Role of Geochemical Interactions in Assuring Permanence of Storage of CO_2 in Geologic Environments

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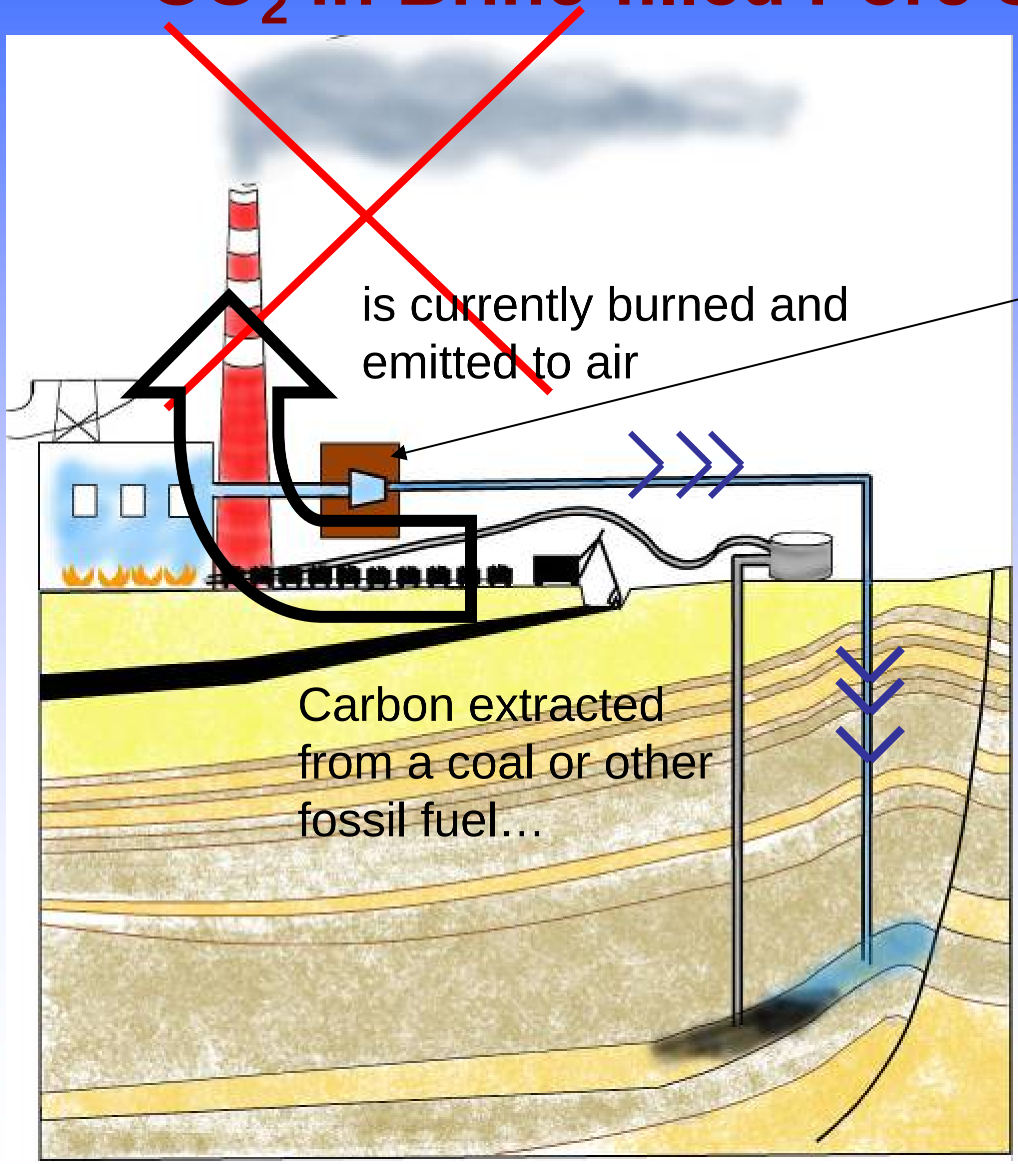
Geologic Sequestration Emplaces Dense-Phase CO_2 in Brine-filled Pore Systems in Rock



To reduce CO_2 emissions to air from point sources..

CO_2 is captured as concentrated high pressure fluid by one of several methods..

CO_2 is shipped as dense-phase fluid via pipeline to a selected, permitted injection site

CO_2 injected at pressure into pore space at depths below and isolated (sequestered) from potable water.

CO_2 stored in pore space over geologically significant time frames.

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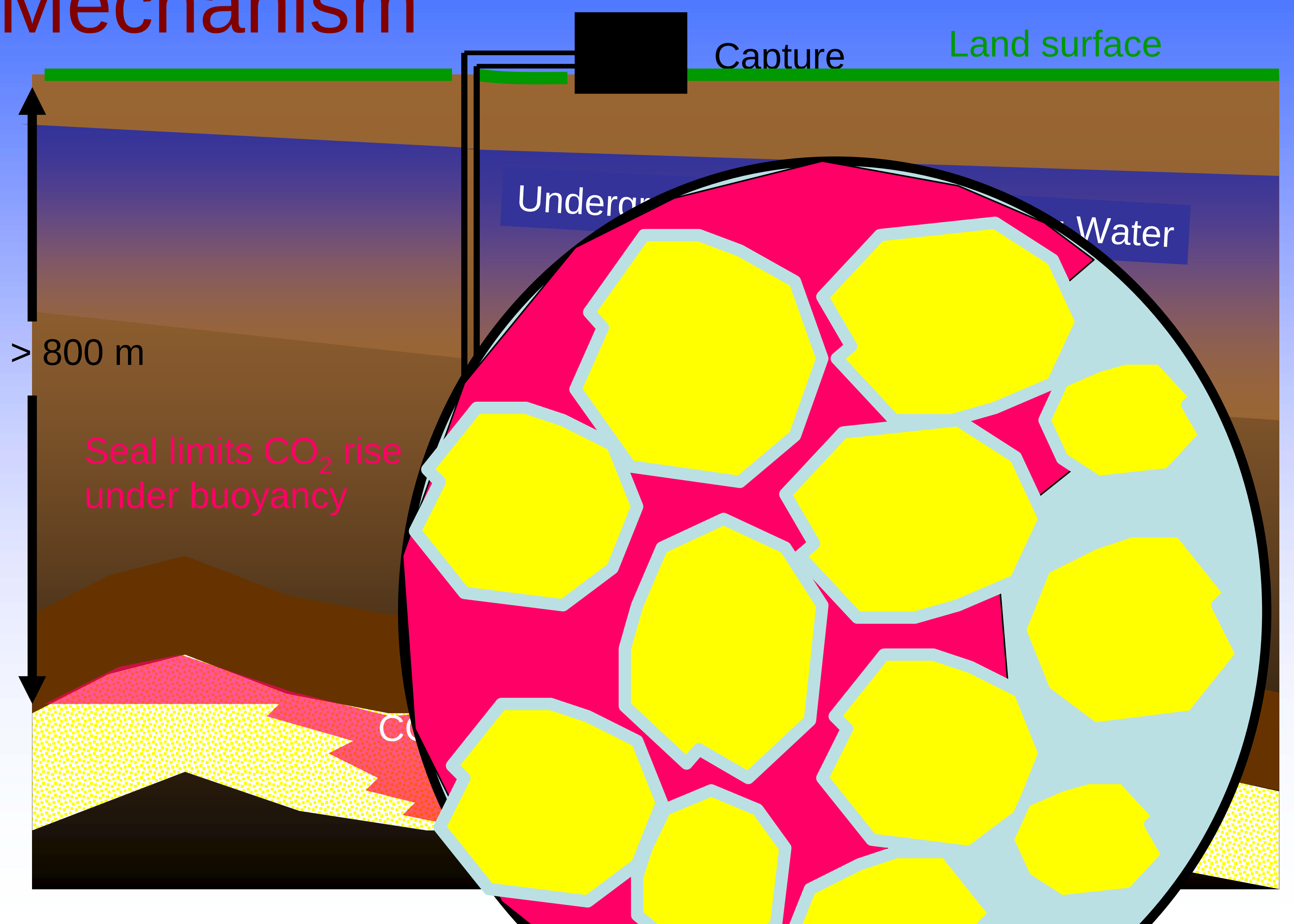
Trapping Mechanisms
Assuring Permanence of Storage

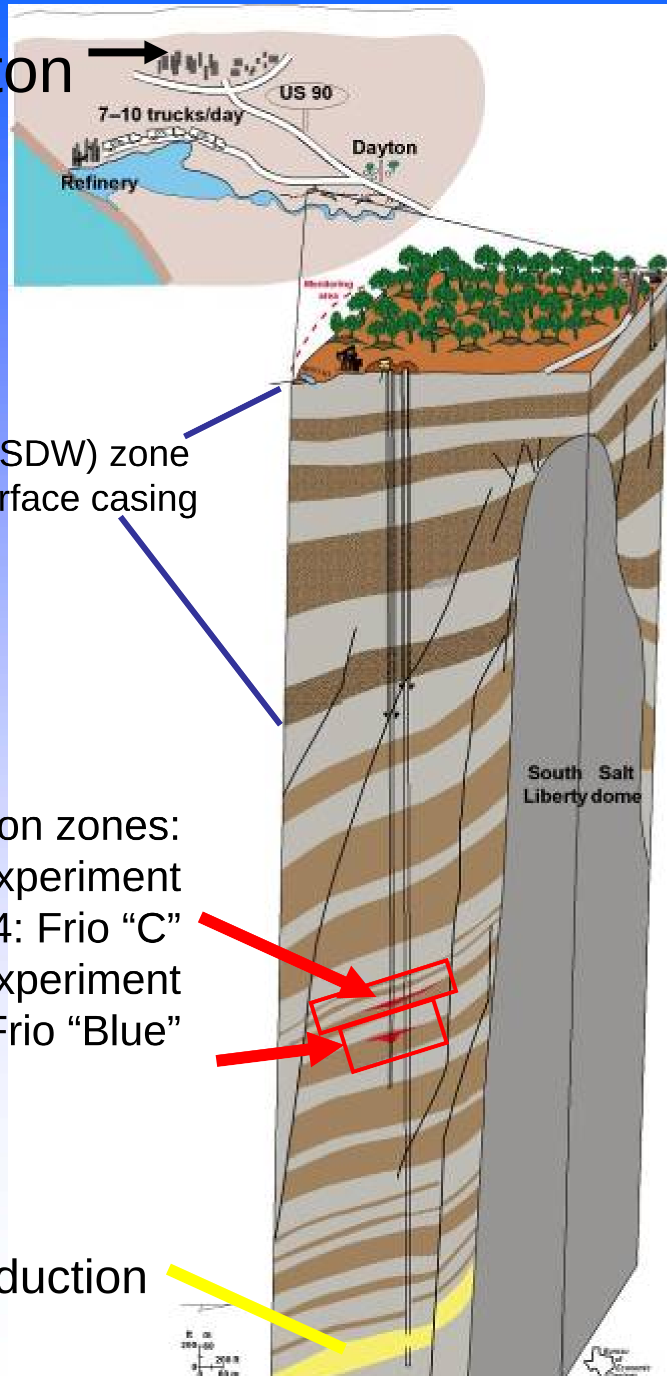
- CO_2 at typical injection depth temperature and pressure is dense phase (supercritical) Density 0.6 to 0.7 = CO_2 is buoyant in brine, low viscosity = Mobile
- Trapping: assure that CO_2 will be retained in injection zone and prevent escape into drinking water and atmosphere over 1000 + year time frames
  - Physical Trapping
    - Seal and capillary effects
  - Chemical trapping
    - Dissolution into water
    - Dissolution and sorbtion into organics (oil and coal)
    - Mineral dissolution and buffering
    - Mineral precipitation

Capillary-Pressure Seal Trapping Mechanism



Frio Brine Pilot Field Test

Houston

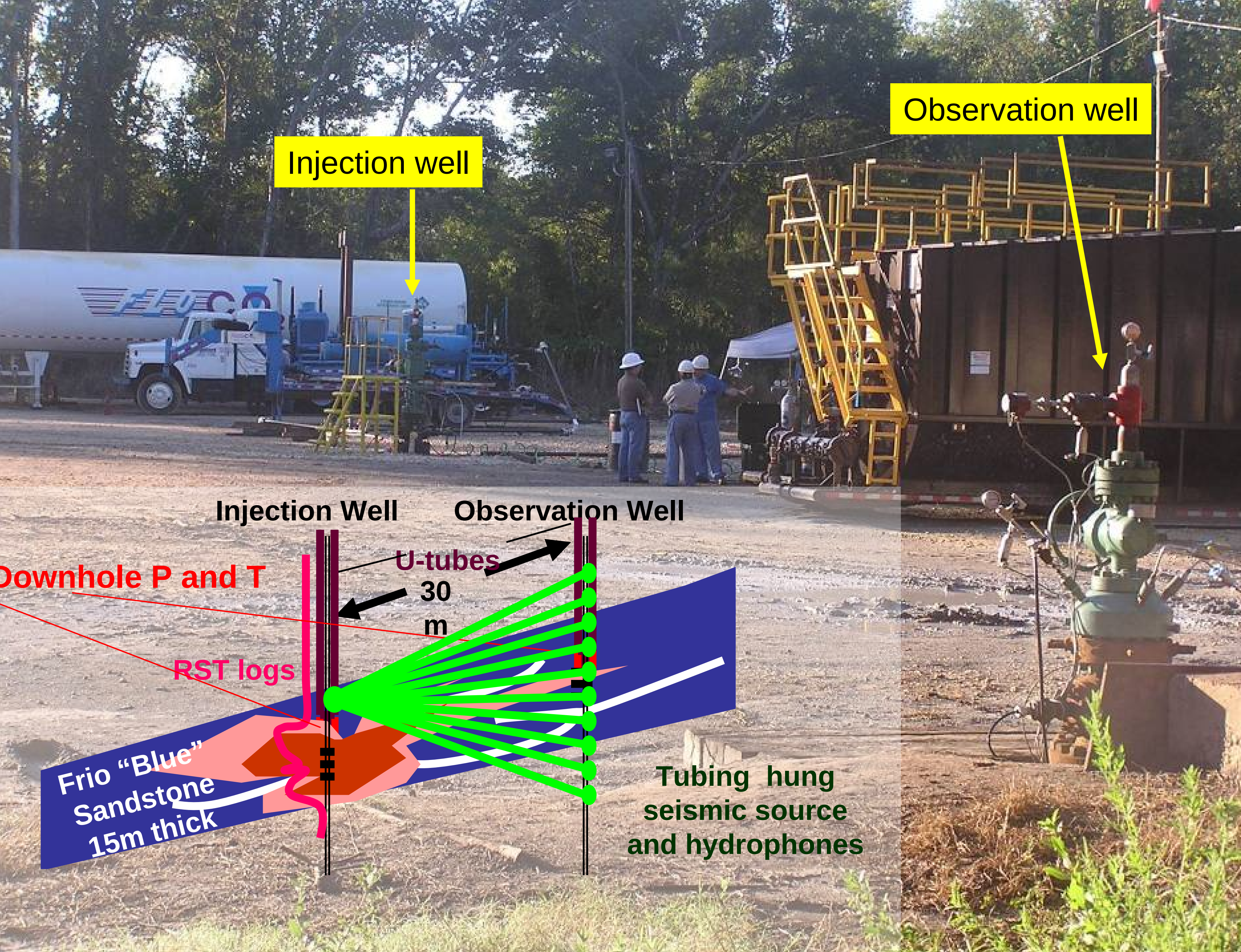


Fresh water (USDW) zone protected by surface casing

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

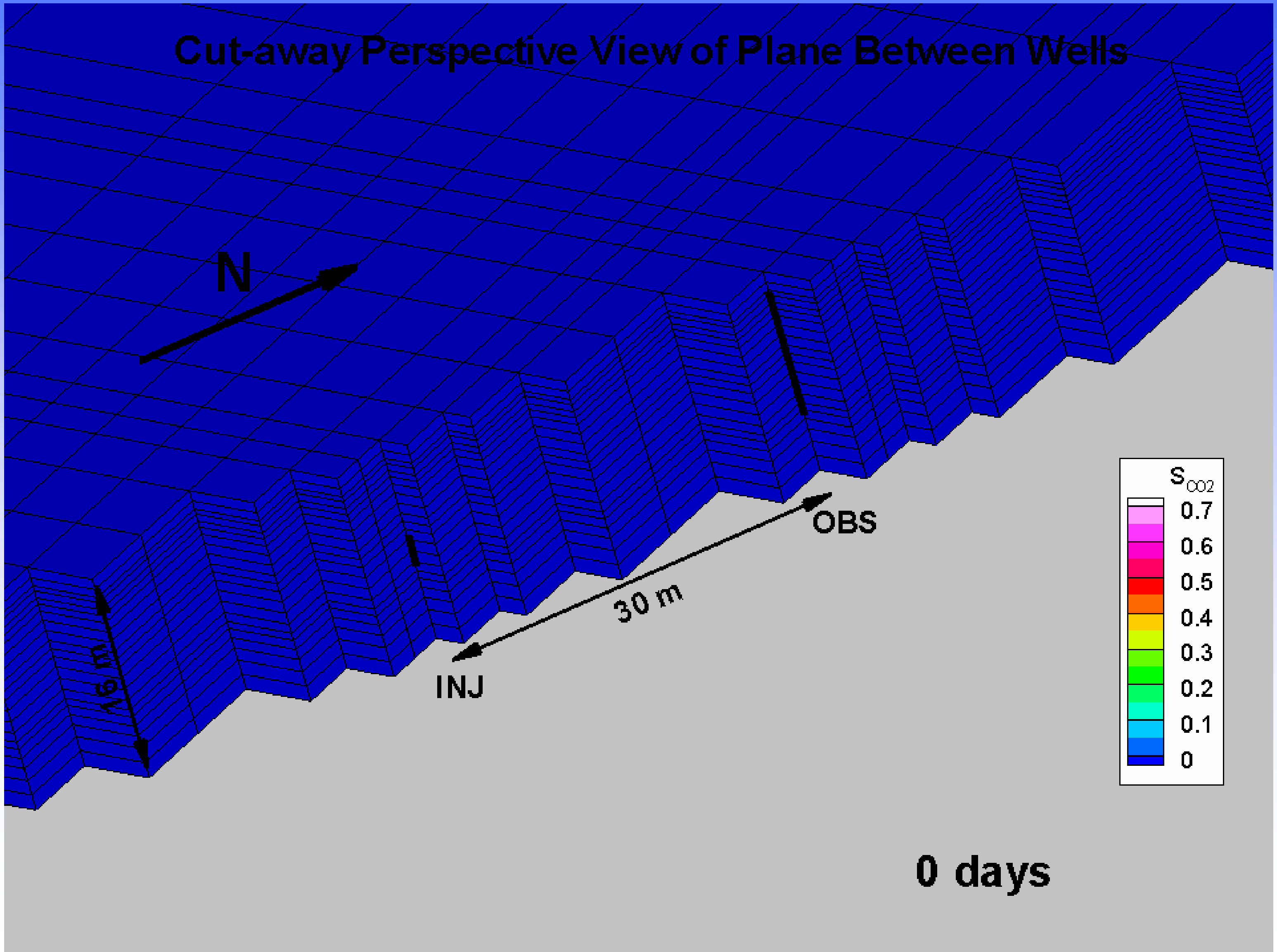
Oil production

- Injection intervals: mineralogically complex Oligocene fluvial and reworked fluvial sandstones, porosity 24%, permeability 4.4 to 2.5 Darcys
- Steeply dipping 11 to 16 degrees
- Seals – numerous thick shales, small fault block
- Depth 1,500 and 1657 m
- Brine-rock system, no hydrocarbons
- 150 and 165 bar, 53 -60 degrees C, supercritical CO_2

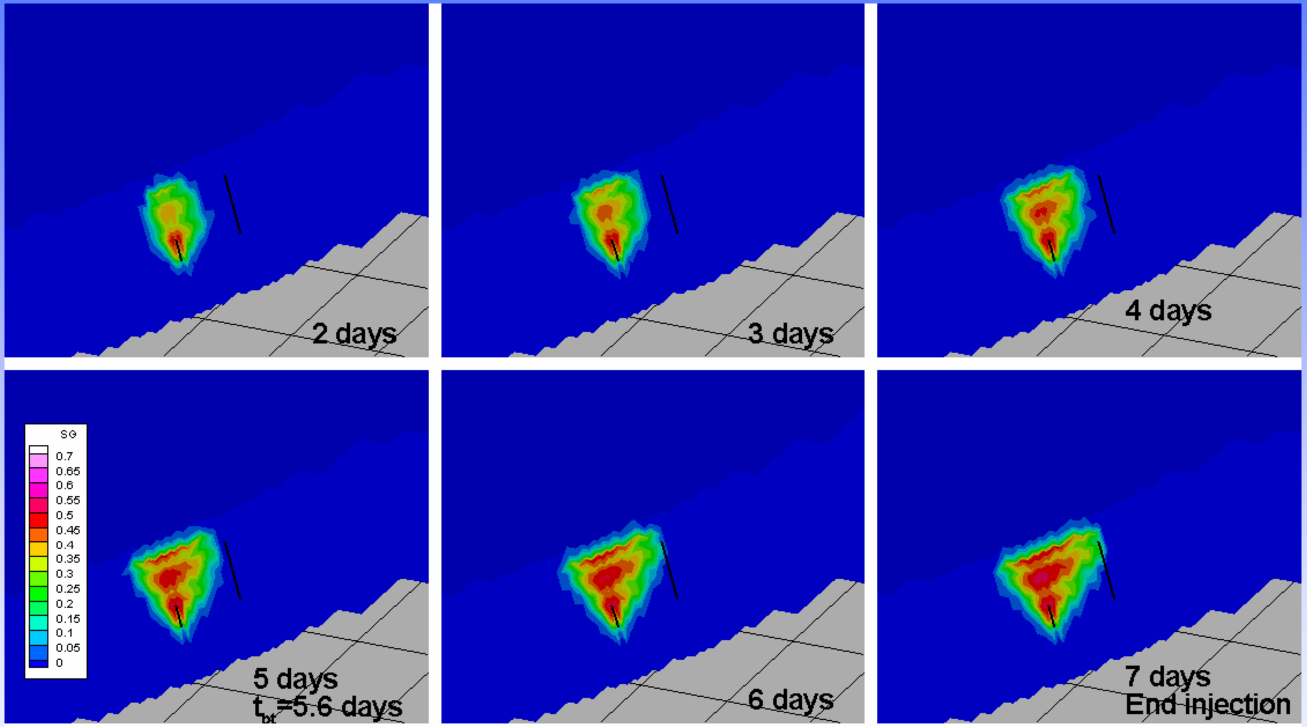


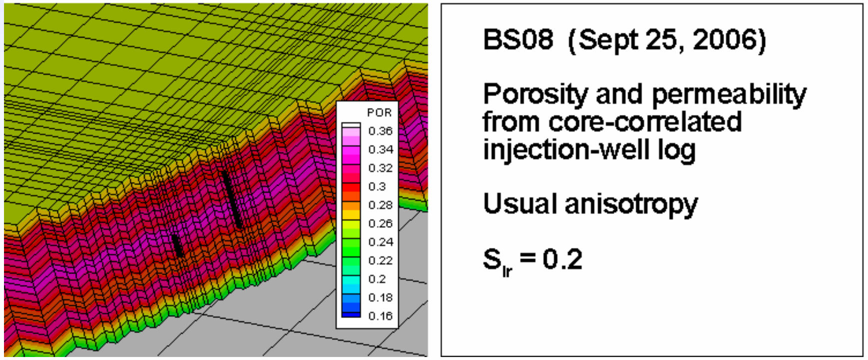
Observation well
Injection well
Injection Well
Observation Well
U-tubes
Downhole P and T
30
m
RST logs
Frio "Blue" Sandstone 15m thick
Tubing hung seismic source and hydrophones

Predicting Evolution of the CO_2 Plume



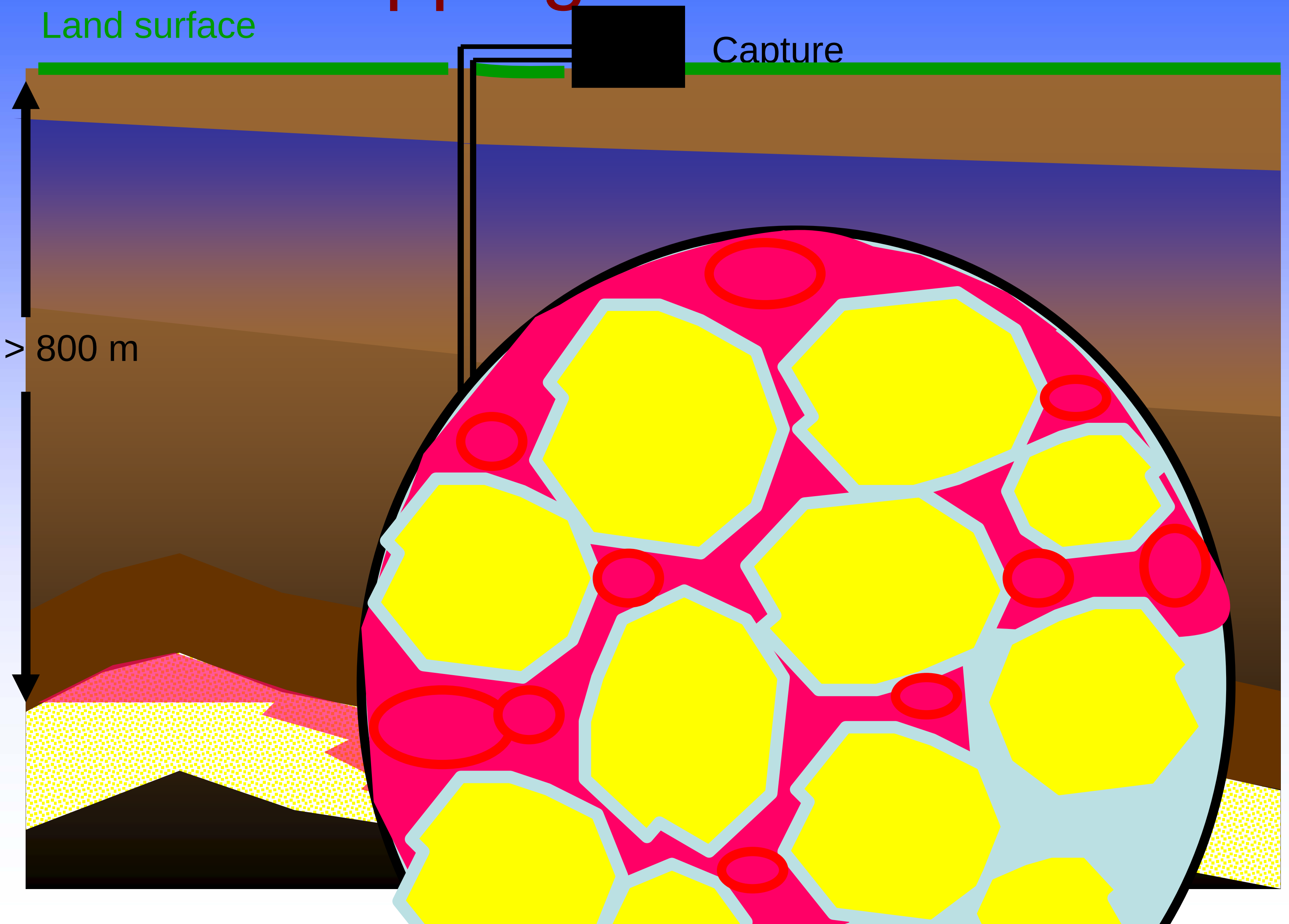
Predicting the Movement of CO_2 after Injection





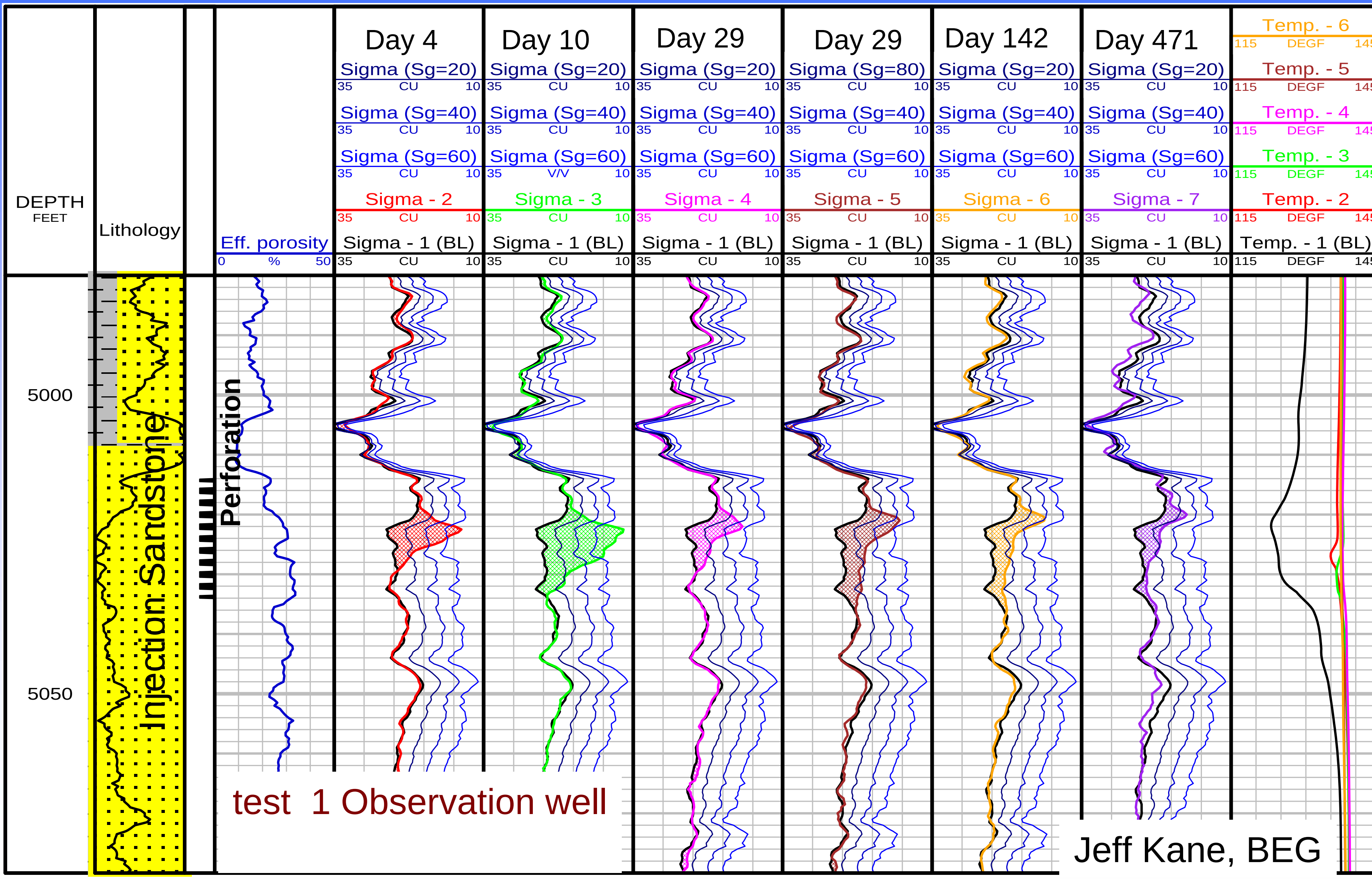
TOUGH2, Christine Doughty LBNL

Non-wetting Residual Phase Trapping Mechanism



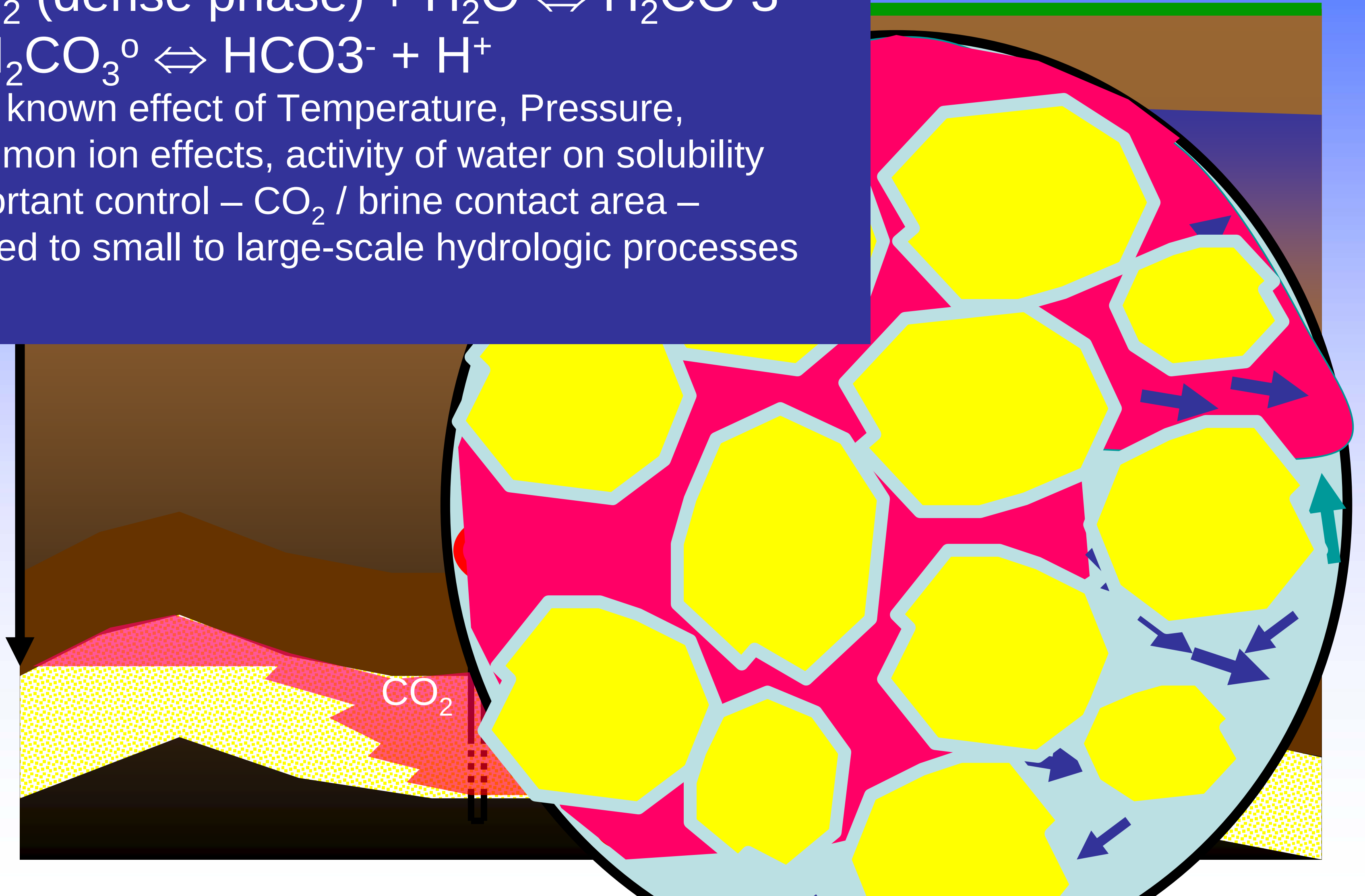
Non-Wetting Phase Trapping

Injection Trapping

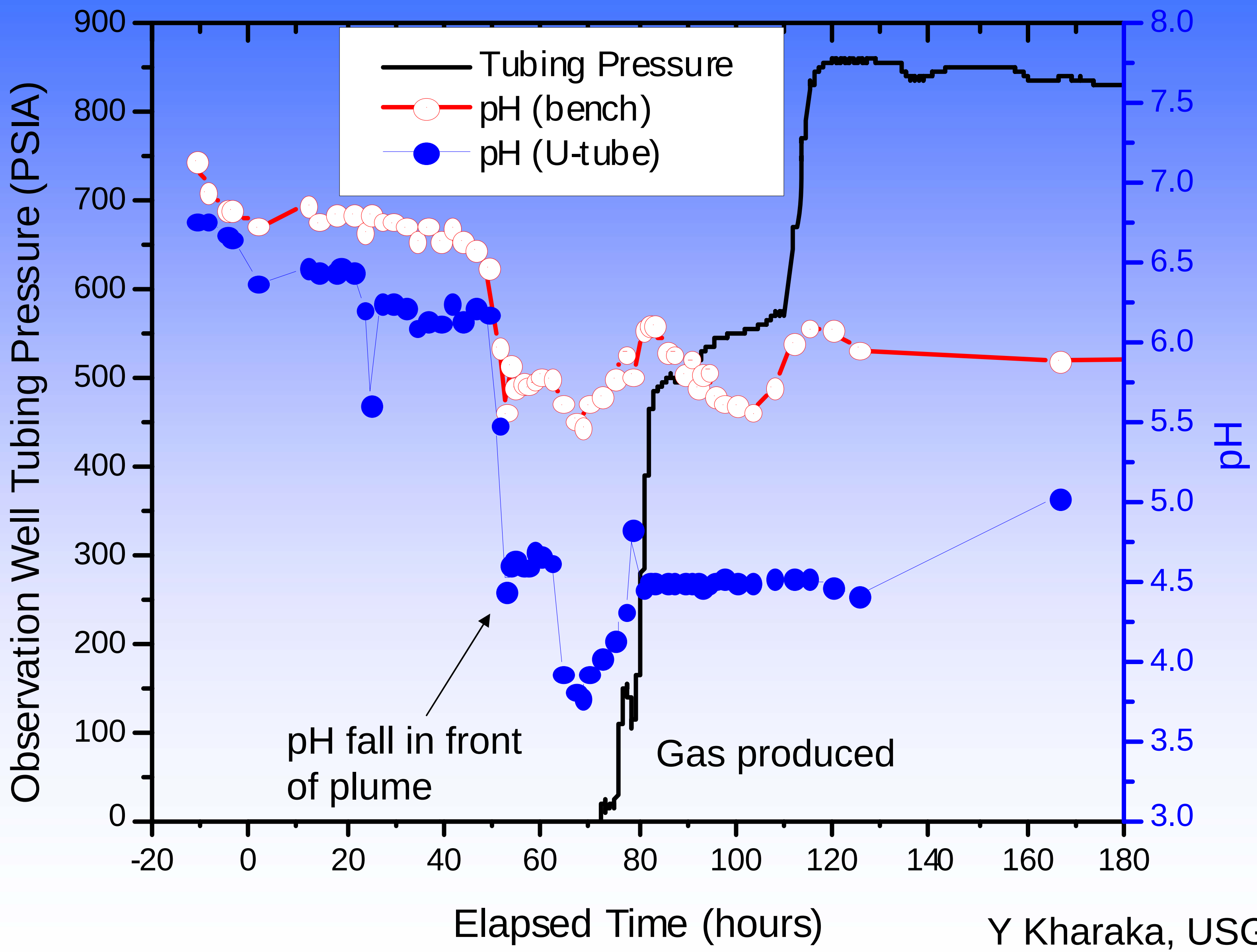


Dissolution into Brine Trapping Mechanism

- CO_2 (dense phase) + $H_2O \Leftrightarrow H_2CO\ 3^o$
- $H_2CO_3^o \Leftrightarrow HCO3^- + H^+$
- Well known effect of Temperature, Pressure,
- Common ion effects, activity of water on solubility
- Important control – CO_2 / brine contact area –
- related to small to large-scale hydrologic processes

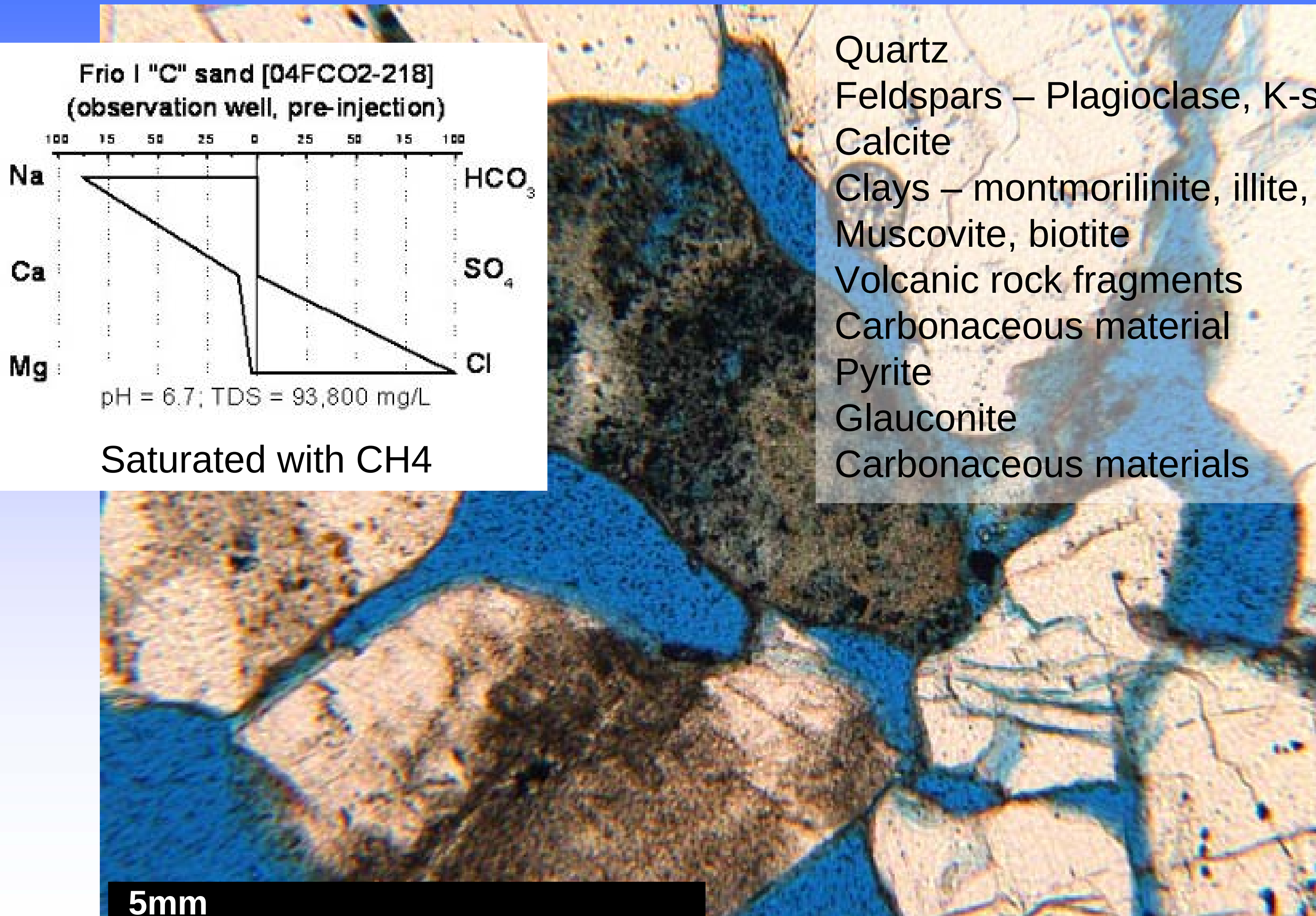


Measured Dissolution of CO_2 in Brine



Y Kharaka, USGS

Rock – Water Reactions- Pre-injection Composition



Saturated with CH4

Quartz
Feldspars – Plagioclase, K-spar
Calcite
Clays – montmorilinite, illite, chlorite
Muscovite, biotite
Volcanic rock fragments
Carbonaceous material
Pyrite
Glauconite
Carbonaceous materials

Major Mineral-Water-Gas Interactions in Rock

CO_2 dissolves into brine

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

$H_2CO_3^o \Leftrightarrow HCO_3^- + H^+$

CO_2 Dissolves calcite

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

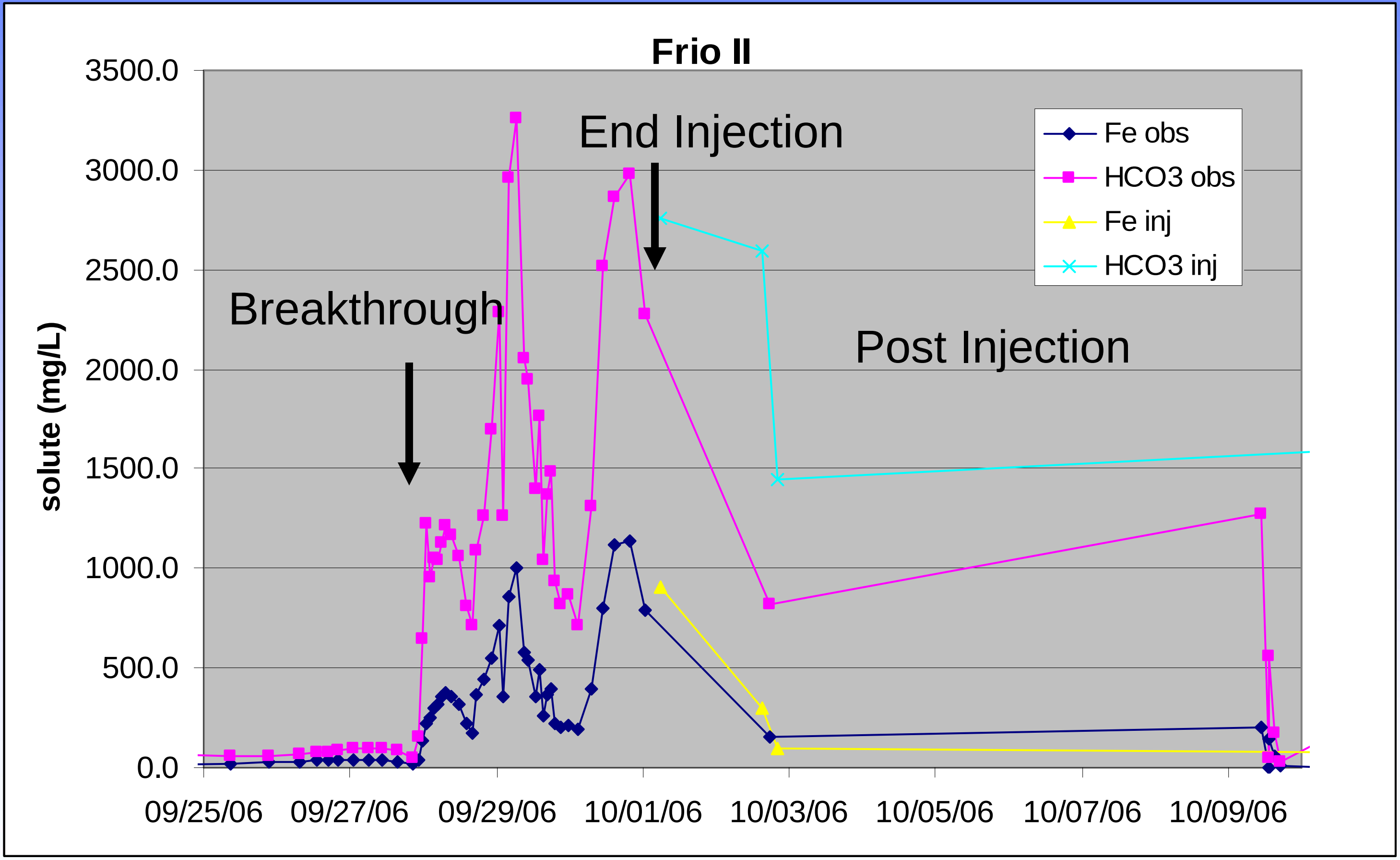
$H^+ + CaCO_3 \Leftrightarrow Ca^{++} + HCO_3^-$

CO2 dissolves feldspar – precipitate minerals (dawsonite

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

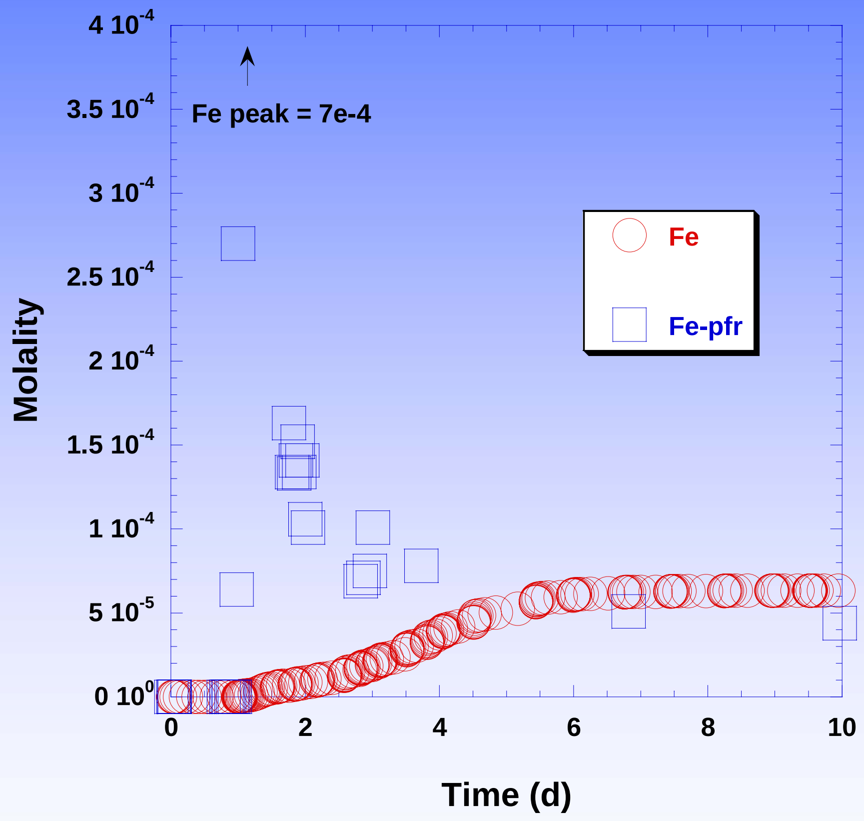
$.2Ca{+}{+} + .8NaAlCO_3(OH)_2 + 0.4Al(OH)_3 + 2.8SiO_2$ -- (10)

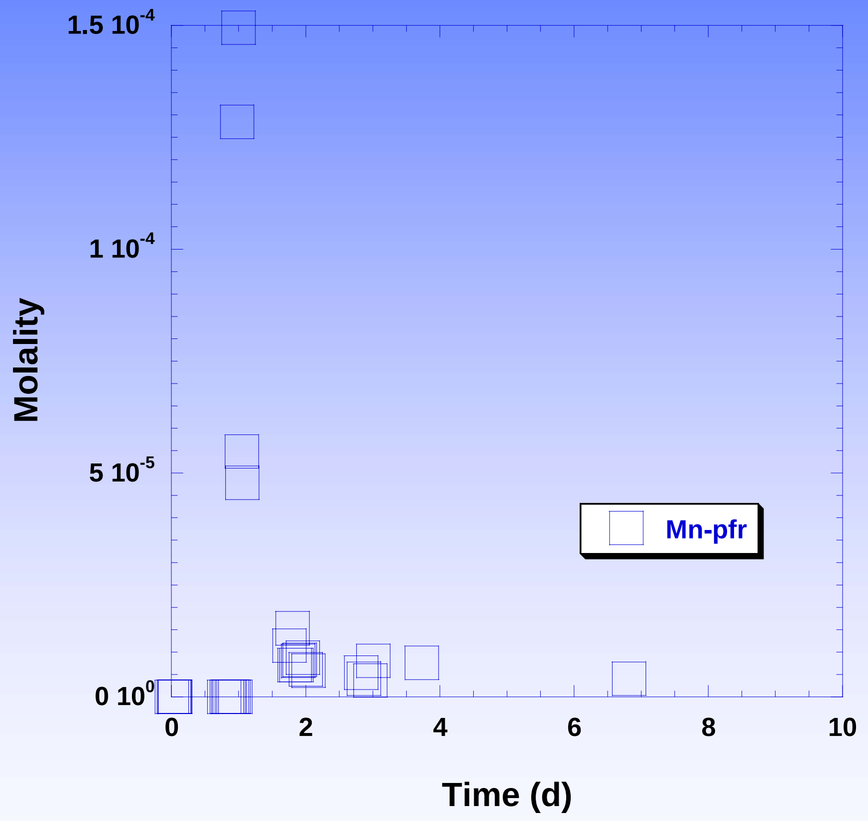
Measured Change in Key Chemical Constituents with Time During and after Injection



Observation Well, Second Test

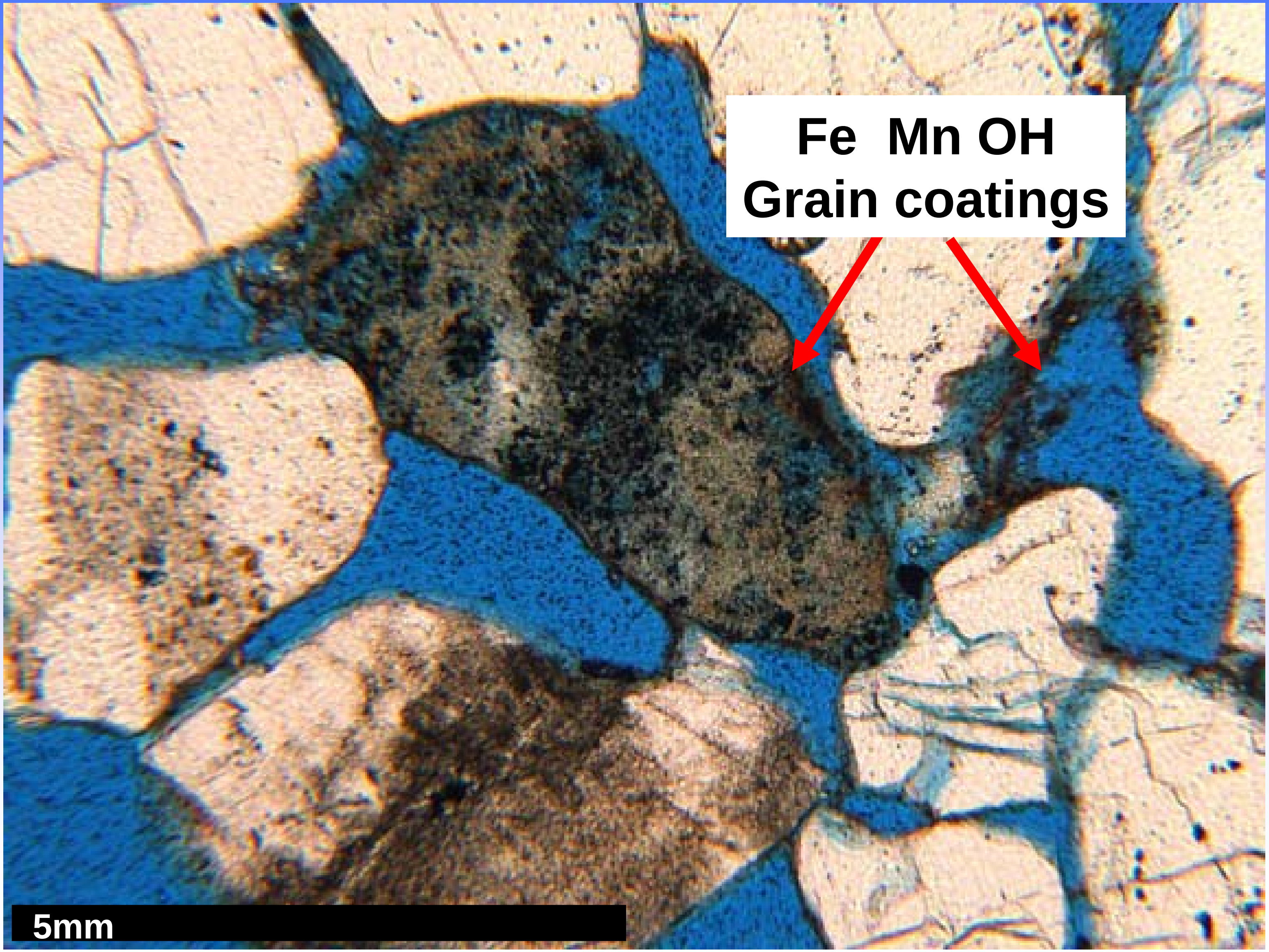
Laboratory Rock-Water Analysis





K. Knauss, LLNL

Rapid Transient Rock – Water Reaction



Fe-Releasing Mineral-Water-Gas Interactions

$CO_{2\,(gas)} + H_2O \Leftrightarrow H_2CO_3^{o}$ CO_2 dissolves into brine

$H_2CO_3^{o} \Leftrightarrow HCO_3^{-} + H^{+}$

$CO_{2\,(gas)} + H_2O + CaCO_3 \Leftrightarrow Ca^{++} + 2HCO_3^{-}$ CO_2 Dissolves calcite

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

$H^{+} + FeCO_3 \Leftrightarrow Fe^{++} + HCO_3$ CO_2 dissolves siderite

$4Fe(OH)_3 + 8H_2CO_3 \Leftrightarrow 4Fe^{++} + 8HCO_3^{-} + 10H_2O + O_2$ CO2 dissolves

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

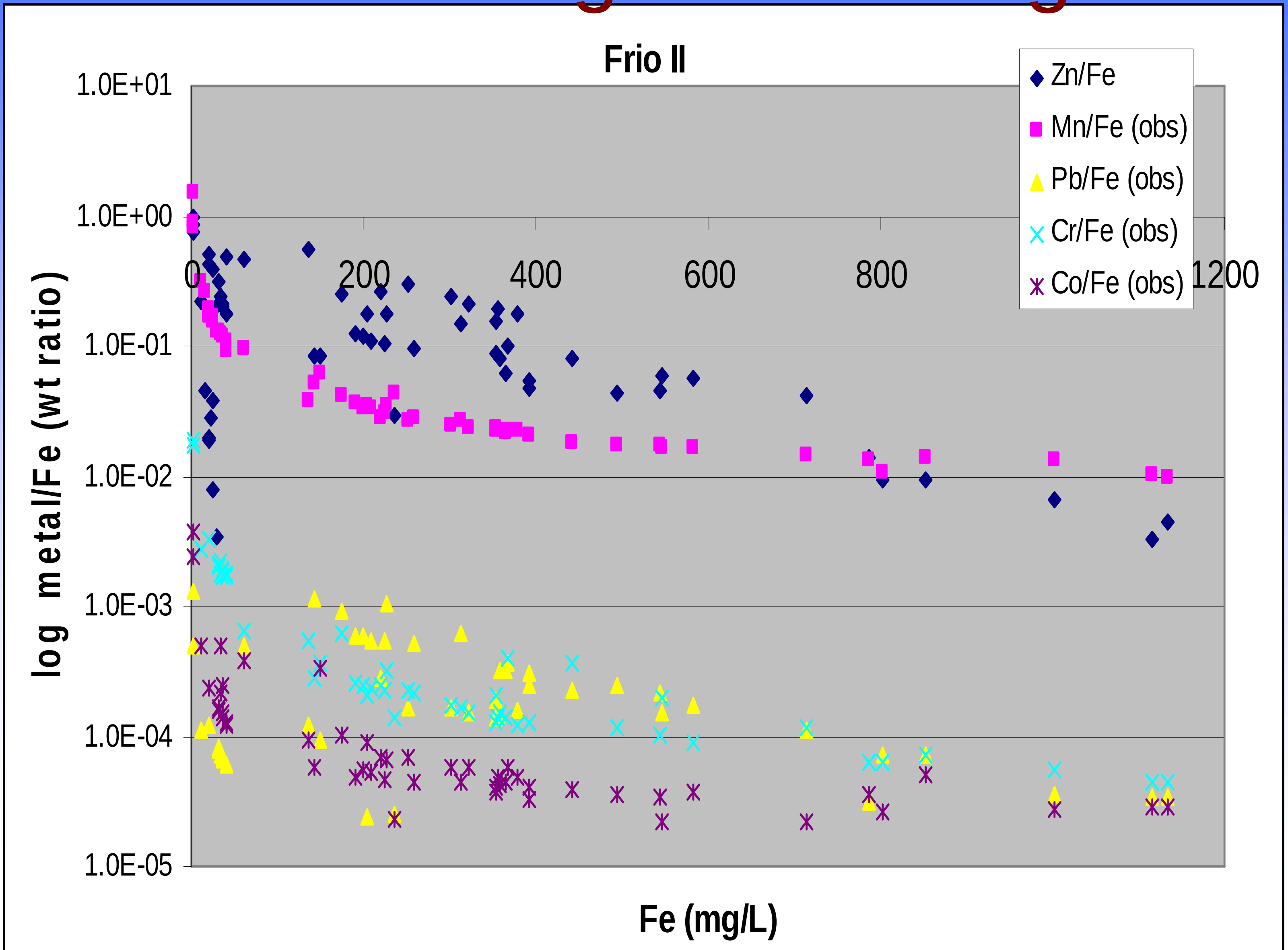
$Fe^{o} + 2H_2CO_3 \Leftrightarrow Fe^{++} + 2HCO_3^{-} + H_2$ CO_2 dissolves steel

$2H^{+} + CaMg(CO_3)_2 \Leftrightarrow Ca^{++} + Mg^{++} + 2HCO_3^{-}$ CO_2 dissolves dolomite

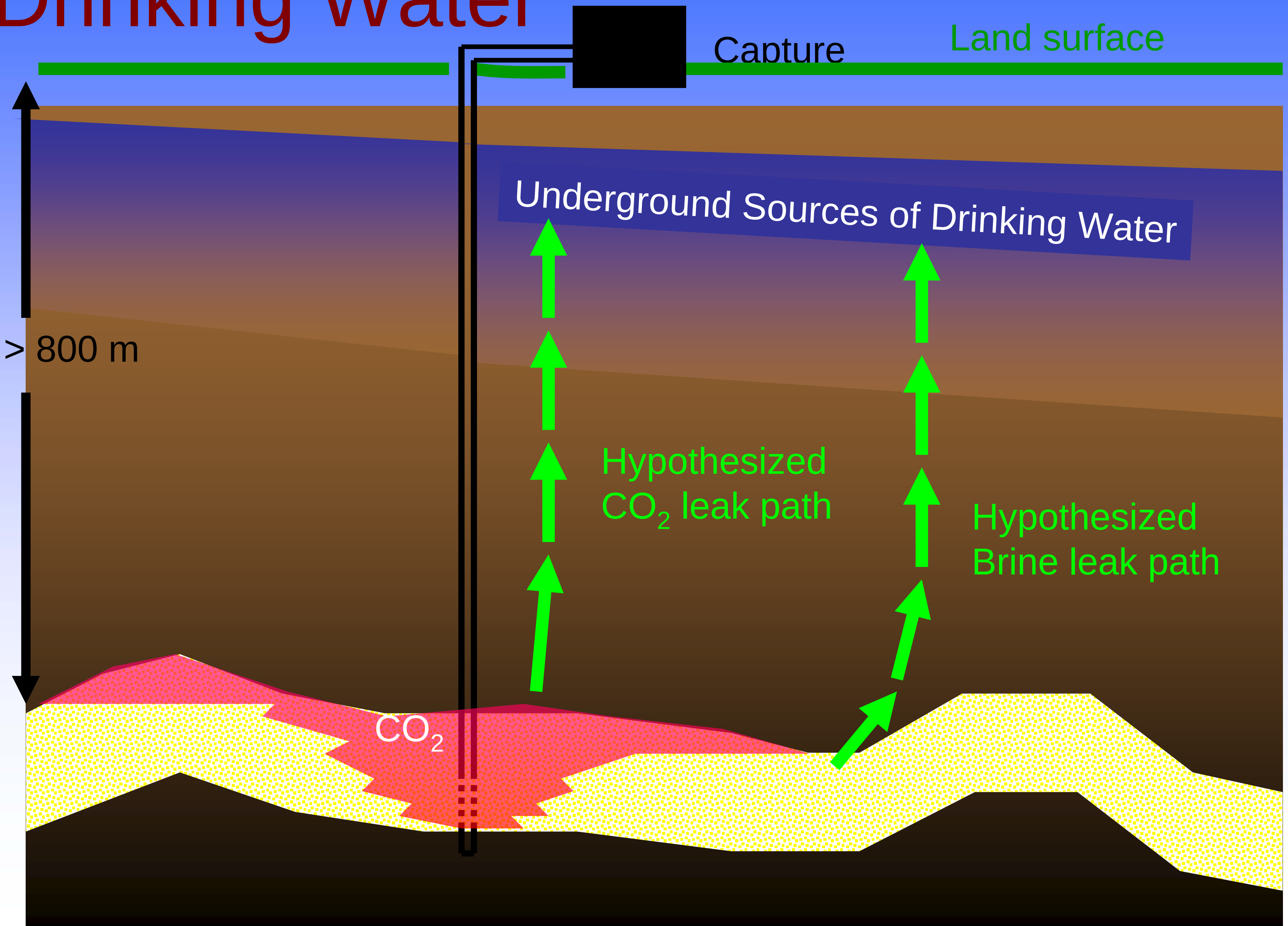
$0.4H^{+} + Ca_{.2}Na_{.8}Al_{1.2}Si_{2.8}O_8 + 0.8CO_2 + 1.2H_2O \Leftrightarrow$ CO_2 dissolves feldspar

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

Other trace metals - Contamination from Casing and Tubing?



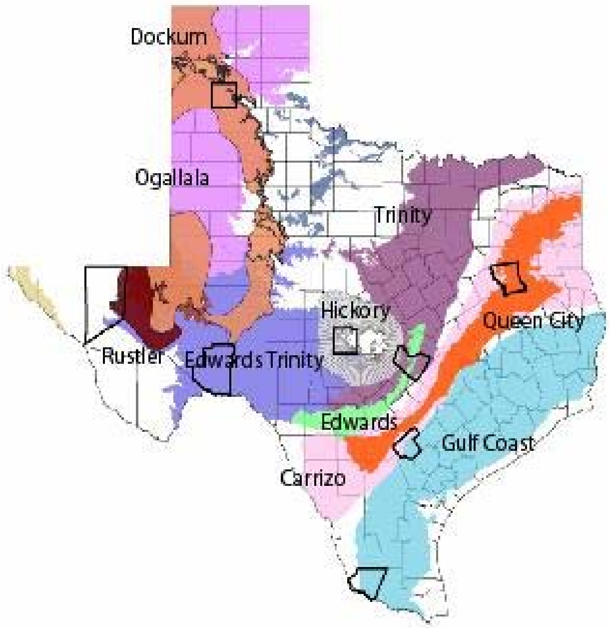
Risk to Underground Sources of Drinking Water

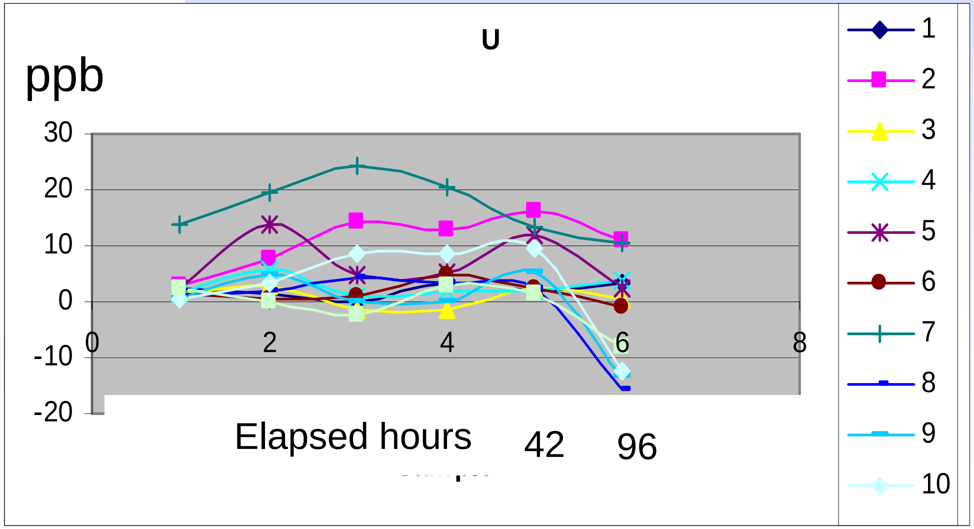


Risk to Potable Water

- Brine + reactants introduced into fresh water
  - Controlled by pressure
  - Main risk is NaCl damage
- CO_2 moves to shallow water & dissolves
  - New results from typical aquifers – fresh water & gas phase CO_2
  - Cations liberated from typical aquifer rocks include Ca, Fe, K, Sr, U, As – potential degradation of drinking water, scaling and process dependent
  - May be transient and self limiting – new study by Corrine Wong

Preliminary Results of Geochemical Risk to Aquifers from CO_2 leakage





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UT Austin

Conclusions

- Physical and capillary barriers to flow play the lead role in assuring permanence of storage
- Geochemical interactions play a secondary but significant role in assuring permanence of storage
  - Dissolution and buffering
  - Mineral precipitation in the long term
- Rock-water reactions provide risk factors that require assessment under current permitting regulations
  - Mineral dissolution in low pH brines
  - Corrodibility of natural and engineered systems
  - Controlled by characterization during site assessment and managed by well engineering