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Iron mineralogy across the oxycline of a lignite mine lake

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ABSTRACT

Iron-rich pelagic aggregates of microbial origin named “iron snow” are formed in the water column of some acidic lignite mine lakes. We investigated the evolution of Fe mineralogy across the oxycline of the Lusatian lake 77, Germany at two sampling sites differing by their pH and mixing profiles. The central basin (CB) of this lake shows a dimictic water regime with a non-permanent anoxic deep layer and a homogeneous acidic pH all over the water column (pH 3). In contrast, the northern basin (NB) is meromictic with a permanently anoxic bottom layer and a pH increase from pH 3 in the mixolimnion (superficial part of the lake) to pH 5.5 in the monimolimnion (anoxic bottom layer). Fe minerals above and below the oxycline were identified using X-ray Absorption Spectroscopy (XAS) at the Fe K-edge and further characterized down to the atomic scale by High Resolution Transmission Electron Microscopy (HRTEM) and Scanning Transmission Electron Microscopy (STEM) coupled to Energy Dispersive X-ray Spectroscopy (EDXS). We explored local Fe redox state and C speciation using Scanning Transmission X-ray Microscopy (STXM) at the Fe $L_{2,3}$-edges and C K-edge. Schwertmannite $[Fe_8O_8(OH)_{8-2x}(SO_4)_x]$ identified as the sole Fe mineral in CB, was polycrystalline, consisting in the aggregation of nanodomains of 2–3 nm each one exhibiting the crystal structure of schwertmannite. In contrast, schwertmannite was partly (40%) converted to aluminous ferrihydrite when reaching the oxycline in NB. This mineralogical transformation was most probably due to a combination of abiotic and microbial anaerobic processes promoting pH increase and release of Fe(II) (e.g. via heterotrophic Fe(III) reduction) that induce the catalytic hydrolysis of schwertmannite to ferrihydrite. Mineral products were stabilized in the monimolimnion by the adsorption of aluminum, silicate and organic matter. Noteworthy, local Fe redox state heterogeneities were observed, with a few areas enriched in Fe(II) as evidenced by STXM analyses at the Fe $L_{2,3}$-edges. These local redox heterogeneities could arise from microbial activity (e.g. Fe(III) and/or sulfate reduction). All these results provide an in-depth mineralogical overview of iron phases forming in lake 77 as a basis for future investigations of microbial vs. abiotic parameters controlling their stability and transformation.

1. Introduction

From early Earth to modern environments, oxidative weathering of Fe sulfides has been a major source of acidity and has supplied high amounts of dissolved sulfate and iron species to surface waters. This process was indeed active since the Archean, as suggested by the Cr isotope record around the Great Oxidation Event (Anbar et al., 2007; Crowe et al., 2013; Konhauser et al., 2011; Reinhard et al., 2013). Nowadays similar processes take place at acid rock or mine drainages (Lu and Wang, 2012) or in acidic lignite mine lakes (Blodau, 2006).

In such ferruginous environments, Fe(III) minerals precipitate massively. For instance iron oxyhydroxide and oxyhydroxysulfate precipitates are emblematic of acid rock drainages such as those located in the Iberian Pyrite Belt (Fernández-Remolar et al., 2005; Sánchez España et al., 2005). Another example of such iron mineralization occurs in acidic lignite mine lakes formed in former coal mine pits (Blodau, 2006; Küsel, 2003). They exhibit high rates of Fe(II) oxidation leading to massive precipitation of Fe(III)-bearing minerals, in the form of iron-rich aggregates termed “iron snow” (Reiche et al., 2011).

The nature of Fe-bearing phases forming in such environments is strongly pH dependent. Schwertmannite $[Fe_8O_8(OH)_{8-2x}(SO_4)_x$; $1 \le x \le 1.75]$ (Bigham et al., 1994) and/or jarosite $[(H, K, Na)Fe_3(OH)_6(SO_4)_2)]$ are usually predominant under acidic conditions (pH 2.8–4.5) (Bigham et al., 1996), whereas at higher pH, ferrihydrite and/or goethite are more stable (Bigham et al., 1996; Gagliano et al., 2004; Sánchez-España et al., 2012, 2011). This diversity of Fe minerals plays a key role in controlling heavy metal(loid) mobility (Burgos et al., 2012; Morin and Calas, 2006; Nordstrom, 2011). For instance, schwertmannite as well as mixed Fe and As oxyhydroxysulfates are

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known to efficiently scavenge arsenic in acid mine drainages (Carlson et al., 2002; Maillot et al., 2013; Morin et al., 2007, Morin et al., 2003). However the mechanisms controlling the precipitation and stability of these various mineral species are not fully understood. In particular, although the atomic structure of nanocrystalline schwertmannite has been elucidated using pair distribution function analysis (Fernandez-Martinez et al., 2010), the nanoscale structure (French et al., 2012; Hockridge et al., 2009), composition and stability (Caraballo et al., 2013; Regenspurg et al., 2004) of this phase remain a matter of debate.

Beyond abiotic factors (pH, redox potential, saturation state), microbial parameters contribute to the formation and/or stabilization of such Fe minerals. Many acidophilic Fe-cycling bacteria are part of the microbial diversity in these environments (Bonnefoy and Holmes, 2012; Johnson et al., 2012; Küsel, 2003) and retrieve energy from Fe(II) oxidation (Nordstrom and Southam, 1997). This leads to Fe minerals closely associated with microbial organic matter in acidic ferruginous environments (Benzerara et al., 2008; Clarke et al., 1997; Hedrich et al., 2011; Inskeep et al., 2004; Mori et al., 2015; Ohnuki et al., 2004) and in laboratory cultures (Egal et al., 2009; Liao et al., 2009; Morin et al., 2003; Sandy Jones et al., 2014; Xu et al., 2014; Zhu et al., 2013). Fe mineralogy may furthermore be modified through the activity of Fe(III)-reducing and sulfate-reducing microorganisms reported in such acidic environments (e.g. Bingjie et al., 2014).

Redox gradients are prone to the activity of such Fe cycling microbes and thus to Fe mineral (trans)formation. Whereas the oxycline is usually located within the sediment, this redox transition zone is present within the water column of some meromictic ferruginous lakes exhibiting either neutral (Crowe et al., 2008; Viollier et al., 1997) or acidic pH (Blodau, 2006; Reiche et al., 2011) that share analogies with early Earth environments (Busigny et al., 2014; Canfield et al., 2008). This oxycline is inhabited by a diversity of microbes involved in the Fe redox cycle (Crowe et al., 2008; Lehours et al., 2009, Lehours et al., 2007; Lehours et al., 2005; Lu et al., 2013; Lu et al., 2010; Walter et al., 2014), some of which are potentially involved in the biomineralization of Fe-bearing phases (Cosmidis et al., 2014; Llirós et al., 2015; Lu et al., 2013; Miot et al., 2016). Interplay of Fe(II)-oxidizing and Fe(III)-reducing bacteria might thus contribute to the control of Fe mineralogy.

Estimating the respective contributions of abiotic vs. microbial processes in controlling Fe mineralogy in redox transition zones remains a critical issue. As a first stage towards understanding these mechanisms, we performed an in-depth study of Fe mineralogy across the oxycline of a lignite mine lake (Lusatian Lake 77, Germany). This lake is characterized by an acidic pH and high dissolved Fe(II) (up to 12 mM in the bottom water) and sulfate (up to 30 mM) concentrations, arising from Fe sulfide oxidative weathering (Blodau, 2006; Küsel, 2003). It is composed of two basins: the northern basin (NB) is meromictic, i.e. permanently stratified with a deep anoxic layer (monimolimnion), whereas the central basin (CB) is dimictic, i.e. undergoes mixing in spring and autumn. A diversity of chemoautotrophic iron oxidizers and heterotrophic iron reducers have been identified as active players of the Fe biogeochemical cycle around the redoxcline of this lake (Lu et al., 2013). In the present study, we used X-ray absorption spectroscopy at the Fe K-edge to determine the nature of Fe minerals, including amorphous or poorly crystalline phases. In addition, we combined High Resolution Transmission Electron Microscopy (HRTEM) and synchrotron-based Scanning Transmission X-Ray Microscopy (STXM) to investigate the speciation of iron and associated organic matter down to the nanometer scale. Our results open a discussion of the stability of Fe minerals across the oxycline of Lake 77.

2. Materials and methods

2.1. Lake characteristics and sampling

The acidic lignite mine lake 77 is located in the Lusatian mining area in east-central Germany and was formed after mining activity had stopped in 1960. The lake is composed of two basins: (a) the central basin (CB) exhibits a dimictic water regime with a full circulation of the water in spring and autumn and (b) the smaller meromictic northern basin (NB) has a deep permanently anoxic water body that is not influenced by lake circulation (Fleckenstein et al., 2009; Reiche et al., 2011). The bottom water of the NB has higher pH value, conductivity and dissolved Fe(II) and sulfate concentrations probably due to the inflow of less acidic contaminated groundwater (Fleckenstein et al., 2009; Neumann et al., 2013; Reiche et al., 2011). At each sampling time, pH, temperature, conductivity and dissolved oxygen content of the lake water were measured over depth with a multi-parameter probe (YSI Pro Plus, YSI, USA). The polarographic dissolved oxygen probe was calibrated with air-saturated water. The resolution for this probe is 0.01 $mg\cdot L^{-1}$ and the accuracy 0.2 $mg\cdot L^{-1}$ in the range 0–20 $mg\cdot L^{-1}$. The pH-meter probe was calibrated by typical two-point calibration, using buffers at pH 4.0 and 7.0. The resolution of this probe is 0.01 units and the accuracy 0.2 units. The decline of the oxygen concentration marked the oxycline. To collect iron rich pelagic aggregates ("iron snow" particles) at different redox conditions, water samples were taken in November 2013 from 6-m depth at CB (after mixing of the CB) and from above, within and below the oxycline (4.5 m, 5.5 m and 6 m depth) at NB. In September 2014, water samples were taken before mixing of the CB from above, within and below the oxycline (5 m, 5.6 m and 6 m depth) and at NB from 4.3 m, 4.9 m and 6 m depth. Water samples were collected using a Ruttner water sampler and filled into bottles pre-flushed with nitrogen gas to avoid further oxygenation, sealed and transferred to laboratory in a cooling box. Bottles were opened in an anaerobic chamber ($O_2 < 0.2\%$) and iron snow particles were transferred to smaller bottles after sedimentation, then kept under cool conditions until further analyses. O_2 contamination is expected to remain limited given the methods used for sampling and given the slow kinetics of Fe(II) oxidation at the acidic pH of the lake water. For samples from NB (September 2014), concentrations of dissolved Fe(II) were measured spectrophotometrically using the phenanthroline method (Tamura et al., 1974). Sulfate concentration was measured turbidimetrically by the barium-chloride method (Tabatabai, 1974).

2.2. X-ray absorption spectroscopy

2.2.1. Sample preparation

For XAS analyses, samples from September 2014 exhibiting the highest content in particulate matter (CB-6.0 m-2014, NB-4.9 m-2014, NB-6.0 m-2014) were prepared in an anoxic glovebox ($pO_2 < 50$ ppm). Water samples were centrifuged at 7000 g for 15 min, then rinsed twice in deoxygenated mQ water (with pH adjusted at the lake water pH using HCl) and vacuum dried. The powder was gently grinded in an agate mortar and pressed as pellets in mixture with appropriate amount of cellulose in order to obtain absorption edge height ($\Delta\mu x$) as close as possible to one.

2.2.2. XAS data collection and analyses

Fe K-edge XAS spectra of the lake samples were recorded at 77 K in transmission detection mode at the XAFS beamline (ELETTRA, Italy), using a Si(111) double-crystal monochromator. Energy was calibrated by setting to 7112 eV the first inflection point of Fe-foil K-edge recorded in double-transmission setup. The spectra were merged and normalized using the Athena program (Ravel and Newville, 2005) and Extended X-ray Absorption Fine Structure (EXAFS) data were extracted using the XAFS program (Winterer, 1997). X-ray Absorption Near Edge Structure (XANES) and k^3-weighted EXAFS spectra were analyzed using a Linear Combination Fit (LCF) procedure thanks to a custom-built software based on the Levenberg–Marquardt minimization algorithm. For this LCF analysis, we used experimental spectra from a large set of Fe-mineral model compounds (Cosmidis et al., 2014; Maillot et al., 2013, Maillot et al., 2011; Noël et al., 2014), among which the following