



## Research papers

## Grain-size effect of biogenic silica in the surface sediments of the East China Sea



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## ABSTRACT

Biogenic silica (BSi) is an important parameter for understanding biogeochemical processes and paleoceanographic records in the ocean, but this proxy still has many challenges when used to reconstruct changes in the paleoproductivity and evolution of the environment, one of which is the grain size effect. We analyzed the BSi distribution in different size fractions from 8 surface sediments collected in the East China Sea (ECS). We observed the particulate characteristics of diatoms in the water and assessed the grain size effect of BSi. The results suggest the following conclusions: (1) the BSi content of the surface sediments in the ECS is generally below 1%, and the BSi content of different size fractions varies significantly, with largest fraction  $< 16 \mu\text{m}$ , which is approximately 1.1–1.8 times that in the bulk sediments. (2) The variation in the BSi content in different size fractions is largely controlled by the species of diatoms and their cell sizes. In the East China Sea, nano-diatoms are the dominant species, with dominant cells of 2–14  $\mu\text{m}$ , resulting in a high BSi content in the fraction  $< 16 \mu\text{m}$ . (3) The hydrodynamic condition affects the diatom cell size distribution and sediment character, and, thus, has a significant influence on the BSi content of different size fractions. Our research suggests that the grain size distribution of the bulk sediment should be considered when using BSi as a proxy for diatom primary production.

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## 1. Introduction

Biogenic silica (BSi) is produced in the euphotic zone by siliceous plankton, such as diatoms or radiolarians. Radiolarians are particularly abundant and diverse in the equatorial latitudes, while diatoms live predominantly in high-latitude areas and along some continental margins, especially in upwelling areas (De Wever et al., 2001; Karleskint et al., 2012). Diatoms play an important role in the global biogeochemical cycle, Nelson et al. (1995) estimated that more than 40% of all primary production is attributable to diatoms, suggesting a close coupling of the ocean's silica and carbon cycles in both the present and the past. They are also responsible for the majority of silica that is extracted from ocean waters in the modern ocean.

The role of diatoms in the biological pump, the global significance of the BSi sedimentary record and the reasonably good overall preservation efficiency of biogenic BSi all indicate that BSi is a potentially important paleoproductivity proxy (DeMaster, 1991; Ragueneau et al., 1996, 2000). However, there are still uncertainties and challenges in using this proxy to interpret the

BSi sedimentary record or to reconstruct changes in paleoproductivity and environmental evolution (Nelson et al., 1995; Anderson et al., 1998). Deriving accurate information from the sediment record requires better calibration for this proxy.

As important BSi accumulation regions, the continental marginal seas receive large amounts of terrigenous materials and strongly influence the global carbon cycle. However, the measurement and employment of BSi in the marginal seas is significantly affected by the sediment grain size, similar to other parameters, such as element concentration, organic carbon content, and magnetic susceptibility (Bergamaschi et al., 1997; Lin et al., 2002; Wang et al., 2009). The grain size distribution of sediment can affect the BSi content because the coarse grain fractions provide a dilution effect that must be eliminated (Bernárdez et al., 2005). To limit the influence of grain size, Bernárdez suggested using BSi from the muddy fraction as an accurate paleoproductivity proxy (Bernárdez et al., 2005). However, the role that the cell size of diatoms that have been buried in the seabed sediments plays in the BSi record needs to be better understood; many physiological processes that occur in planktonic ecosystems are size dependent (Huang et al., 1999; Finkel et al., 2009), and the size distribution of phytoplankton assemblages is a major biological factor that governs the functioning of pelagic food-webs and, consequently, affects the

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rate of carbon export from the upper ocean to deeper layers (Malone, 1980; Huang et al., 1999).

To determine the impact of sediment particle size on the BSi content of the marginal shelf, we selected 8 surface sediments with different grain size patterns and 18 pieces of filter membranes with diatom cells in the East China Sea. We then investigated the BSi content of different grain size fractions together with diatom cell sizes to assess the effect of grain size on the BSi content and its possible connection with diatom cell sizes. This research may also help to identify a more sensitive fraction of BSi in the sediment that may be a preferable proxy in low BSi content areas.

## 2. Geographic setting

The East China Sea (ECS) is an important marginal sea for the research of global change and the carbon cycle, with huge terrigenous inputs and high accumulation rates.

The hydrodynamic conditions in the ECS are complex. The main currents include the Kuroshio Current (KC), the Tsushima Current (TC), the Yellow Sea Warm Current (YSWC), the Taiwan Warm Current (TWC), and the Yellow Sea Coastal Current (YSCC) (Liu et al., 2003, 2007). The warm and salty KC flows northward along the shelf break of the East China Sea and significantly influences the distribution of water masses and sedimentation (Liu et al., 2007). The Changjiang River carries approximately  $9.2 \times 10^{11} \text{ m}^3$  of freshwater and  $4.8 \times 10^8 \text{ t}$  of solid particles to the ECS each year that ranks 5th and 4th in the world, respectively (Milliman et al., 1985; Tian et al., 1993). Approximately 40% of the total suspended load was deposited in the Changjiang River estuary (Milliman et al., 1985), and the rest was temporarily deposited offshore or was later resuspended and transported southward by subsequent winter storms (Milliman et al., 1985; McKee et al., 1983; DeMaster et al., 1985).

The surface sediment distribution in the East China Sea has several apparent patterns. The innermost regions of the shelf are dominated by silty clay, clayey silt, sandy silt and silt, resulting from the rapid accumulation of sediments from the Changjiang River (DeMaster et al., 1985; Qin et al., 1987). The broad middle shelf is characterized by sand and clayey sand, which are known as shelf relic sands and were formed during the late Pleistocene and early Holocene (Niino and Emery, 1961; Milliman et al., 1985). South of Cheju Island, nearly 400 km away from the coast of China, the sediment is strikingly more fine-grained than the surrounding sands (Milliman et al., 1985; Qin et al., 1987). Previous studies have indicated that the inner shelf mud areas are the modern depocenters of the ECS, with deposition rates of  $1\text{--}5 \text{ cm yr}^{-1}$  in the river mouth and inner shelf and  $0.1\text{--}0.5 \text{ cm yr}^{-1}$  in the seaward distal mud area and middle shelf (DeMaster et al., 1985; Liu et al., 2006; Xu et al., 2012). The high deposition rates make the ECS, especially the inner shelf, an important material sink and enables the establishment of high-resolution or ultra-high-resolution sedimentary records (Fan et al., 2011).

Together with the huge freshwater input, plentiful nutrients including dissolved silicate and dissolved inorganic nitrate were delivered to the ECS, and a unique ecosystem was supported and maintained in the estuary and its adjacent areas (Li et al., 2007). Biomarker research has suggested that the sedimentary organic matter in the distal mud area is mainly from marine lower aquatic organisms (Guo et al., 2001) and high contents of brassicasterol and dinosterol in the upwelling areas outside the Changjiang River mouth and the Zhejiang–Fujian coastal zone, suggesting a strong control of marine productivity (Xing et al., 2011).

Diatoms are the dominant phytoplankton and the major contributor to primary production in the ECS, blooming in spring and

summer, especially in August (Luo et al., 2007; Yang et al., 2008). The diatom cell densities ranged from  $0.43 \times 10^3$  to  $23.3 \times 10^3 \text{ cells L}^{-1}$ , with an average of  $4.61 \times 10^3 \text{ cells L}^{-1}$  (Gao et al., 2003). Horizontally, the diatom cell density had a scattered distribution, while vertically, it was commonly higher in the surface water layer than in the middle water layer (Gao et al., 2003). The major diatom species included *Skeletonema*, *Thalassiosira* and *Chaetoceros*, while nano-diatoms and micro-diatoms were the main constituents in the estuary and its adjacent areas (Li, 2006). In this area, many red blooms were induced by these diatoms, especially in the upwelling areas outside the Changjiang River mouth and the Zhejiang–Fujian coastal zone (Xing et al., 2011). In recent years, however, the structure of phytoplankton has changed, along with other algae species that are also increasing due to the change in the ratio of nutrient inputs (Li et al., 2007; Jin et al., 2009).

## 3. Materials and methods

### 3.1. Sample collection

Eight surface sediments of different types were collected from the inshore mud area and outer continental shelf in the ECS using a box sampler that was deployed on the R/V Dong Fang Hong 2 in June 2009. Roughly estimated, the sediments included muddy sand, sandy silt and clayey silt. Within the sample sites, C0401, C0403, C0501 and FJA were located in the Changjiang River mouth or outside of the estuary, C0508 was located in the mud depocenter southwest of Cheju Island and the other sites, C0701, C0802 and C1004, were in the mud wedge off the Zhejiang–Fujian coast from north to south. All of the samples were subsequently separated, following the research procedure. First, 50–80 g of sediment were added to a clean beaker, homogenized, and then dried in an oven at  $103^\circ\text{C}$ . After weighing, a portion was removed for the bulk sediment, and the remaining portion was separated into different fractions by wet sieving through a sieve with a  $63 \mu\text{m}$  mesh size. Then, the fine fractions were gradually extracted on the basis of Stokes' law, following the sequence of  $< 63 \mu\text{m}$ ,  $< 32 \mu\text{m}$ ,  $32\text{--}63 \mu\text{m}$ ,  $< 16 \mu\text{m}$ ,  $16\text{--}32 \mu\text{m}$ . Then the grain size of the bulk sediment and the BSi content in the different size fractions were measured.

For the purpose of understanding the relationship between the distribution of diatoms and their cell size, the character and BSi distribution of different size fractions from ECS were determined. Eighteen suspended matter samples from the surface, middle and bottom layers in the water-column at 6 sites along section DH 3, collected in 2010, were experimented to observe the characteristics of diatoms with a Scanning Electron Microscope (SEM). The sampling sites are depicted in Fig. 1. The water samples were filtered on filters of pore size  $0.45 \mu\text{m}$  to get diatoms. At first, the water was well-mixed by shaking and turning over softly and repeatedly; then, about 10–50 ml water was filtered based on the concentration of suspended particulate material (SPM), so as to obtain enough diatoms and do not interrupt the following observation in SEM. The filters were then dried naturally. Finally, a small piece of filter was cut for diatom observation by SEM.

### 3.2. Grain size analysis

Untreated sediments were wet sieved through a set of Standard Sieves larger than  $63 \mu\text{m}$ . Then, their dry weights were determined with an analytical balance (resolution of  $0.0001\text{g}$ ) at  $1 \Phi$  intervals, and the portion  $< 63 \mu\text{m}$  was measured with a Mastersizer 2000 laser particle size analyzer. Approximately  $0.5 \text{ g}$  of a pre-homogenized,  $< 63 \mu\text{m}$  sediment sample was pretreated using

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