Improved Predictions of Fluid Properties and Mineral Reaction Kinetics

Robert Dilmore

U.S. DOE, NETL, Office of Research and Development
Geological & Environmental Sciences Focus Area

Office of Research and Development
Strategic Center for Coal

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

Improved Prediction of Fluid Properties and Mineral Reaction Kinetics (Geochemical Impacts)

- **International Round Robin comparison of geochemical gas-fluid-rock reactions at elevated pressure-temperature (P-T) conditions**
  - **Team Members:** Craig Griffith, NETL; Robert Dilmore, NETL; Angela Goodman (PI), NETL; Sheila Hedges, NETL; Athanasios Karamalidis, CMU, and 13 International Participants
- **Sensitivity analysis of mineral solution rates in reactive transport**
  - **Team Members:** Victor Balashov, PSU; Sue Brantley (PI), PSU; George Guthrie, NETL; Ale Hakala, NETL; Christina Lopano, NETL
- **Fluid Equilibria in scCO_2-brine systems**
  - **Team Members:** Haining Zhao, PSU; Derek Hall, PSU; Alexander Morse, PSU; Mark Fedkin, PSU; Serguei Lvov (PI), PSU; Robert Dilmore, NETL
- **Multi-Model Predictive System for CO_2 Solubility in Saline Waters**
  - **Team Members:** Zan Wang, CMU; Mitchell J. Small, CMU; Athanasios K. Karamalidis (PI), CMU, Robert. Dilmore, NETL

International Round Robin comparison of geochemical gas-fluid-rock reactions at elevated (P-T) conditions

- Organized and led by the Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany and the USGS, Menlo Park, CA, USA.

Project Objectives

- To compare the results of potential geochemical changes to water chemistry and sedimentary mineral composition over various experimental techniques conducted by several research institutions.
- Assess uncertainty associated with geochemical experiments in gas-fluid-mineral systems.

Programmatic Goal Addressed

- Understand the impacts of CO_2 on mineralization rates in different formation types to improve CCS operations and storage integrity

Invited Participants

USGS (Menlo Park, US)
BGR (Hannover, DE)
GFZ (Potsdam, DE)
RWTH Aachen (Aachen, DE)
MLU Halle (Halle, DE)
IFM-Geomar (Kiel, DE)
BRGM/IFP (Orléans, FR)
CNRS (Nancy, FR)
LMTG (Toulouse, FR)
BGS (Keyworth, GB)
University of Leeds (Leeds, GB)
U. Cambridge (Cambridge, GB)
ETHZ (Zürich, CH)
SINTEF (Trondheim, NO)
IRIS (Stavanger, NO)
TNO (Utrecht, NL)
LBNL (Berkeley, US)
U. Wyoming (Laramie, US)
DOE NETL (Pittsburgh, US)
Washington University (St. Louis, US)
ARC & RECS (Alberta,CA)
CO2CRC (Canberra, AU)
RITE (Kyoto, JP)

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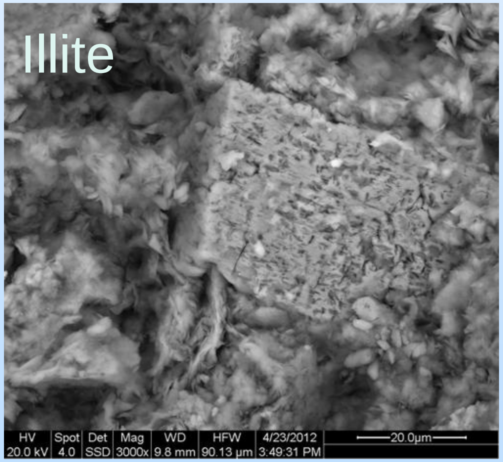
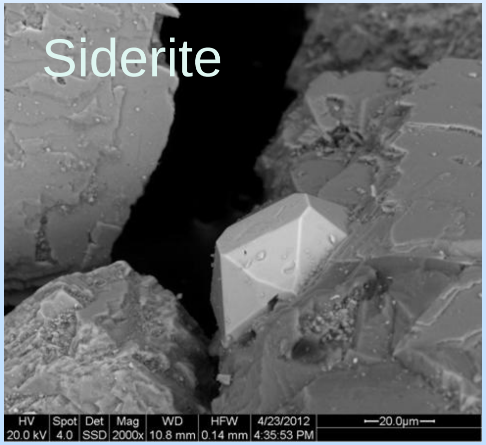
International Inter-lab Round Robin **Overview**

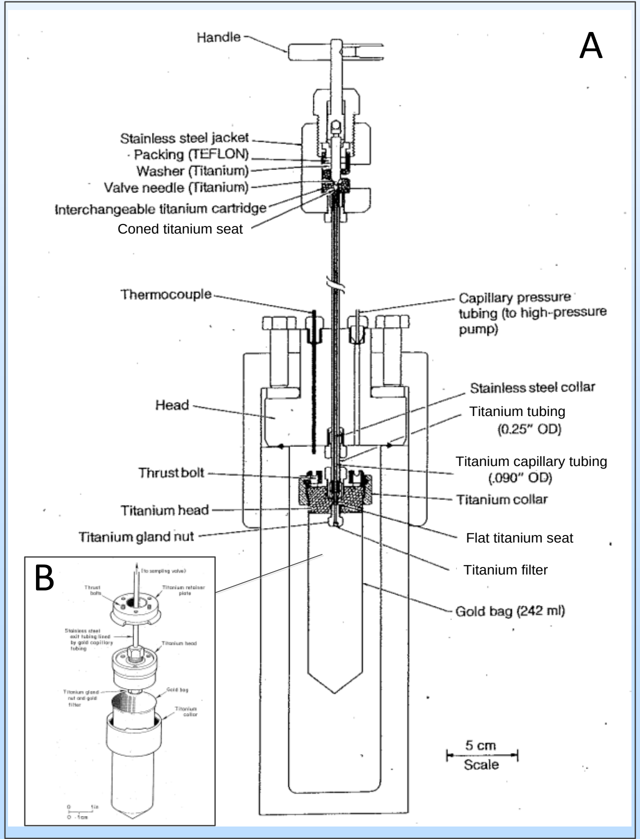
The motivation for this study is threefold:

1. to provide an estimate of potential variance in kinetic (or thermodynamic) data derived from gas-fluid-mineral interaction experiments using different experimental approaches in a variety of labs.
2. to validate kinetic data for three mineral dissolution reactions at relevant in situ pressure and temperature conditions (siderite, labradorite, illite at p=200 bars, T=80°C, CO_2-saturated 2 M NaCl-brine)
3. to strengthen the collaboration among experimental labs around the world and to streamline experimental programs for gas-fluid-mineral reaction studies.





International Inter-lab Round Robin **Accomplishments**



Target Parameters	Target Conditions
Pressure	200 bars
Temperature	80 °C
Initial brine composition	150g NaCl/L H_2O
Brine to mineral initial mass ratio	20:1
CO_2	CO_2 saturated brine and $scCO_2$ in the headspace
Time	Siderite > 1 week Illite > 2 weeks Labradorite > 3 weeks
Sampling	One prior and one at the injection of CO_2; >5 post CO_2 injection at temperature and pressure
Analytes	pH Dissolved ions (Ca, Mg, Fe, Mn, Si, Al, Cl, SO_4) Dissolved inorganic carbon or total CO_2

A) Cross section of Dickson-type, flexible gold-titanium reaction cell, B) gold-titanium reaction cell emphasizing titanium closure configuration. (*Source: modification after Seyfried et al., 1979; Seyfried et al., 1987*)

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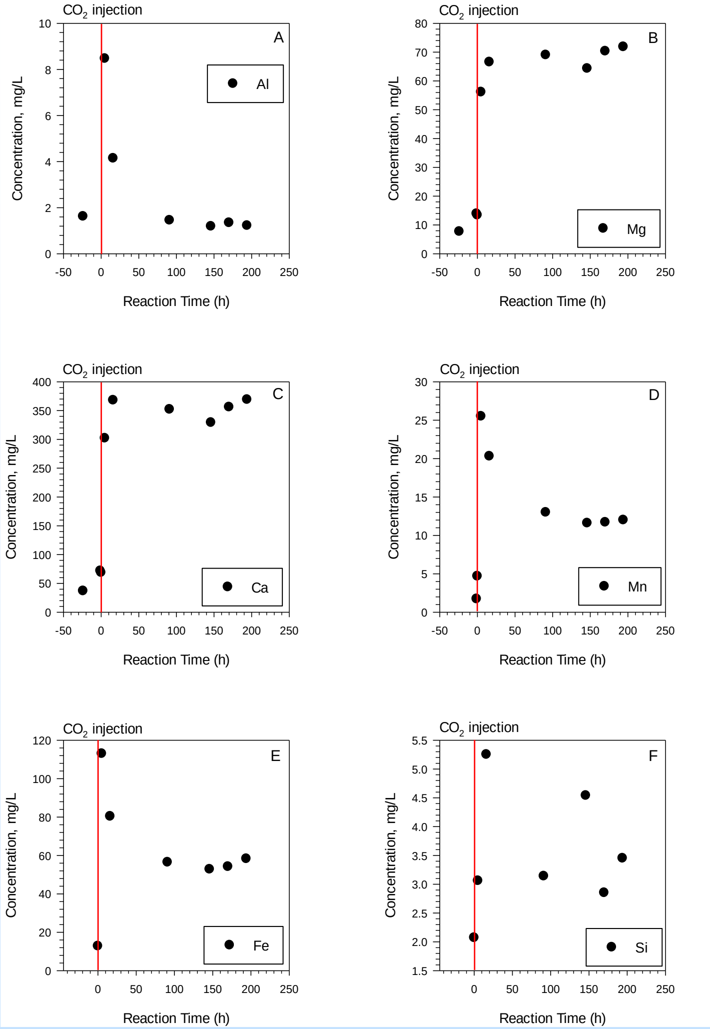
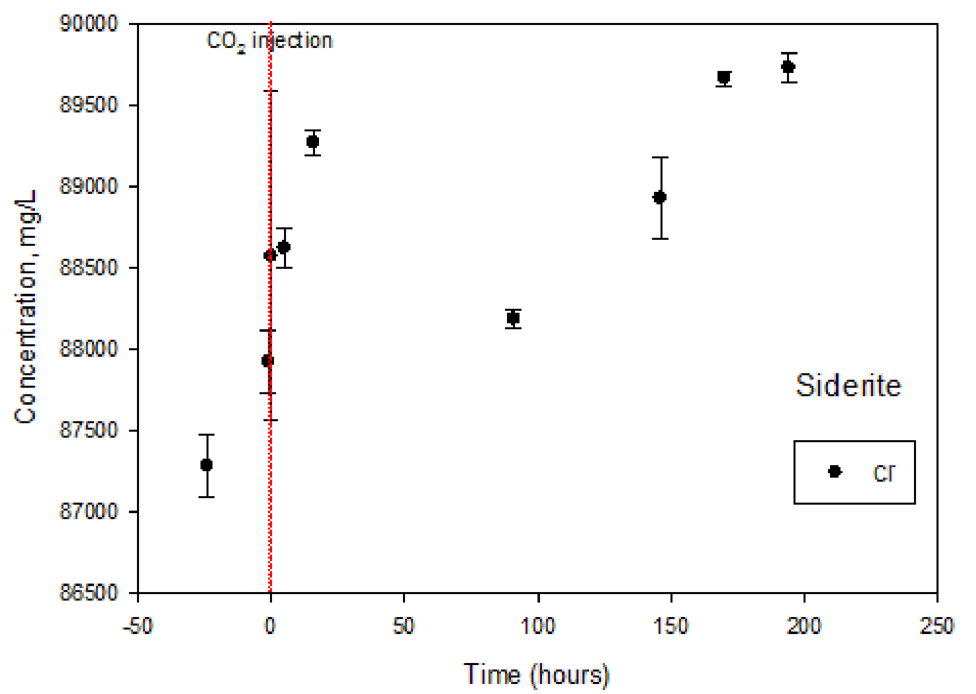
International Inter-lab Round Robin **Accomplishments**





Total concentration (mg/L) of Cl$^-$ measured from Siderite reaction brine before and after CO$_2$ saturation as a function of reaction time (h).

Total concentration (mg/L) of different cations released from Siderite when reacted with or without CO$_2$ saturated brine as a function of reaction time (h) after CO$_2$ injection. Cations of interest: A) Al, B) Mg, C) Ca, D) Mn, E) Fe, and F) Si.

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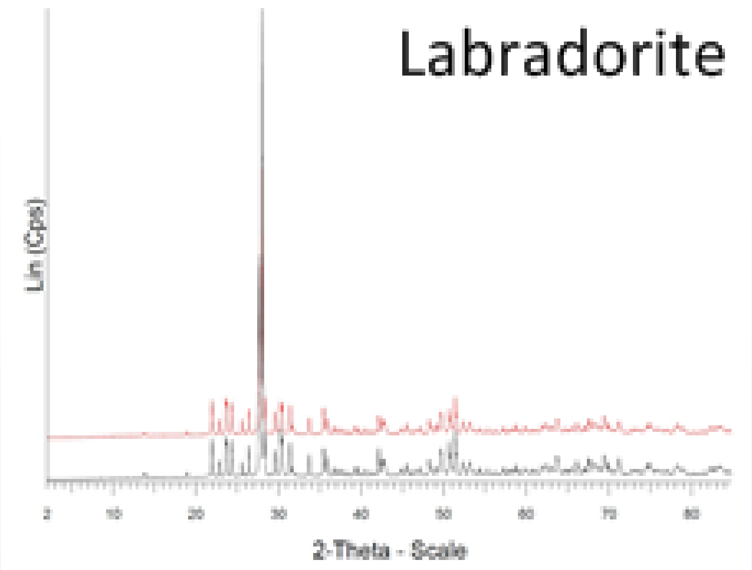
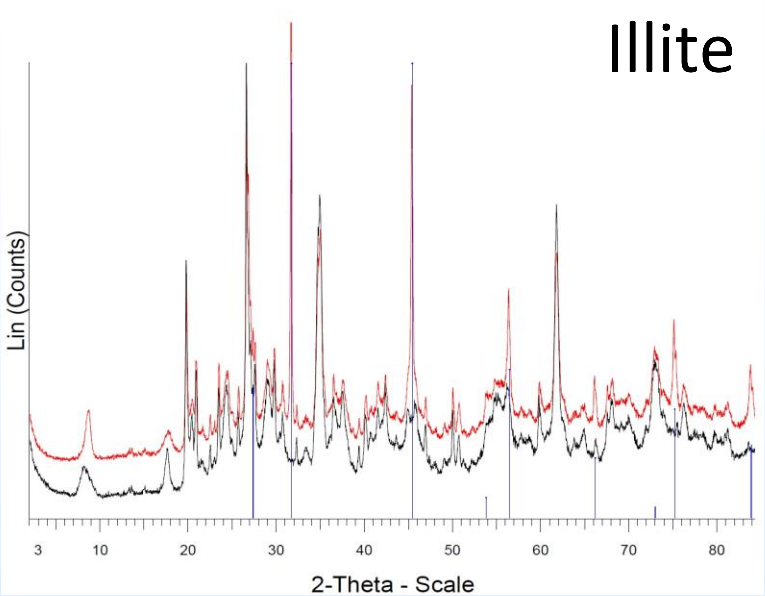
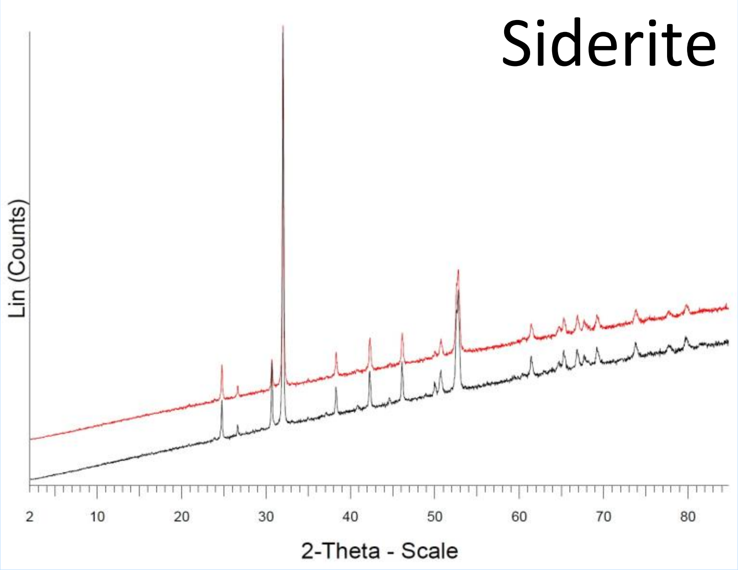
International Inter-lab Round Robin **Accomplishments**







XRD analysis of the three minerals prior (black line) and post (red line) reaction with CO_2. No significant changes are apparent, except for illite where halite is identified (blue lines).

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Technical Status and Future Work

- Gas-fluid-mineral experiments completed (November 30, 2011)

  ACS Spring Meeting 2012, San Diego Geochemical reactions of Illite, Labradorite and Siderite with CO_2-saturated salt solution under geologic CO_2 storage conditions Athanasios Karamalidis[1,2]*, Craig Griffith[2], Robert Dilmore[2], Sheila Hedges[2], Christian Ostertag-Henning[3], Angela Goodman[2]

  [1]Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States,
  [2] Geosciences Division, National Energy Technology Laboratories, U.S. Department of Energy, Pittsburgh, PA 15236, United States, [3] Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany

- Comparison of results with 13 labs near completion
- Publically Available Final International Report (September, 2012)
  - technical report will be available for download from the BGR website
  - joint publication in *Applied Geochemistry* on the comparison of the different (anonymous) data sets
- Continue the collaboration in the GaMin'11 group ... and start GaMin'13 end of 2012.
  - focus on the comparison of mixed-flow/flow-through derived dissolution rates with data from batch type reactor experiments, work on two minerals (calcite & K-feldspar) and use two salinities (again 150
    then seawater)

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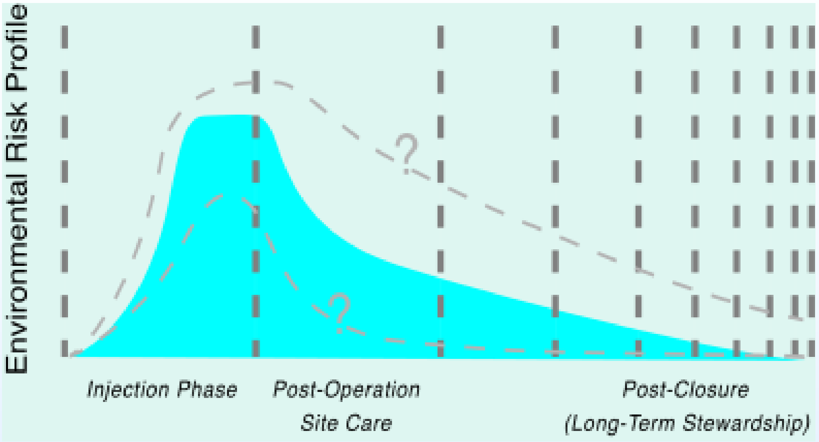
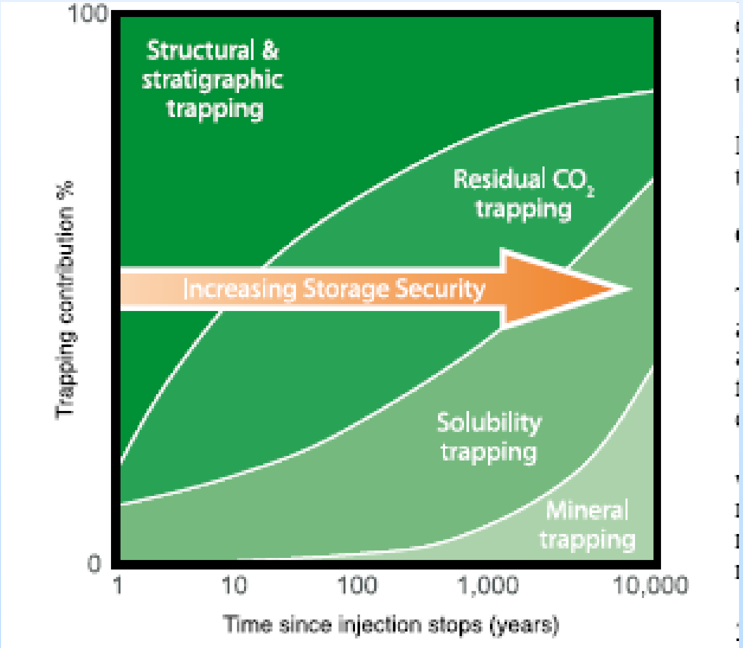
Sensitivity analysis of mineral solution rates in scCO2-brine-sandstone system

- CCUS requires the ability to predict the behavior of geologic system over the near and long term
- Models are needed to understand whether CCUS will effectively store CO_2 to warrant economic investment, meet regulations, and convince the public that CCUS is safe
- Reactive diffusion model to explore rates and extents of water-rock reactions driven by emplacement of CO_2
- Storage security depends on a combination of physical (structural and residual CO_2 trapping) and geochemical (solubility and mineral trapping)





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References: • IPCC, 2005: IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.
• Benson, S.M., 2008. Multi-Phase Flow and Trapping of CO_2 in Saline Aquifers. (Paper No. OTC 19244). Published in the Proceedings of 2008 Offshore Technology Conference held in Houston, TX, USA, May 5–8, 2008

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Sensitivity analysis of mineral solution rates **Overview**

- Overall Goal: Develop a model of a prototypical reservoir based on mineralogical features common to many CO_2 storage targets (using the EHS2 local equilibrium code and MK76 reactive transport code). Determine the mineral precipitation and dissolution processes that are important to storage permanence at brine/aquifer/caprock interfaces. Vary kinetic rates in the model within the known range of uncertainty to determine the most sensitive parameters over various timescales.
- Importance: Geochemical calculations used to predict performance of CO_2 utilization and storage systems
    - These calculations rely on thermodynamic & kinetic databases with inherent uncertainty
    - Uncertainties in kinetic data generally are larger than thermodynamic data
        - lab and field rates vary by factors of 10^5 (White & Brantley, 2005)

References: Balashov V.N., Khudyaev V.S. Numerical modeling of infiltration metasomatic zoning at local equilibrium: program EHS. // Experimental problems in geology. Moscow, Nauka, 1994, p. 456-479.
White, A.F. and Brantley, S.L., 2003. The Effect of Time on the Weathering of Silicate Minerals: Why Do weathering Rates Differ in the Laboratory and Field? Chemical Geology, 202: 479-506.

Sensitivity analysis of mineral solution rates **Accomplishments**

Baseline Case (Sandstone Reservoir)

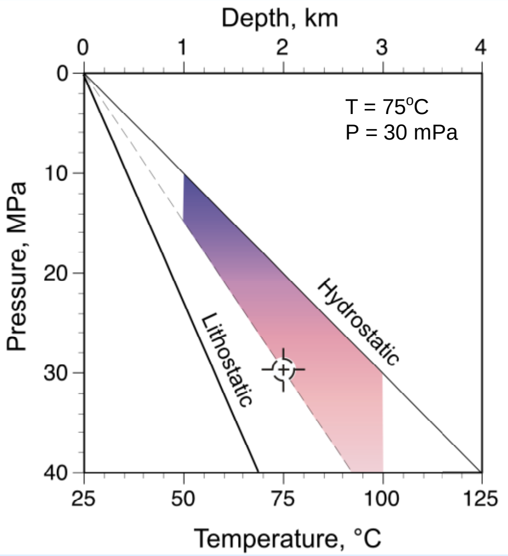
- Comparison among models is difficult (different reservoir characteristics, model approaches, thermodynamic and kinetic databases)
- Offers opportunity for systematic comparisons between models

Geophysical conditions:

- 2 km / 75ºC /30 MPa / Porosity 0.25 / 0-25,000 years

Geochemical conditions:

- 6 mineral system to start
- Brine chemistry derived from average oil-field brine compositions



Baseline brine composition

	Ave. Brine (molality)	Theoretical Brine (molality)
pH	-	7.81
Cl^{3-}	2.146	2.146
Na^+	1.620	1.712
Ca^{2+}	0.258	0.217
K^+	0.012	1.1×10^{-3}
Al^{3+}	-	9.9×10^{-3}
SiO_2	-	3.0×10^{-4}
HCO_3^-	0.0040	9.5×10^{-5}

Baseline sandstone mineralogy

Mineral	Composition	Vol %	Size (mm)	SSA_{geom}[1] (m^2/g)	ng[2] (m^{-3})
Quartz	SiO_2	48.75	1.00	2.3×10^{-3}	4.9×10^8
Microcline	$KAlSi_3O_8$	13.50	0.125	1.9×10^{-2}	6.9×10^{10}
Oligoclase	$Ca_{0.2}Na_{0.8}Al_{1.2}Si_{2.8}O_8$	6.00	0.125	1.8×10^{-2}	3.1×10^{10}
Calcite	$CaCO_3$	3.75	0.500	4.4×10^{-3}	3×10^8
Smectite	$K_{0.03}Ca_{0.39}Al_{1.77}Si_{3.97}O_{10}(OH)_2$	2.25	0.001	2.27×10^0	2.3×10^{16}
Illite	$KAl_3Si_3O_{10}(OH)_2$	0.75	0.001	2.12×10^0	7.5×10^{15}
Porosity	--	25.00		---	

[1] Geometric specific surface area

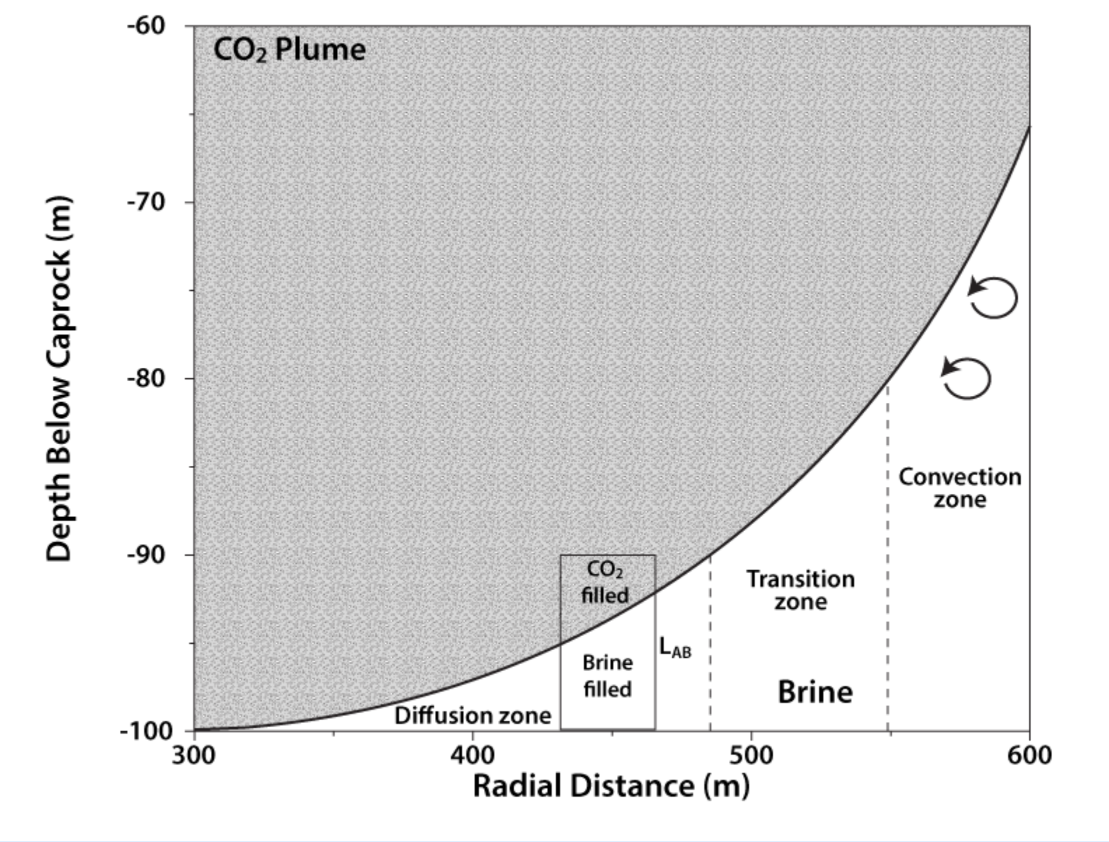
[2] Number of mineral grains per unit volume of a porous medium

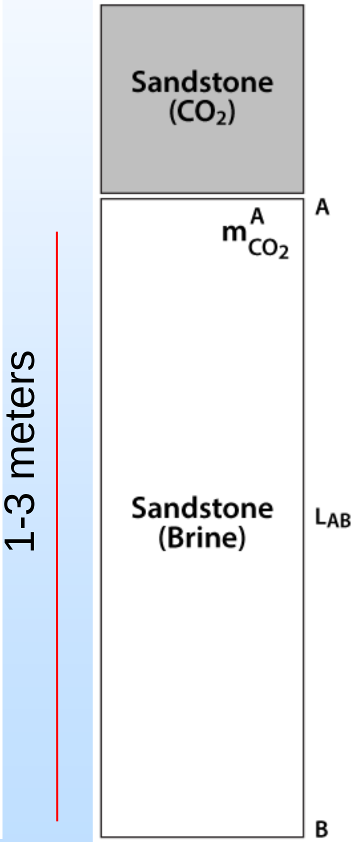
Figures from Balashov et al. (2012) submitted

Sensitivity analysis of mineral solution rates **Accomplishments**

Reactive Transport Modeling (CO_2 & Sandstone Reservoir):

- Numerical reactive transport code with reaction kinetics (MK76)
- Investigate effect of diffusive-reactive partitioning of CO_2 across the interface within the baseline sandstone between sup CO_2 and brine
- Ran sensitivity tests to determine impacts of the use of different reaction rate constants



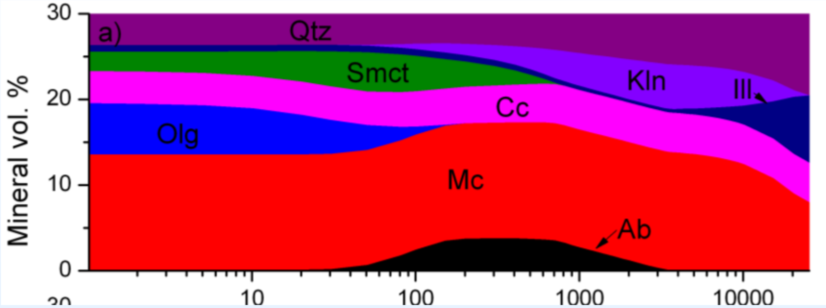


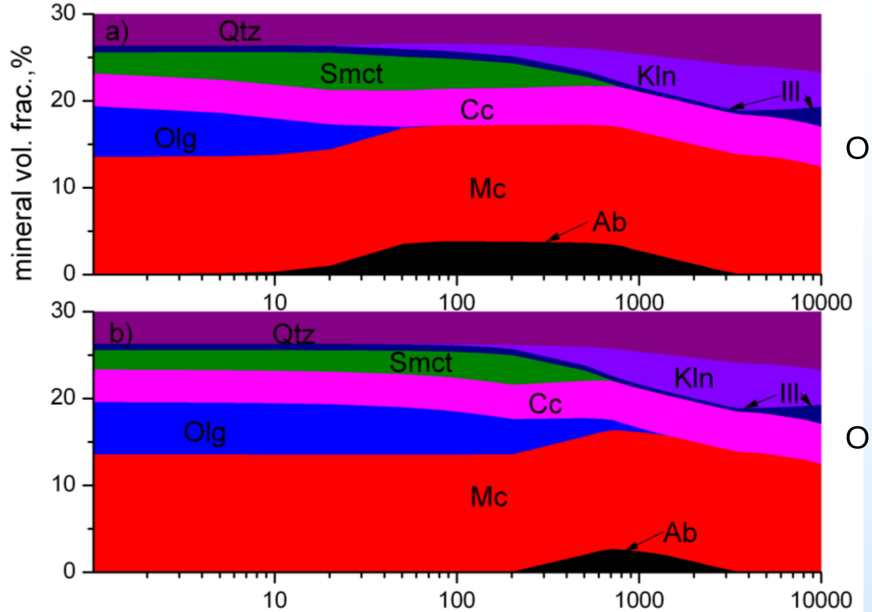
Figures from Balashov et al. (2012) submitted

Sensitivity analysis of mineral solution rates **Accomplishments**

Sensitivity Analysis – Part 1: Important controlling minerals & reaction pathways

“Standard” rate constant values





Olg * 10

Olg * 0.1

Summary of mineral/fluid reactions due to CO$_2$ invasion into sandstone

Reaction Progess	0 – 10 years	10 – 50 years	50 – 100 years	100 – 1000 years	1,000 – 5,000 years	5,000 – 10,000 years
< 0.1	Mc ↓ Cc ↑	Mc ↓ Ab ↑	Mc ↓ Kln ↑	Mc ↑ Ab ↑	Mc ↑	
0.1 – 0.9	Olg ↓	Smct ↑ Olg ↓ Cc ↑	Ab ↑ Smct ↓ Olg ↓	Kln ↑ Smct ↓	Kln ↑ Ab ↓	Ill ↑ Kln ↓ Mc ↓
> 0.9	Smct ↑		Cc ↑	Cc ↑		

↓ dissolution and ↑ precipitation

Model developed and run at PSU

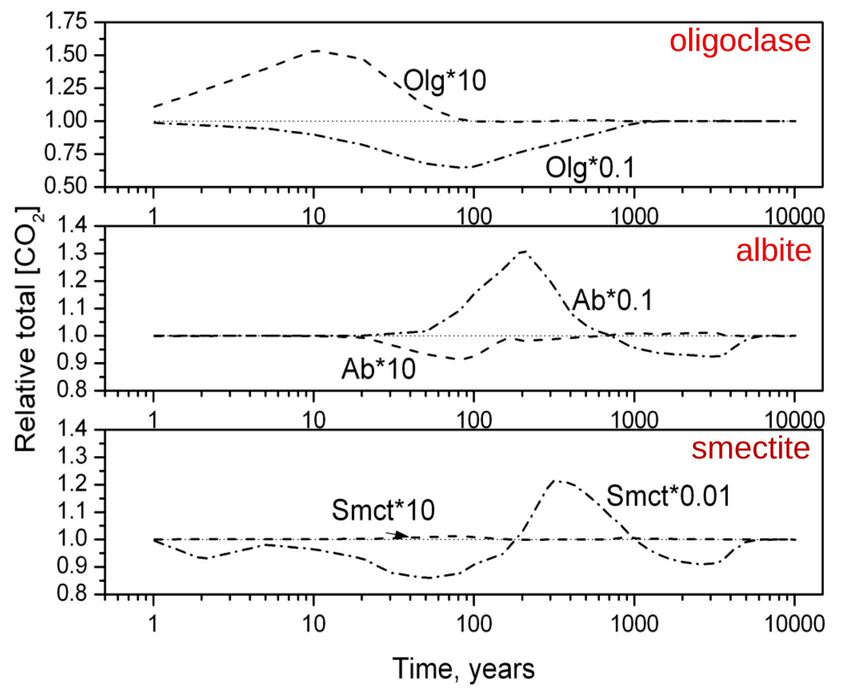
Sensitivity analysis of mineral solution rates **Accomplishments**

Sensitivity Analysis – Part 2: Impacts to overall CO_2 storage

Environmental Risk Profle: Injection Phase ---Post Operation ---Post Closure

Results (CO_2 & Sandstone Reservoir):

- 30 years: CO_2 mostly trapped in solution
- 200-1000 years: replacement of oligoclase with smectite / trapping of some CO_2 as calcite / significant trapping of CO_2 as bicarbonate ion
- 4000 years: CO_2 equilibrium is established
  - – 97% of the maximum stored CO_2 (34.5 kg CO_2/m^3 sandstone) is partitioned as follows:
    - 70% solubility trapping
    - 30% mineral trapping (calcite)
- 25,000 years: final mineral equilibrium established – quartz-illite-calcite-microcline
- Variations in reaction rates mostly affect storage-reservoir behavior in the 10-1000 year time frame, and is dependent on kinetic coupling



The effect of changes in the rate constants for oligoclase, albite and smectite on the relative total CO_2 sequestered in the sandstone (sensitivity factor) plotted versus time.

CO_2 sequestration is sensitive to variability in the mineral rate constants of oligoclase, albite, and smectite to varying degrees (ol > al > sm)

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Figures from Balashov et al. (2012) submitted

Sensitivity analysis of mineral solution rates

On-going & Future Work (FY 2012 +)

- Overall Goal: Determine the mineral precipitation and dissolution processes that are important to storage permanence at brine/aquifer/caprock interfaces. Vary kinetic rates in the model within the known range of uncertainty to determine the most sensitive parameters over different time frames
  - Key focus: Caprock (particularly shale)
    - Develop baseline shale model inputs
    - Include Fe-rich phases such as pyrite (FeS_2)
    - Sensitivity analyses – pinpoint key mineral/brine constituents where variability affects predictive sequestration models
    - Relate modeling results to experimental efforts (compare/contrast mineral dissolution/precipitation)
      - e.g. Isotope tracers, trace metal transport
    - Complete September, 2012
  - Future: Expand work to make links to flow regimes

Baseline shale mineralogy

Mineral	**Composition**	**Mass %**
Quartz	SiO_2	25
Microcline	$KAlSi_3O_8$	1
Oligoclase	$Ca_{0.2}Na_{0.8}Al_{1.2}Si_{2.8}O_8$	0
Calcite	$CaCO_3$	5
Smectite	$K_{0.03}Ca_{0.39}Al_{1.77}Si_{3.97}O_{10}(OH)_2$	5
Illite	$KAl_3Si_3O_{10}(OH)_2$	40
Kaolinite	$Al_2Si_2O_5(OH)_4$	< 1
Pyrite	FeS_2	5
Chlorite	$Mg_5Al_2Si_3O_{10}(OH)_8$	13
Porosity	--	8.0

Complete sensitivity analysis for mineral kinetics for CO_2- saturated brine/aquifer/caprock interface

Sensitivity analysis of mineral solution rates **Time Line**

Overall Scope and Time Line:

- **Reactive transport modeling and kinetic sensitivity study of CO_2-storage in a sandstone reservoir is complete**
    - Manuscript submitted to *Applied Geochemistry* – Jan. 2012

Balashov, V.N., Guthrie, G.D., Hakala, J.A., Lopano, C.L., Rimstidt, J.D., and Brantley S.L. “Predictive Modeling of CO_2 Sequestration in Deep Saline Sandstone Reservoirs: Impacts of Geochemical Kinetics” Submitted January 2012 and under review for a special issue of Applied Geochemistry.

[1] Earth and Environmental Systems Institute, 2217 EES Building, Pennsylvania State University, University Park, PA 16802;

[2] U.S. Department of Energy, National Energy and Technology Laboratory, 626 Cochrans Mill Road, Pittsburgh, PA 15236 :

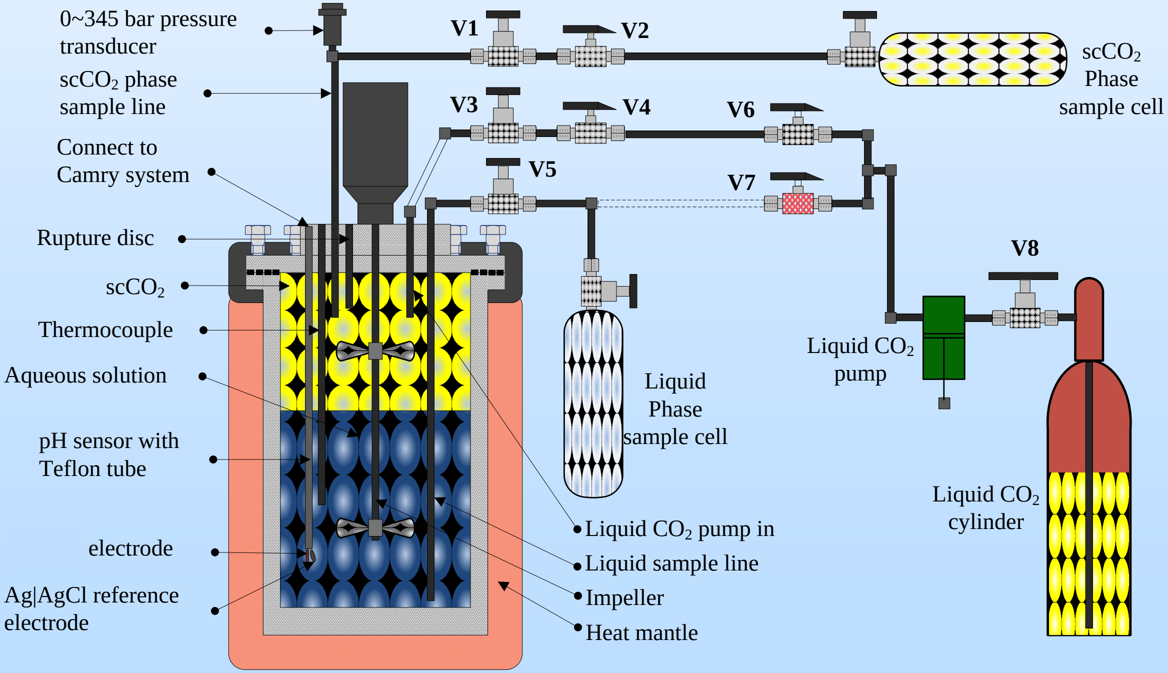
[3] Dept. of Geosciences, 4044 Derring Hall, Virginia Tech University, Blacksburg, VA 24061

- **On-going work expands the model & kinetic sensitivity analyses to include the CO_2-Sandstone-Shale interface**
    - Background research and model set-up complete
    - Thermodynamic input finalized
    - Reaction Transport and sensitivity studies are in development (May 2012 – September 2012)

Fluid Equilibria in $scCO_2$-brine systems

Experimental system for phase equilibria to allow high temperature/pressure pH measurements in $scCO_2$-brine systems

- Experimental measurements of CO_2 solubility in brine
- Experimental measurements water saturation in $scCO_2$
- In-situ pH measurements in $scCO_2$-brine systems at CO_2 storage conditions (up to 200 °C and 150 bar)
- Thermodynamic modeling of the $scCO_2$-brine system and reservoir pH



0~345 bar pressure transducer

$scCO_2$ phase sample line

Connect to Camry system

Rupture disc

$scCO_2$

Thermocouple

Aqueous solution

pH sensor with Teflon tube

electrode

Ag|AgCl reference electrode

V1

V2

V3

V4

V5

V6

V7

V8

$scCO_2$ Phase sample cell

Liquid Phase sample cell

Liquid CO_2 pump

Liquid CO_2 cylinder

Liquid CO_2 pump in

Liquid sample line

Impeller

Heat mantle

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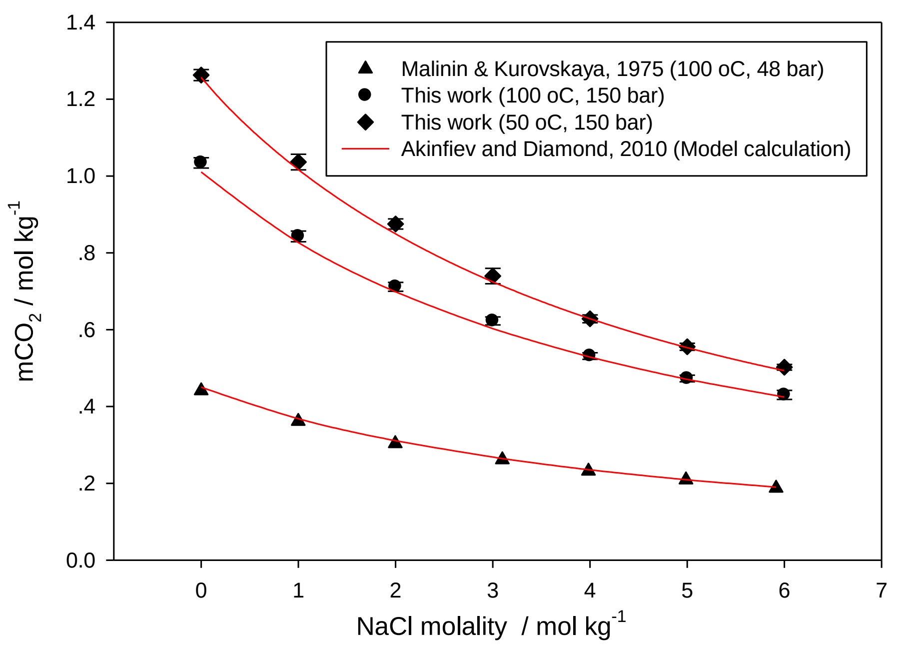
Fluid Equilibria in $scCO_2$-brine systems

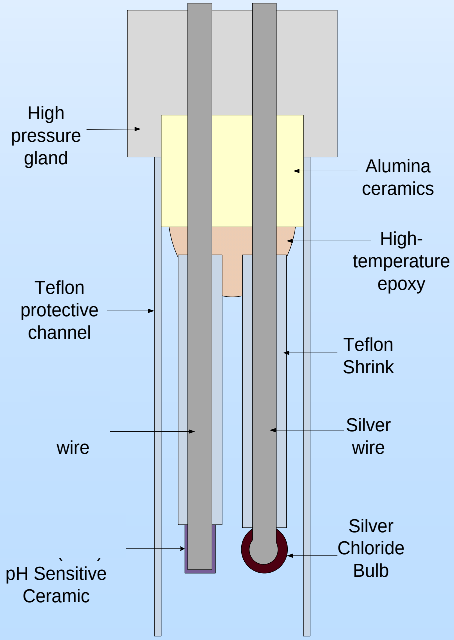
CO_2 solubility measurements completed for:

- 50, 100, and 150 °C at 150 bar.
- Three electrolytes: NaCl, $CaCl_2$, and Na_2SO_4 at ionic strengths up to 6 mol/kg
- NaCl results compare well with Akinfiev and Diamond EOS (2010)



Autoclavable probe development:

- Solid state pH sensor + Ag/AgCl reference
- Stable potentials in hydrothermal conditions up to 100 °C and 5 bar
- Minimal drift over time or with thermal cycling
- Nernstian slope (potential vs. pH)
- All-solid-state electrodes – ideal for high pressure systems



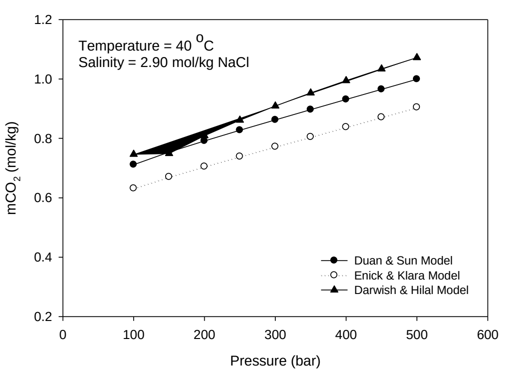
Multi-Model Predictive System for CO_2 Solubility in Saline Formation Waters

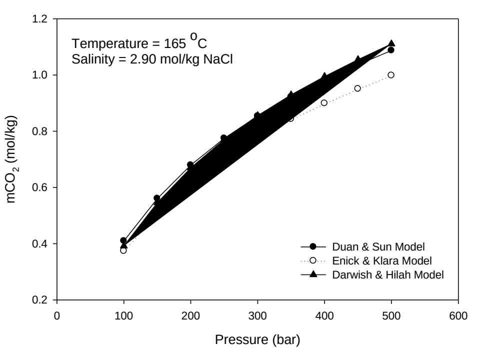
Approach:

- **Assemble database of experimental CO_2 solubility data**
- **Develop codes to model CO_2 solubility in brine at P & T**
- **Apply statistical methodology to identify best-performing CO_2 solubility models based on experimental data (Bayesian Information Criteria)**
- **Develop decision tree to prescribe best performing solubility model at specific T, P, X conditions**

Main Deliverables:

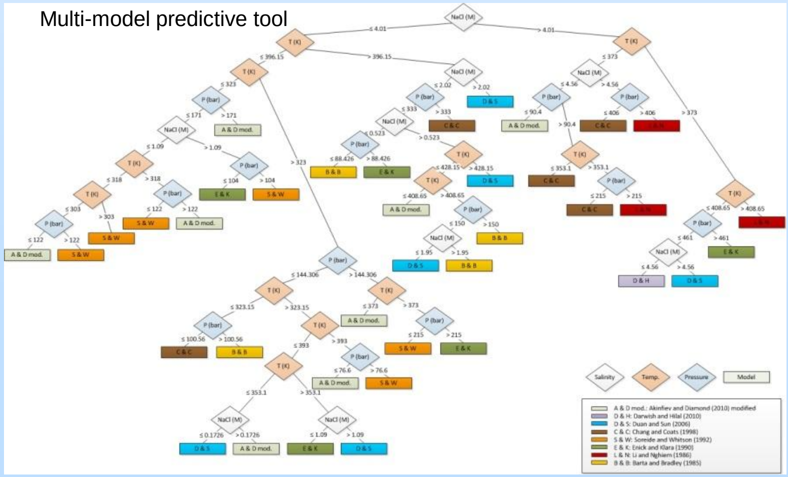
- **Multi-model predictive tool**
- **Manuscript submitted to ACS *Environ. Sci. Technol.***





Zan Wang[1], Mitchell J. Small[1], Athanasios K. Karamalidis[1,2,*] A Multi-Model Predictive System for Carbon Dioxide Solubility in Saline Formation Waters. Submitted March 2012 and under review for a special issue of Environmental Science & Technology. [1]*Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States.* [2]*National Energy Technology Lab, U.S. Department of Energy, P.O. Box 10940, Pittsburgh, PA 15236*

Multi-model predictive tool



Summary

NETL-RUA researchers are engaged in research to address CCUS Programmatic goals related to improving understanding the CO_2 mineralization rates and fluid systems, including:

- Experimental characterization of mineral dissolution rates
- Simulation with sensitivity analyses to understand the potential role of compositional and kinetic uncertainties on mineral trapping
- Experimental characterization of brine/CO_2 equilibrium conditions
- Developing approaches to identify models with best goodness of fit

Questions?

Robert Dilmore
Environmental Engineer
Geosciences Division
NETL, Office of Research and Development
(412)386-5763
dilmore@netl.doe.gov