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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 (bSiO₂%) in marine sediments remains a challenge. The alkaline methods commonly used to
25 quantitatively determine bSiO₂% 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 bSiO₂%. 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 bSiO₂% due to increased leaching of silica mainly from authigenic silicates and clays, whereas
33 weak digestions underestimated the bSiO₂% 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 bSiO₂% 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 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 bSiO₂% in marine sediments (Conley, 1998). Considering the complex
71 sediment composition of CCMZs sediments, a mild alkaline leach (0.1 M Na₂CO₃) 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 bSiO₂% 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 H₂O₂ 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 bSiO₂% 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 bSiO₂% 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 (bSiO₂-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 bSiO₂% (< 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 bSiO₂% determined using several alkaline digestion
104 techniques, such as using different concentrations of alkaline solution (0.1 M Na₂CO₃, 2% Na₂CO₃,
105 2.0 M Na₂CO₃), duration of the alkaline digestion (5 h, 8 h) and pre-treatment process (with HCl and
106 H₂O₂ 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 bSiO₂% using different alkaline
122 solution concentrations (0.1 M, 0.2 M, 2.0 M Na₂CO₃), 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 bSiO₂% determined using the Si/time method (20 h digestion in 0.1 M Na₂CO₃)
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 bSiO₂% 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 bSiO₂% 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 ($0.1 \text{ M Na}_2\text{CO}_3$, 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 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 $10\% \text{ H}_2\text{O}_2$ (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 Ω). 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 (10³ g⁻¹).

171 **3.2.2. Biogenic silica**

172 The content of bSi found in the sediments in this study is expressed as bSiO₂% (molar mass of
173 bSiO₂: 60 g mol⁻¹) 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 bSiO₂%, 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 Na₂CO₃
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 Na₂CO₃) 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 μ 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 Ω cm⁻¹) 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% H₂O₂) and non-pretreated (NP) sediment were performed using 0.1 M, 0.2
194 M, 2.0 M Na₂CO₃ solutions to determine the effect of the concentration of Na₂CO₃ and pretreatment
195 process (P vs. NP) on bSi determination.

196 In this study, the bSiO₂% was determined following the calculation method described by Liu et al,
197 (2002) where sediments undergo an 8 h digestion. In addition, the bSiO₂% 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 Na₂CO₃ 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 bSiO₂% 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, bSiO₂% 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[®], 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⁻¹, 2 mg L⁻¹, 4 mg L⁻¹, 6 mg L⁻¹, 8 mg L⁻¹, 10 mg
215 L⁻¹, 20 mg L⁻¹, 30 mg L⁻¹, and 40 mg L⁻¹ were used for calibration, and only the linear regression curves
216 with correlation coefficients ≥ 0.999 were accepted according to previous studies (Barão et al., 2015).
217 Two independent reference solutions (with concentrations of 3 mg L⁻¹, and 9 mg L⁻¹ 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 Na₂SiO₃·9H₂O (Sigma-Aldrich S4392)
220 and KAl (SO₄)₂·12H₂O (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 bSiO₂% 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 bSiO₂% 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⁻¹, in the reaction
 242 vessel at time t (min). $[Si_{extr}]_0$ is the initial extractable silica present in the vessel in mg L⁻¹, 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⁻¹) and β_1 is the atomic ratio of Si and Al released during the dissolution of
 245 extractable silica fraction. b (mg L⁻¹ min⁻¹) represents the constant dissolution rate of Si from clay
 246 minerals and β_{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 β_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 α 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 (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 bSiO₂ in the CCMZs of East China seas

The burial flux (F_b) of bSiO₂ in sediment can be expressed as follows (Ingall and Jahnke, 1994):

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

288
 289 Where C (mol g^{-1}) is the concentration of 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 mol g^{-1} by dividing it by the molecular weight of 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 bSiO₂% applying a 0.5 M NaOH digestion (Still Pond: 2.74%; R-64:
328 7.23%) and a 0.1 M Na₂CO₃ digestion (Still Pond: 2.00 ± 0.05%; R-64: 5.50 ± 0.10%) are within the
329 acceptable range of bSiO₂% 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 bSiO₂% 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 H₂O₂ (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 bSiO₂%.

345 Figure 3 shows a continuous increase of the SiO₂% 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 Na₂CO₃, P > 0.1 M Na₂CO₃, NP; 0.2 M Na₂CO₃, P > 0.2 M Na₂CO₃, NP; 2.0 M Na₂CO₃, P >
349 2.0 M Na₂CO₃, NP; Figure 4). As shown in Figure S4 and Figure S5, most of the SiO₂ was leached
350 from sediments during the first 4 h (AlkExSi₍₁₋₄₎) and less SiO₂ was extracted during the 5 h to 8 h

351 digestion (AlkExSi₍₅₋₈₎). The quantity of AlkExSi₍₁₋₄₎ and AlkExSi₍₅₋₈₎ correspond to 66% – 86% and
 352 14% – 34% of total amount of silica (TAlkExSi; TAlkExSi = AlkExSi₍₁₋₄₎ + AlkExSi₍₅₋₈₎) extracted
 353 during the 8 h alkaline digestion (Figure S5). In addition, the AlkExSi₍₁₋₄₎ 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₍₅₋₈₎ was low (< 0.2%SiO₂) and showed small variations when digested under different
 356 alkaline solutions (0.1 M, 0.2 M and 2.0 M Na₂CO₃, P vs. NP). Moreover, more silica (AlkExSi₍₁₋₄₎
 357 and AlkExSi₍₅₋₈₎) can be leached in stronger alkaline, but the proportion of AlkExSi₍₁₋₄₎ and AlkExSi₍₅₋₈₎
 358 to TAlkExSi does not change much (Figure S5).

359 Table 3 and Figure S6 showed the bSiO₂% 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 bSiO₂% between 0.1 M Na₂CO₃ (P vs. NP),
 362 0.2 M Na₂CO₃ (P vs. NP) and 2.0 M Na₂CO₃ (P vs. NP) were significant ($p < 0.0001$; Noymer (2008))
 363 (Table S1). The yield, expressed as bSiO₂%, between the P and the NP alkaline digestions are: 0.1 M
 364 Na₂CO₃ (P) = 194% 0.1 M Na₂CO₃ (NP), 0.2 M Na₂CO₃ (P) = 226% 0.2 M Na₂CO₃ (NP) and 2.0 M
 365 Na₂CO₃ (P) = 185% 2.0 M Na₂CO₃ (NP) in average (calculated from Table 3). Besides the pre-
 366 treatment process, a higher concentration of Na₂CO₃ can extract more silica significantly ($p < 0.0001$)
 367 than a lower concentration of Na₂CO₃ (C7, F2, F8 and DC; Figure S6), except for the bSiO₂%
 368 determined using a 0.2 M Na₂CO₃ (P) and the 2.0 M Na₂CO₃ (P) digestion ($p = 0.0726$). For the non-
 369 pretreated (NP) digestion experiment, the average bSiO₂% extracted using 2.0 M Na₂CO₃ solution is
 370 49% and 69% higher than the 0.2 M Na₂CO₃ and 0.1 M Na₂CO₃ digestion, respectively. However, the
 371 bSiO₂% of samples C7 and C12 was approximately the same when the sample was digested using
 372 different concentrations of Na₂CO₃ (0.1, 0.2, 2.0 M), and the bSiO₂% of samples C4, F2, F8, and DC
 373 was higher when using a higher concentration of Na₂CO₃ solution (Figure S6). Compared to the
 374 alkaline concentration, the pretreatment process has a more important influence on bSi determination.
 375 The bSiO₂% determined following the single-step alkaline digestion method proposed for abyssal
 376 deposits (Mortlock and Froelich, 1989) generated much higher bSiO₂% values ($p < 0.0001$) than all
 377 other digestions. Moreover, the bSiO₂% determined using 0.1 M Na₂CO₃ (NP; DeMaster, 1981) was
 378 not significantly different ($p = 0.0726$) compared to the bSiO₂% determined using 0.5 M NaOH (NP;
 379 Koning et al., 2002) (Table S1). The bSiO₂% determined by 2.0 M Na₂CO₃ (P) is about 2.6 times of
 380 the bSiO₂% determined by 0.1 M Na₂CO₃ (NP). The average bSiO₂% of samples C4, C7, C12, F2, F8
 381 and DC determined using different methods (0.1 M, 0.2 M, 2.0 M Na₂CO₃, 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 bSiO₂% was large for low bSiO₂% 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 bSiO₂% estimates, that
395 accord with the duration of digestion, i.e., the 5 h digestion with the shortest time showed the least
396 bSiO₂% ($0.22 \pm 0.18\%$), the moderate duration (8 h) of the attack gave an intermediate bSiO₂% (0.40
397 $\pm 0.29\%$), and the longest duration of digestion produce the highest bSiO₂% ($0.52 \pm 0.34\%$) (Table 4).
398 The ART ANOVA analysis indicated a significant ($p < 0.0001$) difference in the bSiO₂% among the
399 three different time intervals.

400 According to the method described in Conley and Schelske (2001), the diatom bSiO₂%, radiolarian
401 and sponge bSiO₂% were calculated at a 5 h and 20 h digestion interval, respectively (Table 4, Figure
402 S8). The diatom bSiO₂%, radiolarian and sponge bSiO₂% and total bSiO₂% 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 bSiO₂% is approximately equal to the amount
405 of radiolarian and sponge bSiO₂% (Figure S8). ART ANOVA analysis showed a significant difference
406 ($p < 0.0001$) between diatom bSiO₂%, radiolarian and sponge bSiO₂% and the total bSiO₂%. Detailed
407 calculations of the averaged bSiO₂% 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 bSiO₂% 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 bSiO₂%.

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 mg-Si g^{-1} , with a relative constant β_{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 β_1 is higher than the β_2 (except for
 431 D1, table 5). Figure 6 showed a wide range of Si:Al ratios for β_1 ($2 < \beta_1 < 25$) and k_1 ($0.5 < k_1 < 5$), and
 432 small ranges of β_2 ($2 < \beta_2 < 8$) and k_2 ($0 < k_2 < 0.2$). In addition, β_2 has similar Si:Al ratios compare to
 433 β_{lin} , and β_1 is always higher than the β_{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 (β_i) and the reactivity (k_i), the calculated bSiO₂% (dry weight) and lSiO₂% (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 bSiO₂% examined using the Si/time method (0.1 M Na₂CO₃). However, the $ExtrSi_1$ is approximately
 446 equal to diatom bSiO₂% (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 H₂O₂ (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 allocthenic 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 Na₂CO₃, 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 Na₂CO₃ (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 bSiO₂% 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 bSiO₂%. 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 H₂O₂) 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 bSiO₂% 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 bSiO₂% 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% H₂O₂) 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% H₂O₂ 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 bSiO₂ 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 (± 112) Gmol-SiO₂ yr⁻¹, 249 (± 158) Gmol-SiO₂ yr⁻¹ and 329
547 (± 209) Gmol-SiO₂ yr⁻¹ using the bSiO₂% determined at 5 h, 8 h and 20 h digestion interval,
548 respectively. And the estimated bSi burial flux is 253 (± 286) Gmol-SiO₂ yr⁻¹ 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 bSiO₂ (253 \pm 286 Gmol-SiO₂ yr⁻¹) in the East China seas is about one third of the previous
554 studies (924 \pm 693 Gmol-SiO₂ yr⁻¹; Wu et al., 2017, Wu and Liu, 2020). This is mainly due to the
555 methodological bias, because the previous studies determined the bSiO₂% with a pre-treatment (with
556 HCl and H₂O₂) process (Wu et al., 2017; Wu and Liu, 2020) that overestimate the bSiO₂%,
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 bSiO₂%
 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 Na₂CO₃, NP, 5 h digestion) (DeMaster, 1981), which is
 597 commonly used to quantitatively determine bSiO₂% 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 Na₂CO₃ solution can digest
 600 the diatom and radiolarian bSi and ca. 80% of sponge bSi. The determination of the bSiO₂% using
 601 a 2.0 M Na₂CO₃ solution overestimates the bSiO₂% 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 bSiO₂%
 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 H₂O₂ (10%) prior to alkaline digestion can
607 cause an overestimation of the bSiO₂% 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 Na₂CO₃
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 Na₂CO₃ solution
621 resulted in an overestimation of the bSiO₂% owing to silica being digested from clay minerals.
622 Applying a 0.1 M Na₂CO₃ digestion (20 h) can minimize the lSi interference on bSi determination, but
623 can cause at least 20% of underestimation of the bSiO₂% owing to incomplete digestion of sponge
624 spicules. Our results also show that alkaline extractions that apply a pretreatment procedure
625 overestimate the determined bSiO₂% 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 bSiO₂% 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 bSiO₂% 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 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 H₂O₂) 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. H₂O₂). (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 Na₂CO₃ (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 (SiO₂%) was normalized into the dry weight of the sediment. P represents pretreatment
 908 of sediment using HCl (1.0 M) and H₂O₂ (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 Na₂CO₃ solution (P vs. NP). The results presented are the SiO₂% extracted
 913 after 8 h. More SiO₂% 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 (β_i , β_{lin} , k_i) from the modeling results. (A) shows the
 919 relationship between the Si:Al ratio (β_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 β_1 ($1 < \beta_1 < 25$) is bigger than β_2 ($2 < \beta_2 < 10$). (B) shows the relationship of the
 922 Si:Al ratio between the two non-linear dissolving fractions (β_1 , β_2) and lSi (β_{lin}). β_1 is bigger than β_2
 923 and β_{lin} and β_2 is approximately equal to β_{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 H₂O₂ (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 Na₂CO₃ (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 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 μm) of BH; b: observation of low abundance of sponge spicules with intermediate size (length: 50 – 300 μm) of YS; c: observation of high abundance of sponge spicules (length: 100 – 500 μm). 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)		++	–	+ ^a	This study
		13.0 ¹	no data	no data	Other studies
Yellow Sea (n=7)		++	–	+ ^b	This study
		17.0 ²	~0 ⁵	no data	Other studies
East China Sea (n=16)		++	+	+++ ^c	This study
		11.3-19.9 ^{3,4}	0.02-7.3 ^{5,6}	no data	Other studies
	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 bSiO₂% 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 ₂	std	bSiO ₂	std			
2.00	0.05	5.50	0.10	0.1 M Na ₂ CO ₃ ^a	5	This study
2.74	-	7.23	-	0.5 M NaOH ^a	1	This study
1.84	-	7.80	-	0.5 M NaOH ^a	0.5	Barão et al, (2015)
2.68	0.06	-	-	2% Na ₂ CO ₃ ^b	8	Wu and Liu (2015)
3.88	0.19	7.50	0.13	2.0 M Na ₂ CO ₃ ^b	8	Liu et al, (2002)
2.82	1.17	6.49	2.09	Na ₂ CO ₃ /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 H₂O₂ (10%) before the alkaline digestion.

Table 3. The bSiO₂% was determined using 0.1 M, 0.2 M and 2.0 M Na₂CO₃ (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 bSiO₂% of C4 (0.49 ± 0.25%), C7 (0.40 ± 0.23%), C12 (1.82 ± 0.56%), F2 (1.00 ± 0.44%), F8 (1.13 ± 0.49%), DC (1.34 ± 0.57%) determined using different concentrations of alkaline solution (0.1 M, 0.2 M, 2.0 M Na₂CO₃, 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 bSiO₂% determined using different concentrations of Na₂CO₃ (P and NP). MF 1989 represents the bSiO₂% determined following the method described by Mortlock and Froelich (1989), this method (no mineral correction) is presented for comparison with the 2.0 M Na₂CO₃ digestion that applied a mineral correction.

Station	0.1 M Na ₂ CO ₃		0.2 M Na ₂ CO ₃				2.0 M Na ₂ CO ₃				2.0 M Na ₂ CO ₃ MF 1989			
	NP		P		NP		P		NP		P		P	
	bSiO ₂	std	bSiO ₂	std	bSiO ₂	std	bSiO ₂	std	bSiO ₂	std	bSiO ₂	std	bSiO ₂	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 bSiO₂% in sediments of the East China seas (BH, YS, ECS) was determined using the Si/time alkaline digestion method (0.1 M Na₂CO₃; NP). The locations of the samples are shown in Figure 1. The different types of bSi determined (diatom, sponge and total bSiO₂) 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 bSiO₂% calculated at 5 h intervals (DeMaster, 1981; Diatom bSiO₂, 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 ₂		Diatom bSiO ₂		Sponge bSiO ₂		Total bSiO ₂		Total bSiO ₂	
		5	5	5	20	20	20	8	8		
Station	bSiO ₂	std	bSiO ₂	std	bSiO ₂	std	bSiO ₂	std	bSiO ₂	std	
Bohai Sea (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
	Ave.	0.24	0.08	0.27	0.09	0.26	0.09	0.53	0.18	0.43	0.15
Yellow Sea (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
	Ave.	0.23	0.13	0.26	0.16	0.31	0.14	0.58	0.25	0.41	0.11
East China Sea (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
	Ave.	0.19	0.23	0.23	0.27	0.25	0.17	0.48	0.42	0.38	0.37
East China seas (n=24)	Ave.	0.22	0.18	0.25	0.22	0.27	0.15	0.52	0.34	0.40	0.29
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). $ExtrSi_i$ (mg-Si g^{-1}) is the concentration of each Si fraction dissolving nonlinearly, k_i (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 $\text{bSiO}_2\%$ presented here is the bSi content in dry weight. NA represents data that is not available.

Station	Optimum model	$ExtrSi_1$ (mg-Si g^{-1})	$ExtrSi_2$ (mg-Si g^{-1})	TAlkExSi (mg-Si g^{-1})	TAlkExAl (mg-Si g^{-1})	k_1 (min^{-1})	k_2 (min^{-1})	β_1	β_2	b ($\text{mg-Si g}^{-1} \text{ min}^{-1}$)	β_{lin}	$\text{bSiO}_2\%$
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 bSiO₂ (Gmol-SiO₂ yr⁻¹) of the BH, the YS, and the ECS. The total bSiO₂ 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 Na₂CO₃, NP) and the Si/Al method (0.5 M NaOH, NP) was displayed for the determination of bSiO₂%. 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 ₂ yr ⁻¹)	
Si/time (0.1 M Na ₂ CO ₃)	5 h	bSiO ₂ %	0.24 ± 0.08	0.23 ± 0.13	0.19 ± 0.23	132 ± 112
		burial flux (Gmol-SiO ₂ yr ⁻¹)	15.46 ± 5.15	54.03 ± 30.54	62.76 ± 75.98	
	8 h	bSiO ₂ %	0.43 ± 0.15	0.41 ± 0.11	0.38 ± 0.37	249 ± 158
		burial flux (Gmol-SiO ₂ yr ⁻¹)	27.70 ± 9.66	96.31 ± 25.84	125.53 ± 122.22	
	20 h	bSiO ₂ %	0.53 ± 0.18	0.58 ± 0.25	0.48 ± 0.42	329 ± 209
		burial flux (Gmol-SiO ₂ yr ⁻¹)	34.14 ± 11.60	136.24 ± 58.73	158.56 ± 138.74	
Si/Al (0.5 M NaOH)	1 h	bSiO ₂ %	0.23 ± 0.09	0.36 ± 0.34	0.46 ± 0.60	253 ± 286
		burial flux (Gmol-SiO ₂ yr ⁻¹)	14.82 ± 5.80	84.36 ± 79.67	153.49 ± 200.20	

