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Silicon release and its speciation distribution in the surficial sediments of the Pearl River Estuary, China

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Abstract

Liberation experiments have been undertaken to explore silicon release from the surficial sediments of the Pearl River Estuary, China. Three environmental factors are selected including agitation time, pH value, and salinity. Results show that a logarithmic relationship between dissolved silicon concentration and time is observed. After the initial rapid release, a dynamic balance is accessed for ∼14 h and the maximum release is ∼46 μg g^{-1}. There is a decrease trend of silicon release with increasing pH value. The silicon release decreases rapidly from ∼50 to ∼42 μg g^{-1} as pH value increases from 3 to 5, whereas from pH 5 to 9, the decrease trend is mild from ∼42.5 to ∼40.3 μg g^{-1}. Silicon release is intimately related to seawater salinity, illustrating a significant correlation ($r = -0.995$, $p = 0.01$). Liberated silicon is 21.18−22.76 μg g^{-1} at the salinity of 35, reducing by 43.5−44.5% compared to those leached with de-ionized water. Silicon speciation analyses are performed to both the initial and the liberated sediments based on a sequential extraction procedure. The exchangeable fractions in the initial and liberated sediments average 18.89 and 13.6 μg g^{-1}, respectively. This result suggests that silicon liberation with de-ionized water does not exert a prevailing influence on the subsequent exchangeable extraction.

Keywords: silicon release; estuarine sediment; speciation; sequential extraction procedure; Pearl River Estuary

1. Introduction

Silicon is an important component of the marine ecosystem. Silica cycling in ocean is mainly dependent on the marine biogeochemical processes of plankton. Approximately 80% of the dissolved silicic acid into the world ocean is from rivers (Tréguer et al., 1995), and the net accumulation of opal constitutes the net output of silicon from the biogeochemical cycle. Biogenic silica release from marine sediments not only becomes an important reservoir to the overlying water column (Nelson et al., 1995), but also plays a crucial role in the recycling dynamics and in maintaining marine primary production (e.g., Nelson et al., 1995; Tréguer et al., 1995; Giblin et al., 1997; Friedl et al., 1998; Friedrich et al., 2002). Since biogenic silica deposits are extensive in both coastal and abyssal sediments, a more accurate interpretation of the information they contain will result in a better mechanistic understanding of the causal linkages connecting Si cycling, ocean productivity, atmospheric CO_2 levels and global climate on time scales ranging from seasonal to glacial/interglacial (Ragueneau et al., 2000).

The estuarine system is a mixing high-energy region between sea and inland waters, where the water circulation is dominated by river discharge and tidal movements. High turbidity and complex circulation patterns are commonly exhibited especially in the estuary of large river (DeMaster et al., 1986). Former researches indicated that, during estuarine mixing processes, 10−20% of riverine dissolved silicic acid may commonly be scavenged by the adsorption of suspended particulates, flocculation, and seawater electrolyte effect, settling as amorphous silica in the benthic sediment of

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estuary and its adjacent continental shelf to become a potential storage of bioavailable silica (Riley and Chester, 1978). The relationship between silicon concentration in river waters and the amount removed has also been investigated by Liss and Spencer (1970) whose results show that the proportion removed tends to increase with increasing silicon concentration. Biogenic opal is another important contributor to active silicon in depositional phases. It is well established that the surfaces of biogenic silica particles are often quickly coated and enriched in Fe and Al, dramatically affecting solubilities and dissolution behavior of Si in both the oceanic water column and sedimentary deposits (Lewin, 1961; Hurd, 1973; Katamani et al., 1988; Van Bennekom et al., 1989; Rickert et al., 2002), particularly in the estuarine environment with high turbidity and high sedimentation rate. Therefore, undissolved biogenic silica during settling in shallow deltas tends to be buried and be altered into authigenic clays through early diagenetic processes (Michalopoulos and Aller, 2004). This case is different from the silica cycling in pelagic zones where diatom skeletons may stay for a few months to dissolve before settling down to the sea floor of abysses (Tréguer et al., 1995).

Mineralization of organic matter in benthic deposits results in increased concentrations of various nutrients in pore water. The resulting exchange fluxes of dissolved nutrients across the sediment–water interface are an important contribution to the nutrient budget of estuaries. Sediment disturbance induced by wave and current, bioturbation, and faunal irrigation can drive pore-water silicic acid to diffuse across the sediment–water interface into overlying waters. The importance of benthic sediments in governing $Si(OH)_4$-Si concentrations in overlying waters has long been a subject of concern. DeMaster et al. (1996) reported that seabed resuspension by tides and waves in Amazon shelf waters may provide on the order of 5–20% of the silicate reaching the shelf. The regenerated $Si(OH)_4$-Si from the benthic sediments in Boston Harbor, Massachusetts, supplies 60% of the phytoplanktonic requirement (Giblin et al., 1997). Investigations on the continental shelf in the Gulf of Lions (NW Mediterranean Sea) (Denis and Grenz, 2003) showed that, the annual release from the sediments approximates to 165 kt dissolved silica, which represent an amount close to 28% of the nutrient requirements for primary production. Therefore, benthic sediments are an important source of nutrients for waters, and have potential impacts on marine primary production. Recent monitoring (e.g., Lin et al., 1994) demonstrated that there are mainly 26 species of plankton triggering red tides in the marine region of the Pearl River Estuary and its adjacent areas. Among these, 16 species belong to diatom and 10 belong to dinoflagellate, and phytoplankton bloom predominated by dinoflagellate is also based on the over-propagation of diatom (Lin et al., 1994).

In this article, we have quantitatively studied the silicon release from the surficial sediments of the Pearl River Estuary that were exposed in vitro under different environmental conditions of agitation time, pH value, and salinity. Then, the consequent speciation distribution of silicon in the leached sediments was also analyzed through comparing with the silicon speciation in the initial (unleached) sediments. This research might provide novel insight for revealing the effects of environmental factors on the release of $Si(OH)_4$ from estuarine sediments, and the quantification of the partitioning behavior of silicon in estuarine sediment is also of implications for estimating the mobility and bioavailability of silicon in aquatic environments.

2. Materials and methods

2.1. Study area

The Pearl River Estuary, with a watershed area of 453,690 km^2, is located in Guangdong Province, China. It drains three main tributaries, Dongjiang River, Beijiang River and Xijiang River and passes through a complex river network and flows into the South China Sea. The total annual runoff reaches 3.33×10^{11} m^3 and has an annual suspended sediment load of 8.87×10^7 t (Zhao, 1990), as is only next to the Yangtze River and Yellow River in China. The Pearl River shows a strong seasonal variation. About 80% of the water and 95% of the sediment load are delivered during the wet season from April to September. Although the estuary is characterized by micro-tides ranging from 0.9 to 1.7 m (Lin, 1996), it has a strong tidal movement due to the large tidal volume during the flood tide. Because of the strong seasonal variation in runoff, the estuarine hydrodynamics are commonly stratified during the wet season and well mixed during the dry season with regard to the salinity field (Ying and Chen, 1983; Dong et al., 2004). The saltwater wedge and turbidity maximum also shift seasonally (Tian, 1986; Deng et al., 2002). Estuarine circulation is mainly formed by the upper layer of brackish water that flows out and entrains the lower layer of high salinity water from the inner shelf which flows in at the bottom of the estuary. The sedimentation rate averages 2–3 cm yr^{-1} based on ^{210}Pb chronologies (Chen and Luo, 1991).

2.2. Sampling

The surficial sediment samples were collected during July 1999 with a grab corer at three sampling sites, respectively, located in the central submarine delta of the Pearl River (Fig. 1). The lithology of Cores D1 and D2 are silty clay from water depths of 4.7 and 5.5 m, respectively, and Core D3 is fine sand at 9.0 m below water surface. Sediment was immediately frozen and stored in tightly capped vials under ambient conditions. Prior to analytical work, all sediments were freeze-dried and subsequently ground in an agate mortar, homogenized and stored at 4 °C until needed.

2.3. Experimental

Liberation experiments were designed in vitro to observe silicon release from the estuarine sediments under three different environmental conditions including agitation time, pH, and salinity. Silicon phase leached with de-ionized water here is operationally defined as loosely bound fraction (Kryc et al., 2003). We used a modified sequential extraction procedure originally outlined in Tessier et al. (1979), Li et al. (1995),