



Iron sulfide formation in young and rapidly-deposited permeable sands at the land-sea transition zone

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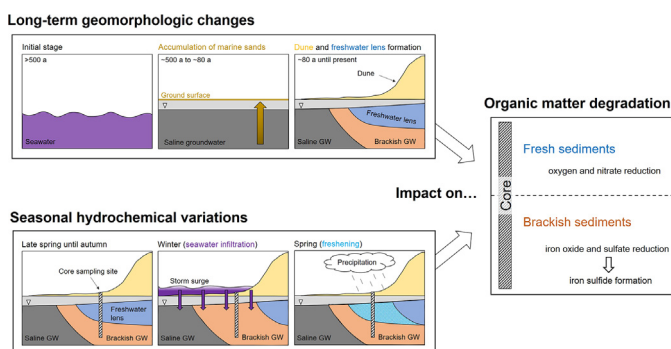
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HIGHLIGHTS

- Biogeochemical cycles in coastal organic-poor, permeable sands are not well studied.
- Our multidisciplinary approach covers aspects of coastal litho- and hydro-spheres.
- Methods include hydrogeochemical, sulfur isotope, DOM, and OSL age investigations.
- SRR are extremely low and organic carbon limits iron sulfide formation.
- Biogeochemical cycles are linked to (seasonal) hydrochemical variations.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic-poor, permeable quartz sands are often present at land-sea transition zones in coastal regions. Yet, the biogeochemical cycles of carbon, sulfur, and iron are not well studied here. The aim of this work was, therefore, to improve our understanding regarding the chemical processes in these prominent coastal sediments. A 10 m core was collected at a dune base of the barrier island Spiekeroog, Germany, for this purpose. Additionally, groundwater was sampled from a multi-level well for one year to record seasonal hydrochemical variations. Methods included the analyses of geochemical (total carbon, total inorganic carbon, reactive iron, total sulfur, reduced inorganic sulfur) and hydrochemical parameters (field parameters, major ions, DOC, and molecular compositions of DOM), as well as stable sulfur isotopes ($\delta^{34}\text{S}$ -sulfate, -sulfide, -total reduced inorganic sulfur). Moreover, optically stimulated luminescence (OSL) dating was applied. Results show that the core sediments are very young (<500 a) and were rapidly deposited. They are characterized by remarkably low contents of organic carbon (<0.1% dw.), reactive iron (~10 mmol/kg), and iron sulfides (<3 mmol/kg). Groundwater salinities were low in the top core sediments and increased at depth during most times of the year. However, the sampling site is subject to (seasonally) varying salinities, which could be linked to the biogeochemical cycles. For instance,

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the infiltration of seawater-derived labile DOM during inundation events drives microbial respiration besides sedimentary organic matter. Oxygen and nitrate were the dominant electron acceptors for the decomposition of organic matter in near-surface groundwater, while sulfate reduction was constrained to the lower brackish sediments. Here, authigenic pyrite formation was inferred based on the detection of dissolved sulfide, intact pyrite framboids, and matching stable sulfur isotope signatures of dissolved and solid sulfides. We concluded that the extremely low organic carbon contents limit pyrite formation in the organic-poor, permeable quartz sands.

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1. Introduction

The environmental cycles of carbon, sulfur and iron are tightly linked to each other. Organic matter is constantly produced, degraded, and deposited in all marine and terrestrial ecosystems (e.g., Burdige, 2007). Sulfur in the form of sulfate is a major constituent in seawater (Howarth, 1984) and present in the atmosphere. Furthermore, iron is delivered to the sea as nanoparticulate (oxyhydr)oxides (e.g., Moore and Braucher, 2008; Raiswell et al., 2008; Tagliabue et al., 2009; Raiswell and Canfield, 2012).

In (marine) sediments, redox conditions rapidly become reducing in the presence of reactive organic matter (e.g., Canfield et al., 1993a; Thamdrup et al., 1994; Al-Raei et al., 2009), resulting in the anaerobic oxidation of organic carbon using mainly sulfate as electron acceptor (Jørgensen, 1982). The reduction of metal oxides (i.e., iron (oxyhydr)oxides and manganese oxides) is often less relevant for the bulk oxidation of organic carbon and may proceed via microbes (e.g., Nealson and Myers, 1990; Lovley, 1991) or coupled to the chemical oxidation of reduced sulfide species (e.g., Canfield, 1989; Thamdrup et al., 1994; Gagnon et al., 1995; Blonder et al., 2017). Methanogenesis classically presents the terminal stage in the redox sequence (Berner, 1981). However, zones of iron (oxyhydr)oxide and sulfate reduction and methanogenesis are often not strictly separated in nature and may overlap, depending on iron (oxyhydr)oxide stability, sulfate concentrations, and substrate levels (e.g., Postma and Jakobsen, 1996; Jakobsen and Postma, 1999). The role of sulfate as the prominent electron acceptor in marine sediments was recently corroborated by Hansel et al. (2015), who suggested that sulfate reduction may precede the reduction of all types of iron (oxyhydr)oxides, including ferrihydrite, even at low sulfate concentrations, a finding challenging classical, thermodynamic-based redox models (e.g., Berner, 1981; Lovley and Phillips, 1987; Lovley and Goodwin, 1988; Chapelle and Lovley, 1992).

As reaction products of anaerobic organic matter degradation, sulfide and ferrous iron are formed that may react to form iron sulfides like mackinawite, greigite, and finally pyrite (e.g., Berner, 1970; Luther, 1991; Wilkin and Barnes, 1996; Passier et al., 1997; Rickard and Luther, 1997; Neretin et al., 2004; Schoonen, 2004; Rickard and Morse, 2005; Raiswell and Canfield, 2012). The formation/transformation processes of iron sulfides are inherently coupled to the availability of reactive organic matter, sulfate, and iron (oxyhydr)oxides (e.g., Berner, 1970; Berner and Raiswell, 1984; Lyons and Berner, 1992; Morse et al., 2007), and the application of geochemical indicators (e.g., C/S ratio, degree of pyritization (DOP), acid volatile sulfide (AVS)/pyrite ratio) proved useful in investigating the environmental conditions during their formation more closely (Raiswell and Canfield, 2012).

Stable sulfur isotope signatures of dissolved sulfate and sulfide as well as solid iron sulfides have been widely used as additional tools to study sulfur sources and biogeochemical processes (e.g., Passier et al., 1997; Böttcher et al., 2004; Kunzmann et al., 2017). This is applicable because bacterially mediated sulfate reduction as well as oxidation of sulfides and disproportionation of sulfur intermediates are associated with distinct isotope fractionations (Nakai and Jensen, 1964; Canfield and Thamdrup, 1994; Habicht et al., 1998; Cypionka et al., 1998; Böttcher et al., 2005). High stable sulfur isotope discrimination between dissolved sulfate and reduced sulfide of up to about 50‰ observed in

the marine environment were previously attributed to a cycling of sulfur species, including re-oxidation of dissolved sulfide and subsequent disproportionation of sulfur intermediates (Canfield and Thamdrup, 1994; Habicht et al., 1998; Habicht and Canfield, 2001). More recent studies, however, demonstrated that high isotope discrimination may also be achieved by dissimilatory sulfate reduction alone (Wortmann et al., 2001; Rudnicki et al., 2001; Canfield et al., 2010; Sim et al., 2011) and that the reactivity of the electron donors may be involved in the developing sulfur isotope discrimination (Kaplan and Rittenberg, 1964; Sim et al., 2011).

Mineral structures of iron sulfides present a further means to investigate chemical conditions during formation (e.g., Wilkin et al., 1996; Böttcher and Lepland, 2000; Merinero et al., 2009; Lin et al., 2016). As an example, size distribution and variability of pyrite framboids were successfully used to infer the redox conditions during sediment deposition or to distinguish between syngenetic and diagenetic pyrite formation (e.g., Wilkin et al., 1996).

The intense study of isotope biogeochemistry in coastal environments has substantially improved our understanding of carbon, sulfur, and iron cycles in the past three decades. Studies were carried out in fully/brackish marine (e.g., Canfield et al., 1993a; Thamdrup et al., 1994; Gagnon et al., 1995; Neretin et al., 2004; Neumann et al., 2005), (semi)euoxic (e.g., Lyons and Berner, 1992; Middelburg, 1991), estuarine (e.g., Morse et al., 2007; Morgan et al., 2012; Kraal et al., 2013), marsh (e.g., Luther and Church, 1988; Dellwig et al., 2002), and freshwater environments (e.g., Marnette et al., 1993; Huerta-Diaz et al., 1998; Canfield et al., 2010). However, very little is known about the cycling of redox sensitive elements, including the formation of iron sulfides, in permeable sands with low organic carbon and reactive iron contents, as only few studies were carried out in such environments (Böttcher et al., 1998, 2004; Jakobsen and Postma, 1999; Al-Raei et al., 2009).

The aim of this study was to assess the cycling of carbon, sulfur, and iron in organic-poor, permeable Holocene sands under the influence of fresh to brackish groundwater salinities. Investigations were carried out at the currently developing Ostplate, which forms the eastern part of the barrier island Spiekeroog, southern North Sea, Germany. Main objectives were to study the geochemical conditions and limiting factors of pyrite formation in such an environment and to assess the effect of varying salinity and redox gradients on the biogeochemical cycles. Interpretations are based on a combination of geochemical, hydrochemical, stable sulfur isotope, and mineral structure investigations, as well as optically stimulated luminescence (OSL) dating.

2. Methodology

2.1. Study site

Core and groundwater sampling were carried out at the Ostplate, which is the eastern part of the barrier island Spiekeroog, Germany (Fig. 1a). Spiekeroog Island is located in the southern North Sea in front of the North German coastline. It has a west-to-east extent of ~9.8 km and a total surface area of ~21.3 km² (Streif, 1990). To the east, the tidal inlet Harle separates it from the neighboring island Wangeroog. The local tidal range of the North Sea is 2.72 m, with a mean high water of 1.39 m above sea level (masl) and a mean low

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