Workshop on the Role of Geochemical Data in Ecological and Human Health Risk Assessment
March 17-18, 2010, Halifax NS

Analytical Methods Used to Characterize the Solid-Phase Speciation of Metal(loid)s

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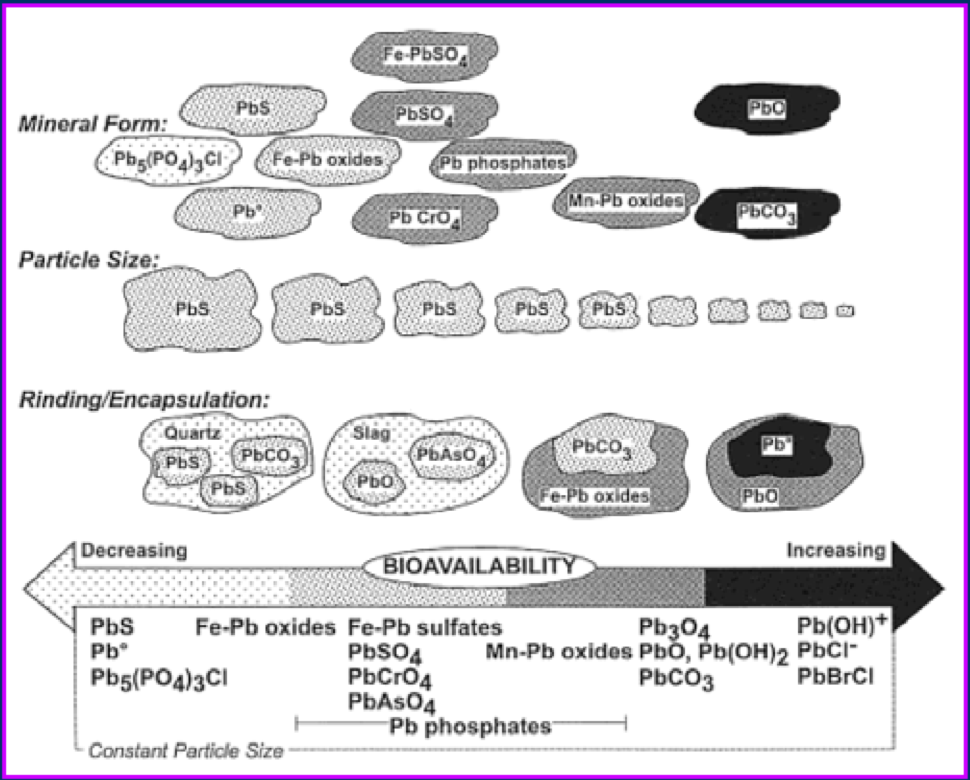
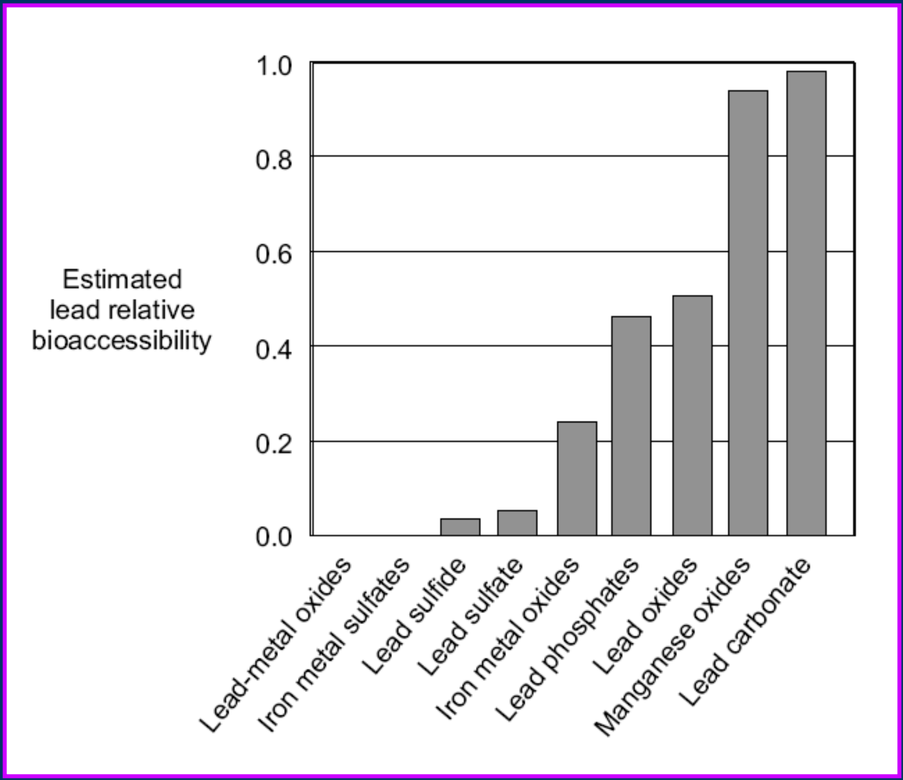
Why is Metal(loid) Speciation Important?

Solubility and bioaccessibility of Pb minerals

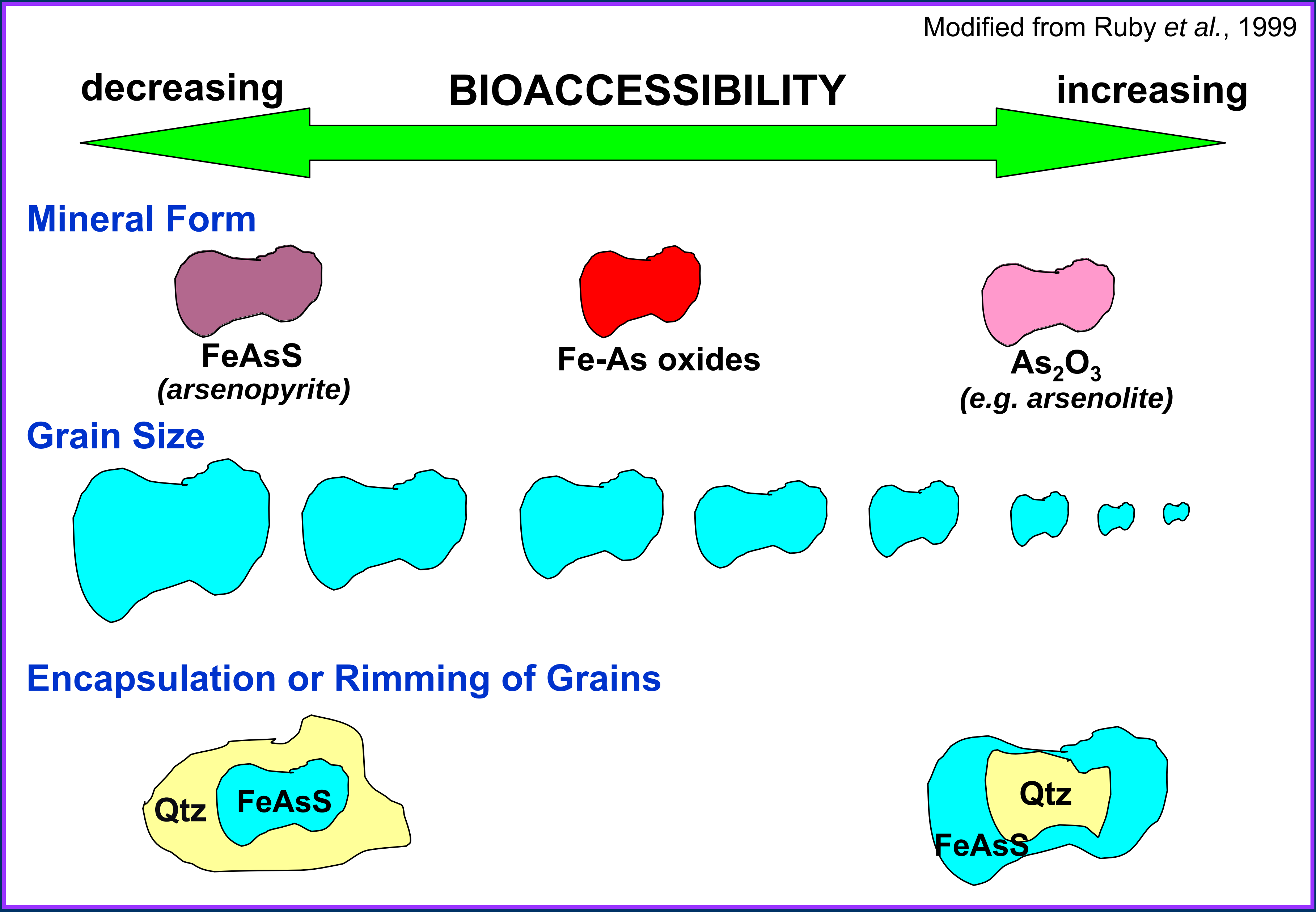


Schematic of how different lead species, particle sizes, and morphologies affect lead bioavailability (*Ruby et al. 1999*).



Relative bioavailability of Pb from soils (determined by swine uptake studies) as a function of the Pb-bearing minerals present in the soil (*Casteel et al. 2006*).

Nature of As-hosting phase affects the risk of As exposure

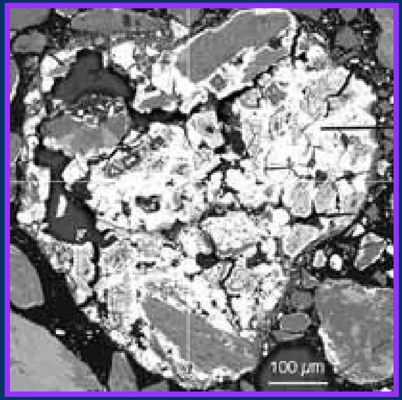


Characterization of Mineral Hosts for As

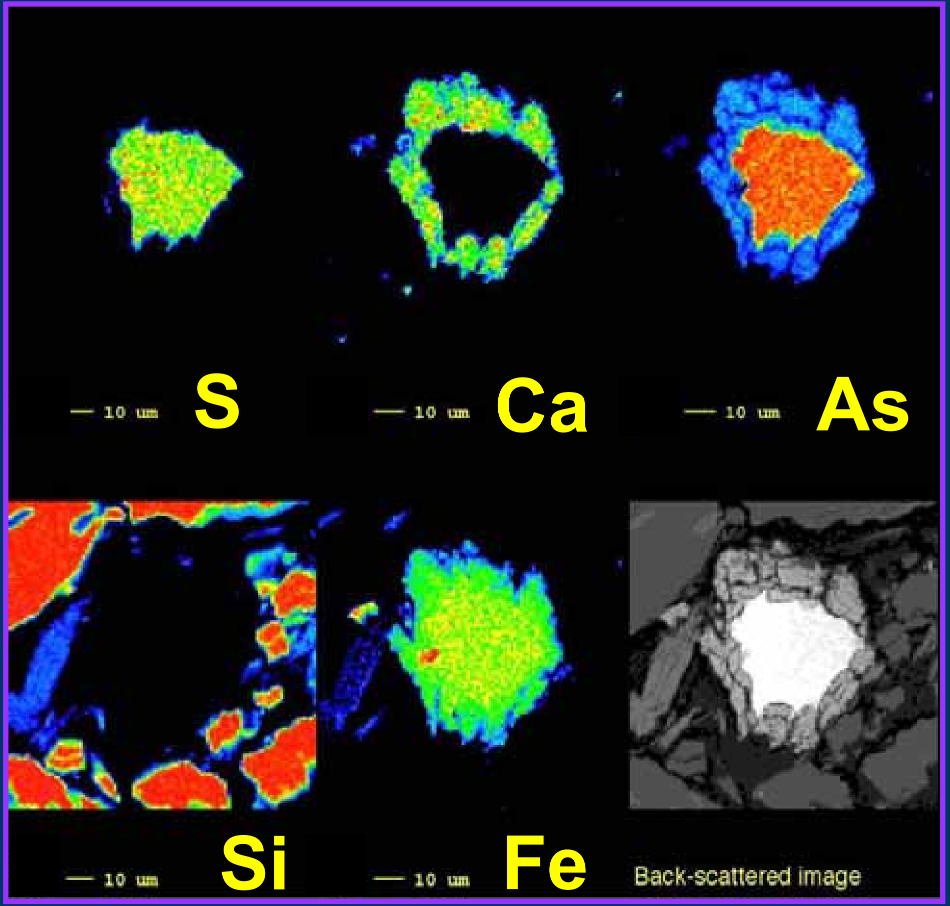
Arsenopyrite (FeAsS)

Crystalline scorodite ($FeAsO_4 \cdot 2H_2O$)

Amorphous Fe arsenate cement

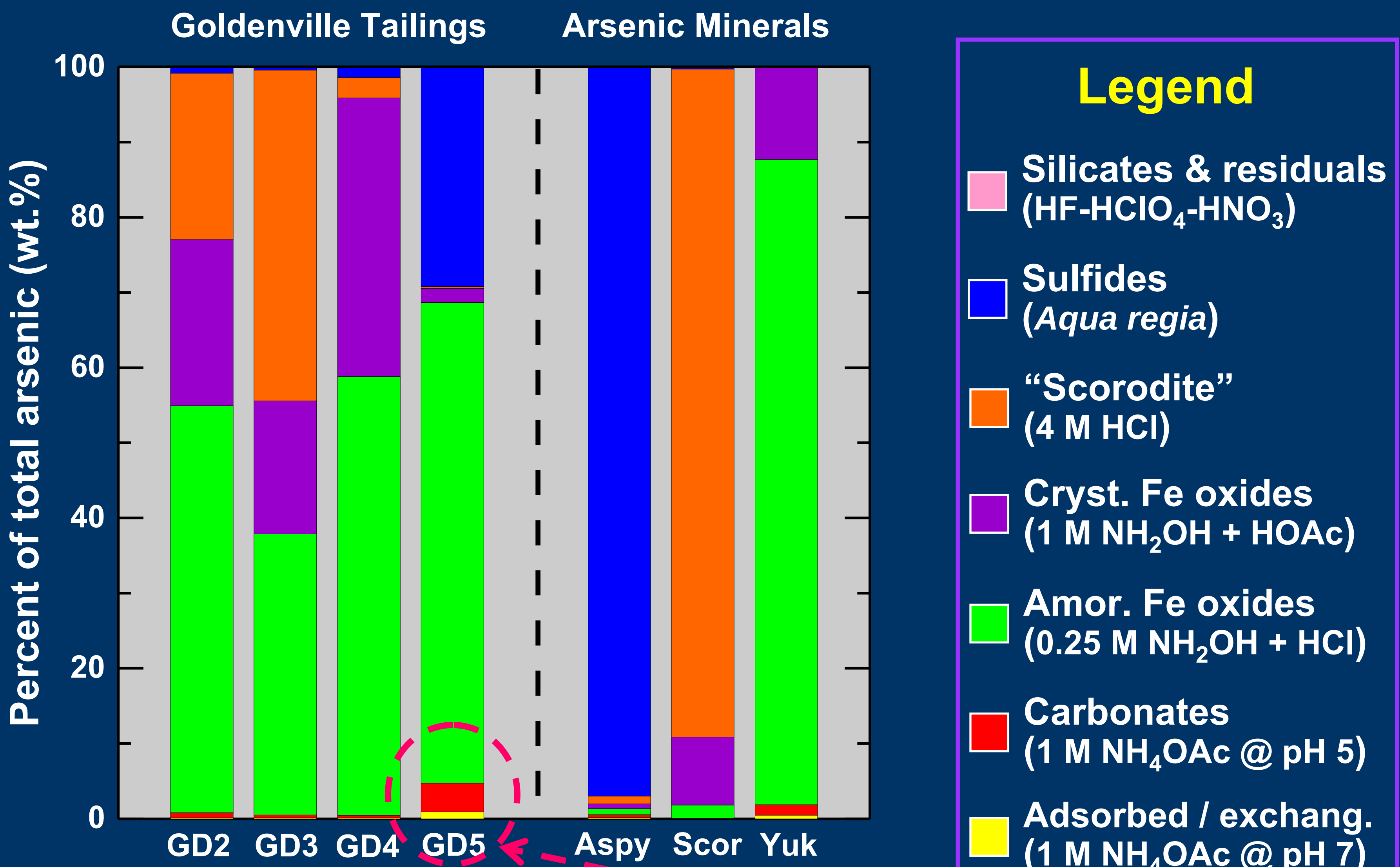


Compositional maps from electron microprobe



As-Ca bearing Fe oxyhydroxide reaction rim on arsenopyrite

Bulk Speciation Methods: Sequential Chemical Extraction



Mineralogy Results

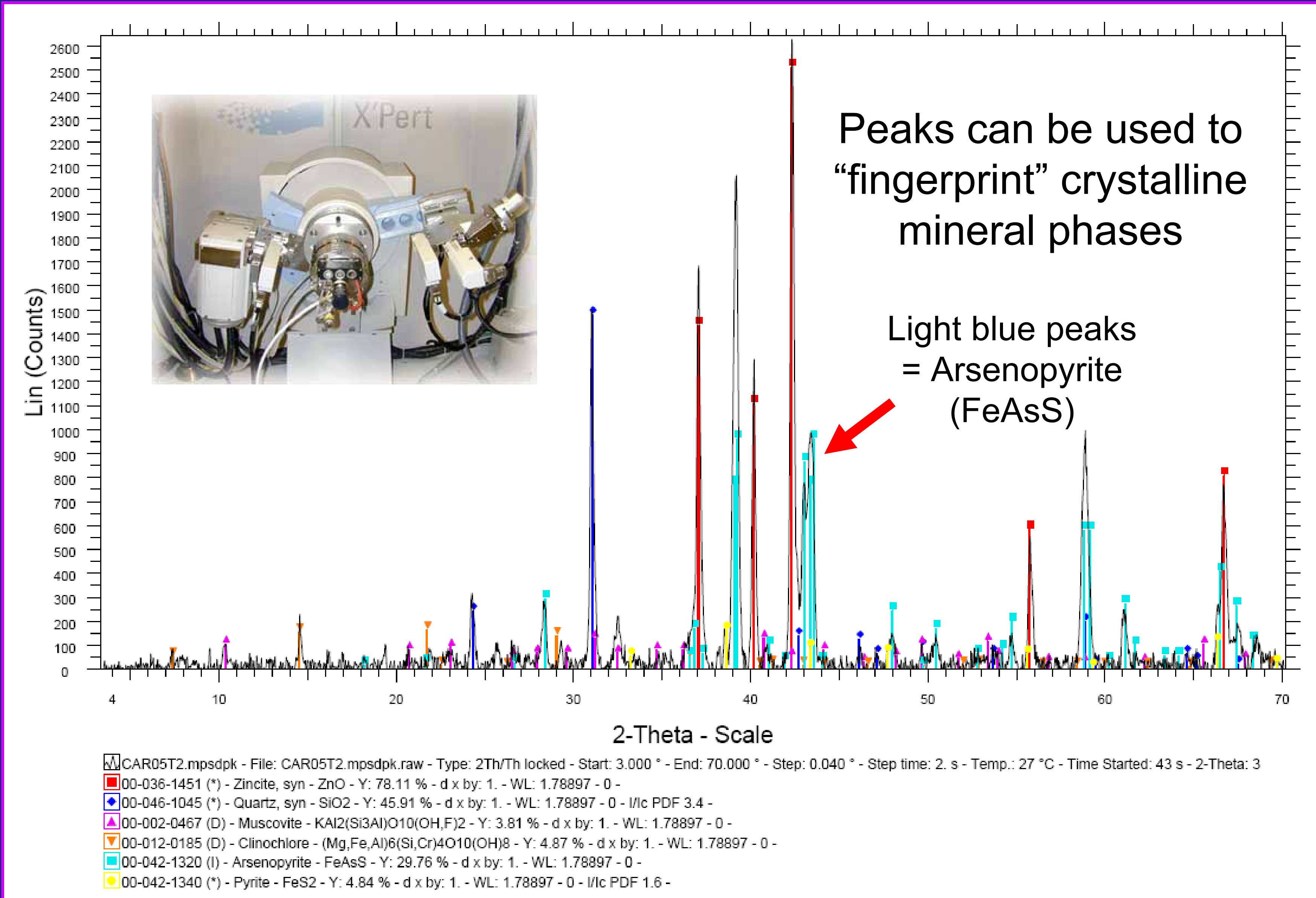
GD2: Scor ≈ Amor. Fe arsenate > Amor. Fe oxide

GD3: Scor ≈ Amor. Fe arsenate

GD4: Amor. Fe arsenate > As-bearing Fe oxides

GD5: Aspy ≈ Yukonite ≈ Amor. Fe oxide

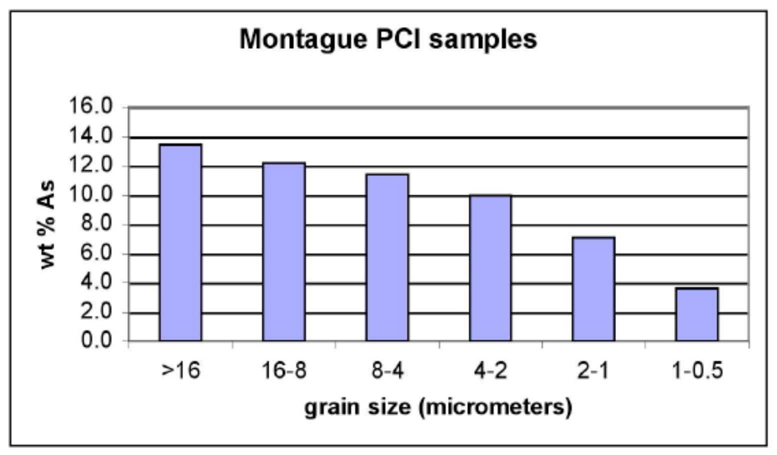
Bulk Speciation Methods: X-ray Diffraction

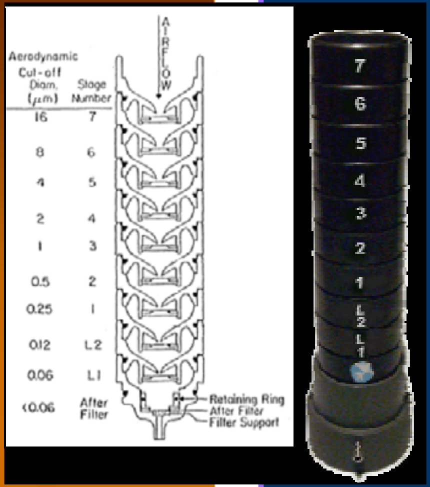


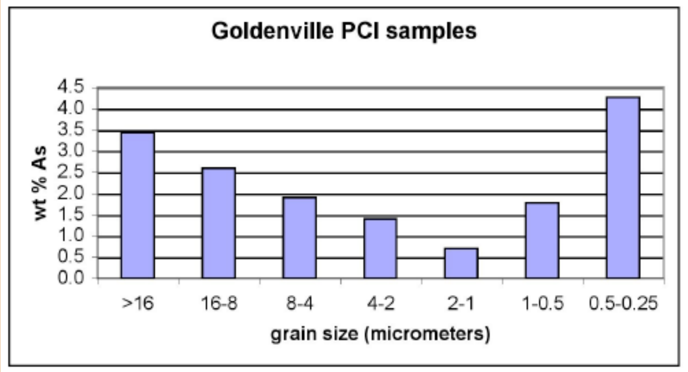
X-ray diffractogram of arsenopyrite-bearing tailings, Caribou Gold District, NS

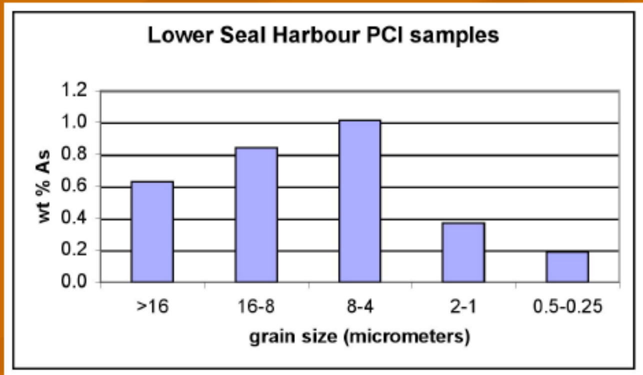
Microbeam Methods: Proton-Induced X-ray Emission

PIXE results





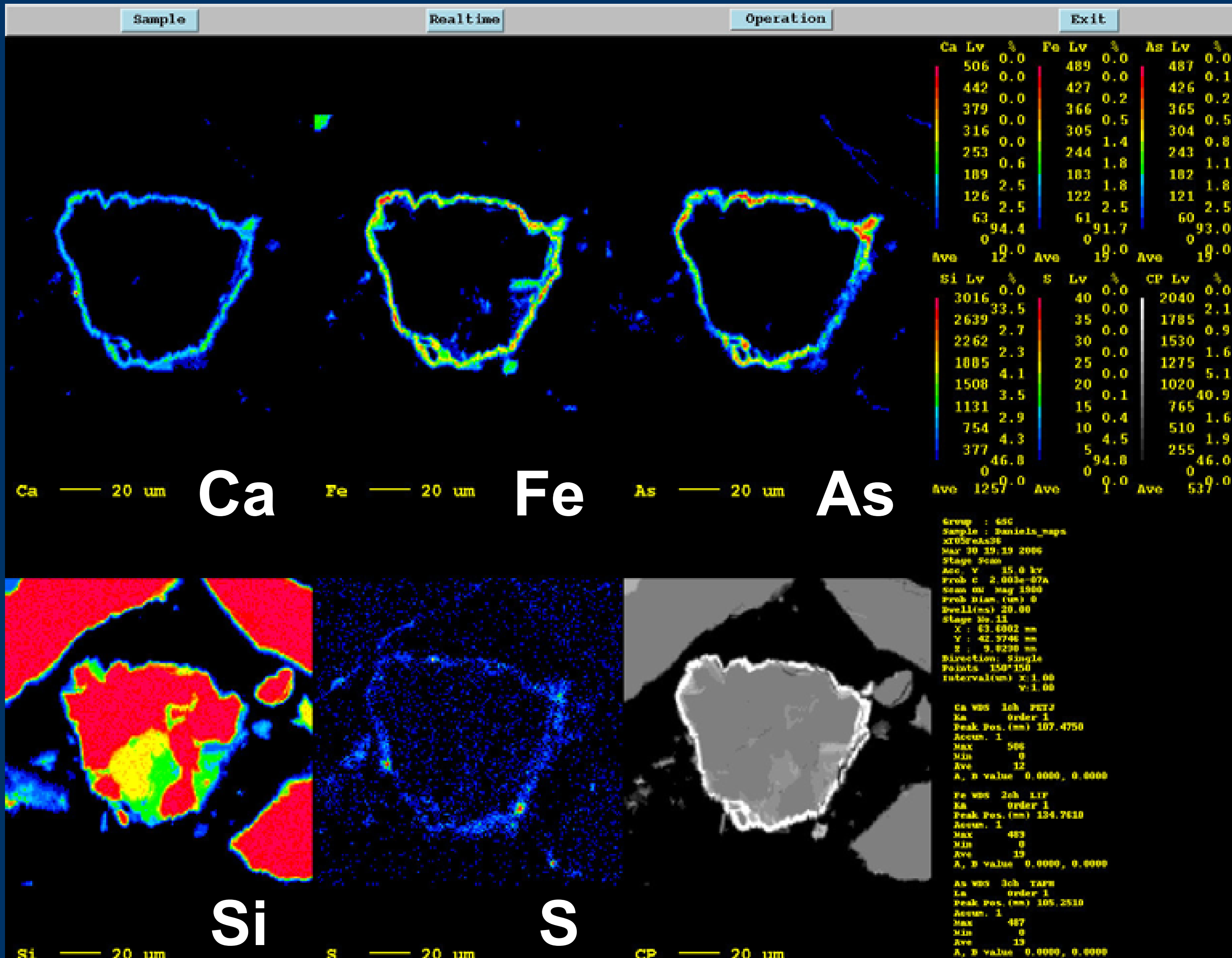




from Corriveau et al. (2010)

Arsenic Content of Airborne Particulates

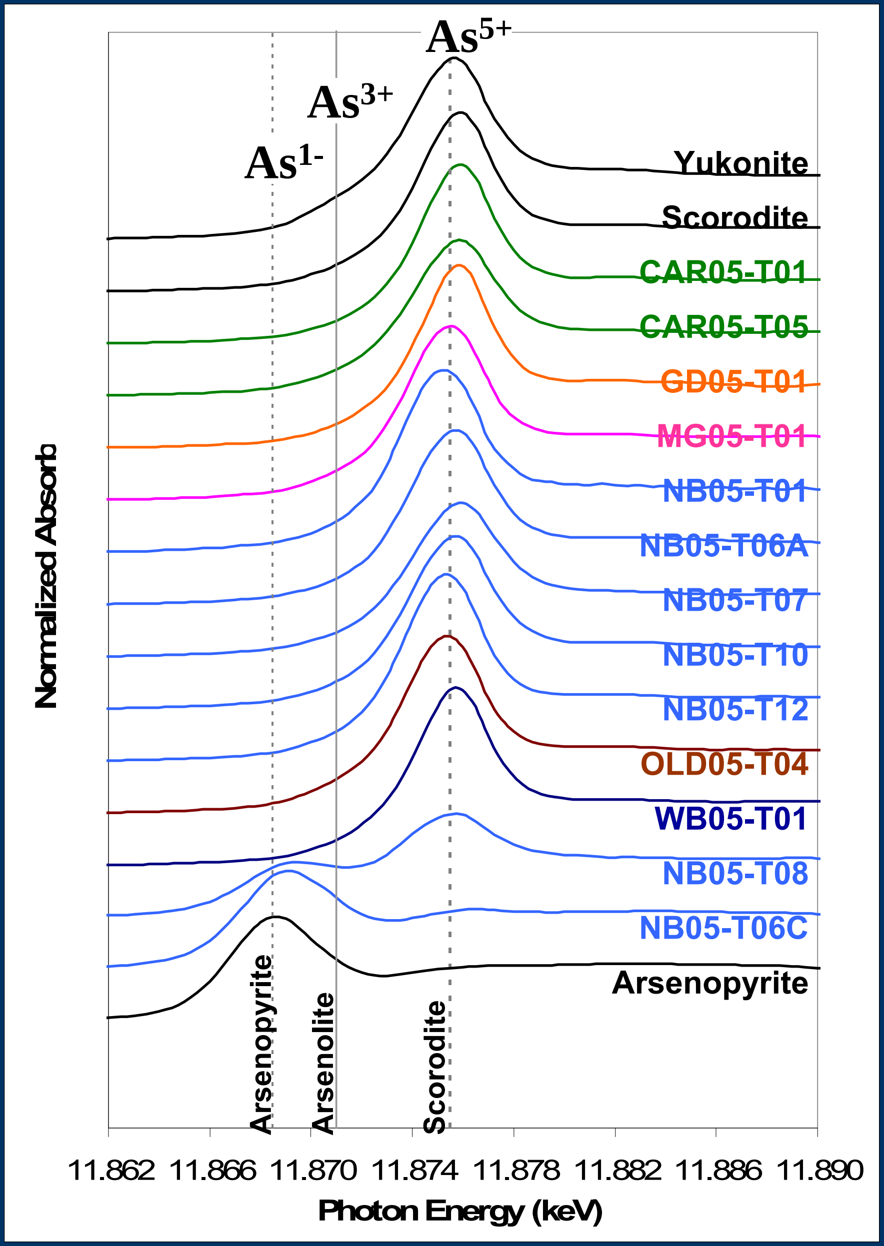
Microbeam Methods: Electron Microprobe Analyses



Ca-Fe-As rim on silicate mineral

Synchrotron Methods

Bulk XANES (X-ray Absorption Near-Edge Structure)



From Meunier et al. (2010)

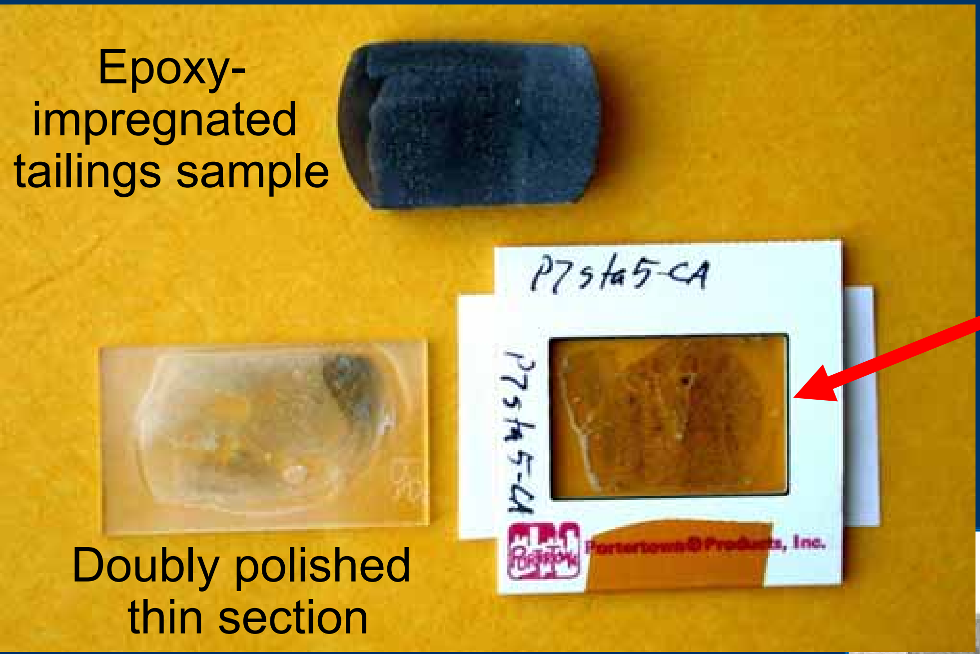
XANES spectra of most gold mine tailings samples analyzed are similar to scorodite (As^{5+})

North Brookfield sample NB05-T08 contains a mixture of arsenopyrite (As^{1-}) and As^{5+}

North Brookfield sample NB05-T06C spectra is similar to that of arsenopyrite

Detached Thin Section Preparation & Location of Targets for EMPA and synchrotron microanalysis

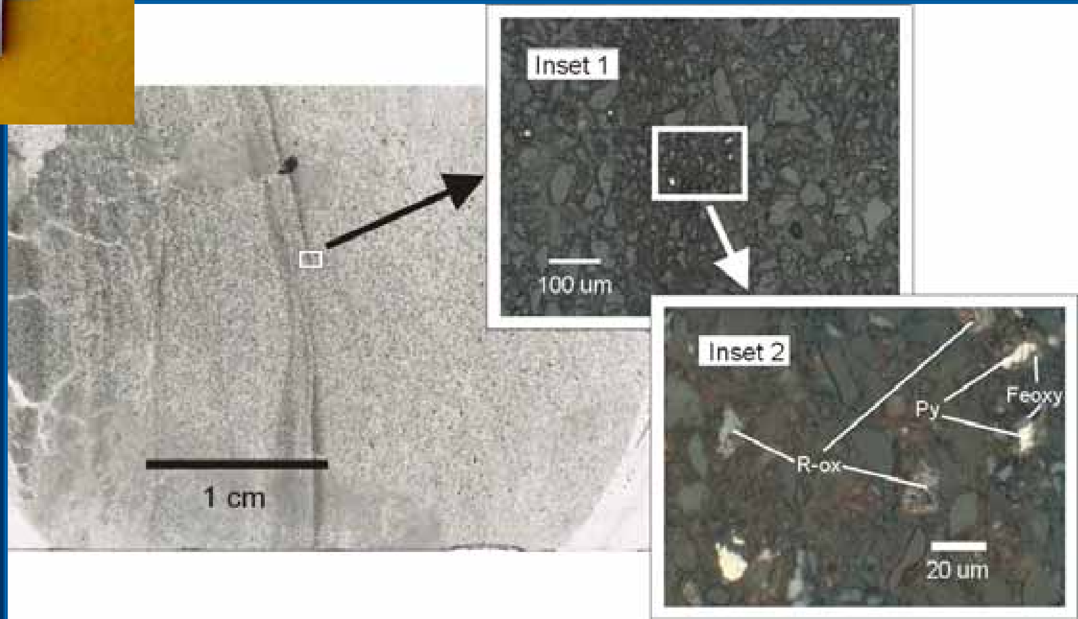
(Slide from Stephen Walker, Queen's University)



Thin-section lifted from slide & mounted on kapton tape- necessary for microXRD

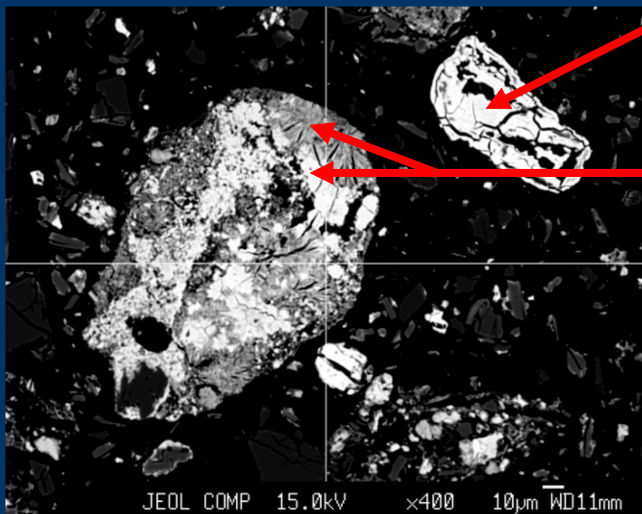
Targets selected petrographically & photographed

Other targets located using element mapping



Combining petrography, electron microprobe (EPMA), micro-synchrotron methods

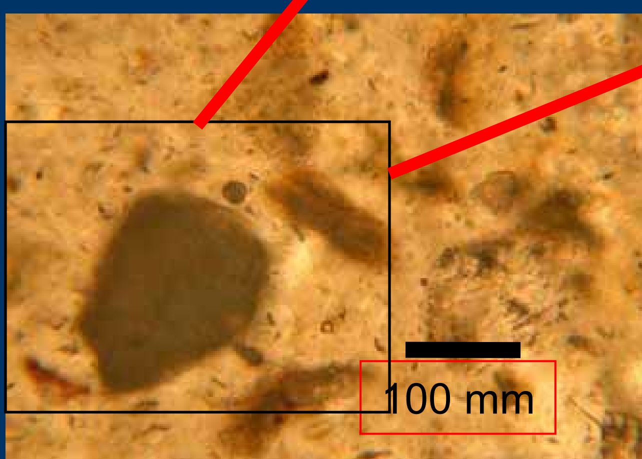
(Slide from Stephen Walker, Queen's University)



Fe/As (molar) = 1.2 (EPMA)

Fe/As (molar) = 0.9 to 1.0 (EPMA)

BSE image



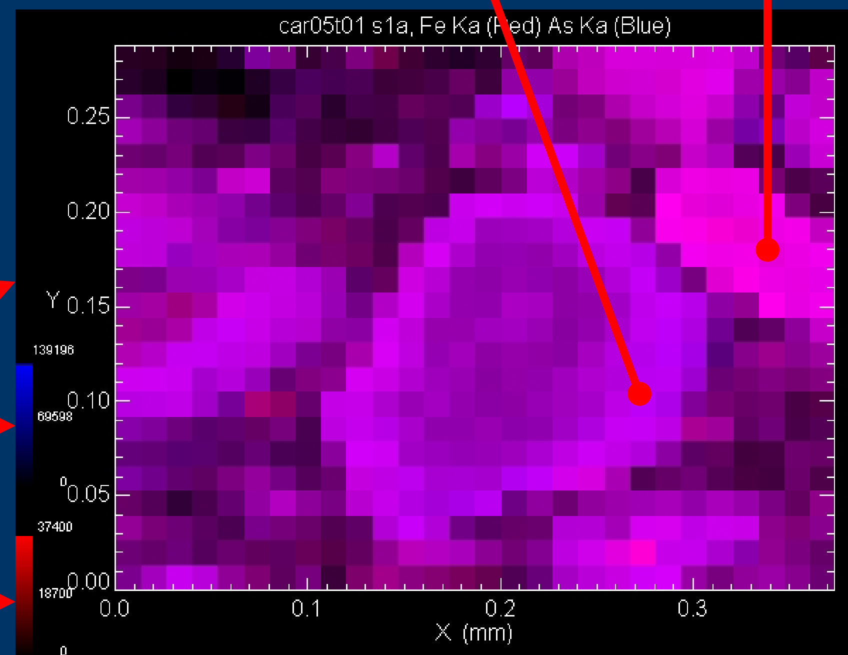
Transmitted and reflected light (20x objective)

Mixture of 2 different 1As:1Fe arsenates

Amorphous

As (Blue)

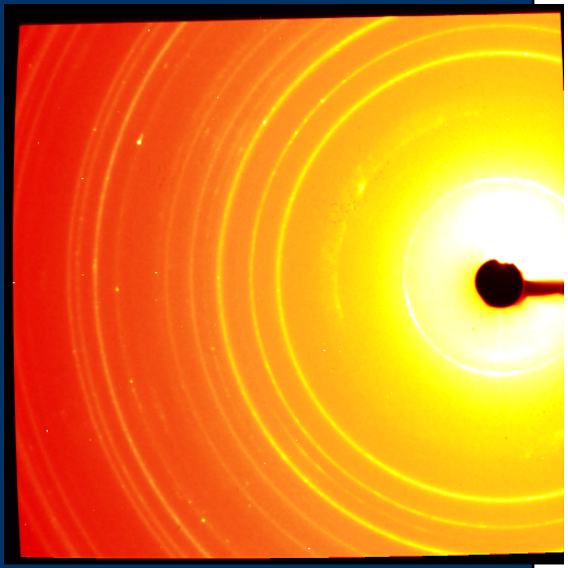
Fe (Red)



μ-XRF map with μ-XRD targets and identities

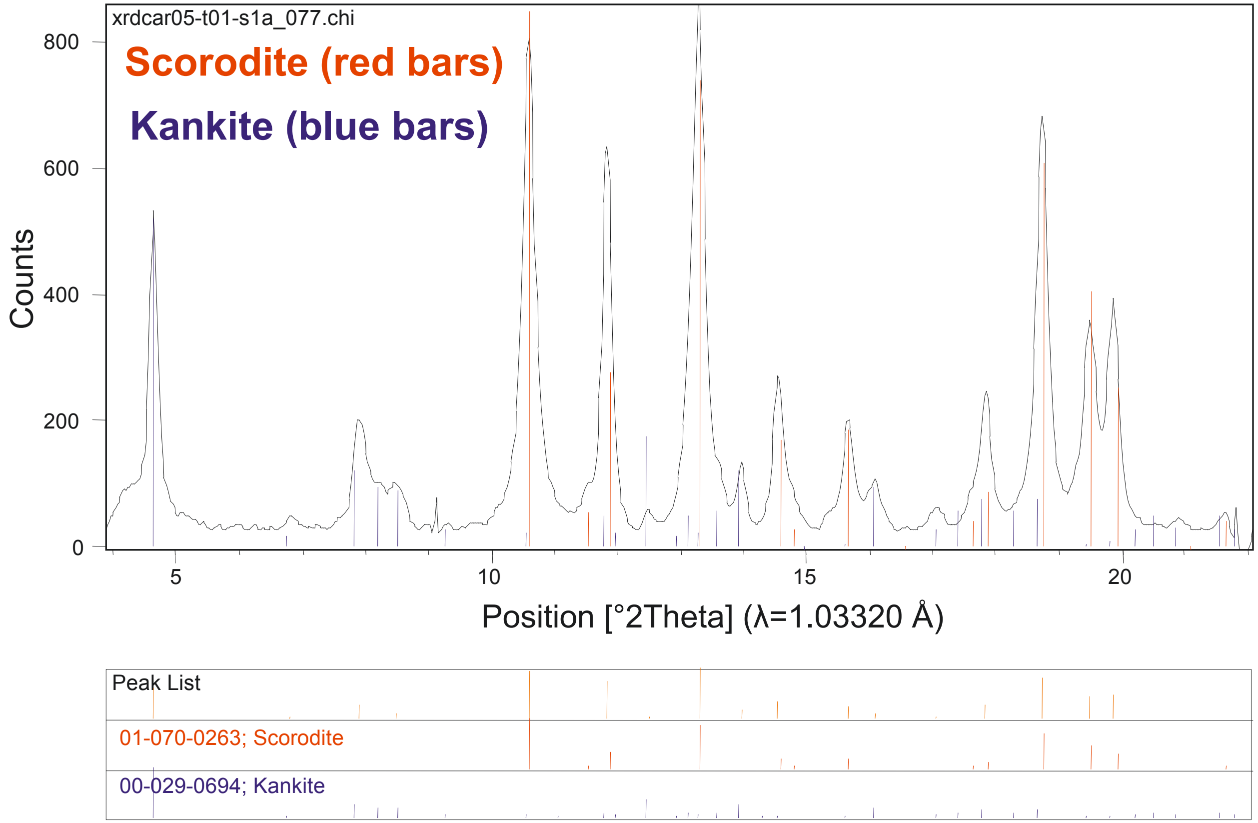
Micro XRD (~10 μm) on larger grain identifies two microcrystalline Fe arsenate minerals

(Slide from Stephen Walker, Queen's University)



Mixture of:
Scorodite ($FeAsO_4 \cdot 2H_2O$)
Kankite ($FeAsO_4 \cdot 3.5H_2O$)

Simulated "powder" pattern (integration of 2-D pattern)

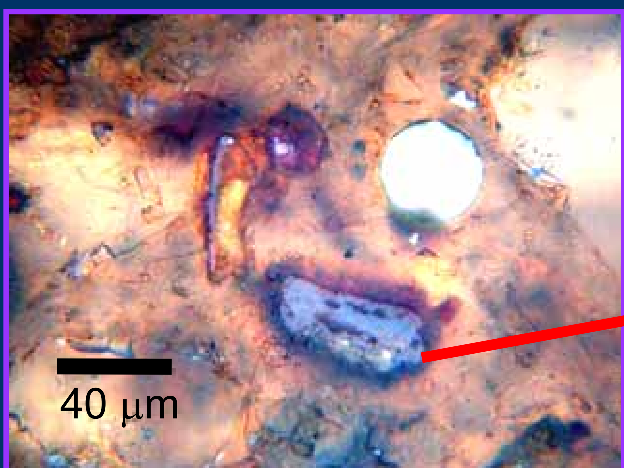


Yukonite: an Ca-Fe arsenate mineral

(Slide from Stephen Walker, Queen's University)

Photomicrographs

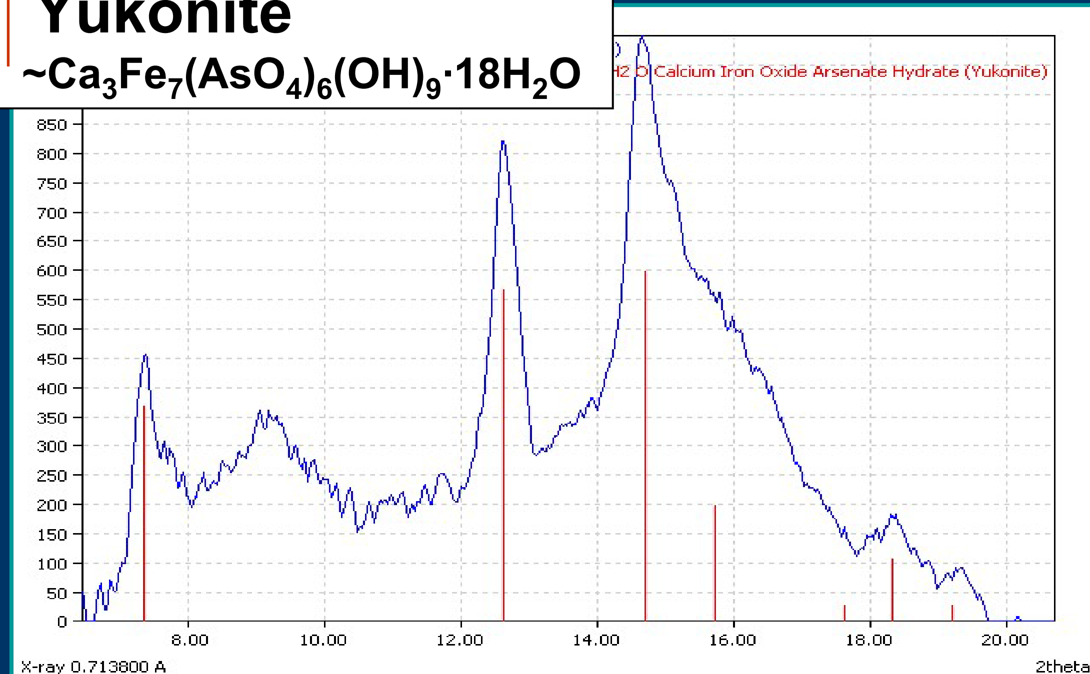
Reflected light



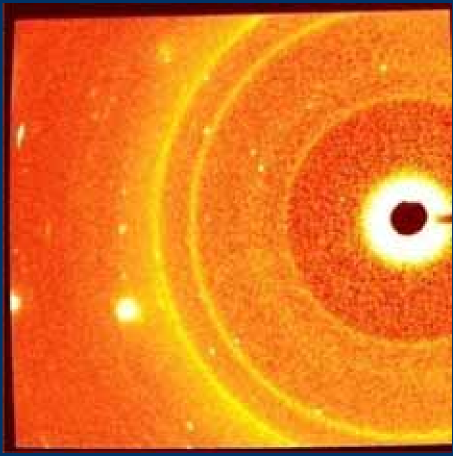
Transmitted and reflected light

Yukonite

~$Ca_3Fe_7(AsO_4)_6(OH)_9{\cdot}18H_2O$



Fe_2O_3 = 32.7%
As_2O_5 = 35.6%
SO_4 = 0.3%
CaO = 7.4%

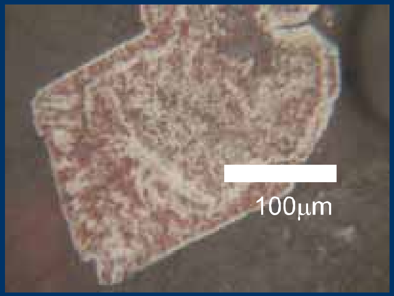


μ-XRD pattern

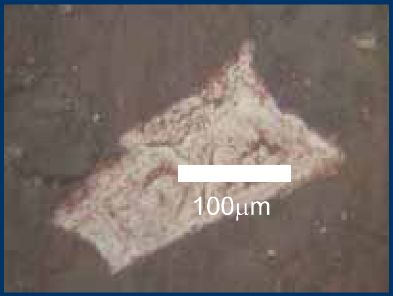
Tailings from historical roasting of gold-ore
North Brookfield Gold District
(*Slide from Stephen Walker, Queen's University*)

μ-XANES data

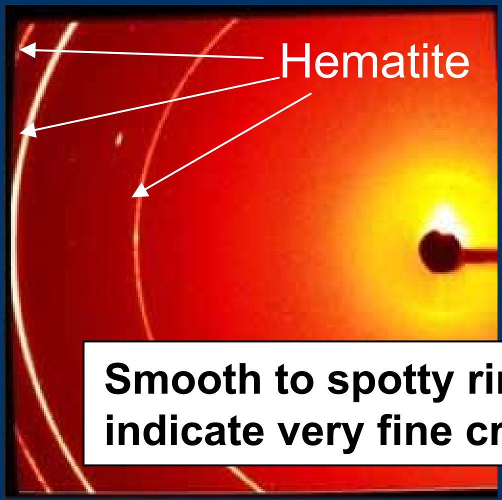
Abundant roaster derived As-bearing Fe-oxide (hematite α-Fe_2O_3 or maghemite γ-Fe_2O_3) in some samples



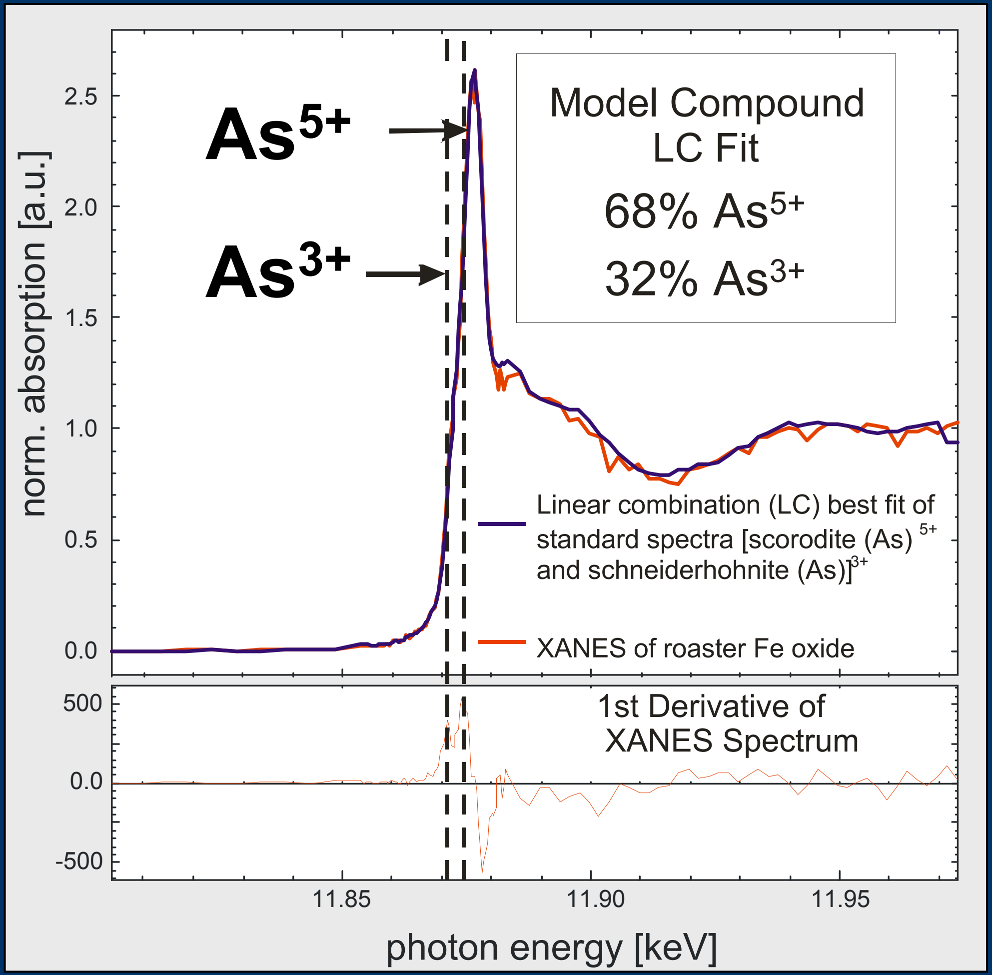
Reflected Light



Reflected Light



Smooth to spotty rings indicate very fine crystallinity



Typically these roaster Fe-oxides contain <2 % As

Key Points

- Metal(loid)s in soils, sediments, and mine wastes can be hosted in a wide range of primary and secondary phases.
- These phases have varying solubilities that strongly influence the environmental fate and bioaccessibility of metal(loid)s.
- The total concentrations of metal(loid)s in solid samples does not give sufficient information on the environmental availability of these elements, or their potential risks to human health.
- In the future, ecological and human health risk assessments should incorporate information on the solid-phase speciation of metal(loid)s to ensure that realistic management guidelines are established.

References

- Ruby, M.V., Schoof, W.B., Brattin, W., Goldade,M., Post, G., Harnois, M., Mosby, D.E., Casteel, S.W., Berti, W., Carpenter, M., Edwards, D., Cragin, D., and Chappell, W., 1999. Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment; Environmental Science and Technology, v. 33 (21), p. 3697–3705.
- Casteel, S.W., Weis, C.P., Henningsen, G.M., and Brattin, W.J., 2006. Estimation of relative bioavailability of lead in soil and soil-like materials using young swine; Environmental Health Perspectives, v. 114, p. 1162-1171.
- Corriveau, M.E., Jamieson, H.E., Parsons, M.B., Campbell, J.L., and Lanzirotti, A. 2010. Direct characterization of airborne particles associated with arsenic-rich mine tailings: Particle size, mineralogy and texture; Submitted to Applied Geochemistry.
- Meunier, L., Walker, S.R., Wragg, J., Parsons, M.B., Koch, I., Jamieson, H.E., Reimer, K.J. (2010) Effects of soil composition and mineralogy on the bioaccessibility of arsenic from tailings and soil in gold mine districts of Nova Scotia; Environmental Science and Technology, DOI: 10.1021/es9035682.