Characterization of ARD Neutralization Sludge: Links between ARD Influent Chemistry, Treatment Process and Sludge Composition.

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- Inmet - Samatosum Mine (BC)
- Teck - Sullivan Mine (BC)
- Hudson Bay Mining and Smelting – Chisel North Mine (MB)

Reviews:

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PREFACE

Neutralization Sludges:

They're not what you think they are…..

BACKGROUND

- At many mine sites the management of ARD involves neutralization with lime to reduce levels of acidity and trace elements prior to discharge to the environment.
- In general, treatment is achieved by raising the pH to values greater than 8.5 and separating the resulting precipitates (sludge) from the treated water prior to discharge.
- Within Canada alone, it is estimated that approximately 7 million m^3 of neutralization sludge are produced on an annual basis from mining/metallurgical operations (MEND, 1997).

BACKGROUND cont.

- In general, trace-element associations (i.e., metal-bearing phases) within lime neutralization sludge are not well understood.
- Due to the extremely fine-grained and often amorphous (*i.e.*, non crystalline) character of sludge solids, metal associations have been difficult to elucidate.
- Given that neutralization sludges represent large inventories of metal-rich material, understanding sludge composition is prerequisite for assessing the long-term chemical stability in various depositional settings (pH and Eh dependent solubility).

OBJECTIVES

- To elucidate the trace metal associations (phase relationships) in sludge materials using high resolution microscopy methods; and
- To assess the links between sludge composition, ARD influent chemistry and treatment process;

Provide basis from which to assess long-term chemical stability.

METHODS - Sludge Samples

Sludges from 7 mines across Canada

1. Equity Mine (B.C.) - Goldcorp Canada
2. Geco Mine (Ontario) – Xstrata Zinc
3. Britannia Mine (BC) - EPCOR
4. Brunswick Mine (New Brunswick) – Xstrata Zinc
5. Samatosum Mine (BC) - Inmet
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Focus of today's presentation (mines 1–3)

Geology and Treatment Process

	Equity	Geco	Britannia
Commodities	Au-Ag-Cu	Cu-Zn	Cu (Zn-Pb-Ag)
Deposit Type	Intrusion-related hydrothermal	Metamorphosed Volcanogenic Massive Sulfide	Massive Sulfide
Treatment Process	High density sludge	High density sludge	High density sludge

HDS: typically 20-30% solids

METHODS – SLUDGE ANALYSIS

Solid Phase:

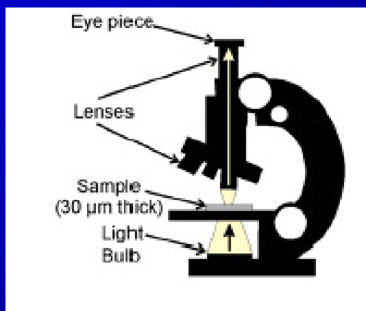
- Elemental Abundance
- X-Ray Diffraction
- High-resolution microscopy
    - Optical Microscopy
    - Scanning Electron Microscopy (SEM)
    - (Scanning) Transmission Electron Microscopy ((S)TEM).
    - X-ray absorption spectroscopy (XAS): synchrotron accelerator at Canadian Light Source – Saskatoon)

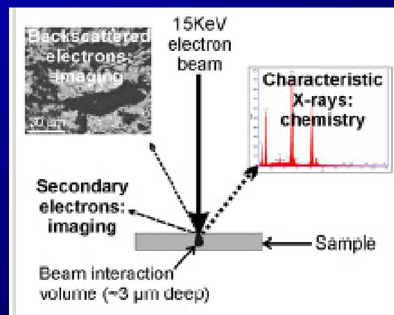
Aqueous Phase:

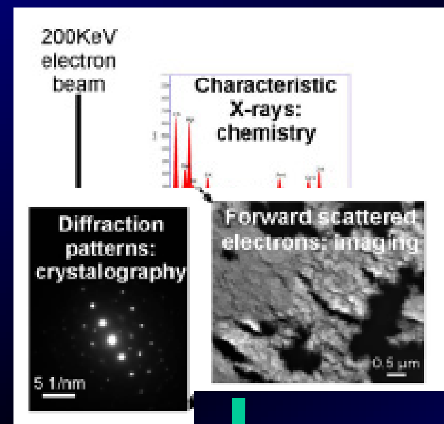
- Influent and effluent chemistry

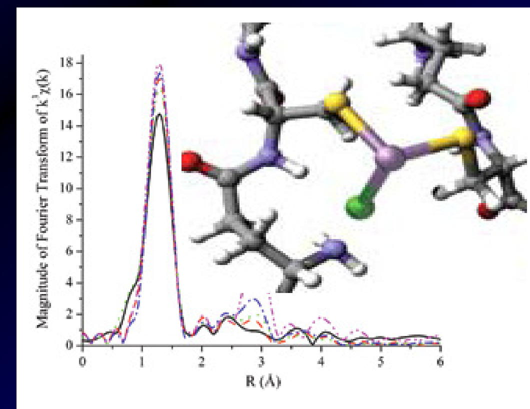
MICROSCOPY METHODS

Optical	SEM	STEM	XAS









0.1 mm — Micrometres — Nanometres — Atomic

Increasing Resolution

Results: ARD Influent (FEED) Chemistry

Parameter	Equity	Geco	Britannia
pH	2.7	3.0	4.05
SO_4	9,900	4,600	1320
Al	776	10	19
Fe	920	1,100	0.6
Mg	919	170	64
Ca	330	338	411
As	6	<0.01	<0.0005
Cd	1.1	0.04	0.09
Zn	123	12	18
Cu	60	0.31	18
Mn	137	7.0	4.2
Ni	8	0.02	0.04
Pb	<0.3	0.01	0.05

All values in mg/L

Equity:
- High sulphate, Al, Fe, Mg
- Priority trace elements: As, Cd, Cu, Ni, Zn

Geco:
- High sulphate, Fe
- Low Al, Mg
- Priority trace elements: Cu, Zn

Britannia:
- Low SO4, Fe, Al, Mg
- High Cu, Zn
- Priority trace elements: Cu, Zn

Results – Sludge Elemental Abundance

Element	Unit	Equity	Geco	Britannia
Aluminum	%	4.0	0.3	5.6
Calcium	%	14	10	13
Iron	%	4.3	26.2	0.7
Magnesium	%	2.5	0.3	3.5
Sulphur	%	11.6	7.4	1.1
Arsenic	ppm	267	<0.5	7
Cadmium	ppm	58	7	262
Copper	ppm	2,693	73	50,000
Zinc	ppm	6,317	2,743	52,000
Lead	ppm	0.3	2.6	150
Manganese	ppm	6,956	1,880	12,000
Nickel	ppm	368	9.2	112

EQUITY Mine: Microscopy

Mineral Assemblage:

- Dominant phase: Gypsum (only phase detected by XRD)

- Other mineral phases identified with SEM:
  - Al hydroxide,
  - Fe-oxyhydroxide,
  - Calcite
  - Apatite

Dominant trace element-bearing phase in the sludge:

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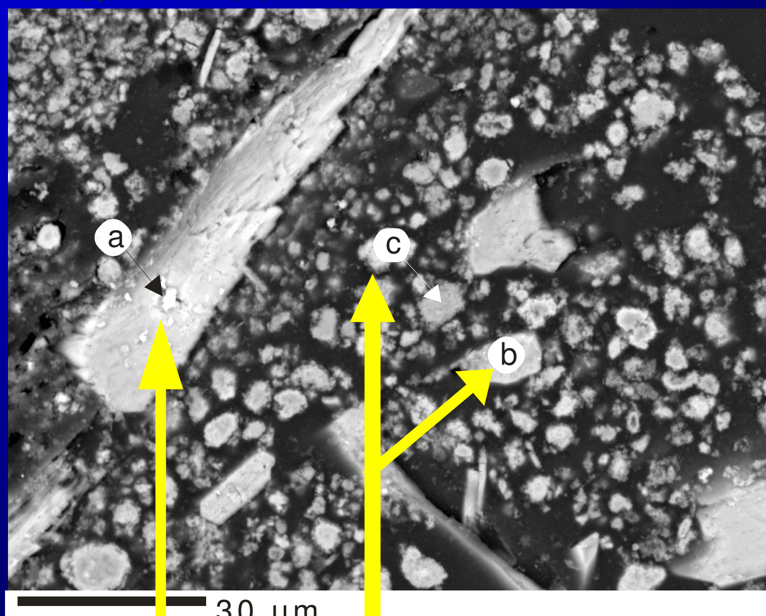
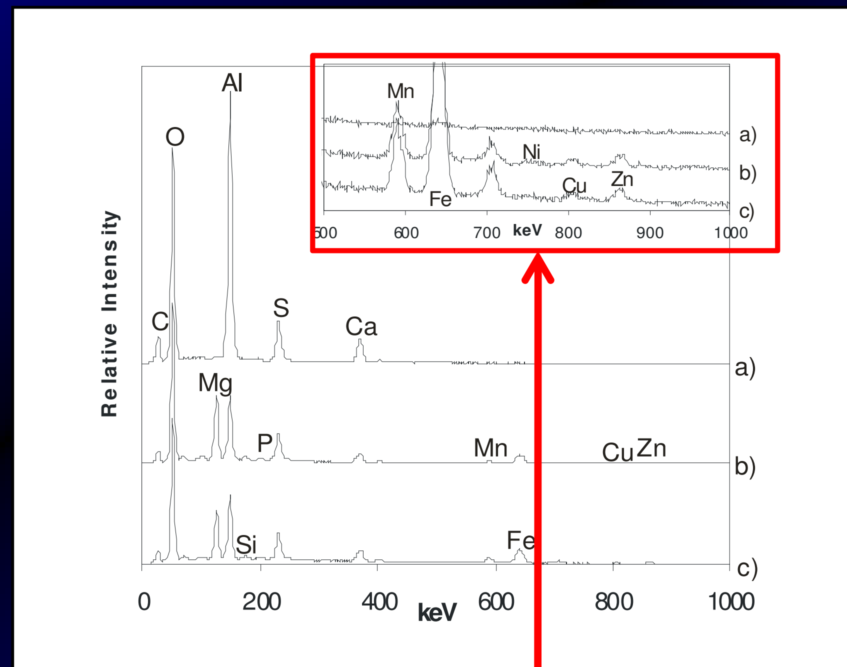
Amorphous Mg-Al-(Fe) hydroxysulphate

Consistent with high Mg, Al and sulfate in ARD

EQUITY HDS - SEM BSE Images



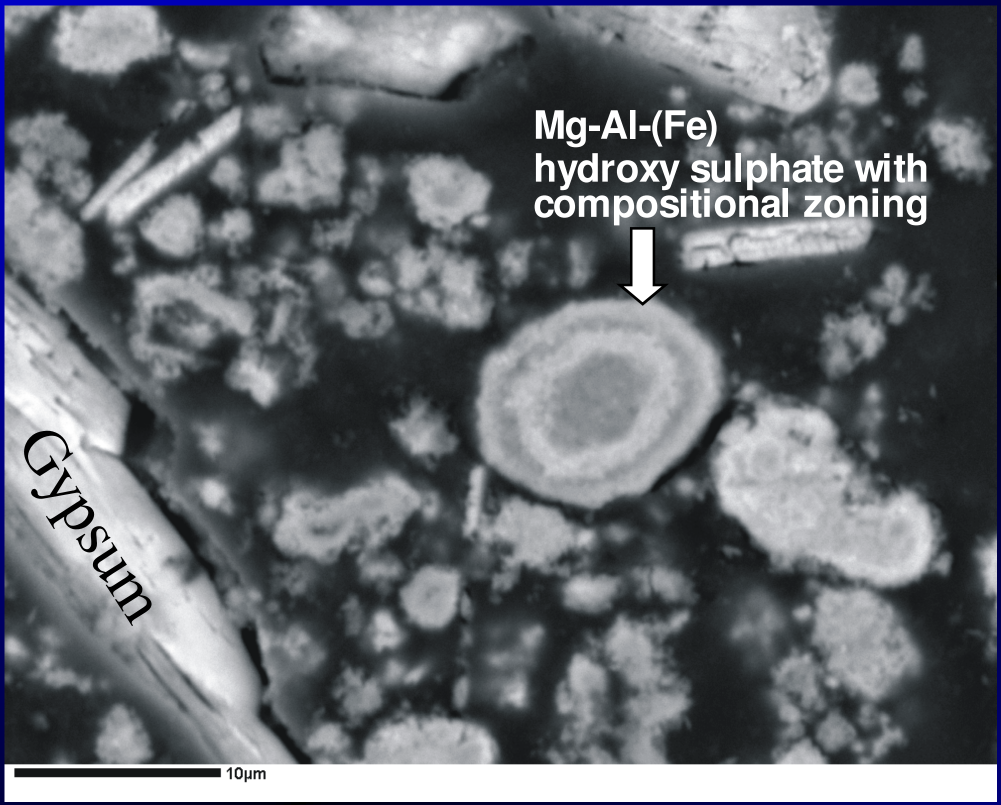


a) Gypsum + Al-Fe hydroxide

Metals associated with Mg-Al hydroxysulfate (spectra b and c)

b) & c) Mg-Al-(Fe) hydroxysulphate (<1 to 15 µm)

EQUITY HDS: Mg-Al-(Fe) hydroxysulphate

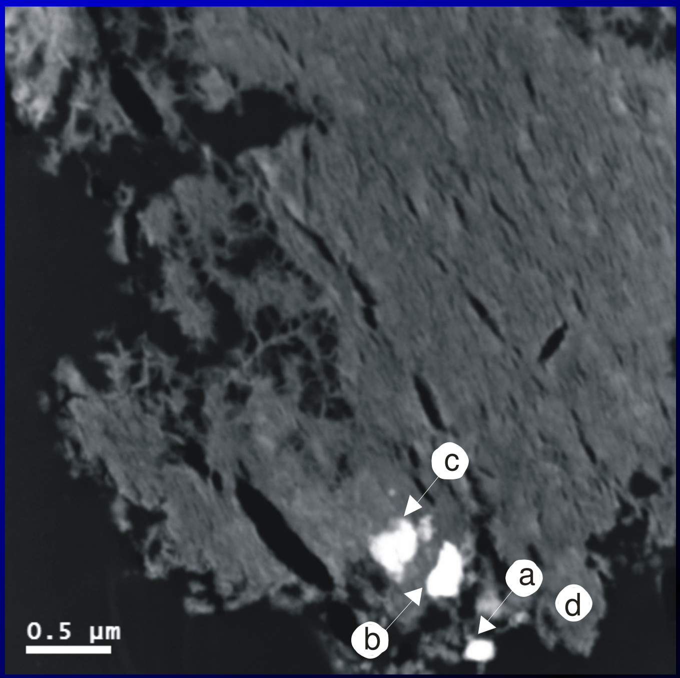


Concentric layers alternating between Mg+Al-rich (Fe-poor) and Fe-rich

Consistent with the dissolution and re-precipitation reactions predicted to occur during sludge recycling in HDS process

EQUITY HDS: (S)TEM Images and EDS spectra

Mg-Al-(Fe) hydroxysulphate



- Zn is more strongly correlated with Mg/Al than Fe.
- Selected-area electron diffraction (SAED) did not produce any discernable diffraction patterns or rings, suggesting that this phase is amorphous.

Geco Mine: Microscopy

Mineral Assemblage:

- Dominant phase: Gypsum (only phase detected by XRD)

- Other mineral phases identified by SEM:
  - Al hydroxide
  - Calcite

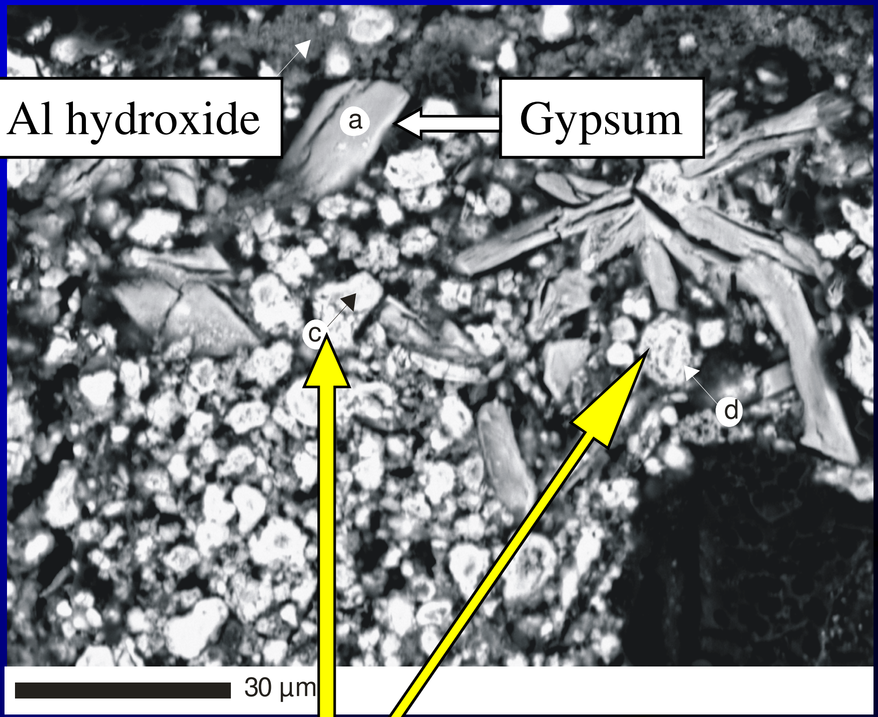
Dominant trace element-bearing phase in the sludge:

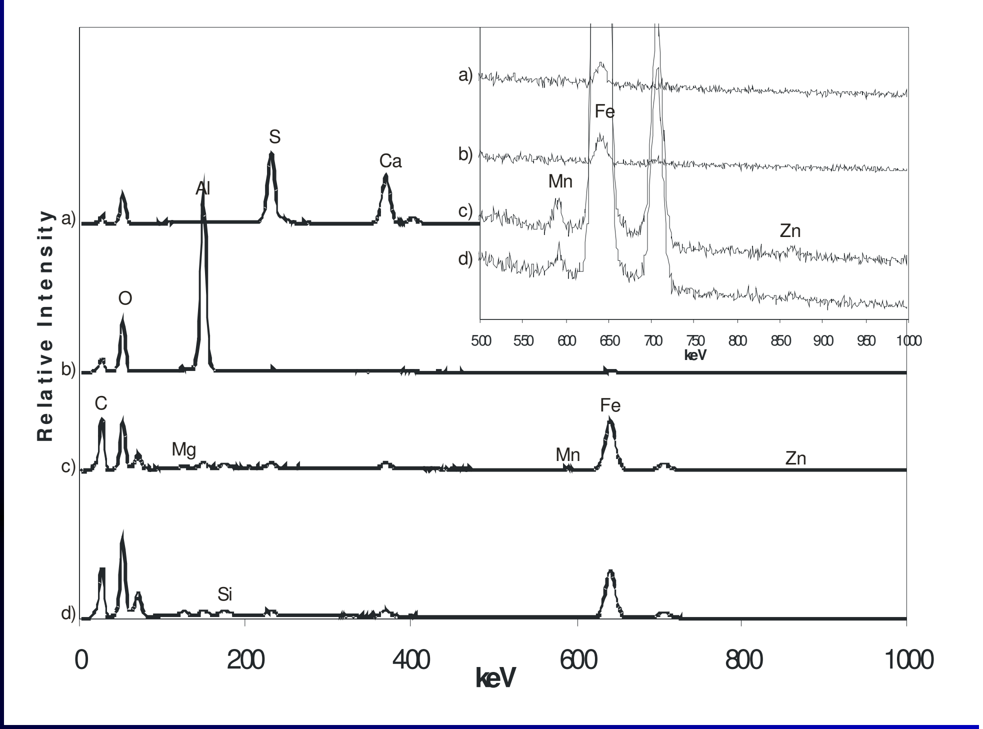
↓

Relatively pure Fe hydroxide

Consistent with high Fe and low Mg & Al in ARD

GECO - SEM BSE Images

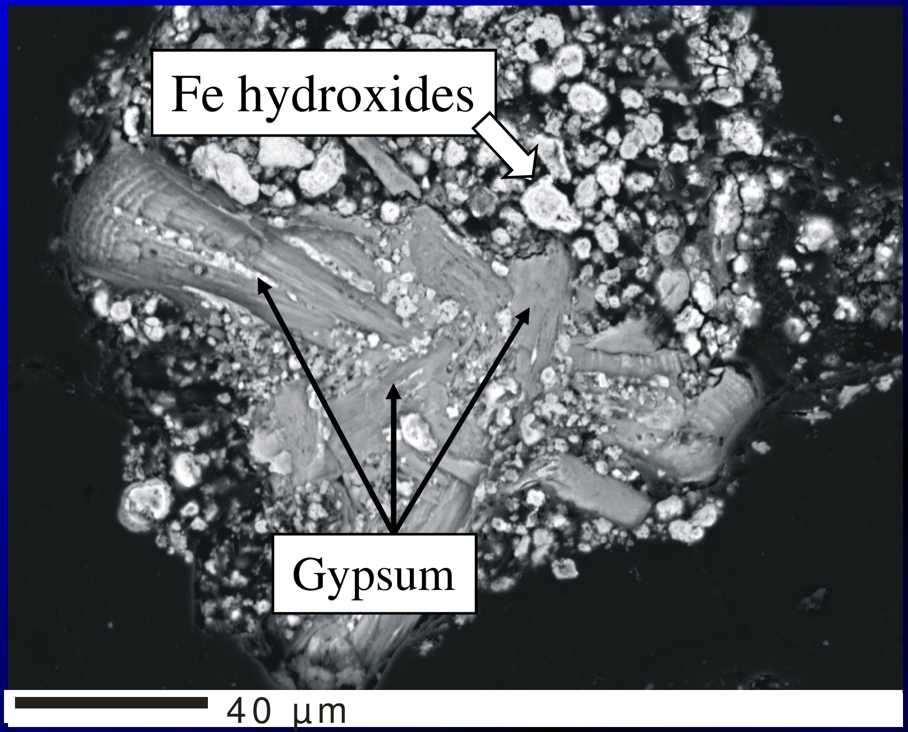




Fe hydroxides: (1-20 µm) well rounded grains that display compositional zoning

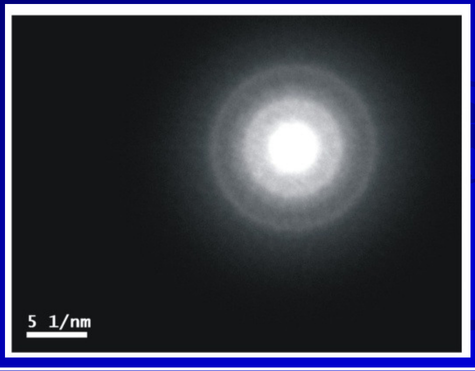
Zn and Cu associated with Fe hydroxides (spectra c and d) and not gypsum (a) or Al hydroxide (b)

GECO - SEM BSE Images



- Fe hydroxide (<1 to 20 µm in size) is essentially pure with only minor amounts of other constituents (e.g. Mg, Al and S).

- Selected area electron diffraction (SAED) indicates the presence of broad diffuse rings, suggestive of poorly crystalline to amorphous Fe oxides.



Britannia Mine: Microscopy

Mineral Assemblage:

- Dominant phases by XRD
  - Calcite and/or Mg-calcite

- Other mineral phases identified by SEM:
  - Quartz
  - Fe oxyhydroxide
  - No gypsum

Dominant trace element-bearing phase in the sludge:

↓

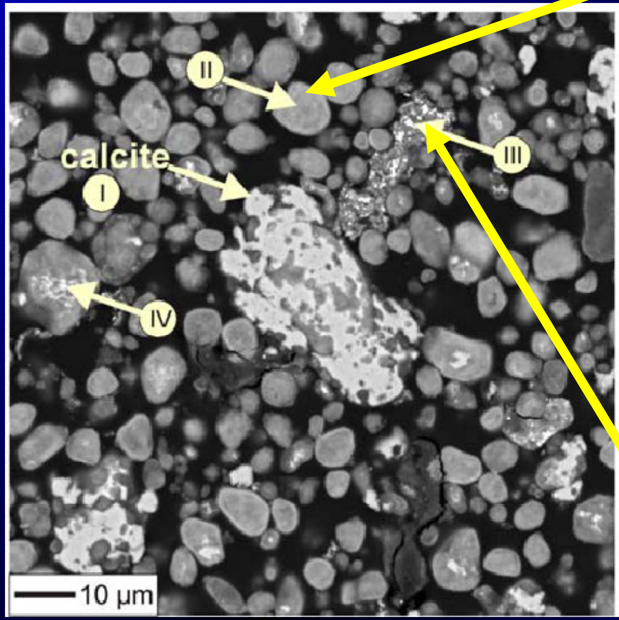
Amorphous Cu-Zn hydroxide

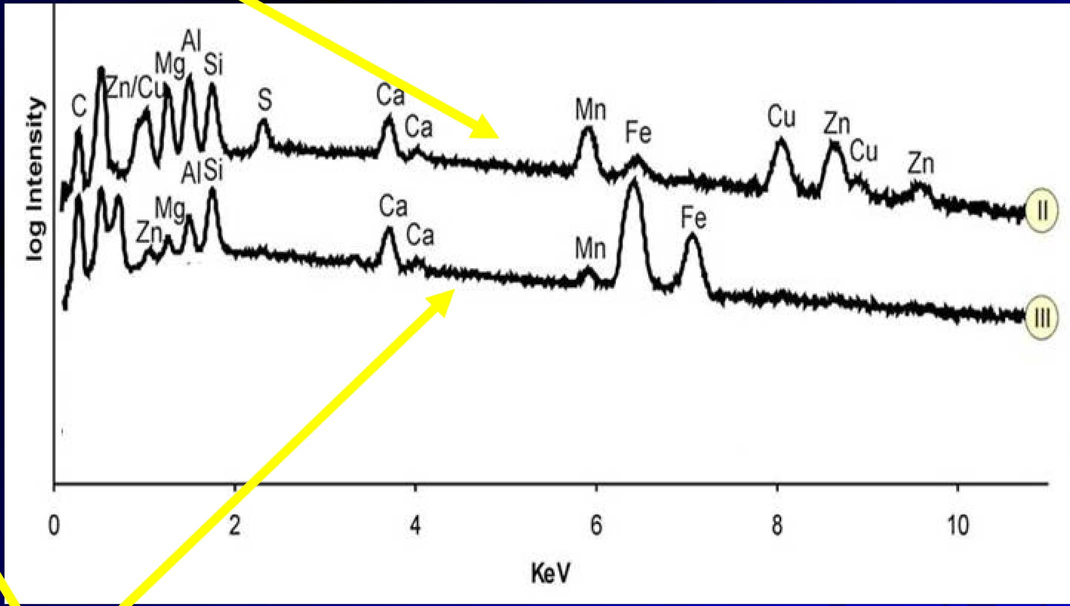
Consistent with low Fe/Al and high Cu and Zn in ARD

Britannia - SEM BSE Images

- Metal bearing phase : fine-grained aggregates of Cu hydroxide
- Contains variable Mg, Al and Si
- Fibrous grains ranging in size from 5 to 100 µm.

Cu-Zn (Mg, Al, Si) hydroxide

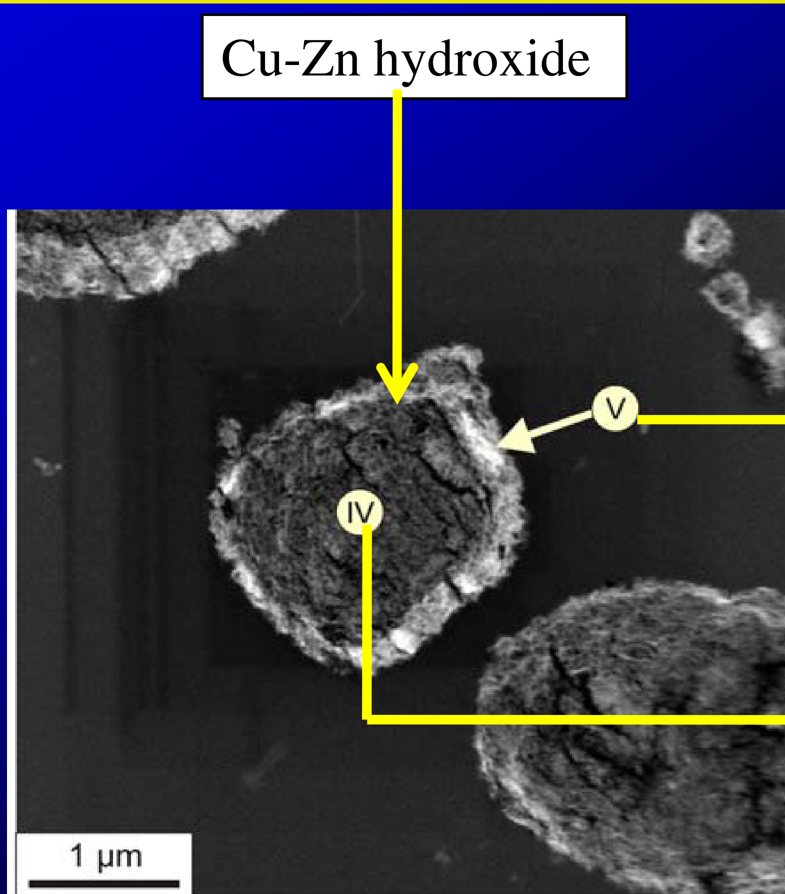


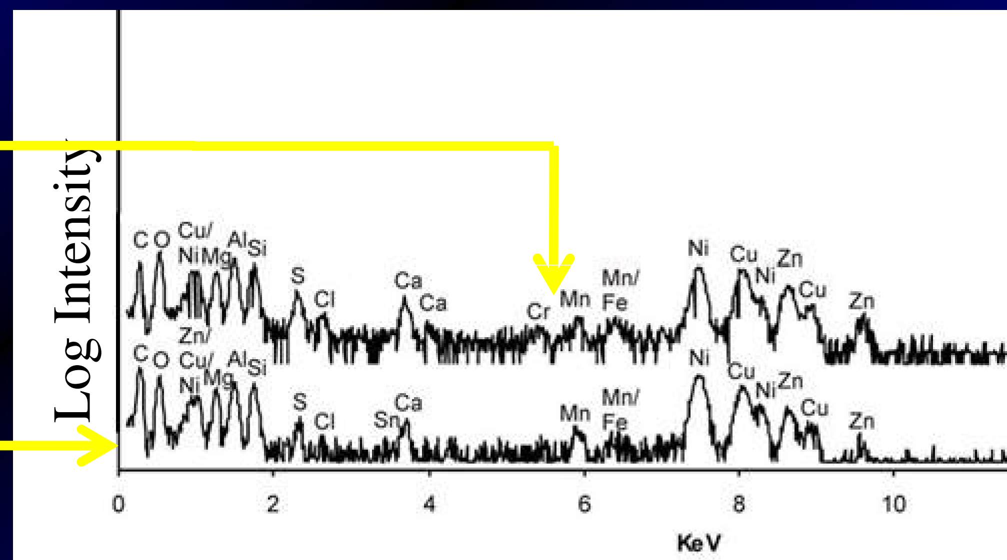


Fe oxyhydroxide

Britannia – STEM Images

Fibrous grains display compositional zoning





Selected area electron diffraction patterns consistent with amorphous or nanocrystalline material

SUMMARY

- In all sludges, metal-bearing phases were amorphous (or poorly crystalline) and variable in composition (relatively pure to heterogeneous).
- Metal-bearing phases largely governed by composition of ARD. Proportions of Fe, Mg, Al and S important. Textures and concentric zoning reflective of HDS process.
- Varied spectrum in metal-bearing phases observed, including: 1) heterogeneous Mg-Al-(Fe) hydroxysulphate; 2) relatively-pure Fe hydroxide; and 3) heterogeneous Cu-Zn hydroxide.
- Different metal-hosting phases can be expected to show contrasting chemical stabilities with respect to pH and Eh conditions. Results therefore highlight need to understand controls governing long-term chemical stability of various sludge phases.

Predictive Tool

ARD Chemistry

↓

"Sludge type"
(metal-bearing phases)

↓

In situ chemical stability, depending on depositional environment

} Further investigation required

Thank you

Questions?