Glacial-Interglacial Variability in Atmospheric CO₂

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Although the complete answer to the question of the glacial-interglacial variability in atmospheric CO_2 remains something of a mystery, important feedbacks, and processes have been identified that have improved our understanding of the modern and future carbon cycle. In this chapter, we will (1) outline the problem posed by the observed glacial-interglacial changes in CO_2 ; (2) provide a brief primer for understanding the basics of the global carbon cycle; (3) summarize some of the common ways in which the marine sediment record can be used to shed light in the problem; (4) describe the most promising candidate hypotheses put forth to explain changes in the carbon cycle, including an assessment of our confidence in our level of understanding of these mechanisms and their magnitude of impact on the carbon cycle and what observational evidence there is for constraining their importance; and (5) suggest some new directions and ideas.

"There are known knowns. These are things we know that we know. There are known unknowns. That is to say, there are things that we know we don't know. But there are also unknown unknowns. There are things we don't know we don't know."

-Donald Rumsfeld, former US Secretary of Defense

1. INTRODUCTION: USING THE PAST TO CONSTRAIN THE FUTURE

The biogeochemical cycling of carbon and nutrients at the Earth's surface is both regulated by, and exerts a controlling influence on, organisms. Biogeochemical cycles, particularly carbon as carbon dioxide (CO_2) and methane (CH_4),

Surface Ocean–Lower Atmosphere Processes Geophysical Research Series 187 Copyright 2009 by the American Geophysical Union. 10.1029/2008GM000845 also affect climate via the greenhouse effect and, in turn, are influenced by changes in climate. We have monitored changes in ocean and atmospheric chemistry over short timescales using instrumental records and gauges, satellites, and large-scale measurement programs. However, the variability in most of these instrumental records remains small in comparison to the scale of responses anticipated from continuing anthropogenic forcing of the Earth system. How can we be sure that we understand how the global carbon cycle and its relationship with climate may change in the future?

One means of improving our knowledge of global biogeochemical processes and their relationship to climate is through study of the geologic record. Geochemical indicators from sedimentary records can shed light on environmental changes that have occurred from decades to millions of years ago and of greater magnitude than that so far seen in instrumental records. These past biogeochemical cycles provide insights into the range of natural variability within the Earth system, insights into the manner in which biogeochemical processes operate under different boundary conditions, and a rigorous test for our models and working knowledge of the Earth system.

A classic example of how knowledge of past biogeochemical cycles contributes to our understanding of modern processes is the phenomenon of glacial-interglacial changes in atmospheric carbon dioxide. Ever since records of atmospheric carbon dioxide were first reliably retrieved from polar ice cores [Delmas, 1980; Neftel et al., 1982], a high-profile goal of Earth, environment, and climate scientists has been to explain how and why these changes have occurred. There have been numerous ideas and proposals, with each new hypothesis stimulating the exploration of new processes and observations, and enriching our understanding of the global carbon cycle, nutrient cycling, and their relationship to climate. This exploration has also resulted in development of a range of simple-to-complex models for understanding the Earth system. Each hypothesis has also predicted observable consequences that can be tested against the geologic record and has identified new data and observations that can help constrain and improve models. Thus, while a full solution to the question of glacial-interglacial variability in atmospheric CO₂ has yet to be found, the search has led to the identification of important feedbacks and processes that have improved our understanding of the modern carbon cycle, and thus presumably improved the fidelity of our future atmospheric CO₂ predictions. Understanding the processes which are capable of generating a significant lowering of CO₂ has gained even greater significance in our current political climate, as technological solutions for manipulating the global environment, "geoengineering" [Keith, 2000], are increasingly considered as a means of sequestering anthropogenically generated CO₂ and re-taking control of climate. Our understanding of the geologic record provides an important perspective for determining the effectiveness of controversial geoengineering proposals such as Fe fertilization [e.g., Zeebe and Archer, 2005] and direct CO₂ injection [Brewer et al., 1999].

In this chapter we will: (a) outline the problem posed by the observed glacial-interglacial changes in CO_2 ; (b) provide a brief primer for understanding the basics of the global carbon cycle; (c) summarize some of the common ways in which the marine sediment record can be used to shed light on the problem, (d) describe the most promising candidate hypotheses put forth to explain glacial-interglacial changes in atmospheric CO_2 , including a detailed assessment of our confidence in our level of understanding of these mechanisms, the potential range in magnitude of their CO_2 impact and what observational evidence there is for constraining their importance; and (e) suggest some new directions and ideas.

2. THE GLACIAL-INTERGLACIAL CO₂ PROBLEM

The warming response of the climate system to anthropogenic carbon dioxide emissions depends on how the carbon released from fossil fuel burning and deforestation is retained in the atmosphere. This, in turn, depends sensitively upon how much is partitioned into other reservoirs (ocean and biosphere) and how quickly this transfer takes place. Much research has gone into understanding how this partitioning occurs today [*IPCC*, 2007], how the partitioning between the ocean and biosphere is likely to change in the future [e.g., *Schmittner et al.*, 2008], and how the potential of each reservoir to hold carbon depends on the interaction between natural and anthropogenic processes [e.g., *Le Quéré et al.*, 2007].

We can test our understanding of the exchange of carbon between the different reservoirs and of how atmospheric CO₂ is regulated by looking at past changes in the global carbon cycle. Ice cores recovered from the Antarctic ice cap and analyzed for air bubble gas composition revealed that the concentration of CO_2 in the atmosphere around 20 thousand years ago (20 ka BP or ka) and at the height of the Last Glacial Maximum (LGM) was about one-third lower than during the subsequent interglacial (Holocene) period [Delmas, 1980; Neftel et al., 1982; Monnin et al., 2001; Flückiger et al., 2002]. The longer ice-core records have shown that the same pattern re-occurs over the past four cycles (Figure 1) and that this glacial-interglacial variability approaches 90 ppm [Lüthi et al., 2008; Siegenthaler et al., 2005]. Furthermore, fluctuations in atmospheric carbon dioxide are highly correlated with changes in temperature (T) [Petit et al., 1999; Indermuhle et al., 2000; Cuffey and Vimeux, 2001; Siegenthaler et al., 2005], as well as with changes in deepocean T as inferred from marine oxygen isotope records [e.g., Shackleton, 2000]. Other interesting relationships are also revealed from these records. For example, dust concentrations within the Vostok ice core only begin to rise once CO_2 has decreased to 220 ppm, hinting that the dust cycle ramps up only after the Earth has progressed at least halfway toward glaciation. The correlations, leads, and lags between these records suggest that multiple biogeochemical feedbacks operate within the Earth system [Bopp et al., 2003; Caillon et al., 2003; Vettoretti and Peltier, 2004; Kohfeld et al., 2005; Peacock et al., 2006; Lambert et al., 2008].

Ultimately, the mystery associated with long-term fluctuations in the carbon cycle has proved a powerful and fertile testing ground for understanding the natural processes controlling the global carbon cycle. Numerous hypotheses have been proposed to explain these fluctuations (Table 1). Each scenario has various implications from which one can make predictions regarding what changes should be observed in



Figure 1. Measured changes in (A) temperature (T) (δ D), (B) carbon dioxide concentrations, and (C) dust concentrations in the European Project for Ice Coring (EPICA) in Antarctica Dome C ice core in Antarctica [data from *Jouzel et al.*, 2007; *Siegenthaler et al.*, 2005; *Lambert et al.*, 2008].

the geological record. Thus, at least in theory, the validity or strength of each hypothesis can be assessed against geologic evidence. But before exploring the likely drivers of the glacial-interglacial variations in atmospheric CO_2 (section 5) and how geologic evidence can be utilized to test theory and model prediction (section 4), we will first outline the principles of how the global carbon cycle operates.

3. HOW IT WORKS: A HITCHHIKER'S GUIDE TO THE MARINE CARBON CYCLE

On timescales of decades and less, the terrestrial biosphere exerts a significant control on atmospheric composition with a pronounced seasonal signal, primarily due to the antiphased seasonal uptake and release of CO_2 by the terrestrial biosphere between the hemispheres in conjunction with the disparity in total land mass between North and South. The terrestrial biosphere thus provides a very responsive modulation of atmospheric CO_2 . At some 39,000 PgC, the reservoir of dissolved carbon in the oceans is over 13 times that of the atmosphere and terrestrial biosphere put together [*IPCC*, 2007]. Thus, the mechanisms responsible for longerterm variability in the concentration of atmospheric CO_2 are more likely to involve the ocean. For this reason, models of the global carbon cycle used in the context of glacialinterglacial change are rooted in numerical representation of the oceanic carbon cycle.

The exchange of CO₂ between the ocean and atmosphere depends on the difference in molar fraction (xCO₂) or, more commonly, partial pressure (pCO₂) of gaseous CO₂ in the atmosphere and that in the surface ocean, which is approximately equal to its fugacity (fCO₂). If one assumes no significant change in terrestrial carbon storage, weathering rates of silicate rocks, volcanic outgassing of CO₂, or the burning of fossil fuels, then the area-weighted, mean ocean surface fCO₂, as modified by local wind speed, determines the value of atmospheric CO₂. The mean ocean surface fCO₂, in turn, is primarily a function of the concentration of total dissolved inorganic carbon (DIC), alkalinity (ALK), salinity (S), and T at the ocean surface [*Zeebe and Wolf-Gladrow*, 2001]. Processes that affect any or all of S, T, DIC, or ALK, will therefore influence atmospheric CO₂.

3.1. A Tale of Three Pumps

Climate alone determines surface *S* and *T* (and wind speed). DIC is affected by the production and export of (mainly) particulate organic matter (POM). ALK is influenced primarily by *S*, less strongly by the precipitation of calcium carbonate (CaCO₃), as calcium ions (Ca²⁺) are removed from solution and, to a more minor extent, by the creation and destruction of POM due to transformations involving nitrate (NO₃⁻). Ocean circulation, by re-distributing all of *T*, *S*, DIC, and ALK exerts an overall modulation of CO₂. From these basic controls, *Volk and Hoffert* [1985] characterized three main cycles of transformation of state and translocation within the ocean system that act to vertically (and horizontally) partition DIC and ALK and thus determine surface ocean *f*CO₂. These three processes were termed "pumps" and consist of:

(1) The "solubility pump," whose action arises through the strong *T*-dependence of the solubility of gaseous CO_2 in water, with cold water exhibiting a much lower fCO_2 than warmer water. Thus, all other things being equal, warm oceanic regions will tend to be sources of CO_2 to the atmosphere and cold regions sinks. The concentration of atmospheric CO_2 is therefore related to a nonlinearly weighted average of global sea surface temperature (SST).

(2) The "soft tissue pump," whose effect is due to the removal of DIC from surface waters through its photosynthetic fixation by phytoplankton and subsequent export in the form of particulate organic carbon (POC) into deeper waters, where it is largely re-mineralized back into DIC. Through this action, there is a vertical partitioning of DIC

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CO ₂ Driver	Estimat	ted ACC	D ₂ , ^a ppm				
(and Section)	Best	Low	High	Timescale ^b	LOSU°	Studies ^d	Assessment
Higher ocean surface temperatures (<i>T</i>) (section 5.1.1)	+26	+21	+30	Fast	High	2, 3, 4, 5, 8, 12, 26, 28, 21	The Δ CO ₂ estimate analysis discounts box model predictions because of the implications of their degree of spatial averaging. The best estimate reflects the predictions of <i>Bopp et al.</i> [2003], extrapolating their sea surface temperature (SST) analysis to a Climate: Long-Range Investigation, Mapping, and Prediction (CLIMAP) glacial SST field with tropical <i>Ts</i> reduced by an additional 2°C. The upper and lower bound estimates reflect the range of intermediate complexity and GCM models and spanning boundary condition assumptions of CLIMAP to CLIMAP –2°C tropical <i>Ts</i> . The lower bound estimate ignores <i>Brovkin et al.</i> [2007] because of problems in separating SST from CO ₂ impacts of circulation chance in that narticular model shudy
Decreased ice sheet volume (section 5.1.2)	-13	-16	-12	Med	High	2, 3, 4, 5, 12, 21, 26	The best estimate reflects the average of available intermediate complexity models that include the effects of both salinity (<i>S</i>) and dissolved tracer changes. The lower CO_2 bound is taken from <i>Kohler and Fisher</i> [2006], while the upper (less negative) bound reflects the model of <i>Browkin et al.</i> [2007]. The effect of changes in <i>S</i> alone is well constrained and close to 6 mm.
Increased terrestrial carbon storage (section 5.1.3)	-22	-36	-12	Med	High	1, 12, 21, 23, 26	The analysis assumes a range of uncertainty in the glacial-interglacial variability in terrestrial carbon storage of 400–900 PgC. The Δ CO ₂ sensitivity as ppm CO ₂ per 100 PgC following carbonate compensation was calculated for the available models and applied to the 400–900 PgC range. The 3.4 ppm per 100 PgC sensitivity of the model of <i>Archer et al.</i> [2000a], in conjunction with an assumed 650 PgC carbon transfer, gives the Δ CO ₂ best estimate of -22 ppm. The low/high range is derived form both the range in carbon transfers (400–900 PgC) and range in model sensitivity. Model studies that are clearly very far from equilibrium by the late Holocene are disconneed.
Altered ocean circulation (section 5.2.1)	+27	+	+57	Med-Fast	Med-Low	2, 5, 8, 21, 25, 28	The preferred estimate for the CO ₂ impact of glacial circulation is taken from <i>Schmittner et al.</i> [2007], although this prediction does not include the Δ CO ₂ contribution from carbonate compensation. This best Δ CO ₂ estimate is also similar to the circulation effect reported by <i>Brovkin et al.</i> [2007]. Upper and lower Δ CO ₂ uncertainty bounds simply span the available GCM and box model estimates and making no indement regarding the "ouality" of the simulated glacial state.
Reduced Fe fertilization (section 5.2.2)	+15	÷ v	+28	Med-Fast	Med-Low	1, 2, 5, 12, 19, 20, 24, 30	Although some potentially important secondary CO ₂ mechanisms such as Si leakage (section 3.4) and carbonate compensation (section 3.5) are missing from current GCM-based estimates using a full occan Fe cycle, the close clustering of results informs the ΔCO_2 best estimate of 15 ppm. The observationally derived maximum contribution of <i>Röthlisberger et al.</i> [2004] informs the upper bound on ΔCO_2 . The lower bound comes from the uncompensated CO ₂ estimate of <i>Archer et al.</i> [2000a]. A number of estimates fall considerably outside the upper bound, suggesting that secondary mechanisms make a net contribution to CO ₂ changes greater than 15 ppm a distinct possibility. Estimates range up to 52.4 ppm assuming Si leakage and rain ratio impacts, but contravene the CaCO ₃ sediment record
Increased <i>T</i> (higher metabolic rate) (section 5.2.3)	+15	0	+30	Fast	Low	16, 17	Little analysis has been made of this mechanism, leading to very poor constraints on the upper and lower bounds. The ΔCO_2 best estimate is derived from the model predictions of <i>Matsumoto et al.</i> [2007] including carbonate compensation, re-scaling these results to a mean global ocean <i>T</i> change of $-2.5^{\circ}C$.

The Δ CO ₂ best estimate of 12 ppm is taken as midway between the available model estimates (6, 12, 20 ppm). It seems unlikely that this mechanism contributes less than 6 ppm, which is set as the lower bound. The upper bound is more problematic: the higher, 40 ppm estimate of <i>Ridgwell et al.</i> [2003] seems unlikely in light of the only 20 ppm total mid-late Holocene CO ₂ rise and so is discounted. The meretiared estimate of <i>Ridowell et al.</i> [2003] of 20 mpm is taken as the unner bound	Only a single model making an explicit assessment as to the impact of marine ecosystems and reporting the atmospheric CO ₂ response to changes in aeolian Si supply to the surface ocean is available [<i>Ridgwell et al.</i> , 2002]. In response to decreasing dust fluxes at the end of the glacial, a 2-ppm CO ₂ change was predicted. Assuming an equivalent contribution from an increased Si sink through opal deposition on newly flooded continental shelves leads to the Δ CO ₂ best estimate of 4 ppm. Uncertainty is estimated as lying between 0 (if little-to-no aeolian Si dissolves) and 4 ppm for aeolian Si supply, and 1 to 4 ppm for changes in the continental shelf sink. Eiving a total uncertainty range of 1 to 8 ppm CO ₂ .	No GCMs have been applied to this question, nor have appropriate glacial wind fields been explicitly assessed in any model. The ΔCO_2 best estimate is thus set at zero in the absence of spatially explicit estimates. The upper limit is from <i>Ridgwell</i> [2001], for elacial wind speeds uniformly 50% higher than during interglacials.	Weathering models [<i>Munhoven</i> , 2002] and proxy reconstructions [<i>Foster and Vance</i> , 2006] suggest little net glacial-interglacial changes in terrestrial weathering rates. The Δ CO ₂ best estimate of the contribution from terrestrial weathering changes is thus set to 0 ppm. A $\pm 25\%$ uncertainty in glacial-interglacial weathering variability would translate to ± 5 ppm based on the model sensitivity of <i>Browkin et al.</i> [2007].	Estimates vary widely depending on the Hemisphere analyzed and the nature of biological impacts taken into account (if any). The model consensus is of a net negative impact on CO_2 as sea ice cover retreats. The ΔCO_2 best estimate splits the difference between available GCM estimates and is in line with <i>Ridgwell</i> [2001]. Lower glacial CO_2 due to increased sea ice seems unlikely, hence a 0-ppm upper bound for this mechanism. The lower CO_2 bound follows <i>Köhler and Fisher</i> [2006]. The results of the box modeling of <i>Stephens and Keeling</i> [2000] are discounted.
5, 11, 21, 23, 13	1, 22	7, 21, 11	5, 18	2, 3, 12, 14, 21, 27
Med	Low	Med	Med	Med-Low
Slow-Med	Slow	Fast	Slow	Fast
+20	& +	+5	+5	0
9+	-	0	Ś	-14
+12	+	0	0	Ϋ́Υ
Coral reef re-growth (section 5.2.4)	Reduced Si fertilization (section 5.2.5)	Lower wind-speed (and gas transfer) (section 5.2.6)	Changes in terrestrial weathering (section 5.2.7)	Reduced sea ice cover (section 5.2.8)

^aSee Assessments for details of derivation of preferred estimate ("best"), and low and high limits.

^bThe timescale of the CO₂ response to each mechanism is loosely characterized as occurring on a comparable timescale to the rapid ~70 ppm CO₂ rise associated with the deglacial transition between 17 and 11 ka, "Fast," and on a timescale comparable to LGM to late Holocene (20 to 0 ka) or slower, "Slow." Note that the CO₂ response to a mechanism is likely to be characterized by multiple timescales, such as carbon removal to the terrestrial biosphere, which has a rapid component and a slower carbonate component. ^cLevel of Scientific Understanding.

^dReferences are numbered as follows: 1, [Archer et al., 2000a]; 2, [Bopp et al., 2003]; 3, [Broecker and Peng, 1986a, 1986b]; 4, [Broecker and Peng, 1993]; 5, [Brovkin et al., 2007]; 6, [Chikamoto et al., 2008]; 7, [Gildor et al., 2002]; 8, [Heinze et al., 1991]; 9, [Keir, 1988]; 10, [Keir, 1993]; 11, [Kohler et al., 2005]; 12, [Köhler and Fischer, 2006]; 13, [Kohler, personal communication]; 14, [Kurahashi-Nakamura et al., 2007]; 15, [Marchal et al., 1998b]; 16, [Matsumoto, 2007]; 17, [Matsumoto et al., 2007]; 18, [Munhoven and Francois, 1996]; 19, [Parekh et al., 2006b]; 20, [Parekh et al., 2006a]; 21, [Ridgwell, 2001]; 22, [Ridgwell et al., 2002]; 23, [Ridgwell et al., 2003]; 24, Rothlisberger et al., 2004]; 25, [Schmittner et al., 2007]; 26, [Sigman and Boyle, 2000]; 27, [Stephens and Keeling, 2000]; 28, [Toggweiler, 1999]; 29, [Toggweiler et al., 2006]; 30, [*Watson et al.*, 2000]. within the ocean, with reduced surface concentrations. The concentration of atmospheric CO_2 is consequently inversely related to the strength of operation of this pump, which responds to physical changes (e.g., *T*, sea ice, and circulation) as well as changes in nutrient, micronutrient, and light availability. This pump is sometimes also called the "biological pump," although strictly, the biological pump encompasses both soft tissue and carbonate (see below) pumps combined.

The strength of the soft tissue pump does not necessarily have a simple relationship to nutrient utilization at the surface. Although *Redfield* [1934] made the observation that carbon, phosphate, and nitrogen are found in the deep ocean at an approximate ratio of 106:16:1, related to the proportions at which these elements are taken up by phytoplankton, these ratios represent a whole ocean average [*Arrigo*, 2005], and there is substantial variability in the actual utilization ratios. Thus, the amount of carbon transferred from surface to deep waters, and hence the strength of the soft tissue pump, could be increased if the amount of carbon that was fixed per unit phosphate and/or nitrate was increased [*Broecker*, 1982].

(3) The "carbonate pump," whose effect arises in a similar way to that of the soft tissue pump, except that the particulate phase in question is calcium carbonate (CaCO₃). When CaCO₃ is produced by certain species of phyto- (e.g., coccolithophores) and zoo-plankton (e.g., foraminifera) and exported below the surface ocean, ALK is decreased at the surface and enhanced at depth in a 2:1 ratio with DIC. The resultant vertical re-partitioning of ALK in the ocean has a greater effect on fCO_2 than the associated changes in DIC and with the opposite sign, i.e., reduced ALK drives an increased partial pressure of CO₂ in surface waters. The concentration of atmospheric CO₂ therefore scales with the strength of the operation of this pump and in opposition to the soft tissue pump. For this reason, this pump is also known as the "counter pump."

The production ratio of CaCO₃ compared to POC, and thus the relative ratio of the strength of the soft tissue and carbonate pumps, was often treated as a constant in early box models. However, significant spatial and seasonal variability in the CaCO₃:POC export ratio exists in the modern ocean. Furthermore, surface ocean chemistry, specifically pH, affects the ability of open-ocean dwelling calcifying plankton, such as coccolithophorids and foraminifera to make CaCO₃ shells [e.g., *Bijma et al.*, 1999; *Riebesell et al.*, 2000]. Future decreases in pH could thus restrict the global production of marine carbonate, weaken the strength of the carbonate pump, and hence reduce atmospheric CO₂ [*Ridgwell et al.*, 2007]. Conversely, higher glacial surface ocean pH, if translated into a stronger counter pump, would tend to increase atmospheric CO_2 and thus oppose the observed changes recorded in ice cores (Figure 1).

3.2. The Principle of Carbonate Compensation

The concentration of DIC and ALK at the ocean surface is affected not only by the gradient between surface and deep, which itself is imposed by the joint operation of the three pumps, but also by the carbon and ALK inventory of the ocean as a whole. The weathering of the continents as well as interactions with biogenic materials such as CaCO₃ in the underlying sediments can bring about such a wholeocean change. The most important process at work in terms of changes in CO₂ on glacial-interglacial timescales is "carbonate compensation."

At steady state, the flux of solutes such as Ca^{2+} and HCO_3^- to the ocean will equal the burial flux of $CaCO_3$ in marine sediments. However, when the ocean's distribution of dissolved carbon and/or ALK is altered, the carbonate ion (CO_3^{2-}) concentration of the deep ocean is also changed and, with it, the stability of $CaCO_3$ and its rate of dissolution in deep-sea sediments [*Ridgwell and Zeebe*, 2005]. In the absence of any concurrent increase in weathering or hydro-thermal inputs, the amount of $CaCO_3$ preservation and burial in marine sediments and hence the deep-sea CO_3^{2-} content must ultimately be restored to that required for steady state to be re-established [*Broecker*, 1982; *Broecker and Peng*, 1987]. The changes to ocean chemistry brought about by a transitory imbalance between sources and sinks of DIC and ALK creates a lasting change in atmospheric CO_2 .

For example, consider a transfer of carbon from the ocean to the terrestrial biosphere (such as associated with the deglacial transition, see section 5.1.3). The immediate impact is a substantial decrease atmospheric CO₂. This removal of carbon drives an increase in the carbonate ion $[CO_3^{2-}]$ concentration of seawater, as $CO_{2(aq)}$ is (partially) replenished:

$$2HCO_3^- \rightarrow CO_{2(aq)} + CO_3^{2-} + H_2O$$

The higher $CO_3^{2^-}$ concentrations are progressively communicated to the entire ocean on the timescale of mixing and overturn of the entire ocean (circa 1000 years), resulting in deepening of the carbonate saturation horizon and reducing the rate of CaCO₃ dissolution in deep-sea sediments. This is manifested in a deepening of the carbonate compensation depth (CCD) and lysocline, the depths at which sediments become CaCO₃-free, and the calcite content of the sediment begins to noticeably decline with increasing ocean depth, respectively [for a review, see *Ridgwell and Zeebe*, 2005]. The stronger CaCO₃ burial sink subsequently draws ocean [CO₃^{2–}] back down:

$$Ca^{2+} + 2HCO_3^{-} \rightarrow CaCO_3 + CO_{2(aq)} + H_2O$$

as some of the released $\mathrm{CO}_{2(aq)}$ reacts to remove carbonate ions:

$$CO_{2(aq)} + CO_3^{2-} + H_2O \rightarrow 2HCO_3^{-}$$
.

(An alternative way to look at it is that with a temporary increase in CaCO₃ preservation, some of the $CO_{2(aq)}$ that was previously consumed at the sediment surface in the CaCO₃ dissolution reaction is available for reaction with $CO_3^{2^-}$, leading to higher $[CO_{2(aq)}]$ and lower $[CO_3^{2^-}]$ deep waters.) The lysocline gradually bounces back up with an efolding time of ~5000 years and atmospheric CO_2 increases in response to the upwelling of deep waters with a higher $CO_{2(aq)}$ content. Once steady state between weathering and sedimentary burial has been re-established, initial seawater carbonate ion concentrations are also re-established. Because of the loss of ALK during the transitory deficit of weathering supply of Ca²⁺ compared to burial in CaCO₃, atmospheric CO₂ is left higher overall. This process of adjustment of ocean chemistry and atmospheric CO₂ as a result of an initial imbalance induced between weathering input to the ocean and burial in deep-sea sediments, is called "carbonate compensation" [Broecker and Peng, 1987].

A variety of glacial-interglacial CO_2 drivers, both internal and external to the marine carbon cycle can result in carbonate compensation. The influx or extraction of terrestrial carbon [*Broecker et al.*, 1999b] or changes in CaCO₃ buried in shallow sediments such as coral reefs [*Broecker*, 1982] represent two external influences. Within the ocean, changes in ocean circulation or the partitioning of nutrients and carbon between intermediate and deep waters [*Boyle*, 1988a; *Keir*, 1988, 1991; *Toggweiler*, 1999] or changes in the rain rates of organic carbon to calcium carbonate [*Archer and Maier-Reimer*, 1994] will also influence the interaction between sediments and ocean. Thus, carbonate compensation mediates the atmospheric CO₂ of many, if not all (if only to a relatively trivial degree), of the potential drivers of glacialinterglacial CO₂ change.

3.3. Rain Ratio Hypotheses: Theme and Variations

One means by which biological activity could affect atmospheric carbon dioxide concentrations is via changes in the relative rates of calcium carbonate and POC supply to the seafloor [*Archer and Maier-Reimer*, 1994]. Diatoms (together with their zooplankton equivalent, radiolarians) are responsible for all of the biogenic opal production in the

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open ocean. Among nonsiliceous plankton species, only phytoplankton such as coccolithophorids (and their zooplankton equivalent, foraminifera) produce globally significant amounts of CaCO₃. Changes in ecosystem structure, specifically the balance between siliceous and nonsiliceous phytoplankton, may then affect the ratio of CaCO₃ to POC exported from the euphotic zone [*Ragueneau et al.*, 2000].

The amount of CaCO₃ that is buried in the sediments of the deep sea is influenced by the flux of CaCO₃ reaching the sediments. It is also affected by the flux of POC reaching the sediments. This is because the CO₂ that is released to sediment pore waters due to the aerobic oxidation of organic carbon within the sediments results in additional dissolution of calcium carbonate in a process referred to as "respiratory calcite dissolution" [*Archer*, 1991, 1996]. Changes in the CaCO₃:POC rain ratio reaching the ocean floor will thus exert an important influence upon the preservation and burial of CaCO₃, ultimately affecting ocean chemistry and atmospheric CO₂ [*Archer and Maier-Reimer*, 1994].

In David Archer and Ernst Maier-Reimer's original study [*Archer and Maier-Reimer*, 1994], which used a coupled ocean and sediment carbon cycle model, a 40% decrease in CaCO₃:POC rain ratio (to the sediments) was sufficient to reduce atmospheric CO₂ by ~90 ppm: the entire difference between glacial and interglacial periods [*Petit et al.*, 1999]. Subsequent variations on this theme have been proposed as mechanisms by which the ratio of organic carbon to calcium carbonate could have been changed, including changes in nutrient distributions ("Si leakage") [*Matsumoto et al.*, 2002b] and *T*-dependent changes in organic matter regeneration and recycling to surface waters [*Matsumoto et al.*, 2007].

3.4. Silica Leakage

If changes in the CaCO₃:POC ratio are to be effective in accounting for a significant portion of the glacial-interglacial CO₂ difference, some means of influencing ecosystem composition on a near-global scale is required. The "silica leakage hypothesis" provides such a mechanism. Observations have suggested that increased iron concentrations and reduced iron limitation in surface waters result in a decrease in the uptake of silicic acid relative to nitrate by diatoms [Watson et al., 2000], leaving excess silicic acid compared to nitrate. This excess silicic acid would be entrained during Antarctic intermediate water formation and transported to more silica-limited oceanic regions, where it could enhance the prevalence of silicate-producing organisms compared to nonsilicifiers. This hypothesis has been used to explain the relationship between $\delta^{15}N$ and $\delta^{30}Si$ in polar regions (see section 4.2.3), as well as the apparent opposite behavior of N and Si in these regions [Brzezinski et al., 2002]. Simple box-modeling studies have suggested that this process could account for 40–50 ppm decrease in atmospheric CO₂ [*Matsumoto et al.*, 2002b].

3.5. Ballasting

Changes in CaCO₃ production due to changes in pH, or due to changes in ecosystem composition, would affect the strength of the carbonate pump and thus atmospheric CO_2 (section 3.1). A secondary, more sensitive but somewhat longer timescale control is exerted on CO₂ via the rain ratio mechanism (section 3.3). "Silica leakage" provides a mechanism to drive regional to global-scale changes in CaCO₃:POC (section 3.4). The potential party spoiler in accounting for a large chunk of the glacial-interglacial CO₂ change in this way is the "ballast hypothesis." This hypothesis rests on the strong correlation observed between the settling fluxes of organic matter and mineral grains (particularly CaCO₃), reconstructed from sediment traps moored in the open ocean [Armstrong et al., 2002; Klaas and Archer, 2002]. The inference made from this correlation is that when CaCO₃, opal, and dust (terrigenous silicate minerals) aggregate with organic matter, they increase mean particulate densities and thus enhance the settling rate of particles, giving bacteria in the water column less time to degrade the organic matter before it reaches the ocean floor. The bottom line is that the flux of organic carbon to the ocean floor is mechanistically dependent on the flux of mineral particles, particularly CaCO₃.

If ballasting is an important mechanism controlling the POC flux reaching the ocean floor, this has implications for how the efficiency of the biological pump, and thus atmospheric CO₂, is regulated. For example, a change in ecosystem composition that reduces the production of CaCO₃ ballast (such as envisioned by the Si-Leakage hypothesis, see section 3.4) would tend to result in an increase in atmospheric CO₂ because organic matter would be recycled closer to the ocean surface [*Barker et al.*, 2003; *Heinze*, 2004]. More importantly, because the CaCO₃:POC rain ratio reaching the sediment surface is buffered, the effectiveness of the rain ratio mechanism (section 3.3) would be substantially diminished [*Ridgwell*, 2003b].

However, alternative interpretations of sediment trap correlations exist and do not require the efficiency of the organic carbon pump to be explicitly dependent on the CaCO₃ flux. It is possible that POC binds together small biogenic carbonate particles, and therefore the production and flux of POC is responsible for the flux of CaCO₃ to the deep ocean and thus the observed correlations [*Passow and de la Rocha*, 2006], not vice versa. Alternatively, the sediment trap observations could simply reflect correlations between ecosystem composition and productivity at the surface [*François et al.*, 2002]. The role of ballasting is currently not fully known, adding a dimension of uncertainty to the ocean carbon cycle processes at work in the glacial ocean (as well as to the modern and future ocean).

3.6. Carbon Cycle Models

There is no unique or "correct" model for the glacial carbon cycle, if for no other reason than to create the perfect model would require that the causes of low glacial CO₂ were a priori precisely known, which is the unanswered question being addressed in the first place. Model structure is inevitably a trade-off between: (1) the degree of complexity in terms of the different mechanisms and processes within the global carbon cycle that are represented, (2) the spatial and temporal resolution of the model, and (3) the required simulation length. This, in turn, is further modified by the best "guess" as to what the key processes operating during the glacial are judged to be. At a minimum, the representation of the ocean must be capable of distinguishing between major water masses and accounting for important vertical and horizontal (ideally: along density surfaces) transports of T, S, and (bio-)geochemical tracers. Models for glacialinterglacial variability in atmospheric CO2 must also resolve the three separate "pumps" (section 3.1) and their associated controls (e.g., nutrient availability). Although changes in CaCO₃:POC rain ratio (section 3.3), silica leakage (section 3.4), and ballasting (section 3.5) may play important roles, there is currently no consensus on this, and their inclusion is somewhat subjective. In contrast, carbonate compensation (section 3.2) is widely believed to be an essential component. However, because a simulation length of circa 10-20 ka is required to calculate its contribution to atmospheric CO₂ [Ridgwell and Hargreaves, 2007], carbonate compensation is omitted in most models (although its effects on ocean chemistry can be approximated, e.g., see Toggweiler [1999]).

Historically, much of the progress in our understanding of the potential causes of low glacial CO₂ has been made with the use of carbon cycle models where the representation of the world ocean is highly simplified. In some of the earliest of these models, the ocean was partitioned into only two or three homogeneous volumes or "boxes" with a prescribed ocean circulation [e.g., *Knox and McElroy*, 1984; *Sarmiento and Toggweiler*, 1984; *Siegenthaler and Wenk*, 1984], soon followed by slightly more complex "multibox" models utilizing up to a few dozen boxes [e.g., *Broecker and Peng*, 1986a, 1986b; *Keir*, 1988]. Despite their apparent oceanographic naivety, they have the advantages of relative ease of interpretation and numerical efficiency, leading to their central role in the development of many of the proposed mechanisms for glacial-interglacial CO_2 variability. However, the general inability of box models to sufficiently finely resolve key regions of CO_2 ocean-atmosphere exchange (such as strong net outgassing from equatorial upwelling zones) can produce a distortion of the predicted atmospheric CO_2 response to perturbation, such as to changes in sea ice extent [*Archer et al.*, 2003], cautioning their use in assessing certain aspects of glacial-interglacial CO_2 variability.

At the opposite end of the spectrum, Ocean General Circulation Models (OGCMs) represent the global ocean on a three-dimensional (3-D) grid, with a typical horizontal resolution of order 3° and with upward of 15–30 separate vertical levels resolved. Ocean circulation is calculated by consideration of forces generated through surface wind stress and ocean density contrasts (driven by heat and S gradients), with surface boundary conditions prescribed from observations or calculated through coupling with an atmospheric general circulation model (AGCM). Although their grid spacing enables most major ocean biogeochemical provinces to be adequately resolved, the sheer number of cells in the 3-D structure results in a considerable computation requirement, even when run "off-line," i.e., utilizing a precalculated circulation [e.g., Archer et al. 2000a; Bopp et al., 2003; Heinze et al., 1999]. Models approaching a resolution of 1° cannot be run long enough to include processes operating on timescales of 1–10 ka and beyond, such as carbonate compensation. Despite this, important dynamics associated with eddies are still not explicitly represented until a resolution of $\sim 0.1^{\circ}$ or less is reached.

A "third way" is provided by Earth system (or "intermediate complexity") models. These seek to maximize spatial resolution, while retaining the 10- to 20-ka run-time capability required to account for ocean-sediment interaction and its modulation of atmospheric CO₂. They also typically account for feedback with climate and many additionally include the response of the terrestrial biosphere. They may be based on zonally averaged [e.g., *Brovkin et al.*, 2007] or 3-D ocean circulation models [e.g., *Ridgwell and Hargreaves*, 2007] and are sometimes designed with the glacial CO₂ question in mind.

The different approaches have their strength and weaknesses, but can be complementary. Box models are particularly useful for rapid assessment of new ideas and exploration of parameter space. Higher resolution 3-D models are important because some mechanisms and processes require a minimum spatial and/or temporal resolution in addition to improvements in the representation of ocean circulation that is generally facilitated by increased resolution. Earth system/intermediate complexity models attempt to bridge this divide within a single model framework and are often developed with a wide range of carbon cycle processes including sediments in mind.

4. HELP FROM OCEAN MUDS: PALEOCEANOGRAPHIC PROXIES

Modelers are not entirely free to vary anything in the search for the desired change in atmospheric CO₂. Reconstructing past changes in the climate system and global biogeochemical cycles provides important constraints on the boundary conditions that are required as input by all but the most highly integrated Earth system models. For instance, ocean-only models will require information about surface winds and Ts; models without a prognostic ice sheet component need to know how much additional volume of water was stored on land during the last glacial period, and thus what sea level and S were. Models invariably require information regarding dust and thus the supply of iron to the ocean surface. Once appropriate changes in the required boundary conditions have been made, further observations can be used to test model predictions. As we will see later, many potential mechanisms operating over the glacial-interglacial cycles and affecting atmospheric CO₂ could produce nearly identical CO₂ changes. How do we chose between them, or correctly elucidate their relative contributions? The geological record, specifically the sedimentary (paleoceanographic) record on the ocean floor, contains the imprints of a multitude of chemical and biological properties of the ocean. Different mechanisms controlling CO₂ give rise to different unique signatures in the paleoceanographic record.

Some of the earliest hypotheses explaining fluctuations in CO_2 have concerned the role of biology and specifically changes in the strength of the biological pump in the ocean [Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Martin, 1990]. Testing the viability of such hypotheses requires a means of reconstructing, either directly or indirectly, changes in primary productivity, export production, changes in surface and deep-ocean nutrient contents, surface nutrient utilization, and changes in the amount of sinking and remineralization. Such a quantification is a tall order even for the modern ocean! But as an example of the importance of sediment proxies in reconstructing past ocean conditions and thus constraining models, in this section, we review in detail how changes in export production, ocean nutrient concentrations and distributions, and nutrient utilization are recorded in muds on the ocean floor.

4.1. Reconstructing Export Production

A relevant measure for understanding biological changes in the ocean carbon cycle is changes in the export of carbon from the surface ocean to the seafloor. Quantifying changes in the modern ocean is already quite challenging and becomes increasingly difficult when examining the marine sediment record. Each paleoceanographic proxy carries its own set of assumptions and complications, and not one represents the perfect indicator of export production.

There are several direct measures of fluxes of biogenic components produced by plankton in surface waters, such as organic carbon, biogenic opal, carbonate, and molecular biomarkers. Biogenic opal is formed by diatoms and radiolaria; carbonate is produced by coccolithophorids and foraminifera; molecular biomarkers are associated with primnesiophytes (coccolithophorids), and diatoms have been identified and measured. Organic carbon is produced by all of these organisms as well as several species that do not form tests. The measured fluxes of these materials are never likely to reflect exactly what falls from the surface to the seafloor but, instead, will reflect balance between the surface flux, what is redistributed by lateral transport, what is preserved, and what is dissolved.

For instance, changes in the timing and pattern of opal accumulation in the sediments of the deep sea could help in assessing the silica leakage hypothesis (section 3.4). The first concerns the timing of events. If changes in the Si/N uptake are dependent on iron fertilization, and iron comes largely from aeolian input, then the changes in northward transport of excess silicic acid would be coincident with input of dust to the ocean. Thus, if this effect contributed to decreases to the atmospheric CO₂, then its major impact would be limited to the latter half of the glacial-interglacial cycle, when dust fluxes to the ocean begin to increase. A second implication of this hypothesis concerns the region of the ocean where changes in silicic acid concentrations and therefore Si fluxes to the seafloor are likely to be observed. Two most likely regions to be affected are the Subantarctic regions and equatorial upwelling regions. These increases are observed in the Subantarctic regions of the Atlantic and Indian Oceans [Kumar et al., 1995; Frank et al., 2000; Anderson et al., 2002] and believed to compensate for reductions in opal burial rates in the Antarctic zone at the LGM. However, increased opal burial rates during the LGM compared with today are not observed in the eastern equatorial Pacific region [Kienast et al., 2006; Bradtmiller et al., 2007].

There are also indirect measures of changes in organic carbon fluxes to the seafloor, including radiogenic isotopes, biogenic barium, and authigenic uranium. Radiogenic proxies (e.g., ²³¹Pa and ¹⁰Be) are scavenged by particles in the water column and therefore are related to particulate fluxes [*Kumar et al.*, 1995]. However, they can be affected by extra particle scavenging near continental margins, and preferential adsorption to certain types of particles may affect their

ability to record export production exclusively [Frank et al., 2000]. Accumulation of biogenic barium in marine sediments is positively related to organic carbon fluxes (specifically diatom frustules), as barite forms during the decomposition of planktonic marine organic matter [Paytan and Kastner, 1996]. However, interpretation of barium depends on variable ratios of barium to organic material, preservation problems under reducing ocean water conditions, and regional variability in the lithogenic contribution to barium concentrations [McManus et al., 1998]. Authigenic U is formed in marine sediments during the degradation of organic material, and thus is indirectly related to organic carbon fluxes [Kumar et al., 1995]. However, it can also be influenced by lateral fluxes of organic carbon during sediment focusing, as well as low oxygen content of overlying bottom waters [*Frank et al.*, 2000].

One approach to estimating paleo-export production is to consider these proxies collectively. Some recent studies [Bopp et al., 2003; Kohfeld et al., 2005] used all measures of export production in each individual core to determine a qualitative consensus, estimating only whether export production at one time period increased, decreased, or did not change relative to another time period. This approach assumes that not all proxies will be affected by the same complications and that the consensus will provide a general representation of changes in carbon export. The reconstruction of the last glacial period compared to today (Plate 1a) shows several distinctive patterns, including decreases or no change in carbon export to the seafloor in high-latitude regions (south of \sim 50°S, and north of approximately 45°–50°N). The data also suggest increases in carbon export to the seafloor during the LGM relative to the late Holocene in the Subantarctic regions of the Atlantic and Indian Oceans, and possibly higher export along the equatorial upwelling regions of the Atlantic Ocean. Data from the equatorial Pacific regions, to the contrary, seem to suggest lower export production overall.

One constraint in this analysis is that all fluxes can be affected by lateral redistribution of sediments. Lateral redistribution can inflate the measured accumulation rates of the sediment components, in some cases, by as much as a factor of 20 [*Francois et al.*, 1993]. Constant flux proxies such as 230 Th and 10 Be have been utilized in several studies to account for these issues [*Bacon*, 1984]. One limitation is that 230 Th can only be used reliably for the last 75,000 years. In this instance, constant flux proxies were used at 89 out of 277 locations. These fewer data in the equatorial and Southern Ocean regions present a more cohesive picture of changes in carbon export to the seafloor (Plate 1b) and also reveal knowledge gaps where normalization for changes in lateral movements of sediments are still needed.



LGM - Late Holocene Change in Export Production

Plate 1. Reconstructed changes in carbon export to the seafloor during the Last Glacial Maximum compared to the late Holocene period, from (A) all deep-sea core records, and (B) only those records for which ²³⁰Th normalization of fluxes are available. Data are from [*Kohfeld et al.*, 2005] with new data added in the equatorial Pacific regions [*Kienast et al.*, 2006; *Bradtmiller et al.*, 2007].

4.2. Reconstructing Changes in Ocean Nutrients and Nutrient Utilization

Changes in the distribution of nutrient concentrations as well as nutrient utilization in the surface waters are also highly relevant for understanding which mechanisms are responsible for changes in atmospheric CO_2 . Several sediment proxies have been used to this end, including the carbon isotope composition of foraminiferal calcite, the ratio of Cd to Ca in foraminiferal calcite, nitrogen isotope composition of organic material, and the silicon isotope composition of diatom frustules.

4.2.1. Carbon isotope composition ($\delta^{13}C$) of biogenic calcite. A global relationship between the carbon isotope com-

position of DIC and oceanic phosphate (PO₄⁻) concentrations was recognized in the late 1960s and early 1970s, when data were collected as part of the Geochemical Ocean Sections Study (GEOSECS) program [*Kroopnick*, 1985]. As carbon is fixed during photosynthesis, isotopically light carbon (¹²C) is taken up by organisms in the surface water (at an average fractionation of ~-19‰), which enriches surface water DIC in ¹³C. When this organic material is remineralized (generally at deeper depths in the ocean), ¹²C is released into the water and decreases the δ^{13} C of DIC. Coincident with this carbon isotope fractionation is the uptake and subsequent release of phosphate in surface and deep waters, respectively. If biological uptake and release were the only processes affecting the carbon isotope composition of DIC, then one would anticipate the δ^{13} C of DIC to decrease by ~1.1‰ for every 1

μ mol/kg of PO₄⁻ that is utilized [*Broecker and Maier-Reimer*, 1992].

In theory, this relationship makes it possible for the carbon isotopic composition of biogenic carbonates to indirectly track changes in ocean nutrient concentrations. As such, paleoceanographic reconstructions of the carbon isotope composition of foraminiferal shells living in intermediate and deep-water masses have provided new insights into glacial-interglacial changes in ocean circulation [*Raymo et al.*, 1989; *Oppo et al.*, 1995]. Attempts to reconstruct oceanic circulation have resulted in numerous measurements of the carbon isotope composition of foraminiferal calcite, bridging several geologic time periods.

However, several factors complicate the use of carbon isotopes as a paleo-nutrient tracer, both in terms of the relationship to PO₄⁻ concentrations and the integrity of the carbon isotope composition of foraminiferal calcite as an accurate measure of δ^{13} C of ocean DIC. First, air-sea gas exchange affects the fractionation of δ^{13} C of DIC of surface waters [Mook et al., 1974; Broecker and Maier-Reimer, 1992] and therefore disrupts the stable relationship between δ^{13} C/P [Lvnch-Stieglitz et al., 1995]. Second, the δ^{13} C in foraminifera can be affected by several "vital" effects which alter carbon isotope fractionation. These include: (a) changes in the carbonate ion concentration of seawater [Spero et al., 1997]; (b) changes in the carbon isotopic concentration of food source [for summary, see Kohfeld et al., 2000], and (c) T-based fractionation factors [Spero et al., 1997]. In the Subantarctic South Atlantic Ocean, carbon isotope disequilibrium in planktonic foraminifera can be as much as three to four times greater than the observed glacial-interglacial difference [Kohfeld et al., 2000]. Mackensen et al. [1993] also demonstrated that the δ^{13} C of benthic foraminifera do not always reflect ambient, deep-ocean δ^{13} C of DIC. This work suggested that there is a tendency for benthic foraminifera to incorporate isotopically "light" ¹²C when the rain of organic carbon to the seafloor is especially high and therefore is not always a faithful indicator of the δ^{13} C of DIC of ambient seawater.

4.2.2. Cd/Ca ratio of foraminiferal calcite. Another means of reconstructing ocean nutrient contents involves measuring the ratio of Cd to Ca in foraminiferal calcite, which reflects the phosphate content of ambient seawater [Boyle, 1981, 1988b]. The principles behind this proxy lay in the global relationship between Cd/P in oceanic deep waters. Like all other proxy indicators of past ocean conditions, Cd/Ca is also affected by other processes [for review, see Marchitto and Broecker, 2006; Marchitto et al., 2006]. McCorkle et al. [1990] demonstrated that the Cd/Ca of benthic-dwelling foraminifera changed with water depth and suggested that the dissociation coefficients are affected by pressure. Rickaby and Elderfield [1999] also suggested that the dissociation coefficients depended on T, with greater Cd incorporation occurring at higher Ts. Furthermore, just as the carbon isotope proxy assumes a stable relationship between $\delta^{13}C$ of DIC and phosphate concentrations, the Cd/Ca proxy is based on the assumption that the relationship between Cd/P in the ocean remains constant. Recent studies suggest that uptake of Cd/P by diatom species varies depending on the degree of iron limitation in the ocean [Lane et al., 2008]. In Antarctic coastal waters, Cd/PO_4^- ratios have been shown to be higher than those observed in ambient, open-ocean waters, most likely as a result of high inputs of Fe and Zn from continental sediments [Hendry et al., 2008]. Both of these recent studies imply that changes in the influx of iron to biologically active regions of the ocean, and subsequent changes in contribution of these waters to deep-water mass formation, could very well alter the deepwater Cd content of seawater and thereby decouple foraminiferal Cd/Ca values from ambient ocean phosphate concentrations.

4.2.3. Nutrient utilization proxies: $\delta^{15}N$ and $\delta^{30}Si$. Information about the utilization of nutrients in the surface waters helps to gauge how much nutrients and CO₂ have been removed from the surface waters (and therefore also removed from contact with the atmosphere). Several utilization proxies have been developed over the past few years.

The nitrogen isotope composition of bulk and diatombound organic matter is one proxy believed to reflect changes in the relative utilization of nitrate in surface waters, based on a Rayleigh distillation process [Altabet and Francois, 1994]. The δ^{15} N of diatom-bound organic matter is believed to increase, as nitrate utilization increases in surface waters and therefore provides us with an overall estimate of the amount of nitrate that is used. Several factors can complicate the interpretation of δ^{15} N measurements, including (a) diagenetic alteration when measurements are made on bulk sedimentary organic material [Altabet and François, 1994; François et al., 1997; Sigman et al., 1999], (b) differences in analytical procedures [Robinson et al., 2004], and (c) regional variability in the fractionation factor for ${}^{15}N/{}^{14}N$, possibly due to remineralization of newly fixed nitrogen and active cycling between NO₃⁻ and NO₂⁻ [DiFiore et al., 2006] and possibly due to the influence of iron availability on phytoplankton growth rates [Karsh et al., 2003].

A second useful measure of changes in nutrient utilization is the change in the silica isotope fractionation observed in diatom frustules, which follows changes in the relative utilization of silicic acid in surface waters [*De la Rocha et al.*, 1998]. Whether modeled as a closed [*De la Rocha et al.*, 1997] or open [*Varela et al.*, 2004] system, the silicon isotope composition of diatom frustules increases with increased utilization of $Si(OH)_4$ in surface waters. As such, this measurement has recently been used most extensively to estimate the changes in silica utilization in Antarctic and Subantarctic regions.

When used together, δ^{15} N and δ^{30} Si records have suggested that the Subantarctic and Antarctic regions of the Atlantic and Indian Oceans experienced enhanced depletion of nitrate but lesser utilization of silicic acid during the LGM when compared with the Holocene [*De La Rocha et al.*, 1998; *Beucher et al.*, 2007]. These records have been interpreted to indicate support for the idea that higher iron fluxes to the ocean increased Si leakage from the Antarctic to Subantarctic zones in these oceans.

4.3. Difficulties in Paleo Reconstruction

The proxies discussed above provide us with valuable clues about changes in ambient ocean conditions, but their real message is frequently obscured by a complex interaction of physical environmental changes that also affect the way in which a particular isotope is fractionated within a biological system. The important lesson to acknowledge is that each change we measure can have a host of meanings, and it is up to us to interpret these proxies in the most meaningful way based on our combined understanding of the physical, biological, and chemical systems.

Another point that must be considered when reconstructing past conditions is age control. The two primary means of determining the age of deep-sea sediments are through the use of absolute chronologies or stratigraphic correlation. The use of radiocarbon dating for the past ~30,000 years is now the standard means of establishing absolute chronologies in marine sediments, although this technique is not without its complications. Several studies have demonstrated that the production of radiocarbon in the atmosphere has varied [Stuiver, 1978], likely as a result of changes in the Earth's magnetic field as well as changes in the amount of radiocarbon stored in the various reservoirs. The calibration of the radiocarbon timescale against other methods such as dendrochronology, laminated marine sediments [e.g., Stein et al., 2000], and U/Th ages in corals [Bard et al., 1990, 1998] has allowed to reconstruct a calendar age scale that is believed to be a truer representation of time. Stratigraphic correlation, such as the oxygen isotope stratigraphy [Imbrie et al., 1984; Martinson et al., 1987], is a second means of determining relative ages of sediments that is used extensively in dating marine sediment records. Other forms of stratigraphic correlation that are used in cores that are more difficult to date include magnetic stratigraphy [e.g., Gebhardt et al., 2009] or other forms of lithographic correlation. Because of these complications, both the exact age of records and the estimation of fluxes must be examined cautiously.

5. WHAT CAUSED THE ~70- TO 90-PPM GLACIAL-TO-INTERGLACIAL CHANGE IN ATMOSPHERIC CO₂?

We need to understand the nature of the climate-CO₂ relationship encapsulated in ice core records, not least for the insights it may offer into the future response of the Earth system to anthropogenic forcing. Numerous hypotheses and mechanisms have been proposed to explain this observation [see, e.g., reviews by Archer et al., 2000a; Broecker and Henderson, 1998; Köhler et al., 2005; Köhler and Fischer, 2006; Ridgwell, 2001; Sigman and Boyle, 2000]. However, taken in isolation, all proposed mechanisms have fallen far short of the simultaneous constraints dictated by marine, terrestrial, and ice core paleoenvironmental records. Thus, despite the continuing lure to researchers of a single and conceptually elegant explanation, it has become increasingly clear that the observed glacialinterglacial variability in CO₂ must result from a combination of processes operating in conjunction (but not necessarily in phase or even in sign) [Köhler and Fischer, 2006]. The difficulty lies in unambiguously identifying the set of mechanisms involved and constraining their relative contributions.

In the preceding section, we discussed ways in which common paleoceanographic tools can come to our aid and provide evidence of past changes in ocean biogeochemical conditions and function. In the following section, we provide a summary and discussion of the most viable drivers of atmospheric CO₂ change that have been hypothesized to explain the ice core record. The mechanisms and their likely impact on CO₂ are summarized in Figure 2 and detailed in Table 1. For each mechanism, we will describe how it works and assess its likely importance toward changing atmospheric CO₂, based on available model estimates. We will also summarize what independent evidence we have to constrain the role of each driver (Table 2). The order of the CO_2 drivers follows that of Figure 2, with the mechanisms grouped into three categories: "known knowns," "known unknowns," and "unknown unknowns," loosely based on our current level of understanding and certainty of their importance. We also distinguish between 'drivers' of CO₂ change, as summarized in Table 1, and marine carbon cycle "processes," covered previously (section 3). The distinction is somewhat artificial, CO2 drivers we consider to be a direct cause of change in CO₂. Processes may be involved and may be equally or more important, but they act as secondary or tertiary processes down the chain of cause-and-effect.

In our analysis, it must be borne in mind that, although we list and discuss the drivers generally in isolation, there may be an important interaction between them, with the impact of the "whole" being greater (or less) than the sum of the parts. We assume that the summation can be done by linear



Glacial-interglacial CO, drivers

Figure 2. Best estimates and associated degree of uncertainty in our level of understanding in the magnitude of impact of the mechanisms contributing to glacial-interglacial changes in atmospheric carbon dioxide concentrations (see Table 1 for details of model simulations and studies included).

addition. In other words, the impact on atmospheric CO_2 of a particular environmental change when measured in isolation and with respect to an otherwise interglacial state of the Earth system may be rather different from that same environmental change when measured against the glacial state [e.g., *Rahmstorf*, 2002; *Rahmstorf et al.*, 2005]. However, where such a comparison has been carried out, the CO_2 impact of adding a process to the interglacial state versus subtracting it from the glacial state does not normally differ by more than a few ppm. Thus far, there is no consistent sign as to whether the glacial or interglacial state is the more "sensitive" [*Köhler and Fischer*, 2006]. We have also chosen to focus on global environmental changes that followed the last glacial maximum and how these contributed to the observed CO_2 rise at deglaciation. There are other ways of viewing the "glacial CO_2 problem," such as the reasons for the *fall* in CO_2 between each interglacial and the subsequent full glacial period, and fluctuations in atmospheric CO_2 between intermediate glacial states and full glacial and interglacial periods [e.g., *Kohfeld et al.*, 2005]. Finally, the assessment of different (primarily) modelbased estimates is not exhaustive, nor can the estimated glacial-interglacial CO_2 contributions a priori be an entirely objective judgment. We have excluded more simplistic models and assumptions (not necessarily box models) for which some basis for exclusion exists, particularly where subsequent papers and analysis has raised some doubt. Otherwise, we have taken available estimates at face value in assessing the "uncertainty" in CO_2 , giving a simple min/max range of feasible values rather attempt to assign a formal likelihood (i.e., 1 or 2 sigma uncertainty). The "level of scientific understanding" is subjective.

5.1. Well-Understood Glacial-Interglacial Changes: The "Known Knowns"

Several of the global environmental changes occurring between glacial and interglacial periods have impacts on atmospheric CO₂ that are reasonably well understood. We term these the "known knowns" of the glacial CO₂ problem. This is not to say that there is no uncertainty in their contribution to observed CO₂ variability, no model is perfect after all. More importantly, different proxy-based (or other) reconstructions used to define the glacial input conditions to carbon cycle models do not always agree, and reconstructions are not always sufficiently well constrained spatially or temporally to allow us to make exact estimates of their CO₂ impact. The "known knowns" concern glacial-interglacial variations in ocean surface T, sea level, and the terrestrial biosphere.

5.1.1. Ocean surface temperature. Ocean surface T (or SST) affects atmospheric CO₂ because the solubility of carbon dioxide in seawater is T sensitive [Zeebe and Wolf-Gladrow, 2001]. Thus, one expects that the ocean will be able to hold more carbon dioxide during glacial periods when surface ocean waters are cooler and CO₂ solubility higher. How much cooler? Paleoceanographic reconstructions of seasurface Ts during the LGM have been made using several faunal and geochemical techniques (e.g., transfer functions using diatoms, dinoflagellates, radiolaria, and foraminifera; alkenone Ts, Mg/Ca ratios in planktonic foraminifera). These T reconstructions vary slightly in their estimates of global T change largely due to differences in methodology [e.g., Kucera et al., 2005; de Vernal et al., 2006], but overall, they suggest that the global ocean was, on average, 3°–5°C cooler during glacial relative to interglacial periods (Figure 3).

One ongoing concern in these *T* reconstructions is the spatial pattern of the SST change, particularly with respect to the *T* suppression in tropical regions at the LGM period. Early reconstructions suggested that this *T* drop was rather small, on the order of $1^{\circ}-2^{\circ}C$ in western equatorial

regions and $2^{\circ}-3^{\circ}$ C in eastern equatorial regions [*CLIMAP*, 1981]. However, *T* reconstructions based on the tropical snowline depressions [*Rind and Peteet*, 1985], land-based *T*s from groundwater [*Stute et al.*, 1995], geochemical-based reconstructions from tropical corals [*Guilderson et al.*, 1994], geochemical estimates from alkenones [*Rosell-Melé et al.*, 2004], and Mg/Ca ratios in foraminifera [*Lea et al.*, 2000] suggest that tropical *T*s might have been an additional $2^{\circ}-3^{\circ}$ C cooler than the original Climate: Long-Range Investigation, Mapping, and Prediction (CLIMAP) reconstruction, in some places. Ongoing efforts to address this problem continue to demonstrate east-west spatial patterns in the *T* gradients at the LGM [*Farrera et al.*, 1999], but that overall *T*s were likely to be approximately 2° C cooler [*Hostetler et al.*, 2006] than the CLIMAP reconstruction.

Quantifying the impact of SSTs on atmospheric CO_2 is simple in principal because the process at work is gas solubility, which is well-constrained from laboratory characterization. Early studies employed simple box models to translate lower glacial SSTs into a CO₂ change [e.g., Broecker and Peng, 1989]. However, biases arise because of the necessity to average large oceanic regions or even entire basins in low-resolution box models, despite the solubility of CO₂ being a nonlinear function of T [Broecker et al., 1999a]. This averaging, together with differences in assumptions about what constitutes a representative mean glacial-interglacial change in SSTs, give rise to a large spread in atmospheric CO₂ estimates: 14-38 ppm. Questions have been raised as to whether these types of models can be relied upon to correctly predict the response of atmospheric composition to SST changes [Archer et al., 2000b; Broecker et al., 1999a, 1999b; Ridgwell, 2001]. Because of the importance of spatial variations in SSTs, 3-D and "2.5-D" [e.g., Marchal et al., 1998a] GCM-based carbon cycle models are arguably more appropriate tools. When glacial SST reconstructions [CLIMAP, 1981] are used and an additional 2°C cooling in the tropics are assumed, ocean GCM carbon cycle models (as well as more highly resolved box models) produce an estimate for the atmospheric CO₂ increase due to ocean surface warming across the glacial-to-interglacial transition with a central value of 26 ppm (ΔCO_2 range: 21 to 30 ppm, see Table 1, Figure 2).

5.1.2. Global sea level, whole ocean salinity, and alkalinity. Another change between glacial and interglacial periods that is reasonably well constrained by data, and whose influence on CO_2 is well understood, is sea level. During the LGM, sea level was much lower than today, as a result of large amounts of water stored on the continents in the form of the massive, northern hemisphere ice sheets. During deglaciation, freshwater was released from continental ice

Fable 2. Constraining the	Contri	butions to Glacial-Interglacial CO ₂ Var	iability From the Geological Record
CO ₂ Driver	ΔCO_2 ,		
(and Section)	ppm^{a}	Ocean Region Impacted	Constraining Observations From the Geologic Record
Higher ocean surface Ts	+26	Whole ocean	Faunal assemblage changes, increased Mg/Ca of foraminiferal shells, Uk37' (alkenone) reconstructions [<i>CLIMAP</i> , 1981; <i>Rosell-Melé et al.</i> , 1998; <i>Sarnthein et al.</i> , 2003; <i>Rosell-Melé et</i> 21, 2004. <i>Knows at al</i> , 2005.
Section 5.1.1) Decreased ice sheet volume (section 5.1.2)	-13	Whole ocean	au., 2004, Matcha et al., 2003]. Coral reconstructions quantify increased sea levels during deglaciation [Fairbanks, 1989; Peltier and Fairbanks, 2006].
ncreased terrestrial carbon storage (section 5.1.3)	-22	Whole ocean	Carbon isotopic evidence from marine sediments [<i>Shackleton</i> , 1978; <i>Curry et al.</i> , 1988; <i>Duplessy et al.</i> , 1988; <i>Matsumoto and Lynch-Stieglitz</i> , 1999]. Reconstructed changes in global vegetation patterns show massive regrowth of boreal forests across deglaciation [e.g., <i>Prentice</i> , 2001a, 2001b].
Altered ocean circulation (section 5.2.1)	+27	Whole ocean	Shifts in meridional overturning circulation from intermediate water depths at the glacial to deep-water depths during the interglacial periods, determined using $^{13}C/^{12}C$ ratios [e.g., <i>Oppo and Fairbanks</i> , 1987; <i>Sarnthein et al.</i> , 1994] and Cd/Ca ratios [e.g., <i>Boyle and Keigwin</i> , 1982] in foraminifera. ²³¹ Pa/ ²³⁰ Th data suggest that rate of overturning is similar between the two time periods [<i>Yu et al.</i> , 1996; <i>McManus et al.</i> , 2004], and $\delta^{13}C$ suggests that Pacific Ocean circulation is similar between two time periods [<i>Matsumoto et al.</i> , 2002a]. Glacial ocean believed to be well-stratified compared to modern interglacial, as evidenced from bore hole sites [<i>Adkins et al.</i> , 2002] and from surface ocean data in polar regions [e.g., <i>François et al.</i> , 1997; <i>Sigman et al.</i> , 2007; <i>Marchitto et al.</i> , 2007] and was a source of CO ₂ to the atmosphere.
deduced Fe fertilization (section 5.2.2)	+15	Iron-limited HNLC regions: North Pacific, eastern equatorial Pacific, Southern Ocean; potential nutrient-related impacts at lower latitudes	Decreased dust fluxes to marine sediments across the deglaciation can, in theory, be reconstructed directly [e.g., <i>Rea</i> , 1994; <i>Kohfeld and Harrison</i> , 2001; <i>Kohfeld and Tegen</i> , 2007]. Ice-core records which show several-fold decreases between the last glacial period and today can be used as regional proxies for changes in high-latitude deposition [e.g., <i>Hammer et al.</i> , 1985; <i>Steffensen</i> , 1997; <i>Petit et al.</i> , 1999; <i>Delmonte et al.</i> , 2002]. Decreases in biogenic fluxes (export production) to marine sediments are observed [<i>Kohfeld et al.</i> , 2005].
ncreased <i>T</i> (higher metabolic rate) (section 5.2.3)	+15	Whole ocean	T-dependent increases in the rate of remineralization and recycling of organic matter will increase the CaCO ₃ :POC rain ratio, resulting in lower respiratory CO ₂ at the seafloor, recorded as a deepening in the CCD and lysocline transition zone thickness between the glacial and interglacial periods. Evidence of these changes is mixed: Reconstructed burial rates of

			dissolution indices estimate that carbonate ion concentrations changed by a maximum of 5
			mmol/kg in the Pacific and 20 mmol/kg in the Atlantic [<i>Anderson and Archer</i> , 2002]; increases in foraminiferal size imply that carbonate ion concentrations were only 4 to 8 mmol/kg different between glacial and interglacial periods [<i>Biima et al.</i> , 2002].
Coral reef re-growth (section 5.2.4)	+12	Impact on whole ocean; driven from changes in tropical and sub-	Changes in coral reef buildup and shallow water CaCO ₃ deposition can be reconstructed directly from the geological record [<i>Kayanne</i> , 1992; <i>Milliman</i> , 1993; <i>Milliman and Droxler</i> , 1996;
		tropical coastal waters and seas	<i>Montaggioni</i> , 2000; <i>Ryan et al.</i> , 2001]. Changes in shallow water CaCO ₃ deposition would affect the CCD with an antagonistic (anti-phased) relationship.
Reduced Si fertilization (section 5.2.5)	+	Whole ocean outside of high H ₄ SiO ₄ regions (North Pacific,	Changes in opal accumulation rates. Shifts in ecosystem structure and CaCO ₃ :POC rain ratio potentially recorded in a change in the CCD and lysocline transition zone thickness. Deep-sea
		Southern Ocean; equatorial Pacific?)	sedimentary impacts likely to generally be extremely small. Evidence of enhanced opal accumulation rates observed in Subantarctic Atlantic during the glacial period, but this may be a
			result of Si leakage from the Antarctic region, where Si deposition was lower during the glacial period [<i>Anderson et al.</i> , 2002; <i>Chase et al.</i> , 2003]. Opal deposition, in fact, lower than today in equatorial Pacific region [<i>Kienast et al.</i> , 2006; <i>Bradtmiller et al.</i> , 2007]. Changes in shallow
Lower wind-speed	0	Surface ocean	water opai deposition can, in theory, be reconstructed directly from the geological record. Coupled measurements $\delta^{13}C$ and Cd/Ca ratios recorded in foraminifera have been used as one
(and gas transfer) (section 5.2.6)			way of estimating the degree of air-sea gas exchange [Lynch-Stieglitz and Fairbanks, 1994]. Other estimates of wind speed involve grain size of terrigenous materials found in ice cores
			[Delmonte et al., 2004] and marine sediments [Rea, 1994], but overall, this parameter is difficult to constrain.
Changes in terrestrial weathering (section 5.2.7)	0	Whole ocean	Changes in the CCD.
Reduced sea ice cover	-5	North Atlantic, North Pacific,	The impact of sea ice on CO ₂ is sensitive to the maximum and minimum extents of the sea ice
(section 5.2.8)		Southern Ocean; potential nutrient-related impacts at lower latitudes	margin in both summertime and winter. Sea ice extent can be reconstructed by the distribution of sea ice diatoms [e.g., <i>Crosta et al.</i> , 1998]. <i>Gersonde et al.</i> [2005b] suggested that Southern Ocean sea ice extent was \sim ⁸⁰ further north at the last olacial neriod A full understanding of the
			impact on biological productivity (and thus CO_2) requires that changes in ecosystem structure are reconstructed [<i>Abelmann et al.</i> , 2006] in addition to bulk fluxes of opal and organic matter [<i>Anderson et al.</i> , 2002; <i>Chase et al.</i> , 2003; <i>Kohfeld et al.</i> , 2005].
^a See Table 1 for explan	ation (a	nd also Figure 2).	

carbonate suggest little or no change [Catubig et al., 1998]; foraminiferal assemblage



Figure 3. Change in average, August sea surface *Ts* (SSTs) as reconstructed by the Climate: Long-Range Investigation, Mapping, and Prediction (CLIMAP) program [*CLIMAP*, 1981] in the top panel, and warm season SSTs, as revised by the Multiproxy Approach for the Reconstruction of the Glacial Ocean surface (MARGO) Project [*Kucera et al.*, 2005] in the bottom panel. CLIMAP SST anomalies were based on a mixture of faunal indices (planktonic foraminifera, diatoms, and radiolarian), and data were later gridded to produce the anomalies recorded above. The MARGO data are SST reconstructions based on planktonic foraminifera (circles), radiolarian (inverted triangles), diatoms (diamonds), alkenones (squares), and Mg/Ca ratios (triangles).

sheets and mixed with the ocean, leading to sea-level rise. *Fairbanks* [1989] quantified this change by recovering and dating fossilized corals that normally live in surface waters from a depth transect off the island of Barbados, and correcting for the average vertical uplift at this location. This reconstruction quantified the deglacial sea level rise at about 117 m.

Removal and replacement of fresh water from the ocean has three distinct impacts on the global carbon cycle. First, mean ocean S during the LGM was approximately 3% greater than today. This affects atmospheric CO_2 almost entirely through its influence on aqueous carbonate equilibria in the surface ocean [*Zeebe and Wolf-Gladrow*, 2001]. An increase in *S* of 1‰ equates to an increase in CO_2 fugacity of ~8 ppm. However, because glacial SSTs (section 5.1.1) tend to reduce the rate of evaporation, the net glacial-interglacial change in surface salinities will be somewhat less than the mean ocean change, meaning that the net *S*-driven CO_2 impact is closer to 6 ppm (Table 1). Second, removing fresh water from the glacial ocean means that dissolved species such as DIC, ALK, and nutrients were more concentrated at the LGM. Increasing DIC and ALK in a 1:1 ratio has the effect of driving atmospheric CO₂ higher. However, complicating this response are further influences on CO₂ related to increased export production and sedimentary opal preservation during glacial periods, both driven by the increased nutrient availability. Finally, since the solubility ratio of CaCO₃ is a sensitive function of pressure, decreasing ambient hydrostatic pressure at the ocean floor at low sea level will drive reduced CaCO₃ dissolution and induce carbonate compensation (section 3.2), decreasing DIC and ALK in the ocean in a 1:2 ratio and driving CO₂ slightly higher. These processes all work in reverse when adding freshwater and diluting solutes and lowering *S* during deglaciation.

The sum of these effects creates a glacial-to-interglacial decrease in atmospheric CO₂ of 13 ppm (Δ CO₂ range: -16 to -12 ppm), toward which the effect of decreasing *S* contributes about 50% (~6 ppm). This occurs in the "wrong" direction compared to the prominent glacial-to-interglacial increase in CO₂ of 70–90 ppm observed in ice cores (Figure 1) and partly cancels out the effect of the deglacial increase in ocean surface *T*s (section 5.1.1). However, the effect is well understood and must be taken into account despite pushing CO₂ in the opposite direction to observed [*Ridgwell*, 2003a].

5.1.3. The terrestrial carbon reservoir. In the past few decades, the terrestrial biosphere has served as a substantial sink for anthropogenic carbon [*IPCC*, 2007]. Is it possible that vegetation and soils served as a larger sink for CO_2 during glacial periods?

Evidence to address this question was first obtained using the carbon isotope composition of marine benthic carbonates (benthic foraminifera), which record changes in the isotopic composition of the ocean's DIC pool. Shackleton [1978] proposed that glacial-interglacial changes in foraminiferal δ^{13} C might indicate that carbon had been transferred between the ocean (and atmosphere) and terrestrial biosphere. Measurements from deep-sea sediment cores suggested ambient glacial δ^{13} C conditions around 0.7% lighter than during the Holocene. From this, Shackleton [1978] estimated that some ~1000 PgC of carbon must have been removed from the ocean since the LGM. Shackleton's hypothesis was consistent with the idea that carbon storage increased in terrestrial ecosystems between glacial and interglacial times, through the CO₂ fertilization of primary productivity together with afforestation of high northern latitudes (both somewhat offset by loss of shelf areas for vegetation growth as the sea level rises at the end of the glacial). If a significant quantity of carbon were removed from the ocean and atmosphere upon deglaciation, this would effectively increase the gross deglacial CO₂ rise that other mechanisms need to explain [Berger and Wefer,

1991; *Maslin et al.*, 1995; *Ridgwell et al.*, 2003]. The magnitude of the change in carbon storage is therefore of primary importance in accounting for glacial-interglacial change.

From an extensive survey of deep-sea sediment cores, *Curry et al.* [1988] concluded that a 0.46‰ increase in mean ocean had taken place during the last deglacial transition, although this value was subsequently reduced to 0.32‰ [*Duplessy et al.*, 1988; *Matsumoto and Lynch-Stieglitz*, 1999], with other analyses of benthic δ^{13} C data suggesting a mean oceanic δ^{13} C increase of about 0.40‰ [*Crowley*, 1995]. A decrease in ocean δ^{13} C at the last glacial was also originally proposed to be consistent with the erosion and oxidation in the ocean of organic matter stored on exposed continental shelves [*Broecker and Peng*, 1982]. However, the consequences of an increase in PO₄³⁻ from eroding shelf sediments and hence productivity globally is not consistent with other lines of paleoceanographic evidence, as we discuss later in section 5.3.1.

Translating a ~0.4‰ ocean δ^{13} C change into an equivalent shift in terrestrial biosphere carbon requires an estimate to be made of the mean isotopic composition of terrestrial organic carbon, which lies in the range -22 to -25% for the preindustrial biosphere [Bird et al., 1994]. However, the mean isotopic composition of land biota cannot be guaranteed to have remained invariant over the course of the late Ouaternary, with a shift in the dominance of C_4 over C_3 species suspected to have occurred since the LGM [Crowley, 1991; Maslin et al., 1995]. Further complications arise as a result of recent culture studies, which have found that the ¹³C fractionation in several planktonic foraminiferal species depends on ambient carbonate ion concentrations [Spero et al., 1997]. If benthic species were to behave in a comparable manner, then changes in deep-sea carbonate ion concentrations might either amplify or diminish apparent variations recorded by foraminiferal tests [Russell and Spero, 2000]. Changes in foraminiferal δ^{13} C would therefore need to be interpreted in light of glacial-interglacial perturbations in oceanic DIC and ALK inventories, both of which are poorly constrained.

There are independent methods available for quantifying the deglacial change in carbon stored in the terrestrial biosphere, primarily through the reconstruction of terrestrial ecosystems (and their associated soils) both for LGM and modern (preindustrial) conditions. This can be done by either interpreting terrestrial proxy evidence [Adams et al., 1990; Crowley, 1995; Maslin et al., 1995; Faure et al., 1996; Prentice, 2001b] or by means of climate-vegetation models [Prentice and Fung, 1990; Prentice et al., 1993; Van Campo et al., 1993; Esser and Lautenschlager, 1994; Francois et al., 1998; Peng et al., 1998; Francois et al., 1999; Friedlingstein et al., 1992; Kaplan et al., 2002; Otto et al., 2002]. Estimates made by these two methods often do not entirely agree, neither among themselves nor when compared with foraminiferal δ^{13} C-based estimates [*Bird et al.*, 1994; *Crowley*, 1995; *Maslin et al.*, 1995]. Reconstructions range from 31 PgC *less* terrestrial carbon stored [*Esser and Lautenschlager*, 1994] to 1900 PgC *more* carbon stored today compared with the LGM [*Adams and Faure*, 1998]. If these values are to be believed, they imply a high degree of uncertainty in our estimate of the transfer of carbon between the terrestrial biosphere and ocean and atmosphere.

Here we assume a more modest uncertainty range of 400–900 PgC, which encapsulates recent vegetation model estimates of over 800 PgC [*Kaplan et al.*, 2002; *Otto et al.*, 2002] and has a mean estimate of 650 PgC, which lies close to the δ^{13} C-based reconstruction of *Crowley* [1995]. Adding this amount of carbon to the terrestrial biosphere implies that atmospheric CO₂ would have dropped by a little over 47 ppm following the LGM. This would make the 70–90 ppm observed rise extremely problematic to explain! However, carbonate compensation (see section 3.5) means that the actual impact on atmospheric CO₂ would be a more manageable 22 ppm (Δ CO₂ range: -12 to -36 ppm), albeit still in the "wrong" direction.

5.2. Less Well-Understood Glacial-Interglacial Changes: The "Known Unknowns"

As is evident from Figure 2, if we combine the individual influences of the global environmental changes taking place between the glacial and interglacial period for which we have the best scientific grasp of their impacts upon CO₂, we are headed in the wrong direction! The net effect of the "known knowns" is a 9-ppm *reduction* in CO₂ following the LGM, rather than the 70- to 90-ppm *increase* that is observed in ice cores (Figure 1). While simple linear addition of the impacts of the individual mechanisms in isolation will not give quite the same answer as when they are all combined, the Δ CO₂ deficit (or "residual") [*Ridgwell et al.*, 2003] requires the simultaneous operation of one or more additional mechanisms.

Although there are a number of additional changes in the global carbon cycle that are likely to contribute to glacialinterglacial CO_2 variability, our level of scientific understanding of how these mechanisms affect atmospheric CO_2 is rather less well developed. These are our "known unknowns," and comprise changes in ocean circulation, iron fertilization (from dust), metabolic rates, reefal (and other shallow water) carbonate production, Si supply from dust, and loss of opal sinks on continental shelves, wind speed (as it affects the air-sea gas transfer coefficient), weathering of terrestrial rocks, and sea ice cover. 5.2.1. Ocean circulation. Because of the importance of the ocean as a store of (dissolved) carbon, circulation is the "elephant in the room" of the glacial CO_2 problem. Both largescale circulation and microscale mixing act to undo the work of the biological pump by transferring nutrient and CO_2 -rich waters back to the surface. Circulation changes have the potential to alter the volume and distribution of deep-water masses, and their degree of connectivity (i.e., how well they are ventilated from the surface), and thus also atmospheric CO_2 [*Boyle*, 1988a; *Toggweiler*, 1999]. Circulation also controls the distribution and rate of supply of nutrients to the surface, and thus, its net carbon cycle impact is intricately linked with biological productivity.

So what is known about ocean circulation during glacial periods? The classical and generally popularized view of oceanic circulation is that it operates like a "conveyor belt" [*Broecker et al.*, 1985], driven by warm, salty surface waters from the Atlantic Gulf Stream that move toward the poles, cool, and become dense enough to sink. These relatively warm, salty, low-nutrient waters sink and fuel the movement of the ocean's deep conveyor, accumulating remineralized nutrients and carbon as they move throughout the ocean. The Atlantic head of this circulation [the Atlantic Meridional Overturning ("AMO")] is susceptible to changes in the freshwater balance [*Broecker et al.*, 1985], and these freshwater inputs during glacial periods would be enough to shutdown this meridional overturning circulation [see, e.g., *Schmittner et al.*, 2002].

Reconstructions of circulation during the LGM suggest that a persistent complete shutdown of the conveyor circulation is unlikely. Instead, evidence from ${}^{13}C/{}^{12}C$ ratios [*Oppo* and Fairbanks, 1987; Sarnthein et al., 1994] and Cd/Ca ratios [e.g., Boyle and Keigwin, 1982] in foraminifera suggest that the predominant meridional overturning circulation occurred at intermediate water depths during glacial periods and shifted to deeper water depths during the interglacial periods [for review of this paleoceanographic evidence, see *Boyle*, 1995]. Although the depth at which meridional overturning occurs appears to have shifted, additional ²³¹Pa/²³⁰Th data suggest that the rate of overturning is similar between glacial and interglacial time periods [Yu et al., 1996; McManus et *al.*, 2004]. Furthermore, δ^{13} C data from benthic foraminifera suggest the overall pattern of circulation remained similar between two time periods [Matsumoto and Lynch-Stieglitz, 1999; Matsumoto et al., 2002a]. Nevertheless, a change in the depth of the meridional overturning circulation would have implications for the volume of deep water in which nutrients and carbon most effectively accumulate. Because of the relative ease of simulating a collapse of the AMO by applying a fresh water forcing to the surface of the North Atlantic, the CO₂ impact of this facet of glacial-interglacial circulation change has been evaluated in a number of different models and, on average, demonstrates a modest 12 ppm change (ΔCO_2 range: 7 to 15 ppm).

Additional evidence from bore hole sites [Adkins et al., 2002] and from surface ocean data in polar regions [Fran*cois et al.*, 1997; *Sigman et al.*, 2004; *Jaccard et al.*, 2005] have led paleoceanographers to believe that the glacial ocean was highly stratified compared to modern interglacial conditions. This stratification may have played a key role in holding a larger store of DIC during glacial times and likely disintegrated during the process of deglaciation [Galbraith et al., 2007; Marchitto et al., 2007]. Conflicting hypotheses exist regarding how this stratification of the deep ocean might have come about. One mechanism for increasing ocean stratification and enhancing carbon sequestration in the deep ocean involves the large northward shift and weakening of midlatitude westerly winds in the Southern Hemisphere, which reduces the amount of CO₂-rich deep waters that upwell around Antarctica during the cold glacial periods [Toggweiler et al., 2006]. A similar mechanism suggests that a combination of more extensive sea ice formation and reduced air-sea buoyancy fluxes resulted in weaker mixing and less upwelling [Watson and Garabato, 2006]. Alternatively, as a result of the nonlinear dependence of seawater density on T, vertical S contrasts have a greater effect on the density structure, as T through the water column is reduced. On this basis, Sigman et al. [2004] suggested that polar stratification could arise as a simple consequence of the cooling of the glacial ocean. The exact mechanism and timing over which stratification may have occurred as well as the exact nature and depth of this stratification remains an open question.

An additional constraint on the stratification of the deep ocean relates to the concentration of dissolved oxygen. The proposal that the glacial ocean was stratified with a deepocean carbon reservoir containing old carbon also presumably implies reduced [O₂]. Both the deep Southern Ocean and deep Pacific Oceans have been proposed as possible locations for this "old carbon," but do we see evidence for extensive anoxia? Evidence from δ^{13} C, excess Ba, and authigenic U suggests that at least some parts of the ocean experienced suboxic conditions during the last glacial period, but this evidence remains somewhat mixed because of the difficulty in pinpointing circulation or increased organic carbon inputs to the sediments as the main cause. Light excursions in the $\delta^{13}C$ of benthic foraminifera in the Southern Ocean [Michel et al., 1995; François et al., 1997] suggest that this region experienced nutrient-rich (and therefore low oxygen) conditions. Similarly, the increased concentrations of authigenic U was ubiquitous in the South Atlantic Ocean at the LGM [Chase et al., 2001]. In both of these instances, it is difficult to ascertain

whether these changes are a result of higher export production or reduced ventilation and therefore poorly oxygenated bottom waters. Some support for a productivity-related cause comes from the low preservation of excess Ba in the same cores that record concurrent increases in export production proxies [*Kumar et al.*, 1995; *Anderson et al.*, 1998], as excess Ba is poorly preserved under suboxic conditions [*McManus et al.*, 1998]. An additional, convincing piece of evidence concerns the very existence of deep-ocean foraminiferal records during the glacial period. Benthic foraminifera require oxygen to metabolize organic matter and respire, and their continuing and widespread abundance through the glacial discounts the occurrence of widespread anoxia.

With these constraints in mind, models in which a glacial state has been assessed indicate a 27-ppm change, although with considerable uncertainty (ΔCO_2 range: 3 to 57 ppm).

5.2.2. (Aeolian) Iron fertilization: The "iron hypothesis." In addition to regions of the ocean where all nutrients are consumed, there are certain regions of the ocean where the primary nutrients (PO_4^{3-} , NO_3^{-}) remain plentiful. These "high-nutrient, low-chlorophyll" (HNLC) regions are areas where some other factor limits biological production, and include the North Pacific, the eastern equatorial Pacific, and the Southern Oceans. The potential for increased consumption of the large unused nutrient inventories in these regions and thus a stronger biological pump led to a series of hypotheses for low glacial CO₂. The Southern Ocean, in particular, is considered to exhibit a powerful control over atmospheric CO_2 because of its cooler Ts, the large pool of nutrients, and high-CO₂ deep water that comes into contact with surface waters [Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984].

The prevailing mechanism by which increased utilization of NO₃⁻ (and PO₄) in HNLC regions can come about is via a relief from the constraint of trace metal limitation. Martin and Fitzwater [1988] first produced data that suggested that the micronutrient iron (Fe) can limit biological production in several regions of the ocean. Over the past decade, iron fertilization has been observed to increase carbon fixation in surface waters in several field experiments [Coale et al., 1998; Boyd et al., 2000; Tsuda et al., 2003] as well as under conditions where the ocean surface has been naturally fertilized with dust [Bishop et al., 2002]. Based on the idea of iron fertilization, the chemical oceanographer John Martin [Martin, 1990] first proposed that iron may have been more abundant during glacial periods when dust fluxes to the ocean were more than two times greater than today in several places. This increased glacial supply of iron-rich dust may have alleviated iron limitation in HNLC regions, leading to increased productivity and thus lower CO₂.

All modeling studies applied to estimating the effect of increased glacial rates of dust deposition, particularly to the surface of the Southern Ocean, agree that some CO₂ drawdown will result. However, the magnitude of the reduction in atmospheric CO_2 is not necessarily proportional to primary production because carbon fixed into additional organic matter must escape remineralization and reach the ocean interior if the atmospheric CO₂ inventory is to be altered [Gnanadesikan et al., 2003; Matsumoto, 2006]. Most open-ocean Fe fertilization experiments conducted to date are generally ambiguous on this question. This uncertainty, in conjunction with substantial differences in how the Fe cycle is represented in the ocean in models (and thus what the balance at the surface is between "new" (aeolian) and preformed (upwelled) dissolved Fe supply [see, e.g., Parekh et al., 2004], gives rise to a wide spread of model estimates (Table 1, ΔCO_2 range: 5 to 28 ppm) with a central estimate of 15 ppm.

If iron fertilization and resulting increases in marine productivity lowered atmospheric CO₂, we should see increased organic carbon and biogenic fluxes to the seafloor in regions that are iron-limited today. Examination of Plate 1 suggests that increased export production is indeed observed in the south Atlantic region and in areas directly downwind of the Australian continent. The effects of Fe fertilization are more ambiguous in areas such as the North Pacific Ocean where dust fluxes were expected to increase during glacial periods, but export production was apparently not enhanced [Kienast et al., 2004]. Recent studies have suggested that lower export production during the height of glacial periods may have occurred because the effects of ocean stratification reduced nutrient availability and therefore also productivity [Jaccard et al., 2005; Brunelle et al., 2007; Galbraith et al., 2008]. However, this does not mean that the efficiency of the soft tissue pump was necessarily reduced.

If aeolian iron fertilization and resulting increases in marine productivity lowered CO₂, one obvious change that one might expect to see is higher dust fluxes to the oceans during periods of decreased atmospheric carbon dioxide concentrations. But are these changes observed? Paleoceanographic reconstructions suggest that dust fluxes to the ocean were increased on the order of two- to fivefold during glacial compared to interglacial time periods [see, e.g., *Rea*, 1994; *Kohfeld and Harrison*, 2001; *Kohfeld and Tegen*, 2007]. Data from polar ice cores suggest even larger changes, with fluxes increasing as much as 20 times during glacial compared with interglacial periods. Model simulations of the dust cycle are basically consistent with these large-scale data reconstructions [*Mahowald et al.*, 1999; *Werner et al.*, 2002; *Mahowald et al.*, 2006].

We can also place constraints on the basis of the timing at which the maximum fluxes of dust to the sediments are expected to occur. In order to account for the total decrease in atmospheric CO₂, one would expect that dust would have to increase during glacial inception. Instead, Figure 1 suggests that dust fluxes only begin to increase after atmospheric CO₂ has dropped to 220 ppm Antarctic ice cores. Therefore, the feedback of Fe fertilization most likely occurs during peak glacial periods [*Watson et al.*, 2000]. *Röthlisberger et al.* [2004] came to a similar conclusion based on correlations between dust and CO₂ in an ice core record.

5.2.3. Temperature-dependent changes in organic matter regeneration. The T of the ocean not only affects density gradients and the solubility of CO_2 (section 5.1.1), but also directly impacts the living organisms within it. T exerts a general influence on metabolic rate, which is manifested as an increasing rate of growth with T up until a critical point, at which conditions steadily become less conducive for organisms [Eppley, 1972; Laws et al., 2000]. Although lower glacial ocean surface Ts should result in slower growth rates, the glacial-interglacial variability in export production may be muted. This is, first, because marine production today is generally nutrient, not T limited. Second, species are able to "habitat track," moving geographically to follow (track) their optimal environmental conditions [see, e.g., Longhurst, 2007]. Thus, in any one location, the gradual replacement of one dominant species by another may mute the impact of changes in SST, although across marine species, the net effect is still a nonlinearly increasing rate of growth with T, known as the Eppley Curve [Eppley, 1972].

However, *T* changes deeper in the water column may be important. Particulate organic matter export from the surface ocean is progressively degraded as it settles through the water column, primarily by the action of bacteria. The result is that on average, only ~5% of export production reaches the ocean floor, and the profile of the fraction remaining with depth resembles a pseudoexponential curve [e.g., *Martin et al.*, 1987]. Any deepening of this profile with a greater fraction of organic matter reaching greater depths will negatively impact on atmospheric CO₂ and vice versa [*Heinze*, 2004]. Lower glacial *Ts* could drive such a deepening of the average depth at which organic matter is remineralized as a result of a reduction in the rate of bacterial metabolism.

Only one model to date has been applied directly in quantifying this effect. *Matsumoto et al.* [2007] found that a uniform 5°C decrease in ocean *T*s could drive a 30-ppm CO₂ decrease (including secondary rain ratio and carbonate compensation effects). The observed glacial-interglacial amplitude in ocean *T* was, on average, rather less than 5°C and likely heterogeneous (e.g., see surface *T*, Figure 3), suggesting a contribution to deglacial CO₂ rise of faster metabolism in a warming ocean somewhat less than 30 ppm, perhaps 15 ppm (ΔCO_2 range: 0 to 30 ppm). GCM studies of future global warming impacts indicate an important positive feedback via this mechanism [*Matsumoto*, 2007; *Schmittner et al.*, 2008], supporting a glacial-interglacial contribution from this effect.

Apart from records of T change, geologic evidence that remineralization in the mesopelagic zone of the ocean changed at the last glacial period is particularly difficult to acquire. We have no direct evidence of changes in the rates of bacterial activity in the ocean. However, one of the major impacts of this mechanism is a shoaling in the depth of organic matter remineralization, as Ts increase across the deglaciation and hence an increase in the CaCO₃:POC rain ratio at depth. An increase in CaCO₃:POC rain ratio to the sediments would reduce the supply of respiratory CO₂ and drive a deepening of the CCD and lysocline between the glacial and interglacial periods. Evidence for this change is mixed: reconstructed burial rates of carbonate between glacial-interglacial periods suggest little or no change [Catubig et al., 1998], and foraminiferal assemblage dissolution indices estimate that carbonate ion concentrations changed by a maximum of 5 µmol/ kg in the Pacific and 20 µmol/kg in the Atlantic [Anderson and Archer, 2002]. Increases in foraminiferal size imply that carbonate ion concentrations were only 4 to 8 µmol/kg different between glacial and interglacial periods [Bijma et al., 2002]. Thus, geologic evidence for shifts in the lysocline is substantially smaller than would be predicted if rain ratio changes were the dominant cause in glacial-interglacial changes in atmospheric CO₂ [Sigman and Boyle, 2000].

5.2.4. Coral reef re-growth. Since the LGM there has been a rise in sea level of ~117 m [*Fairbanks*, 1989], which by flooding the continental shelves produced a substantial, approximately fourfold [*Kleypas*, 1997] increase in the area of shallow water (neritic) environments. More CaCO₃ precipitation and burial globally in shallow marine sediments will return CO₂ to the atmosphere at an increased rate via:

 $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_{2(aq)} + H_2O.$

On this basis, buildup of shallow water carbonates was once proposed as an explanation for the deglacial rise in atmospheric CO₂ concentrations recorded in ice cores, known as the "coral reef hypothesis" [*Berger*, 1982a, 1982b]. While early coupled atmosphere-ocean-sediment carbon cycle box models confirmed that sea level-driven changes in shallow water carbonate deposition could generate a substantial increase in atmospheric CO₂ [e.g., *Berger*, 1982a; *Opdyke and Walker*, 1992; *Munhoven and Francois*, 1996; *Walker and Opdyke*, 1995], atmospheric changes due to this cause must inevitably lag sea level rise. This lag is contrary to the apparent sequence of events at deglaciation [Sowers et al., 1991; Sowers and Bender, 1995; Broecker and Henderson, 1998], meaning that this mechanism cannot contribute significantly to the rapid ~70 ppm CO₂ rise at the deglacial transition (circa 17 to 11 ka) [*Ridgwell et al.*, 2003].

Irrespective of arguments regarding the relative timing of sea level and CO2 rise, observational evidence is unambiguous in indicating an increase in the global rate of shallow water carbonate deposition since the LGM [Kayanne, 1992; Milliman, 1993; Milliman and Droxler, 1996; Montaggioni, 2000; Ryan et al., 2001]. This interpretation is also supported by process-based model studies [Kleypas, 1997]. Full understanding of the glacial to interglacial change in CO₂ must therefore a priori accommodate the effects of reef buildup. Observations also suggest that initial colonization lags shelf inundation, such that the onset of modern reef growth did not occur until as late as perhaps 8 ka BP, with peak CaCO₃ accumulation rates around 5 ka [Kayanne, 1992; Montaggioni, 2000; Ryan et al., 2001]. This timing is contemporaneous with a 20-ppm rise observed starting at ~8 ka [Indermuehle et al., 1999; Flückiger et al., 2002]. Models have confirmed an important role for coral reef re-growth in the observed late Holocene CO₂ rise [see e.g., *Ridgwell et al.*, 2003; *Brovkin* et al., 2007]. The shallow water sedimentary carbonate system thus plays an important role in climate feedback on sea level rise (and fall). Available model estimates suggest 12 ppm (ΔCO_2 range: 6 to 20 ppm) as the relative importance of this carbon cycle phenomenon.

5.2.5. Si fertilization: The "silica hypothesis." Changes in the supply of dissolved silica to the ocean should affect the relative contribution of export production derived from diatoms relative to that derived from phytoplankton that do not make opal frustules. In turn, such ecosystem shifts might affect the CaCO₃:POC rain ratio and thus atmospheric CO₂ via a cascade of mechanisms (see sections 3.2-3.4). One component of the modern ocean Si budget is the supply and bioavailability of dissolved Si (as silicic acid, H₄SiO₄) resulting from the (partial) dissolution of silicate in dust. Silicate from dust accounts for $\sim 10\%$ of the total new supply to the ocean, with riverine supply accounting for much of the remainder [for review, see Tréguer et al., 1995]. Although a decrease in dust (as recorded at Vostok) precedes the increase in atmospheric CO₂ at glacial terminations [*Petit et al.*, 1999], there is an apparent lag of up to 8 ka between initial dust decline and initial CO₂ rise [Broecker and Henderson, 1998]. Since the residence time of H₄SiO₄ in the ocean is of similar order to the observed lag, the aeolian input of dissolved Si to the ocean might play an important role in driving atmospheric CO₂ changes. Harrison [2000] proposed a "Silica Hypothesis," whereby higher aeolian Si supply to the surface ocean during glacial times enhances diatom productivity at the expense of calcium carbonate shell-forming species, producing a substantial second-order effect on atmospheric CO₂ through the rain ratio (section 3.2.) [*Archer and Maier-Reimer*, 1994].

However, models incorporating an explicit marine Si cycle and including deep-sea sediments suggest a relatively long residence time of Si in the ocean of 23 ka. Because of the dominant supply of Si to the ocean surface by upwelling (~120 Tmol Si a⁻¹) rather than dust (~0.5 Tmol Si a⁻¹) [*Ridgwell et al.*, 2002], the reduced dustiness at the end of the glacial is unlikely to explain more than 3 ppm of the observed CO₂ rise. It is possible, however, that increased dustiness plays a more important role in the decline in CO₂ from interglacial into glacial because the timescale is more comparable to that of Si residence in the ocean [*Ridgwell et al.*, 2002].

A corollary of the aeolian silica hypothesis is that an important sink of opal on the continental shelves is lost during glacial periods and re-gained as sea level rises during deglaciation [*Tréguer and Pondaven*, 2000]. This CO₂ driver shares the same difficulties as the Si hypothesis in that the entire dissolved silica inventory of the ocean must be changed. It also shares similar problems of timing with the coral reef hypothesis, in that the CO₂ change must invariably lag sea level rise. The difficulties of modeling coastal environments and shallow water processes mean that no explicit quantification of the importance of changing the magnitude of the neritic sedimentary opal sink for Si is available. The magnitude is likely to be similar to that of aeolian Si fertilization and thus not a major player at deglaciation.

Taken together, changes in the supply of dissolved silica to the open ocean since the last glacial, both via decreased dust and by enhanced burial of opal in coastal and shelf sediments, may be responsible for only 4 ppm (ΔCO_2 range: 1 to 8 ppm).

5.2.6. Wind speed. The degree to which the carbonate chemistry of a parcel of water at the ocean surface is equilibrated with respect to the concentration of CO₂ in the atmosphere is dependent on the speed of the prevailing wind because this sets the value of the air-sea gas transfer coefficient, generally thought to be a strongly nonlinear function of wind speed [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Nightingale et al.*, 2000]. Today, the ocean surface is a patchwork of regions of outgassing (where the fugacity of $CO_{2(aq)}$ in seawater (fCO_2) exceeds atmospheric pCO_2) and uptake (where $pCO_2 > fCO_2$). This variability, coupled with the nonlinear response of CO_2 gas transfer rates to wind speed, means that glacial-interglacial variations in winds could potentially exert an important control on atmospheric composition [*Erickson*, 1989, 1993; *Keir*, 1993].

Using a box model, *Keir* [1993] was able to account for around 50 ppm of the observed glacial-interglacial difference in atmospheric CO₂. However, a massive 80–150% increase in glacial wind speeds was assumed by *Keir* [1993]. Furthermore, this study restricted changes to a single high-latitude box and used a class of model strongly suspected to overestimate the effect of high-latitude perturbations [*Broecker et al.*, 1999a; *Archer et al.*, 2003]. Analysis with a more highly resolved model in which a simple 50% change in wind speed was applied globally resulted in only a ~4 ppm decrease in glacial CO₂ [*Ridgwell*, 2001]. The lack of available explicit estimates using 3-D ocean GCMs, in conjunction with glacial and interglacial wind fields, leads us to an assessment of 0 ppm for the importance of this CO₂ driver (Δ CO₂ range: 0 to 5 ppm).

The effect of changing wind speed on gas transfer leaves little imprint in sediments, making model results difficult to constrain against the paleoceanographic record. However, because of the difference in δ^{13} C of DIC in surface waters, with higher latitudes generally lighter than lower latitudes [Lynch-Stieglitz et al., 1995], the effect of changes in wind speed can be tested against the variations in the $\delta^{13}C$ of CO₂ recorded in ice cores [Smith et al., 1999]. For instance, Ridgwell [2001] found a ~0.2‰ deglacial increase in atmospheric δ^{13} CO₂ due to weaker interglacial winds, a change consistent with observations of higher Holocene $\delta^{13}CO_2$ [Marino et al., 1992; Smith et al., 1999]. Furthermore, because the process involved is reasonably well understood, improved reconstructions and simulations of glacial wind fields applied to the glacial flow fields of 3-D ocean circulation models should be sufficient to place strong constraints on this mechanism in future.

5.2.7. *Terrestrial weathering*. Carbon dioxide in the atmosphere dissolves in rainwater to form a weak carbonic acid solution, which dissolves carbonate minerals in rocks exposed at the land surface and mineral grains in soils:

$$CO_{2(aq)} + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^{-}$$

In this reaction, for each mole of $CaCO_3$ that dissolves, 1 mol of $CO_{2(aq)}$, originally derived from CO_2 in the atmosphere, is removed. The solutes that result from this reaction are carried by rivers to the ocean, where biological precipitation of carbonate shells and skeletons and $CaCO_3$ burial in marine sediments results in the return of CO_2 (to the atmosphere):

$$Ca^{2+} + 2HCO_3^{-} \rightarrow CaCO_3 + CO_{2(aq)} + H_2O_{-}$$

Hence, at steady state, there is no net impact of terrestrial carbonate weathering on atmospheric CO₂.

A second weathering reaction involves calcium silicate minerals (particularly the feldspar family, which are the most abundant group of minerals in continental rocks), which can be conceptually written:

$$2CO_2 + 3H_2O + CaAl_2Si_2O_8 \rightarrow Ca^{2+} + 2HCO_3^{-}.$$
$$+Al_2Si_2O_5(OH)_4$$

This reaction differs from the weathering of carbonate rocks in one fundamental regard: it takes 2 mol of CO_2 to weather each mole of $CaAl_2Si_2O_8$ and release a single mole of calcium ions (plus two of bicarbonate ions). The calcium ion is subsequently removed from solution in the same precipitation reaction as before, meaning that only 1 mol of CO_2 is released back to the ocean (and atmosphere). The weathering of silicate rocks is thus a net sink for atmospheric CO_2 [*Berner*, 1992], with 1 mol of CO_2 being sequestered for each mole of Ca-silicate mineral weathered. On the longterm, the rate of silicate weathering is balanced by the rate of volcanic release of CO_2 to the atmosphere [*Berner and Caldeira*, 1997].

Any glacial enhancement in the rate of weathering, if not balanced by an increase in CaCO₃ burial (both weathering mechanisms) and mantle CO2 outgassing (Ca-silicate weathering only), will result in a drawdown of atmospheric CO₂. Could this help explain the glacial-interglacial variability in CO₂? The rate at which the weathering reaction proceeds also depends on variables such as ambient T, and ambient (soil) CO₂ concentration, which is enhanced in soils through the metabolic activity of plants, animals, and microbes, [Berner, 1990, 1992], and the influence of plants more directly, in excreting organic acids. None of these factors is likely to be higher during glacial than interglacial periods. Thus, if anything, the rate per unit area of terrestrial weathering should have increased during deglaciation, driving CO₂ lower just when it is observed to increase. Countering this weathering effect is the effect of ice sheets and glaciers in physical weathering, transforming solid rock into fine glacial flour, which is more susceptible to weathering. These interplays of total area and lithology, the total mineral surface area available for weathering and rate of creation of fresh surfaces, and kinetic accelerations (T and acidity), make the net effect of weathering on glacial-interglacial CO₂ variability highly uncertain as reflected in the status report (Figure 2; ΔCO_2 range: 0 to 5 ppm). Because of the long timescale of this process (tens of ka) and uncertainty in sign, the best estimate for contribution to the deglacial increase in CO₂ is 0 ppm.

Have weathering inputs to the ocean changed on glacialinterglacial timescales? It is difficult to answer this question given existing proxies. One commonly cited proxy is the ratio of germanium to silicon (Ge/Si) in diatomaceous material, which has been thought to reflect changes in riverine fluxes to the oceans, with lower ratios suggesting lower riverine fluxes during glacial compared with interglacial periods [Mortlock and Froelich, 1987; Shemesh et al., 1989; Froelich et al., 1992; Bareille et al., 1998]. However, the exact interpretation of this proxy is complicated by possible variability in opal diagenesis [e.g., Hammond et al., 2000] or even possible changes in the fluxes of low Ge/Si opal phytoliths, which were mobilized and added to the ocean during glacial periods [Derry et al., 2005; Street-Perrott and Barker, 2008]. These complications could be substantial enough to bring this proxy in line with Sr and Pb isotopic proxies that suggest little change in glacial-interglacial weathering rates [Henderson et al., 1994; Foster and Vance, 2006].

5.2.8. Sea ice cover: A change in sea ice extent is another means by which the rate of air-sea gas exchange can be modified in polar oceans. Reconstructions of the cryosphere at the time of the LGM suggest that seasonal sea ice cover was much more extensive than today [*CLIMAP*, 1981; *Crosta et al.*, 1998; *Gersonde and Zielinski*, 2000; *Gersonde et al.*, 2003; *Sarnthein et al.*, 2003].

At first glance, this mechanism appears a seductively simple and potentially powerful means of controlling atmospheric CO₂. For instance, in a box modeling study, over half (>45 ppm) of the entire glacial-interglacial amplitude of CO₂ variability could be explained as a consequence of changing sea ice coverage in the Southern Ocean [*Stephens and Keeling*, 2000]. However, the particular configuration of this model had virtually all outgassing of CO₂ in the modern ocean occurring from the surface of the Antarctic box, whereas in present-day data-based reconstructions, it occurs primarily in equatorial regions [*Takahashi et al.*, 2003], making it prone to being overly sensitive to sea ice changes.

One of the difficulties in assessing the impact on atmospheric CO_2 of changes in sea ice cover is that the pattern of circulation and biological productivity and thus surface CO₂ uptake and outgassing will not be invariant over the glacial-interglacial cycles, and will respond to changing sea ice extent. Some OGCM-based carbon cycle models have examined effects of changing sea ice cover by prescribing sea ice cover in experiments [see, e.g., Kurahashi-Nakamura et al., 2007] but ideally, sea ice extent (climate) and ocean carbon cycling need to be modeled interactively (fully coupled). In simulating a colder glacial climate with increased sea ice extent, the isolation of the impact of changing sea ice cover alone then becomes impossible and arguably something of a nonsensical question to pose. In models that do attempt to isolate a sea ice impact, the CO_2 change is -5 ppm $(\Delta CO_2 \text{ range: } -14 \text{ to } 0 \text{ ppm})$, and thus slightly opposing the observed deglacial CO2 increase.

There are also difficulties in accurately reconstructing the limits of sea ice extent, which complicates the overall assessment of its CO₂ impact, both in summertime (minimum extent) and wintertime (maximum extent). Original CLIMAP [1981] reconstructions were based on changes in sediment lithology and suggested that the winter sea ice extent was several degrees equatorward of its present position and that summer sea ice extent was comparable to the modern-day winter sea ice extent. More recent reconstructions rely on the distribution and abundance of certain diatom species, whose preferred habitats are associated with either sea ice or open-water conditions [Crosta et al., 1998; Gersonde and Zielinski, 2000]. These reconstructions are, more or less, in agreement with the CLIMAP reconstruction of winter sea ice distributions at the LGM in the Southern Ocean [Gersonde et al., 2005a]. However, while Gersonde et al. [2005a] estimate that LGM sea ice was greater than present during summer months, Crosta et al. [1998] suggest little difference between the modern and LGM summer sea ice extent. These distinctions are important because a large seasonal ice zone (SIZ) has the potential to be an efficient CO_2 sink, with blooms drawing down CO₂ in the summer but with that CO_2 being isolated from the atmosphere during winter. Significant ecosystem changes are also associated with the changing limits of sea ice [Abelmann, 1992; Abelmann et al., 2006], further complicating the understanding of the net carbon cycle effect. This type of dynamic interaction leads to perhaps the greatest problem for modelers: simulating how carbon and nutrient cycling is impacted not only within the glacial maximum limits of sea ice extent, but also far outside of this region, as is relevant when considering mechanisms such as Si leakage (section 3.4).

5.3. The Wildcards of the Glacial-Interglacial Pack: The "Unknown Unknowns"

The search for an explanation for why atmospheric CO_2 during the LGM was around one-third lower than during the Holocene has proved fertile intellectual ground, with myriad hypotheses devised since the first unambiguous evidence for low glacial CO_2 was presented from ice core samples crushed under vacuum [*Delmas*, 1980; *Neftel et al.*, 1982]. As additional information has become available, particularly concerning the relative timing of deglacial CO_2 rise and sea level and also of productivity in the ocean, many of the ideas have been left by the wayside or reformulated with a much smaller role than originally envisaged. Some of the earlier propositions that have been little (if at all) considered probably have a grain of truth in them. These mechanisms, of which very little is understood if only because of a historical deficit of analysis, are our "unknown unknowns." We summarize some of them here for completeness, although most researchers are of the opinion that their overall contributions are expected to be relatively small. As the uncertainty is progressively reduced in the known knowns and known unknowns (Figure 2), we will home in on the solution for the glacial-interglacial variability in CO_2 and pinpoint the role (if any) that additional "unknown unknown" mechanisms must play.

5.3.1. Nutrient storage on continental shelves and denitrification. Some early hypotheses to explain the observed glacial-interglacial variability in atmospheric composition envisioned an oceanic NO_3^- inventory higher during glacial periods than interglacials. Comparisons made between the predictions of ocean N cycle models and paleoceanographic $\delta^{15}N$ proxy data go some way to supporting this assertion [*Altabet and Curry*, 1989; *Altabet and Francois*, 1994].

One hypothesis required the existence of a critical threshold within the oceanic nitrogen cycle. During glacial inception, dissolved O_2 concentrations in the ocean gradually decrease until widespread denitrification rapidly proceeds. Since the oceanic residence time of NO_3^- is relatively short (3–10 ka) [Codispoti, 1995], the oceanic nitrate inventory could be quickly depleted, resulting in decreased biological productivity and thus a steep rise in atmospheric CO₂ [Knox and McElroy, 1984; Shaffer, 1990]. Declining [O₂] during glacial periods could be driven by increased productivity fuelled by nutrients (PO₄³⁻ and/or NO₃⁻) eroded from shelf sediments exposed as sea level falls [McElroy, 1983; Shaffer, 1990]. An associated hypothesis draws upon the likelihood that the modern ocean nitrogen cycle is far from steady state, with nitrogen losses from the ocean through denitrification (particularly on continental shelves) exceeding the combined input from rivers, atmosphere, and nitrogen fixation in the surface ocean [McElroy, 1983; Berger and Vincent, 1986; Codispoti, 1995]. As sea level fell during glacial inception, denitrification within neritic sediments ceased on the newly exposed shelf area. This increased the oceanic N inventory, fueled greater productivity, and led to CO₂ drawdown [Berger and Vincent, 1986; Altabet and Curry, 1989; Codispoti, 1995; Ganeshram et al., 1995].

Both variants on this hypothesis imply increased carbon production during glacial compared with interglacial periods, particularly in the regions of the ocean where nutrients are limiting today, such as the tropical regions and subtropical gyres. Such an increase in biological productivity would also likely increase the export of carbon to the seafloor and thus also manifest itself as an increase in fluxes of biogenic materials in marine sediments.

Do we see evidence of coherent global-scale changes? First, reconstructions of export production at the LGM (Plate 1) do show increases at the last glacial period compared to today, although these changes are not globally coherent. Furthermore, analyses of changes in export production over different time periods seem to limit the impact of this process to the full glacial period rather than during the glacial inception [Kohfeld et al., 2005]. Increased global nutrient inventories and productivity also has implications for the concentration of dissolved O_2 in the ocean, as O_2 is consumed during the (aerobic) degradation of organic matter. Our review of the data concerning changes in deepwater O_2 contents in section 5.2.1 suggests that changes in deep-water oxygen concentrations seem to be regional in nature and are not conclusively the result of globally enhanced carbon export. A final implication for productivity mechanisms tied to shelf area is that deglacial CO₂ increases should lag sea level change, which is contrary to observed temporal relationships and thus limits their potential importance.

5.3.2. N-fixation. Another means of monkeying around with NO₃⁻ availability in the glacial ocean is via increased Fe availability arising from aeolian dust deposition. This influx of iron stimulates the activity of diazotrophs such as Trichodesmium spp. in the surface ocean, thereby increasing the rate of N₂ fixation [Falkowski, 1997; Broecker and Henderson, 1998]. As a consequence, biological productivity and thus CO₂ drawdown follow (lagged) changes in aeolian dust supply, in general agreement with ice core records. A compilation of nine sedimentary δ^{15} N records from deepsea sediments globally demonstrates coherent behavior in δ^{15} N of nitrate [Galbraith et al., 2004]. These authors hypothesize that low SSTs and strong winds in high-latitude regions at the LGM likely resulted in higher O₂ solubility and greater ventilation of the thermocline. Although regional changes in export production and nitrate utilization are likely to modulate this $\delta^{15}N$ signal [e.g., Galbraith et al., 2008], these cooler and well-ventilated thermocline waters suggest that, in fact, glacial periods were likely marked by more limited denitrification and reduced N-fixation overall, thereby limiting the overall effectiveness of this mechanism.

6. SUMMARY AND OUTLOOK

The purpose of this review has been to summarize the different mechanisms that have been proposed as a means of explaining glacial-interglacial changes in atmospheric CO₂ (Table 1), to provide an assessment of our best estimates and degree of uncertainty regarding the relative magnitude of the impacts of these mechanisms (Figure 2), and to describe the basis for these mechanisms that is found in geologic evidence (Table 2). It should be recognized that this summary has, for the most part, taken the approach of teasing apart the magnitude of the impact of each mechanism separately. In the real world, synergisms between mechanisms might exist, and the overall, combined effect of some of these processes on atmospheric CO_2 might be larger (or smaller) than the simple linear sum. For example, model simulations that incorporate interactive sea ice might reveal a different picture of the impacts that sea ice might have on vertical mixing and biological activity in polar regions, which might result in a different drawdown of CO₂ than otherwise anticipated. A second point in this study is that we have focused primarily on the increase in atmospheric CO₂ concentrations that occurred during the transition between the Last Glacial Maximum and the pre-Industrial era of the Holocene. Of equal importance is our need to study the Earth's transition as it moves into a period of glaciation, from which we may gain insights into the relative phasing of the processes we have described here. Modeling studies of this nature have been initiated [Vettoretti and Peltier, 2004; Peacock et al., 2006].

A quick glance at Figure 2 highlights that there is no "smoking gun" that can account for the entire glacial-interglacial change in atmospheric CO₂. Instead, the combination of and interaction between a number of different mechanisms and feedback are required to account for the total observed ice core changes. It is also apparent that there are substantial uncertainties in each of the mechanisms contributing to glacial-interglacial CO₂ variability and that progress toward a full understanding of this problem requires development on several fronts, including: (a) expansion of key observations, (b) development of new and more realistic ways of modeling the problem, and (c) examining the problem from different perspectives.

Aside from glacial-interglacial changes in ocean *T*, *S* (and volume), and terrestrial biosphere carbon inventory, for which we have a relatively high level of scientific understanding, two controls clearly dominate the residual change in atmospheric CO₂ that needs to be explained (79–99 ppm, depending on the deglacial time interval considered), ocean circulation and the strength and efficiency of the biological pump. Thus, we believe that the greatest advances toward solving the (low) "glacial CO₂ problem" will come through improved constraints and understanding of the role of physics and biology. Specifically, an increased appreciation of the development of deep-ocean stratification during glacials and how this interacts with the biological pump to affect atmospheric CO₂ is likely to lead to major advances in our overall understanding of the problem in the next few years.

Observational evidence is progressively providing new insights into the physical oceanographic conditions prevailing during the last glacial, but crucial information that we still need includes the distribution of ocean water masses and their spatial evolution with time, and an understanding of the cause and mechanism driving the changes in physical conditions. Addressing the spatial distribution will involve a quantification of the partitioning of ocean water masses between the different ocean basins and with depth. Knowing their relative volumes and properties will allow greatly improved estimates of carbon storage. Understanding what triggers changes in the physical oceanography requires knowledge of the relative timing of changes in winds, T, upwelling, and overturning circulations in the Northern and Southern Hemispheres. Studies are attempting to ascertain this information indirectly through new chemical oceanographic tracers (e.g., radiocarbon measurements in deep-sea corals) but also through more extensive data collection and synthesis of existing tracers (e.g., carbonate and opal preservation indices).

The second main term in the glacial CO_2 equation is the response of ocean biology to physical and geochemical environmental changes, and the consequences of these biological changes for ocean chemistry. Several studies have brought us a long way in understanding changes in ocean export production, but detailed knowledge of what happened in surface waters between glacial and interglacial remains quite limited. Development and more extensive application of nutrient utilization proxies may take us a long way in both quantifying the global role of ocean biology as well as serving as a test of whether our physical understanding of the ocean is correct.

To interrogate the expanded observational data sets, improvements are also required in models that parallel the two primary facets of glacial-interglacial CO₂ change, physics and biology. 3-D ocean circulation models are necessary to make use of and attempt to reproduce observed spatial patterns and at sufficient resolution. Appropriate models must have the "physics" and parameters that allow adequate reproduction of observed modern patterns and historical trends [*Cao et al.*, 2008; *Doney et al.*, 2004]. Further refinements to representations of the marine iron cycle and controls on the fate of particulate organic matter exported from the surface are also needed.

It is important to recognize the iterative nature of this exploratory process in our search for understanding natural processes of glacial-interglacial CO₂; new data further constrain models which then make revised predictions that can be tested through observations [*Archer et al.*, 2009]. The combination of Earth system modeling with available data reconstructions have vastly improved our understanding of natural processes and how they are likely to interact with anthropogenic perturbations and what changes we are likely to see on the carbon cycle in the future [see, e.g., *Archer and*

Ganopolski, 2005; Montenegro et al., 2007; Schmittner et al., 2008].

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REFERENCES

- Abelmann, A. (1992), Diatom assemblages in arctic sea ice—Indicator for ice drift pathways, *Deep Sea Res., Part A*, 39, s525.
- Abelmann, A., et al. (2006), Extensive phytoplankton blooms in the Atlantic sector of the glacial Southern Ocean, *Paleoceanography*, 21, PA1013, doi:10.1029/2005PA001199.
- Adams, J., and H. Faure (1998), A new estimate of changing carbon storage on land since the last glacial maximum, based on global land ecosystem reconstruction, *Global Planet. Change*, 17, 3–24.
- Adams, J. M., et al. (1990), Increases in terrestrial carbon storage from the Last Glacial Maximum to the present, *Nature*, 348(6303), 711–714.
- Adkins, J. F., et al. (2002), The salinity, temperature and δ^{18} O of the glacial deep ocean, *Science*, 298, 1769–1773.
- Altabet, M. A., and W. B. Curry (1989), Testing models of past ocean chemistry using foraminiferal ¹⁵N/¹⁴N, *Global Biogeochem. Cycles*, 3(2), 107–119.
- Altabet, M. A., and R. Francois (1994), Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization, *Global Biogeochem. Cycles*, 8(1), 103–116.
- Anderson, D. M., and D. Archer (2002), Glacial-interglacial stability of ocean pH inferred from foraminifer dissolution rates, *Nature*, 416, 70–73.
- Anderson, R. F., et al. (1998), Late-Quaternary changes in productivity of the Southern Ocean, J. Mar. Syst., 17, 497–514.
- Anderson, R. F., et al. (2002), The Southern Ocean's biological pump during the Last Glacial Maximum, *Deep Sea Res, Part II*, 49, 1909–1938.
- Archer, D. (1996), A data-driven model of the global calcite lysocline, *Global Biogeochem. Cycles*, 10(3), 511–526.
- Archer, D., and A. Ganopolski (2005), A movable trigger: Fossil fuel CO₂ and the onset of the next glaciation, *Geochem., Geophys., Geosystems*, 6, Q05003, doi:10.1029/2004GC000891.
- Archer, D., and E. Maier-Reimer (1994), Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration, *Nature*, 367(6460), 260–263.
- Archer, D., A. Winguth, D. Lea, and N. Mahowald (2000a), What caused the glacial/interglacial atmospheric pCO₂ cycles?, *Rev. Geophys.*, 38(2), 159–189.

- Archer, D., G. Eshel, A. Winguth. W. Broecker, R. Pierrehumbert, M. Tobis, and R. Jacob (2000b), Atmospheric pCO₂ sensitivity to the biological pump in the ocean, *Global Biogeochem. Cycles*, *1*(4), 1219–1230.
- Archer, D. E. (1991), Equatorial Pacific calcite preservation cycles: Production or dissolution?, *Paleoceanography*, 6, 561–571.
- Archer, D. E., P. A. Martin, J. Milovich, V. Brovkin, G.-K. Plattner, and C. Ashendel (2003), Model sensitivity in the effect of Antarctic sea ice and stratification on atmospheric pCO₂, Paleoceanography, 18(1), 1012, doi:10.1029/2002PA000760.
- Archer, D., et al. (2009), Atmospheric lifetime of fossil-fuel carbon dioxide, *Annu. Rev. Earth Planet. Sci.*, in press.
- Armstrong, R. A., et al. (2002), A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals, *Deep Sea Res., Part II*, 49(1–3), 219–236.
- Arrigo, K. R. (2005), Marine microorganisms and global nutrient cycles, *Nature*, 437, 349–355.
- Bacon, M. P. (1984), Glacial to interglacial changes in carbonate and clay sedimentation in the Atlantic Ocean estimated from ²³⁰Th measurements, *Isot. Geosci.*, *2*, 97–111.
- Bard, E., et al. (1990), Calibration of the ¹⁴C time scale over the past 30,000 years using mass spectrometric U-Th ages from Barbados corals, *Nature*, *345*, 405–410.
- Bard, E., et al. (1998), Radiocarbon calibration by means of mass spectrometric Th-230/U-234 and C-14 ages of corals: An updated database including samples from Barbados, Mururoa and Tahiti, *Radiocarbon*, 40(3), 1085–1092.
- Bareille, G., et al. (1998), Glacial-interglacial changes in the accumulation rates of major biogenic components in Southern Indian Ocean sediments, J. Mar. Syst., 17(1–4), 527–539.
- Barker, S., et al. (2003), The future of the carbon cycle: Review, calcification response, ballast and feedback on atmospheric CO₂, *Philos. Trans. R. Soc. London, Ser. A*, *361*(1810), 1977–1998.
- Berger, W. H. (1982a), Increase of carbon-dioxide in the atmosphere during deglaciation—The coral reef hypothesis, *Naturwissenschaften*, 69(2), 87–88.
- Berger, W. H. (1982b), Deglacial CO₂ buildup: Constraints on the coral-reef model, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 40, 235–253.
- Berger, W. H., and E. Vincent (1986), Sporadic shutdown of North Atlantic deep water production during the Glacial–Holocene transition?, *Nature*, *324*, 53–55.
- Berger, W. H., and G. Wefer (1991), Productivity of the glacial ocean—Discussion of the iron hypothesis, *Limnol. Oceanogr.*, 36(8), 1899–1918.
- Berner, R. A. (1990), Atmospheric carbon dioxide levels over Phanerozoic time, *Science*, 249(4975), 1382–1386.
- Berner, R. A. (1992), Weathering, plants, and the long-term carbon cycle, *Geochim. Cosmochim. Acta*, 56(8), 3225–3231.
- Berner, R., and K. Caldeira (1997), The need for mass balance and feedback in the geochemical carbon cycle, *Geology*, 25(10), 955–956.
- Beucher, C. P., M. A. Brzezinski, and X. Crosta (2007), Silicic acid dynamics in the glacial sub-Antarctic: Implications for the

silicic acid leakage hypothesis, *Global Biogeochem. Cycles*, 21, GB3015, doi:10.1029/2006GB002746.

- Bijma, J., et al. (1999), Reassessing foraminiferal stable isotope geochemistry: Impact of the oceanic carbonate system (Experimental Results), in *Use of Proxies in Paleoceanography: Examples from the South Atlantic*, edited by G. Fischer and G. Wefer, pp. 489–512, Springer, Berlin.
- Bijma, J., B. Hönisch, and R. E. Zeebe (2002), Impact of the ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deep waters of the Caribbean Sea" by W. S. Broecker and E. Clark, *Geochem., Geophys., Geosyst.*, 3(11), 1064, doi:10.1029/2002GC000388.
- Bird, M. I., et al. (1994), Terrestrial carbon storage at the LGM, *Nature*, 371(6498), 566.
- Bishop, J. K. B., et al. (2002), Robotic observations of dust storm enhancement of carbon biomass in the North Pacific, *Science*, 298(5594), 817–821.
- Bopp, L., K. E. Kohfeld, C. Le Quéré, and O. Aumont (2003), Dust impacton marine biota and atmospheric CO₂ during glacial periods, *Paleoceanography*, 18(2), 1046, doi:10.1029/2002PA000810.
- Boyd, P. W., et al. (2000), A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, *Nature*, *407*, 695–702.
- Boyle, E. A. (1981), Cadmium, zinc, copper and barium in foraminifera tests, *Earth Planet. Sci. Lett.*, 53(1), 11–35.
- Boyle, E. A. (1988a), The role of vertical chemical fractionation in controlling late Quaternary atmospheric carbon dioxide, *J. Geophys. Res.*, 93(C12), 15,701–15,714.
- Boyle, E. A. (1988b), Cadmium: Chemical tracer of deepwater paleoceanography, *Paleoceanography*, 3, 471–489.
- Boyle, E. A. (1995), Last Glacial Maximum North Atlantic deep water—On, off, or somewhere in-between, *Philos. Trans. R. Soc. London, Ser. B*, 348(1324), 243–253.
- Boyle, E. A., and L. D. Keigwin (1982), Deep circulation of the North Atlantic over the last 200,000 years—Geochemical evidence, *Science*, 218(4574), 784–787.
- Bradtmiller, L. I., R. F. Anderson, M. Q. Fleisher, and L. H. Burckle (2007), Opal burial in the equatorial Atlantic Ocean over the last 30 ka: Implications for glacial-interglacial changes in the ocean silicon cycle, *Paleoceanography*, 22, PA4216, doi:10.1029/ 2007PA001443.
- Brewer, P. G., et al. (1999), Direct experiments on the ocean disposal of fossil fuel CO₂, *Science*, 284, 943–945.
- Broecker, W. S. (1982), Ocean chemistry during glacial time, Geochim. Cosmochim. Acta, 46, 1689–1705.
- Broecker, W. S., and G. M. Henderson (1998), The sequence of events surrounding Termination II and their implications for the cause of glacialinterglacial CO₂ changes, *Paleoceanography*, *13*(4), 352–364.
- Broecker, W. S., and E. Maier-Reimer (1992), The influence of air and sea exchange on the carbon isotope distribution in the sea, *Global Biogeochem. Cycles*, 6(3), 315–320.
- Broecker, W. S., and T.-H. Peng (1982), *Tracers in the Sea*, Eldigio Press, Palisades, N. Y., 690pp.
- Broecker, W. S., and T.-H. Peng (1986a), *Tracers in the Sea*, Lamont-Doherty Geological Observatory, Columbia University, New York.

- Broecker, W. S., and T.-H. Peng (1986b), Glacial to interglacial changes in the operation of the global carbon cycle, *Radiocarbon*, 28(2A), 309–327.
- Broecker, W. S., and T.-H. Peng (1987), The role of CaCO₃ compensation in the glacial to interglacial atmospheric CO₂ change, *Global Biogeochem. Cycles*, *1*(1), 15–29.
- Broecker, W. S., and T.-H. Peng (1989), The cause of the glacial to interglacial atmospheric CO₂ change: A polar alkalinity hypothesis, *Global Biogeochem. Cycles*, *3*(3), 215–239.
- Broecker, W. S., and T.-H. Peng (1993), What caused the glacial to interglacial CO₂ change?, in *The Global Carbon Cycle*, edited by M. Heimann, Springer, Berlin.
- Broecker, W. S., et al. (1985), Does the ocean-atmosphere have more than one stable mode of operation, *Nature*, 315, 21–25.
- Broecker, W. S., J. Lynch-Stieglitz, D. Archer, M. Hofmann, E. Maier-Reimer, O. Marchal, T. Stocker, and N. Gruber (1999a), How strong is the Harvardton-Bear constraint?, *Global Biogeochem. Cycles*, 13(4), 817–820.
- Broecker, W. S., D. C. McCorkle, T.-H. Peng, I. Hajdas, and G. Bonani (1999b), Evidence for a reduction in the carbonate ion content of the deep sea during the course of the Holocene, *Paleoceanography*, 14(6), 744–752.
- Brovkin, V., A. Ganopolski, D. Archer, and S. Rahmstorf (2007), Lowering of glacial atmospheric CO₂ in response to changes in oceanic circulation and marine biogeochemistry, *Paleoceanography*, 22, PA4202, doi:10.1029/2006PA001380.
- Brunelle, B. G., D. M. Sigman, M. S. Cook, L. D. Keigwin, G. H. Haug, B. Plessen, G. Schettler, and S. L. Jaccard (2007), Evidence from diatom-bound nitrogen isotopes for subarctic Pacific stratification during the last ice age and a link to North Pacific denitrification changes, *Paleoceanography*, 22, PA1215, doi:10.1029/2005PA001205.
- Brzezinski, M., C. J. Pride, V. M. Franck, D. M. Sigman, J. L. Sarmiento, K. Matsumoto, N. Gruber, G. H. Rau, and K. H. Coale (2002), A switch from Si(OH)(4) to NO₃-depletion in the glacial Southern Ocean, *Geophys. Res. Lett.*, 29(12), 1564, doi:10.1029/2001GL014349.
- Caillon, N., et al. (2003), Timing of atmospheric CO₂ and Antarctic temperature changes across Termination III, *Science*, 299, 1728–1731.
- Cao, L., et al. (2008), The importance of ocean transport in the fate of anthropogenic CO₂, *Biogeosci. Discuss.*, *5*, 4521–4557.
- Catubig, N. R., D. E. Archer, R. Francois, P. deMenocal, W. Howard, and E. F. Yu (1998), Global deep-sea burial rate of calcium carbonate during the last glacial maximum, *Paleoceanography*, *13*(3), 298–310.
- Chase, Z., R. F. Anderson, and M. Q. Fleischer (2001), Evidence from authigenic uranium for increased productivity of the glacial Subantarctic Ocean, *Paleoceanography*, 16(5), 468–478.
- Chase, Z., et al. (2003), Accumulation of biogenic and lithogenic material in the Pacific sector of the Southern Ocean during the past 30,000 years, *Deep Sea Res., Part II, 50*.
- Chikamoto, M., K. Matsumoto, and A. Ridgwell (2008), Response of deep-sea CaCO₃ sedimentation to Atlantic meridional overturning circulation shutdown, *J. Geophys. Res.*, *113*, G03017, doi:10.1029/2007JG000669.

- CLIMAP Project Members (1981), Seasonal reconstructions of the Earth's surface at the last glacial maximum, *Geol. Soc. Am. Map Chart Ser.*, *MC-36*, 1–18.
- Coale, K. H., et al. (1998), IronEx-I, an in situ iron-enrichment experiment: Experimental design, implementation and results, *Deep Sea Res., Part II*, 45(6), 919–945.
- Codispoti, L. (1995), Biogeochemical cycles—Is the ocean losing nitrate, *Nature*, 376(6543), 724.
- Crosta, X., J.-J. Pichon, and L. H. Burckle (1998), Application of modern analog technique to marine Antarctic diatoms: Reconstruction of maximum sea-ice extent at the Last Glacial Maximum, *Paleoceanography*, 13, 284–297.
- Crowley, T. J. (1991), Ice-age carbon, Nature, 352(6336), 575-576.
- Crowley, T. J. (1995), Ice-age terrestrial carbon changes revisited, *Global Biogeochem. Cycles*, 9(3), 377–389.
- Cuffey, K. M., and F. Vimeux (2001), Covariation of carbon dioxide and temperature from the Vostok ice core after deuteriumexcess correction, *Nature*, 412(6846), 523–527.
- Curry, W., J. C. Duplessy, L. D. Labeyrie, and N. J. Shackleton (1988), Changes in the Distribution of δ^{13} C of deep water ΣCO_2 between the Last Glaciation and the Holocene, *Paleoceanography*, *3*(3), 317–341.
- De la Rocha, C. L., et al. (1997), Fractionation of silicon isotopes during biogenic silica formation, *Geochim. Cosmochim. Acta*, *61*(23), 5051–5056.
- De la Rocha, C. L., et al. (1998), Silicon-isotope composition of diatoms as an indicator of past oceanic change, *Nature*, 395, 680–683.
- Delmas, R. (1980), Atmospheric carbon-dioxide in the past, *Re-cherche*, 11(114), 992–994.
- Delmonte, B., et al. (2002), Glacial to Holocene implications of the new 27000-year dust record from the EPICA Dome C (East Antarctica) ice core, *Clim. Dyn.*, 18, 647–660.
- Delmonte, B., et al. (2004), Dust size evidence for opposite regional atmospheric circulation changes over east Antarctica during the last climatic transition, *Clim. Dyn.*, *23*, 427–438.
- Derry, L., et al. (2005), Biological control of terrestrial silica cycling and export fluxes to watersheds, *Nature*, 433, 728–731.
- de Vernal, A., et al. (2006), Comparing proxies for the reconstruction of LGM sea-surface conditions in the northern North Atlantic, *Quat. Sci. Rev.*, 25(21–22), 2820–2834.
- DiFiore, P. J., D. M. Sigman, T. W. Trull, M. J. Lourey, K. Karsh, G. Cane, and R. Ho (2006), Nitrogen isotope constraints on subantarctic biogeochemistry, *J. Geophys. Res.*, 111, C08016, doi:10.1029/2005JC003216.
- Doney, S. C., et al. (2004), Evaluating global ocean carbon models: The importance of realistic physics, *Global Biogeochem. Cycles*, *18*, GB3017, doi:10.1029/2003GB002150.
- Duplessy, J. C., N. J. Shackleton, R. G. Fairbanks, L. Labeyrie, D. Otto, and N. Kallel (1988), Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation, *Paleoceanography*, 3(3), 343–360.
- Eppley, R. W. (1972), Temperature and phytoplankton growth in the sea, *Fish. Bull.*, *70*, 1063–1085.
- Erickson, D. J., III (1989), Variations in the global air-sea transfer velocity field of CO₂, *Global Biogeochem. Cycles*, 3, 37–41.

- Erickson, D. J., III (1993), A stability dependent theory for air-sea gas-exchange, *J. Geophys. Res.*, *98*(C5), 8471–8488.
- Esser, G., and M. Lautenschlager (1994), Estimating the change of carbon in the terrestrial biosphere from 18000-BP to present using a carbon-cycle model, *Environ. Pollut.*, 83(1–2), 45–53.
- Fairbanks, R. G. (1989), A 17,000-year glacio-eustatic sea-level record—Influence of glacial melting rates on the Younger Dryas Event and deep-ocean circulation *Nature*, 342(6250), 637–642.
- Falkowski, P. G. (1997), Evolution of the nitrogen cycle and its influence on the biological pump in the ocean, *Nature*, *387*, 272–275.
- Farrera, I., et al. (1999), Tropical palaeoclimates at the Last Glacial Maximum: A new synthesis of terrestrial data I. Vegetation, lake levels and geochemistry, *Clim. Dyn.*, *15*(1), 823–856.
- Faure, H., et al. (1996), Carbon storage and continental land surface change since the Last Glacial Maximum, *Quat. Sci. Rev.*, 15(8–9), 843–849.
- Flückiger, J., E. Monnin, B. Stauffer, J. Schwander, T. F. Stocker, J. Chappellaz, D. Reynaud, and J.-M. Barnola (2002), Highresolution Holocene N₂O ice core record and its relationship with CH₄ and CO₂, *Global Biogeochem. Cycles*, 16(1), 1010, doi:10.1029/2001GB001417.
- Foster, G., and D. Vance (2006), Negligible glacial-interglacial variation in continental chemical weathering rates, *Nature*, 444(7121), 918–921.
- Francois, L., et al. (1998), Modelling the glacial-interglacial changes in continental biosphere, *Global Planet. Change*, 17, 37–52.
- Francois, L., et al. (1999), Carbon stocks and isotopic budgets of the terrestrial biosphere at mid-Holocene and last glacial maximum times, *Chem. Geol.*, 159(1–4), 163–189.
- Francois, R., M. P. Bacon, M. A. Altabet, and L. D. Labeyrie (1993), Glacial/interglacial changes in sediment rain rate in the SW Indian sector of subantarctic waters as recorded by 230 Th, 231 Pa, U, and δ^{15} N, *Paleoceanography*, *8*, 611–629.
- Francois, R., et al. (1997), Contribution of Southern Ocean surfacewater stratification to low atmospheric CO₂ concentrations during the last glacial period, *Nature*, 389, 929–935.
- Francois, R., S. Honjo, R. Krishfield, and S. Manganini (2002), Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, *Global Biogeochem. Cycles*, 16(4), 1087, doi:10.1029/2001GB001722.
- Frank, M., R. Gersonde, M. R. van der Loeff, G. Bohrmann, C. C. Nürnberg, P. W. Kubik, M. Suter, and A. Mangini (2000), Similar glacial and interglacial export bioproductivity in the Atlantic sector of the Southern Ocean: Multiproxy evidence and implications for glacial atmospheric CO₂, *Paleoceanography*, 15(6), 642–658.
- Friedlingstein, P., C. Delire, J. F. Müller, and J. C. Gérard (1992), The climate induced variation of the continental biosphere—A model simulation of the Last Glacial Maximum, *Geophys. Res. Lett.*, 19(9), 897–900.
- Froelich, P. N., V. Blanc, R. A. Mortlock, S. N. Chillrud, W. Dunstan, A. Udomkit, and T.-H. Peng (1992), River fluxes of dissolved silica to the ocean were higher during glacials: Ge/Si in diatoms, rivers, and oceans, *Paleoceanography*, 7(6), 739–767.

- Galbraith, E. D., M. Kienast, T. F. Pedersen, and S. E. Calvert (2004), Glacial-interglacial modulation of the marine nitrogen cycle by high-latitude O₂ supply to the global thermocline, *Pale-oceanography*, 19, PA4007, doi:10.1029/2003PA001000.
- Galbraith, E. D., et al. (2007), Carbon dioxide release from the North Pacific abyss during the last deglaciation, *Nature*, 449(7164), U890–U899.
- Galbraith, E. D., M. Kienast, S. L. Jaccard, T. F. Pedersen, B. G. Brunelle, D. M. Sigman, and T. Kiefer (2008), Consistent relationship between global climate and surface nitrate utilization in the western subarctic Pacific throughout the last 500 ka, *Paleoceanography*, 23, PA2212, doi:10.1029/2007PA001518.
- Ganeshram, R. S., et al. (1995), Large changes in oceanic nutrient inventories from glacial to interglacial periods, *Nature*, *376*(6543), 755–758.
- Gebhardt, H., M. Sarnthein, P. M. Grootes, T. Kiefer, H. Kühn, F. Schmieder, and U. Röll (2008), Paleonutrient and productivity records from the subarctic North Pacific for Pleistocene glacial terminations I to V, *Paleoceanography*, 23, PA4212, doi:10. 1029/2007PA001513.
- Gersonde, R., and U. Zielinski (2000), The reconstruction of late Quaternary Antarctic sea-ice distribution—The use of diatoms as a proxy for sea-ice, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 162, 263–286.
- Gersonde, R., et al. (2003), Last glacial sea surface temperatures and sea-ice extent in the Southern Ocean (Atlantic-Indian sector): A multiproxy approach, *Paleoceanography*, *18*(3), 1061, doi:10.1029/2002PA000809.
- Gersonde, R., et al. (2005a), Sea-surface temperature and sea lee distribution of the Southern Ocean at the EPILOG Last Glacial Maximum—A circum-Antarctic view based on siliceous microfossil records, *Quat. Sci. Rev.*, 24(7–9), 869–896.
- Gersonde, R., et al. (2005b), Sea-surface temperature and sea ice distribution of the Southern Ocean at the EPILOG Last Glacial Maximum—A circum-Antarctic view based on siliceous microfossil records, *Quat. Sci. Rev.*, 24(7–9), 869–896.
- Gildor, H., E. Tziperman, and J. R. Toggweiler (2002), Sea ice switch mechanism and glacial-interglacial CO₂ variations, *Global Biogeochem. Cycles*, 16(3), 1032, doi:10.1029/2001GB001446.
- Gnanadesikan, A., J. L. Sarmiento, and R. D. Slater (2003), Effects of patchy ocean fertilization on atmospheric carbon dioxide and biological production, *Global Biogeochem. Cycles*, 17(2), 1050, doi:10.1029/2002GB001940.
- Guilderson, T. P., et al. (1994), Tropical temperature variations since 20,000 years ago: Modulating interhemispheric climate change, *Science*, 263, 663–665.
- Hammer, C. U., H. B. Clausen, W. Dansgaard, A. Neftel, P. Kristinsdottir, and E. Johnson (1985), Continuous impurity analysis along the Dye 3 deep core, in *Greenland Ice Core: Geophysics, Geochemistry, and the Environment, Geophys. Monogr. Ser.*, vol. 33, edited by C. Langway Jr., H. Oeschger, and W. Dansgaard, pp. 90–94, AGU, Washington, D. C.
- Hammond, D., et al. (2000), Diagenetic fractionation of Ge and Si in reducing sediments: The missing Ge sink and a possible mechanism to cause glacial/interglacial variations in oceanic Ge/ Si, *Geochim. Cosmochim. Acta*, 64(14), 2453–2465.

- Harrison, K. G. (2000), Role of increased marine silica input on paleo-*p*CO₂ levels, *Paleoceanography*, *15*(3), 292–298.
- Heinze, C. (2004), Simulating oceanic CaCO₃ export production in the greenhouse, *Geophys. Res. Lett.*, 31, L16308, doi:10.1029/ 2004GL020613.
- Heinze, C., E. Maier-Reimer, and K. Winn (1991), Glacial *p*CO₂ reduction by the world ocean: Experiments with the Hamburg carbon cycle model, *Paleoceanography*, *6*, 395–430.
- Heinze, C., E. Maier-Reimer, A. M. E. Winguth, and D. Archer (1999), A global oceanic sediment model for long-term climate studies, *Global Biogeochem. Cycles*, 13, 221–250.
- Henderson, G., et al. (1994), Evolution of seawater Sr-87/Sr-86 over the last 400 ka—The absence of glacial-interglacial cycles, *Earth Planet. Sci. Lett.*, *128*(3–4), 643–651.
- Hendry, K. R., et al. (2008), Cadmium and phosphate in coastal Antarctic seawater: Implications for Southern Ocean nutrient cycling, *Mar. Chem.*, 112(2008), 149–157.
- Hostetler, S., et al. (2006), Sensitivity of Last Glacial Maximum climate to uncertainties in tropical and subtropical ocean temperatures, *Quat. Sci. Rev.*, 25(11–12), 1168–1185.
- Imbrie, J., et al. (1984), The orbital theory of Pleistocene climate: Support from a revised chronology of the marine δ 180 record, in *Milankovitch and Climate Part 1*, edited by A. Berger et al., pp. 269–305, Springer, Dordrecht.
- Indermuehle, A., et al. (1999), Holocene carbon-cycle dynamics based on CO₂ trapped in ice at Taylor Dome, Antarctica, *Nature*, 398, 121–126.
- Indermuehle, A., E. Mannin, B. Stauffer, T. F. Stocker, and M. Wahlen (2000), Atmospheric CO₂ concentration from 60 to 20 kyr BP from the Taylor Dome ice core, Antarctica *Geophys. Res. Lett.*, 27(5), 735–738.
- IPCC (2007), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 996 pp., Cambridge Univ. Press, Cambridge, U. K.
- Jaccard, S. L., et al. (2005), Glacial/Interglacial changes in subarctic North Pacific stratification, *Science*, 308, 1003–1006.
- Jouzel, J., et al. (2007), Orbital and millennial Antarctic climate variability over the past 800,000 years, *Science*, 317(5839), 793– 797, doi:10.1126/science.1141038.
- Kaplan, J. O., I. C. Prentice, W. Knorr, and P. J. Valdes (2002), Modeling the dynamics of terrestrial carbon storage since the Last Glacial Maximum, *Geophys. Res. Lett.*, 29(22), 2074, doi:10. 1029/2002GL015230.
- Karsh, K. L., et al. (2003), Relationship of nitrogen isotope fractionation to phytoplankton size and iron availability during the Southern Ocean Iron RElease Experiment (SOIREE), *Limnol. Oceanogr.*, 48(3), 1058–1068.
- Kayanne, H. (1992), Deposition of calcium carbonate into Holocene reefs and its relation to sea-level rise and atmospheric CO₂, paper presented at Proceedings of the Seventh International Coral Reef Symposium, Univ. of Guam Press, Mangilao, Guam.
- Keir, R. S. (1988), On the late Pleistocene ocean geochemistry and circulation, *Paleoceanography*, *3*, 413–445.
- Keir, R. S. (1991), The effect of vertical nutrient redistribution on surface ocean δ¹³C, *Global Biogeochem. Cycles*, 5(4), 351–358.

- Keir, R. S. (1993), Are atmospheric CO₂ content and Pleistocene climate connected by wind-speed over a polar Mediterranean Sea, *Global Planet. Change*, 8(1–2), 59–68.
- Keith, D. W. (2000), Geoengineering the climate: History and prospect, Annu. Rev. Energy Environ., 25, 245–284.
- Kienast, S. S., et al. (2004), Export production in the Subarctic Pacific: No evidence for iron fertilization?, J. Oceanogr., 60, 189–203.
- Kienast, S. S., M. Kienast, S. Jaccard, S. E. Calvert, and R. Francois (2006), Testing the silica leakage hypothesis with sedimentary opal records from the eastern equatorial Pacific over the last 150 kyrs, *Geophys. Res. Lett.*, 33(15), L15607, doi:10.1029/2006GL026651.
- Klaas, C., and D. E. Archer (2002), Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio, *Global Biogeochem. Cycles*, 16(4), 1116, doi:10.1029/2001GB001765.
- Kleypas, J. A. (1997), Modeled estimates of global reef habitat and carbonate production since the Last Glacial Maximum, *Pale-oceanography*, 12(4), 533–545.
- Knox, F., and M. B. McElroy (1984), Changes in atmospheric CO₂: Influence of the marine biota at high latitude, *J. Geophys. Res.*, *89*(D3), 4629–4637.
- Kohfeld, K. E., and S. P. Harrison (2001), DIRTMAP: The geologic record of dust, *Earth Sci. Rev.*, 54(1–3), 81–114.
- Kohfeld, K. E., and I. Tegen (2007), The record of soil dust aerosols and their role in the earth system, in *Treatise on Geochemistry Update 1*, vol. 4.13, edited by H. D. Holland, and K. K. Turekian, pp. 1–26, Elsevier Ltd., Oxford.
- Kohfeld, K. E., R. F. Anderson, and J. Lynch-Stieglitz (2000), Carbon isotopic disequilibrium in polar planktonic foraminifera and its impact on Modern and Last Glacial Maximum reconstructions, *Paleoceanography*, 15(1), 53–64.
- Kohfeld, K. E., et al. (2005), Role of marine biology in glacialinterglacial CO₂ cycles, *Science*, 308(5718), 74–78.
- Köhler, P., and H. Fischer (2006), Proposing a mechanistic understanding of changes in atmospheric CO₂ during the last 740 000 years, *Clim. Past Discuss.*, 2, 1–42.
- Köhler P., H. Fischer, G. Munhoven, and R. E. Zeebe (2005), Quantitative interpretation of atmospheric carbon records over the last glacial termination, *Global Biogeochem. Cycles*, 19, GB4020, doi:10.1029/2004GB002345.
- Kroopnick, P. M. (1985), The distribution of δ13C of TCO₂ in the world oceans, *Deep Sea Res.*, *Part A*, *32*, 57–84.
- Kucera, M., et al. (2005), Multiproxy approach for the reconstruction of the glacial ocean surface (MARGO), *Quat. Sci. Rev.*, 24(7–9), 813–819.
- Kumar, N., et al. (1995), Increased biological productivity and export production in the glacial Southern Ocean, *Nature*, 378, 675–680.
- Kurahashi-Nakamura, T., A. Abe-Ouchi, Y. Yamanaka, and K. Misumi (2007), Compound effects of Antarctic sea ice on atmospheric pCO₂ change during glacial-interglacial cycle, *Geophys. Res. Lett.*, 34, L20708, doi:10.1029/2007GL030898.
- Lambert, F., et al. (2008), Dust-climate couplings over the past 800,000 years from the EPICA Dome C ice core, *Nature*, 452(7187), 616–619.

- Lane, E. S., et al. (2008), The interaction between inorganic iron and cadmium uptake in the marine diatom *Thalassiosira oceanica*, *Limnol. Oceanogr.*, 53(5), 1784–1789.
- Laws, E. A., P. G. Falkowski, W. O. Smith Jr., H. Ducklow, and J. J. McCarthy (2000), Temperature effects on export production in the open ocean, *Global Biogeochem. Cycles*, 14(4), 1231– 1246.
- Lea, D., et al. (2000), Climate Impact of Late Quaternary Equatorial Pacific Sea Surface Temperature Variations, *Science*, 289, 1719–1724.
- Le Quéré, C., et al. (2007), Saturation of the Southern Ocean CO₂ sink due to recent climate change, *Science*, *316*(5832), 1735–1738.
- Liss, P. S., and L. Merlivat (1986), Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp. 113–129, Springer, Boston.
- Longhurst, A. R. (2007), *Ecological Geography of the Sea*, 560 pp., Elsevier, San Diego.
- Lüthi, D., et al. (2008), High-resolution carbon dioxide concentration record 650,000–800,000 years before present, *Nature*, 453, 379–382.
- Lynch-Stieglitz, J., and R. G. Fairbanks (1994), A conservative tracer for glacial ocean circulation from carbon isotope and palaeonutrient measurements in benthic foraminifera, *Nature*, *369*(6478), 308–310.
- Lynch-Stieglitz, J., T. F. Stocker, W. S. Broecker, and R. G. Fairbanks (1995), The influence of air-sea exchange on the isotopic composition of oceanic carbon: Observations and modeling, *Global Biogeochem. Cycles*, 9(4), 653–665.
- Mackensen, A., H.-W. Hubberten, T. Bickert, G. Fischer, and D. K. Fütterer (1993), The δ^{13} C in benthic foraminiferal tests of *Fontbotia-wuellerstorfi* (Schwager) relative to the δ^{13} C of dissolved inorganic carbon in Southern Ocean deep water: Implications for glacial ocean circulation models, *Paleoceanography*, *8*, 587–610.
- Mahowald, N., K. Kohfeld, M. Hansson, Y. Balkanski, S. P. Harrison, I. C. Prentice, M. Schulz, and H. Rodhe (1999), Dust sources and deposition during the Last Glacial Maximum and current climate: A comparison of model results with palaeodata from ice cores and marine sediments, *J. Geophys. Res.*, 104(D13), 15,895–15,916.
- Mahowald, N. M., D. R. Muhs, S. Levis, P. J. Rasch, M. Yoshioka, C. S. Zender, and C. Luo (2006), Change in atmospheric mineral aerosols in response to climate: last glacial period pre-industrial, modern and doubled carbon dioxide climates, *J. Geophys. Res.*, 111, D10202, doi:10.1029/2005JD006653.
- Marchal, O., et al. (1998a), A latitude-depth circulation-biogeochemical ocean model for paleoclimate studies, *Tellus, Ser. B*, *B50*, 290–316.
- Marschal, O., T. F. Stocker, and F. Joos (1998b), Impact of oceanic reorganizations on the ocean carbon cycle and atmospheric carbon dioxide content, *Paleoceanography*, 13(3), 225–244.
- Marchitto, T. M., and W. S. Broecker (2006), Deep water mass geometry in the glacial Atlantic Ocean: A review of constraints from the paleonutrient proxy Cd/Ca, *Geochem., Geophys. Geo*syst., 7, Q12003, doi:10.1029/2006GC001323.

- Marchitto, T. M., et al. (2007), Marine radiocarbon evidence for the mechanism of deglacial atmospheric CO₂ rise, *Science*, *316*(5830), 1456–459.
- Marino, B. D., et al. (1992), Glacial-to-interglacial variations in the carbon isotopic composition of atmospheric CO₂, *Nature*, *357*(6378), 461–466.
- Martin, J. H. (1990), Glacial-interglacial CO₂ change: The iron hypothesis, *Paleoceanography*, 5, 1–13.
- Martin, J. H., and S. E. Fitzwater (1988), Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic, *Nature*, *331*, 341–343.
- Martin, J. H., et al. (1987), VERTEX: Carbon cycling in the northeast Pacific, *Deep Sea Res., Part A*, 34, 267–285.
- Martinson, D. G., et al. (1987), Age dating and the orbital theory of the ice ages—Development of a high-resolution 0 to 300,000-vear chronostratigraphy, *Ouat. Res.*, 27(1), 1–29.
- Maslin, M. A., et al. (1995), Estimating the carbon transfer between the ocean, atmosphere and the terrestrial biosphere since the Last Glacial Maximum, *Terra Nova*, 7(3), 358–366.
- Matsumoto, K. (2006), Model simulations of carbon sequestration in the northwest Pacific by patch fertilization, *J. Oceanogr.*, 62(6), 887–902.
- Matsumoto, K. (2007), Biology-mediated temperature control on atmospheric *p*CO₂ and ocean biogeochemistry, *Geophys. Res. Lett.*, *34*, L20605, doi:10.1029/2007GL031301.
- Matsumoto, K., and J. Lynch-Stieglitz (1999), Similar glacial and Holocene deep water circulation inferred from southeast Pacific benthic foraminiferal carbon isotope composition, *Paleoceanography*, 14(2), 149–163.
- Matsumoto, K., et al. (2002a), Interior hydrography and circulation of the glacial Pacific Ocean, *Ouat. Sci. Rev.*, 21(14–15), 1693–1704.
- Matsumoto, K., et al. (2002b), Silicic acid leakage from the Southern Ocean: A possible explanation for glacial atmospheric *p*CO₂, *Global Biogeochem. Cycles*, *16*(3), 1031, doi:10.1029/2001GB001442.
- Matsumoto, K., T. Hashioka, and Y. Yamanaka (2007), Effect of temperature-dependent organic carbon decay on atmospheric pCO₂, J. Geophys. Res., 112, G02007, doi:10.1029/2006JG000187.
- McCorkle, D. C., L. D. Keigwin, B. H. Corliss, and S. R. Emerson (1990), The influence of microhabitats on the carbon isotopic composition of deep-sea benthic foraminifera, *Paleoceanography*, 5(2), 161–185.
- McElroy, M. (1983), Marine biological controls on atmospheric CO₂ and climate, *Nature*, *302*(5906), 328–329.
- McManus, J., et al. (1998), Geochemistry of barium in marine sediments: Implications for its use as a paleoproxy, *Geochim. Cosmochim. Acta*, 62(21/22), 2453–2473.
- McManus, J., et al. (2004), Collapse and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes, *Nature*, 428(6985), 834–837.
- Michel, C., L. D. Labeyrie, J.-C. Duplessy, N. Gorfty, N. Labracherie, and J.-L. Turon (1995), Could deep Subantarctic convection feed the world deep basins during the Last Glacial Maximum?, *Paleoceanography*, 10, 927–942.
- Milliman, J., and A. Droxler (1996), Neritic and pelagic carbonate sedimentation in the marine environment: Ignorance is not bliss, *Geol. Rundsch.*, 85(3), 496–504.

- Milliman, J. D. (1993), Production and accumulation of calcium carbonate in the ocean: Budget of a nonsteady state, *Global Bio*geochem. Cycles, 7(4), 927–957.
- Monnin, E., et al. (2001), Atmospheric CO₂ concentrations over the last glacial termination, *Science*, 291(5501), 112–114.
- Montaggioni, L. (2000), Postglacial reef growth, Comptes rendus de l'Academie des Sciences Serie II Fascicule A-Sciences de la Terre et des Planetes, 331(5), 319–330.
- Montenegro, A., V. Brovkin, M. Eby, D. Archer, and A. J. Weaver (2007), Long term fate of anthropogenic carbon, *Geophys. Res. Lett.*, 34, L19707, doi:10.1029/2007GL030905.
- Mook, W. G., et al. (1974), Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon-dioxide, *Earth Planet. Sci. Lett.*, 22, 169–176.
- Mortlock, R. A., and P. N. Froelich (1987), Continental weathering of Germanium—Ge/Se in the global river discharge, *Geochim. Cosmochim. Acta*, 51(8), 2075–2082.
- Munhoven, G., and L. M. François (1996), Glacial-interglacial variability of atmospheric CO₂ due to changing continental silicate rock weathering: A model study, *J. Geophys. Res.*, *101*(D16), 21,423–21,437.
- Neftel, A., et al. (1982), Ice core sample measurements give atmospheric CO₂ content during the past 40,000 yr, *Nature*, 295(5846), 220–223.
- Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, 14, 373–387.
- Opdyke, B. N., and J. C. G. Walker (1992), Return of the coral-reef hypothesis—Basin to shelf partitioning of CaCO₃ and its effect on atmospheric CO₂, *Geology*, 20(8), 733–736.
- Oppo, D., et al. (1995), A δ^{13} C record of Upper North Atlantic Deep Water during the past 2.6 million years, *Paleoceanography*, *10*(3), 373–394.
- Oppo, D. W., and R. Fairbanks (1987), Variability in the deep and intermediate water circulation of the Atlantic Ocean during the past 25,000 years—Northern Hemisphere modulation of the Southern Ocean, *Earth Planet. Sci. Letters*, *86*(1), 1–15.
- Otto, D., et al. (2002), Biospheric carbon stocks reconstructed at the Last Glacial Maximum: Comparison between general circulation models using prescribed and computed sea surface temperatures, *Global Planet. Change*, *33*(1–2), 117– 138.
- Parekh, P., M. J. Follows, and E. Boyle (2004), Modeling the global ocean iron cycle, *Global Biogeochem. Cycles*, 18, GB1002, doi:10.1029/2003GB002061.
- Parekh, P., S. Dutkiewicz, M. J. Follows, and T. Ito (2006a), Atmospheric carbon dioxide in a less dusty world, *Geophys. Res. Lett.*, 33, L03610, doi:10.1029/2005GL025098.
- Parekh, P., M. J. Follows, S. Dutkiewicz, and T. Ito (2006b), Physical and biological regulation of the soft tissue carbon pump, *Paleoceanography*, *21*, PA3001, doi:10.1029/2005PA001258.
- Passow, U., and C. De La Rocha (2006), Accumulation of mineral ballast on organic aggregates, *Global Biogeochem. Cycles*, 20, GB1013, doi:10.1029/2005GB002579.

- Paytan, A., and M. Kastner (1996), Benthic Ba fluxes in the central Equatorial Pacific, implications for the oceanic Ba cycle, *Earth Planet. Sci. Lett.*, 142(3–4), 439–450.
- Peacock, S., E. Lane, and J. M. Restrepo (2006), A possible sequence of events for the generalized glacial-interglacial cycle, *Global Biogeochem. Cycles*, 20(2), GB2010, doi:10.1029/ 2005GB002448.
- Peltier, W. R., and R. G. Fairbanks (2006), Global glacial ice volume and Last Glacial Maximum duration from an extended Barbados sea level record, *Quat. Sci. Rev.*, 25(23–24), 3322– 3337.
- Peng, C., et al. (1998), Estimating changes in terrestrial vegetation and carbon storage: Using palaeoecological data and models, *Quat. Sci. Rev.*, 17(8), 719–735.
- Petit, J. R., et al. (1999), Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, 399(6735), 439–436.
- Prentice, I. C. (2001a), Interactions of climate change and the terrestrial biosphere, in *Geosphere-Biosphere Interactions and Climate*, edited by L. O. Bengtsson and C. U. Hammer, pp. 176– 195, Pontifical Academy of Sciences, Cambridge.
- Prentice, I. C. (2001b), Last Glacial Maximum and Mid-Holocene vegetation: Data and Models, in *Klimawechsel vor dem Einfluß des Menschen*, edited by M. Sarnthein, pp. 61–70, Deutsche Adademie der Naturforscher Leopoldina, Halle (Saale).
- Prentice, I. C., et al. (1993), Modelling global vegetation patterns and terrestrial carbon storage at the last glacial maximum, *Global Ecol. Biogeography. Lett.*, *3*, 67–76.
- Prentice, K. C., and I. Y. Fung (1990), The sensitivity of terrestrial carbon storage to climate change, *Nature*, *346*, 48–51.
- Ragueneau, O., et al. (2000), A review of the Si cycle in the modern ocean: Recent progress and missing gaps in the application of biogenic ipal as a paleoproductivity proxy, *Global Planet*. *Change*, 26, 317–365.
- Rahmstorf, S. (2002), Ocean circulation and climate during the past 120,000 years, *Nature*, 419, 207–214.
- Rahmstorf, S., et al. (2005), Thermohaline circulation hysteresis: A model intercomparison, *Geophys. Res. Lett.* 32, L23605, doi:10. 1029/2005GL023655.
- Raymo, M. E., W. F. Ruddiman, J. Backman, B. H. Clement, and D. G. Martinson (1989), Late Pliocene variation in Northern Hemisphere ice sheets and North Atlantic Deep Water circulation, *Paleoceanography*, 4(4), 413–446.
- Rea, D. K. (1994), The paleoclimatic record provided by eolian deposition in the deep sea: The geologic history of wind, *Rev. Geophys.*, 32(2), 159–195.
- Redfield, A. C. (1934), On the proportions of organic derivations in sea water and their relation to the composition of plankton, in *James Johnstone Memorial Volume*, edited by R. J. Daniel, pp. 177–192, Univ. Press of Liverpool, Liverpool.
- Rickaby, R. E. M., and H. Elderfield (1999), Planktonic foraminiferal Cd/Ca: Paleonutrients or paleotemperature?, *Paleocean*ography, 14(3), 293–303.
- Ridgwell, A., and J. Hargreaves (2007), Regulation of atmospheric CO₂ by deep-sea sediments in an Earth System Model, *Global Biogeochem. Cycles*, 21, GB2008, doi:10.1029/2006GB002764.

- Ridgwell, A., and R. E. Zeebe (2005), The role of the global carbonate cycle in the regulation and evolution of the Earth system, *Earth Planet. Sci. Lett.*, 234, 299–315.
- Ridgwell, A. J. (2001), Glacial-interglacial perturbations in the global carbon cycle, Ph.D. thesis, 134 pp, University of East Anglia, Norwich, U. K.
- Ridgwell, A. J. (2003a), Implications of the glacial CO₂ "iron hypothesis" for Quaternary climate change, *Geochem. Geophys. Geosyst.*, 4(9), 1076, doi:10.1029/2003GC000563.
- Ridgwell, A. J., (2003b), An end to the 'rain ratio' reign?, *Geochem. Geophys. Geosyst.*, 4(6), 1051, doi:10.1029/2003GC000512.
- Ridgwell, A. J., A. J. Watson, and D. E. Archer (2002), Modeling the response of the oceanic Si inventory to perturbation, and consequences for atmospheric CO₂, *Global Biogeochem. Cycles*, *16*(4), 1071, doi:10.1029/2002GB001877.
- Ridgwell, A. J., A. J. Watson, M. A. Maslin, and J. O. Kaplan (2003), Implications of coral reef buildup for the controls on atmospheric CO₂ since the Last Glacial Maximum, *Paleoceanographv*, 18(4), 1083, doi:10.1029/2003PA000893.
- Ridgwell, A., et al. (2007), Significant long-term increase of fossil fuel CO₂ uptake from reduced marine calcification, *Biogeosci*ences, 4, 481–492.
- Riebesell, U., et al. (2000), Reduced calcification of marine plankton in response to increased atmospheric CO₂, *Nature*, 407, 364–367.
- Rind, D., and D. Peteet (1985), Terrestrial conditions at the last glacial maximum and CLIMAP sea-surface temperature estimates: Are they consistent?, *Quat. Res.*, 24, 1–22.
- Robinson, R. S., B. G. Brunelle, and D. M. Sigman (2004), Revisiting nutrient utilization in the glacial Antarctic: Evidence from a new method for diatom-bound N isotopic analysis, *Paleocean*ography, 19(3), PA3001, doi:10.1029/2003PA000996.
- Rosell-Melé, A. (1998), Project takes a new look at past sea surface temperatures, *Eos Trans. AGU*, *79*(33), 393.
- Rosell-Melé, A., E. Bard, K.-C. Emeis, B. Grieger, C. Hewitt, P. J. Müller, and R. R. Schneider (2004), Sea surface temperature anomalies in the oceans at the LGM estimated from the alkenone-U^{*}₃₇ index: Comparison with GCMs, *Geophys. Res. Lett.*, 31, L03208, doi:10.1029/2003GL018151.
- Röthlisberger, R., M. Bigler, E. W. Wolff, F. Joos, E. Monnin, and M. A. Hutterli (2004), Ice core evidence for the extent of past atmospheric CO₂ change due to iron fertilisation, *Geophys. Res. Lett.*, *31*, L16207, doi:10.1029/2004GL020338.
- Russell, A. D., and H. J. Spero (2000), Field examination of the oceanic carbonate ion effect on stable isotopes in planktonic foraminifera, *Paleoceanography*, 15(1), 43–52.
- Ryan, D., et al. (2001), Holocene sediments of Wistari Reef: Towards a global quantification of coral reef related neritic sedimentation in the Holocene, *Palaeogeogr., Palaeoclimatol., Palaeoecol., 175*(1–4), 173–184.
- Sarmiento, J., and J. R. Toggweiler (1984), A new model for the role of the oceans in determining atmospheric pCO₂, *Nature*, 308, 621–624.
- Sarnthein, M., K. Winn, S. J. A. Jung, J.-C. Duplessy, L. Labeyrie, H. Erlenkeuser, and G. Ganssen (1994), Changes in the East Atlantic deep-water circulation over the last 30,000 years:

Eight time slice reconstructions, *Paleoceanography*, 9(2), 209–267.

- Sarnthein, M., R. Gersonde, S. Niebler, U. Pflaumann, R. Spielhagen, J. Thiede, G. Wefer, and M. Weinelt (2003), Overview of Glacial Atlantic Ocean Mapping (GLAMAP 2000), *Paleoceanography*, 18(2), 1030, doi:10.1029/2002PA000769.
- Schmittner, A., K. J. Meissner, M. Eby, and A. J. Weaver (2002), Forcing of the deep ocean circulation in simulations of the Last Glacial Maximum, *Paleoceanography*, *17*(2), 1015, doi:10.1029/2001PA000633.
- Schmittner, A., E. D. Galbraith, S. W. Hostetler, T. F. Pedersen, and R. Zhang (2007), Large fluctuations of dissolved oxygen in the Indian and Pacific oceans during Dansgaard-Oeschger oscillations caused by variations of North Atlantic Deep Water subduction, *Paleoceanography*, 22, PA3207, doi:10.1029/2006PA001384.
- Schmittner, A., A. Oschlies, H. D. Matthews, and E. D. Galbraith (2008), Future changes in climate, ocean circulation, ecosystems, and biogeochemical cycling simulated for a business-as-usual CO₂ emission scenario until year 4000 AD, *Global Biogeochem. Cycles*, 22, GB1013, doi:10.1029/2007GB002953.
- Shackleton, N. J. (1978), Carbon-13 in Uvigerina: Tropical Rainforest History and the Equatorial Pacific Carbonate Dissolution Cycles., in *The Fate of Fossil Fuel CO₂ in the Oceans.*, edited by N. R. Andersen and A. Malahoff, pp. 401–427, Springer, New York.
- Shackleton, N. J. (2000), The 100,000-year ice-age cycle identified and found to lag temperature, carbon dioxide, and orbital eccentricity, *Science*, 289(5486), 1897–1902.
- Shaffer, G. (1990), A non-linear climate oscillator controlled by biogeochemical cycling in the ocean: An alternative model of Quaternary ice age cycles, *Clim. Dyn.*, 4, 127–143.
- Shemesh, A., R. A. Mortlock, and P. N. Froelich (1989), Late Cenozoic Ge/Si record of marine biogenic opal: Implications for variations of riverine fluxes to the ocean, *Paleoceanography*, 4(3), 221–234.
- Siegenthaler, U., and T. Wenk (1984), Rapid atmospheric CO₂ variations and ocean circulation, *Nature*, *308*, 624–626.
- Siegenthaler, U., et al. (2005), Stable carbon cycle-climate relationship during the late Pleistocene, *Science*, 310(5752), 1313–1317.
- Sigman, D. M., and E. A. Boyle (2000), Glacial/interglacial variations in atmospheric carbon dioxide, *Nature*, 407(6806), 859–869.
- Sigman, D. M., M. A. Altabet, R. Francois, D. C. McCorkle, and J.-F. Gaillard (1999), The isotopic composition of diatom-bound nitrogen in Southern Ocean sediments, *Paleoceanography*, 14(2), 118–134.
- Sigman, D. M., et al. (2004), Polar ocean stratification in a cold climate, *Nature*, 428, 59–63.
- Smith, H., et al. (1999), Dual modes of the carbon cycle since the Last Glacial Maximum, *Nature*, 400(6741), 248–250.
- Sowers, T., and M. Bender (1995), Climate records covering the last deglaciation, *Science*, 269, 210–214.
- Sowers, T., M. Bender, D. Reynaud, Y. S. Korotkevich, and J. Orchardo (1991), The δ^{18} O of atmospheric O₂ from air inclusions in the Vostok ice core: Timing of CO₂ and ice volume changes during the penultimate deglaciation, *Paleoceanography*, *6*(6), 679–696.

- Spero, H. J., et al. (1997), Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes, *Nature*, 390, 497–500.
- Steffensen, J. P. (1997), The size distribution of microparticles from selected segments of the Greenland Ice Core Project ice core representing different climatic periods, J. Geophys. Res., 102, 26,755–26,763.
- Stein, M., et al. (2000), Radiocarbon calibration beyond the dendrochronology range, *Radiocarbon*, *42*(3), 415–422.
- Stephens, B. B., and R. F. Keeling (2000), The influence of Antarctic sea ice on glacial-interglacial CO₂ variations, *Nature*, 404, 171–174.
- Street-Perrott, F. A., and P. A. Barker (2008), Biogenic silica: A neglected component of the coupled global continental biogeochemical cycles of carbon and silicon, *Earth Surf. Processes Landforms*, 33, 1436–1457.
- Stuiver, M. (1978), Radiocarbon timescale tested against magnetic and other dating methods, *Nature*, 273, 271–274.
- Stute, M., et al. (1995), Cooling of tropical Brazil (5-degrees-C) during the last glacial maximum, *Science*, 269(5222), 379–383.
- Takahashi, T., et al. (2003), Decadal variation of the surface water PCO₂ in the western and central equatorial Pacific, *Science*, *302*(5646), 852–856.
- Toggweiler, J., J. L. Russell, and S. R. Carson (2006), Midlatitude westerlies, atmospheric CO₂, and climate change during the ice ages, *Paleoceanography*, 21, PA2005, doi:10.1029/ 2005PA001154.
- Toggweiler, J. R. (1999), Variation of atmospheric CO₂ by ventilation of the ocean's deepest water, *Paleoceanography*, *14*(5), 571–588.
- Tréguer, P, and P. Pondaven (2000), Global change: Silica control of carbon dioxide, *Nature*, 486, 358–359.
- Tréguer, P., et al. (1995), The silica balance in the world ocean: A reestimate, *Science*, *268*, 375–379.
- Tsuda, A., et al. (2003), A mesoscale iron enrichment in the western Subarctic Pacific induces a large centric diatom bloom, *Science*, *300*(5621), 958–961.
- Van Campo, E., et al. (1993), A data-based re-appraisal of the terrestrial carbon budget at the last glacial maximum, *Global Planet. Change*, 8, 189–201.
- Varela, D. E., C. J. Pride, and M. A. Brzezinski (2004), Biological fractionation of silicon isotopes in Southern Ocean

surface waters, *Global Biogeochem. Cycles*, 18, GB1047, doi:10.1029/2003GB002140.

- Vettoretti, G., and W. Peltier (2004), Sensitivity of glacial inception to orbital and greenhouse gas climate forcing, *Quat. Sci. Rev.*, 23(3–4), 499–519.
- Volk, T., and M. I. Hoffert (1985), Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO₂ changes, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present, Geophys. Monogr. Ser.*, vol. 32, edited by E. T. Sundquist and W. S. Broecker, pp. 99–110, AGU, Washington, D. C.
- Walker, J. C. G., and B. C. Opdyke (1995), Influence of variable rates of neritic carbonate deposition on atmospheric carbon dioxide and pelagic sediments, *Paleoceanography*, 10, 415–427.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, J. Geophys. Res., 97, 7373–7381.
- Watson, A. J., and A. C. N. Garabato (2006), The role of Southern Ocean mixing and upwelling in glacial-interglacial atmospheric CO₂ change, *Tellus, Ser. B*, 58, 73–87.
- Watson, A. J., et al. (2000), Effect of iron supply on Southern Ocean CO₂ uptake and implications for glacial atmospheric CO₂, *Nature*, 407, 730–734.
- Werner, M., I. Tegen, S. P. Harrison, K. E. Kohfeld, I. C. Prentice, Y. Balkanski, H. Rohde, and C. Roelandt (2002), Seasonal and interannual variability of the mineral dust cycle under present and glacial climate conditions, *J. Geophys. Res.*, 107(D24), 4744, doi:10.1029/2002JD002365.
- Yu, E.-F., et al. (1996), Similar rates of modern and last-glacial ocean thermohaline circulation inferred from radiochemical data, *Nature*, 379, 689–694.
- Zeebe, R. E., and D. Archer (2005), Feasibility of ocean fertilization and its impact on future atmospheric CO₂ levels, *Geophys. Res. Lett.*, *32*, L09703, doi:10.1029/2005GL022449.
- Zeebe, R. E., and D. Wolf-Gladrow (2001), *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*, 346 pp., Amsterdam.

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