

**Hydrogeochemistry and Trace Element Mobility
in an Acidic High-Sulfide Tailings Impoundment After
40 Years of Oxidation**

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

I would like to acknowledge my co-author for Chapter 2, Dr. Eva Pakostova, who contributed to sequence data processing, methods, prokaryotic genera classification, and the creation of figures presenting the results of prokaryotic populations.

Abstract

Abandoned mine sites can create a legacy environmental contamination issue when the generation of acid mine drainage is allowed to continue with insufficient or absent remediation measures. The South Bay mine, a former underground Cu-Zn mine located in northwestern Ontario, is once such site with historical contamination. The mine wastes at South Bay contain high concentrations of sulfide minerals which continue to oxidize decades following mine closure, leading to acidic seepage with high concentrations of dissolved metals impacting the surrounding lakes. This aim of this study is to provide a characterization of the current hydrogeology, geochemistry, mineralogy, and microbiology of the South Bay tailings so that this information can inform future remediation work.

Instrument installation and collection of core samples of the tailings was performed at five locations within the tailings impoundment area. Pore-water samples were collected from piezometer and soil water sampler nests. Sub-samples of tailings cores were collected and analysed using optical microscopy, scanning electron microscopy, selective extractions, total carbon/sulfur, X-ray diffraction, X-ray fluorescence, synchrotron, and DNA sequencing techniques. Mineralogical analysis indicated that pyrite was the main sulfide mineral in the tailings, with lesser amounts of sphalerite and chalcopyrite and trace amounts of pyrrhotite, galena, and arsenopyrite. The oxidation zone in which sulfide minerals are depleted is restricted to the upper 0-15 cm of tailings. The moisture content within the tailings is relatively high, contributing to a low O₂ diffusion rate into the tailings. High proportions of acidophilic microorganisms capable of catalyzing Fe and S oxidation reactions were found in the shallow tailings. Sulfide oxidation modelling has indicated that oxidation of sulfide minerals in the South Bay tailings may continue for decades to millennia before all sulfide minerals are depleted in the vadose zone.

Prolonged sulfide mineral oxidation has led to acidic pore waters with pH as low as 1.26 with high concentrations of dissolved metals, including Fe, Zn, Cu, As, Pb, and Co. The lowest pH and highest concentrations of dissolved metals tends to occur in the shallow tailings near the region of active sulfide-

mineral oxidation. High concentrations of dissolved rare earth elements (REEs), up to 9.45 mg L⁻¹ total REEs, were also found within the shallow acidic pore-waters. Dissolution of gangue minerals and secondary minerals contributes to acid neutralization, with pH increasing to circumneutral values below the water table. Metals and metalloids may be attenuated through adsorption or co-precipitation with secondary mineral phases. Copper was found to be attenuated through covellite precipitation, Pb was attenuated through anglesite precipitation, and As was attenuated by adsorption or co-precipitation with Fe(III) (oxy)hydroxides. Metal(loid)s sequestered within Fe(III) (oxy)hydroxides may be susceptible to remobilization through reductive dissolution should environmental conditions imposed by future remediation efforts induce strong reductive conditions.

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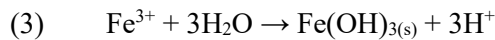
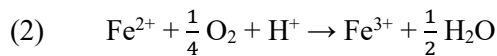
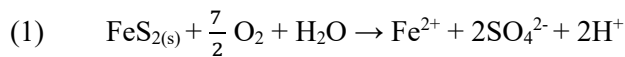
AMD	acid mine drainage
aIOB	acidophilic iron-oxidizing bacteria
aSOB	acidophilic sulfur-oxidizing bacteria
CLS	Canadian Light Source
CMCF	Canadian Macromolecular Crystallography Facility
DI	deionized
EDX	energy dispersive X-ray
HREE	heavy rare earth elements
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectroscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
IOB	iron-oxidizing bacteria
LCF	linear combination fitting
LREE	light rare earth elements
MREE	middle rare earth elements
nIOB	neutrophilic iron-oxidizing bacteria
nSOB	neutrophilic sulfur-oxidizing bacteria
REE	rare earth elements
SAI	sulfide alteration index
SEM	scanning electron microscopy
SI	saturation index
SOB	sulfur-oxidizing bacteria
SRB	sulfate-reducing bacteria
SXRMB	Soft X-ray Microcharacterization Beamline
TEY	total electron yield
VCDT	Vienna Canyon Diablo Troilite
VSMOW	Vienna Standard Mean Ocean Water
XANES	X-ray absorption near-edge spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

Chapter 1: Introduction

1.1 Background: Acid Mine Drainage

Mining activities generate very large volumes of waste material in the form of mill tailings and waste rock. Tailings are the fine-grained crushed residual that remains from the concentration of economically valuable minerals during the ore processing phase. Tailings often contain high amounts of sulfide minerals such as pyrite [FeS₂] (Blowes et al., 2014). Once exposed to O₂ at the surface, these sulfide minerals oxidize to create acidic drainage waters with high concentrations of dissolved metals (Lowson, 1982; Nordstrom, 1982; Evangelou & Zhang, 1995; Moncur et al., 2005; Blowes et al., 2014).

The chemical reactions that govern the oxidation of pyrite are summarized by reactions 1-4 (Nordstrom, 1982; Evangelou & Zhang, 1995; Blowes et al., 2014). Reaction (1) describes the initial oxidation of pyrite by O₂, producing two moles of SO₄²⁻ and H⁺ per mole of pyrite. Ferrous iron is also produced by reaction (1) and can be further oxidized to form Fe³⁺ by reaction (2). The oxidation of pyrite by Fe³⁺ is shown by reaction (4). When pH values are <4.5, pyrite oxidation by Fe³⁺ occurs at a much faster rate than by O₂, allowing oxidation of pyrite to continue even under anoxic conditions (Nordstrom, 1982). Ferrihydrite and other Fe(III) (oxy)hydroxides may precipitate via reaction (3), acting as a sink for Fe³⁺ but generating further acidity.



The oxidation of other sulfide minerals such as pyrrhotite [Fe_(1-x)S], sphalerite [ZnS], and chalcopyrite [CuFeS₂] also contribute to the generation of acid mine drainage (AMD) (Moncur et al., 2009). Pyrrhotite oxidizes up to 100 times faster than pyrite at atmospheric conditions (Nicholson &

Scharer, 1994), demonstrating its importance to acid generation in mining environments. Microorganisms also influence the rate of sulfide mineral oxidation since Fe- and/or S-oxidizing bacteria are often present in acidic mining environments. In abiotic systems with low pH, the oxidation of Fe^{2+} to Fe^{3+} by O_2 is the rate-limiting step in the oxidation of sulfide minerals (Singer & Stumm, 1970). Iron-oxidizing bacteria such as *Acidithiobacillus (A.) ferrooxidans* can oxidize dissolved Fe^{2+} to Fe^{3+} at a more rapid rate than by O_2 , indirectly increasing the overall rate of sulfide oxidation since Fe^{3+} is a more effective oxidant for sulfides than O_2 at acidic pH (Nordstrom, 2003). *A. ferrooxidans* is one of the most well-characterized bacteria present in AMD environments, capable of obtaining energy from both reduced S and Fe oxidation (Gould & Kapoor, 2003). *A. ferrooxidans* is an obligate acidophile and an autotroph, present at pH values between 1.0 to 3.5 and capable of obtaining C through CO_2 fixation (Gould & Kapoor, 2003). Factors controlling the diversity of microorganisms in tailings impoundments include the pH, temperature, mineralogy, and metal concentrations (Baker & Banfield, 2003).

Trace elements, such as Zn, Cu, Pb, As, and Co, are mobilized to tailings pore-waters during the oxidation of sulfide minerals that incorporate these elements. Acidic pore-waters with high concentrations of dissolved metals often occur near the surface where there is active sulfide mineral oxidation. Pore waters can become supersaturated with respect to certain minerals, leading to the precipitation of secondary mineral phases, which are generally fine-grained and have a high sorption capacity (Jamieson, 2011). As acidic pore-waters migrate downwards, the dissolution of non-sulfide gangue minerals such as calcite, dolomite, siderite, Al hydroxides, Fe(III) (oxy)hydroxides, and aluminosilicates, leads to a series of pH neutralization reactions (Blowes & Jambor, 1990; Blowes et al., 2014). The dissolution of gangue minerals can lead to elevated concentrations of elements such as Al, Ca, Mg, and Mn within tailings pore-waters. Rare earth element (REE) concentrations may also be elevated due to dissolution of REE-bearing minerals in acidic waters. As pore-water pH increases with depth, previously mobile elements can become attenuated through adsorption or precipitation reactions with secondary mineral phases. The accumulation of secondary precipitates within shallow areas of sulfide-rich tailings impoundments can create cemented

layers known as hardpans that are enriched in trace elements (Blowes et al., 1991; McGregor & Blowes, 2002; Elghali et al., 2019). Secondary precipitates can also dissolve and re-precipitate at greater depths as the acid front migrates downwards (Moncur et al., 2005).

AMD and metal leaching can have considerable negative environmental impacts to surface water and groundwater systems around mine sites. A major challenge for the mining industry is the prevention and remediation of AMD, with the total liability associated with AMD worldwide previously estimated to be around U.S.\$100 billion (MEND, 2001). More stringent regulations on AMD prevention and effluent quality have been imposed on mining companies in many parts of the world in recent decades to limit environmental impacts (Rezaie & Anderson, 2020). However, there remains many historical abandoned mine sites that are still generating AMD due to insufficient remediation measures (Bussière, 2009). Many of these abandoned or orphaned mines have been reverted to government ownership due to the original owners being absent or financially unable or unwilling to remediate the site (Bussière, 2009; NOAMI, 2009). In Canada alone, there is estimated to be over 10,000 orphaned and abandoned mine sites with different remediation requirements (NAOMI, 2009). Remediation of these abandoned sites is essential, since some sites have the potential to continue generating AMD for hundreds to thousands of years (Nordstrom & Alpers, 1999; Moncur et al., 2005; Tabein et al., 2019).

There are numerous remediation and treatment strategies for AMD, however prevention of AMD is often the preferred strategy if it is feasible (Johnson & Hallberg, 2005). Prevention of AMD can be achieved by limiting the oxidation of sulfide minerals. Physical barriers to oxygen and water transport can be implemented to prevent oxidation; these include capillary barrier soil covers which retain a high saturation content, organic carbon covers, water covers and elevated water tables, or synthetic covers (Bussière, 2009; Blowes et al., 2014). Remediation strategies can be classified into active methods and passive methods. Active remediation requires a continuous input of resources and energy to sustain the process, whereas passive remediation methods do not require continuous resource input (Johnson & Hallberg, 2005). Active remediation techniques often have a high operating cost, require ongoing

maintenance, and can produce toxic by-products (Johnson & Hallberg, 2005). Passive remediation solutions rely on natural geochemical and biological processes to neutralize AMD and precipitate metals and often offer lower capital and operating costs, although they do require some occasional maintenance (Skousen et al., 2017; Park et al., 2019).

Suitable remediation strategies for AMD will be different for operating mine sites in comparison to abandoned mine sites since remediation at abandoned sites must address historical contamination as well as future contamination (Bussière, 2009). The pore waters at abandoned mine sites can be highly acidic with high concentrations of dissolved metals, and mine wastes will have developed colonies of acidophilic bacteria (Bussière, 2009). Many abandoned mine sites are located in remote locations, where active treatment measures may not be suitable due to their need for ongoing maintenance and resource input as well as high operating costs. Passive remediation alongside sulfide oxidation prevention measures are often the most appropriate remediation strategies for abandoned mine sites (Bussière, 2009).

Changes in geochemical and environmental conditions within mine waste areas during remediation may remobilize trace elements (Gunsinger et al., 2006b). For example, reductive dissolution of secondary Fe(III) (oxy)hydroxides due to the installation of an organic carbon cover over an oxidized tailings impoundment has the potential to remobilize metals that were previously attenuated with the secondary minerals (Ribet et al., 1995; Doerr et al., 2005). The dissolution of highly soluble metal-salts and sulfate precipitates may also cause negative environmental impacts due to the high concentrations of metals liable to be released (Valente & Gomes, 2009). A raised water table or subaqueous disposal of oxidized tailings may therefore dissolve secondary minerals and release heavy metals to solution. The long-term stability of secondary minerals and the susceptibility of metals to remobilization under different geochemical conditions must be considered when choosing suitable remediation strategies for abandoned sulfide-rich mine sites (Jamieson et al., 2015). Site characterization of abandoned mine sites is fundamental for designing effective remediation systems since it will provide information about how the system functions and the sources of contamination (Nordstrom et al., 2015).

1.2 Site Description

The South Bay mine is located in northwestern Ontario, 65 km northeast of the township of Ear Falls. The mine was in operation between 1971 to 1981 and is currently abandoned. The mined ore reserves produced an average grade of 14.5% zinc, 2.3% copper, and 3.5 oz/ton silver (Wan & Warburton, 1979). The South Bay mine extracted ore from the Uchi orebody; a Cu-Zn deposit with lenses of massive sulfides within Archean siliceous tuff in contact with the top of a dome of quartz-feldspar porphyry (Pollock et al., 1972). The ore body was primarily composed of pyrite, sphalerite, and chalcopyrite (Pollock et al., 1972; Seccombe & Clark, 1981). The tailings management area lies within a former peat bog basin and currently covers an area of 25 hectares and contains about 785,000 tonnes of tailings.

AMD and metal leaching has been an ongoing problem at the site. The South Bay Mine is situated on a peninsula surrounded by Confederation Lake. There are several smaller lakes near the mine site, including Boomerang Lake and Mud Lake, which have been heavily impacted by mine drainage (Boojum, 2004). Boomerang Lake has been contaminated throughout the life of the mine and receives seepage directly from the tailings management area as well as the mine and mill area (Boojum, 2004). Mud Lake receives drainage from the tailings management area through groundwater flow channeled in a bedrock valley aquifer (Boojum, 2003).

Various remediation strategies have been evaluated and implemented at the site since its closure. A sand and gravel layer, approximately 30 cm thick, was placed over the dry tailings after mine closure in 1981 and was partially revegetated (Boojum, 2003). Passive biological treatment and ecological engineering approaches were tested at the site from the mid 1980's until 2003 (Kalin & Wheeler, 2011; CH2M, 2017). Some of these treatment methods included the addition of carbon sources to ponds and lakes around the site, application of natural phosphate rock to sections of the tailings, lakes, and ponds, magnesium scrap additions to Boomerang Lake, and a pilot project injection trial of urea and sugar mixture to contaminated groundwater (Boojum, 2003; Kalin & Wheeler, 2011). These remediation

approaches had limited success because they were never sufficiently scaled up for the full extent of contamination (CH2M, 2010).

Additional remediation measures have been more recently considered for the South Bay site. The preferred remediation strategy is to cap the tailings in-place with a bituminous geomembrane to limit water and oxygen ingress to the tailings, add a slurry wall around the perimeter of the tailings management area for enhanced groundwater seepage control, and install a permeable reactive barrier to intercept and treat seepage before it enters Boomerang Lake (CH2M, 2017). The goal of these remediation approaches is to reduce the contaminant loading to receiving water bodies such as Confederation Lake (CH2M, 2017).

1.3 Research Objectives

The main objective of this research was to examine how oxidation has affected the geochemistry of sulfide-rich tailings at the South Bay mine 40 years post-closure. Specific research objectives were to:

- Provide a detailed investigation into the hydrogeology, geochemistry, mineralogy, and microbiology of the site.
- Determine the extent to which sulfide minerals in the tailings have oxidized and investigate the factors that affect the rate of oxidation.
- Estimate the timeframe for which sulfide oxidation may continue if no remediation is implemented.
- Determine the mechanisms for acid neutralization in the tailings.
- Examine the mobility of metals, metalloids, and rare earth elements, including their mechanisms of release and potential attenuation in the tailings.

Overall, this research will help enhance our scientific knowledge of sulfide oxidation processes in abandoned tailings impoundments and will be able to better inform regulators regarding remediation decisions at the South Bay site.

1.4 Thesis Organization

This thesis is divided into four chapters. Chapter 1 is a general introduction describing acid mine drainage geochemistry and the research objectives for this thesis. Chapters 2 and 3 were written as separate research papers for submittal to peer-reviewed journals. Chapter 2 describes the hydrogeology, geochemistry, and microbiology of the South Bay tailings, with a focus on the extent of sulfide mineral oxidation. Chapter 3 describes the mobility and abundances of rare earth elements and elements released through sulfide mineral oxidation and the acid neutralization reactions in the tailings. The final chapter, Chapter 4, presents a summary of the conclusions from this research and recommendations of further research.

Chapter 2: Geochemistry of Pyrite-Rich Tailings at an Abandoned Cu-Zn Mine 40 Years Post-Deposition

Executive summary

Acid mine drainage from abandoned mine sites can create long-term environmental contamination. This study investigates the effects of 40 years of oxidation on tailings geochemistry at the abandoned South Bay mine (northwestern Ontario, Canada). Samples of pore-water, pore-gas, and tailings cores were collected for this study. Results indicate a shallow zone of oxidation and sulfide mineral depletion within the upper 0-15 cm of tailings. Factors contributing to the shallow extent of oxidation include a relatively high moisture content, a high sulfide content (average 27 wt. % S in the unoxidized tailings), and the predominance of pyrite over other sulfide minerals. Tailings pore-waters are acidic ($1.27 < \text{pH} < 7.03$) with high concentrations of dissolved Fe (up to $8,320 \text{ mg L}^{-1}$) and SO_4 (up to $23,700 \text{ mg L}^{-1}$). 16s rRNA sequencing indicated an elevated abundance of acidophilic Fe- and S-oxidizing bacteria in the shallow tailings, and an elevated abundance of sulfate-reducing bacteria where the pH transitions from acidic to circumneutral under anaerobic conditions. Sulfide oxidation modelling predicts that the tailings will continue to oxidize for approximately 4000 years if no remediation measures are taken to limit oxidation.

2.1 Introduction

The mining industry produces very large quantities of waste materials worldwide in the form of waste rock and tailings. Sulfide ore deposits often contain high concentrations of sulfide gangue minerals such as pyrite [FeS_2] and pyrrhotite [$\text{Fe}_{(1-x)}\text{S}$], which become concentrated in mine wastes. Acid mine drainage and metal leaching occurs when these sulfide-bearing wastes are exposed to oxidation processes; the overall oxidation reaction of pyrite releases dissolved Fe, SO_4^{2-} and H^+ (Nordstrom, 1982; Evangelou & Zhang, 1995; Blowes et al., 2014). In tailings impoundments, exposure to atmospheric O_2 depletes the sulfide mineral content near the surface and the oxidation front progresses deeper into the tailings over time. The timeline for complete sulfide mineral oxidation at mine sites can range from decades to millennia (Nordstrom & Alpers, 1999; Moncur et al., 2005; Tabelin et al., 2022).

The environment surrounding mine sites can be significantly impacted by acidic drainage and high concentrations of dissolved metals discharging from mine wastes. As such, within recent decades, governments in many parts of the world have imposed regulations to limit the release of contaminants from mine sites through effluent water quality standards (Rezaie & Anderson, 2020). However, many historical mining operations predate requirements for environmental protection associated with acid mine drainage. Long-lasting contamination sources exist at many sites, and efforts to remediate legacy contamination remain in progress. There is estimated to be over 600,000 abandoned and closed mines around the world, many of which pose environmental contamination issues (Park et al., 2019). Optimal remediation strategies differ based on site conditions, and abandoned sites can pose additional issues compared to actively operating mine sites since extensive oxidation can create accumulations of secondary minerals, high concentrations of dissolved metals in pore-waters, and host abundant colonies of acidophilic iron- and sulfur-oxidizing microorganisms. Although many acid-generating abandoned mine sites have been studied in detail, each site possesses different hydrogeochemical characteristics, and the extent of sulfide mineral oxidation and sources of contamination will differ based on site-specific conditions.

This study focuses on a tailings impoundment at the abandoned South Bay mine, a former underground Cu-Zn mine in northwestern Ontario that has been generating acid mine drainage for over 40 years. Commodities recovered from the South Bay mine included Cu, Zn and Ag. Initial characterization of the ore-associated metavolcanic rocks indicated elevated concentrations of some rare earth elements (REE) (Leshner et al., 1986), which were not targeted during metallurgical processing. The objectives of this study were to characterize the current geochemistry, hydrogeology, and microbiology of the tailings, and determine the extent to which the sulfide minerals have been oxidized and how long sulfide oxidation may continue. These results will help inform the development of effective remediation strategies to limit further environmental degradation.

2.2 Site Description

The South Bay mine is located in northwestern Ontario, 65 km NE of the town of Ear Falls. The mine site lies adjacent to Confederation Lake, Boomerang Lake and Mud Lake (Figure 2.1). Mean annual precipitation in the region from 1981-2010 was 686.4 mm (Environment and Climate Change Canada, 2023). The average temperature during the same period was -18.3 °C in January and 18.1 °C in July, with an average annual temperature of 1.3 °C (Environment and Climate Change Canada, 2023).

The ore deposit was associated with felsic volcanic rocks in the Uchi-Confederation greenstone belt (Wan & Warburton, 1979). The ore was composed primarily of pyrite, with sphalerite [ZnS] and chalcopyrite [CuFeS₂] as the other principal sulfides, and minor constituents of galena [PbS], cassiterite [SnO₂], pyrrhotite, magnetite [Fe₃O₄], native silver, argentite [Ag₂S], and arsenopyrite [FeAsS] (Pollock et al., 1972; Thurston et al., 1978; Seccombe & Clark, 1981). Chlorite alteration of the quartz feldspar porphyry wall-rock was commonly observed in close relation to massive sulfide ore lenses (Wan and Warburton, 1979). Gangue within the massive sulfides consisted of dacite and chert fragments, quartz [SiO₂], carbonate, and minor sericite [KAl₂(AlSi₃O₁₀)(OH)₂] and chlorite (Thurston et al., 1978). The

underground mine was in production from 1971 to 1981, with ore deposits producing an average of 14.5% Zn, 2.3% Cu, and 3.5 oz/ton Ag from reserves totalling 1,600,000 tons (Wan and Warburton, 1979).

The tailings were deposited into a peat bog basin north of the mill site, enclosed by natural topography, concrete dams built on top of bedrock, and dykes (Boojum Research Ltd., 2003; CH2M Hill, 2010). The tailings impoundment area currently contains approximately 785,000 tonnes of tailings covering an area of 25 ha (CH2M Hill, 2010). The tailings are deepest near the centre south-west area of the impoundment at over 10 m depth, and thin out towards the edges of the impoundment and the Decant Pond (CH2M Hill, 2010). The tailings are underlain by a thin layer of peat, followed by sand and gravel, then till and finally bedrock (CH2M Hill, 2010). Boomerang Lake has been contaminated throughout the life of the mine, whereas contamination of Mud Lake began in 1994 after a deep groundwater plume arrived at the lake (Boojum Research Ltd., 2004).

Passive biological treatment methods were implemented at the site from the mid 1980's to early 2000's, but acidic drainage persists and additional remediation measures are planned (CH2M Hill, 2010; CH2M Hill, 2017). Ecological engineering remediation work included the addition of various carbon sources and wood ash to Boomerang Lake and Mud Lake, phosphate rock applications to the mill area, portions of the tailings impoundment, and Boomerang Lake, magnesium scrap additions to Boomerang Lake, and trials of urea additions to contaminated groundwater to induce sulfate reduction (Boojum Research Ltd., 2003; CH2M Hill, 2010). Additionally, a sand and gravel layer, approximately 30 cm thick, was placed on top of the tailings and revegetated soon after mine operations ceased. The tailings have continued to oxidize and produce acidic drainage, which has heavily impacted Boomerang Lake and Mud Lake, which were recorded to have pH values between pH 2.7 and pH 3.2 in 2021 and 2022.

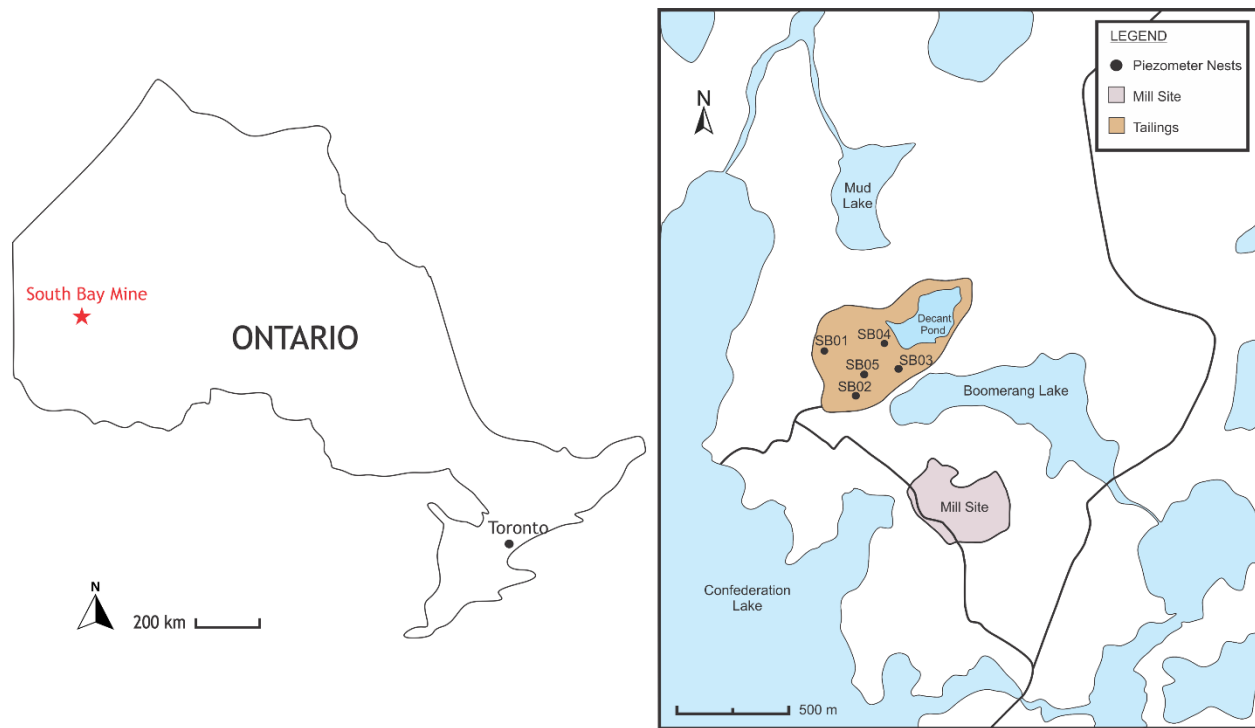


Figure 2.1. Location of the South Bay mine in Ontario, Canada (left). Site map of the South Bay mine with locations of 2021 instrument installations shown on the tailings area (right).

2.3 Methods

2.3.1. Field Installations

Instrumentation nests consisting of drive-point piezometers, soil-water samplers, and soil moisture and temperature sensors were installed in depth profiles at five separate locations (SB01, SB02, SB03, SB04, and SB05) on the South Bay tailings impoundment in the spring of 2021 (Figure 2.1). Piezometers were driven directly into the tailings using a Pionjar 120 portable hammer drill to the desired depth, with the deepest piezometers installed at the bottom of the tailings or at the drill refusal depth. Soil-water samplers (Model 1900) were installed in auger holes and were backfilled with silica flour around the ceramic cup, and with bentonite and soil around the PVC casing. Five additional water table wells were installed around the tailings using steel pipes driven directly into the ground with a slide hammer.

2.3.2. Groundwater Analysis

Water samples were collected from all installed piezometers and soil-water samplers using a peristaltic pump in the spring and fall of 2021 and 2022. The soil-water samplers were placed under suction using a vacuum pump for 1-3 days prior to sampling to allow pore water from the unsaturated zone to enter the porous ceramic cup in the samplers. Measurements of pH and redox potential (Eh) were made in the field during sample collection using an Orion Ross Ultra pH Electrode and Thermo Orion Sure-Flow ORP/Redox Electrode connected to an Orion Star A321 meter. The pH electrode was calibrated daily using pH 4, 7, and 10 buffer solutions, or pH 1.68, 4, and 7 buffer solutions if the sampled groundwater was highly acidic. The Eh electrode was checked daily against Light's solution (Light, 1972) and Zobell's solution (Nordstrom, 1977). Alkalinity was determined in the field using a Hach digital titrator with filtered (0.45 μm) water samples, bromocresol green-methyl red indicator and 0.16 N or 1.6 N sulfuric acid (Hach Method 10244). Filtered (0.45 μm) water samples were collected for geochemical analyses, including cations, anions, dissolved organic carbon (DOC) and aqueous sulfate isotopes.

All samples were stored at 4 °C until analysis. Cation samples were preserved with 67-70% HNO_3 (OmniTrace[®]) and DOC samples were preserved with H_2SO_4 to pH < 2. Cation concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6000, Thermo Fisher Scientific) and inductively coupled plasma mass spectroscopy (ICP-MS, X Series II, Thermo Fisher Scientific). Anion concentrations were determined by ion chromatography (IC, Dionex DX600 IC-CO3 system). DOC concentrations were analysed with an Aurora 1030W TOC Analyzer (O.I Analytical, College Station, TX) using wet oxidation with heated sodium persulfate.

Sulfate isotope ratios for $\delta^{34}\text{S}\text{-SO}_4$ and $\delta^{18}\text{O}\text{-SO}_4$ were measured at the Environmental Isotope Laboratory at the University of Waterloo. Samples were first precipitated as BaSO_4 using BaCl_2 then rinsed with deionized water and oven dried. Measurements of $\delta^{34}\text{S}$ were determined using a 4010 Elemental Analyzer (Costech Instruments, Italy) coupled to an IsoChrom (Micromass, UK) continuous flow isotope ratio mass spectrometer (CF-IRMS). Measurements of $\delta^{18}\text{O}$ were determined by high

temperature combustion with a Vario PYRO Cube elemental analyzer (Elementar) coupled to an IsoPrime CFIRMS (GV Instruments). Values of $\delta^{34}\text{S}$ were corrected to the Vienna Canyon Diablo Troilite (VCDT) standard, and values of $\delta^{18}\text{O}$ were corrected to the Vienna Standard Mean Ocean Water (VSMOW) standard.

2.3.3. Pore-Gas Analysis

Pore-gas concentrations of O_2 and CO_2 in the unsaturated zone were measured in the field at each sampling location. Stainless steel tubes were driven into the ground and pore-gas measurements were analysed every 5-10 cm depth using a portable O_2/CO_2 analyzer (Quantek Instruments Oxygen/Carbon Dioxide Analyzer, Model 902P), until saturation conditions prevented further gas measurements at deeper points.

2.3.4. Tailings Mineralogy and Geochemistry

Continuous cores of tailings material were collected from each of the five instrumentation sites by driving aluminum casing into the tailings with a Pionjar 120 and using a piston core-barrel technique (Starr & Ingleton, 1992). Cores were capped at both ends to limit atmospheric contact and core samples were stored at $-20\text{ }^\circ\text{C}$ prior to subsampling. Frozen core segments were cut in half lengthwise, then subsampled within an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, USA). Subsamples were freeze dried for total C/S measurements, and anaerobically air-dried for oxygen-sensitive mineralogical analysis including optical microscopy, X-ray diffraction (XRD), and synchrotron studies.

Total C and S concentrations were determined using an Eltra CS-2000 C/S Analyzer coupled with a CS800 induction furnace. Powder XRD data was collected at the Canadian Macromolecular Crystallography Facility (CMCF) beamline at the Canadian Light Source (CLS) and mineral phases were determined with semi-quantitative analysis using Sieve+ peak-matching software with the PDF-4+ minerals database. Polished quartz thin section slides were prepared by Vancouver Petrographics Ltd. (Langley, BC) and examined for mineralogical composition using reflected and transmitted light

microscopy (Nikon Eclipse LV100N-POL) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX; FEI Quanta Feg 250 ESEM).

Bulk S X-ray absorption near-edge spectroscopy (XANES) analysis was performed at the Soft X-Ray Microcharacterization Beamline (SXRMB) at the CLS in Saskatoon, Canada. Freeze-dried tailings samples were crushed using a mortar and pestle and stored and transported under anaerobic conditions. The powder was mounted onto C tape for analysis at the CLS. Fluorescence and total electron yield (TEY) spectra were measured simultaneously in a vacuum chamber of 10^{-7} torr. The fluorescence spectra were processed using Larch XAS Viewer version 0.9.56 (Newville, 2013). Reference spectra were measured for pyrrhotite, chalcopyrite, sphalerite, elemental S, jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$, schwertmannite $[\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4]$, gypsum $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$, Na-thiosulfate, K-tetrathionate, and Na-sulfite for use as linear combination fitting (LCF) standards. Because the measured spectra for pyrite showed signs of oxidation, the pyrite spectra from the European Synchrotron Radiation Facility (ESRF) Database of Inorganic Sulfur compounds (ESRF, 2005) was instead used as a LCF standard. Spectra analysed in duplicate were merged prior to normalization to a gypsum E0 reference of 2481.0 eV. LCF was performed over an energy range of 2460-2500 eV to estimate the fractions of S species present in each sample.

2.3.5. Physical and Hydraulic Properties

Moisture content, bulk density, and porosity measurements were obtained from cores collected from the unsaturated zone in September 2021. The cores were subdivided into 10 cm long sections in the field, then transported back to the laboratory for analysis. Each section was weighed, dried in a gravimetric oven at 70 °C for 24 hours, and then re-weighed to obtain the dry mass. Only cores which had minimal compaction during collection were used to determine the average bulk density and porosity. Volumetric water content and matric potential were continuously measured in-situ using TEROS 11 and TEROS 21 sensors (METER) respectively, installed in depth profiles within the walls of pits excavated adjacent to the piezometer nests, and the test pits were backfilled. Particle density was measured using a

Beckman 930 Air Comparison Pycnometer. Particle-size distributions were obtained using laser diffraction analysis (ANALYSETTE 22, Fritsch). Seasonal water levels were recorded in two piezometers using Solinst Leveloggers and corrected for barometric pressure using data from a ZL6 Pro data logger (METER) at site. The hydraulic conductivity was calculated from rising-head tests using the Hvorslev method and estimated based on the porosity and grain size distributions using the Kozeny-Carman equation (Bear, 1972):

$$(1) \quad K = \frac{g}{\nu} \frac{\varphi^3}{(1-\varphi)^2} \frac{d_{10}^2}{180}$$

where K is hydraulic conductivity [m s^{-1}], g is gravitational acceleration [m s^{-2}], ν is kinematic viscosity of water [$\text{m}^2 \text{s}^{-1}$], φ is porosity, and d_{10} is the grain size [m] at 10% passing.

2.3.6. DNA Extraction, PCR Amplification and Illumina MiSeq Sequencing

Core sub-samples from SB02, SB04, and SB05 were analysed for prokaryotic populations using high-throughput amplicon sequencing of 16S rRNA genes (Pakostova et al., 2020a). A total of 26 core sub-samples were analysed, including two samples were from the sand and gravel layer, three samples from oxidized and partially oxidized tailings, 17 samples from unoxidized tailings samples, three samples from the peat layer directly below the tailings, and one sample from the native sand below the peat (Table A1). Four samples were analysed in duplicate, and one sample was discarded before sequence data processing due to a low number of sequences. Total genomic DNA was extracted using a Sox Soil DNA Extraction Kit (Metagenom Bio Life Science) and stored at -20°C . PCR amplification of the V4 region of 16S rRNA genes was performed using the modified universal primers 515F/806R (Walters et al., 2016) prior to Illumina MiSeq sequencing (Metagenom Bio Life Science, Waterloo, Canada).

The method for sequence data processing is described in detail by Pakostova et al. (2020). Sequence data were analysed using the mothur program v.1.48.0 (updated: 20/05/2022; Schloss et al., 2009), and the MiSeq SOP (Kozich et al. 2013; https://www.mothur.org/wiki/MiSeq_SOP) from 08/03/2023. The data was first processed without merging the duplicate samples to compare similarity of

the prokaryotic populations on the phylum and order levels. Duplicate samples were then merged prior to further taxonomic investigations. Chimeric sequences were discarded based on predictions by vsearch using the Silva database for 16S rRNA gene sequences (release 132 for mothur, downloaded 18/03/2019) as a reference. Sequences were clustered into OTUs (operational taxonomic units) at a 97% similarity level by a de novo picking method. Taxonomic annotation of individual OTUs was based on mothur-formatted version of the Silva reference database. Several taxa (unknown, mitochondria, eukaryotes) were not considered for further data processing. The taxonomy files were screened for prokaryotic genera (or for higher taxa when identification to the genus level was not possible) and classified into sulfate-reducing bacteria (SRB), sulfur-oxidizing bacteria (SOB), and iron-oxidizing bacteria (IOB) if at least one species possessed the given metabolic trait.

2.4 Results

2.4.1. Hydrogeology

The temperature in the subsurface ranges throughout the year from 24 °C to 1 °C, with more variation in the shallow subsurface (Figure 2.2, Figure 2.3, Figure 2.4). The sand and gravel layer generally has a lower moisture content than the tailings and shows response to snowmelt in the spring and precipitation events in the summer whereas the moisture content in the tailings shows less variation (Figure 2.3, Figure 2.4). Periods of higher water content in the shallow tailings at SB02 (Figure 2.2) could reflect water mounding above the hardpan or slow propagation of precipitation through the unsaturated zone. The hydraulic gradient in the unsaturated zone is generally downwards except for drier spans during the summer months where there are periods of upwards hydraulic gradient, indicating upward movement of water toward the tailings surface (Figure 2.2, Figure 2.4).

In the unoxidized tailings, the average particle density (ρ_p) is 3.48 g cm⁻³, the average dry bulk density (ρ_b) is 1.74 g cm⁻³, and the average porosity (ϕ) is 50%. In the sand and gravel layer overlying the

tailings, the average ρ_p is 2.76 g cm^{-3} , the average ρ_b is 1.75 g cm^{-3} , and the average ϕ is 36%. The grain size varies from clay to sand-sized particles in the tailings, with less than 10% clay in all measured samples (Figure A1). Location SB04 has a relatively coarser grain size in the top 50 cm of tailings in comparison to SB02 and SB05.

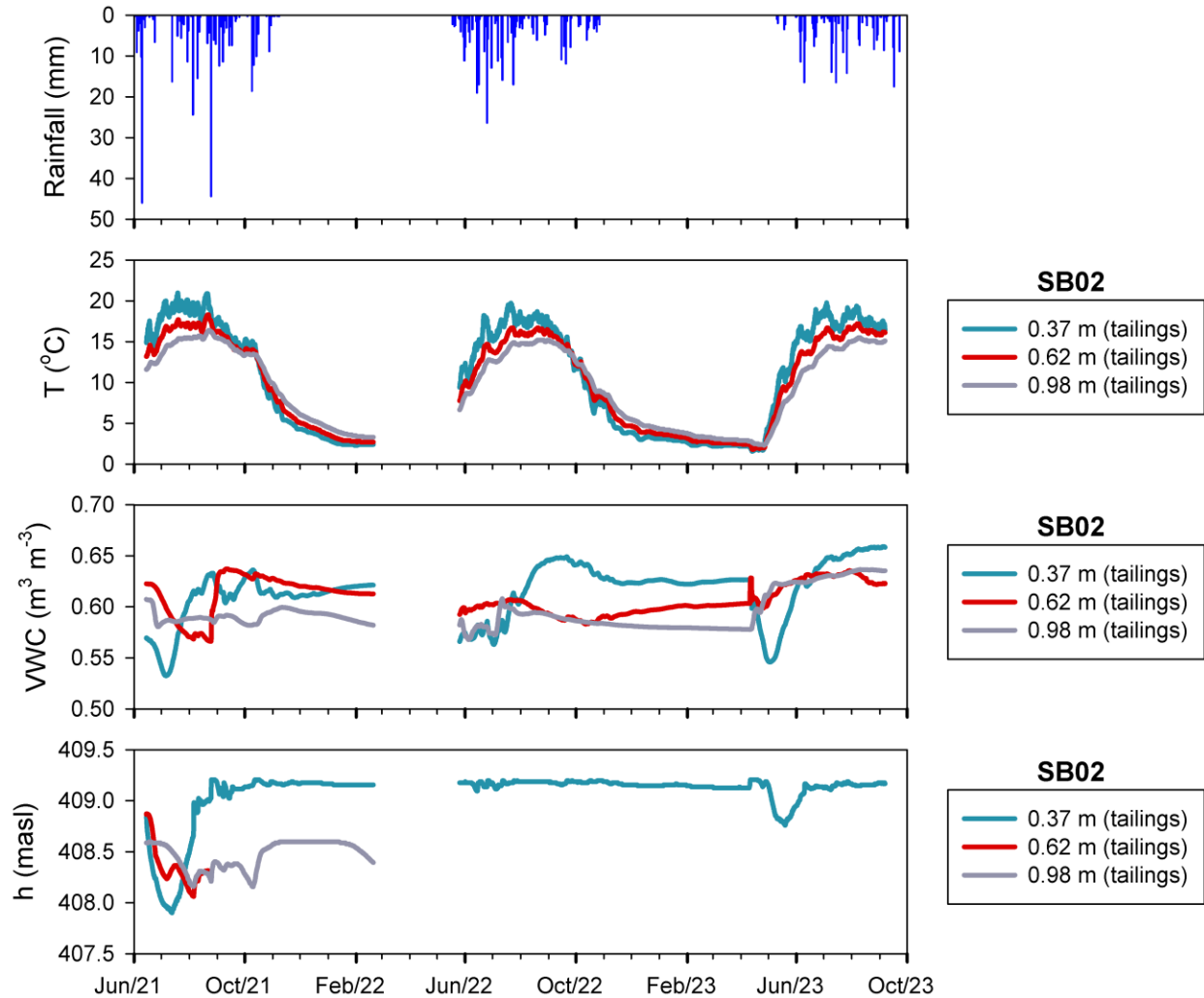


Figure 2.2. Rainfall, temperature, volumetric water content (VWC) and hydraulic head (h) at SB02. The hydraulic head was calculated from matric potential and is shown in metres above sea level (masl). Gaps in the data were due to instrument malfunctions.

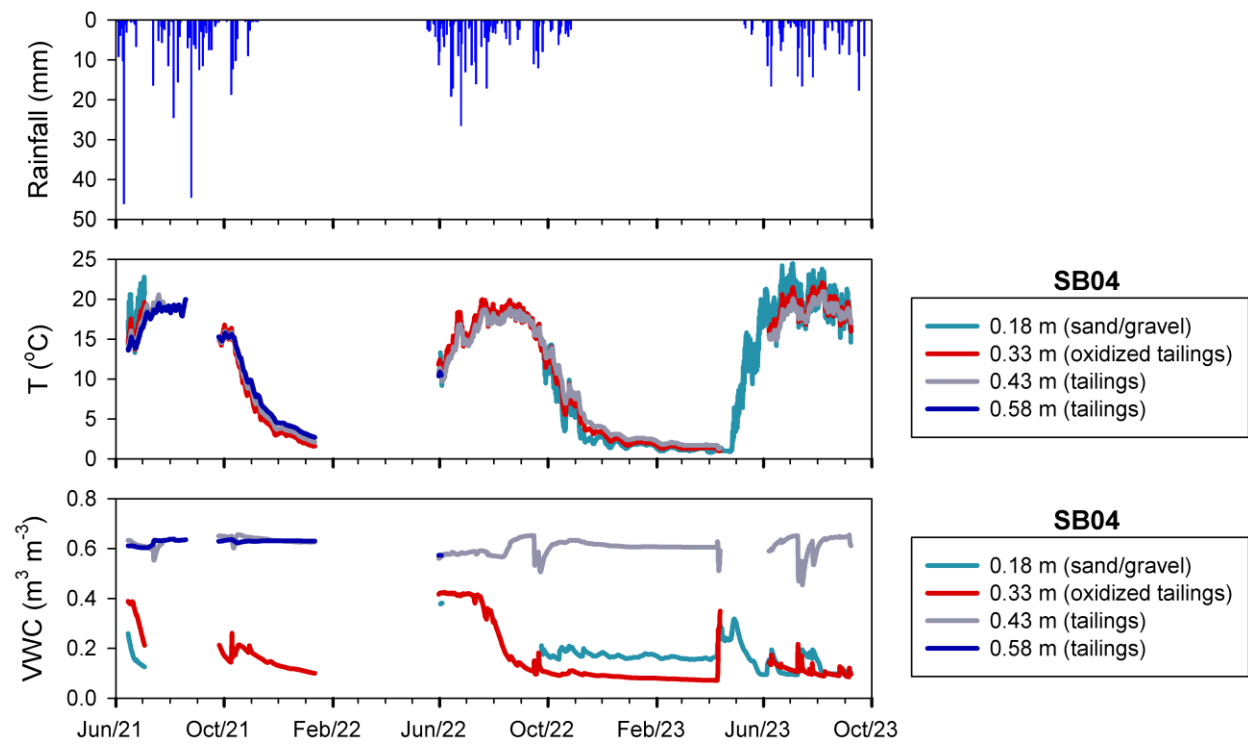


Figure 2.3. Rainfall, temperature, and volumetric water content (VWC) at SB04. Gaps in the data were due to instrument malfunctions, and hydraulic head was not included due to sensor error.

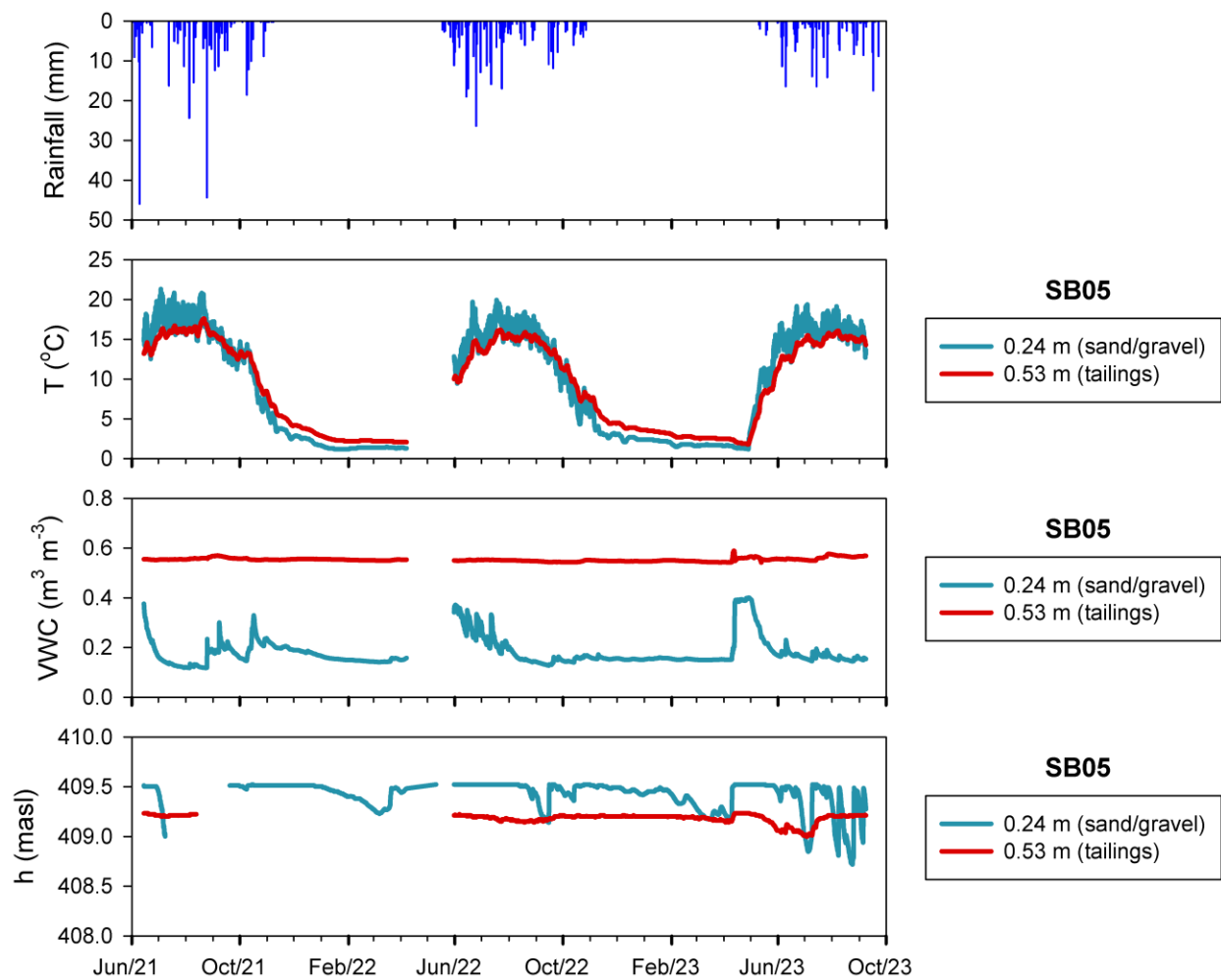


Figure 2.4. Rainfall, temperature, volumetric water content (VWC) and hydraulic head (h) at SB05. The hydraulic head was calculated from matric potential and is shown in metres above sea level (masl). Gaps in the data were due to instrument malfunctions.

A water table map (Figure 2.5) was constructed using water level data from installed piezometers and water table wells from June 2021 and surface water elevations estimated based on LiDAR data from 2009. This water table map represents a high water table period in the spring. The water table within the tailings is higher than the surrounding area and lakes, indicating that the tailings are a groundwater recharge area. Groundwater levels are highest near the southwest-central area of the tailings near location SB05, with flow occurring outwards from SB05 towards the other four sampling locations (Figure 2.5, Figure 2.6). A steep hydraulic gradient was observed between the south-east edge of the tailings and Boomerang Lake. Water levels in the tailings fluctuate seasonally and in response to precipitation events, with up to a 1.4 m seasonal difference measured in water level elevation (Figure A3). The highest water levels occur in the spring due to recharge from snowmelt, and water levels slowly decline throughout the summer, fall, and winter seasons. Previous hydrological modelling of the tailings area has identified that groundwater flow from the north end of the tailings is channeled northwards towards Mud Lake via a bedrock canyon aquifer (SCIMUS, 2003). Seepage from the southwest tailings area is directed towards Boomerang Lake via a diversion ditch, and seepage from tailings south of the Decant Pond flows directly towards Boomerang Lake (SCIMUS, 2003; CH2M Hill, 2010).

Hydraulic conductivity (K) values for the tailings, determined from rising head tests, ranged from $2.8 \times 10^{-8} \text{ m s}^{-1}$ to $5.4 \times 10^{-7} \text{ m s}^{-1}$ (Table A2). The vertical K (K_z) and the horizontal K (K_x) were calculated using the following equations (De Marsily, 1986):

$$(2) \quad K_z = \frac{d}{\sum_{i=1}^n \frac{d_i}{K_i}}$$

$$(3) \quad K_x = \sum_{i=1}^n \left[\frac{K_i d_i}{d} \right]$$

where d_i is the thickness of an individual layer and d is the total thickness of the tailings. The midpoint between each piezometer depth was used to define each new layer.

K_z was $1.0 \times 10^{-7} \text{ m s}^{-1}$ and the K_x was $2.2 \times 10^{-7} \text{ m s}^{-1}$ for the tailings. This K_x value was lower than K_x values determined by a previous groundwater modelling study at the site, which ranged from a median of $7.1 \times 10^{-7} \text{ m s}^{-1}$ to $7.2 \times 10^{-5} \text{ m s}^{-1}$ in different modelled tailings layers (SCIMUS, 2003). K values determined from the Kozeny-Carman equation ranged from $8.6 \times 10^{-8} \text{ m s}^{-1}$ to $2.6 \times 10^{-6} \text{ m s}^{-1}$, corresponding to d_{10} values ranging from $1.9 \text{ }\mu\text{m}$ to $10.4 \text{ }\mu\text{m}$.

The average vertical hydraulic gradient at each location ranged from -0.005 to 0.343, where a positive gradient indicates downward flow (Table A3). The largest average downward vertical hydraulic gradient occurred at location SB04 whereas location SB05 consistently had a vertical hydraulic gradient close to zero. Average vertical groundwater velocities ranged from -0.03 m a^{-1} at SB05 to 2.28 m a^{-1} at SB04 (Table A4). The horizontal hydraulic gradients between SB05 and the other four sampling locations ranged from an average of 0.00332 to 0.0123, with the steepest gradient between SB05 and SB02 (Table A3). The calculated average horizontal groundwater velocities ranged from 0.041 m a^{-1} to 0.153 m a^{-1} (Table A4).

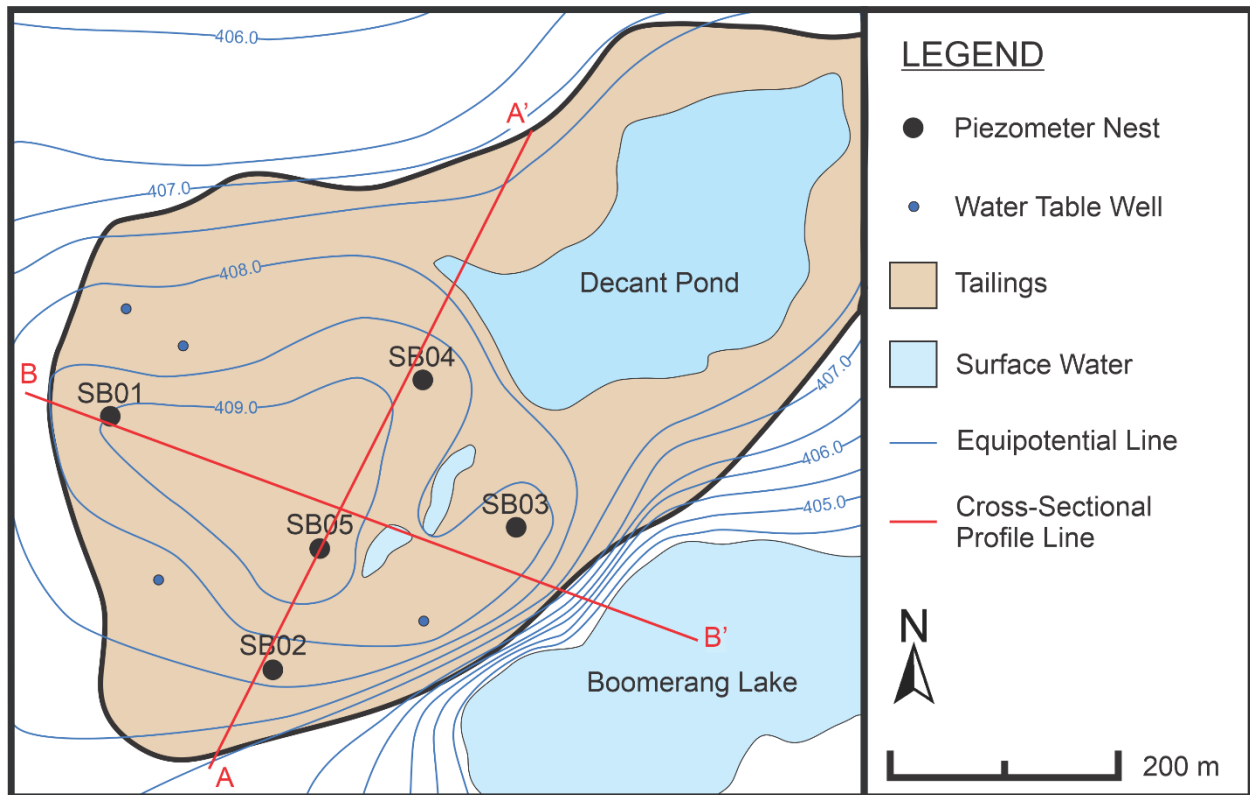


Figure 2.5. Water table map of the South Bay tailings impoundment area. Water levels from the piezometer nests and water table wells were collected in June 2021.

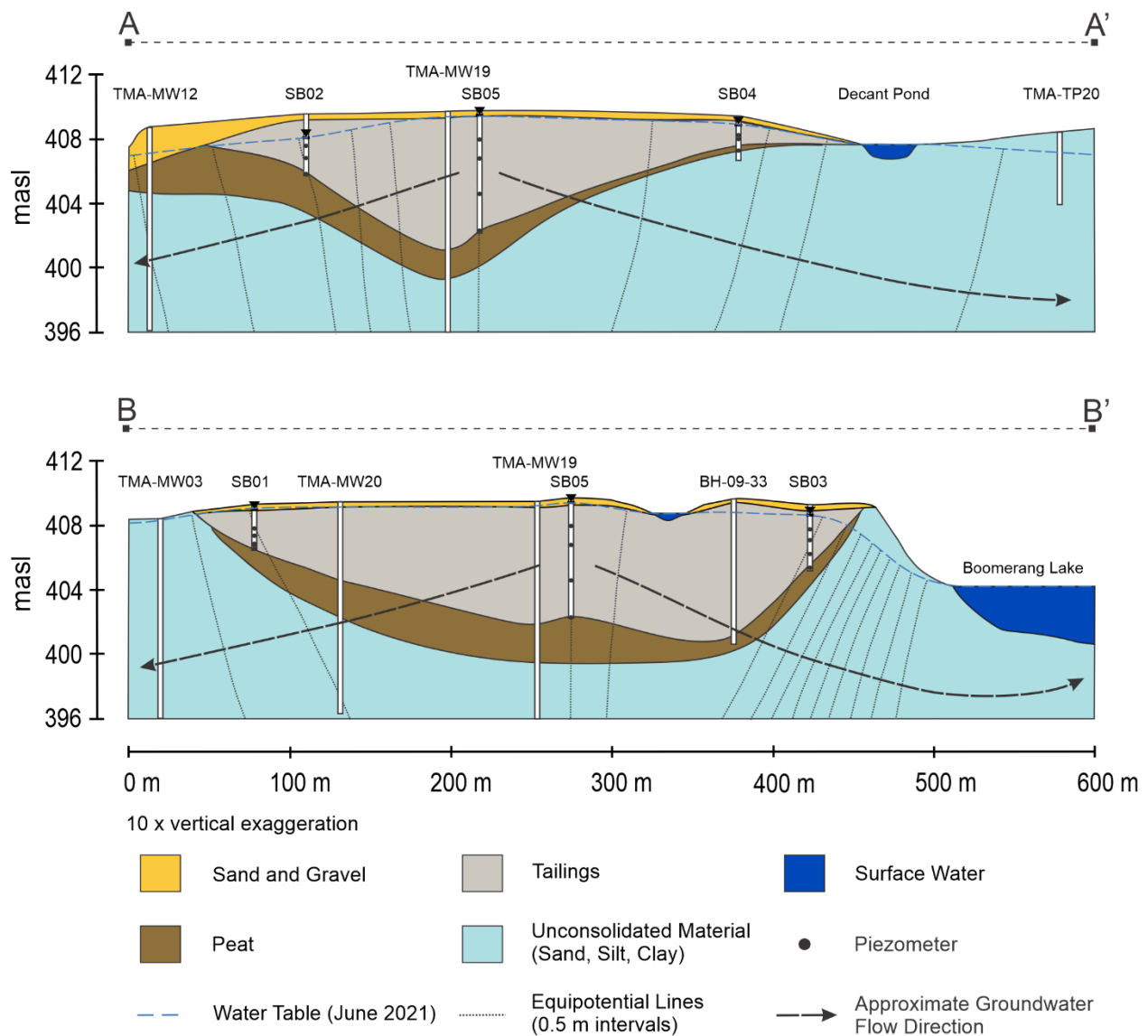


Figure 2.6. Cross-sectional profiles along transects A-A' and B-B' (Figure 2.5) showing tailings stratigraphy, water table elevation, and groundwater flow direction. Borehole data from CH2M Hill (2010; 2017) was used to determine tailings area stratigraphy in addition to cores collected from this study.

2.4.2. Pore-Water Geochemistry

In the sand and gravel layer, pore-waters are near-neutral to acidic, with low dissolved Fe (0.24-1.3 mg L⁻¹, mean (μ)=0.59 mg L⁻¹, standard deviation (sd)=0.36 mg L⁻¹) and SO₄ (37-888 mg L⁻¹, μ =411 mg L⁻¹, sd=415 mg L⁻¹) relative to the tailings, and alkalinity in the range of 0-66 mg L⁻¹ as CaCO₃ (μ =21 mg L⁻¹, sd=25 mg L⁻¹). The tailings pore-waters are acidic within the unsaturated and variably saturated zone near the tailings-sand interface (Figure 2.7). Minimum measured pH values at SB02, SB04, and SB05 were 2.68, 1.27, and 1.49, occurring at 0.83 m, 0.87 m, and 0.36 m depth, respectively.

Geochemical conditions were oxidizing near the top of the tailings where the pore-waters are acidic and became more reducing with depth where the pH increases to near-neutral. Elevated concentrations of sulfide mineral oxidation products, including Fe (μ =1490 mg L⁻¹, sd=1650 mg L⁻¹) and SO₄ (μ =3710 mg L⁻¹, sd=3910 mg L⁻¹) occurred within the tailings profile, with maximum concentrations measured up to 8,320 mg L⁻¹ of Fe and 23,700 mg L⁻¹ of SO₄ at the top of the tailings (0.36 m depth) at location SB05. Thiosulfate concentrations were commonly below detection limit (<0.5 or <1 mg L⁻¹), with maximum concentrations of 3.41 mg L⁻¹. Nitrate concentrations were generally below detection limit (< 1 mg L⁻¹), phosphorus concentrations ranged from <0.07 to 20.7 mg L⁻¹, and DOC concentrations ranged from 4.5 to 69 mg L⁻¹.

The bottom sampling point at location SB05 (7.48 m depth) occurs at the very base of the tailings where it overlays peat. This deepest sampling point shows a sharp increase in alkalinity, up to 650 mg L⁻¹ as CaCO₃, together with reducing conditions and a large decrease in dissolved concentrations of Fe and SO₄. Aqueous sulfate isotopic analysis indicates an enrichment in $\delta^{34}\text{S-SO}_4$ and an enrichment in $\delta^{18}\text{O-SO}_4$ at the base of the tailings (Figure 2.7).

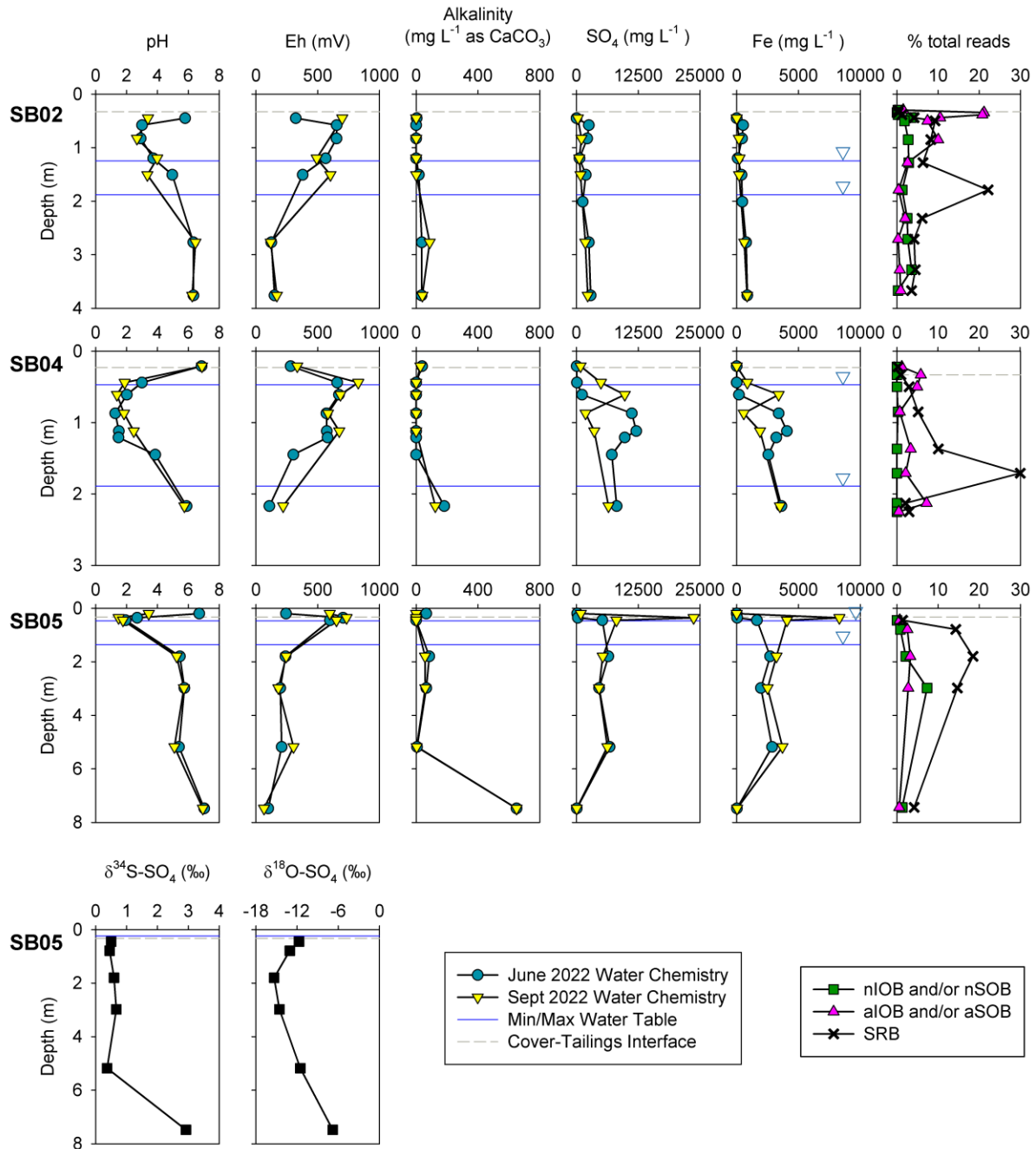


Figure 2.7. Pore-water chemistry, prokaryotic population proportions, and sulfate isotope depth profiles at SB02, SB04, and SB05. Proportions of total reads of neutrophilic sulfur- (nSOB) and/or neutrophilic iron-oxidizing bacteria (nIOB), acidophilic sulfur- (aSOB) and/or acidophilic iron-oxidizing bacteria (aIOB) and sulfate- (and/or sulfur-) reducing bacteria (SRB) are plotted in the right-most column.

2.4.3. Pore-Gas and Sulfide Oxidation Modelling

Oxygen concentrations remained close to atmospheric levels (20.9%) within the sand and gravel layer, then decreased rapidly within the tailings, reaching measured O_2 values of $<0.1\%$ (Figure 2.8). At locations SB02 and SB05, O_2 concentrations decreased sharply within the top 10 cm of tailings, whereas at location SB04, O_2 concentrations displayed a more gradual decline within the top 20 cm of tailings before reaching a concentration of $<1\%$. Pore-gas CO_2 concentrations are elevated in the tailings at location SB02, increasing with depth to a maximum CO_2 concentration of 6.7%.

The rate of O_2 diffusion and sulfide oxidation was modelled using PYROX, a 1-D finite element model for non-homogeneous media based on the shrinking-core model (Wunderly et al., 1996). Table 2.1 indicates the parameters used for the tailings in the PYROX simulations. Values were based on average parameters measured in the unoxidized tailings. The sand and gravel layer overlying the tailings was modelled using the average measured ρ_b of 1751 kg m^{-3} and ϕ of 0.36. The moisture content was variable, with input values similar to the continuous in-situ moisture content measurements collected within test pits, but with some variation to better fit with field-measured data and to account for variable porosity within the tailings. The volumetric moisture content input for the sand and gravel ranged from 0.10-0.12, whereas the moisture content within the tailings was usually set as 0.42, except for the shallow tailings at SB04 which had a lower volumetric moisture content set to 0.10, similar to the values measured in-situ (Figure 2.3). The weight fraction of pyrite was determined from the average weight % S in the top meter of unoxidized tailings at locations SB02, SB04, and SB05, assuming that all S is present as pyrite.

The PYROX model was run with nodes distributed evenly throughout the unsaturated zone at 0.01 m intervals and a time step of 0.01 years. D_2 is the diffusion coefficient for the oxidized coating forming on the sulfide mineral grains and was adjusted as a fitting parameter to obtain a best fit against the field-measured data. Sulfide oxidation was assumed to only occur for 6 months of the year as temperatures near or below freezing inhibit oxidation in the winter months. The impact of the discontinuous hardpan layer at SB02 was not incorporated into these calculations.

Table 2.1. PYROX model input parameters for unoxidized tailings and modelled time for complete sulfide-mineral oxidation.

	SB02	SB04	SB05
D₂ (m² s⁻¹)	5.0 × 10 ⁻¹³	5.0 × 10 ⁻¹³	5.0 × 10 ⁻¹³
Wt. fraction pyrite	0.56	0.56	0.56
Particle size (µm)	30	70	30
Tailings φ	0.5	0.5	0.5
Tailings ρ_b (kg m⁻³)	1738	1738	1738
Temperature (°C)	13	13	13
Average depth of water table (m)	1.6	0.95	0.6
Time to complete oxidation (years)	4260	1480	430

The modelled O₂ concentrations and fraction of sulfide minerals remaining were in good agreement with field-measured values (Figure 2.8). The model results indicate that the rate of sulfate release from the tailings is highest at the initiation of oxidation, and rapidly decreases within the first several decades. However, it is predicted that sulfate will continue to be released from the tailings at a lower rate for many more centuries if no further remediation actions are taken. The time for complete oxidation of sulfide minerals within the vadose zone was calculated to range between 430 – 4,260 years.

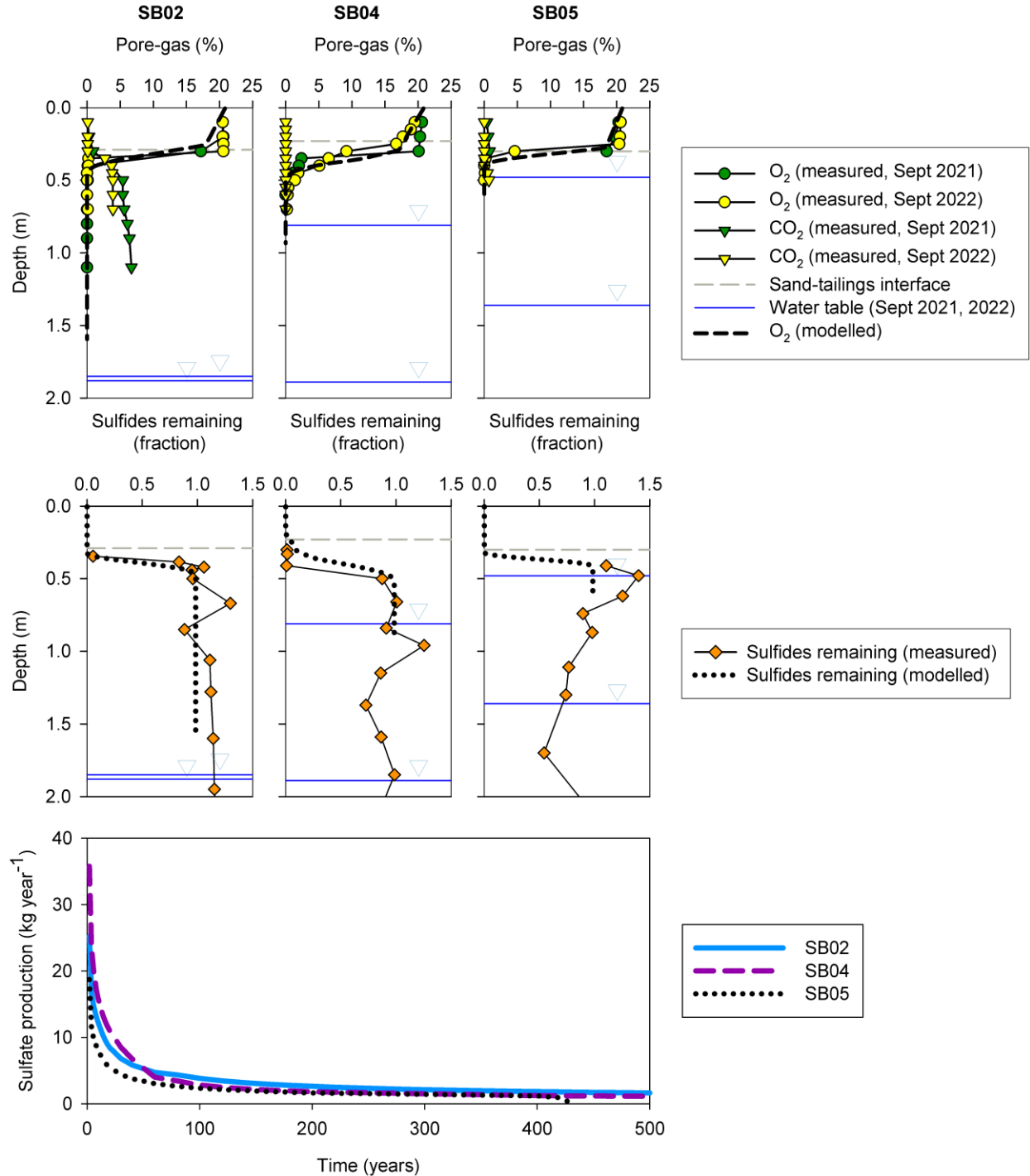


Figure 2.8. Top: depth profiles of measured pore-gas concentrations of O_2 and CO_2 and PYROX-modelled O_2 after 40 years of oxidation. Middle: depth profiles of measured and modelled fraction of sulfides remaining in the tailings. The measured values were calculated by dividing the wt.% S by the average wt.% S in the unoxidized tailings. Values greater than 1.0 represent a sulfide content higher than the average. Bottom: modelled annual sulfate production.

2.4.4. Tailings Mineralogy and Geochemistry

Analysis of tailings solids with XRD indicated that pyrite was the predominant sulfide mineral, comprising between 24-64 weight % of the unoxidized tailings, with sphalerite as the second-most abundant sulfide mineral (Figure A5). Quartz was the primary non-sulfide mineral, with lower amounts of albite [NaAlSi₃O₈], muscovite [KAl₂(Si₃Al)O₁₀(OH)₂], and chlorite. Optical microscopy and SEM-EDX analysis of the tailings confirmed that pyrite is the most abundant sulfide mineral, with minor amounts of sphalerite and chalcopyrite, and trace amounts of pyrrhotite, galena, arsenopyrite, and cassiterite. In the oxidized tailings within the top 5 cm at locations SB02 and SB03, Fe(III) (oxy)hydroxides and hydroxysulfates were observed with optical microscopy. SEM-EDX analysis indicated that the Fe(III) hydroxysulfates have compositions consistent with jarosite and schwertmannite.

A discontinuous hardpan layer was detected at locations SB01, SB02, and SB03, spanning 10-20 cm and starting at 0.5-0.6 m depth (0.2-0.3 m below the top of the tailings). This hardpan layer was identified as a denser layer which was more difficult to excavate within test pits. Observations with optical microscopy indicated that trace amounts of Fe(III) (oxy)hydroxides and hydroxysulfates were present in the hardpan, but these secondary phases could not be identified by SEM-EDX and XRD analyses. No hardpan was identified at locations SB04 or SB05, potentially due to a higher water table at SB05 limiting accumulation of oxidation products and highly acidic porewaters at SB04 limiting secondary mineral precipitation.

The depth progression of sulfide-mineral alteration was examined in thin section at location SB02 (Figure 2.9), with observations classified using the sulfide alteration index (SAI) (Moncur et al, 2005; Blowes and Jambor, 1990) (Table 2.2); ten being the most altered and one being the least altered. Samples near the surface of the tailings showed extensive sulfide-mineral alteration, with abundant Fe(III) (oxy)hydroxides and only trace pyrite. Pyrrhotite is absent in the top several cm of tailings and becomes progressively less altered with depth, displaying extensive alteration at 10 cm below the tailings-sand interface and minor alteration at 33 cm below the tailings-sand interface. Covellite [CuS] is present on

many of the alteration rims surrounding partially oxidized pyrrhotite grains. Below 1 m depth, pyrrhotite, as well as the other sulfide minerals, remain relatively unaltered.

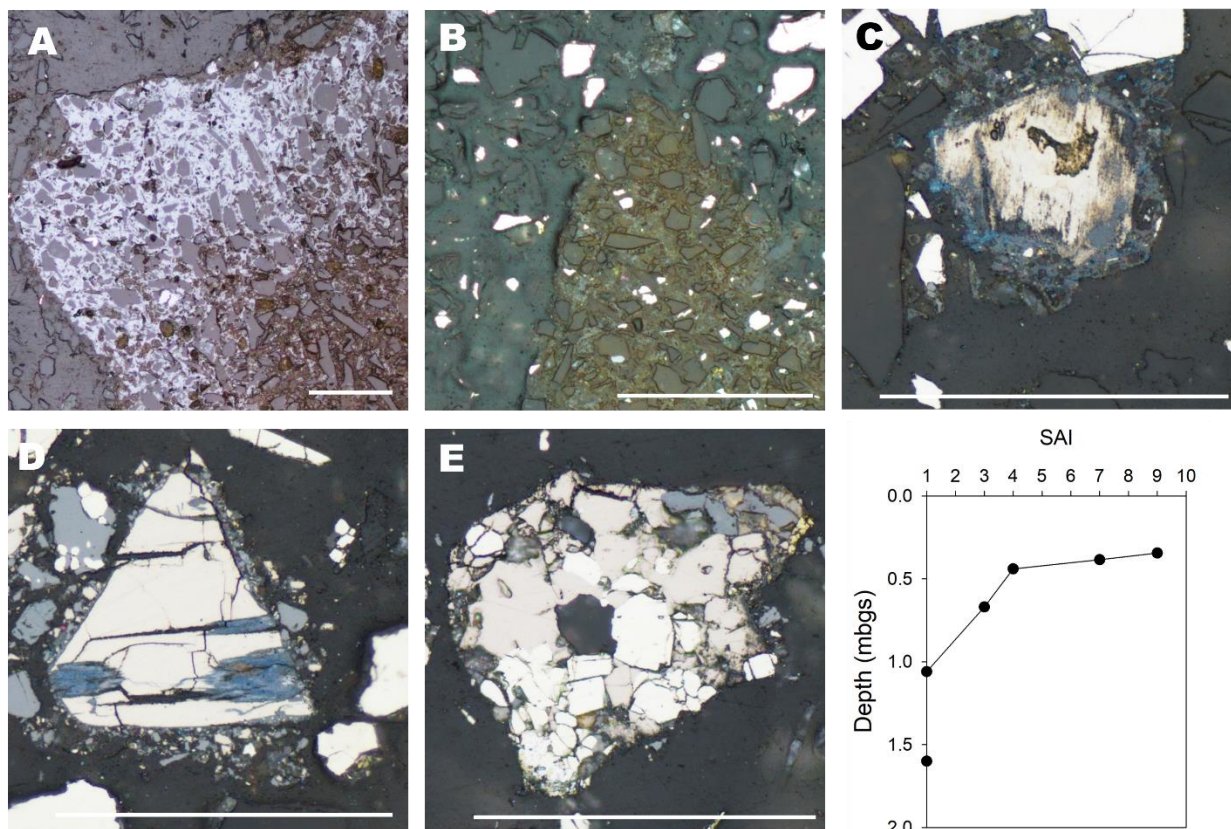


Figure 2.9. Depth progression of sulfide-mineral alteration within the tailings at location SB02. (A) 0.5 cm below tailings-sand interface: Fe(III) (oxy)hydroxides and hydroxysulfates around residual fine-grained silicate minerals. Sulfide minerals are almost all depleted, with only trace pyrite remaining. (B) 4 cm below tailings-sand interface: Fe hydroxysulfates with fine-grained pyrite. (C) 10 cm below tailings-sand interface: Partially oxidized pyrrhotite grain with covellite (blue) in the alteration rim. (D) 33 cm below tailings-sand interface: Pyrrhotite with a narrow alteration rim and covellite (blue). (E) 72 cm below tailings-sand interface: Intergrowth of pyrite and pyrrhotite with minimal alteration. The sulfide alteration index (SAI) indicates the relative alteration intensity of the sulfide minerals with depth in metres below ground surface (mbgs). White scale bar represents 100 μm .

Table 2.2. Sulfide alteration index (Moncur et al, 2005; Blowes and Jambor, 1990)

Index	Alteration
10	Almost complete oxidation of sulfides; traces of chalcopyrite and pyrite
9	Only sparse pyrite and chalcopyrite; no pyrrhotite or sphalerite
8	Pyrite and chalcopyrite common, but chalcopyrite proportion higher than normal possibly because of pyrite dissolution; no pyrrhotite or sphalerite
7	Pyrite and chalcopyrite proportions normal; pyrrhotite absent but sparse sphalerite present
6	Pyrrhotite absent but sphalerite common
5	Pyrrhotite represented by marcasite pseudomorphs
4	First appearance of pyrrhotite, but only as remnant cores
3	Cores of pyrrhotite abundant
2	Well-developed cores of pyrrhotite, with narrower alteration rims; replacement by marcasite decreasing, and pseudomorphs are absent
1	Alteration restricted to narrow rims on pyrrhotite

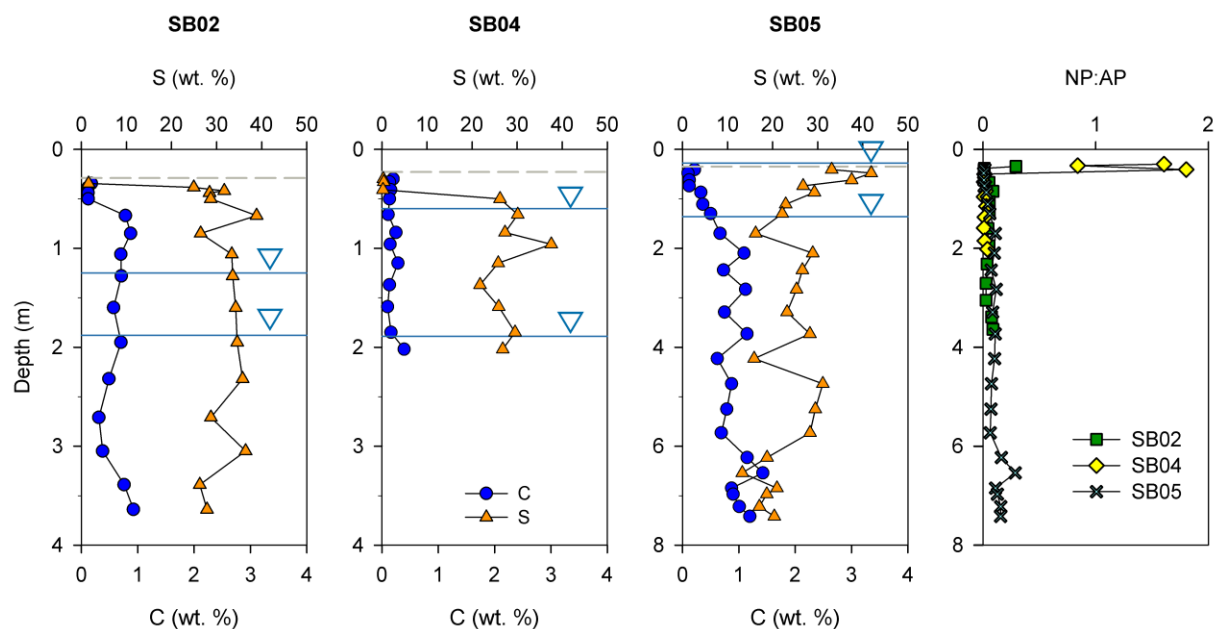


Figure 2.10. Total carbon (blue circles), total sulfur (orange triangles), and neutralization potential (NP) to acid potential (AP) ratio depth profiles. The horizontal grey dashed line represents the interface between the sand and gravel layer and the tailings, the blue lines represent the minimum and maximum measured water table. Note that the vertical axes are not consistent across all plots.

Sulfur concentrations were much higher compared to total C concentrations in the tailings, with depletion of total C near the surface extending deeper than the depletion of total S (Figure 2.10). In the upper few cm of tailings at location SB02, the total S contents have been depleted to <2 wt.% S, whereas

the unoxidized tailings below contain on average 31 wt.% S. Carbon concentrations at SB02 were similarly depleted in the top 30 cm of tailings to <0.3 wt.% C and increased to an average of 0.7 wt.% C at depth. At location SB04, sulfides were oxidized to a greater depth, with <0.5 wt.% S in the top 30 cm of tailings, increasing to an average of 30 wt.% S in the unoxidized tailings. Carbon concentrations remained depleted to <0.2 wt.% C throughout the tailings depth profile at SB04. Elevated concentrations of total S (average 25 wt.% S) occur throughout the depth profile at SB05. The carbon concentrations at SB05 were depleted to <0.4 wt.% C in the top meter but increased to an average of 0.9 wt.% C below 1 m.

The neutralization potential (NP) for the tailings was calculated based on the assumption that all C is present as CaCO_3 , and the acid potential (AP) was calculated using the total S content. The NP:AP ratio for all samples, except for the shallow oxidized tailings at SB04, was <1, indicating potentially acid generating tailings.

2.4.5. X-Ray Absorption Spectroscopy

Sulfur XANES spectra collected on bulk tailings samples from SB02 and SB04 indicate the presence of sulfate species such as schwertmannite and jarosite near the top of the tailings (Figure 2.11). Jarosite and schwertmannite are both Fe(III) hydroxysulfate minerals with very similar S XANES spectra, therefore it is difficult to distinguish between them with LCF. At location SB02, the sulfate species are largely restricted to the very top of the tailings, with low amounts of sulfate (2-4% of total S species) present in samples from 4 cm below the tailings-sand interface and the hardpan at 41 cm below the tailings-sand interface. At location SB04, sulfate species are present in significant proportions from the top of the tailings to 12 cm below the tailings-sand interface, and are present as a minor phase (1-7% of total S species) in deeper tailings (Table 2.3). LCF indicates that pyrite was the major S species in the unoxidized tailings. LCF of the XANES spectra indicated the presence of elemental S, generally in the upper tailings samples, however accurately distinguishing between reduced S species such as elemental S, pyrite, pyrrhotite, sphalerite, and chalcopyrite is difficult due to the similarities in their E0 values. Intermediate S

species including thiosulfate, tetrathionate, and sulfite were not present in sufficient amounts to be accurately detected using LCF in the tailings samples. Gypsum was considered in the linear combination fitting exercise but was not included in any of the best fit results. The apparent absence of gypsum is consistent with the observation of pore-waters that are undersaturated with respect to gypsum which may be attributed to low concentrations of dissolved Ca observed in the shallow tailings where calcite depletion is extensive (Chapter 3). The R-factor and reduced chi-square are goodness-of-fit statistics, with a smaller R factor indicating a lower degree of misfit.

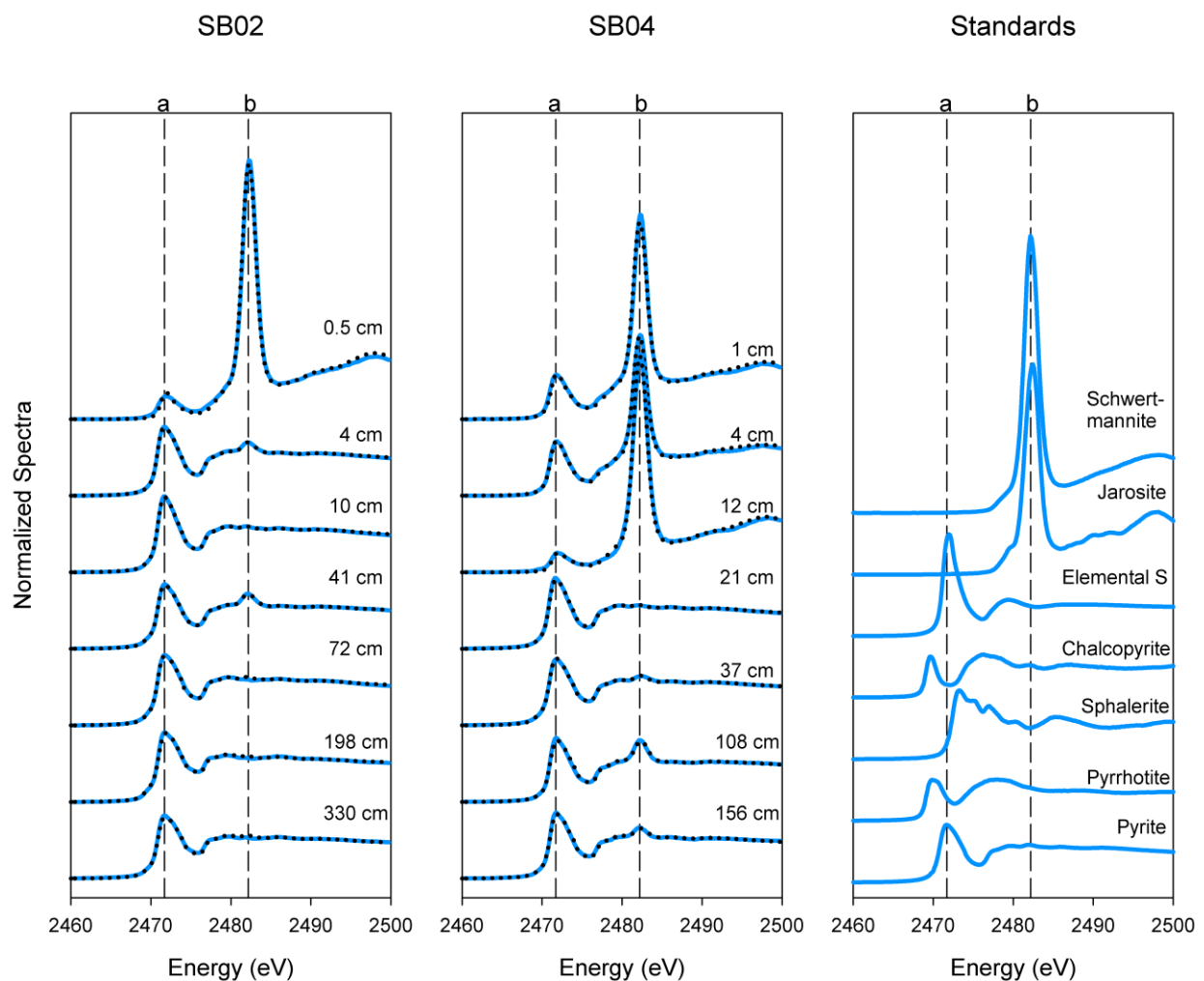


Figure 2.11. Bulk S XANES spectra of tailings samples from SB02 and SB04 and reference spectra used for linear combination fitting. Measured spectra are shown as solid blue lines, and modelled linear combination fitting results are shown as dotted black lines. The spectral peak locations for pyrite (a) and sulfate (b) are indicated as vertical dashed lines. Labels indicate the depth below the tailings-sand interface.

Table 2.3. Linear combination fitting results for S species from bulk XANES analysis.

	Depth Below Sand (mbgs)	Reduced Chi- Square	R Factor	Pyrite (%)	Pyrrhotite (%)	Sphalerite (%)	Chalcopyrite (%)	Elemental S (%)	Schwert- mannite (%)	Jarosite (%)
SB02	0.005	4.2E-03	1.3E-03					20.4	50.8	28.8
	0.04	7.2E-05	6.6E-05	97.4					2.6	
	0.10	1.6E-04	1.4E-04	86.7	4.4			8.9		
	0.41 (Hardpan)	7.5E-05	6.9E-05	88.6		1.3	6.8		3.3	
	0.72	3.2E-04	2.6E-04	87.4	7.2	5.4				
	1.98	7.0E-04	5.9E-04	68.9	13.3	8.2		9.5		
	3.30	5.9E-04	6.1E-04	86.2	8.6	5.2				
SB04	0.01	4.3E-03	1.9E-03	22.6				22.6	43.2	11.6
	0.04	1.9E-03	1.0E-03	39.3				21.5	39.1	
	0.12	2.9E-03	1.3E-03			4.8		16.8	55.5	22.9
	0.21	3.3E-04	3.3E-04	90.1	4.5			5.4		
	0.37	1.3E-04	1.2E-04	90.1			8.4			1.5
	1.08	6.7E-04	6.7E-04	91.3	2.2				6.5	
	1.56	4.6E-04	4.6E-04	92.5	5.2				2.3	

2.4.6. Prokaryotic Populations

The two most abundant phyla were Proteobacteria (mean relative abundance 28.8% of total reads) and Firmicutes (12.0% of total reads), both of which contain many species that catalyze dissimilatory iron and/or sulfur oxidation or reduction. Other phyla present included Actinobacteria (10.2%), Chloroflexi (6.5%), Acidobacteria (5.8%), Planctomycetes (5.3%), and Bacteroidetes (5.0%). Prokaryotes involved in sulfur and iron oxidation/reduction reactions were classified as either SOB/IOB or SRB, and their mean relative abundances grouped by stratigraphic layer (Figure 2.12). No sulfur- and/or iron-oxidizing archaea were detected in the samples. SOB and/or IOB were also classified as either neutrophiles or acidophiles, and their relative abundances along with SRB relative abundances are compared to the pore-water geochemistry in Figure 2.7. Percentages of total reads of SOB/IOB and SRB on the genus level for individual samples are indicated in Figure 2.13.

Sulfur and iron oxidizers were found in highest abundance in the partially oxidized tailings ($16.00 \pm 8.82\%$; mean $\pm$ standard deviation; $n = 3$), with lower concentrations in the unoxidized tailings ($5.37\% \pm 4.06\%$; $n = 16$), peat layer ($3.42 \pm 3.30\%$; $n = 3$), sand and gravel layer ($1.49\% \pm 0.39\%$; $n = 2$), and the native sand (0.45% ; $n = 1$) (Figure 2.12). SB02 contained higher proportions of mineral oxidizing genera in comparison to SB04 and SB05, particularly in the oxidized tailings at 0.345 m and 0.385 m depth. Out of all the mineral-oxidizing species, 77% were acidophilic, and 23% were neutrophilic. Acidophilic SOB/IOB were more abundant relative to neutrophilic SOB/IOB in the shallow tailings where the pore-water is acidic, and proportions of neutrophilic SOB/IOB generally increase with depth at SB02 and SB05 as pore-water pH increases to near-neutral (Figure 2.7). At SB04, nearly all the SOB/IOB in the tailings are acidophilic due to the acidic pH ($1.27 < \text{pH} < 3.86$).

Sulfate reducers ranged from 0.25 to 30.04% of total reads, with mean relative abundance of SRB highest in the unoxidized tailings ($10.12 \pm 7.91\%$). Abundances of SRB were $3.26 \pm 1.09\%$ in the peat, 2.96% in the native sand, $0.84 \pm 0.47\%$ in the partially oxidized tailings, and $0.36 \pm 0.15\%$ in the sand and gravel layer (Figure 2.12). Higher proportions of SRB occur near the interface where pH transitions from acidic to near-neutral (Figure 2.7). The most dominant SRB species across all samples was *Desulfosporosinus* (Figure 2.13). Low abundances of methanogens (0.08% of total reads) and methylotrophs (0.65% of total reads) were detected in the samples, indicating that methane production and reduction is not a significant process in the tailings.

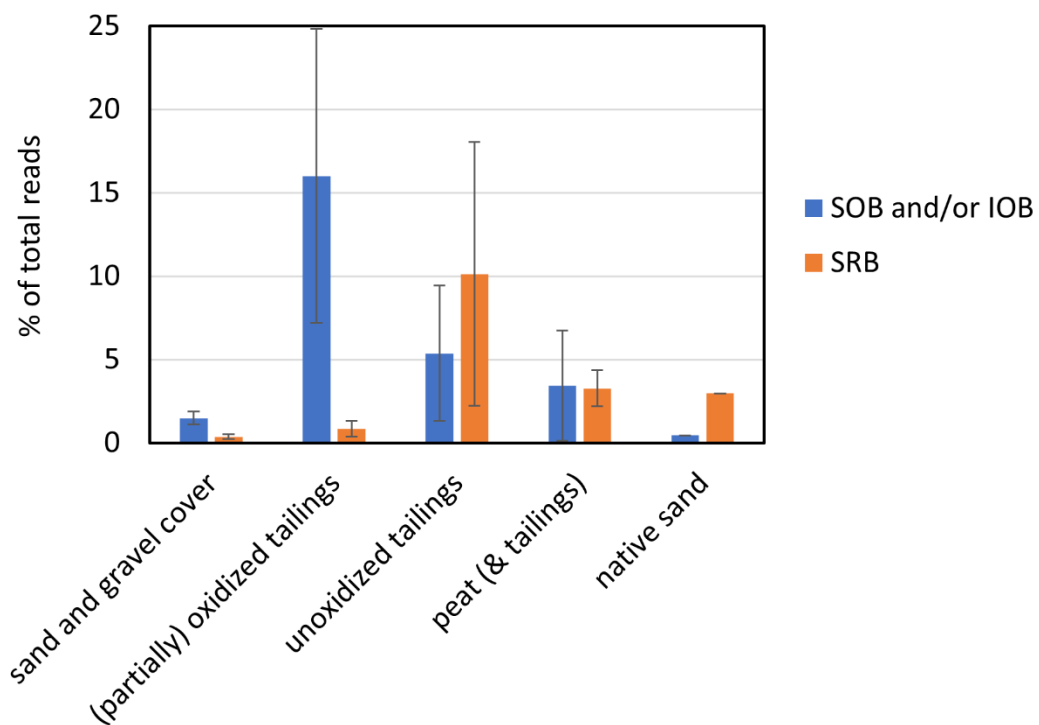


Figure 2.12. Mean proportions of total reads of sulfur- (SOB) and/or iron-oxidizing bacteria (IOB) and sulfate-reducing bacteria (SRB) (both on the genus level) in individual layers of the vertical profile of the tailings impoundment (defined in Table A1). Error bars show standard deviations of samples within each layer.

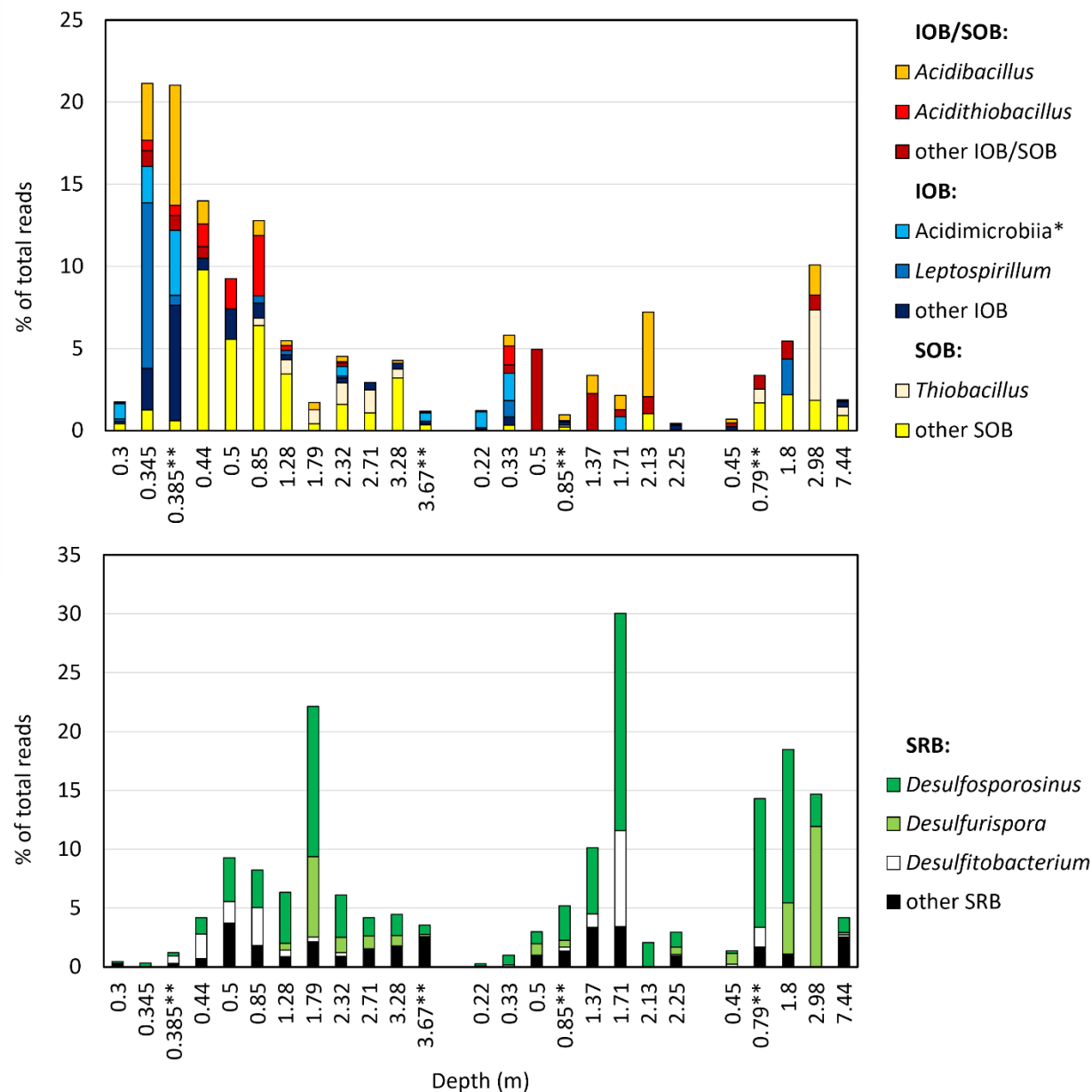
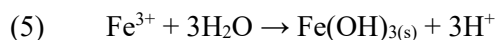
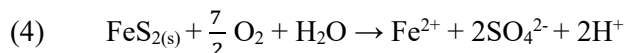


Figure 2.13. Proportions of total reads of (A) sulfur- (SOB) and/or iron-oxidizing bacteria (IOB), and (B) sulfate- (and/or sulfur-) reducing bacteria (SRB), both on the genus level. Higher taxa are marked with an asterisk. Samples that were analysed in duplicate are marked with two asterisks. Depths are presented as metres below ground surface, where the tailings-sand interface lies at 0.34 m at SB02, at 0.29 m at SB04, and at 0.39 m at SB05.

2.5 Discussion

The oxidation of pyrite generates Fe^{2+} , SO_4^{2-} , and H^+ (Equation 4), further oxidation of Fe^{2+} and precipitation of Fe(III) (oxy)hydroxide minerals generates additional H^+ (Equation 5):



Oxidation of other sulfide minerals release dissolved metal(oids) to the tailings pore water (*e.g.*, As, Co, Cu, Pb, Zn). Acidic waters containing high concentrations of dissolved metals have been generated due to sulfide mineral oxidation within the South Bay tailings. Pore-water pH values are highly acidic within the shallow tailings, with pH values reaching a minimum of pH 1.27, and Fe and SO_4 reaching maximum concentrations of 8,320 mg L^{-1} and 23,700 mg L^{-1} respectively. Deeper in the tailings profile, pH values increase as a result of acid neutralization reactions, which occur as pore-waters migrate downwards through the tailings. The dissolution of carbonates through acid neutralization results in elevated pore-gas CO_2 in certain areas of the tailings. Groundwater flow velocity was calculated to be over 100x faster in the vertical direction downwards in comparison to horizontal groundwater velocity within the tailings. Groundwater flow occurs outwards from the tailings impoundment, with acidic seepage containing elevated concentrations of dissolved metals flowing towards receiving surface water bodies Boomerang Lake and Mud Lake.

2.5.1. Sulfide Mineral Oxidation

The South Bay tailings have been undergoing oxidation for over 40 years. However, these tailings show a relatively limited extent of oxidation (0-15 cm depth) in comparison to other sulfide-bearing tailings sites that have been exposed to atmospheric O_2 for several years to several decades (Table 2.4). The sharp decrease in pore-gas O_2 concentrations together with the depletion of total S concentrations and the predominance of sulfate over sulfide species near the top of the tailings provide evidence for this limited extent of oxidation. Differences in the extent and rate of sulfide mineral oxidation may be

attributed to many factors, including the diffusion coefficient, moisture content, concentration of sulfide minerals, and mineralogy.

Gas transport in tailings impoundments is commonly assumed to be dominated by diffusive gas transport (Davis & Ritchie, 1986; Nicholson et al., 1989). The rate of diffusion can be described by Fick's law:

$$(6) \quad J = -D_1 \frac{dC}{dz}$$

where J is the diffusive flux of O_2 in the gas phase ($M L^{-2} T^{-1}$), D_1 is the diffusion coefficient, and dC/dz is the concentration gradient of $O_{2(g)}$ over depth.

The diffusion coefficient in partly water-saturated porous media is dependent on the temperature and moisture content and can be describe by the empirical equation (Reardon & Moddle, 1985):

$$(7) \quad D_1(x) = 3.98 \times 10^{-9} \left[\frac{apor(i) - 0.05}{0.95} \right]^{1.7} \times T^{1.5}$$

where $apor$ is the air-filled porosity and T is the temperature in Kelvin.

Diffusion coefficients in the vadose zone of the South Bay tailings average 8.6×10^{-8} , 2.8×10^{-7} and $5.4 \times 10^{-8} m^2 s^{-1}$ at SB02, SB04 and SB05 respectively. These values are lower than calculated values in the vadose zone at other tailings impoundments, such as 2.8×10^{-7} to $1.9 \times 10^{-6} m^2 s^{-1}$ at Lynn Lake (Gunsinger et al., 2006a), 3.0×10^{-7} to $3.0 \times 10^{-6} m^2 s^{-1}$ at Waite Amulet (Blowes & Jambor, 1990), and 2.6×10^{-8} to $4.0 \times 10^{-5} m^2 s^{-1}$ at Copper Cliff (Coggans et al., 1999; Buis, 2016). The gas diffusion coefficient decreases as saturation increases (Reardon & Moddle, 1985); therefore, the high moisture content within the South Bay tailings contributes to the low diffusion coefficients. A shallow water table and fine grain-size both result in a higher moisture content. In fine-grained materials, capillary action will increase saturation and hence decrease gas diffusion. Gunsinger et al. (2006a) observed that coarse-grained tailings in the proximal area of the Lynn Lake tailings allowed for O_2 to penetrate deeper into the vadose zone and increase the extent of oxidation in comparison to fine-grained tailings in the distal area.

Similarly, Hakkou et al. (2008) observed extensive sulfide oxidation to 0.75 m in coarse-grained tailings located within a dyke, whereas fine-grained tailings were only oxidized to 0.15 m. At South Bay, location SB05 has a water table near the surface with minimal depletion of sulfides, compared to location SB04 which has a coarser grain size near the surface and a lower water table, allowing for deeper O₂ gas penetration and sulfide mineral oxidation to 0.15 m depth.

Although the tailings were deposited more than 40 years prior to sample collection, O₂ gas is consumed within the upper 5-30 cm of the tailings beneath the sand layer. The rapid consumption of O₂ near the surface is in part due to the oxidation of high concentrations of sulfide minerals in the tailings, which prevents O₂ from diffusing deeper into the tailings. The high concentration of sulfide minerals available for oxidation results in longer periods of time before tailings become sulfide depleted. The impact of sulfide concentration has been seen in the Monte Romero district, Spain, where the depletion of sulfide minerals in tailings containing 30 wt.% pyrite extended to 0.20-0.25 m depth, whereas adjacent tailings containing 80 wt.% pyrite showed minimal oxidation (Quispe et al., 2013). The South Bay tailings contain a very high sulfide content, with an average of 27 wt.% S in the unoxidized tailings, higher than many of the other sites summarized in Table 2.4.

The various sulfide minerals within tailings have previously been observed to have different degrees of resistance to oxidation, with pyrrhotite having the lowest resistance, and pyrite and chalcopyrite having a relatively high resistance (Lindsay et al., 2015; Jambor, 1994). This mineralogy-dependent oxidation is reflected by the SAI (Moncur et al., 2005), and was observed within the South Bay tailings, as pyrrhotite was absent near the top of the tailings and showed alteration features to a greater depth in comparison to pyrite. The higher specific surface area and the structural deficiency of Fe in pyrrhotite leads to its rapid oxidation, occurring up to 100 times faster than the oxidation of pyrite when exposed to atmospheric oxygen (Nicholson & Scharer, 1994; Janzen et al., 2000). In the South Bay tailings, pyrite is the predominant sulfide mineral whereas pyrrhotite is at minor amounts. In comparison, other tailings facilities that contain pyrrhotite as the predominant sulfide mineral often show a high degree

of oxidation, such as at Copper Cliff (Buis, 2016), Nickel Rim (Ribet et al., 1995), and Lynn Lake (Gunsinger et al., 2006a) (Table 2.4).

The sand and gravel layer and sparse vegetation on the South Bay tailings does not limit O₂ ingress into the tailings, demonstrated by how the pore-gas O₂ concentrations remain close to atmospheric throughout this layer. Revegetation programs at other sites, such as Waite Amulet, have stabilized tailings and decreased wind and water erosion, but have similarly done little to limit sulfide mineral oxidation (Veldhuizen et al., 1987). At Long Lake, cemented crusts of As-bearing precipitates within a sand cover overlying the tailings have become a secondary contamination source (Sapkota et al., 2023), however at South Bay no cementation within the sand layer was observed and is therefore not anticipated to present further contamination issues.

2.5.2. Duration of Sulfide Oxidation

The formation of secondary Fe(III) (oxy)hydroxide and hydroxysulfate alteration rims surrounding primary sulfide grains at South Bay is similar to oxidation processes at other tailings impoundments, such as Waite Amulet (Blowes & Jambor, 1990), Kidd Creek Mine (Blowes et al., 1995), and the East Tailings Management Area (Gunsinger et al., 2006a). Numerical models have been developed that couple gas diffusion through the unsaturated tailings to shrinking core models that describe diffusion of oxidants (O₂ or Fe³⁺) through the alteration rims (Davis and Ritchie, 1986; Wunderly et al, 1996; Mayer et al, 2002). The governing equations for these models are (Wunderly et al, 1996):

$$(8) \quad \text{apor}(x) \frac{\partial U_A^*(x,t)}{\partial t} = D_1(x) \frac{\partial^2 U_A^*(x,t)}{\partial x^{*2}} - \frac{3[1-\text{por}(x)]D_2}{R^{*3}} \left(\frac{R^* r_c^*(x,t)}{R^* - r_c^*(x,t)} \right) U_W^*(x, t)$$

$$(9) \quad \frac{dr_c^*}{dt} = \frac{D_2(1-\text{por})}{\varepsilon \rho_s r_c^{*2}} \left(\frac{R^* r_c^*(x)}{R^* - r_c^*(x)} \right) U_W^*(x, t)$$

where *apor* is the air-filled porosity, U_A^{*} is the oxygen concentration in the pore space [kg m⁻³], D₁ is the diffusion coefficient for the porous medium [m² s⁻¹], *por* is the porosity, R^{*} is the unreacted radius of the particle [m], r_c^{*} is the radius of the unreacted core or reaction front within the particle [m],

U_w^* is the concentration of oxygen in the water surrounding the particle [kg m^{-3}], ϵ is the mass ratio of O_2 to sulfur based on the oxidation of pyrite (equation 4), D_2 is the diffusion coefficient for the oxidized rim of the particle [$\text{m}^2 \text{s}^{-1}$], and ρ_s is the density of sulfur [kg m^{-3}], calculated by multiplying the bulk density by the fraction of sulfur.

These processes are included in the numerical model PYROX (Wunderly et al., 1996) which has been applied to describe the sulfide oxidation process and duration of oxidation at several tailings impoundments such as Waite Amulet (Blowes & Jambor, 1990), Lynn Lake (Gunsinger et al., 2006a), Copper Cliff (Coggans et al., 1999; Buis, 2016), and Long Lake (Verbuyst, 2020). The time required for complete oxidation of sulfide minerals within the vadose zone was estimated to be between 430 to 4260 years in the South Bay tailings, a much longer extent than the timeframes calculated at other tailings sites (Table 2.4). These findings emphasize the need for additional remediation measures to prevent long-term sulfide oxidation.

Table 2.4. Comparison of sulfide mineral oxidation extents at mine sites in Canada and around the world.

Location	Principal Sulfide(s)	Total S (wt.%)	Depth of Water Table	Years of Oxidation Prior to Study	Depth of Extensive Oxidation	Time to Complete Sulfide Oxidation in Vadose Zone (yrs)
Joutel, Quebec ^a	Pyrite > pyrrhotite	5 (average)	< 2 m	7	0.2 m - 1.0 m	
Waite Amulet, Quebec ^b	Pyrite > pyrrhotite	26.7 ¹ (average)	Surface to > 5 m	>24	0.5 m - 0.7 m	150 - 640
Kettara mine, Morocco ^c	Pyrrhotite and pyrite	1.6 – 14.5 (range)	unknown	25	Fine tailings: 0.05 - 0.15 m Coarse tailings: 0.75 m	
East Tailings Management Area Lynn Lake, Manitoba ^d	Pyrrhotite	0.46 – 14.7 (range) 5.13 (average)	Proximal tailings: 4 m Distal tailings: 1.3 m	26	Proximal (coarse) tailings: 0.9 m Distal (fine) tailings: 0.3 m	350 - 1900
Monte Romero district, Iberian Pyrite Belt, Spain ^e	Pyrite	Yellowish impoundment: 16.0 ² (average) Grayish impoundment: 42.8 ² (average)	0.4 - 0.7 m	>30	Yellowish impoundment: 0.20 - 0.25 m Grayish impoundment: Negligible	
Nickel Rim, Ontario ^f	Pyrrhotite	3 (average)	unknown	33	0.6 m	60
South Bay, Ontario	Pyrite	27 (average)	0.3 m - 2.0 m	40	0 m - 0.15 m	430 - 4260
Haveri, Finland ^g	Pyrite and pyrrhotite	2.9 (average)	< 2 m in central area	45	0.5 - 1.4 m	
Copper Cliff Sudbury, Ontario ^h	Pyrrhotite	4.5 (average)	2.25 m	>50	1.6 m	5 - 386
Camp tailings Sherridon, Manitoba ⁱ	Pyrrhotite > or = pyrite	9 – 25 (range)	4.6 m	>70	0.5 m	
Long Lake Sudbury, Ontario ^j	Pyrite	3 – 8 (range of average S)	Surface - 1.2 m	78	0.7 m	10 - 157

^a Blowes et al. (1998)^b Siwik et al. (1987); Blowes & Jambor (1990); Yanful et al. (1990)^c Hakkou et al. (2008)^d Gunsinger et al. (2006a)^e Quispe et al. (2013)^f Mayer et al. (1999); Ribet et al. (1995)^g Parvianinen et al. (2009)^h Coggans et al. (1999); Buis (2016)ⁱ Moncur et al., (2005)^j Verbuyst (2020); Sapkota et al. (2023)¹ Estimated wt.% S from average sulfide content, assuming pyrite as the sulfide mineral² Converted wt.% pyrite into wt.% total S, assuming pyrite as the only source of total S

2.5.3. Hardpan and Secondary Minerals

The formation and accumulation of secondary minerals often occurs within oxidized tailings as pore-waters become supersaturated with respect to certain mineral phases. Common secondary minerals within tailings include Fe(III) (oxy)hydroxides such as goethite [α -FeOOH], lepidocrocite [γ -FeOOH] and ferrihydrite [$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$], and sulfates such as gypsum, jarosite, schwertmannite, and melanterite [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$] (Jamieson, 2015). In the South Bay tailings, secondary minerals were observed within the thin oxidized zone with compositions consistent with that of jarosite and schwertmannite, and within the discontinuous hardpan layer as unidentified Fe (oxy)hydroxides and hydroxysulfates. Hardpan layers occur when the accumulated precipitation of secondary minerals results in a cemented layer (McGregor & Blowes, 2002). At other abandoned mine sites, hardpans have been observed to range from a few centimetres to several metres thick and have a range of secondary mineral compositions including gypsum, jarosite, goethite, ferrihydrite, and lepidocrocite (Blowes et al., 1991; McGregor & Blowes, 2002; Moncur et al., 2005; Gunsinger et al., 2006a; Hakkou et al., 2008).

2.5.4. Microbial Processes

Geochemical processes within tailings impoundments, such as sulfide mineral oxidation, are often catalyzed by microorganisms. The activity of IOBs increases the rate of sulfide oxidation through the oxidation of dissolved Fe^{2+} to Fe^{3+} under acidic conditions (Johnson & Hallberg, 2003). The abiotic oxidation of pyrite can occur by either molecular O_2 or Fe^{3+} . Under acidic pH conditions, the abiotic oxidation rate of pyrite by Fe^{3+} can be an order of magnitude or more faster than that by O_2 , but the rate-limiting step is the oxidation of Fe^{2+} to Fe^{3+} (Nordstrom, 1982; Nordstrom & Alpers, 1997). Therefore, the presence of IOBs in mine drainage waters can significantly increase the rate of sulfide mineral oxidation. Microorganisms can also play an important role in oxidizing reduced sulfur species such as thiosulfate and elemental sulfur to produce sulfate (Johnson & Hallberg, 2003). Areas of active sulfide oxidation within acid-generating tailings often contain elevated populations of IOBs and SOB.

The South Bay tailings contain high proportions of IOB and SOB up to 21.13% within the oxidized and partially oxidized tailings at location SB02, and lower reads within the unoxidized tailings, indicating increased oxidation within the top several cm through microbial processes. Locations SB05 and SB04 contained lower proportions of IOB and SOB in comparison to SB02, potentially due to a higher water table at SB05 limiting oxidation, and highly acidic pore waters and higher concentrations of dissolved metals at SB04. Pore-water pH influences whether acidophilic or neutrophilic IOB and SOB are dominant in the tailings, with higher proportions of acidophilic SOB/IOB occurring in the shallow tailings where pH is acidic. The ranges of IOB and SOB measured in the oxidized and unoxidized tailings at South Bay are similar to those documented at other acid-generating tailings and waste rock sites (e.g. Pakostova et al., 2020a, 2020b, 2022; Bruneel et al., 2017; Kwon et al., 2015). However, it should be noted that the presence of DNA of prokaryotes with a specific metabolic trait does not necessarily correlate with their metabolic activity in the tailings at the time of sampling.

Sulfate reduction is also an important microbial process in tailings, leading to the precipitation of insoluble metal sulfides. Isotopic fractionation occurs during bacterial sulfate reduction because SRB preferentially reduce the lighter $^{32}\text{S-SO}_4$ and $^{16}\text{O-SO}_4$, creating a relative enrichment of $^{34}\text{S-SO}_4$ and $^{18}\text{O-SO}_4$ in pore waters (Jones & Starkey, 1956; Waybrant et al., 2002; Mayer, 2005). An increase in alkalinity, decrease in dissolved SO_4 , and an enrichment in $^{34}\text{S-SO}_4$ and $^{18}\text{O-SO}_4$ provide indications that sulfate reduction is occurring at the base of the tailings and underlying peat layer at SB05. The relative abundance of SRB detected in the peat samples was greater than that of the sand and gravel layer and oxidized tailings, but lower than that of the unoxidized tailings. Elevated populations of SRB occur within the unoxidized tailings near the transition from acidic to near-neutral pH, indicating the potential for bacterial sulfate reduction. However, isotopic results do not show enrichment of $^{34}\text{S-SO}_4$ or $^{18}\text{O-SO}_4$ in the pore waters near this transition from acidic to near-neutral at SB05. High concentrations of dissolved SO_4 ($>4580 \text{ mg L}^{-1}$) occur in the pore-waters at 1.80 m depth at SB05, corresponding to the depth of maximum SRB abundance, whereas the base of the tailings at SB05 contains lower dissolved SO_4 (<222

mg L⁻¹). The higher concentration of SO₄ may mask the effects of isotopic fractionation during bacterial sulfate reduction within the unoxidized tailings.

2.6 Conclusions

Sulfide oxidation in the South Bay tailings over the past 40 years has led to acidic waters, with pH as low as 1.27, and with elevated concentrations of SO₄, Fe, and other metals, that continue to discharge into the surrounding environment. Mineralogical investigation of the tailings has shown that pyrite is the most abundant sulfide mineral, with minor amounts of sphalerite and chalcopyrite, and trace amounts of pyrrhotite. The oxidized zone of the tailings is restricted to the upper 0-15 cm and is characterized by a depletion of sulfide minerals, a rapid decline of pore-gas O₂, and precipitation of secondary Fe(III) (oxy)hydroxide and hydroxysulfate minerals. Pyrrhotite is depleted and shows alteration features to a greater depth in comparison to pyrite, sphalerite, and chalcopyrite. A discontinuous hardpan between 10-20 cm thick was observed to also contain secondary Fe(III) (oxy)hydroxides and hydroxysulfates. Elevated populations of prokaryotic microorganisms that catalyze Fe and S oxidation were found within the shallow oxidized zone. The peat layer underlying the tailings contains populations of SRB that catalyze SO₄ reduction reactions. The extent of sulfide mineral oxidation within the South Bay tailings was found to be shallower than that observed at many other abandoned sulfide-bearing tailings sites. Various factors contribute to this limited extent of oxidation, including a high concentration of sulfide minerals, the predominance of pyrite instead of pyrrhotite, a relatively high water table, and a fine grain-size in the tailings. Due to the high amounts of unoxidized tailings still available for sulfide oxidation, acidic drainage from the South Bay tailings is estimated to continue for decades to millennia in the absence of additional remediation measures.

Chapter 3: Mobility of Metal(loid)s and Rare Earth Elements in High Sulfide Tailings

Executive Summary

For more than 40 years, since mine closure, tailings at the South Bay mine in northwestern Ontario, Canada, have generated acid mine drainage and released elevated concentrations of dissolved metals. The mobility of metal(loid)s and rare earth elements (REEs) in the South Bay tailings was investigated through selective extractions and geochemical methods to determine attenuation and potential release mechanisms of trace elements. Shallow pore-waters are acidic, and pH increases to circumneutral with depth. Acid neutralization within the tailings results from dissolution of gangue minerals including calcite, dolomite, siderite, Al hydroxides, Fe(III) (oxy)hydroxides, and aluminosilicates. The shallow acidic pore-waters contain high concentrations of dissolved REEs, up to 9.45 mg L⁻¹ total REEs, indicating elevated REE mobility under acidic conditions. Dissolved Zn is mobile and present at high concentrations within the tailings, up to 818 mg L⁻¹ Zn. Copper, Pb, and As have lower mobility in the tailings and are sequestered through adsorption, precipitation, or co-precipitation with secondary minerals such as covellite, anglesite, and Fe(III) (oxy)hydroxides and hydroxysulfates. Secondary phases with sequestered metals may be susceptible to remobilization under reductive dissolution conditions if the geochemical conditions of the tailings are altered during remediation efforts.

3.1 Introduction

Sulfide-bearing mine wastes often pose a hazard to the environment due to their potential to generate acid mine drainage. Exposure of sulfide minerals such as pyrite [FeS_2] and pyrrhotite [$\text{Fe}_{(1-x)}\text{S}$] within tailings to atmospheric O_2 results in the release of acidity and metals contained within the oxidized sulfides to the pore waters (Blowes et al., 2014). Neutralization of acidity can occur through the dissolution of gangue minerals, principally carbonate minerals, and secondary minerals within tailings (Blowes et al., 2014). A series of successive acid-neutralizing dissolution reactions has been documented at tailings sites, with different phases such as carbonates, oxyhydroxides, and aluminosilicates contributing to buffering pH at different levels (Jurjovec et al., 2002; Blowes et al., 2014; Lindsay et al., 2015). As a result of these buffering reactions, pH plateaus can form *versus* depth within tailings impoundments. Low pH often occurs in the upper tailings where oxidation is occurring and the neutralization capacity has been depleted, and pH generally increases with depth to near-neutral values.

Metals and other trace elements can be released through sulfide mineral oxidation and acid neutralization reactions. These elements may be attenuated through secondary mineral precipitation or adsorption, especially while these contaminants migrate downwards through the tailings and the pH increases. Sequestered metals may be susceptible to re-mobilization if remediation designs such as cover systems change the geochemical conditions within the tailings impoundment. Reductive conditions may promote the reductive dissolution of secondary phases or desorption of metals, whereas an elevated water table can dissolve soluble phases.

The occurrence and speciation of rare earth elements (REEs) in tailings have been a topic of growing interest due to the importance of these elements to the green energy transition and the potential for mine wastes to contain economical concentrations of REEs or other metals. Studies have examined REE concentration, speciation and mobility within seeps, surface waters, and groundwaters affected by acid mine drainage (Leybourne et al., 2000; Ferreira da Silva et al., 2009; Khorasanipour & Jafari, 2018; Soyol-Erdene et al., 2018; Lozano et al., 2020). However, limited information is available on the mobility

and fractionation of REEs between the solid and dissolved phases within sulfide-rich tailings that have undergone partial oxidation.

The tailings impoundment selected for this study was derived from the South Bay mine, an abandoned Cu-Zn mine in northwestern Ontario, 65 km north-east of the town of Ear Falls (Figure 3.1). A detailed description of the site is provided in Chapter 2. The mine has been abandoned since 1981, and remediation efforts to prevent acid mine drainage from contaminating the surrounding environment were not fully implemented. A sand and gravel layer, approximately 30 cm thick, covers the tailings, but does little to limit O₂ ingress to the tailings below. The tailings contain very high concentrations of sulfide minerals (average 27 wt. % as S), principally in the form of pyrite and with lesser amounts of sphalerite [ZnS], chalcopyrite [CuFeS₂] and pyrrhotite. Prolonged oxidation of the tailings over the past 40 years has generated acidic pore waters with elevated concentrations of dissolved metals. The oxidized zone is relatively thin, with depletion of sulfide minerals restricted to the upper 0-15 cm of tailings.

This study aims to characterize the mobility of dissolved metals and trace elements and the attenuation of these elements through precipitation and adsorption to secondary phases within the South Bay tailings. Although the mobility and sequestration of metals in tailings has previously been studied in detail at other mine sites (McGregor et al., 1998; Moncur et al., 2005; Gunsinger et al., 2006b), this research offers a new opportunity to study these processes at a site with different mineralogy and geochemical conditions. The results will also give insight into what elements may be susceptible to dissolution under differing geochemical conditions imposed by potential remediation efforts, such as reductive dissolution under an impermeable cover. The concentration, mobility, and fractionation of REEs with depth in the tailings was also investigated as a part of this study. This presents a new opportunity to examine REE release and attenuation throughout a depth profile of sulfide-rich tailings with variable pH and geochemical conditions.

3.2 Methods

3.2.1. Geochemical Sampling

Five instrumentation nests; SB01, SB02, SB03, SB04, and SB05 (Figure 3.1) were installed on the tailings in the spring of 2021. Three to five piezometers and four to five soil-water samplers were installed in depth profiles at each location. Water samples were collected in the spring and fall of 2021 and 2022. Continuous cores of tailings solids were collected from each location in the spring of 2021 using the piston core-barrel technique described by Starr & Ingleton (1992). Core samples were collected within 2” and 3” Al casing and capped at each end to limit O₂ exposure. The cores were stored frozen until they were thawed and sub-sampled within an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, USA). Sub-samples of tailings were collected every 2-50 cm, with more frequent sampling in the oxidized tailings near the ground surface. Tailings samples were air-dried anaerobically prior to preparation of thin sections for optical microscopy, and freeze-dried for other analyses including whole-rock geochemistry and selective extractions.

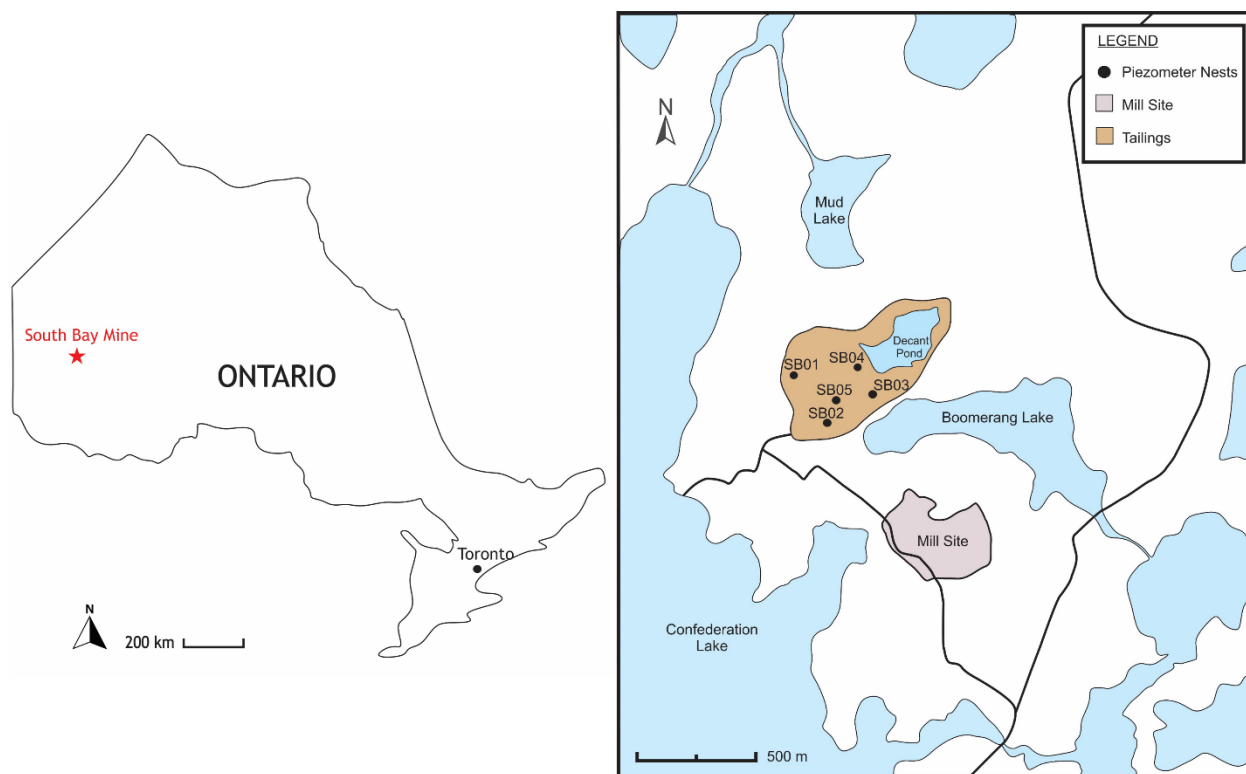


Figure 3.1. Left: map of the South Bay mine location in Ontario, Canada. Right: site map with tailings sampling locations and piezometer nests.

3.2.2. Aqueous Geochemistry

Pore-water samples were filtered (0.45 μm) and stored at 4 $^{\circ}\text{C}$ prior to analysis. Trace-metal grade 67-70% HNO_3 (OmniTrace[®]) was added to samples for cation analysis to maintain pH <2 for preservation. Major cations were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and trace elements by inductively coupled plasma mass spectroscopy (ICP-MS) (iCAP 6000 and X Series II; Thermo Fisher Scientific) and anions were analysed by ion chromatography (IC; DX600, Dionex) at the University of Waterloo. REE concentrations were measured for water samples collected from Sept 2021, with analysis by ICP-MS (Agilent MS7850) performed by SGS Canada Inc. (Lakefield, ON). Measurements for pH, Eh, and alkalinity were made in the field at the time of sample collection. The pH electrode (Orion ROSS Ultra; Thermo Scientific) was calibrated daily using at least three of pH 1.68, 4, 7, and 10 buffer solutions prior to sampling. The Eh electrode (Orion Sure-Flow ORP/Redox Electrode; Thermo Scientific) was checked daily against Zobell's and Light's solutions. Alkalinity was

measured on 0.45 μm filtered samples using a Hach Digital Titrator (Hach Method 10244) and bromocresol green-methyl red indicator with 1.6 N or 0.16 N H_2SO_4 .

Saturation indices (SI) were calculated in PHREEQC (Parkhurst & Appelo, 2013) using the *minteq.v4* database. The SI describes the degree of saturation with respect to a particular mineral or phase; negative values represent undersaturated conditions, positive values represent supersaturated conditions, and a value of zero represents thermodynamic equilibrium. The calculated SI values indicate the thermodynamic tendency of phases to precipitate or dissolve, but do not confirm if a phase is present.

3.2.3. Solid-Phase Geochemistry

Whole-rock geochemical analysis, including REEs, was performed by Actlabs (Ancaster, ON). Following lithium metaborate/tetraborate fusion, samples were digested in a nitric acid solution and analysed by ICP-OES and ICP-MS. Additionally, total elemental composition (Al, As, Ca, Co, Cu, Fe, K, Mg, Mn, Na, P, Pb, Si, Ti, Zn) was analysed on pulverized samples by X-ray fluorescence (XRF; MiniPal4, PANalytical). X-ray diffraction (XRD) semi-quantitative analysis was performed using the PDF-4+ minerals database and Sieve+ peak-matching software, with powder diffraction data collected from the Canadian Macromolecular Crystallography Facility beamline at the Canadian Light Source.

Polished thin sections were prepared from anaerobically air-dried tailings samples (Vancouver Petrographics Ltd.; Langley, BC) and observed under reflected and transmitted light with a microscope (Nikon Eclipse LV100N-POL). Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX; FEI Quanta FEG 250) was used to determine elemental compositions of minerals and secondary phases. Micro X-ray fluorescence (μ -XRF) mapping was conducted at the BioXAS-Imaging beamline at the Canadian Light Source (Saskatoon, Canada). The incident beam energy was 12 keV, and the beam spot size was $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$. Data processing was done using PyMCA (5.9.1) software (Solé et al., 2007), with a fitting region limited to 2 – 11 keV. It was difficult to distinguish between As and Pb in some samples due to the overlap of As $\text{K}\alpha$ and Pb $\text{L}\alpha$ fluorescence lines at 10.5 keV. Fit parameters were

adjusted to include As and Pb separately as well as together to determine the best fit configuration. For the selected pyrrhotite grain, As was excluded from the best fit based on EDX spectra which was operated at 20 keV and could therefore detect the Pb L β fluorescence lines at 12.6 keV.

3.2.4. Selective Extractions

Five non-sequential selective extractions were conducted on a depth profile of tailings samples from location SB02. The samples used for the extractions were collected from a depth profile (0.345-3.39 m) along the same core, except for the hardpan sample which was collected within a test pit at 0.75 m depth because the hardpan was difficult to distinguish within the cores. The hardpan layer, which is described in Chapter 2, extends from approximately 0.65-0.83 m depth at location SB02. The extraction methods were adopted from Gunsinger et al. (2006b) and are described in Table 3.1. The extractions were not performed sequentially due to the overlap in targeted species.

Tailings were mixed with each extraction reagent within a centrifuge tube on an end-over-end rotator for the specified digestion period. After the digestion period, the samples were centrifuged, and the supernatant was filtered through 0.45 μ m PVDF syringe filters. Samples for cation analysis were preserved with 16 N trace-metal grade HNO₃ to pH<2 and analysed by ICP-OES (X Series II; Thermo Fisher Scientific). The deionized (DI) water extractants were also analysed by ICP-MS (Element II; Thermo Fisher Scientific) due to lower concentrations of dissolved metals. The extractant from the DI water and 0.3 M NaOH extractions were analysed for anions by IC (DX600, Dionex). Blank samples were analysed for each extraction, and the blank concentrations were subtracted from the measurement of each element. No tertiary precipitates were observed on the dried samples, and no corrections were made for contributions from pore-water precipitates formed during the drying process.

The DI water extraction targeted weakly adsorbed sulfates and water-soluble phases and was performed with Ar-purged DI water (18.2 M Ω ·cm, Milli-Q® Advantage A10 Water Purification System) within an anaerobic chamber (Ribet et al., 1995). An alkaline extraction of 0.3 M NaOH targeted the

insoluble sulfates, such as jarosite (Yin & Catalan, 2003). The ascorbate solution extraction, composed of 0.12 M Na-ascorbate, 0.6 M Na-bicarbonate, and 0.17 M Na-citrate, is a weak reductant and targeted amorphous Fe(III) oxyhydroxides and any adsorbed metals associated with these phases (Amirbahman et al., 1998). The 0.5 M HCl extraction targeted carbonates and poorly crystalline phases (Heron et al., 1994). Finally, the 2 M hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$, hereafter abbreviated as HHCl) extraction in 25 % acetic acid targeted all Fe(III) oxyhydroxides, from amorphous to crystalline, and any associated adsorbed metals (Ribet et al., 1995). This 2 M HHCl extraction represents the reducible fraction within the tailings, which may be susceptible to reductive dissolution under strongly reducing conditions (Ribet et al., 1995). Extraction results were compared to total elemental concentrations obtained by analysis following lithium metaborate/tetraborate fusion and digestion in nitric acid.

Table 3.1. Selective extraction methods to target specific phases in tailings (from Gunsinger et al., 2006b)

Reagent	Target Phases	Digestion Period (hrs)	Solid: Reagent Ratio	Source
DI water, purged with $\text{Ar}_{(\text{g})}$	Water-soluble phases, weakly adsorbed sulfates	24	1:50	Ribet et al. (1995)
0.3 M NaOH	Insoluble sulfates	16	1:30	Yin and Catalan (2003)
0.12 M Na-ascorbate, 0.6 M Na-bicarbonate, 0.17 M Na-citrate	Amorphous oxyhydroxides	24 (in dark)	1:20	Amirbahman et al. (1998)
0.5 M HCl	Poorly crystalline phases, carbonates, adsorbed metals	24	1:10	Heron et al. (1994)
2.0 M hydroxylamine hydrochloride (HHCl) in 25% (v/v) acetic acid	Amorphous and crystalline oxyhydroxides, adsorbed metals	24 at 95°C	1:30	Ribet et al. (1995)

3.3 Results and Discussion

3.3.1. Acid Neutralization

The oxidation of sulfide minerals generates acidity which can be neutralized by the dissolution of gangue minerals (Jurjovec et al., 2002; Blowes et al., 2014; Lindsay et al., 2015). The pH buffering sequence commonly observed within mine wastes involves the dissolution of calcite/dolomite [CaCO_3] [$\text{CaMg}(\text{CO}_3)_2$], siderite [FeCO_3], Al oxyhydroxides, Fe oxyhydroxides, and aluminosilicates buffering pH at around values of 6.5 - 7.5, 5.5, 4.0, 3.0, and 1.3 respectively (Jurjovec et al., 2002; Lindsay et al., 2015). Pore-water pH will decrease, and the acidic front will progress downwards as gangue minerals attacked by acid neutralization processes are depleted and additional sulfide minerals are oxidized. As the sulfide mineral content of the tailings is depleted, trace elements are released to pore waters that can subsequently be attenuated through the precipitation and adsorption to secondary minerals at greater depths.

Within the pore-waters in the South Bay tailings, pH values tend to stabilize to around pH 6.0 deeper (> 1 m) in the profile, coinciding with an increase in dissolved Ca, indicating the role of calcite dissolution in buffering the pH. Pore-water samples were undersaturated with respect to calcite, except for the base of the tailings at SB05 where pH increases to > 6.8 (Figure B4). Carbonates were not observed in thin section within the South Bay tailings; however, calcite is presumed to be present in minor quantities, indicated by the total Ca present in the 0.5 M HCl extraction solution, which targets carbonates (Figure 3.2).

After primary carbonate dissolution and the release of Fe to pore waters from sulfide oxidation, secondary siderite may precipitate in the tailings (Al et al., 2000). The pore-waters at South Bay are saturated to supersaturated with respect to siderite at depths where the pH is near-neutral (Figure 3.3, Figure B1-Figure B4). Elevated Fe associated with the 0.5 M HCl extraction at depth further suggests siderite precipitation, because this extraction targets carbonate minerals (Figure 3.2). Although siderite

was not observed in thin section, powder XRD analysis indicated that siderite may be a minor phase within the unoxidized tailings. Below the water table at locations SB01 and SB05, pH values generally stabilize to between 5.1 - 5.9, coinciding with the pore-waters approaching saturation, or slight undersaturation with respect to siderite (Figure B1, Figure B4). Therefore, at these locations, siderite may be an important phase for acid neutralization, consistent with previous studies associating siderite dissolution with a pH plateau of around 5.5 (Moncur et al., 2005; Lindsay et al., 2015). However, it should be noted that siderite does not provide any net increase in acid neutralization capacity since dissolution of siderite releases Fe^{2+} , which will generate further acidity upon its oxidation to Fe^{3+} and hydrolysis (Lindsay et al., 2015).

When carbonate minerals have been depleted, dissolution of secondary Al and Fe (oxy)hydroxides and hydroxysulfates can further consume H^+ within the tailings. Aluminum is mobilized as a result of enhanced aluminosilicate dissolution under acidic pH near the surface of the tailings, but may precipitate as secondary Al hydroxysulfates such as alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$ or basaluminite $[\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 4\text{H}_2\text{O}]$ or Al hydroxides such as gibbsite $[\text{Al}(\text{OH})_3]$ where pH is greater than 5.0 (Nordstrom, 1982; Bigham & Nordstrom, 2000). Although no secondary Al phases were observed in the South Bay tailings, geochemical modelling suggests that pore waters are periodically undersaturated to saturated with respect to gibbsite and alunite, with supersaturation more often occurring at greater depths corresponding to near-neutral pH values. The dissolution of Al (oxy)hydroxides has been shown to stabilize pH values around pH 4.0 (Jurjovec et al., 2002; Gunsinger et al., 2006b), and is likely responsible for buffering pH between 3.7-4.1 at SB04 near the base of the tailings, coincident with a sharp increase in dissolved Al up to 1198 mg L^{-1} (Figure B3). Fe (oxy)hydroxide dissolution may also contribute to pH stabilization at pH values less than or close to 3.0 (Johnson et al., 2000). In the shallow tailings at locations SB01 and SB02, pH values remain close to 3.0 and pore-waters are undersaturated with respect to ferrihydrite $[5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}, \text{ or } \text{Fe}(\text{OH})_3]$ (Figure B1, Figure 3.3), suggesting the presence of a shallow Fe (oxy)hydroxide neutralizing zone. Pore waters are commonly at supersaturation with

respect to Fe (oxy)hydroxides such as goethite [α -FeOOH] and lepidocrocite [γ -FeOOH], except at highly acidic pH values occurring at the top of SB05 (Figure B4) and throughout the middle of the tailings at SB04 (Figure B3).

Aluminosilicate dissolution becomes the predominant acid neutralization process after other phases have been depleted. The dissolution of aluminosilicate minerals begins at near-neutral pH, but is kinetically limited in comparison to the dissolution of other phase such as carbonates and (oxy)hydroxides (Jambor, 2003; Gunsinger et al., 2006b). At very low pH values, dissolution of aluminosilicates occurs at a more rapid rate, and becomes the dominant limitation on the rate of acid neutralization (Jurjovec et al., 2002; Gunsinger et al., 2006b). Albite [$\text{NaAlSi}_3\text{O}_8$] was the most common aluminosilicate mineral detected by powder XRD in the South Bay tailings. Albite is relatively slow to dissolve at acidic pH in comparison to many other minerals (Jambor & Blowes, 1998), explaining the retention of total Al in the top tailings. Other aluminosilicate minerals that may be present include chlorite group minerals $[(\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot (\text{Mg,Fe})_3(\text{OH})_6]$, muscovite $[\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2]$, and hornblende $[(\text{Ca,Na})_2(\text{Mg,Fe,Al})_5(\text{Al,Si})_8\text{O}_{22}(\text{OH})_2]$. At location SB04, pH values drop as low as 1.26, similar to the pH plateaus of around pH 1.3-1.4 found at other tailings sites, attributed to aluminosilicate dissolution control on neutralization (Jurjovec et al., 2002; Moncur et al., 2005). However, at location SB04, dissolved Al remains relatively low throughout the acidic zone where $\text{pH} < 2$, with dissolved Al concentrations only increasing deeper in the tailings where the pH buffering is attributed to Al oxyhydroxide dissolution at pH 4.

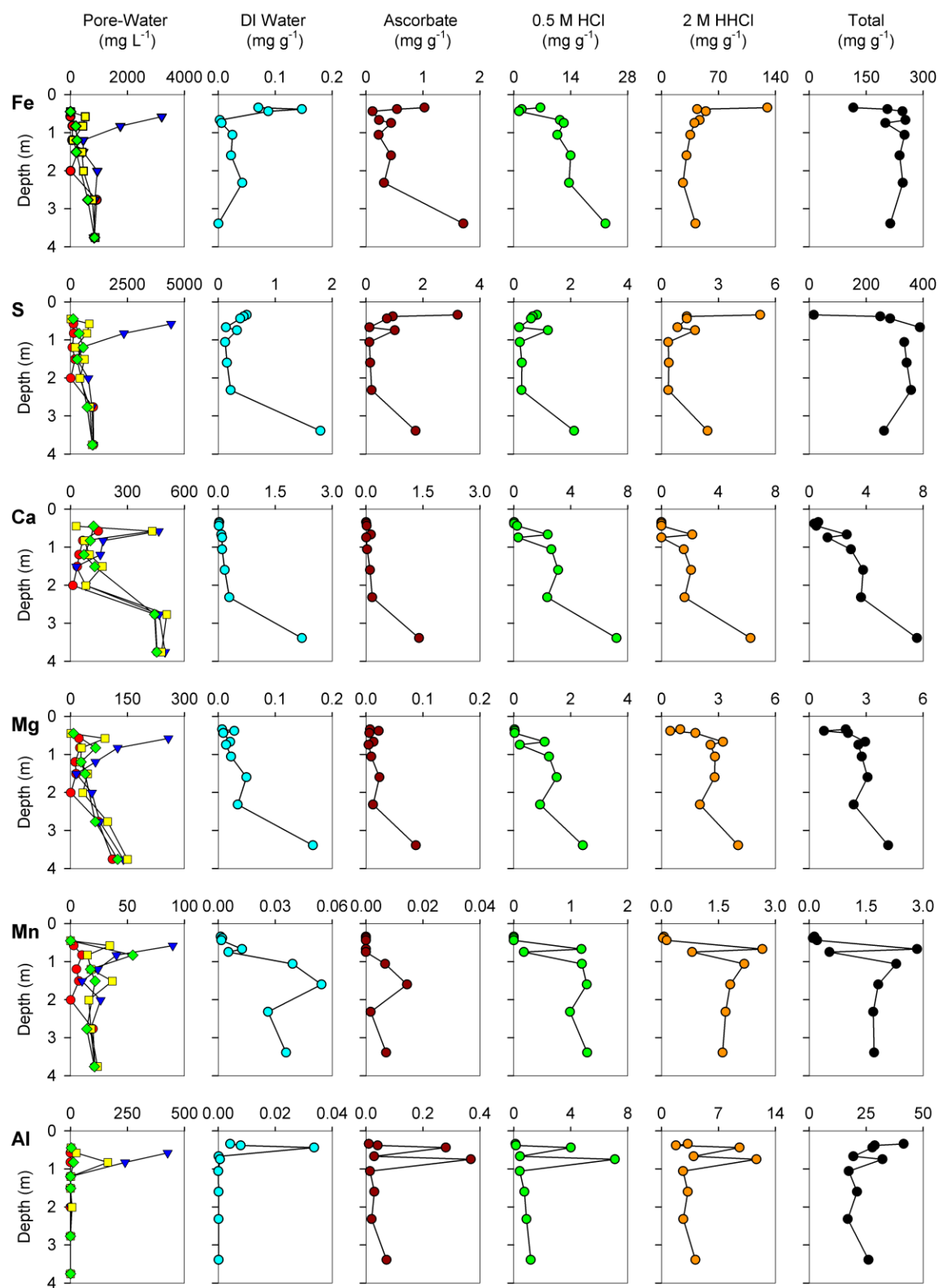


Figure 3.2. Selective extraction profiles for Fe, S, Ca, Mg, Mn, and Al at SB02. Pore-water chemistry for each element is plotted on the left, with data from June 2021 (red circles), Sept 2021 (blue triangles), June 2022 (yellow squares), and Sept 2021 (green diamonds).

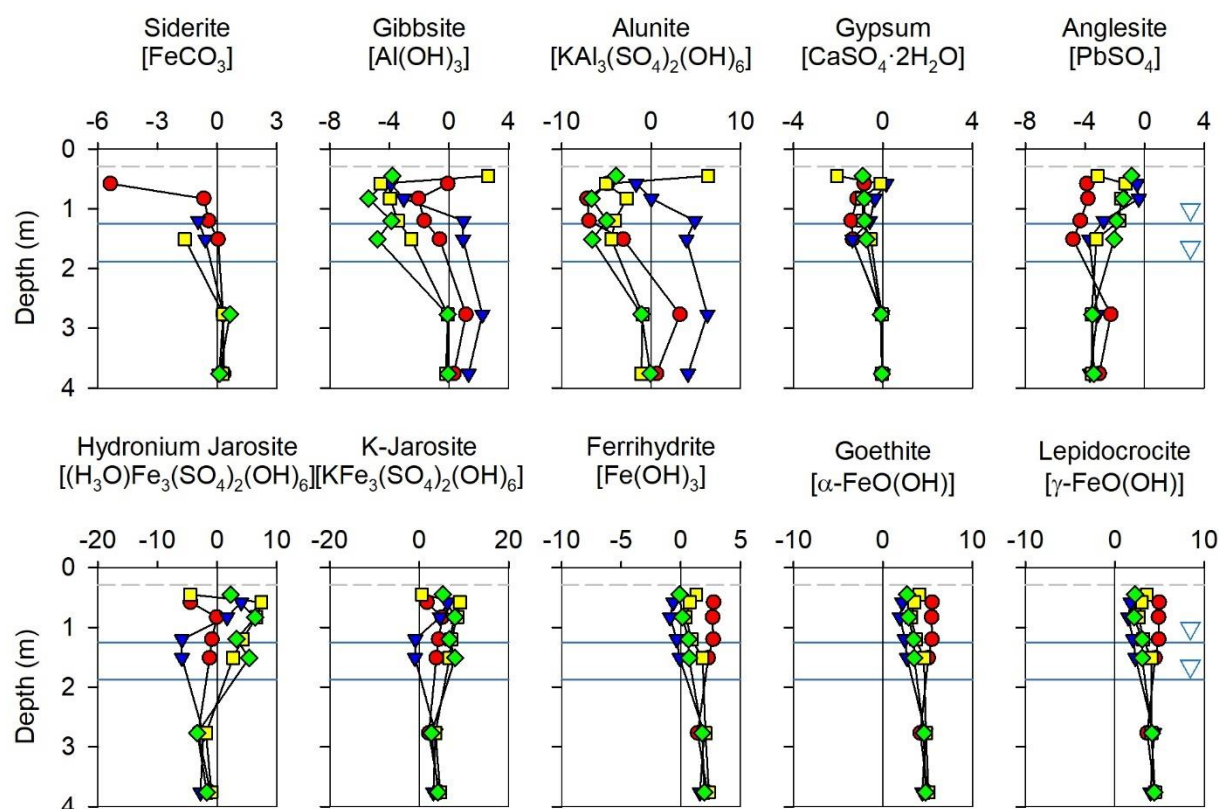


Figure 3.3. Saturation indices for select phases at SB02. The grey dashed line represents the cover-tailings interface, and the solid blue lines represent the maximum and minimum measured water table elevation. Data was from June 2021 (red circles), Sept 2021 (blue triangles), June 2022 (yellow squares), and Sept 2021 (green diamonds).

3.3.2. Mobility of Sulfur and Metal(loid)s

Metals and metalloids are released during sulfide mineral oxidation and their mobility in the tailings pore-water is controlled by adsorption-desorption and precipitation-dissolution reactions with secondary mineral phases. Based on pore-water concentrations, the relative mobility of metal(loid)s in the South Bay tailings was found to be as follows: $\text{Fe} = \text{Mg} = \text{Mn} \geq \text{Zn} > \text{Co} \geq \text{As} \geq \text{Pb} > \text{Cu}$. These findings are similar to results from studies on the geochemistry at other tailings impoundments (Blowes & Jambor, 1990; McGregor et al., 1998; Coggans et al., 1999; Gunsinger et al., 2006b).

3.3.2.1 Iron and Sulfur

Iron and SO_4 are released through sulfide mineral oxidation, leading to elevated pore-water concentrations up to $8,310 \text{ mg L}^{-1}$ Fe and up to $23,700 \text{ mg L}^{-1}$ SO_4 (Figure B4). Calculated saturation indices suggest that precipitation of secondary minerals such as siderite, jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$, or goethite influence the concentrations of dissolved Fe and SO_4 . The pore-waters were undersaturated with respect to the soluble Fe sulfate mineral melanterite $[\text{FeSO}_4 \cdot 7\text{H}_2\text{O}]$ and were variably undersaturated to supersaturated with respect to jarosite, with samples more often displaying supersaturation with respect to K-jarosite in comparison to hydronium-jarosite. The alkaline extraction (0.3 M NaOH) removed higher masses of SO_4 from the upper oxidized tailings and hardpan at SB02, indicating that jarosite may be present at higher amounts at those depths (Figure B10). SEM-EDX data also indicated that a phase with a composition similar to jarosite as well as a phase with a composition similar to that of schwertmannite $[\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}]$ were present in the shallow oxidized tailings. Schwertmannite is a poorly crystalline phase with somewhat variable composition and commonly precipitates from acid mine drainage at acidic pH values between 2-4 (Bigham & Nordstrom, 2000). Schwertmannite is metastable and can transform to either goethite or jarosite over time (Schwertmann & Carlson, 2005; Sánchez-España et al., 2011), however this transformation may be inhibited by high sulfate concentrations and low pH (Chen et al., 2022).

Pore-waters were generally supersaturated with respect to Fe (oxy)hydroxide phases such as goethite, lepidocrocite, and ferrihydrite with the notable exception of the extremely acidic pore-waters ($\text{pH} < 2$) at SB04. High concentrations of Fe in the reducible fraction occurred at the top of the tailings at SB02, suggesting the prevalence of crystalline Fe(III) (oxy)hydroxides in the oxidized zone. In the unoxidized tailings, Fe in the reducible fraction remained relatively consistent indicating that smaller amounts of crystalline Fe(III) (oxy)hydroxides remain through the tailings. The ascorbate extraction only accounted for very small masses of Fe relative to the reducible fraction and the total Fe mass, indicating

that amorphous Fe(III) (oxy)hydroxides such as ferrihydrite are not prevalent within the South Bay tailings.

3.3.2.2 Calcium

Higher concentrations of dissolved Ca occur at depths where pH is near-neutral, with maximum concentrations up to 601 mg L⁻¹. Pore-waters were saturated with respect to gypsum [CaSO₄·2H₂O], also at depths where the pH is near-neutral. Although gypsum was not observed in thin section, water-soluble Ca and S are both significantly higher at the base of SB02, suggesting the presence of gypsum (Figure 3.2). Gypsum is a common secondary precipitate in tailings and has been observed at many other field sites (Blowes et al., 1991; Moncur et al., 2005; Blowes et al., 2014; Lindsay et al., 2015).

3.3.2.3 Magnesium and Manganese

The depth trends for dissolved Mg and Mn are similar, with higher concentrations generally occurring deeper in the tailings where the pH is near-neutral. The maximum concentration of Mg was 258 mg L⁻¹ at SB02 and for Mn was 98 mg L⁻¹ at SB01 (Figure 3.2, Figure B1). Dissolved Mg and Mn are mobile within the pore waters, and no secondary phases for these elements were observed. The similarities in the pore-water profiles for Mg and Mn indicate that they may be derived from the same source. Chlorite group minerals are the most likely source of Mg and Mn in the South Bay tailings, with a general formula of (Mg,Fe,Al)₆(Si,Al)₄O₁₀(OH)₈, but with variable concentrations of Fe, Mg, Mn, Li, or Ni in the structure. Other sources for Mg and Mn may include carbonates, feldspars, and amphiboles. The 2 M HCl extraction removed nearly all the Mg and Mn across the entire depth profile, indicating that Mg- and Mn-bearing minerals are potentially susceptible to reductive dissolution. Total Mg and Mn are depleted in the top oxidized tailings, with Mn depletion occurring to a greater extent suggesting that Mn-bearing minerals may be more soluble at acidic pH.

3.3.2.4 Zinc

Dissolved Zn is derived from the dissolution of sphalerite [ZnS], with the maximum Zn concentration as 818 mg L⁻¹ at SB04 (Figure B3). Relatively high concentrations of total Zn remain in the unoxidized tailings, at an average of 2.27% Zn (n=56) measured by XRF. Zinc is relatively mobile in the tailings pore-waters, with elevated concentrations (>100 mg L⁻¹) occurring at several metres below ground surface at some locations despite pH increasing to around pH 6. Total Zn concentrations are depleted in the top oxidized zone of the tailings due to oxidation of sphalerite. The 2 M HHCl extraction removed between 75-100% of the total Zn within the shallow oxidized tailings where total Zn is depleted, indicating that the Zn remaining may be retained within crystalline oxyhydroxides. Lower in the tailings profiles, the 2 M HHCl extraction accounted for between 29-76% of the total Zn, indicating that secondary Zn phases may be susceptible to reductive dissolution, but also that sphalerite may be partially dissolved within this extraction. Much lower concentrations of Zn were extracted with 0.5 M HCl solution or the ascorbate solution indicating that Zn is not largely sequestered within amorphous oxyhydroxides or poorly crystalline phases. Zinc may be sequestered with jarosite or Fe(III) (oxy)hydroxides through adsorption or co-precipitation reactions (Moncur et al., 2005; Romero et al., 2007). The high mobility of Zn in the pore-waters at South Bay is similar to observations at other field sites (Blowes & Jambor, 1990; Moncur et al., 2005; Gunsinger et al., 2006b)

3.3.2.5 Copper

Chalcopyrite [CuFeS₂] is the main source of Cu in the South Bay tailings, with an average of 0.43 % Cu (n=56) in the unoxidized tailings measured by XRF. Dissolved Cu concentrations reach a maximum of 57.4 mg L⁻¹ at SB05 (Figure B4), with elevated dissolved Cu concentrations occurring near the oxidized zone and/or where the pH is less than 4. Total Cu is depleted in the oxidized zone due to oxidation of chalcopyrite. Within the top 1 cm of tailings at SB02 the total Cu is depleted to < 0.1 mg g⁻¹ and the 2 M HHCl extraction accounted for all the total Cu, indicating that the Cu was associated with crystalline Fe(III) (oxy)hydroxides. Overall, the reducible fraction accounts for between 50-100% of the

total Cu in the top meter of tailings, indicating that it may be susceptible to reductive dissolution (Figure 3.4). Secondary covellite [CuS] was identified in thin section within and near the alteration rims of partially oxidized pyrrhotite (Figure 3.5). Covellite is a common secondary Cu mineral in tailings and has been observed at many other sites (Blowes & Jambor, 1990; McGregor et al., 1998; Holmström et al., 1999; Moncur et al., 2005; Gunsinger et al., 2006b; Buis, 2016; Zhang et al., 2023). Formation of secondary covellite acts as a sink for dissolved Cu^{2+} as it is removed from solution by exchange with Fe^{2+} or Zn^{2+} on the surfaces of pyrrhotite or sphalerite (Blowes & Jambor, 1990; Holmström et al., 1999). Adsorption or co-precipitation of Cu with Fe(III) (oxy)hydroxides and hydroxysulfates may also contribute to reduced Cu mobility (McGregor et al., 1998; Gunsinger et al., 2006b).

3.3.2.6 Lead

The oxidation of galena [PbS] in the tailings is the main source of Pb, with dissolved Pb concentrations reaching up to 4.36 mg L^{-1} at location SB04 (Figure B3). Dissolved Pb concentrations are most elevated at acidic pH values less than pH 4. Despite the susceptibility of galena to oxidation in tailings (Lindsay et al., 2015), the total Pb concentrations in the tailings did not generally decrease in the oxidized zone, indicating that Pb may be retained within secondary phases. In SEM-EDX and optical microscopy analysis, Pb was observed to be present within the alteration zones of some pyrrhotite grains (Figure 3.5) and within a Pb-sulfate phase with a composition consistent with anglesite [PbSO₄] (Figure B12). Geochemical modelling indicates pore waters approach saturation with respect to anglesite at SB04 where pH is highly acidic with $\text{pH} < 2$ and dissolved Pb concentrations are high (Figure B3), corresponding to the locations where Pb-sulfate was observed in thin section. The total Pb in the tailings was almost fully extracted with both acidic extraction solutions (0.5 M HCl and 2 M HHCl), suggesting that galena and any secondary Pb phases are soluble in these acidic solutions. The ascorbate extraction accounted for a relatively small amount of Pb in the shallow tailings, but the Pb in the water-soluble fraction was relatively high in the partially oxidized tailings near the surface (Figure 3.4), indicating that some Pb may be weakly adsorbed onto other phases. Studies from other tailings sites have similarly found

that Pb can be attenuated through secondary anglesite precipitation, as well as through adsorption or co-precipitation with jarosite or Fe(III) (oxy)hydroxides (Romero et al., 2007; Hayes et al., 2012; Murray et al., 2014; Courtin-Nomade et al., 2016).

3.3.2.7 Arsenic

Arsenopyrite [FeAsS] is present in minor quantities in the South Bay tailings and is the primary source of As to the pore-waters through sulfide oxidation processes. The maximum concentration of dissolved As was 11.7 mg L⁻¹ at SB03 (Figure B2). Dissolved As is higher near the top of the tailings where pH is acidic and generally decreases with depth. Total As is depleted in the top 10 cm of tailings at SB02, with the reducible fraction accounting for most of the total As at these shallow depths (Figure 3.4). As was found to be in association with Fe(III) (oxy)hydroxides within the shallow oxidized zone, indicating attenuation through adsorption or co-precipitation (Figure B11). Within the hardpan layer at 0.75 m depth, As is elevated in the reducible fraction, 0.5 M HCl extractable-fraction, and the ascorbate solution fraction, also indicating attenuation of As through adsorption and co-precipitation with secondary oxyhydroxide phases in the hardpan. Relatively low amounts of As occur in the water-soluble fraction and ascorbate-extractable fraction throughout the rest of the profile. Previous studies have identified that dissolved As concentrations are controlled by the precipitation of As with Fe oxyhydroxides and Fe arsenates, as well as adsorption onto Fe oxyhydroxides in the oxidizing zone of tailings (DeSisto et al., 2011; Parviainen et al., 2012; Paktunc, 2013; DeSisto et al., 2016). Under reducing conditions, dissolution of oxides can remobilize As, but adsorption or co-precipitation with other secondary phases such as siderite or gypsum can further control dissolved As concentrations (DeSisto et al., 2016).

3.3.2.8 Cobalt

Cobalt in the South Bay tailings averages 331 ppm (n=56) and likely originates from substitution of Co within other sulfide minerals. No discrete cobalt-bearing minerals such as cobaltite were observed. Previous work by Seccombe (1977) indicated that the chalcopyrite in the South Bay economic deposit contained an average of 1850 ppm Co and pyrite contained an average of 79 ppm Co, accounting for

some of the total Co in the tailings. However, Co may also be associated with other sulfide minerals in the tailings, such as pyrrhotite. Maximum dissolved Co concentrations of 9.99 mg L^{-1} occurred at SB02 near the top of the tailings (Figure 3.4). Cobalt has moderate mobility in the pore-waters, with elevated dissolved Co concentrations occurring at several metres depth at some locations. The water-soluble and ascorbate-extractable Co fractions accounted for <1% of the total Co, indicating that Co is not generally associated with soluble or amorphous phases. The 0.5 M HCl extraction only accounted for up to 2.5% of the total Co, indicating that it is also not greatly associated with poorly crystalline phases. In the top oxidized tailings where total Co concentrations are low and sulfide minerals have been obliterated, the remaining Co is present as the reducible fraction. This Co in the reducible fraction is likely associated with goethite, as Co can incorporate into the goethite structure (Cornell, 1991; Alvarez et al., 2015). Below this zone, the reducible fraction accounts for up to 7% of the total Co, indicating some retention of Co with crystalline oxyhydroxides.

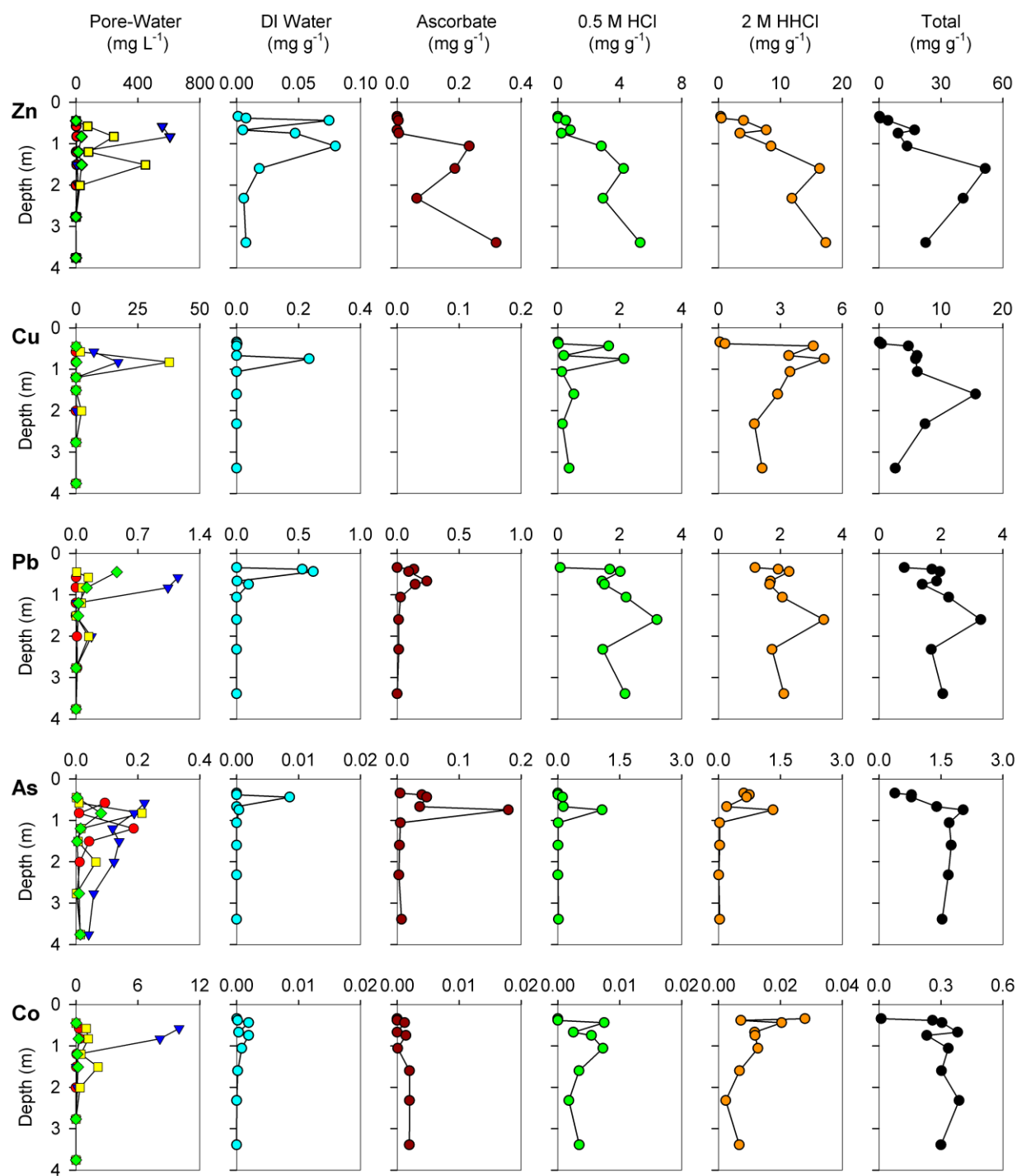


Figure 3.4. Selective extraction profiles for Zn, Cu, Pb, As, and Co at SB02. Pore-water chemistry for each element is plotted on the left, with data from June 2021 (red circles), Sept 2021 (blue triangles), June 2022 (yellow squares), and Sept 2021 (green diamonds).

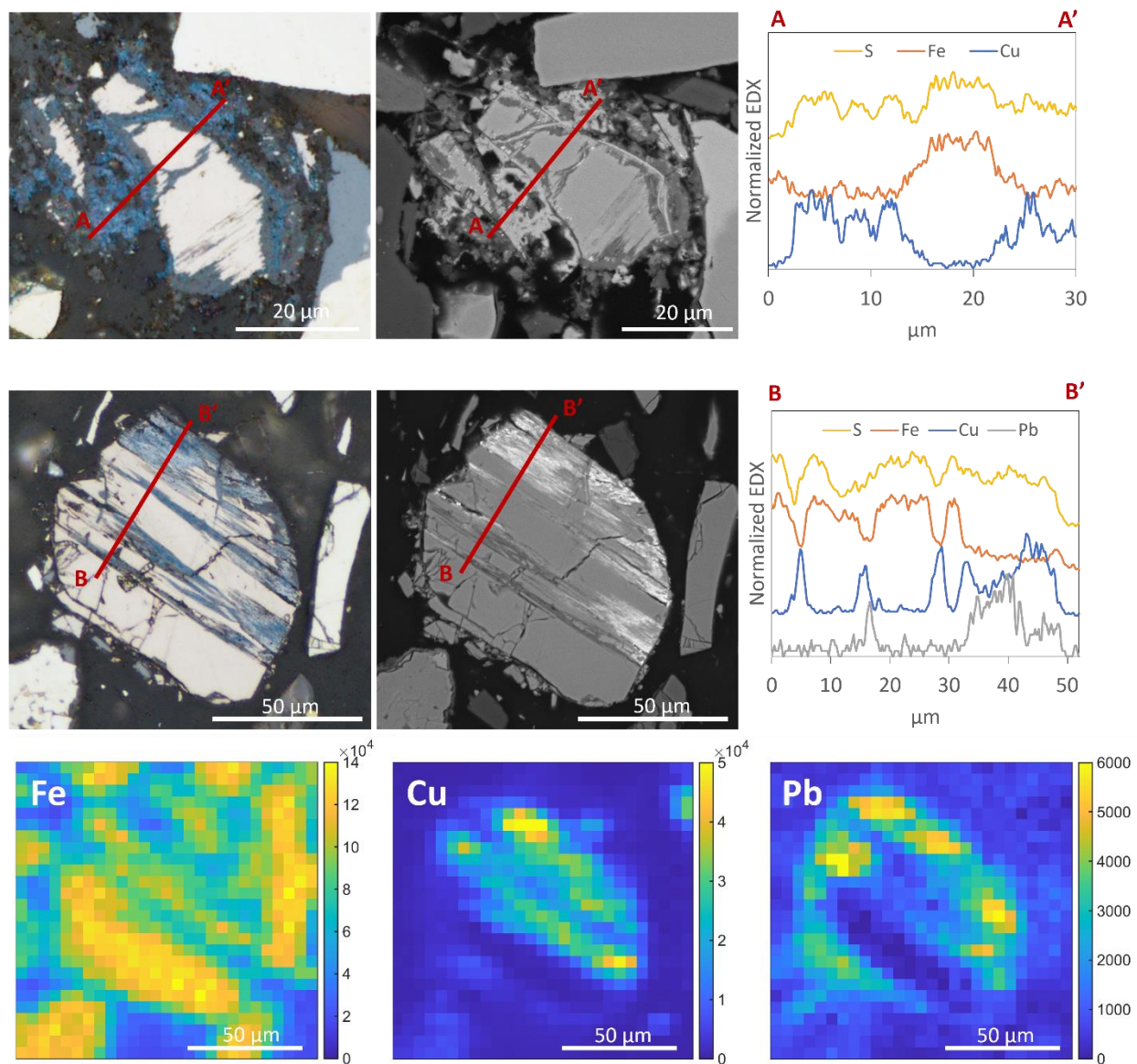


Figure 3.5. Top: microscope image (left) and backscattered electron (BSE) image (middle) of partially oxidized pyrrhotite surrounded by covellite (blue) at 0.44 m depth (0.10 m below sand cover). Middle: microscope image (left) and BSE image (middle) of partially oxidized pyrrhotite at 0.67 m depth (0.33 m below sand cover) with covellite and Pb accumulations within the alteration zone. EDX line profile data (right) was normalized to a maximum intensity of one for each element, and elements were offset along the Y-axis. Bottom: μ -XRF maps of Fe, Cu, and Pb distributions in the pyrrhotite grain from the middle row.

3.3.3. Mobility of Rare Earth Elements

Although there is some variation in REE classification in the literature, for this study REEs have been classified as light rare earth elements (LREE) from La to Eu and heavy rare earth elements (HREE) from Gd to Lu. An additional classification of middle rare earth elements (MREE) from Sm to Dy overlaps both the LREE and HREE classes and is used to describe trends in chondrite-normalized REE patterns (Migaszewski & Gałuszka, 2023).

The tailings at SB02 have a total REE (La-Lu) concentration between 115-236 ppm (average 236 ppm, n=12), and the tailings at SB04 have a total REE concentration between 190-543 ppm (average 361 ppm, n=6). The depth profiles for LREEs and HREEs at SB02 and SB04 are shown in Figure 3.6, whereas the complete depth profiles by element for solid and dissolved REE concentrations are included in Appendix B (Figure B13-Figure B17). HREE concentrations are elevated near the top of the tailings at SB02 relative to deeper in the profile, whereas at SB04 the HREEs in the solid phase appear slightly depleted around 1 m depth where the pH is highly acidic (Figure 3.6). REE concentrations were also analysed in the 2M HHCl in 25%(v/v) acetic acid solution extractant. The LREEs in the unoxidized tailings were almost fully extracted, whereas the HREEs showed limited dissolution in this extraction. In the top oxidized and partially oxidized tailings at SB02, LREEs were more resistant to dissolution by the 2 M HHCl extraction.

Pore-water concentrations reach a maximum of 9.45 mg L⁻¹ total REEs within the top m of tailings at SB02 where the pH is acidic (pH 3.37), and abruptly decrease to <0.1 mg L⁻¹ below 1 m where the pH is > 5. Previous studies have shown that acidic waters often contain elevated concentrations of REEs (Smedley, 1991; Leybourne et al., 2000; Fernández-Caliani et al., 2009; Khorasanipour & Jafari, 2018) and REEs behave conservatively in acid sulfate waters with pH values less than 5.1 (Verplanck et al., 2004), consistent with the observations at this site. Adsorption or co-precipitation with Fe oxyhydroxides is likely responsible for the sharp decrease in dissolved REEs at near-neutral pH (Verplanck et al., 2004; Liu et al., 2017). The 2M HHCl extraction was chosen to target crystalline and

amorphous oxyhydroxides, however this extraction likely also promoted dissolution of some of the primary REE phases and therefore the REE concentrations from this extraction cannot be attributed to adsorption or co-precipitation alone.

At location SB04, the pore-waters are highly acidic, with pH values between 1.26 and 3.75 within the tailings. Total dissolved REE concentrations in the tailings pore-water at SB04 range from 0.25-0.83 mg L⁻¹; much lower than the maximum concentrations measured at SB02. Due to the very low pH present throughout the tailings at SB04, the readily dissolvable REE-bearing minerals may have already been depleted, leading to lower dissolved REE concentrations in comparison to the top of the tailings at SB02. REE-phosphates were detected by SEM-EDX in the shallow oxidized tailings at SB04, however some of these were partially encased by silicates and may therefore be shielded from acidic leaching (Figure B18).

The aqueous speciation of REEs in acid mine waters is usually dominated by sulfate complexes (Gammons et al., 2003; Verplanck et al., 2004; Leybourne et al., 2006; Fernández-Caliani et al., 2009; Perez-Lopez et al., 2010). Spearman's rank correlation was computed to assess the relationship between 15 dissolved sulfate and total dissolved REE (La-Lu) values. There was a strong positive correlation between the two variables, $r(13)=0.69$, $p<0.01$. This correlation suggests aqueous sulfate complexation of REEs within the South Bay tailings.

The maximum concentration of total REEs measured at South Bay (9.45 mg L⁻¹) is comparable to the maximum concentrations measured at some other acidic mine sites such as 1.58 mg L⁻¹ at a former Cu-Zn-Pb-Ag mine (Grawunder et al., 2014), 2.9 mg L⁻¹ at the Berkley Pit lake (Gammons et al., 2003), 4.5 mg L⁻¹ at a former U mine (Grawunder et al., 2014), and 11.7 mg L⁻¹ in the Iberian Pyrite Belt (Ayora et al., 2016). However, other sites have reported even higher total REE concentrations, such as 90.1 mg L⁻¹ of REEs measured in an acid pit pond in south-central Poland (Migaszewski & Gałuszka, 2023).

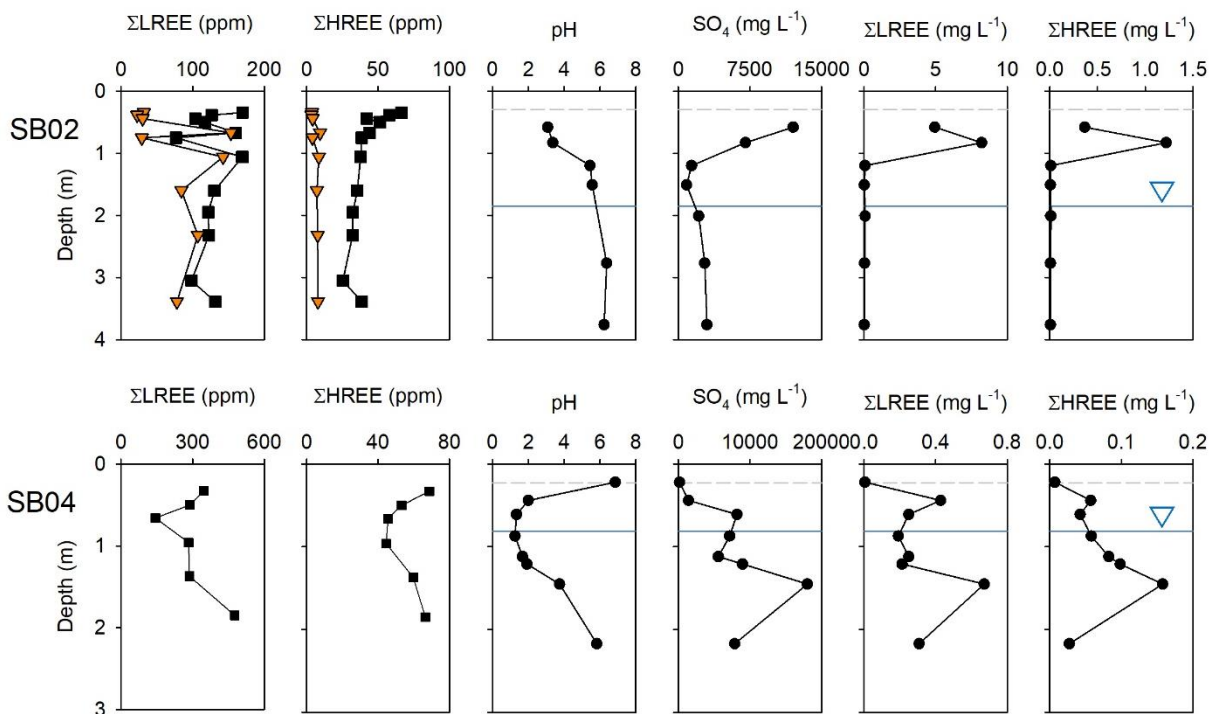


Figure 3.6. Depth profiles of solid phase REEs (black squares), REEs extracted with 2 M HCl solution (orange triangles), pH, sulfate, and dissolved REEs from SB02 (top column) and SB04 (bottom column). Water chemistry data is from Sept 2021 samples. The dashed grey line represent the tailings-sand interface, and the solid blue line represents the water table in Sept 2021.

REE concentrations were normalized to the North American Shale Chondrite (NASC) (Haskin et al., 1968; Gromet et al., 1984) to show potential enrichments or depletions of elements relative to this standard (Figure 3.7). The tailings solids at SB02 are depleted in LREEs relative to HREEs and show a steady increase in NASC-normalized concentration from La to Eu. Pore-water NASC-normalized REE concentrations at SB02 similarly display an upward trend from La to Eu, peaking at Eu, but with HREE depletion relative to the solid-phase. The pore-waters at SB02 are slightly MREE-enriched from Sm to Gd. The deeper pore-water samples from SB02 were not plotted in Figure 3.7 as the REE concentrations were near or below the instrument detection limit. The tailings solids at location SB04 also show a steady increase from La to Eu, but generally show more MREE enrichment from Sm-Gd relative to both LREEs and HREEs. The NASC-normalized trends in the pore-waters at SB04 are generally flat in profile, with several samples displaying HREE enrichment.

It is evident that some fractionation of REEs is occurring between the solid and aqueous phases at both SB02 and SB04, as the pore-waters do not show the same NASC-normalized patterns in the solid phase. However, since these two locations are within the same tailings impoundment but show different types of fractionations, they may be affected by different factors such as pH, secondary precipitates, or mineralogy. The tailings solids at SB02 are more HREE-enriched in comparison to the tailings at SB04, indicating either a difference in REE distributions within the host mineralogy, or increased leaching of HREE-bearing minerals in the highly acidic pore-waters at SB04.

MREE-enrichment is common in acidic waters (Fernández-Caliani et al., 2009; Ferreira da Silva et al., 2009; Pérez-López et al., 2010; Grawunder et al., 2014; Wallrich et al., 2020; Migaszewski & Gałuszka, 2023), with several explanations proposed, such as complexation to intermediate S species during pyrite oxidation (Grawunder et al., 2014), partitioning of REEs into secondary minerals (Welch et al., 2009), adsorption to Fe and Al oxyhydroxides (Leybourne et al., 2000; Gammons et al., 2005; Lozano et al., 2020), or preferential dissolution of MREE-enriched minerals (Johannesson & Zhou, 1999; Sun et al., 2012; Wallrich et al., 2020; León et al., 2023). MREE-enrichment occurs in the pore-waters from SB02 but not at SB04, indicating that the process leading to this fractionation may not be important at location SB04.

The 2 M HCl extraction performed on samples from SB02 indicates that LREEs are preferentially leached in comparison to the HREEs, similar to the trends seen in the pore-waters at SB02. This extraction solution is acidic and may be dissolving the acid-soluble REE-bearing minerals within the tailings, similar to those being dissolved by acidic pore-waters in the tailings. Although a full mineralogical analysis of REE-bearing minerals was not conducted on the tailings samples, a phase with composition consistent with that of monazite $[\text{Ce,L a,Nd,Th}]\text{PO}_4$ was detected by SEM-EDX (Figure B18). Monazite is an LREE-enriched phosphate, whereas xenotime $[\text{YPO}_4]$ is an HREE-enriched phosphate. Experiments by Lazo et al. (2020) indicate that monazite is more susceptible to dissolution in both sulfuric acid and organic acids than xenotime. Therefore, if both monazite and xenotime are present

in the South Bay tailings, the prevalence of dissolved LREE over HREE could be attributed to the preferential dissolution of monazite over xenotime in acidic waters.

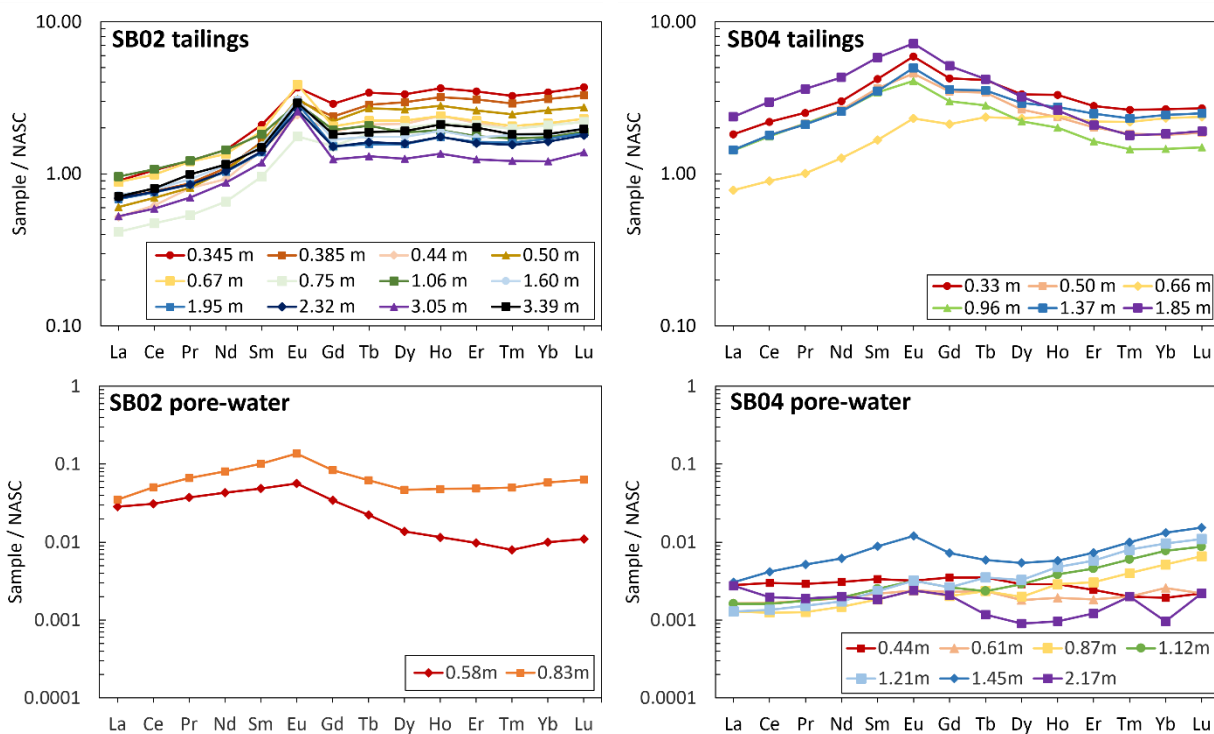


Figure 3.7. NASC-normalized REE patterns from SB02 tailings, SB04 tailings, SB02 dissolved phase, and SB04 dissolved phase.

3.3.4. Implications for the Development of Remediation Strategies

The South Bay tailings are oxidized to between 0-0.15 m depth at the sampling locations, and between 0.3-1.3 m of tailings remain available for oxidation before the water table is reached. Modelling results have indicated that the tailings will continue oxidizing for over 4,000 years (Chapter 2), demonstrating the need for a cover system to limit further sulfide mineral oxidation. However, cover systems may alter the geochemical conditions of the tailings, remobilizing previously sequestered metal(loid)s to the tailings. Organic-carbon rich covers can create reducing conditions, leading to reductive dissolution of Fe(III) (oxy)hydroxides and release of adsorbed or co-precipitated metal(loid)s

(Ribet et al., 1995; Paktunc, 2013). Previous studies have indicated the release of dissolved Fe and As when a biosolids cover or organic carbon amendments were added to tailings (Lindsay et al., 2011; Paktunc, 2013). Methylation of dissolved metals due to methanogenesis under an organic-carbon rich cover may also mobilize metals as highly toxic complexes, creating additional environmental contamination (Tassé et al., 1994).

In this study, the 2 M HCl extraction, referred to as the reducible fraction, was used to indicate what metal(loid)s may be susceptible to reductive dissolution. In the shallow oxidized tailings, the reducible fraction accounted for nearly all the total concentrations for the metal(loid)s, suggesting that metal(loid)s in the oxidized tailings may be remobilized under highly reducing conditions. However, total concentrations of metal(loid)s were often depleted in the oxidized zone in comparison to the unoxidized zone. Elevated concentrations of Fe, Zn and Cu occur in the reducible fraction within the unoxidized tailings, and reducible As was found to be elevated in the hardpan. For Mg, Mn, and Pb, the reducible fraction was comparable or equivalent to the total concentration, suggesting that the host minerals for these elements are susceptible to reductive dissolution. However, a common limitation to these types of extraction methods is that the extractions may not be exclusive to their targeted phases. Although the 2 M HCl extraction was intended to target amorphous and crystalline oxyhydroxides, it is likely that other minerals are also soluble in this extraction solution. For example, the 2 M HCl extraction was found to also dissolve some pyrrhotite in addition to the targeted oxyhydroxides (McGregor, 1994). Further limitations for these extraction methods are that the results are operationally defined and may not be representative of concentrations that could be released under natural conditions (Nirel & Morel, 1990).

Mine tailings are increasingly being examined as a potential economic source of critical minerals (Sarker et al., 2022). Reprocessing of the tailings may also help contribute to the costs of remediation. The South Bay tailings contain elevated concentrations of Cu (0.43%) and Zn (2.27%) among other metals which may prove economically feasible for reprocessing as other higher-grade ore bodies around the world are depleted through mining activities. Acid mine drainage (AMD) waters and treatment by-

products have also previously been identified as a potential economic source of REEs, such as the AMD produced within the Iberian Pyrite Belt (León et al., 2021), or AMD from coal mining districts in the Northern Appalachian Coal Basin (Vass et al., 2019). Further studies are required to determine whether the elevated concentrations of dissolved REEs in the pore-waters in the South Bay tailings present an economically viable opportunity for secondary REE recovery.

3.4 Conclusions

Oxidation of sulfide minerals within the South Bay tailings has led to elevated pore-water concentrations of dissolved sulfate and metal(oids), up to 23,700 mg L⁻¹ SO₄, 8,320 mg L⁻¹ Fe, 818 mg L⁻¹ Zn, 57.4 mg L⁻¹ Cu, 11.7 mg L⁻¹ As, 9.99 mg L⁻¹ Co, and 4.36 mg L⁻¹ Pb. Furthermore, dissolved REEs are elevated within the acidic pore waters, up to a maximum of 9.45 mg L⁻¹ total REEs (La-Lu). Fractionation of REEs between the solid and dissolved phases was evident, although this fractionation may be impacted by the different geochemical conditions in the tailings. Enhanced dissolution of LREE-bearing minerals relative to HREE-bearing minerals may be responsible for this fractionation at SB02. REEs are mobile in the tailings at acidic pH values, and concentrations sharply decrease where pH increases to > 5 suggesting attenuation through adsorption or co-precipitation reactions.

The pore-water pH is buffered through a series of dissolution reactions involving calcite, siderite, Al hydroxides, Fe(III) (oxy)hydroxides, and aluminosilicates. The five locations sampled displayed variations in pH and pH-buffered plateaus within the pore-waters, indicating relatively high spatial variability of pore-water geochemistry within the same tailings impoundment. Extractions results indicate that amorphous and poorly crystalline oxyhydroxide phases are not present in significant amounts in the tailings, but rather crystalline oxyhydroxides are more prevalent. Metals are sequestered through the precipitation of secondary phases such as jarosite, schwertmannite, goethite, gypsum, covellite, and anglesite. Metals that remain relatively mobile in the pore waters include Fe, Mg, Mn, and Zn, with enhanced mobility at lower pH. Some depletion of metals including Cu, Zn, As, and Co occurs in the shallow tailings since the primary host minerals for these metals have been oxidized. The hardpan layer

contains higher concentrations of adsorbed or co-precipitated As relative to the rest of the profile, however other metals were not found to be enriched within the hardpan layer. Relatively high concentrations of Cu and Zn remain in the unoxidized tailings, at approximately 0.43% Cu and 2.27% Zn, indicating that historical mine wastes such as these may have the potential to become an economical source of metals in the future as the more accessible higher-grade deposits become depleted around the world. The elevated concentrations of REEs in the pore-waters may also present an economic source of these elements in the future. Remediation strategies for the South Bay tailings should consider the potential for remobilization of sequestered metals under reductive dissolution conditions, as the reducible fraction accounted for a large portion of the total for many metals and metalloids.

Chapter 4: Conclusions and Recommendations

Since the cessation of mining operations in 1981, the tailings at the South Bay mine have oxidized. Sample collection for this study was conducted in 2021 and 2022 to examine the tailings hydrogeology, geochemistry, mineralogy, and microbiology after 40 years of oxidation. The tailings impoundment is a local groundwater recharge area, with groundwater flow predominantly downward and outward from a water-table mound in the centre of the tailings impoundment towards the Decant Pond, Boomerang Lake, and Mud Lake. Acidic conditions (pH 2.7 - 3.2) prevail in both Boomerang Lake and Mud Lake due to acidic seepage from the tailings and mill site area.

The tailings contain high concentrations of sulfide minerals, with the unoxidized tailings containing an average of 27 wt. % S. Pyrite is the predominant sulfide mineral. Lesser amounts of sphalerite and chalcopyrite, and trace amounts of pyrrhotite, galena, and arsenopyrite are also present in the tailings. Extensive oxidation of the tailings is restricted to the upper 0-15 cm, a notably shallower oxidation extent in comparison to many other abandoned tailings sites that have similarly been oxidizing for several decades. The layer of sand and gravel, placed over the tailings shortly after mine closure, does little to reduce O₂ ingress into the tailings. Pore-gas O₂ remains close to atmospheric concentrations within the sand and gravel layer but decreases rapidly within the top 10-20 cm of tailings.

Factors that were found to contribute to the limited extent of oxidation in the South Bay tailings include a relatively high water table, fine grain-size, and high concentration of pyrite. The water table position, situated close to the surface, along with a fine grain-size within the tailings both contribute to high moisture content, leading to a reduced rate of O₂ diffusion within the vadose zone. High sulfide concentrations also lead to the rapid consumption of O₂ in the shallow tailings. Pyrite is more resistant to oxidation than many other sulfide minerals, therefore its predominance within the South Bay tailings has contributed to the limited oxidation. Pyrrhotite is more susceptible to oxidation than other sulfide

minerals and shows alteration to a deeper extent than pyrite in the South Bay tailings, but was only present in minor quantities.

Pore-waters within the tailings are acidic (as low as pH 1.26) in the shallow tailings where active sulfide mineral oxidation is occurring and pH increases to circumneutral deeper in the profile. The shallow tailings contain elevated populations of acidophilic Fe- and S-oxidizing microorganisms. Elevated populations of SRBs occur where pore-waters transition from acidic to circumneutral in the depth profile. A relative enrichment of $^{34}\text{S-SO}_4$ and $^{18}\text{O-SO}_4$ in the pore-waters occurs at the base of the tailings impoundment at location SB05, indicative of dissimilatory sulfate reduction.

Acid neutralization processes within the tailings include the dissolution of primary and secondary mineral phases within the tailings, including calcite, dolomite, siderite, Al hydroxides, Fe (oxy)hydroxides, and aluminosilicates. The carbonate neutralization potential of the tailings is relatively low, with an average of <1 wt. % total C. As gangue minerals involved in acid neutralization are depleted and sulfide minerals continue to oxidize, the pore-waters will progressively become more acidic, and the acid front will migrate downwards.

High concentrations of dissolved sulfate and metal(oids) occur in the tailings pore-waters, with concentrations of SO_4 up to 23,700 mg L⁻¹, Fe up to 8,320 mg L⁻¹, Zn up to 818 mg L⁻¹, Cu up to 57.4 mg L⁻¹, As up to 11.7 mg L⁻¹, Co up to 9.99 mg L⁻¹, and Pb up to 4.36 mg L⁻¹. The relative mobility of metal(loid)s in the tailings was determined to follow the order $\text{Fe} = \text{Mg} = \text{Mn} \geq \text{Zn} > \text{Co} \geq \text{As} \geq \text{Pb} > \text{Cu}$. The metal(loid)s with the lowest mobility, As, Pb and Cu, may be attenuated through adsorption or co-precipitation with secondary mineral phases. Secondary covellite was observed along the alteration rims of partially oxidized pyrrhotite grains and is responsible for Cu attenuation. Lead was also observed to be attenuated by adsorption or co-precipitation within pyrrhotite alteration rims. Precipitation of secondary anglesite may also be responsible for Pb attenuation. SEM-EDX analysis indicated the presence of a phase with composition consistent with anglesite within the highly acidic oxidized tailings at SB04. Arsenic may be attenuated through adsorption or co-precipitation with Fe(III) (oxy)hydroxides. μ -XRF

mapping of Fe (oxy)hydroxide grains in the shallow oxidized tailings indicated the presences of As. Adsorption or co-precipitation with Fe(III) (oxy)hydroxides and hydroxysulfates may also contribute to the attenuation of other metals and metalloids. Modelling of saturation indices indicates that thermodynamic conditions are favourable for the precipitation of Fe(III) (oxy)hydroxide phases such as ferrihydrite, goethite, and lepidocrocite, and Fe hydroxysulfate phases such as jarosite, throughout most of the tailings except for locations and depths with highly acidic pH.

A discontinuous hardpan layer has developed in some areas of the South Bay tailings due to the accumulation of secondary minerals. This hardpan layer was found at <1 m depth and is between 10-20 cm thick. The precipitation of Fe(III) (oxy)hydroxides and hydroxysulfates has formed a loose cement within this layer. Analysis of the hardpan layer did not indicate any enrichment of total metals or metalloids, although As was enriched within the reducible phase in the hardpan. Selective extractions have indicated that water-soluble phases and amorphous oxyhydroxide phases do not account for a large portion of metal(oids). Relatively high concentrations of metal(oids) are associated with crystalline oxyhydroxides in the reducible phase and may be susceptible to reductive dissolution. Therefore, if any future remediation efforts generate strong reductive conditions within the tailings, metal(oids) that were previously sequestered with Fe(III) (oxy)hydroxides may be remobilized through reductive dissolution.

REEs were found to be mobile in the acidic pore-waters, with concentrations up to 9.45 mg L⁻¹ of total REEs. At depths where the pH is > 5, the concentrations of dissolved REEs sharply decrease, indicating that REEs are not mobile in circumneutral waters. There was some fractionation observed in the LREEs and HREEs between the solid phase and dissolved phase, however this fractionation was not consistent between both sampled locations and further research may be required to understand this fractionation.

Modelling of sulfide mineral oxidation within the South Bay tailings has indicated that it may take centuries to millennia to fully oxidize all the sulfide minerals within the vadose zone. Therefore, it is recommended that future remediation efforts at the site focus on developing a long-term system to limit

sulfide mineral oxidation, such as through an engineered cover. Further research should be undertaken to determine what remediation options may be best suited for this site.

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Appendix A: Additional Figures from Chapter 2

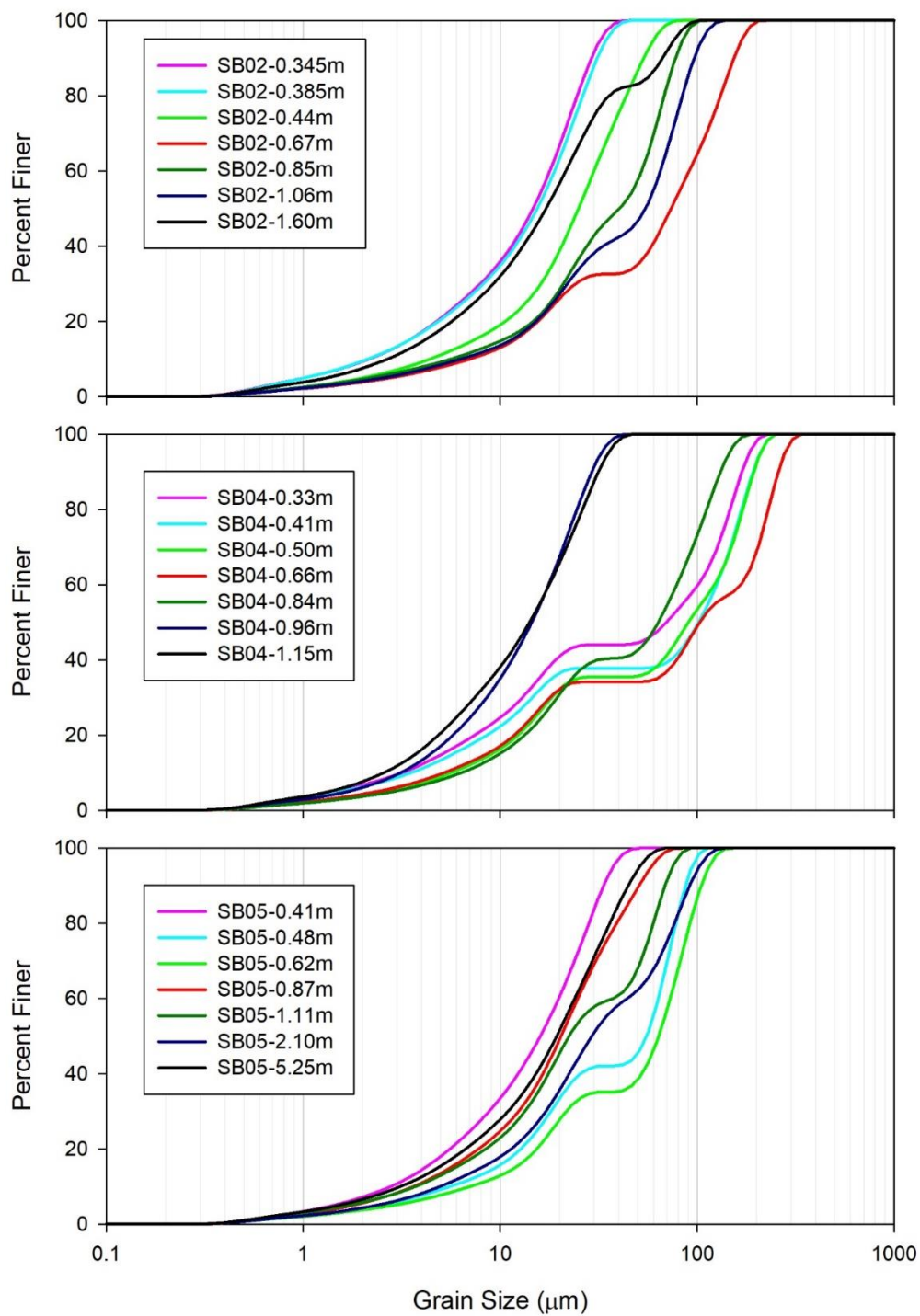


Figure A1. Grain size distributions of tailings samples from SB02, SB04, and SB05

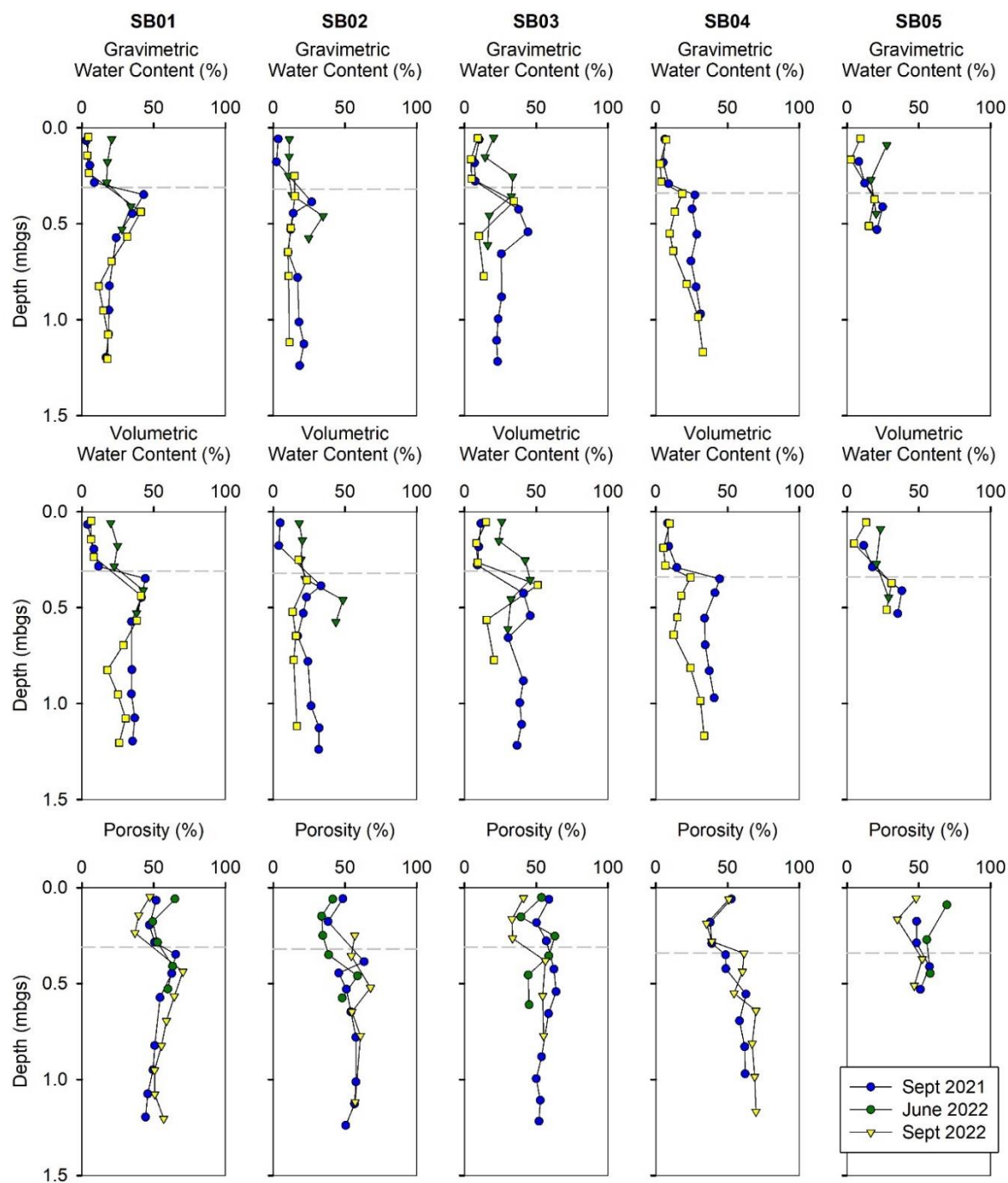


Figure A2. Depth profiles of gravimetric water content, volumetric water content, and porosity calculated from collected cores. The grey dashed line represents the interface between the sand and gravel layer and the tailings. Note that the high porosity values were a result of high compression during core collection.

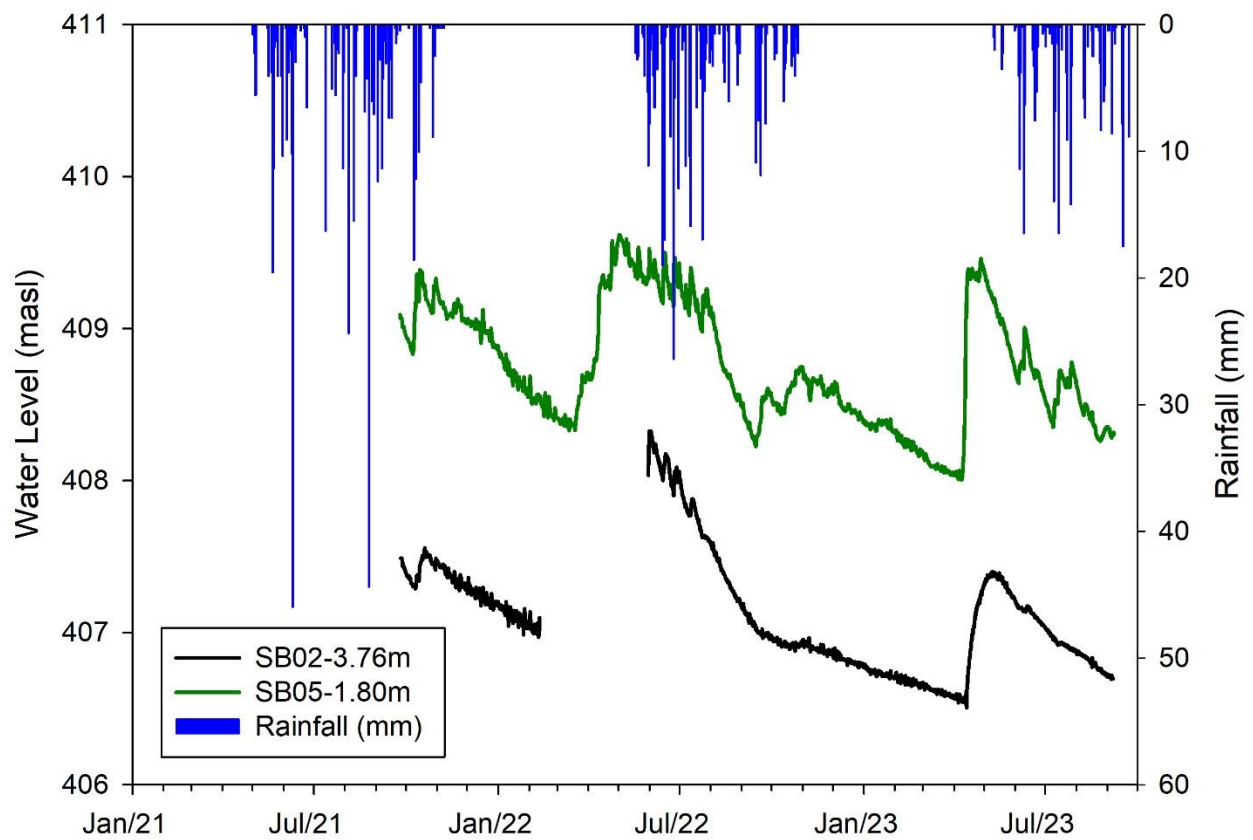


Figure A3. Water level in metres above sea level (masl) and daily rainfall data from 2021-2023. Location SB02-3.76m has missing data from Feb-April 2022. No snowpack data was available.



Figure A4. Test pit photos from all sampling locations showing the sand and gravel layer overlying the tailings, with a thin oxidation zone.

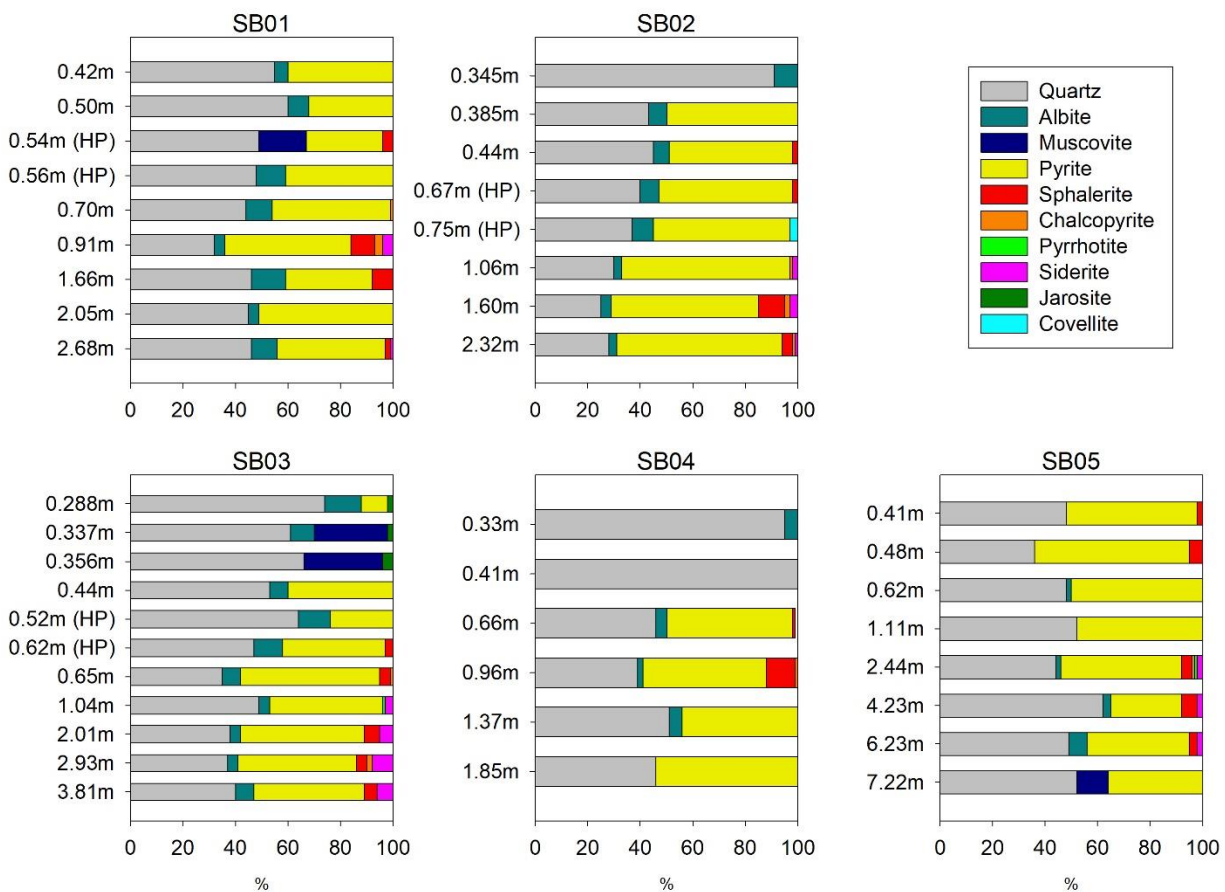


Figure A5. Powder XRD semi-quantitative results of tailings mineralogy. Note: “HP” indicates a hardpan sample. Chlorite was indicated to be present in small quantities in some samples, but was not able to be quantified using the standards present in the database.

Table A1. Samples in which microbial diversity was analysed. Samples that were analysed in duplicate are marked with asterisks. A sample that was discarded before sequence data processing (due to a low number of sequences) is marked with two asterisks.

Location	Depth (m)	Material type
SB02	0.3	sand and gravel layer
	0.345	oxidized tailings
	0.385*	(partially) oxidized tailings
	0.44	unoxidized tailings
	0.5	unoxidized tailings
	0.85	unoxidized tailings
	1.28	unoxidized tailings
	1.79	unoxidized tailings
	2.32	unoxidized tailings
	2.71	unoxidized tailings
	3.28	unoxidized tailings
	3.67*	peat (& tailings)
SB04	0.22	sand and gravel layer
	0.33	oxidized tailings
	0.5	unoxidized tailings
	0.85*	unoxidized tailings
	1.37	unoxidized tailings
	1.71	unoxidized tailings
	2.13	peat
	2.25	native sand
SB05	0.45	unoxidized tailings
	0.79*	unoxidized tailings
	1.8	unoxidized tailings
	2.98	unoxidized tailings
	5.18**	unoxidized tailings
	7.44	peat (& tailings)

Table A2. Calculated hydraulic conductivity values within the tailings

Location	Depth	Date	Hydraulic Conductivity (m s ⁻¹) [Hvorslev]
SB01	1.53 m	12-Jun-21	5.4×10^{-7}
	1.98 m	11-Jun-21	1.3×10^{-7}
	2.48 m	11-Jun-21	2.8×10^{-8}
SB02	3.76 m	09-Jun-21	6.6×10^{-8}
	3.76 m	10-Jun-21	6.3×10^{-8}
SB03	2.28 m	19-Sep-21	5.9×10^{-8}
SB05	2.98 m	12-Jun-21	1.9×10^{-7}
	5.18 m	19-Sep-21	1.5×10^{-7}

Table A3. Calculated vertical and horizontal hydraulic gradients.

Location	June 12, 2021	Sept 19, 2021	May 29, 2022	Sept 18, 2022	Average
	Vertical Hydraulic Gradient				
SB01	0.21	0.03	0.11	-0.01	0.085
SB02	0.18	0.12	0.59	0.41	0.324
SB03	0.14	0.07	0.10	0.03	0.084
SB04	0.19	0.47	0.55	N/A	0.404
SB05	0.00	0.00	-0.02	0.00	-0.005
Direction	Horizontal Hydraulic Gradient				
SB05 → SB01	0.0024	0.0051	0.0017	0.0041	0.00332
SB05 → SB02	0.0131	0.0149	0.0091	0.0122	0.01231
SB05 → SB03	0.0050	0.0069	0.0028	0.0053	0.00500
SB05 → SB04	0.0039	0.0041	0.0020	0.0053	0.00382

Table A4. Calculated vertical and horizontal groundwater velocities

Location	June 12, 2021	Sept 19, 2021	May 29, 2022	Sept 18, 2022	Average
	Vertical Groundwater Velocity (m a ⁻¹)				
SB01	1.20	0.16	0.61	-0.05	0.48
SB02	0.99	0.68	3.30	2.34	1.83
SB03	0.80	0.39	0.55	0.16	0.48
SB04	1.09	2.63	3.11	N/A	2.28
SB05	0.00	-0.02	-0.09	0.00	-0.03
Direction	Horizontal Groundwater Velocity (m a ⁻¹)				
SB05 → SB01	0.029	0.063	0.021	0.051	0.041
SB05 → SB02	0.163	0.184	0.112	0.151	0.153
SB05 → SB03	0.062	0.085	0.035	0.066	0.062
SB05 → SB04	0.049	0.051	0.025	0.065	0.047

Table A5. Example of the six best linear combination fitting results from SB02-0.75m (hardpan). Fit #1 was chosen as the best fit as it had the lowest R factor, and the presence of sphalerite was confirmed by optical microscopy.

Fit #	Number of variables	Reduced Chi-Square	R Factor	Pyrite (%)	Pyrrhotite (%)	Sphalerite (%)	Chalcopyrite (%)	Elemental S (%)	Schwertmannite (%)	Thiosulfate (%)	Gypsum (%)
1	4	7.54E-05	6.90E-05	88.6		1.3	6.8		3.3		
2	4	8.91E-05	8.15E-05	86.6			8.4	1.7	3.3		
3	3	9.99E-05	9.18E-05	89.1			7.7		3.2		
4	4	9.99E-05	9.15E-05	88.9			7.6		3.2	0.3	
5	4	1.00E-04	9.15E-05	89.0			7.7		3.1		0.2
6	4	1.22E-04	1.12E-04	87.4	6.4	2.8			3.4		

Appendix B: Additional Figures from Chapter 3

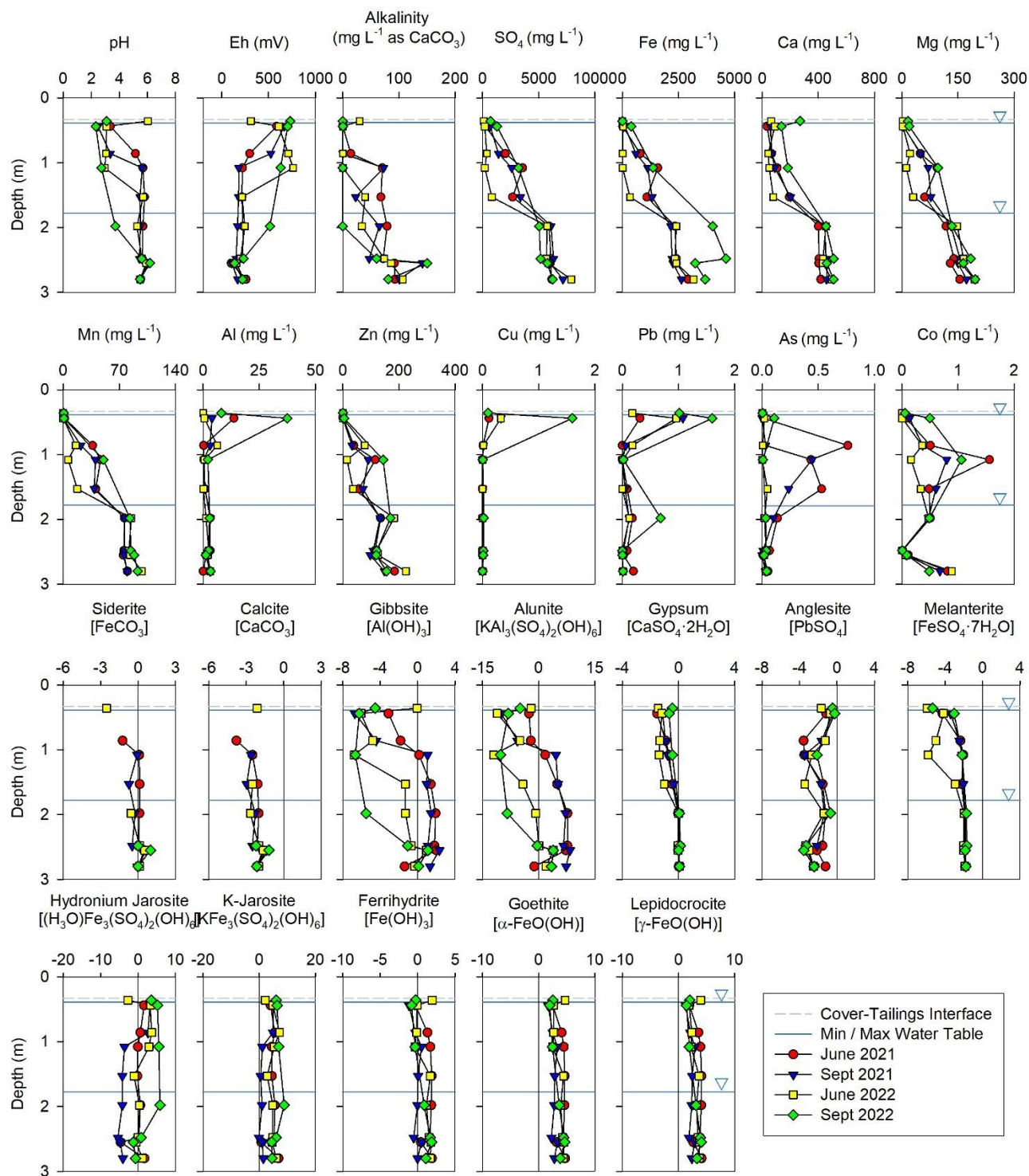


Figure B1. SB01 pore-water chemistry and saturation indices depth profiles.

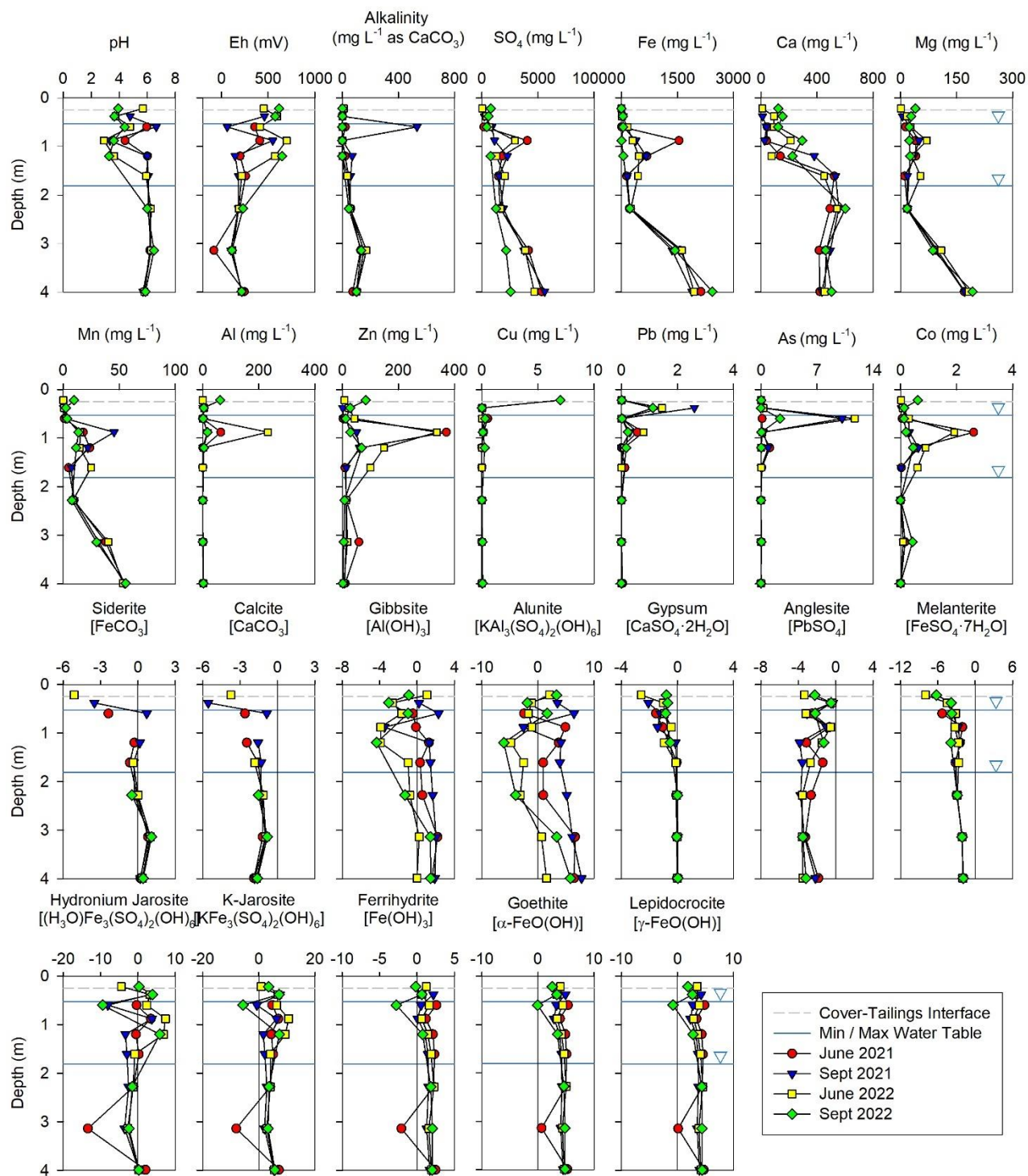


Figure B2. SB03 pore-water chemistry and saturation indices depth profiles.

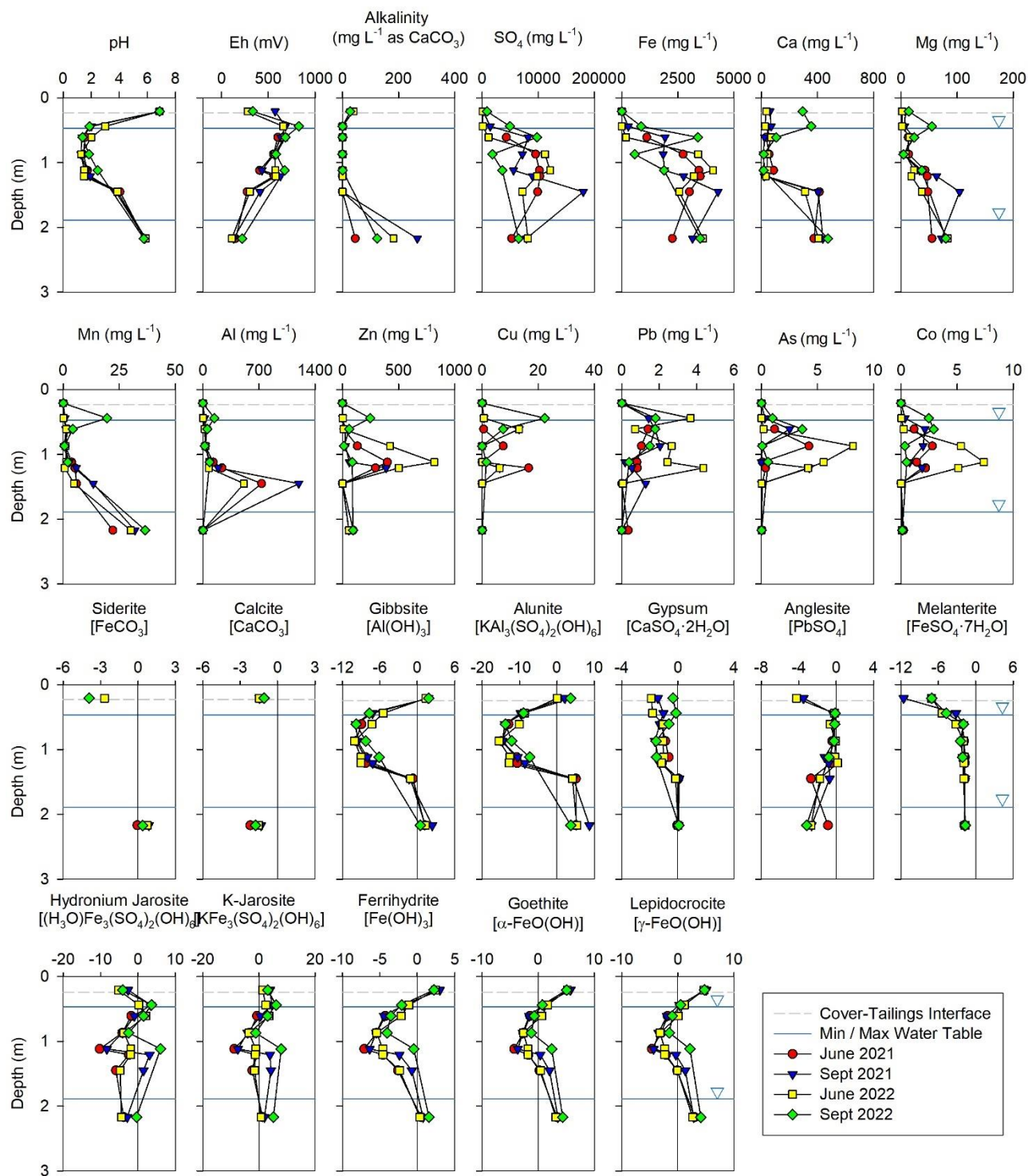


Figure B3. SB04 pore-water chemistry and saturation indices depth profiles. Note: some water chemistry data has previously been presented in Chapter 2 as well as in Figure 6.

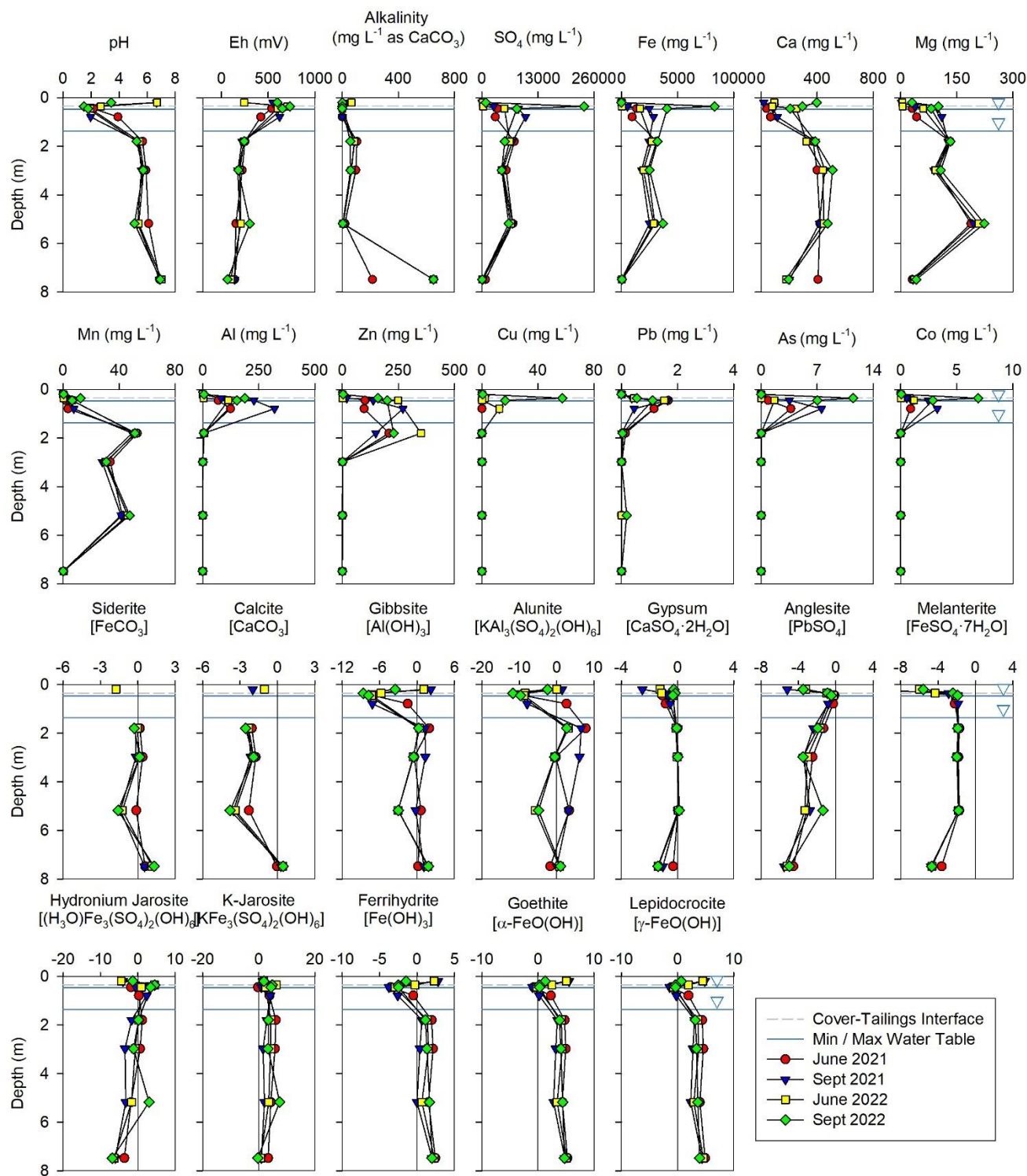


Figure B4. SB05 pore-water chemistry and saturation indices depth profiles. Note: some water chemistry data has previously been presented in Chapter 2.

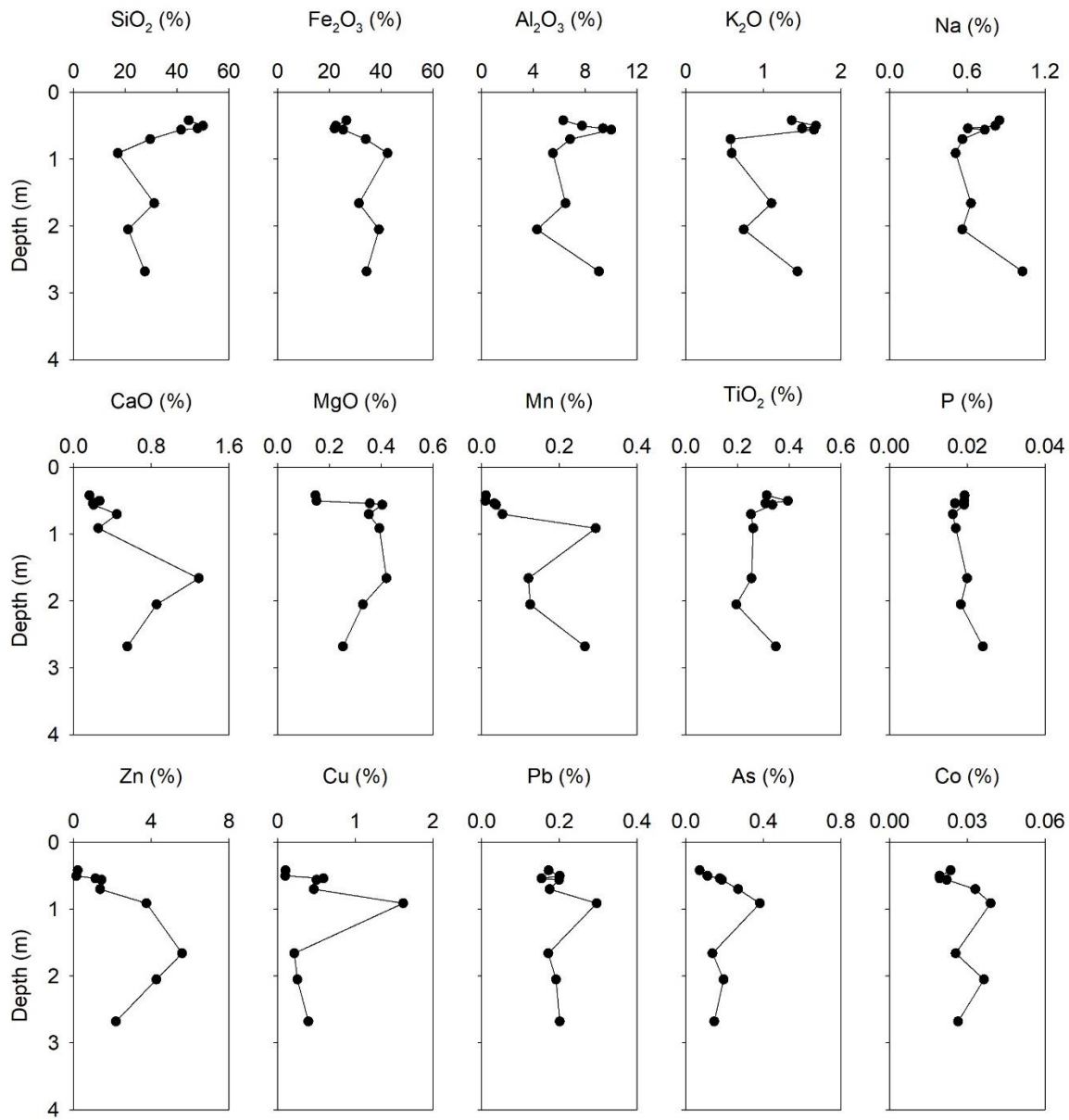


Figure B5. SB01 solid-phase geochemistry profiles determined by XRF analysis.

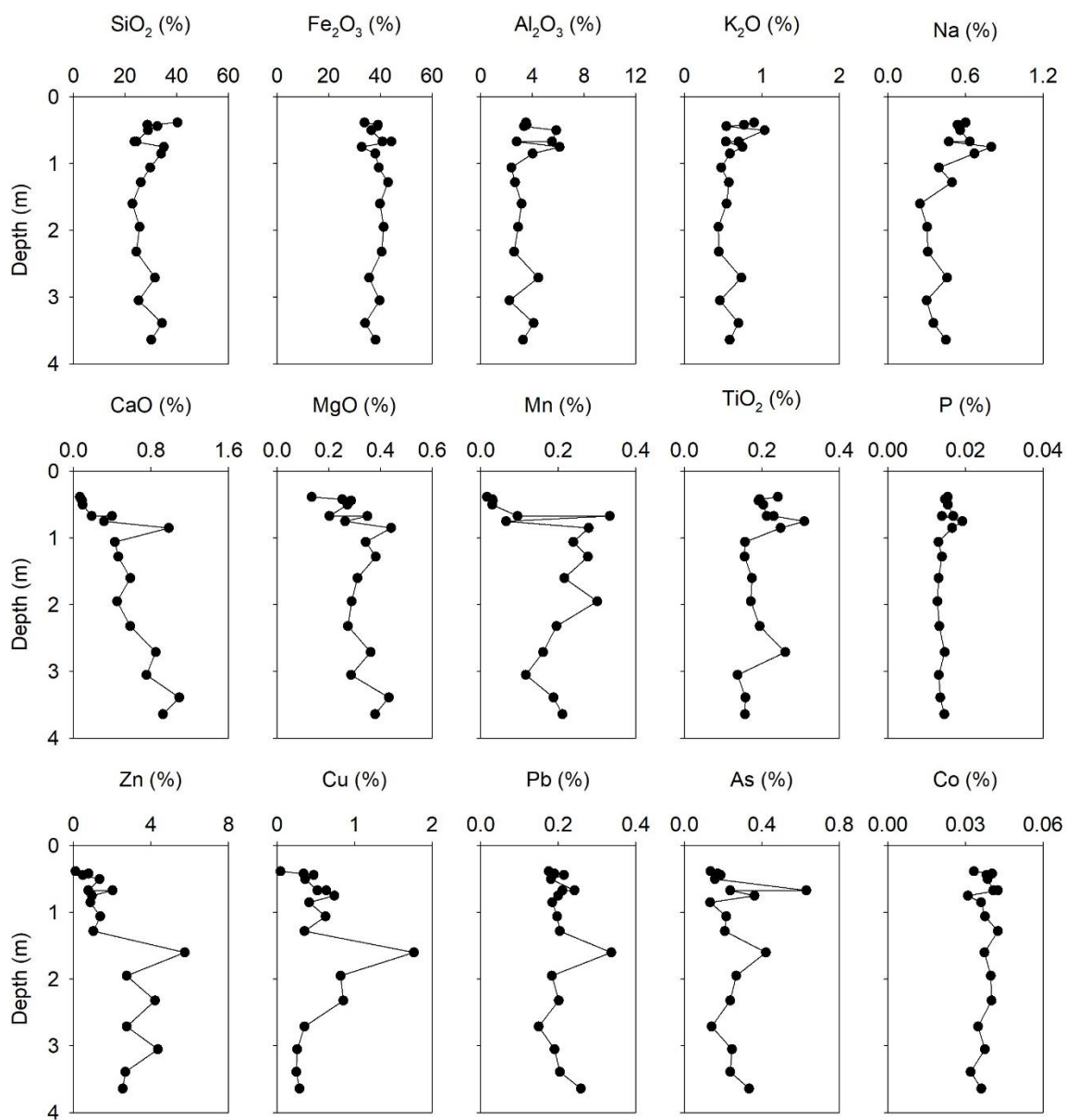


Figure B6. SB02 solid-phase geochemistry profiles determined by XRF analysis.

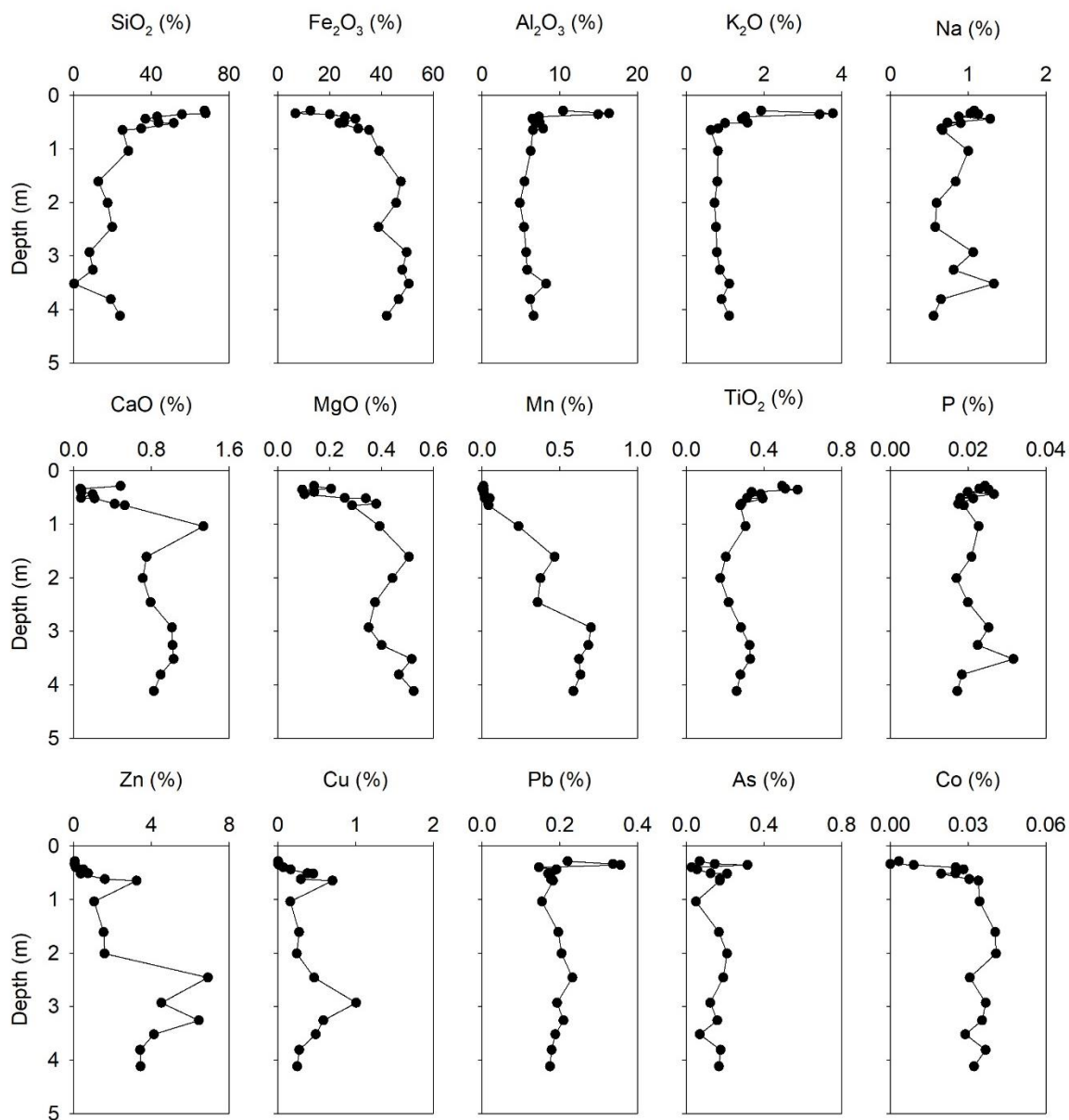


Figure B7. SB03 solid-phase geochemistry profiles determined by XRF analysis.

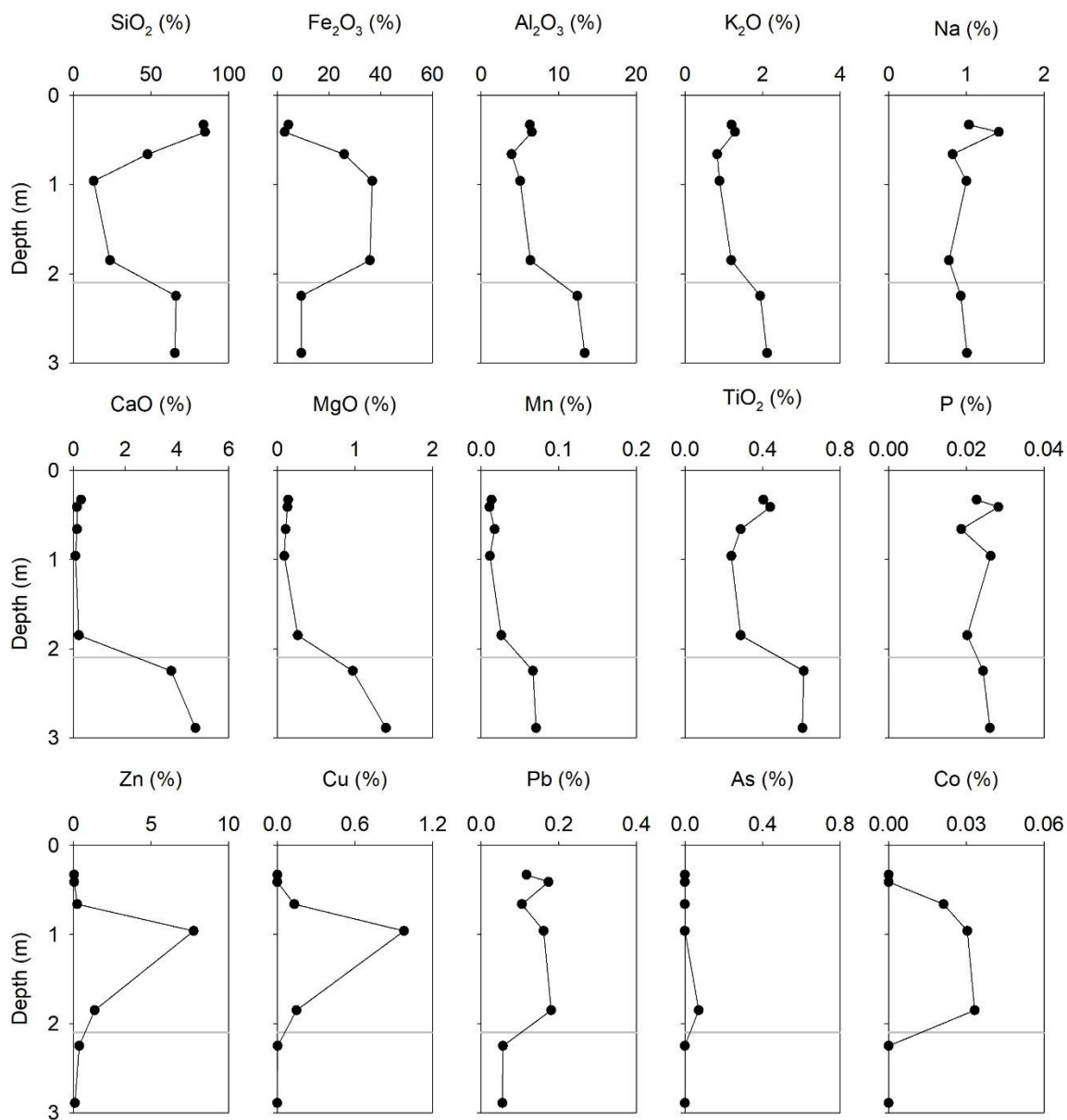


Figure B8. SB04 solid-phase geochemistry profiles determined by XRF analysis. The grey horizontal line represents the base of the tailings, samples below the line are from native sand material.

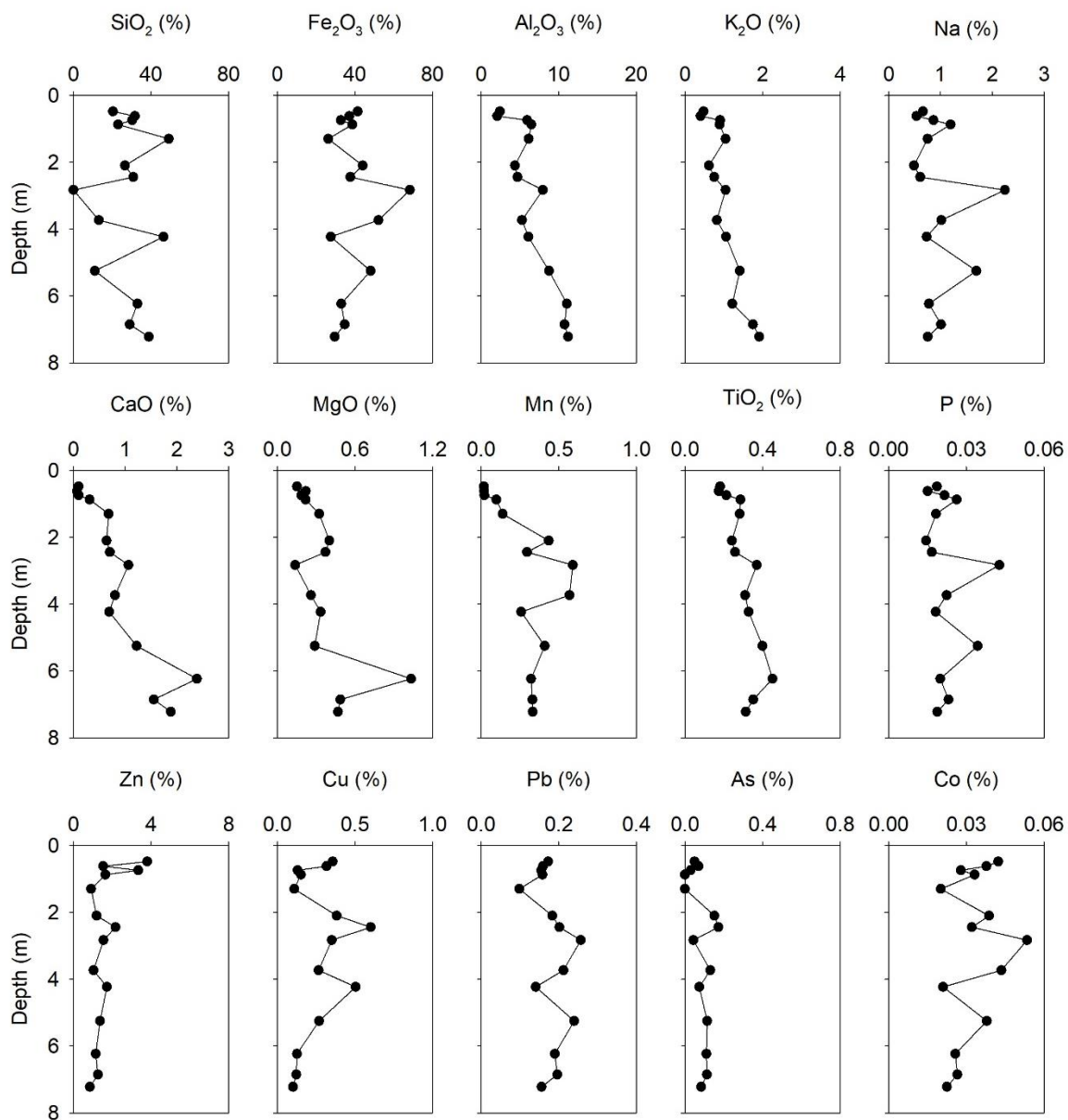


Figure B9. SB05 solid-phase geochemistry profiles determined by XRF analysis.

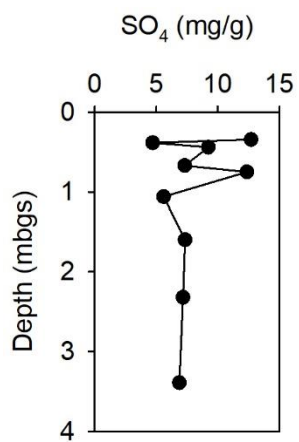
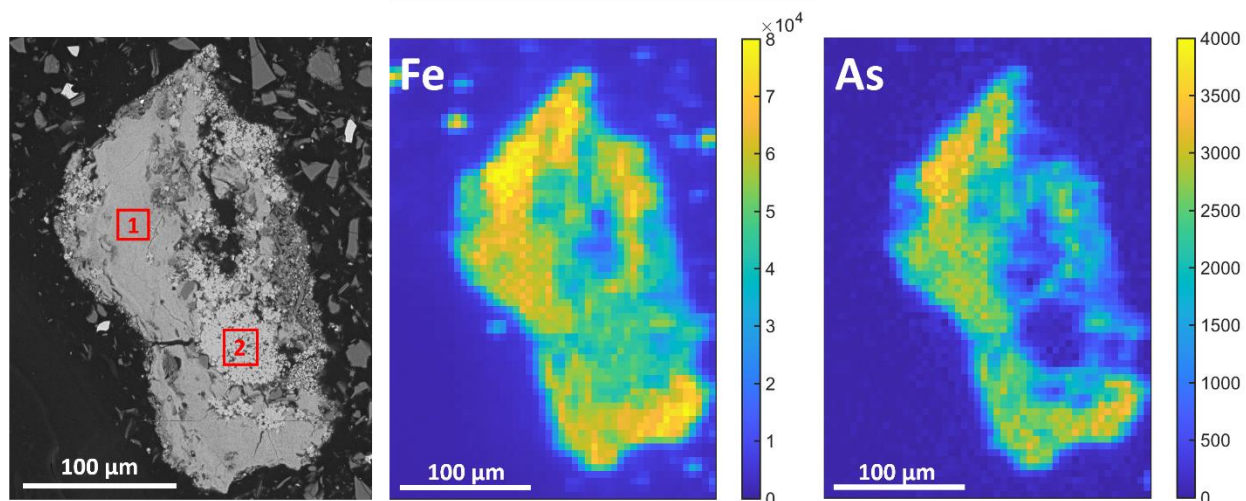


Figure B10. Alkaline extraction (0.3 M NaOH) results for SO_4 at SB02.



	Atomic %				
	O	Si	S	K	Fe
Area 1	65.82	3.02	2.47		28.69
Area 2	68.27	2.08	11.85	2.27	15.53

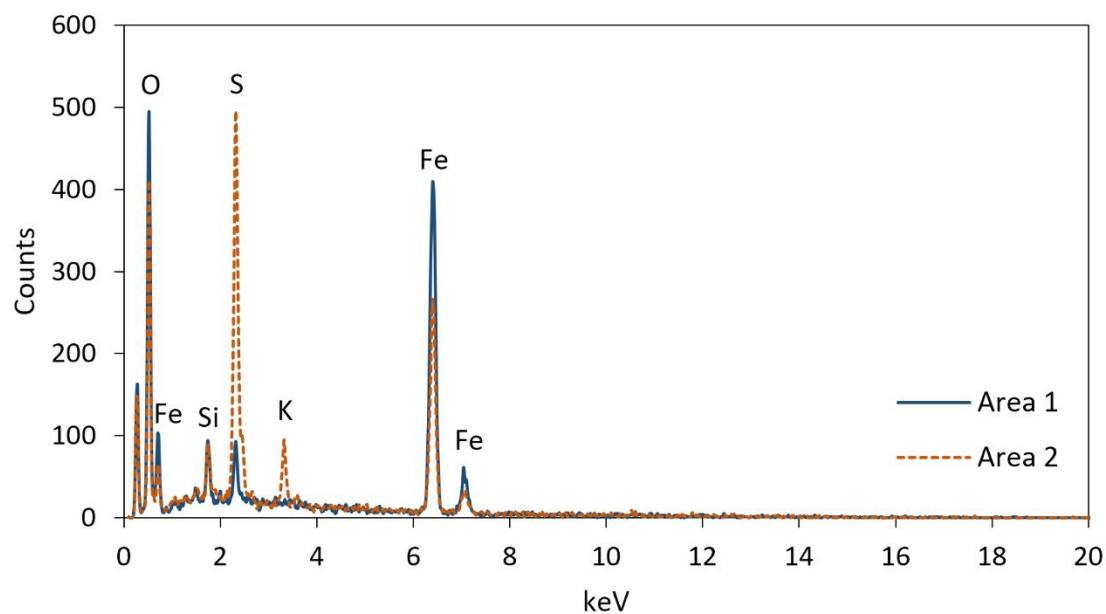


Figure B11. BSE image and Fe and As μ -XRF maps of an Fe oxyhydroxide and Fe hydroxysulfate grain in the top 1 cm of tailings at SB03. EDX data for area 1 indicates that it is an Fe oxyhydroxide, whereas EDX data for area 2 indicates a composition similar to jarosite. EDX profiles for area 1 and 2 are shown below.

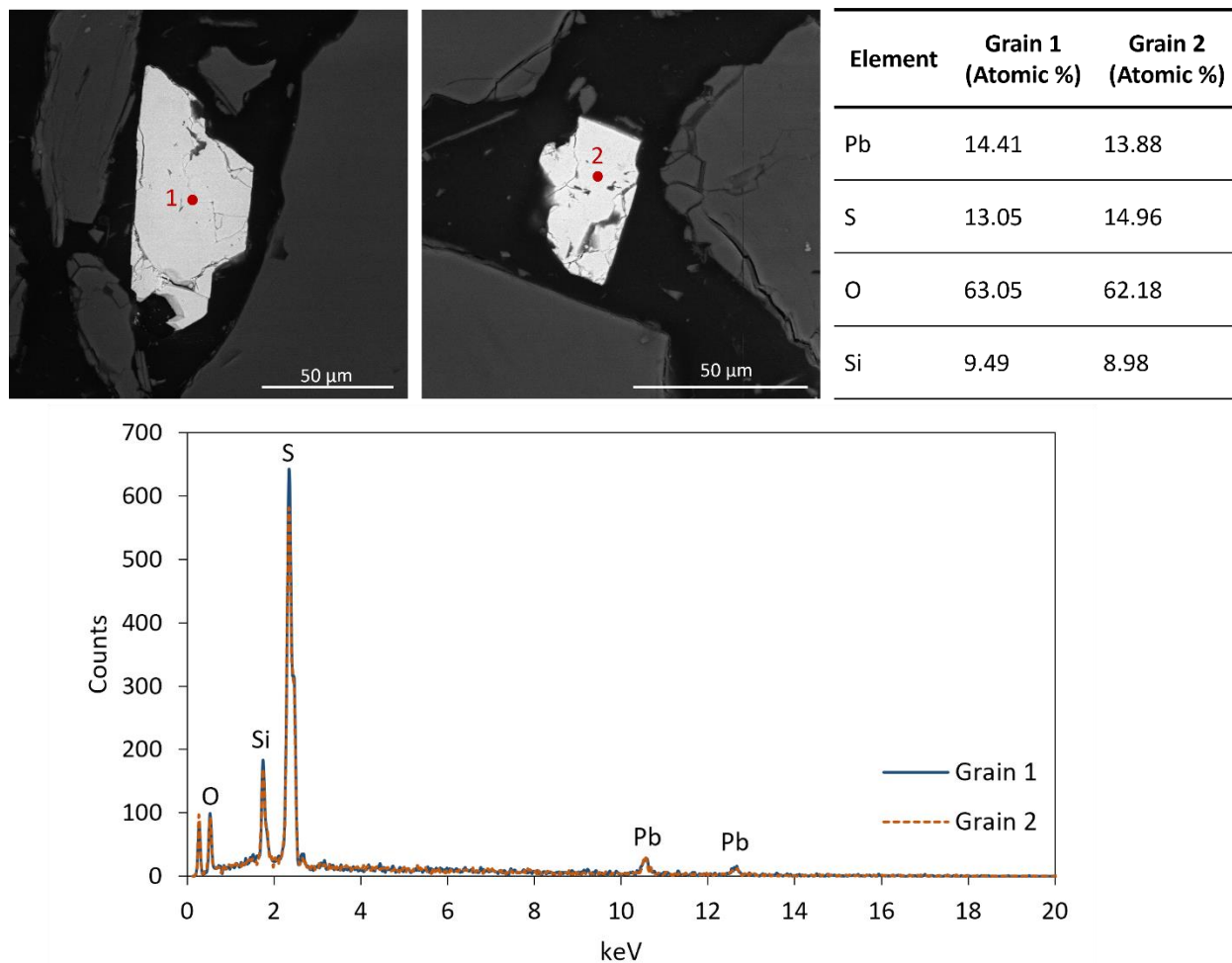


Figure B12. BSE images of a Pb-sulfate phase at 0.41 m depth (0.11 m below top of tailings) at SB04. EDX data for selected points (red circles) is indicated on the right with full EDX spectra displayed below.

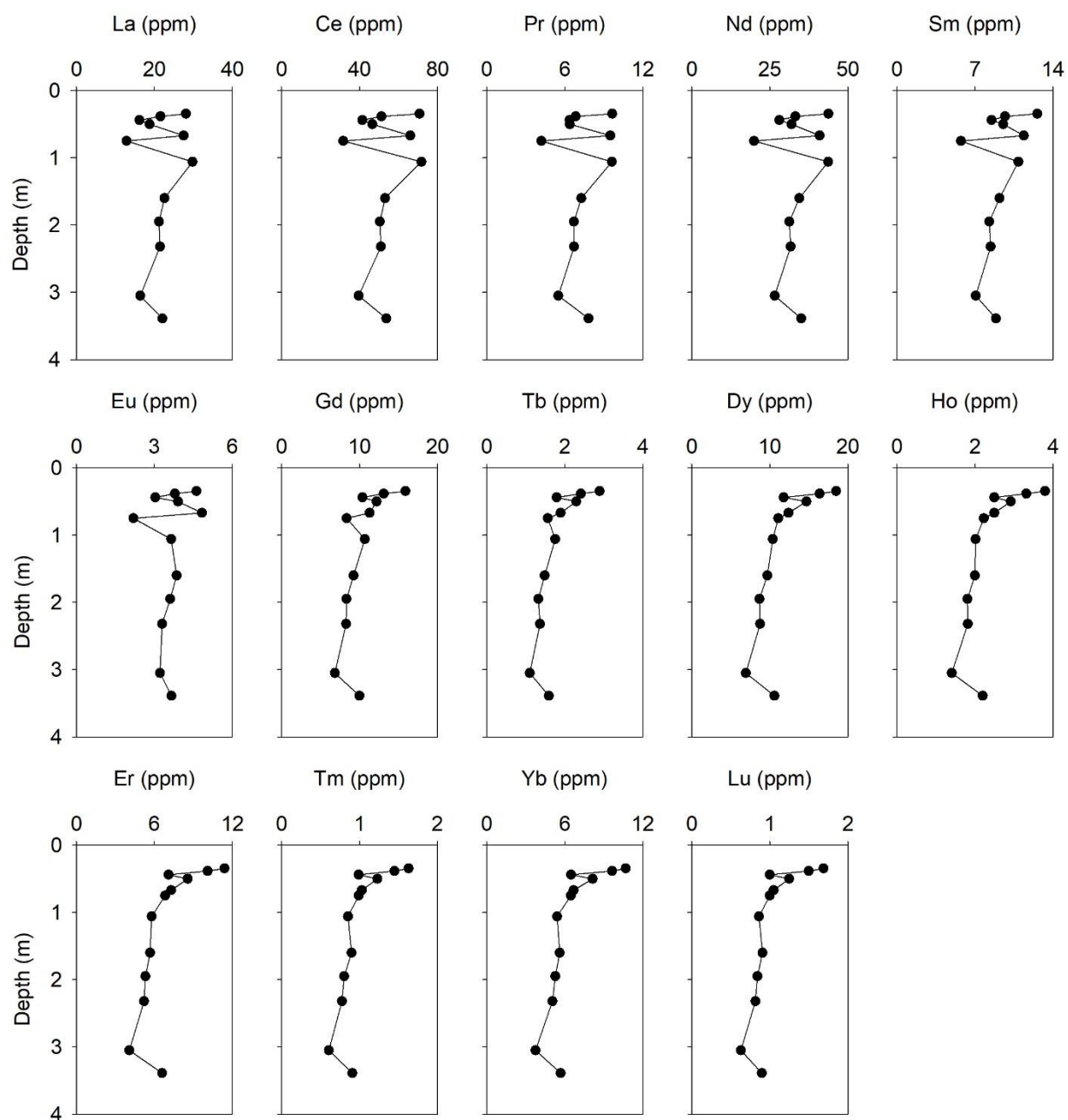


Figure B13. Depth profiles of REE concentrations by element in tailings at location SB02.

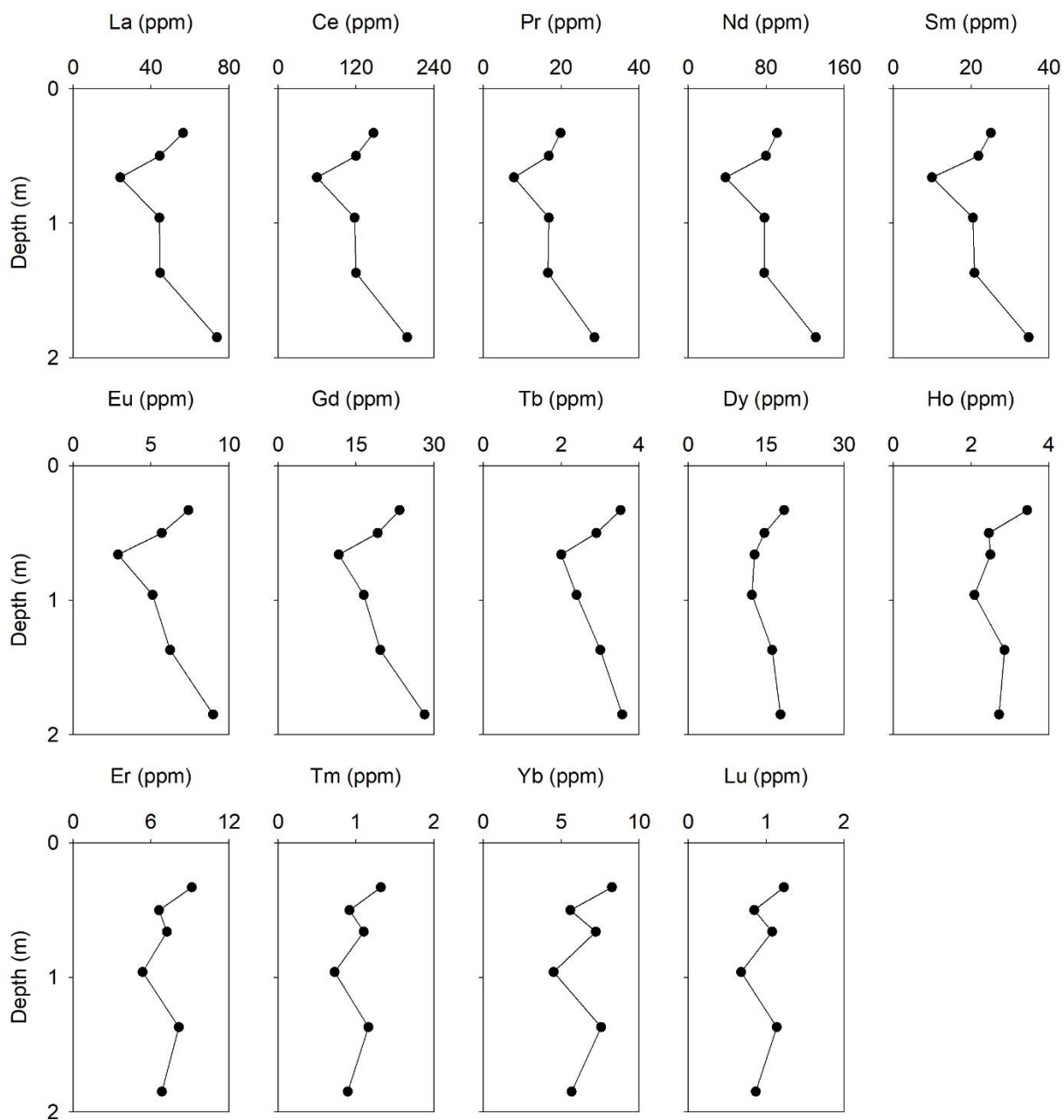


Figure B14. Depth profiles of REE concentrations by element in tailings at location SB04.

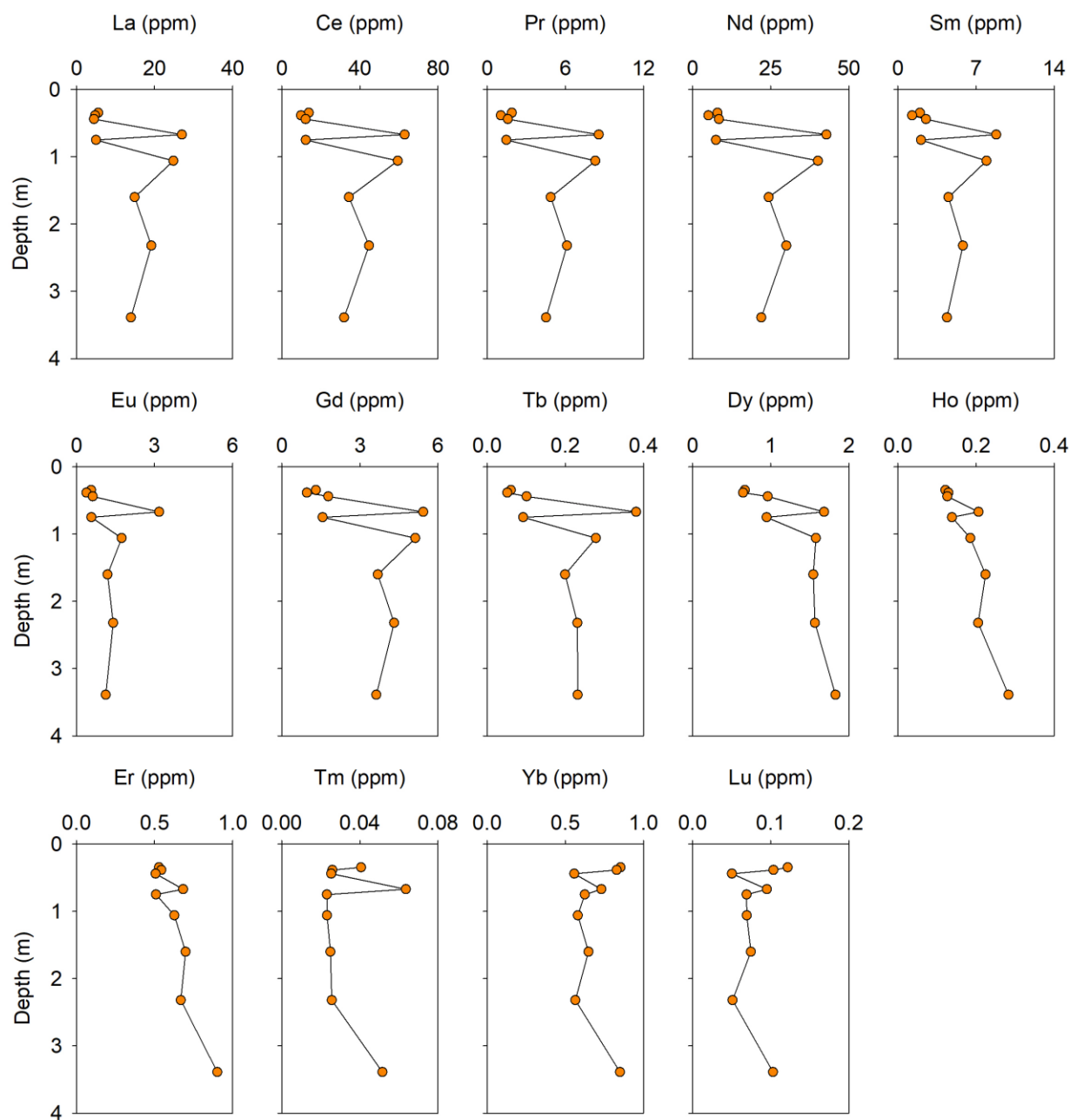


Figure B15. Depth profiles of 2 M HHCl extraction REE concentrations by element at location SB02.

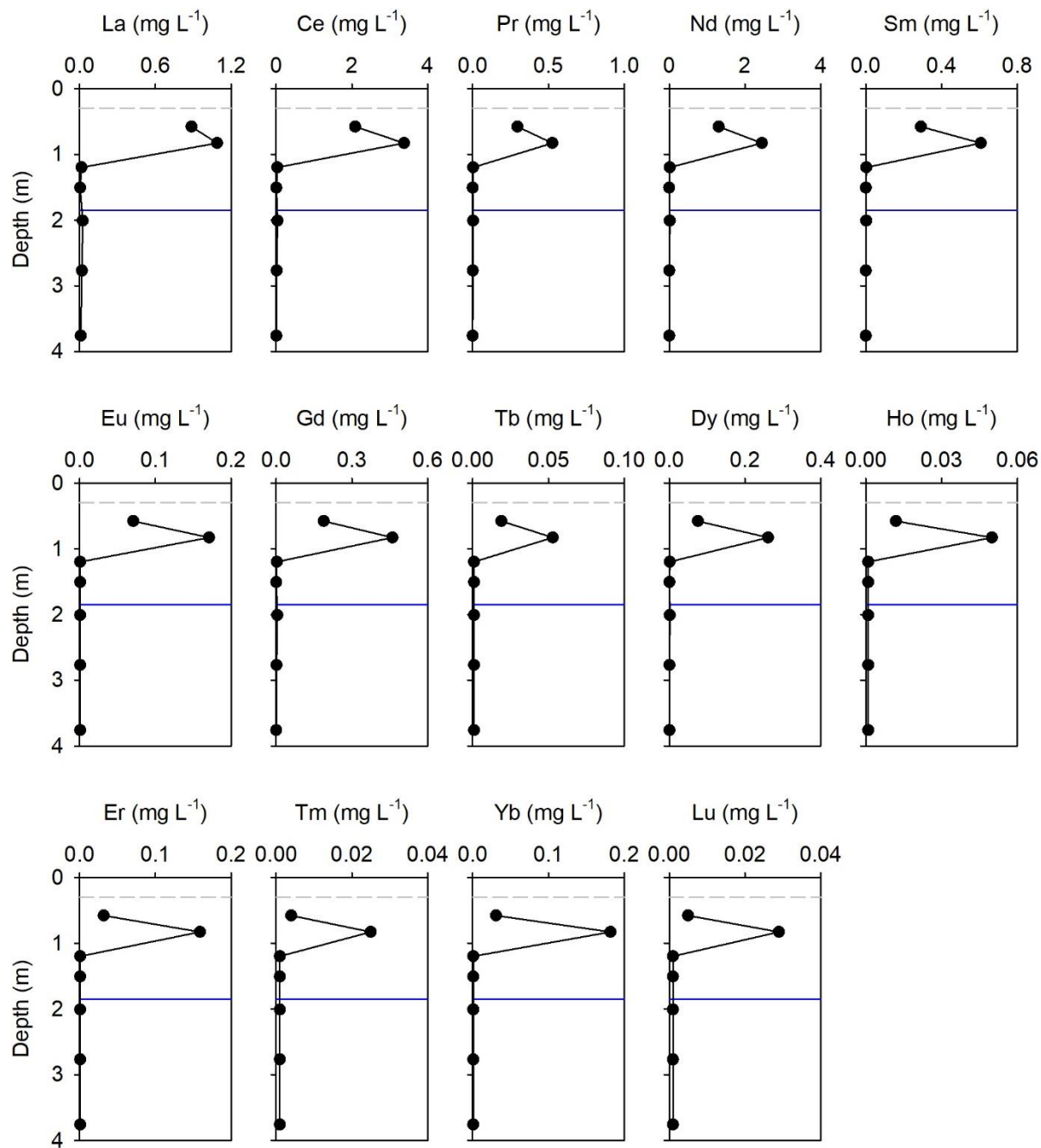


Figure B16. Depth profiles of dissolved REE concentrations by element at location SB02. The grey dashed line represents the interface between the sand and gravel cover and the tailings, the blue line represents the water table.

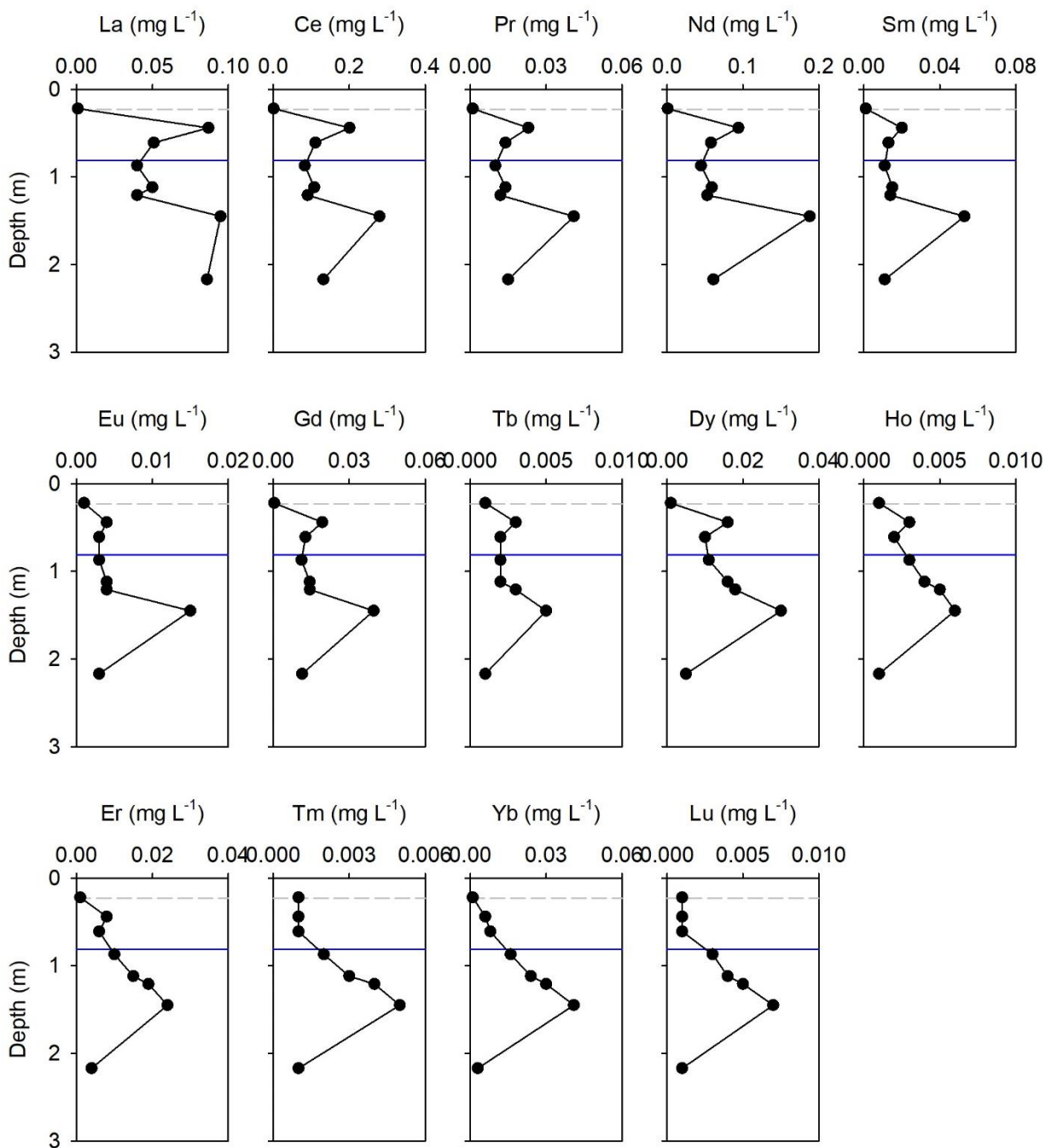


Figure B17. Depth profiles of dissolved REE concentrations by element at location SB04. The grey dashed line represents the interface between the sand and gravel cover and the tailings, the blue line represents the water table.

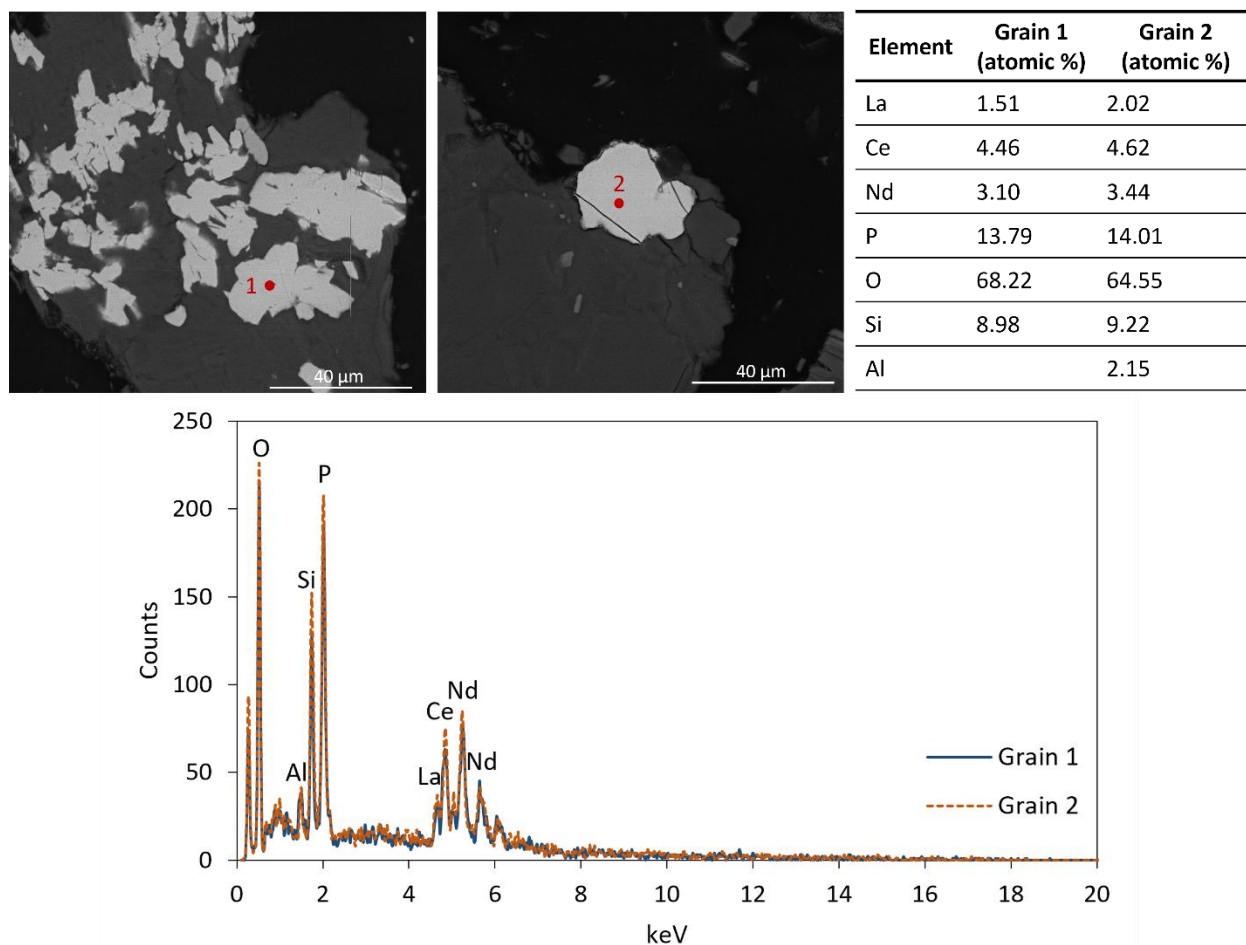


Figure B18. BSE images of an REE-phosphate phase at 0.33 m depth (grain 1, 0.03 m below top of tailings) and 0.41 m depth (grain 2, 0.11 m below top of tailings) at SB04. EDX data for selected points (red circles) is indicated on the right with full EDX spectra displayed below. The minerals surrounding the REE-phosphates are quartz and aluminosilicates.