Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Geologic Storage – Storage Mechanisms

Development of an *in situ* "window" into below-ground geological sequestration reaction processes

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May 8-11, 2006 • Hilton Alexandria Mark Center • Alexandria, Virginia

Background:

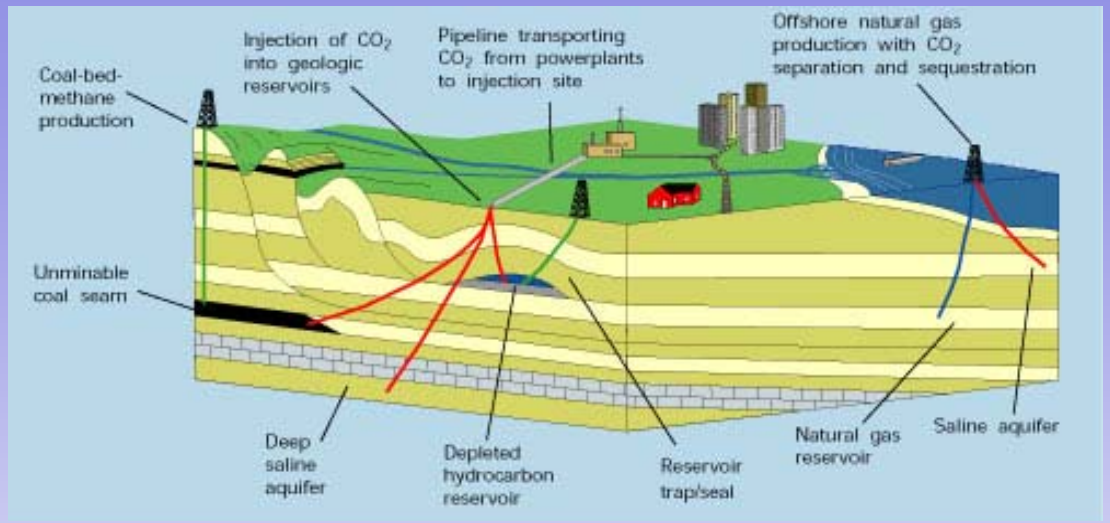
- Mineral Sequestration Working Group (NETL-DOE) (1998-present)
- **ASU:** 5 faculty, 2 postdocs, 4 grad students, 2 undergrads
- Specialization:

  atomic level mechanistic analysis
  in situ process characterization
  atomic level property/reaction simulations
  multi-phase fluid dynamics simulations

- Support:

  DOE-NETL, Argonne National Laboratory

GEOLOGICAL SEQUESTRATION of CO_2



Key concept:

Put the carbon back underground (return your "empties" *Lackner, 2003*)

Promising near-term solution:

1) Enormous storage capacity:

US Reservoirs	Estimated CO_2 Capacity (Gt)
Saline Formations	5-500
Deleted Gas Reservoirs	80-100
Depleted Oil Reservoirs	40-50
Unmineable Coal Beds	15-20

Global: → 320-10,000Gt

2) Geologic formations in close proximity to power generation plants (saline reservoirs).

3) Well established that geologic formations can store oil, gas, methane, CO_2 on a geologic time scale.

4) EOR technology for injecting CO_2 into reservoirs already in use.

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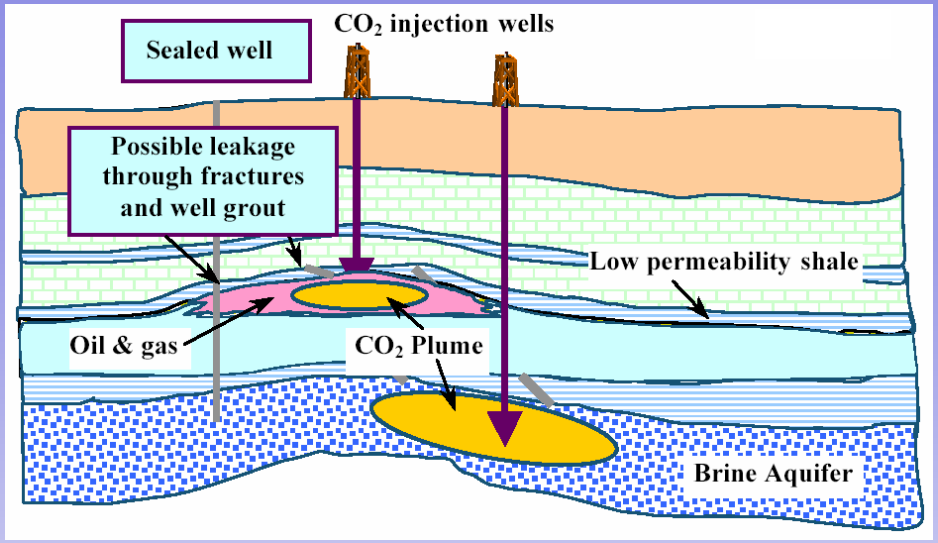


(Carey *et al*, **LANL**, 2005)

Main CO_2 sequestration mechanisms:

(1) structural trapping due to low-permeability

(2) solubility trapping via $scCO_2$ dissolution into oil and/or water

(3) mineral trapping reactions producing permanent mineral products

Factors affecting the redistribution/capacity of injected CO_2 →

- miscibility
- viscous fingering
- reaction kinetics
- gravity segregation
- leakage → natural/artificial pathways

Fundamental knowledge of the physical and chemical behavior of CO_2 in the host geologic environment is highly desirable

Can we study fluid activities, transport, and reaction processes *at actual below-ground conditions* ?

Areas of particular interest include:

- fluid/solid reaction mechanisms
- diffusion rates of carbon-bearing species in solution and porous minerals
- the pressure and temperature dependence of key solution species' activities and the formation of solid carbonate phases and their aqueous complexes.

This talk:

- Development of specialized ***microreactor*** cells which allow study of geological sequestration processes over a broad range of below-ground P and T conditions using:

  (1) x-ray synchrotron
  (2) nuclear magnetic resonance
  (3) Raman

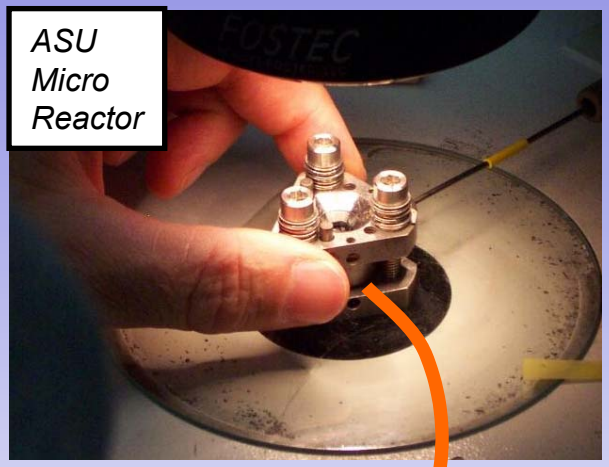
- First principles quantum chemical simulations of structure/properties/ processes.

Examples:

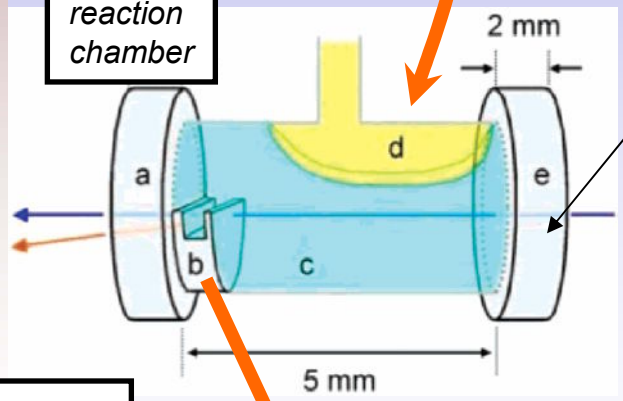
(i) hydrous carbonate phase formation
(ii) aqueous diffusion rates of sequestration species
(iii) temperature dependence of mineral trapping reactions.

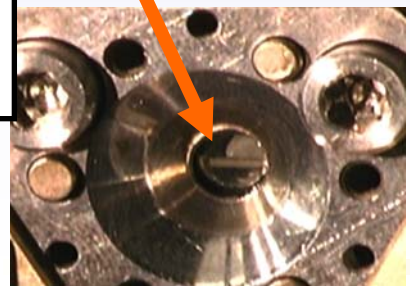
RECENT ADVANCES in CARBON SEQUESTRATION at ASU:

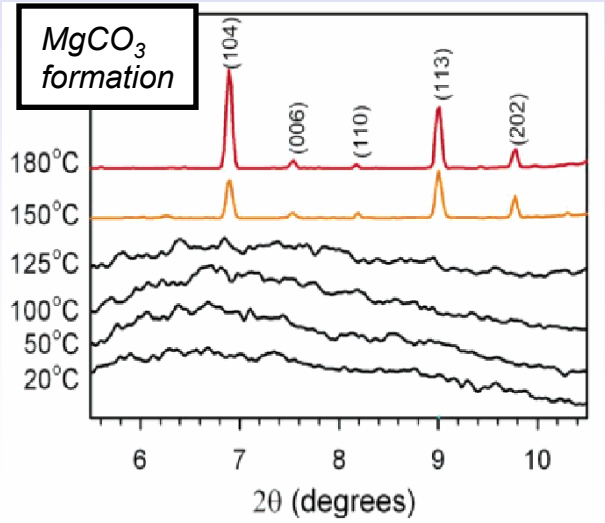
DEVELOPMENT OF A CHEMICAL MICRO-REACTOR for IN-SITU REACTION STUDIES

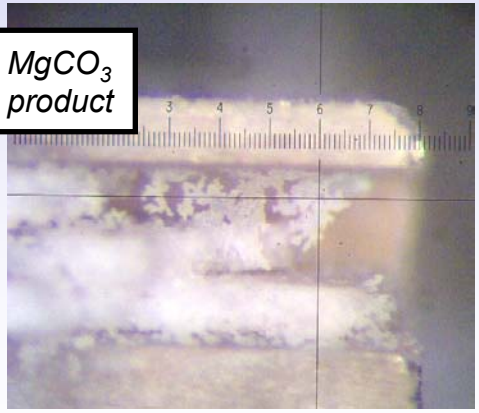


- Moissanite (single crystal SiC) window technology enables spectroscopic access to chemical processes up to T=300 ^{o}C and P=300 atm.
- Use large external ballast to maintain constant chemical activity as reactants are consumed (e.g., <u>unlike</u> closed autoclave systems).
- *in situ* monitoring of reactions allows parameter space to be quickly and accurately mapped (see $MgCO_3$ formation below).









ASU experiments performed at the GeoSoilEnviroCARS synchrotron beamline (Argonne National Laboratory)

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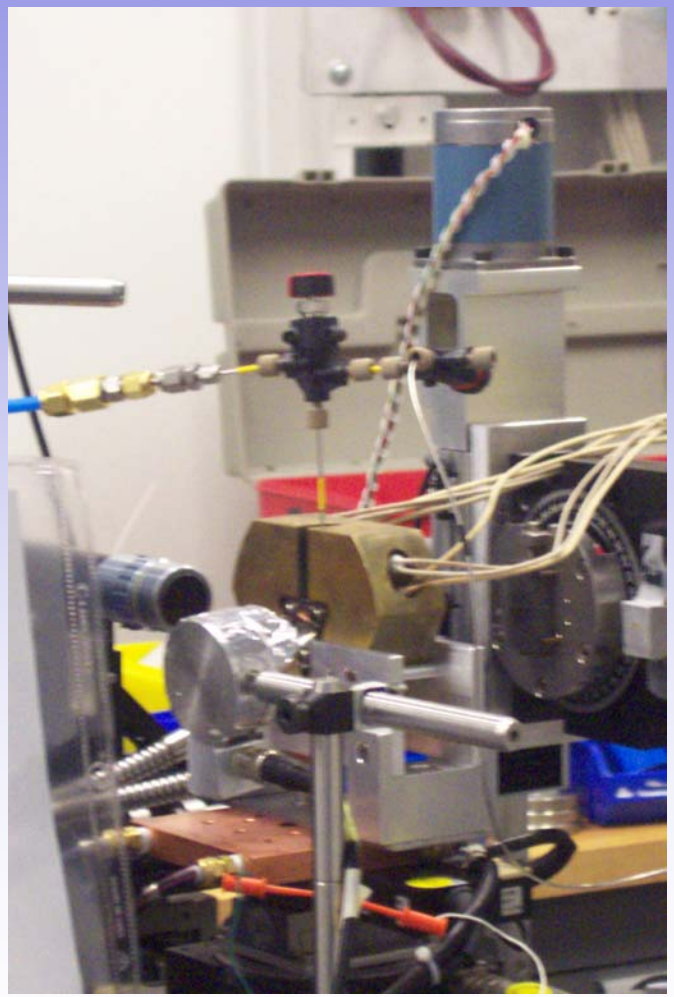
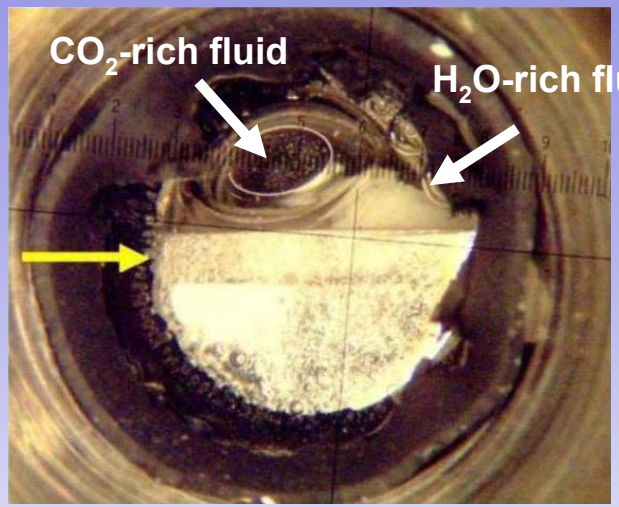
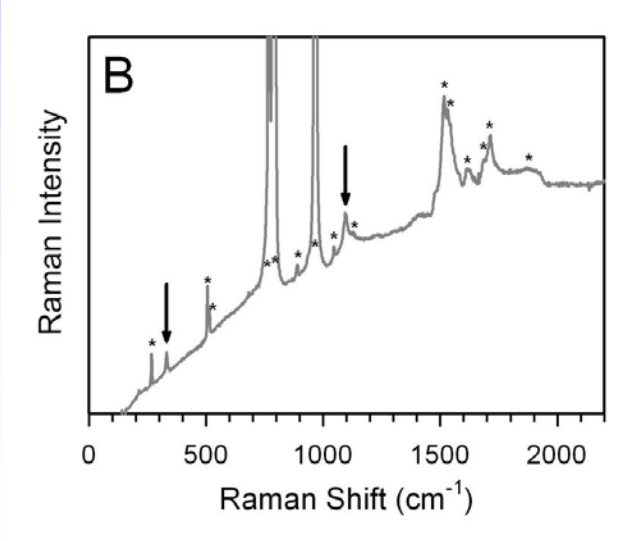




H_2O-CO_2 mixture at 180°C and 150 atm

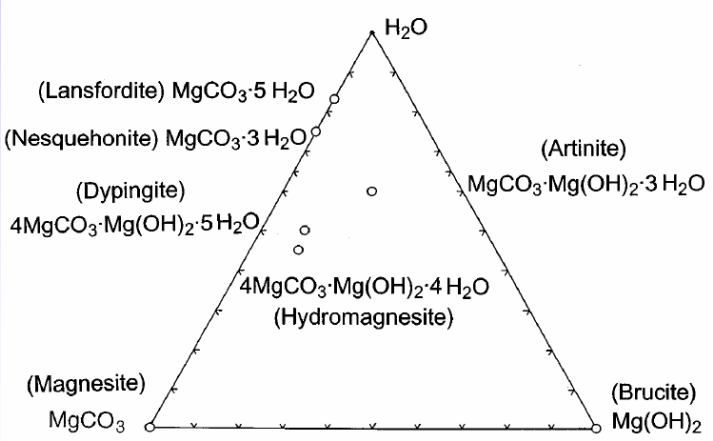


Formation of crystalline $MgCO_3$ confirmed using Raman (shifts at 331 cm^{-1} and 1094 cm^{-1})

FUNDAMENTAL STUDIES OF HYDROUS CARBONATE PHASES

Background and Relevance: Programmatic DOE (Fossil) emphasis on "geologic" CO_2 sequestration (below ground) → how and when do hydrous carbonates form at below ground conditions. MgO is the only engineered barrier certified by EPA for the Waste Isolation Pilot Plant (WIPP) – formation of hydrous carbonates common.

Hydromagnesite	$Mg_5(CO_3)_4\ (OH)_2$	$4H_2O$
Giorgiosite	$Mg_5(CO_3)_4\ (OH)_2$	$4H_2O$
Artinite	$Mg_2(CO_3)\ (OH)_2$	$3H_2O$
Dypingite	$Mg_5(CO_3)_4\ (OH)_2$	$5H_2O$
Nesquehonite	$Mg\ (CO_3)$	$3H_2O$
Lansfordite	$Mg\ (CO_3)$	$5H_2O$



hydromagnesite

nesquehonite

- Mg-rich minerals as potential reservoir well-boar sealing agents (O'Connor *et al*, 2005)
- Formation of Mg-based hydrous carbonates in basaltic geologic sequestration formations.
- Structural data on hydrous phases is scant – large uncertainties in the themodynamic data ($\Delta G, \Delta S$).

Urgent need for fundamental studies

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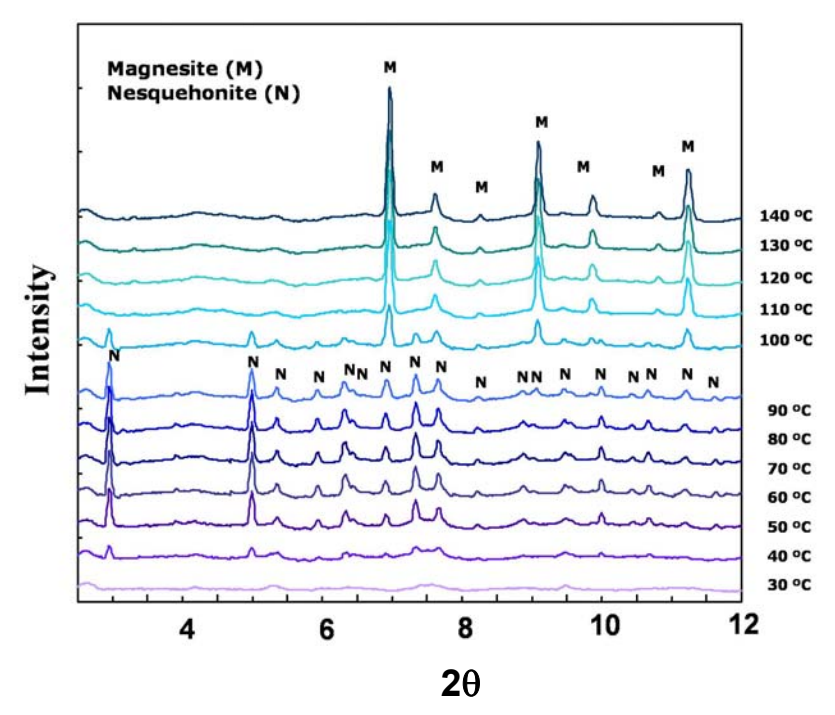
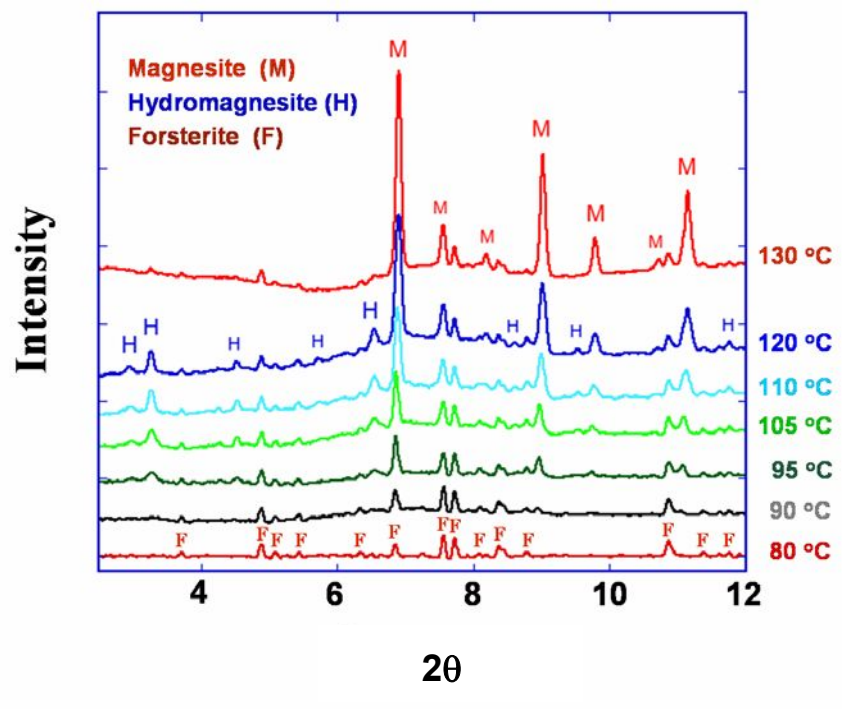
Synchrotron Experiments (Feb 2006)





- Antigorite activated for 2 hours
- reacted @ P_{CO2} ~ 150 atm in buffered (0.64 M NaHCO3 + 1.00 M NaCl) H_2O-CO_2
- **Nesquehonite** onset observed at ~ 40°C
- Recession by 100°C, and onset of $MgCO_3$

- Heat activated lizardite (1% residual OH)
- reacted @ P_{CO2} ~ 150 atm in buffered (0.64 M NaHCO3 + 1.00 M NaCl) H_2O-CO_2
- **Hydromagnesite** + magnesite onset observed at ~ 90°C
- Recession of hydromagnesite by 120°C, continued growth of $MgCO_3$

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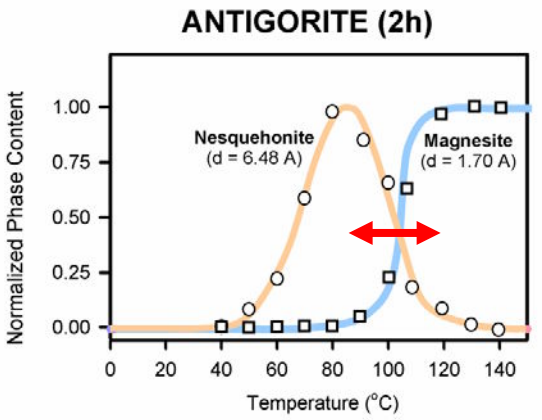
Phase stability field for the $MgO-CO_2-H_2O$

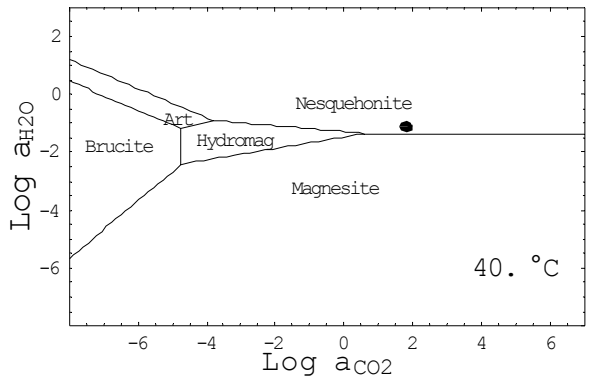
- Activities obtained from Spycher et al EOS
- Dot represents activities corresponding to *in situ* experiment

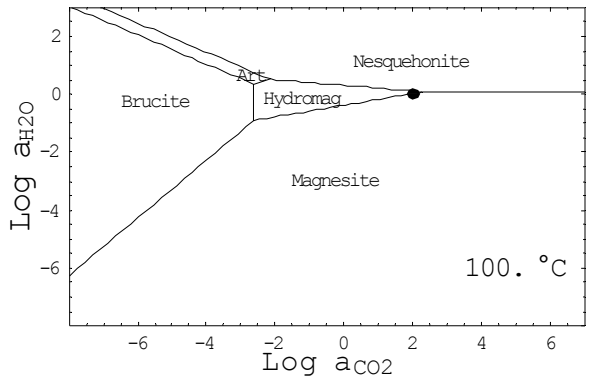


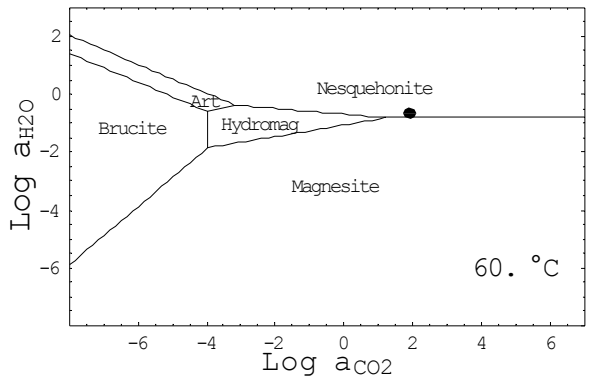
- Kinetic origin of differences observed transitons:

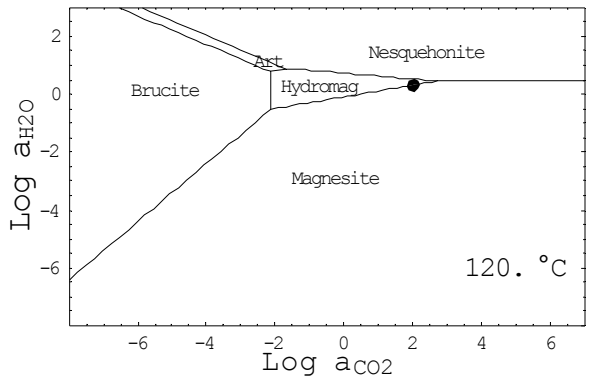
hydromag → magnesite

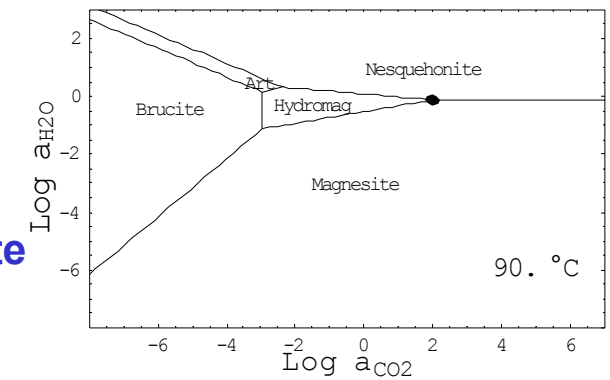
nesquehonite → magnesite

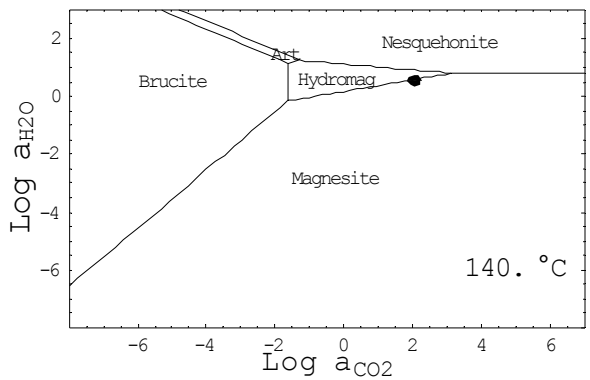












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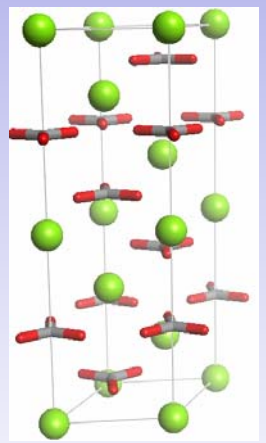
Preliminary Simulations: Connection between structure and kinetics?

- use GGA-based DFT (hydrogen bonding + improved ΔE)

- Excellent agreement with experimental structure from xray (significant effect on lattice constants due to vibrational entropy contribution from confined water

magnesite

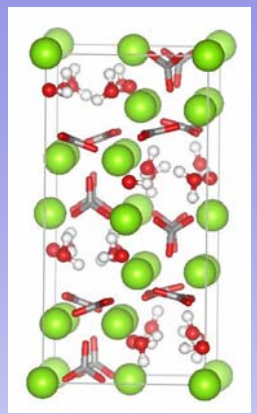


- hydromagnesite contains distribution of CO_3 orientations

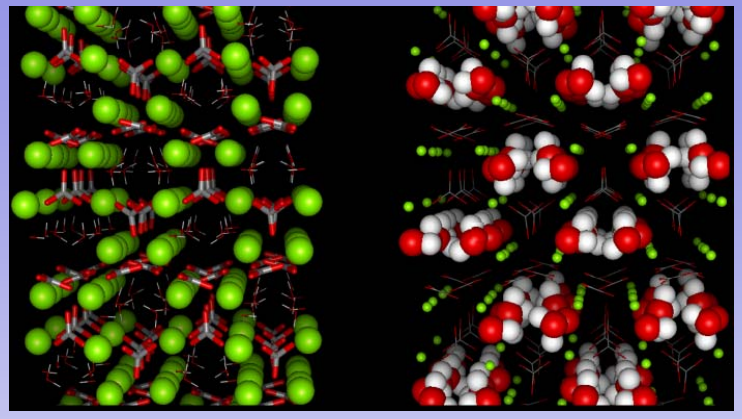
- nesquehonite contains coplanar CO_3 units

- MD simulations suggest **simple kinetic pathway between nesquehonite and magnesite**

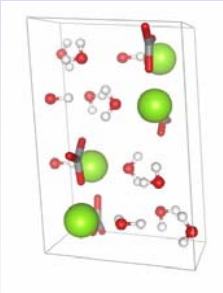
hydromagnesite



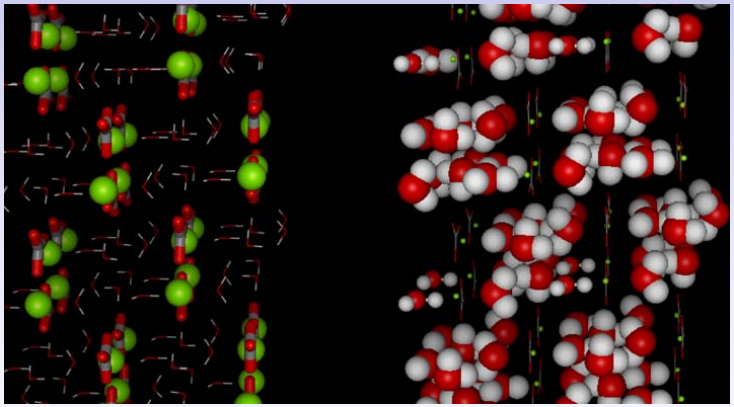
$Mg_5(CO_3)_4(OH)_2 \cdot 4\ H_2O$



nesquehonite



$MgCO_3 \cdot 3\ H_2O$



$$Mg(OH)_2 + CO_2 + 2H_2O \Rightarrow MgCO_3 \cdot 3(H_2O) \qquad \Delta H = -166\ kJ/mol$$

$$5Mg(OH)_2 + 4CO_2 \Rightarrow Mg_5(CO_3)_4(OH)_2(H_2O)_4 \qquad \Delta H = -306\ kJ/mol$$

$$5\ [MgCO_3 \cdot 3(H_2O)] \Rightarrow Mg_5(CO_3)_4(OH)_2(H_2O)_4 + 10\ H_2O + CO_2 \qquad \Delta H = +536\ kJ/mol$$

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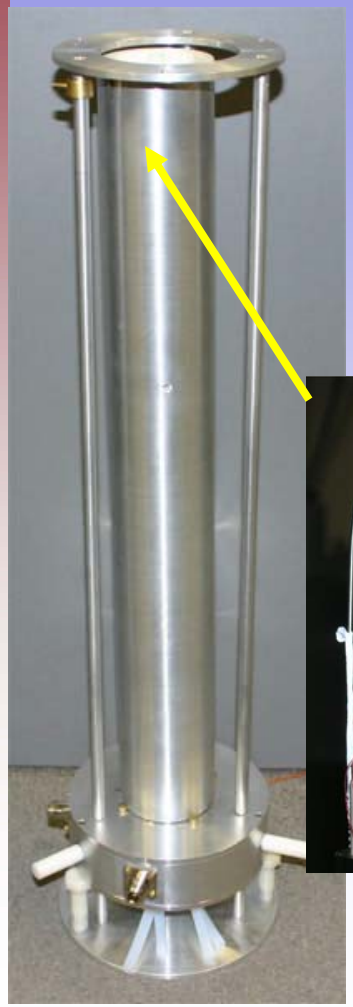
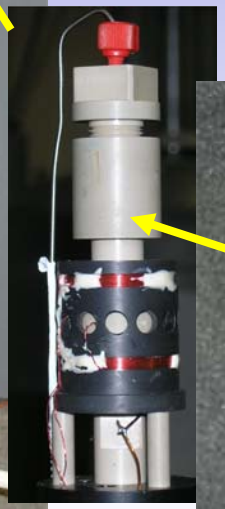
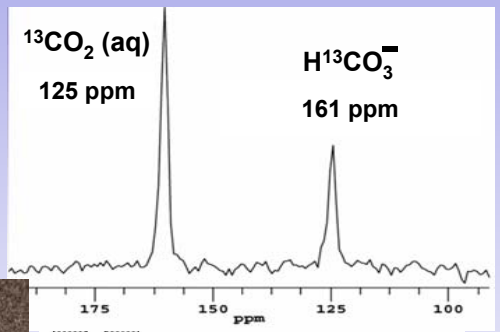
DEVELOPMENT OF AN NMR MICRO-REACTOR for IN-SITU REACTION STUDIES

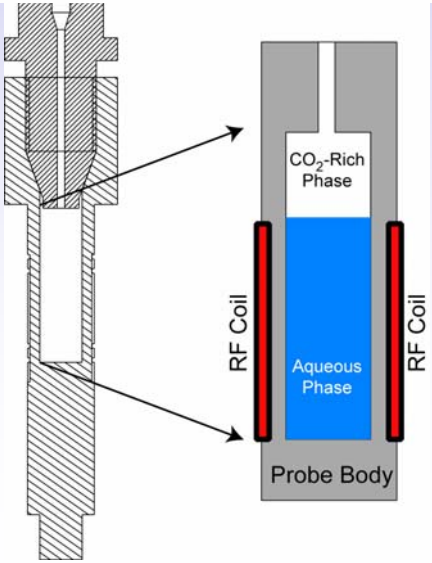




Rapid *In Situ* Chemical Observations

- Study H_2O-CO_2 system at high P & T
- Relative speciation of $CO_{2(aq)}$, HCO_3, etc
- Quantitative
- Interface diffusion
- Self-diffusion





- Designed and developed at ASU
- Wide-bore super-conducting magnet
- 300MHz Varian Infinity Solids NMR
- Chemically inert & non-magnetic Vespel, PEEK
- Pressure, activity & temperature control to 175 °C and 150+ atm
- "double tuning" allows simultaneous measurement of ^1H and ^{13}C signals

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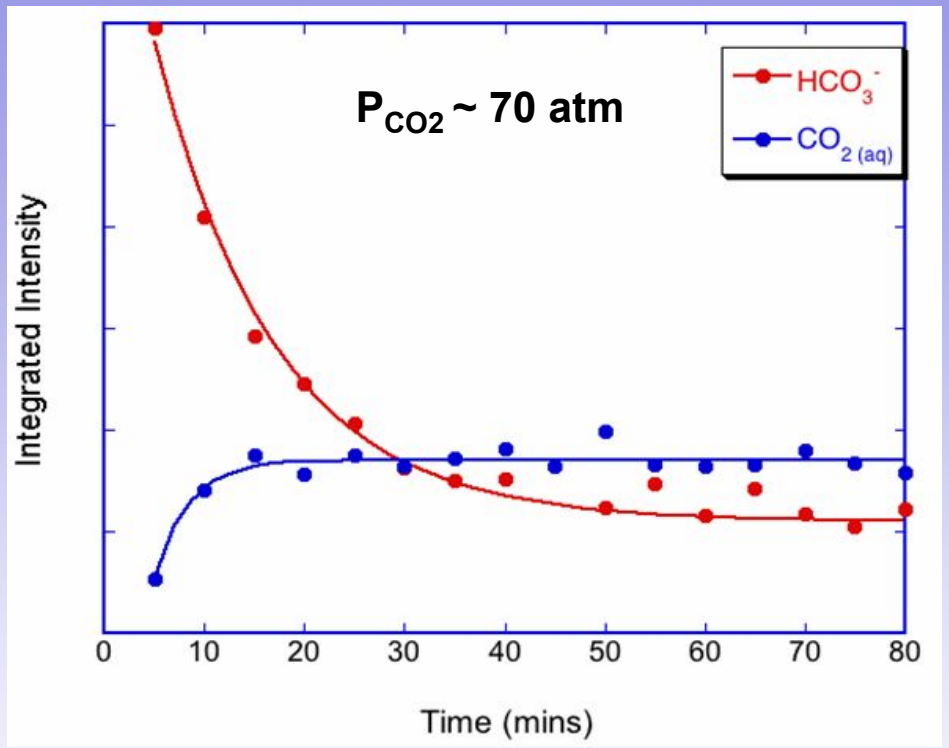
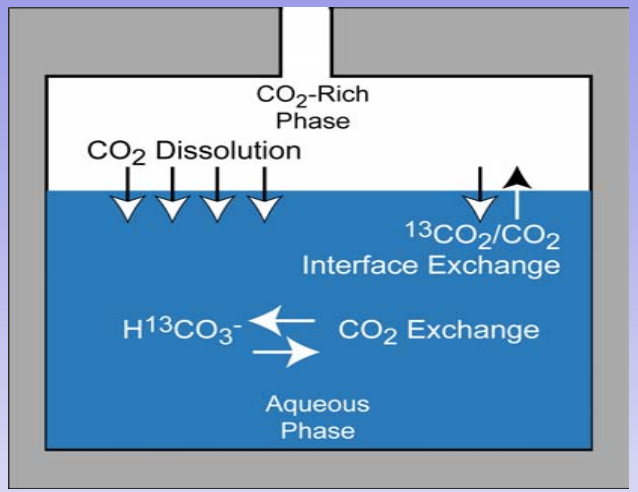
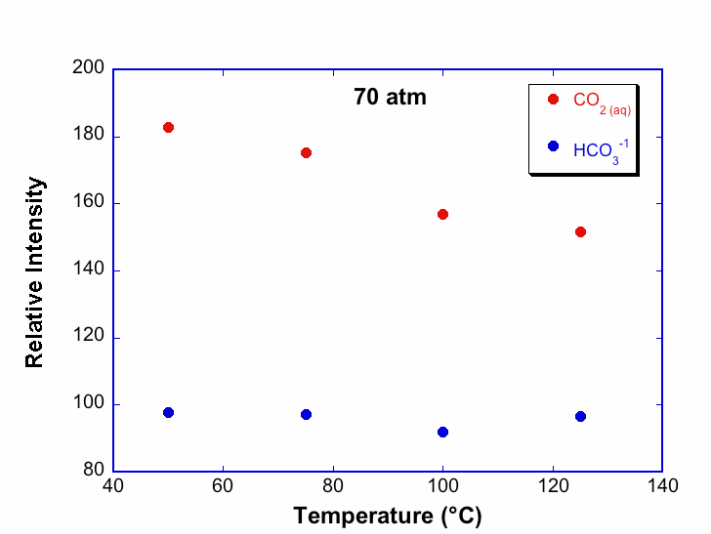




Carbon Speciation vs T (0.64M $NaHCO_3$ + 1M NaCl)



- CO_2 Dissolution
- $H^{13}CO_3/CO_2$ bulk exchange
- $^{13}CO_2/CO_2$ interface exchange

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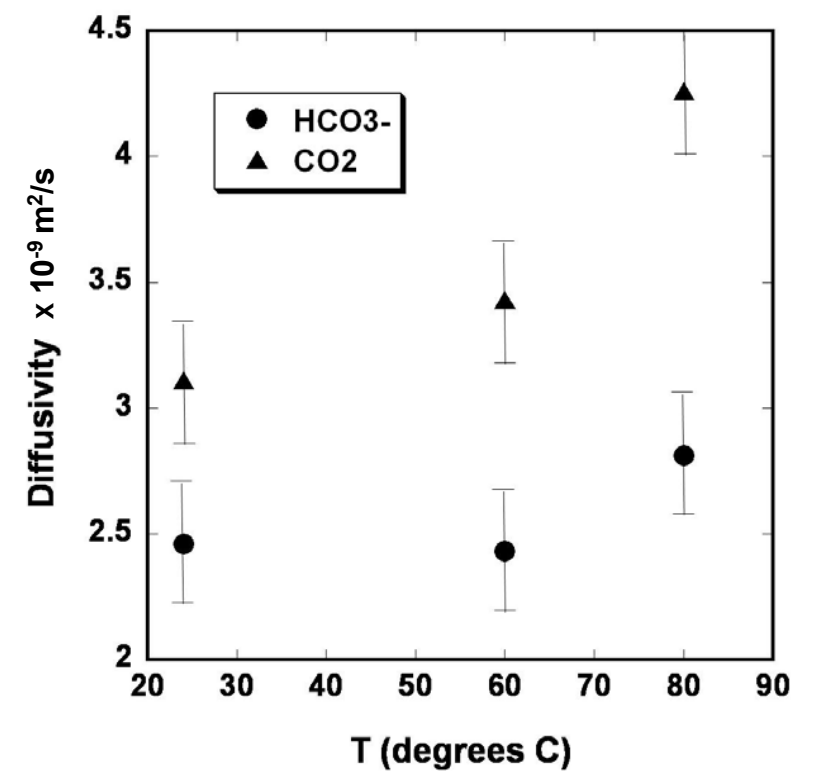
Pressure and Temperature dependence of CO_2 and HCO_3^- diffusivities (self-diffusion)

- Use $NaHCO_3$ containing 99% ^{13}C
- Pressurize to 125 atm CO_2
- Equilibration (CO_2 dissolution, exchange between dissolved CO_2 and bicarbonate, exchange of $^{13}CO_2$(aq) with CO_2 rich fluid)
- Observed $CO_{2(aq)}$ concentration in good agreement with known equilibrium values.
- Analyze intensity vs. gradient pulse length data to obtain diffusivities at desired P and T

Diffusivity of CO_2(aq) and HCO_3^-(aq) vs T at 125 atm



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CONCLUSIONS

- Microreactor cell and high pressure NMR probe enable fundamental *in situ* studies of CO_2 interactions with below ground host geological envrironment

Current *in situ* studies → phase formation and stability of hydrous/anhydrous magnesium carbonate phases as a function of temperature, $P(CO_2)$ and aqueous chemistry.

→ NMR probe has provided first direct determination of $CO_2/HCO_3/CO_3$ transport/diffusion at actual sequestration (above and below ground) conditions

FUTURE DIRECTIONS

- *In situ* observations of the permeability and porosity changes of reservoir core materials under actual CO_2 injection/sequestration conditions

- Long term "in situ" studies using a bank of microreactors to validate "ex situ" measurements of $scCO_2$/brine/mineral reactions.