Copper and iron isotope fractionation in mine tailings at the Laver and Kristineberg mines, northern Sweden

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1. Introduction

During and after mining activities the milled ore material, or mine tailings, is often left exposed to natural weathering processes. Tailings are composed mostly of non-valuable minerals, but since the recovery of target minerals is never 100%, some of the ore minerals could remain in the tailings. The presence of Cu and Fe sulphide minerals such as chalcopyrite (CuFeS2) and pyrite (FeS2) in the tailings and their eventual weathering through oxidation mechanisms may release acid and metals in high concentrations that might leave the impoundment with seepage, or be retained within the tailings via precipitation of supergene minerals (Lottermoser, 2007).

Copper has two oxidation states: Cu+ present in minerals such as chalcopyrite (CuFeS2), chalcocite (CuS) and covellite (CuS2); and Cu2+ which is highly soluble and present in aqueous solutions. Copper is a micronutrient in plants, involved in enzymatic functions during redox reactions, but in high concentrations can cause damage to the plasma membrane of root cells (Marschner, 1995). Depending on parameters such as pH, soil type and redox conditions, Cu can be adsorbed to different surfaces that includes organic matter, Fe-oxides and clays (Bradl, 2004). Copper has two stable isotopes, 62Cu and 64Cu, with global relative isotopic abundances of 69.15% and 30.85%, respectively (De Laeter et al., 2003).

Iron is an element widely present in the Earth’s surface, being the fourth most common element after O, Si and Al (Wedepohl, 1995). The pathways by which Fe is weathered are controlled by the surface conditions, especially O2 presence, and it is in the oxic and circumneutral environment where the species Fe(III) is favoured, compared to Fe(II). However, Fe sulphides are stable under O2-free (anoxic) conditions. Iron is also one of the most important trace nutrients in biological systems (Stumm and Morgan, 1996) and has four stable isotopes 54Fe, 56Fe, 57Fe and 58Fe. Of these, 56Fe is the most abundant (91.75%) followed by 54Fe (5.84%), 57Fe (2.12%) and 58Fe (0.28%) (De Laeter et al., 2003).

In recent years there has been increased interest in the study of Cu and Fe isotopes due to the development of more precise and sensitive mass spectrometers and successful techniques that separate Cu and Fe from a complex matrix (Marechal et al., 1999; Zhu et al., 2000; Borrok et al., 2007). Measurement of Cu and Fe isotope fractionation during redox reactions, but in high concentrations can cause...
between Cu(II)aq and covellite (CuS, with Cu(I)) for the precipitation of $^{63}$Cu isotope fractionation of $3.06 \pm 0.14\%$.

Copper isotope fractionation is influenced by the reactions occurring during the transition between both anoxic and oxic environments, as confirmed by several studies. Ehrlich et al. (2004) showed a mean Cu isotope fractionation of $3.06 \pm 0.14\%$ for the relationship between Cu(II)$_{aq}$ and covellite (CuS, with Cu(I)) for the precipitation of the mineral under anoxic conditions, where Cu(II)$_{aq}$ is reduced to Cu(I). The reduction step from Cu(II) to Cu(I) is the main fractionation. Several studies have shown that the isotope fractionation between Cu(II)$_{aq}$ and the reacting Cu sulphides for the alteration of minerals such as chalcocite, where the unidirectional transfer of $^{65}$Cu from the solution to mineral enriches the solution in $^{65}$Cu, as indicated by Pekala et al. (2011). Fernandez and Borrok (2009) related the Cu isotopic change during the weathering of chalcopryite-rich rocks to a redox transformation of Cu on the mineral surface. Redox processes induced by biological organisms can also cause Cu isotope fractionation, for example during the reduction of Cu(II) to Cu(I) by proteins in live cells which preferentially incorporates the lighter Cu into the cell (Navarrete et al., 2011a). (2) Mineral dissolution. Abiotic dissolution of Cu sulphide minerals such as chalcocite, chalcoctite and bornite has been previously studied (Mathur et al., 2005; Fernandez and Borrok, 2009; Kimball et al., 2009; Maher et al., 2011; Wall et al., 2011) and reveals a redox isotope effect accompanying the oxidation of the Cu(I) present in the minerals, releasing the heavier Cu into solution. In a second stage of the dissolution there is a decrease in the apparent isotope fractionation of Cu, where kinetic isotope effects are the main influence. Dissolution of sulphide minerals in the presence of microorganisms can cause Cu isotope fractionation, but to a lesser extent compared to the abiotic dissolution (Mathur et al., 2005; Kimball et al., 2009). (3) Sorption onto minerals and organic matter. Sulphide dissolution can cause Cu isotope fractionation as a temporary effect when a leach layer enriched in light Cu will develop on the mineral surface. During this process Fe-(oxy)hydroxides are commonly formed and are able to retain trace elements such as Cu by adsorption or coprecipitation. Several studies have shown that Cu(II) sorbed onto minerals such as ferrihydrite (Balistrieri et al., 2008) and goethite and gibbsite (Pokrovsky et al., 2008) is more enriched in the heavy Cu isotope than Cu$_{aq}$. The Cu isotope fractionation due to sorption onto bacteria differs according to the pH of the solutions where it is occurring. At circumneutral pH no isotope fractionation was observed by Pokrovsky et al. (2008) during the sorption of Cu by soil bacteria and diatoms. However, in acidic environments the Cu adsorbed to *Pseudomonas aureofaciens* was enriched in the lighter Cu isotope relative to the solution medium (Pokrovsky et al., 2008). The heavier Cu isotope is preferentially bound to insoluble humic acid during complexation reactions (Bigalke et al., 2010b). (4) Biological processes. Notable examples are the bacterial incorporation of the lighter Cu into bacterial cells and proteins (Zhu et al., 2002; Navarrete et al., 2011a), and the uptake of the lighter isotope in plants, from the soils to the roots and shoots (Navarrete et al., 2011b; Weinstein et al., 2011; Jouvin et al., 2012).

Copper isotope ratios have been measured in several matrices, such as ore minerals (Maher, 2007), sediments (Marechal et al., 1999) and Acid Mine Drainage (AMD) (Kimball et al., 2009) among others. Copper isotope fractionation studies in soil samples have been carried out, such as in hydromorphic soil profiles undergoing oxic soil weathering that exhibit an enrichment in the lighter Cu isotope in the organic layers, which is explained either by plant transfer cycling or complexation by organic matter (Bigalke et al., 2010c, 2011). Weathering of black shales causes a depletion of the heavier Cu isotope in the soil material and a corresponding enrichment in the pore water, compared to the parent material (Mathur et al., 2012). The study of Cu isotopes and its use as a tracer of contamination sources has been applied in soils and lake sediments (Bigalke et al., 2010a; Thapalia et al., 2010).

Three main pathways for stable Fe isotope fractionation can be identified: (1) Redox transformations. Since Fe is a redox sensitive element, it is expected that Fe isotope variations will occur along the redox interfaces in natural systems in either inorganic or microbially mediated processes. A well-studied example is given by the abiotic oxidation of Fe(II)$_{aq}$ to Fe(III) following by its precipitation to Fe$_2$O$_3$ or FeO$_2$H$_3$ which results in enrichment of the heavier Fe isotope in the precipitate, to the same extent as biological processes (Bullen et al., 2001). (2) Dissolution of Fe minerals. During the abiotic dissolution of goethite by proton-promoted mechanisms and dissolution of hematite no isotopic fractionation of Fe was reported (Skulan et al., 2002; Wiederhold et al., 2006). However, during ligand controlled and reductive dissolution of goethite kinetic effects dominated Fe fractionation in the early stages where the solution was enriched in the lighter isotope. In the late stages an equilibrium isotope effect was suggested after a depletion of the light fraction in the solution (Wiederhold et al., 2006). The oxidative weathering of sulphide-rich rocks under acidic conditions results in the enrichment of heavy Fe isotopes in the fluid phase, and the precipitation of Fe(III)-oxide phases under circum-neutral conditions leads to an enrichment of the lighter isotopes in the fluid phase (Fernandez and Borrok, 2009). Iron isotope fractionation has also been observed during the dissolution of phyllosilicates in a soil chronosequence where the solutions from the early dissolution stages were significantly enriched in light Fe isotopes compared to the minerals, being the kinetic effect identified as the dominant fractionation mechanism in the system (Kiczka et al., 2010a). (3) Biological uptake. Iron isotope fractionation by plant uptake has been studied recently, and the isotope signature of the plant biomass depends not only on the metal uptake strategy but also on the nutrient availability in the substrate. Observed variations reveal heavier signatures in soils/roots towards lighter ones in leaves and flowers and a constitutive reductive uptake mechanism of Fe in the substrate is the major determinant of this fractionation (Kiczka et al., 2010b; Guelke-Stelling and van Blackenburg, 2012). The largest Fe isotope fractionation values in natural samples are registered for hydrothermal spring deposits, Fe–Mn nodules and crusts and Banded Iron Formations (BIF), but the terrestrial igneous rocks do not show large variations (Beard et al., 2003). However, the Fe isotopic fractionation ($^{56}$Fe) in natural samples is diverse and varies by $\sim 5\%$ (Bullen, 2011). Diverse field studies have been published regarding field characterisation to interpret geochemical processes and cycles using Fe isotopes (Teutsch et al., 2009; Kiczka et al., 2011). Special mention should be given to the study of the Fe isotope fractionation in mine tailings done by Herbert and Schippers (2008) where processes such as aqueous Fe(II)–Fe(III) equilibrium, microbial Fe(II) oxidation and Fe(oxo)hydroxide precipitation are the main pathways that lead to slightly higher $^{56}$Fe values below the oxidation front, compared to the values above the front.

Since sulphide mine tailings often have high concentrations of Cu and Fe, it is possible that isotope fractionation of these metals due to the effects of surface geochemical processes such as dissolution and reduction/oxidation of metals could be traceable, as shown for example by Johnson et al. (2008) and Fernandez and Borrok (2009). The aim of this study was to investigate the fractionation of Cu and Fe stable isotopes occurring during the oxidation of primary sulphides and formation of secondary Cu minerals below the oxidation front in tailings material in order to relate the possible observed variations to the geochemical processes.
occurring within the tailings. For this purpose a pyrrhotite-containing tailings profile from the Laver Mine (northern Sweden) and plant samples of grass from the same area were characterised using chemical elemental data and Cu isotopic composition. The mineralogy, hydrology and geochemistry of tailings at Laver have been well studied previously (Ljungberg and Öhlander, 2001). There is a distinctive boundary between an oxidised zone, a Cu-enriched zone and an unoxidised zone (Holmström et al., 1999; Alakangas et al., 2009), and thus the site is well suited to study Cu isotope fractionation during sulphide oxidation. In addition, Cu and Fe isotope compositions in a profile through relatively fresh pyrite-rich tailings from the Kristineberg test site in northern Sweden was studied to account for aspects of different mineral composition, ageing and other variables. This is one of the first studies of Cu and Fe isotopes performed on samples collected directly from oxidising mine waste.

2. Site description

2.1. Laver Mine

Laver Mine is an abandoned Cu mine located in northern Sweden (Fig. 1). Approximately 1.537 million tons of ore with Cu, Ag and Au were extracted by Boliden AB. The operational period of the mine was 10 years, ending in 1946, when approximately 1.2 million tons of tailings were deposited in a valley near the mine area. Approximately 25% of the tailings were washed away due to snowmelt runoff in 1951 and 1952. It was then necessary to construct a second clarification pond, 3 km downstream of the tailings (Ljungberg and Öhlander, 2001). In 1974, the eroded parts of the tailings were limed, fertilised and seeded with a grass mixture (Lindgren, 1975), in order to neutralise the acidic water derived from the oxidation of sulphide minerals and slow down further sulphide mineral oxidation. The vegetation in the area could be classified as a coniferous forest with some areas of deciduous forest and bog lands and the major soil type is a podzol weathered till (Fromm, 1965). The area is drained by the small brook Gräbergsbäcken that flows on the side of the impoundment. Currently, the tailings have a vegetation cover and in the lower zones where the groundwater reaches the surface, layers of metal precipitates such as Fe-(oxy)hydroxides can be seen.

It was confirmed by Holmström et al. (1999) that the tailings deposit has a chemical zonation, with two distinct zones. As a top layer there is a strongly oxidised zone that extends to a variable depth of 50–150 cm and below it, a non-oxidised zone. The main minerals present in the non-oxidised tailings are quartz, plagioclase, pyrrhotite, chalcopyrite, pyrite and sphalerite, while in the oxidised tailings only remnants of sulphides are left and the minerals have a coating of Fe-hydroxides. The chemical analysis of these two zones show that the oxidised zone is depleted in Cd, Co, Cu, Ni and Zn compared to the non-oxidised zone. The Laver tailings are relatively poor in sulphides, with a S content of

![Fig. 1. Location of the Kristineberg test site and Laver Mine and their surroundings.](image-url)
7300 ppm in the non-oxidised tailings and 2140 ppm in the oxidised section. In the same study by Holmström et al. (1999) it was determined that there is also a secondary Cu-enrichment zone between the oxidised and non-oxidised zones, where the content of Cu and S is higher than in the other two described zones due to the ongoing process of covellite formation.

The visual appearance of the profile of the pit dug at Laver for this study consisted of two distinct zones with characteristic colours. The uppermost 100 cm layer had a yellow–brown colour. Beneath this layer, the tailings had a distinctly blue–grey colour. These observations are consistent with the ones reported by Holmström et al. (1999) where the top layer had a yellow–brown colour to a depth of 50–150 cm, classifying this layer as the oxidised zone and the bottom layer as the unoxidised zone.

### 2.2. Kristineberg test cells

In 2001, at the Kristineberg mine site in northern Sweden, operated by Boliden AB, six test cells were constructed. The test cells consisted of concrete (5 × 5 × 3 m³), isolated with an inert high density polyethylene liner, and containing fresh unoxidised tailings from the Kristineberg Pb–Zn–Cu mine. Five of these tests were covered with diverse materials such as apatite and sewage sludge, with the purpose of evaluating different dry covers that would help to decrease sulphide oxidation in tailings materials. One cell (cell 6) was not filled completely with tailings material and was left uncovered for reference use. The fresh tailings consisted of sandy–silt particles where the main sulphide minerals were pyrite (FeS₂) 48%, and pyrrhotite (Fe₁₋₀S) 4.8%. The concentration of As, Cu, Cd, Pb and Zn was high in the tailings (Table 1).

Five years after construction, the uncovered test cell already showed evidence of on-going oxidation of minerals such as pyrite, pyrrhotite and sphalerite. Iron and S were released in the leachate waters along with Mn, Co, Ni and Zn in high concentrations. Dissolved Cu and Pb concentrations in the leachate waters were low because both elements were removed from solution by coprecipitation or sorption due to relatively high pH values. The buffering capacity of the alkaline process water deposited together with the tailings had not been exhausted (Alakangas and Ohlander, 2006). The tailings samples at Kristineberg used for this study did not show a striking change of colour between the layers as in Laver. However, the deeper samples were unoxidised, similar to the original material used to fill up the test cell.

### 3. Materials and methods

#### 3.1. Sampling

Tailings and humus samples from Laver were taken in October 2009 from a pit dug using a mechanical excavator and collected manually using metal-free tools. The coordinates of the pit are N65°46'18.3” E20°14'95.8” (Fig. 1). The tailings samples were collected at 20 cm intervals to a depth of 150 cm and a humus sample composed by degrading litterfall material (O-horizon) was also collected. All samples were stored in plastic non-diffusive bags that were kept refrigerated until later preparation and analysis was performed. Grass samples from the Festuca genus were taken in the surrounding areas where the pit was dug, and samples of the white cottongrass (Eriophorum scheuchzeri) were taken from a boggy area where the groundwater from the tailings reaches the surface, and crusts of goethite and lepidocrocite (Holmström et al., 1999) can be seen on the surface. The data for the pH of the soil samples given in Fig. 2 is the median from 5 replicates, using a sample–water ratio of 3:5.

Tailings samples in a profile from the reference (uncovered) cell at Kristineberg were taken during the summer of 2009. Samples were collected every 10 cm to a depth of 1.1 m. The samples were stored in closed plastic cups and kept refrigerated until further analysis. For more details, see Nason (2012).

#### 3.2. Chemical analysis

All the chemical analysis for tailings samples in both study sites and plant samples in Laver Mine were performed by a certified analytical laboratory, ALS Scandinavia AB in Luleå.

##### 3.2.1. Tailing and humus samples

- **Elemental analysis.** The tailings and humus samples were digested by alkali fusion or microwave-assisted acid digestion in closed vessels. Solutions were analysed for Cd, Co, Hg, Ni, Pb using ICP-SFMS (Inductively Coupled Plasma-Sector Field Mass Spectrometry) and Al, Ca, Fe, K, Mg, Mn, Na, P, Ti, As, Ba, Be, Cr, Cu, Mo, Nb, S, Sc, Sr, V, W, Y, Zn, Zr using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) according to US EPA methods 200.8 (modified) and 200.7 (modified). The instrumental precision was better than 5% based on long-term variations.

##### 3.2.1.2. Cu and Fe purification

In this study, Cu from sample digests was purified using anion exchange chromatography following the procedure described by Marechal et al. (1999) and Mason et al. (2005) with calibration of the elution profiles for individual columns, as recommended by Borrok et al. (2007). The anion-exchange columns were made of polyethylene, had a height of 5 cm and were filled with 1 g of AGMP-1 resin, mesh 100–200 (Bio-Rad Laboratories). Due to differences in Cu and Fe concentrations in the two tailings sites, the load and the eluent volume used in the separation procedure varied. For some samples, Cu was partially co-eluted with Fe resulting in incomplete separation of analytes. Two or even three separations were then required in order to achieve quantitative Cu recovery (>95%) based on the measurement of the Cu concentration in the digests before and after the anion exchange chromatography. The final volumes and eluent used during the anion exchange chromatography are shown in Table 2. The purified fractions were evaporated to dryness and re-dissolved in 5 mL 0.7 M HNO₃ for the Cu fractions and 0.3 M HNO₃ for the Fe fractions.

##### 3.2.1.3. Cu and Fe isotope analysis

The purified Cu and Fe fractions were analysed by single-collector ICP-SFMS (Element2, Thermo Fisher Scientific, Bremen, Germany) prior to isotope analyses in order to obtain accurate analyte concentrations, as well as to ensure the absence of interfering elements. Typical operational conditions and measurement parameters can be found elsewhere (Axelsson et al., 2002; Engström et al., 2004).

Prior to Cu isotope analysis samples, working-and isotope standards were diluted to a Cu concentration of 1 mg L⁻¹ and matrix matched to 0.34 M HNO₃ (sp) followed by addition of Zn at 2 mg L⁻¹, for on-line mass bias correction. In this study, the ERM-AE633 was used as delta zero reference material for Cu. According
to a personal communication from the supplier and the material certificate, the isotopic composition of the ERM-AE633 is traceable and identical to the NIST Cu reference standard SRM 976 (NIST, 1994; IRMM and ERM, 2002).

For Fe isotope analyses, the purified Fe fractions, working standards and isotope standard IRMM-014 (delta zero reference material) were diluted to a concentration of 2 mg L⁻¹ and matrix matched to 0.34 M HNO₃ (sp). Additionally, the samples and standards were spiked with Ni (internal standard) at 4 mg L⁻¹ for on-line mass bias correction.

Copper and Fe isotope analyses were performed by multi-collector inductively coupled plasma-sector field mass spectrometry (MC-ICP-MS) using a Neptune (Thermo Fischer Scientific, Bremen, Germany) operated in medium resolution mode. A Pt guard electrode was used to maximise the ion transmission. Typical operating conditions and measurement are detailed elsewhere (Stenberg et al., 2003, 2004). The isotopic analyses of all the samples and standards were performed in duplicate, using Ni for on-line mass discrimination correction in combination with the sample-standard bracketing technique, as explained by Malinovsky et al. (2003). The reported error is 2σ of the standard deviation on instrumental long-term reproducibility, based on both on-line data processing that included baseline subtraction, calculation of ion beam intensity ratios and filtering of outliers and further off-line statistical treatment. Eqs. (1) and (2) were used to calculate Cu and Fe delta values in ‰ where the measured ratios are corrected for mass discrimination following the procedure of Baxter et al. (2006).

\[
\delta^{65}\text{Cu (‰)} = \left( \frac{^{65}\text{Cu} / ^{63}\text{Cu}}{^{65}\text{Cu} / ^{63}\text{Cu}_{\text{ERM-AE633}}} - 1 \right) \times 1000 \tag{1}
\]

\[
\delta^{56}\text{Fe (‰)} = \left( \frac{^{56}\text{Fe} / ^{54}\text{Fe}}{^{56}\text{Fe} / ^{54}\text{Fe}_{\text{IRMM-014}}} - 1 \right) \times 1000 \tag{2}
\]

3.2.2. Plant samples

Plant samples (grass and white cottongrass) were prepared in a similar fashion prior to chemical analysis. First, the roots and the withered leaves were removed and a filter paper was used to clean the rest of the plant by rubbing. The samples were rinsed with deionised water to remove additional external impurities and then dried at room temperature. Ten-30 g of the dried plant and humus samples were ashed at 550 °C overnight followed by digestion of the residue with 10 mL of hot 14 M HNO₃. Digests were evaporated.
to dryness and re-dissolved in 4 mL 7 M HCl. An internal standard (In) was added to a final concentration of 25 \mu{g}/L. These digests were analysed for metal concentration, according to Section 3.2.1.1. The method for Cu separation for isotope analysis was the same as in the one reported for the tailings and humus samples.

### 4. Results

#### 4.1. Profile characterisation

##### 4.1.1. Laver Mine

The pH from the tailings samples ranged from 3.99 to 7.35 through the profile, with a pronounced increase in the most superficial samples as seen in Fig. 2a. In the profile, the Cu concentration (Fig. 2b) ranges from 18.4 mg/kg in grass samples, to an average of 261 mg/kg in the oxidised zone and 2940 mg/kg in the unoxidised zone. The upper oxidised zone at Laver Mine showed an increase in Cu concentration profile from the oxidation front to the surface of the tailings is seen in the profiles shown in Fig. 3c and d. However, the Cu concentration profile showed fewer differences between the oxidised and unoxidised zones (Fig. 3b).

##### 4.1.2. Kristineberg

The sulphide tailings in the test cell in Kristineberg had been oxidised for approximately 8 years before sampling. An oxidation front was indicated by the low pH value (Fig. 3a) and this feature stands out in the pH profile. High Fe and S concentrations occurred at the oxidation front (S = 324,000 mg/kg; Fe_2O_3 = 38.4%). A marked decrease in the Fe and S concentrations from the oxidation front to the surface of the tailings is seen in the profiles shown in Fig. 3c and d. However, the Cu concentration profile showed fewer differences between the oxidised and unoxidised zones (Fig. 3b).

#### 4.2. Metals in plant samples

Two sets of plants from Laver were analysed for metal concentration (Cd, Co, Cr, Cu, Ni, Pb, Zn). The first set consisted of a selection of wild grass species that were located in the area where the soil profile was taken. The second set consisted of specimens of cottongrass. In Table 4 the metal concentrations in the organic layer and Festuca samples are shown. The white cottongrass samples contained a higher concentration of Cu than the grass samples.

#### 4.3. Copper and Fe isotopic composition in the profiles

##### 4.3.1. Laver Mine

The Cu isotopic composition along a profile in the tailings at Laver Mine is shown in Fig. 4. The \delta^{65}\text{Cu} values ranged from -4.35 ± 0.02‰ to 1.31 ± 0.03‰. The lowest value occurs in the transition from the oxidised to the unoxidised zone, where the secondary Cu enrichment zone is located, and the highest value is measured for the deepest sample in the unoxidised zone. In the oxidised zone most values are close to zero.

##### 4.3.2. Kristineberg test-cell

The \delta^{65}\text{Cu} profile for the test cell at Kristineberg showed a range that goes from 0.16 ± 0.01‰ to 0.39 ± 0.03‰, with a clear shift in the values from the unoxidised zone with an average of 0.35 ± 0.04‰ to the oxidation front with a value of 0.17 ± 0.04‰ (Fig. 5a). In the case of the \delta^{56}\text{Fe} profile at this site, the highest value −0.24 ± 0.01‰ was found at the oxidation front and two specific areas can be observed according to their values of \delta^{56}\text{Fe}: An unoxidised zone with an average value of −0.49 ± 0.05‰, and an oxidised zone with an average value of −0.58 ± 0.06‰ (Fig. 5b). The two latter delta values can be considered identical given their value ranges.

#### 5. Discussion

##### 5.1. Metal and S concentration in the tailings zones

The upper oxidised zone at Laver Mine showed an increase in pH values compared to the ones from the unoxidised zone, probably as a product of the remaining liming process back in 1974, but other causes such as a high buffering capacity due to the presence of organic matter could also explain this increase. In the layers of the profile where the pH is below 5.5, such as the lower oxidised zone, the release of acidity caused by sulphide oxidation under aerobic conditions and the lack of anionic ligands, enhances Cu\textsuperscript{5+} mobility, biological availability and toxicity (Martínez and Motto, 2000). In the presence of H_2S under anoxic conditions, a pH close to 4 favours the precipitation of Cu sulphides (Morse, 1987), which could cause an accumulation of Cu in the boundary between the oxidised and unoxidised zones and it is in the latter where reducing conditions prevail (Holmström et al., 1999). A distinctive Cu enrichment zone that was found by Ljungberg and Öhlander (2001) below the oxidation front could not be differentiated from the Cu concentration profile, since the samples at the oxidation front and the deepest one at the unoxidised zone have roughly the same Cu concentration. Therefore, it could be assumed that the Cu-enrichment zone extends for over 30 cm below the oxidation front. This idea is supported by the fact that in the work of Holmström et al. (1999), the Cu concentration in the Cu-enrichment zone varied from 2000 to 3000 mg/kg, in layers that...
could be more than 100 cm wide. Iron is mainly bound in (oxy)hydroxides in the oxidised zone and mainly to sulphides in the non-oxidised zone. There is a marked decrease in the Fe concentration towards the surface, likely the product of the presence of organic matter through litter input that could be causing a dilution effect on the concentration of Fe in the upper areas of the profile. The elemental profile for S shows the same pattern as the Cu profile, with a good correlation ($r^2 = 0.904$), which supports the idea that this metal is present in the form of S-bound minerals, such as chalcopyrite in the unoxidised zone and also covellite in the zone with secondary Cu-enrichment (Ljungberg and Öhlander, 2001).

The elemental profiles in the Kristineberg test cells do not show a clear view of concentration variation of the elements along the profile, especially not in the case of Cu. However, the decrease in the concentrations of Fe and S in the oxidised zone provide support that oxidation processes occur, which are promoting the leaching of $SO_4^{2-}$ and immobilisation of Fe in the oxidation front caused by its precipitation as Fe-(oxy)hydroxides (Fig. 4). Due to buffering by the carbonates and Ca(OH)$_2$ added to process water and mixed with the tailings, pH has not been sufficiently low for the transport of soluble Cu downwards in the profile. Instead it has been sorbed to minerals in the oxidised zone (Alakangas and Öhlander, 2006).

As a way to examine the transport and redistribution of Cu, Fe and S within the Laver and Kristineberg profiles, the elemental mass change compared to an immobile element was calculated using Eq. (3), where $C_i$ and $C'_i$ are the initial and final concentrations of the normalised element, respectively (Cu, Fe and S in this study). The results obtained are shown in the Fig. 6. In Laver a similar trend for Cu and S is seen, being both enriched at the oxidation front and depleted in the oxidised zone. The presence of possible Cu sulphide minerals

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Table 4

<table>
<thead>
<tr>
<th>Metal</th>
<th>Humus</th>
<th>Festuca sp.</th>
<th>E. scheuchzeri</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>&lt;0.06</td>
<td>&lt;0.02</td>
<td>0.11</td>
</tr>
<tr>
<td>Co</td>
<td>0.29</td>
<td>0.03</td>
<td>0.18</td>
</tr>
<tr>
<td>Cr</td>
<td>2.43</td>
<td>0.47</td>
<td>0.38</td>
</tr>
<tr>
<td>Cu</td>
<td>16.6</td>
<td>7.47</td>
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<tr>
<td>Fe</td>
<td>2871</td>
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<td>1170</td>
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<td>K</td>
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<tr>
<td>Zn</td>
<td>65</td>
<td>23</td>
<td>13</td>
</tr>
</tbody>
</table>

95% Confidence level.
in the oxidised zone is limited (Holmström et al., 1999). Therefore Cu is partly retained below the oxidation front and partly lost as a dissolved fraction. Through all the profile Fe has a positive mass balance change in both oxidised and unoxidised zones, this element being present not only in primary sulphides but also as (oxy)hydroxides species to different extents as reported previously by Holmström et al. (1999).

Elemental mass change (\%) = \left( \frac{C_f}{C_i} \times \frac{C_i}{C_n} - 1 \right) \times 100 \quad (3)

The mass change profile in Kristineberg shows a slight release of Cu in the oxidation front where sulphide oxidation is prevalent due to the overall reaction of pyrite (Nason, 2012). The mass change results at both sites should be interpreted with caution, because of the marked heterogeneities in the samples from the oxidised to the unoxidised zones. A possible input of materials and elements via airborne transportation, illuviation, lateral flow and/or capillary rise could eventually be adsorbed in the Fe-(oxy)hydroxide surfaces modifying the mass balance. In the case of Laver, the sample at 130 cm used as the original material could also be part of the secondary enrichment zone of the tailings based on its high Cu concentration.

5.2. Cu bioaccumulation in plants and humus

The Cu bioaccumulation coefficient, which is the ratio between the total metal content in plants and the total metals in soil (Alloway, 1995), for the Festuca sample in Laver is roughly 6%, a moderate value compared to other autochthonous plants in different Cu-contaminated sites that can reach values of 14% (Guo et al., 2009). The white cottongrass samples had a higher concentration of Cu than the grass samples. Specific metabolic processes in the grass and cottongrass plants can cause this variation in Cu concentration to some extent. Nevertheless, the acidic pH values from the nearby Gråbergsbäcken creek (Alakangas et al., 2009) can give some idea of the pH conditions in the water saturated area where the cottongrass grows. These acidic conditions can cause higher

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**Fig. 5.** Vertical distribution of the Cu and Fe isotopic composition in the test cell in Kristineberg. The dashed-dotted line indicates the oxidation front. Bars represent 2σ.

**Fig. 6.** Mass balance plots of the profiles. (a) Laver and (b) Kristineberg, modified from Nason (2012). Zirconium was used as the immobile element. Original materials were the samples at 130 cm (Laver) and 110 cm depth (Kristineberg). Dotted lines indicate the oxidation front.
mobility and bioavailability of Cu (Tyler and Olsson, 2001), that can also explain the larger Cu uptake by the cottongrass. The Cu bioaccumulation coefficient of the white cottongrass at Laver (12.1%) is similar to the one in plants of the same genus grown in wetlands (11.8%) (Nyquist and Greger, 2009).

5.3. Cu isotope fractionation in the tailings

The original value of $\delta^{65}$Cu of the fresh tailings before the oxidation of sulphide minerals started could be assumed to be 1.31 ± 0.03‰. This assumed value corresponds to the deepest sample in the unoxidised zone. While the oxidation process continues, the values of the Cu isotope ratio will change according to the geochemical processes that are occurring in the tailings. In the early stages of oxidation of sulphide-bearing rocks, there is a preferential partitioning of the heavier Cu isotope into the solution phase, leaving the solid phase (chalcopyrite) enriched in the lighter Cu isotope, as pointed out by Fernandez and Borrok (2009) and in a chalcopyrite leaching study done by Kimball et al. (2009).

The difference in the Cu isotope fractionation values between the fresh, unoxidised tailings and the oxidation front is $\Delta^{65}$Cu (fresh tailings-oxidation front) = 5.66‰. This large value is caused by several reactions, starting with the oxidative dissolution of minerals such as chalcopyrite when the infiltrated water reaches the unoxidised tailings. This process is known for the release of isotopically heavy Cu into the solution, leaving the mineral surface enriched in the lighter Cu isotope as a transient effect (Mathur et al., 2005). The process following this dissolution is covellite formation. After the release of Cu(II) into the solution by the oxidation of Cu-bearing sulphides, Fe(II) is replaced by Cu(II) at the pyrrhotite surfaces through an ion exchange reaction, as reported by Holmström et al. (1999). The formation of covellite involves the reduction of Cu, from Cu(II)$_{ox}$ to Cu(I)$_{cov}$ in which the lighter Cu isotope is preferentially transferred from the solution to the newly formed mineral (Ehrlich et al., 2004; Pekala et al., 2011), causing an enrichment of $^{65}$Cu in the covellite. Since this is an open system it is expected that the kinetic transfer of $^{65}$Cu to the covellite continues without reaching equilibrium fractionation. The samples taken along the profile to obtain the $\delta^{65}$Cu value are bulk samples, and it is probable that in the oxidation front sample not only covellite, but also primary Cu sulphide minerals such as chalcopyrite contribute to the observed value. In this case, the $\delta^{65}$Cu value for the precipitated covellite could be lower than −4.35‰ because the higher Cu isotopic value of minerals such as chalcopyrite present in the unoxidised and the enrichment zone, contribute to some extent to the Cu isotopic fractionation value. In the oxidation zone there is an abrupt enrichment in heavy Cu compared to the value observed in the oxidation front. In this layer of the tailings the weathering processes of minerals such as pyrrhotite and chalcopyrite leave the area depleted in such sulphide minerals and its associated metals. Copper has been mobilised to the deeper parts of the tailings, released in the groundwater flow or adsorbed/coprecipitated with Fe-(oxy)hydroxides. The process of sorption of Cu(II) onto ferrihydrite preferentially takes the heavier Cu isotope (Ballistrieri et al., 2008) and it is achieved mainly under equilibrium conditions. As the oxidation front moves downwards in the Laver tailings, the dissolution of the previously precipitated covellite could be a main source for Cu(II). Some of this dissolved Cu(II) might be transported upwards by capillarity through the clay/silt material and sorbed or coprecipitated with the Fe-(oxy)hydroxides. During the latter process, isotope fractionation occurs through preferential binding of heavy Cu.

The vegetation growing on the fertilised surface of the tailings may also play a role in the fractionation of Cu isotopes in the area. The humus, a product of the decomposition of the vegetation layer, is enriched in heavy Cu compared to the soil samples in the oxidised zone, because of the complexation of insoluble humic substances with Cu in solution. Heavy Cu forms the stronger bonds with the organic compound, as reported by Bigalke et al. (2010b). The bacteria present in the upper layers of the tailings are a sink for heavy Cu, due to the probable precipitation of amorphous nanoparticles of Cu and Fe oxides around cell membranes, as described by Mathur et al. (2005). Annual plant recycling and soil-humus mixing could contribute to the enrichment of $^{65}$Cu in the upper soil and organic layers compared to the oxidised zone, even when there is little Cu mass change between the oxidised layers and the organic layer.

At the surface, an increase in $^{65}$Cu in the O-horizon (humus) sample compared to that in the uppermost soil sample is seen. The latter is an indication of the complexation of Cu with organic ligands which is associated with isotopically heavier species (Bigalke et al., 2010b). The resulting $^{65}$Cu variation from the humus sample to the grass sample towards a preferential enrichment in light Cu is described by the principle that the lighter isotopes are taken up preferentially by the plants from the substrate (Weinstein et al., 2011). According to the model proposed by Jouvin et al. (2012), speciation and diffusion of Cu in the solution leads to an increase in the light Cu isotope pool to be taken up by the roots of the plants. Due to the limited amount of data in the present study, the referenced model cannot be related to the tailings profile. However, it can be inferred that the isotopically light Cu pool from the litterfall is reutilised during plant uptake enriching the organic layers of the profile in heavy Cu isotope to some extent. The recycling of litterfall by plants in organic-soil materials has been considered for the cycle of Ca isotope fractionation in higher plants systems (von Blackenburg et al., 2009).

The graph for the Cu isotope composition in the test cell in Kristineberg (Fig. 5) has similarities to the one in Laver, with a marked enrichment of $^{63}$Cu in the oxidation front, caused by the oxidative dissolution of Cu-sulphide minerals and later covellite formation occurring in this zone. Holmström et al. (2001) reported a Cu enrichment zone below the oxidation front in a tailings impoundment at Kristineberg caused by the formation of covellite via transformation of pyrrhotite, chalcopyrite, galena and pyrite.

The values of $^{65}$Cu at Laver and Kristineberg differ, caused probably by two main reasons. First, there is no major Cu concentration change over the Kristineberg profile, but at Laver there is over an 85% loss of Cu in the oxidised zone (Fig. 6a). In the Laver case, $^{65}$Cu has preferentially left the system in the fluid phase leaving the remaining minerals enriched in $^{63}$Cu. This difference in Cu loss between the two tailings is a consequence of the amount of time for which the tailings have been exposed to weathering. This time is longer at Laver than at Kristineberg, while at the latter site $^{65}$Cu has not left the system to the same magnitude. Second, the initial Cu isotope ratio values that will depend on the amount and nature of the Cu-bearing minerals present in the unoxidised tailings is different for both sites, which allows expression of kinetic factors in Cu isotope fractionation within the tailings.

5.4. Species contribution to the Cu isotopic fractionation at Laver

Chalcopyrite is the main mineral regulating the Cu isotope composition in the unoxidised tailings at Laver (Holmström et al., 1999). The Cu isotope composition in the Cu enrichment zone in Laver is mainly regulated by the presence of chalcopyrite and especially the newly precipitated covellite. The tailings are enriched in $^{65}$Cu mainly as a function of the amount of covellite precipitated, reaching a minimum $^{65}$Cu value at the depth of minimum chalcopyrite abundance (i.e. 100 cm depth sample). The sample at 112 cm depth can be considered to be a mixture of both chalcopyrite and covellite contributing to the Cu isotopic composition.
The presence of Cu minerals in the oxidised zone is limited. Most of the Cu present in this zone is sorbed onto Fe-(oxy)hydroxides and this sorbed fraction mainly determines the Cu isotope composition. However, in the deeper layers of the oxidised zone some covellite might still be present since the $\delta^{63}$Cu values are slightly lighter than the ones registered in the upper layers. Biotite and muscovite contribution to the Cu isotope fractionation in the unoxidised zone could be neglected in this case. Both minerals were found as gangue in the Laver tailings and their Cu content can be considered low compared to the one in chalcopyrite (Ljungberg and Ohlander, 2001).

5.5. Fe isotope fractionation in the Kristineberg test cell

The original $\delta^{56}$Fe values in the tailings can be considered to be the average of the results obtained in the unoxidised zone, where the fresh tailings are present. This statement is considered to be valid because in this layer of the tailings no Fe-sulphide oxidation has occurred and this process is considered the main factor for a variation of Fe isotope composition in the system. In the test cell in Kristineberg, Fe-sulphide oxidation is the major process that occurs in this zone (Alakangas and Ohlander, 2006). Pyrite is the main sulphide mineral in the unoxidised zone, and along with other minerals such as chalcopyrite is oxidised as soon as the oxidation front reaches the unoxidised zone. Oxidation of pyrite is regulated by the oxidation of Fe(II) via O$_2$ or Fe(III) (Reactions 4 and 5). For the weathering via Fe(III) to be continued, Fe(II) has to be oxidised, according to reaction 6.

$$\text{FeS}_2 + 7/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (4)$$

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (5)$$

$$\text{Fe}^{2+} + 1/4\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{Fe}^{3+} + 1/2\text{H}_2\text{O} \quad (6)$$

Since the test cell has a pH $> 5$, it would be expected that Fe-(oxy)hydroxides would precipitate when the newly oxidised Fe(III) is in contact with O$_2$ and water (Banks et al., 1997). Abiotic Fe(II)$_{aq}$ oxidation and subsequent ferricydrate precipitation favours an enrichment of the heavier Fe isotope in the solid phase as a product of a prior preferential partitioning of the isotopes in the coexisting Fe(II)$_{aq}$ species (Bullen et al., 2001). Iron-(oxy)hydroxides can also precipitate at the surfaces of pyrite, which contributes to an increase of the bulk $\delta^{56}$Fe values at the oxidation front. It is also noted that the oxidation of pyrite-bearing rocks leads to an enrichment on $^{56}$Fe in the solid phase under circumneutral pH conditions (Fernandez and Borrok, 2009). These two studies provide an explanation for the increase of $^{56}$Fe around the oxidation front where Fe oxide phases are precipitating, assuming that light Fe(II) is removed from the system. The leached fraction containing low concentrations of Fe (Alakangas and Ohlander, 2006) might be enriched in the lighter Fe isotope needed to establish an isotopic balance in the system. Leachate water was not analysed in this study, but this inference is based on the results obtained by Herbert and Schippers (2008).

Overall pyrite oxidation in the test cell causes a slight depletion of $^{56}$Fe in the oxidised zone relative to the unoxidised zone. This change cannot be explained by the precipitation of Fe-(oxy)hydroxides alone. Previous steps along the flow path such as Fe(II) oxidation (Bullen et al., 2001) and the relationship between the dominant Fe(II) and Fe(III) species in natural waters (Bullen et al., 2001; Johnson et al., 2002), can cause Fe isotope fractionation along the oxic/anoxic interphase and in the oxidised zone. However, other factors such as the presence of Fe bearing silicates in the bulk material may influence the $\delta^{56}$Fe values, as reported by Herbert and Schippers (2008). In addition, biological fractionation of Fe in the tailings may have contributed to Fe isotope variability, but the data set did not include information on pore water in the tailings and thus it is not possible to establish the possible extent of biological fractionation of Fe in the tailings.

The studied profile shows a relationship between the oxidation of pyrite and Fe isotope variation along the profile. The $\Delta^{56}$Fe$_{unoxidised}$-oxidised in the profile is in the range of the analytical error and it could be interpreted that this variation is low or absent. However it is expected that this variation may increase with time as long as the pyrite in the test cell is still oxidising and more Fe(ox)/hydroxide precipitates as a product.

6. Conclusions

Copper isotopes were fractionated within the tailings in Laver due to the different redox-driven reactions that occur at this site. Processes such as the reduction of Cu(II) to Cu(I) and subsequent covellite precipitation in a redox-boundary zone at the tailings site can preferentially enrich the precipitated mineral in $^{63}$Cu. Dissolution of covellite as the result of the downward movement of the oxidation front leads to mobilisation of Cu(II) followed by its sorption onto Fe-(ox)/hydroxides. This sorption process preferentially removes $^{63}$Cu (Balistrieri et al., 2008) from the dissolved Cu(II) pool in the oxidised zone of the tailings. Hemic substances contained in the uppermost organic layer of the tailings can form complexes with the Cu in solution, preferentially removing $^{65}$Cu, which forms stronger bonds than $^{63}$Cu (Bigalke et al., 2010b). This observation in a natural system has not been reported before. The Cu fractionation profile along the tailings material in the Kristineberg test site has a similar pattern as at Laver, with an enrichment of $^{62}$Cu at the oxidation front. The processes that cause Cu fractionation in the sulphide-rich tailings in Kristineberg are comparable to the ones in Laver, especially the reduction of Cu(II) to Cu(I). Differences such as the mineral composition of the tailings and time since the weathering started result in different Cu isotope ratios at the respective oxidation front and in the oxidised and unoxidised zones.

Iron isotope ratios in the Kristineberg test cell ranged from $-0.24\%$ to $-0.60\%$ with a small enrichment in $^{56}$Fe at the oxidation front, linked to pyrite oxidation under circumneutral conditions occurring in that zone.

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