Geoscience Perspectives in Carbon Sequestration – Educational Training and Research Through Classroom, Field, and Laboratory Investigations

Project Number DE-FE0002416

David J. Wronkiewicz

Missouri University of Science & Technology

U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the Infrastructure for CO_2 Storage

August 21-23, 2012

Presentation Outline

1. Education & training of students – enhancing undergraduate curriculum.
2. Graduate Student Research Projects
   a) Investigation of Midcontinent Rift (MCR) for CO_2 sequestration.
   b) Natural analogs for a leaking CO_2 system, mineral precipitation in an upwelling spring.
   c) Biomineralization processes in CO_2 sequestration.

MISSOURI S&T University of Science & Technology

Benefit to the Program

- Program Goals
  - Demonstrate 99% retention of CO_2 for injection zones.

- Project Benefits
  - Identify and characterize CO_2 + water + rock interaction processes.
  - Carbonate mineralization is a key component towards ensuring carbon capture on ***geologic time scales***.
  - Natural analog studies provide validation to laboratory and model results

MISSOURI S&T University of Science & Technology

Project Overview:
Goals and Objectives

- Project goals and objectives for support to DOE program objectives for long-term carbon retention.
  - Success criteria:
    - Number of undergraduate & graduate students integrated into field investigations (176) and laboratory research (12).
    - Demonstrate carbonate mineralization processes in laboratory and field studies for as an aid in predicting retention of injected CO_2 --- both site specific reactions and mineral specific reactions.

MISSOURI S&T University of Science & Technology

Technical Status

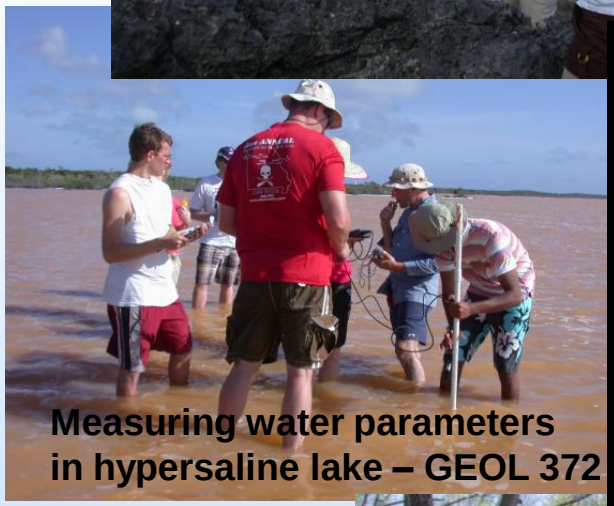
1) Education & Training of Students – Tomorrow's workforce in CO_2 sequestration

- Students from diverse academic disciplines: Geology, Chemistry, Biology, Environmental Engineering, Geological Engineering, & Petroleum Engineering.
- Undergraduate level courses; ~90% undergrads.
- DOE funding used for purchase of field instrumentation and travel to local field sites.
  - GEOL 275 Introductory Geochemistry
  - GEOL 372 Carbonate Geology Bahamas
  - GEOL 376 Aqueous Geochemistry

MISSOURI S&T University of Science & Technology


Examination of Pleistocene-aged coral reef from past sea level rise GEOL 372


Microbialite mat from tailings pond – GEOL 376


Measuring water parameters in hypersaline lake – GEOL 372

Enhancing the Educational Experience Through Curriculum Development & Research

Number of Students Affected

	2010	2011	2012	Total
GEOL 275-Introductory Geochemistry	42	59	55	156
GEOL 372 - Carboante Geology of Bahamas		10		10
GEOL 376 - Aqueous Geochemistry		10		10
Undergraduate Research Assistants	3	3	2	8
Graduate Students (year starting)	4			4
Totals	49	82	57	188

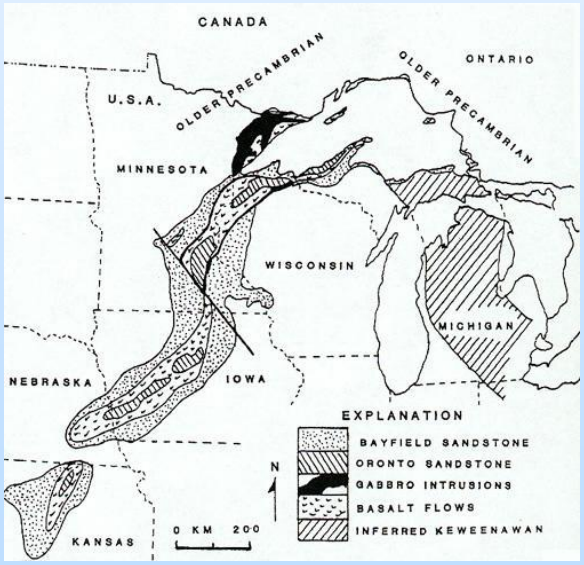

Group photograph at Maramec Spring GEOL 275


Measuring alkalinity by titration GEOL 275

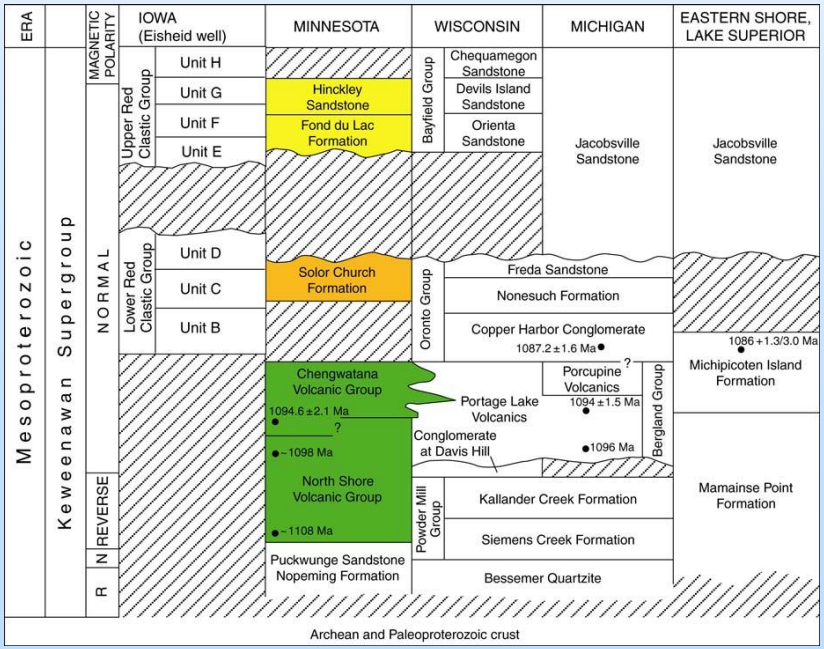
MISSOURI S&T University of Science & Technology

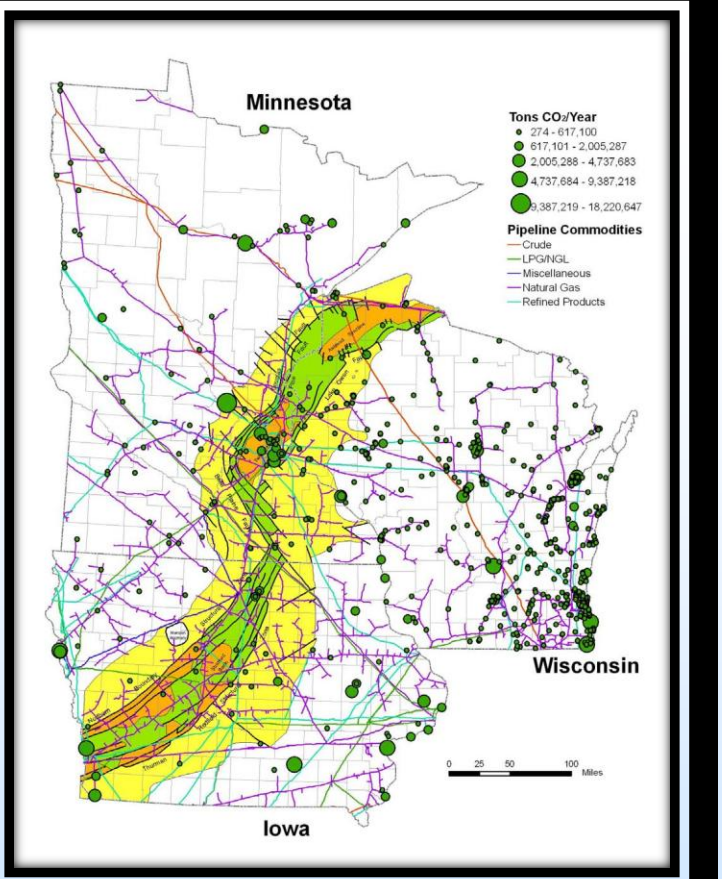
Technical Status

- 2a) Graduate Student Research Projects
  - Investigating the potential of the Midcontinent Rift (MCR) sequence for CO_2 sequestration (Alsedik Abousif).
    - 1.1 billion year old failed rift system.
    - Two arms: SW trend into Kansas & SE trend into Michigan.
    - Lake Superior exposure sedimentary and volcanic rocks (basalt).



LaBerge, 1994





Point sources for CO_2 & pipelines relative to the Midcontinent Rift (Chandler et al., 1989). Bayfield Group in yellow, Oronto Group in orange, and volcanic rocks in green.

Advantageous Features:

- Large target - rift basin trends through six or more Midwest states.
- Ca-, Mg-, & Fe-rich minerals will promote carbonate precipitation following alteration (Oronto Group and basal volcanics).
- MCR basin compartmentalized into numerous fault bounded sub-basins.
- Nonesuch Formation shale and siltstone represents potential confining unit.
- Most of sequence buried >2500' depth.

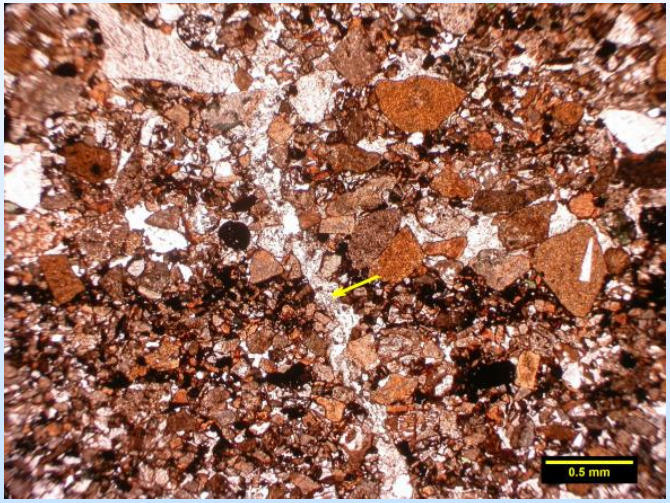
Concerns:

Low porosity & permeability of Oronto Group sediments may limit injection volume/rate (Minnesota Geol. Survey Open File Report OFR-08-01, 2008).

MISSOURI S&T University of Science & Technology

Technical Status

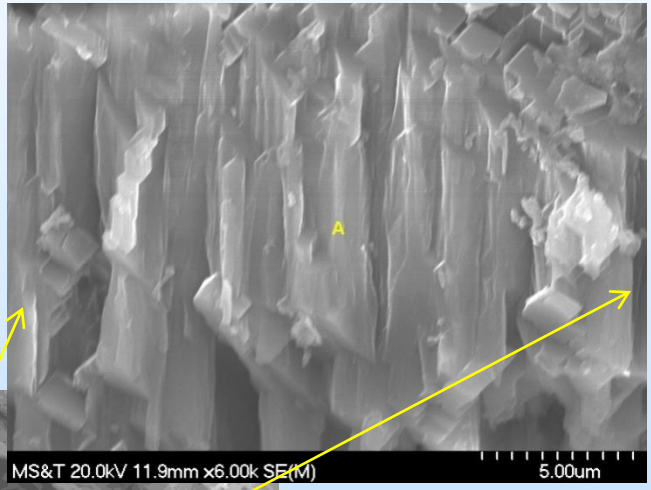
– ***Near Field Reactions:*** acidified water reacts with calcite, zeolite, and epidote cement in pores and fractures – permeability increase.

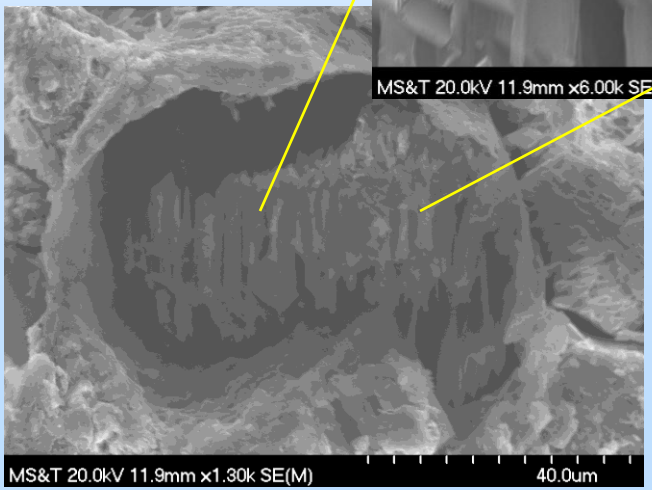


Pore and fractures filled with calcite (arrow) in Copper Harbor Conglomerate.

Average porosity of sandy matrix samples = 5.4 +/- 4.5%, with additional 13 +/- 5% calcite cement.

Preferential dissolution of pore-filling calcite 143 hrs., 90°C, CO_2 + DIW





MISSOURI S&T University of Science & Technology

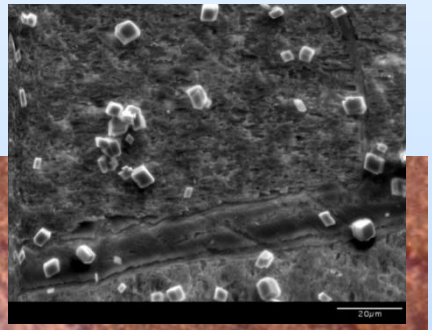
Technical Status

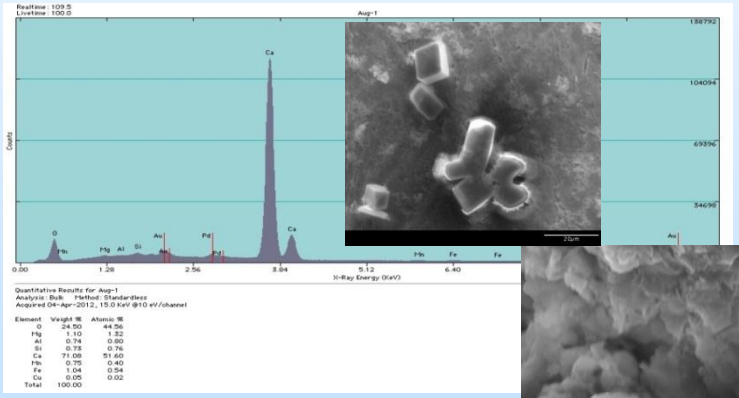
- ***Near Field Reactions:*** Dissolution of pore cement will increase surface area exposure of sediment grains, increasing reaction rates.
  - Sample KEW4-2 (Copper Harbor Conglomerate); reacted 2106 hours at 90^{o}C; in CO_2 + DIW
    - Ca release = 4.15E-03 moles / cm^2
    - Mg release = 6.25E-04 moles / cm^2
    - Leachate Ca/Mg molar ratio 7:1 << calcite cement Ca/Mg ratio 185:1
    - Excess Mg release from dissolution of pyroxenes, amphiboles, and/or phyllosilicates.

MISSOURI S&T University of Science & Technology

Technical Status

– ***Far Field Reactions:*** Precipitation of dissolved mineral components (Ca^{2+} Mg^{2+}) as carbonate minerals following dissolution of olivine, augite–pyroxene, and MCR sedimentary rocks.

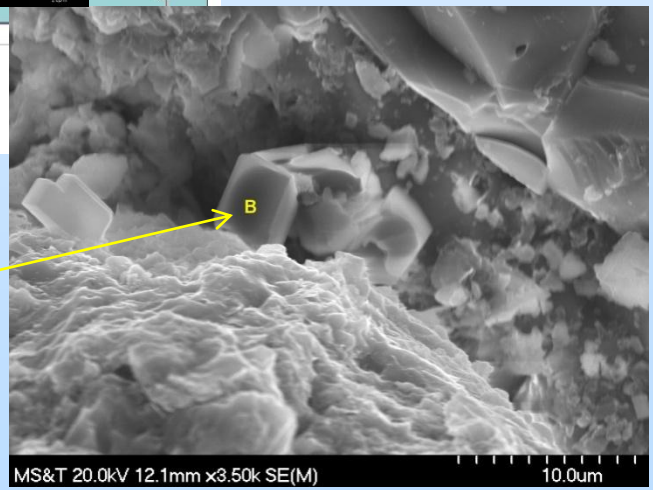




Ca-carbonate precipitation on reacted augite 236 hr. 90°C

Mg-carbonate precipitation on reacted olivine 236 hr. 90°C

Ca-carbonate mineral precipitation on reacted MCR sample 2446 hours 90°C



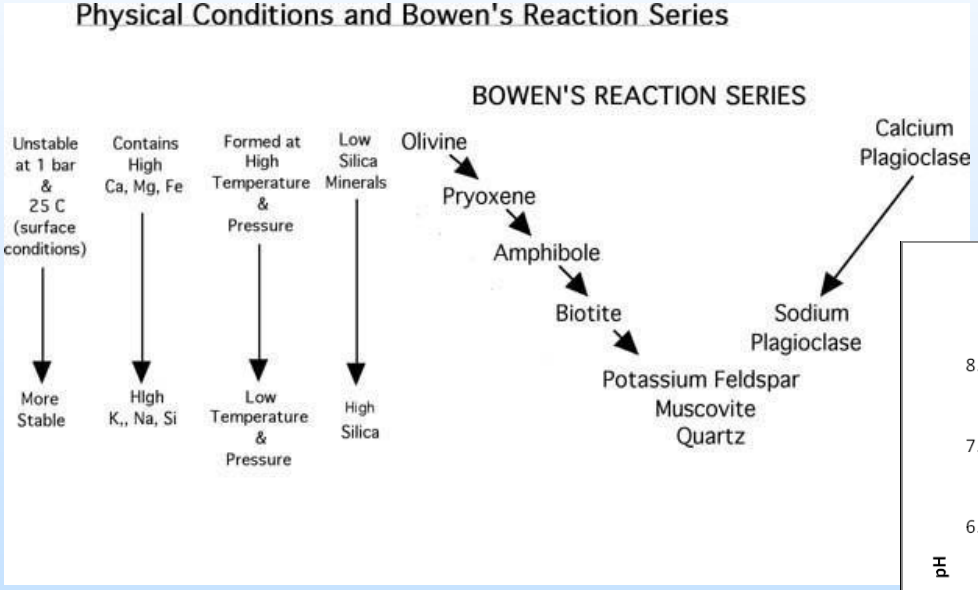
Technical Status

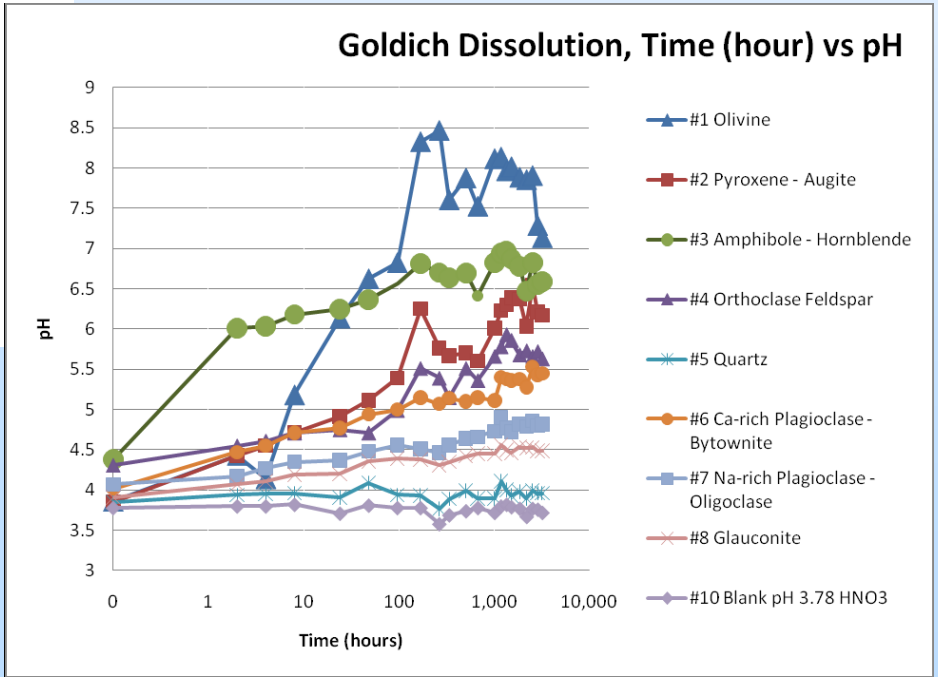
- *Near Field-Far Field* ⇔ dissolution-precipitation reactions in experiments match modeled results of Knauss et al., 2005 for the Frio Formation.
- Calcite cement dissolution followed by reprecipitation is a *zero gain* carbon capture process, cement dissolution may however:
  - Connect isolated pores.
  - Increase surface area exposure of sediment grains leading to increased dissolution rates.
  - Provide additional accommodation space for carbonates through accelerating dissolution of sediment particles.

MISSOURI S&T University of Science & Technology

Technical Status

– Additional quantitative assessment on mineral dissolution rates is needed.



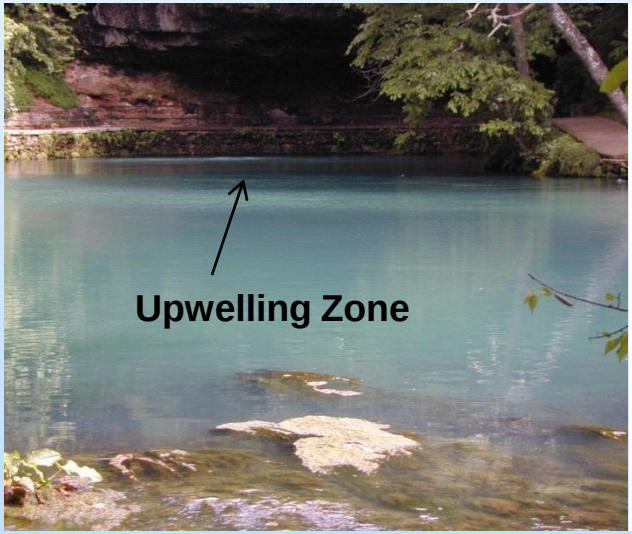


MISSOURI S&T University of Science & Technology

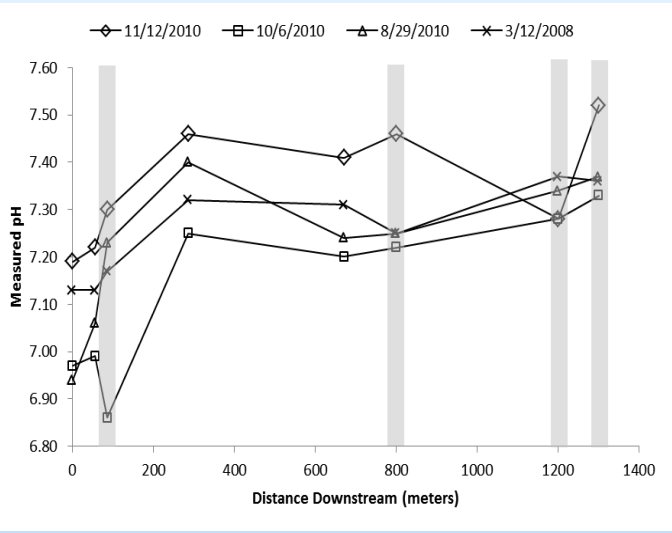
Technical Status

– 2b) Graduate Student Research Projects

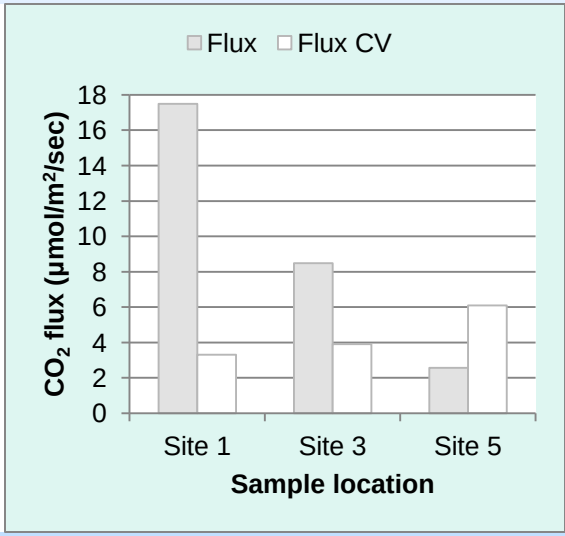
- Maramec Spring, Missouri – natural analog for CO_2 leakage (Kyle Rybacki).
- Cold water (~14^{o}C) Ca-Mg-bicarbonate system.
- Water upwelling from estimated depth of ~400'.



Turbidity produced at Maramec Springs point of upwelling



pH rise moving downstream from upwelling zone

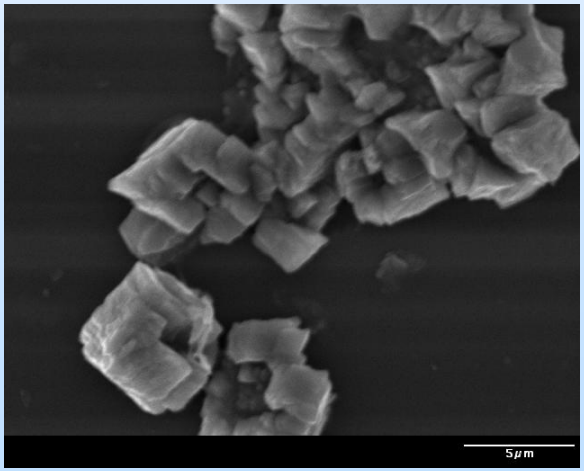


Decreasing CO_2 loss moving downstream from upwelling

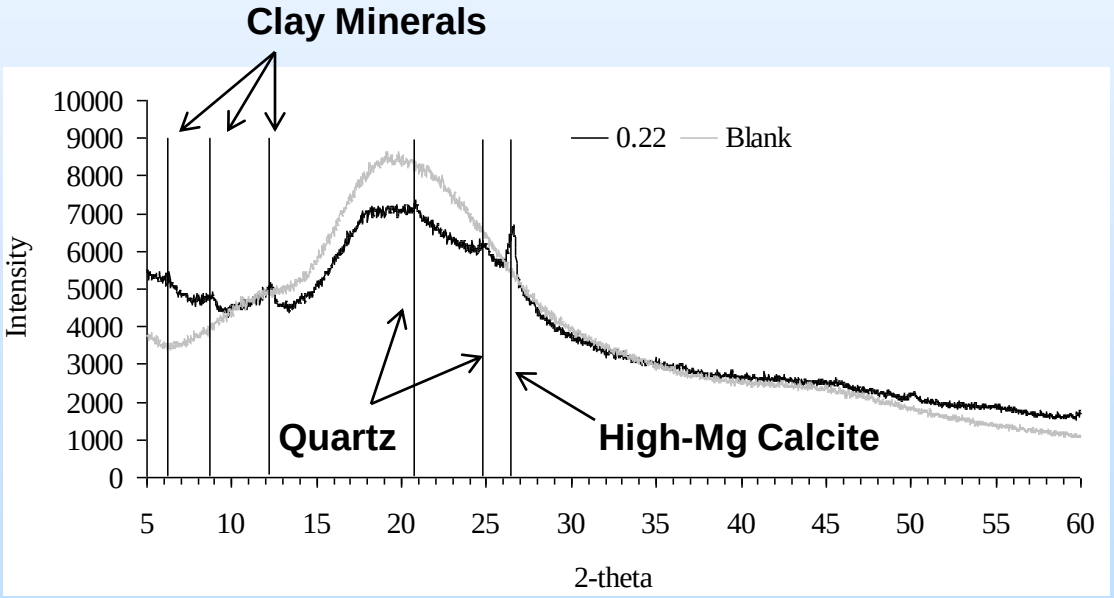
Technical Status

– 2b) Graduate Student Research Projects

- CO_2 loss $\rightarrow$ pH rise results in saturation for calcite.
- Rhombohedral calcite grains (~8 mole% Mg) captured by: 1) centrifuging, and 2) filtering trapping.



Rhombohedral calcite crystals From Maramec Spring



X-Ray diffraction 2θ angles of 6.3°, 8.8°, 12.3°, 20.8°, 24.8°, and 26.6°, 29.7. "Blank" refers to the spectra collected from unused 0.22 µm filter.

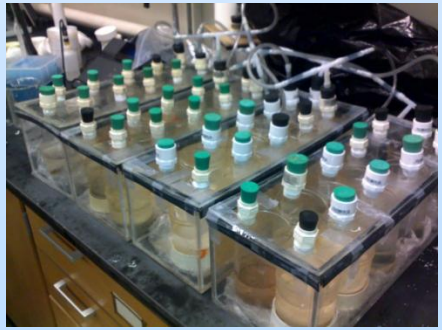
Technical Status

- 2c) Graduate Student Research Projects
  - Carbonate biomineralization in aphotic zones (Varun Paul).

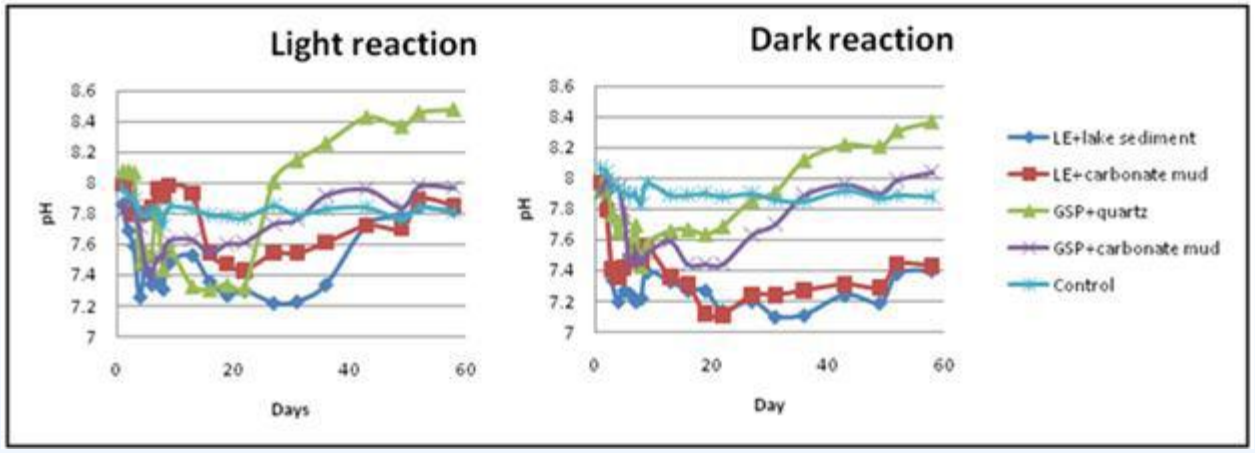
    $SO^{2-}_4 + 2[CH_2O] + OH^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + 2H_2O + HS^-$
  - Sulfur reducing bacteria (SRB) enrichments:
    - Lake Estancia, NM - subsurface sediments
    - Great Salt Plains Lake, OK - subsurface sediments
    - Storr's Lake Bahamas – high turbidity hypersaline lake

SRB enrichment - sulfides as black precipitates

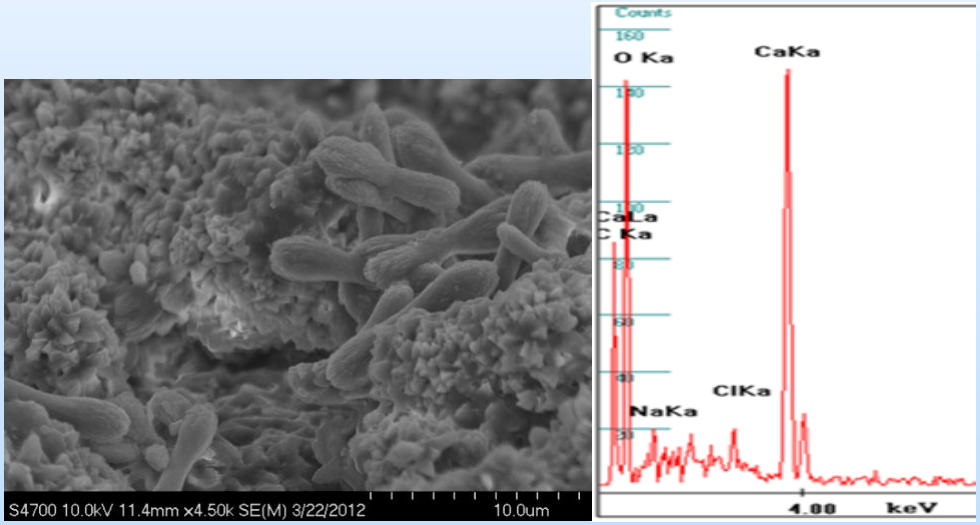
- artificial Seawater-20^{o}C
- microbe inoculations
- quartz vs. carbonate substrate
- 24 hr. light vs. dark
- 390 vs. 1200 ppm CO_2



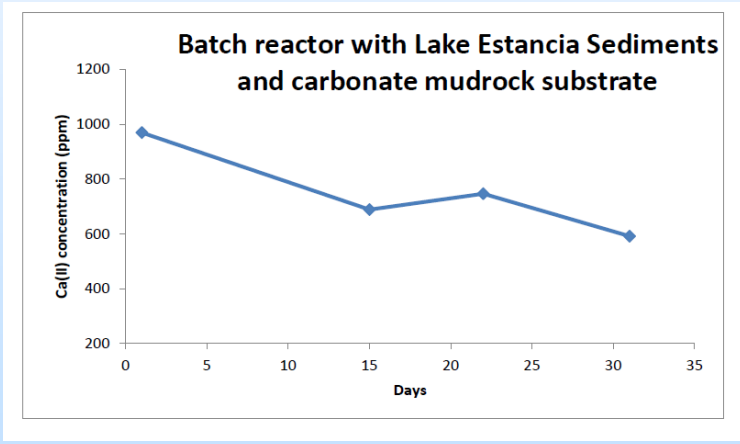
MISSOURI S&T University of Science & Technology



Variable pH trends for batch reactors with SRB enrichments from Lake Estancia (LE) and Great Salt Plains (GSP).



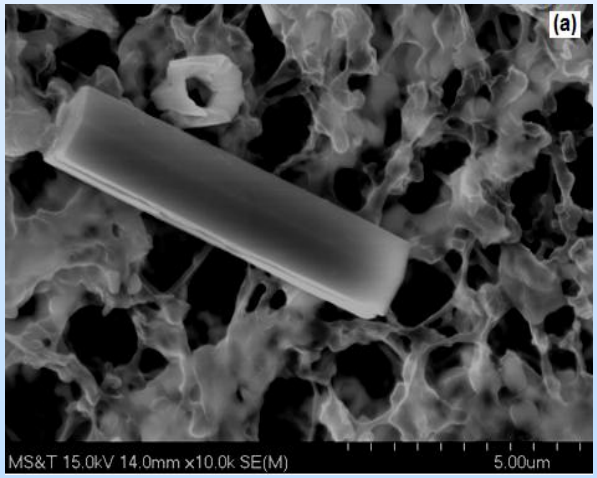
Dumbbell- and rhombohedron-shaped carbonates deposited on quartz. Batch tests with Lake Estancia cultures.



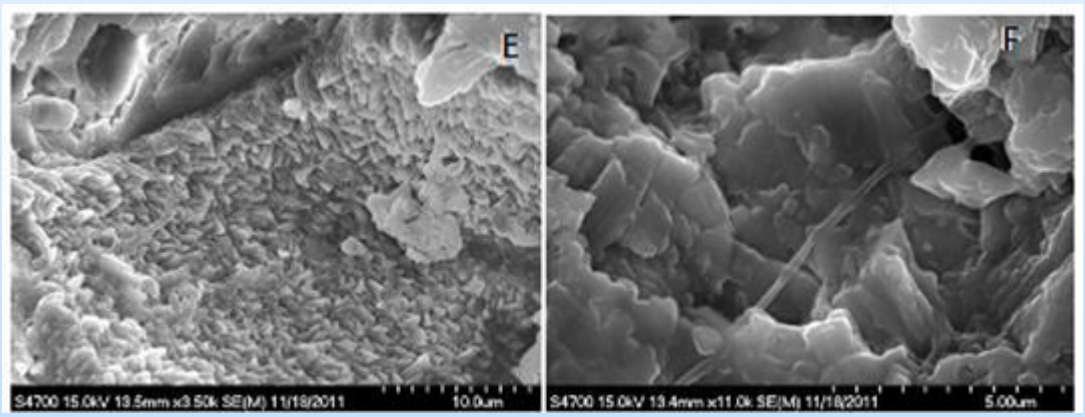
Decrease in aqueous Ca content during testing with Lake Estancia Sediments.

Technical Status

- 2c) Graduate Student Research Projects
  - Dumbbell carbonate morphology often associated with incipient biogenic formation of carbonates:
    - Dolomite (Warthmann et al., 2000; Van Lith et al., 2003)
    - Aragonite (Krumbein et al., 1977)



Twinned hexagonal Ca carbonate from Lake Estancia culture. Substrate is cellulose acetate filter.



Internal cavity of stromatolite from Storr's Lake. Elongate microbial form entombed by calcium carbonate.

Accomplishments to Date

- Funding for travel and instrumentation enhanced the educational experience for 176 students enrolled in courses and 12 research students; 186 total.
- MCR - attractive *chemical system* for mineral sequestration, but hindered by *low porosity-permeability*. Dissolution of calcite and other cement material will improve porosity-permeability features.
- Maramec Springs as analog for leaking CO_2 system.
  pressure decrease $\rightarrow$ CO_2 loss $\rightarrow$ pH increase $\rightarrow$ calcite precipitation
- Carbonate mineralization rate enhanced in the presence of Lake Estancia microbial community.

MISSOURI S&T University of Science & Technology

Summary

- Key Findings:
  - Combined porosity + cement in MCR – Oronto Group ≈18%. Cements rapidly dissolve in presence of carbonic acid, increasing permeability and increasing surface area exposure of reactive sedimentary grains.
  - Carbonate mineralization is expected in both *far field* migration of injection fluids and following pressure decrease associated with leakage.
- Continuing Research:
  - Quantify rock/mineral dissolution rates, changes in permeability, and net mineralization process for MCR sequence.
  - Testing with deep well MCR samples from Iowa and Kansas
  - Identify microbialite communities involved in mineralization process – gene sequencing
  - Identify role of organic carbon vs. bicarbonate in mineralization.

MISSOURI S&T University of Science & Technology

Acknowledgments

- Melanie Mormile – Biological Sciences Department, MS&T
- Graduate Students – Alsedik Abousif, Varun Paul, Kyle Rybacki, & David Davison
- Kansas & Iowa Geological Surveys for providing MCR well samples
- DOE – NETL for funding

Appendix

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

MISSOURI S&T University of Science & Technology

Organization Chart

- Project Team
  - Missouri University of Science & Technology, Department of Geological Sciences and Engineering
  - David J. Wronkiewicz PI and faculty mentor
  - Graduate Students (4 total):

- Varun Paul; Ph.D. student - biomineralization processes in carbonate systems.
- Alsedik M. Abousif; Ph.D. student – Study of the Midcontinent Rift System
- David Davison; M.S. Student – Study of Lamotte Formation sandstone
- Kyle Rybacki; M.S. Student – Geochemical processes at Maramec Springs (graduated).

  - Undergraduate Student Assistants (8 total):

- Joshua Silverstein, Hang Deng, Airin Price, Hanani Tajul Nahar, Robert Swain, Coleen Conrad, Thomas Herbst, & Rebecca Nuckolls -

MISSOURI S&T University of Science & Technology

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.

MILESTONE STATUS REPORT

Task/ Subtask #	Project Milestone Description*	Project Duration - Start: / End												Planned Stary Date:	Planned End Date:	Actual Start Date:	Actual End Date:
		Year (PY) 1				PY 2				PY 3							
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12				
Enhancement Undergrad. Curriculum																	
1a	Intro. Geochemistry	√	√			√	√			√	√			January	May	1/1/2010	5/7/2012
1b	Field Studies-Bahamas					√	√							1/1/2011	6/1/2011	1/1/2011	6/1/2011
1c	Aqueous Geochemistry							√	√					8/1/2011	12/20/2011	8/1/2011	12/20/2011
Training Through Student Research																	
2-1a	MidContinent Rift West Arr	√	√	√	√	√	√	√	√	√				8/1/2010	12/31/2011	1/1/2010	
2-1b	MidContinent Rift East Arm									√	√	√		8/1/2011	12/31/2012	12/31/2011	
2-1c	Lamotte Formation	√	√	√	√	√	√	√	√					1/1/2010	12/31/2011	1/1/2010	12/31/2011
2-2a	Long-term Mineral Trapping			√	√	√	√	√	√	√	√	√		6/1/2010	12/31/2012	6/1/2010	
2-2b	Dissolution Processes	√	√	√	√	√	√	√	√	√	√			1/1/2010	12/31/2011	1/1/2010	
2-2c	Self-Sealing Fractures				√	√	√	√	√	√	√	√		1/1/2011	12/31/2012	10/15/2010	

MISSOURI S&T University of Science & Technology

Bibliography

- Journal:
  - Fang, Y., Bai, B., Dazhen, T., Dunn-Norman, S., and Wronkiewicz, D., 2010, Characteristics of CO_2 sequestration in saline aquifers. *Petroleum Science* v. 7, p. 83-92, available at http://www.springerlink.com/content/y40t761146488p11/fulltext.pdf

- Masters Thesis:
  - Rybacki, K.S., 2010, Calcium carbonate precipitation mechanisms and geochemical analysis of particulate material found within the waters of Maramec Spring, St. James, Missouri. Masters Thesis, Missouri University of Science & Technology.

- Abstracts:
  - D.J. Wronkiewicz, V.G. Paul, and E. Bohannan: Changes in aragonite/calcite & Ca/Mg Ratios in Microbialite Deposits of Storr's Lake, San Salvador Island, The Bahamas. The 16th Geology Conference, The College of the Bahamas, Gerace Research Centre, San Salvador Island, Bahamas, 6/15/12.
  - Paul, V.G., Wronkiewicz, D.J. and Mormile, M.R., Characterization of Modern Microbialites of the Storrs Lake Ecosystem, The 16th Geology Conference, The College of the Bahamas, Gerace Research Centre, San Salvador Island, Bahamas, 6/15/12.
  - Paul, V.G., Wronkiewicz, D.J., Mormile, M.R., and Sanchez-Botero, C.A., Modern Microbialites of Storr's Lake, San Salvador Island, Bahamas, Missouri S&T Graduate Student Showcase, Rolla, MO, 4/17/12 (Student won 2nd Place Award Campus Poster Session).

Bibliography (cont.)

- **Abstracts (cont.):**
  - Herbst, T., Nahar-Nurul, H., Swain, R., and Wronkiewicz, D.J., Investigation of Mineral Weathering Products Following CO_2 Injection and High Pressure Tests, Missouri S&T Undergraduate Student Showcase, Rolla, MO, 4/10/12.
  - Paul, V.G., Wronkiewicz, D.J., and Mormile, M.R., Sulfate Reducing Bacteria and Their Potential Role in CO_2 Sequestration. American Society of Microbiology Warrensburg, Missouri 3/31/2012.
  - Paul, V.G., Wronkiewicz, D.J., and Mormile, M.R., Biomineralization of carbonates in modern microbial sediments, Geol. Soc. America, Minneapolis, MN, 10/10/11. https://gsa.confex.com/gsa/2011AM/finalprogram/abstract_197955.htm
  - Wronkiewicz, D.J., and Rybacki, K.S., Processes controlling Mg-calcite colloid precipitation within Maramec Spring, Missouri, Geol. Soc. America, Minneapolis, MN, 10/11/11. https://gsa.confex.com/gsa/2011AM/finalprogram/abstract_198154.htm
  - Abousif, A.M., and Wronkiewicz, D.J., Mineralogical and geochemical attributes of the Midcontinent Rift: Application as a target for CO_2 sequestration, Geol. Soc. America, Minneapolis, MN, 10/12/11. https://gsa.confex.com/gsa/2011AM/finalprogram/abstract_197878.htm
  - Paul, V.G., Wronkiewicz, D.J. and Mormile, M.R., Biomineralization of carbonates in modern microbial sediments and its application in CO_2 sequestration**,** American Inst. Professional Geologists (AIPG) Bloomingdale, IL, 9/14/11.
  - Fang, Y., Bai, B., Dunn-Norman, S., and Wronkiewicz, D.J., Modeling CO_2 Injection in the Lamotte Formation, Southwest Missouri, Geol. Soc. America, Branson Missouri, 4/12/10. https://gsa.confex.com/gsa/2010NC/finalprogram/abstract_171452.htm

Bibliography (cont.)

Abstracts (cont.):

- Davison, D.A., and Wronkiewicz, D.J., Potential Geochemical Reactions from Carbon Sequestration in the Lamotte and Bonneterre Formations in Southwest Missouri, Geol. Soc. America, Branson Missouri, 4/12/10. https://gsa.confex.com/gsa/2010NC/finalprogram/abstract_171394.htm
- Rybacki, K.B. and Wronkiewicz, D.J., Calcium Carbonate precipitation induced by CO2 degassing and pH changes at Maramec Spring, Missouri, Geol. Soc. America, Portland, OR October, 2009.

- Chaired Meeting Sessions:
  - David J. Wronkiewicz co-chaired Geological Society of America sectional meeting in Branson, Missouri on 4/12/10. Nine abstracts were presented in the session.

MISSOURI S&T University of Science & Technology

Bibliography (cont.)

- Papers in Preparation for Future Submission:
  - Abousif, A.M. and Wronkiewicz, D.J., Carbonate Dissolution and Precipitation during Mineral-Water-CO_2 Interactions: Potential for Enhanced Porosity and Permeability during CO_2 Sequestration in the Midcontinent Rift, To be submitted to: *Environmental Science and Technology.*
  - Paul, V.G., Wronkiewicz, D.J., and Mormile, M.R., Influence of Sulfate Reducing Bacteria on Carbonate Precipitation and Potential Impact on CO_2 Sequestration. To be submitted to: *Environmental Science and Technology.*
  - Rybacki, K.B. and Wronkiewicz, D.J. Processes controlling Mg-calcite colloid precipitation within Maramec Spring, Missouri, To be submitted to: *Chemical Geology*
  - D.J. Wronkiewicz, V.G. Paul, and E. Bohannan: Changes in aragonite/calcite & Ca/Mg Ratios in Microbialite Deposits of Storr's Lake, San Salvador Island, The Bahamas. The 16th Geology Conference. Proceedings volume to be published following Gerace Research Centre conference in June 2012.
  - Paul, V.G., Wronkiewicz, D.J. and Mormile, M.R., Characterization of Modern Microbialites of the Storrs Lake Ecosystem, The 16th Geology Conference. Proceedings volume to be published following Gerace Research Centre conference in June 2012.

MISSOURI S&T University of Science & Technology