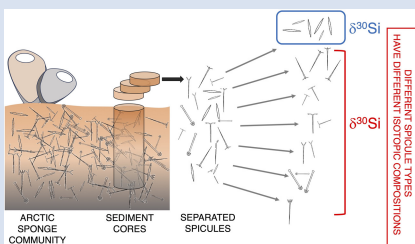# Spicule morphology impacts stable silicon isotopic composition of sponge archives

K.R. Hendry[1,2]*, H. Pryer[3], S.L. Bates[1], F. Mienis[4], J.R. Xavier[5,6]

OPEN ACCESS

Abstract

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The stable silicon isotopic composition of siliceous sponge skeletal elements, spicules, forms a potential proxy for past dissolved silicon (DSi) concentrations of bottom waters. Field-based studies have shown that there is a non-linear relationship between the concentration of ambient DSi and both the isotopic composition (denoted by $\delta^{30}Si$) of spicules and apparent isotopic fractionation by sponges during growth. There is considerable scatter in the calibration, with some studies highlighting variation within an individual sponge, and between individuals, in both monospecific and more diverse communities. Furthermore, some derived sponge forms, including hypersilicified and carnivorous sponges, appear to have anomalous isotopic fractionation, deviating significantly from other sponges. When reconstructing past DSi, it is only possible to differentiate spicules by their morphology, which in many cases will not be taxonomically diagnostic. However, there has yet to be a systematic study of core top and downcore $\delta^{30}Si$ measurements from different spicule types. Here we address that gap using spicules extracted from two sediment cores taken at the summit of the Schulz Bank, a seamount located on the Arctic Mid-Ocean Ridge between the Norwegian and Greenland Seas. Mean isotopic compositions of downcore spicules of a given morphology were similar between nearby cores and mainly did not show any significant differences. Our results did reveal a systematic difference between spicule types extracted from a given sediment horizon, and a significant difference in the downcore mean compositions, between needle-like Oxea and other morphologies. These new findings imply that picking a single spicule type is best practice for palaeoceanographic applications of sponge archives, but the choice of Oxea spicules could bias these reconstructions towards high DSi concentrations.

Introduction

The global marine silicon cycle plays a critical role in the Earth's climate system *via* carbon uptake and sequestration (Struyf *et al.*, 2009; Tréguer *et al.*, 2021). Diatoms, a siliceous phytoplankton group common to most marine ecosystems, are one of the most important contributors to organic matter export production. As they form their cell walls from silica, diatoms have an absolute requirement for dissolved silicon (silicic acid, or DSi), and largely rely on upwelling of deeper waters to obtain the nutrients required for growth. As such, archives of past deep and bottom water DSi concentrations in addition to surface conditions are essential for understanding past ocean biogeochemistry and climate impacts (Ellwood *et al.*, 2010; Fontorbe *et al.*, 2016; Sutton *et al.*, 2018; Hendry *et al.*, 2019; Dumont *et al.*, 2020).

Surface and subsurface silicon cycling processes can be reconstructed using the geochemistry of siliceous microfossils, such as diatoms and radiolarians, extracted from marine sediments (Hendry *et al.*, 2014; Abelmann *et al.*, 2015). In deeper waters benthic siliceous sponges create a skeleton of sponge spicules, which have the potential to act as archives of past bottom water conditions, providing a unique source of the critical information required to reconstruct past changes in DSi supply to the surface ocean from upwelling waters (De La Rocha, 2003; Łukowiak, 2020). Several field-based studies have shown that there is a non-linear relationship between the concentration of ambient DSi and both the isotopic composition (denoted by $\delta^{30}Si$) of spicules and apparent isotopic fractionation by sponges during growth that is apparently insensitive to temperature and other seawater properties (Hendry *et al.*, 2010; Wille *et al.*, 2010; Hendry and Robinson, 2012). At present, there is no evidence for any systematic difference in isotopic fractionation behaviour between the major groups of siliceous sponges, demosponges and hexactinellids, after differences in habitat and depth preference are taken into account (Cassarino *et al.*, 2018; Hendry *et al.*, 2019; Pack *et al.*, 2023). However, there is considerable scatter in the spicule $\delta^{30}Si$-DSi calibration that remains poorly understood. Whilst some studies show good agreement in measurements of spicules taken from individual sponges and good agreement between laboratories (*e.g.*, Hendry *et al.*, 2011), other studies highlight variation within

1. School of Earth Sciences, University of Bristol, Queen's Road, Bristol, BS8 1RJ, UK
2. British Antarctic Survey, High Cross, Madingley Road, Cambridge, CB3 0ET, UK
3. Department of Earth Sciences, University of Cambridge, Downing Street, CB2 3EQ
4. NIOZ Royal Netherlands Institute for Sea Research, Department of Ocean Sciences, P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands
5. CIIMAR – Interdisciplinary Centre of Marine and Environmental Research of the University of Porto, Matosinhos, Portugal
6. Department of Biological Sciences, University of Bergen, 5006 Bergen, Norway
* Corresponding author (email: kathen@bas.ac.uk)

an individual sponge, and between individuals, in both mono-specific and more diverse communities (Hendry *et al.*, 2019). Genetically-controlled biomineralisation pathways appear to be strong drivers of spicule isotopic heterogeneity, with some derived sponge forms, including hypersilicified demosponges, glass sponges, and carnivorous sponges, exhibiting anomalous isotopic fractionation that deviates significantly from other sponges (Hendry *et al.*, 2015; Jochum *et al.*, 2017; Cassarino *et al.*, 2018).

Sponge spicules, when buried in sediments, can become part of the geological record forming a palaeo-archive that could potentially be used to reconstruct past bottom water DSi concentrations. In most cases, the sponge skeleton completely disintegrates and spicules in marine sediment cores are found as separate elements. The larger spicules (megascleres) are generally preserved better, and more readily isolated, than the smaller and more taxonomically diagnostic microscleres. As such, it can be highly challenging to determine from which sponge any given fossil spicule derived. Earlier palaeoceanographic studies simply extracted all spicule material for analysis (*e.g.*, Hendry *et al.*, 2010; Hendry *et al.*, 2012), but more recent studies have taken the conservative approach of picking only one spicule type, usually selecting only the needle-like monaxonic spicules (*e.g.*, Fontorbe *et al.*, 2016; Fontorbe *et al.*, 2017). Developments in the use of secondary ion mass spectrometer (SIMS) methodologies have also allowed the targeting of individual spicules for isotopic analysis (*e.g.*, Trower *et al.*, 2021). However, to date, there has been no systematic study into the impact of spicule type on $\delta^{30}Si$ records and – so – palaeoceanographic reconstructions.

In this study, we address this gap using spicules extracted from box cores collected from a sponge ground in the Arctic Ocean. We ask the questions: do spicules of a given morphology picked from a given sediment horizon have consistent isotopic compositions? Do spicules of a given morphology picked from nearby sediment cores have consistent isotopic compositions? Is there a significant offset between different spicule morphologies picked from a given sediment horizon?

Methods

Box cores were collected from the Schulz Bank (SB) aboard the R/V G.O. Sars expedition GS2016109A in 2016. The summit of the SB is at approximately 560–600 m water depth, with a thick (~20 cm) sponge spicule mat characterising the upper reaches of the slope and summit (Meyer *et al.*, 2023). The oceanographic conditions around the SB are beneficial to sponge growth, with relatively nutrient-rich bottom waters frequently flushed with high oxygen, warm Arctic Intermediate Waters (Hanz *et al.*, 2021). Mean nutrient concentrations from between 600 and 800 m on SB are 7.56 mM (2 s.d. 0.63), 13.97 mM (2 s.d. 0.30), and 0.95 mM (2 s.d. 0.01) for DSi, nitrate and phosphate respectively (full details in Roberts *et al.*, 2018). A high organic particulate matter supply is maintained by strong diurnal currents, which also act to prevent sedimentation (Roberts *et al.*, 2018).

These conditions support a dense benthic community of sponges, or 'sponge ground' on the SB (Fig. 1a). The SB sponge ground is diverse including several species of demosponges and hexactinellids (see Supplementary Information).

Box cores BC1 and BC2 were collected from 73.81° N, 7.51° E, from 773 m and 765 m water depth respectively, less than 5 m apart on the seafloor. BC1 and BC2 were subsampled using plastic tubes, which were extruded and wrapped in clean foil and frozen for transport (Fig. 1b,c). Although age models do not exist for these subcores, the age model based on radiocarbon age dating of a nearby core GS2017-47 collected during an

expedition in 2017 would indicate that the top 16 cm as sub-sampled in this study should be approximately 6,000 years old (unpublished data).

The sediments were thawed in the UK, photographed (Fig. 1b,c) and sectioned into 1 cm slices. These slices were air dried in a cool oven (40 °C), washed and sieved at 63 μm, and then re-dried. Monoaxonic spicules were hand picked from the sediments using a very fine brush under a stereomicroscope and categorised into different spicule morphologies (see Fig. 1d). The categories represented are: Oxea, Plagiotriaene, Cladotylote, Dichotriaene, Protriaene, Dichodiaene (rare), and Prodiaene (rare) (Łukowiak *et al.*, 2022). It should be noted that these spicule morphologies are not diagnostic of sponge species and may be present across different taxonomic groups within classes of demospongiae (including carnivorous sponges). One sample of Pentactine spicules (from hexactinellid sponges) was recoverable from BC1.

The spicules (3 to 10 spicules *per* replicate, depending on size and availability) were cleaned for organic matter by heating for 1 hr at 80 °C in 30 % reagent grade hydrogen peroxide before being rinsed in 18 MΩ cm Milli-Q. The samples were dried down in concentrated in house distilled nitric acid (HNO_3) at 120 °C, and then dissolved in 1 ml 0.4 M sodium hydroxide (Analar) at 100 °C for 24–72 hours. The solutions were acidified with 50 μl 8 N HNO_3, and diluted with 1 ml Milli-Q. All samples and standards were chemically purified using cation exchange resin (Bio-Rad AG50W-X12) following published protocols, which have shown quantitative Si yield and cation retention under neutral or acidic conditions (*e.g.*, Georg *et al.*, 2006; Zambardi and Poitrasson, 2011; Savage and Moynier, 2013). Before analysis, the solutions were doped with a magnesium solution. The samples were analysed within 72 hours of purification for ^{28}Si, ^{29}Si, ^{30}Si, ^{24}Mg, ^{25}Mg, and ^{26}Mg using a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (Thermo Neptune MC-ICP-MS) in medium resolution mode. Sample blank corrections and Mg isotope mass bias corrections were carried out offline, before being normalised to NBS28 (RM8546) (Hendry *et al.*, 2015). A three isotope plot shows that all analyses fall on a mass-dependent $\delta^{29}Si$ and $\delta^{30}Si$ line, with a gradient of 0.510 ± 0.003, within the range of equilibrium or kinetic fractionation (Reynolds *et al.*, 2007). Repeat measurements of reference standards Diatomite and LMG08 (sponge material) reveal a long term $\delta^{30}Si$ reproducibility of 1.24 ± 0.11 ‰ (n = 64) and -3.46 ± 0.12 ‰ (n = 65) respectively (2 s.d.), within published ranges (Reynolds *et al.*, 2007; Hendry *et al.*, 2011). Each sample aliquot was measured at least twice and most were measured in triplicate. When possible, duplicate analyses were carried out on true replicates (*i.e.* analyses of separate aliquots of spicules that were picked from the same horizon). Statistical analyses (ANOVA and t-tests) were carried out using MATLAB R2021b for the more abundant spicule types, after testing for normality using an Anderson-Darling test ($\alpha = 0.05$).

Results

Oxea spicule $\delta^{30}Si$ compositions ranged from -1.47 to -2.05 ‰. The other spicule types exhibited similar ranges, from -0.94 to -1.76 ‰ (Fig. 2a,b). The one sample of hexactinellid Pentactine spicules from BC1 (10–11 cm depth) had an isotopic composition of -1.11‰. The mean difference between $\delta^{30}Si$ values of the true replicates was 0.14 ‰, with a maximum of 0.42 ‰ (Fig. 2c).

Within each core, there was a significant difference between the mean isotopic composition of the different spicule
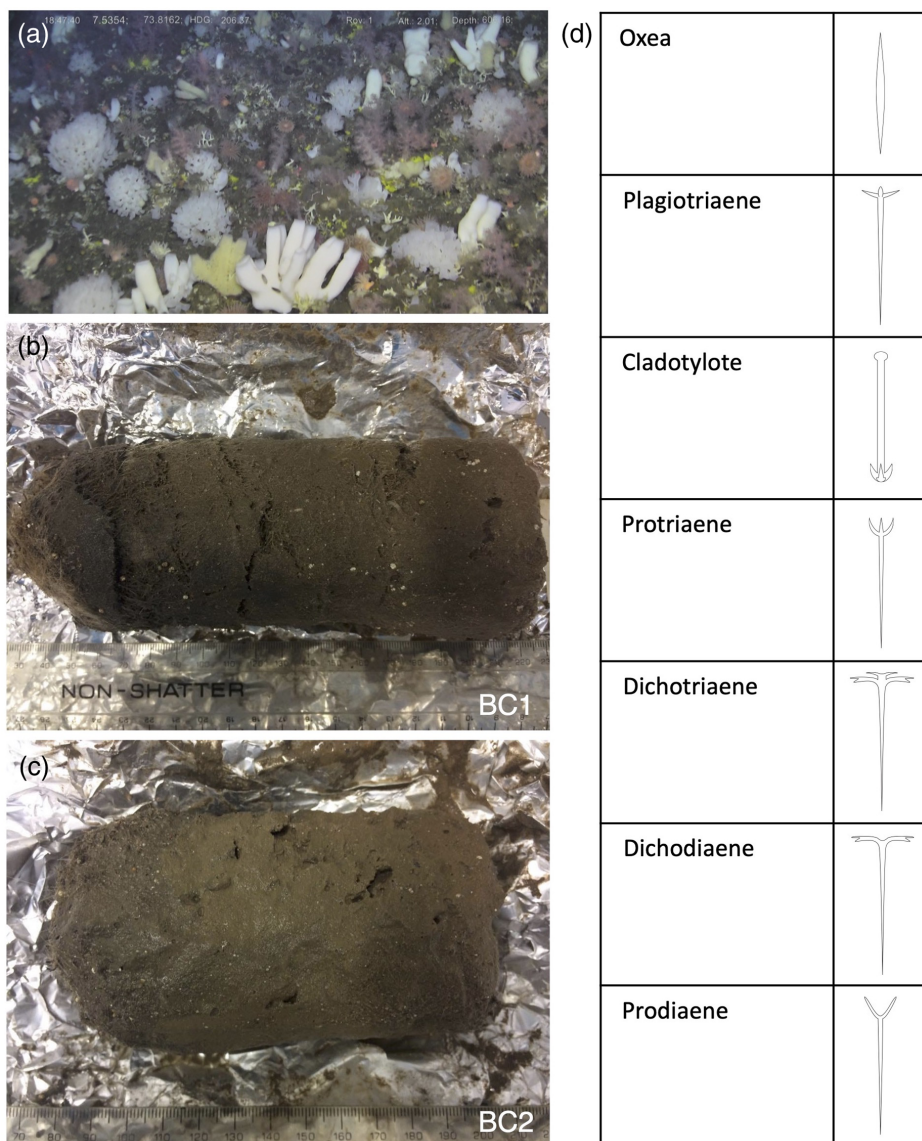
Figure 1 **(a)** Remotely Operated Vehicle image of the sponge ground of the Schulz Bank summit (image courtesy of the University of Bergen). **(b-c)** Photographs of the subcores from BC1 and BC2. **(d)** Spicule morphology definitions used in this study.

morphologies downcore (for BC1, F-statistic= 24.77, d.f. = 3, p << 0.001; for BC2, F-statistic= 6.39, d.f. = 3, p = 0.001), with *post hoc* analysis indicating that the Oxea spicules were significantly different from the other spicule morphologies analysed. There was no significant difference for either core between the isotopic compositions of the Plagiotriaene, Dichotriaene, and Protriaene spicule morphologies (Fig. 3).

There was no significant difference between the mean downcore isotopic composition of same spicule morphologies between BC1 and BC2, except for a weak difference between the Dichotriaene spicules (p = 0.025). Note that there is an inherent caveat in taking averages of δ^{30}Si values downcore, in that changes in environmental parameters through time could influence the spicule geochemical compositions.

Discussion

Comparison between Schulz Bank and other North Atlantic sponge grounds. To put our findings in a broader context, we can compare these findings from sedimentary spicules to field studies investigating stable silicon isotopic compositions of individual intact sponges. The SB study site is bathed in water with a similar DSi concentration to North Atlantic *Geodia* sponge aggregations at Orphan Knoll in the Labrador Sea and coastal Greenland (Hendry *et al.*, 2019). The δ^{30}Si values from different species of *Geodia* were assessed from these locations by taking subsamples from individual specimens, likely comprising a mixture of different spicule morphology types. The range of δ^{30}Si values between the specimens was similar (−1.0 to −2.4 ‰) to the range from the differentiated sedimentary spicules measured in this study. Our observations show that spicule morphology likely contributes to variation in δ^{30}Si between individuals of similar species, but other factors including localised differences in environmental conditions and growth rate will also play a role (Hendry *et al.*, 2019).

Impact of spicule morphology on DSi concentration reconstructions. Here, we discuss the differences in δ^{30}Si values obtained between spicule morphologies within and between the nearby box cores to address three key questions surrounding the impact of spicule form on palaeoceanographic archives.
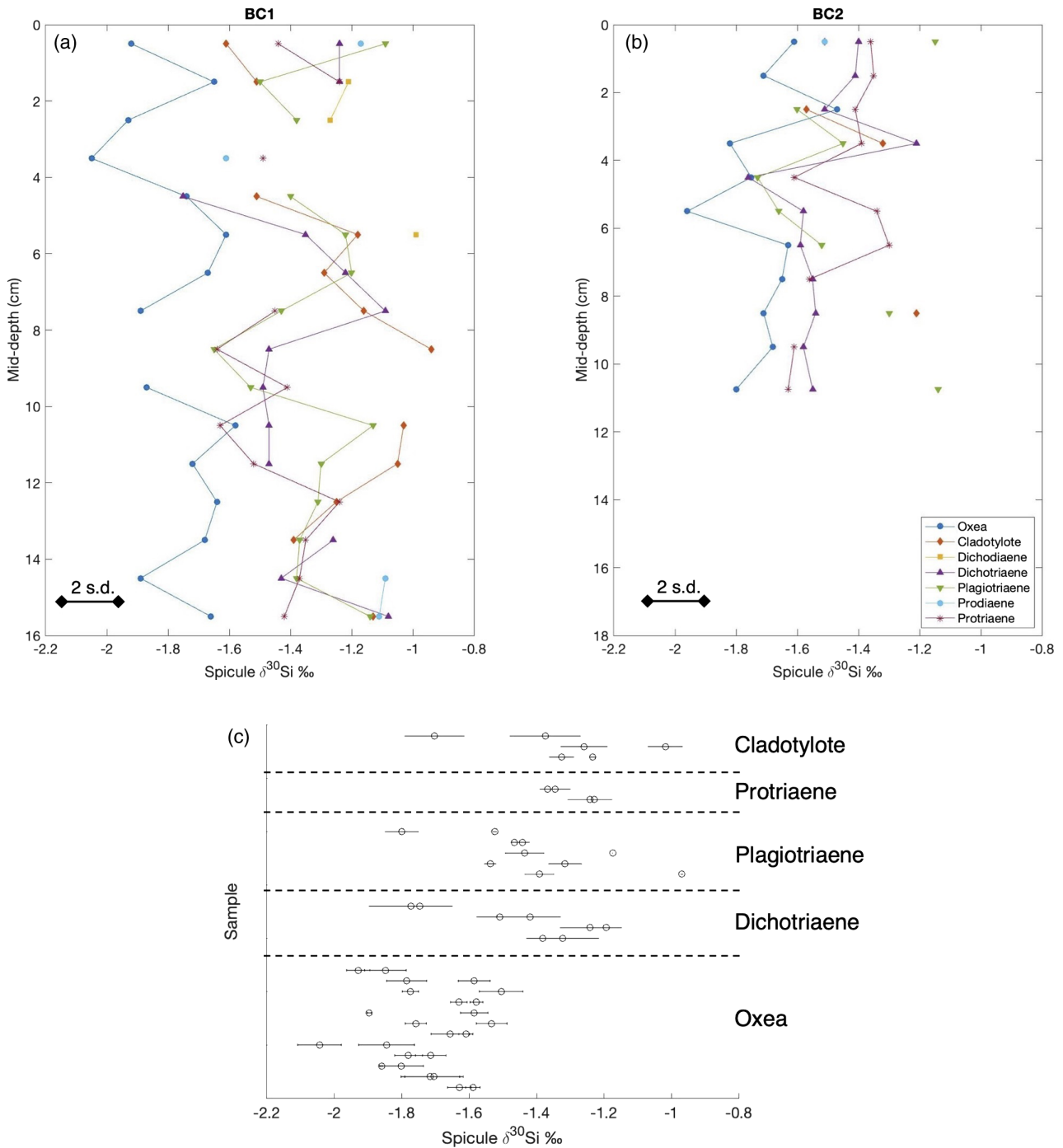
Figure 2 Downcore δ^{30}Si values from the different spicule types extracted from **(a)** BC1 and **(b)** BC2. Error bar shows 2 σ based on repeat measurements of reference materials. Each point represents the mean of repeat measurements of a sample aliquot (n = 2 or 3). **(c)** Assessment of true replicates of separate aliquots from a given horizon. Each symbol represents the mean of repeat measurements (n = 2 or 3, error bar 1 s.d.) of each of multiple aliquots (n = 2) of spicules extracted from the same horizon.

1. Do spicules of a given morphology picked from a given sediment horizon have consistent isotopic compositions? The analyses of true replicates indicates that there is some variability in δ^{30}Si within a given horizon for a particular spicule morphology. No differences were observed between column replicates (one aliquot of dissolved spicule passed through two columns), showing that the variability was not caused by sample processing. The mean difference between true duplicates was 0.14 ‰ – similar to the long term reproducibility based on repeat measurements of reference materials – and is often considerably less. However, there were some samples where there were larger differences between duplicate δ^{30}Si measurements, up to 0.3 to 0.4 ‰, indicating significant environmental heterogeneity. There does not appear to be any relationship between duplicate offset and spicule type, indicating no clear link between isotopic variability and biomineralisation. Instead, these offsets could be due to recycling of silica (*i.e.* partial dissolution effects), localised differences in environmental conditions, or spicule growth rate (Hendry *et al.*, 2019).

2. Do spicules of a given morphology picked from nearby sediment cores have consistent isotopic compositions? Our findings indicate that spicules of a given morphology
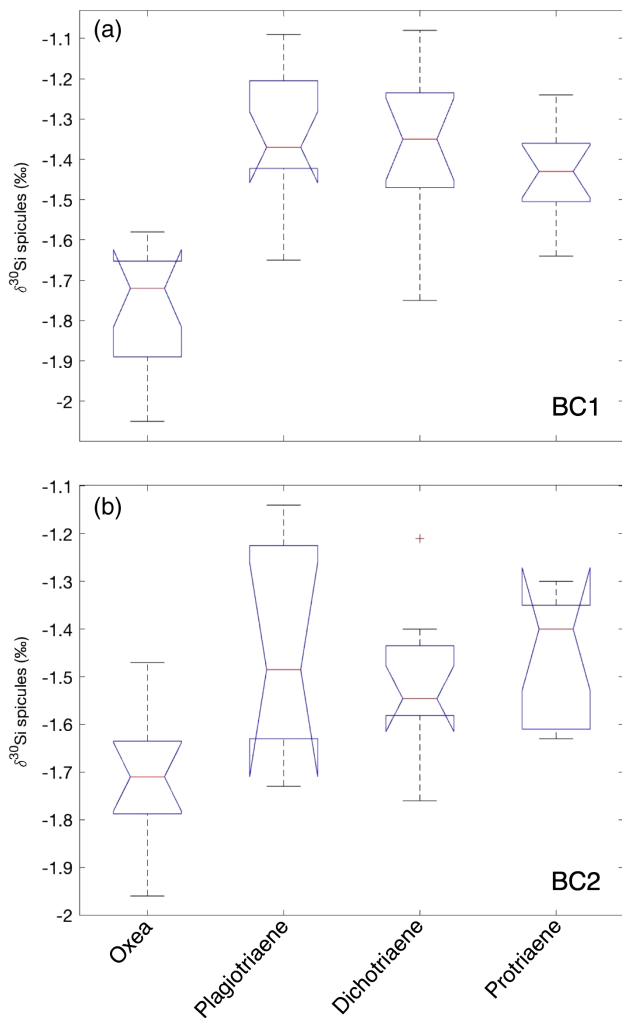
Figure 3 Box and whisker plots summarising downcore δ^{30}Si data from **(a)** BC1 and **(b)** BC2 for the main spicule types present in the sediment. The notches represent the median values, the bottom and top edges of the box represent the 25 th and 75 th percentiles, and the whiskers encompass all data points not considered statistical outliers (outliers are shown by a red cross).

Figure 4 New spicule isotopic data from this study (grey hollow circles are non-Oxea Demosponge spicules; solid circles are Oxea spicules) plotted with existing field calibration of ambient DSi concentrations against **(a)** sponge spicule δ^{30}Si values and **(b)** apparent isotopic fractionation (Δ^{30}Si = δ^{30}Si$_{sponge}$ − δ^{30}Si$_{sw}$), assuming ambient seawater δ^{30}Si$_{sw}$ at the SB of +1.7 ‰ (Brzezinski *et al.*, 2021). Blue symbols = demosponges without Cladorhizidae, red symbols = hexactinellids without hypersilicifiers.

extracted from the two sediment cores do not have statistically different δ^{30}Si compositions, and so should yield consistent [DSi] reconstructions. It is possible that there are differences in fossil age between spicules from the same 1 cm slice horizon in different cores due to small scale heterogeneities in sedimentation rate. However, given the assumed age of the core, there is only likely a 6,000 year age difference between the core top and 16 cm depth, and no large scale shifts in Arctic Ocean circulation that would have influenced bottom water conditions and nutrient dynamics are likely over this timescale (Rasmussen *et al.*, 2014).

3. Is there a significant offset between different spicule morphologies picked from a given sediment horizon? Our analyses of different spicule morphologies extracted from the same core horizons indicated that the δ^{30}Si composition of sponge silica, used to reconstruct past bottom water DSi, depends on the spicules chosen during the picking process. Oxea spicules could be a potential target for palaeoceanographic research as they are commonly found, are often large and so provide a useful amount of silica for analysis, and are readily identified as simple double-pointed needles. However, our findings reveal a significant offset between Oxea spicules and tetraxonic
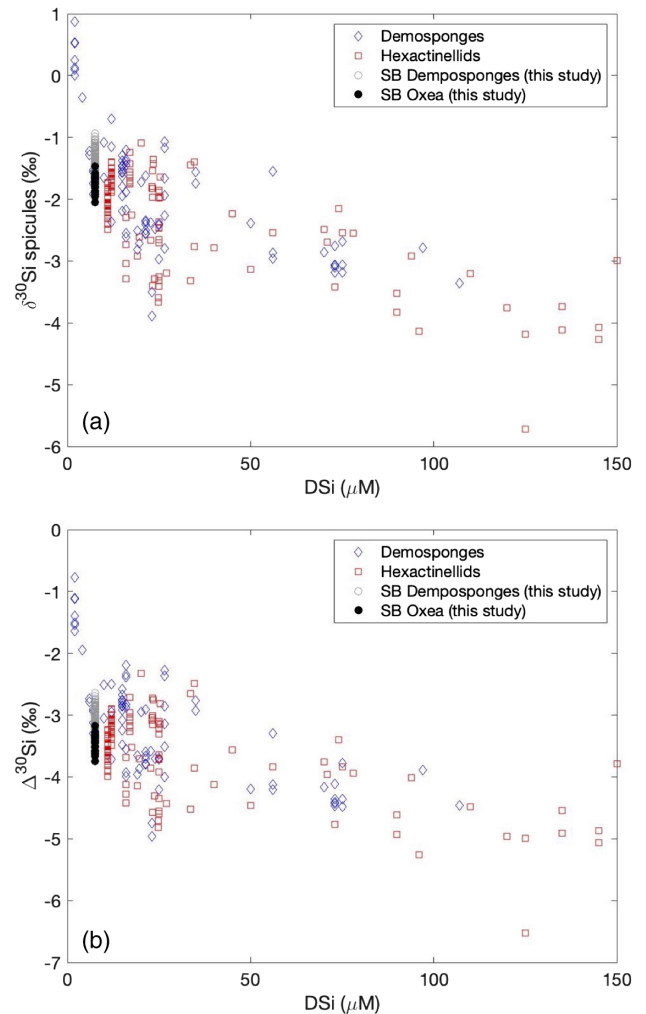
spicules analysed (common forms being Plagiotriaene, Dichotriaene, and Protriaene). There was no significant difference downcore between Plagiotriaene, Dichotriaene, and Protriaene spicules. In other words, the Oxea spicules form the outlier, yielding significantly lighter isotopic compositions than tetraxonic spicules, potentially reflecting an impact of biomineralisation processes, differential preservation, or redistribution by currents. When the shallow core spicule data are added to the δ^{30}Si-DSi calibration plot (Fig. 4a), it is apparent that Oxea plot towards the isotopically lighter region of the observed scatter, with the other spicules falling more in the mid-range of the variability seen in field studies. This observation is robust even when taking into consideration any possible bias due to the isotopic composition of ambient seawater (Fig. 4b). Our results could imply that using Oxea could bias [DSi] reconstructions towards higher values. To test this possibility, we have substituted the range in spicule compositions into Equation 1 (adapted from Hendry *et al.*, 2019):

$$[\text{DSi}] = (27.6/(\delta^{30}\text{Si}_{\text{Sponge}} − \delta^{30}\text{Si}_{\text{DSi}} + 4.6)) − 7.4 \qquad \text{Eq. 1}$$

where we have assumed the bottom water isotopic composition, $\delta^{30}Si_{DSi}$, to be +1.7 ‰, similar to the deep Central Arctic Basin (Brzezinski *et al.*, 2021). Reconstructed [DSi] for Oxea ranged from 12 to 25 mM, with a mean of 16 mM, whereas the range for the other spicules was 7 to 17 mM (mean 11 mM), matching better with modern [DSi] observations (mean value approximately 8 mM; Roberts *et al.*, 2018). As such, our findings suggest that Oxea may not be the best spicule morphology to select when using the existing field-based calibration, or that a new calibration using core top Oxea spicules is required.

Synthesis

We have presented a systematic study of core top and downcore $\delta^{30}Si$ measurements from different sponge spicule types extracted from box core material. Mean $\delta^{30}Si$ compositions of the spicules of a given morphology in the top ~16 cm were invariant with depth and largely did not show any significant differences between the subcores. Our results revealed a difference between spicule types extracted from a given sediment horizon, and significant differences between morphologies in the downcore mean $\delta^{30}Si$ values. Our new findings imply that picking a single spicule type is best practice for palaeoceanographic applications of sponge archives, and the choice of Oxea spicules could bias these reconstructions towards high DSi concentrations.

Acknowledgements

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2423.

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