Monitoring of Geological CO_2 Sequestration Using Isotopes and Perfluorocarbon Tracers

Project Number FEAA-045

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Transforming Technology through Integration and Collaboration
August 18-20, 2015

Presentation Outline

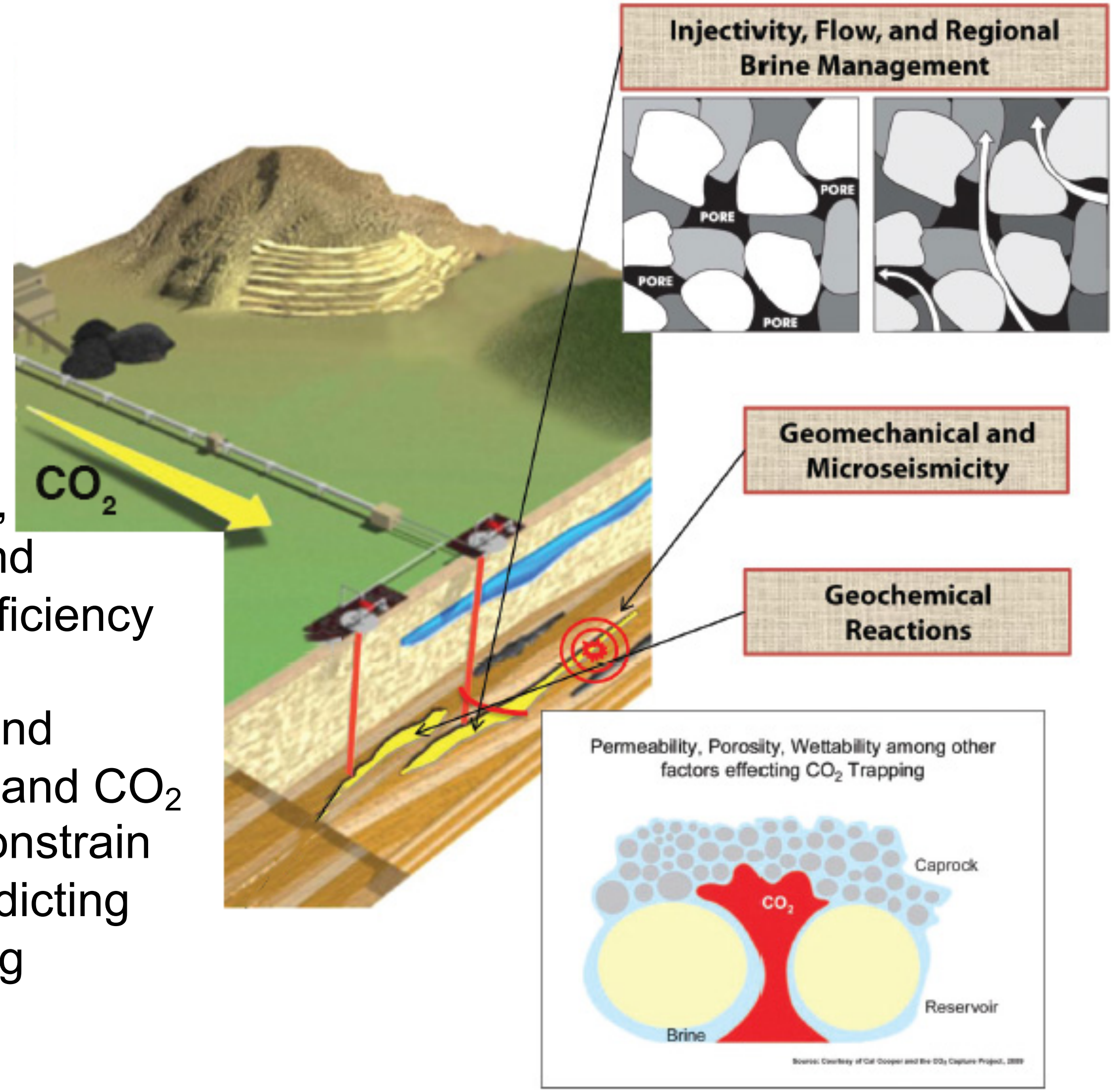
- Tracers for CO_2 storage programs
- Cranfield, Mississippi SECARB project
- Conservative perfluorocarbon tracers
- Gas and isotope geochemistry
- Lessons learned from tracers in brine CO_2 storage
- Future plans

Benefit to the Program:
Geologic Storage and Simulation and Risk Assessment

Provide information on physical and geochemical changes in the reservoir, ensuring CO_2 storage permanence

Facilitate a fundamental understanding of processes impacting the behavior of fluids —diffusion, dispersion, mixing, advection, and reaction— to improve storage efficiency

Ground-truth behavior of fluids and gases, CO_2 transport properties and CO_2 saturation that can be used to constrain reservoir simulation models, predicting CO_2 storage capacity & designing efficient MVA programs



Modified from NETL Carbon Storage GSRA Technology Research Areas Illustration

Project Overview

Develop complementary tracer methods to interrogate the subsurface for improved CO_2 storage efficiency and permanence

- Complete geochemical and PFT analysis from 5-year Cranfield, Mississippi storage project
- Transfer technology to storage project partners
- Improve ultra-trace detection methods for PFT mixtures
- Integrate geochemical, isotope and PFT results into an advanced reservoir simulator for improved storage predictions

Candidate Tracers
(*complementing hydrology and geophysics*)

Brines: Native non-conservative tracers that respond to changes

pH, alkalinity, electrical conductivity

Cations: Na, K, Ca, Mg, ΣFe, Sr, Ba, Mn

Major anions: Cl, HCO_3, SO_4, F, Br

Organic acids: acetate, propionate, formate, oxalate, etc.

Other organics: DOC; methane, CO_2, benzene, toluene

Gases: Native conservative tracers or added conservative tracers

Gases: N_2, H_2, O_2, CO_2, CO, CH_4, $C_2 – C_{n+}$

Noble gas tracers: Ar, Kr, Xe, Ne, He (and their isotopes)

Perfluorocarbon tracers (PFTs):

PMCP, PECH, PMCH, PDCH, PTCH (SF_6)

Isotopes: D/H, $^{18}O/^{16}O$, $^{87}Sr/^{86}Sr$ in water, DIC, minerals;

$^{13}C/^{12}C$ in CH_4, CO_2, DIC, DOC, carbonates

Processes Impacting Tracer Signals

Hydrodynamic: Mixing, dispersion, advection

Dissolution and/or exsolution at gas/brine/HC interfaces

Diffusion into brine

Sorption onto mineral surfaces

Partitioning into hydrocarbons: liquid or solid (e.g. kerogen)

Microbial activity → biomineralization

Fluid-rock interaction (weathering, digenesis, hydrothermal)

Diffusion in porous/fractured media; minerals

fast

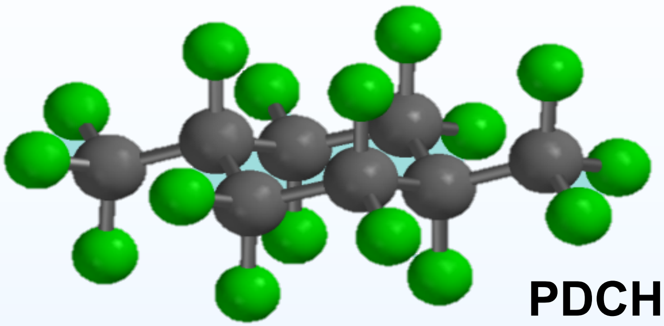
KINETICS

slow

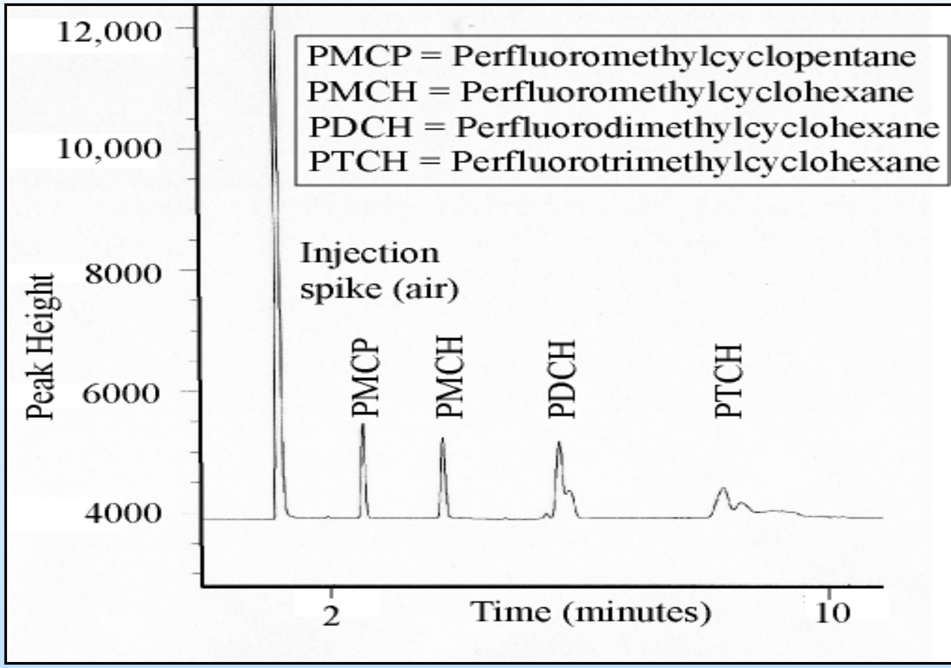
A combination of tracers assesses the multiple length and time scales relevant to Carbon Storage.

Benefits of PFTs & SF_6 Conservative Tracers

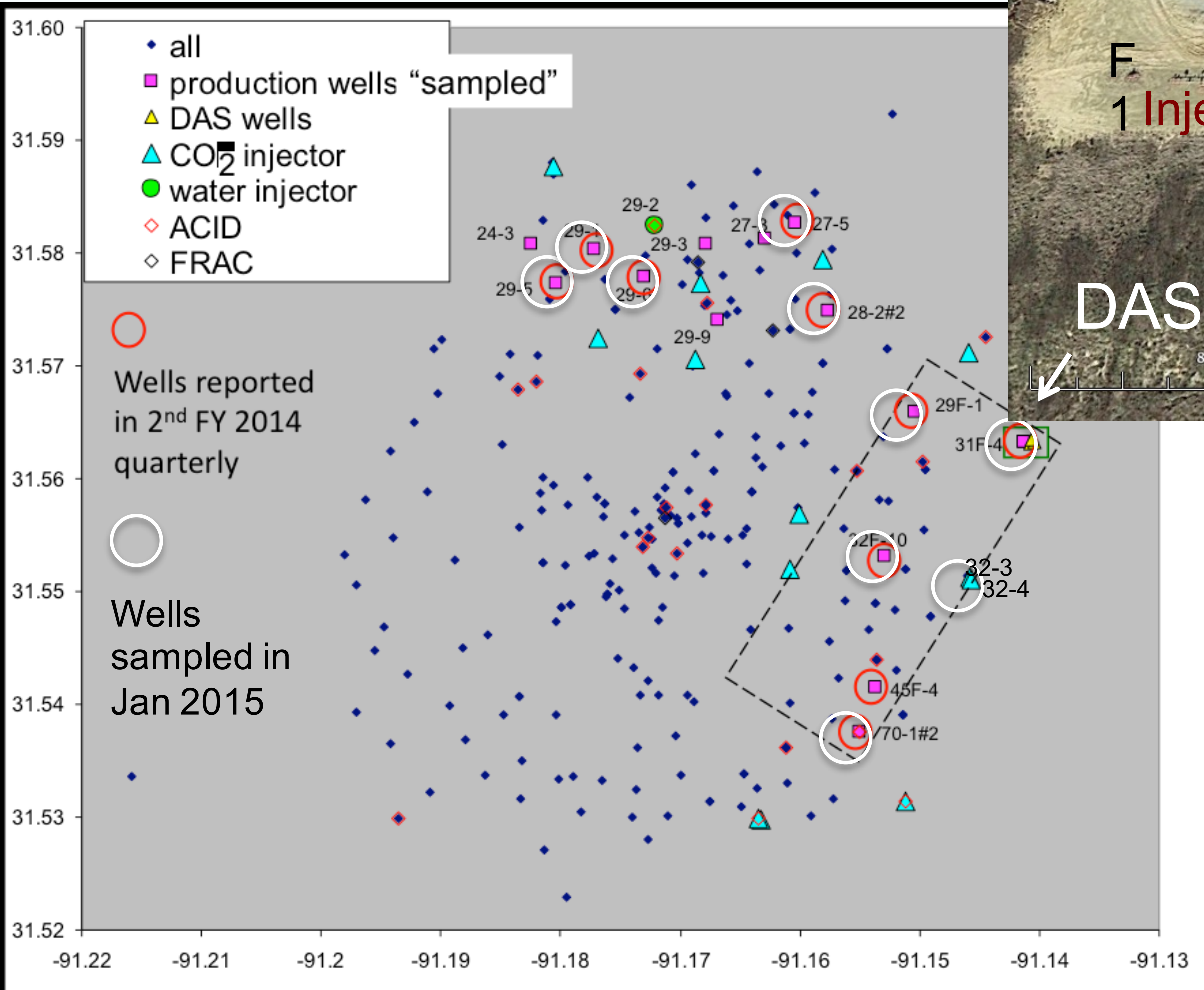
- Non-reactive, non-toxic, inexpensive & stable to 500°C
- Detectable at pg-fg levels
- Several PFTs can be quantified in a single analysis
- Scalable to 1000s of samples
- Different PFT "suites" assess multiple breakthroughs → *flow regime indicator*
- Complements stable isotopes and geochemistry for modeling heterogeneous flow

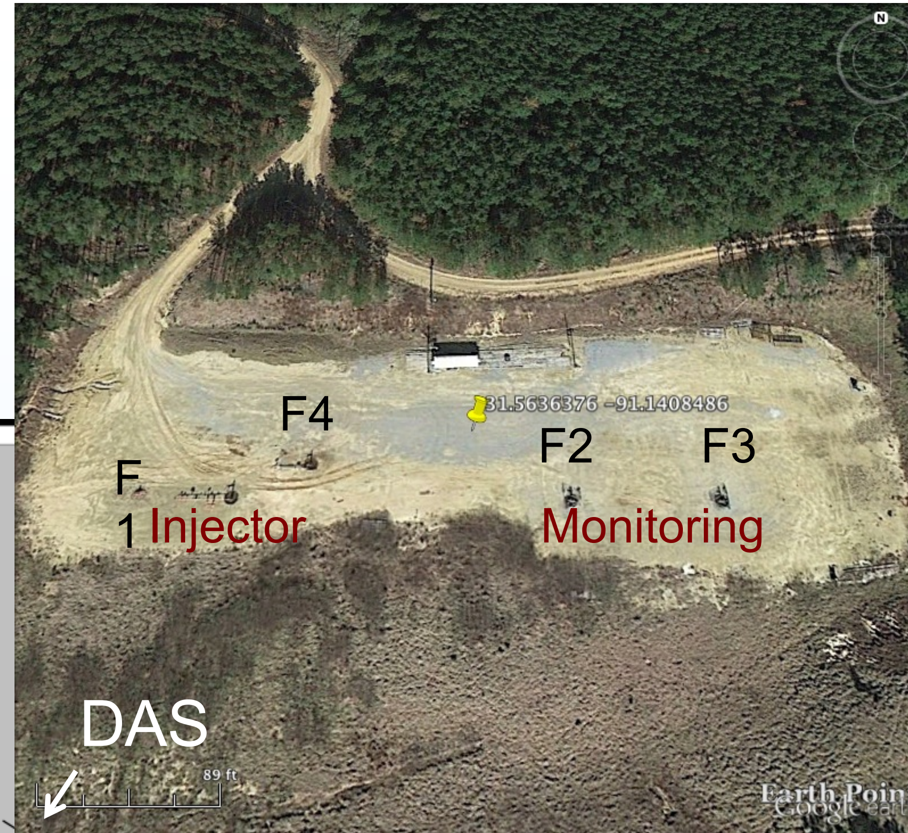


PDCH



Cranfield, MS Wells

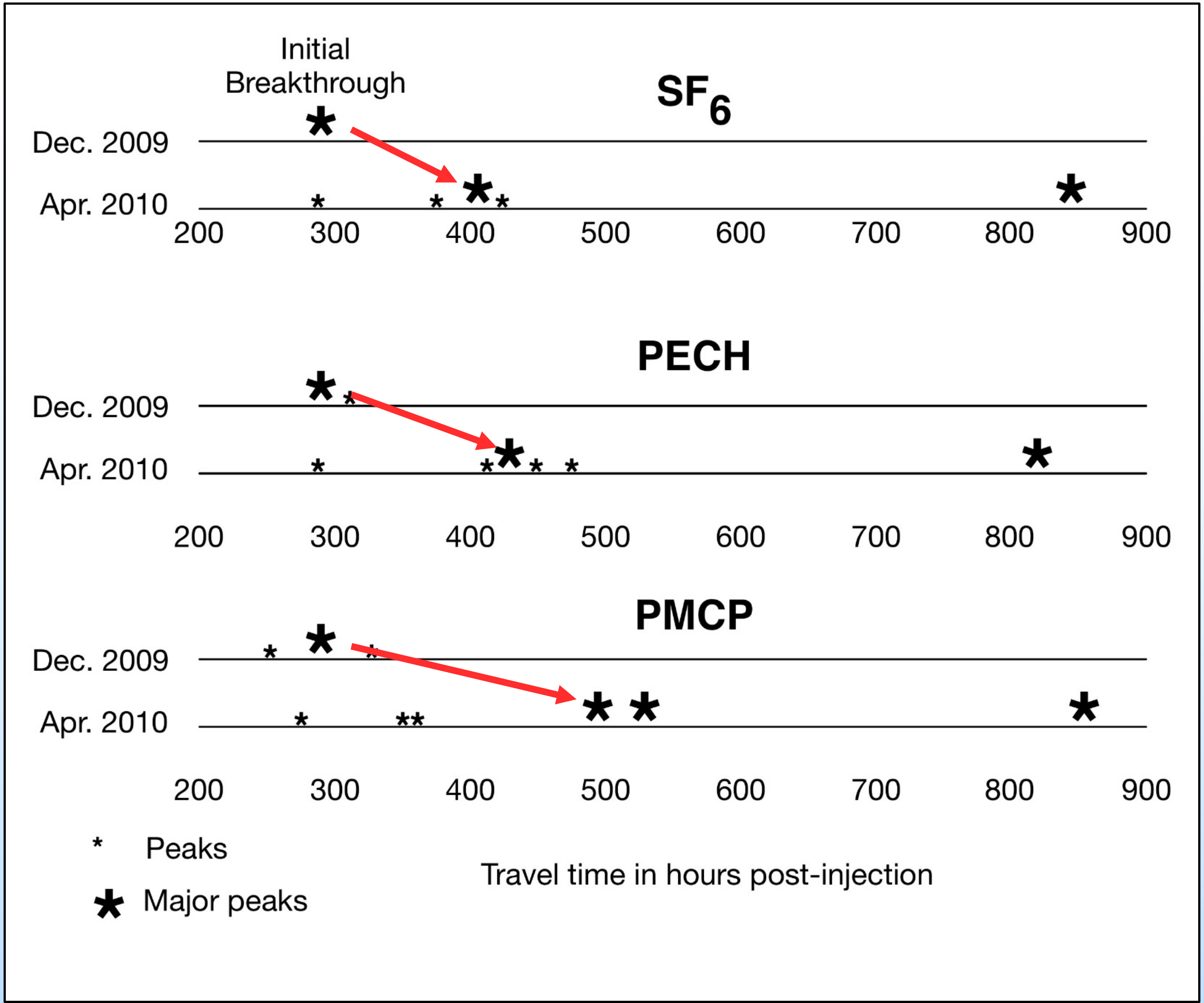




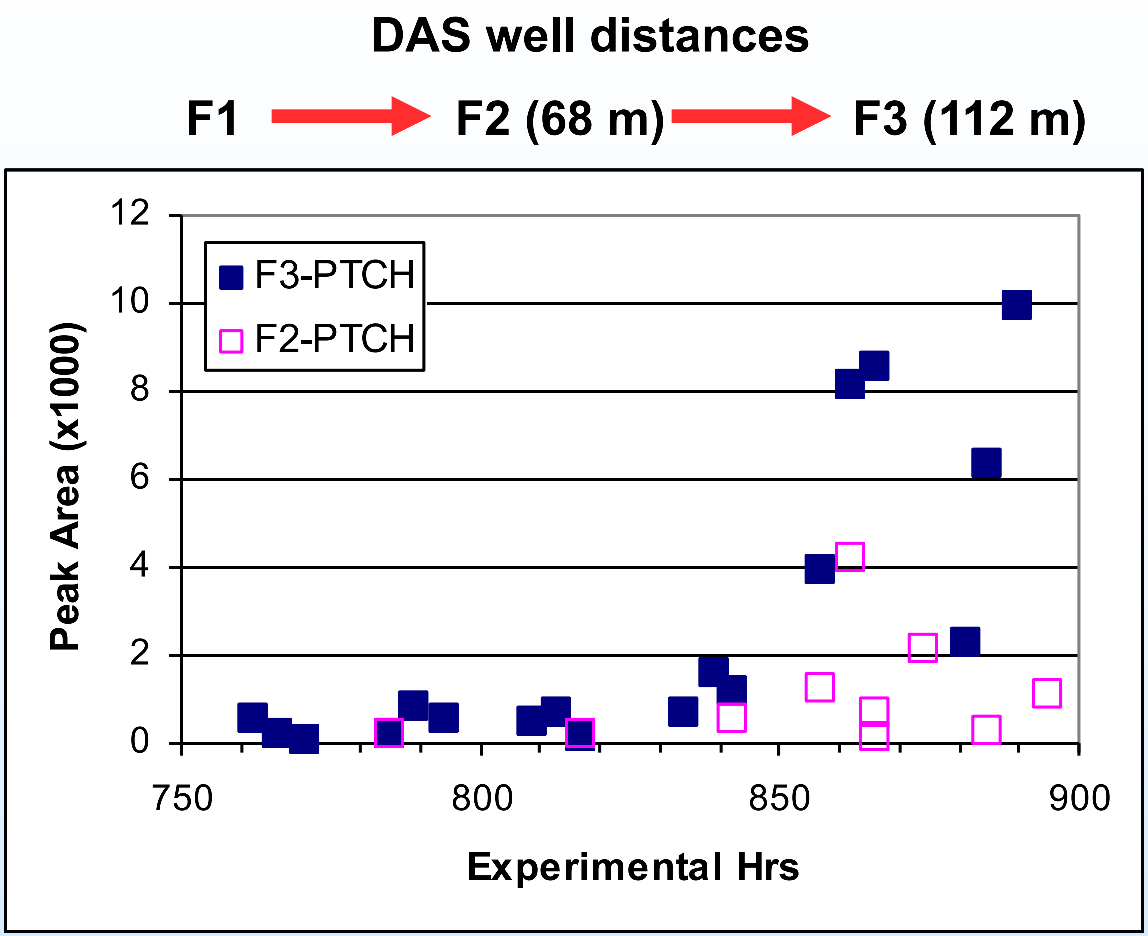
Thanks to:

- SECARB
- Jiemin Lu @ Bureau of Economic Geology (UT-Austin)
- LBNL
- Sandia Technology
- Denbury Resources

PFTs at Cranfield – F2 Well



PTCH Tracer Results from Cranfield



April 2010 campaign:

PTCH was added at t = 693 hr

F2 – Closer to F1, delayed breakthrough compared to F3, smaller peak areas

F3 – Further from F1, Earlier breakthrough compared to F2, larger peak areas

Radial-like flow in 2009

Multi-flow paths in 2010 with short circuits to F3

Final Cranfield Campaign January 2015

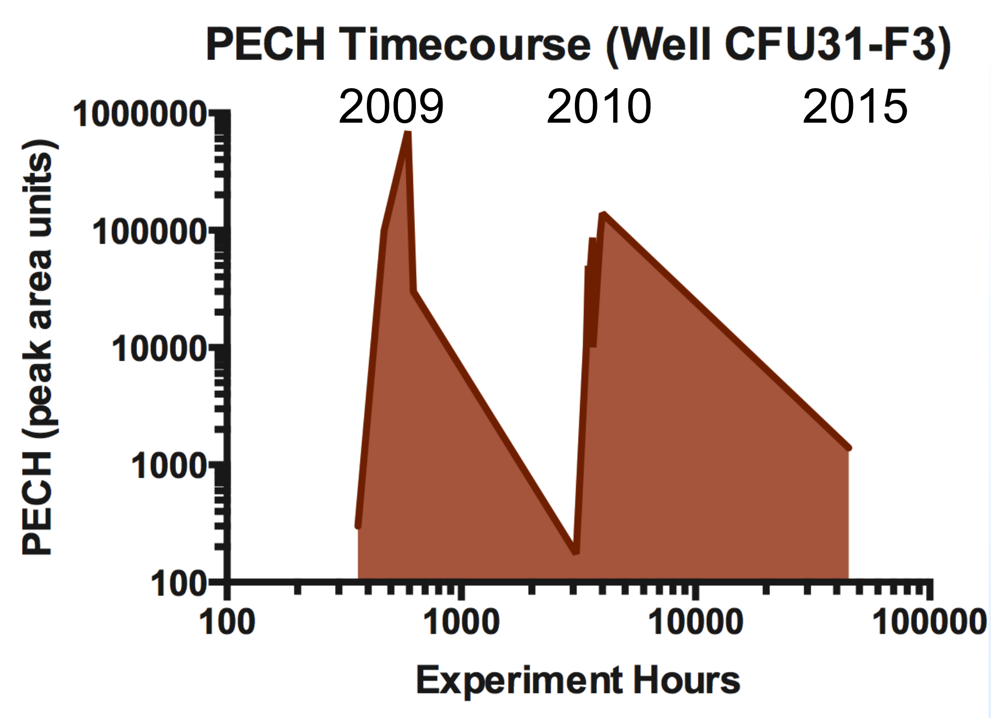
- Gas and water samples for PFT, water chemistry and stable isotope analyses from the DAS site and from nearby production and separation wells
- 14 wells sampled for PFTs
- Additional samples from various CO_2 injection wells, Jackson Dome CO_2 and recycled CO_2 used for injection.

Gas collection into steel canister directly at well fitting.

Gas/water separator for gas collection. Fluids were collected into a carboy.

PFTs Present After 5 Years of Experiment

- Long-term diffusive tail (50 X longer than Frio)
- Tracer reservoir in F3 vicinity (>20,000 hr of previous inactivity)
- Revealed differential transport of SF_6 and PECH (and others)



PFTs Observed as Peak Area Units for the F3 Observation Well

PFT	F3 Pre-Vent 01-13-15	F3 Post Vent 01-23-15	F3 Post Vent 01-26-15
SF6	185,245	0	0
PMCP	571	173	37
PMCH	1079	428	121
PECH	2017	1233	377
PTCH	541	376	107

Lessons Learned

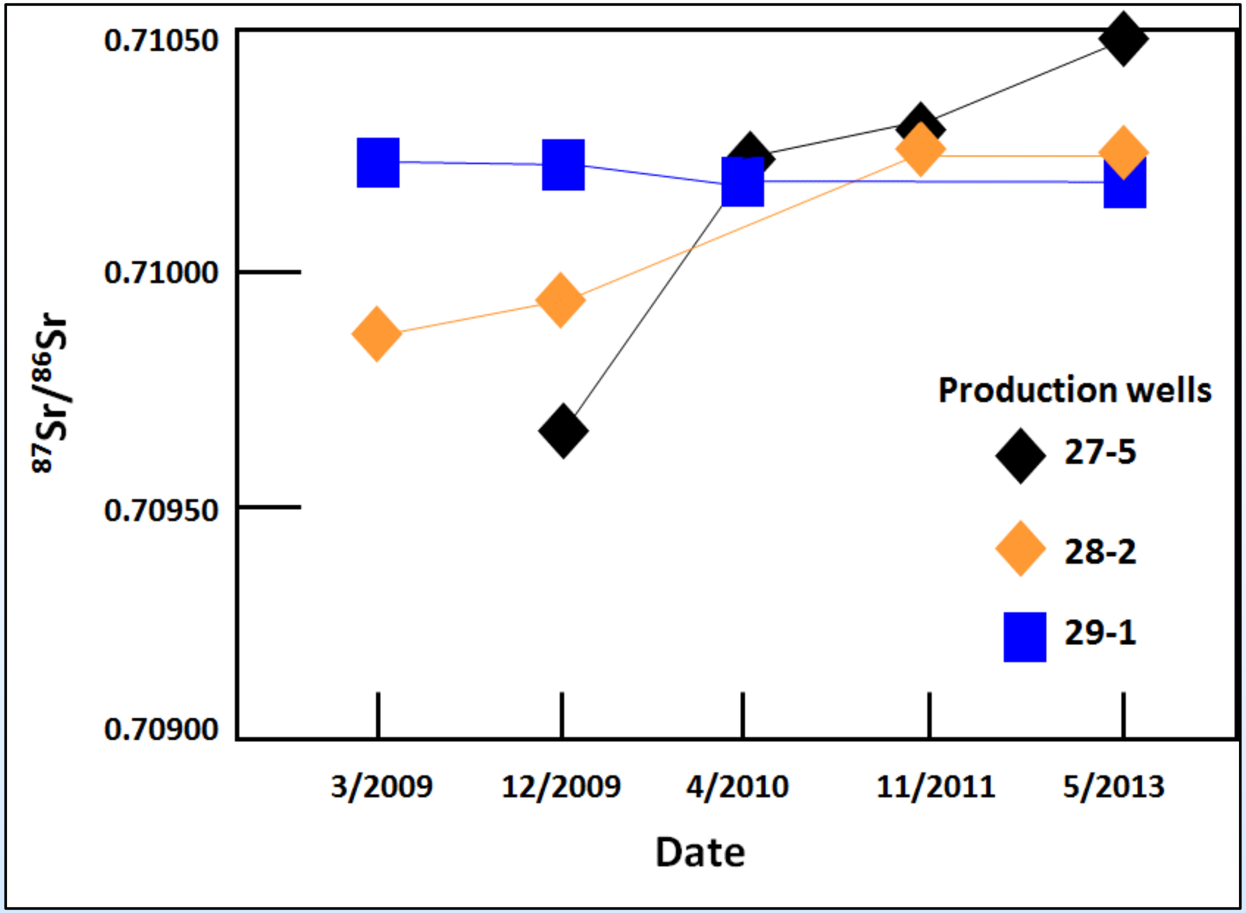
- Long-term experiments are important (long-tail)
- Flow paths evolve in the reservoir
- Sensitive tracer detection is critical
- Suites of tracers are essential for interpreting flow
- Multiple suites of tracers are required for monitoring with repeated injections

Benefits of Stable Isotopes as Nonconservative Tracers

($^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, $^{87}Sr/^{86}Sr$)

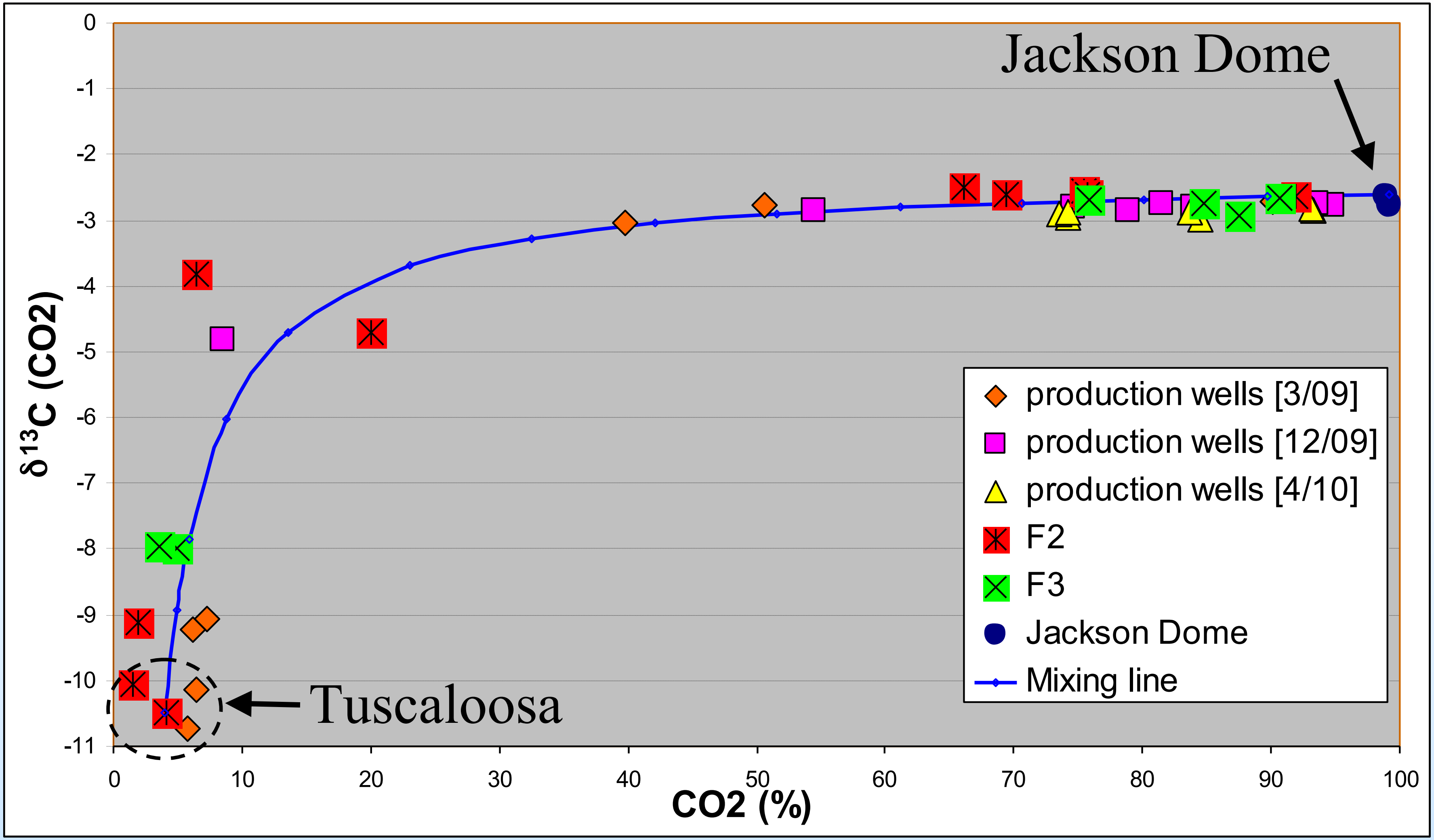
- Naturally occurring in gases, brines, rocks
- Sensitive, established mass spectrometric methods
- Kinetic & equilibrium partitioning constrained
- Assess gas-brine-rock interaction processes
- Assess leakage from reservoir; well bore
- Complementary to gas and brine chemistries

Strontium Isotope Variation with Time



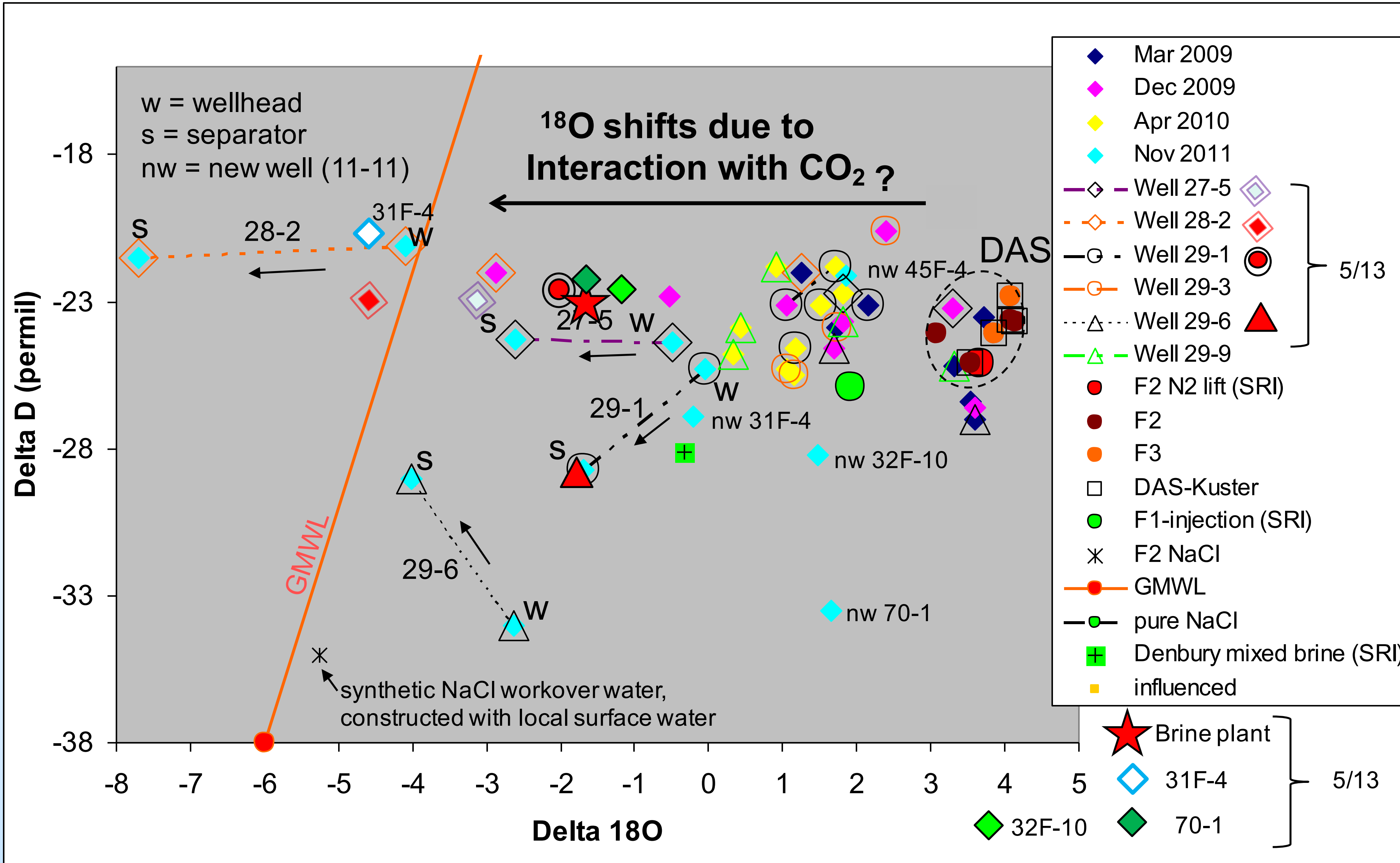
The presence of CO_2 dissolved in the Cranfield brine may have enhanced reactivity with the sandstone thus releasing some additional ^{87}Sr from feldspars or clays.

Carbon Isotopes ($^{13}C/^{12}C$) of Injected CO_2 Gas from Jackson Dome Show Good Mixing with Tuscaloosa CO_2

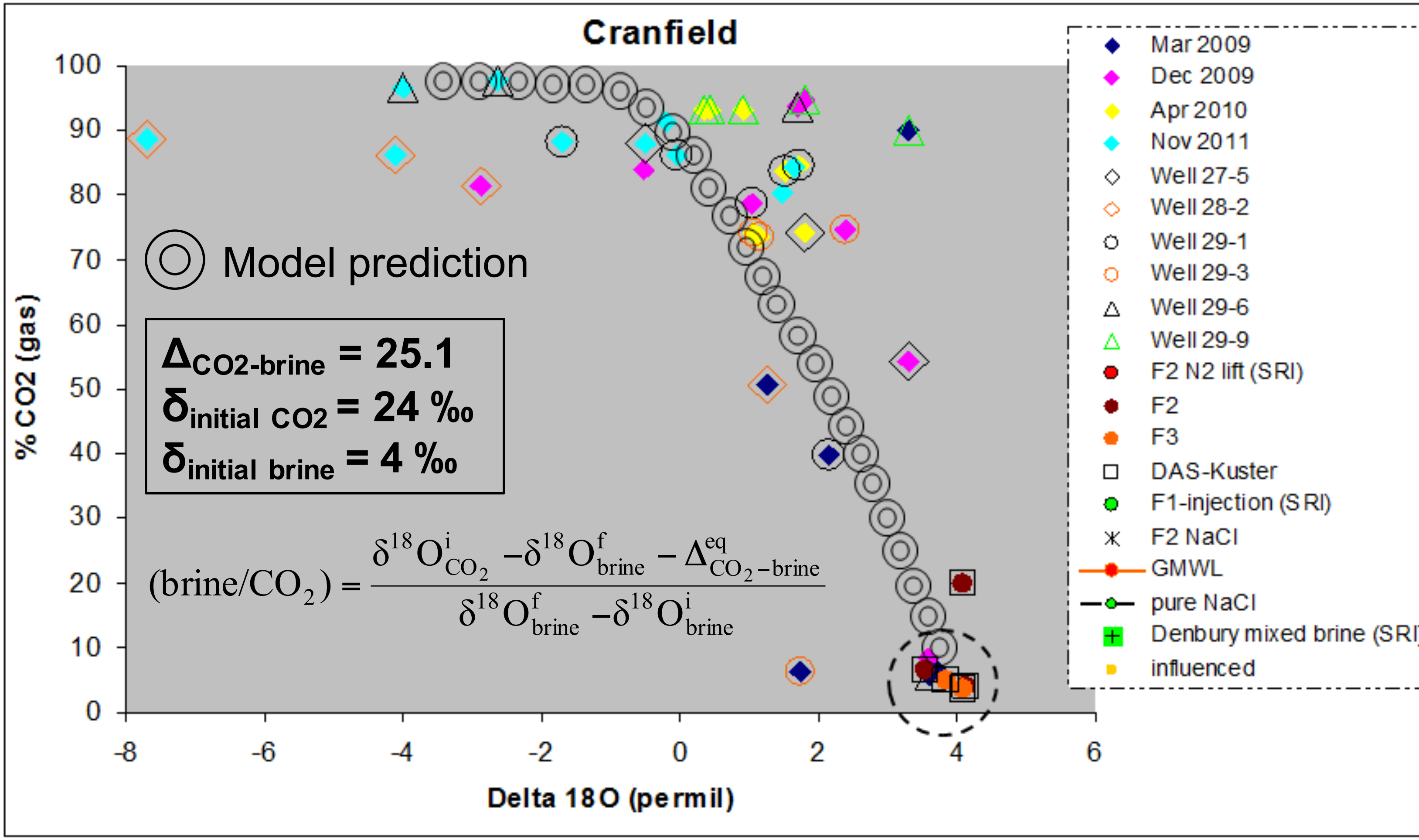


Simple two-component fluid mixing dominates at the DAS site
No obvious evidence of CO_2 reaction with reservoir rock carbonates

Cranfield: Brine O and H Isotopes

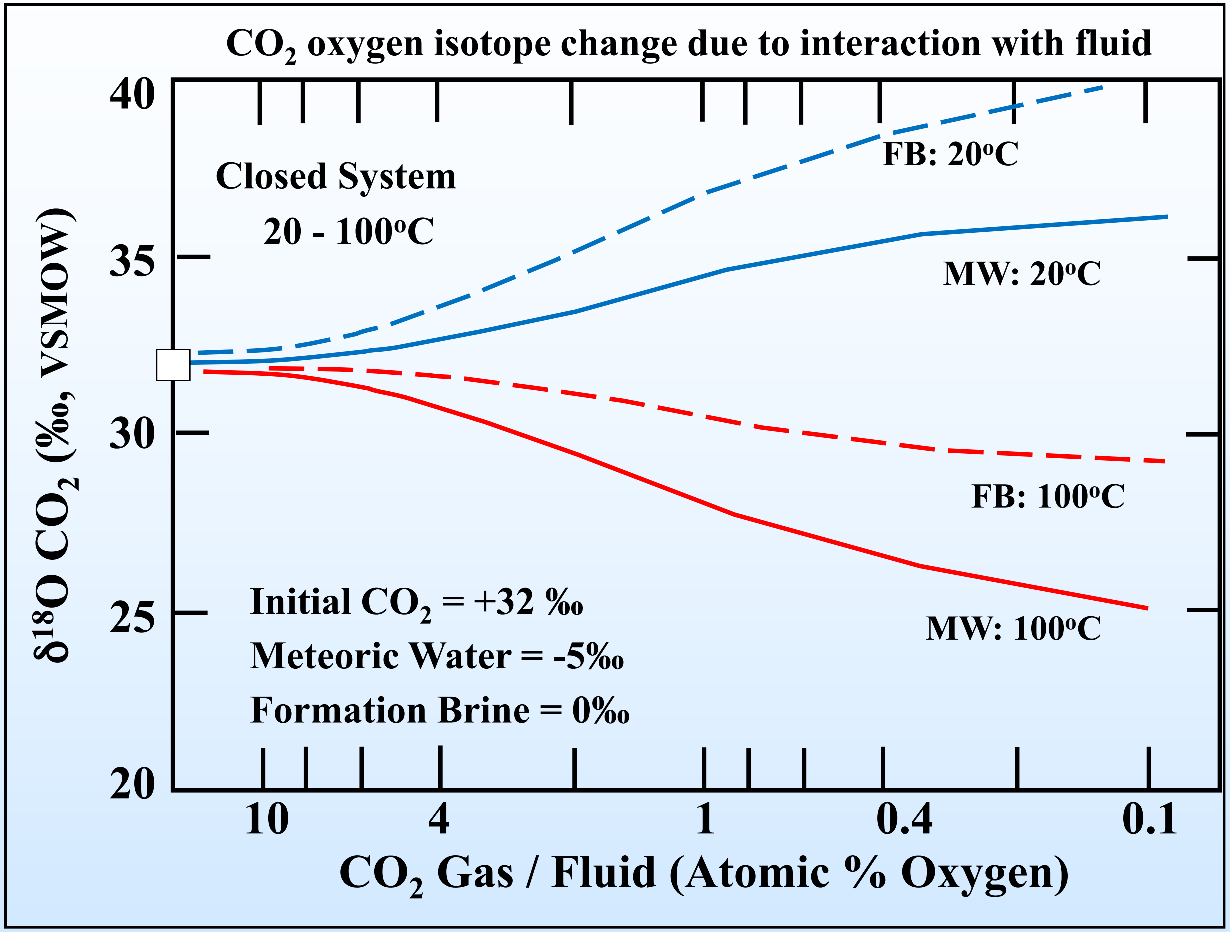


Modeling of O isotope shifts in CO_2



Magnitude of oxygen isotope shift largely a function of brine/CO_2 ratio vs carbon isotope variation due to mixing of formation CO_2 with injectate

Effect of brine O isotope composition and temperature on CO_2 O isotopes



O isotope change in CO_2 reacted with two different fluid types at two different temperatures, 20 and 100°C.

Summary of Key Isotope Results

Possible dual source for Sr – formation brine + dissolution of sediment (more $^{87}Sr/^{86}Sr$ in progress)

Mixing of CO_2 injectate and reservoir CO_2 revealed by carbon isotopes ⇒ ensure storage permanence, MVA

Oxygen isotope shifts in CO_2 and brine yield estimates of CO_2/brine mass ratios complementary to RST

Incorporating Tracer Results in a Reservoir Simulator

Leverage a state-of-the-art reservoir simulator for compositional multicomponent multiphase flow

Tracers added as conservative or weakly non-conservative species, with advection-diffusion-dispersion transport

EOS compositional modeling to predict local changes in density & viscosity

Dr. Joachim Moortgat (OSU)

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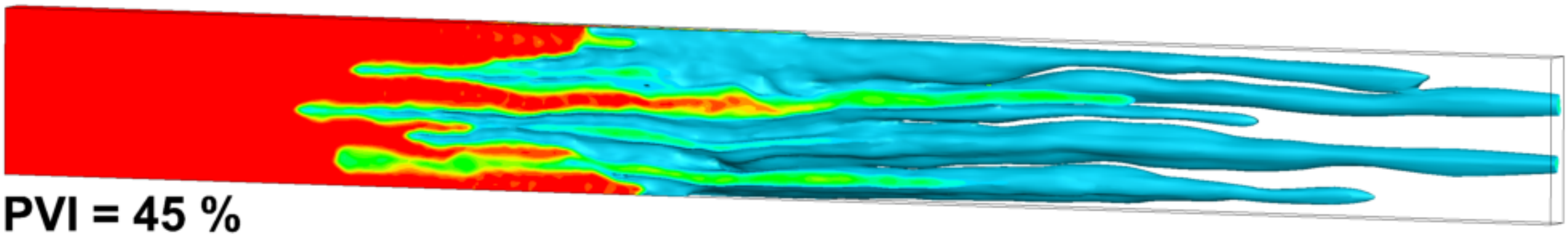

EOS compositional modeling to predict local changes in density & viscosity

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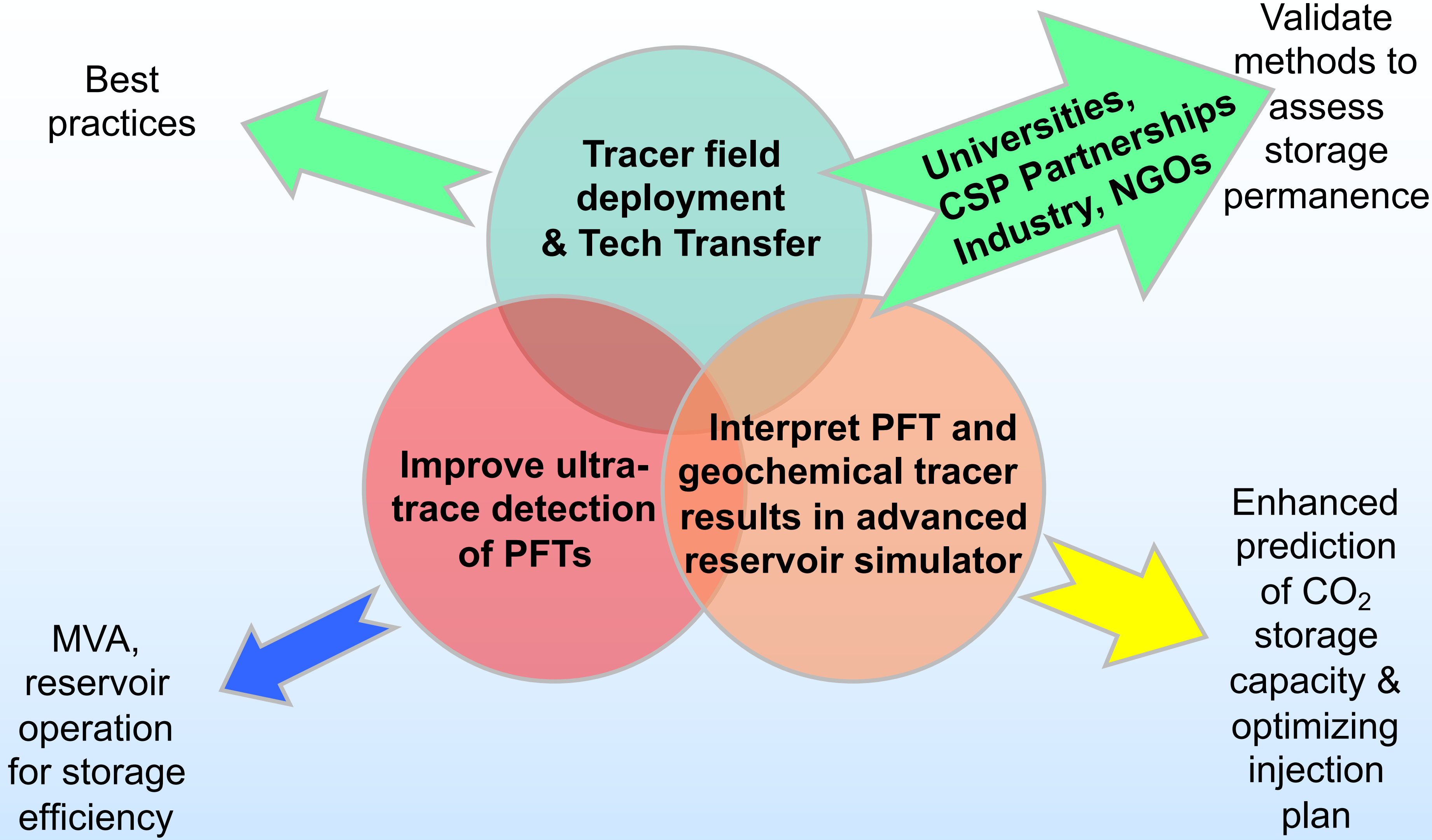
Future Plans & Synergies



Appendix

Project Organization

U.S. DEPARTMENT OF ENERGY | NETL

Oak Ridge National Laboratory

David Graham, PI

The University of Tennessee Knoxville

Tommy Phelps
Susan Pfiffner

The Ohio State University

David Cole
and team

Collaborators:

RCSPs

Bureau of Economic Geology
John A. and Katherine G. Jackson School of Geosciences

Berkeley Lab

USGS
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Gantt Chart

	2015				2016				2017			
Task Description	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Sampling plan	■											
Initial gas-brine isotope model	■	■										
PFT comparison		■	■									
Geochem comparison		■	■	■								
Tech transfer update			■	■								
Technology survey				■	■							
Geochem and isotope integration				■	■	■						
10X PFT Implementation plan						■	■					
Brine-CO2 & PFT transport						■	■	■				
Tech transfer update							■	■				
Test 10X PFT enhancement							■	■	■			
100X PFT implementation plan									■	■		
Test 100X PFT enhancement										■	■	
Isotope simulation reactive transport									■	■	■	■
Field test enhanced PFT analysis											■	■
Tech transfer update											■	■

Bibliography

DePaolo, D. J., Cole, D. R., Navrotsky, A. and Bourg, I. C. (2013, Editors) Geochemistry of Geologic CO_2 Sequestration. In: Geochemistry of Geologic Carbon Sequestration (D.J. DePaolo, D. R. Cole. A. Navrotsky and I. Bourg, eds.), *Rev. Mineral. Geochem*. 77, 539p.

DePaolo, D. J and Cole, D. R. (2013) Geochemistry of geologic carbon sequestration. An overview. *Rev Mineral. Geochem*. 77, 1-14.

Yousif K. Kharaka, David R. Cole, James J. Thordsen, Katherine D. Gans, and R. Burt Thomas, (2013) Geochemical Monitoring for Potential Environmental Impacts of Geologic Sequestration of CO_2. In: Geochemistry of Geologic Carbon Sequestration (D.J. DePaolo, D. R. Cole. A. Navrotsky and I. Bourg, eds), *Rev. Mineral. Geochem.* **77**, 399-430.

Wilkins, M. J., R. Daly, P. J. Mouser, R. Trexler, K. C. Wrighton, S. Sharma, D. R. Cole, J. F. Biddle, E. Denis, J. K. Fredrickson, T. L. Kieft, T. C. Onstott, L. Petersen, S. M. Pfiffner, T. J. Phelps, and M. O. Schrenk. 2014. Trends and Future Challenges in Sampling the Deep Terrestrial Biosphere. *Frontiers in Microbiology* 5:481.

Accomplishments and Benefits to Program

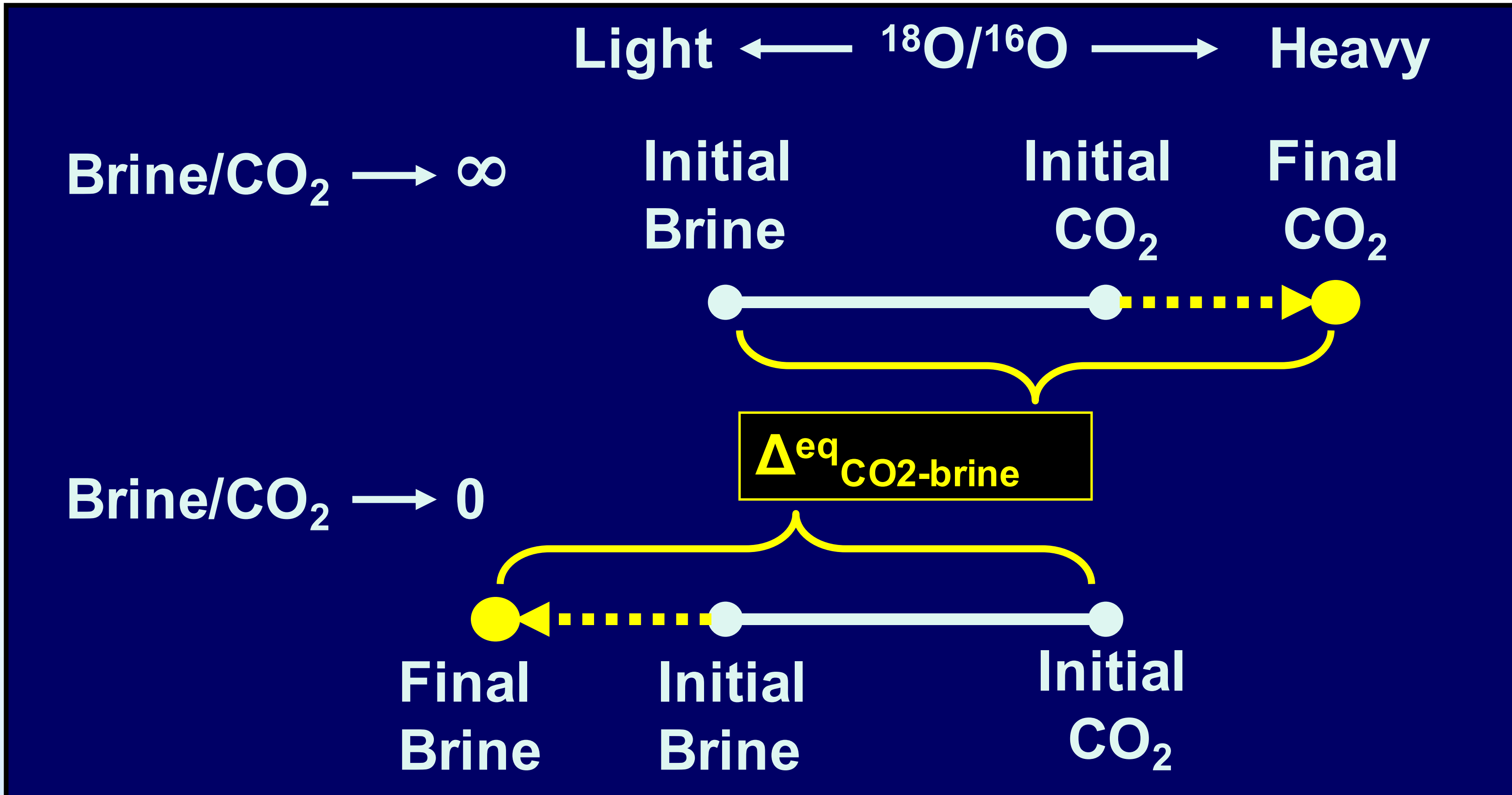
- Accomplishments
- **Assessing water-mineral-CO_2 interactions using geochemical modeling and isotopic signatures in baseline, during and post injection for multiple sites and campaigns.**
- **Determine behavior of perfluorocarbon tracer suites, breakthrough, development of reservoir storage over time at multiple sites.**
- **Delineate CO_2 fronts with PFT's, isotopes and on-line sensors (T, pH, Cond.).**
- **Established methods, proven successful, inexpensive, ongoing collaborations.**
- ***Procedures for monitoring, verification and accounting (MVA) as tech transfer for larger sequestration demonstrations complementing other sites/partnerships.***

- Benefits,
- **Fate, Breakthroughs, Transport, Interactions, MVA, and Technology Transfer.**
- **Established, successful, inexpensive, Technology Transfer collaborations.**
- **Lessons Learned of baseline needs and multiple natural and added tracers.**
- **Publications: 13 journal/book articles and a dozen proceedings papers.**
- **Education: 4 Students and 2 postgraduates.**

Oak Ridge National Laboratory

The Ohio State University

Brine/CO_2 Ratios Based on Shifts in $^{18}O/^{16}O$



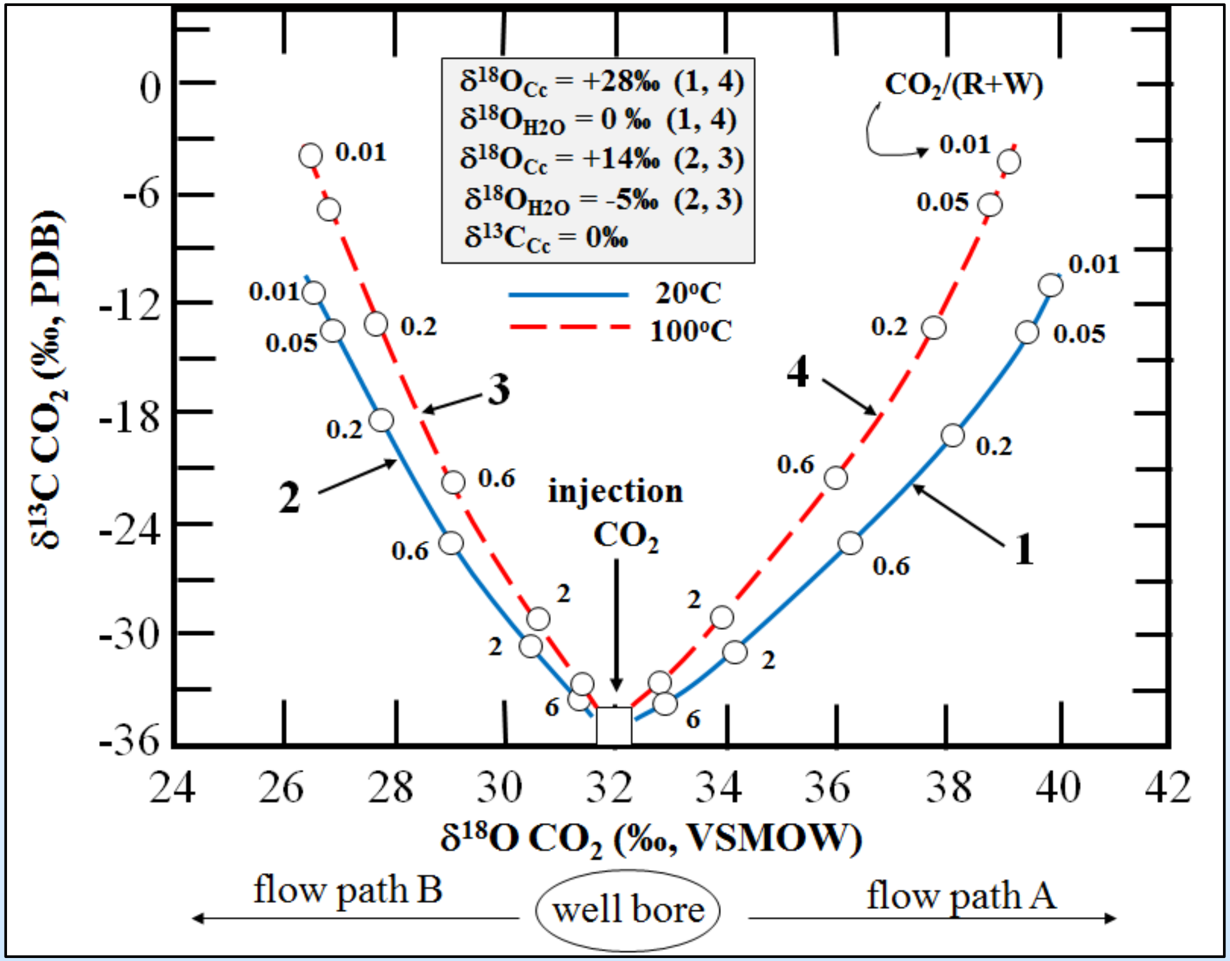
Attainment of equilibrium is not a prerequisite

$$\frac{X_{H2O}}{X_{CO2}} = \frac{\delta^{18}O^{f}_{CO2} - \delta^{18}O^{i}_{CO2}}{\delta^{18}O^{i}_{H2O} - \delta^{18}O^{f}_{H2O}}$$

Pronounced $^{18}O/^{16}O$ Shifts in Brines

Possible Mechanisms	$^{18}O/^{16}O_{brine}$ depletion	$^{18}O/^{16}O_{brine}$ enrichment
Mixing with groundwater	X	
Evaporation/boiling		X
Reaction with reservoir rock		X
Interaction with CO_2	X	X

O and C isotope exchange in a Gulf Coast CO_2-brine-carbonate system



Changes in C and O isotopes in CO_2 as a result of reaction-path modeling. Circles on trend lines refer to the mole ratio of CO_2/(rock + brine).

Reservoir modeling of tracers

Backbone: State-of-the-art reservoir simulator for compositional multicomponent multiphase flow

Higher-order Finite Elements for high accuracy on coarse (unstructured) grids with permeability anisotropy & heterogeneity (including fractures and faults)

EOS-based phase-split computations and phase behavior

Tracers added as conservative or weakly non-conservative species, with advection-diffusion-dispersion transport

Additional complexities (reaction, hysteresis) can be incorporated if required