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Impact of electrogenic sulfur oxidation on trace metal cycling in a coastal sediment

Sebastiaan van de Velde^{a,*}, Ine Callebaut^a, Yue Gao^a, Filip J.R. Meysman^{a,b}

^a Department of Analytical, Environmental and Geo-Chemistry, Vrije Universiteit Brussel (VUB), Pleinlaan 2, 1050, Brussel, Belgium

^b Centre for Microbial Ecology and Technology, Universiteit Gent, Coupure Links 653, 9000 Ghent, Belgium

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ABSTRACT

Electrogenic sulfur oxidation (e-SOx) is a newly discovered pathway of microbial sulfide oxidation, mediated by so-called cable bacteria. The reduction of oxygen near the sediment-water interface is coupled by long-distance electron transport to the oxidation of sulfide in deeper sediment, and in this way, electrical currents are induced within the seafloor that range over centimeter scale distances. Previously, electrogenic sulfur oxidation has been shown to generate extreme pH excursions in the pore water, and as a result, the process strongly amplifies the cycling of various pH-sensitive minerals, such as sulfide minerals and carbonates. Here we show that e-SOx also strongly influence the early diagenesis of trace metals in coastal sediments. For this, field observations at a shallow subtidal site in the North Sea were combined with dedicated laboratory incubations of repacked sediments. High resolution microsensor profiling (pH, H₂S and O₂) confirmed the typical geochemical signature of e-SOx both in situ as in the laboratory experiments. Pore water analysis revealed a strong mobilization of both arsenic and cobalt within the electro-active sediment zone. The dissolution of iron sulfides, resulting from the acidification of the pore water by e-SOx, appears to be the main driver for the observed release of cobalt and arsenic. The current generated by e-SOx affects charged species. In this manuscript, we have proposed a new estimation method for the associated current density, based on the rate of sulfide oxidation.

Overall, electrogenic sulfur oxidation has a major impact on the cycling of arsenic and cobalt in coastal sediments, and may substantially increase the effluxes of these trace metals to the coastal ocean.

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1. Introduction

Most trace metals (e.g. cobalt, cadmium ...) play a dual role in the biogeochemical cycles of marine environments. They act as essential micro-nutrients at low concentrations, but exhibit toxic effects for marine biota at higher concentrations (Driscoll et al., 1994). In marine sediments, the mobility and toxicity of trace metals is often highly redox dependent, as trace metals can cycle between stable oxidized and reduced forms, depending on the redox state of the pore water (Edenborn et al., 1986; Langmuir et al., 1999; Swanner et al., 2014). Although most pore waters are enriched in trace metals compared to the overlying water, the effluxes of these metals from the sediment are generally low, as long as oxygen levels are sufficiently high in the overlying bottom water. However, as the oxygen concentrations in the bottom water decrease, and hypoxia and anoxia develops, the sediment may see a substantial increase in the efflux of trace metals (Riedel et al., 1999; Banks et al., 2012a). Furthermore, resuspension of anoxic sediment can lead to a strong increase in

metal release to the overlying water, associated with the oxidation of reduced minerals like FeS (Sullivan and Aller, 1996; Saulnier and Mucci, 2000).

Overall, marine sediments can act both as a source or a sink of trace metals, and the magnitude of the benthic efflux will depend both on the local bottom water conditions (Sundby et al., 1986), sediment resuspension activity (Sullivan and Aller, 1996) as well as the local geochemical cycling regime in the sediment. Accordingly, to assess their impact on water quality, one requires a comprehensive understanding of trace metal cycling in the seafloor.

A first important control on trace metal cycling in marine sediments is exerted by adsorption onto various solid phases. Trace metals enter the sediment mainly in particulate form. Some metals (e.g. Cd, Cu) are principally adsorbed onto organic matter (Johnson et al., 1988; Gendron et al., 1986), while others (e.g. Co, As, Ni) are typically associated with manganese and iron (oxyhydr)oxides (Gendron et al., 1986; Giménez et al., 2007; Kay et al., 2001; Stockdale et al., 2010). In deeper sediment layers, organic matter becomes mineralized or iron and manganese (oxyhydr)oxides become subject to dissimilatory reduction, and so, trace metals are released into the pore water. Yet, also removal processes are in place. Part of the trace metals that are released in the pore water, will diffuse

* Corresponding author.

E-mail address: sevdevel@vub.ac.be (S. van de Velde).

upwards. Upon passing through the oxic layer near the sediment-water interface, they can be captured by iron and manganese (oxyhydr)oxides (Sundby et al., 1986; Mucci et al., 2000; Kay et al., 2001). Furthermore, in sulfidic environments, some metals (e.g. As, Cd, Co, Cu, Pb and Ni) are captured during the formation of iron sulfides and pyrite, and in this way, they can become buried (Huerta-diaz and Morse, 1992; Huerta-diaz et al., 1998; Bostick and Fendorf, 2003; Lesven et al., 2008).

A second important control on trace metal cycling in aquatic sediments is exerted by the pH (O'Connor and Kester, 1975; Harbison, 1986). Trace metals typically form complexes in seawater, with the most common organic ligands being polymeric humic and fluvic acids (Gardner, 1974), while typical inorganic ligands are the hydroxyl ion (e.g. for Cr), carbonate ion (e.g. for Cu) and chloride (e.g. for Cd). The stability of these ligand complexes is dependent on pH, with a lower pH being responsible for higher free element concentrations (Byrne et al., 1988). At the same time, the pore water pH conditions also regulate the dissolution and precipitation of various minerals, such as carbonates and sulfides, and therefore, shifts in pore water pH can substantially influence the mobilization of trace metals that are associated with pH-sensitive minerals (Bergkvist, 1987). Overall, pH is a controlling factor for the bioavailability of trace metals in marine sediments.

Here we examine the impact of long-distance electron transport by cable bacteria on trace metal cycling in coastal sediments. The process of long-distance electron transport has only been recently discovered (Nielsen et al., 2010; Pfeffer et al., 2012), but forms a truly paradigm shifting concept in geochemistry. By inducing electrical currents, cable bacteria are able to segregate the half reactions of sulfide oxidation over centimeter distances (a process referred to as electrogenic sulfur oxidation). This remote spatial coupling of redox half reactions defies conventional ideas of how redox cycling occurs within marine sediments (Nealson, 2010). Long-distance electron transport short-circuits the conventional redox cascade (Froelich et al., 1979) and allows electron acceptors and electron donors to interact with each other without being in close proximity. Moreover, it turns the seafloor into an electro-active environment, characterized by electrical fields that induce the electro-migration of ions. In this process, the reduction of oxygen and the oxidation of sulfide are spatially separated over centimeter-scale distances (Nielsen et al., 2010) and coupled with the generation of electrical currents (Damgaard et al., 2014; Risgaard-Petersen et al., 2014).

Electrogenic sulfur oxidation (e-SOx; Meysman et al., 2015) has a strong impact on the two dominant factors that control trace metal cycling in marine sediments. Firstly, e-SOx influences the distribution of adsorbing mineral phases as it strongly impacts the cycling of iron (oxyhydrox)oxides, metals sulfides and carbonates (Rao et al., 2016; Risgaard-Petersen et al., 2012; van de Velde et al., 2016). Secondly, e-SOx substantially affects the depth profile of pore water pH, as it induces strong pH excursions in the pore water. This pH effect results from the spatial segregation of two redox half reactions of e-SOx (Nielsen et al., 2010). Oxygen reduction near the sediment-water interface (SWI) creates strong proton consumption (high pH), while sulfide oxidation in the deeper layers of the sediment creates a strong proton generation (low pH) – see Meysman et al. (2015) for a model analysis. The acidification of the pore water at depth promotes the dissolution of sulfide and carbonate minerals and releases Ca^{2+} , Fe^{2+} and Mn^{2+} , while the alkaline conditions near the SWI stimulates the precipitation of carbonates and iron oxides (Risgaard-Petersen et al., 2012; Rao et al., 2016). Given its impact on adsorbing mineral phases and pore water pH, one can expect that electrogenic sulfur oxidation also has a major influence on the cycling of trace metals in marine sediments. To verify this hypothesis, we investigated the geochemical cycling of trace metals in a coastal sediment in the southern North Sea, which is naturally impacted by electrogenic sulfur oxidation.

2. Materials & methods

2.1. Field site location

Station BCZ 130 (N51°16.3', E2°54.3'; Fig. 1) is located in the Southern North Sea, ~5 km offshore from the Belgian coastal city of Oostende. The site has an average water depth of ~12 m, a tidal amplitude of ~4.5 m and is exposed to strong tidal currents, which are directed in parallel to the coast (Vlaamse Hydrografie, 2012). The sediment at the site consists of fine-grained mud enriched in organic matter and carbonate (Van Lancker et al., 2004; van de Velde et al., 2016). Benthic macrofauna are largely absent throughout the year, and so the sediment likely experiences little bioturbation (Braeckman et al., 2014). Station BCZ 130 was selected as the field site for this study because of suitably available background knowledge on the sediment geochemistry. The site was one of the three sites where the natural occurrence of cable bacteria was first demonstrated by Malkin et al. (2014). This study revealed the characteristic geochemical fingerprint of e-SOx, as well as the presence of high filament densities of cable bacteria (investigations in two different periods; October 2011 and March 2013). In a follow-up study (executed in January, March and May 2014), van de Velde et al. (2016), showed a strong impact of e-SOx on the geochemical transformations of the major elements (C, S, N, P, Fe, Mn) in the sediment. Finally, an earlier study (Gao et al., 2009), conducted in the spring of 2008, already showed that some trace metals are present in measurable concentrations in the pore water at BCZ 130.

2.2. Sediment collection

Sediment was collected on board of the RV Simon Stevin on two different occasions (26 November 2014 and 23 February 2015). In a first sampling campaign (26 November 2014), bottom water samples and intact sediment cores for in situ geochemistry were collected. Water column depth profiles of temperature (T), salinity (S) and oxygen (O_2) saturation were recorded with a CTD instrument (Seabird 19plusV2, USA). Bottom water was sampled with 5 L NISKIN bottles attached to the CTD carousel (Seabird 55 ECO, USA) and analyzed for O_2 , cations (Ca^{2+} , Mg^{2+} , dissolved Fe, dissolved Mn), trace metals (cadmium, lead, chromium, zinc, copper, nickel, arsenic, cobalt), sulfate (SO_4^{2-}), nutrients (NH_4^+ , PO_4^{3-}), dissolved inorganic carbon (DIC) and total alkalinity (A_T). Sediment cores were collected with a single core gravity corer (UWITEC, Austria) using transparent PVC core liners (inner diameter: 6 cm; length: 60 cm). Upon retrieval, sediment cores were carefully inspected and only cores with an apparent undisturbed sediment-water interface were kept for further analysis. Intact sediment cores ($n = 12$) were transported back to the shore-based laboratory in a thermally insulated container (transit time ~2 h). In a second campaign (23 February 2015), sediment was collected for laboratory incubation experiments using a Van Veen grabcorer. The sediment was subsequently homogenized and transferred into a PVC container, which was closed with an airtight lid and stored in the dark at 4 °C until further usage.

2.3. Sediment handling and pore water collection

Upon arrival at the laboratory, intact sediment cores were inspected again for any sign of disturbance, and subsequently, 8 out of 12 cores were selected for microsensor depth profiling (see Section 2.5), which commenced within 4 h after sampling. After microsensor profiling, the cores were left submerged in an air-saturated water tank, which was located in a climate-controlled room at in situ temperature and filled with bottom water collected from the sampling site. The next day, 2 cores were sectioned for pore water collection in an anaerobic glove box (N_2 atmosphere; Coy lab products, USA), randomly selected from the 8 cores that were microsensor profiled the day before. Cores were sectioned at 0.5 cm resolution from 0 to 5 cm depth, at 1 cm resolution between 5 and 10 cm depth, and at 2 cm slices from 10 to 16 cm depth.

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