Zero Emissions Research and Technology (ZERT) II – Investigating the Fundamental Scientific Issues Affecting the Long-term Geologic Storage of Carbon Dioxide
Project Number DE-FE0000397

Lee H Spangler
Energy Research Institute
Montana State University

• U.S. Department of Energy
• National Energy Technology Laboratory
• Carbon Storage R&D Project Review Meeting
• Developing the Technologies and Infrastructure for CCS
• August 12-14, 2014
Presentation Outline

• Laboratory studies to understand subsurface CO$_2$ behavior
• Mitigation method development bio-sealing of shales
• Fiber sensor development
  – Soil CO$_2$ sensor
  – Distributed borehole seismic sensor
• Coal bed methane enhancement / mitigation
• Analog studies to inform risk analysis
Benefit to the Program

Program goals being addressed.

- Develop technologies that will support industries’ ability to predict CO₂ storage capacity in geologic formations to within ±30 percent.
- Develop technologies to demonstrate that 99 percent of injected CO₂ remains in the injection zones.
- Conduct field tests through 2030 to support the development of BPMs for site selection, characterization, site operations, and closure practices.

Project benefits statement.

ZERT II supports Storage Program goals by 1) developing computational tools for simulating CO₂ injection, storage and trapping, 2) performing basic geoscience experiments to address relationships between properties such as wetting, relative permeability, saturation, and capillary pressure that will improve understanding of CO₂ behavior in the reservoir and help with model parameterization 3) investigating analogs to understand risks to storage security 4) conducting field experiments to test near surface monitoring technologies and 5) developing novel bio-controlled leakage mitigation technology.
Project Overview: Goals and Objectives

Fundamental Geosciences
- Objective: Develop methods to perform in situ measurements during core flood and flow experiments

Biofilms, Biomineralization and Biogenic Processes
- Objective: Perform a comprehensive evaluation of techniques for current and novel CO₂ sequestration concepts associated with microbial biofilms.
- Objective: Evaluate the potential for coal-bed mediated CO2 sequestration and enhanced methane production.

Natural Analogs of Escape Mechanisms
- Objective: Characterize the physical, mineralogical, and geochemical characteristics of outcrops of hydrothermal plume related rocks to determine their usefulness as natural analogs of breached and healed caprocks for carbon sequestration.

Optical Detection for Carbon Sequestration Site Monitoring
- Objective: Demonstrate the feasibility of creating an in-line fiber optic sensor for CO₂ that utilizes sections of photonic bandgap (PBG) fibers interspersed with sections of single mode optical fiber.
- Objective: Develop a low cost multispectral imager to detect CO₂-induced plant stress

Validation of Near-surface CO₂ Detection Techniques and Transport Models
- Objective: Determine, via field experimentation, the efficacy and detection limits for existing and emerging near-surface CO₂ detection technologies.
Technical Status

• Focus the remaining slides, logically walking through the project. Tell the story of your project and highlight the key points as described in the Presentation Guidelines. Organize the remainder of the talk as though it was being given at a technical conference.

• When providing graphs or a table of results from testing or systems analyses, also indicate the baseline or targets that need to be met in order to achieve the project and program goals.
Capabilities for *in-situ* MRI studies of CO$_2$/brine in rock cores at Montana State University

Sarah L. Codd, Joseph D. Seymour, Joshua M. Bray, and Cody A. Prather

Magnetic Resonance Microscopy (MRM) lab

June 22, 2014
Temco custom FCH Core Holder

Core Holder Schematic

A. Core-challenge fluid (outlet)
B. Recirculating fluid (outlet)
C. Recirculating fluid (inlet)
D. Core-challenge fluid (inlet)
E. Thermocouple
F. PEEK composite sheath

Max. pressure: 5000 psi
Max. temperature: 150°C

Core holder
Flow loop mock-up
ISCO 500D syringe pumps

H₂O/CO₂
Fluorinert
Previous strategy: 3D spin-echo imaging

MRI Sequence Comparison

Spin-echo imaging (SEI)
- High resolution
- Slower, repetition-time-limited acquisition
- High power demands
- Gradient noise/vibration

Zero echo time imaging (ZTE)
- Bandwidth limited (lower resolution)
- Rapid, steady-state k-space acquisition
- Low power demands
- “Silent mode”, low vibration

Total scan time: 30 hours
Image resolution: 270 × 270 × 1500 µm

SEI

Total scan time: 53 sec
Image resolution: (781 µm)³
ZTE imaging demonstration: H$_2$O displacement by injected CO$_2$ gas in Berea core

1. Initially dry core
2. Mount in core holder/RF coil
3. Acquire 3D images with ZTE
4. Water distribution in 1D
   a) Dry core
   b) Inject H$_2$O (full saturation)
   c) Inject CO$_2$ (H$_2$O displacement)
Rock core images – Background signal subtraction

Sources of $^1$H background signal:
- Plastics of the RF coil currently having them retrofitted!
- AFLAS overburden sleeve have a FEP heat-shrink sleeve with no signal
Rock core images – CO$_2$ injection test

- 1 sagittal plane (lengthwise); 3 axial planes: top, middle, bottom
- FOV: $100 \times 100 \times 100$ mm$^3$
- Resolution: 781 µm
- Time step: 3 min. 30 sec. (53 second scan time)

Fully-saturated core

CO$_2$ pulse in transit

Signal attenuation when water is displaced
Rock core images – CO$_2$ injection test

- 1-D projection of signal intensity
- Time step is 3 min. 30 sec.
Acidic solutions

Bright spots in the overburden sleeve?...

Late-time point

Acid damage in the headspace!

Align distribution plugs to avoid dead volume.

Temco is sending replacements free of charge.

Switching between liquid/CO2 in pump
Extra ISCO 500D pump

Potential for long-duration studies
Capabilities summary

*The Temco MRI-compatible core holder enables us to:*

1. Observe water in real, porous rock cores
2. Inject liquids, gases, or supercritical fluids (brine, CO$_2$, etc.)
3. Acquire 3D images in 50 sec. with ~1 mm resolution
4. Observe transport and structural changes *in situ*
Microbially Induced Carbonate Precipitation (MICP)

**Cunningham, Gerlach**

+ pH and alkalinity (increase in OH⁻ and HCO₃⁻) increase SATURATION STATE OF CALCITE

\[
\begin{align*}
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} &\rightarrow \text{NH}_2\text{COOH} + \text{NH}_3 \\
\text{NH}_2\text{COOH} + \text{H}_2\text{O} &\rightarrow \text{NH}_3 + \text{H}_2\text{CO}_3 \\
\text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} &\rightarrow 2\text{NH}_3 + \text{H}_2\text{CO}_3 \quad \text{(Urea hydrolysis)}
\end{align*}
\]

\[
\begin{align*}
2\text{NH}_3 + 2\text{H}_2\text{O} &\leftrightarrow 2\text{NH}_4^+ + 2\text{OH}^- \quad \text{(pH increase)}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{CO}_3 + 2\text{OH}^- &\leftrightarrow \text{HCO}_3^- + \text{H}_2\text{O} + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + 2\text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
\text{CO}_3^{2-} + \text{Ca}^{2+} &\leftrightarrow \text{CaCO}_3 \quad \text{(carbonate precipitation)}
\end{align*}
\]

**Model ureolytic organism: Sporosarcina pasteurii**

Ureolysis is only one possible way to manipulate the saturation state of carbonates

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Bio-sealants in Mont Terri
Conducted by Montana State University

Permeability reduction due to biomineralization in one-inch diameter Opalinus shale core drilled from original shale sample, July 18, 2013

Core locations on the Opalinus shale sample
X-Ray CT scans for two locations along the axis of core OP1-4

Before

Slice 1

Slice 2

After
Permeability Tests With & Without Propants

Split OP2-3 core and core wrapped in PTFE tape. Core length was 5.77 cm

OP2-4 Core showing proppant placement and wrapping pieces with PTFE tape.
Table 1  Initial Permeability values prior to biomineralization

<table>
<thead>
<tr>
<th>Core</th>
<th>Area (cm²)</th>
<th>Average Length (cm)</th>
<th>Flow Rate (ml/min)</th>
<th>Pressure drop (meters H₂O)</th>
<th>Calculated Permeability (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP2-3</td>
<td>5.43</td>
<td>5.77</td>
<td>10.0</td>
<td>7.3</td>
<td>249</td>
</tr>
<tr>
<td>OP2-4</td>
<td>5.43</td>
<td>4.01</td>
<td>40.0</td>
<td>2.2</td>
<td>2,420</td>
</tr>
</tbody>
</table>

Mont Terri Shale Permeability
OP2 Cores

Table 2  Permeability values following biomineralization

<table>
<thead>
<tr>
<th>Core</th>
<th>Flow Rate (ml/min)</th>
<th>Pressure drop (meters H₂O)</th>
<th>Final Permeability (mD)</th>
<th>Permeability Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP2-3</td>
<td>0.015</td>
<td>15.6</td>
<td>0.18</td>
<td>99.93%</td>
</tr>
<tr>
<td>OP2-4</td>
<td>0.03</td>
<td>19.5</td>
<td>0.20</td>
<td>99.99%</td>
</tr>
</tbody>
</table>
The inline fiber sensor uses a series of segmented photonic bandgap (PBG) fiber in series to form an inline fiber sensor array.

Each segment is addressed using time of flight of the laser pulse.

CO₂ diffuses into the PBG fiber to allow spectroscopic measurements of CO₂ concentration.

**Challenge:** PBG fiber is larger diameter than SMF and conventional splicing collapses hollow core.
Fiber Sensors

Schematic of the inline fiber sensor. Carbon dioxide measurements can be made in each of the photonic bandgap (PBG) fibers.

After each PBG fiber section, a gap allows a portion of the light to be reflected back to the detector while the remainder of the light couples into a SMF fiber. The gap spacing determines the reflectivity.

V-groove structures were designed and manufactured allowing precise and repeatable alignment of the PBG fiber and SMF fiber.

The transmitted light during a wavelength scan is shown as the red line. The light reflected from the second segment of the inline fiber sensor is shown as the blue line. Dividing these two signals would yield a transmission spectrum. The carbon dioxide absorption feature is seen in the reflected signal and can be used to monitor carbon dioxide concentrations.
A single section of the distributed fiber seismic sensing system schematic, the 400ns pulse is sent down the FGB line, the fiber stretcher will alter the path length between the two FBG’s which will change the amplitude of the 200ns interference signal created by the two overlapping reflected 400ns pulses. A fiber stretcher was used to mimic the effects of a seismic wave.

The fiber seismic sensor set up for laboratory testing. The ability to measure seismic events over a distributed fiber seismic sensor array has the potential to allow monitoring of the injected carbon dioxide plum.
Careful filtering of the signal is needed to achieve good signal to noise performance. An active filter was designed as shown in the upper schematic with the Bode plot showing the filter frequency response in the lower plot. The corner frequency can be changed while maintaining the 60 dB/decade falloff.

Fiber sensor signal as a function of time. The blue line for the plots on the left represent the unfiltered signal while the red line represents the filtered signal. The right hand plots utilizes a sliding window averaging. The strain sensitivity of the fiber sensor is measured to be 60 x 10^{-9} indicating this sensor can work for subsurface seismic monitoring.
CO₂

Lipids and Biofuels

Re-inject treated water with algal extracts

Algae/Microbes

CH₄ gas to pipeline

Recharge aquifer. Stimulate additional CH₄.

Aquifer / Coal seam
Algae enhanced CBM Microcosm experiments

Three sets of microcosm experiments have been run and are continuing at present. These microcosm experiments all involve the addition of algae extract as a stimulant to methane production from coal, compared to methane production from the same coal without algae addition. The description of each experiment is as follows.

**Experiment 1.** Coal from a surface mine in Decker, MT, inoculum from a USGS well in the Powder River Basin, synthetic CBM produced water (main ingredients magnesium, potassium, calcium, ammonium, (as chloride), sodium bicarbonate, experiment started 9/10/2010.

**Experiment 2.** Decker coal, same inoculum, Synthetic CBM water plus sulfate, started 5/4/2011,

**Experiment 3.** Decker coal, filtered CBM produced water from a USGS well, Same Inoculum. Started 4/5/2012
Lab Results: Biostimulation of methane production from coal

- Batch systems with native PRB microbes
- Increased methane with algae extract

![Graph showing methane concentration over time for different media treatments.]

Barnhart et al. in prep.
Coal from a surface mine in Decker, MT, Inoculum from a USGS well in the Powder River Basin, Water synthetic CBM produced water Started 9/10/2010
**Experiment 1**


**Graph:**

- **X-axis:** Media conditions (Media + Coal, Media + Yeast + Coal, Media + Algae Extract + Coal)
- **Y-axis:** Methane concentration (umols/10 mL culture)
- **Legend:**
  - Day 165
  - Day 1406

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### Experiment 1 Details

- **Media + Coal**
- **Media + Yeast + Coal**
- **Media + Algae Extract + Coal**

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**ZERT Zero Emissions Research and Technology**

**Montana State University**
Coal from a surface mine in Decker, MT, Inoculum from a USGS well in the Powder River Basin, Water synthetic CBM produced water + Sulfate
Coal from a surface mine in Decker, MT, **Inoculum** from a USGS well in the Powder River Basin, **Water** filtered CBM produced water from USGS well.
Fall 2013 drilling and sampling program in the Flowers-Goodale coal horizon near Birney MT. Coal samples were recovered along with samples of produced water from the coal seam.

Elliott Barnhart
Ph.D. Candidate, Microbiology
Center for Biofilm Engineering
USGS – Pathways student
Microbial inoculum samples were recovered from Flowers-Goodale coal in June 2014 using Diffusive Microbial Sampler (DMS)
### Large Number of Participants / Methods

**47 investigators**

**31 instruments / sensor arrays**

**5 univ. 6 DOE labs, 4 companies**

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Institution</th>
<th>Monitoring Technology</th>
<th>Number of Sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arthur Wells</td>
<td>National Energy Technology Laboratory</td>
<td>Atmospheric tracer plume measurements</td>
<td>1 tower (4m)</td>
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<tr>
<td>Rod Diehl</td>
<td></td>
<td>Bee hive monitoring for tracer with sorption tube and pollen trap</td>
<td>2 hives</td>
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<tr>
<td>Brian Straszar</td>
<td></td>
<td>Automated Soil CO₂ flux system</td>
<td>4 chambers</td>
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<td>William Pickles</td>
<td>University of California- Santa Cruz</td>
<td>Hand held hyperspectral measurements (plant health)</td>
<td>1 instrument</td>
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<tr>
<td>Eli Silver</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Erin Male</td>
<td></td>
<td></td>
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<tr>
<td>Yousif Kharaka</td>
<td>United States Geological Survey*</td>
<td>Ground water monitoring</td>
<td>1 EC and temperature probe, Dissolved oxygen probe, lab analysis of water samples</td>
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<tr>
<td>James ThorsdenGil</td>
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<tr>
<td>AmbatsSarah Beers</td>
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<tr>
<td>Henry Rauch</td>
<td>West Virginia University</td>
<td>Water monitoring well headspace gas sampling</td>
<td>1 sensor</td>
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<tr>
<td>Lucian Wielopolski</td>
<td>Brookhaven National Laboratory*</td>
<td>Inelastic neutron scattering (total soil carbon)</td>
<td>1 instrument</td>
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<tr>
<td>Sudeep Mitra</td>
<td></td>
<td></td>
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<tr>
<td>Martha Apple</td>
<td>Montana Tech*</td>
<td>Soil moisture, temp. Chlorophyll Content Meter, Fluorescence Meter, LI-COR 2000 to measure leaf area index Leaf Porometer to measure stomatal conductance</td>
<td>5 sensors</td>
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<tr>
<td>Xiaobing Zhou</td>
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<tr>
<td>Venkata Lakkaraju</td>
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<tr>
<td>Bablu Sharma</td>
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<td></td>
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<tr>
<td>+2 students</td>
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<td></td>
<td></td>
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<tr>
<td>Marth Apple</td>
<td></td>
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<tr>
<td>Xiaobing Zhou</td>
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<td>Bablu Sharma</td>
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<tr>
<td>William Holben</td>
<td>University of Montana*</td>
<td>Microbial studies</td>
<td>Lab analysis</td>
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<tr>
<td>Sergio Morales</td>
<td></td>
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* indicates non-university research institutions.
<table>
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<th>Number of Sensors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee Spangler &amp; Laura Dobeck &amp; Kadie Gullickson</td>
<td>Montana State University</td>
<td>Water content reflectometers (soil moisture)</td>
<td>15 sensors</td>
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<td></td>
<td>Automated soil CO₂ flux system</td>
<td>5 long term chambers, 1 portable survey chamber</td>
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<td></td>
<td></td>
<td>CO₂ soil gas concentration</td>
<td>6 sensors</td>
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<tr>
<td>Kevin Repasky (PI) &amp; Jamie Barr</td>
<td>Montana State University</td>
<td>Underground fiber sensor array (CO₂ soil gas concentration)</td>
<td>4 sensors</td>
</tr>
<tr>
<td>Rand Swanson</td>
<td>Resonon*</td>
<td>Flight based hyperspectral imaging system</td>
<td>1 instrument</td>
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<tr>
<td>Joseph Shaw (PI) &amp; Justin Hogan &amp; Nathan Kaufman</td>
<td>Montana State University</td>
<td>Multi-spectral imaging system (plant health)</td>
<td>1 instrument</td>
</tr>
<tr>
<td>Julianna Fessenden &amp; +3 students</td>
<td>Los Alamos National Laboratory</td>
<td>In situ (closed path) stable carbon isotope detection system</td>
<td>1 instrument</td>
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<tr>
<td>Sam Clegg &amp; Seth Humphries</td>
<td>Los Alamos National Laboratory</td>
<td>Frequency-modulated spectroscopy (FMS) open-air path</td>
<td>1 instrument</td>
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<tr>
<td>Thom Rahn</td>
<td>Los Alamos National Laboratory</td>
<td>Eddy covariance</td>
<td>1 tower</td>
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<tr>
<td>James Amonette &amp; Jon Barr</td>
<td>Pacific Northwest National Laboratory</td>
<td>Soil CO₂ flux (steady-state)</td>
<td>27 chambers</td>
</tr>
<tr>
<td>Sally Benson (PI) &amp; Sam Krevor &amp; Jean-Christophe Perin &amp; Ariel Esposito &amp; Chris Rella (Picarro)</td>
<td>Stanford University* / Picarro Instruments*</td>
<td>Commercial cavity ringdown real-time measurements of δ¹³C and CO₂ in air</td>
<td>1 instrument</td>
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<tr>
<td>Greg Rau &amp; Ian McAlexander (LGR)</td>
<td>Lawrence Livermore National Laboratory / Los Gatos Research*</td>
<td>Commercial cavity ringdown real-time measurements of δ¹³C and CO₂ in air</td>
<td>1 instrument</td>
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<tr>
<td>Jennifer Lewicki</td>
<td>Lawrence Berkeley National Laboratory</td>
<td>CO₂ soil gas concentration</td>
<td>8 sensors</td>
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<td>CO₂ atmospheric concentration</td>
<td>2 sensors</td>
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<td>Chamber soil CO₂ flux measurements</td>
<td>1 instrument</td>
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<td>Meteorological measurements</td>
<td>1 tower</td>
</tr>
</tbody>
</table>
Flux Chamber

07/08/2008

07/09/2008: Injection begins

07/10/2008

07/11/2008

07/12/2008

07/13/2008

Log CO₂ flux (g m⁻² d⁻¹)

J.L. Lewicki, LBNL
Accomplishments to Date

• Modified two computational codes used for CO$_2$ simulations
• Studied multiple analogs to inform risk assessment
• Developed and performed initial field tests on three prototype moderate area near surface detection technologies
• Performed studies to deepen understanding of capillary trapping mechanism
• Hosted other academic institutions, gov. agencies and private sector entities in field experiment
Accomplishments to Date

- We have demonstrated biomineralization sealing of fractured shales achieving four orders of magnitude permeability in fractures with several mm apertures.

- Methods for monitoring biogenic methane production from coal have been successfully developed and three sets of long term coal-to-methane experiments are on-going.

- We now have the capability to study biogenic coal-to-methane conversion using coal samples, formation water, and microbial inoculum from the same location (Flowers-Goodale coal layer near Birney MT)

- An MRI-compatible core holder and new pulse sequence enables us to: 1) Observe water in real, porous rock cores, 2) Inject liquids, gases, or supercritical fluids (brine, CO2, etc.) 3) Acquire 3D images and 4) Observe transport and structural changes in situ in ~50 sec. with ~1 mm resolution

- Achieved strain sensitivity for a fiber sensor of $60 \times 10^{-9}$. Next step is to develop non-Bragg grating technique for downhole distributed seismic sensing
Summary

– **Key Findings** Enrichment of coal microcosm experiments with Algae extract and ____ resulted in increased methane production of ____ to ___% compared to the same coal with out AE. These findings suggest that algae can be farmed in produced water impoundments, processed for biofuel production, and the extract used on-site to stimulate additional methane production underground. Algae farming will increase the CO2 uptake from the atmosphere thereby reducing the carbon footprint of the overall CBM operation.

– **Lessons Learned** There are many factors which affect the rate of biogenic methane production in laboratory microcosm experiments including maintaining field-relevant redox conditions and water chemistry. Utilizing samples of inoculum, formation water and coal from the same coal formation will minimize these and other related problems.

– **Future Plans** Batch microcosm experiments will continue. We are also beginning the design of flowing column coal-to-methane conversion experiments to assess methane production kinetics under representative groundwater flow conditions.
What We Have Learned

• Many near surface methods are quantitative but
  – Diurnal, seasonal, annual variations in ecosystem background flux affect detection limits
  – Appropriate area integrated, mass balance is a challenge
• Nearly all methods could detect 0.15 tonnes / day release at ZERT site.
• Scaling, 6 tonnes per day would be detectable over an area 40 times as large
• Surface expression was “patchy” – 6 areas of ~5m radius
• Natural analogs also seem to have “patchy” surface expression
Summary

• Multiple computational codes have been improved
• Near surface detection technologies have been tested
• Analogs are providing important information to understanding of risk
ZERT II

Natural Analogs of CO$_2$ Escape Mechanisms
Pryor Mountain and Big Snowy study areas
Carbon Storage R&D
Slides
Big Snowy Mountains Field Area
Pryor Mountain Study Area
Favorable sites for Hydrothermal Dolomite formation

A. Cartoon figure of paleohighs and strike slip faults showing favorable sites for hydrothermal dolomite formation, figure adapted from Davis and Smith, 2006. The Pryor Mountains are divided N-S by the Nye-Bowler lineament a major sinistral strike slip fault and the Snowy Mountain Study area has a strike slip faults which may source migrating fluids. Little Sheep Mountain and Little Mountain areas formed over paleohighs which influence the fracture density and may concentrate fluid flow in these areas.

B. Cartoon figure showing greater fault intensity in paleokarst situated over paleohigh, figure adapted from Eldam, 2012. $t_1$ and $t_2$ (green boxes) represent fracture intensity/density before and after uplift. The small arrow beneath the high could correspond to the location of the fault in the core of Little Sheep Mountain and be an area of concentrated fluid flow and breccia formation in the Madison Limestone a reservoir rock being considered in some carbon sequestration sites.
Model for the formation and fluid source of a hydrothermal breccia pipe

A. Fluid Migration Pathways
In this model, hydrothermal fluids are sourced by a combination of meteoric and basement fluids that flow along pre-existing structures in the subsurface. Hydrothermal fluids rise along pre-existing structures, preferentially hydrofracturing the hanging wall side of features (modified from Huntoon, 1993; Katz et al., 2006).

B. Formation of Breccia Bodies
Brecciation continues along the thrust sheet, forming shatter breccias in an increasingly vertical pattern. In both cases, hot fluids rise through strata in unpredictable patterns, creating off-shoots near sequence boundaries due to major changes in mechanical properties (modified from Katz et al., 2007). Depleted $\delta^{18}$O and $\delta^{13}$C in late-stage calcite and dolomite precipitated along brecciated zones and fracture systems in Mississippian limestone the Pryor Mountain and Big Snowy study areas are fingerprints of these processes. These areas are major avenues of enhanced porosity and permeability in the subsurface and have important applications at some sites in Montana where carbon sequestration is under consideration.

C. Similar model for the formation of hydrothermal breccia pipes.
Hydrofracturing at the fault tip results in three stages of progressively damaged and mineralized zones. These stages include (a) a zone of permeation at the propagating fault tip, causing extensive hanging wall dolomitization; (b) a region of hydraulic fracturing and brecciation of the previously dolomitized halo, resulting in the precipitation of hydrothermal minerals; and (c) the repetition of seismic events, allowing the brecciated area to become progressively more vertical with continued activity (modified from Phillips, 1972; Davies and Smith, 2006; Jeffrey, 2014).
Hydrothermal Breccias and fluid flow examples in Little Sheep Mountain, WY

A. Hydrothermal breccia formed along an oblique to strike fracture in Madison Limestone in the LSMA. Note bleached rock along fracture and bedding planes.

B. Small dolomitized, possibly silicified breccia pipe protruding from roof of Lower Kane Cave.

C. Sample LSM-RRC008 silicified floating clast breccia near Lower Kane Cave. Matrix sampled has a $\delta^{18}O$ value of -11.07 and $\delta^{13}C$ value of 0.02 reflecting warm fluid migration.

D. Oil impregnated breccia clast from Little Sheep Mountain. SM-RRC001 sample location. Three samples were analyzed from this site for stable C and O isotopes: LSM-001 a silicified Permian limestone had the most depleted $\delta^{18}O$ value of -14.09 and the most depleted $\delta^{13}C$ value of all the samples in the Pryor Mountain study area of -10.31.

E. Gypsum coated breccia Lower Kane Cave. The walls have dried bitumen which seeped along breccia clasts and along fractures. Twenty centimeter arrow for scale is in lower portion of photo.

F. Hydrothermal breccia which may be associated with the breccias in Lower Kane Cave (B above) has a $\delta^{18}O$ value of -12.80 and $\delta^{13}C$ value of -0.03. Breccia formed along oblique to strike of the anticline axis fractures bleaching is evident on the side of the breccia.
Stable O and C Isotope Data
Madison & Permian Limestone

A. Stable carbon and oxygen isotope analyses data from brecciated host rock and vein fill material from the Pryor Mountain Study area. The black symbols are from the Little Mountain area and the Pryor Mountains. The red and blue symbols are from Little Sheep Mountain. Squares are host rock, triangles vein fill material, circles breccias and crosses are the standards which are circled in the figure. The dashed boxes represent approximate value for Mississippian and Permian seawater carbonate based on Veizer et al., 1999. The oval shape shows the most depleted $\delta^{13}C$ and $\delta^{18}O$ values are mainly the late stage vein fill material and breccias.

B. Carbon and oxygen graphs of Phanerozoic $\delta^{13}C$ and $\delta^{18}O$ trend. Carbon is for combined Bochum/Ottawa (based on 1564 brachiopod (secondary layer) and belemnite (laminae pelucidae) measurements at Bochum and Ottawa and literature data (compiled from 3918 measurements for low Mg calcite (brachiopods, belemnites, oysters, foraminifera) and 96 measurements for aragonite (mollusk shells). The running mean is based on 20 Ma window and 5 Ma forward step. The shaded areas around the running mean include the 68% (+/- 1$\sigma$ for a strictly Gaussian distribution) and 95% (+/- 2$\sigma$) of all data (From Veizer et al., 1999 and references within). Dashed boxes are values represented in top graph.
Porosity change accompanies brecciation and dolomitization

SEM and BoneJ analyses of matrix material from breccias A & B highlight the amount of porosity present. SEM images were used to determine secondary porosity associated with matrix dolomitization, which was too fine to see through petrographic analysis. The Mission Canyon Formation in the Snowy Mountain study area is characterized by poor intrinsic porosity and permeability; however, in brecciated regions matrix material of the Mission Canyon Fm. added a strong secondary fabric to the rock, creating open vuggy space and intercrystalline porosity.

SEM (left) and the BoneJ plug-in of ImageJ (right) analyses were of matrix material from breccias located along the Big Snowy fault system. SEM images (greyscale) were analyzed using a color thresholds (light blue) highlighting the amount of porosity present. Such two-dimensional area calculations suggest that pore space increased by 5-25% as a result of hydrothermal brecciation.
Hydrothermal brecciation characterized by multiple episodes of fluid flow

A. Breccia with boxwork texture
B. Thin section of stained breccia with late stage calcite (pink), bitumen (black) and purple fluorite filling in void space created during brecciation.
C. Cathodoluminescence image of fracture fill shows multiple episodes of fluid migration with iron rich, darker bands alternating with regular late stage calcite.
D. Breccia with vugs filled with dark purple to black fluorite.
E. Inset SEM image of a corroded fluorite crystal, 1000x magnification
F. F. & G. Large silicified, dolomitic floating clast breccia Red Pryor Mountain; clast (F) was cut, polished and stained for carbonate identification. The matrix is ferroan dolomite and there were at least two late stage calcite vein filling episodes. The last was ferroan calcite. The sample was drilled for isotope analyses from the veining and the matrix. The late stage ferroan calcite was the most depleted in $\delta^{18}O$ with a value of -15.99 and a $\delta^{13}C$ value of -0.40. The clast shows fractures healed by calcite (arrow) and later fracturing along edge of clast and through matrix.
Some factors for CO$_2$ Reservoir Characterization in Paleozoic reservoir rocks

- Porosity and permeability may be influenced by tectonic hydrothermal breccias:
  - Heterogeneity is created by hydrothermal breccias which may serve to increase porosity or occlude it.
  - Dolomitization may increase the porosity while late stage calcite may serve to occlude it.
  - Faulting and brecciation within perspective reservoir units must be thoroughly characterized for such secondary networks of permeability, as they create unpredicted anisotropy within the reservoir.

- Structural position may influence the flow of fluids in the subsurface.
  - Paleohighs may serve as areas of increased density of fractures and fracture intensity thus increasing porosity and permeability of the fractured units.
  - Preexisting faults, fractures and joints may serve as conduits for the migration of fluids in the subsurface.
  - Position on a structure such as the axis of an anticline vs. the forelimb or backlimb will influence the fluid migration and trapping capabilities of the reservoir system.

- Stratigraphy and mechanical stratigraphy in Paleozoic reservoir rocks may influence fluid migration locally within a unit.
  - Mechanical stratigraphy can influence the migration of fluids in a reservoir rock.
  - Thickness of layers within a formation respond differently to applied stress.
    - Thinner units may have greater density of fractures within a stratigraphic unit and provide greater fracture permeability in that unit influencing fluid flow.
Appendix

– These slides will not be discussed during the presentation, but are mandatory
Organization Chart

• Describe project team, organization, and participants.
  – Link organizations, if more than one, to general project efforts (i.e. materials development, pilot unit operation, management, cost analysis, etc.).

• Please limit company specific information to that relevant to achieving project goals and objectives.
Gantt Chart

• Provide a simple Gantt chart showing project lifetime in years on the horizontal axis and major tasks along the vertical axis. Use symbols to indicate major and minor milestones. Use shaded lines or the like to indicate duration of each task and the amount of that work completed to date.
The tasks are continued in the no-cost extension awarded in August 2012.
<table>
<thead>
<tr>
<th>Task 1.0 – Project Management, Planning, and Reporting</th>
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<td>Subtask 1.3  Presentations and Briefings</td>
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<td>Subtask 2.1  Conduct experiments on CO₂ biominalization deposits on flat coupons and in porous media bead packs.</td>
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<td>Subtask 2.2  Develop method to control deposition rate of biominalized calcium carbonate with distance along a porous media flow path.</td>
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<td>Subtask 2.3  Optimize biominalization of isotopically labeled CO₂ carbon under variable head space pressure.</td>
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<td>Subtask 2.4  Evaluate the potential for coalbed mediated CO₂ sequestration.</td>
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<td>Subtask 2.5  Construct a system capable of flowing supercritical fluids through the bore of the magnet of the NMR spectrometer.</td>
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<tr>
<td>Subtask 2.6  Evaluate transport phenomena for brine and supercritical CO₂ using magnetic resonance techniques.</td>
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<tr>
<td>Subtask 2.7  Evaluate transport phenomena for brine and supercritical CO₂ in a bead pack or other model porous media.</td>
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<th>Task 3.0 – Natural Analogs of Escape Mechanisms</th>
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<td>Subtask 3.2  Ancient Hydrothermal Plumes as a Natural Analog of Hydrofracing Caprocks and Geochemical Healing Mechanisms</td>
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<td>Subtask 5.2  Coordinate experimental season with ZERT team.</td>
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<tr>
<td>Subtask 5.3  Collect data in support of ZERT research project goals.</td>
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<tr>
<td>Subtask 5.4  Investigate opportunities for greater involvement outside of the ZERT team.</td>
</tr>
<tr>
<td>Subtask 5.5  Support optical remote sensing group</td>
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<tr>
<td>Subtask 5.6  Support pollen capture of tracers experiments:</td>
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<tr>
<th>Task 6.0 – Tracking Emerging Issues That Could Influence CCS Research Needs</th>
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<tr>
<td>Subtask 6.1  Provide information to government at the state, federal and international levels.</td>
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<tr>
<td>Subtask 6.2  Provide information to NGOs, industry groups, and professional groups relevant to CCS.</td>
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<tr>
<th>Task 7.0 – Sequestration of Carbon Dioxide in Appalachian Coal Deposits (WVU Subcontract)</th>
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<tr>
<td>(Detailed Task and Subtask descriptions will be provided at a later date.)</td>
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Bibliography


Vegetation imaging and meteorological sensing at the ZERT site – 2014 summary

Joseph Shaw
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Bozeman, Montana, USA
jshaw@montana.edu
Vegetation imaging test at ZERT field
Principle: detect leaking gas from induced plant stress
Visible & NIR imaging to locate CO2 leak via plant stress

Normalized Difference Vegetation Index

\[ NDVI = \frac{\rho_{NIR} - \rho_{RED}}{\rho_{NIR} + \rho_{RED}} \]
Tethered balloon multispectral imaging

Compact, ultra-low-cost multispectral imager on balloon
NDVI measured with balloon camera & scaffold camera

2012 ZERT
NDVI vs. Time

- Scaffold camera (control)
- Scaffold camera (hotspot)
- CO₂ flow started
- CO₂ flow stopped
- CO₂ flow resumed
- Power outage interrupts CO₂ flow
- Power outage interrupts CO₂ flow
- Flow rate up from 0.15 to 0.3 tonne/day
- CO₂ flow ended
- Balloon imager (control)
- Balloon imager (hotspot)
Thermal imaging also detects leaking gas

10 μm IR images before & after CO$_2$-induced plant stress

<table>
<thead>
<tr>
<th>Before</th>
<th>After</th>
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<tr>
<td><img src="before.png" alt="Image" /></td>
<td><img src="after.png" alt="Image" /></td>
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*Figure showing before and after 10 μm IR images of CO$_2$-induced plant stress.*
Hot spot emits higher IR radiation after start of CO$_2$ flow.
ZERT weather station study

Two identical sensors at ZERT and MSU
3rd identical sensor mounted on backpack

- Confirmed calibration of each weather station
- Temperature variation map indicates existence of campus heat island

MSU - mobile
Heat island also varies throughout town
Thermal camera used to understand heat island

Two sample regions: grass and concrete
Higher IR radiation from concrete warms the air.
Higher IR radiation from concrete warms the air (2)

IR & air temps

Sidewalk is warmer except in direct Sun

Clouds explain wiggles in daytime IR temps
• Leaking CO$_2$ gas has been detected via plant stress with visible and NIR imaging and with thermal IR imaging;

• Balloon-borne vis-NIR camera gives same results, but over much larger area and without airplane;

• ZERT weather station is accurate, but difference from MSU station helped us understand heat islands...