Role of $\text{CO}_2$-$\text{H}_2\text{O}$ fluids in vein formation: Observational and experimental studies

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Today’s Talk

- Hypothesis for mixed fluid (H$_2$O+CO$_2$)-rock interactions
  - Laboratory perspective
  - Aqueous geochemistry
  - Rocks and minerals
- Proposed Henderson experiments
  - Geophysics on behalf of Jim Rutledge
- Broader applications
- Questions and discussion
General Hypothesis

Reactive properties of a supercritical CO₂ phase that may coexist with brine at low T and P has not been evaluated or appreciated for a broader range of geologic systems. Potential examples:

• Sedimentary basins
  • Deep burial diagenesis, Kootenay Fm, BC and Alberta (Hutcheon et al., 1980)

• Thermal aureoles in siliceous carbonate rocks
  • Alta Stock Aureole, Utah, USA (Bowman & Pollington, 2004; Pollington et al., 2005; Kaszuba et al., 2006).
Specific Henderson-DUSEL Hypothesis

- Origin of some quartz-carbonate veins (e.g., in ore deposits)
  - Supercritical CO₂ buffers aqueous fCO₂,
    - provide carbonate from small fluid volumes
    - concomitant brine acidity promotes silica supersaturation

- Proposed examples
  - Butte porphyry Cu, Montana, USA (Rusk et al., 2000)
  - ‘Au-only’ provinces and deposits (Phillips & Evans, 2004)
    - CO₂ plays critical role during Au transportation - buffers pH to elevate dissolved Au (S complexes). Not critical in transportation, CO₂-H₂O fluid immiscibility may be important to gold deposition
Relevance for Other Geologic Environments?

Temperature (°C)

Pressure (MPa)

Depth (km)

- CO₂ critical point
- Diagenesis Begins
- Metamorphism Begins
- Carbonate Veins
- CO₂-H₂O Saddle Point
- H₂O critical point
- Deep Saline Aquifers
- Deep Natural Gas Resources
- X₂₀°C/km
- X₂₀°C/km
- X₂₀°C/km
- X₂₀°C/km

after Kaszuba et al., 2006, in press
Magnesite (Mg Brine)

after Kaszuba et al., 2003
Magnesite (NaCl Brine)

after Kaszuba et al., 2005
Siderite (NaCl Brine)

after Kaszuba et al., 2005
Brine Chemistry – Silica

![Graph showing the dissolution of silica in NaCl brine and Mg-NaCl brine with CO₂ injection.](image)

- **Quartz** dissolution starts at around 4 mM/Kg and decreases with time.
- **Chalcedony** dissolution shows a sharp increase after CO₂ injection.
- **Mg-NaCl brine** shows a slight increase in SiO₂ with time.

The graph is based on data from Kaszuba et al., 2006.
EXPERIMENTAL SETUP: Hassler vessel
Pore pressure 2880 psi
Confining pressure 3800 psi
Temperature 54°C

PROCEDURE
Saturation with 3 M brine over 174 hours
Injection of SCCO₂ over 2163 hours

after Wigand et al., 2006
Saturation and permeability evolution over time

after Wigand et al., 2006
Observations after the experiment

- Formation of an orange-colored and a gray-colored zone divided by a dense contact zone.
- Fracture heeled in parts during experiment but also opened due to the reaction with \( \text{SCCO}_2 \) and brine.

after Wigand et al., 2006
Geochemical reactions inside the fracture

Surface structure before experiment

Surface structure after experiment

Cross section of fracture after experiment

Opening of the fracture due to calcite formation
Heeling of the fracture

Diagram after Witschko & Morse (2001)

after Wigand et al., 2006
Proposed Henderson Experiments

- DUSEL as an Earth Observatory
  - Substantial vertical profile through a well-documented, deep hydrothermal vein system that is needed to test and calibrate hypotheses
    - Well-studied history of the Henderson mine
    - Initial drilling and coring
  - First two stages of Geoscience work (Site Characterization and Pre- or Syn-Construction Tasks)
Proposed Henderson Experiments

• DUSEL as an Experimental Laboratory
  • Inject synthetic hydrothermal veins
  • Track geochemistry
  • Synergy with hydrogeology, geophysics, and microbiology
  • Begin in the 3rd stage of Geoscience work (Initial Suite of Experiments) and monitor throughout the 4th stage (Long-Term Vision)
Broader Applications

- Fluid mass transfer in crust
- Carbon budgets and cycles
- Developing issues of geologic sequestration of anthropogenic carbon.
  - “Non-traditional” analogue
Geophysics on behalf of Jim Rutledge

- Hydraulic-fracture mineback experiments
  - Collect extensive microseismic or acoustic emissions data during a series of controlled hydraulic fracture operations
  - Obtaining source mechanisms along with precise locations from induced seismicity could provide detailed information on the fracture growth and deformation processes associated with artificial injections as well as natural hydrothermal processes
  - Subsequent mineback operations would provide the ground truth
Let’s Talk about Veins

- Conceptual and detailed geochemical reactions in mixed CO$_2$-rich and brine solution systems are only beginning to be explored
  - Reaction trends and kinetics of silicate reactions in the presence of mixed brine and CO$_2$-rich fluids can be characterized
  - Isotopic behavior is unexplored
  - Fluid inclusions from a wide range of natural systems should be re-examined
Extra Slides
Phase Compositions, System H₂O-CO₂

after Takenouchi and Kennedy, 1964
Brine Chemistry – Saturation States

- Time (hours)
- Log (Q/K)
- Log mM/kg CO₂

- Total carbon as carbon dioxide
- Magnesite
- Calcite
- Siderite
- Dawsonite (0.4 uM Al)
- Dolomite

inject CO₂
Example Reactions

\[ 3\text{Annite} + 11\text{CO}_2 \rightarrow \]
\[ \text{Muscovite} + 9\text{Siderite} + 6\text{Quartz} + \text{H}_2\text{O} + 2\text{K}^+ + 2\text{HCO}_3^- \]

\[ 3\text{Albite} + 2\text{H}_2\text{O} + 2\text{CO}_2 + \text{K}^+ \rightarrow \]
\[ \text{Muscovite} + 6\text{Quartz} + 3\text{Na}^+ + 2\text{HCO}_3^- \]