Implications of coral reef buildup for the controls on atmospheric CO$_2$ since the Last Glacial Maximum

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[1]   We examine the effect on atmospheric CO$_2$ of the occurrence of increased shallow water carbonate deposition and regrowth of the terrestrial biosphere following the last glacial. We find that contrary to recent speculations that changes in terrestrial carbon storage were primarily responsible for the observed ∼20 ppmv late Holocene CO$_2$ rise, a more likely explanation is coral reef buildup and other forms of shallow water carbonate deposition during this time. The importance of a responsive terrestrial carbon reservoir may instead be as a negative feedback restricting the rate of CO$_2$ rise possible in the early stages of the deglacial transition. This separation in time of the primary impacts of regrowth of the terrestrial biosphere and increased shallow water carbonate deposition explains the occurrence of an early Holocene carbonate preservation event observed in deep-sea sediments. We demonstrate that their combined influence is also consistent with available proxy estimates of deep ocean carbonate ion concentration changes over the last 21 kyr. Accounting for the processes that act on the carbonate chemistry of the ocean as a whole then allows us to place strong constraints on the nature of the remaining processes that must be operating at the deglacial transition. By subtracting the net CO$_2$ effect of coral reef buildup and terrestrial biosphere regrowth from recent high-resolution ice core data, we highlight two periods, from 17.0 to 13.8 kyr and 12.3 to 11.2 kyr BP characterized by sustained rapid rates of CO$_2$ increase (>12 ppmv kyr^{-1}). Because these periods are coincident with Southern Hemisphere "deglaciation," we argue that changes in the biogeochemical properties of the Southern Ocean surface are the most likely cause.   *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4842 Oceanography: Biological and Chemical: Modeling; *KEYWORDS:* carbon dioxide, coral reef, deglacial

1.   Introduction

[2]   Ice cores recovered from the Antarctic ice cap and analyzed for air bubble gas composition reveal that the concentration of CO$_2$ in the atmosphere around 21 thousand years ago (21 kyr BP) and at the height of the Last Glacial Maximum (LGM) was about one third lower than during the subsequent interglacial (Holocene) period [*Delmas et al.*, 1980; *Neftel et al.*, 1982]. More recent, higher sampled resolution ice cores have confirmed the ∼90 ppmv magnitude of this glacial to interglacial CO$_2$ increase [*Flückiger et al.*, 2002; *Monnin et al.*, 2001] (Figure 1a). This also appears to be a robust feature of each of the last (four)

glacial to interglacial transitions for which ice core CO$_2$ data are currently available [*Petit et al.*, 1999]. The nature of the climate-CO$_2$ relationship that this data represents is clearly an important question, not least for the insights it may offer into the future response of the Earth system to anthropogenic forcing. Numerous different hypotheses and mechanisms have therefore been proposed to try and explain this observation (for reviews of some of these, see *Archer et al.* [2000], *Broecker and Henderson* [1998], *Ridgwell* [2001]). However, taken in isolation all have fallen 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 is becoming increasingly clear that the observed glacial-interglacial variability in CO$_2$ must result from a combination of processes operating in conjunction (but not necessarily in phase or even in sign) during the Late Quaternary. The difficulty lies in identifying the mechanisms involved and constraining their relative contribution.

[3]   Although there is still no accepted explanation for the most prominent feature of the ice core CO$_2$ record; the 70−80 ppmv increase associated with the deglacial transition (∼17−11 kyr BP) [*Monnin et al.*, 2001], it is interesting to note attention recently focused on the much smaller and more gradual 20 ppmv rise occurring over the last 7−8 kyr

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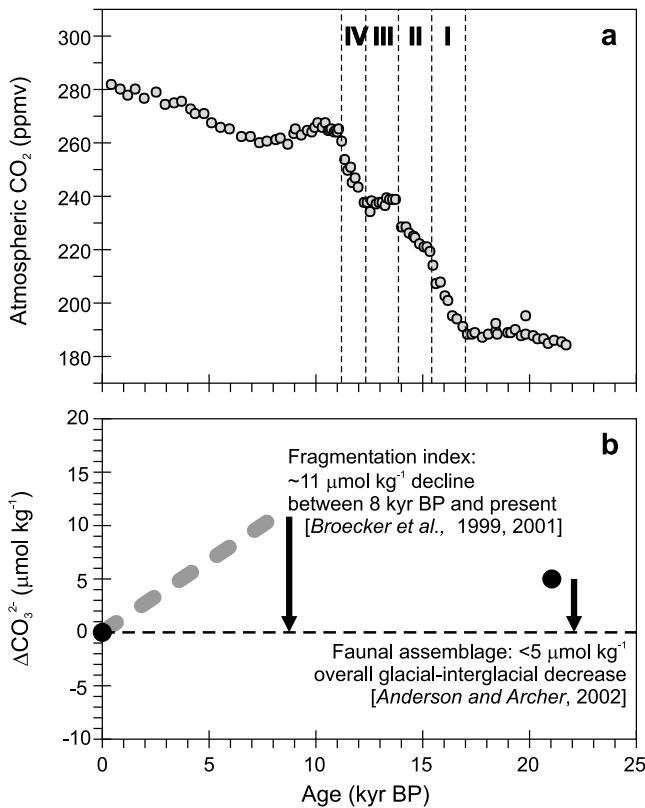
Figure 1. Proxy data for changes in global carbon cycling occurring since the Last Glacial Maximum. (a) Changes recorded in the high-resolution dome C CO_2 record [*Flückiger et al.*, 2002; *Monnin et al.*, 2001]. The four deglacial intervals designated by *Monnin et al.* [2001] are indicated "I" through "IV." (b) Inferred changes in deep-sea (Pacific) carbonate ion concentration. The occurrence of a $\sim$11 μmol kg^{-1} decrease over the last 8 kyr estimated with a foraminiferal size fraction index [*Broecker et al.*, 1999, 2001] is shown as a dotted gray line. The (maximum estimate) -5 μmol kg^{-1} overall LGM to present-day difference based on foraminiferal abundance [*Anderson and Archer*, 2002] is shown as a pair of solid circles. Carbonate ion concentrations are plotted as the deviation from end Holocene (preindustrial) values.

of the Holocene [*Broecker and Clark*, 2003; *Broecker et al.*, 1999, 2001; *Brovkin et al.*, 2002; *Indermühle et al.*, 1999; *Kaplan et al.*, 2002] (Figure 1a). To date, explanations for this particular feature of the CO_2 record have centered on changes in the quantity of carbon stored in the terrestrial biosphere (both vegetation biomass and soil carbon). An important part of the motivation behind this focus then concerns the possibility that the terrestrial biosphere may thus be sensitive to relatively small changes in climate [*Broecker et al.*, 2001; *Broecker and Clark*, 2003], with obvious implications for future global change. One hypothesis, based on inverse modeling of measurements made of the carbon isotopic ($\delta^{13}C$) signature of ice core CO_2, posits a 195 GtC reduction in terrestrial carbon storage since the time of the mid-Holocene climatic optimum ($\sim$8–6 kyr BP)

[*Indermühle et al.*, 1999] associated with a secular cooling and drying trend in the Northern Hemisphere. Although there are no data (specifically of past changes in the global terrestrial carbon inventory) available to either support or refute this, model reconstructions for the late Holocene suggest either a much lower 90 GtC reduction occurred [*Brovkin et al.*, 2002], or that carbon stocks did the opposite, and continued to increase [*Kaplan et al.*, 2002].

[4] A more widely aired explanation is that the CO_2 rise is a consequence of early Holocene ($\sim$11–8 kyr BP) regrowth of the terrestrial biosphere [*Broecker and Clark*, 2003; *Broecker et al.*, 1993, 1999, 2001]. In this scenario, the initial "direct" effect of CO_2 uptake by the rejuvenating terrestrial biosphere, which in itself can only drive a reduction in atmospheric CO_2, is subsequently (partly) ameliorated on a timescale of $\sim$7 kyr through a response induced in the preservation of calcium carbonate ($CaCO_3$) in deep-sea sediments. This is the process of "carbonate compensation" [*Broecker and Peng*, 1987; *Broecker et al.*, 1993], whereby removal of CO_2 from the ocean, by shifting the aqueous carbonate equilibrium; $CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$ [*Zeebe and Wolf-Gladrow*, 2001] to the left to compensate for degassing of CO_2 to the atmosphere, results in an increase in carbonate ion (CO_3^{2-}) concentrations in the ocean. This, in turn, enhances the preservation and burial of $CaCO_3$ in deep-sea sediments because carbonate solubility is inversely related to CO_3^{2-} [*Zeebe and Wolf-Gladrow*, 2001]. Drawdown of oceanic CO_3^{2-} through greater $CaCO_3$ burial rates then leads to a (partial) reversal of the initial atmospheric CO_2 fall.

[5] It is implicitly assumed in this hypothesis that regrowth of the terrestrial biosphere occurs primarily during the early Holocene [*Broecker et al.*, 1993, 1999, 2001]. However, as with the proposed 195 GtC late Holocene decline [*Indermühle et al.*, 1999], there are no data available to directly support or refute the timing and magnitude of the assumed event. Once again, the predictions of terrestrial ecosystem models also do not support the underlying assumptions. Time-dependent reconstruction of the terrestrial biosphere between LGM and preindustrial times [*Kaplan et al.*, 2002] suggests that almost three quarters of the glacial-interglacial magnitude of regrowth occurs prior to the start of the Holocene. This earlier than previously expected response is ascribed primarily to a "CO_2-fertilization" effect on the biota of rising atmospheric CO_2 [*Kaplan et al.*, 2002]. The dominance of a CO_2 control on the terrestrial carbon inventory is supported by the results of other recent model studies [*Otto et al.*, 2002].

[6] As an alternative to changes in the terrestrial biosphere as the explanation for late Holocene CO_2 rise, we introduce a new data-supported hypothesis and revisit the role of coral reef and other forms of shallow water carbonate buildup. Since the LGM there has been a rise in sea level of $\sim$117 m [*Fairbanks*, 1989], which by flooding the continental shelves produced a very substantial (approximately four-fold [*Kleypas*, 1997]) increase in the area of shallow water (neritic) environments; a necessary precondition for coral reef buildup and other forms of shallow water carbonate deposition to occur. By reducing oceanic carbonate ion concentrations, increased rates of $CaCO_3$ deposition will

drive the partial pressure of CO_2 in the surface ocean higher (the aqueous carbonate equilibrium; $CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2HCO_3^-$ driven to the left to compensate for removal of CO_3^{2-} in precipitated $CaCO_3$). On this basis, buildup of shallow water carbonates was once proposed as an explanation for the deglacial rise in atmospheric CO_2 concentrations recorded in ice cores; the "coral reef hypothesis" [*Berger*, 1982a, 1982b]. While early coupled atmosphere-ocean-sediment carbon cycle models confirmed that sea level-driven changes in shallow water carbonate deposition could generate a substantial (60 ppmv or more) increase in atmospheric CO_2 [e.g., *Berger*, 1982a, 1982b; *Munhoven and François*, 1996; *Opdyke and Walker*, 1992; *Walker and Opdyke*, 1995], because atmospheric changes due to this cause must inevitably lag sea level rise contrary to the apparent sequence of events at deglaciation [*Broecker and Henderson*, 1998; *Sowers et al.*, 1991], this particular control on CO_2 received little further attention.

[7] Irrespective of arguments regarding the relative timing of sea level and CO_2 rise, all 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], an interpretation also supported by process-based model studies [*Kleypas*, 1997]. Full understanding of the glacial to interglacial change in CO_2 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 kyr BP, with peak $CaCO_3$ accumulation rates around 5 kyr BP [*Kayanne*, 1992; *Montaggioni*, 2000; *Ryan et al.*, 2001] (Figure 2a). Although this timing is not consistent with the prominent $\sim 70-80$ ppmv CO_2 rise at the deglacial transition as originally envisaged in the "coral reef hypothesis" [*Berger*, 1982a, 1982b], it is, however, contemporaneous with the 20 ppmv rise observed starting at ~ 8 kyr BP [*Flückiger et al.*, 2002; *Indermühle et al.*, 1999]. We therefore explicitly test whether postglacial buildup of shallow water carbonates is a viable explanation (or partial explanation) for the observed late Holocene CO_2 rise. We then go on to examine the role of both this forcing and that of the regrowth of the terrestrial biosphere in the wider context of atmospheric CO_2 changes taking place since the Last Glacial Maximum.

2. Methods

[8] We employ a coupled atmosphere-ocean-sediment carbon cycle model to quantify the effect on atmospheric CO_2 of changes in shallow water carbonate deposition and terrestrial carbon storage. The model is based on a zonally averaged representation of ocean circulation [*Stocker and Wright*, 1996], with biogeochemical cycling and validation against present-day observations described in full in the work of *Ridgwell* [2001] and *Ridgwell et al.* [2002]. However, we include a brief overview of model carbon cycling as follows. Tracers advected in the ocean include dissolved inorganic carbon (DIC), oxygen (O_2), alkalinity (ALK), temperature, and salinity. Of these, CO_2 and O_2 are exchanged with a "well-mixed" atmosphere across the air-
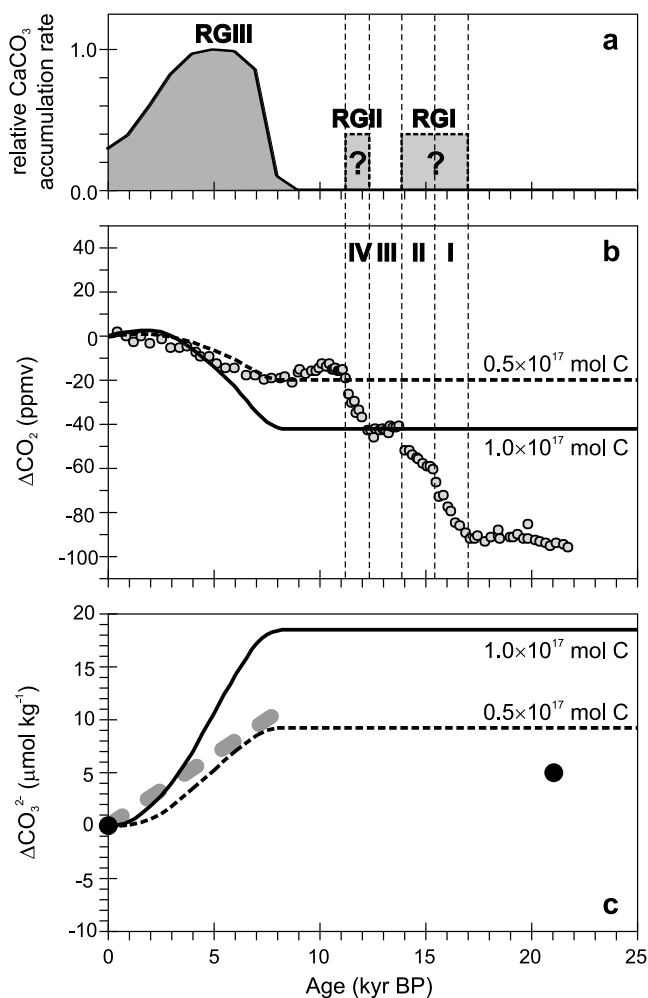

Figure 2. Reconstructed postglacial coral reef buildup and response of the atmosphere-ocean-sediment carbon cycle. (a) Assumed Holocene time history of (relative) coral reef-derived $CaCO_3$ accumulation rates ("RGIII"), shown normalized to a value of 1.0. Also indicated is the likely timing of two minor preceding phases of reef-building ("RGI" and "RGII") [*Montaggioni*, 2000]. (b) Model-predicted CO_2 response to prescribed changes in shallow water carbonate deposition. Shown is the effect of 0.5×10^{17} and 1.0×10^{17} mol C carbonate deposition scenarios (dashed and solid lines, respectively). For comparison, observed CO_2 changes [*Flückiger et al.*, 2002; *Monnin et al.*, 2001] are shown as gray filled circles. In each case, CO_2 is plotted as a change relative to preindustrial values. (c) Model-predicted response of deep equatorial Pacific carbonate ion concentrations. Show is the effect of 0.5×10^{17} and 1.0×10^{17} mol C carbonate deposition scenarios (dashed and solid lines, respectively), with proxy-estimated CO_3^{2-} concentration changes shown for comparison (see Figure 1b for symbol legend). All carbonate ion concentration data are plotted as the deviation from end Holocene (preindustrial) values.

sea interface. Three nutrients potentially limiting to biological activity in the ocean are also considered; phosphate (PO_4), silicic acid (H_4SiO_4), and iron (Fe). Nutrients, together with DIC and ALK, are taken out of solution in

the surface ocean layer through biological action, and exported in particulate form to depth (export of nutrients and carbon in the form of dissolved organic matter is not considered here). Particulate material is subject to remineralization processes as it settles through the water column resulting in the release of dissolved constituent species to the ocean. Material reaching the ocean floor may undergo diagenetic alteration (representing a further release of dissolved species to the ocean) and/or (semi-) permanent burial. To accomplish this, the ocean is everywhere underlain by a series of discrete sediment modules handling ocean-sediment interactions, in which the fractional preservation of biogenic CaCO$_3$ (and opal) reaching the sediment surface is calculated. Thus the buffering response of the deep-sea sedimentary CaCO$_3$ reservoir to changes in overlying ocean chemistry; ''carbonate compensation'' is explicitly and mechanistically accounted for in our model. Loss of material through burial in the sediments is balanced over the long-term by prescribed inputs to the ocean from continental weathering and volcanic/geothermal processes; DIC (20 Tmol C a^{-1}) and ALK (40 Tmol eq a^{-1}) fluxes follow *Walker and Opdyke* [1995] (but omitting terms representing the erosion and formation of sedimentary kerogen), H$_4$SiO$_4$ input (5 Tmol Si a^{-1}) follows *Ridgwell et al.* [2002], and aeolian Fe input (3.0 × 10^9 mol Fe a^{-1}) is derived from model simulated dust fluxes [*Mahowald et al.*, 1999]. It should be noted that the phosphate cycle is ''closed'' and no PO$_4$ input is required. Although the stable isotopes of carbon (^{12}C and ^{13}C) and major fractionation processes between them are treated explicitly in the model, we make no specific δ^{13}C predictions or data-model comparisons in this current study.

[9] Before perturbing the atmosphere-ocean-sediment system by increasing rates of shallow water carbonate deposition and/or transferring carbon to the regrowing terrestrial biosphere, the model is first ''spun-up'' for a period of 100 kyr. This is sufficient time to bring burial of CaCO$_3$ (and opal) in deep-sea sediments into balance with the prescribed input fluxes. Because the global carbon cycle is arguably far from steady state at every point of the glacial-interglacial cycle, perturbing a steady state, particularly of modern conditions, is obviously not an ideal basis for assessing the nature of the observed CO$_2$ variability. However, start from a ''true'' LGM state would require that all changes in the carbon cycle occurring since the penultimate interglacial (Eemian) be taken into account. Because it is the causes themselves that are unknown and under scrutiny, we take the modern system as the point of reference.

[10] To assess whether a revised ''late'' role for enhanced carbonate deposition is consistent with the observed 20 ppmv rising trend in atmospheric CO$_2$, the model is forced with alkalinity and carbon withdrawn from the surface ocean in a 2:1 ratio according to a reconstructed time history of shallow water carbonate buildup. We adopt a recent reconstruction of changes in CaCO$_3$ accumulation in a modern reef system [*Ryan et al.*, 2001] as a template (Figure 2a). Because this is similar in form to previous reconstructions [*Kayanne*, 1992] we have some confidence that our chosen (single reef) reconstruction is representa-

tive. Our assumption is also supported by the dominant control on reef buildup exerted by sea level [*Kleypas*, 1997], first order changes of which being global in scope. Deposition rates are scaled to achieve a value for total Holocene (reef-derived) shallow water CaCO$_3$ accumulation of 1 × 10^{17} mol C [*Kayanne*, 1992]; equivalent to a mean deposition rate over the last 5 kyr of about 12 Tmol C a^{-1}, and consistent with available estimates [*Kleypas*, 1997; *Milliman*, 1993; *Ryan et al.*, 2001]. Two earlier growth phases, occurring around 15 and 12 kyr BP [*Montaggioni*, 2000] (Figure 2a) are much more difficult to quantify, and because of their brevity (both being abruptly terminated by meltwater events) may only have had a minor effect on the global carbon cycle. We therefore take no account of their possible influence, although we note that their timing is coincident with periods of rising CO$_2$ (phases ''I'' + ''II,'' and ''IV'' in Figure 2b).

[11] To assess speculations that the terrestrial biosphere may have driven the observed 20 ppmv late Holocene CO$_2$ rise, we utilize the results of a recent modeling study [*Kaplan et al.*, 2002]. In this, a dynamic vegetation model (DVM) was forced with continuously varying climatic boundary conditions (derived by interpolating between a series of 1 kyr interval time-slice climate reconstructions from 21 to 0 kyr BP) and observed atmospheric CO$_2$. While wholly a model-generated reconstruction (and alternative simulations are possible), in the absence of data with which to constrain the evolving terrestrial reservoir, such model results are an invaluable starting point in understanding the time-dependent response of atmospheric CO$_2$. In the atmosphere-ocean-sediment carbon cycle model, carbon is now withdrawn from the ocean according to the increase in terrestrial carbon storage implied by the reconstruction of *Kaplan et al.* [2002] (Figure 3a).

[12] In addition to ice core records, evidence with which to guide our analysis of the respective roles of shallow water carbonate deposition and regrowth of the terrestrial biosphere is available from deep-sea sediments. Proxy measures have been developed for past changes in ambient carbonate ion concentrations. One, based on analysis of foraminiferal size fractions [*Broecker and Clark*, 1999] suggests an ∼11 μmol kg^{-1} decline in deep-sea CO$_3^{2-}$ concentration over the last 8 kyr [*Broecker et al.*, 1999, 2001]. Another, based on planktonic foraminifer abundance indicates only slightly higher (<5 μmol kg^{-1}) deep Pacific CO$_3^{2-}$ at the LGM compared to present [*Anderson and Archer*, 2002]. These two data sets are shown in Figure 1b. These are not the only possible measures for paleocarbonate ion concentration. The analysis of foraminiferal shell weight [*Broecker and Clark*, 2001] for instance, shows promise. However, unambiguous interpretation of this is problematic [*Barker and Elderfield*, 2002; *Bijma et al.*, 2002]. A potentially useful relationship is also exhibited between ambient *p*H (and thus CO$_3^{2-}$) and the degree of isotopic fractionation between the two stable isotopes of boron (^{10}B and ^{11}B) during the precipitation of calcite in foraminifers [*Sanyal et al.*, 1995, 1997]. Initial benthic reconstructions for the deep Pacific implied a ∼100 μmol kg^{-1} decrease in carbonate ion concentration since the LGM, which is difficult to reconcile with other paleoceanographic
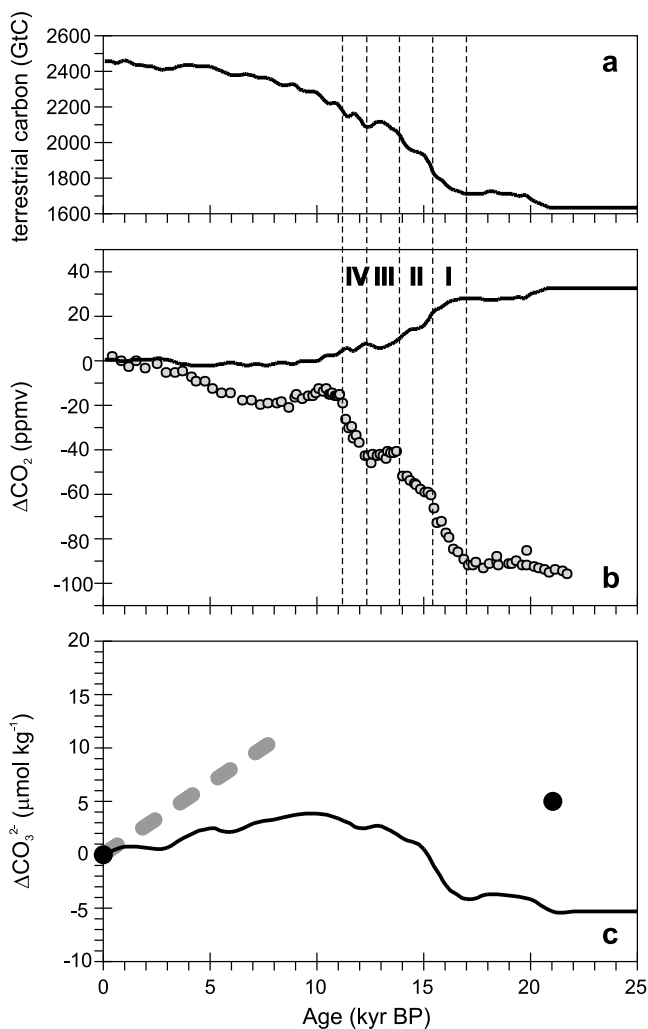
Figure 3. Reconstructed postglacial changes in the terrestrial biosphere and response of the atmosphere-ocean-sediment carbon cycle. (a) Assumed deglacial history of terrestrial carbon storage [*Kaplan et al.*, 2002]. (b) Model-predicted CO_2 response to prescribed changes in terrestrial carbon storage (solid line), with observed CO_2 changes [*Flückiger et al.*, 2002; *Monnin et al.*, 2001] plotted for comparison (gray filled circles). (c) Model-predicted response of deep equatorial Pacific carbonate ion concentrations, with proxy-estimated CO_3^{2-} changes shown for comparison.

observations. We will therefore restrict our attention to paleo CO_3^{2-} estimates based on shell fragmentation and faunal assemblage.

3. Results and Discussion

[13] We find that the onset of higher rates of carbonate deposition has a marked impact on atmospheric CO_2 (Figure 2b), driving a ∼40 ppmv increase after 8 kyr BP. However, the predicted effect is clearly greater than observed. It is possible that the sensitivity of our model is

somewhat overstated; perhaps a consequence of the zonally averaged nature of the ocean configuration [*Stocker and Wright*, 1996] and/or the assumed (modern) steady state initial conditions [*Ridgwell*, 2001; *Ridgwell et al.*, 2002]. It is also possible that current global estimates of Holocene $CaCO_3$ accumulation are too high. For instance, assuming 50% lower $CaCO_3$ deposition rates and total Holocene shallow water $CaCO_3$ accumulation of 0.5×10^{17} mol C (equivalent to a ∼50% reduction in model CO_2 sensitivity) results in model-predicted atmospheric CO_2 now tracking the observed rise rather well (Figure 2b). Alternatively, coral reef buildup might be capable of driving a CO_2 increase of 40 ppmv, but in practice the magnitude of this rise is partly offset by a secondary antagonistic factor. This would be consistent with an important role for increased carbon storage in Northern Hemisphere peatlands, which is known to have occurred during the late Holocene [*Gajewski et al.*, 2001; *Gorham*, 1991; *Laine et al.*, 1996]. This is a component of the global carbon cycle that has received relatively little attention in the context of glacial-interglacial cycles [e.g., *Klinger et al.*, 1996], and is currently not accounted for in terrestrial biosphere reconstructions such as that of *Kaplan et al.* [2002].

[14] Regrowth of the terrestrial biosphere drives an overall 33 ppmv CO_2 decrease since the LGM (Figure 3b). In contrast to assumptions that the impact of this occurs during the early Holocene (∼11–8 kyr BP) [*Broecker et al.*, 1993, 1999, 2001], we find that the major influence on atmospheric CO_2 occurs some five thousand years earlier, and corresponds with a punctuation (between 15.4 and 13.8 kyr BP; "II" in Figure 3b) of the early rapid deglacial CO_2 increase recorded in the dome C ice core [*Monnin et al.*, 2001]. Since dynamic vegetation models ascribe much of the deglacial increase in terrestrial carbon to a "CO_2-fertilization" effect on the biota [*Kaplan et al.*, 2002; *Otto et al.*, 2002], this can be thought of as a negative feedback on CO_2, with the terrestrial biosphere acting (after a lag) to temporarily counter initial ocean-driven increases in atmospheric CO_2. The reason we find little net effect on CO_2 during the late Holocene is because small continuing increases in terrestrial biomass are sufficient to offset the residual $CaCO_3$ compensation remaining from the much earlier primary period of regrowth.

[15] It is noticeable that neither the "coral reef" or terrestrial biosphere mechanisms alone can reproduce the inferred $[CO_3^{2-}]$ history of the deep ocean (Figures 2c and 3c). This negative result is independent of the assumed timing of the reconstructions used. However, forcing the model with both coral reef (0.5×10^{17} mol C carbonate buildup) and terrestrial biosphere carbon cycle perturbations simultaneously we predict a 12 μmol kg⁻¹ decrease in deep-sea $[CO_3^{2-}]$ over the last 8 kyr BP, but only a −3 μmol kg⁻¹ overall change since the LGM. Both forcings combined can therefore explain the available proxy data estimates (Figure 4). In addition, analysis of "historical" sediment composition recorded by the model [*Heinze*, 2001; *Ridgwell*, 2001] reveals a clear deglacial $CaCO_3$ preservation event (not shown) in response to the positive $[CO_3^{2-}]$ anomaly. This is consistent with analyses of changes in bulk sediment composition which indicate the onset around 15 kyr BP of a
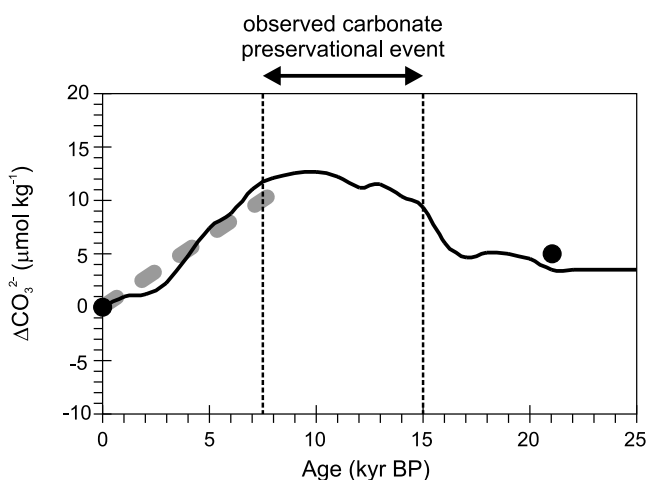
Figure 4. Changes in deep-sea carbonate ion concentration over the deglacial transition. Shown is the model predicted response to a combined forcing of 0.5×10^{17} mol C Holocene carbonate deposition and regrowth of the terrestrial biosphere. Proxy-estimated CO_3^{2-} changes are shown for comparison, as well as the approximate timing of observed deep-sea calcite and aragonite preservation maxima [*Berger*, 1982b; *Broecker et al.*, 1993, 1999, 2001].

period of enhanced preservation [*Berger*, 1982b; *Broecker et al.*, 1993, 2001] followed by a return to markedly lower $CaCO_3$ content in sediments younger than ~8 kyr BP [*Broecker et al.*, 1999, 2001]. We therefore interpret the observed preservation event as a consequence of the two perturbations of deep ocean carbonate chemistry being separated in time; (1) relatively early in the deglacial sequence of events (~16–14 kyr BP), extraction of carbon from the ocean due to regrowth of the terrestrial biosphere drives high $[CO_3^{2-}]$ and thus a strong increase in $CaCO_3$ preservation, (2) later coral reef buildup starting at 8 kyr BP reverses the $[CO_3^{2-}]$ change and carbonate dissolution increases once again.

[16] An alternative explanation for the preservation spike requires a change in the flux ratio of biogenic calcium carbonate to particulate organic carbon (the $CaCO_3$:POC "rain" ratio) delivered to deep-sea sediments [*Archer et al.*, 2000]. This works as follows. An increase in the $CaCO_3$: POC "rain" ratio at the beginning of the deglacial transition, perhaps due to ecological shifts in the surface ocean biota [*Archer et al.*, 2000; *Ridgwell et al.*, 2002; *Ridgwell*, 2003a] would result in a rapid increase in sedimentary carbonate content and global burial rate. The resulting drawdown in ocean carbonate ion concentration taking place on a timescale of ~7 kyr drives gradually increasing rates of sedimentary $CaCO_3$ dissolution until balance is restored between the sources and sinks to the ocean of CO_3^{2-}. The overall result would be to produce a high $[CO_3^{2-}]$ transient in the deep ocean. This "rain ratio" mechanism [*Archer and Maier-Reimer*, 1994] has the additional advantage that decreasing ocean *pH* and CO_3^{2-} could potentially help explain the deglacial CO_2 rise [*Archer and Maier-Reimer*, 1994; *Archer et al.*, 2000]. However, it is difficult to envisage how the "rain ratio" mechanism, which

by itself would drive a postglacial CO_3^{2-} decrease of 29 μmol kg^{-1} [*Archer and Maier-Reimer*, 1994], can be fully reconciled with planktonic foraminifer abundance proxy evidence [*Anderson and Archer*, 2002] (Figure 1b). Furthermore, recent research regarding the potential role of "ballast" minerals in the control of POC export to the deep ocean [*Armstrong et al.*, 2002; *Klaas and Archer*, 2002] casts doubt on whether a sufficient change in the $CaCO_3$: POC rain ratio at the sediment surface can be plausibly achieved in the first place [*Ridgwell*, 2003a]. However, because of the uncertainties inherent in both proxy data and our assumed forcing reconstructions, a role for rain ratio changes cannot currently be ruled out.

4. Implications

[17] We hypothesize that increased shallow water carbonate deposition and the rejuvenation of the terrestrial biosphere are the primary controls on the carbonate chemistry of the ocean as a whole since the LGM. The remaining mechanisms affecting atmospheric CO_2 must then involve the partitioning of carbon between surface and deep ocean (which disproportionately affects the much smaller surface reservoir), and between surface ocean and atmosphere. We highlight the role of what could be considered "surface ocean" mechanisms by subtracting the calculated net effect of the "whole ocean" changes we have discussed from the high-resolution dome C CO_2 record [*Flückiger et al.*, 2002; *Monnin et al.*, 2001] (Figure 5a). One further subtraction is made to form the CO_2 "target" record; the effect of diluting dissolved species in the ocean as a result of the ice sheet melting and sea level rise. By itself this drives a ~14 ppmv decrease since the LGM (but only a minimal −2 μmol kg^{-1} change in CO_3^{2-} concentration).

[18] The early impact of regrowth in the terrestrial biosphere increases the magnitude of the deglacial atmospheric CO_2 increase that other mechanisms must account for at the deglacial transition; rather than an increase of ~77 ppmv between 17.0 and 11.1 kyr BP, we now require 109 ppmv. Furthermore, with the exception of the Bølling/Allerød interval, the rate of increase exceeds 12 ppmv kyr^{-1}; twice the minimum rate exhibited by the raw data (Figure 5b). Relatively few mechanisms have the potential to change atmospheric CO_2 this rapidly, and in a manner which does not lead to significant residual rise occurring during the Bølling/Allerød (13.8–12.3 kyr BP) or extending into (and throughout) the Holocene. For instance, if progressive changes in the oceanic supply rate of any of the phytoplankton nutrients; H_4SiO_4, NO_3^-, or PO_4^{3-} were primarily responsible for the two periods of "rapid" deglacial CO_2 rise (17.0–13.8 and 12.3–11.1 kyr BP), one might expect substantial CO_2 increases continuing after 13.8 and 11.1 kyr BP. This is because they all have a residence time of order >1 kyr. That this is not observed argues against an important role for changes in the oceanic inventories of these nutrients at the deglacial transition. Similarly, for a change in the $CaCO_3$:POC "rain ratio" [*Archer and Maier-Reimer*, 1994; *Archer et al.*, 2000] to be the driver of increasing CO_2, the characteristic time constant of carbonate compensation must be sufficiently short to allow abrupt cessation of rising CO_2 at the start of both the Bølling/Allerød and Holocene.
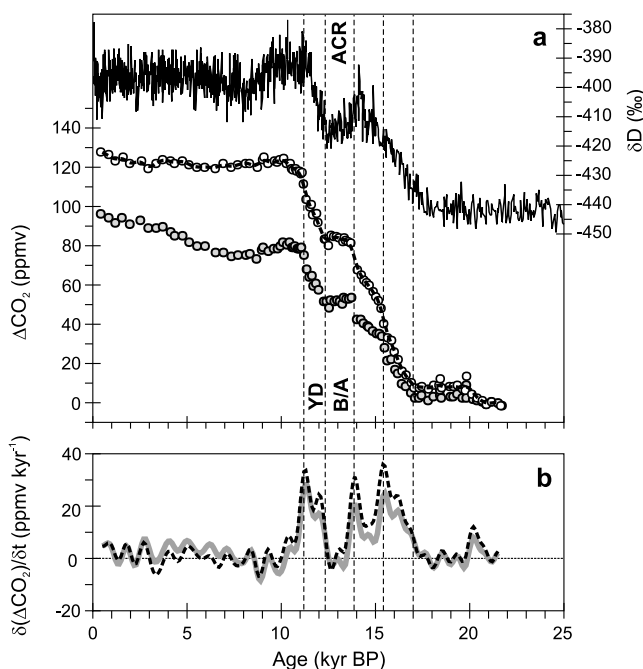
Figure 5. Residual CO$_2$ "target" record to be accounted for by upper ocean processes. (a) Shown are the dome C δD record [*Jouzel et al.*, 2001] (solid curve, top) highlighting the relative timing of the Antarctic Cold Reversal (ACR), Bølling/Allerød (B/A), and Younger Dryas (YD) intervals (assigned after *Monnin et al.* [2001]), observed atmospheric CO$_2$ changes [*Flückiger et al.*, 2002; *Monnin et al.*, 2001] as grey filled circles, and our "residual" CO$_2$ record as empty circles, formed by subtracting the effects of regrowth of the terrestrial biosphere and reef buildup (assuming the lower 0.5×10^{17} mol C carbonate deposition scenario), along with the effect of dilution of dissolved species in the ocean resulting from the melting of the ice sheets and sea level rise [*Fairbanks*, 1989]. Both data sets are now plotted as a change relative to LGM values. It should be noted that to form the CO$_2$ residual, the influences on CO$_2$ of changes in the terrestrial biosphere, neritic carbonate deposition, and sea level are not subtracted individually from the observed record (which would assume a linear, additive response), but by subtracting the results of a model integration with all three forcings acting simultaneously. Shown as a red dotted line in the residual CO$_2$ record interpolated at 0.1 kyr intervals and FFT smoothed, which forms the basis of the rate-of-change curve in Figure 5b. (b) Rate of change of observed (thick gray line) and "residual" (dashed red line) CO$_2$ since the LGM. The timing of the sharp spikes at 13.8 and 11.1 kyr BP, corresponding to discernable "jumps" in observed CO$_2$ record (Figure 5a) appear to be coincident with prominent warming transitions in the North Atlantic (not shown). It is therefore likely that they reflect the effect of Northern Hemisphere ocean surface temperature increases increase, sea ice retreat, and/or a rapid strengthening of the Atlantic overturning circulation. See color version of this figure at back of this issue.

The ~7 kyr adjustment time for this process therefore argues against a significant role for this mechanism.

[19] Possible mechanisms can therefore be constrained to changes in; the control of the biological pump by iron availability [*Bopp et al.*, 2003; *Ridgwell and Watson*, 2002; *Watson et al.*, 2000; *Ridgwell*, 2003b], sea surface temperatures (SSTs) [*Archer et al.*, 2000; *Bacastow*, 1996; *Bopp et al.*, 2003], sea ice cover [*Stephens and Keeling*, 2000], and ocean circulation [*Francois et al.*, 1997; *Sigman and Boyle*, 2000; *Toggweiler*, 1999]. Because the marked cessation of increasing CO$_2$ is associated with the Antarctic Cold Reversal of the Bølling/Allerød (an interval during which the Southern Hemisphere climate experienced a partial reversal toward glacial conditions) rather than the Younger Dryas (when Northern Hemisphere deglaciation reversed), mechanisms in which the Southern Hemisphere dominates are additionally strongly implicated. Higher SSTs since the LGM fulfill both criteria, and can account for 20–30 ppmv [*Archer et al.*, 2000; *Bopp et al.*, 2003].

[20] The predicted effect of decreasing aeolian fluxes of iron to the surface ocean biota is consistent with the timing of the initial CO$_2$ rise [*Ridgwell and Watson*, 2002; *Watson et al.*, 2000] and has its greatest impact in the Southern Ocean, making it an obvious candidate. Experiments carried out both with the present model [*Ridgwell*, 2001, 2003b] and also with a simpler "box" model [*Watson et al.*, 2000] suggest the potential for iron-driven changes in biological export production to account for 30–40 ppmv, although other model studies predict smaller effects [*Archer et al.*, 2000; *Bopp et al.*, 2003]. This leaves a similar portion (~40 ppmv) to be accounted for by reductions in seasonal sea ice limits and/or changes in ocean circulation and mixing. Depending on how ocean circulation is represented, different models give widely varying estimates for the potential effects from these mechanisms. For example, "box"-type models in which upper ocean mixing between water masses is strictly controlled and deep waters contact the surface only in polar regions, give high sensitivity to sea ice [*Stephens and Keeling*, 2000], whereas 3-D general ocean circulation model studies do not reproduce this result [*Bopp et al.*, 2003]. A fundamental difficulty here is that, for numerical reasons, spatially realistic ocean circulation models usually have effective near-surface open-ocean diapycnal mixing rates much larger than observed, with the result that it is not yet possible to positively identify any particular model as having the "correct" response.

5. Conclusions

[21] Working from a data-based hypothesis for environmental changes since the Last Glacial Maximum, we find that the buildup of coral reefs and other forms of shallow water carbonate deposition, rather than changes occurring in the terrestrial biosphere is the more likely underlying cause of the observed rising trend in atmospheric CO$_2$ during the late Holocene. In contrast, the primary effect of the rejuvenating terrestrial biosphere appears to be as negative feedback on early deglacial CO$_2$ rise, and might be responsible for a previously unexplained reduction in the rate of CO$_2$ rise several thousand years prior to the onset of the Bølling/

Allerød. We propose that the occurrence of the ~15–7 kyr BP preservation "spike" observed in deep-sea sedimentary calcium carbonate content is a direct consequence of the separation in time of these two antagonistic perturbations of ocean carbonate chemistry.

[22] The "residual" CO_2 record we have discussed here highlights the existence of a period when "fast" acting mechanisms appear to have driven an increase of almost 110 ppmv in just a few thousand years. While we are unable to quantitatively account for the entirety of this portion of the residual signal, our analysis points to changes in the ocean iron cycle and circulation as critical, particularly with respect to the Southern Ocean.

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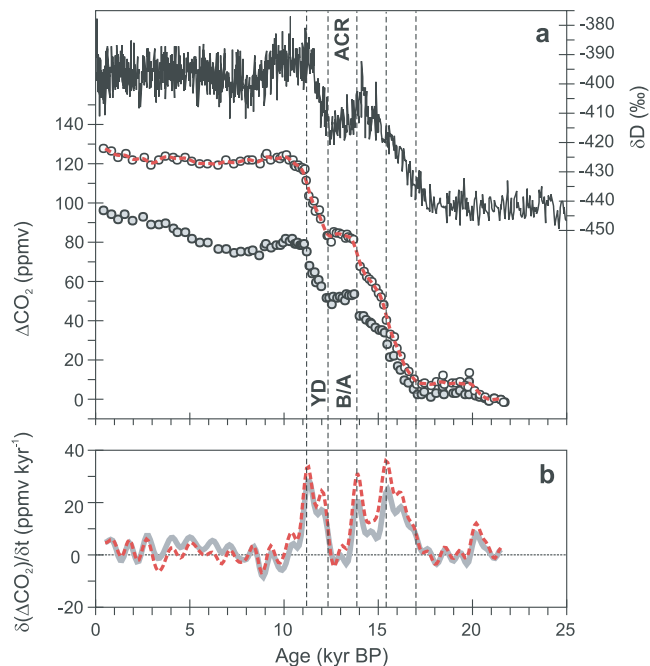
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