



Evidence for elevated alkalinity in the glacial Southern Ocean

R. E. M. Rickaby,¹ H. Elderfield,² N. Roberts,² C.-D. Hillenbrand,³ and A. Mackensen⁴

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[1] An increase in whole ocean alkalinity during glacial periods could account, in part, for the drawdown of atmospheric CO₂ into the ocean. Such an increase was inevitable due to the near elimination of shelf area for the burial of coral reef alkalinity. We present evidence, based on downcore measurements of benthic foraminiferal B/Ca and Mg/Ca from a core in the Weddell Sea, that the deep ocean carbonate ion concentration, [CO₃²⁻], was elevated by ~25 μmol/kg during each glacial period of the last 800 kyr. The heterogeneity of the preservation histories in the different ocean basins reflects control of the carbonate chemistry of the deep glacial ocean in the Atlantic and Pacific by the changing ventilation and chemistry of Weddell Sea waters. These waters are more corrosive than interglacial northern sourced waters but not as undersaturated as interglacial southern sourced waters. Our inferred increase in whole ocean alkalinity can be reconciled with reconstructions of glacial saturation horizon depth and the carbonate budget if carbonate burial rates also increased above the saturation horizon as a result of enhanced pelagic calcification. The Weddell records display low [CO₃²⁻] during deglaciations and peak interglacial warmth, coincident with maxima in percent CaCO₃ in the Atlantic and Pacific oceans. Should the burial rate of alkalinity in the more alkaline glacial deep waters outstrip the rate of alkalinity supply, then pelagic carbonate production by the coccolithophores at the end of the glacial maximum could drive a decrease in ocean [CO₃²⁻] and act to trigger the deglacial rise in pCO₂.

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1. Introduction

[2] Despite nearly three decades of research, an unexplained explanation for the 100 kyr cycle of ~90 ppmv fluctuations in atmospheric carbon dioxide (pCO₂) associated with each glacial-interglacial cycle of the late Pleistocene remains elusive. The smorgasbord of hypotheses rely on a dominant change in either the physical, biological or chemical nature of the glacial Southern Ocean [e.g., Knox and McElroy, 1984; Broecker and Peng, 1989; Elderfield and Rickaby, 2000; Stephens and Keeling, 2000; Matsumoto et al., 2002; Jaccard et al., 2005; Kohfeld et al., 2005; Marchitto et al., 2005; Watson and Naveira Garabato, 2006; Toggweiler et al., 2006].

[3] Almost all models invoke elevated deep ocean carbonate ion concentrations, [CO₃²⁻], and carbonate compensation for part of the glacial CO₂ decrease [e.g., Boyle, 1988; Toggweiler, 1999]. The average ocean [CO₃²⁻] is regulated by the global alkalinity cycle [Broecker and Peng, 1982]. Production of calcite in the surface ocean exceeds the supply rate of alkalinity from rivers, so in order for the alkalinity fluxes to balance, only a fraction of the calcite production

can be removed from the oceans by burial. The burial fraction is controlled by the depth of the carbonate compensation depth (CCD: the horizon beneath which no carbonate is preserved). This CCD is the sedimentary expression of the thermodynamic saturation horizon (the water depth at which Δ[CO₃²⁻] (measured [CO₃²⁻] minus the saturation [CO₃²⁻]) is zero), but lies at greater depth due to the kinetics of dissolution of the pelagic carbonate production. Therefore, while the average ocean [CO₃²⁻] controls the saturation horizon and moves to help maintain an alkalinity balance in the ocean, pelagic carbonate production can ultimately dictate the alkalinity burial from the ocean via its influence on the CCD and therefore holds the potential to drive the deep ocean [CO₃²⁻] and influence pCO₂ [Rickaby et al., 2007].

[4] On timescales of thousands of years the average depth of the CCD is maintained such that the total ocean burial rate of calcite matches the input rate of alkalinity from the rivers. An increase in the pH of the whole ocean, would force a greater burial of carbonate and would drive CO₂ into the ionic forms HCO₃⁻ and CO₃²⁻, decreasing the equilibrium pCO₂ of the atmosphere.

[5] One proposal for increasing ocean pH is the “coral reef hypothesis” [Berger and Keir, 1984; Opdyke and Walker, 1992]. CaCO₃ burial is normally partitioned between shallow, and deep waters, the latter of which is sensitive to ocean pH. Deposition on the continental shelves today is approximately equal to deep sea deposition [Milliman, 1993], although there are major uncertainties in

¹Department of Earth Sciences, Oxford University, Oxford, UK.

²Godwin Laboratory for Paleoclimate Research, Department of Earth Sciences, Cambridge University, Cambridge, UK.

³British Antarctic Survey, Cambridge, UK.

⁴Alfred Wegener Institute, Bremerhaven, Germany.

these estimates [Milliman and Droxler, 1996]. Because sea level dropped below the depth of the continental shelves during glacial time, and because temperatures were colder, carbonate deposition on the shelves all but ceased during the Last Glacial Maximum (LGM) [Kleypas, 1997]. The elimination of shallow-water burial would leave a greater burial load for the deep sea, which would be accomplished in the steady state by increasing ocean pH, and thus deep ocean $[\text{CO}_3^{2-}]$ by the mechanism of CaCO_3 compensation, which acts to draw down $p\text{CO}_2$ by ~ 25 ppm for every 1 km of saturation horizon deepening [Sigman and Boyle, 2000]. However, the coral reef hypothesis has been “shelved” because, despite a deepening of the saturation horizon in the glacial Pacific, it shallowed in the Atlantic such that a spatial time slice reconstruction implies little net change at glacial times [Catubig et al., 1998]. Furthermore, although the re-deposition of carbonate onto the shelves at the deglaciation as sea level rises would act as a positive feedback on the release of CO_2 at the termination by decreasing $[\text{CO}_3^{2-}]$, the sea level rise occurs too late in the deglaciation for this mechanism to trigger the initial rise in CO_2 [Broecker and Henderson, 1998]. Therefore, alternative models, which increase the average $[\text{CO}_3^{2-}]$ within a closed system, have been invoked to explain glacial CO_2 drawdown (i.e., no change in input or output of alkalinity to the ocean system). Either the production rate of calcium carbonate decreased or the dissolution rate increased, as a result of respiration-driven dissolution for example, or there was a transient redistribution of alkalinity and dissolved inorganic carbon (DIC), which required a higher ocean pH to maintain the burial rate in balance with the input of carbonate alkalinity [Archer and Maier-Reimer, 1994; Sigman et al., 1998; Sigman and Boyle, 2000].

[6] There are difficulties in using an LGM time slice to constrain global changes in the saturation horizon. The modern ocean carbonate system bears the imprint of circulation on the steady state carbonate system. It is difficult to capture the intricacies of the slowly responding steady state carbonate system (5–10 kyr) to potentially rapid, transient and spatially varying changes in both hydrography and partitioning of CO_2 between water masses. The majority of time slice data are based on percent CaCO_3 , and therefore subject to dilution and other fluxes, as well as the kinetics of carbonate dissolution.

[7] Changes in the steady state carbonate budget of the ocean can only be determined by reconstructing the global alkalinity (carbonate) flux to the deep ocean or the carbonate accumulation rate out of the deep ocean. Alternatively, changes in the balance will be reflected in the pH, saturation state or $[\text{CO}_3^{2-}]$ of the deep ocean. Here, we use glacial-interglacial changes in the carbonate chemistry of the Weddell Sea as a sensitive monitor of the global deep ocean preservation potential and hence how it modifies carbonate output from the ocean during the glacial cycle. Within this framework we reevaluate the coral reef hypothesis.

2. Study Area, Samples, and Method

[8] The Weddell Sea region of the Southern Ocean is responsible for the formation of 50%–70% of the major

carbon and nutrient rich deepwater mass of the global oceans, Antarctic Bottom Water (AABW) [Orsi et al., 1993, 1999; Naveira-Garabato et al., 2002]. The chemistry of AABW, with an origin in the Weddell Sea, ultimately determines the carbonate chemistry and dissolution rate of calcium carbonate in the deep modern ocean. In the modern ocean, the waters of the Weddell Sea are the most acidic of the global ocean with a pH down to 7.7–7.9 and $[\text{CO}_3^{2-}]$ of 55–70 $\mu\text{mol/kg}$ (Figure 1) based on data from Chen [1984] and a very shallow saturation horizon, at approximately 1100 m. “Old” nutrient- and carbon-rich waters enter the Weddell sea and intense shallow remineralization of organic carbon [Fischer et al., 2000; Usbeck et al., 2002] gives rise to the carbon-charged waters of the central Weddell Gyre, with DIC concentrations >2270 $\mu\text{mol/kg}$. This Central Intermediate Water (CIW) acts as a major source of DIC to the global ocean and is responsible for the highest DIC found at depth in each of the major ocean basins (>2260 $\mu\text{mol/kg}$) [Wanninkhof and Feely, 1998; Hoppema, 2004]. Therefore, abyssal waters sourced from the Weddell Sea are primarily responsible for the global rate of calcium carbonate dissolution by providing the end-member for mixing with other deep waters to create the lowest $[\text{CO}_3^{2-}]$ in each of the deep South Atlantic, deep Pacific and Indian oceans. Any change in their carbonate chemistry should be irrespective of any other water mass influence and will have a profound influence on global carbonate burial and atmospheric $p\text{CO}_2$.

[9] Gravity core PS1506, a repeat of core PS1387, was collected from a mid-slope bench on the continental margin on the southern limb of the Weddell Gyre at 68.73°S, 5.85°W [Mackensen et al., 1994], in the vicinity of cores PS1388 and PS1389 [Grobe et al., 1990; Grobe and Mackensen, 1992]. At these core sites in the Weddell Sea, polynyas enabled continuous primary productivity and benthic life during glacial periods [Mackensen et al., 1996; Thatje et al., 2008]. PS1506 is situated at 2426 m water depth. The core is beneath the depth of the average modern saturation horizon (Figure 2) based on the carbonate chemistry of eastern Weddell Sea waters [Chen, 1984] but above the local CCD [Mackensen et al., 1990]. The site is partly influenced in the modern ocean by CIW, a unique water mass originating in the subsurface of the Weddell Sea, which feeds into the lowest parts of the Antarctic Circumpolar Current and AABW, and is responsible for major carbon sequestration in the deep oceans [Hoppema, 2004]. Stable isotope data from both benthic and planktonic foraminifera and CaCO_3 content have already been published [Mackensen et al., 1994; Thatje et al., 2008] (see also Data Set S1).¹ *N. pachyderma* (s) is the only planktonic foraminifera present, but *Epistominella exigua*, *Oridorsalis umbonatus* and *Cibicidoides* (spp.) can be found as part of the benthic assemblage. The age model for the core was developed by tuning the planktonic $\delta^{18}\text{O}$ to that by Lisiecki and Raymo [2005], incorporating the paleomagnetic constraint of the Brunhes-Matuyama boundary, and is shown in Figure 3a.

[10] Trace metal analyses focused on *Cibicidoides* spp. Ten to fifteen tests were handpicked from the 250–355 μm

¹Auxiliary materials are available at <ftp://ftp.agu.org/apend/pa/2009pa001762>.

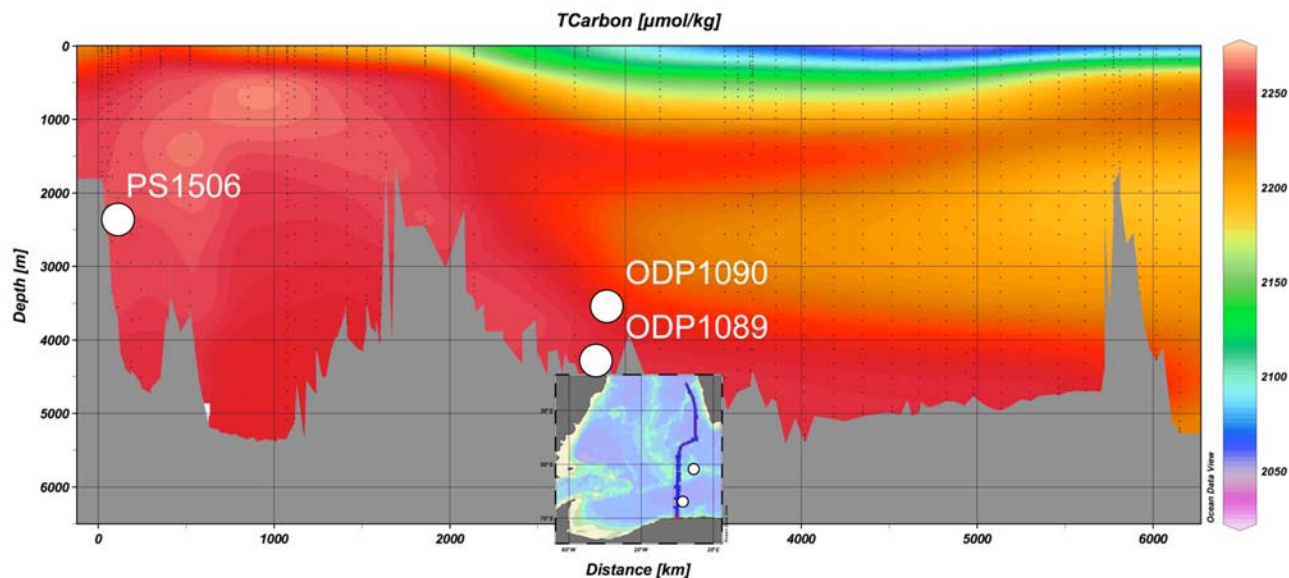


Figure 1. Hydrographic section of total carbon content (TCarbon = $\text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}$ and equivalent to DIC) from WOCE [Schlitzer, 2000] based on data from Hoppema [2004], intersecting the Weddell Sea and the southern ACC with the location of core PS1506 (marked by the white circle) on the southern limb of the Weddell Gyre, close to the site of formation of Central Intermediate Water. Also marked are the locations of ODP Sites 1090 and 1089, discussed in the text, marked with white circles and collapsed onto the longitude of the section. A map showing the location of the transect is inset.

fraction and cleaned by reductive and oxidative procedures [Boyle and Keigwin, 1985]. B/Ca, and Mg/Ca ratios were analyzed by inductively coupled plasma–mass spectrometer (ICP-MS) according to the method described by Yu *et al.* [2005]. By ICP-MS, the B blank is <2% of the consistency standards (B/Ca = 150 $\mu\text{mol/mol}$). When possible, duplicate measurements on the same solution were made. Based on replicate analyses of standard and samples, the precisions are <2.3% (RSD) for B/Ca and <1.4% (RSD) for Mg/Ca. All data are available in Data Set S2 and from the PANGAEA world data center.

3. Results

[11] During each glacial cycle of the last 800 kyr, B/Ca and Mg/Ca of *Cibicidoides* (spp.) show a cyclic behavior with high values at glacial times and low values at interglacial times (Data Set S2 and Figures 4a and 4b). Because there were insufficient *C. wuellerstorfi* for single species analysis of every sample (72% were single *wuellerstorfi* species analysis) we show data for both *C. wuellerstorfi* and *Cibicidoides* spp. The results obtained from mixed species track those for *C. wuellerstorfi* with the former on average lower by roughly 1 mmol/mol Mg/Ca and 15 $\mu\text{mol/mol}$ B/Ca.

[12] It has been demonstrated that B/Ca in benthic foraminifera is a measure of the $[\text{CO}_3^{2-}]$ of bottom waters with a sensitivity of 1.14 $\mu\text{mol/mol}$ per $\mu\text{mol/kg}$ $[\text{CO}_3^{2-}]$ for *Cibicidoides wuellerstorfi* and 0.69 $\mu\text{mol/mol}$ per $\mu\text{mol/kg}$ $[\text{CO}_3^{2-}]$ for *Cibicidoides mundulus* [Yu and Elderfield, 2007]. Benthic Mg/Ca is normally interpreted as a paleothermometer which would indicate that the waters surrounding Antarctica were warmer during the

glacial period by 2°C–3°C. However, it has been shown that epifaunal benthic foraminiferal Mg/Ca is also strongly sensitive to $[\text{CO}_3^{2-}]$ by ~ 0.009 mmol/mol per $\mu\text{mol/kg}$ $[\text{CO}_3^{2-}]$ [Elderfield *et al.*, 2006; Yu and Elderfield,

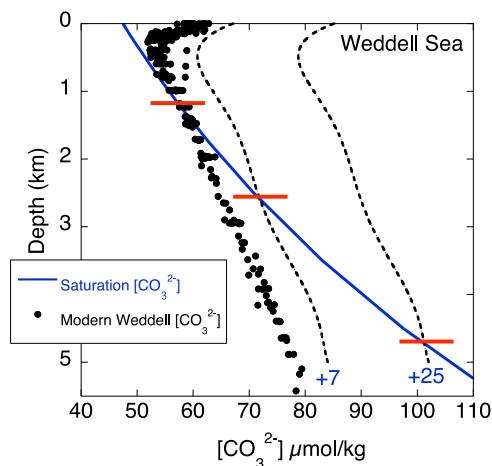


Figure 2. Depth profile of $[\text{CO}_3^{2-}]$ (black dots) at site PS1506 calculated with CO2.sys using data from Chen [1984] compared with the saturation $[\text{CO}_3^{2-}]$ concentration profile (blue line). Profiles corresponding to increases in $[\text{CO}_3^{2-}]$ of 7 and 25 $\mu\text{mol/kg}$ (dashed lines) are shown, and red horizontal lines show the modern saturation horizon at ~ 1100 m and the saturation horizons required for carbonate preservation at the core depth ($[\text{CO}_3^{2-}] \sim +7$ $\mu\text{mol/kg}$) and for the extension of saturation to 4.7 km ($[\text{CO}_3^{2-}] \sim +25$ $\mu\text{mol/kg}$).

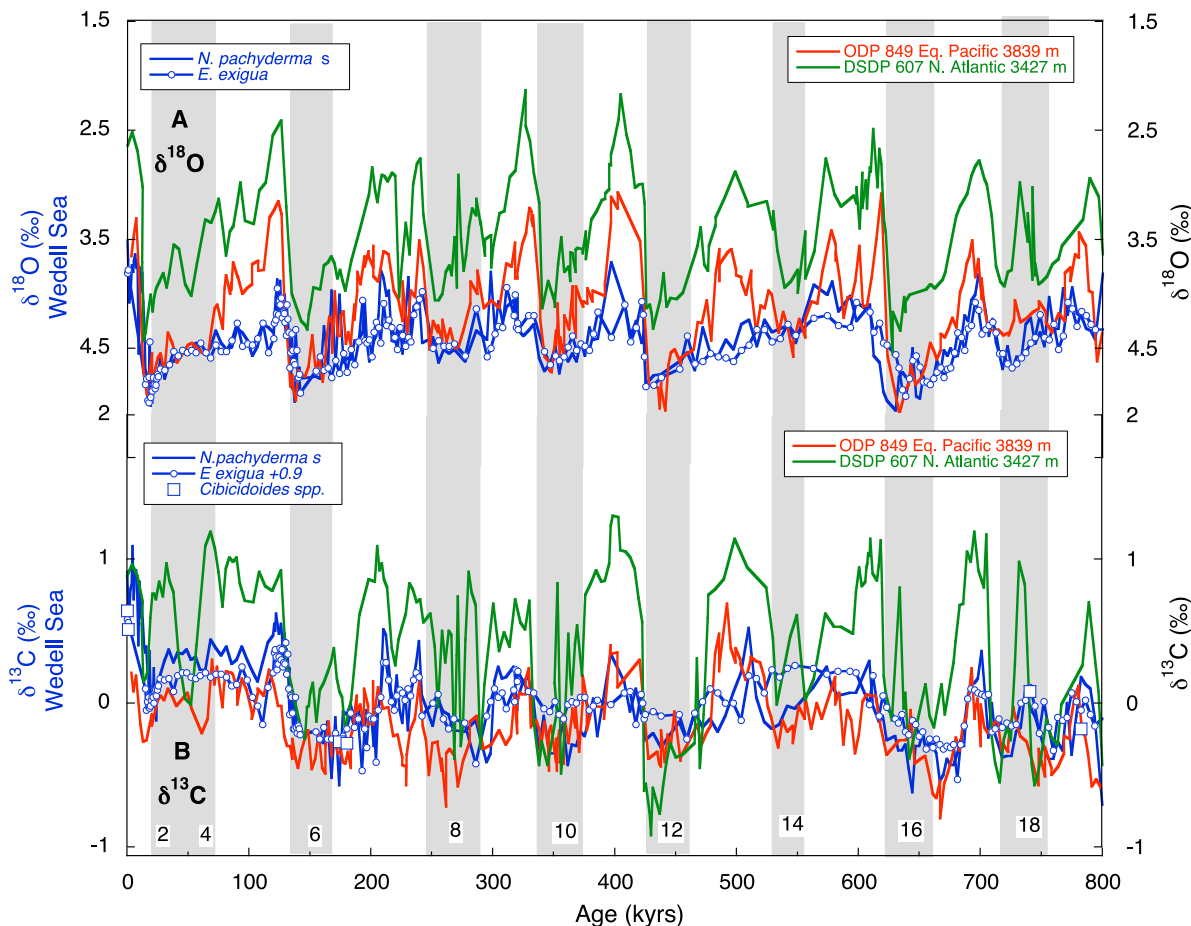


Figure 3. (a) The $\delta^{18}\text{O}$ (‰) records of *Epistominella exigua* (blue line with open circles) and of *Neogloboquadrina pachyderma* s (blue line without symbols) from core PS1506, 68.7°S, 5.85°W (2426 m) and (b) $\delta^{13}\text{C}$ (‰) records of *N. pachyderma* s (blue line without symbols); *E. exigua* (blue line with open circles), corrected by +0.9‰; and *Cibicides* spp. (blue squares) from PS1506 compared with benthic $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records from ODP 849, equatorial Pacific (red), 0°10.98'N, 110°31.18'W (3837 m) in Circumpolar Deep Water [Mix, 2000], and DSDP 607, North Atlantic (green), 41°00'N, 32°57'W (3427 m) in North Atlantic Deep Water [Raymo et al., 1989]. In PS1506, the $\delta^{18}\text{O}$ record of *E. exigua* matches exactly that of *N. pachyderma* s such that the surface-dwelling foraminifera records deepwater conditions in the well-mixed water column of the Weddell Sea. Furthermore, the $\delta^{13}\text{C}$ record of *N. pachyderma* s matches the record of *E. exigua*, known to be offset to lighter values by ~ -0.9 ‰ due to its preference for periods of high seasonal productivity, and the sparse data points of *Cibicides* spp. so they provide a record of Weddell Sea $\delta^{13}\text{C}$ of DIC. Due to the low resolution of the PS1506 benthic $\delta^{18}\text{O}$ record, during the tuning some minor differences have arisen between our age model and the age model recently published by Hillenbrand et al. [2009], but this does not affect the general pattern of glacial-interglacial change. The gray bars identify the glacial periods, and each is labeled with the MIS number.

2008] and that, at the extreme low temperatures of the high-latitude Southern Ocean, variability in concentrations of several trace metals in foraminifera may be largely controlled by variations in $[\text{CO}_3^{2-}]$ [Hendry et al., 2009]. Mg/Ca ratios of planktonic foraminifera have been shown to be sensitive to dissolution [e.g., Brown and Elderfield, 1996; Regenberg et al., 2006]. SEM images show that *Cibicides* spp. from PS1506 appears robust and is well preserved downcore. Dissolution has a minimal influence on the B/Ca content of foraminifera [Yu and Elderfield, 2007] and since there is a good correlation

between B/Ca and the Mg/Ca we rule out dissolution as a major artifact. Furthermore, ion probe analyses have demonstrated that benthic foraminiferal shells are homogeneous in their B content [Kasemann and Schmidt, 2007].

[13] On this basis we have assumed that both B/Ca and Mg/Ca data are a measure of $\Delta[\text{CO}_3^{2-}]$. A number of issues arise in converting elemental data into $\Delta[\text{CO}_3^{2-}]$. In the case of *C. wuellerstorfi* we have converted B/Ca to $\Delta[\text{CO}_3^{2-}]$ using the established calibration for this species. For *Cibicides* spp. we show $\Delta[\text{CO}_3^{2-}]$ based on both the *C. wuellerstorfi* and *C. mundulus* calibrations (Figure 4c).

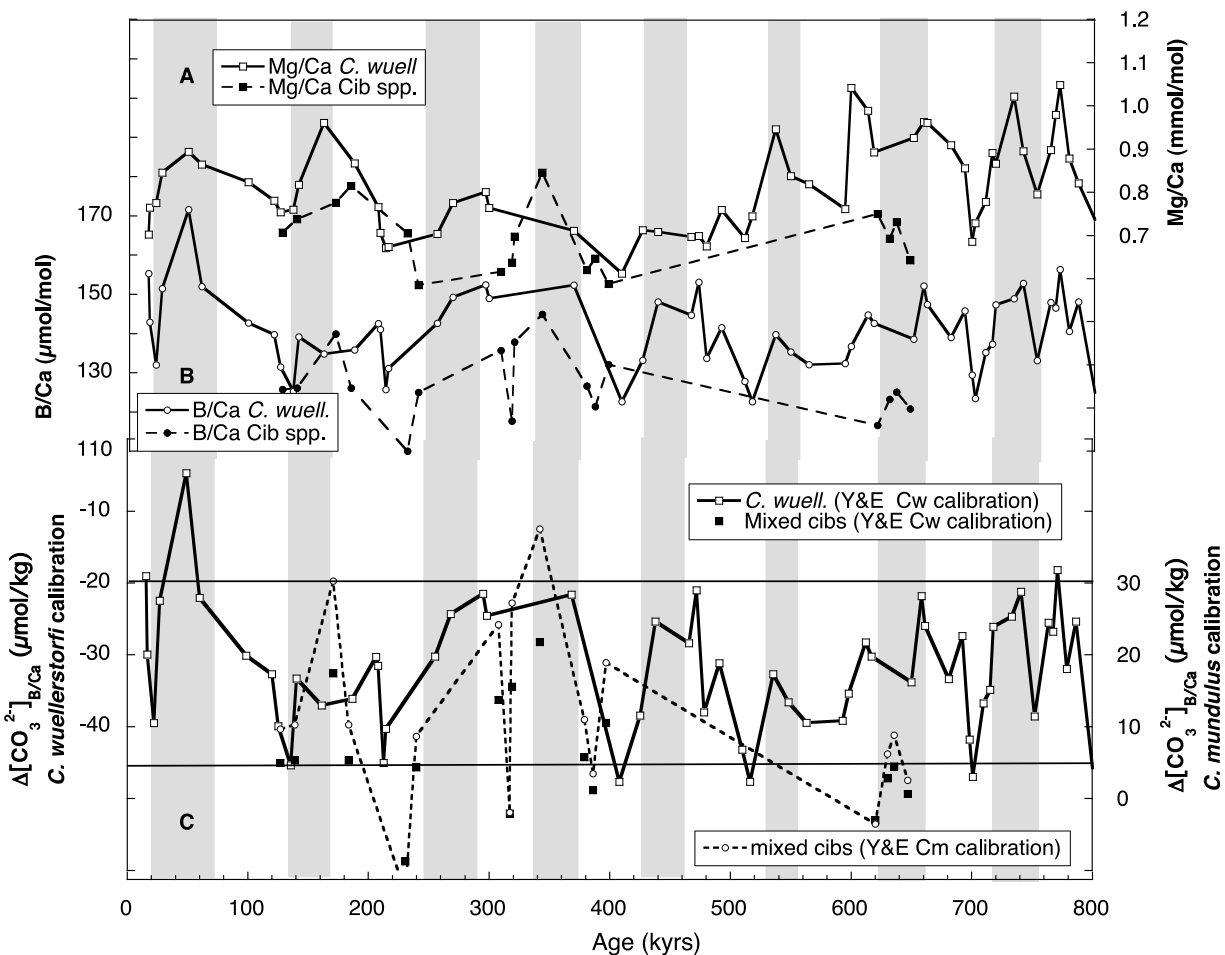


Figure 4. Trace element data from PS1506, Weddell Sea (a) Mg/Ca. Open squares joined by solid lines refer to *C. wuellerstorfi*, and solid squares joined by dashed lines refer to *Cibicidoides* spp. (b) B/Ca. Open circles joined by solid lines refer to *C. wuellerstorfi*, and solid circles joined by dashed lines refer to *Cibicidoides* spp. (c) $\Delta[\text{CO}_3^{2-}]_{\text{B/Ca}}$ derived from B/Ca. Open squares joined by solid lines refer to *C. wuellerstorfi*, and solid squares refer to *Cibicidoides* spp., in both cases using the *C. wuellerstorfi* calibration (Y&E Cw): $\text{B/Ca} = 1.14 \Delta[\text{CO}_3^{2-}] + 177$ [Yu and Elderfield, 2007]. Open circles joined by dashed lines refer to *Cibicidoides* spp., using the *C. mundulus* calibration (Y&E Cm): $\text{B/Ca} = 0.69 \Delta[\text{CO}_3^{2-}] + 119$ [Yu and Elderfield, 2007]. Note the offset between the two ordinate scales. The horizontal lines define the range of -20 to $-45 \mu\text{mol/kg}$ seen in values obtained from the *C. wuellerstorfi* calibration and the range of $+5$ to $+30 \mu\text{mol/kg}$ in values obtained from the *C. mundulus* calibration. The gray bars identify the glacial periods.

Estimated values of $\Delta[\text{CO}_3^{2-}]$ using the *C. wuellerstorfi* calibration show about $5 \mu\text{mol/kg}$ lower values for *Cibicidoides* (spp.), simply mirroring the B/Ca data (Figure 4b). However, the striking feature of data obtained using this calibration is the range in estimated $\Delta[\text{CO}_3^{2-}]$ from -20 to $-45 \mu\text{mol/kg}$: interglacial values are much lower than the modern $[\text{CO}_3^{2-}]$ undersaturation of $-7 \mu\text{mol/kg}$ at the depth of the core site (Figure 2). It would be illogical to apply the *C. mundulus* calibration to *C. wuellerstorfi* data but we have tested *Cibicidoides* (spp.) against this calibration. In contrast, we see $\Delta[\text{CO}_3^{2-}]$ estimated from the *C. mundulus* calibration falls in the range $+5$ to $+20 \mu\text{mol/kg}$, higher than the modern $[\text{CO}_3^{2-}]$ undersaturation of $-7 \mu\text{mol/kg}$ at the depth of the core site. Clearly there is uncertainty to the absolute values obtained

from the *Cibicidoides* spp. specimens in core PS1506 because a mixed species calibration does not exist (and is unlikely to be unique) and there is also uncertainty to the absolute values obtained from *C. wuellerstorfi* specimens because they are so much lower than expected from the modern carbonate saturation at the core site. We have tried to address this problem through examining the consistency of the data set with what is known of the sensitivity of both B/Ca and Mg/Ca to $\Delta[\text{CO}_3^{2-}]$ for the two *Cibicidoides* species.

[14] We estimated $\Delta[\text{CO}_3^{2-}]$ from all the B/Ca using the equation for *C. wuellerstorfi* [Yu and Elderfield, 2007] based on core top data adjusted by a constant to place the average interglacial values at about $-7 \mu\text{mol/kg}$ reflecting

the average modern $[\text{CO}_3^{2-}]$ undersaturation at the depth of the core site in the Weddell Sea (Figure 2) giving

$$\text{B/Ca} = 1.14 \Delta[\text{CO}_3^{2-}] + 135. \quad (1)$$

Next we compared B/Ca and Mg/Ca data. They are significantly correlated ($r = 0.50$, $p < 0.001$), and comparison of Mg/Ca with $\Delta[\text{CO}_3^{2-}]$ estimated from B/Ca gives

$$\text{Mg/Ca} = 0.749 + 0.0058 \Delta[\text{CO}_3^{2-}] \quad (2)$$

a sensitivity of Mg/Ca to $\Delta[\text{CO}_3^{2-}]$ of 0.0058 ± 0.0002 mmol/mol per $\mu\text{mol/kg}$. In comparison, estimates of sensitivity of Mg/Ca to $\Delta[\text{CO}_3^{2-}]$ reported for *C. wuellerstorfi* from core top data [Elderfield et al., 2006] are 0.0087 ± 0.0007 mmol/mol per $\mu\text{mol/kg}$. While not identical, the similarity of the two independently estimated values of Mg/Ca sensitivity to $\Delta[\text{CO}_3^{2-}]$ suggests that the application of the *C. wuellerstorfi* calibration, adjusted to core top undersaturation, is justifiable. When we repeat this exercise using *C. mundulus* we obtain a sensitivity of Mg/Ca to $\Delta[\text{CO}_3^{2-}]$ of 0.0035 ± 0.0007 mmol/mol per $\mu\text{mol/kg}$. This is significantly above zero, whereas it has been found that core top Mg/Ca of *C. mundulus* has zero (or very weak) sensitivity to $\Delta[\text{CO}_3^{2-}]$ [Yu and Elderfield, 2008]. This leads us to prefer the *C. wuellerstorfi* calibration, although we recognize that this exercise has revealed a sensitivity for *C. wuellerstorfi* of 0.0029 mmol/mol per $\mu\text{mol/kg}$ below the core top estimate and a sensitivity for *C. mundulus* 0.0035 mmol/mol per $\mu\text{mol/kg}$ above the core top estimate (of zero). Perhaps a more powerful argument is that were we to ignore the mixed species data we would, naturally, use the *C. wuellerstorfi* calibration for *C. wuellerstorfi* samples and this would require the adjustment to core top undersaturation.

[15] We are more interested in changes in $\Delta[\text{CO}_3^{2-}]$ rather than absolute values and therefore this approach is logical. The use of *Cibicides* (spp.) was necessitated by species availability and the calibration equation based on *C. wuellerstorfi* is the most appropriate choice. Further application of benthic foraminiferal B/Ca may help resolve the calibration issues highlighted here. One issue may well be that of habitat since we are examining a site of overall very low carbonate saturation. Another issue is the viability of core top calibration for infaunal species for which pore water $\Delta[\text{CO}_3^{2-}]$ would be expected to be offset from bottom waters toward zero values such that calibrations should be steeper than implied from core top calibration plots.

[16] To avoid any circularity in estimation of $\Delta[\text{CO}_3^{2-}]$ from Mg/Ca from the approach above, we have used the calibration based on core top data [Elderfield et al., 2006] again adjusted by a constant to place the average interglacial values at about $-7 \mu\text{mol/kg}$ reflecting the modern $[\text{CO}_3^{2-}]$ undersaturation at the depth of the core site

$$\text{Mg/Ca} = 0.749 + 0.0087 \Delta[\text{CO}_3^{2-}]. \quad (3)$$

[17] The records of $\Delta[\text{CO}_3^{2-}]$ derived in this manner from B/Ca and the Mg/Ca (shown with $\delta^{18}\text{O}$ and CaCO_3 from

PS1506 in Figure 5) are broadly very similar in their shape. The low sedimentation rates of core PS1506 and small offsets between B/Ca and Mg/Ca based reconstructions makes precise estimates of timings difficult. However, the principal characteristic of the record of $\Delta[\text{CO}_3^{2-}]$ is of similar strong cyclic behavior over eight glacial-interglacial periods. Within each cycle, $\Delta[\text{CO}_3^{2-}]$ is at its maximum at glacial periods (maxima in $\delta^{18}\text{O}$) and its minimum at interglacial periods (minima in $\delta^{18}\text{O}$). Overall, minima in $\Delta[\text{CO}_3^{2-}]$ (i.e., at each interglacial) based on B/Ca average $-4.9 \pm 5.5 \mu\text{mol/kg}$ and based on Mg/Ca average $-8.4 \pm 6.6 \mu\text{mol/kg}$. Corresponding maxima (at each glacial) average 21.9 ± 7.9 and $16.0 \pm 13.5 \mu\text{mol/kg}$, respectively. The glacial minus interglacial values are $\sim 25 \mu\text{mol/kg}$ ($26.6 \pm 6.2 \mu\text{mol/kg}$ from B/Ca and 24.3 ± 15.3 from Mg/Ca).

[18] The correspondence of high $\Delta[\text{CO}_3^{2-}]$ and glacial maxima is clear at glacial Marine Isotope Stages (MIS) in the Weddell Sea. $\Delta[\text{CO}_3^{2-}]$ decreases during deglaciations reaching minima during peak interglacial warmth after which $\Delta[\text{CO}_3^{2-}]$ increases. Although the similarity in records based on B/Ca and Mg/Ca is striking, the difference between these records, although arbitrary in absolute terms because of the normalization used, is not constant; the estimates based on Mg/Ca are proportionally higher before MIS 12. This may suggest a secondary longer-term embedded influence of temperature on Mg/Ca, also reflected in the higher σ value. Our results correspond to elevated $\Delta[\text{CO}_3^{2-}]$ in southern Weddell Sea deep waters of $\sim 25 \mu\text{mol/kg}$ during the cold phases of the glacial cycles compared to the deglacial transitions and warmest stages of the interglacial periods (Figure 5). Such an increase in $\Delta[\text{CO}_3^{2-}]$ of the Weddell Sea water column, is of a consistent order of magnitude with original estimates of a whole ocean change of $20 \mu\text{mol/kg}$ by Broecker and Clark [2001].

[19] An increase in $\Delta[\text{CO}_3^{2-}]$ of $25 \mu\text{mol/kg}$ predicts an overall shift in carbonate preservation in the Weddell Sea (with an average modern saturation horizon of ~ 1100 m) to greater depth, and up to ~ 4700 m during the cold periods (Figure 2). There is great variability in the modern depth of the Weddell Sea CCD depending on the ventilation and chemistry of different water masses [Mackensen et al., 1990]. We shall use the carbonate chemistry of the waters [Chen, 1984] as an indication of the average Weddell Sea conditions in order to derive a semiquantitative inference about glacial Weddell Sea CCD depth change. We must assume that, in this region, the CCD closely approximates the saturation horizon. This is a reasonable assumption because the modern average saturation horizon of ~ 1100 m (Figure 2), dictated by the water chemistry, is within an estimate of the depth of the CCD, based on sediment observations, between 713 and 1190 m near our core site [Anderson, 1975a, 1975b]. The small vertical carbonate flux appears to be insufficient to offset significantly the CCD from the saturation horizon in the Weddell Sea. Further we must assume that the vertical gradient in $[\text{CO}_3^{2-}]$ remains invariant. This gradient in $[\text{CO}_3^{2-}]$ is largely driven by productivity: the remineralization of organic matter primarily dictates the depth at which the water column becomes

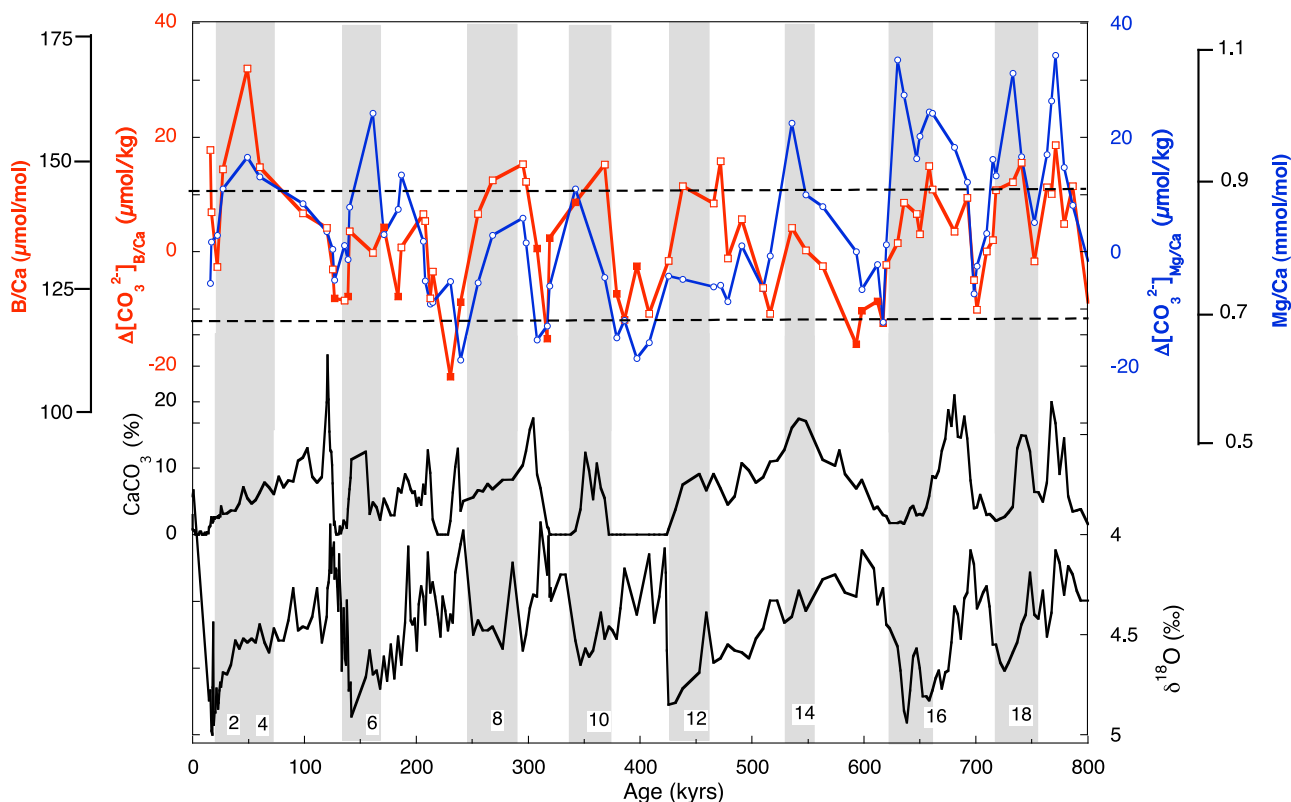


Figure 5. B/Ca (red showing data points as squares: open symbols based on *C. wuellerstorfi* and solid symbols based on *Cibicidoides* spp.) and Mg/Ca (blue with data points as circles) in *Cibicidoides* spp. from PS1506, Weddell Sea, together with $\Delta[\text{CO}_3^{2-}]$ derived from B/Ca and Mg/Ca, derived as discussed in text using $\text{B/Ca} = 1.14 \Delta[\text{CO}_3^{2-}] + 135$ and $\text{Mg/Ca} = 0.749 + 0.0087 \Delta[\text{CO}_3^{2-}]$. The records change largely in parallel with the percent CaCO_3 records from PS1506 (top solid black line), implying that increases in the $\Delta[\text{CO}_3^{2-}]$ in deep waters in the Weddell Sea are responsible for enhanced preservation of carbonate in the Weddell Sea during glacial periods. Also presented is the $\delta^{18}\text{O}$ in *Epistominella exigua* (bottom solid black line) to show the phasing of change in the carbonate system relative to the climate record and the cold glacial stages highlighted in gray. There is a significant long-term trend in Mg/Ca (but not in B/Ca) with age, described by a linear increase to older values of ~ 0.0002 mmol/mol (or $\sim 0.02 \mu\text{mol/kg} \Delta[\text{CO}_3^{2-}]$) per kyr ($r = 0.41$; $p = 0.00013$) or a second-order polynomial fit to the data ($r = 0.59$) with a minimum centered on ~ 400 kyr. The dotted lines represent the average increase in $\Delta[\text{CO}_3^{2-}]$ from interglacial to glacial periods of $\sim 25 \mu\text{mol/kg}$.

undersaturated in the Weddell Sea since the vertical alkalinity gradient is very small. Our core was collected from the present seasonally sea ice covered zone. At this site a polynya enabled biological productivity in surface waters (at least seasonally) even at glacial times [Mackensen et al., 1996; Thatje et al., 2008]. It is reasonable to assume that, to a first order, the vertical $[\text{CO}_3^{2-}]$ gradient remained similar at glacial times. Our PS1506 CaCO_3 record implies that the saturation horizon at the site of PS1506 deepened to at least ~ 2300 m (accounting for 120 m sea level change), requiring a glacial increase in $[\text{CO}_3^{2-}]$ of about $7 \mu\text{mol/kg}$ (Figure 2). Records of CaCO_3 contents [Bonn et al., 1998] and foraminiferal counts in other Weddell Sea cores [Anderson and Andrews, 1999] show that carbonate is preserved at glacial periods down to at least 4200 m water depth. Given our assumptions, qualitatively at least, these sedimentary ob-

servations support an increase in $\Delta[\text{CO}_3^{2-}]$ of similar magnitude to $\sim 25 \mu\text{mol/kg}$ (Figure 2).

4. Discussion

4.1. An Increased Influence of NADW in the Glacial Weddell Sea?

[20] A glacial increase in the $\Delta[\text{CO}_3^{2-}]$ of waters of the Weddell Sea could be interpreted as a greater influence of less corrosive waters from the North Atlantic reaching the Antarctic continental margin. This interpretation is at odds with other proxies which show that the influx of glacial northern sourced waters to the Southern Ocean was reduced greatly [Diekmann et al., 1996, 1999, 2003; Rutberg et al., 2000; Piotrowski et al., 2005; Lynch-Stieglitz et al., 2007]. Indeed, examination of abyssal $\delta^{13}\text{C}$, an indicator of major changes to the pattern of ocean circulation [Mackensen et

al., 1994, 2001; Hodell et al., 2003] show the exact reverse, that there was a greater influence at glacial times of southern sourced waters at more northerly sites and into the Pacific (see discussion in section 4.3.1).

4.2. Alkaline Glacial Waters at the Poles and Global Alkalinity Change

[21] Fluctuations in $\Delta[\text{CO}_3^{2-}]$ of Weddell Sea deep waters largely resemble in timing and direction changes in the percent CaCO_3 content of core PS1506 (Figure 5). Although low-carbonate sediments typical of the Southern Ocean, are sensitive to dilution by other fluxes such as opal or terrigenous input, deposition of carbonate during the cool parts of interglacial periods and during glacial periods was higher than during peak warm times on the Antarctic continental margin in the Weddell Sea [Grobe et al., 1990; Grobe and Mackensen, 1992; Bonn et al., 1998; Anderson and Andrews, 1999; Forsberg et al., 2003]. Thus, in the Weddell Sea, carbonate is better preserved during the cool periods of interglacials and during glacials due to less undersaturated deep waters. These water masses emanate from the Weddell Sea, and therefore may influence the rest of the Southern Ocean (see section 4.3.1). Support for this suggestion comes from sediment cores recovered on the Pacific continental margin of the Antarctic Peninsula, which is influenced by bottom water formed in the Weddell Sea [e. g., Hillenbrand et al., 2008]. These cores show a similar glacial-interglacial pattern in carbonate deposition as those from the Weddell Sea [Pudsey and Camerlenghi, 1998; Pudsey, 2000; Hillenbrand and Fütterer, 2002]. On the Antarctic continental margin, the carbonate deposition during most glacials is lower than during the cool periods of interglacials [Grobe et al., 1990; Grobe and Mackensen, 1992], which can be attributed to an overall decrease in productivity [Shimmiel et al., 1994; Frank et al., 1995; Bonn et al., 1998; Pudsey and Camerlenghi, 1998; Pudsey, 2000; Hillenbrand and Fütterer, 2002].

[22] It is arguable that the high-latitude abyss close to sources of ventilation of deep waters for the rest of the global oceans may provide the best approximation of the steady state carbonate chemistry of the deep glacial ocean since ventilation changes should be minimal close to the source area of deepwater masses. Evidence from the Nordic seas and from North Atlantic sites proximal to inflow of northern sourced waters suggests this is the case. Planktonic foraminiferal shell weight records (a measure of carbonate preservation) in two cores from the Nordic Seas are characterized by the same preservation patterns as the Weddell Sea [Helmke and Bauch, 2002] with deglacial and interglacial dissolution maxima [Henrich, 1986] and enhanced carbonate preservation during the remaining cold periods of the glacial cycle but contrast with the Atlantic and Pacific carbonate histories. Thus, reconstructed $\Delta[\text{CO}_3^{2-}]$ in both the northern and southern high latitudes highlights the deglaciation and the peak interglacial warmth as the periods of the lowest reconstructed $\Delta[\text{CO}_3^{2-}]$. Estimates of bottom water $\Delta[\text{CO}_3^{2-}]$ from B/Ca at sites from 1 to 2 km water depth in the northern North Atlantic are $\sim 20\text{--}30 \mu\text{mol/kg}$ higher at the LGM than during the Holocene [Yu and Elderfield, 2007].

4.3. Influence of Higher-Alkalinity Weddell Sea Waters in the Glacial Deep Ocean

[23] Rationalizing whether the higher-alkalinity waters from the Weddell Sea also control the carbonate chemistry of the rest of the glacial deep ocean requires disentangling of circulation and carbonate production superimposed on “typical” patterns of carbonate preservation history. The Atlantic and Pacific preservation histories prove to be predominantly controlled by changing ocean circulation.

4.3.1. Ocean Circulation

[24] A greater influence at glacial times of Weddell sourced waters at more northerly sites and into the Pacific is exemplified (Figure 3b) by comparison of the record of benthic $\delta^{13}\text{C}$ from the Weddell Sea with those of a site in the deep North Atlantic (DSDP site 607 at 3427 m [Raymo et al., 1989]), and a deep Pacific Site (ODP Site 849 at 3839 m [Mix, 2000]). During the warm stages, there is a $\delta^{13}\text{C}$ gradient between all the core sites, which indicates ventilation, entrainment and aging of water masses from the deep North Atlantic to the Weddell Sea and ultimately the Pacific. At the end of each interglacial period the magnitude of this gradient diminishes markedly, driven in large part by a shift in the heavier deep North Atlantic $\delta^{13}\text{C}$ toward the lighter values of the Weddell Sea and Pacific Ocean. Concurrently, where any interglacial $\delta^{13}\text{C}$ gradient exists between the Weddell Sea and the Pacific Ocean, this gradient is largely eliminated during each glacial period from stage 18 to stage 2. Both the deep Pacific and deep Atlantic records could be interpreted to reflect a greater influence of Weddell Sea deepwater, consistent with a globally reduced ventilation gradient, hence more sluggish passage of deepwater from the Atlantic to the Pacific and a weaker contribution of northern sourced waters to the Southern Ocean at glacial times, as is suggested by changes in the clay mineralogical and geochemical composition of terrigenous and authigenic sediment components [e.g., Diekmann et al., 2003; Piotrowski et al., 2005]. At core sites in the Cape Basin sector of the Southern Ocean, this circulation signal in the isotopic composition of foraminifera tests maybe overprinted by a repartitioning of carbon [Hodell et al., 2003; Piotrowski et al., 2005] independent of circulation which leads to anomalously light benthic $\delta^{13}\text{C}$. Such an overprint may be due to build up of respired carbon in a chemically segregated Southern Ocean reservoir, or an artifact associated with a large flux of organic carbon to the seafloor [Mackensen et al., 1994].

[25] Further suggestion of an increased influence of waters sourced from the Weddell Sea in the rest of the glacial ocean comes from inspection of benthic $\delta^{18}\text{O}$ records (Figure 3a), a proxy which combines temperature and salinity and captures the conservative property, density, of a water mass [Lynch-Stieglitz et al., 1999] at the above sites. During the interglacials, the density of deep waters in the Pacific reflects a mixture of the warm and saline northern sourced waters and the near-freezing but fresh Weddell sourced waters. During each glacial period, the density of the deep Pacific increases to become identical to the saltier glacial waters [Adkins et al., 2002] in the Weddell Sea. While the density difference between the deep Atlantic and

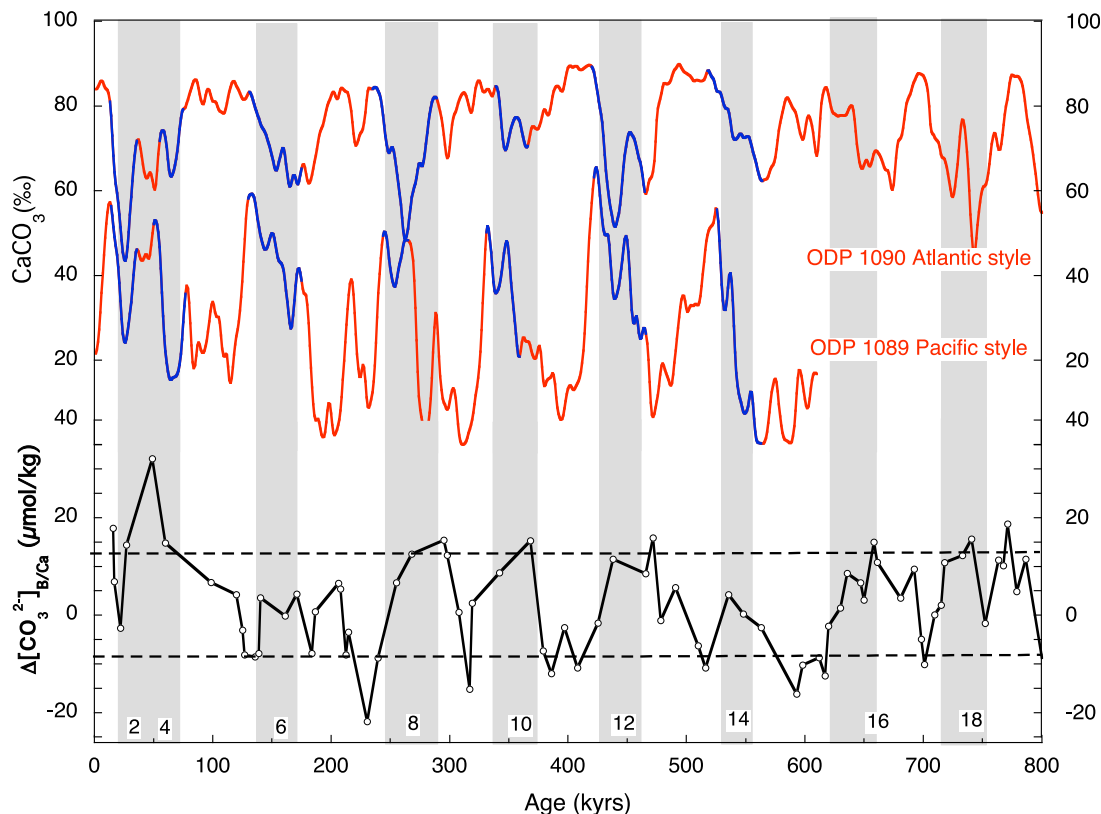


Figure 6. Percent CaCO_3 records in red from ODP site 1090 (top curve) and ODP site 1089 (bottom curve) typical of Atlantic and Pacific preservation, respectively [Hodell *et al.*, 2003], compared with Weddell Sea core PS1506 ΔCO_3^{2-} (black line with open circles). The periods during the glacial periods (marked by gray bars) where the Atlantic- and Pacific-style preservation records coevolve are highlighted in blue. These parallel changes are due to the increased influence of the same Weddell Sea sourced waters in each of these deep ocean basins at glacial times. The influence of the increased extent of the higher glacial alkalinity Weddell Sea waters is to reduce glacial preservation in the Atlantic relative to the interglacial baseline but increase glacial preservation in the Pacific relative to the interglacial baseline.

the Weddell Sea is diminished during the glacial periods indicative of a greater influence of southern sourced waters, likely from the Weddell Sea, the whole Atlantic remains either warmer or fresher than the rest of the deep glacial ocean. Coupled with the $\delta^{13}\text{C}$ evidence, deep waters originating from the Weddell Sea appear to play a major role in the deep glacial ocean. Weddell sourced waters at glacial times have an increased influence on the deep Atlantic and flush the entire deep Pacific. An increase in Weddell Sea alkalinity will therefore exert an influence on carbonate preservation in a large proportion of the deep glacial ocean.

4.3.2. Typical Atlantic- and Pacific-Style Percent CaCO_3 Records

[26] In order to demonstrate how the higher-pH Weddell Sea waters influence carbonate preservation in the glacial ocean, we have selected two “typical” oceanic sites from the many cores which show identical “Atlantic-style” (high percent CaCO_3 with light $\delta^{18}\text{O}$ found in the deep North and intermediate depth South Atlantic) or “Pacific-style” (high percent CaCO_3 with heavy $\delta^{18}\text{O}$ found in the deep Indian,

Pacific and deep Southern Ocean) histories. Cape Basin ODP Site 1090 provides a typical Atlantic preservation history [Hodell *et al.*, 2001] and Site 1089 a typical Pacific preservation history [Anderson *et al.*, 2008]. The Atlantic and Pacific are considered out of phase over glacial interglacial cycles with the major changes in carbonate preservation occurring between cooler and warmer periods (Figure 6). The higher carbonate content of deep Pacific, Southern and Indian Ocean sediments [Farrell and Prell, 1989; Hodell *et al.*, 2001; Anderson *et al.*, 2008] during glacial periods has been attributed to better preservation by higher- $[\text{CO}_3^{2-}]$ waters and the lower carbonate content of deep Atlantic sediments during glacial periods has been attributed to replacement of deep northern sourced water by southern sourced waters. We note that cores from the Southern Ocean show either Atlantic- or Pacific-style carbonate histories. In particular, shallower sediment cores from the northern Antarctic Zone and the Polar Frontal Zone show highest carbonate deposition and preservation during peak warm times [e.g., Howard and Prell, 1994; Diekmann,

2007]. The style of percent CaCO_3 record is the sedimentary expression of the preservation history relative to an interglacial “baseline” and depends on the *relative* change in the $\Delta[\text{CO}_3^{2-}]$ of the waters at that site so is sensitive to the changing water mass as well as how the chemistry of that water mass evolves.

[27] During interglacial periods, the percent CaCO_3 records of Atlantic preservation history (Site 1090) show high carbonate preservation because of the influence of the higher-alkalinity northern sourced waters. During the same periods Pacific preservation is low (Site 1089). The deep South Atlantic (Site 1089) is decoupled from any influence by Weddell Sea sourced waters during interglacial periods since evidence from the modern ocean shows that this site is exclusively flushed by waters sourced from the low-alkalinity Lower Circumpolar Deep Water (LCDW), while Site 1090 is located at the boundary between high-alkalinity lower NADW and LCDW [Hodell *et al.*, 2001, 2003]. The true abyssal waters sourced from the Weddell Sea are constrained by the ridge systems to remain proximal to Antarctica during interglacial periods and only escape through a deep gap in the South Scotia Ridge into the Argentine, Brazil, Mozambique, and Crozet basins to the north [Orsi *et al.*, 1999; Naveira-Garabato *et al.*, 2002] with a minimal influence at Site 1089. Thus, interglacial preservation patterns reflect the proportionally greater influence of the higher-alkalinity northern sourced waters (NADW) at Site 1090 and indicative of Atlantic wide patterns, compared to the greater influence of the lower-alkalinity waters sourced from pure LCDW at Site 1089, indicative of conditions in the deep Pacific and Indian oceans [Hodell *et al.*, 2003].

[28] During glacial periods the percent CaCO_3 records of both Atlantic and Pacific preservation history show an increased influence of southern sourced waters. However, the influence in the Atlantic is to reduce preservation whereas in the Pacific it is to increase preservation. The waters sourced from the Weddell Sea escape to the north (as discussed in section 4.3.1), independently or through increased entrainment in Glacial LCDW to influence the deep Atlantic, deep Indian and deep Pacific (Figures 3 and 6). In the Pacific and Indian oceans, the greater influence of the higher-alkalinity glacial Weddell Sea water compared with lower-alkalinity LCDW increases preservation. In the Atlantic, the greater influence of the higher-alkalinity Weddell water compared with even higher-alkalinity northern sourced deepwater of the interglacial decreases preservation. That the same water mass from the Weddell Sea influences the entire deep ocean during the glacial periods and controls the glacial carbonate preservation is reflected by parallel increases in percent CaCO_3 records through the glacial periods at Atlantic- and Pacific-style sites (Figure 6).

[29] Thus the heterogeneity of the carbonate preservation histories in the different ocean basins reflect control of the carbonate chemistry of the deep glacial ocean in both the Atlantic and Pacific by the waters sourced from the Weddell Sea. While these glacial southern sourced waters are more corrosive than interglacial northern sourced waters (hence the poorer preservation in the deep Atlantic relative to the interglacial), our data from core PS1506 suggest that during glacial periods the southern sourced waters were not as

undersaturated as during peak interglacials. This is also suggested by data presented by Volbers and Henrich [2004], Anderson and Archer [2002] and Yu and Elderfield [2008]. The low $[\text{CO}_3^{2-}]$ characterizes the Weddell Sea during deglacial transitions and peak interglacial warmth. Although the record from the Weddell Sea is not high resolution, there is an indication that alkalinity increases here during the interglacial after the peak warmth, but the circulation change with invasion of the global deep ocean by an increased influence of Weddell Sea water does not take place until the interglacial-glacial transition (Figures 3 and 5).

[30] What could have caused the increase in $\Delta[\text{CO}_3^{2-}]$ in glacial waters of the Weddell Sea? The corrosive, carbon-charged nature of the modern Weddell Sea waters is due in part to almost complete remineralization of export flux at shallow depth in the Weddell Gyre [Hoppema, 2004], and in part because the supply of waters to the Weddell Sea is rich in DIC and nutrients which remain unutilized in the Weddell Sea before returning as “preformed” nutrients to the deep ocean. A decrease in organic matter remineralization efficiency, or a shift to the production of more calcifiers which dissolve and transport alkalinity to the shallow depths of the Weddell Gyre which ventilate the rest of the deep ocean could result in the 25 $\mu\text{mol/kg}$ increase in $\Delta[\text{CO}_3^{2-}]$ in the Weddell Sea. Alternatively, an increase in $\Delta[\text{CO}_3^{2-}]$ could arise as a result of increased sea ice formation which raised both the conservative properties of the salinity and alkalinity of the Weddell Water, and was associated with increased uptake of DIC by organic matter production [Bakker *et al.*, 2008], or as a result of increased dissolution of carbonate associated with sea ice formation such as ikaite [Dieckmann *et al.*, 2008]. Another option is that the nutrient and DIC rich deep waters which enter the modern Weddell Sea had an increased Alk:DIC ratio at glacial times, or gain an increased Alk:DIC ratio through increased air-sea exchange and carbon loss to the atmosphere with higher glacial wind velocities across polynyas during transit through the Weddell Sea. The increased alkalinity and $[\text{CO}_3^{2-}]$ of these waters then spills northward to fill the deep Atlantic and deep Pacific making the global deep ocean more alkaline. One further possibility is that the switch in ocean circulation to an increased extent of Weddell Sea water in the abyssal glacial Atlantic Ocean means that these corrosive, carbon-charged waters encountered carbonate-rich sediments deposited during the previous interglacial period, and elevated the dissolution rate of any carbonate particles raining into the water mass over the larger proportion of the global oceans [Toggweiler, 1999]. While the short-term response in the Atlantic to such an invasion of Weddell Sea waters is one of dissolution, like the rain ratio hypothesis a globally elevated deep dissolution rate of carbonate must result ultimately in a raised $\Delta[\text{CO}_3^{2-}]$ in this deep water mass in order to maintain the steady state alkalinity balance of deep carbonate burial.

4.4. Whole Ocean Increase in Alkalinity During the Glacial Period

[31] The Weddell Sea is also a sensitive monitor to a whole ocean alkalinity increase. Since it is the end-member of low $[\text{CO}_3^{2-}]$ in the modern ocean, then any increase in

whole ocean alkalinity should be reflected first in the Weddell Sea chemistry. Assuming our reconstructed $\Delta[\text{CO}_3^{2-}]$ reflects a change in the steady state chemistry of the glacial deep ocean, the inferred increase in $\Delta[\text{CO}_3^{2-}]$ of the glacial Southern Ocean implies that the global ocean was more alkaline and absorbed more CO_2 from the glacial atmosphere. A rise in deep ocean $[\text{CO}_3^{2-}]$ of $\sim 25 \mu\text{mol/kg}$ could be consistent with a number of scenarios.

[32] First, in a closed system which experiences no change in the flux of alkalinity into the ocean, a rise in deep ocean $[\text{CO}_3^{2-}]$ is consistent with a decrease in carbonate production by pelagic calcifiers or a change in the rain ratio. If less alkalinity is precipitated into calcite rain, then to maintain a burial of carbonate alkalinity in balance with the flux of carbonate alkalinity into the ocean, it is necessary to preserve a greater proportion of the calcite rain by increasing the $[\text{CO}_3^{2-}]$ in the deep ocean. This scenario draws down CO_2 in two ways: a decrease in carbonate production raises the $[\text{CO}_3^{2-}]$ of the surface waters and the increase in $[\text{CO}_3^{2-}]$ of the deep ocean also titrates $p\text{CO}_2$ to depth. Alternatively, decreasing the $\text{CaCO}_3:\text{C}_{\text{org}}$ ratio of the pelagic rain [Archer and Maier-Reimer, 1994] or the partitioning of respired carbon to a segregated water mass at depth [Boyle, 1988; Toggweiler, 1999] drives a higher rate of CaCO_3 dissolution, which also requires a higher ocean pH to compensate. Near-glacial $p\text{CO}_2$ can be generated, in box models, by doubling the opal flux which results in increasing deep ocean $[\text{CO}_3^{2-}]$ by $\sim 20 \mu\text{mol/kg}$.

[33] Second, in an open system scenario, an increase in deep ocean $[\text{CO}_3^{2-}]$ of $\sim 25 \mu\text{mol/kg}$ could account for $\sim 50\%$ of LGM $p\text{CO}_2$ drawdown accounting for reduced deposition of carbonate alkalinity from the glacial ocean onto the restricted area of the shelves and an additional alkalinity input from the weathering of exposed coral reefs [Opdyke and Walker, 1992; Walker and Opdyke, 1995]. All else being equal, a rise in $[\text{CO}_3^{2-}]$ of $25 \mu\text{mol/kg}$ would equate to a CCD deepening of $\sim 1\text{--}1.5 \text{ km}$ [Archer et al., 2000] which may be reconcilable within the large uncertainties of the reconstructions of the glacial CCD [Catubig et al., 1998].

[34] If we invoke this coral reef hypothesis, however, there is a problem with our reconstructed magnitude. Shallow water deposition, responsible for an estimated 50% of the alkalinity output from the modern ocean was nearly shut down during the LGM [Kleypas, 1997]. A shift of carbonate deposition from the shelf to the deep ocean implies that for the glacial steady state, there should be an LGM accumulation rate of at least double the modern day pelagic accumulation rates. As the average CCD sits at $\sim 4 \text{ km}$ in the modern ocean and 50% of the modern ocean floor is beneath 4 km, it follows that, in order to accommodate this doubling of carbonate accumulation, the CCD would drop at least 2 km (to the bottom of the ocean), consistent with an increase in whole ocean $[\text{CO}_3^{2-}]$ of $40 \mu\text{mol/kg}$ (nearly double our reconstructed value) and allow ubiquitous carbonate accumulation.

[35] There are three ways to reconcile this mismatch in the magnitude of our resultant change in $[\text{CO}_3^{2-}]$ compared to that predicted from the coral reef alkalinity change. Either the current shelf carbonate accumulation rate is over-

estimated globally [Milliman, 1993], but the ongoing discovery of significant additional sources of shelf carbonate production such as *halimeda* bioherms [e.g., Rees et al., 2007] makes this unlikely. Alternatively, the ocean DIC pool may increase in concert with the transfer of coral reef alkalinity and DIC (in a 2:1 ratio) and offset a fraction of the rise in $[\text{CO}_3^{2-}]$ yielding a resultant increase of $25 \mu\text{mol/kg}$ in $[\text{CO}_3^{2-}]$. The ocean DIC could rise due to the transfer of $\sim 500 \text{ PgC}$ of organic carbon from the shelves or the terrestrial biosphere [Sigman and Boyle, 2000] but it is unknown whether such a transfer occurs as pulses (with transient phases of dissolution) or is ongoing during the increasingly severe glacial conditions. A transfer of 10 kyr of shelf alkalinity accumulation (29×10^{16} moles) to the ocean with an alkalinity:DIC ratio of 2:1 yields a net rise of $[\text{CO}_3^{2-}]$ of $\sim 80 \mu\text{mol/kg}$, whereas the transfer of 500 PgC organic carbon yields a decrease in carbonate ion of $\sim 55 \mu\text{mol/kg}$ due to the rise in DIC alone.

4.5. Biological Calcification Feedback

[36] Alternatively, an increase in pelagic carbonate accumulation above the saturation horizon, due to increased pelagic carbonate production, could act as a part substitute for the burial of this additional coral reef alkalinity. Indeed, an increase in the $\text{CaCO}_3:\text{C}_{\text{org}}$ production ratio provides the optimal solution to the inverse multiparameter modeling of the glacial carbon cycle [Heinze and Hasselmann, 1993]. Since the Atlantic comprises only 15% of the total ocean area, the general pelagic carbonate accumulation rate (as indicated by Pacific-style preservation) was likely higher in the glacial ocean as we suggest earlier. Halving the glacial flux of carbonate in the Atlantic [Francois et al., 1990] is more than compensated by the up to 6 times greater glacial carbonate accumulation rates in the Pacific [Anderson et al., 2008]. However, this mechanism requires a natural response and feedback of increasing surface ocean carbonate production with sea level and $p\text{CO}_2$ fall with increasing alkalinity or transfer of DIC to the oceans during the growth of the ice sheets. Certainly, pelagic calcifiers such as planktonic foraminifera [Barker and Elderfield, 2002] and some species of coccolithophore [Beaufort et al., 2008; Riebesell et al., 2000] increase their degree of calcification as waters become more alkaline as well as shifting toward assemblages dominated by larger more heavily calcified forms [Colmenero-Hidalgo et al., 2002]. The pelagic alkalinity flux to the deep ocean and burial above the saturation horizon could increase to substitute for the coral reef alkalinity without a change in phytoplankton composition. There is also a general pattern of increasing carbonate nannofossil accumulation rates [Flores et al., 2003] and alkenone-producing coccolithophores [Rickaby et al., 2007] during the cold periods in the Southern hemisphere, to peak accumulation rates on the deglacial transitions while interglacials are characterized by low coccolithophore accumulation rates and occasionally barren intervals. Of course, should the increased alkalinity from coral reefs be completely matched by increased pelagic carbonate production the effect on $p\text{CO}_2$ would be zero.

4.6. A Deglacial Alkalinity Hypothesis

[37] A feature of each carbonate cycle is exceptional deglacial and peak interglacial corrosive waters in the Weddell Sea (minimum percent CaCO_3 and $\Delta[\text{CO}_3^{2-}]$) which are coincident with maximal percent CaCO_3 in both the Atlantic and the Pacific oceans (Figure 6). While the broad glacial Pacific preservation pattern may originate from the Weddell Sea, such a mismatch toward the end of glacial maxima and into the terminations hints that generally increased pelagic carbonate productivity could be exerting an influence on ocean carbonate chemistry and the Weddell $\Delta[\text{CO}_3^{2-}]$ record. Toward the end of the LGM, the pelagic alkalinity burial rate (carbonate production) may outstrip the rate of alkalinity supply (decreased shelf area and weathering/diagenesis of shelf carbonates) to the ocean. This is evidenced by increasing nannofossil accumulation rates throughout the cold periods, with a peak on the deglaciation which is coincident with a deglacial dissolution peak. This would result in a decrease in deep ocean $[\text{CO}_3^{2-}]$ (first sensed in the sediments in areas of lowest $[\text{CO}_3^{2-}]$ such as the Weddell Sea) and could trigger the release of CO_2 at the deglaciation. Within the uncertainties of the modern carbonate budget, a doubling of “overproduction” and burial of calcite relative to the supply rate of alkalinity could yield a drop in deep ocean $[\text{CO}_3^{2-}]$ of 10–20 $\mu\text{mol/kg}$ and an increase in $p\text{CO}_2$ of 10–25 ppm [Zeebe and Westbroeck, 2003; Sigman et al., 1998]. This hypothesis implies that deep ocean $[\text{CO}_3^{2-}]$, hence the saturation horizon, is not just a passive responder to, e.g., weathering, but may, at times, be actively driven by the pelagic production of carbonate which exerts a greater influence on deep ocean alkalinity burial through the depth of the CCD.

[38] Further, we postulate that the high- $p\text{CO}_2$ interglacial periods (e.g., MIS 5.5 and today) could arise from the resultant nonsteady state in the carbonate system. The low deep ocean $[\text{CO}_3^{2-}]$ at the end of the glacial period occurs quickly because it is a change in the seawater equilibria, and forces the process of deep sea dissolution [Berelson et al., 1997; Mackenzie et al., 2004; Anderson et al., 2008]. But this dissolution is kinetically slow (order of 5–10 kyr). So alkalinity burial is able to continue to outstrip alkalinity supply to the ocean into the peak interglacial, and accentuated by the highstand coral reef production [Vecsei and Berger, 2004]. Only when the accelerated alkalinity sup-

ply by weathering under warm conditions then balances and ultimately outstrips alkalinity burial in the ocean is the end of the peak interglacial warmth triggered and the start of the next cooling cycle.

5. Conclusion

[39] Benthic foraminiferal Mg/Ca and B/Ca in the Weddell Sea are controlled by the $\Delta[\text{CO}_3^{2-}]$ of the ambient water and demonstrate that the deep waters in the Weddell Sea experienced elevated alkalinity by $\sim 25 \mu\text{mol/kg}$ during the cool period of each glacial cycle. This signal of less corrosive deep water emanating from the Southern Ocean likely accounts for the higher carbonate accumulation seen across the glacial Southern and Pacific Ocean. An increase in the alkalinity of the ocean by 25 $\mu\text{mol/kg}$ could account for the entirety of glacial $p\text{CO}_2$ drawdown in a closed system with a doubling of opal production. A more likely scenario explains $\sim 50\%$ of the atmospheric $p\text{CO}_2$ drawdown and involves changes in the alkalinity budget associated with reduced shelf carbonate accumulation, which are partially compensated by increased pelagic carbonate production and accumulation above the CCD. Increased pelagic carbonate accumulation throughout the glacial period could drive alkalinity burial to outstrip alkalinity supply into the ocean, resulting in a decrease in deep ocean $[\text{CO}_3^{2-}]$, degassing of CO_2 from the ocean and provide a trigger for the rise in $p\text{CO}_2$ at the beginning of deglaciations. We hypothesize that pelagic production of carbonate may, at times, and via its influence on the CCD and alkalinity burial, drive the carbonate chemistry of the deep ocean and atmospheric change of $p\text{CO}_2$.

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- H. Elderfield and N. Roberts, Godwin Laboratory for Paleoclimate Research, Department of Earth Sciences, Cambridge University, Downing Street, Cambridge CB2 3EQ, UK.
- C.-D. Hillenbrand, British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET, UK.
- A. Mackensen, Alfred Wegener Institute, Columbusstrasse, D-27568 Bremerhaven, Germany.
- R. E. M. Rickaby, Department of Earth Sciences, Oxford University, Parks Road, Oxford OX1 3PR, UK. (rosr@earth.ox.ac.uk)