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## Spatial distribution of organic and pyritic sulfur in surface sediments of eutrophic Jiaozhou Bay, China: Clues to anthropogenic impacts

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## ABSTRACT

Anthropogenic perturbations exert important impacts on sulfur geochemistry in marine sediments. In the study, chemical extraction was used to quantify four sulfur pools, i.e., pyrite, humic-acid sulfur (HA-S), fulvic-acid sulfur (FA-S), and residual organic sulfur (ROS), in surface sediments of eutrophic Jiaozhou Bay. Results show that riverine inputs are the main control on organic matter (OM) distribution in the sediments. OM enrichment in the eastern coast is mainly due to discharges of anthropogenic wastes. Spatial coupling of pyrite and FA-S vs. TOC points to the impacts of OM enrichment on formation and preservation of pyrite and FA-S. Poor spatial coupling of HA-S vs. TOC is due to low fractions of diagenetic OS in the pool. ROS is mainly from riverine inputs and anthropogenic OS has been superimposed on this pool. Spatial coupling among TOC, pyrite-S and FA-S is a sensitive indicator of anthropogenic impacts on benthic processes of the bay.

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### 1. Introduction

Pyrite (FeS<sub>2</sub>) is quantitatively the most important sulfur pool in modern marine sediments (Goldhaber, 2004; Rickard, 2014). Its permanent burial manifests an end of diagenetic cycling of sulfur and iron, and has played an important role in regulating atmospheric O<sub>2</sub> and CO<sub>2</sub> concentrations, the redox state of the earth's surface, and ultimately seawater chemistry over geologic time-scales (Holland, 1984; Berner, 1999). Quick formation and accumulation of pyrite via polysulfide pathway is often observed in the redox interface of coastal sediments (Rickard and Morse, 2005), whereas variable contents of pyrite could also be observed in the uppermost layers (<2 cm) of sediments subjected to physical reworking and/or bioturbation, even though acid volatile sulfides (AVS, mainly FeS and dissolved sulfide) are almost absent (Rickard and Morse, 2005; Zhu et al., 2013a; Ding et al., 2014). Pyrite formation is commonly limited by the availability of labile organic matter (OM) in marine sediments (Berner, 1982; Burdige, 2006). Thus increased inputs of OM induced by natural processes or anthropogenic perturbations, be they pulsed and prolonged, can substantially enhance the rate of bacterial sulfate reduction and thus the accumulation of AVS and/or pyrite in the impacted

sediments (Otero et al., 2006, 2009; Valdemarsen et al., 2009, 2010; Hyun et al., 2013). For example, up to a 25-time increase in sedimentation of labile OM in marine areas affected by eutrophication and mariculture markedly alters benthic biogeochemical processes, leading to enhanced accumulations of AVS and/or pyrite (Otero et al., 2006; Kraal et al., 2013). Whether pyrite dominates over AVS or not in the impacted sediments depends primarily on the availability of reactive iron. High availability of reactive iron generally favors rapid conversion of AVS to pyrite, whereas low availability of dissolved iron in iron-lean sediments limits the conversion (Gagnon et al., 1995; Otero et al., 2006, 2009; Kraal et al., 2013). Thus, the content and spatial variability of pyrite in the uppermost layer of sediments can be used to indicate C–S–Fe cycling and the impacts of anthropogenic perturbations on benthic biogeochemistry.

Organic sulfur (OS) is quantitatively the second most important sulfur pool in marine sediments. It is formed through two basic pathways: one is assimilatory sulfate reduction and subsequent formation of sulfur-requiring cellular components, that is, biosynthetic OS (bio-OS) (Francois, 1987; Werne et al., 2008); the other is diagenetic sulfuration, that is, incorporation of various species of reduced inorganic sulfur, particularly polysulfides, into OM, i.e., diagenetic OS (diag-OS) (Brüchert, 1998; Bottrell et al., 2009, 2010). In most marine settings sedimentary OS is a mixture of bio- and diag-OS (Brüchert, 1998; Zhu et al., 2013b, 2014). Base extraction (0.1–0.5 N NaOH) is commonly used to quantify

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sedimentary OS (Ferdelman et al., 1991; Henneke et al., 1997; Brüchert, 1998; Yücel et al., 2010). Base-extractable OS is regarded as humic sulfur, which can be further subdivided into humic-acid sulfur (HA-S) and fulvic-acid sulfur (FA-S) by precipitation and separation of humic acids. Base-nonextractable residual OS (ROS) can be quantified after removal of pyrite. Previous study indicates that HA-S in one selected sediment core of Jiaozhou Bay is dominated by bio-OS fraction (65–68%), whereas FA-S is dominated by diagenetic fraction (53–73%) (Zhu et al., 2014). In coastal marine sediments, fulvic-acid moieties are generally more active than humic-acid ones in diagenetic sulfurization (Brüchert, 1998; Zhu et al., 2013b, 2014), and thus the contents of sedimentary FA-S are more dependent on the availability of sulfide and in turn the availability of labile OM. ROS consists principally of refractory OS pool (Ferdelman et al., 1991), and its amount, chemical compositions, and spatial distribution in surface sediments are probably strongly controlled by terrestrial inputs (see later discussion for details). Thus spatial distribution of ROS may provide insightful information on riverine inputs and fingerprint anthropogenic impacts.

Environmental and ecological responses of Jiaozhou Bay to anthropogenic perturbations have been of a particular concern in the recent one decade (Liu et al., 2010; Yang et al., 2011). Nutrient dynamics and budget (Liu et al., 2005; Shen et al., 2006), phytoplankton biomass (Shen, 2001; Wu et al., 2005), and contaminant chemistry (Deng et al., 2010; Dai et al., 2007; Ye et al., 2011) have been studied. However, information about the impacts of anthropogenic perturbations on benthic biogeochemistry, particularly sulfur chemistry, still remains in scarcity. Sedimentary sulfides (including pyrite) in the bay have been reported only at selected stations (Huo et al., 2001; Zhang and Zhang, 2007; Pu et al., 2009; Zhu et al., 2012). Available results indicate that AVS is almost undetectable in the uppermost layer of most sites studied (except for some river mouths in the eastern coast of the bay), while pyrite is present at variable levels at all the sites. Humic sulfur in the bay has been characterized using sulfur stable isotope and XANES spectroscopy in only one sediment core (Zhu et al., 2014). Up to date, no spatial pattern of pyrite and OS in the bay surface sediments and potential relevance to anthropogenic perturbations has been revealed.

Given the fact that content and distribution of pyrite and some forms of OS in coastal sediments are strongly influenced by OM inputs and thus by anthropogenic perturbations, high contents of TOC, pyritic-S, and OS in sediments receiving high OM inputs may be well coupled to each other, and the spatial coupling may be used as a diagnostic trait to trace anthropogenic perturbations. To test this conjecture, chemical extraction was used in this study to quantify four sulfur pools, i.e., pyrite-S, HA-S, FA-S, and ROS, in surface sediments of Jiaozhou Bay and to reveal their spatial patterns. The spatial patterns were then used to trace potential anthropogenic impacts on sediment biogeochemistry of the bay.

## 2. 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). This study area has been detailed elsewhere (Zhu et al., 2012), therefore only a brief description is presented here as required for later discussion. About 10 rivers, notably Dagu River, Moshui River, Baisha River, Licun River, and Yanghe River, discharge seasonally into the bay with variable freshwater discharges and sediment loads (Liu et al., 2005). Several rivers in the east and northeast of the bay, particularly Licun River and Haibo River, have become the conduits of industrial and domestic waste 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 Dagu River and Yanghe River in the northwestern and western coasts of the bay are much less polluted in terms of heavy metal levels (Deng et al., 2010). Jiaozhou Bay has received large amounts of nutrient inputs from the rivers around the bay since the 1980s, among which, Dagu River, Moshui River, Baisha River, and Licun River are the main sources of nutrient supply (Liu et al., 2005). High nutrient loading has caused seasonal eutrophication of the bay and frequent red tide events since 1997 (Wu et al., 2005).

Twenty-three surface sediments (0–4 cm) were sampled on May 21st and 22nd, 2012 (Fig. 1). Upon retrieval of a box core at each station, surface sediments were collected into zip-lock plastic bags with a plastic trowel and covered with ice. The samples were transported to our home laboratory within 9 h, and then frozen at  $-18^{\circ}\text{C}$  until further handling within two months. After thawing at room temperature under  $\text{N}_2$  atmosphere, samples were subjected to a series of chemical extractions.

## 3. Analytical methods

### 3.1. Wet/dry weight ratio and organic carbon

Accurately preweighed wet sediment samples in duplicate were dried at  $105^{\circ}\text{C}$  until constant weight for determination of wet/dry weight ratios. For TOC analysis, sediment subsamples of known weight ( $\sim 1$  g) were treated with excess 1 N HCl (20 mL) overnight (stirring once a while) and washed twice with deionized water to remove carbonates, then the samples were dried at  $\sim 60^{\circ}\text{C}$  for 12 h and ground to  $\sim 100$  mesh for TOC analysis using a PE2400II CN element analyzer, with variability between duplicates better than 5.0% (Zhu et al., 2014).

### 3.2. Speciation of sulfur

#### 3.2.1. Humic sulfur

Three main OS species, HA-S, FA-S, and ROS, in the surface sediments were determined by sequential extractions (Ferdelman et al., 1991). Wet sediment subsamples of known weight ( $\sim 5$  g) in duplicate were washed with 1 M HCl twice under  $\text{N}_2$  atmosphere to convert organic polysulfides to elemental sulfur and to remove porewater sulfate and sulfides (pyrite excluded) (Henneke et al., 1997; Yücel et al., 2010), and then washed twice with 20 mL acetone to remove elemental sulfur. The washed sediment pellets were treated immediately with 15 mL NaOH (0.5 N) under  $\text{N}_2$  for extraction of humic substances. After 24-h extraction while stirring, the humic substances were separated by centrifugation (4800 rpm) and filtration (0.22  $\mu\text{m}$ ). The procedure was repeated six times for a thorough extraction. The separated humic substances were then treated with dilute HCl to pH 2 to precipitate humic acids. Precipitated humic acids were separated by centrifugation for HA-S analysis, and supernatant was collected for FA-S analysis. HA-S was determined according to the Eschka's procedure. Briefly, the separated HA was mixed with the Eschka's agents and combusted at  $800^{\circ}\text{C}$  to convert HA-S to sulfate. Resultant sulfate was dissolved in deionized water at  $60^{\circ}\text{C}$  for 30 min and then collected by filtration. Upon adjustment of pH to 2, sulfate in filtrates was quantitatively precipitated as  $\text{BaSO}_4$  by adding excess 10% (w/v)  $\text{BaCl}_2$  (10 mL). After dryness at  $60^{\circ}\text{C}$ , precipitated  $\text{BaSO}_4$  was saved for determination of HA-S by gravimetry and expressed in  $\mu\text{mol S}$  per gram dry sediment ( $\mu\text{mol/g}$ ). For FA-S quantification, fulvic-acid supernatants were treated with 20 mL  $\text{H}_2\text{O}_2$  (30% v/v) at  $60^{\circ}\text{C}$  for 1 h to oxidize FA-S to sulfate, and this procedure was repeated 3 times for complete oxidization. The sulfate was precipitated as  $\text{BaSO}_4$  and recovered with the same procedure for HA-S

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