



## Reactive iron and its buffering capacity towards dissolved sulfide in sediments of Jiaozhou Bay, China

Mao-Xu Zhu\*, Juan Liu, Gui-Peng Yang, Tie Li, Ru-Jun Yang

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

Reactive iron (Fe) oxides in marine sediments play a critical role in removal of free sulfide. In this study, 0.5 and 6 N HCl-extractable Fe, acid volatile sulfide (AVS), and pyrite were examined in sediments at three sites of eutrophic Jiaozhou Bay to investigate the interactions of sulfur and Fe and possible influences of eutrophication on free sulfide removal. The results indicate that formation and accumulation of AVS and pyrite are limited by low availability of labile organic matter, despite eutrophication of the bay water. Quick buffering of free sulfide proceeded mainly via consumption of 0.5 N HCl-extractable Fe (labile Fe), however, the consumption did not result in a depletion of the Fe pool. High residual buffering capacity enables a quick removal of free sulfide in porewater, and thereby it is difficult for sulfide to accumulate and to cause detrimental effects on benthic organisms at the present steady state. Significant effects of eutrophication on Fe and sulfur geochemistry is restricted only to the estuarine sediments which were subject to direct wastewater discharges, whereas no such effects were observed in other sediments of the bay.

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### 1. Introduction

In coastal marine sediments rich in organic matter (OM), oxygen quickly becomes depleted within millimeters below the sediment–water interface and, thereby, an anoxic environment develops. Microbial sulfate reduction is commonly the most important pathway for OM oxidation in coastal sediments, accounting for, on average, 50% or more of total OM mineralization (Jørgensen, 1982; Thullner et al., 2009). Sulfide produced via sulfate reduction can be removed by three types of reactions (Azzoni et al., 2005; Sell and Morse, 2006): (1) oxidation by O<sub>2</sub> predominantly through microbial processes, (2) abiotic oxidation mainly by manganese and iron (Fe) oxides, or (3) precipitation as Fe sulfide minerals, which can transform into thermodynamically more stable pyrite (FeS<sub>2</sub>). The first reaction is termed biological buffering of free sulfide, and the combination of the latter two termed chemical buffering (Heijs et al., 1999; Heijs and van Gemerden, 2000). Although sedimentary total buffering capacity towards sulfide is a combination of chemical removal and microbial oxidation, it has been suggested that biological buffering capacity becomes effective only after chemical buffering capacity is exhausted. Therefore, chemical buffering is a critical

process for dissolved sulfide removal and the last protection against sulfide accumulation in porewater (Kanaya and Kikuchi, 2004; Giordani et al., 2008; Valdemarsen et al., 2009).

Reactive Fe oxides are an important player in chemical buffering of dissolved sulfide, while their reactivity towards reaction with sulfide varies considerably due to widely varying mineralogy, crystallinity and morphology of Fe oxides. Amorphous and poorly crystalline Fe oxides, for example, ferrihydrite and lepidocrocite, react very quickly with dissolved sulfide (with half-lives from hours to days); well crystalline Fe oxides, for example, goethite and hematite, react slightly more slowly (with half-lives less than 31 days); magnetite can have variable chemical reactivity depending on its source, mineralogy and grain-sized distribution (with half-lives from two months to ~100 a), poorly reactive sheet silicate Fe(III) reacts very slowly with dissolved sulfide over geological timescales (with half-lives from 10<sup>2</sup> to 10<sup>5</sup> a) (Canfield et al., 1992; Raiswell and Canfield, 1998; Poulton et al., 2004). Therefore, differentiating reactivity of Fe oxides is essential for evaluating their buffering towards dissolved sulfide over specific timescales, and many extraction methods have been employed for this purpose (Canfield, 1989; Kostka and Luther, 1994; Poulton and Canfield, 2005). According to Azzoni et al. (2005) and Giordani et al. (2008), 0.5 N HCl-extractable Fe oxides can be used as an estimate of amorphous and poorly crystalline Fe oxides which are available for quick sulfide buffering over short-term timescales, and

\* Corresponding author. Tel.: +86 532 66782513; fax: +86 532 66782540.  
E-mail address: zhumaoxu@ouc.edu.cn (M.-X. Zhu).

6 N HCl-extractable Fe oxides as an estimate of the sum of amorphous and well crystalline Fe oxides which are available to react with dissolved sulfide over long-term timescales during early diagenesis.

Eutrophication of coastal waters caused by excess inputs of nutrients from river runoff or mariculture may enhance primary production and thereby burial flux of OM in the sediments. As a consequence, enhanced labile OM in the sediments stimulates OM oxidation mainly via sulfate reduction pathway (Otero et al., 2006). Under this circumstance, dissolved sulfide may accumulate in the porewater and diffuse upward to the overlying water, and consequently cause detrimental effects on benthic ecosystem, unless it is quickly buffered *in situ* within the sediment (Sorokin and Zakusina, 2012). Therefore, chemical buffering of dissolved sulfide in eutrophic marine areas is an important process for regulation of dissolved sulfide concentration and its toxic effects on benthic organisms (Valdemarsen et al., 2010; Morgan et al., 2012). Potential buffering capacity and buffering saturation degree are important parameters for assessment of health status of the benthic ecosystem and its resilience to rapid environmental changes (Neira and Rackemann, 1996; Rusch et al., 1998; Böttcher et al., 1998; Al-Raei et al., 2009). The capacity and saturation degree may be influenced by several factors such as sedimentation rate, availability of reactive OM and Fe oxides, activity of sulfate reducer, and even anthropogenic perturbations (Rusch et al., 1998).

Short- and long-term environmental and ecological responses of Jiaozhou Bay to anthropogenic perturbations, particularly eutrophication, have been of a particular concern in the recent decade (Liu et al., 2010; Yang et al., 2011). Nutrient dynamics and budget (Liu et al., 2005, 2007; Shen et al., 2006), phytoplankton biomass (Shen, 2001; Wu et al., 2005), and contaminant chemistry (Dai et al., 2007; Ye et al., 2011) have been studied. Studies on sulfide (including pyrite) in the bay have been reported only in selected estuarine (Pu et al., 2009), intertidal (Zhang and Zhang, 2007), and mariculture sediments (Huo et al., 2001). Up to date, buffering capacity and its saturation degree of the bay sediment towards dissolved sulfide have not been reported, thus the impacts of river discharges and eutrophication of the bay water on sedimentary Fe and sulfur diagenetic geochemistry remain unknown. The objectives of this study are: (1) to investigate diagenetic interactions between sulfur and Fe in Jiaozhou Bay sediments, (2) to examine possible impacts of eutrophication of the water on sedimentary sulfur diagenesis, and (3) to compare sulfur geochemistry and buffering capacity towards dissolved sulfide of the bay sediments with other nearshore/coastal marine sediments in China and around the world with different impacts of eutrophication.

## 2. Material and methods

### 2.1. Study area and sampling

Jiaozhou Bay is a semi-closed water body, surrounded by Qingdao City and linked by a narrow channel (maximum width: 3.1 km) to the Yellow Sea (Fig. 1). It has an area of 390 km<sup>2</sup>, of which one fifth is intertidal, and an average water depth of 7 m. Strong turbulent mixing caused by Jiaozhou Bay tides results in nearly homogeneous vertical profiles of temperature and salinity (Liu et al., 2004). About 10 rivers, notably Daguhe, Moshuihe, Baishaha, Licunhe, and Yanghe River, discharge seasonally into the bay with variable freshwater discharges and sediment loads (Liu et al., 2005). Most of the rivers are affected by anthropogenic perturbations from agriculture, urbanization, and industrialization, which have increased in the past fifty years (Dai et al., 2007; Yang et al., 2011). Several rivers in the east and northeast of the bay, particularly Licunhe River, have become the conduits of industrial and domestic wastewater discharges due to the region's rapid economic development and population growth (Pu et al., 2009; Liu et al., 2010). Jiaozhou Bay has received large amounts of nutrients since the 1980s and nutrient loads peaked in the 1990s. After 2000, eutrophication of the water has been mitigated to some extent by more stringent measures aiming at improving the environment (Dai et al., 2007). Due to the influence of eutrophication, nutrient stoichiometry of the water (Shen, 2001; Liu et al., 2005, 2008b) and, thereby, dominant phytoplankton species have been substantially changed (Liu et al., 2008a); red tide events have been increasing in number, frequency, and intensity since 1997 (Wu et al., 2005). Unexpectedly, the eutrophication events have not caused an increase in OM burial in the sediments. On the contrary, it seems that top-down pressure due to large-scale shellfish mariculture in the bay has led to a decrease in net burial of organic carbon within the upper 30 cm of the sediments in comparison with the deeper sediments (Zhu and Zhang, 2007; Liu et al., 2010).

Three sites (J1: 120.33°E, 36.17°N; J2: 120.25°E, 36.12°N; J3: 120.18°E, 36.12°N) were chosen for study based on distance to river outlets at the east and northeast of the bay (Fig. 1), since the impacts of industrial and domestic wastewater discharges are mainly from these rivers (particularly, Licunhe River). Water depths at sites J1, J2 and J3 are about 6, 10 and 4 m, respectively. Two to three sediment cores were collected at each site using a box corer on November 8th, 2010. After retrieval of box cores onto the deck at each site, PVC tubes (inner diameter: 8 cm) were immediately inserted for coring (note that at each site only the box-core with the lowest population of macrofauna was used for tube

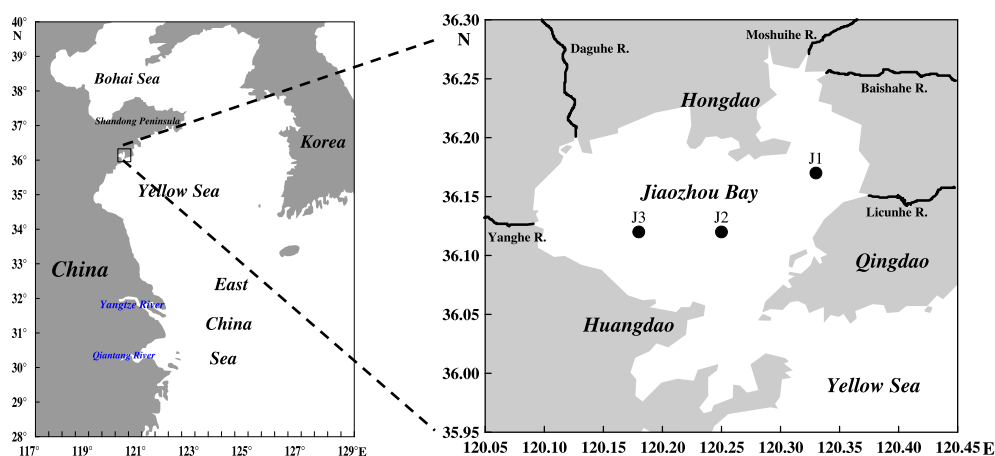


Fig. 1. Map of sampling sites in Jiaozhou Bay, China.

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