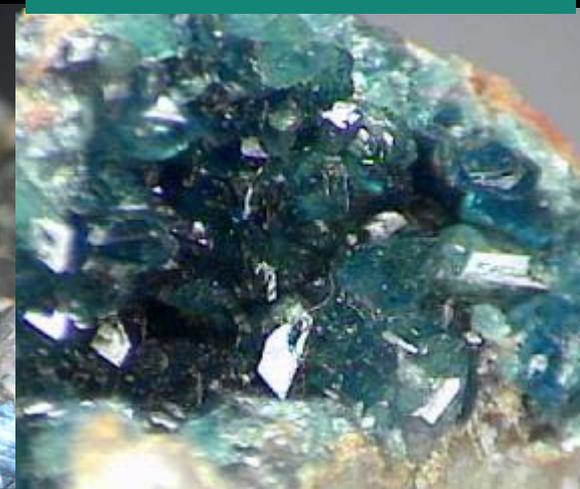


# ENVIRONMENTAL GEOCHEMISTRY OF ARSENIC AND ITS BIOREMEDIATION IN CONTAMINATED GROUNDWATER

Orpiment (yellow)  $\text{As}_2\text{S}_3$

Scorodite  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$



Realgar (red)  $\text{AsS}$

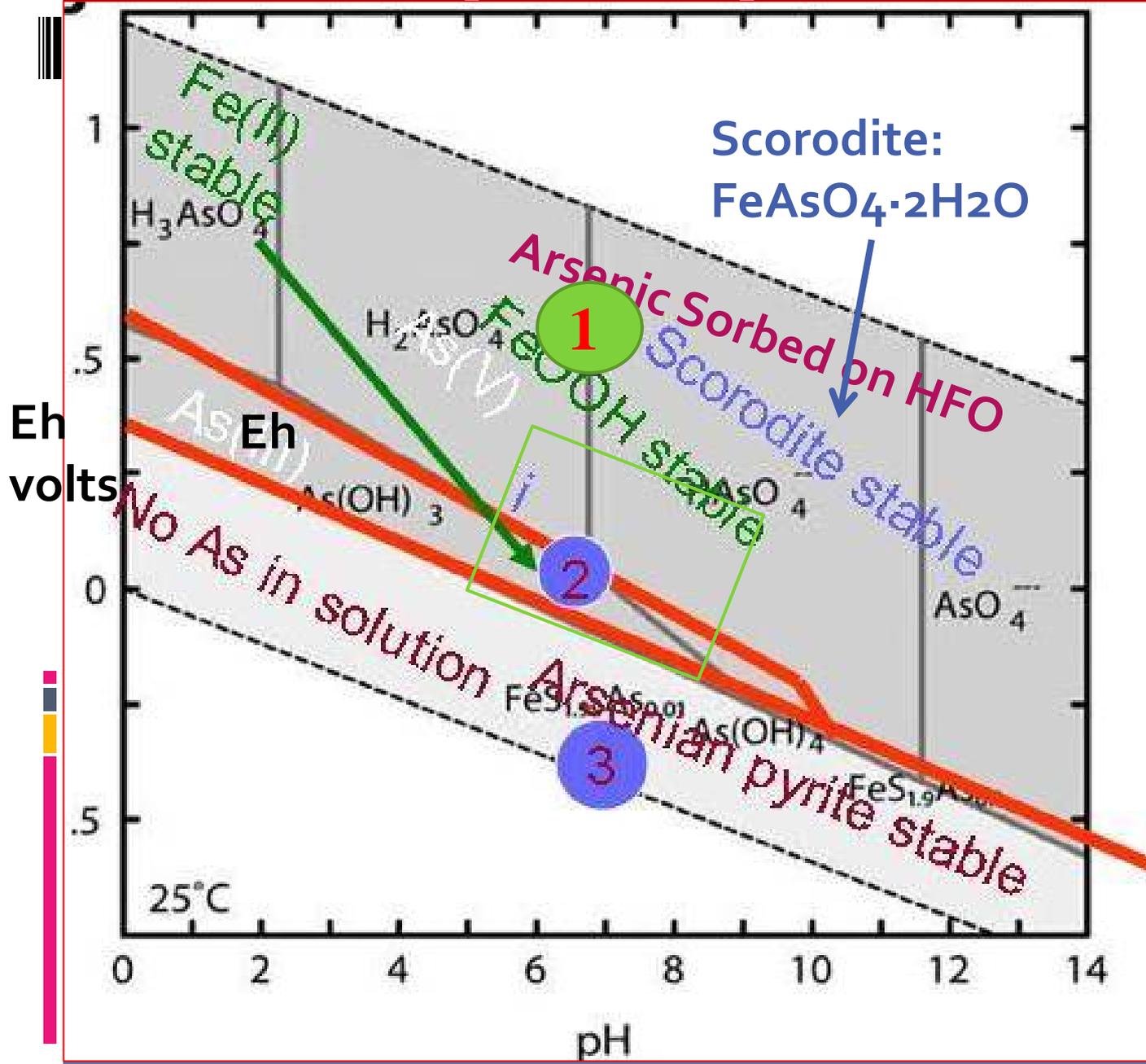
Arsenopyrite (silver)  $\text{FeAsS}$

James A. Saunders, P.G.  
Professor (emeritus) of Geochemistry  
Dept. of Geosciences  
Auburn University

# Arsenic Aqueous Geochemistry

- Mobile under OXIDIZING conditions as arsenate oxy-anion ( $\text{As-V}$ ;  $\text{H}_2\text{AsO}_4^-$ ) but **WILL** sorb onto Fe-oxyhydroxides (HFO, FeOOH) under oxidizing conditions (immobile): like other “ates” (phosphate, molybdate, chromate, permanganate, selenate, vanadate)
- Mobile under “moderately” reducing conditions as arsenite oxy-anion ( $\text{As-III}$ ;  $\text{H}_3\text{AsO}_3^0$ ); EPA regulates total As!
- Immobile under sulfate-reducing conditions if dissolved iron content is high: Makes **Arsenian Pyrite**
- Somewhat mobile under sulfate-reducing conditions if **iron content is low**,  $\text{H}_2\text{S}$  elevated; e.g., As-combines with  $\text{H}_2\text{S}$  to make aqueous species and perhaps amorph.  $\text{AsS}$  (“**realgar**”),  $\text{As}_2\text{S}_3$  (“**orpiment**”) although the As-S phases DO NOT remove enough As from ground water to be meet DWS or clean up goals in USA

# Arsenic, Iron, S Geochemistry



As(V) ( $H_2AsO_4^-$ , arsenate) Sorbed onto HFO, and immobile

2) As(III) ( $H_3AsO_3$ , arsenite) and Fe(II) occur together and are mobile and elevated!

3) As occurs IN arsenian pyrite, immobile

NOTE: Arsenian pyrite is  $Fe(S,As)_2$ ; Arsenopyrite is  $FeAsS$  (rare or perhaps unknown at low-T?)

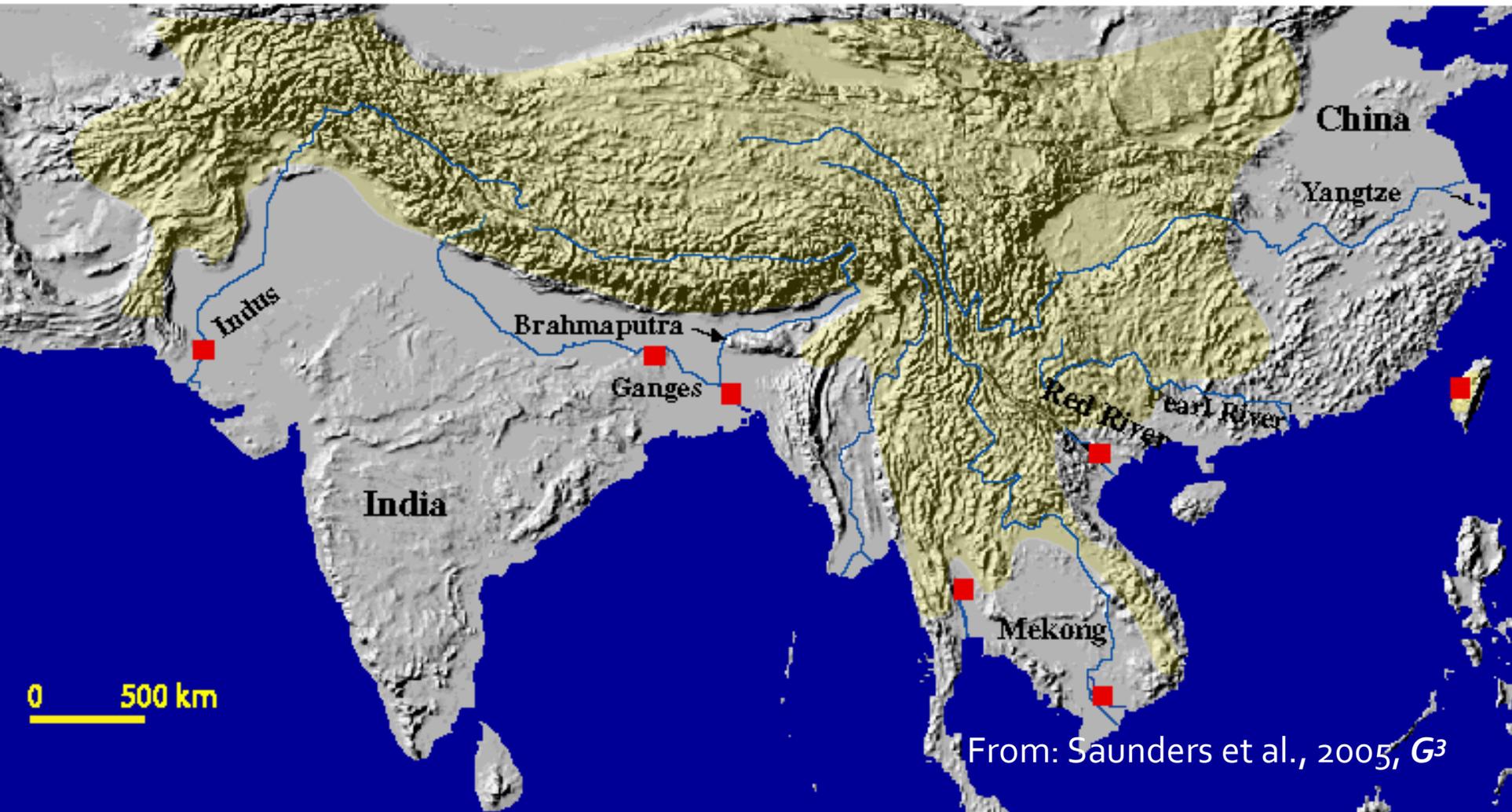
# As Contamination of Groundwater

- NATURAL: Probably most problematic worldwide as this process contaminates **DRINKING** water for hundreds of millions of people, mainly in developing nations
- ANTHROPOGENIC: Arsenic compounds have been used for many industrial purposes, including: wood treatment, as a herbicide, and also as a pesticide
- BOTH!?: release of organic carbon from storage tanks, landfills, airport runways (de-icers), etc. can trigger release of sorbed As on HFO if the geology and biogeochemistry is right (wrong?)....first documented “natural” arsenic contamination at KC MO was this (Korte, 1989)

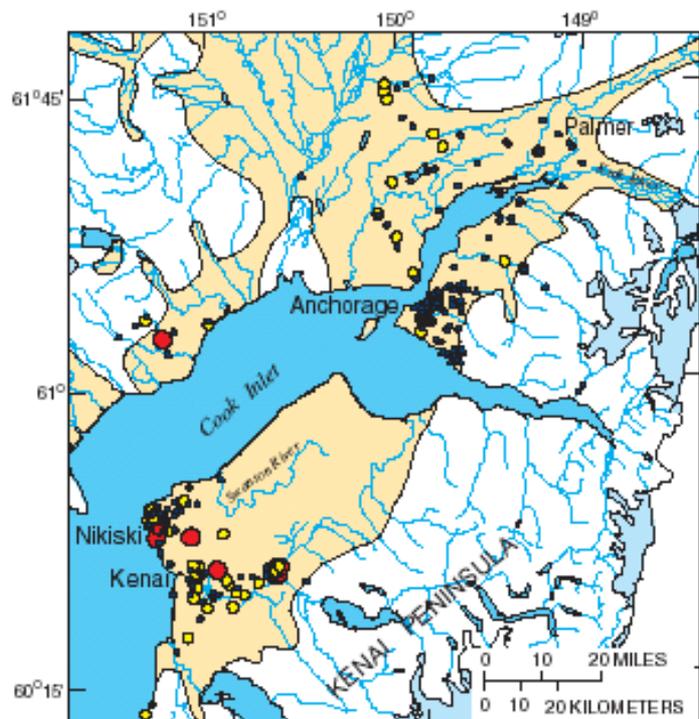
# The Natural As Problem

- Average arsenic content of crustal rocks is ~1-15 ppm (occurs in metal sulfides, biotite, basalts, glacial till, etc.)
- US-EPA and WHO arsenic drinking water standard is 10 ppb
- Thus, crustal rocks contain ~3 orders of magnitude more arsenic than the drinking water standard
- A VARIETY of water-rock-bacteria-organic matter reactions can release this natural arsenic to solution
- As geochemistry largely controlled by the geochemistry of iron, sulfur, and organic carbon (more abundant redox sensitive elements!)

# Some NATURALLY Arsenic-Contaminated River Basins in Southern Asia



# As-Glaciers (till) Connection



## EXPLANATION

Unconsolidated aquifer materials:

- Present
- Thin or absent
- Glaciers and perennial snow and ice

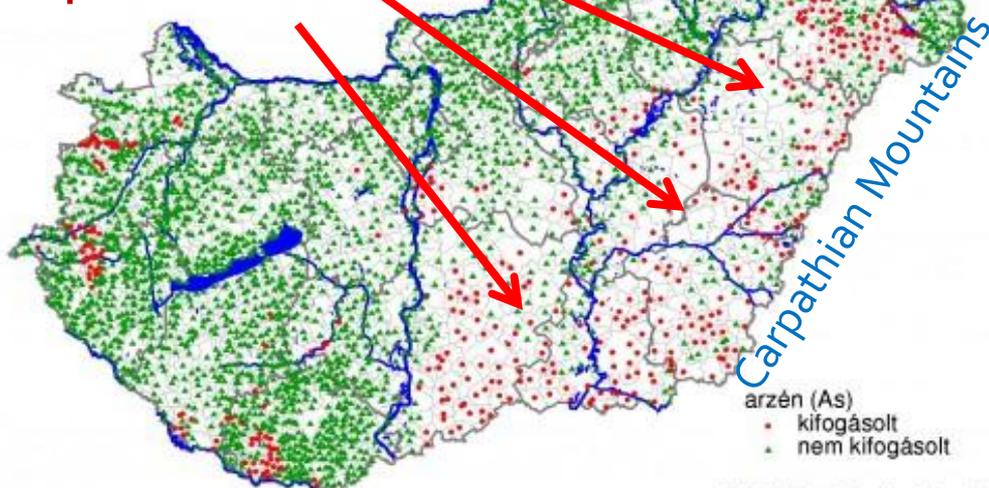
Dissolved arsenic in water from wells:

- Less than 10 micrograms per liter
- 10 to 49 micrograms per liter
- Greater than or equal to 50 micrograms per liter

Dissolved arsenic in water from streams:

- Less than 10 micrograms per liter

Vezetékes ivóvizek arzén (As) tartalma Magyarországon  
**Holocene fluvial-glacial deposits undifferentiated**



Magyarországon a 2011/2001 (10. 25) Kormányrendeletben felsorolt településeken 2009. december 25-ig az itt megadottól eltérő, ideiglenes határértékek érvényesek

Készült az Országos Környezetegészségügyi Intézetben, 2007. 1. negyedév

## Pannonian Basin, Hungary

## Anchorage, Alaska

# Why don't they just drink river water?

River water is often contaminated by human and animal feces in the "Third World"

Where? Bangladesh, India, Pakistan, China, Viet Nam, Nepal, Bhutan, Cambodia, Thailand, Taiwan, Hungary, etc.,

Bangladesh: flat  
and wet!



Flood plain of two of world's largest  
rivers: Ganges, Brahmaputra



# Bangladesh Drinking Water



Tube Well Installation



Red paint=  
As-rich  
water



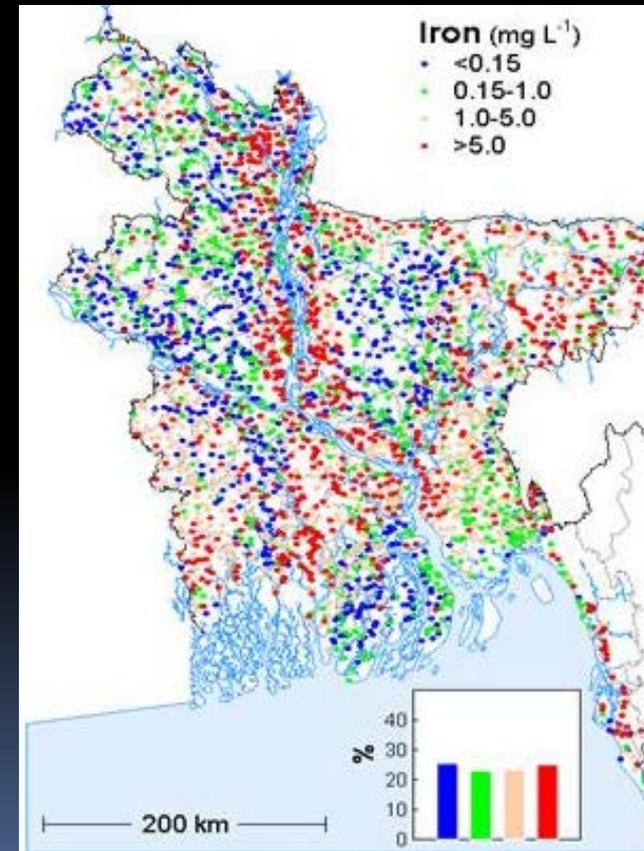
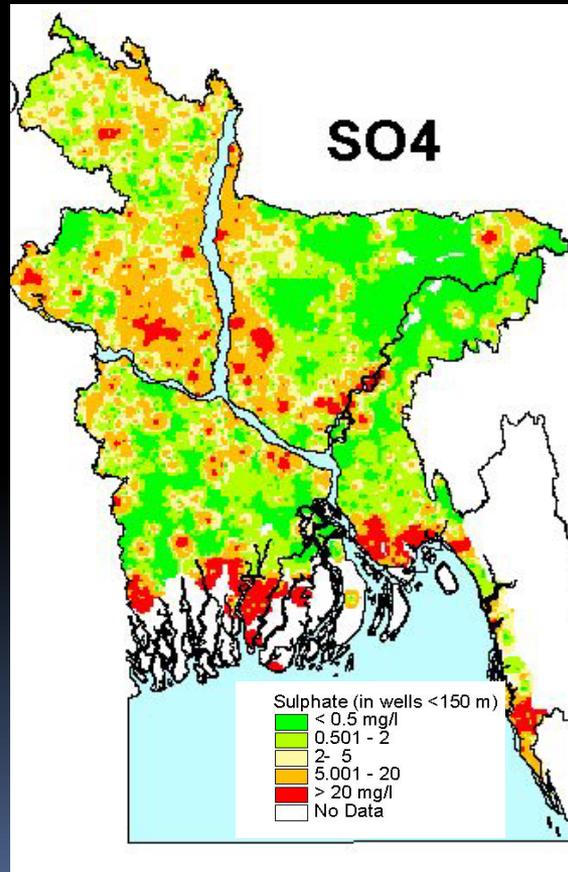
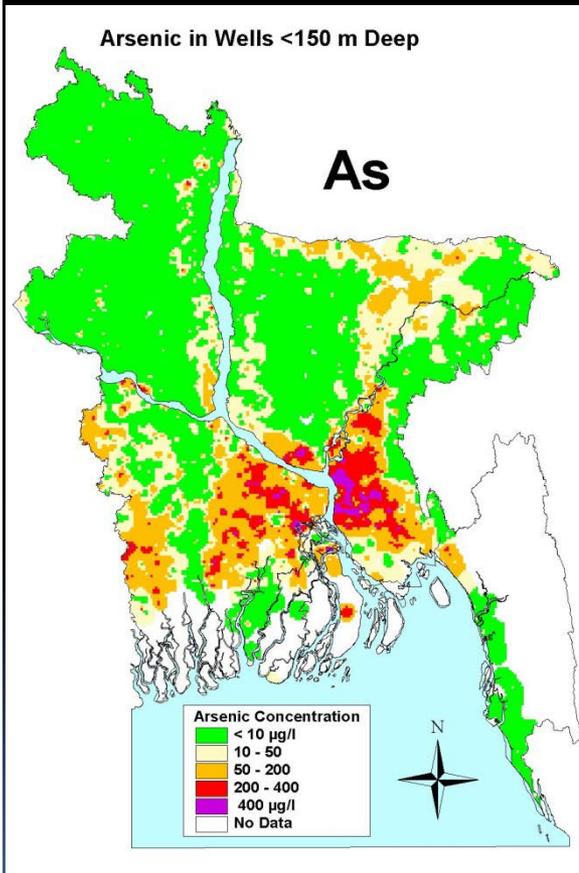
“Dug” Well

# Bangladesh: Arsenic Poisoning

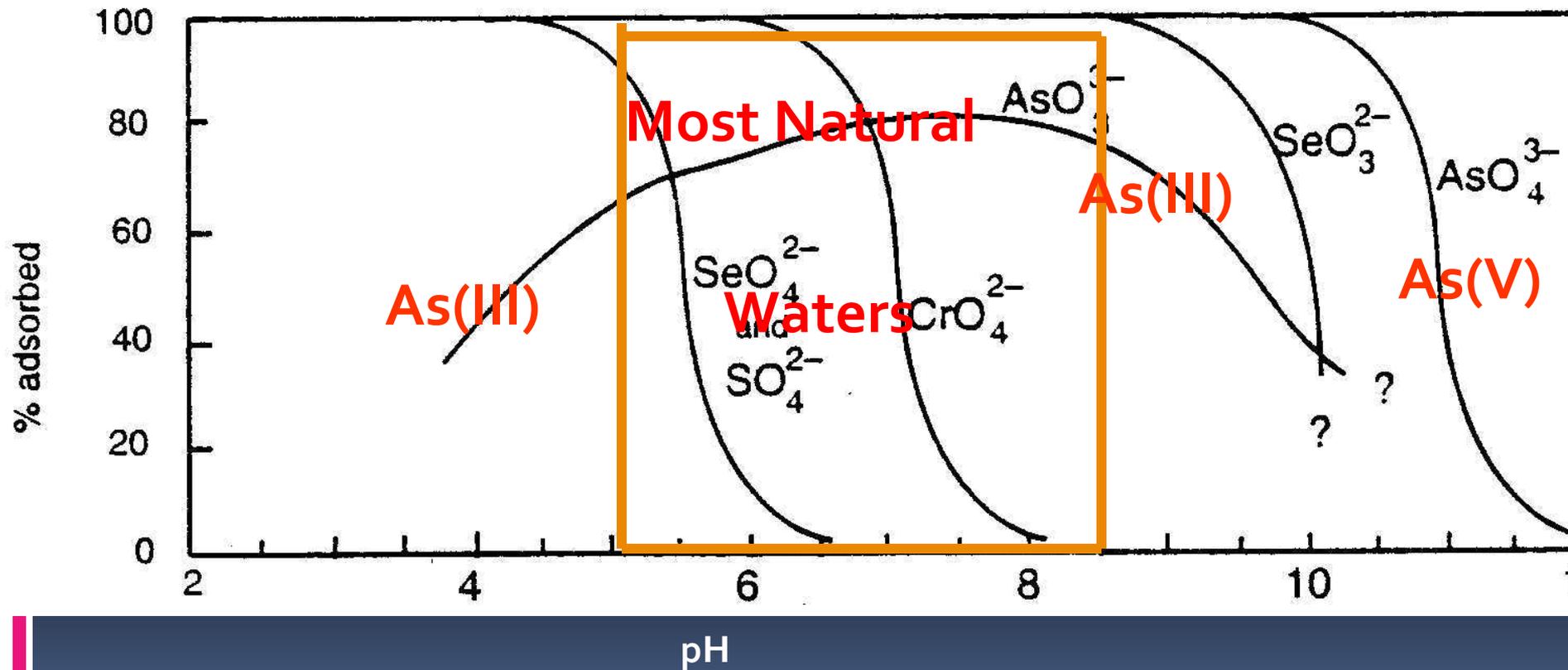


**melanosis**

# Bangladesh Tube Well Geochemistry (Depth < 150m)



# Sorption of Oxyanions on HFO, Diffuse Layer Model of Dzombak and Morel (1990)



As mostly sorbed by HFO at typical pH's

MOST natural As contamination caused by anaerobic iron-reducing bacteria release arsenic to groundwater



- Common Fe-reducer:  
*Geobacter metallireducens*



- $\text{FeO(OH) * As} = \text{HFO}$ , hydrous ferric oxide containing sorbed and coprecipitated arsenic

# Manikganj, Bangladesh, Water treatment Plant



Iron oxidizes in holding ponds,  
sorbs As, water then put into city  
distribution system



Get the HFO out, get the arsenic out..  
(or ~75% of it)

- 1) Let  $\text{Fe}^{2+}$  oxidize to HFO, sorbs As
- 2) Filter HFO\*As out, pour water into second jug
- 3) Repeat step 2, pour water into lower jug for drinking



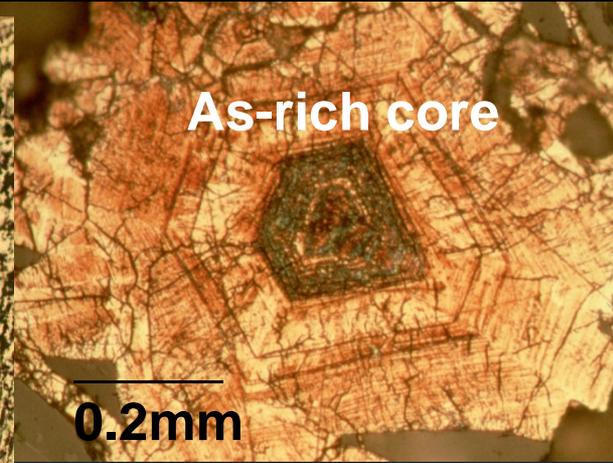
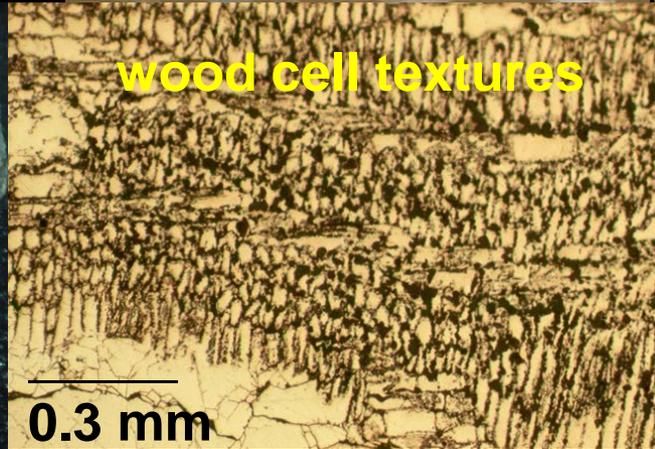
# Holocene (<7000 year old) Biogenic As-bearing Pyrite from Macon County, AL

Exploration geologist,  
Exxon Mobil

IT Consultant, Sogento  
CPA, Price-Waterhouse



First found in 1974 when  
Saunders was a BS  
student at AU!

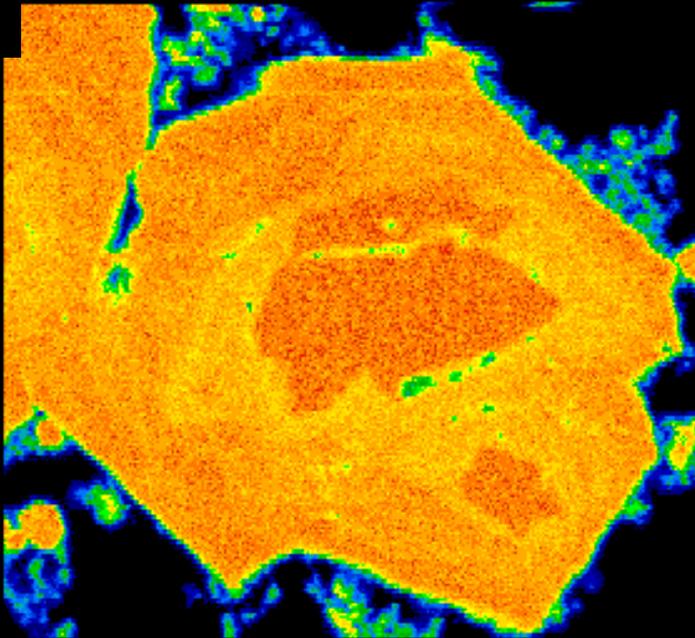


- Occurs in Iron-rich water, low dissolved sulfate
- SRB use wood fragments for organic C source

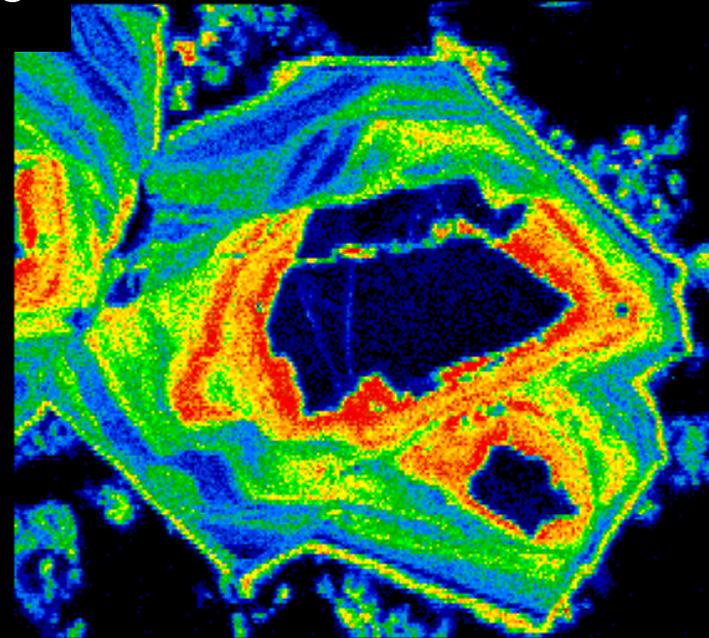
# Arsenic substituting into hydrothermal pyrite, Carlin-Type gold ores, NV (Meikle Mine)

*As-S Substitution in pyrite*

S



As



50 microns

50.µm Score 20.kV

500

438

375

312

250

188

125

62

0

200

175

150

125

100

75

50

25

0

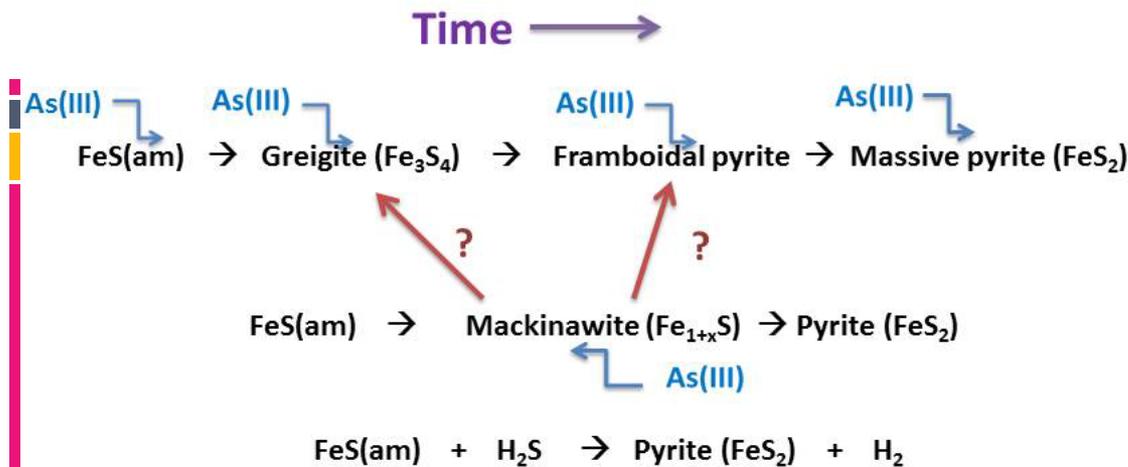
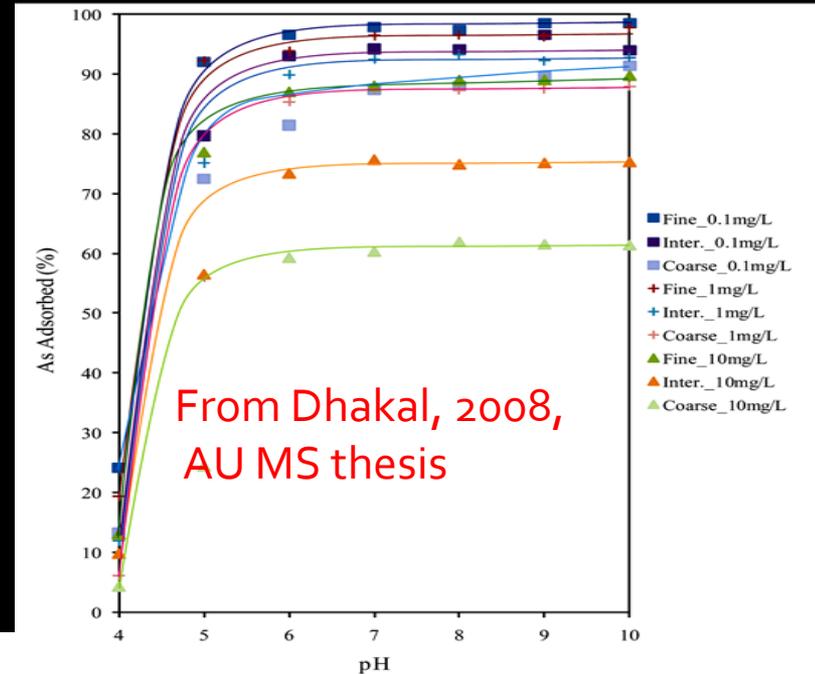
50.µm Ascore 20.kV

Source: Steve Kesler->



# So how does As get into pyrite?? First it is sorbed, then “co-pprted”

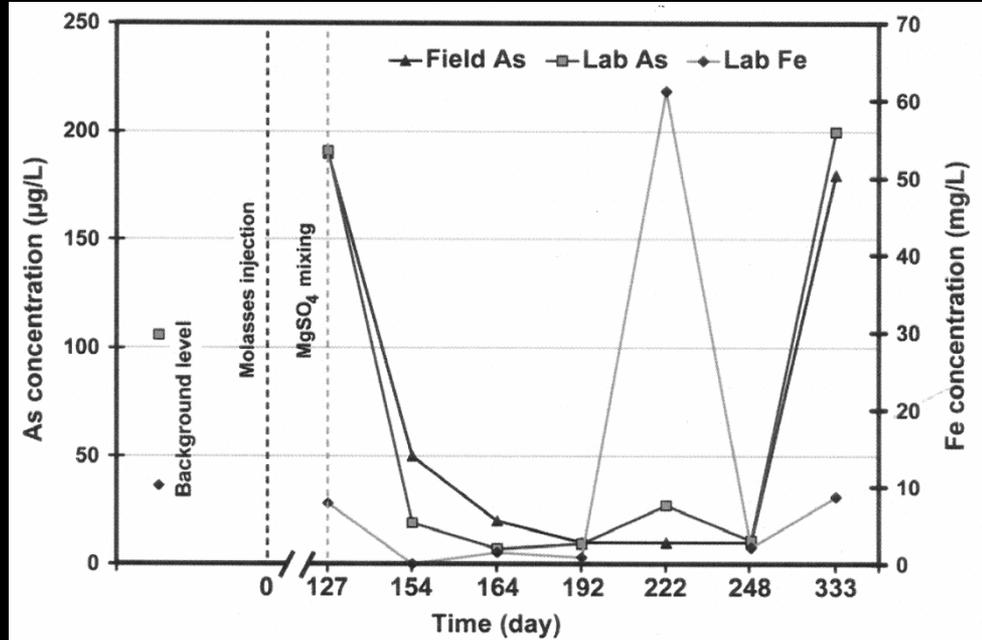
Fe-sulfide-Arsenic processes under reducing conditions



Plot showing As (III) sorption per unit mass adsorbent as a function of pH for fine, intermediate, and coarse-grained pyrite grains for different concentrations of added arsenic (0.1 mg/L, 1 mg/L, 10 mg/L)

As(III,V) sorption on FeS phases may retard inversion to pyrite?? →

# Field site 1: Bangladesh

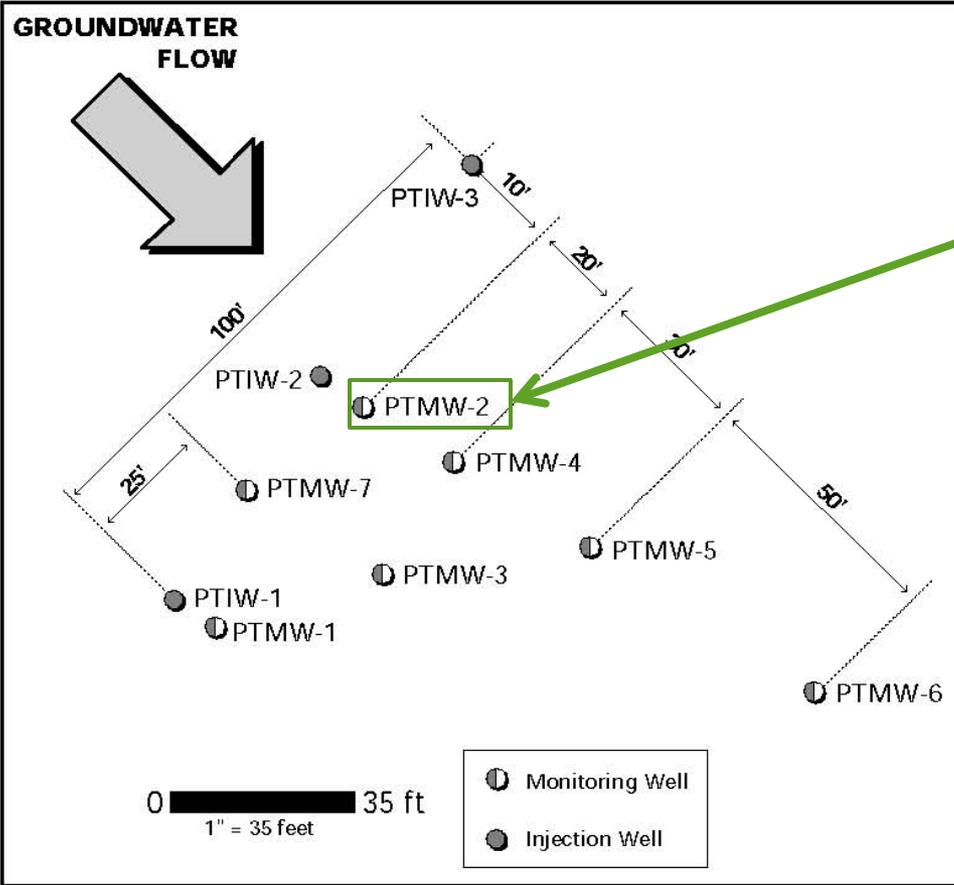


Field "Bioremediation" tests in Bangladesh done on a single "tube" well with  $>100$  ppb As

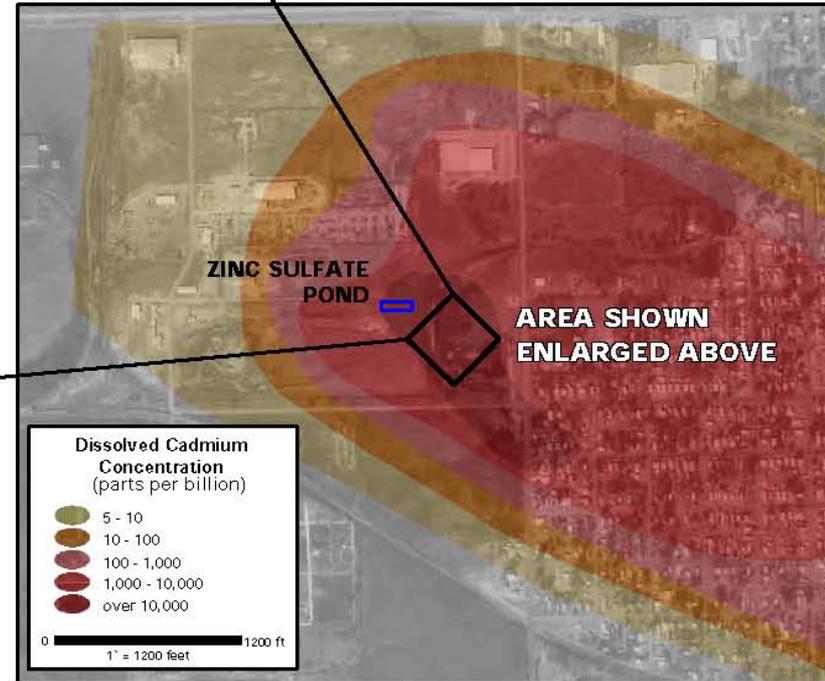
First experiment was to inject molasses and Epsom's salt ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ); Arsenic decreased to  $<10$  ppb, then returned to higher levels as "un-remediated" background groundwater displaced the remediated groundwater due to natural flow

Second experiment involved injecting molasses and ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ); arsenic removal was longer lasting (poorly quantified due to field problems)

# Field Site 2; Blackwell, OK

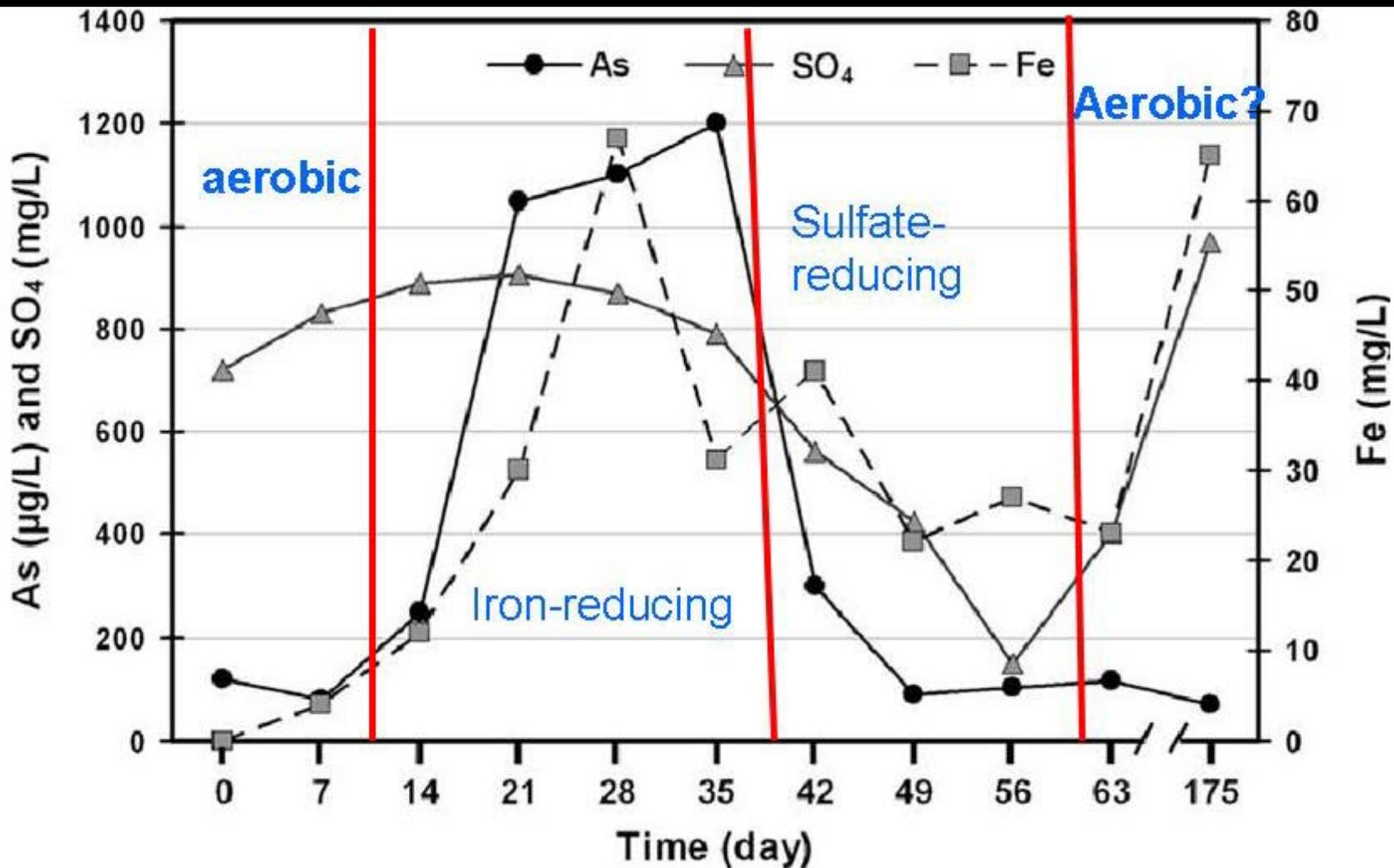


Data from this monitoring well shown on next slide

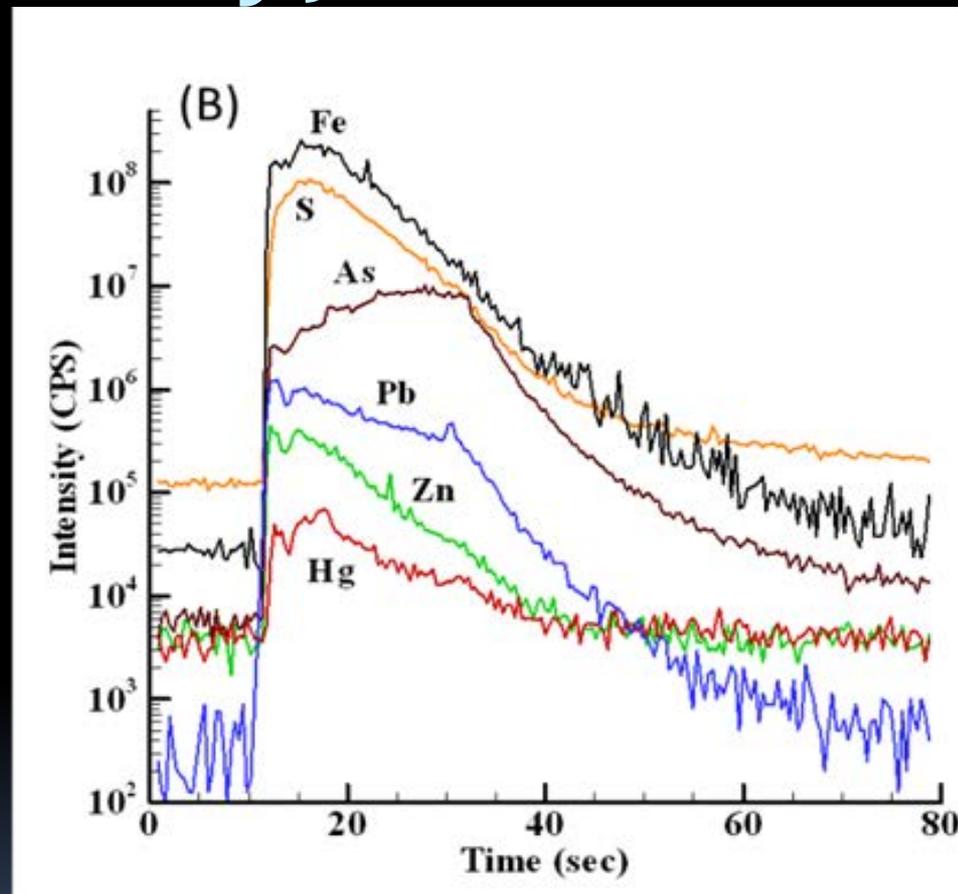
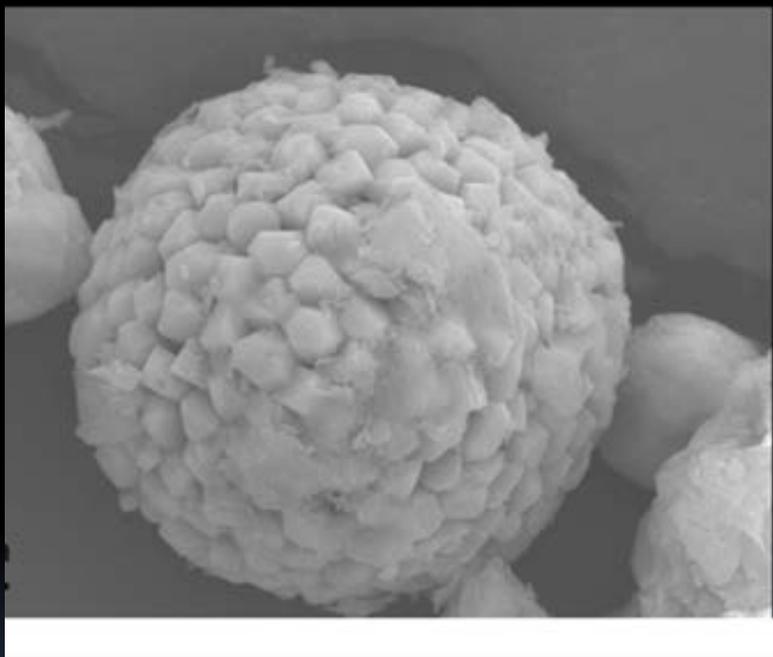


Groundwater contaminated by Zn, Cd, and sulfate from an old zinc smelter. No arsenic in the system but the geology of the site was conducive to As release from alluvial sediments that host shallow groundwater

# Geochemical data (6 months) for monitoring well PTMW-2



# Field site 3: Biogenic pyrite framboids, Weeks Bay, AL



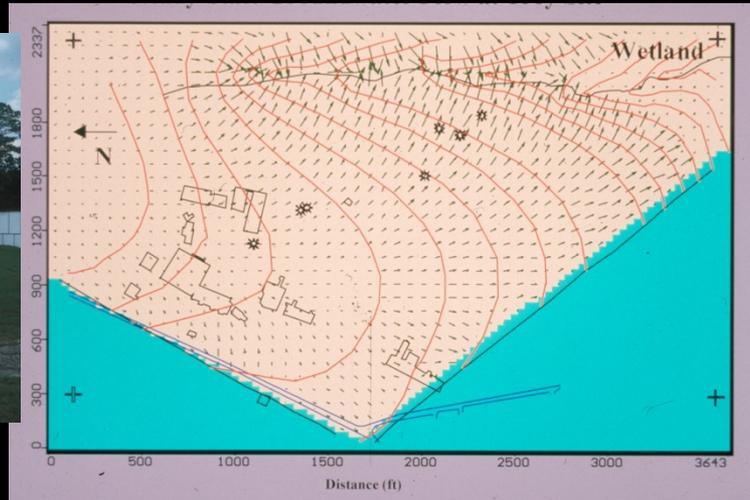
Seawater sulfate + BP oil --> pyrite with As!!

Laser-Ablation ICP-MS Analysis of Arsenian Pyrite from Weeks Bay

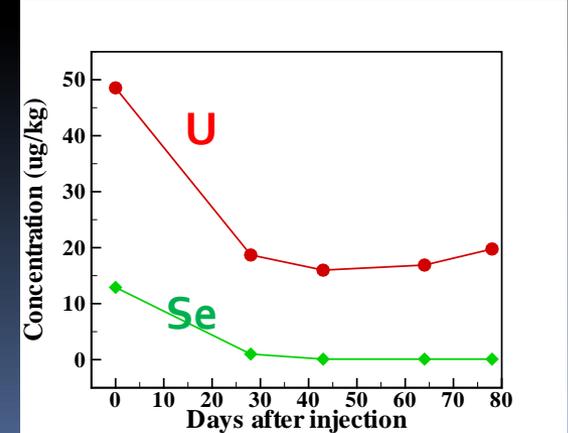
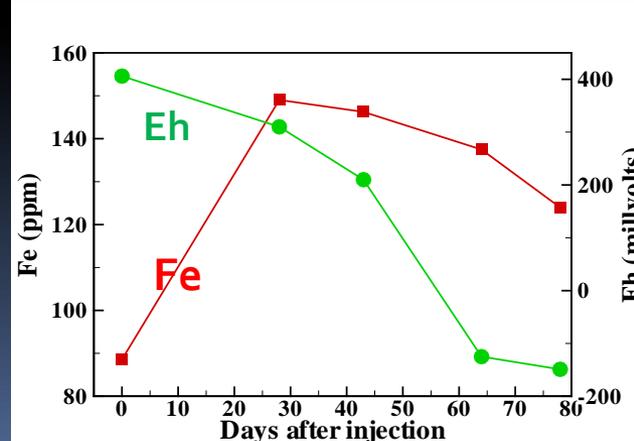
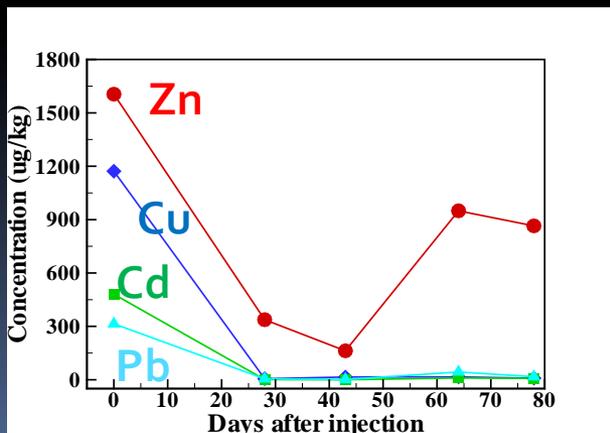
# Field Site 4: Troy, AL: No As, but interesting implications!



Sanders Lead site

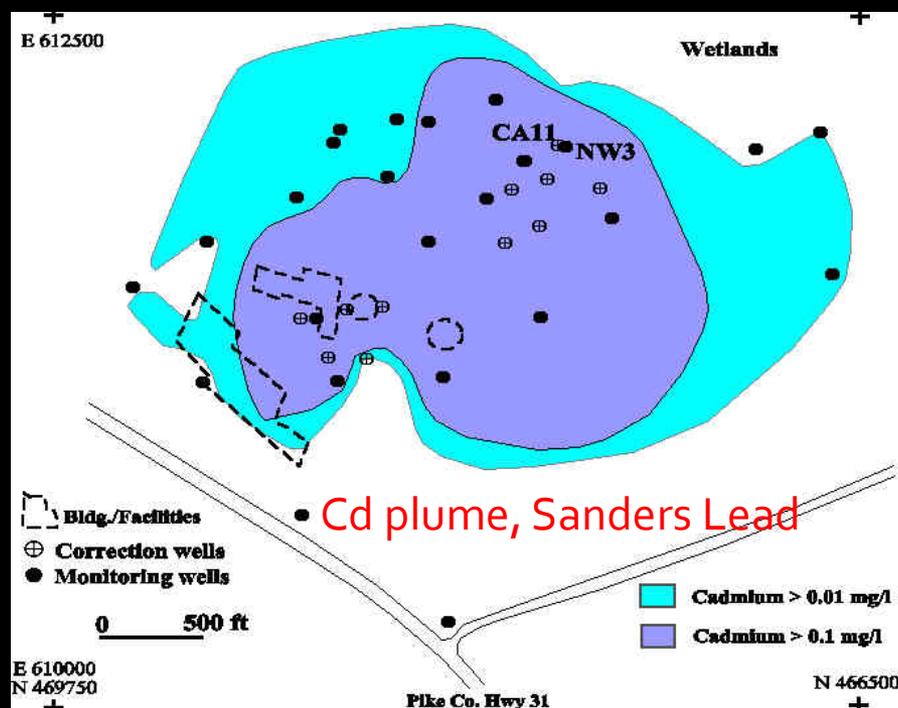


Nanafalia Fm (Paleocene)

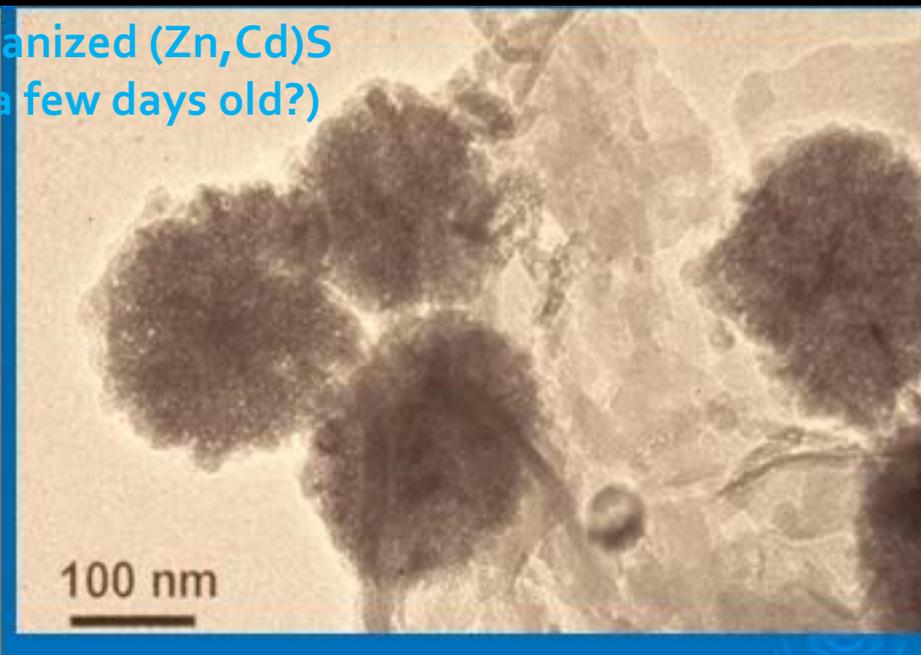
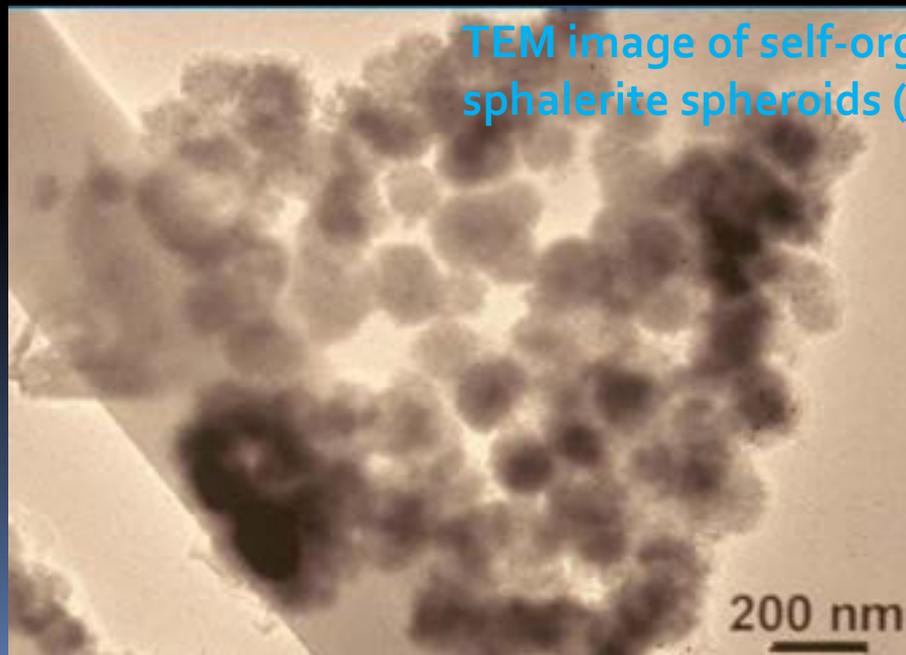


# Troy, AL site

Metal-Sulfide colloids on filter



TEM image of self-organized (Zn,Cd)S sphalerite spheroids (a few days old?)



# Field Site 5: As-biormediation, In progress, north Florida site (working?)



# Arsenic Geochemistry Summary

- As (V) is soluble (mobile) under OXIDIZING, conditions, may ppt. as the mineral scorodite, will sorb onto FeOOH (HFO) if present
- As(III) is soluble (mobile) under MODERATELY REDUCING conditions, might sorb onto HFO if present and/or stable [As(III) and Fe(II) commonly occur together in solution]
- As is relatively insoluble under very reducing conditions (can smell H<sub>2</sub>S?) as it forms As-sulfide minerals (maybe) but also Fe(S, As)<sub>2</sub> (for sure!)
- Pyrite is a little recognized but strong sorber of As under reducing conditions!!