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Influence of Equatorial Diatom Processes on Si Deposition and Atmospheric CO(2) Cycles at Glacial/Interglacial Timescales

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The causes of the glacial cycle remain unknown, although the primary driver is changes in atmospheric CO2, likely controlled by the biological pump and biogeochemical cycles. The two most important regions of the ocean for exchange of CO2 with the atmosphere are the equatorial Pacific and the Southern Ocean (SO), the former a net source and the latter a net sink under present conditions. The equatorial Pacific has been shown to be a Si(OH)4-limited ecosystem, a consequence of the low source Si(OH)4 concentrations in upwelled water that has its origin in the SO. This teleconnection for nutrients between the two regions suggests an oscillatory relationship that may influence or control glacial cycles. Opal mass accumulation rate (MAR) data and δ15N measurements in equatorial cores are interpreted with predictions from a one-dimensional Si(OH)4-limited ecosystem model (CoSINE) for the equatorial Pacific. The results suggest that equatorial Pacific surface CO2 processes are in opposite phase to that of the global atmosphere, providing a negative feedback to the glacial cycle. This negative feedback is implemented through the effect of the SO on the equatorial Si(OH)4 supply. An alternative hypothesis, that the whole ocean becomes Si(OH)4 poor during cooling periods, is suggested by low opal MAR in cores from both equatorial and Antarctic regions, perhaps as a result of low river input. Terminations in this scenario would result from blooms of coccolithophorids triggered by low Si(OH)4 concentrations.

INDEX TERMS: 1615 Global Change: Biogeochemical processes (4805); 4267 Oceanography: General: Paleoceanography; 3344 Meteorology and Atmospheric Dynamics: Paleoclimatology; 4231 Oceanography: General: Equatorial oceanography; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); KEYWORDS: diatoms, CO2, silicate


1. Introduction

CO2 increased before the melting of the ice sheets in the last two terminations [Petit et al., 1999] and appears to be a primary driver in glacial cycles [Shackleton and Pisias, 1985; Archer et al., 2000]. Interglacial to glacial decreases in atmospheric CO2 concentration change regularly in step with the Milankovitch solar insolation cycles [Sigman and Boyle, 2000]. Although these solar cycles appear to initiate the glacial periods, the decreases in heat input from this source are insufficient to bring about the inferred cooling and glacier formation. Instead they create feedbacks that result in decreased atmospheric CO2 and increased cooling. Shackleton [2000] identified a 100,000 year cycle in ice volume lagging atmospheric temperature, atmospheric CO2 and deep water temperature, all three found to be in phase with orbital eccentricity, indicating that carbon cycle changes apparently lead the changes in ice volume.

Broecker [1982] first proposed that the cause of the CO2 changes was the oceanic biological pump. His hypothesis would require changes in the nutrient concentrations or supply, since increased nutrients would result in increased new production [Dugdale and Goering, 1967] and increased export of carbon to the deep ocean [Eppley and Peterson, 1979] and decreased atmospheric CO2. In particular increased supply of Si(OH)4 for diatoms, usually considered to be the engines of export production [Smetacek, 1998], would be important. Dust deposition, as a source of Si [Harrison, 2000], should stimulate diatom productivity. Archer et al. [2000] considered that doubling of the Si(OH)4 inventory of the ocean could drive the atmospheric CO2 changes and glacial cycles, but had difficulty in explaining how the ocean content of Si(OH)4 would have increased by that amount. Sigman and Boyle [2000] showed that any credible NO3 increments would be insufficient to account for the reduction in pCO2 of 80–100 ppmv that was observed during glacial periods. Also Loubere [2000] concluded from carbon isotope data from the foraminiferan Neogloboquadrina dutertrei that the Equatorial Undercurrent (EUC) supply of nutrients was lower during the last full glacial (around the Last Glacial Maximum, LGM, 21 kyr) period than at present.

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The two major oceanic regions involved in the glacial to interglacial changes in CO2 are the equatorial Pacific and Southern Ocean that likely interact to influence the global CO2 and glacial cycles [e.g., Brzezinski et al., 2002]. The equatorial Pacific is the major ocean region where net CO2 efflux to the atmosphere occurs [e.g., Takahashi et al., 1986, 1997; Feely et al., 1997] and which has considerable influence on the global carbon budget of the atmosphere. The eastern equatorial Pacific (EEP) upwelling area is considered as a HNLC (high nitrate, low chlorophyll) region due to the presence of considerable NO3 in the surface waters but low chlorophyll concentration [e.g., Minas et al., 1986; Dugdale and Wilkerson, 1998]. The lack of iron (Fe) from atmospheric dust input, was proposed initially as a cause of the incomplete utilization of NO3 by phytoplankton and hence of surplus CO2 to be exchanged to the atmosphere from the equatorial Pacific Ocean [e.g., Chavez et al., 1990]. However, Ku et al. [1995] using 228Ra showed upwelled Si(OH)4 would be limiting for diatom growth and the equatorial upwelling system has subsequently been designated more accurately as low silicate-HNLC (LSHNLC) [Dugdale et al., 1995]. Confirmation of equatorial Si(OH)4 limitation was obtained from 32Si uptake kinetics [Leynaert et al., 2001]. In this paper we explore the role of equatorial diatoms in Si flux and CO2 cycles at glacial/interglacial timescales by applying results from an ecosystem model constructed using modern-day data to understand relationships observed in paleoceanographic core data. Although diatoms in the equatorial upwelling system are low in abundance relative to other non-Si-using phytoplankton [Bidigare and Ondrusek, 1996; Chavez et al., 1990]), they may have a dominating effect on other phytoplankton, the nutrient environment and overall productivity. For example, enclosure experiments in a Norwegian fjord showed when Si(OH)4 concentrations were greater than 2 mmol/m3, diatoms were able to grow faster than the non-Si-users, and inhibited their growth [Egge and Aksnes, 1992]. Consideration of interactions between diatoms and other phytoplankton led to the construction of a 1-D biogeochemical model, (CoSINE: carbon, silicate, nitrogen ecosystem model) of the equatorial upwelling system [Chai et al., 2002] (Figure 1). It includes two functional groups of phytoplankton (the numerically dominant small-sized non-Si-using picoplankton, and the Si-requiring diatoms), three nutrients (NO3, NH4 and Si(OH)4), two size classes of zooplankton grazers, and detrital N and Si. The influence of Fe is included as a fixed factor reducing photosynthesis below optimal levels. Si(OH)4 and NO3 are supplied in upwelled water in ratios always less than the 1:1 ratio usually occurring in diatoms [Brzezinski, 1985] ensuring that diatom growth will be limited by Si. NO3, largely unavailable to the picoplankton which primarily use NH4, will remain in substantial amounts in the surface waters, a well known feature of the eastern equatorial Pacific.

The model can be manipulated to simulate the LSHNLC conditions. One experiment in which the
concentration of Si(OH)$_4$ in the upwelling source waters was increased while holding the NO$_3$ concentration constant [Dugdale et al., 2002a] showed a two phase response (Figures 2a–2d). The initial response, termed phase 1, is an increase in diatom and decrease in picoplankton biomass (Figure 2a), with accompanying increases in surface nutrient concentrations (Figure 2b), surface TCO$_2$ (Figure 2c), and Si export (Figure 2d). With a further increase in Si(OH)$_4$ (from 7.5 mmol/m$^3$ to 15 mmol/m$^3$), phase 2 then occurs and the biomass of diatoms continues to increase.

**Figure 2.** Surface response (phases 1 and 2) of the 1-D CoSINE model to changes in source Si(OH)$_4$ concentration: (a) picoplankton and diatom biomass, mmol/m$^3$; (b) NO$_3$ and Si(OH)$_4$ concentrations, mmol/m$^3$; (c) TCO$_2$, mmol/m$^3$; (d) integrated export production of N and Si, mmol/m$^2$/d. Stars are present-day equatorial data from Leynaert et al. [2001]. Dotted lines show range of mean Si(OH)$_4$ at 120 m from 140$^\circ$W, JGOFS.
2. Differences in Source Si(OH)₄ Concentrations to the Equatorial Pacific and the Paleoceanographic Consequences

The primary source for nutrients to the modern Pacific equatorial upwelling ecosystem is the EUC, that is deficient in Si(OH)₄ with respect to NO₃ resulting in Si(OH)₄ limitation for diatoms [Ka et al., 1995; Dugdale and Wilkerson, 1998, 2001; Leynaert et al., 2001; Jiang et al., 2003]. The EUC forms at the western end of the equator where water from the Northern and Southern Hemispheres meet. The contribution of water volume to the EUC is roughly equal between the Northern and Southern Hemispheres. The southern water is low in Si(OH)₄ relative to NO₃, while the northern water has about equal concentrations of Si(OH)₄ and NO₃ [Dugdale et al., 2002b]. Changes in Si(OH)₄ in the Southern Ocean should be reflected in changes in equatorial Si(OH)₄ supply and diatom production. In the Southern Ocean, waters strongly deficient in Si(OH)₄ compared to NO₃ (i.e. with increased Si trapping) are formed during the austral summer productivity season [Hiscock et al., 2003] and advected northward as Sub-Antarctic Mode Water (SAMW) [Toggweiler et al., 1991; Dugdale et al., 2002b]. Diatomaceous sedimentation rates in the Antarctic, south of the polar front were lower during the last Ice Age [Sigman and Boyle, 2000; Mortlock et al., 1991; Charles et al., 1991] suggesting less Si trapping and more Si(OH)₄ available for northward transport in the SAMW to the equatorial Pacific: the silicate leakage hypothesis of Brzezinski et al. [2002]. If so Southern Ocean productivity can influence equatorial Si(OH)₄ concentrations and the Si flux and regulate the resulting CO₂ cycles.

Tropical Pacific cores (central equatorial Pacific, eastern equatorial Pacific, and the Guatemala Basin) [Lyle et al., 1988] exhibit alternating periods of biogenic silica (opal) and carbonate deposition with the major peaks in opal deposition occurring every 100 kyr (the Milankovitch major frequency), suggesting that the supply of Si(OH)₄ to the equator has varied in concert with 100 kyr glacial/interglacial cycles. However, high opal burial occurred on the transitions between glacial and interglacial periods, rather than being in phase with either glacial or interglacial periods. To search for a link between glacial equatorial Si burial and changes in atmospheric CO₂, opal deposition from the central equatorial Pacific core W8402-14GC [Lyle et al., 1988] and CO₂ changes from Vostok ice core data [Petit et al., 1999] were compared. We chose to compare W8402-14GC (recovered at 1°N, 139°W) to the ice core record because the largest CO₂ flux from the oceans takes place in the equatorial Pacific between 110° and 160°W [Takahashi et al., 1997]. We assume that Si(OH)₄ introduced into surface waters is efficiently incorporated into diatom tests so that the opal rain is a reasonable indicator of Si(OH)₄ supply to the surface ocean. We also assume that the majority of opal being deposited in the central equatorial Pacific is of diatom origin. Murray [1987] measured the opal flux at a 2-year sediment trap deployment at the location of W8402-14 by partitioning the opal flux into diatom and radiolarian fractions. By using size separations he was able to determine that 75–80% of the total opal flux was of diatom origin. Comparisons of opal flux as determined from the sediment traps with opal sediment deposition [Dymond and Lyle, 1985] showed a positive correlation between opal deposition/preservation and opal rain from the surface ocean, perhaps driven, at least in part, by changes in flux of other sedimentary components [Archer et al., 1993]. We also assume that the opal record of W8402-14GC is a reasonable representation of opal deposition in the central equatorial Pacific but recognize that there may be considerable zonal variability, e.g. in the eastern Pacific a 50 kyr opal depositional event is much stronger than to the west [Lyle et al., 1988].

Sediment focusing evaluated by ²³⁰Th and ³He may have influenced the apparent burial rates of equatorial sediments [Marcantonio et al., 1996, 2001]. Marcantonio et al. [2001] argue that the presence of high concentrations of phytodetritus at the sediment surface from 2°N to 2°S is the result of sediment focusing. However, the latitude band, 2°N to 2°S is the maximum in equatorial upwelling and new production. The simplest explanation is that the phytoplankton blooms resulting from upwelling productivity events are being deposited under the surface where the phytoplankton biomass was produced. The freshness of these deposits argues for a rapid sinking of surface production, a characteristic of diatom blooms in many localities [Smetacek, 1985]. In any case W8402-14GC is at a location where Marcantonio et al. [1996, 2001] claimed there was no sediment focusing. We are thus inclined to accept the sediment record of biogenic silica (opal) as a record of the overlying productivity, a conclusion based on our understanding of the functioning of the equatorial upwelling system.

The mass accumulation rate of opal (opal MAR) in core W8402-14GC was averaged to 5 kyr intervals (Figure 3). Changes in opal MAR show a strong similarity to changes in atmospheric CO₂, with peak values of both at or near terminations 1 (~12 kyr) and 2 (~130 kyr). These data are combined together in a plot of atmospheric CO₂...
also averaged to 5 kyr intervals) versus equatorial opal MAR (Figure 4). This plot was made to enable the paleo Si and C trends to be compared with those predicted by the CoSINE model. Opal mass accumulation rate is considered here as a proxy for Si(OH)₄ supply or concentration in equatorial source water. If Si(OH)₄ source water concentrations varied over glacial cycles in the full range considered in the CoSINE model and the global atmospheric CO₂ concentration varied in phase with the surface TCO₂ at the equator then the CO₂ versus source Si(OH)₄ pattern shown in Figure 2c should appear in Figure 4. However, the basic pattern for the core data (Figure 4) is that low opal MAR occurs when Vostok CO₂ is low and high opal MAR occurs when CO₂ is high; i.e. the relationship between opal MAR and global atmospheric CO₂ is almost always positive. There is no evidence from the relationship of global atmospheric CO₂ and opal MAR of a phase 2 limb that would appear to the right in Figure 4 at the high opal MAR values and with negative slope. While it is tempting to interpret the data in Figure 4 as indicating a model phase 1 at the equator, the conclusion would only be valid if the changes in TCO₂ at the equator were in phase with the global atmosphere changes and we have no evidence for such an in-phase condition. Consequently Figure 4 can only be used to indicate that equatorial opal MAR appears to have a positive relationship with the global atmosphere CO₂ changes.

3. Paleoceanographic Nutrient Conditions Resolved by Natural Isotope Abundances

Variations in the natural abundance of N, C and Si isotopes in core material provide another tool for understanding paleoceanographic nutrient conditions. [Farrell et al., 1995; Altabet and Francois, 1994]. The basis for the method is the fractionation of isotope pairs, e.g. ¹⁵N/¹⁴N, ¹³C/¹²C, ³⁰Si/³²Si during phytoplankton uptake and assimilation. Although various outcomes are possible depending on the particular environmental conditions, the change in isotope composition depends on the degree of utilization of the element [Altabet and Francois, 1994] such that as available nutrient is reduced to near source levels, the isotope composition of the phytoplankton becomes heavier by Rayleigh fractionation. In the case of nitrogen this is expressed as an increase in δ¹⁵N and occurs with decreased NO₃ concentration.

Our analysis suggests the equatorial upwelling system experienced decreased source Si(OH)₄ supply (i.e. low opal MAR) over most of the last cooling cycle, 125–25 kyr (Figure 4) i.e. model phase 1. The CoSINE model output can also be used to predict changes in utilization of NO₃ and Si(OH)₄ and changes in δ¹⁵N as a function of source Si(OH)₄ (Figures 5a and 5b). δ¹⁵N natural abundance variations were obtained from CoSINE model predicted values of surface NO₃ by calculating the relative NO₃ utilization (Figure 5a), as the difference between the 120 m source NO₃ (12 mmol/m², held constant in the model) and the surface NO₃ concentration divided by the source NO₃ concentration as the 120 m source Si(OH)₄ was varied (Figure 2b) and inserting that value into Altabet [2001, equation (4)] for first order Rayleigh fractionation. The model predicts a U-shaped curve (Figure 5b) with a minimum in δ¹⁵N at the transition between phase 1 and 2. Farrell et al. [1995] measured nitrogen isotope ratios in bulk nitrogen in three cores from the eastern equatorial Pacific. Their δ¹⁵N measurements cover the periods, 24–12 kyr including the LGM, termination 1 (12 kyr), and 12–0 kyr warming (Holocene). Minimum values occurred at the LGM and increased toward the Holocene. Farrell et al. [1995] attributed low δ¹⁵N values at the LGM to an elevated NO₃ supply to the euphotic zone due to increased upwelling apparently without a compensating increase in NO₃ uptake (new production). However, the CoSINE model results suggest that the low δ¹⁵N at the LGM was due to low
Si(OH)₄ supply to the equator, resulting in high unused NO₃ (Figure 2b), rather than to an increase in NO₃ supply. The subsequent increase in A¹⁵N was due to an improved Si(OH)₄ supply. The minimum in A¹⁵N during the LGM may represent the transition point in Figure 5b, between model phases, which is also the point of maximum surface TCO₂ (Figure 2c). The range of mean Si(OH)₄ concentrations at 120 m measured on U.S. JGOFS cruises to 140⁰W [Dugdale et al., 2002a, Table 2] are shown as vertical lines in Figures 2 and 5. This range of contemporary source Si(OH)₄ concentrations along with indications of increasing export of Si at the equator (Figure 3) from the LGM to the Holocene are consistent with the CoSINE results suggesting a transition from phase 1 to phase 2. The evidence from A¹⁵N analyses of equatorial cores interpreted with the CoSINE model suggests the LGM was at the transition point between phase 1 and phase 2. Increased Si(OH)₄ flux to the sediments from the glacial minima to the transitions combined with CoSINE results also point to phase 2 changes as suggested by the vertical lines in Figures 2 and 5. The CoSINE model and A¹⁵N results indicate a maximum in TCO₂ at the equator at the glacial maximum, specifically the LGM, and at that time the equator would have been a maximum source to the atmosphere. However, low equatorial opal MAR correlates with low global atmospheric CO₂ and high equatorial MAR opal with high atmospheric CO₂ suggesting that the equator is out of phase with some other process influencing atmospheric CO₂ in an opposite way. The suggestion of maximum CO₂ flux to the atmosphere at the equator during glacial periods is consistent with the analysis of Pedersen et al. [1991] who suggest cooler temperatures and higher CO₂ flux to the atmosphere for the eastern equatorial Pacific over the last 30 kyr.

[13] Altabet [2001] obtained A¹⁵N values from a JGOFS core at 0⁰, 140⁰W, within a degree of where W8402-14GC was collected. The A¹⁵N values have cyclic saw-tooth like changes over the last 600 kyr with a periodicity of ~100 kyr [Altabet, 2001] (Figure 6). The period recorded by this core includes both termination 2 and termination 1. Both terminations are periods of increasing opal MAR (Figures 3 and 4a). The rapid rise in A¹⁵N from 150–125 kyr, which includes termination 2 (128 kyr) is correlated with an increase in opal MAR. The rapid decrease from 125–110 kyr coincides with a decrease in opal MAR. The period from 25–0 kyr which includes the LGM (21 kyr) and termination 1 (12 kyr) is also a period of rapid increase in opal MAR (Figure 3) and increasing A¹⁵N. In both terminations, the positive relationship between opal MAR and A¹⁵N suggests model phase 2 conditions, in agreement with the termination 1 data from Farrell et al. [1995]. Altabet [2001] interpreted increases in A¹⁵N; i.e. increased NO₃

Figure 5. (a) Modeled utilization of NO₃ or Si(OH)₄ and (b) modeled A¹⁵N in trap particles versus source Si(OH)₄ concentration computed with CoSINE model and Altabet [2001, equation (4)]. Dotted lines show range of mean Si(OH)₄ at 120 m from 140⁰W, U.S. JGOFS.

Figure 6. Bulk sediment A¹⁵N at the equator for the last 600 kyr from Piston core PC 72 collected during U.S. JGOFS EqPac Program [from Altabet, 2001, Figure 11].
utilization as a consequence of increased Fe availability and higher new production. However, the changes predicted by the CoSINE model are consistent with the Altabet [2001] N isotope measurements and provide an alternate explanation, i.e., increased $\delta^{15}$N is due to increased Si(OH)$_4$ supply resulting in increased NO$_3$ utilization.

4. Hypothetical Si-Driven Glacial Cycle

[14] The equatorial Pacific is a chronically Si(OH)$_4$-limited ecosystem receiving Si(OH)$_4$ from the Southern Ocean through SAMW that is rich in NO$_3$ and low in Si(OH)$_4$. Our modeling shows Si(OH)$_4$-limited diatoms to control the success of other non-Si-using phytoplankton in the equatorial ecosystem in such a way that a bell-shaped curve emerges of surface TCO$_2$ as a function of Si(OH)$_4$ source concentration (Figure 2c). For the cores considered here, the relationship between Si deposition and Vostok atmospheric CO$_2$ appears to be always positive. Interpretation of this pattern requires recognition that although the opal MAR represents local equatorial processes, the atmospheric CO$_2$ values are global, the result of both local and remote processes. If we take the $\delta^{15}$N isotope data to indicate the equator is in model phase 2 (increasing and decreasing source Si(OH)$_4$ over glacial cycles) then when source Si(OH)$_4$ is low, $\delta^{15}$N is low and equatorial TCO$_2$ is highest (Figure 2). However, at low source Si(OH)$_4$ concentrations, global atmospheric CO$_2$ is at a minimum (Figure 4), indicating the equatorial CO$_2$ cycle is in opposite phase to global atmospheric CO$_2$. The link between Southern Ocean and equatorial Si(OH)$_4$ biogeochemical processes provides a negative feedback in the warming and cooling cycle. In a cooling period the Southern Ocean exhibits high diatom productivity, high CO$_2$ influx from the atmosphere; Si(OH)$_4$ export to the equator is reduced. As equatorial diatom productivity declines due to reduced source Si(OH)$_4$, equatorial CO$_2$ flux to the atmosphere increases. At some point equatorial CO$_2$ flux becomes dominant over Southern Ocean CO$_2$ absorption and warming begins. In an alternative scenario, as equatorial Si(OH)$_4$ continues to decline, the equatorial system enters model phase 1 and CO$_2$ changes in the surface waters are in synchrony with the Southern Ocean resulting in a rapid decline in atmospheric CO$_2$ leading to full glacial conditions. When a critical low source Si(OH)$_4$ concentration is reached, blooms of coccolithophorids are triggered [Aksnes et al., 1994], releasing CO$_2$ to the surface waters and to the atmosphere. The equator has been converted from a sink to a source of atmospheric CO$_2$. Warming begins rapidly with increased Si(OH)$_4$ supply to the ocean, e.g. from river input and glacial melting and the cycle begins again. In this scenario, the equator is initially a brake on decreasing atmospheric CO$_2$, later falls into synchrony with the Southern Ocean and finally triggers rapid CO$_2$ release and warming.

5. Causes of the Changes in Source Si(OH)$_4$

[15] This hypothetical cycle based upon the CoSINE model simulations, is driven by changes in Si(OH)$_4$ supply to the equatorial Pacific. The causes of the changes in Si(OH)$_4$ supply, besides the reduced supply from the Southern Ocean to the EUC, include weathering, glacial melting, drying of the climate, river inputs and dust. Rapid increases in opal MAR and CO$_2$ occurred from 150–135 kyr, just prior to termination 2 (128 kyr), and 35–5 kyr including the LGM and termination 1. CO$_2$ and air temperature are in phase with the 100,000 year ice age cycle, but changes in ice volume lags both [Shackleton, 2000]. Since opal MAR changes in the central equatorial core are in phase with CO$_2$, ice volume also lags opal MAR in this case. The lag in ice volume change, i.e. melting, eliminates increased weathering and also glacial melting with inputs of glacial flour [Pollock, 1997] as the sources of increased Si(OH)$_4$ at the terminations. Re-dissolution from the continental shelf sediments does not appear to be a viable source of Si(OH)$_4$ since CO$_2$ rose before sea level increased at terminations [Broecker and Henderson, 1998]. The dust pulses shown in the work of Petit et al. [1999, Figure 2], occurred also with a 100 kyr frequency but declined to low levels just before the rise in air temperature and CO$_2$ at termination 2, the “demise of the dust” [Broecker and Henderson, 1998]. The low dust period lasted until about 60 kyr. Although aeolian inputs of Si are only about 10% of river inputs [Tréguer et al., 1995], the dust falls on the surface and can have an immediate effect on the euphotic zone. However, the high dust period precedes the increase in Si deposition at termination 2 and so is unlikely to be the source of increased Si at terminations.

[16] Another possible explanation for decreasing input of Si(OH)$_4$ to the ocean is a progressive drying of the climate which would affect both the inputs of Si(OH)$_4$ from both local, western Pacific rivers, and to the EUC from both the Northern and Southern Hemispheres. River inputs are the primary source of Si(OH)$_4$ (~90%) to the modern ocean, with hydrothermal vents and basalt dissolution making up the remaining 10% [Tréguer et al., 1995]. Input from the North Pacific would be affected both directly through lower river Si(OH)$_4$ supply to the ocean and perhaps by a decrease in the estuarine effect with deepening of the nutricline. Si(OH)$_4$ input from the rivers of the western tropical Pacific [Dugdale et al., 2002b] would decrease with the drying of the climate. The southern source of Si(OH)$_4$ to the EUC would also be reduced by reduced river input to the Atlantic and Indian Oceans. A shutdown or decrease in the conveyer belt transporting nutrients in deep water from the Atlantic toward the south would also starve the Southern Ocean of Si(OH)$_4$. The timescales for precipitation induced changes to the Si budget of the world oceans would be somewhere close to the turnover time for Si(OH)$_4$ as a function of river input, about 15,000 years [Tréguer et al., 1995] and so match the timescale of the slow equatorial opal decline. During the long cooling phase (107–23 kyr), Southern Ocean productivity south of the polar front declined; a fourfold decrease according to Mortlock et al. [1991] and Charles et al. [1991], but this reduction in southern Si demand did not result in increased export to the equator. On balance, at least the regions south of the polar front in the Southern Ocean were starved of Si(OH)$_4$ along with the equatorial system.
[17] Decreased Si(OH)$_4$ and opal accumulation during interglacial cooling, might also occur if the global supply of Si(OH)$_4$ became progressively sequestered in the coastal margins [Berger et al., 1994]. Berger et al. [1994] observed that the global ocean must have had a very different chemistry during periods of glacial accumulation. However, the diatom record from cores taken from three Atlantic coastal upwelling sites [Abrantes, 2000] shows the same pattern as the equatorial Pacific and the Southern Ocean, i.e. very low opal accumulation during the post termination 2 interglacial period with large accumulations beginning in isotope stage 2 and reaching peak values in termination 1. The apparent global decline of Si(OH)$_4$ as indicated by core isotope stage 2 and reaching peak values in termination 1, 2 interglacial period with large accumulations beginning in i.e. very low opal accumulation during the post termination pattern as the equatorial Pacific and the Southern Ocean, coastal upwelling sites [].

The diatom record from cores taken from three Atlantic chemistry during periods of glacial accumulation. However, that the global ocean must have had a very different leakage hypothesis []. SAMW to the EUC []. The result of diatom suppression of non-Si-requiring deposition at terminations when atmospheric CO$_2$ is high. 6. Discussion

[18] We have shown that equatorial Pacific cores show low opal deposition in interglacial periods when CO$_2$ is low, increasing opal MAR at glacial maxima and high opal deposition at terminations when atmospheric CO$_2$ is high. Cores north of the polar front in the Southern Ocean and Atlantic coastal upwelling areas [Abrantes, 2000] also show the same pattern, as do cores from the California margin [Kienast et al., 2002; Lyle et al., 1992; Gardner et al., 1997], consistent with the pattern predicted and recreated by the 1-D CoSINE model for low source Si(OH)$_4$ concentrations, i.e., phase 1 [Dugdale et al., 2002a]. In the model this direct relationship between source Si(OH)$_4$ and surface TCO$_2$ is the result of diatom suppression of non-Si-requiring phytoplankton.

[19] The Southern Ocean has been suggested as a source of the varying Si deposition in the equatorial region, through decreased Si trapping during glacial periods communicated as increased Si(OH)$_4$ to the equator through advection of SAMW to the EUC [Dugdale et al., 2002a], and the silicate leakage hypothesis [Brzezinski et al., 2002]. The present study however, suggests that Antarctic and equatorial changes in opal MAR vary together. Alternatively, the supply of Si(OH)$_4$ remains constant during glacial cycles, but is re-distributed between different parts of the Southern Ocean and equatorial systems. However, it may emerge that different regions of the equatorial/southern ocean system are in different, opposite deposition phases, e.g. the more direct effect of the SAMW water may be to the eastern equatorial Pacific, through the lower EUC which transits under the equatorial upwelling system, upwells along the Peru coast and turns north to supply some of the water to the EEP upwelling system [Toggweiler and Carson, 1995; Dugdale et al., 2002b]. The upper part of the EUC is supplied from shallower waters to the south and north and so is less influenced by SAMW water. In this case, the pattern of Si deposition in the central and eastern equatorial Pacific could be either in or out of phase with each other. Enhanced export production north of the polar front during glacial periods would send water with decreased Si concentration northward. Additional studies of opal deposition in both equatorial and Antarctic cores will be useful in corroborating or refuting the silicate leakage hypothesis, the general conclusion of Berger et al. [1994] and our results suggesting that opal deposition tends to be low in glacial periods.

[20] We have interpreted variations in natural abundance of N, Si and C isotopes from the equatorial Pacific and our model results to indicate that the equatorial Pacific provides a negative feedback on CO$_2$ processes in the Southern Ocean. Additional measurements of stable isotope natural abundances in cores from the two regions would allow further tests of the hypothesis that variations in Si and N isotopes are the result of changes in Si(OH)$_4$ supply rather than changes in Fe or other drivers of enhanced production. The possibility that low Si(OH)$_4$ conditions are necessary for the blooming of coccolithophorids, adds another dimension to the hypothesis that variations in Si(OH)$_4$ supply during glacial/interglacial cycles affect the emission of CO$_2$ through diatom control of upwelling ecosystem functioning. Dymond and Lyle [1985] suggested that a reduction in the proportion of diatoms to coccolithophorids would lead to more calcite export from the equatorial surface waters and an increase in CO$_2$. An attractive element of this hypothesis is that it predicts the alternating opal-rich and carbonate-rich deposits under the equatorial Pacific.

[21] The purpose of this study was to add a new biological dimension and new theory to the quest for understanding glacial CO$_2$ cycles. Our major conclusion from data and modeling is that the role of diatoms in carbon export needs to be considered in a more complex way than the commonly accepted mode where increased diatom production equals increased carbon export. At low Si(OH)$_4$ source levels, diatom interaction with other non-Si-requiring phytoplankton may have the counter-intuitive result that increased Si(OH)$_4$ source concentration and increased diatom populations result in greater surface TCO$_2$ concentrations and increased evasion of CO$_2$ to the atmosphere. At even higher Si(OH)$_4$ source concentrations, increased diatom populations result in lower TCO$_2$ and decreased CO$_2$ flux to the atmosphere. Although the changes in TCO$_2$ in equatorial surface waters predicted by the CoSINE model are relatively small, they are enough to change the equator from a net source to a net sink and so lead to a new equilibrium value for the atmosphere. The possibility that the equatorial Pacific may provide either negative or positive feedback
to Southern Ocean processes is intriguing. The observed relationship between Si(OH)₄ deposition and glacial/interglacial CO₂ may be causal or artifact, but in any case should be considered in the context of climate changes on short or long timescales. Of particular interest is the question of the source of increased Si(OH)₄ just prior to or at terminations. Field studies to test these model driven hypotheses need to be made in the equatorial Pacific. We hope some contribution will be made by these efforts to the puzzle of glacial/interglacial feedback systems in Earth’s biogeochemical system.

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