



Distribution and accumulation of biogenic silica in the intertidal sediments of the Yangtze Estuary

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Abstract

Sedimentary biogenic silica is known to be an important parameter to understand biogeochemical processes and paleoenvironmental records in estuarine and coastal ecosystems. Consequently, it is of great significance to investigate accumulation and distribution of biogenic silica in sediments. The two-step mild acid-mild alkaline extraction procedure was used to leach biogenic silica and its early diagenetic products in intertidal sediments of the Yangtze Estuary. The results showed that total biogenic silica (t-BSi) in the intertidal sediments varied from 237.7–419.4 $\mu\text{mol Si/g}$, while the mild acid leachable silica (Si-HCl) and the mild alkaline leachable silica (Si-Alk) were in the range of 25.1–72.9 $\mu\text{mol Si/g}$ and 208.1–350.4 $\mu\text{mol Si/g}$, respectively. Significant correlations were observed for the grain size distributions of sediments and different biogenic silica pools in intertidal sediments. This confirms that grain size distribution can significantly affect biogenic silica contents in sediments. Close relationships of biogenic silica with organic carbon and nitrogen were also found, reflecting that there is a strong coupling between biogenic silica and organic matter biogeochemical cycles in the intertidal system of the Yangtze Estuary. Additionally, the early diagenetic changes of biogenic silica in sediments are discussed in the present study.

Key words: biogenic silica; early diagenesis; intertidal flats; the Yangtze Estuary

Introduction

Silicate is one of the major nutrient elements for estuarine and coastal ecosystems, which often dominate phytoplankton communities and have important roles in planktonic microorganisms (e.g., diatoms, radiolaria and silicoflagellate) (Srithongouthai *et al.*, 2003; Wu and Chou, 2003; Natori *et al.*, 2006). Relatively excessive silicate has been considered to be the cause of the increase in toxic phytoplankton blooms observed in estuarine and coastal waters during recent decades (Kuuppo *et al.*, 1998; Escaravage and Prins, 2002; Wu and Chou, 2003; Parsons *et al.*, 2006). Biogenic silica in sediments is known to be an important parameter to understand the biogeochemical processes and paleoenvironmental records in estuarine and coastal ecosystems. The content of biogenic silica in sediments is found to have a close link with biosiliceous productivity in overlying waters (Legovic *et al.*, 1996; Romero and Hebbeln, 2003), alterations of phytoplankton species composition are likely to have a large effect on levels of CO₂ in the atmosphere, and have a strong potential as a powerful proxy for paleoproductivity reconstructions (Ragueneau *et al.*, 2000; Tréguer

and Pondaven, 2000; Bernárdez *et al.*, 2005). Therefore, it is of great significance to investigate the accumulation and distribution of biogenic silica in estuarine and coastal sediments. However, data on biogenic silica contents in estuarine and coastal sediments are relatively scarce, and factors controlling the preservation of biogenic silica in such complex systems still remain unclear.

The Yangtze Estuary is of particular interest to nutrient cycling because of its importance for transportations of terrigenous nutrients to coastal seas. Numerous reports have been published on the distributions and variations of nitrogen and phosphorus in Yangtze estuarine waters (Edmond *et al.*, 1985; Hou *et al.*, 2002) and in coastal sediments (Yu *et al.*, 1990; Zhang *et al.*, 2002), nutrient fluxes across the intertidal sediment-water interface (Hou *et al.*, 2006), and adsorption of ammonium and phosphate on sediments in the Yangtze Estuary (Liu *et al.*, 2002; Hou *et al.*, 2003). To the best of our knowledge, this is the first report dealing with silica cycling in the intertidal flats of the Yangtze Estuary. The main objectives of the present study are to investigate the spatio-temporal variations in biogenic silica in intertidal sediments and to explore the factors and mechanisms that affect the distributions of biogenic silica.

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1 Materials and methods

1.1 Study area

The Yangtze Estuary (121°50′–122°30′E and 30°50′–31°45′N) is situated on the east coast of China (Fig. 1). For nearly 6,000 km before discharging through the Yangtze Estuary near Shanghai, the Yangtze River traverses Central China in an approximately westerly direction into the East China Sea. The Yangtze River is a primary source of sediments for the widely developed continental shelf of the East China Sea. The river annually transports a runoff discharge of $9.0 \times 10^{11} \text{ m}^3$ that carries approximately $5.0 \times 10^8 \text{ t}$ of sediments (Milliman *et al.*, 1984). Approximately, 78% of the suspended matter is transported during high runoff periods of the river. About 25% of suspended sediment is deposited in the near shore area of the river mouth; in addition, 25% is transported southwards where it settles and remains in the coastal zone. Very little suspended sediment is transported offshore and even less escapes to the north (Milliman *et al.*, 1985).

The extensive tidal flats, which develop along the Yangtze estuarine and coastal zone and from land to sea, can be divided into high, medium, and low tidal flats. The high tidal flats are generally characterized by clayey sediments, the middle tidal flats by silts mixed with clays, and the low tidal flats by silts with fine sands. In addition, the high tidal flats are overgrown mainly by *Phragmites communis* and *Scirpus triquetus* flourishes in the middle tidal flat while there is almost no vegetation in the low tidal flat.

1.2 Collection and pretreatment of sample

According to the background settings of the study area, nine typical sampling stations were selected along the Yangtze estuarine and coastal tidal flats, including Liuhokou (LHK), Shidongkou (SDK), Wusongkou (WSK), Bailonggang (BLG), Chaoyang (CY), Donghai (DH), Fengxin (FX), Luchao (LC), and Jinshan (JS) locations (Fig. 1). Triplicate surface (0–5 cm) sediment samples at each of the stations were taken with a Petite Ponar grab

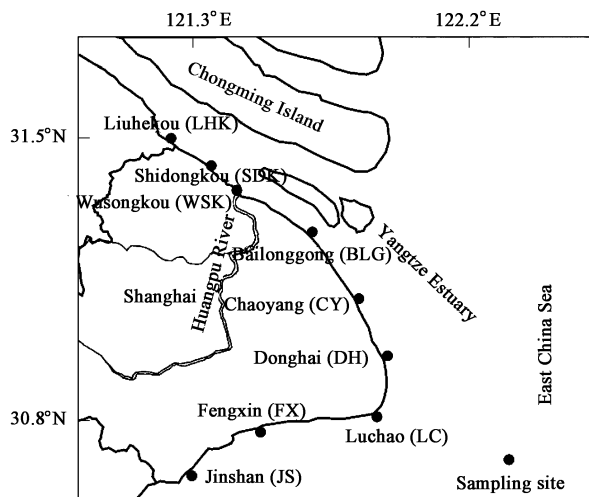


Fig. 1 Location of Yangtze Estuary and the sampling station during field investigation.

sampler from the intertidal flats during the dried and flooded seasons (February and August of 2006, respectively) and were thoroughly homogenized at the sealed polyethylene plastic bags. After carried back to the laboratory, all sediment samples were immediately freeze-dried, crushed, and homogenized for later chemical analysis.

1.3 Extraction of biogenic silica

Numerous techniques and modifications have been used for the determination of biogenic silica in sediments (Eisma and van der Gaast, 1971; Leinen, 1985; Müller and Schneider, 1993; Koning *et al.*, 2002). However, these operational analytical methods do not explicitly target the possible early diagenetic products of biogenic silica. As a consequence, the amounts of biogenic silica stored in sediments are usually underestimated. In this study, for the analysis of biogenic silica and its diagenetic derivatives, the two-step mild acid-mild alkaline extraction procedure was used to leach biogenic silica in sediments, which is evaluated to be more efficient in dissolving sedimentary biogenic silica and its altered products (Michalopoulos and Aller, 2004). In brief, triplicate about 50–70 mg sediment samples were leached for 18 h with 40 ml of 0.1 mol/L HCl in 50 ml polyethylene centrifuge tubes at 25°C. Tubes were periodically shaken. HCl leaches were analyzed for dissolved silica. After centrifugation and removal of HCl, sediment was rinsed briefly and centrifuged twice with 20 ml of distilled water to remove residual acid. Remaining sediment was subsequently extracted for 7 h with 40 ml of 1% Na₂CO₃ at 85°C and serially sampled at 1 h interval. The extracted silica was plotted versus time, and the extrapolated concentration (y intercept) was used to estimate the silica content of the sediment sample (DeMaster, 1981). These various operational pools were defined as: Si-HCl (mild acid leachable), Si-Alk (mild alkaline leachable after acid pretreatment), and t-BSi (total biogenic silica released by mild acid and subsequent mild alkaline treatments = Si-HCl + Si-Alk). To explore early diagenetic changes of biogenic silica, potassium (K) extracted by mild acid and mild alkaline solutions was also analyzed. Therefore, analogous operational pools are defined for K⁺.

1.4 Chemical analysis

Sediment grain size was analyzed using a LS 13 320 Laser grain sizer. Chlorophyll-*a* (Chl-*a*) in sediments was extracted with a 45:45:10 solvent mixture (acetone:methanol:water) for 24 h at 0°C and determined using a spectrophotometric assay and standard equations (Liu *et al.*, 2006). The contents of organic carbon and nitrogen were determined using a CHN elementary analyzer (VVAiro ELIII, Elementar, Germany) after removing carbonate by leaching with 0.1 mol/L HCl (Liu *et al.*, 2006). Dissolved silica in the extractions was measured by the molybdate blue spectrophotometric method (Mortlock and Froelich, 1989). K and Fe in the extraction solutions were analyzed using flame emission or atomic absorption spectroscopy (Liu, 1996).

2 Results

2.1 Physio-chemical characteristics of sediments

Table 1 shows the grain size distributions of sediments from the intertidal flats along the Yangtze estuarine and coastal zone. Intertidal sediments at most sampling stations mainly consisted of fine particles with the grain size less than 63 μm . One-way ANOVA analysis showed that there were the dramatic spatial and seasonal changes in the grain size distribution of sediments at the study area ($p < 0.05$).

Concentrations of sedimentary organic carbon in intertidal sediments from the Yangtze Estuary were relatively low, being 68.9–1,010 $\mu\text{mol/g}$. Remarkable seasonal and spatial differences were observed for the concentrations of sedimentary organic carbon along the Yangtze estuarine and coastal zone (ANOVA, $p < 0.05$; Table 1). Sedimentary organic carbon had a close relationship with fine particles ($< 63 \mu\text{m}$) in sediments ($r = 0.53$, $p = 0.02$).

The contents of organic nitrogen in intertidal sediments varied between 15.2 and 100.1 $\mu\text{mol/g}$. The spatial and temporal variations of organic nitrogen were similar to those of sedimentary organic carbon (Table 1). There was a dramatic and linear correlation of organic nitrogen with organic carbon in the intertidal sediments from the Yangtze Estuary ($r = 0.94$, $p < 0.0001$). Table 1 presents that C/N molar ratios of intertidal sediments were higher than the Redfield ratio of 6.65, except FX station in August. The elevated C/N ratios in the intertidal flats were generally consistent with higher contributions of organic matter from terrigenous sources, which usually showed higher C/N ratios (C/N molar ratios > 12 ; Kukal, 1971; Aitkenhead and McDowell, 2000, Liu *et al.*, 2006).

Chl-*a* concentrations in intertidal sediments ranged from 0.6 to 6.8 and from 0.3 to 3.9 $\mu\text{g/g dw}$ in February and August, respectively. The significant temporal variations of Chl-*a* in sediments were observed (ANOVA, $p < 0.05$),

with the averages of 2.78 and 2.09 $\mu\text{g/g dw}$ in February and August, respectively. Dramatic relationship of Chl-*a* with clay ($< 4 \mu\text{m}$) and sand ($> 63 \mu\text{m}$) were observed ($r = 0.79$, $p < 0.0001$; $r = -0.53$, $p = 0.02$, respectively), which indicated that the grain-size distributions of sediments had a significant influence on Chl-*a*. There was no significant relationship between organic carbon and Chl-*a* in the freshwater area from LHK to CY station ($r = 0.01$, $p = 0.97$), whereas a significant correlation was found for organic carbon and Chl-*a* ($r = 0.92$, $p < 0.0001$) in the brackish area from DH to JS station. This indicated that benthic alga made more contribution to the accumulation of organic matter in intertidal sediments seawards (Liu *et al.*, 2006).

2.2 Biogenic silica pools

The spatial and seasonal distributions of Si-HCl, Si-Alk, and t-BSi in intertidal sediments are shown in Fig. 2.

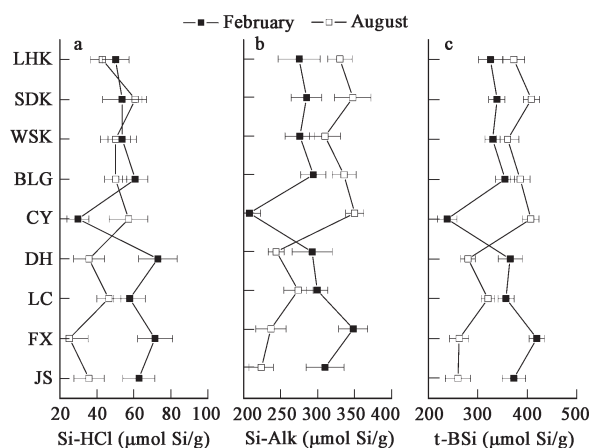


Fig. 2 Concentrations of Si-HCl (a), Si-Alk (b) and t-BSi (c) in August and February intertidal sediments of the Yangtze Estuary. Error bars represent the standard deviation of replicate ($n = 3$) sediment samples.

Table 1 Physio-chemical characteristics of the intertidal sediments in the Yangtze Estuary in February and August, respectively

Station	Grain-size distribution (%)			OC ($\mu\text{mol/g}$)	ON ($\mu\text{mol/g}$)	C/N ratio	Chl- <i>a</i> ($\mu\text{g/g}$)
	Clay ($< 4 \mu\text{m}$)	Silt ($4-63 \mu\text{m}$)	Sand ($> 63 \mu\text{m}$)				
February							
LHK	18.5 \pm 2.2*	67.6 \pm 4.1	13.9 \pm 1.9	472.2 \pm 7.2	39.7 \pm 0.7	11.9 \pm 0.03	0.8 \pm 0.1
SDK	21.9 \pm 1.5	57.7 \pm 5.2	20.4 \pm 3.7	808.0 \pm 18.3	63.9 \pm 1.1	12.6 \pm 0.07	1.5 \pm 0.5
WSK	10.9 \pm 3.4	74.3 \pm 7.8	14.8 \pm 4.4	394.1 \pm 11.3	35.2 \pm 0.7	11.2 \pm 0.1	3.5 \pm 0.4
BLG	20.1 \pm 4.2	76.1 \pm 5.4	3.8 \pm 1.2	403.4 \pm 9.7	36.9 \pm 1.4	10.9 \pm 0.2	1.0 \pm 0.2
CY	6.3 \pm 2.1	23.1 \pm 6.1	70.6 \pm 4.0	176.5 \pm 15.4	15.3 \pm 0.9	11.5 \pm 0.3	0.6 \pm 0.1
DH	35.2 \pm 6.7	57.9 \pm 6.8	6.9 \pm 0.1	576.2 \pm 9.9	64.6 \pm 0.8	8.9 \pm 0.04	6.0 \pm 1.1
LC	13.3 \pm 3.2	82.6 \pm 4.9	4.1 \pm 1.7	200.7 \pm 6.8	19.1 \pm 1.0	10.5 \pm 0.2	0.7 \pm 0.1
FX	27.9 \pm 3.3	69.7 \pm 3.6	2.4 \pm 0.3	386.4 \pm 14.2	42.6 \pm 1.3	9.1 \pm 0.06	4.1 \pm 0.9
JS	45.0 \pm 7.5	52.9 \pm 8.9	2.1 \pm 1.4	617.9 \pm 7.3	71.4 \pm 0.7	8.7 \pm 0.02	6.8 \pm 1.2
August							
LHK	16.9 \pm 2.5	66.6 \pm 7.8	16.5 \pm 5.3	412.1 \pm 6.5	42.6 \pm 0.8	9.7 \pm 0.03	2.4 \pm 0.3
SDK	27.0 \pm 6.4	68.7 \pm 8.6	4.3 \pm 2.2	1,010 \pm 9.3	100.1 \pm 0.6	10.2 \pm 0.03	2.8 \pm 0.2
WSK	18.1 \pm 3.6	68.9 \pm 7.1	12.9 \pm 3.5	531.6 \pm 10.2	41.1 \pm 1.1	12.9 \pm 0.1	3.9 \pm 0.2
BLG	25.3 \pm 5.8	71.6 \pm 8.9	3.1 \pm 3.1	385.4 \pm 6.9	36.4 \pm 0.7	10.6 \pm 0.01	2.9 \pm 0.1
CY	31.1 \pm 3.3	67.2 \pm 3.4	1.7 \pm 0.1	438.4 \pm 12.8	55.3 \pm 0.9	7.9 \pm 0.1	3.8 \pm 0.4
DH	12.4 \pm 2.6	27.9 \pm 6.8	59.7 \pm 4.2	153.1 \pm 13.6	21.6 \pm 1.5	7.1 \pm 0.1	0.3 \pm 0.1
LC	20.5 \pm 6.1	67.6 \pm 7.8	11.9 \pm 1.7	325.1 \pm 8.6	35.5 \pm 0.6	9.2 \pm 0.09	0.4 \pm 0.2
FX	6.3 \pm 2.3	53.8 \pm 8.4	39.9 \pm 6.1	68.9 \pm 17.4	15.2 \pm 1.3	4.5 \pm 0.8	1.1 \pm 0.1
JS	14.9 \pm 4.1	47.1 \pm 6.9	38.0 \pm 2.8	246.2 \pm 12.7	32.5 \pm 0.8	7.6 \pm 0.2	1.3 \pm 0.3

* Mean \pm SD ($n = 3$). LHK: Liuhekou; SDK: Shidongkou; WSK: Wusongkou; BLG: Bailonggang; CY: Chaoyang; DH: Donghai; LC: Luchao; FX: Fengxin; JS: Jinshan. OC: organic carbon; ON: organic nitrogen.

The contents of Si-HCl in sediments were in the range of 25.1–72.9 $\mu\text{mol Si/g}$, with the averages of 56.9 and 44.9 $\mu\text{mol Si/g}$ in February and August, respectively. Si-HCl in February sediments gradually increased seawards while Si-HCl in August sediments had a tendency opposite to those of February (Fig.2a). As shown in Fig.3, Si-HCl had a close relationship with Fe extracted by 0.1 mol/L HCl, suggesting that Si released by 0.1 mol/L HCl may be derived from Fe, Mn, and Al oxides (Michalopoulos and Aller, 2004). Si-Alk in February and August sediments has the concentrations of 208.1–348.2 and 224.3–350.4 $\mu\text{mol Si/g}$, respectively. Fig.2b shows that Si-Alk in February sediments gradually increased from LHK to JS station, whereas it decreased in August sediments. Total biogenic silica (t-BSi) in intertidal sediments varied from 237.7 to 419.4 and from 259.7 to 408.2 $\mu\text{mol Si/g}$ in February and August, respectively. The ratios of Si-HCl/t-BSi and Si-Alk/t-BSi in intertidal sediments were in the range of 9.6%–19.9% and 80.1%–90.4% respectively, indicating that the t-BSi pools were dominated by Si-Alk. Additionally, it is found that the distribution patterns of t-BSi in sediments were similar to Si-Alk (Figs.2b and 2c).

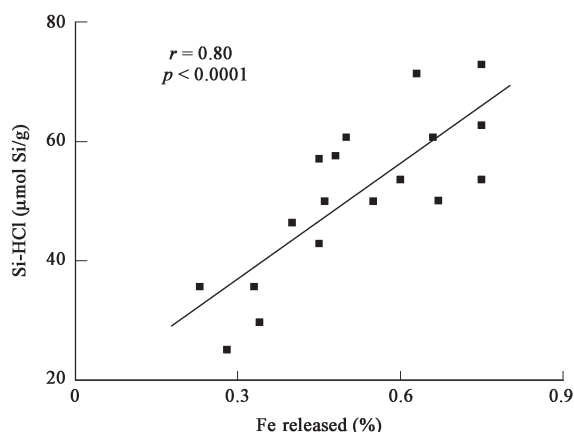


Fig. 3 Correlation of Si-HCl with Fe released from intertidal sediments during mild acid extraction.

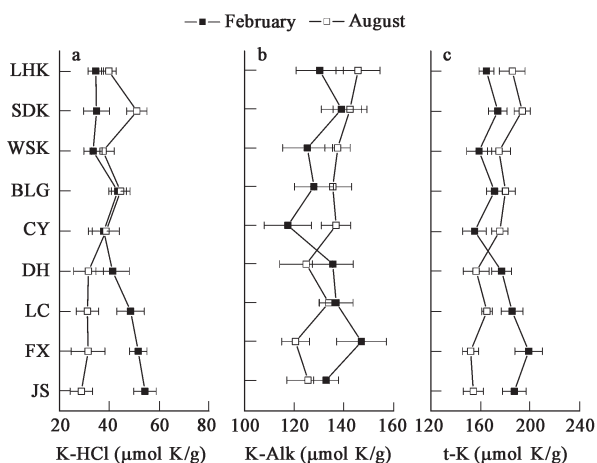


Fig. 4 Concentrations of K-HCl (a), K-Alk (b) and t-K (c) in August and February intertidal sediments of the Yangtze Estuary. Error bars represent the standard deviation of replicate ($n = 3$) sediment samples.

2.3 Labile K pools

As in the case of Si, a well-defined labile K pool in sediments is given in Fig.4. K-HCl in intertidal sediments ranged from 33.5 to 54.4 and from 28.8 to 51.1 $\mu\text{molK/g}$ in February and August, respectively (Fig.4a). K-Alk in sediments was in the range of 117.5–147.1 $\mu\text{molK/g}$, with averages of 132.5 and 133.7 $\mu\text{molK/g}$ in February and August, respectively (Fig.4b). Total labile K (t-K) in February and August sediments respectively ranged from 155.3 to 198.8 and from 152.1 to 193.6 $\mu\text{molK/g}$ (Fig.4c). K-HCl/t-K and K-Alk/t-K in sediments had the values of 18.7%–29.0% and 71.0%–81.3%, respectively. This showed that t-K was mainly released from sediments during mild alkaline extraction.

3 Discussion

3.1 Sediment characteristics and biogenic silica relations

The effects of sediment grain-size on the accumulation of biogenic silica were discussed in previous studies (Bernárdez *et al.*, 2005, 2006). For example, Bernárdez *et al.* (2005) found that there was a general tendency for higher values of biogenic silica in muddy fractions and lower values in sandy fractions. Similarly, significant correlations were also found for the grain size distributions of sediments and different biogenic silica pools in the intertidal sediments of the Yangtze Estuary (Fig.5). It is shown that both Si-HCl and Si-Alk had positive relationships with the $< 4 \mu\text{m}$ and $4\text{--}63 \mu\text{m}$ fractions of sediments, whereas they showed negative relationships with the $>63 \mu\text{m}$ fractions. This further confirms that grain size distribution can significantly affect biogenic silica contents in sediments, mainly because coarser grains provide a dilution effect (Bernárdez *et al.*, 2005). In addition, there were the pronounced spatial and seasonal changes in the grain size distribution of sediments at the study area (ANOVA, $p < 0.05$). However, the grain size distribution of sediments was significantly controlled by the strong and complicated hydrodynamic conditions in the Yangtze estuarine and coastal zone (Chen, 1988). Therefore, it is considered that the complicated hydrodynamic mechanisms might play an important role in dominating the spatial distributions of biogenic silica along the Yangtze estuarine and coastal zone.

Close relationships of biogenic silica with organic carbon and nitrogen were found in the present study (Fig. 6). This reflects that there was a strong coupling between biogenic silica and organic matter biogeochemical cycles in the intertidal sediments of the Yangtze Estuary. OC/Chl-*a* weight ratio can be commonly used to evaluate the contribution of phytomicrobenthic production to organic matter in sediments (Wassmann *et al.*, 1990; Descy and Gosselain, 1994; Bernárdez *et al.*, 2005). The ratios of OC/Chl-*a* in the intertidal sediments at the study area ranged from 779.7 to 9,071.5, and were considerably higher than the values considered to be the representatives

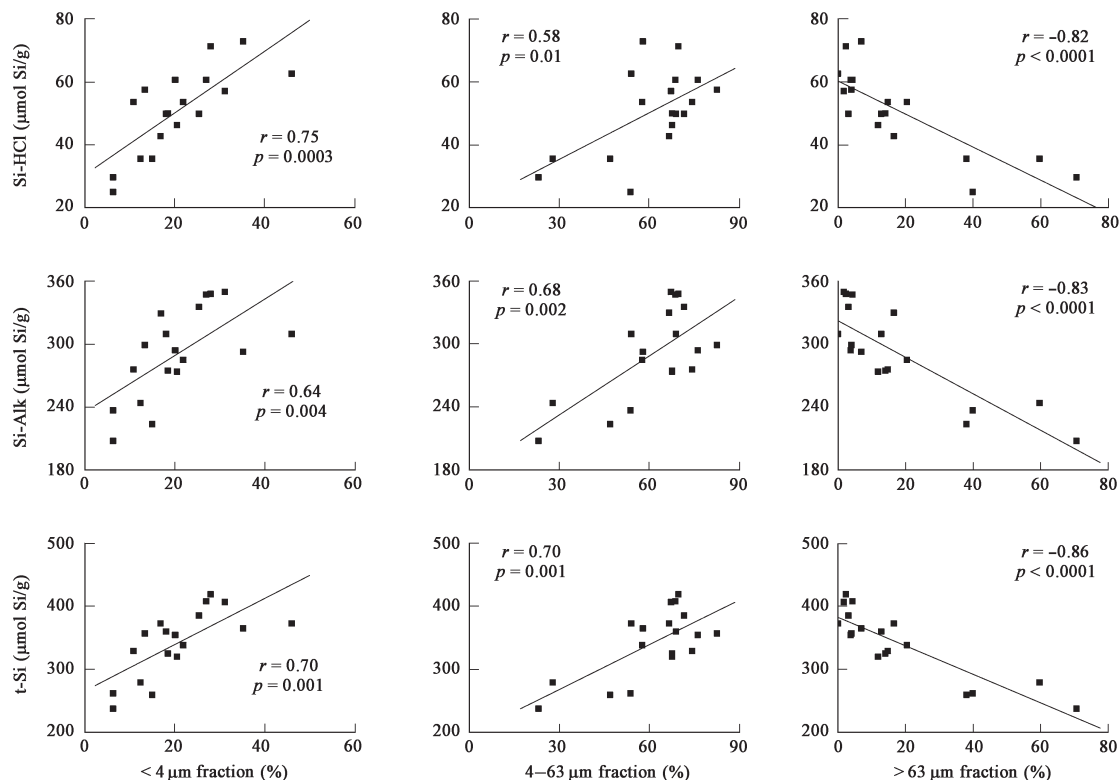


Fig. 5 Correlation of Si-HCl, Si-Alk and t-BSi with the grain size distributions (< 4 μm, 4–63 μm, and > 63 μm fractions) of intertidal sediments.

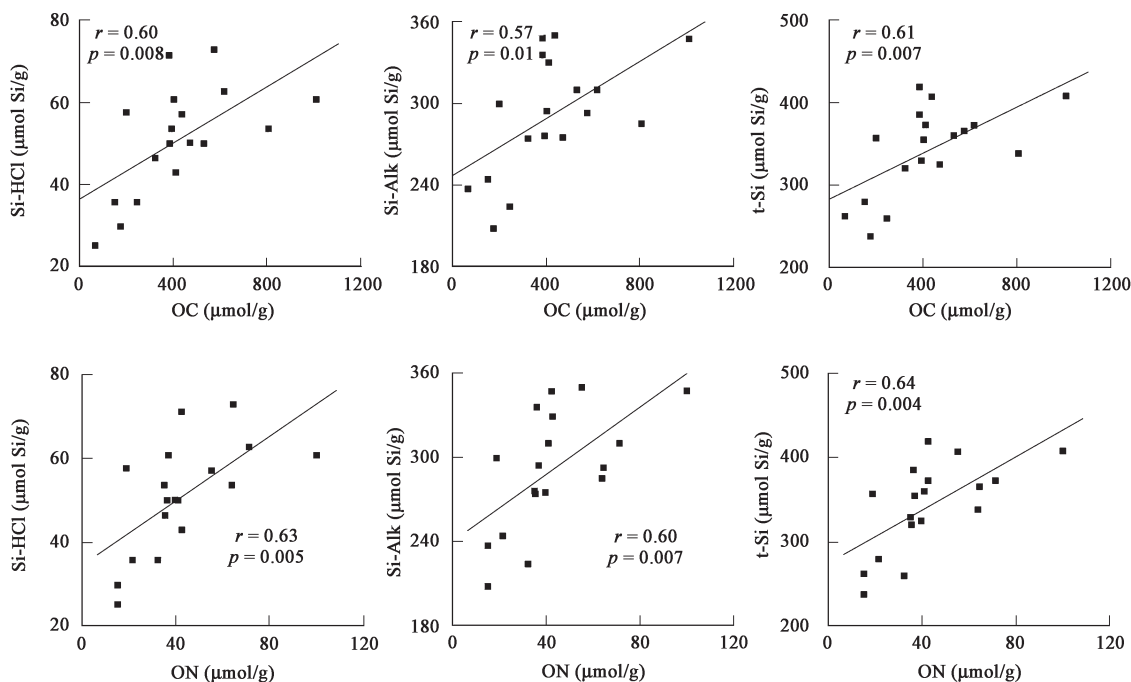


Fig. 6 Correlation of Si-HCl, Si-Alk, and t-BSi with organic carbon (OC) and organic nitrogen (ON) in intertidal sediments.

of living autotroph communities (Redfield *et al.*, 1963), which strongly supported the presence of detrital matter from riverine inputs (Liu *et al.*, 2006) and microbiological decomposition of salt marsh plants (e.g., *P. communis* and *S. triquetra*) (Norris and Hackney, 1999). Therefore, it is hypothesized that detrital biogenic silica makes a significant contribution to accumulation of biogenic silica in intertidal sediments. Additionally, dramatic correlations were observed for biogenic silica and Chl-*a* in sediments

(Fig. 7), suggesting that *in situ* phytomicrobenthic production is also an important source of biogenic silica in the intertidal environment (Bernárdez *et al.*, 2005). The OC/t-BSi and ON/t-BSi molar ratios in intertidal sediments were in the range of 0.3–2.5 and 0.05–0.24, respectively. The values were lower than their corresponding Redfield ratios (OC/BSi \approx 6.63, ON/BSi \approx 1). This implies more rapid recycling of OC and ON in the intertidal sediments of the Yangtze Estuary as compared to biogenic silica.

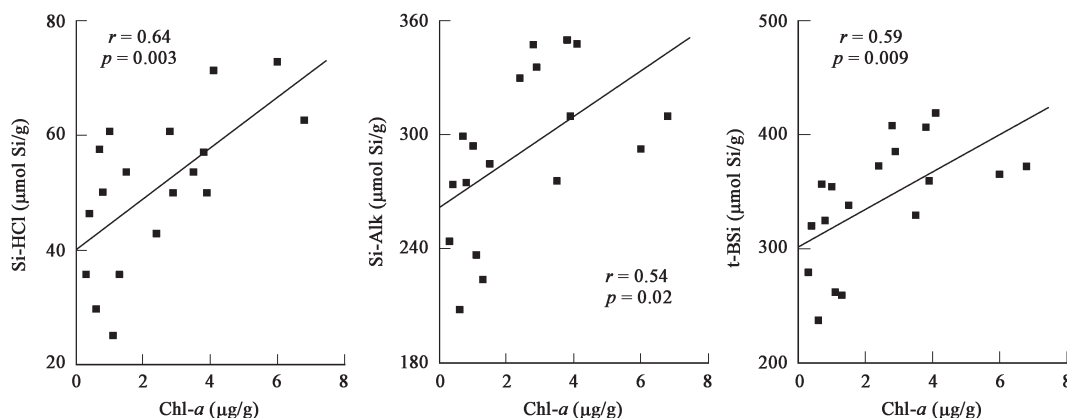


Fig. 7 Correlation of Si-HCl, Si-Alk, and t-BSi with chlorophyll-a (Chl-a) in intertidal sediments.

3.2 Early diagenetic changes of biogenic silica

It is well established that the surfaces of biogenic silica particles in sediments are often quickly coated and enriched with Fe and Al oxides (Katamani *et al.*, 1988; Machin, 1989; Richert *et al.*, 2002). This is also supported by the significant relationship of Si-HCl with Fe released by 0.1 mol/L HCl in the present study ($r = 0.80$, $p < 0.0001$). The close association of Si-HCl with Fe was believed to be mainly due to the precipitation of Fe oxides with silicate from early diagenetic processes of biogenic silica in the intertidal sediments (Machin, 1989; McManus *et al.*, 1995). In addition, significant correlations were observed for the labile K and Si released during the successive mild acid-mild alkaline extractions of sediment (Fig.8). This shows that reactive K and Si pools are highly coherent in intertidal sediments of the Yangtze Estuary. The geometric mean regression slopes (dSi/dK) in intertidal sediments are 2.5, 6.0, and 4.2 for Si-HCl/K-HCl, Si-Alk/K-Alk, and t-BSi/t-K, respectively. These slopes correspond closely to the Si/K ratio found in authigenic clays and altered diatom material obtained in both the field and laboratory experiments (Michalopoulos and Aller, 2004). Therefore, it is concluded that biogenic silica in the intertidal sediments was involved in the formation of aluminosilicate phases by reverse-weathering reactions during early diagenesis (Hover *et al.*, 2002; Michalopoulos and Aller, 2004).

4 Conclusions

Si-HCl and Si-Alk in February sediments were respectively in the range of 29.7–72.9 and 208.1–348.2 $\mu\text{mol Si/g}$, while they respectively varied from 25.1 to 60.7 $\mu\text{mol Si/g}$ and from 224.3 to 350.4 $\mu\text{mol Si/g}$ in August sediments. Total biogenic silica in February and August sediments respectively had the values of 237.7–419.4 and 259.7–408.2 $\mu\text{mol Si/g}$. The ratios of Si-HCl/t-BSi and Si-Alk/t-BSi showed that t-BSi was mainly dominated by Si-Alk, which averagely occupied 83% and 87% of total biogenic silica in February and August sediments, respectively. Significant correlations between grain size distributions of sediments and biogenic silica pools suggested that grain size distributions exerted a significant influence on the accumulation of biogenic silica contents in intertidal sediments. It is also concluded that the complicated hydrodynamic mechanisms might play an important role in dominating the spatial distributions of biogenic silica along the Yangtze estuarine and coastal zone. Close relationships of biogenic silica with organic carbon and nitrogen indicated the strong coupling between biogenic silica and organic matter biogeochemical cycles in intertidal sediments. Compared with Redfield ratios, the relatively lower OC/t-BSi and ON/t-BSi molar ratios implied more rapid recycling of OC and ON in intertidal sediments than biogenic silica. Additionally, the close association of labile K with Si indicated that biogenic silica

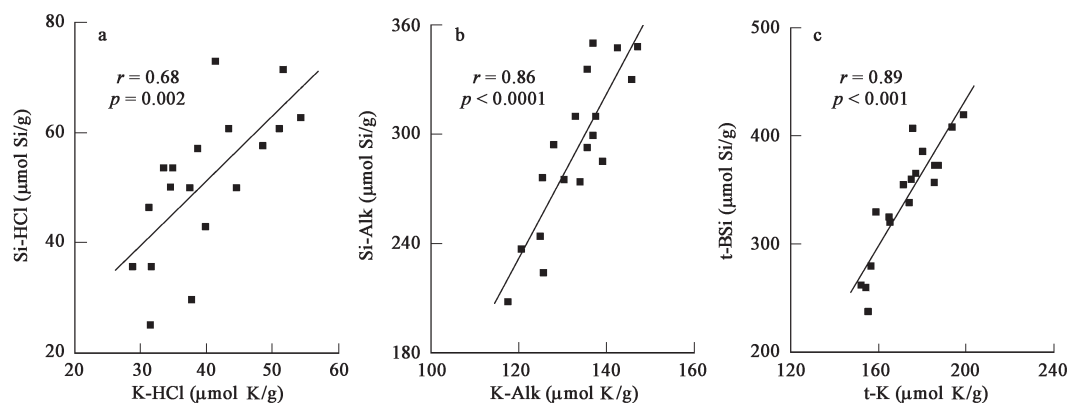


Fig. 8 Correlation between Si and K released from intertidal sediments during mild acid-mild alkaline extraction. (a) K-HCl vs. Si-HCl; (b) K-Alk vs. Si-Alk; (c) t-K vs. t-BSi.

in the intertidal sediments was involved in the formation of aluminosilicate phases by reverse-weathering reactions during early diagenesis.

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