Water Quality Implications of Brine and CO_2 Leakage on USDW

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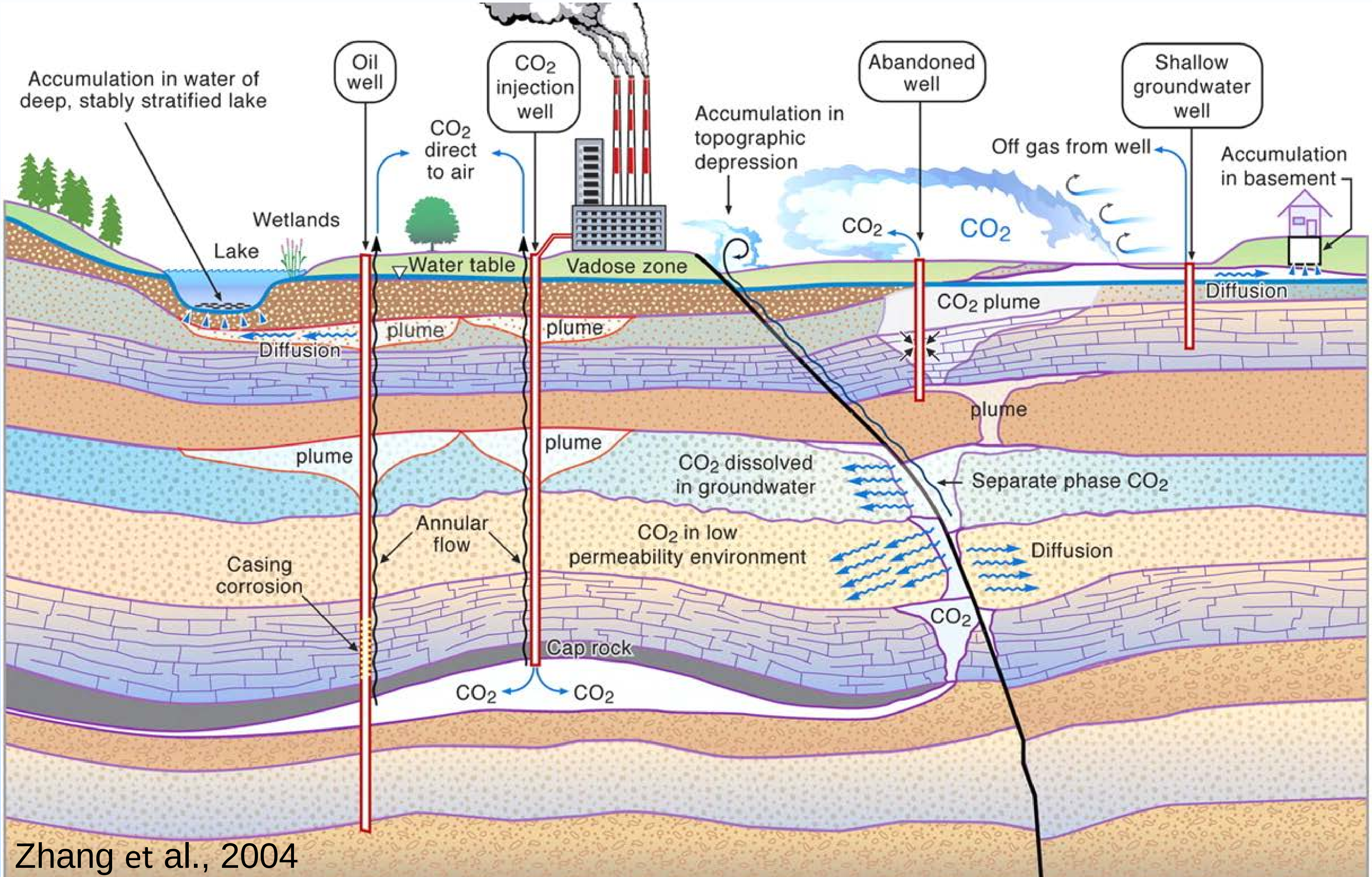
Impacts of CO_2 + Brine Leakage



Project Work Accomplished

Experiments to evaluate potential release of trace metals in the injection formation (high P & T).

Experiments to understand impacts of CO_2 leakage on aquifer water quality at the leak location.

- Carbonate and sandstone aquifers

Screening level assessment of potential impacts of brine leakage using national database.

Multiphase, multi-species reactive-transport modeling to assess human-health risk of potentially released metals

Paper, Papers, Papers……

Atchley, A.L., Maxwell, R.M., Navarre-Sitchler, A.K. 2013. Using streamlines to simulate stochastic reactive transport in heterogeneous aquifers: Kinetic metal release and transport in CO_2 impacted drinking water aquifers, *Adv. Water Resour*., *In Press.*

Atchley, A.L., Maxwell, R.M., Navarre-Sitchler, A.K, Siirila, E.R., and McCray, J.E. 2012. Using streamlines for highly-resolved, reactive transport for CO_2 leakage contamination in groundwater, *Proceedings of the conference ModelCARE2011: Models – Repositories of knowledge. IAHS Publ. 3XX,* Leipzig, Germany.

Atchley, A.L., Maxwell, R.M., Navarre-Sitchler A.K., 2013. Human health risk assessment of CO2 leakage into underlying aquifers using a stochastic, geochemical reactive transport approach, in preparation for *Water Resour. Res*.

Bearup, L., Navarre-Sitchler, A., Maxwell, R.M., McCray, J.E., 2012. Kinetic metal release from competing processes in aquifers, *Environ. Sci* Technol., doi/10.1021/es203586y

Kirsch, K., Navarre-Sitchler, A., Wunsch, A., McCray, J.E. 2012. Assessing the impact of CO_2 leakage on groundwater chemistry in siliclastic aquifers: an experimental investigation of CO_2-water-rock reactions, in preparation for *Applied Geochemistry*.

Marcon, V., Kaszuba, J., 2013. Mobilization of trace metals in an experimental carbon sequestration scenario, in preparation.

Navarre-Sitchler, A.K., R.M. Maxwell, E.R. Siirila, G.E. Hammond, P.C. Lichtner, 2012. Elucidating geochemical response of shallow heterogeneous aquifers to CO2 leakage using high-performance computing: implications for monitoring of CO2 sequestration, *Adv Water Resour*, http://dx.doi.org/10.1016/j.advwatres.2012.10.005

Siirila, E.R., Navarre-Sitchler, A., Maxwell, R.M., McCray, J.E., 2012, A quantitative methodology to assess the risks to human health from CO2 leakage into groundwater, *Adv Water Resour., 36*, p. 146-164: http://www.sciencedirect.com/science/article/pii/S0309170810002149.

Siirila, E.R, et al., 2013. A model comparison of statistically anisotropic, heterogeneous aquifers 1. Effect on macrodispersion, in preparation for *Water Resour. Res*.

Siirila, E.R, et al., 2013, A model comparison of statistically anisotropic, heterogeneous aquifers 2. Interplay between local dispersion and macrodispersion, in preparation for *Water Resour. Res*.

Wunsch, A., Navarre-Sitchler, A.K., McCray, J.E. 2013. Geochemical implications of brine leakage into freshwater aquifers, *Ground Water*, http://onlinelibrary.wiley.com/doi/10.1111/gwat.12011/abstract.

Wunsch, A., Navarre-Sitchler, A.K., Moore, J., McCray, J.E. 2013. Metal release from limestone aquifer rocks at elevated CO_2 pressures, in preparation for *Chemical Geology.*

Wunsch, A., Navarre-Sitchler, A.K., Moore, J., McCray, J.E. 2013. Metal release from dolomite aquifer rocks at elevated CO_2 pressures, in preparation.

Wunsch, A., Navarre-Sitchler, A.K., Moore, J., McCray, J.E. 2013. Metal release from clayey limestone aquifer materials at elevated CO_2 pressures, in preparation.

Metal Release from Natural Limestone Rocks at Elevated CO_2

Submitted to *Chemical Geology*

Assaf Wunsch[1], Alexis Navarre-Sitchler[1], Joel Moore[2], John McCray[1]

1 COLORADO SCHOOL OF MINES
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2 TOWSON UNIVERSITY

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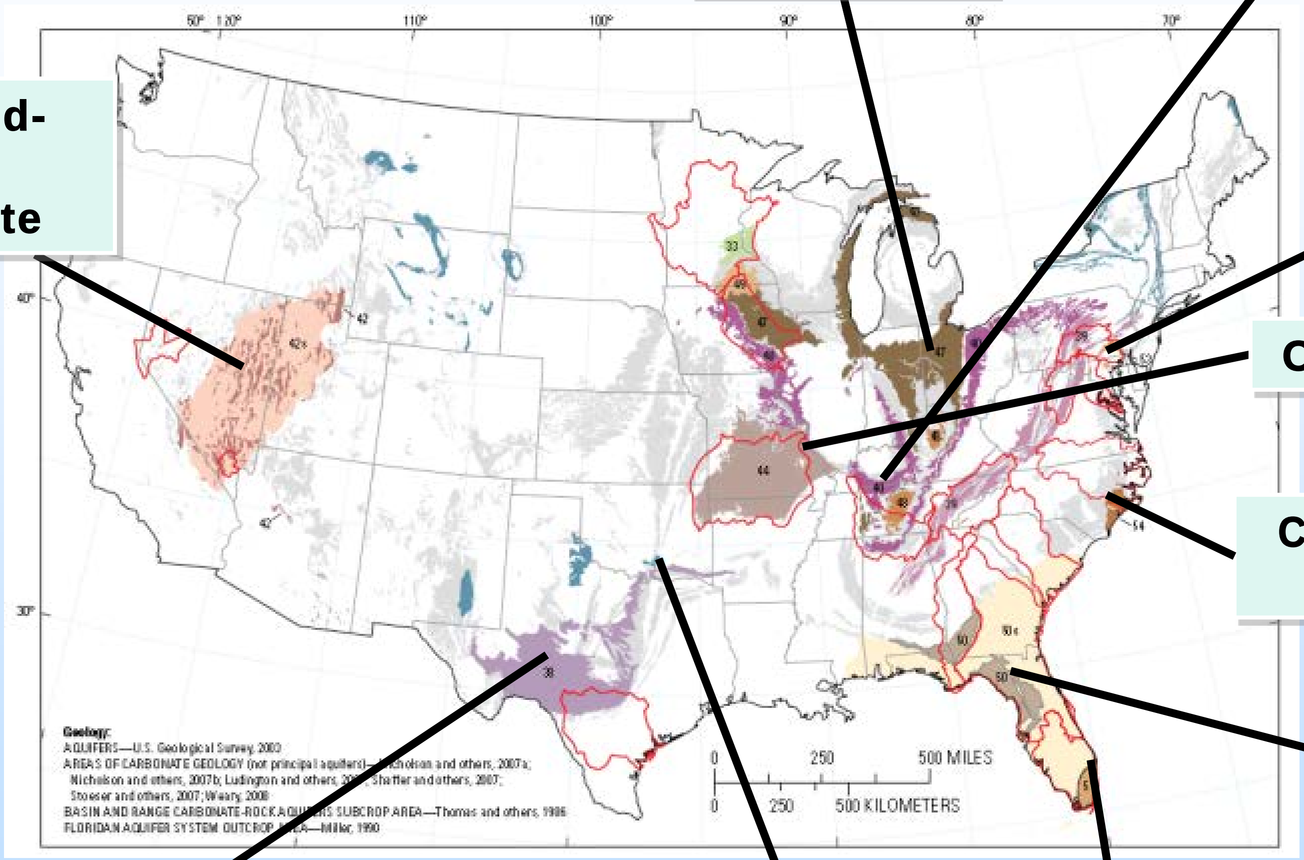
Carbonate Aquifers

… Supply 20-25% of earth's drinking water; 17% for U.S.



Carbonate Aquifers…

…have been largely ignored in leakage scenarios

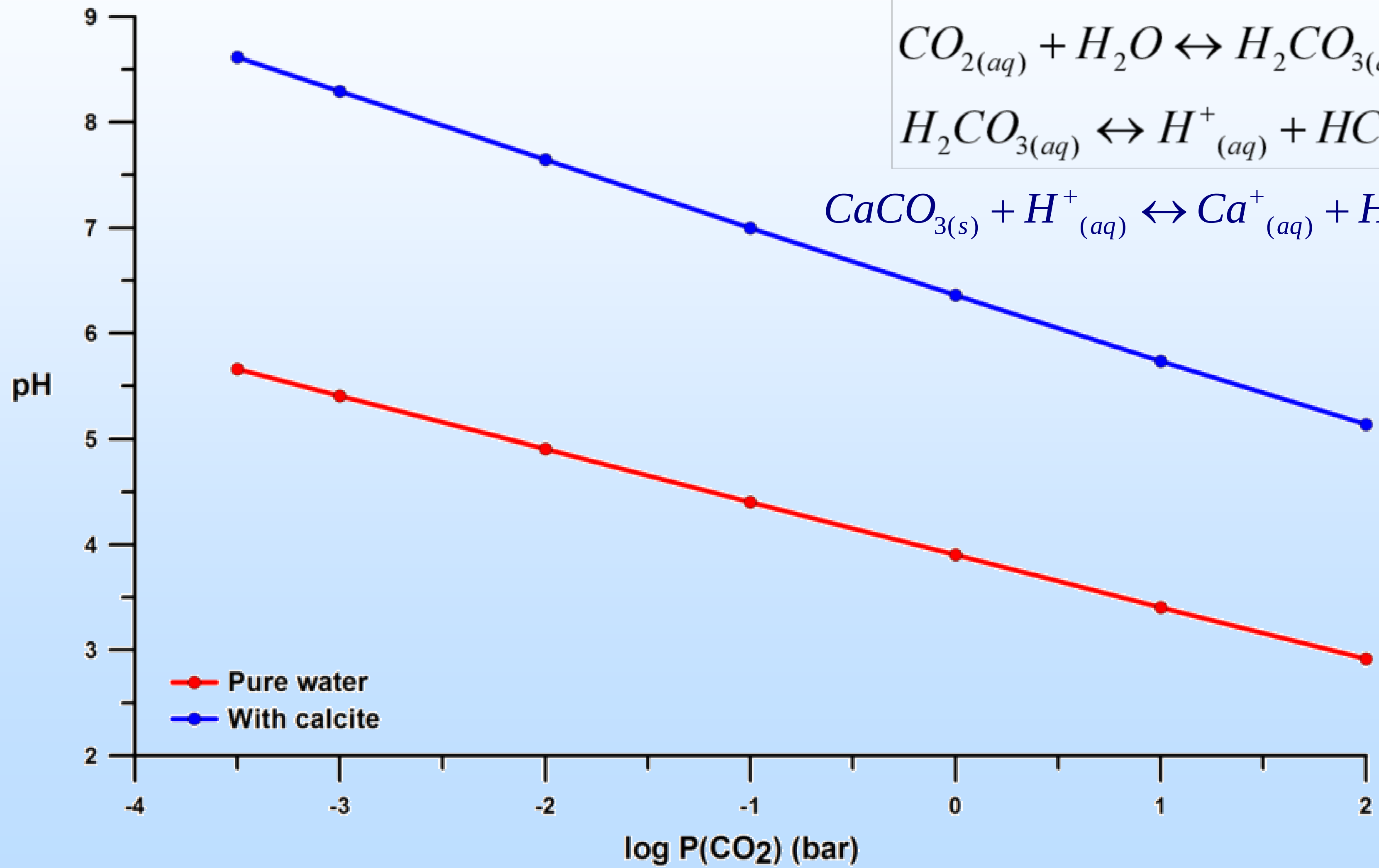
– expect pH buffering as carbonate dissolves

$$\frac{CO_{2(g)}}{K_H} \leftrightarrow CO_{2(aq)}$$

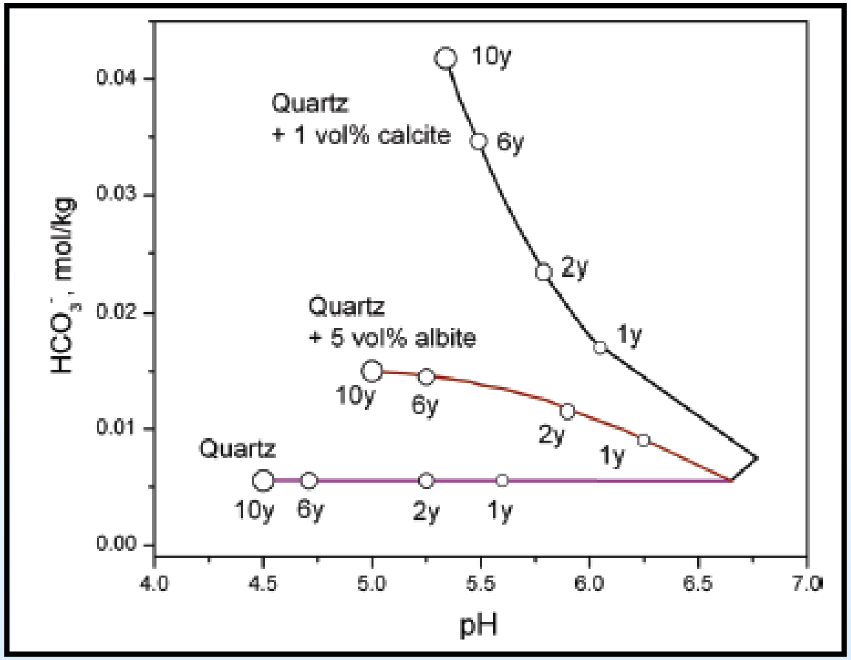
$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} \leftrightarrow H^+{}_{(aq)} + HCO_3^-{}_{(aq)}$$

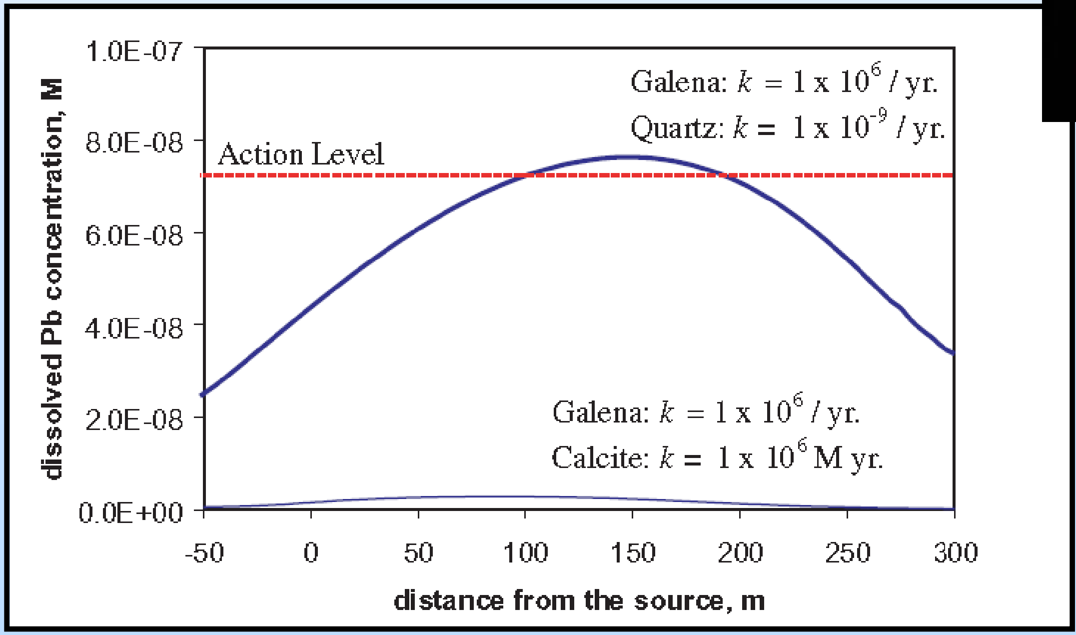
$$CaCO_{3(s)} + H^+{}_{(aq)} \leftrightarrow Ca^+{}_{(aq)} + HCO_3^-{}_{(aq)}$$



Previous Works…



Wilkin, R.T., DiGiulio, D.C., 2010. Geochemical Impacts to Groundwater from Geologic Carbon Sequestration: Controls on pH and Inorganic Carbon Concentrations from Reaction Path and Kinetic Modeling. Environmental Science & Technology 44, 4821-4827.

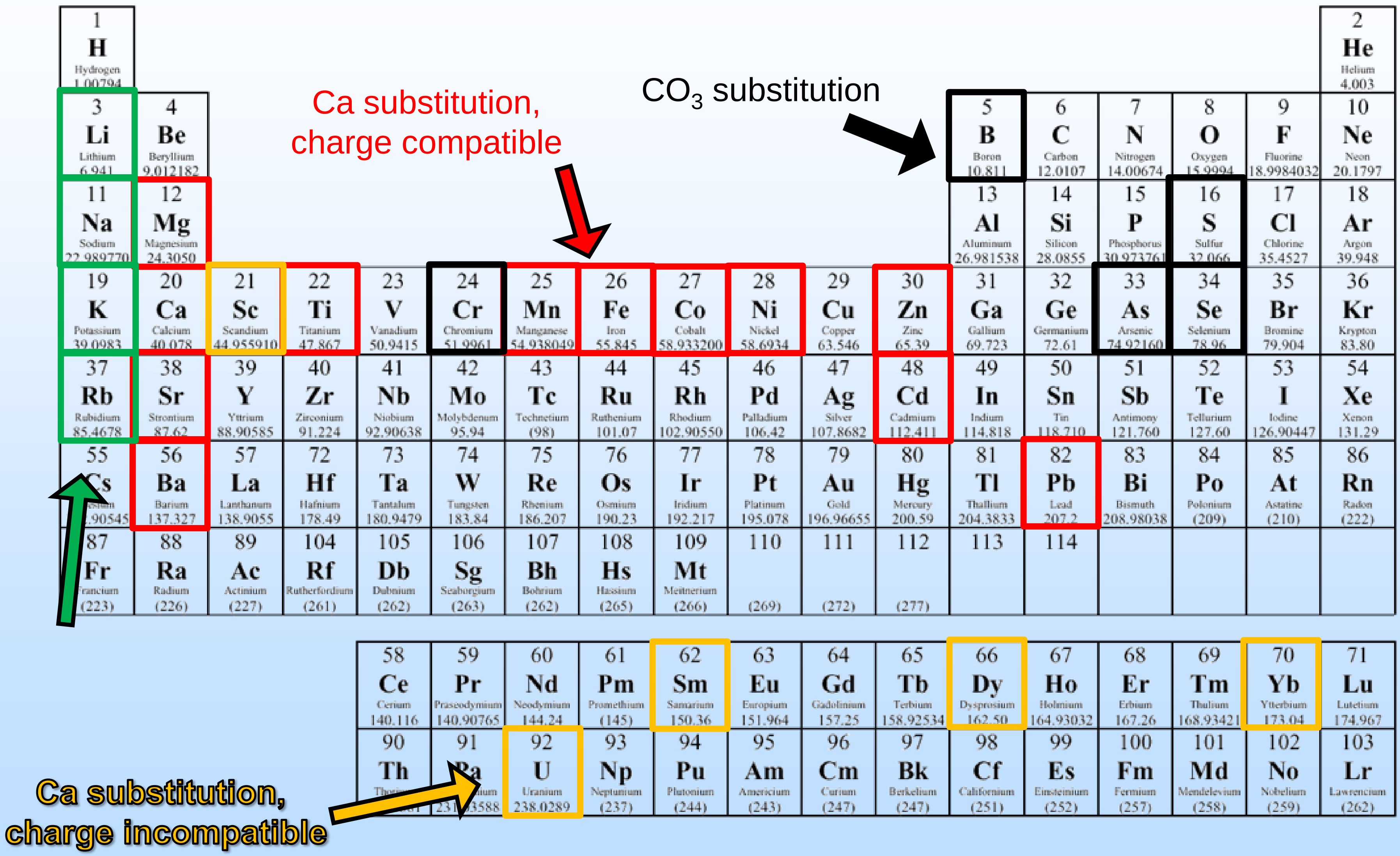


Wang, S., Jaffe, P.R., 2004. Dissolution of a mineral phase in potable aquifers due to CO_2 releases from deep formations; effect of dissolution kinetics. Energy Conversion and Management 45, 2833-2848.

Impurities in Calcite

$$Ca_{1-x}M_x(CO_3)_{1-y}(MO_3)_{y(s)} + H^+_{(aq)} \leftrightarrow (1-x)Ca^{2+}_{(aq)} + xM^{z+}_{(aq)} + (1-y)HCO^-_{3\,(aq)} + yMO^{z-}_{3\,(aq)}$$

$$CaCO_{3(s)} + H^+_{(aq)} \leftrightarrow Ca^{2+}_{(aq)} + HCO^-_{3\,(aq)}$$

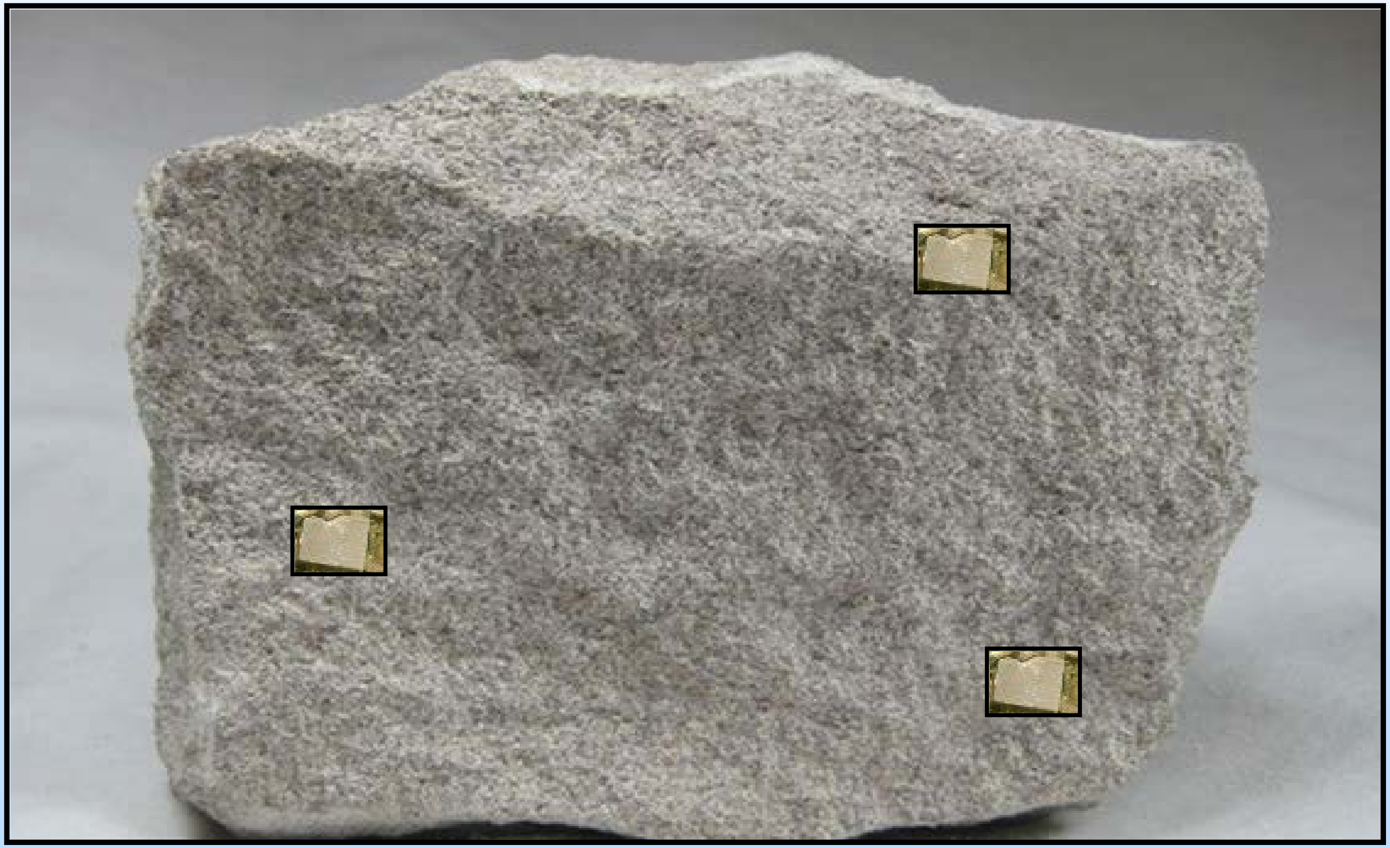


Conceptual Model:

Metals are released from dissolving calcite, exposing pyrite and other minerals, which also release metals

Research Question:

How much does each mineral phase contribute?



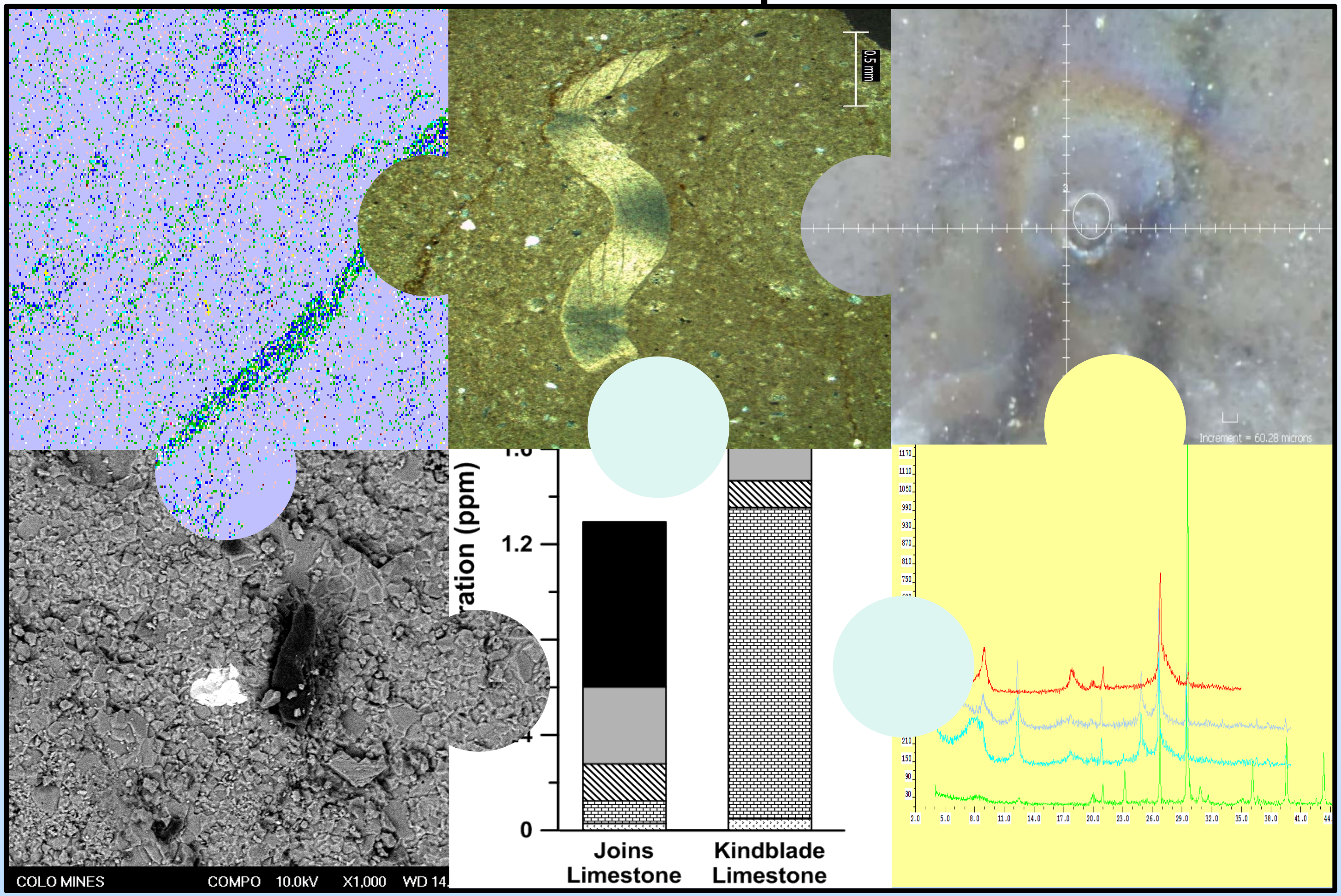
Experimental Work

Characterization (What's in the rock?)

QEMSCAN

Optical Microscope

LA-ICP-MS



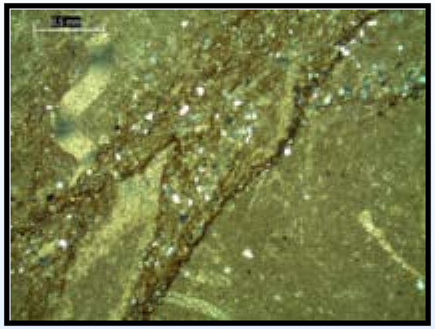
FE-SEM

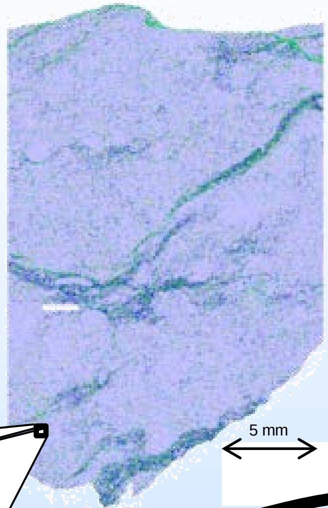
Sequential Extraction

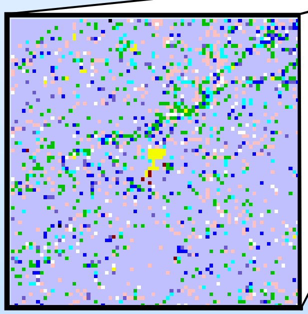
XRD

Rock Characterization for Carbonates

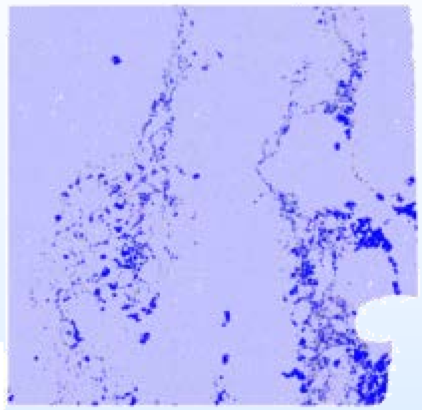
"Beaker 1" – Joins Limestone

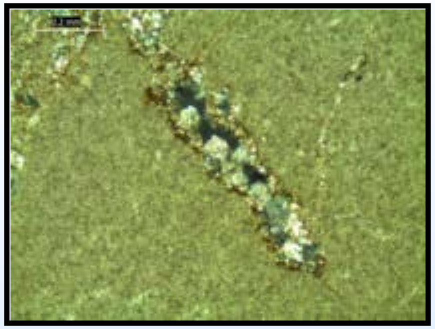






"Beaker 2" – Kindblade Limestone



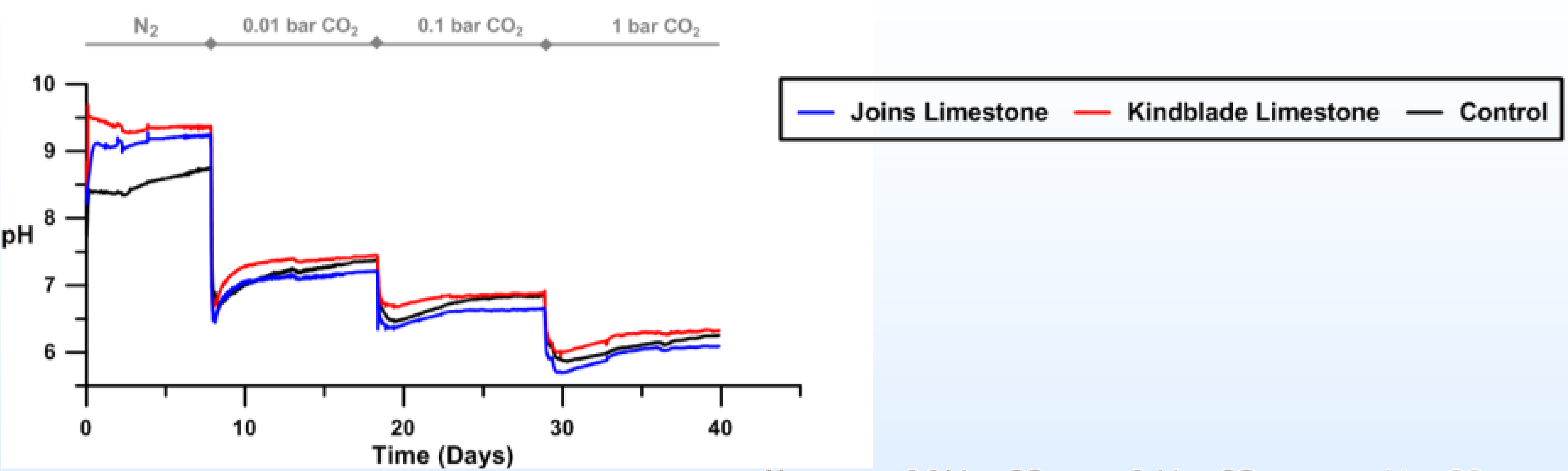


Mineral Abundance (%)		
	Joins	**Kindblade:**
Calcite	77.04	89.23
Quartz	7.04	3.58
Clay	**6.65***	0.43
Dolomite	4.68	5.58
Feldspar	2.25	0.01
Calcite (Mg-Bearing)	1.94	1.12
Pyrite	0.20	0.03
Ca-SO_4/Anhydrite/Gypsum	0.13	0.01
Others	0.07	0.01
Apatite	0.01	0.00
BET Surface Area (m^2/g)	0.245	0.152

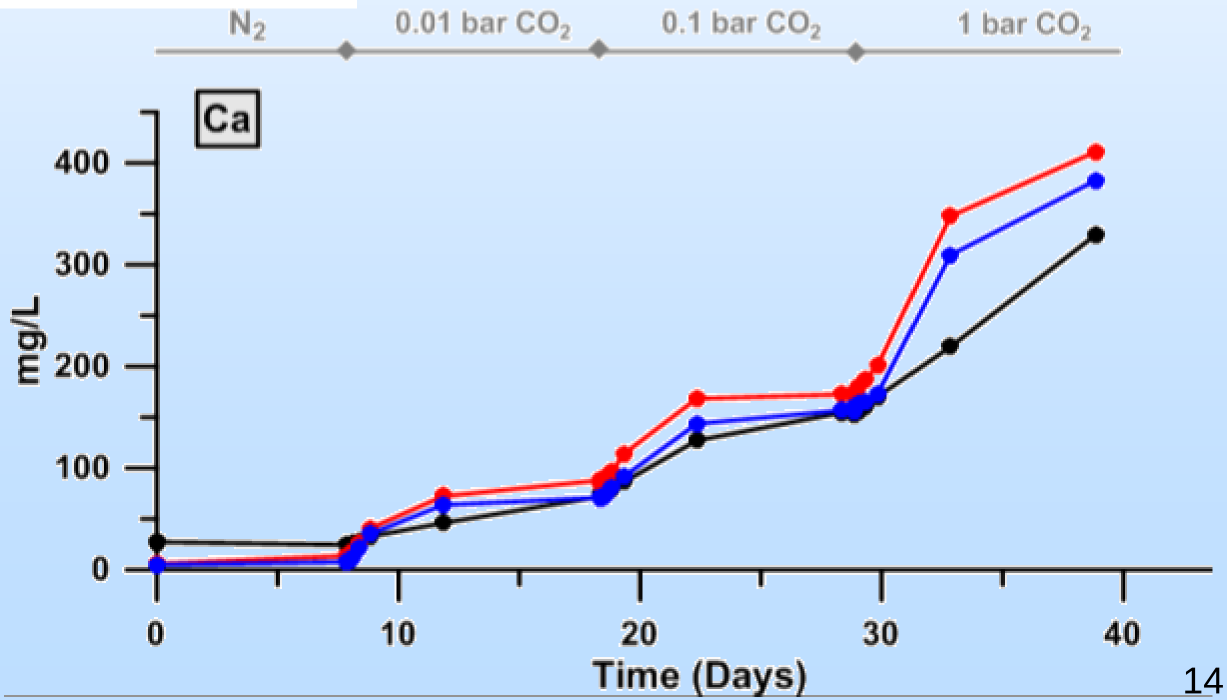
*** Illite / Glauconite**

Control - >99.999% Pure $CaCO_3$

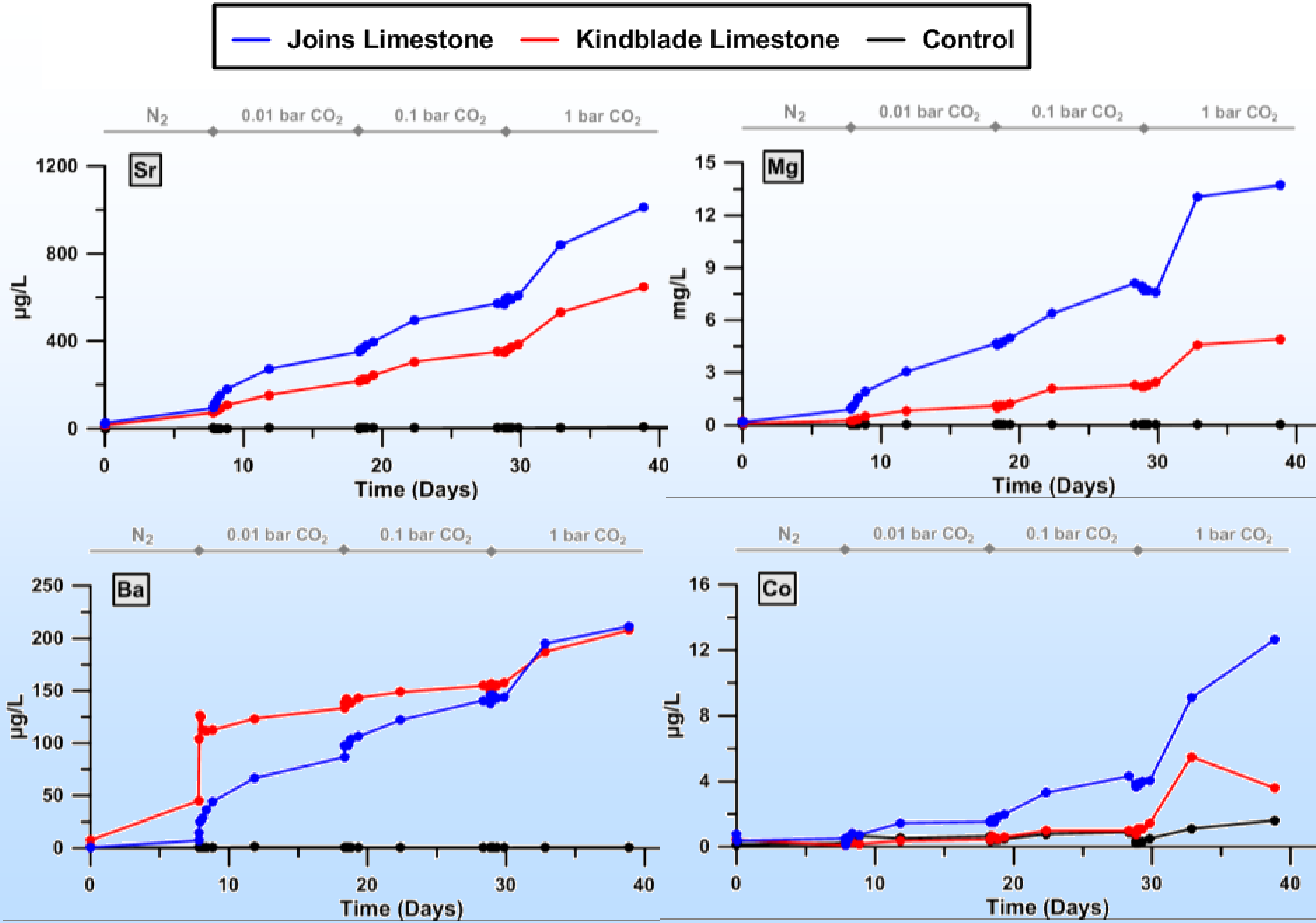
Results



N2
0.01 bar CO2
0.1 bar CO2
1 bar CO2
pH
10
9
8
7
6
0
10
20
30
40
Time (Days)
Joins Limestone
Kindblade Limestone
Control



N2
0.01 bar CO2
0.1 bar CO2
1 bar CO2
Ca
mg/L
400
300
200
100
0
0
10
20
30
40
Time (Days)

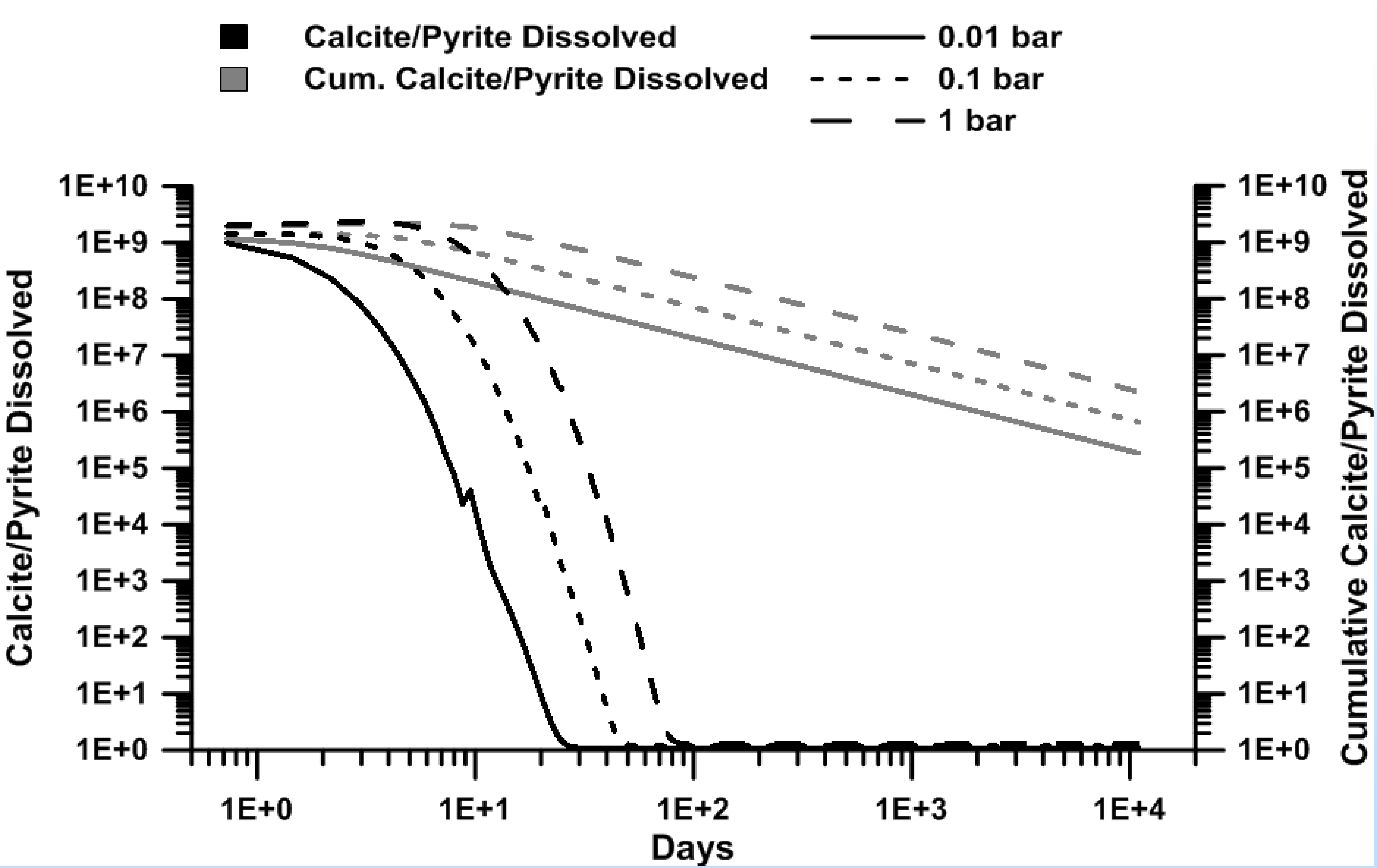


Joins Limestone
Kindblade Limestone
Control
N_2
0.01 bar CO_2
0.1 bar CO_2
1 bar CO_2
Sr
μg/L
Time (Days)
Mg
mg/L
Ba
Co

Placing the experimental results in context: Dissolution of “dirty” pyrite vs.“clean” calcite

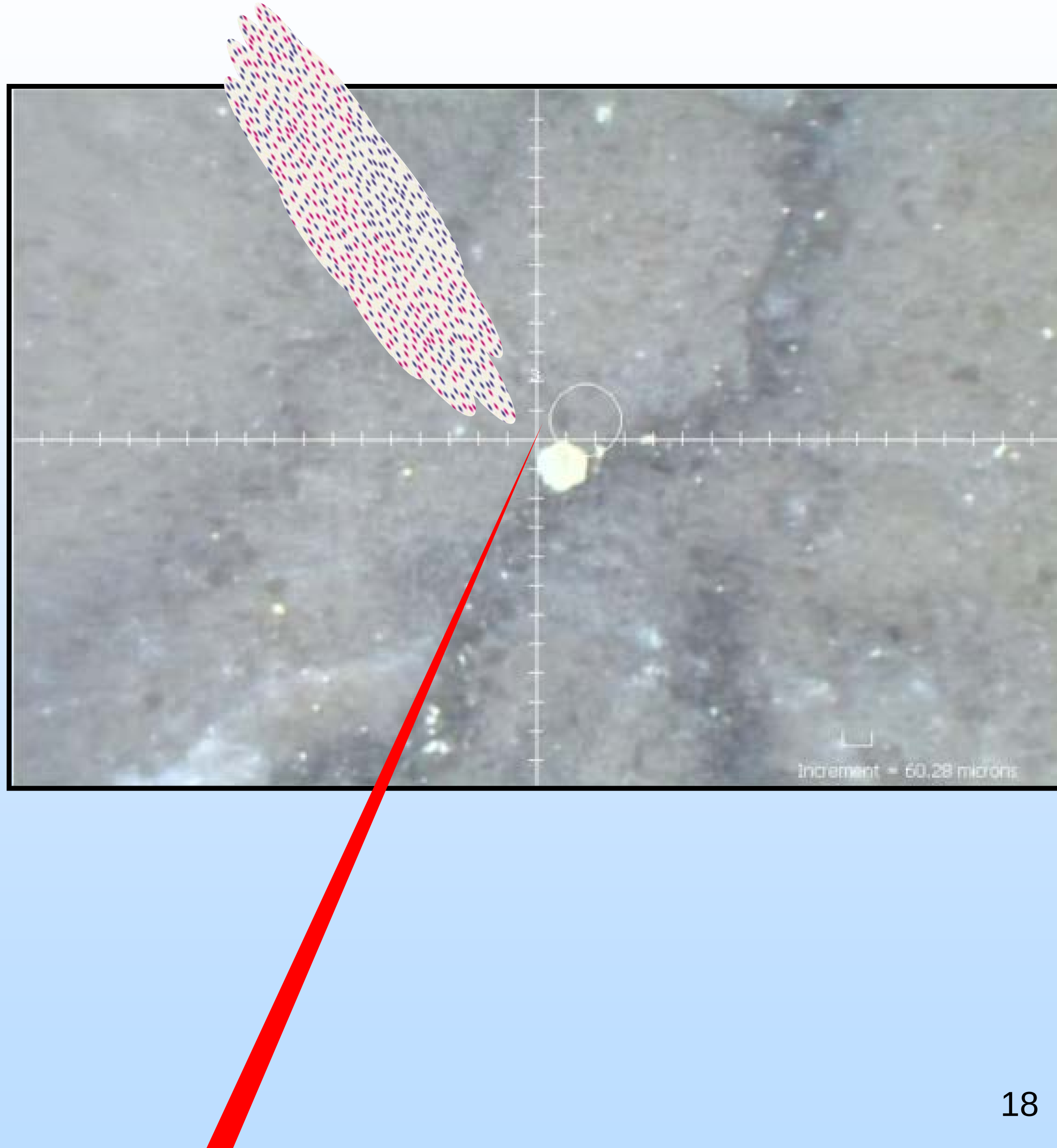
- Carbon sequestration operations could occur over 30 years.
- Use a geochemical model (PHREEQC) to extrapolate experimental results to longer time periods
- Develop reliable conceptual and mathematical models
- First step, do the QEMScan mineral assemblages enable us to simulate our experimental data?
- Adjust and parameterize model to simulate long-term impacts of leakage under simple conditions.

Long-Term Predictions



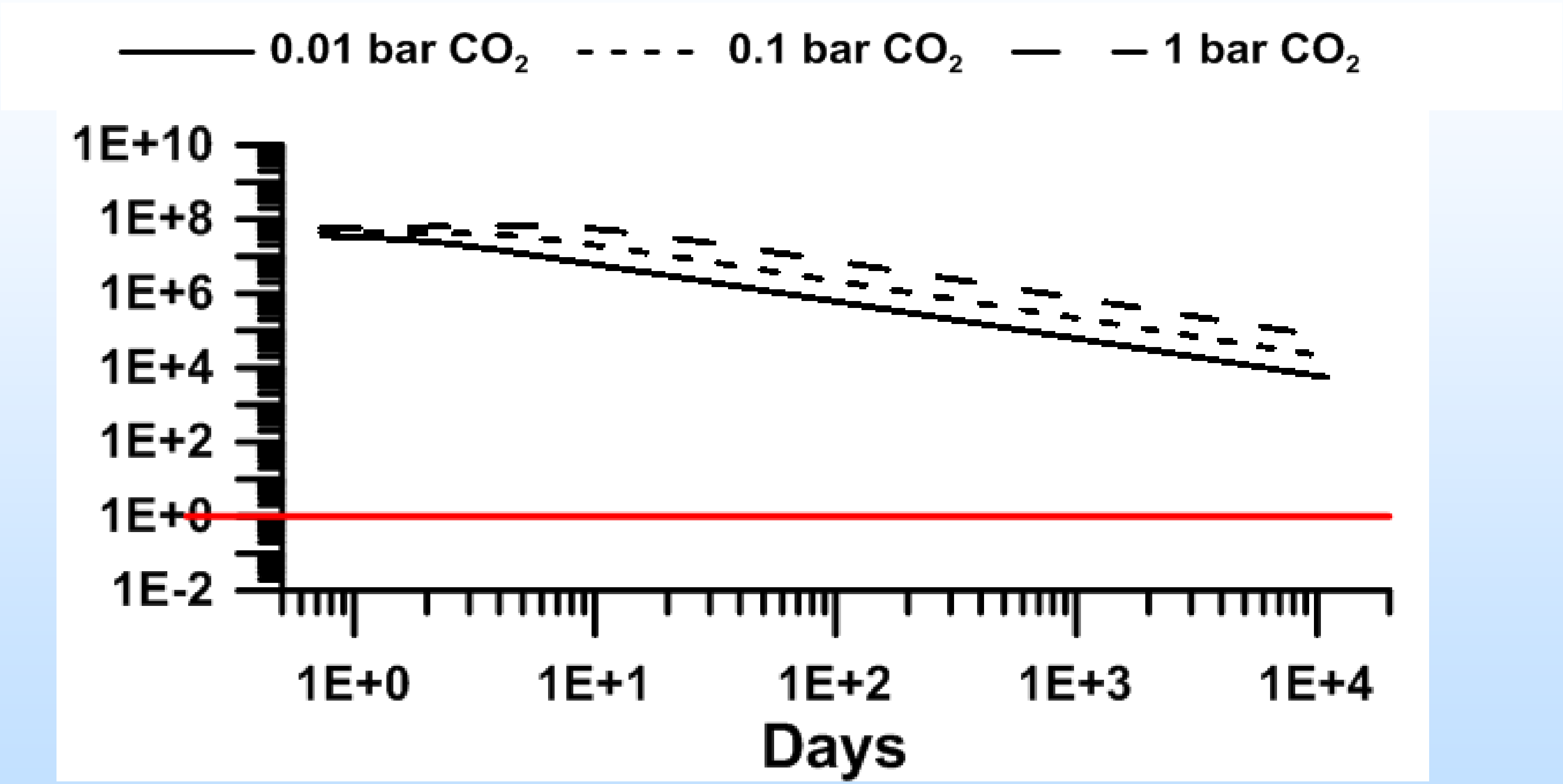
Higher concentration of impurities in Pyrite

	Pyrite/Calcite
Cr	1.49
Co	29.06
Ni	24.12
As	74.82
Rb	2.45
Sr	1.06
Tl	20.72
Pb	20.43
U	9.46



Cumulative Cobalt Release from Calcite

Cumulative Cobalt Release from Pyrite



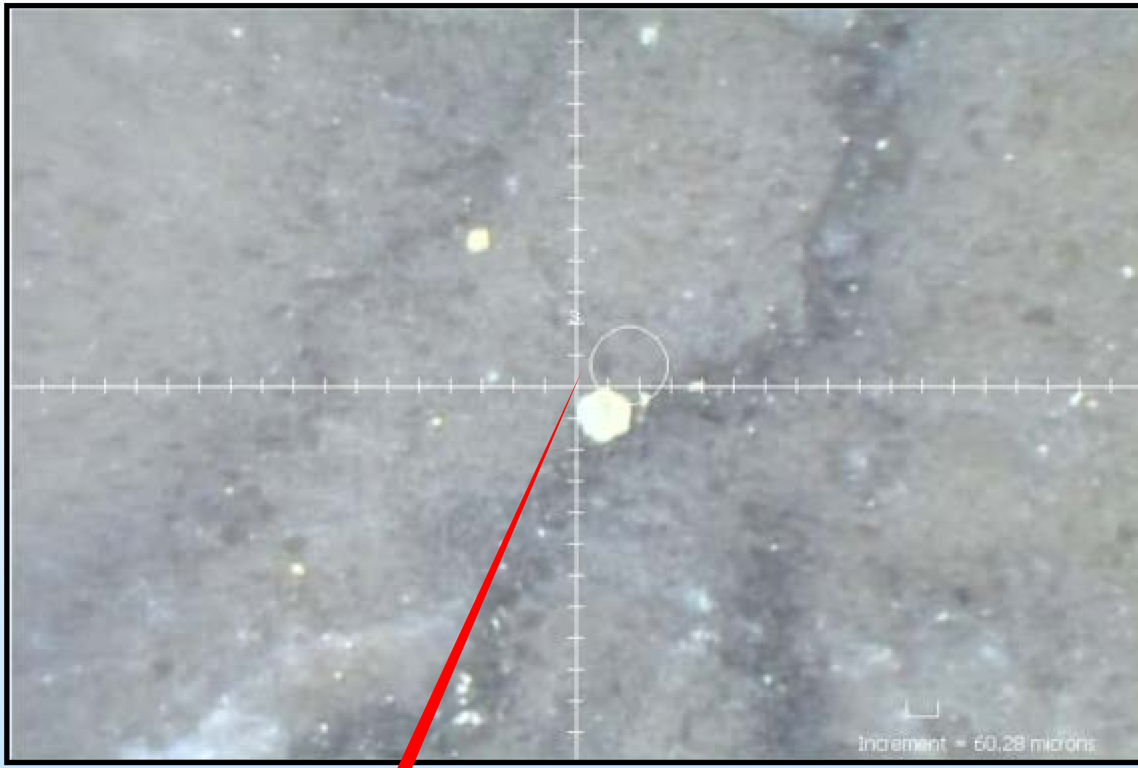
Pyrite dissolution is more sensitive to oxidizing conditions. Our *experiments* were under conducted under somewhat reducing conditions, but many *aquifers* have oxidizing conditions.

Use modelling to investigate the influence :

pO_2 varied up to -2.5 (D.O. ~ 0.15 mg/L)

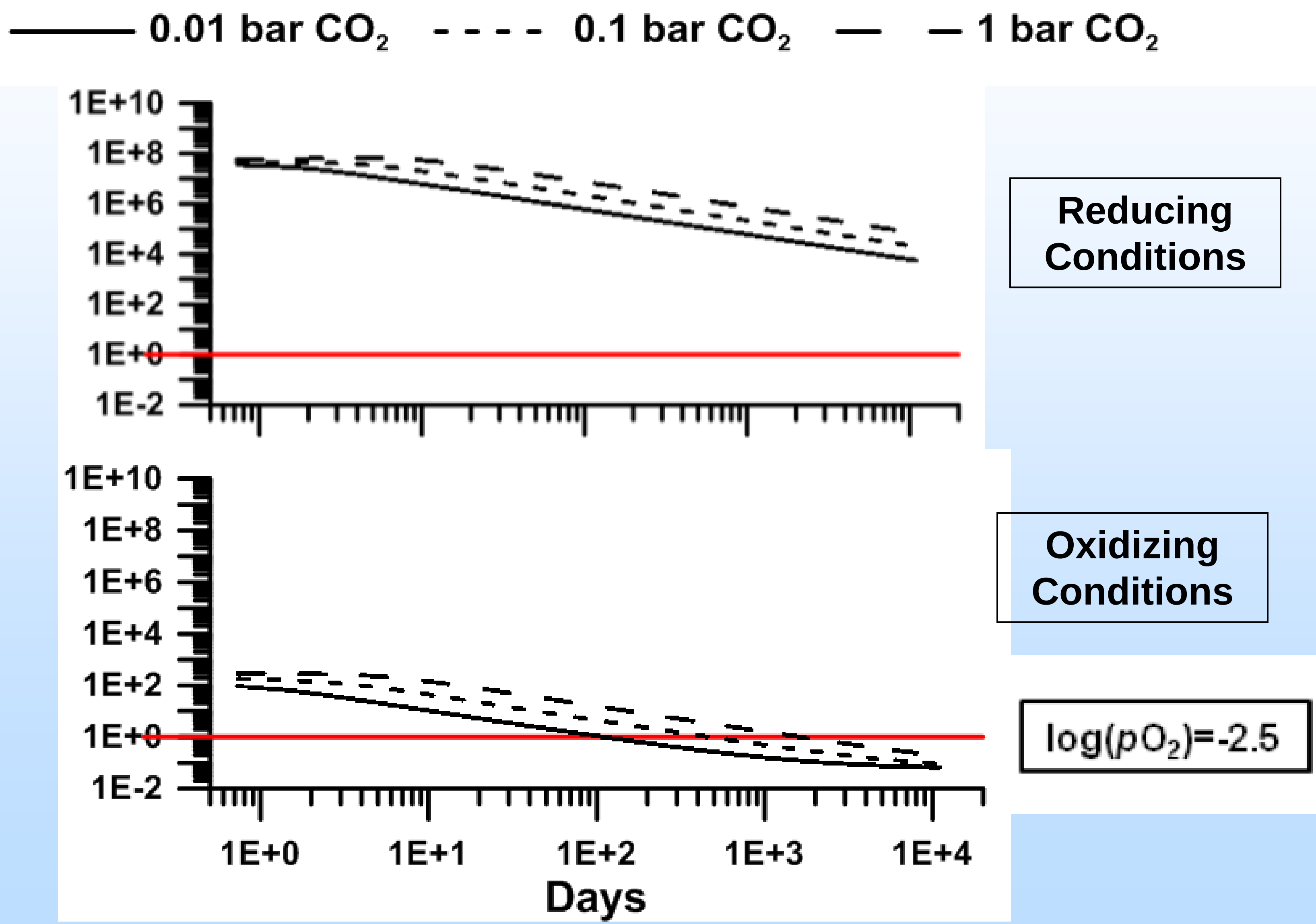
Conceptual Model for Pyrite dissolution in Oxidizing aquifers

Carbonate dissolves to expose pyrite that did not previously participate in the dissolution process.



Cobalt Release from Calcite

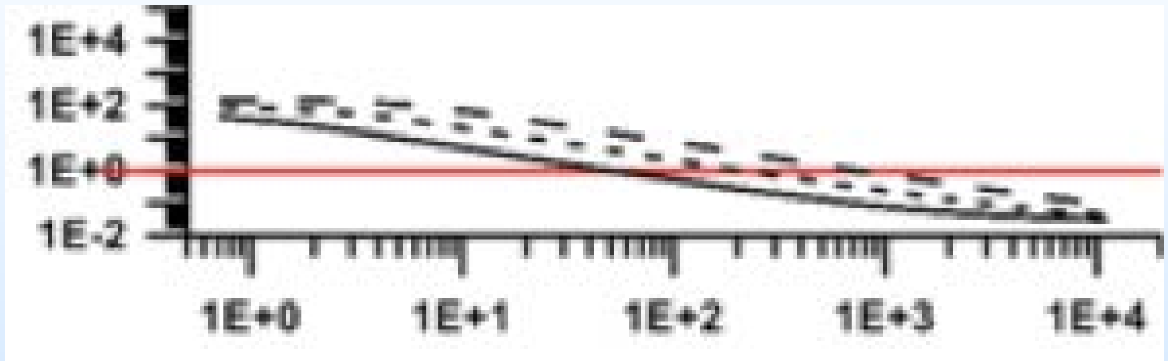
Cobalt Release from Pyrite



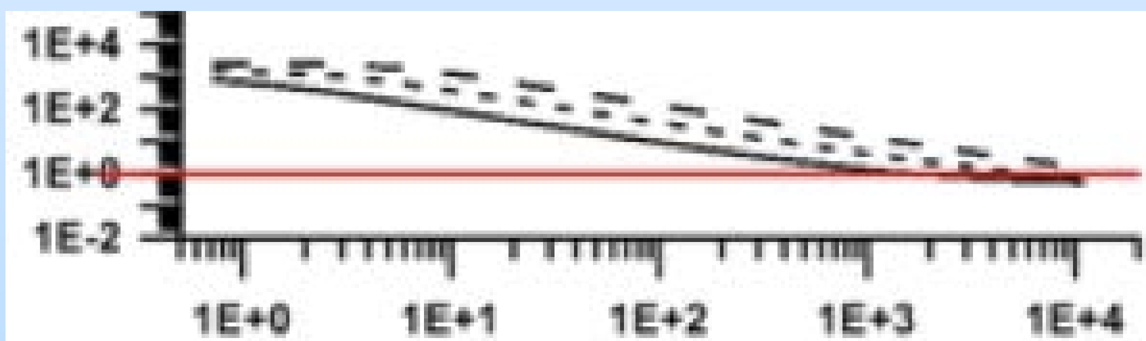
$\log(pO_2)=-2.5$

——— 0.01 bar CO_2 - - - - 0.1 bar CO_2 — — 1 bar CO_2

Arsenic



Barium



Days

Conclusions: CO_2 Leakage into Limestone

- Carbonate minerals can buffer pH at elevated pCO_2, but at the "cost" of carbonate minerals dissolution.

- Dissolution of carbonate minerals contributes to release of metals.

- In both short and long term, calcite dissolution controls release of several trace elements in carbonate aquifers, BUT

- Under oxidizing conditions, pyrite is the major metal source (as expected)

- Most trace elements did not exceed MCL (exceptions: Cr, As, Ni)

- Experiments could be successfully modeled using PHREEQC if the appropriate rate expressions were chosen.

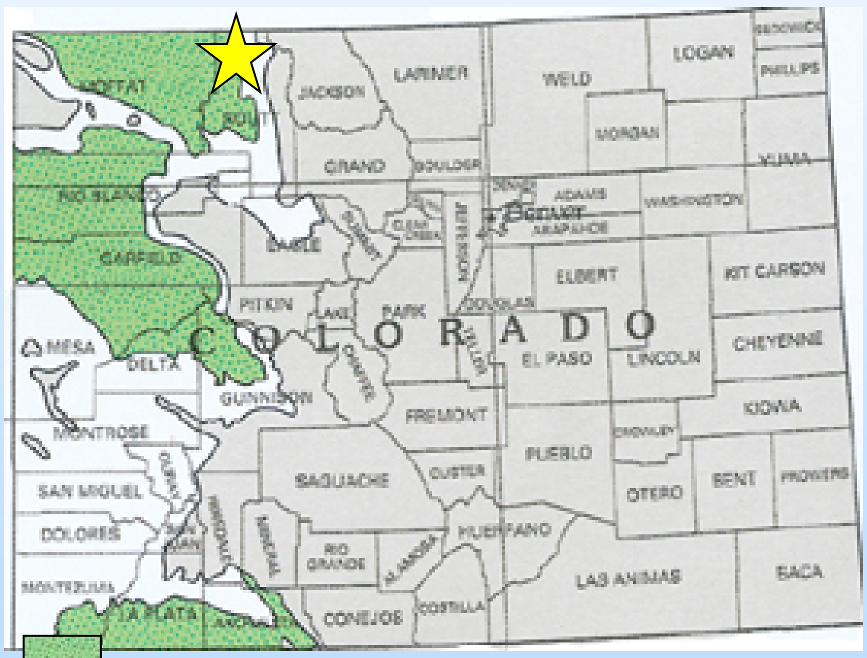
4 types of experiments: ***Limestones***, Dolomites, Clayey Limestones, **Silliclastic Rocks**

CO_2 Leakage into ***Siliclastic Aquifer Rocks***

Katie Kirsch, Alexis Sitchler, Assaf Wunsch, John McCray

Pressured leakage experiments for aquifer sandstone sediments

Sequential extractions to understand specific mechanism of metal release

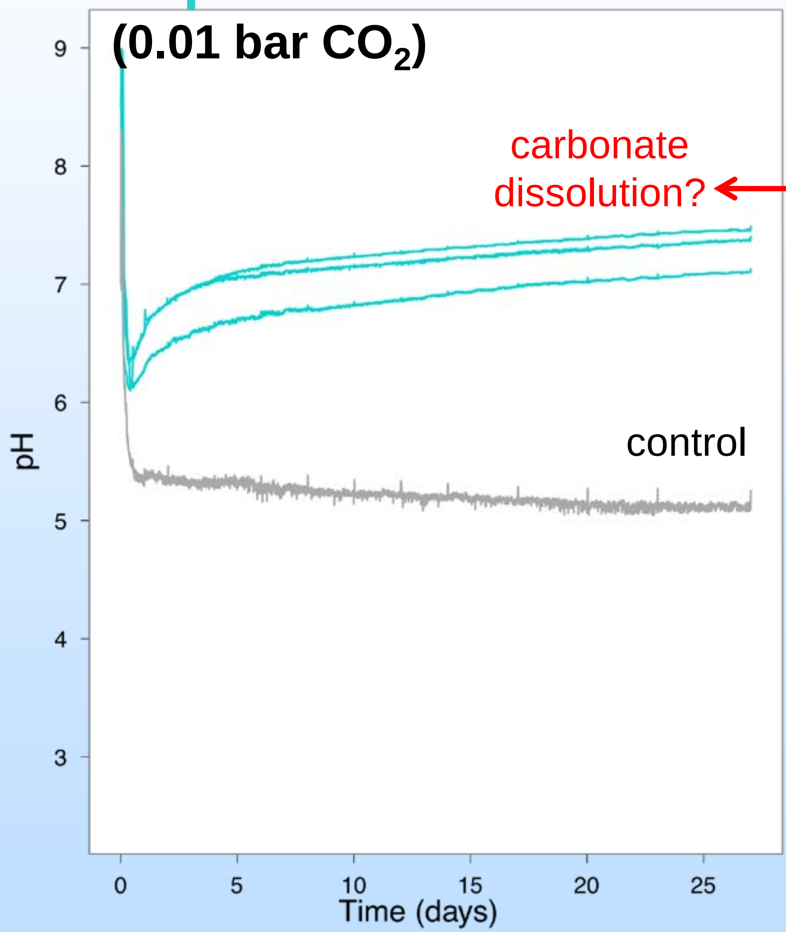


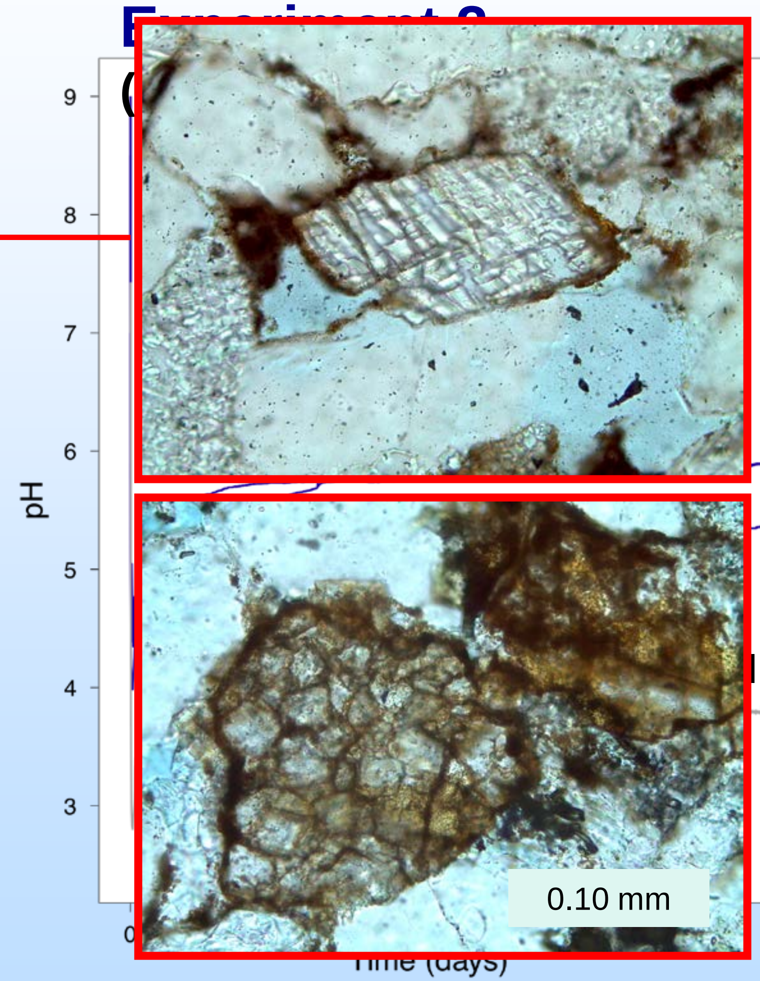
Outcrop of the Mesaverde Group

Significant pH buffering

Experiment 1:

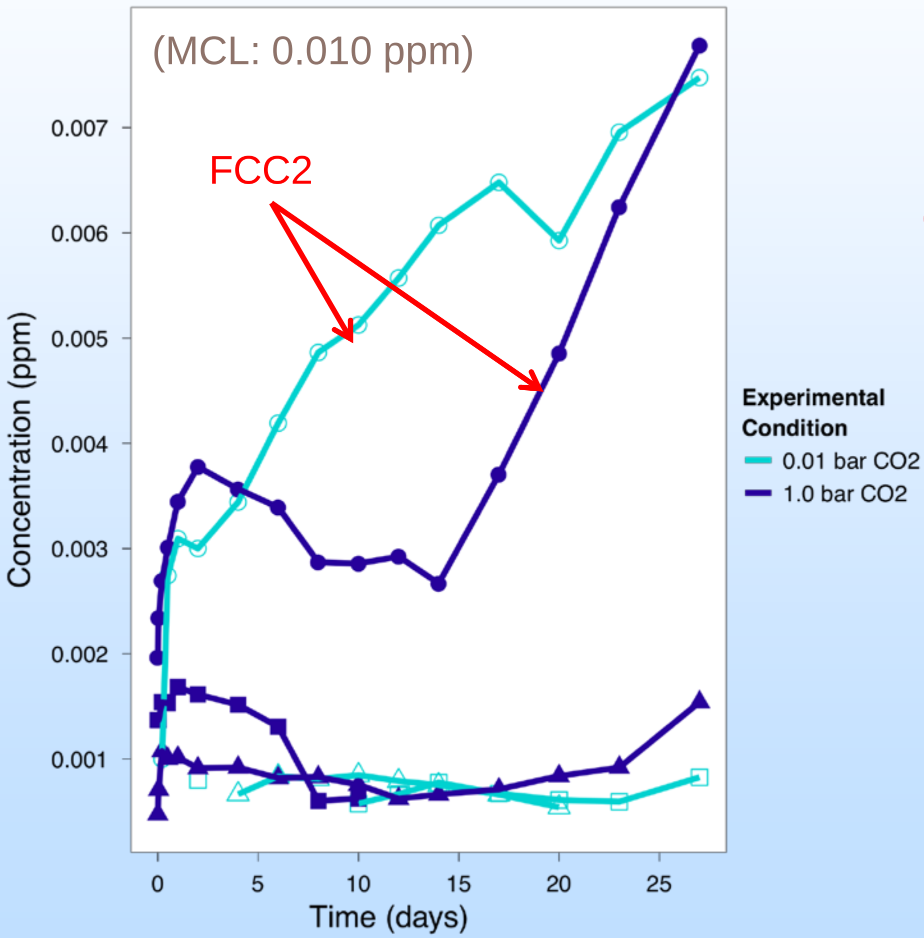
(0.01 bar CO_2)

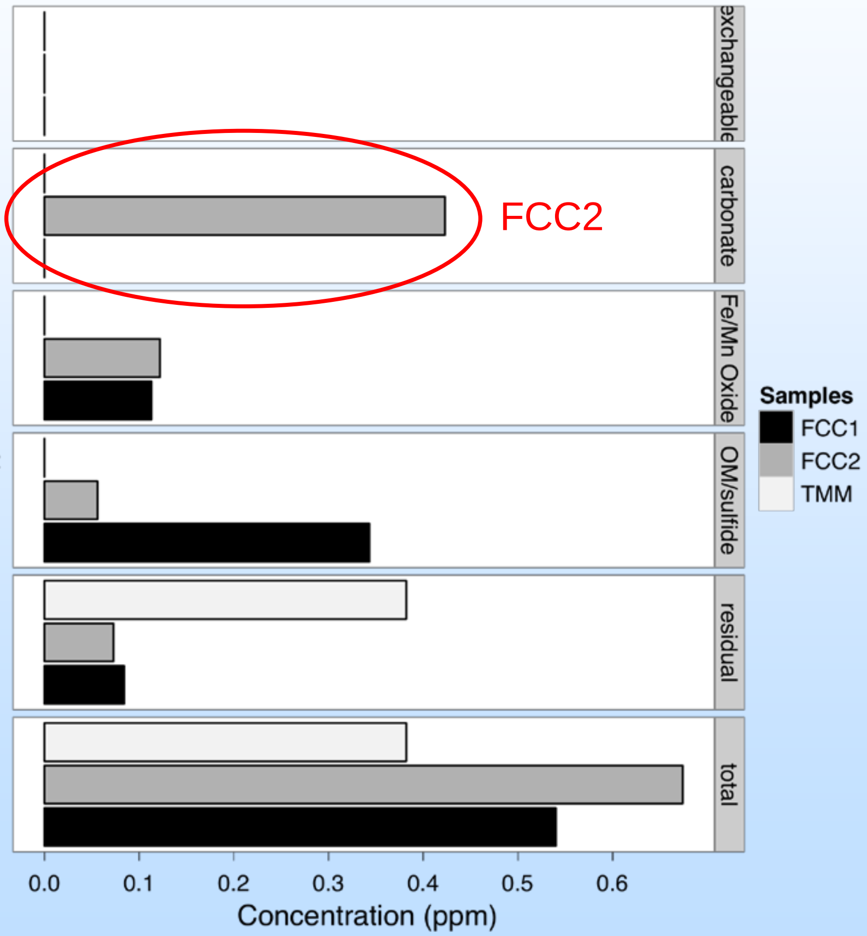




Carbonate dissolution – likely source of metals

Arsenic





Conclusions: CO_2 Leakage into Sandstone

Sandstones may have a significant pH buffering capacity, probably due to carbonate cement.

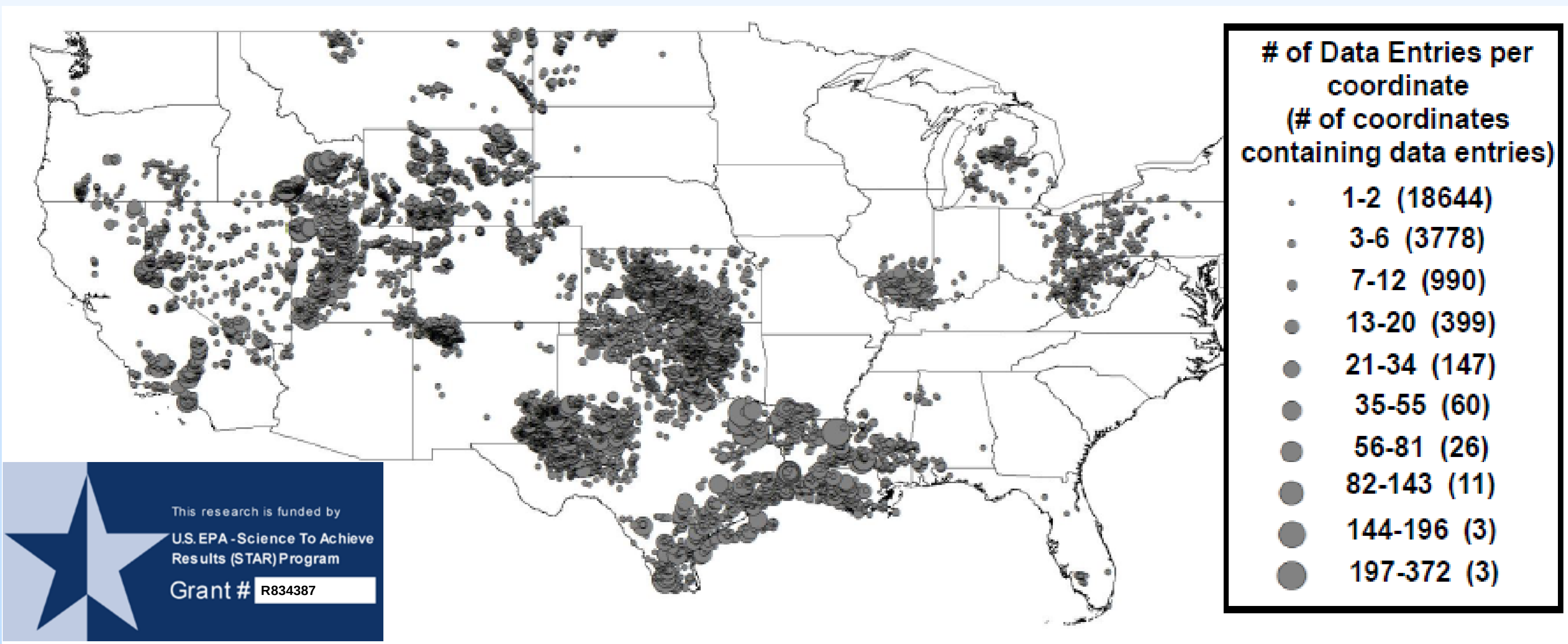
Metals are released after CO_2 exposure, although MCL concentrations were not achieved in these batch-”equilibrium” experiments.

Carbonates are a significant source, along with oxides.

groundwater

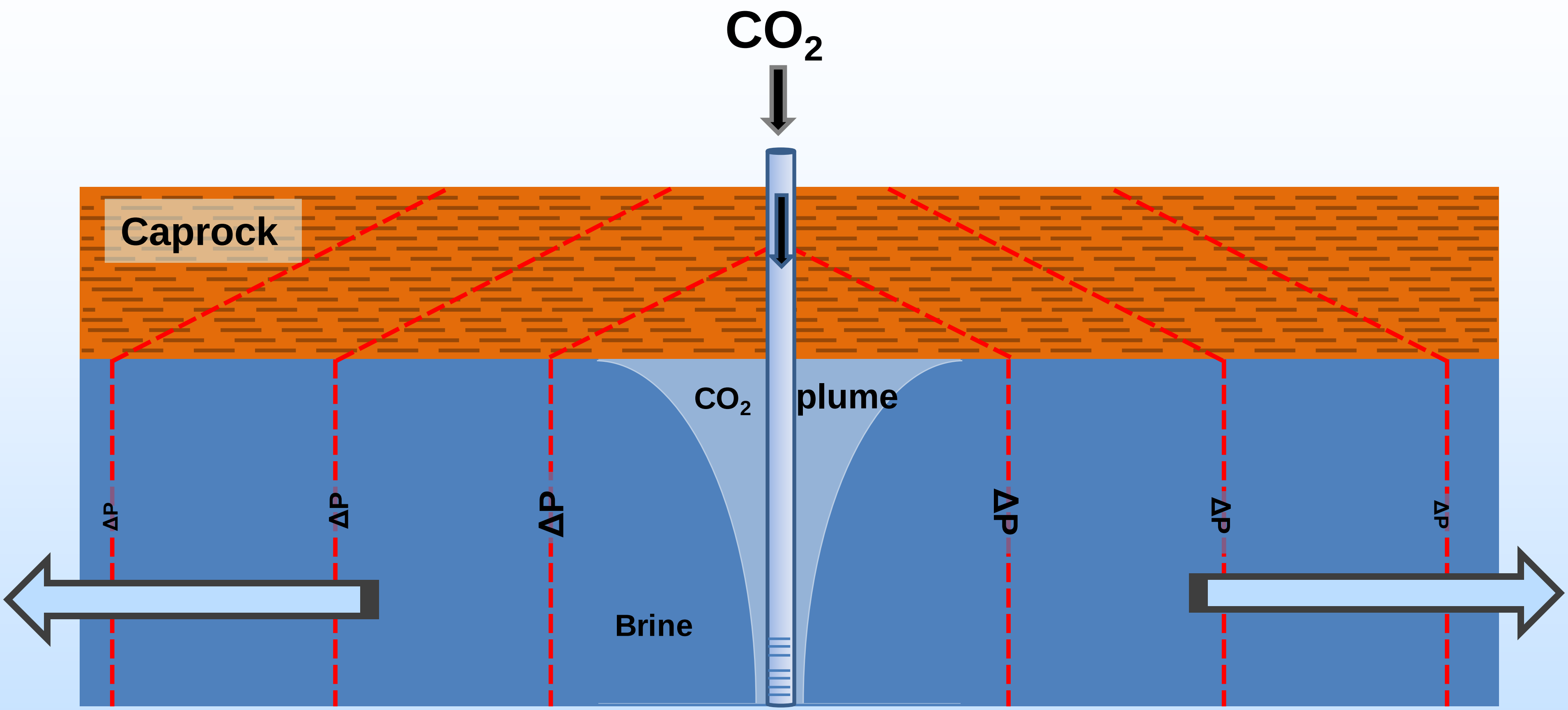
Geochemical Implications of Brine Leakage into Freshwater Aquifers

by Assaf Wunsch[1,2], Alexis K. Navarre-Sitchler[2,3], and John E. McCray[2,4]

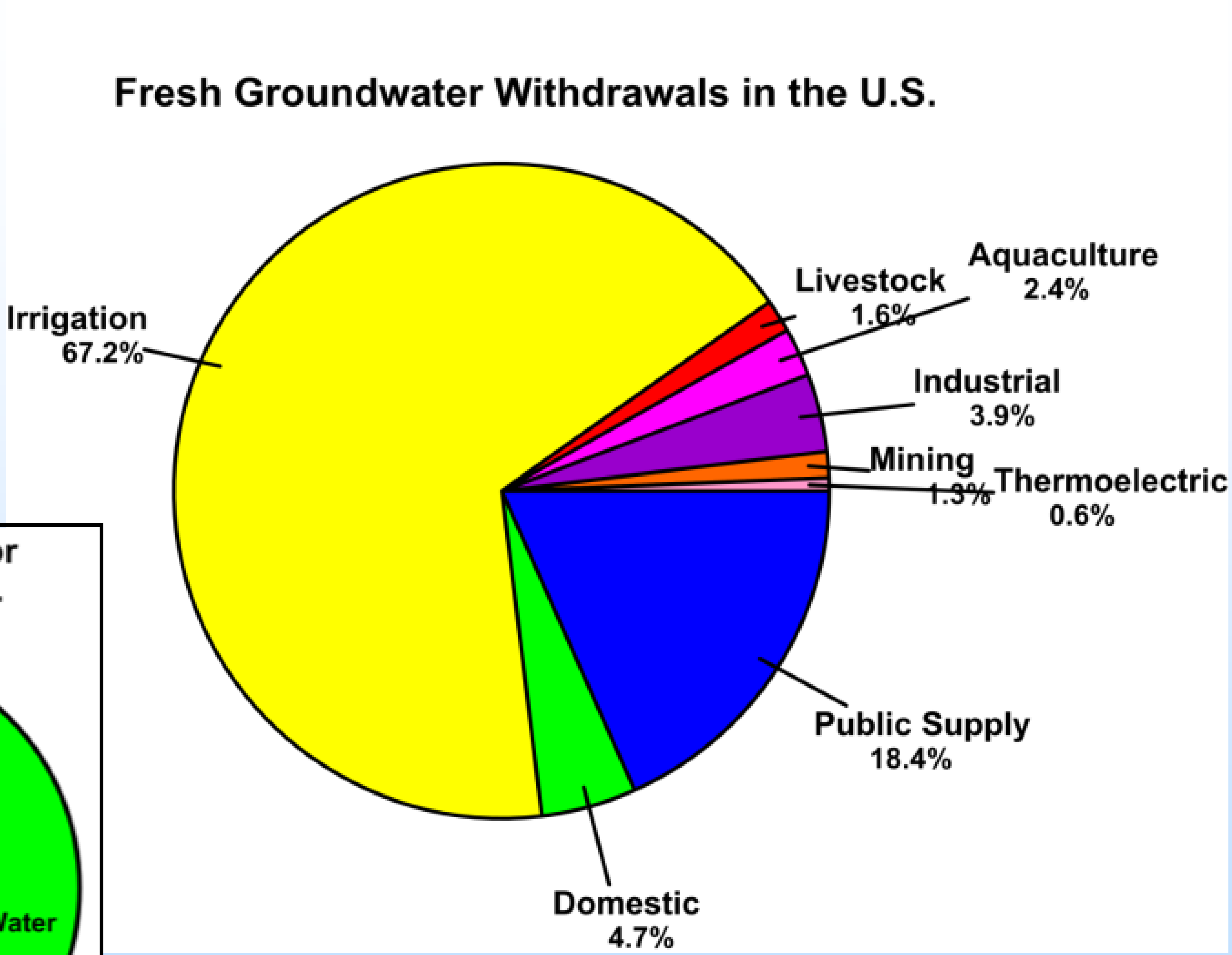


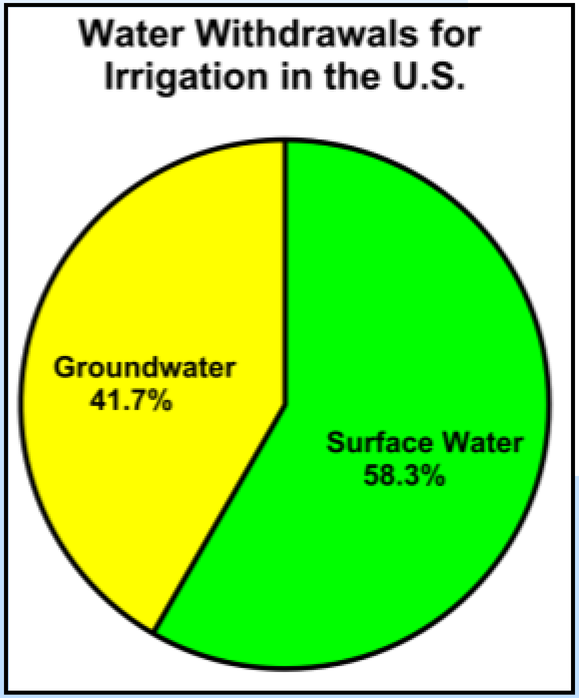
Statistical analysis of the NETL NatCarb Brine Database

Saline leakage may occur far outside CO_2 plume



Drinking Water and Agricultural Impacts





Data from: Kenny, J.F., N.L. Barber, S.S. Hutson, K.S. Linsey, J.K. Lovelace, and M.A. Maupin. 2009. Estimated use of water in the United States in 2005. U.S. Department of the Interior, U.S. Geological Survey, Circular 1344.

Drinking Water Statistical Analysis

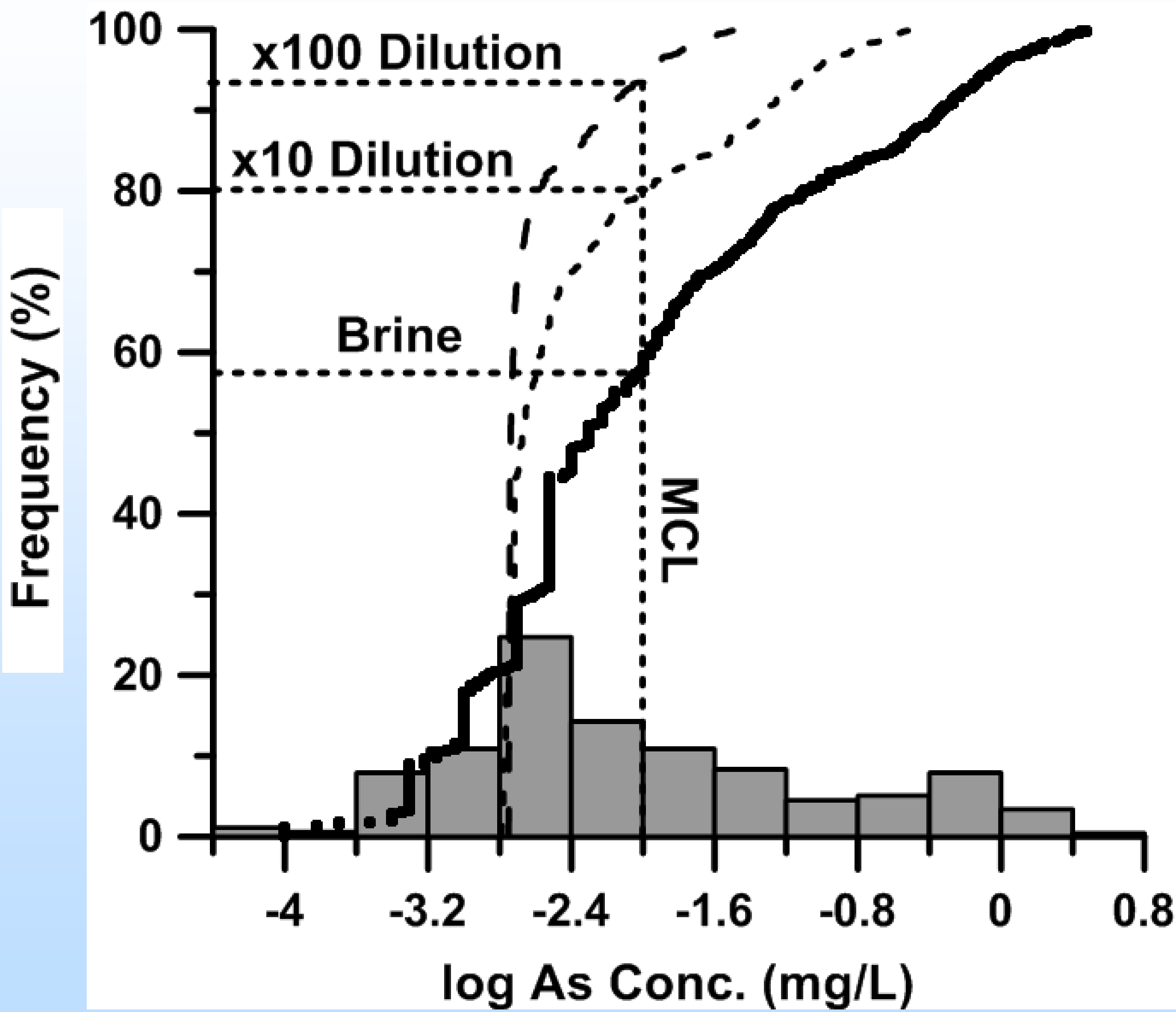
- **"Representative values" (medians) were mostly below regulatory limits for drinking water**

- **Except…**

Parameter	n	Median	95th Percentile	Regulatory Value	Percentage Above Regulatory Value
Cl	49634	<u>50,900</u>	160,000	250[b]	98.0
Fe	2213	<u>7</u>	431	0.3[b]	78.4
Mn	878	<u>0.07</u>	124	0.05[b]	53.0
NO_3	54	<u>11</u>	84	10[a]	51.2
SO_4	43024	<u>549</u>	5300	250[b]	63.55
TDS[f]	46990	<u>84407</u>	251662	500[b]	100
pH	37958	7.10	5.6 / 8.21[e]	6.5<pH<8.5[b]	74.98% are within regulatory limits

[a] EPA maximum contaminant level (MCL) for drinking water
[b] EPA secondary standard for drinking water
D [f] Total dissolved solids, in mg/L

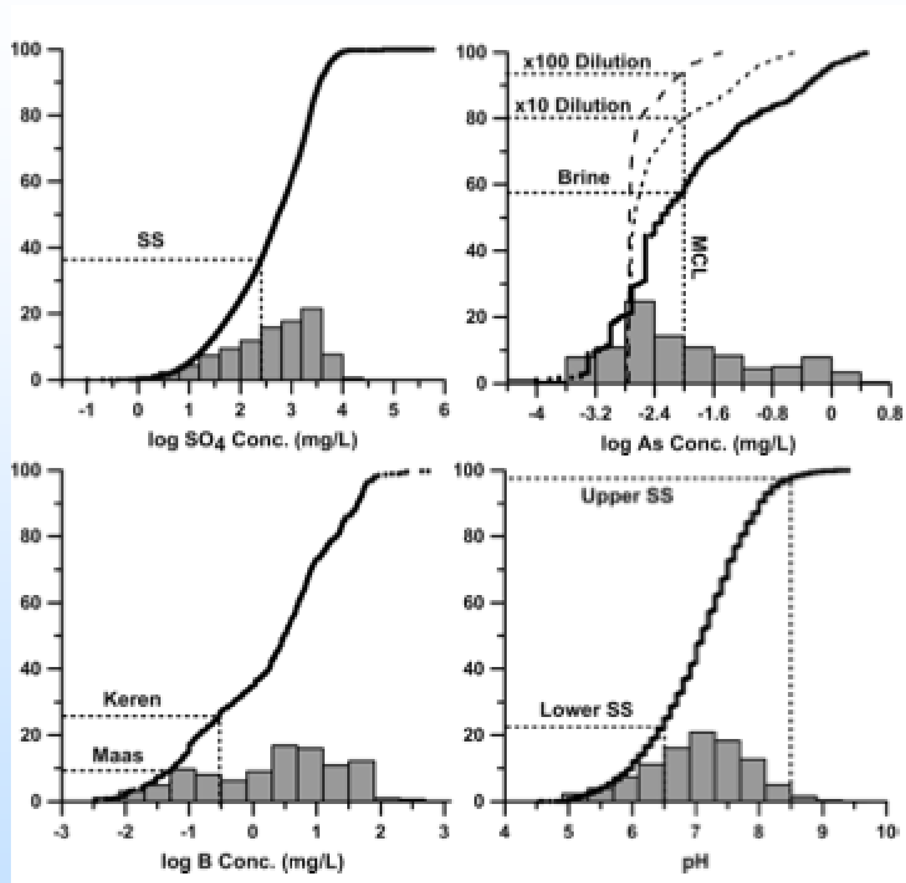
Cumulative Frequency Diagrams



Selected Conclusions: Drinking Water

Median concentrations of **chloride, iron, manganese, sulfate and nitrate** are expected to exceed regulatory standards.

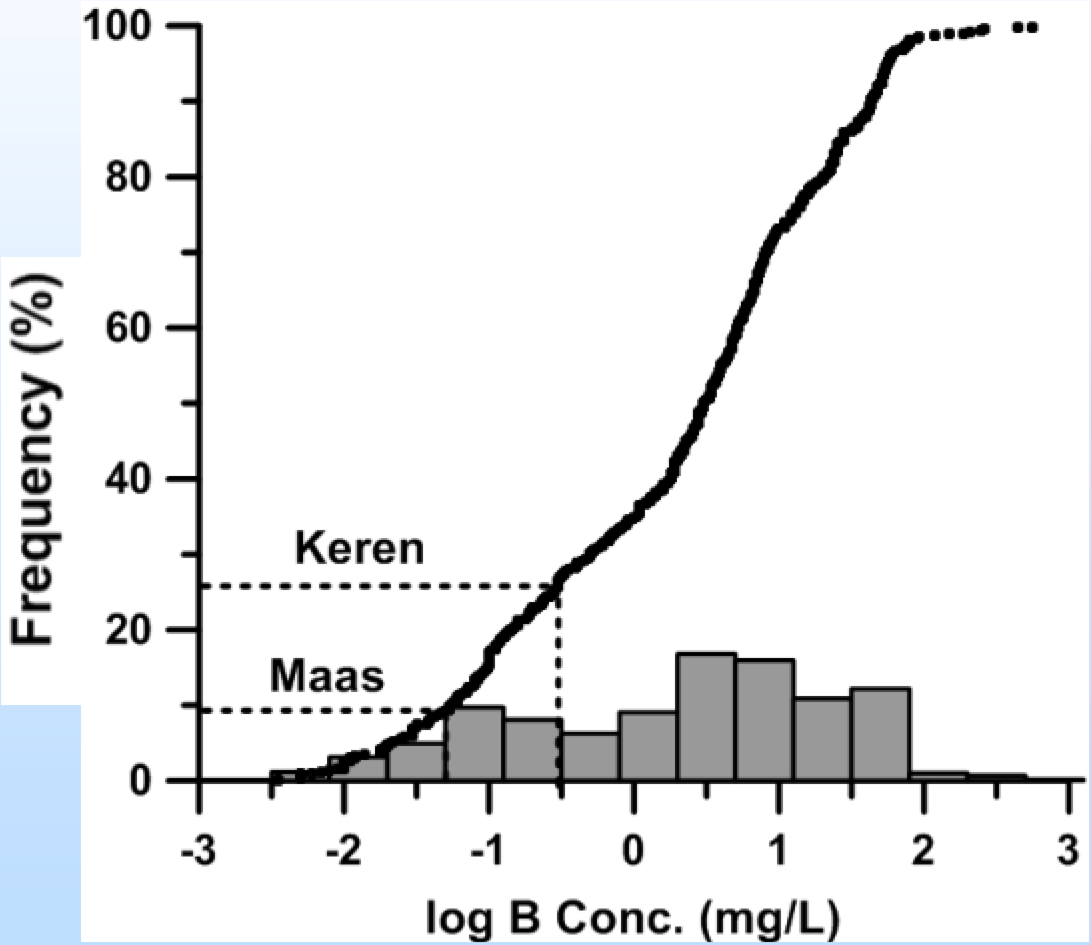
Arsenic - low risk of exceeding regulatory levels. However, overall distributions span orders of magnitude above regulatory levels, causing concern even upon dilution with fresh groundwater.

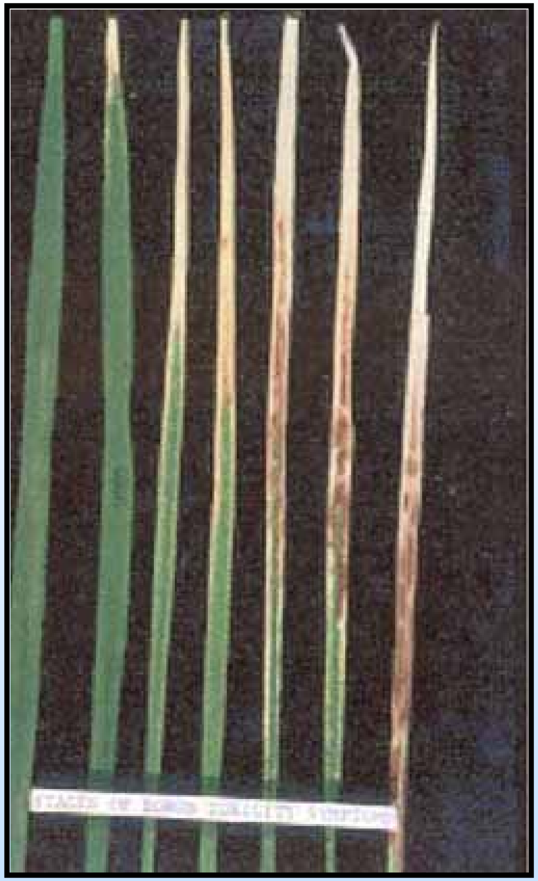


TDS concentrations in aquifers may exceed USEPA secondary standard for a brine fraction > 0.004.

pH not a good indicator for brine leaks into aquifers.

Agricultural Impacts: Boron

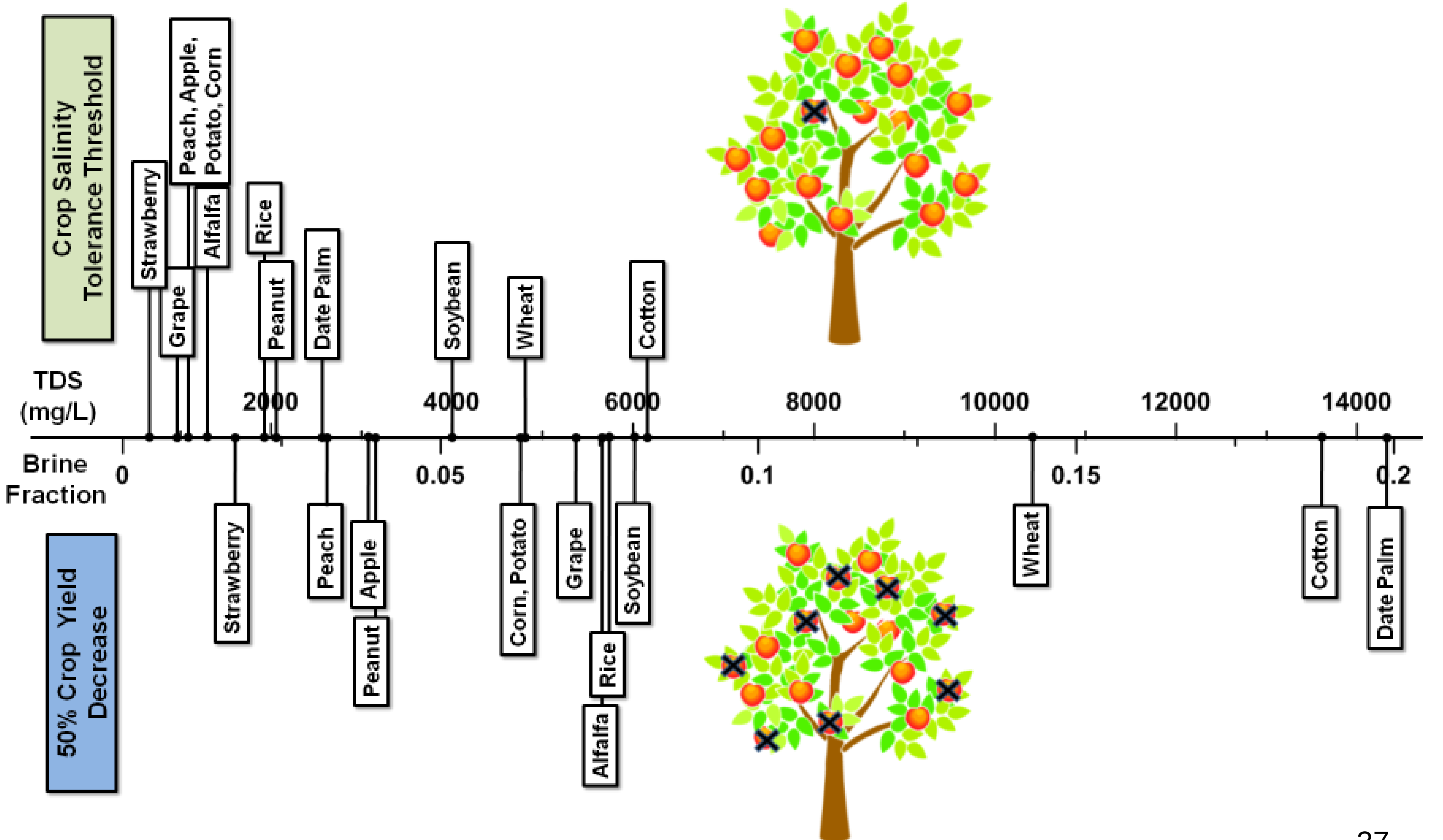




http://www.agnet.org/library.php?func=view&id=20110804094714&type_id=2

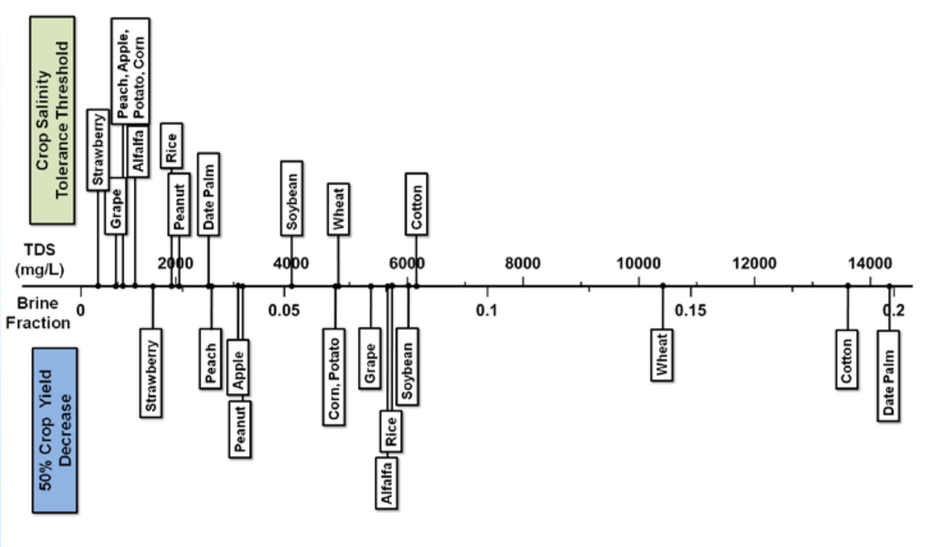
Agricultural Impacts: Total Dissolved Solids

$$TDS_{mix} = f_b TDS_b + (1 - f_b) TDS_w$$



Selected Conclusions: Agriculture

A brine fraction of 0.1 in a brine-aquifer mixture, will cause reduction in crop yield of most US crops due to salinity.



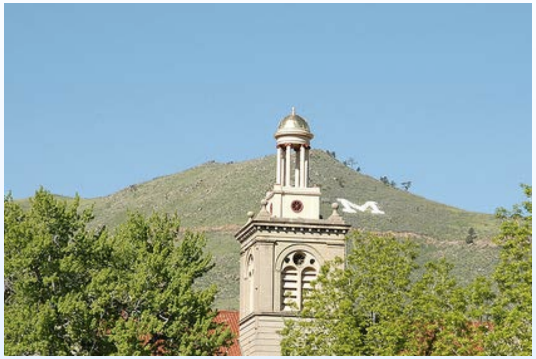
Some crops may become affected at brine fractions as low as 0.004.

High boron concentrations may affect crop development.

Iron- or manganese-rich brine may damage irrigation pipes through precipitation of oxides.

Questions?

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R834387



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