Carbon Sequestration in Basalts: Laboratory Studies and Field Demonstration

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Needles of aragonite growing on Columbia River basalt grain during exposure to wet scCO$_2$ for 377 days at 100°C and 90 bar.
Presentation Outline

► Research Program Overview and Objectives
  ■ Reasons for sequestering carbon in basalts
  ■ Unique basalt characteristics
► Laboratory Based Studies
  ■ Basalt carbonation
  ■ Phase behavior of CO₂-H₂O mixtures
► Wallula Field Pilot Demonstration
  ■ Project background and regional setting
  ■ Field characterization program
► Side Wall Core Analysis
  ■ 3D imaging of carbonate precipitates
  ■ Carbonate identification (XRD, SEM-EDX)
  ■ Isotopic analysis on pre and post injection samples
► Summary and Conclusions
Why Carbon Sequestration in Basalts?

Favorable Attributes of Basalt

- Highly reactive with supercritical $\text{CO}_2$
- Self-sealing for leakage scenarios
- Common rock type with worldwide distribution

Flood Basalt = large volumetric thickness
Flood Basalt Features Relevant to CO₂ Sequestration

- **Formation process**
  - Giant volcanic eruptions
    - Low viscosity lava
    - Large plateaus
  - Multiple layers

- **Primary structures**
  - Thick impermeable seals
    - Caprock (flow interior)
    - Regional extensive interbeds
  - Permeable vesicular and brecciated interflow zones
    - Injection targets
    - 15-20% of average flow

- **Mineralogy**

  - **Augite** \((\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6\)
  - **Plagioclase** \((\text{Ca}, \text{Na})\text{Al}_2\text{Si}_2\text{O}_8\)
  - **Mesostasis** \((\text{Ca}, \text{Mg}, \text{Fe}, \text{Na}, \text{Mn})_2\text{Si}_4\text{O}_{10}\)
Carbon Sequestration in Basalts

**Aqueous Dissolved CO₂**

- Static basalt experiments
  - Crushed basalt
  - 2.5 years or longer
  - 100 Bar, 100°C
- Carbonate precipitation
  - Rates of formation
  - Chemistry
  - Various morphologies

**Variable Pressure/Temperature**

- Experimental Conditions
  - 2591-3048 m (180 days)
  - 116-137°C
  - 25.5-31.0 MPa (3188-4496 psi)
- Carbonate precipitates occur as discrete individual growths on the basalt surface
  - Long fibers
  - Spheres and globs
- Carbonate chemistry is heavily substituted with Fe²⁺, Mn²⁺, and Mg²⁺
- Carbonate structure transitions from calcite to ankerite/kutnahorite, similar to dolomite
Early laboratory studies at PNNL indicated high reactivity with water bearing liquid and scCO₂ fluids. Key questions emerged:

- What is the role of water activity in mineral transformations (water threshold)?
- What are relevant time scales for mineral transformations with respect to fluid flow through fractures?
- How do we predict conditions for fluid transmission through fractures (opening/self sealing)?
- How do we represent water-wet scCO₂ reactions in simulators?
Wallula Basalt Carbon Sequestration Pilot Project
Early and aggressive characterization program to reduce uncertainties

Include backup option of injecting into sub-basalt sediments

Siting in densely populated areas makes almost every aspect of CCS projects more challenging
Wallula Basalt Carbon Sequestration Pilot Project

Project Background:
- Seismic survey conducted December 2007
- Drilling initial test characterization and well completion: Jan. – May 2009
- Injection permit issued: March 2011
- Extended hydraulic test characterization: Sept. – Nov. 2012
- ~1,000 MT CO₂ injection: July 17th – August 11th, 2013
- Post-injection air/soil monitoring and downhole fluid sampling performed for ~2 years following injection

Current Status:
- Final well characterization activities: June – July 2015
- Detailed wireline survey
- Targeted sidewall coring
- Extended hydrologic tests
- Final well decommissioning/site demobilization: August 2015
Wallula Basalt Pilot Well: Detailed Wireline Survey and Reservoir Tests

- Detailed wireline survey
  - Pre injection: zone 1 & 2 are water saturated
  - Post injection: zone 1 & 2 contain CO₂
  - Thermal signature
- Extended duration hydrologic injection test
  - Zone of increased compressibility detected
- 7 low-stress (i.e. $\Delta P \approx 13$ psi), near-field pressurized slug tests (i.e. pulse tests)
- Short-duration constant rate drawdown and recovery test
  - Zone of increased compressibility detected

Injection zone still exhibits a well-defined temperature signature (+2.2 °C) 22-months after injection termination.
Detailed resistivity wireline log surveys (pre and post) indicate two large spikes that identifies two highly resistive layers of free phase supercritical CO$_2$. These spikes correlate well with the top of two injection zones.
Wallula Basalt Pilot Well: Post Injection Downhole Fluid Sampling

- Significant increases (factor of 10 to 100 higher) in post-injection fluid sample concentrations (e.g., TDS, alkalinity, Na, Ca, Mg, K)
- Concentrations continued to increase during post injection period (although at a declining rate)
50 sidewall cores were collected across the open borehole section between 828-884 m (2,716 – 2,900 ft bgs)

Potential carbonate reaction products observed on SWC samples occur both as large (up to ~1mm) nodules within open vesicles and as a coating on the borehole wall face of a few core samples

XRD analysis of selected carbonate nodules identified ankerite as the only carbonate mineral present
Wallula Basalt Pilot Well: Initial Sidewall Core Characterization

- XMT imaging shows likely ankerite nodules existing throughout core
- Chemically, these ankerite nodules are initially dominated by Ca, but become Fe rich as the precipitation progresses.
**Isotopic Characterization of Nodules**

- Nano Secondary Ion Mass Spectrometry (NanoSIMS) was utilized to measure delta oxygen-18 ($\delta^{18}O$) and delta carbon-13 ($\delta^{13}C$) isotope ratios.
- ~10 mg of ankerite nodules removed from SWC 857.1m.
- Subsamples from natural calcite vein recovered in pre-CO$_2$ injection sidewall core.
- Individual nodules mounted in epoxy and polished to obtain cross sections.
Wallula Basalt Pilot Well: Isotopic Analysis on pre and post injection samples

Isotopic Data

- Ankerite nodules were depleted in $\delta^{13}$C relative to natural occurring calcite
- Formation water, evolved CO$_2$, & CO$_2$ source, were depleted in $\delta^{13}$C (analyzed by outside laboratory)
- Natural calcite from wellbore and carbonates in drill cuttings (pre injection) enriched in $\delta^{13}$C

Key Findings

- Pre injection carbonate containing samples are enriched in $^{13}$C compared to post injected carbonates
- Metal cations such as Fe and Mn appearing in the ankerite nodules indicate a reaction between the basalt and CO$_2$
- Clear evidence of the injected CO$_2$ mineralizing into ankerite.
Reactions occurring between basaltic rocks and H$_2$O-scCO$_2$ fluids produce well crystallized carbonate minerals at laboratory time scales
- Carbonates incorporate basalt components
- Water bearing scCO$_2$ fluids are highly reactive

Wallula Basalt Pilot Field Demonstration Test
- Injection of 977 metric tons occurred August 2013
- Thermal signature persists after 24 months
- Increasingly complex injection zone geochemical environment
- Presence of free-phase CO$_2$ detected in upper two zones

Sidewall core analysis post CO$_2$ injection
- 3D imaging reveal nodules located within open vesicles throughout SWCs
- Ankerite nodules identified
- Isotopically distinct from native calcite

First field evidence of in-situ carbonation occurring from a free phase supercritical CO$_2$ injection into a flood basalt reservoir

Validation of rapid carbonation rates that were first speculated in our 2006 publication
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