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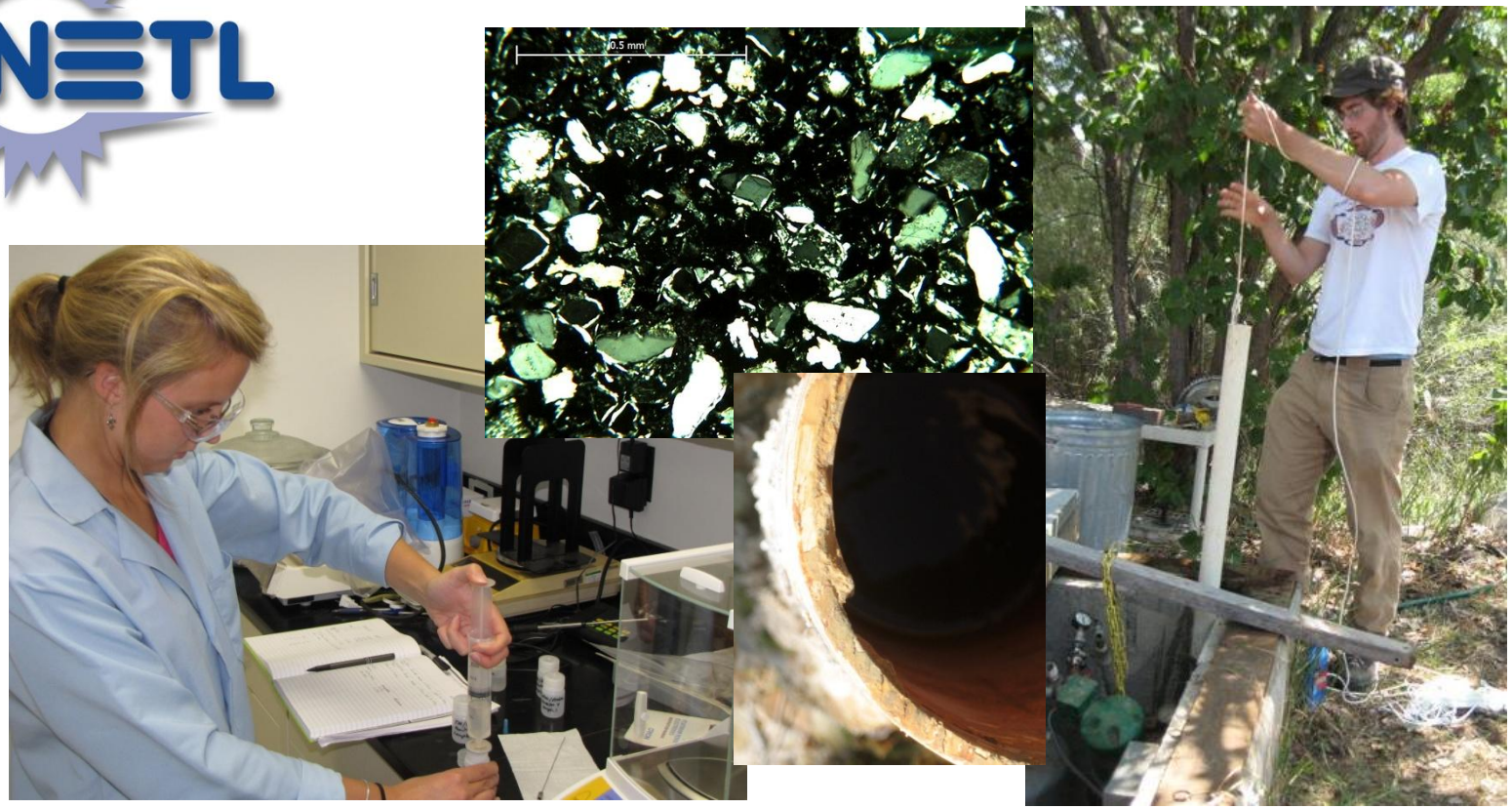

Groundwater Monitoring to Verify Storage Permanence

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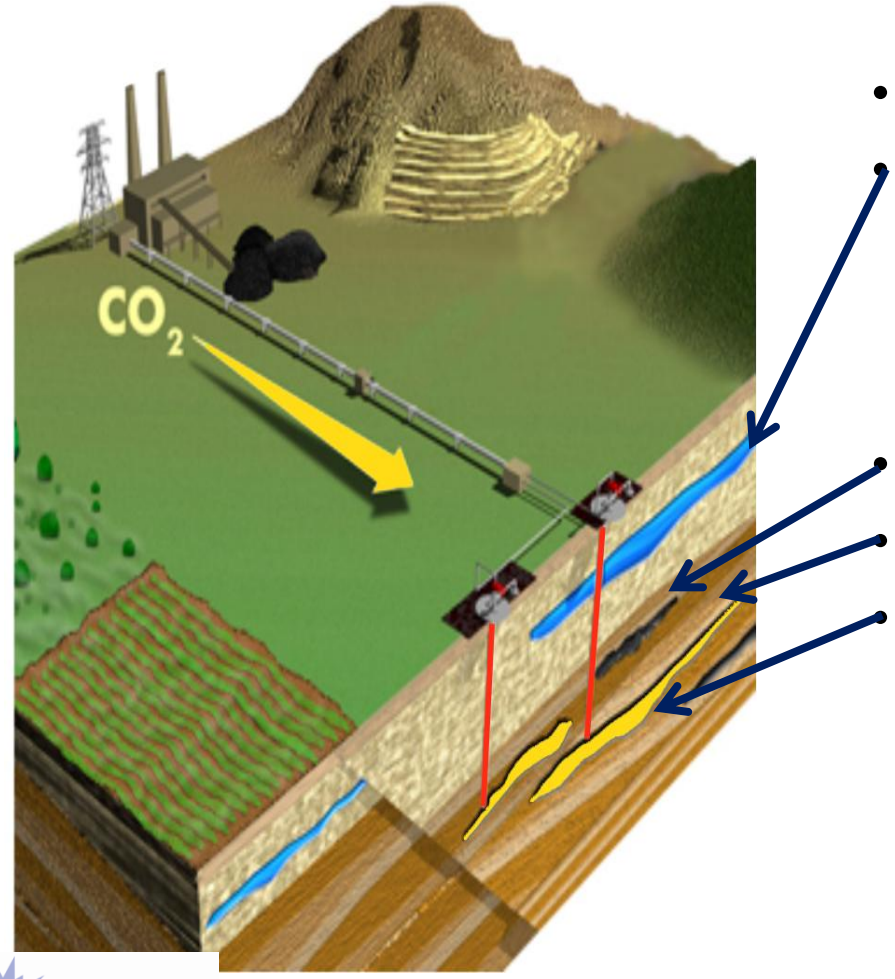
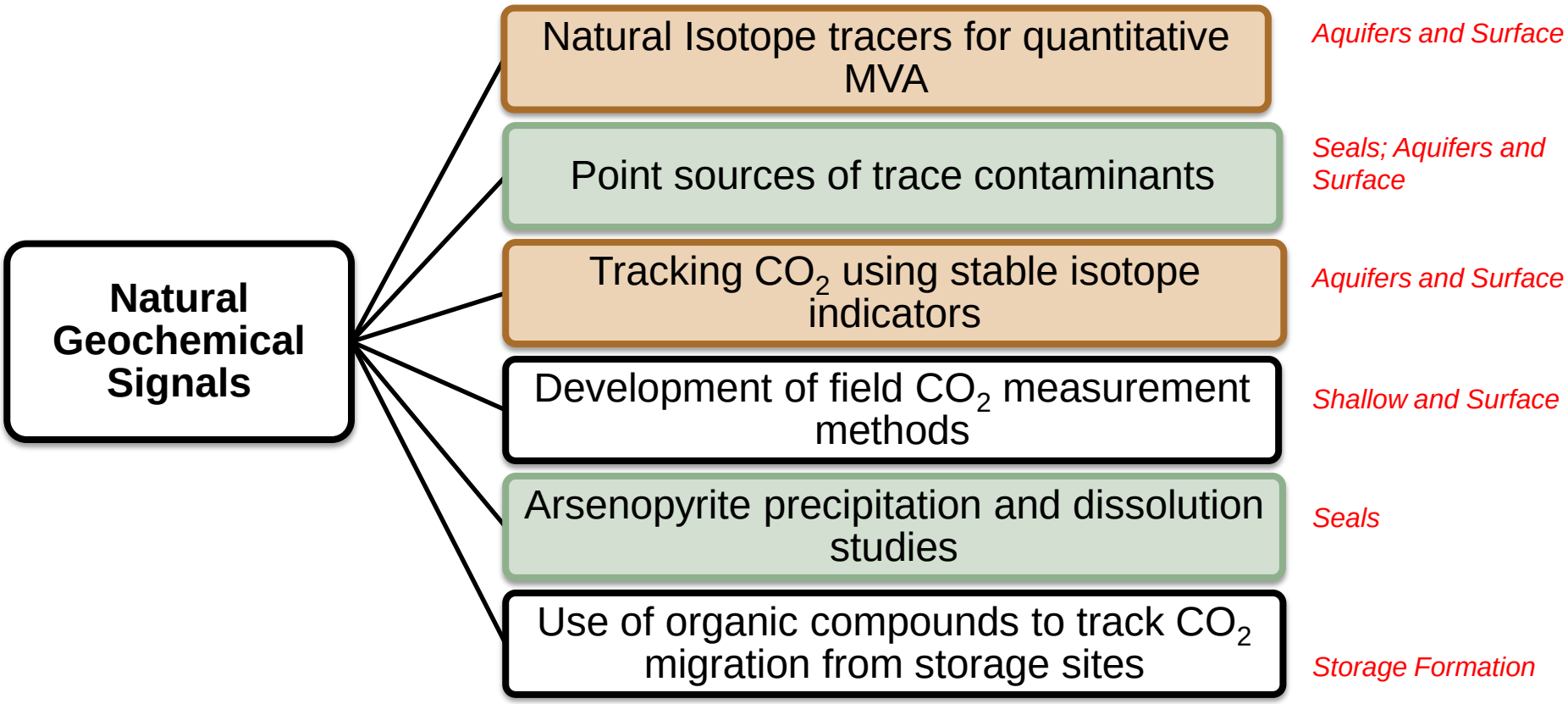
U.S. DEPARTMENT OF ENERGY

Geochemistry plays an important role in all aspects of a geological CO_2 storage system



- **Monitoring techniques**
- **Groundwater aquifers**
  - Liability issues
  - EPA Class VI rules (also includes injection well integrity)
- **Other subsurface resources**
- **Seals: Wells and Natural Rocks**
- **Storage formation**
  - CO_2 plume behavior
  - Long-term permeability and porosity
  - Organics with CCUS

Objective: provide a suite of natural geochemical signals to monitor leakage of CO_2 to groundwater. Ultimate objective: develop a suite of techniques that, when used alone or in combination, can indicate CO_2 losses in excess of the 99% over 100 years target.

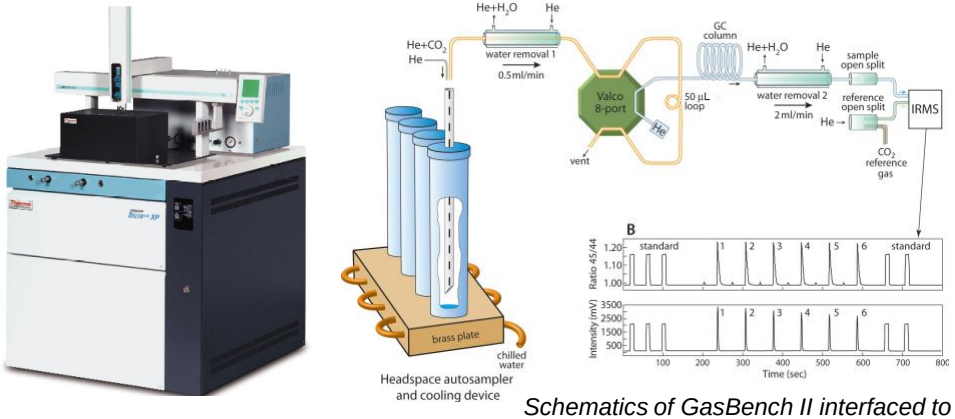


Tracking CO_2 using stable isotope indicators

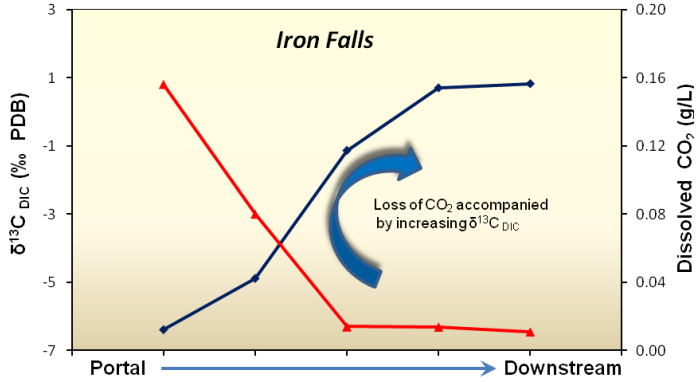
Develop methodologies to use stable isotope mass spectrometry for quantitative measurement of C, H, O, S isotopic signatures to determine their ability to signal CO_2 intrusion.

- *The $\delta^{13}C_{DIC}$ can prove to be a very effective natural geochemical MVA tracer because it is very sensitive to shifts in carbonate chemistry in the reservoir.*
- *Samples collected from high CO_2 natural analogue sites show that the $\delta^{13}C_{DIC}$ shift towards higher values as isotopically lighter dissolved CO_2 species is lost.*

Gas Bench Coupled to IRMS for $\delta^{13}C_{DIC}$ measurement



Schematics of GasBench II interfaced to a gas source IRMS (Torres et al., 2005)



$\delta^{13}C_{DIC}$ (blue) and dissolved CO_2 (red) trends from portal to downstream at two coal mine discharge sites in Allegheny County, PA. Note the sharp rise in $\delta^{13}C_{DIC}$ signatures as CO_2 is lost via degassing

Natural Isotope tracers for quantitative MVA

Develop methodologies using the NETL Multicollector ICP-MS facility for quantitative measurement of trace element isotopic signatures to determine their ability to signal CO_2 intrusion.

➢ Isotopes currently of interest include:

- ➢ Strontium (Sr)
- ➢ Uranium (U)
- ➢ Neodymium (Nd)
- ➢ Boron (B)
- ➢ Lithium, (Li)
- ➢ Iron (Fe) and,
- ➢ Copper (Cu).

➢ Develop analytical techniques specific to storage fluids.

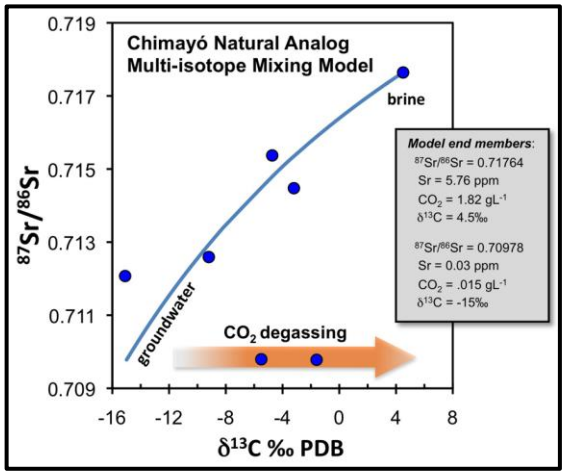
➢Determine the quantitative relationship between changes in isotopic signatures and the extent of CO_2 intrusion.

Isotope systems can be useful for:

- **Tracking brine migration**
- **Determining seal rock leakage**
- **Studying fluid/rock reactions**

❖ **Quantification of CO_2-water-rock signatures using natural strontium (Sr) isotope signatures**

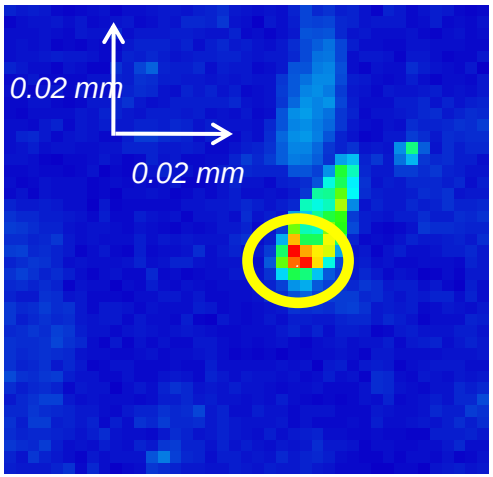
- Sr isotope mixing models indicate admixing of up to 5% of CO_2-charged brine
- Evidence for CO_2-induced dissolution of aquifer carbonate – decoupling of brine CO_2(aq) and exsolved CO_2(g)



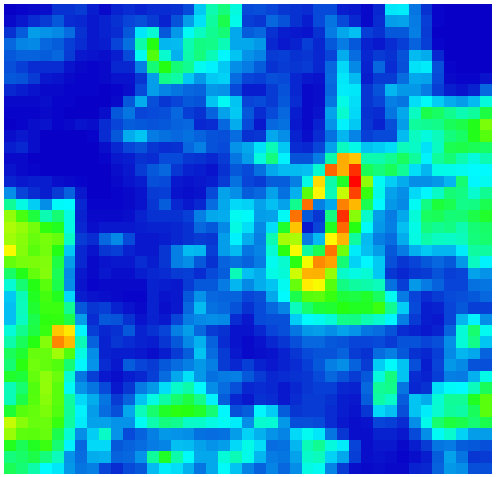
Stewart – Pitt; Capo – Pitt; Wall – ORISE

Point sources of trace contaminants

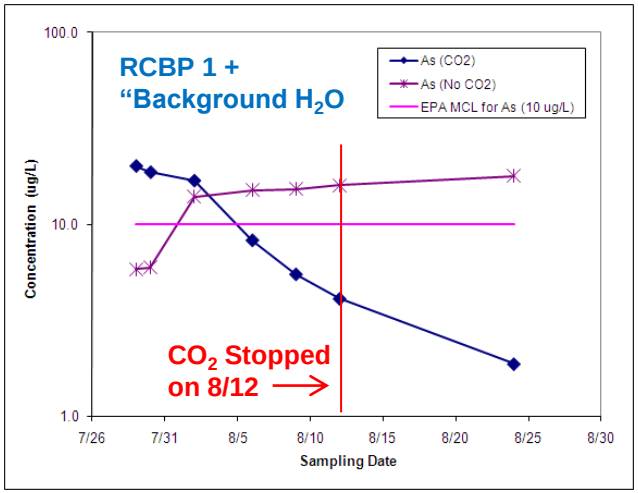
Characterize the distribution and speciation of EPA Drinking Water Standard contaminants in groundwater aquifer solids to provide input for reactive transport simulations



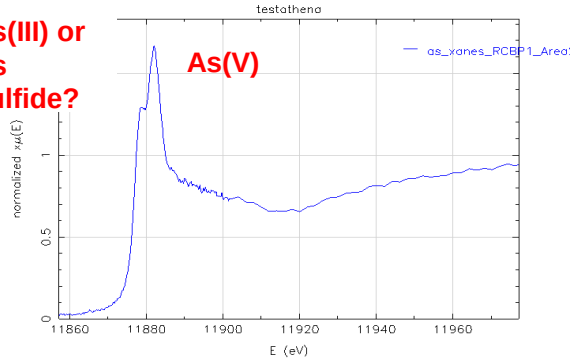
As *Kα*/***Pb*** *Lα1*



Fe *Kα*



As(III) or As sulfide?



- **μ-XRF Mapping and preliminary XANES results show that As is present in multiple redox states and/or is present in different coordination environments in the oxidized aquifer system**

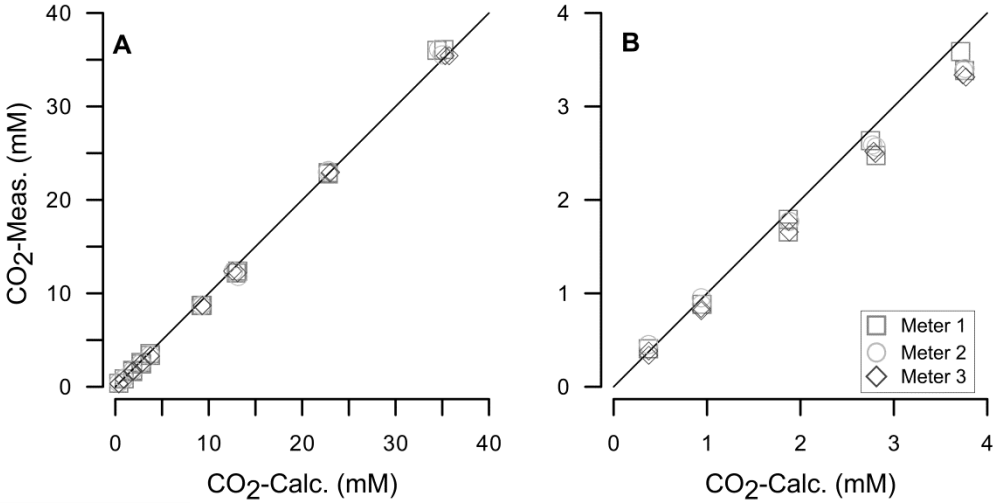
- **As behaves differently in sediment + water solutions with elevated CO_2 relative to sediment + water solutions with ambient CO_2.**

Development of field CO_2 measurement methods

Develop method to directly measure CO_2 in groundwater in the field.

- ❖ *Over 40 natural emergent waters containing elevated CO_2 have been tested*
- ❖ *Gave more rapid and accurate results than traditional methods based on pH and alkalinity titration*
- ❖ *Not sensitive to the presence of non-carbonate alkalinity*
- ❖ *Further field testing on deeper well waters and higher pressure samples is planned.*

Beverage Carbonation Measuring Module: CarboQC

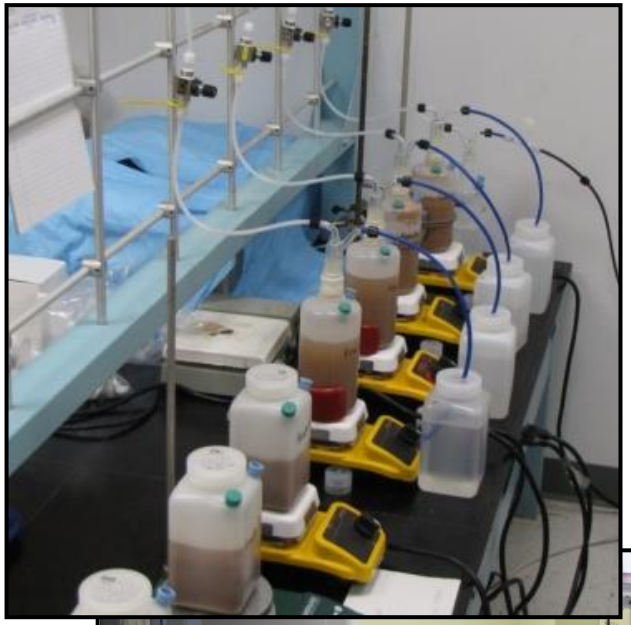


Vesper and Edenborn, "Determination of free CO_2 in emergent groundwaters using a commercial beverage carbonation meter" submitted to Journal of Hydrology

Arsenopyrite precipitation and dissolution studies

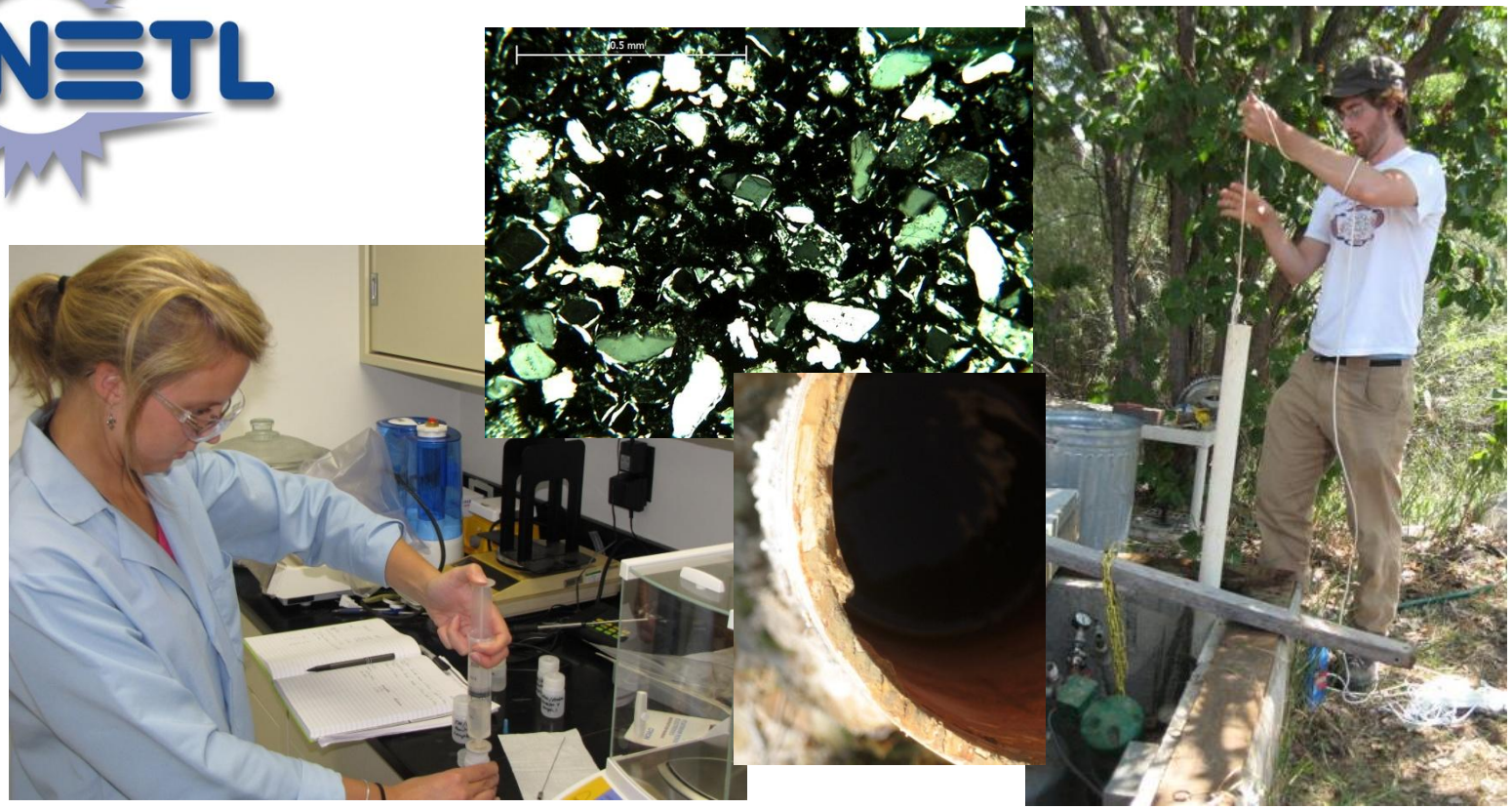
Develop a comprehensive understanding of arsenopyrite reactivity in CO_2-rich systems of varied pressure and temperture.

- **As is a potential groundwater concern**
  - **Arsenopyrite (FeAsS) and arsenian pyrite $Fe(S,As)_2$, major forms of As in sedimentary rocks, (includes CO_2 reservoir seals)**
- **Review of existing literature during FY11 – many gaps in knowledge regarding arsenopyrite reactivity in the presence of CO_2**
  - **Need information for predictive models**
- **Development of experimental system to probe key gaps within the reaction matrix**
- **Coordination with Fe isotopic measurements for determining mechanisms of As release**



Use of organic compounds to track CO_2 migration from CO_2-EOR (or other storage) sites

- Which organic compounds will be relevant in geologic CO_2 storage formations and in shallow groundwaters potentially affected by CO_2?
- Which organics will be soluble in and rendered mobile by supercritical CO_2?
- Research focused on developing input for multiphase flow simulations for predicting organics migration and behavior
  - Laboratory and field-based studies
  - Use of liquid and gas phase analytical techniques
- Review article on “Partitioning Behavior of Organic Contaminants in Carbon Sequestration Environments” (Bruant, A.; Lowry, G. V.; Karamalidis, A.)



Questions?