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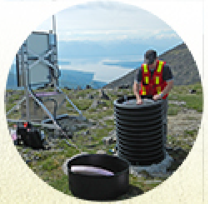


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Hydrogeochemistry of mine tailings from a carbonatite-hosted Nb-REE deposit, Oka, Québec, Canada

A.J. Desbarats[1] and J.B. Percival[1]

[1]Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario

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Abstract

Environmental impacts associated with the mining of carbonatite deposits are an emerging concern due to the demand for critical metals. This study investigates the chemistry of tailings seepage at the former Saint Lawrence Columbium mine near Oka, Québec, Canada, which produced pyrochlore concentrate and ferroniobium from a carbonatite-hosted Nb-REE deposit. Its objectives are to characterize the mineralogy of the tailings and their pore water and effluent chemistries. Geochemical mass balance modeling, constrained by aqueous speciation modeling and mineralogy, is then used to identify reactions controlling the chemical evolution of pore water along its flow path through the tailings impoundment. The tailings are composed mainly of REE-enriched calcite (82 wt. %), biotite (12 wt. %) and fluorapatite (4 wt. %). Minor minerals include chlorite, pyrite, sphalerite, molybdenite and unrecovered pyrochlore. Secondary minerals include gypsum, barite and strontianite. Within the unsaturated zone, pore water chemistry is controlled by sulfide oxidation and calcite dissolution with acid neutralization. With increasing depth below the water table, pore water composition reflects gypsum dissolution followed by sulfate reduction and FeS precipitation driven by the oxidation of organic carbon in the tailings. Concomitantly, incongruent dissolution of biotite and chlorite releases K, Mg, Fe, Mn, Ba and F, forming kaolinite and Ca-smectite. Cation exchange reactions further remove Ca from solution, increasing concentrations of Na and K. Fluoride concentrations reach 23 mg/L and 8 mg/L in tailings pore water and effluent, respectively. At a pH of 8.3, Mo is highly mobile and reaches an average concentration of 83 µg/L in tailings effluent. Although U also forms mobile complexes, concentrations do not exceed 16 µg/L due to the low solubility of its pyrochlore host. Adsorption and the low solubility of pyrochlore limit concentrations of Nb to less than 49 µg/L. Cerium, from calcite dissolution, is strongly adsorbed although it reaches concentrations (unfiltered) in excess of 1 mg/L and 100 µg/L in pore water and effluent, respectively. Mine tailings from carbonatite deposits are enriched in a variety of incompatible elements with mineral hosts of varying reactivity. Some of these elements, such as F and Mo, may represent contaminants of concern because of their mobility in alkaline tailings waters.

Carbonatites

- Intrusions consisting of > 50% carbonate minerals (calcite, dolomite, ankerite)
- Enriched in incompatible elements (REE, U, Th, Nb, Ta, Zr)
- Attractive exploration targets for REE and Nb
- Examples: Bayan Obo, Mountain Pass, Araxa, Palabora
- Knowledge Gap: Little published information on the environmental signature of mining carbonatites for REE or Nb

Saint Lawrence Columbium mine, Oka, Québec

- Typical carbonatite-hosted Nb deposit mined between 1961 and 1976 (underground and open pit)
- Different types of mine wastes and mine waters are present: pit lakes, waste rock, tailings, ferroniobium slag
- Focus here on mine tailings and their drainage chemistry
- What are the issues of potential environmental concern associated with mine tailings drainage?

"Two-Scale" Approach

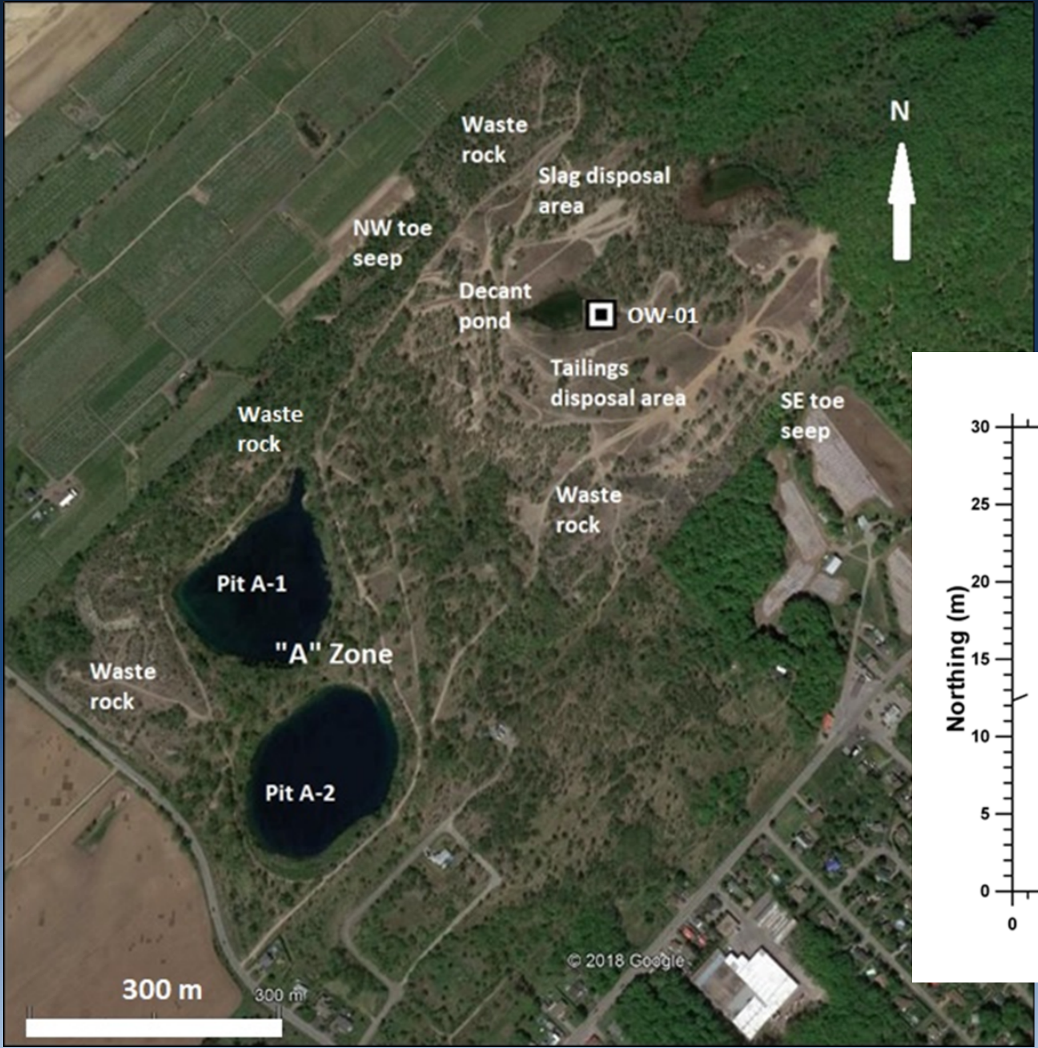
1. Analysis of tailings effluent chemistry: composite water chemistry of the tailings impoundment as a whole
2. Detailed analysis of tailings porewater evolution along a vertical flow path through the impoundment:

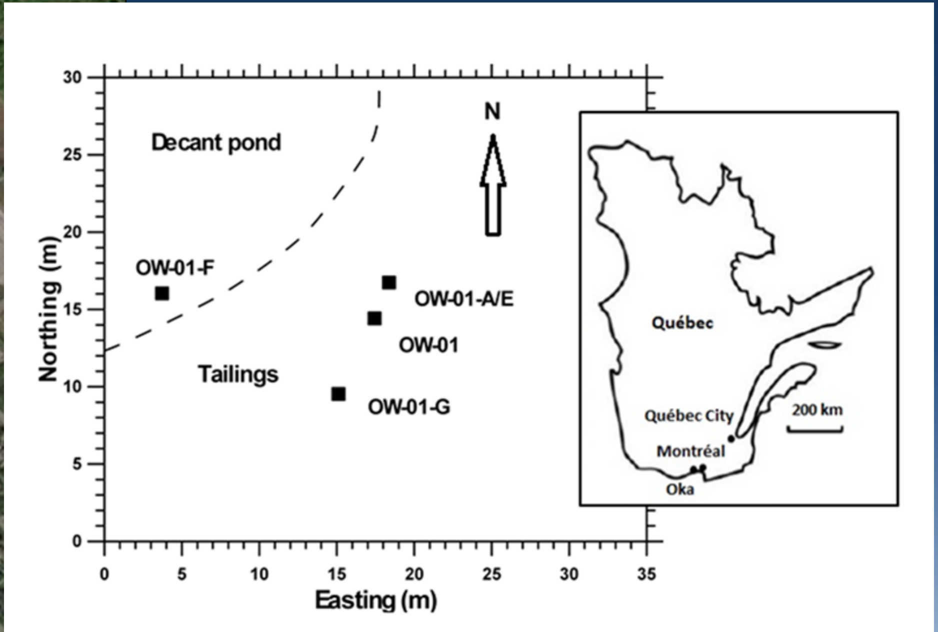
   Mineralogy (XRD, SEM-EDS, EPMA) with aqueous speciation and mass balance modeling of porewater to understand reactions and contaminant mobilization

Objectives

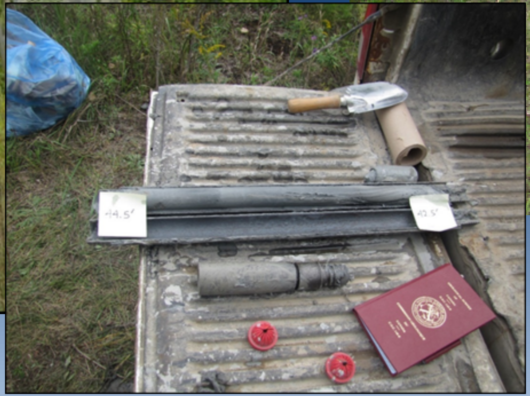
- Characterize the physical properties, geochemistry and mineralogy of the tailings
- Characterize the evolution of tailings porewater chemistry within the impoundment
- Identify the aqueous contaminants of potential environmental concern
- Elucidate the geochemical processes controlling tailings hydrogeochemistry and the mobilization of contaminants

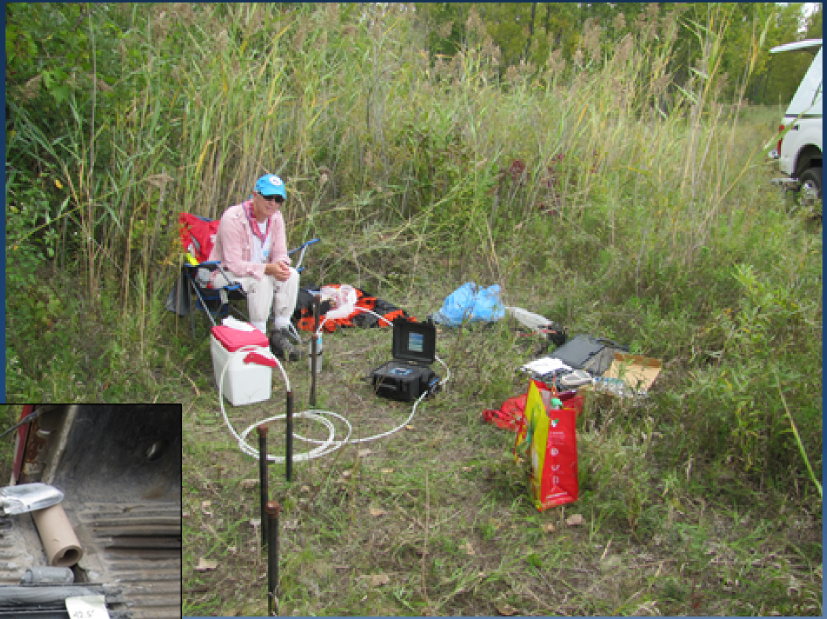
Main features of the Saint Lawrence Columbium mine site



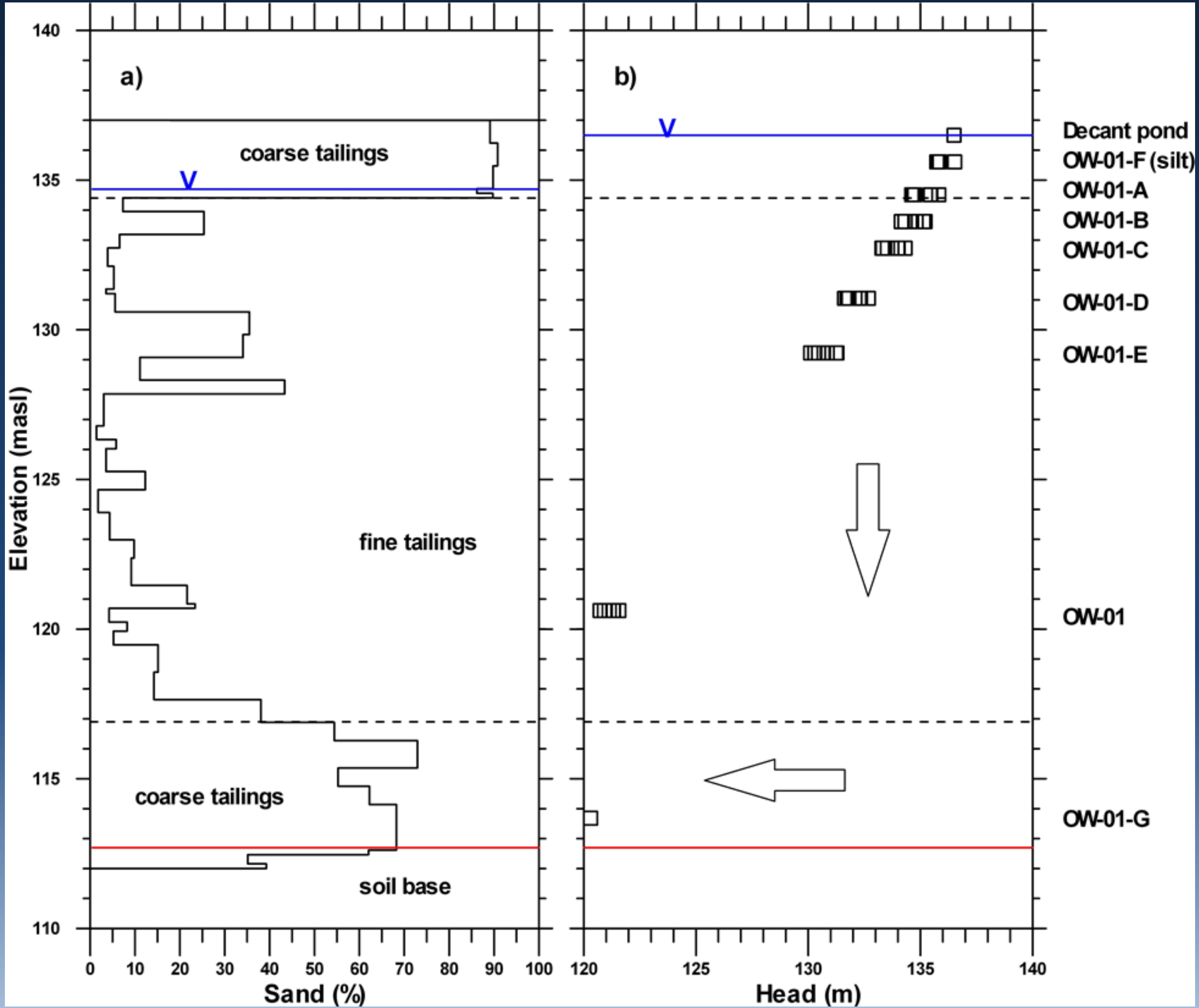


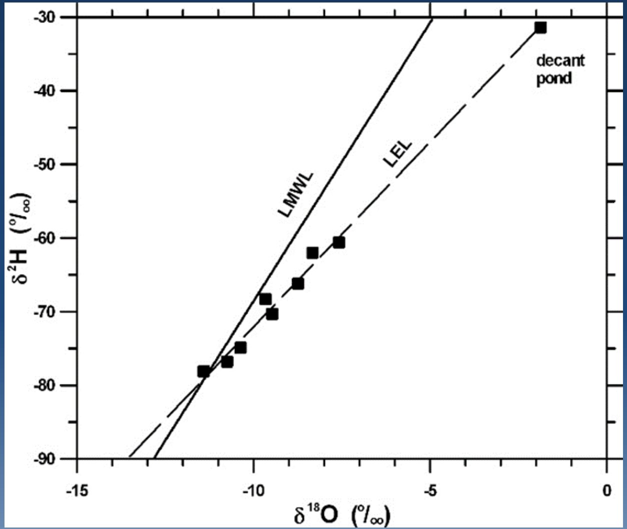
Continuous core drilling through the tailings and multilevel drive-point piezometers



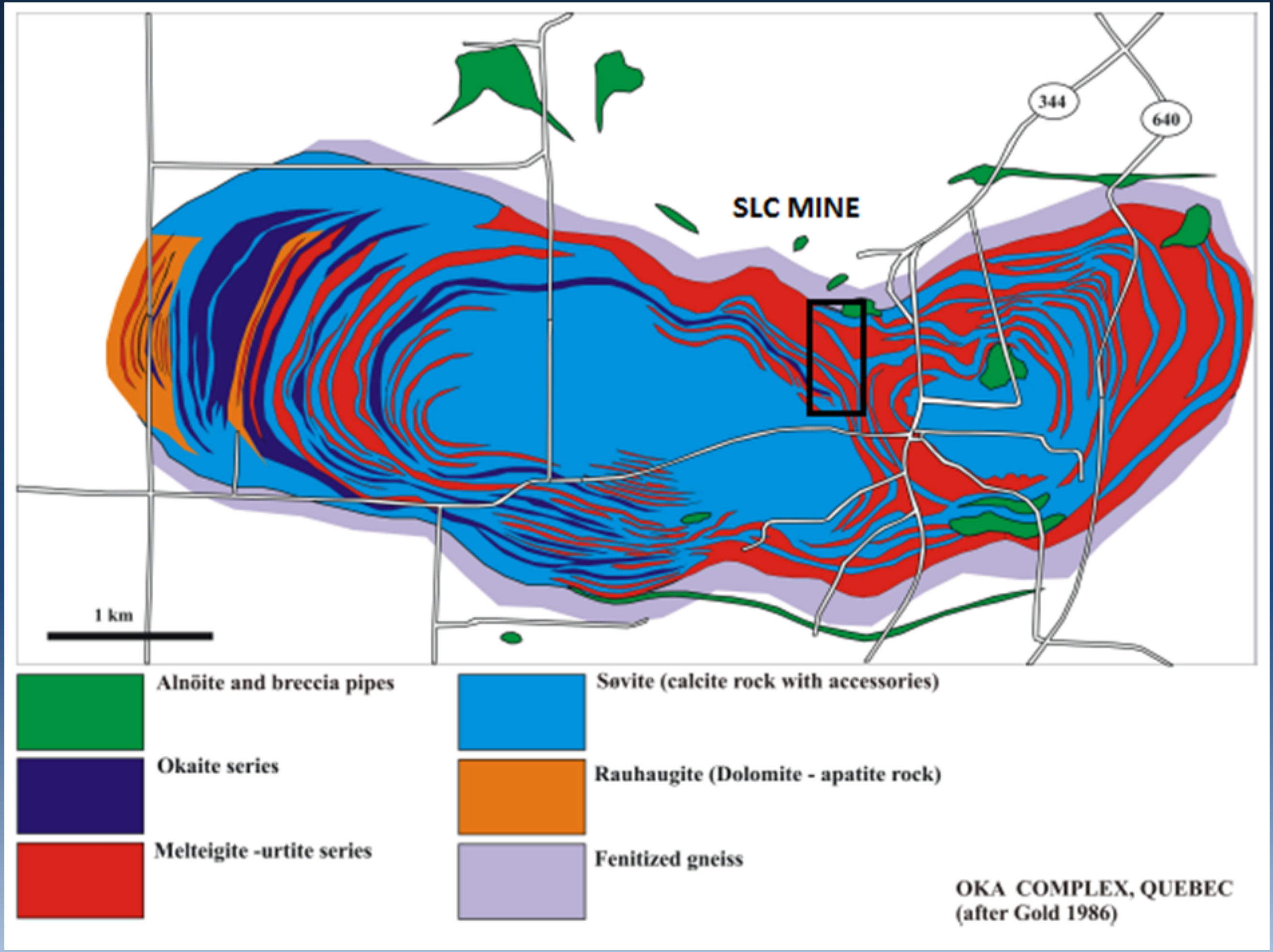


Physical flow system





Simplified geology of the Oka carbonatite complex (from Lentz, 2006)



Nb ore mineral: Pyrochlore

- Hosted in sövites
- Nb oxide with general formula: $A_{2-x}B_2O_6(OH,F)$
- A: Na, Ca, Mn, Sr, U, Th, REE
- B: Nb, Ta, Ti, Al, Fe, Zr

- Oka example (Petruk & Owens, 1975):

$Na_{.15}Ca_{.48}Sr_{.01}Mn_{.01}Fe_{.16}U_{.38}Ce_{.08}Nd_{.01}La_{.02}Nb_{1.66}Ta_{.05}Ti_{.27}Zr_{.01}O_6(OH,F)$

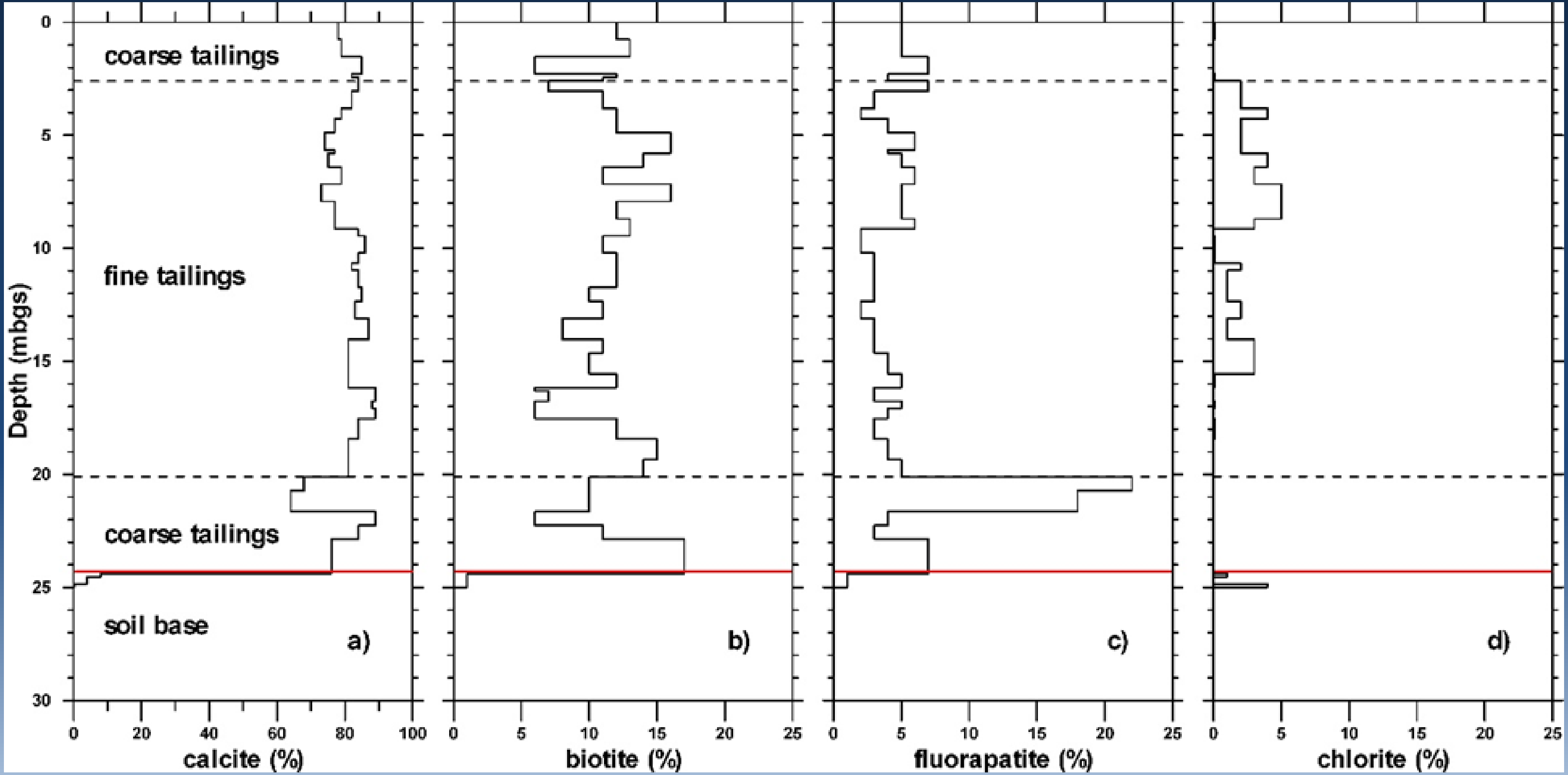
Accessory minerals (SEM-EDS, EPMA)

Silicates	biotite	$K_{0.84}\,Na_{0.11}\,Mg_{2.33}\,Fe_{0.55}\,Mn_{0.09}\,Ba_{0.06}\,Al_{1.21}\,Si_{2.84}\,O_{10}\,(OH)_{1.72}\,F_{0.28}$
	chlorite	$Mg_{2.11}\,Ca_{0.73}\,Mn_{0.1}\,Fe_{1.62}\,Al_{1.42}\,Si_{3.25}\,O_{10}\,(OH)_8$
	kaolinite	$Ca_{0.16}\,Mg_{0.06}\,Fe_{0.06}\,Al_{1.76}\,Si_{2.04}\,O_5\,(OH)_4$
	smectite	$Ca_{0.88}\,Mg_{0.67}\,Mn_{0.04}\,Fe_{0.45}\,Al_{1.37}\,Si_{3.34}\,O_{10}(OH)_2$
Carbonates	ankerite	$Ca_{1.05}\,Mg_{0.6}\,Fe_{0.32}\,Mn_{0.03}\,(CO_3)_2$
	calcite	$Ca_{0.976}\,Mg_{0.002}\,Mn_{0.004}\,Sr_{0.016}\,Ba_{0.002}\,CO_3$
	strontianite	$Sr_{0.84}\,Ca_{0.16}\,CO_3$
Sulfates	barite	$Ba_{0.89}\,Ca_{0.11}\,SO_4$
	gypsum	$Ca_{0.96}\,Sr_{0.04}\,SO_4: 2H_2O$

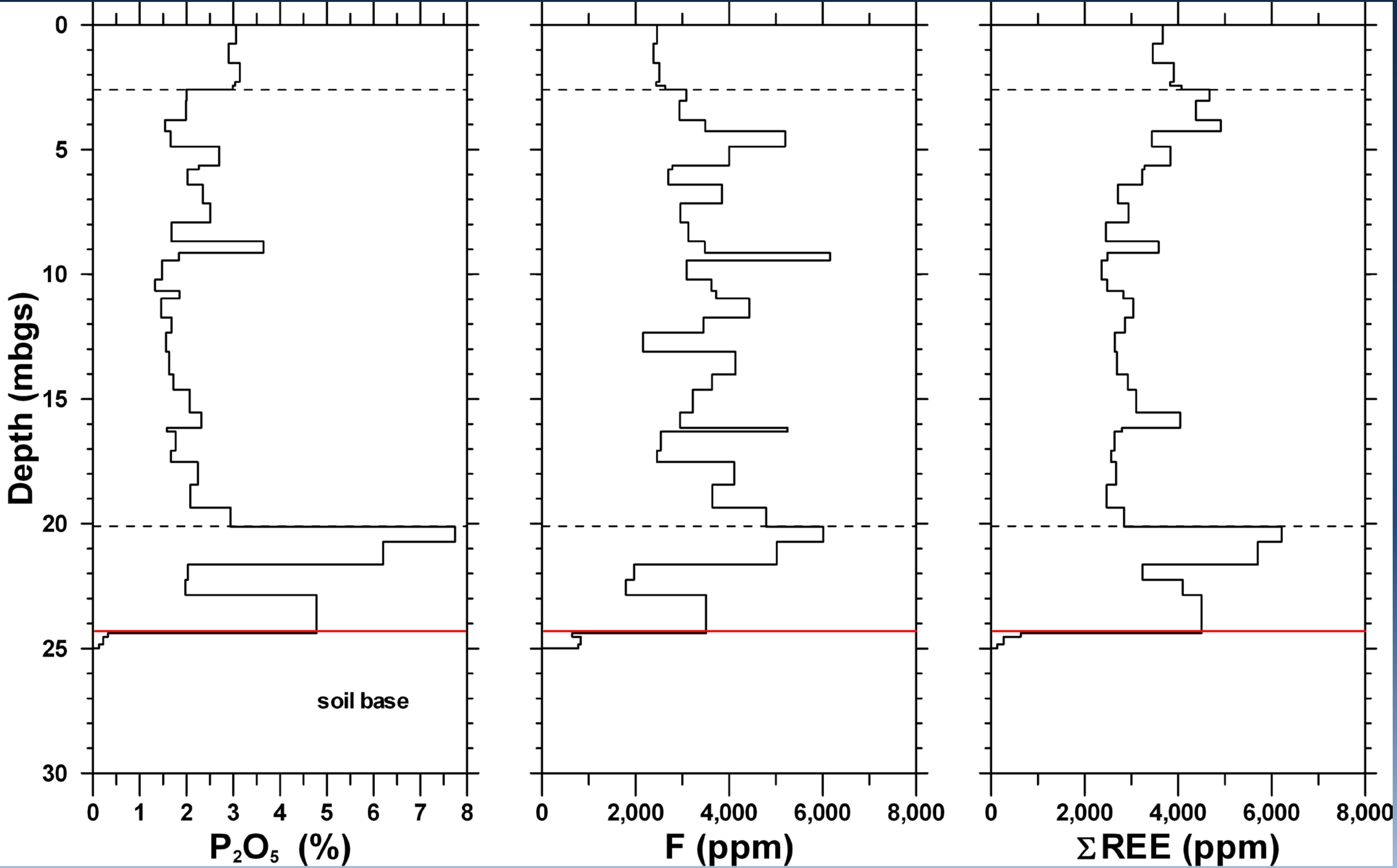
Accessory minerals (continued)

- Silicates: nepheline, clinopyroxene, monticellite, richterite, zeolites, niocalite, etc.
- Carbonates: rhodochrosite, parisite (REE-F)
- Phosphates: fluorapatite (REE-rich)
- Sulfides: pyrite, pyrrhotite, sphalerite, molybdenite
- Oxides: magnetite, ilmenite, Nb-perovskite

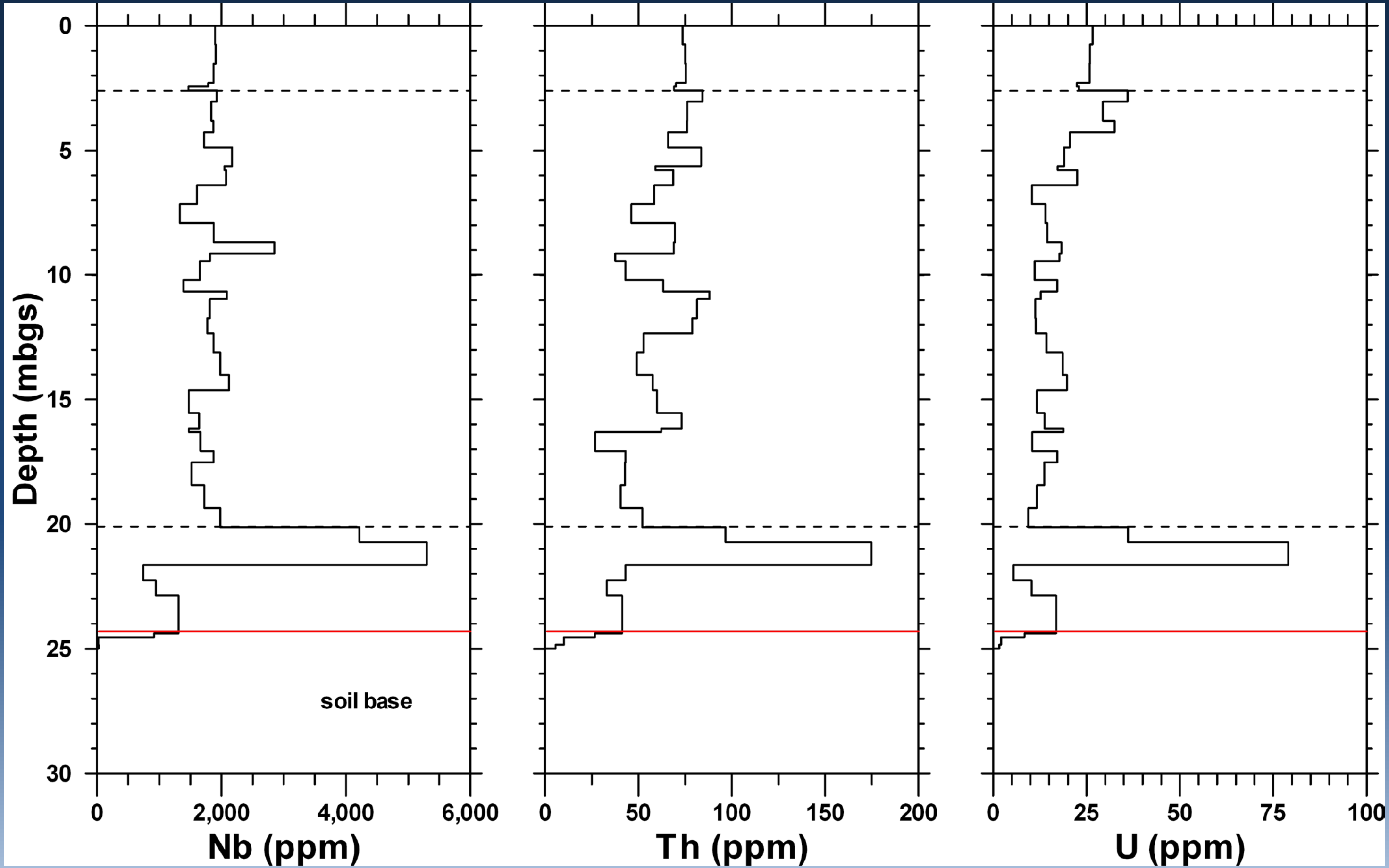
Bulk XRD mineralogy



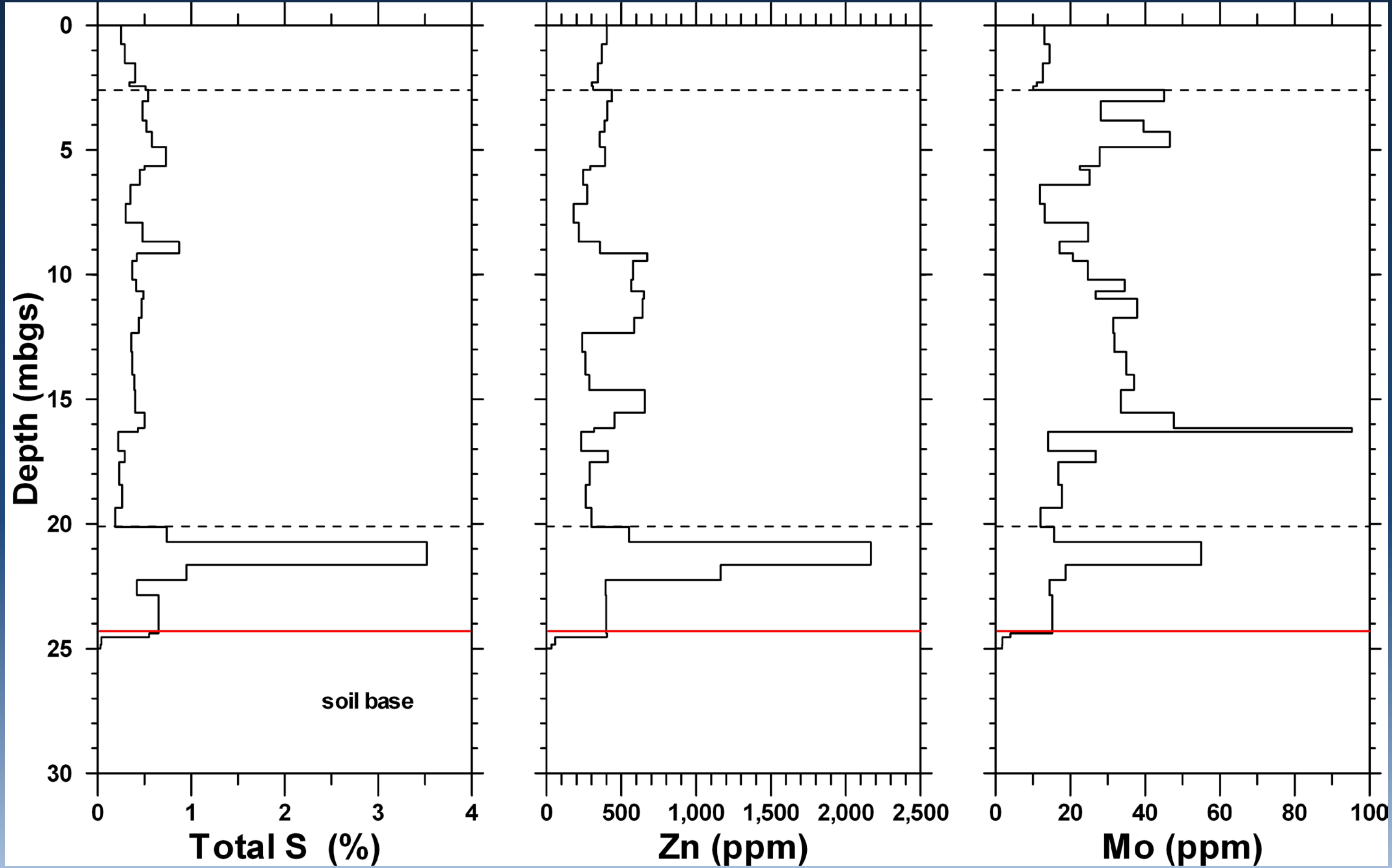
Geochemical profiles through the tailings



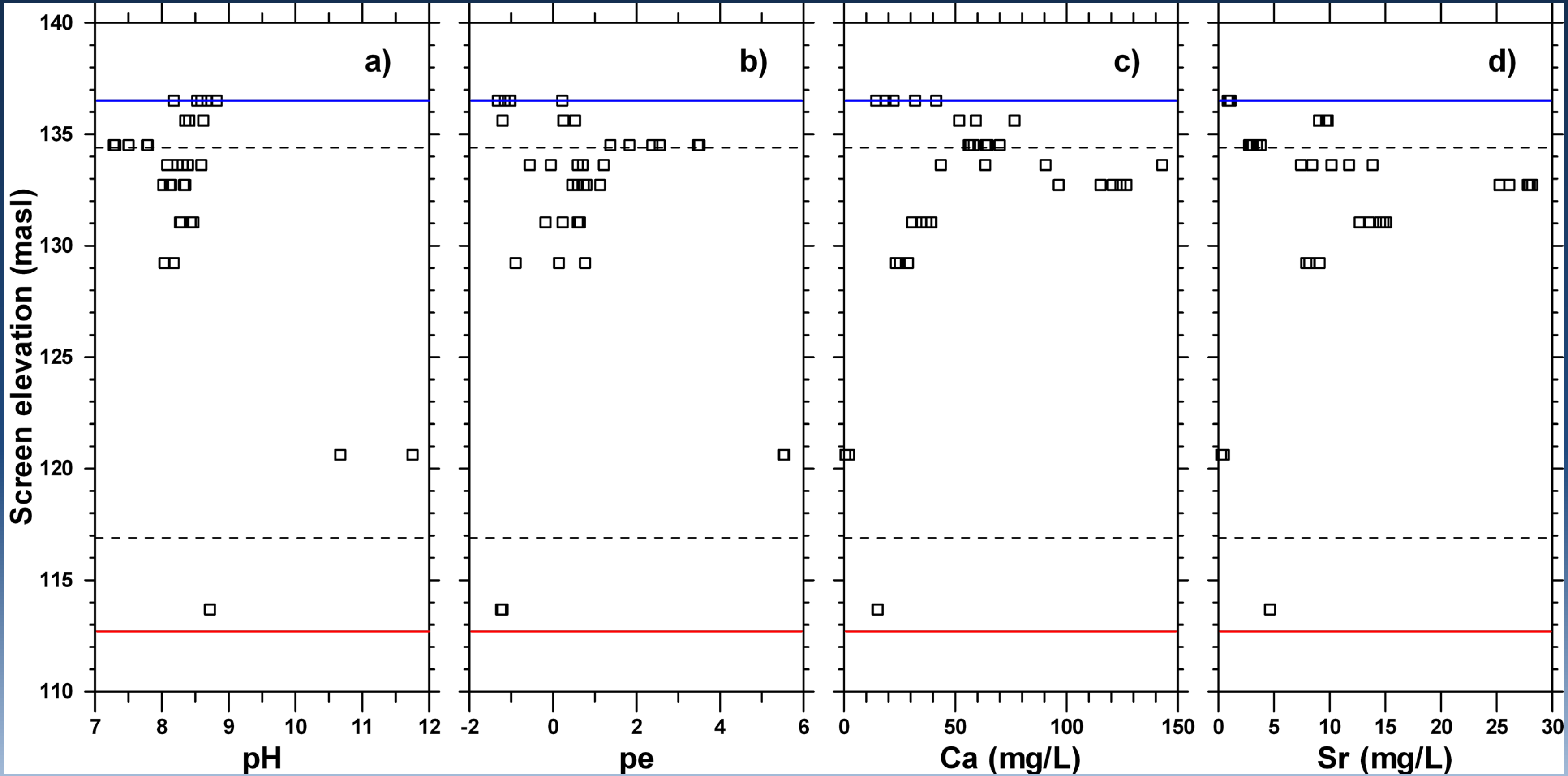
Geochemical profiles through the tailings



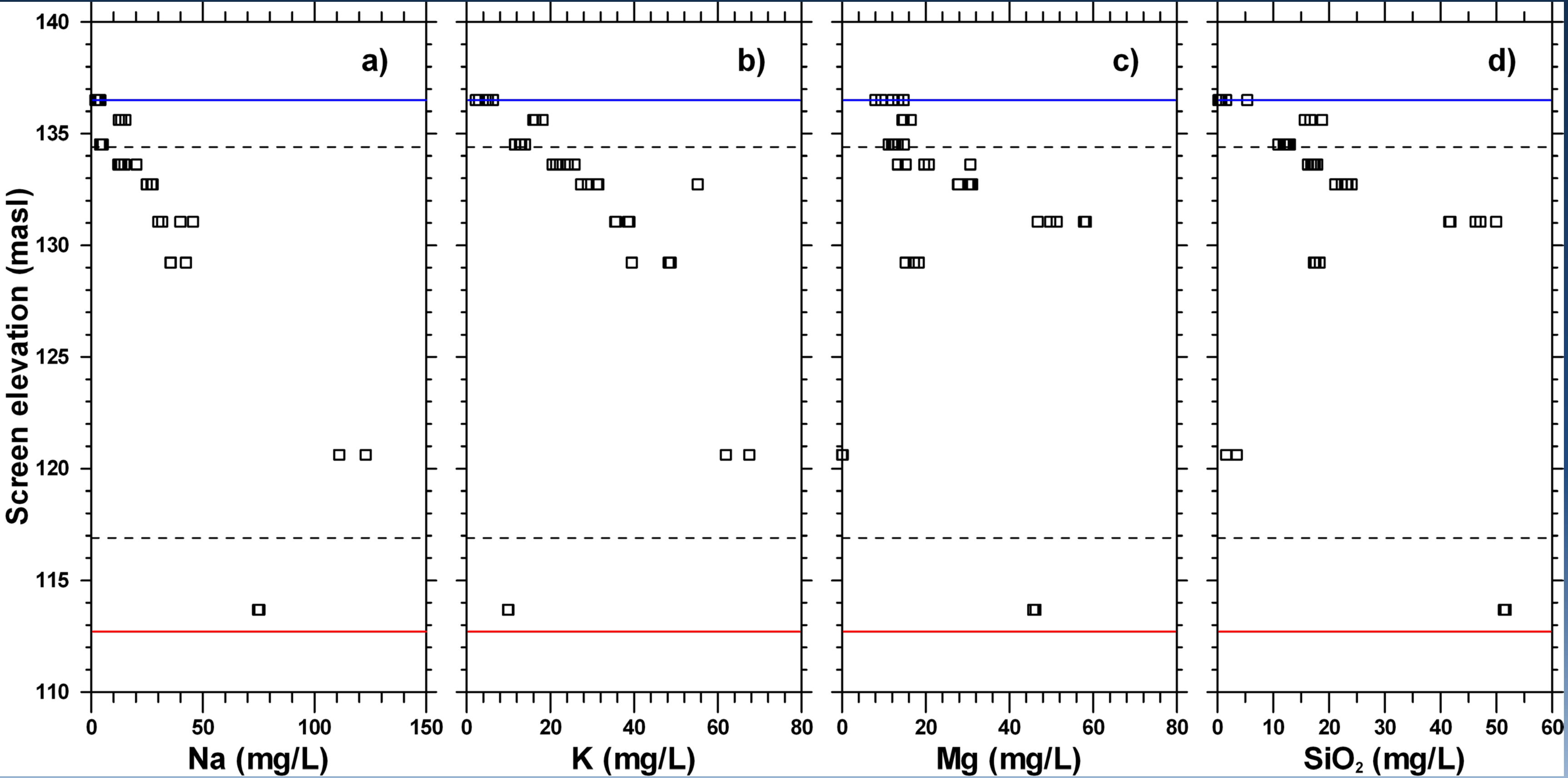
Geochemical profiles through the tailings



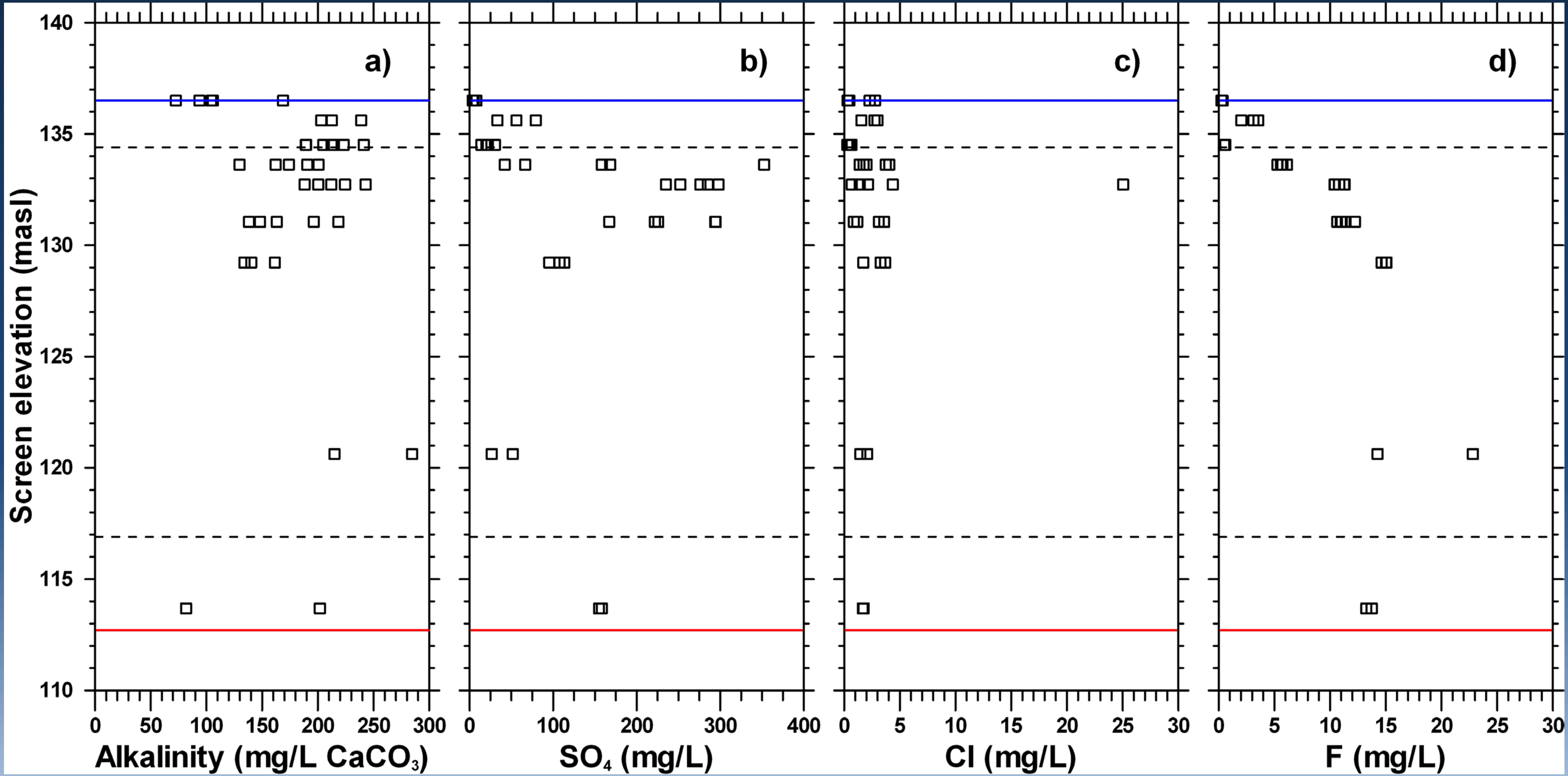
Depth profiles of pore water chemistry: pH, pe, Cations



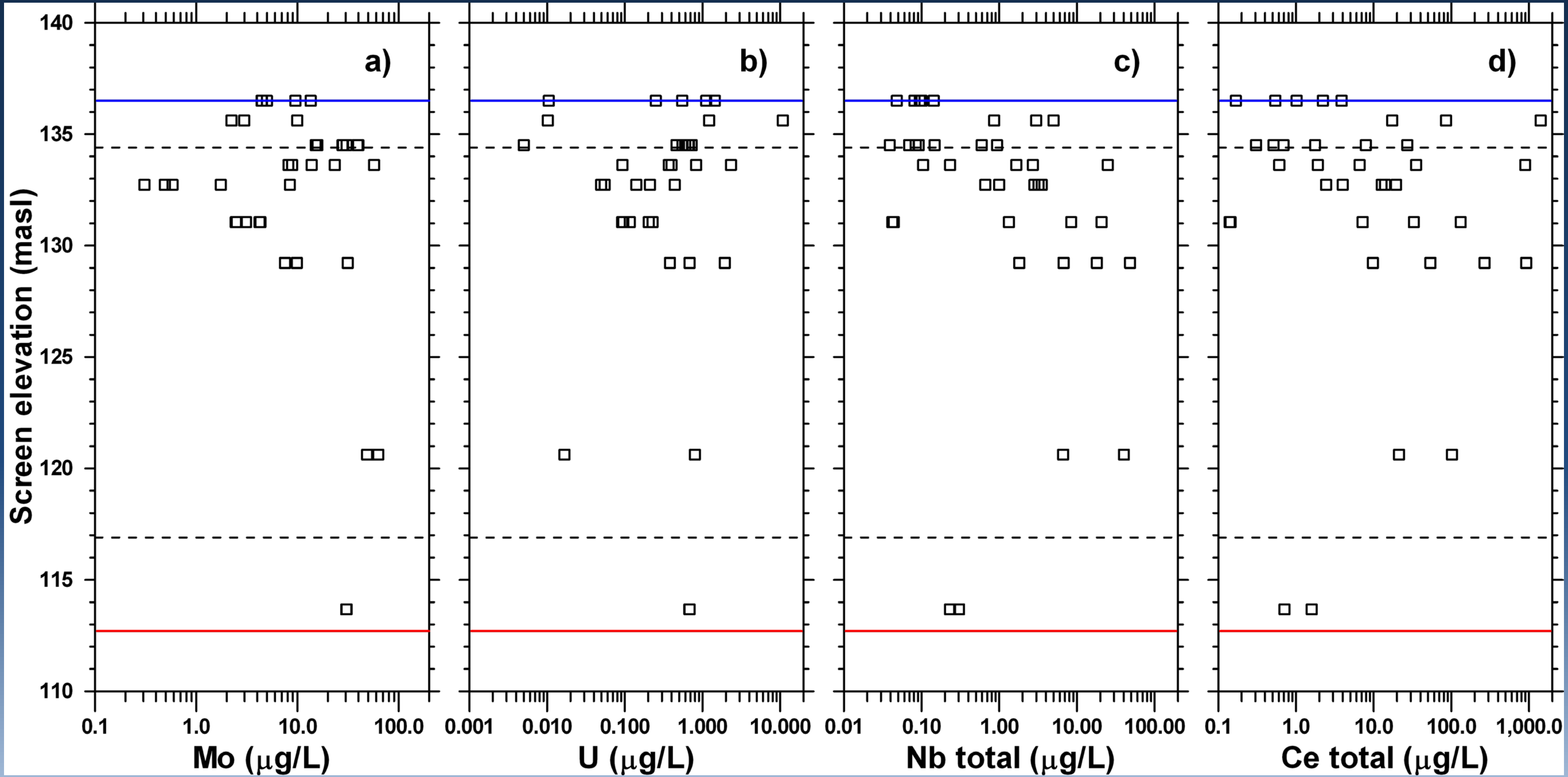
Depth profiles of pore water chemistry: Cations



Depth profiles of pore water chemistry: Anions



Depth profiles of pore water chemistry: trace metals



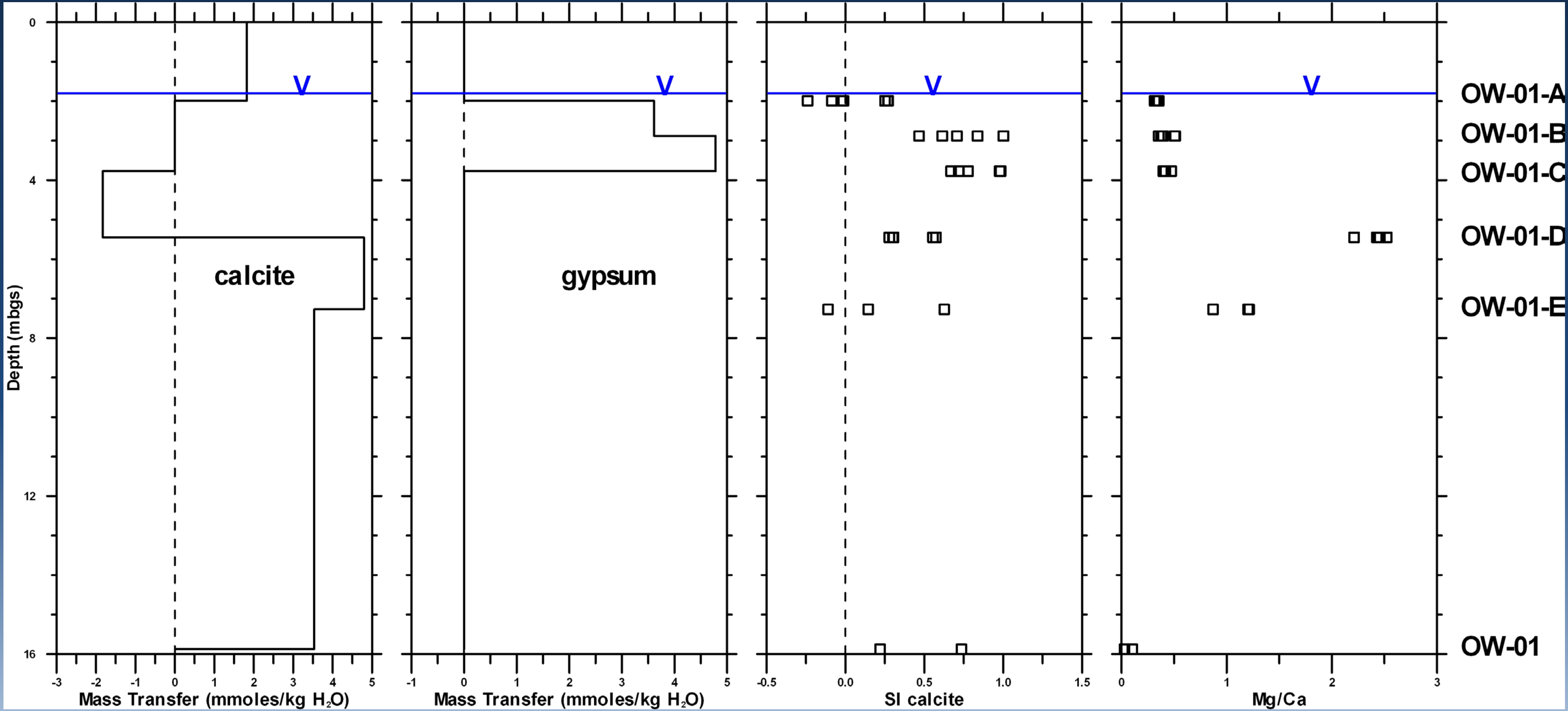
Geochemical Mass Balance (Inverse) Modeling

- Simultaneous solution of mass balance equations for each groundwater constituent (cations, anions):

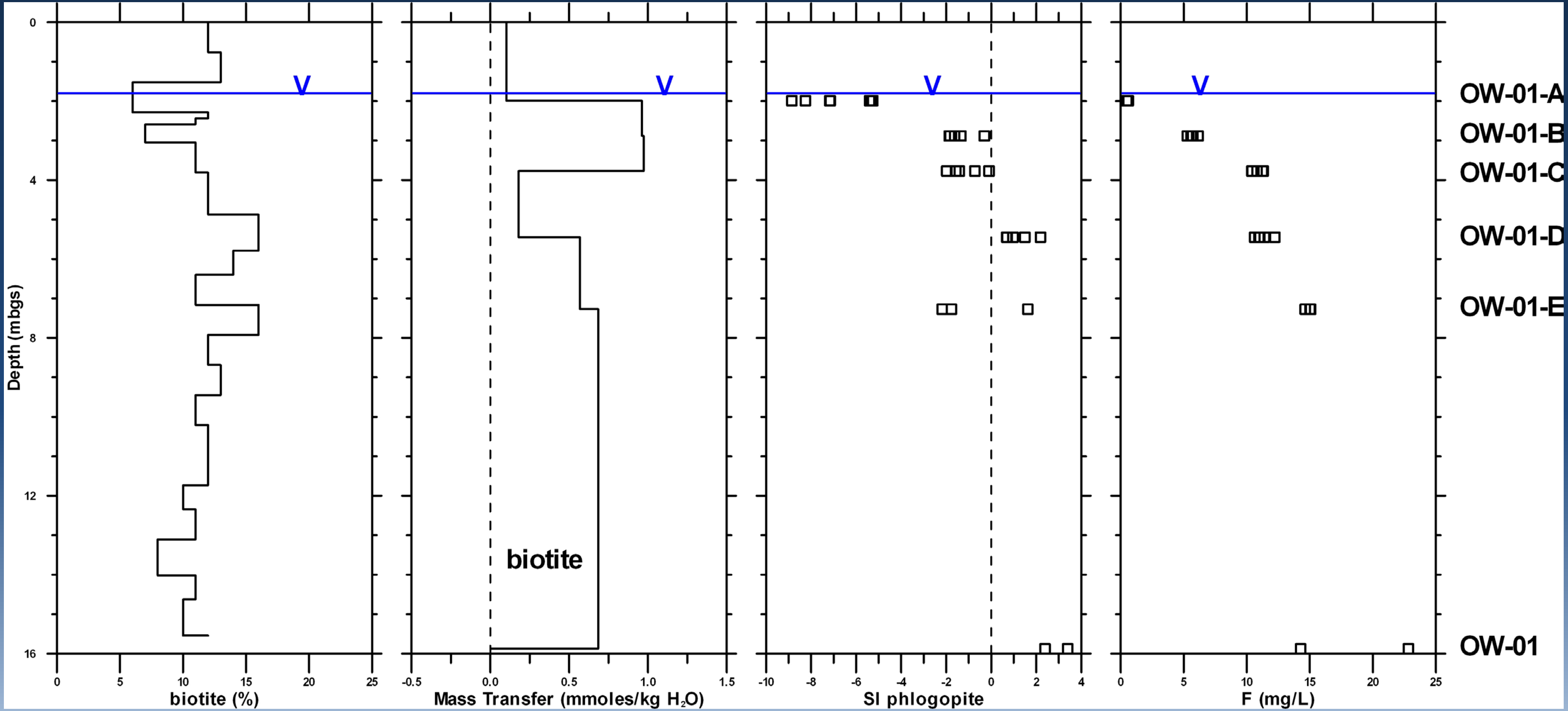
  Initial water composition + reactants = Final water composition + products

- Reactants: mineral or gas phases of known stoichiometry that dissolve (saturation index < 0)
- Products: mineral or gas phases of known stoichiometry that precipitate from solution (saturation index > 0)
- Piecewise solution of mass balance equations between piezometer pairs along flow path through tailings (precip-A, A-B, B-C, C-D, D-E, E-OW1)
- Results: mass transfers (mmol /kg H_2O) dissolving, precipitating, exchanging

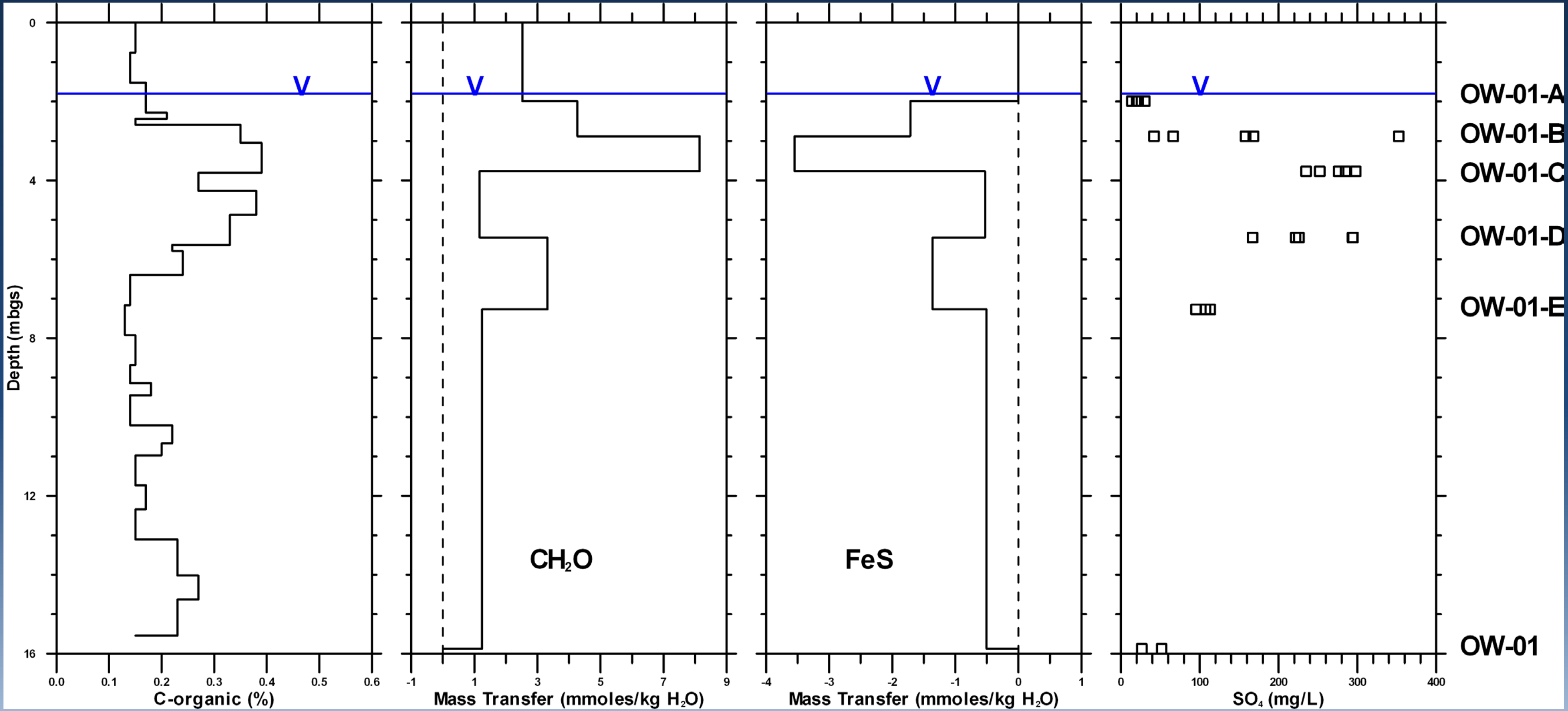
Mass balance modeling: calcite dissolution



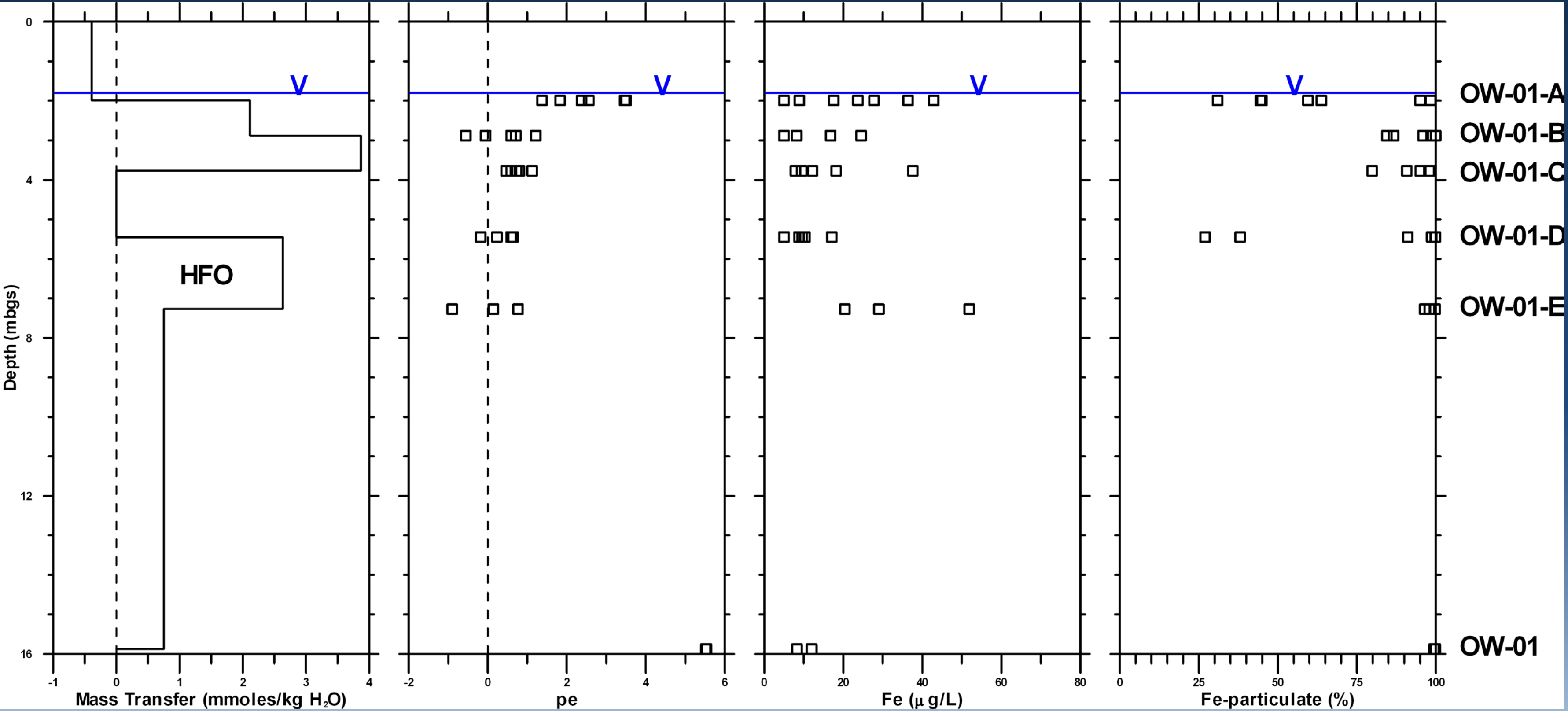
Mass balance modeling: biotite weathering



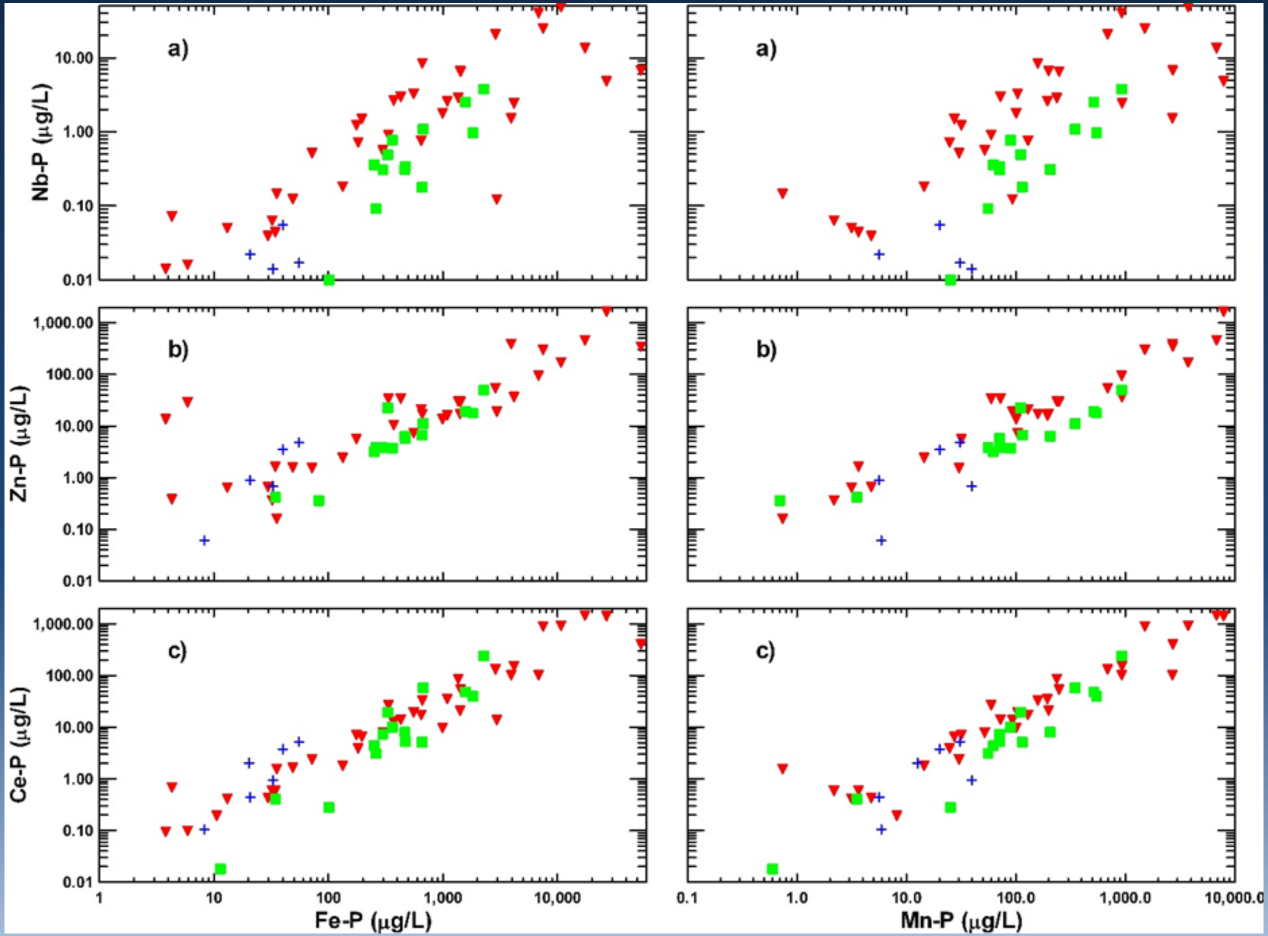
Mass balance modeling: organic carbon oxidation and sulfate reduction



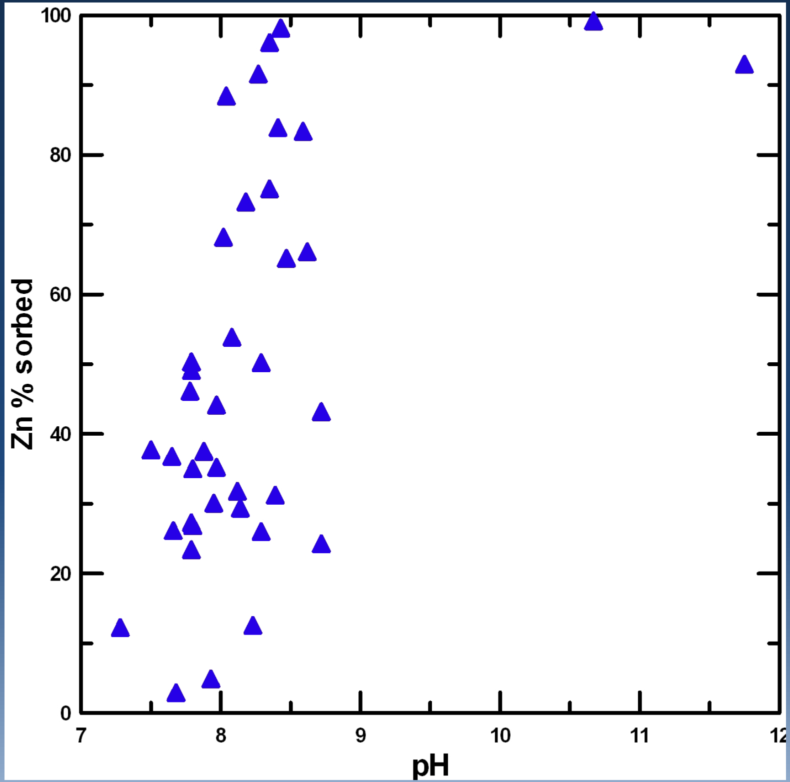
Mass balance modeling: HFO dissolution



Geochemistry of tailings seepage: Trace metal adsorption

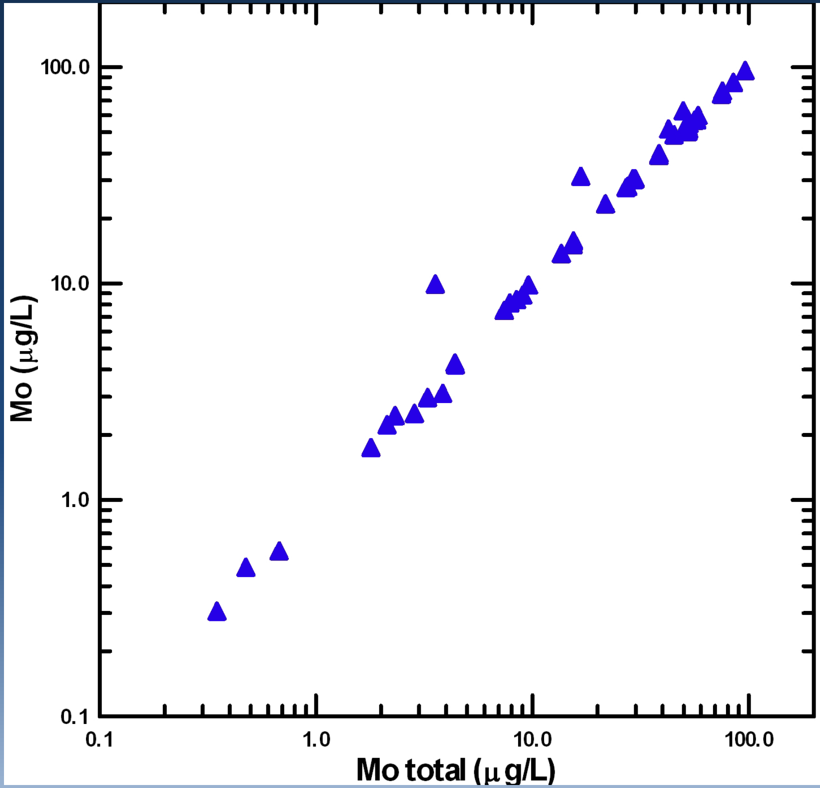


Geochemistry of tailings seepage: Zn adsorption edge

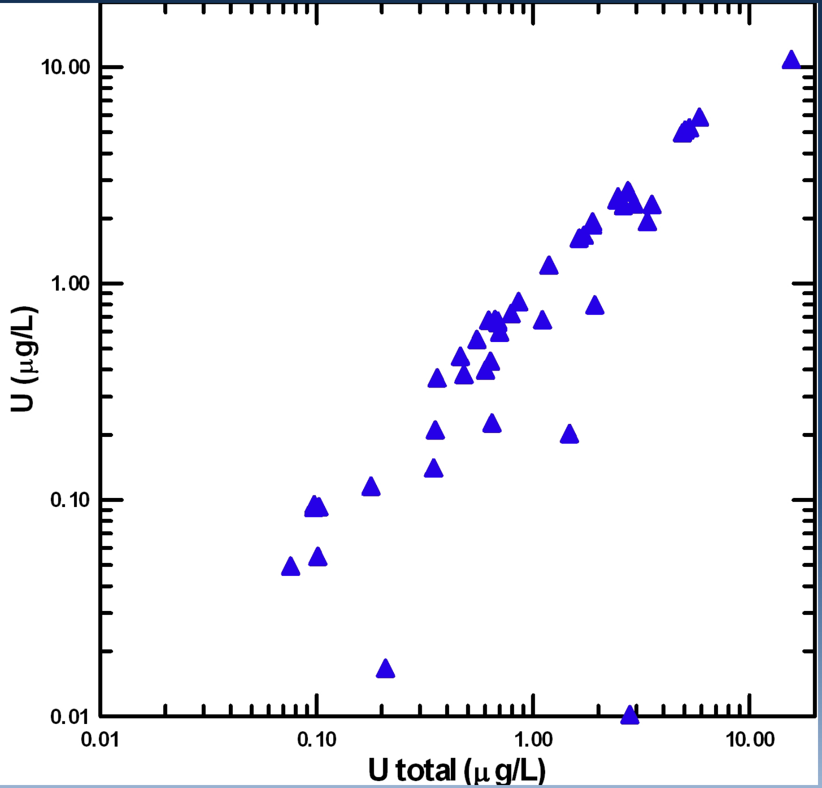


Geochemistry of tailings seepage: Trace metal mobility

Mo mainly as MoO_4^{-2}



U mainly as $Ca_2UO_2(CO_3)_3^0$



Conclusions

- Carbonatite tailings contain minerals enriched in incompatible and other trace elements (Nb, REE, U, Mo, Zn, Ba, F, P, etc.)
- Environmental hazard from a trace element depends on abundance and solubility of its mineral host(s) under conditions (pH, pe) within the tailings
- SLC Tailings contain sulfide minerals (pyrite, sphalerite, molybdenite) with average 0.5 % total S but are not PAG

Conclusions

- Pyrite oxidation and calcite dissolution in the unsaturated zone
- Organic matter oxidation drives sulfate reduction and reductive dissolution of HFO with precipitation of sulfides
- Sulfide minerals are stable in reducing environment below tailings water table
- Fluoride (from biotite dissolution) in tailings porewater (up to 23 mg/L) exceeds regulatory limits for protection of aquatic life
- Chlorite dissolution increases Mg/Ca ratio causing dolomitization of calcite, and may also release Zn

Conclusions

- Mo is highly mobile in mildly alkaline (pH 8.3) tailings porewater but concentrations are limited by low abundance of host mineral(s)
- U is mobile in tailings porewater but concentrations are limited by low pyrochlore solubility
- Nb is strongly adsorbed at pH 8.3 and concentrations are limited by low pyrochlore solubility
- Zn is strongly adsorbed at pH 8.3 but total concentrations can exceed 1 mg/L
- REE (from calcite dissolution) are strongly adsorbed at pH 8.3 but total concentrations in porewater can exceed 1 mg/L.

Acknowledgments

- Project funding from the GSC's Environmental Geoscience Program
- Unrestricted access to the SLC site granted by the Municipality of Oka
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- SEM-EDS analyses by Matt Polivchuk (GSC)
- Water chemistry analyses by the GSC's Inorganic Geochemistry Research Laboratory (P. Pelchat, J. Sekerka, P. Gammon)


Questions?