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
Developing the Technologies and Infrastructure for CCS
August 12-14, 2014

Presentation Outline

- **Benefits of Tracers to MVA Program**
- **Project Objectives**
- **Background on MVA Tracers**
- **Results on PFTs**
- **Results on Gas and Isotope Geochemistry**
- **Summary of Key Results**
- **Lessons Learned**
- **Future Plans**

Benefit to the MVA Program

- **Tracer studies of subsurface fluids and gases can provide information on physical and geochemical changes occurring in the host reservoir due to CO_2 plume migration.**
- **Tracers used in concert with other monitoring methods like geophysics can lead to a fundamental understanding of processes impacting the behavior of fluids – diffusion, dispersion, mixing, advection, reaction.**
- **Tracer data can provide ground-truth on behavior of fluids and gases, CO_2 transport properties, and CO_2 saturation that can be used to constrain reservoir simulation models.**

Project Overview:
Overarching Goals

Develop complementary tracer methods to interrogate subsurface for improved CO_2 sequestration, field test methods for application to MVA, demonstrate CO_2 remains in zone, and benefit industry through tech transfer.

Specific Objectives:

1. **Assessment of injections in field. PFT gas tracers are analyzed by GC-ECD to <pg levels. GC and IRMS is used for gas chemistry and stable isotope ratios, respectively. (e.g. D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$, $^{87}Sr/^{86}Sr$).**

2. **Integrate PFT and isotopic results to quantify the behavior of CO_2 interaction with brine-rock leading to better predictive models beneficial for MVA.**

3. **Develop MVA strategy to decipher the fate, transport and breakthrough of CO_2, estimate residence time and reservoir capacity, assess the potential leakage → transfer technology to partnerships and industry.**

Candidate MVA 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 (PFT's):

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

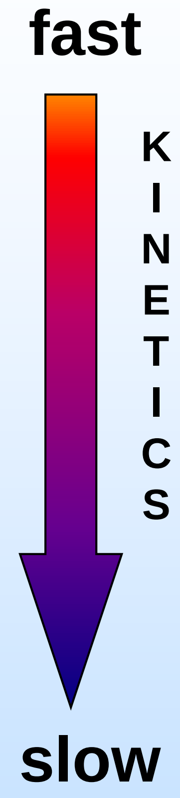
Sorption onto mineral surfaces

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

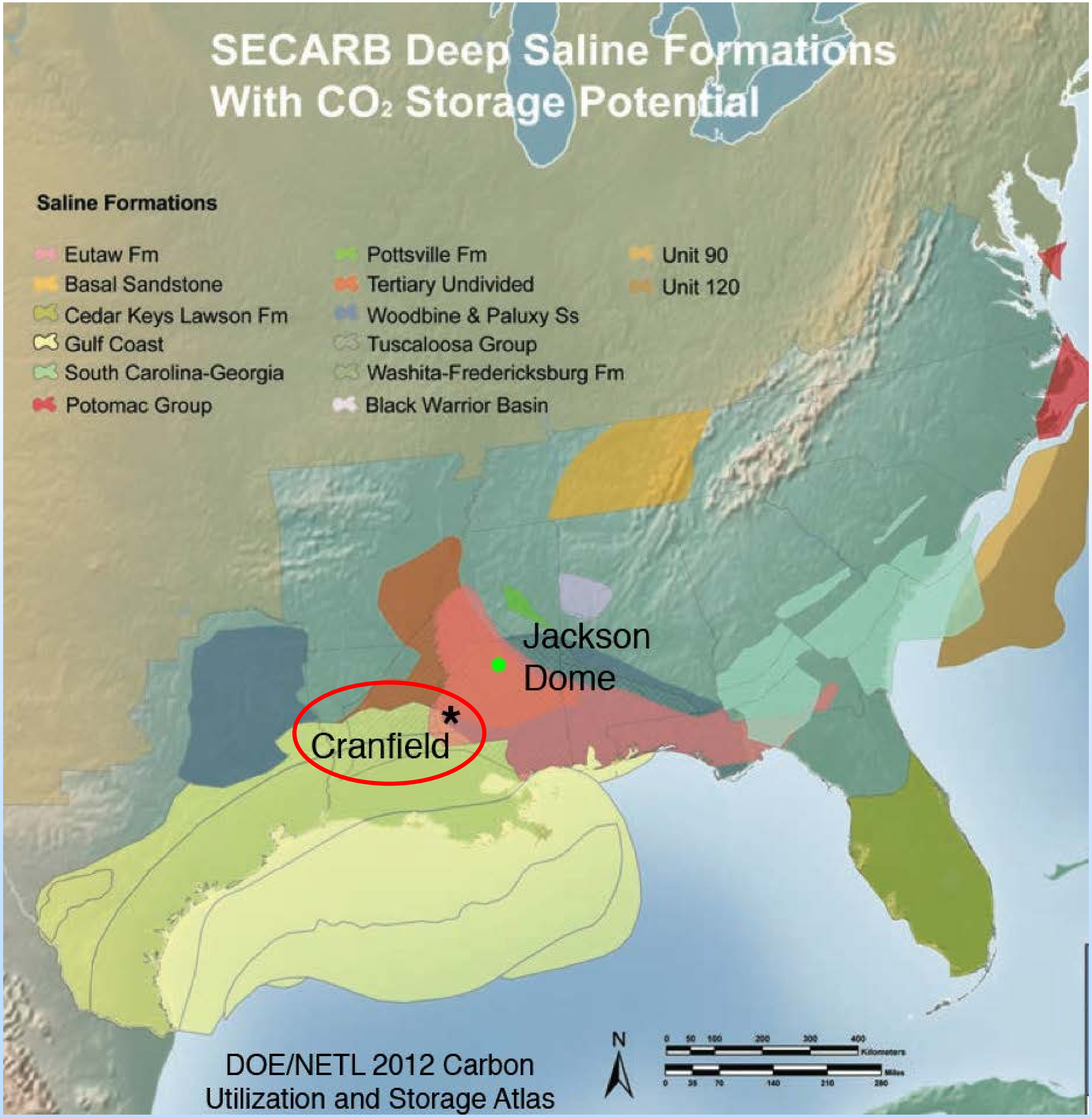
Microbial activity → biomineralization

Fluid-rock interaction (weathering, digenesis, hydrothermal)

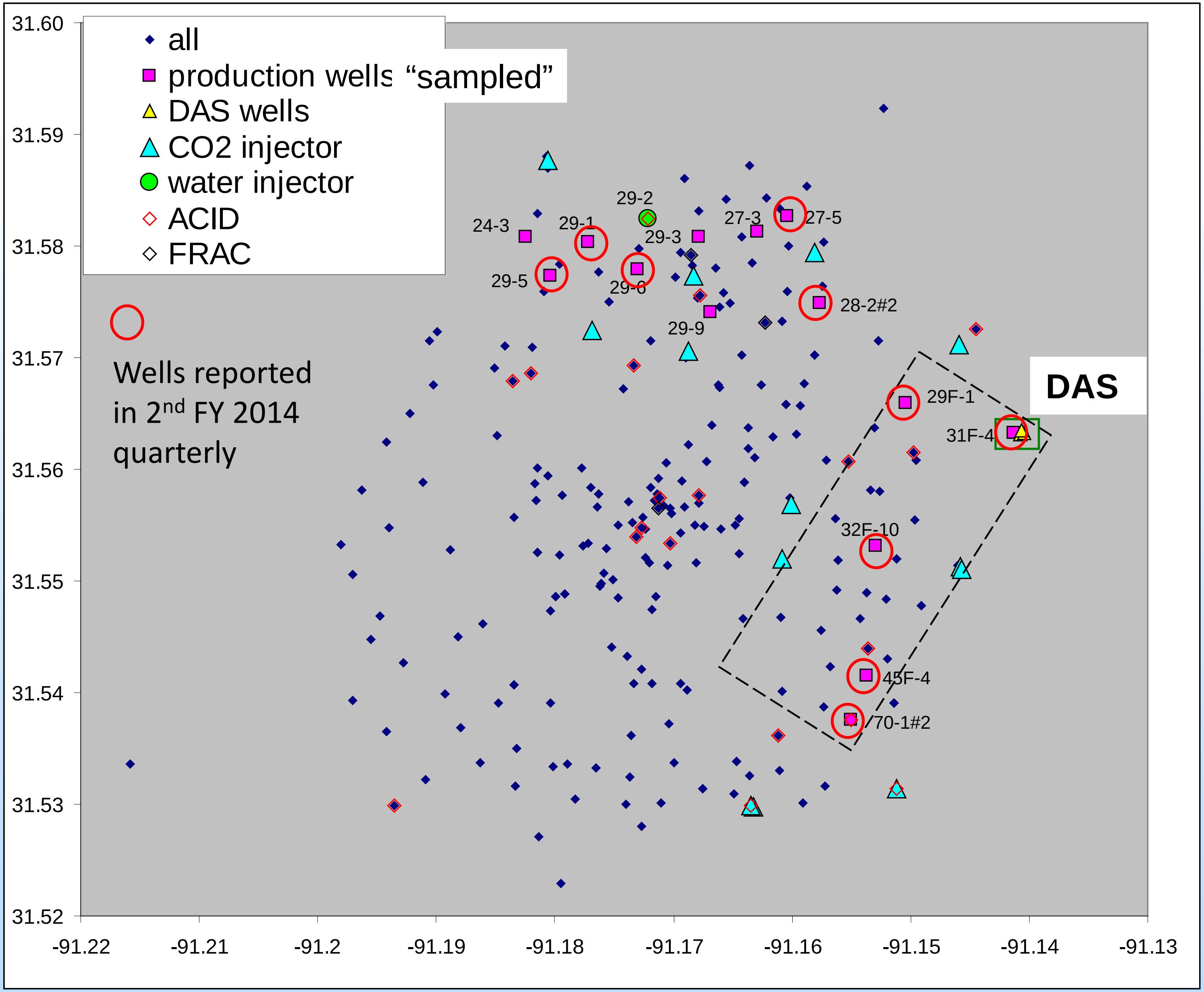
Diffusion in porous/fractured media; minerals



Possible consequence: chromatographic zoning along flow path dependent on length and time scales.

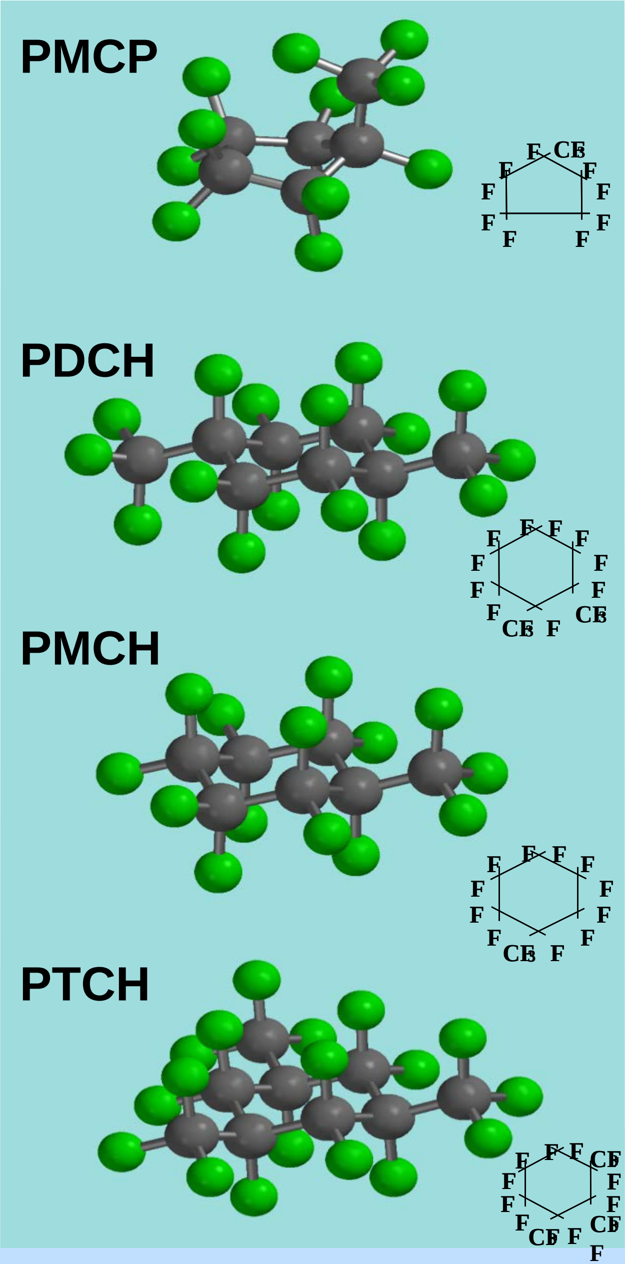

SECARB Deep Saline Formations
With CO_2 Storage Potential
Saline Formations
Eutaw Fm
Basal Sandstone
Cedar Keys Lawson Fm
Gulf Coast
South Carolina-Georgia
Potomac Group
Pottsville Fm
Tertiary Undivided
Woodbine & Paluxy Ss
Tuscaloosa Group
Washita-Fredericksburg Fm
Black Warrior Basin
Unit 90
Unit 120
Jackson Dome
Cranfield
N
DOE/NETL 2012 Carbon Utilization and Storage Atlas

Cranfield Well Locations



Benefits of Conservative Tracers – PFTs & SF_6

- **Non-reactive & non-toxic**
- **Stable to elevated temperatures up to 500^{o}C**
- **PFT's sensitive at pg-fg, versus isotopes at ppt**
- **Several PFTs can be quantified in a single analysis**
- **Can be analyzed in the field or preserved for the lab**
- **Scalable to thousands of samples**
- **Easy and cheap; different PFT "suites" used to assess multiple breakthroughs – *flow regime indicator***
- **Applicable near-surface or at depth**
- **Complementary to stable isotopes and geochemistry for modeling heterogeneous flow – crucial for MVA**

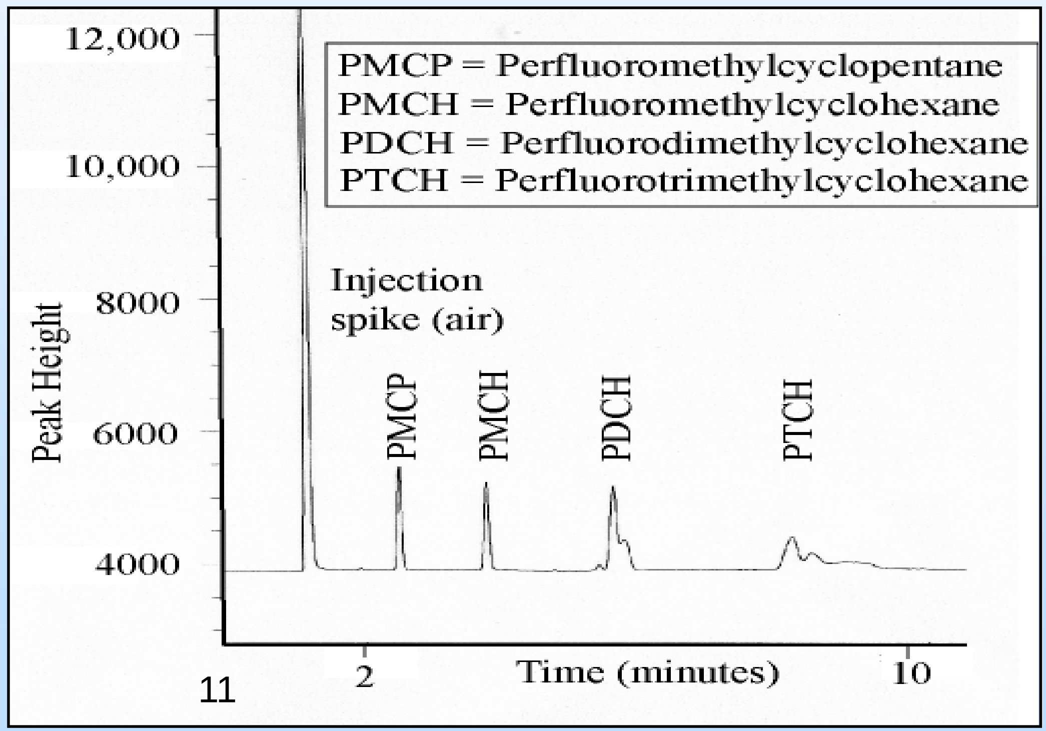


Examples of PFTs

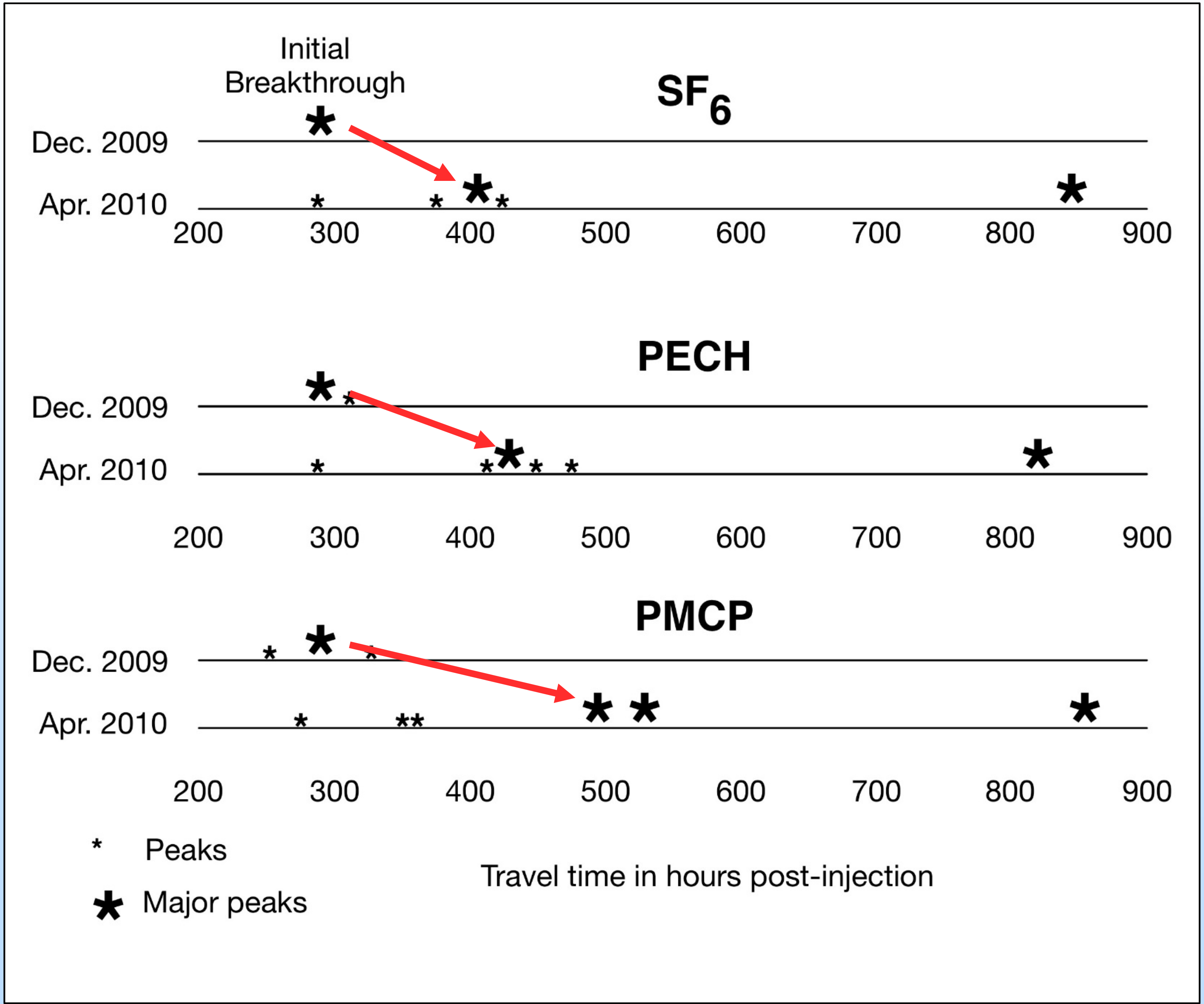
Deploy multiple-tracer suites (others available)
Different molecular weights, solubilities, and structure may enable chromatographic separation in reservoirs

Pressure cylinders for sample collection (U-tube)

PFT Analyses performed in the field or preserved



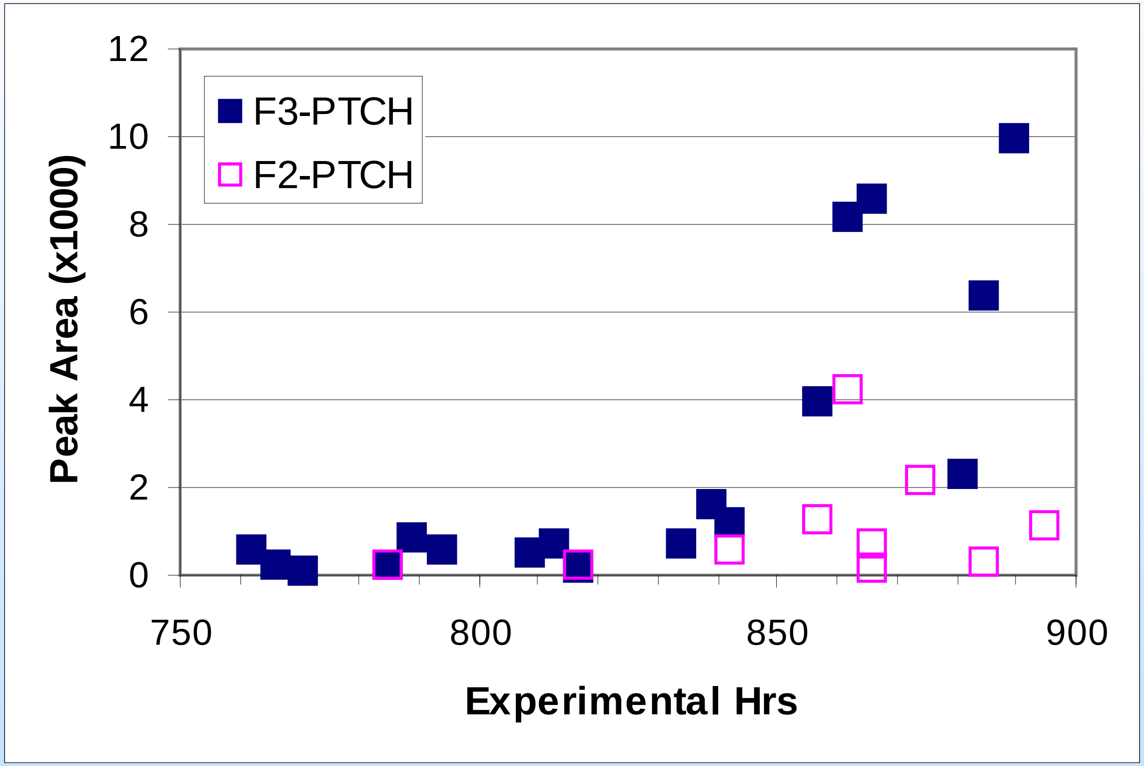
PFTs at Cranfield – F2 Well



PTCH Tracer Results from Cranfield, MS

DAS well distances

F1 → F2 (68m) → F3 (112m)



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

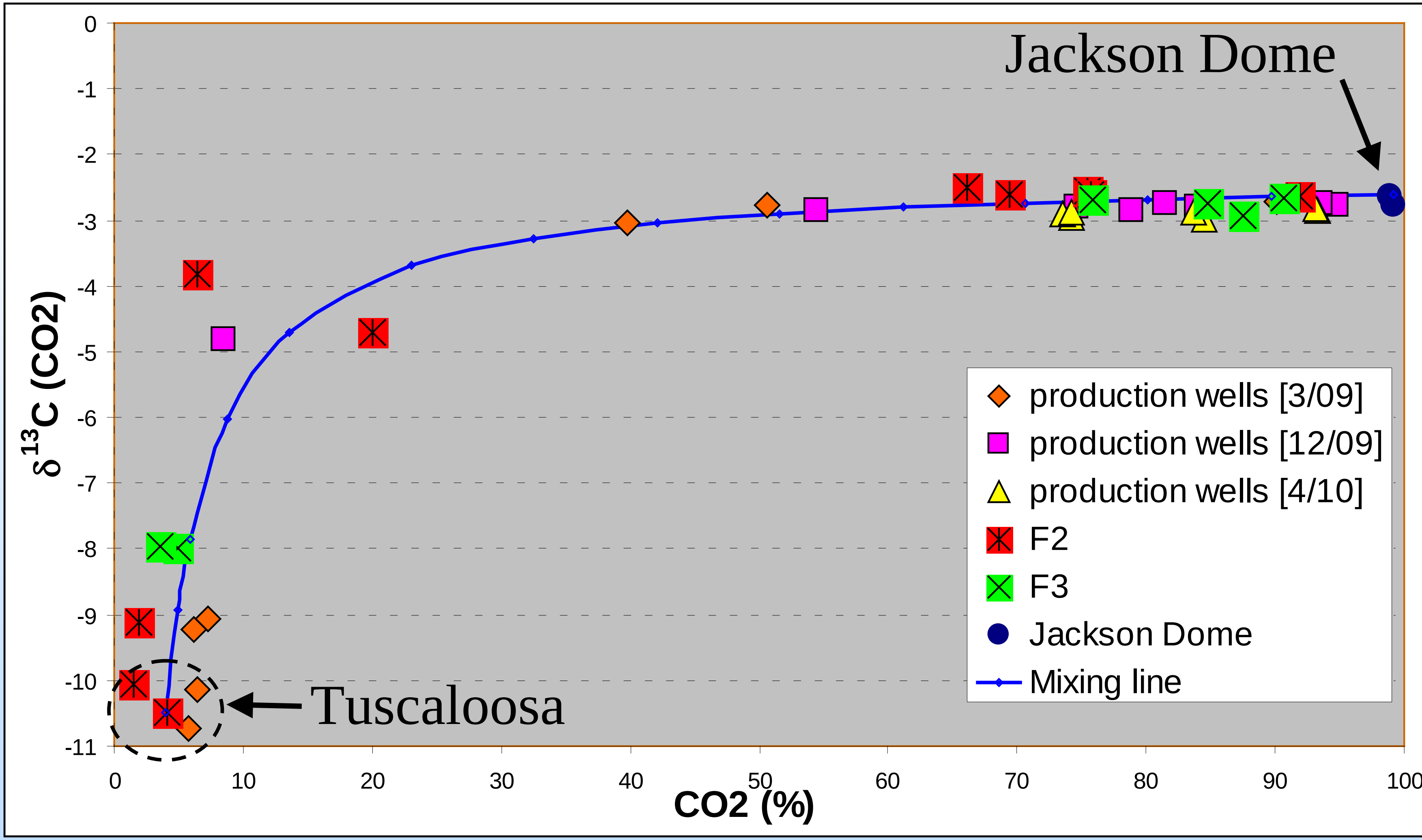
Radial-like flow in 2009; Multi-flow paths in 2010 with short circuits

Benefits of Nonconservative Tracers – Stable Isotopes

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

- **Naturally occurring in gases, brines, rocks**
- **Sensitive mass spectrometric methods**
- **Kinetic & equilibrium partitioning constrained**
- **Can be analyzed in the field or the lab**
- **Assess gas-brine-rock interaction processes**
- **Assess leakage from reservoir; well bore**
- **Complementary to gas and brine chemistries**
- **Proven and established procedures**

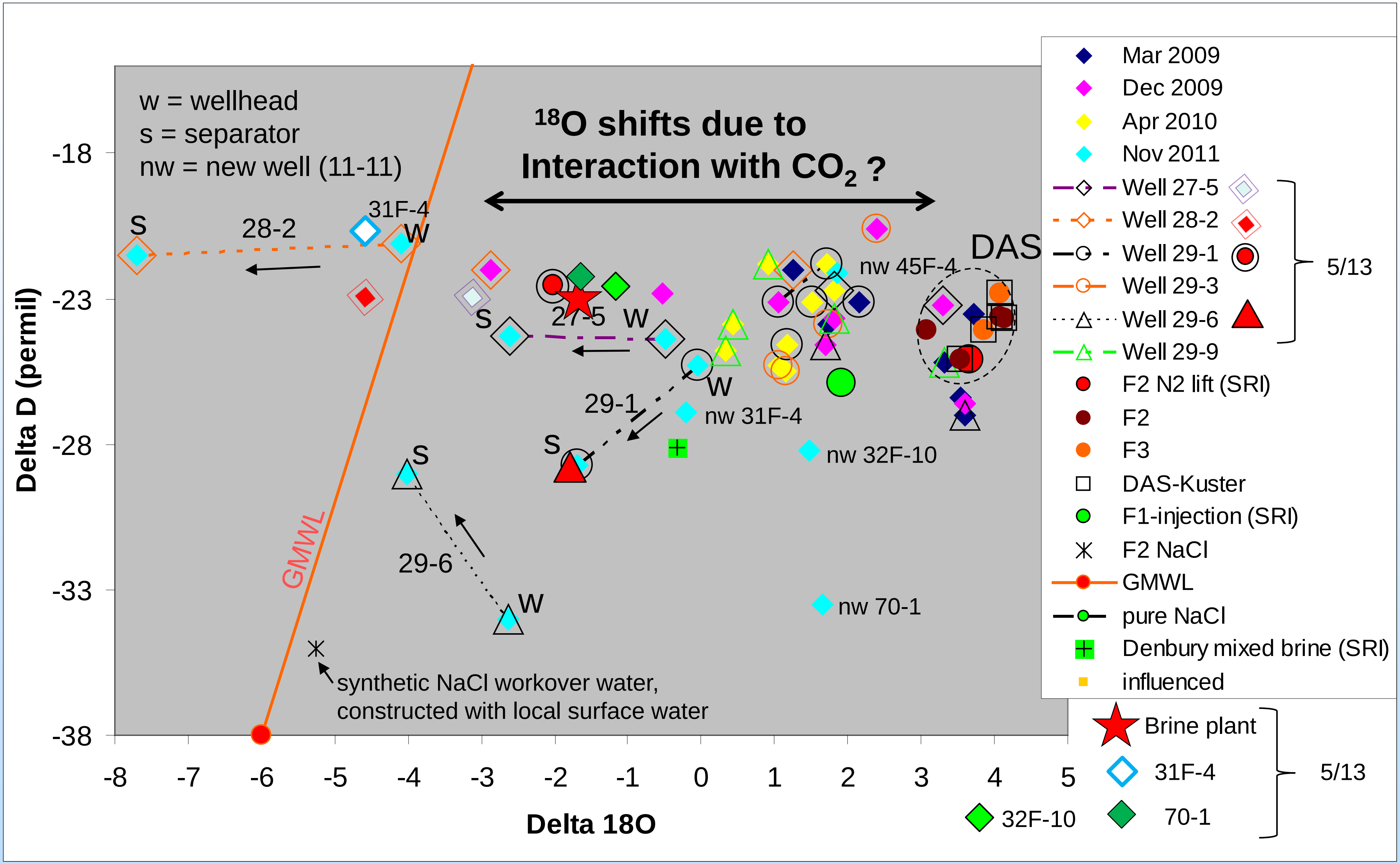
Carbon Isotopes ($^{13}C/^{12}C$) of Injected CO_2 Gas from Jackson Dome Show Good Mixing with Tuscaloosa CO_2



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



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

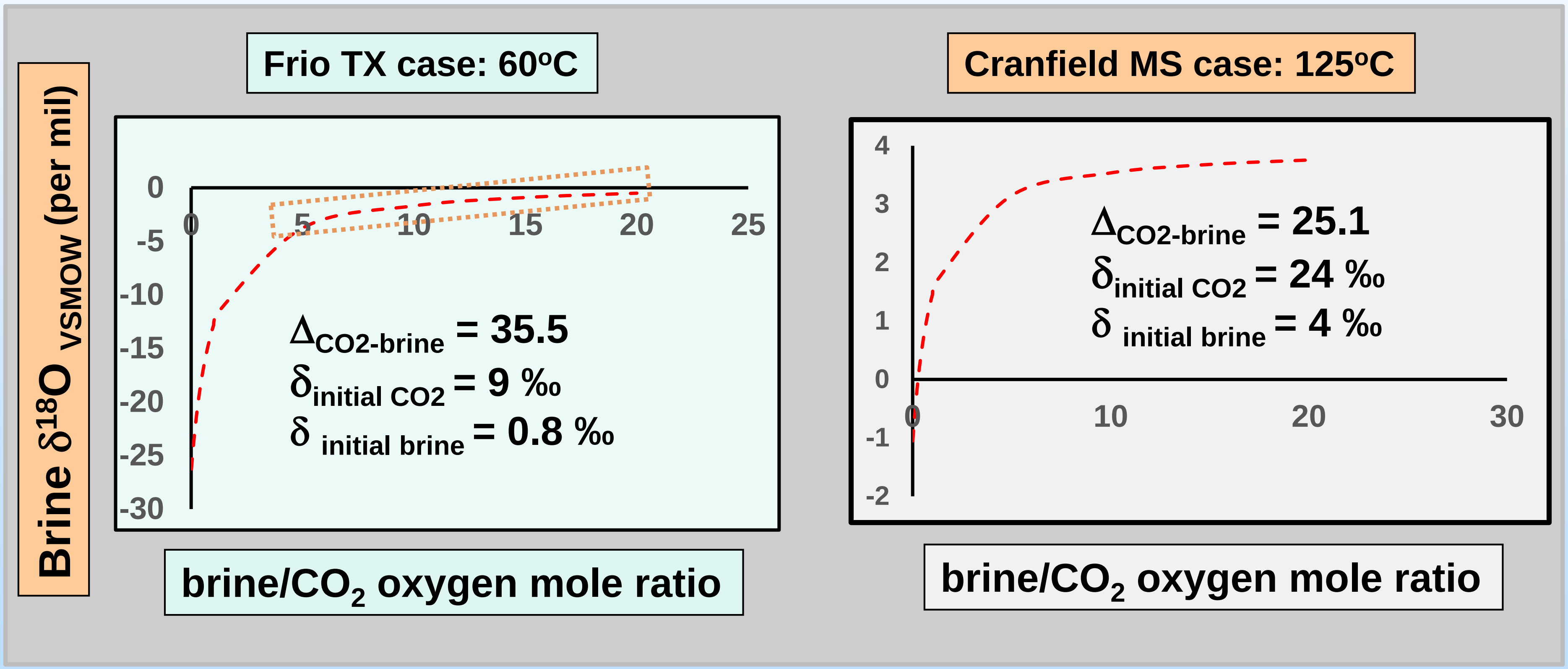
Possible Mechanisms	$^{18}O/^{16}O_{brine}$ depletion	$^{18}O/^{16}O_{brine}$ enrichment
Mixing with groundwater	X	
Evaporation/boiling		X
Reaction with reservoir rock		X
Interaction with CO_2	X	X

Oxygen isotope shifts in CO_2 and Brine add value to MVA

Brine-CO_2 oxygen isotopes equilibrate rapidly
Use mass balance relationships to estimate brine/CO_2 ratios

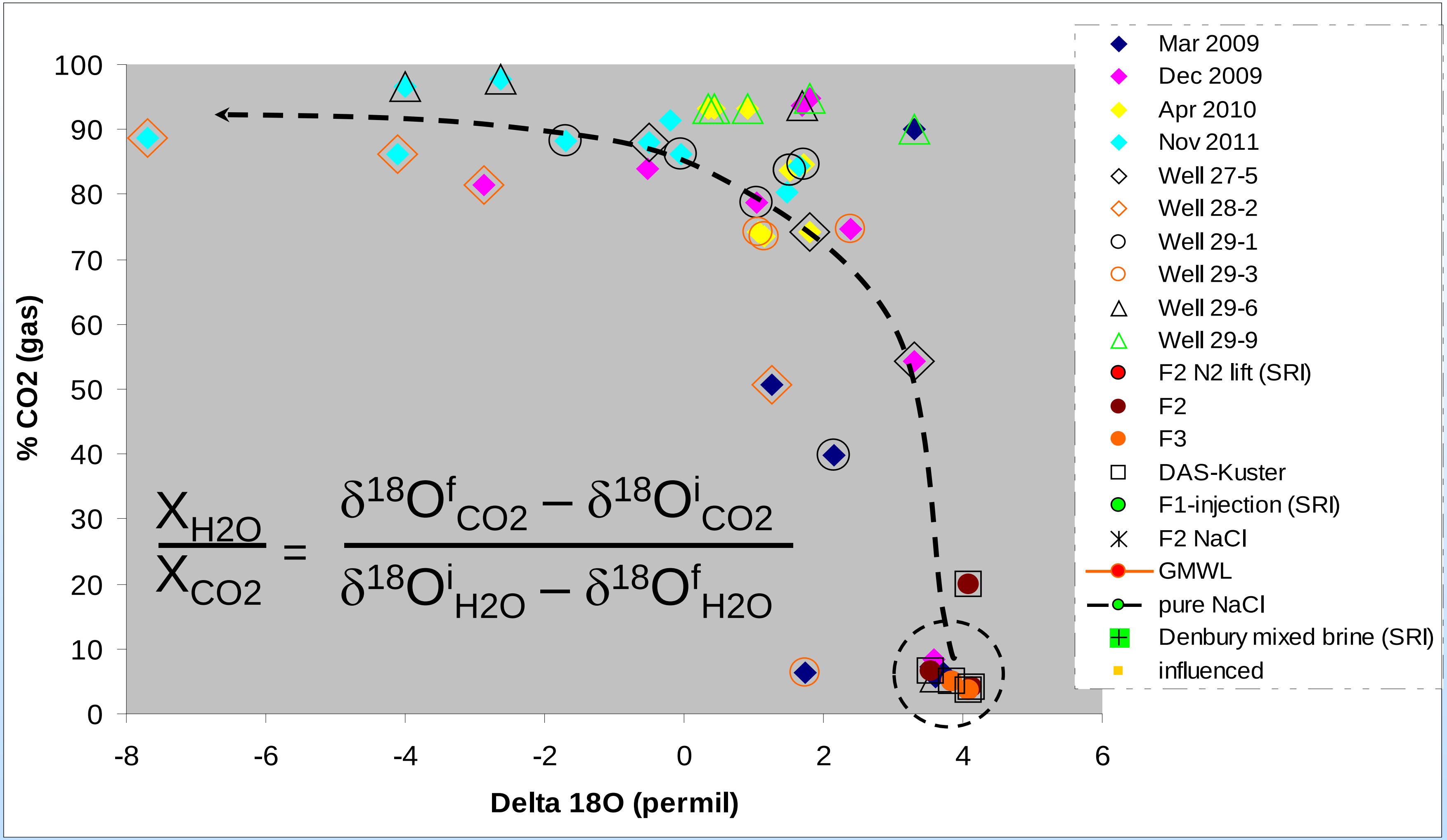
$$(\text{brine}/\text{CO}_2) = \frac{\delta^{18}\text{O}^{i}_{\text{CO}_2} - \delta^{18}\text{O}^{f}_{\text{CO}_2}}{\delta^{18}\text{O}^{f}_{\text{CO}_2} - \delta^{18}\text{O}^{i}_{\text{brine}} - \Delta^{eq}_{\text{CO}_2-\text{brine}}}$$

$$(\text{brine}/\text{CO}_2) = \frac{\delta^{18}\text{O}^{i}_{\text{CO}_2} - \delta^{18}\text{O}^{f}_{\text{brine}} - \Delta^{eq}_{\text{CO}_2-\text{brine}}}{\delta^{18}\text{O}^{f}_{\text{brine}} - \delta^{18}\text{O}^{i}_{\text{brine}}}$$



Geochemical analog to RST

Relationship between $^{18}O/^{16}O_{brine}$ and CO_2



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

Magnitude of oxygen isotope shift largely a function of brine/CO_2 ratio

Summary of Key Results

Suite of PFTs reveal multiple flow paths; short circuit connectivity between injection and monitoring wells

Mixing of CO_2 injectate and reservoir CO_2 revealed by carbon isotopes

Oxygen isotope shifts in CO_2 and brine yield estimates of saturation conditions – analog to RST

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

Lessons Learned for MVA Applications

Conduct base line characterization of system prior to CO_2 injection – gas, brine, & solid compositions (mineralogy), and characterize input CO_2 chemistry and isotopes

Down-hole samples preferred over well-head samples; Kuster (USGS); U-Tube (LBNL)

Deploy multiple introduced conservative gas tracers and natural isotopes

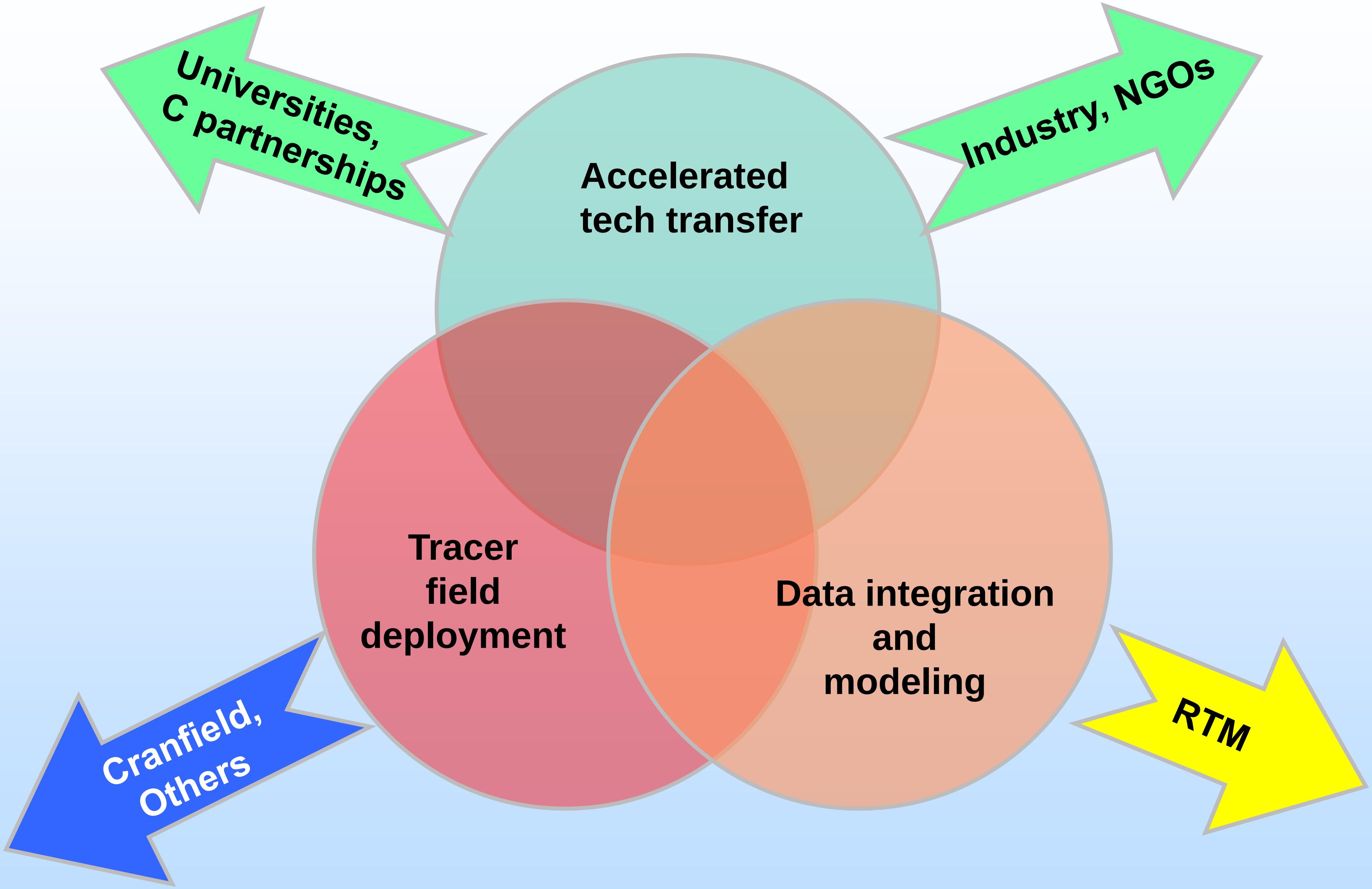
Sample prior to and during test at injection well and the monitoring wells; frequency dictated by pre-test modeling, timing of actual breakthrough, test length and availability

Continue monitoring injection well and monitoring wells after completion of test.

Continue long-term monitoring to assess signal decay; leakage in well bore above primary sample horizon; leakage to environment

Calibrate and validate models for CO_2 residence time, storage capacity and mechanisms (integrate results with hydrology and geophysics)

Future Plans



Appendix

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.**

Project Organization

Oak Ridge National Laboratory

David Graham, PI

The University of Tennessee Knoxville

Tommy Phelps
Susan Pfiffner
and team

The Ohio State University

Dave Cole
and team

DOE-NETL & Partnerships

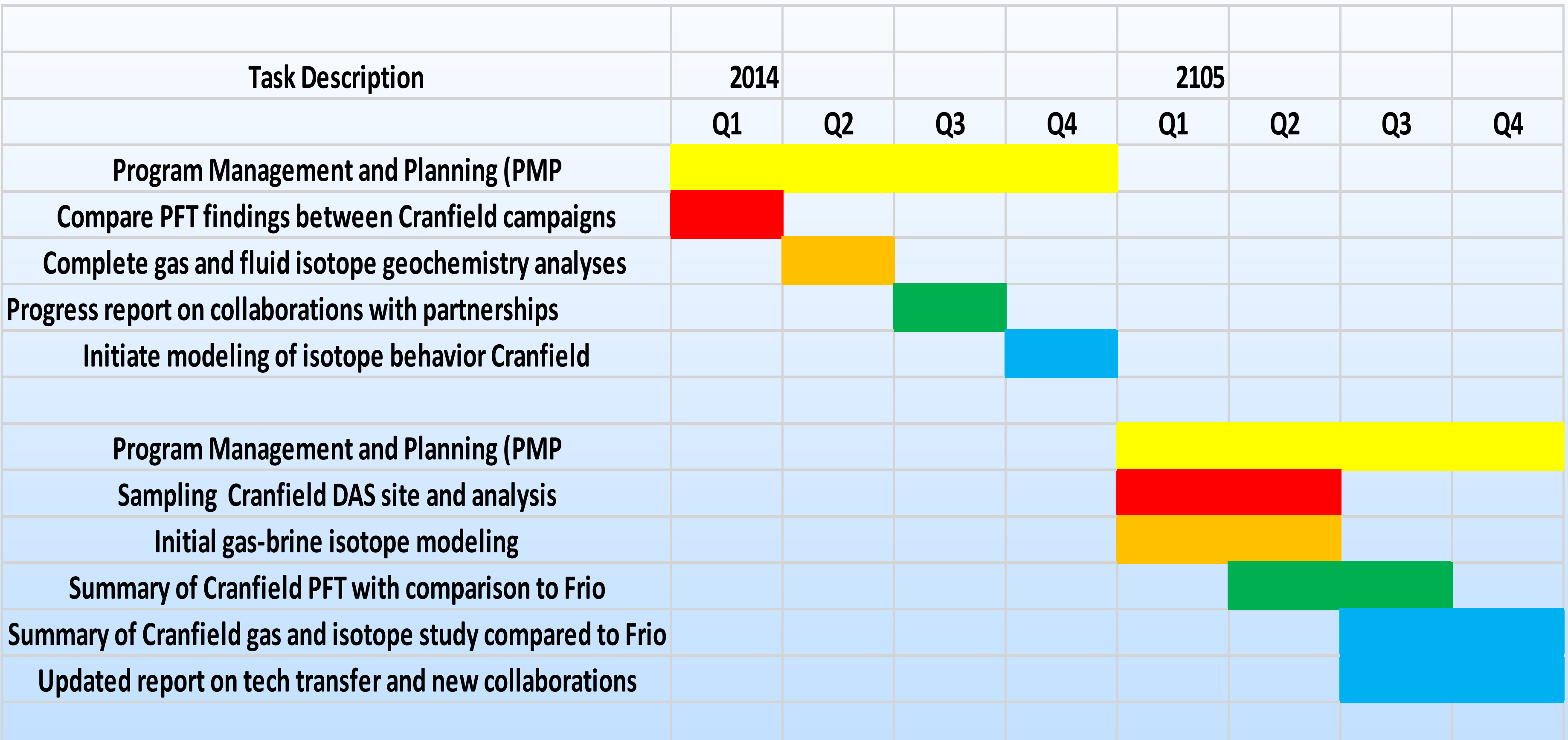
Collaborators

USGS science for a changing world

Berkeley Lab

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

Gantt Chart


Task Description
2014
2105
Q1
Q2
Q3
Q4
Q1
Q2
Q3
Q4
Program Management and Planning (PMP
Compare PFT findings between Cranfield campaigns
Complete gas and fluid isotope geochemistry analyses
Progress report on collaborations with partnerships
Initiate modeling of isotope behavior Cranfield
Program Management and Planning (PMP
Sampling Cranfield DAS site and analysis
Initial gas-brine isotope modeling
Summary of Cranfield PFT with comparison to Frio
Summary of Cranfield gas and isotope study compared to Frio
Updated report on tech transfer and new collaborations

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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, 539 p.

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

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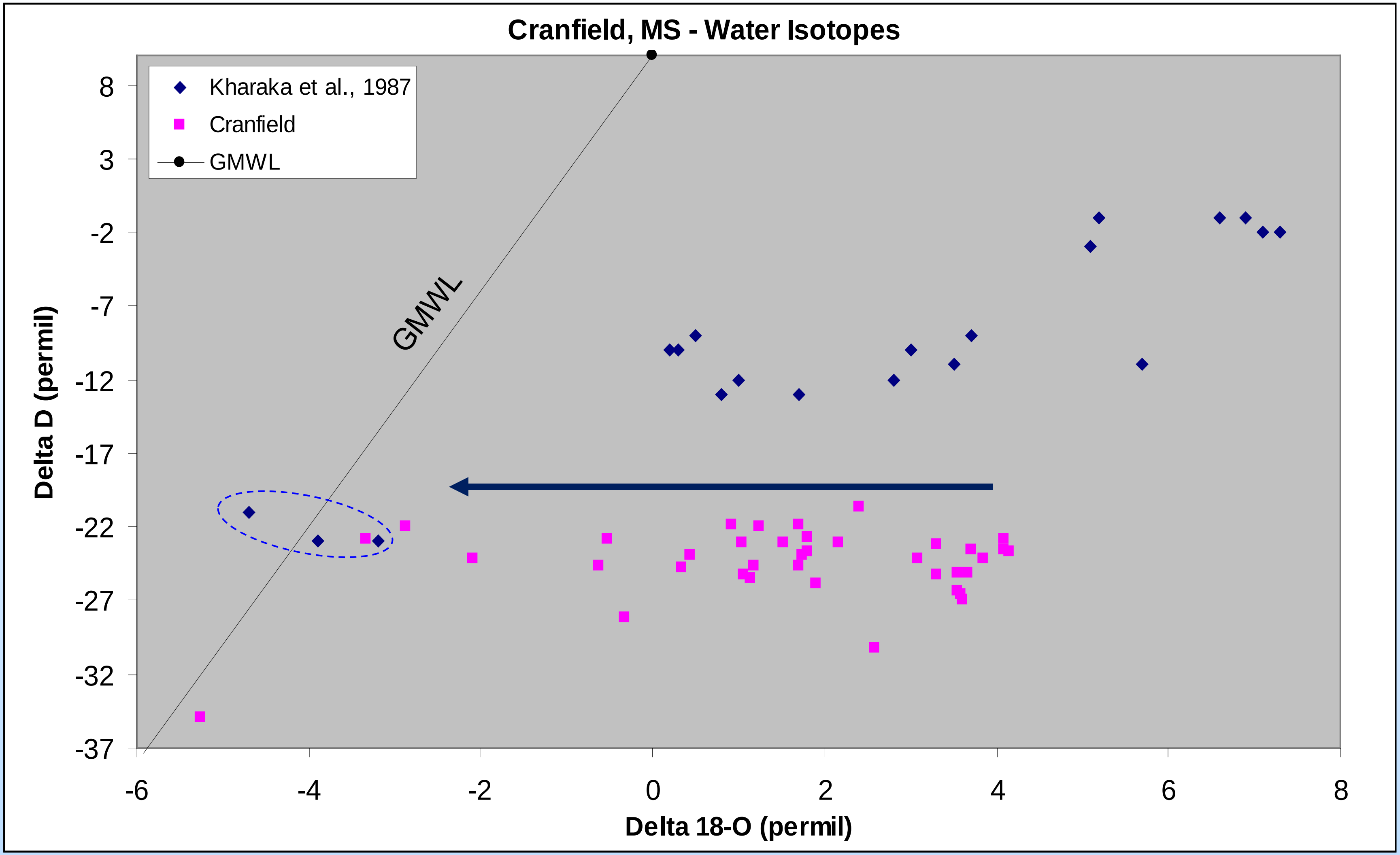
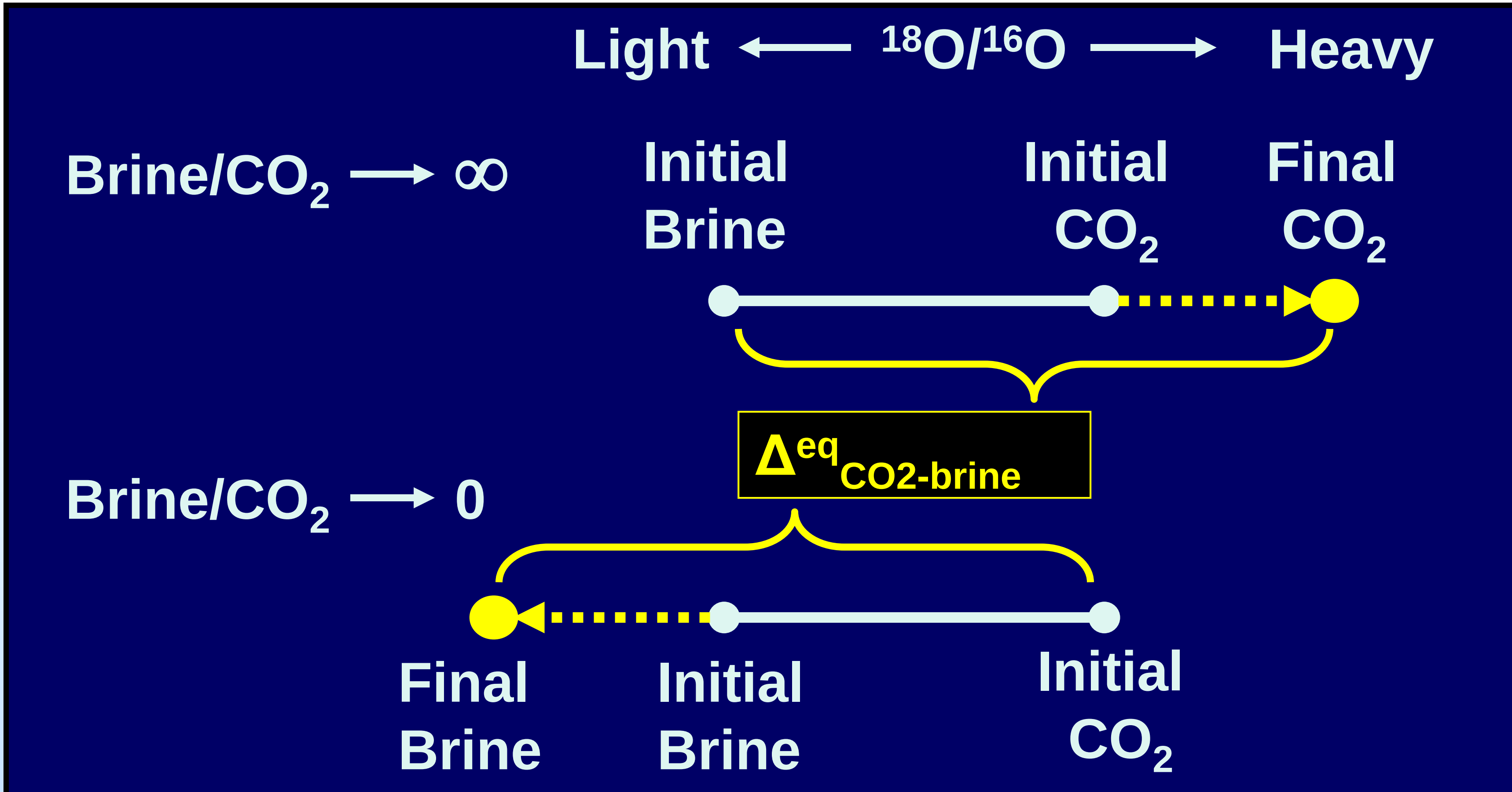
Pronounced $^{18}O/^{16}O$ Shifts



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



Attainment of equilibrium is not a prerequisite

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