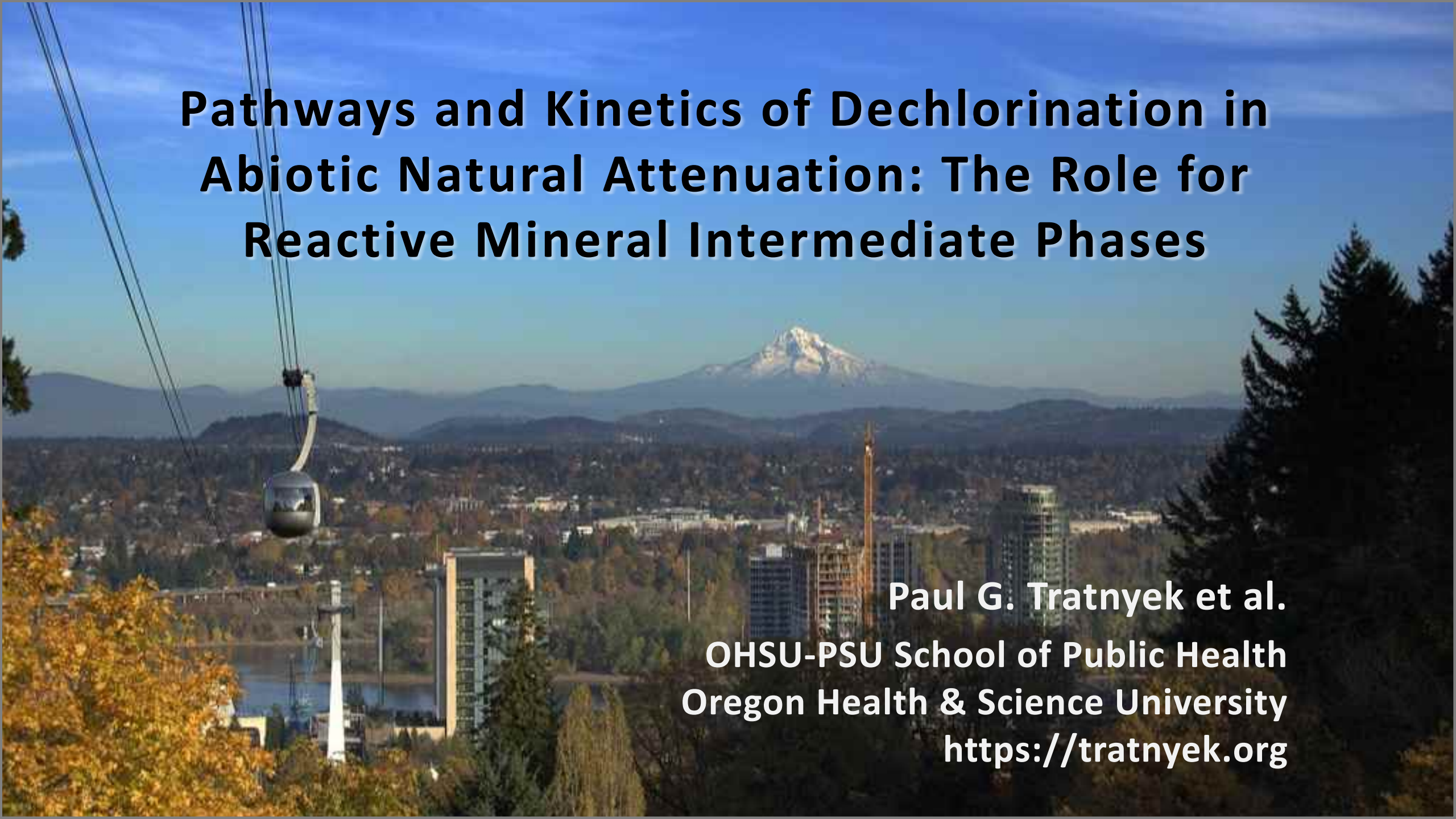

# Pathways and Kinetics of Dechlorination in Abiotic Natural Attenuation: The Role for Reactive Mineral Intermediate Phases

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# Modeling Abiotic Attenuation of Chlorinated Ethenes under Natural and Transitional Site Management Scenarios

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*Oregon Health & Science University*

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*University of Iowa*

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SERDP Project No. ER20-1357

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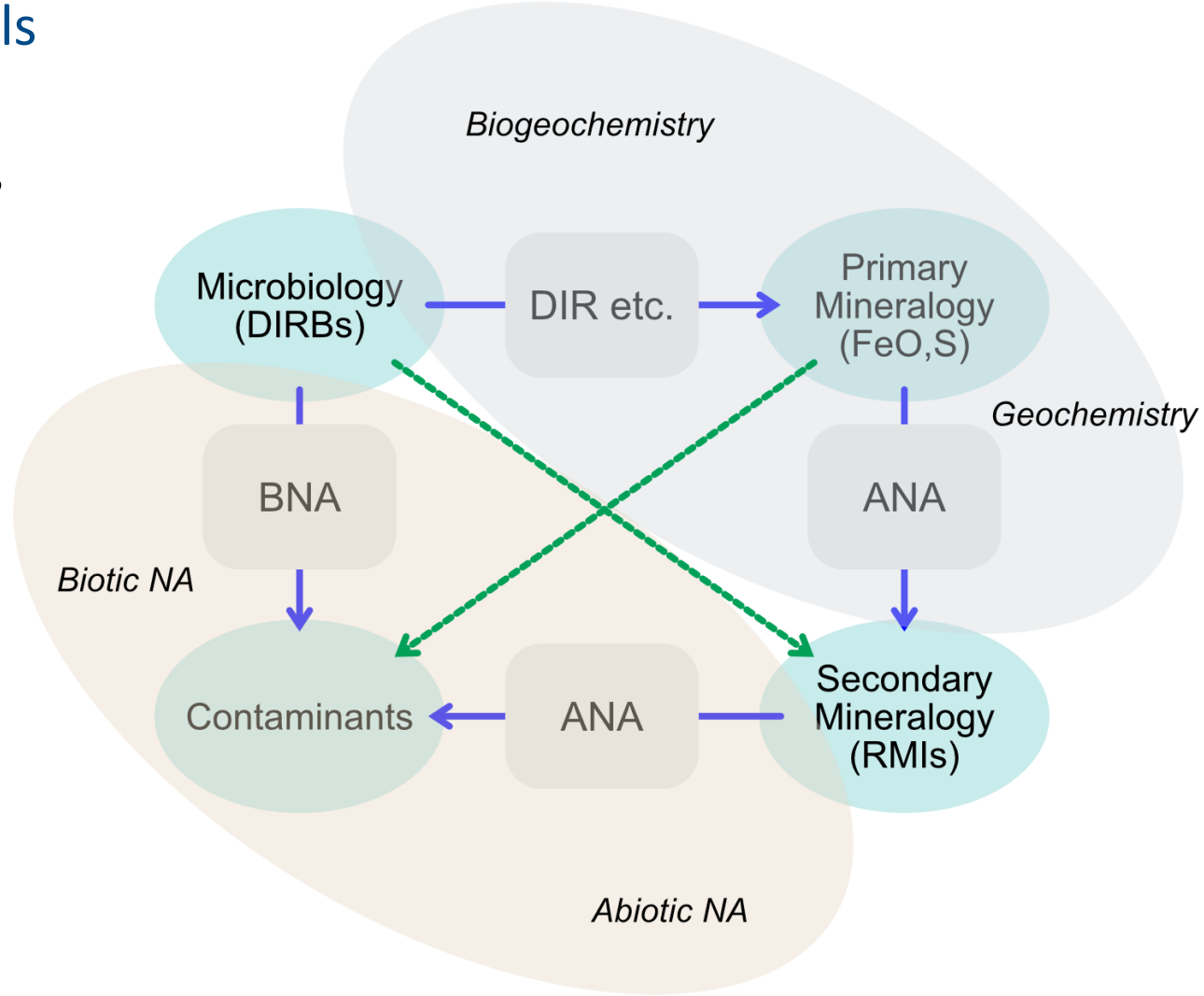
# Abiotic Natural Attenuation (ANA)

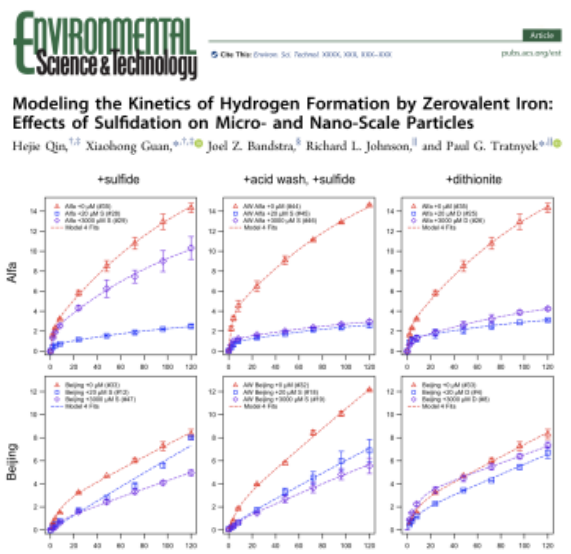
## Geomicrobiology of Reactive Minerals

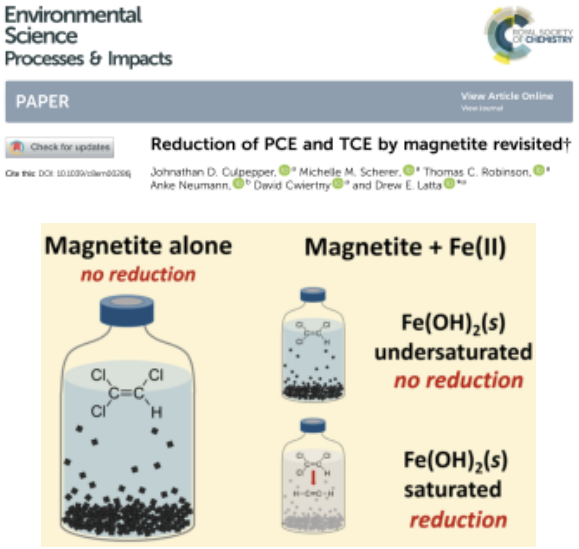
- **Microbiology** (e.g., DIRBs) drives formation of reducing mineral phases directly (①,③) and indirectly (②).
- **Contaminants** can be reduced by Microbes (⑥), **1°Minerals** (④), and/or **2°Minerals** (RMIs)(⑤).
- **Hypothesis**: ANA of CEs is mostly by RMIs (⑤), not 1°FeO/S (④).
- **Hypothesis**: Active precipitation of RMIs may be altered by Natural Hydrobiogeochemical (**HBGC**) fluctuations or Active-Passive Transitions (**APTs**).

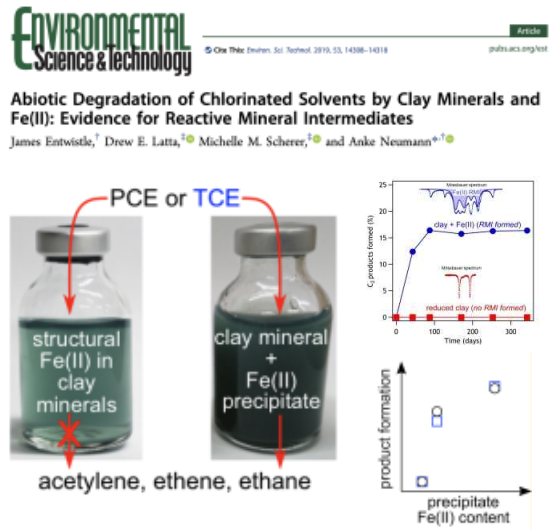


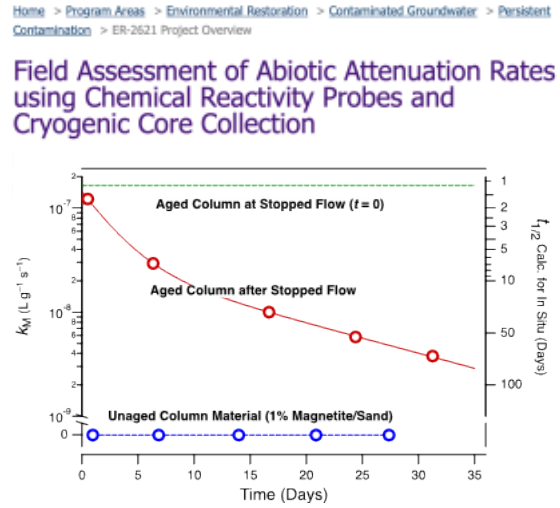
# Reactive Mineral Intermediates (RMIs): Introduction

- **RMI Hypothesis:**
  - *Active precipitation* leads to
  - *Metastable phases* that serve as
  - *Reactive mineral intermediates* (RMIs)
  - Which are the main cause of ANA
- **RMI Characteristics:**
  - Authigenic (formed in situ); transient when sampled for ex situ analysis.
  - Life-time and concentration deter-mined by the balance of source and sink processes.
  - Low steady-state concentration with high turnover can give significant contaminant degradation.



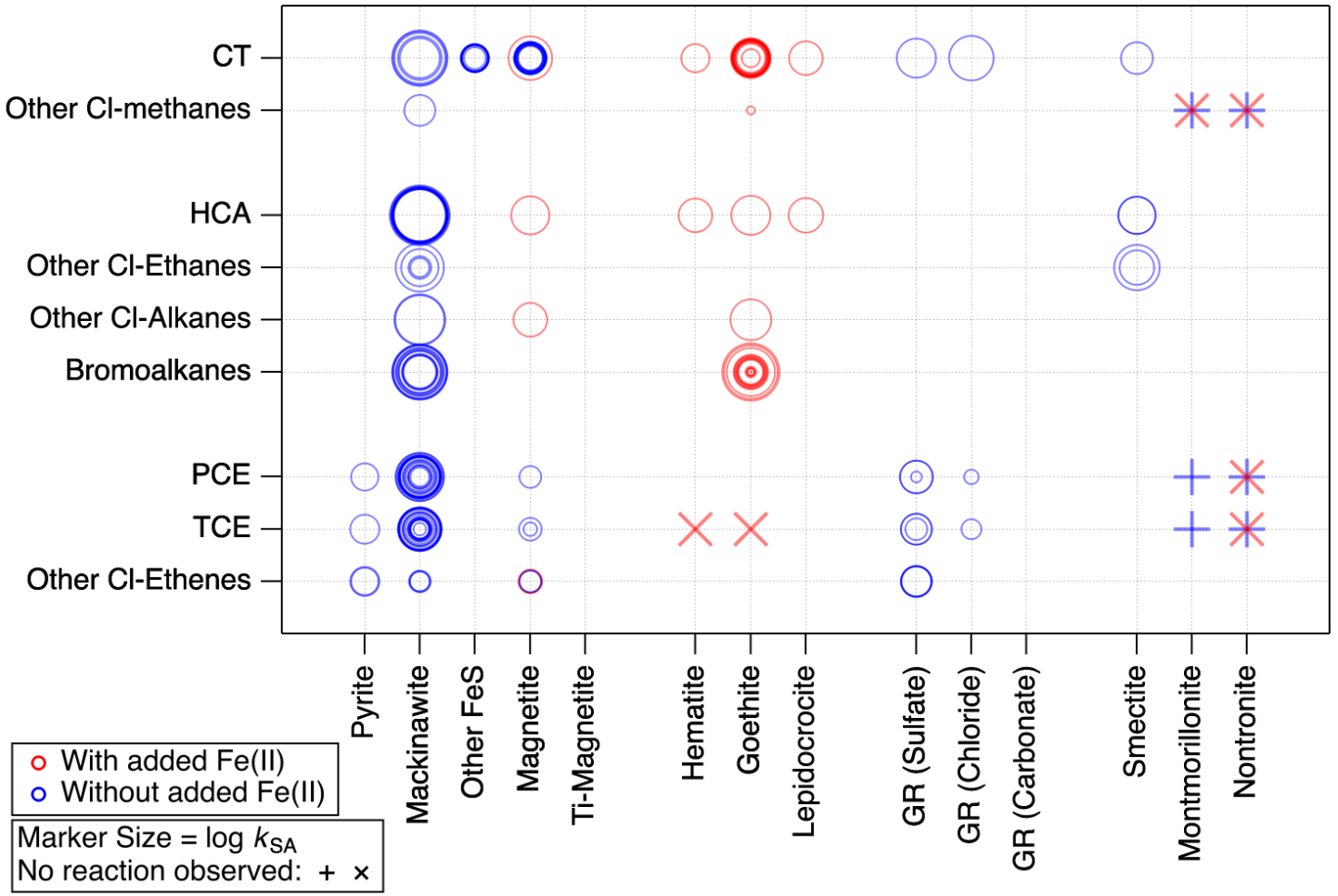



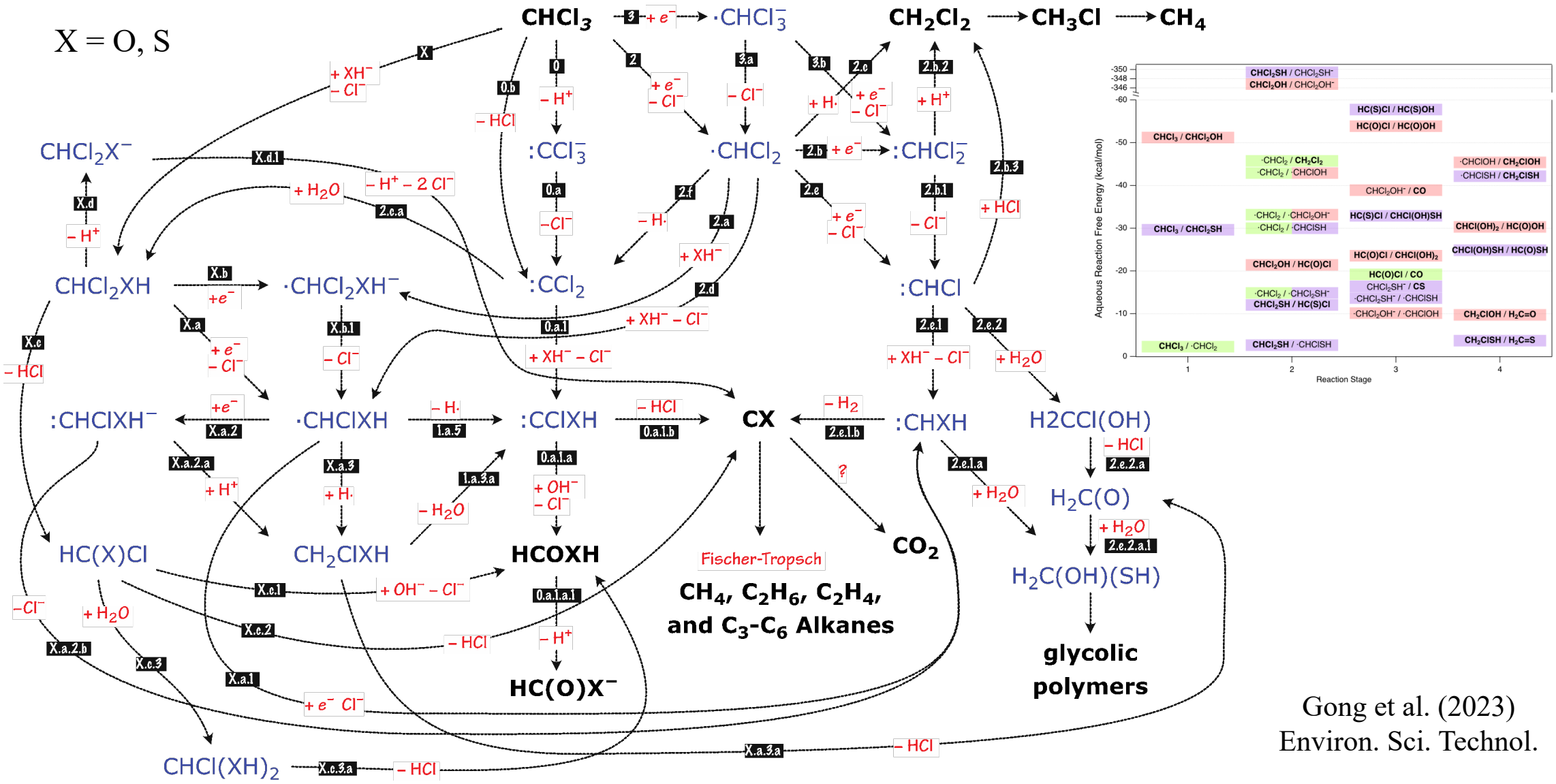
# Reactive Mineral Intermediates (RMIs): Dechlorination Kinetics

- Available Data:
  - Literature data mining and meta-analysis
  - Primary Variables: Contaminant vs. Reductant
  - Marker size ∝ Rate
  - Secondary Variables: Fe(II), S(−II), pH, etc.
- Data Gaps:
  - DCEs, all other LHHCs
  - Fe(III) Oxides, Clays, etc.
  - RMI/RAMP-ness




Draft, Adapted from Figure 3 in Huang et al. (2021) Chemical Reviews 121(13): 8161-8233

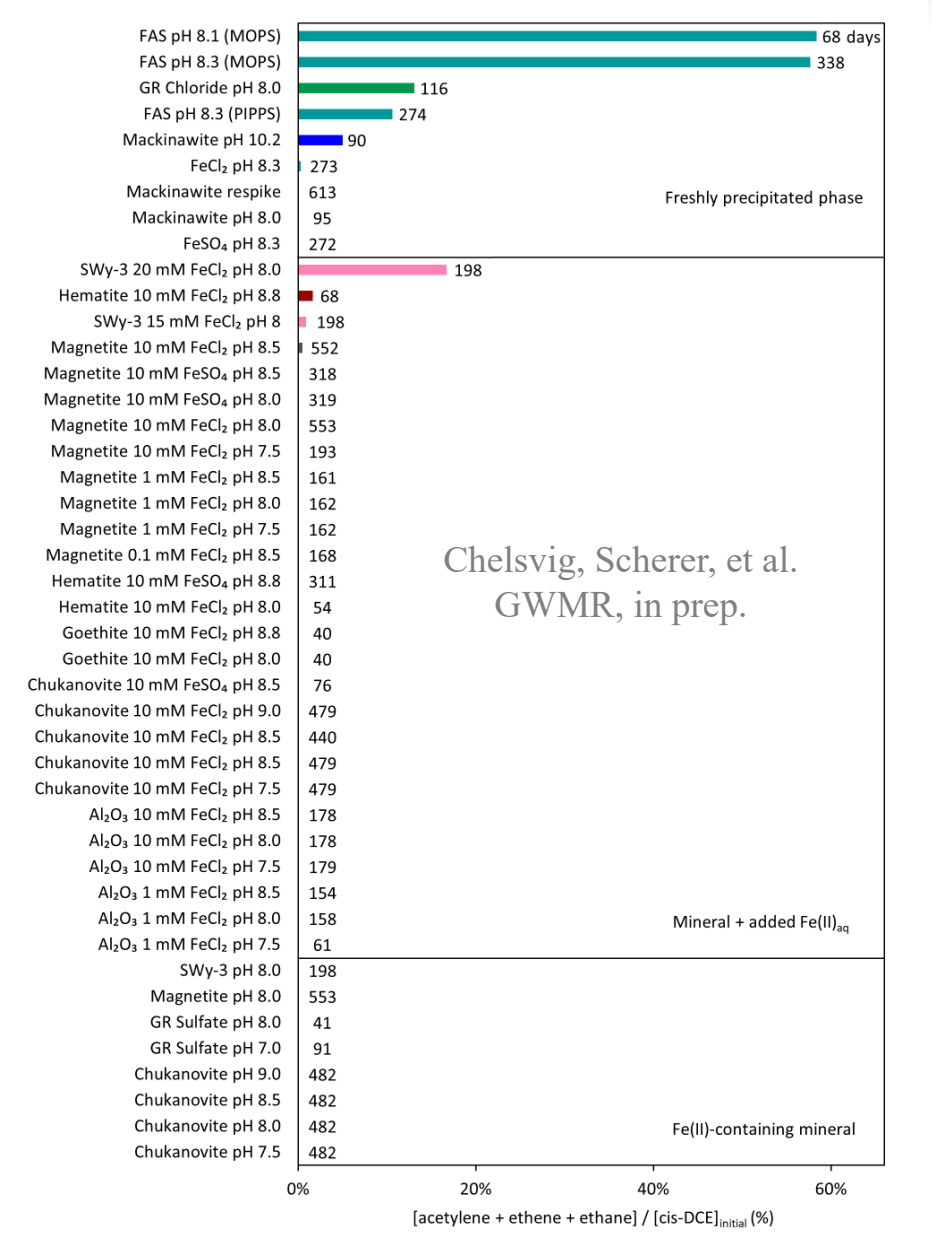
# Pathways and Kinetics of Dechlorination: Chloroform




Gong et al. (2023)
Environ. Sci. Technol.

# Reactive Mineral Intermediates (RMIs): Batch Results

- Reduction of CEs vs. Fe(II) Minerals:
  - Disappearance of **cis-DCE** too slow, but products (**acetylene + ethene + ethane**) accumulate.
  - Measured % product recovery vs. pH, Eh, Fe(II), various types of minerals (estimated $k^0$).
  - Little to no reduction of cis-DCE in most Fe mineral suspensions (anoxic; batch) in up 1 yr.
  - Including magnetite ±Fe(II), and RMI-conditions that did reduce TCE in Culpepper/Scherer et al.
  - Some reduction of cDCE by very fresh, amorphous ferrous hydroxides (e.g., precipitate from concentrated ferrous ammonium sulfate (FAS).



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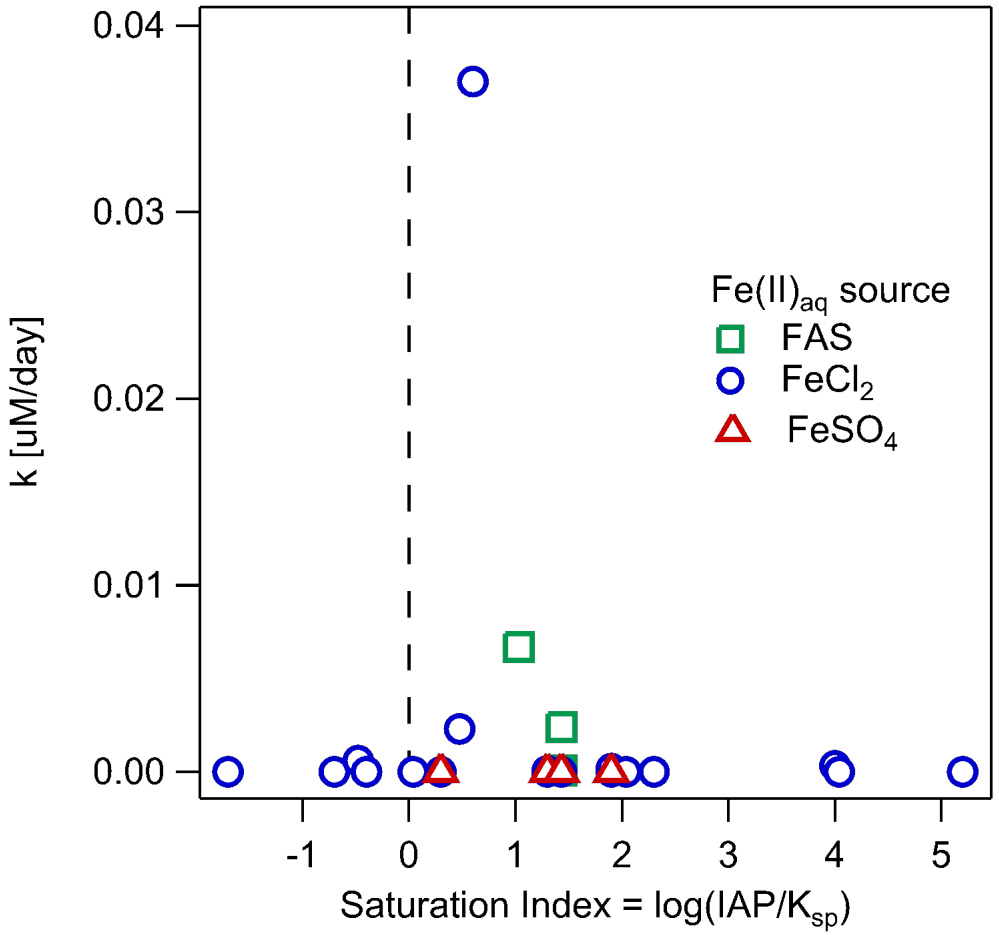
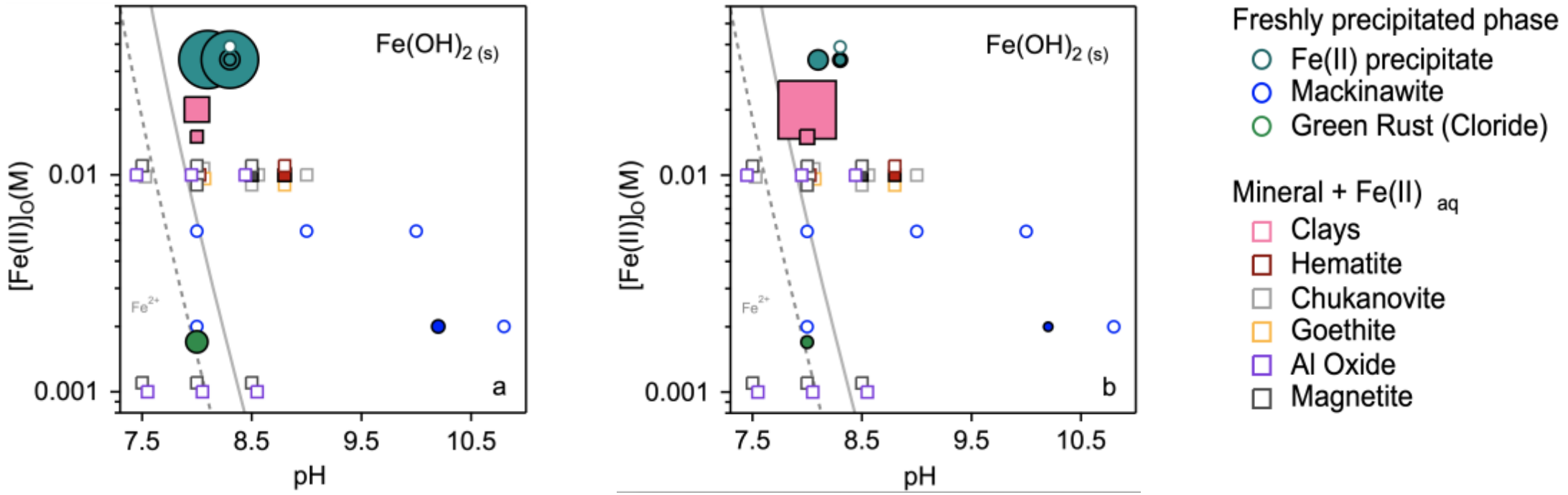
  - Some reduction of cDCE by very fresh, amorphous ferrous hydroxides (e.g., precipitate from concentrated ferrous ammonium sulfate (FAS).
  - Most reaction at initial conditions near of slightly above saturation index for $Fe(OH)_2$.

Chelsvig, Scherer, et al. GWMR, in prep.



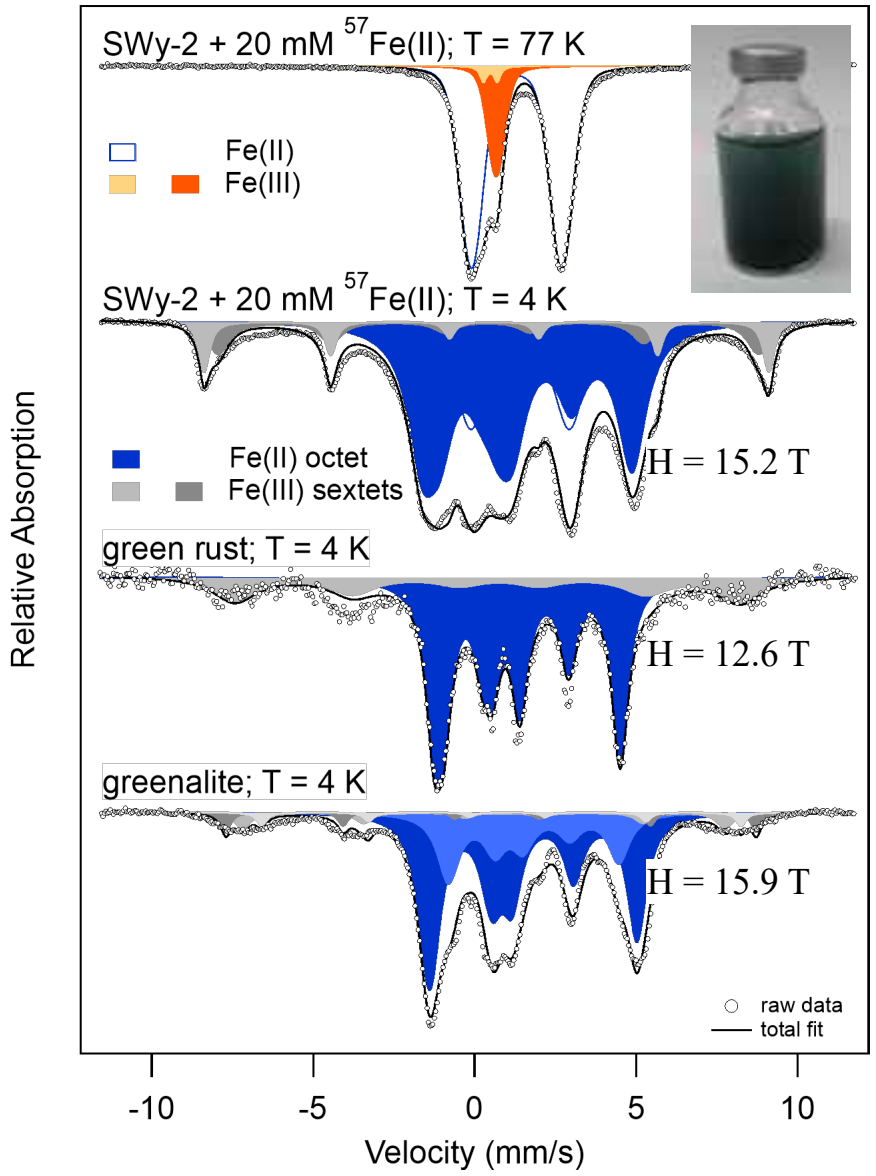
# Reactive Mineral Intermediates (RMIs): Batch Results

- Reduction of CEs vs. Fe(II) Minerals:
  - $Fe(OH)_2(s)$ solubility diagrams for reactors containing added aqueous Fe(II).
  - Marker size and color representing degree of cDCE reduction to acetylene, ethene, and/or ethane: (A) Amount of products produced (ranging up to 58.4%) and (B) Zero order rate of product appearance (ranging up to 0.037 uM/day).



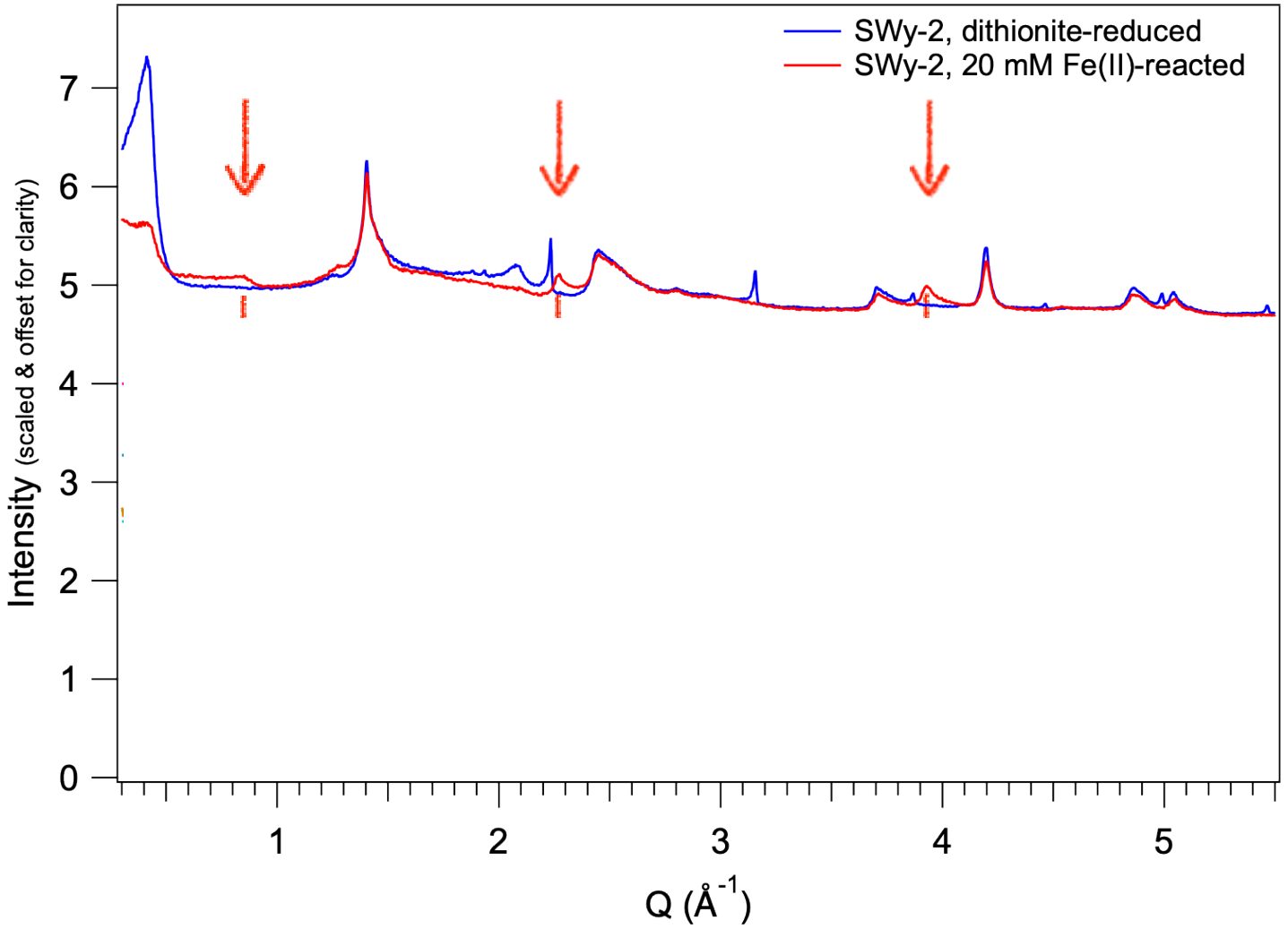
# Reactive Mineral Intermediates (RMIs): Batch Results

- Reduction of CEs vs. Fe(II) Minerals:
  - Up to 25% reduction of **PCE and TCE to acetylene, ethene, and/or ethane** (not shown).
  - Various combinations of clays, Fe(II), pH, etc.
  - Detailed mineralogical characterization under conditions that give PCE/TCE dechlorination.
  - **Mössbauer** spectra collected at both 77 K and 4 K show both Fe(II) (in blue) and Fe(III) components (in yellow/orange).
  - At 4 K, the Fe(II) octet has a hyperfine field (H = 15.2 T), which is *low* compared to **$Fe(OH)_2$** (H ≈ 19 T) and *high* compared to **Green Rust** (measured here ~12.6 T).
  - Best match is **Greenalite** ($Fe^{II}/Fe^{III}$ hydroxy silicate).



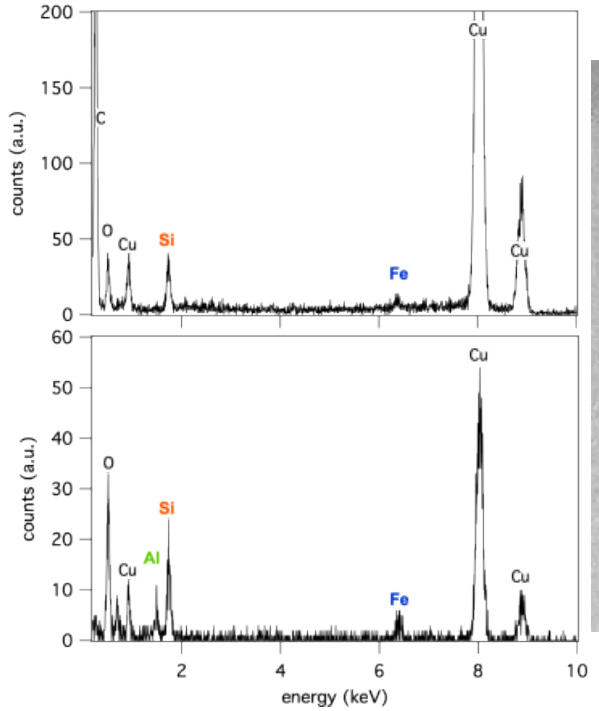
# Reactive Mineral Intermediates (RMIs): Batch Results

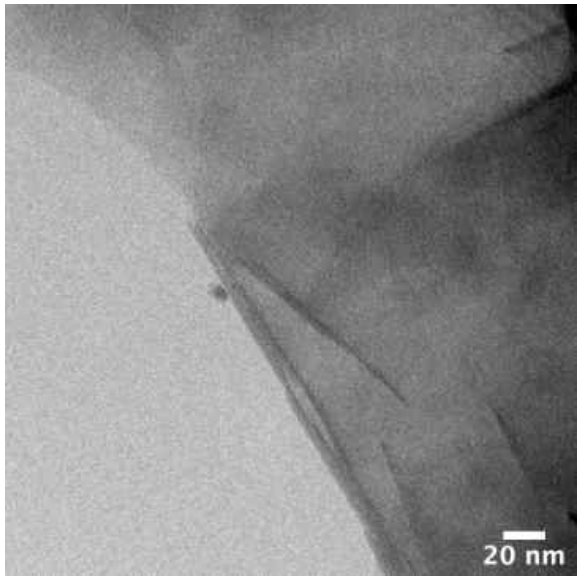
- Reduction of CEs vs. Fe(II) Minerals:
  - XRD of clay (Swy-2)
  - Powers vs. Suspensions
  - Red arrows = new features
  - $Fe(OH)_2$ > No Match
  - Green Rust > Poor Match
  - Magnetite > No Match
  - Greenalite > Best Match
  - Consistent with Mössbauer and TEM

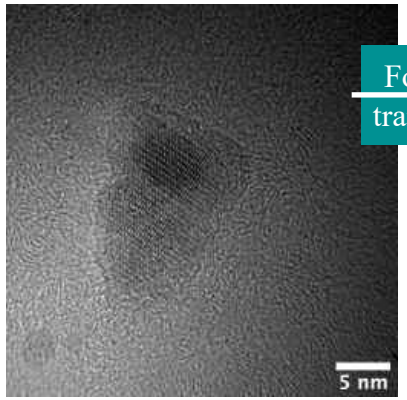


# Reactive Mineral Intermediates (RMIs): Batch Results

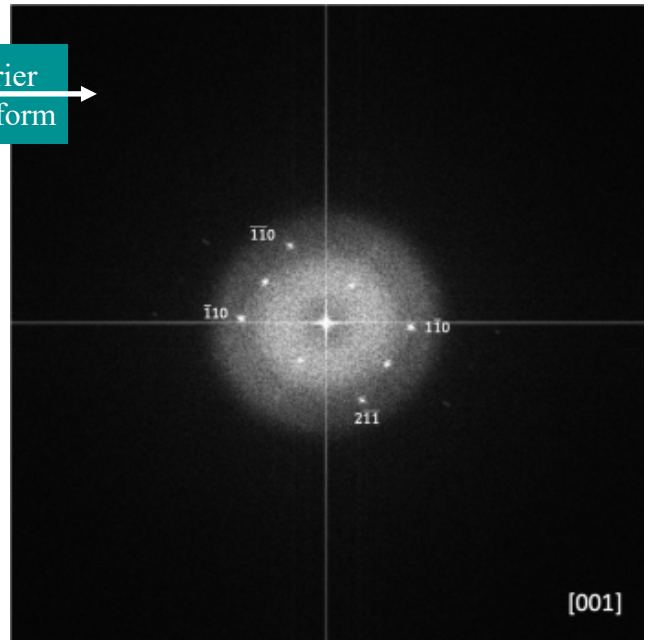
- Reduction of CEs vs. Fe(II) Minerals:
  - TEM images display nano-sized particles that are absent in unreacted SWy-2.
  - EDS showed that these particles comprise Fe and Si only whereas the clay mineral matrix contains (as expected) Fe, Si, and Al.
  - Best match is **Greenalite** ($Fe^{II}/Fe^{III}$ hydroxy silicate) ⇒ "Greenalite Precursor".



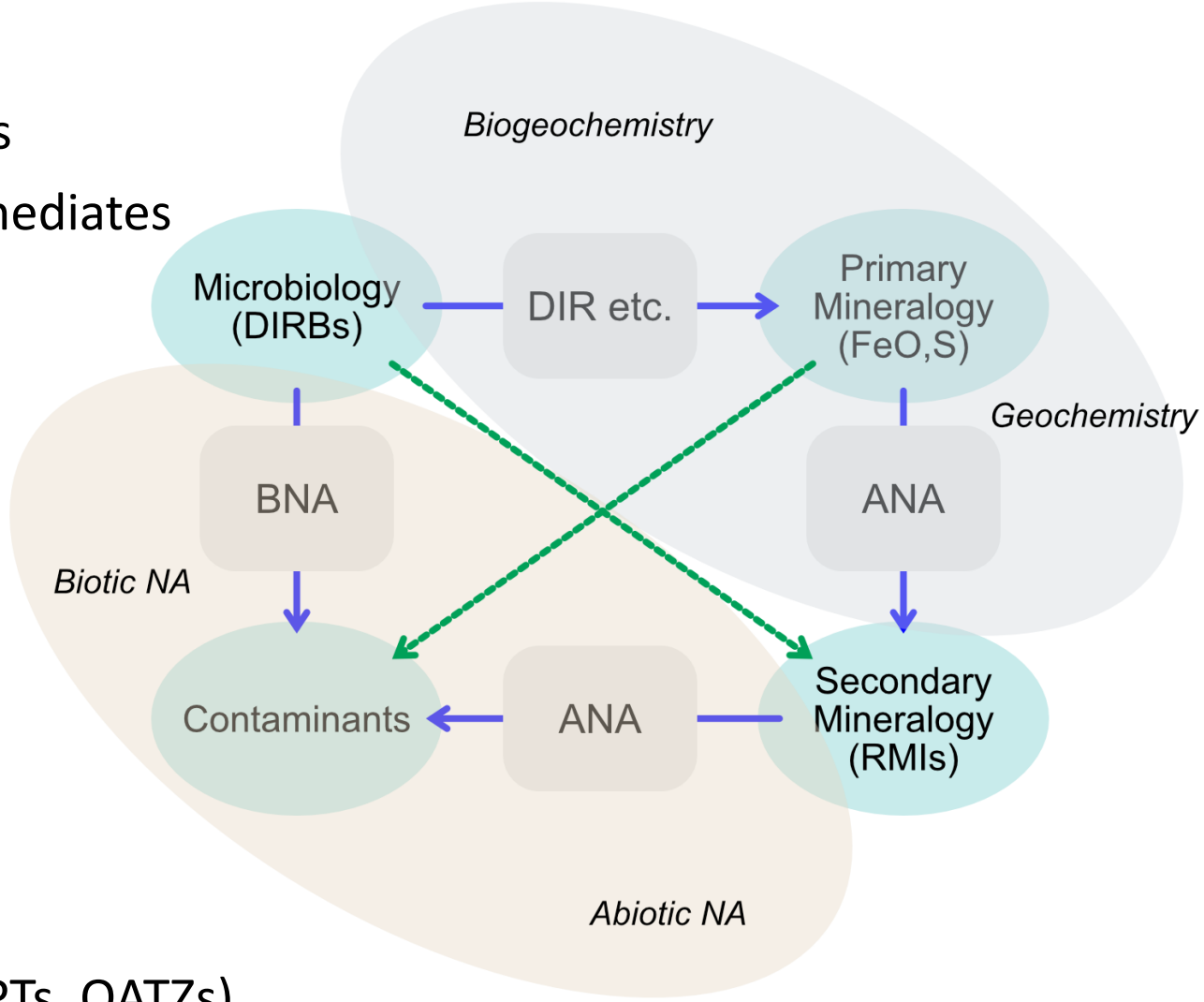

Fourier transform

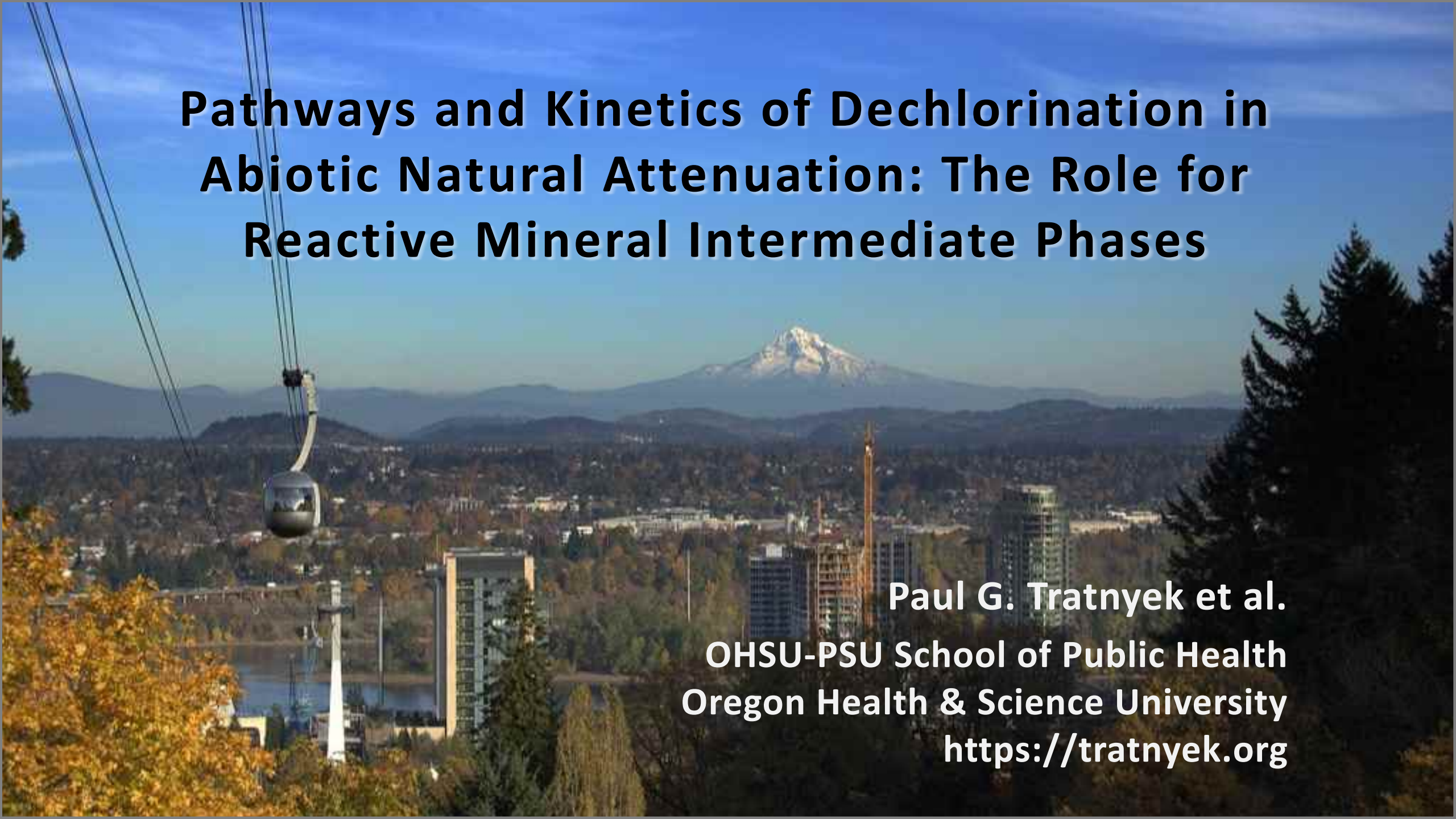



consistent with known structure of greenalite

# Summary and Implications

- RMI Model for ANA
  - ANA requires activated mineral phases
  - RMIs are metastable, transient, intermediates
  - Identification in progress
  - $Fe(OH)_2$-like or “Greenalite Precursor”
- Contaminant Reduction by RMIs
  - Requires “in situ” conditions
  - Rates slow and sensitive to [RMI]
  - Indirectly reflected in pH + Eh etc.
- Implications of RMIs in ANA
  - Not 1° minerals (e.g., magnetite)
  - Fluctuations in hydrogeochemistry (APTs, OATZs)





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# Reactive Mineral Intermediates (RMIs)

- RMI Hypothesis (Variations):

Journal of Hazardous Materials 420 (2021) 126600

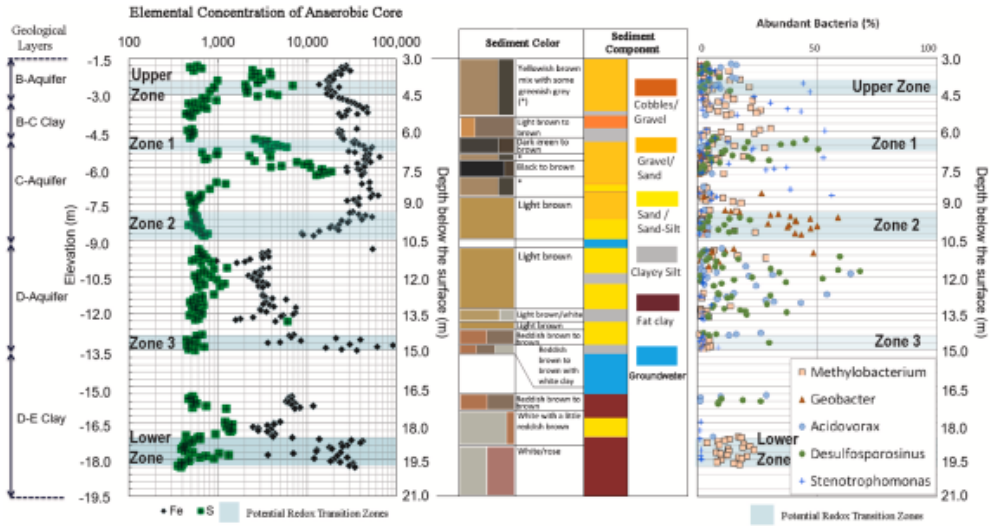
Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

## Roles of reactive iron mineral coatings in natural attenuation in redox transition zones preserved from a site with historical contamination

Han Hua [a], Xin Yin [a], Donna Fennell [b], James A. Dyer [c], Richard Landis [d], Scott A. Morgan [e], Lisa Axe [f,*]



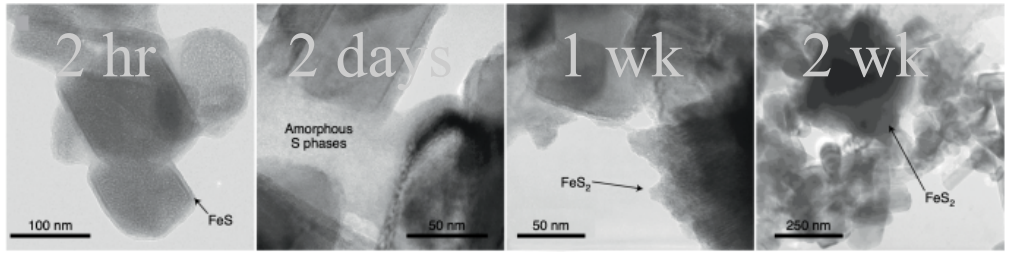

nature geoscience

REVIEW ARTICLE

https://doi.org/10.1038/s41561-021-00742-z

## A biogeochemical–hydrological framework for the role of redox-active compounds in aquatic systems

S. Peiffer [1✉], A. Kappler [2], S. B. Haderlein [3], C. Schmidt [2], J. M. Byrne [2], S. Kleindienst [4], C. Vogt [5], H. H. Richnow [5], M. Obst [6], L. T. Angenent [7], C. Bryce [2], C. McCammon [8] and B. Planer-Friedrich [9]




Dynamic processes involving the formation of RAMPs. TEM images showing the reaction between sulfide and lepidocrocite over time.

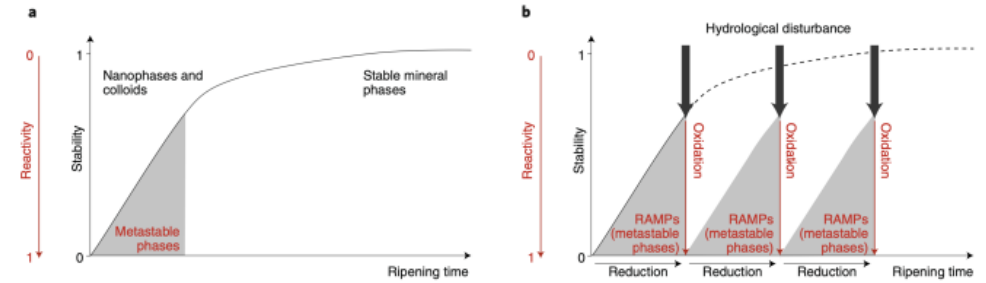
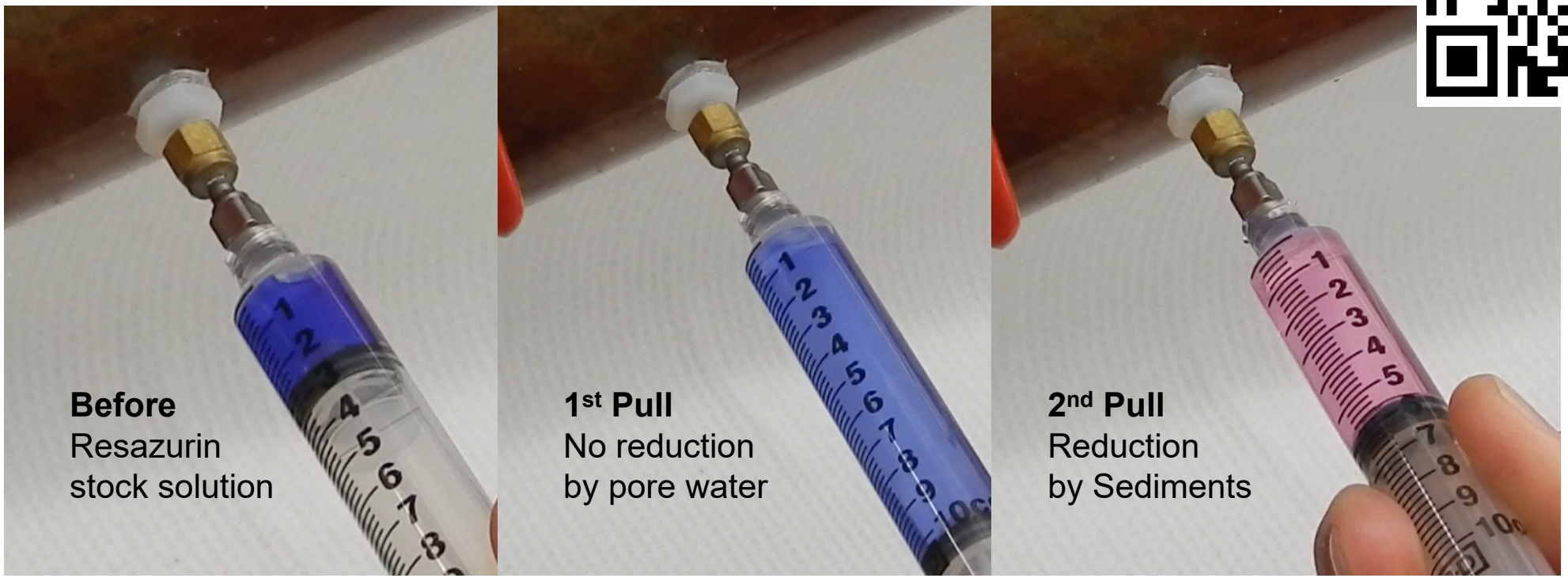



**Fig. 3 | Influence of hydrological fluctuations on RAMPs. a**, Ripening time enhances the stability of RAMPs and decreases their reactivity. **b**, Hydrological events with suitable recurrence frequencies interrupt the ripening process and lead to the regeneration of RAMP properties.

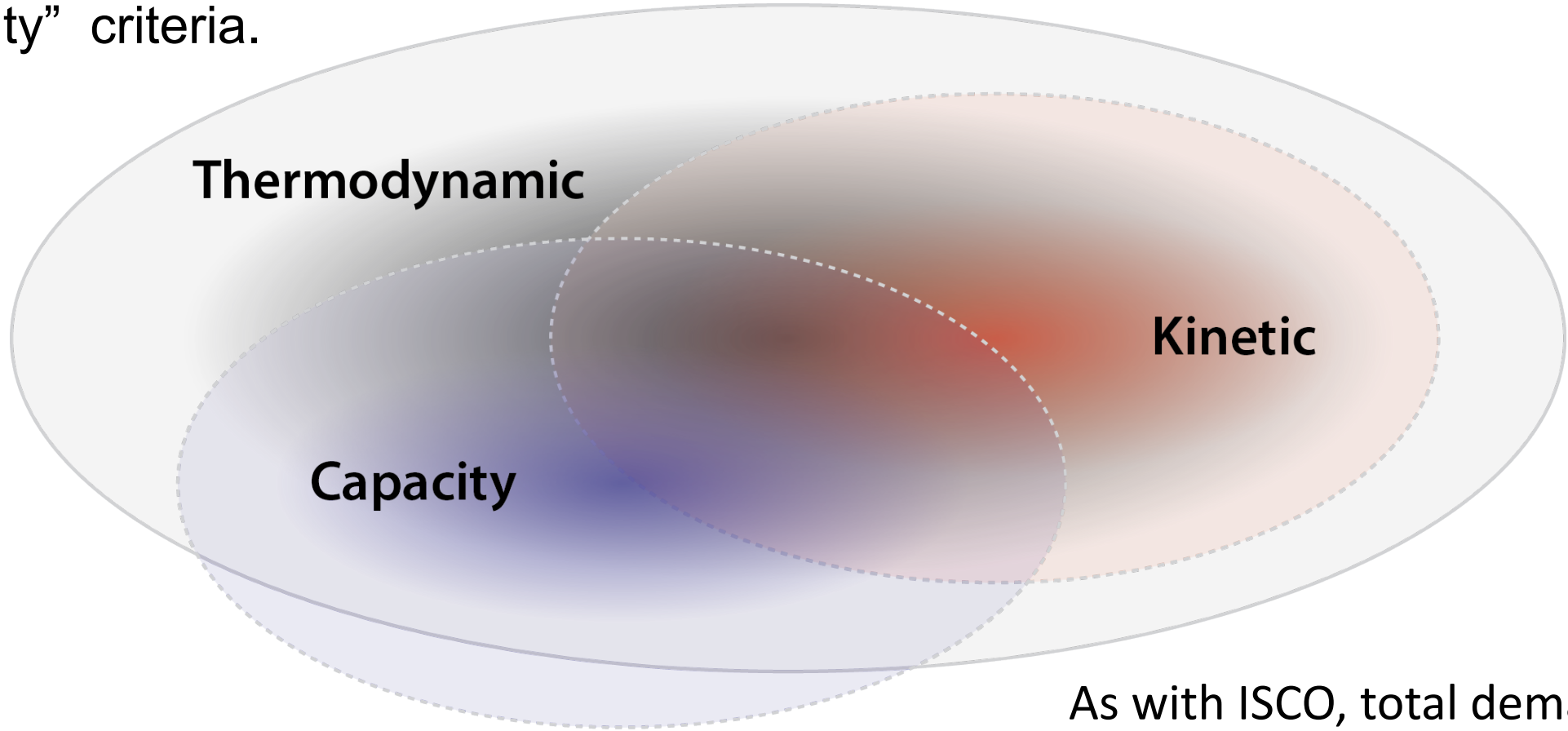
## Reactive Surface Area:

- Not reflected in remote solution phase measurements (e.g., ORP)
- Chemical reactivity probe (CRP) like resazurin shows reactivity
- Resazurin: (1) purple = oxidized, (2) pink = reduced.

YouTube Video



Overall success requires meeting thermodynamic, kinetic, and "capacity" criteria.




As with ISCO, total demand = contaminant demand + aquifer demand