Degradation of Wellbore Cement Due to CO_2 Injection — Effects of Pressure and Temperature

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Why should we be concerned about existing wellbore integrity?

- **Over 360,000 active oil/gas wells registered with the Railroad Commission of Texas**
- **Estimated 1.5 million total deep holes in state of Texas (over 5 wells per square mile)**

Degradation of Well Cement Under Geologic Sequestration Conditions

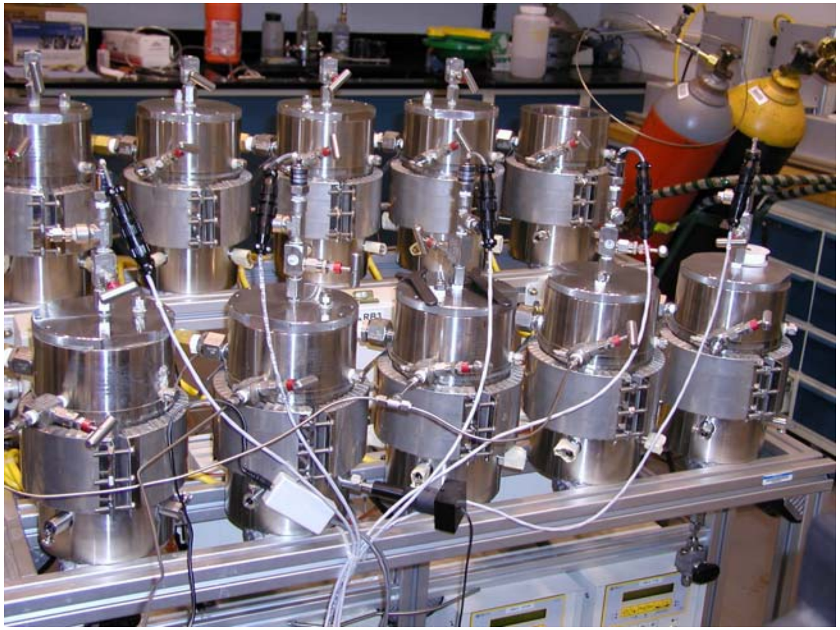
Objective:

To determine the effect of exposure to CO_2 on the physical and chemical properties of cements under geologic sequestration conditions.

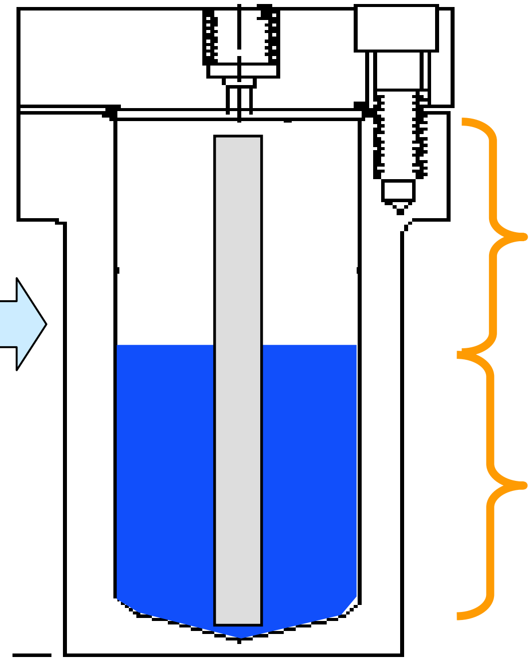
- **How does degradation depend on conditions?**
  - Temperature?
  - Pressure?
  - Salinity?

Hydration and Degradation Experiments

- **Samples prepared according to API Recommended Practice 10B**
  - Class H neat
  - Class H with 6% bentonite
- **Hydrated for 28 days in 1%NaCl solution**
  - T = 50°C, P = 4400 psi
    - Simulating depth of ~1300 m
  - T = ambient, P = 4400 psi
  - T = 50°C, P = ambient
  - T = ambient, P = ambient



CO_2 - Sequestration Exposure Experiments



Headspace: water saturated CO_2

Aqueous phase saturated with CO_2

Results – Class H Neat

- **Top (above water):**
  - Visible grey on surface, rough texture
    - Lack of water to diffuse ions
    - Calcite deposits

- **Bottom (under water):**
  - Visible orange on surface, smooth texture
  - Soft, weak

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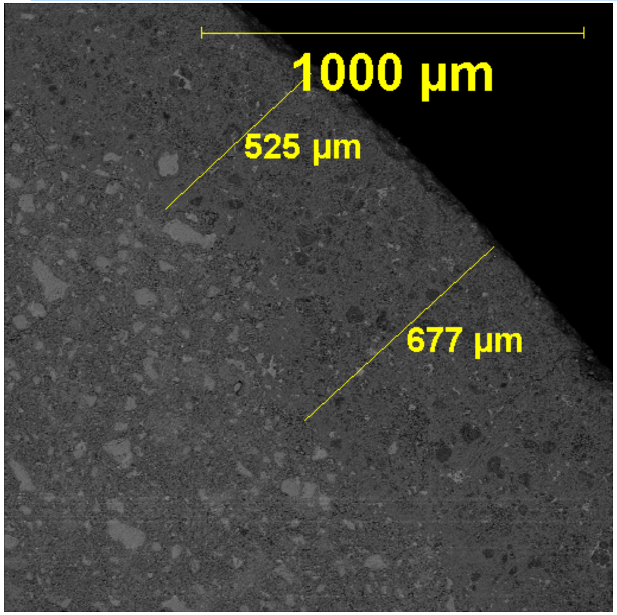

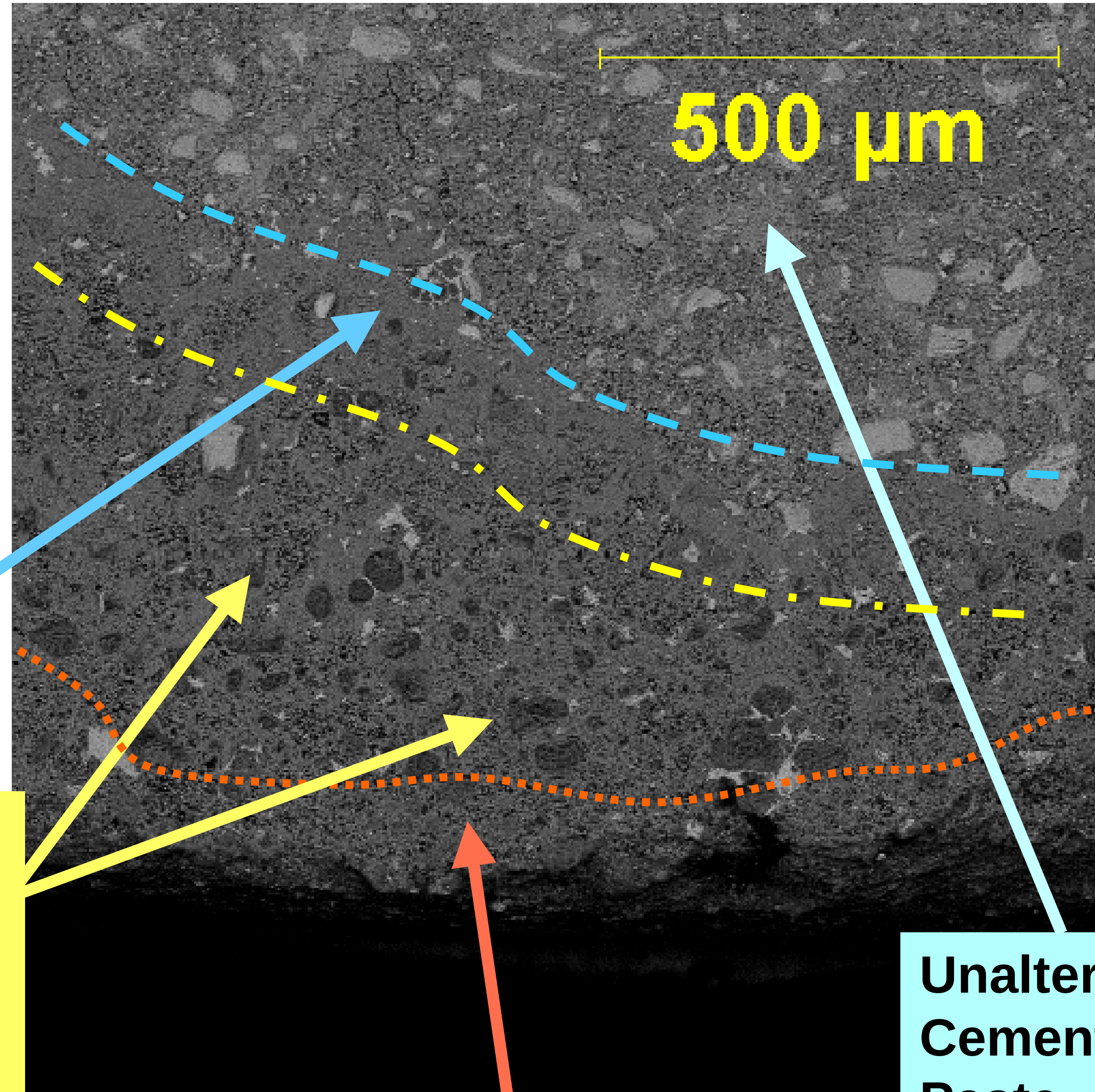

Calcite-rich zone

Calcium depleted zone

•mixture of porosity, partly decalcified CSH and calcium carbonate

Unaltered Cement Paste

Highly porous rim

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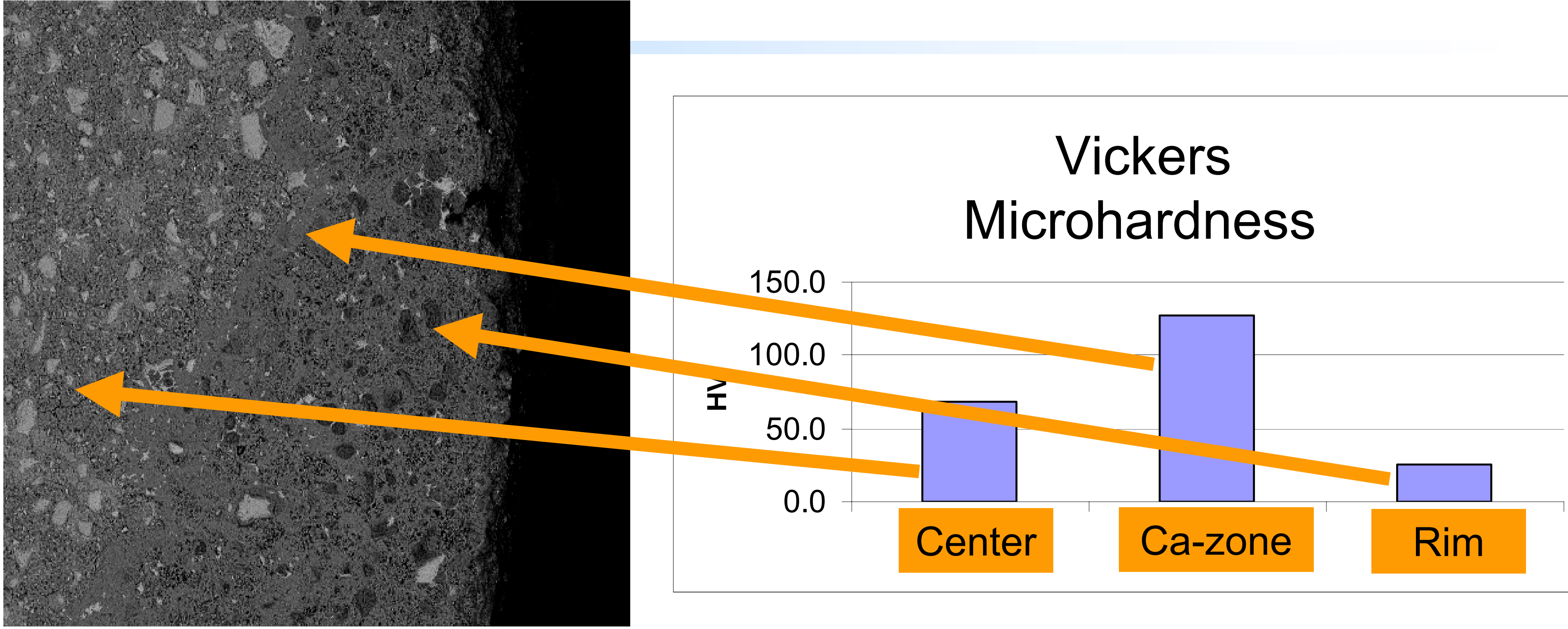


1. Carbonation

Acid attack on calcium hydroxide:

$Ca(OH)_2$ (s) + H_2CO_3 (aq) → $CaCO_3$ (s) + 2 H_2O

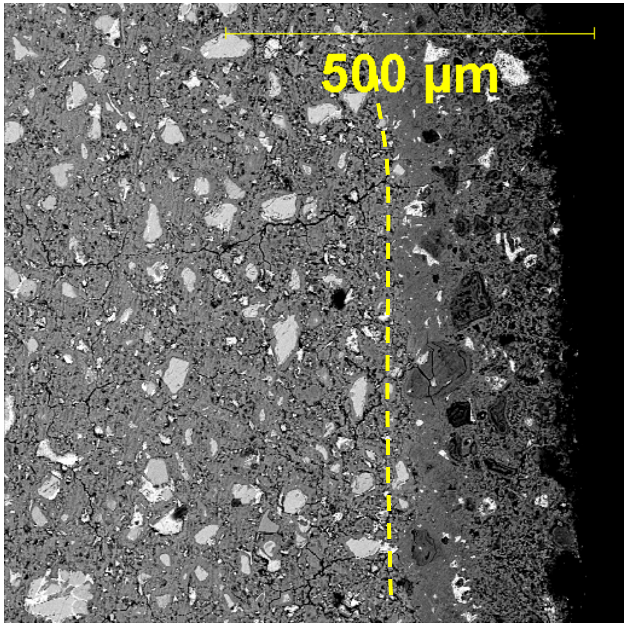
Degradation of Calcium-Silicate-Hydrate:

C-S-H + H_2CO_3 (aq)→ $CaCO_3$ + amorphous silica gel

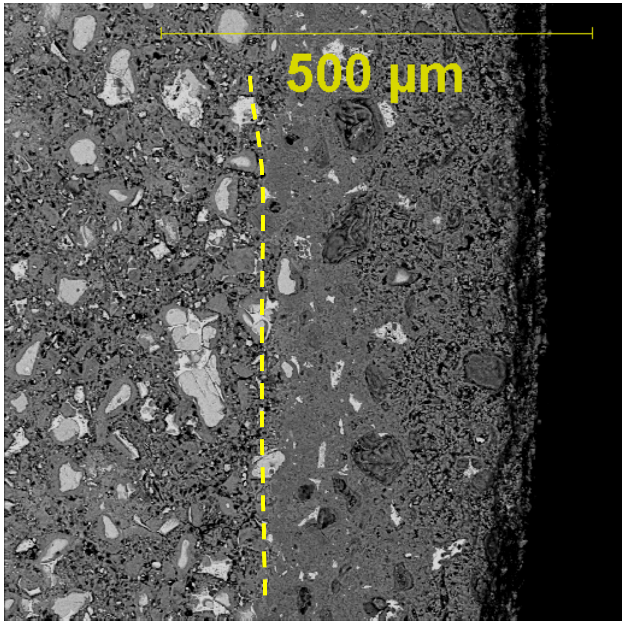
2. Bicarbonation

CaCO3 (s) + H2CO3 (aq) → Ca(HCO3)2 (aq)

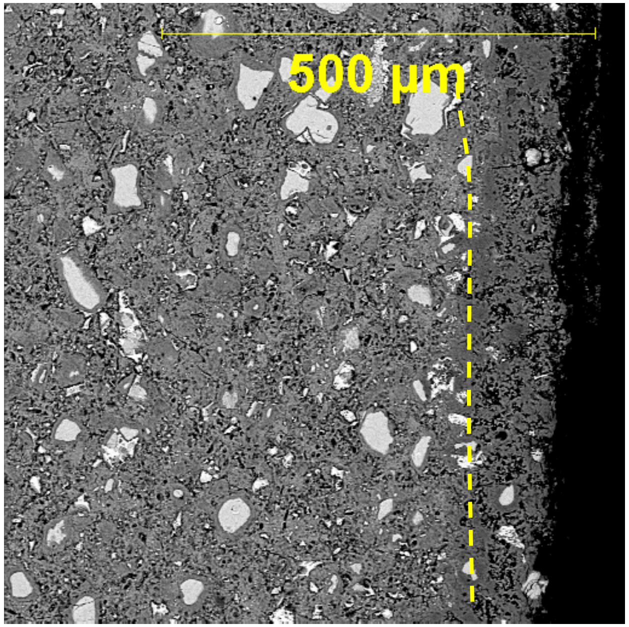
Headspace vs. Aqueous Phase



Aqueous Phase: 9 days HTHP CO_2 exposure



Aqueous Phase: 60 days HTHP CO_2 exposure



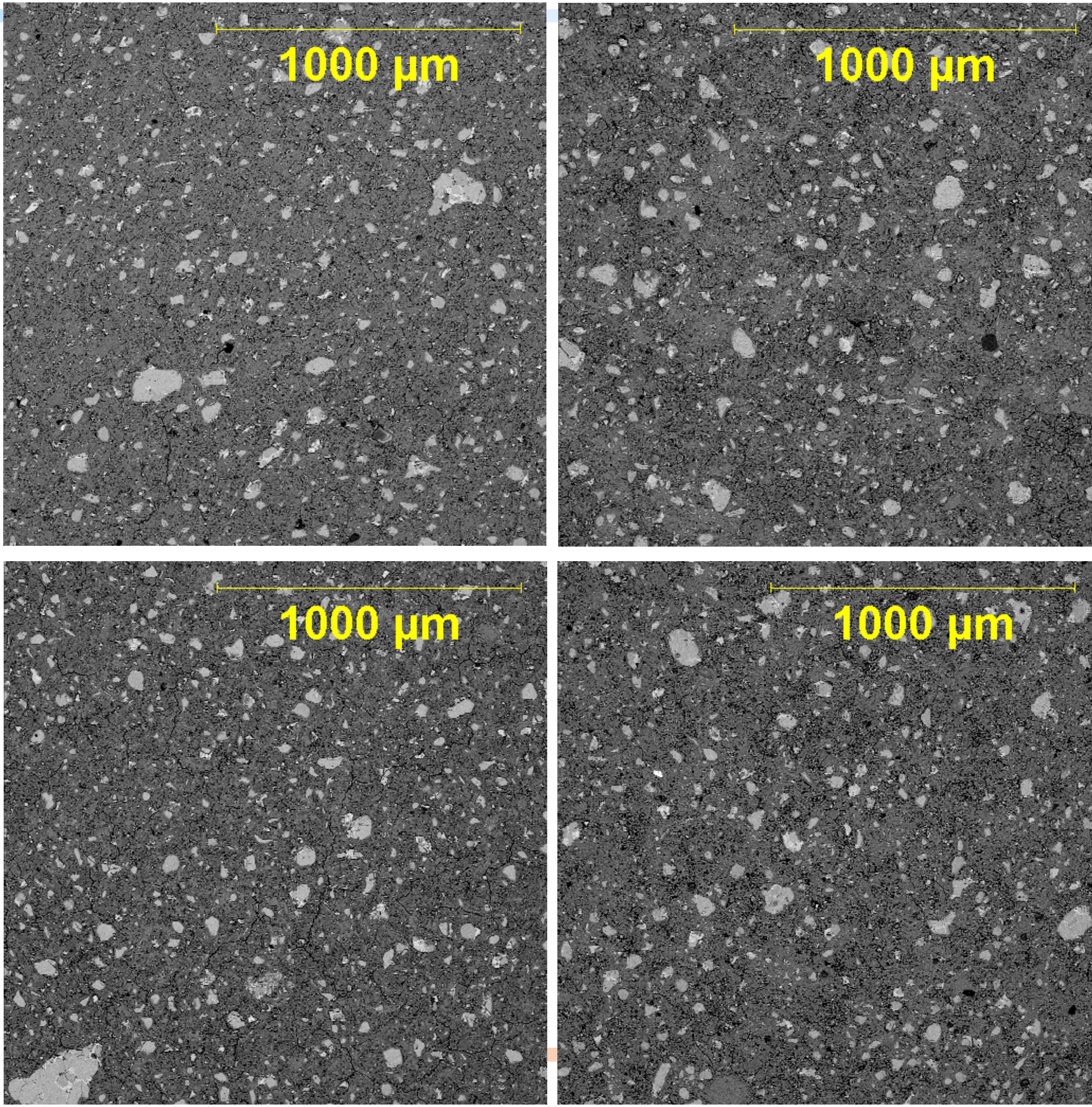
Headspace: 60 days HTHP CO_2 exposure

4400 psi
50°C

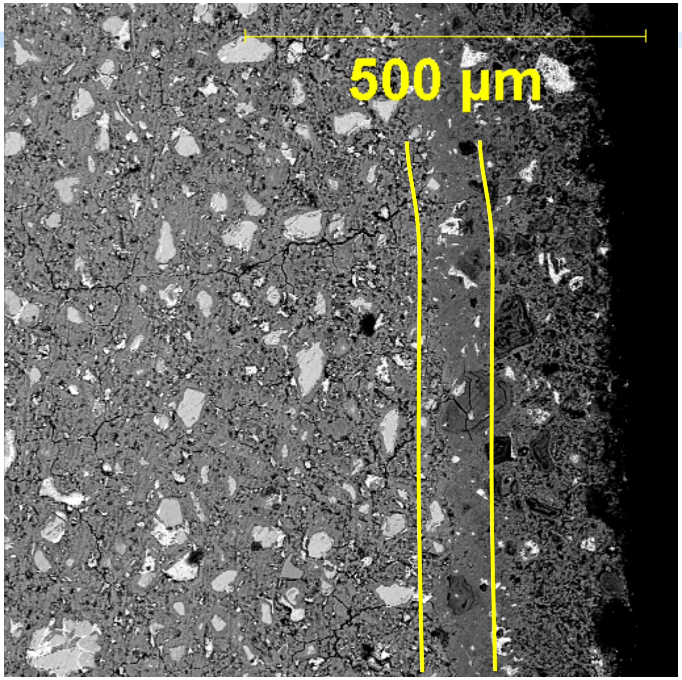
4400 psi
22°C

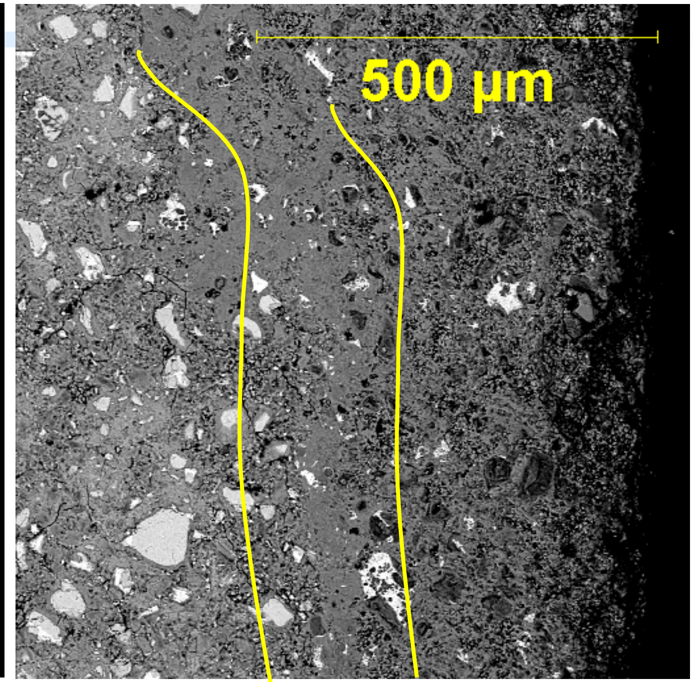
Atm.
50°C

Atm.
22°C



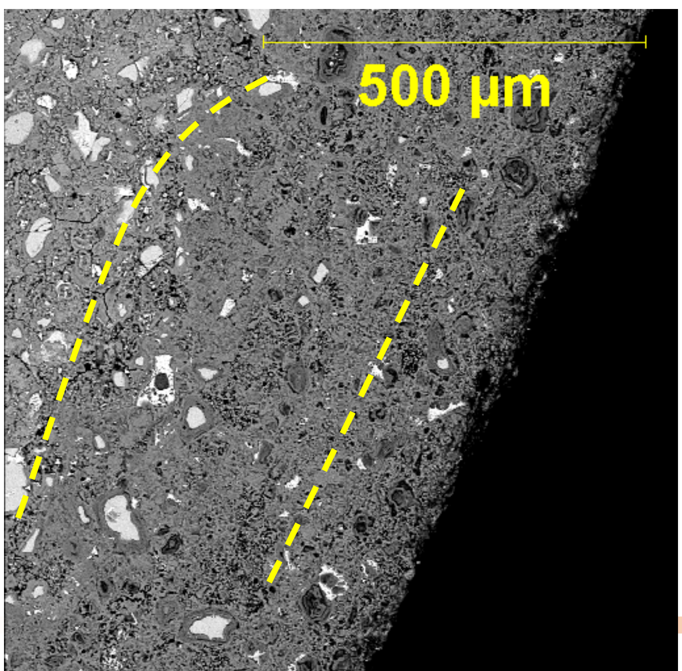
4400 psi
50°C

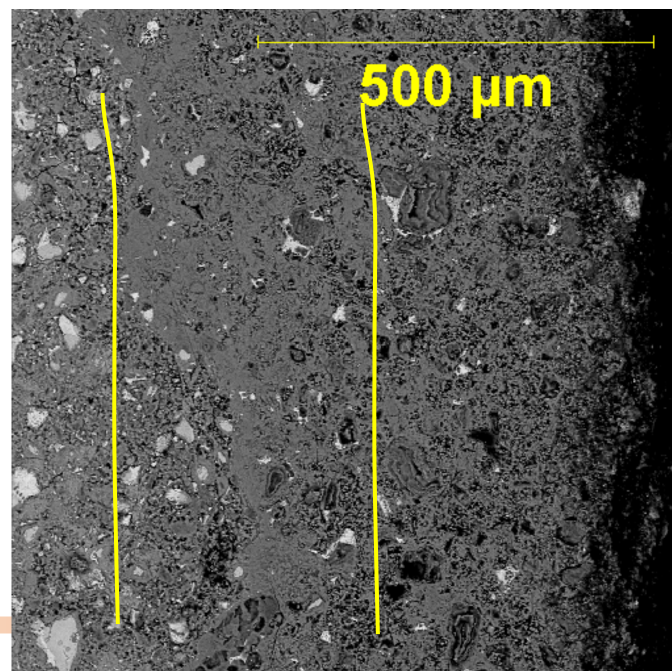




4400 psi
22°C

Atm.
50°C

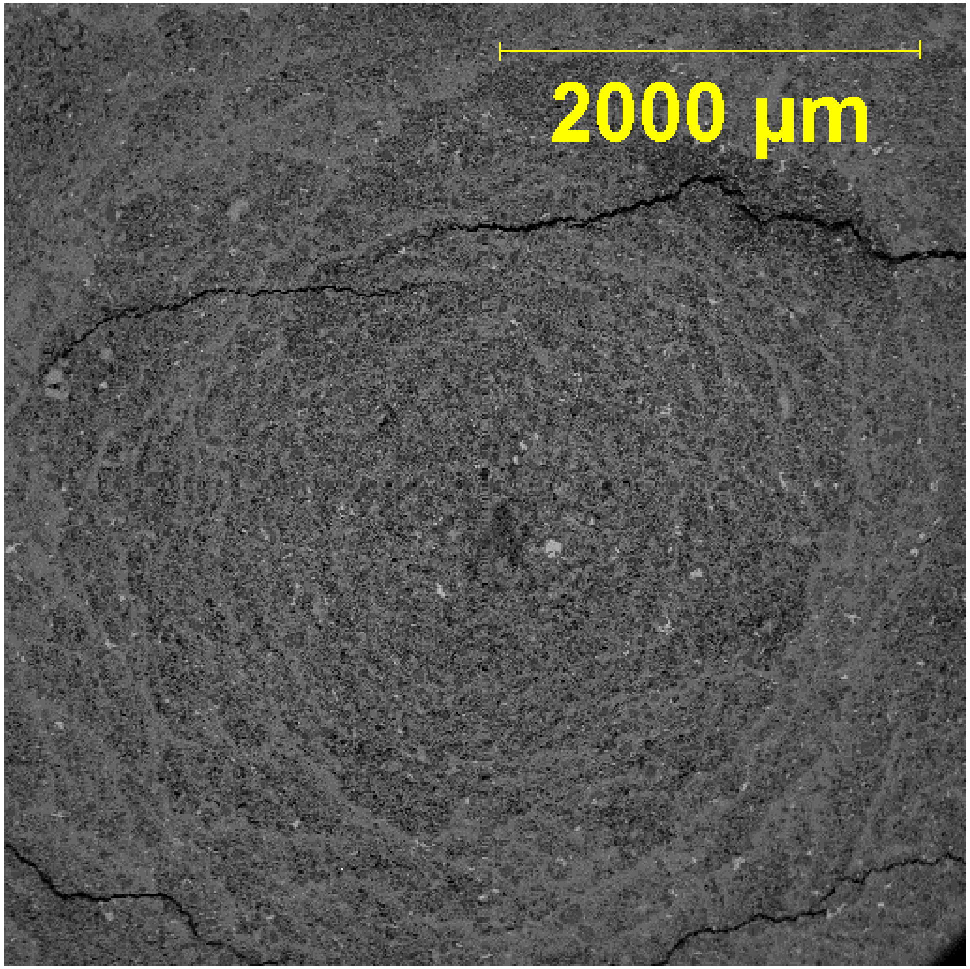




Atm.
22°C

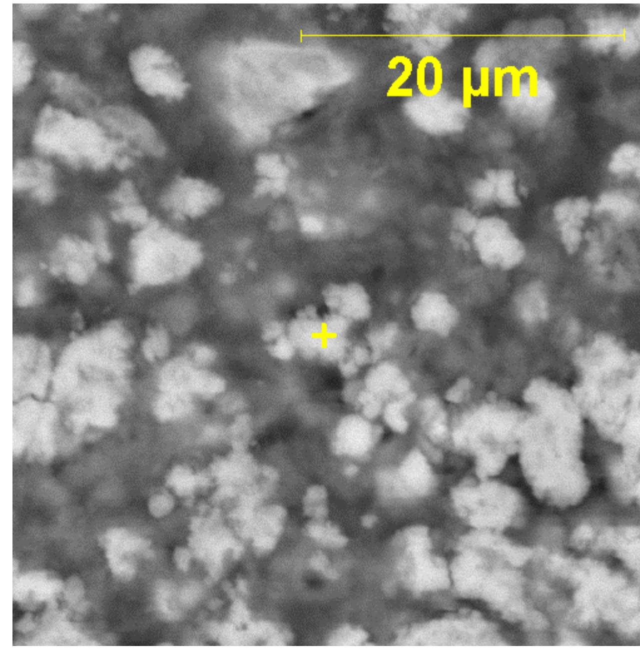
Class H with 6% Bentonite

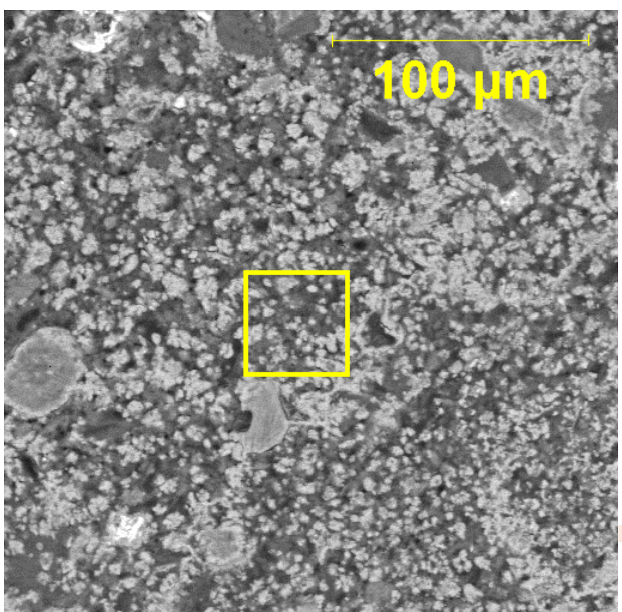
- **Water to solids ratio of 0.70**
- **Highly degraded**
  - Extreme porosity, “popcorn” carbonation
  - Shows importance of water/cement ratio
  - Liesegang rings
    - “Formed by the **complex interplay of diffusion, chemical reaction, and precipitation**. …”

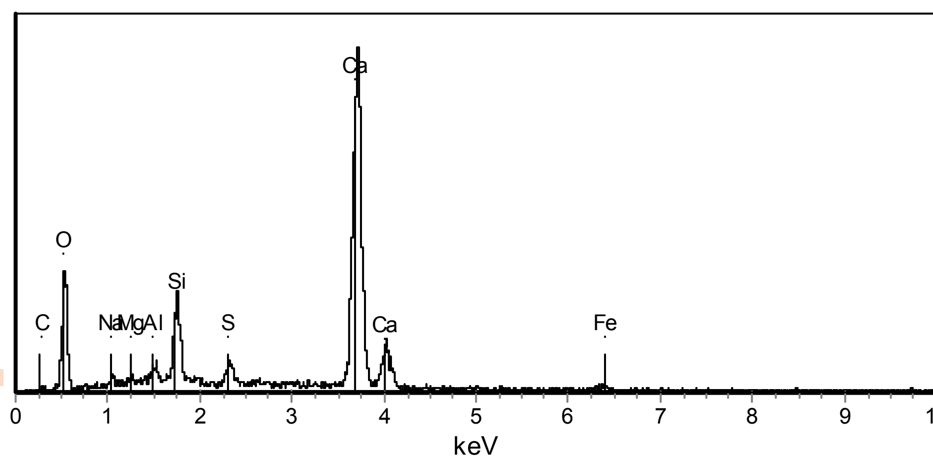


Class H with 6% Bentonite

- **Bicarbonation leaves behind "Popcorn" crystals of calcite in an isotropic matrix of silica gel**
  - Act as sand grains rather than binding agent.
  - New binding agent is now the decalcified silica gel







Conclusions (so far…)

- **Importance of simulated geologic sequestration conditions**
  - Free gas phase
  - Dissolved aqueous phase
  - HTHP cure
    - increased hydration
    - Smaller CH crystals
    - lower rate of attack
- **Degradation of cement in headspace significantly less than in aqueous phase**
- **Additive bentonite resulted in complete degradation**

Future Work

- **Continue with longer exposure times**
- **Additional cement additives**
- **Different conditions**
  - Salinity
  - Temperature
  - Pressure

Acknowledgements

- **George Scherer**
  - Princeton University
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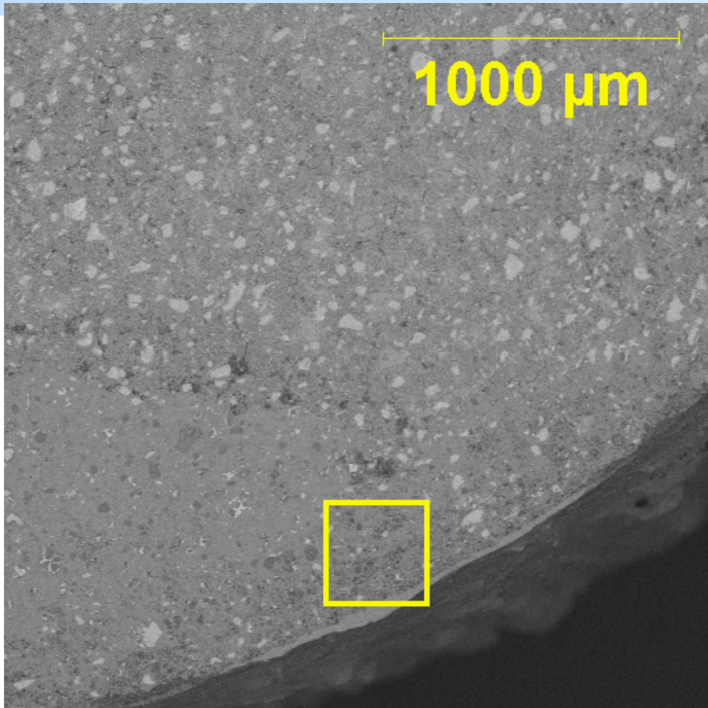
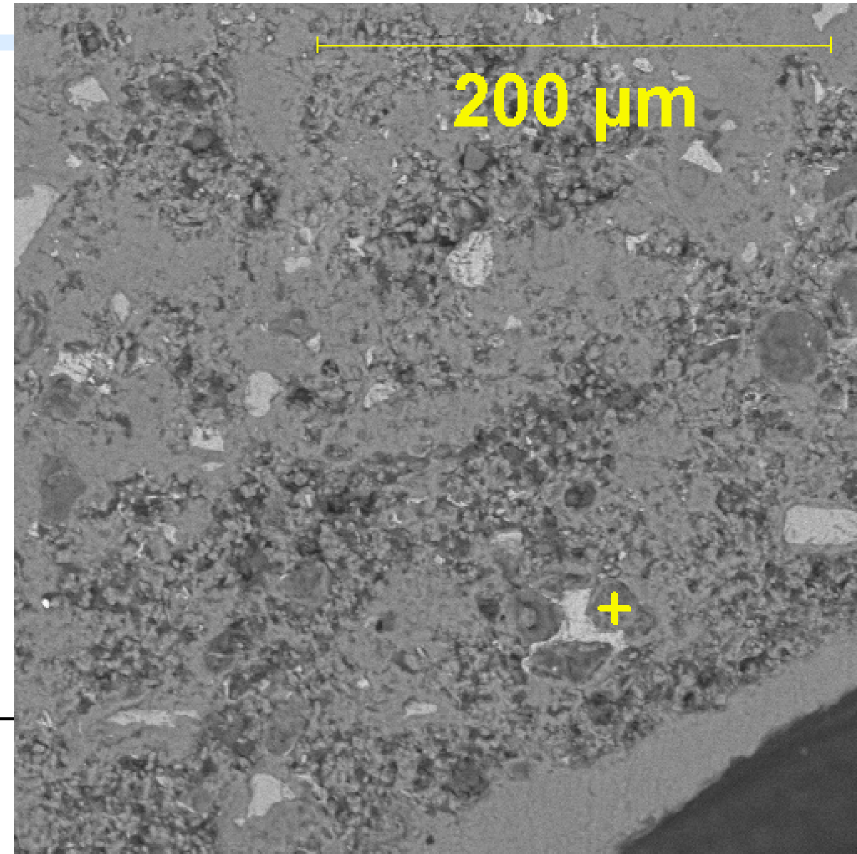
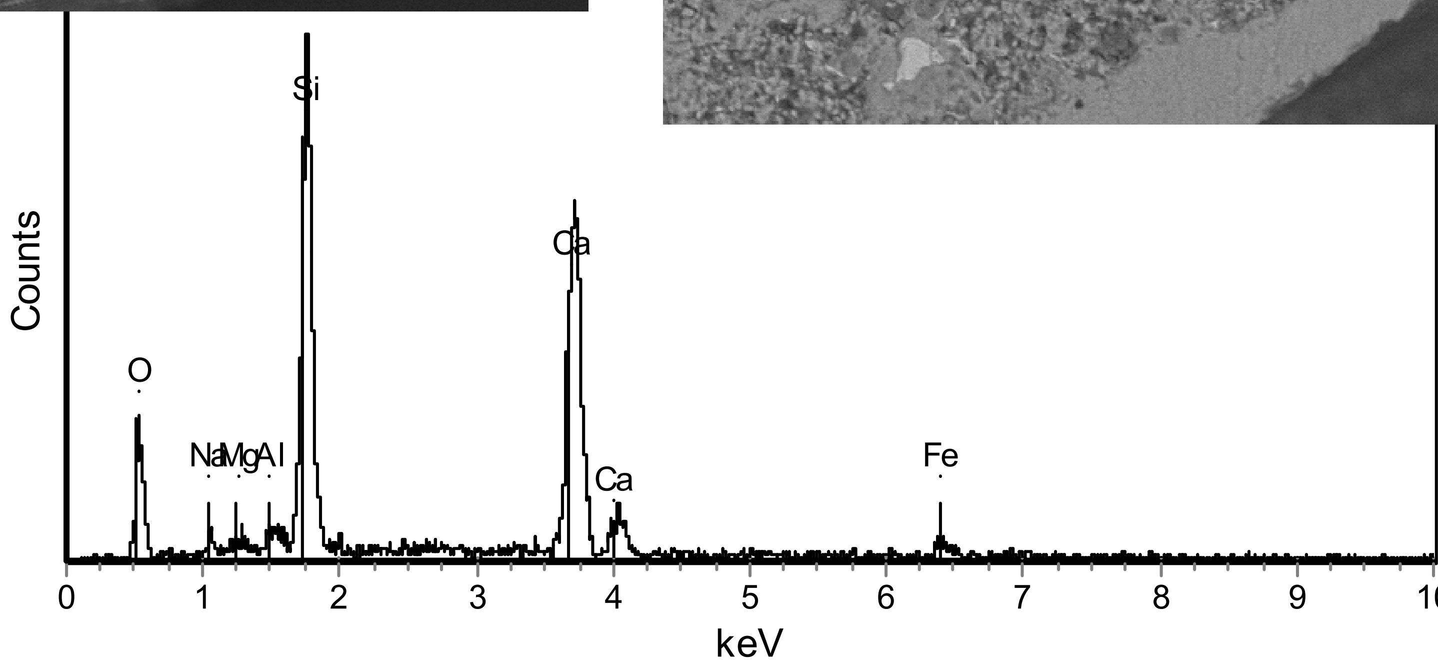
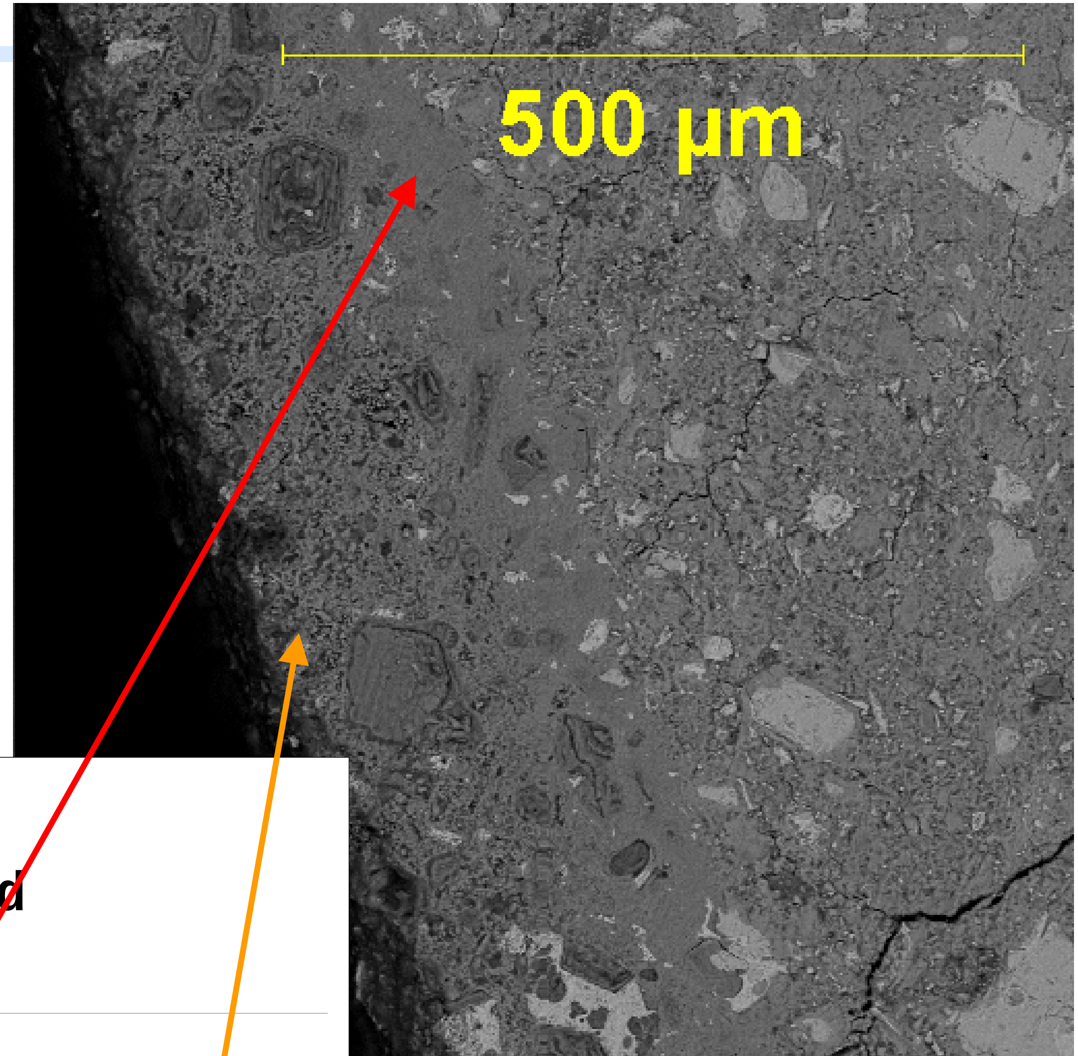
  - Carnegie Mellon University
- **Greg Lowry**
  - Carnegie Mellon University

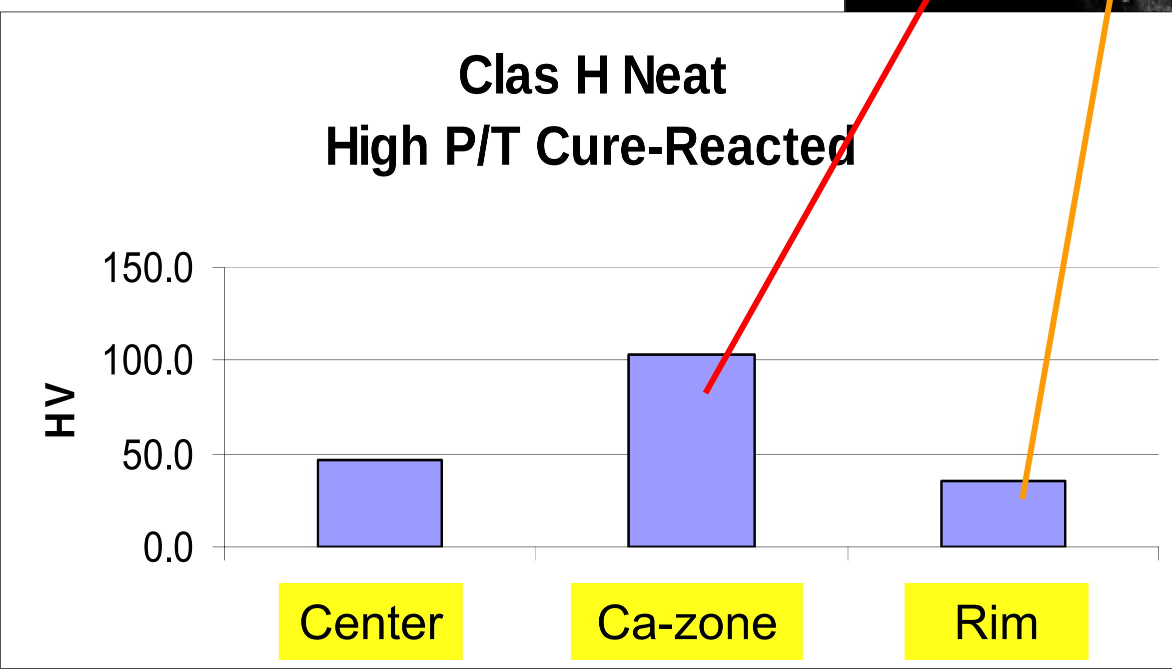

1000 µm

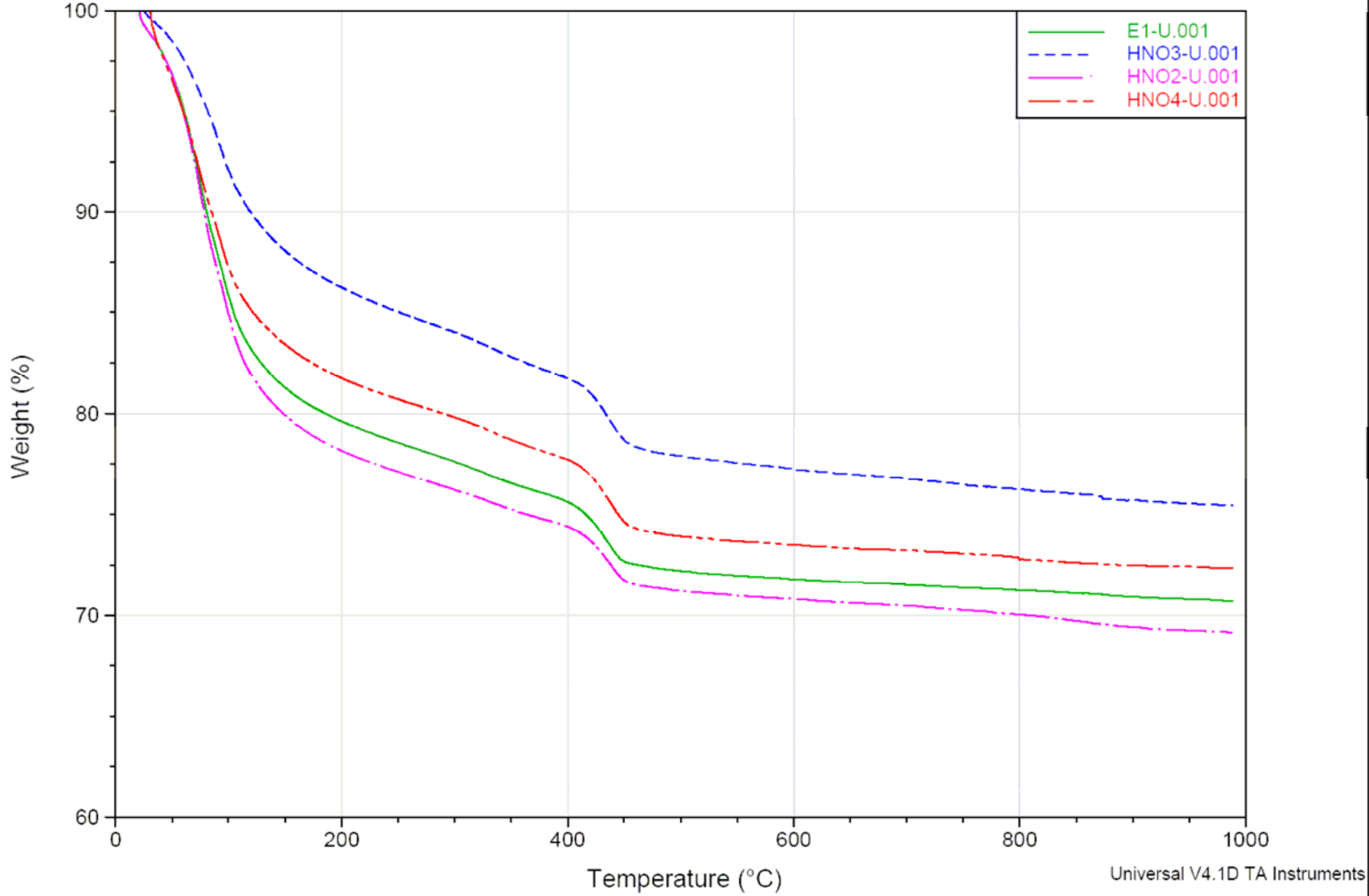

200 µm


Counts
O
Na
Mg
Al
Si
Ca
Ca
Fe
0
1
2
3
4
5
6
7
8
9
10
keV

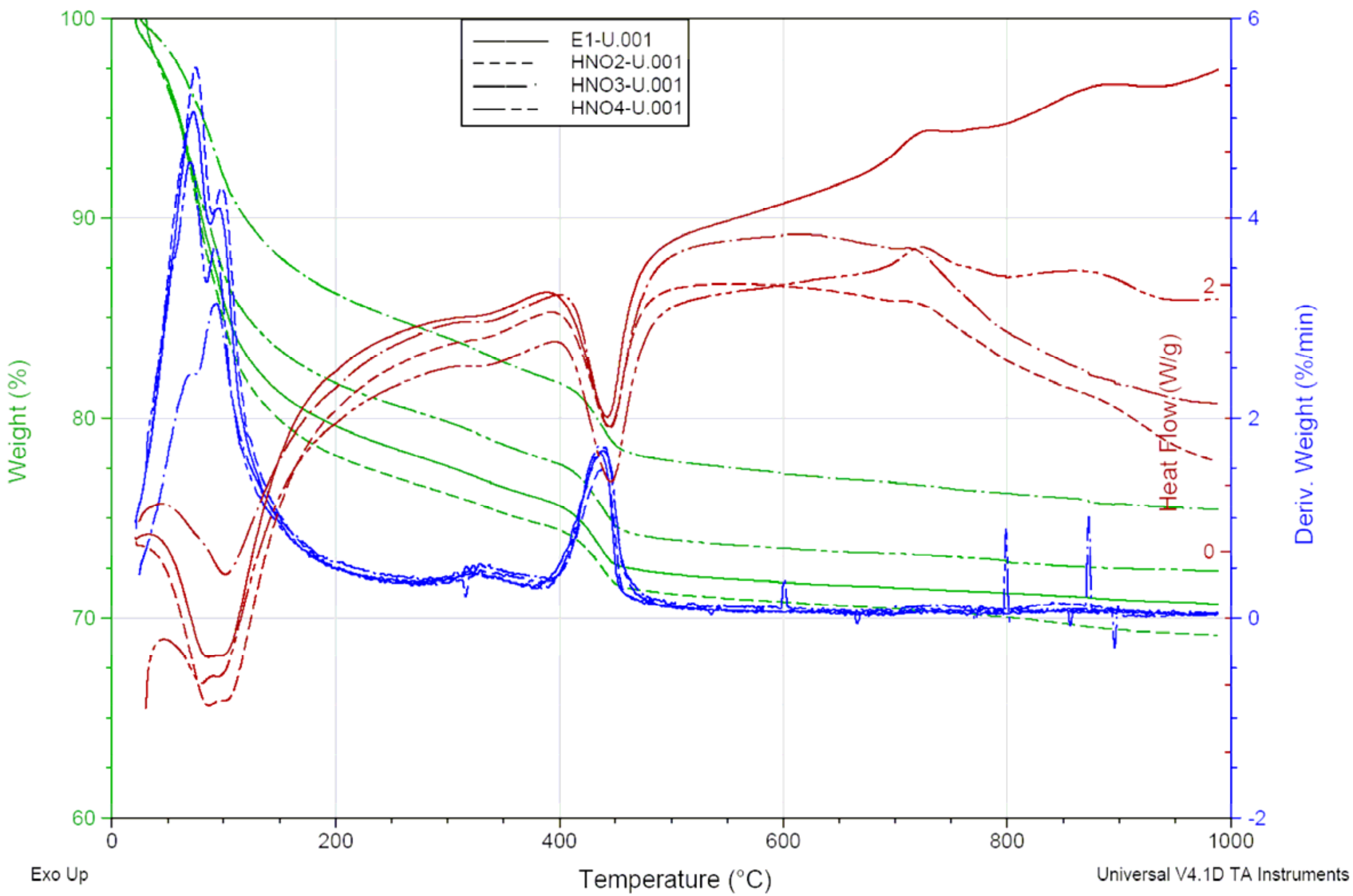
Vickers Microhardness



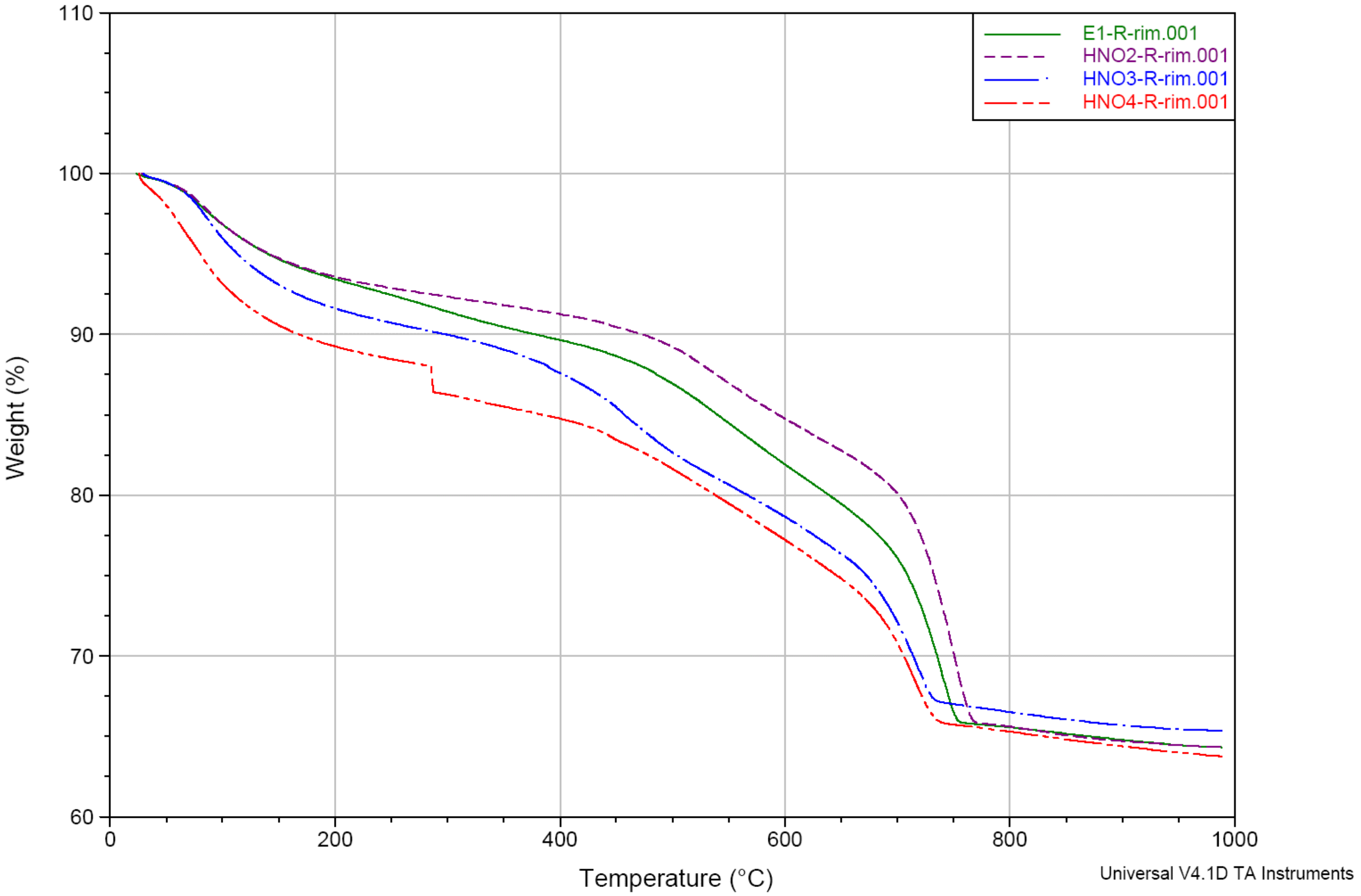




100
90
80
70
60
Weight (%)
0
200
400
600
800
1000
Temperature (°C)
E1-U.001
HNO3-U.001
HNO2-U.001
HNO4-U.001
Universal V4.1D TA Instruments



E1-U.001
HNO2-U.001
HNO3-U.001
HNO4-U.001
Weight (%)
Heat Flow (W/g)
Deriv. Weight (%/min)
Temperature (°C)
Exo Up
Universal V4.1D TA Instruments



110
100
90
80
70
60
Weight (%)
0
200
400
600
800
1000
Temperature (°C)
E1-R-rim.001
HNO2-R-rim.001
HNO3-R-rim.001
HNO4-R-rim.001
Universal V4.1D TA Instruments

Observations

High P/ High T

- Smaller CH
- AFt present
- Fewer unhydrated cement grains
- Smaller unhydrated cement grains

High P/ Low T

- High abundance of CH
- Abundance of C_4AF
- No AFt observed
- Greater abundance of unhydrated cement grains
- Low Cl observed

Low P/ High T

- Outside/surface “dimples”
- AFt present
- Several voids observed
- Typical CH observed

Low P/ Low T

- Abundant CH visible
- No AFt observed
- Unhydrated cement grains

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High P/
High T

- Well defined boundaries
  - Porous "popcorn carbonation" Rim
- Ca-rich "front"
  - Porous area behind "front"
  - Little intermixing
- Symmetrical reaction rim
- Depth: 188 μm to 239 μm
- Ave depth: 220 μm

High P/
Low T

- Intermixing Boundaries
  - "popcorn carbonation"
  - Somewhat well defined Ca-rich "front"
- Near-symmetrical reaction rim
- Depth: 311 μm to 572 μm
- Ave depth: 442 μm

Low P/
High T

- Intermixing boundaries
  - Porous "popcorn carbonation"
  - Ca-rich "front"
  - Variable reaction rim
  - Depth: 89.5 μm to 1930 μm
  - Ave depth: 437 μm with blob, 271 μm without blob

Low P/
Low T

- Intermixing Boundaries
  - "popcorn carbonation"
  - Ca-rich "front"
  - Porous area behind front
- Near-symmetrical reaction rim
- Depth: 465 to 741 μm
- Ave depth: 587 μm

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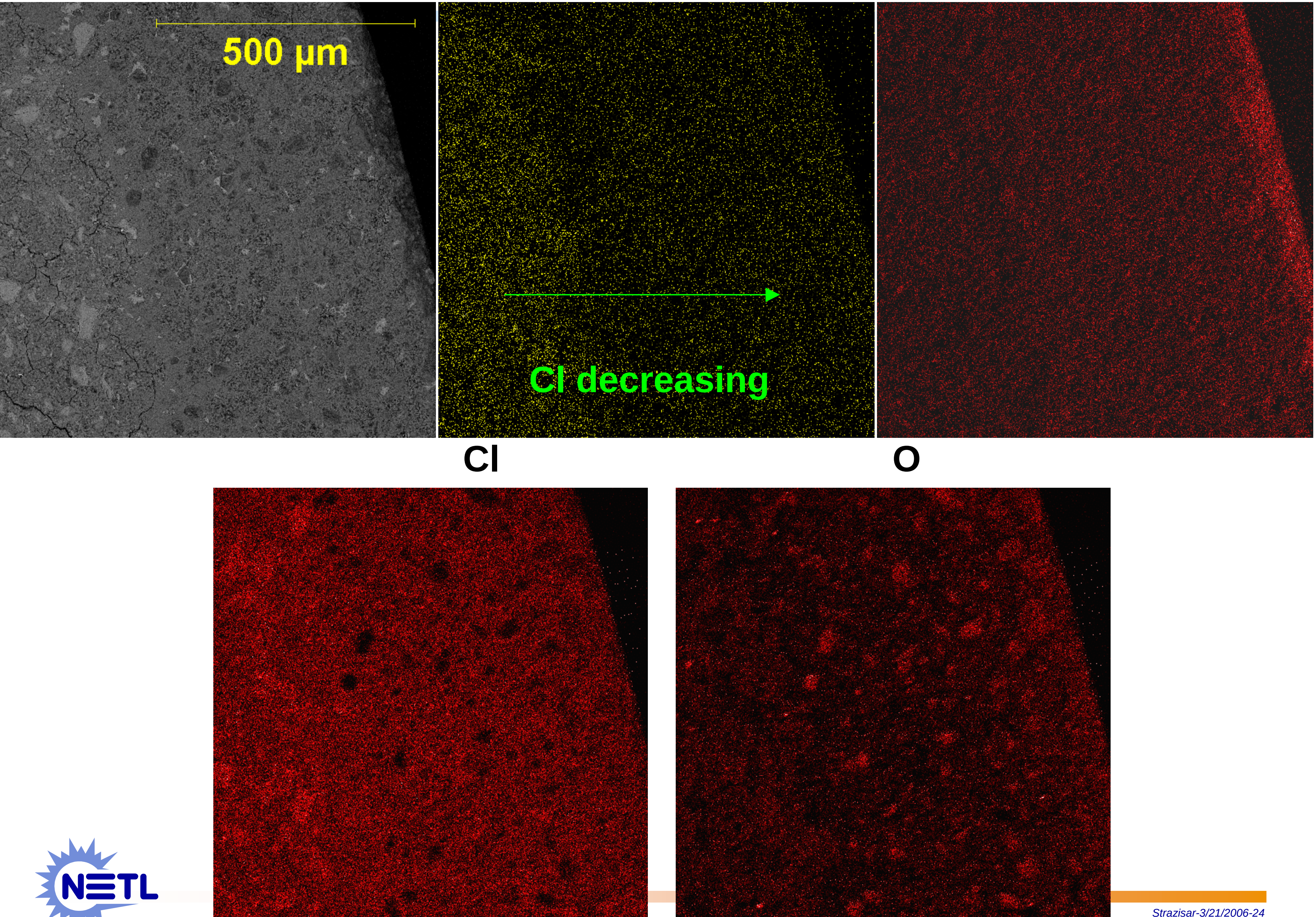
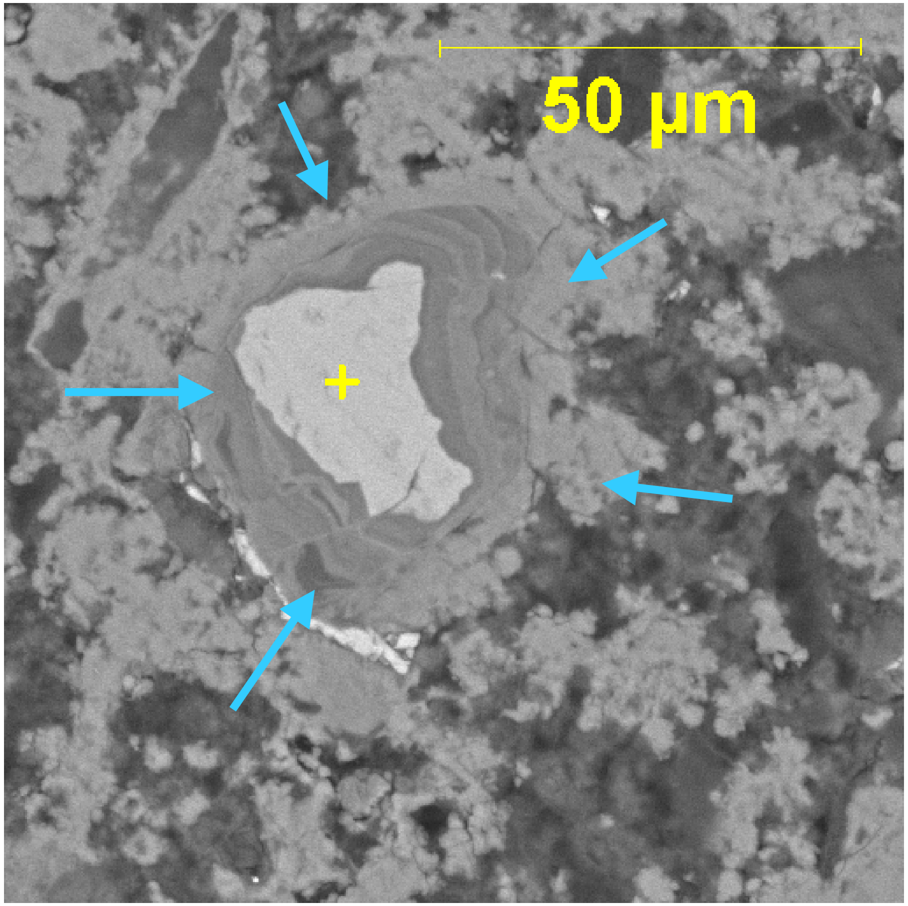
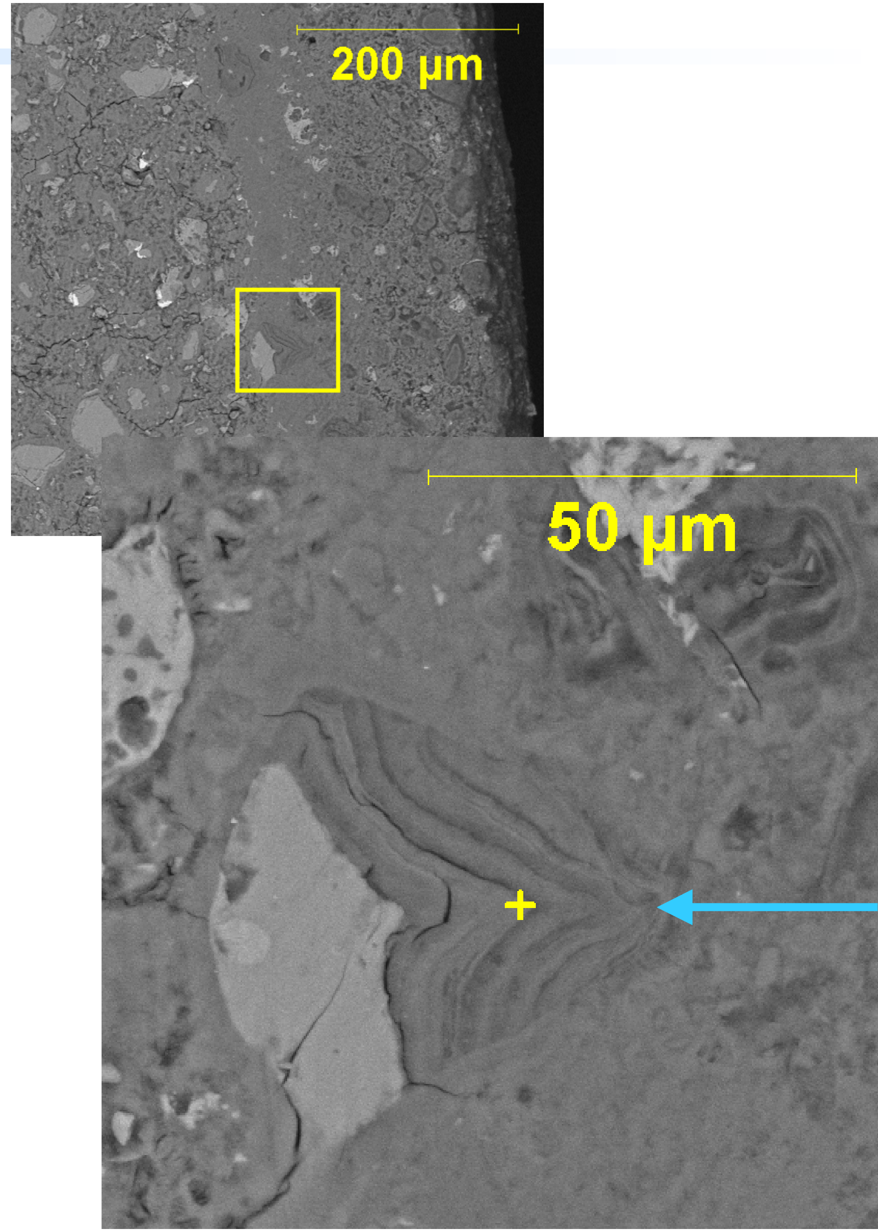


Ca Si

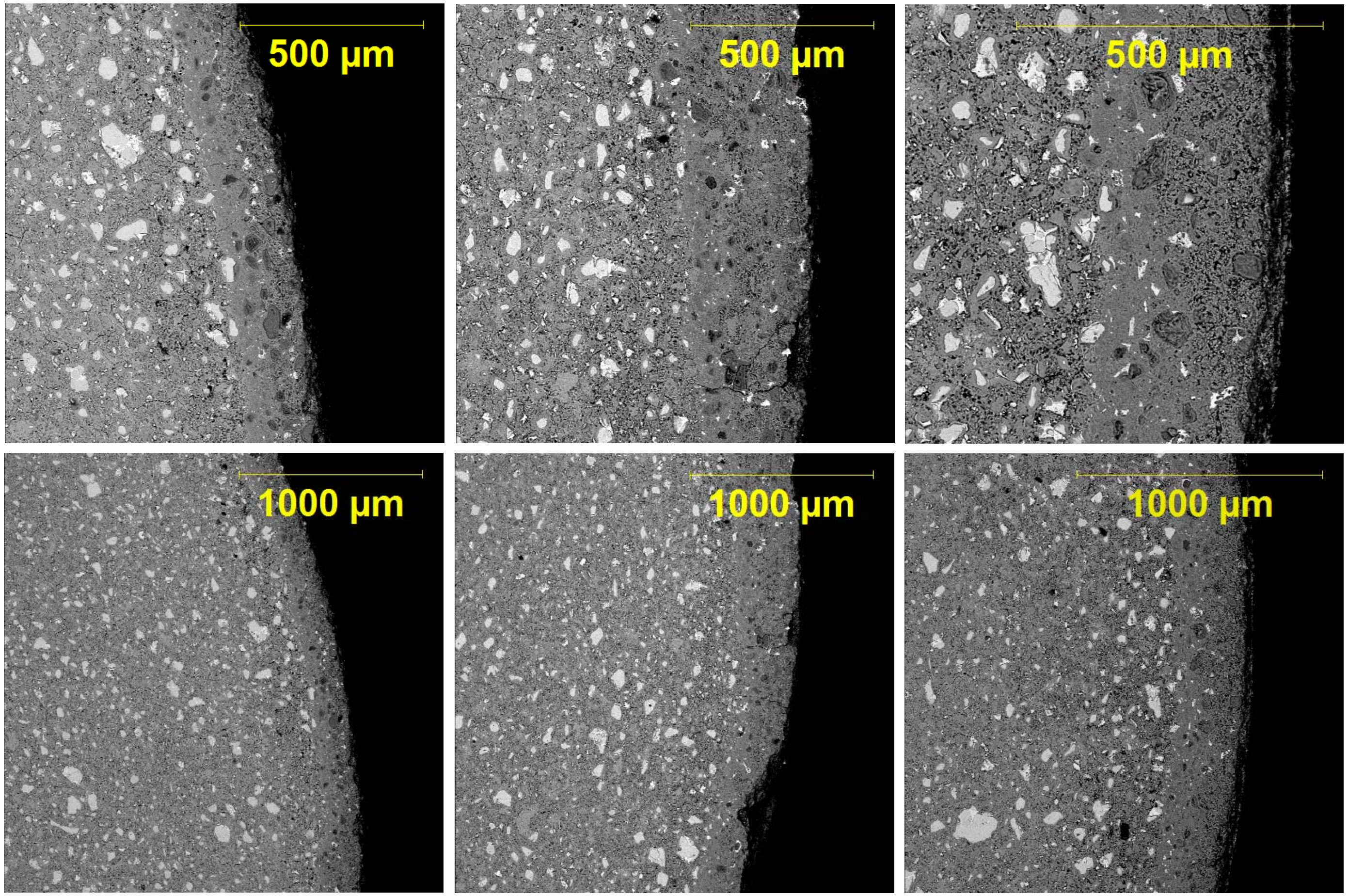


Class H with bentonite



Class H high P/T cure

Progression of HTHP – Aqueous Phase



9 days
~200 µm

23 days
~330 µm

61 days