

Post-Depositional Formation of Metal-Rich Cyanide Phases in Saturated Tailings Deposits

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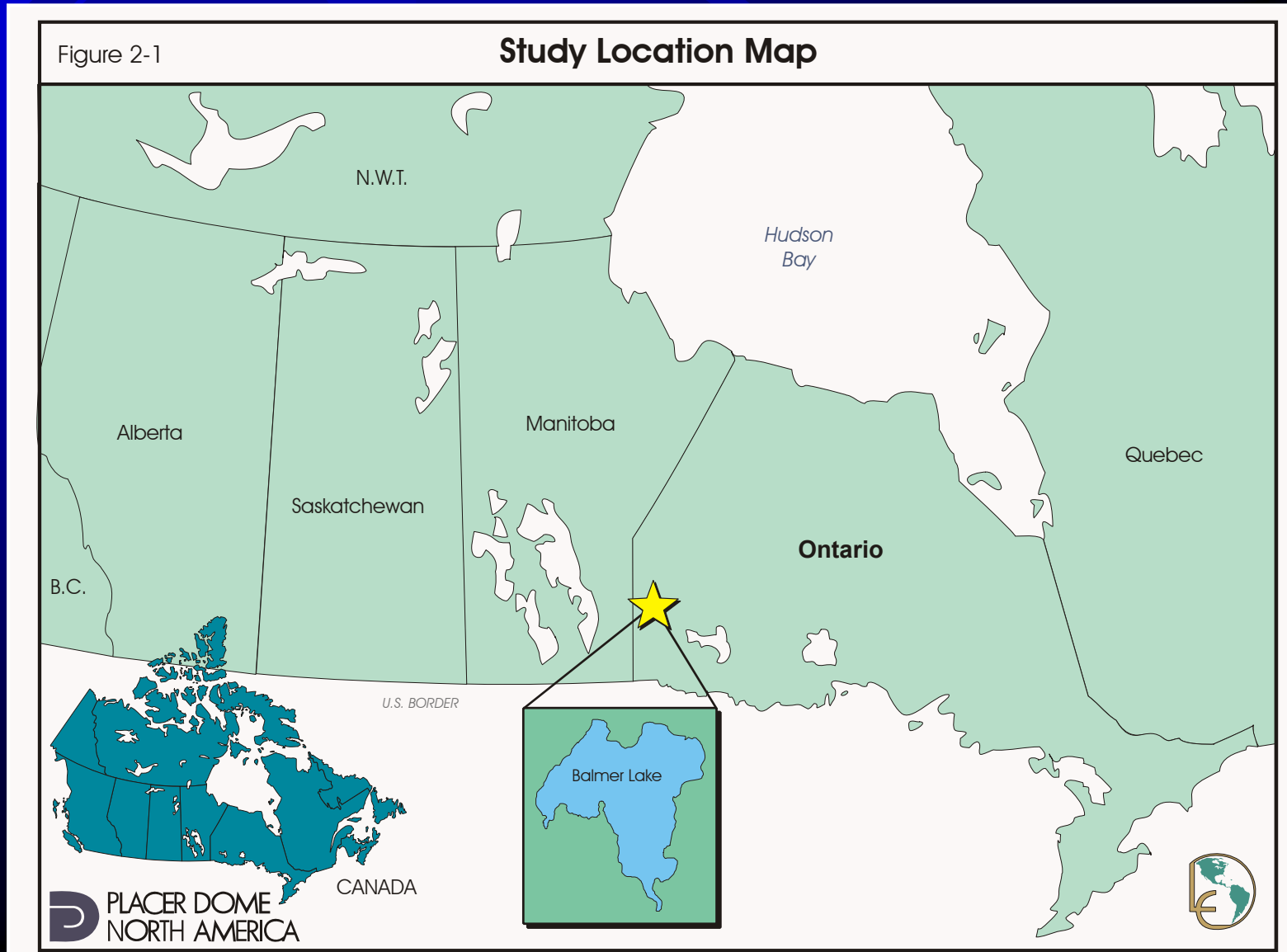
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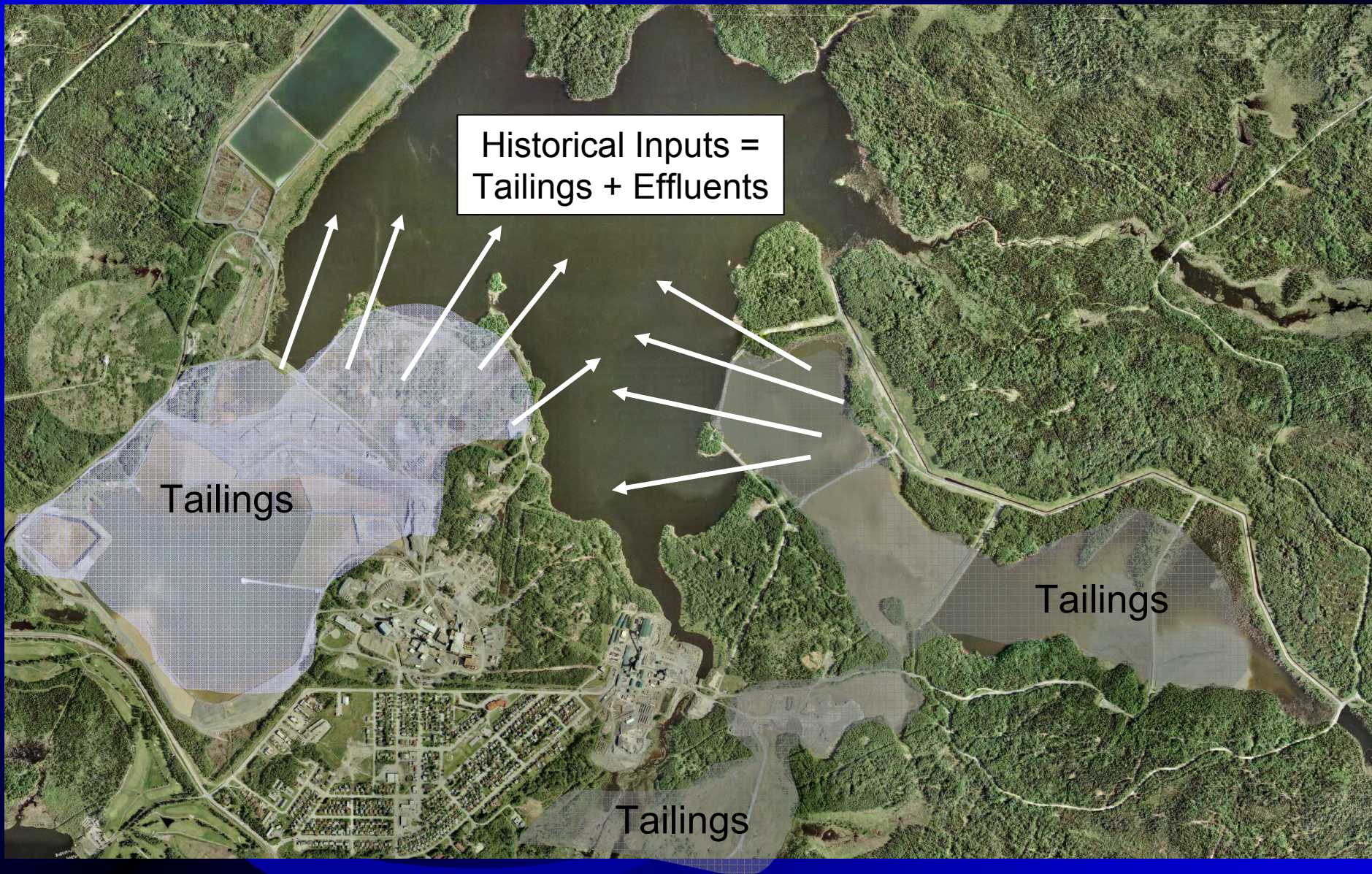
Study Site – Balmer Lake, Ontario



History of Mine-Related Discharges

- Milling of gold ores since 1940's (carbon in pulp processing, using cyanide leaching)
- Direct tailings deposition to Balmer Lake prior to 1970 (predominantly roaster tailings)
- Tailings pond overflow (1940's to present)
- Sediments contaminated with respect to Cu, Pb, Ni, Zn and As.
- Arsenic is focus of environmental management

Balmer Lake



STUDY OBJECTIVES (1993-present)

- Since 1993: Assessment of controls governing post-depositional behaviour of arsenic and other trace elements in Balmer Lake and tailings management areas;



Discovery of Cyanide Phases (2006)

STUDY OBJECTIVES – CYANIDE PHASES

- Composition/texture?
- Importance as repository for trace elements?
- Mechanism of formation?
- Environmental management (benefit or liability?)

METHODS

Overall approach: detailed assessment of sediments and porewaters:

I. Sediment Analysis:

- Whole-rock analysis (minor/major elements, cyanide)
- Mineralogy: optical microscopy, scanning electron microscopy, electron microprobe, Rietveld XRD

II. Porewater Analysis:

- High resolution sampling of dissolved species across sediment-water interface (trace elements, pH, redox-sensitive parameters)

III. Geochemical Modelling: Aqueous speciation using PHREEQC

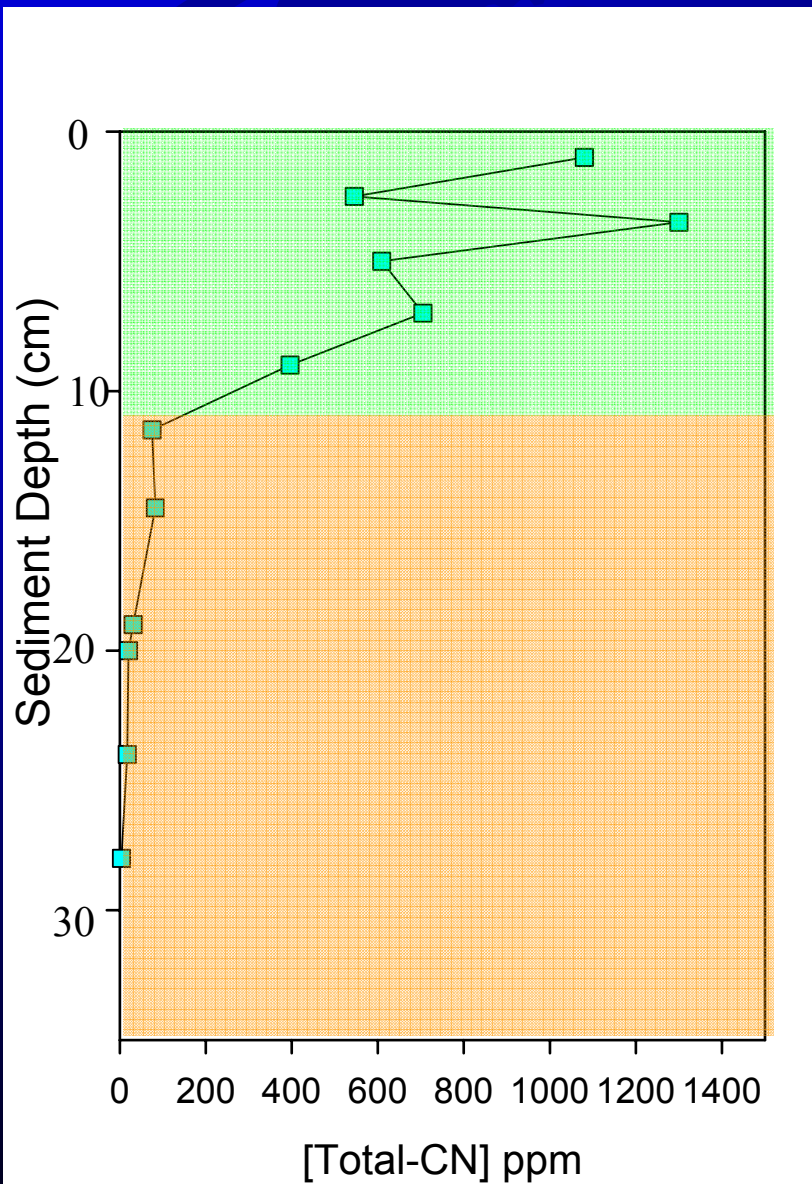
CYANIDE DEGRADATION MECHANISMS

- Volatilization HCN(g) at circum-neutral pH
- Hydrolysis to ammonia
- Oxidation to cyanate (CNO⁻)
- Formation of thiocyanate (SCN⁻)
- Photodegradation
- Biodegradation
- Complexation of free cyanide (CN⁻), *e.g.* Fe(CN)₆⁻³
- Adsorption (hydrous Fe/Mn oxides, organic matter)
- Precipitation of cyanide complexes, *e.g.* Fe₄[Fe^{II}(CN)₆]₃

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CYANIDE IN SEDIMENTS



- Mine-related signature evident in upper 10 cm of deposits

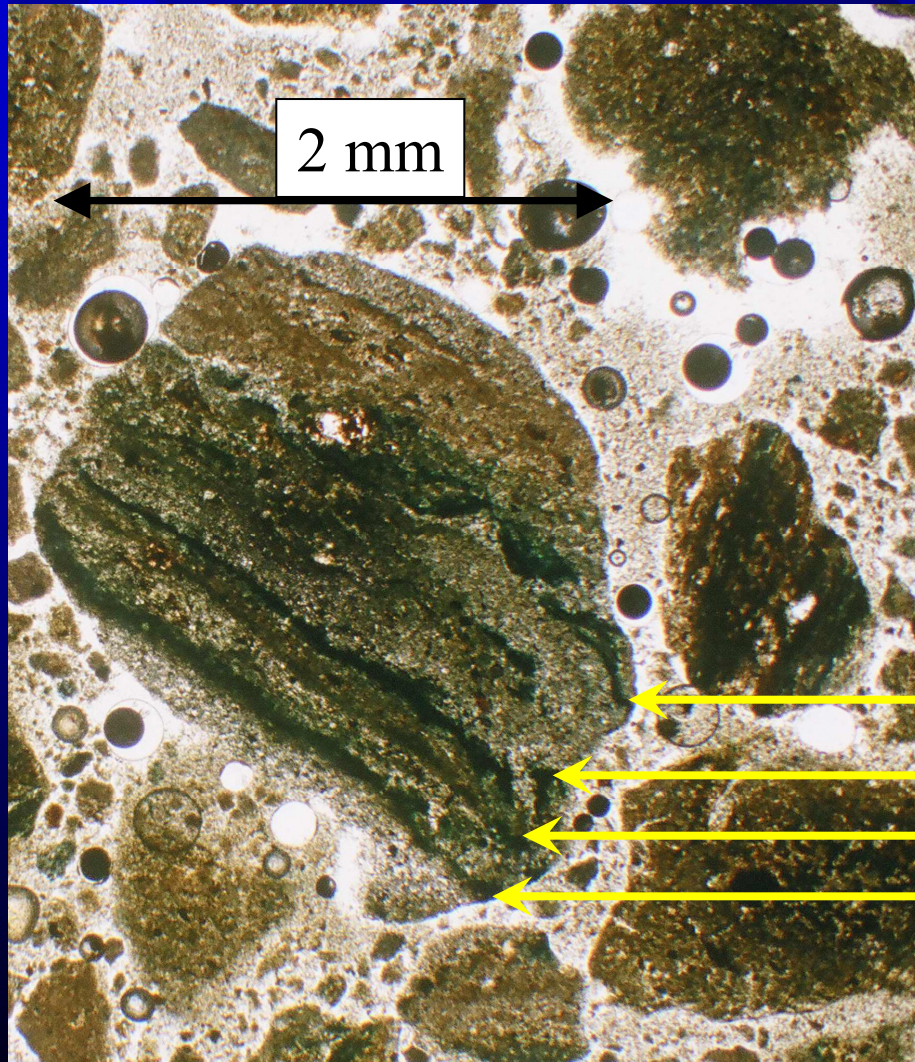
Tailings: elevated CN, trace elements, dolomite, roaster Fe-oxides

Natural sediments: organic-rich, low carbonate, low levels of trace elements

Cyanide Phases

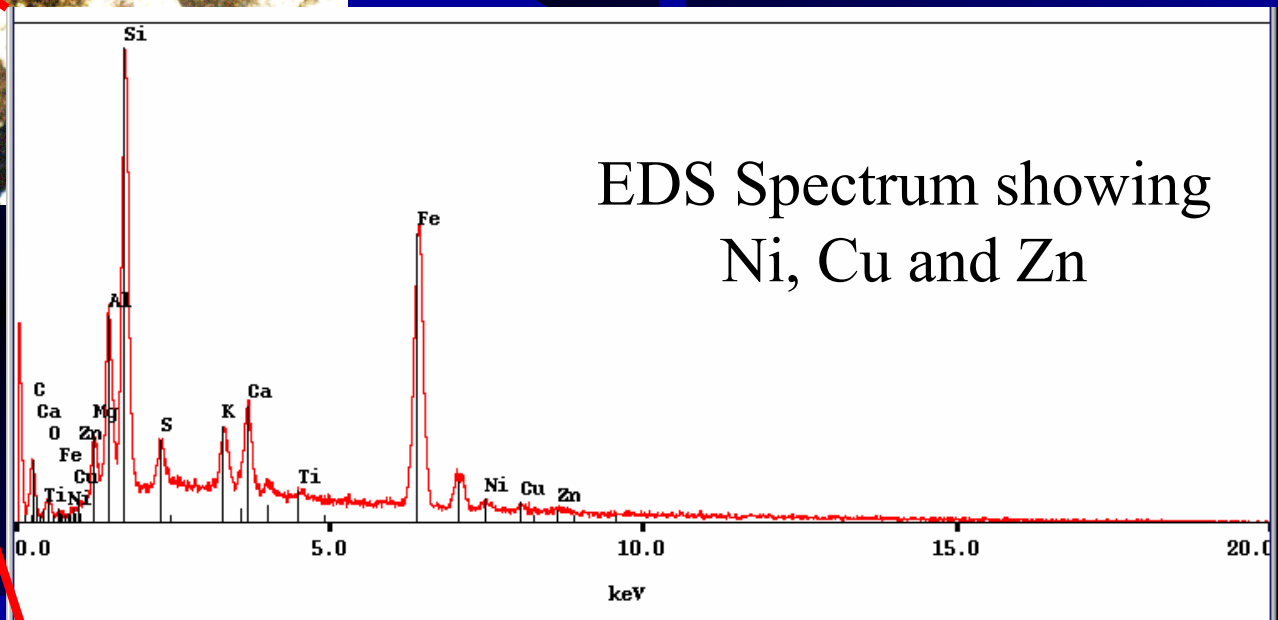
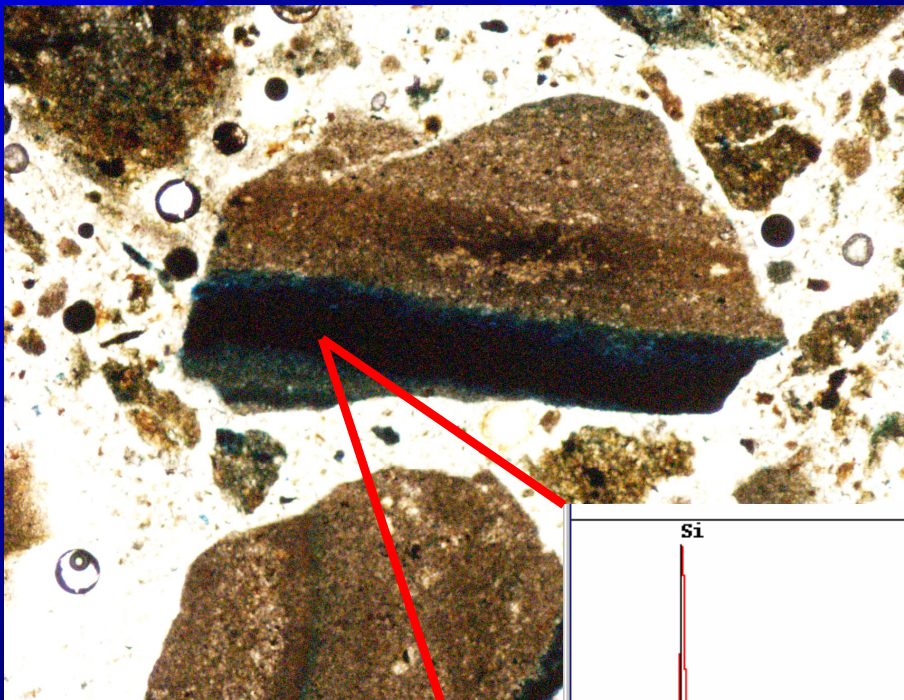
- Total cyanide concentrations range from 220 to 1,300 ppm in top 10 cm of deposit
- Cyanide occurs as bedded layers and as discrete particles that have crystallized *in situ* in the tailings (authigenic phases).
- Cyanide phases are all Fe-bearing (e.g., hexacyanoferrates)
- XRD on a hand-picked specimen confirmed the presence of a mixed ferri/ferro cyanide = $\text{Fe}^{\text{III}}_4(\text{Fe}^{\text{II}}\text{CN})_6)_3$, commonly referred to as “Prussian Blue”

CN Compounds - Plain Transmitted Light

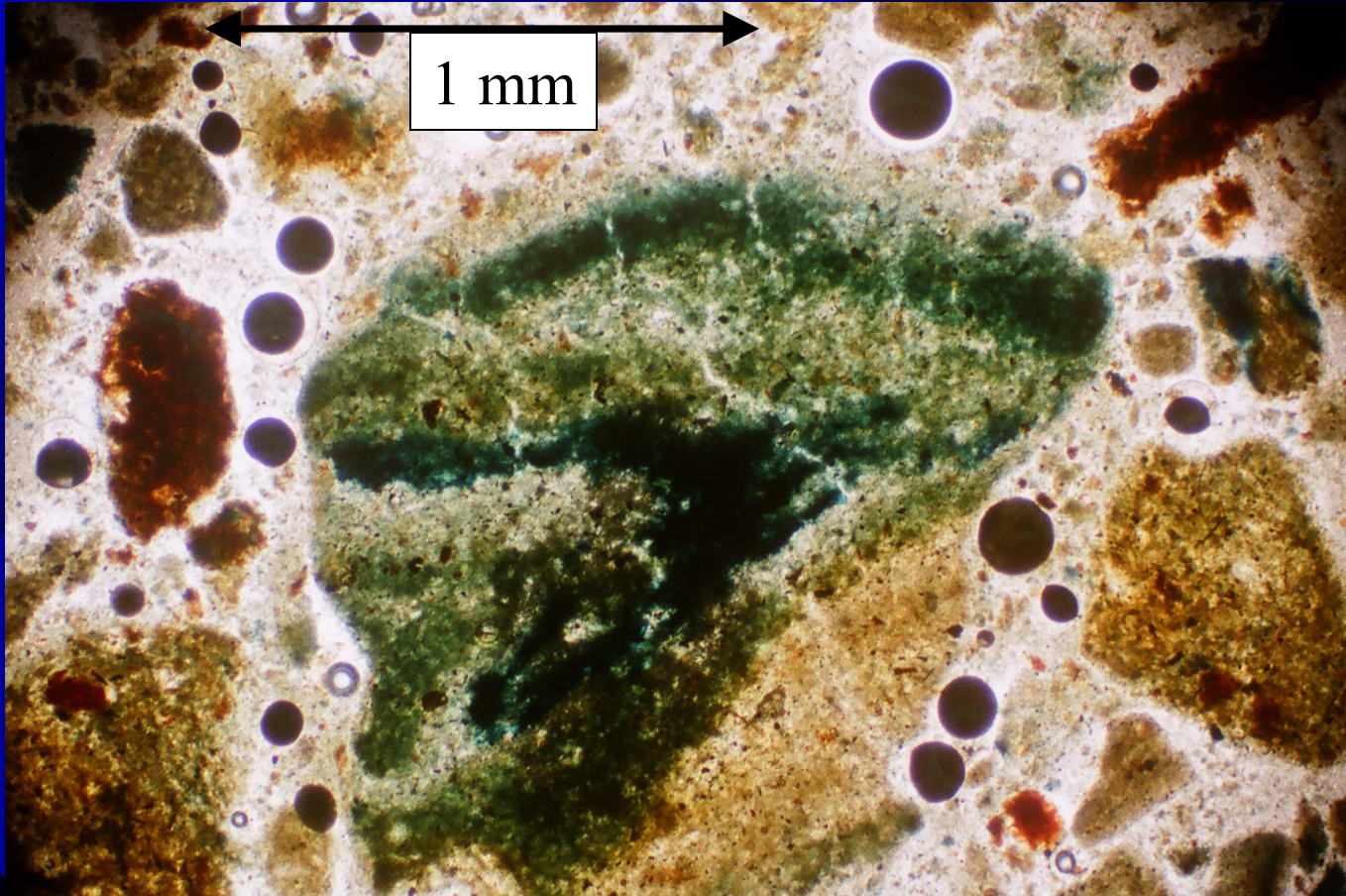


- Cyanide-rich bands 100-500 μM in thickness
- Contain Cu, Ni and Zn.

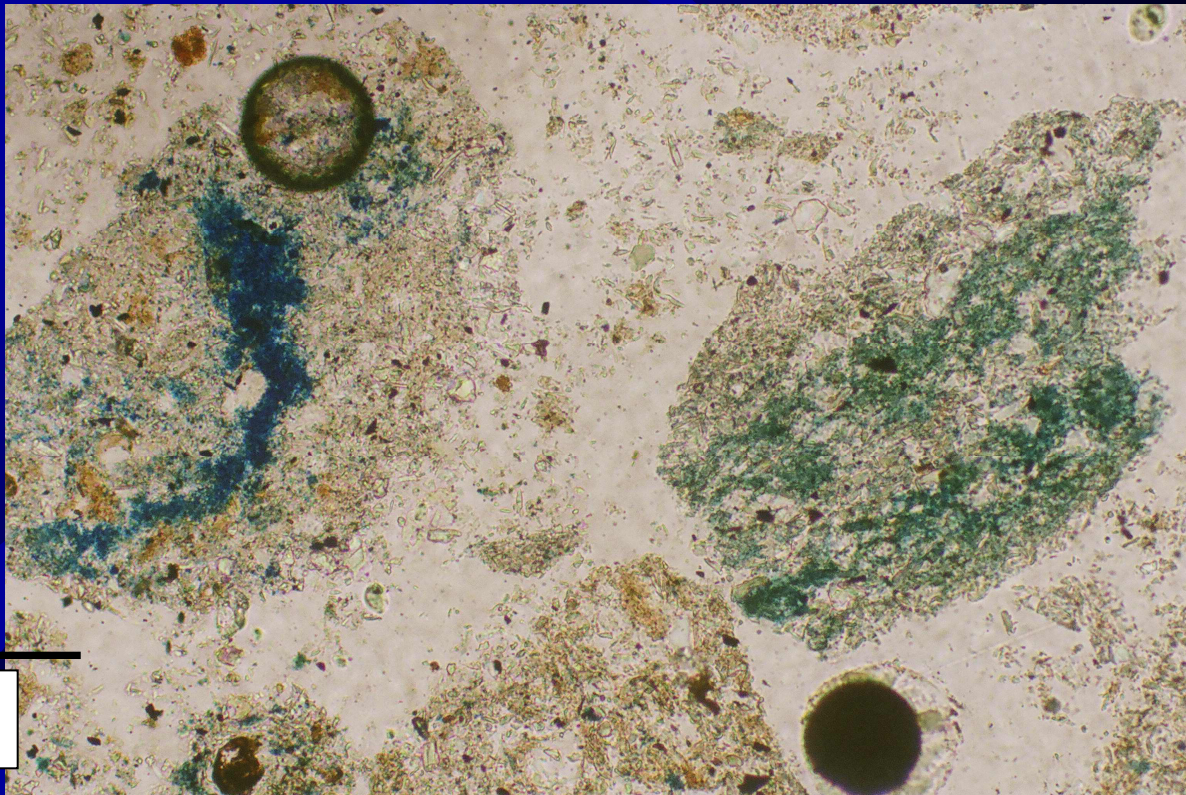
Cyanide Compounds – Trace Element Content



CN Compounds - Plain Transmitted Light



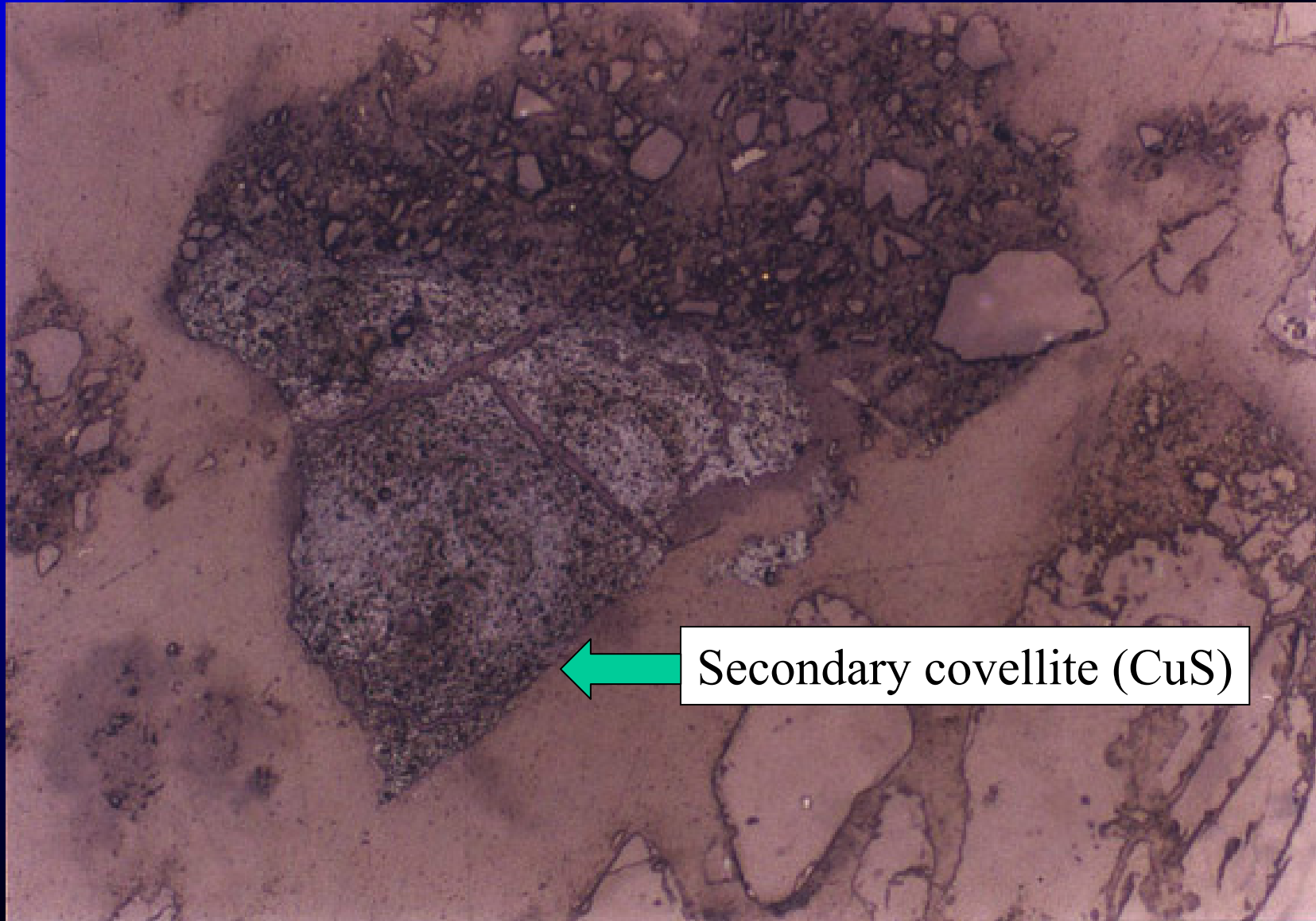
Cyanide Compounds – Colour Variation



200 μm

- Cyanide phases range in colour from green to blue
- Colour variations could not be linked to trace element content

CN Compounds - Impostors



Cyanide Compounds – Trace Element Content

- In all cases, cyanide phases are Fe-dominant and contain variable amounts of Ni, Cu and Zn.
- Electron microprobe results indicate variable Ni, Cu and Zn contents ranging from 1-5 wt.% in cyanide phases.
- Cyanide phases are dominant host for Cu in Balmer Lake sediments.
- Cyanide phases are second most important host for Ni and Zn (Ni and Zn dominantly associated with Fe oxyhydroxides)

Metal-Cyanide Phases Quantitatively Significant!

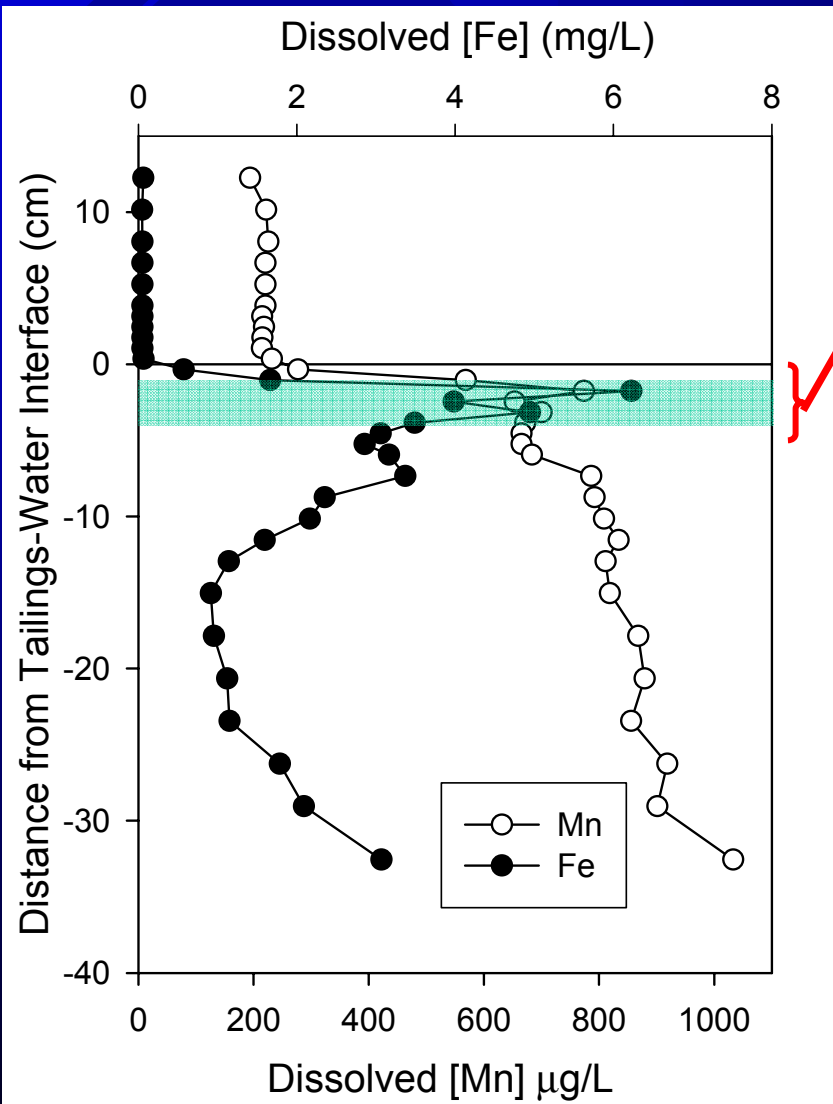
IRON CYANIDE - MECHANISM OF FORMATION

- The concentrated distribution of cyanide along bedding planes implies *in situ* formation (authigenic origin)
- Strong evidence that the formation of cyanide complexes in Balmer Lake sediments is a microbially-mediated process, linked to redox potential, cyanide concentration and the availability of dissolved Fe (both Fe^{II} and Fe^{III})



Requirement for reduction of Fe^{III} (i.e., suboxia)

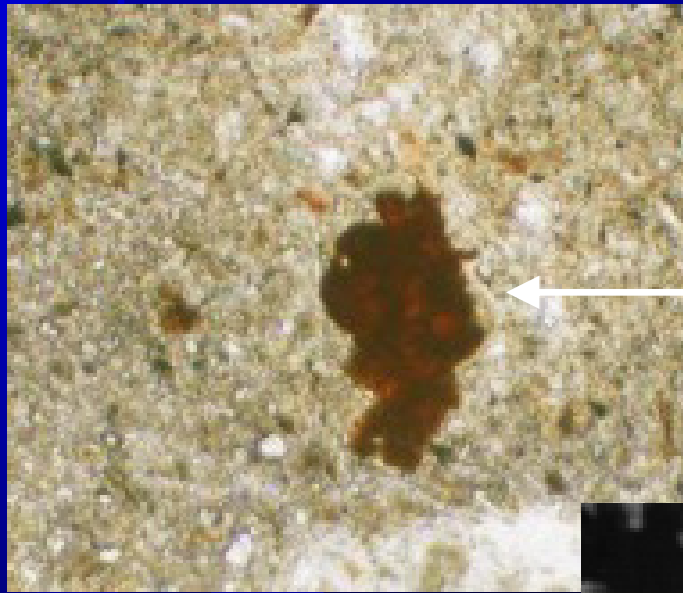
Balmer Lake –Redox Conditions in Porewater



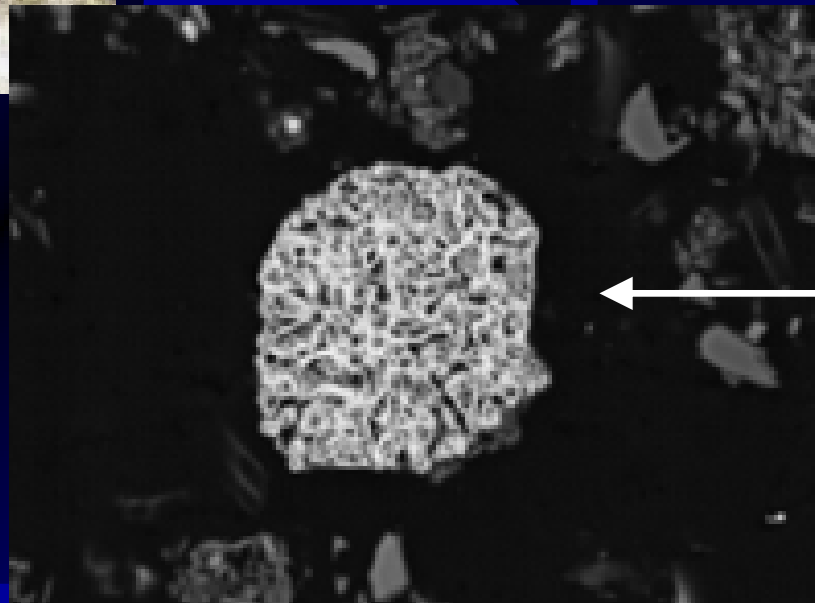
Reductive dissolution of Fe^{III} and $\text{Mn}^{\text{III/IV}}$ phases in close proximity to sediment-water interface.

Strong suboxia below sediment depths of 2-3 cm

Balmer Lake – Sedimentary Fe(III) phases



Fe oxyhydroxides



Roaster
Fe oxides

IRON CYANIDE – Solubility in Porewater

Solubility Equilibrium:

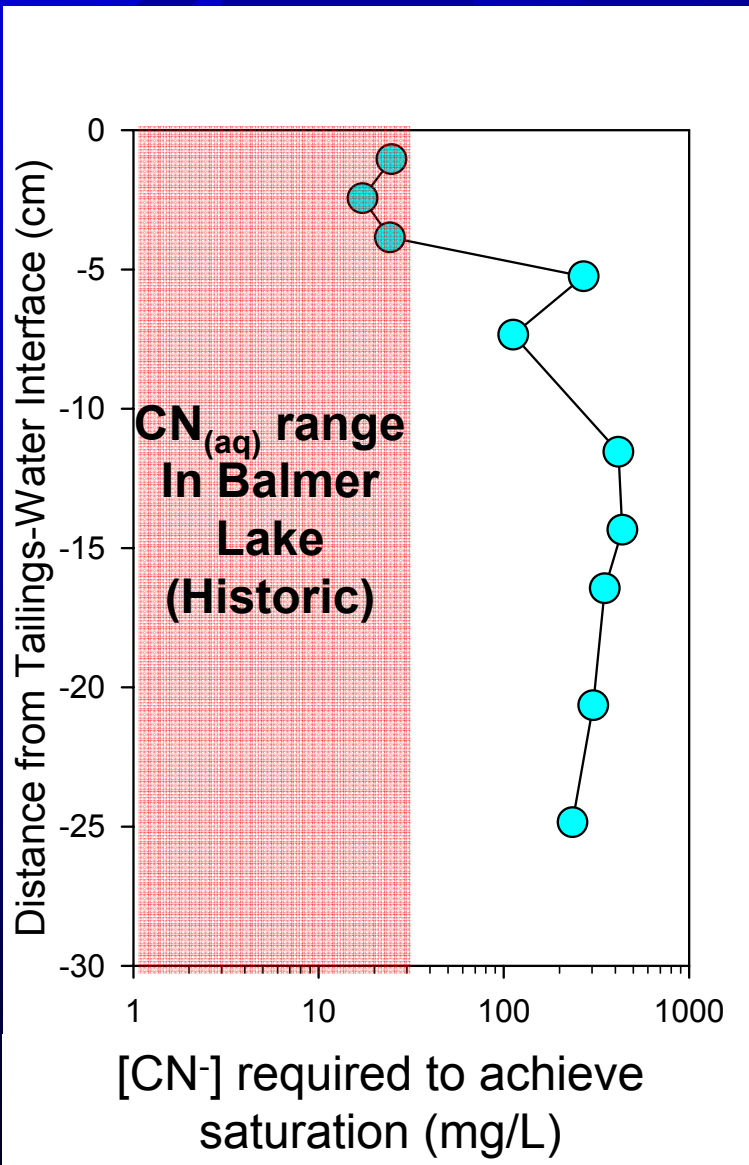


$$\log K = -84.5 = 4\log[\text{Fe}^{3+}] + 3\log[\text{Fe}(\text{CN})_6^{3-}] - 3pe$$

Variables:

- $[\text{Fe}^{3+}]$ and pe obtained from aqueous speciation of porewater data for Balmer Lake
- $[\text{Fe}(\text{CN})_6^{3-}]$ calculated from $\log K$ equation
- (CN) derived from calculated $[\text{Fe}(\text{CN})_6^{3-}]$

IRON CYANIDE – Solubility in Porewater



- CN levels in porewater ranging from 17 to 440 mg/L are required to achieve saturation with respect to $\text{Fe}_4(\text{FeCN})_6)_3$
- Historic CN concentrations in Balmer Lake waters have ranged as high as 20 mg/L, and most likely higher.
- Given changes in CN levels in Balmer Lake, precipitation of authigenic cyanide phases possibly a feature of the past and not current scenario.

FATE OF TRACE METALS?

- If cyanide phases dissolve, what will the fate be for associated trace elements (Cu, Ni and Zn)?
- In Balmer Lake, Cu, Ni and Zn currently show no evidence of release to water column.
- Presence of free sulfide (HS^-) in porewater, and solubility considerations, suggest any Cu, Ni and Zn remobilized from CN phases would be consumed via formation of secondary sulfides.
- i.e., Conditions required for formation of cyanide phases also serve well for attenuation of trace elements upon remobilization.

IMPLICATIONS FOR ENVIRONMENTAL MANAGEMENT - BENEFITS

Formation of metal-cyanide complexes offers several potential advantages with respect to water quality management:

- Reduction in cyanide and metal loadings to groundwater and surface water reservoirs
- Decreased mobility, bioavailability, and hence toxicity of trace metals.

IMPLICATIONS FOR ENVIRONMENTAL MANAGEMENT - RISKS

Under what conditions could cyanide compounds be remobilized?

- Change in pH
- Increase in redox potential (exposure to oxidizing conditions)
- Exposure to sunlight

- Studies that have examined of cyanide degradation suggest that decomposition proceeds very slowly in absence of UV radiation.
- In the absence of light, the speciation of cyanide is likely governed by decomposition kinetics (not chemical equilibrium).

CONCLUSIONS

- Formation of secondary (*in situ*) formation of cyanide phases can present a dominant control on the mobility and accumulation of metals in permanently saturated tailings deposits.
- Behaviour observed at Red Lake Gold Mines likely occurring at many other sites.
- Conditions which may result in CN remobilization are not well understood.
- Need for further study.

Special issue of Applied Geochemistry in honour of John Jambor

- Publication date: summer fall of 2009.