Geological Sequestration of CO$_2$ - An Exploratory Study of the Mechanisms and Kinetics of CO$_2$ Reaction with Mg-Silicates

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Some Strategies for Carbon Storage

- Injection into deep sedimentary formations
- Injection into saline aquifers
- Mineral carbonation (i.e. reaction with basalt)
- CO$_2$ disposal in the deep sea
- Others (e.g., green cement)
“I am convinced that, in the long term, we must turn to solutions that involve chemical neutralization (immobilization) of CO$_2$, as opposed to simply storing it in gaseous form. Hence, I consider petroleum reservoirs and saline aquifers as interim storage solutions. Ultimately, we must learn to economically bind CO$_2$ with the magnesium and calcium contained in silicate rocks, whether it be under in situ or ex situ conditions.”
Lifetime of 1mm$^3$ Crystal in Dilute Water @25°C
Mineral Carbonation

- Reaction between divalent cations (Mg$^{2+}$, Ca$^{2+}$, Fe$^{2+}$) and CO$_2$ to generate carbonate minerals
  - Chemically benign product
  - Stable over geologic time
- Most abundant cation source is silicate minerals
- 0.1 Gt of CO$_2$ sequestered annually by silicate weathering (vs. 30 Gt emitted)

Model System Study of Surface Carbonation Reactions

Ambient Pressure XPS Study of MgO(100) + CO$_2$ ± H$_2$O
Scanning transmission X-ray microscope (in cubicle)

High-pressure photoelectron spectroscopy endstation

X-ray emission spectroscopy endstation
Ambient-Pressure XPS of the Interaction of CO₂ and H₂O with MgO(100)

Conditions

UHV

RT 0.2 CO₂

RT 0.2 CO₂ + 0.1 Torr H₂O

-19°C, 0.2 CO₂ + 0.1 Torr H₂O

This study clearly shows that the presence of water on the MgO (100) surface inhibits the formation of Mg-carbonate and helps explain the enhanced carbonation of preheated Mg-silicate minerals presumably due to the dehydration of their surfaces.
The Reaction of Olivine with CO$_2$–rich Fluid

- Natural process, thermodynamically favored in CO$_2$-rich environments, including our atmosphere
- Net reaction:
  \[
  \text{Mg}_2\text{SiO}_4 + 2\text{CO}_2 \rightarrow 2\text{MgCO}_3 + \text{SiO}_2
  \]
  \[
  \text{Mg}_2\text{SiO}_4 + 4\text{H}^+ \rightarrow 2\text{Mg}^{2+} + \text{SiO}_2^{aq} + 2\text{H}_2\text{O}
  \]
  \[
  \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+
  \]
  \[
  \text{Mg}^{2+} + \text{HCO}_3^- \rightarrow \text{MgCO}_3 + \text{H}^+
  \]
- Goals: understand mechanisms and improve kinetics; understand consequences of +20% volume increase during carbonation reaction vis-à-vis porosity and permeability changes in basaltic rocks.
Potential Problems

- Surfaces of Mg-silicates may become passivated due to deposition of SiO$_2$ or MgCO$_3$ coatings.

- Reactions are relatively slow under “mild” conditions and may not be economically feasible at present, requiring crushing of rock to increase surface areas or heat treatment to increase reactivity.

- Large positive volume changes of solid products relative to reactants may cause significant reductions in porosity and permeability. However, if silica concentrations are maintained below quartz saturation, the volume change resulting from conversion of Mg-olivine to MgCO$_3$ is -23%.
Natural Analogues

Underlying hydrocarbon deposits are thought to have contributed organic acids which dissolved zeolite-rich veins and facilitated conversion of olivine to magnesite.

MgCO₃ veins in serpentinite, Red Mountain Magnesite Mines, near Livermore, CA (courtesy of K. Maher)
Massive MgCO₃ veins in basalt, Nuussuaq, West Greenland (courtesy of D. Bird)
Olivine \((\text{Mg,Fe})_2\text{SiO}_4\)

\((\text{Mg,Fe}^{2+})\text{O}_6\) octahedral sites, isolated \(\text{SiO}_4^{4-}\) tetrahedra

Olivine from San Carlos, AZ

Olivine structure produced using CrystalMaker
Olivine sample image from: http://skywalker.cochise.edu/wellerr/mineral/olivine/olivineL.htm
Olivine Dissolution: Past Work

- Decades of work to understand weathering
- Dissolution rate increases with temperature, acidity, exposed surface area
- Organic acids increase rate

Stability of Mg-Olivine Relative to Magnesite as a Function of Aqueous H$_2$ and Acetic Acid
Olivine Dissolution: Mg-O bonds

- Cation exchange reaction
- Proton promoted dissolution
- Ligand promoted dissolution

\[
\text{rate}_{\text{dissolution}} = k_{\text{MgOH}^+} \{\text{MgOH}_2^+\} + k_L \{\text{MgL}\}
\]
Olivine Dissolution: Si Removal

- Si-O bonds stronger than Mg-O
- Isolated SiO$_4$ tetrahedra: no bridging oxygens
- Formation of Si-O polymers?
  - Hypothesized by Pokrovsky and Schott (2000)
  - No evidence found by Zakaznova-Herzog et al. (2008)

XPS O 1s peak
Olivine leached for 27 days at pH=2

Past Work: Olivine carbonation

- Harsh conditions (Teir et al., 2007: 4M HCl and HNO$_3$, NaOH)
- No MgCO$_3$ formation (Giammar et al., 2005)
- Strive for mild conditions

Starting Material

- Olivine (natural), Oregon
- BET surface area: 1.13 m²/g
- Composition:
  \[(\text{Mg}_{0.85}\text{Fe}_{0.15})_2\text{SiO}_4\]
  \[
  \text{Al (0.75%)}
  \]
  \[
  \text{Ca (0.75%)}
  \]
  \[
  \text{Mn (0.23%)}
  \]
  \[
  \text{Ni (0.88%)}
  \]
“Dickson-Type Rocker Bomb” (developed at Stanford University in 1970’s)

Photos courtesy of Bob Rosenbauer
Solution Analysis

• Elemental Composition
  – Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

• Alkalinity titration

• Total carbon analysis
  – DIC
  – DOC

Image from: http://em-1.stanford.edu/Schedule/ICP/Index.htm
Experimental Studies

- Initial trial (A)
- Repeat A (B)
- Coal: contains dissolved organic acids
- Salicylic acid: naturally abundant

<table>
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<tr>
<th></th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>Water: Rock</th>
<th>Time (days)</th>
<th>Moles CO₂/volume of separate phase</th>
<th>Ionic Strength</th>
<th>Other additions</th>
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<tbody>
<tr>
<td>A</td>
<td>77</td>
<td>100</td>
<td>10:1</td>
<td>44</td>
<td>0.23/10.3 mL</td>
<td>0.05</td>
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<tr>
<td>B</td>
<td>60</td>
<td>100</td>
<td>20:1</td>
<td>39</td>
<td>0.21/15.0 mL</td>
<td>0.50</td>
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<tr>
<td>C</td>
<td>60</td>
<td>100</td>
<td>20:1</td>
<td>39</td>
<td>0.31/15.0 mL</td>
<td>0.50</td>
<td>20:1 water: coal</td>
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<tr>
<td>D</td>
<td>60</td>
<td>100</td>
<td>20:1</td>
<td>39</td>
<td>0.27/15.0 mL</td>
<td>0.50</td>
<td>1 g/L salicylic acid</td>
</tr>
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</table>
Phase Analysis: Quantitative XRD

- MgCO$_3$ peaks
- 33% conversion
- Salicylic Acid
- 9% conversion
- control
- coal
- olivine
Salicylic Acid

MgCO₃

SiO₂

2 μm

100 μm

10 μm

MgCO₃ crystal
Coal

Olivine grain
Elemental Analysis: XPS

- Si 2s
- Mg 2s
- Mg 2p
- C 1s
- Mg Auger
- O 1s

Graph showing binding energy (eV) with peaks for O 1s, Mg Auger, C 1s, Si 2s, Si 2p, Mg 2s, Mg 2p. Samples include olivine, Salicylic acid, control, and coal.
XPS Evidence for Si-rich layer

- Also reported by
  - Pokrovsky & Schott, 2000 – Schultze et al. 2004

Expected Mg/Si ratio based on bulk composition $\text{Mg}_{1.7}\text{Fe}_{0.3}\text{SiO}_4$
Solution Composition

![Graphs showing the concentration of Mg and Si over time for different samples: Coal, Control, and Salicylic acid.](image_url)
Numerical Modeling of $\text{H}_2\text{O}-\text{CO}_2$ “Flow-Through” Experiments with Mg-Silicates using “CrunchFlow”

a kinetic rate constants ($k$) for dissolution reactions calculated from a compilation of existing experimental data by Palandri and Kharaka (2004) unless otherwise specified.
b activation energy ($E_a$) as calculated from a compilation of existing experimental data by Palandri and Kharaka (2004) unless otherwise specified.
c for pH < 9 the dependence on $a_{H^+}^{0.46}$ (Pokrovsky and Schott, 2000).
d for the present study we assume that dissolution and precipitation are reversible.

**Transition State Theory Rate Law:**

$$R_j = A k_f \beta \Delta G_r n^m \sigma$$

where $R_j$ is the rate of an individual reaction pathway or mechanism (in units of mol/m$^3$ porous medium/s), $A$ is the reactive surface area (m$^2$/m$^3$ porous medium), $k_f$ is the surface normalized rate constant (mol/m$^2$/s) determined far from equilibrium, $\beta$ is a term describing the inhibition or catalysis of the reaction, $\Delta G_r$ is the Gibbs free energy of reaction (and the entire term in parentheses describes the dependence on reaction affinity), $n$ and $m$ are fitting parameters, and $\sigma$ is Temkin’s average stoichiometric coefficient.
Reactive transport simulations: interaction of CO$_2$-rich fluids with Mg-silicate rocks

- Initial work suggests that aggressive CO$_2$-rich fluids create sufficient porosity to allow for MgCO$_3$ precipitation to occur.
- Effect is strongly dependent on porosity-permeability relationship and flow rate.
- Future work with 2-D flow and natural analogue data.

1-D simulations of reactions within a fracture zone
Progress in Experimental Studies

• Produced MgCO₃ under mild conditions
• Salicylic acid significantly enhanced reaction kinetics
• Si-rich layer found on all reaction products, but quartz is rare in natural basaltic and serpentinitic rocks that have undergone mineral carbonation.
Future Plans

- TEM, XPS with Ar sputtering
- Continue ambient-P XPS studies of interaction of CO$_2$ +H$_2$O with mineral surfaces
- Dissolution only experiments
  - Vary ionic strength
  - Vary salt composition
  - Stay below SiO$_2$ saturation
- Extract kinetic parameters from data
- Further modeling of flow-through reactions
- Explore the use of the Zn-enzyme Human Carbonic Anhydrase II to speed up conversion of CO$_2$ in aqueous solution to HCO$_3^-$.
- Field studies of natural magnesite deposits to help guide our experimental and modeling studies
Longer Term Questions

- What are the kinetics of serpentinite mineral (hydrated Mg-silicates) carbonation?
- How would this reaction proceed in a flow-through process?
  - Porosity
  - Surface area considerations
  - CrunchFlow2007
- Other reactant materials for mineral carbonation?
Thanks for your attention and thanks to the organizers for the invitation to speak.