Sixth Annual Conference on Carbon Capture & Sequestration

Session: Evaluation of Geological Formations (1)

Mobilization of metals as a result of CO_2 injection into sedimentary basins: Results from the Frio-II Brine test, Texas, USA

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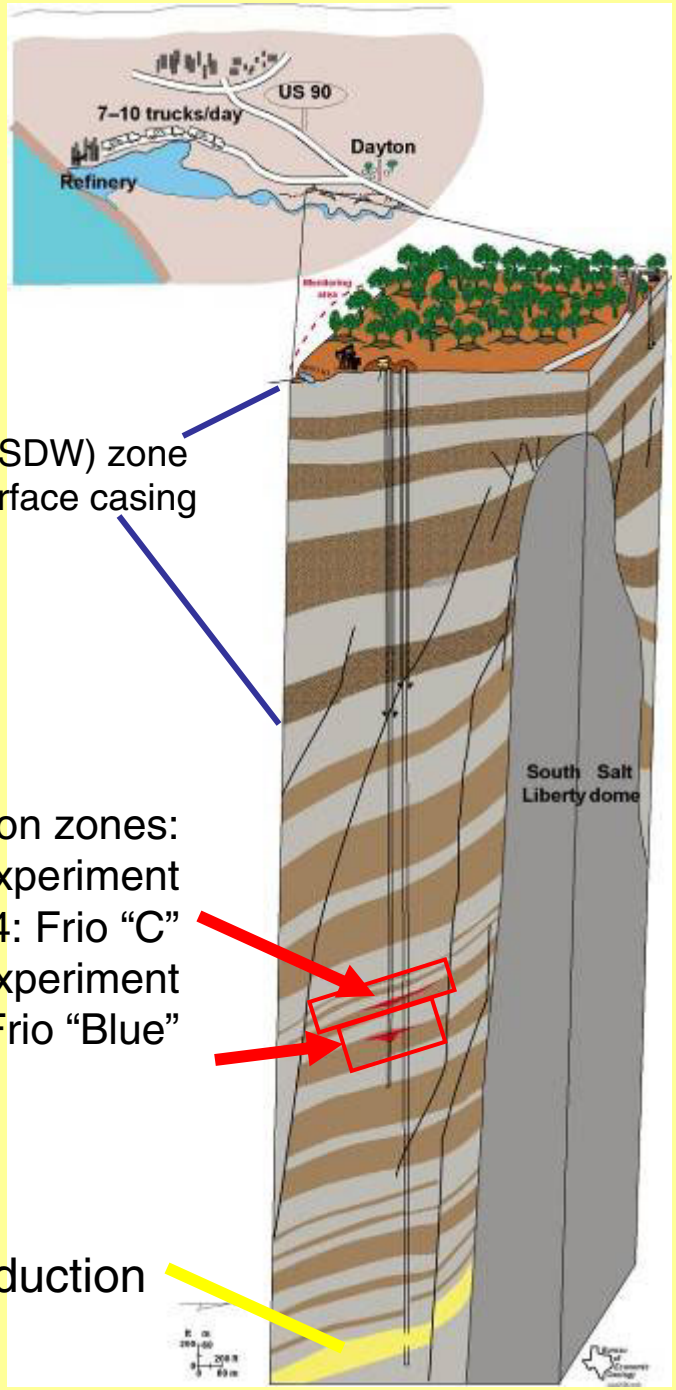

Fresh water (USDW) zone protected by surface casing

Injection zones:
First experiment 2004: Frio "C"
Second experiment 2006 Frio "Blue"

Oil production

Frio Brine Pilot Site

- Injection intervals: Oligocene fluvial and reworked sandstones, porosity 34-24%, permeability 4.4-2.5 Darcys
- Steeply dipping 11 to 16°
- Seals – several thick shales
- Depth 1,500 and 1,657 m
- Brine-rock system, no hydrocarbons
- 150 and 165 bar, 53 -60°C, supercritical CO_2

Hovorka, 2007

Topics Discussed

- Composition of water and gases in Frio "Blue" sand vs "C" & "B". Baseline, during and post injection results.
- Water-mineral-CO_2 interactions in the Frio.
- **Mobilization of Fe and other metals.**
- **Environmental implications of post-injection results.**
- Frio II future plans and concluding remarks.

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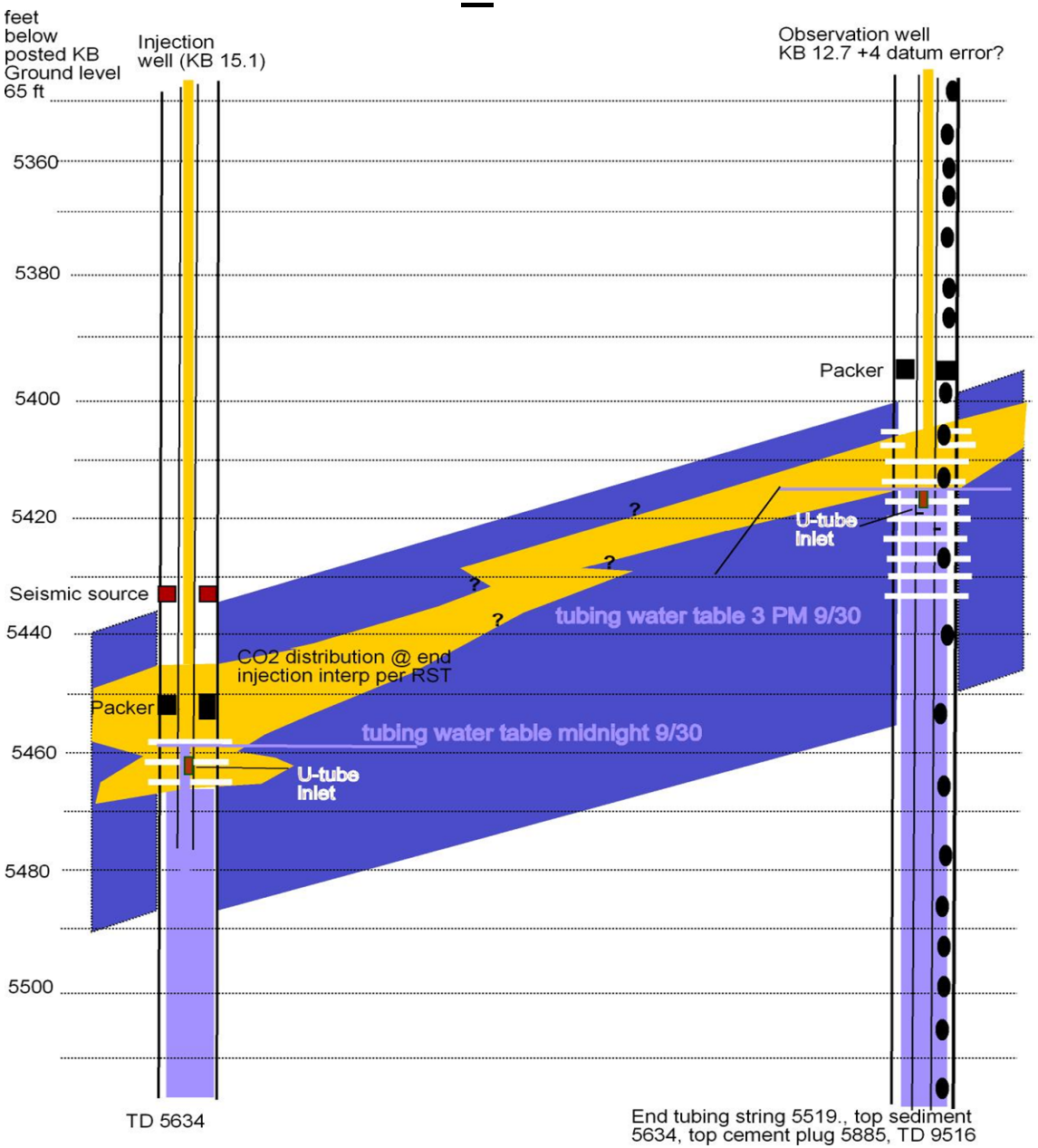
Inferred CO_2 distribution in Blue sandstone



Approximate well completion and sketch of inferred CO_2 distribution at end injection, based on RST log response and compatible with well production performance

Inferred CO2 distribution

Blue sandstone

Water-filled wells

Receivers

Hovorka, 2006

Frio II CO_2 Field sampling

Drilling & test water tagged with dye tracers

Sampling date	Sampling site	Sampling tool
Sep 6-12, 2006	injection & observation wells	surface sampling (N_2), Kuster
Sep 25-Oct 2, 2006	observation & injection wells	U-tube
Oct 9-10, 2006	observation & injection well	U-tube and Kuster
March 20, 2007	observation well	U-tube

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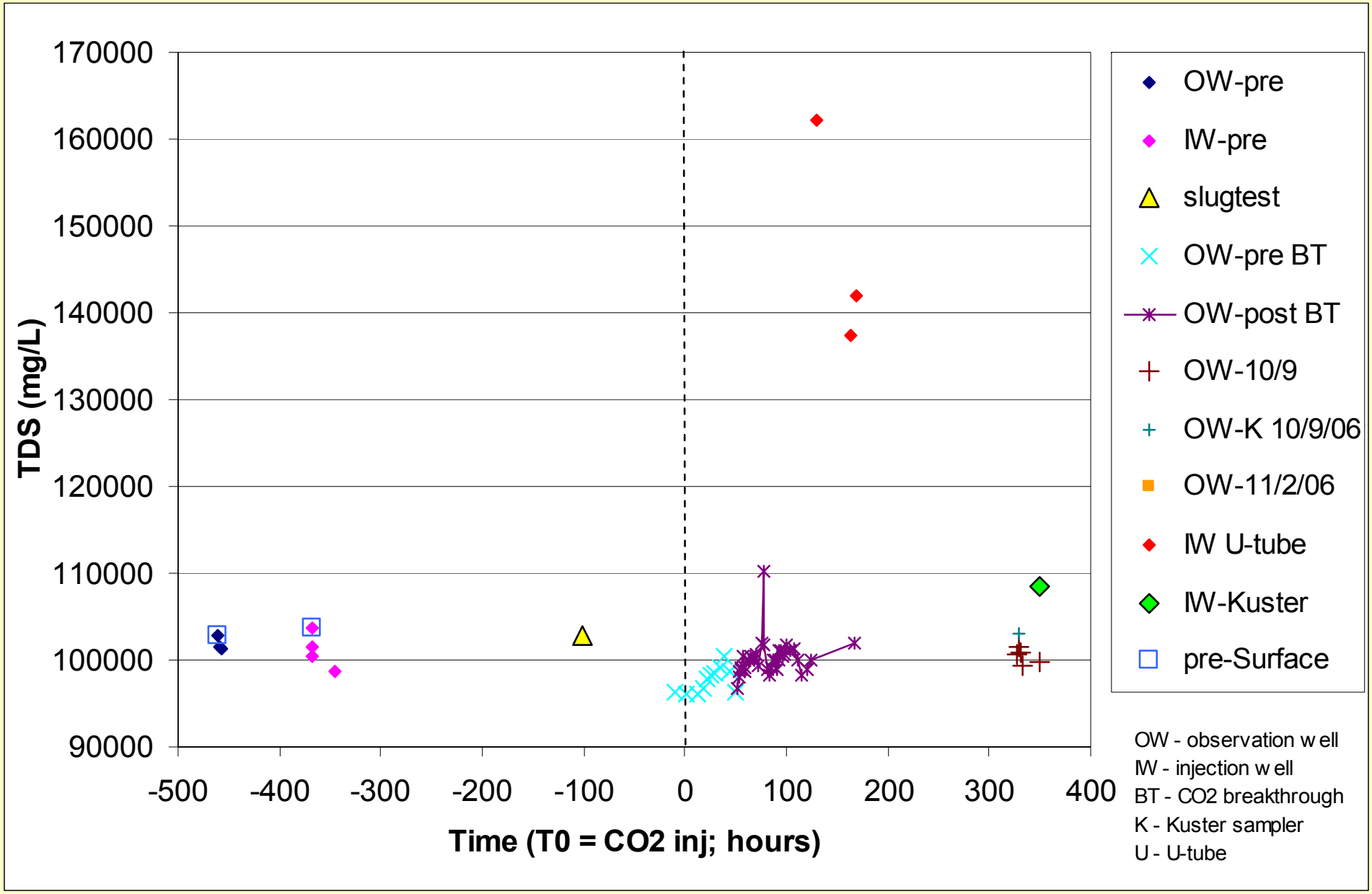
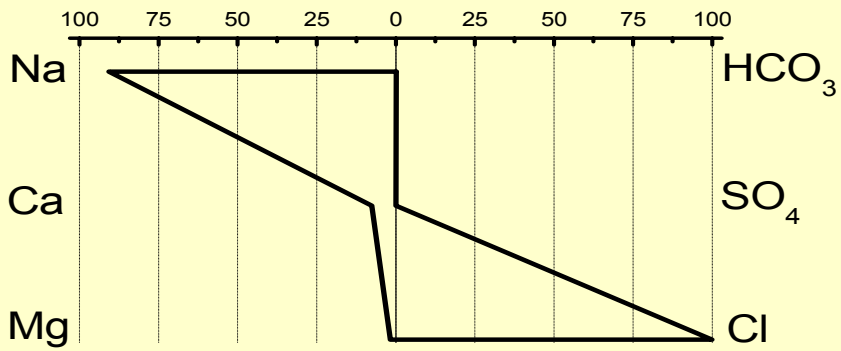
Salinity of brine from Frio II



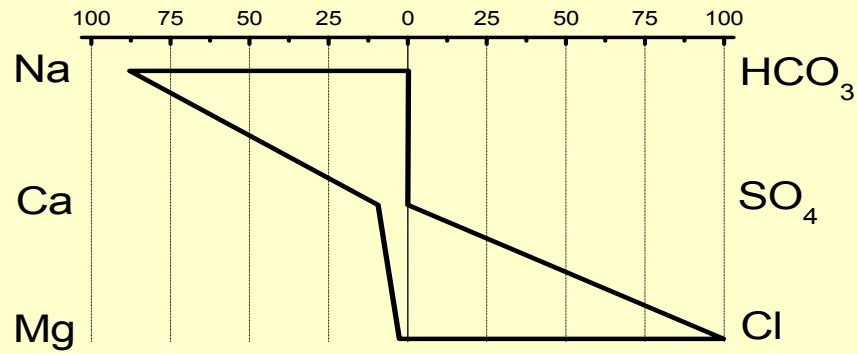
Normalized concentrations of Major cations and anions in Frio brines

Frio II "blue" sand [06FCO2-212]
(observation well; pre-injection)



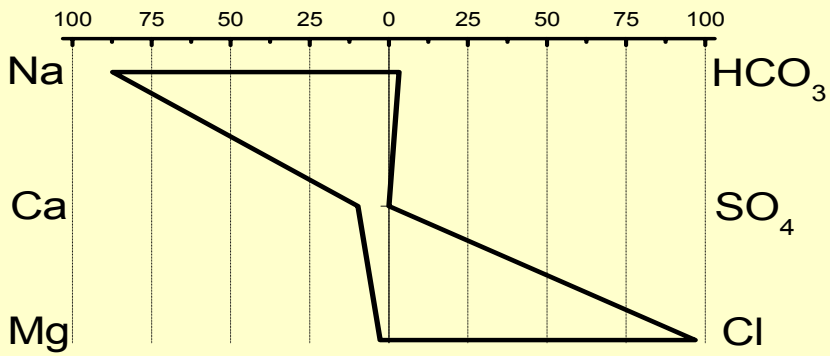
pH = 6.7; TDS = 101,600 mg/L

Frio I "C" sand [04FCO2-218]
(observation well, pre-injection)



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

Frio I "C" sand [04FCO2-337]
(observation well; post injection)

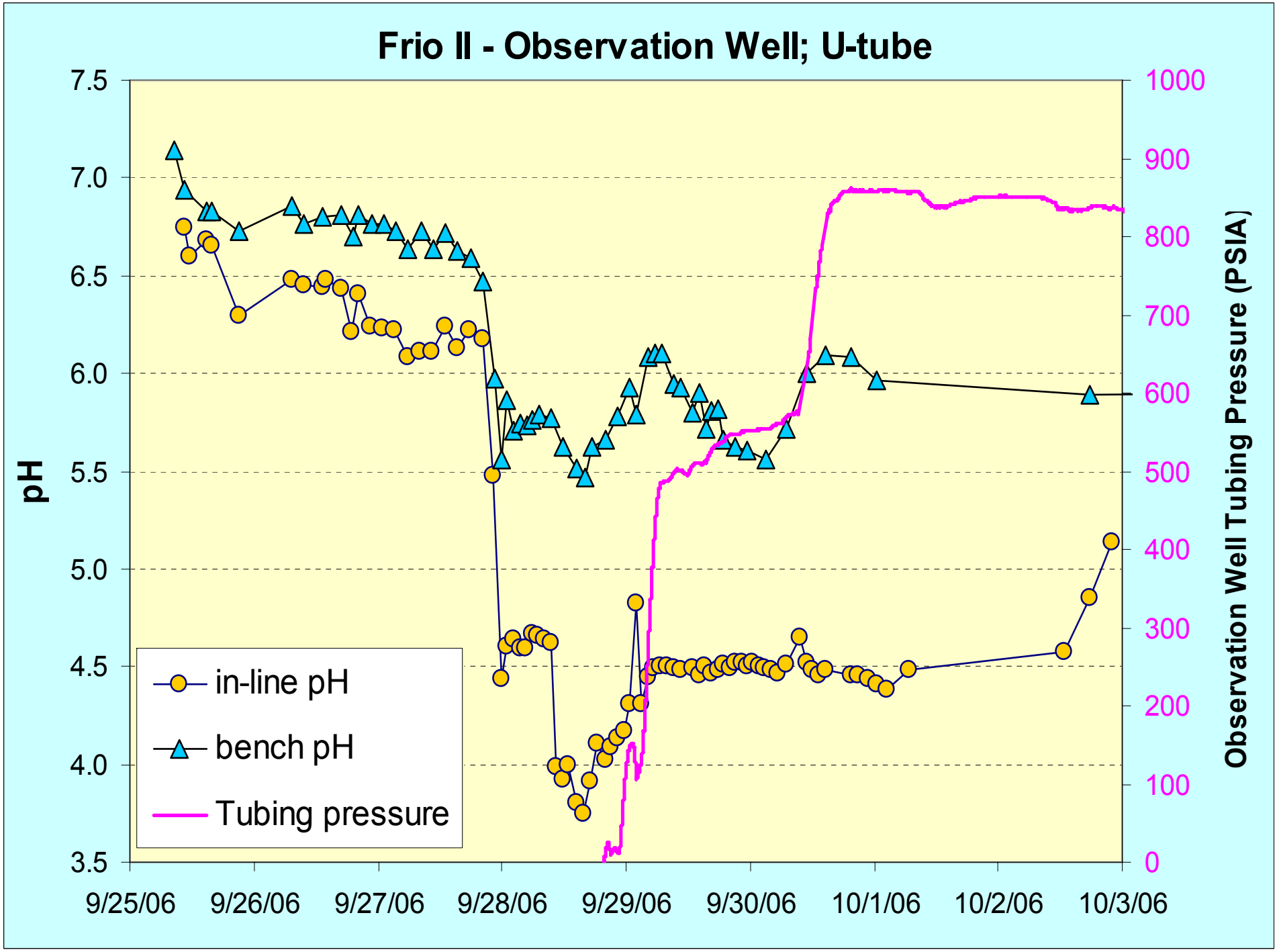


pH = 6.03; TDS = 92,600 mg/L

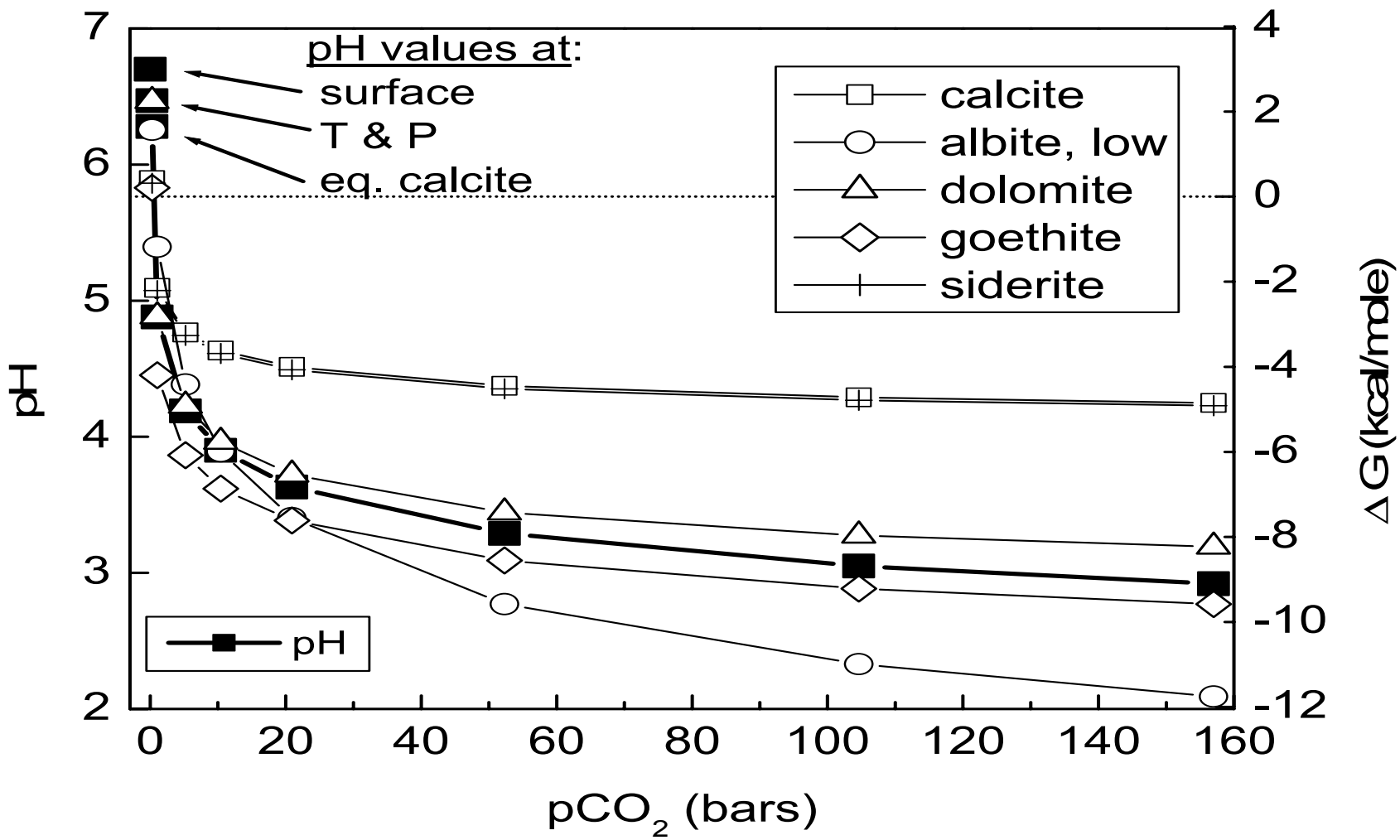
Frio "B" sand [05FCO2-110]
(observation well)

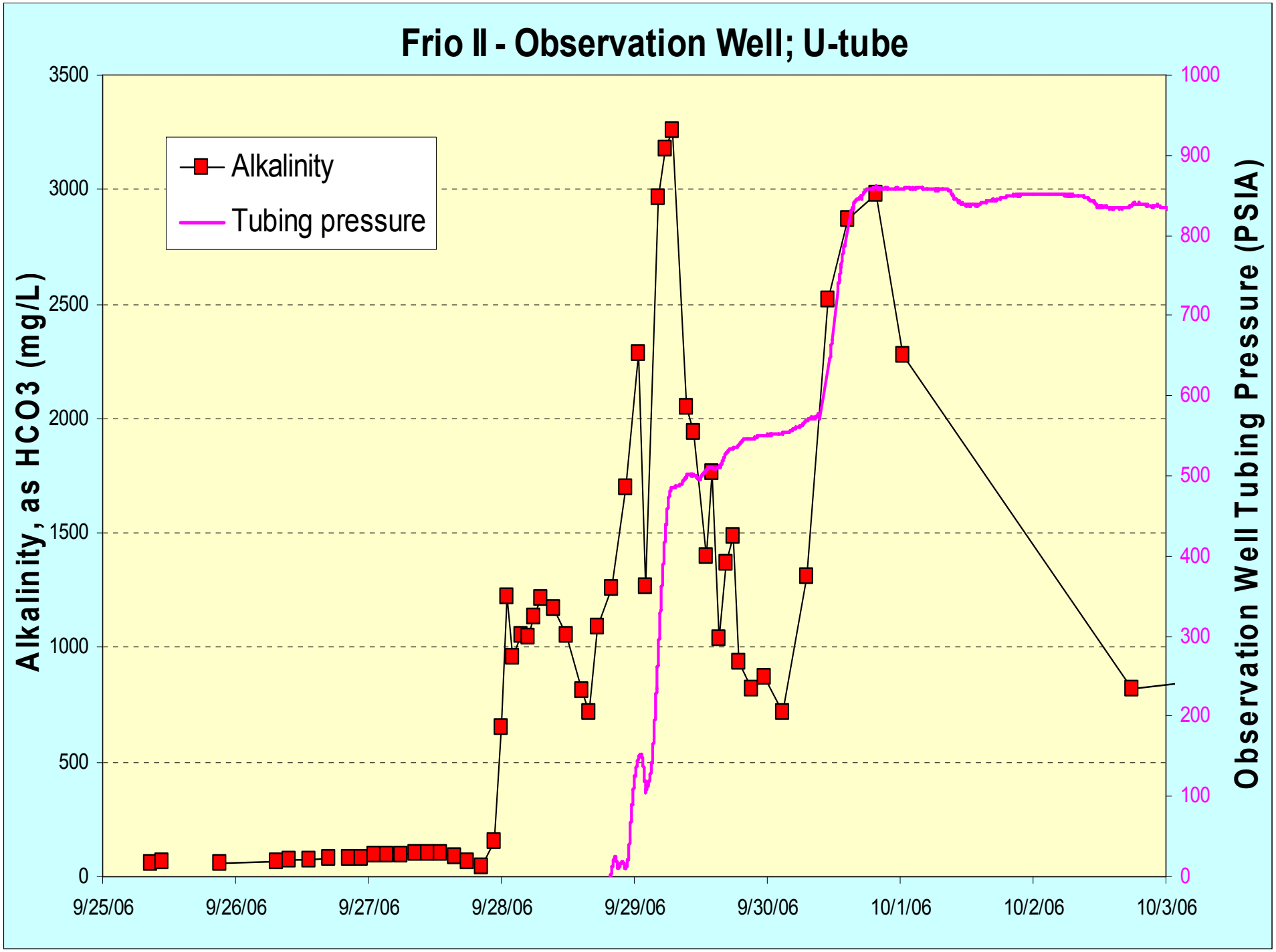
pH = 6.6; TDS = 92,200 mg/L

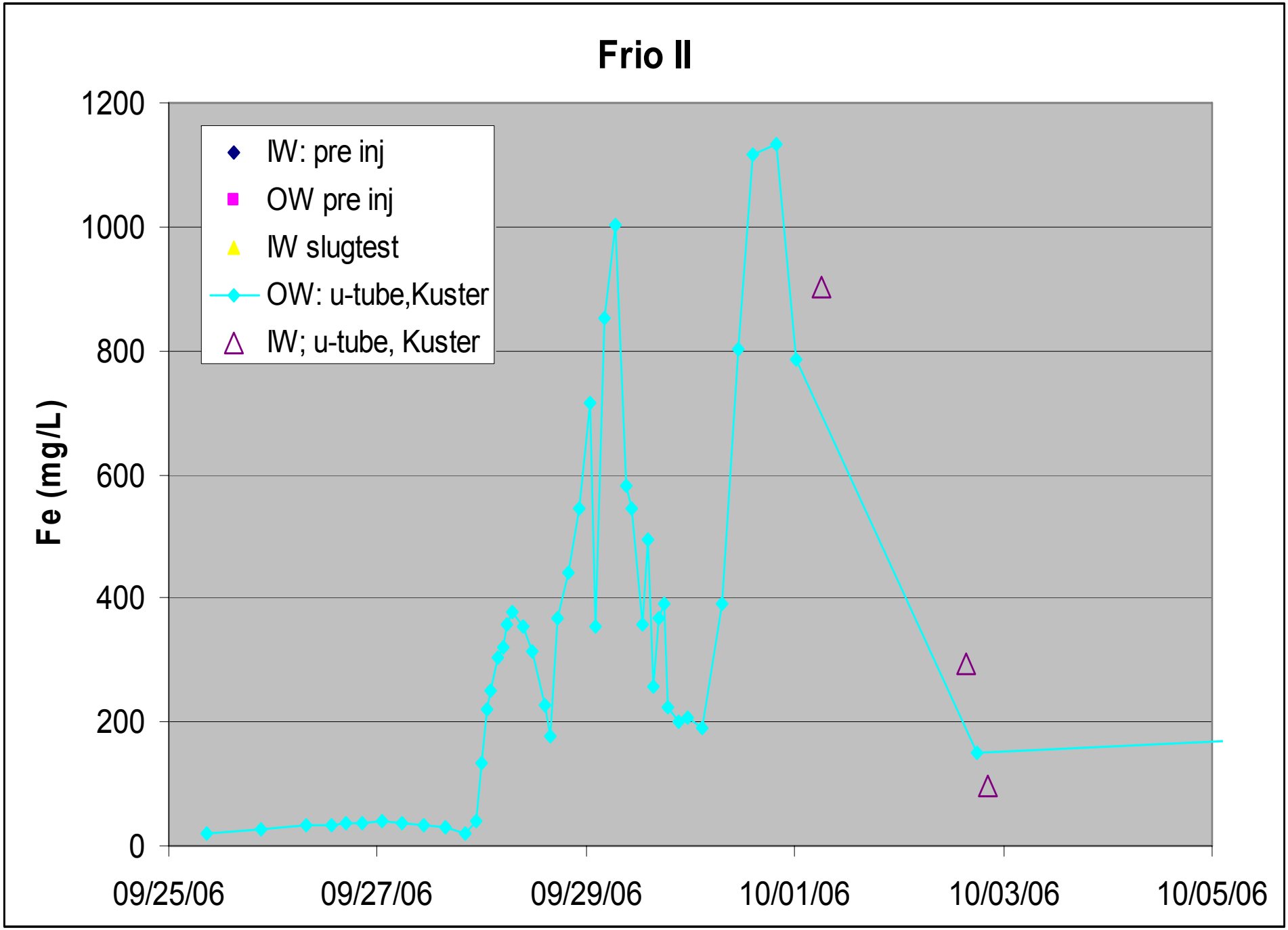
[milliequivalents/liter, normalized to 100%]


Frio II - Observation Well; U-tube
pH
Observation Well Tubing Pressure (PSIA)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
1000
900
800
700
600
500
400
300
200
100
0
9/25/06
9/26/06
9/27/06
9/28/06
9/29/06
9/30/06
10/1/06
10/2/06
10/3/06
in-line pH
bench pH
Tubing pressure

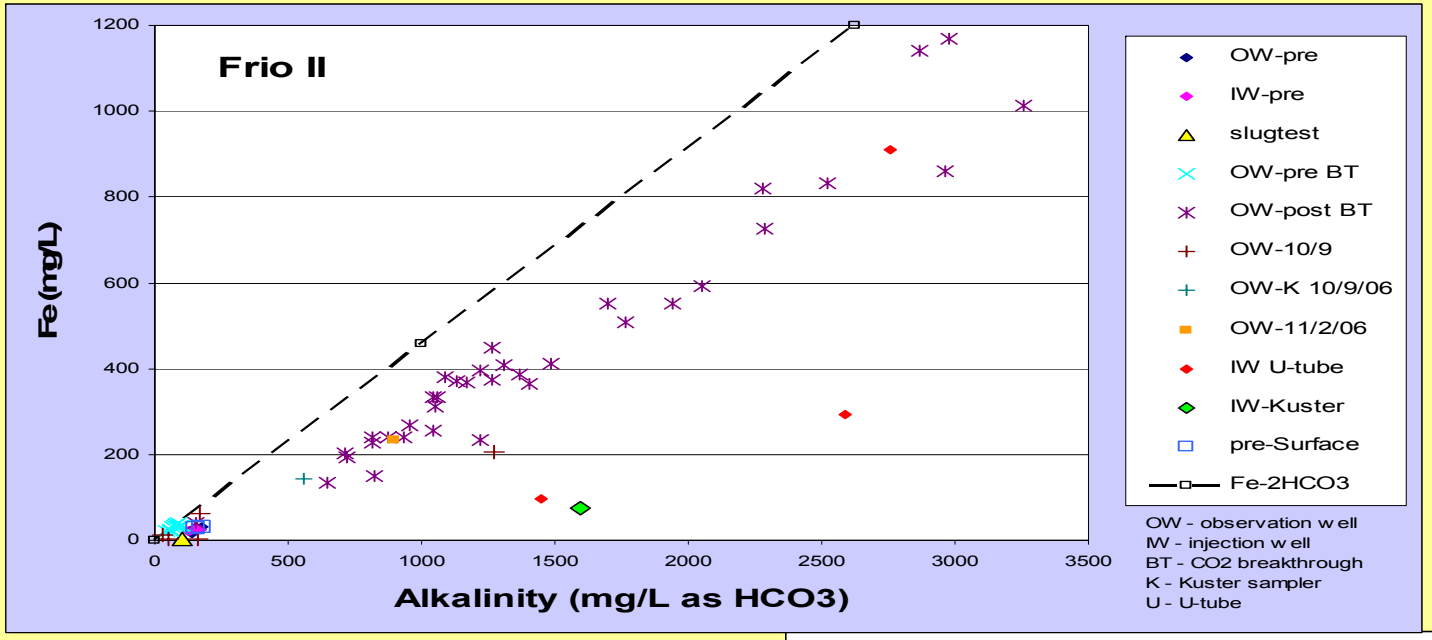
Computed pH and saturated states of selected minerals at T & P

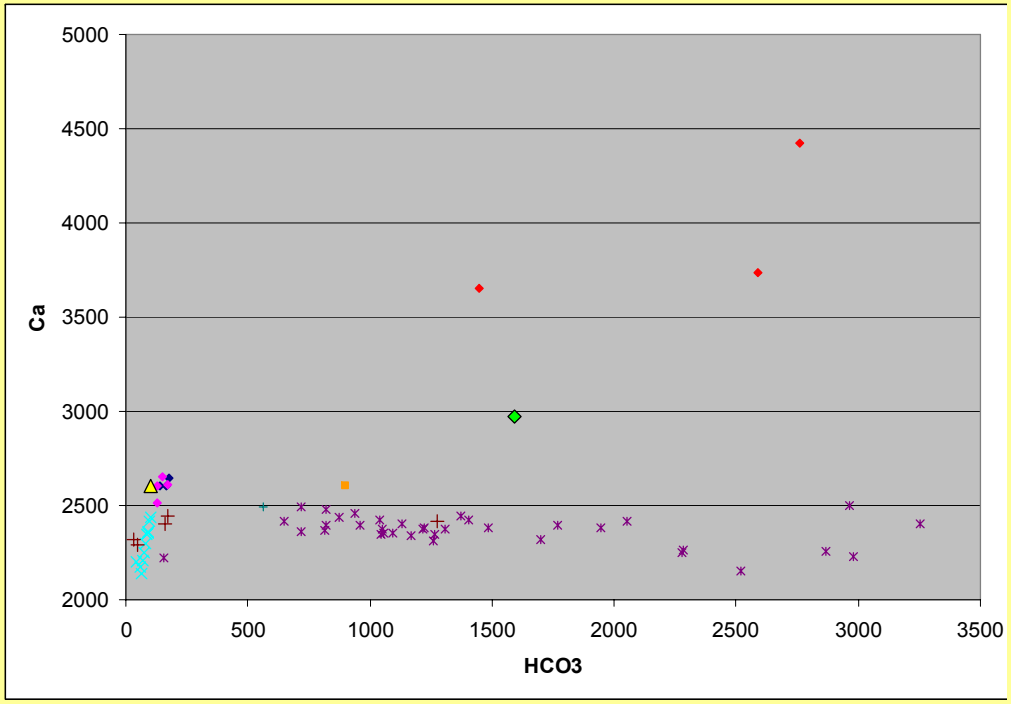


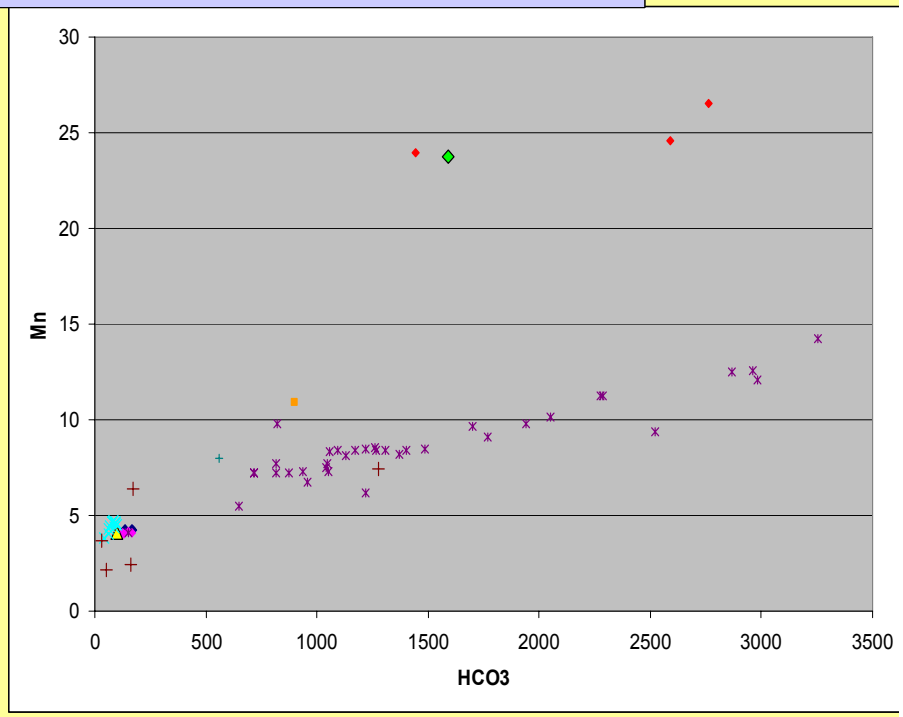

Frio II - Observation Well; U-tube
Alkalinity
Tubing pressure
Alkalinity, as HCO3 (mg/L)
Observation Well Tubing Pressure (PSIA)
3500
3000
2500
2000
1500
1000
500
0
1000
900
800
700
600
500
400
300
200
100
0
9/25/06
9/26/06
9/27/06
9/28/06
9/29/06
9/30/06
10/1/06
10/2/06
10/3/06


Frio II
Fe (mg/L)
1200
1000
800
600
400
200
0
09/25/06
09/27/06
09/29/06
10/01/06
10/03/06
10/05/06
IW: pre inj
OW pre inj
IW slugtest
OW: u-tube,Kuster
IW; u-tube, Kuster

Concentration of Fe and HCO3 in Frio II brines







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)

$4Fe(OH)_3 + 8H_2CO_3 \Leftrightarrow 4Fe^{++} + 8HCO_3^- + 10H_2O + O_2$ ------ (6)

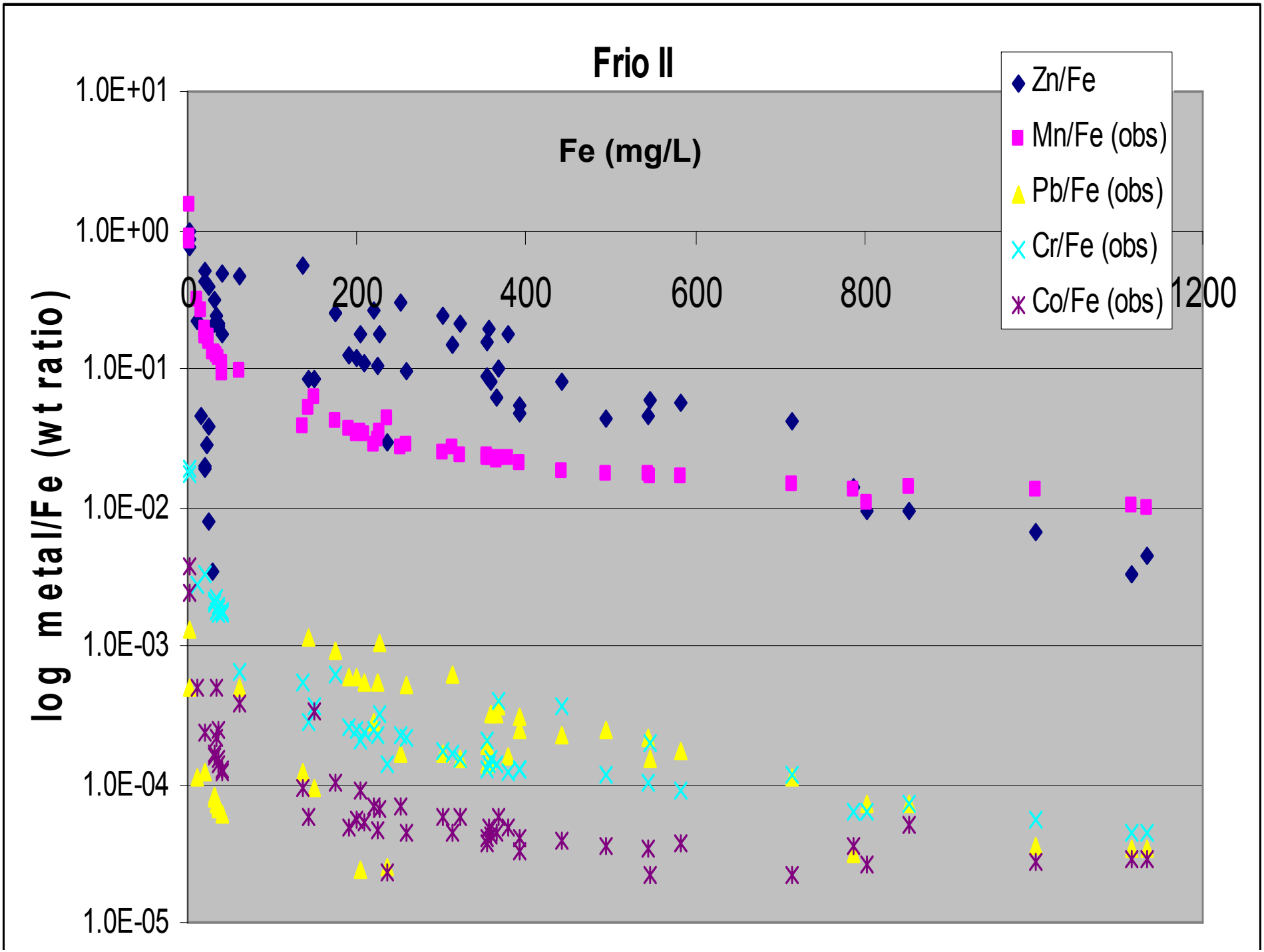
$2Fe(OH)_3 + 4H_2CO_3 + H_2 \Leftrightarrow 2Fe^{++} + 4HCO_3^- + 6H_2O$ ------ (7)

$Fe^o + 2H_2CO_3 \Leftrightarrow Fe^{++} + 2HCO_3^- + H_2$ ------ (8)

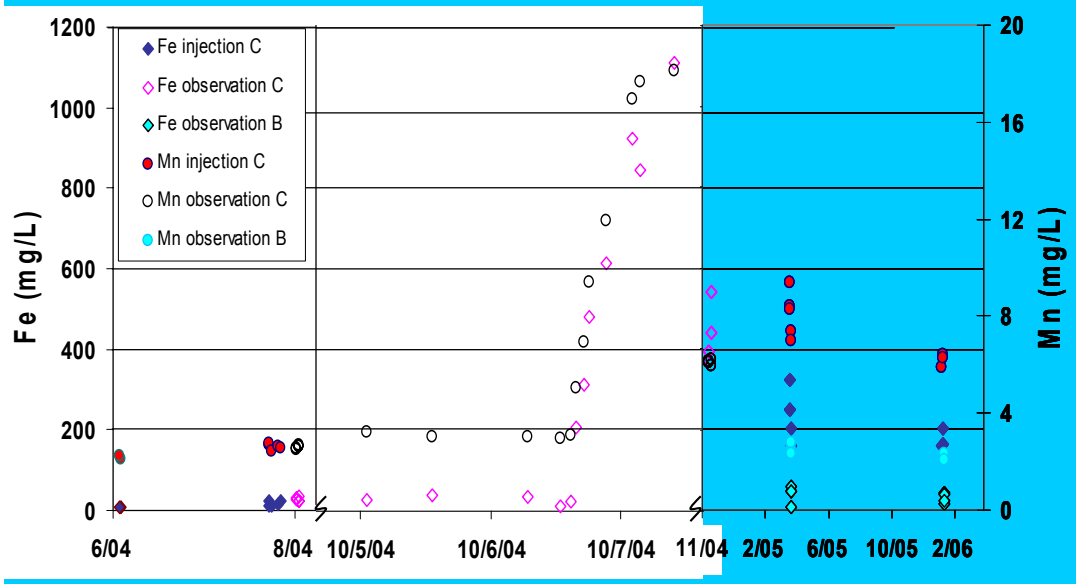
$2H^+ + CaMg(CO_3)_2 \Leftrightarrow Ca^{++} + Mg^{++} + 2HCO_3^-$ ------ (9)

$0.4H^+ + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 0.8CO_2 + 1.2H_2O \Leftrightarrow$

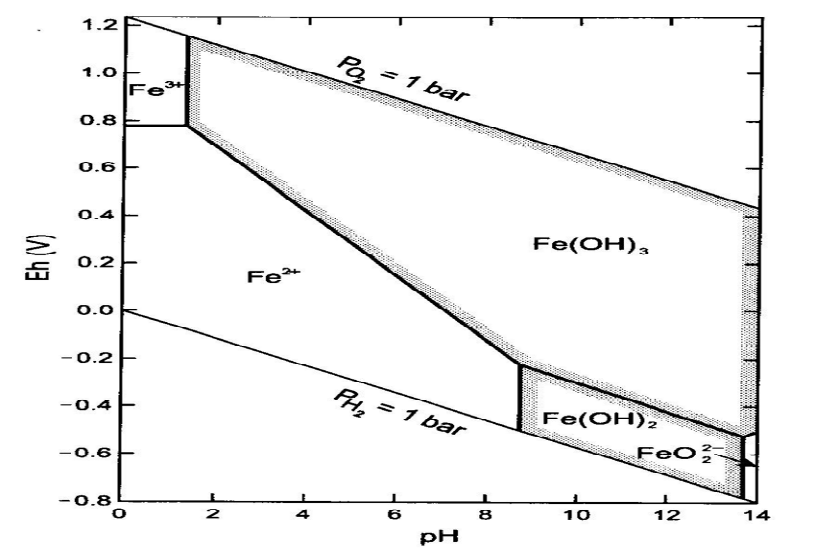
$.2Ca^{++} + .8NaAlCO_3(OH)_2 + 0.4Al(OH)_3 + 2.8SiO_2$ -- (10)


Frio II
Fe (mg/L)
log metal/Fe (wt ratio)
1.0E+01
1.0E+00
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
0
200
400
600
800
1200
Zn/Fe
Mn/Fe (obs)
Pb/Fe (obs)
Cr/Fe (obs)
Co/Fe (obs)

Frio I (Fe & Mn)

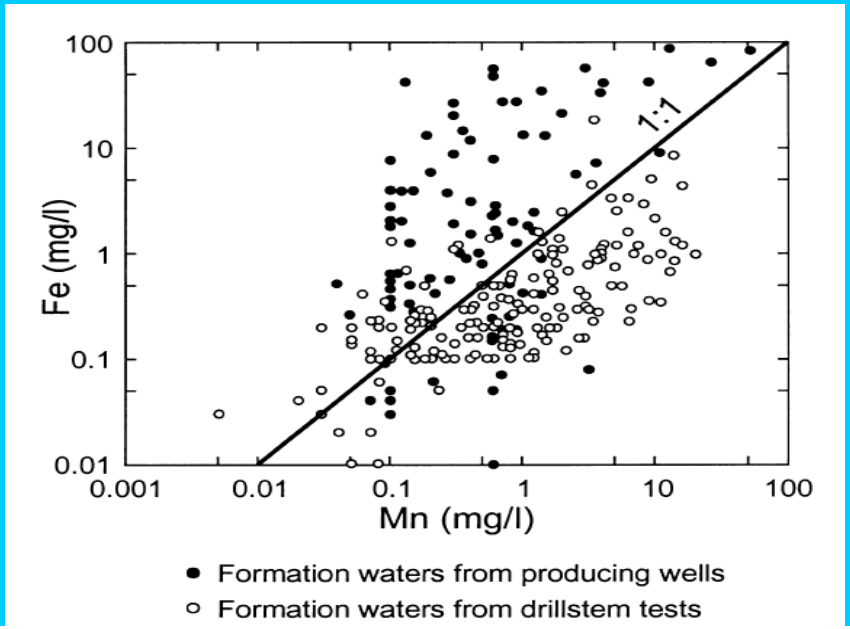


Eh-pH diagram for selected Fe species



Fe and Mn in formation waters from Alberta Basin, Canada

Hitchon, 2000



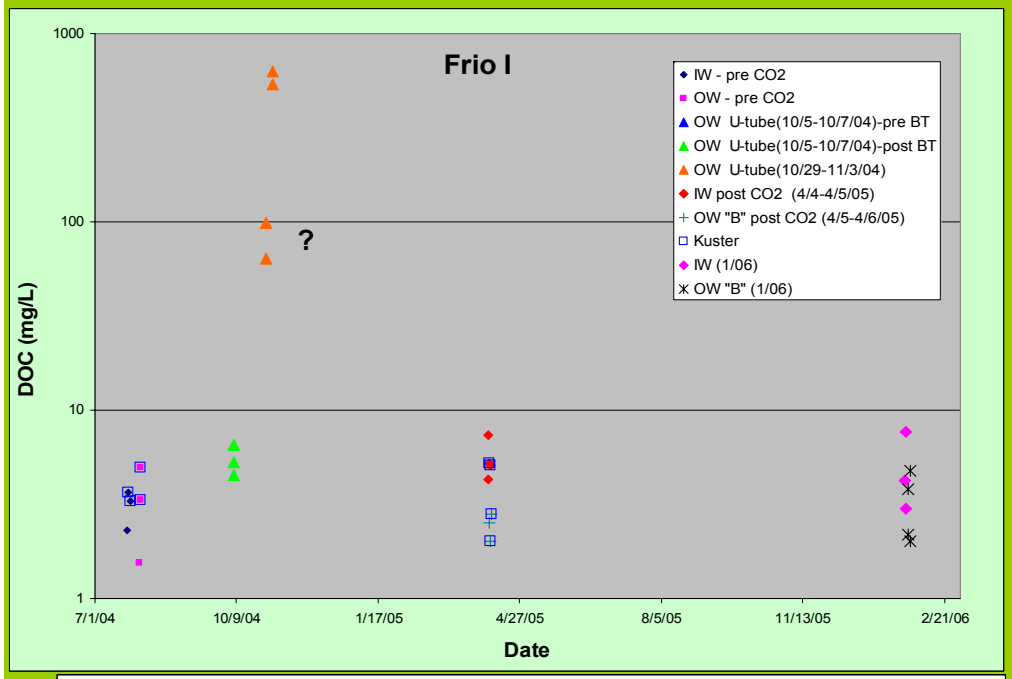
"TRACE" METALS

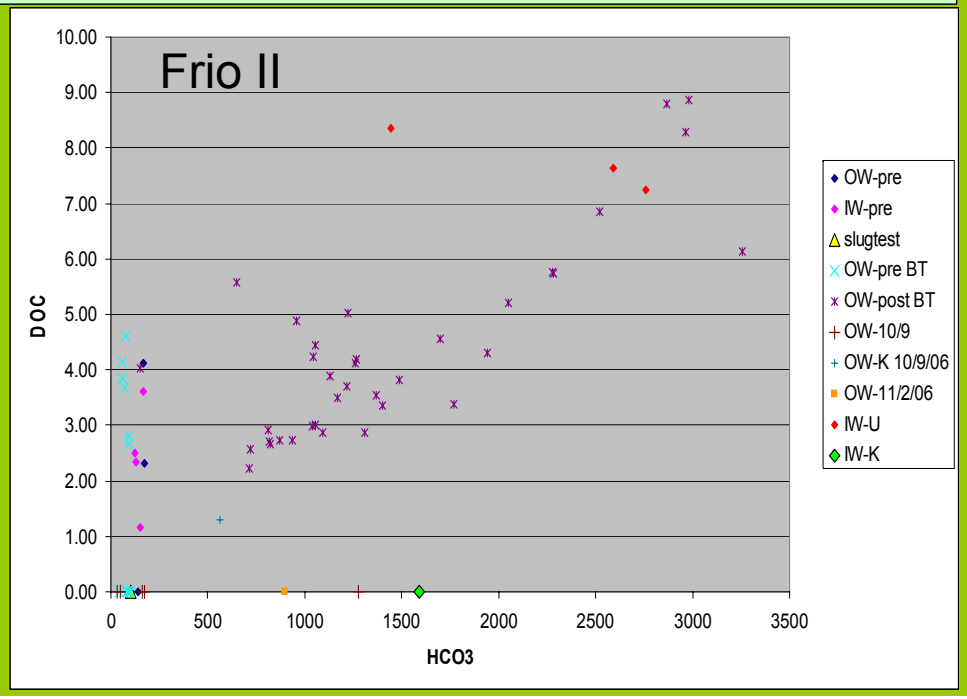
mg/L	Fe	Mn	Pb	Zn	Cd	Cu*
MS 11 Rodessa	465	212	70	243	1.0	21
MS 5 Hosston	407	70	60	243	0.8	61
MS 15 Norphlet	223	53	2.0	4.0	.02	<20
MS 3 Stanley	62	11	.04	.53	.02	<20
MS 19 Smackover	.47	1.6	.04	.06	.03	<20

* µg/L

Kharaka et al., 1987

Concentrations of DOC in Frio I brine





Organics in Oil-Field Water

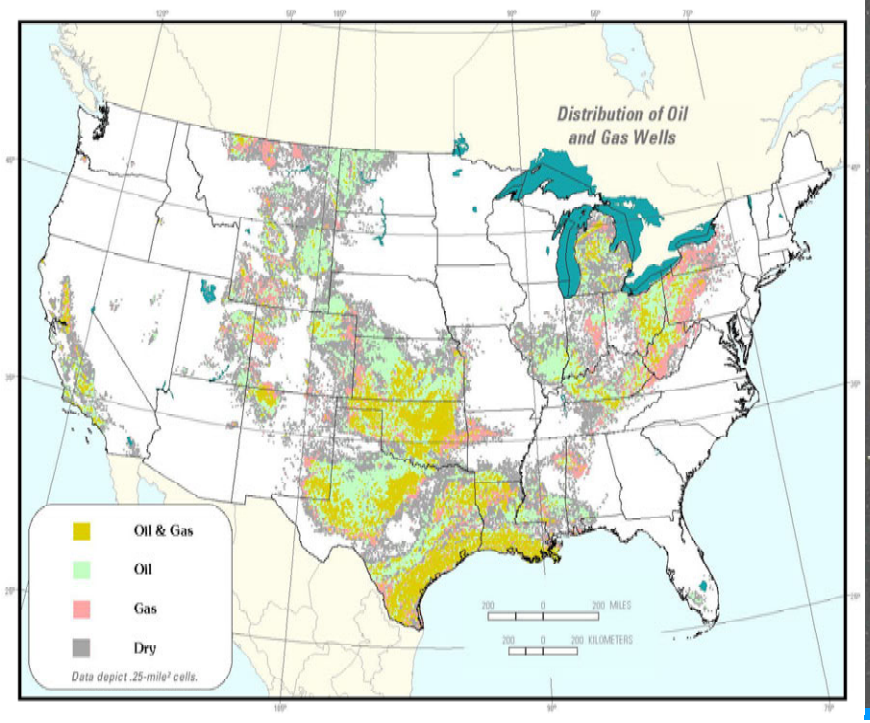
(mg/L)

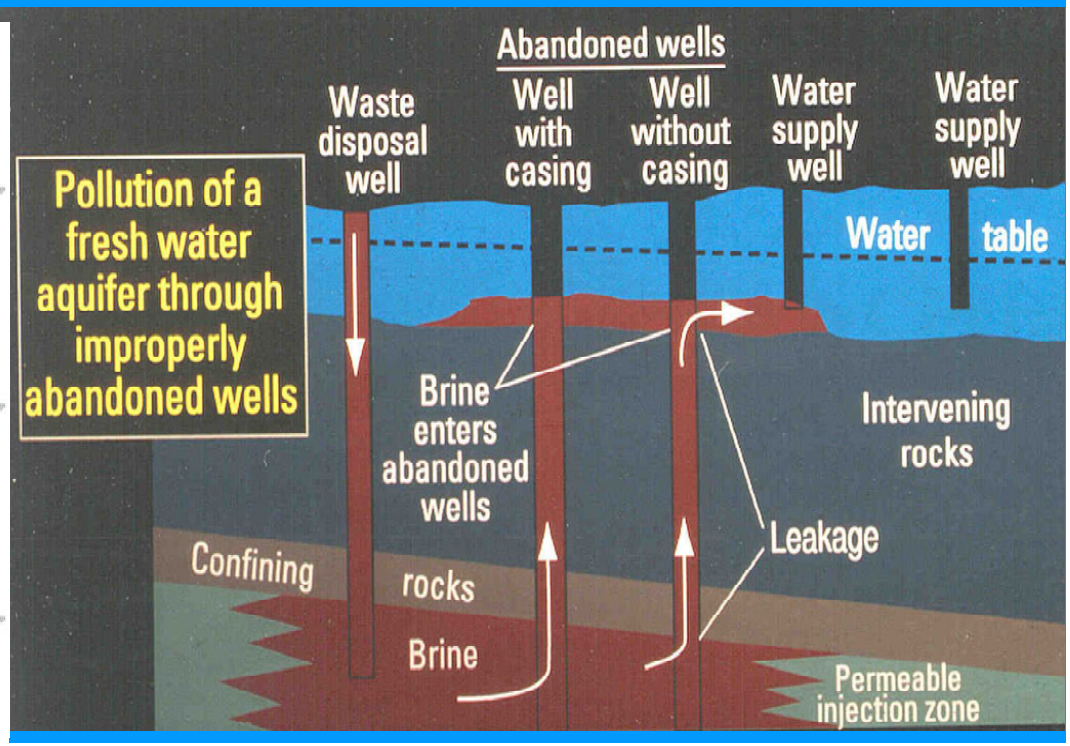
ACETATE & OTHER ACID ANIONS	10,000
BTEX	60
PAHs	10
PHENOL	20
4 – METHYL PHENOL	2
BENZOIC ACID	5
4 – METHYL BENZOIC ACID	4
2 – HYROXY BENZOIC ACID	0.2
3 – HYDROXY BENZOIC ACID	1.2

Kharaka & Hanor, 2004

Importance of Protecting Ground Water

- 50% of drinking water in USA is from GW
- 95% of rural America is dependant on GW
- GW use increased from 13×10^{10} L/day in 1950 to 33×10^{10} L/day in 2000
- Once GW is contaminated, remediation is very costly or impossible





Summary and Conclusions

1- Brine in the Frio Blue sandstone is also a Na-Ca-Cl type water and is saturated with CH_4, but has a higher salinity of 103,000 mg/L TDS.

2- Alkalinity, pH and gas-composition determinations are excellent and rapid field methods for tracking injected CO_2.

3- Low pH values approaching the computed subsurface value of ~3 were measured with in line pH probe.

4- The low pH values resulting from CO_2 injection again mobilized high Fe, other metals and organics.

5- Some metals are from dissolution of Fe-oxyhdroxide minerals; some could be from casing and pipe corrosion.

Hovorka et al., 2006, Environmental Geosciences, v. 13, p. 103-119.
Kharaka et al., 2006, Geology, v. 34, p. 577-580.

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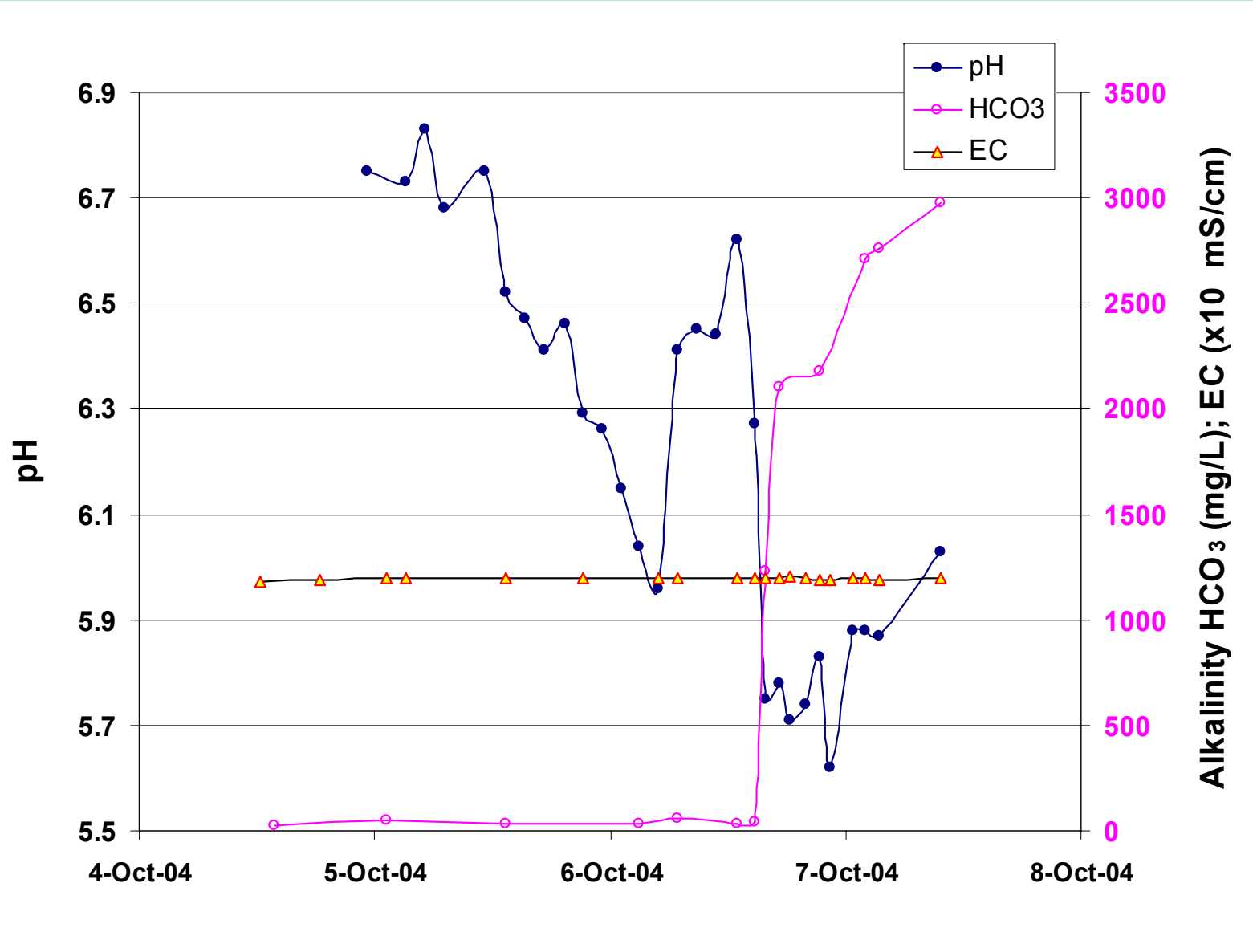
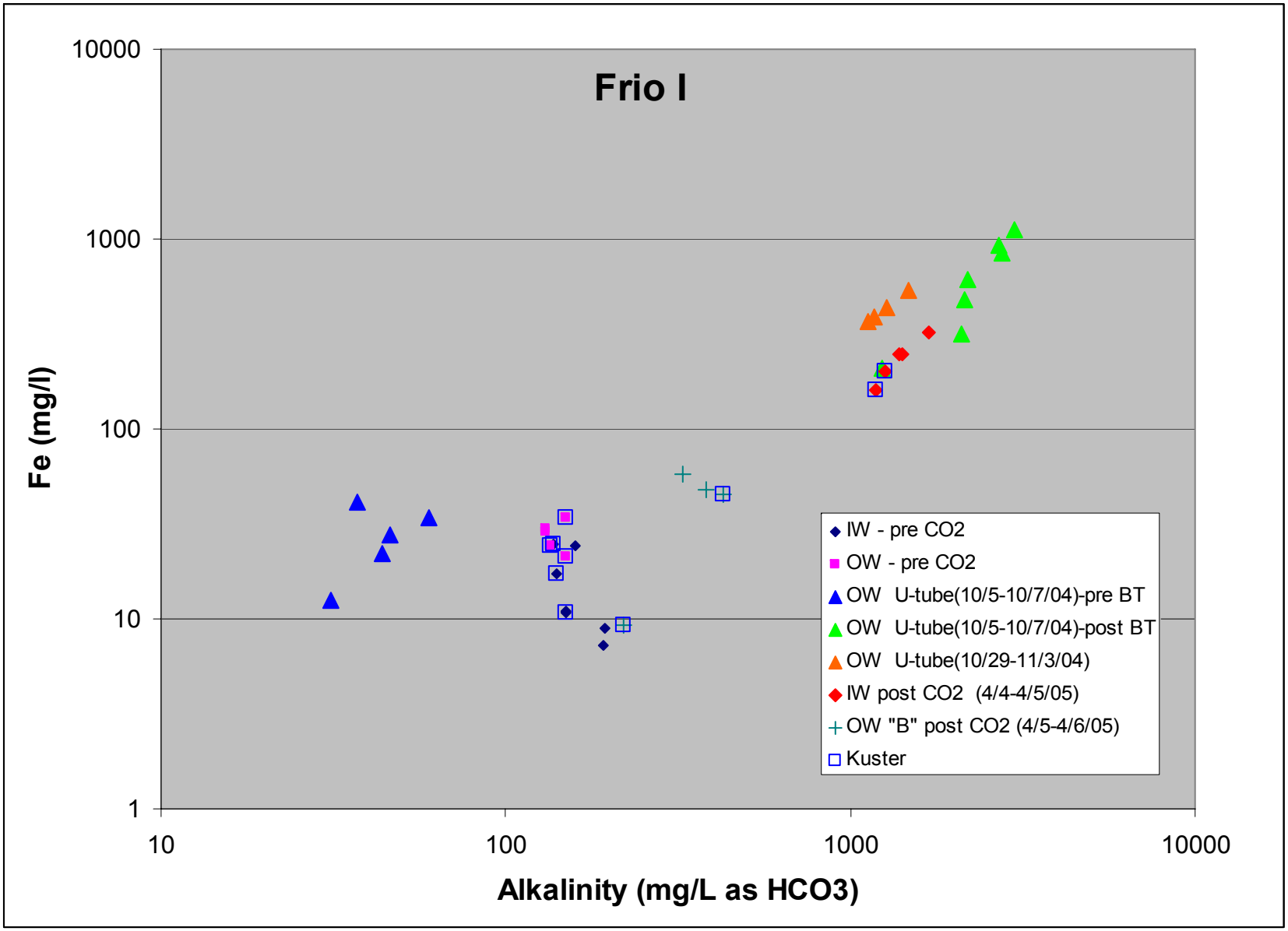
Chemical Composition (%v) of Frio Gases

Frio formation water at saturation with CH_4

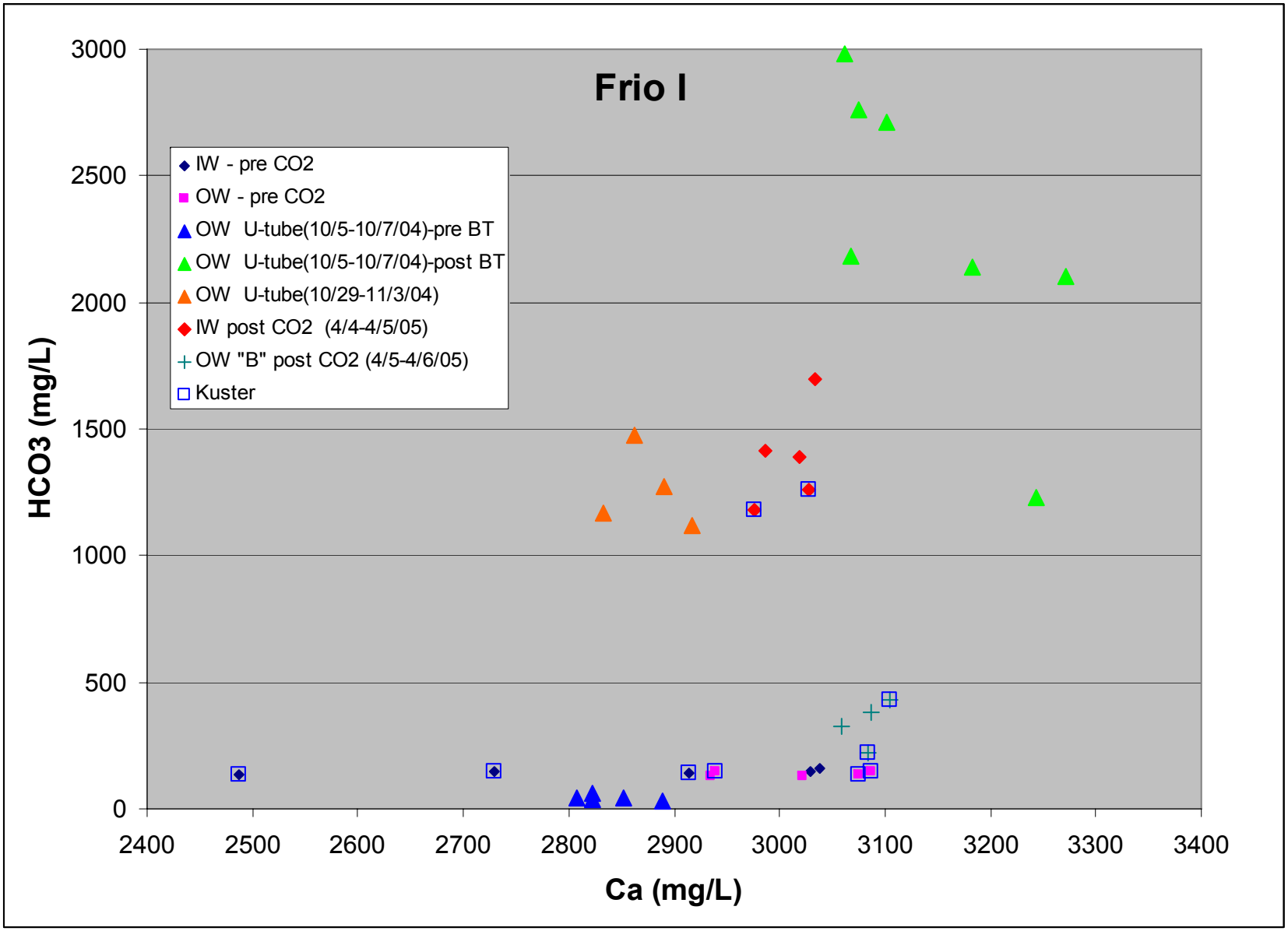
Gas	[1]"C"	[2]"C"	[3]"B"	[4]"Bls"
He	0.0077	0	0.01	0
H_2	0.040	0.19	0.92	0.3-6
Ar	0.041	0	ND	0.061
CO_2	0.31	96.8	2.86	22-96
N_2	3.87	0.037	1.51	2-53
CH_4	93.7	2.94	94.3	0.01-54
C_2H_6+	1.95	0.005	0.12	0-0.23

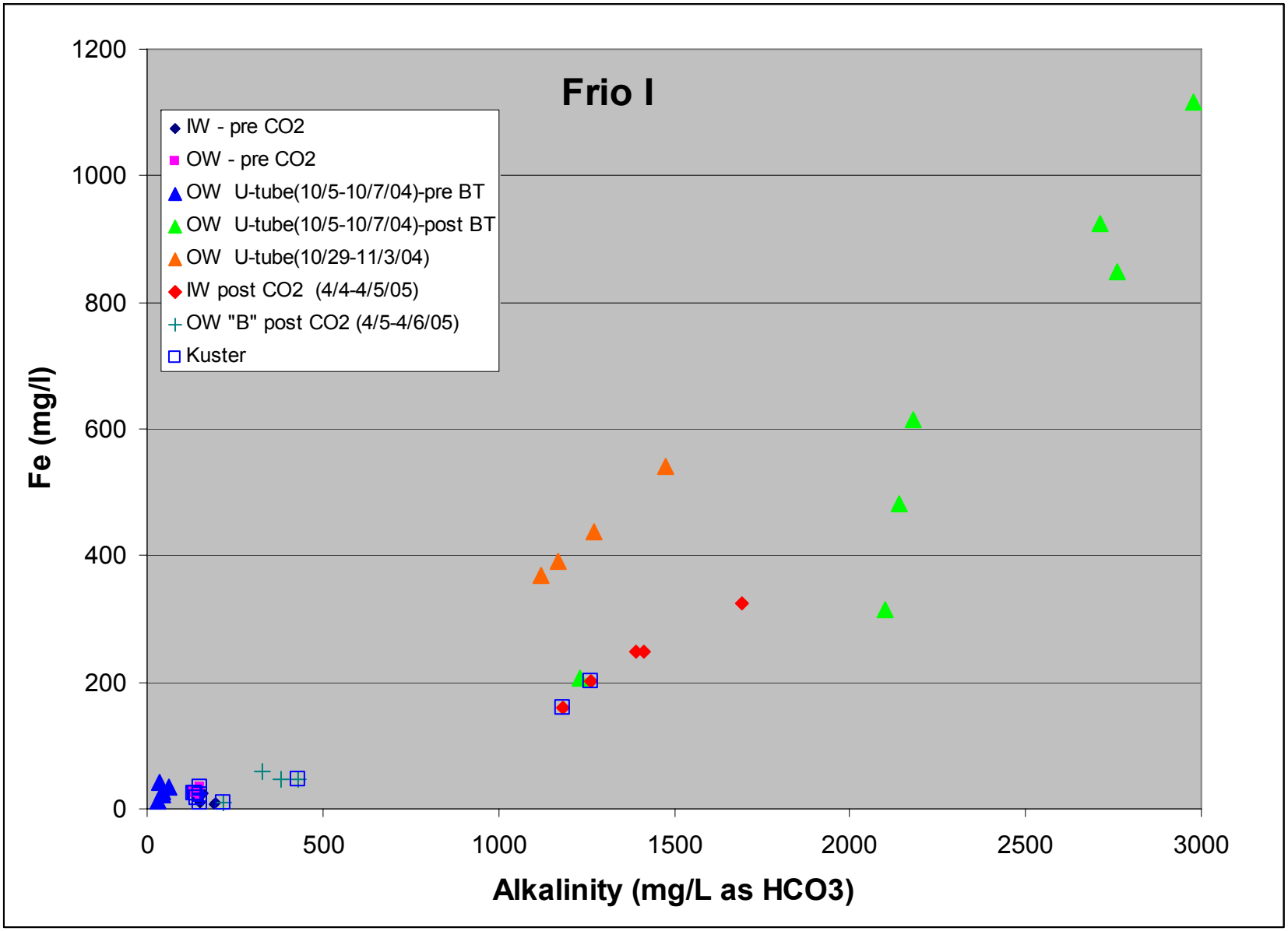
Selected chemical data from monitoring well during CO2 injection



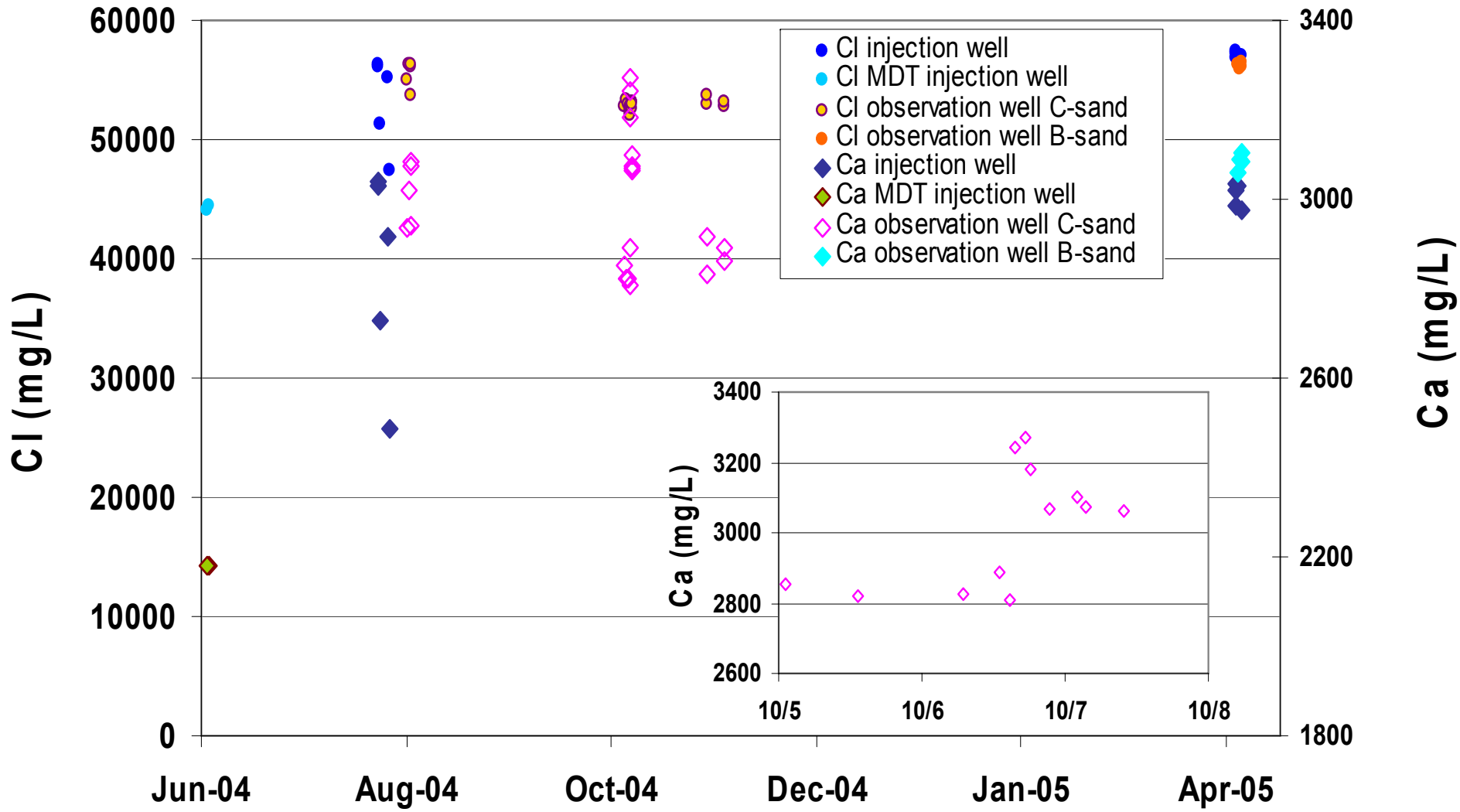

Frio I
Fe (mg/l)
10000
1000
100
10
1
10
100
1000
10000
Alkalinity (mg/L as HCO3)
IW - pre CO2
OW - pre CO2
OW U-tube(10/5-10/7/04)-pre BT
OW U-tube(10/5-10/7/04)-post BT
OW U-tube(10/29-11/3/04)
IW post CO2 (4/4-4/5/05)
OW "B" post CO2 (4/5-4/6/05)
Kuster

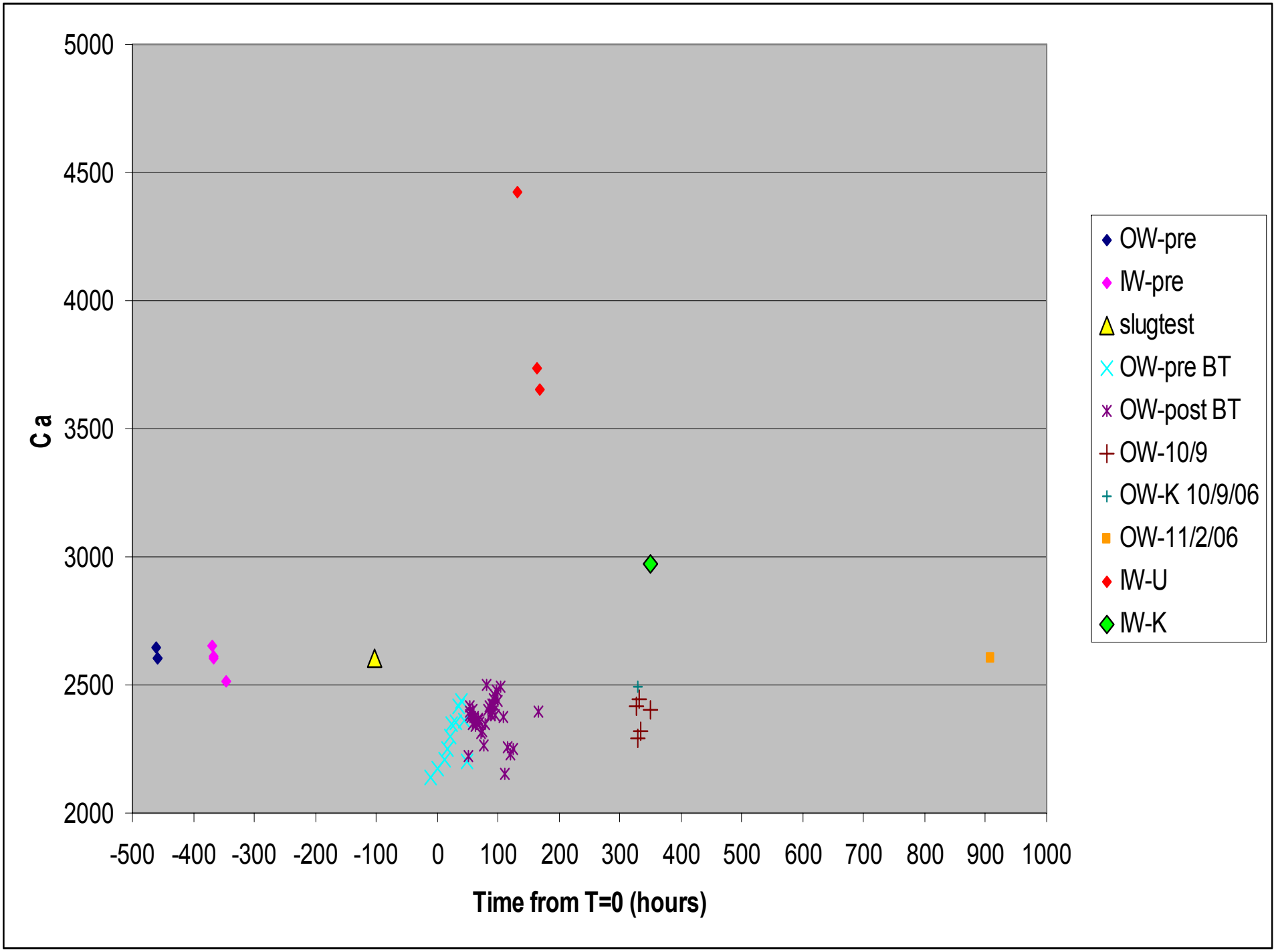
log-log

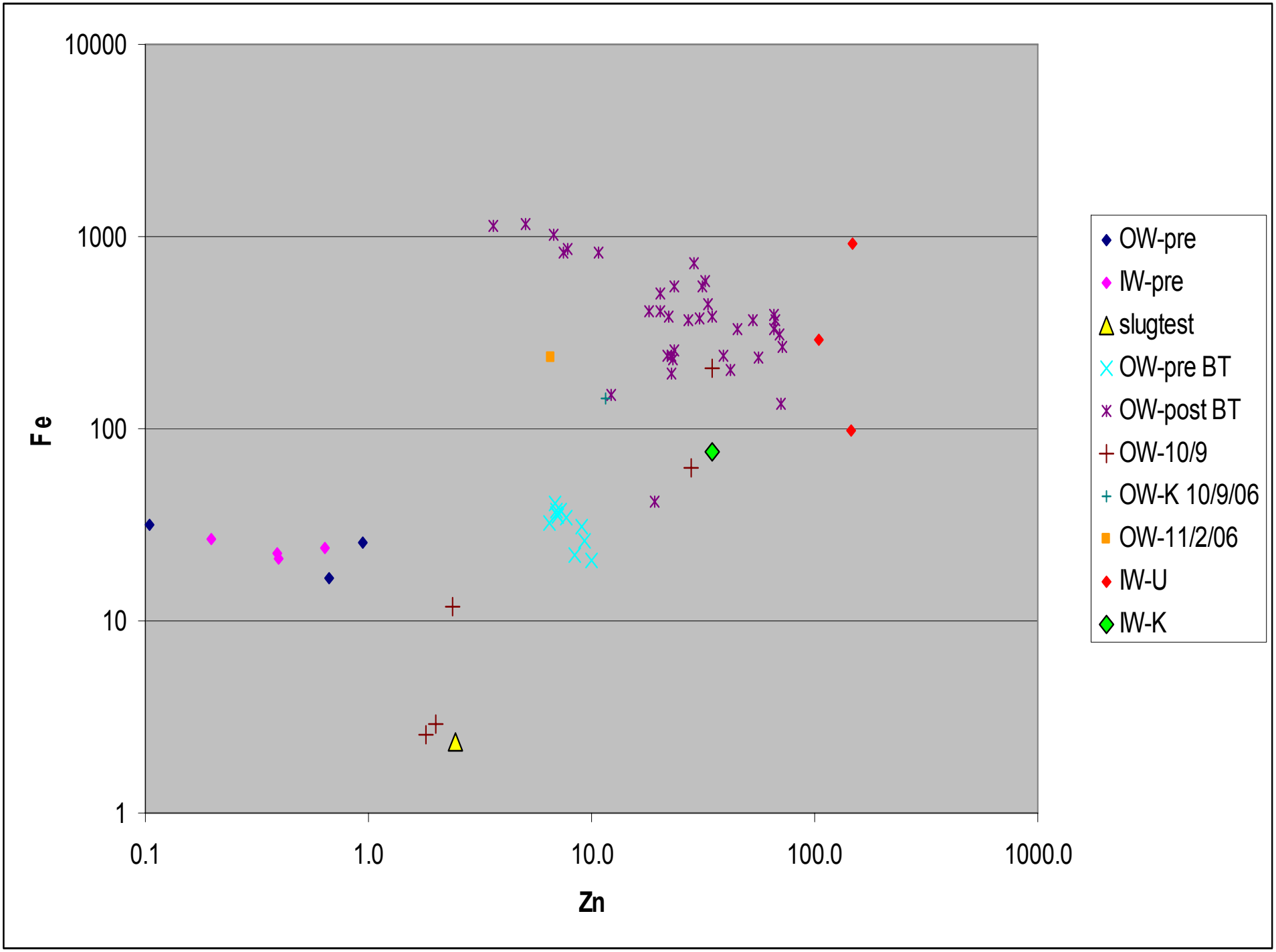

Frio I
IW - pre CO2
OW - pre CO2
OW U-tube(10/5-10/7/04)-pre BT
OW U-tube(10/5-10/7/04)-post BT
OW U-tube(10/29-11/3/04)
IW post CO2 (4/4-4/5/05)
OW "B" post CO2 (4/5-4/6/05)
Kuster
HCO3 (mg/L)
3000
2500
2000
1500
1000
500
0
2400
2500
2600
2700
2800
2900
3000
3100
3200
3300
3400
Ca (mg/L)


Frio I
IW - pre CO2
OW - pre CO2
OW U-tube(10/5-10/7/04)-pre BT
OW U-tube(10/5-10/7/04)-post BT
OW U-tube(10/29-11/3/04)
IW post CO2 (4/4-4/5/05)
OW "B" post CO2 (4/5-4/6/05)
Kuster
Fe (mg/l)
0
200
400
600
800
1000
1200
0
500
1000
1500
2000
2500
3000
Alkalinity (mg/L as HCO3)

Frio Cl & Ca (6/04-4/05)



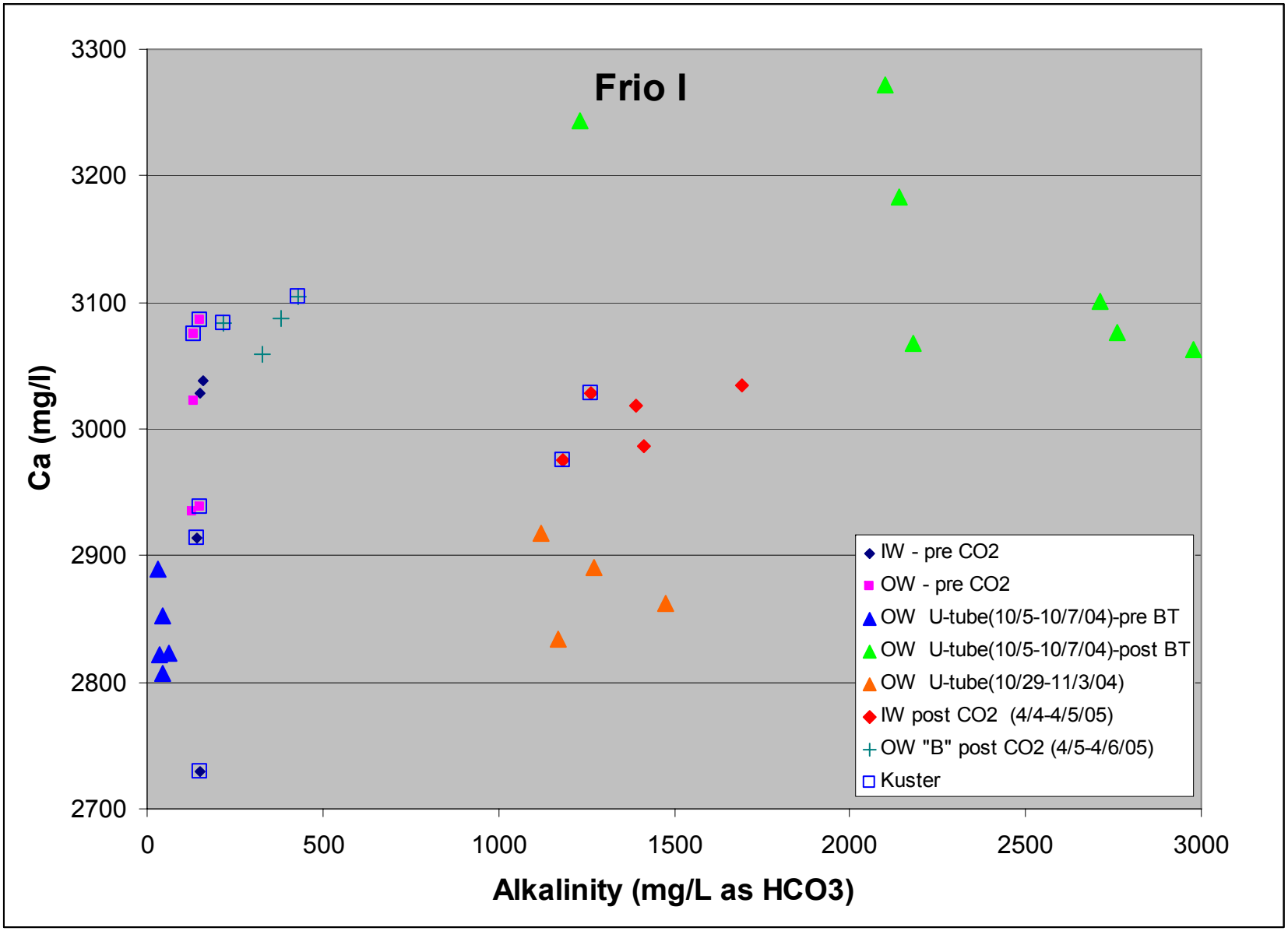
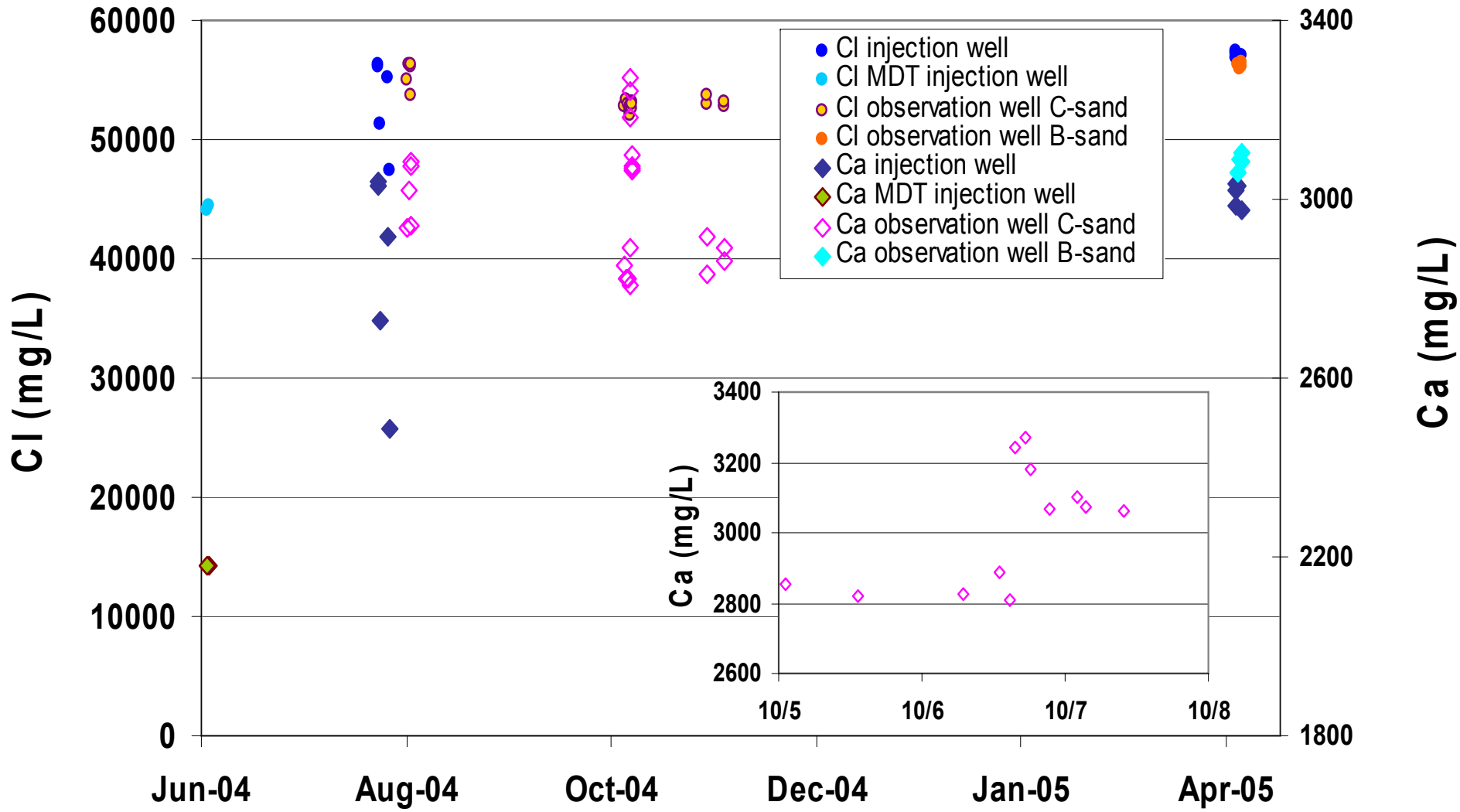

5000
4500
4000
3500
3000
2500
2000
Ca
-500
-400
-300
-200
-100
0
100
200
300
400
500
600
700
800
900
1000
Time from T=0 (hours)
OW-pre
IW-pre
slugtest
OW-pre BT
OW-post BT
OW-10/9
OW-K 10/9/06
OW-11/2/06
IW-U
IW-K


10000
1000
100
10
1
Fe
0.1
1.0
10.0
100.0
1000.0
Zn
OW-pre
IW-pre
slugtest
OW-pre BT
OW-post BT
OW-10/9
OW-K 10/9/06
OW-11/2/06
IW-U
IW-K

Frio I CO_2 Field sampling

Drilling & test water tagged with dye tracers

Sampling date	Sampling site	Sampling tool
June 3, 2004	injection well	MDT tool (Schlumberger)
Jul 23-Aug 2, 2004	injection & observation wells	surface sampling (N_2), Kuster
Oct 4-7, 2004	observation well	U-tube
Oct 29-Nov 3, 2004	observation well	U-tube
April 4-6, 2005	injection (C) & observation (B) wells	Surface sampling (N_2) & Kuster
Jan 23-27, 2006	injection (C) & Observation (B) wells	Surface sampling (swab) & Kuster


Frio I
Ca (mg/l)
3300
3200
3100
3000
2900
2800
2700
0
500
1000
1500
2000
2500
3000
Alkalinity (mg/L as HCO3)
IW - pre CO2
OW - pre CO2
OW U-tube(10/5-10/7/04)-pre BT
OW U-tube(10/5-10/7/04)-post BT
OW U-tube(10/29-11/3/04)
IW post CO2 (4/4-4/5/05)
OW "B" post CO2 (4/5-4/6/05)
Kuster

Frio Cl & Ca (6/04-4/05)