

# 1 **Deep ocean nutrients during the Last Glacial Maximum** 2 **deduced from sponge silicon isotopic compositions**

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## 8 **Abstract**

9 **The relative importance of biological and physical processes within the Southern**  
10 **Ocean for the storage of carbon and atmospheric pCO<sub>2</sub> on glacial-interglacial**  
11 **timescales remains uncertain. Understanding the impact of surface biological**  
12 **production on carbon export in the past relies on the reconstruction of the nutrient**  
13 **supply from upwelling deep-waters. In particular, the upwelling of silicic acid**  
14 **(Si(OH)<sub>4</sub>) is tightly coupled to carbon export in the Southern Ocean via diatom**  
15 **productivity. Here, we address how changes in deep-water Si(OH)<sub>4</sub> concentrations**  
16 **can be reconstructed using the silicon isotopic composition of deep-sea sponges. We**  
17 **report  $\delta^{30}\text{Si}$  of modern deep-sea sponge spicules and show that they reflect seawater**  
18 **Si(OH)<sub>4</sub> concentration. The fractionation factor of sponge  $\delta^{30}\text{Si}$  compared to seawater**  
19  **$\delta^{30}\text{Si}$  shows a positive relationship with Si(OH)<sub>4</sub>, which may be a growth rate effect.**  
20 **Application of this proxy in two down-core records from the Scotia Sea reveals that**  
21 **Si(OH)<sub>4</sub> concentrations in the deep Southern Ocean during the Last Glacial**  
22 **Maximum (LGM) were no different than today. Our result does not support a**  
23 **coupling of carbon and nutrient build up in an isolated deep-ocean reservoir during**

24 **the LGM. Our data, combined with records of stable isotopes from diatoms, are only**  
25 **consistent with enhanced LGM Southern Ocean nutrient utilization if there was also**  
26 **a concurrent reduction in diatom silicification or a shift from siliceous to organic-**  
27 **walled phytoplankton.**

28

29       Keywords: Porifera, spicule, silicic acid, deep-water, silicon cycle, glacial

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## 31           **1. Introduction**

32           Debate still surrounds the relative importance of physical and biological mechanisms  
33 behind glacial-interglacial variations in atmospheric carbon dioxide (pCO<sub>2</sub>; reviewed by  
34 Sigman and Boyle, 2000). The Southern Ocean has been implicated in the regulation of  
35 greenhouse gases through both types of mechanism. Firstly, a physical reduction in the  
36 ventilation of deep waters due to greater glacial sea-ice cover and ocean stratification,  
37 enhanced in a cooler ocean, would result in less outgassing of CO<sub>2</sub> to the atmosphere (e.g.  
38 de Boer et al., 2007). Secondly, an increase in biological export, accompanied by  
39 enhanced burial of carbon, would also reduce atmospheric pCO<sub>2</sub> during glacials (e.g.  
40 Kohfeld et al., 2005). A “biogeochemical divide” has been proposed, whereby biological  
41 export in the Antarctic Zone of the Southern Ocean regulates CO<sub>2</sub> directly, whereas export  
42 in the Subantarctic Zone controls global preformed nutrient supply, such that different  
43 regions around Antarctica may drive or respond to climate change by different mechanisms  
44 (Marinov et al., 2006). An understanding of Southern Ocean nutrients is clearly required  
45 to distinguish the physical and biological mechanisms that impact pCO<sub>2</sub> over glacial-  
46 interglacial timescales.

47           The concentration of silicic acid, [Si(OH)<sub>4</sub>], in deep-waters is governed by tectonics  
48 and silicate weathering on long timescales (>10<sup>4</sup> years) and by ocean productivity and  
49 ocean circulation on glacial-interglacial timescales (10<sup>3</sup>-10<sup>4</sup> years; Ragueneau et al., 2000;  
50 Falkowski et al., 2004). As such the Si cycle is a synergistic driver of, and respondent to,  
51 the carbon (C) cycle and global climatic change. In the modern surface ocean, biological  
52 precipitation of amorphous silica (opal) by diatoms is the dominant process that removes

53  $\text{Si(OH)}_4$  from seawater, efficiently transporting silica and organic C to the seafloor. The  
54 partitioning of C and Si between the surface and deep-ocean is controlled by the export and  
55 remineralization of this biological material relative to vertical mixing rates (Toggweiler et  
56 al., 1999; Ragueneau et al., 2000).

57 Diatom blooms rely on upwelling sources of  $\text{Si(OH)}_4$  because efficient utilization  
58 strips almost all of the Si from surface waters (Ragueneau et al., 2000). The nutrient  
59 composition of upwelling waters, in particular the ratio of Si to other major nutrients, plays  
60 a strong role in the population structure of phytoplankton growing in surface waters and  
61 the biological pumping of C to deep-water (Yool and Tyrell, 2003; Falkowski et al., 2004).  
62 Furthermore, reduced vertical mixing, or enhanced stratification, results in an increase in  
63 deep-water C, and a corresponding reduction in atmospheric  $\text{pCO}_2$ . (Toggweiler, 1999).  
64 Quantifying changes in the  $\text{Si(OH)}_4$  content of deep-water is an important step towards  
65 understanding the link between the sequestration of C, Si and other nutrients over glacial  
66 cycles (Brzezinski et al., 2002; Matsumoto et al., 2002). The Southern Ocean is a key  
67 location for studying paleo- $\text{Si(OH)}_4$  because of the regional and global importance of Si-  
68 based productivity and its potential sensitivity to well documented proximal climatic  
69 changes (Anderson et al., 2002).

70 The silicon isotopic composition ( $\delta^{30}\text{Si}$ ) of biogenic opal provides a direct method  
71 for quantifying seawater  $\text{Si(OH)}_4$  budgets (de la Rocha et al., 1997; de la Rocha, 2003;  
72 Beucher et al., 2007). Siliceous sponges (Phylum Porifera, Classes Demospongea and  
73 Hexactinella) produce needle-like skeletal elements, spicules, composed of hydrated  
74 amorphous silica. Uptake of ambient  $\text{Si(OH)}_4$  occurs via a sodium transporter, which

75 resembles active transporters isolated from other metazoans (Schroeder et al., 2004).  
76 Biosilicification in sponges is controlled by two enzymes silicatein, which promotes  
77 condensation reactions, and silicase, which dissolves silica (Müller et al., 2007). A  
78 previously published study shows that the uptake of  $\text{Si}(\text{OH})_4$  results in fractionation of Si  
79 isotopes, such that spicules have some of the lightest  $\delta^{30}\text{Si}$  signatures known in natural  
80 systems (de la Rocha, 2003). The  $\delta^{30}\text{Si}$  of sponge spicules is a potential proxy to quantify  
81 whole ocean changes in Si cycling over timescales longer than the residence time of Si in  
82 the oceans (~15 ka), as well as changes in intermediate and deep-water  $\text{Si}(\text{OH})_4$   
83 composition on shorter timescales (de la Rocha, 2003; de la Rocha and Bickle, 2005).

84 Here, we investigate the Si isotope composition of modern sponges and ambient  
85 waters from the Southern Ocean, and find a clear relationship between  $[\text{Si}(\text{OH})_4]$  and  
86 sponge spicule  $\delta^{30}\text{Si}$  and Si isotope fractionation. We have then applied this calibration to  
87 sponge spicules picked from two cores in the Scotia Sea (Figure 1) to determine if  
88  $[\text{Si}(\text{OH})_4]$  changed in response to the major climatic shifts since the Last Glacial Maximum  
89 (LGM).

## 90 **2. Methods**

### 91 **2.1. Field setting and sample materials**

92 The modern day Southern Ocean has large  $[\text{Si}(\text{OH})_4]$  gradients (Pollard et al., 2002)  
93 and an abundance of living sponges. Therefore, we have used a transect across the Drake  
94 Passage and Scotia Sea to undertake a calibration of sponge  $\delta^{30}\text{Si}$  fractionation as a  
95 function of ambient  $[\text{Si}(\text{OH})_4]$ . We focus our reconstruction of past  $\text{Si}(\text{OH})_4$  on the Scotia

96 Sea, which plays a disproportionately important role in global oceanography. It contains  
97 both Antarctic and Subantarctic Zone waters, and acts as a bathymetric channel for the  
98 Antarctic Circumpolar Current (ACC) and major oceanographic fronts. This flow results  
99 in intense mixing and modification between the well ventilated and Si-rich Weddell Sea  
100 derived deep-waters and the rest of the global oceans (Naveira Garabato et al., 2002). For  
101 the calibration, we collected and analysed living specimens from a north-south transect  
102 across the Scotia Sea and Drake Passage, encompassing a range of  $[\text{Si}(\text{OH})_4]$  (12 to 120  
103  $\mu\text{M}$ ) and depths (300 to 2500 m; Figure 1A, 1B, Table 1). The  $[\text{Si}(\text{OH})_4]$  increases  
104 polewards and with depth through a combination of water-mass mixing, remineralization  
105 and an isopycnal gradient (Figure 1B; Pollard et al., 2002). Sponges were collected aboard  
106 the *R/V Nathaniel B. Palmer* by either benthic trawl or dredge, and dried or frozen for  
107 transit (April-May 2008). Water samples for  $\text{Si}(\text{OH})_4$  analysis were collected in niskin  
108 bottles attached to deep-water CTD casts and a towed camera system (WHOI TowCam),  
109 filtered immediately through 0.4  $\mu\text{m}$  polycarbonate membranes (Whatman) and stored in  
110 pre-cleaned HDPE bottles.

111 Additional samples were collected from coastal West Antarctic Peninsula (Figure 1)  
112 and the North Atlantic. Core material was obtained from two cores in the Scotia Sea, from  
113 south of the ACC (Piston core PC034, 1652m) and within the ACC (Kaston core KC081,  
114 3662m; Figure 1; Table 2). All core material was sampled from the British Antarctic  
115 Survey.

## 116 **2.2. Laboratory methods**

117 The modern spicules were initially separated from organic matter by repeatedly heating  
 118 and sonicating in concentrated HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (Analar). Sediment grains were removed  
 119 by picking until visual inspection showed the spicules to be clear of detritus. The spicules  
 120 were then cleaned of any remaining organic matter and surface contaminants in a class 100  
 121 laboratory by heating in 50% quartz-distilled HNO<sub>3</sub>/10% quartz-distilled HCl. Sediment  
 122 samples were deflocculated in sodium hexametaphosphate (5% w/v), sieved at 200 μm and  
 123 rinsed thoroughly in 18 MΩ.cm Milli-Q water. Approximately 20-30 spicules were hand  
 124 picked, rinsed with reagent grade methanol to remove clays, and heated with H<sub>2</sub>O<sub>2</sub> to  
 125 remove organic matter.

126 The sponge spicules were then dissolved by heating in 0.2 M NaOH (Analar) at 100 °C for  
 127 3 days (Cardinal et al., 2007). The solution was then acidified to pH~2 using 0.2 N  
 128 thermally distilled HCl. Quantitative separation of Si from major ions was achieved using  
 129 a cation exchange resin (BioRad AG50W-X12; Georg et al., 2006), and diluted to 300-600  
 130 ppb Si depending on machine sensitivity.

131 The Si isotope analyses were carried out for Si isotopes <sup>28</sup>Si, <sup>29</sup>Si and <sup>30</sup>Si using the  
 132 *NuPlasma HR* MC-ICP-MS (University of Oxford) in medium resolution mode. The  
 133 samples were bracketed with a concentration-matched NBS28 standard (Georg et al., 2006,  
 134 2009; Reynolds et al., 2007), and isotope ratios calculated according to Equation 1.

$$135 \quad \delta^x Si = \left( \left[ \frac{R_{sam}}{R_{nbs28}} \right] - 1 \right) \times 1000 \quad (1)$$

136 Each sample was measured 8 times on the mass spectrometer, and mean ratios calculated.  
137 Standards were checked before every batch run to ensure accuracy (either “diatomite” with  
138  $\delta^{30}\text{Si} = +1.26\text{‰}$  (0.08),  $\delta^{29}\text{Si} = +0.65\text{‰}$  (0.03) or “Big Batch” with  $\delta^{30}\text{Si} = -10.67\text{‰}$  (0.08),  
139  $\delta^{29}\text{Si} = -5.48\text{‰}$  (0.05), parentheses indicating  $2\sigma_{\text{SE}} = 2\sigma_{\text{SD}}/\sqrt{n}$ ; Reynolds et al., 2007). Repeat  
140 dissolutions, and repeat aliquots of the same dissolution, indicate an adequate level of  
141 reproducibility comparable to previous studies (repeat measurements agree within  
142  $\sim\pm 0.15\text{‰}$ ). Subsamples from the same modern sponge specimens were also analysed using  
143 in-line gas fluorination followed by Isotope Ratio Mass Spectroscopy (IRMS; Finnigan  
144 MAT 253) by M. Leng at the NERC Isotope Geosciences Laboratory (NIGL, Nottingham,  
145 UK), yielding  $\delta^{30}\text{Si}$  values within error of the measurements made at the University of  
146 Oxford by MC-ICP-MS.

147 The  $[\text{Si}(\text{OH})_4]$  of water samples from the site of sponge collection were analysed at the  
148 WHOI nutrient facility, and were consistent with Southern Ocean data from existing  
149 databases (Schlitzer, 2000; Garcia et al., 2006). If there were no water samples collected in  
150 the vicinity of the sponges, then  $[\text{Si}(\text{OH})_4]$  was estimated from existing data (Schlitzer,  
151 2000; Garcia et al., 2006). For isotopic analysis, Si was quantitatively separated from  
152 seawater using a modified Mg co-precipitation technique (Cardinal et al., 2005; Reynolds  
153 et al., 2006). 2% by volume of 1M NaOH (Aristar) was added to 10-15 ml of seawater to  
154 precipitate  $\text{Mg}(\text{OH})_2$ , shaken, left for 1 hour, centrifuged and the supernatant transferred to  
155 a new, clean tube. To ensure quantitative yields, the process was repeated twice adding  
156 1% by volume NaOH to the supernatant each time. The precipitate was washed twice with  
157  $\sim 0.001\text{M}$  NaOH to remove anions, which can suppress intensity on the MC-ICP-MS. Ion

158 chromatography was used to show the precipitate wash effectively removed excess  $\text{Cl}^-$  and  
 159  $\text{F}^-$  ions. The precipitate was then dissolved in 5% thermally distilled  $\text{HNO}_3$  or  $\text{HCl}$ . The Si  
 160 was then purified using cation exchange as above; as before, matrix tests show the resin  
 161 effectively removes Na and other cations. The  $\delta^{30}\text{Si}$  was measured using the same  
 162 protocol as for the spicules.

### 163 **3. Results and discussion**

#### 164 **3. 1. Modern calibration**

165 Modern Southern Ocean sponge  $\delta^{30}\text{Si}$  ranges from -0.70‰ to -4.13‰ (Figure 2A;  
 166 Table 3), in agreement with the limited published data from archived sponges (de la Rocha,  
 167 2003). A three isotope plot of all the silicon isotope data collected ( $\delta^{29}\text{Si}$  vs.  $\delta^{30}\text{Si}$ ) has a  
 168 slope of 0.51 ( $\pm 0.01$ ) calculated by model II regression (parentheses denotes the 95%  
 169 confidence interval), which is consistent with that anticipated for kinetic equilibrium  
 170 (0.509 or 0.511 depending on whether Si or  $\text{SiO}_2$  undergoes fractionation; Reynolds et al.,  
 171 2007; Figure 2C). We find an inverse linear functional relationship between sponge  $\delta^{30}\text{Si}$   
 172 and  $[\text{Si}(\text{OH})_4]$  ( $r^2 = 0.75$ ) according to Equation 2 (parentheses denotes the 95% confidence  
 173 interval, such that a single measurement of  $\delta^{30}\text{Si}_{\text{sponge}}$  can give a  $\text{Si}(\text{OH})_4$  concentration to  
 174 approximately  $\pm 20 \mu\text{M}$ ).

$$175 \quad [\text{Si}(\text{OH})_4] = -30.3(\pm 8.2)\delta^{30}\text{Si}_{\text{sponge}} - 13.79 \quad (2)$$

176 The measured seawater  $\delta^{30}\text{Si}_{\text{Si}(\text{OH})_4}$  in the collected waters agree well with modeled (Table  
 177 4; Wischmeyer et al., 2003; Reynolds, 2009) and published data from other sectors of the

178 Southern Ocean (de la Rocha et al., 2000). Our  $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$  values were used to calculate a  
 179 fractionation factor,  $\varepsilon$  (Equation 3; de la Rocha, 2003), which ranges from -2.5 to -5.3‰  
 180 and increases with ambient  $\text{Si(OH)}_4$  ( $r^2=0.56$ ; Figure 3A).

$$181 \quad \varepsilon \approx \delta^{30}\text{Si}_{\text{sponge}} - \delta^{30}\text{Si}_{\text{Si(OH)}_4} \quad (3)$$

182 Subsamples from the same specimen, and of two co-existing specimens of the same  
 183 species, show  $\delta^{30}\text{Si}$  is homogeneous within and between individuals bathed in the same  
 184 water mass (Figure 2B). We cannot rule out a  $\sim 0.5\%$  species-specific offset in  
 185 fractionation, but it is small compared to the effect of environmental controls ( $\sim 4\%$ ; Figure  
 186 2A).

187 Other factors that are known to influence biomineralization co-vary with  $[\text{Si(OH)}_4]$   
 188 in the Southern Ocean (e.g. temperature and pH; Foo et al., 2004). However, the samples  
 189 from coastal West Antarctic Peninsula and the deep North Atlantic show similar isotope  
 190 fractionations for a given  $[\text{Si(OH)}_4]$  compared to sponges from the deep Southern Ocean  
 191 despite being collected under very different temperature, salinity and pH conditions  
 192 (Figure 3B-D). Consistent with growth under low  $\text{Si(OH)}_4$  conditions, and in line with our  
 193 data, shallow-water sponges from a low nutrient tropical shelf show relatively heavy  
 194 isotopic compositions ( $\delta^{30}\text{Si}_{\text{sponge}}$  from -2 to +0.5‰; Vroon et al., 2004). Our interpretation  
 195 that  $[\text{Si(OH)}_4]$  is the dominant control over  $\delta^{30}\text{Si}_{\text{sponge}}$  appears to hold in a variety of  
 196 oceanographic settings, providing a robust proxy for paleo- $[\text{Si(OH)}_4]$ .

197 The environmental control over  $\delta^{30}\text{Si}$  in sponges is likely to be a physiological  
 198 growth rate response to varying ambient  $\text{Si(OH)}_4$  concentrations because  $\varepsilon$  is variable, and

199 correlates with  $\text{Si(OH)}_4$  (Figure 3A). This control is not unexpected because silicification  
200 is known to depend on  $\text{Si(OH)}_4$  availability. Sponges produce different types of spicules  
201 under Si limiting and replete conditions (Maldonado et al., 1999). Further, sponge culture  
202 studies show there is a positive correlation between  $\text{Si(OH)}_4$  availability and uptake rates,  
203 and no apparent relationship with temperature (Frølich & Barthel, 1997). If the  
204 fractionation process occurs at the site of Si uptake, greater uptake rates may lead to a  
205 greater fractionation. Alternatively,  $\text{Si(OH)}_4$  availability may control the internal  
206 biochemical pathways involved during silicification, which may in turn determine isotopic  
207 fractionation. For example, ambient  $\text{Si(OH)}_4$  is a known modulating factor that regulates  
208 the expression of silicatein and silicase, and induces expression of genes for other enzymes  
209 involved in biosilicification (Perovic-Ottstadt et al., 2005; Müller et al., 2007). Further  
210 work is required to understand the biosilicification process and, in particular, the reactions  
211 that result in isotopic fractionation.

212       The Si isotope fractionation observed during the formation of sponge spicules is  
213 greater than the fractionation observed during silicification of diatom opal ( $\epsilon = -0.8$  to -  
214 2.1‰; Cardinal et al., 2005, 2007). Although diatoms use uptake transporters and  
215 condensation/dissolution enzymes distinct to sponges, the mechanisms are somewhat  
216 similar and may be homologous (Foo et al., 2004). However, we suggest the two groups  
217 evolved Si acquisition mechanisms, which likely impact Si isotopes differentially, at  
218 distinct points in Earth history. Siliceous sponges originated in the Precambrian (Love et  
219 al., 2009), with a relatively low affinity for Si (Frølich & Barthel, 1997), at a time when  
220 weathering of silicate rocks resulted in high oceanic  $\text{Si(OH)}_4$  (Siever, 1992). In contrast,

221 diatoms evolved in the Jurassic (Sims et al., 2006) with a higher affinity for Si, probably  
222 because biological utilization by other siliceous organisms resulted in lower oceanic  
223  $\text{Si(OH)}_4$  (Maldonado et al., 1999).

### 224 **3.2. Downcore data**

225 We use the modern relationship between  $[\text{Si(OH)}_4]$  and  $\delta^{30}\text{Si}_{\text{sponge}}$ , and analyses of  
226 spicules hand-picked from two Scotia Sea sediment cores, to investigate whether deep-  
227 water  $[\text{Si(OH)}_4]$  changed within the ACC on glacial-interglacial timescales, and to address  
228 the potential consequences for atmospheric  $\text{pCO}_2$  levels in the past.

229 Our modern core-top sample from piston core PC034 (Figure 4A;  $\delta^{30}\text{Si}_{\text{sponge}} = -$   
230  $3.86 \pm 0.17\%$ ,  $\pm 2\sigma_{\text{SD}}$ ) agrees well with the living sponges collected from the southern  
231 Scotia Sea, growing in  $[\text{Si(OH)}_4]$  of approximately  $100 \mu\text{M}$  (Figure 2A, 4B). The  
232 youngest section of the northern site (KC081) has been dated at  $\sim 6 \text{ ka}$  (Figure 4A), so we  
233 are unable to measure a core-top sample at the site. In both cores, the Last Glacial  
234 Maximum (LGM) value is similar to the modern, suggesting deep-water  $[\text{Si(OH)}_4]$  was not  
235 significantly different at the LGM compared to today at either site (within  $\sim 20 \mu\text{M}$ ). The  
236 similarity between LGM and modern  $[\text{Si(OH)}_4]$  in Southern Ocean deep-waters provides  
237 insight into processes occurring in different regions of the water column on glacial-  
238 interglacial timescales.

239 The fractionation factor,  $\epsilon$ , would be the most appropriate parameter to record  
240 because it would account for changes in seawater  $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$ . However,  $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$  of  
241 seawater cannot be constrained directly downcore, and so here we present  $\delta^{30}\text{Si}_{\text{sponge}}$  and

242 assume that  $\delta^{30}\text{Si}_{\text{Si}(\text{OH})_4}$  of deep waters is constant over glacial-interglacial cycles in accord  
243 with recent box modeling (Georg et al., 2009).

244 There are two important caveats when interpreting our downcore data. Firstly, age  
245 models for cores in the Southern Ocean are notoriously challenging due to poor  
246 preservation of benthic foraminifera and other dateable carbonates. Here, we apply the  
247 best dating constraints available, based on radiocarbon measurements and stratigraphic  
248 markers, locating the LGM using the abundance of diatoms and the radiolarian  
249 *Cycladophora davisiana* (Figure 4A). The limited number of tie-points results in an  
250 inherent degree of uncertainty on the age model. Secondly, as is a common problem with  
251 any sedimentary proxy, there is a possibility that core components, such as spicules,  
252 undergo differential transport and are of different ages to surrounding grains. However,  
253 sponges are benthic and, in life, comprise a large proportion of sticky organic matter,  
254 making significant post-mortem transportation of spicules less likely than, for example,  
255 planktonic diatoms or foraminifera. Opal-specific dating methods may resolve any issues  
256 arising from particulate transportation (Ingalls et al., 2004).

### 257 **3.2.1. Deep processes: the glacial carbon reservoir**

258 A leading hypothesis for the reduced  $\text{pCO}_2$  during the glacial is the presence of an  
259 isolated reservoir of C-rich water in the Pacific and Southern Oceans (Marchitto and  
260 Broecker 2006; Marchitto et al., 2007). Radiocarbon records from Baja California and the  
261 Equatorial Pacific point towards a deglacial degassing of old C from a reservoir isolated  
262 during the LGM (Marchitto et al., 2007; Stott et al., 2009). Deglacial age deep-sea corals

263 from the Drake Passage, dated to Heinrich Event 1 (~16.7 ka), also show radiocarbon  
264 depletion, but not to such a great extent as the Baja California record (Robinson & van de  
265 Flierdt, 2009). Benthic foraminiferal records from the Southern Ocean show very light  
266  $\delta^{13}\text{C}$  signatures, indicative of a high nutrient content or significant changes in air-sea  
267 exchange of inorganic C (Curry et al., 1998; Marchitto and Broecker, 2006; Marchitto et  
268 al., 2007). Specifically, there is evidence for a strong vertical  $\delta^{13}\text{C}$  gradient at  
269 approximately 2.5km to the north of the polar front in the South Atlantic during the glacial  
270 (Hodell et al., 2003). However, records of benthic foraminiferal Cd/Ca, a proxy for  
271 dissolved phosphate (P), do not support a significant change between the nutrient content  
272 of the modern and LGM deep Southern Ocean (Boyle, 1992). This discrepancy has led to  
273 considerable debate in the paleoceanographic community surrounding the continued  
274 presence of nutrient-poor North Atlantic derived waters in the ACC. One possibility,  
275 consistent with a continued presence of NADW in the Glacial Southern Ocean, is that the  
276 light  $\delta^{13}\text{C}$  was associated either with changes in air-sea exchange of C (Broecker, 1993;  
277 Lynch-Stieglitz & Fairbanks, 1994; Marchitto & Broecker, 2006) or organic matter with  
278 high C:P content (Arrigo, 1999; Elderfield & Rickaby, 2000). Alternatively, several  
279 studies have highlighted caveats and artifacts associated with both  $\delta^{13}\text{C}$  in regions of high  
280 organic matter accumulation rate (Mackensen et al., 1993) and Cd/Ca where significant  
281 dissolution has occurred (McCorkle et al., 1995). When outliers in Southern Ocean  
282 datasets of individual foraminiferal shells of a single benthic species, potentially arising  
283 from changes in productivity in high organic accumulation rate regions, are removed the  
284 resulting “representative”  $\delta^{13}\text{C}$  brings  $\delta^{13}\text{C}$  more inline with Cd/Ca. These data, together

285 with  $^{231}\text{Pa}/^{230}\text{Th}$  records of water mass export (Yu et al., 1996), are consistent Glacial  
286 NADW entering the ACC followed by transportation to the North Pacific in a similar  
287 fashion to the modern ocean (Matsumoto & Lynch-Stieglitz, 1999).

288 Our  $\delta^{30}\text{Si}$  results from KC081, situated greater than 3km, below the glacial  $\delta^{13}\text{C}$  gradient,  
289 (Hodell et al., 2003), do not show a change between the modern and the LGM, so we infer  
290 that, any isotopically light C in the deep Southern Ocean was not associated with higher  
291 levels of  $\text{Si}(\text{OH})_4$ . Furthermore, our results are consistent with the benthic foraminiferal  
292 Cd/Ca records, suggesting there were insignificant changes in both refractory and labile  
293 nutrient concentrations in Southern Ocean deep-waters during the LGM. In this case, the  
294 light  $\delta^{13}\text{C}$  signature of the LGM Southern Ocean could have been caused by a reduction in  
295 air-sea exchange of inorganic C ( $\text{CO}_2$ ) due to poor ventilation, or changes in the surface  
296 temperature or residence time of subducting deep waters (e.g. Broecker, 1993; Lynch-  
297 Stieglitz & Fairbanks, 1994; Mackensen, 2001). For example, the isolation of a deep-  
298 water mass, due to stratification or sea-ice cover, could lead to a depletion in  $\delta^{13}\text{C}$  and a  
299 decrease in atmospheric  $\text{CO}_2$  without a concurrent change in nutrients (Toggweiler, 1999).

300         Alternatively, the light  $\delta^{13}\text{C}$  could originate from the remineralization of organic C  
301 that is not associated with significant quantities of  $\text{Si}(\text{OH})_4$  or P. This decoupling could be  
302 a result of physiological changes within the diatom populations, or shifts in the  
303 phytoplankton population structure, during the LGM. Firstly, extensive field and  
304 laboratory experiments have shown that diatoms have both lower cellular Si:N and P:N  
305 when grown under Fe replete conditions than when Fe stressed or limited (Timmermans et  
306 al., 2004; Brzezinski et al., 2005; Price, 2005). The higher Fe conditions existing in the

307 Southern Ocean during glacials, due to enhanced dust supply (e.g. Kohfeld et al., 2005),  
308 are thought to promote lower Si:N uptake ratios in diatoms compared to Fe-stressed  
309 diatoms growing during interglacials (Brzezinski et al., 2002). Secondly, the non-siliceous  
310 dinoflagellate *Phaeocystis* shows a high N:P uptake ratio during modern Southern Ocean  
311 blooms. If *Phaeocystis* blooms became more dominant in stratified waters during the LGM  
312 (Arrigo, 1999; Elderfield and Rickaby 2000), then export of the associated organic C, and  
313 subsequent remineralization in deep-waters, could result in a depletion in  $\delta^{13}\text{C}$  and an  
314 increase in  $\text{NO}_3$  without a concurrent increase in either  $\text{Si(OH)}_4$  or P. These two scenarios  
315 are not mutually exclusive, and both may have contributed to the nutrient conditions  
316 prevailing in the glacial Southern Ocean.

### 317 **3.2.2. Surface processes: glacial nutrient utilization**

318 In addition to the deep-water signal, our results provide further information about  
319 biological utilization in surface waters at the LGM. The Silicic Acid Leakage Hypothesis  
320 (SALH) proposes that reduced productivity, due the physiological response of  
321 phytoplankton to Fe fertilization, caused a reduction in the Si to N uptake ratio in the  
322 Southern Ocean during the LGM (Brzezinski et al., 2002; Matsumoto et al., 2002).  
323 According to the SALH, a pool of excess  $\text{Si(OH)}_4$  in Antarctic surface waters was exported  
324 to lower latitudes, via intermediate water, promoting diatom production at the expense of  
325 carbonate-producing coccolithophores. In this scenario, there would be an increase in  
326 export of organic C with respect to inorganic C in the low latitudes associated with a rise in  
327 ocean alkalinity and lowered atmospheric  $\text{pCO}_2$  (Brzezinski et al., 2002; Matsumoto et al.,  
328 2002). Diatom  $\delta^{30}\text{Si}$  records show a 0.5‰ change across the deglaciation, which have

329 been interpreted as a reduction in the fraction of  $\text{Si(OH)}_4$  utilized in the Antarctic (de la  
330 Rocha et al., 1997), subantarctic and subtropics during the LGM (Beucher et al., 2007).  
331 Since whole ocean  $\delta^{30}\text{Si}$  changes are unlikely over this timescale (Georg et al., 2009), our  
332 new record demonstrates that the decrease in  $\text{Si(OH)}_4$  surface depletion in the subantarctic  
333 region (Beucher et al., 2007) was not caused by changes in the  $[\text{Si(OH)}_4]$  concentration of  
334 upwelling waters (Figure 4B). Instead it must have been a consequence of either an  
335 increase in upwelling intensity or reduced surface utilization. We argue above that the  
336 geochemical evidence points towards an increase in stratification in the ACC south of the  
337 polar front during the LGM, so the diatom  $\delta^{30}\text{Si}$  data is best explained by changes in the  
338 efficiency of surface utilization (Beucher et al., 2007). Records of nitrogen isotopes ( $\delta^{15}\text{N}$ )  
339 of diatom-bound organic matter indicate an increase in utilization of nitrate in surface  
340 waters (Sigman et al., 1999; Robinson et al., 2004). This can be reconciled with the  
341 diatom  $\delta^{30}\text{Si}$  data if there was a large-scale physiological change in diatoms reducing Si:N  
342 and P:N uptake ratios (e.g. Brzezinski et al., 2005), or an increase in productivity by non-  
343 siliceous phytoplankton, such as *Phaeocystis* (Arrigo, 1999; Elderfield and Rickaby, 2000).

### 344 **3.2.3. Implications for glacial $\text{pCO}_2$**

345 Our new sponge  $\delta^{30}\text{Si}$  data, when combined with other geochemical proxies, bring  
346 new insight into the mechanisms behind the lower glacial atmospheric  $\text{pCO}_2$ . Deep-water  
347 C and macronutrients are decoupled on glacial-interglacial timescales as a result of  
348 physical processes, such as ocean stratification or sea-ice cover, which lock-up C in the  
349 deep ocean and lower atmospheric  $\text{pCO}_2$  (Toggweiler, 1999; Stephens and Keeling, 2000).

350 An increase in the biological export of C from the surface to the deep ocean is consistent  
351 with all of the currently available data if there was either a concurrent decrease in diatom  
352 silicification, or a shift away from siliceous to organic-walled phytoplankton production, in  
353 the Southern Ocean. Whilst this could increase the C:Si and C:P content of the deep  
354 ocean, without significant mineral ballast a lightly-silicified diatom or *Phaeocystis*  
355 dominated biological pump would not export as C efficiently as one dominated by heavily-  
356 silicified diatoms (Jin et al., 2006), limiting the impact on atmospheric pCO<sub>2</sub>. However,  
357 the excess Si(OH)<sub>4</sub> resulting from a decrease in surface utilization in the Southern Ocean  
358 could have been exported away from the subantarctic via mode waters without impacting  
359 the deep-water Si inventory. This would have the potential to impact atmospheric pCO<sub>2</sub> by  
360 increasing the relative productivity of diatoms in the lower latitudes (Matsumoto et al.,  
361 2002; Bradtmiller et al., 2007).

#### 362 **3.2.4. The deglaciation**

363 During the deglacial (after ~ 18 kyr), our records indicate a depletion in deep-water  
364 [Si(OH)<sub>4</sub>] both within and south of the ACC (Figure 4B). In the late Holocene, deep-water  
365 [Si(OH)<sub>4</sub>] recovers to modern values. Given the uncertainty on the age models, we cannot  
366 pin point the exact timing of these changes but the decline is a robust observation in both  
367 cores. Our best estimate for the maximum rate of change of deep-water [Si(OH)<sub>4</sub>] is  
368 approximately 10 μM ky<sup>-1</sup>

369 We hypothesize two possible mechanisms behind this decline in deep-water  
370 Si(OH)<sub>4</sub>: large scale changes in nutrients arising from decomposition of biogenic particles

371 in the deep Southern Ocean (“remineralized nutrients”) or localized changes in unutilized  
372 nutrients subducted during deep-water formation (“preformed nutrients”; Marinov et al.,  
373 2006). Firstly, our data are consistent with storage of  $\text{Si(OH)}_4$  in the form of a large-scale  
374 opal deposition in the Southern Ocean during the deglacial (10-16 kyr), caused by wind-  
375 driven upwelling of water enriched in  $\text{Si(OH)}_4$  relative to the surface. Enhanced opal  
376 fluxes during the deglaciation, coupled with  $^{231}\text{Pa}/^{230}\text{Th}$  activity ratios, have been observed  
377 in Pacific and Atlantic Sectors of the Southern Ocean and equatorial regions (Anderson et  
378 al., 2009). Such a significant and widespread burial of opal could have resulted in a drop in  
379 deep ACC remineralized  $\text{Si(OH)}_4$ , whilst the enhanced upwelling drove a concurrent rise  
380 in  $\text{pCO}_2$  (Anderson et al., 2009). The decline in deep-water  $[\text{Si(OH)}_4]$  would have led to a  
381 negative feedback, by limiting the amount of productivity that could be supported by  
382 upwelling water and an eventual restoration of export production rates, opal fluxes and  
383  $[\text{Si(OH)}_4]$  gradients over time. Such changes in remineralized nutrients cannot change  
384 global deep-water  $[\text{Si(OH)}_4]$  over timescales of less than the residence time of Si in the  
385 whole ocean (~15 ky; Georg et al., 2009). However, we constructed a simple one-box  
386 model for the deep Southern Ocean alone (south of  $50^\circ\text{S}$ , > 400 m depth, area  $\sim 25 \times 10^{12}$   
387  $\text{m}^2$ ), using a mean modern  $[\text{Si(OH)}_4]$  of  $100 \mu\text{M}$  and mean depth of 4000 m (Garcia et al.,  
388 2006), and modern opal accumulation fluxes of  $\sim 0.2 \text{ mol Si m}^{-2} \text{ yr}^{-1}$  (Pondaven et al.,  
389 2000). Using this model, we estimate changes in the opal burial rate relative to Si inputs of  
390  $\sim 20\%$  (less than observed in core TN057-13-4PC; Figure 4b, Anderson et al., 2009) could  
391 cause changes of the order of  $10 \mu\text{M}$  in 1000 years, which are sufficient to explain our  
392 observations.

393           Alternatively, the rapid rates in change indicate the decline in deep-water  $[\text{Si}(\text{OH})_4]$   
394 during the deglaciation was at least in part a result of localized inputs of preformed  
395 nutrients. For example, the retreat of the Weddell Sea ice shelf during the deglacial and  
396 early Holocene “Hypsithermal” may have changed deep-water formation processes and led  
397 to a decline in the input of highly Si-enriched Weddell Sea Deep Water (WSDW) into the  
398 ACC (Yoon et al., 2007). This could explain both the rapid decline in deep-water  $\text{Si}(\text{OH})_4$   
399 and the apparent divergence in the records between ~ 6-10 ky (higher  $[\text{Si}(\text{OH})_4]$  from the  
400 southern core compared to the northern core; Figure 4B). Resumption of WSDW input to  
401 the ACC could be in part responsible for the recovery in deep-water  $\text{Si}(\text{OH})_4$  in the later  
402 Holocene. Future research should focus on constraining this climatically important time,  
403 in order to understand the response of Southern Ocean deep-water circulation during  
404 periods of global warming.

#### 405           **4. Summary and conclusions**

406           In summary, we show the potential for combined  $\delta^{30}\text{Si}$  records from diatoms and  
407 sponges to constrain the surface and deep components of the Si biological pump. We  
408 investigate fractionation by modern deep-sea sponges, and find the  $\delta^{30}\text{Si}$  of spicules and  
409 fractionation with respect to ambient seawater correlate with the ambient  $[\text{Si}(\text{OH})_4]$ . We  
410 then apply this calibration to two downcore records from the Scotia Sea. Our results show  
411 that the deep-waters of the LGM Southern Ocean were not enriched in  $\text{Si}(\text{OH})_4$ , suggesting  
412 that the isolated reservoir of old, isotopically depleted C was not associated with an  
413 increase in either  $\text{Si}(\text{OH})_4$  or P. Instead, the Southern Ocean resulted in lower atmospheric  
414  $\text{pCO}_2$  during the glacial largely due to reduction in air-sea exchange of C via a physical

415 process. If there was an enhanced glacial biological pump in the Southern Ocean, it was  
416 likely to have been dominated by lightly-silicified diatoms or organic-walled  
417 phytoplankton (e.g. *Phaeocystis*) resulting in a concurrent increase in surface nitrate  
418 utilization, and a change in deep-water nutrient ratios that may not have been associated  
419 with a considerable increase in pump efficiency. Utilization of Si-rich upwelling waters by  
420 diatoms was lower during the LGM, providing a surplus of  $\text{Si(OH)}_4$  that could then be  
421 exported to lower latitudes via intermediate waters, where enhanced export production  
422 could lower atmospheric  $\text{CO}_2$ . During the deglaciation, there is a robust and significant  
423 decrease in deep-water  $\text{Si(OH)}_4$ , which could be associated with a pulse of opal burial  
424 linked with wind-driven upwelling and concurrent rise in  $\text{pCO}_2$ , or a change in water mass  
425 inputs.

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- 622 The authors would like to thank the captain and crew of the *R/V Nathaniel B. Palmer* (cruise NBP0805;  
623 Program Manager Thomas Wagner). Thanks also to Rhian Waller (University of Hawaii), Laura Schejter

624 (INIDEP, Argentina), Jade Berman (University of Victoria, Wellington), Nicky White (University of  
625 Cambridge) and Andy Clarke (British Antarctic Survey) for sponge samples and help with identification.  
626 Thanks to Chris Siebert, Helen Williams, Sune Nielsen, Ros Armytage and Paul Savage (University of  
627 Oxford) for assistance in the laboratory, Melanie Leng (NIGL) for additional silicon isotope measurements,  
628 Maureen Auro and Paul Henderon (WHOI) for assistance with nutrient analyses and Kathy Scanlon (USGS)  
629 for map production. Core material and age model from Claire Allen and Claus-Dieter Hillenbrand (British  
630 Antarctic Survey). Thanks to Louisa Bradtmiller (WHOI), editor Peter deMenocal and three anonymous  
631 reviewers for constructive reviews and discussion. Cruise NBP0805 was funded by NSF Office of Polar  
632 Programs (OPP) Antarctic Sciences (grant number ANT-0636787). Data from the Palmer LTER data archive  
633 were supported by Office of Polar Programs, NSF grants OPP-9011927, OPP-9632763 and OPP-0217282.  
634 The work was funded by the Natural Environment Research Council (NERC) grant NE/F005296/1 and an  
635 Antarctic Science Bursary. The authors declare no competing financial interests.

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637 Figure 1: A) Location of sample sites in the Southern Ocean and coastal  
638 Antarctica. Grey stars indicate modern sponge sample sites; grey squares indicate  
639 deep-water samples; grey dotted circles show cores PC034 and KC081. Map  
640 production by K. Scanlon (USGS).

641 B) Dissolved silicic acid concentrations from across the Drake Passage. Drawn  
642 using Ocean Data View (Schlitzer, 2000).

643 Figure 2: A) The relationship between modern sponge silicon isotope composition  
644 and ambient seawater  $\text{Si}(\text{OH})_4$  concentration ( $r^2=0.75$ ; Equation 2). Filled symbols  
645 show values for Hexactinellid sponges; open symbols show values for  
646 Demosponges. There is no consistent difference between the two classes of  
647 sponges, although there may be species-specific fractionation ( $\sim 0.5\text{‰}$ ). Error bars  
648 show  $2\sigma_{\text{SD}}$ .

649 B) Isotopic homogeneity between individuals of the same species from one  
650 locality, and within an individual. The black symbols show duplicate  
651 measurements of spicule silicon isotopes taken from three different specimens;  
652 the white triangles show the silicon isotopic composition of two specimens of  
653 *Rosella* collected from the same site; the white circles show the silicon isotopic  
654 composition of two different types of spicules from the same specimen (dermal  
655 and perenchymal). Error bars show  $2\sigma_{\text{SD}}$ .

656 C) A three-isotope plot for all sponge samples. The equation was calculated using  
 657 model II regression, and numbers in parentheses indicate 95% confidence  
 658 intervals of the slope and intercept respectively. The relationship between  
 659  $\delta^{29}\text{Si}_{\text{sponge}}$  and  $\delta^{30}\text{Si}_{\text{sponge}}$  is consistent with mass dependent fractionation under  
 660 kinetic equilibrium. Error bars show  $2\sigma_{\text{SD}}$ .

661 Figure 3: Fractionation of silicon isotopes by sponges. The black circles show the  
 662 fractionation by sponges from the deep Southern Ocean; the grey squares show  
 663 the fractionation by sponges from the West Antarctic Peninsula; the white triangles  
 664 show the fractionation by sponges from the deep North Atlantic (assuming Atlantic  
 665 deep water  $\delta^{30}\text{Si}_{\text{Si(OH)}_4} = 1.6\text{‰}$ ; Reynolds, 2009). Fractionation is plotted against  
 666 ambient A)  $\text{Si(OH)}_4$  concentrations; B) salinity; C) temperature and D) pH (data  
 667 from the British Antarctic Survey and Garcia et al., 2006). Error bars are  
 668 propagated from  $\pm 2\sigma_{\text{SD}}$  of  $\delta^{30}\text{Si}_{\text{Si(OH)}_4}$  and  $\delta^{30}\text{Si}_{\text{sponge}}$ .

669 Figure 4: A) Age models for the two cores based on magnetic susceptibility  
 670 (dashed lines) and diatom abundances (squares). Note for PC034, the shallower  
 671 peak in magnetic susceptibility has been interpreted as showing the Antarctic  
 672 Climate Reversal. For KC081, age constraints are also available from the  
 673 occurrence of the radiolarian *Cycladophora davisiana* (triangles), which are  
 674 abundant in glacial sediments, and corrected radiocarbon ages (indicated by black  
 675 arrows) showing core top  $\sim 6.3$  ka, 0.23 mbsf  $\sim 11.3$  ka and 1.59 mbsf  $\sim 23.5$  ka  
 676 (NERC Publication Code AA-28113-5). Data and interpretation from C. Allen  
 677 (BAS). Also shown are locations of the cores with respect to major oceanographic  
 678 fronts, although these can vary by several degrees in the modern setting (SAF =  
 679 Sub-Antarctic Front; PF = Polar Front; SACCF = Southern Antarctic Circumpolar  
 680 Front; SB = Southern Boundary of the ACC, adapted from Naveira Garabato et al.,  
 681 2002). White symbols correspond to the northern core (KC081) and black  
 682 symbols to the southern core (PC034).

683 B) Composition of sponges (error bars show  $2\sigma_{\text{SD}}$ ) and reconstructed deep-water  
 684  $\text{Si(OH)}_4$  concentrations (95% confidence intervals  $\sim 20$   $\mu\text{M}$ ; Equation 2). White  
 685 symbols correspond to the northern core (KC081) and black symbols to the  
 686 southern core (PC034). The white box shows  $\delta^{30}\text{Si}$  of modern sponges found near  
 687 KC081; the black box shows  $\delta^{30}\text{Si}$  of modern sponges found near PC034. The  
 688 age model is based on the information in A). Also shown: opal flux and  
 689  $^{231}\text{Pa}/^{230}\text{Th}$  from core TN057-13-4PC from south of the Polar Front in the Atlantic  
 690 Sector (Anderson et al., 2009); EPICA ice core records of  $\text{pCO}_2$  and  $\delta\text{D}$ , a proxy  
 691 for local temperature (Indermüle et al., 1999; Fluckiger et al., 1999; Monnin et al.,  
 692 2001, 2004).

693

694

Sample code	Classification	Location	Depth (m)	Method	Lat (°S)	Lon (°W)
NBP0805-TB1-3	Unidentified Demosponge	Burdwood Bank	306-333	Blake trawl	54.48	62.18
NBP0805-TB1-6	Mycalidae	Burdwood Bank	306-333	Blake trawl	54.48	62.18
NBP0805-TB1-11	Unidentified Hexactinellid	Burdwood Bank	306-333	Blake trawl	54.48	62.18
NBP0805-TB3-21	Mycalidae	Burdwood Bank	2215-2343	Blake trawl	54.91	62.03
NBP0805-TB4-3	Unidentified Demosponge	Burdwood Bank	804-828	Blake trawl	54.74	62.21
NBP0805-TB4-24	Unidentified Demosponge	Burdwood Bank	804-828	Blake trawl	54.74	62.21
NBP0805-TB4-27	<i>Rosella</i>	Burdwood Bank	804-828	Blake trawl	54.74	62.21
NBP0805-TO1-27	<i>Rosella</i>	Elephant Island	407-428	Otter trawl	61.25	56.42
NBP0805-TO1-57	<i>Rosella</i>	Elephant Island	407-428	Otter trawl	61.25	56.42
NBP0805-TO3-100	Unidentified Demosponge	Drake Passage	689-914	Otter trawl	60.56	65.97
NBP0805-TO3-111	Unidentified Demosponge	Drake Passage	689-914	Otter trawl	60.56	65.97
NBP0805-DR7-47	<i>Acoelocalyx</i>	Scotia Sea	2109-2422	Dredge	54.88	40.69
NBP0805-DR13-47	<i>Acoelocalyx</i>	Scotia Sea	2097-2477	Dredge	59.50	42.50
NBP0805-DR16-47	<i>Acoelocalyx</i>	Scotia Sea	930-	Dredge	61.10	56.45

NBP0805-DR29-47	<i>Acoelocalyx</i>	Drake Passage	1070 758-759	Dredge	60.56	65.91
NBP0805-DR34-47	<i>Acoelocalyx</i>	Drake Passage	899-838	Dredge	59.73	68.74
NBP0805-DR35-111	Unidentified Demosponge	Drake Passage	672-718	Dredge	59.72	68.88
NBP0805-DR40-47	<i>Acoelocalyx</i>	Drake Passage	1294-1351	Dredge	59.73	68.93
CRS-956	Unidentified Demosponge	Anvers Island	600	Dredge	64.78	65.30
RB-Mycale	<i>Mycale</i>	Adelaide Island	10	Hand collection	67.57	68.23

695

696 Table 1: Samples used in the modern calibration collected from the Southern  
697 Ocean. CRS-956 was collected by R. Waller (University of Hawaii) from near  
698 Anvers Island; RB-Mycale was collected by J. Berman (BAS) from near Adelaide  
699 Island.

Core	Depth (m)	Latitude (°S)	Longitude (°W)
PC034	1652	59.79	39.60
KC081	3662	56.74	42.97

700

701 Table 2: Locations of cores used in this study.

702

Sample code	T (°C)	S (psu)	pH	Si(OH) <sub>4</sub> (μM)	δ <sup>30</sup> Si (‰)	δ <sup>29</sup> Si (‰)	*δ <sup>30</sup> Si (‰)
NBP0805-TB1-3	4.3	34.17	7.96	12	-0.70(0.04)	-0.38(0.02)	-0.36
NBP0805-TB1-6	4.3	34.17	7.96	12	-1.01(0.08)	-0.51(0.05)	-0.52

Repeat dissolution					-1.15 (0.04)	-0.61 (0.03)	-0.59
NBP0805-TB1-11	4.3	34.17	7.96	12	-1.69(0.03)	-0.84(0.03)	-0.86
NBP0805-TB3-21	1.8	34.69	7.70	97	-2.79(0.02)	-1.45(0.02)	-1.42
NBP0805-TB4-3	3.1	34.35	7.80	56	-1.55(0.03)	-0.83(0.02)	-0.79
NBP0805-TB4-24	3.1	34.35	7.80	56			
Dermal					-2.87(0.04)	-1.41(0.02)	-1.46
Perenchymal					-2.96(0.04)	-1.51(0.01)	-1.51
NBP0805-TB4-27	3.1	34.35	7.80	56	-2.54(0.04)	-1.28(0.02)	-1.30
NBP0805-TO1-27	1.9	34.65	7.71	90	-3.83(0.05)	-1.94(0.02)	-1.95
NBP0805-TO1-57	1.9	34.65	7.71	90	-3.51(0.04)	-1.83(0.02)	-1.79
NBP0805-TO3-100	2.4	34.63	7.80	75	-3.06(0.04)	-1.59(0.02)	-1.56
NBP0805-TO3-111	2.4	34.63	7.80	75	-2.88(0.09)	-1.46(0.06)	-1.47
Repeat dissolution					-3.18 (0.05)	-1.64 (0.03)	-1.62
NBP0805-DR7-47	1.5	35	7.7	120	-3.76(0.05)	-1.92(0.05)	-1.92
					-3.58(0.02)	-1.77(0.03)	-1.82
NBP0805-DR13-47	1.5	35	7.7	110	-3.20(0.05)	-1.59(0.02)	-1.63
NBP0805-DR16-47	1.48	34.72	7.76	96	-4.13(0.05)	-2.10(0.04)	-2.10
NBP0805-DR29-47	2.4	34.63	7.80	100	-3.91(0.04)	-2.02(0.01)	-1.99
					-3.91(0.05)	-2.02(0.02)	-1.99
NBP0805-DR34-47	2.3	34.62	7.80	75	-2.54(0.03)	-1.31(0.02)	-1.30
NBP0805-DR35-111	2.4	34.64	7.80	70	-2.86(0.04)	-1.44(0.03)	-1.46
NBP0805-DR40-47	1.9	34.70	7.72	94	-2.92(0.03)	-1.47(0.01)	-1.49
CRS-956	1.5	34.72		107	-3.36(0.04)	-1.72(0.02)	-1.71

RB-Mycale	-0.4	33	8.19	50	-2.39(0.05)	-1.21(0.03)	-1.22
Repeat dissolution					-2.34(0.03)	-1.21(0.02)	-1.19
					-2.40(0.03)	-1.24(0.03)	-1.22

703

704 Table 3: Silicon isotopic composition of modern sponge spicules. Temperature,  
 705 salinity, pH and nutrient values courtesy of WHOI, BAS, Palmer LTER, WOCE  
 706 (Schlitzer, 2000) and World Ocean Atlas 05 (WOA05; Garcia et al., 2006).  
 707 Numbers in parentheses are  $2(\sigma/\sqrt{n})$ . \* $\delta^{30}\text{Si}$  is the expected  $\delta^{29}\text{Si}$  value calculated  
 708 assuming mass dependent fractionation:

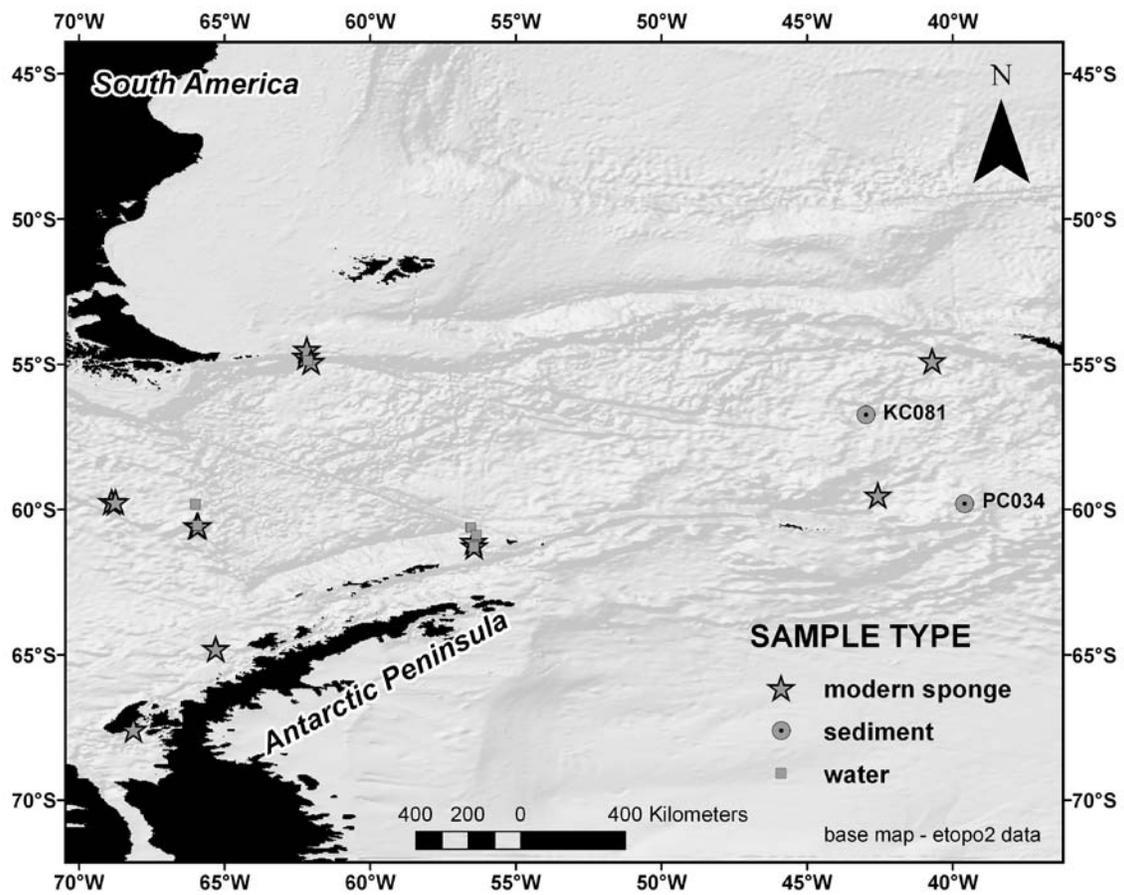
709 
$$*\delta^{30}\text{Si} = 0.51 \times \delta^{30}\text{Si}_{\text{sponge}}$$

Sample	Lat (°S)	Long (°W)	Depth (m)	Si(OH) <sub>4</sub>	$\delta^{30}\text{Si}$
CTD2-1-1	54.88	62.14	2190	96.5	1.06 (0.04)
CTD2-13-7	54.88	62.14	805	56.0	1.28 (0.03)
CTD2-17-9	54.88	62.14	300	11.8	1.76 (0.05)
CAM3-bottom	61.28	56.42	400	95.8	1.03 (0.05)
CAM7-1500	60.55	65.94	1500	100.6	1.10 (0.06)
repeat					1.04 (0.06)
CAM8-600	59.89	68.86	600	40.4	1.40 (0.06)

710

711 Table 4: Seawater Si(OH)<sub>4</sub> and  $\delta^{30}\text{Si}$  values. Si(OH)<sub>4</sub> measured by WHOI nutrient  
 712 facility;  $\delta^{30}\text{Si}$  measured using a co-precipitation method. Numbers in parentheses  
 713 are  $2(\sigma/\sqrt{n})$ .

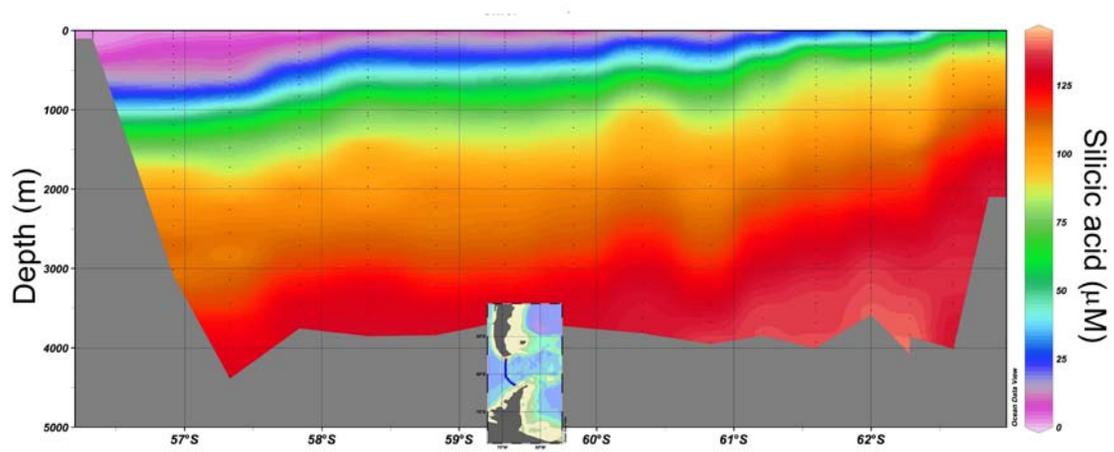
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715

716 Figure 1a

717

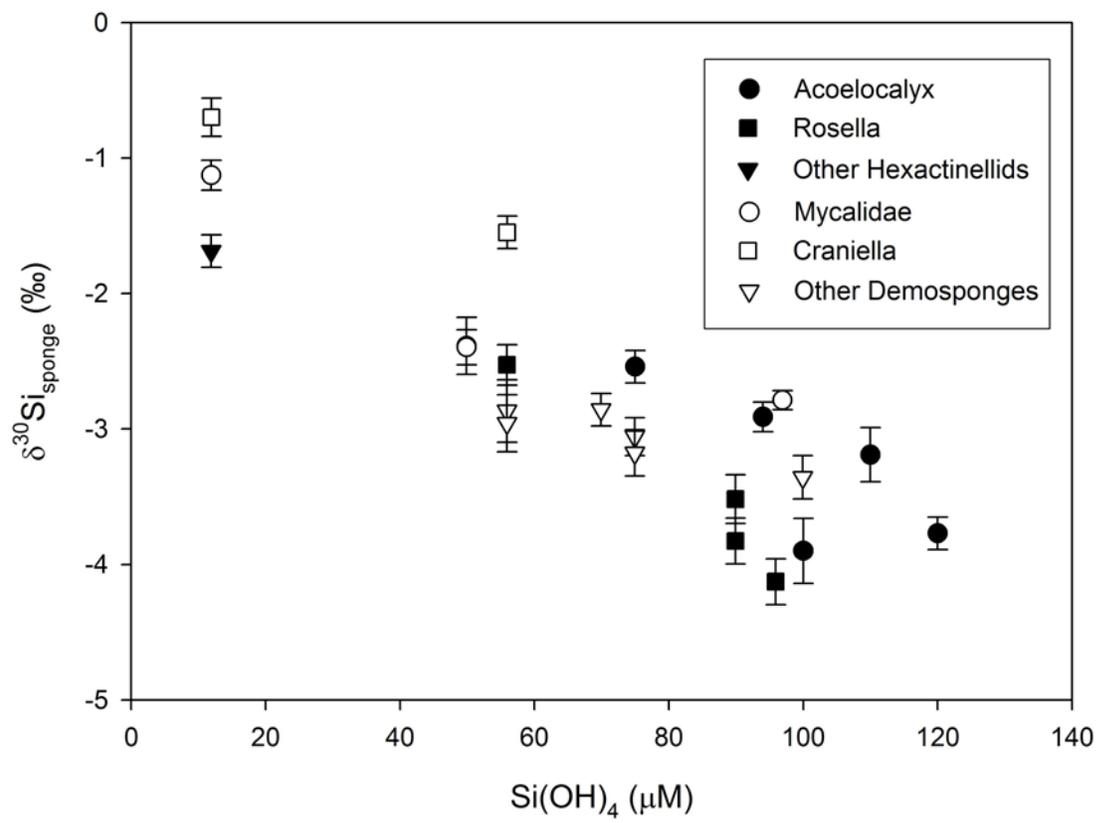


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719 Figure 1b

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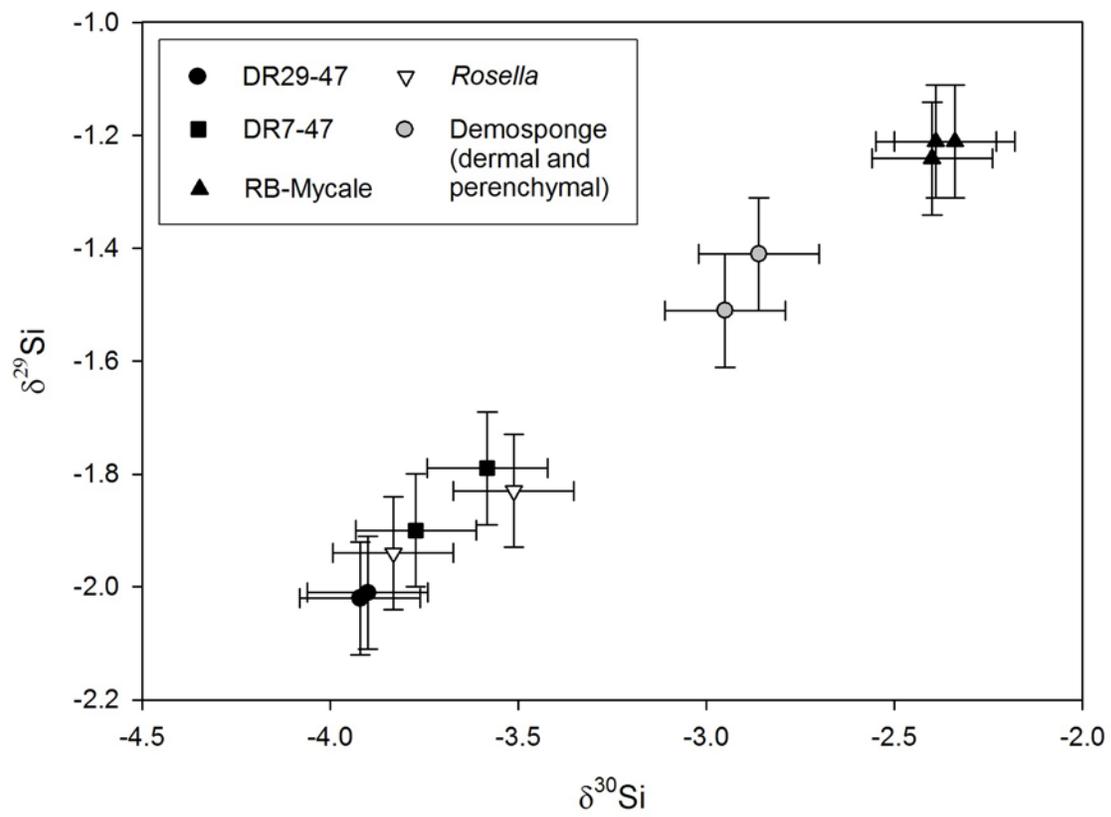
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723 Figure 2a

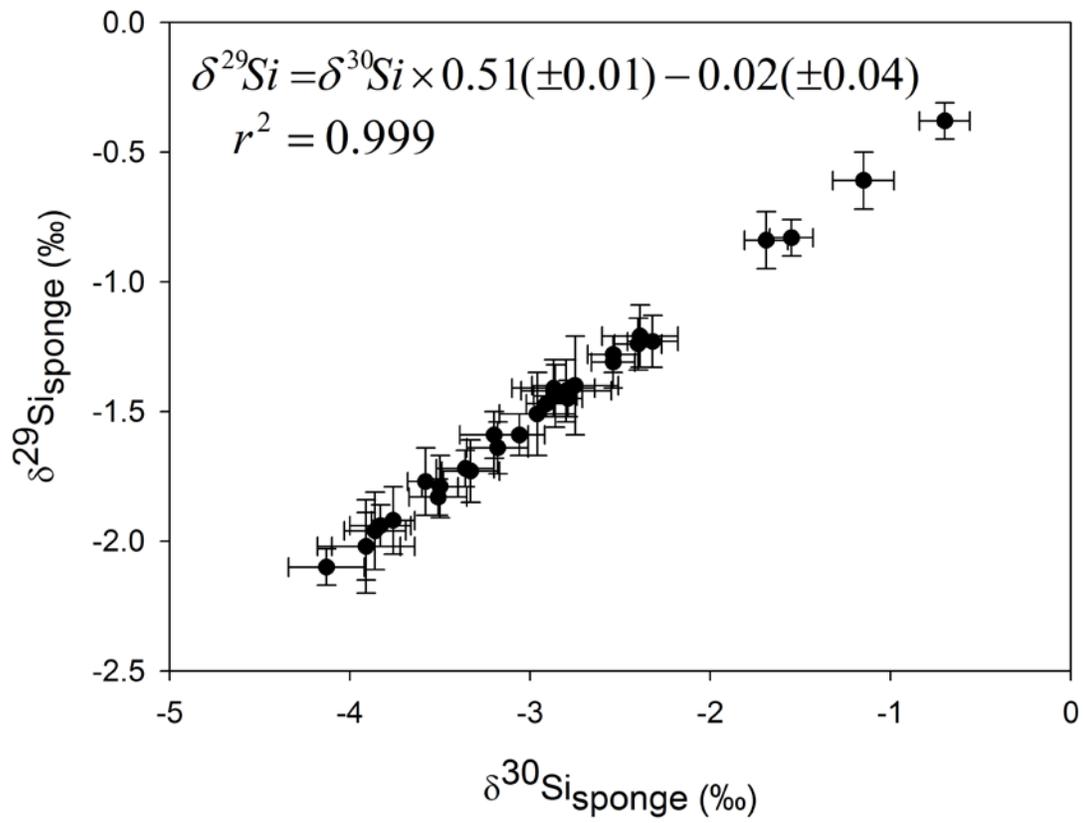
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726 Figure 2b

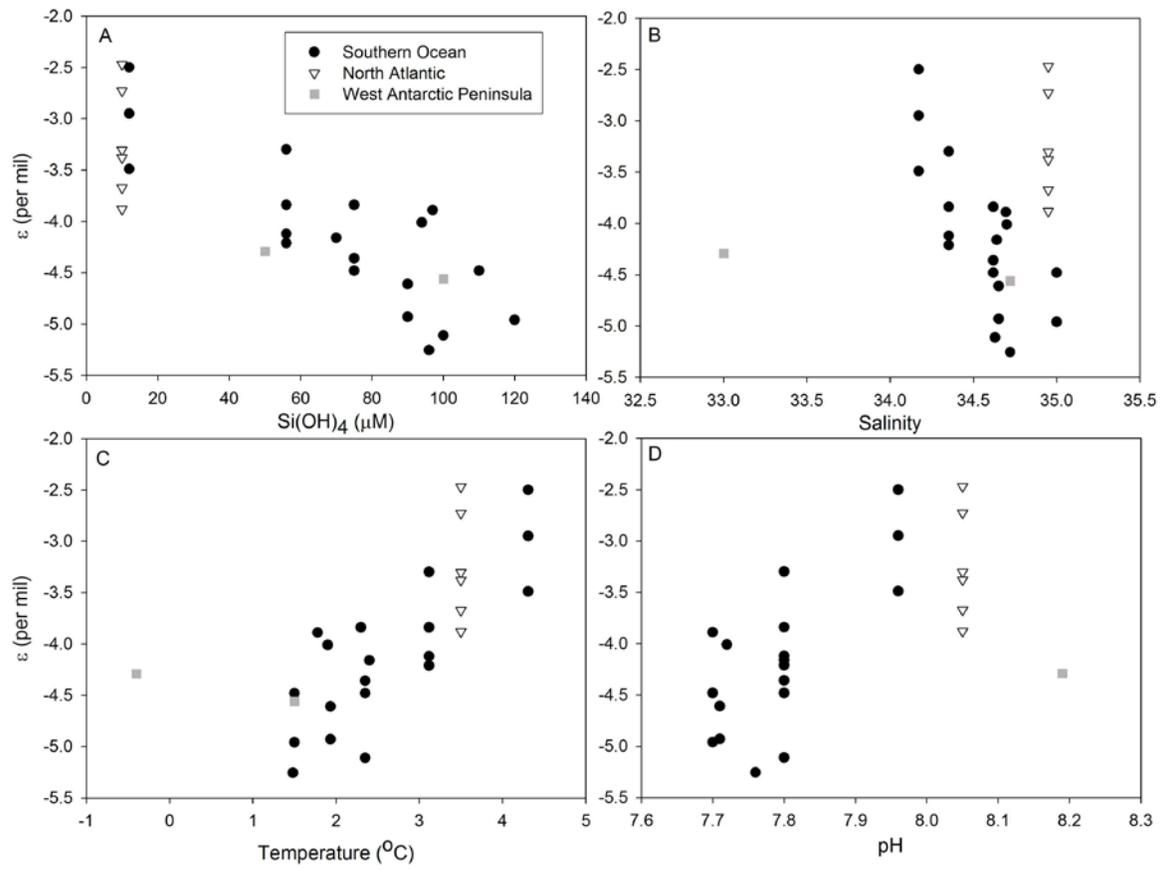
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729 Figure 2c

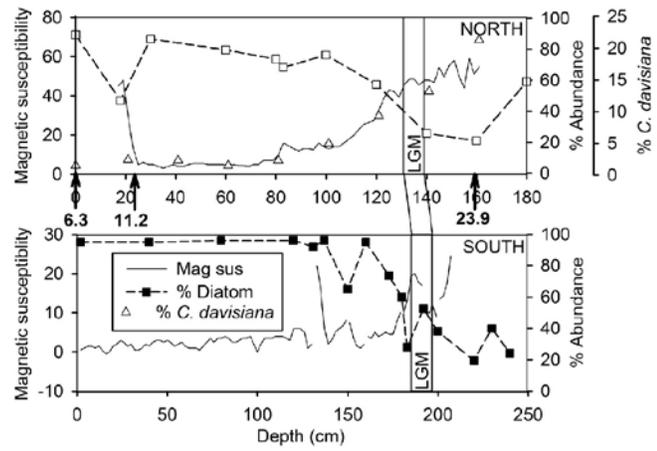
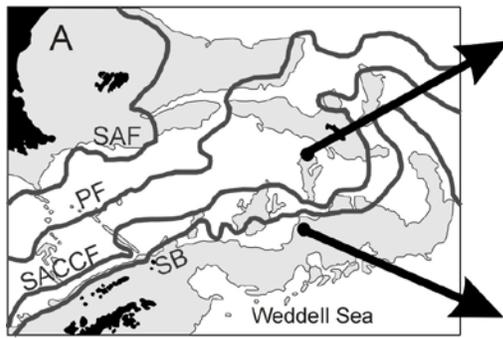
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732 Figure 3

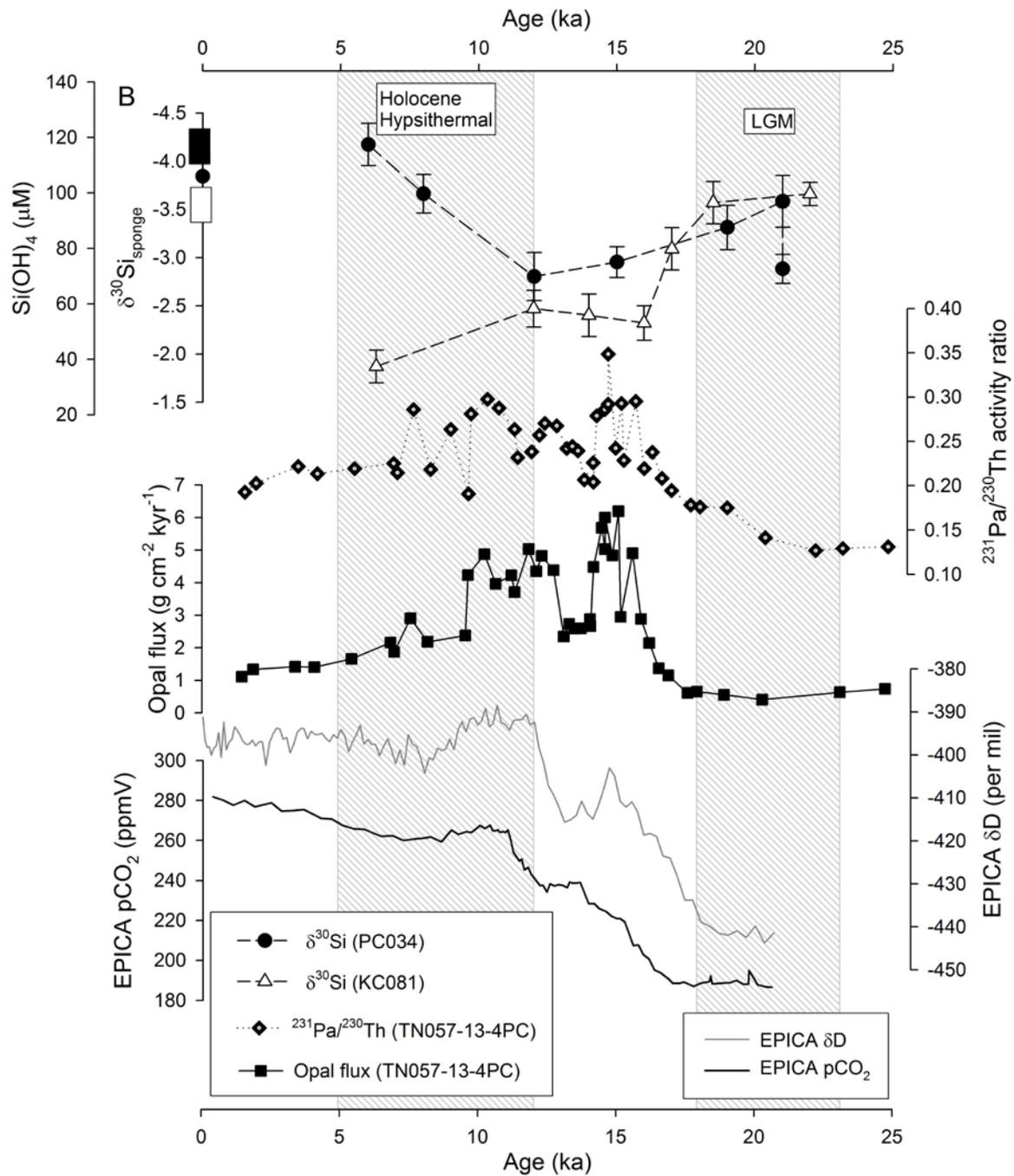
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734

735 Figure 4a

736



737

738 Figure 4b