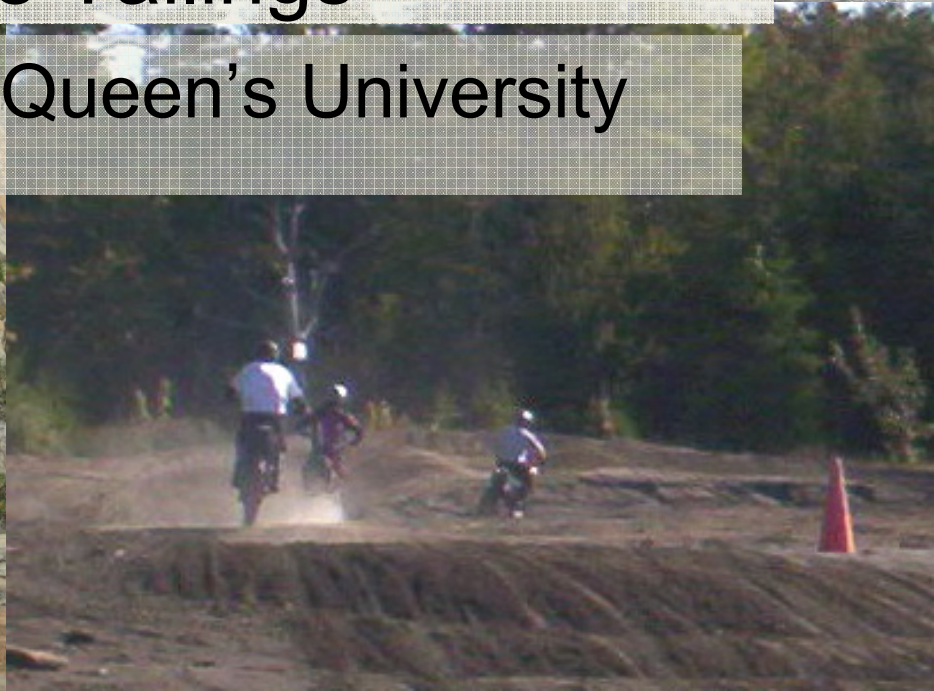


Mineralogical Controls on the Mobility and Bioaccessibility of Arsenic in Gold Mine Tailings

Heather Jamieson, Queen's University



Four examples from recent research at Queen's University

1. Giant Mine Tailings, Yellowknife

*S.R. Walker, H.E. Jamieson, A. Lanzirotti, C.F. Andrade, 2005.
Canadian Mineralogist 43, 1205-1224.*

2. Lake sediments, Yellowknife Bay

*C.F. Andrade, H.E. Jamieson, T.K. Kyser, T. Praharaj, D. Fortin,
Applied Geochemistry (accepted 2008)*

3. Roaster-impacted soils, Yellowknife area

*L. Wrye, H.E. Jamieson, Environmental Science & Technology
(submitted)*

4. Abandoned gold mines, Nova Scotia

*S.R. Walker, M.B. Parsons, H.E. Jamieson, Canadian Mineralogist
(submitted)*

1. In what mineral form is As hosted in gold mine tailings that include roaster waste?



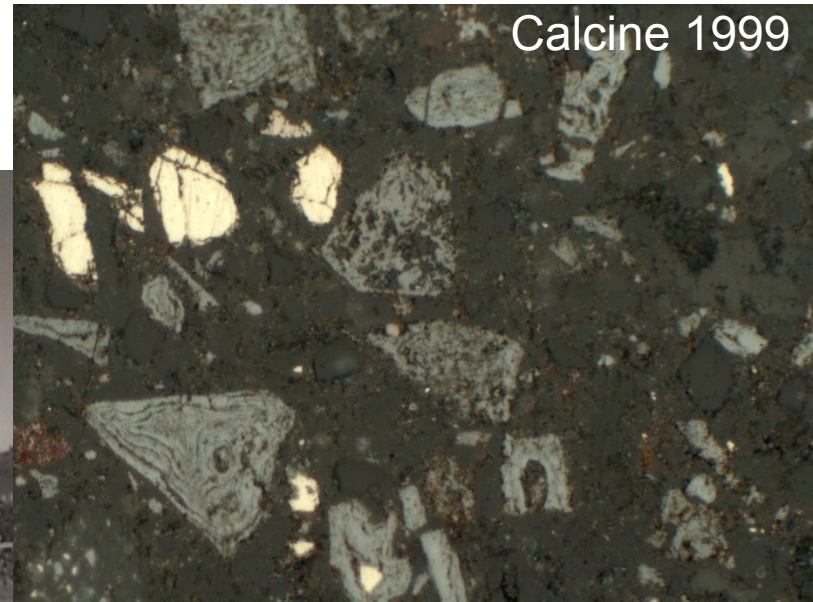
60 yr-old site managed by INAC with controlled public accessibility

Soon to be remediated

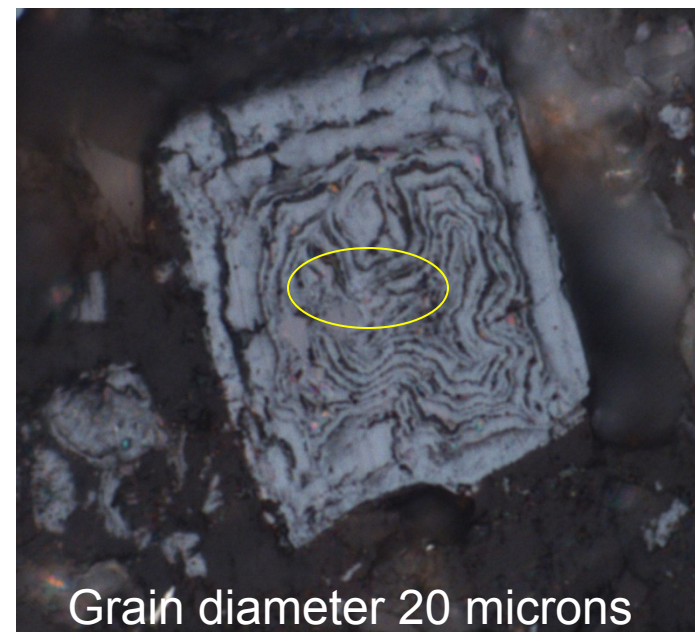
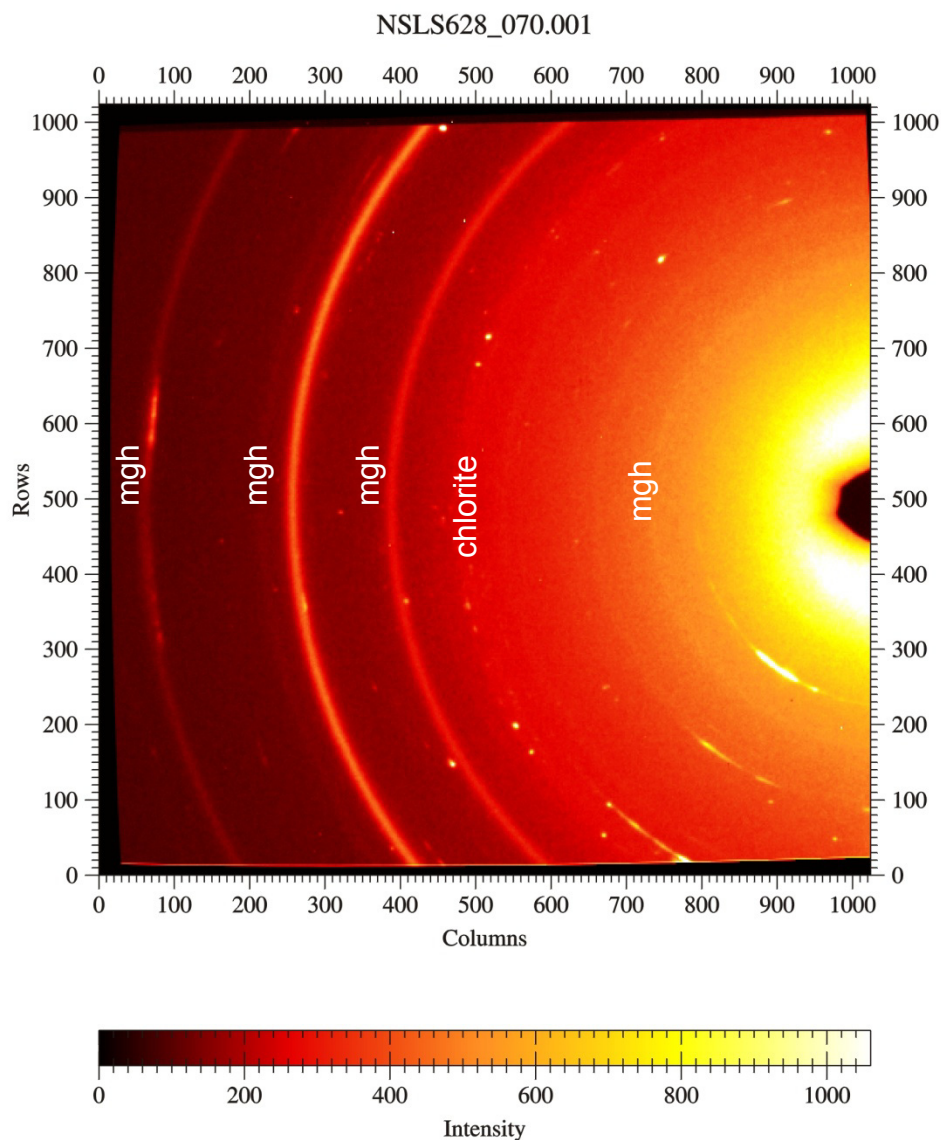
Mixture of flotation tailings & roaster waste (75% of arsenic in tailings from calcine)

Field of view 0.160 mm x 0.120 mm

Calcine 1999

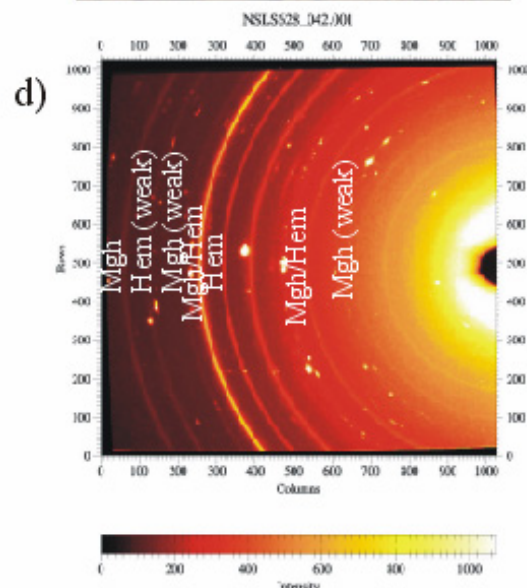
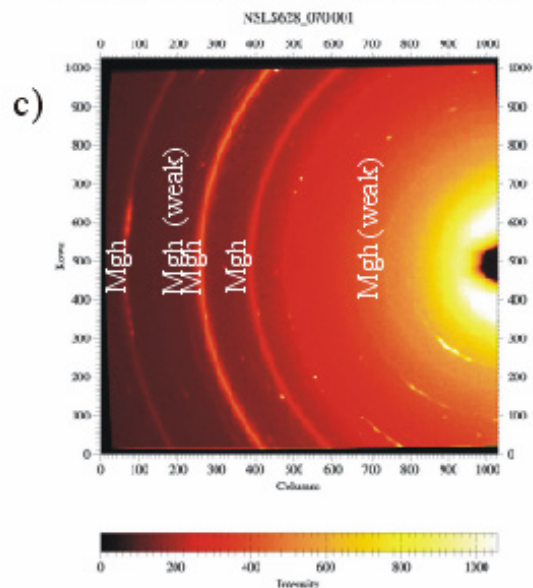
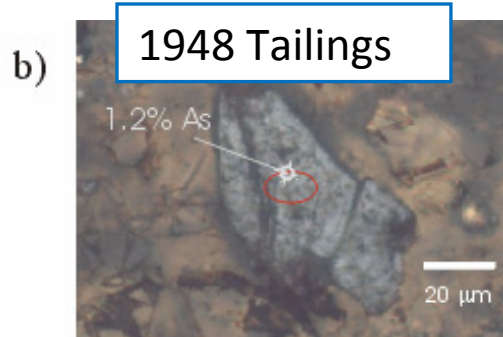
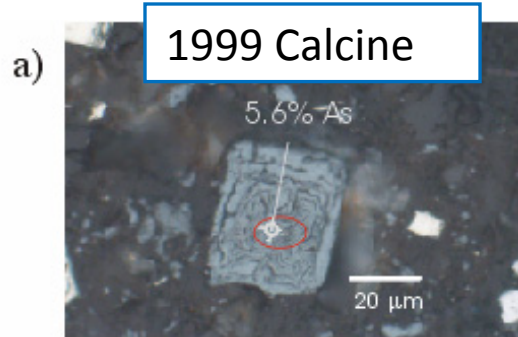


Synchrotron-based microXRD



Roaster oxides behave as powders
and produce Debye rings

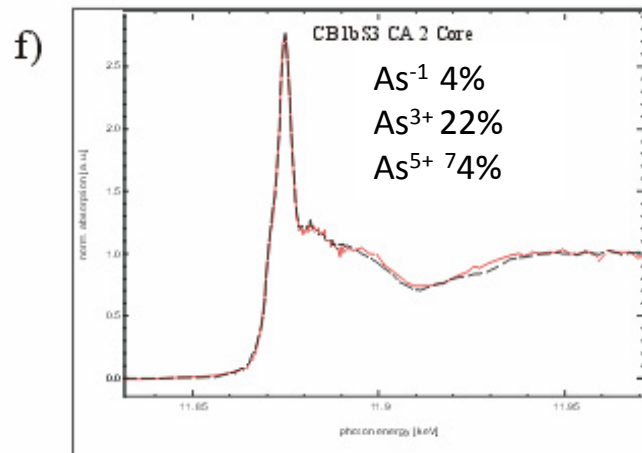
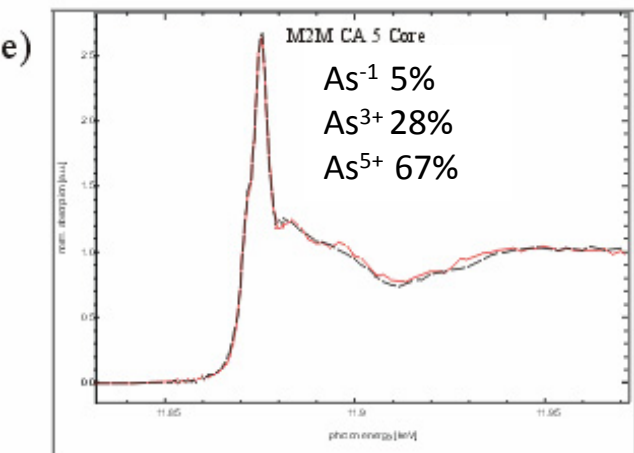
Centre of grain is nanocrystalline maghemite ($\gamma\text{-Fe}_2\text{O}_3$)



Roaster-generated Fe oxides (maghemite and hematite) contain 0.5 to 7% As

This is a mixture of As^{5+} and As^{3+}

Roaster oxides exposed to atmosphere for 60 years still contain As^{3+}



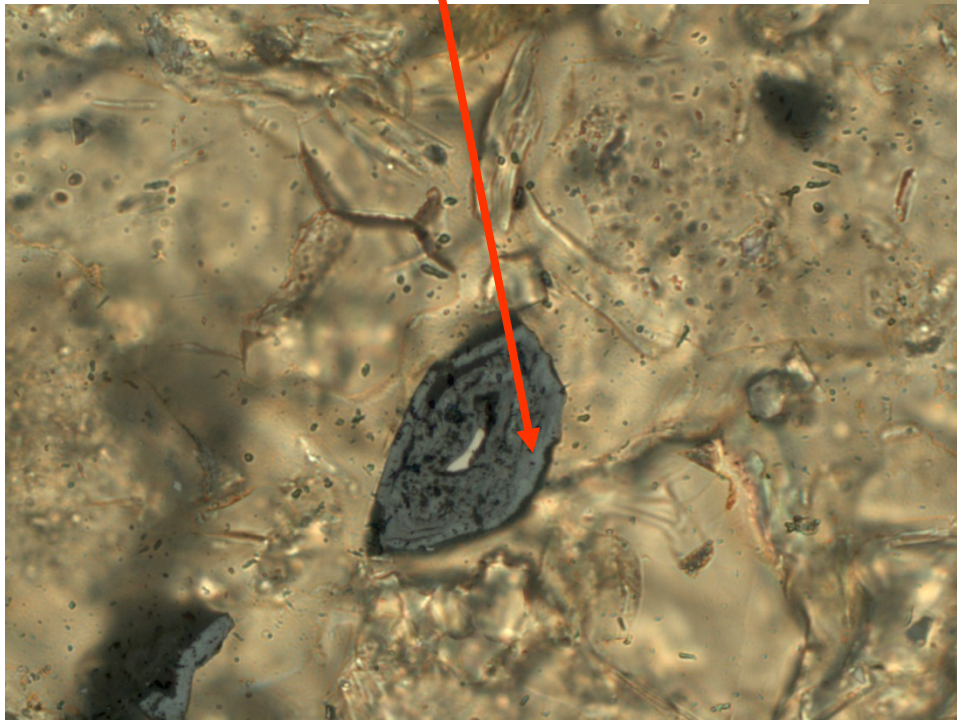
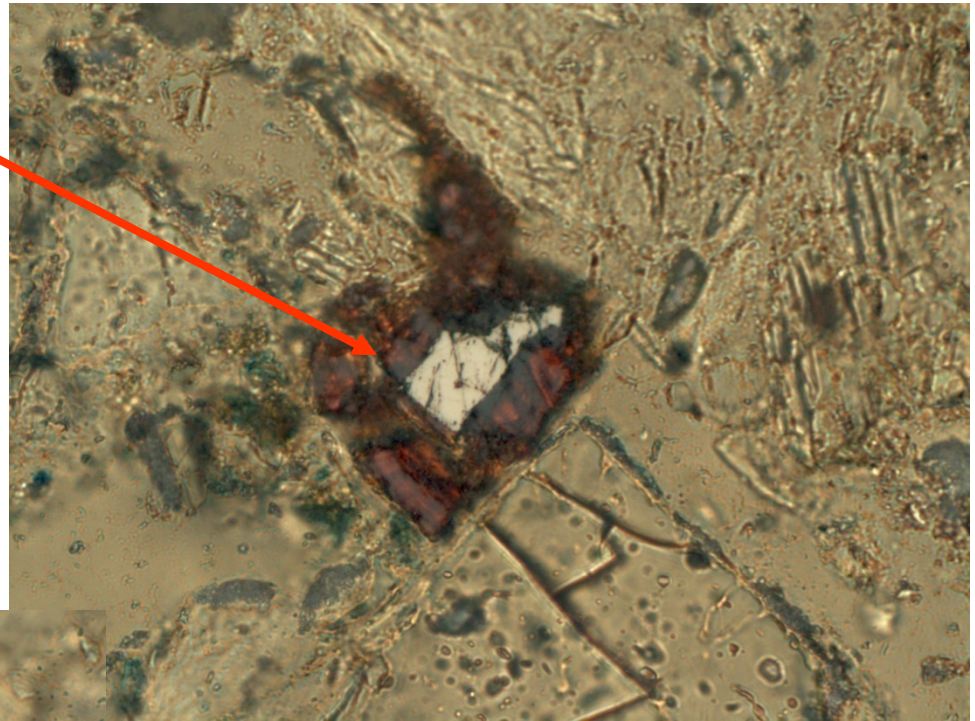
Oxidizing sulfides

Arsenopyrite and pyrite with
AsV-bearing iron oxyhydroxide rim

Roaster iron oxide

AsIII and As V-bearing iron oxide
around sulfide core

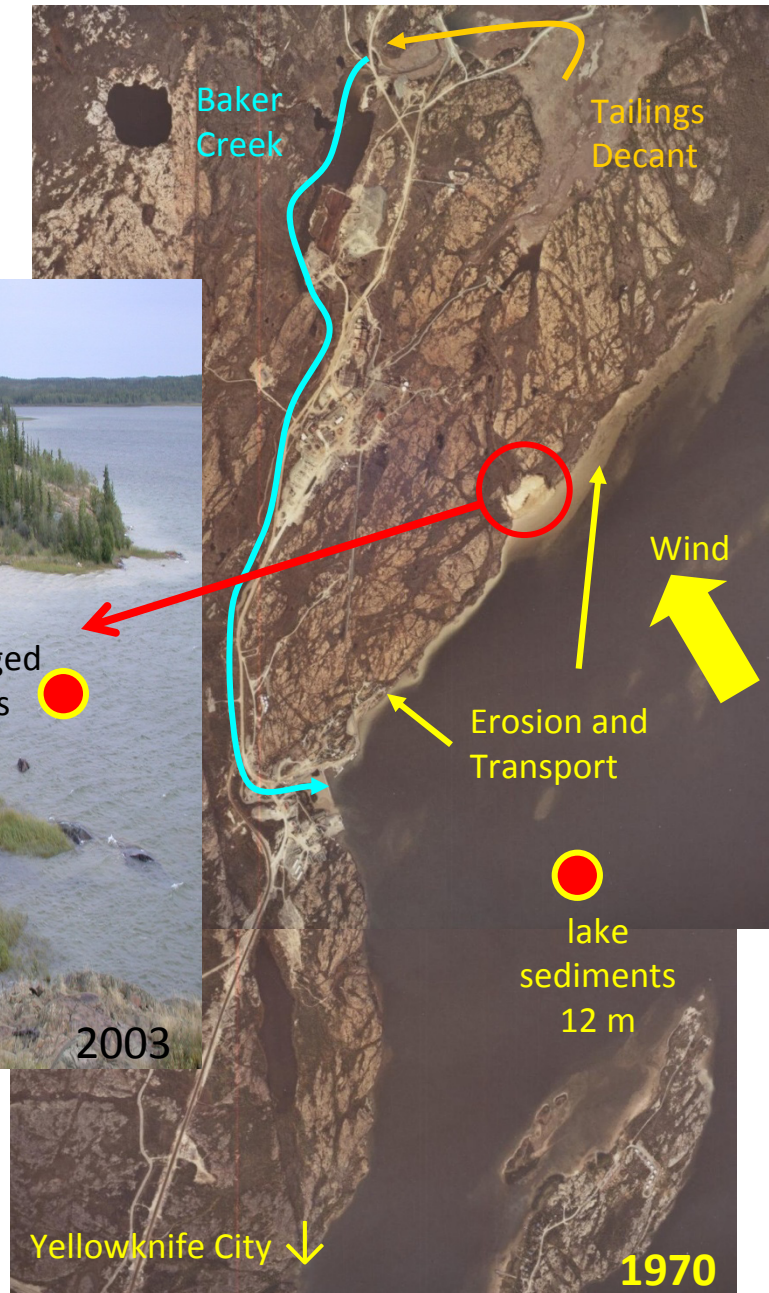
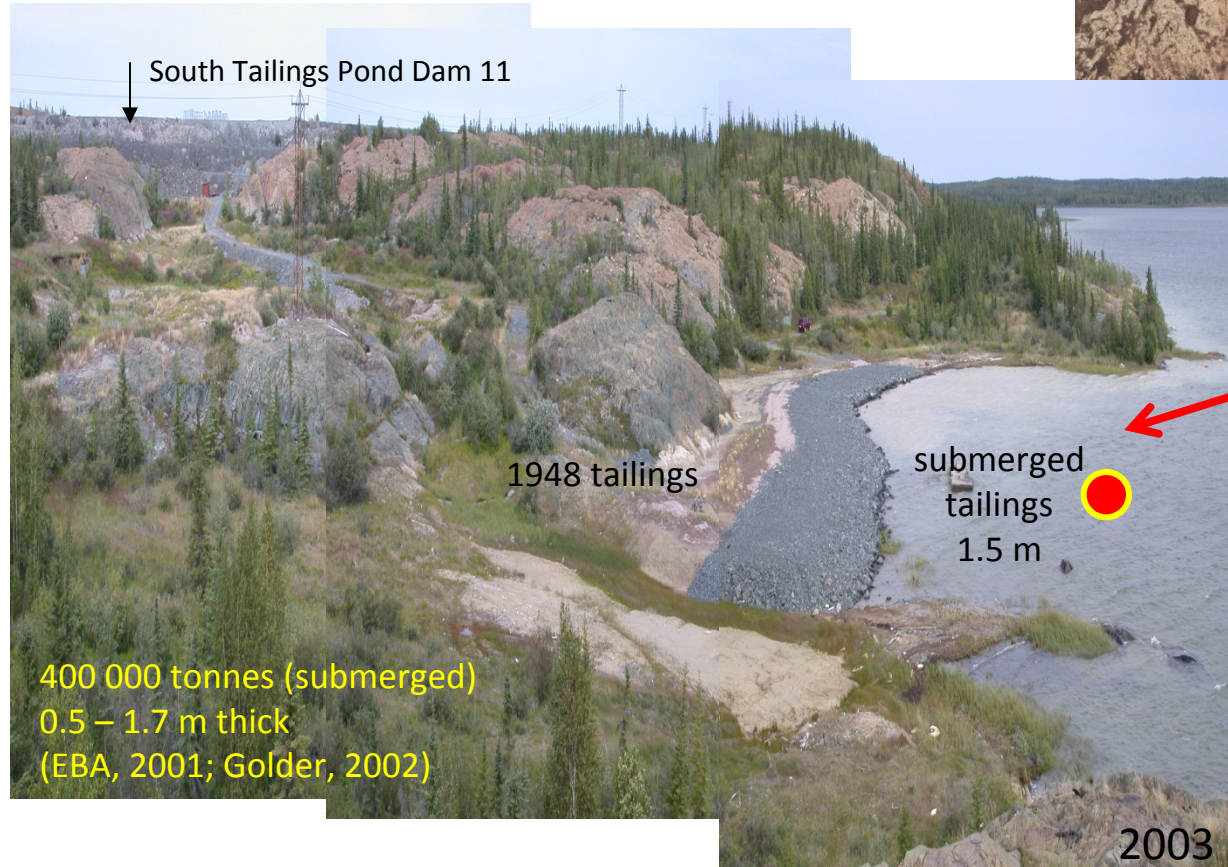
Field of view
0.16 x 0.12 mm



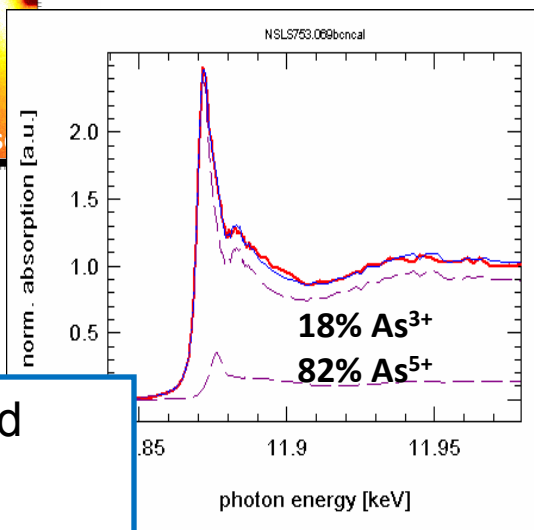
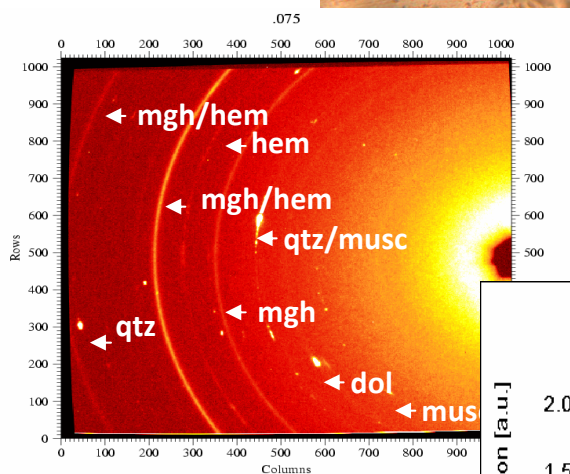
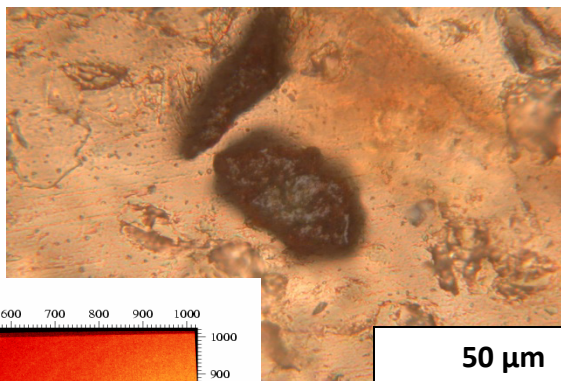
Conclusions

1. Tailings remediation plan designed for a mixture of oxide and sulfide-hosted As: composite cover
2. Understanding processing history is important to predict As mobility

2. Are As-bearing roaster oxides stable in Yellowknife Bay?



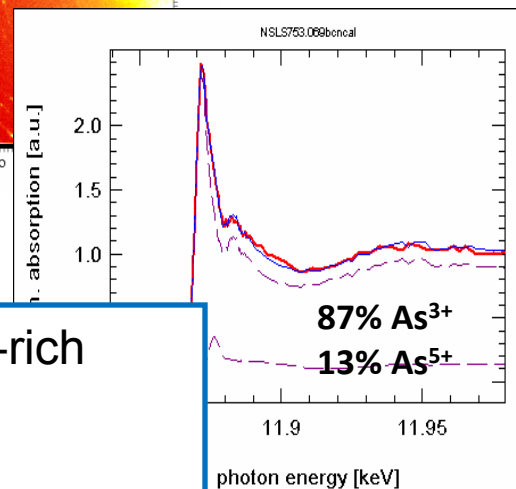
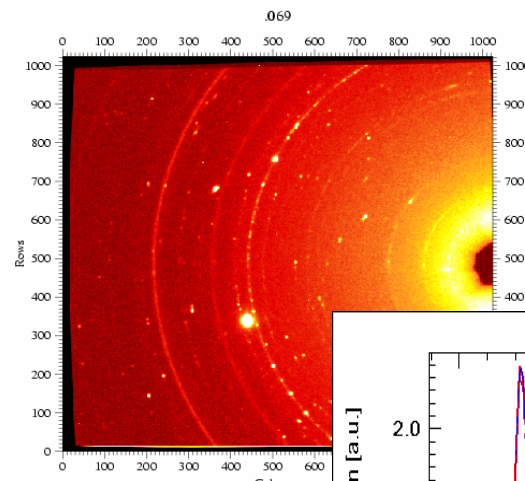
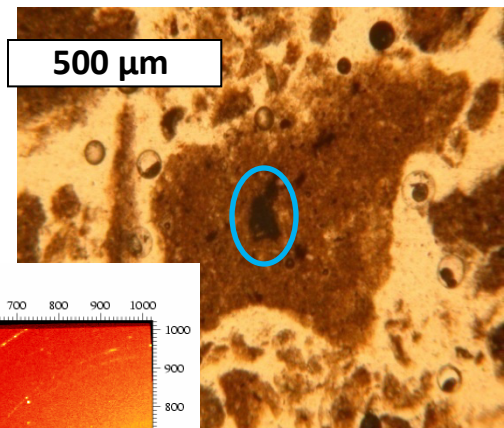
Submerged Tailings (1.5 m)



Shallow, oxygenated
environment

Roaster oxides similar to
subaerial ones

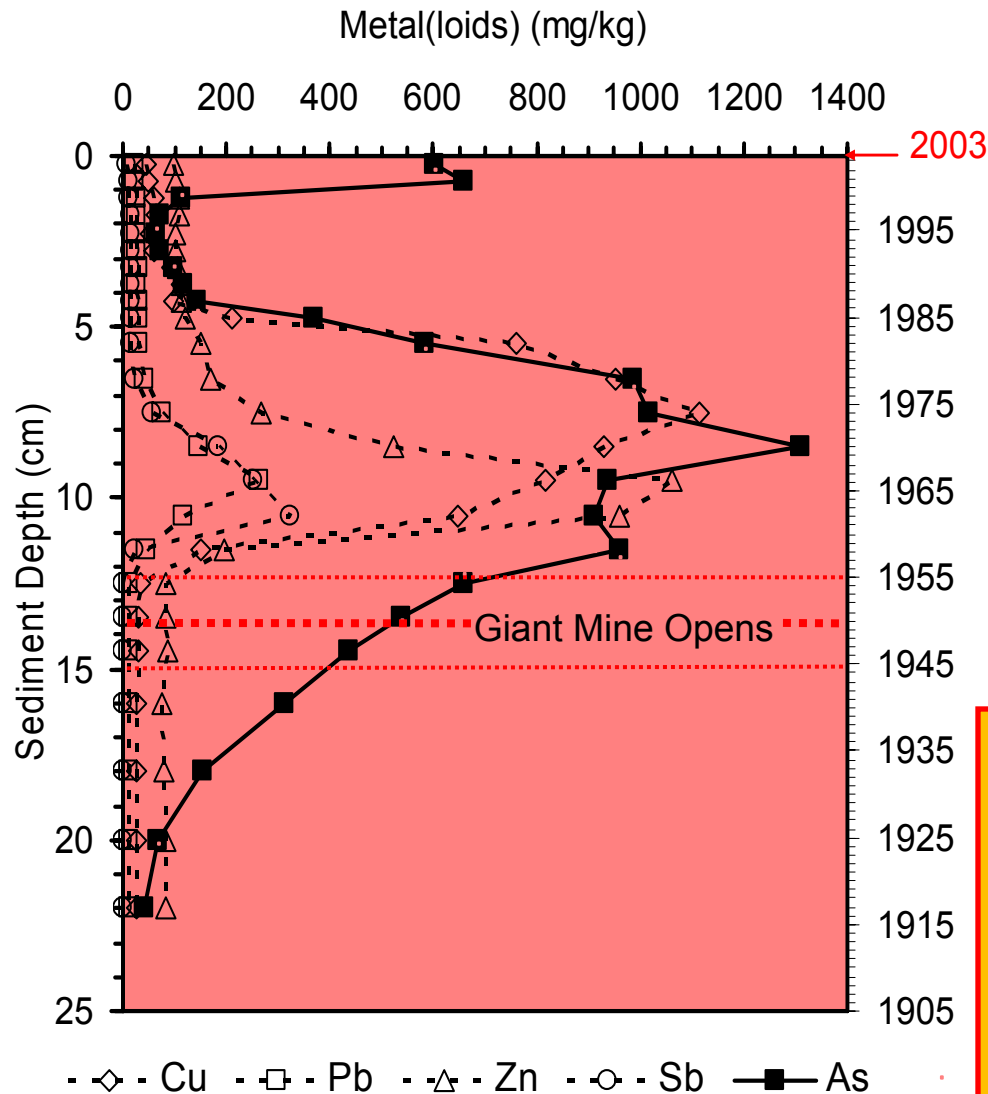
Lake Sediment (12 m)



Deeper, organic-rich
environment

Roaster oxides low in
 As^{5+} - preferentially
leached or reduced

As in Lake Sediments Summer 2003



Sediment core records release of As and metals for ~25 years of mining

Emission controls limited metal release in later years

Pore water data (not shown) shows that As is migrating upwards from mid-core enrichment

As is recaptured near surface by Fe-Mn oxyhydroxide layer

Conclusions

1. Cover not recommended for submerged tailings (As-hosting roaster oxides are stable)
2. Nutrient loading to Yellowknife Bay should be limited to preserve As-hosting Fe oxyhydroxides)

3. Can one distinguish between natural and anthropogenic arsenic in soils near Giant Mine?

~16,000 tonnes of
arsenic trioxide emitted
from roaster over region

Roaster



Shoreline outcrops



West Bay Fault

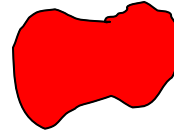


Townsite
(away from houses)

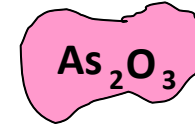


Modified from Ruby et al, 1999

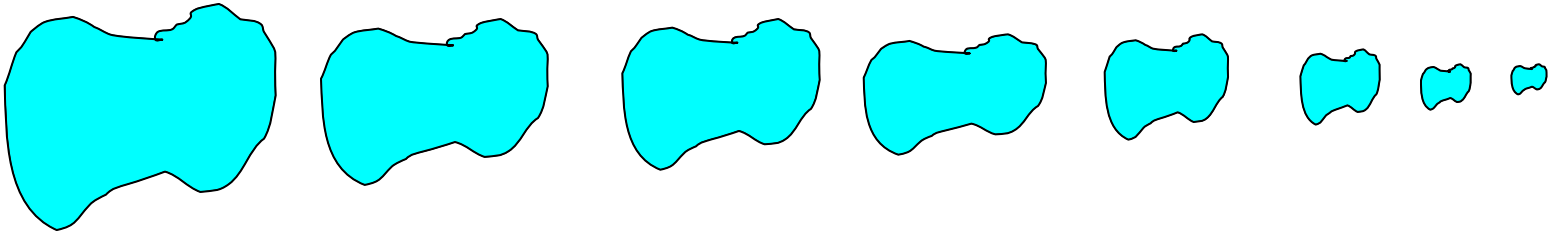
Mineral Form



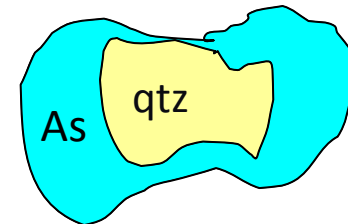
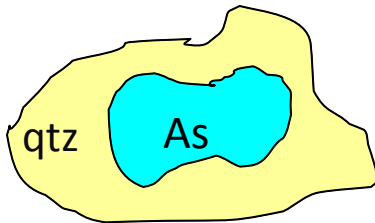
Fe-As oxides



Grain Size



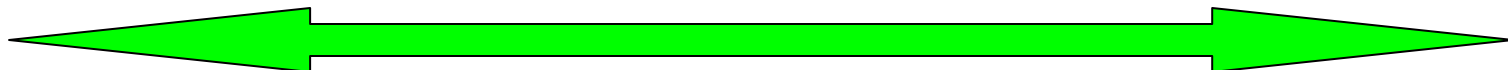
Encapsulation or Rimming of Grains



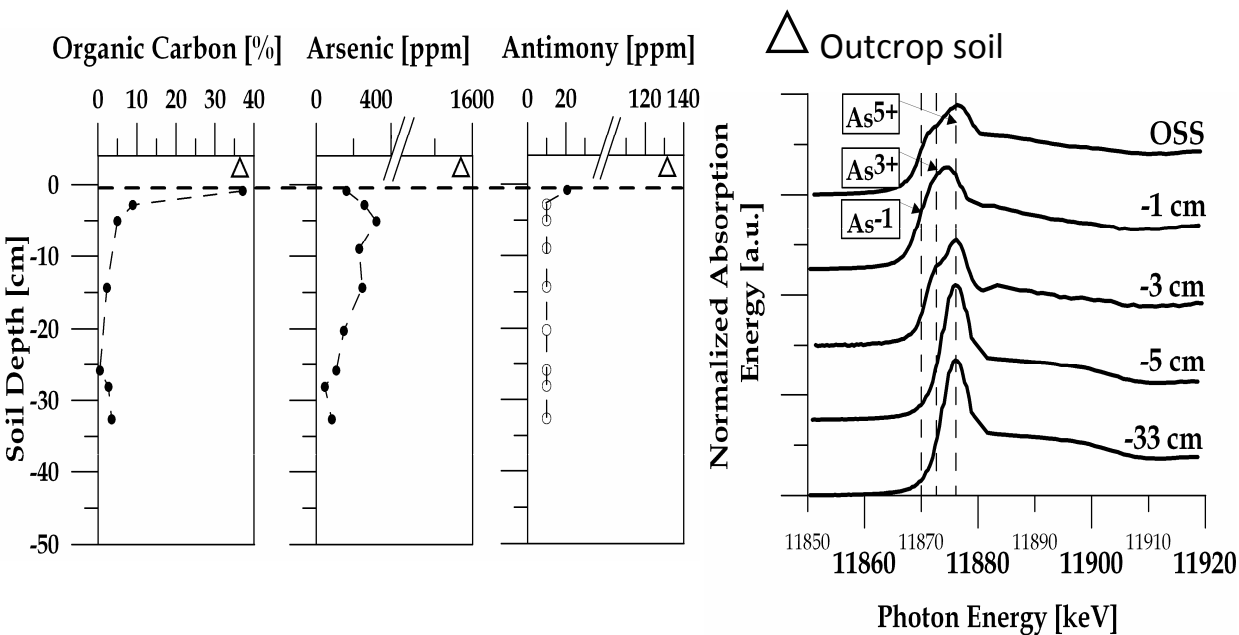
decreasing

BIOAVAILABILITY

increasing



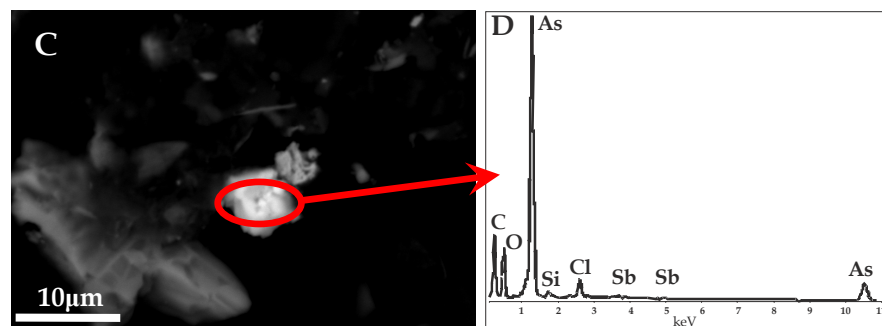
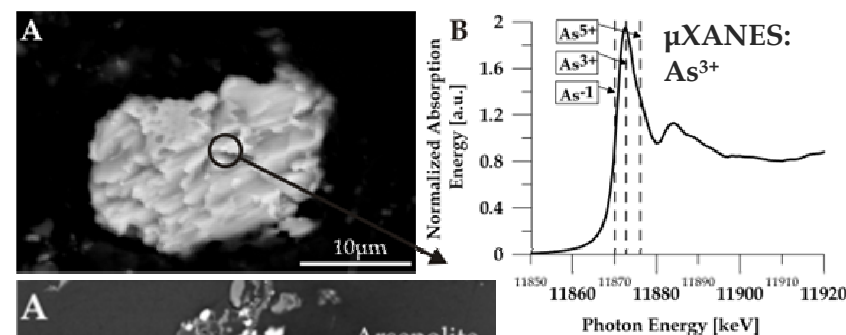
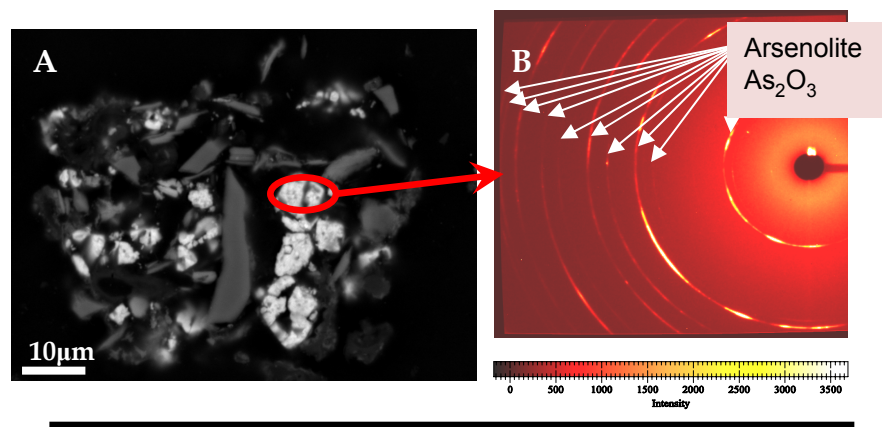
Bioaccessibility = Fraction soluble in relevant body fluids



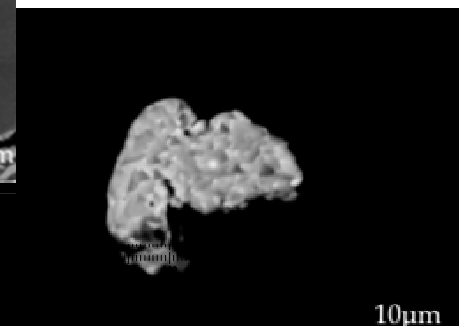
Near surface soils are enriched in:

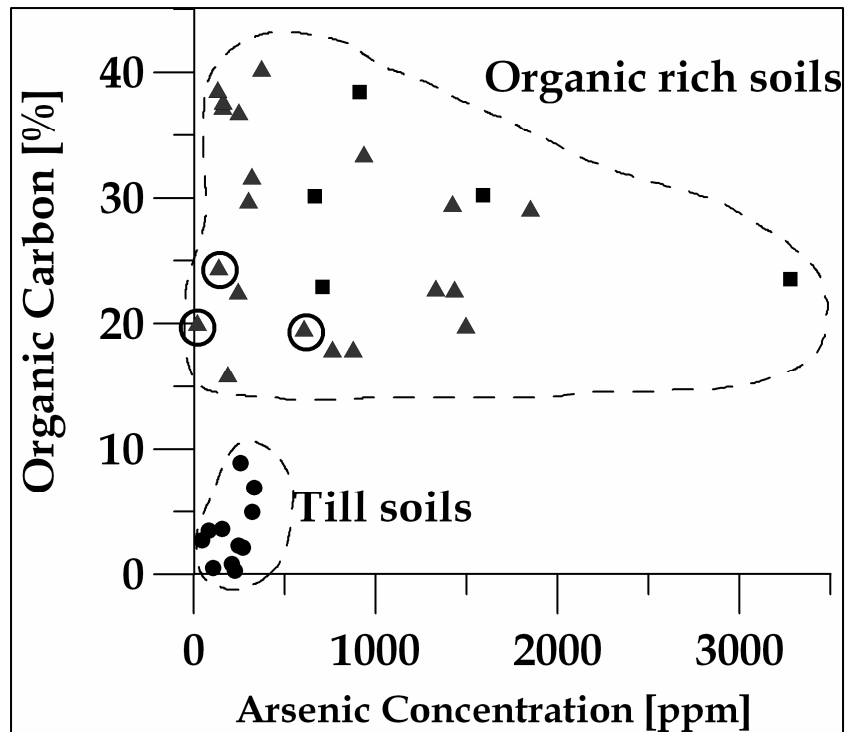
total As
Antimony
As³⁺
organic C

“Outcrop” soils are very high in As



BSE images: As-rich particles appear bright





▲ soil core ■ soil from outcrop

Canadian Soil Quality Guideline 12 ppm total As
Yellowknife Area Soil Guideline 150 ppm total As

All organic-rich soils contain arsenic trioxide particles except those circled

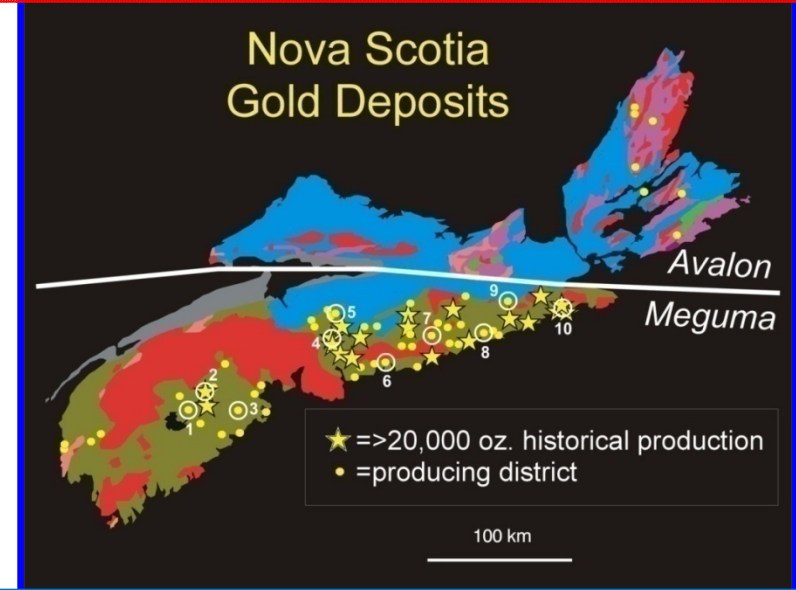
One thin section contained >145 particles of arsenic trioxide

Maghemite (roaster oxide) particles also found

Conclusions

1. As from roaster fallout can be distinguished from natural As
2. Arsenic trioxide particles may be a source of soluble As for decades
3. May represent human health risk through ingestion or inhalation in publicly accessible areas

4. What is the relationship between As mineralogy and bioaccessibility in gold mine tailings in Nova Scotia?



Many historic mine sites are publicly accessible

Some are used for recreational purposes (dirtbikes, ATVs)

As concentrations in tailings
~350 times local soil background

1000's times Soil Quality Guideline

29 samples of near-surface tailings used for mineralogy (Queen's-GSC) and bioaccessibility tests (Royal Military College)

Based on detailed petrography, electron microprobe analysis, and synchrotron-based microanalysis (particularly microXRD), As-bearing grains include:

Primary Sulfides (arsenopyrite and pyrite)

Fe arsenates (scorodite, kankite, amorphous)

As-bearing iron oxyhydroxides (goethite, akaganeite, lepidocrocite, amorphous)

Ca-Fe arsenates (yukonite, amorphous)

Tooeleite (ferric arsenite-sulfate)

Pharmacosiderite (potassium iron arsenate)

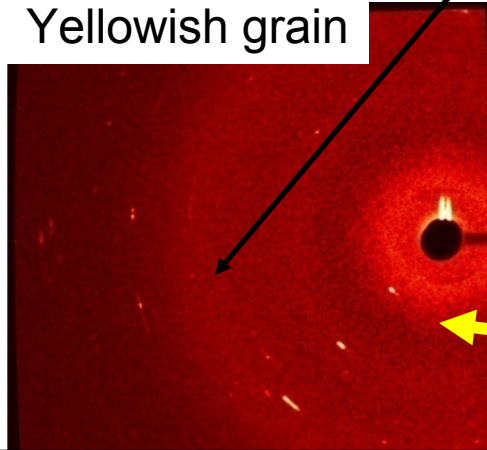
Realgar (secondary arsenic sulfide)

Roaster-generated As-bearing oxides (maghemite, hematite)

Three different Fe-arsenates (As^{5+})

Broad ring at $\sim 3 \text{ \AA}$
- “amorphous” Fe-arsenate

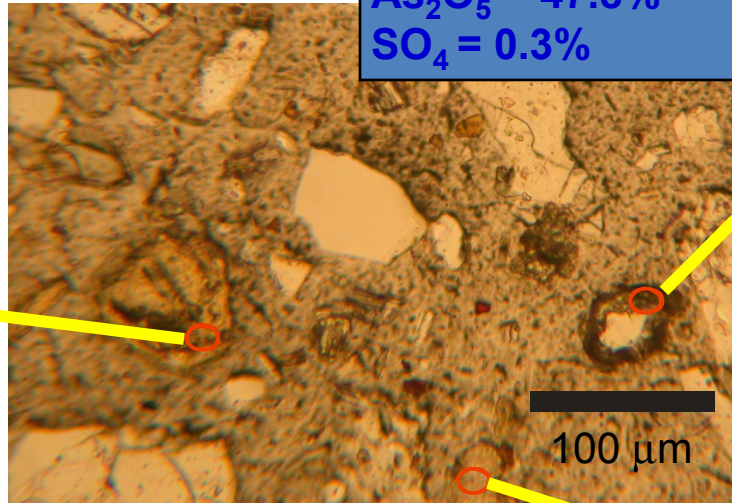
Yellowish grain



Amorphous
- short-range ordered

$\text{Fe}_2\text{O}_3 = 24.0\%$
 $\text{As}_2\text{O}_5 = 27.9\%$
 $\text{SO}_4 = 2.4\%$

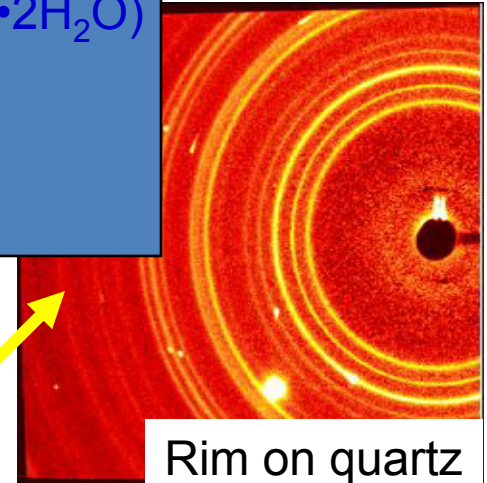
- All concentrations by EPMA



Transmitted Light

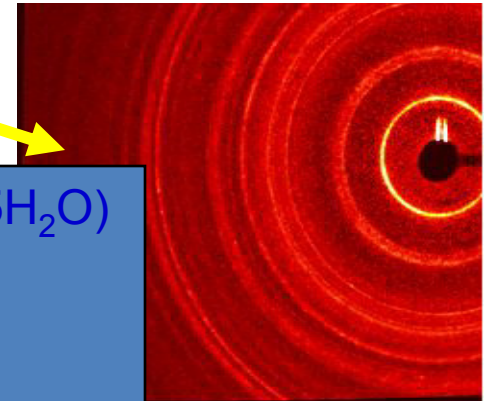
Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$)

$\text{Fe}_2\text{O}_3 = 27.5\%$
 $\text{As}_2\text{O}_5 = 47.8\%$
 $\text{SO}_4 = 0.3\%$



Rim on quartz

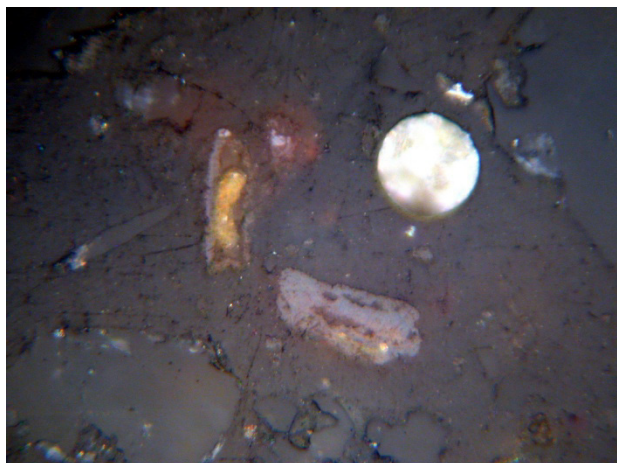
Faint yellowish grain



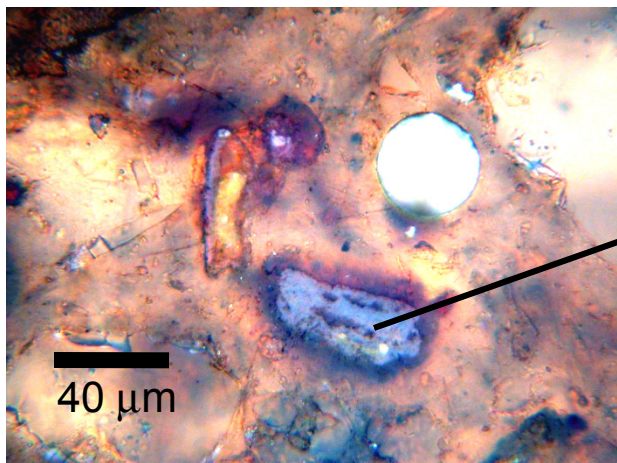
Kankite ($\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$)

$\text{Fe}_2\text{O}_3 = 30.6\%$
 $\text{As}_2\text{O}_5 = 45.5\%$
 $\text{SO}_4 = 0.3\%$

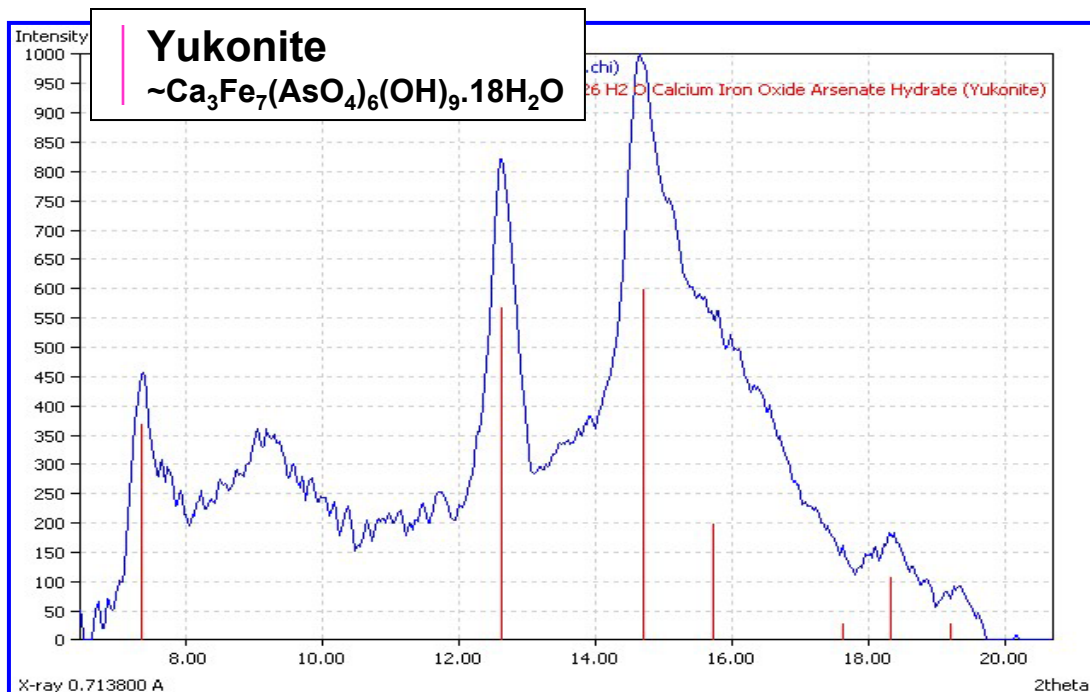
Yukonite



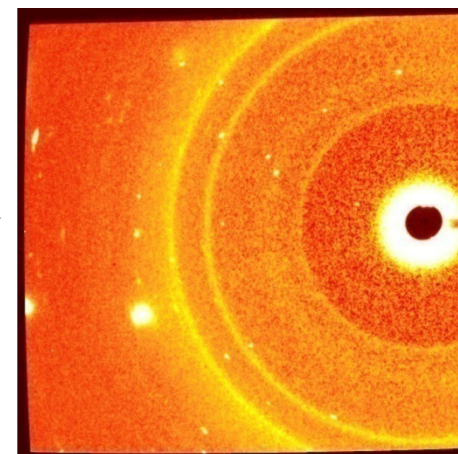
Reflected light



Transmitted and reflected light



$\text{Fe}_2\text{O}_3 = 32.7\%$
 $\text{As}_2\text{O}_5 = 35.6\%$
 $\text{SO}_4 = 0.3\%$
 $\text{CaO} = 7.4\%$



Bioaccessibility tests at RMC:

Simulated gastric (pH= 1.5) and intestinal (pH=7) fluids

Overall , arsenic bioaccessibility is low (0.3 to 48%)



Correlation between As mineralogy and bioaccessibility:

Low bioaccessibility

Arsenopyrite and scorodite

Coarsely crystalline arsenopyrite slow to react

Scorodite known to be stable in acidic environments
(pH ~2)

High bioaccessibility

Yukonite and amorphous Ca-Fe arsenates

Ca-Fe arsenates stable in pH-neutral
solution, soluble under acidic conditions

Conclusions

1. Arsenic bioaccessibility is strongly controlled by mineralogy
2. Ca-Fe arsenates are soluble in gastric fluid, scorodite is not.
3. Remediation needs to consider arsenic mineralogy

Acknowledgements

- Beamline X26a, National Synchrotron Light Source, New York
- Funding for the Yellowknife projects provided by Indian and Northern Affairs Canada, and NSERC
- Funding for the Nova Scotia project provided by the MITHE (Metals in the Human Environment) Strategic Network, NSERC and the Geological Survey of Canada
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