

A switch from $\text{Si}(\text{OH})_4$ to NO_3^- depletion in the glacial Southern Ocean

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[1] Phytoplankton in the Antarctic deplete silicic acid ($\text{Si}(\text{OH})_4$) to a far greater extent than they do nitrate (NO_3^-). This pattern can be reversed by the addition of iron which dramatically lowers diatom $\text{Si}(\text{OH})_4:\text{NO}_3^-$ uptake ratios. Higher iron supply during glacial times would thus drive the Antarctic towards NO_3^- depletion with excess $\text{Si}(\text{OH})_4$ remaining in surface waters. New $\delta^{30}\text{Si}$ and $\delta^{15}\text{N}$ records from Antarctic sediments confirm diminished $\text{Si}(\text{OH})_4$ use and enhanced NO_3^- depletion during the last three glaciations. The present low- $\text{Si}(\text{OH})_4$ water is transported northward to at least the subtropics. We postulate that the glacial high- $\text{Si}(\text{OH})_4$ water similarly may have been transported to the subtropics and beyond. This input of $\text{Si}(\text{OH})_4$ may have caused diatoms to displace coccolithophores at low latitudes, weakening the carbonate pump and increasing the depth of organic matter remineralization. These effects may have lowered glacial atmospheric pCO_2 by as much as 60 ppm. **INDEX TERMS:** 4267 Oceanography: General: Paleooceanography; 4215 Oceanography: General: Climate and interannual variability (3309); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4870 Oceanography: Biological and Chemical: Stable isotopes

1. Introduction

[2] Phytoplankton productivity in the Southern Ocean is thought to be limited by the availability of iron [Boyd *et al.*, 2000; Martin *et al.*, 1990a; Martin *et al.*, 1990b] resulting in a vast reservoir of unused nutrients in Antarctic surface waters. Ice core records showing higher dust inputs to the glacial Antarctic [Petit *et al.*, 1999] inspired the hypothesis that Fe inputs triggered the

consumption of the reservoir of unused nutrients, thus lowering glacial atmospheric pCO_2 through the sequestration of carbon in the ocean interior [Martin, 1990; Martin *et al.*, 1990a]. Recent iron fertilization experiments in the Southern Ocean confirm limitation of phytoplankton productivity by iron in this area [Boyd *et al.*, 2000], and a recent food web model forced with the Antarctic dust record reproduces a significant component of glacial/interglacial pCO_2 changes [Watson *et al.*, 2000]. Testing for an impact of iron on glacial Southern Ocean productivity, however, has proven difficult. Most paleoceanographic data imply that export production was lower, not higher, in the glacial Antarctic [Francois *et al.*, 1997; Kumar *et al.*, 1995].

[3] Here we consider the consequences of glacial iron fertilization for Southern Ocean nutrient dynamics and atmospheric pCO_2 through its effect on the Si:N ratio of diatoms [Hutchins and Bruland, 1998; Takeda, 1998]. New data from the Southern Ocean water column and sediments show that an Fe-induced shift to lower diatom Si:N ratios during glacial periods favors nitrate (NO_3^-) depletion and the creation of a pool of unused silicic acid ($\text{Si}(\text{OH})_4$) in the Antarctic that is transported northward to low latitudes. We then consider the significance of this $\text{Si}(\text{OH})_4$ for low latitude export production and glacial atmospheric pCO_2 .

2. Results and Discussion

[4] The $\text{Si}(\text{OH})_4:\text{NO}_3^-$ depletion ratio in the present day Southern Ocean, 4:1 [Pondaven *et al.*, 2000; Smith *et al.*, 2000], is considerably higher than the ratio of ca. 2:1 in waters upwelling in the Antarctic Circumpolar Current. This can drive the system to $\text{Si}(\text{OH})_4$ depletion with $<1 \mu\text{M}$ [$\text{Si}(\text{OH})_4$] while NO_3^- remains $>15 \mu\text{M}$ [Pondaven *et al.*, 2000; Smith *et al.*, 2000]. Fe inputs can reverse this trend. Both ship-board bottle experiments [Martin *et al.*, 1990a] and in situ Fe-fertilization experiments [Boyd *et al.*, 2000] confirm that Fe limits primary production and nutrient use in the Southern Ocean. Iron additions, however, do not enhance the uptake of all nutrients equally. Additions of Fe consistently favor diatoms over other phytoplankton [Boyd *et al.*, 2000; Coale *et al.*, 1996]. Because diatoms require Si to form their

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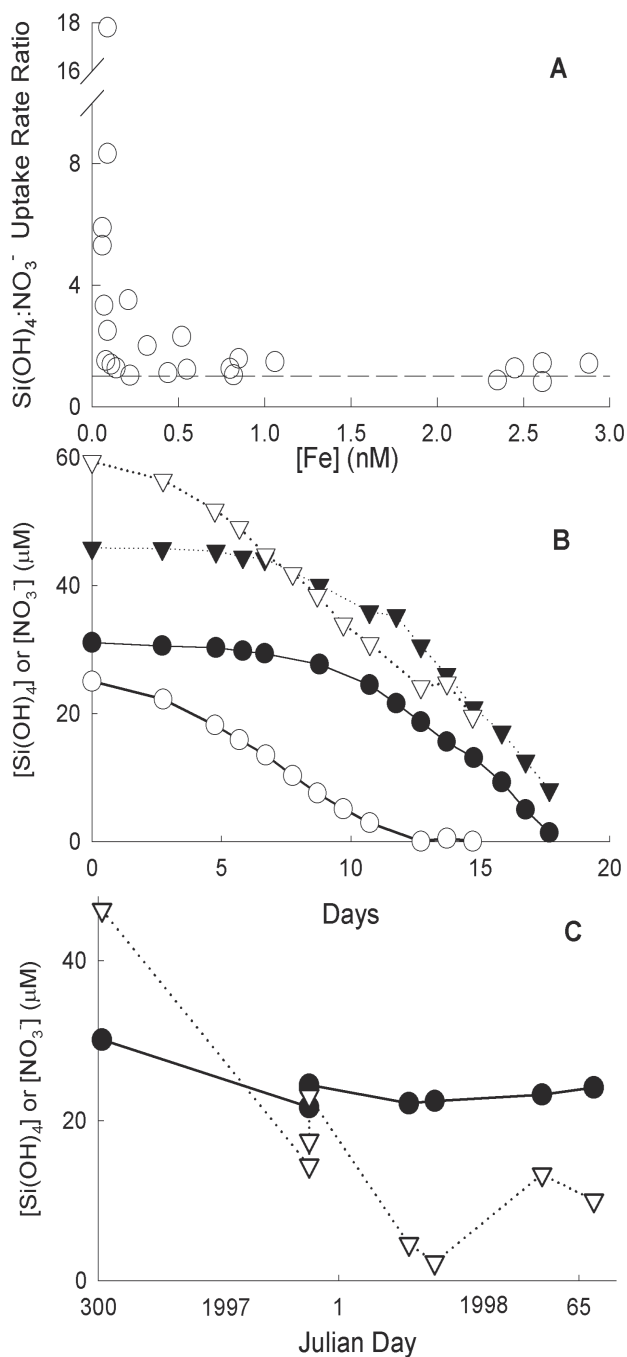


Figure 1. (a) The ratio of Si(OH)₄:NO₃⁻ uptake in Antarctic waters from 170°W longitude as a function of [Fe] (Adapted from [Franck *et al.*, 2000]). (b) Time course of [Si(OH)₄] (inverted triangles) and [NO₃⁻] (circles) from bottle experiments where 1 nM Fe was added to Antarctic waters in October 1997 (filled symbols) and in January 1998 (open symbols). (c) Time course of surface [Si(OH)₄] (∇) and [NO₃⁻] (●) in Antarctic waters between 61–63°S latitude along 170°W longitude.

cell wall [Lewin, 1962], Fe addition should favor Si(OH)₄ depletion. The opposite occurs, however, because Fe concentrations that favor diatom growth also dramatically lower diatom Si:N ratios [Franck *et al.*, 2000; Huchins and Bruland, 1998; Takeda, 1998]. Additions of Fe > 0.5 nM to the high nutrient waters of the Antarctic cause Si(OH)₄:NO₃⁻ uptake ratios to decline from >4:1 to 1:1 (Figure 1c) which is less than the Si(OH)₄:NO₃⁻ upwelling

ratio of ca. 2:1 and would thus favor NO₃⁻ depletion. Additions of Fe to Antarctic surface water produce the predicted switch from Si(OH)₄ to NO₃⁻ depletion. Adding 1 nM Fe to the high-nutrient waters from south of the Polar Front causes NO₃⁻ to be depleted before Si(OH)₄ (Figure 1b) whereas the opposite pattern is observed in the same water mass in situ under natural conditions without added Fe (Figure 1c).

[5] The above observations predict that increased Fe inputs to the glacial Southern Ocean cause a switch from the Si(OH)₄-poor NO₃⁻-rich state of present day Southern Ocean to a Si(OH)₄-rich NO₃⁻-poor condition during glacial times [Matsumoto *et al.*, 2001]. Isotopic records from Antarctic sediments support this hypothesis. Antarctic records of the δ¹⁵N of bulk sedimentary organic matter [Francois *et al.*, 1997] and the organic matter bound within diatom frustules [Sigman *et al.*, 1999a] show maxima during the last glacial maximum (LGM) that indicate greater depletion of NO₃⁻ during the last glacial episode compared to the current interglacial. The opposite is observed in sediment records of δ³⁰Si of diatom frustules, which show minima during the LGM, indicating less Si(OH)₄ depletion in the Antarctic during the last glacial episode compared to the current interglacial [De La Rocha *et al.*, 1998], consistent with lower opal accumulation rates in the glacial Antarctic [Kumar *et al.*, 1995; Mortlock *et al.*, 1991].

[6] A new longer δ³⁰Si record from the Antarctic shows that the pattern of diminished Si(OH)₄ use during glacial periods implied by minima in diatom δ³⁰Si repeats through three glacial cycles (Figure 2). Comparison with the δ¹⁵N of bulk sediment from the same core reveals an inverse correlation between the δ¹⁵N and δ³⁰Si records through all three cycles (Figure 2). Thus the anti-phasing of the Si and N isotopic records established previously for the LGM and Holocene appears to be a regular feature of glacial cycles in the Antarctic suggesting repeated oscillations between Si and N depleted states. The contribution of diatoms to the oscillation in N use is supported by data from nearby core AII-107 22GGC where glacial/interglacial changes in the δ¹⁵N of bulk N are corroborated by those of diatom-bound N [Sigman *et al.*, 1999a] indicating that diatom N use paralleled that of the total phytoplankton assemblage in this region. While such data suggest that the anti-phasing of Si and N depletion could be driven solely by changes in diatom Si(OH)₄:NO₃⁻ uptake ratios, higher Fe levels during glacial times may have also stimulated the growth of nonsiliceous phytoplankton such as *Phaeocystis* [Martin *et al.*, 1990a, 1990b], adding to the greater utilization of NO₃⁻ over Si(OH)₄ attributable to diatoms.

[7] The increase in NO₃⁻ use in the glacial Southern Ocean implied by this argument was apparently not associated with an increase in export production in the Antarctic [Francois *et al.*,

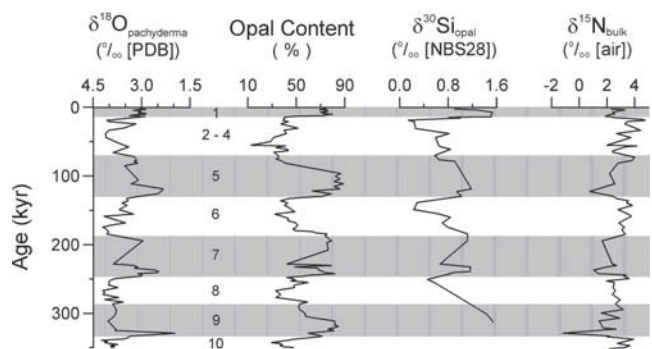


Figure 2. δ¹⁸O (*N. pachyderma*) [Charles *et al.*, 1991], opal content [Charles *et al.*, 1991], δ³⁰Si of diatom opal and δ¹⁵N of bulk sediment [Rau and Froelich, 1993] from RC13-259 (53°53'S; 4°56'W; 2,677 m). Numbers indicate oxygen isotope stages 1–10. The precision of the isotope analyses is 0.13 and 0.20 ‰ (±1 s.d.) for δ³⁰Si and δ¹⁵N measurements, respectively.

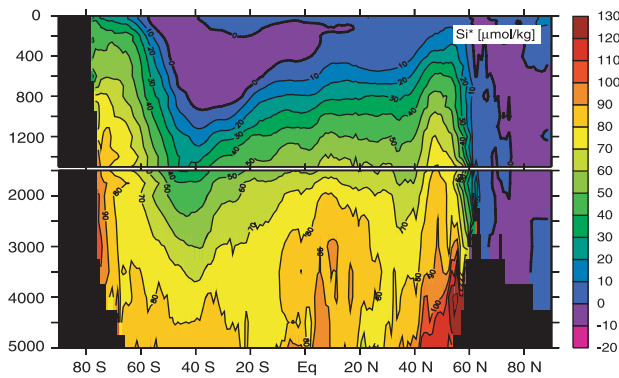


Figure 3. Zonally averaged section of the tracer Si^* ($\text{Si}^* = [\text{Si}(\text{OH})_4] - [\text{NO}_3^-]$) across all ocean basins. A value of zero implies that $\text{Si}(\text{OH})_4$ and NO_3^- are present in the 1:1 ratio required by diatoms [Brzezinski, 1985]. The plot is based on the global gridded nutrient climatology of [Conkright et al., 1994].

1997; Kumar et al., 1995], leading to the interpretation that nutrient supply to the Antarctic surface was reduced, perhaps due to enhanced stratification of the upper water column [Francois et al., 1997]. Under these conditions increases in Fe would still stimulate the depletion of NO_3^- over $\text{Si}(\text{OH})_4$, but the size of the reservoir of excess $\text{Si}(\text{OH})_4$ is diminished. Thus, the creation of surface waters with high $[\text{Si}(\text{OH})_4]$ and low $[\text{NO}_3^-]$ in the glacial Antarctic is a robust result, but the size of the $\text{Si}(\text{OH})_4$ pool can not be determined precisely with the available data.

[8] During glacial periods Antarctic surface waters with high $[\text{Si}(\text{OH})_4]:[\text{NO}_3^-]$ would be transported northward across the Polar Front and become incorporated into intermediate and mode waters by the same circulation that transports the modern NO_3^- excess to lower latitudes [Sigman et al., 1999b]. This mechanism provides a $\text{Si}(\text{OH})_4$ source for the higher accumulation rates of biogenic silica in the glacial Subantarctic [Charles et al., 1991; Mortlock et al., 1991]. Total opal accumulation in the Antarctic and Subantarctic in the Atlantic and Indian sectors of the Southern Ocean are nearly equivalent during the LGM and Holocene [Francois et al., 1997]. All other things being equal, this suggests that the glacial $\text{Si}(\text{OH})_4$ excess may have been largely consumed within the Subantarctic in these sectors. New results from the Pacific sector show a decrease in the preservation of opal in both the Antarctic and Subantarctic during the LGM [Anderson et al., 2002] suggesting that the northward transport of high $[\text{Si}(\text{OH})_4]:[\text{NO}_3^-]$ waters beyond the Subantarctic was most pronounced in this sector.

[9] Analysis of modern nutrient distributions shows that the northward transport of low $\text{Si}(\text{OH})_4$ –high NO_3^- waters extends to at least the subtropics (Figure 3). When the high $[\text{Si}(\text{OH})_4]:[\text{NO}_3^-]$ waters traveling this route during glacial times are brought to the surface by vertical mixing their altered nutrient composition could drive changes in nutrient dynamics and phytoplankton productivity at low latitudes. The amount of NO_3^- in these waters during glacial times is unknown, but it would have been less than in the present-day ocean, consistent with evidence for depletion of nutrients (nitrate, phosphate) and enrichment of O_2 in the mid-depth ocean during glacial times [Boyle, 1988; Herguera et al., 1992; Keigwin, 1998; Kennett and Ingram, 1995]. The upwelling of Antarctic intermediate water at the equator with higher $[\text{Si}(\text{OH})_4]:[\text{NO}_3^-]$ during glacial times also explains a shift toward higher opal accumulation rates in some equatorial regions [Broecker et al., 2000].

[10] If increased diatom productivity at low latitudes in the southern hemisphere occurred at the expense of coccolithophores, the high sinking rates of diatom-derived particulate matter may have facilitated the transport of organic matter through intermediate waters to the deep ocean [Boyle, 1988], consistent with

evidence for greater nutrient content of the deep sea during glacial times [Boyle, 1988; Herguera et al., 1992]. In addition, a floral shift away from coccolithophores to diatoms would have also lowered the CaCO_3 /organic carbon rain ratio weakening the ocean carbonate pump. Both the increase in the remineralization depth of organic carbon and a decrease in the rain ratio would have lowered atmospheric pCO_2 [Archer and Maier-Reimer, 1994; Boyle, 1988; Broecker and Peng, 1987; Keir, 1988].

[11] The depth of the lysocline provides an observable constraint on the role that such changes could have played in glacial pCO_2 reduction [Sigman et al., 1998]: these changes tend to deepen the lysocline, and yet the global mean depth of the lysocline was apparently not more than 1 km deeper during the last ice age [Farrell and Prell, 1989]. In box models such as CYCLOPS [Keir, 1988], this constrains the glacial rain ratio to have been not less than 60% of the interglacial rain ratio, in which case the rain ratio decrease would lower atmospheric pCO_2 by ≤ 40 ppm, according to a box model calculation [Sigman et al., 1998]. The simultaneous deepening of organic matter remineralization could have driven an additional ~ 20 ppm decrease without further deepening the lysocline, so that, in box models, these two changes together could account for up to 60 ppm of the 80–100 ppm amplitude of the glacial/interglacial pCO_2 change [Matsumoto et al., in press; Petit et al., 1999]. Thus, these low-latitude impacts contribute considerably to the overall impact of Southern Ocean iron fertilization in lowering glacial pCO_2 [Watson et al., 2000]. Moreover, ocean general circulation models have a much greater sensitivity of atmospheric pCO_2 to the low- and mid-latitude rain ratio than do box models [Archer et al., 2000], separate from the effects of deep sea calcite preservation. If this higher sensitivity is correct, then the estimated 40% rain ratio change caused by changes in Southern Ocean Si:N utilization ratios, would be an even stronger candidate for explaining a significant fraction of the glacial/interglacial pCO_2 change.

3. Conclusions

[12] Recent assessments of the role of the ocean in atmospheric pCO_2 changes suggest that increases in the ocean inventory of $\text{Si}(\text{OH})_4$ can significantly decrease atmospheric pCO_2 during glacial times by favoring the growth of diatoms over coccolithophores [Archer et al., 2000; Harrison, 2000]. The underlying mechanisms invoked to date require an enhanced supply of silicon to the oceans through increased aeolian [Harrison, 2000] or riverine [Froelich et al., 1992] transport. The mechanism explored here is unique in that the increase in the contribution of diatoms to organic matter production during glacial periods arises through the redistribution and more efficient use of the existing ocean $\text{Si}(\text{OH})_4$ inventory rather than requiring an exogenous source of $\text{Si}(\text{OH})_4$ to the oceans.

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