Advancing Subsurface Monitoring:

Spectral induced polarization for detecting remedial amendment delivery and reactivity

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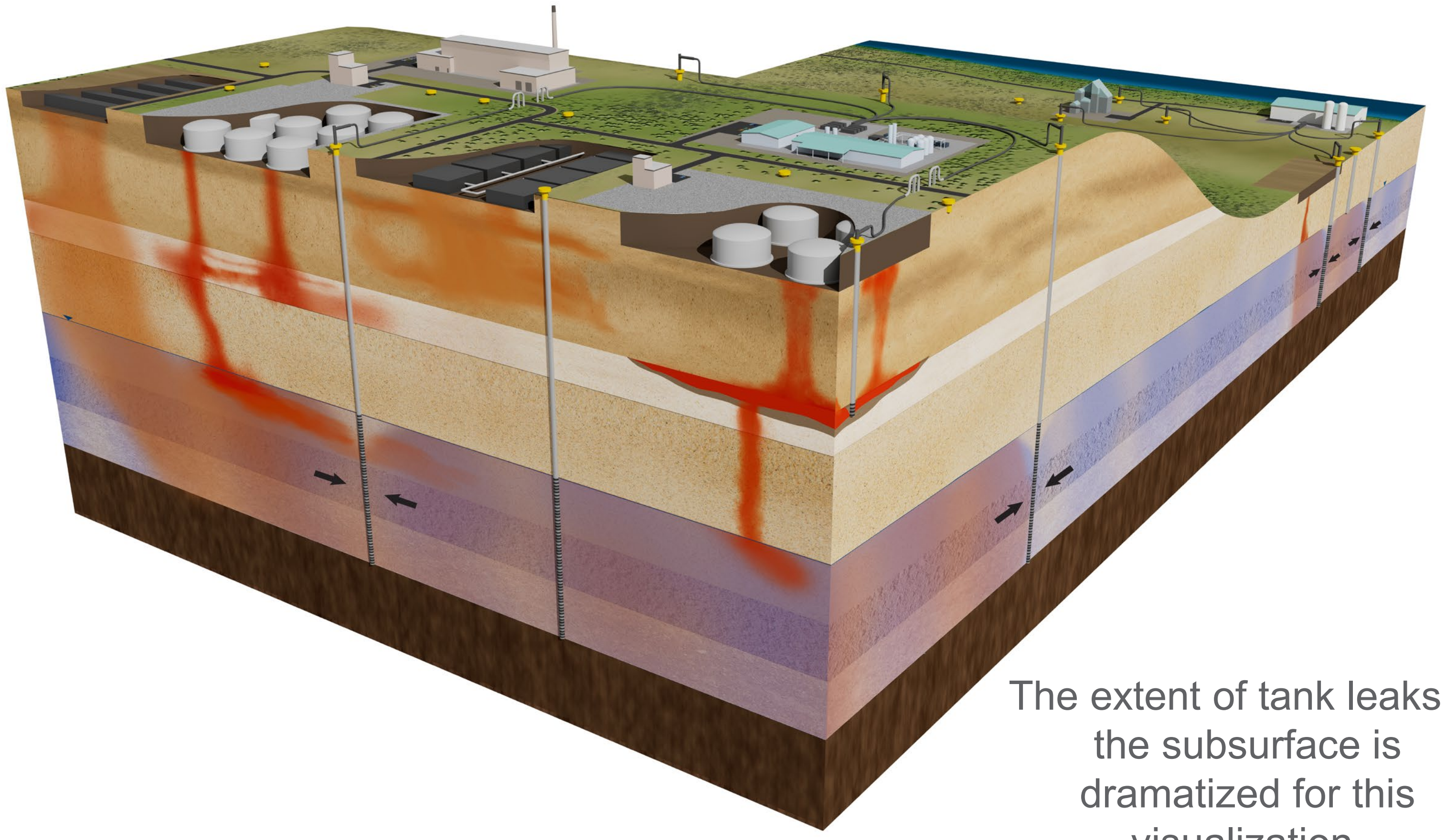
Talk Preview

Objective: Demonstrate electrical geophysics for understanding reactions at the solid-water interface during subsurface remediation

- What is spectral induced polarization (SIP) and how does it relate to commonly used geophysical techniques?
- How can we use SIP to understand mineralogy and interfacial chemistry?
- Can we monitor apatite formation in sediments with SIP?
- Can we characterize iron transformations in sediments with SIP?

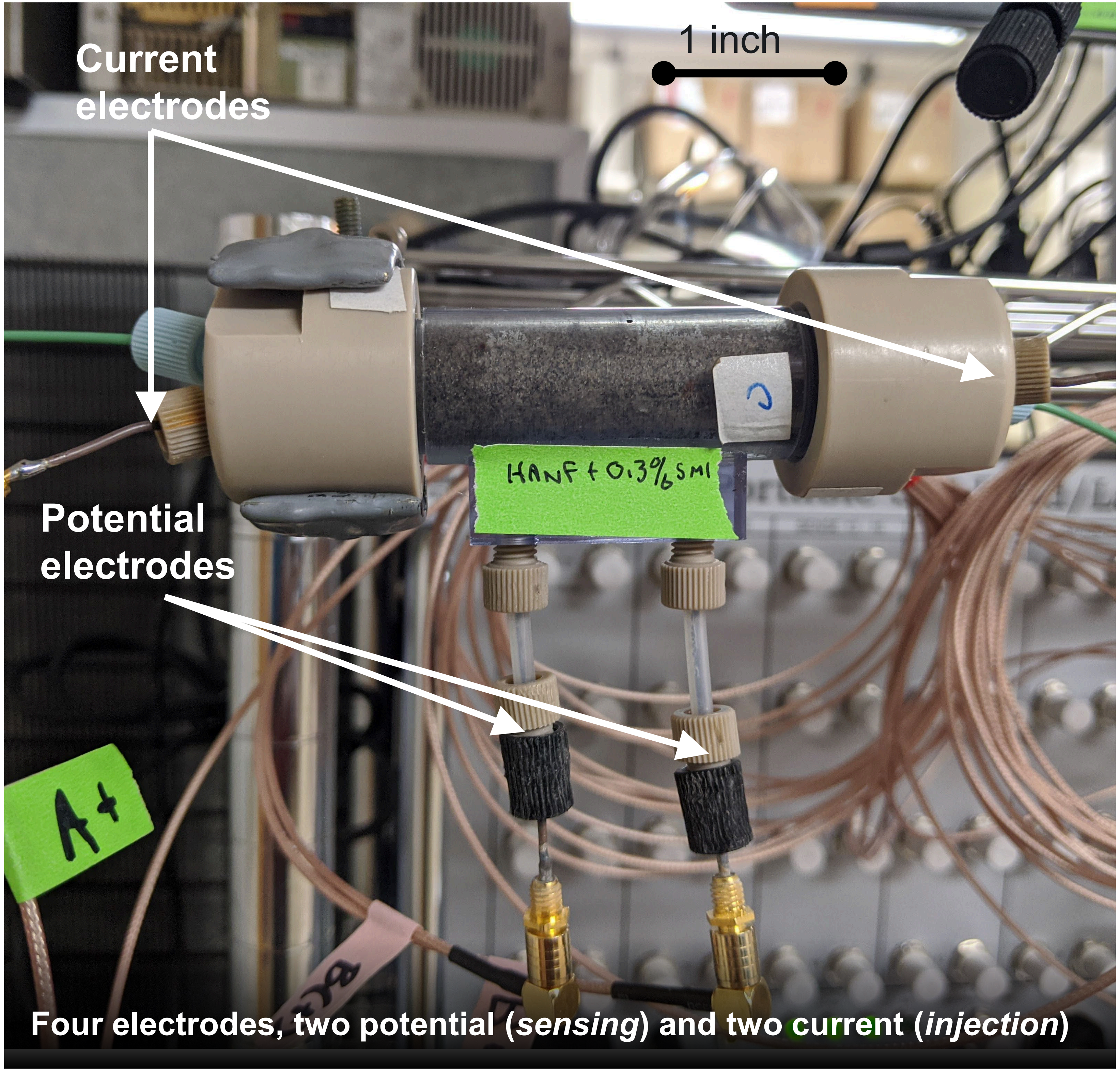


The extent of tank leaks to the subsurface is dramatized for this visualization.

What is Spectral Induced Polarization?

A geophysical technique that applies low alternating electrical current across a pair of electrodes (*current*) and measures a response across sensing (*potential*) electrodes in-between the current electrodes

Collects both *resistivity* (inverse is conductivity) and *phase shifts*

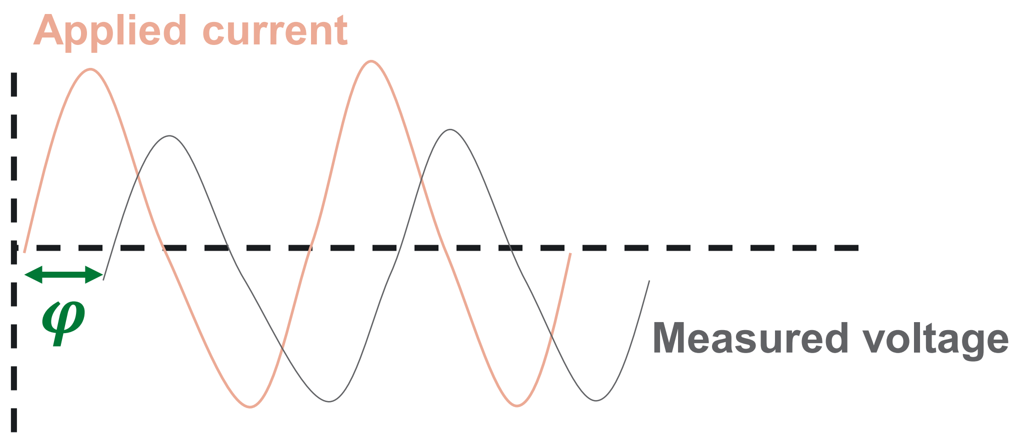


Four electrodes, two potential (*sensing*) and two current (*injection*)

Comparison to Conventional Geophysical Techniques

- Electrical resistivity, ER
  - Commonly used in the field
  - ER does not allow separation of electrolytic (1 – via the fluid-filled pores) and interfacial (2 – via the EDL) charge transport processes
- Spectral induced polarization, SIP
  - Being developed for field, limited use to date
  - SIP measures complex conductivity and phase, φ
  - Allows separation and provides high sensitivity to processes impacting interfacial charge transport mechanisms

*Measured values in orange and green

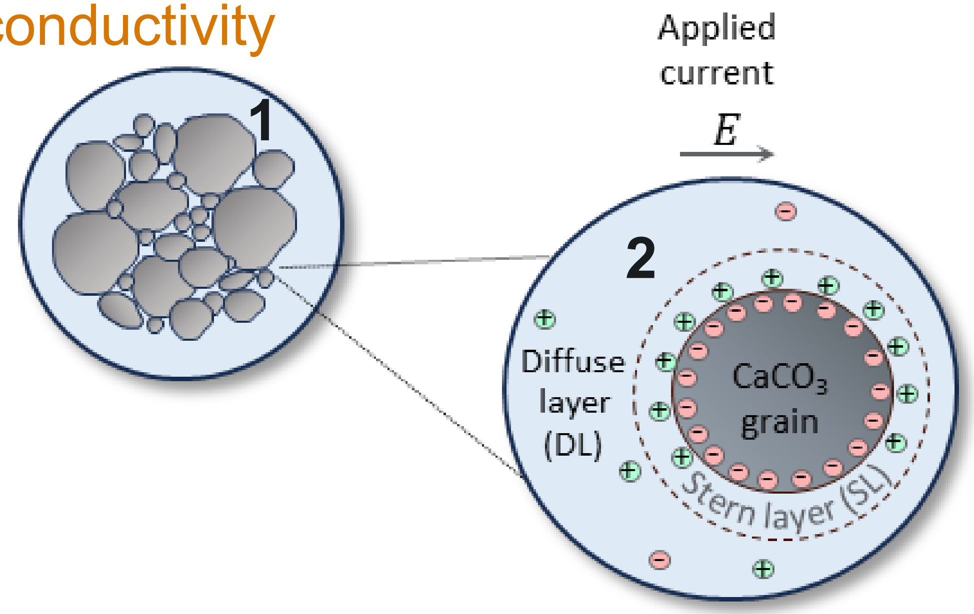


$$Complex = Real + [i \times Imaginary]$$

$$\sigma = \sigma' + i\sigma'' = |\sigma| e^{-i\varphi}$$

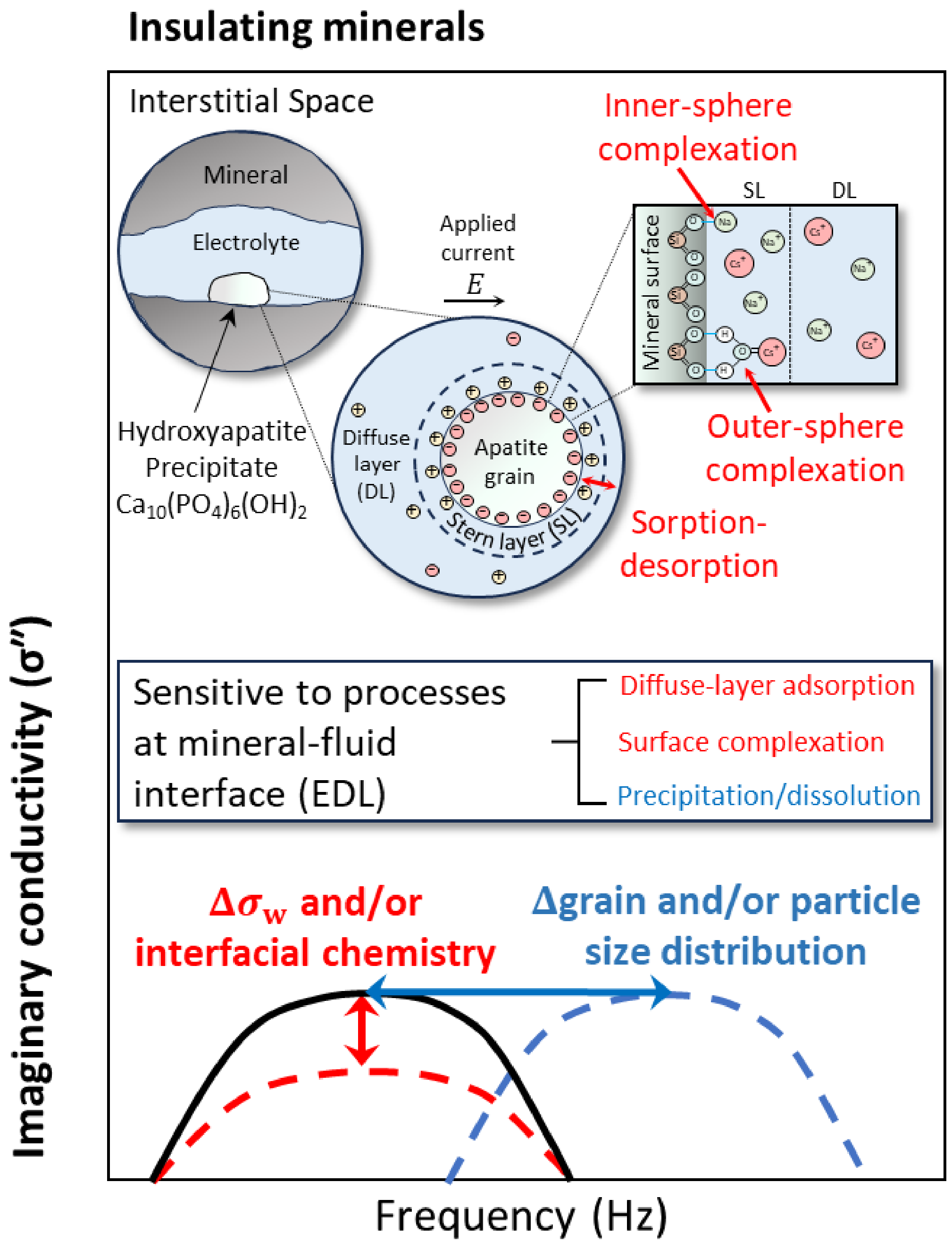
complex conductivity

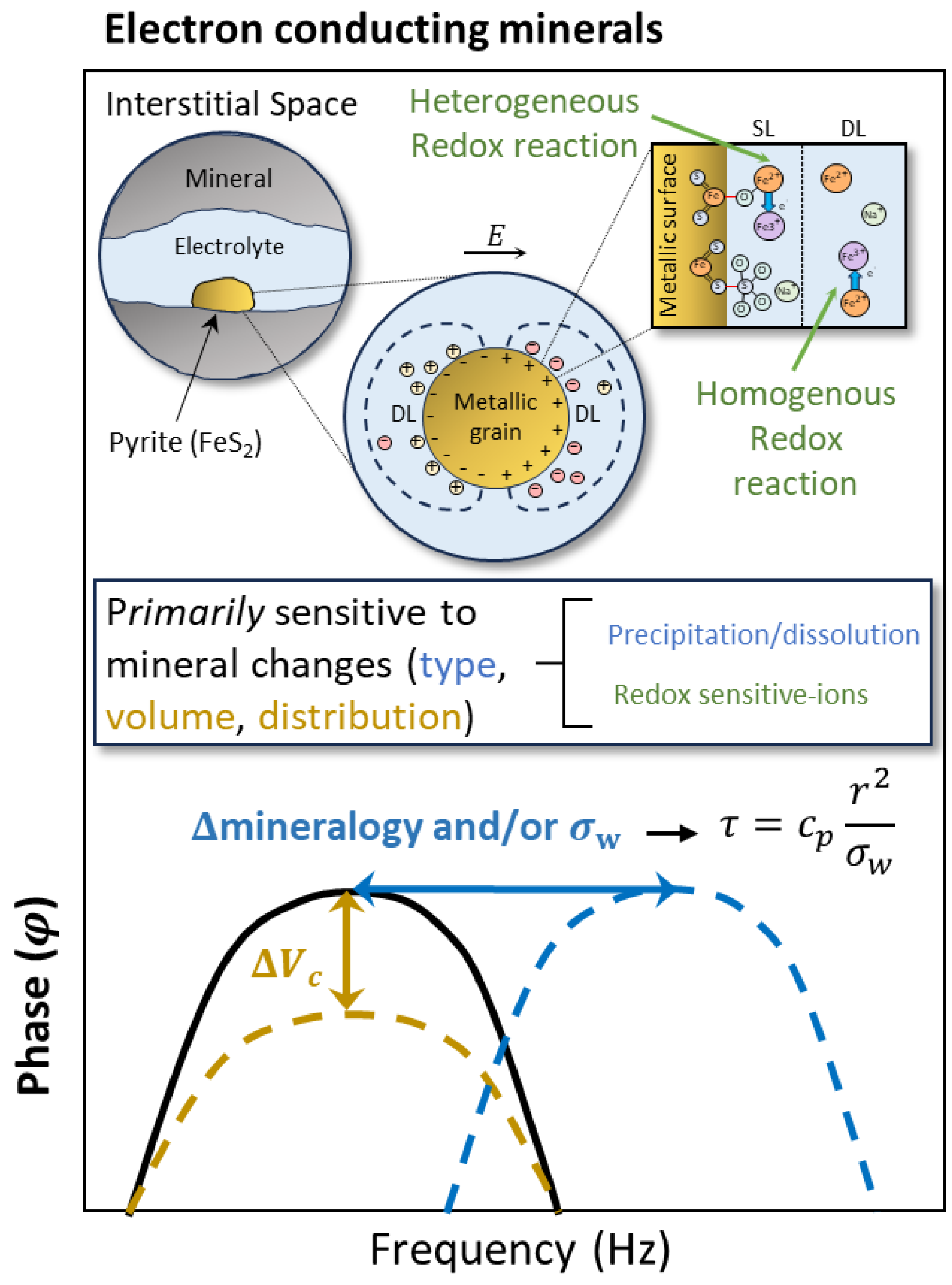
phase



Conceptual Model of SIP

- Significantly different response for *insulating* versus *electron conducting* minerals
- Shifts expected in both *frequency* and *magnitude* of response
- *Physical* and *geochemical* changes impact response



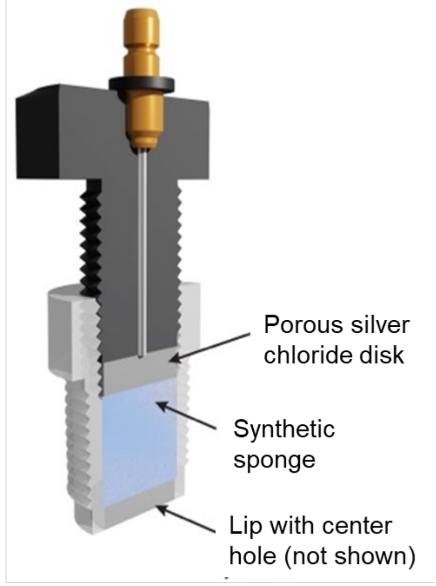


Δ refers to change, σ_w is fluid conductivity, SSA is specific surface area, V_c is volume content (including particle size) of electron conducting minerals, τ is relaxation time, c_p is specific polarizability, arrows delineate change from baseline peak (*black solid line*) after geochemical reaction (*dashed line*)

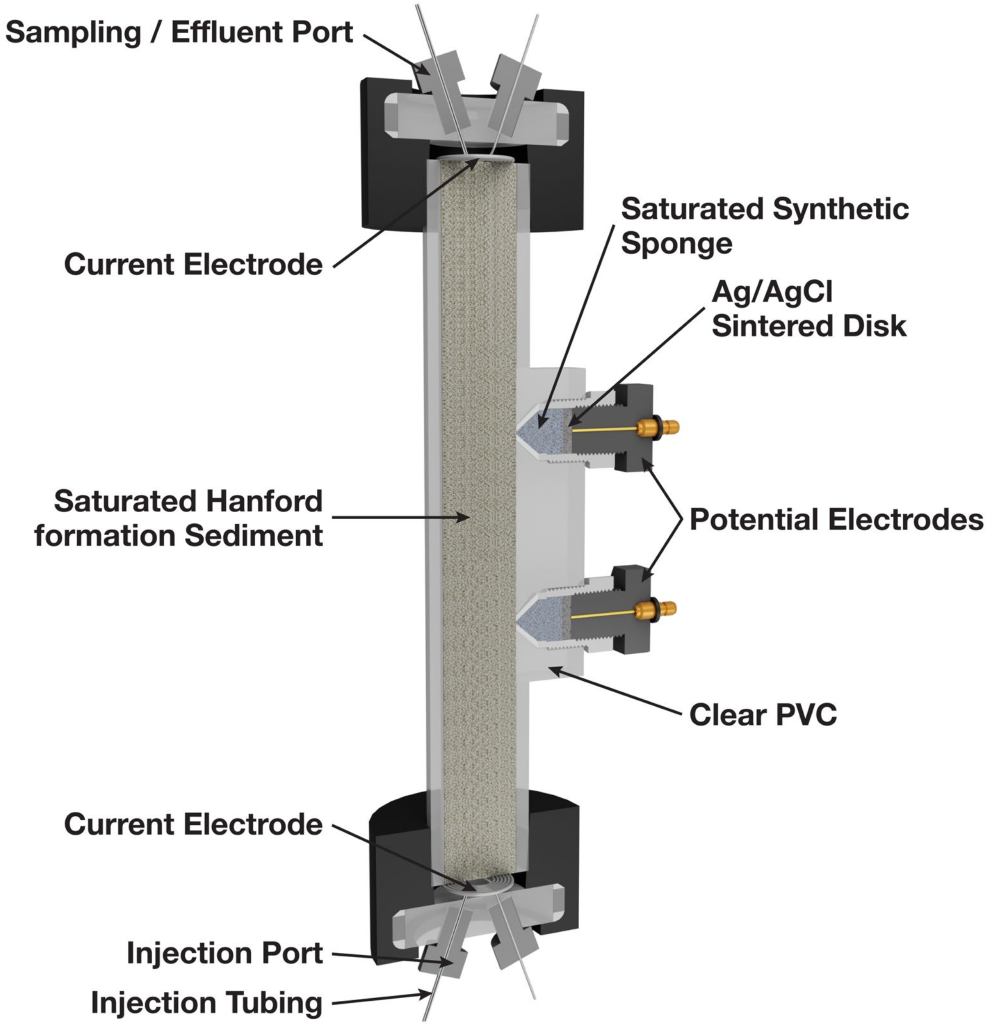
Approach

Objective: Evaluate SIP response for non-intrusively monitoring remediation in the subsurface (including both delivery and subsequent transformations)

1. Determine SIP response during remediation
   - During treatment with particulate zero valent iron or liquid apatite-forming amendments
   - Following groundwater flushing of injected solutions
2. Identify signatures associated with SIP response, if possible
   - Characterize column sediments to quantify physical and geochemical changes



SIP potential electrode



Experimental scale – one-dimensional columns

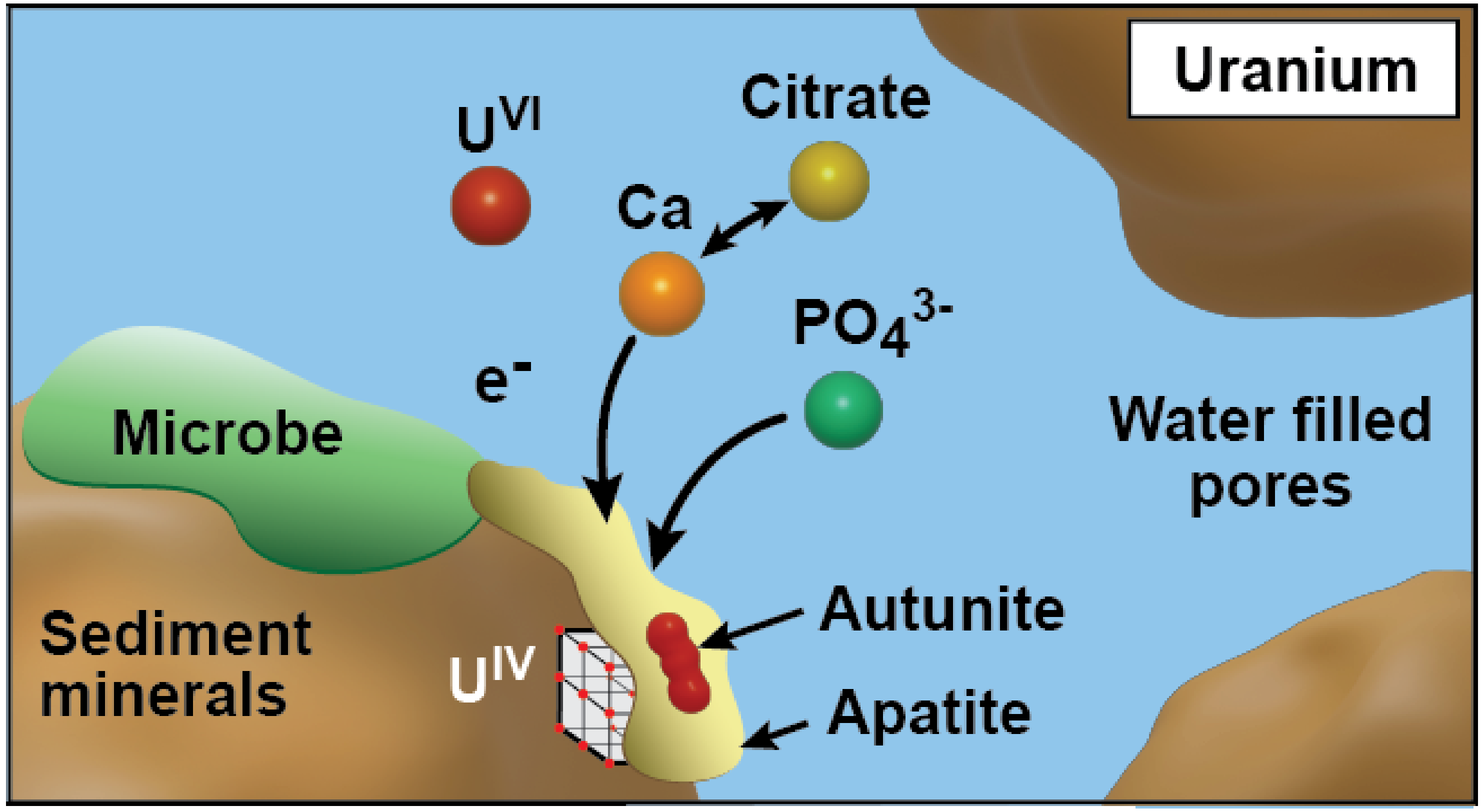
What Happens During Liquid PO_4 Injection?

High ionic strength injection solution fills pore spaces

Ca^{+2} and PO_4^{-3} become available in solution

Apatite $Ca_{10}(PO_4)_6(OH)_2$ precipitates on sediment particles

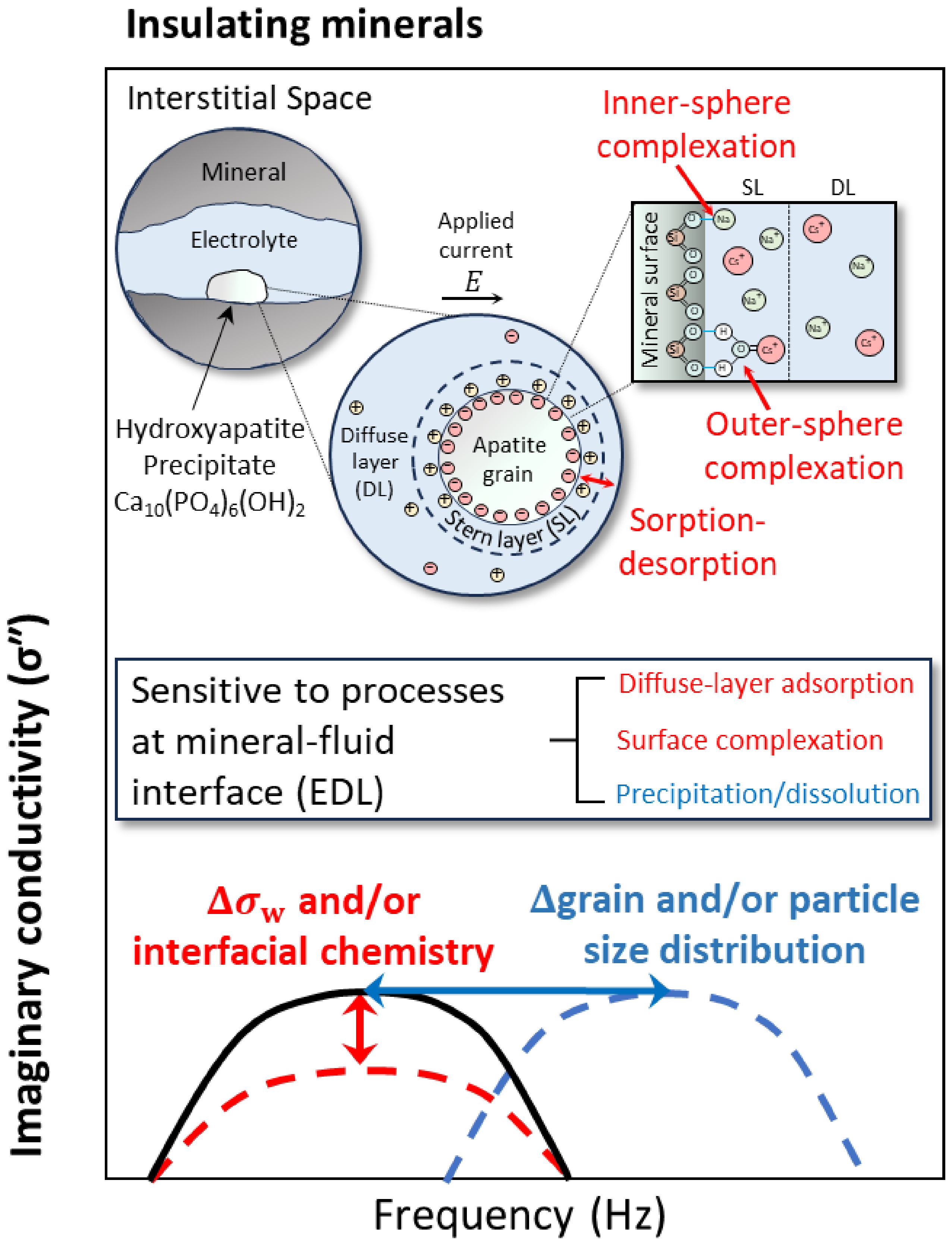
Conceptual diagram of delivery of calcium citrate PO_4 solutions into pore space with subsequent precipitation of apatite and contaminant-specific precipitates (e.g., autunite)



Can we identify when and where apatite is forming?

Conceptual Model of Liquid PO_4 for SIP

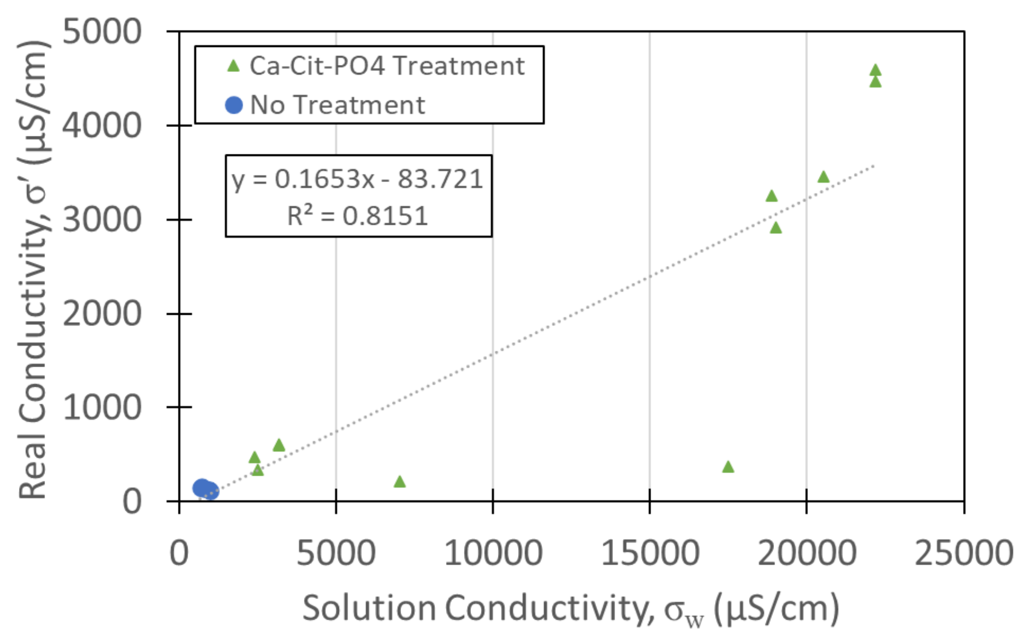
- Initial injection
  - ↑ σ_w contributes to ↑ σ' and ↓ φ
  - ↑ σ'' from ion exchange, adsorption, and/or initial $Ca\text{-}PO_4$ precipitation
- Post injection
  - ↓ σ_w back to natural conditions ↑ φ
  - ↑ σ'' from ion exchange, adsorption, and/or initial $Ca\text{-}PO_4$ precipitation
  - Shift in peak frequency due to pore blocking or particle size and roughness changes

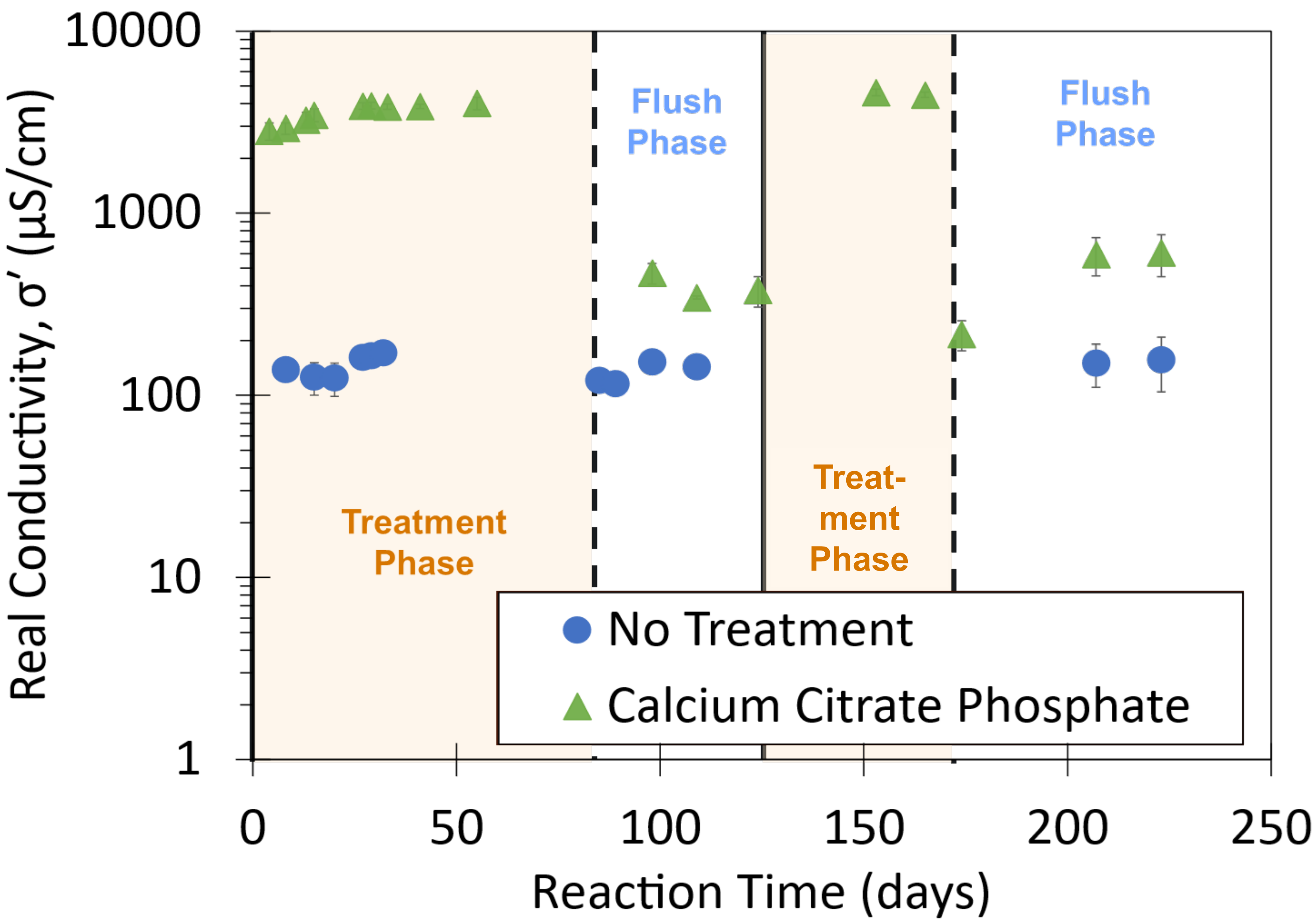


Results: Liquid PO_4 Amendments Column Testing

Significant increase in real conductivity, σ′, only during treatment with apatite-forming solutions

- Similar to ER response
- Correlates with solution conductivity increases

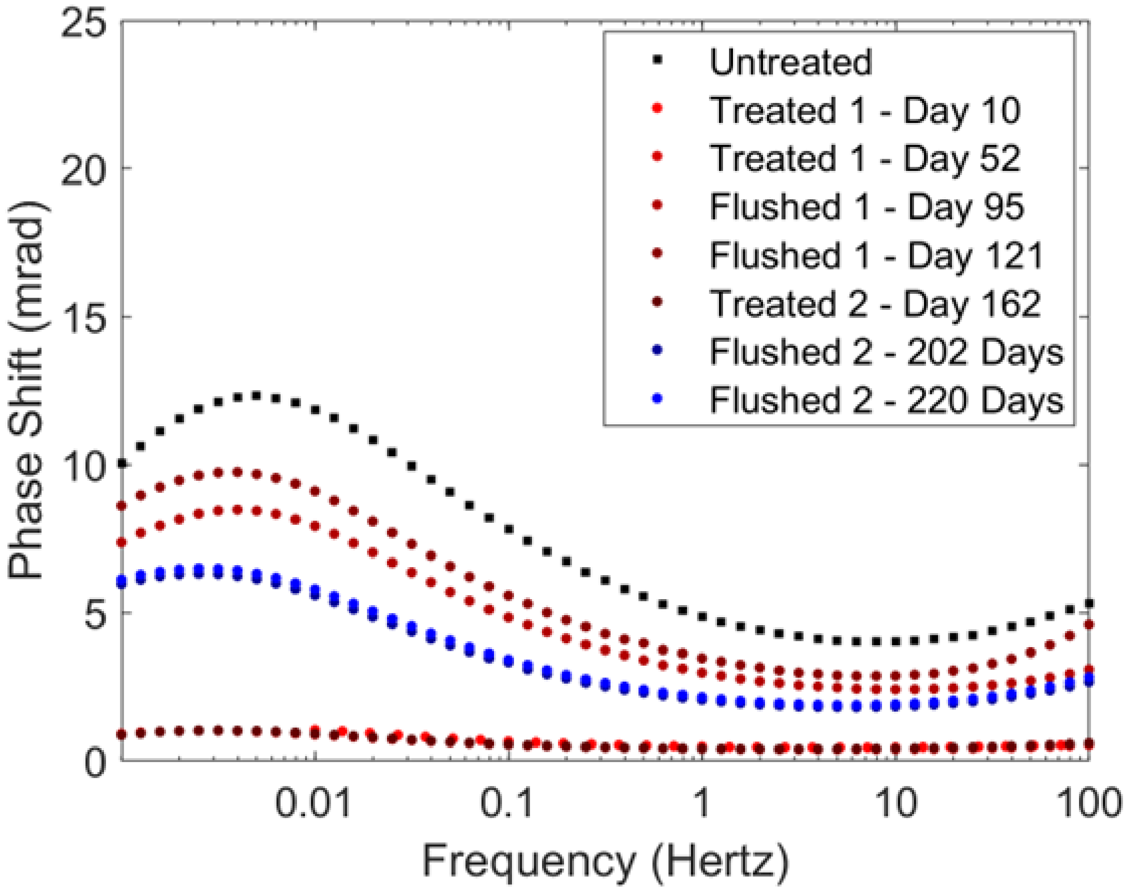


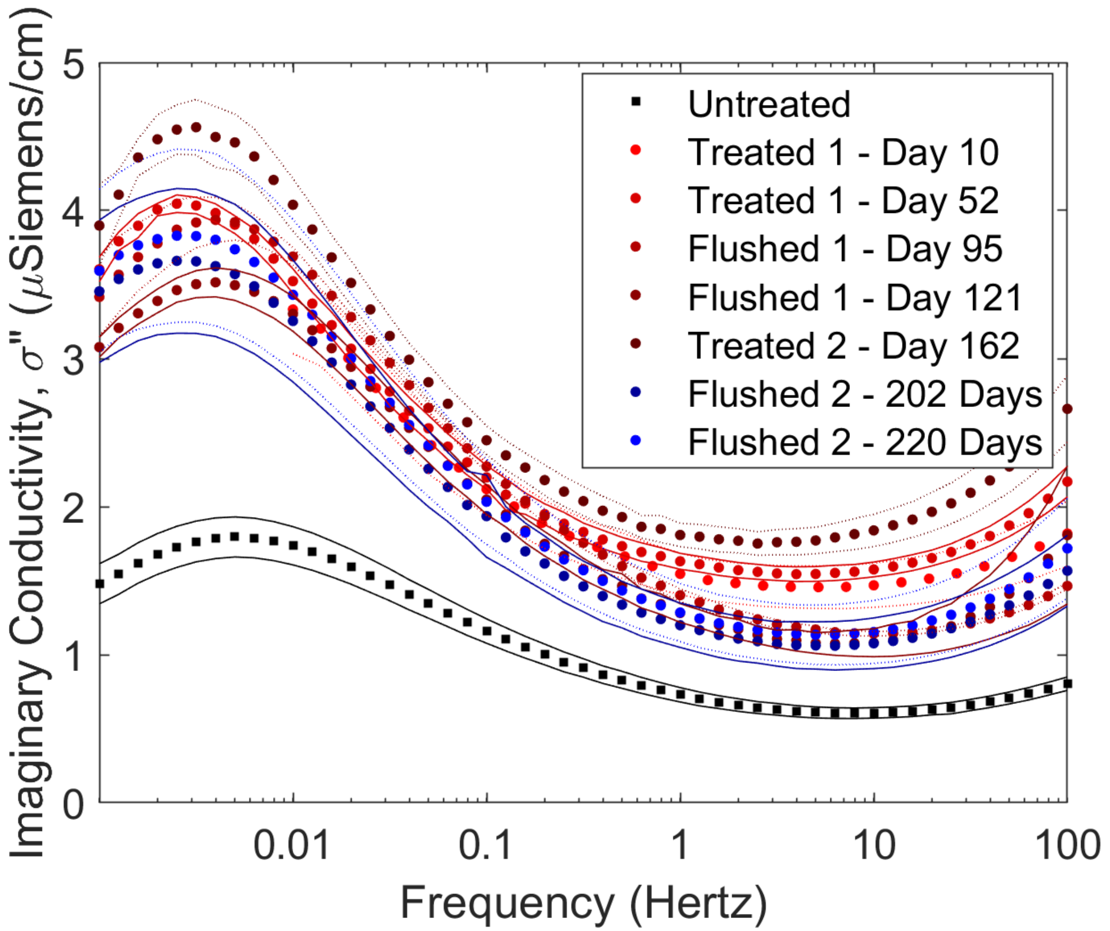


Results: Liquid PO_4 Amendments Column Testing

Increase in imaginary conductivity (σ''), following treatment and after flushing

- Increase consistent after flushing, not impacted by solution ionic strength
- Frequency-specific response (peak at 0.005 Hz)
- Suggests impacts to particle surfaces from precipitation

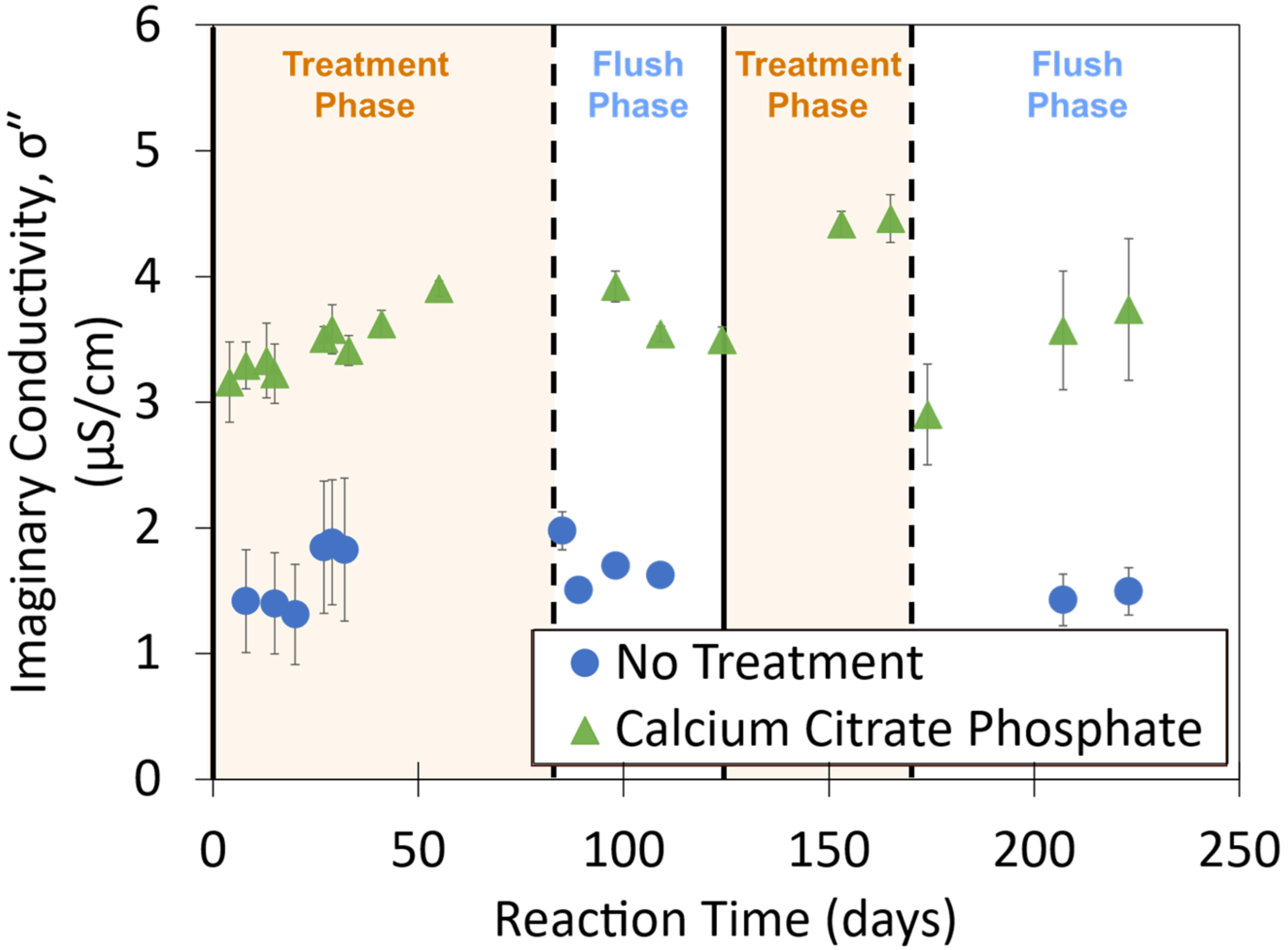




Results: Liquid PO_4 Amendments Column Testing

Increase in imaginary conductivity (at 0.005 Hz), σ″, following treatment and after flushing

- Increase consistent after flushing, not impacted by solution
- Frequency-specific response (at 0.005 Hz)
- Suggests impacts to particle surfaces and interface
- SIP provides additional information not possible with ER



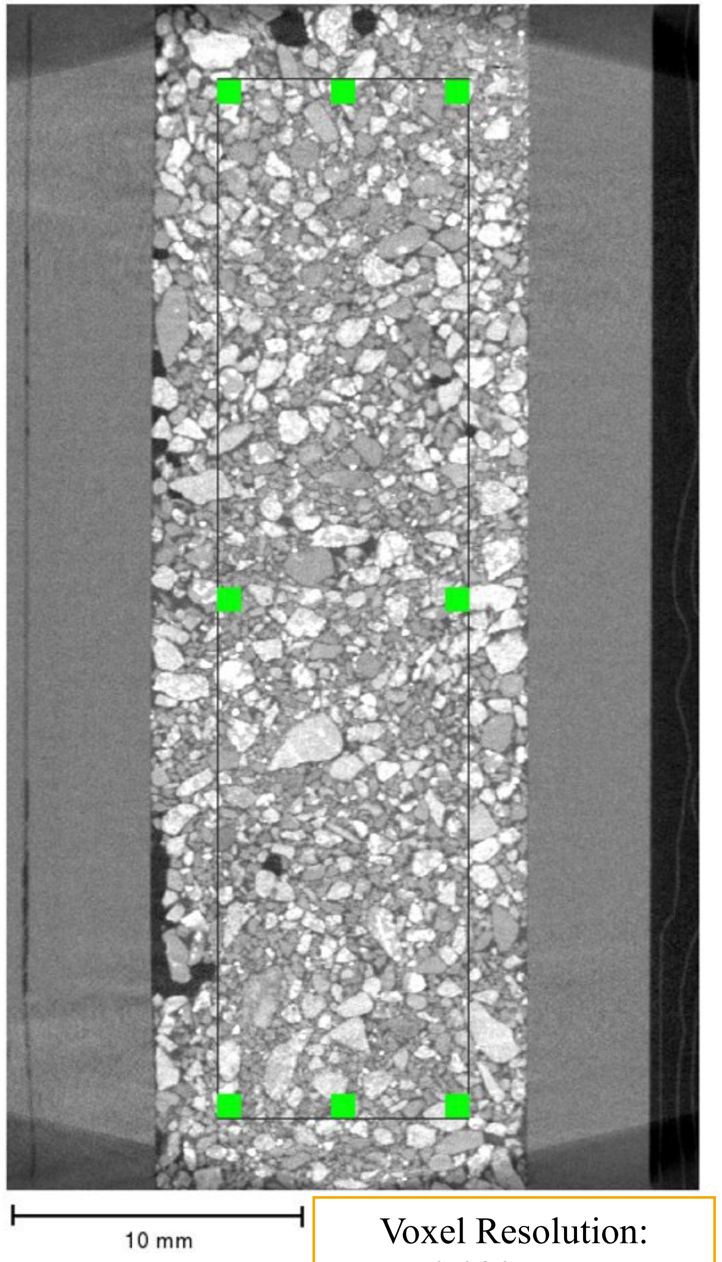
Results: Liquid PO_4 Amendments Post Characterization

Condition	BET Surface Area (m^2/g)
Untreated	7.7 ± 1.6
Before first flush	8.2 ± 0.1
After first flush	10.2 ± 0.6
After second flush	8.4 ± 0.3

Average 2-4 samples from a single column

Sample	Porosity		
	Inject #1	Flush #1	Flush #2
Treated	0.30	0.32	0.33
	0.33	0.31	0.36
	0.30	0.32	NM
	0.31	NM	NM
	0.32	NM	NM
Control	0.33	0.33	0.38
	0.31	0.26	0.29

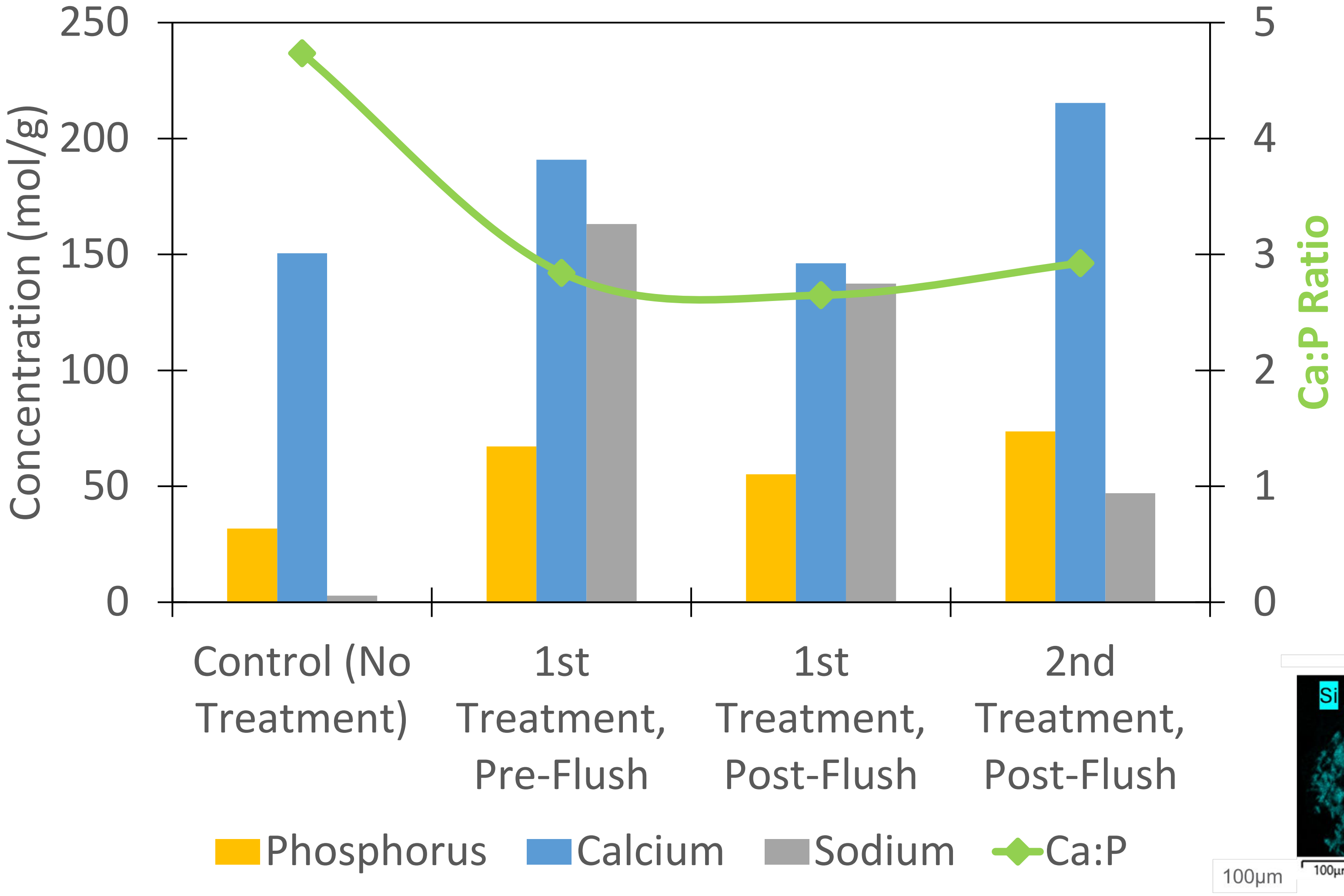
Showing replicates over time; NM = not measured

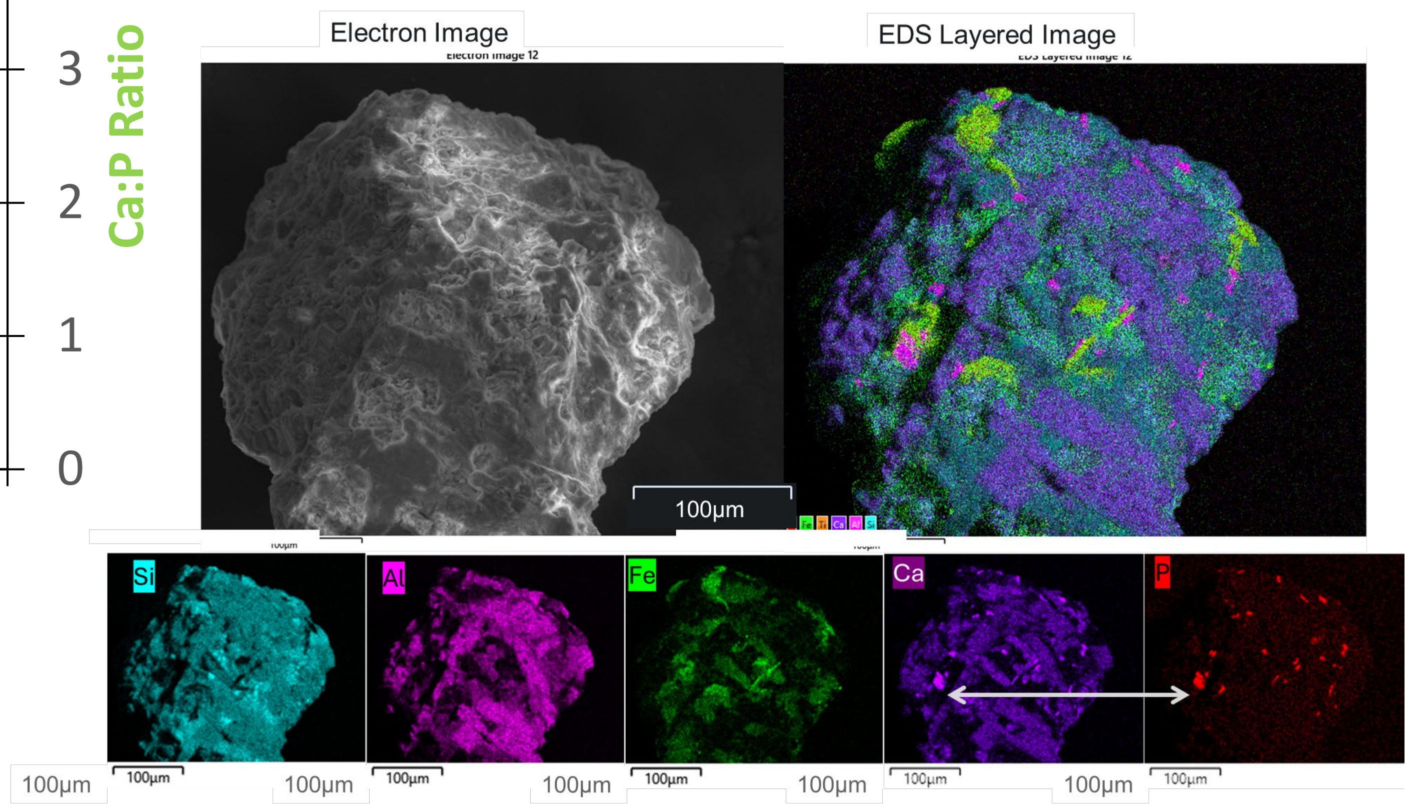


Voxel Resolution: 0.0205 mm

- No significant change in surface area as measured by BET
- No consistent change in porosity, pore connectivity, or pore size as shown by XCT

Results: Liquid PO_4 Amendments Post Characterization

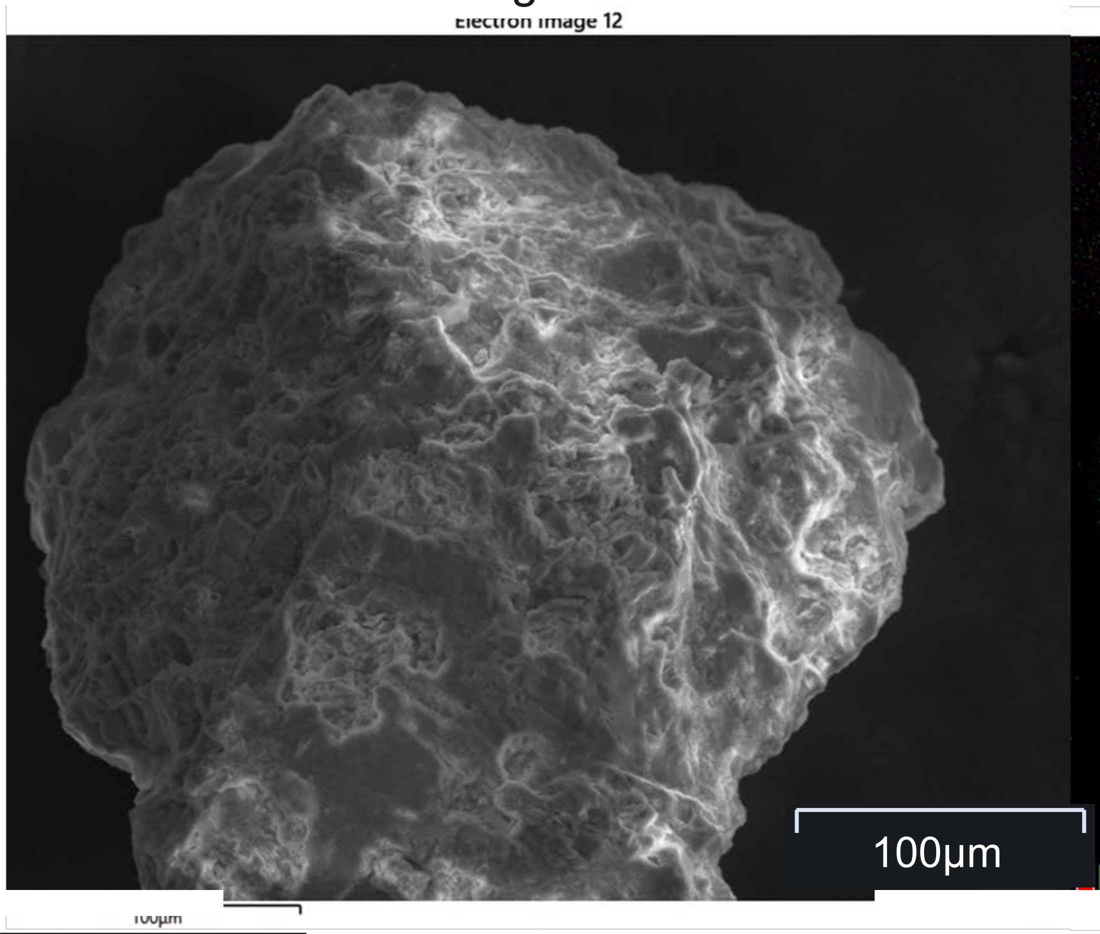




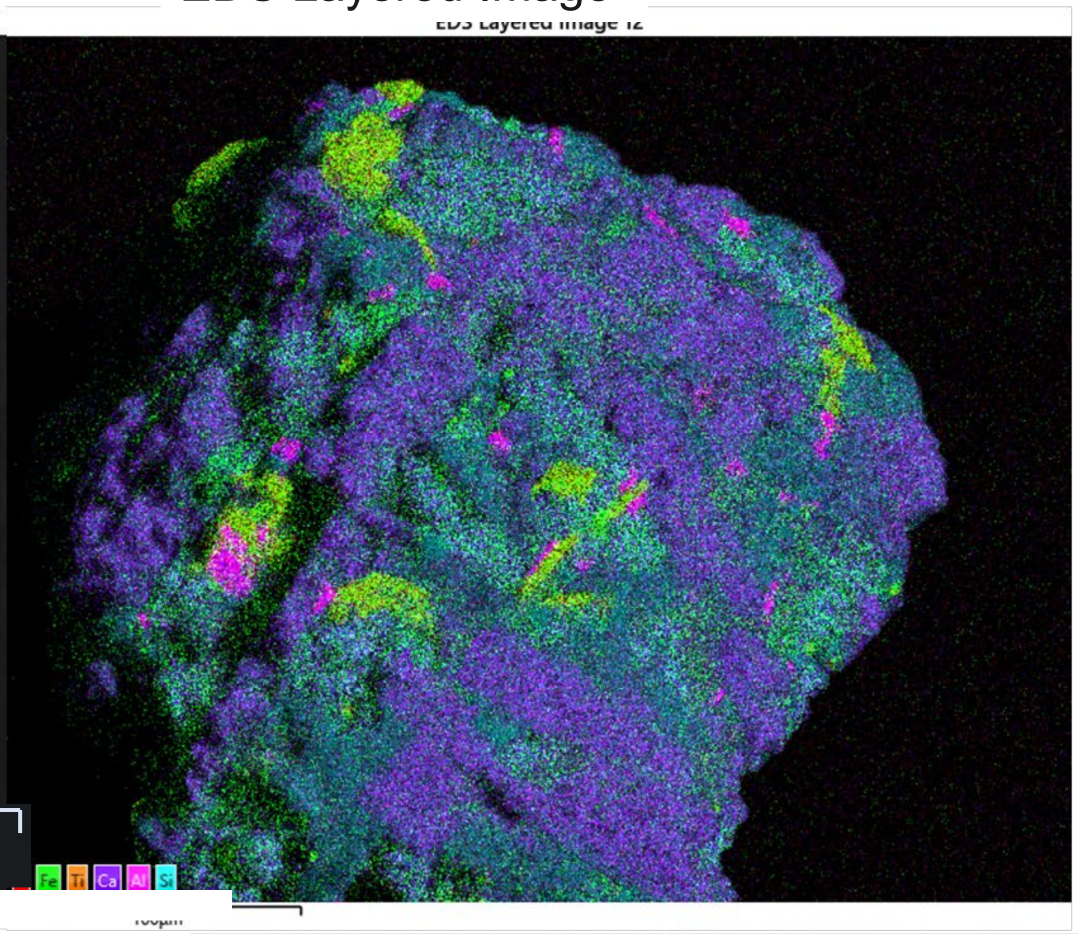
- Significant increase in solid phase phosphorus
- Ca:P ratio moving closer to apatite (1.25), likely significant $CaCO_3$ in sediments

Results: Liquid PO_4 Amendments Post Characterization

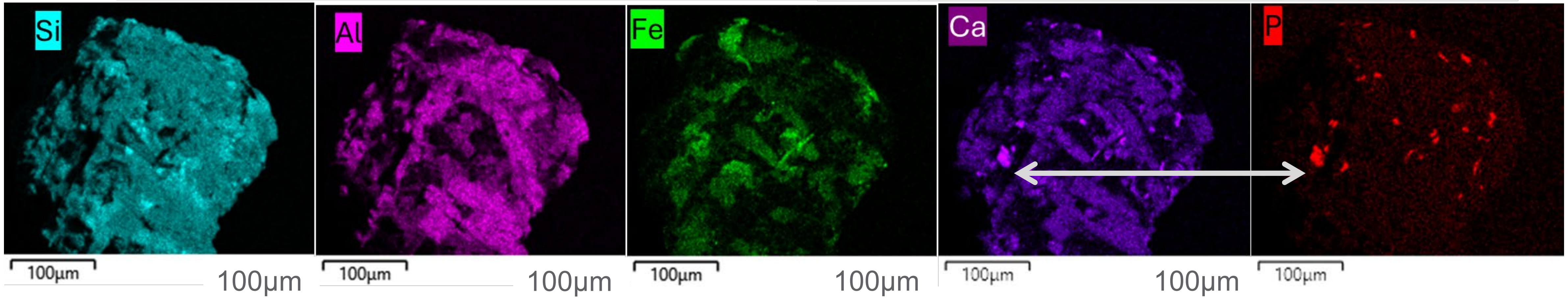
Electron Image



EDS Layered Image



Note: Co-association of Ca and P, potentially $Ca_{10}(PO_4)_6(OH)_2$

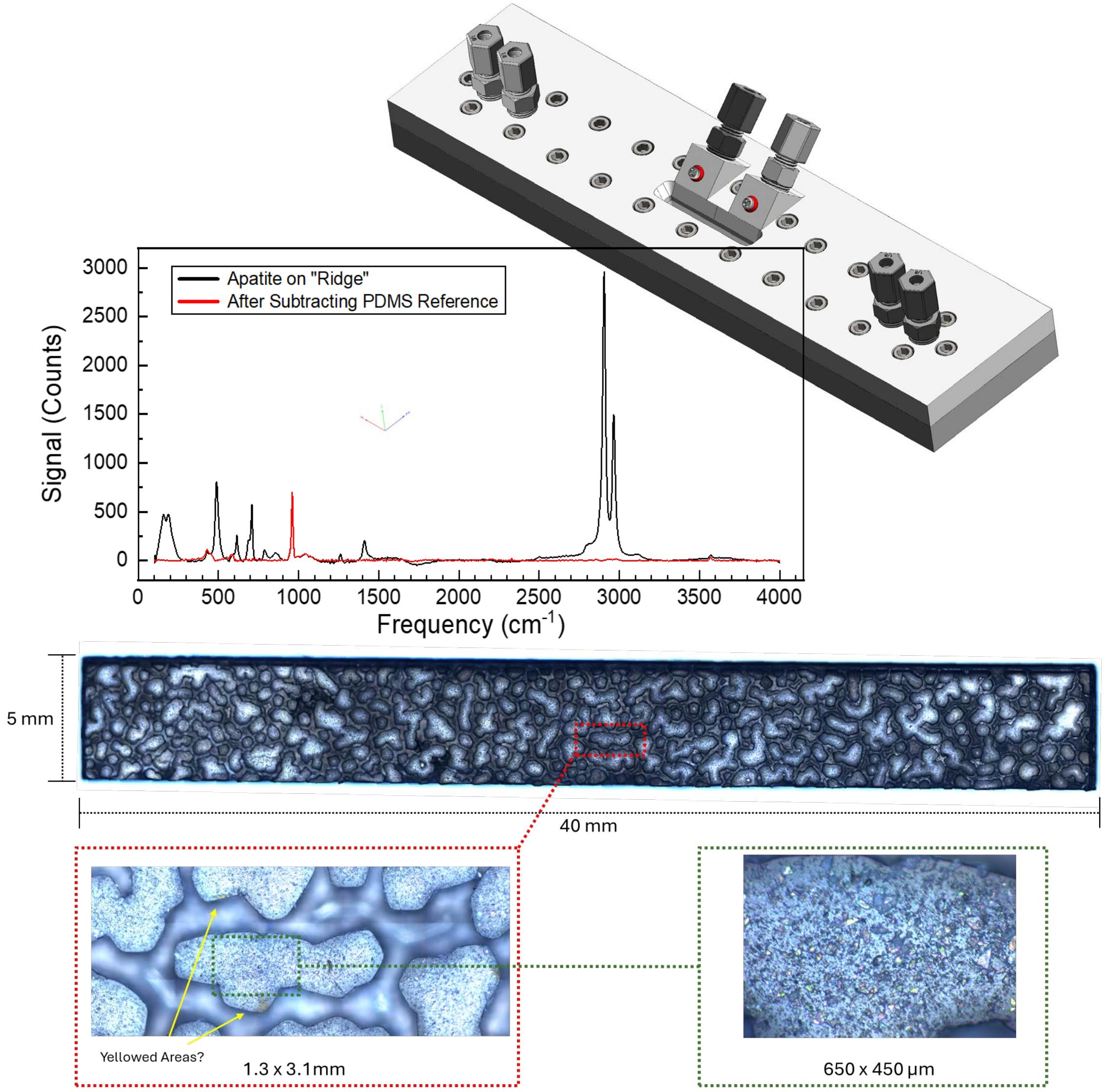


100µm 100µm 100µm 100µm 100µm

Conclusions and Future Work Liquid PO_4

Poster: Peshtani, et al. “Integrating Induced Polarization and Spectroscopy Into Microfluidics to Map Apatite Precipitation”

- Real conductivity, σ' (similar to ER, delivery indicator)
  - Dominated by changes in fluid conductivity
  - Results show where liquid PO_4 was *delivered*
- Imaginary conductivity, σ'' (apatite formation indicator)
  - ↑ as surface of minerals changed, *independent of solution conductivity*
  - Δ likely due to ion exchange, adsorption, apatite precipitation, and coating
- Results show promise for SIP for monitoring both <u>delivery</u> of solutions and <u>formation</u> of apatite coatings
- Ongoing work: Decrease scale to confirm controlling mechanisms via microfluidics



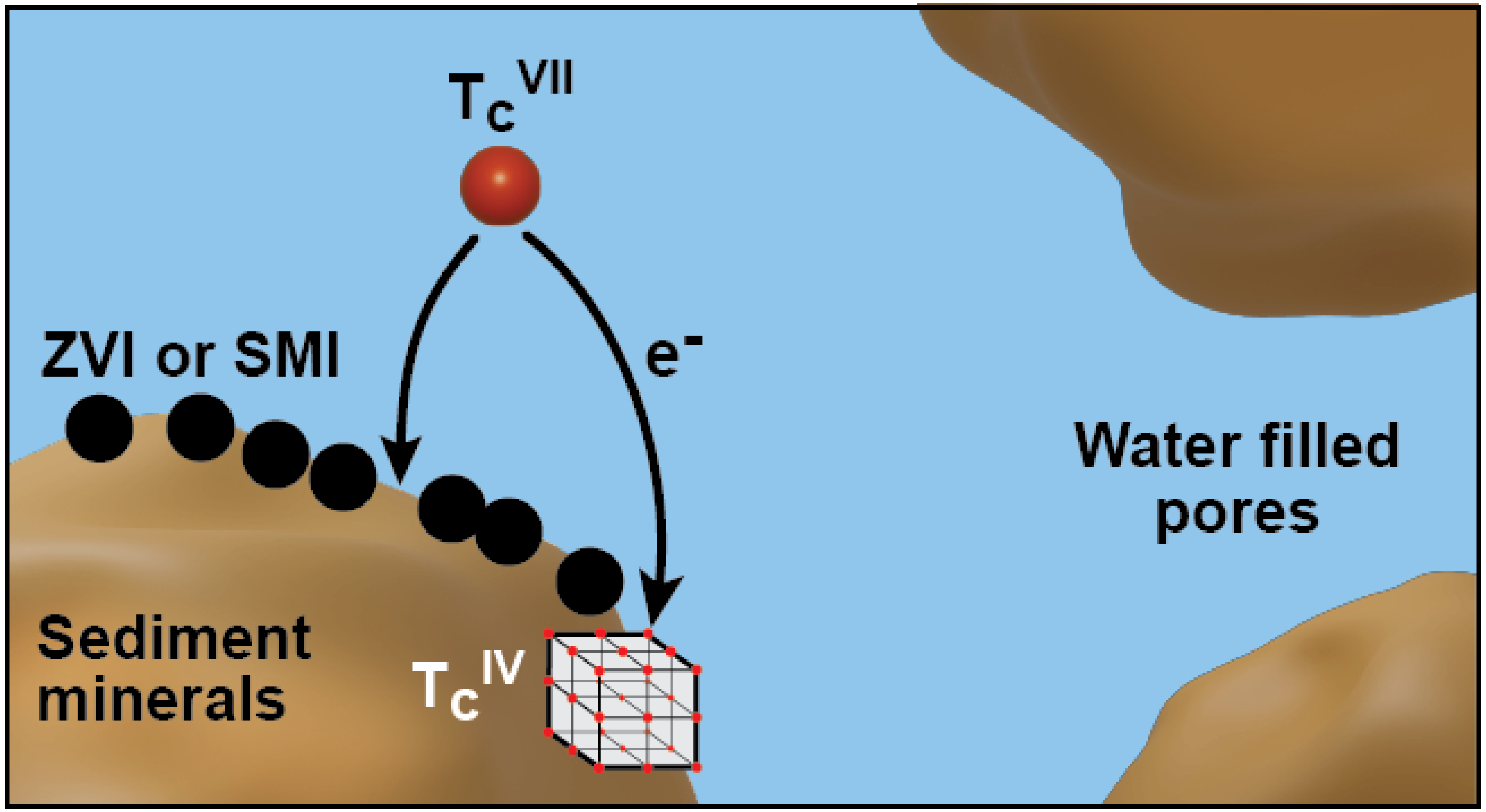
What Happens with Zero Valent Iron?

High ionic strength injection solution fills pore spaces with ZVI or SMI particles

Reducing conditions generated impacting mobility of contaminants

ZVI or SMI corrosion: reduction capacity consumed, iron dissolution, and secondary precipitation

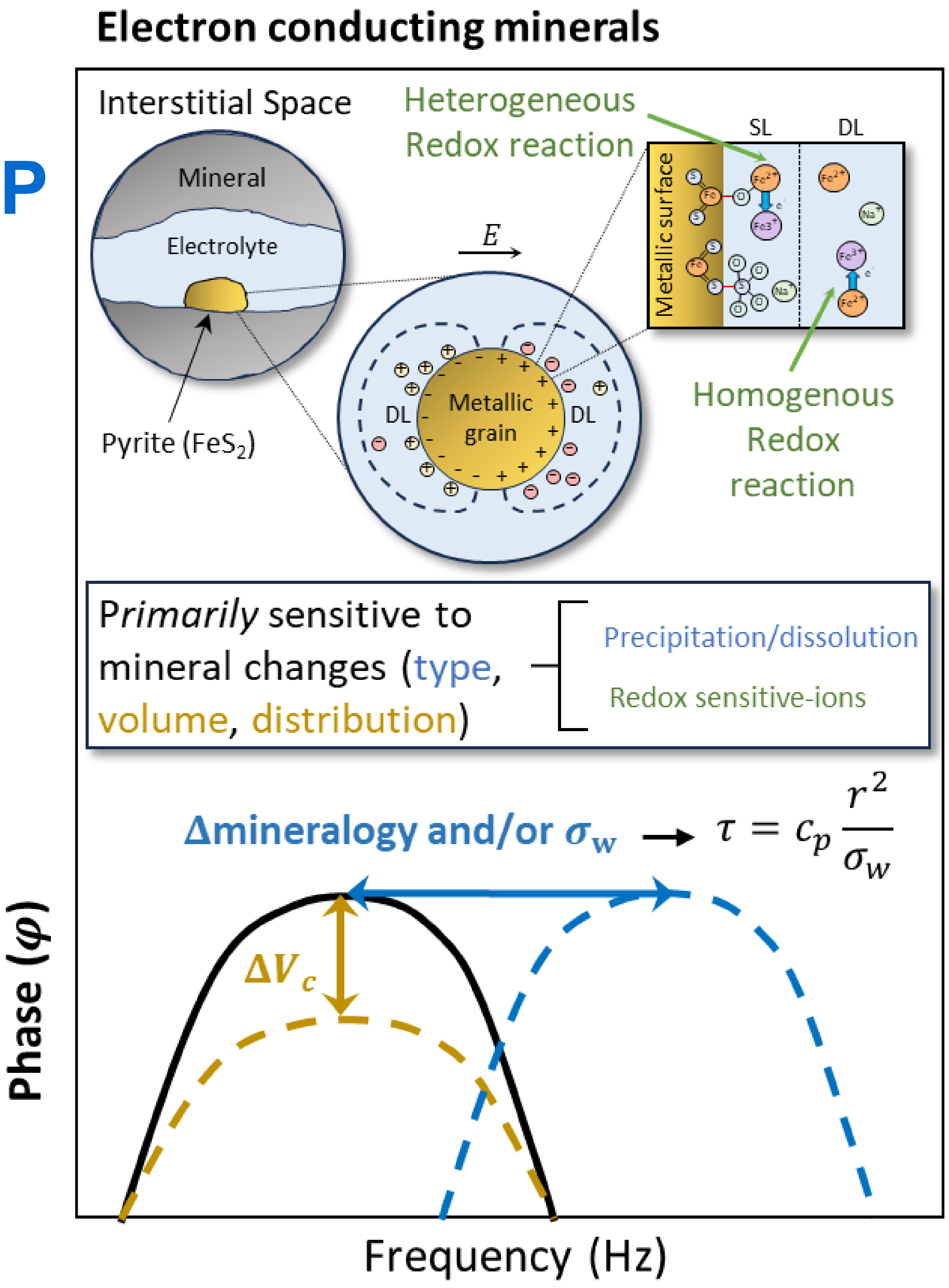
Conceptual diagram of delivery of zero valent iron (ZVI) or sulfur modified iron (SMI) into pore space with subsequent reductive precipitation of contaminants (e.g., TcO_4^-).



Can we predict the point of failure for iron reductants?

Conceptual Model of Iron Amendments for SIP

- Initial injection
  - ↑ σ_w contributes to ↑ σ′ and shift in φ peak
  - ↑ φ coincident with ↑ volume fraction of ZVI or SMI
- Post injection
  - ↓ σ_w back to natural conditions
  - Δφ dependent on volume content of secondary minerals that are polarizable (e.g., magnetite)
  - Shifts in φ peak due to pore blocking or particle size changes

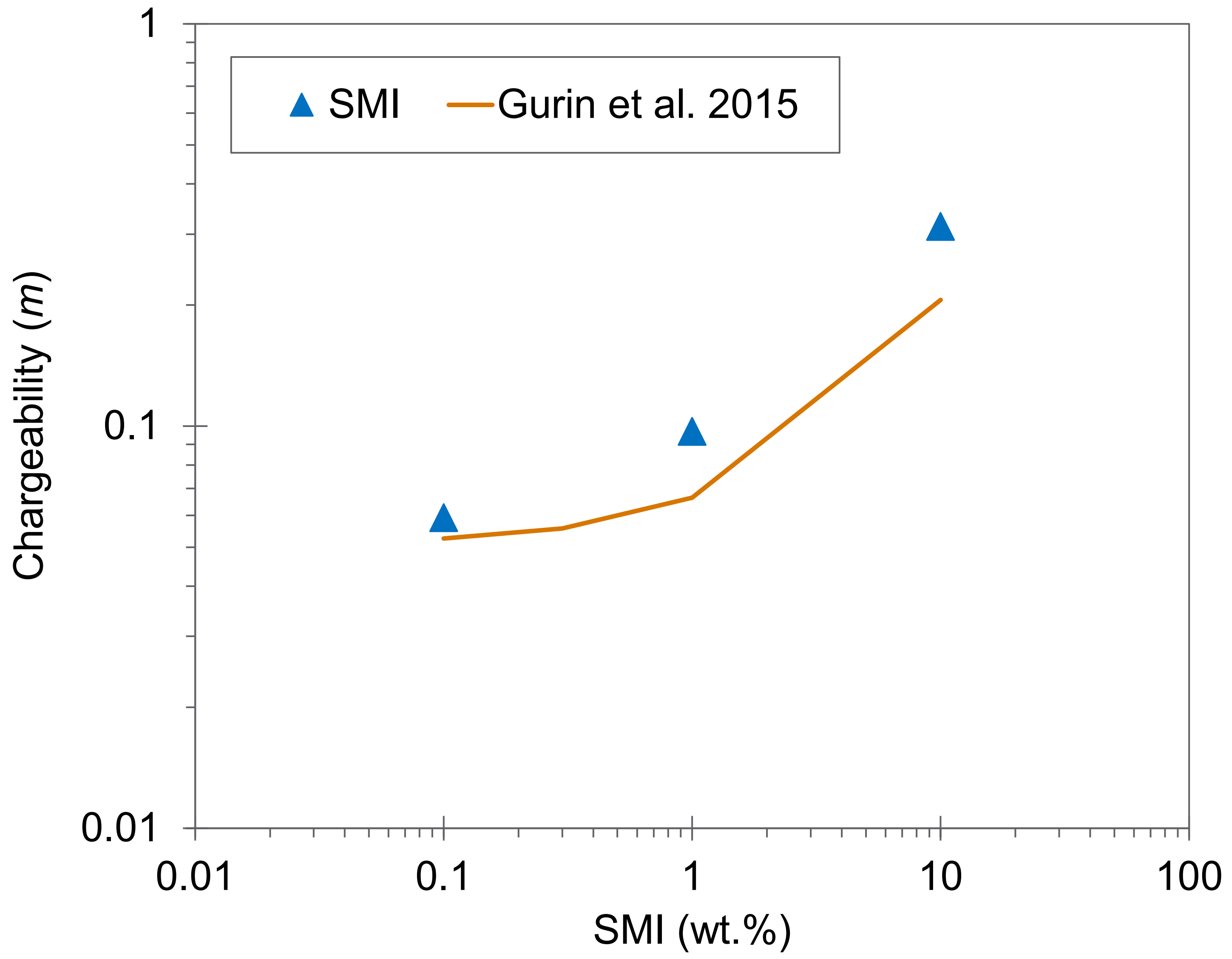


Results: ZVI and SMI Amendments Column Testing

- Volume content strongly correlated with φ and chargeability (*m*)
  - Well-studied concept
  - Background sediment polarization corrected based on previous literature

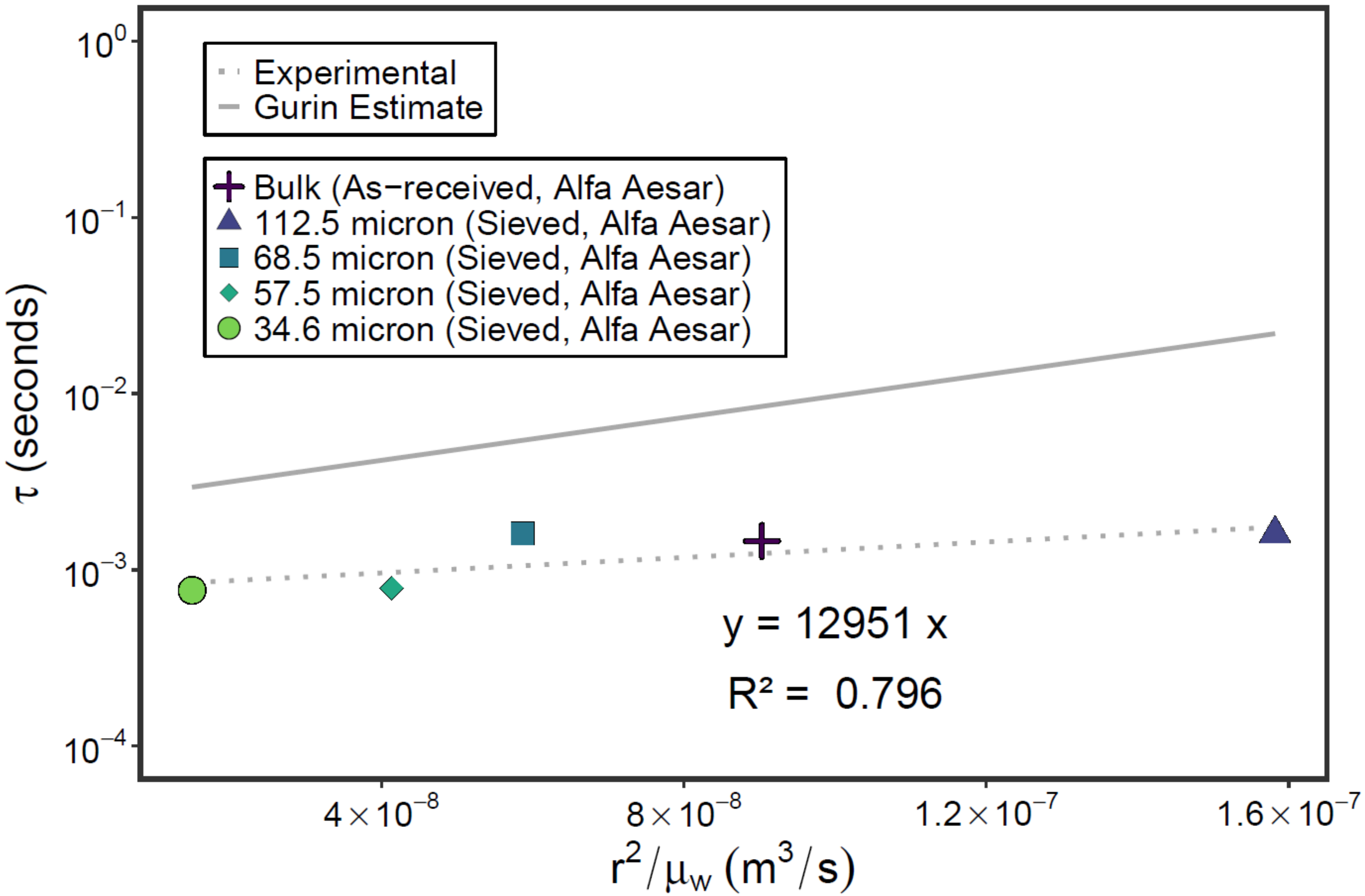
$$m = 1 - (1 - m_b)\frac{2(1-v)^2}{(2+v)(1+2v)}$$

Gurin et al. (2015) Geophys J Int 200
Emerson et al. (2024) J Contam Hydrol 264



Results: ZVI and SMI Amendments Column Testing

- Sieved ZVI materials to isolate different size fractions
- Particle size strongly correlated with τ
  - Consistent with literature, though not previously studied systematically
  - Mineral-dependent, correlated with Fe(II/III) surface ratios

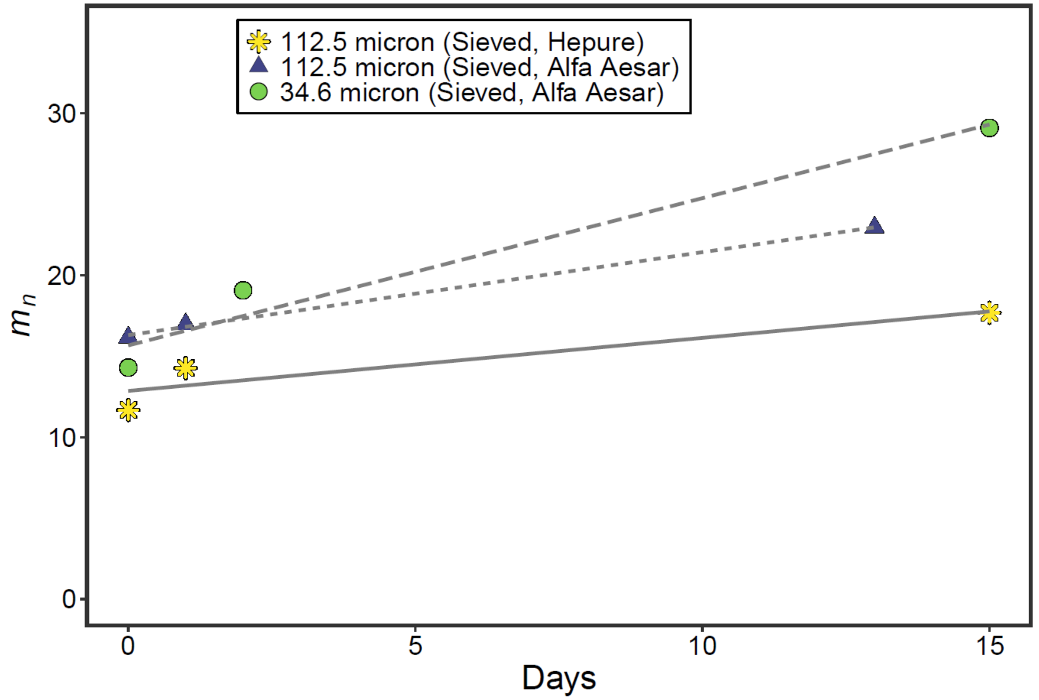


What about changes over time due to corrosion?

Results: ZVI and SMI Amendments Iron Corrosion Testing

ZVI corrosion in silica sand – 14 days

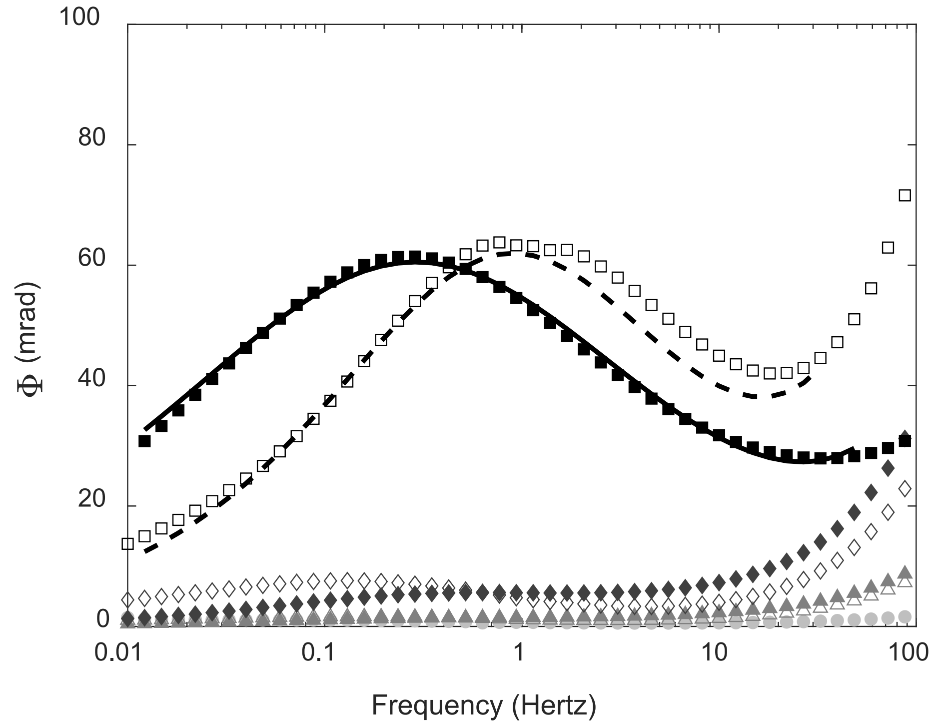
- Significant shifts in τ over time
  - Δ in particle size (via BET)
  - Δ in $Fe^{+2/+3}$ solid phase ratios
- ↑ in normalized chargeability
- What are the primary mechanisms impacting polarization magnitude and frequency?



*Contribution from Δ in mineralogy inconclusive (not detected via XRD but redox condition changed over time, potentially moving to Fe^{+3} oxides)

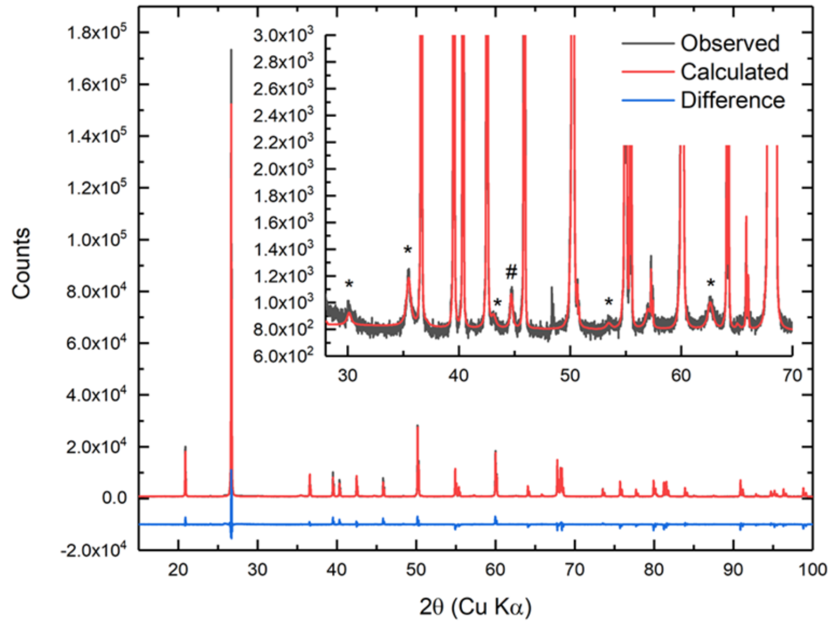
Emerson et al. (2024) J Contam Hydrol 264

Results: ZVI and SMI Amendments Iron Corrosion Testing



SMI corrosion in silica sand – 77 days

- Significant shifts in peak over time, multiple mechanisms are controlling response
  - ∆ in particle size (via BET)
  - ∆ in mineralogy (via XRD)
- No change in the magnitude of φ
  - No *significant* ∆ in volume content



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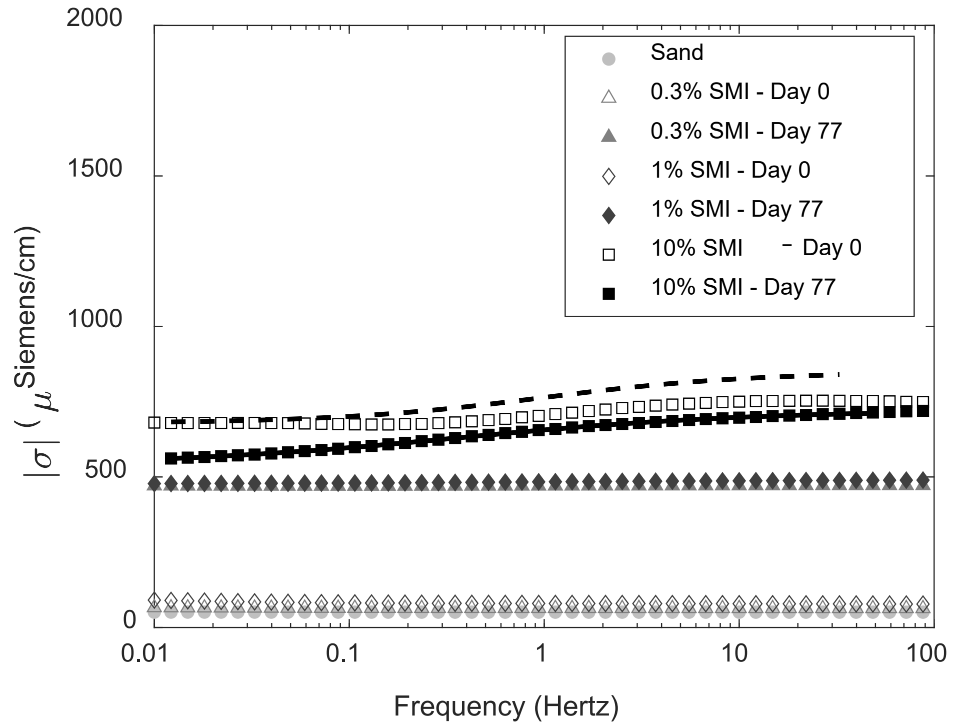
* magnetite
# zero valent iron

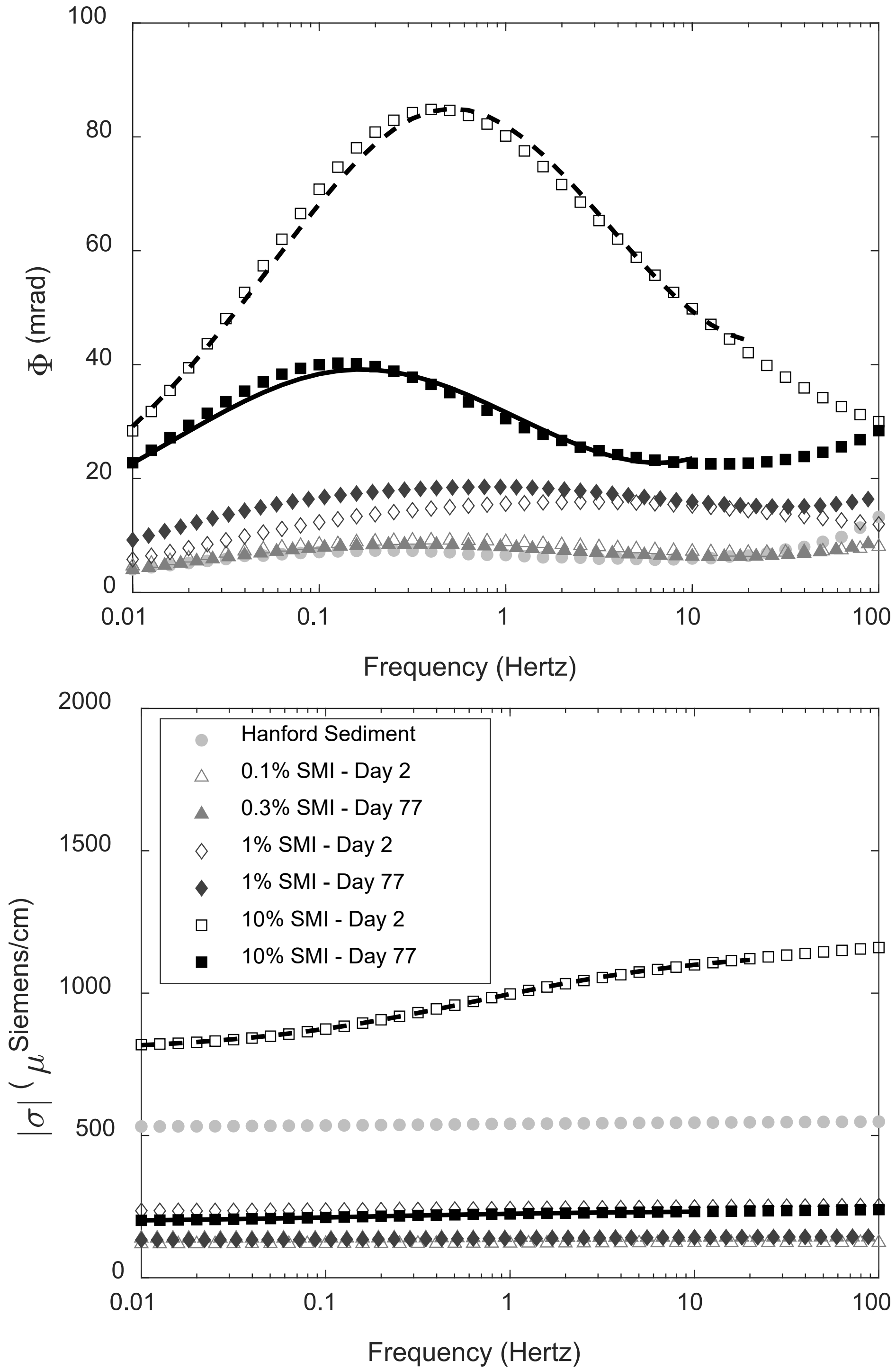


Results: ZVI and SMI Amendments Iron Corrosion Testing

SMI corrosion in Hanford formation sediments

- Significant shifts in peak over time
  - Δ in particle size (via BET)
  - Δ in solution conductivity ($Fe^{+2/+3}$ dissolution)
- Significant shift in the magnitude of φ
  - Conductive phases are oxidizing and/or becoming isolated

*Contribution from Δ in mineralogy inconclusive (not detected via XRD but redox condition changed over time, potentially moving to Fe^{+3} oxides)



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Results: ZVI and SMI Amendments Iron Corrosion Testing

SMI corrosion in Hanford formation sediments

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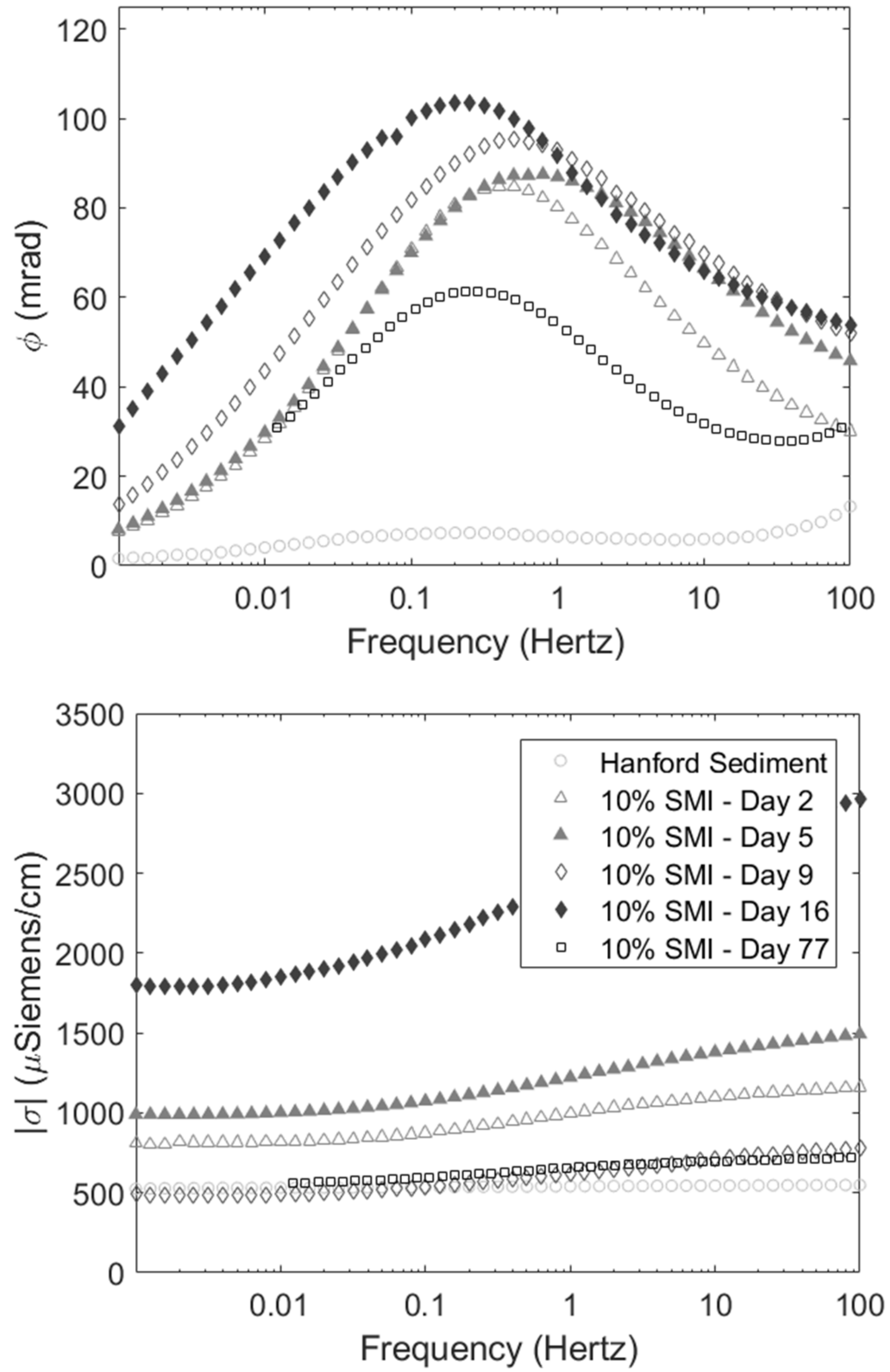
- What are the primary mechanisms impacting polarization magnitude and frequency?



*Contribution from Δ in mineralogy inconclusive (not detected via XRD but redox condition changed over time, potentially moving to Fe^{+3} oxides)

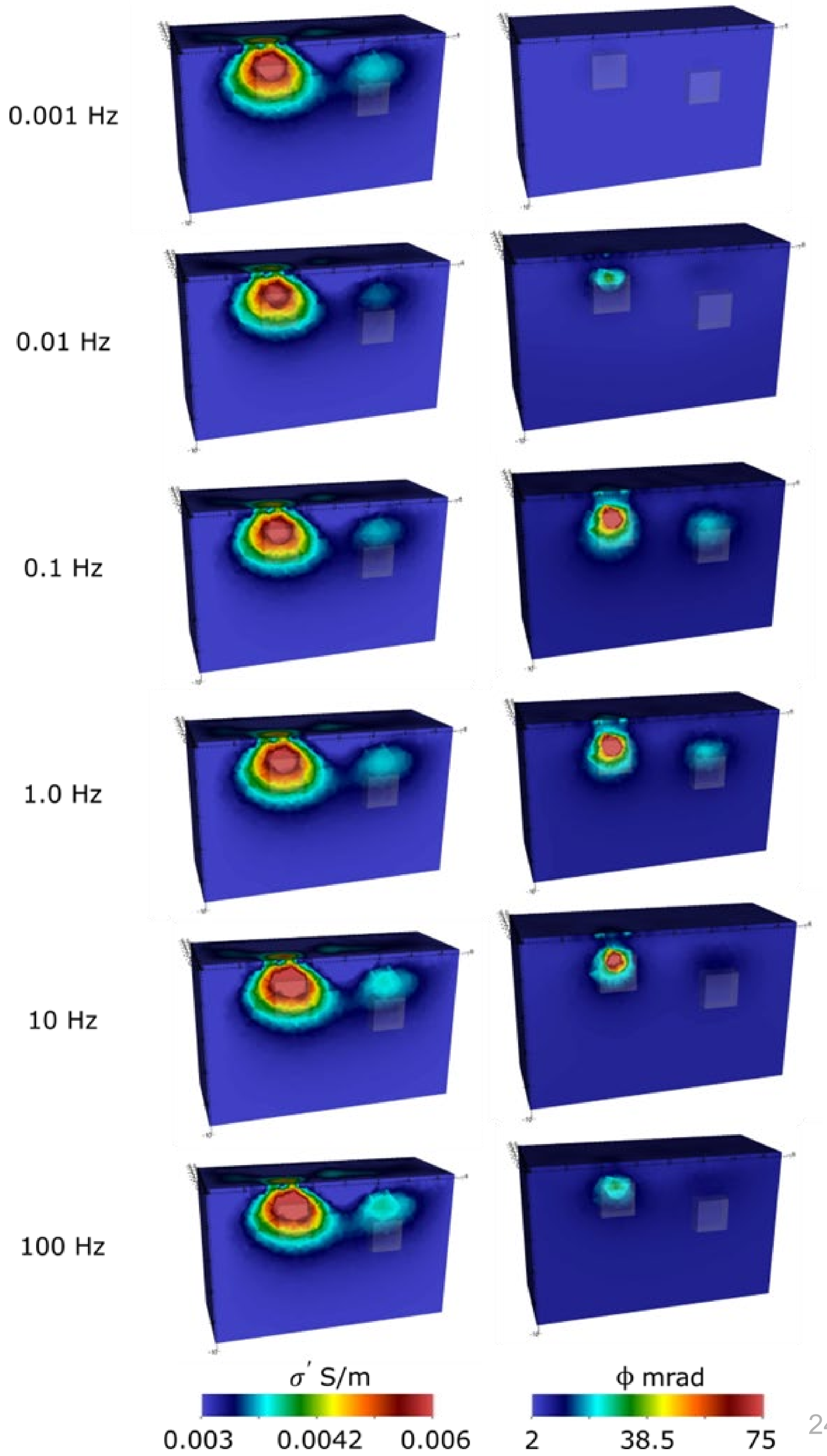
Emerson et al. (2024) J Contam Hydrol 264

Conclusions and Future Work
Iron Amendments

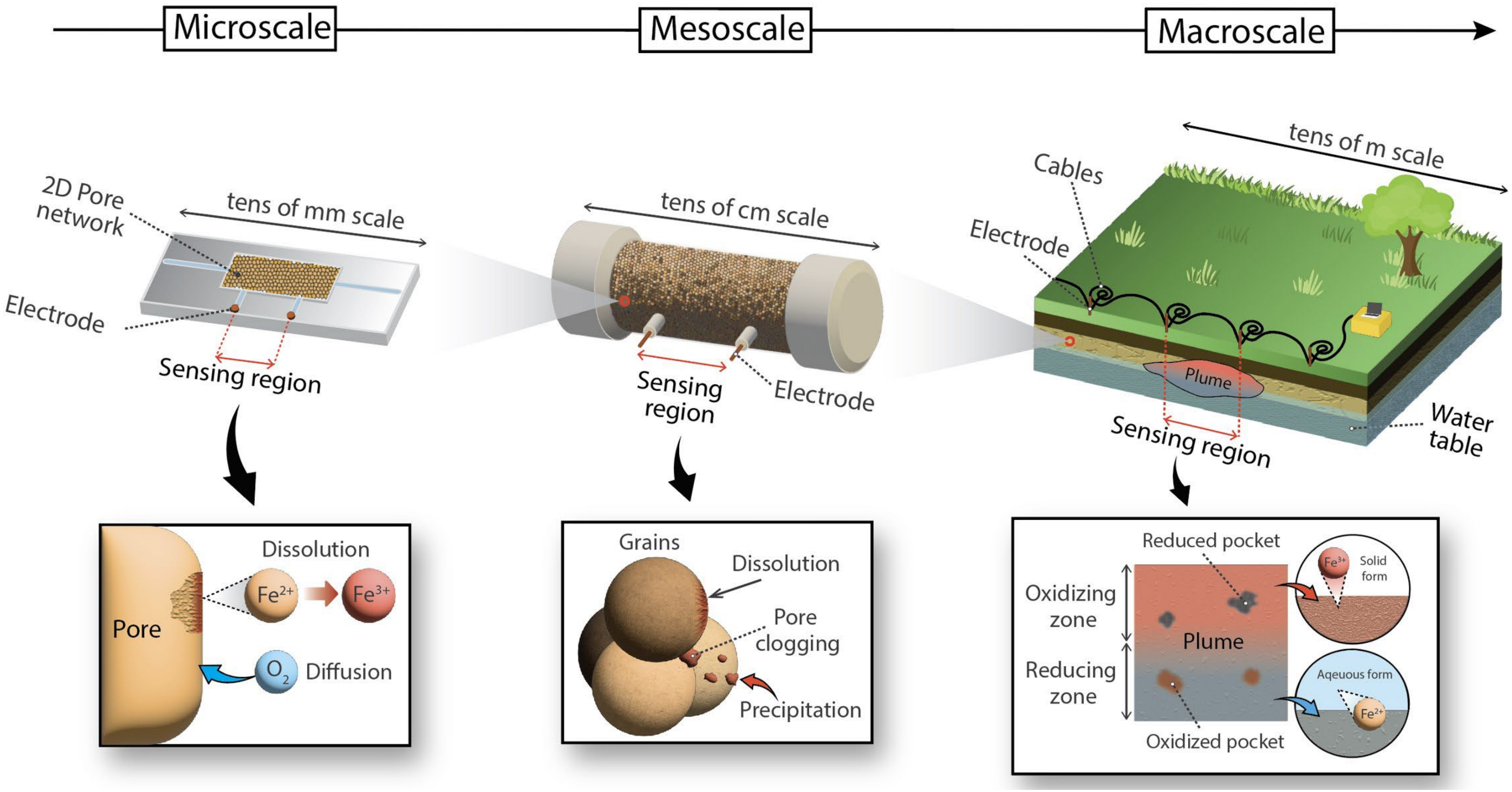
- Real conductivity, σ'
  - Dominated by changes in fluid conductivity
  - Results show where ZVI was *delivered*
- Phase, φ or Chargeability, m or m_n
  - ↑ with volume content
  - Shifts in peak due to Δ in mineralogy, σ_w and particle size
- Results show promise for SIP for monitoring both <u>delivery</u> of solutions and <u>corrosion</u> of ZVI and SMI

Future work: Improve real-time characterization to identify controlling mechanisms during corrosion

E4D inversion for SMI using two blocks model



Conclusions



Potential to monitor amendment delivery and transformation with SIP via φ, σ″, and τ depending on material and alteration

Environmental Significance

Promising technology for monitoring source zones during remediation – including potential to confirm injection solution delivery and amendment precipitation

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Thank you

Questions?
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