



Redox conditions and trace metal cycling in coastal sediments from the maritime Antarctic

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Abstract

Redox-sensitive trace metals (Mn, Fe, U, Mo, Re), nutrients and terminal metabolic products (NO_3^- , NH_4^+ , PO_4^{3-} , total alkalinity) were investigated for the first time in pore waters of Antarctic coastal sediments. The results of this study reveal a high spatial variability in redox conditions in surface sediments from Potter Cove, King George Island, western Antarctic Peninsula. Particularly in the shallower areas of the bay the significant correlation between sulphate depletion and total alkalinity, the inorganic product of terminal metabolism, indicates sulphate reduction to be the major pathway of organic matter mineralisation. In contrast, dissimilatory metal oxide reduction seems to be prevailing in the newly ice-free areas and the deeper troughs, where concentrations of dissolved iron of up to 700 μM were found. We suggest a combination of several factors to be responsible for the domination of metal oxide reduction over sulphate reduction in these areas. These include the increased accumulation of fine-grained material with high amounts of reducible metal oxides, a reduced availability of metabolisable organic matter and an enhanced physical and biological disturbance by bottom water currents, ice scouring and burrowing organisms. Based on modelled iron fluxes we calculate the contribution of the Antarctic shelf to the pool of potentially bioavailable iron (Fe_b) to be 6.9×10^3 to $790 \times 10^3 \text{ t yr}^{-1}$. Consequently, these shelf sediments would provide an Fe_b flux of $0.35\text{--}39.5 \text{ mg m}^{-2} \text{ yr}^{-1}$ (median: $3.8 \text{ mg m}^{-2} \text{ yr}^{-1}$) to the Southern Ocean. This contribution is in the same order of magnitude as the flux provided by icebergs and significantly higher than the input by aeolian dust. For this reason suboxic shelf sediments form a key source of iron for the high nutrient-low chlorophyll (HNLC) areas of the Southern Ocean. This source may become even more important in the future due to rising temperatures at the WAP accompanied by enhanced glacier retreat and the accumulation of melt water derived iron-rich material on the shelf.

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1. INTRODUCTION

The microbially mediated mineralisation of organic material forms a major process controlling redox conditions and therefore the cycling of trace metals and nutrients in marine sediments (e.g., Elderfield et al., 1985; Shaw et al., 1990). Since the oxidation of carbon is coupled to the reactivity and availability of electron acceptors, like O_2 , nitrate,

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Mn(IV), Fe(III) or sulphate, their occurrence or absence in pore waters provides valuable information on redox conditions in the sediment (e.g., Beck et al., 2008b; Canfield and Thamdrup, 2009). Redox-sensitive trace metals (Fe, Mn, V, Mo, U, Re) and nutrients (NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-}) have therefore been successfully used to decipher the redox state and biogeochemical processes in a wide range of coastal marine and deep-sea sediments of the North Atlantic, the North Pacific, the North Sea and off Peru (Froelich et al., 1979; Shaw et al., 1990; Canfield et al., 1993; Morford et al., 2005; Beck et al., 2008a,b; Scholz et al., 2011; Morford et al., 2012). Several studies have shown that in the neritic zone, where the aerobic layer is often only a few millimetres thick, sulphate reduction is considered to be the dominant pathway of anaerobic organic matter degradation, which accounts for up to 92% of carbon oxidation (Jørgensen, 1982; Thamdrup and Canfield, 1996; Kostka et al., 1999). In areas with Mn and Fe-rich surface sediments metal oxide reduction may play a major role as well (Canfield et al., 1993; Thamdrup and Canfield, 1996; Rysgaard et al., 1998; Vandieken et al., 2006).

To date there are only a few studies dealing with geochemical processes and organic matter degradation in coastal marine sediments in the sub-Antarctic or Antarctic. Hartnett et al. (2008), for example, calculated benthic oxygen fluxes and denitrification rates from pore water profiles collected close to Anvers Island at the western Antarctic Peninsula. They could show that O_2 consumption rates on the Antarctic continental margin are comparable to rates found in other typical continental margin sediments. The influence of bioturbation on nutrient, (NH_4^+ , NO_3^-) exchange rates across the sediment–water interface were analysed in sediments from Factory Cove, Signey Island, South Orkney Islands by Nedwell and Walker (1995). Further studies dealt with sulphate reduction rates in Subantarctic sediments off Signey Island (Nedwell, 1989) and in Ellis Fjord, Vestfold Hills, East Antarctica (Franzmann et al., 1988). However, investigations about early diagenetic processes and the behaviour of redox-sensitive trace elements in Antarctic pore waters are rare and restricted to deep sea regions of the Southern Ocean (e.g., King et al., 2000). This gap is astonishing as the Southern Ocean is known to be a high nutrient-low chlorophyll (HNLC) region where primary production is limited by the availability of bioavailable iron (e.g., Martin et al., 1990; Boyd et al., 2007). Consequently, the recycling of trace metals in Antarctic shelf sediments and their subsequent release into the water column could possibly represent an important source of bioavailable iron to the Southern Ocean, as it has been proposed by a number of authors (Planquette et al., 2007; Dulaiova et al., 2009; Lancelot et al., 2009; Tagliabue et al., 2010; Shaw et al., 2011; De Jong et al., 2012; Measures et al., 2012; Raiswell and Canfield, 2012 and references therein; Hatta et al., 2013; Measures et al., 2013).

In this study we report, for the first time, data on redox-sensitive trace metals (Mn, Fe, Mo, U, Re), nutrients (NO_3^- , PO_4^{3-}), sulphate and terminal metabolic products (NH_4^+ , H_2S , total alkalinity) determined in pore waters from Potter Cove, King George Island, maritime

Antarctica. In combination with solid-phase data (bulk parameters, like TOC and TS) we intend to shed light on controlling factors of early diagenetic processes and redox conditions at different locations in this model area. Moreover, based on a modelling approach, the potential of Antarctic shelf sediments as a significant source of bioavailable iron for the Southern Ocean will be discussed.

2. GEOCHEMICAL BACKGROUND

2.1. Trace element geochemistry

2.1.1. Iron

In oxic environments sediment iron is naturally occurring as solid Fe(II) and Fe(III) bearing silicates and (hydr)oxides (Poulton and Raiswell, 2005; Schroth et al., 2009). During early diagenetic processes in the sediment microbially mediated reduction and dissolution of reactive Fe (oxyhydr)oxides can occur leading to an enrichment of dissolved Fe(II) in the pore water (e.g., Canfield et al., 1993). Whereas in the presence of H_2S Fe (hydr)oxides (e.g., ferrihydrite or lepidocrocite) rapidly react to insoluble Fe(II) phases, like FeS and finally pyrite (FeS_2), residual Fe silicates require more than a century for a significant sulphidisation due to their slower reaction kinetics (Canfield, 1989; Canfield et al., 1992; Raiswell and Canfield, 1996).

2.1.2. Manganese

While stable in its oxidised and solid form in oxic seawater, Mn(IV) oxides are reduced to dissolved Mn(II) (and Mn(III)) in suboxic sediments (Stumm and Morgan, 1981; Trouwborst et al., 2006; Madison et al., 2013). With increasing alkalinity production in deeper, anoxic sediment layers Mn(II) is fixed again to the sediments by precipitation of mixed Ca–Mn carbonates (Middleburg et al., 1987; Jakobsen and Postma, 1989; Mucci, 2004). Mn (hydr)oxides are associated with Fe and some trace elements (e.g., As, Co, Mo, Ni, V) which are either incorporated or adsorbed on their surface and whose cycling is directly linked to dissolution and precipitation processes of the respective (hydr)oxide (e.g., Shaw et al., 1990; Burdige, 1993).

2.1.3. Rhenium

Rhenium is characterised by its conservative behaviour in marine waters, presumably present as an oxyanion (Re(VII)O_4^-) at 39.8 ± 0.2 pM (corrected to 35‰ salinity; Anbar et al., 1992; Colodner et al., 1995). In suboxic pore water ReO_4^- is probably reduced to Re(IV) and presumably precipitated as ReS_4 into sediments where conducive conditions for organic matter oxidation by Fe(III) and sulphate reduction are persisting (Colodner et al., 1993; Morford et al., 2012).

2.1.4. Molybdenum

Being generally conservative in oxic marine environments, molybdenum is present as dissolved molybdate (Mo(IV)O_4^{2-}) showing concentrations of around 110 nM at a salinity of 35‰ (Morris, 1975; Algeo and Tribouillard, 2009). However, under certain conditions a

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