

Biogenic silicate accumulation in sediments, Jiaozhou Bay*

LI Xuegang (李学刚)[†], SONG Jinming (宋金明)^{†, **}, DAI Jicui (戴纪萃)[†],
YUAN Huamao (袁华茂)[†], LI Ning (李宁)^{††}, LI Fengye (李凤业)[†],
SUN Song (孙松)[†]

[†]Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

^{††}The Graduate School, Chinese Academy of Sciences, Beijing 100039, China

Received Dec. 21, 2005; revision accepted Apr. 30, 2006

Abstract It has been widely recognized that low silicate content in seawater is a major limiting factor to phytoplankton primary production in Jiaozhou Bay. However the reason of Si-limitation remains poorly understood. In the present study we measured the biogenic silicate content and discussed the accumulation of silicate in Jiaozhou Bay sediment. The results show that the biogenic silica content in the sediment of the Jiaozhou Bay is obviously much higher than those in the Yellow Sea and the Bohai Sea. The BSi:TN ratios and BSi:16P ratios in the sediment are > 1 and the OC:BSi ratio in sediment is lower than these of Redfield ratio (106:16), indicating that the decomposition rate of OC is much higher than that for BSi in similar conditions. Therefore, the majority of the biogenic silicate was buried and thus did not participate in silicate recycling. Silicate accumulation in sediment may explain why Si limits the phytoplankton growth in the Jiaozhou Bay. Comparing the flux of biogenic silicate from sediments with primary production rate, it can be concluded that only 15.5% of biogenic silicate is hydrolyzed during the journey from surface to bottom in seawater, thus approximate 84.5% of biogenic silicate could reach the bottom. The silicate releasing rate from the sediment to seawater is considerably lower than that of sedimentation of biogenic silicate, indicating silicate accumulation in sediment too. In a word, the silicate accumulation in sediment is the key reason of silicate limiting to phytoplankton growth in Jiaozhou Bay.

Key words: biogenic silicate; accumulation; limiting factor; Jiaozhou Bay

1 INTRODUCTION

Silicate, or silicic acid (H_4SiO_4), is a very important nutrient in the ocean. Unlike other major nutrients such as phosphate and nitrate or ammonium, which are needed by almost all marine plankton, silicate is an essential chemical requirement only for certain biota such as diatoms, radiolarian, silicoflagellates and siliceous sponges. But siliceous phytoplankton contributes significantly to the primary production in the world ocean. The estimate by Nelson et al. (1995) shows that more than 40% of entire primary production is contributed by diatoms, which reveals a close coupling of silica and carbon in the ocean. Therefore, silicate cycling has received significant scientific attention in recent years and many scientists have studied silicate behavior in marine environments (Song, 1997; DeMaster, 2002; Quequiner and Brzezinski, 2002; Song et al., 2002).

Biogenic silica is one of amorphous silica or termed biogenic opal, or opal in brief. Biogenic silica in sediments is mainly consisted of fecal pellets and reliquiaes of siliceous plankton such as diatoms, radiolarian, silicoflagellates and siliceous sponges. It is estimated that about 240×10^{12} mol of silica were fixed by marine silica biota every year. Nevertheless, most of the biogenic silica produced in euphotic zone dissolves during settling. Nelson et al. (1995) estimated that on a global scale, at least 50% of the silica produced by diatoms in euphotic zone dissolves in the upper 100 m of a water column. Diatom frustules that escaped from dissolution dur-

*Supported by Qingdao Special Project for Outstanding Scientists (Nos. 04-3-JJ-03 and 05-2-JC-90), the "100 Talents Project" of Chinese Academy of Sciences, the Knowledge Innovation Program of Chinese Academy of Sciences (Nos. KZCX1-SW-01-08 and KZCX3-SW-214)

*Corresponding author: jmsong@ms.qdio.ac.cn

ing settling could reach the sea floor, where a major fraction of the silica dissolves at the sediment–water interface or in surface sediments (Koning et al., 1997), and only 3% of the silica produced in euphotic zone could be finally buried in the sediment (Treguer et al., 1995). As a calculation shows, the silica supplied to the world ocean from biogenic silica dissolution in sediment is 4 times of that from rivers, and the regeneration of biogenic silica in sediment is the main source of silica in seawater (Dixit et al., 2003). There are a number of factors to influence the dissolution of biogenic silica in sediment. Besides the source of silica, the dissolution is related with the water depth, water temperature, the degree of the saturation of silicate in pore water and overlying water, too. Silica accumulation in sediment will strongly influence the silica concentration in seawater. Indeed, silica can limit the growth of diatom under some particular conditions.

Diatoms and dinoflagellates are the dominate genera in Jiaozhou Bay and its adjacent regions, especially diatom in the number of species or cells. Among 116 species of phytoplankton recognized so far in Jiaozhou Bay, 100 species of 35 genera were diatoms, 15 species of 3 genera were dinoflagellates and 1 species of 1 genus belonged to chrysophyta, and the cells number of diatom accounted for 99% of total phytoplankton cells number (Guo and Yang, 1992). Thus, the distribution of species or cells of phytoplankton in the regions was determined by diatom. The growth of these diatoms would consume a huge amount of silica. Yang et al. (2002; 2003a, b; 2005a, b) studied the content of silica, the ratios of Si:N and Si:P, and other parameters in Jiaozhou Bay water, they concluded that silica was an important limiting factor for phytoplankton growth in the bay. Shen (2002) considered Si but N and P in Jiaozhou Bay was a limiting nutrient for phytoplankton growth concluded after a long term investigation.

Silicate received in the bay is mainly from surrounding rivers. Although the runoff has been reducing in recent years, the input amount of silicate is still large (Song, 2004). However, why is it lack of silicate in seawater? What was the reason for silicate limitation? Yang et al. (2002) considered two possible reasons. One is the consumption by phytoplankton growth; the other is the water exchange through bay mouth to the Yellow Sea silicate-poor water. In general, silicate absorbed by phytoplankton would be dissolved in water column during settling and only a minor part of original

production of biogenic silica could deposit and be buried. Moreover, the depth of Jiaozhou Bay is shallow with a mean of 7 m, the silica would be settled down to bottom in a short time before its decomposition. As the result, the biogenic silica would be buried and moved from seawater. This explained why Si became a limiting factor in the bay. In this paper, concentrations of silica in the sediments of the bay were chemically analyzed and statistically presented for understanding the details of accumulation of biogenic silica and its ecological significance.

2 MATERIALS AND METHODS

2.1 Sampling

Three sediment cores in Jiaozhou Bay were collected with a gravity corer on board of “*Jinxing (Venus) II*” in September, 2003 (Fig.1). B3 is located in the bay center with 6 m water depth. The core is ca. 94 cm long and its surface sediment is yellow-grey silty mud. D4 is located in the south of the bay near the bay mouth with 21 m water depth. The core length is ca. 104 cm and its surface sediment is grey-black muddy ooze. D7 is located in the outer bay with 17 m water depth. The core is ca. 82 cm long and its surface sediment is yellow-grey muddy silt. The cores were cut into 2.0 cm long slices from surface to bottom. All the samples were sealed in polyethylene bags. The sedimentation rate, biogenic silica, nitrogen, phosphorus, organic carbon and other indicators were determined in laboratory.

2.2 Chemical analysis of biogenic silica (BSi)

The content of biogenic silica in sediment was determined in dried sediments using technique proposed by Mortlock and Froelich (1989). The sediment sample is dried at 40°C, then allowed to re-equilibrate with the atmosphere at room temperature for at least 24 h. A portion of 0.100 0 g is weighed and put into a 100 ml polypropylene centrifuge tube. 5 ml of a 10% H₂O₂ solution is added to the tube, and after about 30 min, 5 ml 1 mol/L HCl solution is added. The tube is capped and placed on a rack for about 30 min. Addition of acid and peroxide removes diluting phase such as car

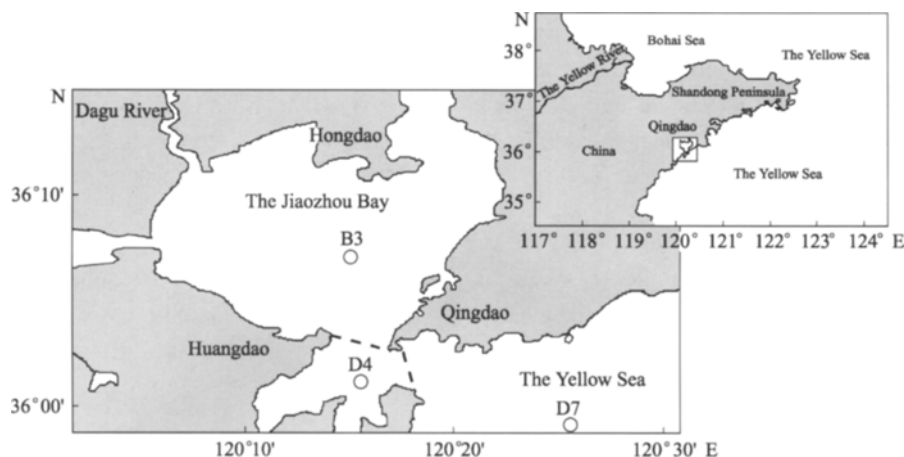


Fig.1 The sampling localities

bonate and organics and assists in disaggregating the sediment, exposing opal surface to dissolution. About 20 ml of deionized water is added to the tube and then centrifuged for about 5 min. The supernatant is decanted to remove residual acid and peroxide. The tube is then placed in an oven to dry at 60°C over night. Exact 40 ml of 2 mol/L Na₂CO₃ solution is added to the tube, which is then capped, mixed well and placed in a covered constant-temperature bath pre-heated to 85°C. The tube is taken out at about two hours and four hours later respectively from the water bath and shaken vigorously to resuspend the solids and quickly returned to the water bath. After a total of 5 h, the tube is removed and centrifuged immediately for 5 min. 125 µl of the clear supernatant was used to determine biogenic silica by modified molybdate-blue spectrophotometry. The mean reproducibility was 2% in a range of 0.05% to 8%.

2.3 Organic carbon analysis

0.500 0 g dried sediment sample that dried at 40°C in natural grain size is weighed into a 300 ml flask. Exact 10 ml of 1 mol/L K₂Cr₂O₇ solution is added to the sediment and mixed by swirler in the flask. 20 ml of concentrated H₂SO₄ are added and then mixed by gently waggling the flask for about one minute. This should be done carefully to insure complete mixing of the reagents with the sediment, avoiding splashing the sediment onto the wall of the flask out of the contact with the reagents. The mixture is allowed to stay for 30 min. A standardization blank without sediment is run with each new batch

of samples. After 30 min, the solution is diluted to 150ml volume with distilled water, and 10 ml 85% H₃PO₄, 0.2 g NaF, and 10 drops of diphenylamine indicator are added to the sample flask. The solution is back titrated with 0.5 mol/L ferrous ammonium sulfate solution to the color change from opaque green-brown to a brilliant green. The standard deviation was less than ±0.25% for all samples (Gaudette et al., 1974).

2.4 N and P analyses

N and P contents in sediments were simultaneously determined by colorimetric method at analytical precision of 0.5%. Inorganic N and P were extracted by 0.1 mol/L HCl with vibration for 2 hours, and then determined after centrifugation. Total N and total P were extracted by potassium persulfate-sodium hydroxide mixture solution in stainless steel autoclave and maintained 124 for 1 hour. The contents were determined after cooling down naturally. Organic N and P were calculated from the difference between the total N, P and inorganic N, P (Li, 2005).

3 RESULTS AND DISCUSSIONS

3.1 High content of biogenic silica in Jiaozhou Bay sediment

The biogenic silica contents in sediments from the three cores in Jiaozhou Bay are shown in Table

1 and Fig.2, by which an overall low discrimination of biogenic silica content is indicated. From the contrast between the biogenic silica content in surface sediment (0–10 cm) and sub-surface sediment (10–20 cm), supposing the sedimentation rate is constant, the content of biogenic silica in recent years is obviously higher than early years in the inner bay, indicating a faster accumulation of biogenic silica in recent years. On the whole, the average of biogenic silica in location B3, D4 and D7 is 1.54%, 1.48% and 1.39%, respectively, having a same trend that the biogenic silica content decreases from inner bay to bay mouth then outer bay, which is the same to that of phytoplankton distribution (Wu et al., 2004). Therefore, the biogenic silica content in Jiaozhou Bay sediment is positively correlated to the biomass of phytoplankton.

Table 1 The content (%) of biogenic silica in Jiaozhou Bay sediments

Depth	B3(inner bay)	D4(bay mouth)	D7(outer bay)
0–10 cm	1.58	1.44	1.48
10–20 cm	1.29	1.49	1.40
Total	1.54	1.48	1.39

The vertical distribution of biogenic silica in Jiaozhou Bay sediment is shown in Fig.2. Their vertical changes are small in bay mouth and outer bay, but bigger in the inner bay, where several high value intervals at 4–6 cm, 22–24 cm, 68–70 cm, and 92–94 cm are denoted. The distribution is due to slow water exchange with the Yellow Sea in the inner bay, and massive N, P nutrient input from surrounding rivers, who would bring about eutrophication and result in algae bloom if condition favors.

Consequently, biogenic silica that accumulated in sediment could fluctuate with the bloom. Because the frequency and scale of algae bloom in the inner bay is often higher than that in bay mouth and outer bay. Therefore, the biogenic silica content in the inner bay is more variable.

In addition, water exchange continuously increases from the inner bay to outer bay, with which the concentration of nutrient would decrease. As the results, the frequency and scale of the bloom would decrease from the inner bay to outer bay. Therefore, the content of biogenic silica in sediment remains more stable in outer bay than in inner bay. According to the sedimentation rate we calculated for Jiaozhou Bay, the high content of biogenic silica at 4–6 cm in location B3 was probably related to the event of large red tide in 1998.

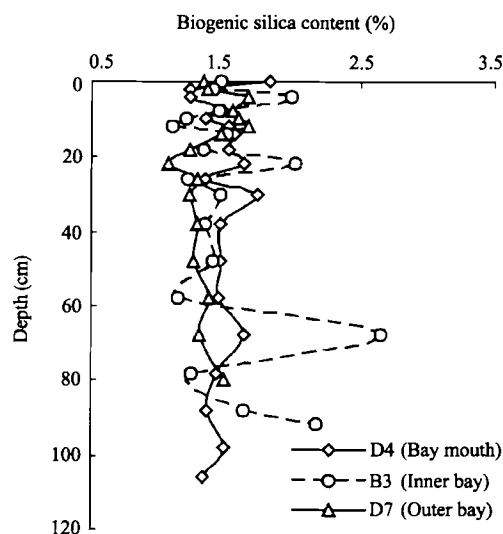


Fig.2 The vertical distribution of biogenic silica in Jiaozhou Bay sediment

Table 2 Comparison of biogenic silica contents in surface sediments of different marine regions

Region	BSi content(%)	Extraction method	Data source
The Jiaozhou Bay	1.44–1.58	2 mol/L. Na ₂ CO ₃	This study
The Yellow Sea	0.21–0.46	2 mol/L. Na ₂ CO ₃	Liu (2002)
The Bohai Sea	0.25–0.58	2 mol/L. Na ₂ CO ₃	Liu (2002)
The northern Arabian Sea	2.3–3.9	0.5 mol/L. NaOH	Weijden et al., (2002)
The Southern Ocean	6.5–38	2 mol/L. Na ₂ CO ₃	Cappellen et al., (1997)
Mesohaline Tidal marsh	0.76–1.0	1% Na ₂ CO ₃	Norris (1999)
Ross Sea	0.7–2.1	1% Na ₂ CO ₃	Demaster et al., (1996)

3.2 The ratios of Si:N and Si:P

The ratios of Si:N and Si:P can be used to estimate limitation nutrient factors for phytoplankton growth. In general, when Si:P < 10 and Si: DIN < 1 in seawater, silica would become an important limiting factor to phytoplankton growth (Song, 1997; Shen, 2002). Since Si:DIN and Si:16P are less than 1 in Jiaozhou Bay seawater, Yang et al. (2003a) thought silica is a limiting factor in Jiaozhou Bay to phytoplankton growth. However, although the reason of making silica limitation is complicated, the most important reason is that in the author's viewpoint, silica in seawater are absorbed and delivered to the bottom in biological pumping, and buried finally by sediment. The accumulation of silica in sediment may reflect the ratios of Si to C, N or P. The ratio of Si:N:P in marine alga is 16:16:1 (Wang, 2003), if all Si, N and P in sediment came from phytoplankton, the ratio of Si:N:P in sediment should be close to 16:16:1. The ratios of BSi:TN and BSi:TP in Jiaozhou Bay core sediment are listed in Table 3 showing that the ratios of BSi:TN in every location are much greater than 1, and the ratios of BSi:TP are well above 16, which indicates that biogenic silica was accumulated in sediment. In

general, BSi:TN and BSi:TP increase with depth, illustrating that the rates of N and P decomposition are faster than that of biogenic silica in early diagenesis, and silica continuously accumulates in sediment resulting in silica depletion in seawater. In addition, the fact that BSi:TN and BSi:TP are greater in surface layer than in subsurface layer in location B3 confirmed that the silicate accumulation rate in the inner bay has been increasing in recent years.

3.3 The relationship between biogenic silica and organic carbon

Silica plays an important role in controlling carbon cycle (Treguer, 2002). Remero et al. (2003) observed a good correlation between biogenic silic in sediment and primary production in overlying water in the region of the Peru-Chile upwelling, viz: higher biogenic silica content means higher primary production. Preservation of silicate in sediment has close relationship with its dissolution rate. And the dissolution rate depends mainly on the factors including under-saturation of Si(OH)₄ in bottom pore water, depth pressure, temperature, pH, the o

Table 3 The ratios of Si/TN and Si/TP in Jiaozhou Bay sediments

Layer	B3 (inner bay)			D4 (bay mouth)			D7 (outer bay)				
	BSi/TN	BSi/TP	OC/BSi	Layer	BSi/TN	BSi/TP	OC/BSi	Layer	BSi/TN	BSi/TP	OC/BSi
0-2	18	56	0.30	0-2	37	84	0.20	0-2	33	67	0.11
2-4	20	60	0.35	2-4	28	57	0.28	2-4	25	66	0.07
4-6	43	85	0.25	4-6	28	54	0.26	4-6	42	84	0.07
8-10	15	55	0.34	8-10	41	74	0.22	8-10	32	75	0.12
10-12	13	46	0.37	10-12	23	65	0.24	10-12	53	93	0.07
12-14	12	42	0.37	12-14	24	65	0.17	12-14	41	76	0.08
14-16	18	73	0.29	14-16	28	69	0.23	14-16	41	135	0.09
18-20	24	64	0.35	18-20	32	71	0.27	18-20	36	97	0.11
22-24	30	124	0.19	22-24	30	70	0.30	22-24	18	70	0.16
26-28	23	47	0.31	26-28	34	62	0.25	26-28	41	80	0.08
30-32	43	62	0.27	30-32	40	77	0.28	30-32	37	91	0.12
38-40	20	47	0.36	38-40	37	67	0.25	38-40	31	80	0.18
48-50	21	50	0.35	48-50	43	67	0.29	48-50	32	93	0.13
58-60	29	37	0.21	58-60	52	55	0.30	58-60	33	117	0.06
68-70	83	98	0.08	68-70	34	67	0.27	68-70	60	154	0.19
78-80	31	73	0.06	78-80	25	59	0.26	80-82	57	110	0.11
88-90	30	67	0.29	88-90	49	60	0.24				
92-94	54	92	0.26	98-100	42	59	0.18				
				106-108	45	57	0.25				
Average	29	65	0.28	Average	35	65	0.25	Average	38	93	0.11

ganic coating. In fact, the generation of $\text{Si}(\text{OH})_4$ from biogenic silicate increases with sediment permeability. In general, organically poor sands have relatively higher mineralization rates. Silica depletion in overlying water can boost the dissolution of biogenic silica (Ehrenhauss et al, 2004). Therefore, relation between biogenic silicate and organic carbon in sediment is a very important issue in this regard for scientists, as shown by Jiaozhou Bay case (Fig.2).

In Fig.2, the correlation coefficient between biogenic silica and organic carbon at B3 (inner bay) is obviously greater than that at D7 (outer bay), and the ratios of OC:BSi in inner bay and bay mouth is close but higher than in outer bay, which might resulted from different hydrodynamics, structures and compositions of sediment between inner bay and outer bay. Sediment in outer bay is coarser than that of the inner bay and have better permeability with which OC and BSi could leak out resulting in low contents of them. In addition, exchange between pore water and overlying water result in not only the low OC content and silicate unsaturation but also the acceleration in biogenic silica dissolution. This is why we observed very low biogenic silica content in sediment and smaller correlation coefficient in the outer bay than that in the inner bay.

In OC:BSi ratio, the maximum value is 0.37 in Jiaozhou Bay sediment, much smaller than the Redfield ratio, indicating that OC was decomposed much faster than biogenic silica did in the same environment. Most OC but biogenic silica that preserved in sediment would decompose then participate in the carbon recycle, which may explain why Si becomes a limiting factor in Jiaozhou Bay.

According to Ma et al. (2002), the order of decomposition rate of biogenic element is $\text{N} > \text{P} > \text{OC} > \text{Si}$, which is consistent with the phenomenon that the decomposition rates of C, N, and P are faster than that of biogenic silica indicated by the ratios of OC:BSi, BSi:TN, and BSi:TP in the sediment of Jiaozhou Bay, which proved that the BSi do accumulated in Jiaozhou Bay sediment.

3.4 Flux of biogenic silica sedimentation in Jiaozhou Bay sediment

Sedimentation flux can reflect quantitatively how much sediment may accumulate. Being compared with primary production, the amount of matter that decomposed and came back to water during set-

tlng can be estimated. By comparing it with the flux across the interface of sediment and water, we can calculate how much matter is buried. Therefore, how much biogenic silica can be buried and how much biogenic silica can be taken back to the sea water in Jiaozhou Bay can be determined.

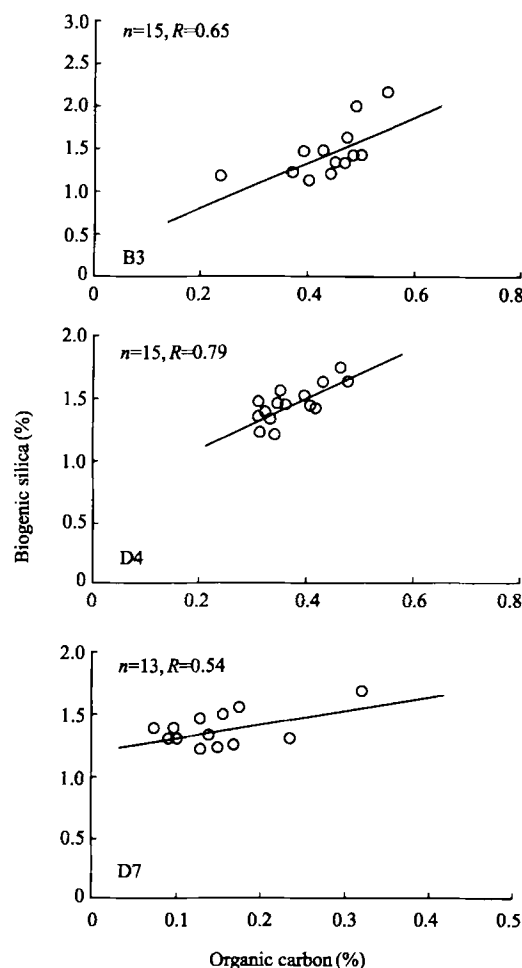


Fig.3 Relationship between biogenic silica and organic carbon in Jiaozhou Bay sediments

Based on the Jiaozhou Bay sedimentation rate, the flux of biogenic silica sedimentation can be calculated by Eqs (1) and (2) (Zhao, 1991) and the results are shown in Table 4.

$$BF = C \times S \times \rho_d \quad (1)$$

$$\rho_d = (1 - W_c) / ((1 - W_c) / \rho_s + W_c / \rho_w) \quad (2)$$

where BF is flux of biogenic silica sedimentation; C is the content of biogenic silica; S is sedimentation rate; ρ_d is dry density of sediment; W_c is water con-

Table 4 The fluxes of biogenic silica sedimentation in Jiaozhou Bay

Region	Water content(%)	Sedimentation rate (cm/a)	Sedimentation flux [mmol/(m ² /d)]
Inner bay	65.6	0.85	5.34
Bay mouth	65.4	1.63	9.87
Outer bay	80.3	0.45	2.08

tent; ρ_s is sediment density; and ρ_w is water density (here is 1.027 g/cm³).

According to the primary production of (41.9±15.3) mmol/(m²·d) (Wang, 1995), the biogenic silica production from diatom, which calculated in the Redfield ratio, is (6.32±2.35) mmol/(m²·d). Using the sedimentation flux at B3 (inner bay) as average flux of biogenic silica sedimentation in the bay, we found that only about 15.5% of diatom-produced biogenic silica can be decomposed during sinking down to the bottom, about 84.5% of biogenic silica can reach the bottom and deposited. Because the water depth of Jiaozhou Bay is small (7 m in average), most primary production can deposit before decomposition takes place. The flux of biogenic silica from the sediment-water interface to water, which can represent the silicate release rate, is 3.3 mmol/(m²·d) (Jiang et al., 2002), less than the inner bay sedimentation flux. Consequently, silica continuously transported from seawater to sediment, resulting in low silica concentration in seawater for phytoplankton growth. Above all, the accumulation of biogenic silica in sediment is a major mechanism or the Si limitation for phytoplankton growth in the Jiaozhou Bay.

4 CONCLUSIONS

Based on the information of biogenic silica revealed from three sediment cores of Jiaozhou Bay, the reasons of silica limitation to local phytoplankton growth were discussed. Main conclusions can be summarized as follows:

(1) The biogenic silicate content in Jiaozhou Bay sediment is obviously much higher than those in the Yellow Sea and the Bohai Sea. The sediment of the bay is characterized by high content of biogenic silicate, being 1.58%, 1.44% and 1.48% in location B3, D4, D7, respectively. In the inner bay, the content at sediment surface is higher than that underneath, indicating that the accumulation rate in

recent years is greater than that in earlier years.

(2) In the sediment of Jiaozhou Bay, OC, N and P decompose much faster than biogenic silicate does in similar conditions; thus most biogenic silicate would be buried and separated from silicate recycling.

(3) Only 15.5% of biogenic silicate is hydrolyzed during the journey from the surface to bottom in seawater, thus approx. 84.5% of them can deposit at the bottom. The silicate release rate through sediment and seawater interface is quite lower than its accumulation rate from water to sediment. They are the main reasons for constantly low silicate concentration in the seawater and Si-limitation to phytoplankton primary production. In one word, silicate accumulation in sediment is the key factor for silicate limiting on phytoplankton growth in the Jiaozhou Bay.

Reference

- Cappellen, P. V. and L. Qiu, 1997. Biogenic silica dissolution in sediments of the Southern Ocean I Solubility. *Deep-Sea Research II* **44**: 1 109-1 128.
- DeMaster, D. J., 2002. The accumulation and cycling of biogenic silica in the Southern Ocean: revisiting the marine silica budget. *Deep-Sea Research II* **49**: 3 155-3 167.
- DeMaster, D. J., O. Ragueneau and C. A. Nitouer, 1996. Preservation and accumulation rates for biogenic silica and organic C, N, and P in high-latitude sediments: The Ross Sea. *J. Geophys. Res.* **101** (8): 18 501-18 518.
- Dixit, S. and P. V. Cappellen, 2003. Predicting benthic fluxes of silicic acid from deep-sea sediments. *Journal of Geophysical Research* **108**(c10): 3 334-3 353.
- Ehrenhauss, S., U. Witte, F. Janssen and M. Huettel, 2004. Decomposition of diatom and nutrient dynamics in permeable North Sea sediments. *Continental Shelf Research* **24**: 721-737.
- Gaudette, H. E., W. R. Flight and L. Toner, 1974. An inexpensive titration method for the determination of organic carbon in recent sediment. *Journal of Sedimentary Petrology* **44**(1): 249-253.
- Guo, Y. J. and Z. Y. Yang, 1992. Biological environment in Jiaozhou Bay: primary productivity. In: Liu, R. Y. et al., Ecology and Living Resources of Jiaozhou Bay. Science Press, Beijing, p. 110-125. (in Chinese)
- Jiang, F. H., X. L. Wang, X. Y. Shi, C. J. Zhu, X. R. Han and L. Zhang, 2002. Benthic Exchange Rate and Flux of Dissolved Silicate at the Sediment—Water Interface in Jiaozhou Bay. *Journal of Ocean University of Qingdao* **32**(6): 1 012-1 018.
- Koning E., G. J. Brummer, W. van Raaphorst, A. J. van

- Bennekom, W. Helder and J. van Iperen, 1997. Settling, dissolution and burial of biogenic silica in the sediments off Somalia (northwestern Indian Ocean). *Deep-Sea Research II* **44**: 1 341-1 360.
- Liu, S. M., X. W. Ye, J. Zhang and Y. F. Zhao, 2002. Problems with biogenic silica measurement in marginal seas. *Marine Geology* **192**: 383-392.
- Ma, H. B., J. M. Song and X. X. Lu, 2002. Nitrogen forms and decomposition of organic carbon in the south Bohai Sea core sediment. *Acta Oceanologica Sinica* **24**(5): 64-70. (in Chinese)
- Mortlock, R. A. and P. N. Froelich, 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediment. *Deep-Sea Research II* **36**: 1 415-1 426.
- Nelson, D. M., P. Treguer and M. A. Brzezinski, 1995. Production and dissolution of biogenic silica in the ocean: revised global estimates comparison with regional data and relationship to biogenic sedimentation. *Global Biogeochemistry Cycle* **9**: 359-372.
- Norris, A. R., 1999. Silica content of a mesohaline tidal marsh in North Carolina. *Estuarine, Coastal and Shelf Science* **49**: 597-605.
- Queguiner, B. and M. A. Brzezinski, 2002. Biogenic silica production rates and particulate organic matter distribution in the Atlantic sector of the southern ocean during austral spring 1992. *Deep-Sea Research II* **49**: 1 765-1 786.
- Romero, O. and D. Hebbeln, 2003. Biogenic silica and diatom thanatocoenosis in surface sediments below the Peru-Chile Current: controlling mechanisms and relationship with productivity of surface waters. *Marine Micropaleontology* **48**: 71-90.
- Shen, Z. L., 2002. Long-term changes in nutrient structure and its influence on ecology and environment in Jiaozhou Bay. *Oceanologia et Limnologia Sinica* **33**(3): 322-330. (in Chinese)
- Song, J. M. 2004. Biogeochemistry of the China Seas. Shandong: Shandong Science and Technology Press, 1-591. (in Chinese)
- Song, J. M., 1997. Chemistry of sediment-sea water interface of the China Sea. China Ocean Press, Beijing, p. 1-222. (in Chinese)
- Song, J. M., Y. X. Luo, X. X. Lu and P. C. Li, 2002. Biogeochemical processes of phosphorus and silicon in southern Bohai Sea surface sediments. *Chinese Journal of Oceanology and Limnology* **20**(4): 378-383.
- Tréguer, P. D. A. Nelson, A. J. van Bennekom, D. J. Demaster, A. Leynaert and B. Queguiner, 1995. The silica balance in the world ocean: a re-estimate. *Science* **268**: 375-379.
- Tréguer, P. D., 2002. Silica and the cycle of carbon in the ocean. *C. R. Geoscience* **334**: 3-11.
- Wang, B. D. 2003. Nitrogen distribution and their limitation on phytoplankton in the yellow Sea and the East China Sea. *Chinese Journal of Applied Ecology* **14**(7): 1 122-1 126. (in Chinese)
- Wang, R., N. Z. Jiao and C. L. Li, 1995. Study on primary production and new production of the Jiaozhou Bay. In: Dong, J. H., N. Z. Jiao ed., *Ecological Studies of Jiaozhou Bay*, Science Press, Beijing, p. 125-137. (in Chinese)
- Weijden, A. J. and C. H. Weijden, 2002. Silica fluxes and opal dissolution rates in the northern Arabian Sea. *Deep-Sea Research I* **49**: 157-173.
- Wu, Y. L., S. Sun and Y. S. Zhang, 2004. Quantitative Study on Long-Term Variation of Phytoplankton in Jiaozhou Bay. *Oceanologia et Limnologia Sinica* **35**(6): 518-523. (in Chinese)
- Yang, D. F., J. J. Zhang, J. B. Lu, Z. H. Gao and Y. Chen, 2002. Examination of silicate limitation of primary production in Jiaozhou Bay, China I: Silicate being a limiting factor of phytoplankton primary production. *Chinese Journal of Oceanology and Limnology* **20**(3): 208-225.
- Yang, D. F., J. Zhang, Z. H. Gao, Y. Chen and P. Y. Sun, 2003a. Examination of silicate limitation of primary production in Jiaozhou Bay, China II: Critical value and time of silicate limitation and satisfaction of the phytoplankton growth. *Chinese Journal of Oceanology and Limnology* **21**(1): 46-63.
- Yang, D. F., Z. H. Gao, Y. Chen, J. Zhang and P. G. Wang, 2003b. Examination of silicate limitation of primary production in Jiaozhou Bay, China III: Judgment method, rules and uniqueness of nutrient limitation among N, P, and Si. *Chinese Journal of Oceanology and Limnology* **21**(2): 114-133.
- Yang, D. F., Y. Chen, Z. H. Gao, J. Zhang and F. Wang, 2005a. Silicon limitation on primary production and its destiny in Jiaozhou Bay, China IV: Study on cross-bay transect from estuary to ocean. *Chinese Journal of Oceanology and Limnology* **25**(1): 72-90.
- Yang, D. F., Z. H. Gao, Y. Chen, P. G. Wang, P. Y. Sun and S. Liu, 2005b. Silicon limitation on primary production and its destiny in Jiaozhou Bay, China V: Silicon deficit process. *Chinese Journal of Oceanology and Limnology* **25**(2): 169-175.
- Zhao, Y. Y., F. Y. Li, Demaster, C. A. Nittrouer and J. D. Milliman, 1991. Primary studies on sedimentation rate and sediment flux of the south Huanghai Sea. *Oceanologia et Limnologia Sinica* **22**(1): 38-43. (in Chinese)