Coupling of the distribution of silicon isotopes to the meridional overturning circulation of the
North Atlantic Ocean

Mark A. Brzezinski*^{1,2} & Janice L. Jones¹

¹Marine Science Institute, University of California, Santa Barbara, CA 93106

mark.brzezinski@lifesci.ucsb.edu, 805-893-8605, ²Department of Ecology Evolution and Marine
Biology, University of California, Santa Barbara, CA 93106

*corresponding author

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Abstract

The distribution of silicon isotopes within silicic acid, $\delta^{30}\text{Si}(\text{OH})_4$, was examined along a section in the North Atlantic from the Cape Verde Islands off Africa to Cape Cod, Massachusetts in North America. Surface water displayed elevated $\delta^{30}\text{Si}(\text{OH})_4$ associated with biological fractionation of Si during silica production. Below 300 m variations in $\delta^{30}\text{Si}(\text{OH})_4$ were closely tied to the distribution of water masses as diagnosed through optimum multiparameter analysis, confirming a tight relationship between $\delta^{30}\text{Si}(\text{OH})_4$ and the meridional overturning circulation in the Atlantic. A linear relationship between $\delta^{30}\text{Si}(\text{OH})_4$ and the inverse of silicic acid concentration supported control of Si isotope distribution by conservative mixing of end member water masses of different isotopic composition in the Atlantic. There was a suggestion of a weak local minimum in $\delta^{30}\text{Si}(\text{OH})_4$ in deep waters above the Trans-Atlantic Geotraverse hydrothermal zone on the mid-Atlantic Ridge consistent with the light $\delta^{30}\text{Si}(\text{OH})_4$ of hydrothermal waters. The lightest $\delta^{30}\text{Si}(\text{OH})_4$ values were observed in the deep western and deep eastern basins where Antarctic Bottom Water (AABW) dominated. The heaviest values in subsurface waters occurred in North Atlantic Deep Water due to strong ventilation and the contribution of heavy northern source waters that are influenced by the Arctic Ocean. The concept of a silicon isotope bipole is introduced to explain how the isotopic differences between the northern and southern end-member water masses arise, and how they influence Si isotope distributions. Northern end-member water masses are heavy due to the influence of the Arctic Ocean. Bottom topography prevents light deep waters from entering the Arctic and the further removal of light isotopes through local biological productivity results in extremely heavy $\delta^{30}\text{Si}(\text{OH})_4$ within the Arctic. Light AABW dominates the southern end member. The Southern Ocean silicic acid trap distills heavier isotopes of Si out of the Southern Ocean as preformed silicic acid within Antarctic mode

waters, while retaining light isotopes that become incorporated into AABW. The influence of the silicon isotope bipole is predicted to be strongest in the Atlantic as the net flow of waters through the Arctic Ocean is from the Pacific to the Atlantic.

1.1 Introduction

Silicon isotopes have proven to be a powerful tool for understanding diatom productivity on unprecedented spatial and temporal scales in both the modern and past ocean (e.g. Beucher *et al.*, 2007; Brzezinski *et al.*, 2002; De La Rocha *et al.*, 1998; Fripiat *et al.* 2011; Reynolds *et al.*, 2008). Silicon isotopes in biogenic silica, $\delta^{30}\text{Si-bSiO}_2$, and in silicic acid, $\delta^{30}\text{Si}(\text{OH})_4$, are increasingly being used to assess the roles of diatoms and of changes in silicic acid supply in past shifts in ocean productivity and their implication for climate. Application of the proxy requires several untested assumptions. Two of the most common assumptions made when interpreting sedimentary silicon isotope records are that both the silicic acid concentration, $[\text{Si}(\text{OH})_4]$, and the silicon isotopic composition of ventilating waters masses are unique and invariant over time (Beucher *et al.*, 2011; Fripiat *et al.*, 2011; Reynolds *et al.*, 2006). The issue of changes in water mass $[\text{Si}(\text{OH})_4]$ over time is being addressed through recent advances in the use of Si isotopes within sponge spicules as a proxy for the $[\text{Si}(\text{OH})_4]$ of deep waters (Ellwood *et al.*, 2010; Hendry *et al.*, 2010; Wille *et al.*, 2010). Here we address the fundamental issue of whether major water masses in the modern ocean possess the unique $\delta^{30}\text{Si}(\text{OH})_4$ signatures predicted by models (Matsumoto *et al.*, 2012; Reynolds, 2009; Wischmeyer *et al.*, 2003).

Both laboratory (De La Rocha *et al.*, 1997; Demarest *et al.*, 2009) and field (e.g. Cardinal *et al.*, 2005; Cardinal *et al.*, 2007; De La Rocha *et al.*, 2000; Fripiat *et al.*, 2011; Varela *et al.*, 2004) studies indicate that the production and recycling of diatom silica are the dominant

biogeochemical processes controlling silicon isotope distributions in the global ocean. Fractionation of isotopes of Si occurs during both the production of opal by diatoms (De La Rocha *et al.*, 1997) and during opal dissolution (Demarest *et al.*, 2009) with each process favoring the incorporation (production) or release (dissolution) of the lighter isotopes of Si. Silica production and dissolution are decoupled in space and time with silica production being confined to surface waters following the injection of nutrients from depth, while silica dissolution occurs mainly following cell death, and throughout the water column, with a vertical distribution governed by the remineralization length scale for biogenic silica. Numerical simulations suggest that the coupling of these processes to the meridional overturning circulation (MOC) creates predictable and unique $\delta^{30}\text{Si}(\text{OH})_4$ signatures within major ocean basins and water masses (Reynolds, 2009).

Reynolds (2009) used a seven box model based on Toggweiler (1999) and the ten box PANDORA model of Broecker and Peng (1986) to examine global marine silicon isotope distributions. Incomplete silicic acid use in the surface waters of the Southern Ocean was a major driver of the model results. $\delta^{30}\text{Si}(\text{OH})_4$ values within waters that subduct to form Antarctic Bottom water (AABW) are light due to high preformed $[\text{Si}(\text{OH})_4]$. Stronger biological depletion of $\text{Si}(\text{OH})_4$ occurs in the waters incorporated into Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) giving those water masses relatively heavy $\delta^{30}\text{Si}(\text{OH})_4$ signatures. The northward flow of deep waters formed in the Southern Ocean strongly influenced the isotopic composition of modeled bottom waters in the Atlantic and Pacific basins. The modeled isotopic signature of North Atlantic Deep Water (NADW) was heavy, largely due to strong ventilation in the North Atlantic resulting in high productivity and low nutrient content. One caveat of current model results is that they do not include the

contribution of the Arctic Ocean to the MOC of the north Atlantic. New data indicate that waters in the Arctic are the heaviest of all oceans with deep-water $\delta^{30}\text{Si}(\text{OH})_4$ of +1.9 ‰ (Varela, pers. com.) such that exchange between the Arctic and the Atlantic will influence the isotopic composition of northern source waters.

The focus of this study was a section across the North Atlantic conducted by the US GEOTRACES program in 2010 and 2011. The North Atlantic Ocean resides at one extreme of the MOC. More than any other basin, nutrient distributions in the North Atlantic are affected by advection. NADW transports waters to the south with northward counter flows in surface waters, AAIW, SAMW and at depth via AABW. Lateral injection is also important, most notably water from the Mediterranean outflow through the Strait of Gibraltar, and water from the Arctic Ocean entering through the Fram Strait off Greenland and through the Canadian Archipelago. The GEOTRACES cruise track from the African Coast near the Cape Verde Islands to the North American coast near Cape Cod, Massachusetts (Figure 1) traverses the deep western and eastern basins at latitudes where there is a contrast in deep water silicic acid concentrations between basins, and it also intersects a major hydrothermal zone along the mid-Atlantic ridge. The section also spans a large range in diatom productivity from the highly productive upwelling zone off West Africa to the oligotrophic subtropical gyre. This diversity of water masses, silicic acid concentrations and gradients in productivity provide an ideal context for evaluating the coupling of Si isotope distributions and the MOC.

2.1 Material and methods

2.1.1 Sample collection –

Samples for the measurement of the silicon isotope composition of silicic acid were collected at nine stations from the Cape Verde Islands to the shelf waters off the Northeast coast of the United States (Figure 1). Two stations were sampled in 2010 on cruise KN199-4 (USGT10-9 and USGT10-12). USGT10-12 was resampled along with six other stations during 2011 on cruise KN204-1. Comparison of data from the one station that was sampled during both years (station USGT10-12 during 2010, station USGT11-24 during 2011) allows an assessment of combined sampling, analytical and environmental variability. The 2011 section also sampled the Bermuda Atlantic Time Series (BATS) station (USGT11-10) which was the site on the earlier US GEOTRACES intercalibration exercise in the Atlantic (Cutter, 2013).

Seawater samples were obtained using a conventional CTD rosette equipped with 30L Niskin samplers, an oxygen probe, and a seabird 911 CTD. Two liters of seawater were filtered directly from each Niskin sampler into acid-washed polypropylene or polyethylene bottles through silicone tubing using in-line AcroPak® filter capsules containing 0.8/0.45 µm Supor® membrane filters that had been washed with trace-metal-grade HCl prior to use. Filter capsules and sample bottles were rinsed extensively with sample prior to sample collection. Individual capsules were reused to filter up to 500 liters and stored refrigerated between uses. The water samples were tightly capped and stored in the dark at room temperature until analysis. Samples for silicic acid concentration analysis were also drawn from all Niskin bottles.

2.1.2 Sample processing –

Subsamples were prepared for Si isotope analysis by reacting subsamples with acid-molybdate and precipitation of the resulting silicomolybdic acid with triethylamine using a modification of the method of De La Rocha *et al.* (1996). The original method quantitatively

precipitates the Si in samples with $> 10 \mu\text{M Si(OH)}_4$. It was learned that quantitative precipitation of samples containing as little as $1 \mu\text{M}$ silicic acid could be accomplished by waiting a week rather than the recommended 24 h for the precipitate to form. The precipitate was collected by filtration, rinsed and combusted to form solid SiO_2 as in the original method. The SiO_2 was dissolved in HF, precipitated as Cs_2SiF_6 by the addition of CsCl, and analyzed by acid decomposition by IRMS using a modified Kiel III inlet system coupled to a Finnigan MAT 252 IRMS mass spectrometer (Brzezinski *et al.*, 2006). The in house standard, Big Batch (Brzezinski *et al.*, 2006), was analyzed approximately every 8th sample to monitor system performance. Seawater samples were analyzed in duplicate or triplicate with each analysis performed on separate analytical runs of the mass spectrometer yielding an average external precision of $\pm 0.04 \text{ ‰}$ (1 SD). All isotope values are expressed in delta notation relative to the NBS28 standard.

2.1.3 Nutrient concentration analysis –

Silicic acid and nitrate concentrations were determined at sea using a Seal Analytical continuous flow Autoanalyzer according to Armstrong (1967) with a measurement precision of $\pm 0.27 \mu\text{M}$ for silicic acid and $\pm 0.12 \mu\text{M}$ for nitrate (uncertainties are standard deviations; Boyle and Cutter, 2011). The silicic acid concentration in each sample was re-assessed ashore using the manual acid-molybdate analysis of Strickland and Parsons (1972) and the reagent blank as described by Brzezinski and Nelson (1986).

3.1 Results

3.1.1 Data Calibration –

Silicic acid concentration analyses performed ashore agreed well with shipboard autoanalyzer results (laboratory concentration = $0.9998 \times \text{at sea concentration} + 0.2 \mu\text{mol kg}^{-1}$; Major axes Model II regression of laboratory versus at sea measurements) indicating high sample integrity. The $[\text{Si}(\text{OH})_4]$ values determined at sea are used for all data interpretation.

We were generally not successful in measuring $\delta^{30}\text{Si}(\text{OH})_4$ in 2 L water samples with $[\text{Si}(\text{OH})_4] < 2.5 \mu\text{M}$ as our analytical method requires five micromoles of Si for an accurate reading on the mass spectrometer (Brzezinski *et al.*, 2006). Given the low silicic acid concentrations in the Atlantic, this limitation resulted in few data from depths < 300 m at the more oligotrophic stations. Subsamples of near-surface waters (250 mL) have been archived for analysis at a later date with more sensitive methods.

The resampling of the station near the Cape Verde Islands in 2010 and 2011 allows an assessment of measurement precision. Comparison of values for the seven samples below 890 m where Si isotope values are not expected to show strong interannual variation shows agreement to within 0.1‰ with values from 2011 being more positive than those from 2010 by an average of 0.07 ± 0.03 (S.E., $n = 7$).

Two approaches were used to control data quality. The first was the use of an in-house standard, Big Batch, to monitor variability among individual runs on the mass spectrometer. No drift corrections were applied. Runs where the isotope value of Big Batch deviated by more than 0.1‰ from the consensus value were rejected. The average $\delta^{30}\text{Si}$ value for Big Batch for all runs yielding acceptable data was $-10.44 \pm 0.08 \text{ ‰}$ ($n = 87$) compared to the consensus value of -

$10.48 \pm 0.04 \text{ ‰}$ from the international intercalibration study of Reynolds *et al.*(2007). The average $\delta^{30}\text{Si}/\delta^{29}\text{Si}$ for these analyses was $1.959 \pm 0.003\text{‰}$.

The second approach employed the use of reference sea water collected as part of the prior US GEOTRACES intercalibration study at the BATS station (Cutter, 2013) to check data accuracy. Prior analysis of the reference waters collected on the intercalibration cruise from 4,000 m in our laboratory gave an average $\delta^{30}\text{Si}(\text{OH})_4$ value of $+1.41 \pm 0.08 \text{ ‰}$ compared to the overall average from analyses by four participating laboratories of $+1.45 \pm 0.05\text{‰}$ (Brzezinski, unpublished). The present section also sampled this same site. Measurement of the sample from 4,000 m from the BATS site on the current section yielded a slightly heavier $\delta^{30}\text{Si}(\text{OH})_4$ value of $+1.56 \text{ ‰}$. The possible offset implied by these data was explored further through comparison of our entire data set with data from the North and South Atlantic reported by de Souza *et al.* (2012b). $\delta^{30}\text{Si}(\text{OH})_4$ behaves as a quasi-conservative property in the Atlantic (de Souza *et al.*, 2012b) justifying comparison to samples from other locations within the Atlantic. The slope of the linear relationship between $\delta^{30}\text{Si}(\text{OH})_4$ and the inverse of $[\text{Si}(\text{OH})_4]$ between the two studies agrees to better than 2%, but there is an offset between the two data sets of 0.22 ‰ with the data from the US GEOTRACES section being more positive (Figure 2). This indicates that each study resolved relative differences in $\delta^{30}\text{Si}(\text{OH})_4$ values similarly, but with a bias in the absolute magnitude of the values obtained between studies.

We have not corrected the $\delta^{30}\text{Si}(\text{OH})_4$ data for the observed offset. The data from the present study at UCSB and that of de Souza *et al.* (2012b) at ETH are both well calibrated and quality controlled. Analysis of the 4,000 m BATS seawater samples during the earlier intercalibration exercise gave values of $+1.40 \text{ ‰}$ and $+1.55 \text{ ‰}$ by the UCSB and ETH laboratories, respectively (unpublished results), which implies a bias opposite of that in the

current pattern. These offsets will need to be accounted for during future syntheses involving multiple data sets generated by different laboratories. All data from this study are available from the Biological and Chemical Oceanography Data Management Office (BCO-DMO) repository.

3.1.2 Nutrient distributions –

The highest silicic acid concentrations (Figure 3a) were observed in the deep western basin with a maximum concentration of $53.1 \mu\text{mol kg}^{-1}$. Concentrations in the deep eastern basin were somewhat lower with a maximum of $48.1 \mu\text{mol kg}^{-1}$. This trend reversed at depths $< 3,000$ m with lower concentrations in the west compared to the east. Silicic acid concentrations were relatively uniform between 1,000 and 2,000 m east of station USGT11-20 with values between $22.6 - 25.3 \mu\text{mol kg}^{-1}$. Near surface (20 – 30 m) concentrations were $< 1 \mu\text{mol kg}^{-1}$ at all stations. In the western basin a subsurface minimum in silicic acid concentration occurred between 1,000 and 2,000 m that extended eastward to at least the mid-Atlantic ridge.

Si^* , defined as $[\text{Si}(\text{OH})_4] - [\text{NO}_3^-]$ (Sarmiento *et al.*, 2004), was high in the deep waters with maximum values of $+29 \mu\text{mol kg}^{-1}$ and $+24 \mu\text{mol kg}^{-1}$ in the deep western and deep eastern basins, respectively (Figure 3b). Si^* became negative at shallower depths reaching a minimum between 500 and 1,000 m across the section tracking the subsurface oxygen minimum (Figure 3b). The most negative values of Si^* , $-17 \mu\text{mol kg}^{-1}$, occurred in the upper 700 m in the eastern basin associated with the Mauritanian oxygen minimum zone off West Africa.

3.1.3 Silicon isotopes –

Figure 4 shows profiles of $\delta^{30}\text{Si}(\text{OH})_4$ and $[\text{Si}(\text{OH})_4]$ from station USGT11-22 in the eastern basin (See Figure 1 for station location). The commonly observed inverse correlation between $\delta^{30}\text{Si}(\text{OH})_4$ and $[\text{Si}(\text{OH})_4]$ is clear. $\delta^{30}\text{Si}(\text{OH})_4$ values are heaviest in the low $[\text{Si}(\text{OH})_4]$

surface waters becoming increasingly lighter through the nutricline. In this particular profile, silicic acid concentrations continue to increase, and $\delta^{30}\text{Si}(\text{OH})_4$ continues to decline, below 1,000 m until both properties become relatively uniform below 4,000 m. When $\delta^{30}\text{Si}(\text{OH})_4$ values for all stations are plotted against the inverse of silicic acid concentration, values fall along a straight line implying conservative mixing across end members (Figure 2).

While we were not able to obtain isotope measurements in surface waters in the most oligotrophic regions, at the more nutrient-rich coastal sites $\delta^{30}\text{Si}(\text{OH})_4$ values increase rapidly towards the surface in the upper 200 m associated with silicic acid depletion due to surface diatom production (Figure 3a, 5). Values between +1.8 ‰ and +2.0 ‰ are observed at intermediate depths (Figure 5). Waters with these characteristics span a greater depth range in the western basin compared to the east (Figure 5) associated with higher O_2 content of waters in the west (Figure 3b) mirroring the spatial trends in $[\text{Si}(\text{OH})_4]$ (Figure 3a). The lightest $\delta^{30}\text{Si}(\text{OH})_4$ values are observed in the deep western basin (station USGT11-12) (Figure 5). Values are slightly heavier in the deep eastern basin (station USGT11-20).

A unique feature along the section is the minimum in $\delta^{30}\text{Si}(\text{OH})_4$ observed near the bottom at station USGT11-16 that sampled directly over the Trans-Atlantic Geotraverse (TAG) hydrothermal zone (Figure 5). The near-bottom isotope profile shows a hooked pattern with a minimum near 3,300 m, while $[\text{Si}(\text{OH})_4]$ remains nearly constant (Figure 6). These variations are within analytical limits so the trends are highly uncertain, but they are consistent with the location of anomalies in several other trace elements and isotopes measured on this section.

4.1 Discussion

4.1.1 Data quality –

The overall precision for Si isotope measures of the seawater samples was ± 0.04 ‰ (1 SD); however, an offset of 0.22 ‰ was noted between $\delta^{30}\text{Si}(\text{OH})_4$ values obtained in this study and those of de Souza *et al.* (2012b) (Figure 2). Although there is close agreement between laboratories on the $\delta^{30}\text{Si}$ value for secondary standards (Reynolds *et al.*, 2007), the methods used to prepare these standards (all are solids) for analysis differs from those used to prepare seawater samples, such that the standards cannot be used to evaluate biases introduced during seawater sample processing. While the analysis of seawater from the BATS site gave values that agreed to within 0.15 ‰ among laboratories in the past, it is unclear whether that level of agreement has been maintained over time. Improved intercalibration will require laboratories to prepare and analyze the same reference seawaters in parallel with field samples. It is presently premature to apply a correction to account for the observed offset. Fortunately, its existence does not impede the ability to compare differences among water masses along the section or comparisons with other data sets when differences in $\delta^{30}\text{Si}(\text{OH})_4$ are large.

4.1.2 Ties between the MOC and $\delta^{30}\text{Si}(\text{OH})_4$ –

The observed trend of increasing $\delta^{30}\text{Si}(\text{OH})_4$ with declining silicic acid concentration in surface waters is observed commonly and is associated with the fractionation of Si during silicic acid consumption by siliceous plankton. The influence of fractionation during silica dissolution on the observed isotope distributions is more difficult to evaluate. Fractionation during opal dissolution would be predicted to release light isotopes of Si as frustules sink through the water

column (Demarest *et al.*, 2009). The input of light isotopes at depth coupled to their removal during silica production in surface waters would intensify the observed gradient in $\delta^{30}\text{Si}(\text{OH})_4$ across the nutricline, but this anticipated effect is difficult to separate from the influence of water mass changes with depth without direct knowledge of the depth distribution of rates of silica dissolution and of silica production.

To examine the relationship between the distribution of $\delta^{30}\text{Si}(\text{OH})_4$ and water masses, the results of the Optimum Multi-Parameter Analysis (OMPA) of Jenkins *et al.* (this issue) were used to identify the mixture of water masses present within each sample. The OMPA shows AABW to be the dominant contributor to the light $^{30}\text{Si}(\text{OH})_4$ values in the deep basins below 3,000 m (34 - 41% AABW, Figure 5) with the highest percent contribution of AABW in the deepest regions of the western basin. AABW is rich in silicic acid relative to nitrate (Sarmiento *et al.*, 2004) resulting in the very positive Si^* values in the deepest portions of the eastern and western basins (Figure 3). The high silicic acid concentration of AABW means that this water mass accounts for 90% and 86% of the $\text{Si}(\text{OH})_4$ in the deepest regions of the western and eastern basins, respectively. The remainder comes from the north, in the form of Iceland Scotland Overflow Water (ISOW), Denmark Strait Overflow Water (DSOW) and Central Labrador Sea Water (CLSW) with very minor (< 4 %) contribution from Mediterranean Outflow Water (MOW) (Jenkins *et al.*, this issue; Figure 5). $\delta^{30}\text{Si}(\text{OH})_4$ values for northern component waters that have been measured are all > +1.7 ‰ (de Souza *et al.*, 2012b). As a result, waters in the deep basins have a $\delta^{30}\text{Si}(\text{OH})_4$ value, +1.5 ‰ (or +1.3 ‰ after adjustment for the offset between data sets, Figure 2), that is intermediate between that of AABW, +1.2 ‰ (Cardinal *et al.*, 2005; de Souza *et al.*, 2012b; Fripiat *et al.*, 2012), and the northern component waters, > +1.7 ‰. The higher fraction of $\text{Si}(\text{OH})_4$ from the north in the deep eastern basin below 4,000 m is consistent

with the heavier $\delta^{30}\text{Si}(\text{OH})_4$ values in that basin compared to the values in the deep western basin (Figure 5).

There are significant differences in the proportions of northern end member water masses present in the deep eastern and deep western basins. ISOW and DSOW are the dominant northern water masses in the deep western basin (USGT11-12), while CLSW largely displaces ISOW in the eastern basin (station USGT11-20) (Figure 5). Still further east at station USGT11-22, ISOW completely displaces DSOW (Figure 5). The range in $\delta^{30}\text{Si}(\text{OH})_4$ among these water masses is, 0.18 ‰, with ISOW, CLSW and DSOW having $\delta^{30}\text{Si}(\text{OH})_4$ values of +1.68 ‰, +1.79 ‰ and +1.86 ‰, respectively (de Souza *et al.*, 2012b) each considerably heavier than the value of +1.2 ‰ in AABW (Cardinal *et al.*, 2005; de Souza *et al.*, 2012b; Fripiat *et al.*, 2012). However, these water masses collectively account for < 15 % of the silicic acid in the deep basins such that even large changes in their relative abundance has little influence on $\delta^{30}\text{Si}(\text{OH})_4$. The difference in calculated deep basin $\delta^{30}\text{Si}(\text{OH})_4$ values when all northern component waters are assumed to have the light signature of ISOW (+1.68 ‰) versus the heavier isotopic signature of DSOW (+1.86 ‰) is only 0.01 ‰.

The upper limb of the northward flowing component of the MOC is represented by AAIW in the OMPA (Jenkins *et al.*, this issue). Waters at approximately 800 m depth in the easternmost reaches of the section contain up to 62% AAIW with MOW and Irminger Sea Water (ISW) contributing the remainder (Figure 5). Currently, the best measures of the isotopic composition of AAIW come from the South Pacific where AAIW was measured to have a $\delta^{30}\text{Si}(\text{OH})_4$ value of +1.6 to +2.0 ‰ and $[\text{Si}(\text{OH})_4]$ of 10 to 15 $\mu\text{mol kg}^{-1}$ with the Irminger Sea having a $\delta^{30}\text{Si}(\text{OH})_4$ of +1.8 ‰ and $[\text{Si}(\text{OH})_4]$ of 10 $\mu\text{mol kg}^{-1}$ (de Souza *et al.*, 2012b). No measurements of $\delta^{30}\text{Si}(\text{OH})_4$ are available from the Mediterranean Sea, but based on the low

silicic acid content of Mediterranean waters, relatively heavy isotope values are anticipated. The observed AAIW-ISW-MOW mixture is heavy as expected, but there is little contrast between the isotopic value of the mixture and surrounding waters, such that AAIW does not appear as a distinct feature in the distribution of $\delta^{30}\text{Si}(\text{OH})_4$.

Upper Labrador Sea Water (ULSW) and Upper Circumpolar Deep Water (UCDW) are found just beneath AAIW across the section (Jenkins *et al.*, this issue). The contribution of ULSW is most pronounced in the west where it comprises 80% of the water between 1,000 and 1,500 m, while UCDW is most prevalent in the east where it comprises 60% of the water between 1,500 and 2,000 m (Figure 5). ULSW is the shallow limb of NADW and is apparent as a minimum in $[\text{Si}(\text{OH})_4]$ (Figure 3) and a local maximum in $\delta^{30}\text{Si}(\text{OH})_4$ in the west between 1,000 and 2,000 m (Figure 5). The dominance of UCDW in the east is not apparent in the distribution of either silicic acid concentration or silicon isotopes, but it may contribute to the general eastward increase in $[\text{Si}(\text{OH})_4]$ and decrease $\delta^{30}\text{Si}(\text{OH})_4$ along the 1,500 – 2,000 m depth horizon.

Surface waters between 300 and ~ 600 m are overwhelmingly dominated by North Atlantic Central water (>90%) except near the Mauritanian oxygen minimum zone off Africa where Atlantic Equatorial Water dominates (Jenkins *et al.*, this issue). These water masses do not appear as unique features in either the $[\text{Si}(\text{OH})_4]$ or in the $\delta^{30}\text{Si}(\text{OH})_4$ distributions, but they may contribute to the higher near-surface $[\text{Si}(\text{OH})_4]$ and heavier isotopic signatures in the east compared to the west. SAMW was not included in the OMPA, but this water mass also carries a strong Southern Ocean imprint (Sarmiento *et al.*, 2004). The 26.80 σ_θ isopycnal used by Sarmiento *et al.* (2004) to identify the location of the SAMW pycnostad in the Atlantic lies near

the top of the oxygen minimum zone at ~300 – 400 m depth along the section (Figure 3b). $\delta^{30}\text{Si}(\text{OH})_4$ data were largely not obtained in this depth zone.

The section sampled directly over the TAG hydrothermal zone on the mid-Atlantic ridge. Hydrothermal vents emit high concentrations of dissolved Si accounting for 10% of the global input of Si to the oceans (Tréguer and De La Rocha, 2013). The silicon isotopic composition of hydrothermal waters has only been measured in two samples from the East Pacific Rise. Those waters have highly negative $\delta^{30}\text{Si}(\text{OH})_4$ values, -0.2 ‰ and -0.4 ‰ (De La Rocha *et al.*, 2000) compared to the average value of +1.2 ‰ to +1.5 ‰ for the deep ocean silicic acid reservoir. A plume of hydrothermal waters from TAG hydrothermal zone is thus consistent with the suggestion of a local minimum in $\delta^{30}\text{Si}(\text{OH})_4$ above the ridge (Figure 5, 6). Interestingly, there is no apparent silicic acid anomaly in the same depth interval (Figure 6). Mortlock *et al.* (1993) observed positive silicic acid anomalies up to tens of kilometers away from vent sites on the East Pacific rise. Assuming that hydrothermal waters at TAG have a $\delta^{30}\text{Si}(\text{OH})_4$ value of -0.4 ‰, the observed ~0.05 ‰ minimum in $\delta^{30}\text{Si}(\text{OH})_4$ in waters of $36 \mu\text{mol kg}^{-1} [\text{Si}(\text{OH})_4]$ and $\delta^{30}\text{Si}(\text{OH})_4$ of +1.5 ‰ should be accompanied by a $1 \mu\text{mol kg}^{-1}$ positive silicic acid anomaly which should be detectable given the $\pm 0.27 \mu\text{M}$ precision of the dissolved silicon analysis (Boyle and Cutter, 2011, see Methods). Our horizontal resolution is extremely coarse making it difficult to resolve a true background silicic acid concentration for detecting concentration anomalies, but there isn't even a suggestion of a local maximum in $[\text{Si}(\text{OH})_4]$ associated with the minimum in the $\delta^{30}\text{Si}(\text{OH})_4$ profile (Figure 6). Further analysis of the entire North Atlantic GEOTRACES data set at stations near the TAG hydrothermal zone may help resolve these issues.

4.1.3 Controls on $\delta^{30}\text{Si}(\text{OH})_4$ distribution in the Atlantic –

The Southern Ocean plays a key role in setting the preformed nutrient content of the global ocean. The strong influence of the Southern Ocean on the distribution of Si isotopes in the Atlantic has been highlighted by de Souza *et al.* (2012b). Box models that incorporate Southern Ocean dynamics reproduce key features of the Si isotope distribution in the Atlantic including the heavy isotopic signature of NADW (de Souza *et al.*, 2012b; Reynolds, 2009). While mass balance requires that the relatively heavy $\delta^{30}\text{Si}(\text{OH})_4$ in northward flowing AAIW and SAMW be incorporated in the southward return flow, there is a second source of isotopically heavy $\text{Si}(\text{OH})_4$ in the north Atlantic, the Arctic Ocean.

Recent measurements show that the waters of the Arctic Ocean contain the heaviest $\text{Si}(\text{OH})_4$ of all ocean basins (Varela, pers. com.). Waters leave the Arctic through the Fram Strait as the East Greenland Current and through the Canadian Archipelago as the Baffin Island Current (Aksenov *et al.*, 2010) transporting between 2 – 30 Sv (Hopkins, 1991). The heavy isotopic signature predicted for the entire deep Arctic by models (Varela, pers. com.) would contribute to the heavy Si isotope values that have been measured in the Labrador and Irminger Basins (de Souza *et al.*, 2012b). In the present section, the heavy isotopic composition of these and other northern end-member waters had a clear impact on the isotopic composition of NADW as revealed by the minimum in $[\text{Si}(\text{OH})_4]$ and maximum in $\delta^{30}\text{Si}(\text{OH})_4$ between 500 and 1,000 m in the west. These waters also likely influence the deeper layers within NADW maintaining low silicic acid concentration, and relatively heavy $\delta^{30}\text{Si}(\text{OH})_4$ values, to depths of 2,500 m in the west whereas similar values occur no deeper than ~1,200 m in the east.

The developing global $\delta^{30}\text{Si}(\text{OH})_4$ data set indicates that the deep waters of the two polar oceans lay at opposite ends of the range of $\delta^{30}\text{Si}(\text{OH})_4$ in the ocean, with the heaviest $\delta^{30}\text{Si}(\text{OH})_4$ in the Arctic, +1.9 ‰ (Varela, pers. com.), and the lightest $\delta^{30}\text{Si}(\text{OH})_4$ in the Southern Ocean, +1.2 ‰ (Cardinal *et al.*, 2005; de Souza *et al.*, 2012b; Fripiat *et al.*, 2012), compared to an average of +1.3 to +1.4 ‰ for most of the deep ocean (Beucher *et al.*, 2008; Reynolds, 2009). The contrasting isotopic signatures between the two polar oceans arise through dynamics that are unique to each region (Figure 7).

AABW originates at the Antarctic Divergence which is the one area of the surface ocean that is in direct contact with abyssal waters. The deep waters ventilating at the divergence have high silicic acid concentration and a light silicon isotope signature (Cardinal *et al.*, 2005; de Souza *et al.*, 2012b; Fripiat *et al.*, 2012) due to Si trapping in the Southern Ocean. The trap involves strong diatom production in the surface waters as they are driven equatorward from the Divergence by the West Wind Drift (Figure 7). Strong depletion of silicic acid results in a heavy isotopic signature of the residual preformed silicic acid that is incorporated into AAIW at the Polar Front and into SAMW in the Subantarctic. In contrast, the light diatom frustules sink, and because of the long remineralization length scale for biogenic silica, they dissolve at relatively deep depths reintroducing isotopically light $\text{Si}(\text{OH})_4$ into the deep waters flowing southward back towards the Divergence (Figure 7). This process essentially distills heavy isotopes of Si out of the Southern Ocean via the northward flowing mode waters, while light isotopes accumulate in the meridional recirculation cell imparting low $\delta^{30}\text{Si}(\text{OH})_4$ to the waters ventilating at the Antarctic Divergence. The East Wind Drift drives water poleward from the Antarctic Divergence (Figure 7). These waters experience little biological consumption before subducting and turning northward at abyssal depths resulting in the AABW having a relatively light

$\delta^{30}\text{Si}(\text{OH})_4$ signature of +1.2 ‰ (Cardinal *et al.*, 2005; de Souza *et al.*, 2012b; Fripiat *et al.*, 2012).

In contrast to the major role of deep waters in $\delta^{30}\text{Si}(\text{OH})_4$ dynamics in the Southern Ocean, shallow sills restrict exchange between the Arctic and adjacent oceans to < 50 m in the Bering Strait in the Pacific, and to < 2,600 m in the Fram Strait off Greenland and to <1,000 m along the Atlantic inflow to the Norwegian Sea (Skagseth *et al.*, 2008). This means that waters entering the Arctic from the Atlantic and Pacific Oceans originate at depths with relatively low $[\text{Si}(\text{OH})_4]$ and heavy $\delta^{30}\text{Si}(\text{OH})_4$ compared to the deep ocean (Figure 3). This initially heavy signature would be amplified within the Arctic Ocean through the production and burial of diatom frustules that have preferentially incorporated light Si isotopes. The combined effect of these two processes is that the subsurface waters of the Arctic are the heaviest of all ocean basins. River inputs into the Arctic are large, but current models suggest only a minor impact on $\delta^{30}\text{Si}(\text{OH})_4$ (Varela, pers. com.).

The third prominent component of the MOC in the Atlantic is the northward flow of Southern Ocean mode waters. Between 5 and 10 Sv of AAIW flow across the equator into the North Atlantic (Jochum and Malanotte-Rizzoli, 2003; and references therein). The distillation of heavy isotopes of Si from the Southern Ocean silicic acid trap into SAMW and AAIW results in those water masses having moderately low $[\text{Si}(\text{OH})_4]$ and heavy $\delta^{30}\text{Si}(\text{OH})_4$ compared to AABW. SAMW is present at relatively shallow depths along the section where low $[\text{Si}(\text{OH})_4]$ prevented us from obtaining isotope data. Data was obtained in the region dominated by AAIW in the east (Figure 4). AAIW did not appear as a distinct feature in the $\delta^{30}\text{Si}(\text{OH})_4$ distribution along the section from the North Atlantic. The isotopic value observed in the region of AAIW dominance (Figure 5) is heavy as expected (de Souza *et al.*, 2012a), but the water mass is both

diluted with other components and embedded in the gradient in $\delta^{30}\text{Si}(\text{OH})_4$ that is characteristic of the main nutricline which obscures its presence.

$\delta^{30}\text{Si}(\text{OH})_4$ in the Atlantic is therefore heavily influenced by a Si isotope bipole that to first order represents mixing between end members originating in each polar ocean. In Figure 8 we plot the $\delta^{30}\text{Si}(\text{OH})_4$ values measured along the GEOTRACES transect together with those of de Souza *et al.* (2012b) to illustrate key aspects of the bipole. The data in the figure have been adjusted for the offset between data sets by subtracting 0.22 ‰ from the GEOTRACES values. After this adjustment the two data sets form a single line on a plot of $\delta^{30}\text{Si}(\text{OH})_4$ versus $[\text{Si}(\text{OH})_4]^{-1}$ (Figure 8). The consistency between data sets is remarkable considering that the data of de Souza *et al.* (2012b) come from stations in the Atlantic that span a wide range of latitude (~64°N to 60°S) sampled over five years, while the present data set spans a large range in longitude in only the North Atlantic with sampling occurring largely during a single year. The coherence between these geographically and temporally distinct data sets reinforces the idea that silicon isotopes behave as a quasi-conservative property in the Atlantic (de Souza *et al.*, 2012b).

The end members reside in each polar ocean with the light $\delta^{30}\text{Si}(\text{OH})_4$ end member being the AABW from the Southern Ocean and the heavy end member being Arctic Water (AW) (Figure 8). The bipole is dominated by the Southern Ocean end member as the concentration of silicic acid in AABW exceeds that in northern end members by an order of magnitude (Figure 8). AABW enters the MOC in the Atlantic unaltered, and thus falls on the two-end member mixing line (Figure 8). In contrast, the $\delta^{30}\text{Si}(\text{OH})_4$ value of Arctic Waters (AW) falls off of the mixing line for two reasons. First, the value of AW was taken from the Canada Basin far from the North Atlantic and variations in deep water $\delta^{30}\text{Si}(\text{OH})_4$ may exist in the Arctic. Second, AW is significantly altered upon entering the Atlantic during the formation of LSW (and

subcomponents), ISOW, and DSOW. LSW and ISOW are the dominant contributors to the southward transport of waters of Arctic origin in the north Atlantic (e.g. Smethie and Fine, 2001), and thus constitute the effective northern end member of the bipole (Figure 8). AAIW and SAMW constitute a third end member that is intermediate in both silicic acid concentration and $\delta^{30}\text{Si}(\text{OH})_4$. The properties of these water masses fall very close to the mixing line (Figure 8) and thus mixing involving these waters does not produce strong deviations from the apparent two end-member mixing relationship.

4.1.4 Differences in Si and N isotope systems –

The strong ties between the MOC and $\delta^{30}\text{Si}(\text{OH})_4$ distribution is very different from its relationship to the distribution of other macronutrient isotopes, most notably the nitrogen isotopic composition of nitrate. $\delta^{15}\text{NO}_3$ in the deep ocean is nearly uniform at +4.8 ‰ with little variation within the MOC outside of oxygen minimum zones (Sigman *et al.*, 2000) and the Southern Ocean (Rafter *et al.*, 2013). The two main arguments put forth to explain the uniformity of deep $\delta^{15}\text{NO}_3$ are both related to the severe depletion of nitrate in surface waters over most of the ocean outside of the Southern Ocean. The effects are two-fold: 1) the average $\delta^{15}\text{N}$ of sinking PON and the $\delta^{15}\text{N}$ of deep nitrate converge at local scales on an annual basis and 2) the lack of preformed nitrate in surface waters outside of the Southern Ocean means that the mixing of surface waters to depth alters subsurface $[\text{NO}_3^-]$, but not subsurface $\delta^{15}\text{NO}_3$ (Sigman *et al.*, 2000). These factors cannot explain the difference between deep $\delta^{15}\text{NO}_3$ and $\delta^{30}\text{Si}(\text{OH})_4$ distributions as silicic acid is also highly depleted in surface waters over most of the global ocean. The role of differences in preformed $\text{Si}(\text{OH})_4$ and NO_3^- in the Southern Ocean is also equivocal. Preformed silicic acid concentration in AABW is higher than that of nitrate, which would buffer $\delta^{30}\text{Si}(\text{OH})_4$ within the water mass against alteration due to mixing to a greater

extent than would occur for $\delta^{15}\text{NO}_3$. However, the reverse is true in AAIW and SAMW where the concentration of preformed nitrate exceeds that of preformed silicic acid.

A clear difference between the N and Si cycles that may be responsible for the contrasting distributions of their isotopes is that Si is not involved in redox reactions, while such reactions dominate nitrogen cycling, especially at low latitudes. Nitrification and denitrification act on the dissolved NO_3 pool altering $\delta^{15}\text{NO}_3$ which is then mixed and distributed by currents. Other processes, like the fixation of atmospheric N_2 , affect the isotopic signature of sinking particles that are remineralized to nitrate at depth. These processes pull the isotopic signature of nitrate in different directions and they are not spatially uniform with, for example, denitrification being most intense in oxygen minimum zones. The Si cycle is simple by comparison. Unlike inorganic N, dissolved silicon in the sea has only one molecular form, silicic acid, which is predominantly (~97%) present in its undissociated state. Like nitrate, silicic acid depletion in surface waters is nearly complete. Biogenic silica production is overwhelmingly supported by vertical mixing of silicic acid from beneath the euphotic zone. Atmospheric inputs do occur in the form of the dissolution of dust, but the impact of aeolian inputs on the dissolved Si inventory is small (Treguer and De La Rocha, 2013). The fractionation associated with silica production from field observations is relatively consistent at -1.1 ‰ (Fripiat *et al.*, 2012; Fripiat *et al.*, 2011; Varela *et al.*, 2004) although some interspecific variation is observed in culture (Sutton *et al.*, 2013). Silica dissolution also fractionates isotopes of Si (Demarest *et al.*, 2009). The effects of fractionation during dissolution on global Si isotope distributions are currently poorly understood, but would be expected to have their largest impact on $\delta^{30}\text{Si}(\text{OH})_4$ in the upper kilometer of the ocean where most sinking opal dissolves. Thus, while there are multiple

processes that can affect $\delta^{15}\text{NO}_3$, only fractionation during silica production in surface waters and fractionation during silica dissolution throughout the water column alter $\delta^{30}\text{Si}(\text{OH})_4$.

More critical may be differences in the spatial distribution of new N and new Si production. Thermocline waters fueling phytoplankton productivity over most of the global ocean are rich in nitrate, but low in silicic acid, due to Si trapping in the Southern Ocean (Sarmiento *et al.*, 2004). As a result, well over half of global marine new N production occurs in the low latitude ocean (Sarmiento and Gruber, 2006), while these areas account for <10% of global marine new silica production (Brzezinski *et al.*, 2011). This means that in the low latitudes the remineralization of locally produced new organic N plays a large role in determining deep water $\delta^{15}\text{NO}_3$ compared to the impact of the dissolution of locally produced new silica on deep water $\delta^{30}\text{Si}(\text{OH})_4$. The diminished role of local processes in the Si cycle of the low latitude ocean means that $\delta^{30}\text{Si}(\text{OH})_4$ and $[\text{Si}(\text{OH})_4]$ have a stronger link to thermohaline circulation and to the characteristics of preformed nutrients in the high latitudes than do $\delta^{15}\text{NO}_3$ and $[\text{NO}_3^-]$. High latitudes, especially the Southern Ocean, are also the dominant source of regenerated $\text{Si}(\text{OH})_4$ to most of the deep ocean as supported by recent numerical simulations (Holzer *et al.*, 2013). Dominance of the Southern Ocean for both preformed and regenerated Si would diminish the role of local inputs at low latitude to Si isotope distribution contributing to the quasi-conservative nature of $\delta^{30}\text{Si}(\text{OH})_4$ in the Atlantic (de Souza *et al.*, 2012b).

The greater role of the Southern Ocean in Si isotope versus N isotope dynamics is the result of differences in how nitrate and silicic acid are cycled within the Southern Ocean overturning circulation. Silicic acid concentration in waters upwelled at the Antarctic Divergence, $\sim 65 \mu\text{mol kg}^{-1}$, exceeds that of nitrate by two fold. The biological consumption of silicic acid within waters that form AAIW and SAMW is high relative to that of nitrate due to Fe

stress on phytoplankton (e.g. Franck *et al.*, 2000) and the inherent heavy silicification of some Southern Ocean diatom species (Smetacek, 1998). Silicic acid concentrations can be depleted by >70% compared to only about 20% for nitrate. The result is that the preformed silicic acid and preformed nitrate in AAIW and SAMW are both heavier than in deep waters, with Si isotopes exhibiting the greater relative difference. Light isotopes of both Si and N are returned to depth by the remineralization of sinking particles imparting a lighter character to the Si and N upwelling at the Antarctic Divergence. Thus, heavy isotopes of both elements are distilled out of the Southern Ocean in mode waters with light isotopes incorporated into Antarctic deep waters making the deep Southern Ocean the lightest of all deep ocean basins for both $\delta^{30}\text{Si}(\text{OH})_4$ and $\delta^{15}\text{NO}_3$ (de Souza *et al.*, 2012b; Rafter *et al.* 2013), but the effect is stronger for Si given it's greater retention efficiency within the Southern Ocean overturning circulation. The nitrogen isotope signatures of AABW, AAIW, and SAMW are reset at low latitudes through the complex series of processes discussed above, while $\delta^{30}\text{Si}(\text{OH})_4$ behaves more like a conservative property with a distribution governed by mixing among end member water masses.

The relationship between N and Si isotopes in the Arctic Ocean differs from that in the Southern Ocean. The first N and Si isotope data from the Arctic were obtained on the Canadian GEOTACES cruise to the Canada Basin. Unlike the Southern Ocean which is light in both $\delta^{15}\text{NO}_3$ and $\delta^{30}\text{Si}(\text{OH})_4$, the deep waters of the Canada Basin contain the heaviest $\delta^{30}\text{Si}(\text{OH})_4$ of any deep ocean basin (Varela, pers. com.), while $\delta^{15}\text{NO}_3$ was $\sim +5$ ‰ similar to other deep ocean basins outside of the Southern Ocean (Julie Granger, pers. com.). As discussed above, shallow exchange between the Arctic and the Pacific and between the Arctic and the Atlantic likely contributes to the heavy $\delta^{30}\text{Si}(\text{OH})_4$ of the deep Arctic, but the effects of this process on $\delta^{15}\text{NO}_3$ are less clear. The shorter remineralization length scale for particulate organic nitrogen

versus biogenic silica combined with the relative shallow depth of exchange between the north Atlantic and Arctic means that the water entering the Arctic will be closer to deep water values for $\delta^{15}\text{NO}_3$ than for $\delta^{30}\text{Si}(\text{OH})_4$, but as in other basins, local processes within the Arctic may also be important in setting deep water $\delta^{15}\text{NO}_3$.

4.1.5 Conclusions –

This study confirms a tight relationship between $\delta^{30}\text{Si}(\text{OH})_4$ and the MOC in the North Atlantic and that Si isotopes behave as a quasi-conservative property in the Atlantic Ocean. At depths below ~300 m spatial patterns in $\delta^{30}\text{Si}(\text{OH})_4$ were closely related to water mass distribution due to the strong contrasts in the isotopic composition of waters originating in the two polar oceans. The Southern and Arctic Oceans lie at opposite extremes in the range of $\delta^{30}\text{Si}(\text{OH})_4$ in the global ocean with the Southern Ocean containing the lightest, and the Arctic Ocean the heaviest, $\delta^{30}\text{Si}(\text{OH})_4$. Northward flowing Southern Ocean deep waters attain their light $\delta^{30}\text{Si}(\text{OH})_4$ through Si trapping in the Southern Ocean, which also distills heavy isotopes out of the Southern Ocean via the northward flow of mode waters. The heavy $\delta^{30}\text{Si}(\text{OH})_4$ of the Arctic Ocean arises from the long remineralization length scale of opal coupled to the shallow depth of exchange between the Arctic and adjacent oceans forced by bottom topography. The resulting silicon isotope bipole maximizes the contrast in the isotopic composition of $\text{Si}(\text{OH})_4$ entering the northern and southern extremes of the MOC in the Atlantic with isotopically heavy NADW and isotopically light AABW clearly evident along the section.

The heavy signature of northern end member components of the bipole is predicted to be diluted relatively quickly along the MOC given the low $[\text{Si}(\text{OH})_4]$ of northern end members compared to their high $[\text{Si}(\text{OH})_4]$ counterparts from the Southern Ocean. The Atlantic is the only

major ocean that receives significant inputs from both polar oceans as the net flow of water through the Arctic Ocean is from the Pacific to the Atlantic. Thus, the influence of the silicon isotope bipole will be likely confined to the Atlantic causing meridional gradients in $\delta^{30}\text{Si}(\text{OH})_4$ in the Atlantic to be far stronger than in either the Pacific or Indian Oceans. Additional data from the International GEOTRACES program will allow a rigorous test of these assertions.

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Figure Legends:

Figure 1: Map of station locations where $\delta^{30}\text{Si}(\text{OH})_4$ was measured. Numbers denote GEOTRACES station numbers. The prefix USGT11 denotes stations occupied in 2011 with USGT10 denoting stations sampled in 2010.

Figure 2: $\delta^{30}\text{Si}(\text{OH})_4$ as a function of the inverse of $[\text{Si}(\text{OH})_4]$ for this study (white circles) and for the study of (de Souza *et al.*, 2012b) (black circles) for waters from > 1,000 m depth.

Figure 3. A. Contours of $[\text{Si}(\text{OH})_4]$ across the section. B. Contours of Si^* , colored contouring, and oxygen, line contours.

Figure 4. Representative profile of $\delta^{30}\text{Si}(\text{OH})_4$ (black circles) and $[\text{Si}(\text{OH})_4]$ (white circles) from station USGT11-22.

Figure 5. Section of $\delta^{30}\text{Si}(\text{OH})_4$ for stations illustrated in Figure 1. Data from both GT10-12 and GT11-24 that sampled at 24°W longitude were used in constructing the contours of $\delta^{30}\text{Si}(\text{OH})_4$. Pie charts indicate the percent of dominant water masses present at the sampling points indicated by the arrows. Water mass abbreviations: Antarctic Intermediate Water (AAIW), Upper Circumpolar Deep Water (UCPDW), Denmark Straits Overflow Water (DSOW), Mediterranean Outflow Water (MOW), Irminger Sea Water (ISW), Iceland-Scotland Overflow Water (ISOW), Central Labrador Sea Water (CLSW), Upper Labrador Sea Water (ULSW).

Figure 6. Profile of $\delta^{30}\text{Si}(\text{OH})_4$ and $[\text{Si}(\text{OH})_4]$ in the bottom waters at station USGT11-16 above the TAG hydrothermal zone. Error bars are standard errors. $\delta^{30}\text{Si}(\text{OH})_4$ at the closest density surfaces at adjacent stations (stations USGT11-12 and USGT11-20, gray symbols, are shown for reference).

Figure 7. Conceptual diagram of the silicon isotope bipole. Arrows denote the flows of major water masses with their relative $\delta^{30}\text{Si}(\text{OH})_4$ indicated by color. Blue colors denote light Si isotope values (low $\delta^{30}\text{Si}(\text{OH})_4$) with red colors representing heavy values (more positive $\delta^{30}\text{Si}(\text{OH})_4$). Blue circles represent diatoms that have preferentially incorporated the lighter isotopes of Si. Small blue arrows represent the release of light isotopes of Si via dissolution. The major Antarctic Provinces are: the Antarctic Zone, ANT; the Polar Frontal Zone, PFZ; and the SubAntarctic Zone, SAZ. The major fronts in the Southern Ocean are the Antarctic Divergence (Southern ACC Front), AD; Antarctic Polar Front, APF, the Subantarctic Front, SAF and the Subtropical Front, STF. The Antarctic Divergence is driven by the opposing East Wind Drift (EWD) and West Wind Drift (WWD). Water mass abbreviations as defined in the text.

Figure 8. Characteristics of end member waters masses of the silicon isotope bipole. Antarctic Bottom Water (AABW) and the Arctic Water (AW) shown in red form the high nutrient isotopically-light and low-nutrient isotopically-heavy end members, respectively. Shallow exchange between the Arctic and North Atlantic cause Labrador Sea Water (LSW), Iceland-Scotland Overflow Water (ISOW) and Denmark Strait Overflow Water (DSOW) to be heavy. Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) fall close to the two-end member mixing line. The line drawn was calculated by linear regression for the observations of de Souza *et al.* (2012b), filled circles, and this study, open circles (adjusted for the 0.22 ‰ offset between studies, see text) together. Data are values from > 1,000 m. Characteristics of major water masses (large symbols) from de Souza *et al.* (2012b) and Varela (pers. com.).

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