# Carbon Dioxide Solubility and Mineral Trapping Estimates

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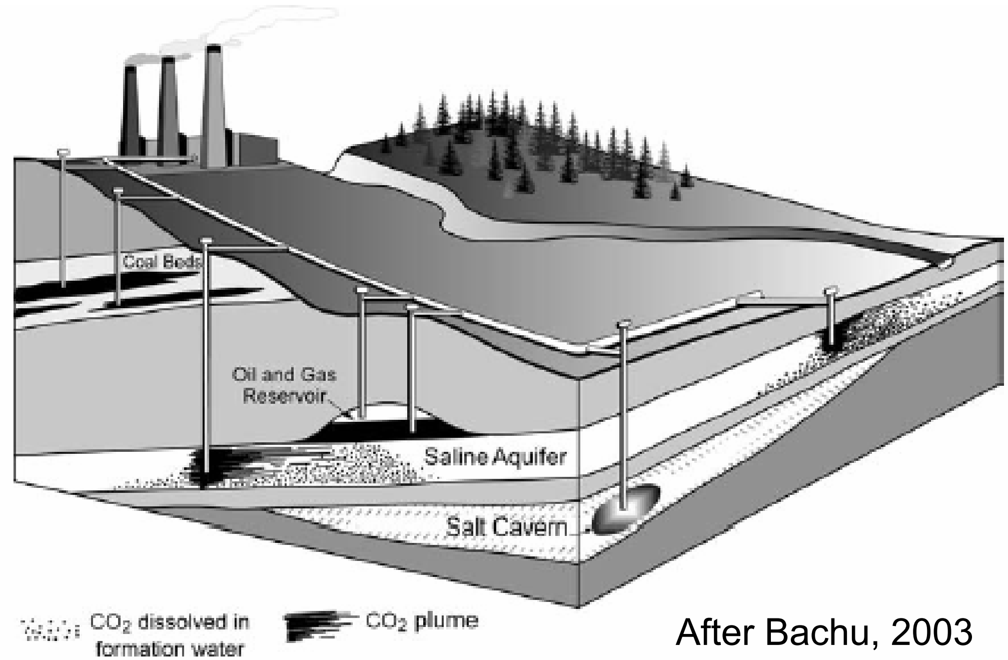
# Mechanisms of Geologic Sequestration

- **Hydrodynamic trapping**
  - $CO_2$ trapped as supercritical fluid or gas under low-permeability caprock
  - Most important mechanism, in short term (?)
- **Solubility trapping**
  - $CO_2$ dissolved in brine
  - Reduces likelihood that $CO_2$ will return to atmosphere quickly
- **Mineral trapping**
  - Consume $CO_2$ by reaction with minerals
    - Precipitate carbonate minerals
    - Silicate reactions
  - The most permanent solution: stable repositories




After Bachu, 2003

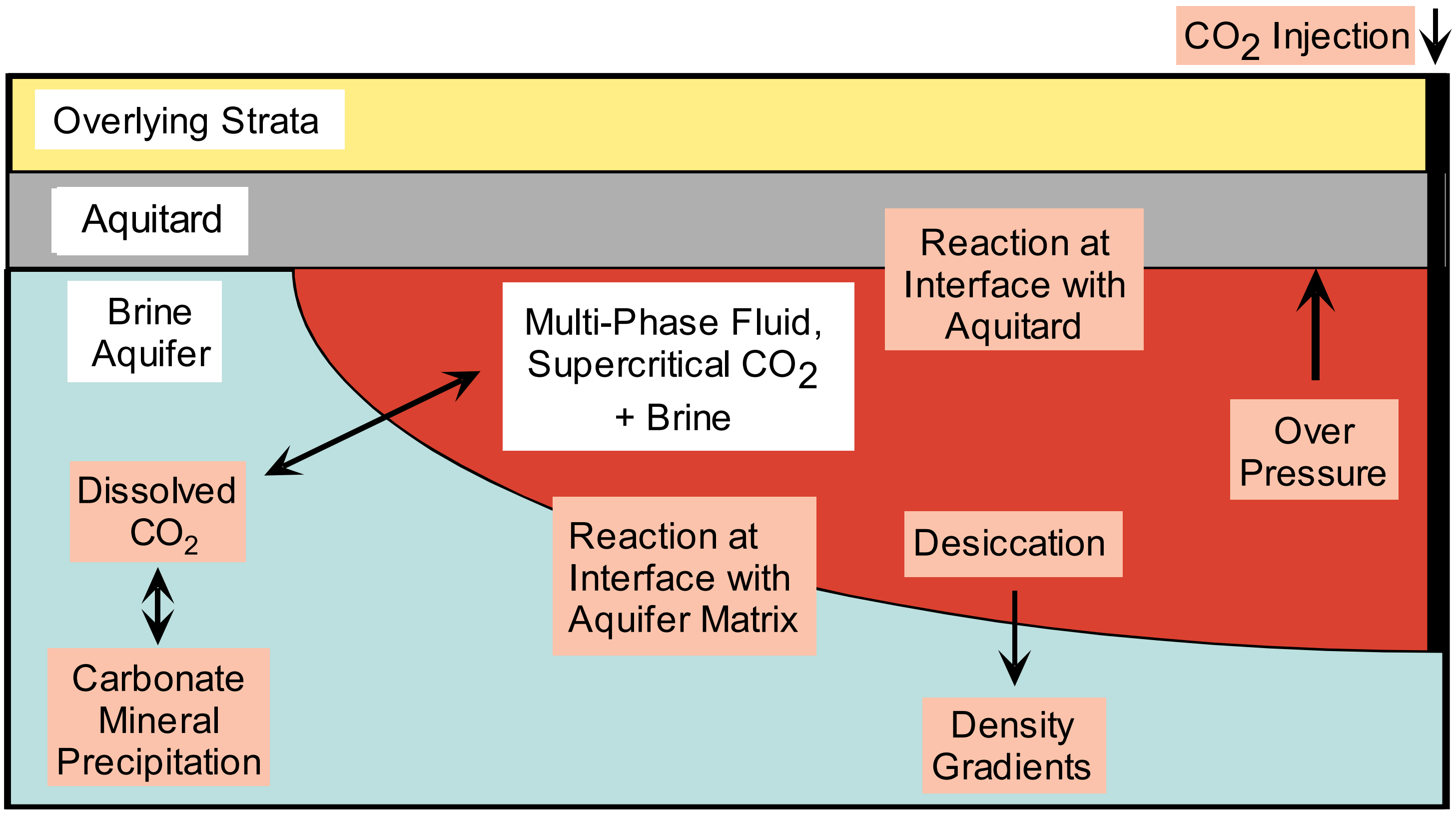
# Long-Term Goals

- Simulate critical processes within aquifer-aquitard-brine-supercritical $CO_2$ system using laboratory and computational experiments
- Key questions to address
  - Once injected into a brine aquifer, what are the time frames for supercritical $CO_2$ to dissolve, carbonate and acidify brine, and induce subsequent chemical reaction within reservoir rock (and caprock)?
  - How rapid is the shift from a rock-dominated to a fluid-dominated system?

# Outline for Today's Talk

- Approach
  - Theoretical/Modeling
  - Experimental
- Results
- Interpretation
- Summary and Conclusions
- Discussion

# Conceptual Model

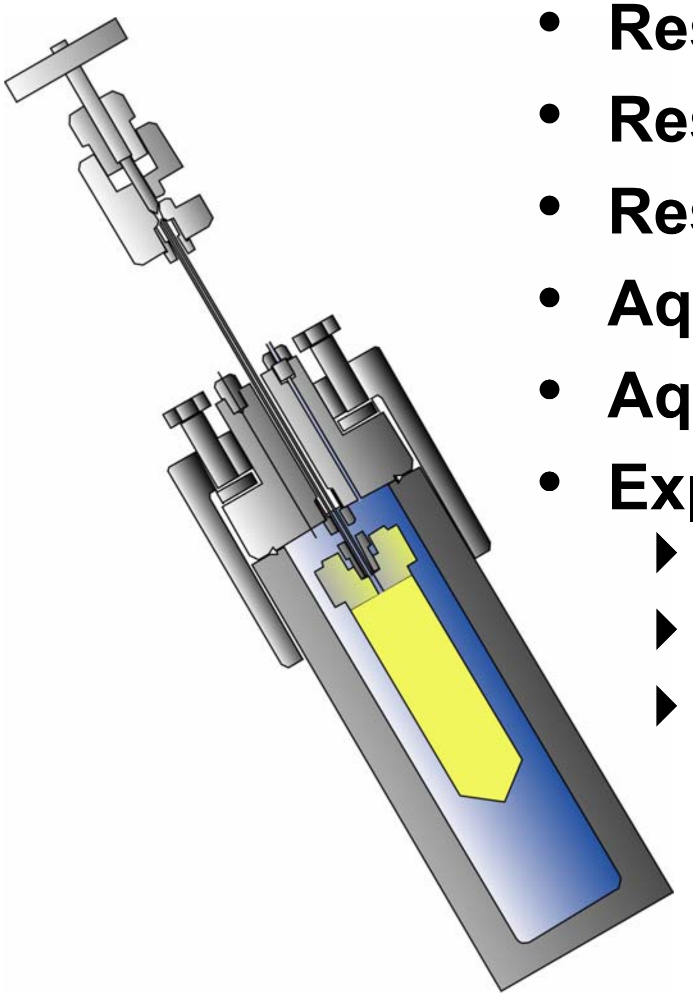



- "Batch" experiments to duplicate reservoir conditions
- Focus on $CO_2$ dissolution and subsequent mineralization
  - Dissolution a quick process
  - Mineralization a slow process

# Reactions and Processes

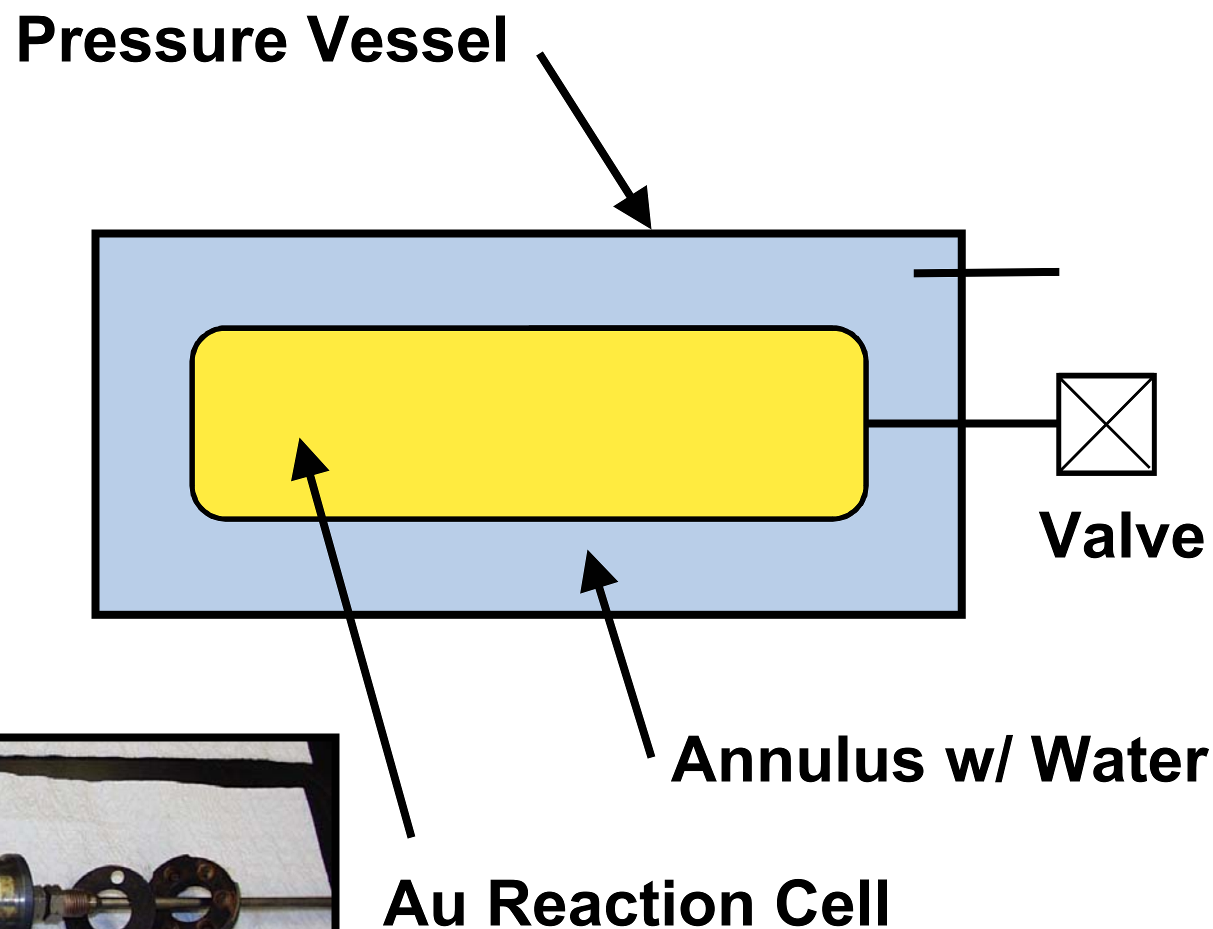
- A variety of geochemical rate processes are implicit in these questions:
  - dissolution of supercritical $CO_2$
  - formation and dissociation of carbonic acid
  - dissolution and re-precipitation of minerals in acidic brine
- Once injected, $CO_2$ first has to dissolve in brine
  - $CO_2(sc) \Leftrightarrow CO_2(aqueous)$, large $\Delta V$
  - Rate = $k_f[CO_2(sc)] - k_r[CO_2(aq)]$
- Carbonic acid equilibria follows soon after
- Mineralization a process that occurs later

# Experimental Approach



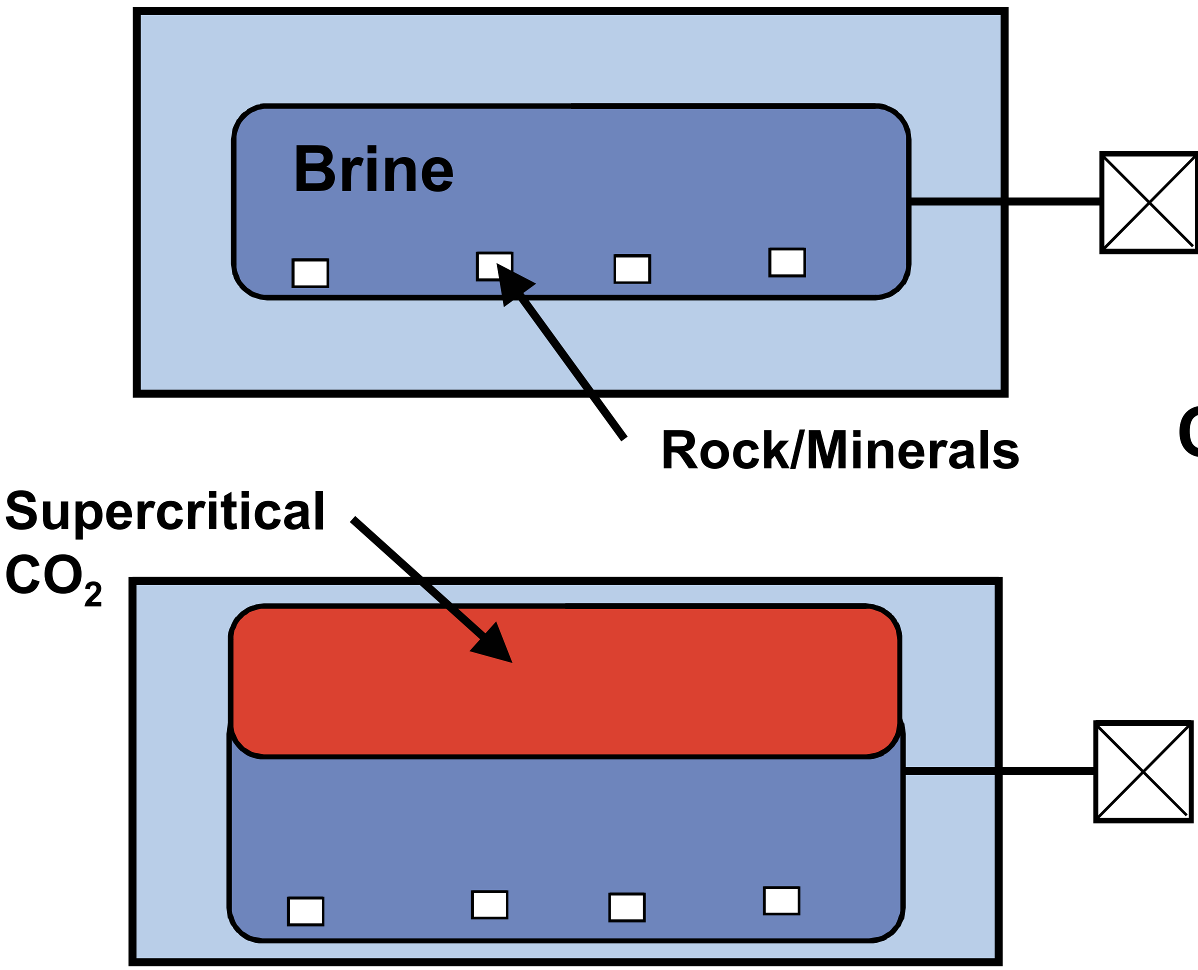
- Flexible cell hydrothermal apparatus (batch)
- Reservoir temperatures, 50 to 200°C
- Reservoir pressure, ~200 bars (~3000 psi)
- Reservoir brines, 1 to 5.5 molal
- Aquifer = arkose, carbonate
- Aquitard = shale
- Experiment
  - Brine
  - Brine + rock
  - Inject $CO_2$ into ongoing reaction

# Experimental Approach




# Experimental Approach

Pre-injection, brine + rock

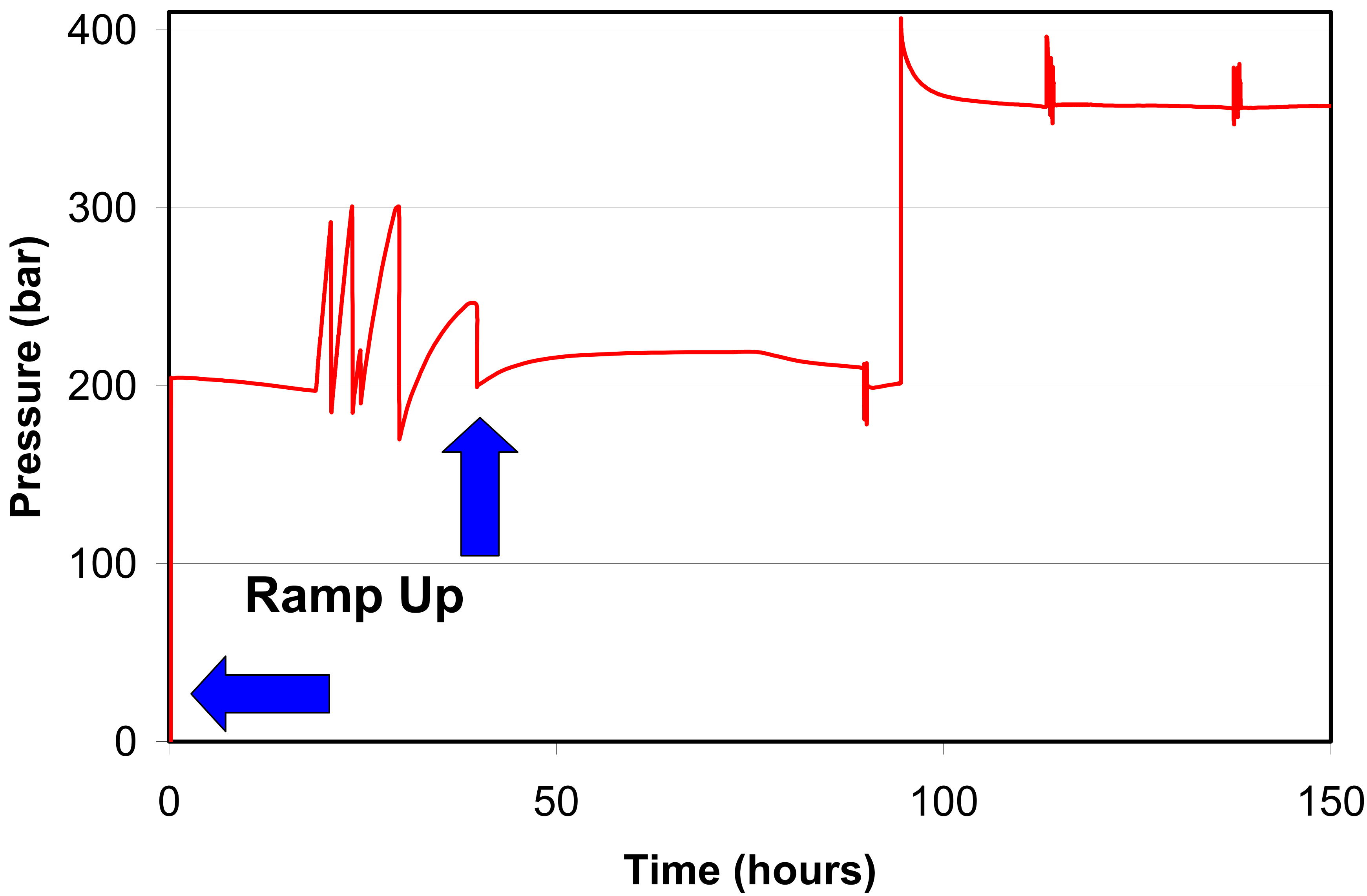



Post-injection, brine + rock + $CO_2$

$CO_2(sc) \Leftrightarrow CO_2(aq)$

large $\Delta V$

# Pressure Evolution in 1M NaCl Brine



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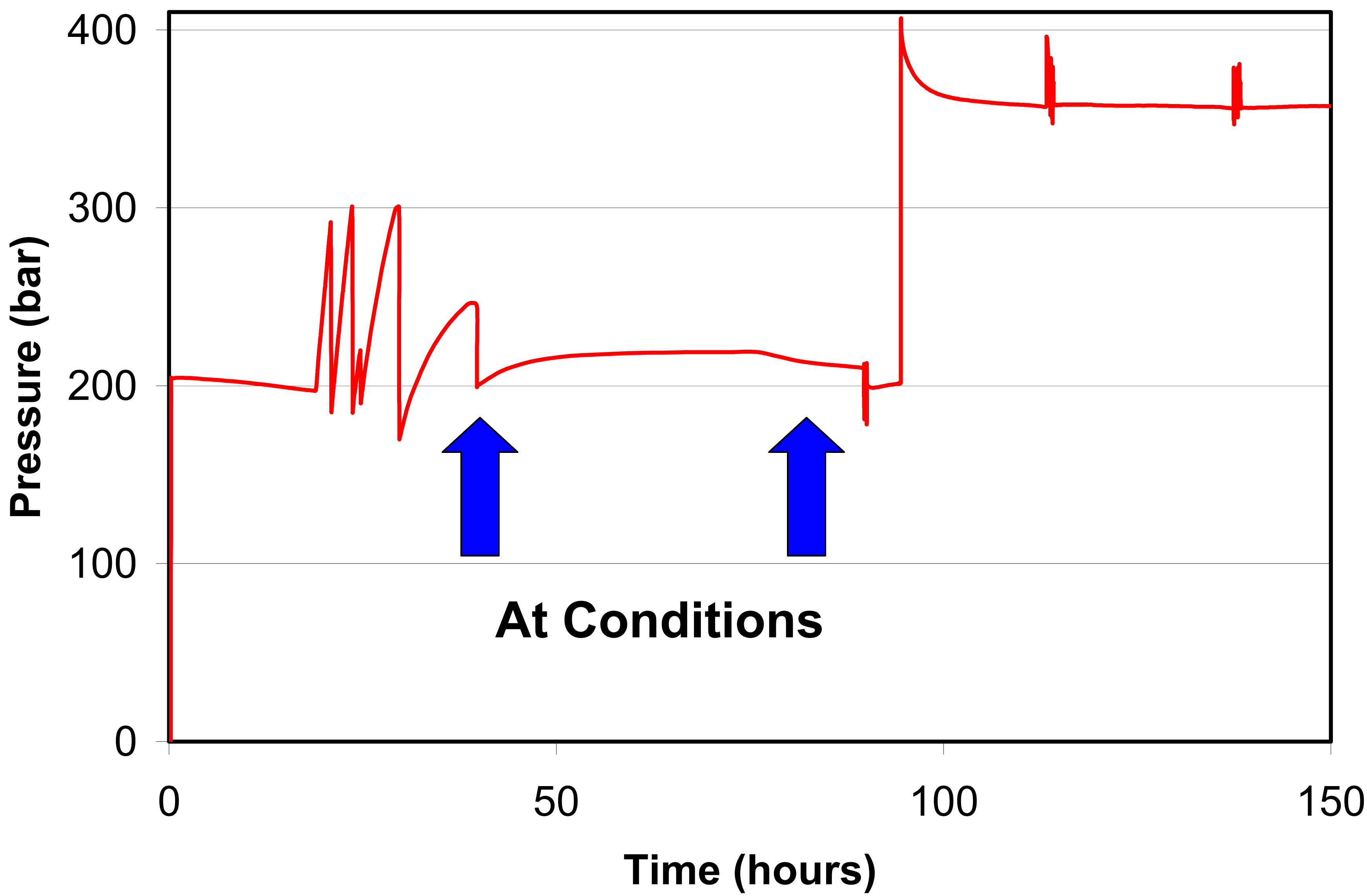

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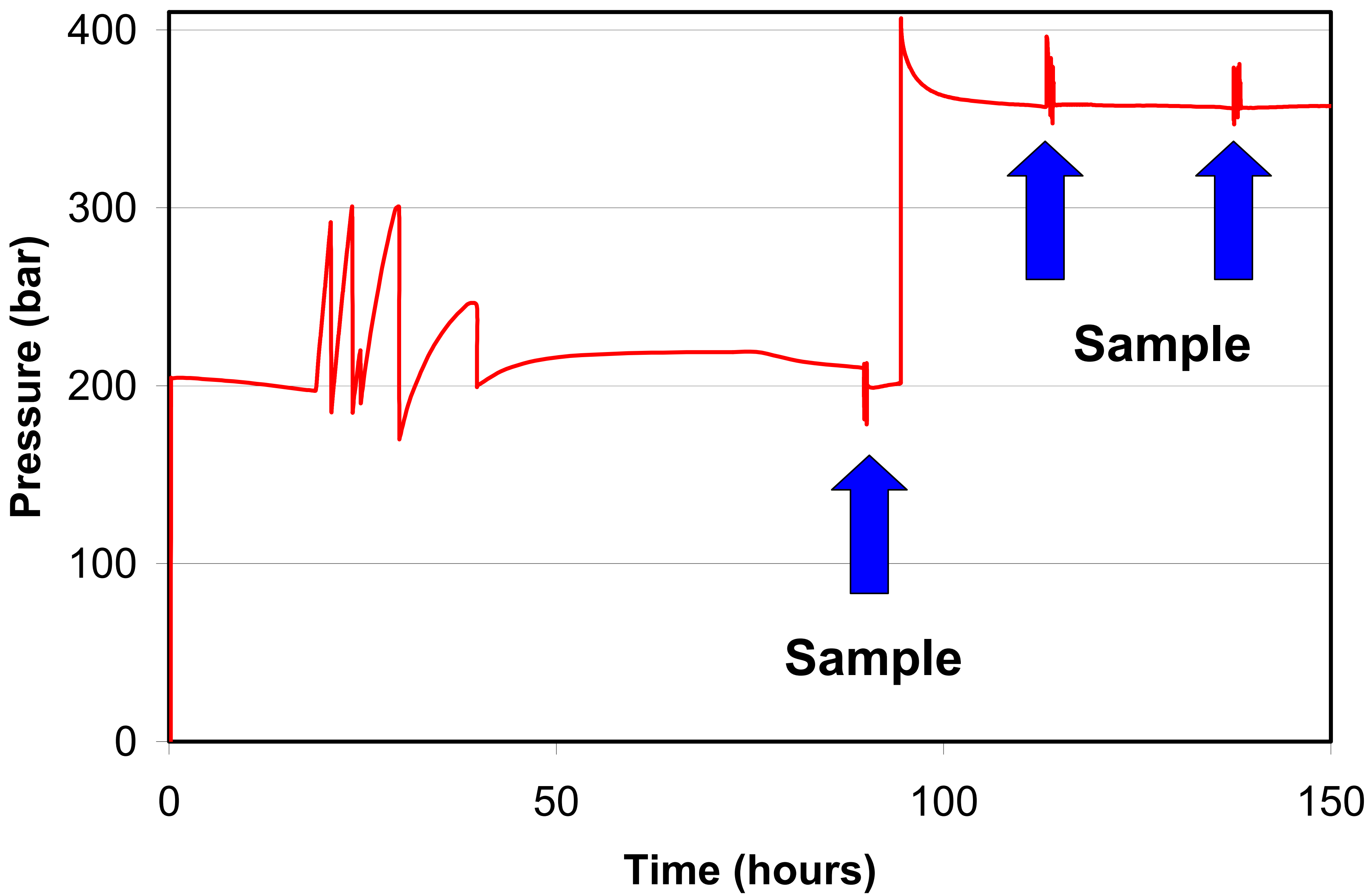

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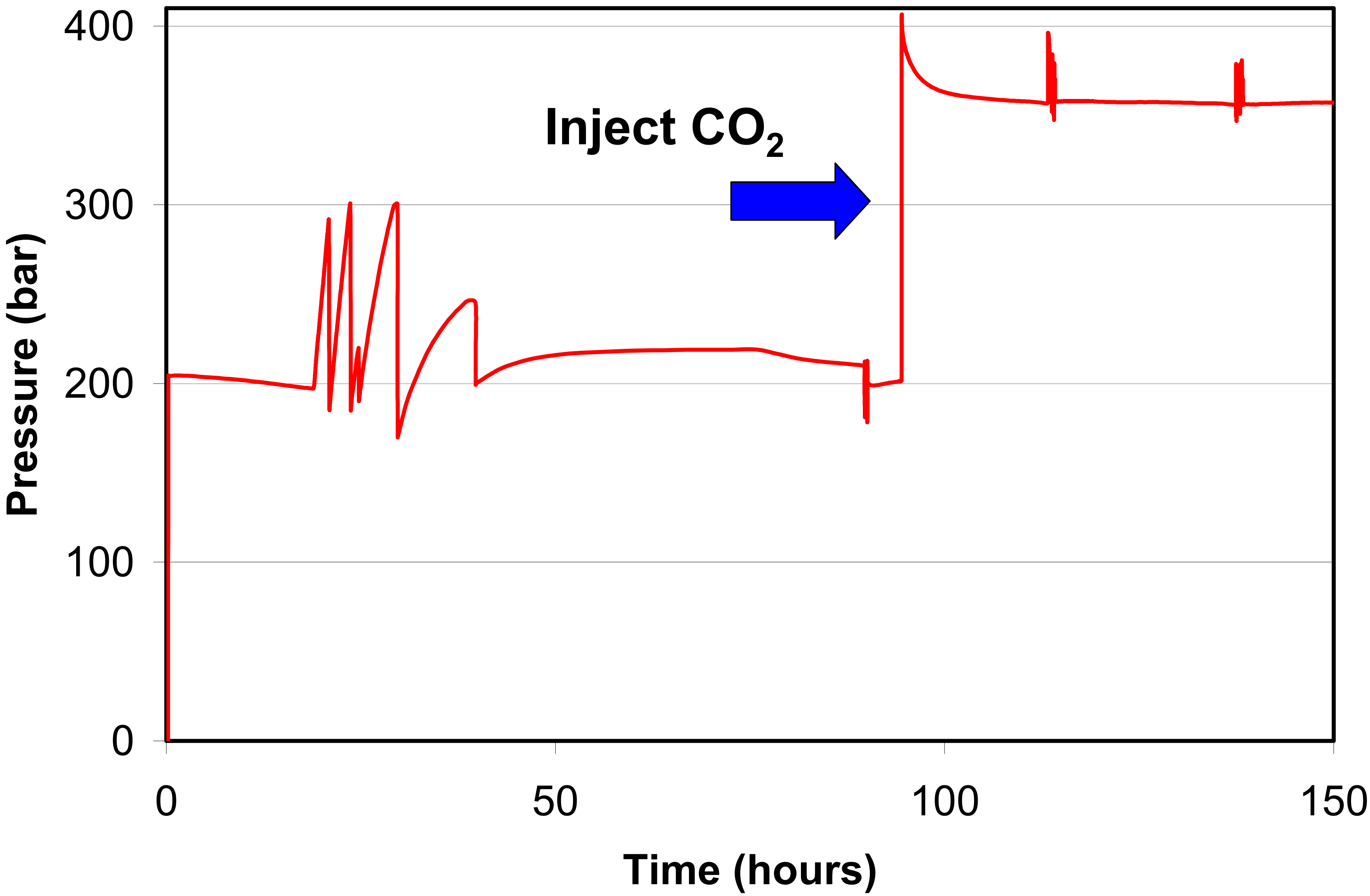

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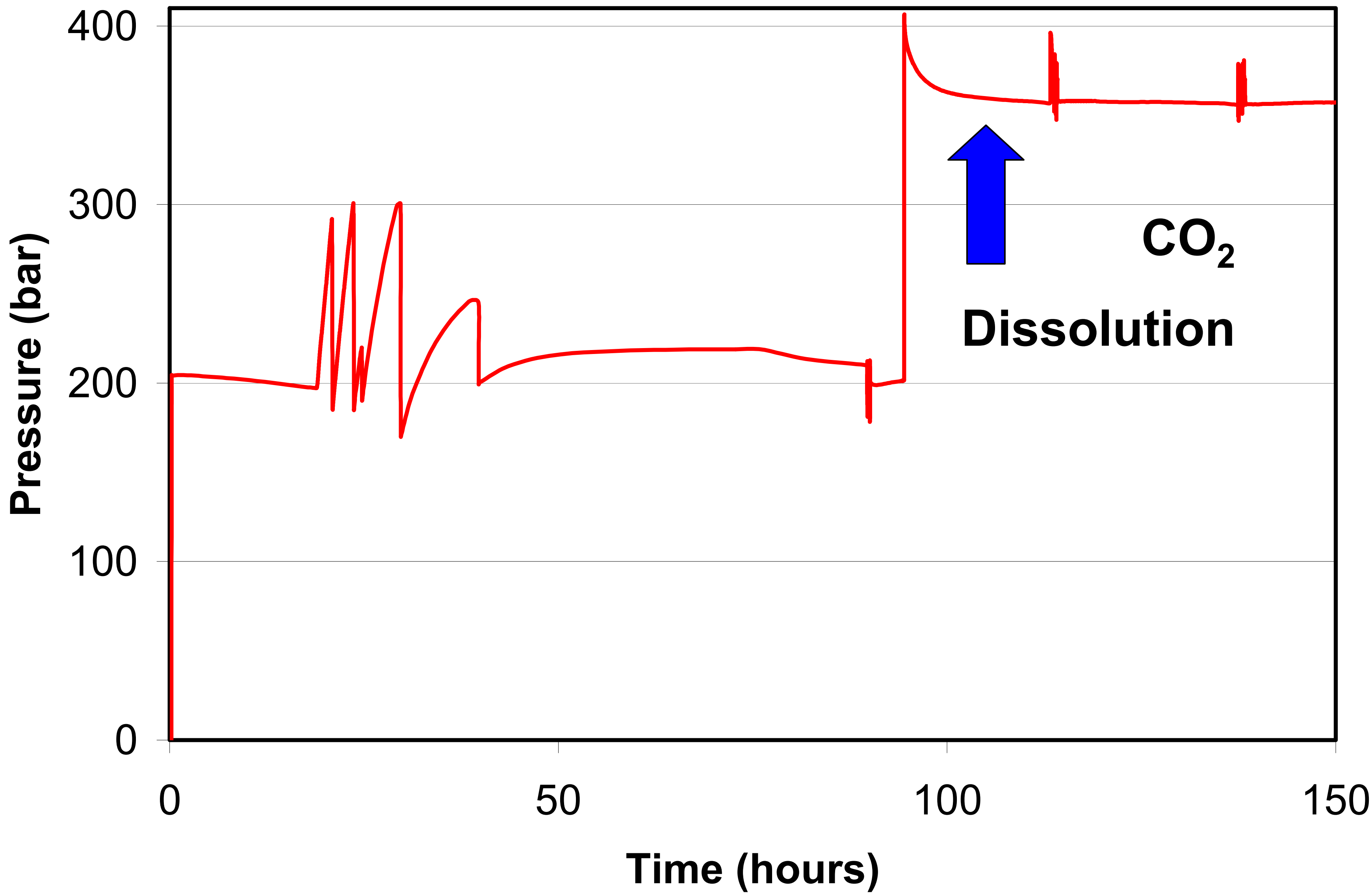
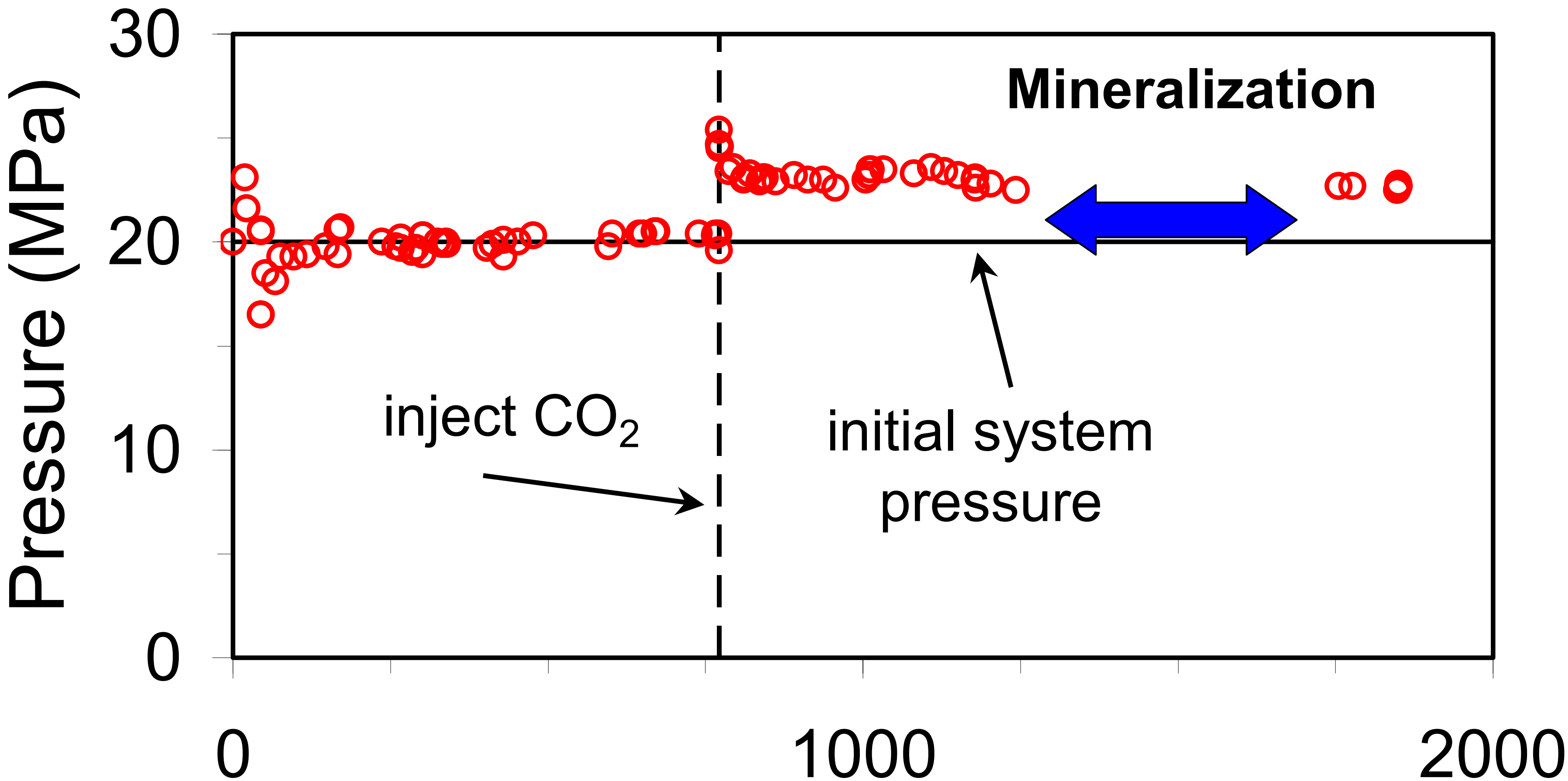
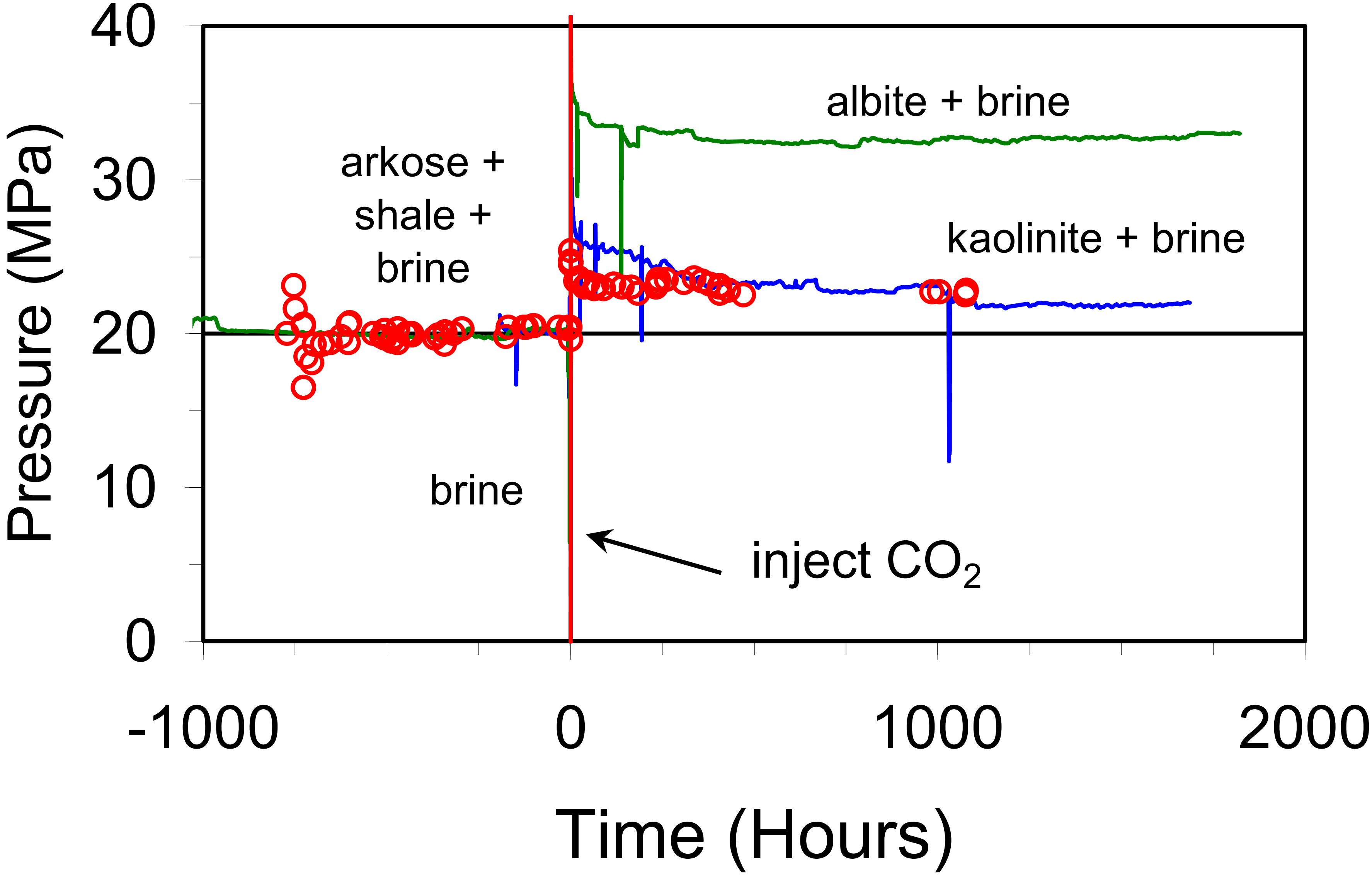


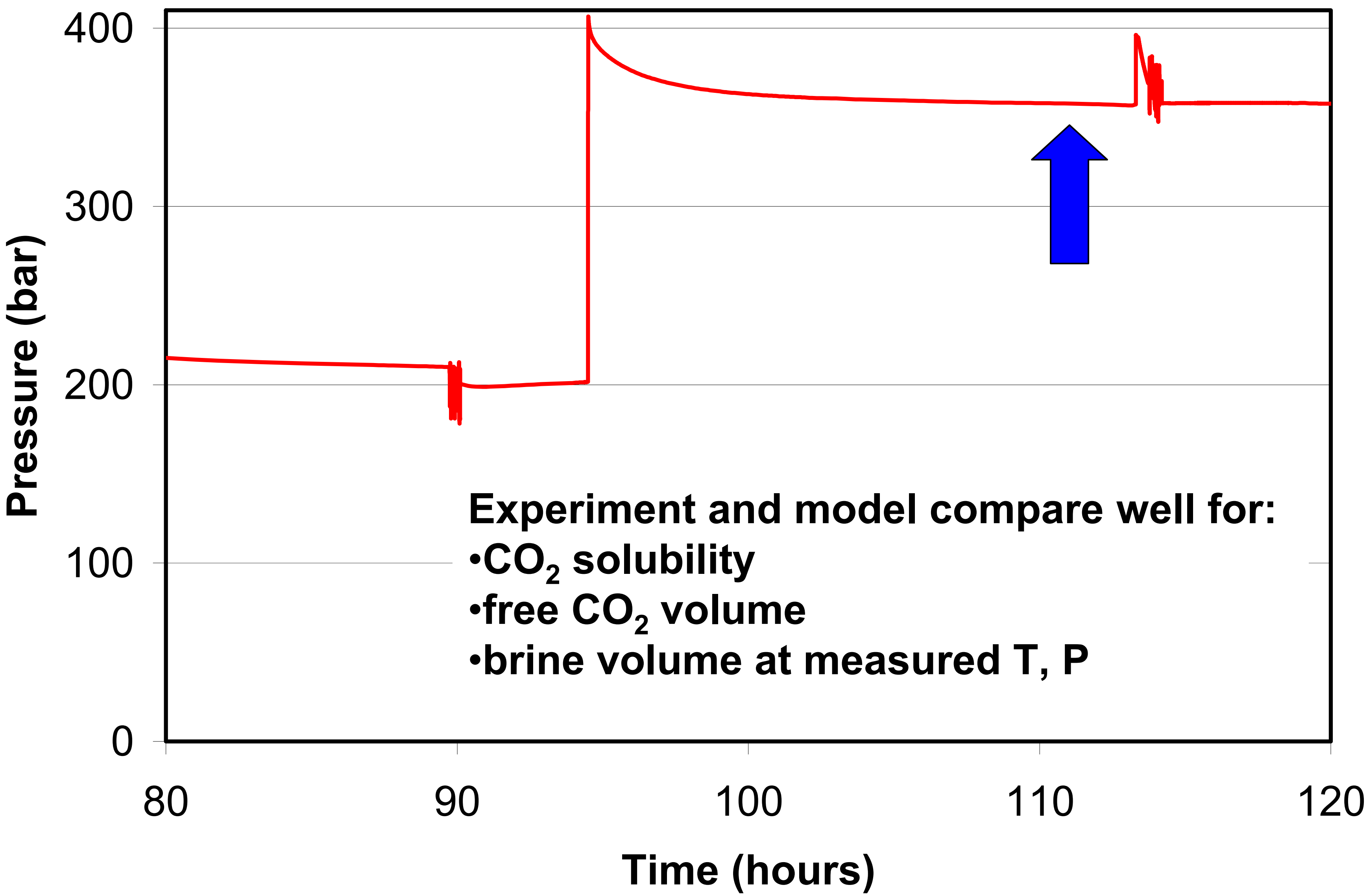
# Pressure Evolution in 5M NaCl Brine + Rock



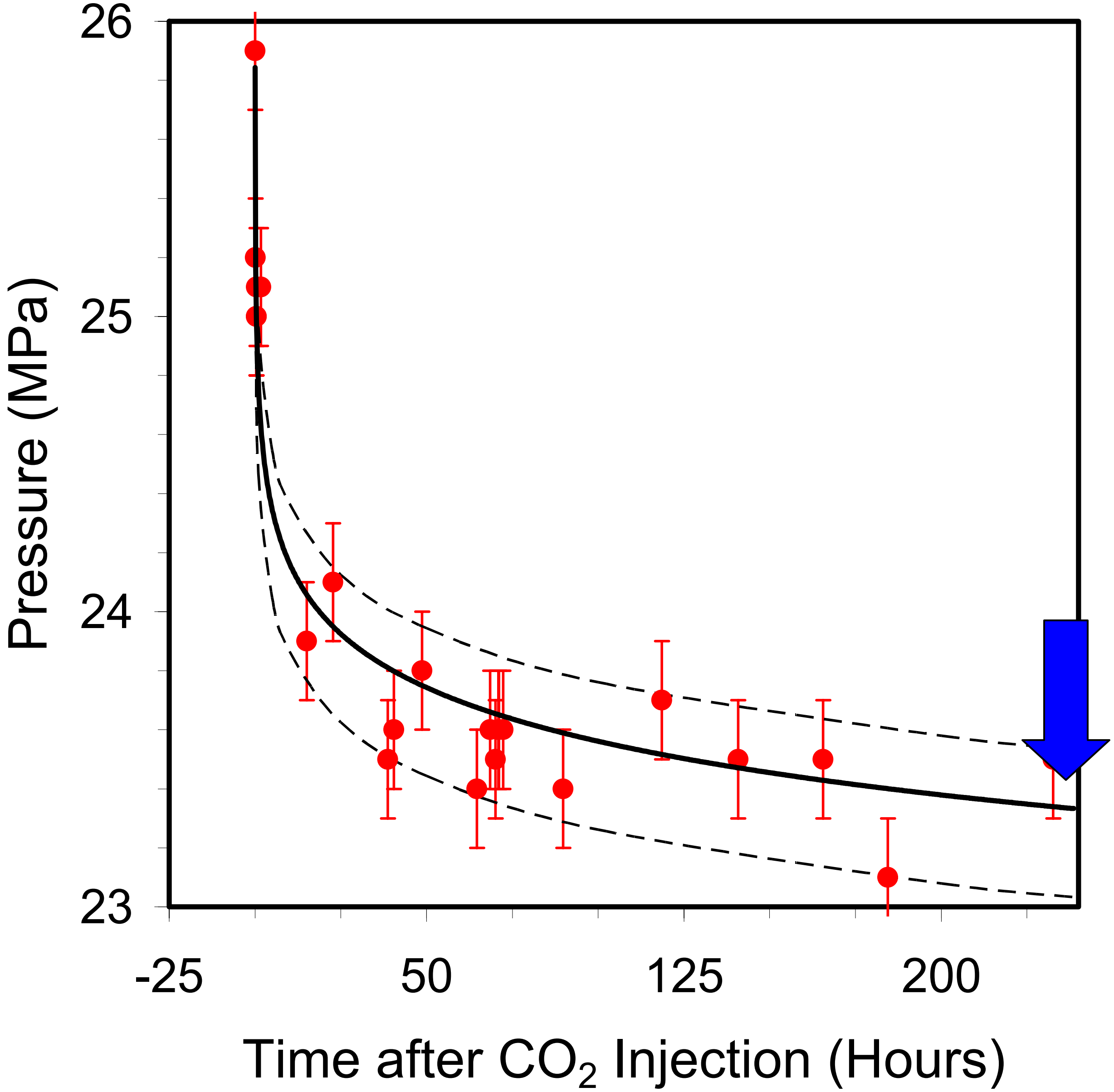
# Pressure Evolution



# Pressure Evolution in 1M NaCl Brine

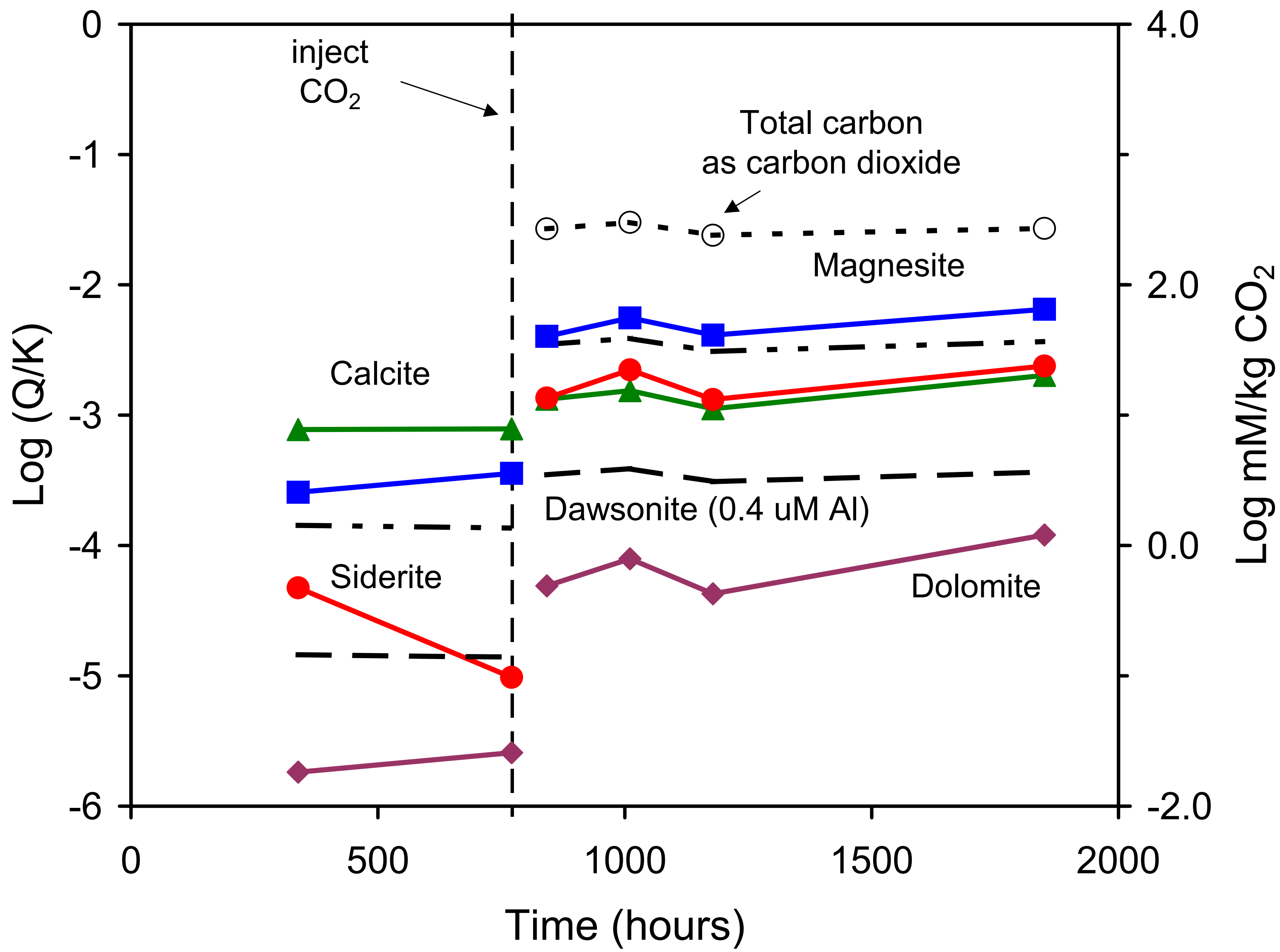


# Pressure Evolution in 1M NaCl Brine + Rock



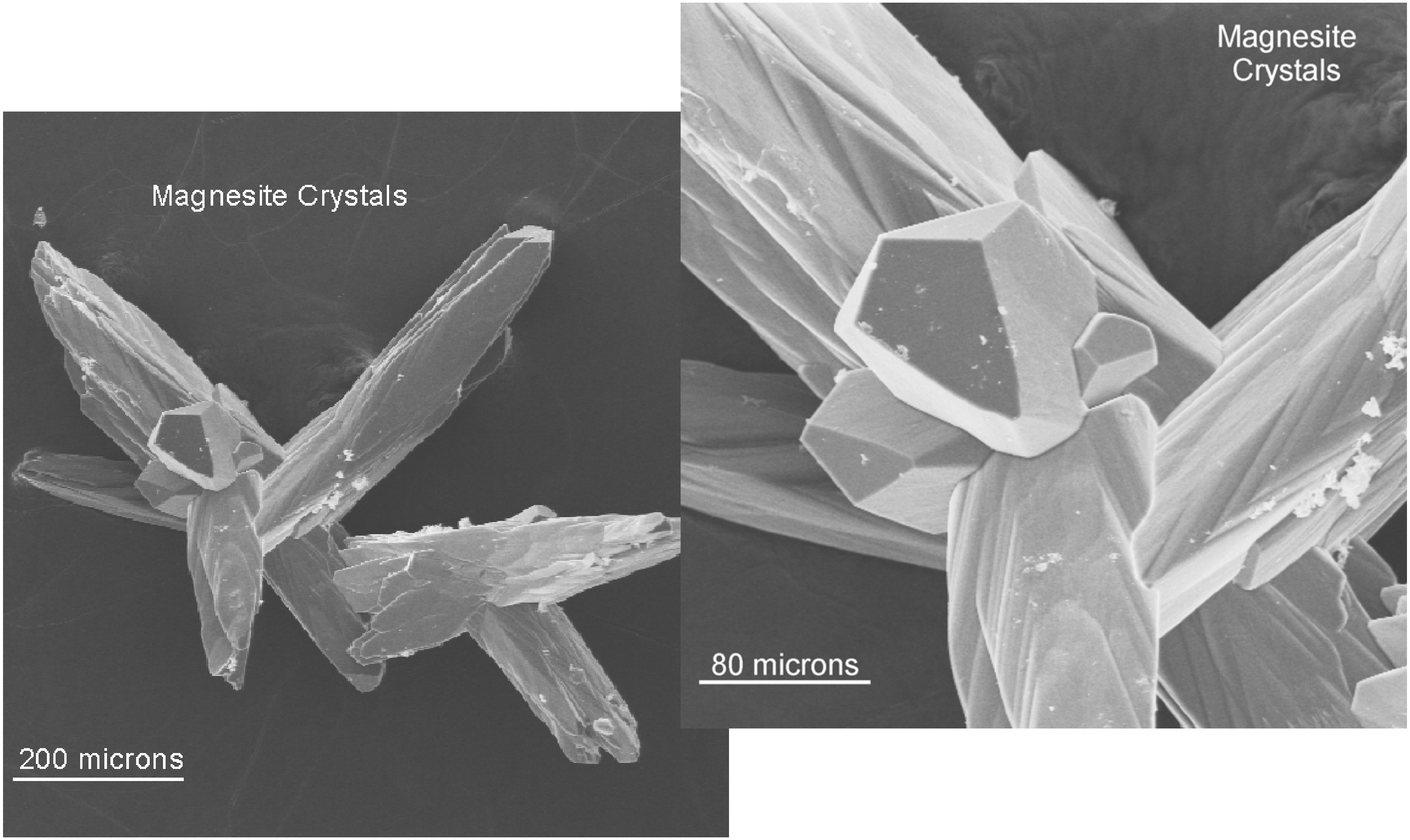

**after Kaszuba *et al.*, 2006 submitted**

# Brine Chemistry – Saturation States



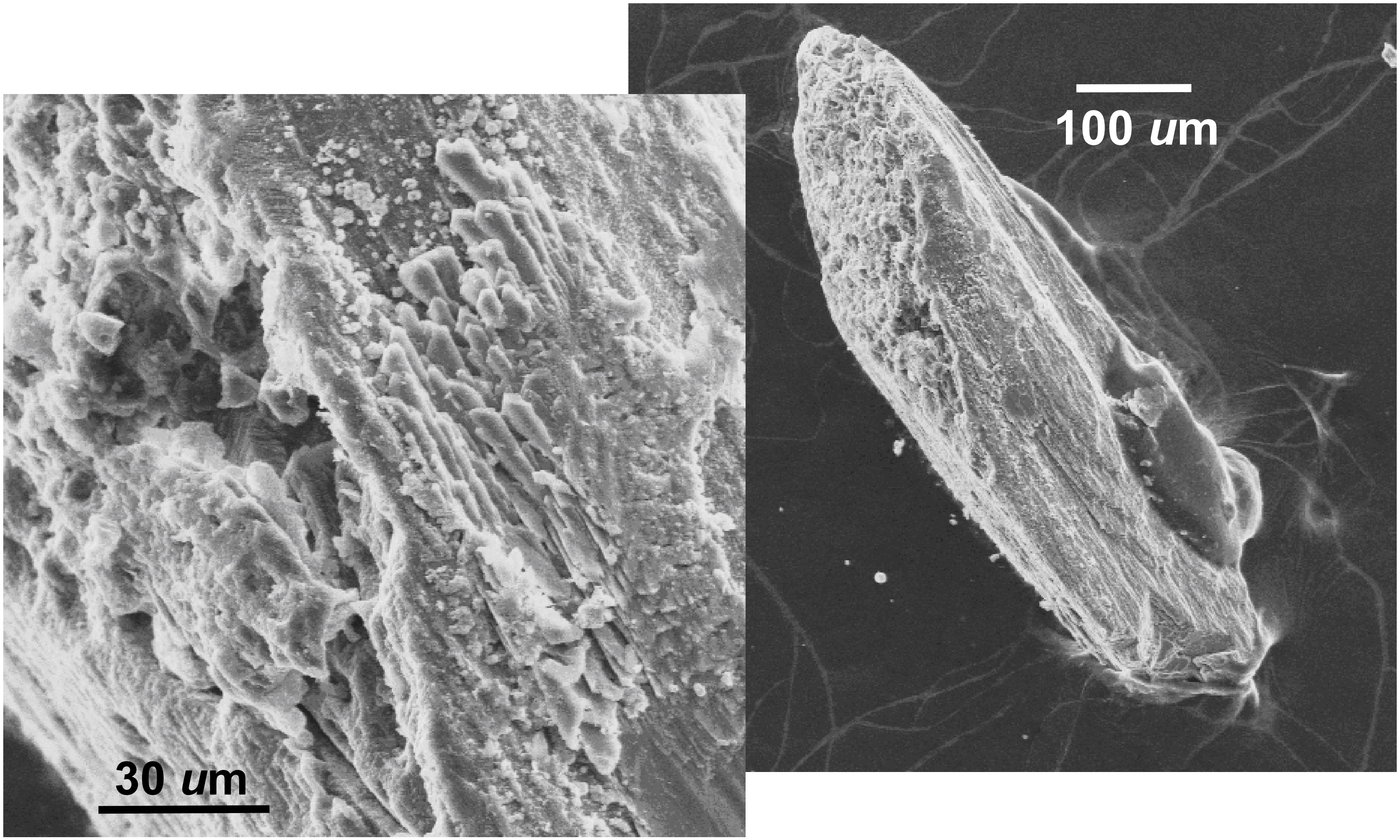

**after Kaszuba *et al.*, 2005**

# Magnesite (Mg Brine)



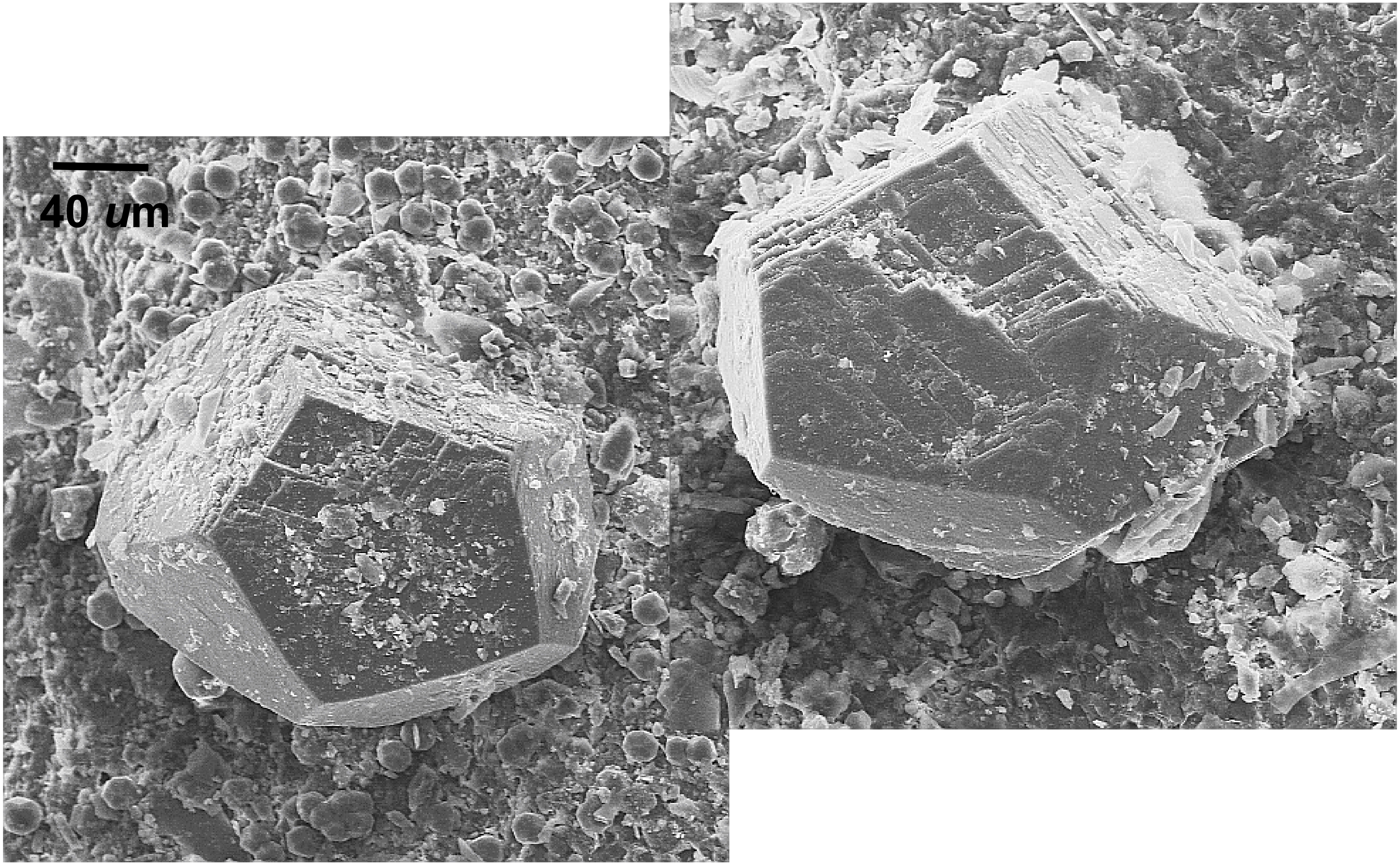

**after Kaszuba *et al*., 2003**

# Magnesite (NaCl Brine)




after Kaszuba *et al.*, 2005

# Siderite (NaCl Brine)




after Kaszuba *et al*., 2005

# Summary

- Reaction among supercritical carbon dioxide, brine, and rock exhibits relatively rapid kinetics
- Experiment and model compare well for equilibrium end state for $CO_2$ solubility (Duan et al., 2006), free $CO_2$ volume
- Experiment and model do not compare well for prediction of mineral phases at measured T, P
- Next steps
  - Initial overpressure
  - Kinetic model
  - minerals

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# Carbon Dioxide Solubility and Mineral Trapping Estimates

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Once it is injected into a brine aquifer, how long does it take supercritical $CO_2$ to carbonate and acidify brine and induce subsequent chemical reaction within reservoir rock? How rapid is the shift from a rock-dominated to a fluid-dominated system? A variety of geochemical rate processes are implicit in these questions, including dissolution of supercritical $CO_2$, formation and dissociation of carbonic acid, and dissolution and re-precipitation of minerals in acidic brine.

In closed system laboratory experiments, we recreate the geochemical conditions of a carbon repository at steady state, wherein brine, rock, and supercritical $CO_2$ coexist. We estimate overall kinetic rates for the variety of processes as identified in the previous paragraph by measuring the pressure changes that accompany the addition of supercritical $CO_2$ into ongoing brine-rock reactions. For example, following an initial pressure increase (5.8 MPa) due to injection of $CO_2$ into a steady state brine-rock (siliciclastic aquifer and illite-rich shale caprock) system at 20 MPa, pressure decreases 2.4 MPa within ~40 hours and subsequently remains stable at ~23 MPa for the life of the experiment. The pressure decrease is interpreted as a decrease in the volume of the system due to consumption of supercritical $CO_2$ by dissolution into brine and subsequent reaction with aquifer to produce carbonate mineral. We model a full suite of laboratory experiments, including different siliciclastic, mafic, and ultramafic rock aquifers, shales, and $CO_2$+$H_2O$ fluids, using geochemical simulations to help identify the processes that are revealed by the overall kinetic rate measured in the experiments.

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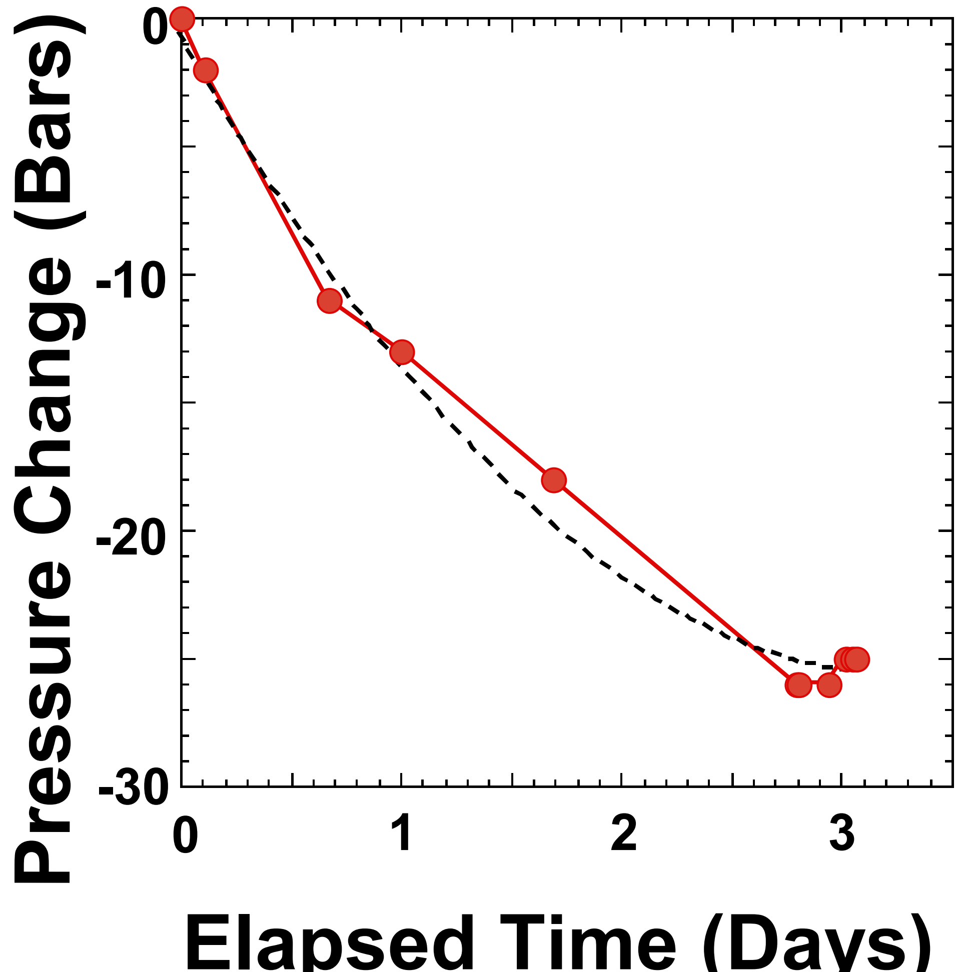
# Change in Pressure after Injection of $CO_2$




- increased 30 bars following injection
- decreased 26 bars over 3 days
- interpret as consumption of supercritical $CO_2$ and precipitation of carbonate mineral

after Kaszuba *et al.*, 2003