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Dynamics of biogenic silica dissolution in Jiaozhou Bay, western Yellow Sea

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ABSTRACT

Dissolution of biogenic silica (BSi) in coastal environments is important for marine productivity. Understanding this process is central to assessing the global silicon cycle, which is closely linked to the global carbon cycle. BSi dissolution experiments were conducted to explore factors influencing this process, and to better understand the regeneration of silicic acid in Jiaozhou Bay sediments. The results showed that the BSi content in sediments varied from 0.44% to 2.73% (average, 1.90%). The horizontal distribution of BSi was slightly greater in the north of the bay than in the south, and was similar to the distributions of Chl-a and phytoplankton abundance. Experiments conducted under continuous flow conditions showed that the dissolution kinetics of BSi was non-linear; based on these data the mean solubility of BSi was calculated to be 277 μM-Si for sediment samples, 297 μM-Si for sediment trap samples and 559 μM-Si for diatom–sediment mixture. The dissolution rate constant for BSi in surface sediments varied from 1.7 to 6.8 yr^{-1}. The highest rate was found for tidal flat sediments, and the lowest rate was found in the mouth of the bay; these values for sediment material are higher than those reported for sediments from the Arabian, Scotia and Norwegian seas. For the sediment trap samples the dissolution rate constant ranged from 1.5 to 3.0 yr^{-1}, and showed no obvious variation among the different sampling periods. Structural incorporation of trace aluminum to the BSi surface, and the specific surface area and the reactivity of BSi affected both the solubility and dissolution dynamics of BSi in Jiaozhou Bay sediment. BSi dissolution in the water column and sediment appears to be the key process that sustains diatoms as the dominant phytoplankton species in Jiaozhou Bay.

1. Introduction

Biogenic silica (BSi) is produced in the upper ocean by siliceous organisms, primarily diatoms. These latter organisms contribute up to 50% of global primary production (Van Cappellen et al., 2002) and up to approximately 75% of the primary production in coastal and nutrient-replete waters (Nelson et al., 1995; Liu et al., 2008c). Dissolution of BSi begins when a siliceous organism dies. Globally, an average of approximately 56% of the BSi produced is dissolved in the euphotic zone, before it reaches the seabed (Tréguer and De La Rocha, 2013). In sediments, the dissolution of BSi continues, increasing the silicic acid concentration in pore water, and finally leading to a global mean preservation efficiency estimated at 3% (Tréguer et al., 1995; Tréguer and De La Rocha, 2013). The global average benthic silicic acid flux at the sediment–water interface is approximately an order of magnitude greater than the amount that of riverine input (Tréguer and De La Rocha, 2013). Dissolution of BSi in the water column and sediments dominates the recycling of nutrient silicon in the ocean (Van Cappellen and Qiu, 1997a). The growth of diatoms can be limited by the availability of silicic acid. This phenomenon has been observed worldwide, including in the northern Gulf of Mexico (Nelson and Dortch, 1996), the Bay of Biscay (Loyer et al., 2006) and the Bay of Brest (Le Pape et al., 1996). Dissolution of BSi is thus central to marine productivity, the global silicon cycle and the global carbon cycle (Nelson et al., 1995). The dynamics of this process has been extensively studied worldwide, with a focus on deep sea sediments, of the Atlantic Ocean (Ragueneau et al., 2001; Gallinari et al., 2002, 2008); the Equatorial Pacific Ocean (Gallinari et al., 2002); the Arabian, Weddell, Norwegian and Scotia seas (Rickert, 2000; Rickert et al., 2002); the Porcupine Abyssal Plain (Gallinari et al., 2008); the Antarctic Peninsula shelf (Gallinari et al., 2008); the Congo margin (Ragueneau et al., 2009); and the southern California borderland basins (Cheng et al., 2009). In particular, research on this topic has been carried out in the Southern Ocean (Van Cappellen, 1996; Van Cappellen and Qiu, 1997a,b; Dixit et al., 2001; Van Cappellen et al., 2002). Dissolution of BSi is affected by many factors, including the siliceous organism species involved (Kamatani, 1982; Tréguer et al., 1989), the degree of silicification (Loucaides et al., 2012), temperature (Van Cappellen and Qiu, 1997a, b), pressure (Loucaides et al., 2012), pH (Loucaide et al., 2008), the seawater electrolyte composition (Loucaide et al., 2008), salinity (Loucaide

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et al., 2008), the presence of organic or inorganic coatings on the siliceous organism (Lawson et al., 1978; Kamatani, 1982; Natori et al., 2006), the presence of bacteria (Roubeix et al., 2008), the specific surface area of the diatoms involved (Dixit et al., 2001; Van Cappellen et al., 2002; DeMaster, 2003), and the presence of aluminum (Van Cappellen, 1996; Van Cappellen and Qiu, 1997a,b; Rickert, 2000; Dixit et al., 2001; Cheng et al., 2009).

Jiaozhou Bay is a semi-enclosed bay that is connected to the Yellow Sea through a narrow channel of approximately 2.5 km in length; it has a surface area of 390 km^2 and an average water depth of approximately 6–7 m. More than ten small seasonal rivers carrying various amounts of water and sediment enter the bay. Among these rivers are the Yanghe, Daguhe, Moshuihe, Baishahe and Licunhe rivers, of which the largest is the Dagu River. However, most of these rivers have become contaminated with industrial and domestic waste from the adjacent city of Jiaozhou Bay. From the 1960s to the 1990s, the concentrations of dissolved inorganic nitrogen and phosphate increased by factors of 3.9 and 1.4, respectively. The silicic acid concentration remained at a very low level from the 1980s to the 1990s (Shen, 2001), and consequently the Si/N and Si/P ratios decreased, and the possibility of silicon limitation increased (Zhang and Shen, 1997). This might explain a change in the phytoplankton community structure (Liu, 2004), and the frequent occurrence of red tide events (Sun et al., 1993; Hao et al., 2000; Huo et al., 2001; Lu et al., 2001).

Phosphorus and silicon remain the limiting elements for phytoplankton growth in Jiaozhou Bay (Liu et al., 2005), and consequently the regeneration of silicic acid in this ecosystem is particularly important. Understanding the processes that control the dissolution of BSi requires knowledge of the regeneration of silicic acid, and the silicon cycle. The aims of this study are to investigate factors influencing the dissolution of BSi, and to obtain a better understanding of the regeneration of silicic acid in Jiaozhou Bay sediments.

2. Materials and methods

2.1. Sampling

Field studies were carried out in August and November 2001, March and September 2002, and September 2004. The sampling sites are shown in Fig. 1. Surface sediments were collected using a box sampler, except for the tidal flat surface sediments, which were sampled by hand. At stations J1 and J2 in 2001, and stations J3 and Z in 2002 (Fig. 1), the core sediments were carefully collected using a multicorer with an inner diameter of 9 cm and a length of 60 cm, to avoid resuspension of seabed sediments. The core sediments were sectioned at 1-cm intervals, and all sediments were packed in sealed bags and stored in −20 °C until analyzed. In the laboratory the sediments were freeze dried and ground gently using a mortar and a pestle. The water content of the sediment was estimated from the change in weight prior to and following freeze drying. Sediment trap samples were collected at station M from 13 to 28 August 2001, using sediment trap moorings. The average water depth was 19.2 m during this period. Each sediment trap comprised a polyvinyl chloride cylinder (opening diameter, 14.6 cm; length, 59 cm) with a polyvinyl chloride baffle to reduce turbulence and prevent the entrance of large organisms. A 450-ml polyethylene sample cup was attached to the bottom of each cylinder by threaded screws. To prevent bacterial decomposition/degradation of settled particles during deployment, the receiving cups in the traps were filled with a saturated $HgCl_2$ solution in filtered seawater. Based on the turbidity of the bottom water in the station, the sediment traps were placed 0.5 m above the sea bed using a winch, in order to avoid the influence of sediment resuspension on sediment trap samples as much as possible. On recovery of each trap, the trapped particles were filtered onto a pre-weighed 0.45 μm pore-size acetate cellulose filter. Large organisms were carefully removed by hand, using a pair of fine-tipped tweezers. The filters were freeze dried. Each sampling period lasted four days, and encompassed tidal variation (neap tide: 13–16 and 25–28 August; moderate tide: 16–19 and 22–25 August; spring tide: 19–22 August). The average wind speed was 4 m s^{-1} during the sampling periods; however, on 23–24 August the maximum wind speed was 15 m s^{-1}.

2.2. BSi solubility and dissolution kinetic experiments

The dissolution behavior of BSi (i.e. apparent solubility and dissolution kinetics) was measured using flow-through experiments, to mirror the dissolution of BSi under natural conditions (Van Cappellen and Qiu,

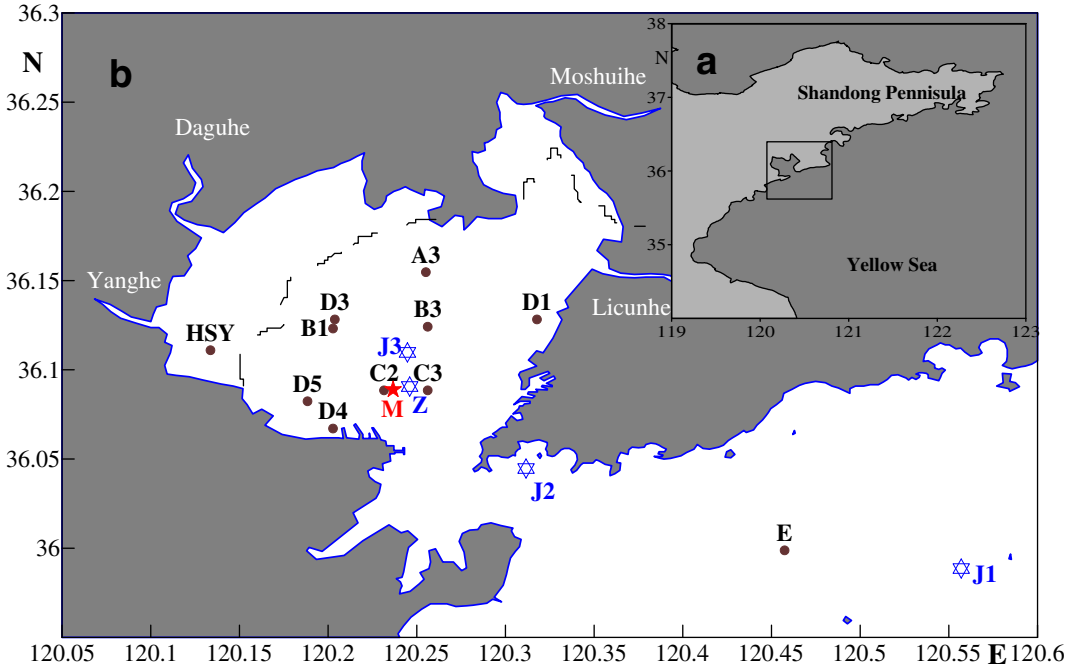

Fig. 1. (a) Location of Jiaozhou Bay. (b) Map of Jiaozhou Bay showing the surface sediment stations (●), the core sediment stations (✡) and the sediment trap station M (★). Among these stations J1 and E are in the Yellow Sea.