Geochemistry of Water and Gases in the Frio Brine Pilot Test: Baseline Data and Changes During and Post CO_2 Injection

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Fourth Annual Conference on Carbon Capture & Sequestration

Developing Potential Paths Forward Based on the Knowledge, Science and Experience to Date

Geologic - Frio Brine Field Project (1)

Geochemistry of Water and Gases in the Frio Brine Pilot Test: Baseline Data and Changes During and Post CO2 Injection

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- Sandia Technologies: Dan Collins, “Spud” Miller, David Freeman; Phil Papadeau
- BP: Charles Christopher, Mike Chambers
- Schlumberger: T. S. Ramakrishna and others
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- Praxair: Joe Shine, Dan Dalton
- Australian CO2CRC (CSRIO): Kevin Dodds
- Core Labs: Paul Martin and others

Hovorka et al., 2004

Topics Discussed

- Composition of water and gases in the Frio– Baseline, during and post injection results.
- How are such data obtained and why are they important to CO_2 sequestration?
- Water-mineral-CO_2 interactions in the Frio.
- Environmental implications of post injection results.
- Future plans and concluding remarks.

USGS

Frio CO_2 Field sampling

Drilling & test water tagged with dye tracers

Date	Site	Sampling info	Sample series
June 3, 2004	injection well	MDT tool	$04FCO_2$-100
Jul 23-Aug 2, 2004	injection well, monitoring well & gw wells	surface sampling (N_2), Kuster, submers.pump	$04FCO_2$-200
Oct 4-7, 2004	monitoring well	U-tube	$04FCO_2$-300
Oct 29-Nov 3, 2004	monitoring well	U-tube	$04FCO_2$-400
April 4-6, 2005	injection well & monitoring well	surface sampling (N_2) & Kuster	$05FCO_2$-100

A national produced-water geochemistry database

James K. Otton

George N. Breit

Yousif K. Kharaka

Cynthia A. Rice

internet at:

http://energy.cr.usgs.gov/prov/prodwat/intro.htm

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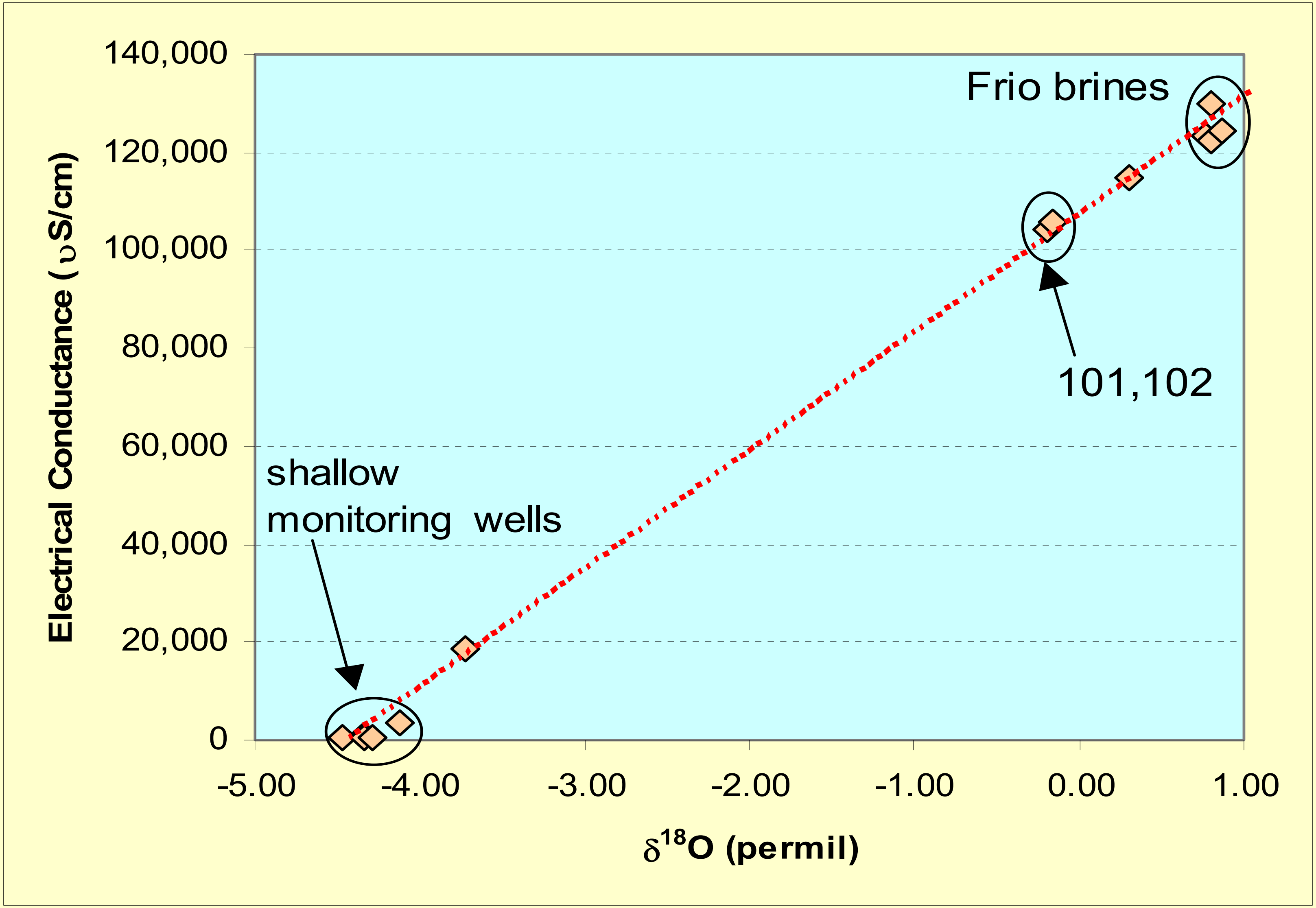
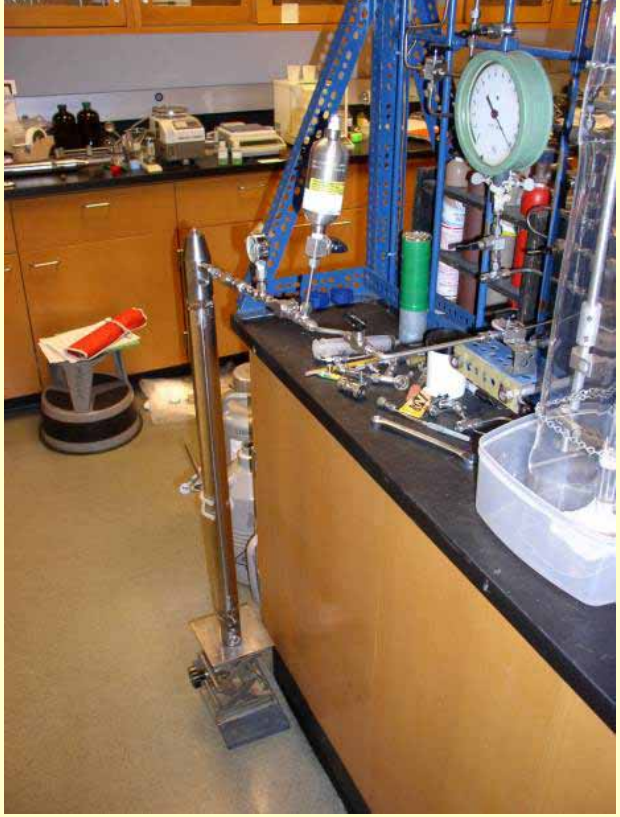
Use of water isotopes and chemistry to determine mixing with drilling water





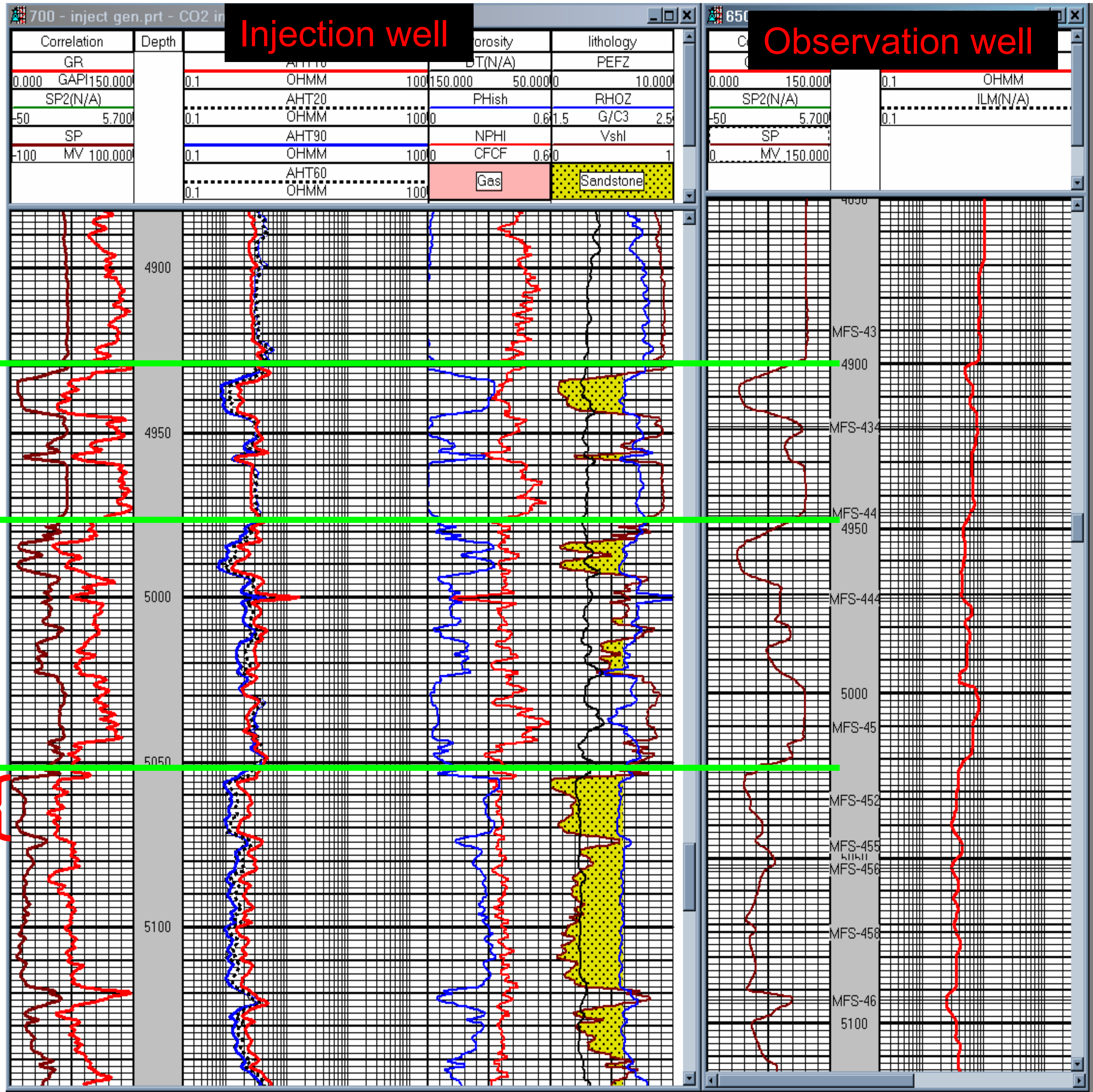
Open Hole logs

Top A ss

Top B ss

Top C ss

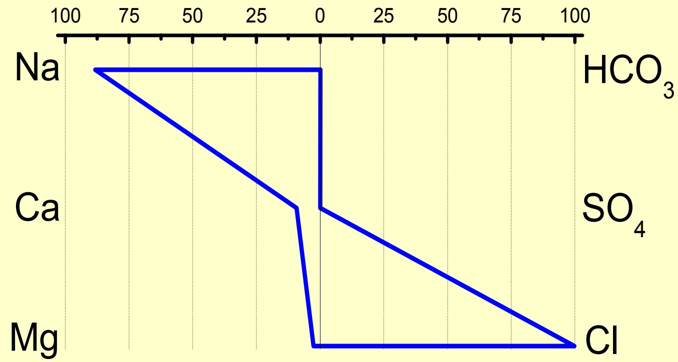
Proposed injection zone



Hovorka et al., 2004

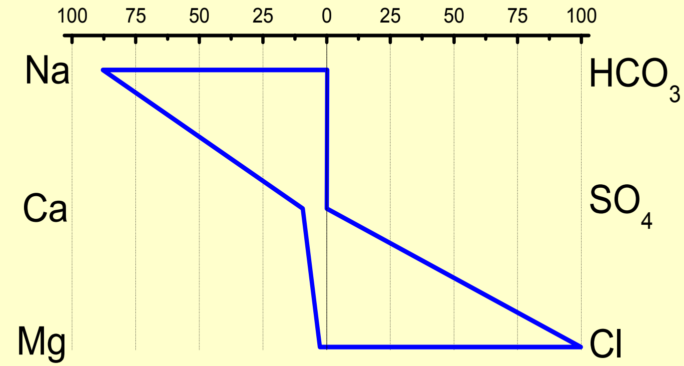
Salinity and normalized conc. of major cations and anions

04-FCO2-208 (injection well)



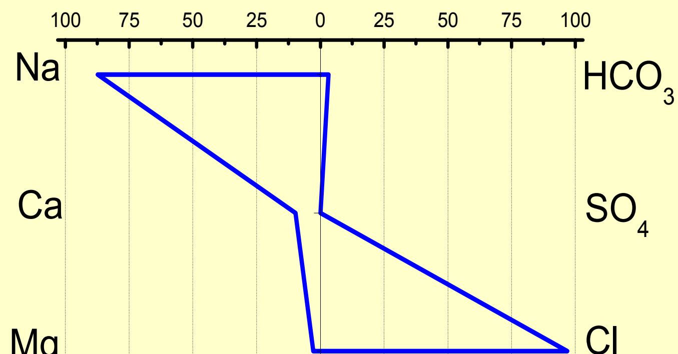
pH = 6.86; TDS = 91,500 mg/L

04FCO2-218 (monitoring well, C-sand)



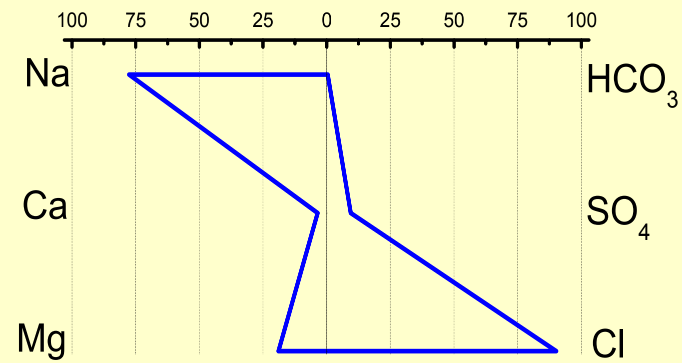
pH = 6.7; TDS = 93,800 mg/L

04FCO2-337 (monitoring well; post injection)



pH = 6.03; TDS = 92,600 mg/L

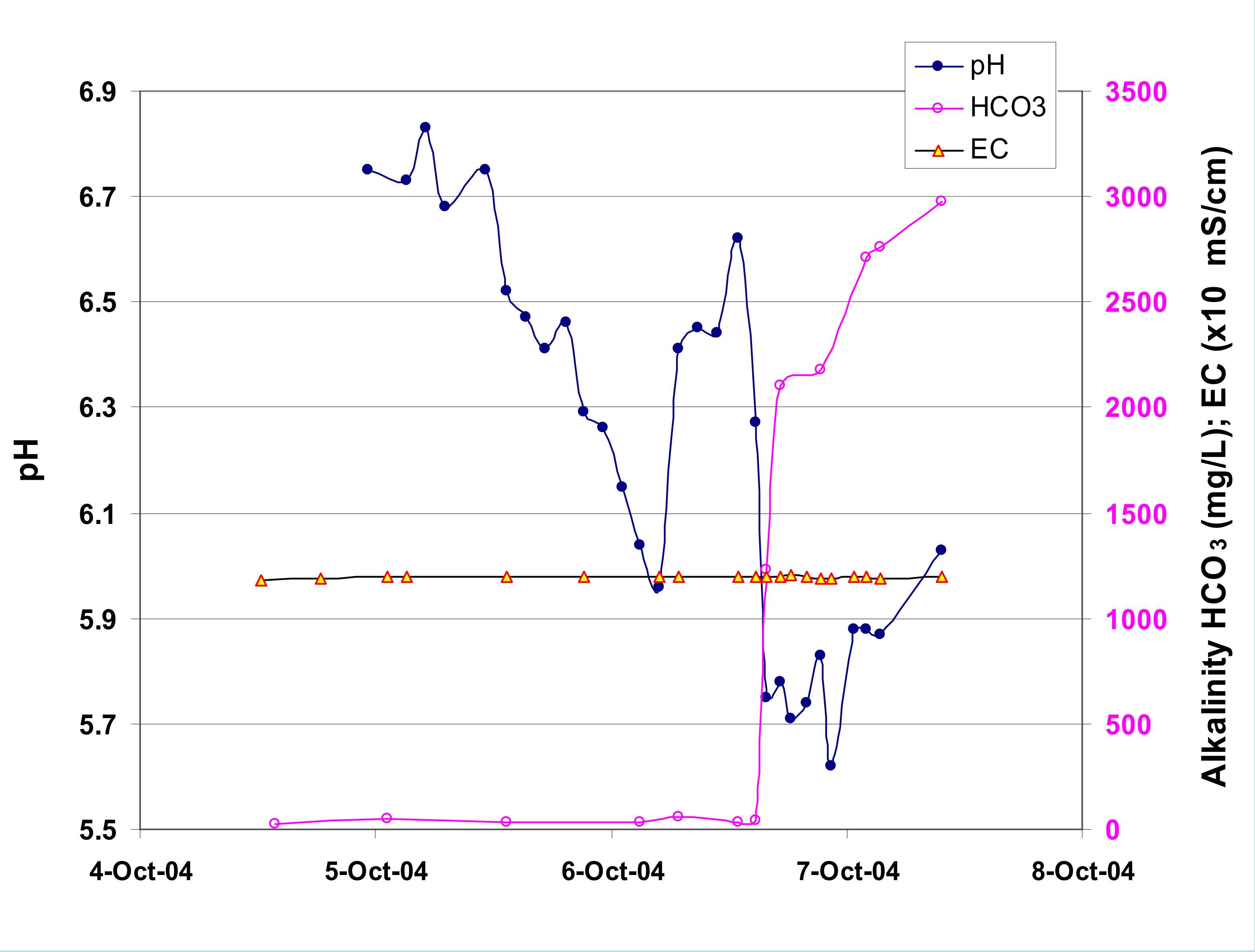
seawater

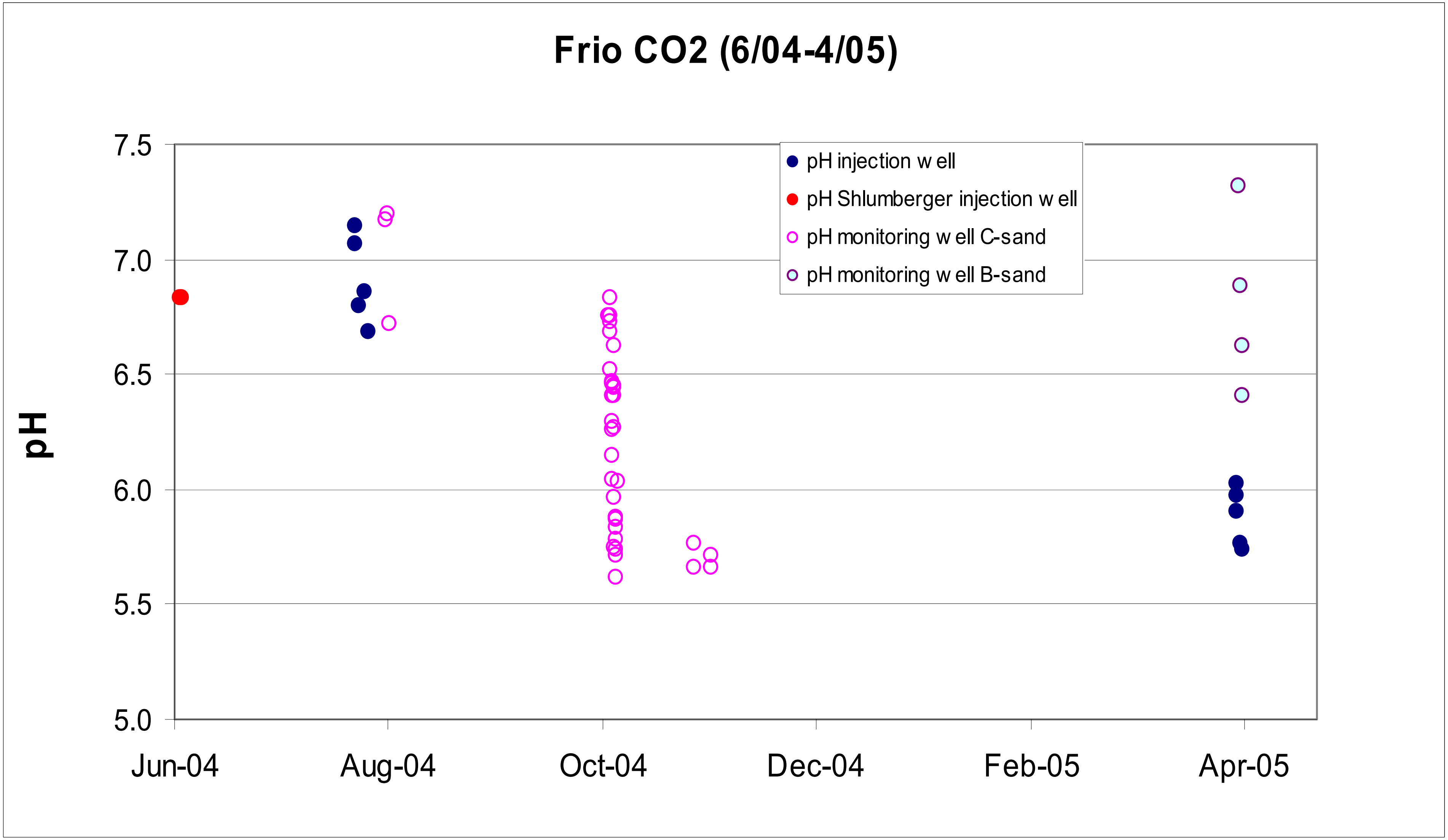


pH = 8.2; TDS = 36,900 mg/L

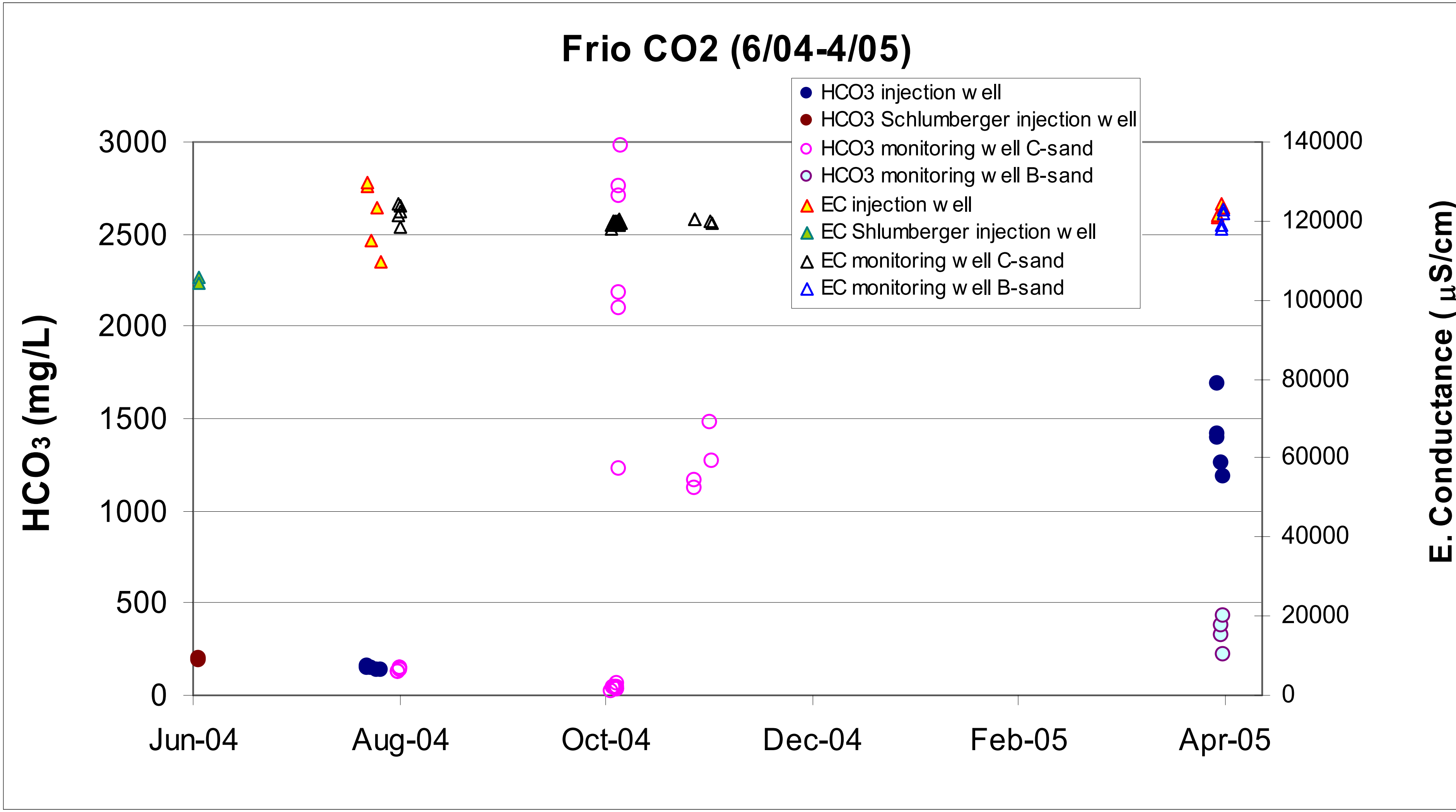
[milliequivalents/liter, normalized to 100%]

Selected chemical data from monitoring well during CO2 injection



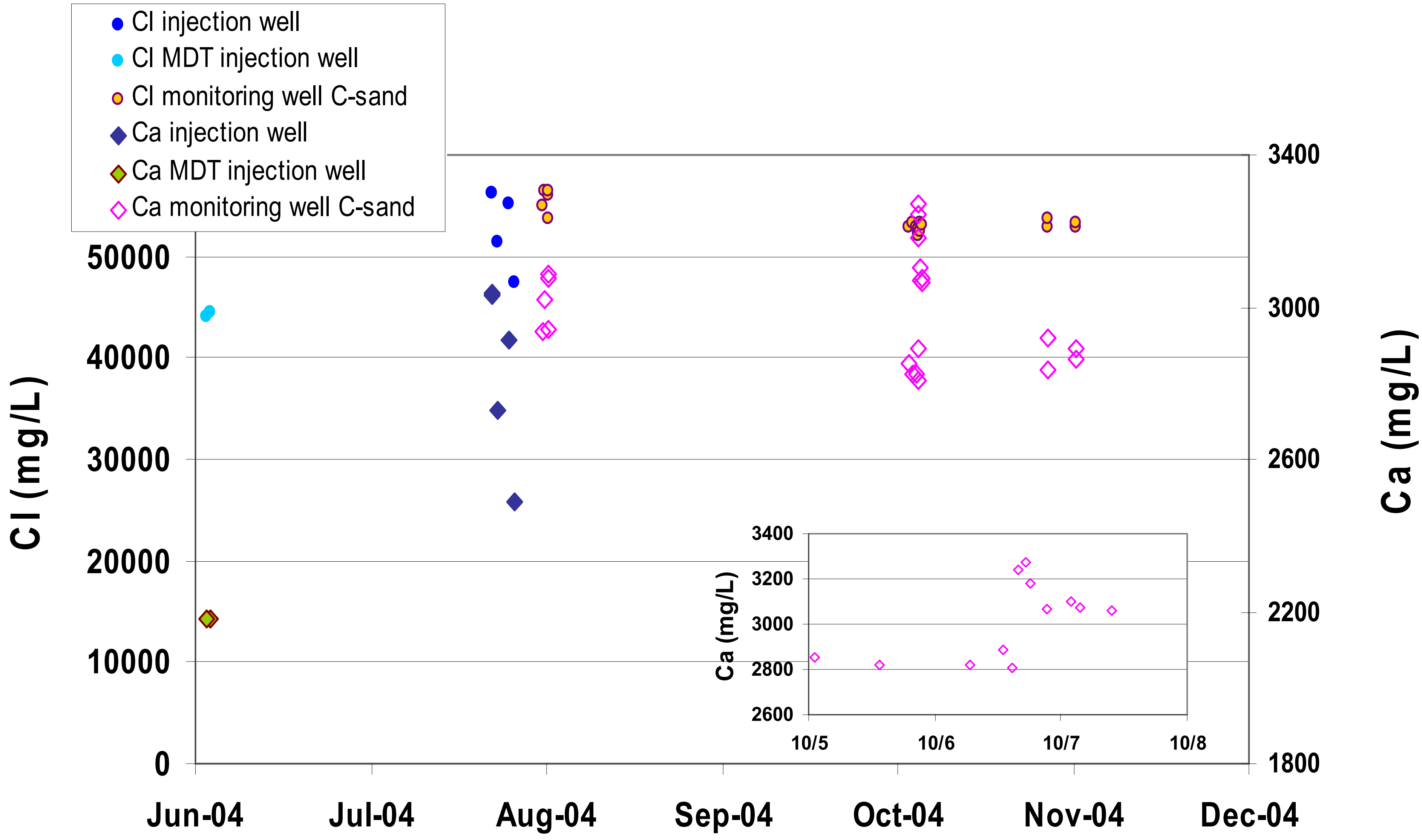


Frio CO2 (6/04-4/05)
pH
7.5
7.0
6.5
6.0
5.5
5.0
Jun-04
Aug-04
Oct-04
Dec-04
Feb-05
Apr-05
pH injection w ell
pH Shlumberger injection w ell
pH monitoring w ell C-sand
pH monitoring w ell B-sand

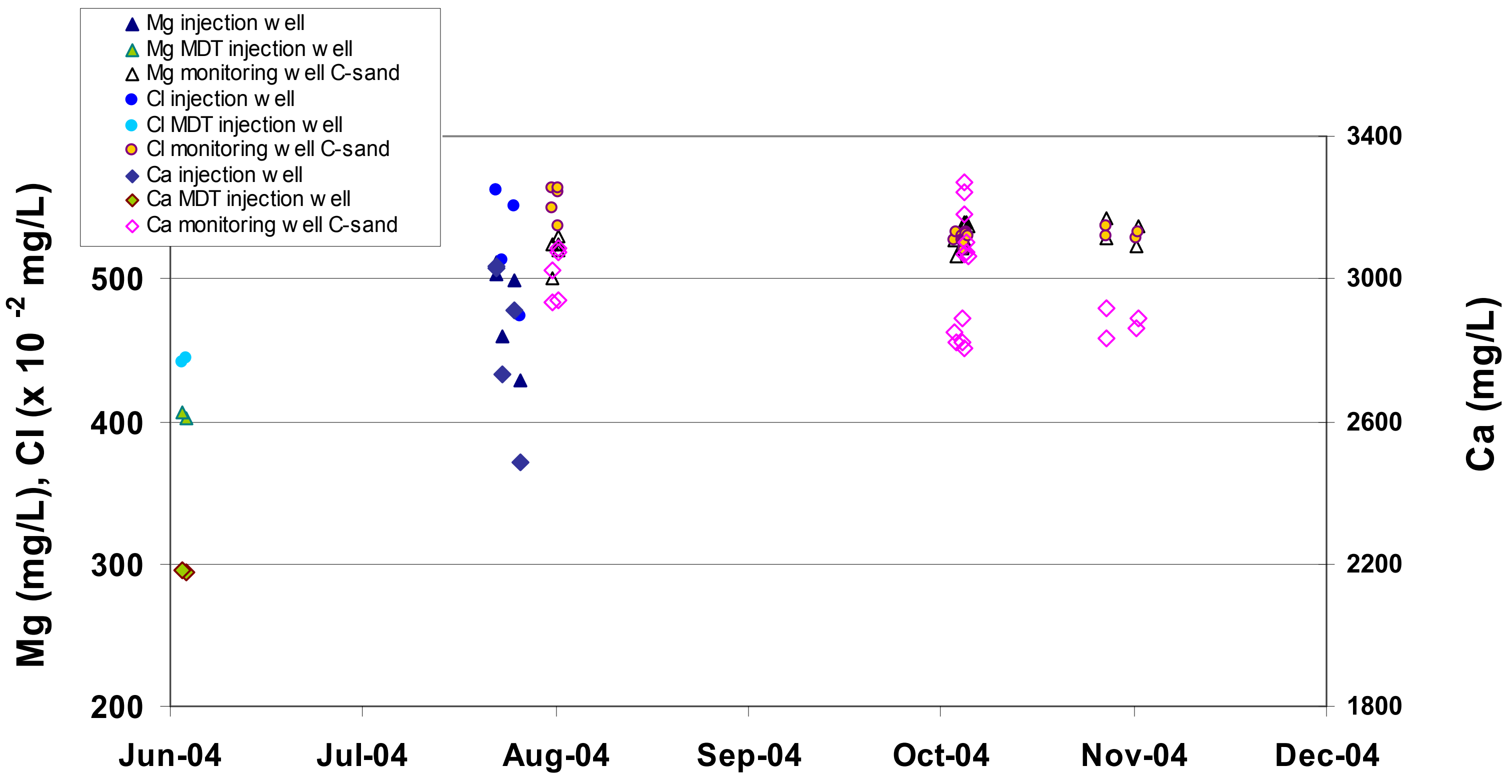


Frio CO2 (6/04-4/05)
HCO3 injection w ell
HCO3 Schlumberger injection w ell
HCO3 monitoring w ell C-sand
HCO3 monitoring w ell B-sand
EC injection w ell
EC Shlumberger injection w ell
EC monitoring w ell C-sand
EC monitoring w ell B-sand
HCO3 (mg/L)
E. Conductance (μS/cm)
3000
2500
2000
1500
1000
500
0
140000
120000
100000
80000
60000
40000
20000
0
Jun-04
Aug-04
Oct-04
Dec-04
Feb-05
Apr-05

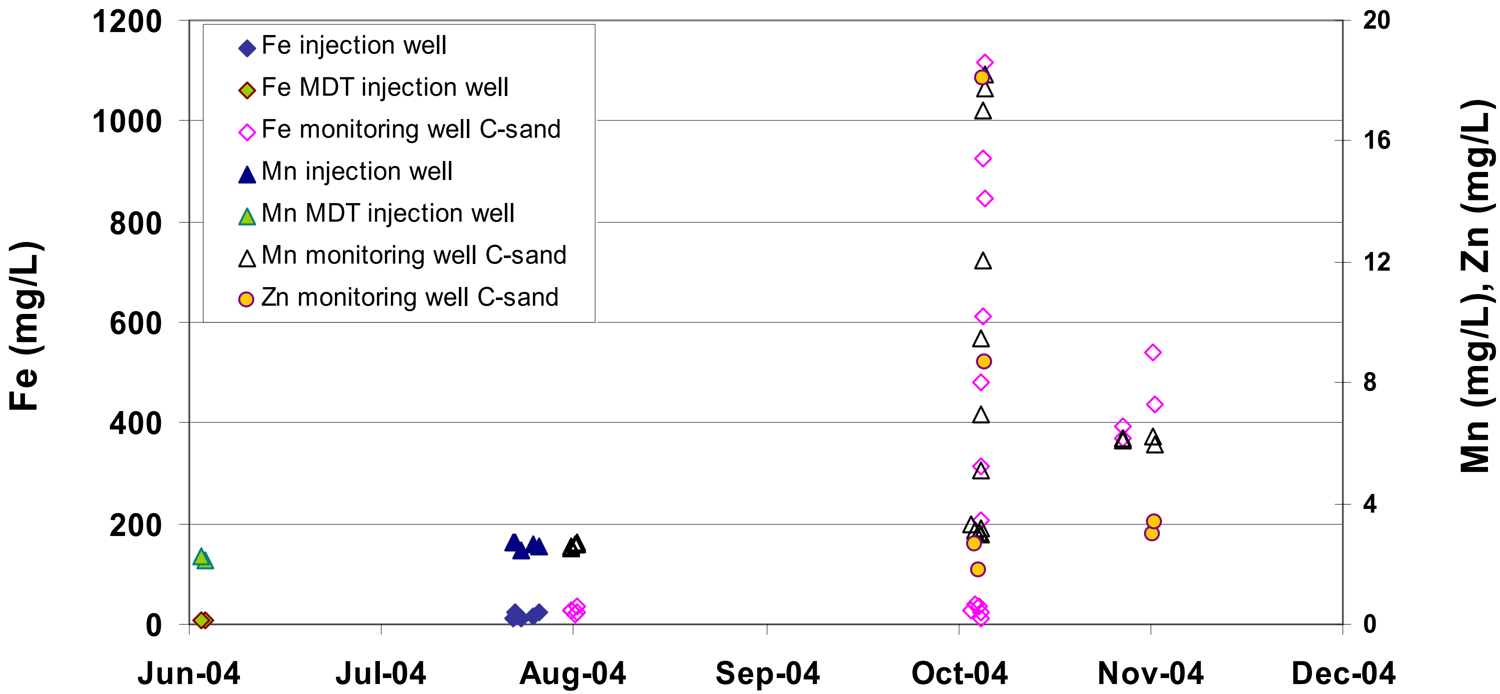
Frio Cl & Ca (6/04-11/04)



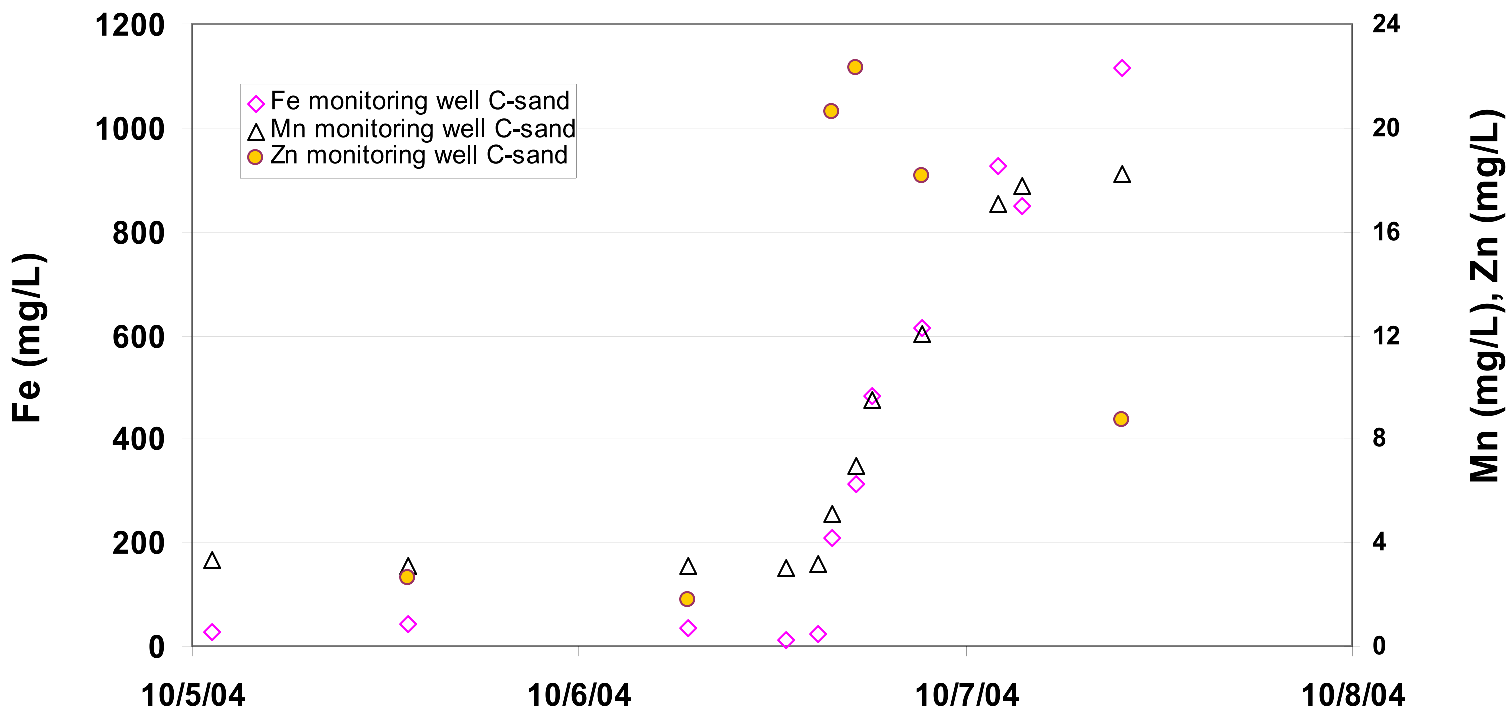
Frio CO2 (6/04-11/04)

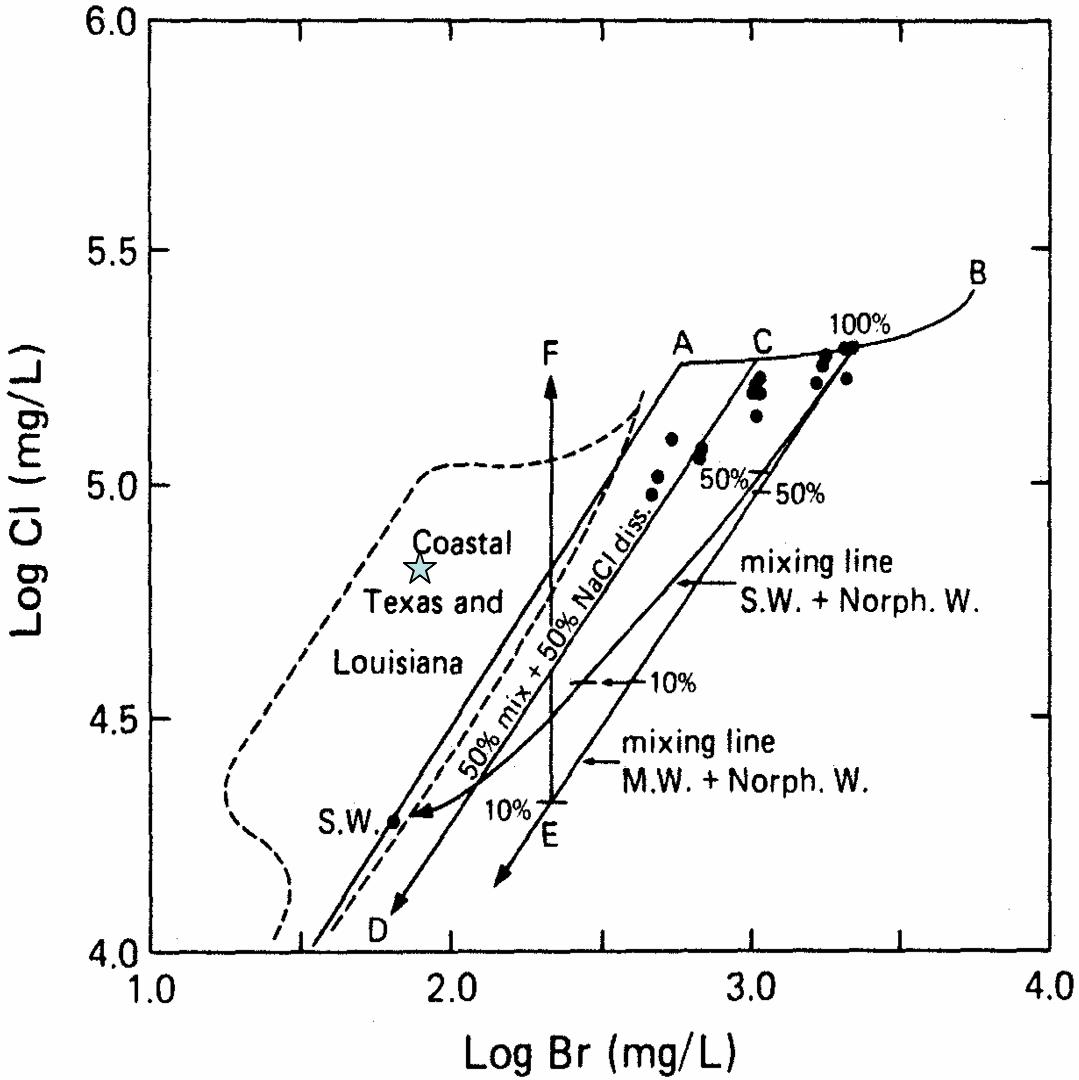


Frio CO2 (6/04-11/04)



Frio CO2 (10/5/04-10/7/04)



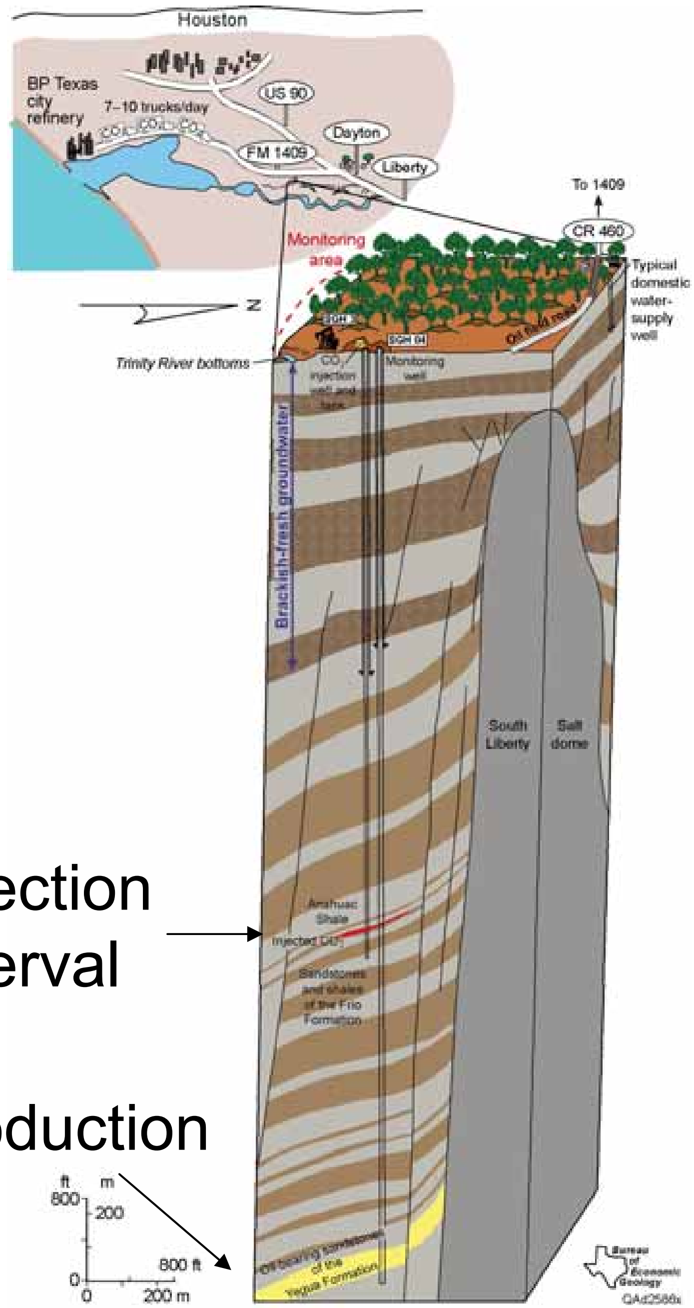


Br-Cl as indicator of origin of solutes

(* Frio value)

Kharaka & Hanor, 2004

Frio Brine Pilot

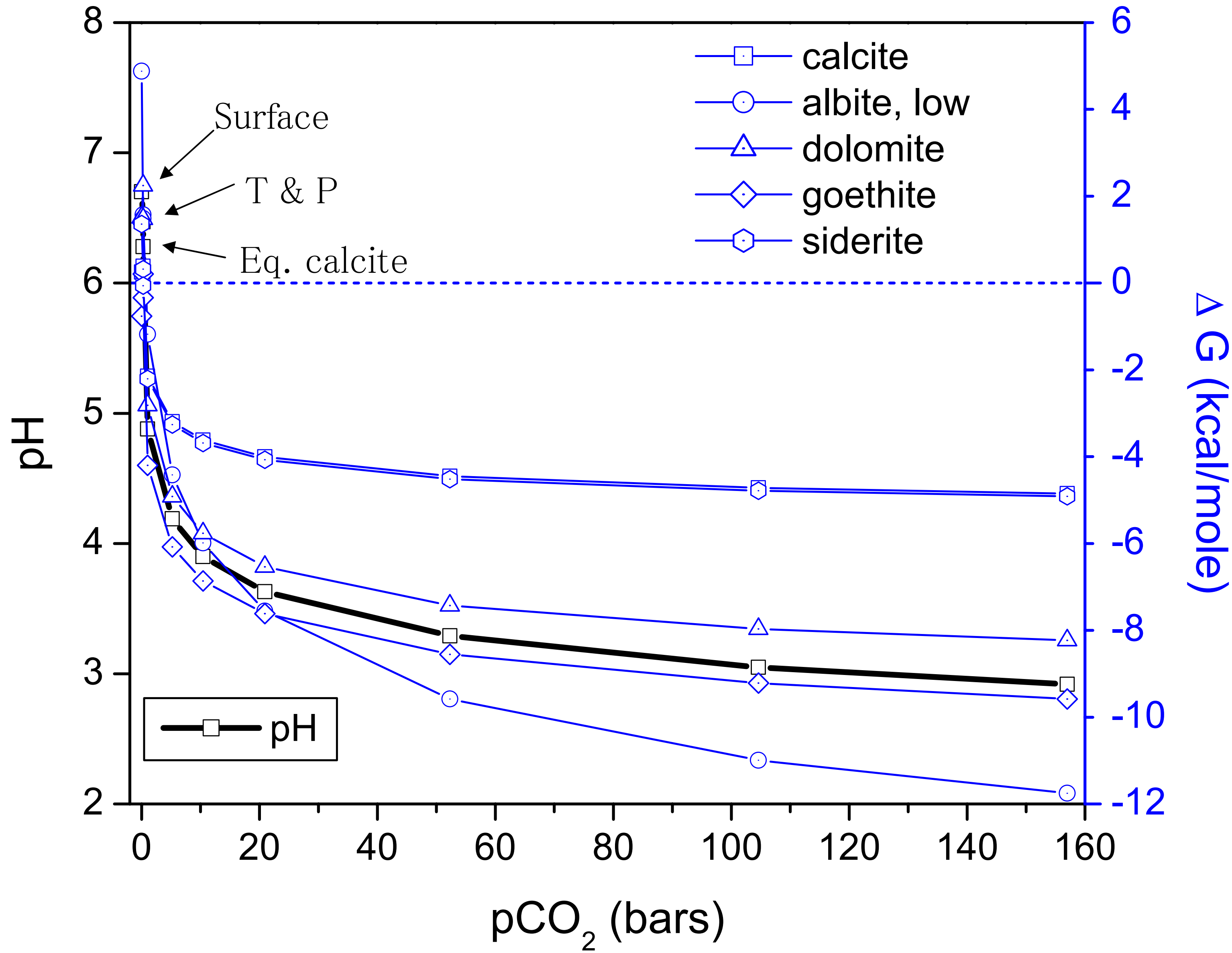


Injection interval

Oil production

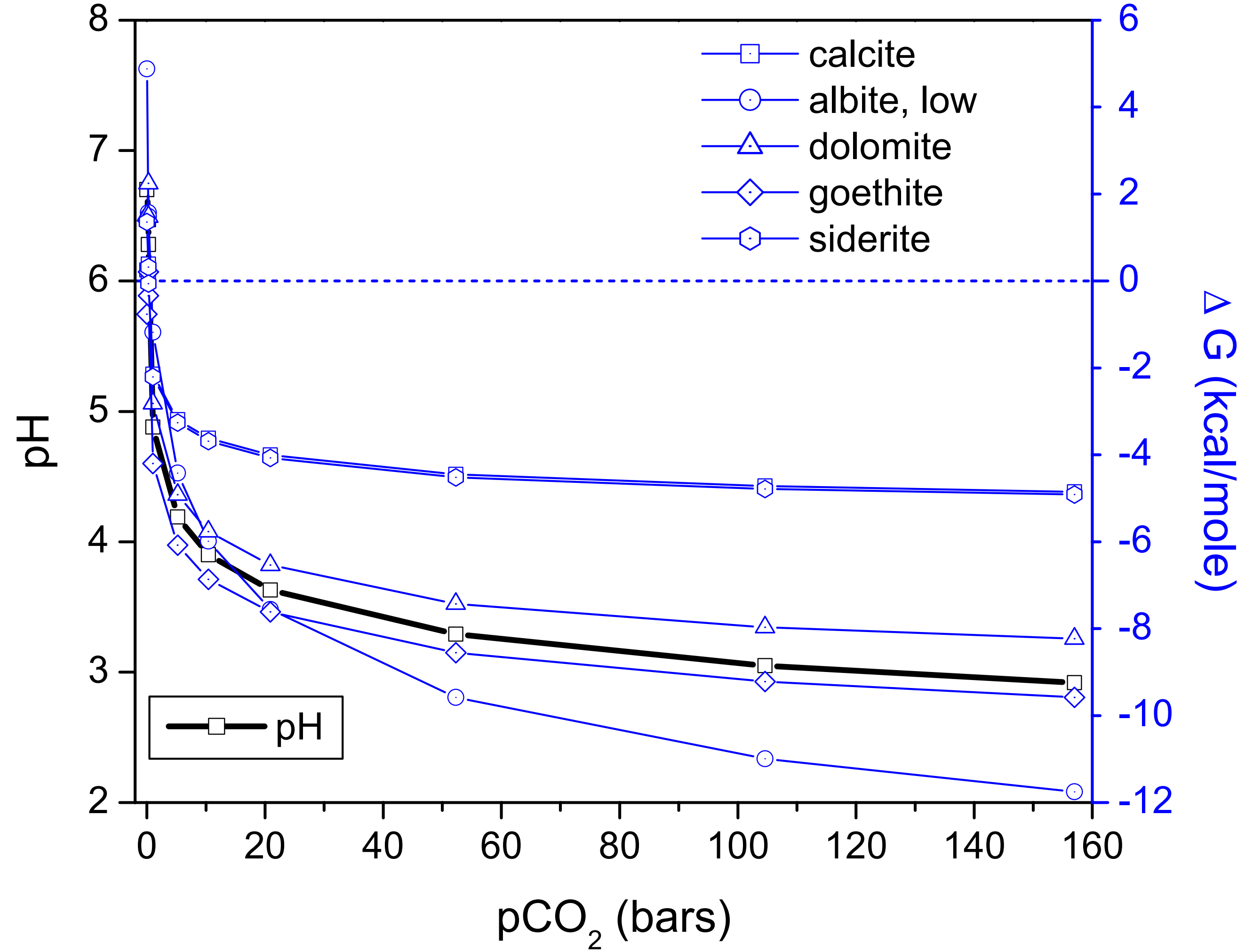
- Injection interval: 24-m-thick, mineralogically complex Oligocene reworked fluvial sandstone, porosity 24%, Permeability 2-3 Darcys
- Seals – numerous thick shales, small fault block
- Depth 1,500 m
- Brine-rock system, no hydrocarbons
- 67°C; 150 bar

Hovorka et al., 2004

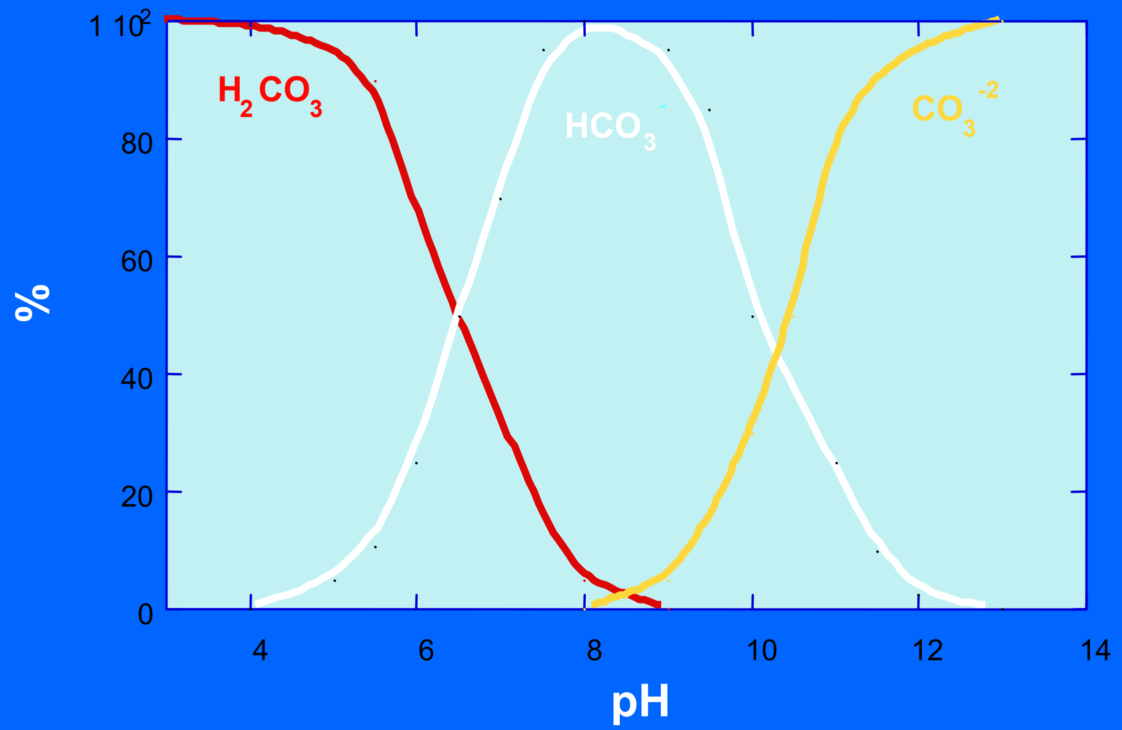


8
7
6
5
4
3
2
pH
6
4
2
0
-2
-4
-6
-8
-10
-12
Δ G (kcal/mole)
0
20
40
60
80
100
120
140
160
pCO2 (bars)
Surface
T & P
Eq. calcite
calcite
albite, low
dolomite
goethite
siderite
pH

Computed pH and saturated states of selected minerals at T & P



Idealized carbonate speciation



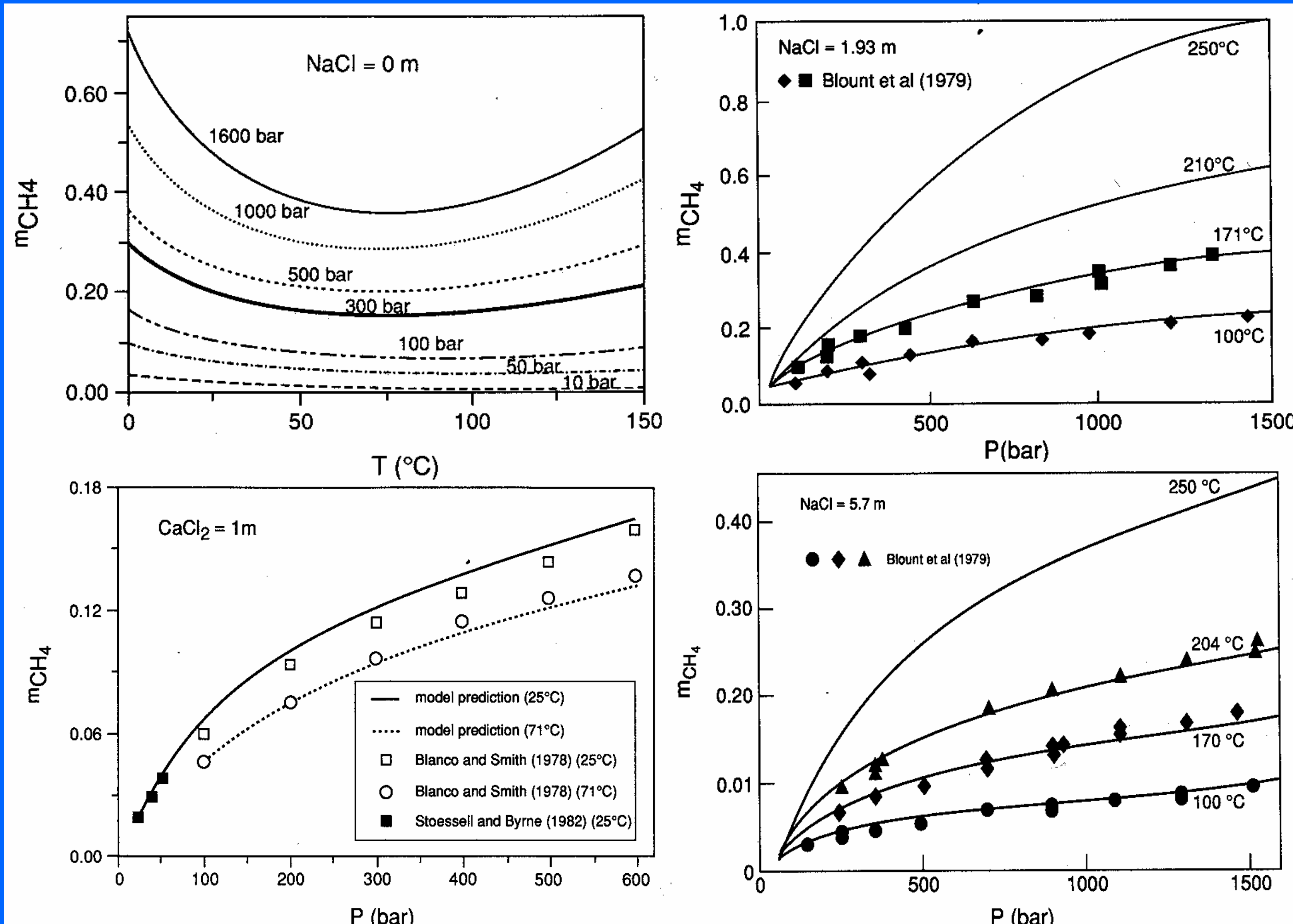
Chemical Composition of Frio Gases

Frio formation water at saturation with CH_4

	Injection well before CO_2 injection 04FCO2-102	Monitoring well before CO_2 injection 10-7-04 @ 2:15 am	Monitoring well after CO_2 injection 10-13-04 @ 20:37	Monitoring well "B" sand 05FCO2-110
He	0.0077	0.0026	0	0.0124
H_2	0.0401	1.36	0.191	0.285
Ar	0.0418	0.0207	0	0.0608
O_2	0.0719	0	0	0.748
CO_2	0.31	0.0040	96.8	0.208
N_2	4.15	3.60	0.037	5.17
CO	0	0	0	<0.001
CH_4	93.4	94.8	2.94	93.4
C_2H_6	0.149	0.161	0.0052	0.103
C_3H_8	0.0086	0.0021	0	0.0012
C_4H_{10}+	1.76	0.0037	0	<0.0005

volume%, normalized

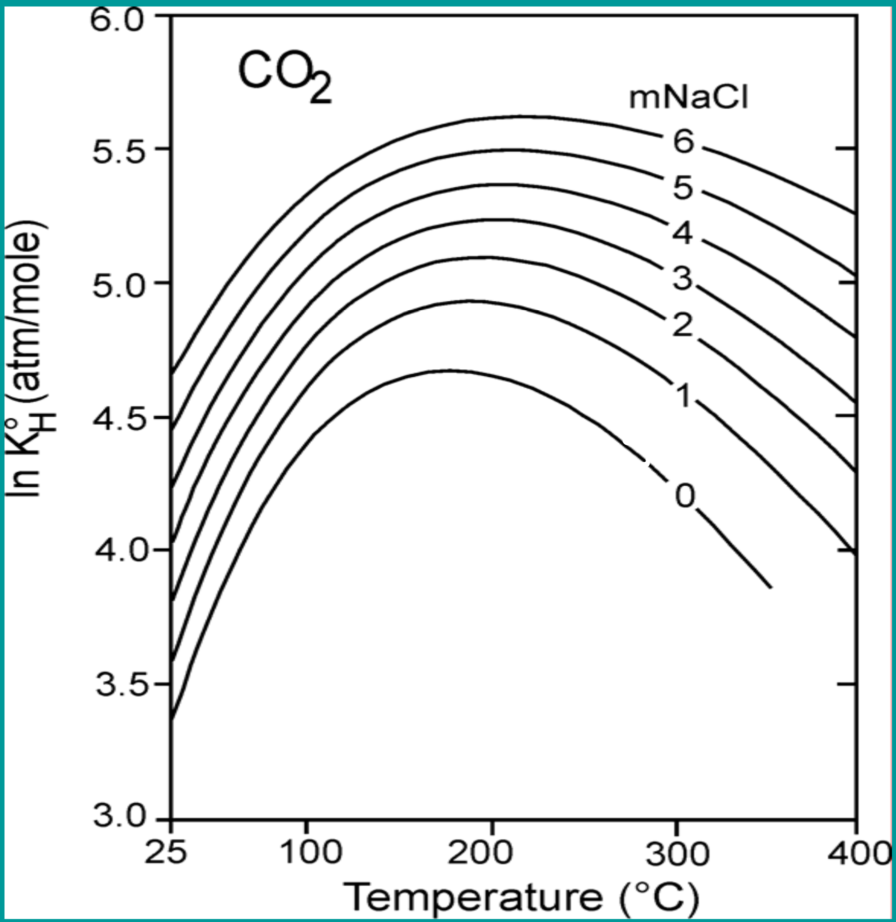
Solubility of CH_4 in Aqueous Solutions

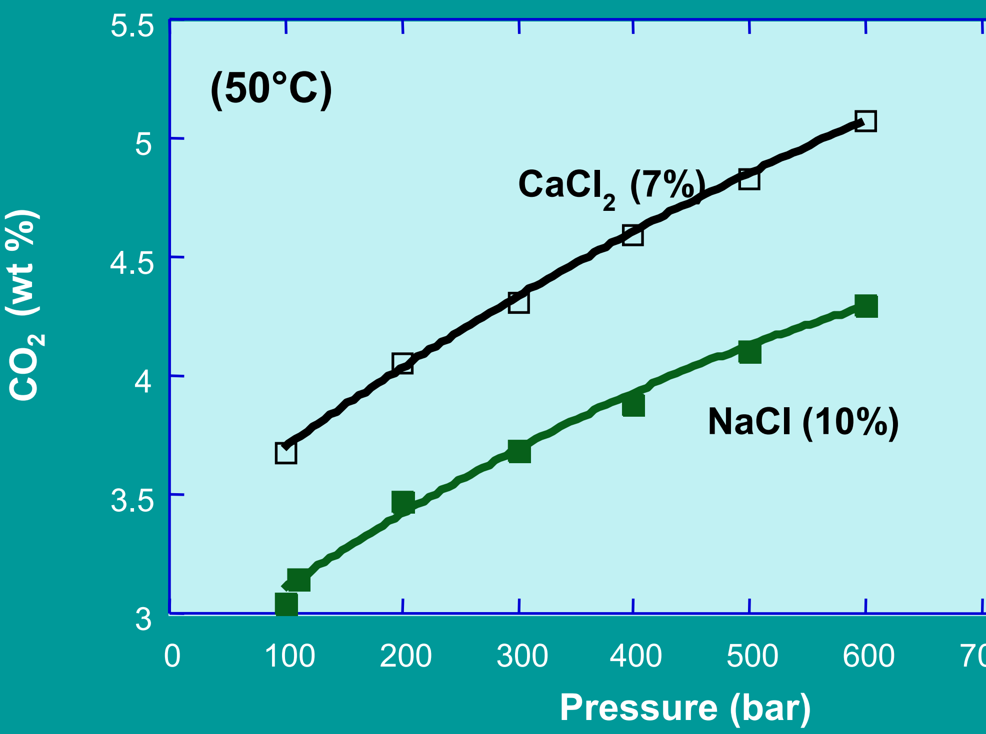


Duan et al., 1992

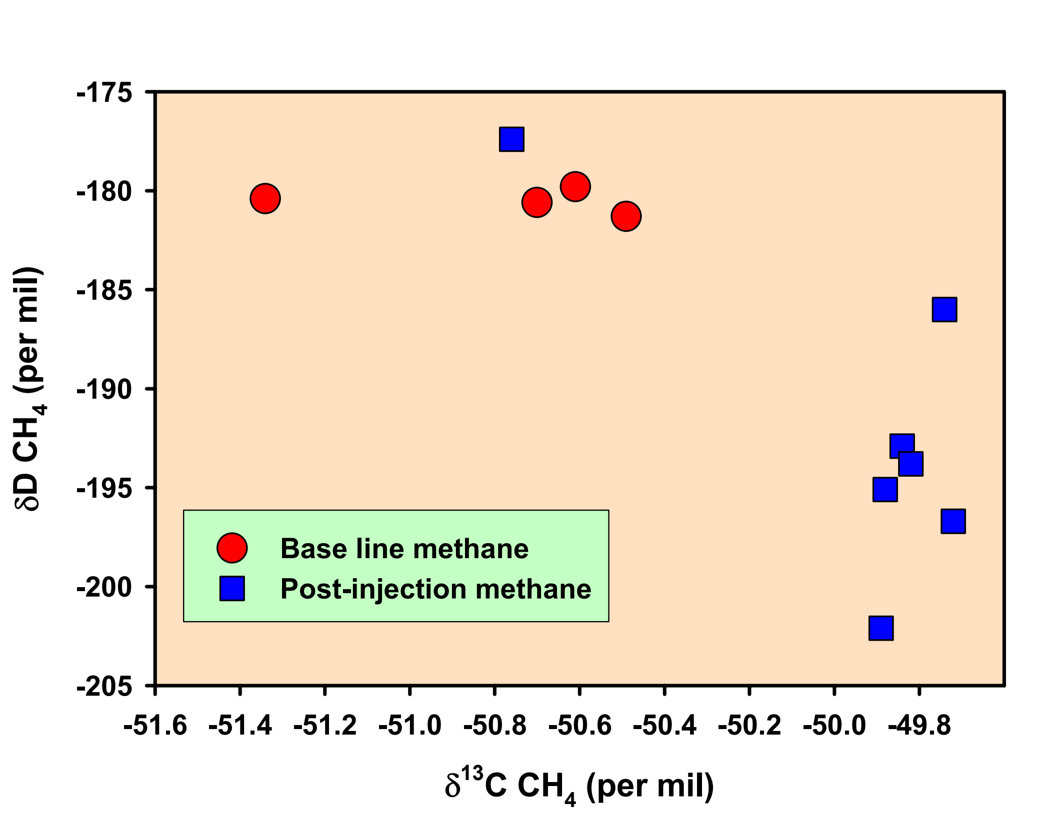
Solubility of CO_2 in water as f (t, P & chemical composition)

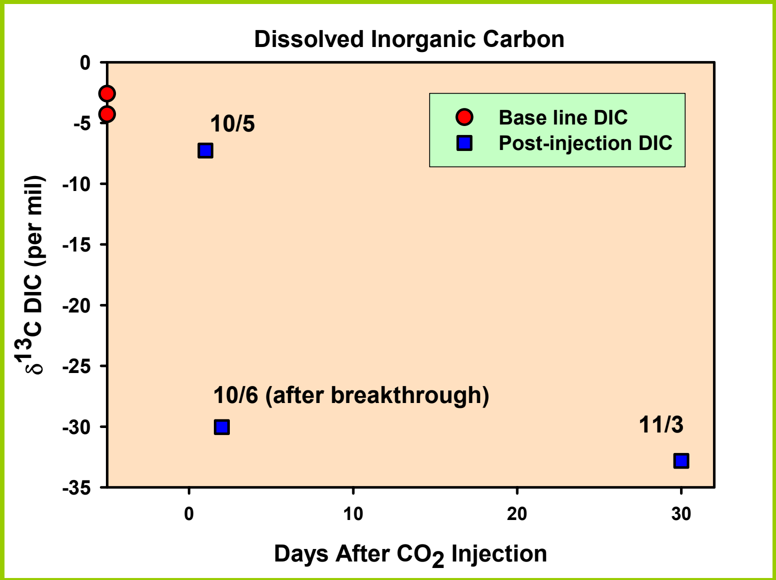
Drummond (1981); Rosenbauer et al., 2003

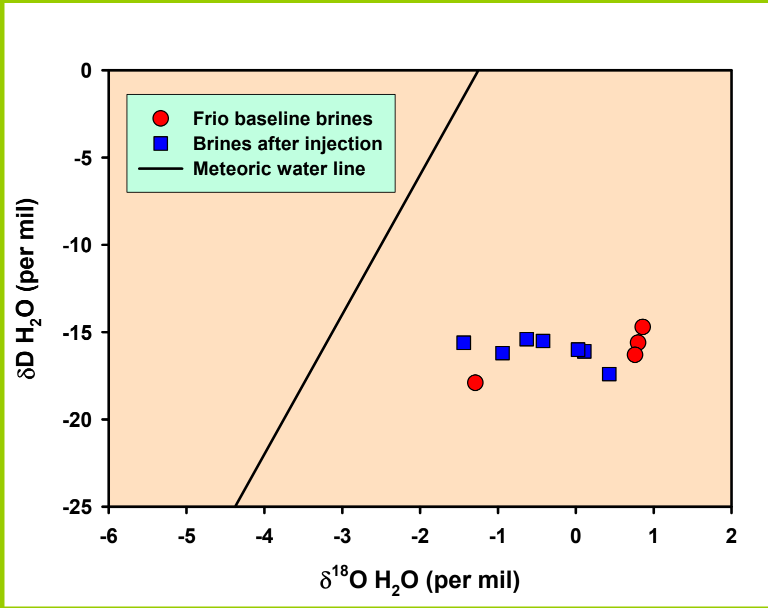




Isotope data- H_2O, CH_4 & DIC







KINETICS OF MINERAL DISSOLUTION AND PRECIPITATION

$$\frac{dm}{dt} = -SA\sum_i [A_i e^{-E_i / RT} \prod_j a_{i,j}^{n_{i,j}} f_i(\Delta \mathrm{G}_\mathrm{r})]$$

The surface area is SA (m^2), A is the Arrhenius pre-exponential factor (mol m^{-2} s^{-1}), E is the activation energy (J mol^{-1}), T is the temperature (K), R is the gas constant, $a_{i,j}$ is the activity of the j^{th} species in the i^{th} reaction mechanism, and $n_{i,j}$ is the reaction order. The term f (ΔG_r) is a dimensionless function of the chemical affinity to account for slowing of reactions as equilibrium is approached:

$$f(\Delta G_r) = (1 - \Omega^{p_i})^{q_i} = (1 - \left[\frac{Q}{K}\right]^{p_i})^{q_i}$$

Omega (Ω = Q/K) is the mineral saturation index where Q is the activity product, and K is the equilibrium constant. The parameters p_i and q_i are empirical and dimensionless, although p_i can be predicted from transition state theory.

$$\frac{dm}{dt} = SA\left[\begin{aligned} & k_{acid}^{25°C} e^{\frac{-E_{acid}}{R(T-298.15)}} a_{H^+}^{n_{1a}} a_{Fe^{3+}}^{n_{1b}} (1-\Omega^{p_1})^{q_1} + k_{neut}^{25°C} e^{\frac{-E_{neut}}{R(T-298.15)}} (1-\Omega^{p_2})^{q_2} \\ & + k_{base}^{25°C} e^{\frac{-E_{base}}{R(T-298.15)}} a_{H^+}^{n_3} (1-\Omega^{p_3})^{q_3} + k_{HCO_3^-}^{25°C} e^{\frac{-E_{base}}{R(T-298.15)}} a_{HCO_3^-}^{n_4} (1-\Omega^{p_4})^{q_4} \end{aligned}\right]$$

Important Mineral-Water-Gas Interactions in Frio

$CO_{2\,(gas)} + H_2O \Leftrightarrow H_2CO_3^o$ ------ (1)

$H_2CO_3^o \Leftrightarrow HCO_3^- + H^+$ ------ (2)

$CO_{2\,(gas)} + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^-$ ------ (3)

$H^+ + CaCO_3 \Leftrightarrow Ca^{++} + HCO_3^-$ ------ (4)

$H^+ + FeCO_3 \Leftrightarrow Fe^{++} + HCO_3^-$ ------ (5)

$4Fe^{++} + O_2 + 10H_2O \Leftrightarrow 4Fe(OH)_3 + 8H^+$ ------ (6)

$2H^+ + CaMg(CO_3)_2 \Leftrightarrow Ca^{++} + Mg^{++} + 2HCO_3^-$ ------ (7)

$4.8H^+ + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 3.2H_2O \Leftrightarrow$

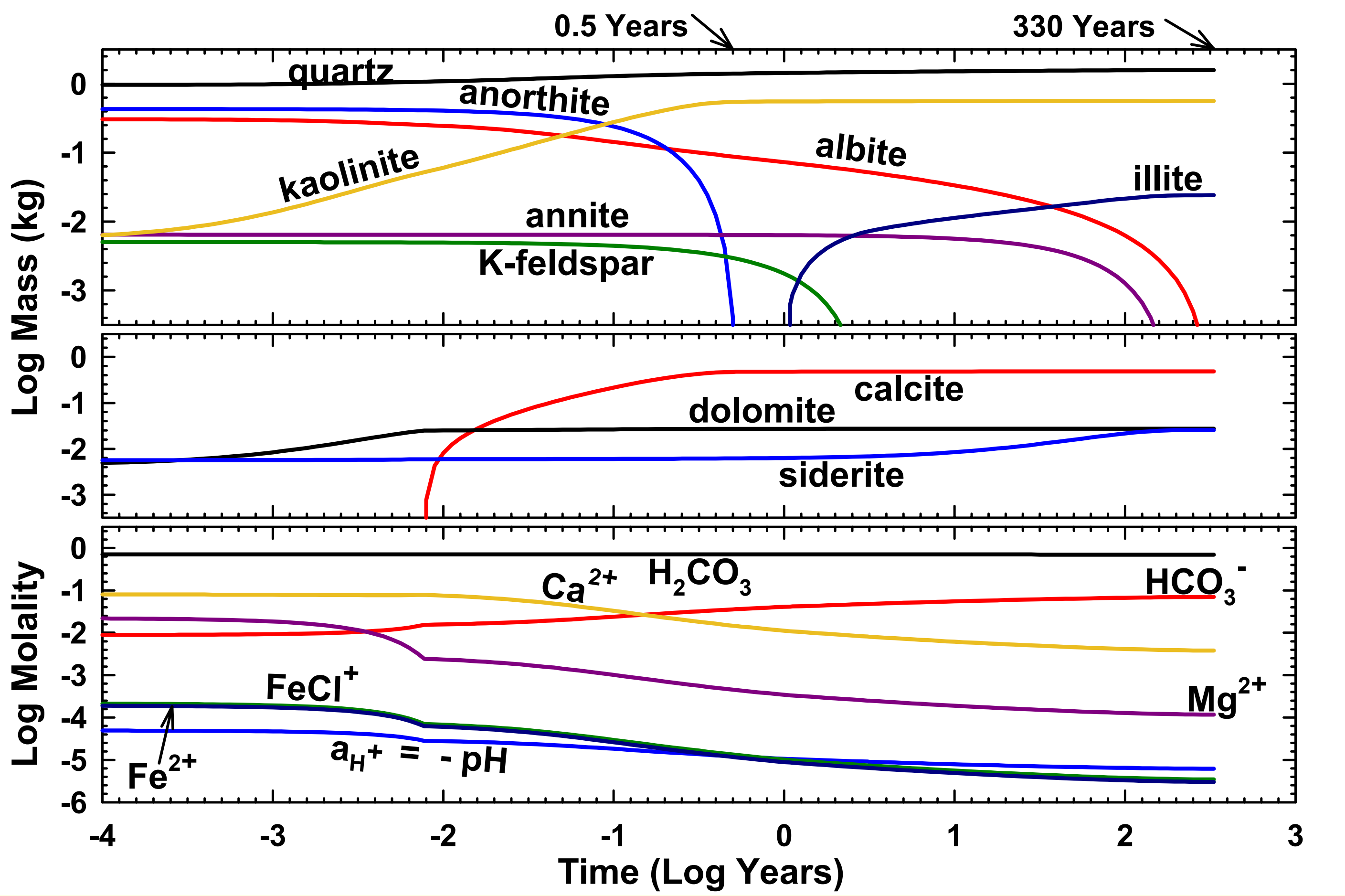
$.2Ca^{++} + .8Na^+ + 1.2Al^{+++} + 2.8H_4SiO_4$ ------ (8)

CO_2 Sequestration: Theoretical studies

(Palandri, Kharaka, 2004)

Compilation of a database of rate parameters for mineral dissolution and precipitation for use in geochemical modeling: Prediction of rates of water/ rock/gas interaction

Example simulation: CO_2 sequestration in Ca-bearing arkose



Summary and Conclusions

1- The Frio brine is saturated with CH_4 has a salinity of ~93,000 mg/L TDS, and is a Na-Ca-Cl type water; composition of formation water that determines CO_2 interactions in sedimentary basins is highly variable—TDS=2,000-460,000 mg/L.

2- Though useful parameters may be obtained from electrical logs and the National Geochemical Database, careful sampling & analysis of brine samples are necessary to study interactions.

3- Alkalinity and pH determinations are excellent and rapid field methods for tracking injected CO_2.

4- The low pH values resulting from CO_2 injection could have important environmental implications:

a)-Dissolution of minerals, esp. iron oxyhdroxides could mobilize toxic components;

b) dissolution of minerals may create pathways for CO_2 and brine leakage.

5- Where residual oil and other organics are present, CO_2 may mobilize organic compounds; some may be toxic.

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