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# Microbial and geochemical controls on waste rock weathering and drainage quality

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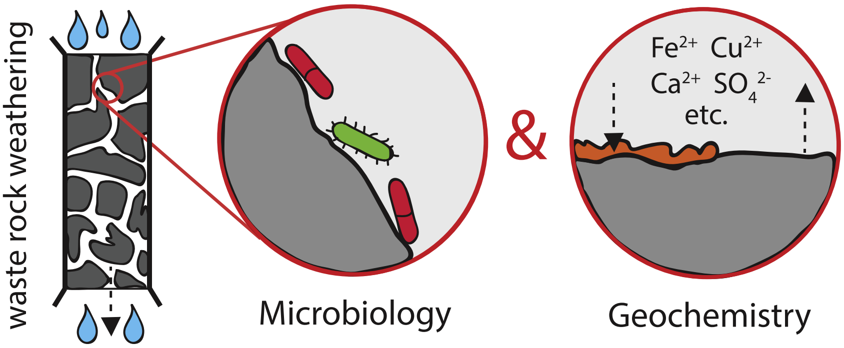
## HIGHLIGHTS

- Integrated approach to study microbial and geochemical controls on drainage quality.
- Characterization of microbial abundance and community structures in waste rock.
- Waste-rock weathering under simulated field conditions using column experiments
- Demonstration of microbial catalysis of waste-rock weathering
- Discrete secondary minerals and adsorption affect waste-rock drainage quality.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Bacteria can adversely affect the quality of drainage released from mine waste by catalyzing the oxidation of sulfide minerals and thereby accelerating the release of acidity and metals. However, the microbiological and geochemical controls on drainage quality from unsaturated and geochemically heterogeneous waste rock remain poorly understood. Here, we identified coexisting neutrophilic and acidophilic bacteria in different types of waste rock, indicating that robust endemic consortia are sustained within pore-scale microenvironments. Subsequently, natural weathering was simulated in laboratory column experiments with waste rock that contained either in-situ microbial consortia or suppressed populations with up to 1000 times smaller abundance and reduced phenotypic diversity after heating and drying. Drainage from waste rock with in-situ populations was up to two pH units lower and contained up to 16 times more sulfate and heavy metals compared to drainage from waste rock bearing treated populations, indicating significantly higher sulfide-oxidation rates. The drainage chemistry was further affected by sorption and formation of secondary-mineral phases (e.g., gypsum and hydroxycarbonates). This study provides direct evidence for the existence of diverse microbial communities in waste rock and their important catalytic role on weathering rates, and illustrates the mutual controls of microbiology and geochemistry on waste-rock drainage quality.

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## 1. Introduction

Open-pit mining produces significant quantities of waste rock that are typically deposited in large dumps that can reach up to several 100 s of meters in height. These mostly unsaturated piles constitute complex systems that have highly heterogeneous physical, mineralogical, and geochemical properties (Amos et al., 2015) and consequently contain many potential niche environments for microbes (Nordstrom et al., 2015). The important role of lithoautotrophic prokaryotes on catalyzing the oxidative dissolution of minerals has been established for decades (Singer and Stumm, 1970; Baker and Banfield, 2003; Johnson and Hallberg, 2003) and the biotic oxidation rate of sulfidic minerals (e.g., pyrite, pyrrhotite) exceeds abiotic oxidation rates by orders of magnitude (Singer and Stumm, 1970; Elberling et al., 2000). This catalysis by acidophilic bacteria mainly stems from the microbially mediated regeneration of ferric iron ($Fe^{3+}$) and the oxidation of ferrous iron ($Fe^{2+}$) and reduced inorganic sulfur ($S^{2-}$).(Johnson and Hallberg, 2003) Major Fe- and S-oxidizing bacteria include *Acidithiobacillus ferrooxidans*, *A. thiooxidans*, *Leptospirillum ferriphilum*, *L. ferrooxidans*, and *Sulfobacillus* and *Thiobacillus* species (Schippers et al., 2010; Aliaga Goltsman et al., 2009; Johnson et al., 2001; Korehi et al., 2014; Benner et al., 2000).

The abovementioned Fe- and S-oxidizing bacteria are ubiquitous in acidic sulfide mineral-bearing environments, but have also been identified in more neutral and even alkaline pH environments (Nordstrom et al., 2015; Baker and Banfield, 2003; Dockrey et al., 2014). Microenvironments may exist in the pore spaces of unsaturated waste rock, which can protect microbes from unfavorable conditions and sustain biodiversity (Benner et al., 2000; Mesa et al., 2017; Blowes et al., 1995; Dockrey et al., 2014). For instance, acidophilic bacteria have been identified in biofilms in acid-neutralizing carbonate-rich waste rock that also harbored a robust consortium of neutrophilic bacteria, indicating acidic microenvironments protected these acidophiles (Dockrey et al., 2014). Generally, the microbial abundance and community diversity in (circum)neutral mine waste is less studied compared to that of acidic mine-waste environments (Lottermoser, 2010). Furthermore, the majority of microbial studies on mine wastes have focused on relatively homogeneous and saturated tailing materials (Schippers et al., 2010; Silver, 1987; Groudev and Groudeva, 1993) but acidic tailings have been shown to harbor a relatively low genetic variability (Méndez-García et al., 2015) and most open-pit mines produce significantly larger volumes of waste rock compared to tailings (Amos et al., 2015; Lottermoser, 2010). Since waste-rock piles are typically unsaturated and more heterogeneous than tailings, they also have the potential to host more diverse microbial communities; yet, there are to date only a few studies that have described the distributions, sizes, and diversity of microbial populations in waste rock (Schippers et al., 2010; Dockrey et al., 2014; Smith et al., 2013; Bailey et al., 2016; Bosecker et al., 2004; Sand et al., 2007; Schippers et al., 1995; Selenska-Pobell et al., 2001). In addition, the role of microbes on accelerating weathering rates observed in waste rock under natural (field) conditions remains poorly constrained. This paucity of knowledge ultimately complicates the quantitative and timely prediction of the quality of drainage from waste-rock piles.

Therefore, this study is aimed at: i) characterizing the in-situ microbial abundance and community structures in acid-generating and non-acid-generating waste-rock types, ii) discerning the role of microbes on accelerating waste-rock weathering under natural conditions, and iii) identifying a variety of major geochemical and microbial controls on the drainage quality originating from waste rock. To do so, laboratory column experiments and a combination of microbiological tools (i.e., cell counting and pyrosequencing) and geochemical analyses (i.e., XRD, XRF, and ICP-MS) were used to simultaneously study microbial populations, primary and secondary mineralogy, as well as the geochemical composition of the column drainage during waste-rock weathering.

## 2. Materials and methods

### 2.1. Collection and characterization of waste rock

Waste rock was collected from the Antamina Mine, one of the world's largest Cu-Zn mines, located in the Peruvian Andes, about 270 km north of Lima. The climate at Antamina shows a distinct monsoonal pattern with a wet season (October–April) accounting for ~80% of the mean-annual precipitation (~1200 mm) (Blackmore et al., 2014). Two end-member classes of waste rock were collected: class A, acid-generating monzogranitic intrusive exoskarn assemblages and class C, non-acid-generating carbonate-rich hornfels and marbles. Class A was subdivided into classes A1 and A2, which were mined from two distinct locations, but otherwise had comparable material properties (Table S1). The class A and C waste rock was originally excavated from the open pit as ~10 t blasts, from which representative 150 kg samples were collected, homogenized using the coning- and quartering method, and subsequently stored on-site in bags for 2 to 4 years prior to experiment initiation. This storage permitted minor ingress of oxygen and moisture, thereby allowing for some waste-rock weathering as well as survival of endemic microbial populations.

For geochemical and mineralogical characterization of the waste rock, ~100 g subsamples were pulverized to <10 μm using a McCrone micronizing mill. The major chemical composition of the waste rock was analyzed with X-ray fluorescence (XRF; PW-2400 from PANalytical, Almelo, The Netherlands), carbon- and sulfur concentrations were determined using a LECO CNS-analyzer (NS-1000, LECO Corp., St. Joseph, USA) and trace-element concentrations were determined after *aqua-regia* digestion using inductively coupled plasma–mass spectrometry (ICP-MS). The primary waste-rock mineralogy was characterized with X-ray diffraction (XRD; Siemens D8000 Diffractometer) using a corundum spike and Rietveld refinement. Spectra were qualitatively and quantitatively referenced with EVA software and Topas v.3.0 software, respectively, using the ICDD database (2016 version). Additional samples of secondary mineral precipitates were collected from the column outflows after the weathering experiments and similarly analyzed with XRD. Acid-base accounting was performed using the modified Sobek method, using sulfide-S to determine acid-generating potential and an HCl-digestion at ambient temperature to determine neutralizing potential (Price, 2009; Dold, 2017). The mineralogical and geochemical properties of the waste rock are given in Table S1. Particle size distributions (Fig. S1), soil-water characteristics curves (Fig. S2) and hydraulic parameters of the waste rock (Table S2) were previously determined (Blackmore et al., 2014).

### 2.2. Sample treatment and experimental design

Each of the collected 150 kg waste-rock samples was thoroughly homogenized and split into equal halves. One half was heated and dried at 50 °C for 48 h in an oven to suppress the endemic microbial population, whereas the other half was left untreated. This heating and drying treatment was preferred over alternative and more effective sterilization methods because for example autoclaving or irradiation was impractical for >1 m columns with >150 kg of waste rock, and because chemical sterilization was deemed undesirable. The three different waste-rock classes were stacked in layers in two identical experimental columns that were different only in their microbiology: column 1 contained treated waste rock with altered ('suppressed') microbial populations whereas column 2 contained untreated waste rock with unaltered, in-situ, populations (Fig. 1). The stacking sequence and relative quantities of the different waste-rock classes were similar in both columns; both columns contained a total of ~175 kg waste rock. After the waste rock had been placed into the columns, 10 L of a filter-sterilized (0.45 μm) solution was applied over 24 h to remove salts that had accumulated on mineral surfaces during storage and to promote bacterial growth at the start of the experiment. The solution was a salt solution reflecting