Science of the Total Environment 616–617 (2018) 647–657

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Role of microbial activity in Fe(III) hydroxysulfate mineral transformations in an acid mine drainage-impacted site from the Dabaoshan Mine

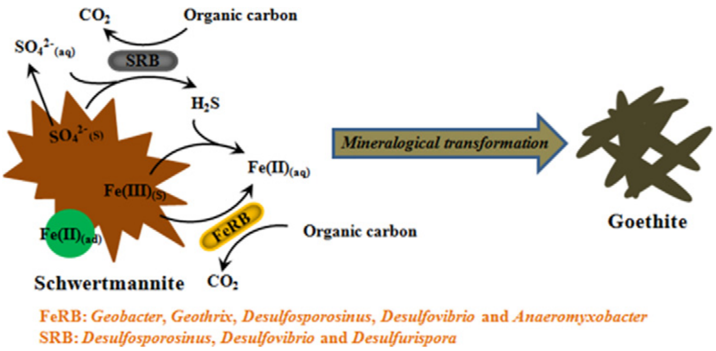
Yanping Bao [a], Chuling Guo [a,b,*], Guining Lu [a,b], Xiaoyun Yi [a,b], Han Wang [a], Zhi Dang [a,b]

[a] *School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China*
[b] *The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, South China University of Technology, Guangzhou 510006, PR China*

HIGHLIGHTS

- Schwertmannite and jarosite were used as electron acceptors by indigenous microbes from the Dabanshan Mine.
- Organic carbon was the major factor limiting the microbial transformation of Fe(III) hydroxysulfate minerals in AMD sites.
- FeRB and SRB are the functional groups that mediate the transformation of Fe(III) hydroxysulfate minerals.
- Microbial transformation of schwertmannite was much faster than that of jarosite.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 June 2017
Received in revised form 26 October 2017
Accepted 26 October 2017
Available online 2 November 2017

Editor: F.M. Tack

Keywords:
Acid mine drainage
Schwertmannite and jarosite
Bacterial community
Iron-reducing bacteria
Sulfate-reducing bacteria
Mineralogical transformation

ABSTRACT

Fe(III) hydroxysulfate minerals are secondary minerals commonly found in acid mine drainage (AMD) sites and have a major impact on water and soil quality in these environments. While previous studies showed that the Fe(III) hydroxysulfate mineral transformation could be mediated by some bacterial strains under laboratory conditions, the role of indigenous microbial activity in Fe(III) hydroxysulfate mineral transformation in natural environment has received little attention. In this study, microcosms were constructed with AMD-affected river water and sediment from the Dabaoshan Mine that was either left unamended or enriched with nutrients (lactate, nitrogen, and phosphorus (LNP)) and biosynthetic minerals (schwertmannite or jarosite). The results show that microbial activity played a decisive role in the mineralogical transformation of schwertmannite/jarosite in the AMD-contaminated site when organic carbon was available. The accumulation of Fe(II) and sulfide in microcosms amended with LNP indicates that schwertmannite/jarosite transformation is mediated by microbial reduction. XRD, SEM and FTIR analyses suggest that schwertmannite was completely transformed to goethite in the Sch-LNP microcosms at the end of their incubation. Jarosite in the Jar-LNP microcosms was also transformed to goethite, but at a much slower rate than schwertmannite. Bacterial community analysis reveals that the stimulated indigenous bacteria promote the mineralogical transformation of schwertmannite/jarosite. Most of these bacteria, including *Geobacter*, *Desulfosporosinus*, *Geothrix*, *Desulfurispora*, *Desulfovibrio*, and *Anaeromyxobacter*, are known to reduce iron and/or sulfate. The mineralogical transformation of schwertmannite and jarosite exerts significant control on the geochemistry of AMD-contaminated systems.

---

[*] Corresponding author at: School of Environment and Energy, South China University of Technology, HEMC, Guangzhou 510006, PR China.
E-mail address: clguo@scut.edu.cn (C. Guo).

https://doi.org/10.1016/j.scitotenv.2017.10.273

1. Introduction

Acid mine drainage (AMD), which is generated by biotic and abiotic oxidation of sulfide minerals (e.g., pyrite, pyrrhotite, and chalcopyrite), contaminates soil and water, leading to severe acidification and accumulation of toxic elements, and induces the erosion, sedimentation, and precipitation of secondary Fe(III) minerals (Bigham et al., 1996; Bigham and Nordstrom, 2000; Chen et al., 2015). In many AMD-polluted rivers and lakes, the uppermost layers of the sediment mainly consist of Fe(III) minerals, such as hematite, schwertmannite, jarosite and goethite (Silva et al., 2013; Chen et al., 2015; Vithana et al., 2015). Among these secondary Fe(III) minerals, Fe(III) hydroxysulfate minerals are particularly important for water and soil quality in AMD-contaminated sites (Peretyazhko et al., 2009; Vithana et al., 2015).

Schwertmannite ($Fe_8O_8(OH)_{8-2x}(SO_4)_x$ (x:1–1.75)) and jarosite ($KFe_3(SO_4)_2(OH)_6$) are two of the principal secondary Fe(III) hydroxysulfate minerals commonly found in AMD sites (Peretyazhko et al., 2009; Valente and Gomes, 2009; Vithana et al., 2015). Schwertmannite and jarosite act as important sinks for minor elements (e.g., As, Zn, Cu, Hg, Pb, Cr) through adsorption or co-precipitation reactions (Peretyazhko et al., 2009; Vithana et al., 2015). However, schwertmannite and jarosite are unstable. Both will progressively transform to more crystalline, thermodynamically stable forms (e.g., goethite and lepidocrocite), resulting in the release of acidity and previously held heavy metals (Bigham and Nordstrom, 2000; Welch et al., 2007; Jones et al., 2009).

In natural environments, the stability of schwertmannite and jarosite depends on a range of physical and chemical factors and the activity of microorganisms (Coggon et al., 2012; Vithana et al., 2015). Laboratory studies have shown that both iron-reducing bacteria (FeRB) and sulfate-reducing bacteria (SRB) can mediate the transformation of schwertmannite and jarosite (Jones et al., 2006; Senko et al., 2009; Coggon et al., 2012; Bertel et al., 2012). These studies were conducted using pure bacterial cultures with well-defined metabolisms and synthetic minerals under laboratory conditions. Bridge and Johnson (2000) showed that a variety of Fe(III) minerals, including jarosite, could be solubilized by the heterotrophic acidophilic iron-reducer *Acidiphilium* SJH. Jones et al. (2006) showed that two *Geobacter* species were able to reduce structural Fe(III) in jarosite and Senko et al. (2009) found that a Fe(III)- and sulfate-reducing bacterium enhanced the transformation of schwertmannite to goethite.

Dissimilatory iron and sulfate reduction widely occurs in the natural environment and is involved in the microbial transformation of schwertmannite and jarosite (Coggon et al., 2012; Vithana et al., 2015). However, the microbially-mediated transformation of schwertmannite and jarosite in AMD sites has not received much attention (Chen et al., 2015; Vithana et al., 2015). The environments that receive AMD are often characterized by very low biodiversity (Baker and Banfield, 2003; Delavat et al., 2013; Bao et al., 2017), because the extreme toxicity and acidity of AMD destroy aquatic ecosystems and render water resources less habitable to various biota. Previous studies of microbial reduction of Fe(III) hydroxysulfate minerals were often conducted under circumneutral pH, which is optimal for most FeRB and SRB. However, only a few species (e.g., *Acidiphilium* (Bridge and Johnson, 2000) and *Acidithiobacillus* (Hallberg et al., 2011)) can reduce Fe(III) minerals under acidic conditions. Moreover, FeRB can outcompete SRB for limited electron donors when the environment is non-limiting in ferric iron (Chapelle and Lovley, 1992; Küsel and Dorsch, 2000; Küsel et al., 2001); thus, SRB may be suppressed in AMD sites characterized by low pH, low nutrient level, and high concentrations of iron and sulfate.

In this work, we used a microcosm-based approach to investigate the role of microbial activity in the transformation of schwertmannite and jarosite under the AMD condition. The objectives were (i) to examine the potential role of microbial activity in the transformation of schwertmannite and jarosite in an AMD site, (ii) to identify the potential bacterial groups that may mediate the transformation of schwertmannite and jarosite, and (iii) to explore the possible mechanisms of microbial transformation of Fe(III) hydroxysulfate minerals in AMD sites.

2. Materials and methods

2.1. Sampling area and field sampling

The sediment and water samples used in this study were collected from a river contaminated by AMD in the Dabaoshan Mine area (24°30′19.93″N; 113°44′47.13″E) (Fig. 1), which is the largest mine in South China. The Dabaoshan Mine is a multi-metallic mine and metal ores (mainly iron and copper) have been mined extensively there since the 1970s. Most of the metal ores are sulfur-containing ores such as pyrite, pyrrhotite, and chalcopyrite, which are very important for AMD generation. The area has a humid subtropical climate that can accelerate AMD formation (Chen et al., 2015).

Our research team has conducted many studies in the Dabaoshan Mine area (Chen et al., 2015; Bao et al., 2017). Seven sampling sites were previously selected to monitor physicochemical, mineralogical, and microbiological characteristics of the river, that receives AMD from this mining area (Bao et al., 2017). Site S6 (circled in Fig. 1), located at the confluence of the effluent streams from the mud impoundment and the tailing impoundment, was selected as the basis for this study based on our prior work that showed the existence of FeRB (e.g., *Geobacter* and *Geothrix*) and Fe(III) reduction in the sediment at this site (Bao et al., 2017).

Schwertmannite and jarosite were two of the main Fe(III) hydroxysulfate minerals found in the river affected by AMD at the Dabaoshan Mine (Chen et al., 2015; Bao et al., 2017). Large amounts of iron-sulfate minerals, especially schwertmannite (accounted for >6 wt% of the dry weight), were present at site S6 (Chen et al., 2015 and unpublished data). In this study, X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that schwertmannite was one of the most abundant minerals in the sediment from site S6 (Fig. S1).

The sampling site S6 is within the AMD attenuation zone, where the pH has remained in the range of 3.0–4.0 since 2012 (Chen et al., 2015; Bao et al., 2017). Only surface water and surface sediment (up to 5 cm deep) samples were collected at site S6 in the Dabaoshan Mine area in November 2014 (Bao et al., 2017); 1 kg of sediment and 5 L of water were collected using sterile serum bottles and stored at 4 °C until use (within 2 days). The geochemical conditions of the water were measured at the time of sampling (Table S1).

2.2. Schwertmannite and jarosite preparation

Schwertmannite and jarosite were biosynthesized using a strain of *Acidithiobacillus ferrooxidans* (Liao et al., 2009; Ouyang et al., 2014). This strain of *A. ferrooxidans* was isolated from the AMD of a pyrite mine in South China (Zhang et al., 2013) and cultivated in a 9 K medium. In the biosynthesis systems, we inoculated the solution with ~10^8 cells/-mL of *A. ferrooxidans*. The solution used for jarosite synthesis contained 0.2 M $FeSO_4$ and 0.067 M K_2SO_4; The solution for schwertmannite synthesis contained 0.16 M $FeSO_4$. The biosynthesis reactors were incubated at 30 °C and an initial pH of 2.5 in a rolling incubator at 150 rpm. After two weeks, the precipitate was collected on a 0.45 μm filter paper, washed with deionized water until the pH of the washed water was near neutral, and dried at room temperature. XRD and Raman analysis showed that the synthesized schwertmannite and jarosite were pure (Fig. S2).

2.3. Microcosm construction and sampling

A series of microcosm experiments were performed, including Sch, Sch-LNP, Jar, Jar-LNP, and LNP microcosms (Table 1). Each microcosm