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Early diagenetic alterations of biogenic and reactive silica in the surface sediment of the Yangtze Estuary

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ABSTRACT

Sedimentary biogenic silica (BSi) is an important parameter for understanding biogeochemical processes in estuarine ecosystems. In this study, a two-step mild acid–mild alkaline extraction procedure was used to leach BSi and its early diagenetic products from the sediments of the Yangtze Estuary. A Si/Al correction of the mild alkaline leachable silica (Si-Alk) was applied to estimate the contents of BSi in the sediments. The BSi contents varied from 18.90 to 120.10 μmol Si/g in the sediments, whereas mild acid leachable silica (Si-HCl) and Si-Alk levels ranged from 17.43 to 73.56 and from 19.56 to 185.63 μmol Si/g, respectively. Furthermore, the degrees of diagenetic alteration of biogenic and reactive silica were also calculated and discussed. The diagenetic alteration ratios of biogenic and reactive silica increased seaward during May, August and November 2012, whereas an opposite trend was observed in March 2013. The diagenetic alteration of the biogenic and reactive silica was mainly controlled by the redox conditions in benthic sediments. Additionally, the deposition of fresh diatoms and authigenic products could temporarily affect the distribution of silica pools in the sediments and ultimately affect the diagenetic alteration ratios of biogenic and reactive silica. Detailed investigations are still necessary to understand the early diagenetic processes of biogenic and reactive silica in this warm temperate area.

1. Introduction

Silicon (Si) is an essential elemental requirement for some biota (e.g. diatoms, radiolaria, silicoflagellates, and siliceous sponges) which utilize dissolved silica (DSi) to form their structural elements of amorphous hydrated silica, known as BSi or opal (Ragueneau et al., 2000; Van Cappellen et al., 2002). As particulate materials, BSi particles can settle and dissolve, and some frustules eventually reach the seafloor, where dissolution continues. BSi dissolves and rejoins the hydrosphere Si cycle, whereas some of the buried biogenic opal is transitioned from the marine ecosystem to the geological cycle through diagenetic processes (Kastner et al., 1977). The accumulation of BSi in the sediments can reveal important information of past productivity in the ocean and coastal regions (Ragueneau et al., 2000; Nelson et al., 2002; Romero and Hebbeln, 2003; Bernárdez et al., 2005). However, advection of water masses, sediment reworking and variations of BSi frustules during sedimentation and burial processes affect the signature produced in the water column and sediments, which may cause misinterpretation of productivity in the overlying water column. On the other hand, sediments disturbance caused by hydrodynamics and bioturbation can drive interstitial-water silicates to diffuse into overlying waters (Qin and Weng, 2006). Many researches have confirmed that the benthic sediment was an important source of DSi for overlying waters (e.g. DeMaster et al., 1996; Nelson et al., 1996; Giblin et al., 1997; Denis and Grenz, 2003; Liu et al., 2005), and have potential impacts on marine primary productivity.

The coastal and shelf environments represent a dynamic interface between the continents and open sea, and approximate 40% of all marine BSi burials occur in these regions (Laruelle et al., 2009). BSi levels in the coastal and shelf sediments are typically less than 10% SiO_2 (DeMaster, 2002), which can most likely be attributed to the dilution effect of high terrigenous sediment loads and the rapid early diagenetic alteration of biogenic opal to authigenic aluminosilicate (DeMaster, 2002; Liu et al., 2005; Qin et al., 2012). Extensive intergrowth of authigenic clay minerals with opal particles has been observed in many deep-sea sites (e.g. Hurd, 1973; Sayles and Bischoff, 1973; Johnson, 1976; Hein et al., 1979; Cole, 1985; Odin and Frohlich, 1988) and saline lakes (Badaut and Risacher, 1983). The specific aluminosilicate phases even can associate intimately with living diatoms in nearshore marine water column (Van Bennekom and Van Der Gast, 1976). The involvement of opal in the formation of cation-reach authigenic

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aluminosilicate has been discussed in the content of “reverse weathering” processes in marine sediments (Mackenzie and Garrels, 1966; Wollast, 1974; Mackenzie et al., 1981; Wollast and Mackenzie, 1983), which has been proposed as an important factor controlling the oceanic elemental mass balance. More recently, experimental and field observations demonstrated the presence of rapid alteration of BSi to authigenic clays in many deltaic regimes (Michalopoulos and Aller, 1995; Michalopoulos et al., 2000; Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008; Qin et al., 2012). Furthermore, early diagenetic reactions of BSi have also been involved to interpret variations of asymptotic interstitial-water DSi concentrations and benthic DSi fluxes in both pelagic and coastal zones (e.g. Dixit and Van Cappellen, 2003; Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008). However, the most widely used wet-chemical digestion method to measure sedimentary BSi proposed by DeMaster (1981) do not explicitly target the possible early diagenetic derivatives (Michalopoulos and Aller, 2004). As a consequence, previous estimates of burial of reactive silica in the deep-ocean or coastal regions (e.g. Tréguer et al., 1995; DeMaster, 2002; Liu et al., 2005; Laruelle et al., 2009) may have been biased. Recent estimates based on improved leaching techniques suggested that river deltas may bury more reactive silica than previously thought (Michalopoulos and Aller, 2004; Presti and Michalopoulos, 2008), which would have major impacts on models of global silicon cycling (DeMaster, 2002).

The Yangtze Estuary and its adjacent area is a productive and resource-rich coastal region (Zhao et al., 2001; Ning et al., 2004). Diatoms have become the dominant phytoplankton species and generate biogenic silica because of relatively shallow, warm water rich in nutrients (Liu et al., 2001; Li, 2006). In past decades, the Yangtze River riverine fluxes of dissolved inorganic nitrogen (DIN) and phosphate (DIP) transport into the East China Sea (ECS) have increased dramatically (Li et al., 2007; Chai et al., 2009; Jiang et al., 2010; Dai et al., 2011; Gao et al., 2012), causing significant increase of phytoplankton biomass. However, riverine input of DSi has decreased (Li et al., 2007; Chai et al., 2009), resulting in sharp decreases in the ratio of DSi/DIN and DSi/DIP in the estuary, which was probably the main reason causing a significant decrease of the percentage of diatoms in phytoplankton in the Yangtze Estuary (Dai et al., 2011; Jiang et al., 2014). The percentage of diatoms in phytoplankton composition decreased from 85% in 1980s to 64% in 2002 (Ning et al., 2004; Zhou et al., 2008), and yet, diatoms still dominate the phytoplankton composition, indicating that BSi may be an important constituent of the Si cycle in the Yangtze Estuary. Furthermore, the sediment load transported by the Yangtze River was decreased sharply after completion of the Three Gorges Dam (TGD) (Dai et al., 2014; Dai and Lu, 2014). Although sediment load transported into the estuary had an obvious decrease, the Yangtze Subaqueous Delta (YSD) continued to accumulate and prograde, but with varying depocenter (Dai et al., 2014). Based on bathymetric changes, the average accumulation rate of the entire YSD was estimated as 1.5 cm/yr in 2007–2009 (Dai et al., 2014). Admittedly, partial erosion of the seabed was also observed in the Yangtze Estuary (e.g. Yang et al., 2011; Dai et al., 2014). The complicated distribution patterns of deposition/erosion of the seabed in the Yangtze Estuary may play an important role in the distribution of the silica pools in the surface sediments. Previous works on Si cycling in sediments of the Yangtze Estuary and adjacent shelf have mainly focused on the distribution and its relationships with grain size (Fan et al., 2011; Wang et al., 2014), with very few on silica balance and preservation of BSi (Liu et al., 2005). However, these studies rarely focused on the authigenic alteration of biogenic silica during early diagenesis in the Yangtze Estuary, which has most likely resulted in the misunderstanding of the silica cycle and an underestimation of the silica burial flux in this warm temperate area. The objectives of the present study include the following: (1) to investigate the biogenic and reactive silica contents in surface sediments of the Yangtze Estuary and (2) to estimate the degree of diagenetic alteration of biogenic and reactive silica. The results of this study will have important implications for further understanding of the early diagenetic processes of biogenic and reactive silica and the geochemical cycle of Si in this warm temperate regime, and will supply useful data for re-estimating the burial of reactive silica in the coastal regions in models of global silicon cycling.

2. Investigations and methods

2.1. Study area

The Yangtze River is one of the largest rivers in the world in terms of water and sediment discharge, and it contributes over 90% of the runoff and sediment load input into the ECS (Zhang et al., 2007). The river catchment features the East Asian monsoonal climate, which causes higher rainfall in summer and lower in winter. The average runoff at Datong hydrological station (located 624 km to the west of the Yangtze River mouth) was about 900 km^3/yr (Dai and Lu, 2014), which was mainly formed from May to October (i.e., during the wet season). Compared with the runoff, the sediment load of the Yangtze River varied drastically over past decades. After completion of the TGD in 2003, the sediment load from the Yangtze River into the estuary (Datong station) has been reduced from 4.3×10^8 t/yr for the period of 1950–2000 to less than 1.5×10^8 t/yr for the period of 2003–2009 (Dai et al., 2014). The partition of the sediment load among the branching channels varied in the estuary during different periods since 1950s. In 1958–1978 more than 55% of the Yangtze River sediment load transported through the South Passage, whereas in 1978–1989 60% of the sediment load passed through the North Passage (Dai et al., 2014). In 1989–1997, sediment load was discharged through the North Channel (Dai et al., 2014). Recently, in 1997–2002, over 50% of the sediment went through the South Passage (Dai et al., 2014).

At the mouth of the Yangtze River there are three tiers of bifurcation forming a branching estuary which has four openings to ECS (Dai et al., 2014) (Fig. 1). A turbidity maximum zone (TMZ) exists all year round in the river mouth-bar area between outlet of South Channel and -10 m isobath (Shen et al., 2008). Tides in the estuary are regular semi-diurnal type (Shen et al., 2008) with a mean and maximum tidal range of 2.76 m and 5.0 m respectively in the river mouth area (Fan et al., 2011). The mean velocity of tidal currents at the river mouth area is 1.2 m/s, and the maximum is greater than 2.0 m/s off the river mouth (Fan et al., 2011). Waves also play an important role in controlling hydrodynamics and sedimentation processes in the Yangtze Estuary. Affected by monsoon climate, the significant waves are caused by typhoons in summer, whereas those in winter are mainly caused by cold winds (Fan et al., 2011). As reported by Xu (1996), from 1966 to 1999, the frequency of significant waves (wave height greater than 6 m) over the winter half of the year was higher than during the summer. The sea surface temperature (SST) in the estuary has significantly seasonal changes, with an annual range of 21 °C (Zhou, 2005). Highest SST (~27 °C) always occurs in August, while lowest SST (~6 °C) appears in February (Zhou, 2005). Due to the seasonal changes of the runoff of the Yangtze River, the salinities in the estuary also exhibit obvious variations. For example, in the South Passage, the mean salinity in a tidal cycle can reach as 18‰ in dry season, while that only 3‰ in flood season (Kong et al., 2004).