ENVIRONMENTAL GEOCHEMISTRY OF ARSENIC AND ITS BIOREMEDIATION IN CONTAMINATED GROUNDWATER

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

Realgar (red) AsS

Orpiment (yellow) As$_2$S$_3$

Arsenopyrite (silver) FeAsS

Scorodite FeAsO$_4$·2H$_2$O
• Mobile under OXIDIZING conditions as arsenate oxy-anion (As-V; H₂AsO₄⁻) 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 (As-III; H₃AsO₃⁻); 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, H₂S elevated; e.g., As-combines with H₂S to make aqueous species and perhaps amorph. AsS (“realgar”), As₂S₃ (“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

1) As(V) \((H_2AsO_4^{\circ})\), arsenate) Sorbed onto HFO, and immobile

2) As(III) \((H_3AsO_3^{\circ})\), 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?)

Scorodite: FeAsO\(_4\)·2H\(_2\)O

No As in solution. Arsenian pyrite stable
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

From: Saunders et al., 2005, G3
As-Glaciers (till) Connection

Pannonian Basin, Hungary

Anchorage, Alaska

Holocene fluvial-glacial deposits undifferentiated
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

“Dug” Well

Red paint = As-rich water
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

- \( \text{FeO(OH)} \ast \text{As} + C_{\text{org}} \rightarrow \text{Fe}^{2+} + \text{HCO}_3^- + \text{As(III)} \)

- Common Fe-reducer: \textit{Geobacter metallireducens}

- \( \text{FeO(OH)} \ast \text{As} = \text{HFO}, \text{hydrous ferric oxide containing sorbed and coprecipitated arsenic} \)
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 Fe2+ 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

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

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

Exploration geologist, Exxon Mobil

IT Consultant, Sogento
CPA, Price-Waterhouse

wood cell textures

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

As-S Substitution in pyrite

Source: Steve Kesler->
So how does As get into pyrite?? First it is sorbed, then “co-ppted”

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)

From Dhakal, 2008, AU MS thesis
Field site 1: Bangladesh

Field “Bioresmediation” tests in Bangladesh done on a single “tube” well with >100 ppb As

First experiment was to inject molasses and Epsom’s salt (MgSO₄*7H₂O); 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 (FeSO₄*7H₂O); arsenic removal was longer lasting (poorly quantified due to field problems).
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

![Graph showing Geochemical data for PTMW-2](image)

- **As (µg/L)** and **SO₄ (mg/L)**
- **Fe (mg/L)**

- **aerobic**
- **Sulfate-reducing**
- **Iron-reducing**
- **Aerobic?**
Field site 3: Biogenic pyrite frambooids, 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!

Nanafalia Fm (Paleocene)

Sanders Lead site

- Zn
- Cu
- Cd
- Pb

- Fe (ppm)
- Eh (millivolts)

- U
- Se

Concentration (ug/kg)

Days after injection
Troy, AL site

Metal-Sulfide colloids on filter

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

Cd plume, Sanders Lead
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 H2S?) as it forms As-sulfide minerals (maybe) but also Fe(S, As)2 (for sure!).
- Pyrite is a little recognized but strong sorber of As under reducing conditions!!