Training Students in Simulation & Risk Assessment for Carbon Sequestration

DE-FE0002059

John McCray

Department of Civil and Environmental Engineering

COLORADOSCHOOL**OF**MINES
EARTH ● ENERGY ● ENVIRONMENT

Presentation Outline

- Benefits to Program

- Project Overview: Goals, objectives, tasks

- Accomplishments

- Technical Status and Findings

- Summary: Lessons Learned & Future Work

- Bibliography

Benefit to the Program

Program goals being addressed.

- Develop technologies that will support industries' ability to predict CO_2 storage capacity in geologic formations to within ± 30 percent.

From the RFP: "… provide training opportunities for graduate and undergraduate students that will provide the human capital and skills required for implementing and deploying CCS technologies. Training can be accomplished through fundamental research ….   Fundamental research is needed to advance science in: simulation and risk assessment; …. verification, and accounting; ….and integrity for long-term CO_2 storage and capture.

Benefit to the Program

Benefits are related to both <u>training</u> and <u>research</u>.

<u>Training</u>:

- Train advanced professionals to enter the CCS field

<u>Research</u>:

- Enhance public confidence in sequestration (maintain license to operate and reduce costs)
- Reduce environmental footprint

Project Overview:
Goals and Objectives

The primary objectives of the project are to *train students* and *advance the science* in two critical areas of risk assessment:

(1) multi-process, multi-scale model simulation: risks associated with leakage into overlying aquifers;

(2) pore-scale geochemical processes in CO_2 sequestration needed to assess the environmental impact and the likelihood of an successful sequestration effort.

Project Overview:
Goals and Objectives

Success criteria:

- MS students complete thesis & receive graduate degrees

- PhD student completes dissertation, & receives PhD degree.

- Post-doctoral researcher achieves career position

- Simulations and experiments are completed.

- 5 peer-reviewed journal articles are submitted/accepted (goal: 1 per MS student and 3 per PhD student)

Accomplishments to Date

- – Alexis Sitchler (PhD Penn State) has received training as a project manager for this project, and recently agreed to a tenure-track faculty position in the Geology & Geological engineering Dept at CSM. She will continue a career in GCS research.

- – Erica Siirilla (B.S. Univ. Colorado) completed PhD degree in May 2013.   Moving to Post-doc position in Spain.

- – Hannah Menke (B.S. Columbia Univ) completed her M.S. degree (Environmental Engineering). Currently in PhD program in CCS at Imperial College (London).

- – Katy Kirsch (BS Middlebury College) completed M.S. Thesis (Hydrology) in May.

Accomplishments to Date

- Developed and delivered (twice) a graduate-level course on carbon sequestration, focusing on fundamental applied concepts and papers from the literature.   More than 35 graduate students received training via course.

- 2 M.S. Theses completed (Siirilla and Menke)

- 5 peer-reviewed papers completed.

- Risk assessment methodology created.

- Experimental protocol developed, experiments complete

Technical Status

Because this is a training grant, we have arranged this section by student:

- Erica Siirilla
- Hanna Menke
- Katie Kirsch

- Will focus on the work of Katy Kirsch (presented other work last year)

Overview: Development of a Quantitative Human Health Risk Framework for CO_2 Leakage
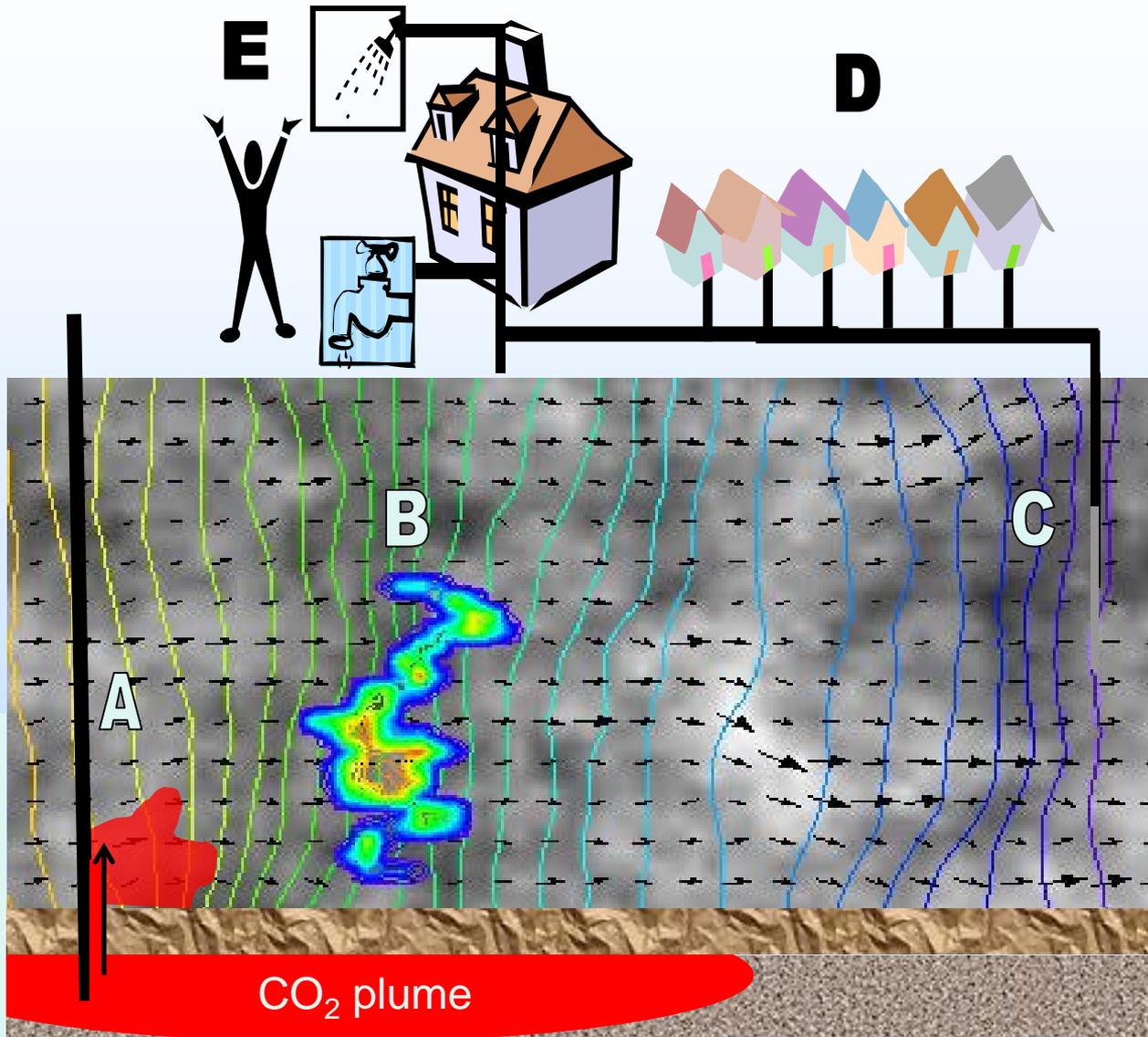
A: CO_2 leakage and dissolution of metals

B: Heterogeneous flow and transport of metals

C: Possible capture in one or more down-gradient wells

D: Water delivery system to many different households

E: Household exposure and health risk via multiple pathways to varying individuals

CO_2 plume

A quantitative methodology to assess the risks to human health from CO_2 leakage into groundwater

Erica R. Siirila [a,c,*], Alexis K. Navarre-Sitchler [b], Reed M. Maxwell [a,c], John E. McCray [b,c]

[a] Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, United States
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[c] Hydrologic Science and Engineering Program, Colorado School of Mines, Golden, CO 80401, United States

ARTICLE INFO

ABSTRACT

Leakage of CO_2 and associated gases into overlying aquifers as a result of geologic carbon capture and sequestration may have adverse impacts on aquifer drinking-water quality. Gas or aqueous-phase leakage may occur due to transport via faults and fractures, through faulty well bores, or through leaky confining materials. Contaminants of concern include aqueous salts and dissolved solids, gaseous or aqueous-phase organic contaminants, and acidic gas or aqueous-phase fluids that can liberate metals from aquifer minerals. Here we present a quantitative risk assessment framework to predict potential human health risk from CO_2 leakage into drinking water aquifers. This framework incorporates the potential release of CO_2 into the drinking water aquifer; mobilization of metals due to a decrease in pH; transport of these metals down gradient to municipal receptors; distributions of contaminated groundwater to multiple households; and exposure and health risk to individuals using this water for household purposes. Additionally, this framework is stochastic, incorporates detailed variations in geological and geostatistical parameters and discriminates between uncertain and variable parameters using a two-stage, or nested, Monte Carlo approach. This approach is demonstrated using example simulations with hypothetical, yet realistic, aquifer characteristics and leakage scenarios. These example simulations show a greater risk for arsenic than for lead for both cancer and non-cancer endpoints, an unexpected finding. Higher background groundwater gradients also yield higher risk. The overall risk and the associated uncertainty are sensitive to the extent of aquifer stratification and the degree of local-scale dispersion. These results all highlight the importance of hydrologic modeling in risk assessment. A linear relationship between carcinogenic and noncarcinogenic risk was found for arsenic and suggests action levels for carcinogenic risk will be exceeded in exposure situations before noncarcinogenic action levels, a reflection of the ratio of cancer and non-cancer toxicity values. Finally, implications for ranking aquifer vulnerability due to geologic configuration, aquifer mineralogy, and leakage scenarios are discussed.

Drawing Connections Between Geochemical Reactions and Aquifer Transport at Different Scales

(A) At the leakage source: aquifer:

- Multi-component, nonlinear geochemical reactions and fluid transport

- Run until a steady-state metal concentration and pH are achieved

?"

CO_2 plume

| Steady-state Concentration | ⟷ | Initial Concentration |
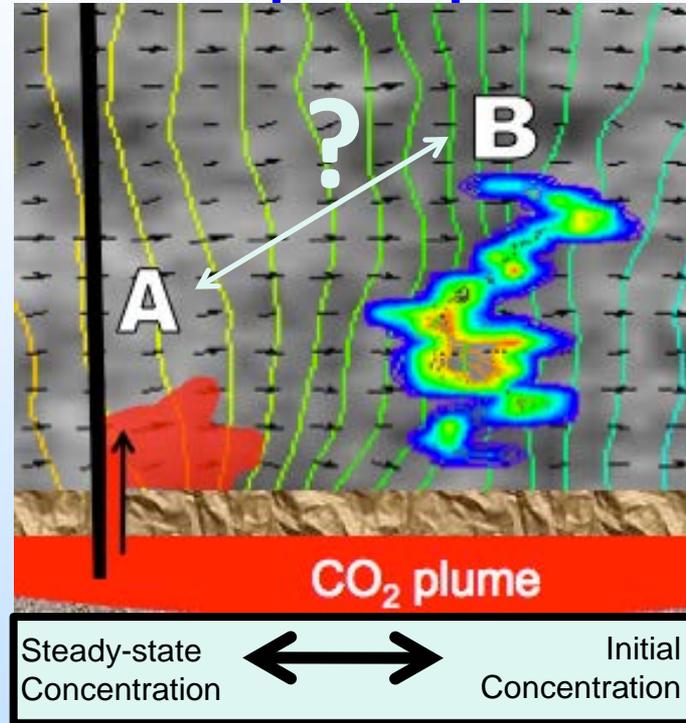
(B) Far-field

- Steady-state concentration from (A) used as initial metal concentration

- Contaminant plume modeled with a particle-tracking technique

- Linear reactions

Includes a Robust, Probabilistic Treatment of Risk:
The Nested Monte Carlo Approach

Outer, Uncertainty Loop

Stochastic Monte Carlo Simulations

Realization 3

Time (d)

Inner, Variability Loop
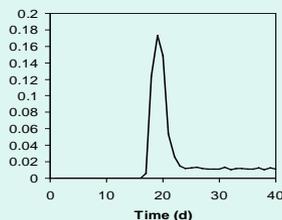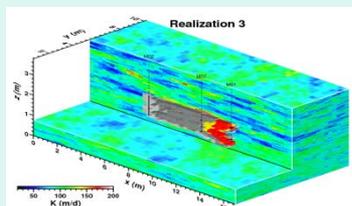
Uncertainty loop

- Calculate individual household exposure from all three pathways
- Calculate risk

- Sort risk results for variability between individuals

E

Yields Risk as a Function of Uncertainty and Variability

Example simulations show:

1. The specific metal mobilized in the event of CO_2 leakage greatly affects the outcome of risk

1. Hydrologic aquifer properties such as the degree of stratification and local dispersion greatly affect the magnitude and *distribution (i.e. uncertainty)* of risk

1. Risk is sensitive to the hydrologic flow parameters and warrants further examination in CCS risk assessment
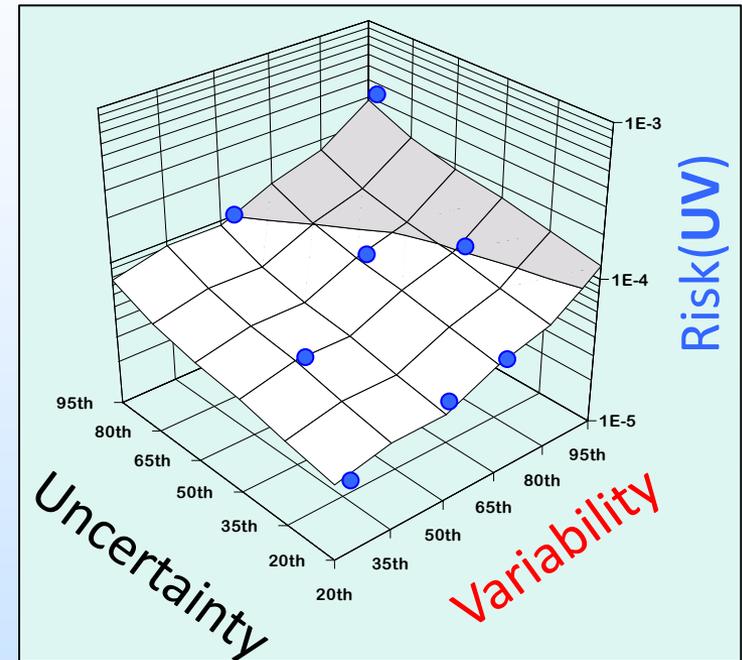
Evaluating effective reaction rates of kinetically driven solutes in large-scale, statistically anisotropic media: Human health risk implications

Erica R. Siirila[1,2] and Reed M. Maxwell[1,2,3]

[1]   The interplay between regions of high and low hydraulic conductivity, degree of aquifer stratification, and rate-dependent geochemical reactions in heterogeneous flow fields is investigated, focusing on impacts of kinetic sorption and local dispersion on plume retardation and channeling. Human health risk is used as an endpoint for comparison via a nested Monte Carlo scheme, explicitly considering joint uncertainty and variability. Kinetic sorption is simulated with finely resolved, large-scale domains to identify hydrogeologic conditions where reactions are either rate limited (nonreactive), in equilibrium (linear equilibrium assumption is appropriate), or are sensitive to time-dependent kinetic reactions. By utilizing stochastic ensembles, effective equilibrium conditions are examined, in addition to parameter interplay. In particular, the effects of preferential flow pathways and solute mixing at the field-scale (marcrodispersion) and subgrid (local dispersion, LD) are examined for varying degrees of stratification and regional groundwater velocities (v). Results show effective reaction rates of kinetic ensembles with the inclusion of LD yield disequilibrium transport, even for averaged (or global) Damköholer numbers associated with equilibrium transport. Solute behavior includes an additive tailing effect, a retarded peak time, and results in an increased cancer risk. The inclusion of LD for nonreactive solutes in highly anisotropic media results in either induced solute retardation or acceleration, a new finding given that LD has previously been shown to affect only the concentration variance. The distribution, magnitude, and associated uncertainty of cancer risk are controlled by the up scaling of these small-scale processes, but are strongly dependent on v and the source term.

Significant Findings Include:

Even when equilibrium conditions were expected based on Da number (i.e. slow groundwater velocities), the effect of kinetic reactions is apparent

- Faster breakthrough, lower peak concentration, but more tailing

- *Higher overall risk*

Equilibrium Scenario
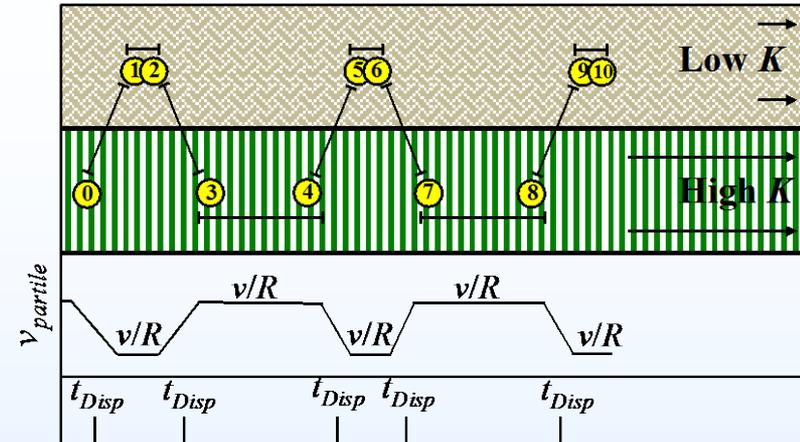
Kinetic Scenario
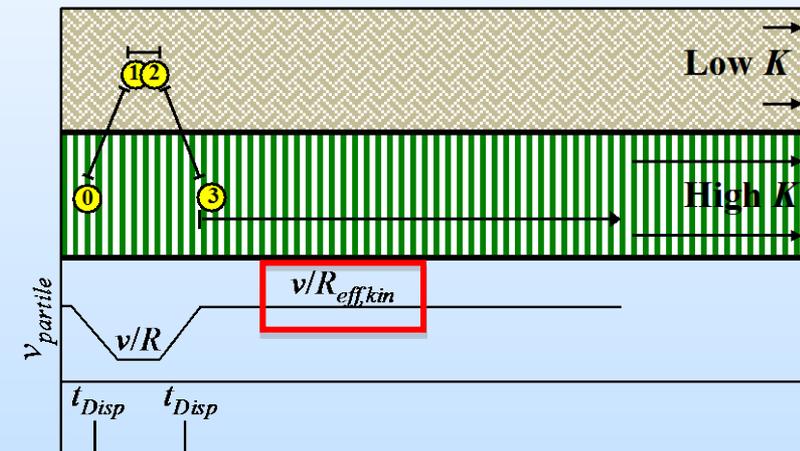
A new perspective on human health risk assessment: Development of a time dependent methodology and the effect of varying exposure durations

Erica R. Siirila [a,c,*], Reed M. Maxwell [a,b,c,1]

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ARTICLE INFO

ABSTRACT

We present a new Time Dependent Risk Assessment (TDRA) that stochastically considers how joint uncertainty and inter-individual variability (JUV) associated with human health risk change as a function of time. In contrast to traditional, time independent assessments of risk, this new formulation relays information on when the risk occurs, how long the duration of risk is, and how risk changes with time. Because the true exposure duration (ED) is often uncertain in a risk assessment, we also investigate how varying the magnitude of fixed size durations (ranging between 5 and 70 years) of this parameter affects the distribution of risk in both the time independent and dependent methodologies. To illustrate this new formulation and to investigate these mechanisms for sensitivity, an example of arsenic contaminated groundwater is used in conjunction with two scenarios of different environmental concentration signals resulting from rate dependencies in geochemical reactions. Cancer risk is computed and compared using environmental concentration ensembles modeled with sorption as 1) a linear equilibrium assumption (LEA) and 2) first order kinetics (Kin). Results show that the information attained in the new time dependent methodology reveals how the uncertainty in other time-dependent processes in the risk assessment may influence the uncertainty in risk. We also show that individual susceptibility also affects how risk changes in time, information that would otherwise be lost in the traditional, time independent methodology. These results are especially pertinent for forecasting risk in time, and for risk managers who are assessing the uncertainty of risk.

Siirilla: The Development of a Time Dependent Risk Assessment (TDRA) framework

Shaded Area: ED

Black line: Environmental concentration

Blue line: $\langle C \rangle$ average obtained from a moving ED window

$$ADD_i = \langle C \rangle_{max} \left[\frac{IN_i}{BW} \right] \frac{ED \times EF}{AT}$$

$$\sum_{i=1}^{i=p} Risk = 1 - \exp^{-(CPF_z \times ADD_i)}$$
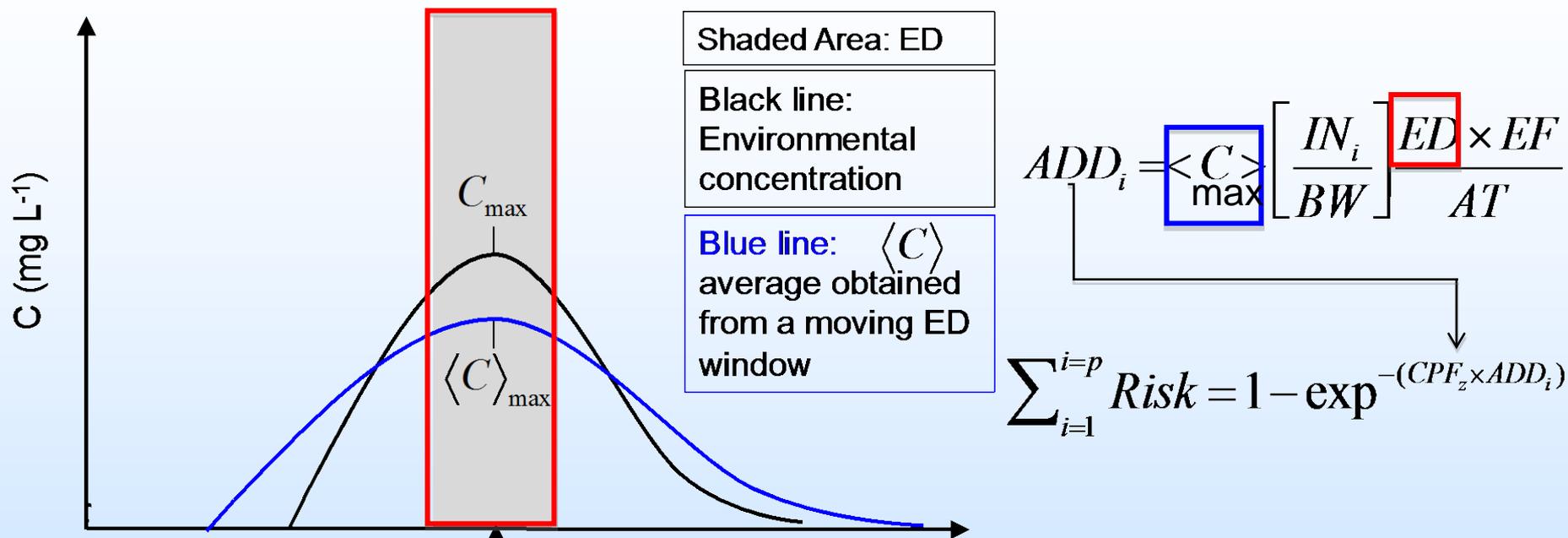
Traditional: Risk calculated during this time of contamination

1. Information on how risk changes as a function of time: d(Risk) / dt
2. A comparison of risk duration versus magnitude

Overall risk may be higher if we consider a lower exposure over a longer period of time

Understanding Multiphase Fluid Leakage through Fault Zones during Geological Carbon Sequestration Using Numerical Simulations

Paper in preparation for submission to
International Journal of Greenhouse Gas Control

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[4] Guest Scientist Los Alamos National Laboratory, Los Alamos NM, USA

[4] Pacific Northwest National Laboratory, Richland WA, USA

Menke: Numerical multiphase simulations to investigate leakage through a fault
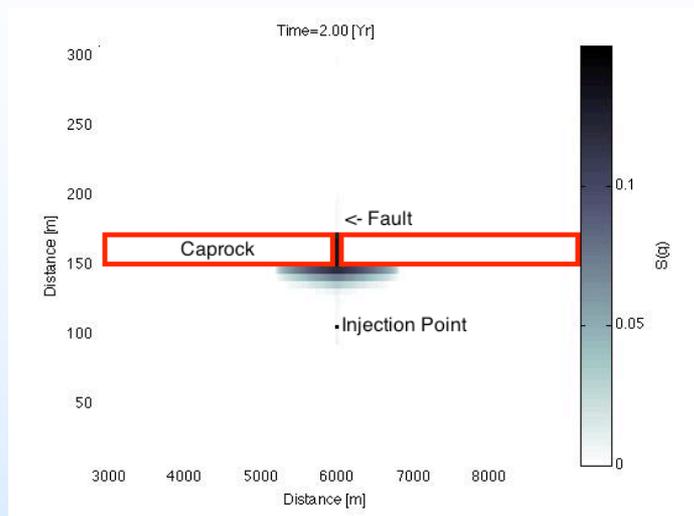
Won the best student presentation at the Front Range Consortium for Research Computing Symposium

• Simulations Conducted at Golden Energy Computing Organization (GECO). Run for 3 years of injection, then 0.5 years for pressure/saturation equilibration.

• Variables included: variations in fracture permeability, injection rate, and distance from injection to fracture.

Menke: Findings

-Initially (which might be a long time), brine leakage is significantly higher than CO2 leakage on a mass basis. We should pay attention to brine leakage.

-Brine leakage may increase for conditions where CO2 leakage decreases (lower injection pressures, further distance from fault) due to relative permeability considerations

-Leakage ends more quickly after stopping injection for lower injection rates and shorter injection periods. Suggests pulsed injection might reduce leakage risks.

CO$_2$-induced metal release from sandstones: implications for geologic carbon sequestration

Katie Kirsch,[†,‡] Alexis K. Navarre-Sitchler,[*,†,‡] Assaf Wunsch,[†,¶] and John E. McCray[†,¶]

Hydrologic Science and Engineering Program, Colorado School of Mines, USA, Department of Geology and Geological Engineering, Colorado School of Mines, USA, and Department of Civil and Environmental Engineering, Colorado School of Mines, USA

Kirsch: Dissolution Experiments with *Siliclastic Rocks*

Investigate the geochemical response of sandstone aquifers to CO_2 leakage

Outcrop of the Mesaverde Group

Samples were collected from outcrop of the Mesaverde Group in northwestern Colorado

These sandstones currently yield water to wells for local domestic and agricultural purposes, and have the potential for increased groundwater development in a water-scarce future.

(1)

(2)

(3)

Rock characterization: which minerals are likely controlling the aqueous concentration of metals?

- XRD
- SEM/EDX
- Point count
- Sequential extraction

FCC1
2% carbonate

FCC2
1% carbonate

TMM
<1% carbonate
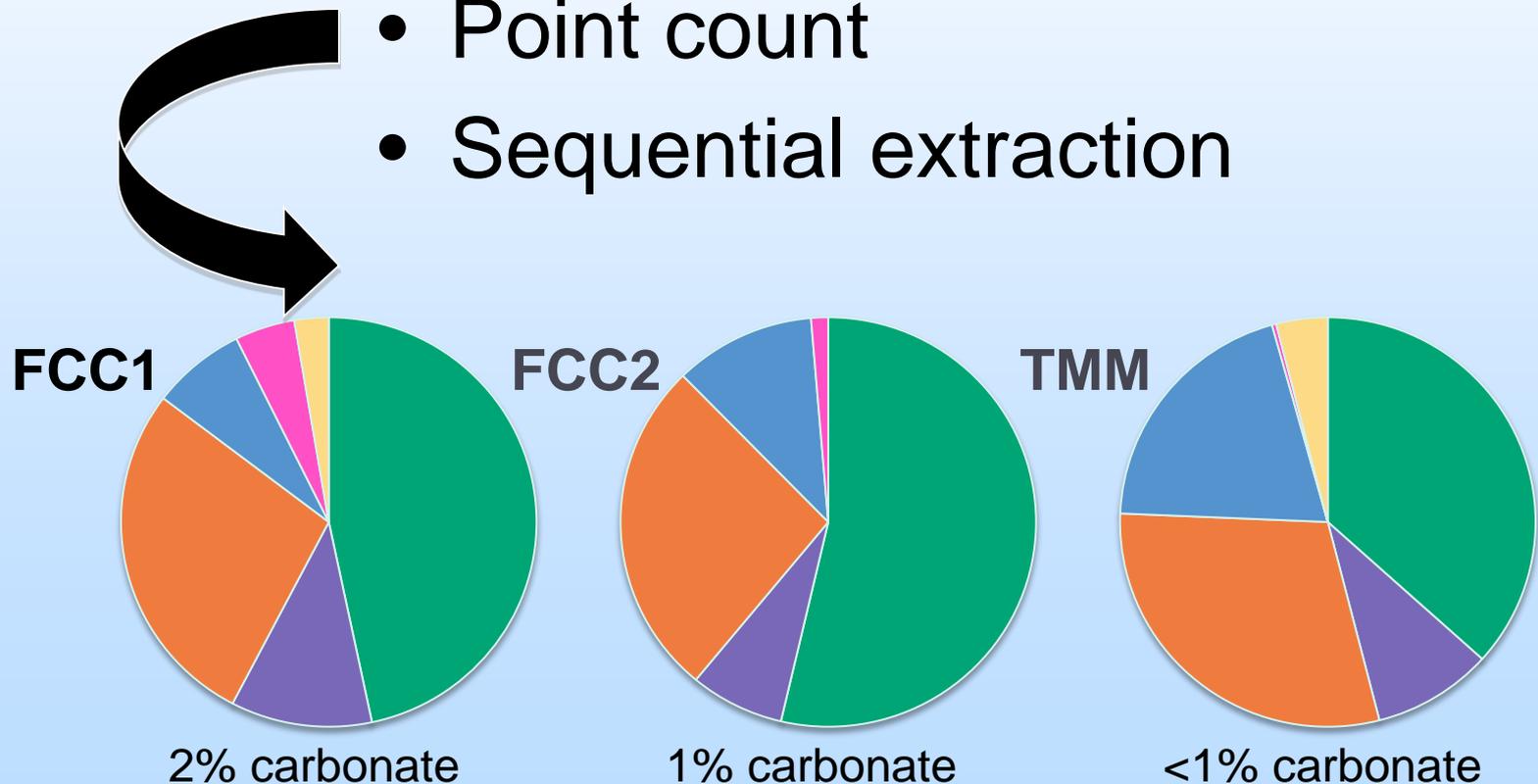
Experiments: How does the fluid composition and microbiology change with time at elevated CO_2 partial pressures?
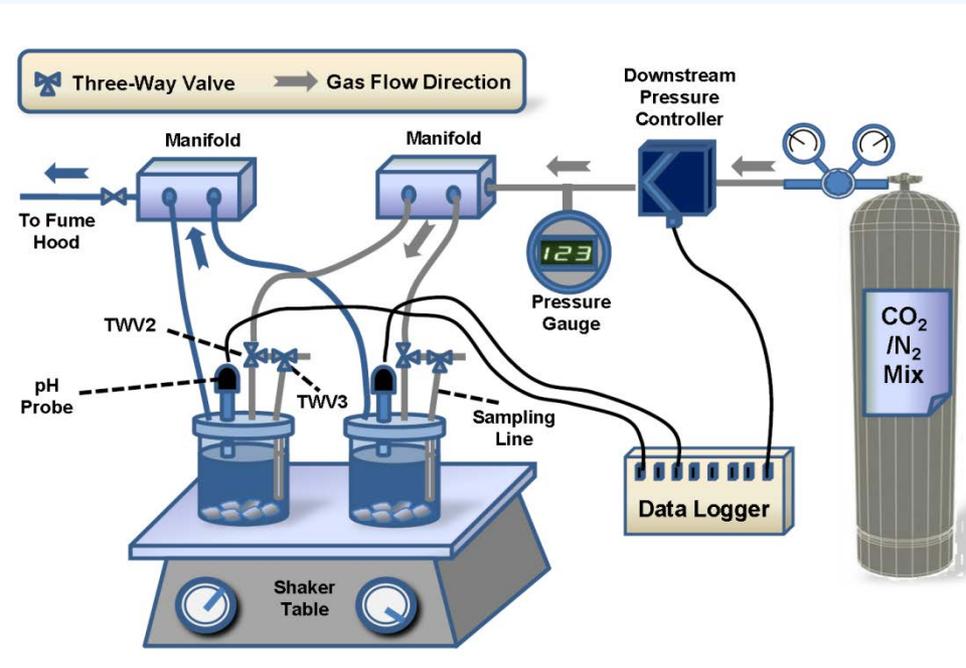

Pressures up to 1 bar above atmospheric, representative of aquifers, yet small enough to enable cost-effective experimental apparatus.

# Dissolution of carbonate minerals in silicate rock can significantly buffer pH
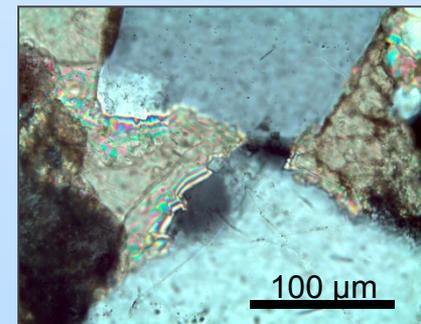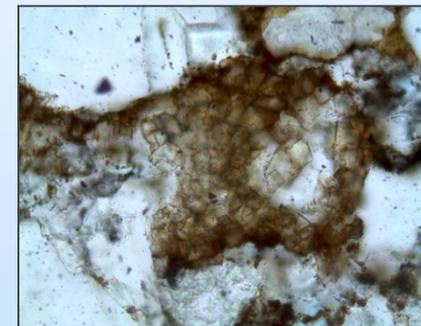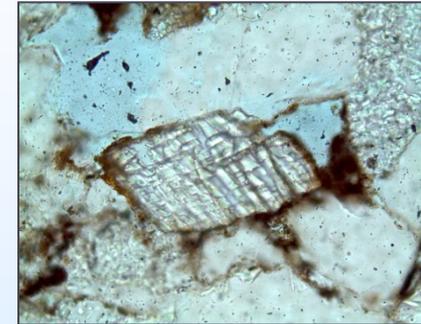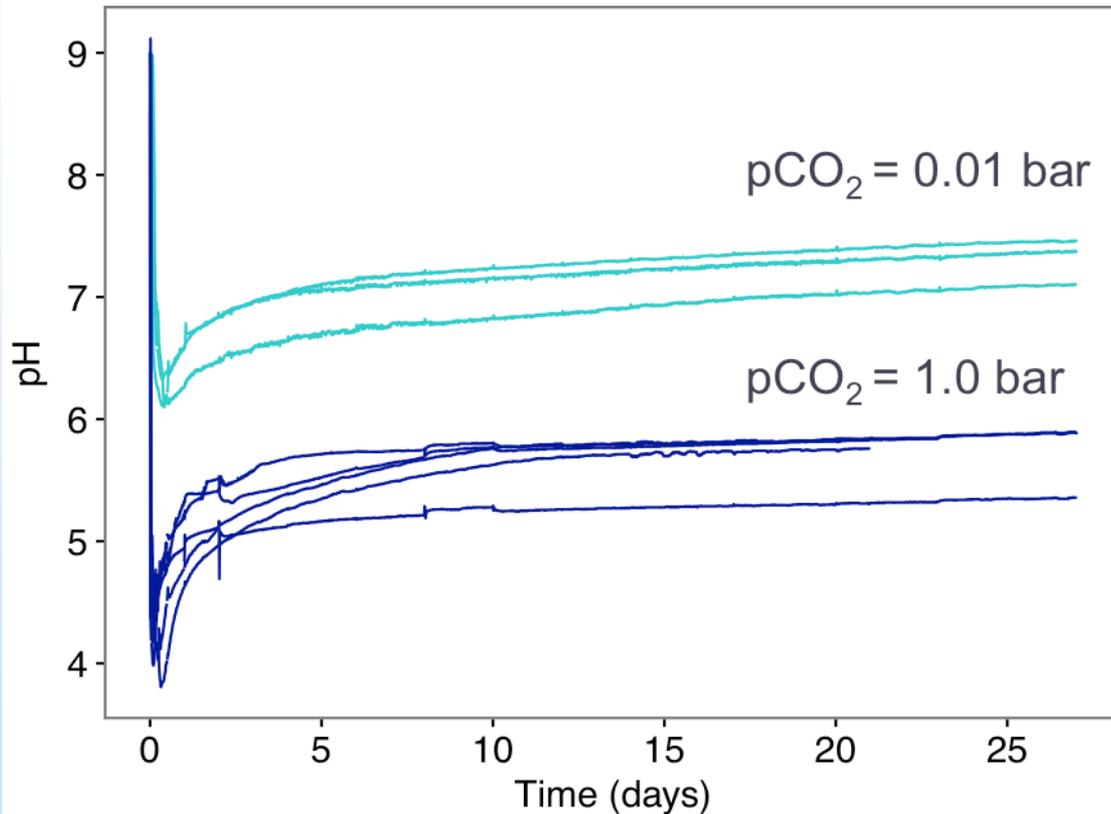
CO$_2$-acidified water induces the mobilization of metals (Note: none above MCL)
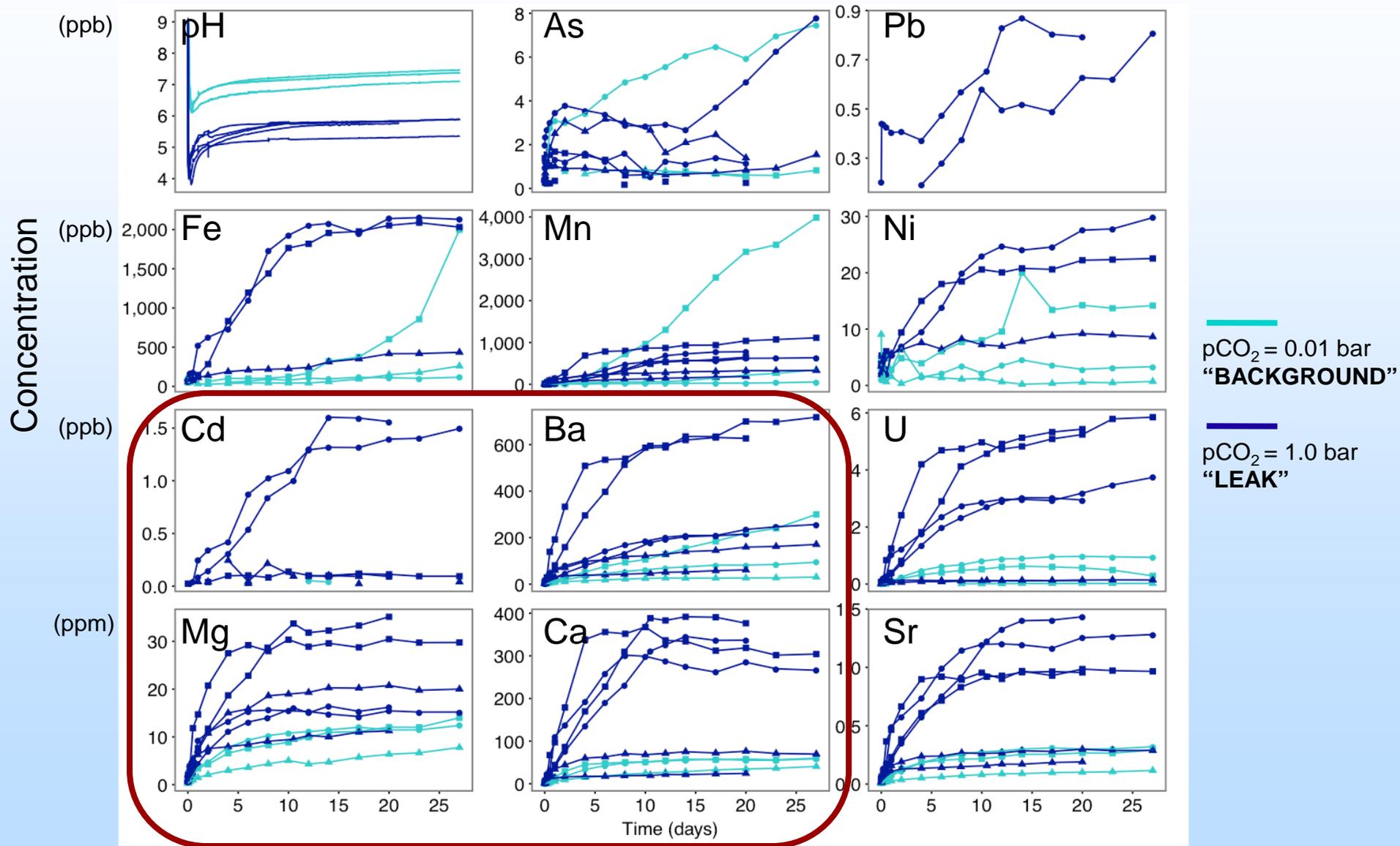
Metal concs varied ~ linearly with Calcium, suggesting a CaCO$_3$ source
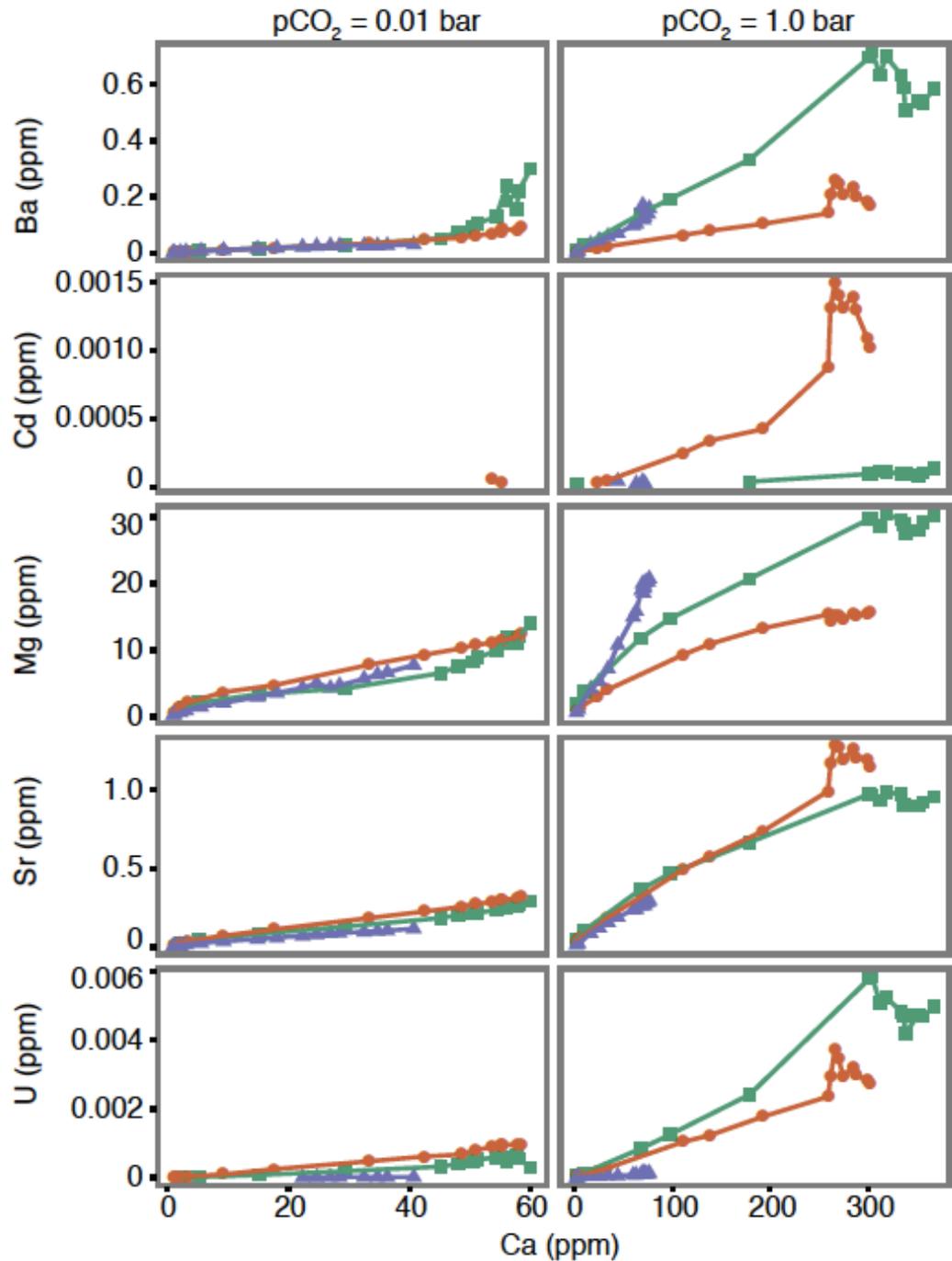
Mechanisms: Which mineral phases are the source of the metal release?
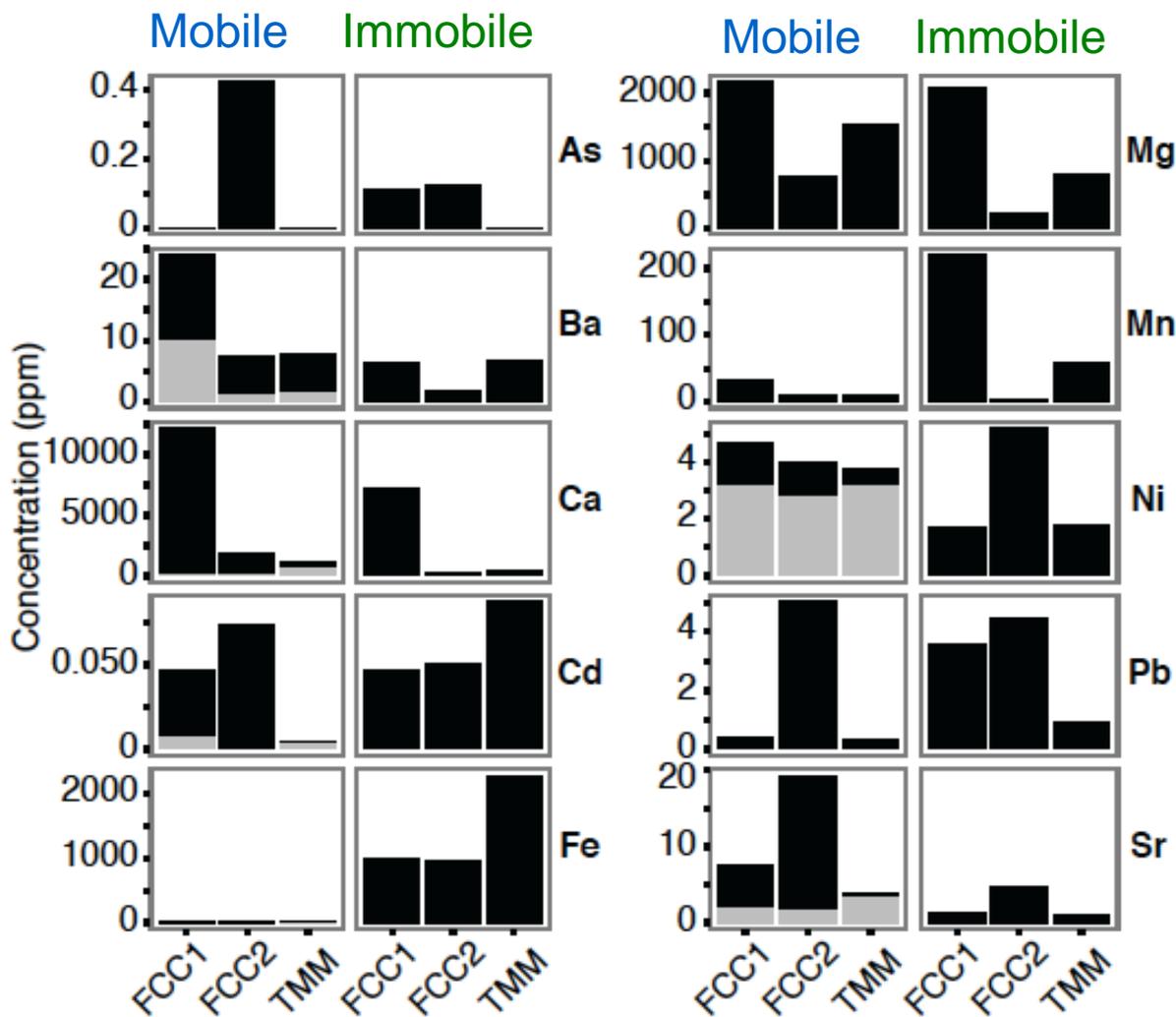

Sequential Extractions

Mobile

- Ion-exchangable

- Carbonate dissolution

**Immobile**

- Fe-Mn Oxides

- Sulfides, Organic Matter

Trace elements released from carbonate fraction
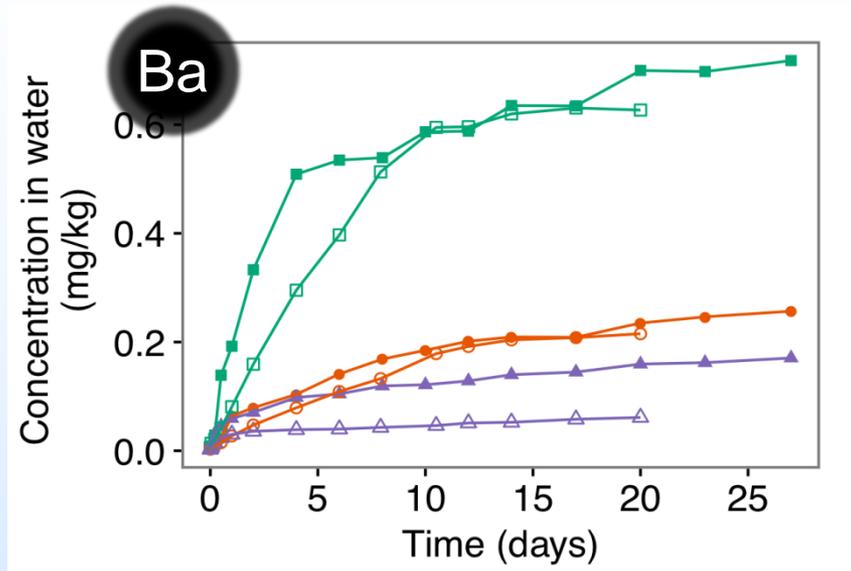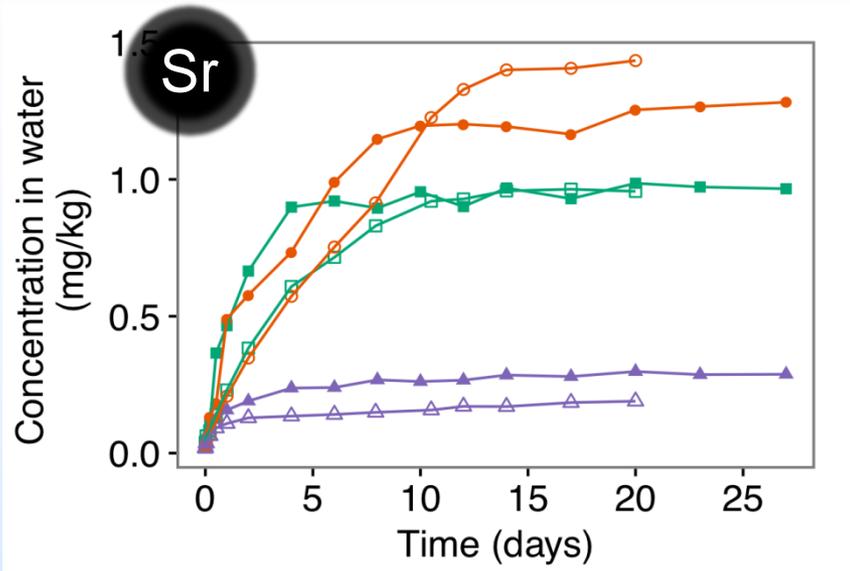

Sr — Mobile Fraction
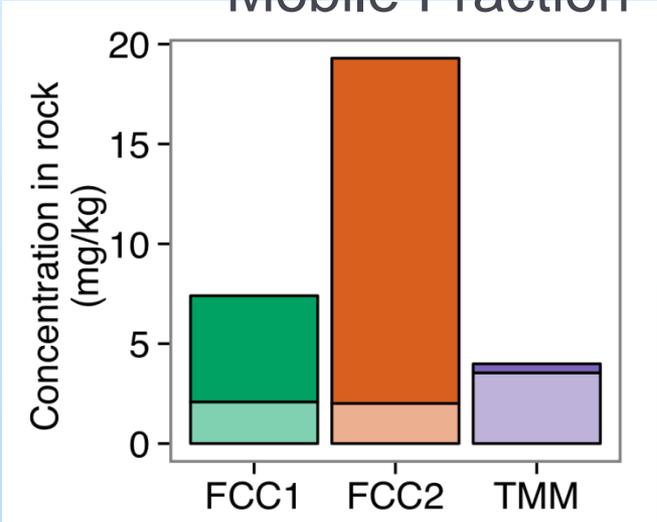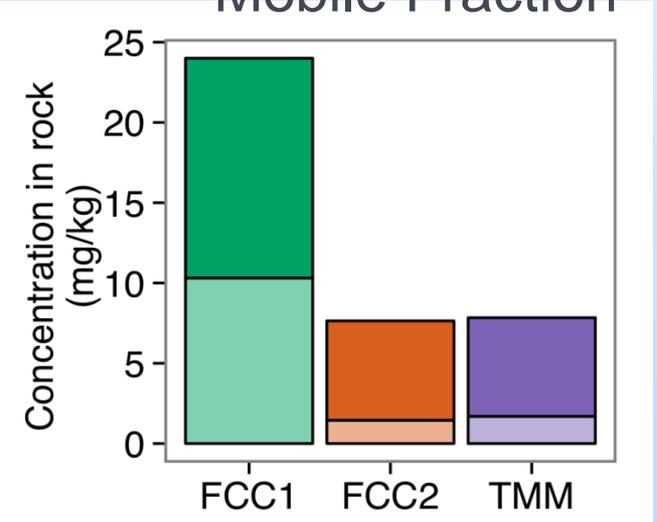
Ba — Mobile Fraction

Carbonates

Ion Exchange

Trace elements released from carbonate fraction
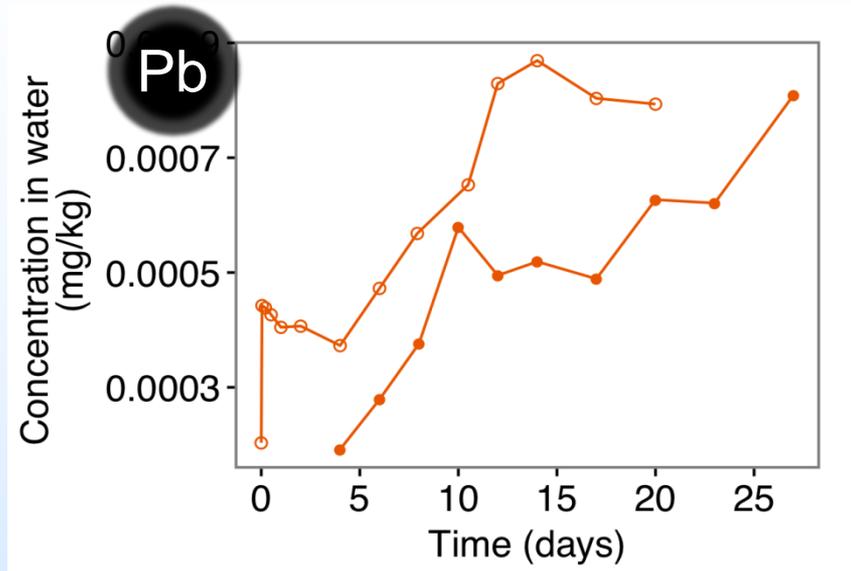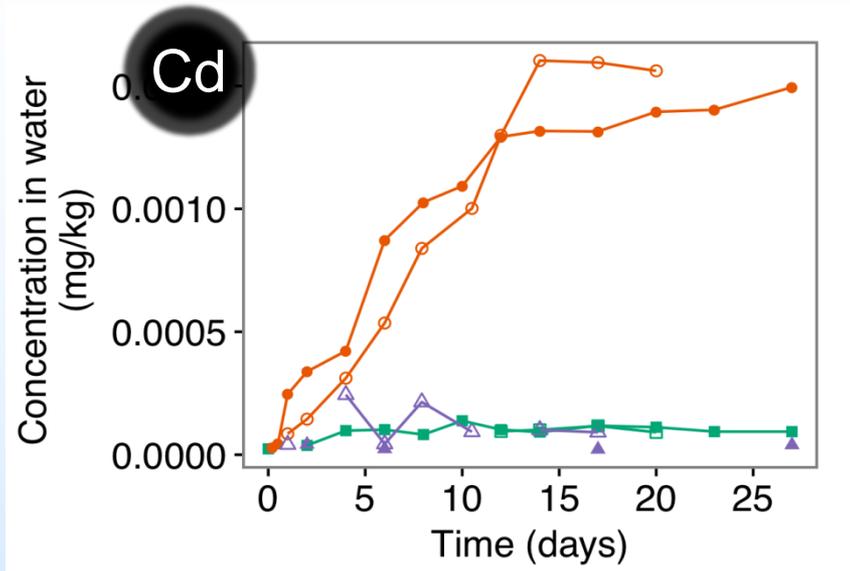
Cd — Mobile Fraction
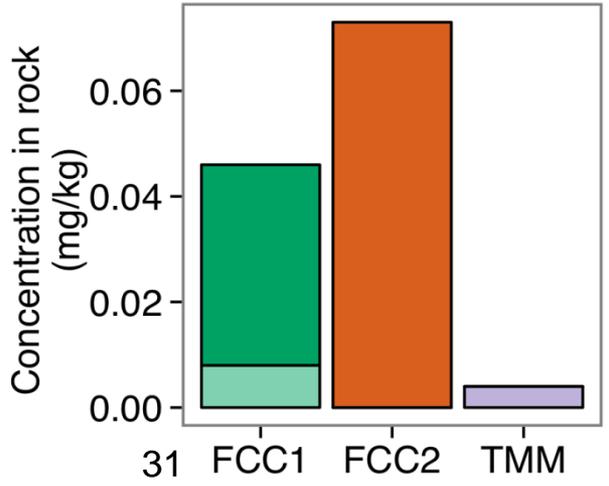
Pb — Mobile Fraction
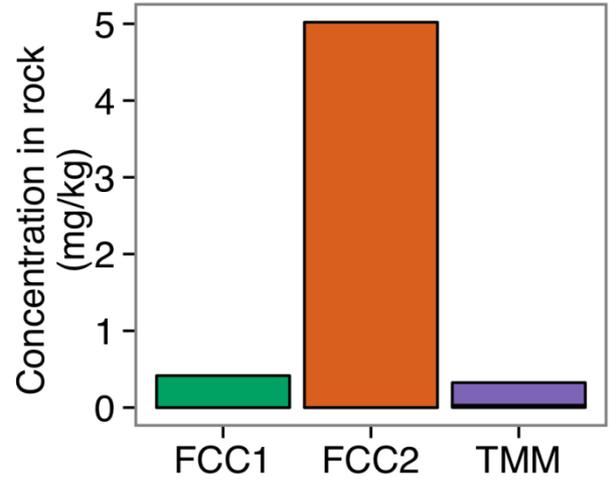
Carbonates

Ion Exchange

Geochemical modeling of experimental data re-affirms hypothesis of carbonate dissolution

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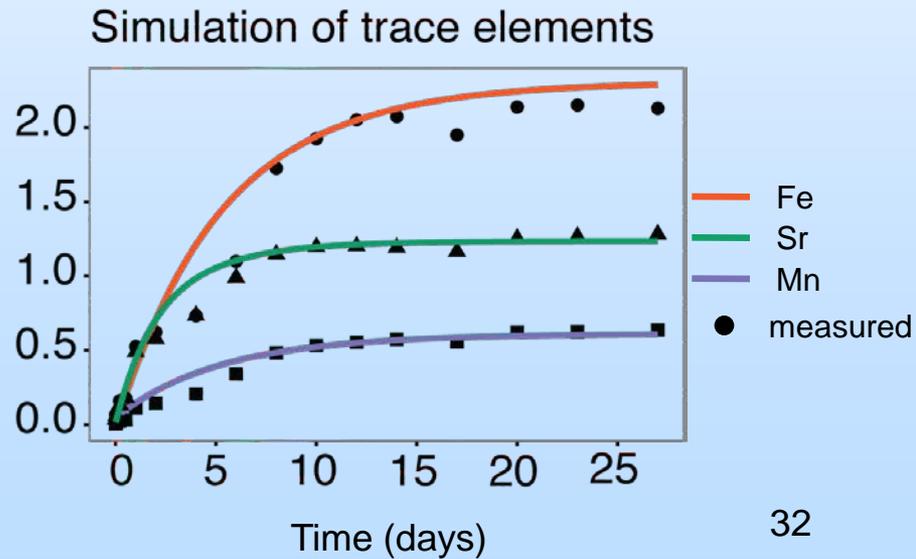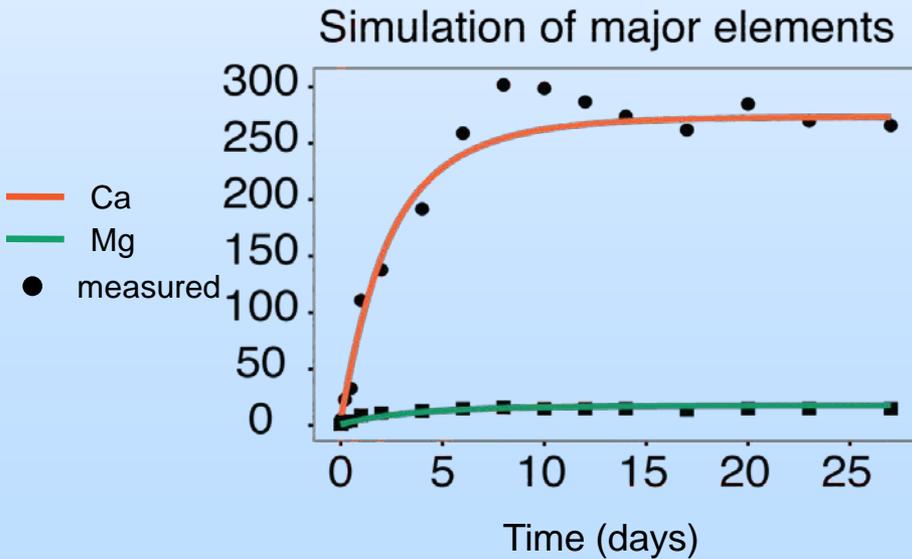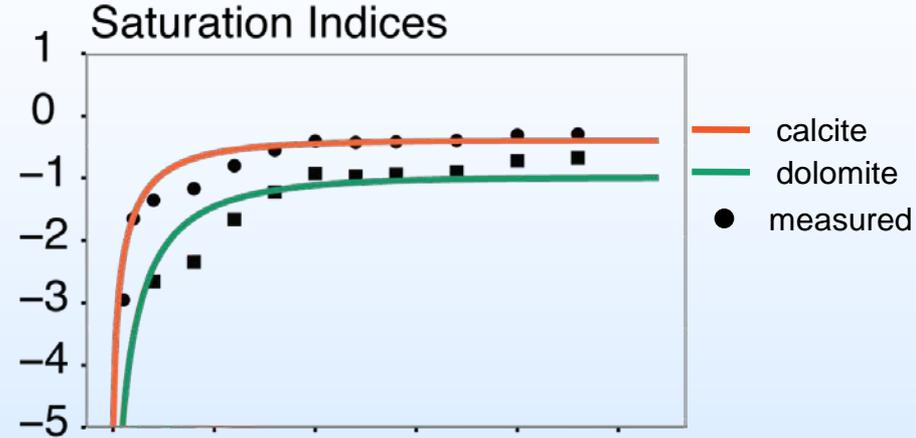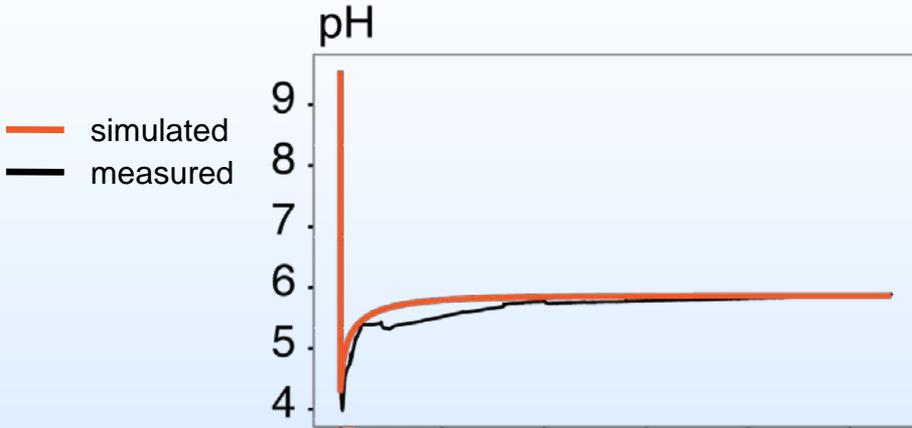
Summary: Lessons Learned

-Aquifer heterogeneities are important in risk calculations

-Kinetic reactions with local dispersion result in lower peak concentrations, but earlier arrival and longer tails: higher calculated risk

-Temporal risk calculations that consider longer exposure durations with smaller concentrations are important in evaluating the true risk

-Brine leakage may increase for conditions where CO_2 leakage decreases (lower injection pressures, further distance from Fault) due to relative permeability-pressure considerations

-Carbonate minerals in sandstones can buffer acidity during leakage into aquifers, but may also be the dominant source of mobile trace metals

-In experiments, one aquifer rock resulted in exceeding secondary MCL for Fe and Mn: rock type is important!

Summary: Future Work

- Project ends this fall.

- Wrap up publication on multiphase modeling of brine and CO_2 leakage (Menke) and hydrochemical changes from CO_2 leakage into sandstone aquifers.

Bibliography

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Theses Completed

Menke, H., 2012. Evaluating storage of geologically sequestered CO2 using numerical simulations, M.S. Thesis in Environmental Science and Engineering, Colorado School of Mines, Golden CO.

Siirilla, E.R., 2012. A quantitative methodology to assess the risks to human health from CO2 leakage into groundwater, M.S. Thesis in Hydrologic Science and Engineering, Colorado School of Mines, Golden CO.

Kirsch, K., 2013. CO_2-induced metal release from sandstones: implications for geologic carbon sequestration, M.S. Thesis in Hydrology, Colorado School of Mines, Golden CO.

Siirilla, E.R., 2013. On the interplay between scaling small-scale reactions, mixing, and aquifer heterogeneity: Human health risk implications. PhD Dissertation in Hydrology, Colorado School of Mines, Golden CO.

Abstracts More than 15:

American Geophysical Union Fall Meeting

Geological Society of America Annual Meeting

ASCE Environmental Water Resources Institute Annual Meeting

Goldschmidt Meeting on Geochemistry

National Ground Water Association Summit

Questions?
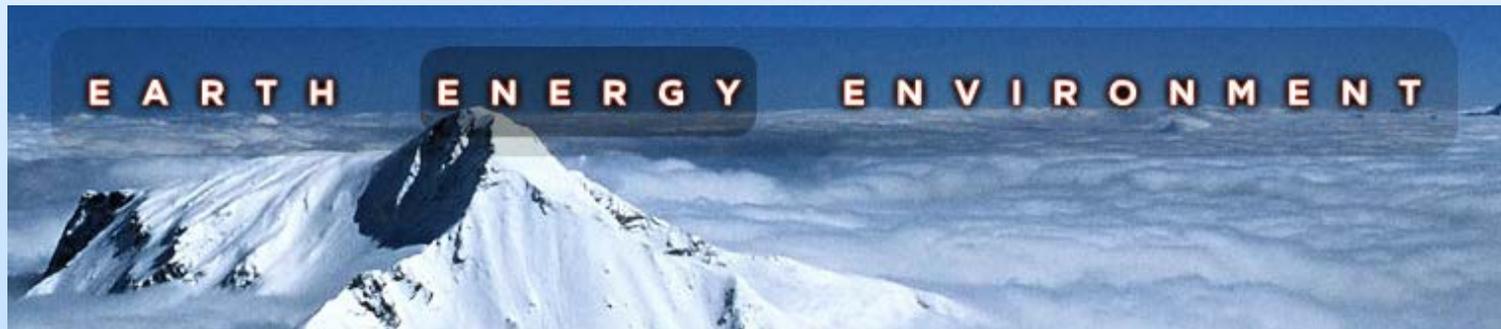
Appendix

Organization Chart

John McCray, Principal Investigator

Ralph Brown Contracts, ARRA Reports

Reed Maxwell co-PI

Alexis Navarre-Sitchler, PM

Erica Siirilla PhD Student

Hannah Menke MS Student

Katie Kirsch MS Student
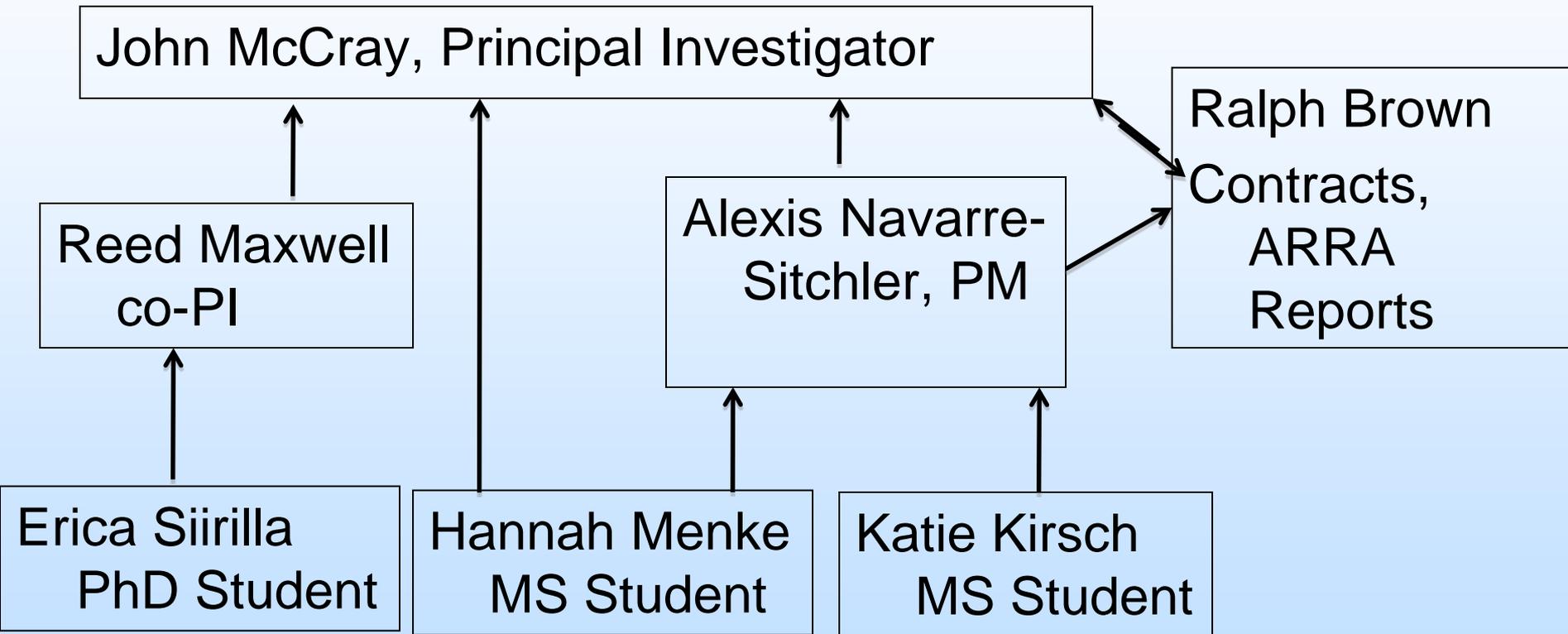
Task	Percent Complete	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13
		FY 2010				FY 2011				FY 2012				FY 2013
Taks 1: Project Management Plan and Reporting	90%													
1.1 Project Management Plan (PMP)	100%	▓	▓											
1.2 Planning and Reporting	90%	▓	A	B	C		D				E			
Task 2: Quantifying risk associated with leakage of CO_2 into overlying aquifers														
2.1 Lit review on CO_2 leakage and impacts on aquifer water quality	100%	▓	▓	▓	▓	▓	▓	▓						
2.2 Lit review on toxicity of CO_2 leakage byproducts.	100%				▓	G						▓		
2.3 Identification of scenarios	90%				F		J	K				▓	▓	▓
2.4 Risk assessment modeling	90%				▓							N		P
Task 3: Laboratory experiments and associated modeling to elucidate pore-scale geochemical processes associated with carbon injection, storage and sequestration														
3.1 Detailed sample characterization	60%	▓	▓	▓		H								
3.2 Laboratory experiments	60%				▓			L						
3.3 Reanalysis of samples from experiments	25%							▓	▓	▓	▓			
3.4 Geochemical modeling	10%									▓	▓	▓	▓	O
Task 4: Seminar taught for course credit on risk-assessment associated with CO_2 sequestration														
4.1 Develop course syllabus	100%						I				▓			
4.2 Develop course materials	100%										▓			
4.3 Deliver Course	100%					▓		M			▓			

Task/ Subtask #	Project Milstone Description	Project Duration - Dec 2009 - Nov 2012 FY 2010 Q1	Q2	Q3	Q4	FY 2011 Q5	Q6	Q7	Q8	FY 2012 Q9	Q10	Q11	Q12	FY 13 Q13	Planned Start Date	Planned End Date	Actual Start Date	Actual End Date	Comments
1.2	A - Project Kickoff meeting	■													12/1/09	12/31/09	12/1/09	12/31/09	Completed as planned
1.2	B - Educational Program Instituted		■												1/1/10	6/30/10	1/1/10	1/30/10	Completed ahead of schedule
1.2	C - Semi-Annual Progress Report				■										9/1/10	9/30/10	7/1/10	7/31/10	Quarterly report for Q3 - 2010 FY serves as semi-annual report per email from Joshua Hull
1.2	D - Yearly Review Meeting						■								11/1/11	11/1/11	11/1/11	11/1/11	Participation in NETL webinar
1.2	E - Yearly Review Meeting									■					9/30/12	9/30/12			
2.3	F - Determine most probable leakage scenarios			■											4/1/10	6/30/10	4/1/10	6/30/10	Completed as planned
2.2	G - List of EPA-regulated byproducts of reaction between aquifer materials and CO2			■											4/1/10	12/31/10	4/1/10	9/30/10	Completed ahead of schedule
3.1	H - Initial characterization of injection and caprock formation begun		■												1/1/10	12/31/10	1/1/10	12/31/10	Completed as planned
4.1	I - Development of course syllabus complete					■									12/1/10	8/15/11	11/1/10	8/1/11	Completed as planned
2.3	J - Identify and rank aquifer sites for use in risk simulations complete				■										7/1/10	3/31/11	1/1/11	3/31/11	Completed as planned
2.3	K - Identify and rank aquifer-leakage scenarios for use in risk simulations complete							■							10/1/10	6/30/11	10/1/10	6/30/11	Completed as planned
3.2	L - Determine rate parameters of important geochemical reactions				■										7/1/10	6/30/11	7/1/10	6/30/11	Completed as planned
4.3	M - Summary on demographics and grades for the university course								■						6/1/11	12/31/11	8/1/11		in progress
2.4	N - Complete screening risk assessment simulations								■						7/1/11	6/30/12	7/1/11	6/30/12	Completed as planned
3.4	O - Complete geochemical modeling for relevant carbon injection scenarios									■					10/1/11	11/30/12	10/1/11		in progress
2.4	P - Complete primary risk simulations for aquifer leakage											■			7/1/12	11/30/12	7/1/11		in progress