Silicon isotopic fractionation in marine sponges: A new model for understanding silicon isotopic variations in sponges

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A B S T R A C T

The silicon (Si) isotope (δ30Si) composition of deep-sea sponges from near Antarctica, subantarctic waters (Tasmania Seamounts) and subtropical waters north of New Zealand vary widely between +0.87‰ and −3.40‰ (vs. NBS28). Depth profiles show that sponge δ30Si compositions trend to lower values with increasing depth. This is exemplified by sponges from the Tasmania Seamounts where δ30Si varies from +0.87‰ to −3.13‰ over a depth range from 100 m to 1200 m. These changes in δ30Si of sponges are inconsistent with a Rayleigh type isotope fractionation model requiring constant δ30Si fractionation between sponge and seawater. We conclude that overall Si isotope fractionation Δ30Si (δ30Si sponge − δ30Si seawater) is influenced by seawater Si concentration, with more fractionated (lower) isotope values being associated with sponges collected from waters high in Si. We invoke and model how it relates to the Si concentration of the water in which they live. Herein, we investigate the δ30Si composition of diatoms and seawater and we propose model how it relates to the Si concentration of the water in which they live.

1. Introduction

Understanding the current and past inventory and distribution of silicon (Si) in the deep Southern Ocean is central to determining the links between diatom productivity and atmospheric pCO2, especially during the glacial period (Matsumoto et al., 2002; Brzezinski et al., 2002). Currently the only proxies for reconstructing the inventory and distribution of Si during the past are based on the germanium:silicon (Ge:Si) composition of diatoms and sponges and the silicon isotope (δ30Si) composition of diatoms. The main issue with using the Ge:Si proxy is that it is dependent on the oceanic inventory of both Ge and Si. Detailed work has revealed that there is an extra oceanic sink for Ge, thus Ge and Si cycling in the ocean can decouple leading to uncertainties in their overall inventories (Hammond et al., 2004, 2000; King et al., 2000; McManus et al., 2003).

The δ30Si composition of diatoms has been used to reconstruct surface ocean Si concentrations (De La Rocha et al., 1998; Wischmeyer et al., 2003), based on a constant Si isotopic fractionation factor relative to seawater (0.9989 ± 0.0004) (De La Rocha et al., 1997). Recent studies have assumed that variations in the δ30Si composition of diatoms and seawater is governed by a closed-system Rayleigh fractionation process or by an open-system steady-state model (Cardinal et al., 2005; Beuchner et al., 2008; Reynolds et al., 2006). However, field studies reveal that the δ30Si compositions of diatoms do not strictly conform to Rayleigh behaviour nor consistently fit proposed models that assume constant fractionation of δ30Si between seawater and diatoms (Cardinal et al., 2007; Varela et al., 2004). In addition, diatoms are surface dwellers thus they only give a surface water signal.

Herein, we investigate the δ30Si composition of sponges and its relationship with ambient seawater Si concentration and isotopic composition. Sponges were chosen because they can be found throughout the water column and across a range of latitudes, thus potentially allowing the Si inventory of the ocean to be reconstructed. In this study siliceous sponges from both the Hexactinellid and Demosponge classes were obtained from the three distinct geographic regions and across a range of depths. The Si concentration varied significantly between sites thus providing a “natural” laboratory setting to explore δ30Si fractionation within sponges. The specific aim of this work is to describe δ30Si fractionation in sponges and model how it relates to the Si concentration of the water in which they live.
2. Materials and methods

2.1. Sample acquisition

Sponge samples were collected using a beam trawl from sites near Antarctica (63–67°S and 139–150°E), Tasmania (43–44°S and 146–150°E), and northern New Zealand (30–35°S and 172–179°E) (Fig. 1). After collection, sponges were frozen. For the Antarctic sponges, seawater samples from the overlying water column were collected with 10 L Niskin bottles attached to a standard rosette-CTD unit (SeaBird, USA). Water samples were filtered through 0.45 µm polycarbonate filters (Millipore type) and stored in 1 L acid-cleaned, low-density polyethylene bottles.

2.2. Sample preparation and measurements

The concentration of Si in seawater was determined colourimetrically using matrix-matched standards (Koroleff, 1976). Sponge samples were cleaned prior to digestion following a method modified after Ellwood et al. (2006), using a solution (w/v) of 12 M hydrochloric acid (reagent grade, Sigma) and 30% hydrogen peroxide (reagent grade, Sigma) at +50 °C for 24 h to remove extraneous organic matter. The samples were then rinsed with deionized water (Millipore, Milli-Q) and dried at +50 °C overnight before milling in a tungsten-carbide TEMA mill. The ne powders were subsequently heated at 550 °C for 16 h in alumina crucibles to oxidize any remaining organic matter.

After weighing ~5 mg of sample powder into a 10 mL Teflon bomb, sodium hydroxide monohydrate (Fluka, TraceSelect) was added (ratio NaOH.H2O/sample ~30 by weight) (van den Boorn et al., 2006). One milliliter of deionized water was added to the mixture which was then decomposed in a Parr bomb for 2 days in a furnace at 200 °C. Additional deionized water was added to the sample and it was reheated for 1 h at ~60 °C. The sample solution was then diluted to 30 mL with deionised water and stored in pre-cleaned high-density polyethylene bottles.

Poly-Prep® chromatographic columns (Bio-Rad) loaded with 1 mL cation exchange resin (Dowex AG-X8, 200–400 mesh) were used to remove sodium. After cleaning the resin with HCl and deionised water (van den Boorn et al., 2006), each column was loaded with 2 mL of sample solution containing a total Si concentration of ~20 mg/L. The Si was then eluted from the column bed using 9 mL of deionised water and the eluant acidified with 1 mL of 2 M HNO3. The resulting silicon concentration in the solution was ~4 mg/L.

Silicon isotopic ratios were determined by multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) (Finnigan Neptune, Germany) operated in medium-resolution (M/ΔM ~2000) and dry plasma mode. The sample was introduced to the MC-ICP-MS via an ESI-Apex nebulizer fitted with a Teflon inlet system and a demountable torch fitted with an alumina injector to minimize the Si background. Data acquisition and reduction were carried out using a standard-sample-standard bracketing technique (Albarede et al., 2004). Prior to each sample run, blank measurements are made to ensure that the combined blank and background contribute less than 1% of the total sample signal. The reproducibility of the δ30Si signal (Δ30Si=[30Si/28Si]sample/[30Si/28Si]std−1)×1000] measured on the NBS28 standard prepared in-full on four separate occasions was ±0.21‰ (2σ standard deviation (SD)), which agrees with the calculated δ30Si regression error of ±0.23‰ (2 SE, n = 32) from the plot of δ29Si vs. δ30Si (Fig. 2). The best-fit mass dependent fractionation line (δ30Si/δ29Si = 0.510) is consistent with the consensus slope of 0.511 obtained by inter-laboratory silicon standard measurements and is in agreement with a theoretical kinetic Si isotope fractionation of 0.5092 (Reynolds et al., 2007). Measurements of the inter-laboratory diatomite standard prepared and measured on different days produced average values for δ30Si of +0.64 ± 0.08‰ and δ29Si of +1.29 ± 0.14‰ (2 SD, n = 32) (Table 1). These values are in good agreement with values obtained by other laboratories (Reynolds et al., 2007). Because of the low number of measurements, the small errors obtained for this standard underestimates the true long-term errors for the method which is closer to ±0.23‰, δ30Si (2σ) (Fig. 2). Most of this error appears to be associated with instrumental instability.

Fig. 1. Map showing the location of sampling stations for coupled sponge and seawater profiles sponge adjacent to Tasmania (circles, n = 15), Antarctica (squares, n = 12), and New Zealand (diamonds, n = 5). Yellow triangles showing the location of sampling stations for seawater profiles CTD17 and CTD124 (Cardinal et al., 2005).
Fig. 2. Mass dependent fraction (MDF) of δ²⁹Si vs. δ³⁰Si plot for samples collected from 3 depth profiles in the southern ocean including Tasmania (circles), Antarctica (squares) and New Zealand (diamonds). MDF line represented by δ³⁰Si=0.51°δ²⁹Si, R²=0.99, 2 SE = 0.23°δ³⁰Si.

3. Results

Profiles of measured δ³⁰Si in siliceous sponges collected from the three ocean regions are presented in Fig. 3 and Table 1. Also shown are seawater δ³⁰Si values (calculated by dividing δ³⁰Si values by 0.5092 (Reynolds et al., 2006) for nearby stations determined by Cardinal et al. (2005) and the seawater δ³⁰Si composition of bottom waters measured at each site. Our use of the Cardinal et al. (2005) δ³⁰Si data from nearby stations to estimate the seawater δ³⁰Si versus depth profiles. For example, the difference in δ³⁰Si between stations CTD87, 63.9°S versus CTD124, 64.9°S across a similar depth range is around 0.4‰ (Cardinal et al., 2005). And the overall δ³⁰Si across all the Cardinal et al., 2005 stations is 1.3‰. This is much smaller than the range for deep sponges of 4.3‰ (Table 1).

The Tasmanian profile is characterised by a large increase in seawater Si concentration from 2 µM at the surface to 50 µM at depth (1200 m). This increase is accompanied by a large change in the δ³⁰Si composition of sponges, with values become lower with depth (+0.87‰ to −3.13‰). This contrasts the seawater δ³⁰Si values which show only a slight decline in the upper water column 0–1200 m (+1.64‰ to +1.13‰, station CTD17, 46.9°S) (Cardinal et al., 2005). These results indicate a systematic increase in Δ³⁰Si (δ³⁰Si Sponges–δ³⁰Si Seawater) fractionation between sponges and seawater with increasing depth.

Table 1

<table>
<thead>
<tr>
<th>Sponge Class</th>
<th>Sponge Order</th>
<th>Sponge Family</th>
<th>Depth (m)</th>
<th>Si water [µmol/kg]</th>
<th>Latitude/Longitude</th>
<th>δ³⁰Si sponge</th>
<th>δ³⁰Si sponge</th>
<th>δ³⁰Si-water</th>
<th>Δ³⁰Si F</th>
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</thead>
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<tr>
<td>Demospongiae</td>
<td>Hadromerida</td>
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<td>100</td>
<td>2 ± 0.02</td>
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</table>

Average 2 S.D. | 0.64 | 1.29 |

Average 2 S.D. | 0.08 | 0.15 |
In contrast to the Tasmanian profile, Si concentrations in the Antarctic waters are high with benthic concentrations around 78 µM between 390 m to 1200 m (Fig. 3B, Table 1). With the exception of one sample from 212 m depth, with a δ³⁰Si of −0.6‰, the δ³⁰Si values for sponges in these waters occupy a narrow range between −2.15‰ and −3.42‰. The lower Si fractionation of sponge sample at 212 m is attributed to close proximity to seasonal sea ice production which may produce localised δ³⁰Si variations. Thus we choose to exclude this sample from further discussion. When our sponge δ³⁰Si results are compared to the seawater δ³⁰Si results as calculated from Cardinal et al. (2005), a large offset between the sponge and seawater values is observed, with the sponge data being about 4‰ lower.

The δ³⁰Si for sponges collected from north of New Zealand show a similar δ³⁰Si profile behaviour as the Tasmanian samples with values ranging from −0.16‰ to −3.40‰. Water samples have not been collected at these sites, consequently no direct seawater Si concentrations are available nor is there seawater δ³⁰Si data. The Si concentration data presented in Fig. 3C were obtained from the World Ocean Circulation Experiment (WOCE) database for location 173.49°E, 30.086°S. Similar to the Tasmanian profile, the δ³⁰Si data for sponges collected north of New Zealand systematic changed to lower values with increasing depth and increasing Si concentration.

Our results show that δ³⁰Si composition of sponges are systematically lower than the surrounding seawater δ³⁰Si, consistent with the preferential incorporation of lighter Si isotopes into siliceous spicules (De La Rocha, 2003; Douthitt, 1982) (Table 1). Indeed, when the δ³⁰Si sponge signal is subtracted from δ³⁰Si seawater signal, Δ³⁰Si fractionation trends to lower, more negative values with increasing silicon concentration (Fig. 4). A Rayleigh type fractionation model with a constant fractionation factor between sponges and seawater is inadequate in describing the observed variations in the sponge dataset. Only large changes in the proportion of Si utilised from seawater over the sponges’ lifetime could have lead to a variable fractionation factor between seawater and sponges. Since the δ³⁰Si seawater variations versus depth and latitude are in the order of 1.3‰ while differences in δ³⁰Si sponge values are up to 4.3‰ such changes are very unlikely of have been occurred.
4. Discussion

Our observation that $\Delta^{30}\text{Si}$ fractionation increases with increasing Si concentration (Fig. 3) suggest that previous interpretation of $\delta^{30}\text{Si}$ fractionation in sponges needs revision. Whereas previous studies have assumed a constant fractionation factor between the bio-siliceous and aqueous phases and ascribed variations to Rayleigh type fractionation within a closed or open-system to a constant fractionation factor (Cardinal et al., 2007; De La Rocha et al., 1997; Reynolds et al., 2006; Varela et al., 2004). Our results indicate that fractionation is variable with fractionation increasing at higher Si concentrations (Fig. 4). While our results indicate that Si availability appears to be the main factor influencing the $\delta^{30}\text{Si}$ composition of sponges, other variables that also change in a similar manner to Si need to be considered and will be discussed at the end of this section.

Studies have shown that low Si concentrations are limiting the silicon uptake in sponges (Maldonado et al., 1999, 2005) and that the formation of biogenic silica in sponges is governed by Michaelis–Menten uptake and efflux kinetics which can be described with the following equation (Reincke and Barthel, 1997):

$$v_{\text{Si}} = \frac{v_{\text{max}}[\text{Si}]}{K_{m} + [\text{Si}]}$$  \hspace{1cm} (1)

where $v_{\text{max}}$ is the maximum Si velocity, $K_{m}$ is the half saturation constant and $[\text{Si}]$ is the external Si concentration. The results of Reincke and Barthel (1997) for Si uptake by the sponge Halichondria panicea (Pallas, 1766) conform to the equation, although their results are different values for $K_{m}$ and $v_{\text{max}}$. Based on the data from Reincke and Barthel (1997) different values for $K_{m}$ and $v_{\text{max}}$ can be applied across a range of Si concentrations (Fig. 6). Because $^{28}\text{Si}$ is the lighter isotope and requires less energy to diffuse to and be transported across the cell membrane it is expected to have a larger $v_{\text{max}}$ than $^{30}\text{Si}$. This results in a constant $\Delta^{30}\text{Si}$ with changing Si concentration (Fig. 6), as is thought to occur in diatoms. However this is inconsistent with our sponge data where $\Delta^{30}\text{Si}$ increases with increasing Si concentration. Since both isotopes have identical chemical behaviour, their transport mechanism(s) should be identical and they should share the same $K_{m}$ value. Even with scenarios where $K_{m}^{30}\text{Si} > K_{m}^{28}\text{Si}$ or $K_{m}^{28}\text{Si} > K_{m}^{30}\text{Si}$, $\Delta^{30}\text{Si}$ fractionation is large at a low Si concentration and decreases with increasing silicon concentration, the opposite of the observed $\Delta^{30}\text{Si}$ trends (Fig. 6).

Model 1: Fractionation only occurs during uptake.

If isotopic fractionation occurs during uptake it likely occurs in a Michaelis–Menten like fashion where the lighter isotope, $^{28}\text{Si}$, is transported at a faster rate than its heavier counterpart $^{30}\text{Si}$. Following Ellwood et al. (2006) who used a similar model to describe Ge:Si fractionation in sponges, the Michaelis–Menten uptake of these two isotopes can be expressed as:

$$\frac{^{30}\text{Si}}{^{28}\text{Si}} = \frac{v_{\text{max}}^{30}\text{Si}}{v_{\text{max}}^{28}\text{Si}} = \frac{K_{m}^{30}\text{Si} + [\text{Si}]}{K_{m}^{28}\text{Si} + [\text{Si}]}$$  \hspace{1cm} (2)

where $K_{m}^{30}\text{Si}$ and $K_{m}^{28}\text{Si}$ are the half saturation constants for $^{30}\text{Si}$ and $^{28}\text{Si}$, respectively. Based on the data from Reincke and Barthel (1997) the Michaelis–Menten uptake process described in Eq. (2). Note the decreased $\Delta^{30}\text{Si}$ fractionation with increasing Si concentration, the opposite that is observed from sponges.

![Fig. 5. $\Delta^{30}\text{Si}$ plotted versus Si concentration along with the kinetic uptake data for Halichondria panicea (Pallas, 1766). Silicon uptake data taken from Reincke and Barthel (1997). Note that the $\Delta^{30}\text{Si}$ scale has been reversed.](image)

![Fig. 6. $\Delta^{30}\text{Si}$ fractionation as a function of isotope uptake based on Michaelis–Menten uptake process described in Eq. (2). Note the decreased $\Delta^{30}\text{Si}$ fractionation with increasing Si concentration, the opposite that is observed from sponges.](image)
Substituting Eq. (4) into Eq. (3) yields:

$$\varepsilon_t = \varepsilon_{t1} + (\varepsilon_P - \varepsilon_{t2}) \left(1 - \frac{v_{\text{Si,P}}}{v_{\text{Si,I}}}\right)^{-1}(5)$$

As expressed, the net $\delta^{30}\text{Si}$ fractionation $\varepsilon_t$ should be a linear function of the Si polymineralisation to Si influx ratio. Thus a plot of $\Delta^{30}\text{Si}$ versus $(1-v_{\text{Si,P}}/v_{\text{Si,I}})$ should be linear with an intercept being equal to $\varepsilon_{t1}$ and slope equal to $(\varepsilon_P - \varepsilon_{t2})$. Since $v_{\text{Si,I}}$ and $v_{\text{Si,P}}$ are both Michaelis–Menten functions, Eq. (5) can be expressed as:

$$\varepsilon_t = \varepsilon_{t1} + (\varepsilon_P - \varepsilon_{t2}) \left(1 - \frac{v_{\text{max,P}}}{v_{\text{max,I}}}\right)^{-1}(6)$$

where $v_{\text{max,P}}$ is the maximum incorporate rate for Si and $K_{m,P}$ is the half saturation rate for Si incorporation. Eq. (6) shows that $\varepsilon_P$, the $\delta^{30}\text{Si}$ composition of sponge spicules, is directly dependent on the external Si concentration. If $v_{\text{max,P}}$ and $K_{m,P}$ are known (Reincke and Barthel, 1997), four constants ($\varepsilon_{t1}$, $\varepsilon_P - \varepsilon_{t2}$), $v_{\text{max,I}}$ and $K_{m,I}$) remain undefined. However, as external Si concentration approaches zero, then Eq. (6) asymptotes to:

$$\lim_{[\text{Si}] \rightarrow 0} \varepsilon_t = \varepsilon_{t1} + \Delta \varepsilon_{P} \left(1 - \frac{v_{\text{max,I}}}{v_{\text{max,P}}}\right)^{-1}(7)$$

with $\Delta \varepsilon_{P}$ replacing $(\varepsilon_P - \varepsilon_{t2})$ for ease of notation. At very low Si concentration, most or all of the Si entering the sponge is consumed for spicule formation. Consequently $v_{\text{Si,P}} = v_{\text{Si,I}}$ and $\varepsilon_t = \varepsilon_{t1}$. The last term of Eq. (7) will go to zero and the ratio term must be unity, thus $K_{m,I}$ can be expressed as a function of $v_{\text{max,I}}$, i.e.:

$$K_{m,I} = \frac{v_{\text{max,I}}}{v_{\text{max,P}}}(8)$$

Substituting Eq. (8) into Eq. (6) eliminates $K_{m,I}$, but we are still left with 3 unknowns: $\varepsilon_{t1}$, $\Delta \varepsilon_{P}$ and $v_{\text{max,P}}$.

To estimate the three remaining unknowns and to demonstrate that Eq. (6) represents an adequate theoretical expression reflecting the isotopic data, we used a least squares data fitting approach (Aster et al., 2005). By varying the three unknowns in Eq. (6) a set of predicted $\varepsilon_{\text{pred}}$ values are obtained for corresponding Si concentrations. The difference between predicted $\varepsilon_{\text{pred}}$ and observed $\varepsilon_{\text{obs}}$ values (Table 1) can be represented by a least squares misfit function. Specifically, we can write the misfit function as:

$$\phi(\varepsilon_{t1}, \Delta \varepsilon, v_{\text{max}}) = \sum_{[\text{Si}]} (\varepsilon_{\text{obs}}([\text{Si}]) - \varepsilon_{\text{pred}}([\text{Si}]))^2(9)$$

where $\varepsilon_{\text{pred}}$ are the values produced by using Eq. (6) for specific values of the three unknowns, across defined Si concentrations. Since the misfit function tells us how well measured and predicted data agree, the $\varepsilon_{t1}, \Delta \varepsilon_{P}$ and $v_{\text{max}}$ values obtained from this function at its minimum represent the best fit to the measured isotope data (Fig. 7A, B). While there is a minimum in the misfit function leading to a single $\varepsilon_{t1}$ value of $-1.34\%$ (Fig. 7A), there are multiple combinations for $\Delta \varepsilon_{P}$ and $v_{\text{max}}$ that correspond to this minimum (Fig. 7B). The value $\varepsilon_{t1}$ of $-1.34\%$ represents $\Delta^{30}\text{Si}$ fractionation associated during uptake and closely matches values obtained for diatoms where $\delta^{30}\text{Si}$ fractionation is dominated by uptake transport (De La Rocha et al., 1997; Milligan et al., 2004).

Conversely when the Si concentration approaches infinity Eq. (6) has the asymptotic form:

$$\lim_{[\text{Si}] \rightarrow \infty} \varepsilon_t = \varepsilon_{t1} + (\varepsilon_P - \varepsilon_{t2}) \left(1 - \frac{v_{\text{max,P}}}{v_{\text{max,I}}}\right)^{-1}(10)$$

At infinitely high Si concentrations, Eq. (6) reduces to a set of constants thus forcing $\varepsilon_t$ to be constant. Since $\varepsilon_{t1}$, $v_{\text{max,P}}$ and the relationship between $\Delta \varepsilon_{P}$ and $v_{\text{max,I}}$ are known, we compute a maximum $\varepsilon_t (\Delta^{30}\text{Si})$ of $-6.02\%$ at $\text{Si} \rightarrow \infty$. Using a value of $-1.34\%$ for $\varepsilon_{t1}$, and best-fit values for the $\varepsilon_P - \varepsilon_{t2}$ and $v_{\text{max,P}}$ pair obtained from the misfit function (Fig. 7A, B), we generated a set of model isotope data (predicted) and then compared this to the measured isotope data (Fig. 8A). Since the model is a best-fit representation of our measured data all values should correlate linearly. Indeed, a linear correlation is obtained with a correlation coefficient of $R^2 = 0.86$ with a $p$-value < 0.0001 demonstrating that the model is a reasonable representation of Si isotope fractionation in sponges. Application of this model allows calculation of $\Delta^{30}\text{Si}$ ($\varepsilon_t$) in biogenic silica across a range of Si concentrations and vice versa.

The asymptotic behaviour of the model indicates that at higher Si concentration, $\Delta^{30}\text{Si}$ tend towards a value of $-6.02\%$. Indeed, two sponges collected from North Pacific had $\Delta^{30}\text{Si}$ of $-3.8\%$ and $-3.9\%$ (De La Rocha, 2003) which is in line with the high Si concentration for...
this region (∼170 μmol/L Si for location 34.817°N 124.582°E at 3992 m depth).

The agreement between the model and observed Δ\text{30Si} values does not unambiguously prove the validity of the model; other variables that also change with depth need to be considered. A good correlation between nitrate and phosphate concentration with Si concentration and Δ\text{30Si} values can be observed. However it is difficult to see how phosphate and nitrate influence sponges directly because they obtain these two nutrients directly from the organic material that they filter. In coastal waters phosphate and nitrate have been found to be negatively to sponge growth rate for costal sponge *Halichondra oculata* (Koopmans and Wijffels, 2008). However this influence is likely to be a direct influence on phytoplankton productivity which will influence sponge food supply. Indeed, in coastal settings, sponges consume ∼75% of the daily organic carbon produced by these planktonic communities (Duckworth and Pomponi, 2005). It is known that availability of phosphate and nitrate can influence surface water community composition and biomass (Jacobsen et al., 1995). However for our Tasmanian and the Antarctic sponges, phosphate and nitrate concentrations are generally not regarded as growth limiting to phytoplankton (the phosphate and nitrate concentrations in surface waters near our Tasmanian site were c. 0.6 μmol L\(^{-1}\) and 7 μmol L\(^{-1}\), respectively). And since the sponges in this study were collected from depths ≥100 m, a direct effect of these nutrients on deep water sponges seems to be unlikely. Sponges are active suspension feeders, therefore a more direct correlation between growth rates and suspended particulate organic matter (POM) would be logical and has been observed (Koopmans and Wijffels, 2008). To estimate the potential influence of POM on sponge growth and Si isotope fractionation, we estimated the Apparent Oxygen Utilization (AOU) for each sponge site and correlated this to Δ\text{30Si}. We obtained a correlation coefficient of R\(^2\) = 0.19 between Δ\text{30Si} and AOU. This thereby excludes AOU as a significant factor controlling the Si isotope fractionation in sponges (Water column data: Cruise PR13N_09FA1089_1, stn = 19, Long = 149.33, Lat = 43.25; PR12_09AR9407_1, stn = 71, Long = 140.20, Lat = 66.46). Looking at the Δ\text{30Si} compositions from sponges at the Tasmanian and Antarctic sites separately, different behaviours versus nitrate and phosphate concentration, depth and pressure can be observed also proving independence of the Si cycle from these variables.

The one remaining factor that needs to be considered is temperature. As with phosphorous and nitrate, one of the problems in deconvoluting the influence of Si from temperature is the fact that colder waters also tend to have higher Si concentration. Theoretical studies have shown that fractionation is a linear function of 1/T\(^2\), where T is temperature (Hoefs, 2009). Indeed, when the Tasmanian data is plotted versus 1/T\(^2\) a good correlation is obtained where Δ\text{30Si} fractionation increases as temperature decreases (Fig. 8B). However, two observations make us favour Si concentration as the main factor controlling Si isotope fractionation in sponges:

1. The Tasmanian sponges from c. 1200 m have similar Δ\text{30Si} values to their Antarctic counterparts despite a temperature difference of 4 °C. Indeed, the Δ\text{30Si} values for Antarctic sponge fall to right of the Δ\text{30Si} versus 1/T\(^2\) relationship for the Tasmanian sponge set (Fig. 8B);

2. The δ\text{30Si} composition of warm (c. +30 °C), tropical surface water sponges from Indonesia (Vroon et al., 2004) range between 0.5‰ and +2.0‰ and have similar δ\text{30Si} compositions to the temperate (c. +10 °C) shallow-water sponges from Tasmanian sponges (0.00‰ and +0.87‰). If δ\text{30Si} fractionation was strongly temperature dependent, one might expect the Indonesian sponges to have much more positive δ\text{30Si} composition.

The definitive experiment to completely rule out temperature as a factor strongly influencing δ\text{30Si} fractionation in sponges would be to obtain contemporary sponges from the North Atlantic where Si concentrations are low. If temperature is a significant factor influencing δ\text{30Si} fractionation, North Atlantic sponges should have an isotopic composition similar to that of Antarctic sponges. If temperature plays only a minor or no role in δ\text{30Si} fractionation, as we believe, North Atlantic sponges should have an isotopic composition similar to shallow-water Tasmanian sponges.

The Indonesian δ\text{30Si} dataset also shows some variability despite sponges coming from the same sampling site (Spermonde Archipelago) assuming similar Si concentrations. These variations may result from symbiotic associations between photosynthetic bacteria and these shallow-water sponges (Peter Vroon personal communication). In addition to changing Si concentrations, some of the variability within our dataset may also result from sponge–bacterial associations, although these would be non-photosynthetic in nature because the sponges are from deeper waters. However these associations are likely to be difficult to quantify.

The dependence of Si isotope fractionation in sponges upon the external Si concentration of seawater provides a new framework for reconstructing past changes in Si concentration and δ\text{30Si} composition of the ocean. The asymptotic nature of Δ\text{30Si} versus Si concentration...
indicates that application of this isotope proxy to fossil sponge spicules will be prone to high uncertainties at more negative δ30Si values. However, this does not negate its usefulness as a paleo-Si proxy, because the proxy is highly sensitive to changes in Si concentration below c. 100 µmol/L. Because δ30Si composition of seawater is largely invariant in deep waters (Reynolds, 2009) and is relatively insensitive to changes in terrestrial Si inputs (De La Rocha and Bickle, 2005) this proxy is potential useful for recording changes in the Si concentration of the deep ocean through time.

5. Conclusion

Sponge sponges inhabit a broad range of locations and depths throughout the ocean making them ideal for studying the Si cycle in oceans. Large variations in the δ30Si composition of sponges and isotopic fractionation relative to ambient seawater are linked to changes in seawater Si concentration. More fractionated (lighter) isotope values occur in sponges growing in waters with more Si. Since the Si isotopic data in sponges show good agreement with a Michaelis–Menten function for Si uptake, δ30Si fractionation appears to be biological controlled. Based on previous theoretical considerations describing the carbon and Si isotopic fractionation in terrestrial plants and marine diatoms, respectively, a model is proposed by which δ30Si fractionation is regulated by the Si influx to efflux ratio which, in turn, is controlled by the external Si concentration of seawater. The model indicates that isotope fractionation associated with uptake transport is constant at 1.34‰ whereas fractionation during spicule formation increases as a function of external Si concentration. The model developed is asymptotic in nature with Δ30Si trending towards lighter values as the seawater Si concentration increases. However the model also predicts that the observed Δ30Si in sponges will never exceed −6.02‰. Application of the model allows us to calculate Δ30Si for spicules at a given Si concentration and vice versa. The asymptotic behaviour of the model also allow us to indirectly determine the δ30Si composition of seawater for spicules of a late Proterozoic to early Phanerzoic age when the overall Si concentration of the ocean was believed to have been much higher compared to the present-day ocean (Kidder and Erwin, 2001).

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References


