Monitoring Geological CO_2 Sequestration using Perfluorocarbon and Stable Isotope Tracers

Project Number FEAA-045

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U.S. Department of Energy
National Energy Technology Laboratory
Carbon Storage R&D Project Review
Developing the Technologies and Building the Infrastructure for CO_2 Storage
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Project Overview: Goals and Objectives

Goal: Develop methods to interrogate subsurface for improved CO_2 sequestration, field test characterization and MVA, demonstrate CO_2 remains in zone, and tech transfer.

Objectives:

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

2. Integrate PFT and isotopic results to assess the nature of CO_2-brine-rock interactions for better model understanding & MVA strategies.

3. Develop MVA strategy to decipher the fate and transport of CO_2, estimating residence time, reservoir capacity/interactions, process optimization, and assessing the potential leakage and transfer technology to partnerships.

MVA Tracer Strategy and Approach

Strategy: Use natural (isotopic) and introduced perfluorocarbon (PFT) tracers to decipher fate, breakthrough, transport, mixing and interactions of CO_2 into reservoir rock. Information used to optimize, calibrate and validate models for CO_2 residence time, storage capacity and mechanisms, injection scenarios, and assessing MVA and enhance safety confidence with stakeholders/regulators.

Approach:

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; 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

Candidate MVA Tracers (complementing 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, formate, oxalate, etc.

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

Gases: Native conservative tracers or added conservative tracers

Gases: N_2, H_2, CO2, 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

PFTs complement stable isotopes and geochemistry for MVA and modeling heterogeneous flow

Conservative, Non-reactive & Non-Hazardous tracers

PFT's sensitive at pg-fg, versus isotopes at ppt

PFT's easy and cheap as multiple combinations or suites for multiple breakthroughs

Complemented by geochemistry providing multiple lines of evidence for MVA, flow path assessment and modeling

Applicable at near-surface or depth

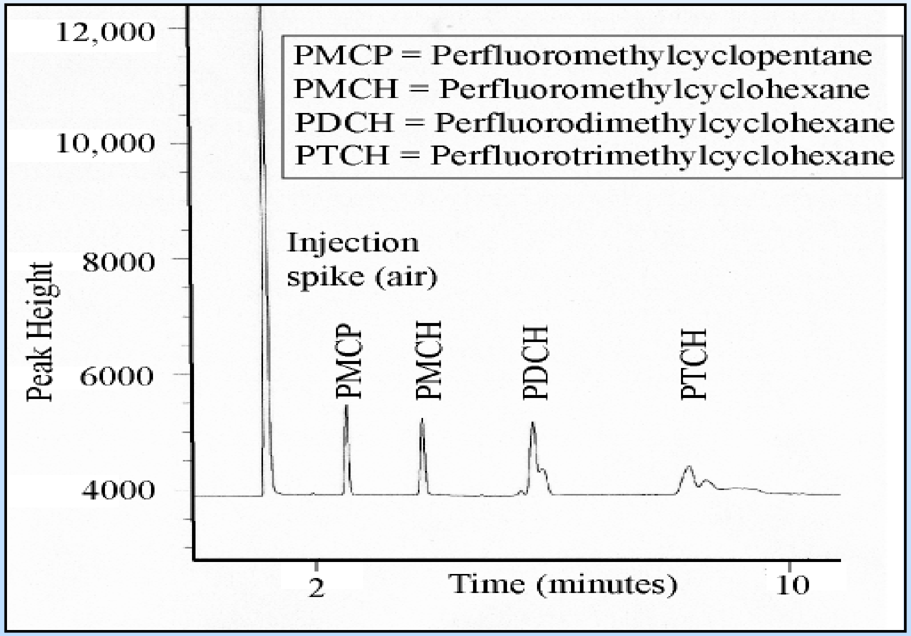
Scalable to thousands of samples

Can be analyzed in the field or preserved for analysis in the lab

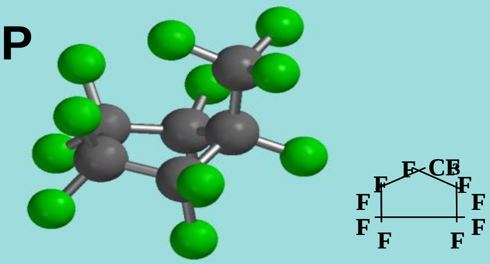
PFTs cost < 1 cent per ton injectate

Geochemistry and isotope analyses readily available at universities

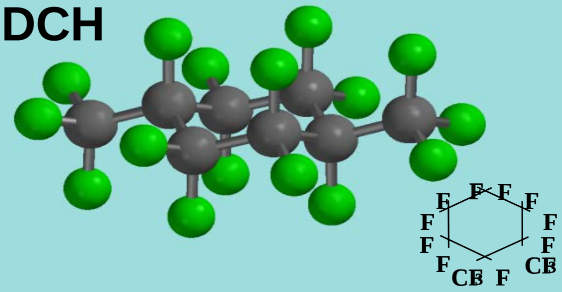
Isotopes, PFTs, and MVA make excellent dissertation projects



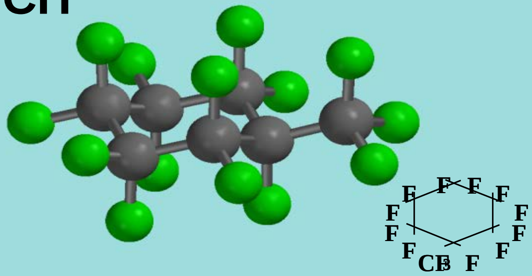
PMCP



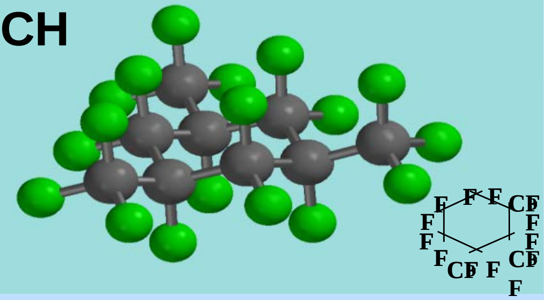
PDCH



PMCH



PTCH



Examples of PFTs used and sample collection

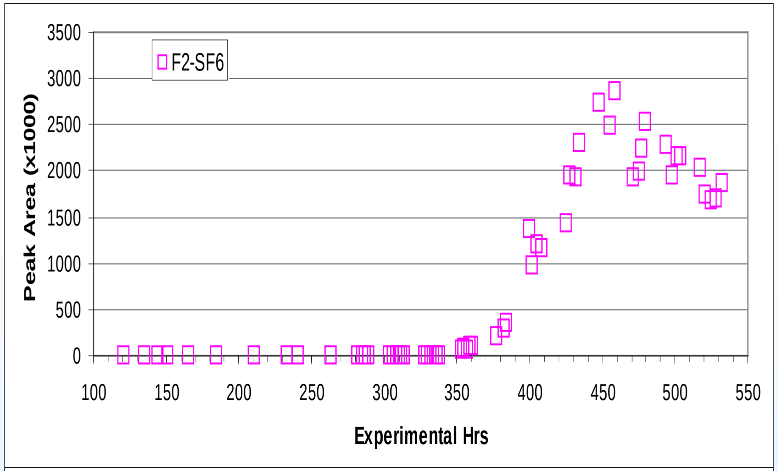
Deploy multiple-tracer suites (others available)
Different molecular weights, solubilities, and structure may enable chromatographic separation in reservoirs

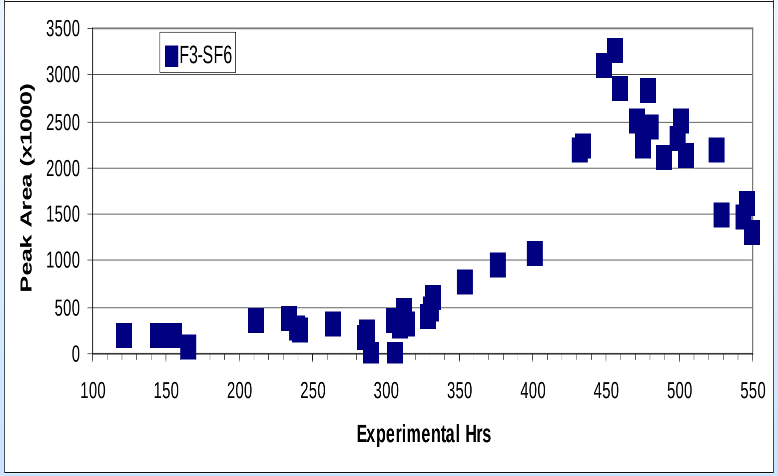
Pressure cylinders for sample collection (U-tube)

PFT Analyses performed in the field or preserved

Stable isotope analyses from pressurized samples

SF$_6$ and PTCH Tracer Results from Cranfield, MS





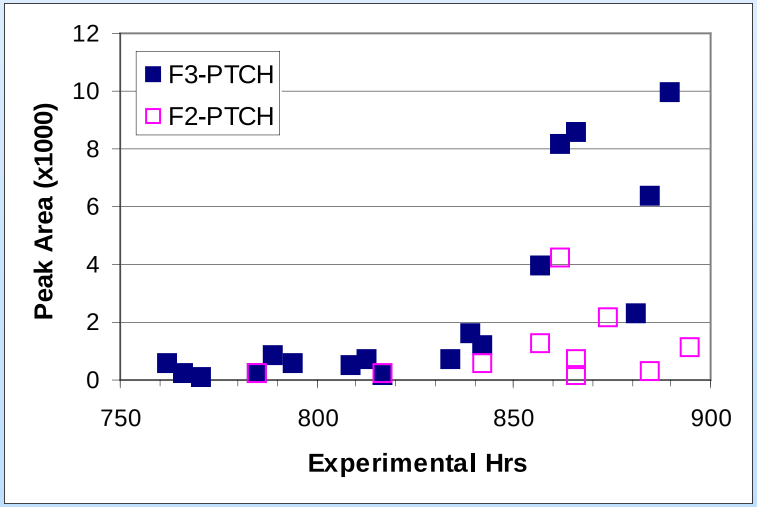
***LEFT:* SF$_6$ Breakthrough and peaks at F2 & F3**
F2 monitoring well was 68m and F3 was 112m east

SF$_6$ was added at t = 54 hr

SF$_6$ Breakthrough: F2 exp hr 342 (**288** travel h)
F3 exp hr 312 (**258** travel h)

F2 Closer but later breakthrough with sharper peak

F3 Exhibited earlier breakthrough with more complex peak shape (likely fingering of multiple flowpaths)



***Right*: PTCH was added at t = 693 hr,**
F2 - Closer, slower, smaller peak
F3 - Earlier arrival and far larger mass
(PMCH exhibited similar profile (data not shown)

(Each 1600 peak area units represents ~10 pg PFT in a 100 ul analysis or ~100 ng/L of tracer in monitoring well fluids.)

Travel Times of Initial Breakthrough and Major Peaks

December 2009 **Initial Breakthrough/** Peaks**, Major Peaks, ***		**April 2010** **Initial Breakthrough /** Peaks, **Major Peaks,***	

Monitoring Well F2

PMCP	- /**250**, **291*,** 328	PMCP	288/ 352, 360, **497*, 530*, 861***
PECH	- / **293**, 319	PDCH	286/ 303, 376, **497***, **861,** 894
SF6	- / **296***	PECH	284/ 407, **423*,** 446, 480, **810**
PTCH	167/ 344, 397	SF6	284/ 374^a**,405*,** 426, **841***
PMCH	155/ 203, 280, **324**	PTCH	>169/ #
		PMCH	>169/ **#**

Pressure front from increased flow 35/ 38

Monitoring Well F3

Pressure front from increased flow 140/ 158

Peaks difficult to distinguish at F3, Dec, 2009

Breakthroughs >150 ~210 <287

*Major Peaks ~ **320**,392,445,**470,**650,701*

PMCP	238/ 313, 470, 488, **838*,** 857
PDCH	238/ 327, 470, **812*, 861**
PECH	262/ 280, **419, 437**, **787**,803
SF6	258/ **424***, **803***
PTCH	169/ 197, #
PMCH	169/197, #

Data as travel time in hrs after injection. * Among maximal peaks; - Missed result from U-tube issues.; # Experiment ended hr 906.

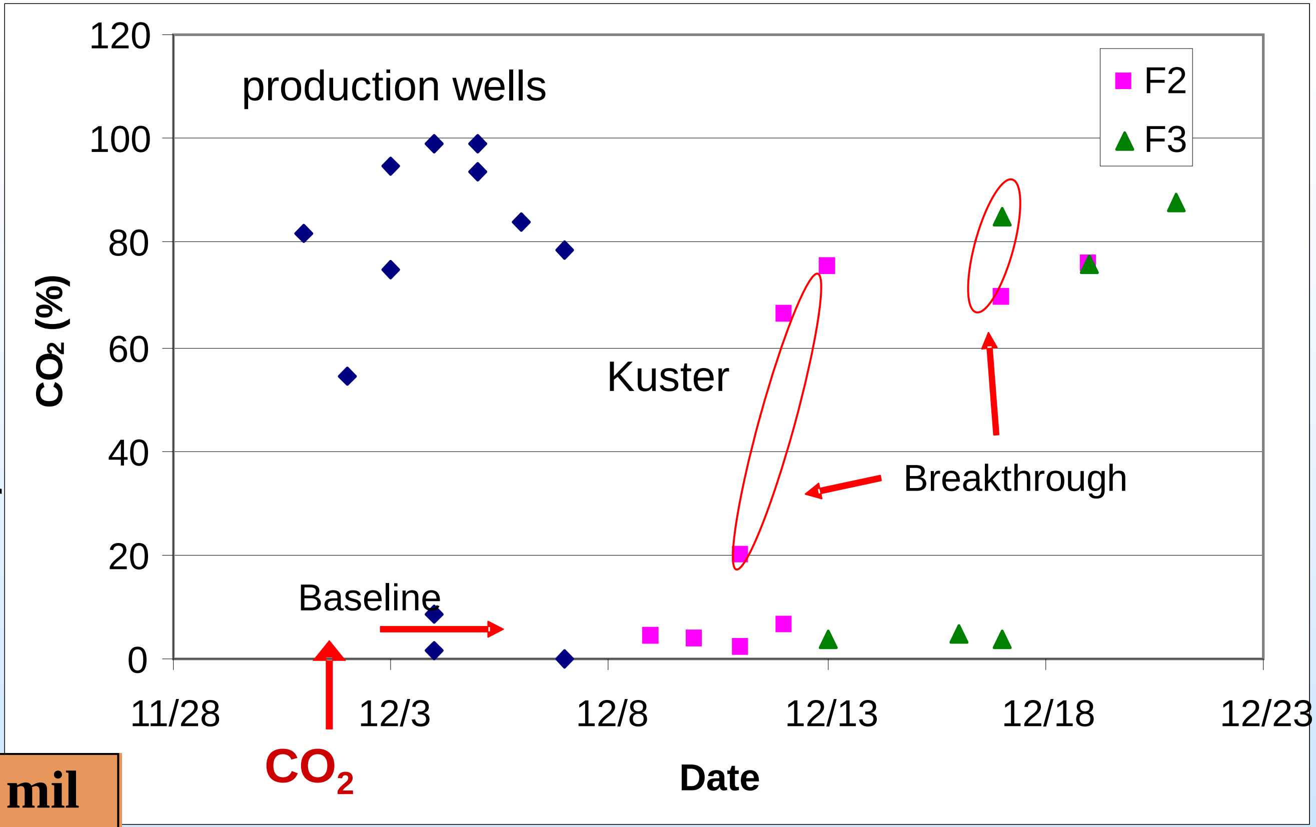
Note: By April the breakthroughs and major peaks required longer travel times indicating more developed flowpaths while breakthrough was faster at the more distant F3 well.

CO_2 Concentration Change vs Time: Production and Monitoring wells (example from 2009 sampling)

Initial brine at DAS had high CH_4/CO_2 ratios

Breakthrough CO_2 values similar to production wells

F2 well experienced CO_2 breakthrough much sooner than F3



$\delta^{13}CO_2$=-2.5 to -10.5 per mil

Baseline $\delta^{13}C$= -10 per mil

Injection $\delta^{13}C$= -2.6 per mil w/99% CO_2 (Jackson Dome)

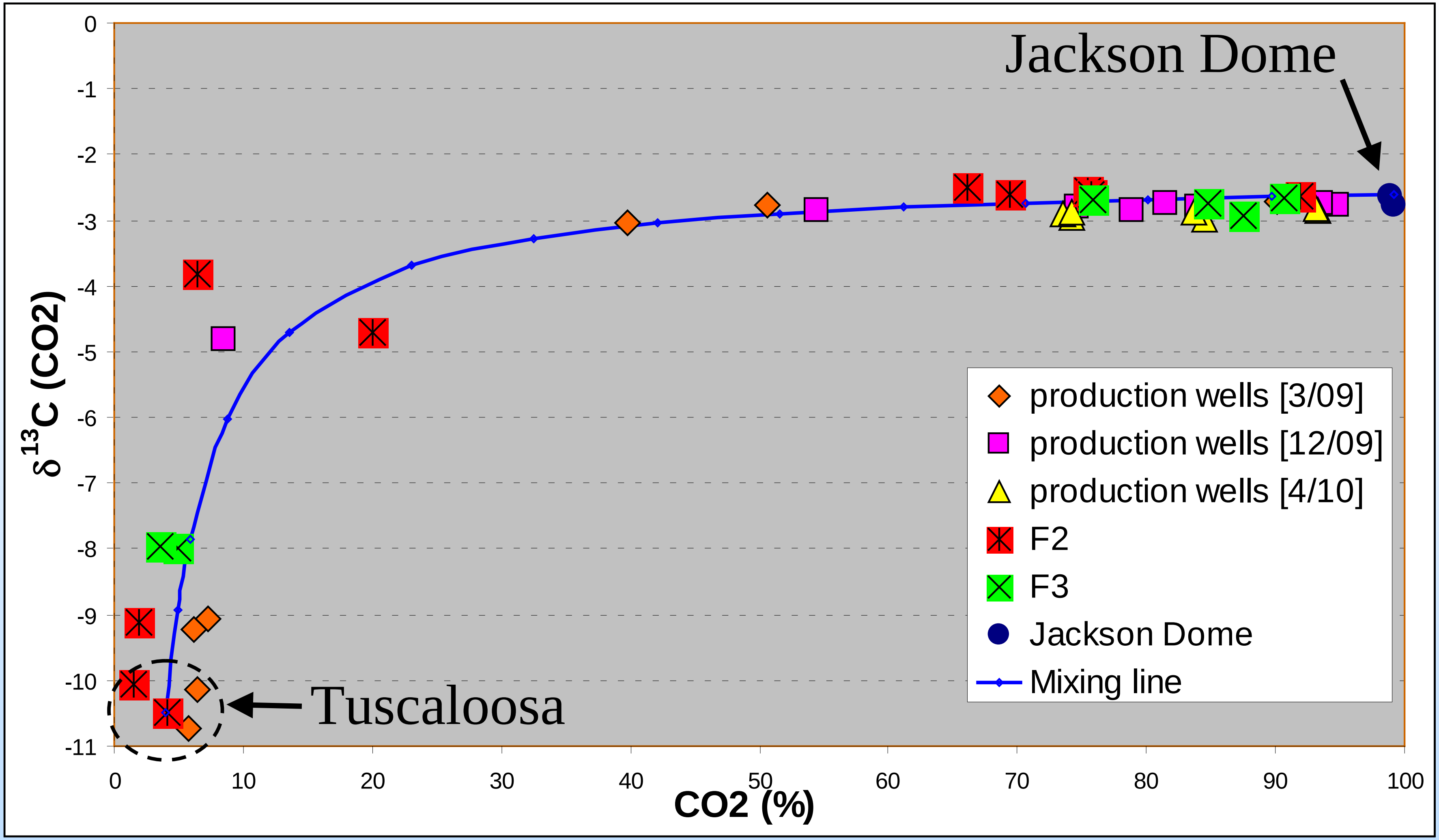
F2/F3: CO_2 (% and $^{13}C/^{12}C$) respond to injection

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**

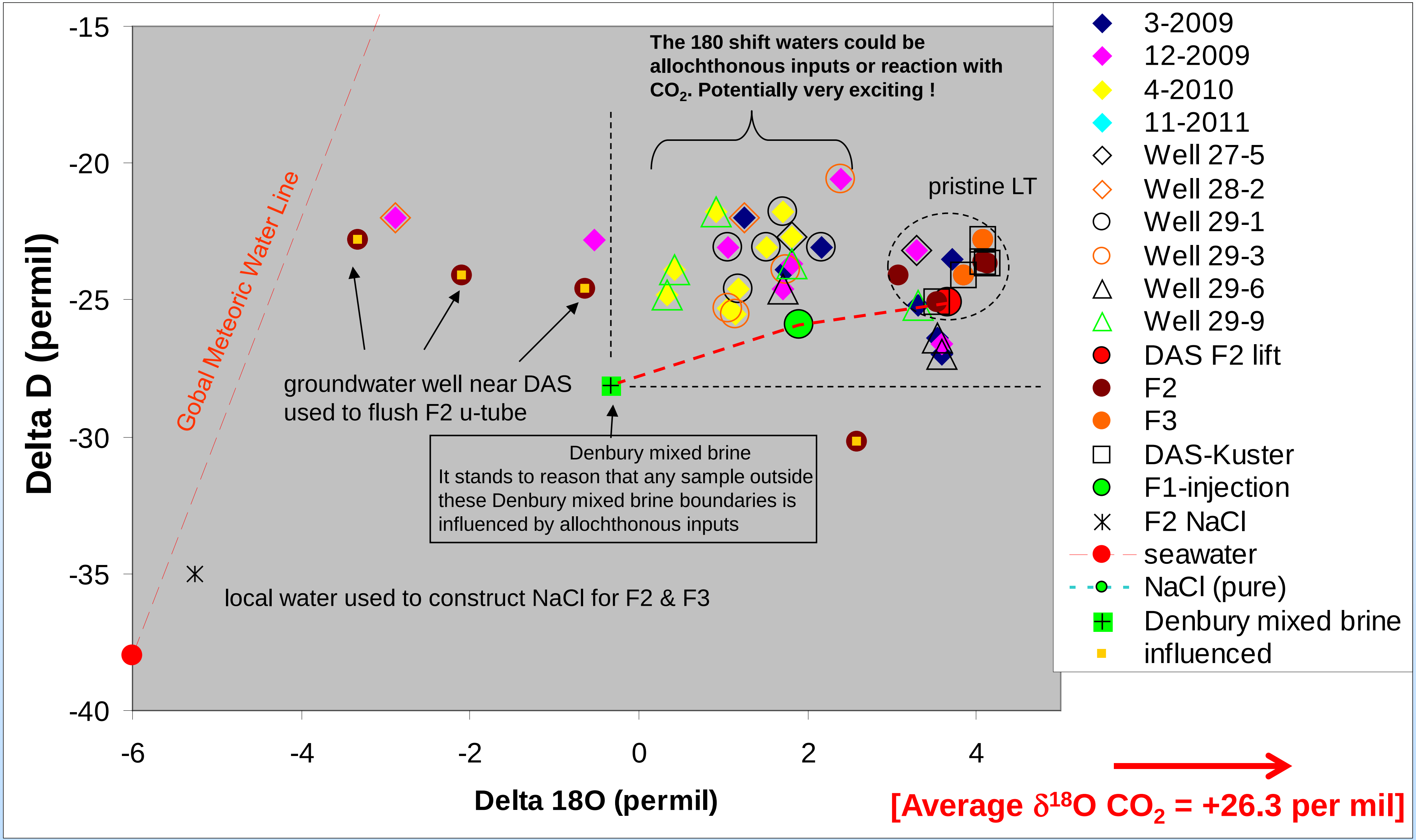
Carbon Isotopes ($^{13}C/^{12}C$) of Injected CO_2 Gas from Jackson Dome Show Good Mixing with Tuscaloosa CO_2



Simple two-component fluid mixing dominates at the DAS site

No evidence of CO_2 reaction with reservoir rock carbonates

Oxygen Isotopes of Brine May Reveal the Effects of Reactions with CO_2 [The isotopic shifts can be used to quantify the CO_2/Brine ratios]



The 180 shift waters could be allochthonous inputs or reaction with CO_2. Potentially very exciting !

groundwater well near DAS used to flush F2 u-tube

Denbury mixed brine
It stands to reason that any sample outside these Denbury mixed brine boundaries is influenced by allochthonous inputs

local water used to construct NaCl for F2 & F3

[Average $\delta^{18}O$ CO_2 = +26.3 per mil]

Water isotopes appear to be very good tracer, especially in combination with conservative solutes. We should be collecting Denbury brine routinely.

Lessons Learned Leading to future Plans for Technology Transfer

Conduct base line characterizations before system is perturbed

Deploy different suites of PFTs for surface and subsurface tests (< 3 sets per week)

Utilize multiple chemical and isotopic probes (some need further testing like $^{87}Sr/^{86}Sr$)

Deploy as many on-site analysis methods as possible – e.g. pH, alkalinity

Dual source of CO_2 with different isotopic values may be helpful

Obtain down-hole samples during base line and during tests; U-tube type design

Sample injection and monitoring wells above injection horizon to test for leakage

Continue to monitor both injection well and monitoring wells after completion of injection test (and above injection horizon)

Integrate results with coupled reactive-transport modeling efforts

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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: 10 journal articles (+4 submitted) and a dozen proceedings papers.**
- **Education: 4 Students and 2 postgraduates.**

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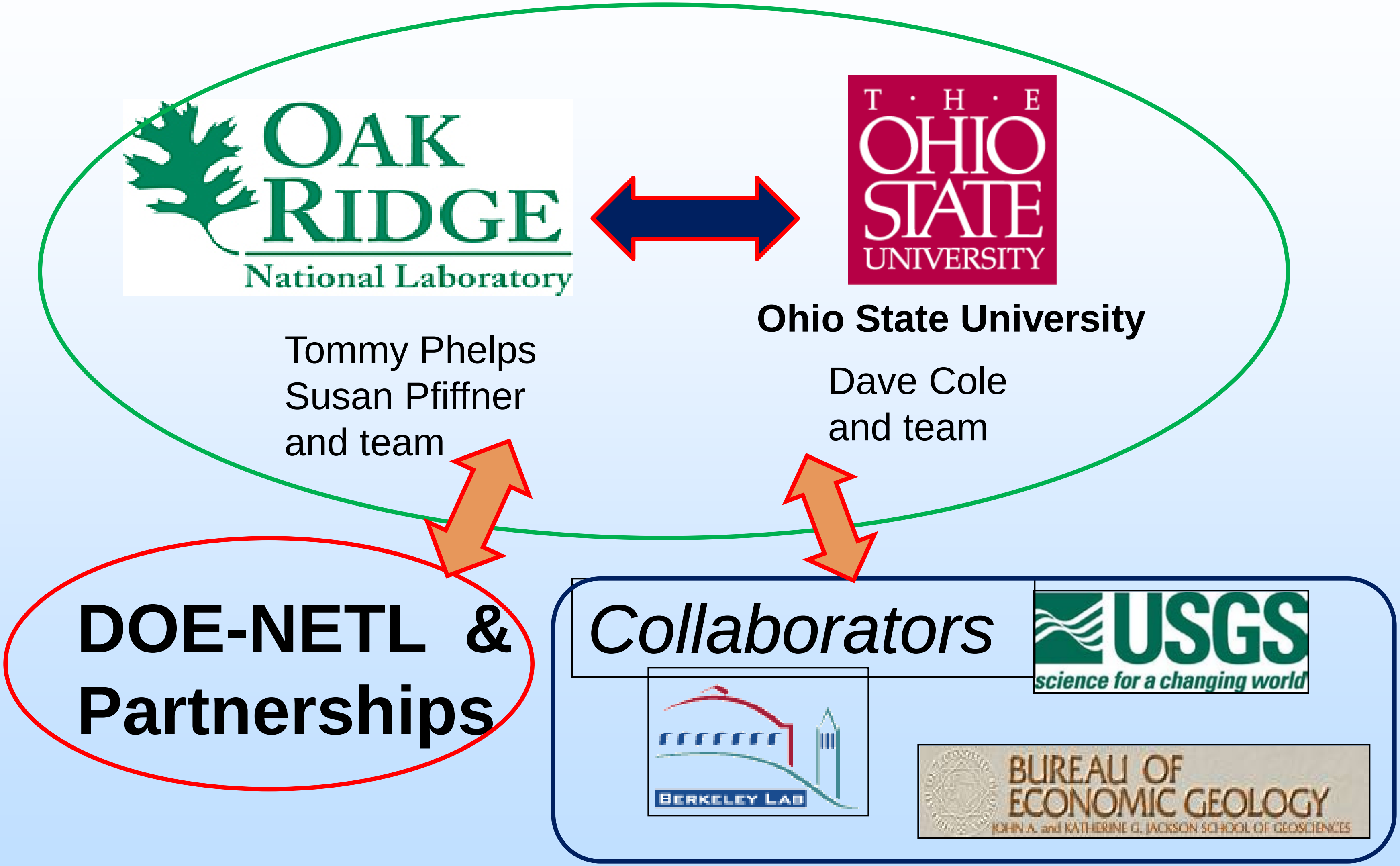
Acknowledgement and Organization Chart



Ohio State University

Tommy Phelps
Susan Pfiffner
and team

Dave Cole
and team

DOE-NETL & Partnerships

Collaborators

Appendix: Gantt Chart

Task	Task Description	Start : 10/1/2010	End: 9/30/2016									
		2014				2015						
		Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12			
1.1	Task 1 Program management and planning (PMP)	🟨	🟨	🟨 75	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
1.2	Analysis (injection/post injection samples) Cranfield **Milestone 6-2013*	🟧	🟧	🟧 80	🟧	🟧	🟧	🟧				
1.2.1	Injection and post-injection analysis	🟩	🟩	🟩 60	🟩	🟩	🟩	🟩				
1.2.2	Compare evolving changes: pre- and post injection	🟨	🟨	🟨 80	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
1.3	Integration of PFT/isotope results	🟪	🟪	🟪 30	🟪	🟪	🟪	🟪	🟪	🟪	🟪	
1.4	Develop PFT/isotope MVA strategy **Milestone update report 09/14*	🟦	🟦	🟦 20	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦

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Since 2006 there have been:

12 proceedings papers, plus 6 abst. presentations (national/international meetings)

8 peer reviewed journal papers; plus 2 submitted

3 book chapters

More papers planned.