Geochemistry of Magnesium Silicate Carbonation in an Aqueous Medium (Carbon Mineralization)

Jon Benner, Deb Bergfeld, Dave Bish, Darrin Byler, Bill Carey, Steve Chipera, George Guthrie, Klaus Lackner, Hans Ziock

Hydrology, Geochemistry, Geology Group
Los Alamos National Laboratory

LA-UR-01-4206

George Guthrie
gguthrie@lanl.gov
505-665-6340

Mineral Carbonation:
Conversion of CO_2 into Carbonates

- alkali carbonates too soluble
- alkaline earth carbonates ideal

sources:

Ca-silicates (feldspar)

Mg-silicates (olivine, serpentine, clays)

$$\mathbf{Mg_2SiO_4 + 4H^+ \Rightarrow 2Mg^{2+} + SiO_{2(aq)}}$$

$$\mathbf{Mg^{2+} + CO_3^{2-} \Rightarrow MgCO_3}$$

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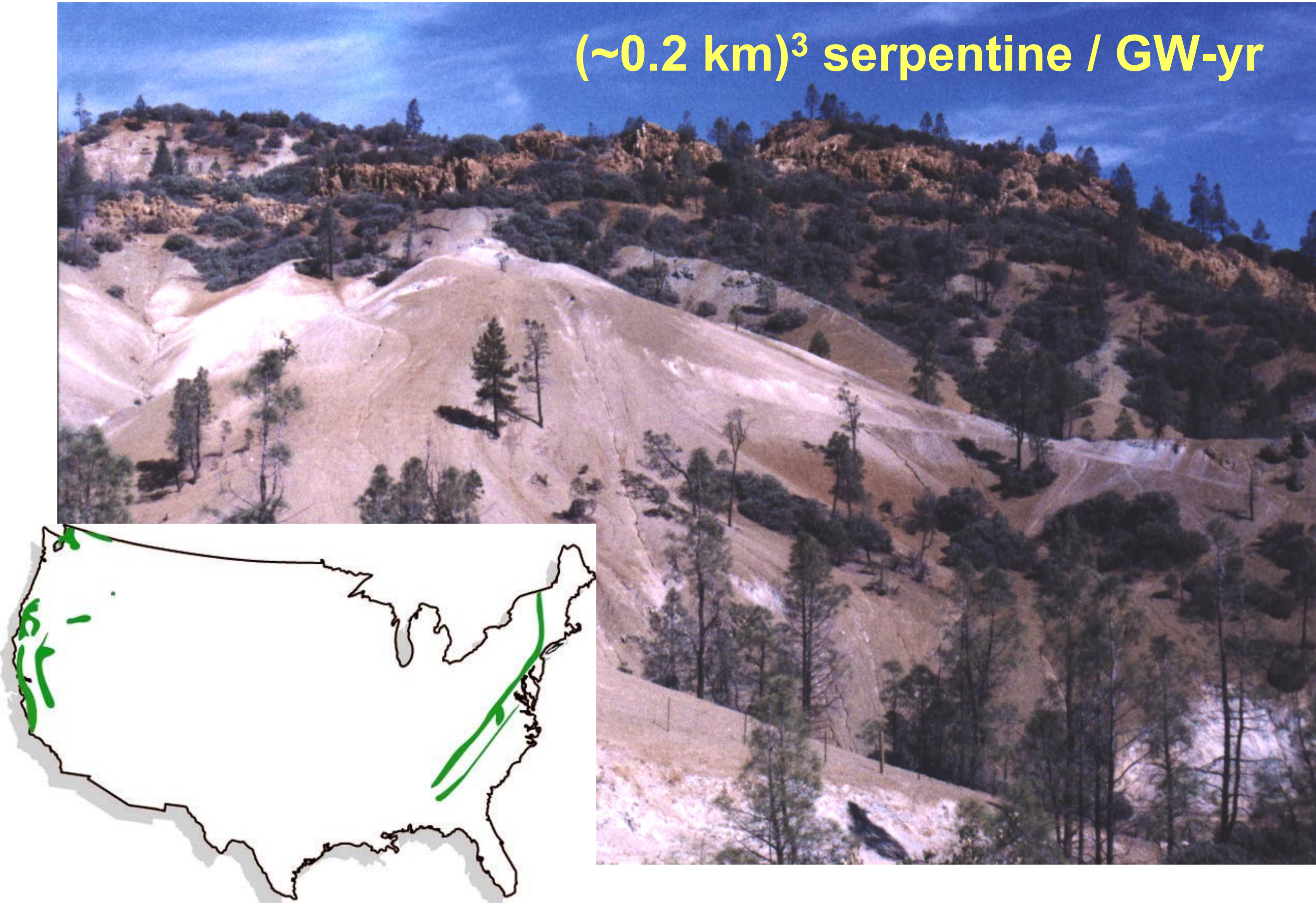
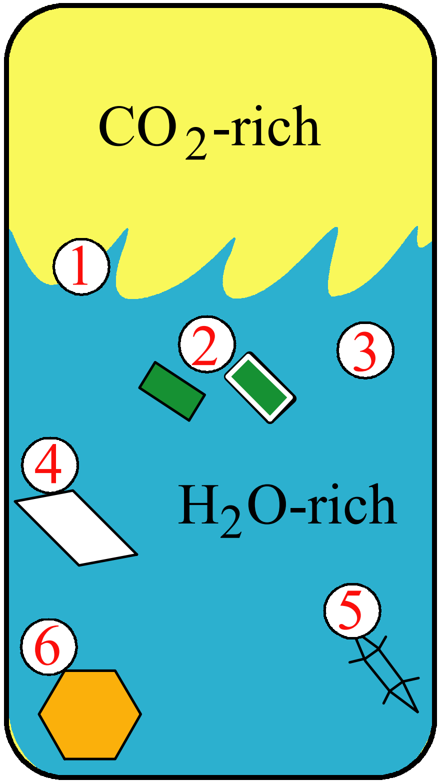
Ultramafic rocks are an abundant Mg source



Challenges for Mineral-Carbonation

- **thermodynamic optimization**
  - **What conditions are necessary for carbonation?**
- **kinetic optimization**
  - **What controls carbonation rate?**
  - **Is carbonation rate sufficient for a power plant?**
    (1 GW plant = 20kton CO_2/day = ~$5x10^3$ mol/sec)



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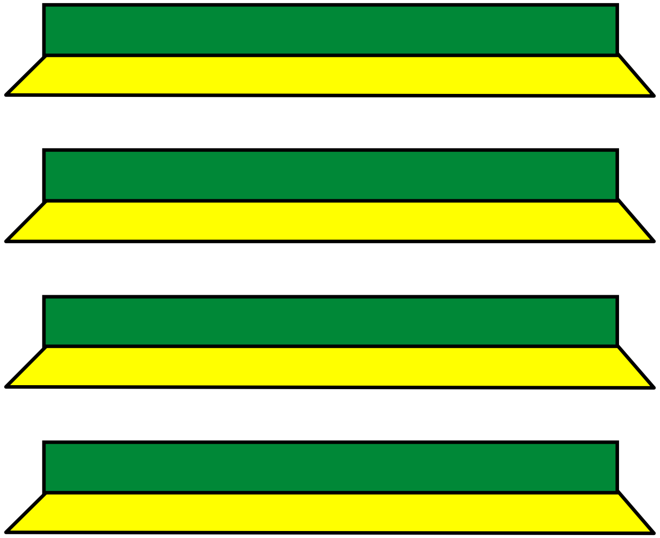
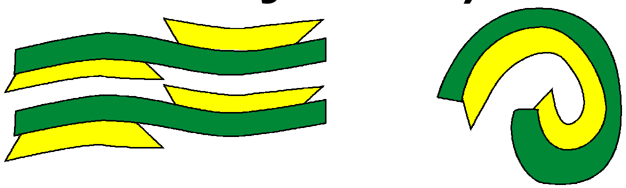
Serpentine and olivine are the common Mg silicates

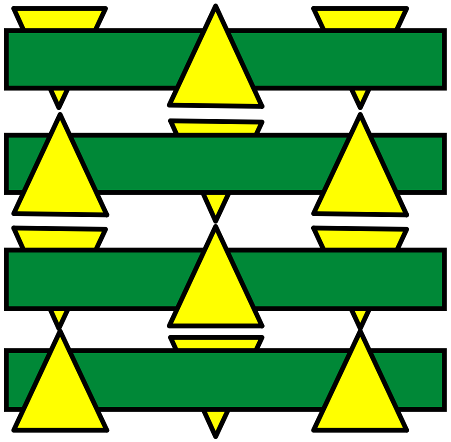
$Mg_3Si_2O_5(OH)_4$
serpentine



(lizardite, antigorite, chrysotile)



$Mg_4Si_2O_8$
olivine



(forsterite)

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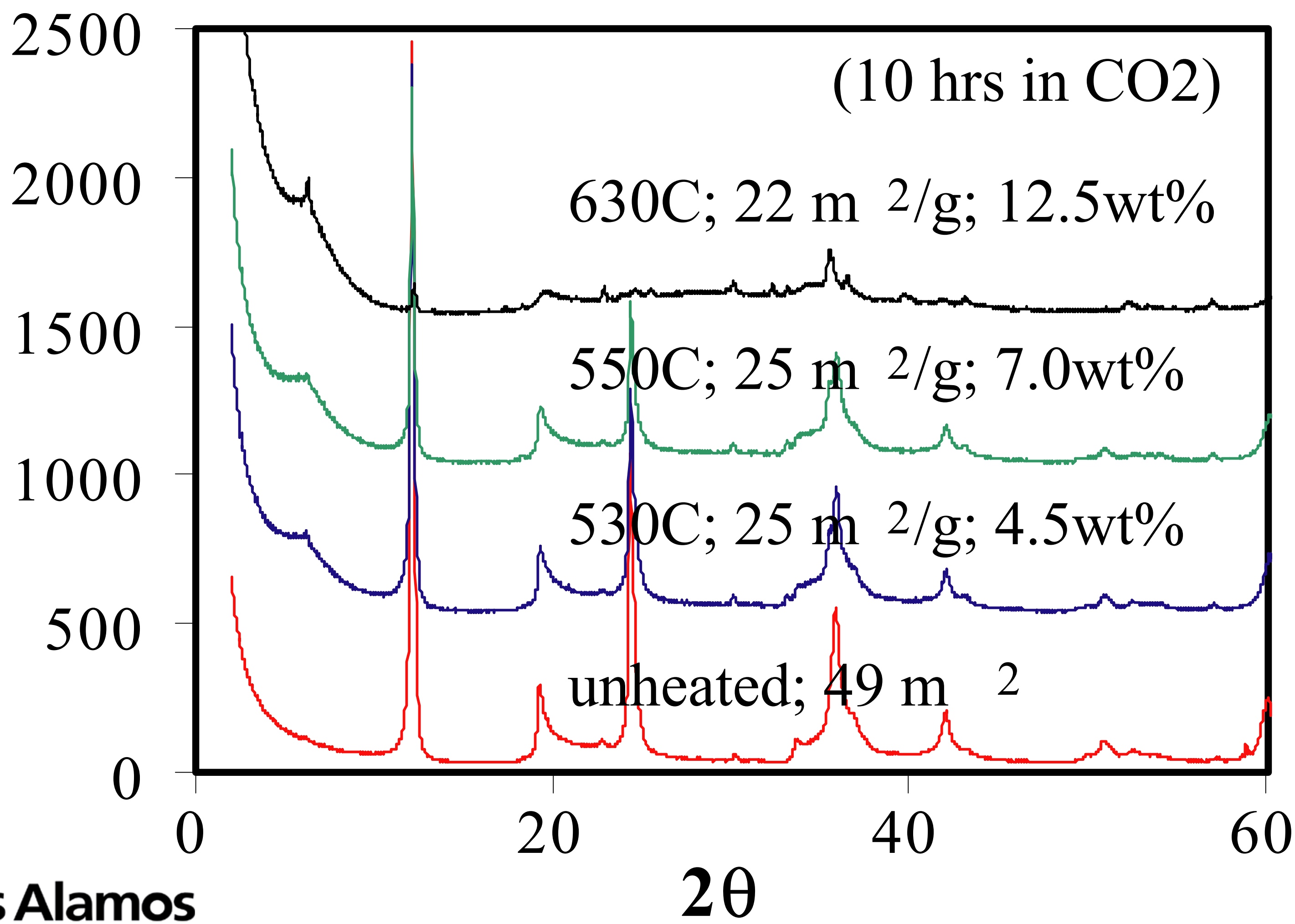
Heat treatment of serpentine

$$Mg_3Si_2O_5(OH)_4 = Mg_3Si_2O_5(O)_2 + 2H_2O \ ?$$



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Magnesium Mineralogy

silicates

lizardite
antigorite
chrysotile
(HT serpentine)

forsterite

talc

pyroxenes/amphiboles

carbonates

magnesite

hydromagnesite

nesquehonite

artinite

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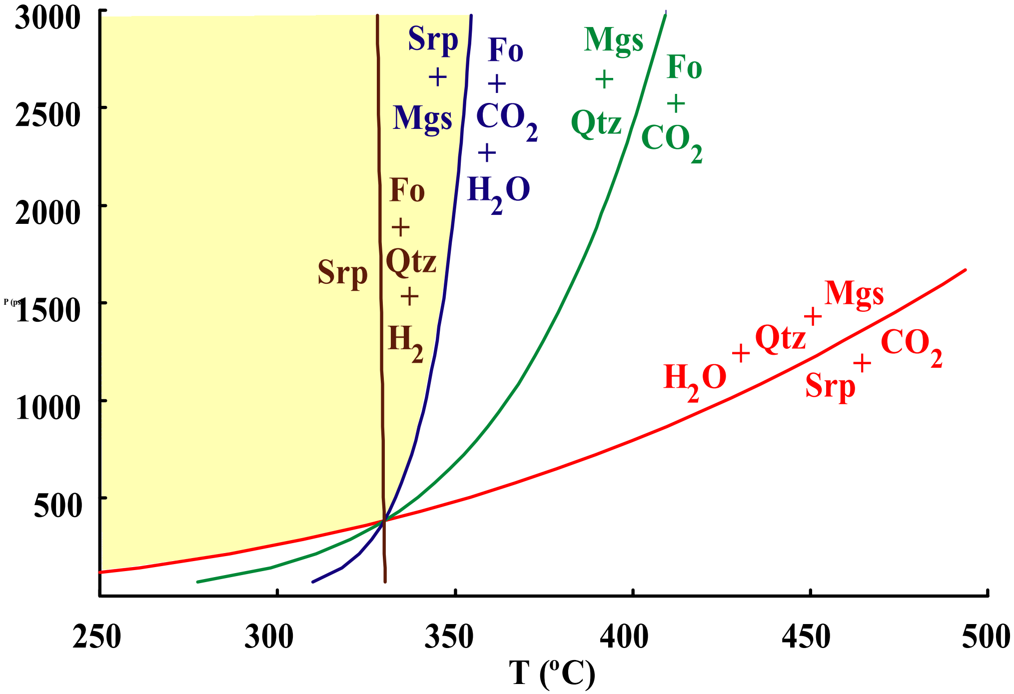
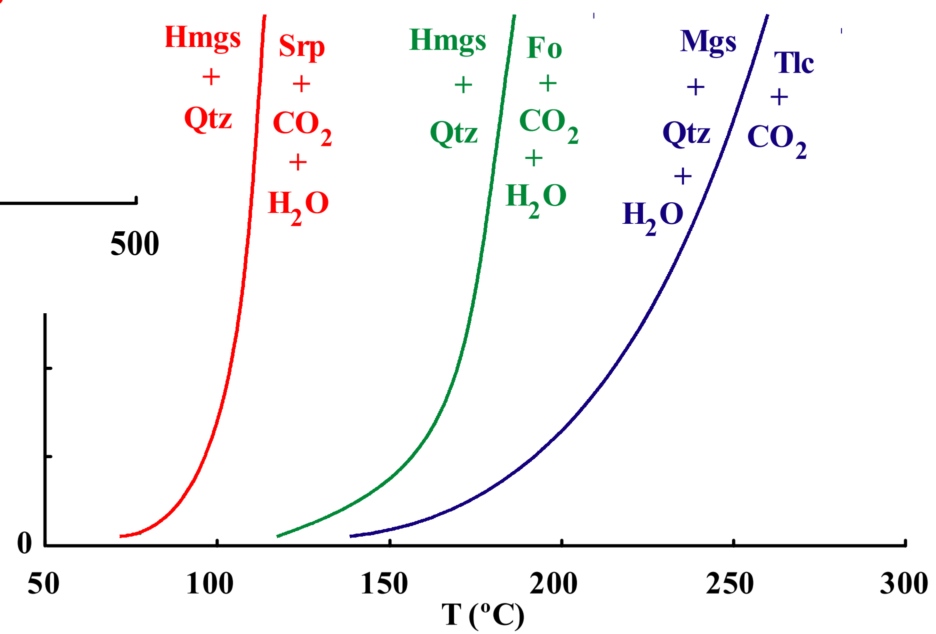
Thermodynamic Constraints in a Multicomponent System





Mgs=magnesite

Srp=serpentine

Fo=forsterite

Qtz=quartz

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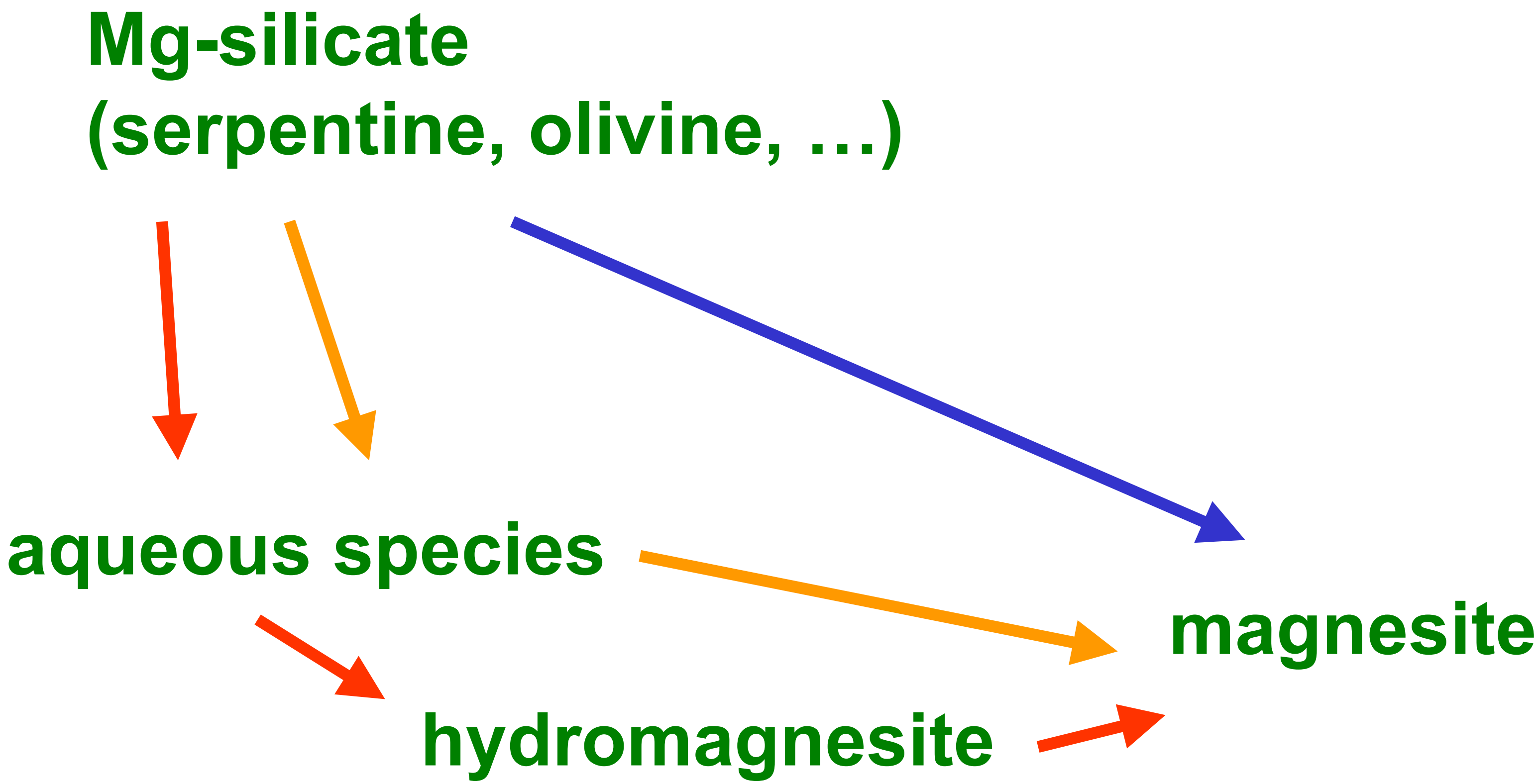
Possible Pathways for Magnesium Silicate Carbonation in an Aqueous Medium



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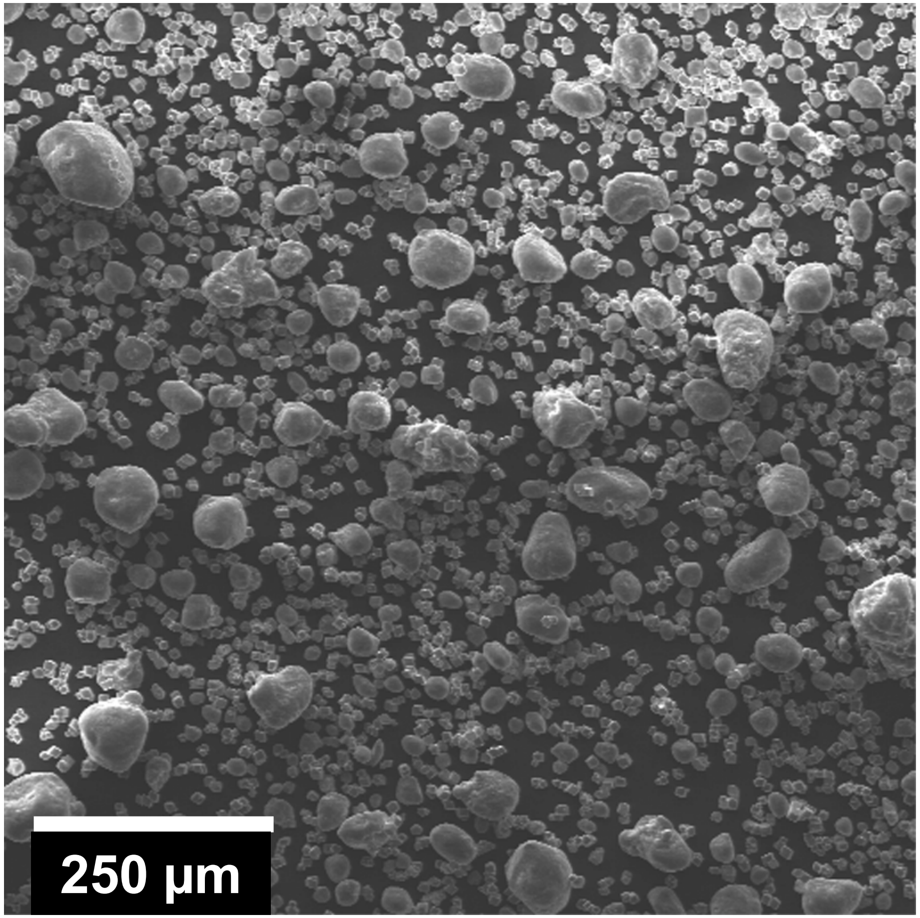
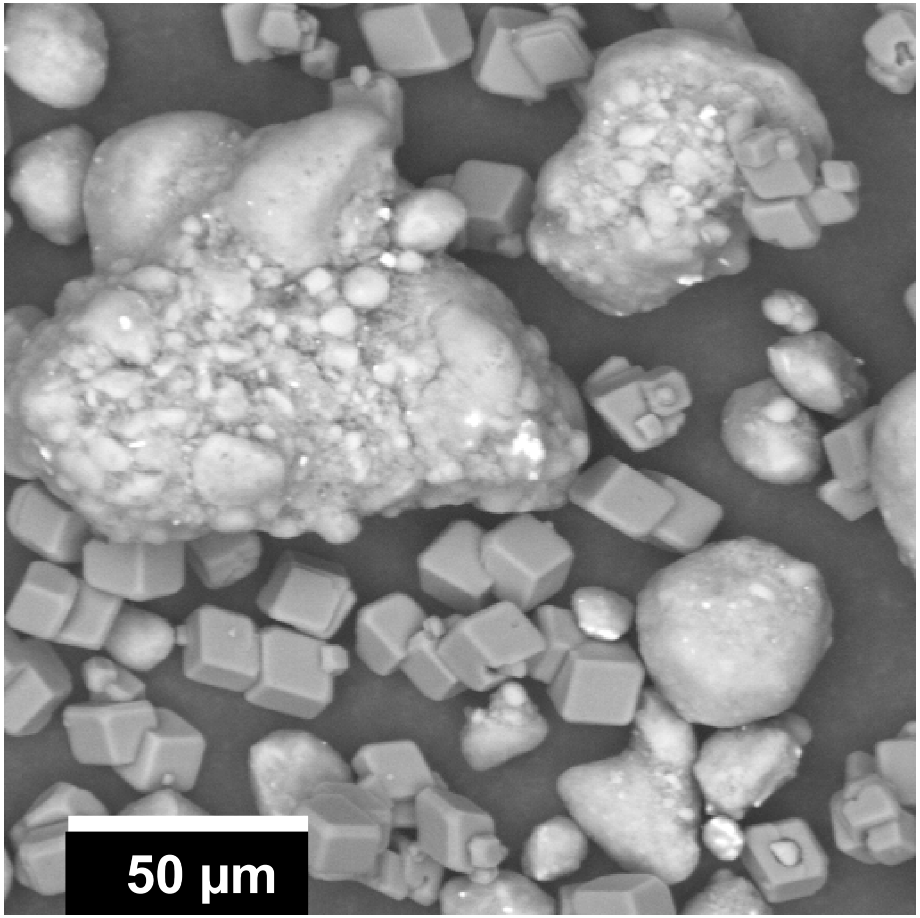
Autoclave results are consistent with a dissolution-precipitation mechanism





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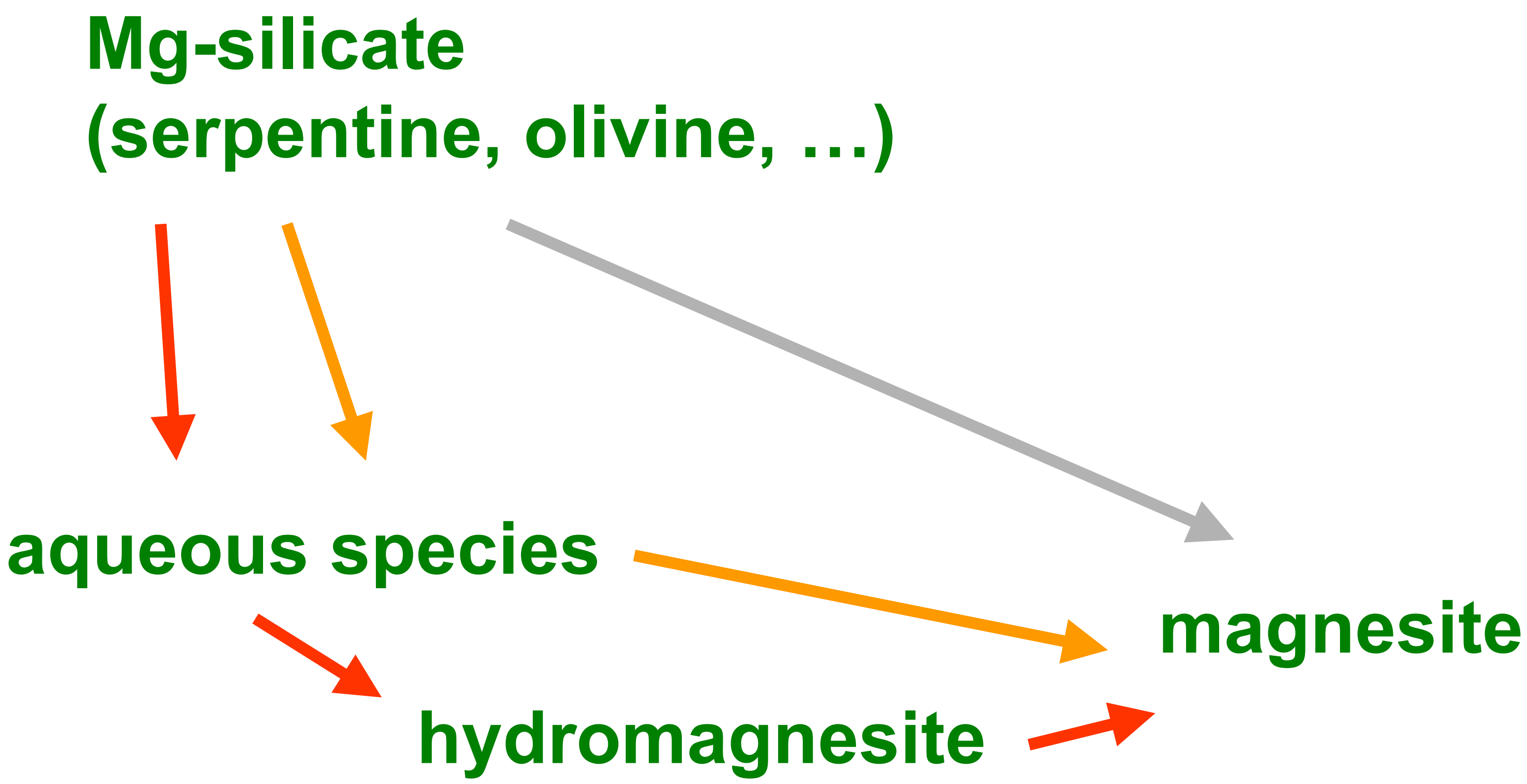
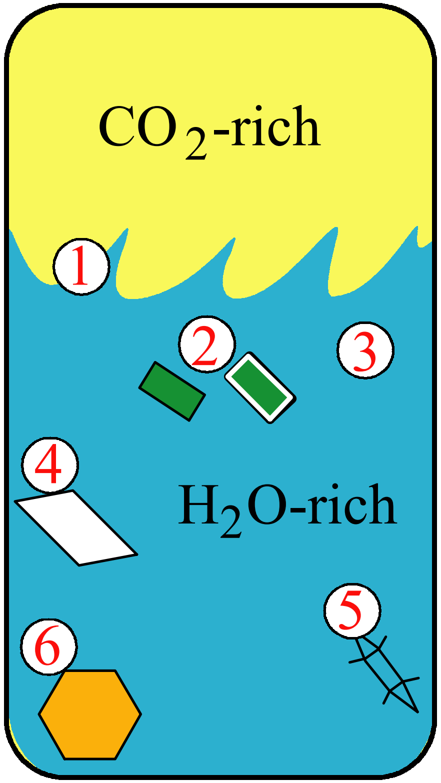
Possible Pathways for Magnesium Silicate Carbonation in an Aqueous Medium



Challenges for Mineral-Carbonation

- **thermodynamic optimization**
  - **What conditions are necessary for carbonation?**

- **kinetic optimization**
  - **What controls carbonation rate?**



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Will the reaction go?
(Thermodynamic Considerations)

$$\Delta G_{PTX} = \Delta H_{STD} - T\Delta S_{STD} + \text{“P”} + \text{“T”} + \text{“X”} = 0$$

ideal correction = f(concentration)

non-ideal correction = ???

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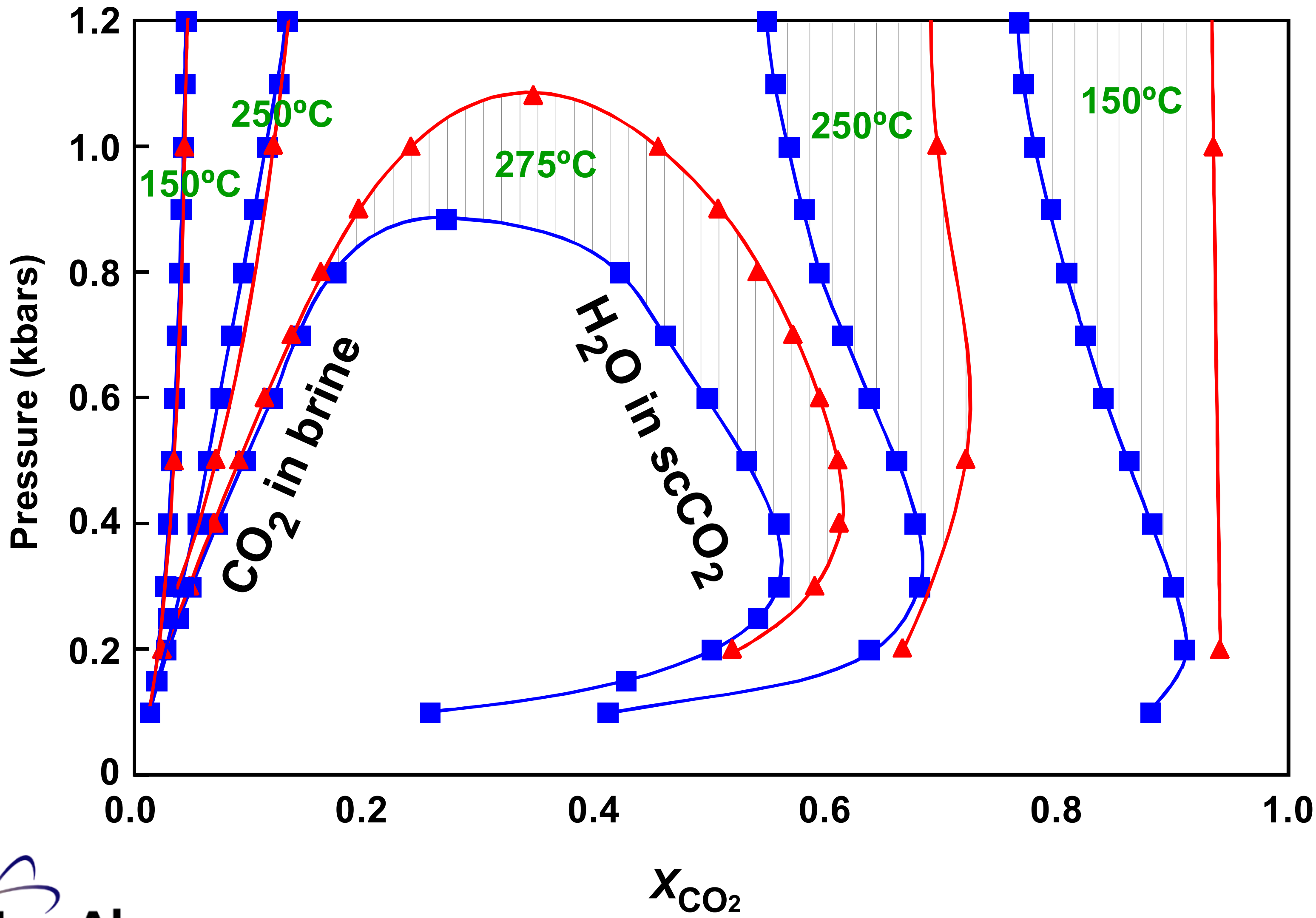
Uncertainty in Pure CO_2-H_2O Fluids



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Will the reaction go?
(Thermodynamic Considerations)

$\Delta G_{PTX} = \Delta H_{STD} - T\Delta S_{STD}$ + "P" + "T" + "X" = 0

Mg-silicate → aqueous species

aqueous species → Mg-carbonate
silica

log (Q/K_{sp}) is a measure of fluid saturation state

$K_{sp} = [a_{Mg++}]\,[a_{CO3--}]$ (magnesite ppt)

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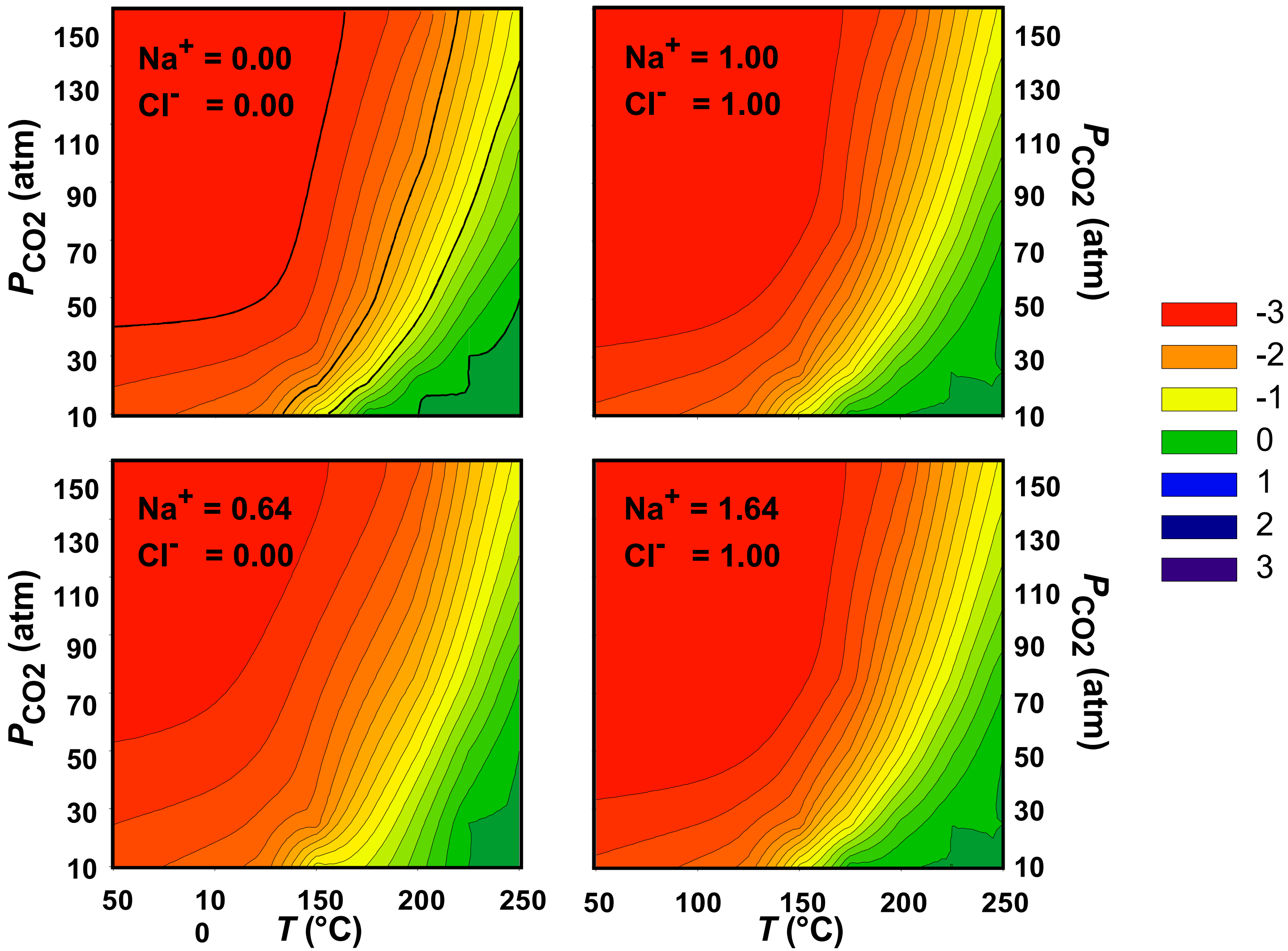
Finding the Geochemical Sweet Spot: Chrysotile Saturation State (log [Q/K])



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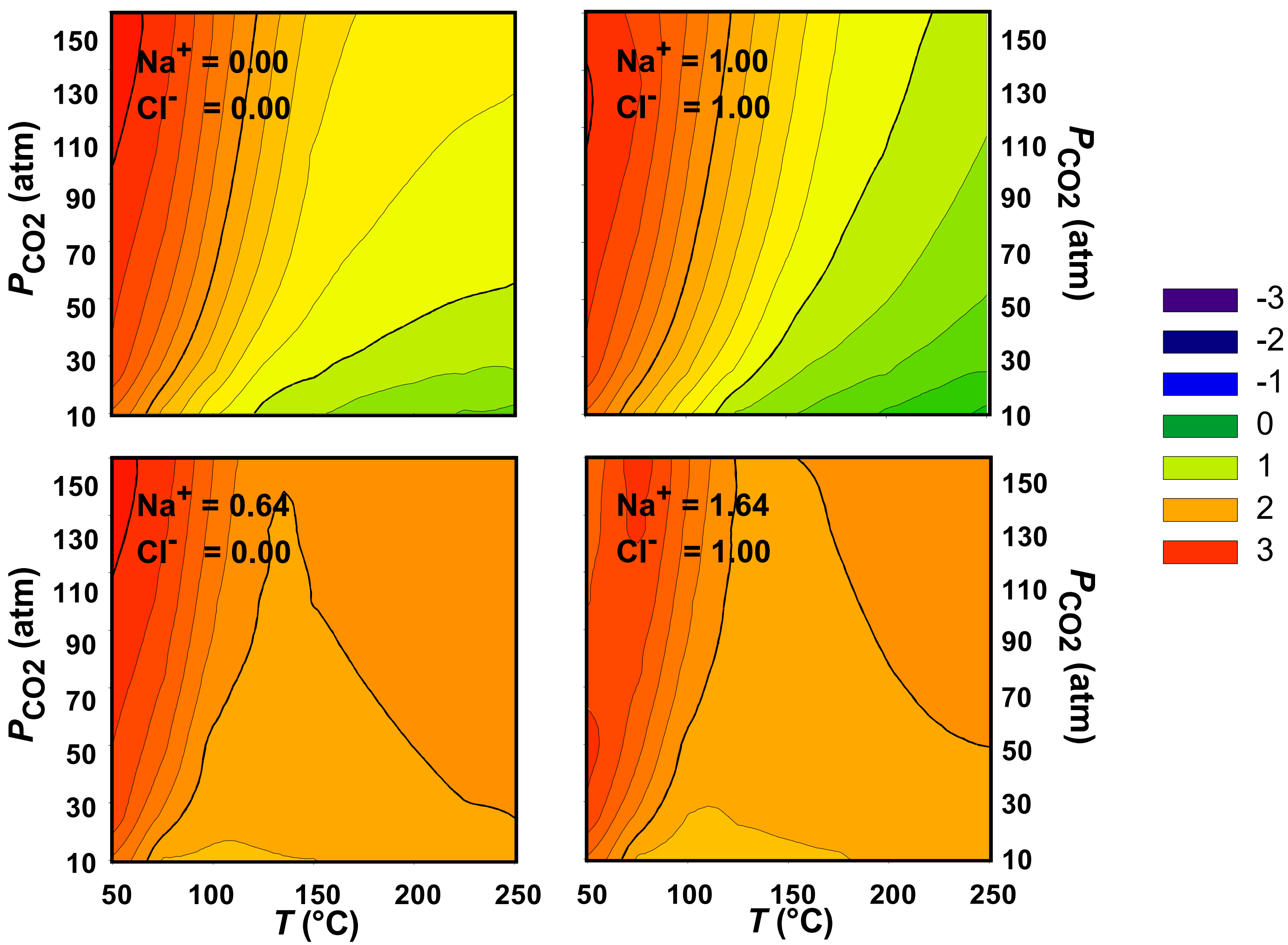
Finding the Geochemical Sweet Spot: Magnesite Saturation State (log [Q/K])



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Finding the Geochemical Sweet Spot: Kinetic Considerations

- **What is the rate of carbonation?**
  - **autoclave experiments on aqueous system**
  - **geochemical modeling**

- **What controls the rate of carbonation?**
  - **autoclave experiments on aqueous system**
  - **batch dissolution experiments**
  - **geochemical modeling**
  - **mineralogical/structural analysis**

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Stirred Autoclave Experiments
(~1.8 litres; ~120-250 ºC; ~10-2500 psi)

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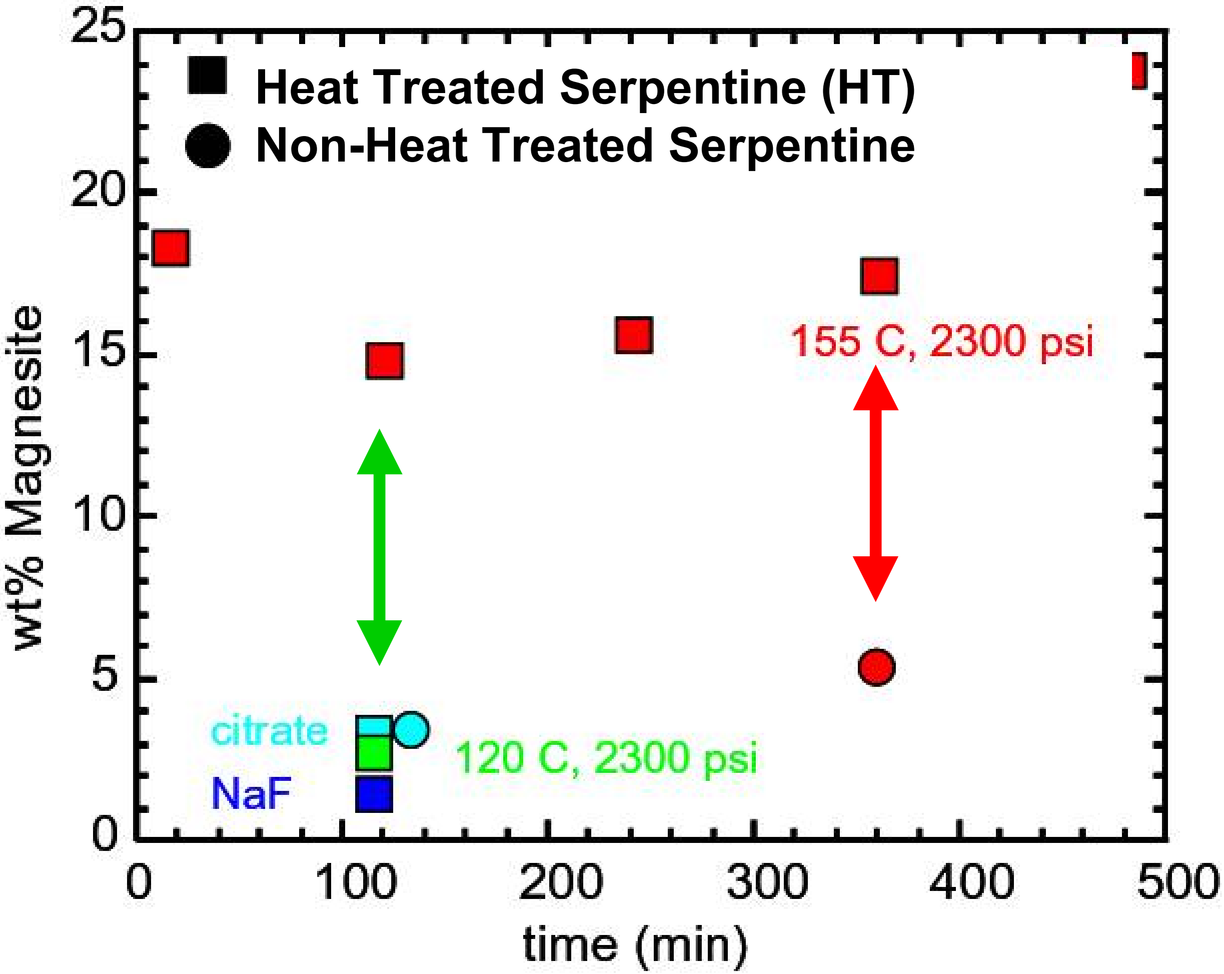
Summary of Autoclave Experiments



HT increases carbonation

HT carbonation rapid but plateaus

T increases carbonation

silica modifiers impact reaction

Na^+ increases carbonation

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Dissolution Kinetics of Minerals

- **surface-controlled dissolution**

  $$\text{rate}_{P,T} = k_{P,T}\ A\ \text{f}(\text{pH}, \text{Q/K}, I, T, a_{Na+})$$

- **diffusion-controlled dissolution**

  $$\text{rate}_{P,T} = k_{P,T}\ A\ \text{f}(t^{-0.5})$$

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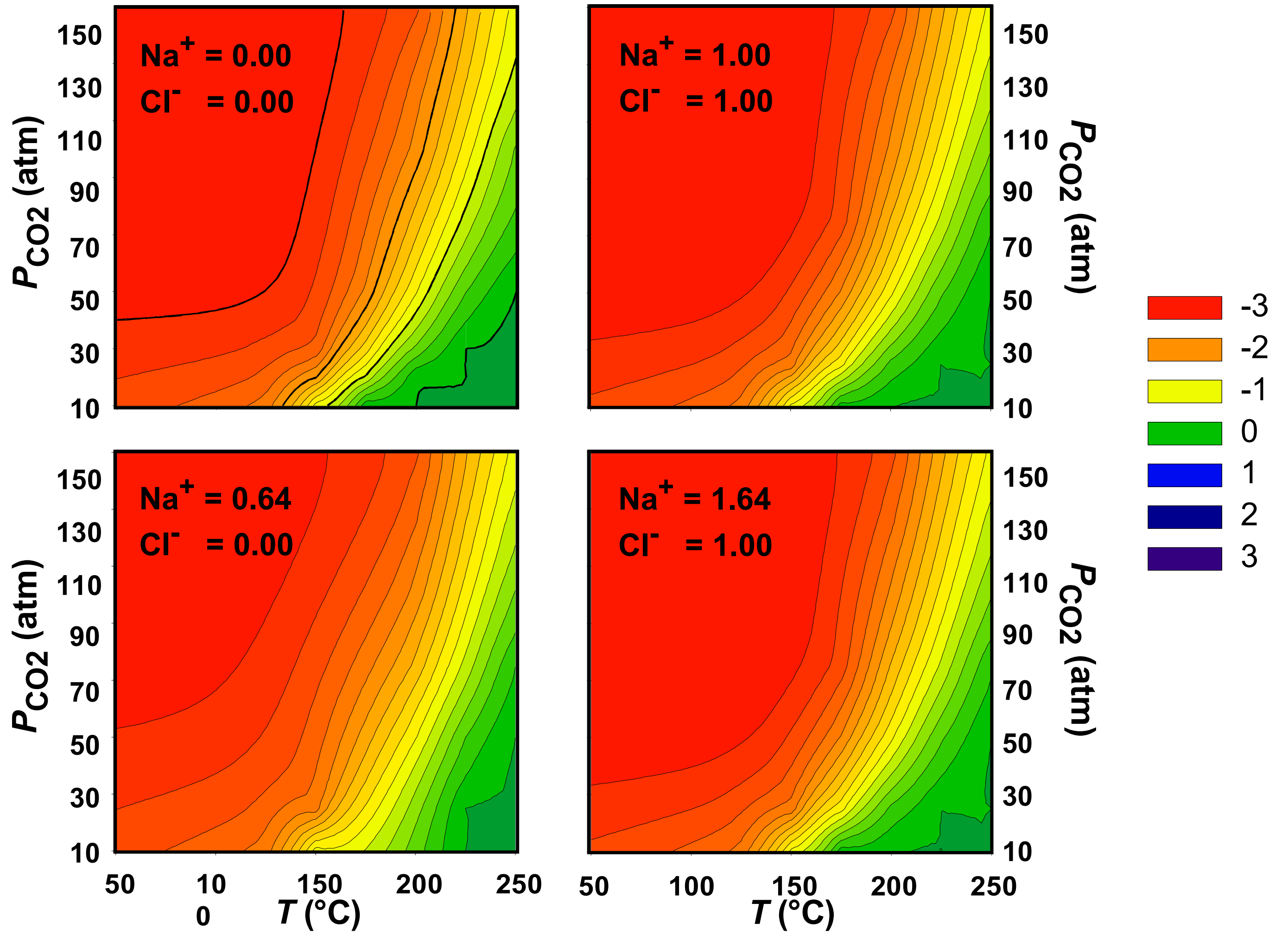
Finding the Geochemical Sweet Spot: Undersaturation speeds dissolution



Chrysotile Saturation State (log [Q/K])

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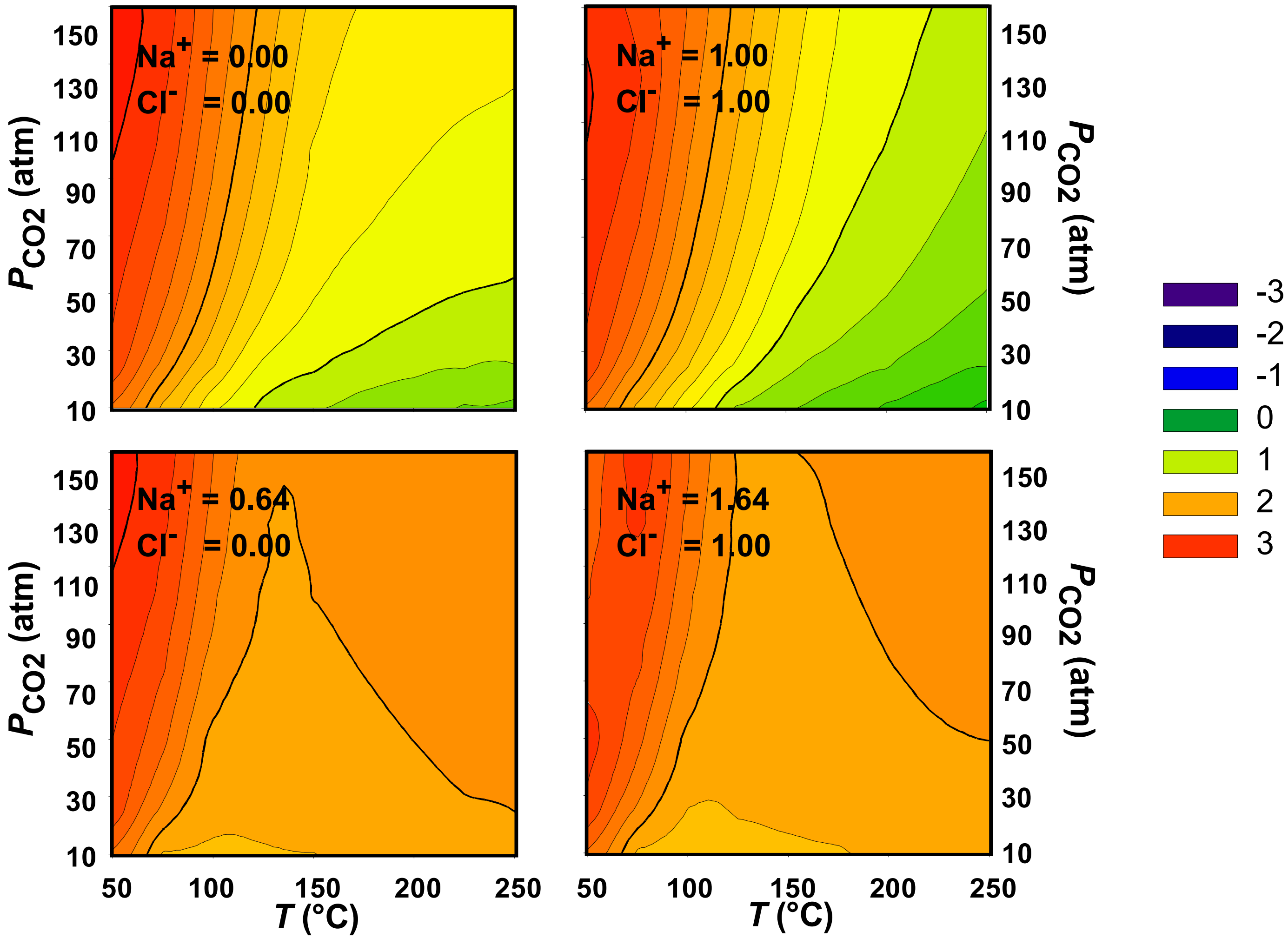
Finding the Geochemical Sweet Spot: Supersaturation promotes precipitation



Magnesite Saturation State (log [Q/K])

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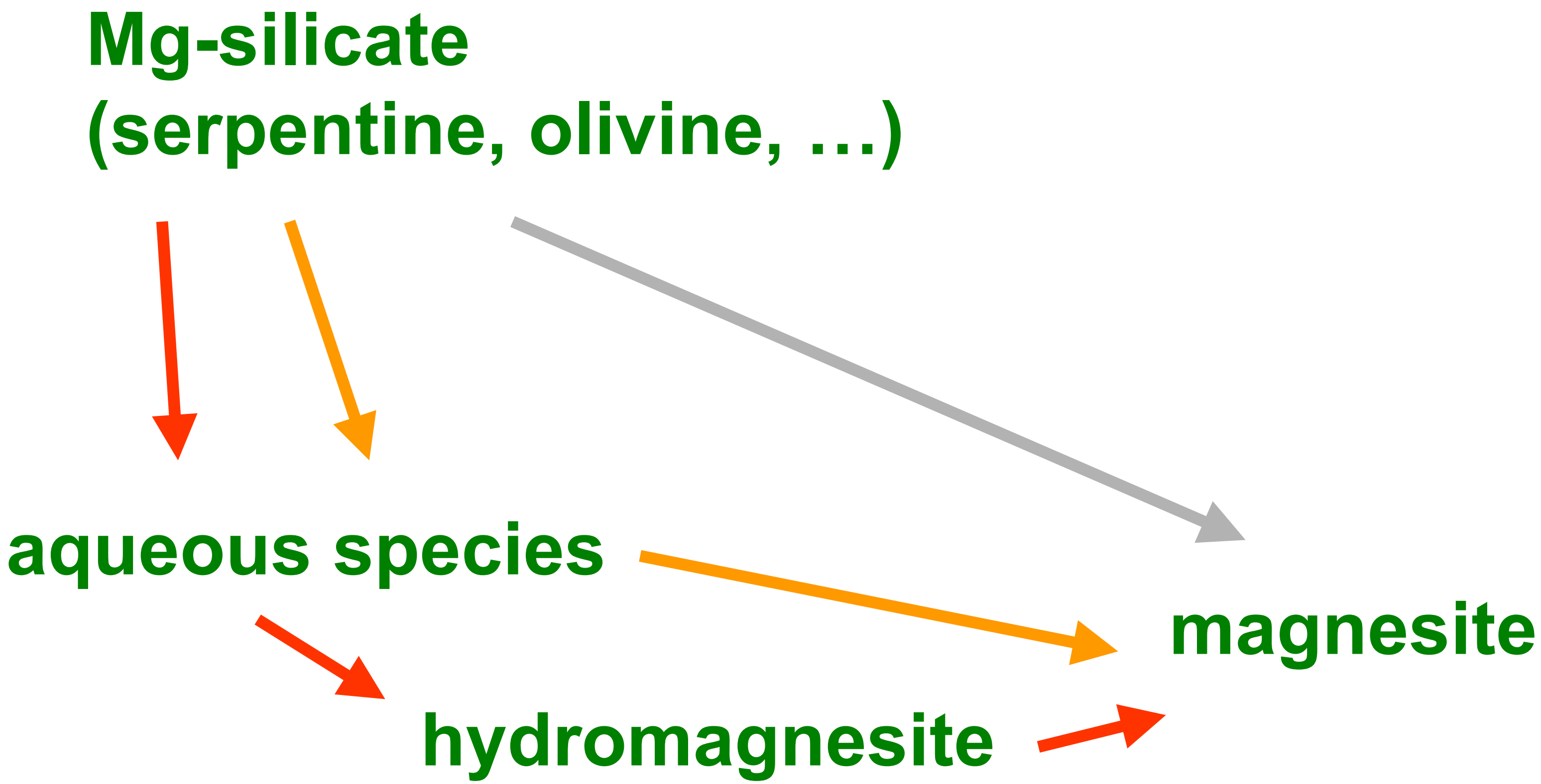
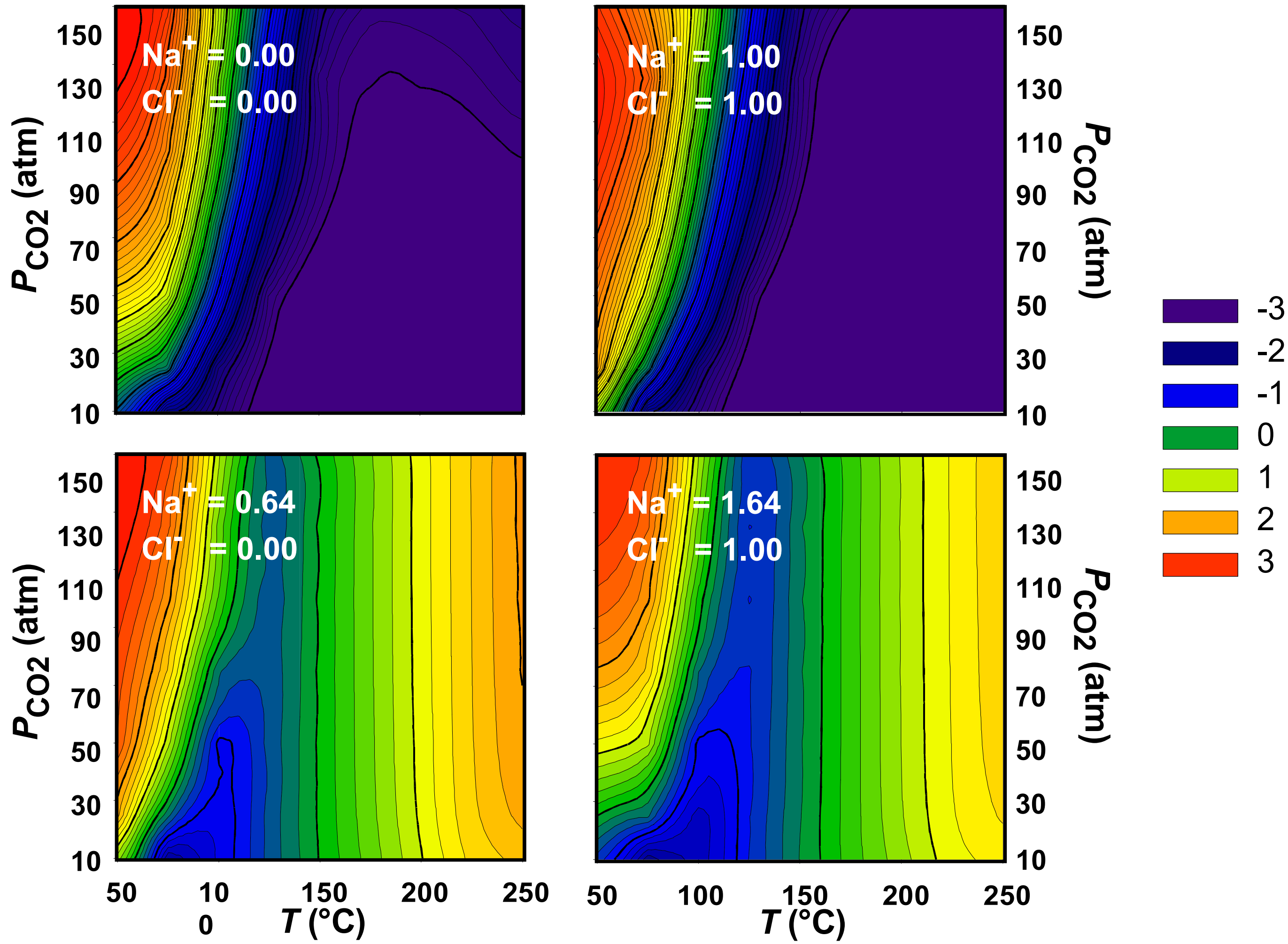


Finding the Geochemical Sweet Spot: Hydromagnesite is kinetically favored



Hydromagnesite Saturation State (log [Q/K])

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Dissolution Kinetics of Minerals

- **surface-controlled dissolution**

  $$\text{rate}_{P,T} = k_{P,T}\ A\ f(\text{pH}, Q/K, I, T, a_{Na+})$$

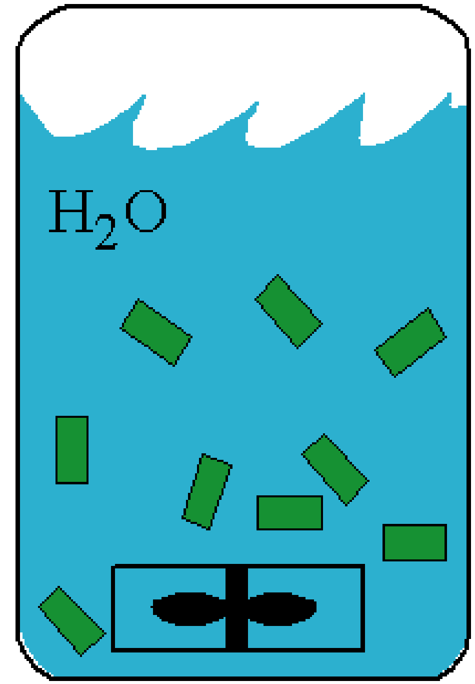
- **diffusion-controlled dissolution**

  $$\text{rate}_{P,T} = k_{P,T}\ A\ f(t^{-0.5})$$

at 25 °C

$Mg(OH)_2$	(k=10^{-5}-10^{-4} mol/m^2/sec)
MgO	(k=10^{-6} mol/m^2/sec)
olivine	(k=10^{-10}-10^{-8} mol/m^2/sec)
serpentine	(k=10^{-11}-10^{-9} mol/m^2/sec)

Batch experiments for investigating the dissolution properties



T = 40-80 °C

both "atmospheric" and CO_2-free systems

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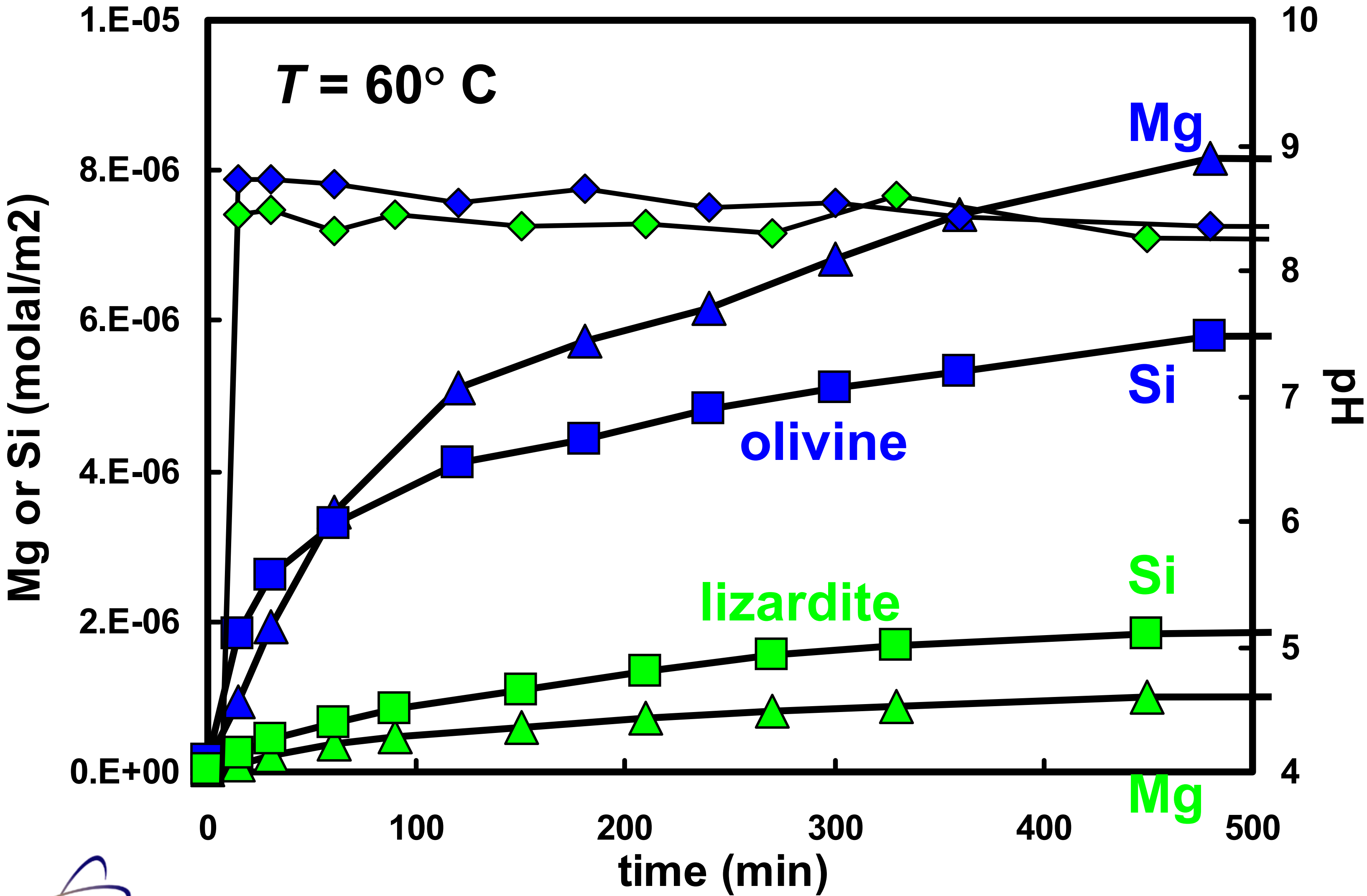
Olivine has much higher dissolution rate than lizardite



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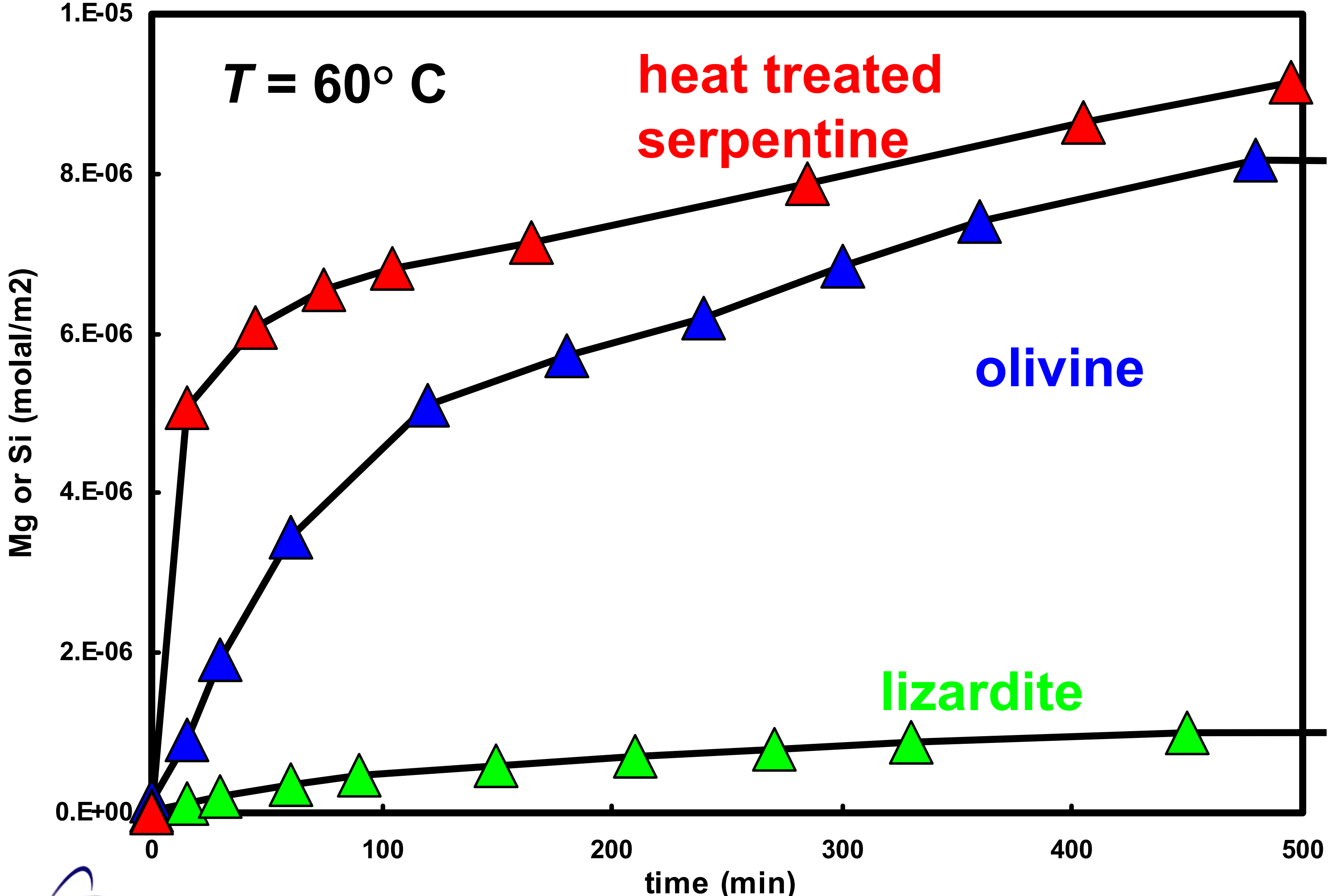
Heat treatment increases dissolution rate & solubility



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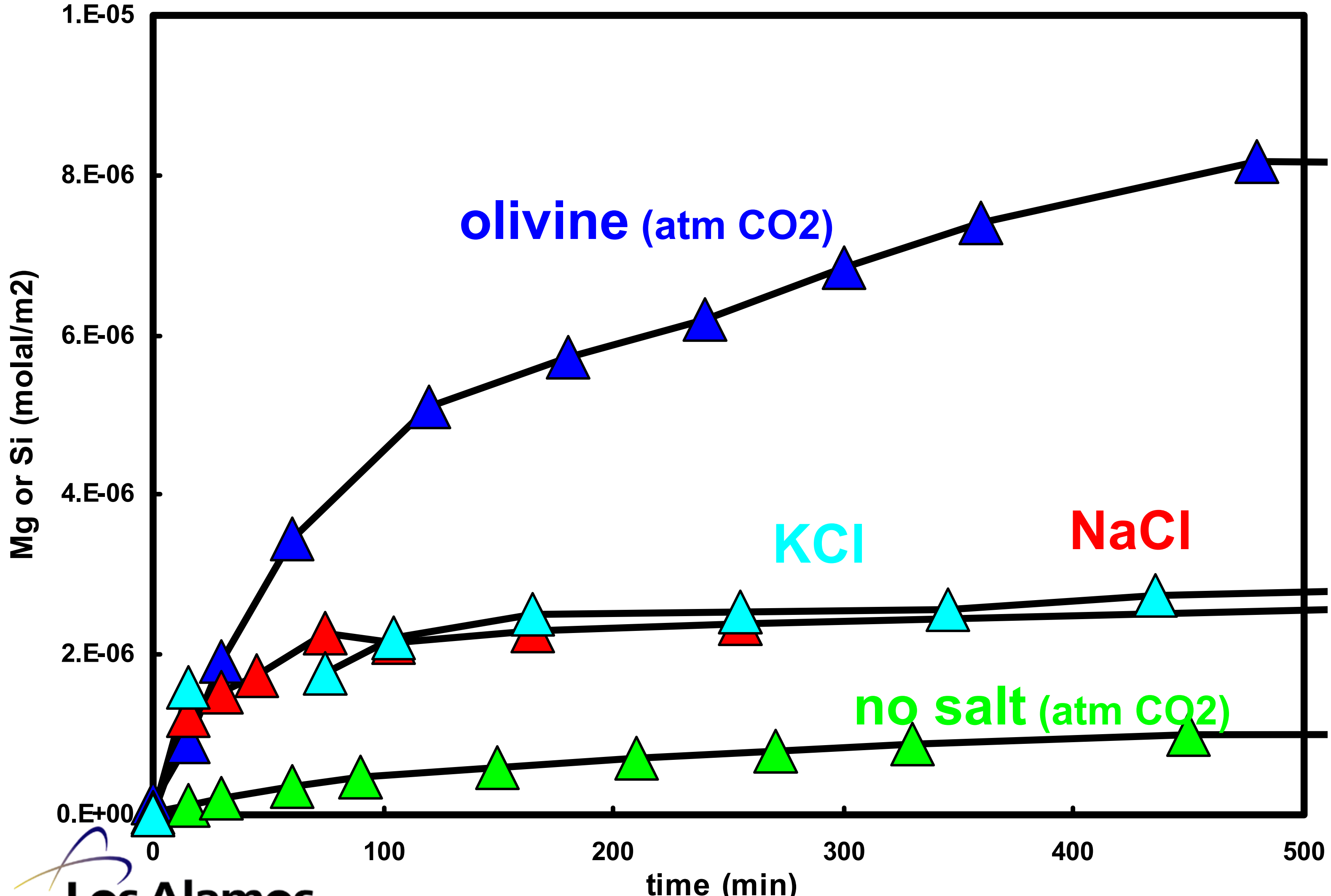
Effect of Na and K on Dissolution



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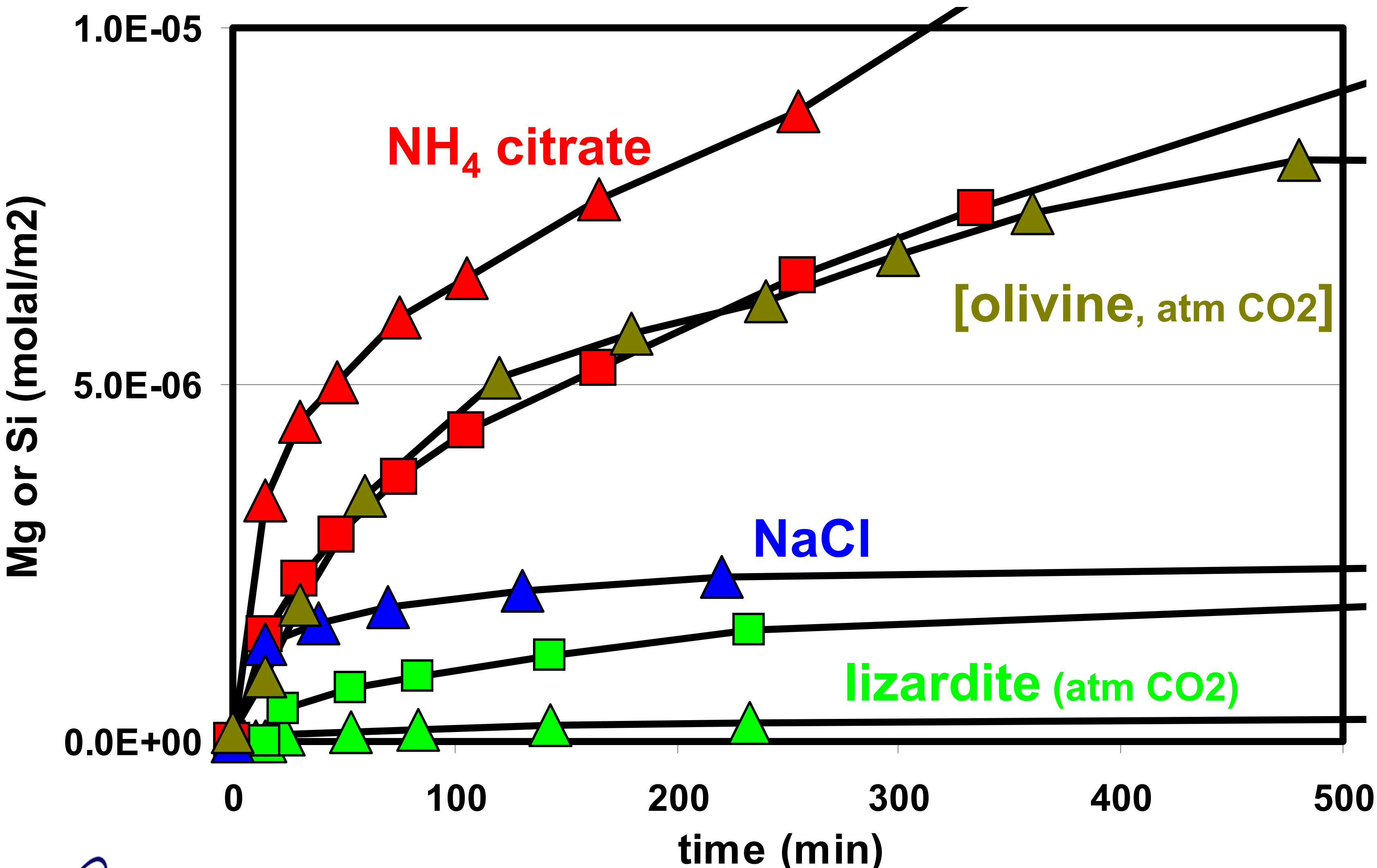
Citrate mobilizes silica and Mg^{2+}



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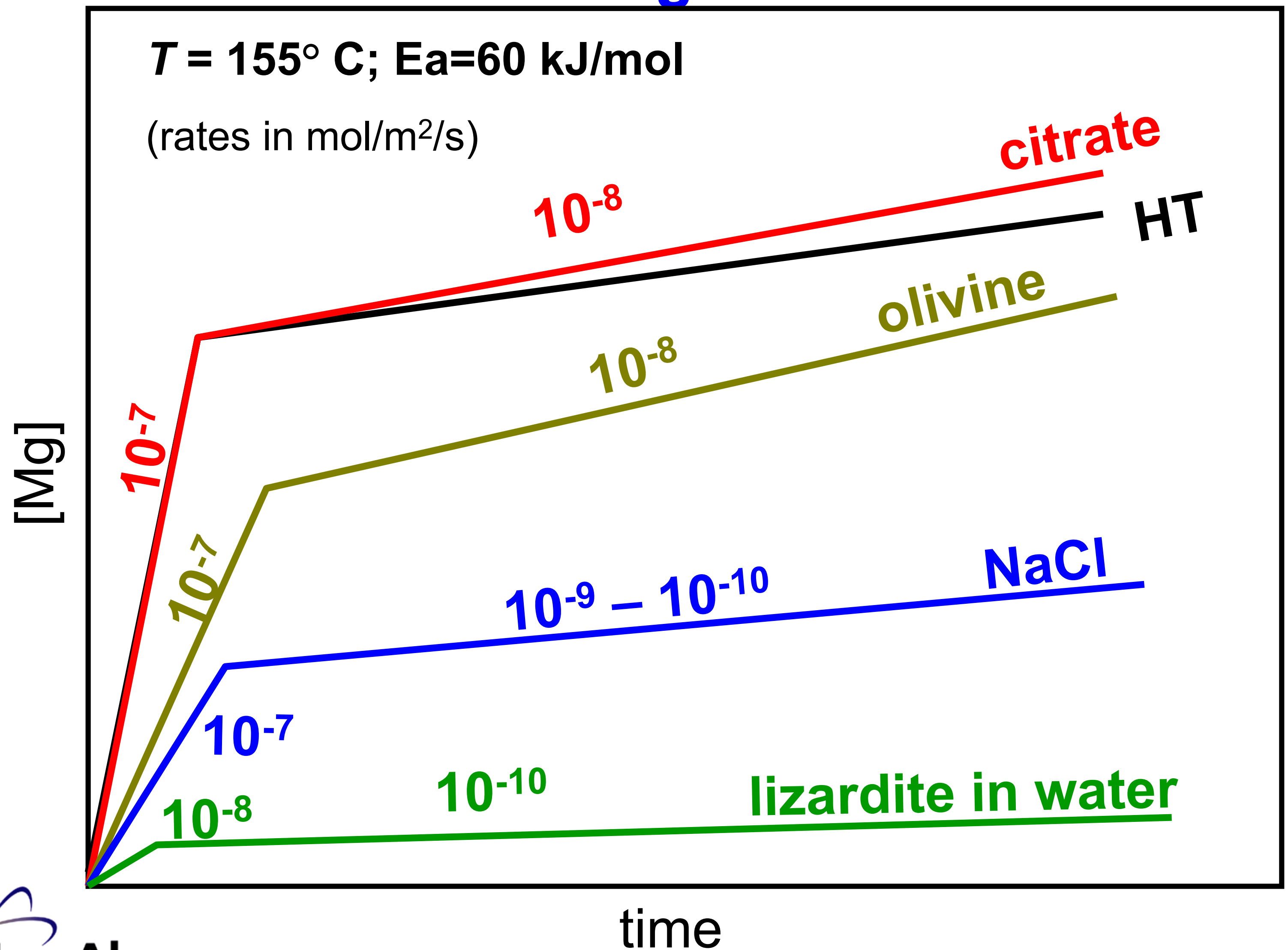
General Aspects of Dissolution Rates for the Mg Silicates



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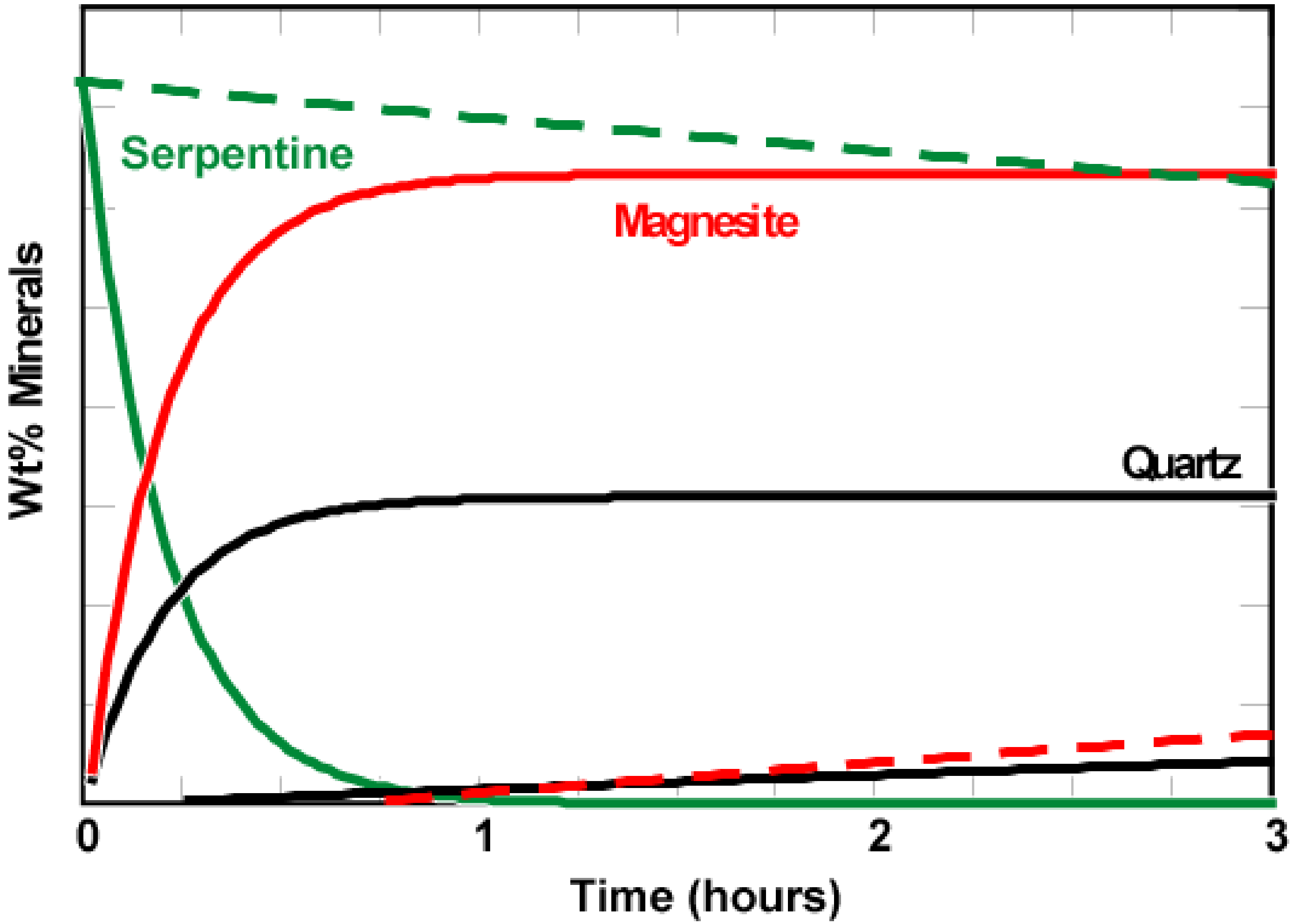
Dissolution can explain many of the carbonation observations



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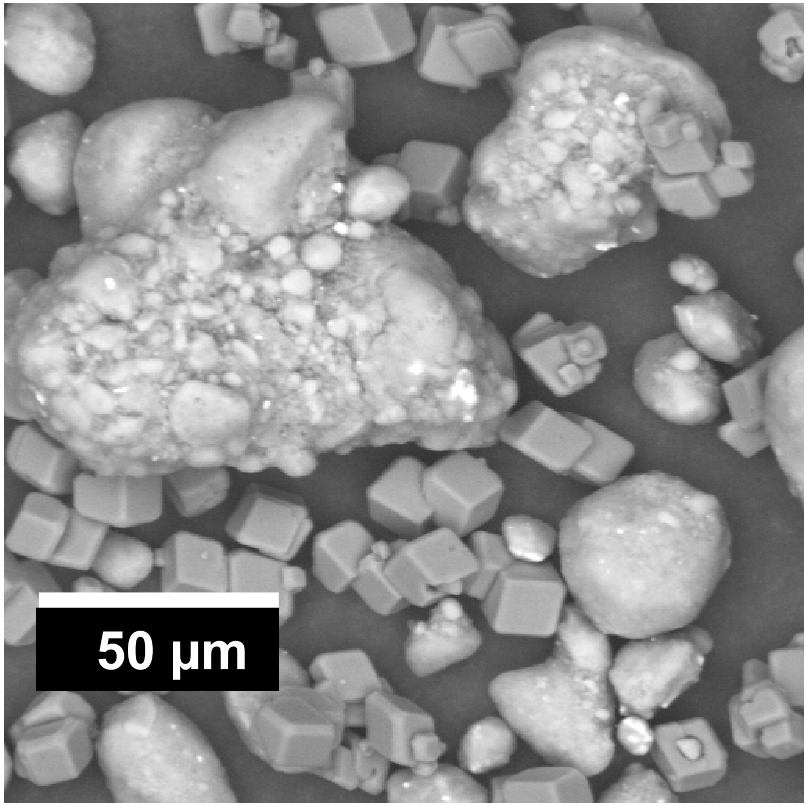
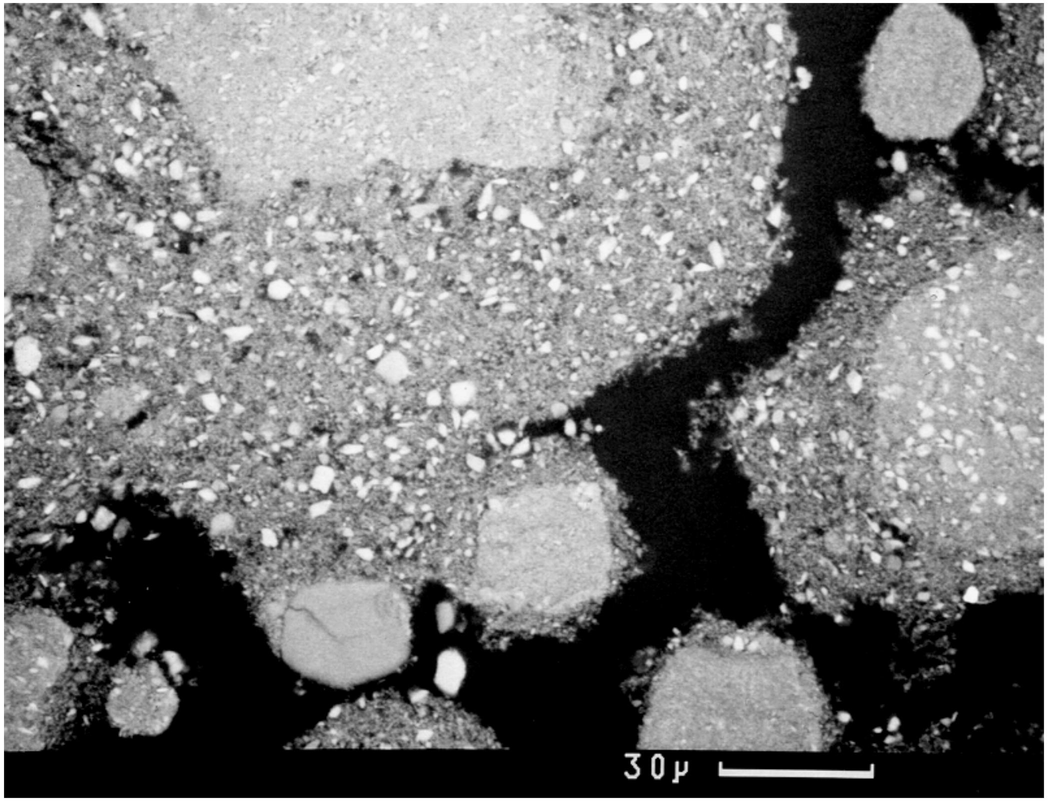
Scanning electron microscopy of autoclave run products





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Conclusions

- thermodynamics are favorable
  - need better thermodynamic information
- kinetics should be favorable
  - dissolution important rate-limiting step
  - need to determine role of precipitation
  - need to determine reaction mechanism (hydromagnesite? fate of silica? etc.)