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Chemical speciation of iron in sediments from the Changjiang Estuary and East China Sea: Iron cycle and paleoenvironmental implications

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Chemical speciation of iron (Fe) in sediment offers a better understanding on iron cycle, early diagenesis, paleoredox condition and paleoclimatic changes. This study reports the Fe chemical speciation (total concentration Fe_T, highly reactive Fe_{HR}, poorly reactive Fe_{PR} and unreactive Fe_U) in the surface sediments from the Changjiang (Yangtze River) Estuary and the East China Sea shelf. The Fe_{HR} concentrations in the estuarine and shelf sediments are much lower than those from the Changjiang and other rivers in the world, confirming the previous observations on geochemical fractionation effect in estuarine and shelf sediments. The high correlations of Fe_{HR} with Fe_T and Al concentrations and sediment surface area, suggest the dominance of clay minerals on Fe_{HR} composition in the sediments. The apparent enrichments of Fe_{HR}, total organic carbon and surface area in the hypoxia zone off the Changjiang Estuary are primarily caused by the local hydrodynamics and sedimentary processes. Despite the wide application of Fe_{HR}/Fe_T ratio for redox condition, its spatial distribution from the Changjiang river mouth to open shelf reveals no obvious enrichment in the hypoxia zone. This suggests that the episodic occurrence of hypoxia off the Changjiang Estuary (mostly in August) is hardly imprinted in particulate iron speciation. The distributions of Fe chemical speciation along the “river-estuary-open shelf” transect suggest the complex controls of particulate iron “shuttle transport” and deposition in the continental margin where fluvial input dominates and intense anthropogenic impact exists. Our study sheds new light on the source-to-sink process of particulate iron in the estuary and open shelf, and also provides important constraints of Fe speciation in modern and ancient archives from various depositional environments.

1. Introduction

Iron (Fe) is the fourth most abundant element in the earth's crust and is intimately involved in geochemical, mineralogical, and biological processes of earth surface. In particular, the Fe cycle through earth history is closely related to the redox condition over the geological past (Raiswell and Canfield, 2012), for example the vast deposits of Precambrian iron-rich sediments, the “banded iron formations” (Klein, 2005). On the short time scales, Fe is an essential nutrient and energy source for the growth of microbial organisms, which has great impacts on the ocean plankton productivity and climate changes as well (Martin, 1990).

Fluvial inputs in terms of terrestrial runoff are estimated to deliver approximately half of the global surface Fe input to the oceans (Jickells et al., 2005; Raiswell, 2006); however, fluvial inputs of Fe are extremely variable at spatial and temporal scales and are efficiently trapped in near-coastal areas (Poulton and Raiswell, 2002). It is widely reported that most of the dissolved riverine Fe decreases along the estuary due to the flocculation and precipitation processes associated with the increase of salinity (Boyle et al., 1977; Raiswell, 2006; Jones et al., 2011; Schroth et al., 2014), while particulate Fe, which accounts for the majority of the total Fe flux from rivers (Martin and Meybeck, 1979), is also readily precipitated with sediment before reaching the continental shelf and open ocean (Moore et al., 1979). In addition, geomorphological factors, like relief and gradient, also influence the scale of Fe removal in estuaries (Raiswell, 2011). In this regarding, the estuary region acts as an important “sink” of

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dissolved terrigenous Fe input during the Fe transport from continent to deep ocean. Whereas, much of the previously deposited Fe can resuspend from estuary/shelf and forms nanoparticles that can be transported in a long distance, known as *Iron Shuttle* (Raiswell, 2011). Even, some large particulates are found on the open shelf during high river discharge (Buck et al., 2007). On this account, the estuary may not only represent a sink of terrigenous Fe but also act as a source for Fe transport to the deep ocean (Bruland et al., 1991; Jones et al., 2011). For example, the lateral advection of particulate Fe mobilized from continental shelf sediments has been proposed to be an important Fe contributor to the High Nutrient Low Chlorophyll zones (Lam and Bishop, 2008).

Thus, the Fe transport in estuary and continental shelf is of great significance for Fe geochemical cycle from continent to deep ocean. However, previous research attempts on the fluvial Fe flux mostly focus on the total Fe concentration and flux, although the Fe geochemical cycles is strongly affected by its solid phase speciation (Poulton and Raiswell, 2002; Poulton and Canfield, 2005). For instance, the total Fe/Al ratio remains almost constant in suspended sediment across the salinity gradient, but the amounts of Fe extracted by citrate-buffered dithionite change apparently towards the open ocean (Trefry and Presley, 1982).

Various methods were proposed to determine the particulate Fe speciation, and most of them are operationally defined by its reactivity towards dissolved sulphide (Berner, 1970; Canfield, 1989; Poulton et al., 2004b; Poulton and Canfield, 2005). In the past decade, the Fe speciation has been widely concerned in paleoenvironmental reconstruction (Poulton et al., 2004a; Lyons and Severmann, 2006; Poulton and Canfield, 2011), tracing the biogeochemical cycle (Hyacinthe et al., 2006; Raiswell and Canfield, 2012) and sediment provenance study (Mao et al., 2010). In particular, the Fe speciation has proven to be a good indicator of paleoredox condition (Lyons and Severmann, 2006). Extensive studies of various marine sediments have demonstrated that the ratio of highly reactive Fe to total Fe does not exceed 0.38 during normal deposition under oxic water column conditions (Poulton and Canfield, 2011). This recognition of paleoredox condition based on Fe speciation ratio has been widely applied in ancient rock/sediment (Canfield et al., 2007; Kendall et al., 2010; Poulton and Canfield, 2011), but is seldom validated in modern depositional environments (Wijsman et al., 2001; Anderson and Raiswell, 2004), particularly in surface seafloor sediment (Zhu et al., 2012).

The Changjiang (Yangtze River) is the largest river in Asia and the fifth largest river in the world in terms of water discharge. Based on the long-term observation (1950–2010), the Changjiang empties 8.96×10^{11} m^3 of freshwater and 390×10^6 t/yr of sediment into the East China Sea (ECS) annually. Most of the sediment inputs are trapped in Changjiang Estuary to build a large delta and form an estuarine mud patch, i.e. prodelta mud system (Gao, 2014). The interaction between the Changjiang freshwater and ECS saline water in the estuary plays a key role on sedimentary and geochemical processes in the estuary and open shelf (Milliman et al., 1985; Zhang, 1996; Zhao et al., 2008; Switzer et al., 2011; Yang et al., 2015). As an important nutrient limiting element, the Fe geochemistry in the Changjiang and the ECS has been widely documented in previous studies (Zhang et al., 1990; Chen et al., 2002; Lin et al., 2002; Zhang and Liu, 2002). However, these studies mainly focused on total Fe concentration and flux and paid little attention to Fe speciation. Recently, Fe speciation studies were carried out in the Changjiang (Mao et al., 2010) and China's marginal seas (Zhu et al., 2012, 2014, 2015). These researches based on Fe speciation provide new insight for Fe geochemical reaction with organic matter and sulfides, and for the kinetic characterization of sediment Fe reductive processes. However, the Fe speciation and source-to-sink transport in the Changjiang Estuary, where strong freshwater-saline water mixing happens, are still unknown. Moreover, the indications of different Fe speciation in estuarine and shelf environments await more investigations.

With the rapid development of economy, agriculture and industry in the large Changjiang catchment (ca. 1.8×10^6 km^2), a large volume of nitrogen, phosphorus and pollutants are transported from the Changjiang into the East China Sea. Like many other large rivers in the world, the Changjiang Estuary has been suffering from severe ecological and environmental problems such as eutrophication and hypoxia (Diaz and Rosenberg, 2008), mostly due to the dramatic increase of nutrient load and seasonal changes in regional water stratification (Li et al., 2002; Wang et al., 2012). Different from the nearly persistent hypoxia in the Black Sea and on the continental shelf of Gulf of Mexico, the hypoxia off the Changjiang Estuary is episodic (mostly in August) and less recurrent primarily because of the complex control of hydrodynamics (Rabouille et al., 2008). The hypoxia off the Changjiang Estuary has been increasingly investigated in terms of its temporal and spatial variability, oxygen depletion mechanism, biogeochemical and ecologic impacts (Li et al., 2002; Wang, 2009; Zhu et al., 2011; Wang et al., 2012). Whereas, these findings were primarily based on modern observations, while a complete record of the hypoxia evolution on geological time scales is still insufficient. For example, the history of hypoxia off the Changjiang Estuary is poorly constrained mostly because the proxy for paleoredox indication in the ECS is not well established yet.

In this study, the Fe speciation in sediments from the Changjiang Estuary to open ECS shelf are analyzed, and the major constraints on spatial variation of Fe speciation are systematically discussed. In particular, the distributions and behaviors of Fe speciation in the sediments from the hypoxia zone are further discussed. Our major objectives are to examine the particulate Fe "shuttle transport" and source-to-sink process along a "river-estuary-open shelf" transect, and to further validate whether particulate Fe speciation can indicate the hypoxia off the Changjiang Estuary.

2. Study area and analytical methods

2.1. Physiography of the Changjiang Estuary and the hypoxia

The Changjiang is the largest river in East Asia and empties about 8.96×10^{11} m^3/yr of freshwater into the ECS with abundant of nutrient and organic matter (Zhang, 1996). The Changjiang water discharge is highly variable on seasonal scale with the change of East Asia summer monsoon, with 75% of the river runoff occurring during the flood/rainy season between May and October. The huge amount of detrital sediment from the Changjiang mostly deposits in the estuary and the inner shelf along the Zhe-Min coast, which has formed unique sedimentary systems in the delta-estuarine area and inner shelf during the Holocene (Youn and Kim, 2011; Yang et al., 2015).

The ECS is one of the river-dominated marginal seas located in the West Pacific, characterized by huge terrestrial inputs from the large rivers in Asian continent and small mountainous rivers in Taiwan. The dominant ocean current along the Zhe-Min coast is the Zhe-Min Coastal Current (ZMCC) (Fig. 1). To the east of the ZMCC offshore, is the Taiwan Warm Current (TWC), a warmer and saline