Faithful transfer of radiolarian silicon isotope signatures from water column to sediments in the South China Sea

Qiang Zhang[1, 2], George E. A. Swann[2], Vanessa Pashley[3], and Matthew S. A. Horstwood[3]

[1]Key Laboratory of Ocean and Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
[2]School of Geography, University of Nottingham, University Park, Nottingham, NG7 2RD, UK
[3]National Environmental Isotope Facility, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

Correspondence: Qiang Zhang (zhangqiang210@scsio.ac.cn)

Abstract. Radiolarian silicon isotopes ($\delta^{30}Si_{rad}$) hold significant potential as a proxy for constraining past silicon cycling in seawater. However, the extent to which $\delta^{30}Si_{rad}$ signatures in sediments accurately represent the isotopic signals of the overlying water column remains unclear, particularly under the influence of radiolarian shell dissolution during sinking and burial in the sediment record. This study presents the first comparative analysis of $\delta^{30}Si_{rad}$ compositions and the radiolarian assemblage community using water column and surface sediment samples collected from the South China Sea (SCS). The results indicate that $\delta^{30}Si_{rad}$ values range from 1.56-1.83‰ (mean = 1.74‰) in the water column, and from 1.61-1.85‰ (mean = 1.73‰) in surface sediments, with the fractionation factor for $\delta^{30}Si_{rad}$ varying from –0.33‰ to –0.92‰ (mean = 0.58‰). $\delta^{30}Si_{rad}$ signatures in the water column are primarily contributed to by radiolarians from the 0-100 m water depth layer. No significant discrepancies in $\delta^{30}Si_{rad}$ values were observed between plankton and sediment samples at each sampling station, as evidenced by the paired t-test ($p = 0.75$), implying that dissolution has a minimal impact on $\delta^{30}Si_{rad}$ during the transfer of radiolarian shells to the sediment record. This finding may be enhanced by the dominance of more dissolution-resistant Spumellaria and Nassellaria taxa (>99% relative abundance) within the radiolarian community, coupled with the scarcity or absence of the readily dissolvable radiolarian taxa in the analysed samples. This study demonstrates the faithful preservation of the $\delta^{30}Si_{rad}$ signature and its potential for studying past changes in the marine silicon cycle.

1 Introduction

Silicon (Si) is a crucial nutrient in marine ecosystems, playing a significant role in both the global carbon cycle and climate change. For example, during glacial periods the Southern Ocean exhibits reduced rates of primary productivity and silicon utilization efficiency due to the alleviation of iron (Fe) limitation by enhanced aeolian deposition, resulting in an excess of silicic acid ($Si(OH)_4$) in the water column (Matsumoto et al., 2002; Brzezinski et al., 2002). Based on this, the "silica acid leakage hypothesis" (SALH) was proposed, in which excess $Si(OH)_4$ within glacial Antarctic intermediate water was transported to lower latitudes, leading to enhanced diatom productivity at the expense of carbonate export (Brzezinski et al., 2002). This shift to diatom growth over carbonate export was expected to result in higher seawater alkalinity, and lower atmospheric pCO₂ (Matsumoto et al., 2002; Matsumoto and Sarmiento, 2008; Ellwood et al., 2010) and is supported by significant increases in glacial siliceous productivity in lower latitude regions of the equatorial Atlantic and low-latitude Pacific Oceans (e.g., Kienast

et al., 2006; Bradtmiller et al., 2007; Arellano-Torres et al., 2011; Hendry et al., 2021). However, other findings have challenged this hypothesis by suggesting that siliceous productivity and surface water $Si(OH)_4$ concentrations were ~~actually~~ higher during interglacials (e.g., Bradtmiller et al., 2006; Dubois et al., 2010). To gain a deeper insight into the mechanisms~~,~~ and impact~~,~~ of marine silicon cycling in both glacials~~,~~ and other temporal/spatial scales across the geological record, it is essential to have a

30 more comprehensive understanding of the relationships between marine $Si(OH)_4$ concentrations, primary productivity and the ~~wider~~ climate system.

The silicon isotope ($\delta^{30}Si$) composition of biogenic silica (BSi), primarily comprising radiolarians, diatoms, and sponge spicules, serves as a key indicator for quantifying marine silicon cycling and its response to changing oceanographic and climate processes. Whereas the $\delta^{30}Si$ of diatoms, inhabiting the photic zone of the water column, primarily reflects changes in

35 silicic acid utilization/supply in the surface ocean (De La Rocha et al., 1998; Reynolds et al., 2006; Egan et al., 2012; Abelmann et al., 2015; Swann et al., 2016, 2017; Hendry et al., 2021; Worne et al., 2022), the $\delta^{30}Si$ of sponge spicules, inhabiting bottom waters, are closely related to deep ocean $Si(OH)_4$ concentrations (De La Rocha, 2003; Wille et al., 2010; Hendry et al., 2010; Hendry and Robinson, 2012; Hendry et al., 2014; Fontorbe et al., 2016). More recently, attempts have been made to use the $\delta^{30}Si$ of radiolaria shells ($\delta^{30}Si_{rad}$), which typically occupy intermediate water depths in high latitudes (Boltovskoy, 2017),

40 to fill in the gaps between surface (diatom) and bottom (sponge) measurements of $\delta^{30}Si$ and so allow whole water column reconstructions of silicon cycling (e.g., Abelmann et al., 2015).

Numerous studies have demonstrated that c. 97% of biogenic silica, specifically for diatoms in surface waters, is dissolved during sinking through the water column and/or early diagenesis (Tréguer et al., 1995; Ragueneau et al., 2000; Tréguer and De La Rocha, 2013). The potential for this dissolution to fractionate and ~~so~~ alter BSi $\delta^{30}Si$ is under debate.

45 Cardinal et al. (2007) reported a positive relationship between the silicon isotopic fractionation factor and net diatom production in the Southern Ocean, implying a dissolution-driven isotope effect. Demarest et al. (2009) then conducted dissolution experiments on natural diatom frustules, observing a silicon isotope fractionation factor of -0.55 ± 0.05‰ with lighter isotopes preferentially released. However, others have showed that diatom dissolution is not associated with significant silicon isotope fractionation in both laboratory experiments (Wetzel et al., 2014) and in studies monitoring the

50 sinking and burial of diatoms in the natural environment (Varela et al., 2004; Fripiat et al., 2012; Egan et al., 2012; Closset et al. 2015; Panizzo et al., 2016; Grasse et al. 2021). These inconsistent findings make it unclear to what extent silicon isotopic fractionation might impact the $\delta^{30}Si$ records of ~~also~~ other forms of biogenic silica preserved in the sediments.

Polycystine radiolarians, a primary component of biogenic silica in tropical ocean surface sediments (Lisitzin, 1972; Zhang et al., 2015), typically inhibit the water column from the surface to the deep ocean (e.g. Kling, 1979; Hu et al., 2015;

55 Boltovskoy et al., 2017) and exhibit a greater resistance to dissolution (Suzuki and Aita, 2011; Morley et al., 2014) than the more fragile and soluble diatoms. However, existing investigations of $\delta^{30}Si_{rad}$ have been limited by difficulties in successfully culturing radiolarians and/or purifying their tests from the natural environment (Suzuki and Aita, 2011; Suzuki and Not, 2015; Zhang and Swann, 2023). Whilst a few studies have explored $\delta^{30}Si_{rad}$ compositions in surface sediments and their correlations with $Si(OH)_4$ concentrations in the overlying water column (Ding et al., 1996; Egan et al., 2012; Abelmann et al., 2015;

60 Doering et al., 2021), as well as their response to changing climatic conditions (Hendry et al., 2014; Fontorbe et al., 2016),

the impact of dissolution on $\delta^{30}Si_{rad}$ during the sinking and burial of radiolarian shells into sediments remains unknown. Given the lightweight nature of shells and high diversity of radiolarians, particularly in low-latitude oceans (Moore, 1969; Takahashi, 1982; Boltovskoy et al., 2010), combined with the observation that most species typically comprise less than 10% of the total radiolarian assemblage in both the water column and the sedimentary record (Boltovskoy et al., 2010; Chen et al., 2008a), obtaining sufficient material from individual radiolarian taxa for silicon isotopic analysis remains a considerable challenge. Using a new method for extracting and purifying bulk radiolarain tests from sediments (Zhang and Swann, 2023), this study documents the $\delta^{30}Si_{rad}$ in water column and surface sediments in the South China Sea (SCS), and then assesses determines 1) the water column depth interval from which the radiolarian community contributes to $\delta^{30}Si_{rad}$; 2) the magnitude of silicon isotope fractionation by radiolarians, and 3) whether there is evidence of a dissolution impact on values of $\delta^{30}Si_{rad}$.

2 Material and methods
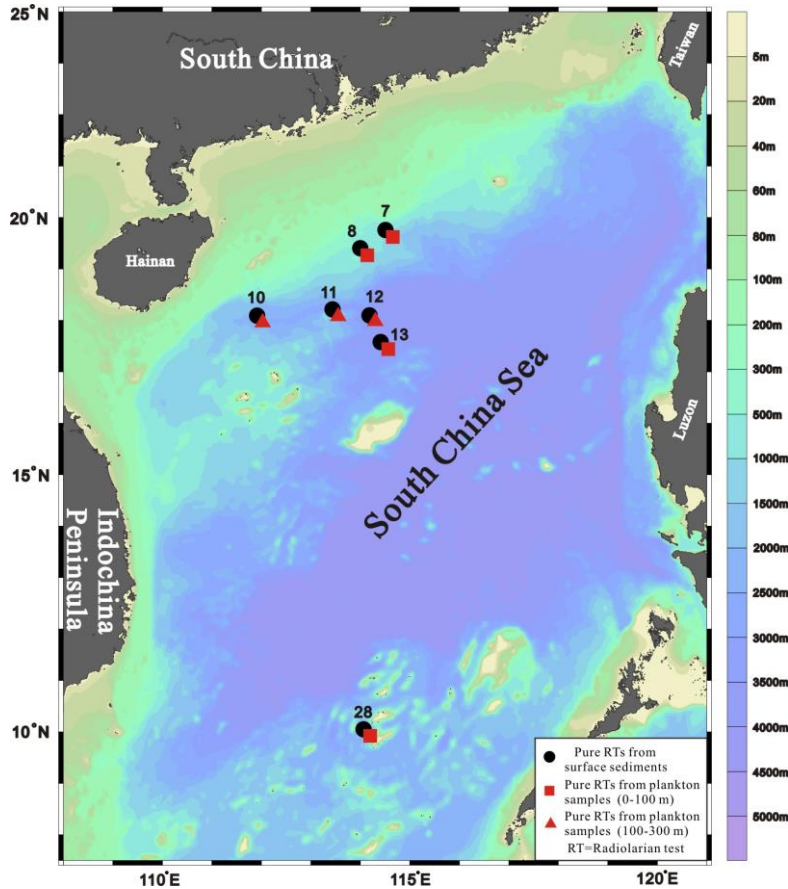
2.1 Sample material

Figure 1. Locations of sampling stations in the South China Sea (base map created using Ocean Data View software, version 5.3.0).

3

A total of 21 samples, comprising 14 plankton samples and 7 surface sediment samples, were collected at seven stations spanning the upper continental slope to the deep basin in the northwestern and southern SCS (Figure 1). All samples were collected during SCS cruises by R/V Shiyan 3 and Shiyan 1 of the South China Sea Institute of Oceanology, Chinese Academy of Sciences, in September 2016, November 2020 and August 2021 (Table S1 in the Supplementary Material 1). Plankton samples were collected from the 0-100 m and 100-300 m water layers at each station using a Hydro-Bios MultiNet with an aperture area of approximately 0.25 m² and a 63 μm mesh size, and were preserved in 5% buffered formalin. Each plankton sample was then divided into two or four aliquots, washed through a 63 μm sieve with deionized water, reacted with 30% H₂O₂ in a water bath at 75 ℃ for 24 hours, and freeze-dried. Due to insufficient radiolarian tests, only one plankton sample from either the 0-100 m or 100-300 m layer was used for isotopic analysis at each station. Surface sediments were sampled from the top 1 cm of the seabed using a box corer, and stored in the cold storage at 5 ℃. No discernible evidence of bioturbation or disturbance from turbidity currents was observed in the sediment samples at these stations. Based on regional variability in Holocene sedimentation rates in the SCS (Sheng et al., 2024), the estimated age of the uppermost 1cm of sediment used in this study ranges from < 40 to 133 years.

2.2 Radiolarian composition and preservation analysis

To determine the species composition of radiolarians, in both plankton samples and surface sediments, all samples were wet-sieved through a 63 μm sieve and prepared into radiolarian slides following the method described by Zhang et al. (2014). Briefly, samples were treated with a sufficient volume of 5% HCl solution for 15 minutes to eliminate calcareous organisms. Subsequently, the residual was processed using a sonic oscillator for one minute, and subjected to differential settling to remove impurities potentially adhering to the radiolarian tests. Following these procedures, all residual material was strewn nearly homogenously onto microscope slides and permanently mounted with Canada Balsam. Radiolarian species were then identified and counted under a Nikon optical microscope at x100 or x200 magnification, with more than 500 specimens identified on slides using the publications of Chen and Tan (1996) and Tan and Chen (1999). Radiolarian diversity was determined by the species richness in each sample. The total number of radiolarian individuals in each sample was estimated from the count data as follows:

$$T = A * \left(\frac{Vt}{V}\right) * S * N \tag{1}$$

Where T is the total number of radiolarian individuals; A is the number of radiolarian shells counted from V fields of view on the slide; Vt is the total number of view fields on the radiolarian slide; V is the number of view fields examined under the microscope for the radiolarian individual count; S is the number of radiolarian slides; and N is the aliquot size of the sample (eight for the plankton sample, and one for the sediment sample in this study). Relative abundances of various species were then calculated based on individual counts of each species and the total number of radiolarian specimens observed under the microscope.

To assess the preservation of radiolarian shells both within the water column and sediments, the proportion of fractured radiolarian shells was quantified in each studied sample under a Nikon optical microscope at x100 magnification. Further

105 scanning electron microscopy (SEM) was employed to examine the potential for dissolution-induced alteration of the radiolarian skeleton.

2.3 Silicon isotope analysis

For isotope analysis, a minimum of 1 mg of~~sufficient~~ radiolarian tests were extracted and purified from 7 plankton samples and 7 surface sediment samples following the method of Zhang and Swann (2023). Overall, the procedure for extracting
110 and purifying radiolarian tests from marine sediments in Zhang and Swann (2023) comprises four stages: chemical treatment, initial sieving and differential settling, subsequent sieving, and finally density separation. In the first stage, raw samples were treated with ~30% H_2O_2 and 15% HCl to remove the organic matters and calcareous components, and to facilitate particle dispersal. Following chemical treatment, the particles were rinsed and filtered using a 53 μm sieve to remove fine detritus, small diatoms, seaweed spines, and some sponge spicules. The filtered particles then underwent differential settling two to
115 three times, followed by sonication, to further isolate radiolarians from large diatoms. Subsequently, particles were filtered three times using a 53 μm sieve by half immersing the sieve in a container filled with distilled deionized water (DDW) and gently tapping the base of the sieve for 10-15 minutes. This process aimed to remove monoaxonic spicules and a portion of the small non-monoaxonic spicules. Finally, the retained fraction was further refined by density separation, using specific gravities from 2.1-2.0 g/cm^3 at 0.5-unit interval, to remove any remaining coarse detritus and non-monoaxonic sponge
120 spicules. The purity of extracted radiolarian tests in each sample was visually assessed under a Zeiss inverted light microscope at x100 magnification, with selected samples further examined using a ~~scanning electron microscopy~~ (SEM) (JEOL JSM-IT200) equipped with an energy dispersive X-ray spectroscopy (EDS) detector at the Nanoscale and Microscale Research Centre, University of Nottingham.

Pure radiolarian samples were digested using ~~the~~ NaOH fusion ~~method~~, with 1-~~3~~ 1.5 mg radiolarian tests fused with a 200
125 mg NaOH pellet. Subsequent purification was achieved via ion exchange chromatography at a pH of ~~between~~ 2-8 to ensure complete removal of cations, such as magnesium (Mg) and/or sodium (Na) (Georg et al., 2006; van den Boorn et al., 2006). Prior to analysis, each sample was filtered through a Millipore PTFE 0.2 nm filter to remove any particulate matter. The samples were then acidified using hydrochloric acid (HCl, to a concentration of 0.05 M, using twice quartz-distilled acid) and sulfuric acid (H_2SO_4, to a concentration of 0.001 M using Romil UPA). Swamping the natural abundance of chloride (Cl^-)
130 and sulfate (SO_4^{2-}) ions, in both samples and reference materials alike, will induce a similar mass bias response in each (Hughes et al., 2011). Finally, all samples are spiked with approximately 300 ppb magnesium (Mg, Alfa Aesar SpectraPure, $^{24}Mg/^{25}Mg$ = 0.126633) to enable correction of the data for instrument-induced mass bias (Cardinal et al., 2003). Any deviation of the measured $^{24}Mg/^{25}Mg$ value from the known value is attributed to the effects of mass bias. The isotopes of Si are assumed to be similarly affected, and consequently, an exponential drift correction is applied (Cardinal et al., 2003).
135 Silicon isotope analysis was performed in dry plasma mode using the high mass-resolution capability of a Thermo Fisher Scientific Neptune Plus MC-ICP-MS (multi collector inductively coupled plasma mass spectrometer) at the Geochronology and Tracers Facility, British Geological Survey. Samples were typically prepared to yield a Si concentration of approximately

2 ppm and introduced to the MC-ICP-MS via an Aridus de-solvating unit, incorporating a PFA nebulizer with an uptake rate of 50 µL/min. In high-resolution mode, the instrument typically exhibited a mass-resolution between approximately 9,000 to 140 10,000, and a sensitivity of 4-5 V/ppm. Analytical replicates of the standard sample bracketing procedure were conducted where sample volume allowed, with repeated ~~sampling~~ analysis of the standard (diatomite) to validate the data and sample bracketing with the international Si standard NBS28 to correct for any instrumental drift (Panizzo et al., 2016). The silicon isotope results are present in δ-notation in per mille (‰) deviations relative to the standard NBS28 ($\delta^{30}Si = [(^{30}Si/^{28}Si)_{sample}/(^{30}Si/^{28}Si)_{NBS28}-1] \times 1000$), using within-run aliquots of NBS28. All uncertainties are reported at 2 standard 145 deviations (2 SD)~~2σ absolute~~, and are propagated to incorporate an excess variance derived from the diatomite validation material, which was quadratically added to the analytical uncertainty of each measurement. The reproducibility and instrument accuracy were assessed by analyzing the secondary reference material (Diatomite). Repeated measurements of diatomite yielded average $\delta^{30}Si$ values of 1.26 ± 0.14‰(2 SD, n = 16), which agree well with the ~~published~~ values obtained from the inter-laboratory comparison experiment (consensus value of 1.26‰ ± 0.2‰, 2 SD) (Reynolds et al., 2006). $\delta^{29}Si$ and 150 $\delta^{30}Si$ values of radiolarian tests fall on the expected mass-dependent fractionation line $\delta^{29}Si = 0.51 \times \delta^{30}Si$ (Reynolds et al., 2006) (Figure S1 in the Supplementary Material 1), indicating the effective removal of all polyatomic interferences during measurement.

2.4 Paired t-tests and Wilcoxon signed-rank tests

To assess ~~for~~ potential differences in radiolarian species composition and $\delta^{30}Si_{rad}$ values between water and surface sediment 155 samples at each sampling station, paired t-tests and Wilcoxon signed-rank tests were employed. These statistical analyses were conducted using IBM SPSS Statistics Version 28, with the selection of the appropriate test determined by whether the data for relative abundances of prominent radiolarian species and $\delta^{30}Si_{rad}$ values conformed to a normal distribution.

3   Results

More than 400 radiolarian species have been reported in the SCS (Chen and Tan, 1996; Chen et al., 2008a), with 67-134 160 radiolarian species (mean = 114) identified in individual samples in this current study. The radiolarian diversity and the number of their shells in the plankton samples collected from the 0-100 m water layer, ranged from 67 to 116 species and from 28,025 to 102,443 individuals, respectively (Figure 2). These values represent 70-93% (mean = 83%) and 52-86% (mean = 72%) of the total observed in the upper 300 m of the water column (Figure 2). To characterize the radiolarian composition of each sample, species with a relative abundance exceeding 2% were defined as prominent species. Based on this, 29 prominent species 165 belonging to Polycystine radiolarians were identified (Figure 3), most of which are typical tropical-subtropical species dwelling in warm surface to subsurface waters at low latitudes (Chen and Tan, 1996; Boltovskoy et al., 2010). The total abundance of prominent radiolarian species constitutes 62-80% (mean=68%) of the radiolarian community in the studied samples (Figure 3 and radiolarian count data in supplementary material 2). Wilcoxon test analysis for relative abundances indicated no statistically significant differences in the radiolarian community between plankton and sediment samples at each sampling sta-
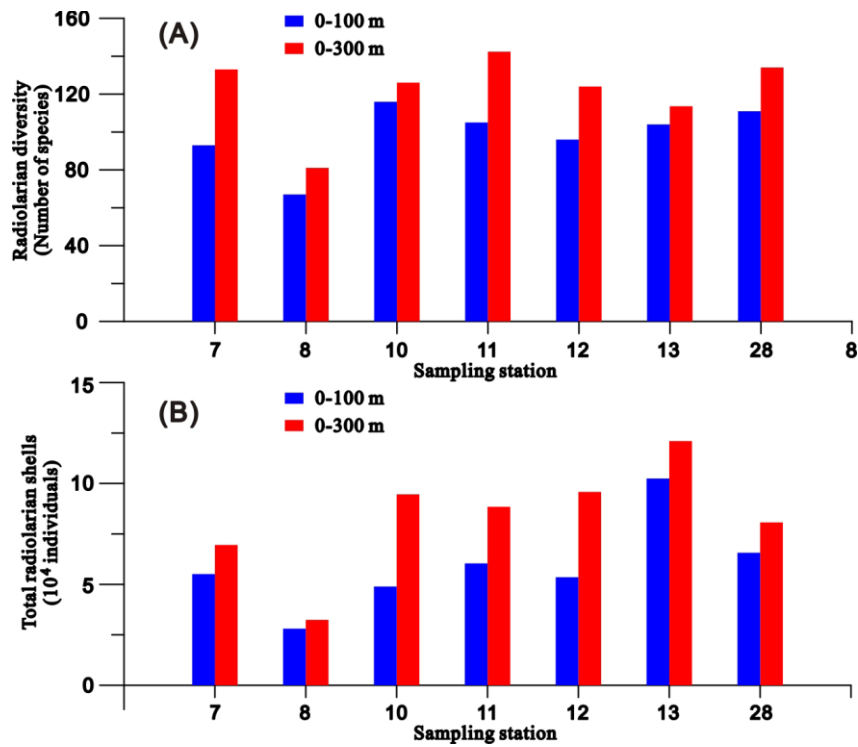
Figure 2. Radiolarian diversity (A) and shell numbers (B) in the upper 0-100 m and 0-300 m water columns at each sampling station.
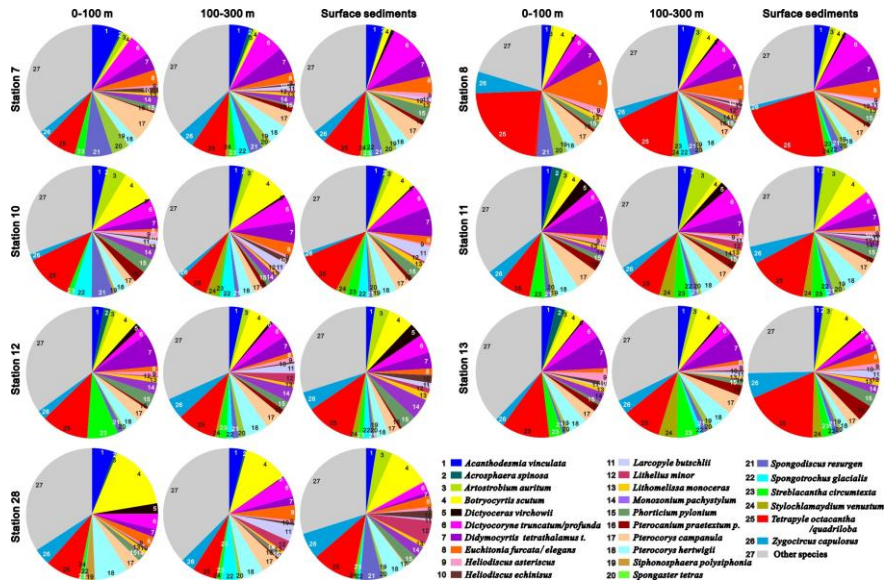

Figure 3. The prominent species and their relative abundances in plankton samples and surface sediments at each sampling station.

170 tion ($p = 0.19$-0.98) (Table S2 in supplementary material 1).

The proportion of fractured shells was low in the studied samples (Figure 4), generally ranging from 2 to 5% (mean = 3%) in plankton samples and from 3 to 9% (mean = 6%) in surface sediments. SEM images reveal a typical morphology of the pores on the radiolarian shell (Figure 4E), along with a high degree of integrity in the delicate skeletal structures (Figure 4F). These observations suggest good preservation of radiolarian shells, with no significant dissolution evident in either the water column or
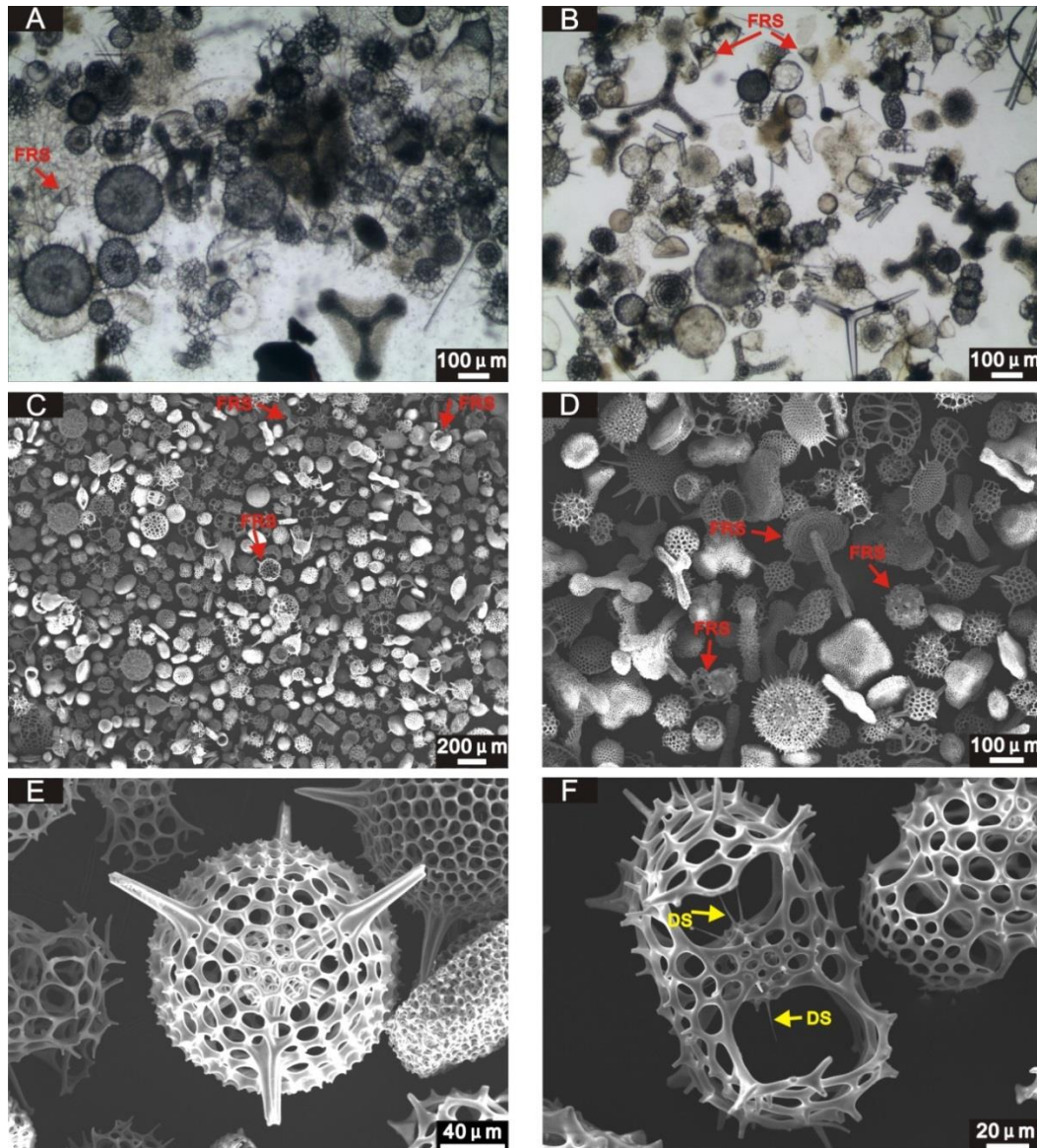175 sediment samples.

Figure 4 Observations of radiolarian shell preservation at station 12 (water depth: 3,497 m) in the plankton sample (100-300 m) (A and C) and surface sediments (B, D, E, and F) using optical microscope and the SEM. FRS=Fractured radiolarian shells; DS=Delicate skeletons

Visual inspection, by light microscopy and SEM, indicated a high degree of purity (>99%) and cleanliness in the radiolarian tests used for silicon isotope analysis, ~~that were free from~~ with negligible contamination from clay minerals or fine detrital particles on their shells (Figure ~~4).~~5). EDS analysis further showed that Si and O were the primary constituents~~constitutes~~ of pure radiolarian test samples, with their combined concentration exceeding 99%. Other elements (Fe, Al, Mg, Sr, Na, K and Cl) flagged in red within the EDS spectrum images (Figure 5) indicate that either their concentrations were below the minimum detectable limit (~ 0.1 %) for the EDS detector, or the software lacked a 99% statistical confidence in the presence of these elemental signatures within the analysed sample.~~The concentrations of other elements (Fe, Al, Mg, Sr, Na, K and Cl) were all below the minimum detectable limit for the EDS detector (Figure 4).~~
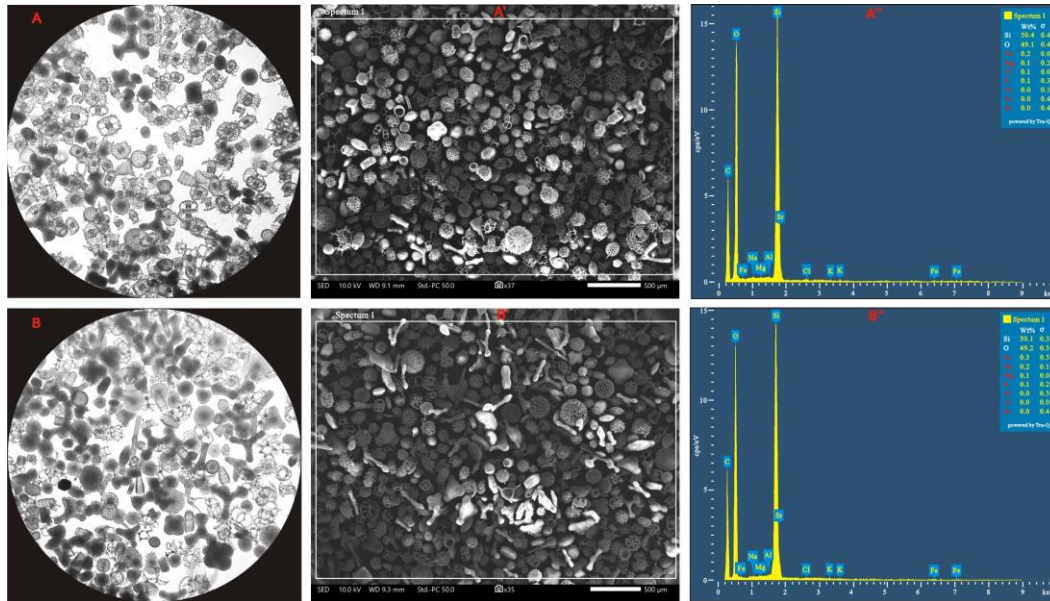

Figure 4_5. Pure radiolarian tests extracted from the plankton sample at station 8 (A) and the surface sediment at station 28 (B) under an inverted microscope at x100 magnification, as well as their SEM (A' and B') and EDS (A" and B") spectrum images.

$\delta^{30}Si_{rad}$ values ranged from 1.68‰ $\pm$0.20 to 1.81‰ $\pm$0.20 (mean = 1.76 $\pm$0.20‰) between 0-100 m of the water column, from 1.56‰ $\pm$0.20 to 1.83‰ $\pm$0.20 (mean = 1.72 $\pm$0.20‰) between 100-300 m, and from 1.61‰ $\pm$0.10 to 1.85‰ $\pm$0.21 (mean = 1.73 $\pm$0.17‰) in surface sediments (Figure ~~5A~~ 6A and Table S1 in the supplementary material_1). A paired t-test indicates no significant difference between the plankton and surface sediment $\delta^{30}Si_{rad}$ values at each station ($p = 0.75$) (Figure ~~5B).~~6B).
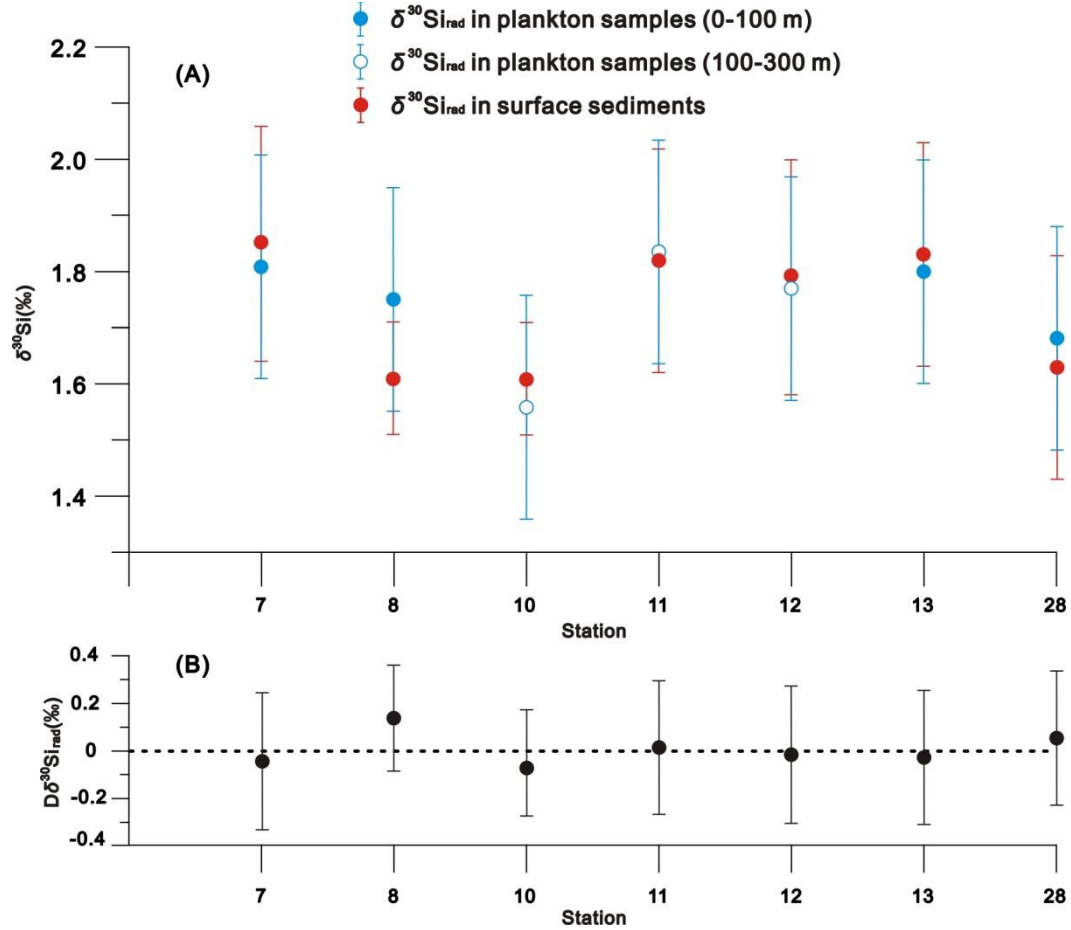
Figure 56. Comparison (A) and differences ($\Delta D\delta^{30}Si_{rad}$) (B) of $\delta^{30}Si_{rad}$ values between plankton samples and surface sediments at each sampling station. The vertical bar denotes the analytical uncertainty (2σ) of $\delta^{30}Si_{rad}$ compositions in (A), and the combined uncertainty (2σ) of $\Delta D\delta^{30}Si_{rad}$ in (B). The horizontal dashed line in (B) represents the zero line, indicating no differences in $\delta^{30}Si_{rad}$ compositions between plankton samples and surface sediments.

4   Discussions

4.1   ~~Contributors to Radiolarian~~ radiolarian δ^{30}Si signatures in water column plankton ~~and surface sediment~~ samples

δ^{30}Si$_{rad}$ values (1.56 to 1.85‰) of water column and surface sediment samples in this study fall within the range of published data for sediment cores across the globe (-1.87 to 2.00 ‰; Hendry et al., 2014; Abelmann et al., 2015; Fontorbe et al., 2016, 2017, 2020), and are approximately consistent with δ^{30}Si$_{rad}$ values of *Dictyocoryne profunda/truncatum* (1.42   to 1.74 ‰; Doering et al., 2021), a species of Spumellaria radiolarians dwelling between 50–100 m along the Peruvian coast (eastern East Pacific). However, they are higher than reported δ^{30}Si compositions of mixed radiolarians in surface sediments from the mid-Pacific (-0.2 to 0.3 ‰, Ding et al., 1996), the Southern Ocean (-0.74 to 1.33‰; Abelmann et al., 2015), and off the Peruvian coast (0.86 to 1.22‰, Doering et al., 2021).

In the oceans, radiolarians are distributed throughout the water column from surface to bottom waters (e.g., Kling, 1979; Abelmann and Gowing, 1996; Zhang et al., 2009; ~~Boltovskoy et al., 2010;~~ Hu et al., 2015; Boltovskoy, 2017). In this study from the SCS, the radiolarians extracted from plankton samples and surface sediments for isotopic analysis comprise a mix of species from the bulk community, theoretically representing the average δ^{30}Si$_{rad}$ signature across different water layers. Indeed, radiolarians in the SCS inhabit water depths from the surface to c. 2000 m (Hu et al., 2015). However, we suggest that the δ^{30}Si$_{rad}$ signal in our samples primarily originates from radiolarians dwelling in surface to subsurface water (0-100 m). Firstly, the diversity and abundance of radiolarians in the SCS generally peak between 25 and 75 m water depth, declining significantly below 100 m (Zhang et al., 2009; Hu et al., 2015). This is consistent with global observations, which show that standing stock and species richness of polycystine radiolarians typically reach their highest values at 0-100 m in tropical and subtropical oceans (Boltovskoy, 2017). Secondly, radiolarians living above 100 m in the SCS account for a mean of 72% of the radiolarian shells in the plankton δ^{30}Si$_{rad}$ samples analyzed in this current study (Figure 2), aligning with the observation that living radiolarians above 150 m contribute c. 77% of ~~the~~ all the radiolarian shells from the surface to a depth of 2000 m (Hu et al., 2015).

Given the differences in both the abundance and dominant species composition of living radiolarians between 0-75 m and the 75-300m water depth in the SCS (Hu et al., 2015), it is expected that δ^{30}Si$_{rad}$ values from plankton samples at 0-100 m water depth might potentially differ from those at 100-300 m. However, ~~Whilst δ^{30}Si$_{rad}$ values from plankton samples at 100-300 m water depth were expected to potentially differ from those at 0-100 m,~~ no significant difference was detected ($p =$ 0.52). We suggest that the similarity of δ^{30}Si$_{rad}$ values from samples at 0-100 m and 100-300 m water depth may be attributed to the fact that radiolarians at 100-300 m water depth primarily consist of dead individuals settling from the upper 100 m of the water column. This is supported by the observation that: 1) the radiolarian species present in this study at 100-300 m water depth are normally found within the 0-100 m layer; and 2) no statistically significant differences were found between the prominent radiolarian species in these two water layers at each station (Wilcoxon signed-rank tests: $p =$ 0.32 to 0.98) (Table S2 in supplementary material 1).

Wilcoxon signed-rank tests also show no statistical difference between the relative abundances of prominent radiolarian species in plankton water column samples and surface sediment samples at each station ($p =$ 0.19 to 0.98, Table S2 in sup-

plementary material 1). This is in agreement with previous studies demonstrating that the radiolarian thanatocoenose in surface sediments generally reflect the major species of living radiolarian assemblage in the overlying water column in the SCS (Hu et al., 2014) and other oceans (Takahashi, 1982; Itaki, 2003; Itaki et al., 2003). Although discernibleminor differences in the relative abundances of some prominent radiolarian species are observed, these likely result from the varying temporal coverage of each sample. The SCS, influenced by the East Asian Monsoon, exhibits seasonal and interannual variability in its hydrological environment (Ning et al., 2009; Palacz et al., 2011) and radiolarian community (Wang et al., 2000; Zhang et al., 2020). Plankton samples were collected during a single snapshot in time, capturing radiolarians in a particular season, whereas radiolarians in the sediment samples represent an average record accumulated over multiple seasons and years. Although variations in the δ^{30}Si composition (vital effects) have been documented among different radiolarian taxa (Doering et al., 2021), the relative abundance differences in certain prominent species, such as *Botryocyrtis scutum, Didymocyrtis tetrathalamus t., Tetrapyle octacantha/quadribola,* and *Zygocircus capulosus* between plankton and surface sediment samples (Figure 3) do not result in significant δ^{30}Si$_{rad}$ disparities in our study in the SCS. This may be attributed to two factors: 1) the minor differences in the relative abundance of most prominent taxa between water column and sediment samples (Wilcoxon signed-rank tests: p = 0.19 to 0.98, Table S2 in supplementary material 1); and 2) the high diversity of radiolarians in each sample averaging out the δ^{30}Si$_{rad}$ signal across different taxa, mitigating potential bias from individual taxathe risk of vital effects in some taxa distorting the measured isotopic value.

Overall, we conclude that δ^{30}Si$_{rad}$ signatures in the water column, and subsequently incorporated in surface sediments, are primarily influenced by radiolarians from the 0-100 m water depth layer (surface to subsurface water), due to the substantial contribution of radiolarians in this depth range to the bulk radiolarian community in the SCS water column and sediment record.

4.2 Radiolaria silicon isotope fractionation

The isotope fractionation factor between radiolaria and seawater is a critical parameter for reconstructing past silicon cycle in the mid-upper ocean using δ^{30}Si$_{rad}$ in downcore records (Hendry et al., 2014; Abelmann et al., 2015; Doering et al., 2021). As discussed previously, the δ^{30}Si$_{rad}$ signatures in the water column of the SCS are predominantly contributed to by radiolarians from the 0-100 m depth layer. Therefore, seawater δ^{30}Si (δ^{30}Si$_{sw}$) data pertinent to constraining silicon isotope fractionation by radiolarians in the SCS should be derived primarily from this depth interval. Currently, there is no corresponding δ^{30}Si$_{sw}$ data from the stations in the SCS where water column radiolaria samples were collected. Previous work, however, has measured seasonal changes in δ^{30}Si$_{sw}$ in the northern SCS (Cao et al 2012). At the two sites from that study situated off the continental shelf (A10 and SEATS), δ^{30}Si$_{sw}$ above 100m varies from 1.4‰ to 2.9‰. Assuming: 1) these values are broadly comparable to stations where δ^{30}Si$_{rad}$ was measured; and 2) that radiolarians construct their skeletons in equilibrium with ambient seawater (Abelmann et al., 2015, Fontorbe et al., 2016, Doering et al 2021), the isotope fractionation factor (ε) by radiolarians can be calculated as:

$$\varepsilon \sim \Delta^{30}\text{Si} = \delta^{30}\text{Si}_{rad} - \delta^{30}\text{Si}_{sw} \tag{2}$$

Using Monte Carlo simulations (10,000 replicates) to account for the 2SD uncertainty of both δ^{30}Si$_{rad}$ and δ^{30}Si$_{sw}$, ε is

estimated to range from –0.33‰ to –0.92‰ (mean = 0.58‰) (Table S1 in supplementary material 1). Due to the difficulties in culturing radiolaria (e.g. Suzuki and Not, 2015), relatively little is known about the fractionation factor for $\delta^{30}Si_{rad}$. Values for ε obtained here from the SCS are comparable to those measured by Abelmann et al. (2015) in the Southern Ocean (–0.54‰ to –0.91‰, mean = –0.75‰) and by Doering et al. (2021) along the Peruvian Shelf (–0.35‰ to –0.79‰, mean = –0.62‰, mixed radiolaria). The large range of values for ε has been suggested to indicate species/order-specific fractionation during the uptake of silicic acid by radiolaria (Doering et al., 2021). Such a process would necessitate the extraction of species-specific radiolarian samples for isotope analysis in future palaeoceanographic research (e.g., Zhang and Swann, 2023). However in this current study from the SCS, whilst the species compositions of the $\delta^{30}Si_{rad}$ samples is known (Figure 3), an absence of matching $\delta^{30}Si_{sw}$ data from exactly the same stations prevents this issue being further investigated at this time.

4.2 4.3 Transfer of radiolarian $\delta^{30}Si$ signatures into the sediment record

At each sampling station, $\delta^{30}Si_{rad}$ compositions (mean = 1.73‰) in the surface sediment closely resembles those (mean = 1.74‰) in the overlying water column evidenced by the paired t-test (p=0.75) (Figure 6), indicating a faithful transfer of the $\delta^{30}Si$ signal incorporated into radiolarian skeletons from the water column to sediments. This suggests that dissolution and other processes have has a minimal impacts on the $\delta^{30}Si_{rad}$ signatures of as radiolarians as shells sink through the water column and become incorporated into the sediment record. One of two possibilities may account for this observation: 1) the radiolarian shells may not have undergone substantial dissolution during sinking; 2) the radiolarian shells have experienced substantial dissolution, but this process may not significantly alter their isotope composition. As shell fracture of microfossils preserved within sediments is commonly attributed to partial dissolution (e.g. Murray and Alve, 1999; Ryves et al., 2001), the proportion of fractured radiolarian shells may indicate the potential for radiolarian shell dissolution during sinking. In this study, fractured radiolarian shells comprised only a mean of 3% in plankton samples and 6% in surface sediment (Figure 4). Considering the low proportion of fractured radiolarian shells, the well-preserved state of radiolarian shells (Figure 4), and the minor differences in the relative abundances of prominent radiolarian species between plankton samples and surface sediments at each sampling station (as detailed in section 4.1), we propose that radiolarian shells have not experienced substantial dissolution or remineralisation during their transfer from the water column to the sediments.

The susceptibility of radiolarian shells to dissolution vary considerably with different taxonomic groups due to the differences in the chemical constituent of their skeletons. It is generally accepted that radiolaria comprise three classes: Polycystinea, Acantharea, and Taxopodida (Adl et al., 2019), despite debate concerning radiolarian classification schemes (Chen and Tan, 1996; Suzuki et al., 2015; Adl et al., 2019; Biard, 2022). Acantharians are composed of celestite $SrSO_4$, and their skeletons are highly susceptible to dissolution due to the significant undersaturation of seawater with respect to this mineral (Bernstein et al., 1992; De Deckker, 2004; Shimmen et al., 2009). However, their absence of a silicon based skeletons renders their dissolution inconsequential for $\delta^{30}Si_{rad}$ measurements in the water column and sediment. Taxopodida, though composed of silica, are generally rare in the water column, and no fossil records of this Class have been discovered in surface sediments of the world ocean to date (Biard, 2022). In our studied samples from the SCS, both Acantharea and Taxopodida taxa are trace components (<0.1%) in plankton samples and absent in surface sediments.

In the oceans, particularly in the SCS, polycystine radiolarians are the predominant group of the radiolarian community in both the water column and in sediments (Chen and Tan, 1996; Chen et al., 2008a, b; Suzuki and Aita, 2011) and are

13

comprised of three Orders: Spumellaria, Nassellaria, and Collodaria. Collodaria radiolaria, with skeletons composed of both opal and Celestine (Afanasieva et al., 2005; Afanasieva and Amon, 2014), are generally susceptible to dissolution in seawater and poorly preserved in sediment samples. However, Collodaria radiolaria are less common in the oceans (Probert et al., 2014; Zhang et al., 2018) and generally represent a low abundance in both the water column and sediments (Suzuki et al., 2015; Biard, 2022). In the SCS, the abundance of Collodaria radiolarians in the water column ranges from 2-270 individuals/m^3 (mean = 30 individuals/m^3) (Zhang et al., 2020; Cheng et al., 2023), while the mean abundance of Spumellaria and Nassellaria in the upper water exceeds 3000 individuals/m^3 (Zhang et al., 2009; Hu et al., 2015). Spumellaria and Nassellaria taxa, which have been widely used as proxies for paleoenvironmental reconstruction (e.g., Itaki et al., 2004; Abelmann and Nimmergut, 2005; Zhang et al., 2014; Cortese and Prebble, 2015), are characterized by a greater resistance to dissolution and are generally well preserved in sediments (Takahashi, 1982; Morley et al., 2014). In this current study, Collodaria taxa have very low relative abundance in the analysed samples (mean < 1%), which are instead dominated by the more dissolution-resistant Spumellaria and Nassellaria taxa (Figure 3). Since Spumellaria and Nassellaria radiolarians, the primary constituent of the radiolarian community in the SCS, are characterized by a great resistance to dissolution, dissolution is expected to have limited impacts on these radiolarian shells, and thus on $\delta^{30}Si_{rad}$ compositions during sinking and burial.

As discussed above, we suggest that the effect of dissolution on radiolarian shells and the $\delta^{30}Si_{rad}$ composition in the SCS is negligible during the transfer from the water column to the surface sediment, based on the well-preserved state of radiolarian shells and the comparable $\delta^{30}Si_{rad}$ compositions observed in plankton samples and surface sediment at each sampling station. This is likely attributed to the dominance of Spumellaria and Nassellaria taxa in the radiolarian community, which generally exhibit a high resistance to dissolution, as well as the scarcity or absence of the readily dissolvable Taxopodida, Acantharea, and Collodaria taxa.

5   Conclusions

To investigate the potential effects of dissolution on $\delta^{30}Si_{rad}$ signatures during the sinking and burial processes from the water column to sediments, we conducted a comparative analysis of radiolarian community and $\delta^{30}Si_{rad}$ compositions between plankton samples and surface sediments from seven stations in the SCS. The key findings are summarized as follows:

1. $\delta^{30}Si_{rad}$ compositions ranged from 1.56-1.83‰ (mean = 1.74‰) in the plankton samples and from 1.61-1.85‰ (mean = 1.73‰) in surface sediments, with the fractionation factor for $\delta^{30}Si_{rad}$ varying from −0.33‰ to −0.92‰ (mean = 0.58‰). No statistically significant differences in $\delta^{30}Si_{rad}$ values were observed between the water column and surface sediment samples at each sampling station.

2. Minor differences in the relative abundance of prominent taxa between the water column and sediments are not statistically significant. As most radiolarians in the water column originate from depths above 100 m in this study, we suggest that the $\delta^{30}Si_{rad}$ signature preserved in surface sediments is primarily contributed from radiolarians within this depth range in the SCS.

3. The similar $\delta^{30}Si_{rad}$ compositions in plankton samples and surface sediment at each station suggest a faithful transfer of

$\delta^{30}Si_{rad}$ signatures from the water column to the surface sediment in the SCS. This is aided by the dominance of the more dissolution-resistant Spumellaria and Nassellaria taxa (>99%) within the radiolarian community, coupled with the scarcity or absence of the readily dissolvable taxa (Taxopodida, Acantharea, and Collodaria).

330 *Data availability.* The $\delta^{30}Si_{rad}$ data and original radiolarian count data from this paper can be found in supplementary material 1 and 2, respectively. Data from this paper can be found in Table S1 of the Supplement

Author contributions. QZ and GEAS conceived and designed the study. QZ analysed the radiolarian assemblages and prepared the samples for isotope analysis, supported by GEAS. Isotope samples were prepared and analysed by VP and QZ with additional support from MSAH. All authors contributed to the writing of the paper and commented on drafts.

335 *Competing interests.* The authors declare that they have no conflict of interest.

References

Abelmann, A., Gersonde, R., Knorr, G., Zhang, X., Chapligin, B., Maier, E., Esper, O., Friedrichsen, H., Lohmann, G., Meyer, H., Tiedemann, R.: The seasonal sea-ice zone in the glacial Southern Ocean as a carbon sink, Nat. Commun., 6(1), 8136, https://doi.org/10.1038/ncomms9136, 2015.

345 Abelmann, A., Gowing, M. M.: Horizontal and vertical distribution pattern of living radiolarians along a transect from the Southern Ocean to the South Atlantic subtropical region, Deep-Sea Res. Pt. I, 43(3), 361-382, https://doi.org/10.1016/0967-0637(96)00003-9, 1996.

Abelmann, A., Nimmergut, A.: Radiolarians in the Sea of Okhotsk and their ecological implication for paleoenvironmental reconstructions, Deep-Sea Res. Pt. II, 52(16-18), 2302-2331, https://doi.org/10.1016/j.dsr2.2005.07.009, 2005.

Adl, S. M., Bass, D., Lane, C. E., Lukeš, J., Schoch, C. L., Smirnov, A., Agatha, A., Berney, C., Brown, M. W., Buki, F., Cárdenas, P.,
350 Čepička, I., Chistyakova, L., Campo, J., . . . Youssef, N., Zlatogursky, V., Zhang, Q.: Revisions to the classification, nomenclature, and diversity of eukaryotes, Journal of Eukaryotic Microbiology, 66(1), 4-119, https://doi.org/10.1111/jeu.12691, 2019.

Afanasieva, M. S., Amon, E. O.: Biomineralization of radiolarian skeletons, Paleontological Journal, 48, 1473-1486, https://doi.org/10.1134/S0031030114140020, 2014.

Afanasieva, M. S., Amon, E. O., Agarkov, Y. V., Boltovskoy, D. S.: Radiolarians in the geological Record, Paleontological Journal, 39,
355 135-392, https://doi.org/10.1666/0094-8373(2005)031, 2005.

Arellano-Torres, E,, Pichevin, L. E., Ganeshram, R. S.: High-resolution opal records from the eastern tropical Pacific provide evidence for silicic acid leakage from HNLC regions during glacial periods, Quaternary Sci. Rev., 30(9-10), 1112-1121, https://doi.org/10.1016/j.quascirev.2011.02.002, 2011.

Biard, T.: Diversity and ecology of Radiolaria in modern oceans, Environmental Microbiology, 24(5), 2179-2200, https://doi.org/10.1111/1462-2920.16004, 2022.
360

Bernstein, R. E., Byrne, R. H., Betzer, P. R., Greco, A.: Morphologies and transformations of celestite in seawater: The role of acantharians in strontium and barium geochemistry, Geochim. Cosmochim. Ac., 56(8), 3273-3279, https://doi.org/10.1016/0016-7037(92)90304-2, 1992.

Boltovskoy, D., Kling, S. A., Takahashi, K., Bjørklund, K.: World atlas of distribution of recent polycystina (Radiolaria), Palaeontologia Electronica, 13, 1–229, 2010.

365 Boltovskoy, D.: Vertical distribution patterns of Radiolaria Polycystina (Protista) in the World Ocean: living ranges, isothermal submersion and settling shells, Journal of Plankton Research, 39(2), 330-349, https://doi.org/10.1093/plankt/fbx003, 2017.

Bradtmiller, L. I., Anderson, R. F., Fleisherm, M. Q., Burckle, L. H.: Diatom productivity in the equatorial Pacific Ocean from the last glacial period to the present: A test of the silicic acid leakage hypothesis, Paleoceanography, 21(4), https://doi.org/10.1029/2006PA001282, 2006.

Bradtmiller, L. I., Anderson, R. F., Fleisher, M. Q., Burckle, L. H.: Opal burial in the equatorial Atlantic Ocean over the last 30 ka: Im-
370 plications for glacial-interglacial changes in the ocean silicon cycle, Paleoceanography, 22(4), https://doi.org/10.1029/2007PA001443, 2007.

Brzezinski, M. A., Pride, C. J., Franck, V. M., Sigman, D. M., Sarmiento, J. L., Matsumoto, K., Gruber, N., Rau, G. H., Coale, K. H.: A switch from Si $(OH)_4$ to NO_3^- depletion in the glacial Southern Ocean, Geophys. Res. Lett., 29(12), 5-1, https://doi.org/10.1029/2001GL014349, 2002.

375 Cardinal, D., Alleman, L. Y., De Jong, J., Ziegler, K., & André, L.: Isotopic composition of silicon measured by multicollector plasma source mass spectrometry in dry plasma mode. Journal of Analytical Atomic Spectrometry, 18(3), 213-218, https://doi.org/10.1039/B210109B, 2003.

Cardinal, D., Savoye, N., Trull, T. W., Dehairs, F., Kopczynska, E. E., Fripiat, F., Tison, J. L., André, L.: Silicon isotopes in

spring Southern Ocean diatoms: Large zonal changes despite homogeneity among size fractions, Mar. Chem., 106 (1-2), 46-62. https://doi.org/10.1016/j.marchem.2006.04.006, 2007.

Chen, M. H., Tan, Z. Y.: Radiolaria from Surface Sediments of the Central and Northern South China Sea, Science Press, Beijing, China, 271 pp., ISBN 7-03-004945-4/Q.611, 1996. (in Chinese with English abstract).

Chen, M. H., Zhang, L. L., Zhang, L. L., Xiang, R., Lu, J.: Preservation of radiolarian diversity and abundance in surface sediments of the South China Sea and its environmental implication, J. China Univ. Geosci., 19, 217–229, https://doi.org/10.1016/S1002-0705(08)60041-2, 2008a.

Chen, M. H., Zhang, L. L., Xiang, R., Lu, J.: Radiolarian assemblages in surface sediments of the South China Sea and their marine environmental correlations, J. China Univ. Geosci., 33(6), 775-82, https://doi.org/10.3799/dqkx.2008.093, 2008b.

Cheng, X. W., Zhang, L. L., Qiu, Z. Y., Xiang, R., Chang, H.: Biodiversity, biogeography and seasonal variation of zooplankton Collodarians (Radiolaria) in surface waters from the northern Indian Ocean to the South China Sea, Journal of Tropical Oceanography, 42(2), 97-112, https://doi.org/10.11978/20220472023, 2023. (in Chinese with English abstract)

Closset, I., Cardinal, D., Bray, S. G., Thil, F., Djouraev, I., Rigual−Hernández, A. S., Trull, T. W.: Seasonal variations, origin, and fate of settling diatoms in the Southern Ocean tracked by silicon isotope records in deep sediment traps. Global Biogeochemical Cycles, 29(9), 1495-1510. https://doi.org/10.1002/2015GB005180, 2015.

Cortese, G., Prebble, J.: A radiolarian-based modern analogue dataset for palaeoenvironmental reconstructions in the southwest Pacific, Mar. Micropaleontol., 118, 34-49, https://doi.org/10.1016/j.marmicro.2015.05.002, 2015.

De Deckker, P.: On the celestite-secreting Acantharia and their effect on seawater strontium to calcium ratios. Hydrobiologia, 517, 1–13, https://doi.org/10.1023/B:HYDR.0000027333.02017.50, 2004.

De La Rocha, C. L., Brzezinski, M. A., DeNiro, M., Shemesh, A.: Silicon isotope composition of diatoms as an indicator of past oceanic change, Nature, 395, 680–683, https://doi.org/10.1038/27174, 1998.

De La Rocha, C. L.: Silicon isotope fractionation by marine sponges and the reconstruction of the silicon isotope composition of ancient deep water. Geology, 31, 423–426, https://doi.org/10.1130/0091-7613(2003)031<0423:SIFBMS>2.0.CO;2, 2003.

Demarest, M. S., Brzezinski, M. A., Beucher, C. P.: Fractionation of silicon isotopes during biogenic silica dissolution, Geochim. Cosmochim. Ac., 73(19), 5572–5583, https://doi.org/10.1016/j.gca.2009.06.019, 2009.

Ding, T., Jiang, S., Wan, D., Li, Y., Li, J., Song, H., Liu, Z., Yao, X.: Silicon Isotope Geochemistry. Geological Publishing House, Beijing, China. 125 pp., 1996.

Doering, K., Ehlert, C., Pahnke, K., Frank, M., Schneider, R., Grasse, P.: Silicon isotope signatures of radiolaria reveal taxon-specific differences in isotope fractionation, Front. Mar. Sci., 8, 666896, https://doi.org/10.3389/fmars.2021.666896, 2021.

Dubois, N., Kienast, M., Kienast, S., Calvert, S. E., Francois, R., Anderson, R.: Sedimentary opal records in the eastern equatorial Pacific: It is not all about leakage. Global Biogeochem. Cy., 24(4), https://doi.org/10.1029/2010GB003821, 2010.

Egan, K. E., Rickaby, R. E. M., Leng, M. J., Hendry, K. R., Hermoso, M., Sloane, H. J., Bostock, H., Halliday, A. N.: Diatom silicon isotopes as a proxy for silicic acid utilisation: A Southern Ocean core top calibration, Geochim. Cosmochim. Ac., 96, 174–192, https://doi.org/10.1016/j.gca.2012.08.002, 2012.

Ellwood, M. J., Wille, M., Maher, W.: Glacial silicic acid concentrations in the Southern Ocean, Science, 330(6007), 1088-91, https://doi.org/10.1126/science.1194614, 2010.

Fontorbe G, Frings P J, De La Rocha, C., Hendry, K. R., Conley, D. J.: A silicon depleted North Atlantic since the Palaeogene: Evidence from sponge and radiolarian silicon isotopes, Earth Planet. Sci. Lett., 453, 67-77, https://doi.org/10.1016/j.epsl.2016.08.006, 2016.

Fontorbe, G., Frings, P. J., De La Rocha, C. L., Hendry, K. R., Carstensen, J., Conley, D. J.: Enrichment of dissolved silica in the deep

17

equatorial Pacific during the Eocene-Oligocene, Paleoceanography, 32(8), 848-863, https://doi.org/10.1002/2017PA003090, 2017.

Fontorbe, G., Frings, P. J., De La Rocha C. L., Hendry, K. R., Conley, D. J.: Constraints on Earth system functioning at the Paleocene-Eocene thermal maximum from the marine silicon cycle, Paleoceanogr. Paleocl., 35(5), https://doi.org/10.1029/2020PA003873, 2020.

Fripiat, F., Cavagna, A. J., Dehairs, F., De Brauwere, A., André, L., Cardinal, D.: Processes controlling the Si-isotopic composition in the Southern Ocean and application for paleoceanography, Biogeosciences, 9(7), 2443-2457, https://doi.org/10.5194/bg-9-2443-2012, 2012.

Georg, R. B., Reynolds, B. C., Frank, M., Halliday, A. N.: New sample preparation techniques for the determination of Si isotopic compositions using MC-ICP-MS, Chem. Geol., 235(1-2), 95-104. https://doi.org/10.1016/j.chemgeo.2006.06.006, 2006.

Grasse, P., Haynert, K., Doering, K., Geilert, S., Jones, J. L., Brzezinski, M. A., Frank, M.: Controls on the silicon isotope composition of diatoms in the peruvian upwelling. Front. Mar. Sci., 8, 697400, https://doi.org/10.3389/fmars.2021.697400, 2021.

Hendry, K. R., Georg, R. B., Rickaby, R. E. M., Robinson, L. F., Halliday, A. N.: Deep ocean nutrients during the Last Glacial Maximum deduced from sponge silicon isotopic compositions. Earth Planet. Sci. Lett., 292(3-4), 290–300, https://doi.org/10.1016/j.epsl.2010.02.005, 2010.

Hendry. K. R., Robinson, L. F., McManus, J. F., Hays, J. D.: Silicon isotopes indicate enhanced carbon export efficiency in the North Atlantic during deglaciation. Nat. Commun., 5(1), 3107, https://doi.org/10.1038/ncomms4107, 2014.

Hendry, K. R., Robinson, L. F.: The relationship between silicon isotope fraction-ation in sponges and silicic acid concentration: modern and core-top studies of biogenic opal, Geochim. Cosmochim. Ac., 81, 1–12, https://doi.org/10.1016/j.gca.2011.12.010, 2012.

Hendry, K., Romero, O., Pashley, V.: Nutrient utilization and diatom productivity changes in the low-latitude south-eastern Atlantic over the past 70 ka: response to Southern Ocean leakage. Clim. Past, 17(2), 603-14, https://doi.org/10.5194/cp-17-603-2021, 2021.

Hu, W. F., Zhang, L. L., Chen, M. H., Chen, R. Y., Zhou, W. H., Xiang, R., Zhang, Q.: Spitial distribution of dead radiolarians in spring upper waters of the South China Sea, and its comparision with the surface sediment record. Acta Micropalaeontologica Sinica, 31 (3), 213-227, https://doi.org/CNKI:SUN:WSGT.0.2014-03-001. 2014. (in Chinese with English abstract).

Hu, W. F., Zhang, L. L., Chen, M. H., Zeng, L. L., Zhou, W. H., Xiang, R., Zhang, Q., Liu, S. H.: Distribution of living radiolarians in spring in the South China Sea and its responses to environmental factors, Sci. China Earth Sci., 58, 270-85, https://doi.org/10.1007/s11430-014-4950-0, 2015

Hughes, H. J., Delvigne, C., Korntheuer, M., De Jong, J., André, L., Cardinal, D. Controlling the mass bias introduced by anionic and organic matrices in silicon isotopic measurements by MC-ICP-MS. J. Anal. At. Spectrom., 26(9), 1892-1896, https://doi.org/10.1039/C1JA10110B, 2011.

Itaki, T.: Depth-related radiolarian assemblage in the water-column and surface sediments of the Japan Sea, Mar. Micropaleontol., 47(3-4), 253-270, https://doi.org/10.1016/S0377-8398(02)00119-6. 2003.

Itaki, T., Ito, M., Narita, H., Ahagon, N., Sakai, H.: Depth distribution of radiolarians from the Chukchi and Beaufort Seas, western Arctic, Deep-Sea Res. Pt. I, 50(12), 1507-1522, https://doi.org/10.1016/j.dsr.2003.09.003, 2003.

Itaki, T., Ikehara, K., Motoyama, I., Hasegawa, S.: Abrupt ventilation changes in the Japan Sea over the last 30 ky: evidence from deep-dwelling radiolarians, Palaeogeogr. Palaeocl., 208(3-4), 263-78, https://doi.org/10.1016/j.palaeo.2004.03.010, 2004.

Kienast, S. S., Kienast, M., Jaccard, S., Calvert, S. E., François, R: Testing the silica leakage hypothesis with sedimentary opal records from the eastern equatorial Pacific over the last 150 kyrs, Geophys. Res. Lett., 33(15), https://doi.org/10.1029/2006GL026651, 2006.

Kling, S. A.: Vertical distribution of polycystine radiolarians in the central North Pacific, Mar. Micropaleontol., 4, 295-318, https://doi.org/10.1016/0377-8398(79)90022-7, 1979.

Lisitzin, A. P.: Sedimentation in the world ocean. Society of Economic Paleontologists and Mineralogists, Special Publications. No. 17, 218 pp. https://doi.org/10.2110/pec.72.17, 1972.

Matsumoto, K., Sarmiento, J. L.: A corollary to the silicic acid leakage hypothesis, Paleoceanography, 23(2), https://doi.org/10.1029/2007-PA001515, 2008.

Matsumoto, K., Sarmiento, J. L., Brzezinski, M. A.: Silicic acid leakage from the Southern Ocean: A possible explanation for glacial atmospheric pCO$_2$, Global Biogeochem. Cy., 16(3), https://doi.org/10.1029/2001GB001442, 2002.

Moore, JR. T. C: Radiolaria: change in skeletal weight and resistance to solution. Geological Society of America Bulletin, 80(10), 2103-2108. https://doi.org/10.1130/0016-7606(1969)80[2103:RCISWA]2.0.CO;2, 1969

Morley, J. J., Shemesh, A., Abelmann, A.: Laboratory analysis of dissolution effects on Southern Ocean polycystine Radiolaria, Mar. Micropaleontol., 110, 83-86, https://doi.org/10.1016/j.marmicro.2013.05.001, 2014.

Murray, J. W., Alve, E.: Natural dissolution of modern shallow water benthic foraminifera: taphonomic effects on the palaeoecological record, Palaeogeogr. Palaeocl., 146(1-4), 195-209, https://doi.org/10.1016/S0031-0182(98)00132-1, 1999.

Ning, X., Lin, C., Hao, Q., Liu, C., Le, F., Shi, J.: Long term changes in the ecosystem in the northern South China Sea during 1976–2004, Biogeosciences, 6(10), 2227-2243, https://doi.org/10.5194/bg-6-2227-2009, 2009.

Palacz, A. P., Xue, H. J., Armbrecht, C., Zhang, C. Y., Chai, F.: Seasonal and inter-annual changes in the surface chlorophyll of the South China Sea, J. Geophys. Res.: Oceans, 116(C9) https://doi.org/10.1029/2011JC007064, 2011.

Panizzo, V. N., Swann, G. E. A., Mackay, A. W., Vologina, E., Sturm, M., Pashley, V., Horstwood, M. S. A.: Insights into the transfer of silicon isotopes into the sediment record, Biogeosciences, 13(1), 147-157, https://doi.org/10.5194/bg-13-147-2016, 2016

Probert, I., Siano, R., Poirier, C., Decelle, J., Biard, T., Tuji, A., Suzuki, N., Not, F.: *Brandtodinium* gen. nov. and *B. nutricula* comb. Nov. (Dinophyceae), a dinoflagellate commonly found in symbiosis with polycystine radiolarians. Journal of Phycology, 50(2), 388-399, https://doi.org/10.1111/jpy.12174, 2014

Ragueneau, O., Tréguer, P., Leynaert, A., Anderson, R. F., Brzezinski, M. A., DeMaster, D. J., Dugdale, R. C., Dymond, J., Fischer, G., Francois, R., Heinze, C., Maier-Reimer, E., Martin-Jézéquel, V. Nelson D. M., Quéguiner, B.: A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy, Global. Planet. Change, 26(4), 317-365, https://doi.org/10.1016/S0921-8181(00)00052-7, 2000.

Reynolds, B. C., Frank, M., Halliday, A. N.: Silicon isotope fractionation during nutrient utilization in the North Pacific, Earth Planet. Sci. Lett., 244(1-2), 431–443, https://doi.org/10.1016/j.epsl.2006.02.002, 2006.

Ryves, D. B., Juggins, S., Fritz, S. C., Battarbee, R. W.: Experimental diatom dissolution and the quantification of microfossil preservation in sediments. Palaeogeogr. Palaeocl., 172(1-2), 99-113, https://doi.org/10.1016/S0031-0182(01)00273-5, 2001.

Sheng, J., Qiao, S., Shi, X., Liu, J., Liu, Y., Liu, S., Wang, K., Mohamed, C., Khokiattiwong, S., Kornkanitnan, N.: Modern sedimentation and sediment budget in the South China Sea and their comparisons with the eastern China seas, Marine Geology, 475, 107348, https://doi.org/10.1016/j.margeo.2024.107348, 2024.

Shimmen, K., Takahashi, O., Yuasa, T.: SEM observations of the fracture morphology of Acantharea (Radiolaria) from the East China Sea, Okinawa, Japan. Bulletin of Tokyo Gakugei University, Division of Natural Sciences, 61: 55-62, 2009.

Suzuki, N., Aita, Y.: Radiolaria: achievements and unresolved issues: taxonomy and cytology, Plankton and Benthos Research, 6(2), 69-91, https://doi.org/10.3800/pbr.6.69, 2011.

Suzuki, N., Not, F: Biology and Ecology of Radiolaria, In: Marine Protists, edited by: Ohtsuka, S., Suzaki, T., Horiguchi, T., Suzuki, N., Not, F., Springer, Tokyo, Japan, https://doi.org/10.1007/978-4-431-55130-0_8, 2015.

Swann, G. E. A., Snelling, A. M., Pike, J.: Biogeochemical cycling in the Bering Sea over the onset of major Northern Hemisphere Glaciation, Paleoceanography, 31(9), 1261-1269, https://doi.org/10.1002/2016PA002978, 2016.

Swann, G. E. A., Pike, J., Leng, M. J., Sloane, H. J., Snelling, A. M.: Temporal controls on silicic acid utilisation along the West Antarctic Peninsula, Nat. Commun., 8, 14645, https://doi.org/10.1038/ncomms14645, 2017.

19

Takahashi, K.: Vertical flux, ecology and dissolution of radiolaria in tropical oceans: implications for the silica cycle. PhD thesis. (Cambridge MA: Massachusetts Institute of Technology and Woods Hole Oceanographic Institution), 461 pp., https://doi.org/10.1575/1912/2420, 1982.

500 Tan, Z. Y., Chen, M. H.: Chinese Offshore Radiolarians. Science Press, Beijing, China, 404 pp., ISBN 7-03-006675-8, 1999. (in Chinese with English abstract)

Tréguer, P., Nelson, D. M., Van Bennekom, A. J., DeMaster, D. J., Leynaert, A., Quéguiner, B. The silica balance in the world ocean: a reestimate, Science, 268(5209), 375-379, https://doi.org/10.1126/science.268.5209.375, 1995.

Tréguer, P. J., De La Rocha, C. L.: The world ocean silica cycle. Annu. Rev. Mar. Sci., 5(1), 477-501, https://doi.org/10.1146/annurev-marine-121211-172346, 2013

van den Boorn, S. H., Vroon, P. Z., van Belle, C. C., Van der Wagt, B., Schwieters, J., van Bergen, M. J.: Determination of silicon isotope ratios in silicate materials by high-resolution MC-ICP-MS using a sodium hydroxide sample digestion method, J. Anal. Atom. Spectrom., 21(8), 734-742, https://doi.org/10.1039/B600933F, 2006.

Varela, D. E., Pride, C. J., Brzezinski, M. A.: Biological fractionation of silicon isotopes in Southern Ocean surface waters. Global biogeochemical cycles, 18(1). https://doi.org/10.1029/2003GB002140, 2004.

Wang, R., Lin, J., Zheng, L., Chen, R., Chen, J.: Siliceous microplankton fluxes and seasonal variations in the central South China Sea during 1993–1995: monsoon climate and El Niño responses, Chinese Sci. Bull., 45, 2168-72, https://doi.org/10.1007/BF02886323, 2000.

Wetzel, F., De Souza, G. F., Reynolds, B. C.: What controls silicon isotope fractionation during dissolution of diatom opal?, Geochimica et Cosmochimica Acta, 131, 128-37, https://doi.org/10.1016/j.gca.2014.01.028, 2014.

Wille, M., Sutton, J., Ellwood, M. J., Sambridge, M., Maher, W., Eggins, S., Kelly, M.: Silicon isotopic fractionation in marine sponges: A new model for understanding silicon isotopic variations in sponges. Earth Planet. Sci. Lett., 292(3-4), 281-289, https://doi.org/10.1016/j.epsl.2010.01.036, 2010.

Worne, S., Swann, G. E. A., Kender, S., Kender, S., Lacey, J. H., Leng, M. J.: Silicic acid cycling in the Bering Sea during the Mid-Pleistocene Transition, Paleoceanogr. Paleocl., 37 (2), https://doi.org/10.1029/2021PA004284, 2022.

520 Zhang, Q., Swann, G. E. A.: An effective method to extract and purify radiolaria from tropical marine sediments, Front. Mar. Sci., 10, 1150518, https://doi.org/10.3389/fmars.2023.1150518, 2023.

Zhang, L. L., Chen, M. H., Xiang, R., Zhang, J. L., Liu, C. J., Huang, L. M., Lu, J.: Distribution of polycystine radiolarians in the northern South China Sea in September 2005, Mar. Micropaleontol., 70(1), 20–38, https://doi.org/10.1016/j.marmicro.2008.10.002, 2009.

Zhang, Q., Chen, M. H., Zhang, L. L., Hu, W. F., Xiang, R.: Variations in the radiolarian assemblages in the Bering Sea since Pliocene and their implications for paleoceanography, Palaeogeogr. Palaeocl., 410, 337-50, https://doi.org/10.1016/j.palaeo.2014.05.048, 2014.

Zhang, L. L., Wang, R. J., Chen, M. H., Liu, J. G., Zeng, L. L., Xiang, R., Zhang, Q.: Biogenic silica in surface sediments of the South China Sea: Controlling factors and paleoenvironmental implications, Deep-Sea Res. Pt. II, 122, 142-152, https://doi.org/10.1016/j.dsr2.2015.11.008, 2015.

Zhang, L. L., Suzuki, N., Nakamura, Y., Tuji, A.: Modern shallow water radiolarians with photosynthetic microbiota in the western North Pacific, Mar. Micropaleontol., 139, 1-27, https://doi.org/10.1016/j.marmicro.2017.10.007, 2018.

530 Zhang, J., Zhang, L., Xiang, R., Suzuki, N., Qiu, Z., Zhang, Q.: Radiolarian biogeographic contrast between spring of 2017 and winter of 2017–2018 in the South China Sea and Malacca Strait. Cont. Shelf Res., 208, 104245, https://doi.org/10.1016/j.csr.2020.104245, 2020.