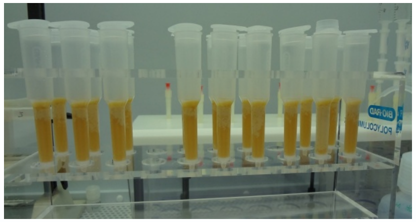
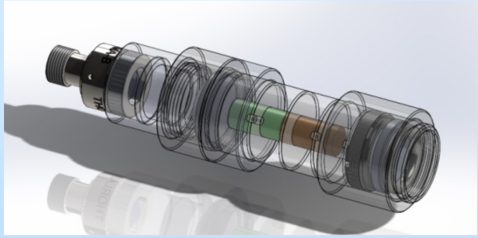


Methods and Tools for Monitoring Groundwater Impacts

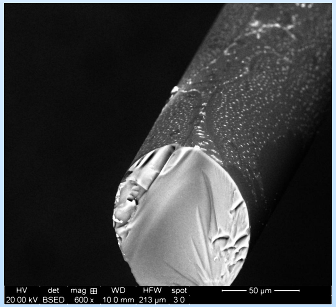
Project Number 1022403 (Task 4)

Christina Lopano

NETL - ORD



U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Transforming Technology through Integration and Collaboration
August 18-20, 2015



Natural geochemical signals to monitor leakage to groundwater

FY 2015 Team

- Christina Lopano, NETL-ORD
- Ale Hakala, NETL-ORD
- Hank Edenborn, NETL-ORD
- J. Rodney Diehl, NETL-ORD
- Sheila Hedges, NETL-ORD
- Dustin McIntyre, NETL-ORD
- Paul Ohodnicki, NETL-ORD
- Tom Brown, NETL-ORD
- Djuna Gulliver, NETL-ORD
- Thai Phan, ORISE-NETL
- James Gardiner, ORISE-NETL
- Mengling Stuckman, ORISE-NETL
- Cantwell Carson, ORISE-NETL
- Brian Stewart, Pitt, ORISE
- Shikha Sharma, WVU, ORISE
- Dorothy Vesper, WVU
- Jinesh Jain, AECOM, NETL

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

Presentation Outline

- Project Goals and Benefits
- Project Overview and Background
- Technical Status:
  - Isotope methodology
  - Sensor development
  - Field Validation
- Accomplishments
- Summary and Future Direction

Benefit to the Program

- Program Goals:
  - Validate/ensure 99% storage permanence.
  - Develop Best Practice Manuals for monitoring, verification, accounting, and assessment; site screening, selection and initial characterization…
- Project benefits:
  - *There is a need to be able to quantify leakage of CO_2 to the near surface and identify potential groundwater impacts. This project works to develop a suite of complementary monitoring techniques to identify leakage of CO_2 or brine to USDW's and to quantify impact.*

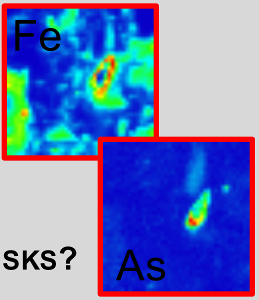
Project Overview:
Goals and Objectives

Monitoring Groundwater Impacts – What suite of measurements and/or tools can used in groundwater to detect CO_2 and/or brine leakage and to evaluate the impact?

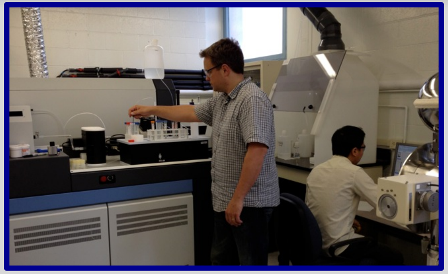
- Establish the utility of stable isotopes to track migration of a CO_2 plume
- Develop and apply metal isotope tracers for QMVA
- Develop novel materials and sensors for in-situ monitoring
- Test and validate the use of CO_2 monitoring devices under field conditions
- Understand natural variability in background
- Better understand physical-chemical-biological parameters impacting signals for geochemical tracers

Monitoring Groundwater Impacts

UNDERSTAND NATURAL BACKGROUND VARIABILITY

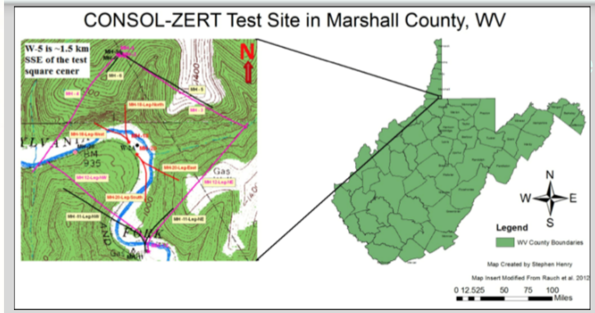


RISKS?

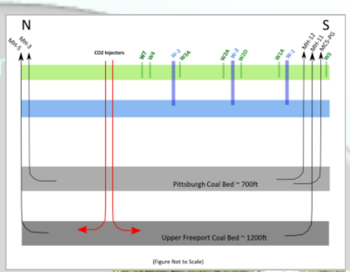


METHODS?

ESTABLISH THE UTILITY OF STABLE ISOTOPES TO TRACK MIGRATION OF A CO_2 PLUME



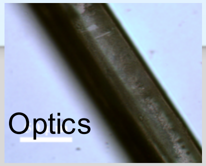
CONSOL-ZERT Test Site in Marshall County, WV



Thermal springs (Natural Analog)

EOR Field Site

Developing and demonstrating a suite of geochemically-based monitoring strategies for groundwater systems, and developing a statistical understanding of natural groundwater variability in CO_2 storage systems.

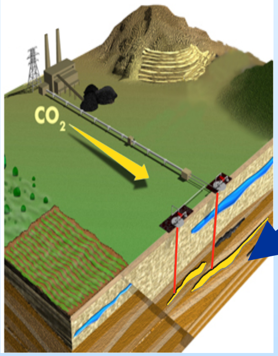


Fiber Optics

LIBS

Continuous CO2 Monitoring Devices

TEST AND VALIDATE THE USE OF CO_2 MONITORING DEVICES UNDER FIELD CONDITIONS



Migration into Shallow Aquifers

Migration into other Deep Formations

VALIDATE/ENSURE 99% STORAGE PERMANENCE

Progress to Date on Key Technical Issues

- Issue #1 – Determining what natural geochemical signals can be used to monitor changes in groundwater chemistry
  - Natural samples are complex, thus interferences and contamination are common issues
    - Stable isotopes have been shown to be effective – having robust background measurements of groundwater and injected substrate are key
    - Developed protocols for sample preparation and analysis of metal isotopes on samples with complex matrices: Sr and recently Li
  - Lab measurements can be time intensive, so some in-situ methods are also being explored:
    - Volumetric expansion and NDIR for in-situ field CO_2 measurements
    - Fiber optic sensors for CO_2 and/or proxies (e.g. pH)
    - In-situ LIBS analysis for changes in water chemistry
- Issue #2 – Deconvoluting interferences and determining sensitivities of these techniques

Stable Isotope: CBM Site validation

International Journal of Greenhouse Gas Control 41 (2015) 107–115

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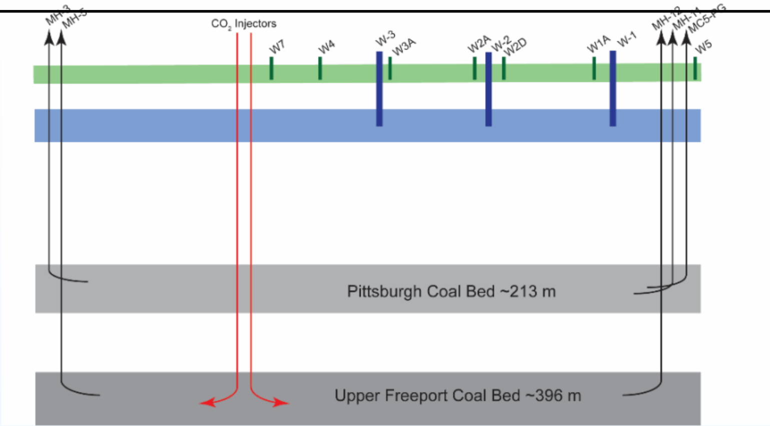
journal homepage: www.elsevier.com/locate/ijggc

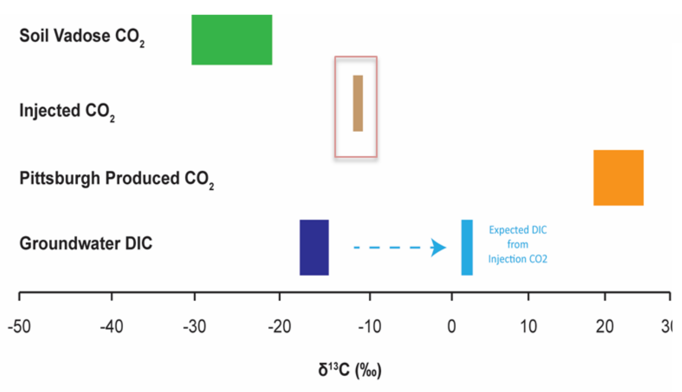
Using stable carbon isotopes to track potential leakage of carbon dioxide: Example from an enhanced coal bed methane recovery site in West Virginia, USA

Bethany Meier, Shikha Sharma*

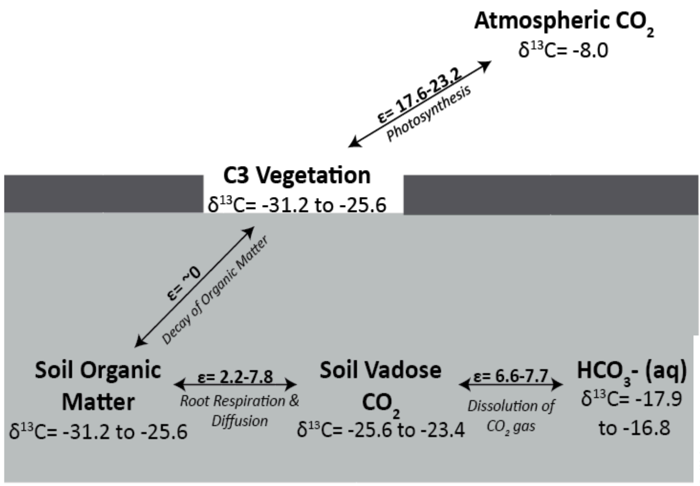
Department of Geology & Geography, West Virginia University, Morgantown, WV 26506, United States

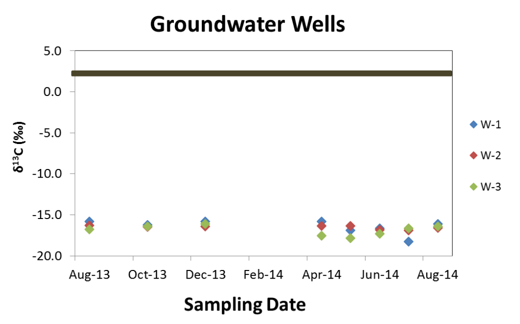


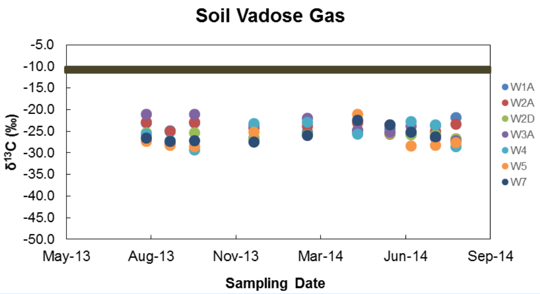
Schematic cross sectional view across A-A'



$\delta^{13}C_{CO2}$ values of the distinct isotopic end members at study site







Schematic of expected isotope fractionation processes

PIs – Hakala, Sharma

Similar study is in progress at an EOR site in TX

Plans for Remaining Technical Issues – How?

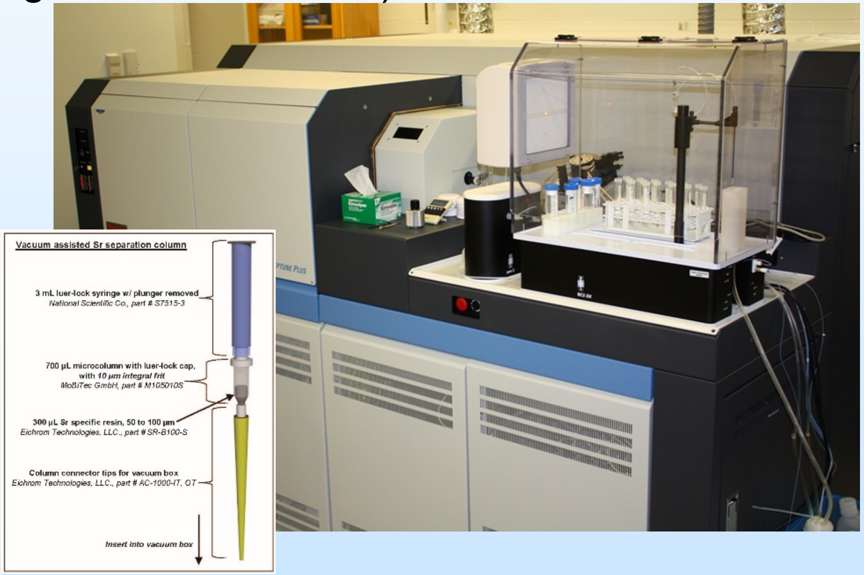
1. Natural Geochemical Tracers in Groundwater
   - develop and demonstrate a protocol for the use of a combination of natural geochemical tracers (e.g., isotopic, chemistry, trace elements, etc.) to monitor groundwater systems
   - Utilize NETL's MC-ICP-MS system for metal isotopes (with Pitt)
2. Assessment of Continuous CO_2 Monitoring Devices
   - understand the response and limitations of CO_2 monitoring devices (volumetric methods and direct measurement via NDIR) relative to CO_2 detection , including in the context of potential interference by other constituents (e.g. H_2S).
3. Development and Assessment of LIBS for In-situ Measurement of CO_2 Impacts in Groundwater
   - Use LIBS as a tool to monitor chemical signals in groundwater (in-situ) that reflect potential impacts to groundwater resulting from the introduction of CO_2 and/or brine.
4. Development and Assessment of Novel Fiber-Optics Technologies for Downhole Measurement of Potential Groundwater Impacts
   - develop and demonstrate robust fiber-optic based materials & tool(s) capable of sensing (at elevated P & T) the introduction of CO_2 and/or brine into overlying formations or groundwater systems

Groundwater Monitoring:

Metal Isotope Tracers

NETL ORD - Application to Complex Field Samples

- Metal isotope systems: track fluid-rock interaction, fluid origin, fate & transport. Use distinct isotope end-members to trace movement of plume in injected formation & to monitor leakage into overlying formations. Examples:
  - Mineral-fluid exchange (e.g., $^{87}Sr/^{86}Sr$, $^{7}Li/^{6}Li$, $^{234}U/^{238}U$)
  - Subsurface redox conditions (e.g., $^{56}Fe/^{54}Fe$, $^{238}U/^{235}U$)
  - Origin and environmental tracking of brines (e.g., $^{87}Sr/^{86}Sr$, $^{7}Li/^{6}Li$)
- Isotopes available FY15 (MC-ICP-MS):
  - **$^{87}Sr/^{86}Sr$** (24 samples/16 hours)
  - **$^{7}Li/^{6}Li$** (16 samples/24 hours)
  - **$^{234}U/^{238}U$** and **$^{235}U/^{238}U$** (24 samples/48 hrs)
- Type of samples: water & rock
  - Field sampling: filtered and acidified samples
  - Water surface waters or monitoring wells
  - Transport & Analyze in lab
    - Separations from matrix (NETL ORD methods)
    - Run using MC-ICP-MS



NETL's Thermo Scientific NEPTUNE PLUS MC-ICP-MS at University of Pittsburgh, Dept. of Geology & Planetary Science

PIs – Hakala, Phan, Stewart

Metal Isotopes: Methodology

Li isotope separation procedure:

Pack 2.0 mL AG50W-X8 (200-400 mesh) resin in a Poly-Prep column

↓

Wash with 10 mL 2% HNO_3, and then 10 mL 6N HCl

↓

Condition with 10 mL 1.50 N HNO_3:70% CH_3OH

↓

Wash with 10 mL 18.2 MΩ.cm water

↓

Condition with 5 mL 1.50 N HNO_3:70% CH_3OH. Collect for pre-column check for Li

↓

Load 0.5 mL sample in 1.0 N HNO_3, add drop wise 0.5 mL 1.50 N HNO_3:70% CH_3OH to "push" down sample. Discard

↓

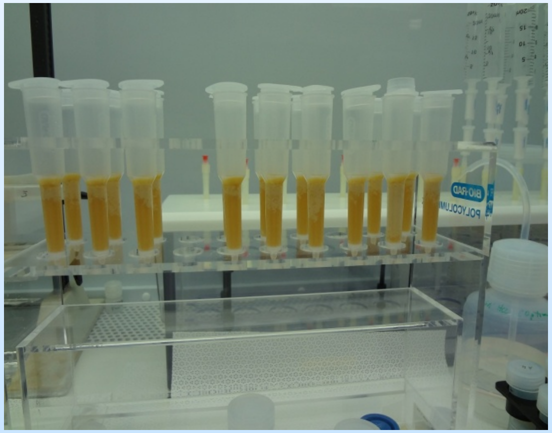
Collect Li fraction with 18.7 mL 1.50 N HNO_3:70% CH_3OH. Dry down. Redissolve in 2% HNO_3 prior to isotopic measurement

↓

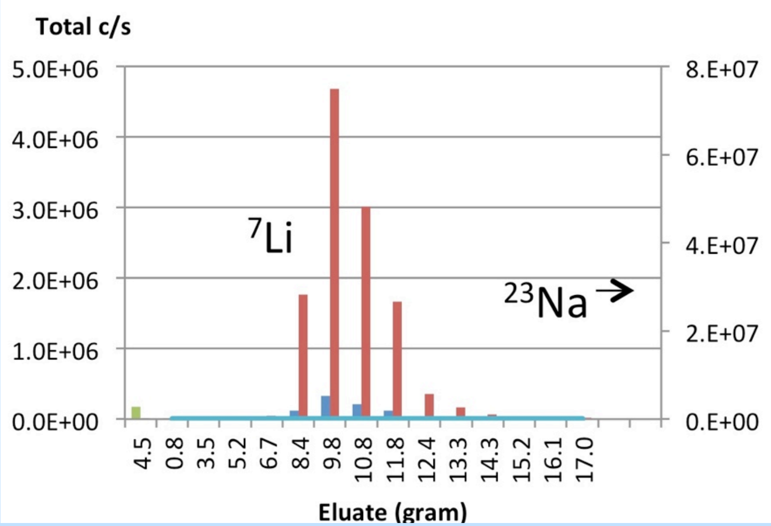
Pass 2 mL 1.50 N HNO_3:70% CH_3OH. Collect for post-column check

Robust separation procedures are fully developed for Sr and Li isotopes

- Li separation for $^7Li/^6Li$
- Disposable cation columns – low blank, high yields
- Effective separation from sample matrix for a variety of sample matrices : brines, surface water, and sedimentary rocks.
- 16-20 samples/8 hrs

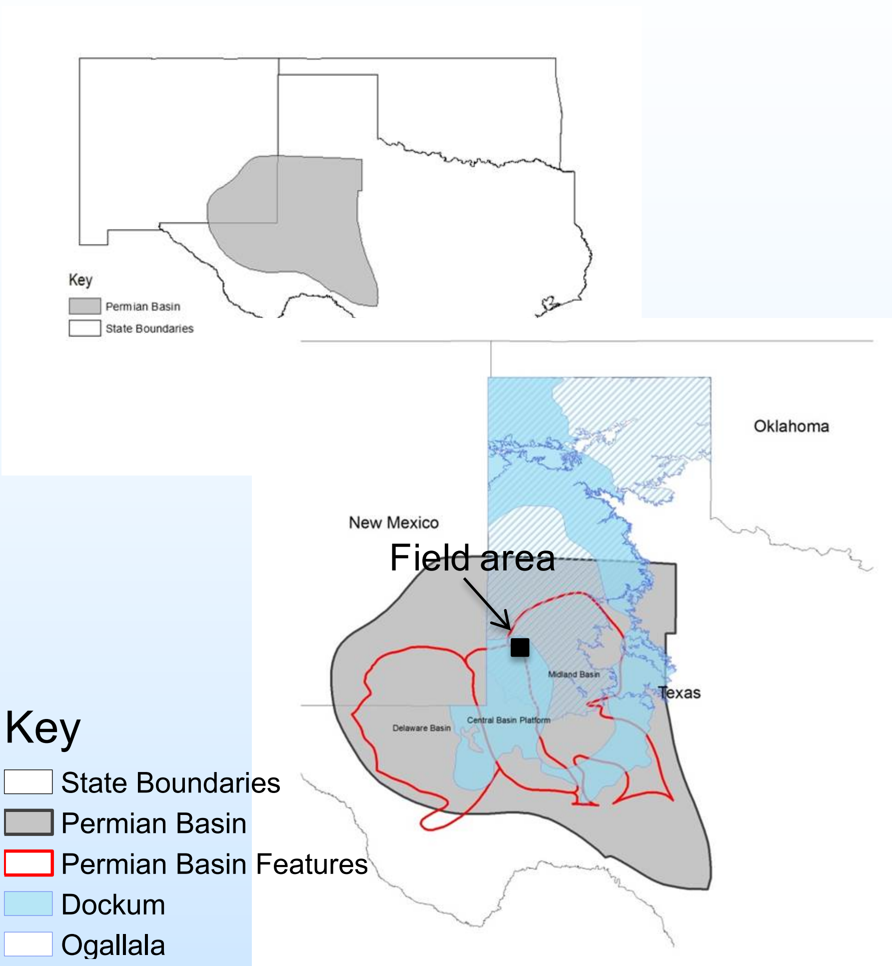


Li isotope separation setup (Phan et al., in prep)



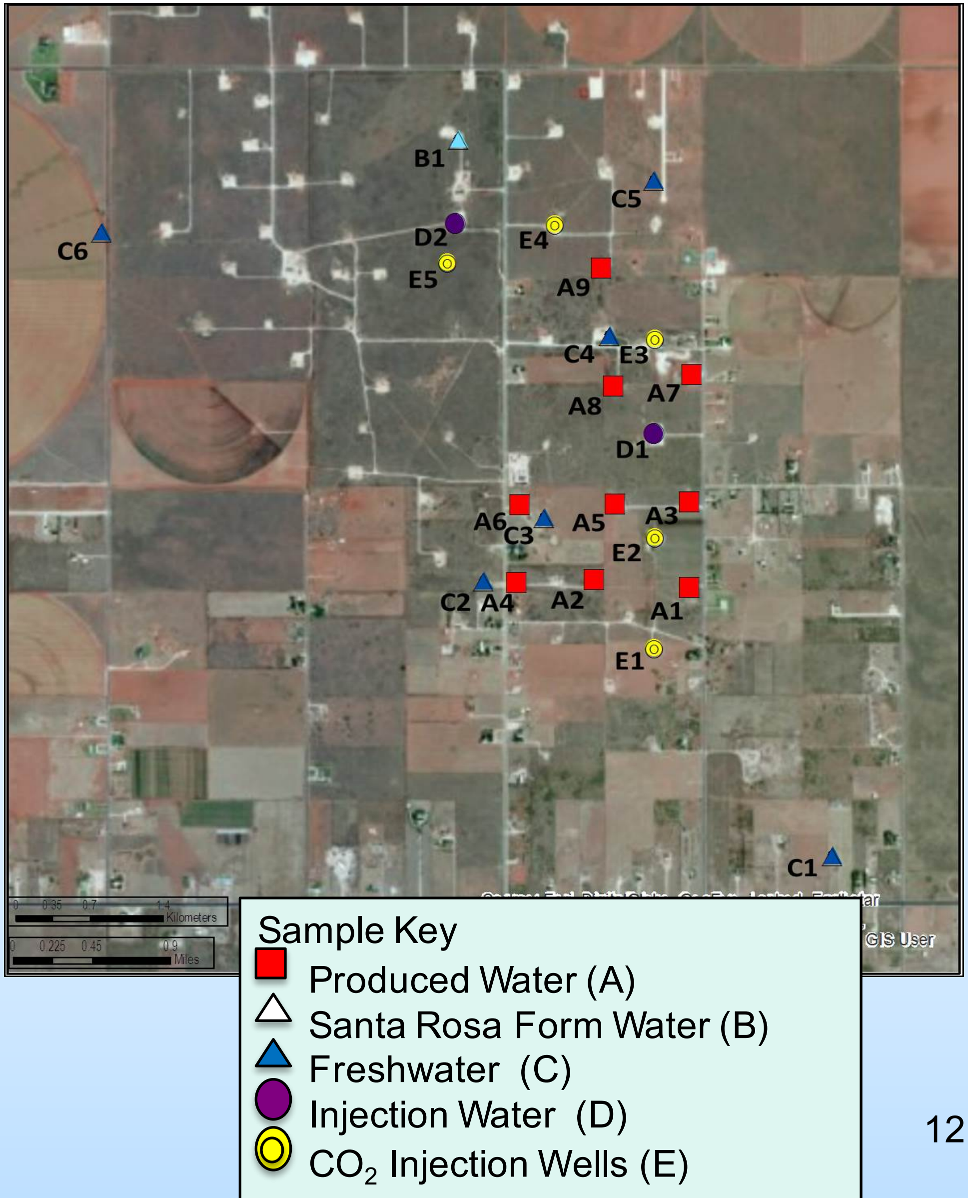
Metal Isotopes: In Practice

EOR Site – East Seminole, TX



Key

- ☐ State Boundaries
- ▨ Permian Basin
- 🟥 Permian Basin Features
- 🟦 Dockum
- ☐ Ogallala



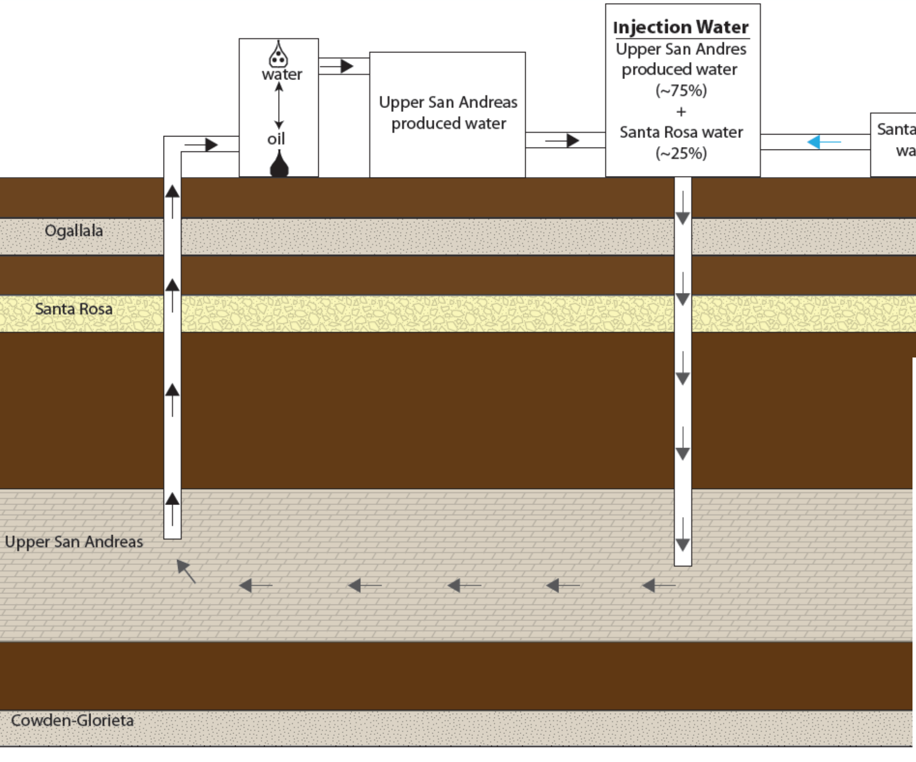
Sample Key

- 🟥 Produced Water (A)
- △ Santa Rosa Form Water (B)
- ▲ Freshwater (C)
- ● Injection Water (D)
- ◎ CO_2 Injection Wells (E)

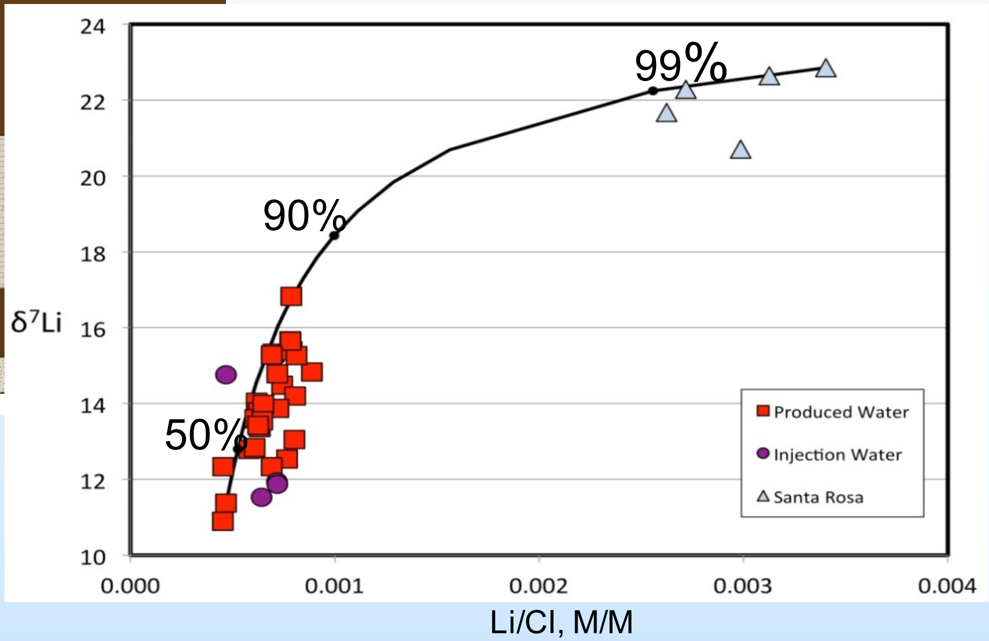
From Pfister et al. (2014)

Metal Isotopes: In Practice

Li Isotope Preliminary Results – EOR Site (TX)



Mixing curve for Santa Rosa Formation waters mixed with produced water. The % values shown indicate the percent of Santa Rosa water in the mixture.



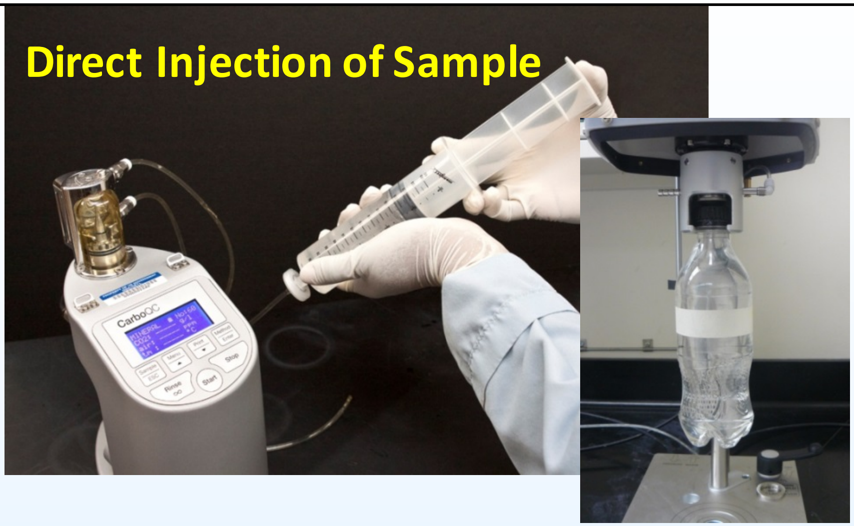
→ ***Sr and Li isotopes are effective geochemical tracers of potential brine migration from the subsurface upward to shallow groundwater system***

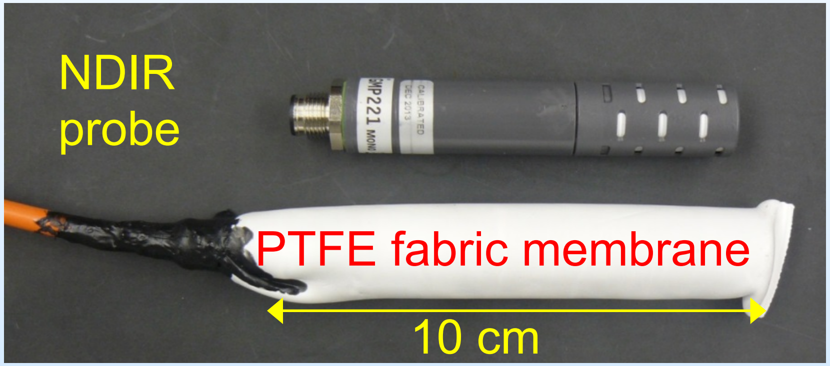
Groundwater Monitoring:
Direct CO_2 Measurements

TECHNIQUES

1. CarboQC (CQC)– measure CO_2 via volumetric expansion (FY15)
    - Grab sampling (i.e. not continuous)
    - Surface or shallow depth (~ 25 – 180 ft depth using a pump)
    - Measurements directly in the field or analysis of sealed field samples in the lab

2. NDIR – non-dispersive infrared real time analysis (FY 15)
    - Continuous measurement
    - Start at surface – shallow borehole
    - Ideally a dedicated monitoring well
    - Currently testing “hybrid” method



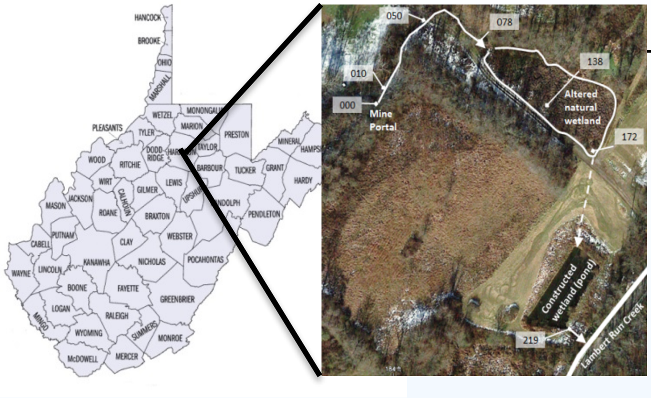


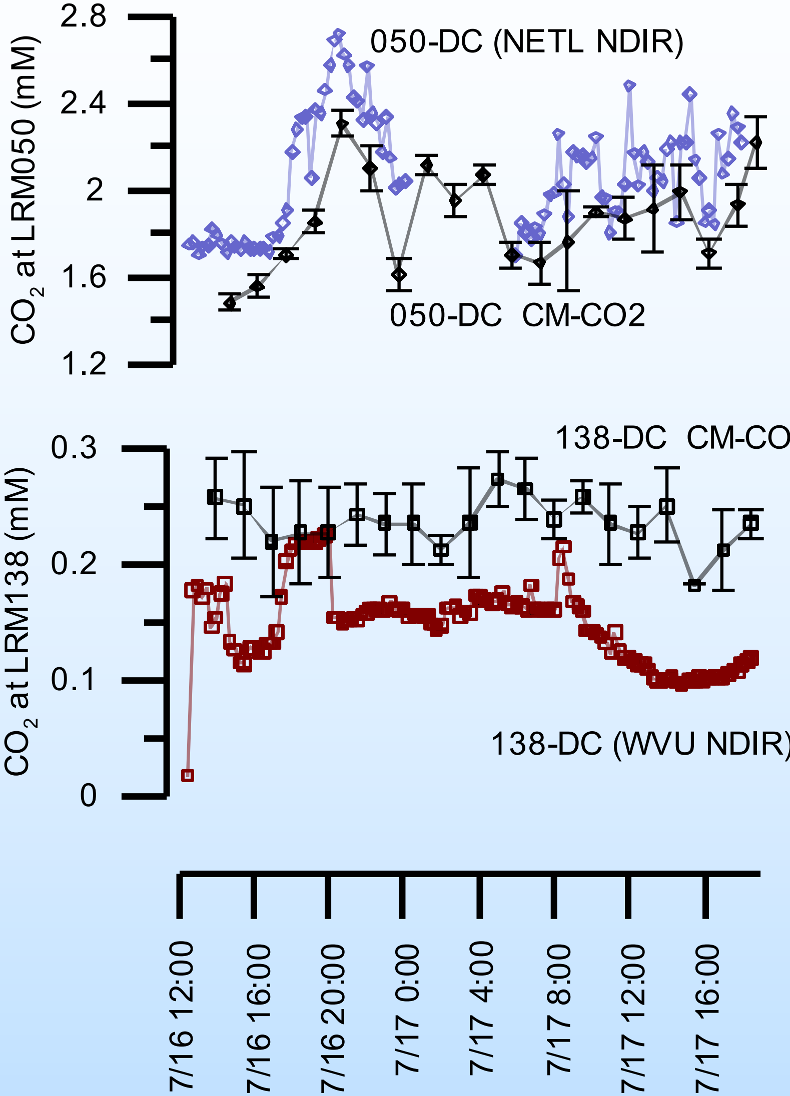
TURNER CO_2 SENSOR

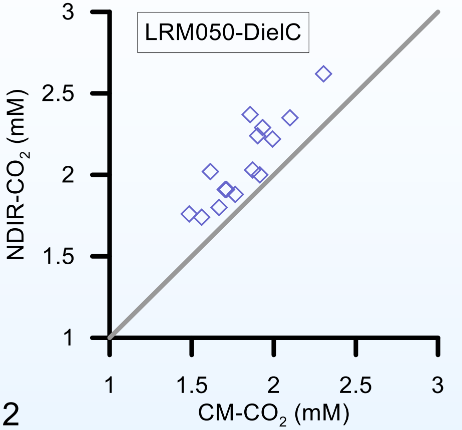
PIs – Edenborn, Vesper

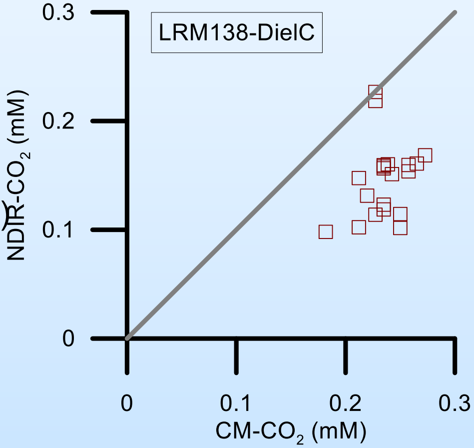
Direct Field CO_2 Measurements

Side-by-Side Comparison of Methods (NDIR vs CQC)





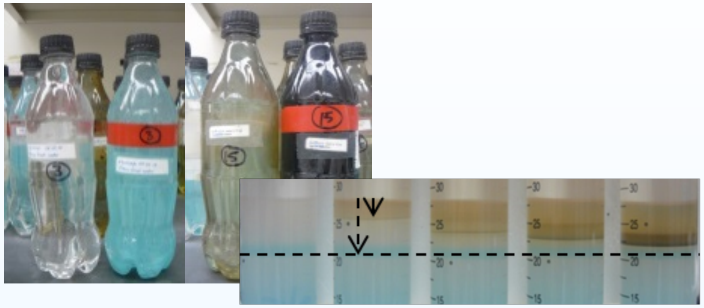


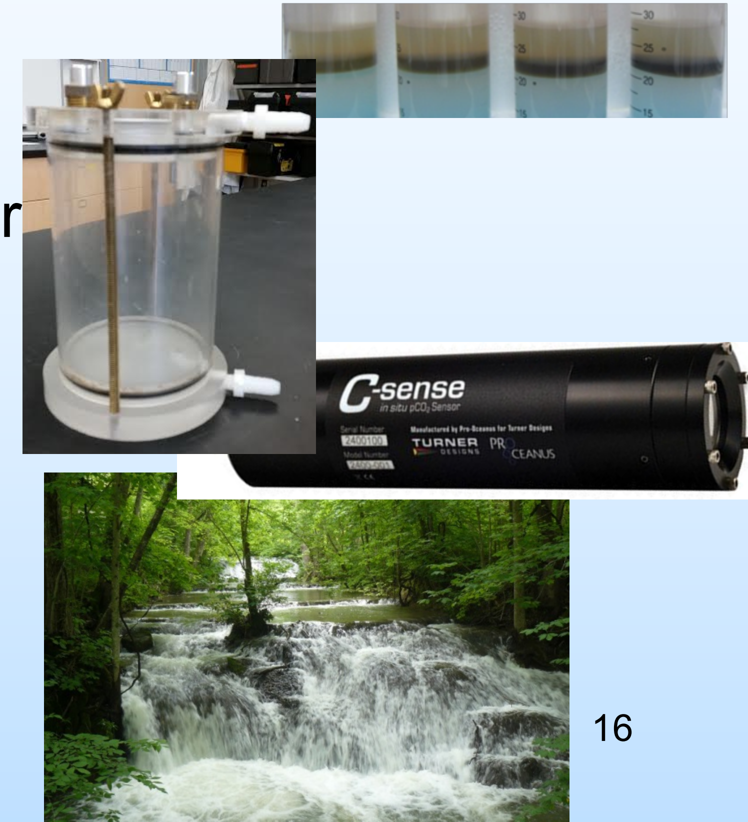


Direct Field CO_2 Measurements

Upcoming Field Work

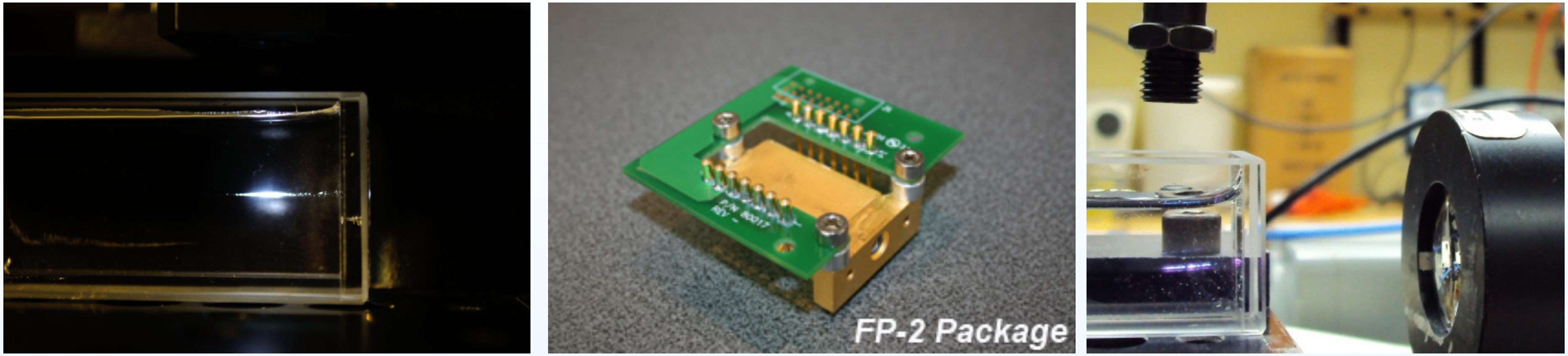
- Eliminate H_2S interferences with CO_2
  - Analysis of Texas EOR samples using lab methods (precipitation and/or sol-gel techniques). (CQC)
- Shakedown trips to high CO_2 sites to test newly-fabricated flow-through apparatus and the simultaneous measurement of CO_2 on pumped water using multiple methods
- Preliminary plans to test NDIR & CQC in groundwater monitoring wells at the Illinois Basin – Decatur Project (IBDP), a large-scale carbon capture and storage project. (~ Sept 2015)





Groundwater Monitoring: LIBS

Laser Induced Breakdown Spectroscopy

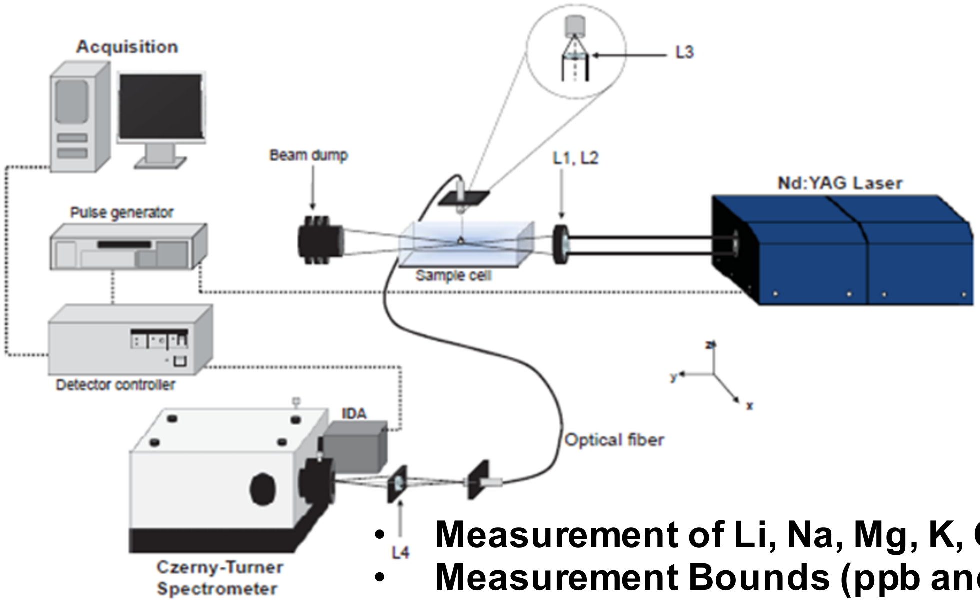


- ***How -*** Miniaturized laser technology produces sparks underwater, resulting atomic emission from sparks can be used to measure concentrations (ICP-MS). Probe can be placed down-hole for ***in-situ measurements*** of groundwater chemistry.
- ***What -*** Qualitative and Quantitative analysis of brine (Na, Li, Mg, Ca, K, Sr). Concentrations measured from the ppb and ppm range to the % range using synthetic brines in the lab. Measurements performed at elevated pressure (1800psi) in carbonated brine
- ***When -*** Mark 1 prototype development underway. Atomic interferences and enhancements currently being studied. Anticipated time frame for initial field testing – end FY 2016

PI – McIntyre, Carson

LIBS Sensor:

Lab testing in brine



- **Measurement of Li, Na, Mg, K, Ca, Sr**
- **Measurement Bounds (ppb and ppm)**
- **Matrix Effects (Enhancements with Na)**

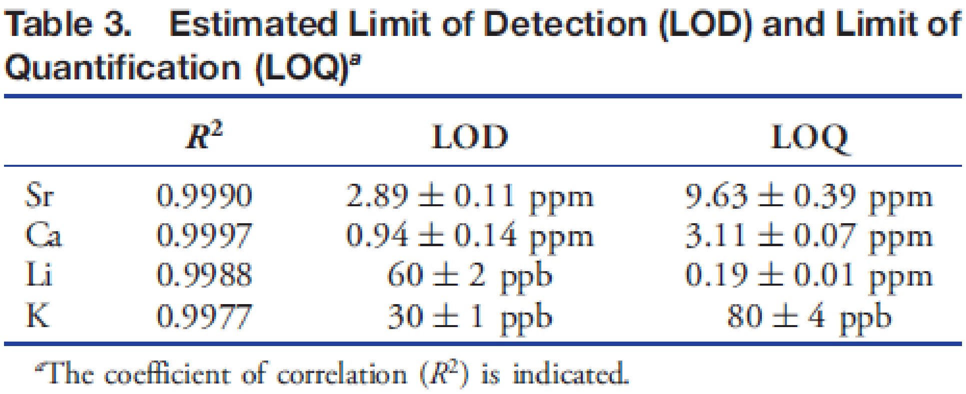
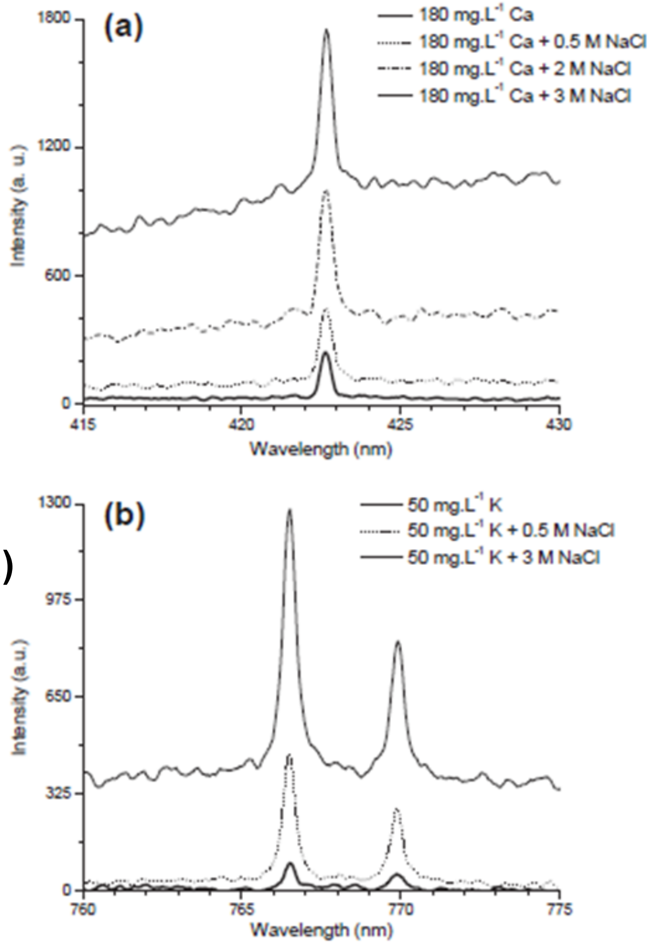


Table 3. Estimated Limit of Detection (LOD) and Limit of Quantification (LOQ)[a]

	R^2	LOD	LOQ
Sr	0.9990	2.89 ± 0.11 ppm	9.63 ± 0.39 ppm
Ca	0.9997	0.94 ± 0.14 ppm	3.11 ± 0.07 ppm
Li	0.9988	60 ± 2 ppb	0.19 ± 0.01 ppm
K	0.9977	30 ± 1 ppb	80 ± 4 ppb

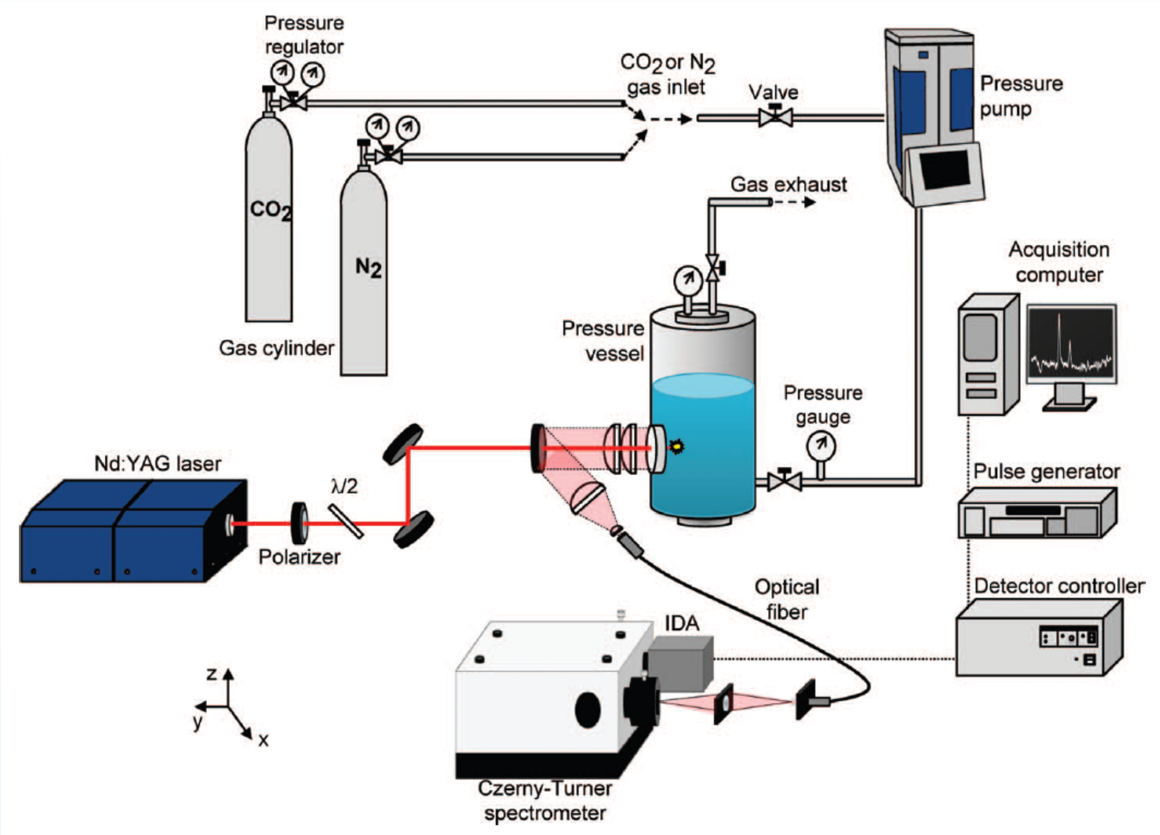
[a] The coefficient of correlation (R^2) is indicated.

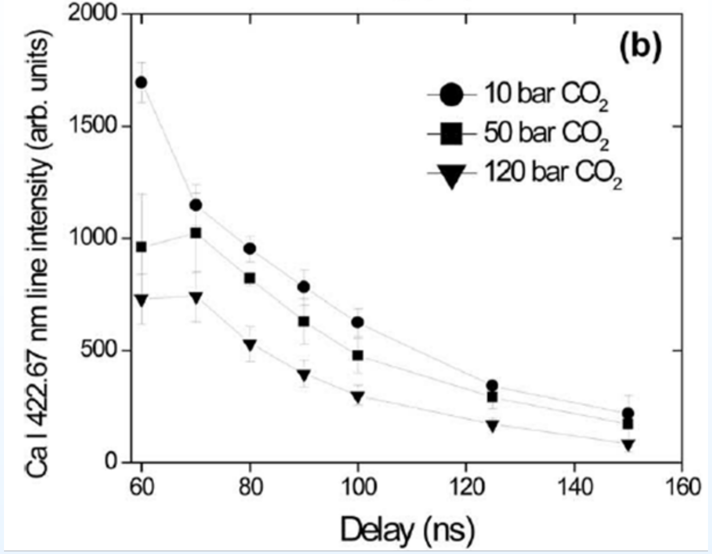


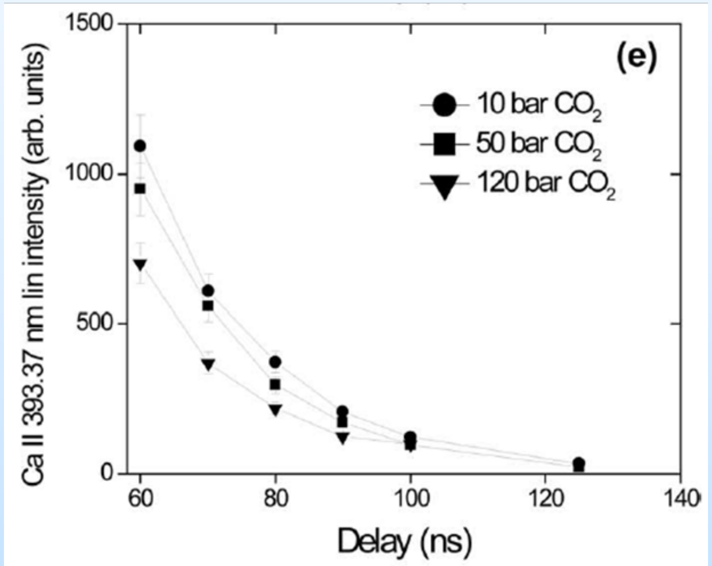
Goueguel et al (2015)

LIBS Sensor:

Lab testing at pressure







- Elevated temperature and pressure
- Investigate effect on atomic emission
- Investigate measurement capability

LIBS Sensor:

Miniaturization

Towards enabling downhole deployment of measurement optics

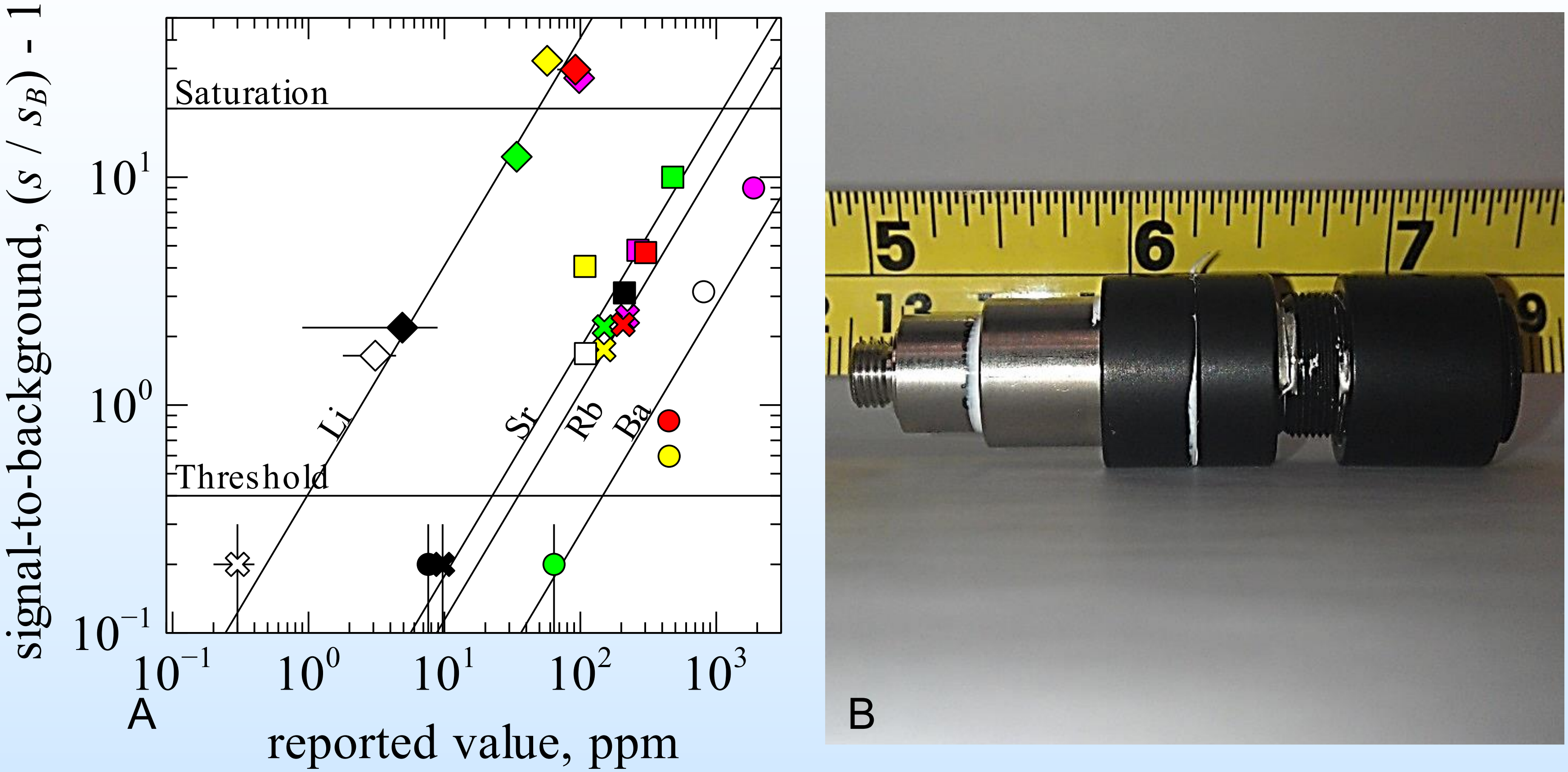


Figure 1: In A, the calibration curves for Li, Sr, Rb, and Ba are shown for a series of calibrated rock glasses using LIBS from a passively q-switched laser. In B, a photograph of the prototype downhole passively q-switched laser is shown.

1 Patent, 4 Pending

Groundwater Monitoring:

Fiber Optic Sensors

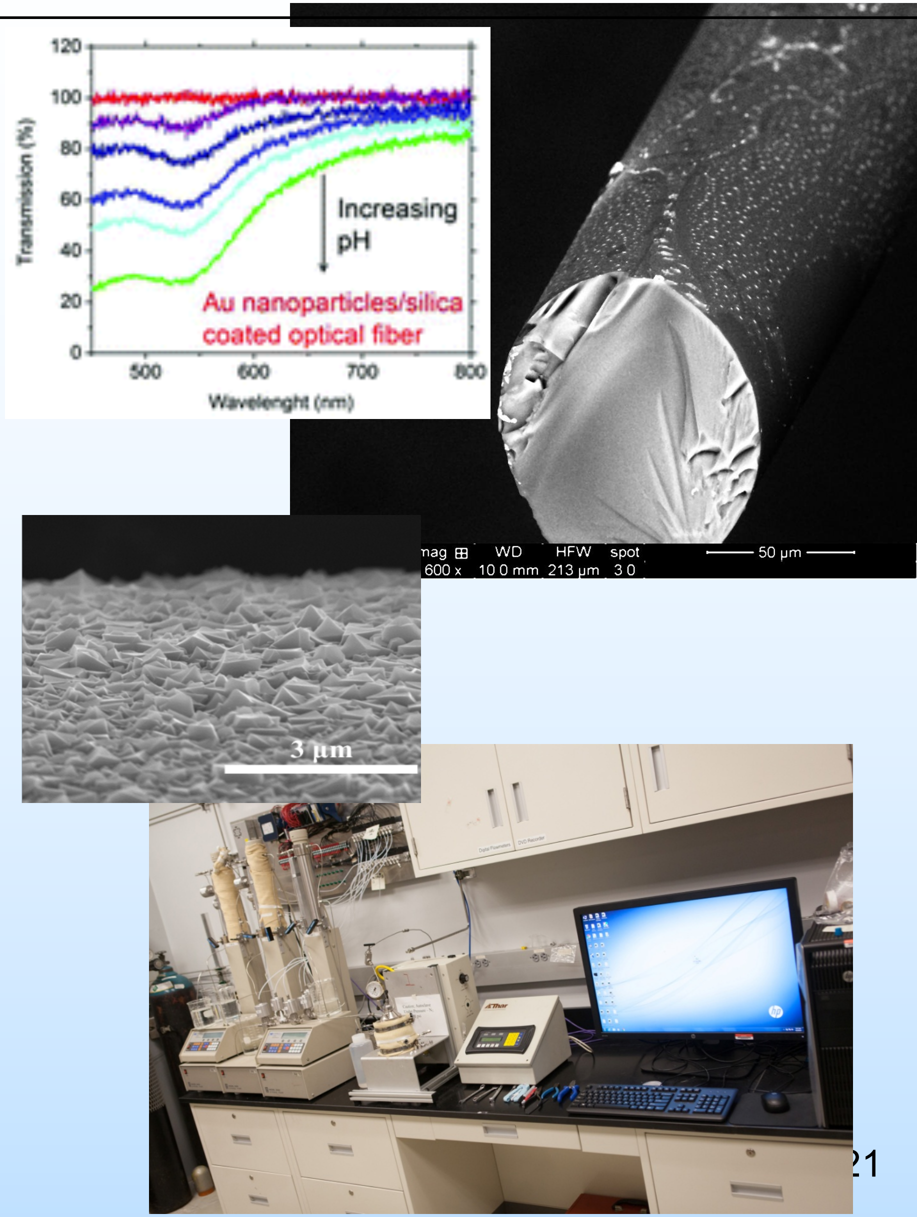
PI – Ohodnicki

GOAL: Extending the Capabilities of Fiber Optic Sensors for Chemical Sensing (e.g. CO_2 Monitoring) Through Integration with ***Functional Nanomaterials***

1) pH – controlling silica surface charge density using silica optical fibers coated with nanoparticles to optimize pH sensing under a range of T & P
2) CO_2 – directly measure using chemical specific MetalIorganic Framework (MOF) coatings on optical fibers

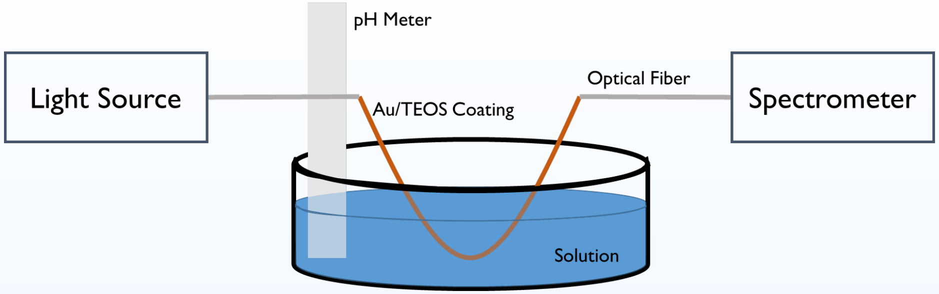
Time Line

- Investigate and characterize novel functional materials for potential use & future optimization – FY 2015 - 2016
- Couple with other sensor initiatives to adopt packaging and deployment strategies - FY2016 - 2017
- First sensor deployment (ideally in a water monitoring well) – FY2017



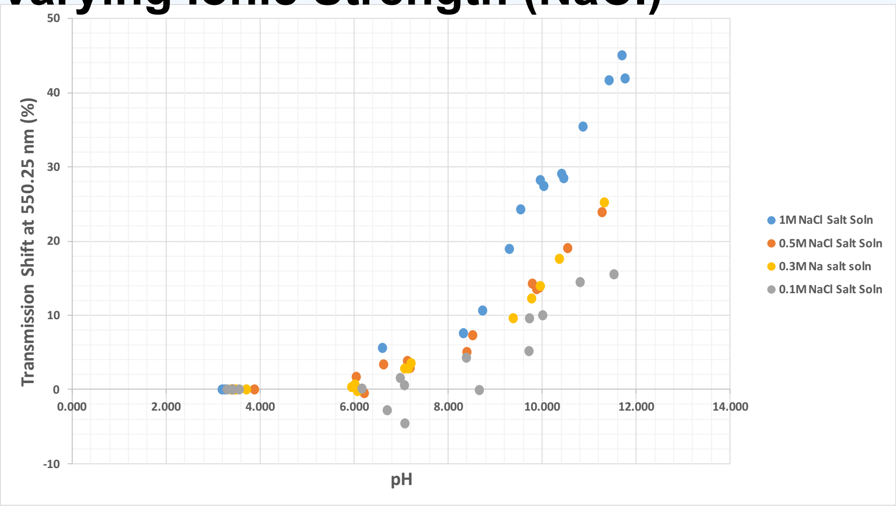
Novel FO Materials:

Understanding Transmission in Brines

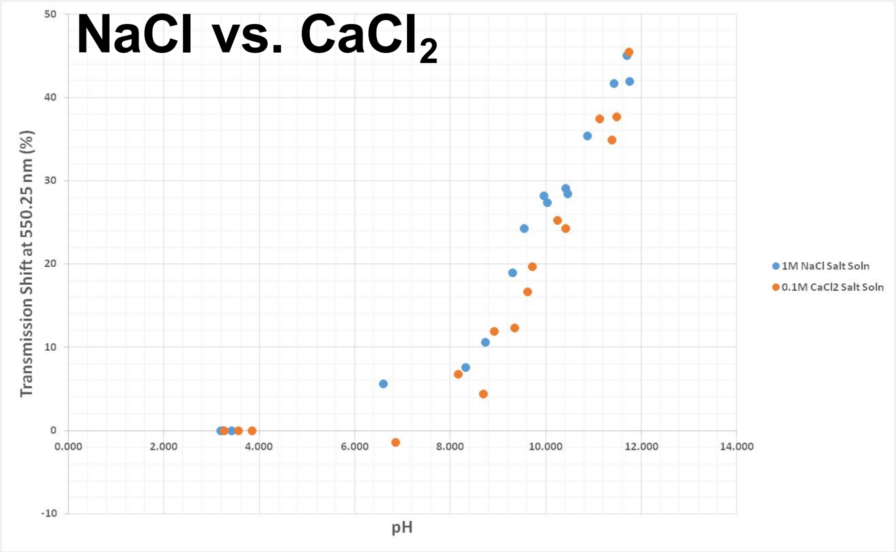


Is there a correlation between optical response and salt solutions for optical fibers coated with Au/TEOS sol solutions?

Varying Ionic Strength (NaCl)



NaCl vs. $CaCl_2$

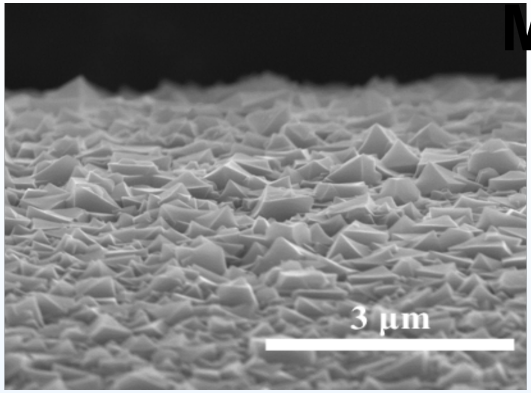


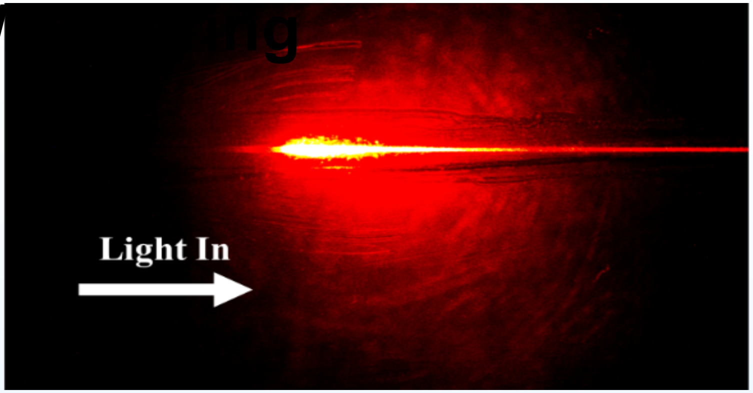
○ The porosity of the silica coating determines how salinity will affect optical response

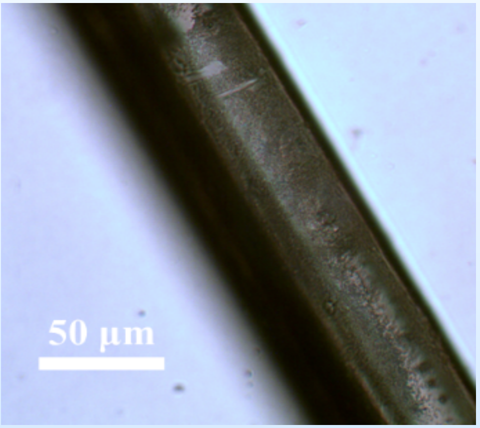
○ pH dependence of response is intimately linked with the surface charging behavior of the matrix phase so alternative oxide matrices will be investigated: TiO_2 and ZrO_2

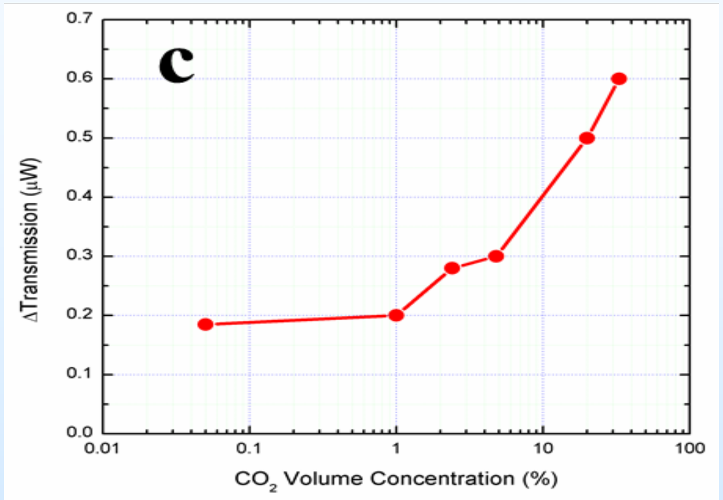
Fiber Optic Sensor

Metallorganic Framework (MOF) Based Sensors for CO_2 M ng









Chemical-Specific Interactions of Metallorganic Framework Based Materials Have Recently Been Utilized for Optical Fiber Based Sensing of CO_2 in collaboration with Oregon State U.

A provisional patent application on the concept has been filed.

Key Findings to Date (FY2015)

- Team has successfully utilized stable isotopes for monitoring a coal-bed CO_2 sequestration site (GW and Soil Gas)
- Team developed a methodology for high through-put Sr and Li isotope measurements in complex sample matrices using novel sample prep techniques and the MC-ICPMS
- Team has used novel in-situ CO_2 field measurement techniques at surface conditions and is developing methods for accurate in-situ downhole measurements
- Team has identified and eliminated interference (H_2S) with measurements of CO_2 at EOR sites via volumetric techniques (CarboQC).

Key Findings to Date (FY2015)

- LIBS lab measurements of atomic species for potential leak detection (ppb and ppm)
- Lab investigations of interferences and enhancements in ground water LIBS sensing
- FOS lab measurements successfully show CO_2 detection in harsh environments
- MOF show promise as novel sensing material
- Publication of various journal papers, conference papers, and Patents

Summary

- Lessons Learned: Real world field conditions may present a lot of natural interferences
  - Baseline measurements are key to the success of understanding mixing and method sensitivity
  - Multiple measurement techniques are key
  - Fundamental research helps de-convolute interferences
- Future Plans:
  - Further field testing of methods at CO_2 storage sites
    - Different Geologies (sandstone, carbonate, etc.)
    - Different activities (CO_2 only, EOR etc.)
  - Lab experimentation on novel sensors for eventual field testing (in-situ, real-time data collection)
  - Statistical analysis of lab data and forward modeling

Synergy Opportunities

- Compile data and results from different field sites throughout the country
  - Look for data trends between types of reservoir, storage conditions, etc.
- Deploy sensing tools and collection methods at different sites – collaboration & tool validation
- Use real world experiences to help inform “best practices” for monitoring

Appendix

Organization Chart

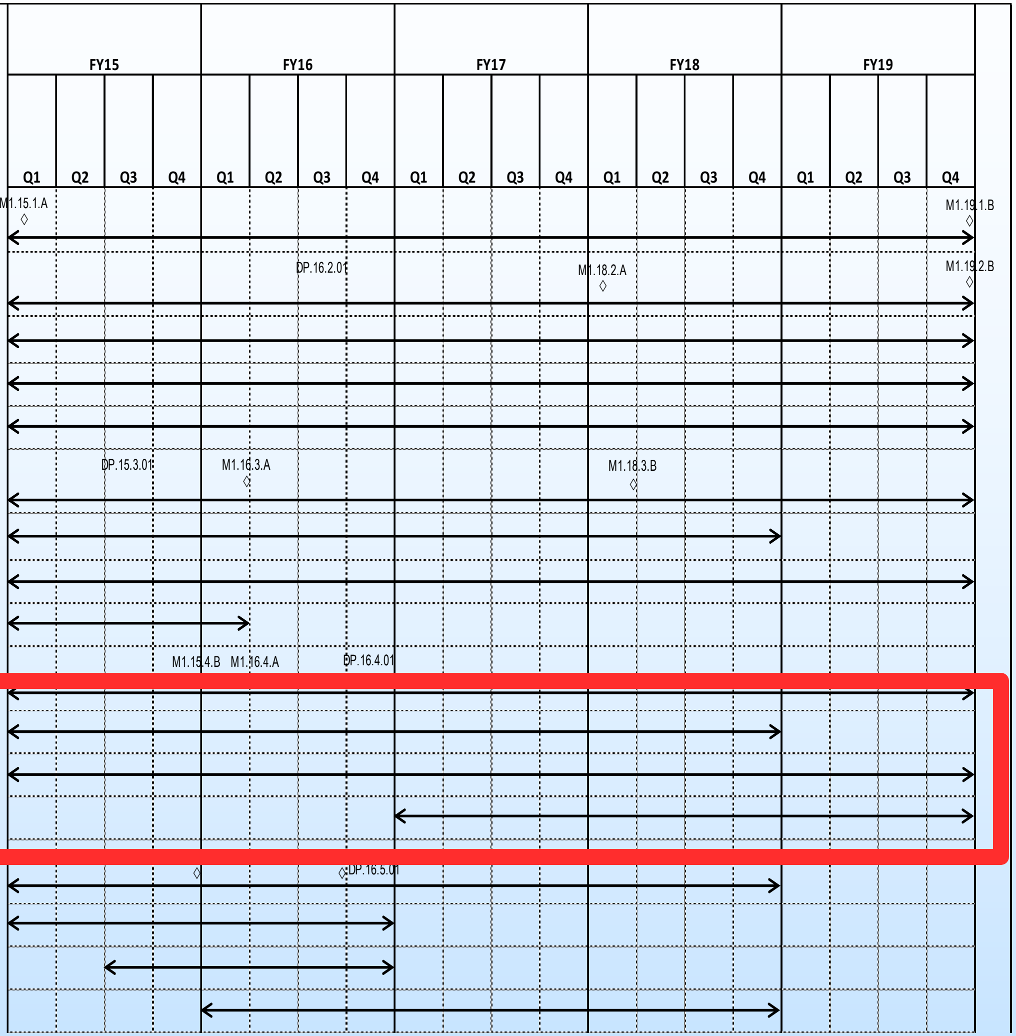
4.1.1	Natural Geochemical Tracers in Groundwater	To develop and demonstrate a protocol for the use of a combination of natural geochemical tracers (e.g., isotopic, trace elements, etc.) to monitor groundwater systems.	Hakala, Hedges, Phan, Stuckman, Bank
4.1.2	Assessment of Continuous CO2 Monitoring Devices	To understand the response and limitations of (commercially available) continuous CO2 monitoring devices relative to CO2 detection , including in the context of potential interference by other constituents (e.g. H2S).	Edenborn, Vesper (WVU) , Lopano
4.1.3	Development and Assessment of LIBS for Measurement of CO2 Impacts in Groundwater	To develop and demonstrate LIBS as a tool to monitor chemical signals to groundwater that reflect potential impacts to groundwater resulting from the introduction of CO2 and/or brine.	McIntyre, Jain, Carson, Goueguel, Sanghapi
4.1.4	Development and Assessment of Fiber-Optics Technologies for Downhole Measurement of Potential Groundwater Impacts	To develop and demonstrate fiber-optic based tool(s) to monitor the introduction of CO2 and/or brine into groundwater systems either by direct measurement of CO2 or by other geochemical indicators such as pH.	Ohodnicki, Brown

Organization Chart (cont'd)

4.2.1	Assess impacts: natural groundwater variability	Document baseline variability for key monitoring signals in groundwater for aquifers prior to and during CO2 injection and to document baselines in potential source terms from the CO2 reservoir.	Hakala, Hedges, Diehl, Stanko, Paukert, Phan, Bank
4.3.1	Experimental studies on (bio)geochemical behavior of aquifers in response to the introduction of CO2 and/or brine	This activity is focused on experimental studies on samples from a variety of aquifer classes to identify expected (bio)geochemical behavior of aquifers in response to the introduction of CO2 and/or brine, focusing on how the responses change based on aquifer class; how they change over time.	Lopano, Gulliver, Bank, Phan

Gantt Chart

	Project Dates For each Task, Subtask, Sub-subtask of your WBS	
FY15 Carbon Storage (Project Period: 10/01/14 – 09/30/19)	**Start** Reflects the date the work is scheduled to begin	**Finish** Reflects the date the work is scheduled for completion
1. Project Management and Planning	**10/1/2014**	**9/30/2019**
2. Reservoir and Seal Performance	**10/1/2014**	**9/30/2019**
2.1 Understanding Relative Permeability, Residual Saturation, and Porosity in Reservoirs to Reduce Uncertainty in Long-Term CO_2 Storage and Efficiency	10/1/2014	9/30/2019
2.2 Improve Characterization of Physical Changes in Reservoir and Seal Rock due to CO_2	10/1/2014	9/30/2019
2.3 Determine Impact of Microbial Induced Changes on Reservoir Performance	10/1/2014	9/30/2019
3. Shales as Seals and Unconventional Reservoirs	**10/1/2014**	**9/30/2019**
3.1 Understanding Permeability, Residual Saturation, and Porosity in Shale to Reduce Uncertainty in Long-Term CO_2 Storage and Efficiency	10/1/2014	9/30/2018
3.2 Improve Characterization of Physical Changes in Shale with Exposure to CO_2	10/1/2014	9/30/2019
3.3 Field Activity to Obtain, Log, Ship, and Store Shale Core from South Dakota	10/1/2014	12/31/2015
4. Monitoring Groundwater Impacts	**10/1/2014**	**9/30/2019**
4.1 Develop and Demonstrate Monitoring Tools and Protocols for Groundwater Systems	10/1/2014	9/28/2018
4.2 Assess Impacts: Natural Groundwater Variability	10/1/2014	9/30/2019
4.3 Fundamental Controls on Groundwater Composition	10/1/2016	9/30/2019
5. Resource Assessments	**10/1/2014**	**9/30/2018**
5.1 Develop Defensible Department of Energy Methodology for Regional Assessment	10/1/2014	9/30/2016
5.2 Expand Methodology to Include Stochastic Approach for Key Parameters	4/1/2015	9/30/2016
5.3 Expand Methodology to Include Geospatially Variable Key Parameters	10/1/2015	9/30/2018



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