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# 1 Revisiting the biogenic silica burial flux determinations: A case study 2 for the East China seas

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19 **Keywords: biogenic silica, alkaline digestion, analytical methods, burial flux, Coastal and**  
20 **Continental Margin Zones, East China seas, marine silicon cycle.**

## 21 1. Abstract

22 The Coastal and Continental Margin Zones (CCMZs) contribute to 40% of the total burial flux of  
23 biogenic silica (bSi) of the world ocean. However, the accurate determination of the bSi content  
24 (bSiO<sub>2</sub>%) in marine sediments remains a challenge. The alkaline methods commonly used to  
25 quantitatively determine bSiO<sub>2</sub>% can completely digest the amorphous silica of diatoms but are less  
26 effective at digesting radiolarians and sponge spicules. In addition, the lithogenic silica (lSi) found in  
27 sediments is partly digested during these alkaline extractions, which can bias the accuracy of the  
28 determined bSiO<sub>2</sub>%. This is of importance in CCMZs where the lSi:bSi ratio is high. In this study, we  
29 examined sediments collected in the CCMZs of East China seas, an environment of peculiar interest  
30 given the large amount of lSi deposited by the Yellow River and the Yangtze River. The results show  
31 that alkaline digestions using stronger solutions and pretreatment steps resulted in an overestimate of  
32 the bSiO<sub>2</sub>% due to increased leaching of silica mainly from authigenic silicates and clays, whereas  
33 weak digestions underestimated the bSiO<sub>2</sub>% owing to incomplete digestion of sponge spicules. We  
34 found that the use of the Si/Al method accurately corrects for the lSi fraction in marine sediments, and  
35 thereby improves the determinations of bSiO<sub>2</sub>% in the sediments of East China seas CCMZs. Ensuring

36 full digestion of all bSi remains challenging, in particular for sponge spicules, motivating both  
37 verifications via microscopy and longer extraction times. To emphasize the influence of these  
38 methodological differences, we revised the bSi burial flux in the East China seas and provide a new  
39 estimate of  $253 (\pm 286) \text{ Gmol-SiO}_2 \text{ yr}^{-1}$ , which is one third of the previous estimates. We discuss the  
40 potential contribution from radiolarian and sponges and we propose a new general protocol for the  
41 determination of bSi in sediments that minimizes the methodological bias in bSi determination.

## 42 **2. Introduction**

43 Coastal and Continental Margin Zones (CCMZs) are distinct settings for the interrogation of global  
44 marine biogeochemical cycling of silica (Si), climate change and marine ecological processes (Jeandel  
45 and Oelkers, 2015; Jeandel, 2016; Tréguer et al., 2018; Rahman et al., 2019). The CCMZs represent  
46 approximately 10% of the global marine surface area ( $3.61 \times 10^8 \text{ km}^2$ ) (Costello et al., 2010), and  
47 account for 40% of the total biogenic silica (bSi) burial ( $\sim 9.2 \text{ Tmol-Si yr}^{-1}$ ) in the global ocean  
48 (DeMaster, 2019; Tréguer et al., 2021). This estimate was based solely on the burial of diatom bSi.  
49 However, marine Si is also removed through reverse weathering in major tropical and subtropical deltas  
50 (Rahman et al., 2016, 2017), the burial of siliceous sponges spicules predominantly on the continental  
51 shelf and margins (DeMaster, 2019; Maldonado et al., 2019), and the burial of radiolarian tests  
52 (Maldonado et al., 2019). Recent work estimated that if all of these processes are taken into account,  
53 the burial flux of Si that occurs mainly within the CCMZs, removes 5.0 to 10.1  $\text{Tmol-Si yr}^{-1}$  (DeMaster,  
54 2019; Tréguer et al., 2021), which is equivalent to roughly one to two-thirds of the global Si output  
55 flux ( $15.6 \text{ Tmol-Si yr}^{-1}$ ) from the marine environment (DeMaster, 2019; Tréguer et al., 2021).

56 The calculation of the marine Si budget at the global or local level is dependent on the precision  
57 and accuracy of the bSi measurements (DeMaster, 1991). Within the CCMZs, the combination of lSi  
58 with bSi decreases the reactive surface area of biogenic opal and lowers its solubility (Dixit and Van  
59 Cappellen, 2003; Varkouhi et al., 2020; Varkouhi and Wells, 2020), which enhances the bSi burial  
60 efficiency. However, high precipitation rates of terrestrial lSi dilute the bSi and result in an opal-  
61 depleted coastal sediment (DeMaster, 2002; Wu et al., 2017; Wu and Liu, 2020). Therefore, accurate  
62 determination of the bSi content ( $\text{bSiO}_2\%$ ) in the CCMZs sediment is particularly challenging owing  
63 to its characteristically low  $\text{bSiO}_2\%$ , high lithogenic silica (lSi; clay mineral, authigenic aluminosilicate,  
64 quartz) content (DeMaster, 1991), and complexity of bSi types (e.g. diatoms, phytolith, radiolarians,  
65 sponge spicules; Figure 1A) (DeMaster, 1991; Maldonado et al., 2019). Among several different  
66 techniques (e.g., X-ray Diffraction (Goldberg, 1958; Eisma and van der Gaast, 1971), point counts of  
67 siliceous microfossil (Pudsey, 1992; Varkouhi et al., 2020a), infrared analysis (Fröhlich, 1989),

68 normative calculation technique (Leinen, 1977), wet chemical method (DeMaster, 1981; Muller and  
69 Schneider, 1993; Mortlock and Froelich, 1989)), wet chemical method is the most commonly used  
70 method for determining the bSiO<sub>2</sub>% in marine sediments (Conley, 1998). Considering the complex  
71 sediment composition of CCMZs sediments, a mild alkaline leach (0.1 M Na<sub>2</sub>CO<sub>3</sub>) is recommended to  
72 minimize the interference of lSi in bSi determination when using the wet chemical method (DeMaster,  
73 1981). However, a mild alkaline leach underestimates the quantity of bSi due to an incomplete  
74 extraction of more resistant bSi (Figure 1A), such as radiolarians (Mortlock and Froelich, 1989; Müller  
75 and Schneider, 1993) and siliceous sponge spicules (Maldonado et al., 2019). Nonetheless, complete  
76 digestion of resistant bSi using a strong alkaline solution can introduce additional bias due to the  
77 inevitable attack on lSi. To accurately determine bSiO<sub>2</sub>% in sediment from different marine  
78 environments, various kinds of wet alkaline methods with different digestion conditions (i.e., alkaline  
79 solution, sample to solution ratio, extraction temperature, duration of extraction and pre-treatment of  
80 sediment by HCl and H<sub>2</sub>O<sub>2</sub> prior to alkaline digestion) have been proposed and applied in the literature  
81 (DeMaster, 1981; Mortlock and Froelich, 1989; Müller and Schneider, 1993; Kamatani and Oku, 2000;  
82 Conley and Schelske, 2001; Koning et al., 2002; Liu et al., 2002; Olivarez Lyle and Lyle, 2002). These  
83 methods were grouped into two different types: (1) Si/time alkaline digestion and (2) Si/Al alkaline  
84 digestion (Swann, 2010). The Si/time method (Figure 1B), which is the conventional wet alkaline  
85 method, requires the measurement of alkaline extracted Si concentration and corrects the lSi fraction  
86 based on the assumption of the difference in dissolution kinetics between bSi (non-linear dissolution)  
87 and lSi (linear dissolution) (DeMaster, 1981). The Si/Al alkaline digestion method (Figure 1B) requires  
88 the measurement of alkaline extracted Si and Al concentrations, and corrects the lSi fraction based on  
89 the assumption that the Si:Al ratio of lSi is low (Si:Al < 5, Figure 1A) and the extracted Al is mainly  
90 lSi origin (Kamatani and Oku, 2000; Koning et al., 2002). Previous studies found methodological  
91 differences in the bSiO<sub>2</sub>% between Si/time and Si/Al methods in both lacustrine (Swann, 2010) and  
92 marine sediments (Barão et al., 2015). It has been noted that major biases in the bSiO<sub>2</sub>% can be  
93 generated among different wet alkaline methods (DeMaster, 1991; Gehlen and van Raaphorst, 1993;  
94 Schlüter and Rickert, 1998; Kamatani and Oku, 2000; Barão et al., 2015), influencing the estimation  
95 of the bSi burial flux especially in the opal-depleted (bSiO<sub>2</sub>-depleted) sediment of the CCMZs  
96 (DeMaster, 1991, 2002; Tréguer et al., 2021).

97 The East China seas, which consists of the Bohai Sea (BH), the Yellow Sea (YS), and the East  
98 China Sea (ECS), is one of the largest CCMZs in the Northwest Pacific Ocean. The East China seas  
99 are characterized by high sedimentation rates (Qiao et al., 2017), low bSiO<sub>2</sub>% (< 3%) and high  
100 lithogenic material content (> 70%) (Liu et al., 2002; Wu et al., 2017; Wu and Liu, 2020). Previous

101 studies demonstrated that the burial of bSi in the East China seas is  $924 (\pm 693) \text{ Gmol-SiO}_2 \text{ yr}^{-1}$  (Liu  
102 et al., 2016; Wu et al., 2017; Wu and Liu, 2020), accounting for ~5% of the bSi burial in the global  
103 ocean. These estimations were based on the bSiO<sub>2</sub>% determined using several alkaline digestion  
104 techniques, such as using different concentrations of alkaline solution (0.1 M Na<sub>2</sub>CO<sub>3</sub>, 2% Na<sub>2</sub>CO<sub>3</sub>,  
105 2.0 M Na<sub>2</sub>CO<sub>3</sub>), duration of the alkaline digestion (5 h, 8 h) and pre-treatment process (with HCl and  
106 H<sub>2</sub>O<sub>2</sub> prior to alkaline extraction) that may underestimate or overestimate the bSi content due to the  
107 incomplete digestion of bSi or the interference of lSi in bSi determination (Kamatani and Oku, 2000;  
108 Barão et al., 2015) and leaching of authigenic silicates activated by acid treatment (Michalopoulos and  
109 Aller, 2004; Rahman et al., 2016; Pickering et al., 2020). Such an under- or overestimate of the bSi  
110 content will influence the magnitude of the burial flux of bSi determined for the CCMZs where the  
111 sediment load is high and the bSi content is low. In addition, diatoms, radiolarians (Liu et al., 2017;  
112 Qu et al., 2020a, 2020b), sponge spicules (Chou et al., 2012) and living siliceous sponges (Zhang et  
113 al., 2003) were observed in the sediment of the East China seas. However, the influence of their  
114 presence on the determination of bSi content and consequent role in marine Si cycling for this region,  
115 is still not defined. The radiolarians and siliceous sponge spicules are more resistant to alkaline attacks  
116 than diatoms (DeMaster, 1981; Muller and Schneider, 1993), thus the types of bSi need to be  
117 considered when characterizing the bSi content of sediments (DeMaster, 1991).

118 This study aims to provide an accurate determination of the burial flux of the East China seas  
119 CCMZs by conducting a thorough evaluation of the potential methodological biases influencing the  
120 determination of bSi. To evaluate these methodological biases, multiple samples of characteristically  
121 diverse marine sediment from the East China seas were measured for bSiO<sub>2</sub>% using different alkaline  
122 solution concentrations (0.1 M, 0.2 M, 2.0 M Na<sub>2</sub>CO<sub>3</sub>), with and without pretreatment. In addition, the  
123 types of marine bio-siliceous structures (diatoms, radiolarian tests, and sponge spicules) and their  
124 abundances in the different sediment samples were quantified to select an appropriate wet alkaline  
125 method. Further, the bSiO<sub>2</sub>% determined using the Si/time method (20 h digestion in 0.1 M Na<sub>2</sub>CO<sub>3</sub>)  
126 and the Si/Al method (1 h digestion in 0.5 M NaOH) were compared for an accurate evaluation of the  
127 alkaline extracted Si (bSi and lSi) from sediments of the CCMZs. The detailed evaluation of these  
128 methodological biases resulted in the production of a revised evaluation of the burial flux of bSi for  
129 the East China seas CCMZ and a discussion on the implementation of a standardized method for the  
130 determination of bSiO<sub>2</sub>% in similar depositional environments.

### 131 **3. Materials and methods**

#### 132 **3.1. Study area and sample locations**

133 The East China seas (Figure 2) consists of the BH (surface area:  $7.73 \times 10^4 \text{ km}^2$ ), the YS (surface  
134 area:  $38 \times 10^4 \text{ km}^2$ ), and the ECS (surface area:  $77 \times 10^4 \text{ km}^2$ ) (Qiao et al., 2017). The semi-enclosed  
135 BH and YS are shallow water bodies with an average water depth of 18 m (maximum 85 m) and 44 m  
136 (maximum 140 m) respectively. About 21 large rivers (length of mainstream  $> 100 \text{ km}$ ) deliver  $782.2$   
137  $\times 10^9 \text{ kg yr}^{-1}$  of sediment to the BH, with more than 90% delivered by the Yellow River. Roughly 30  
138 rivers discharge  $13.0 \times 10^9 \text{ kg yr}^{-1}$  of sediment into the YS (Qiao et al., 2017). However, up to 90% of  
139 its total sediment burial flux ( $414.6 \times 10^9 \text{ kg yr}^{-1}$ ) is transported from the BH and 5.7% is eroded  
140 sediment from the old Yellow River (Qiao et al., 2017). The ECS consists of a broad continental shelf  
141 and the Okinawa Trough, with an average water depth of 349 m (maximum 2700 m). About 18 rivers  
142 deliver  $490.5 \times 10^9 \text{ kg yr}^{-1}$  of sediment into the ECS, of which approximately 80% is delivered from  
143 the Yangtze River (Qiao et al., 2017). The bSiO<sub>2</sub>% in surface sediments of the BH, YS and ECS were  
144  $0.92 \pm 0.24\%$  (Liu et al., 2002),  $2.20 \pm 0.79\%$  (Wu et al., 2017) and  $1.97 \pm 0.53\%$  (Wu and Liu, 2020),  
145 respectively, and are considered to be relatively low values ( $< 3\%$  is considered a threshold value for  
146 bSi concentrations) and requires an accurate determination (Koning et al., 2002; Liu et al., 2002;  
147 DeMaster, 2019; Tréguer et al., 2021).

148 Field observations were conducted in the East China seas from 2008 to 2013. The sampling sites  
149 are shown in Figure 2. At each sampling site, surface sediment samples (0 – 2 cm) were collected using  
150 a stainless-steel box sampler and subsequently packed in sealed plastic bags at  $-20 \text{ }^\circ\text{C}$  on board. Frozen  
151 samples were then freeze-dried in the laboratory and stored at room temperature ( $\sim 20 \text{ }^\circ\text{C}$ ) until analysis.  
152 Two sediment samples for interlaboratory comparison (sample code: Still Pond, R-64) were also  
153 measured using the Si/time (0.1 M Na<sub>2</sub>CO<sub>3</sub>, 20 h digestion) and the Si/Al (0.5 M NaOH, 1 h digestion)  
154 alkaline digestion method. The location of these sampled sediments and their descriptions are given in  
155 Conley (1998).

## 156 **3.2. Analytical methods**

### 157 **3.2.1. The biogenic silica types and abundance**

158 The different types of bSi and their abundance in the sediment of the East China seas were  
159 determined using an inverted microscope (Zeiss Axio Observer A1) at 10X magnification. The  
160 abundance (numbers per gram:  $10^3 \text{ g}^{-1}$  dry sediments) of different marine bSi organisms in samples A3,  
161 C4, C7, C12, and F2 were examined optically (see Figure 2 for sample locations). The samples were  
162 selected based on their water depth and sediment type (A3, F2: silty-clay; C4, C7: sandy; C12: clay-  
163 silt). In order to prepare the samples for microscopic observation, ca. 5 – 10 mg of homogenized dry  
164 sediment was pretreated using 1.0 M HCl (10 mL) and 10% H<sub>2</sub>O<sub>2</sub> (10 mL) and heated at  $60 \text{ }^\circ\text{C}$  for 2 h.

165 The solution was subsequently discarded after centrifugation (4000 rpm, 5 min) and the residual  
166 sediment was rinsed three times using Milli-Q water (18.2 M $\Omega$ ). The decarbonated sediment samples  
167 were homogenized in Milli-Q water (1 mL) and the samples were put on a glass microscope slide for  
168 optical observation. The abundance of individuals for different types of bSi (i.e., diatom frustules,  
169 radiolarian skeletons and siliceous sponge spicules) was counted and normalized as the number of  
170 individuals per gram of dry sediment (10<sup>3</sup> g<sup>-1</sup>).

### 171 **3.2.2. Biogenic silica**

172 The content of bSi found in the sediments in this study is expressed as bSiO<sub>2</sub>% (molar mass of  
173 bSiO<sub>2</sub>: 60 g mol<sup>-1</sup>) to avoid potential errors associated with the difference in bond water content of  
174 different types of bSi and/or ages of siliceous organisms.

175 Two wet chemical methods were used to quantify the bSiO<sub>2</sub>%; the Si/time method (DeMaster, 1981;  
176 Conley and Schelske, 1993, 2001; Liu et al., 2002) and the Si/Al method (Koning et al., 2002; Barão  
177 et al., 2014, 2015). For the Si/time alkaline digestion, samples were digested using a 0.1 M Na<sub>2</sub>CO<sub>3</sub>  
178 solution for 20 h. Before wet-alkaline digestion, freeze-dried marine sediment was gently ground using  
179 an agate pestle and mortar. The grinding process aims to homogenize the sediment. Sediment (~100  
180 mg) was then weighed into a 50 mL polypropylene copolymer centrifuge tube (Nalgene no. 3119-0050;  
181 Caps no. DS3132-0024) or 50 mL fluorinated ethylene propylene (FEP) centrifuge tube (Nalgene no.  
182 3114-0050; Caps no. DS3131-0024). An alkaline solution (40 mL, 0.1 M Na<sub>2</sub>CO<sub>3</sub>) was added to the  
183 centrifuge tube using a calibrated 10 mL pipette (10 ± 0.01 mL, Eppendorf). The sample to liquid ratio  
184 (S/L) was ca. 2.5 g/L. The tubes were tightly capped after the addition of the alkaline solution and the  
185 sediments were well mixed using a Vortex. Samples were immediately placed into a shaking water  
186 bath (Julabo SW22) pre-heated to 85 °C with an oscillation frequency of 100 rpm. An aliquot of 200  
187  $\mu$ L clear centrifugation supernatant was taken from the extraction solution at each time interval and  
188 neutralized using 1.0 M HCl solution. Later, the neutralized samples were diluted by Milli-Q water  
189 (18.2 M $\Omega$  cm<sup>-1</sup>) to 10 mL, then the dissolved silicic acid (dSi) was measured following the molybdate-  
190 blue method (Grasshoff et al., 1983) using a spectrometer as described in Mortlock and Froelich (1989).  
191 Determination of the blanks during each extraction experiment showed the Si from both the reagent  
192 and tube were negligible. Additionally, alkaline digestion of pre-treated (P; pretreating the sediment  
193 using 1.0 M HCl and 10% H<sub>2</sub>O<sub>2</sub>) and non-pretreated (NP) sediment were performed using 0.1 M, 0.2  
194 M, 2.0 M Na<sub>2</sub>CO<sub>3</sub> solutions to determine the effect of the concentration of Na<sub>2</sub>CO<sub>3</sub> and pretreatment  
195 process (P vs. NP) on bSi determination.

196 In this study, the bSiO<sub>2</sub>% was determined following the calculation method described by Liu et al,  
197 (2002) where sediments undergo an 8 h digestion. In addition, the bSiO<sub>2</sub>% was also calculated  
198 following the method described in DeMaster (1981), Liu et al, (2002) and Conley and Schelske, (1993,  
199 2001) when sediment was digested in a 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution for 20 h. The method described in  
200 Conley and Schelske (1993, 2001) was applied for quantifying the diatom bSi, radiolarian and/or  
201 sponge bSi (Figure 1B). Moreover, the bSiO<sub>2</sub>% analyzed according to the method described by  
202 Mortlock and Froelich (1989) was also performed.

203 The Si/Al method refers to the continuous analysis of Si and Al concentrations in the alkaline  
204 digestion at a high sampling resolution time (Figure S1). In this study, bSiO<sub>2</sub>% was measured following  
205 the continuous analysis method (Koning et al., 2002; Barão et al., 2015) at the University of Antwerp  
206 (Belgium). The dSi and dissolved Al (dAl) in alkaline solution (0.5 M NaOH) were measured  
207 continuously at 1 second (s) resolution (Müller and Schneider, 1993). Freeze-dried sediment samples  
208 (~100 mg) were added into a stainless-steel vessel with an initial 180 mL of 0.5 M NaOH pre-heated  
209 to 85 °C. The S/L ratios of all the analyses range from 0.56 to 0.89 g/L. The closed vessel (to avoid  
210 evaporation) is directly connected to a continuous analyzer (Skalar<sup>®</sup>, The Netherlands) and a rotating  
211 motor continuously homogenizes the sample in the extraction liquid, maintaining a constant S/L ratio.  
212 The dSi concentration is determined according to the molybdate-blue method (Grasshoff et al., 1983),  
213 while dAl is determined according to the fluorometric method (Hydes and Liss, 1976). Standard  
214 samples of dSi and dAl with concentrations of 1 mg L<sup>-1</sup>, 2 mg L<sup>-1</sup>, 4 mg L<sup>-1</sup>, 6 mg L<sup>-1</sup>, 8 mg L<sup>-1</sup>, 10 mg  
215 L<sup>-1</sup>, 20 mg L<sup>-1</sup>, 30 mg L<sup>-1</sup>, and 40 mg L<sup>-1</sup> were used for calibration, and only the linear regression curves  
216 with correlation coefficients  $\geq 0.999$  were accepted according to previous studies (Barão et al., 2015).  
217 Two independent reference solutions (with concentrations of 3 mg L<sup>-1</sup>, and 9 mg L<sup>-1</sup> of dSi and dAl)  
218 were tested before and after the continuous alkaline extractions to guarantee an analytical error below  
219 5%. The stock standard solutions for Si and Al were made using Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O (Sigma-Aldrich S4392)  
220 and KAl (SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (Merck 101047).

### 221 3.2.3. Scanning Electron Microscopy (SEM)

222 The observed siliceous organisms in the sediment samples were imaged using Scanning Electron  
223 Microscopy (SEM; FEI Quanta 200, and Hitachi TM4000). To chemically characterize the bSi and its  
224 associated authigenic aluminosilicate ‘coating’, the Scanning Electron Microscopy was coupled with  
225 an Energy Dispersive Spectrometer (SEM-EDS) analysis using FEI Quanta 200 and OXFORD X-  
226 MAX Silicon Drift Detector (detector size: 80 mm) at Ifremer-LCG (France). Typically, the bio-  
227 siliceous structures were handpicked under a stereomicroscope and mounted on an adhesive carbon tab



228 (Leit) using a brush. The carbon tab was pasted on pin stubs and coated with gold (Cheize et al., 2019).  
 229 The major elements were quantitatively determined under a high vacuum at 20 kV.

### 230 3.3. Analytical procedures for Si/Al data

231 Each extraction in the continuous analysis procedure provides Si and Al concentrations through  
 232 time at a one-second resolution (Figure S1), and the unit of parameter  $t$  in the models (Eq. 1 – 3) was  
 233 normalized into minutes (min). Determination of the bSiO<sub>2</sub>% follows the procedure that assumes the  
 234 presence of two discrete phases: (1) a linear phase indicating lithogenic silicate (lSi) dissolution and  
 235 (2) a nonlinear phase indicating bSi and/or non-bSi dissolution (DeMaster, 1981; Koning et al., 2002).  
 236 The bSiO<sub>2</sub>% was calculated following the 4 models (Eq.1 = Model 1; Eq.2 = Model 2 and Model 3;  
 237 Eq.3 = Model 4) described by Koning et al, (2002) using the Origin 2021b software.

238 Model 1 demonstrates the first-order dissolution of a single Si phase ( $Si_{extr}$ ) as shown in Eq.1:

$$239 \quad Si_{aq} = [Si_{extr}]_0 (1 - e^{-kt}) + bt$$

$$240 \quad Al_{aq} = \frac{1}{\beta_1} [Si_{extr}]_0 (1 - e^{-kt}) + \frac{1}{\beta_{lin}} bt \quad (1)$$

241 Here,  $Si_{aq}$  and  $Al_{aq}$  are the concentrations of silicic acid and aluminum in mg L<sup>-1</sup>, in the reaction  
 242 vessel at time  $t$  (min).  $[Si_{extr}]_0$  is the initial extractable silica present in the vessel in mg L<sup>-1</sup>, equivalent  
 243 to the final concentration of  $Si_{aq}$  reached when all extractable silica (bSi and lSi) has dissolved,  $k$  is the  
 244 reactivity constant (min<sup>-1</sup>) and  $\beta_1$  is the atomic ratio of Si and Al released during the dissolution of  
 245 extractable silica fraction.  $b$  (mg L<sup>-1</sup> min<sup>-1</sup>) represents the constant dissolution rate of Si from clay  
 246 minerals and  $\beta_{lin}$  is the Si:Al ratio in the lithogenic fraction.

247 Natural sediment samples may consist of several types of extractable bSi. For natural samples  
 248 containing two  $Si_{extr}$  fractions ( $Si_{extr1} = ExtrSi_1$ ,  $Si_{extr2} = ExtrSi_2$ ;  $n = 2$ ), the increases of the silicic acid  
 249 concentration in the reaction vessel with time can be as the sum of two first-order dissolution processes  
 250 (Model 2, Eq. 2), using the same parameters as described in Eq.1. For natural samples containing three  
 251  $Si_{extr}$  fractions ( $n = 3$ ), the increase in silicic acid concentration with time can be the sum of three first-  
 252 order dissolution processes (described as Model 3).  $[Si_{extr}]_{0,i}$  is the initial extractable silica present in  
 253 the extractable silica fraction  $i$ ,  $k_i$  is the reactivity constant and  $\beta_i$  is the Si:Al ratio for fraction  $i$ .

$$254 \quad Si_{aq} = \sum_i^n [Si_{extr}]_{0,i} (1 - e^{-k_i t}) + bt$$

$$255 \quad Al_{aq} = \sum_i^n \frac{1}{\beta_i} [Si_{extr}]_{0,i} (1 - e^{-k_i t}) + \frac{1}{\beta_{lin}} bt \quad (2)$$

256 Model 4 demonstrates the reactive continuum dissolution of the infinite number of fractions ( $i$ ) (Eq.  
 257 3) (Koning et al., 1997) and can be described as:

$$Si_{aq} = [Si_{extr}]_0 \left(1 - \left(\frac{\alpha}{\alpha + t}\right)^v\right) + bt$$

$$Al_{aq} = \frac{1}{\beta_1} [Si_{extr}]_0 \left(1 - \left(\frac{\alpha}{\alpha + t}\right)^v\right) + \frac{1}{\beta_{lin}} bt \quad (3)$$

Where the parameter  $\alpha$  represents the average lifetime of the alkaline extractable components in sediment and  $v$  represents a non-dimensional parameter solely related to the shape of the distribution curve. Model 4 allows a continuum of reactivity of bSi and lSi and assumes one Si:Al ratio for all the bSi components, it is not justified by data fitting in this study. The highest number of bSi components justified by model fitting was model 2, in agreement with Barão et al. (2015) and Raimonet et al. (2015).

The alkaline extractable Si (AlkExSi) may contain several non-linear fractions, based on the Si:Al ratio and reactivity constant ( $k$ ). The origin of different extractable Si fractions (bSi, lSi) can be evaluated (Koning et al., 2002). The lSi fraction (Figure 1A) is normally characterized by low reactivity (Koning et al., 2002) and small Si:Al ratios (authigenic silicates: Si:Al < 2, Mackin, 1989, Michalopoulos and Aller, 1995; Kaolinite: Si:Al = 1, Illite: Si:Al = 2, Montmorillonite, Si:Al < 5, Koning et al., 2002), the bSi fraction is characterized by high reactivity ( $k > 0.1 \text{ min}^{-1}$  and  $\beta_i > \beta_{lin}$ ) and high Si:Al ratios ( $\beta_i > 5$ ) (Koning et al., 2002; Barão et al., 2015). Moreover, chemically altered bSi structures were characterized by a nonlinear dissolution with low reactivity ( $k < 0.1 \text{ min}^{-1}$ ) and low Si:Al ratio (< 5) (Koning et al., 2002).

For the fitted results from the above-mentioned models, optimization was carried out by maximizing the likelihood statistic  $\log(L)$  (Armstrong et al., 2002; Moriceau et al., 2009) as described as follows:

$$\log(L) = -\frac{N}{2} \log \left( \frac{\sum (\log(\hat{C}_j) - \log(C_j))^2}{N} \right) \quad (4)$$

Where  $N$  is the total number of data points,  $C_j$  is the measured concentration ( $\text{mg L}^{-1}$ ) for data point  $j$ . and the  $\hat{C}_j$  is the corresponding model prediction. The difference in  $\log(L)$  ( $\Delta \log(L)$ ) between fits of different models to the same data gives the goodness of fit of one model compared to the other (Figure S1). As described in Moriceau et al. 2009, if the  $\log(L)$  of one model is at least two points higher per added parameter than another, it is considered a better model (Hilborn and Mangel, 1997). In this study, the results from the fitted model were used for methodology comparison. A non-parametric Aligned Ranks Transformation (ART) Analysis of Variance (ANOVA) was performed using R. studio software to test for significant differences between methods.

### 3.4. Burial flux of bSiO<sub>2</sub> in the CCMZs of East China seas

The burial flux ( $F_b$ ) of bSiO<sub>2</sub> in sediment can be expressed as follows (Ingall and Jahnke, 1994):

$$F_b = C * w \quad (5)$$

288  
 289 Where  $C$  ( $\text{mol g}^{-1}$ ) is the concentration of  $\text{bSiO}_2$ , and is calculated from the  $\text{bSiO}_2\%$  determined in dry  
 290 sediment (in  $\text{g of SiO}_2 \text{ g}^{-1}$ ), and converted to  $\text{mol g}^{-1}$  by dividing it by the molecular weight of  $\text{SiO}_2$  ( $6$   
 291  $\times 10^{-3} \text{ g mol}^{-1}$ ),  $w$  ( $\text{g cm}^{-2} \text{ yr}^{-1}$ ) is the mass accumulation rate. The  $w$  used in this study is averaged  
 292 sediment accumulation rate at BH ( $0.50 \text{ g cm}^{-2} \text{ yr}^{-1}$ ), YS ( $0.37 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) and ECS ( $0.26 \text{ g cm}^{-2} \text{ yr}^{-1}$ )  
 293 reported previously (Qiao et al., 2017). Note, a primary objective of this study was to determine the  
 294 potential influence that methodological biases can have on the bSi burial flux Therefore, an average  
 295 sedimentation rate of the study area was applied. The  $F_b$  was then multiplied by the respective area of  
 296 the BH, the YS and the ECS to calculate the burial flux of bSi of each region and the East China seas.

## 297 4. Results

### 298 4.1. Biogenic silica types and their abundances

299 Table 1 shows the abundance of the three types of marine bSi in sediment obtained from the East  
 300 China seas (see Figure 2 for sample sites). All of the samples used in this study were examined under  
 301 a microscope to determine the relative composition of different bSi types. Among the three major types  
 302 of marine bSi (i.e., diatoms, radiolarians, sponge spicules), diatoms and sponge spicules were observed  
 303 in the sediments of BH, YS, and ECS. Radiolarian skeletons were only observed in the sediment of YS  
 304 and ECS. The abundance of sponge spicules and their size (length) and the number of radiolarian tests  
 305 varied between samples from the BH, the YS and the ECS. Microscopic observations indicated that  
 306 radiolarian skeletons were rare in the sediment of the YS, whereas more radiolarian tests were found  
 307 in the sediment samples of ECS. Although sponge spicules were found in all sediment samples (Table  
 308 1), the size of sponge spicules in the sediment of the BH (length:  $10 - 40 \mu\text{m}$ ), and YS (length:  $50 -$   
 309  $300 \mu\text{m}$ ) are smaller than that of the ECS ( $100 - 500 \mu\text{m}$ ). The abundance of sponge spicules in the  
 310 sediment of BH and YS is less than what was observed for diatoms. In contrast, the abundance of  
 311 sponge spicules was greater than diatoms in ECS sediment samples (Table 1).

312 We found that radiolarians and sponge spicules were more abundant in the sediment of the ECS  
 313 than the BH and the YS from the microscopic observations. Therefore, five samples (C4, C7, C12, F2,  
 314 and A3) were selected from the ECS for determining the abundance of different types of bSi. The  
 315 radiolarians and sponge spicules are more abundant in the offshore sediment (C7, C12) than in  
 316 nearshore sediment (A3, F2, C4). The abundance of sponge spicules is greater than that of diatom tests  
 317 in the 5 samples (C4, C7, C12, F2, A3) from ECS, especially in sample C12 where the abundance of  
 318 sponge spicules ( $231.7 \times 10^3 \text{ g}^{-1}$ ) is ca. 15 times greater than that of diatoms ( $14.8 \times 10^3 \text{ g}^{-1}$ ). The  
 319 abundance of diatoms is similar for the BH, YS and ECS, which is in agreement with previous research

320 (Chen et al., 2014; Wang et al., 2016; Li et al., 2018, Li et al., 2020). However, radiolarians and sponge  
321 spicules are more abundant in the ECS, especially in the sediment of the outer shelf of the ECS.

## 322 **4.2. Wet alkaline digestions**

### 323 **4.2.1 Evaluation of reference samples**

324 Two interlaboratory comparison sediment samples (Still Pond, R-64) were measured using Si/time  
325 (Figure S2) and Si/Al (Figure S3) alkaline digestion to assess the accuracy of the biogenic silica  
326 measurement. Similar results were obtained to previous works (Table 2), but also showed dependence  
327 on the extraction method. The bSiO<sub>2</sub>% applying a 0.5 M NaOH digestion (Still Pond: 2.74%; R-64:  
328 7.23%) and a 0.1 M Na<sub>2</sub>CO<sub>3</sub> digestion (Still Pond: 2.00 ± 0.05%; R-64: 5.50 ± 0.10%) are within the  
329 acceptable range of bSiO<sub>2</sub>% values (Still Pond: 2.82 ± 1.17%; R-64: 6.49 ± 2.09%) reported in Conley  
330 (1998) (Table 2). The wide range of data presented in Conley (1998) is likely due to the influence of  
331 methodological differences applied (alkaline solution concentration and/or chemical pretreatment), the  
332 act of crushing the sediment prior to the alkaline attack, and the existence of sponge spicules in Still  
333 Pond and R-64 which was not previously reported in Conley (1998), because siliceous sponge spicules  
334 were observed in both reference samples. The coefficient of variability (i.e., relative standard deviation)  
335 for five parallel extractions was < 3%, indicating good reproducibility.

### 336 **4.2.2. Comparison of the extraction methods**

337 The results presented here compare the analysis of bSiO<sub>2</sub>% determined using different Si/time  
338 methods. Triplicate digestion of the pre-treated (P) and non-pretreated (NP) sediment (Figure 3) was  
339 performed to determine the influence of the pre-treatment process on bSi determination. As expected,  
340 stronger solutions and pretreatment of sediment led to a greater release of silica (Table 3, Figure 3 and  
341 Figure 4). According to the different alkaline digestion and microscopic observation, this is mainly due  
342 to the extraction of lSi rather than bSi (e.g., sponge spicules). The pre-treatment of sediment using HCl  
343 (1.0 M) and H<sub>2</sub>O<sub>2</sub> (10%) as described by Mortlock and Froelich (1989) will activate the authigenic  
344 silicate phases and the clay minerals, thus cause an overestimation of the bSiO<sub>2</sub>%.

345 Figure 3 shows a continuous increase of the SiO<sub>2</sub>% over time. The alkaline extracted silica  
346 (AlkExSi) content is higher for the pretreated sediments than the non-pretreated sediments. Similar  
347 result was obtained for the total amount of alkaline extracted silica (TAlkExSi) after the 8 h digestion  
348 (0.1 M Na<sub>2</sub>CO<sub>3</sub>, P > 0.1 M Na<sub>2</sub>CO<sub>3</sub>, NP; 0.2 M Na<sub>2</sub>CO<sub>3</sub>, P > 0.2 M Na<sub>2</sub>CO<sub>3</sub>, NP; 2.0 M Na<sub>2</sub>CO<sub>3</sub>, P >  
349 2.0 M Na<sub>2</sub>CO<sub>3</sub>, NP; Figure 4). As shown in Figure S4 and Figure S5, most of the SiO<sub>2</sub> was leached  
350 from sediments during the first 4 h (AlkExSi<sub>(1-4)</sub>) and less SiO<sub>2</sub> was extracted during the 5 h to 8 h

351 digestion (AlkExSi<sub>(5-8)</sub>). The quantity of AlkExSi<sub>(1-4)</sub> and AlkExSi<sub>(5-8)</sub> correspond to 66% – 86% and  
 352 14% – 34% of total amount of silica (TAlkExSi; TAlkExSi = AlkExSi<sub>(1-4)</sub> + AlkExSi<sub>(5-8)</sub>) extracted  
 353 during the 8 h alkaline digestion (Figure S5). In addition, the AlkExSi<sub>(1-4)</sub> leached from the pre-treated  
 354 sediment was higher than from the non-pretreated sediment (Figure S4 and Figure S5), and the amount  
 355 of the AlkExSi<sub>(5-8)</sub> was low (< 0.2%SiO<sub>2</sub>) and showed small variations when digested under different  
 356 alkaline solutions (0.1 M, 0.2 M and 2.0 M Na<sub>2</sub>CO<sub>3</sub>, P vs. NP). Moreover, more silica (AlkExSi<sub>(1-4)</sub>  
 357 and AlkExSi<sub>(5-8)</sub>) can be leached in stronger alkaline, but the proportion of AlkExSi<sub>(1-4)</sub> and AlkExSi<sub>(5-8)</sub>  
 358 to TAlkExSi does not change much (Figure S5).

359 Table 3 and Figure S6 showed the bSiO<sub>2</sub>% calculated from the 8 h digestion experiment. Through  
 360 ART ANOVA analysis, a significant difference between different alkaline digestions was identified  
 361 (Table S1). ART ANOVA analysis showed the increase of bSiO<sub>2</sub>% between 0.1 M Na<sub>2</sub>CO<sub>3</sub> (P vs. NP),  
 362 0.2 M Na<sub>2</sub>CO<sub>3</sub> (P vs. NP) and 2.0 M Na<sub>2</sub>CO<sub>3</sub> (P vs. NP) were significant ( $p < 0.0001$ ; Noymer (2008))  
 363 (Table S1). The yield, expressed as bSiO<sub>2</sub>%, between the P and the NP alkaline digestions are: 0.1 M  
 364 Na<sub>2</sub>CO<sub>3</sub> (P) = 194% 0.1 M Na<sub>2</sub>CO<sub>3</sub> (NP), 0.2 M Na<sub>2</sub>CO<sub>3</sub> (P) = 226% 0.2 M Na<sub>2</sub>CO<sub>3</sub> (NP) and 2.0 M  
 365 Na<sub>2</sub>CO<sub>3</sub> (P) = 185% 2.0 M Na<sub>2</sub>CO<sub>3</sub> (NP) in average (calculated from Table 3). Besides the pre-  
 366 treatment process, a higher concentration of Na<sub>2</sub>CO<sub>3</sub> can extract more silica significantly ( $p < 0.0001$ )  
 367 than a lower concentration of Na<sub>2</sub>CO<sub>3</sub> (C7, F2, F8 and DC; Figure S6), except for the bSiO<sub>2</sub>%  
 368 determined using a 0.2 M Na<sub>2</sub>CO<sub>3</sub> (P) and the 2.0 M Na<sub>2</sub>CO<sub>3</sub> (P) digestion ( $p = 0.0726$ ). For the non-  
 369 pretreated (NP) digestion experiment, the average bSiO<sub>2</sub>% extracted using 2.0 M Na<sub>2</sub>CO<sub>3</sub> solution is  
 370 49% and 69% higher than the 0.2 M Na<sub>2</sub>CO<sub>3</sub> and 0.1 M Na<sub>2</sub>CO<sub>3</sub> digestion, respectively. However, the  
 371 bSiO<sub>2</sub>% of samples C7 and C12 was approximately the same when the sample was digested using  
 372 different concentrations of Na<sub>2</sub>CO<sub>3</sub> (0.1, 0.2, 2.0 M), and the bSiO<sub>2</sub>% of samples C4, F2, F8, and DC  
 373 was higher when using a higher concentration of Na<sub>2</sub>CO<sub>3</sub> solution (Figure S6). Compared to the  
 374 alkaline concentration, the pretreatment process has a more important influence on bSi determination.  
 375 The bSiO<sub>2</sub>% determined following the single-step alkaline digestion method proposed for abyssal  
 376 deposits (Mortlock and Froelich, 1989) generated much higher bSiO<sub>2</sub>% values ( $p < 0.0001$ ) than all  
 377 other digestions. Moreover, the bSiO<sub>2</sub>% determined using 0.1 M Na<sub>2</sub>CO<sub>3</sub> (NP; DeMaster, 1981) was  
 378 not significantly different ( $p = 0.0726$ ) compared to the bSiO<sub>2</sub>% determined using 0.5 M NaOH (NP;  
 379 Koning et al., 2002) (Table S1). The bSiO<sub>2</sub>% determined by 2.0 M Na<sub>2</sub>CO<sub>3</sub> (P) is about 2.6 times of  
 380 the bSiO<sub>2</sub>% determined by 0.1 M Na<sub>2</sub>CO<sub>3</sub> (NP). The average bSiO<sub>2</sub>% of samples C4, C7, C12, F2, F8  
 381 and DC determined using different methods (0.1 M, 0.2 M, 2.0 M Na<sub>2</sub>CO<sub>3</sub>, P vs. NP; Table 3) were  
 382  $0.49 \pm 0.25\%$ ,  $0.40 \pm 0.23\%$ ,  $1.82 \pm 0.56\%$ ,  $1.00 \pm 0.44\%$ ,  $1.13 \pm 0.49\%$  and  $1.34 \pm 0.57\%$

383 respectively, showed a large variation (31 – 57%) of the standard deviation. The proportion of standard  
384 deviation to the averaged bSiO<sub>2</sub>% was large for low bSiO<sub>2</sub>% samples (C4: 51%, C7: 57%) than other  
385 samples. After the alkaline digestions, microscopic observations (10X; Zeiss Axio Observer A1)  
386 showed complete digestion of diatoms and radiolarians, whereas sponge spicules remain present.

#### 387 **4.2.3. Separation of bSi from lSi using dissolution rates**

388 A 20 h-alkaline digestion (Figure S7) was performed for separating different bSi (diatom,  
389 radiolarian and sponge) from lSi using the Si dissolution rate (Conley and Schelske, 2001).  
390 Microscopic observations of the sediment residual indicated that diatoms and radiolarian skeletons  
391 were digested completely while sponge spicules were not fully extracted. The time-dependent methods  
392 (e.g., 5 h, DeMaster (1981); 8 h, Liu et al. (2002); 20 h, Conley and Schelske (2001)) all showed  
393 variations which emphasize that the fixed duration approach (Mortlock and Froehlich, 1989) is  
394 insufficient in the study area. The time-dependent methods yield different bSiO<sub>2</sub>% estimates, that  
395 accord with the duration of digestion, i.e., the 5 h digestion with the shortest time showed the least  
396 bSiO<sub>2</sub>% ( $0.22 \pm 0.18\%$ ), the moderate duration (8 h) of the attack gave an intermediate bSiO<sub>2</sub>% ( $0.40$   
397  $\pm 0.29\%$ ), and the longest duration of digestion produce the highest bSiO<sub>2</sub>% ( $0.52 \pm 0.34\%$ ) (Table 4).  
398 The ART ANOVA analysis indicated a significant ( $p < 0.0001$ ) difference in the bSiO<sub>2</sub>% among the  
399 three different time intervals.

400 According to the method described in Conley and Schelske (2001), the diatom bSiO<sub>2</sub>%, radiolarian  
401 and sponge bSiO<sub>2</sub>% were calculated at a 5 h and 20 h digestion interval, respectively (Table 4, Figure  
402 S8). The diatom bSiO<sub>2</sub>%, radiolarian and sponge bSiO<sub>2</sub>% and total bSiO<sub>2</sub>% in sediment used in this  
403 study averaged  $0.25 \pm 0.22\%$  ( $0.003 - 0.97\%$ ),  $0.27 \pm 0.15\%$  ( $0.03 - 0.52\%$ ) and  $0.52 \pm 0.34\%$  ( $0.04 -$   
404  $1.49\%$ ), respectively (Table 4). The amount of diatom bSiO<sub>2</sub>% is approximately equal to the amount  
405 of radiolarian and sponge bSiO<sub>2</sub>% (Figure S8). ART ANOVA analysis showed a significant difference  
406 ( $p < 0.0001$ ) between diatom bSiO<sub>2</sub>%, radiolarian and sponge bSiO<sub>2</sub>% and the total bSiO<sub>2</sub>%. Detailed  
407 calculations of the averaged bSiO<sub>2</sub>% of the BH, YS and ECS were also presented (Table 4).

#### 408 **4.2.4. Separation of bSi form lSi using Si/Al ratios**

409 The Si/Al method is proposed based on the assumption that Si is extracted continuously from bSi  
410 and lSi whereas the Al is extracted mainly from lSi (Koning et al., 1997, 2002; Kamatani and Oku,  
411 2000), therefore the quantity of bSi and lSi can be corrected using the Si:Al ratio (Kamatani and Oku,  
412 2000). The purpose of determining the bSiO<sub>2</sub>% using the Si/Al method is to fully digest bSi and correct  
413 the lSi properly. It should be noted that after 1 h digestion using 0.5 M NaOH, diatoms were not

414 observed whereas a few radiolarian skeletons and some sponge spicules were observed within the  
 415 residual sediment of ECS samples (Figure S9). Therefore, the Si/Al alkaline digestion method  
 416 determines mostly diatom bSi and radiolarian bSi and partly sponge bSi, instead of the total bSiO<sub>2</sub>%.

417 The measured dSi and dAl results and the best fit models were shown in Figure S3. After the  
 418 likelihood statistic (Eq. 4) analysis, we found most samples (27/30 samples including sample Still Pond  
 419 and R-64) were fitted better with 2 components (Model 2) than 1 component (Model 1), and the time  
 420 evolution of release rates and Si:Al ratios were never sufficient to justify higher component models  
 421 (Models 3 or 4). Generally, Si and Al were released non-linearly during the first 20 minutes and  
 422 followed by a linear dissolution, and the AlkExSi was always higher than the AlkExAl (Figure S3).  
 423 The bulk Si:Al ratios ( $2 < \text{Si:Al} < 20$ ) were high at the beginning of digestion and decreased to a  
 424 relatively constant value ( $2 < \text{Si:Al} < 5$  for most samples, except D12 and C12) after 30 min (Figure 5),  
 425 showing a rapid bSi dissolution during the  $< 30$  min and complete extraction of bSi after  $> 50$  min.  
 426 The TAlkExSi ranged from  $0.65 \text{ mg-Si g}^{-1}$  to  $24.0 \text{ mg-Si g}^{-1}$ , whereas the total alkaline extracted Al  
 427 content (TAlkExAl) ranged from  $0.14 \text{ mg-Si g}^{-1}$  to  $6.0 \text{ mg-Si g}^{-1}$ , with a relative constant  $\beta_{lin}$  ( $2.71 \pm$   
 428  $0.63$ , Table 5).

429 The reactivity constant ( $k$ ) of the first non-linear fraction (average  $k_1 = 1.96 \text{ min}^{-1}$ ) was greater than  
 430 the second fraction (average  $k_2 = 0.084 \text{ min}^{-1}$ ) (Figure 6), and the  $\beta_1$  is higher than the  $\beta_2$  (except for  
 431 D1, table 5). Figure 6 showed a wide range of Si:Al ratios for  $\beta_1$  ( $2 < \beta_1 < 25$ ) and  $k_1$  ( $0.5 < k_1 < 5$ ), and  
 432 small ranges of  $\beta_2$  ( $2 < \beta_2 < 8$ ) and  $k_2$  ( $0 < k_2 < 0.2$ ). In addition,  $\beta_2$  has similar Si:Al ratios compare to  
 433  $\beta_{lin}$ , and  $\beta_1$  is always higher than the  $\beta_{lin}$  (Figure 6). The  $ExtrSi_1$ ,  $ExtrSi_2$  and the linear lSi fraction  
 434 account for  $19.3 \pm 9.9\%$ ,  $27.4 \pm 12.6\%$  and  $53.3 \pm 10.1\%$  of the TAlkExSi, respectively (Table S2).  
 435 Based on Si:Al ratio ( $\beta_i$ ) and the reactivity ( $k_i$ ), the calculated bSiO<sub>2</sub>% (dry weight) and lSiO<sub>2</sub>% (linear  
 436 lSi fraction + non-linear lSi fraction) in sediments of East China seas were  $1.82 \pm 2.28 \text{ mg-Si g}^{-1}$  ( $0.39$   
 437  $\pm 0.49\% \text{ bSiO}_2$ ) and  $5.95 \pm 4.69 \text{ mg-Si g}^{-1}$  ( $1.28 \pm 1.00\% \text{ bSiO}_2$ ), respectively (calculated from Table  
 438 5). However, the definition of bSi ( $\beta_i > 5$  or  $\beta_{lin} < \beta_i < 5$  &  $k > 0.1 \text{ min}^{-1}$ ) and lSi ( $1 < \text{Si/Al} < 4$ ) (Koning  
 439 et al., 2002; Barão et al., 2015) based on Si/Al ratios and reactivity may limit our understanding of the  
 440 different Si fractions. Our results showed that sometimes  $\beta_2 < \beta_{lin}$  (B01, H32, A3, E6, F2; Table 5),  
 441 suggest that the  $ExtrSi_2$  is lSi origin. However, whether this fraction is authigenic silicate is not clear,  
 442 because the Si:Al ratio of authigenic silicates ( $< 2$ , Mackin (1989), Michalopoulos and Aller (1995))  
 443 and clay mineral (1- 4, Koning et al. (2002)) are both below 5. Barão et al, (2015) found the non-linear  
 444 Si fractions ( $ExtrSi_1$ ,  $ExtrSi_2$ ) obtained using the Si/Al alkaline digestion method is higher than the  
 445 bSiO<sub>2</sub>% examined using the Si/time method (0.1 M Na<sub>2</sub>CO<sub>3</sub>). However, the  $ExtrSi_1$  is approximately  
 446 equal to diatom bSiO<sub>2</sub>% (Barão et al., 2015). Implies the reactive non-linear fraction originates from

447 the diatom bSi and the less reactive non-linear fraction originates from less soluble Si fractions  
448 (implicating resistant bSi, such as radiolarians, sponge spicules and/or altered diatoms, or lSi). So far,  
449 we cannot differentiate the less soluble Si fractions. A future study looking at the alkaline digestion of  
450 diatoms, radiolarian skeletons, sponge spicules and synthesized sediment using both Si/Al method and  
451 Si/time method would improve our understanding of the definition of different Si fractions.

#### 452 **4.3. SEM and SEM-EDS analysis**

453 The existence of a clay mineral “coating” on the surface of the siliceous organism was observed by  
454 SEM (Figure 7 and Figure S10) in samples before alkaline digestion. Generally, the diatoms and  
455 radiolarian tests were coated with more clay minerals than the siliceous sponge spicules. Diatom  
456 frustules in sample A1 were pre-treated using HCl (1.0 M) and H<sub>2</sub>O<sub>2</sub> (10%), showing the partial  
457 removal of the coated clay minerals after the pre-treatment process. Additionally, Si, Al, K, Mg, Ca,  
458 Fe, Ti, S and As were detected from the diatom tests in sample A1 (Figure S10), indicating incomplete  
459 removal of clay materials (authigenic and/or allochthonous clays) after pre-treatment. Besides Si and O, the  
460 major metal elements from reaction products of the reverse weathering process, such as Al, Mg, K and  
461 Fe (Michalopoulos and Aller, 2004), were commonly detected through EDS-SEM analysis (Figure  
462 S10).

463 In addition, diatoms and radiolarian tests were not observed in sediment residuals after the alkaline  
464 digestions (0.1 M, 0.2 M, 2.0 M Na<sub>2</sub>CO<sub>3</sub>, 8 h digestion, P vs. NP; 0.5 M NaOH, 1 h digestion, NP),  
465 whereas sponge spicules were found in the sediment residuals (post-digestion), especially in sediment  
466 from the outer shelf and slope of ECS. The digestion and destruction of the sponge spicule structures  
467 by the alkaline solution are visible from the SEM image (Figure 8). Different types of sponge spicules  
468 (i.e., *strongyle*, *acanthostyle*, *tignule*) were observed and picked from sediment residuals of sample  
469 C12, which was previously extracted in a 2.0 M Na<sub>2</sub>CO<sub>3</sub> (P, 85 °C) solution for 8 h. Nevertheless, the  
470 degree of destruction of the different shapes/types of sponge spicules by alkaline solution is variable.  
471 For example, the *strongyle* sponge spicules (Figure 8 G, H, I) are more heavily digested than the  
472 *acanthostyle* sponge spicules (Figure 8 A, B, C) and the *tignule* sponge spicules (Figure 8 D, E, F).

#### 473 **5. Discussion**

474 This study determined the bSiO<sub>2</sub>% in sediment from the CCMZs of the East China seas using  
475 both the Si/time and the Si/Al methods and estimated the abundance of different types of bSi in  
476 sediment. The results show that the commonly used pretreatment step and different alkaline digestion  
477 methods inherently bias the accurate determination of bSiO<sub>2</sub>%. For example, this study found that



478 strong alkaline digestion can overestimate bSi content and does not completely digest sponge bSi, in  
479 agreement with Maldonado et al, (2019), which are important factors to consider when evaluating total  
480 bSi fluxes in the marine environment. These technical biases are important to understand since  
481 pretreatment procedures (e.g., HCl and H<sub>2</sub>O<sub>2</sub>) can overestimate the burial flux of bSi in CCMZs. To  
482 emphasize the influence of these methodological differences, we present a revised bSi burial flux for  
483 the East China seas. The causes of the methodological biases are discussed below (section 5.1) and the  
484 importance of resistant bSi in the East China seas is presented (section 5.2). Finally, a general procedure  
485 (section 5.3) is proposed to ensure that determination of bSi burial flux is supported by an accurate  
486 quantification of bSiO<sub>2</sub>% in coastal sediments.

### 487 **5.1. Re-evaluated burial flux of bSi in the CCMZs of East China seas**

488 Considering the complex bSi types (diatoms, radiolarians and sponge spicules) (Table 1) and high  
489 AlkExSi from lSi from East China seas sediments (Table 5), an accurate determination of the bSi  
490 content is challenging due to the technical problems highlighted by Maldonado et al. (2019) and  
491 Koning et al. (2002) for coastal sediments. In this study, we assessed the Si/time and Si/Al methods in  
492 order to define the optimal method for the determination of the bSi content. This information is  
493 necessary to accurately evaluate bSi burial in the CCMZs of East China seas.

494 This study found two major limitations for the Si/time method: 1) insufficient correction of the lSi  
495 phase and 2) inadequate digestion of the resistant bSi (mainly sponge spicules). Applying a weak  
496 alkaline digestion completely digests the diatoms but cannot fully digest sponge spicules (Figure 8),  
497 whereas a strong alkaline digestion extracts more lSi from the sediment and resulting in an  
498 overestimation of the bSi content. In addition, the AlkExSi concentration continues to increase during  
499 an alkaline extraction (Figure 3, Figure S7, Figure S11) and a flat “plateau” as shown in Figure S2 is  
500 never reached, suggesting a continuous dissolution of resistant bSi (e.g., sponge spicules) and lSi.  
501 Therefore, a complete digestion of the bSi using the Si/time method cannot be defined for the sediment  
502 of East China seas, and the use of a simple tangent line to calculate bSi content (DeMaster, 1981) is  
503 insufficient.

504 Furthermore, authigenic silicates precipitate on the structure of bSi (Figure 7 and Figure S10) can  
505 decrease the reactive surface area of bSi and decrease its solubility (Williams et al., 1985; Varkouhi  
506 and Wells, 2020). Applying an acid and peroxide pretreatment procedure can remove the authigenic  
507 silicates and enhance the reactivity of bSi (Mortlock and Froelich, 1989). However, our results showed  
508 the bSiO<sub>2</sub>% increased by more than 100% after the pretreatment (Table 3, Figure S6), a significant ( $p$   
509  $< 0.0001$ ) statistical increase (Table S1), which is not in agreement with our microscopic observations

510 (Table 1, Figure 8). Ohlendorf and Sturm (2008) and Dai et al. (2017) found that using a pretreatment  
511 step increased the bSi yield and they suggested that more bSi was being digested after the removal of  
512 the mineral coating. We argue that this observed increase bSi yield is mainly due to an enlarged amount  
513 of Si extracted from authigenic silicate and clay minerals. This argument is supported by observations  
514 made by Michalopoulos and Aller (2004), who concluded that a mild acid pretreatment step (0.1 M  
515 HCl) can activate the authigenic silicate in the Amazon delta sediment. They also suggested that the  
516 mild acid pre-treatment can activate the neo-formed reverse weathering product (authigenic silicates)  
517 without changing the structure of crystallized clay minerals. However, applying a stronger acid (1.0 M  
518 HCl) and peroxide (10% H<sub>2</sub>O<sub>2</sub>) pretreatment can weaken the structure of clay minerals (Komadel and  
519 Madejová, 2006; Hu et al., 2022), therefore, enhancing the solubility of the clay mineral. The chemical  
520 composition differences between bSi and authigenic silicates suggest that they are two different marine  
521 Si pools (Michalopoulos and Aller, 2004; Rahman et al., 2016; Pickering et al., 2020). Applying pre-  
522 treatment can cause an overestimation of the bSi pool, therefore, further studies on disentangling the  
523 different Si pools are required (DeMaster, 1991; Frings et al., 2014, 2021a, 2021b; Ehlert et al., 2016;  
524 Pickering et al., 2020; Michalopoulos and Aller, 2004; Rahman et al., 2016).

525 Although the Si/time method determines the bSi content based on a simple Si vs. time tangent line,  
526 the mineral interference still needs to be corrected. This is typically done with the Si/Al method for  
527 CCMZs sediment (Koning et al., 2002; Barão et al., 2015). However, the quantification of the bSi  
528 content by Si/Al method is underestimated since the sponge bSi is not completely digested (Figure S9).  
529 Previous studies concluded that all sponge spicules and most (> 70%) of radiolarians were digested  
530 after 1 h continuous alkaline digestion using 0.5 M NaOH (Muller and Schneider, 1993). Maldonado  
531 et al, (2019) found that only 10% to 20% of fresh sponge spicules were dissolved after 1.5 h of alkaline  
532 digestion using 0.5 M NaOH. The sponge spicules used by Muller and Schneider, (1993) were treated  
533 in acid solution and 10% H<sub>2</sub>O<sub>2</sub> for removing the organic matter and then ground, thus can be digested  
534 completely. However, the sponge spicules used by Maldonado et al, (2019) were not crushed, and were  
535 therefore harder to be digested completely. Thus, 30 to 90% of the sponge spicules may not be  
536 determined by the Si/Al method. Moreover, crushing the sediment or pre-treating the samples would  
537 enhance the digestion efficiency of the sponge bSi, but inevitably increase the surface area of lSi and  
538 bring out an overestimation of the bSi content. Therefore, pretreatment of sediment should be applied  
539 with caution, and we suggest applying a Si/Al method with an extension of extraction time to > 12 h  
540 (Maldonado et al. 2019). Unfortunately, this is not currently possible for the Si/Al method proposed  
541 by Koning et al, (2002).

542 The burial flux of bSi ( $F_b = C * w$ ) in the CCMZs of the East China seas was re-evaluated,  
543 considering the sediment mass accumulation rate ( $w$ ) from previously published studies and the  
544 concentration of bSiO<sub>2</sub> in sediments ( $C$ ). The variations of the estimated bSi burial flux are dependent  
545 on the determination of the bSi content of the study area. The total bSi burial flux of the East China  
546 seas thus re-evaluated varied from 132 ( $\pm 112$ ) Gmol-SiO<sub>2</sub> yr<sup>-1</sup>, 249 ( $\pm 158$ ) Gmol-SiO<sub>2</sub> yr<sup>-1</sup> and 329  
547 ( $\pm 209$ ) Gmol-SiO<sub>2</sub> yr<sup>-1</sup> using the bSiO<sub>2</sub>% determined at 5 h, 8 h and 20 h digestion interval,  
548 respectively. And the estimated bSi burial flux is 253 ( $\pm 286$ ) Gmol-SiO<sub>2</sub> yr<sup>-1</sup> based on the Si/Al method  
549 (Table 6). Given the presence of high lSi content in the sediment samples of the East China seas, a  
550 well-known opal-depleted CCMZs influenced by the terrestrial input delivered from the Yellow River  
551 and the Yangtze River, we opted for the Si/Al (1 h digestion in 0.5 M NaOH) method as the optimal  
552 method for the determination of the bSi content in the East China seas. Our best estimate of the burial  
553 flux of bSiO<sub>2</sub> (253  $\pm$  286 Gmol-SiO<sub>2</sub> yr<sup>-1</sup>) in the East China seas is about one third of the previous  
554 studies (924  $\pm$  693 Gmol-SiO<sub>2</sub> yr<sup>-1</sup>; Wu et al., 2017, Wu and Liu, 2020). This is mainly due to the  
555 methodological bias, because the previous studies determined the bSiO<sub>2</sub>% with a pre-treatment (with  
556 HCl and H<sub>2</sub>O<sub>2</sub>) process (Wu et al., 2017; Wu and Liu, 2020) that overestimate the bSiO<sub>2</sub>%,  
557 subsequently, the bSi burial flux is over-estimated. The Si/Al method can correct the lSi properly, but  
558 still digest the sponge spicules insufficiently. Therefore, our estimation of the bSi burial flux is an  
559 underestimate.

560 Notably, the difference in bSi burial flux is also influenced by the sampling technique (sampling at  
561 different locations and seasons) and the calculation of sediment mass accumulation rate. We adopted  
562 an average mass accumulation rate for the BH, YS and ECS (see section 3.4) and the potential factors  
563 (such as riverine sediment input, resuspension of sediment by currents and primary production) that  
564 influence the sediment mass accumulation rate were not discussed in this study but are necessary for  
565 future works. The substantial decrease in the estimation of Si burial flux in the East China seas raises  
566 the question of whether it can have an impact on the global scale and on the balance of the silica cycle  
567 in the ocean.

## 568 **5.2. Contribution of radiolarian and sponge in bSi burial of the East China seas**

569 Our findings emphasize that radiolarian and sponge bSi are important sinks of marine Si for the  
570 East China seas, especially the ECS. Microscopic observations indicate the sediment of BH is  
571 composed principally of diatoms (Li et al., 2020), YS is composed of diatoms (Wang et al., 2016), and  
572 the ECS is composed of diatoms (Chen et al., 2014; Li et al., 2018), radiolarians (Liu et al., 2017; Qu  
573 et al., 2020b) and sponge spicules (Table 1). No significant differences were observed in the average

574 abundance of diatoms in the surface sediment of BH, YS and ECS. However, the abundance of sponge  
 575 spicules is of the same magnitude as diatoms in the sediment of ECS (Table 1), and the abundance of  
 576 radiolarians is of the same magnitude as diatoms in the outer shelf and slope of ECS (Qu et al., 2020).  
 577 Besides the observational data, our alkaline digestion results confirm the quantity of the less soluble  
 578 bSi fraction (i.e., sponge spicules and radiolarians) is approximately equivalent to diatom bSiO<sub>2</sub>%  
 579 (Table 4). Our data showed the abundance of radiolarians and sponge spicules was not as important as  
 580 diatoms in the BH and YS (Table 1), thus the origin of the less soluble bSi in BH and YS may be partly  
 581 due to phytolith discharged from rivers. Since phytoliths are less soluble than diatoms (Meunier et al.,  
 582 2014) and can contribute 14% – 64% of bSi in estuaries and coastal sediment (Ran et al., 2017).

583 Although little is known about the quantity of radiolarian and sponge bSi in the East China seas  
 584 (Zhang et al., 2003; Liang et al., 2021), the current results imply that the burial of “dark bSi”  
 585 (radiolarian skeleton and sponge spicules, as defined by Maldonado et al. (2019)) is possibly as  
 586 important as diatoms in East China seas. The burial of silicon associated with siliceous sponges was  
 587 mainly found on continental slopes/margins (Maldonado et al., 2019), as one of the largest CCMZs in  
 588 the Northwest Pacific, the Si burial through siliceous sponges would be more important than previously  
 589 expected (Chou et al., 2012; Ran et al., 2017).

### 590 **5.3. General protocol for the determination of bSi in coastal sediments**

591 Our findings emphasize that besides diatoms, the less soluble types of bSi (i.e., radiolarians and  
 592 sponge spicules) also act as an important marine Si sink in the CCMZs of the East China seas. However,  
 593 the accurate determination of the magnitude of these marine Si sinks is complicated by different types  
 594 of methods to determine the bSi content in sediments. The following is a brief summary of the different  
 595 wet alkaline methods employed in this study and their technical limitations:

- 596 (1) The Si/time alkaline method ( 0.1 M Na<sub>2</sub>CO<sub>3</sub>, NP, 5 h digestion) (DeMaster, 1981), which is  
 597 commonly used to quantitatively determine bSiO<sub>2</sub>% in the sediment of CCMZs, incompletely  
 598 digests the skeletal structures of radiolarians and sponge spicules and partly digests lSi, similar to  
 599 the findings from Maldonado et al. (2019). A 20 h extraction in 0.1 M Na<sub>2</sub>CO<sub>3</sub> solution can digest  
 600 the diatom and radiolarian bSi and ca. 80% of sponge bSi. The determination of the bSiO<sub>2</sub>% using  
 601 a 2.0 M Na<sub>2</sub>CO<sub>3</sub> solution overestimates the bSiO<sub>2</sub>% because silica is digested from clay minerals,  
 602 which biases the accuracy of the method.
- 603 (2) The one-hour Si/Al method (0.5 M NaOH, NP) (Koning et al., 2002) underestimate the bSiO<sub>2</sub>%  
 604 due to incomplete digestion of radiolarian skeleton and sponge spicules. Therefore, an extension of  
 605 the digestion time is necessary.

606 (3) The pre-treatment of sediment using HCl (1.0 M) and H<sub>2</sub>O<sub>2</sub> (10%) prior to alkaline digestion can  
607 cause an overestimation of the bSiO<sub>2</sub>% due to the digestion of authigenic silicates and/or clay  
608 minerals. Thus, a pre-treatment procedure should be avoided.

609 To resolve these technical problems, we propose the following general wet alkaline digestion  
610 procedure for the appropriate determination of bSi content in the sediments of CCMZs:

611 (1) Determine the types of bSi in sediment using a microscope.

612 (2) Selecting an appropriate alkaline solution according to the type of sediments.

613 - For sediment samples containing mainly diatoms, a 5 h alkaline digestion using 0.1 M Na<sub>2</sub>CO<sub>3</sub>  
614 solution is capable of extracting bSi.

615 - For sediment samples containing diatoms, sponge spicules and/or radiolarian skeletons, alkaline  
616 digestion > 2 h in 0.5 M – 1.0 M NaOH (Si/Al method) solution is suggested.

617 (3) Checking the residue sediment (post-digestion) using a microscope to observe if there are no more  
618 radiolarian tests and /or sponge spicules.

## 619 **6. Conclusion**

620 Our results showed that alkaline extractions of CCMZs sediments using 2.0 M Na<sub>2</sub>CO<sub>3</sub> solution  
621 resulted in an overestimation of the bSiO<sub>2</sub>% owing to silica being digested from clay minerals.  
622 Applying a 0.1 M Na<sub>2</sub>CO<sub>3</sub> digestion (20 h) can minimize the lSi interference on bSi determination, but  
623 can cause at least 20% of underestimation of the bSiO<sub>2</sub>% owing to incomplete digestion of sponge  
624 spicules. Our results also show that alkaline extractions that apply a pretreatment procedure  
625 overestimate the determined bSiO<sub>2</sub>% due to the digestion of the authigenic silicate phases and clays  
626 and subsequently overestimate the bSi burial flux. Consequently, we propose the general alkaline  
627 digestion protocol to accurately determine bSiO<sub>2</sub>% in marine sediments of CCMZs using the Si/Al  
628 method by either applying the continuous analysis method (Koning et al., 2002) or the time-series  
629 digestion method (Kamatani and Oku, 2000). Based on these new results and the application of the  
630 Si/Al method in order to produce accurate bSiO<sub>2</sub>% results, we revised the current estimate of bSi burial  
631 flux to  $253 \pm 286 \text{ Gmol-SiO}_2 \text{ yr}^{-1}$ , which is one third of the previously reported ( $924 \pm 693 \text{ Gmol-SiO}_2$   
632  $\text{yr}^{-1}$ ). Our estimate still underestimates the bSi burial flux of the East China seas, and further work on  
633 examining the resistant bSi (i.e., phytolith, radiolarian and sponge spicule) content is still required. We  
634 argue that the pre-treatment process (with HCl and H<sub>2</sub>O<sub>2</sub>) applied in previous estimates is the main  
635 reason that bSi burial flux was previously over-estimated. In order to ensure the accurate determination  
636 of bSi from different depositional settings in the future, we strongly suggest the development of an  
637 international intercalibration exercise.

638 **Conflict of Interest**

639 The authors declare that the research was conducted in the absence of any commercial or financial  
640 relationships that could be construed as a potential conflict of interest.

641 **Author Contributions**

642 DDZ, JNS, SML, AL and PT designed this study. DDZ conducted the experiments, did the analysis  
643 and wrote the first manuscript. DDZ, JNS, SML, AL, PT, JS, MG, MYW edited the manuscript. All  
644 authors contributed to the article and approved the submitted version.

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880 **Figure 1.** The schematic diagram shows the: (A) components in the sediment of CCMZs and (B) Wet  
 881 chemical methods (B1: Si/time method; B2: Si/Al method). (A) shows the types of bSi in sediment and  
 882 their dissolution capability : diatom < phytolith < radiolarian < sponge spicule (Muller and Schneider,  
 883 1993; Mortlock and Froelich, 1989; Meunier et al., 2014) and types of lSi in sediment and their Si:Al  
 884 ratio: authigenic clay: Si:Al < 2 (Mackin, 1989; Michalopoulos and Aller, 1995); Kaolinite: Si:Al = 1,  
 885 Illite: Si:Al = 2, Montmorillonite: Si:Al < 5 (Koning et al. 2002). The ‘stronger attack’ represents high  
 886 alkaline concentration / pH, longer extraction time and sample pretreatment with acid (e.g. HCl) and/or  
 887 oxidizing agents (e.g. H<sub>2</sub>O<sub>2</sub>). (B) shows the alkaline digestion (85°C) of bSi and correction of lSi using  
 888 the Si/time method (B1) modified from DeMaster (1981), the Si/time method (B2) modified from  
 889 Conley and Schelske (2001) and the Si/Al method (B3) modified from Kamatani and Oku (2000). The  
 890 Si/time method (B1 and B2) assumes the bSi dissolves non-linearly through time whereas the lSi  
 891 dissolves linearly (the slope equals to dissolution rate ‘b’) through time, the different types of bSi  
 892 (diatom, radiolarian and sponge spicules) can be quantified based on their dissolution rate ( $k_1$ , and  $k_2$ ).  
 893 The Si/Al method (B3) assumes that the ratio of alkaline extractable Si vs. Al is constant, and the  
 894 alkaline extractable Al is mainly lSi origin, the Si:Al ratio of bSi is higher (> 5) than lSi (< 5) (Koning  
 895 et al., 2002). The Si: Al vs. time plot shows a decrease of Si:Al ratios to constant value after a complete  
 896 digestion of bSi.

897 **Figure 2.** Map of the study area indicating the sampling stations. The location of samples are grouped  
 898 in different colors at the Bohai Sea (black dots ●), Yellow Sea (blue dots ●), and the East China Sea  
 899 (red dots ●). The surface sediment samples (0 – 2 cm) were obtained during several research cruises  
 900 during 2008-2013. The distributions of currents are based on Liu et al, (2007) and Qin et al, (1996).  
 901 White arrows represent the Yellow River and Yangtze River discharge. (YSCC: Yellow Sea Coastal  
 902 Current; ZFCC: Zhejiang Fujian Coastal Current; TWWC: Taiwan Warm Current; KWC: Kuroshio  
 903 Warm Current). The map is created using Ocean Data View (ODV) software (Schlitzer, Reiner, Ocean  
 904 Data View, <https://odv.awi.de>, 2021).

905 **Figure 3.** Conventional wet alkaline digestion using Na<sub>2</sub>CO<sub>3</sub> (0.1 M, 0.2 M and 2.0 M; P vs. NP)  
 906 solution. A subsample was removed at each 1 h with a total extraction of 8 h. The alkaline extracted  
 907 silica content (SiO<sub>2</sub>%) was normalized into the dry weight of the sediment. P represents pretreatment  
 908 of sediment using HCl (1.0 M) and H<sub>2</sub>O<sub>2</sub> (10%) before digestion; NP represents no pretreatment  
 909 before alkaline digestion. The error bars were averaged from triplicate digestions. The locations of  
 910 samples C4, C7, C12, F2, F8, and DC are shown in Figure 1.

911 **Figure 4.** The total alkaline extracted silica content (TAlkExSi) of sample C4, C7, C12, F2, F8, DC  
 912 using 0.1 M, 0.2 M, 2.0 M Na<sub>2</sub>CO<sub>3</sub> solution (P vs. NP). The results presented are the SiO<sub>2</sub>% extracted  
 913 after 8 h. More SiO<sub>2</sub>% was extracted in a high concentration of the alkaline solution and after the pre-  
 914 treatment process.

915 **Figure 5.** The Si:Al ratio during alkaline digestion. Sediments were digested following the method  
 916 described in Koning et al. (2002) and Barão et al. (2015). The grey area represents the Si:Al below 5,  
 917 indicating the extraction of lSi.

918 **Figure 6.** The plots show parameters ( $\beta_i$ ,  $\beta_{lin}$ ,  $k_i$ ) from the modeling results. (A) shows the  
 919 relationship between the Si:Al ratio ( $\beta_i$ ) and the reactivity ( $k_i$ ) of the nonlinear dissolving Si  
 920 fractions, the reactivity of the first nonlinear fraction ( $k_1$ ) is higher than the second nonlinear fraction  
 921 ( $k_2$ ). The range of  $\beta_1$  ( $1 < \beta_1 < 25$ ) is bigger than  $\beta_2$  ( $2 < \beta_2 < 10$ ). (B) shows the relationship of the  
 922 Si:Al ratio between the two non-linear dissolving fractions ( $\beta_1$ ,  $\beta_2$ ) and lSi ( $\beta_{lin}$ ).  $\beta_1$  is bigger than  $\beta_2$   
 923 and  $\beta_{lin}$  and  $\beta_2$  is approximately equal to  $\beta_{lin}$ .

924 **Figure 7.** SEM images show different siliceous organisms found in sediment samples (A1, C4, C7,  
925 and C12) before alkaline digestion. A: diatom frustule in sample A1, B: diatom frustule and sponge  
926 spicule in sample C4, C: diatom frustule and sponge spicule in sample C7, D, E and F: diatom frustules  
927 and radiolarian skeletons in sample C12. Sample A1 was pretreated using HCl (1.0 M) and H<sub>2</sub>O<sub>2</sub> (10%)  
928 for 1 h, sample C4, C7, and C12 were not pretreated.

929 **Figure 8.** SEM images of three types of siliceous sponge spicule structures observed in the residual  
930 sediment of sample C12 after 8 h digestion using 2.0 M Na<sub>2</sub>CO<sub>3</sub> (P). A-C: *acanthostyle* sponge spicule,  
931 D-F: *tignule* sponge spicule, G-I: *strongyle* sponge spicule. B and C, E and F, H and I are zoom-in  
932 views of images A, D and G, respectively.

**Table 1.** Different types of marine bSi (diatoms, radiolarians, sponge spicules) and their abundances ( $10^3 \text{ g}^{-1}$  dry sediments) in the surface sediment of East China seas. “+”, “++”, “+++”: observation of bSi from low to high abundance; “–”: not observed; a: observation of low abundance of small sponge spicules (length: 10 – 40  $\mu\text{m}$ ) of BH; b: observation of low abundance of sponge spicules with intermediate size (length: 50 – 300  $\mu\text{m}$ ) of YS; c: observation of high abundance of sponge spicules (length: 100 – 500  $\mu\text{m}$ ). Note that phytolith and siliceous dinoflagellate are not counted in this study.

Region		Biogenic silica types/abundance			
		Diatom	Radiolarians	Sponge spicules	
Bohai Sea (n=5)		++	–	+ <sup>a</sup>	This study
		13.0 <sup>1</sup>	no data	no data	Other studies
Yellow Sea (n=7)		++	–	+ <sup>b</sup>	This study
		17.0 <sup>2</sup>	~0 <sup>5</sup>	no data	Other studies
East China Sea (n=16)		++	+	+++ <sup>c</sup>	This study
		11.3-19.9 <sup>3,4</sup>	0.02-7.3 <sup>5,6</sup>	no data	Other studies
East China Sea (n=16)	A3	3.8	0	5.2	This study
	F2	6.1	0.4	17.6	This study
	C4	2.2	0	3.3	This study
	C7	5.2	0.1	8.4	This study
	C12	14.8	12.4	231.7	This study

Note: the numbers in the table are references. 1: Li et al, 2020; 2: Wang et al, 2016; 3: Chen et al, 2014; 4: Li et al, 2018; 5: Qu et al, 2020; 6: Liu et al, 2017; n represents the number of samples used for evaluating the types of bSi of each region.

1 **Table 2.** The bSiO<sub>2</sub>% of interlaboratory comparison sediment samples (Still Pond and R-64). The  
 2 location of the two samples is described in Conley (1998). Note that sponge spicules were observed in  
 3 the two sediment samples. NA represents not available.

Still Pond		R-64		Alkaline	Digestion time (h)	References
bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std			
2.00	0.05	5.50	0.10	0.1 M Na <sub>2</sub> CO <sub>3</sub> <sup>a</sup>	5	This study
2.74	-	7.23	-	0.5 M NaOH <sup>a</sup>	1	This study
1.84	-	7.80	-	0.5 M NaOH <sup>a</sup>	0.5	Barão et al, (2015)
2.68	0.06	-	-	2% Na <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	8	Wu and Liu (2015)
3.88	0.19	7.50	0.13	2.0 M Na <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	8	Liu et al, (2002)
2.82	1.17	6.49	2.09	Na <sub>2</sub> CO <sub>3</sub> /NaOH	NA	Conley (1998)

4 a: no pre-treatment before the wet alkaline digestion; b: pre-treatment of sediment using HCl (1.0 M)  
 5 and H<sub>2</sub>O<sub>2</sub> (10%) before the alkaline digestion.

**Table 3.** The bSiO<sub>2</sub>% was determined using 0.1 M, 0.2 M and 2.0 M Na<sub>2</sub>CO<sub>3</sub> (P vs. NP). The standard deviations were based on triplicate digestion. Detailed information on the digestion conditions (S/L, temperature, concentration of alkaline solution) and pretreatment process was described in section 3 (i.e., Materials and methods). The averaged bSiO<sub>2</sub>% of C4 ( $0.49 \pm 0.25\%$ ), C7 ( $0.40 \pm 0.23\%$ ), C12 ( $1.82 \pm 0.56\%$ ), F2 ( $1.00 \pm 0.44\%$ ), F8 ( $1.13 \pm 0.49\%$ ), DC ( $1.34 \pm 0.57\%$ ) determined using different concentrations of alkaline solution (0.1 M, 0.2 M, 2.0 M Na<sub>2</sub>CO<sub>3</sub>, P vs. NP), showed a large variation of standard deviation (30 – 60%), which was also reported previously in Conley (1998). ART ANOVA analysis showed a significant difference ( $p < 0.0001$ ) of the bSiO<sub>2</sub>% determined using different concentrations of Na<sub>2</sub>CO<sub>3</sub> (P and NP). MF 1989 represents the bSiO<sub>2</sub>% determined following the method described by Mortlock and Froelich (1989), this method (no mineral correction) is presented for comparison with the 2.0 M Na<sub>2</sub>CO<sub>3</sub> digestion that applied a mineral correction.

Station	0.1 M Na <sub>2</sub> CO <sub>3</sub>		0.2 M Na <sub>2</sub> CO <sub>3</sub>				2.0 M Na <sub>2</sub> CO <sub>3</sub>				2.0 M Na <sub>2</sub> CO <sub>3</sub> MF 1989			
	NP		P		NP		P		NP		P		P	
	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std
C4	0.27	0.02	0.39	0.03	0.21	0.01	0.51	0.18	0.44	0.13	0.65	0.09	0.95	0.04
C7	0.17	0.03	0.47	0.03	0.14	0.05	0.56	0.02	0.18	0.03	0.52	0.10	0.78	0.02
C12	1.41	0.09	1.40	0.16	1.46	0.03	2.10	0.07	1.28	0.22	2.31	0.34	2.75	0.12
F2	0.55	0.04	0.72	0.13	0.55	0.03	1.18	0.07	0.86	0.05	1.42	0.23	1.74	0.08
F8	0.41	0.01	0.79	0.08	0.76	0.10	1.33	0.03	1.22	0.27	1.50	0.10	1.89	0.05
DC	0.80	0.04	1.35	0.07	0.84	0.04	1.39	0.07	1.24	0.34	1.71	0.29	2.15	0.11
Ave.	0.56	0.42	0.90	0.49	0.66	0.45	1.17	0.56	0.84	0.46	1.35	0.67	1.72	0.71



**Table 4.** The bSiO<sub>2</sub>% in sediments of the East China seas (BH, YS, ECS) was determined using the Si/time alkaline digestion method (0.1 M Na<sub>2</sub>CO<sub>3</sub>; NP). The locations of the samples are shown in Figure 1. The different types of bSi determined (diatom, sponge and total bSiO<sub>2</sub>) are specified according to the digestion time or method used. The “n” represents the total amount of samples used for bSi determination. ART ANOVA analysis showed a significant difference (p < 0.0001) between the bSiO<sub>2</sub>% calculated at 5 h intervals (DeMaster, 1981; Diatom bSiO<sub>2</sub>, Conley and Schelske, (2001)), 8 h intervals (Liu et al., 2002) and 20 h intervals (Conley and Schelske, 2001).

Region	Methods digestion time (h)	DeMaster (1981)		Conley and Schelske (2001)				Liu et al, (2002)			
		Total bSiO <sub>2</sub>		Diatom bSiO <sub>2</sub>		Sponge bSiO <sub>2</sub>		Total bSiO <sub>2</sub>		Total bSiO <sub>2</sub>	
		5	5	5	5	20	20	20	20	8	8
Station	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	bSiO <sub>2</sub>	std	
<b>Bohai Sea</b> (n=5)	B01	0.22	0.02	0.25	0.02	0.27	0.01	0.52	0.01	0.43	0.01
	B10	0.24	0.02	0.27	0.03	0.27	0.01	0.54	0.03	0.43	0.04
	B19	0.25	0.005	0.28	0.02	0.26	0.02	0.54	0.03	0.42	0.02
	B23	0.37	0.01	0.42	0.01	0.39	0.01	0.80	0.03	0.67	0.03
	B18	0.13	0.02	0.15	0.003	0.11	0.01	0.26	0.01	0.21	0.03
	<b>Ave.</b>	<b>0.24</b>	<b>0.08</b>	<b>0.27</b>	<b>0.09</b>	<b>0.26</b>	<b>0.09</b>	<b>0.53</b>	<b>0.18</b>	<b>0.43</b>	<b>0.15</b>
<b>Yellow Sea</b> (n=7)	B43	0.51	0.03	0.60	0.02	0.37	0.02	0.97	0.03	0.79	0.07
	H20	0.13	0.03	0.15	0.00	0.25	0.03	0.40	0.03	0.28	0.03
	B09	0.11	0.04	0.11	0.01	0.05	0.04	0.15	0.01	0.12	0.04
	B02	0.29	0.01	0.34	0.02	0.38	0.01	0.72	0.03	0.57	0.03
	H06	0.20	0.05	0.21	0.08	0.50	0.01	0.71	0.07	0.47	0.07
	H32	0.19	0.02	0.22	0.02	0.30	0.01	0.51	0.03	0.33	0.02
	C07	0.19	0.01	0.23	0.01	0.34	0.02	0.57	0.01	0.40	0.02
	<b>Ave.</b>	<b>0.23</b>	<b>0.13</b>	<b>0.26</b>	<b>0.16</b>	<b>0.31</b>	<b>0.14</b>	<b>0.58</b>	<b>0.25</b>	<b>0.41</b>	<b>0.11</b>
<b>East China Sea</b> (n=12)	A09	0.09	0.01	0.09	0.01	0.16	0.002	0.26	0.01	0.13	0.01
	F10	0.13	0.05	0.17	0.02	0.39	0.02	0.57	0.04	0.34	0.02
	E6	0.02	0.01	0.003	0.01	0.03	0.01	0.04	0.01	0.01	0.02
	D1	0.20	0.02	0.27	0.02	0.41	0.01	0.68	0.01	0.41	0.01
	D12	0.51	0.03	0.59	0.03	0.48	0.02	1.07	0.03	0.73	0.05
	A3	0.12	0.01	0.13	0.01	0.17	0.01	0.29	0.02	0.24	0.02

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	C4	0.09	0.01	0.11	0.01	0.20	0.01	0.31	0.01	0.27	0.02
	C7	0.06	0.01	0.07	0.01	0.11	0.01	0.18	0.01	0.17	0.03
	C12	0.83	0.07	0.97	0.06	0.52	0.03	1.49	0.09	1.41	0.09
	B8	0.04	0.01	0.05	0.01	0.11	0.00	0.16	0.01	0.14	0.01
	F2	0.20	0.03	0.25	0.03	0.33	0.02	0.58	0.05	0.55	0.04
	F5	0.06	0.02	0.06	0.02	0.06	0.01	0.12	0.02	0.13	0.04
	<b>Ave.</b>	<b>0.19</b>	<b>0.23</b>	<b>0.23</b>	<b>0.27</b>	<b>0.25</b>	<b>0.17</b>	<b>0.48</b>	<b>0.42</b>	<b>0.38</b>	<b>0.37</b>
East China seas (n=24)	<b>Ave.</b>	<b>0.22</b>	<b>0.18</b>	<b>0.25</b>	<b>0.22</b>	<b>0.27</b>	<b>0.15</b>	<b>0.52</b>	<b>0.34</b>	<b>0.40</b>	<b>0.29</b>
Interlaboratory comparison sample	Still Pond	1.31	0.09	1.55	0.10	0.43	0.13	1.98	0.10	2.00	0.05
	R-64	4.06	0.07	4.30	0.03	1.57	0.43	5.87	0.44	5.50	0.10

**Table 5.** Parameters from the Si and Al continuous dissolution (Si/Al method) with 0.5 M NaOH (1 h digestion).  $ExtrSi_i$  ( $\text{mg-Si g}^{-1}$ ) is the concentration of each Si fraction dissolving nonlinearly,  $k_i$  ( $\text{min}^{-1}$ ) is their respective reactivity and  $Si_i: Al_i$  ratio. Parameter  $b$  refers to the slope of the fraction dissolving linearly. SP-1, SP-2 and R-64-1, R-64-2 represent duplicate digestions of sample Still Pond and R-64. TAlkExSi and TAlkExAl represent the total alkaline extracted Si and Al. The bSiO<sub>2</sub>% presented here is the bSi content in dry weight. NA represents data that is not available.

Station	Optimum model	$ExtrSi_1$ ( $\text{mg-Si g}^{-1}$ )	$ExtrSi_2$ ( $\text{mg-Si g}^{-1}$ )	TAlkExSi ( $\text{mg-Si g}^{-1}$ )	TAlkExAl ( $\text{mg-Si g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$k_2$ ( $\text{min}^{-1}$ )	$\beta_1$	$\beta_2$	$b$ ( $\text{mg-Si g}^{-1} \text{min}^{-1}$ )	$\beta_{lin}$	bSiO <sub>2</sub> %
B01	Model 2	0.82	2.34	6.13	2.89	1.90	0.08	4.40	1.83	0.07	2.13	0.18
B10	Model 2	1.26	3.73	12.25	5.14	1.45	0.07	3.16	2.53	0.12	1.95	0.27
B19	Model 2	0.96	1.97	6.16	2.24	1.63	0.08	7.14	2.81	0.07	2.32	0.21
B23	Model 2	1.64	4.91	14.88	5.79	1.66	0.08	10.44	2.36	0.16	2.30	0.35
B18	Model 2	0.58	0.83	3.22	1.01	3.10	0.09	12.83	3.08	0.03	2.45	0.12
B43	Model 2	1.49	6.01	15.29	5.18	1.52	0.08	3.86	3.86	0.16	2.45	0.32
H20	Model 2	0.73	1.56	4.21	1.56	1.84	0.06	4.36	2.64	0.04	2.40	0.16
B09	Model 1	0.66	NA	1.58	0.36	0.69	NA	10.71	NA	0.03	3.23	0.14
B02	Model 2	1.40	3.80	10.83	3.77	2.46	0.10	7.83	3.06	0.17	2.38	1.11
H06	Model 2	1.46	4.50	12.21	4.26	1.64	0.08	11.89	2.81	0.16	2.45	0.31
H32	Model 2	1.10	1.69	5.83	1.94	2.23	0.09	12.15	2.13	0.07	2.82	0.24
C07	Model 2	1.04	2.48	7.00	2.29	2.79	0.08	9.01	2.88	0.08	2.65	0.22
A09	Model 2	0.46	0.68	2.19	0.65	2.46	0.09	8.05	3.44	0.02	2.66	0.10
F10	Model 2	0.88	1.74	7.50	2.72	2.17	0.11	6.75	2.81	0.11	2.45	0.56
A3	Model 2	0.66	0.64	2.92	1.02	2.50	0.10	13.83	1.83	0.03	2.74	0.28
D1	Model 2	0.89	4.08	10.59	4.95	0.99	0.07	2.00	2.29	0.09	2.07	0.19
D12	Model 2	2.47	2.63	23.31	3.73	1.89	0.12	8.94	7.84	0.08	5.07	1.09
DC	Model 2	4.99	5.88	17.82	3.72	1.32	0.05	7.91	5.44	0.15	3.60	2.33
E6	Model2	0.40	0.16	0.97	0.24	3.32	0.13	22.44	2.72	0.01	2.82	0.12
B8	Model 2	0.39	0.39	2.02	0.56	3.57	0.10	9.47	3.22	0.02	3.12	0.17
C4	Model 1	1.14	NA	2.97	1.20	0.06	NA	2.31	NA	0.03	2.71	0.24
C7	Model 2	0.25	0.39	2.25	0.68	4.50	0.09	9.21	3.35	0.02	2.98	0.05
C12	Model 2	5.29	5.67	17.10	3.54	1.17	0.06	7.86	4.79	0.10	3.80	1.13
F2	Model 2	0.90	3.52	9.15	3.93	1.52	0.07	4.80	2.09	0.09	2.27	0.19

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F5	Model 2	0.39	0.44	1.68	0.51	2.56	0.08	6.92	3.26	0.02	2.69	0.08
F8	Model 2	2.50	4.62	10.69	2.77	1.06	0.05	7.35	4.15	0.08	2.70	0.54
A1	Model 2	0.81	2.72	6.35	2.84	1.46	0.08	3.44	2.22	0.06	2.09	0.17
A4	Model 1	0.21	NA	0.65	0.14	1.34	NA	25.02	NA	0.01	3.14	0.05
SP-1	Model 2	6.53	6.45	18.73	4.42	1.49	0.13	9.96	4.50	0.10	2.47	2.78
SP-2	Model 2	7.44	5.18	17.11	4.81	0.50	0.05	5.88	5.18	0.09	1.79	2.70
R-64-1	Model 2	19.20	15.32	46.09	7.97	0.64	0.15	20.39	6.37	0.19	2.49	7.40
R-64-2	Model 2	15.16	17.76	43.65	11.26	1.26	0.18	22.06	11.00	0.18	2.96	7.05

**Table 6.** Burial flux of bSiO<sub>2</sub> (Gmol-SiO<sub>2</sub> yr<sup>-1</sup>) of the BH, the YS, and the ECS. The total bSiO<sub>2</sub> burial flux of the East China seas equals the sum of the burial flux of the BH, YS, and ECS. The Si/time method (0.1 M Na<sub>2</sub>CO<sub>3</sub>, NP) and the Si/Al method (0.5 M NaOH, NP) was displayed for the determination of bSiO<sub>2</sub>%. The Si/Al method was defined as an optimum method due to an accurate correction of lSi.

Methods	Time interval of digestion	BH	YS	ECS	Total burial flux (Gmol-SiO <sub>2</sub> yr <sup>-1</sup> )	
Si/time (0.1 M Na <sub>2</sub> CO <sub>3</sub> )	5 h	bSiO <sub>2</sub> %	0.24 ± 0.08	0.23 ± 0.13	0.19 ± 0.23	132 ± 112
		burial flux (Gmol-SiO <sub>2</sub> yr <sup>-1</sup> )	15.46 ± 5.15	54.03 ± 30.54	62.76 ± 75.98	
	8 h	bSiO <sub>2</sub> %	0.43 ± 0.15	0.41 ± 0.11	0.38 ± 0.37	249 ± 158
		burial flux (Gmol-SiO <sub>2</sub> yr <sup>-1</sup> )	27.70 ± 9.66	96.31 ± 25.84	125.53 ± 122.22	
	20 h	bSiO <sub>2</sub> %	0.53 ± 0.18	0.58 ± 0.25	0.48 ± 0.42	329 ± 209
		burial flux (Gmol-SiO <sub>2</sub> yr <sup>-1</sup> )	34.14 ± 11.60	136.24 ± 58.73	158.56 ± 138.74	
Si/Al (0.5 M NaOH)	1 h	bSiO <sub>2</sub> %	0.23 ± 0.09	0.36 ± 0.34	0.46 ± 0.60	253 ± 286
		burial flux (Gmol-SiO <sub>2</sub> yr <sup>-1</sup> )	14.82 ± 5.80	84.36 ± 79.67	153.49 ± 200.20	

