D.5 Arsenic Remobilization: Geochemical Controls, Case Histories and Prediction

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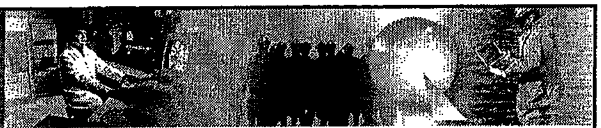

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Geochemical Controls

- **Solubility of secondary & Tertiary arsenates**
- **As(V)-As(III) conversion in the "geochemical rubber band"**
- **Schurmann's solubility series**
- **Galvanic interaction**
- **Carbonation reactions**

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Solubility of Some Arsenates

Metal Arsenate	$Log_{10}Ksp$	Moles/Litre
$Ca_3(AsO_4)_2$	-18.2	8.98×10^{-5}
$Ba_3(AsO_4)_2$	-50.1	3.74×10^{-11}
$Zn_3(AsO_4)_2$	-27.9	1.03×10^{-6}
$FeAsO_4$	-20.2	7.94×10^{-11}
$Co_3(AsO_4)_2$	-28.1	9.40×10^{-7}
$Ni_3(AsO_4)_2$	-25.5	3.11×10^{-6}
$Cu_3(AsO_4)_2$	-35.1	3.74×10^{-8}
$AlAsO_4$	-15.8	1.26×10^{-8}

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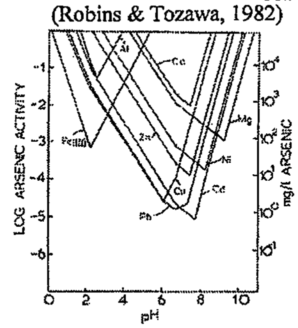
Stability of Arsenates in Water, $P_{CO2} = 10^{-3.52}$ ats (Robins & Tozawa, 1982)



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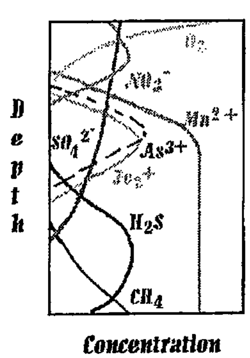

Aerobic Oxidation

Denitrification

Fe + Mn Oxyhydroxide Reduction

Sulfate Reduction

Methanogenesis

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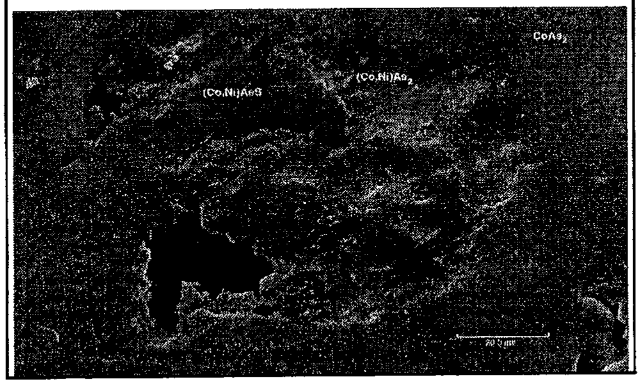
Sulfide Stability Sequence (Schurmann, 1888)

Ion affinity for S	Metal	Sulfide Solubility
High	Palladium	Low
	Mercury	
	Silver	
	Copper	
	Bismuth	
	Cadmium	
	Antimony	
	Tin	
	Lead	
	Zinc	
	Nickel	
	Cobalt	
	Iron	
	Arsenic	
	Thallium	
Low	Manganese	High

Preferential weathering of Ni-rich safflorite through galvanic interaction



Arseno-Carbonate Complexes

- Kim et al. (2000) found that As release from the Marshall sandstone varied directly with the bicarbonate concentration
- Carbonation of As_2S_3 and As_2S_2 is an important leaching process under anaerobic conditions
- $As(CO_3)_2^-$, $As(CO_3)(OH)_2^-$ and $AsCO_3^+$ are stable in groundwater

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Case Histories

- Mount Washington, Vancouver Island, B.C.
  - As mobilization and ARD
- High-grade uranium mines, northern Saskatchewan
  - As levels in basic tailings porewaters
- Former Cobalt Mining Camp, Ontario
  - As mobilization and attenuation in near-neutral drainage

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Some As-Related Observations at Mt. Washington

- As-minerals include arsenopyrite, scorodite, realgar, amorphous Cu-AsO_4 compound in green stream
- Low As levels (<0.1 - 0.5 mg/L) in both surface and ground waters
- Green stream in South Pit with neutral toslightly basic pH has higher dissolved As than most acidic drainage in North Pit
- Pyrrhotite Lake (pH 4.6-4.9) gave <0.06 mg/L As but sediment contained up to 2310 ppm As (1997 data)

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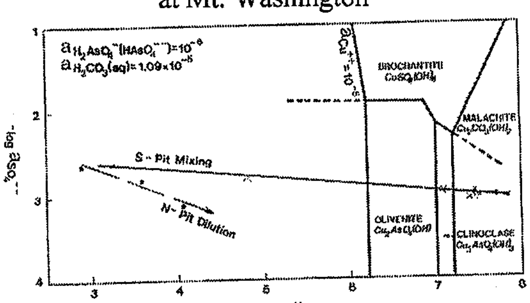
Mineralogical Controls of Cu/As Mobilization at Mt. Washington



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Factors Controlling As Mobility at Mt. Washington

- High sorption affinity of ferrihydrite for As, ~1 mole As / mole Fe (Pierce and Moore, 1982)
- Stability of trace metal arsenates at slightly basic pH conditions
- (Thus no As remobilization observed when lime was added to Pyrrhotite Lake sediment to bring leachate pH to near-neutral values in a batch test)

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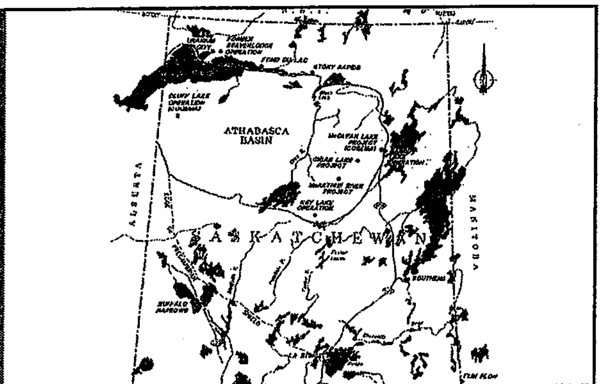

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Arsenic Issue with Uranium Mining in Saskatchewan

- Many high-grade deposits (e.g., Key Lake, Rabbit Lake, Collins Bay, McClean Lake and Midwest) also host arsenide mineralization
- Proposed control of tailings porewater As at 1 mg/L for the McClean Lake Operation has received much scrutiny
- In situ porewater As analysis at Rabbit Lake gave 6-132 (1993/4) and 0.06-85 (1997) mg/L, at Key Lake, 3.5-29 mg/L
- Reverse osmosis is relied upon to bring As level to acceptable levels prior to discharge

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Rabbit Lake In-Pit Tailings Facility

(with chemical data from Moldovanet al., 2000)

- 425 x 300 x 98 m^3; 15 years history; 4.6M tonnes to Sept. 1999
- Tailings composed of residues from ore leach process and precipitates from acid neutralization (88% As in arsenates, 12% in arsenides/sulfides)
- Porewater analyses
  - pH: 8.4 - 11.1; Eh: -64 - 268 mV; T= 0 - 6.5°C
  - As: 0.2 - 140 mg/L with 11% in trivalent state; highest value measured at a depth of 59 m

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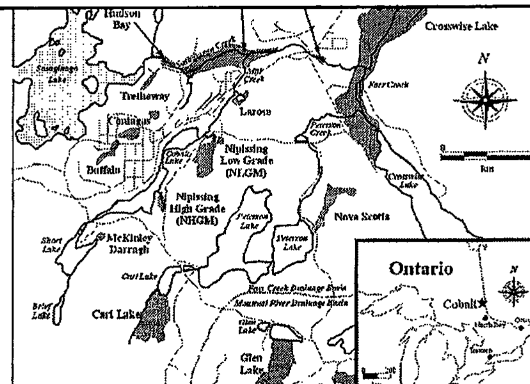

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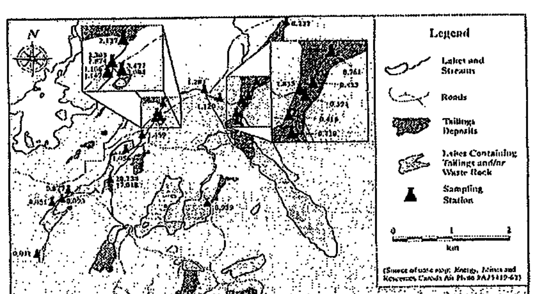
Total Arsenic Concentrations (ppm), Summer, 1994



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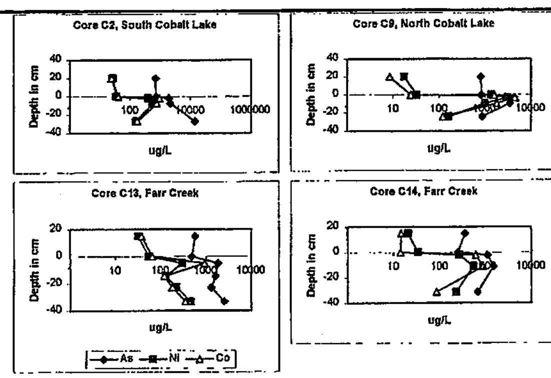

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Prediction of Arsenic Leaching Prerequisites

- Material characterization
  - primary and secondary minerals or tertiary products
- Geological setting
  - associated minerals
  - geology of drainage basin
- Environmental setting
  - pH, Eh, availability of sorption sites (clays, Fe-oxides)
  - site hydrology

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Prediction of Arsenic Leaching Methods and Limitations

- Use of solubility data
  - equilibrium may not occur (thus over-estimate)
  - complications resulting from solid solutions
- Geochemical modeling
  - incomplete data base
  - galvanic interaction not considered
- "Educated guess" based on monitoring results
  - sensible perhaps but relatively expensive

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Observed As Levels in Natural Drainage

pH	Other Conditions	mg/L As
pH ≤ 2.5	Oxic	1 - >100
pH > 8.5	Oxic or reducing	1 - > 100
Mildly acidic to basic	Oxidic, Fe-oxide rich Oxidic, no Fe-oxide Reducing	0.x 0.x – 10x 1 - >100

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Concluding Remarks

- An integrated approach is required to
  - predict arsenic leaching
  - manage As-bearing mine waste
    - *subaqueous versus subaerial disposal*
    - *separate versus co-disposal*

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