Supplementary Material to

Silicon stable isotope distribution traces Southern Ocean export of Si to the eastern South Pacific thermocline

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A. Influence of filtration blank on δ^{30}Si values of near-surface samples

As noted in the main text, we determined a filtration blank of 0.35-0.45 μM for the Whatman GF/F filters used on expedition 33RO20071215. Whilst negligible for most samples, this contribution is a considerable fraction of sample Si for 8 near-surface samples with low [Si] of < 7 μM (highlighted in Supplementary Table 1), but we are unable to directly assess the influence of the filtration blank on measured δ^{30}Si values, because its low absolute contribution precludes analysis of its isotope composition. Since the source of Si in borosilicate glass, sand, should impart it a low δ^{30}Si value (~0‰), the samples most vulnerable to the influence of filtration blank are the low-[Si], high-δ^{30}Si summer mixed layers of the high-latitude stations. As Fig. S4 shows, our high-latitude summer mixed layer data are in good agreement with similarly high values in the published literature, with no indication of a systematic offset to lower values, which gives us reasonable confidence that the values we report are not strongly affected by the influence of the filtration blank. However, the scatter in these data precludes a satisfactorily robust conclusion. If the filtration blank does indeed contribute Si with a δ^{30}Si value near 0‰, we cannot conclusively rule out the possibility that the δ^{30}Si values of the 8 samples with [Si] < 7 μM are affected by blank to levels greater than analytical uncertainty. These potential systematic offsets range from –0.2‰ for the sample at Sta 70/133m (in fact within the analytical uncertainty on this datapoint) as well as the summer mixed layer at 62ºS (Sta 158/4m, 32m) to –0.4‰ for the high-latitude summer mixed layer at 58ºS (Sta 149/15m). Importantly, the winter mixed layer data, on which our analysis mainly focuses, are insignificantly affected (always < 0.1‰) by this contamination.

B. Monte Carlo *t*-test

A Monte Carlo method was adopted to compare deepwater δ^{30}Si values in the South Pacific, since variability is small compared to the analytical uncertainty of the data. All δ^{30}Si datapoints from two datasets being compared were perturbed 10^4 times by a normally-distributed random variable with a variance corresponding to the analytical uncertainty of the datapoints (as reported in Supplementary Table 1). After each perturbation, a two-sided unequal variance *t*-test (Welch's *t*-test) was performed on these dataset pairs and the *p*-value corresponding to the test statistic recorded. The probabilities reported in the main text refer to the relative proportion of *p*-values that were smaller than $\alpha = 0.05$.

C. Influence of NADW on the Southern Ocean δ^{30}Si distribution

We use the distribution of the quasi-conservative tracer PO_4^* (Broecker et al, 1991) in order to calculate the volume fraction of NADW along a longitudinal section of the Southern Ocean along 30ºE (CLIVAR I06S re-occupation). We calculate the volume fraction of NADW, f_{NADW}, from the relation:

$$f_{NADW} = \frac{PO^*_{4,CDW} - PO^*_4}{PO^*_{4,CDW} - PO^*_{4,NADW}}$$

with $PO_4^*{}_{,CDW}$ = 1.71 µmol/kg and $PO_4^*{}_{,NADW}$ = 0.76 µmol/kg and

$$PO^*_4 = PO_4 + \frac{O_2}{170} - 1.95 \text{ µmol/kg}$$

following the revised definition of Sarmiento et al. (2007). We then draw on de Souza et al. (2012) and Broecker et al. (1991) to estimate the [Si] and δ^{30}Si of the high North Atlantic and the deep Southern Ocean endmembers. With this, we can calculate the expected Si concentration and isotope composition distribution along the I06S section using:

$$Si_{mix} = f_{NADW} \cdot Si_{NADW} + (1 - f_{NADW}) \cdot Si_{CDW}$$

$$\delta^{30}Si_{mix} = \frac{f_{NADW} \cdot Si_{NADW} \cdot \delta^{30}Si_{NADW} + (1 - f_{NADW}) \cdot Si_{CDW} \cdot \delta^{30}Si_{CDW}}{Si_{mix}}$$

with Si_{NADW} = 12 µmol/kg, Si_{CDW} = 120 µmol/kg, $\delta^{30}Si_{NADW}$ = +1.7‰ and $\delta^{30}Si_{CDW}$ = +1.2‰. The resulting variation in Southern Ocean δ^{30}Si values is exceedingly small, with a range of about 0.05‰, as can be seen in Fig. S8. This result is unsurprising, considering the extremely small Si mass flux associated with NADW, due to its low Si concentration.

SUPPLEMENTARY FIGURES

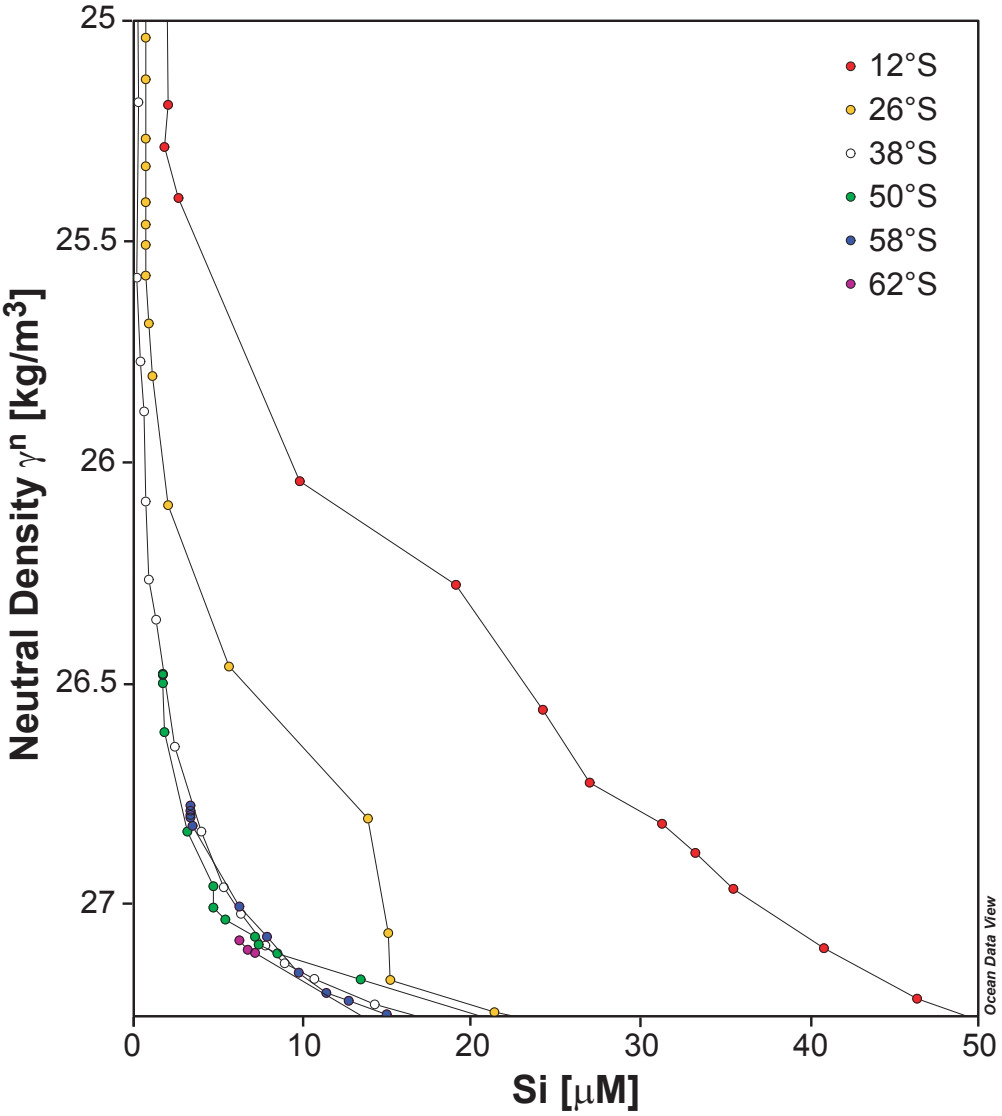

Figure S1: Silicon concentrations at thermocline to intermediate depths, plotted against neutral density γ^n. This is a more detailed view of concentration data presented in Fig. 5b of the manuscript, highlighting the constancy of [Si] along isopycnals in the eastern South Pacific. The elevated [Si] around γ^n = 26.75 kg/m^3 at 26°S is also apparent. Data are from the CLIVAR & Carbon Hydrographic Data Office (http://cchdo.ucsd.edu/).

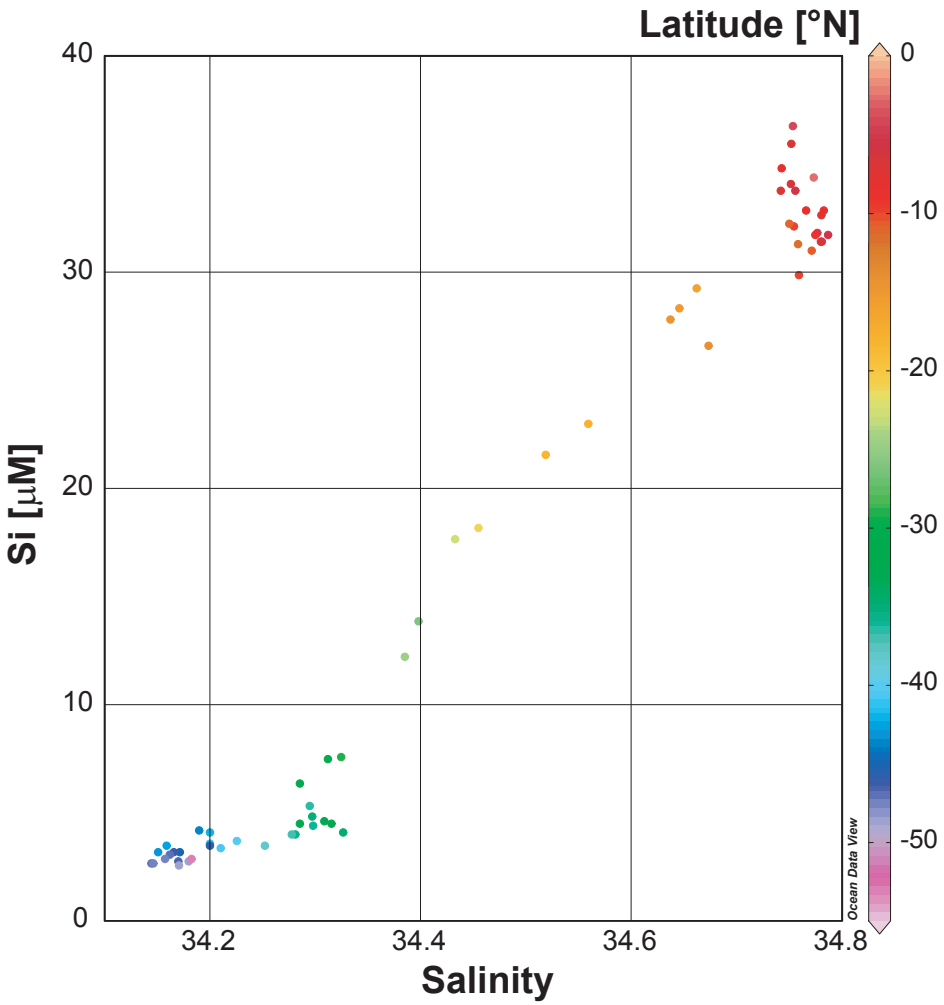

Figure S2: Isopycnal covariation of silicon concentration [Si] and seawater salinity for 26.75 kg/m^3 ≤ γ^n ≤ 26.85 kg/m^3 below 100 dbar along line P18. Datapoint color denotes sampling latitude. Note the linear increase in [Si] with salinity centered around ~30°S, documenting the mixing of saline and Si-rich equatorial waters into the subtropics. Data are from the CLIVAR & Carbon Hydrographic Data Office (http://cchdo.ucsd.edu/).

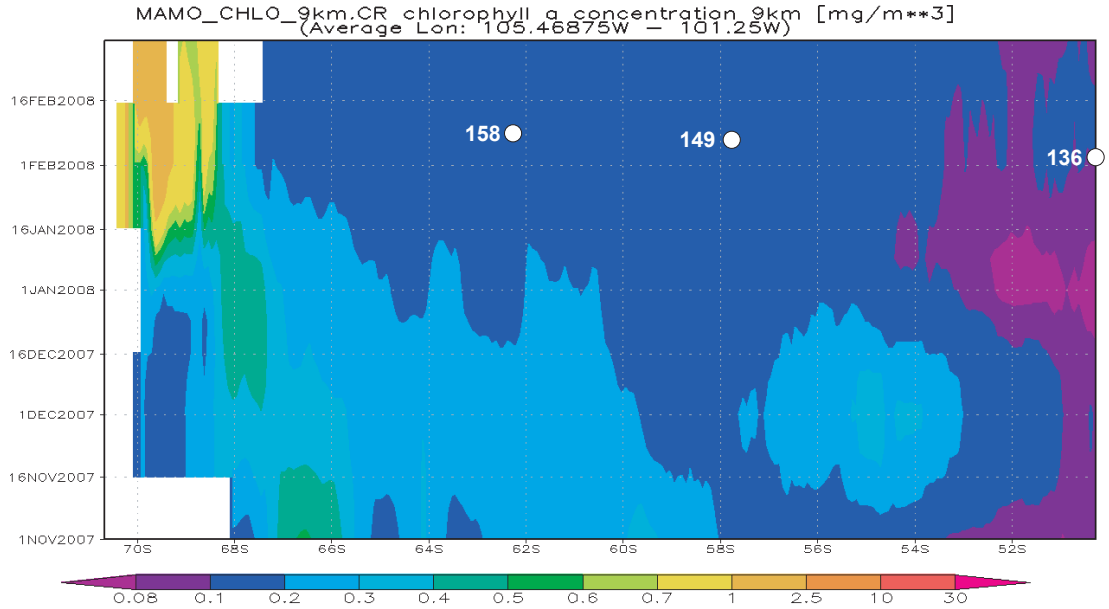

Figure S3: Hovmöller (latitude–time) plot of chlorophyll *a* concentrations (mg/m^3; colorbar) in the Subantarctic and Antarctic Zones at ~103°W, from November 2007 to February 2008. The expedition 33RO20071215 of R/V *Ronald H. Brown* reached these high southern latitudes in February 2008, as indicated by the white circles representing sampled stations. From satellite data (MODIS Aqua), accessed using the Giovanni online data system (http://reason.gsfc.nasa.gov/Giovanni), developed and maintained by the NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC).

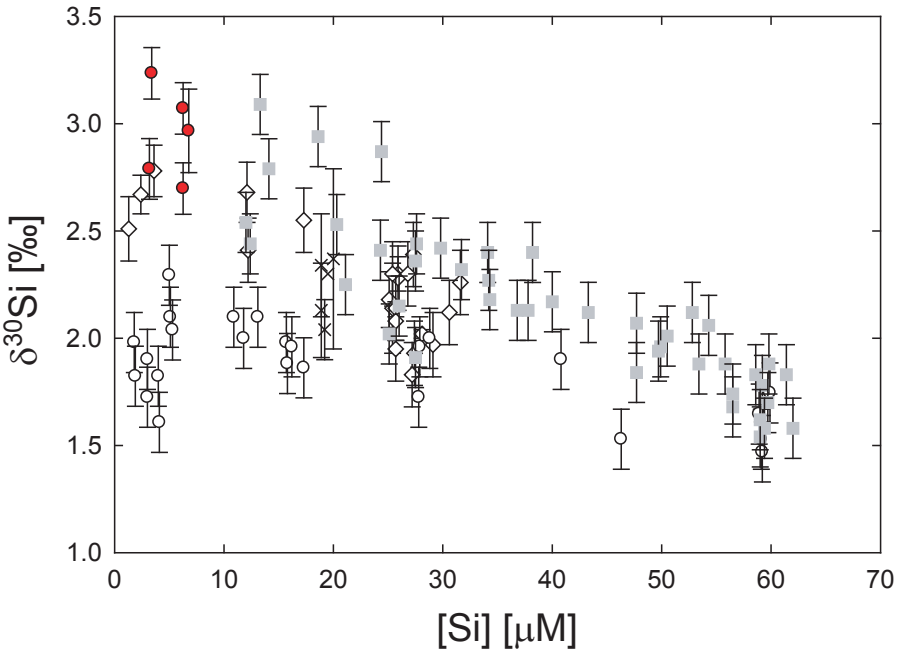

Figure S4: A comparison of surface Southern Ocean δ^{30}Si data from 62°S–50°S at 103°W (this study; red circles) with published data (gray squares: *Varela et al.* [2004], open circles: *Cardinal et al.* [2005], crosses: *Cavagna et al.* [2011], open diamonds: *Fripiat et al.* [2011a]). Our data are consistent with the high values seen by most authors; the reason for the comparatively low values observed by *Cardinal et al.* [2005] is not known.

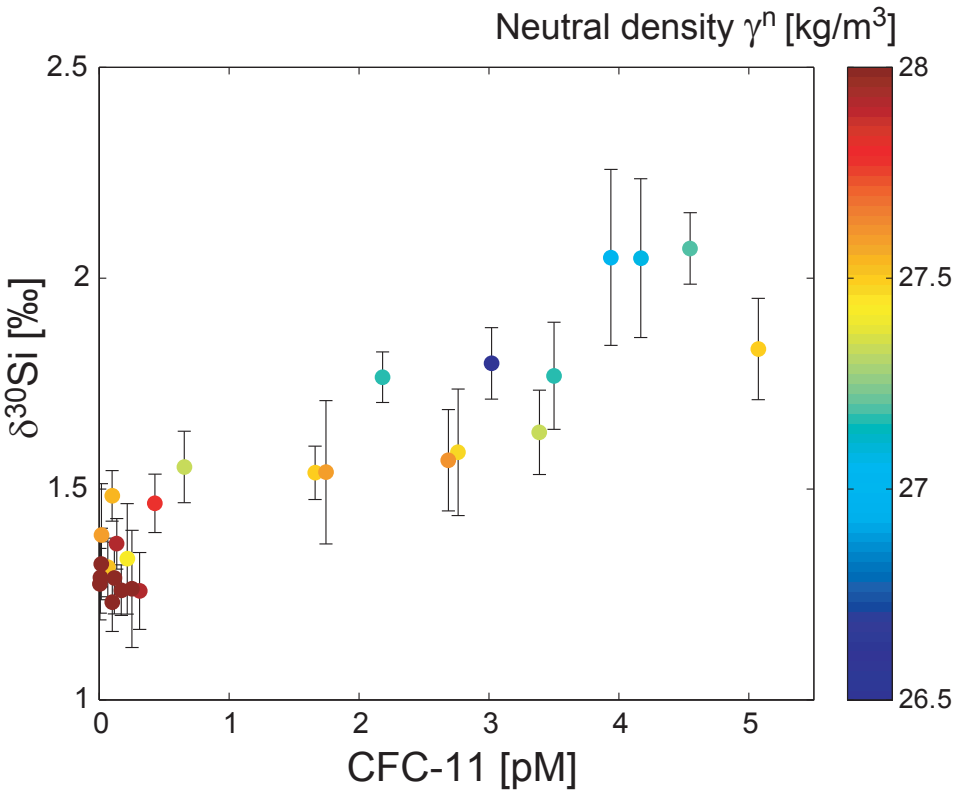

Figure S5: CFC-11 concentrations plotted against $\delta^{30}Si$ values for samples below the depth of the mixed layer. The poorly-ventilated equatorial Pacific station (12°S) is excluded. Datapoint color corresponds to neutral density. CFC-11 and density data are from the CLIVAR & Carbon Hydrographic Data Office (http://cchdo.ucsd.edu/).

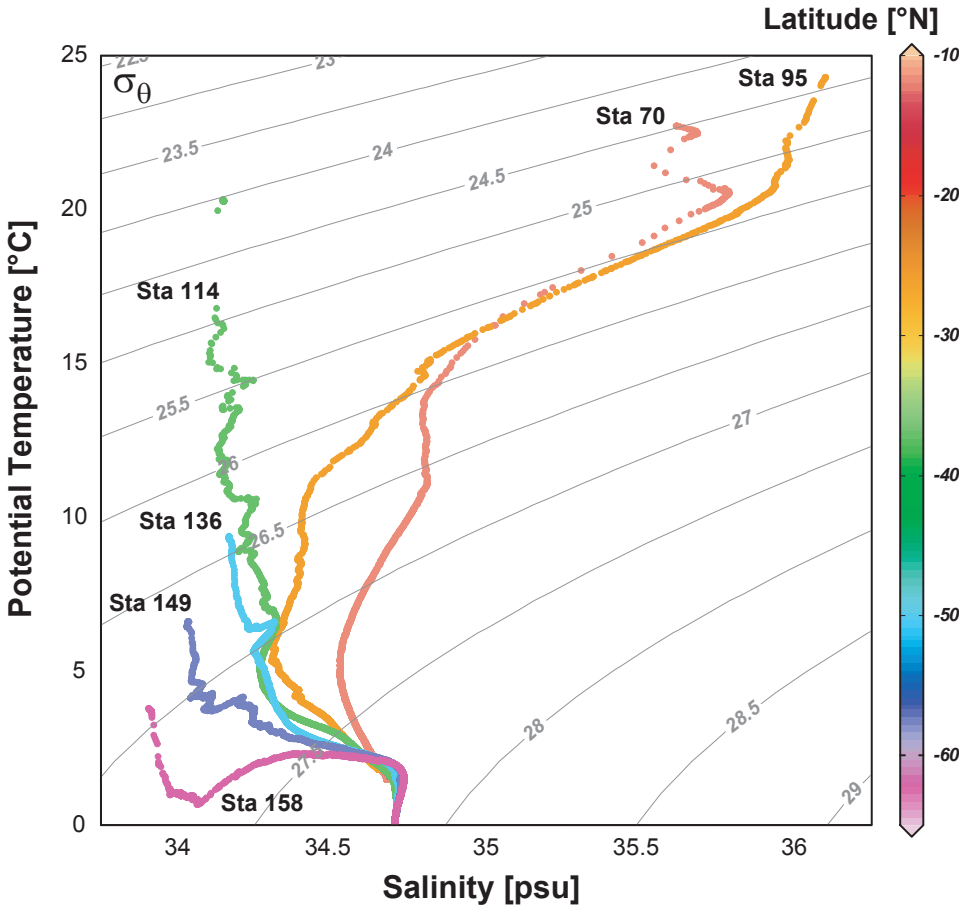

Figure S6: Potential temperature–salinity diagram for 33RO20071215 stations from which samples were analysed for $\delta^{30}Si$ (see Fig. 1 of the main text for station locations). Data are from the CLIVAR & Carbon Hydrographic Data Office (http://cchdo.ucsd.edu/).

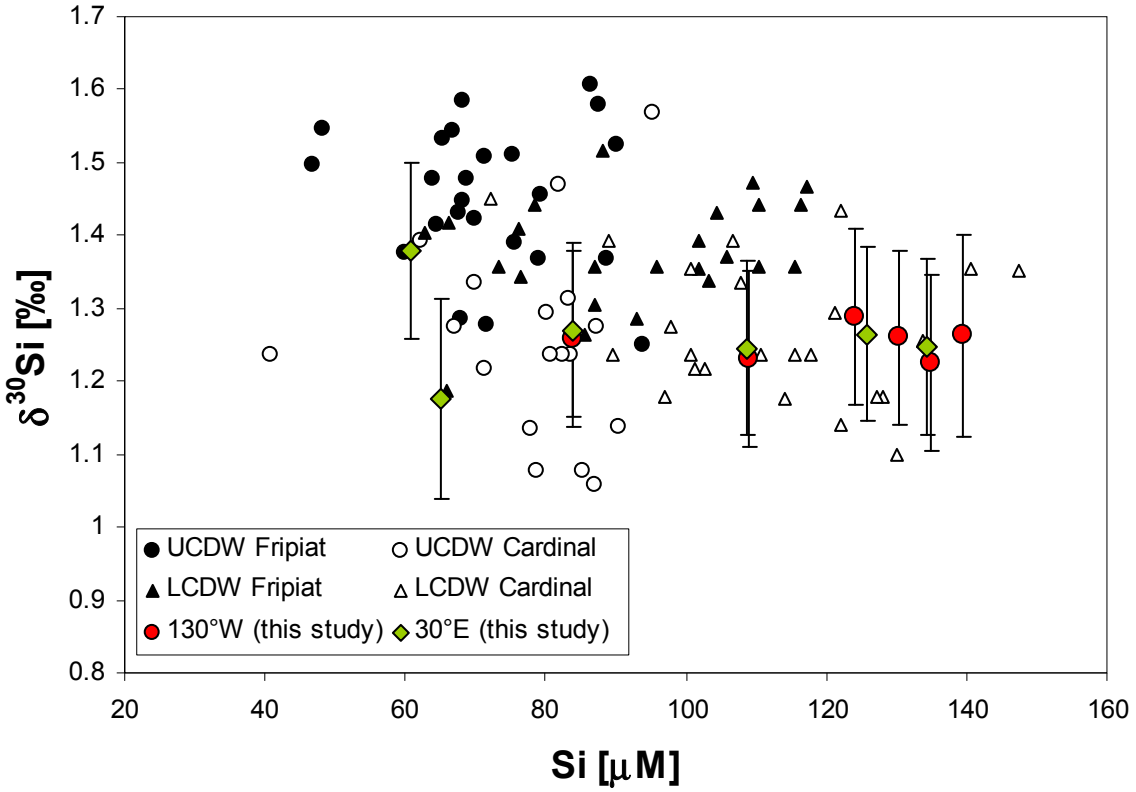

Figure S7: A comparison of deep Southern Ocean δ^{30}Si data from this study ($\gamma^n \geq 27.93$ kg/m^3) with those from *Fripiat et al.* [2011b] and *Cardinal et al.* [2005] (their data as plotted in Fig. 8b of *Fripiat et al.* [2011b]). Our data show no variability in deep Southern Ocean δ^{30}Si values from the Indo-Atlantic to the eastern Pacific sectors, whilst *Fripiat et al.* [2011b] inferred a 0.2‰ decrease in deepwater δ^{30}Si values from the Atlantic to the Australian sectors based on their and *Cardinal et al.'s* [2005] data plotted above. Error bars on our data are external $2\sigma_{SD}$ as given in Supplementary Table 1. The external reproducibility of *Cardinal et al.*'s [2005] analytical protocol is ±0.14‰ ($2\sigma_{SD}$); errors estimated by *Fripiat et al.* [2011b] from replicate analyses range from ±0.02‰ to ±0.68‰ ($2\sigma_{SD}$).

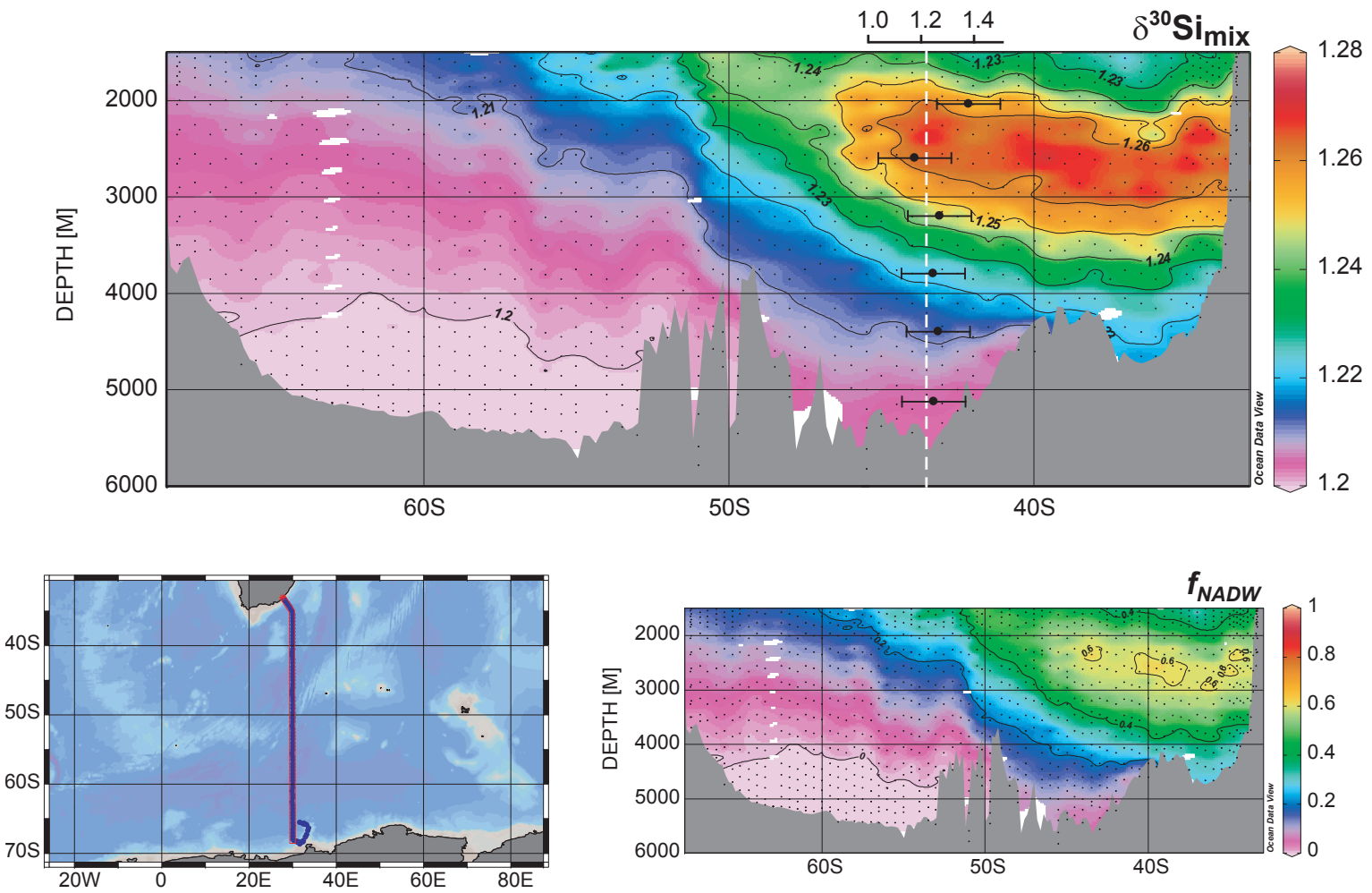

Fig. S8: Distribution of f_{NADW} (small panel) and predicted $\delta^{30}Si$ values (main panel) in a section south of Africa (CLIVAR I06S re-occupation) based on the calculations detailed in Suppl. Mat. C. Note that while values of f_{NADW} reach as high as 0.6, the low Si concentration of NADW results in it having an insignificant influence on Southern Ocean $\delta^{30}Si$. Overlain on the large panel are observed $\delta^{30}Si$ values from CLIVAR I06S (Supplementary Table 1), which show no influence of the high f_{NADW} waters on $\delta^{30}Si$ values. Dashed white line marks station location and mean CDW $\delta^{30}Si$ of +1.22‰.

References

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