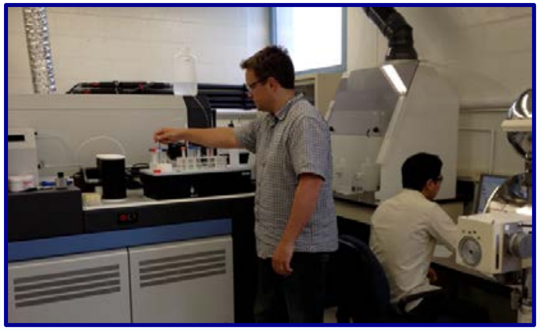

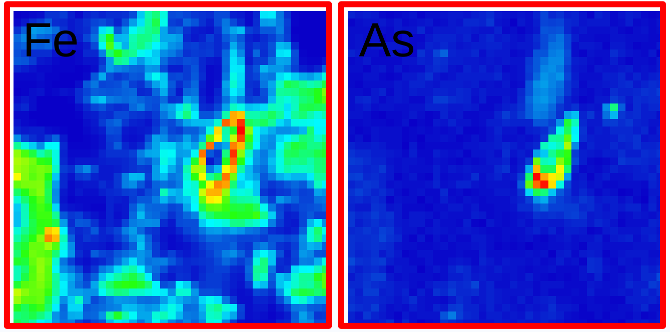

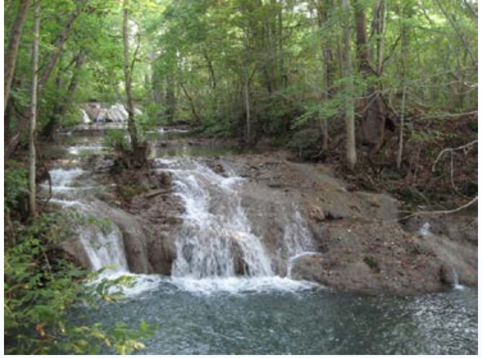

Evaluating Potential Groundwater Impacts and Natural Geochemical Signals with CO_2 Storage: Trace Metals

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U.S. Department of Energy

National Energy Technology Laboratory
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Developing the Technologies and
Infrastructure for CCS

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NETL-RUA
Regional University Alliance

Project Overview: Benefits of Technology to the Program

Chemical tracers and geochemistry-based tools can address technical and scientific gaps related to:

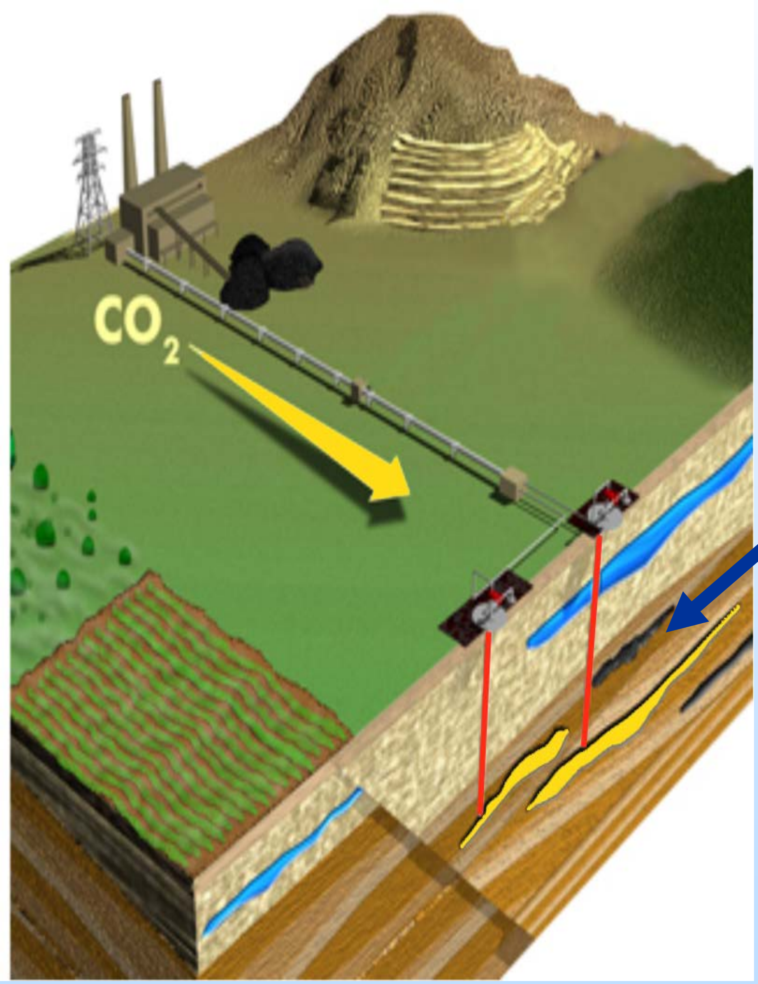
- Verifying predictions of CO_2-water-rock reactions at a storage site
- Tracking subsurface CO_2 plume migration, potential leakage pathways
- Early detection of CO_2 or brine breach from a storage formation
- Potential impacts on groundwater aquifer quality

Geochemical signals may be used to differentiate among different scenarios, for example:

- Is the observed pressure drop due to in-situ mineralization or a slow leak?
- Is the observed degradation in a nearby water supply due to displaced sub-surface brine associated with the target formation?
- Is the leak occurring due to poor cement bonding or a natural fracture

- Natural geochemical signals include only species already present in the environment
  - Do not rely on man-made tracers
  - Avoid costs of materials and injection equipment
  - No additional environmental impacts
  - Potential limitations:
    - Most environmental studies are for surface or near-surface conditions (e.g. are thermo and kinetic parameters relevant)
    - Complex redox chemistry may limit usefulness
    - Need more detailed knowledge of water-rock-CO_2 chemistry
    - Multiple sources may hamper source identification

Project Overview: Background



Natural geochemical signals

Migration into Shallow Aquifers

Migration into other Deep Formations

Develop natural tracers that can be used for

- **Detecting (1) CO$_2$ or (2) brine leakage from storage formations**
- **Understanding potential impacts to shallow environments (groundwater aquifers, vadose zone)**

Project Overview: Objectives

- Immediate Objectives:
  - Identify potential natural geochemical signals to monitor leakage of CO_2 to groundwater.
  - Better understand sources of potential GW impacts (work towards evaluating "No Impacts")
- Ultimate Objective:
  - develop a suite of techniques (best practices) that, when used alone or in combination, can indicate CO_2 losses in excess of the 1% over 100 years target.

Natural geochemical signals to monitor leakage to groundwater

Team

- Ale Hakala, NETL
- Christina Lopano, NETL
- Hank Edenborn, NETL
- Karl Schroeder, NETL
- Rosemary Capo, Pitt
- Brian Stewart, Pitt
- Shikha Sharma, WVU
- Dorothy Vesper, WVU
- Athanasios Karamalidis, CMU
- Kim Carter, ORISE
- Andrew Wall, ORISE
- Jinesh Jain, URS
- a host of supporting analysts, graduate students and undergraduate students

Technical approach employs a multidisciplinary team (chemists, geologists, microbiologists, environmental scientists) in both laboratory and field work

Natural geochemical signals to monitor leakage to groundwater

Sub-Teams

Natural Geochemical Signals

- **Field CO_2 measurements** (WVU, NETL)
  Carbonation meter
- **Natural Isotope tracers** (Pitt)
  Sr, Li, U, Cu, Fe
- **CO_2 stable isotope indicators** (WVU)
  C, H, O, S
- **Point sources of trace contaminants** (NETL) As, U, Pb ★
- **Precipitation and dissolution studies** (CMU)
  Arsenopyrite, caprock ★
- **Organic compounds to track CO_2 migration** (CMU) Volatile organic carbon

Research Summary

The Immediate Objective, to provide a suite of natural geochemical signals to monitor leakage of CO_2 to groundwater, is being met on multiple fronts:

- **Direct CO_2 measurements**
- **Carbon and other stable isotope ratios**
- **Sr and other geochemical isotopic tracers**
- **Identification of organic compounds mobilized during EOR or other sequestration activities**
- **Chemistry of trace element mobilization (Arsenic)**

Using a combination of Laboratory and Field Studies

Technical Status: Groundwater Impacts

- Study trace metals (e.g. As) to fill science gaps –
  - evaluate impacts and any perspective signals (isotope and/or chemical trends) ***“No Impact“***
- Previous work:
  - Chimayo Natural Analogue site (LANL, NETL, Pitt)
    - As, U in shallow groundwater (in places above MCL)
      - upwells with CO_2 from deep aquifer (Keating 2009, 2013)
    - Models indicate that As then sorbs in shallower sediments to clay materials *(Viswanathan et al. 2012)*
- Current studies:
  - Mineral (arsenopyrite) dissolution studies (CMU)
  - Caprock materials
    - Characterization of point source (NETL)
    - In-situ experiments under sequestration conditions

Point Sources of Trace Contaminants: As

Develop a comprehensive understanding of arsenopyrite reactivity in CO_2-rich systems of varied pressure and temperature.
(H. Parthasarathy & A. Karamalidis – CMU)

- Literature review: occurrence of arsenic in sedimentary formations:
  - Major sources of arsenic are arsenopyrite: FeAsS, arsenian pyrite: $Fe(S,As)_2$, and iron oxy hydroxides: FeOOH - As(ads) (considered a secondary source)
  - Concentrations range up to 50 mg/kg
  - Geochemistry (thermo or kinetics) at GCS conditions are not well understood (Needed for predictive models)
- For the purpose initial project development it was desirable to use a mineral having a well defined crystal structure (FeAsS).
- Developed a unique high T&P flow-through reaction cell

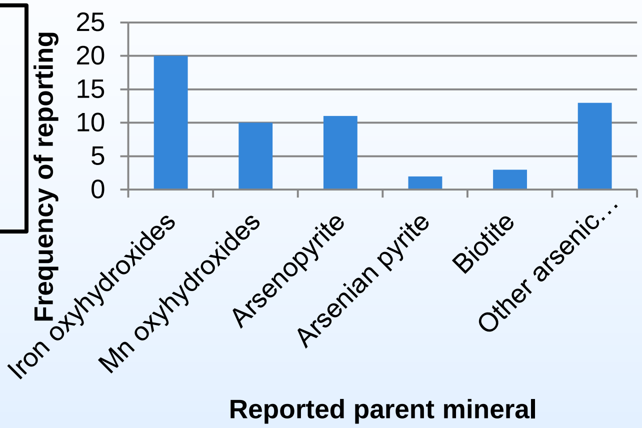


Figure 1: *Arsenic parent material in* ***high permeability*** *sedimentary formations*

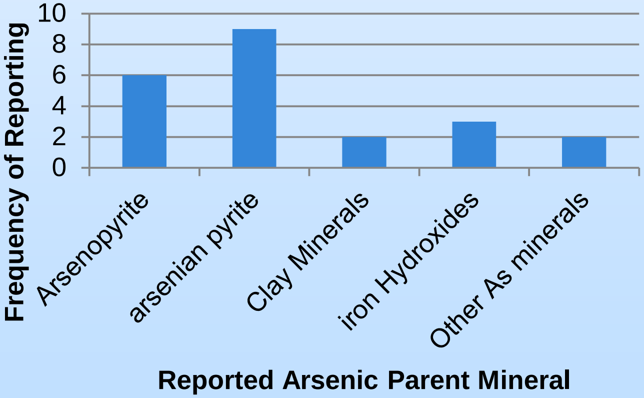


Figure 2*: Arsenic parent material in* ***low permeability*** *sedimentary formations*

Point Sources of Trace Contaminants: As

Develop a comprehensive understanding of arsenopyrite reactivity in CO_2-rich systems of varied pressure and temperature. (H. Parthasarathy & A. Karamalidis – CMU)

- 2011-2013
  - Developed a small-scale flow-through system (patent pending)
  - System sucessfully validated for mineral dissolution (arsenopyrite) for a range of T,P, and solution conditions
- 2012-present
  - Dissolution experiments with formation rocks to test the validity of system in simulating real geologic formations

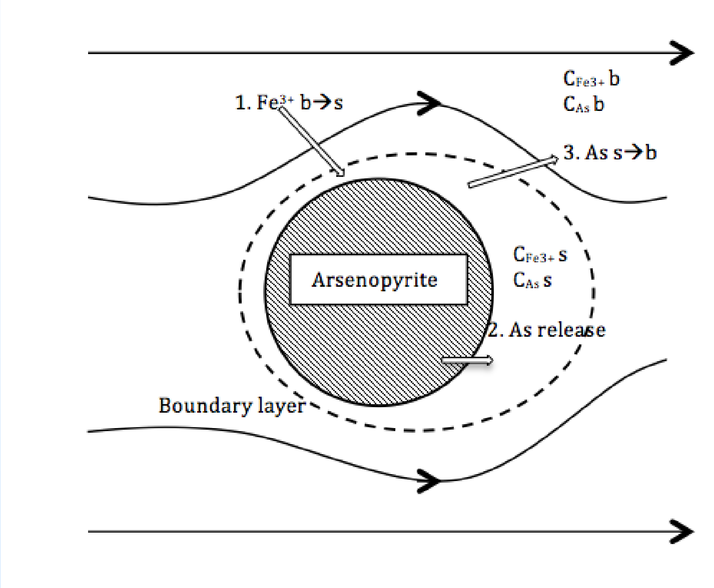


Figure 1. Schematic of proposed flow pattern around a spherical arsenopyrite particle and mass transfer processes

Parthasarathy H., Dzombak D., Karamalidis A.K., Dissolution of Arsenopyrite under Geologic Carbon Storage Conditions, Goldschmidt 2013, Florence, Italy, August 25-30 (2013).

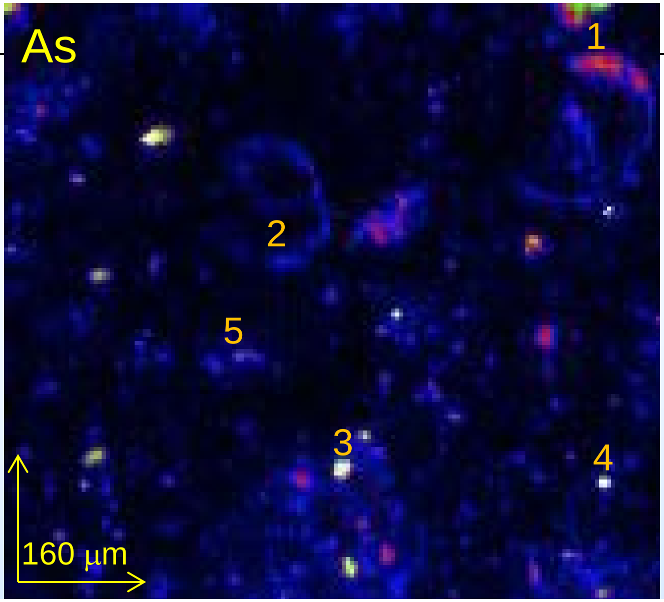
Karamalidis et al., 2012, provisional patent application 61/797,302

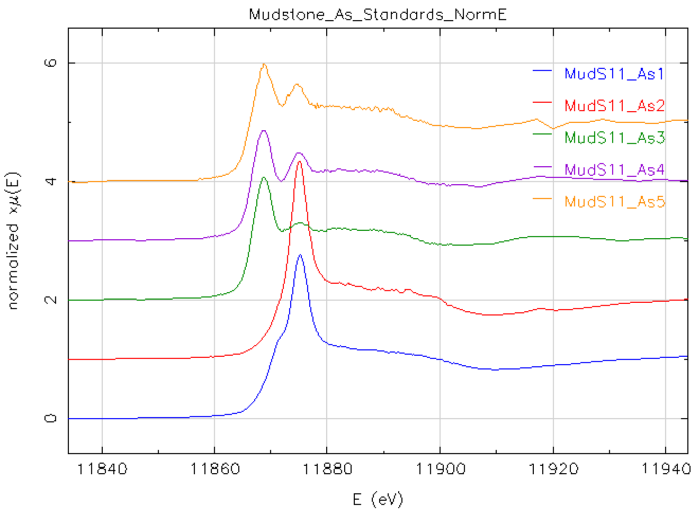
Trace Metal Point Sources: Caprock

- Expand study to more complex natural systems – caprock materials
- Characterization of caprock material
  - XRD: Major clay, quartz, pyrite is common
  - ICP-MS: As levels on the order of 17 mg/kg
  - Synchrotron µXRF and XANES (APS, Argonne National Lab)
    - µXRF used to evaluate elemental associations and to find the As (As trends with Fe)
    - XANES used to determine As speciation and binding environment (compare to standards – Linear Combination Fitting)
  - Additional characterization pre & post reaction

Trace Metal Point Sources: Caprock

- Middle Tuscaloosa Mudstone (d = 10135 ft) Caprock material
  - As bound primarily in two forms:
    - As (III) in sulfide (e.g. arsenopyrite)
      - “Hot spots” in μ-XRF map (spots 3, 4, 5)
    - As (V) sorbed to Fe-oxides
      - Rim features in μ-XRF map (spots 1 & 2)
  - Also evidence for intermediate binding
    - As (III) sorbed to Fe-oxides (spots 1 & 2)
    - As (III) sorbed to sulfides (spots 1 & 5)
- Middle Tuscaloosa Mudstone (d = 10186 ft) Caprock material
  - Similar trends
- Ideal candidate for testing in-situ lab experiments





Data collected on BL 20-ID and 13-ID at APS

Point Sources of Trace Contaminants

Linear Combination Fitting (LCF) results for XANES data collected on samples from the Middle Tuscaloosa Mudstone samples (%) (Athena software)

Sample ID	As(V)-FeOxides	As(III) – FeOxides	As(III) – Sulfide	As(III) *in* sulfide	R-factor
MudS11_As1	59	30	11	0	0.006
MudS11_As2	78	22	0	0	0.018
MudS11_As3	16	0	0	84	0.002
MudS11_As4	28	0	0	72	0.002
MudS11_As5	21	9	39	31	0.002
Mudstone_As1	19	0	0	81	0.004
Mudstone_As2	14	3	4	80	0.003
Mudstone_As3	18	11	28	44	0.002
Mudstone_As4	29	9	27	35	0.002
Mudstone_As5	16	0	3	81	0.003
Mudstone_As6	81	9	11	0	0.005

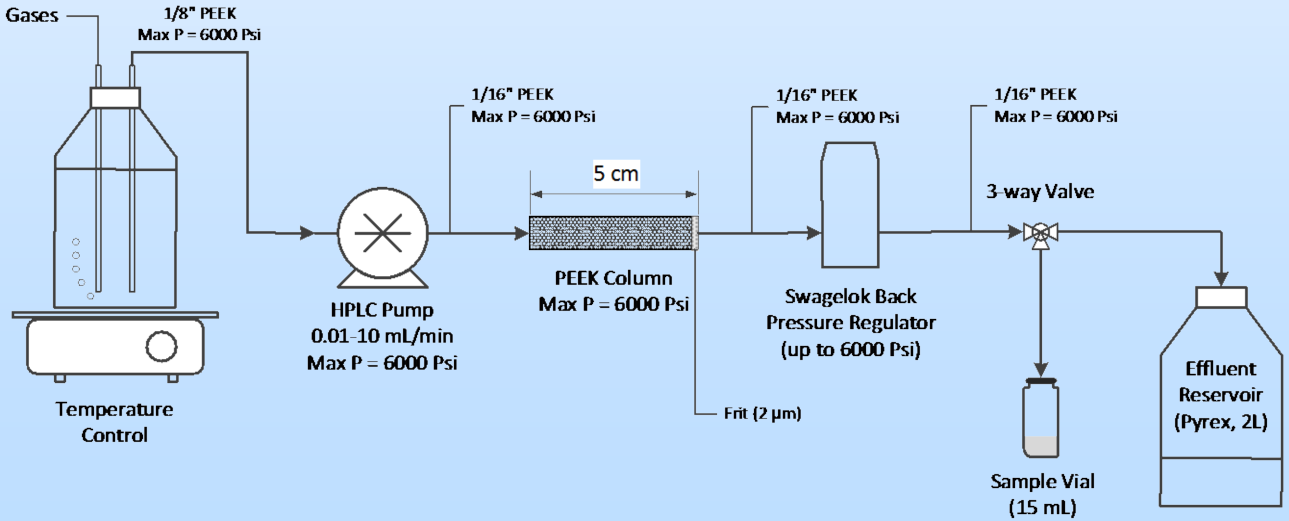
As(V)-FeOxides: Sum of As(V) sorbed to ferrihydrite and scorodite
As(III)-FeOxides: As(III) sorbed to ferrihydrite
As(III)-Sulfide: Sum of As(III) sorbed to pyrite and machinawite
As(III) in Sulfide: Sum of orpiment, realgar, and arsenopyrite
R-factor = $[((\text{data-fit})^2)]/[\text{sum}(\text{data}^2)]$

Standard data provided by K. Scheckel - US EPA

Caprock Dissolution Experiments

Flow-through column experiments

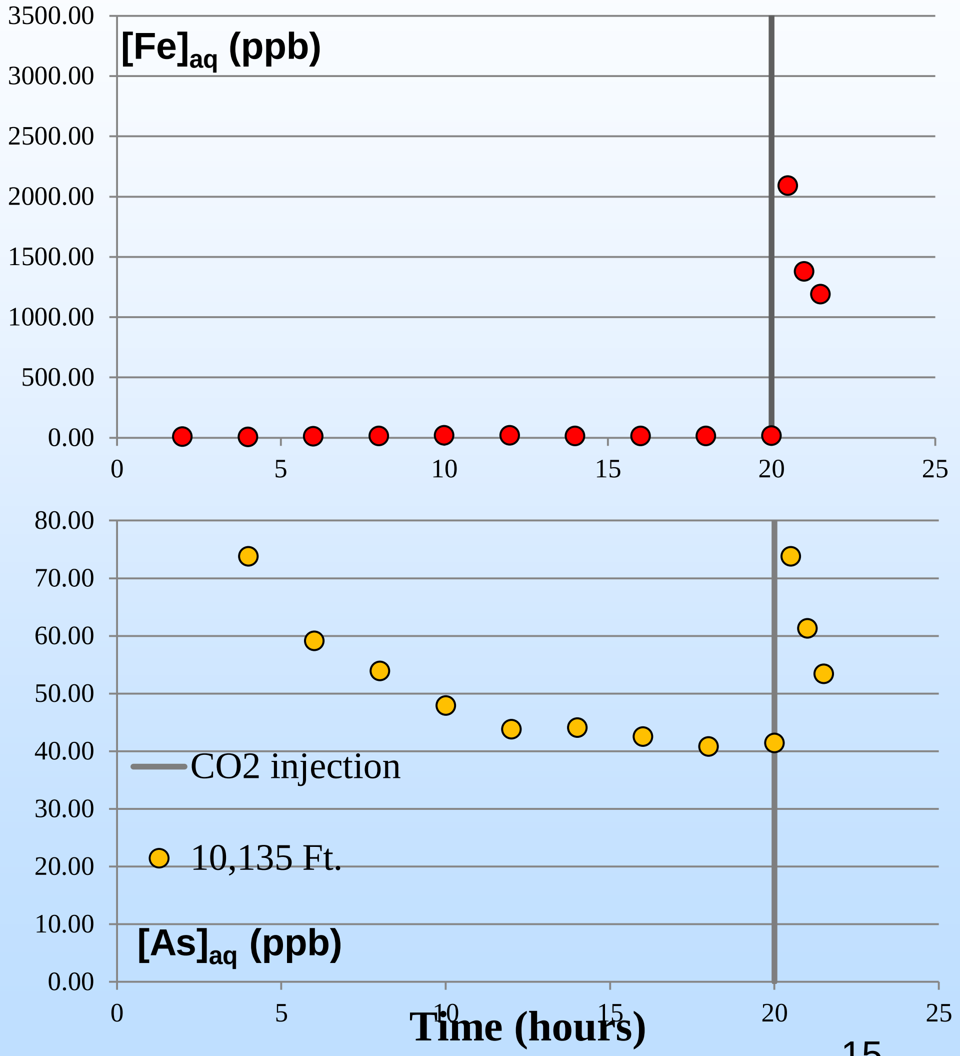
- Flow through column system was used
- Cap-rock samples : Crushed (150-250μm) and packed in PEEK column
- Influent : NaCl (105 g/L, deoxygenated). T= 60 °C, P= 100 bars
- At t= 20h, CO_2 injection
- Fluid phase samples collected for ICP-MS for dissolved Fe and As concentrations



Parthasarathy H., Dzombak D., Karamalidis A.K., "A Small-Scale, Flow-through Column System to determine the Rates of Mineral Dissolution at High Temperature and Pressure and Salinity". Chemical Geology, 354, 65-72 (2013).

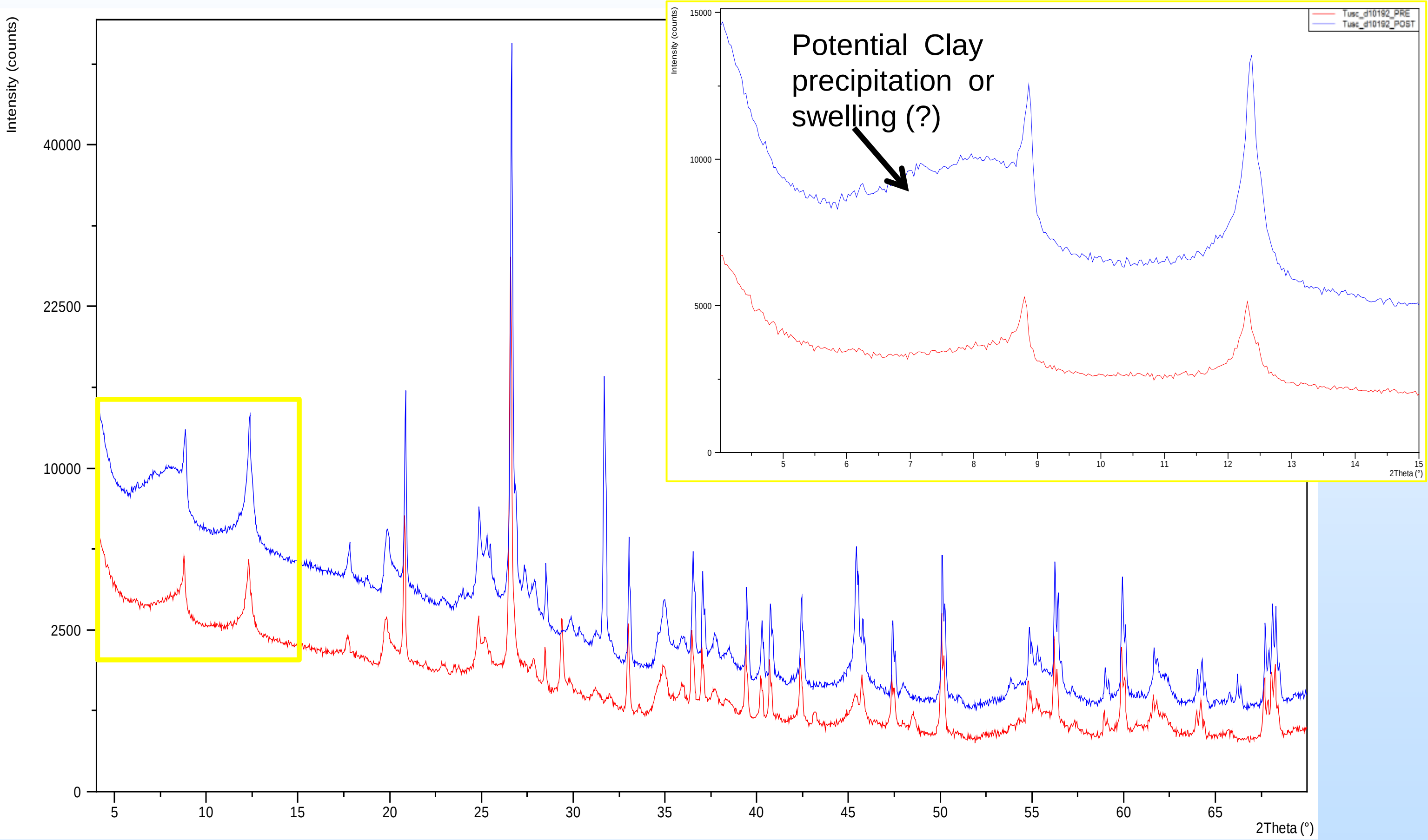
Preliminary Dissolution Experiments: Caprock

- Experiments conducted at CMU
  - Summer 2013
  - Additional shallower secondary caprock will also be analyzed
- Initial results indicate dissolved Fe & As increase with injection of CO_2
  - Similar to trend in Lu et al. (2010) batch experiments
  - Experiment clogged the flow column
    - Clay precipitation or swelling (?)
  - Experiments with secondary caprocks have not clogged to date



Parthasarathy H., Lopano C., Hakala A., Dzombak D., Karamalidis A.K., Dissolution of Arsenic and Iron from Reservoir and Cap-Rocks of Geologic Carbon Dioxide Storage Sites, Goldschmidt 2013, Florence, Italy, August 25-30 (2013).

Preliminary Dissolution Experiments: Caprock



Potential Clay precipitation or swelling (?)

XRD Patterns: sample MT10,135 ft. – Pre (red) and Post (blue) reaction.

Summary: Trace Metal Point Source

- Successful development of a unique flow-through system *(Parthasarathy, 2013)*
  - Arsenic (and Iron) mobilization supercritical CO_2
    - Mineral scale (Arsenopyrite studies)
    - Rock scale (Middle Tuscaloosa Mudstones)
- Ongoing experiments (CMU) explore the effects of pH and DIC independently
- Future work: Link experiments with isotope tracer work (Pitt)
- Iron isotope study of arsenopyrite dissolution mechanism
  - Controlled leaching experiments of water and arsenopyrite under varying redox conditions
  - Isotope fractionation associated with the formation of a passivation surface layer
  - Continue with mudstone caprock material

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- J. Lu – UT BEG: Mudstone samples
- K. Scheckel – US EPA: As standard patterns and aid with data-fitting in Athena
- Synchrotron User Facilities:

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