Deconvolving the controls on the deep ocean’s silicon stable isotope distribution

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1. Introduction

Diatoms are siliceous phytoplankton with an obligate requirement for silicon (Si) to form their opaline cell walls, or frustules. As a result of their large cell size and boom–bust ecological strategy, diatoms are important contributors to the ocean’s biological carbon pump (Buesseler, 1998; Henson et al., 2012), and are the dominant driver of the oceanic Si cycle (Tréguer and De La Rocha, 2013). The resulting link between the oceanic cycles of silicon and carbon (e.g. Dugdale and Wilkerson, 2001; Ragueneau et al., 2006) has motivated much research into the controls on the biogeochemical Si cycle, both in the modern ocean and during past glacial–interglacial cycles (e.g. Dugdale et al., 2002; Brzezinski et al., 2003; Griffiths et al., 2013; Meckler et al., 2013). A promising tool for such research is the stable isotope composition of silicon, expressed as δ30Si (defined in permil units as (Rsample/Rstd − 1) × 1000, where Rsample is the 30Si/28Si isotope ratio in a sample and Rstd is this ratio in the standard NBS28).

Diatoms preferentially incorporate the lighter isotopes of Si into their frustules during silicification (De La Rocha et al., 1997; Milligan et al., 2004; Sutton et al., 2013). As a result, biological utilization of Si in surface waters enriches dissolved Si in its heavier isotopes, imparting an elevated δ30Si signature to surface waters that have experienced diatom Si uptake (Varela et al., 2004; Cavagna et al., 2011). Within the ocean interior, the dissolution of sinking diatom opal that has been exported from the surface also influences the δ30Si value of dissolved Si, an effect that might be enhanced by Si isotope fractionation during dissolution (Demarest et al., 2009). Since these two processes, diatom Si uptake and opal export, drive the largest Si fluxes in the ocean (Tréguer and De La Rocha, 2013), the oceanic δ30Si distribution bears information on the dominant pathways and processes by which Si is cycled within the ocean (e.g. Cardinal et al., 2005; Fripiat et al., 2011a; de Souza et al., 2012a).

Due to isotope fractionation by diatom Si uptake at the surface, δ30Si values of dissolved Si reach their maximum at the surface, and exhibit lower values in the subsurface water column.
In addition to this intuitive vertical $\delta^{30}\text{Si}$ gradient, $\delta^{30}\text{Si}$ values also vary in deep waters at the global scale. Values of $\delta^{30}\text{Si}$ exhibit a systematic inter-basin gradient along the deep limb of the ocean’s meridional overturning circulation (MOC), decreasing from high values in the deep Atlantic, through intermediate values in the Southern Ocean, to low values in the deep North Pacific (De La Rocha et al., 2000; Cardinal et al., 2005; Reynolds et al., 2006). The exact controls on this large-scale deep water $\delta^{30}\text{Si}$ gradient—and thus the nature of oceanic Si cycling reflected by this feature—remain incompletely understood. Early observational and modeling studies invoked a variety of processes to explain its origin. For instance, De La Rocha et al. (2000) attributed the difference between Atlantic and Pacific deep water $\delta^{30}\text{Si}$ values to the cumulative effect of the dissolution of low-$\delta^{30}\text{Si}$ opal along the deep limb of the MOC. A later study by Beucher et al. (2008), however, used $\delta^{30}\text{Si}$ observations in the deep Pacific and Southern Oceans to argue that opal dissolving in the deep Pacific bears a higher $\delta^{30}\text{Si}$ value than deep waters. Wischmeyer et al.’s (2003) early general circulation model simulation, using the Large-Scale Geostrophic model of Maier-Reimer et al. (1993), was unable to shed light on this issue, since the model did not produce the inter-basin deep water $\delta^{30}\text{Si}$ gradient. The box models implemented by Reynolds (2009) did simulate systematic $\delta^{30}\text{Si}$ variation along the deep limb of the MOC, which he attributed to a combination of physical Si transport by the MOC and high Southern Ocean opal export fluxes.

Recently, a number of observational studies have documented strong regional- to basin-scale coherence in $\delta^{30}\text{Si}$ values, implying a strong physical control on the $\delta^{30}\text{Si}$ distribution at a range of depths in the water column. Fripiat et al. (2011b) and de Souza et al. (2012b) demonstrated the importance of physical processes in communicating the elevated $\delta^{30}\text{Si}$ signal produced at the surface into the ocean interior. These studies revealed that high $\delta^{30}\text{Si}$ values produced during summer are retained in the deep winter mixed layers of the Southern Ocean, and that this utilization signal is transported into the subtropical interior by Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW), consistent with the $\text{Si}^*$ distribution ($\text{Si}^* = \text{Si}-\text{NO}_3$; Sarmiento et al., 2004). Similarly, equatorial Pacific studies suggest that the Equatorial Undercurrent’s $\delta^{30}\text{Si}$ signature may be traced across 60 degrees of longitude (Beucher et al., 2008, 2011; Ehler et al., 2012; Grasse et al., 2013). Furthermore, a dominant control of the circulation has been observed on deep water $\delta^{30}\text{Si}$ variations at the basin scale: de Souza et al. (2012a) demonstrated that the meridional $\delta^{30}\text{Si}$ gradient within the deep Atlantic Ocean is related not to opal dissolution, but rather to the quasi-conservative mixing of Si between North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW).

The recent increase in the volume and spatial resolution of oceanic $\delta^{30}\text{Si}$ observations has thus provided powerful evidence for the largely conservative behavior of $\delta^{30}\text{Si}$ values in the ocean interior. The implied dominance of the physical circulation on the large-scale oceanic distribution of $\delta^{30}\text{Si}$—and hence that of Si—is somewhat surprising for a biogeochemically-cycled nutrient. In this study, we aim to identify the processes that determine this behavior, with a focus on the global deep water $\delta^{30}\text{Si}$ distribution. We deconvolve the physical and biogeochemical influences on the Si and $\delta^{30}\text{Si}$ distributions in an ocean general circulation model (OGCM) simulation that explicitly traces the preformed and regenerated components of Si.

Our conceptual distinction between preformed and regenerated Si is motivated by the differing controls on their distributions in the ocean interior. At the ocean’s surface, the balance between Si supply by the circulation on the one hand, and Si uptake & export by biology on the other, determines Si concentrations in the mixed layer. The properties of the winter mixed layer, including its Si concentration and $\delta^{30}\text{Si}$ value, are communicated to the ocean interior during subduction or deep water formation (Stommel, 1979; de Souza et al., 2012b), giving rise to the preformed component of the interior ocean Si inventory. Thus, whilst the concentration of preformed Si and its $\delta^{30}\text{Si}$ value reflect the physical-biogeochemical Si balance in the mixed layer at the sites of deep water formation, this component enters the ocean interior in dissolved form, without being cycled by biology. Once within the ocean interior, preformed Si behaves conservatively, such that its interior concentration and isotopic distributions are influenced only by the physical circulation. Differences in the $\delta^{30}\text{Si}$ value of preformed Si sourced from different deep water formation regions thus leads to variations in deep ocean $\delta^{30}\text{Si}$ values that are purely related to the physical transport of these conservative source signals. The regenerated component, on the other hand, is added to the ocean interior by the dissolution of sinking opal that has been exported from the euphotic zone, representing the non-conservative component of the interior Si inventory that has been cycled biogeochemically. The distribution of total dissolved Si in the ocean interior is governed by the combination of these two components. Our approach of separating preformed and regenerated Si in the context of a model simulation, and tracing their isotopic compositions, thus allows assessment of the relative importance of physical versus biogeochemical controls on the distribution of Si and its isotopes in the deep sea.

2. Methods

2.1. Model description

The physical ocean model used in this study is the Modular Ocean Model 3.0 (MOM3; Pacanowski and Griffies, 1999). MOM3 is a z-level primitive-equation ocean general circulation model, run here with 3.75° × 4.5° (longitude–latitude) horizontal resolution and 24 vertical levels. Our study uses the P2A configuration of MOM3 (Gnanadesikan et al., 2004). This configuration conforms to the observational constraints of low diapycnal diffusivity in the low-latitude thermocline (e.g. Ledwell et al., 1993, 1998) and enhanced diapycnal mixing in the Southern Ocean (e.g. Naveira Garibato et al., 2004), and forces deep water formation in the model’s Southern Ocean via strong winter salinity-restoring in four grid cells. It reproduces observed distributions of ocean ventilation tracers such as radiocarbon and chlorofluorocarbons (CFC-11), as well as biogeochemical variables such as particle export, dissolved phosphate and dissolved oxygen with good fidelity (Gnanadesikan et al., 2004; Matsumoto et al., 2004).

The physical model is coupled to a slightly modified version of the biogeochemical model of Jin et al. (2006). The representation of Si cycling follows the OCMIP-2 protocol (Najjar and Orr, 1998) of restoring nutrient concentrations to observations in the surface ocean (<85 m), with an e-folding timescale of 3 months. The surface nutrient-restoring drives a diagnosed Si uptake in the surface ocean, which is exported as a sinking opal flux that dissolves with an e-folding lengthscale of 1000 m. The oceanic Si cycle in this model is closed, with no external inputs from riverine or aeolian sources and no losses to sediment, such that sinking opal reaching the sea floor is converted to dissolved Si. Unlike the simulations of Jin et al. (2006), biogeochemical tracers are fully prognostic in the ocean interior in our simulation.

We have expanded Jin et al.’s (2006) model to also (a) simulate Si isotope fractionation and trace its stable isotope composition, and (b) explicitly trace the preformed component of Si and its stable isotope composition. Silicon stable isotope composition is traced by including an additional tracer of the isotope $\text{Si}^{30}$, scaled to a $\text{Si}^{30}/\text{Si}^{32}$ ratio of 1 in order to minimize potential numerical errors associated with the model’s advection scheme.
(cf. Somes et al., 2010). Isotope fractionation during diatom Si uptake in the surface ocean is simulated by scaling the Si uptake flux diagnosed from nutrient-restoring by the fractionation factor (e.g. Maier-Reimer, 1993; Schmittner et al., 2013):

\[ J^{30\text{Si}}_{\text{prod}}(t) = \alpha \cdot J^{\text{Si}}_{\text{prod}}(t) \cdot \frac{\delta^{30}\text{Si}}{\delta\text{Si}}(t) \]  

(1)

where \( J^{30\text{Si}}_{\text{prod}} \) is the uptake flux of the tracer \( \alpha \) is the fractionation factor associated with diatom Si uptake, and \( 30\text{Si} \) and Si(t) are the concentrations of \( 30\text{Si} \) and Si respectively. This general formulation represents kinetic Si isotope fractionation without relying on assumptions of isotope systematics (e.g. open- or closed-system behavior), which instead emerge from interaction of the biogeochemical model with the circulation. The fractionation factor \( \alpha \) is set to a constant value of 0.9989 (i.e. an isotope effect of \(-1.1\%\)), consistent with the isotope effect of diatom Si uptake documented by the culture studies of De La Rocha et al. (1997) and inferred from in situ Southern Ocean observations by Fripia et al. (2011a), although the recent culture study of Sutton et al. (2013) has shown that individual diatom species’ isotope effects vary from \(-0.5\%\) to \(-2.1\%\).

Our model does not consider Si isotope fractionation during opal dissolution (Demarest et al., 2009). Unlike Si isotope fractionation during uptake, which directly imposes an isotopic signal upon seawater Si, fractionation during dissolution occurs at the level of the individual diatom frustule. Since the downward decrease in opal flux is primarily due to the complete dissolution of more easily dissolved members of the diatom assemblage (Shemesh et al., 1989; Demarest et al., 2009, and references therein), the isotopic effect of fractionation during dissolution is likely strongly muted (Demarest et al., 2009). This inference is supported by observations that the \( \delta^{30}\text{Si} \) value of sinking opal remains constant throughout the water column (Fripia et al., 2012), and by preliminary OGCM results (Gao et al., 2013), which indicate that simulating fractionation during dissolution results in seawater \( \delta^{30}\text{Si} \) depth profiles inconsistent with observations. Based on these considerations, our model treats \( 30\text{Si} \) and Si identically during regeneration.

Simulated silicon stable isotope composition is calculated offline using the simplified formula (\( 30\text{Si}/\text{Si} - 1 \)) \times 1000 in order to derive \( \delta^{30}\text{Si} \) values. Due to the low abundance of \( 30\text{Si} \), this simplification slightly (\( \sim 8\% \)) underestimates \( \delta^{30}\text{Si} \) relative to the standard delta notation, well within the uncertainty associated with the isotope effect of diatom Si uptake (De La Rocha et al., 1997; Milligan et al., 2004; Sutton et al., 2013).

The preformed component of Si is traced by defining an additional prognostic tracer. Following the definition of preformed nutrients, preformed Si is set equal to total Si in the surface ocean (the uppermost 85 m, in which Si uptake takes place), and behaves conservatively in the ocean interior. Its isotopic composition is traced by including an analogous tracer of preformed Si. Regenerated Si (and \( 30\text{Si} \)) are calculated ex post facto by subtracting preformed Si (and \( 30\text{Si} \)) from total Si (and \( 30\text{Si} \)). This calculation ensures mass balance, such that the combination of preformed Si and regenerated Si always equals total Si in terms of both concentration and isotope composition. In the following, we use italics for clarity when referring to the components derived from our model’s tracer deconvolution.

2.2. Simulation: initialization, forcing, and equilibrium diagnostics

As described in Gnanadesikan et al. (2004), the physical model is forced by heat and salt fluxes from da Silva et al. (1994) including flux corrections diagnosed from restoring surface temperatures and salinities towards observational climatologies (Levitus and Boyer, 1994; Levitus et al., 1994), with additional salinity forcing as described in Section 2.1. Wind stress forcing is derived from the ECMWF reanalysis of Trenberth et al. (1989). Initial physical ocean fields are taken from a multi-millennial spin-up simulation, whilst biogeochemical tracers are initialized to the objectively-analyzed annual mean climatologies of World Ocean Atlas 2009 (WOA09; Garcia et al., 2010a, 2010b). This initialization yields an oceanic Si inventory of 1.19 × 10^23 Tmol, similar to the value of 0.97 × 10^23 Tmol estimated by Tréguier and De La Rocha (2013). Oceanic \( \delta^{30}\text{Si} \) is initialized to a globally constant value of +1.2%, the mean \( \delta^{30}\text{Si} \) value of the Si-rich deep Southern and Pacific Oceans (\( \geq 2000 \) m) that dominate the ocean’s Si mass balance (Cardinal et al., 2005; Beucher et al., 2008, 2011; Fripia et al., 2011b; de Souza et al., 2012a, 2012b; Grasse et al., 2013). Tracer fields used as targets for nutrient-restoring are derived from WOA09’s objectively-analyzed monthly nutrient climatologies.

The model is integrated forward for 5000 model years to steady-state. Over the last 100 years of the simulation, \( \delta^{30}\text{Si} \) values in the deep Pacific Ocean, the basin slowest to approach equilibrium, vary by <0.0001%. Similarly, the oceanic inventories of preformed and regenerated Si are near equilibrium, the preformed inventory increasing by only \(-0.07 \) Tmol century\(^{-1} \) (a negligible fraction of the oceanic preformed Si inventory of 6.23 × 10^24 Tmol), whilst its isotopic composition (+1.42%) remains constant to within 0.0003%. The model’s average opal export flux in the last century of the simulation is 189 Tmol Si yr\(^{-1} \) (with a \( \delta^{30}\text{Si} \) value of +0.98%), slightly different from the value of 178 Tmol yr\(^{-1} \) reported by Jin et al. (2006), likely due to Si-restoring below the euphotic zone in their model. The value we obtain is at the higher end of the range of estimates in the literature (69–185 Tmol yr\(^{-1} \); Dunne et al., 2007, and references therein) and consistent with a recent optimized data-assimilating model of the Si cycle (171 ± 31 Tmol yr\(^{-1} \); Holzer et al., 2014).

3. Results

3.1. Model validation: comparison to \( \delta^{30}\text{Si} \) data

The oceanic Si isotope systematics of open-ocean observations and our model simulation are compared in Fig. 1, which plots \( \delta^{30}\text{Si} \) values against Si concentrations. The model reproduces the observed non-linear relationship between Si concentration and its isotopic composition in the global ocean (Fig. 1a). Furthermore, the model captures a key feature of the regional variability in oceanic \( \delta^{30}\text{Si} \) systematics (Fig. 1b): the simulated isotope systematics of the Southern Ocean south of 50°S faithfully reproduces the observed enhanced trend towards elevated \( \delta^{30}\text{Si} \) values at intermediate Si concentrations (20–60 \( \mu \text{M} \)). Note, however, that at very low Si concentrations (<5 \( \mu \text{M} \)), the model \( \delta^{30}\text{Si} \) extends to higher values than observed. This mismatch may partially reflect analytical constraints on the observations (i.e. inability to analyze extremely Si-depleted samples), but also results from the model’s overprediction of subtropical \( \delta^{30}\text{Si} \) values (see below).

Fig. 2 shows a latitudinal section of \( \delta^{30}\text{Si} \) values in the model’s southeast Pacific at \(-103^\circ\text{W} \), overlain by data from 85°S to 110°W. A more detailed comparison between the model’s \( \delta^{30}\text{Si} \) field and data from 103°W is presented in the Supplementary Information (Fig. S1). The model exhibits considerable fidelity in reproducing the observed \( \delta^{30}\text{Si} \) distribution in the deep ocean, as well as in the intermediate/mesopelagic regions of the high southern latitudes and the tropics, both in terms of the range of \( \delta^{30}\text{Si} \) values and their distribution in the water column. However, in the subtropical thermocline, the model strongly overestimates \( \delta^{30}\text{Si} \) values compared to the sparse observations in these severely nutrient-depleted waters (Fig. 2). This discrepancy, which results from the subduction of preformed Si with greatly elevated \( \delta^{30}\text{Si} \) values at the sites of thermocline ventilation in the model, may
Fig. 1. Comparison of the $\delta^{30}\text{Si}$ systematics in the open-ocean observational dataset (open blue circles) and the model (red dots). Isotope systematics are shown for (a) the global ocean and (b) the ocean south of 50°S. The model reproduces the observed $\delta^{30}\text{Si}$ systematics in terms of degree of Si and $\delta^{30}\text{Si}$ variability as well as the shape of their non-linear relationship (panels a, b), and captures the elevated $\delta^{30}\text{Si}$ values at intermediate Si concentrations of 20–60 μM at high southern latitudes of the Southern Ocean (panel b). Typical 2σ SD analytical reproducibility of the data is ±0.15h, whilst data from different laboratories agree to within ±0.2h (Reynolds et al., 2007). Data are from De La Rocha et al. (2000, 2011), Varela et al. (2004), Cardinal et al. (2005), Reynolds et al. (2006), Beucher et al. (2008, 2011), Cavagna et al. (2011), Fripiat et al. (2011a, 2011b), de Souza et al. (2012a, 2012b), Ehler et al. (2012) and Grasse et al. (2013). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Model-data comparison of the $\delta^{30}\text{Si}$ distribution in the eastern equatorial and southeastern Pacific Ocean. Good agreement is seen between the observations (colored dots) and the simulation (color map) in the deep ocean and over the entire water column at tropical and high southern latitudes, in terms of gradients as well as absolute values (see also Fig. S1). However, the model strongly overestimates $\delta^{30}\text{Si}$ values in the subtropical thermocline and in the shallow tropical ocean (40°S–10°S; see Section 3.1 for discussion). The model section is from 103W; data are from Beucher et al. (2008), de Souza et al. (2012b) and Grasse et al. (2013).

result from our nutrient-restoring approach, which leads to nutrient uptake that is temporally smoother than the episodic diatom blooming in these Si-poor regions (e.g. Brown et al., 2008). Such episodic Si uptake and export may limit the expression of isotope fractionation due to near-complete mass transfer to the opal pool. However, it is beyond the scope of this work to include a discussion of this effect and its potential influence on the $\delta^{30}\text{Si}$ distribution.

The model’s positive $\delta^{30}\text{Si}$ bias in the subtropical thermocline does not affect our deep-ocean analysis here. A comparison of the model’s $\delta^{30}\text{Si}$ field at a depth of ~2000 m with a compilation of observations shows that the model captures the main characteristics of the deep ocean $\delta^{30}\text{Si}$ distribution well (Fig. 3).

Note the high $\delta^{30}\text{Si}$ values in the northern North Atlantic associated with the downward penetration of NADW; this Si-poor water mass bears an elevated $\delta^{30}\text{Si}$ signature of +1.79‰, consistent with de Souza et al. (2012a) observations in the North Atlantic Ocean (+1.58‰ to +1.78‰). Values of $\delta^{30}\text{Si}$ in the deep Arctic are also uniformly high at +1.63‰, consistent with the elevated $\delta^{30}\text{Si}$ values (+1.69‰ to +1.86‰) observed in Nordic Sea overflows by de Souza et al. (2012a). The high-$\delta^{30}\text{Si}$ North Atlantic signal propagates into the South Atlantic and even south of Africa, extending in a tongue of very slightly elevated $\delta^{30}\text{Si}$ values (Fig. 4b) associated with a tongue of low [Si] (Fig. 4a). Southward of this feature, the Si-rich deep Southern Ocean exhibits uniformly low $\delta^{30}\text{Si}$ values, with the model’s average value of +1.14‰ being
highly consistent with observations (+1.2%; Cardinal et al., 2005; Fripiat et al., 2011a, 2011b; de Souza et al., 2012a, 2012b). In contrast to observations, model δ30Si values do not decrease between the deep Southern Ocean and the North Pacific. The model’s North Pacific exhibits δ30Si values largely similar to those in the Southern Ocean, and higher than observations by ~0.3% (De La Rocha et al., 2000; Reynolds et al., 2006). The model is also insufficiently Si-rich in the North Pacific, with concentrations ranging up to 130 μM at 2000 m, contrasting with observed concentrations of >170 μM (Garcia et al., 2010b).

3.2. Distribution of preformed and regenerated components

Having documented the model’s skill at reproducing both oceanic δ30Si systematics and the main features of the deep δ30Si distribution, we now turn to the distributions of the preformed and regenerated components of Si. Here and in the following discussion of the deep ocean, we present model results from a depth level of ~2000 m, which best illustrates the main features of the deep ocean Si and δ30Si distributions (additional figures are in the Supplementary Information). The maps at ~2000 m depth in Fig. 4 illustrate the distributions of both preformed and regenerated Si differ from that of total Si, and bear a number of interesting features central to the deconvolution of the Si cycle. Preformed Si constitutes almost 100% of total Si at 2000 m at the primary sites of deep water formation in the model, the North Atlantic and the Weddell Sea, where deep waters are freshly ventilated from the surface (Figs. 4c, e). Its contribution decreases away from these regions to about half of total Si in the deep Pacific (the global preformed Si inventory is 52% of the total Si inventory). The two sites of deep water formation are associated with preformed Si bearing strongly differing isotope compositions (Fig. 4d); in the Weddell Sea, preformed Si has a low δ30Si signature of +1.29%, whereas the high-latitude North Atlantic has a preformed δ30Si value of +2.1%.

The high North Atlantic values propagate southward through the Atlantic basin along its western boundary, and as a tongue of elevated δ30Si values (> +1.4%) extending eastward south of Africa. Over the entire Indo-Pacific, the δ30Si value of deep water preformed Si is essentially constant (+1.38%).

Unlike the systematic inverse relationship between the concentration and δ30Si value of the preformed component (Figs. 4c, d), the deep ocean distributions of regenerated Si and its isotope composition show little relation (Figs. 4f, g). The concentration of regenerated Si at 2000 m is, as expected, lowest at the sites of deep water formation (where Si is almost entirely preformed), and increases steadily along the deep limb of the MOC (Figs. 4f, h). In strong contrast to this steady progression in concentrations of regenerated Si, regenerated δ30Si values display remarkable regional constancy (Fig. 4g). Apart from a small region of elevated δ30Si values in the northern North Atlantic, the δ30Si value of regenerated Si in the deep Atlantic, Indian and Pacific Oceans is essentially uniform: integrated from 2000 m to the sea floor, the δ30Si value of regenerated Si in these basins ranges between +0.91% and +0.93%. In the deep Southern Ocean south of 50°S, regenerated Si bears a lower δ30Si value, averaging +0.82% in a roughly zonal band around Antarctica. The deep Arctic Ocean, in contrast, exhibits an elevated regenerated δ30Si value of +1.48%.

4. Discussion

The deconvolution of deep ocean Si into its physically-controlled preformed component and its biogeochemically-cycled regenerated component enables us to take a detailed look at the manner in which these two controls interact to determine the oceanic Si and δ30Si distributions. We begin our discussion with a consideration of the most striking feature of the deep δ30Si distribution, the meridional δ30Si gradient in the deep Atlantic Ocean.
Fig. 4. Simulated distributions of Si concentration (left column), isotopic composition (center column) and component fractions (right column) at a model depth of 2063 m. (a) concentration of total Si; (b) δ$_{30}$Si value of total Si; (c) concentration of preformed Si; (d) δ$_{30}$Si value of preformed Si; (e) fractional contribution of preformed Si to total Si; (f) concentration of regenerated Si; (g) δ$_{30}$Si value of regenerated Si; (h) fractional contribution of regenerated Si to total Si. Note the differing color bars between panel a and panels c and f. δ$_{30}$Si color bar applies to entire center column.

4.1. Influence of preformed Si on the deep Atlantic δ$_{30}$Si distribution

It is apparent from Fig. 4 that the strongest δ$_{30}$Si signals in the deep Atlantic are found in preformed Si, which exhibits a δ$_{30}$Si difference of ∼0.8‰ between the high-latitude North Atlantic and the Weddell Sea. Indeed, the close similarity between the spatial distribution of total and preformed δ$_{30}$Si in the deep Atlantic Ocean (Figs. 4b,d) implies that the systematic δ$_{30}$Si variability here is primarily determined by the preformed component. This strong preformed influence on total δ$_{30}$Si is clearly illustrated by the linear correlation ($r^2 = 0.91$) with a slope near unity between the isotopic compositions of preformed Si and total Si (Fig. 5).

Preformed Si is transported into the deep ocean from the surface by deep water formation, a result of the buoyancy loss of surface waters at high latitudes. Since it is, by definition, conservative within the ocean interior, the preformed Si distribution in the deep ocean is determined solely by the circulation. The preformed δ$_{30}$Si gradient in the deep Atlantic Ocean (Fig. 4d) thus reflects a difference in preformed δ$_{30}$Si values between NADW and AABW, the two sources of deep water in the Atlantic. This preformed δ$_{30}$Si difference can be related to the degree of Si utilization in the formation regions of NADW and AABW. North Atlantic Deep Water forms from Si-depleted surface waters of the high North Atlantic and the Nordic seas (Dickson and Brown, 1994). Its high preformed δ$_{30}$Si value reflects the elevated surface δ$_{30}$Si signature of these waters due to isotope fractionation during Si uptake by diatoms. de Souza et al. (2012a) suggested that this elevated δ$_{30}$Si value is ultimately derived from the northward transport of the high-δ$_{30}$Si signature of SAMW and AAIW in the upper limb of the MOC. Whilst our physical model has been shown to produce significant inter-hemispheric nutrient transport via this pathway (Palter et al., 2010), it is not possible to firmly establish such a causal relationship in the absence of additional model diagnostics.

The low preformed δ$_{30}$Si signature of AABW, on the other hand, is a result of its formation from nutrient-replete waters of the high-nutrient, low chlorophyll Southern Ocean that have experienced little Si utilization (Huhn et al., 2008; de Souza et al., 2012a). The lack of high-latitude Si drawdown imparts AABW a low preformed δ$_{30}$Si value and a preformed Si concentration almost an order of magnitude higher than that of NADW (Fig. 4c). This high preformed Si content gives AABW considerable leverage during mixing, allowing it to strongly affect the deep preformed δ$_{30}$Si distribution as it flows northward in the abyssal Atlantic and mixes diapycnally into the overlying water column. Fig. 4d shows that the
A closer look at the correlation between the $\delta^{30}\text{Si}$ values of preformed and total Si in the deep Atlantic (Fig. 5) reveals that the slope of this correlation is less than unity ($m=0.83$), indicating that total $\delta^{30}\text{Si}$ values vary less strongly than preformed $\delta^{30}\text{Si}$. This reduced gradient is the result of the influence of regenerative Si on the total $\delta^{30}\text{Si}$ distribution. Despite the fact that regenerative $\delta^{30}\text{Si}$ values bear a rather complex relationship to total $\delta^{30}\text{Si}$ in the deep Atlantic (Fig. 5), and exhibit their strongest variability in this basin (Fig. 4g), the primary influence of regenerative Si is to homogenize total $\delta^{30}\text{Si}$ values in the deep Atlantic, slightly damping the strong preformed $\delta^{30}\text{Si}$ signal. In the rest of the deep ocean, regenerative $\delta^{30}\text{Si}$ values display remarkable regional homogeneity, and it is to an explanation of this feature that we now turn.

### 4.2. Circulation control on the regenerative component

The regenerative component of Si is added to the ocean interior by dissolution of sinking opal. Fig. 6a shows the latitudinal distribution of the model’s zonally-averaged opal export flux: fluxes are high in the Southern Ocean south of $50^\circ$S and low elsewhere, with the exception of a minor peak at northern subpolar latitudes. This latitudinal distribution is consistent with Dunne et al.’s (2007) estimate from satellite observations and biogeochemical data products, although tropical export fluxes are underestimated in the model (the mean low-latitude opal flux is 3% of the mean Southern Ocean flux in our simulation, as opposed to 10% in Dunne et al., 2007; see the Supplementary Information).

In Fig. 6b, we compare the flux-weighted mean $\delta^{30}\text{Si}$ value of the sinking opal flux with the $\delta^{30}\text{Si}$ value of regenerative Si in the deep ocean. These isotopic distributions clearly document a fundamental feature of the oceanic Si distribution that is not apparent from concentrations alone. The $\delta^{30}\text{Si}$ value of regenerative Si in the global deep ocean north of $50^\circ$S is $+0.93\%$. This $\delta^{30}\text{Si}$ value is considerably lower than that of the opal flux sinking into the deep ocean here, which has a flux-weighted average $\delta^{30}\text{Si}$ value of $+1.70\%$. This large disparity between the isotopic composition of Si being added to the deep ocean north of $50^\circ$S by sinking opal and that of regenerative Si present within this volume demonstrates, unambiguously, that a dominant fraction of the regenerative Si in the Atlantic, Pacific and Indian basins (cf. Fig. 4g) is not added to the deep ocean locally. This low-$\delta^{30}\text{Si}$ regenerative Si must in fact be transported into these basins from a region where the dissolving opal flux releases regenerative Si with a low $\delta^{30}\text{Si}$ value to the deep ocean. From Figs. 6a and b, it is clear that this region must be the Southern Ocean. As we detail in Section 4.3 below, our $\delta^{30}\text{Si}$ deconvolution thus reveals with striking clarity not only that the Southern Ocean is dominantly important in the global Si cycle.
Table 1
Values of parameters used in the mixing equations to calculate the Southern Ocean contribution to the global deep water Si inventory, and details of their calculation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{30}\text{Si}_{\text{AABW}}$</td>
<td>+1.29%</td>
<td>$\delta^{30}\text{Si}$ value of preformed Si within $(80^\circ\text{S}, 50^\circ\text{W})$, $(65^\circ\text{S}, 15^\circ\text{W})$, from 1500 to 5000 m, year 5000</td>
</tr>
<tr>
<td>$\delta^{30}\text{Si}_{\text{NADW}}$</td>
<td>+2.08%</td>
<td>$\delta^{30}\text{Si}$ value of preformed Si within $(70^\circ\text{N}, 60^\circ\text{W})$, $(40^\circ\text{N}, 30^\circ\text{W})$, from 1500 to 2000 m, year 5000</td>
</tr>
<tr>
<td>$\delta^{30}\text{Si}_{\text{SO}}$</td>
<td>+0.82%</td>
<td>$\delta^{30}\text{Si}$ value of total opal flux at 2063 m South of $50^\circ\text{S}$, years 4900–5000</td>
</tr>
<tr>
<td>$\delta^{30}\text{Si}_{\text{nonSO}}$</td>
<td>+1.70%</td>
<td>$\delta^{30}\text{Si}$ value of total opal flux at 2063 m North of $50^\circ\text{S}$, years 4900–5000</td>
</tr>
</tbody>
</table>

(cf. Sarmiento et al., 2007), but also that due to this localized over-representation, the distribution of regenerated Si and its isotopic composition in the global deep ocean is strongly influenced by the northward spreading of deep waters from the Southern Ocean.

4.3. Quantifying the influence of the Southern Ocean

As discussed above, the $\delta^{30}\text{Si}$ distributions of both the preformed and the regenerated components of Si document a strong Southern Ocean influence on the deep Si and $\delta^{30}\text{Si}$ distributions. Here, we use simple isotopic mixing relationships in order to quantify this influence in the context of our simulation. The isotopic composition of preformed Si in the deep sea is determined by conservative mixing of preformed Si from NADW and AABW, and can be represented as:

$$\delta^{30}\text{Si}_{\text{pre}} = \delta^{30}\text{Si}_{\text{AABW}} \cdot X_{\text{AABW}} + \delta^{30}\text{Si}_{\text{NADW}} \cdot (1 - X_{\text{AABW}}) \quad (2)$$

where $\delta^{30}\text{Si}_{\text{pre}}$ is the isotopic composition of preformed Si, $\delta^{30}\text{Si}_{\text{AABW}}$ is the preformed $\delta^{30}\text{Si}$ signature of water mass $x$, and $X_{\text{AABW}}$ is the proportion of preformed Si contributed by AABW (errors in $X_{\text{AABW}}$ introduced by using $\delta$-values in Eq. (2) are < 0.001). Eq. (2) can be solved for $X_{\text{AABW}}$ at each grid point in the deep ocean, giving the proportion of preformed Si derived from the Southern Ocean. Similarly, we can approximately parse the proportion of regenerated Si added to the deep sea by the high opal fluxes of the Southern Ocean by using a similar mixing equation:

$$\delta^{30}\text{Si}_{\text{regen}} = \delta^{30}\text{Si}_{\text{SO}} \cdot X_{\text{SO}} + \delta^{30}\text{Si}_{\text{nonSO}} \cdot (1 - X_{\text{SO}}) \quad (3)$$

where $\delta^{30}\text{Si}_{\text{regen}}$ is the isotopic composition of regenerated Si, $\delta^{30}\text{Si}_{\text{SO}}$ is the flux-weighted mean $\delta^{30}\text{Si}$ value of sinking opal in region $x$, SO stands for the Southern Ocean south of $50^\circ$S, nonSO is the global ocean North of $50^\circ$S, and $X_{\text{SO}}$ is the proportion of regenerated Si contributed by Southern Ocean opal fluxes. Note that the use of average $\delta^{30}\text{Si}$ values for the opal fluxes North and South of $50^\circ$S means that this calculation is only approximate. Parameter values used in the formulation of Eqs. (2) and (3) are given in Table 1.

Figs. 7a, b show the distributions of $X_{\text{AABW}}$ and $X_{\text{SO}}$, respectively, in the deep ocean at ~2000 m. The distribution of $X_{\text{AABW}}$ (Fig. 7a) demonstrates a strong influence of the upward mixing of abyssal AABW in the Atlantic Ocean, with numerous regions even in the North Atlantic exhibiting >50% Si contribution from AABW at this depth level. Whilst this is broadly consistent with observations (van Aken and de Boer, 1995; van Aken, 2000), our model overestimates the influence of AABW at this depth in the Atlantic Ocean, since the physical model produces insufficiently-dense NADW that is consequently restricted to shallower layers than observed, allowing the model’s abyssal Atlantic to fill with Si-rich AABW. Elsewhere in the deep ocean, the high preformed Si content of AABW results in this water mass contributing the dominant fraction (>80%) of deep preformed Si. The sensitivity of regenerated $\delta^{30}\text{Si}$ to the low-$\delta^{30}\text{Si}$ Southern Ocean opal fluxes is revealed by the $X_{\text{SO}}$ distribution in Fig. 7b: our relatively coarse unmixing calculation (Eq. (3)) picks up the increased proportion of locally-regenerated Si under the coastal upwelling regions of the eastern Atlantic and Pacific, and in the recirculating waters of the Angola Basin, west of southern Africa. Interestingly, regenerated $\delta^{30}\text{Si}$ values are so sensitive to the Southern Ocean opal flux that $X_{\text{SO}}$ integrated over the deep ocean traces the inflows of Southern Ocean water into the abyssal southwestern Atlantic, Indian and Pacific Oceans (Fig. S4).

In a final calculation, we estimate the amount of total Si that is derived from the Southern Ocean by combining $X_{\text{AABW}}$ and $X_{\text{SO}}$ with the distributions of preformed and regenerated Si:

$$\text{Si}_{\text{SO}} = X_{\text{pre}} \cdot X_{\text{AABW}} + X_{\text{regen}} \cdot X_{\text{SO}} \quad (4)$$

where $\text{Si}_{\text{SO}}$ is the concentration of Si derived from the Southern Ocean and $X_{\text{pre}}$ ($X_{\text{regen}}$) is concentration of preformed (regenerated) Si. We show the result of this calculation in Fig. 7c, which illustrates the deep distribution of the proportion of total Si derived from the Southern Ocean (i.e. $\text{Si}_{\text{SO}}$). The combination of the high preformed Si content of AABW (Fig. 7a) and the strong Southern Ocean control on regenerated Si (Figs. 6b, 7b) results in an overwhelmingly large contribution of Southern Ocean-sourced Si to the global deep ocean: integrated from 2000 m to the sea floor, 89% of Si in the deep ocean north of $50^\circ$S is of Southern Ocean origin.

4.4. Implications for the deep ocean’s $\delta^{30}\text{Si}$ distribution

Our deconvolution of Si into its preformed and regenerated components allows assessment of the mechanisms driving the global deep water $\delta^{30}\text{Si}$ gradient, and their implications for the marine biogeochemical Si cycle. To a considerable extent, the influence of the physical circulation on the deep $\delta^{30}\text{Si}$ distribution results from the important contribution of preformed Si, whose isotopic composition bears strongly contrasting signals in NADW and AABW. However, our simulation also illustrates that, as a result of the highly non-uniform distribution of opal export, even the distribution of the biogeochemically-cycled regenerated component of Si is significantly determined by the circulation. These two mechanisms combine to produce the observed strong water mass control on the $\delta^{30}\text{Si}$ distribution.

Furthermore, our analysis in Section 4.3 suggests that this quasi-conservation of $\delta^{30}\text{Si}$ values within the ocean interior reflects the dominance of Southern Ocean processes in Si cycling. Firstly, AABW plays a key role in determining the distribution of the circulation-controlled preformed component due to its high preformed Si content. Secondly, the elevated opal fluxes in the Southern Ocean contribute the dominant fraction of the deep ocean’s regenerated Si inventory. As a result, the mass-balance of Si in deep waters, and hence its stable isotope composition, is strongly determined by Si – both preformed and regenerated – from the Southern Ocean. This inference is consistent with the recent modeling study of Holzer et al. (2014), who find that the ocean’s preformed and regenerated Si inventories are dominantly sourced from the Southern Ocean south and north of the Antarctic Divergence, respectively (see also the Supplementary Information). Since the preformed and regenerated Si inventories cannot be calculated from data, the finding of Holzer et al. (2014) could not be validated against observations. Our study fills this gap by tying the Southern
Fig. 7. Quantifying the influence of the Southern Ocean on the simulated Si distribution at 2063 m. (a) Fraction of preformed Si sourced from AABW, calculated from the preformed δ^{30}Si distribution using Eq. (2). (b) Fraction of regenerated Si added south of 50°S, calculated from the regenerated δ^{30}Si distribution using Eq. (3). (c) Fraction of total Si sourced from the Southern Ocean, calculated in Eq. (4) by combining the information in panels a and b.

Ocean's controlling role on these two components directly to the observed δ^{30}Si distribution.

The high Si content of the Southern Ocean and its low δ^{30}Si value are mechanistically linked to each other, and to the MOC. Strong southern westerly winds drive upwelling in the Southern Ocean (Marshall and Speer, 2012), producing a dynamic, nutrient-rich system that favors diatom-dominated ecosystems (Ragueneau et al., 2000). Heavily-silicified diatoms strip Si from these waters as they are transported northward by Ekman drift (Brzezinski et al., 2003; Sarmiento et al., 2004), efficiently exporting it as opal to depth, trapping Si within the Southern Ocean (Sarmiento et al., 2007; Holzer et al., 2014). Since this opal bears a low δ^{30}Si value (Cardinal et al., 2007; Egan et al., 2012), it lowers the deep Southern Ocean's δ^{30}Si signature, whilst leading to the transport of a residual high-δ^{30}Si signal into the regions where SAMW and AAIW are formed (Fripiat et al., 2011b; de Souza et al., 2012b). Importantly, the shoaling of deep isopycnals in the Southern Ocean favors the regeneration of the low-δ^{30}Si signal in dense waters that will exit the Southern Ocean as AABW (cf. Lumpkin and Speer, 2007; Talley, 2013), even if a large proportion of the exported opal dissolves within the upper water column, as suggested by Holzer et al. (2014). The low-δ^{30}Si, high-Si signatures of AABW's preformed and regenerated components thus reflect the Southern Ocean's unique physical-biogeochemical regime.

Our results thus reconcile the intuitive expectation that the oceanic δ^{30}Si distribution should reflect biological uptake and opal dissolution with the observed strong hydrographic control (e.g. Fripiat et al., 2011b; de Souza et al., 2012a, 2012b). Returning to the published hypotheses put forward for the origin of the interbasin deep water δ^{30}Si gradient, we see that explanations invoking the influence of opal dissolution (De La Rocha et al., 2000; Beucher et al., 2008) only capture part of the picture. Dissolution of opal does indeed add regenerated Si with a low δ^{30}Si value to the deep ocean (our model's global opal flux has a δ^{30}Si value of +0.98‰); however, since most regenerated Si is contained in waters of Southern Ocean origin, the isotopic composition of this component is rather homogeneous globally (Fig. 4g), and contributes little to the large-scale δ^{30}Si gradient. In this regard, our simulation agrees with Reynolds' (2009) box model analysis in highlighting the importance of the physical transport of a
high-$^{30}$Si signal in NADW, whilst also emphasizing the role of the contrasting low-$^{30}$Si signal in AABW, one that our model indicates is reflective of the strong trapping of Si in the Southern Ocean.

However, whilst our model performs considerably better at reproducing the oceanic $^{30}$Si distribution than the OGCM simulation of Wischmeier et al. (2003) (see the Supplementary Information), it does not reproduce the high Si concentrations and low $^{30}$Si values observed in the deep North Pacific (De La Rocha et al., 2000; Reynolds et al., 2006). This isotopic feature is poorly constrained, and its origin remains both enigmatic and debated in the literature (Beucher et al., 2008; de Souza et al., 2012b; Grasse et al., 2013). Our results suggest one possible origin for such a low-$^{30}$Si signature. Higher nutrient supply to the surface subarctic Pacific than simulated by our model would lead to an increased inventory of locally-regenerated Si in the deep North Pacific, as a result of larger opal fluxes (cf. Gnanadesikan and Toggweiler, 1999; Gnanadesikan et al., 2002). Since Si utilization in the subarctic Pacific is incomplete (e.g. Whitney, 2011), the regenerated Si released by dissolution of this opal should possess a low $^{30}$Si value, such that it would lower $^{30}$Si values in the mid-depth North Pacific. Such an influence would mean that the contribution of regenerated Si to the global deep $^{30}$Si gradient is greater than our simulation indicates. Alternatively, however, deep North Pacific $^{30}$Si values may be influenced by Si derived from hydrothermal sources (e.g. Johnson et al., 2006). The resolution of this question must await a clearer observational picture of the North Pacific $^{30}$Si distribution.

5. Conclusions

By parsing dissolved Si into its preformed and regenerated components in an OGCM simulation, we have separated the influence of physical and biogeochemical processes on the deep ocean's $^{30}$Si distribution. The results indicate a strong control of the preformed component of Si, whose interior distribution is determined solely by the circulation, on the systematic meridional $^{30}$Si gradient in the deep Atlantic Ocean. Furthermore, we have shown that, due to the pronounced regional differences in opal export flux, the $^{30}$Si value of regenerated Si acts as a sensitive tracer of oceanic regions with large opal export fluxes, which in the model are almost completely restricted to the Southern Ocean. The importance of the Southern Ocean in cycling Si helps explain the strong physical control on the oceanic Si distribution indicated by $^{30}$Si observations: the small opal fluxes north of the Southern Ocean's opal belt lead to the surprising result that most of the regenerated Si in the deep Atlantic and Indo-Pacific Oceans is in fact transported into these basins in dissolved form, by deep waters flowing northwards from the Southern Ocean. Our model's mechanistic explanation of the observed water mass control on the oceanic $^{30}$Si distribution thus provides further support for the dominance of the Southern Ocean in the oceanic Si cycle.

Acknowledgements

Fruitful discussions with Irina Marinov, Mark Brzezinski, Ben Reynolds and Robbie Toggweiler are gratefully acknowledged. Feedback from Florian Wietzel helped considerably improve an earlier version of this manuscript. The authors thank the observational $^{30}$Si community for generously sharing data, Damien Cardinal and an anonymous reviewer for their constructive reviews, and Gideon Henderson for editorial handling. This work was supported by Swiss National Science Foundation postdoctoral fellowship PBEZ2P-140169 granted to GFDS, and NOAA grant NA11OAR4310066 to JLS.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.04.040.

References
