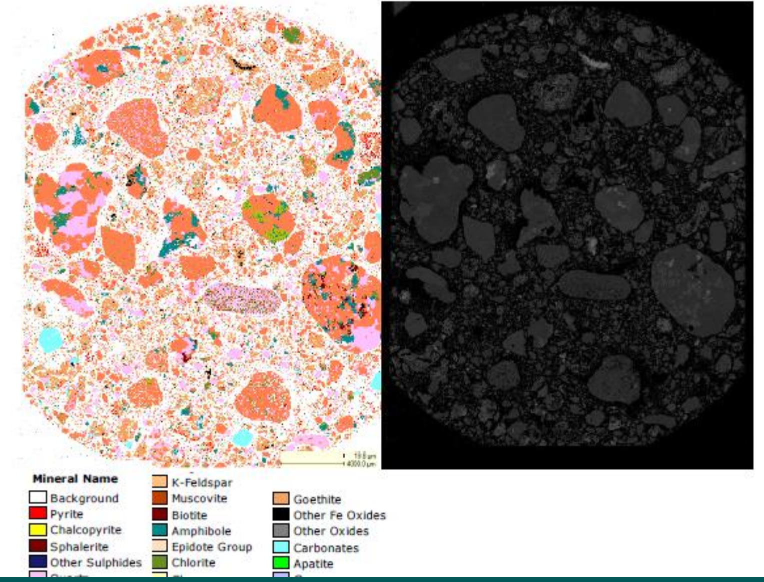
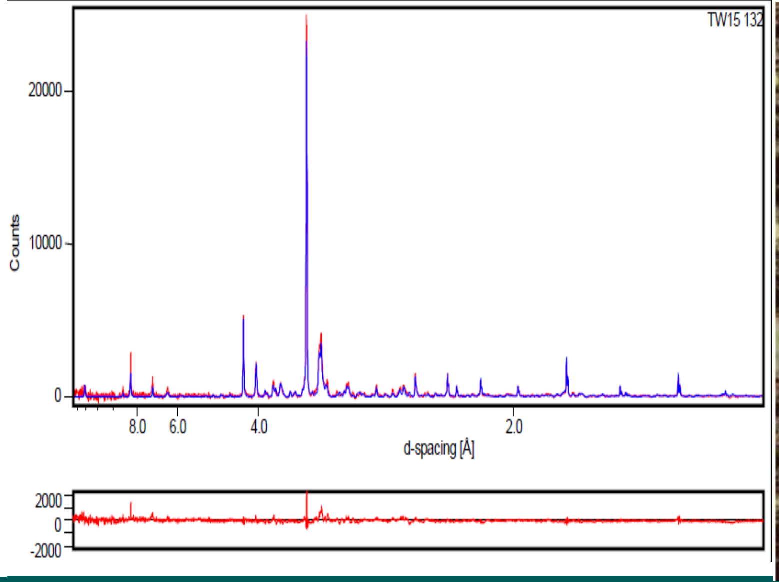
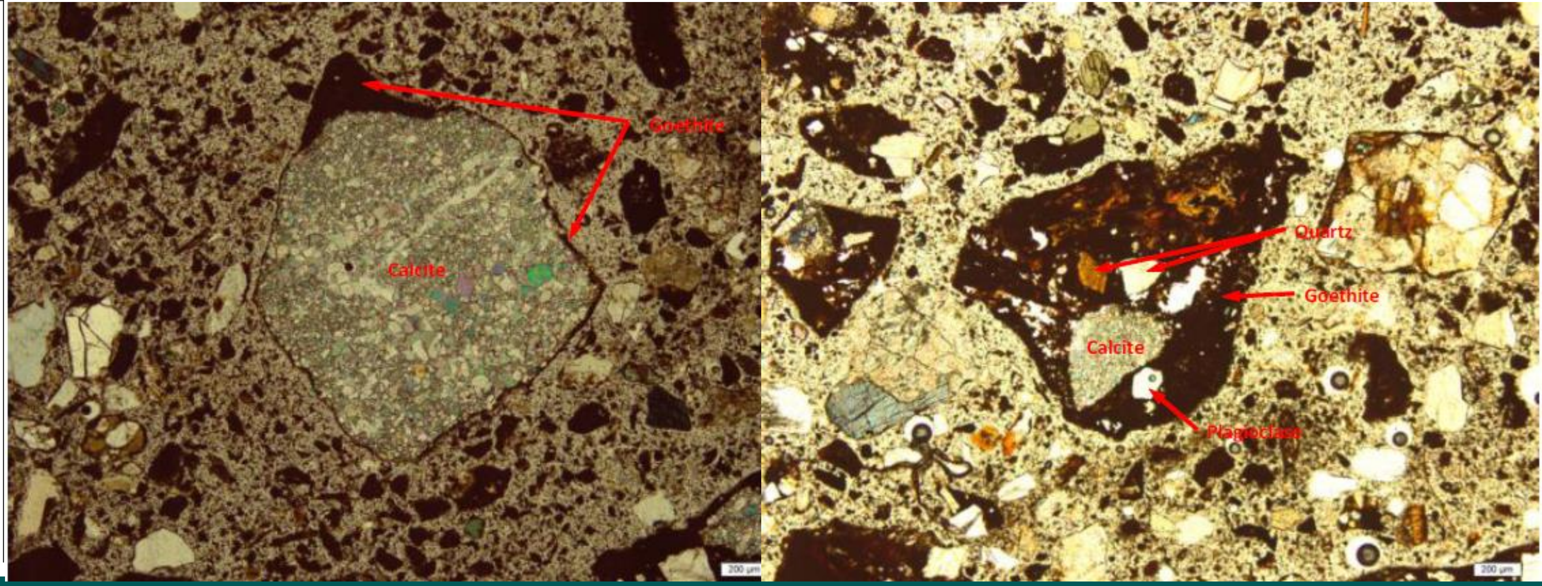






The Aquifer Solid Phase: Reactive Minerals and Their Effect on Remedial Success

By: Jake Gossen, P.Eng, Engineering Hydrogeologist, Hemmera

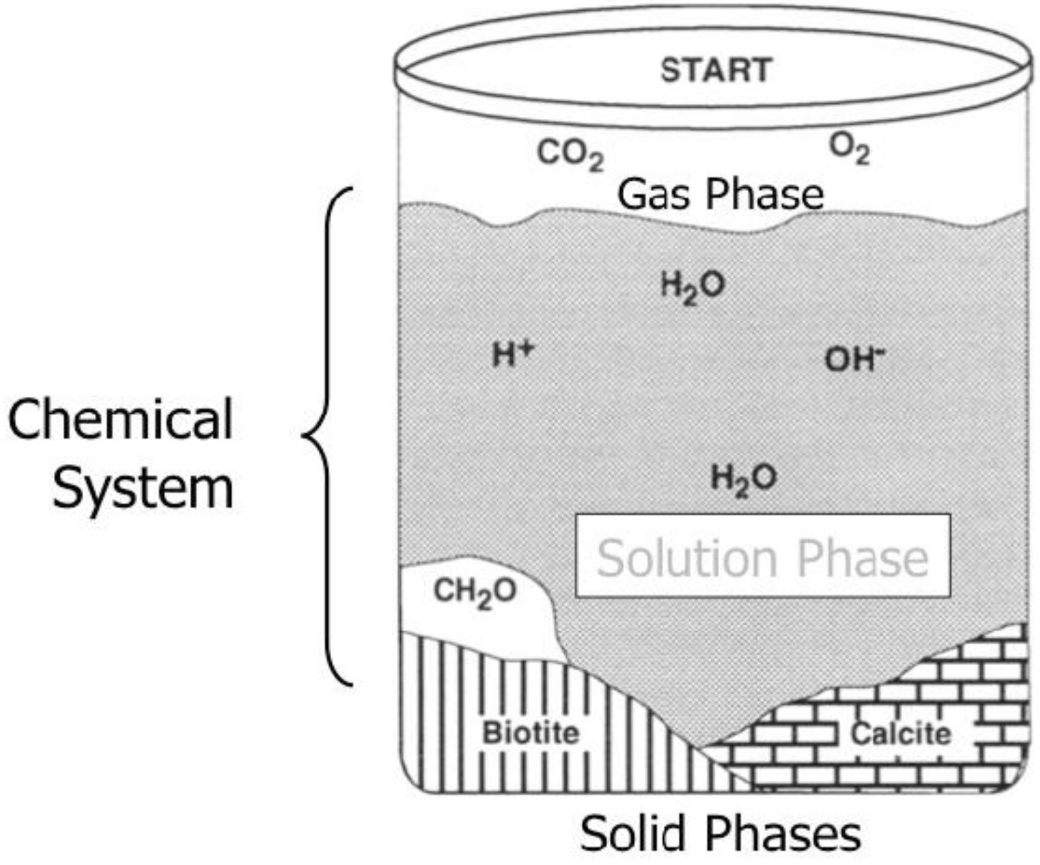
13 October 2016

HEMMERA

Outline

- Definitions: Solid Phase, Reactive Mineral
- Examples of Reactive Minerals
- Properties of Reactive Minerals
- Analytical Techniques + Limitations
- Case Studies
- Remedial Considerations
- Questions/Comments?

Definition – Aquifer Solid Phase



Soil Sample ≠ Solid Phase Characterization

BUT

Solid Phase Characterization = Soil Sample

Definition – Reactive Mineral

- Minerals that dissolve and/or re-precipitate within a human time-scale in response to changes to pH, redox, or solution composition
- Control dissolved concentration of some metals/anions
- Adsorbent surface for other metals
- Minerals that reach equilibrium with the groundwater composition at the pH and E_H of the aquifer system
- Sources and sinks

Reactive Mineral Examples

- **Adsorbents**
  - Iron oxyhydroxides: ferrihydrite [$Fe(OH)_3$], goethite [αFeOOH], etc
    - Hydrous ferric oxide (HFO) minerals
  - Manganese oxides: pyrolusite [MnO_2]
  - Aluminum hydroxide: gibbsite [$Al(OH)_3$]
- Dzombak – up to 600m^2/g surface area for ferrihydrite!
- Stage 8 Amendments to BC CSR

Reactive Minerals - Adsorbents

General Affinity of Dissolved Species for $Fe(OH)_3$

As^{5+} = Cu^{2+} = Be^{2+} = Pb^{2+} = PO_4^{3-}

>Zn^{2+} > Cd^{2+} > As^{3+} > Ni^{2+} > SO_4^{2-}

>> Ba^{2+} >> Ca^{2+} >> B^{3+}

Reactive Mineral Examples

- **Solubility Controls**
  - Salts: halite [NaCl], $MgCl_2$, KCl, gypsum [$CaSO_4 \cdot 2H_2O$]
- **Buffering Agents**
  - Limestone: calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$]

Reactive Mineral Examples

- **Acid Rock Drainage**
  - Sulphides: pyrite [FeS_2], galena [PbS], sphalerite [(Zn,Fe)S], etc
- Acid Rock Drainage is a result of oxidation of reactive minerals
- Metals plume after injection of chemical oxidant?

Reactive Mineral Examples

- Honourable mention to:
  - Clay minerals
  - Organic Carbon (i.e. foc)
  - Both adsorbents (inorganic and organic, respectively)
  - Not technically reactive minerals, but important solid phase constituents to understand

Properties of Reactive Mineral

- Factors that influence mineral reactivity
  - Structure: crystalline, cryptocrystalline, amorphous
    - Surface area
  - Reaction rims
  - Solution composition
  - **pH and redox**

Analytical Techniques

- Batch sequential extraction (BCR procedure)
- Column sequential extraction
- Polished thin-sections
- XRD
- SEM-EDS
- QEMSCAN

Batch Sequential Extraction

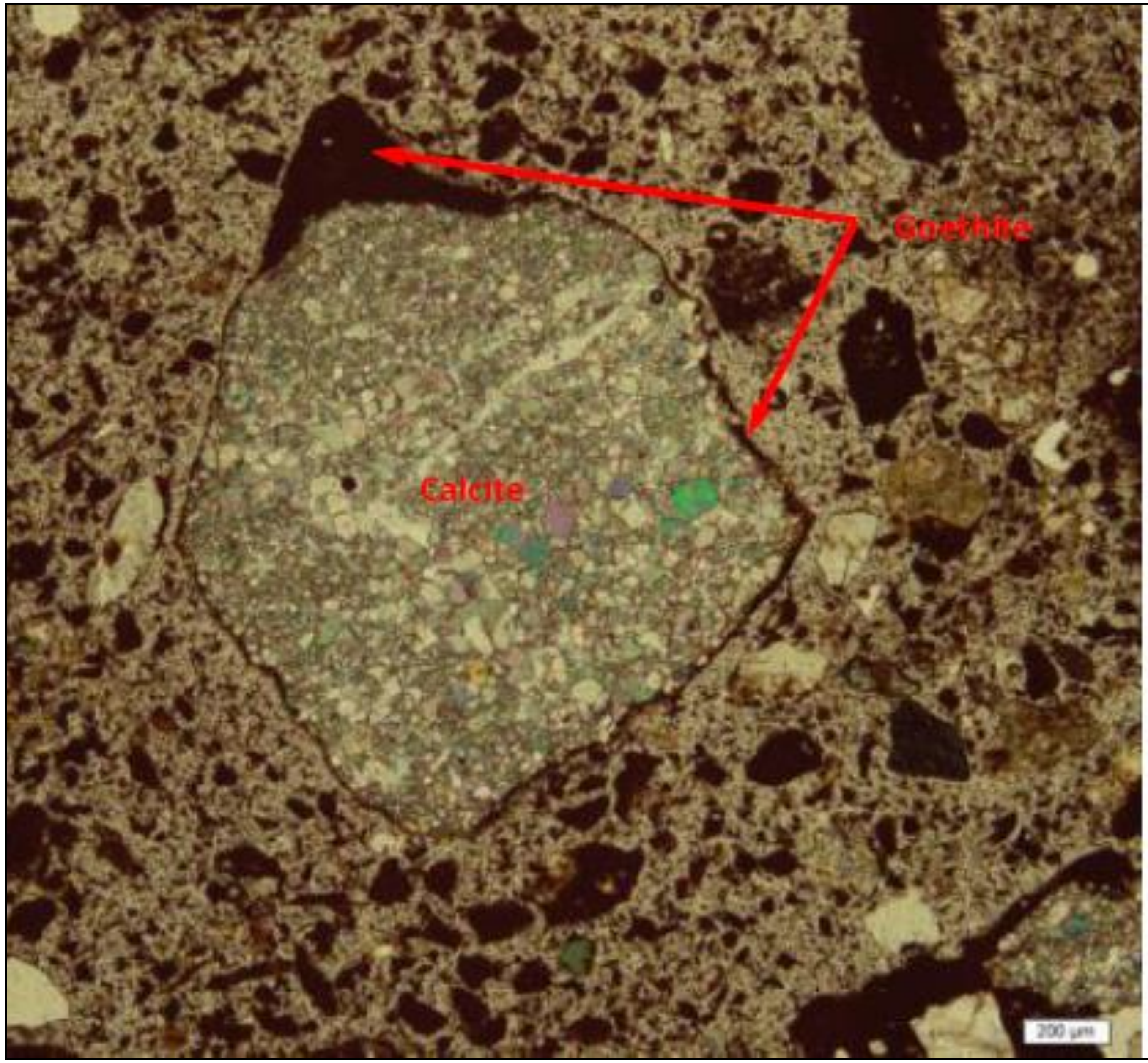
- BCR Procedure – EU methodology
- Extraction solutions
  - 1 – acetic acid: water, exchangeable and acid soluble
  - 2 – hydroxylammonium chloride: reducible
  - 3 – hydrogen peroxide: oxidizable
  - 4 – ammonium acetate: aqua regia
- Total reactive mineral concentrations
- Some math/stoichiometry to calculate [mineral]

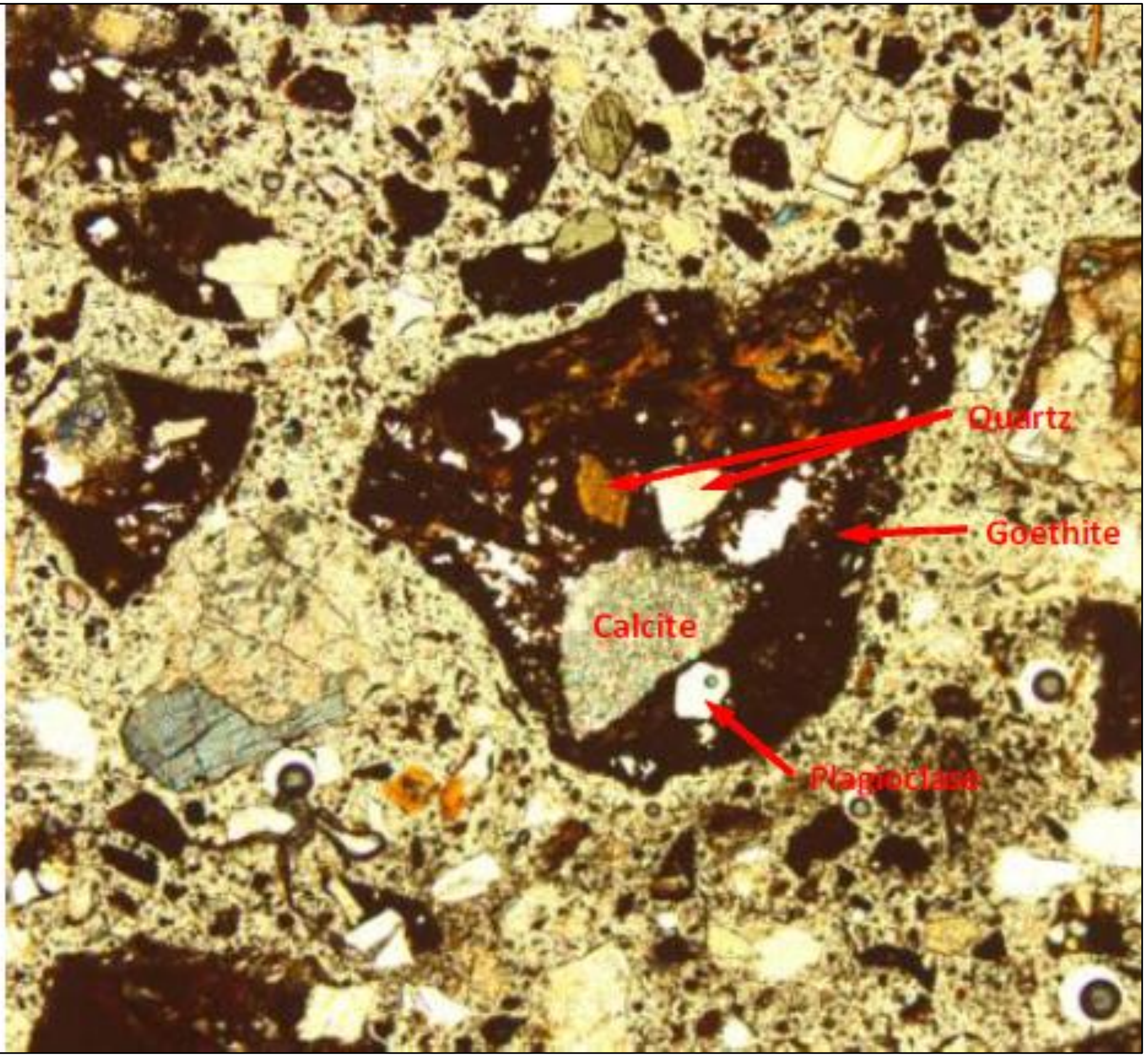
Column Sequential Extraction

- Modified Tessier
  - 1 – DI water: water soluble minerals
  - 2 – ammonium chloride: exchangeable cations
  - 3 – sodium acetate + acetic acid: carbonates
  - 4 – ammonium oxalate + oxalic acid: oxides/hydroxides
- Mimics reactions along a flow path
- Accounts for reaction rim and reaction kinetics
- Mineral stability across range of geochemical conditions

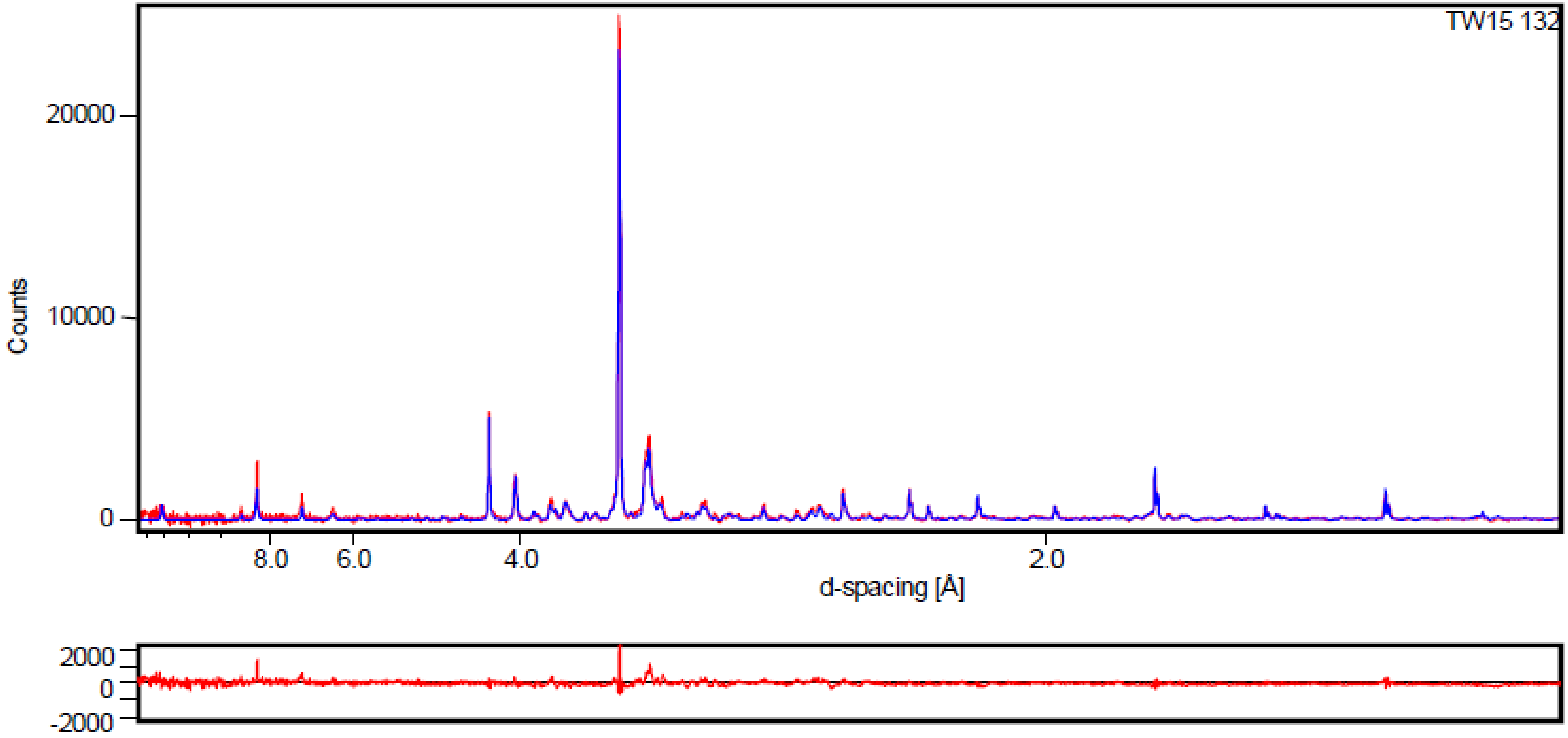
Column Sequential Extraction

Polished Thin-sections





XRD

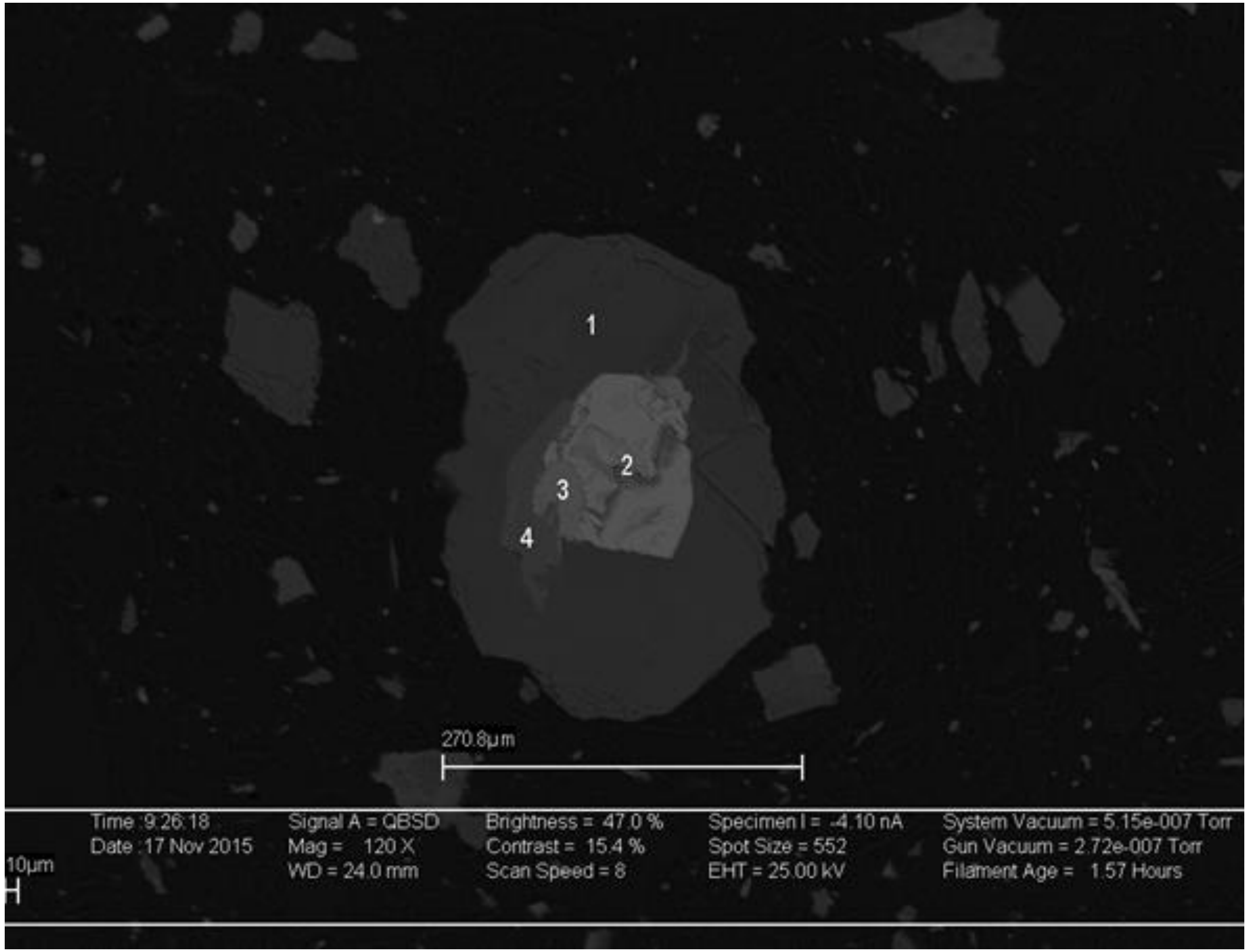


TW15 132
Counts
20000
10000
0
8.0
6.0
4.0
2.0
d-spacing [Å]
2000
0
-2000

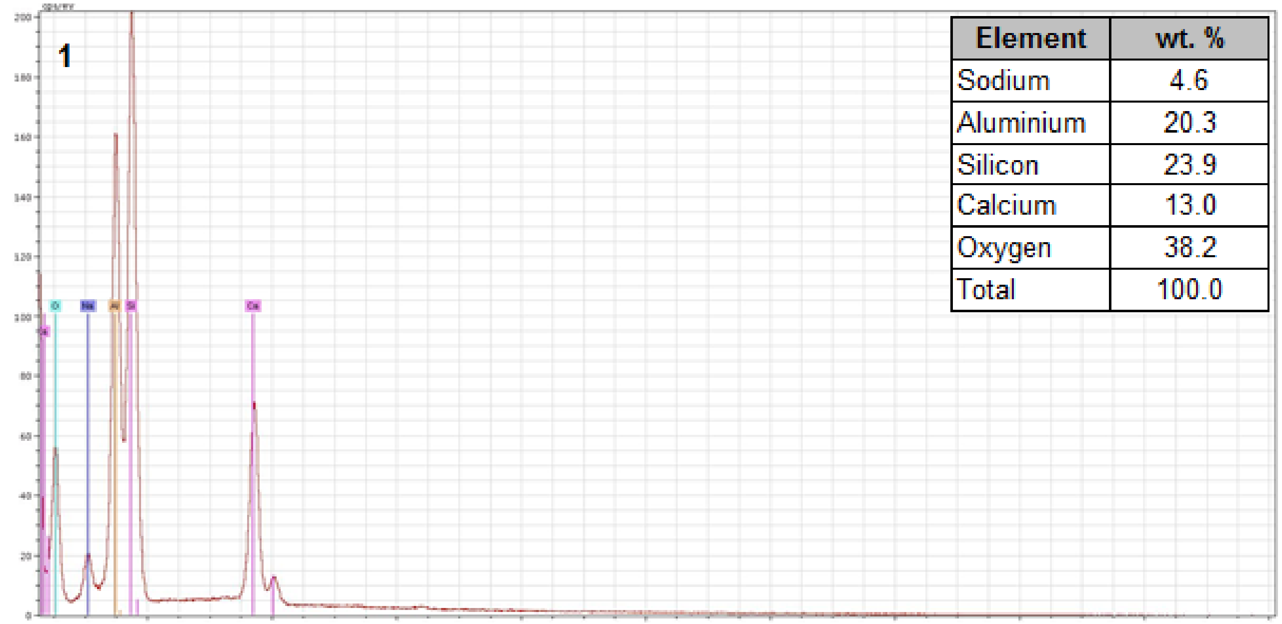
XRD

Mineral Name	Approximate Mineral Formula	Abundance					
		TW15 112	TW15 122	TW15 132	MW15 142	TW15 152	TW15 162
Amphibole	$Ca_2(Mg,Fe)_5(OH)_2(Si_4O_{11})_2$	2.5	3.6	8.7	4.9	5.5	4.5
Calcite	$CaCO_3$	5.8	0.3	0.5	0.0	0.0	3.0
Chlorite	$(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$	3.7	3.0	0.9	0.3	1.0	2.9
Epidote	$Ca_2Al_2O.(Al,Fe)OH(Si_2O_7)(SiO_4)$	1.0	0.0	0.0	0.1	0.7	0.0
K-feldspar	$KAlSi_3O_8$	0.4	1.1	0.3	6.0	2.0	0.6
Magnetite	Fe_3O_4	0.6	0.4	0.6	0.6	0.0	3.0
Mica	$KMg_3(Si_3Al)O_{10}(OH)_2$	0.8	0.1	0.0	0.2	0.4	0.0
Plagioclase	$(Na,Ca)(Al,Si)_4O_8$	48.4	50.0	46.2	54.1	55.9	42.9
Pyroxene	$Ca_2(Mg,Fe)_5(OH)_2(Si_4O_{11})_2$	0.0	2.6	1.4	2.6	1.2	2.9
Quartz	SiO_2	36.8	38.8	41.3	31.3	33.4	40.2
Sphalerite	ZnS	-	-	-	0.1	-	-

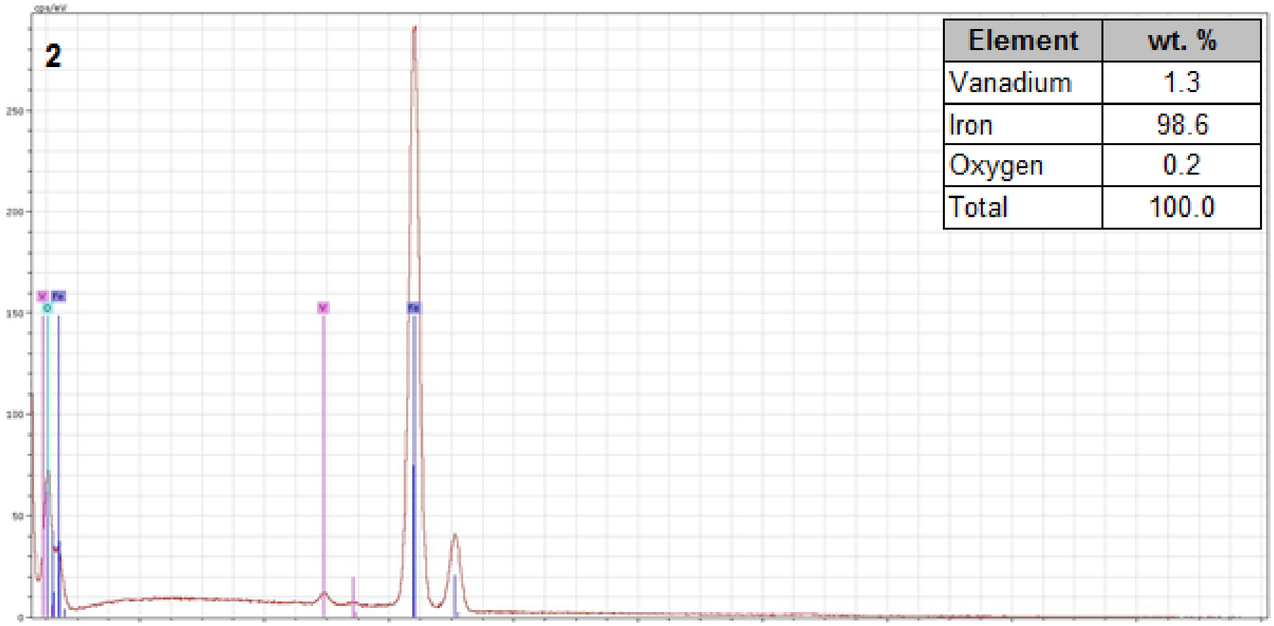
SEM-EDS


1
2
3
4
270.8µm
Time :9:26:18
Date :17 Nov 2015
Signal A = QBSD
Mag = 120 X
WD = 24.0 mm
Brightness = 47.0 %
Contrast = 15.4 %
Scan Speed = 8
Specimen I = -4.10 nA
Spot Size = 552
EHT = 25.00 kV
System Vacuum = 5.15e-007 Torr
Gun Vacuum = 2.72e-007 Torr
Filament Age = 1.57 Hours
10µm

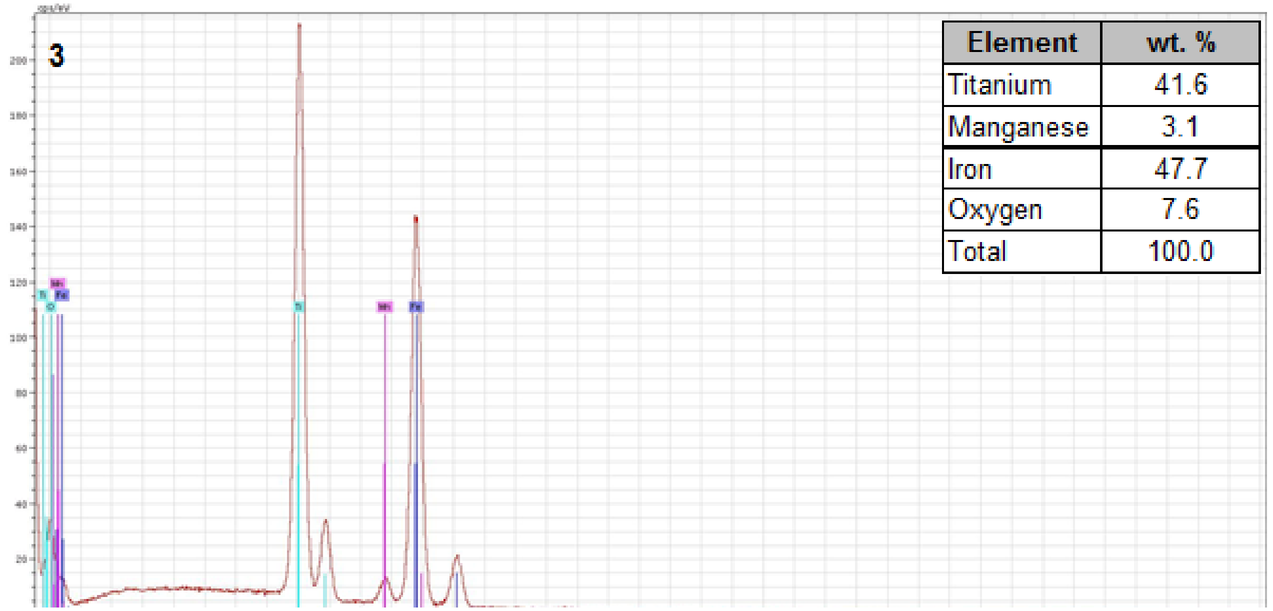
SEM-EDS



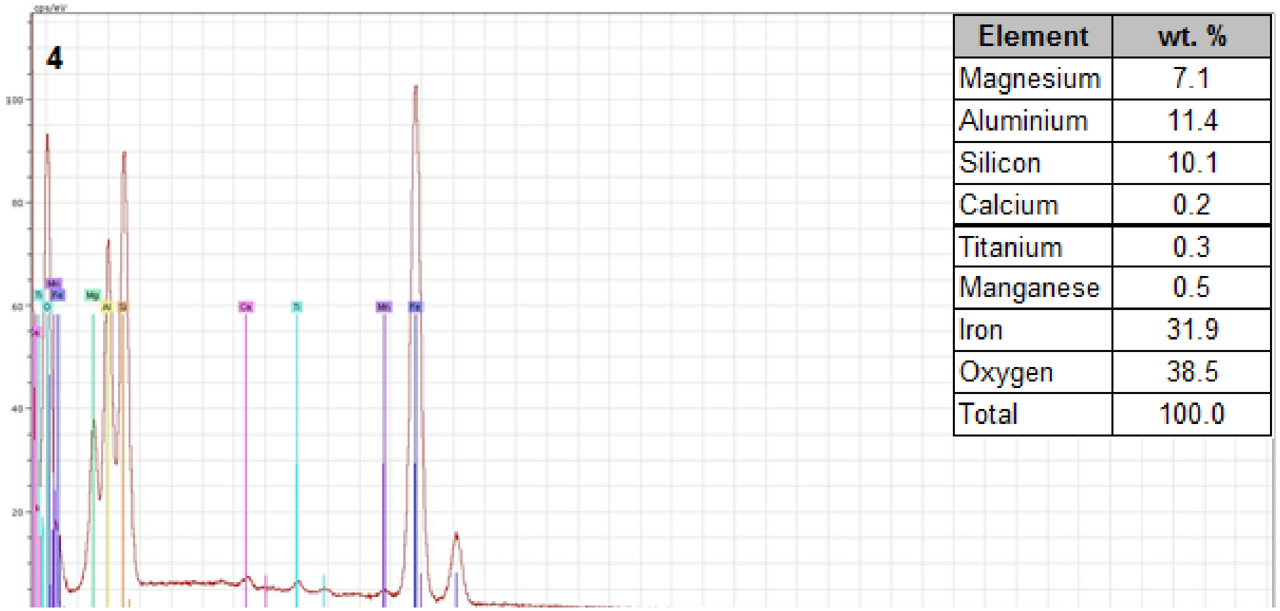
Element	wt. %
Sodium	4.6
Aluminium	20.3
Silicon	23.9
Calcium	13.0
Oxygen	38.2
Total	100.0



Element	wt. %
Vanadium	1.3
Iron	98.6
Oxygen	0.2
Total	100.0

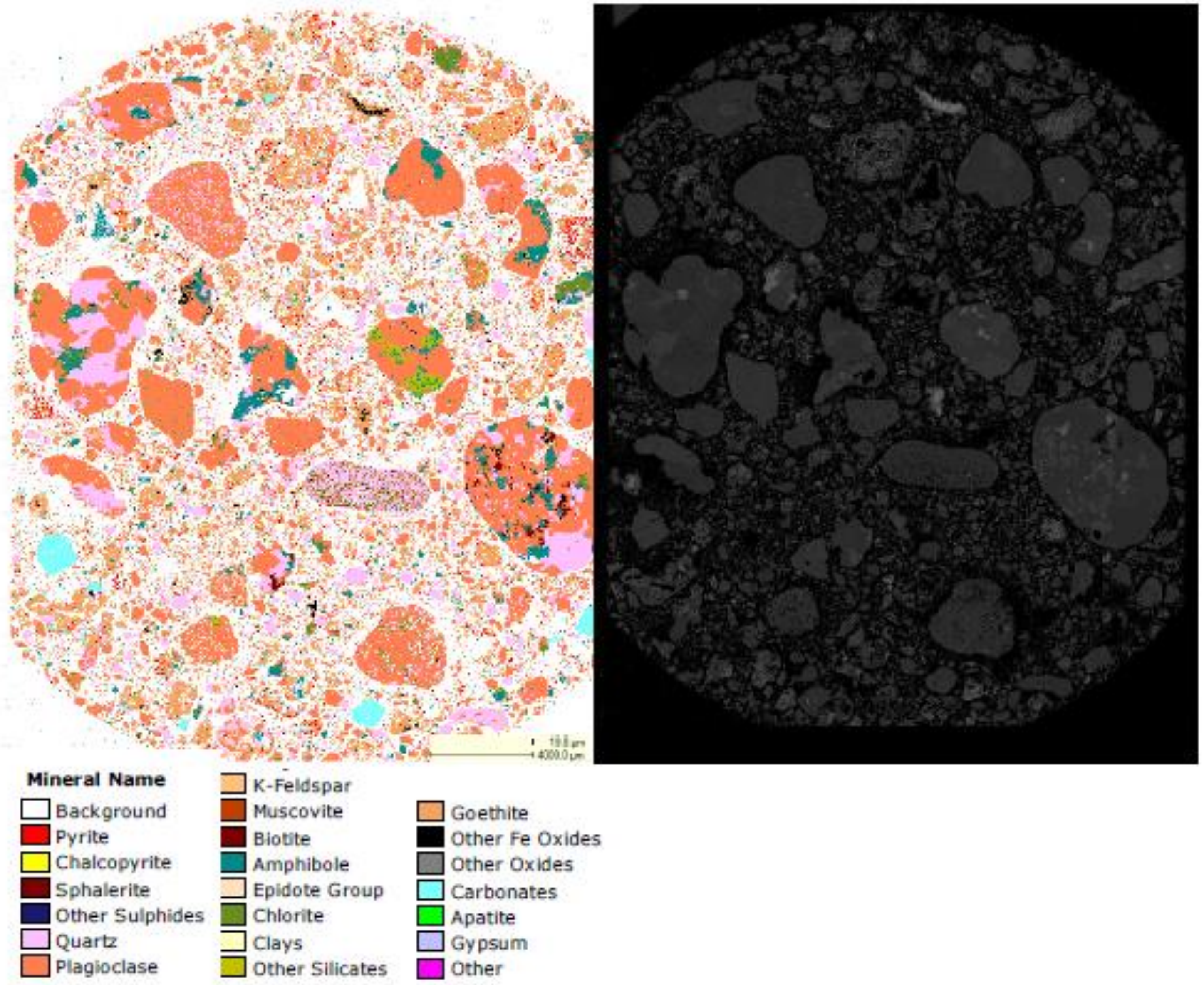


Element	wt. %
Titanium	41.6
Manganese	3.1
Iron	47.7
Oxygen	7.6
Total	100.0

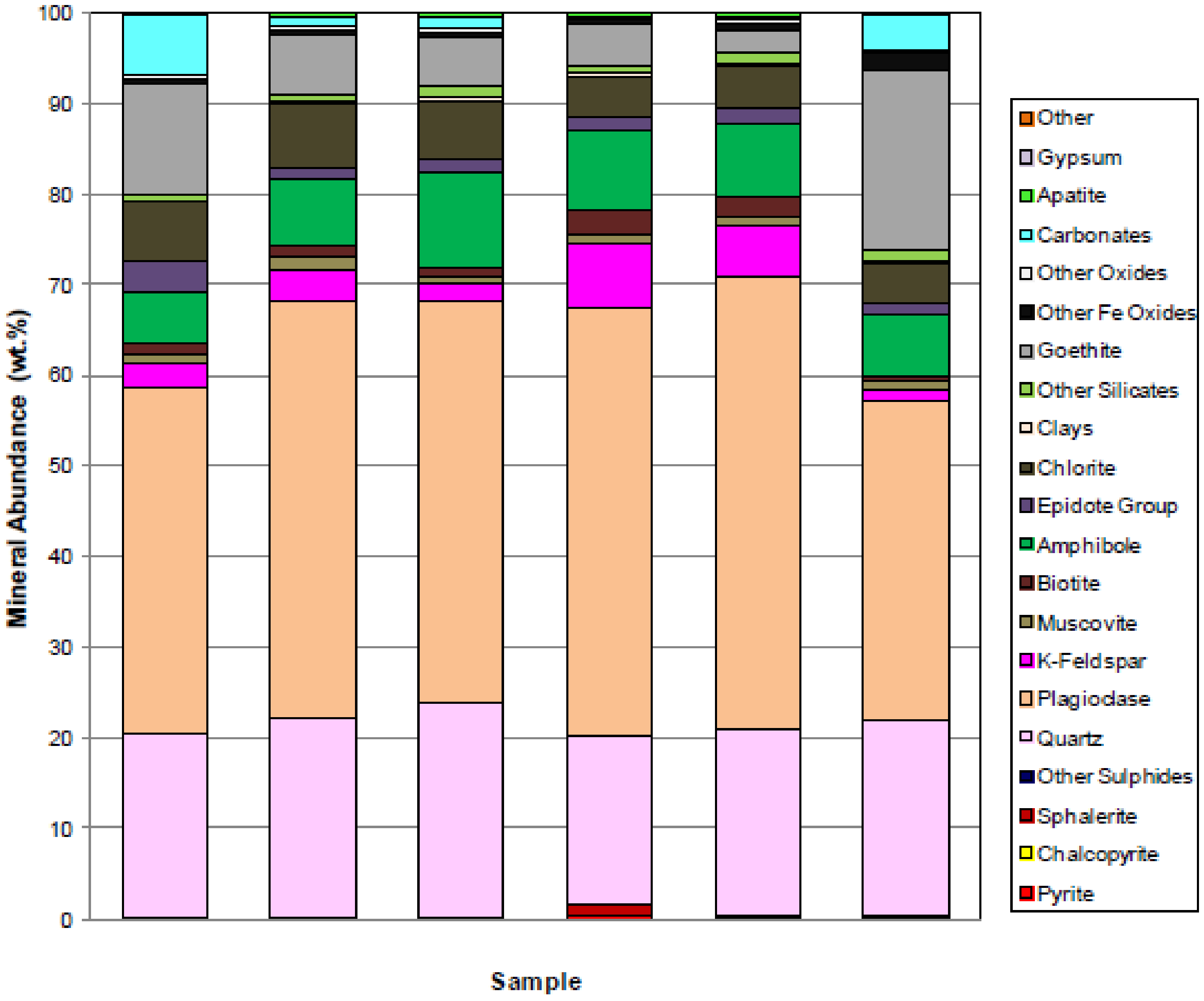


Element	wt. %
Magnesium	7.1
Aluminium	11.4
Silicon	10.1
Calcium	0.2
Titanium	0.3
Manganese	0.5
Iron	31.9
Oxygen	38.5
Total	100.0

QEMSCAN – Automated SEM-EDS



QEMSCAN – Automated SEM-EDS



Analytical Limitations

- Sample collection, preservation, preparation (nitrogen!)
- Sample size/volume
- Natural heterogeneity (nugget effect)
- Crystalline vs Amorphous
- Resolving mineralogy from EDS
- Mineralogist/Petrologist

Case Studies

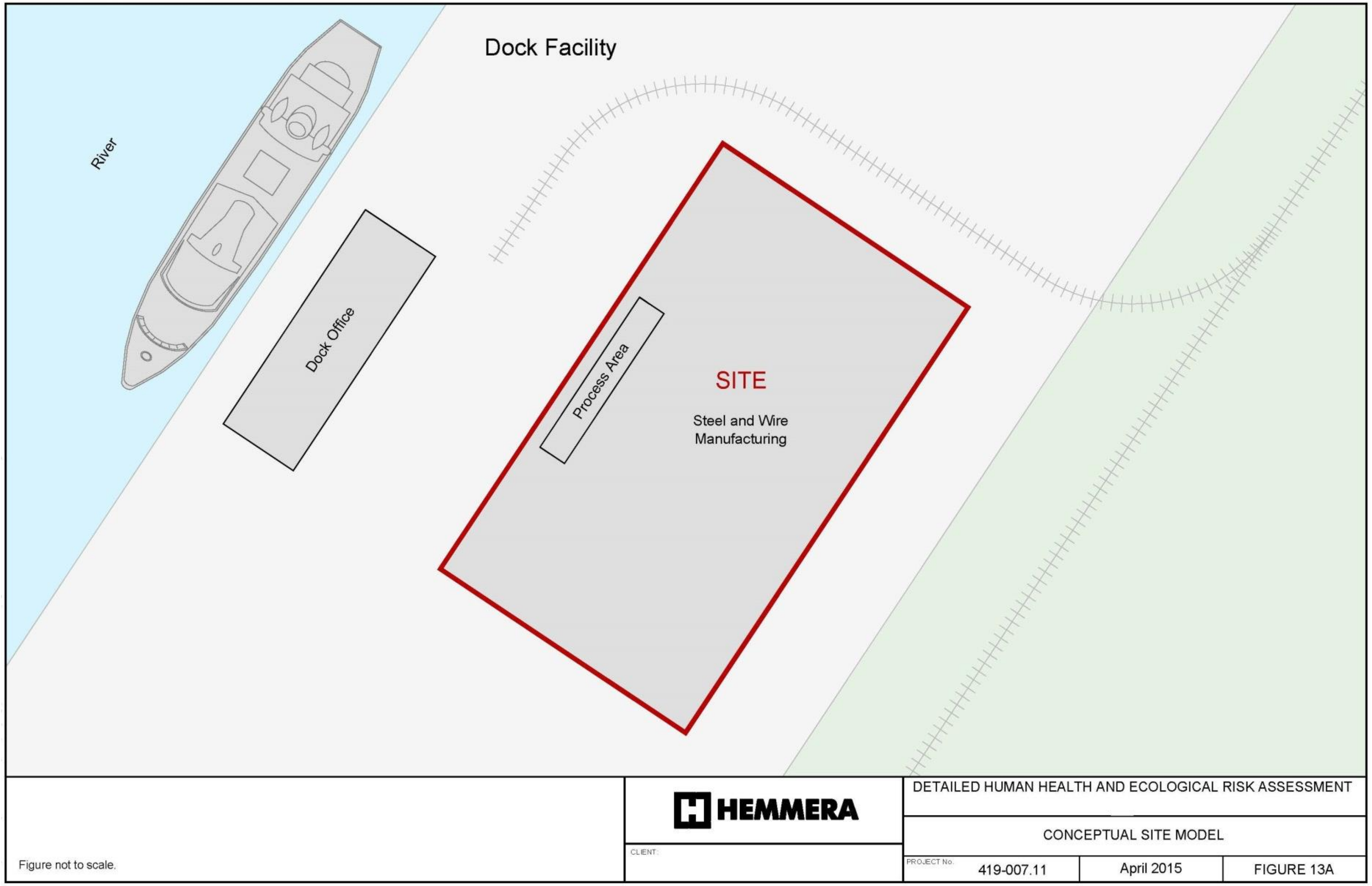
- Reactive Minerals as Source
- Reactive Minerals as a Sink
- Reactive Minerals as Sink → Source

- All Sites are confidential

Case Study 1 - Source

- WaterTech 2015 presentation
- Multiple dissolved metals plume in tidally influenced Industrial Site – Steel and wire manufacturer
- Source and Release Mechanism(s)
  - **B**, **Zn** and **sulphuric acid** used at Process Area; but
  - **Al**, B, **Cd**, **Cu**, **Ni** and Zn in groundwater
- Source of Al, Cd, Cu and Ni?

Case Study 1 - Source



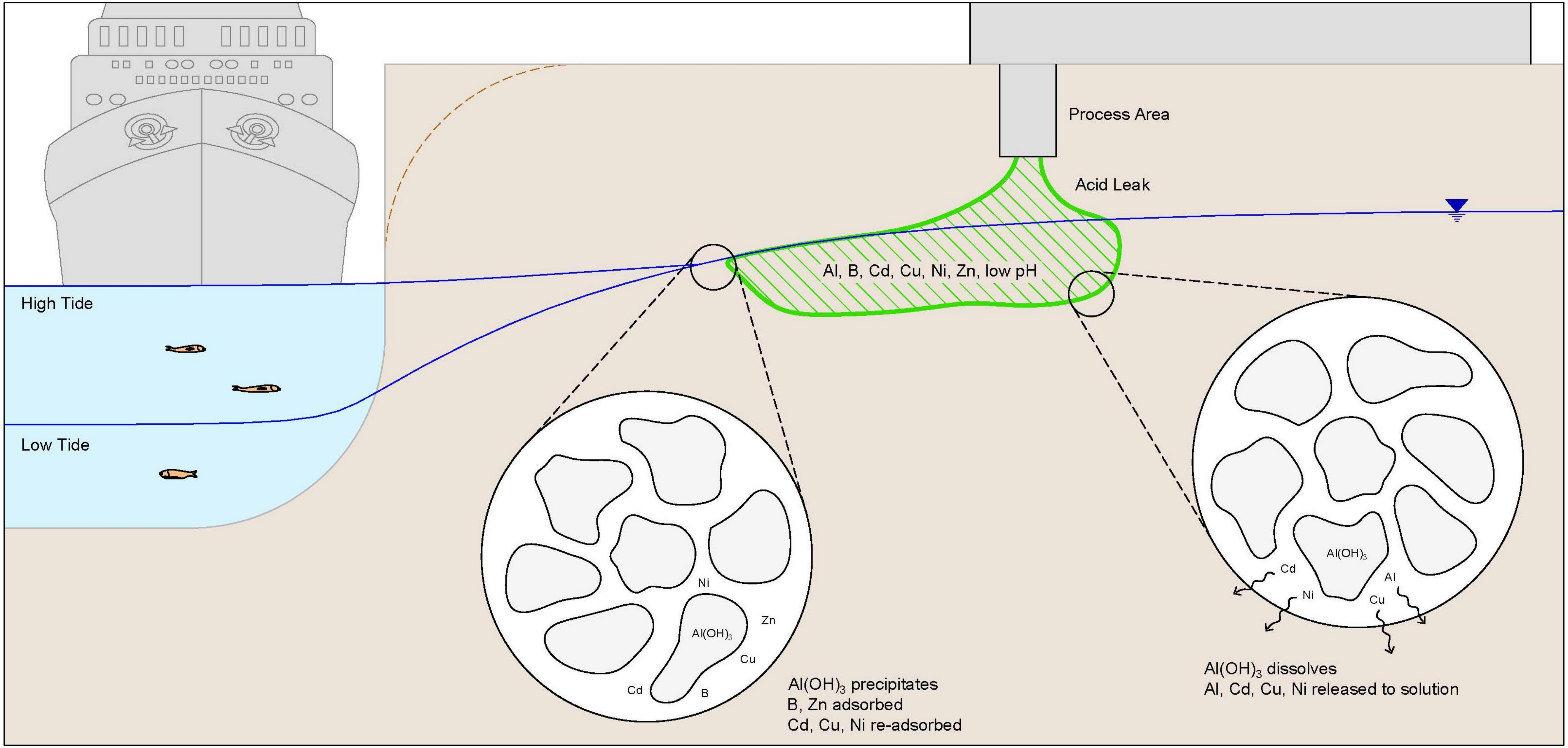
Case Study 1 - Source

- Analytical results indicated:
  - Dissolved iron generally <DL
  - DO ~ 3 mg/L
  - **pH <4 in vicinity of Process Area**
- Gibbsite [$Al(OH)_3$] is an adsorbent and exhibits amphoteric behavior
  - Soluble at pH ~<6 and ~>8.5
- Low pH (acidic dissolution) inferred release mechanism

Case Study 1 - Source

- Source 1 – Chemical Leak through Process Area Floor, contaminating groundwater with B, Zn and acidity
- Source 2 – Acidic dissolution of gibbsite and release of metals adsorbed onto mineral surface
- **Reactive Minerals as a Secondary Source of GW contamination**

Case Study 1 - Source



Case Study 1 - Summary

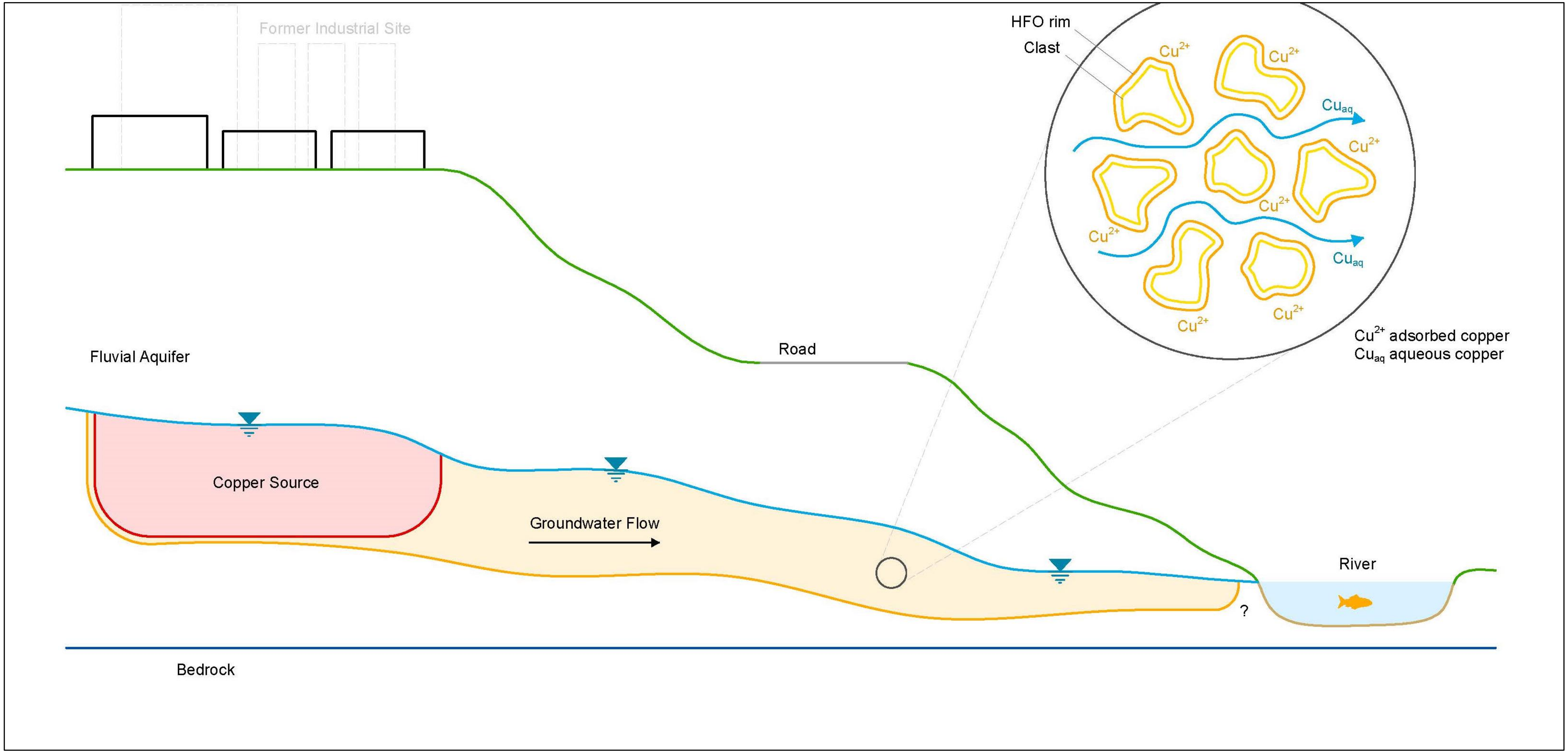
- Reactive Minerals were source of dissolved metals
- Reacted to pH change (pH <4)
- Acidic dissolution
- Stop acid leak, pH buffers, gibbsite re-precipitates, metals re-adsorb

Case Study 2 - Sink

- Former Industrial Facility adjacent to river
  - Freshwater aquatic habitat – fish rearing
- Dissolved metals plume (primarily copper)

- Is plume at steady state? – limited temporal and spatial data
- Will concentrations at receptor get worse?

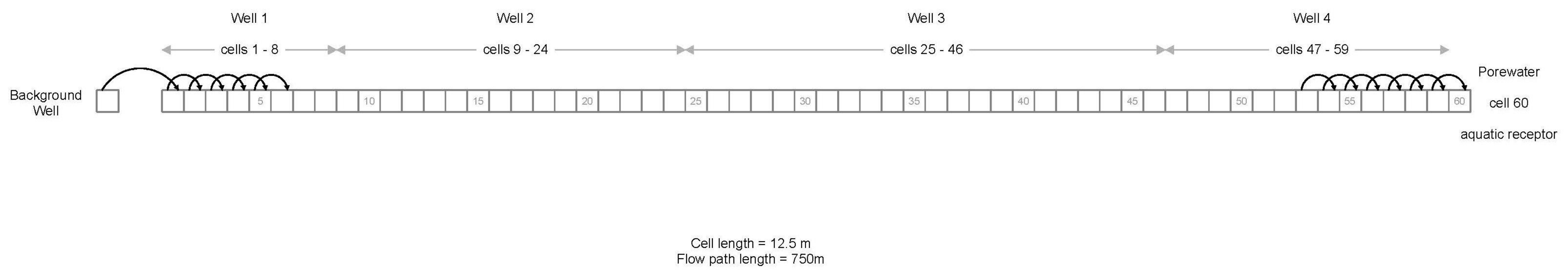
Case Study 2 - Sink



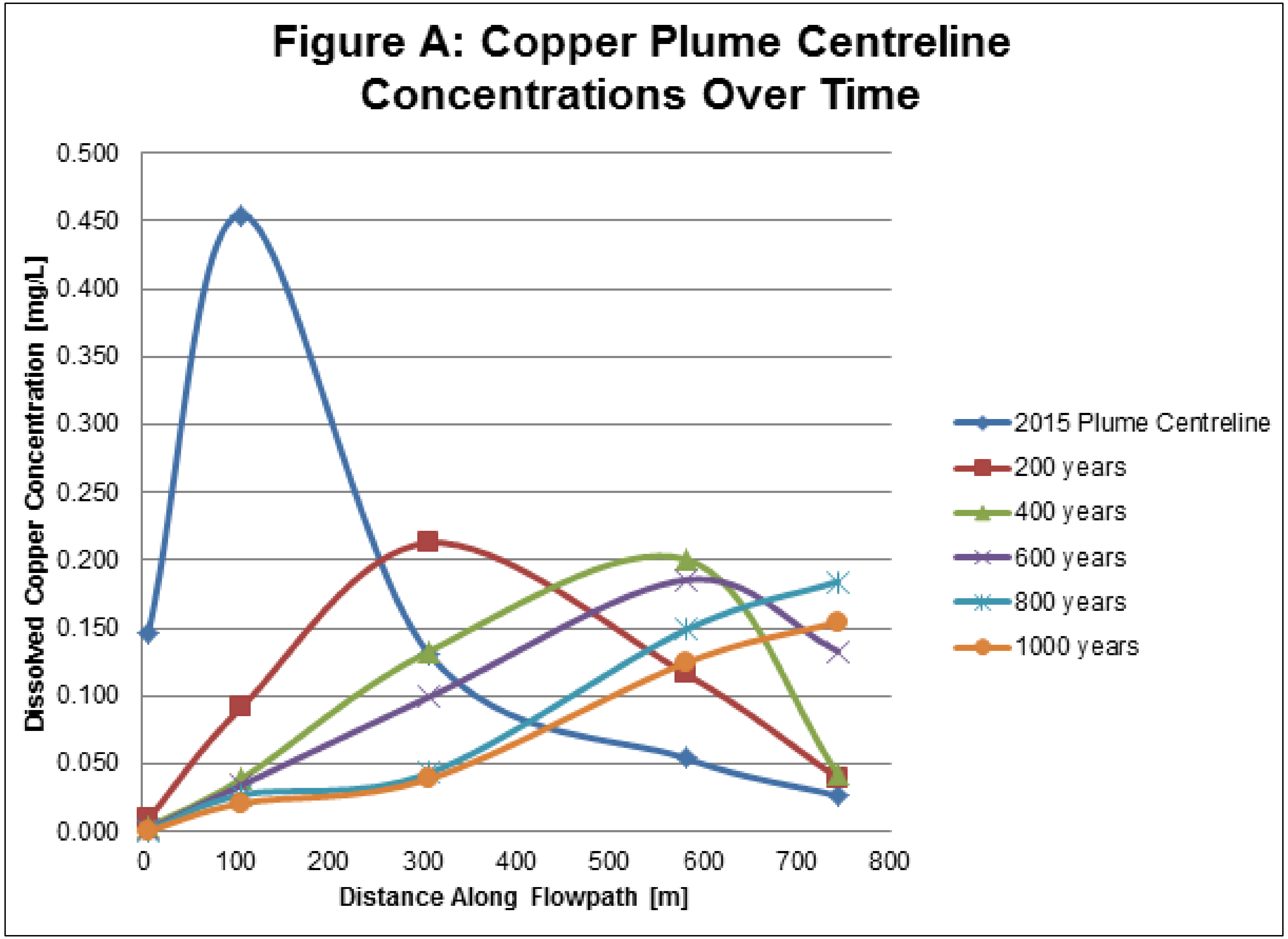
Case Study 2 - Sink

- Collected samples for BCR analysis along flow path
  - Ferrihydrite and calcite molar concentrations!
- Prepared reactive transport model using PHREEQC
  - Ferrihydrite and calcite set as equilibrium phases
- Predict long-term behavior of plume and concentration at receptor
  - [Cu] to increase by >5x!

Case Study 2 - Sink



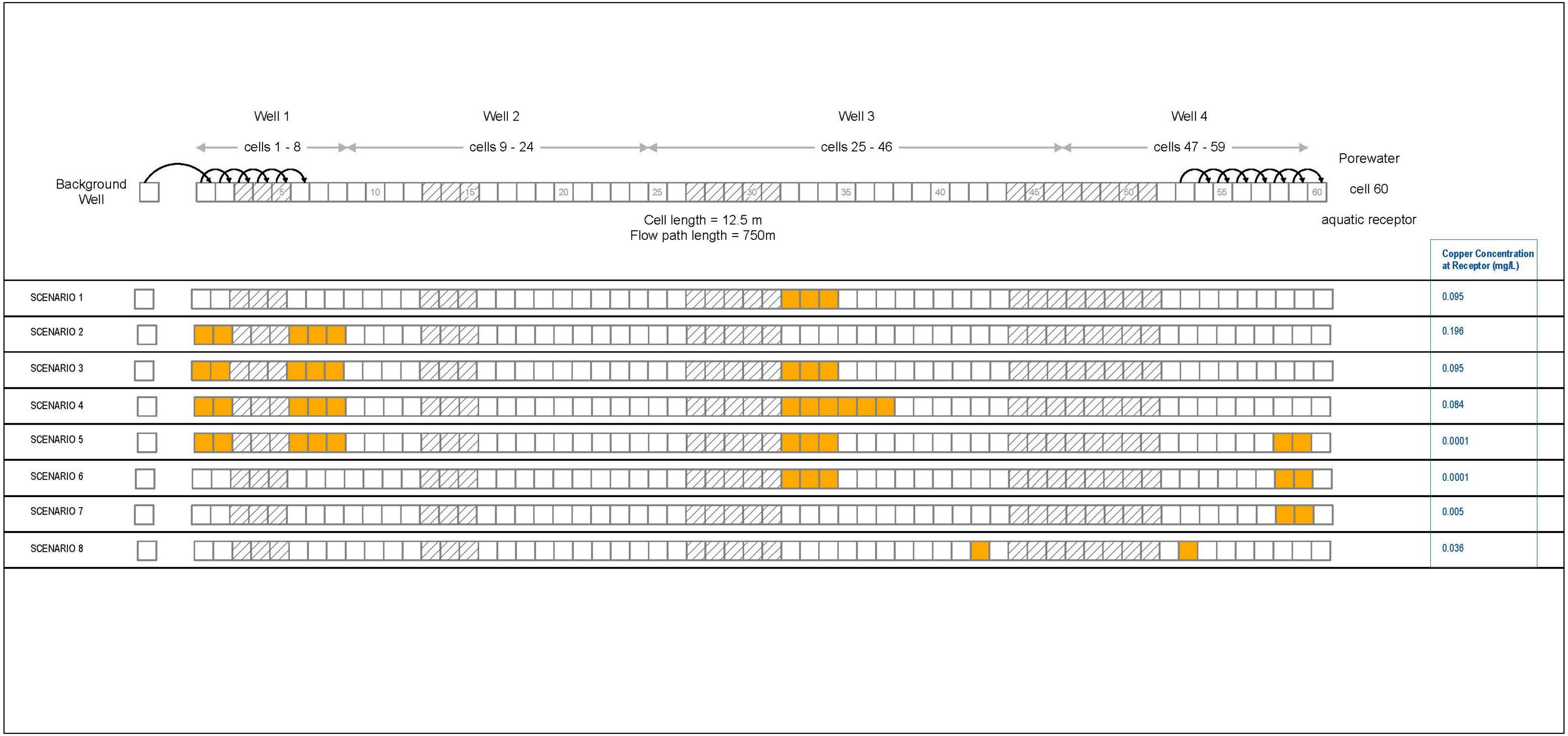
Case Study 2 - Sink



Case Study 2 - Sink

- Proposing to inject ferric sulphate
- Precipitate iron oxyhydroxides
- Adsorb metals = decrease dissolved concentration
  - $Fe_2(SO_4)_3 + 4.5H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$
    - Reaction needs buffering
- Protect Fish Habitat!

Case Study 2 - Sink



Case Study 2 - Summary

- Metals being “flushed” by clean up-gradient water resulting in migration of plume mass over time
- Inject ferric sulphate to precipitate ferrihydrite
- Reaction needs oxygen and buffering
- Model if sufficient calcite or if need to inject NaOH

- **Stay tuned! RemTech2017?**

Case Study 3 – Sink to Source

- Former mining site – sulphide minerals
- Multiple dissolved metals plume (Cu, Cd, Ni, Pb, Zn)
- Concentrations > 100,000 µg/L
- Tidally influenced Permeable Reactive Barrier (PRB)
- Treatment mechanism
  - Sulphate reduction followed by metal sulphide precipitation, carbonate precipitation, and adsorption onto iron oxyhydroxide minerals

Case Study 3 – Sink to Source

- PRB near end of design life (depleted reactive media)
- Observed dissolved metals rebound d/g of PRB
- Secondary source or re-dissolution of sulphides?
- To what extent are secondary mineral precipitates stable as PRB loses reactivity?

Case Study 3 – Sink to Source

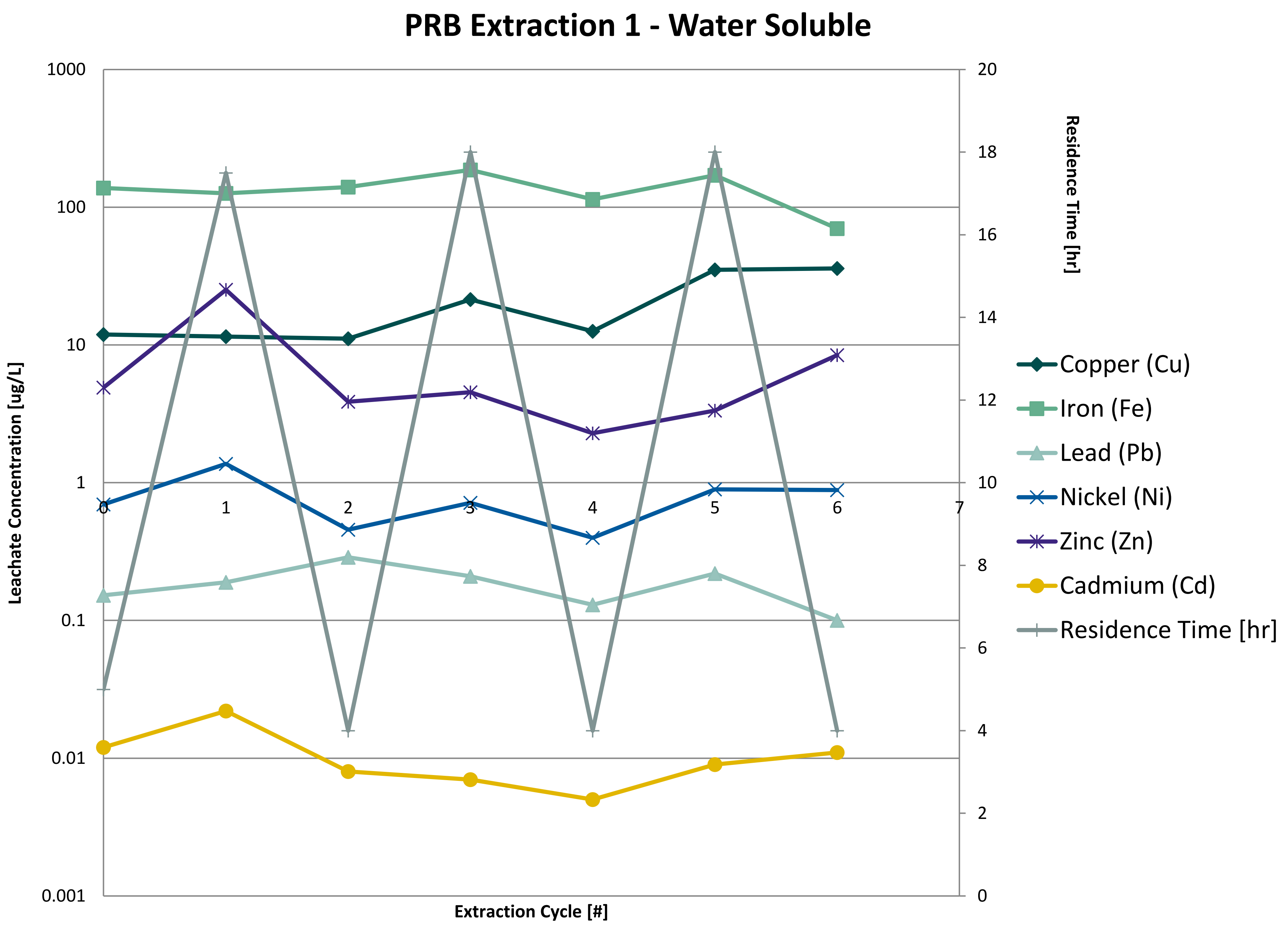
- Challenges
  - PRB relies on anoxic conditions. How to sample?
  - How to evaluate mineral stability/solubility?
  - How to evaluate mineral texture (crystalline, cryptocrystalline, amorphous)
- Solutions
  - Nitrogen during sample collection
  - Custom Column Sequential Extraction (modified Tessier)
  - Thin-sections, XRD, SEM-EDS, QEMSCAN

Case Study 3 – Sink to Source

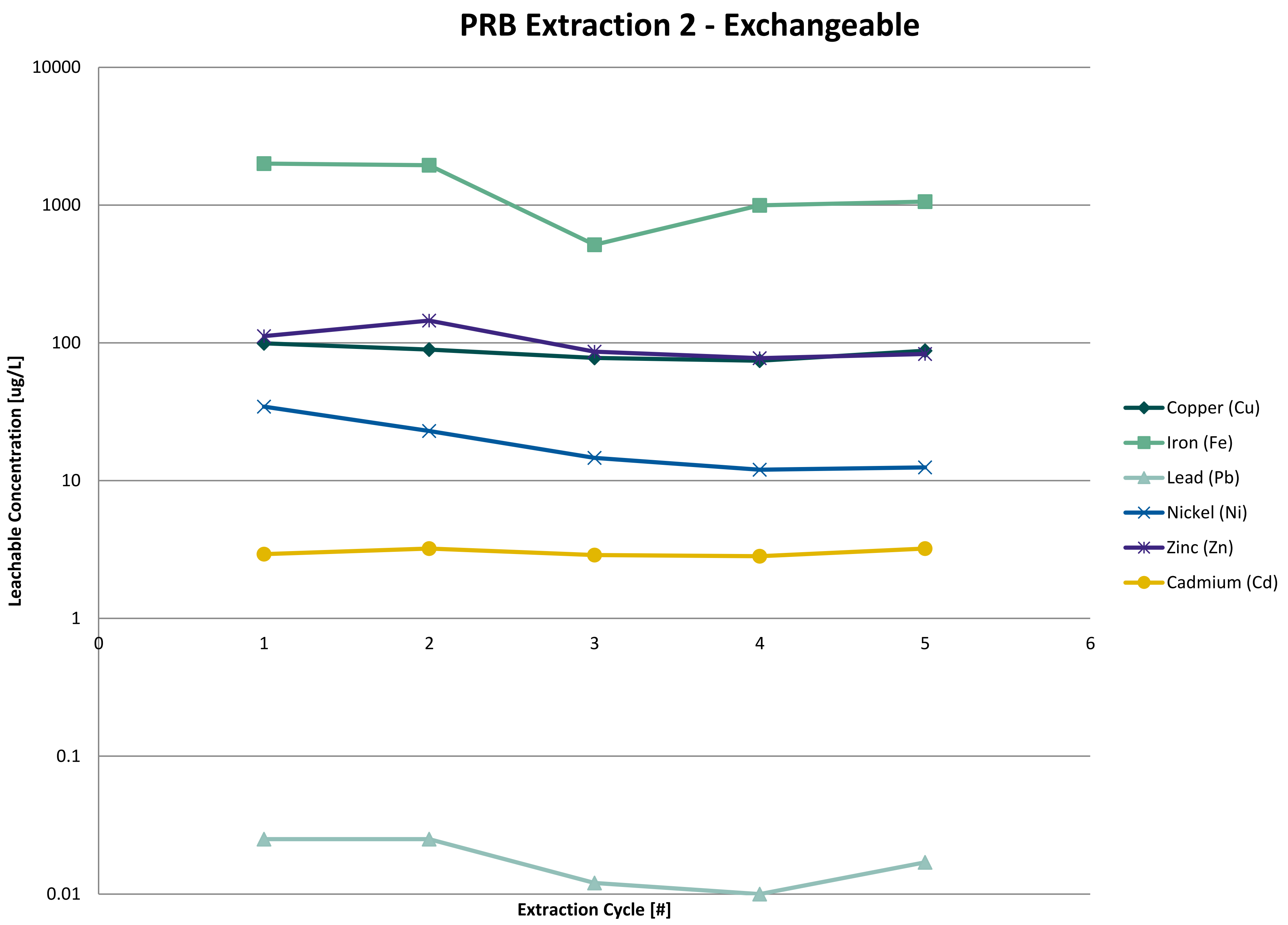
Case Study 3 – Sink to Source

- Modified Tessier
  - 1 – DI water: water soluble minerals
  - 2 – ammonium chloride: exchangeable cations
  - 3 – sodium acetate + acetic acid: carbonates
  - 4 – ammonium oxalate + oxalic acid: oxides/hydroxides
- Residence Time

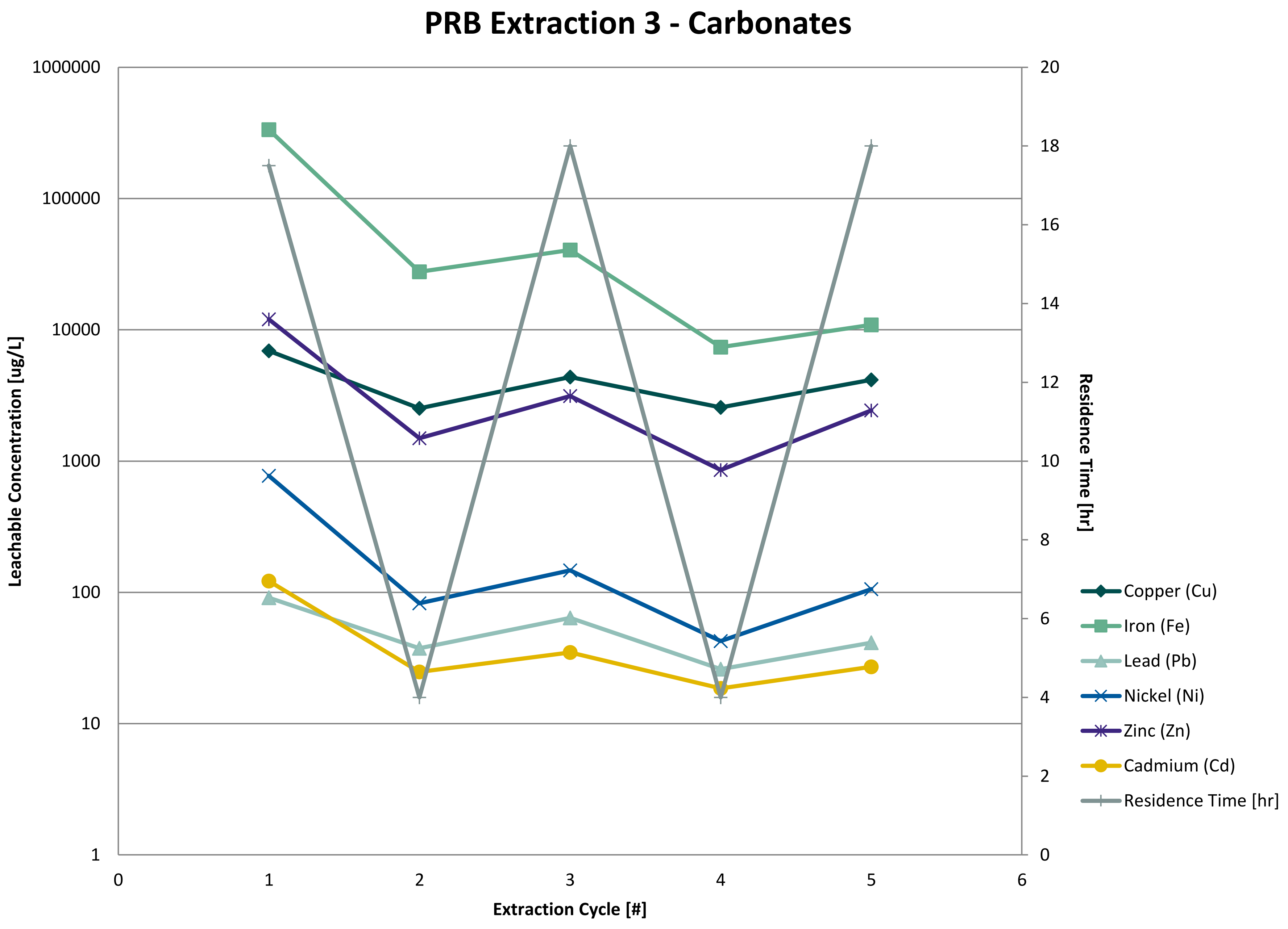
Case Study 3 – Sink to Source



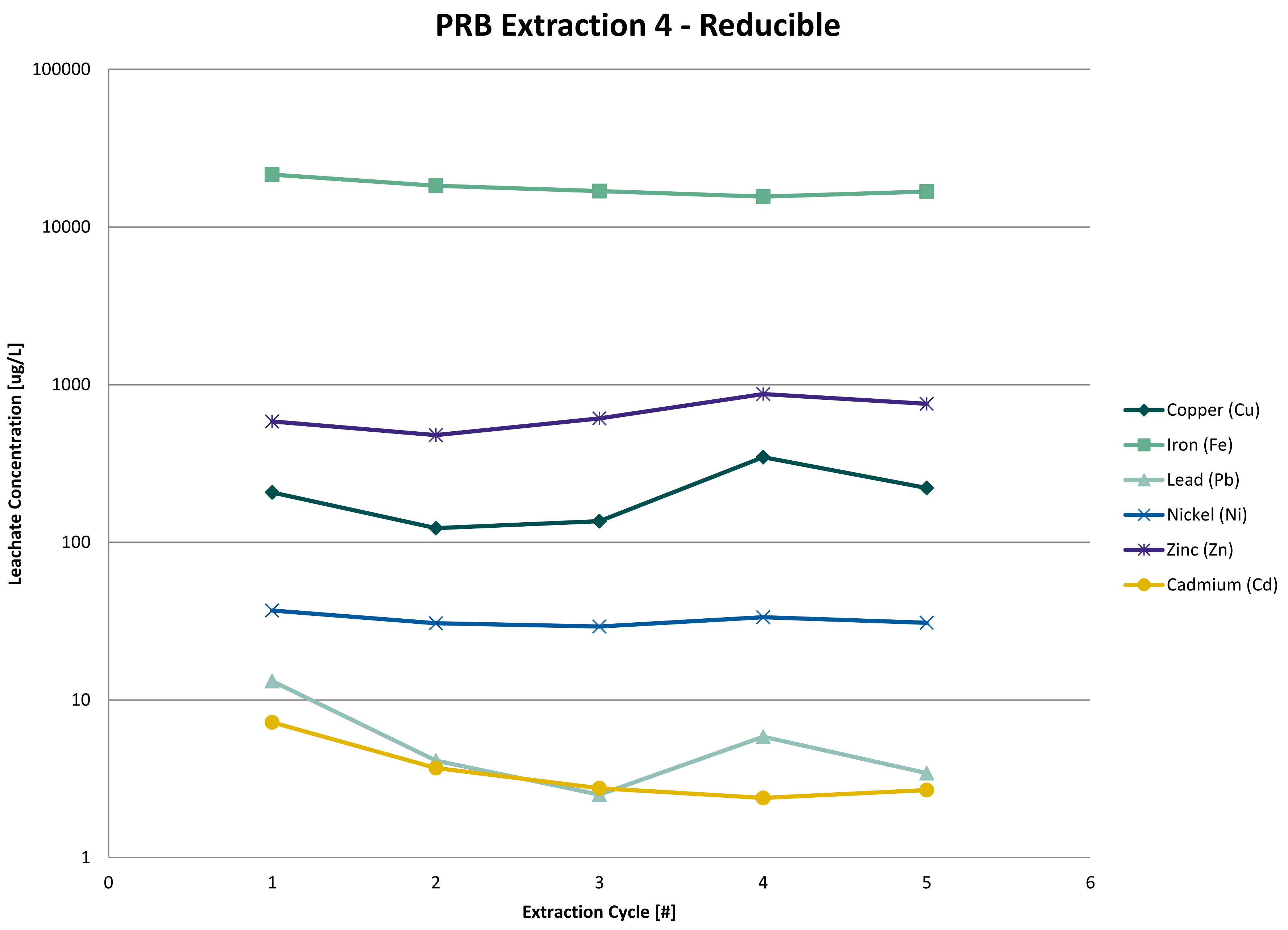
Case Study 3 – Sink to Source



Case Study 3 – Sink to Source



Case Study 3 – Sink to Source



Case Study 3 – Sink to Source

General Affinity of Dissolved Species for $Fe(OH)_3$

As^{5+} = Cu^{2+} = Be^{2+} = Pb^{2+} = PO_4^{3-}

$>Zn^{2+}$ > Cd^{2+} > As^{3+} > Ni^{2+} > SO_4^{2-}

$>>$ Ba^{2+} $>>$ Ca^{2+} $>>$ B^{3+}

Case Study 3 – Summary

- Dissolved metals attenuated as carbonates and adsorbed onto iron oxyhydroxides (goethite)
- Exchangeable cations – high ionic strength solution
- Loss of reactivity and daily tidal influence "bumps" metals off of mineral surface into solution

- Reactive Minerals as a source and a sink!

Remedial Considerations

- Reactive Minerals can be sources, sinks or both
- Manipulating pH and E_H of an aquifer for remediation?
- Characterize the Aquifer Solid Phase!
  - Identify minerals incompatible with remedial approach
  - Buffering agents when acidity produced
  - Naturally present adsorbents minerals

Thank you. Questions?

Contact Us

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