Identification and Quantification of Arsenic Species in Gold Mine Wastes Using Synchrotron-Based X-ray Techniques

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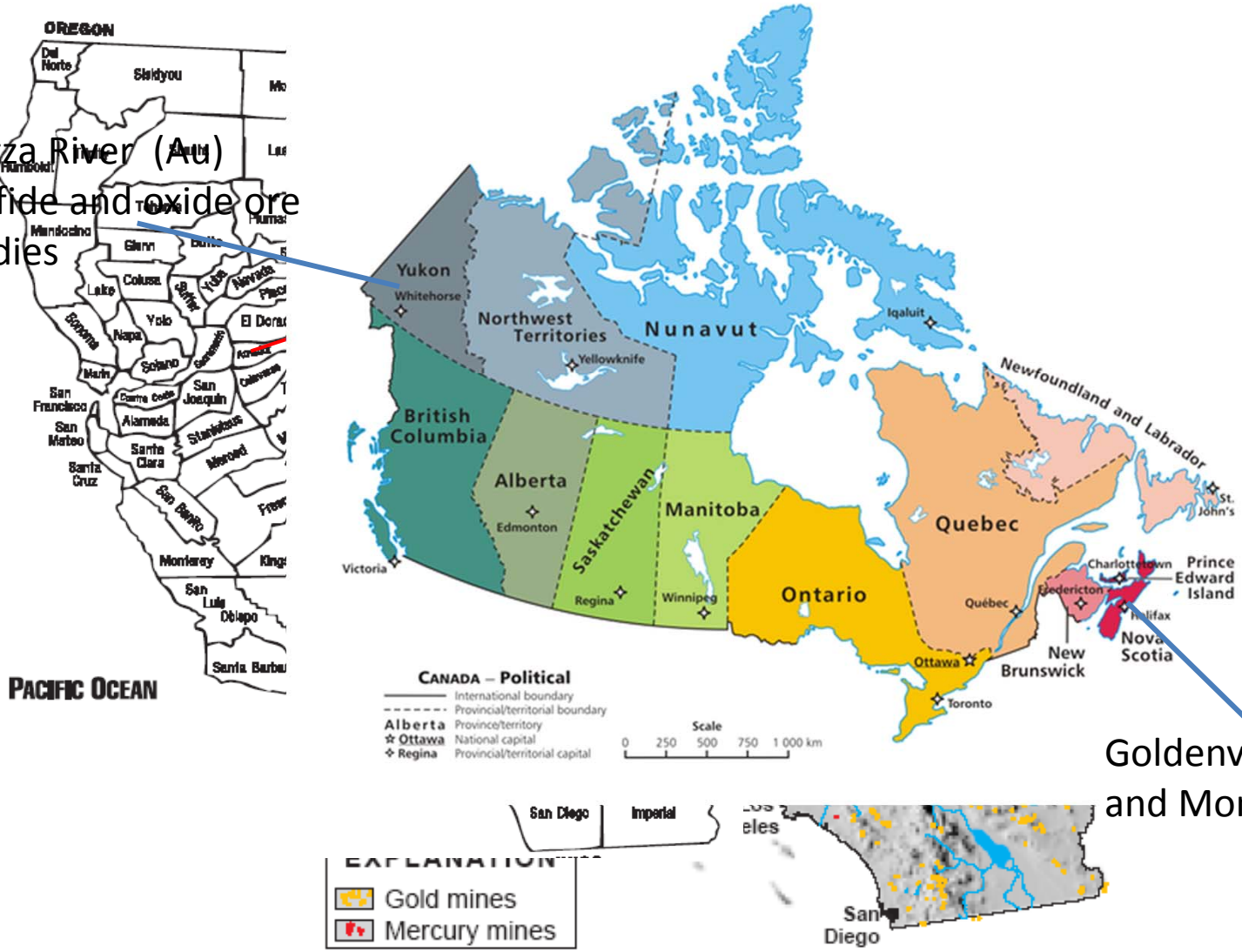
Arsenic is an element of concern in mined gold deposits around the world

Ketza River (Au) sulfide and oxide ore bodies



Goldenville, Caribou, and Montague (Au)

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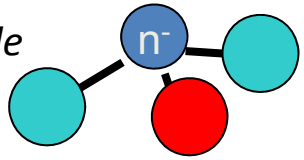
The common arsenic-rich particles in hard-rock gold mines have long been known

Primary

"arsenian" pyrite
As^{-1} pyrite $Fe(As,S)_2$

Reich and Becker (2006):
maximum of 6% As^{-1}

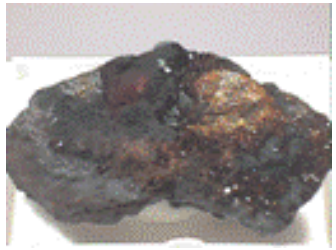
Arsenopyrite FeAsS



arsenide
n = 1-3

Secondary

Scorodite $FeAsO_4$ $2H_2O$
Kankite : FeAsO4•3.5H2O



Jarosite $KFe_3(SO_4)_2(OH)_6$
Tooleite $[Fe_6(AsO_3)_4(SO_4)(OH)_4•4H_2O$
Pharmacosiderite $KFe_4(AsO_4)_3(OH)_4•6–7H_2O$

Secondary/Tertiary

Iron oxyhydroxide ("rust")
containing arsenic up to 20 wt%

Arseniosiderite $Ca_2Fe_3(AsO_4)_3O_2·3H_2O$
Yukonite $Ca_7Fe_{12}(AsO_4)_{10}(OH)_{20}•15H_2O$

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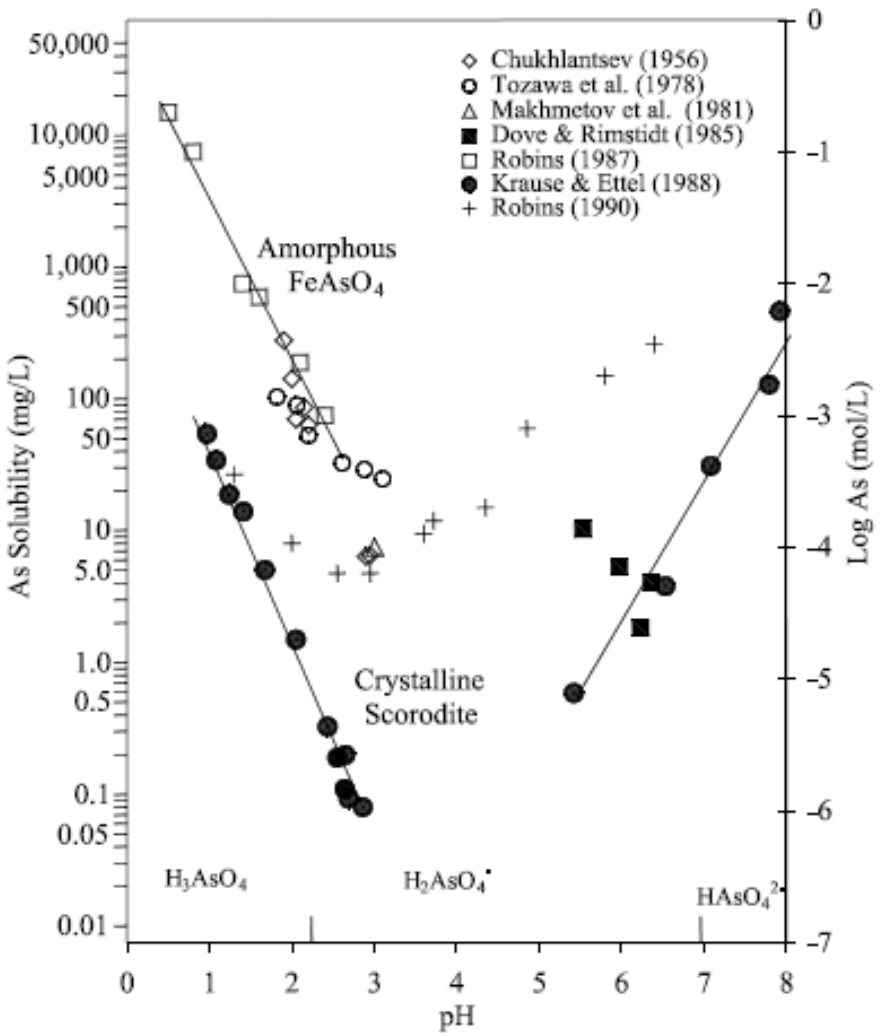
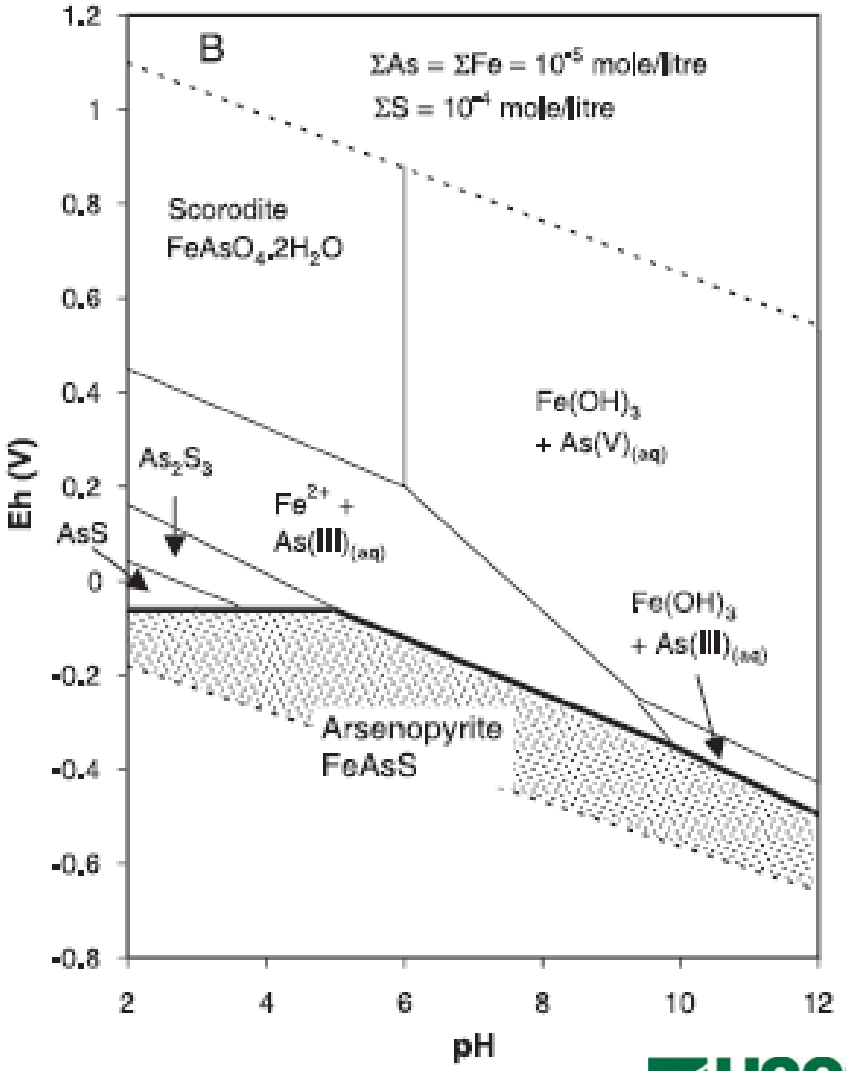
But it is still difficult to predict with an acceptable degree of uncertainty which forms will be present





Langmuir et al. (2006) GCA v70

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Lava Cap Mine Superfund Site, Nevada Cty, CA

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Typical exposure pathways at arsenic-contaminated sites are linked to particles and their dissolution in aqueous fluids

ingestion of arsenic-bearing water

solid-phase arsenic → dissolution → near-neutral, low dissolved organic carbon, low salinity waters

inhalation or ingestion of arsenic-rich particles

solid-phase arsenic → dissolution → lung and gastic/intestinal tract fluids (saline, aqueous solutions-high dissolved organic carbon, enzymes, bile, some low pH, most near-neutral)

- critical to know the form(s) of arsenic in the solid phase
- only a subset of those forms may be reactive

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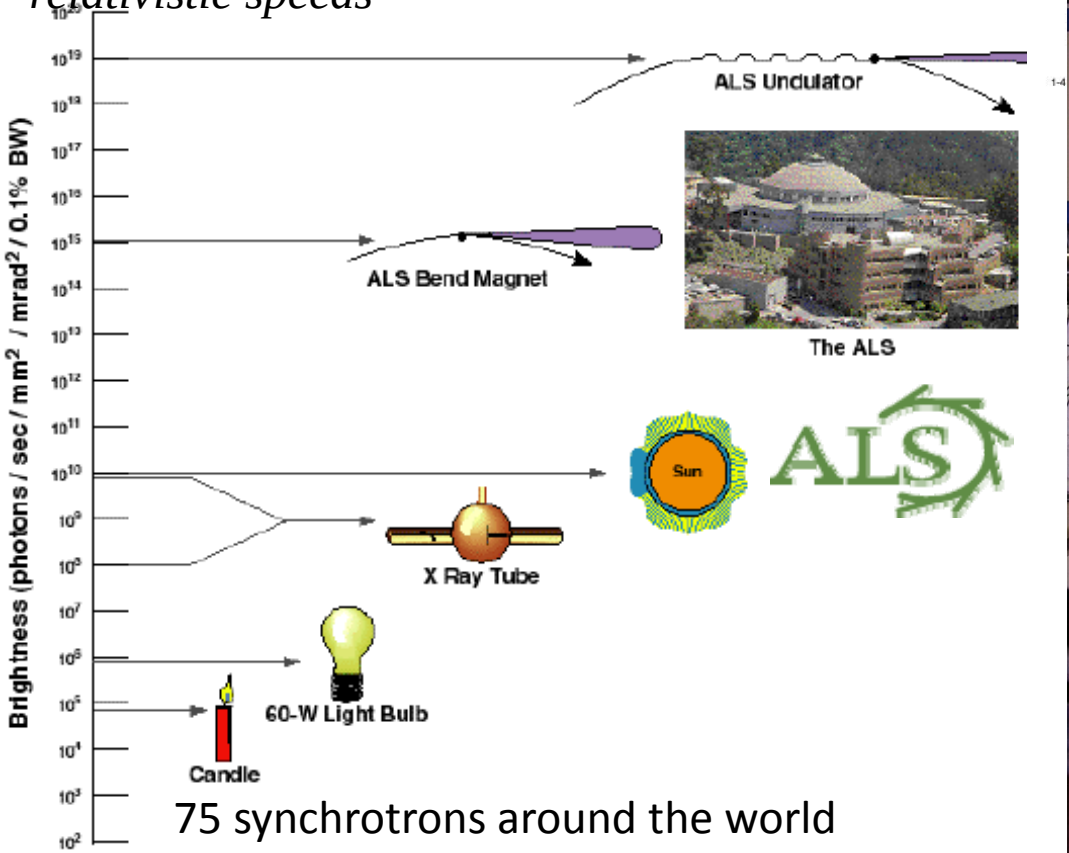
This talk will review the results of synchrotron
X-ray studies of arsenic speciation, with focus on gold mine wastes

Brilliant, high flux radiation produced at points tangent to
a circular orbit of electrons moving at near-relativistic speeds



75 synchrotrons around the world
10 in US (**4 suitable for environmental work**)

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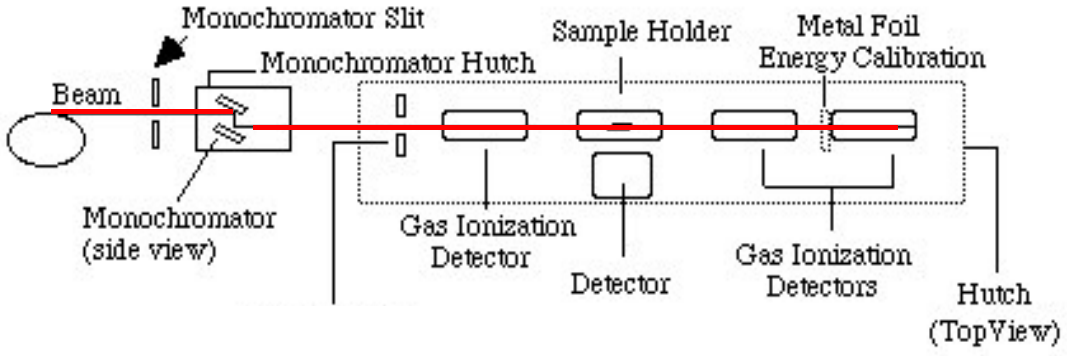
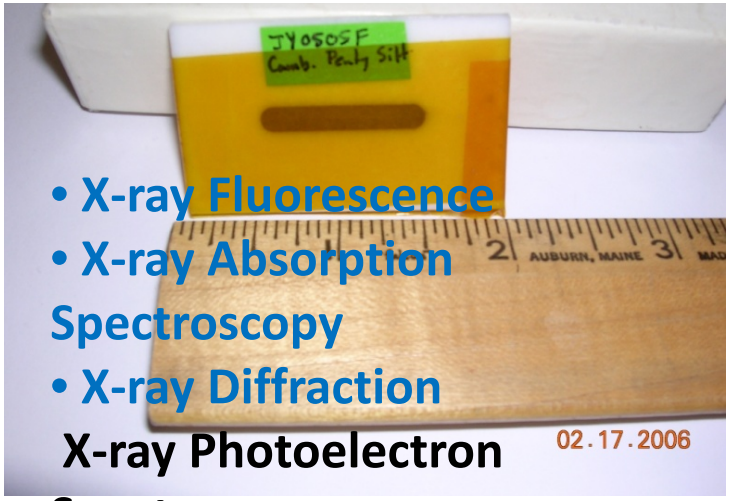
Large (1-10 mm) or small (2 -150 µm) X-ray beams are available for most techniques

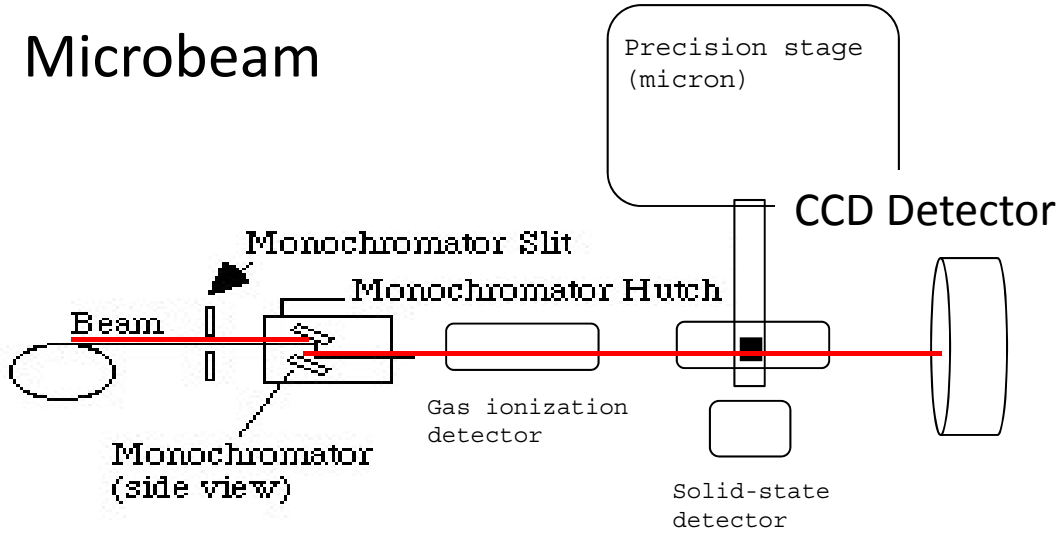
Bulk

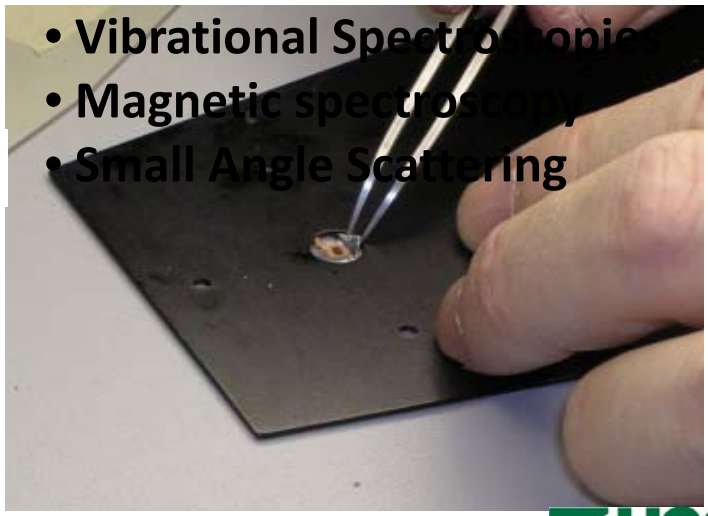




- X-ray Fluorescence
- X-ray Absorption Spectroscopy
- X-ray Diffraction
- X-ray Photoelectron Spectroscopy
- Vibrational Spectroscopies
- Magnetic spectroscopy
- Small Angle Scattering

Microbeam





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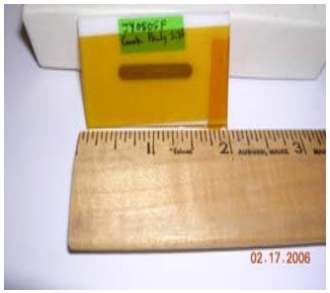
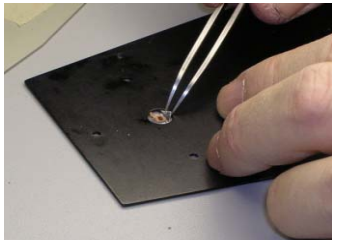
Synchrotron X-ray Fluorescence (XRF) Spectrometry



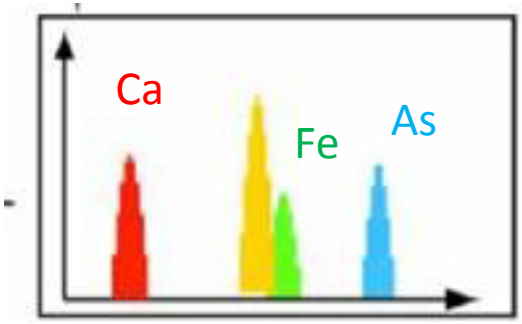
Bulk

Microbeam



One average Spectrum

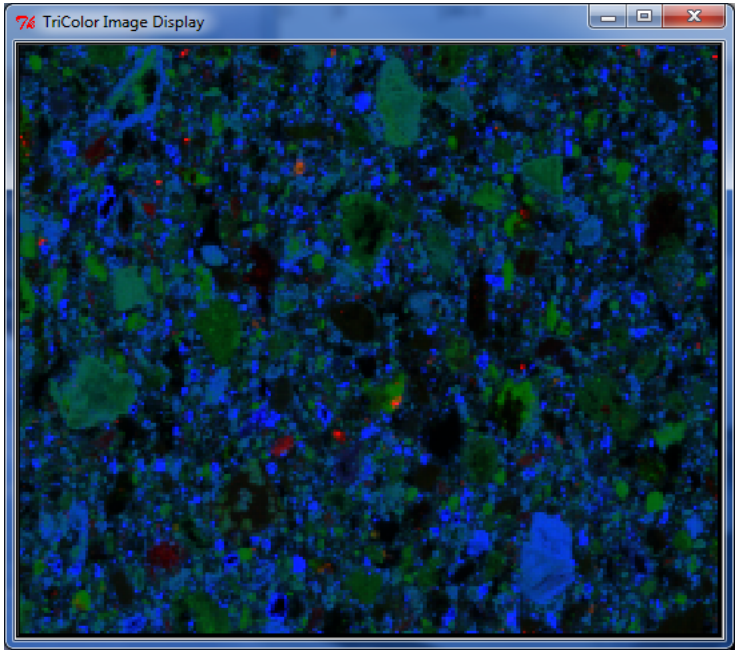
Elemental ID



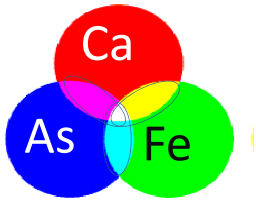
Voltage (energy)

One EDS spectrum
Per point (> 1000)

Elemental ID
Element Correlation
Spatial distribution



1800 microns



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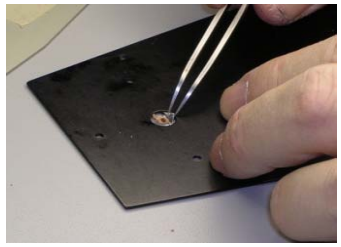
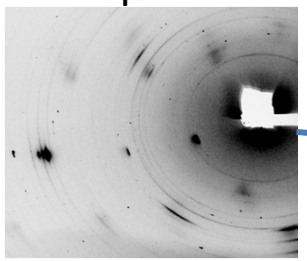
Synchrotron-based X-ray Diffraction (SXRD)



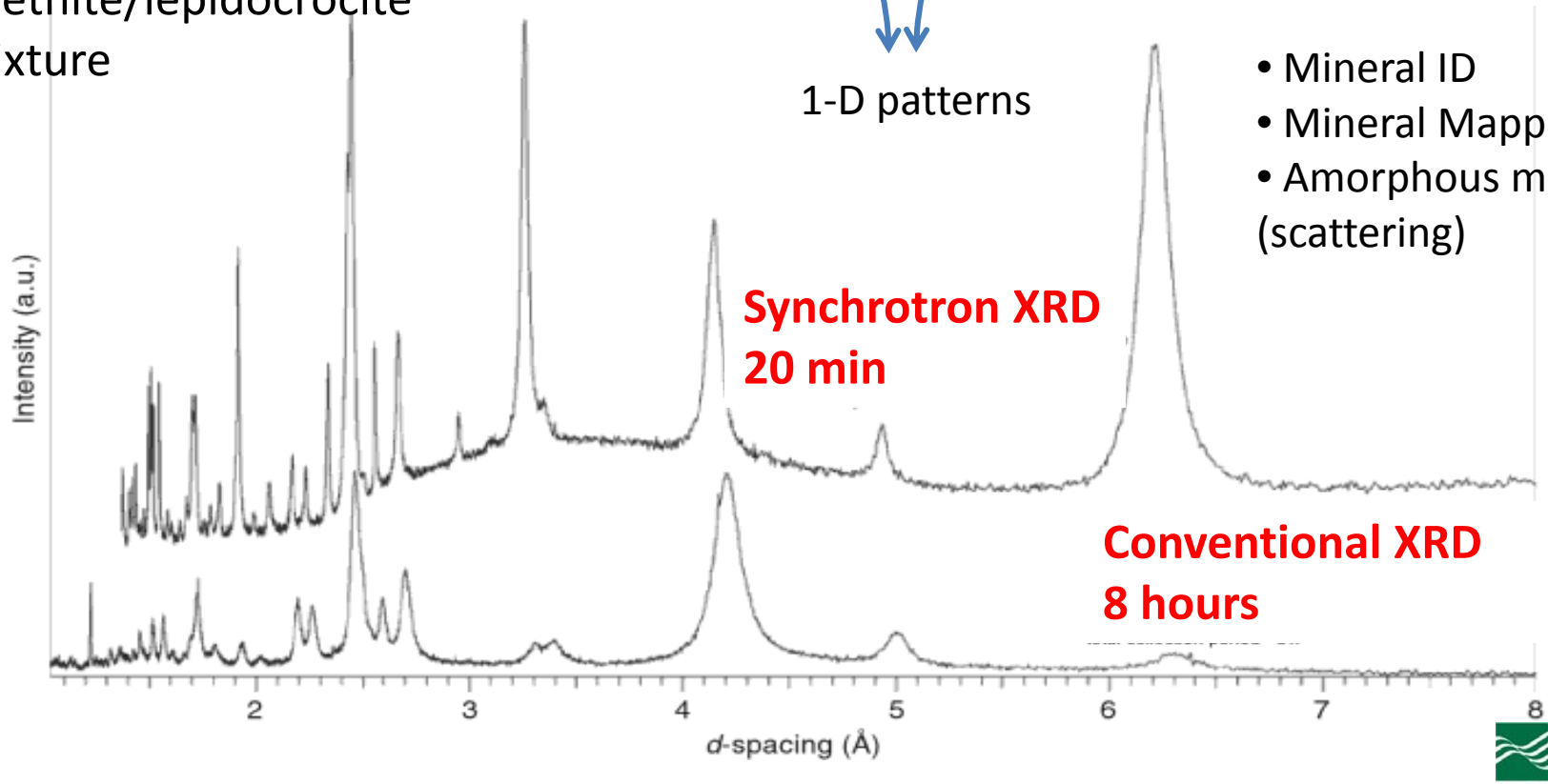
goethite/lepidocrocite mixture

2-D pattern



1-D patterns

- Mineral ID
- Mineral Mapping
- Amorphous materials (scattering)



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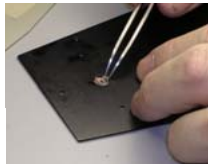
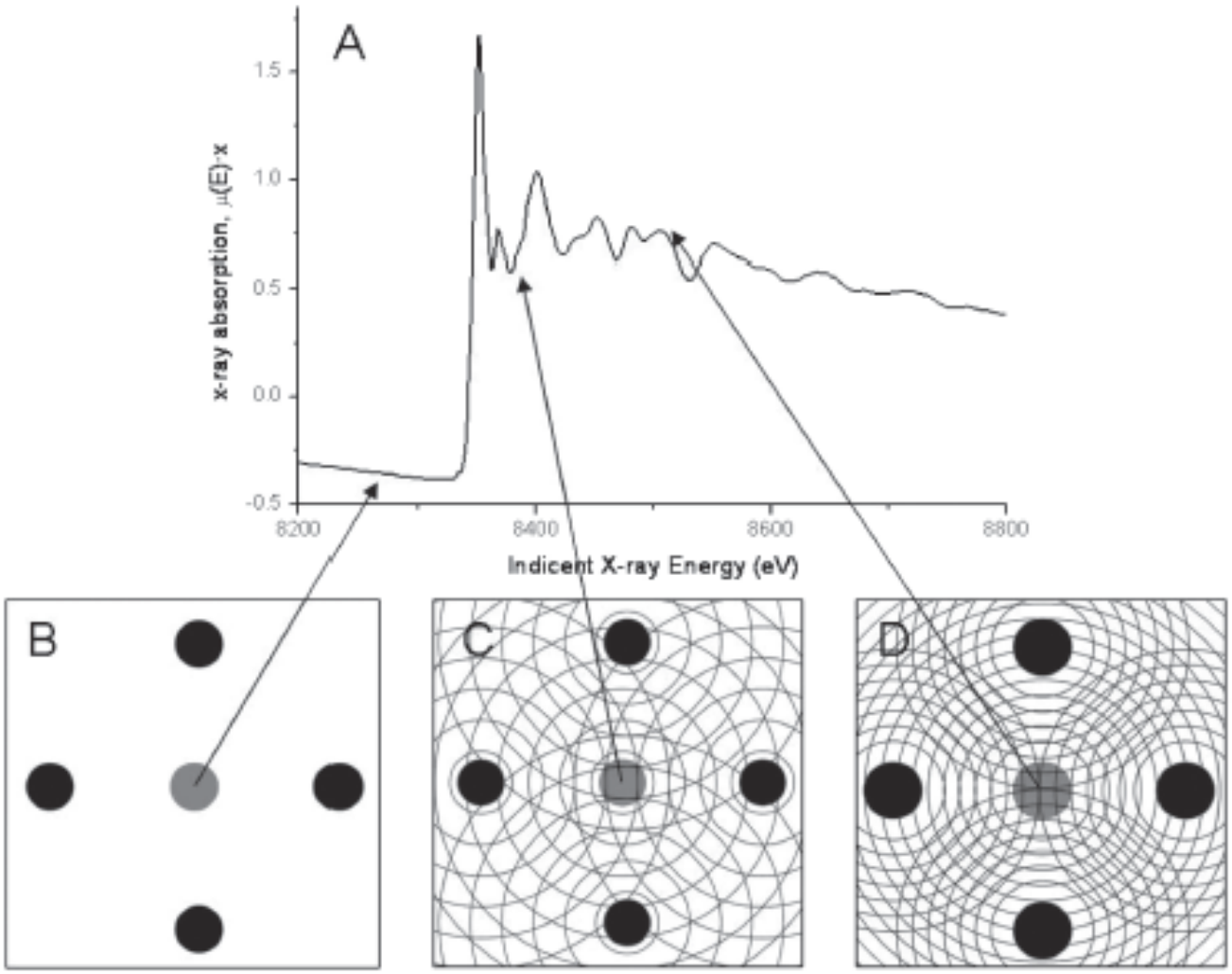
X-ray Absorption Fine Structure Spectroscopy

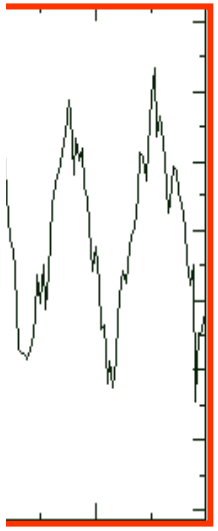


X-ray
Edge S
Oxida

Absorbance



XAFS)
ing atoms



Photoelectron **Wave vector k (Å^{-1})**

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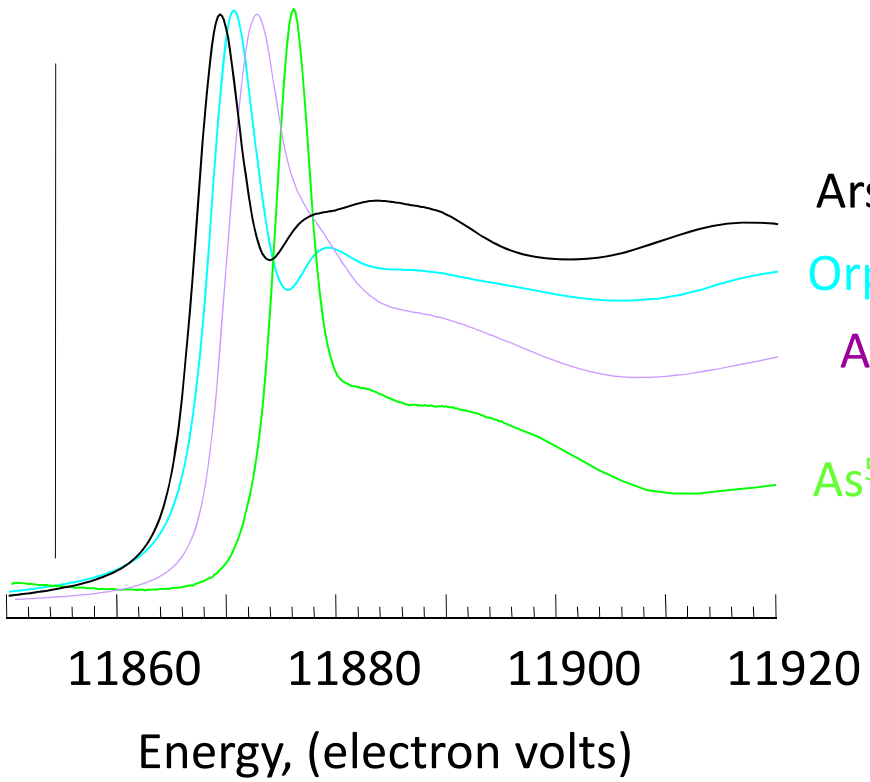
Spectral Deconvolution by Least-Squares Fits

XANES spectra



Energy increases with oxidation state

Arsenopyrite (As^{1-})

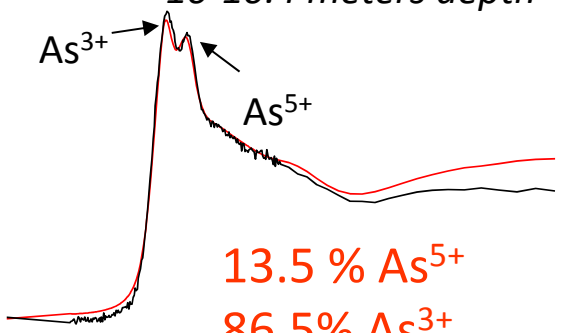
Orpiment (As^{3+}-S)

As^{3+} in water (As^{3+}-O)

As^{5+} on rust (iron oxyhydroxide)

Unique spectral shape

Bangladesh Aquifer Sediment
10-10.4 meters depth



13.5 % As^{5+}

86.5% As^{3+}

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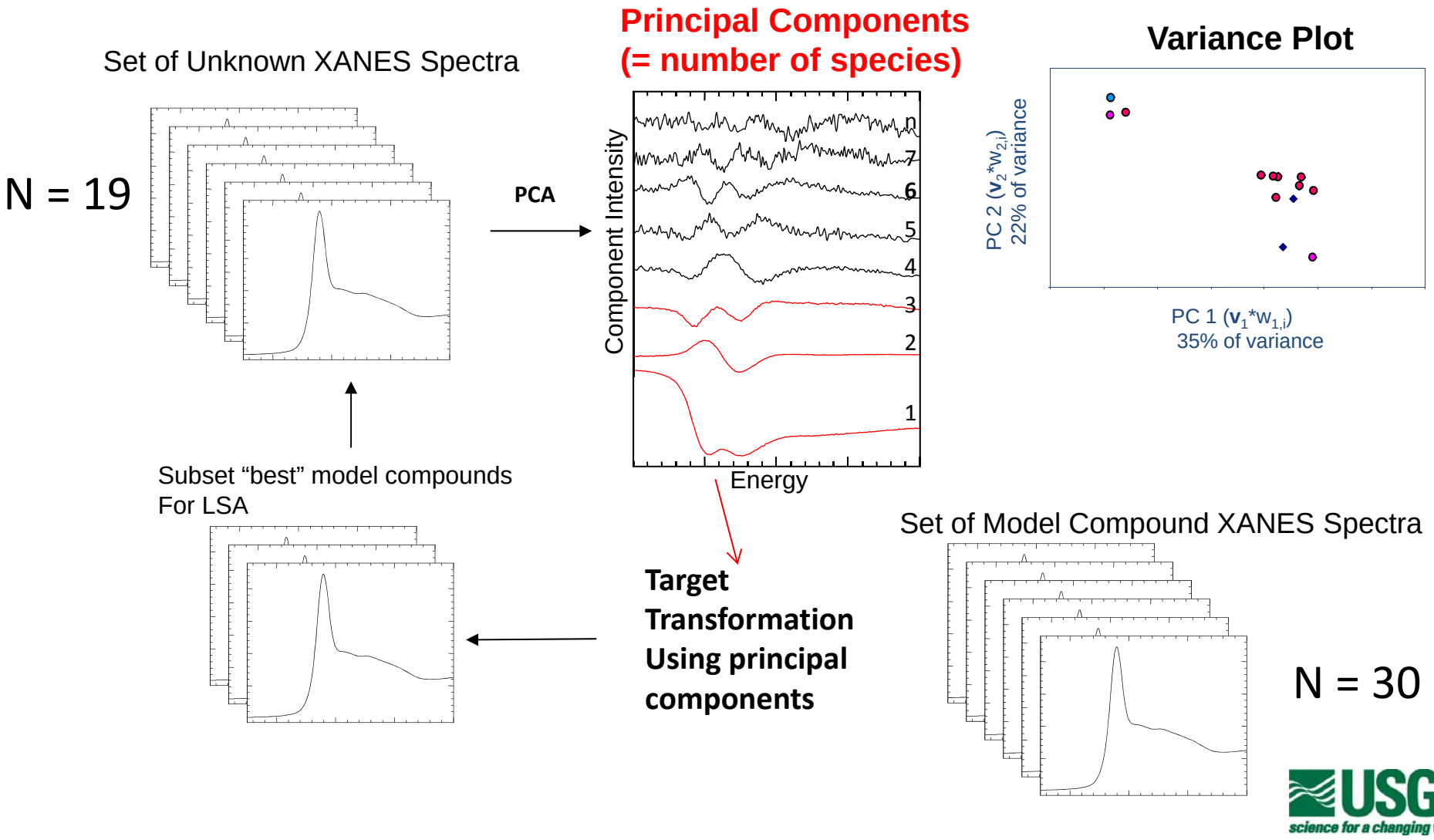
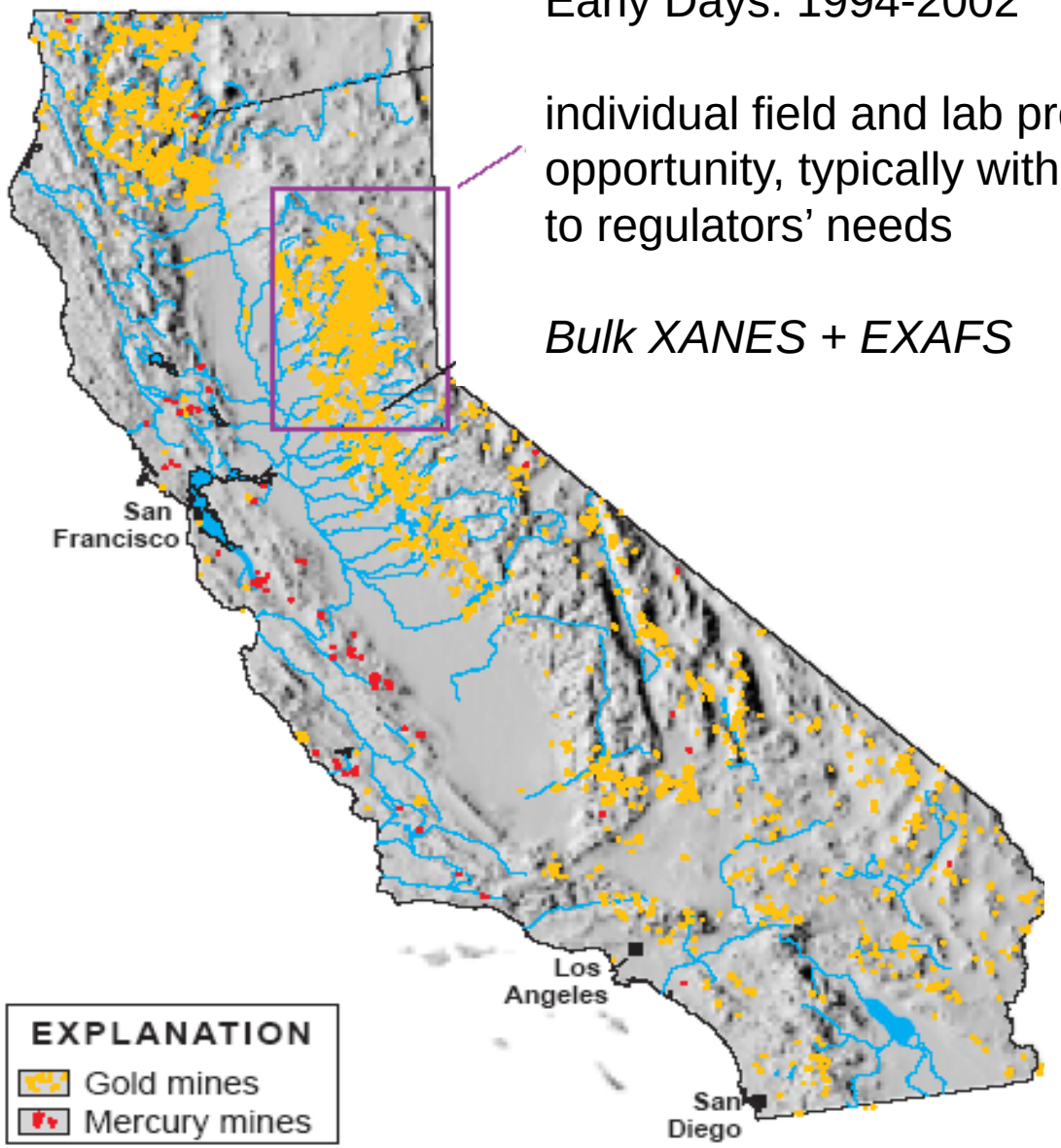
Principal Component Analysis of XANES or EXAFS Spectra



Synchrotron studies of As in Gold Mine Wastes



Early Days: 1994-2002

individual field and lab projects at "targets of opportunity, typically with limited connection to regulators' needs

Bulk XANES + EXAFS

2003- present

collaborative projects at high-profile sites; research focused on addressing needs

Microbeam studies: 2005 and later
Coupled XAFS, XRD XRF
Coupled bulk and microbeam
Multi-metal XAFS

Complimentary Lab-based techniques
Micro Raman, XRD

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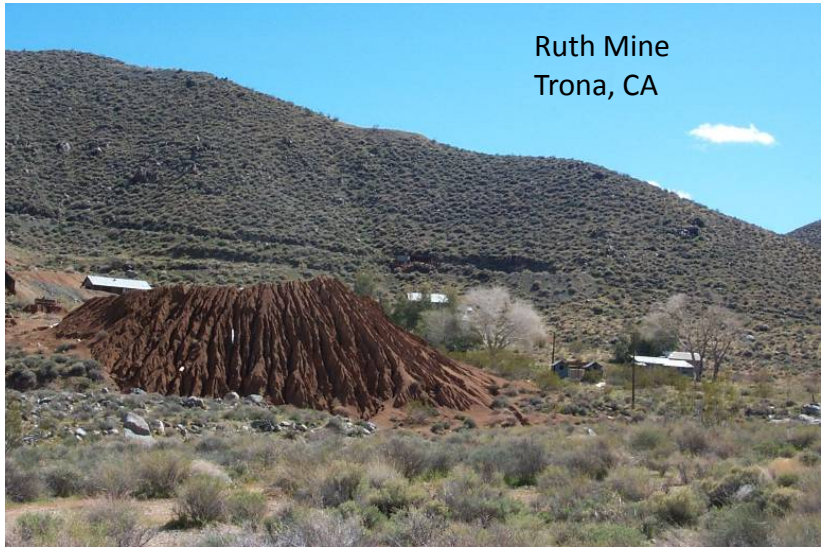
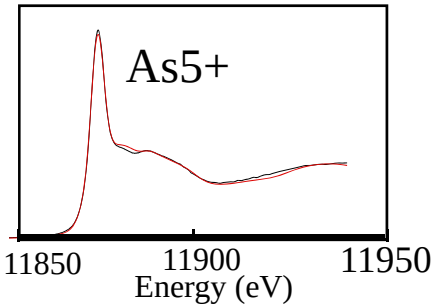
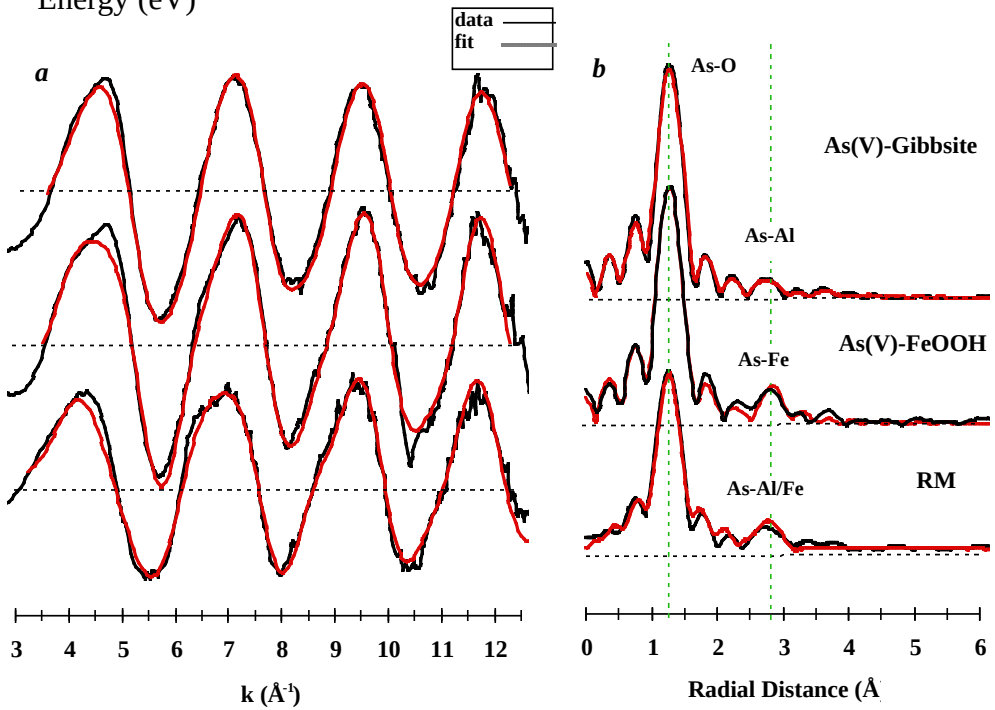
Ruth Mine: Ballarat District (Trona, CA)

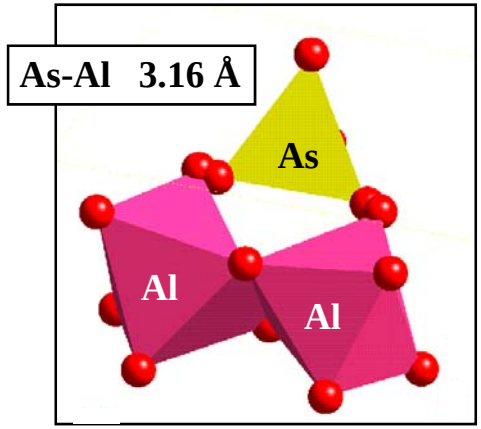
Tailings (ca 1000 mg/kg As) used for residential landscaping

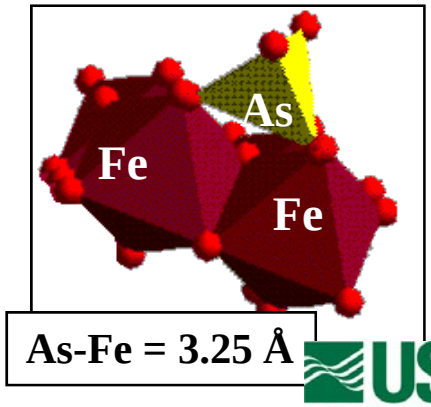


D. Lawler, BLM









Foster et al., (1998) *American Mineralogist* **83**, 553-568

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Mesa De Oro: Should be “Mesa de Arsenico”

- Gold tailings with 115 – 1320 mg/kg arsenic
- 40 homes developed on Mesa between 1975-1985
- EPA emergency response
  - halted new home construction
  - removed and replaced about 1 foot of soil
  - shored up sides of Mesa

Residents won 2,000,000 for loss of property value

http://consumerlawpage.com/article/environmental_pollution_1.shtml

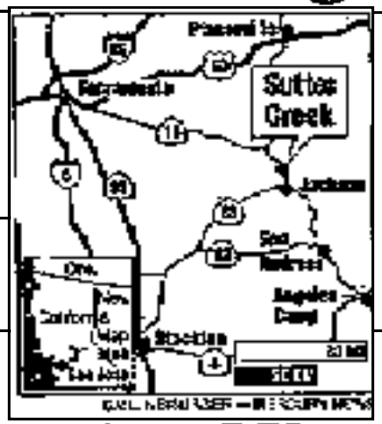
http://www.pbs.org/newshour/bb/environment/superfund_4-16.html (transcript of 1996 show called “Paying for the Past”)

George Wheeldon, “geologist”: arsenic from the mine is in a form that is not dangerous

San Jose Mercury News

Foothills hazard: Homes built on mine tailings

■ Arsenic: Residents have been warned to avoid touching soil.



■ ENVIRONMENT

Arsenic and Old Mines

As Montanans battle a new gold rush, Californians are dealing with the poisonous legacy of the past

Time Magazine Sept 25, 2000

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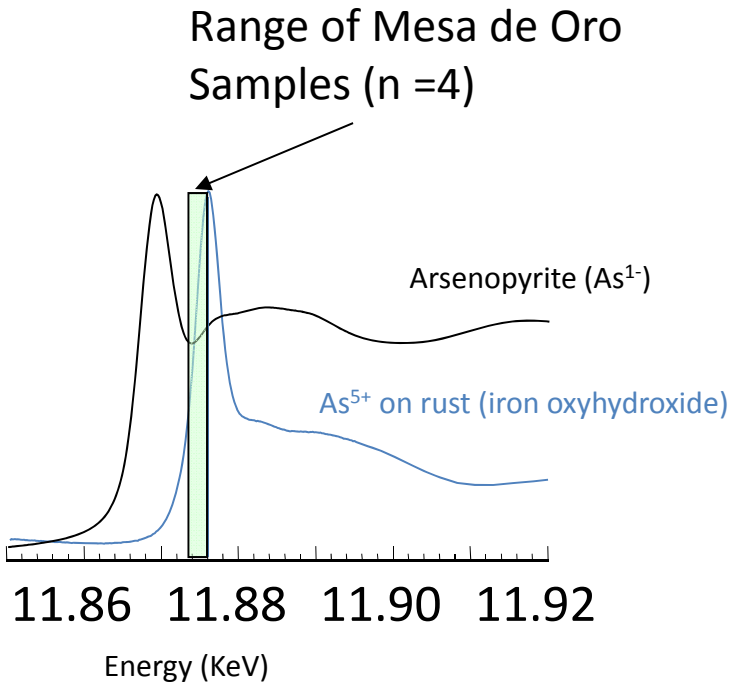
XANES spectra of Mesa de Oro soil samples demonstrate that arsenic is **not** in arsenopyrite form

Arsenopyrite FeAsS

Arsenic (V) on Rust



Mr Wheeldon's Error: assuming that arsenic stays in original form

A. Foster, R. Ashley, and J. Rytuba, USGS: unpublished data

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Lava Cap Mine Superfund Site, Nevada Cty, CA

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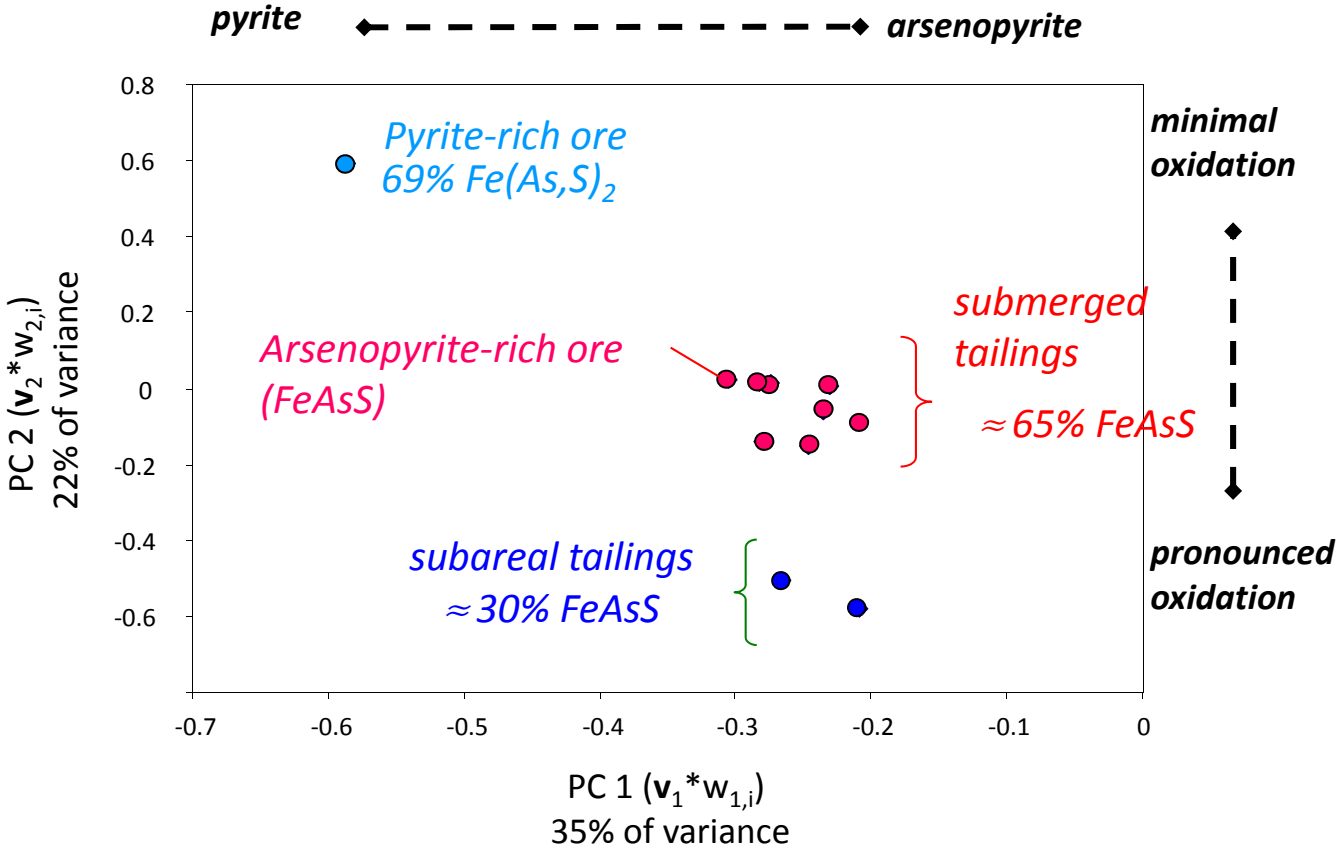
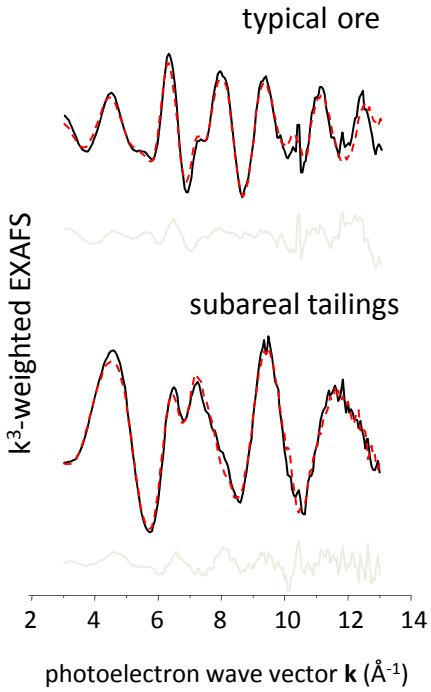
Arsenic species in mine-impacted sediment from the Lava Cap Mine

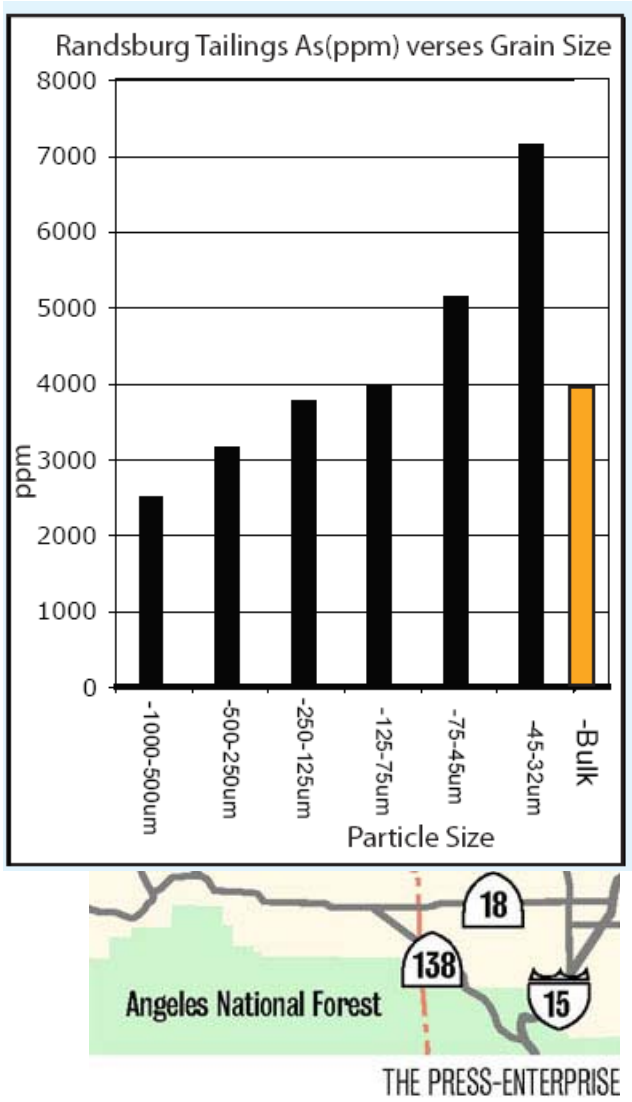
Our first studies at Lava Cap showed that submerged tailings from the private lake contain As in its original forms. Tailings exposed to air after the burst of a log dam in 1998 have oxidized considerably.





Foster et al., (2010) Geochemical Transactions

Kelly/Rand Mines: Ultra-high arsenic in mine tailings



- gold-silver mines operated until 1947
- *approximate volume:* 100,000 tons
- breach of tailings levee; migration of tailings into residences in Randsburg
- 3000->10,000 mg/kg As
- remote, Federal Land (BLM), popular with OHVers

Kim, C.S., Wilson, K.M., and Rytuba, J.J. (2011) Particle-size dependence on metal distributions in mine wastes: implications for water contamination and human exposure. *Applied Geochemistry* **26**, 484-495.

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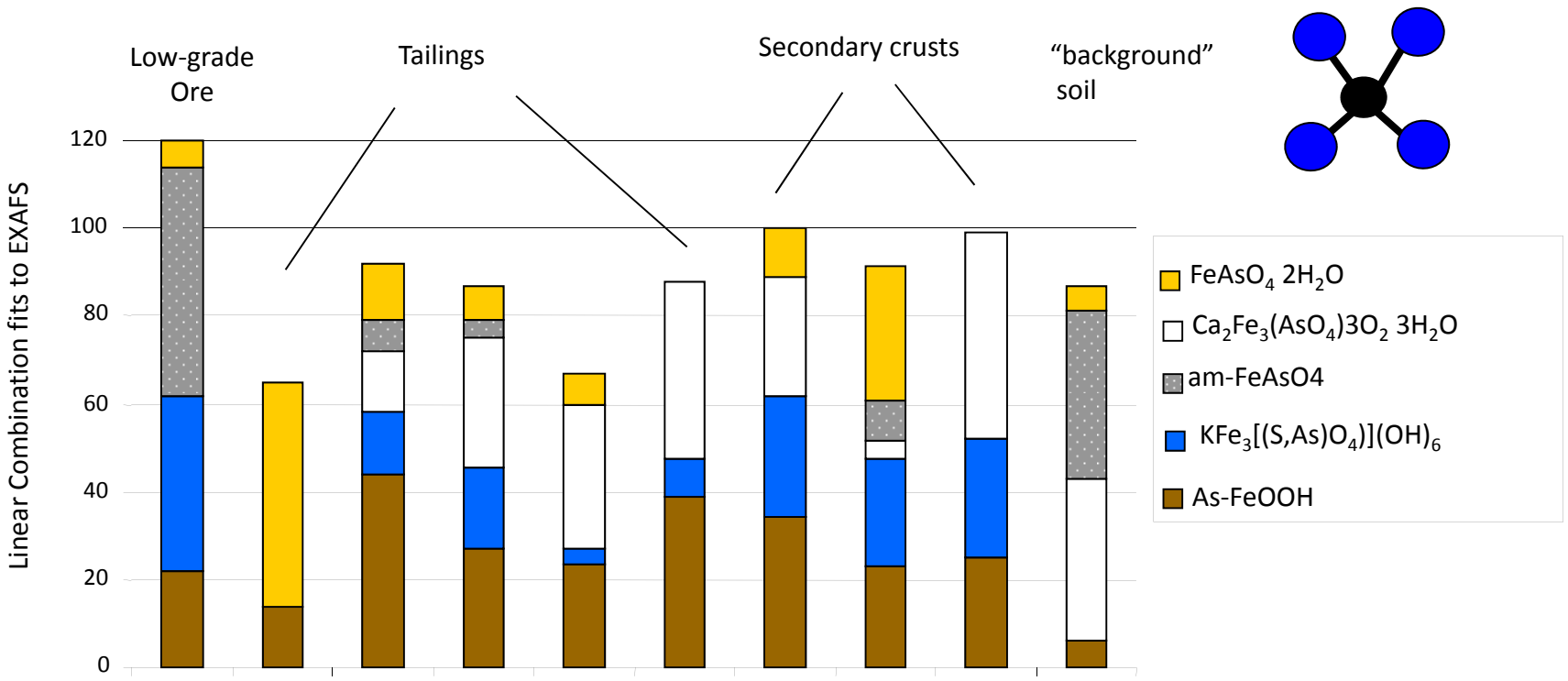
Secondary arsenates and As^{5+}-rich sulfate phases predominate in Kelly/Rand tailings



- no evidence for primary sulfide phases (below detection? Oxidized?)

- solubility and kinetics of dissolution of precipitates is expected to be very different than that of arsenic on ferric oxyhydroxide

Kim, C.S., Wilson, K.M., and Rytuba, J.J. (2011) Particle-size dependence on metal distributions in mine wastes: implications for water contamination and human exposure. *Applied Geochemistry* **26**, 484-495.

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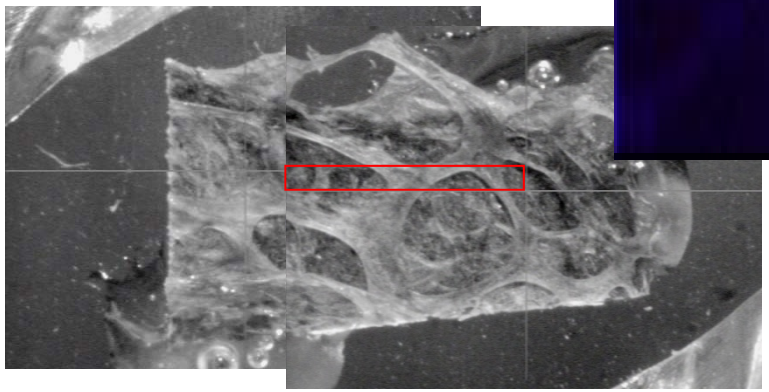
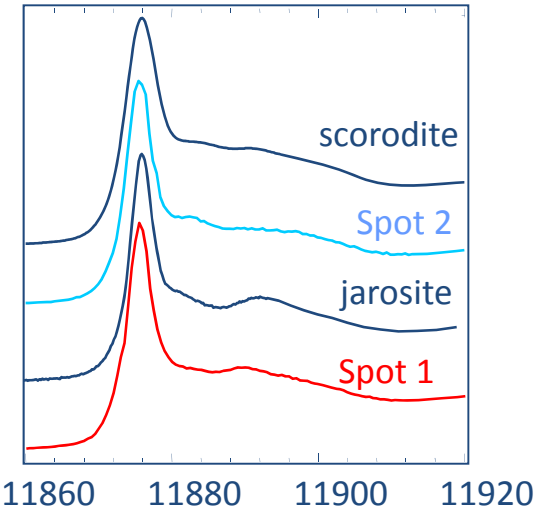
Lungs of tortoises collected near mines contain particles similar to those found in mine tailings

687 lung tissue





A. Foster, unpublished data

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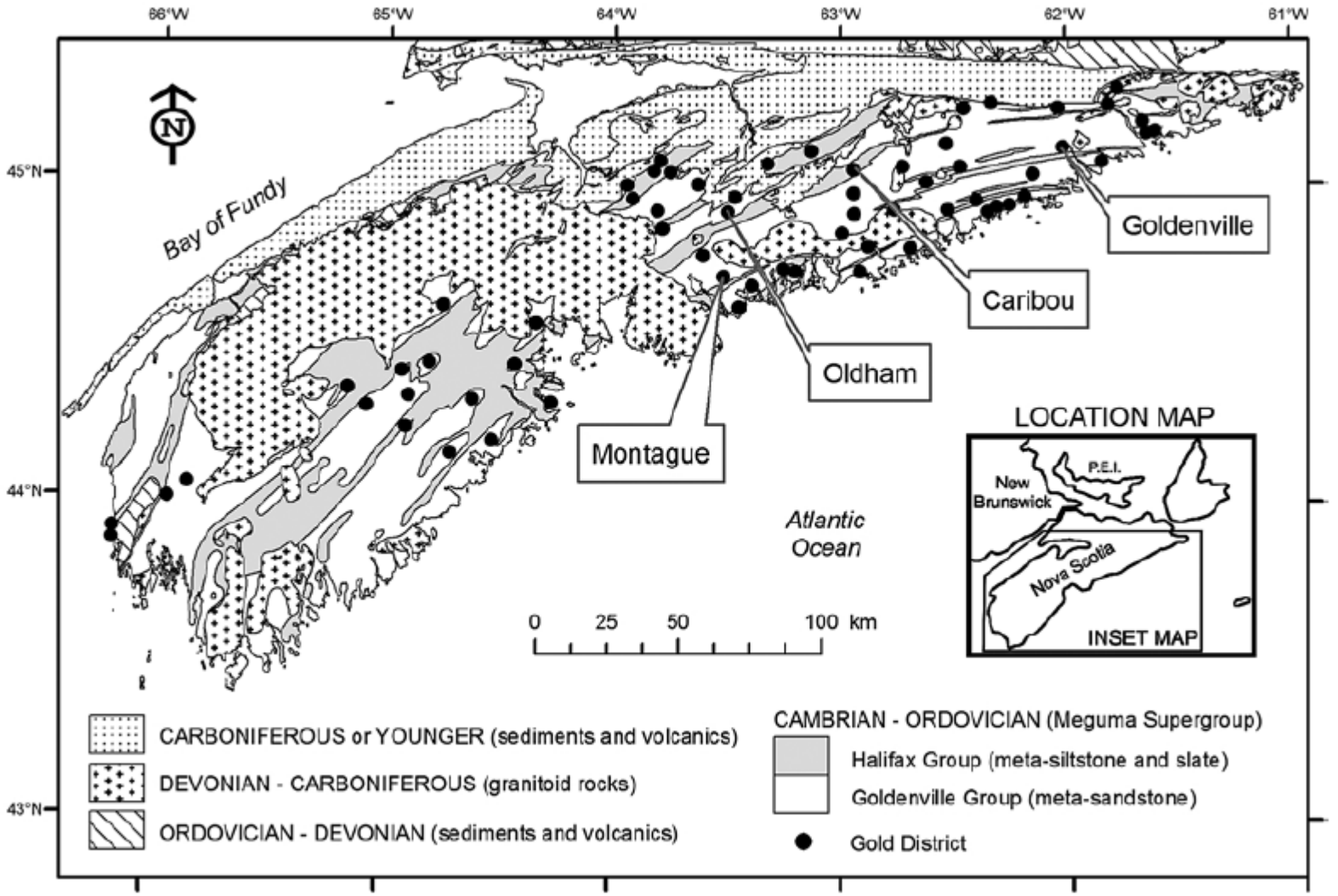
Ultra-high As gold mines in Nova Scotia, Canada



Walker et al (2009) Canadian Mineralogist v 47

Current and Future directions in synchrotron-based arsenic research

- Validated method for As bioaccessibility test
  - Coupled to geochemistry, As speciation
- Bioreactors (anaerobic and aerobic)
  - Aerobic: naturally-occurring microbial consortia?
  - Anaerobic: relative bioaccessibility of As in neo-sulfides vs. organic compounds (biomass)
- Plants
  - Finding more accumulators, maximizing uptake
  - Coupling genetics, protein expression, and location of metal (As) sequestration

Arsenic Relative Bioavailability Project (Empire Mine State Historic Park)

Helping to find a cost-effective means of evaluating the potential for re-development of mined lands contaminated with arsenic

N =25

EMPIRE 1850 1956 MINE

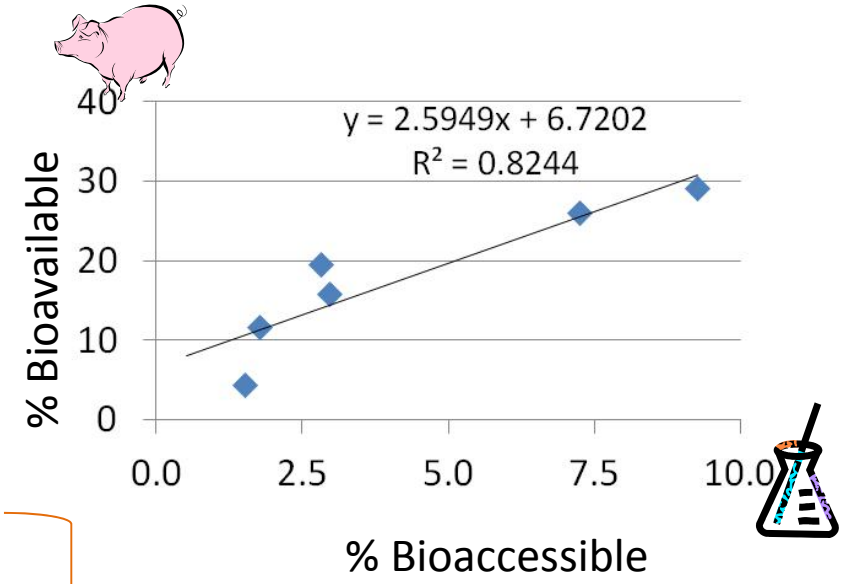
In vitro

25

In vivo

Chemistry
X-ray diffraction
Electron Probe
QEMSCAN
Particle size analysis
"Bulk" Synchrotron studies

"Microfocused" Synchrotron studies

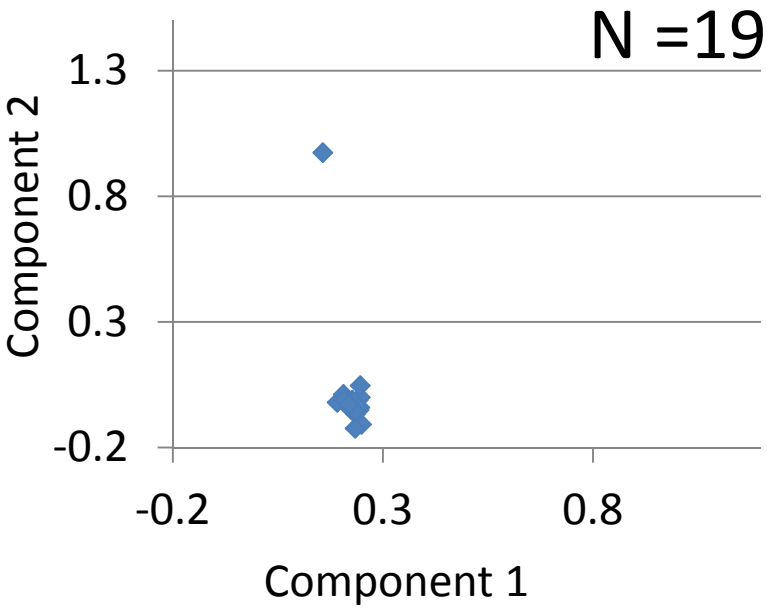


Model of mineralogical control on As bioaccessibility

Correlation with easily-measured parameter

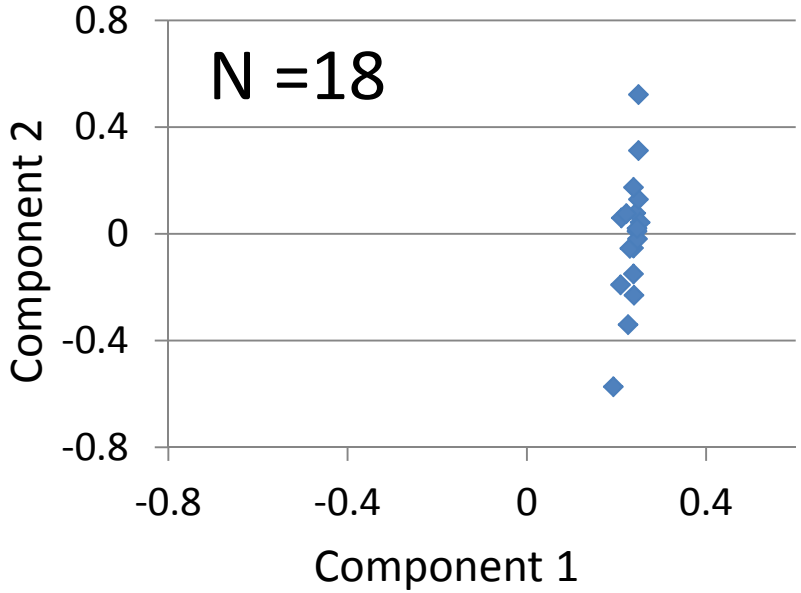
This study is conducted through a proposal by CA Department of Toxic Substances Control and USGS that was funded by US-EPA (Brownfields Program)

Principal Component Analysis predicts 4-5 unique arsenic species

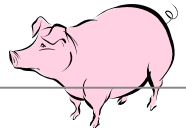


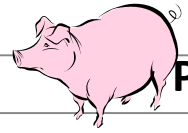
Variance can be visualized on additional Component axes (3, 4, 5)

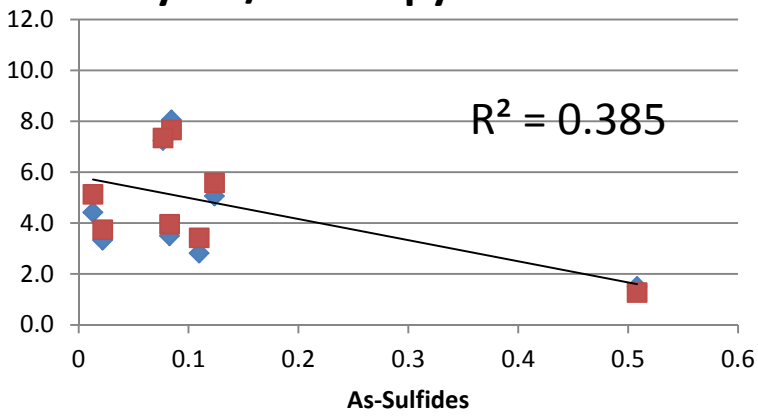
Outlier removed



Bioaccessibility and Bioavailability have similar trends with key arsenic species







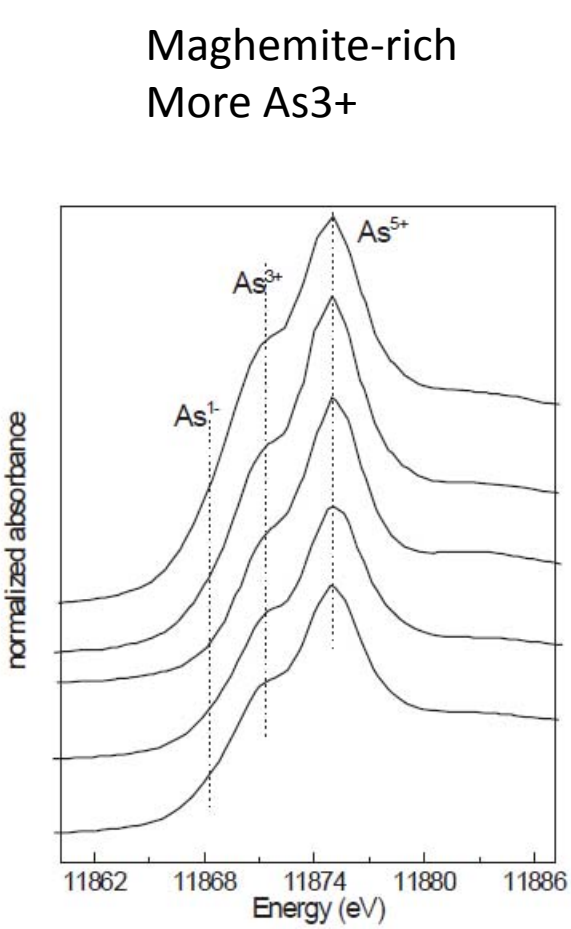
SEE MORE AT ALPERS TALK TOMORROW SESSION 10

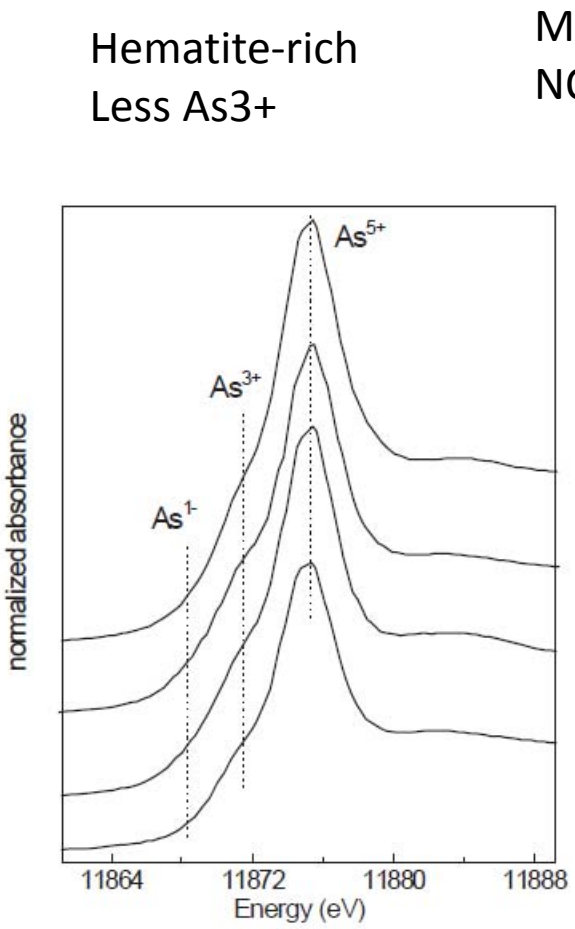
Arsenic in roasted ore treated by an anerobic biochemical reactor

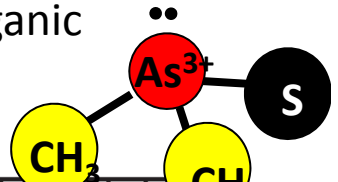
Maghemite-rich
More As3+

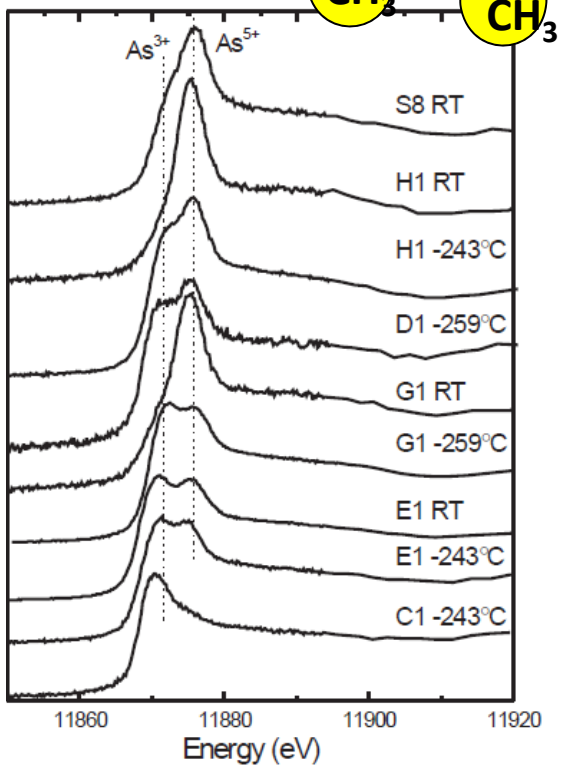
Hematite-rich
Less As3+

Anerobic Reactor Samples
Mostly As3+, but organic
NOT SULFIDE (??)









Paktunc et al. (2008) Proceedings of the 9th Intl Conference for Appl. Mineralogy

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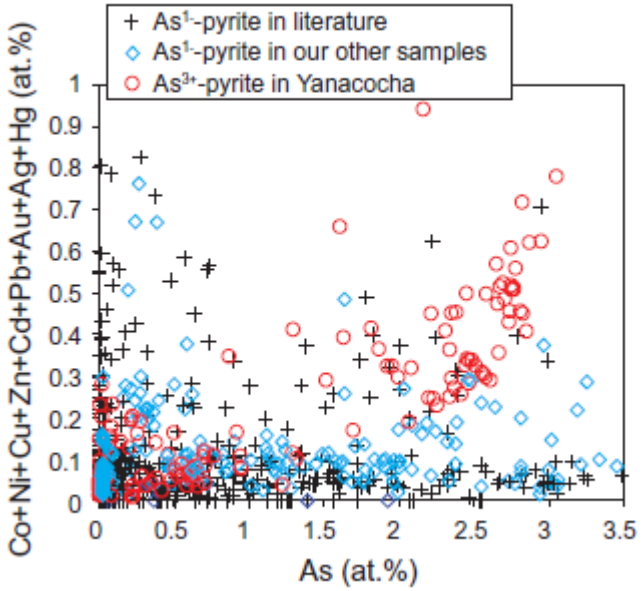
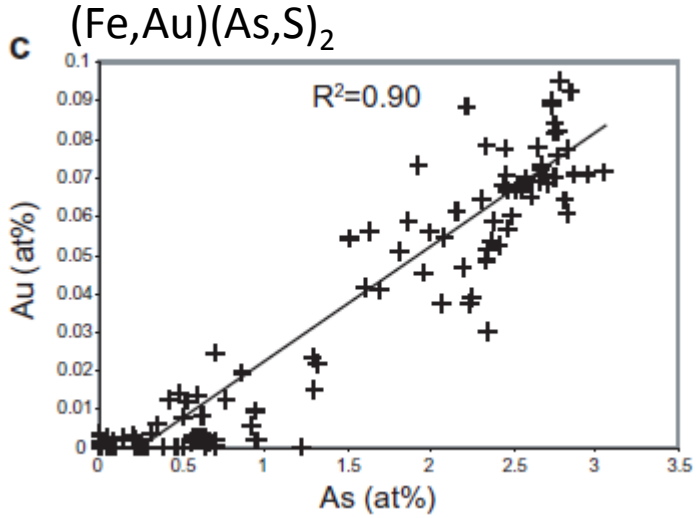
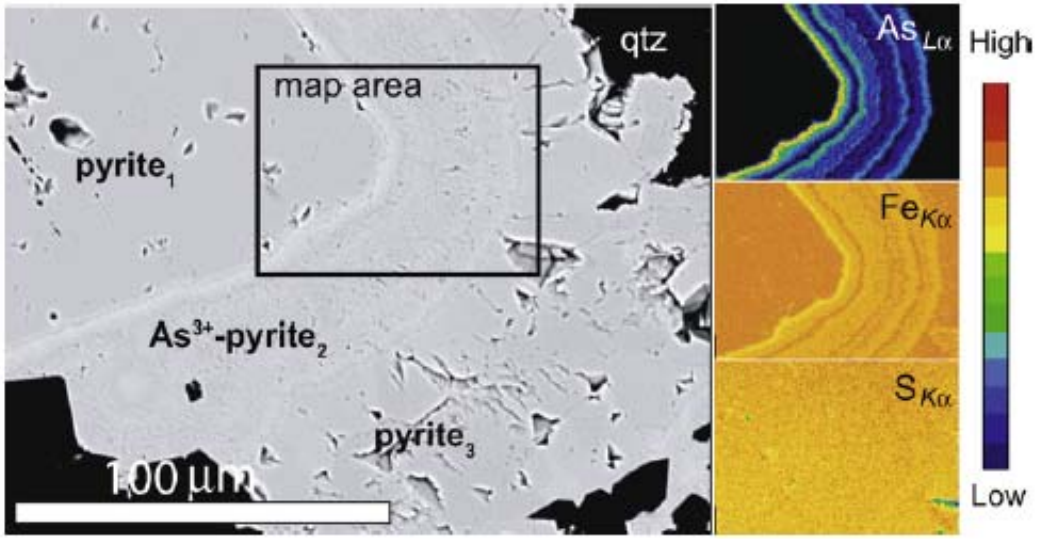
New and improved pyrite: now with As^{3+}

Deditius et al (2008)
Yanacocha , Peru

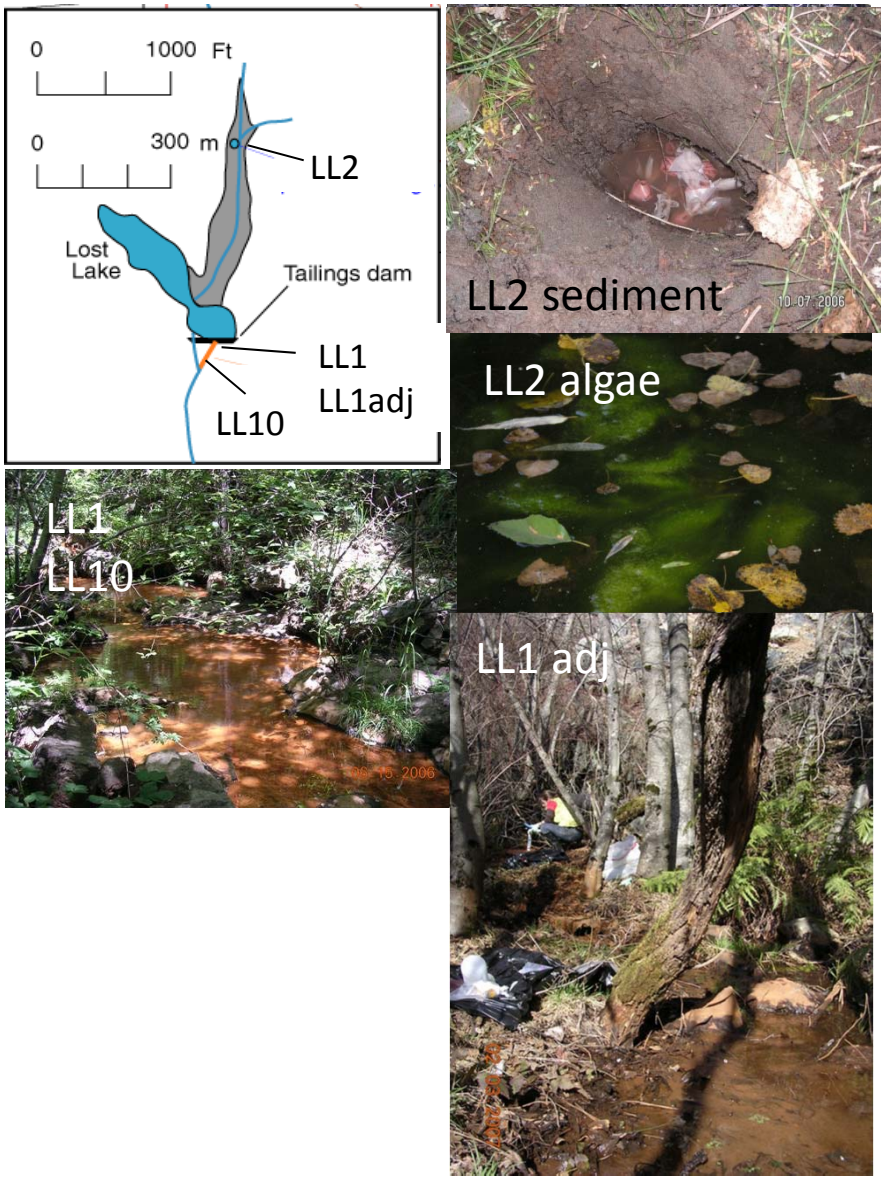


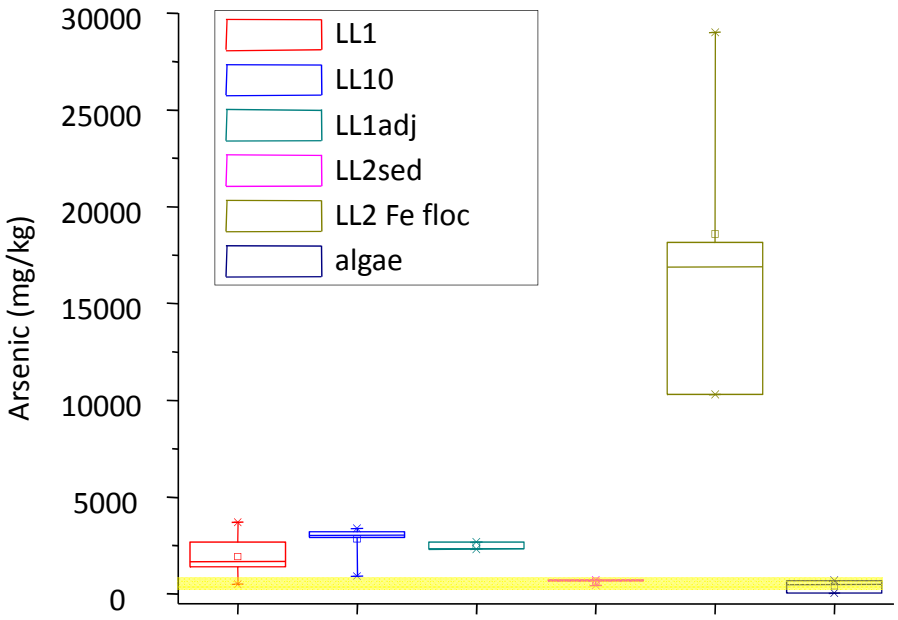




Should be present in other low-sulfidation epithermal deposits: Nevada Au?

Arsenic attenuation by naturally-occurring microbial consortia: Lava Cap Mine (NPL), CA

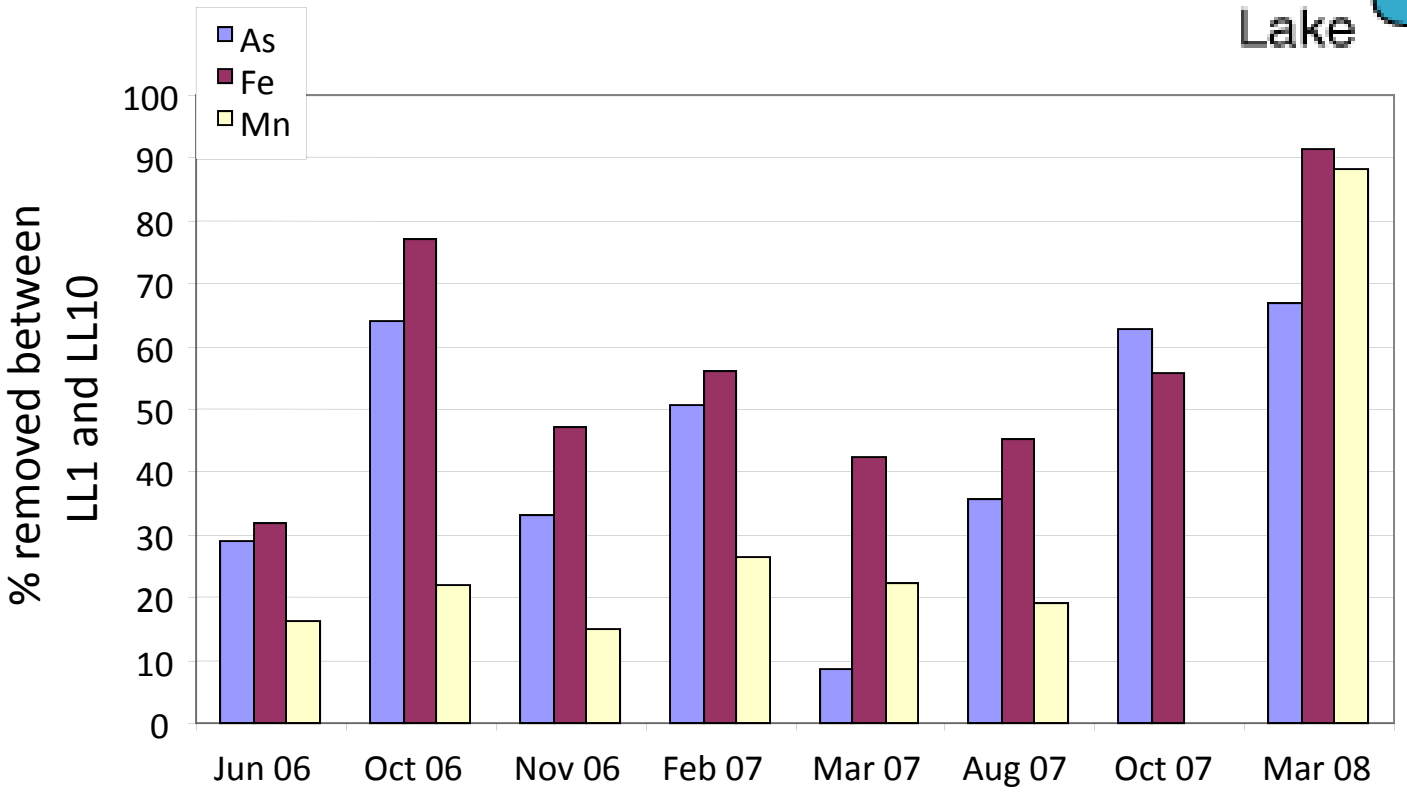


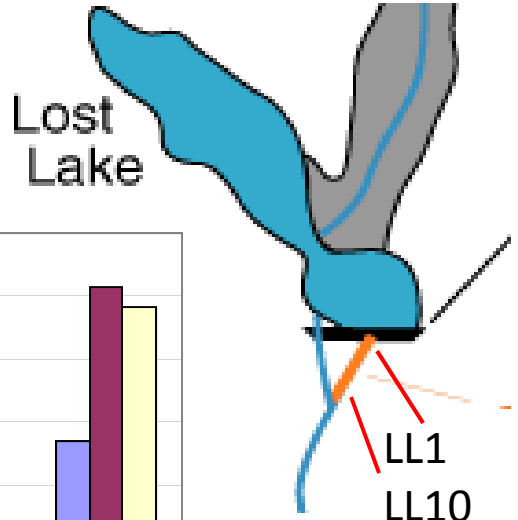


Foster et al, USGS Open File Report 2009-1268

Biogenic Fe-(hydroxide) accumulates arsenic to levels several times to orders of magnitude greater than the original mine tailngs (yellow horizontal line)

Monitoring the performance of a natural passive bioreactor





Concentration range at LL10	EPA cleanup goal:
As: 12-30 µg/l	10 µg/l
Mn: 235-2000 µg/l	300 µg/l

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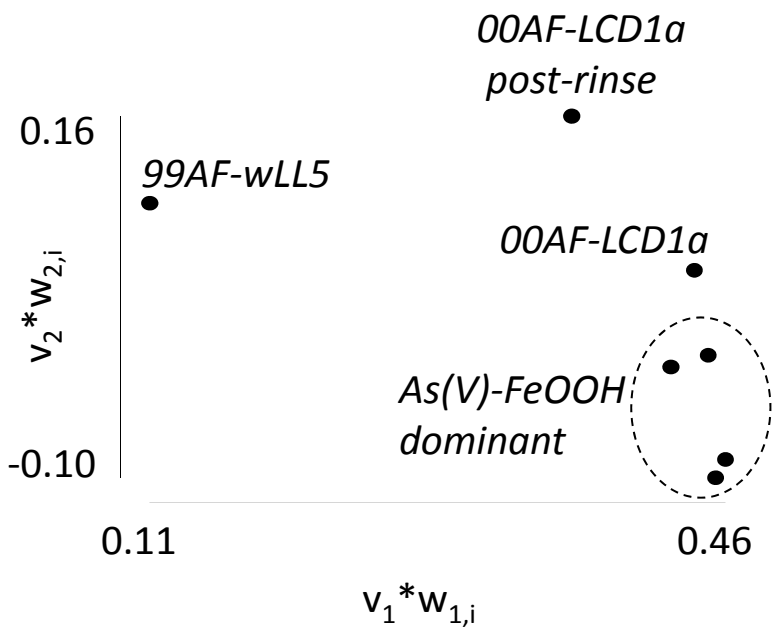
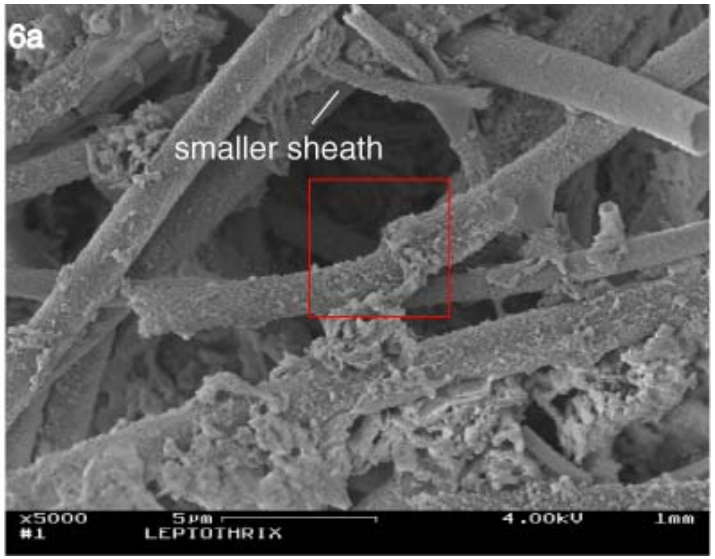
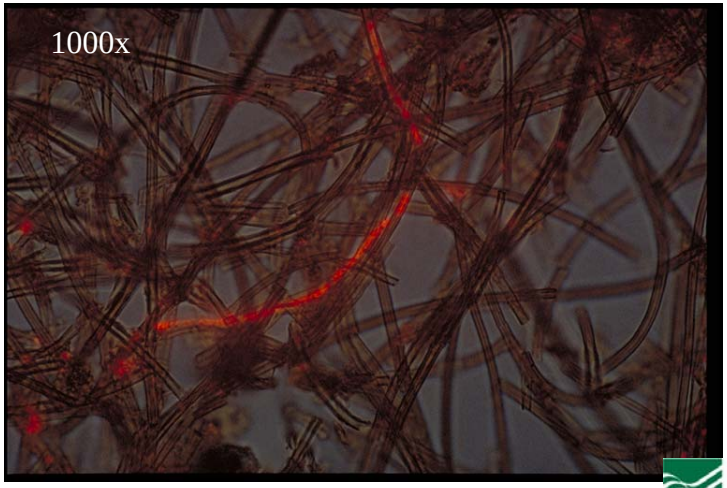
Arsenic is associated with Fe Oxyhydroxides rather than with biological materials (contrast the anerobic treatment of Paktunc)







EPA region 9 Superfund has a pilot aerobic /anerobic treatment in place at the adit, but is not supplanting it with the native microorganisms

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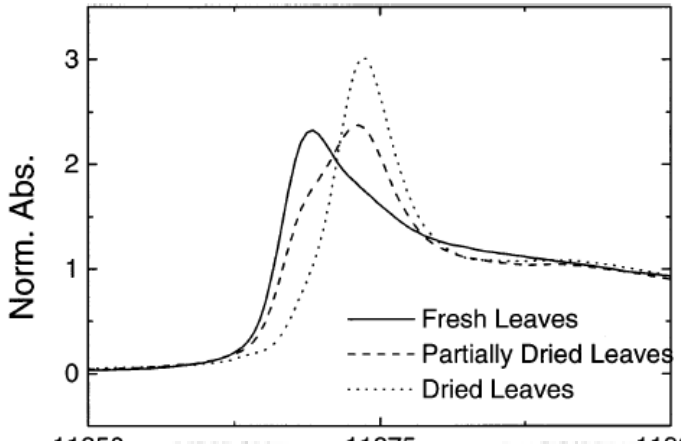
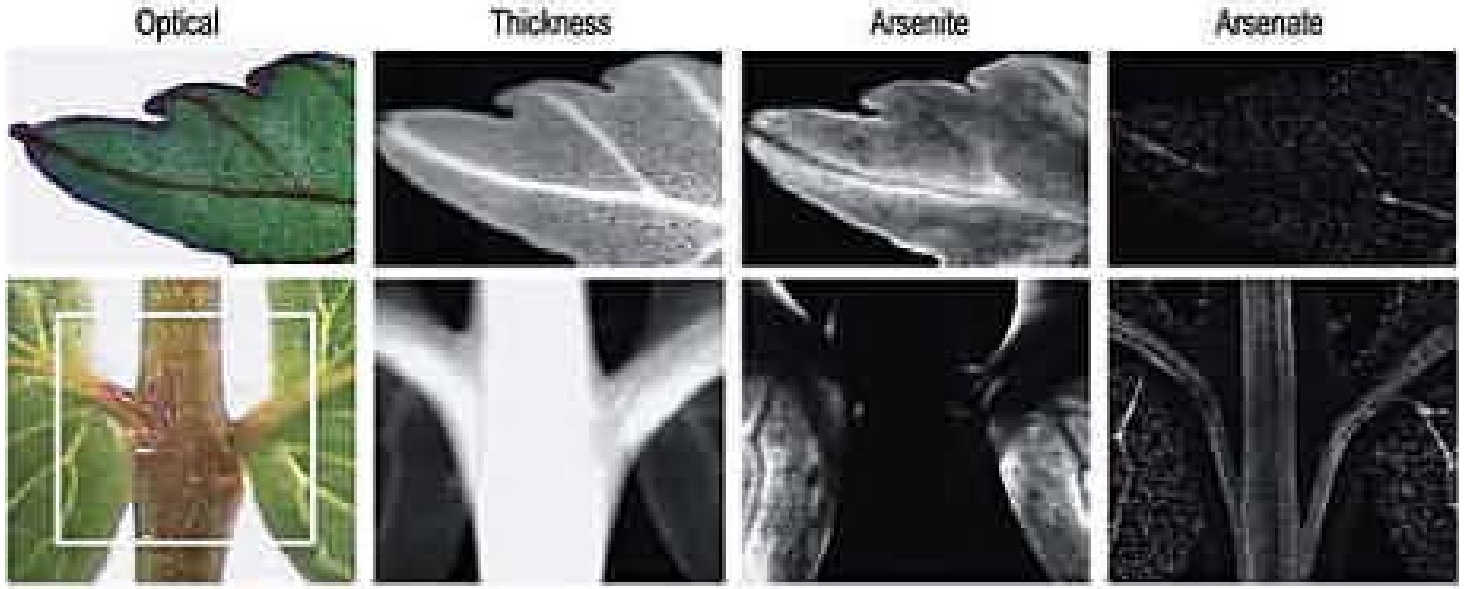
As Speciation in *Pteris vittata* Hyperaccumulating Fern





Webb et al (2003) ES&T

Pickering et al. Environ. Sci. Technol., 40 (2006) 5010-5014.

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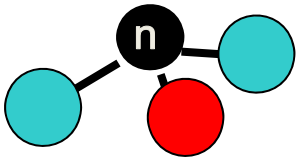
Synchrotron techniques have had great utility in the study of arsenic speciation in gold mines..there is more to come!

Primary (ore, concentrates)

Pyrite

Arsenopyrite



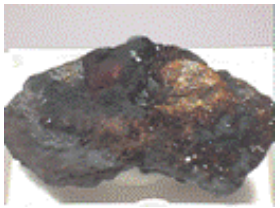
n = -1, +3

Near-neutral Ca minerals

Ca-Fe arsenates

acidic

As-poor

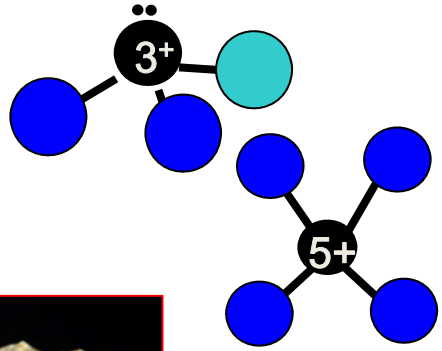


Fe sulfates

As-rich

Fe arsenates

+ Ca



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The End

Leptothrix ochracea from the Lava Cap Mine

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