A switch from Si(OH)₄ to NO₃⁻ depletion in the glacial Southern Ocean

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1] Phytoplankton in the Antarctic deplete silicic acid (Si(OH)₄) to a far greater extent than they do nitrate (NO₃⁻). This pattern can be reversed by the addition of iron which dramatically lowers diatom Si(OH)₄:NO₃⁻ uptake ratios. Higher iron supply during glacial times would thus drive the Antarctic towards NO₃⁻ depletion with excess Si(OH)₄ remaining in surface waters. New δ⁳⁰Si and δ¹⁵N records from Antarctic sediments confirm diminished Si(OH)₄ use and enhanced NO₃⁻ depletion during the last three glaciations. The present low-Si(OH)₄ water is transported northward to at least the subtropics. We postulate that the glacial high-Si(OH)₄ water similarly may have been transported to the subtropics and beyond. This input of Si(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 pCO₂ by as much as 60 ppm. INDEX TERMS: 4267 Oceanography: General: Paleocenography; 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

[1] Phytoplankton productivity in the Southern Ocean is thought to be limited by the availability of iron [Boyd et al., 2000; Martin et al., 1999a; Martin et al., 1999b] 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 pCO₂ 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 pCO₂ 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 pCO₂ 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 (NO₃⁻) depletion and the creation of a pool of unused silicic acid (Si(OH)₄) in the Antarctic that is transported northward to low latitudes. We then consider the significance of this Si(OH)₄ for low latitude export production and glacial atmospheric pCO₂.

2. Results and Discussion

[4] The Si(OH)₄:NO₃⁻ 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 Si(OH)₄ depletion with <1 μM [Si(OH)₄] while NO₃⁻ remains >15 μM [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
Additions of Fe > 0.5 nM to the high nutrient waters of the Southern Ocean cause a switch from the Si(OH)₄-poor NO₃⁻-poor 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 [Kumar et al., 1995; Mortlock et al., 1991].

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 antiphasing 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 diatom frustules 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 antiphasing 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.

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., 1997; Matsumoto et al., 2001].

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] (Δ) and [NO₃⁻] (○) in Antarctic waters between 61 – 63°S latitude along 170°W longitude.

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.
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 NO3 over Si(OH)4, but the size of the reservoir of excess Si(OH)4 is diminished. Thus, the creation of surface waters with high [Si(OH)4] and low [NO3] in the glacial Antarctic is a robust result, but the size of the Si(OH)4 pool cannot be determined precisely with the available data.

During glacial periods Antarctic surface waters with high [Si(OH)4]/[NO3] would be transported northward across the Polar Front and become incorporated into intermediate and mode waters by the same circulation that transports the modern NO3 excess to lower latitudes [Sigman et al., 1999b]. This mechanism provides a Si(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 Si(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 [Si(OH)4]/[NO3] waters beyond the Subantarctic was most pronounced in this sector.

Analysis of modern nutrient distributions shows that the northward transport of low Si(OH)4–high NO3 waters extends to at least the sub tropics (Figure 3). When the high [Si(OH)4]/[NO3] 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 NO3 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 O2 in the mid-deep 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 [Si(OH)4]/[NO3] during glacial times also explains a shift toward higher optical accumulation rates in some equatorial regions [Broecker et al., 2000].

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 CaCO3/organic carbon ratio weakening the ocean carbonate. Both the increase in the remineralization depth of organic carbon and a decrease in the rain ratio would have lowered atmospheric pCO2 [Archer and Maier-Reimer, 1994; Boyle, 1988; Broecker and Peng, 1987; Keir, 1988].

The depth of the lysocline provides an observable constraint on the role that such changes could have played in glacial pCO2 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 pCO2 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 pCO2 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 pCO2 [Watson et al., 2000]. Moreover, ocean general circulation models have a much greater sensitivity of atmospheric pCO2 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 pCO2 change.

3. Conclusions

Recent assessments of the role of the ocean in atmospheric pCO2 changes suggest that increases in the ocean inventory of Si(OH)4 can significantly decrease atmospheric pCO2 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 herein 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 Si(OH)4 inventory rather than requiring an exogenous source of Si(OH)4 to the oceans.

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