Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

CO_2 Conversion

Enhancing Aqueous Olivine Carbonation Reactivity, While Avoiding the Cost of Mineral Pretreatment Activation

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Enhancing Aqueous Olivine Carbonation Reactivity, While Avoiding the Cost of Mineral Pretreatment Activation

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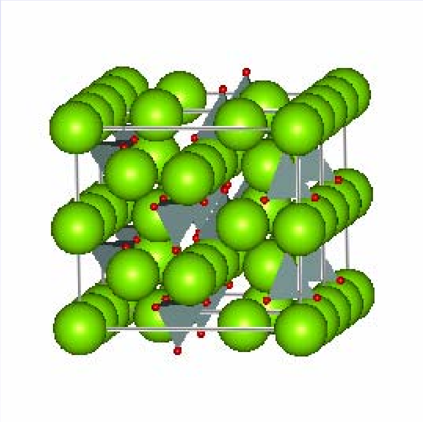

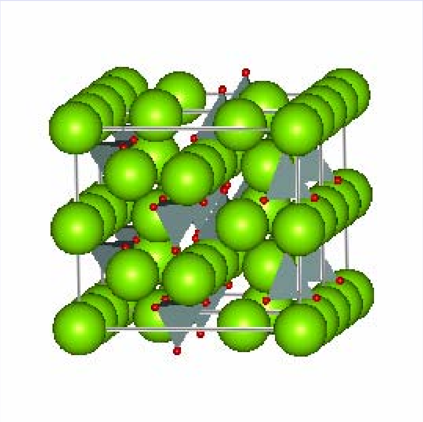

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CARBON DIOXIDE SEQUESTRATION VIA Mg-RICH MINERAL CARBONATION

ADVANTAGES

- **The process occurs naturally and yields *environmentally benign and geologically stable products* (e.g., $MgCO_3$ and SiO_2).**
- **It offers the capacity for *large scale sequestration.* Mg-rich minerals are widely available globally as relatively *low cost feedstocks* (e.g., olivine and serpentine).**
- **It *minimizes the ongoing costs* associated with long term storage (e.g., site monitoring, leakage, liability, etc.).**
- ***Carbonation is exothermic* for both serpentine and olivine, enhancing the potential for low-cost process development.**

PRIMARY CHALLENGE

Economically viable process development.

AQUEOUS SOLUTION MINERAL CARBONATION

$$\underset{olivine}{Mg_2SiO_4} + 2CO_2 \xrightarrow[0.64\ M\ NaHCO_3 + 1M\ NaCl]{\sim 185\ ^oC,\ \sim 150\ atm\ CO_2} 2MgCO_3 + SiO_2$$

<u>An Intriguing Process</u>

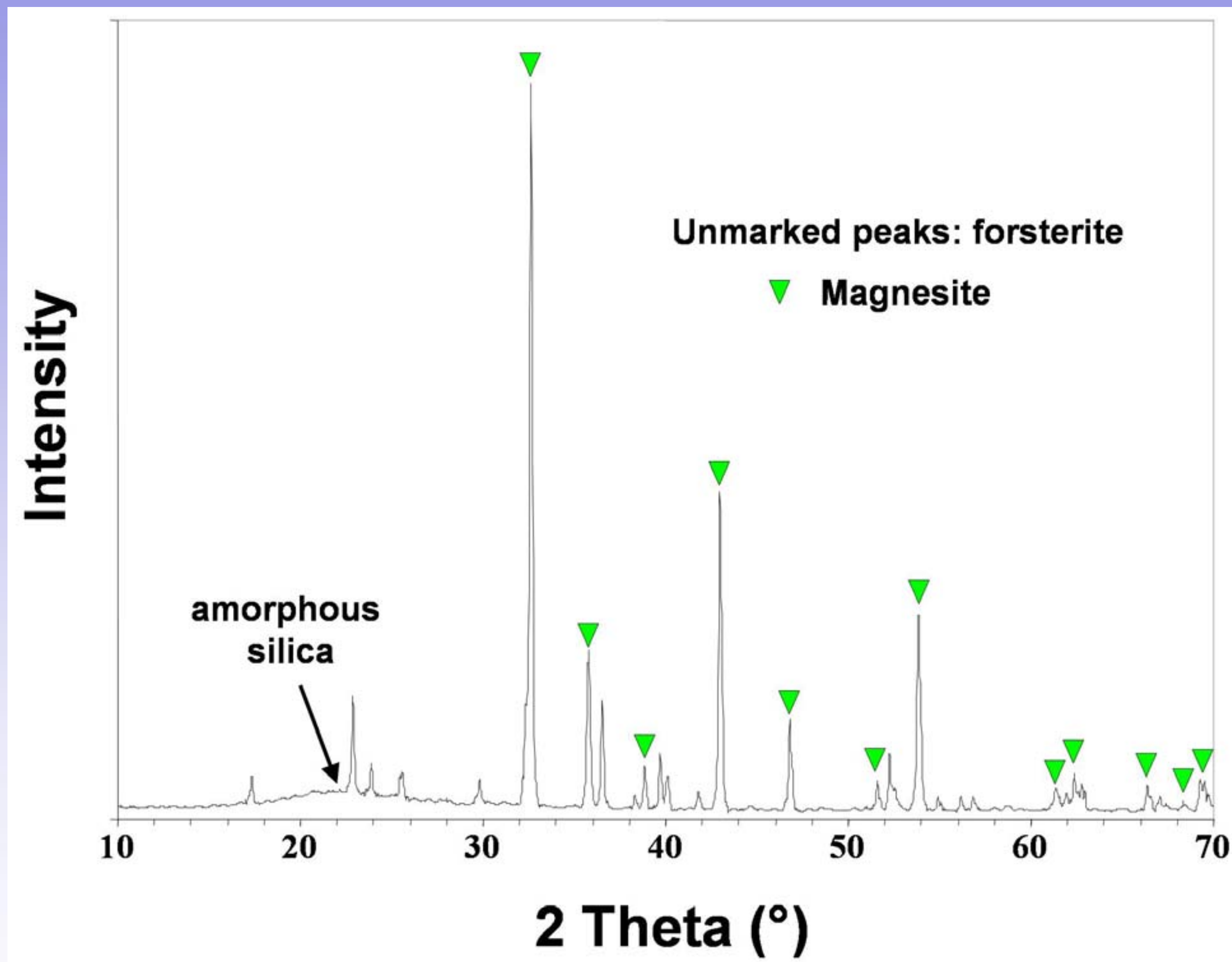
- **Developed by the Albany Research Center (ARC).**
- **Accelerated Mg-rich mineral carbonation from geological time to < 1 hour via heat and mechanical feedstock activation.**

<u>The Primary Challenge</u>

- **Reducing Process Cost**

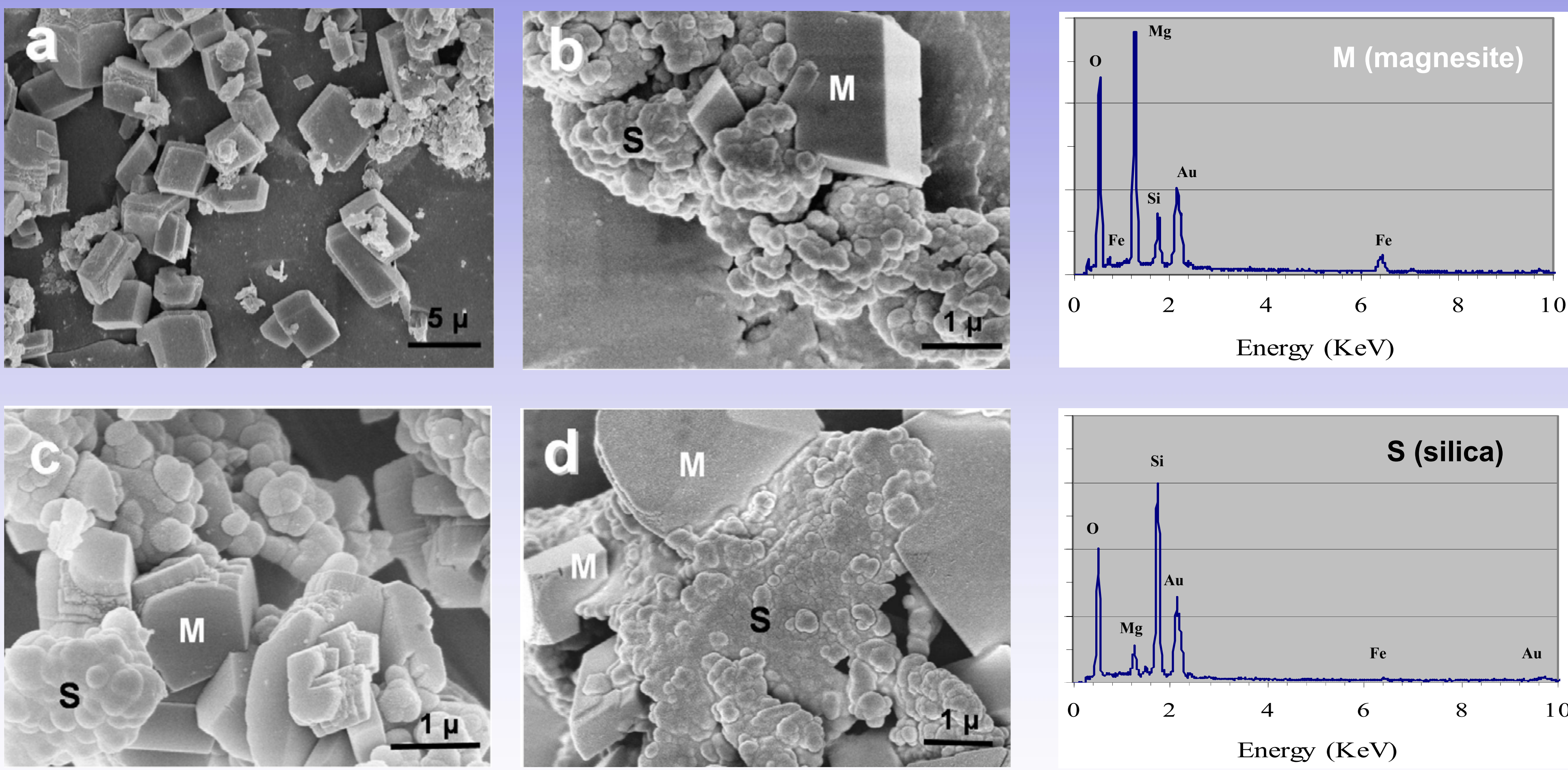
  In particular, *reducing or eliminating the cost of mineral activation*, while enhancing carbonation.

X-RAY POWDER DIFFRACTION OF PARTIALLY CARBONATED OLIVINE



$$\underset{\text{olivine}}{Mg_2SiO_4} + 2CO_2 \longrightarrow \underset{\text{magnesite}}{2MgCO_3} + \underset{\text{silica (amorphous)}}{SiO_2}$$

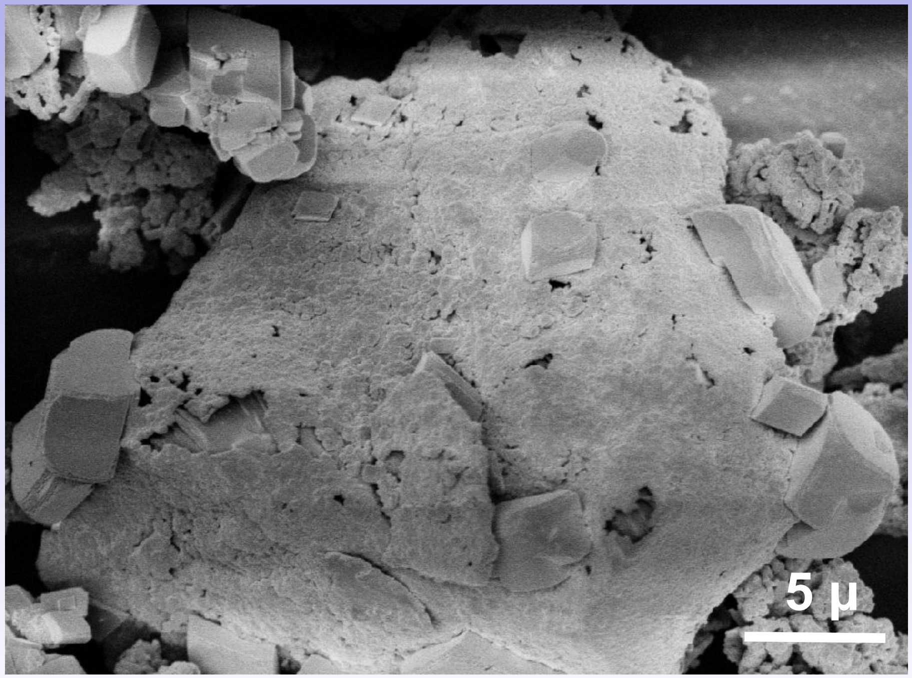
FESEM/EDS ANALYSIS OF SAN CARLOS OLIVINE MINERAL CARBONATION PRODUCTS*

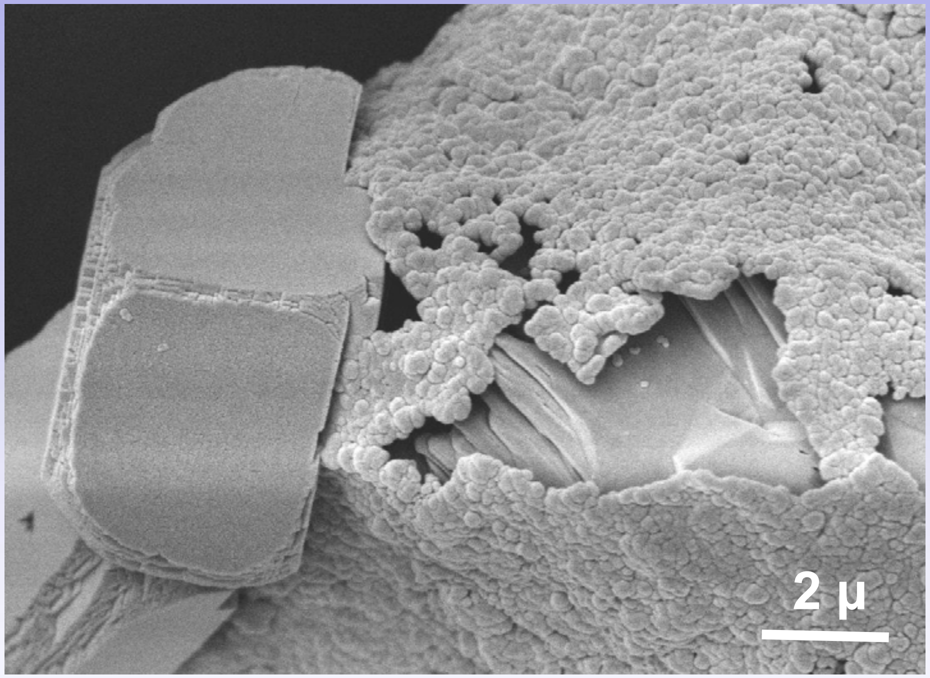


*** 1,500 rpm stirring)**

DEVELOPING A MECHANISTIC UNDERSTANDING OF OLIVINE MINERAL CARBONATION

SILICA-RICH PASSIVATING LAYER FORMATION AND MAGNESITE INTERGROWTH *

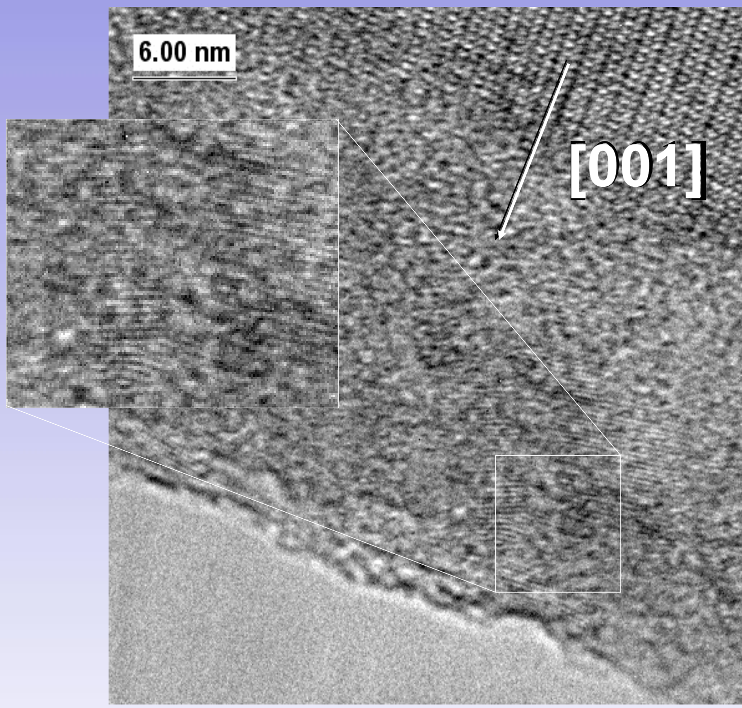




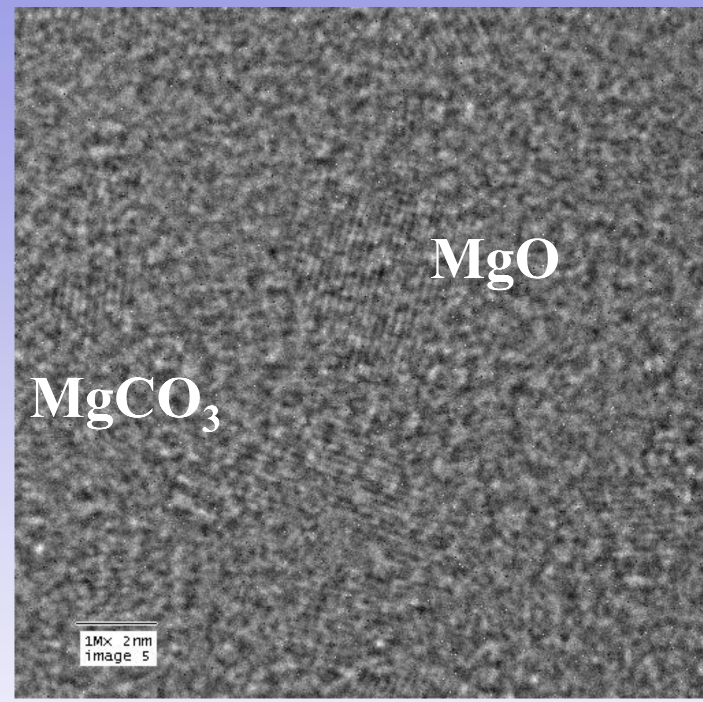
Substantial particle abrasion is evident on the external magnesite edges

***1,500 rpm stirring**

MAGNESITE NANOCRYSTAL FORMATION IN THE SILICA-RICH PASSIVATING LAYERS*



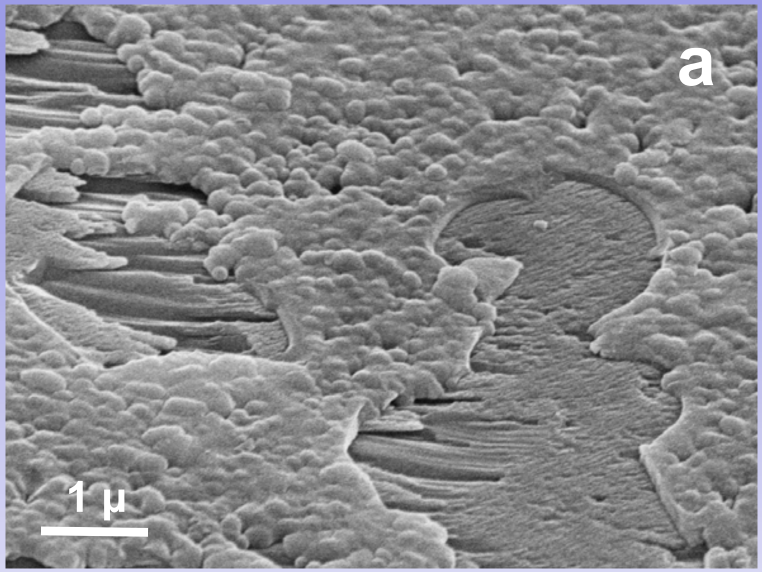
A high-resolution HRTEM image of nanocrystals that form in the silica-rich passivating layers during mineral carbonation. The olivine host crystal is in the upper right of the image.

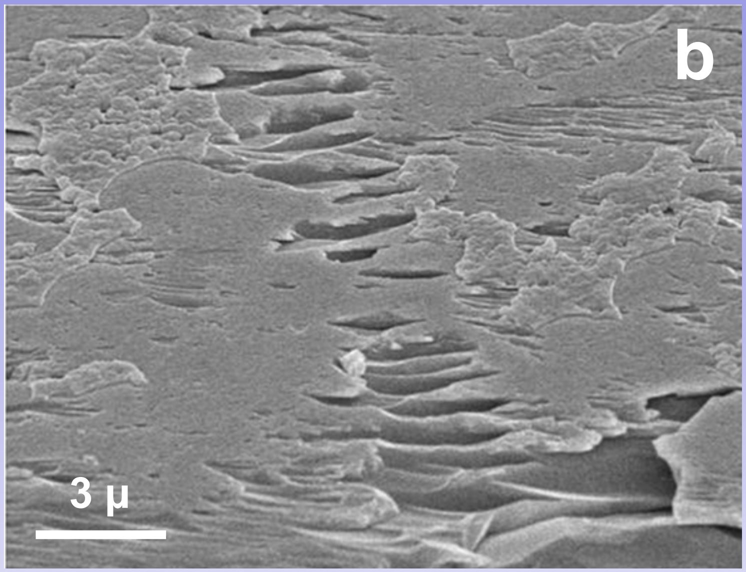


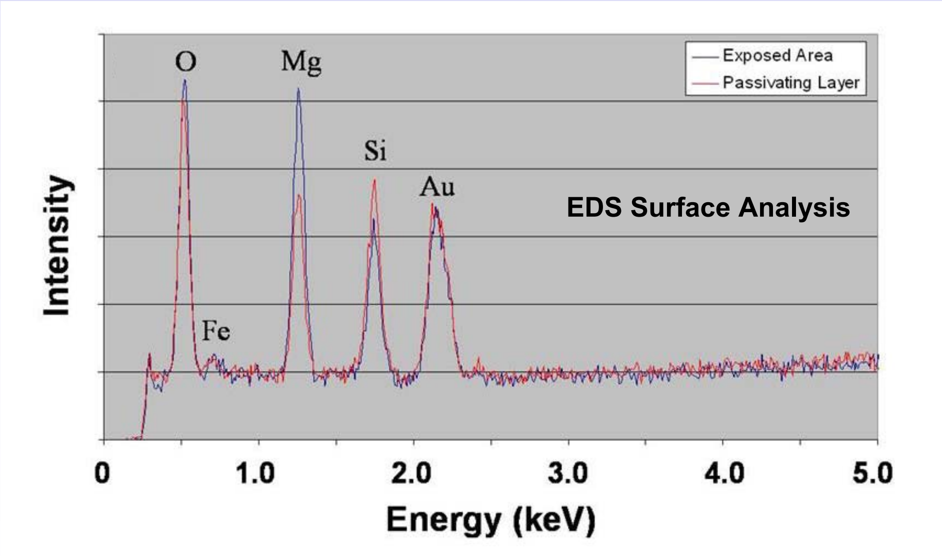
High resolution image of $MgCO_3$ and MgO nanocrystals observed in the disordered silica-rich passivating layer. $MgCO_3$ decomposes in the electron beam to give the MgO particles observed.

* Unstirred carbonation

SILICA-RICH PASSIVATING LAYER EXFOLIATION: ABRASIVE REMOVAL AND REGROWTH







***1,500 rpm stirring**

CAN CARBONATION BE ENHANCED BY CONTROLLING PASSIVATING LAYER FORMATION/EXFOLIATION?

Objective: **to identify key parameters that can enhance olivine carbonation, while avoiding the cost of pretreatment activation.**

***Approaches include*:**

- **chemical studies that probe the potential aqueous ion size and concentration (e.g., Li^+, Na^+, K^+, HCO_3^-, Cl^-) offer to mitigate passivating layer effectiveness and enhance exfoliation,**
- **multi-phase slurry flow modeling and experimental studies that elucidate key flow parameters and slurry interactions that can enhance exfoliation,**
- **investigations that elucidate the potential that cost effective sonication offers to enhance exfoliation and particle cracking.**

SOLUTION CHEMISTRY: EFFECT OF ALKALI CATION SPECIES ON CARBONATION $A^+ = Na^+, Li^+$, or K^+

Comparison with the Optimum ARC Solution: 0.64M $NaHCO_3$ + 1.00M NaCl*

0.64M $AHCO_3$ (A = Li,Na,K)

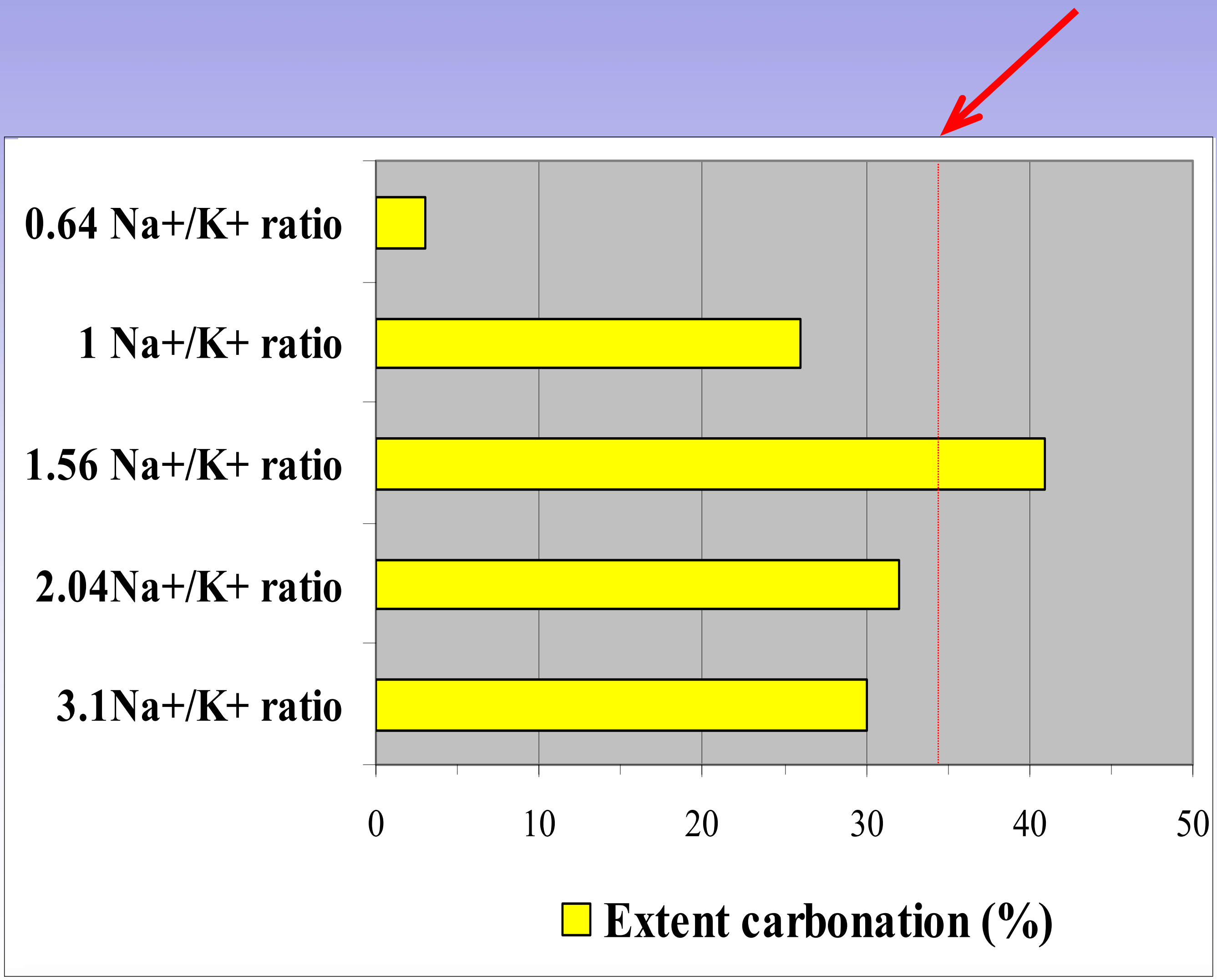
1.00M ACl (A = Li,Na,K)	Li	Na	K
Li	23%	18%	24%
Na	4%	34%*	41%
K	2%	3%	15%

- Note: Solution chemistry studies use single crystal San Carlos olivine fragments and the ASU batch reactor to explore the reaction products and mechanisms. This reaction combination exhibits significantly lower carbonation compared with the prior Albany Research Center (ARC) Flow Loop Reactor carbonation of Twin Sisters olivine.

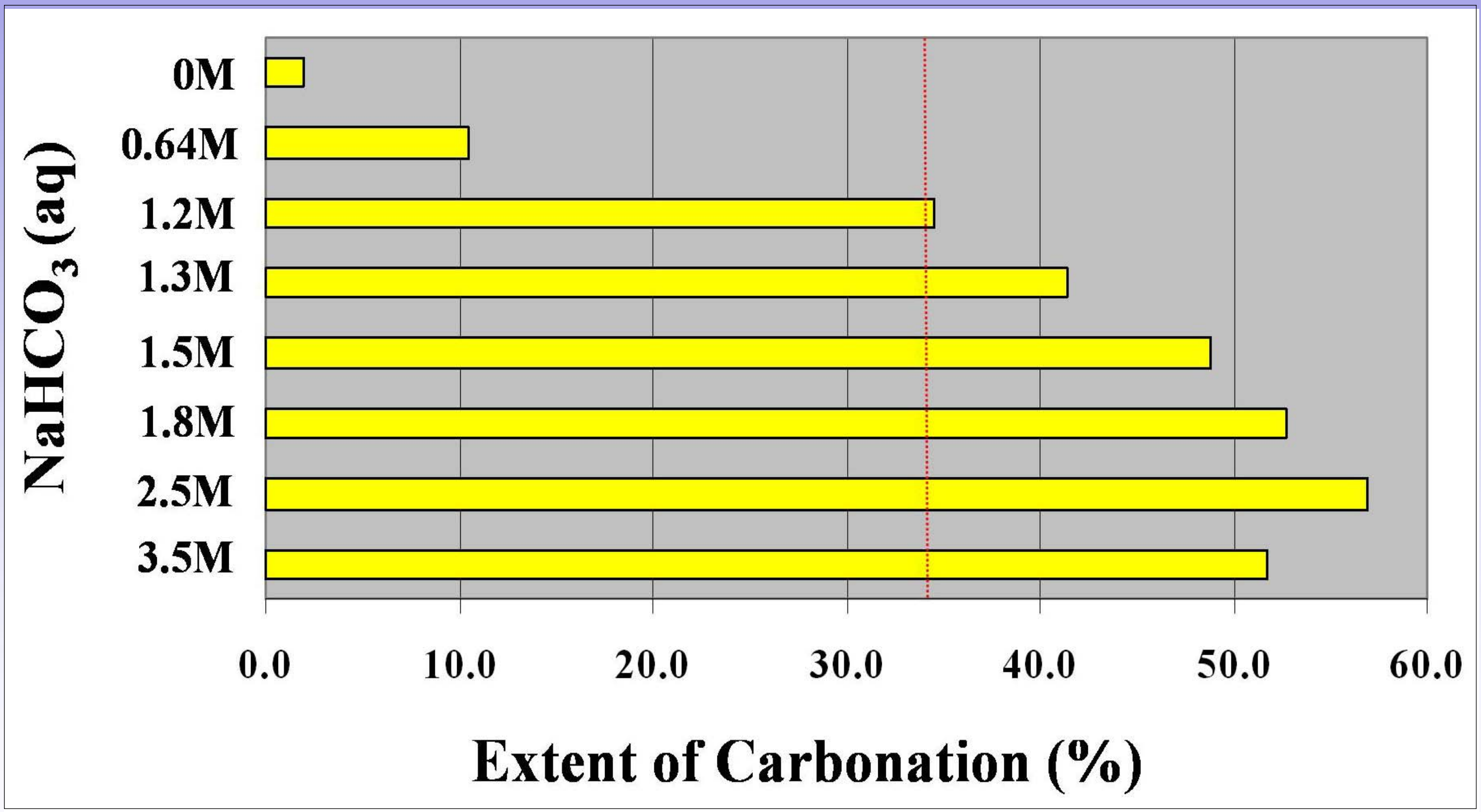
SOLUTION CHEMISTRY: EFFECT OF Na^+/K^+ MOLAR RATIO

0.64M $AHCO_3$ + 1.0M ACl (A = Na + K).

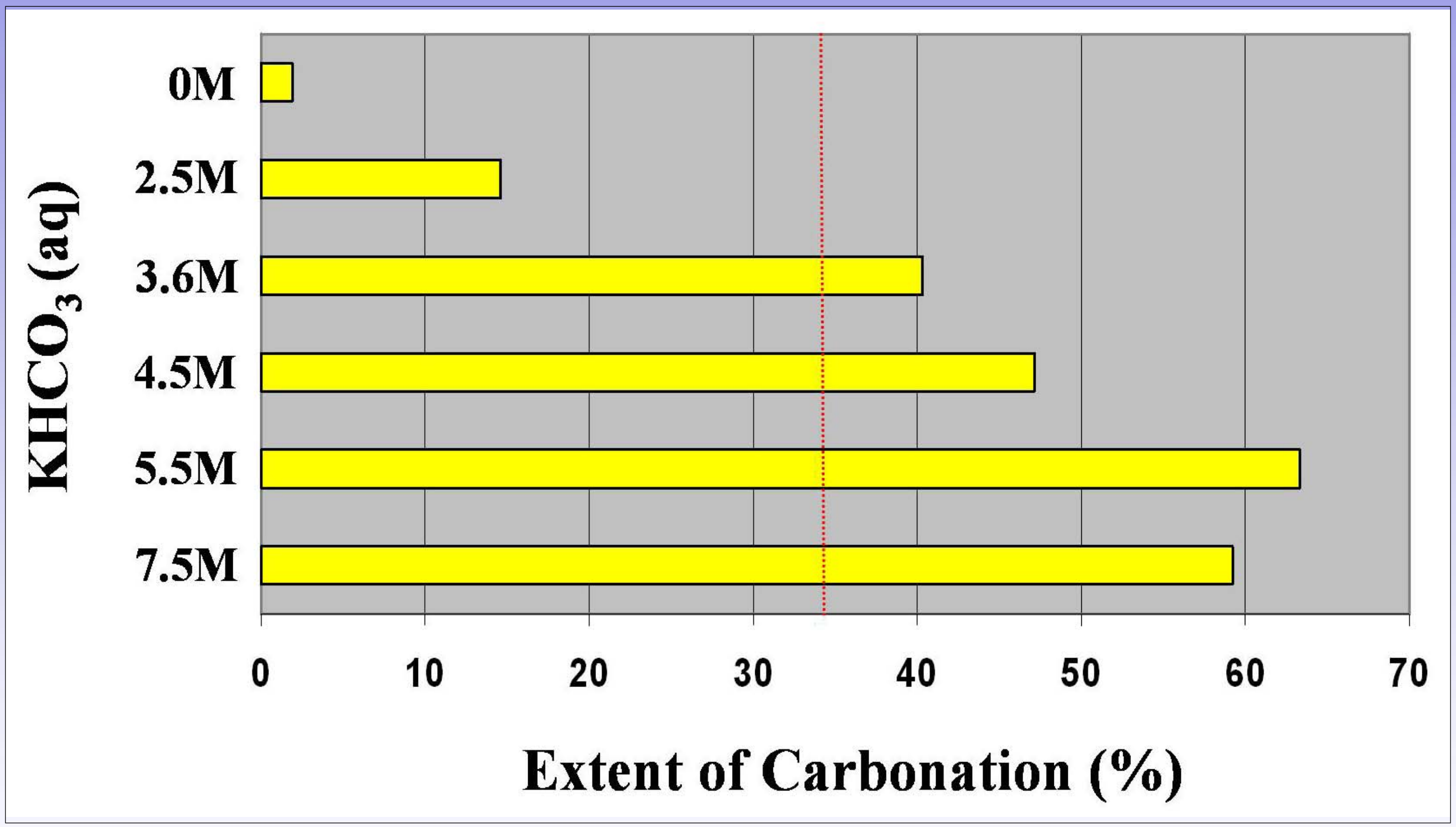
Comparison with the Optimum ARC Solution: 0.64M $NaHCO_3$ + 1.00M NaCl



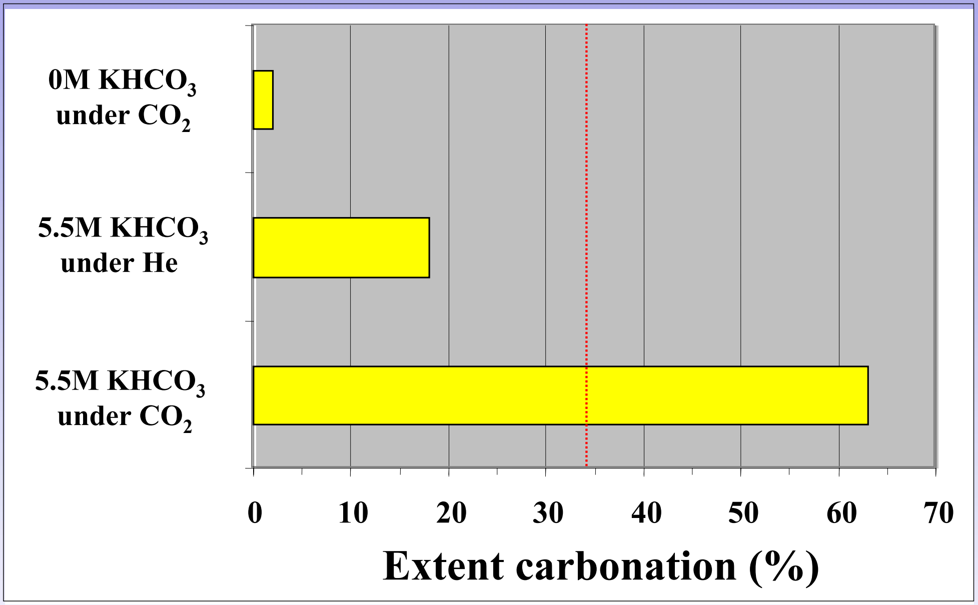
SOLUTION CHEMISTRY: EFFECT OF AQUEOUS SODIUM BICARBONATE CONCENTRATION ON CARBONATION



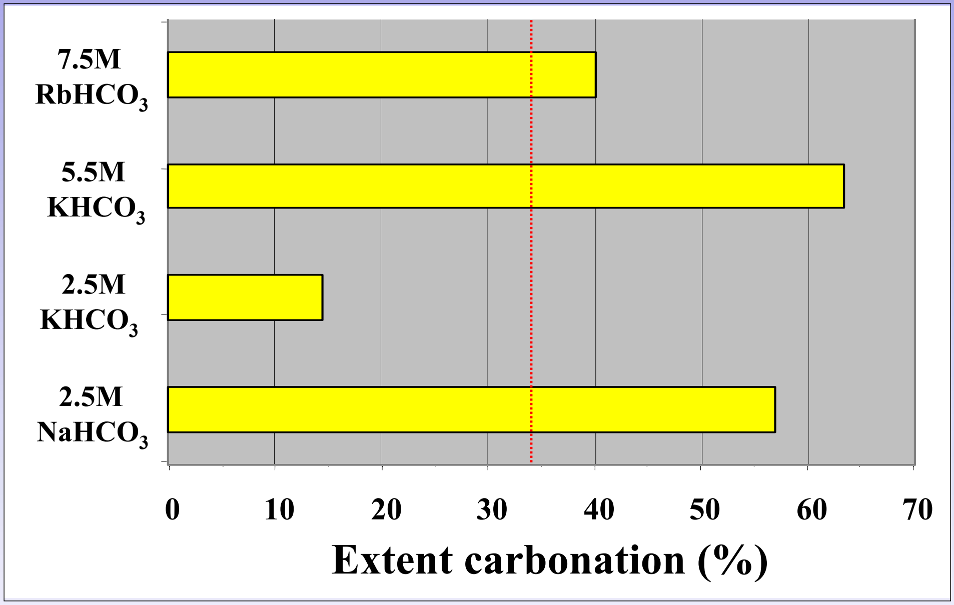
SOLUTION CHEMISTRY: EFFECT OF AQUEOUS POTASSIUM BICARBONATE CONCENTRATION ON CARBONATION



SOLUTION CHEMISTRY: SYNERGISTIC SPECIES INTERACTIONS ARE KEY TO ENHANCING CARBONATION REACTIVTY



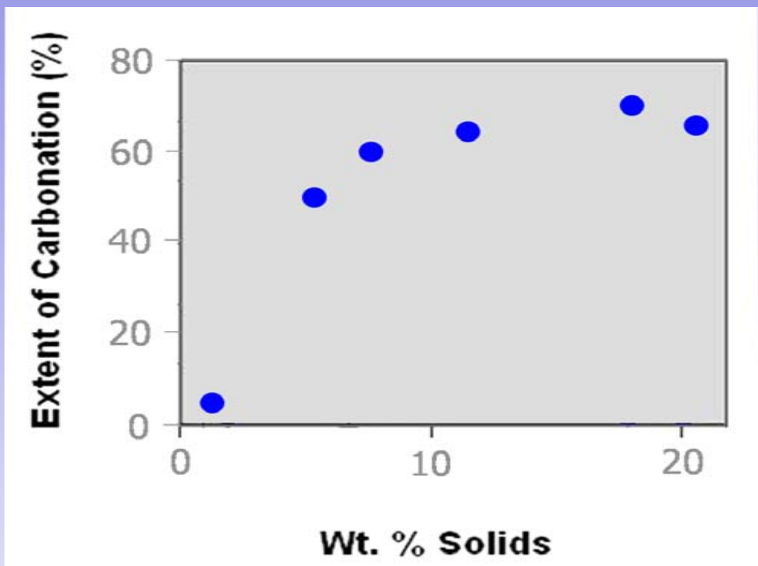
Synergism between $KHCO_3$ and CO_2(aq)



Importance of the HCO_3^- cation species

SLURRY FLOW EFFECTS ON CARBONATION EXTENT

Particle density



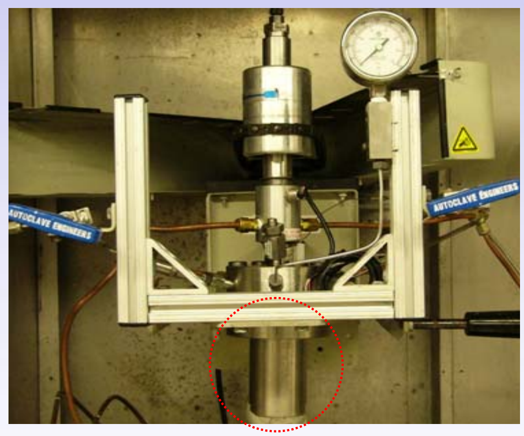
Carbonation of synthetic olivine (Mg_2SiO_4) @ 185 °C, 150 atm CO_2, with 1,500 rpm stirring for 1hr (ASU).

Particle size distribution

ARC Flow Loop Reactor

Initial Studies of the Effect of Pump Speed and Particle Size On Olivine Carbonation in the ARC Flow Loop Reactor

Pump Speed (rpm)	Particle Size Fraction	Extent of Carbonation
1198	< 38 µ	72.0%
1002	< 75 µ	66.9%
1198	< 75 µ	63.2%
1450	< 75 µ	73.8%
1750	< 75 µ	77.9%



ASU Batch Reactor

Olivine Size vs. % Carbonation

<38µ SC olivine → 35%

<75µ SC olivine → 31%

<75µ SC olivine exhibits a 0-12% increase in carbonation compared with the prorated average of its <38µ and 38-75µ size fractions.

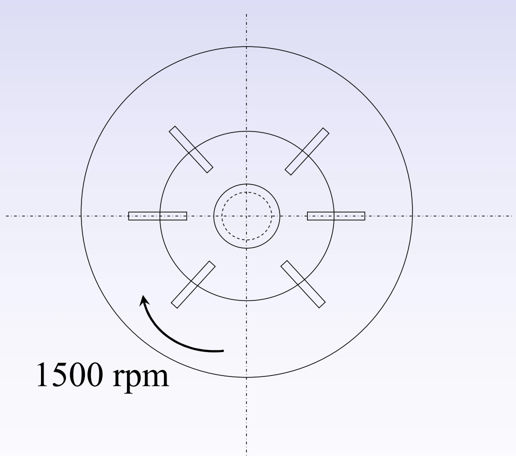
- **Understanding slurry flow reaction dynamics is critical for optimizing carbonation efficiency.**
- **Increasing olivine feedstock size from <38 to <75µ can greatly reduce grinding cost**

FLOW MODELING – ASU BATCH REACTOR

- **Solution of two-fluid equations describing the slurry mixture**
  - **Coupling between the phases via pressure and interphase momentum transfer terms**
  - **Inter-particle collisions modeled via granular pressure**
  - **Particle-particle friction modeled via frictional viscosity**

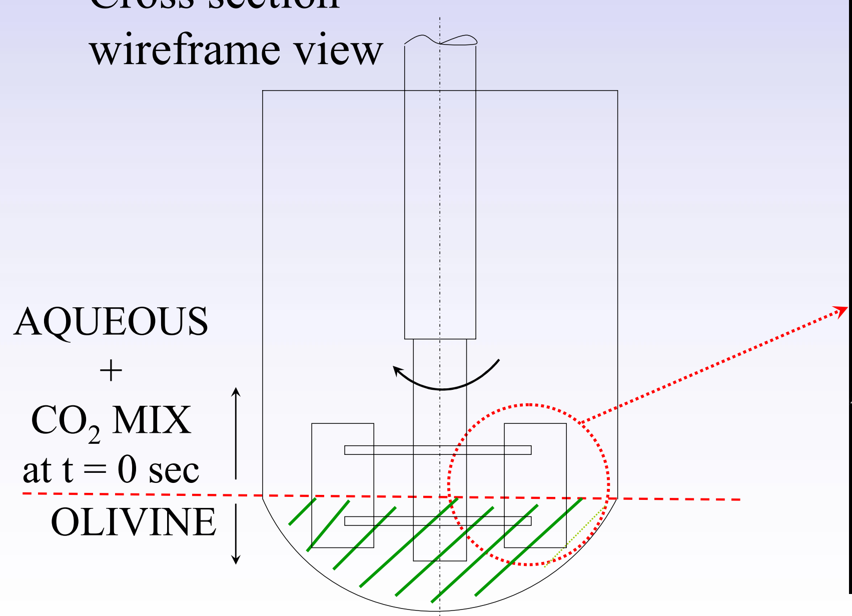
- **Computational setup**
  - **One–sixth of the reactor, impose periodicity along the side faces**
  - **Single size fractions considered to date: 37μ, 75μ, and 150μ**

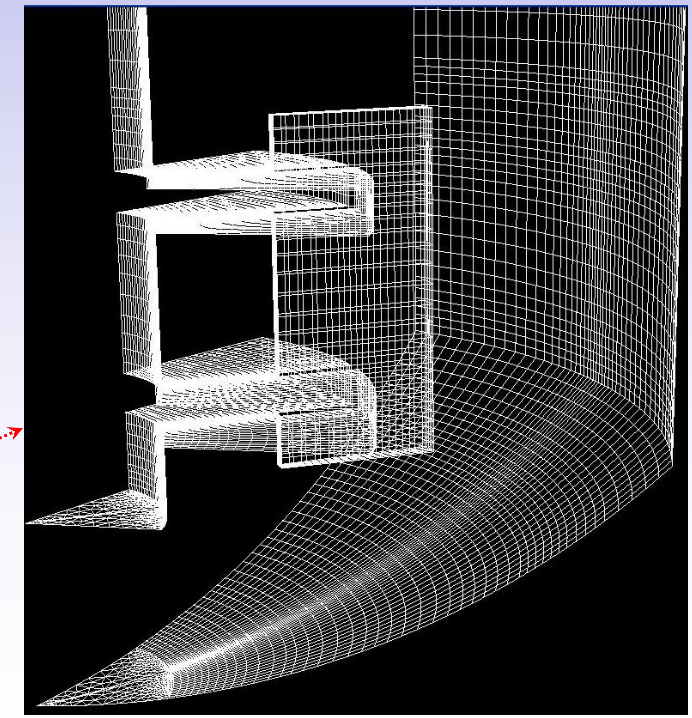
Top View



CAD wireframe of ASU batch reactor

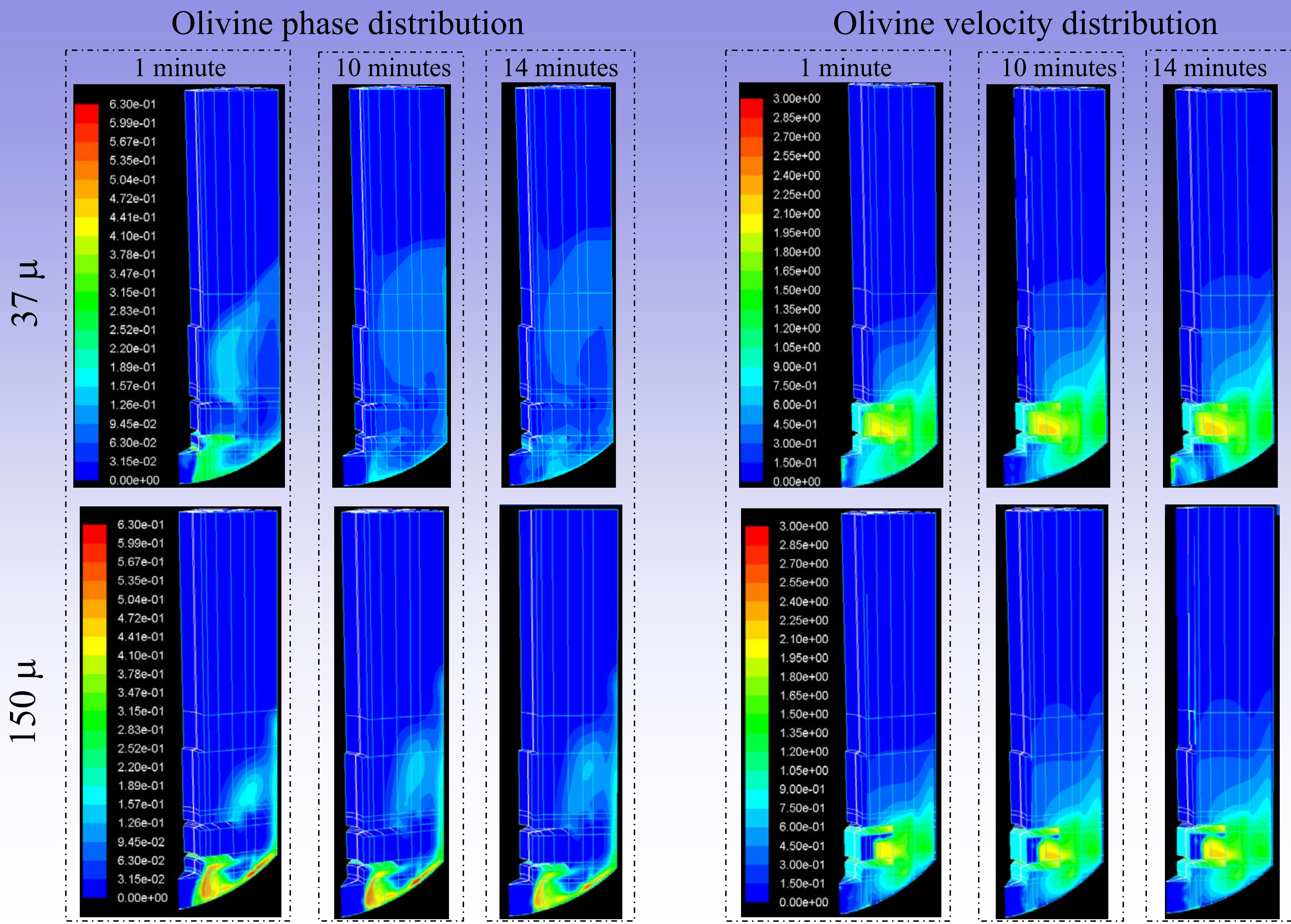
Cross section wireframe view



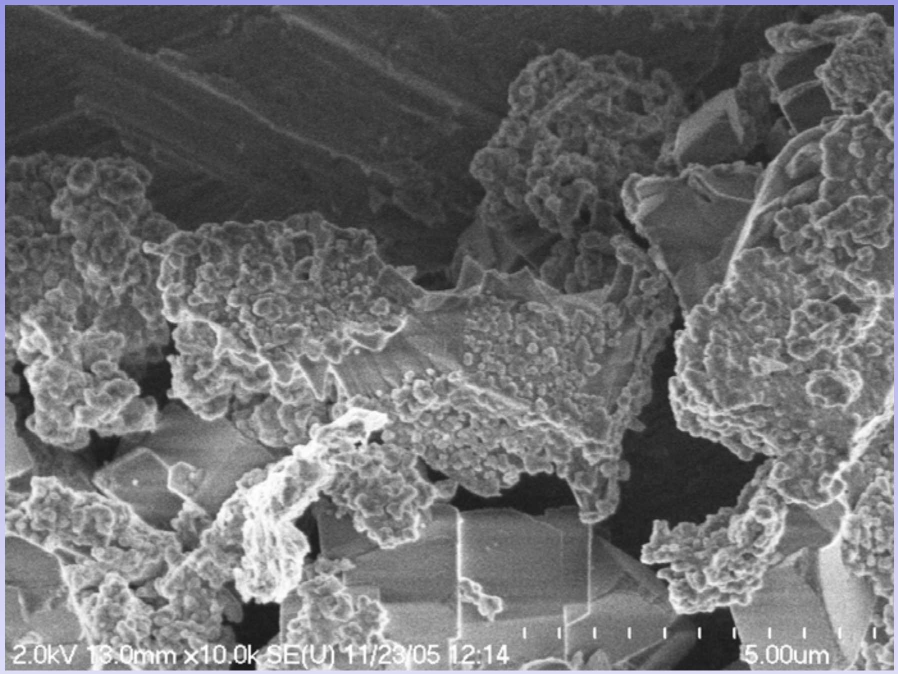


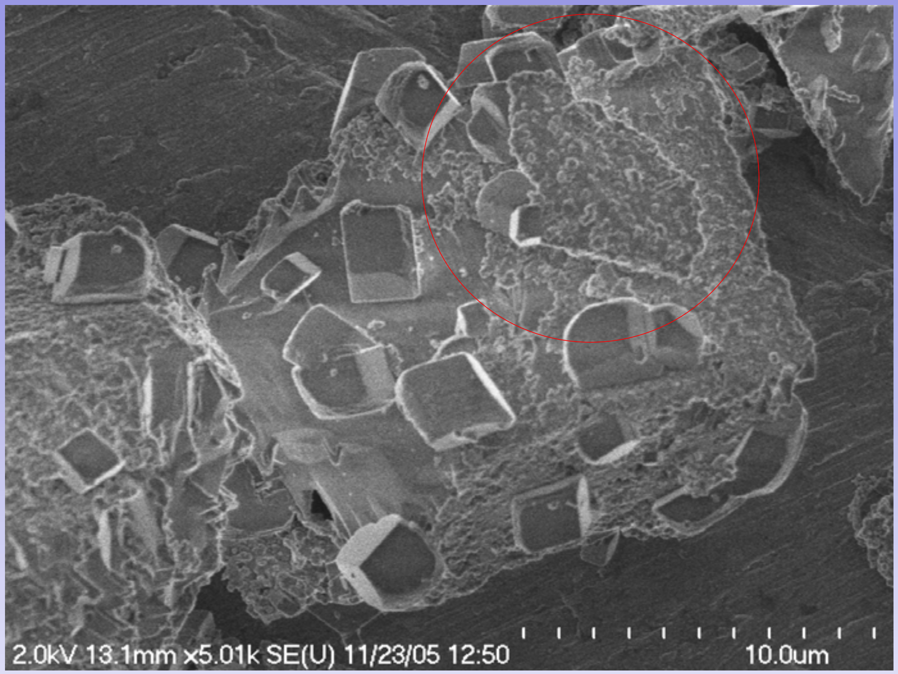
paddle wheel region

INITIAL CFD MODELING RESULTS



INVESTIGATING THE EFFECTS OF SONICATION ON PASSIVATING LAYER GROWTH & CARBONATION





FESEM showing passivating layers are only modestly affected by brief sonication

No significant improvement in carbonation has been observed using brief (1-10 min.), high intensity sonication from ambient conditions to 150 bar CO_2 and 185 ^oC.

- **sonication causes minimal disruption of the passivating layers and olivine particle cores. Layer sections that exfoliate can readily regrow.**
- **longer sonication exposure is likely too energy intensive**

Studies are continuing as a function of P, T, fluid composition, wt% solids, etc.

CONCLUSIONS

- **We have nearly doubled the extent of carbonation observed for the optimum aqueous carbonation solution to date using high alkali bicarbonate concentrations (e.g., 5.5M $KHCO_3$).**

- **Controlling the wt% solids and particle size distribution during aqueous carbonation offers intriguing potential to reduce process cost by enhancing passivating layer exfoliation *in situ* during carbonation.**
  - **Slurry flow modeling may offer an important tool to optimize key parameters.**

- **Controlling slurry flow conditions may allow efficient carbonation of larger < 75µ olivine, greatly reducing feedstock grinding costs.**

- **Studies to date have not yet found evidence that controlled sonication can cost effectively enhance carbonation.**