

**Training Students to Analyze Spatial and Temporal Heterogeneities in
Reservoir and Seal Petrology, Mineralogy, and Geochemistry: Implications
for CO₂ Sequestration Prediction, Simulation, and Monitoring**

FINAL SCIENTIFIC/TECHNICAL REPORT

Start date: December 1, 2009 - End date: September 30, 2013

Brenda B. Bowen

January 2014

DOE Award No. DE-FE0001852

Recipient: Purdue University

Earth, Atmospheric, and Planetary Sciences Department

550 Stadium Mall Drive

Purdue University

West Lafayette, IN 47907-2051

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

The objective of this project was to expose and train multiple students in geological tools that are essential to reservoir characterization and geologic sequestration including but not limited to advanced petrological methods, mineralogical methods, and geochemical methods; core analysis, and geophysical well-log interpretation. These efforts have included training of multiple students through geologically based curriculum and research using advanced petrological, mineralogical, and geochemical methods. In whole, over the last 3+ years, this award has supported 5,828 hours of student research, supporting the work of several graduate and undergraduate students. They have all received training directly related to ongoing CO₂ sequestration demonstrations. The students have all conducted original scientific research on topics related to understanding the importance of lithological, textural, and compositional variability in formations that are being targeted as CO₂ sequestration reservoirs and seals. This research was linked to the Mount Simon Sandstone reservoir and overlying Eau Claire Formation seal in the Illinois Basin- a system where over one million tons of CO₂ are actively being injected with the first large-scale demonstration of anthropogenic CO₂ storage in the U.S. Student projects focused specifically on 1) reservoir porosity characterization and evaluation, 2) petrographic, mineralogical, and geochemical evidence of fluid-related diagenesis in the caprock, 3) textural changes in reservoir samples exposed to experimental CO₂ + brine conditions, 4) controls on spatial heterogeneity in composition and texture in both the reservoir and seal, 5) the implications of small-scale fractures within the reservoir, and 6) petrographic and stable isotope analyses of carbonates in the seal to understand the burial history of the system. The student-led research associated with this project provided real-time and hands-on experience with a relevant CO₂ system, provided relevant information to the regional partnerships who are working within these formations, and provides more broadly applicable understanding and method development for other carbon capture and storage systems.

TABLE OF CONTENTS

Executive Summary.....	4
------------------------	---

Report Details

Experimental Methods, Results and Discussion

1) Porosity Characterization and Diagenetic Facies Analysis of the Cambrian Mount Simon Sandstone: Implications for a Regional CO ₂ Sequestration Reservoir.....	5
2) Petrographic, Mineralogical, and Geochemical Evidence of Diagenesis in the Eau Claire Formation, Illinois Basin: Implications for Sealing Capability in a CO ₂ Sequestration System.....	7
3) Geochemical and Mineralogical Evaluation of CO ₂ -Brine-Rock Experiments: Characterizing Porosity and Permeability Variations in the Cambrian Mount Simon Sandstone	8
4) Investigating Changes in Composition and Texture in the Mount Simon Sandstone and Eau Claire Formation within the Illinois Basin.....	9
5) Characterizing Fractures and Deformation Bands: Implications for Long-Term CO ₂ Storage within the Cambrian Mount Simon Sandstone.....	11
6) Petrographic and Stable Isotope Analysis of Carbonates in the Eau Claire Formation.....	11
Conclusions.....	13
References.....	14

Executive Summary:

The complex issues related to energy demands and the environmental impacts of increasing carbon emissions are not doubt some of the most pressing and challenging issues facing society today. There is significant potential for geologic CO₂ sequestration to provide a mitigation strategy to reduce atmospheric CO₂ inputs while the energy industry transitions to renewable non-carbon energy sources. If the policy and economics are able to move in a direction that instigates large-scale carbon capture and storage (CCS), there is the potential that a new workforce of geologic experts would be needed to immediately move forward with nation-wide CCS initiatives. These workers would need to be informed in many of the same skills that other subsurface geologic resource industries have developed (i.e. the oil and gas industry), but will need to combine classic subsurface geoscience tools (e.g., well log correlation and mapping, core descriptions, basin-scale seismic interpretation) with other tools that specifically address the unique geochemical and hydrologic parameters the influence a CCS system. The project has focused on working with multiple geoscience students in collaboration with the Regional Carbon Sequestration Partnerships to provide focused training opportunities related to ongoing CO₂ sequestration demonstrations. This work has addressed the Carbon Storage Program's major goals by helping to develop technologies that will support the industries' abilities to predict CO₂ storage capacity, and by helping to develop best management practices for site characterization. Other benefits to the carbon capture and storage program included analyses of samples relevant to active demonstration projects, improved understating of reservoir and seal characteristics and the potential for reactivity post-injection. All of the student projects focused on the Cambrian Mount Simon Sandstone reservoir and the overlying Eau Claire Formation seal, the primary storage system within the Illinois Basin in the Midwest United States. The overall research goals were to understand how different depositional and diagenetic histories influence the reservoir and seal quality, and to identify important soluble mineral phases with emphasis on those that are in contact with pore space and would be reactive with CO₂-saturated brines. This work utilized a suite of tools including sedimentological and petrophysical core analyses, microscopy (e.g., transmitted and reflected light petrography, cathodoluminescence, scanning electron microscopy), mineralogy (e.g., reflectance spectroscopy, x-ray diffraction), and geochemistry (e.g., major oxide whole rock analyses, trace element analyses, in-situ x-ray analyses, geochemical modeling).

Experimental Methods, Results, and Discussion:

This work has provided extensive new information about spatial differences in the textural, mineralogical, and geochemical characteristics that impact the reservoir and seal quality of the Mount Simon Sandstone and Eau Claire Formation in the Illinois Basin. The students and PI worked with the Midwest Geologic Sequestration Consortium and the Midwest Regional Carbon Sequestration Partnership, particularly through a close collaboration with John Rupp at the Indiana Geologic Survey, to acquire samples of both the Mount Simon Sandstone and the Eau Claire Formation for the student to work on.

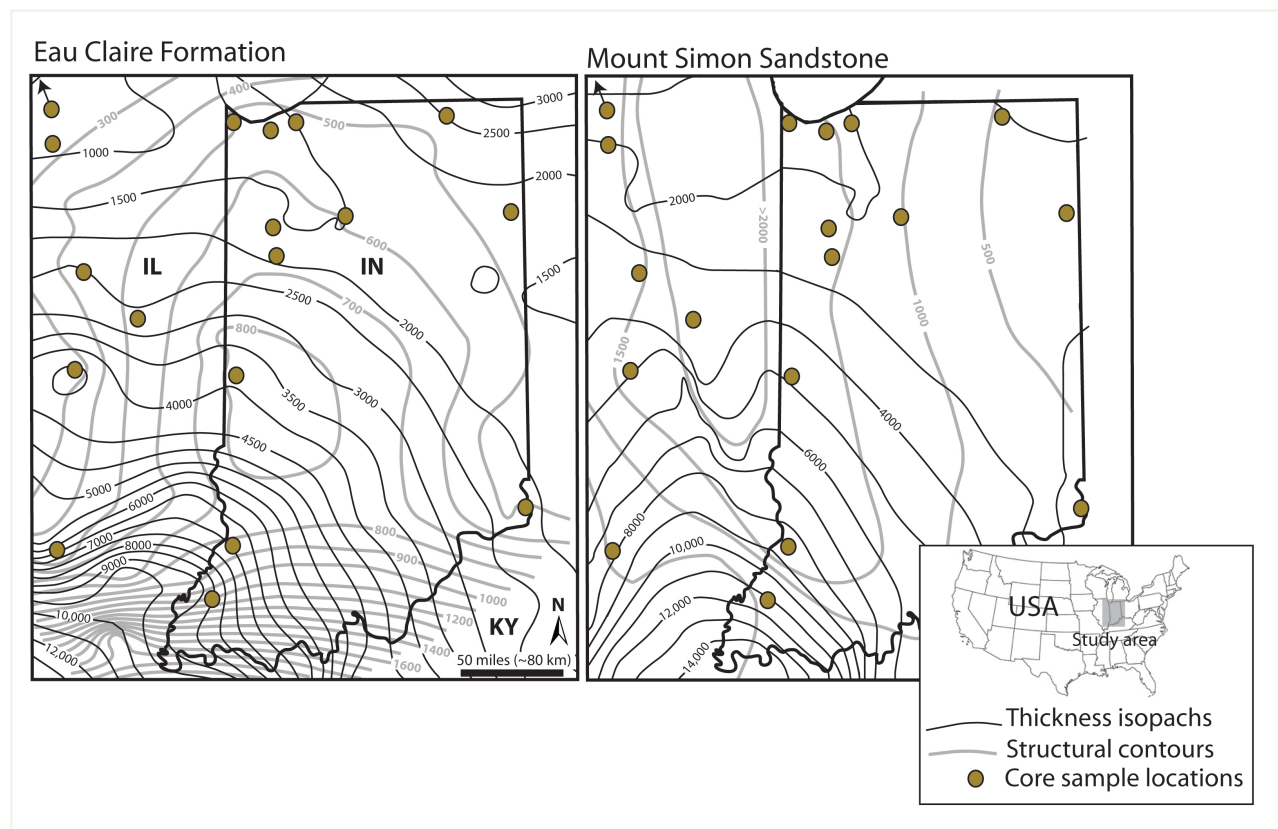


Figure 1. Map of well locations where subsurface cores of the Mount Simon Sandstone and Eau Claire Formation were utilized for research related to this project.

Through the life of the project, this award supported six major student projects, which each had specific methodological approaches, results, and conclusions that will be discussed:

- 1) Raul Ochoa, 2010, M.S. (Purdue University), Porosity Characterization and Diagenetic

Facies Analysis of the Cambrian Mount Simon Sandstone: Implications for a Regional CO₂ Sequestration Reservoir.

The objective of this project was to quantify and understand the spatial variations in porosity in the Mount Simon Sandstone and to identify the processes that have influenced the observed variation. Samples of Mount Simon Sandstone were obtained basin-wide from representative burial depths and lithofacies. Thin sections were made from these samples and porosity was embedded with blue epoxy so that petrographic image analyses could be utilized to quantify and evaluate porosity. Over 150 individual samples from seven different wells were analyzed petrographically to quantify porosity. Images were analyzed using ENVI software to quantify

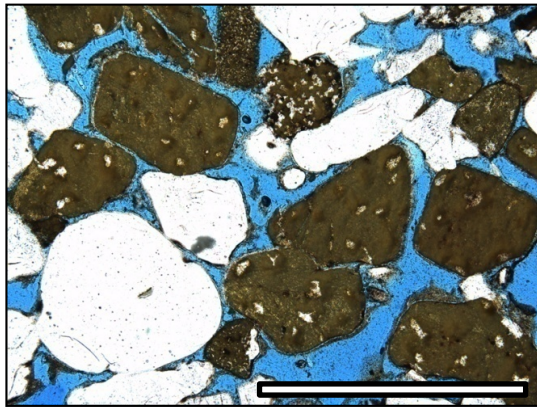
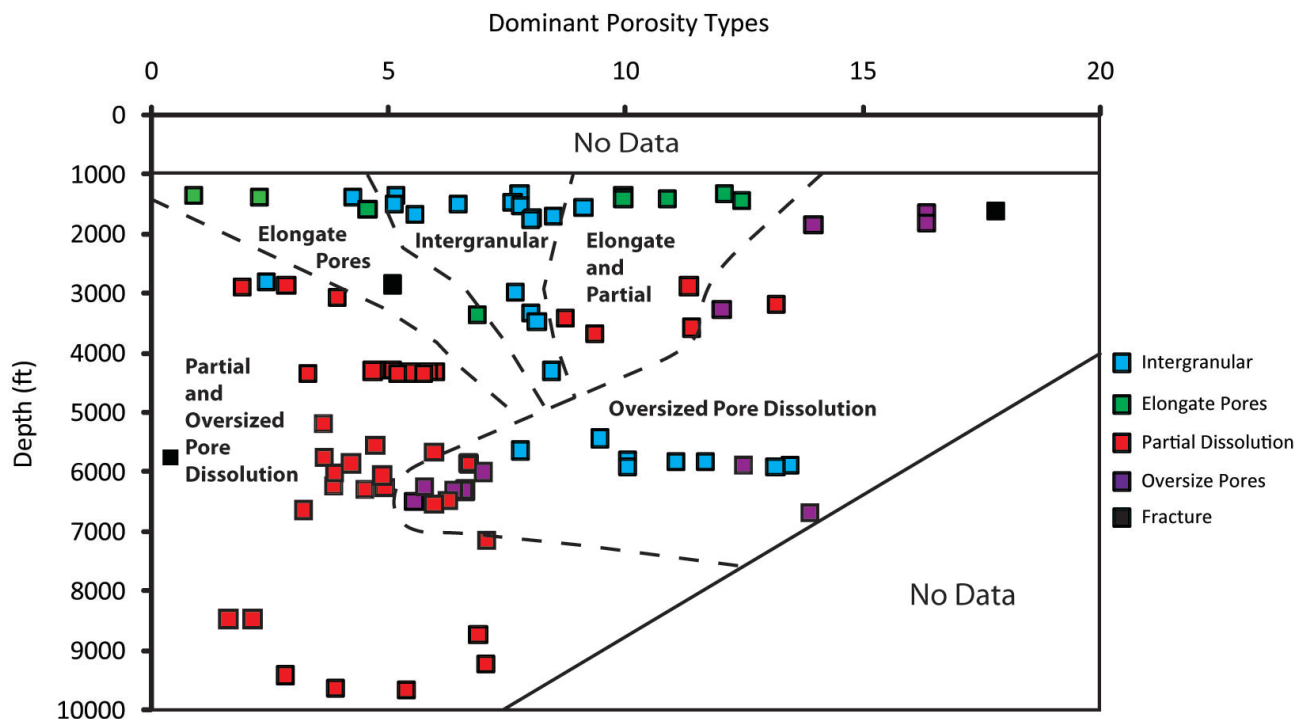


Figure 2. Left: Example of a Mount Simon Sandstone micrograph where porosity is shown in blue (vacuum-embedded epoxy), quartz grains are white, and feldspar grains are brown. The scale bar is 1 mm across. Below: Synthesis of Mount Simon Sandstone porosity and porosity types.



the percentage of the imagery that contains blue epoxy. In addition, the types of porosity were classified for each of these samples to that an analyses of depth, porosity, and porosity type could be assessed.

- 2) Ryan Neufelder, 2011, M.S. (Purdue University), Petrographic, Mineralogical, and Geochemical Evidence of Diagenesis in the Eau Claire Formation, Illinois Basin: Implications for Sealing Capability in a CO₂ Sequestration System.

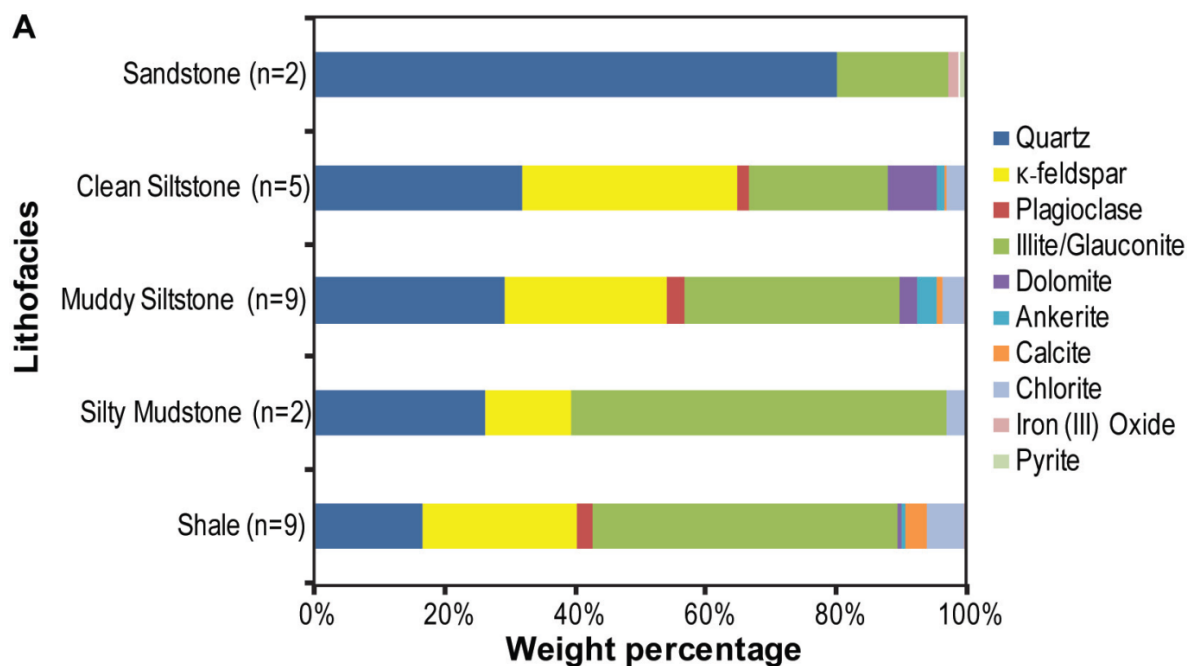


Figure 3. Average mineralogy (via x-ray diffraction) of the five major lithofacies identified in the Eau Claire Formation showing the systematic variations in potentially reactive phases.

The objective of this project was to quantify compositional and textural variability within the Eau Claire Formation to evaluate the history of fluid-related alteration in this unit and to consider how it might react with future introduction of CO₂-saturation brines. For this work, sixty core-derived Eau Claire Formation samples from seven wells across the Illinois Basin were analyzed visually, petrographically, mineralgically, and geochemically. This work showed that the sealing capabilities of the Eau Claire Formation are quite variable depending on depositional fabric and diagenetic history. The samples revealed substantial dissolution porosity and evidence of fluid-related diagenetic alteration in some areas, suggesting the need for detailed intraformational

mapping of lithofacies to identify the location of more shale-rich lithofacies that provide an appropriate seal.

- 3) Alexander Gonzalez, 2013, M.S. (University of Utah), Geochemical and Mineralogical Evaluation of CO₂-Brine-Rock Experiments: Characterizing Porosity and Permeability Variations in the Cambrian Mount Simon Sandstone.

The objective of this work was to examine any compositional and textural changes in samples that were exposed to experimental CCS conditions for six months at the National Energy and Technology Laboratory (NETL) in Pittsburgh (in collaboration with Yi Soong at NETL). Samples were selected to provide a “typical” representative Mount Simon Sandstone sample (the “Vermillion” sample) and to analyze changes in a very low porosity and low permeability sample from deep in the basin (the “Knox” sample). Methods for evaluating the samples included petrographic examination, scanning electron microscopy and energy dispersive chemical analyses, brine geochemical analyses, and geochemical modeling.

Knox		Vermillion
1.5%	Pre-Experimental Porosity	7.9%
1.1% (-27%)	Post-Experiment Porosity	6.3% (-20%)
19nD	Pre-Experimental Permeability	1.6 mD
23 nD (+21%)	Post-Experiment Permeability	.5mD (-69%)
Quartz: 71% Feldspar: 20% Authigenic: 1% Porosity: 8%	Mineral Composition	Quartz: 71% Feldspar: 4% Authigenic: 3% Porosity: 22%
All major ions and trace elements increased	Brine Composition	All major ions and trace elements increased
Center: 1288 μ^2 Middle: 628 μ^2 Edge: 2747 μ^2	Pore Surface Area	Center: 10969 μ^2 Middle: 12566 μ^2 Edge: 12947 μ^2
1.39	Pore Al/K Ratio	4.92

Figure 4. Table of experimental conditions and results comparing pre-experiment and post-experiment analyses.

Results from these analyses showed that there were in fact changes in the porosity and the chemical composition of the samples over the six months of the experiment. There was no evidence of mineral precipitation, but there was both geochemical and textural evidence of dissolution. Geochemical modeling (using Geochemist's Workbench) was used to extrapolate the observed changes over longer time scale and over differing spatial scales.

- 4) Thomas Lovell, Ph.D. research (Purdue University), Investigating Changes in Composition and Texture in the Mount Simon Sandstone and Eau Claire Formation within the Illinois Basin.

The goal of this research was to characterize and explain regional compositional and textural trends within the Mount Simon Sandstone and Eau Claire Formation. Tools for this work included integrated well-log analyses, core descriptions, thin section microscopy and compositional point counting, and geochemical analyses of detrital zircons. A detailed analyses was undertaken for the only known core that spans the entire section of the Mount Simon Sandstone, from Stephenson County, Illinois. This work demonstrated changes in composition and sedimentary provenance through the section, which can then be linked to spatial patterns in reservoir quality.

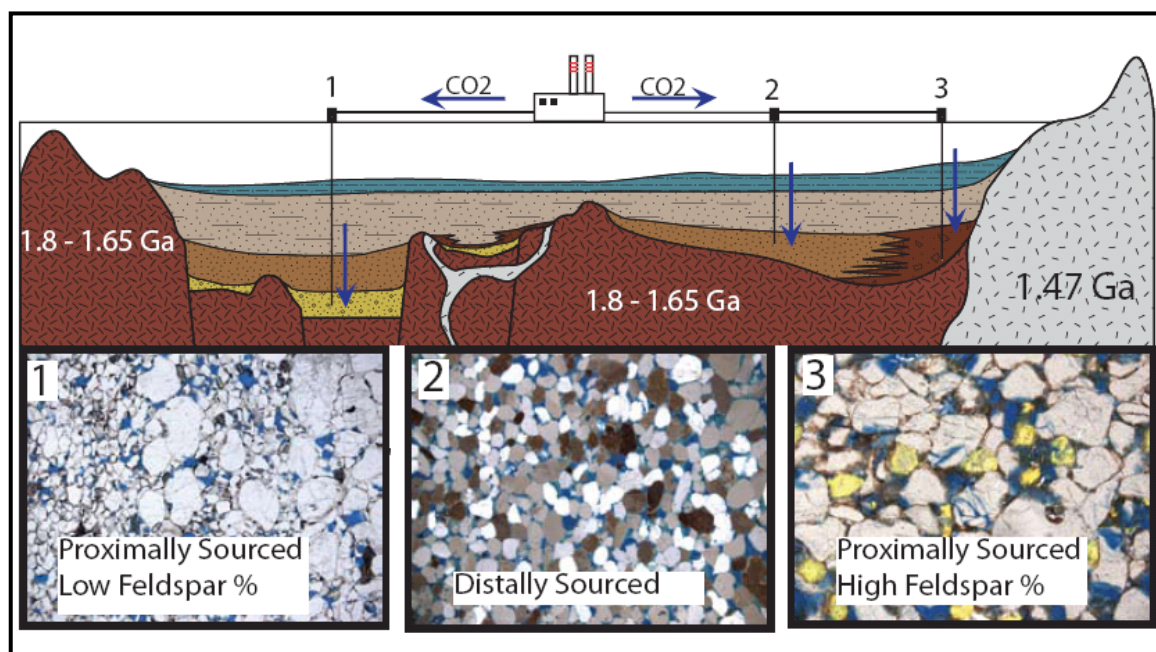


Figure 5. Schematic diagram illustrating how detrital composition and reservoir quality can be

affected by differences in sedimentary provenance. In this example, strata sourced proximally from the 1.8-1.65 Ga terrane yields low feldspar percentages (1), distally sourced strata contain a moderate amount of feldspar (2), and strata sourced from the 1.47 Ga terrane yield high feldspar content (3). Much of the porosity in the Mount Simon Sandstone is seen to occur due to feldspar dissolution, thus the spatial distribution and geologic controls on feldspar content is an important aspect of predicting reservoir potential.

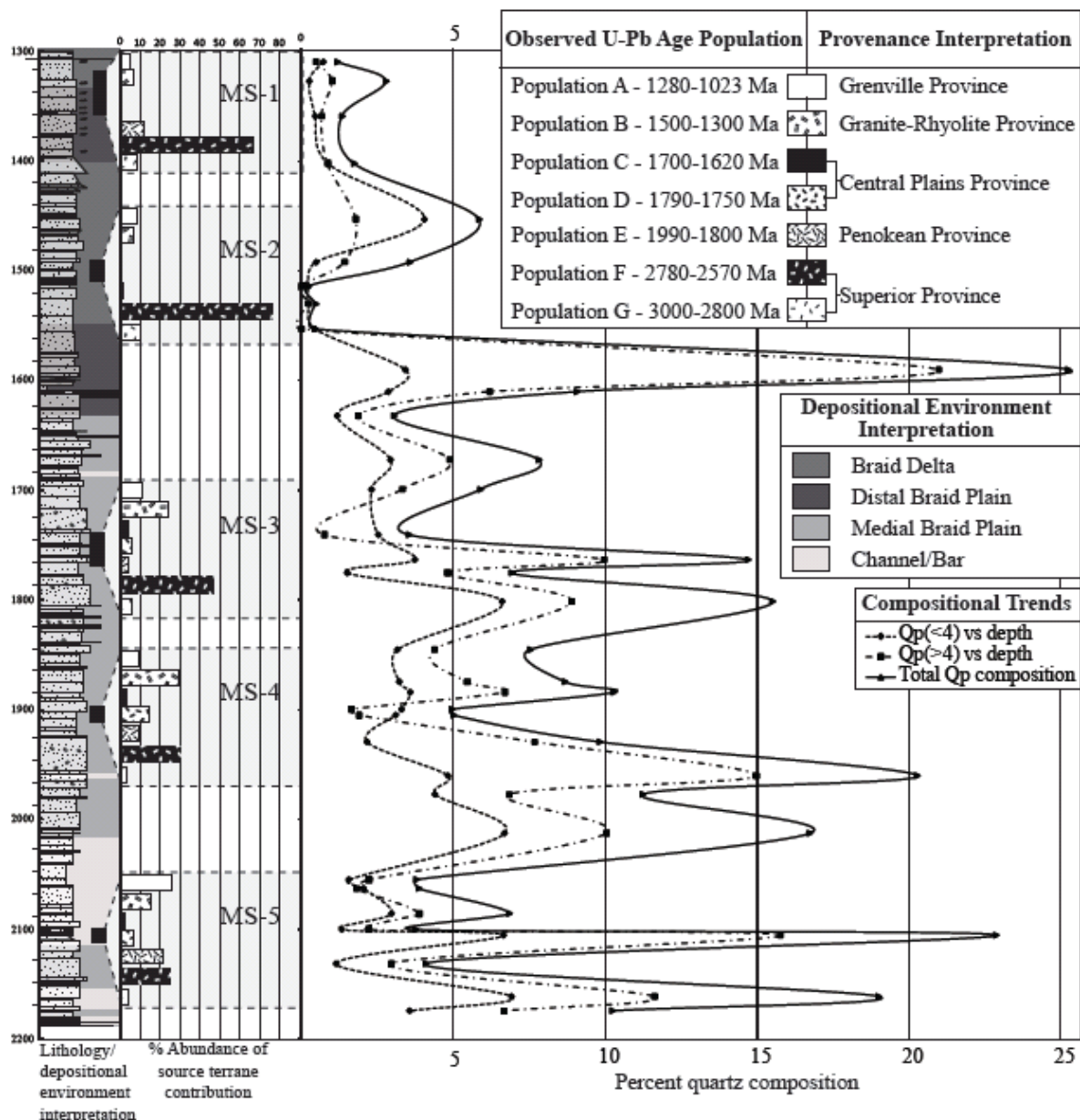


Figure 6. Stratigraphic changes in lithology, depositional environment, observed U-Pb age populations, and types of detrital quartz through the Mount Simon Sandstone (after Lovell and

Bowen, 2013).

- 5) Brenton Chentnik, 2012, undergraduate research (Purdue University), Characterizing Fractures and Deformation Bands: Implications for Long-Term CO₂ Storage within the Cambrian Mount Simon Sandstone.

This project was focused on evaluating any evidence of structural textures such as deformation bands or fractures within the Mount Simon Sandstone and to use petrographic and geochemical analyses to evaluate whether these types of structures have been either conduits and/or barriers to fluid flow within this unit. This work demonstrated that deformation bands and grain-scale fracturing are not uncommon in these samples, and that in some cases the fractures seem to have been conduits for diagenetic fluids.

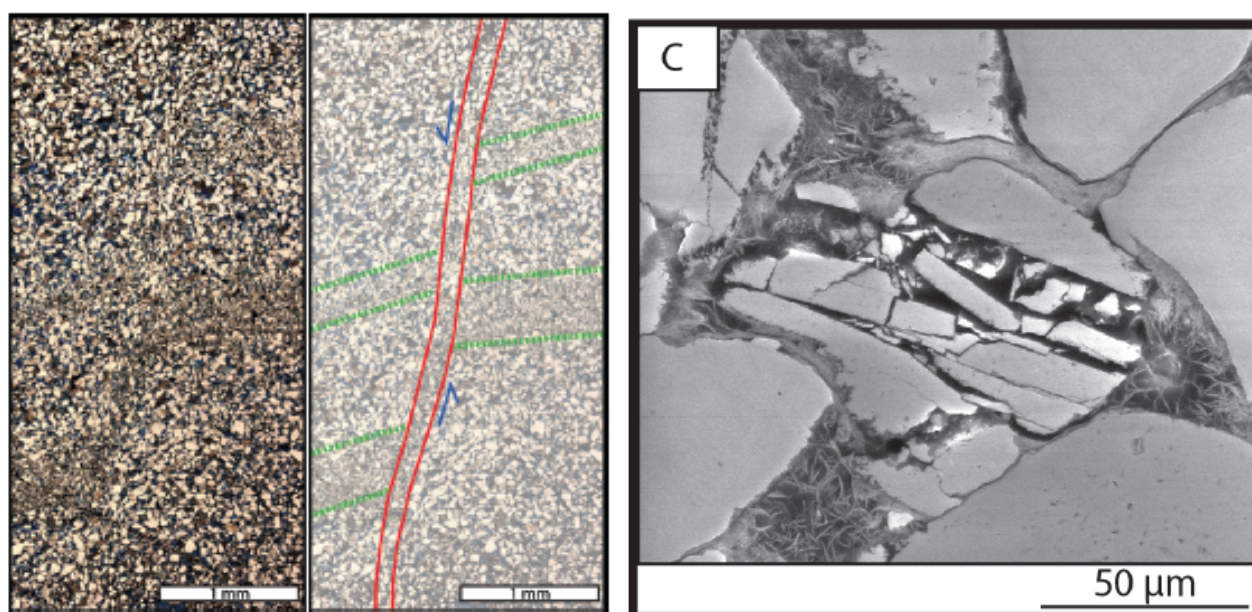


Figure 7. Left- micrograph mosaic for the Mount Simon Sandstone showing interpreted overlay of locations of compaction bands that are offset a small amount by a zone of cataclastic deformation bands. Right- grain-scale scanning electron microscopy image showing a shattered grain with surrounding authigenic clay cement.

- 6) John Shufflebarger, 2011, undergraduate research (Purdue University), Petrographic and Stable Isotope Analysis of Carbonates in the Eau Claire Formation.

This project followed up on the observations made by Ryan Neufelder about the abundance

of authigenic carbonates within the Eau Claire Formation, and attempted to evaluate the history of the fluids responsible for their formation using carbon and oxygen stable isotope analyses. Samples with observed carbonate were sub-sampled with a micro-drill and analyzed at the Purdue Stable Isotope facility. These data showed differences based on the type of carbonate as well as a spatial differences that could indicate a difference in the carbon source in the depositional environment or could be the result of the differences in burial depth and the temperature and composition of diagenetic fluids.

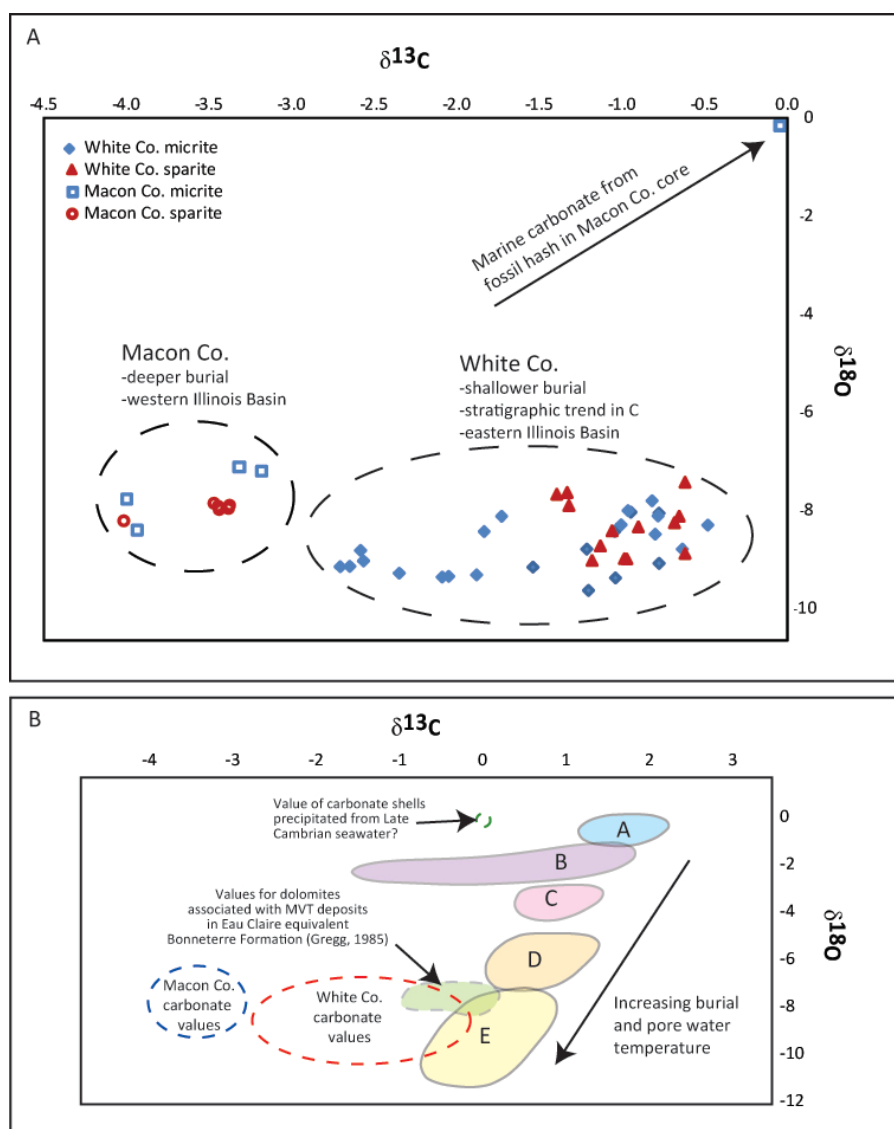


Figure 8. Part A- the isotopic composition of carbonates in the Eau Claire Formation classified as either dominantly “micrite” or “sparite” based on petrographically observed textures. Part B - the hypothetical trends of marine carbonates undergoing burial diagenesis.

Conclusions:

We have successfully completed the objectives of this project, having supported multiple graduate students and undergraduates in research and training related to geologic CO₂ sequestration. PI Bowen worked closely with each of the students to guide their research and to provide training with the various mineralogical, geochemical, petrological, and petrographic techniques. Each study yielded valuable results and led to development of new questions for future work. It is ironic that most of these student were quickly hired by employers in the oil and gas industry as the types of questions they were working on and the tools they developed expertise in are very similar to those used in this field. As of now, the CO₂ sequestration related jobs that were anticipated when this solicitation was announced have not been created. Thus, while this project has focused on identifying methods for training this future workforce, the need for students with these skills has not be realized.

References (student authors supported by this project are underlined)

Bowen, B.B., Ochoa, R., Wilkens, N.P., Neufelder, R., Lahann, R., Brophy, J., Medina, C., and Rupp, J., 2010, Distribution and abundance of potentially reactive minerals with geologic CO₂ sequestration in the Mount Simon - Eau Claire sedimentary system: AAPG Eastern Section Meeting, Kalamazoo, MI, September 25-29, 2010.

Bowen, B.B., Ochoa, R., Wilkens, N.D., Brophy, J., Lovell, T.R., Fischietto, N., Medina, C., and Rupp, J., 2011, Depositional and diagenetic variability within the Cambrian Mount Simon Sandstone: Implications for carbon dioxide sequestration: *Environmental Geosciences*, v.18, p. 69-89.

Bowen, B.B., Lovell, T., Neufelder, R., Rupp, J., Brophy, J., Lahann, R., 2011, Mineralogy and geochemistry of a potential CO₂ sequestration reservoir and seal system, Illinois Basin, USA: Goldschmidt Conference abstract, Mineralogical Magazine, v. 75, p. 566.

Chentnik, B.M., and Bowen, B.B., 2011, Fracture analysis in the Mount Simon Sandstone and implications for carbon sequestration: Geological Society of America Abstracts with Programs, V. 43, No. 5, p. 279.

Chentnik, B.M., 2012, Characterizing Fractures and Deformation Bands: Implications for Long-Term CO₂ Storage within the Cambrian Mount Simon Sandstone, *The Journal of Purdue Undergraduate Research*: Vol. 2, Article 3. DOI: 10.5703/jpur.02.1.02

Gonzalez, A., and Bowen, B.B., 2012, Geochemical and mineralogical evaluation of CO₂-brine-rock experiments: Characterizing porosity and permeability variations in the Cambrian Mount Simon Sandstone: American Geophysical Union annual meeting, abstract # H23A-1325, in *Advances in geochemical and hydrogeological studies of CO₂ fate and transport at geological CO₂ sequestration sites*.

Lovell, T.R., Bowen, B.B., and Fischietto, N., 2011, Temporal changes in composition and detrital Zircon U-Pb ages in the Upper Cambrian Mount Simon Sandstone, Midwest United States: Implications for fluctuations in sedimentary provenance: Geological Society of America Abstracts with Programs, V. 43, No. 5, p. 443.

Lovel, T.R. and Bowen, B.B., 2012, Variations of Laurentian provenance recorded in the Upper Cambrian Mount Simon Sandstone and Eau Claire Formation of the Illinois Basin: Geological Society of America Abstracts with Programs, V. 44, No. 7, p. 379.

Lovell, T., and Bowen, B.B., 2013, Fluctuations in sedimentary provenance of the Upper Cambrian Mount Simon Sandstone, Illinois Basin, United States: *Journal of Geology*, v. 121, p. 129-154.

Neufelder, R.J., Bowen, B.B., Lahann, R.W., and Rupp, J.A., 2012, Lithologic, mineralogical, and petrophysical characteristics of the Eau Claire Formation: Complexities of a carbon storage system seal: *Environmental Geosciences*, v. 19, p. 81-104.

Ochoa, R., Bowen, B.B., and Rupp, J.R., 2010, Porosity characterization and diagenetic facies analysis of the Mount Simon Sandstone, Illinois Basin: Implications for a regional CO₂ sequestration reservoir: Geological Society of America Abstracts with Programs Vol. 42, No. 5.

Shufflebarger, J., Bowen, B.B., and Neufelder, R., 2011, Petrographic and stable isotope analysis of carbonates in the Eau Claire Formation: Geological Society of America Abstracts with Programs, V. 43, No. 5, p. 2.