

Iron geochemistry in surface sediments of a temperate semi-enclosed bay, North China



Mao-Xu Zhu^{*}, Xiang-Li Huang, Gui-Peng Yang, Liang-Jin Chen

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

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ABSTRACT

Iron (Fe) speciation and microbial reducible Fe(III) oxides (MR-Fe(III)) in surface sediments of semi-enclosed Jiaozhou Bay were quantified to reveal Fe geochemistry in the settings subjected to anthropogenic perturbations. Results indicate that sedimentary Fe in the bay is mainly of natural weathering source, without appreciable anthropogenic Fe inputs, as indicated by a generally good linear coupling of total Fe to aluminum. Among the three highly reactive Fe(III) (Fe(III)_{HR}) pools, well crystalline Fe(III) oxides (Fe(III)_{WC}) were always the predominant phase, followed by poorly crystalline Fe(III) oxides (Fe(III)_{PC}), and amorphous Fe(III) oxides (Fe(III)_{AM}) were only of minor importance. The dominance of non-sulfidized Fe(II) over sulfidized Fe in the sediments points to the importance of microbial iron(III) reduction (MIR) in the free sulfide-starved conditions. High riverine inputs of TOC leads to outliers in the Fe(III)_{HR} versus total organic carbon (TOC) ratio compared the rest of the bay. OM-dependent MIR as the common driving force has rendered all Fe(II)-bearing phases linearly coupled to TOC. MR-Fe(III) in the surface sediments covered all Fe(III)_{AM} and a fraction of less reactive Fe(III) phases, while Fe(III)_{WC} was at most a minor contributor. Highly reactive Fe appears to be enriched to some extent in the temperate semi-enclosed bay, as in the wet-tropical counterparts.

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1. Introduction

Iron (Fe) is the most abundant redox-sensitive metal on Earth's surface. Its redox cycling in aquatic environments has profound influences on cycling and fate of carbon, sulfur, phosphorus, and a variety of trace elements (Hamilton-Taylor and Price, 1983; Burdige, 1993; Otero et al., 2009; Taylor and Konhauser, 2011). Solid-phase Fe occurs in various phases in the natural environment: ions adsorbed to mineral surfaces, amorphous or crystalline Fe(II, III) (oxyhydr)oxides, structurally coordinated Fe in silicate minerals, Fe(II, III) phosphates, Fe(II) sulfides, and Fe(II) carbonates (Haese et al., 1997; Whiteley and Pearce, 2003; Hyacinthe and van Cappellen, 2004; Poulton and Canfield, 2005; März et al., 2012). In marine surface sediments underlying oxic water, secondary Fe(III) oxides, hydroxides, and oxyhydroxides (collectively referred to as Fe(III) oxides hereafter) are usually the most important components of reactive Fe pool. But they have a wide spectrum of

mineralogy, crystallinity, morphology and chemical composition, and, therefore, display quite variable reactivity in both microbially mediated reduction (Hines et al., 1991; Thamdrup, 2000; Canfield et al., 2005; Hyacinthe et al., 2006) and abiotic reduction by dissolved sulfide. For instance, in abiotic reductions half-lives for amorphous and poorly crystalline Fe oxides are hours or days, but weeks for well crystalline Fe oxides (Canfield, 1989; Poulton et al., 2004; Jones et al., 2009). Intensive cycling of Fe is commonly observed at the redox interface of organic matter (OM)-rich sediments, and usually highly reactive Fe(III) (Fe(III)_{HR}) is preferentially involved in the cycling. Here Fe(III)_{HR} refers to Fe(III)-bearing minerals that are highly reactive towards reaction with free sulfide under anoxic conditions (Canfield, 1989; Canfield et al., 1992; Poulton et al., 2004), and total highly reactive Fe (Fe_{HR}) is defined as the sum of Fe(III)_{HR} and Fe(II), assuming that Fe(II) is the product of reduction of previous Fe(III)_{HR}.

Different reactivity and pool sizes of various Fe phases in coastal marine sediments are a combined result of terrestrial inputs and post-depositional diagenesis, which are, in turn, influenced by a multitude of factors, such as sedimentation rate, sediment composition, redox conditions, and quantity and quality of OM

^{*} Corresponding author. No. 238, Songling Rd., College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China.
E-mail address: zhumaxu@ouc.edu.cn (M.-X. Zhu).

(Canfield, 1989; Raiswell and Canfield, 2012). Comprehensive Fe speciation based on chemical extraction and kinetic dissolution are two commonly used methods to differentiate various Fe pools and to deduce Fe(III) oxide reactivity. Concentration, spatial distribution, and (de)coupling of various Fe pools may provide insights into geochemical processes/properties in relation to depositional conditions, such as enrichment/depletion of Fe_{HR} , redox conditions of water column and ancient/modern sediments, diagenetic reactions of Fe and sulfur, and even anthropogenic Fe inputs (Lyons and Severmann, 2006; Taylor et al., 2007; Attri et al., 2011; Scholz et al., 2014).

In this contribution, Fe geochemistry in surface sediments of semi-enclosed Jiaozhou Bay was investigated using both selective chemical extraction and kinetic dissolution. One objective of this study is to reveal biogeochemical characteristics of sedimentary Fe and potential impacts of excess inputs of nutrients and industrial/domestic wastewaters on sediment records in the semi-enclosed bay. Another objective is to examine whether Fe_{HR} is also enriched in the temperate semi-enclosed bay as in semi-protected settings of the wet-tropical regions (Ku et al., 2008), by comparison with the tropical counterparts and also with the East China Sea (ECS), one of the world's largest shelf seas. The comparison is helpful to reveal whether Fe_{HR} enrichment is a common nature of all semi-enclosed bays, regardless of their geographic conditions. This is of geochemical importance because this feature, if proven true, should be considered in global budgets of Fe_{HR} (Ku et al., 2008).

2. Study area and sampling

Semi-enclosed Jiaozhou Bay is surrounded by Qingdao City and linked by a narrow channel (maximum width: 3.1 km) to the Yellow Sea (Fig. 1). This study area has been described in detail elsewhere (Zhu et al., 2012a), and thus only some important aspects are presented here as required for later discussion. Among ~10 main rivers flowing into Jiaozhou Bay, some in the eastern coast, particularly Haibo River and Licun River, have become the conduits of industrial and domestic wastewater discharges due to the region's rapid economic development and population growth (Dai et al., 2007; Deng et al., 2010; Liu et al., 2010), whereas the rivers discharging

into the (north)western parts of the bay (i.e., Dagu River and Yanghe River) have been much less polluted in terms of heavy metal levels (Deng et al., 2010). Since the 1980s, large amounts of nutrients have been delivered to the bay annually via the rivers, particularly Dagu River, Moshui River, Baisha River, and Licun River (Liu et al., 2005). The high nutrient loading in association with human activities has resulted in enhanced primary productivity and frequent occurrences of algal blooms since 1997 (Wu et al., 2005). Sediment geochemistry of the bay has also been impacted by some human activities. For instance, large-scale benthic shellfish mariculture has resulted in lower OM burial in the upper 30 cm relative to the deeper layers (Liu et al., 2010), rather than an increase of OM burial, as usually expected, under the circumstance of enhanced primary productivity.

Twenty three surface sediments (0–4 cm) were sampled on May 21st and 22nd, 2012 (Fig. 1). This surface layer (0–4 cm) which receives direct sedimentation is involved in active Fe cycling (Zhu et al., 2012a), which allows us to reveal variations of Fe diagenesis in the uppermost layer exposed to varying depositional settings. Upon retrieval of a box core at each station, surface sediments were collected and sealed in zip-lock plastic bags leaving no headspace and then covered with ice. The samples were transported to the laboratory within 9 h, and then frozen at -18°C until further handling within two months. After thawing at room temperature under N_2 atmosphere, samples were mixed in the plastic bags and then subjected to a series of chemical extractions as described below.

3. Analytical methods

3.1. Selective extractions for Fe speciation

Preweighed wet sediment samples in duplicate were dried at 105°C until constant weight for gravimetric analysis of water contents. Contents of Fe in all extractions below were expressed in μmol per gram dry weight of sediments ($\mu\text{mol/g}$).

A combination of several previously used extraction methods (Lovley and Phillips, 1987; Raiswell et al., 1994; Poulton and Canfield, 2005) was employed to quantify five operational Fe phases: (1) acid volatile sulfide (AVS) Fe(II) and carbonate Fe(II)

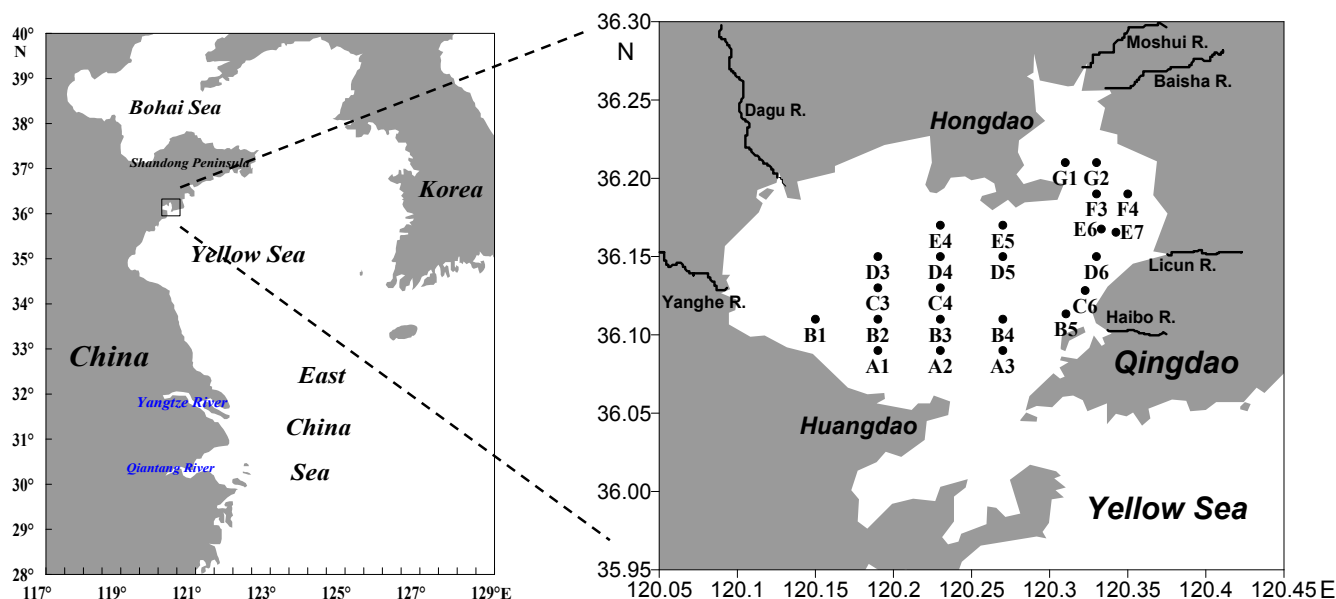


Fig. 1. Map of sampling sites in Jiaozhou Bay, China.

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