

2019-04-15

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<http://hdl.handle.net/10026.1/14573>

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10.1016/j.quascirev.2019.02.017

Quaternary Science Reviews

Elsevier

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# 1 **Silicon isotopic systematics of deep-sea sponge grounds in the North Atlantic**

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11 Keywords: Porifera, isotopes, silicic acid, geochemical archives

12

## 13 **Abstract**

14 Reconstruction of silica cycling in the oceans is key to a thorough understanding of past  
15 climates because of the inherent links between the biogeochemistry of silicifiers and sequestration  
16 of organic carbon. Diatoms are one of the most important phytoplankton groups in determining  
17 export production from surface waters, and rely largely on upwelling deeper waters as a source of  
18 dissolved silicon, an essential nutrient for their growth. Quantification of changes in deep water  
19 dissolved silicon concentrations in the past allows a more robust understanding of changes in  
20 surface nutrient supply and whole-ocean silicon cycling, but cannot be achieved using surface-  
21 derived geochemical archives. In the last few years, there has been increasing focus on the use of  
22 geochemical archives in siliceous skeletal elements, or spicules, from seafloor-dwelling sponges to  
23 fill this gap. The stable silicon isotopic composition of spicules has been shown to be a function of  
24 ambient dissolved silicon, providing a potential archive for past changes in bottom water nutrients.  
25 However, biomineralisation processes impact silicon isotope fractionation and silica formed by  
26 atypical processes (derived from carnivorous sponges, hypersilicified spicules, and giant basal  
27 spicules) result in anomalous geochemical signatures. Furthermore, there is considerable scatter in  
28 the calibration between spicule silicon isotopes and dissolved silicon in seawater, even when the  
29 atypical groups have been removed. Here, we explore this variability further, by examining  
30 aggregation and assemblage-level differences in isotopic fractionation, using silicon isotopic  
31 measurements of specimens from two monospecific sponge groups (*Pheronema carpensteri* and

32 *Vazella pourtalesi*), and one mixed-species population (genus *Geodia*) from the North Atlantic. Our  
33 new data reveal that variability within the monospecific aggregations is less than mixed-species  
34 assemblage, pointing towards a genetic control in isotopic fractionation. However, there is still  
35 variability within the monospecific aggregations, which cannot be explained by macroscale  
36 environmental differences: such variability is likely a reflection of the physiological health of the  
37 individuals, or highly localised heterogeneities in sponge habitats.

38 Other challenges remain in the interpretation of spicule silicon isotopes as proxies for  
39 dissolved silicon changes through time, especially when investigating periods of Earth history that  
40 extend back considerably further than the residence time of dissolved silicon in the oceans. Despite  
41 all the questions still surrounding the use of sponge silicon isotopes in palaeoceanographic  
42 applications, they are still the only known archive of bottom water dissolved silicon. Continued  
43 efforts to understanding sponge biomineralisation and to incorporate silicon isotopes into oceanic  
44 models will help to improve further the reliability of the archive.

## 45 **1. Introduction**

### 46 *1.1. The marine silicon cycle: why study the deep?*

47 The marine biological pump plays a key role in the carbon cycle, through the uptake of  
48 carbon from the atmosphere (CO<sub>2</sub>) during algal growth and subsequent sequestration of carbon via  
49 the burial of organic matter at depth. The majority of marine production, occurring away from direct  
50 inputs of nutrients, is supported by upwelled nutrients supplied through the remineralisation of  
51 sinking particles or release from seafloor sediments. Diatoms, a photosynthetic algae, are  
52 responsible for a significant proportion, up to 40%, of primary production in the oceans (Tréguer et  
53 al., 2018). Their absolute requirement for dissolved silicon (DSi, in the form of silicic acid) to build  
54 their silica tests or frustules, means that there is a fundamental link between both the cycling of  
55 silicon and carbon within the climate system (first described by DeMaster, 1979; more recently  
56 reviewed by Tréguer and De la Rocha, 2013). The robust quantification of DSi within deep and  
57 upwelling waters through time is essential if we are to understand the growth of diatoms in the  
58 surface of the world's oceans, the drawdown of CO<sub>2</sub>, and the burial of organic matter (Hendry and  
59 Brzezinski, 2014).

60 In addition to diatoms, there are a wide range of other organisms that precipitate DSi from  
61 seawater (silicifiers) including bacteria (Baines et al., 2012), other single-celled eukaryotes (e.g.  
62 radiolarians, silicoflagellates, choanoflagellates, some haptophytes, plants, and animals (Hendry et  
63 al., 2018; Marron et al., 2016)). Sponges are the most significant group of animals that contribute to

64 the marine silicon cycle, because the phylum contains a number of silicifying groups requiring a large  
65 supply of DSi to form their skeletal elements, or spicules. Unlike diatoms, sponges are seafloor-  
66 dwelling and obtain the required DSi from bottom waters rather than surface waters. Given the  
67 cosmopolitan distribution of sponges and the high preservation potential of siliceous spicules  
68 (Maldonado et al., 2011; Schrader, 1972), they may possibly form a substantial standing stock of  
69 sedimentary biogenic silica (BSi) in some continental shelf regions (Maldonado et al., 2011), but will  
70 also provide an important archive of the geochemical signature of bottom waters. The occurrence of  
71 sponge spicules, over the entire Phanerozoic (Antcliffe et al., 2014), has led to their investigation as  
72 potentially useful archives of past oceanic change, especially for deep-water DSi through time (De La  
73 Rocha, 2003).

## 74 *1.2. Aims of this review*

75         Given the reliance of diatoms, and other surface-dwelling silicifiers, on upwelling supplies of  
76 DSi, there is substantial motivation to understand the geochemical signatures recorded in marine  
77 sponges, which could act as palaeoceanographic proxies for past changes in marine silicon cycling.  
78 The silicon isotope composition (denoted by  $\delta^{30}\text{Si}$ ) of sponges has shown promise as a proxy for past  
79 bottom-water DSi, due to the discovery of a statistically significant correlation between sponge  
80 silicon isotopic fractionation and ambient DSi (Hendry et al., 2010; Wille et al., 2010). Here, we  
81 review the developments in the understanding of silicon isotope fractionation by sponges during  
82 spicule formation, including recent studies highlighting anomalous fractionation during some forms  
83 of biomineralisation, and their use in palaeoceanographic studies. We will present new  $\delta^{30}\text{Si}$  data  
84 investigating populations of sponges from North Atlantic sponge grounds, specifically to assess  
85 variation in isotopic composition of individuals from mono-specific aggregations and multi-specific  
86 assemblages. Variation between these individuals, which have grown under almost identical  
87 environmental conditions, can be used to address physiological impacts (e.g. growth rate, food  
88 supply, health) on spicule  $\delta^{30}\text{Si}$  compositions, and the potential impact of these biogeochemically  
89 important grounds on the use of spicules as geochemical archives. Finally, we will use our new data  
90 together with published data in the literature to re-evaluate the  $\delta^{30}\text{Si}$ -DSi calibration.

## 91 **2. Sponges as geochemical archives**

### 92 *2.1. Sponge silicification: the role of enzymatic processes*

93         Sponges are predominantly filter-feeding benthic animals (Phylum Porifera), with an  
94 ancestral body plan comprising a gelatinous mesohyl surrounded by two layers of cells. Water is  
95 circulated throughout the body via a series of pores in an aquiferous “canal” system, aided by

96 flagellated choanocyte cells. Other cells have specialised and changeable functions, including  
97 reproduction, digestion, collagen production, and spicule formation. Spicules are produced from  
98 carbonate, proteins, or BSi in the case of Classes Demospongea, Homoscleromorpha, and  
99 Hexactinellida. These siliceous structures are highly diverse in their morphology, and are produced in  
100 – at least initially – and assembled in specialised sclerocytes before being exported out of the cell,  
101 where silicification is completed. Spicules can be separated, joined at nodes, or fused by secondary  
102 silica (Hooper and Van Soest, 2002). Despite being of great interest for biomaterials research (Jo et  
103 al., 2016), the biochemical pathways involved in spicule silicification are not fully understood.  
104 Silicification in sponges is generally considered to be controlled by two enzymes: silicatein, which  
105 promotes polycondensation reactions, and silicase, which dissolves silica (Müller et al., 2013; Müller  
106 et al., 2007; Schroeder et al., 2003). Most spicules are formed in layers around a central filament of  
107 silicatein (Shimizu et al., 1998), resulting in a central “axial” canal structure in the final form.  
108 However, molecular data suggest the enzymes involved in silicification may have evolved  
109 independently multiple times, occurring in individuals that do not express the silicatein gene, and  
110 may have been lost as a trait in some non-silicifying lineages (Riesgo et al., 2015).

111           Regardless of the specific biochemical pathway, DSi is a requirement for silicification, and  
112 DSi availability is an important factor in determining the distribution of sponges in the oceans  
113 (Howell et al., 2016). The uptake of DSi is regulated by availability, and growth experiments in  
114 laboratory-cultured sponges reveal that there is a Michaelis-Menten relationship between uptake  
115 and DSi concentration, indicative of enzymatic control (López-Acosta et al., 2018; López-Acosta et  
116 al., 2016; Maldonado et al., 2011; Reincke and Barthel, 1997). For some shallow-water species, such  
117 experiments have shown that significant uptake only occurs when DSi concentrations far exceed  
118 natural ambient conditions, which has led to the proposition that these sponges suffer chronic  
119 silicon limitation (Maldonado et al., 2012). The measured kinetic parameters vary both between and  
120 within species, indicating both an evolutionary control on the nature and functioning of these  
121 enzymes, in addition to an influence of physiological factors such as food availability and health on  
122 DSi uptake (López-Acosta et al., 2016).

## 123 *2.2. Silicon isotopes in sponges*

124           Sponge biogenic silica is relatively pure, with a general formula  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , with a greater and  
125 more variable degree of hydration relative to diatom silica. Given the trace abundance of  
126 incorporated metals, the majority of proxy calibration studies have focused on the use of silicon  
127 isotopes as geochemical tracers, although there have been some studies into the use of some trace  
128 elements and their isotopes e.g. zinc and germanium (Guillermic et al., 2017; Hendry and Andersen,

129 2013). Oxygen isotopes in spicules have been the focus of a small number of studies, and appear to  
 130 exhibit a high degree of variability, which is not yet mechanistically understood (reviewed in Hendry  
 131 et al., 2015).

132 Silicon has three stable isotopes ( $^{28}\text{Si}$ ,  $^{29}\text{Si}$  and  $^{30}\text{Si}$ ), and fractionation of these isotopes  
 133 occurs in natural systems as a result of physical, chemical or biochemical reactions. The silicon  
 134 isotopic composition ( $\delta^{30}\text{Si}$ , Equ. 1) of spicules, and the associated fractionation of silicon with  
 135 respect to seawater (denoted by  $\Delta^{30}\text{Si}$ , Equ. 2), is highly variable (Hendry et al., 2010; Wille et al.,  
 136 2010) and under certain conditions can be greater than fractionation observed for other silicifiers  
 137 such as diatoms or radiolarians (Abelmann et al., 2015; Hendry et al., 2014).

$$138 \quad \delta^{30}\text{Si} = \left\{ \left[ \frac{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{NBS28}}} \right] - 1 \right\} \times 1000 \quad (1)$$

$$139 \quad \Delta^{30}\text{Si} = \delta^{30}\text{Si}_{\text{sponge}} - \delta^{30}\text{Si}_{\text{seawater}} \quad (2)$$

140

141 Although sponge  $\delta^{30}\text{Si}$  values were measured for the first time in the 1980s (Douthitt, 1982),  
 142 spicule silicon isotopes were first postulated as a potential archive of seawater chemistry decades  
 143 later (De La Rocha, 2003). Later studies of modern filter-feeding sponges (both hexactinellid and  
 144 demosponges) revealed a statistically significant non-linear relationship between  $\delta^{30}\text{Si}$  (and  $\Delta^{30}\text{Si}$ )  
 145 and ambient DSi concentrations in Southern Ocean sponges (Hendry et al., 2010; Hendry et al.,  
 146 2011; Wille et al., 2010), and in core-top spicules and living sponges from the Atlantic and Pacific  
 147 Oceans (Hendry and Robinson, 2012) (Fig. 1). The same relationship between  $\delta^{30}\text{Si}$  and DSi was  
 148 found in sponges from the different ocean basins, despite growing in contrasting temperature,  
 149 salinity and pH conditions, without any systematic difference between hexactinellid and  
 150 demosponges, suggesting that DSi availability is the main driving factor behind  $\delta^{30}\text{Si}$  variability in  
 151 sponges (Hendry & Robinson, 2012). The  $\delta^{30}\text{Si}$ -DSi relationship is thought to derive from the similar  
 152 non-linear dependence of sponge growth rate on DSi availability (Hendry and Robinson, 2012; Wille  
 153 et al., 2010), where the silicon isotopic fractionation can be expressed following Milligan et al.  
 154 (2004), according to Equ. 3.

$$155 \quad \Delta\delta^{30}\text{Si} \approx \varepsilon_f = \varepsilon_{tI} + (\varepsilon_p - \varepsilon_{tE}) \frac{v_E}{v_I} \quad (3)$$

156 where  $\varepsilon_f$  = the total Si isotopic fractionation factor,  $\varepsilon_{tI}$  = Si isotopic fractionation due to transport into  
 157 the cell,  $\varepsilon_p$  = Si isotopic fractionation due to polymerisation and  $\varepsilon_{tE}$  = Si isotopic fractionation due to  
 158 transport out of the cell;  $v_E$  = rate of Si efflux and  $v_I$  = rate of Si influx. This equation can be  
 159 rearranged (Equ. 4-5, Wille et al., 2010):

$$160 \quad \varepsilon_f = \varepsilon_{tl} + \Delta\varepsilon_p \left\{ 1 - \frac{\frac{v_{\max p}}{\left(\frac{K_{mp}}{[DSi]}\right)^{+1}}}{\frac{v_{\max l}}{\left(\frac{K_{ml}}{[DSi]}\right)^{+1}}} \right\} \quad (4)$$

$$161 \quad K_{ml} = v_{\max l} \times \frac{K_{mp}}{v_{\max p}} \quad (5)$$

162 where  $\Delta\varepsilon_p = (\varepsilon_p - \varepsilon_{tl})$ ;  $K_{ml}$  and  $K_{mp}$  are the half saturation constants for DSi incorporation and silica  
 163 precipitation respectively, and  $v_{\max l}$  and  $v_{\max p}$  are the maximum incorporation and precipitation rates  
 164 respectively. This relationship was used to reconstruct the general behaviour of silicon isotopic  
 165 fractionation by filter-feeding sponges, lending strength to the hypothesis that this fractionation is  
 166 driven by enzymatic processes within sclerocytes (Hendry and Robinson, 2012; Wille et al., 2010).

167 More recent work has highlighted that this simple non-linear relationship can breakdown  
 168 when distinct biomineralisation processes are active within different groups of sponges. For  
 169 example, carnivorous sponges (Vacelet, 2006) that are currently classed in the family Cladorhizidae  
 170 (Order Poecilosclerida) are thought to have different isotopic systematics compared to the more  
 171 ancestral body forms. Cladorhizids secondarily evolved the carnivorous habit as an adaptation to  
 172 low-nutrient conditions (Vacelet and Dupont, 2004), and have abandoned the ancestral body  
 173 organisation (i.e. the aquiferous “canal” system) and instead possess specialised feeding apparatus  
 174 and a closed “circulation” system. One specimen in the genus *Asbestopluma* from the Southern  
 175 Ocean (Fig. 2A) (Goodwin et al., 2016) was found to be isotopically heavier than expected for given  
 176 ambient DSi concentration, likely a result of different biomineralising mechanisms and internal  
 177 fractionation (Hendry et al., 2015). Specialised spicules, desmas, which reinforce the skeleton,  
 178 appear to be particularly linked with anomalous  $\delta^{30}\text{Si}$ . These desmas lack a central canal, and are  
 179 thought to grow via a mechanism different to filter-feeding relatives, in agreement with the  
 180 hypothesis that some biochemical pathways for sponge biosilicification evolved independently  
 181 between different lineages (Maldonado and Riesgo, 2007).

182 Other unusual forms of biosilicification have been shown to exhibit  $\delta^{30}\text{Si}$  values that deviate  
 183 significantly from the original calibration (Fig. 1). The giant spicules of the Indian and Western Pacific  
 184 hexactinellid sponge, *Monorhaphis chuni* (Hooper and Van Soest, 2002), are an extreme example of  
 185 biosilicification, with large, basal spicules observed to grow over a metre in length (Jochum et al.,  
 186 2017; Wang et al., 2009) (Fig. 2B). Laser analysis of *M. chuni* spicule silicon isotope composition  
 187 reveals significantly heavy signatures relative to other sponges, again most likely a result of a  
 188 fundamentally different silicification process. Despite this offset, there does appear to be a  
 189 significant trend between  $\delta^{30}\text{Si}$  and DSi concentrations in *M. chuni*, indicating that they have  
 190 potential as a complementary palaeoceanographic archive (Jochum et al., 2017). Analyses of mixed-

191 sponge assemblages from seamounts within the Equatorial Atlantic revealed that heavily fused  
192 hexactinellid spicules, exhibiting a “dictyonal-type” framework (Fig. 2C), are isotopically lighter than  
193 expected. The sponge specimens in the study were graded according to degree of secondary silica  
194 fusion: the more secondary silica deposited, the greater the isotopic anomaly (Cassarino et al.,  
195 2018). These results indicate that, again, there is a different process involved in producing secondary  
196 silica “cement” that fuses primary spicules within hexactinellids.

197 To date, studies have identified anomalous silicon isotope fractionation behaviour in  
198 sponges relating to fundamentally different biosilicification mechanisms. However, filter-feeding,  
199 non-fused sponges also exhibit variation, as shown by the scatter in the original  $\delta^{30}\text{Si}$ -DSi calibration  
200 (Fig. 1). Whilst localised changes in environmental parameters (notably DSi) could be responsible for  
201 some of this scatter, there has not been a full investigation of how physiological factors, such as  
202 growth rate, health and food supply, could impact silicon isotopic fractionation.

### 203 *2.3. Palaeoclimate applications*

204 Despite the uncertainties in understanding biomineralisation and silicon isotopic  
205 fractionation in sponges, there have already been several studies to utilise the sponge silicon isotope  
206 proxy for deep-water formation. There are a number of caveats to consider when applying sponge  
207  $\delta^{30}\text{Si}$  to the geological record, including the observed variability in fractionation associated with  
208 different biosilicification mechanisms. However, this concern can – to a large part – be assuaged  
209 through avoiding potentially anomalous spicules, such as desmas (Hendry et al., 2015), or framework  
210 structures (Cassarino et al., 2018). Some palaeoceanographic studies have circumvented potential  
211 issues by picking only one form of spicule from marine sediments for archive generation (Fontorbe  
212 et al., 2016).

213 Other caveats in the use of the sponge  $\delta^{30}\text{Si}$  proxy are more challenging to circumvent. Most  
214 critically, the residence time of silicon in the oceans is estimated as 10-15 ka (Georg et al., 2009),  
215 with the consequence that whole-ocean silicon concentration – and isotopic budgets – could shift on  
216 glacial-interglacial timescales. Changes in terrestrial weathering relating to the growth and retreat of  
217 ice sheets are likely to be one of the most important causes of regional or global seawater silicon  
218 isotope composition ( $\delta^{30}\text{DSi}$ ) relevant to the majority of silica  $\delta^{30}\text{Si}$  records to date (Frings et al.,  
219 2016; Hawkings et al., 2018; Opfergelt et al., 2013). Changes in regional DSi utilisation, and so  
220 isotopic distillation, by diatoms over abrupt climatic events also need to be taken into consideration  
221 (e.g. Hendry et al., 2012). Shifts in whole-ocean silicon isotope systematics could be even more  
222 substantial (and challenging to constrain) over long-term geological timescales, in response to  
223 changes in continental silicate weathering due to mountain building or macroevolutionary changes.



224 Whilst there is no available proxy for secular changes in silicon budgets, ocean modelling can be  
225 used to constrain potential changes through time (De La Rocha and Bickle, 2005).

226 Most palaeoclimate studies have focussed on the Late Quaternary, especially the last  
227 deglaciation and into the Holocene, during periods of time that are less likely to have witnessed  
228 large shifts in whole-ocean silicon cycling budgets. The first continuous sponge  $\delta^{30}\text{Si}$  records  
229 investigated impact of whole-ocean circulation shifts of the silicon cycle between glacial and  
230 interglacial states by comparing spicule composition at the Last Glacial Maximum (LGM,  
231 approximately 20 ka) and the modern. A shift in sedimentary sponge  $\delta^{30}\text{Si}$  records between the LGM  
232 and today indicate increased deep water DSi concentrations in some sectors of the Southern Ocean,  
233 especially the Pacific Sector, consistent with changes in diatom productivity and opal export (Chase  
234 et al., 2003; Ellwood et al., 2010; Hendry et al., 2010). Higher resolution spicule archives are  
235 beginning to reveal that changes in intermediate and mode water DSi concentrations are also basin-  
236 specific. In the Pacific, spicule records suggest that DSi concentrations in intermediate and mode  
237 waters were higher throughout the LGM and into the deglaciation, only declining at the beginning of  
238 the Holocene, potentially as a result of DSi-enriched deep-water upwelling (Rousseau et al., 2016). In  
239 contrast, Atlantic Ocean sedimentary spicule  $\delta^{30}\text{Si}$  signatures only record lighter signatures during  
240 the abrupt climate events of the deglaciation (Heinrich Event 1 and the Younger Dryas), indicative of  
241 enhanced bottom-water DSi concentrations in the mid-depth Atlantic as a result of the millennial-  
242 scale reorganisation of ocean circulation (Hendry et al., 2016; Hendry et al., 2014; Hendry et al.,  
243 2012).

244 These new Late Quaternary sponge archives have added substantially to the debate over the  
245 extent of DSi supply, or “leakage” from the Southern Ocean to the low latitudes on glacial-  
246 interglacial timescales, and the subsequent impact on atmospheric  $\text{pCO}_2$ . The “silica hypothesis”  
247 posited that diatom productivity was promoted by an increase in DSi supplied from dust dissolution  
248 during colder glacials (Harrison, 2000). A similar theory, the Silicic Acid Leakage Hypothesis (SALH),  
249 was proposed, suggesting that the addition of iron via enhanced dust deposition in the Southern  
250 Ocean impacted diatom physiology and macronutrient uptake ratios, resulting in a lower Si:N  
251 utilisation ratio and a relative increase in mode or intermediate water DSi (Brzezinski et al., 2002).  
252 Low-latitude waters would then receive a relatively high Si:N supply, promoting diatoms relative to  
253 other phytoplankton, contributing to  $\text{pCO}_2$  drawdown via alkalinity changes (Matsumoto and  
254 Sarmiento, 2008). However, the new sponge archives, in combination with other novel proxy data,  
255 suggest an alternative theory, termed the Silicic Acid Ventilation Hypothesis (SAVH), which proposes  
256 that changes in ventilation of deep waters in the Southern Ocean during these periods enhanced the

257 relative DSi concentration of waters leaking into the lower latitudes, rather than surface productivity  
258 (Hendry and Brzezinski, 2014).

259 Spicule records have also been combined with other geochemical archives, including  $\delta^{30}\text{Si}$   
260 records from diatoms and other silicifiers, to capture the whole silicon cycle (Abelmann et al., 2015;  
261 Hendry et al., 2014; Horn et al., 2011). For example, Horn et al. (2011) combined diatom  $\delta^{30}\text{Si}$  and  
262 nitrogen isotope ( $\delta^{15}\text{N}$ ) archives with sponge  $\delta^{30}\text{Si}$  records from the Southern Ocean (Hendry et al.,  
263 2010) to show that DSi utilisation was high during the deglacial at the same time as deep-water DSi  
264 concentrations and supply rates were enhanced, suggesting a strong biological pump and  $\text{CO}_2$   
265 drawdown. Spicule archives can also be combined with diatom and sponge germanium-to-silicon  
266 ratios (Ge/Si) to take whole-ocean changes in silicon inventories into consideration (Ellwood et al.,  
267 2010). This approach is based on the observation that diatoms record Ge/Si of surface seawater,  
268 whereas sponge Ge/Si is highly fractionated and related to their ambient DSi concentrations  
269 (Ellwood et al., 2006). Any common change between Ge/Si in the two siliceous groups can be used  
270 to isolate whole-ocean changes in seawater Ge/Si. Whilst a change in this ratio could signify a  
271 change in either element, or both, modelling can be used to extract any signal of whole-ocean  
272 changes in silicon budgets from sponge  $\delta^{30}\text{Si}$  archives (Ellwood et al., 2010).

273 The giant spicules of *M. chuni* have also been used to construct palaeoceanographic records,  
274 using laser ablation to derive  $\delta^{30}\text{Si}$  profiles across latitudinal sections of individual spicules, which are  
275 thought to be able to live up to 18 ka (Jochum et al., 2017). The offset from the original calibration  
276 profile (Fig. 1) can be taken into consideration using a novel species-specific calibration (Jochum et  
277 al., 2017). However, whilst *M. chuni* represents a novel and independent proxy, there are still  
278 challenges in deriving independent age models with which to link the observed geochemical signals  
279 with climatic events.

280 Over longer, geological timescales, the influences of whole-ocean changes become more  
281 significant, and robust interpretation of sponge  $\delta^{30}\text{Si}$  archives requires modelling to assess potential  
282 influences of seawater DSi isotopic shifts. Cenozoic sponge  $\delta^{30}\text{Si}$  records have been constructed, and  
283 combined with isotopic evidence from other silicifiers to track changes in silicon cycling as far back  
284 as the Palaeogene (Egan et al., 2013; Fontorbe et al., 2016; Fontorbe et al., 2017). These records  
285 highlight that a “modern-like” marine silicon cycle was established early in the Cenozoic, with a  
286 proto-Southern Ocean silicon cycle characterised by upwelling of DSi-rich deep-waters and strong  
287 utilisation by diatoms (Egan et al., 2013), and an Atlantic-Pacific gradient in DSi concentrations  
288 (Fontorbe et al., 2017), from Eocene-Oligocene boundary. Isotopically heavy spicules and  
289 radiolarians from Atlantic sediments indicate low DSi concentrations in low-latitude waters well

290 before the Eocene diversification of diatoms (Fontorbe et al., 2016). This early drawdown of DSi has  
291 been used, in combination with molecular studies (Marron et al., 2016), as evidence that other  
292 pelagic silicifiers and early diatoms may have had more impact on the marine silicon cycle than  
293 previously thought (Conley et al., 2017).

### 294 **3. Sponge grounds in the North Atlantic: silicon isotopes at the population level**

#### 295 *3.1. Sponge grounds of the North Atlantic*

296 Sponge grounds, comprising dense aggregations or assemblages of sponges, are found  
297 throughout the North Atlantic. These environments are important for biogeochemical cycling,  
298 biodiversity, and natural products (Cathalot et al., 2015; Hogg et al., 2010; Kenchington et al., 2013;  
299 Maldonado et al., 2017), and are highly vulnerable to anthropogenic damage and oceanic change  
300 (Beazley et al., 2018; Howell et al., 2016). Given that these sponge grounds are well-characterised,  
301 they are also ideal testing grounds for population-level isotopic variation.

302 We have selected three different locations to test population level  $\delta^{30}\text{Si}$  variation (Fig. 3,  
303 Table 1):

- 304 i) Porcupine Seabight: *Pheronema carpenleri* (Order Amphidiscosida, Family  
305 Pheronematidae) monospecific ground from the Northeast Atlantic (Howell et al., 2016;  
306 Rice et al., 1990);
- 307 ii) Nova Scotia: *Vazella pourtalesi* or 'Russian Hat' sponge (Order Lyssacinosida, Family  
308 Rosselidae) monospecific ground, from Emerald Basin (2016) and Sambro Bank Closure  
309 (2017) of the Northwest Atlantic shelf (Beazley et al., 2018);
- 310 iii) Labrador Sea: *Geodia* spp. (Order Tetractinellida, Family Geodiidae) multi-specific  
311 assemblages from the Boreal-Arctic astrophorid grounds/"boreal ostur" of Orphan Knoll  
312 and shelf-environments of Southwest Greenland within the Labrador Sea (Beazley et al.,  
313 2013; Howell et al., 2016; Knudby et al., 2013; Murillo et al., 2012).

#### 314 *3.2. Conductivity, temperature, depth (CTD) profiles and water sampling*

##### 315 *3.2.1. Porcupine Seabight*

316 Water data for the Porcupine Seabight were obtained from the electronic World Ocean  
317 Circulation Experiment database eWOCE (<http://www.ewoce.org/>).

##### 318 *3.2.2. Nova Scotia*

319 During the expedition to the Emerald Basin in 2016, a continuous, full-depth profile of temperature,  
320 salinity, oxygen, and fluorescence, to within 10 m of bottom was made using an SBE 19plus CTD  
321 close to the site of sponge collection. A 10-L sampling bottle was closed to collect water for  
322 biological and chemical analyses 10 m off the seabed (Fig. A1). During the Sambro Bank expedition in  
323 2017, a continuous, full-depth profile of temperature and salinity was made using an SBE 25 CTD  
324 close to the site of sponge collection (Fig. A2). Nutrient data were obtained from archived data  
325 collected as part of the Atlantic Zone Monitoring Program (AZMP).

### 326 3.2.3. Labrador Sea and coastal Greenland

327 Samples were collected from Orphan Knoll and Southwest Greenland during RRS Discovery  
328 cruise DY081 in July/August 2017. All CTD casts (Fig. A3, A4) were undertaken during DY081 using a  
329 SBE 9plus underwater unit with an array of sensors, with 10L Niskin water samplers used to collect  
330 water for geochemical analysis (Hendry, 2017).

### 331 3.3. Sponge collection

332 *Pheronema carpenteri* (Hexactinellida) were sampled using the Irish national remotely  
333 operated vehicle (ROV), *Holland I*, from Porcupine Seabight (North East Atlantic) aboard the R/V  
334 Celtic Explorer, EUROFLEETS2 cruise CE15011 (Howell et al., 2015). The manipulator arm on the ROV  
335 was used to either grab sponges at the base via the anchor spicules, or to scoop sponges up using a  
336 metal mesh scoop. Sponges were then placed into bio-boxes mounted on the ROV.

337 *Vazella pourtalesi* (Hexactinellida) were collected using either a box corer or by ROV, *ROPOS*,  
338 from the Emerald Basin (North West Atlantic) aboard the R/V Hudson (cruise HUD16019) in July and  
339 August 2016 (Kenchington et al., 2016), and using *ROPOS* from the Sambro Bank on the CCGS  
340 Martha L. Black (cruise MLB2017001) in July 2017 (Beazley et al., 2017). Hexactinellid morphometrics  
341 were recorded when possible (body width and height).

342 *Geodia* sp. (Demosponge) were collected from Orphan Knoll (Labrador Sea) by the ROV, *Isis*,  
343 aboard the RRS Discovery in July 2017 (cruise DY081; Hendry et al., 2017). Sponges were collected  
344 either using the manipulator arms, or using a suction system.

345 In each case, upon recovery of the ROV to the surface, sponge samples were transferred to  
346 buckets and taken into a wet lab for processing. In the wet lab each sponge sample was labelled,  
347 measured and photographed. A sub-sample of each sponge was air-dried, before being placed in  
348 individual plastic bags or boxes for transportation.

### 349 3.4. Sample preparation and analysis

350 3.4.1. *Sponge analyses*

351 Small subsamples were cleaned chemically for organic matter by soaking at room  
352 temperature for 24 hours in 30% hydrogen peroxide (reagent grade H<sub>2</sub>O<sub>2</sub>) and then heating for three  
353 hours at 80°C in fresh 30% H<sub>2</sub>O<sub>2</sub>. The samples were then rinsed in 18 MΩ.cm Milli-Q, heated for  
354 three more hours at 80°C in fresh 30% H<sub>2</sub>O<sub>2</sub>, and rinsed again. Lastly, the samples were rinsed in  
355 concentrated nitric acid (in-house distilled HNO<sub>3</sub>) a total of two times, rinsed between each stage  
356 with Milli-Q water. Approximately 1 mg of cleaned spicules (Fig. 4) were then physically separated by  
357 hand from any lithogenic particles, weighed into clean Teflon, and dried down in concentrated HNO<sub>3</sub>  
358 (in-house distilled) at 120°C. The spicules were then dissolved over three days in 0.4M sodium  
359 hydroxide (Analar) at 100°C, before being acidified with 8N HNO<sub>3</sub> (in-house distilled), diluted with  
360 Milli-Q and purified using cation exchange resin (Bio-Rad AG50W X12, 200-400 mesh in H<sup>+</sup> form)  
361 following published protocols (Georg et al., 2006; Hendry and Robinson, 2012).

362 The purified solutions were spiked with a magnesium solution and analysed for <sup>28</sup>Si, <sup>29</sup>Si, and  
363 <sup>30</sup>Si using a Multi-Collector Inductively Coupled Plasma Mass Spectrometer in medium resolution  
364 mode. Sample signals were blank-corrected offline, and mass-bias corrected using magnesium  
365 isotope ratios (<sup>24</sup>Mg, <sup>25</sup>Mg, and <sup>26</sup>Mg) before being normalised to NBS28 (RM8546) following  
366 published methods to calculate both δ<sup>29</sup>Si and δ<sup>30</sup>Si values (Hendry et al., 2015). A three-isotope plot  
367 shows that δ<sup>29</sup>Si and δ<sup>30</sup>Si values for samples and standards fall on a mass-dependent linear curve,  
368 with a gradient of 0.51 (Fig. A5). Long-term reproducibility was assessed by repeat measurements of  
369 reference standards Diatomite and LMG08, yielding δ<sup>30</sup>Si of +1.24 ± 0.03‰ and -3.47 ± 0.05‰  
370 respectively (2SE, n = 14 and 19 respectively), which fall within error of published values (Hendry et  
371 al., 2011; Reynolds et al., 2007). Internal errors, fully propagated from blocks of 20 measurements  
372 including blank and mass-bias corrections, were typically 0.05‰ for δ<sup>29</sup>Si and 0.10‰ for δ<sup>30</sup>Si.  
373 Repeat measurements of δ<sup>29</sup>Si and δ<sup>30</sup>Si (e.g. *Vazella* 5-022 from MLB2017001) agreed within ±0.04  
374 and ±0.03‰ respectively.

375 3.4.2. *Seawater DSi analyses*

376 Samples for inorganic nutrients were all analysed by comparable methods either at the  
377 Bedford Institute of Oceanography (BIO) or in the Plymouth Marine Laboratory (PML) using the  
378 latest GO-SHIP protocols (Hydes et al., 2010). The analysis was carried out using a SEAL analytical  
379 AAll segmented flow colorimetric auto-analyser using classical analytical techniques for nitrate,  
380 nitrite, DSi and phosphate, as described in Woodward and Rees (2001). Seawater nutrient reference  
381 materials (KANSO Ltd. Japan), or cross-checked in-house standards, were analysed to check analyser  
382 performance and to guarantee the quality control of the final reported data. The typical

383 uncertainties of the analytical results were between 2-3%, and the limits of detection were 0.02  $\mu\text{M}$   
384 for nitrate and phosphate, 0.01  $\mu\text{M}$  for nitrite, and DSi did not ever approach the limits of detection.

385 Water DSi silicon isotope ( $\delta^{30}\text{DSi}$ ) analysis methods are fully described in Cassarino et al.,  
386 2018. Briefly, silicon was pre-concentrated twice by the additional of sodium hydroxide (1.2% v/v 1M  
387 NaOH, followed by 1% v/v 1M NaOH 24 hours later) to precipitate magnesium hydroxide. The  
388 precipitate is rinsed with dilute sodium hydroxide (0.001M NaOH) before redissolution in 8M  
389 distilled  $\text{HNO}_3$ , dilution in 18 M $\Omega$ .cm Milli-Q water, and chemical purification using cation exchange  
390 resin as outlined above. Mass spectrometric analysis was carried out as for the sponge samples, with  
391 the addition of 0.05M HCl and 0.003M  $\text{H}_2\text{SO}_4$  to standards and samples prior to analysis to account  
392 for any potential matrix effects (Hughes et al., 2011). The ALOHA “300” and “1000” seawater  
393 standards were measured alongside the seawater samples to assess analytical accuracy and  
394 precision, and yielded values within error of published data ( $\delta^{30}\text{Si} = +1.10 \pm 0.15 \text{‰}$  and  $+1.43 \pm 0.19$   
395  $\text{‰}$  (2SD internal precision), respectively) (Cassarino et al., 2018; Grasse et al., 2017).

#### 396 3.4.3. *Sponge identification*

397 Sponges from the genus *Geodia* collected during DY081 were identified to species level after  
398 collection. To isolate the spicules, sponge tissue was digested in bleach (15% Sodium Hypochlorite).  
399 Spicules were then washed twice with water and once in 95% ethanol, allowing the spicules to settle  
400 out of the washing solution for ~45 minutes between each change. A few drops of the final ethanol  
401 solution were placed on a slide and then this was placed on a heat plate, evaporating the alcohol  
402 and leaving the spicules behind. The spicules were mounted in Canada balsam covered with a glass  
403 coverslip. A thick tissue section ( $\approx 0.2\text{mm}$ ) was cut using a scalpel and also mounted using Canada  
404 balsam. Spicule measurements were made using an Olympus BX43 microscope, with thirty spicules  
405 measured per spicule type. Digital photos were taken using the combination of the Olympus BX43  
406 microscope with a SC50 camera and are available upon request.

#### 407 3.5. *Sponge ground results: insight into population variance*

408 The new  $\delta^{30}\text{Si}$  sponge and seawater  $\delta^{30}\text{DSi}$  data are shown in Table A1. The  $\delta^{30}\text{Si}$  values for  
409 the hexactinellid specimens range from  $-1.24$  to  $-2.49 \text{‰}$ ; the *Geodia* specimens ranged from  $-1.08$   
410 to  $-2.37 \text{‰}$ .

#### 411 3.5.1. *Monospecific aggregations*

412 The *P. carpenteri* aggregation specimens show a mean  $\delta^{30}\text{Si}$  value of  $-2.07\text{‰}$  and a variance  $0.04\text{‰}$   
413 ( $n = 29$ ; Fig. 5). There is no significant correlation between  $\delta^{30}\text{Si}$  and calculated body volume

414 (correlation coefficient = 0.238;  $p > 0.05$ ; Fig. A6), assuming an ellipsoid form. There is also no  
415 significant correlation between temperature or salinity and spicule  $\delta^{30}\text{Si}$  ( $p > 0.05$ ).

416 Compared to the *P. carpenteri* samples, the specimens from the *V. pourtalesi* aggregations show  
417 higher mean  $\delta^{30}\text{Si}$  values of  $-1.59\text{‰}$  (variance of  $0.03\text{‰}$ ) and  $-1.65\text{‰}$  (variance of  $0.02\text{‰}$ ) for the  
418 Emerald Basin and Sambro Basin specimens respectively. There is no significant difference between  
419 either the means (note the low power of this statistical test) or the medians of the two aggregations  
420 of *V. pourtalesi* (one-tailed t-test,  $p = 0.198$ , power = 0.210; rank sum test,  $p = 0.603$ ). The overall  
421 variance of the *V. pourtalesi* specimens was  $0.02\text{‰}$  ( $n = 24$ ). There is a significant correlation with  
422 body volume (correlation coefficient = 0.758;  $p < 0.01$ ,  $n = 12$ ; Fig. A6), assuming a cylindrical body  
423 form. Note not all of the specimens have morphometric data available, so the statistical analysis in  
424 this case was carried out on a small subset of specimens, and the correlation is largely driven by one  
425 outlier (Fig. A6). Both hexactinellid populations passed a Shapiro-Wilk normality test (Table 2; Fig.  
426 5B).

427 Silicon isotope fractionation was calculated using Equation 2 (Table A1), using the measured  
428 isotopic composition of the sponge spicules and seawater samples (Fig. 7A). The closest located  
429 seawater sample was used for each specimen (or mean values if specimen was located between two  
430 Niskin sampling events). Seawater samples were not available for the *P. carpenteri* samples, so a  
431  $\delta^{30}\text{DSi}$  value of  $+1.5\text{‰}$  was chosen for the ambient composition based on published water column  
432 profiles from the Atlantic Ocean (de Souza et al., 2012). The mean  $\Delta^{30}\text{Si}$  values for the *V. pourtalesi*  
433 and *P. carpenteri* groups were calculated to be  $-3.21\text{‰}$  and  $-3.57\text{‰}$  respectively. The two groups  
434 show equal variance in their population fractionation factors (Brown-Forsythe test passed,  $p = 0.438$ ;  
435 both groups have a variance of  $\sim 0.04\text{‰}$ ) but have significantly different means (two-tailed t-test,  $p <$   
436  $0.001$ , power 0.998 for  $\alpha = 0.05$ ) with the greater mean fractionation factor observed for the *P.*  
437 *carpenteri* population (one-tailed t-test,  $p < 0.001$ , power 0.999 for  $\alpha = 0.05$ ).

### 438 3.5.2. Multi-specific assemblages

439 The mean  $\delta^{30}\text{Si}$  composition for all the *Geodia* specimens was  $-1.64\text{‰}$ , with a variance of  
440  $0.09\text{‰}$  ( $n = 20$ ). All *Geodia* specimens, taken as one population, passed a Shapiro-Wilk normality  
441 test (Table 2). Although variability between individual is greater for the astrophorids compared to  
442 the hexactinellid monospecific aggregations, this group represents a number of different species  
443 within the same genus. Dividing the group into species (Fig. 6) shows that some of the variability  
444 could be a result of genetic differences. For most of the astrophorids, the variance is more aligned  
445 with the hexactinellid populations when separated into species: *G. atlantica*, *G. hentscheli*, *G.*  
446 *macandrewii*, and *G. nodostrella* all have closely aligned isotopic compositions despite not having

447 close phylogenetic relationships (Cardenas et al., 2013). However, *G. hentscheli*, *G. parva* and *G.*  
448 *phlegraei* are more variable (*G. parva* and *G. phlegraei* groupings both have lighter isotopic  
449 specimens, and are closely allied on the molecular phylogeny of the genus). *G. barretti* is significantly  
450 heavier than the majority of the other specimens, although the specimen was the only one located  
451 in the northern-most collection site off west Greenland.

452 Initial tests indicated that different spicules from an astrophorid from the Southern Ocean  
453 have the same  $\delta^{30}\text{Si}$  composition within uncertainty ( $\delta^{30}\text{Si}$  of  $-2.87 \pm 0.21\text{‰}$  and  $-2.96 \pm 0.23\text{‰}$  for  
454 subsamples of a sterraster-dominated dermal layer and a parenchymal layer respectively) (Hendry et  
455 al., 2010). The results here also support a relatively uniform isotopic composition between  
456 individuals, at least for most *Geodia* species.

457 Again, the fractionation of silicon isotopes was calculated using Equation 2 (Table A1), using  
458 the measured sponge and seawater  $\delta^{30}\text{DSi}$  values (Fig. 6). The different *Geodia* species show some  
459 variation in  $\Delta^{30}\text{Si}$ , with mean of  $-2.94\text{‰}$  with a variance of  $0.08\text{‰}$ . However, taking the  
460 environmental differences in ambient  $\delta^{30}\text{DSi}$  between sampling locations, through the calculation of  
461 fractionation factors, can only eliminate some of the variation between species. For example, the *G.*  
462 *barretti* specimen from the northern sampling site was collected from somewhat isotopically heavier  
463 waters than the other specimens (Table A1). The remaining variability must be due to other  
464 environmental differences, in addition to physiological differences between the specimens.

#### 465 **4. Discussion**

##### 466 *4.1. New calibration between sponge silicon isotopes and ambient dissolved silicon concentrations*

467 A compilation of all published data reveals the extreme variation in the fractionation of  
468 stable silicon isotopes during spicule growth (Fig. 7A and B). There are some significant outliers from  
469 the original calibration curve (Fig. 1), which comprise sponges with atypical biosilicification processes  
470 including heavily fused hexactinellids (Cassarino et al., 2018); carnivorous sponges (Hendry et al.,  
471 2015), and the giant spicules of *M. chuni* (Jochum, 2017). If the atypical silicifiers are removed from  
472 the calibration (Fig. 7B), the remaining sponge specimens (largely comprising filter-feeding sponges  
473 that produce loose spicules) still show a significant correlation between isotopic fractionation and  
474 DSi (Equ. 6):

$$475 \quad \Delta^{30}\text{Si} = -4.6(0.1) + \frac{27.6(1.9)}{(7.4(1.9) \times \text{DSi})} \quad (6)$$

476 (Adjusted  $R^2 = 0.46$ ,  $p < 0.001$ ).

##### 477 *4.2. Potential biological driving mechanisms behind silicon isotopic fractionation in sponges*



478 4.2.1. Differences within species: isotopic variations at the population-level

479 Our new data from the North Atlantic sponge grounds are consistent with the original non-  
480 linear DSi- $\delta^{30}\text{Si}$  relationship found previously, especially in comparison to sponges with atypical  
481 silicification mechanisms that form clear outliers. However, there is still scatter in the empirical  
482 relationship, which can be explored with the results from the monospecific assemblages, and can be  
483 used to largely exclude genetic differences as a driving factor in isotopic fractionation. Northwest  
484 Atlantic *P. carpenteri* aggregation is isotopically light for the given ambient DSi concentrations and so  
485 plots below the main calibration line (Fig. 7A). Given that both the *Pheronema* and *Vazella* genera  
486 belong to orders (Amphidiscosida and Lyssacinosa respectively) that are not characterised by  
487 fused, dictyonal spicules (Tabachnick et al., 2017), and the specimens analysed here comprised  
488 either loose spicules or spicules fused lightly at nodes (Fig. 4), secondary hypersilicification is not a  
489 possible mechanism for driving silica isotopic compositions towards lighter values (Cassarino et al.,  
490 2018).

491 One possible reason behind this variation within a monospecific aggregation is that there are  
492 variations in the growth rate (linked with food supply, or health) between the individuals and, so,  
493 differences in the specific values of the uptake kinetics parameters and a variation in isotopic  
494 fractionation (Equation 4). However, a lack of relationship between body size and  $\delta^{30}\text{Si}$  in the *P.*  
495 *carpenteri* samples, and only a statistically weak relationship between the parameters in the *V.*  
496 *pourtalesi* specimens, argues against a growth rate effect in this case (Fig. A6).

497 An alternative explanation as to why these sponge ground specimens have more negative  
498  $\delta^{30}\text{Si}$  values than expected – or predicted by the biological model shown in Equation 4 – is that the  
499 sponges obtain DSi for biomineralising partially from recycled sponge silica, which is available as a  
500 result of the close proximity of the densely aggregated individuals. We have constructed a simple  
501 model to test this hypothesis, varying the percentage of DSi taken up by the sponge originating from  
502 recycled spicules rather than bottom waters, and using isotopic mass balance to calculate the  
503 subsequent impact on spicule  $\delta^{30}\text{Si}$  values (Table A2). Our model implies that the *P. carpenteri*  
504 sponges could be biomineralising from a solution comprising 40-60% recycled silica, with a lower  
505 degree of recycling (<40%) occurring in the *V. pourtalesi* aggregations (Fig. 8). A high degree of  
506 recycling in *P. carpenteri* sponge grounds is consistent with the observation of thick spicule mats,  
507 with aggregations of living and dead sponges commonly found together (Barthel et al., 1996; Bett  
508 and Rice, 1992). Variations in the extent of spicule recycling could be responsible for the isotopic  
509 fractionation scatter observed in population level in dense sponge grounds.

510 4.2.2. Differences between species in a mixed assemblage

511 The relationship between DSi and  $\delta^{30}\text{Si}$  for filter-feeding, non-hypersilicified sponges that are  
512 found in mixed assemblages still shows a degree of scatter, even when atypical silicification processes  
513 are accounted for and removed from the calibration. Despite growing under almost identical  
514 environmental conditions, mixed assemblages of sponges from a particular area exhibit a wide range  
515 in  $\delta^{30}\text{Si}$ , a larger range than for monospecific aggregations (e.g. Cassarino et al., 2018). Part of this  
516 variability could be a result of silica recycling (Fig. 8), although this mechanism can only drive the  
517 system towards lighter isotopic compositions.

518 Instead, the variation could be a result of a combination of genetic variation and physiology.  
519 Our new *Geodia* results show that, generally, a good proportion of the scatter in isotopic composition  
520 can be accounted for by species-specific variations in fractionation (Fig. 6). The half saturation  
521 constant and maximum incorporation rate for polymerisation varies between species, and potentially  
522 even within species as a result of differences in food availability or health (López-Acosta et al., 2018;  
523 López-Acosta et al., 2016). We have explored the impact on silicon isotopic fractionation of such  
524 differences in uptake parameters using the simple biological model in Equation 4 (Cassarino et al.,  
525 2018), and found that a large degree of variability can be explained by differences in kinetics between  
526 species (Fig. 9A and B).

527 The majority of the analyses of sponge  $\delta^{30}\text{Si}$  variation to date have been carried out in deep  
528 water sponges, where environmental variability is relatively low. Shallow water sponges, especially  
529 those in the littoral or sublittoral zone, are likely to be subject to extreme environmental changes on  
530 a range of timescales (diurnal, seasonal, annual), and so could be expected to show a larger degree  
531 of isotopic variability driven by ambient conditions. Any differences in silicon isotope fractionation  
532 between species may also be expected to be amplified, depending on factors such as growing season  
533 and growth rate. Quantifying the variability in sponge  $\Delta^{30}\text{Si}$  in these ecosystems may be particularly  
534 challenging, given the requirement to characterise changes in sponge growth and ambient  
535 conditions (e.g. seawater  $\delta^{30}\text{Si}$  variations) over a range of spatial scales.

#### 536 4.2.3. Differences between higher taxonomic rankings

537 There are fundamental differences in biosilicification between hexactinellids and  
538 demosponges, which might be expected to manifest in contrasting isotopic fractionation (Cassarino  
539 et al., 2018). Demosponges fuse the concentric silica layers that form around the axial canal,  
540 whereas they remain distinct layers in hexactinellids (Aizenberg et al., 2005; Müller et al., 2009;  
541 Wang et al., 2011). Furthermore, the organic composition of the silicification proteins in the two  
542 groups differ: hexactinellids have higher molecular weight proteins than those isolated from

543 demosponges (Weaver et al., 2003). The interaction between the polymerising silica and these  
544 different organic molecules could result in divergent isotopic fractionation (Cassarino et al., 2018).

545         Despite these clear differences in silicification mechanism, there is no clear answer at this  
546 stage as to what extent are there differences in isotopic behaviour between hexactinellids and  
547 demosponges. A qualitative analysis of the whole dataset (excluding 'lithistids', *Asbestopluma* sp.  
548 and *M. chuni*) suggests that the DSi- $\delta^{30}\text{Si}$  relationships are different between hexactinellids and  
549 demosponges (Fig. 7B). However, this whole dataset also illustrates that the two groups are  
550 separated in DSi "space", with demosponges able to grow under lower DSi concentrations than  
551 hexactinellids, such that the difference in isotopic fractionation could be a consequence of distinct  
552 habitat preferences. To account for any DSi influence, one approach is to normalise the  $\delta^{30}\text{Si}$  data, by  
553 calculating a residual for each datapoint relative to the best-fit hyperbolic regression. This method  
554 has previously revealed a lack of systematic differences between demosponges and hexactinellids  
555 (Cassarino et al., 2018). Alternatively, it is possible to statistically assess the differences in  
556 fractionation between the two groups, but only within the DSi range under which both groups are  
557 present (10 to 100  $\mu\text{M}$  DSi). Under these constraints, there is no significant difference between the  
558 mean  $\delta^{30}\text{Si}$ , or DSi- $\delta^{30}\text{Si}$  intercepts, of hexactinellids and demosponges once DSi differences are taken  
559 into account (ANCOVA,  $F=0.045$ ,  $p=0.833$ ; Fig. A7). This suggests that, despite some fundamental  
560 differences in silicification behaviour between hexactinellids and demosponges, there is no  
561 significant impact on stable silicon isotopic fractionation, at least for filter-feeding sponges without  
562 dictyonal framework skeletons. This suggests that using a mixture of hexactinellid and demosponge  
563 spicules, which are often challenging to distinguish within sediments, to measure  $\delta^{30}\text{Si}$  variations in  
564 marine cores should produce robust and interpretable archives of past oceanic change provided  
565 spicules with clearly different morphology (e.g. giant spicules, desmas, heavily fused spicules) are  
566 avoided.

## 567 **Conclusion and outlook**

568         Diatom productivity, and oceanic export production, relies on the upwelling of deep-waters  
569 for a supply of dissolved silicon. If we are to quantify future changes in marine carbon cycling, we  
570 need to be able to predict future changes in diatom growth and, so, changes in the supply of DSi and  
571 other nutrients to the surface through physical and chemical processes. One of the best analogues  
572 we have for how the oceans may respond in the future is the geological record: understanding how  
573 diatoms have responded to past climate events can inform greatly on potential upcoming change.  
574 However, because of the reliance of diatoms on deep-waters, we need an archive of bottom water  
575 DSi concentrations if we are to tease apart the relative impacts of changes in physical upwelling as

576 opposed to water mass variability and remineralisation. To date, sponge spicules are the only  
577 available archive of deep-water silica, especially spicule  $\delta^{30}\text{Si}$  values, which have been shown by a  
578 number of studies to have a statistically significant relationship with ambient DSi. There are  
579 important caveats, as common to all novel geochemical proxies, which must be taken into  
580 consideration for robust interpretation of downcore archives. Atypical biomineralisation processes  
581 (hypersilicification, the growth of giant basal spicules, and silica production in carnivorous sponges)  
582 have an impact on silicon isotopic compositions. However, these spicule types can largely be  
583 disregarded for palaeoceanographic studies as they are morphologically distinct.

584         There are further, more complex challenges surrounding unknown variations in ambient DSi  
585 and seawater  $\delta^{30}\text{Si}$ , either on the small scale in the immediate surroundings of the growing sponge  
586 (e.g. silica recycling within dense sponge aggregations or within individuals as shown in this study) or  
587 secular changes on large spatial scales and over long periods of time that exceed the residence time  
588 of silicon in seawater. However, multi-proxy approaches and modelling efforts will help to  
589 understand these challenging caveats. Robust dating methods and age models are also required,  
590 which have in spicule  $\delta^{30}\text{Si}$  studies – to date – relied entirely on the dating of surrounding material  
591 (e.g. by radiocarbon dating or foraminiferal isotope stratigraphy) and do not take into consideration  
592 the potential age-differential between sedimentary components. Improvements in radiocarbon  
593 dating of sponge organic matter may provide a better handle on how long sponges live, and the  
594 absolute ages of spicules within sediments (Fallon et al., 2010). Lastly, and perhaps most  
595 fundamentally, we do not have a full understanding of the biochemical pathways that lead to  $\delta^{30}\text{Si}$   
596 variations between sponges. Our new results show that there is scatter in the spicule DSi-  $\delta^{30}\text{Si}$   
597 relationship, even between specimens from monospecific aggregations that have grown under the  
598 same environmental conditions, indicating that there is more to understand about how the health of  
599 individuals can impact biological fractionation of silicon isotopes. A greater understanding of  
600 biomineralisation pathways, and how they differ between sponge groups, will aid our mechanistic  
601 understanding of how sponges fractionate silicon isotopes.

## 602 **Acknowledgements**

603         This research was funded by European Research Council project ICY-LAB (ERC-2015-STG  
604 grant agreement number 678371), and EU Horizon 2020 project SponGES (H2020-BG-2015-2 grant  
605 agreement number 679849). K. L. Howell is funded by the EU Seventh Framework Programme  
606 EUROFLEETS2 (FP7/2007-2013 grant agreement number 312762). Thanks to Christopher D. Coath  
607 for assistance with mass spectrometry, and Paco Cárdenas for advice on *Geodia* identification. Many  
608 thanks to Ellen Kenchington and Lindsay Beazley for collection of *Vazella pourtalesi* sponges and co-

609 located seawater samples, and for supplying details of their previous benthic surveys on Orphan  
610 Knoll which assisted with cruise planning. Canadian funding was received from the International  
611 Governance Strategy (IGS) fund of the Department of Fisheries and Oceans Canada Project “Marine  
612 Biological Diversity Beyond Areas of National Jurisdiction (BBNJ): 3-Tiers of Diversity (Genes-Species-  
613 Communities)” to E. K. We also thank Joana Xavier, Manuel Maldonado and Hans Tore Rapp for  
614 support through the SponGES project. Many thanks to two anonymous reviewers for their  
615 constructive comments.

616 Data availability: An electronic copy of the new data from this study is available at  
617 <https://doi.pangaea.de/10.xxxx/PANGAEA.xxxxx>

| Location           | Species                     | n  | Depth (m)   | Temperature (°C) | Salinity    | Oxygen (μmol/L)        | DSi (μM)                 | NO <sub>3</sub> (μM)     |
|--------------------|-----------------------------|----|-------------|------------------|-------------|------------------------|--------------------------|--------------------------|
| Porcupine Seabight | <i>Pheronema carpenteri</i> | 29 | 1204 - 1407 | 6.5 - 7.1        | 35.2 - 35.4 | 245 - 255 <sup>a</sup> | 11.3 - 11.6 <sup>a</sup> | 18.1 - 18.4 <sup>a</sup> |
| Emerald Basin      | <i>Vazella pourtalesi</i>   | 8  | 184 - 206   | 11.0 - 11.1      | 35.2        | 121 - 126              | 16.9 ± 0.5               | 18.9 ± 0.2               |
| Sambro Basin       | <i>Vazella pourtalesi</i>   | 16 | 154 - 161   | ~10              | ~34.7       | 200 - 220 <sup>a</sup> | 12.0 ± 0.4               | 17.5 ± 2.6               |
| Orphan Knoll       | <i>Geodia</i>               | 13 | 1763 - 3463 | 2.1 - 3.4        | 34.9        | 265 - 272              | 6 - 15                   |                          |
| Coastal Greenland  | <i>Geodia</i>               | 2  | 846 - 1146  | 3.9 - 4.5        | 34.9        | 280 - 290              | 9 - 10                   |                          |

620

|     | <b>Species</b>              | <b>n</b> | <b>W-Statistic</b> | <b>P value</b> | <b>Passed?</b> |
|-----|-----------------------------|----------|--------------------|----------------|----------------|
|     | <i>Pheronema carpenteri</i> | 29       | 0.975              | 0.706          | yes            |
|     | <i>Vazella pourtalesi</i>   | 25       | 0.975              | 0.796          | yes            |
| i)  | <i>Emerald Bank</i>         | 17       | 0.851              | 0.097          | yes            |
| ii) | <i>Sambro Bank</i>          | 8        | 0.956              | 0.592          | yes            |
|     | <i>Geodia sp.</i>           | 20       | 0.932              | 0.170          | yes            |

621

622 **Figure captions**

623 Figure 1: Original calibration studies figure (Hendry et al., 2010, Wille et al., 2010; Hendry &  
624 Robinson, 2012) of apparent sponge silicon isotope fractionation (denoted by  $\Delta^{30}\text{Si}$ , Equation 2) and  
625 ambient dissolved silicon concentrations (DSi). Symbols highlight the different collection expeditions.  
626 Error bars show ranges for DSi in  $\mu\text{M}$ , and 2SD for isotopic fractionation.

627 Figure 2: Scanning Electron Microscope images of sponge spicules. A) basal spicules from  
628 *Asbestopluma* sp. (Hendry et al., 2015) where des = desmas and ani = anisostrongyes; B) cross-  
629 section through spicule of *Monorhaphis chuni* (Jochum et al., 2017); C) fused framework of  
630 hexactinellid from the tropical Atlantic (Cassarino et al., 2018).

631 Figure 3: Location of collection sites of the new sponge specimens, from North Atlantic sponge  
632 grounds. Black symbols show hexactinellids, yellow symbols show demosponges. Squares show  
633 *Vazella pourtalesi* samples from Emerald Basin (solid) and Sambro Basin (hollow); triangles show  
634 *Pheronema carpenteri* samples from Porcupine Seabight; stars show *Geodia* (demosponge)  
635 specimens from boreal sponge grounds.

636 Figure 4: Scanning Electron Microscope images of *Vazella*, *Pheronema* and *Geodia* specimens, after  
637 chemical cleaning and before dissolution. Scale bar shows 100  $\mu\text{m}$ .

638 Figure 5: Silicon isotopic composition ( $\delta^{30}\text{Si}$ ) of sponge-ground forming hexactinellids: A) all  
639 datapoints and B) all *Vazella* and *Pheronema* data plotted as histograms. Scale bars show  
640 uncertainties based on repeat measurements of sponge standard LMG08 ( $\pm 2\text{SD}$ ).

641 Figure 6: Silicon isotopic composition ( $\delta^{30}\text{Si}$ ) of *Geodia* specimens (black circles). Scale bars show  
642 uncertainties based on repeat measurements of sponge standard LMG08 ( $\pm 2\text{SD}$ ). Grey circles show  
643 silicon isotopic fractionation ( $\Delta^{30}\text{Si}$ , see Equation 2).

644 Figure 7: A) Compilation of all Si isotopic fractionation data ( $\Delta^{30}\text{Si}$ , see Equation 2) for all available  
645 sponge spicule studies. Scale bars show fully propagated errors ( $\pm 2\text{SD}$ ). Symbols show different  
646 sponge types, where FF = filter-feeding (non-carnivorous) sponges excluding heavily fused  
647 hexactinellids and *M. chuni*. (NB: "lithistids" have been removed from the Wille et al., 2010 dataset).  
648 B) spicule Si isotope data comparing hexactinellids and demosponges, excluding carnivorous, heavily  
649 fused sponges and *M. chuni*.

650 Figure 8: Sponge ground modelling results. Large circles show new data from sponge-ground forming  
651 hexactinellids; small grey circles show published data, where FF = filter-feeding (non-carnivorous)  
652 sponges excluding heavily fused hexactinellids and *M. chuni*. For model details, see main text.



653 Figure 9: Uptake of silicon by sponges modelled using Michaelis-Menten kinetics. For model details,  
654 see main text. A) DSi consumption and B) Si isotopic fractionation (Cassarino et al., 2018). Silicon  
655 uptake data from (López-Acosta et al., 2018; López-Acosta et al., 2016; Maldonado et al., 2011;  
656 Reincke and Barthel, 1997).

657 **Table captions**

658 Table 1: Specimen sample table, including environmental parameters. <sup>a</sup> From GLODAP dataset.

659 Table 2: Shapriro-Wilk normality test results for specimens from the three sponge grounds.

660

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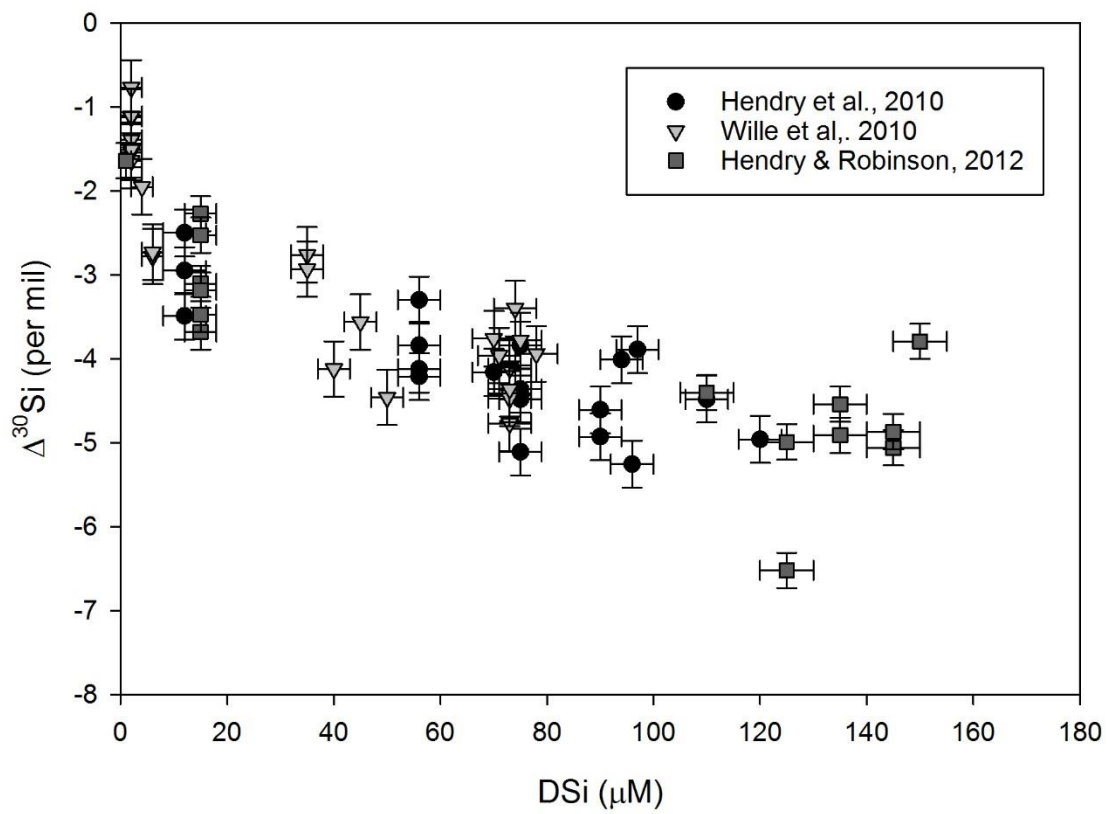
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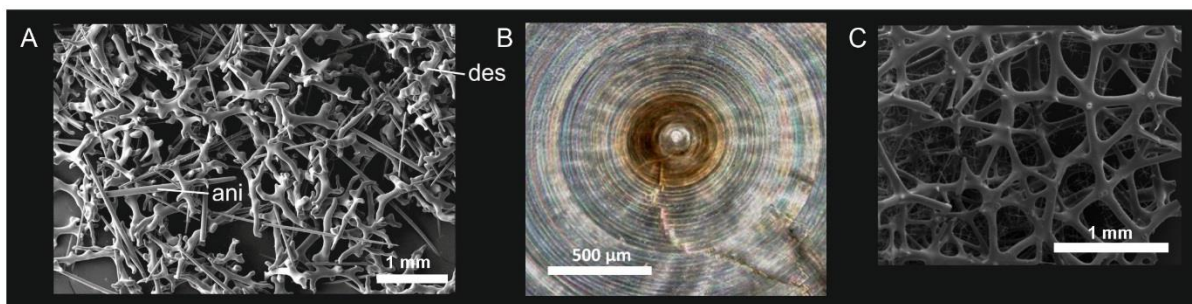
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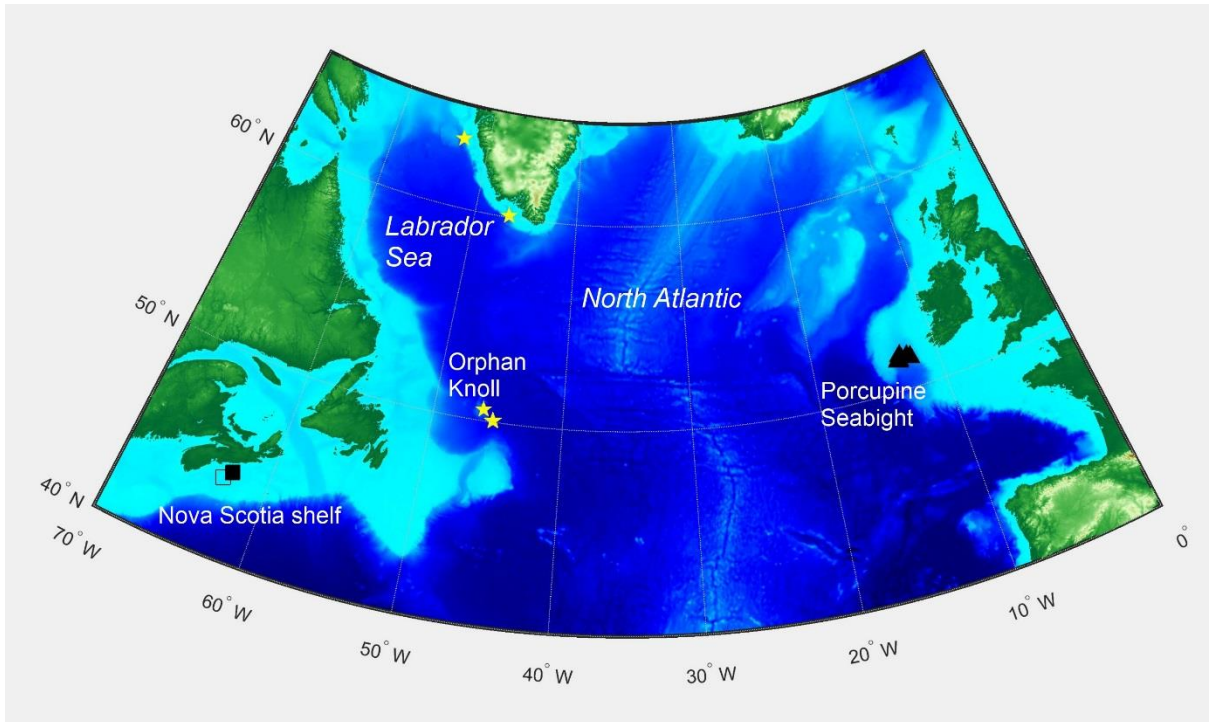
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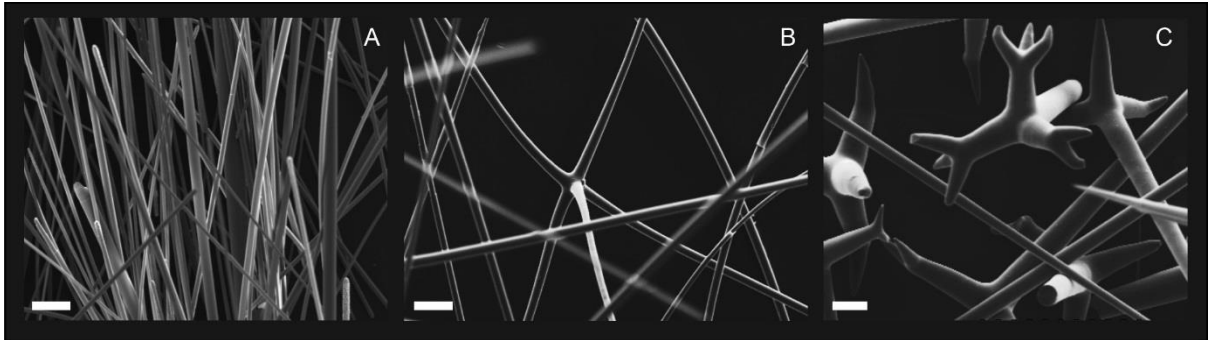
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