Deep Ocean Carbonate Chemistry and Glacial-Interglacial Atmospheric CO$_2$ Changes

BY JIMIN YU, ROBERT F. ANDERSON, AND EELCO J. ROHLING

ABSTRACT. Changes in deep ocean carbonate chemistry have profound implications for glacial-interglacial atmospheric CO$_2$ changes. Here, we review deep ocean carbonate ion concentration ([CO$_3^{2-}$]) changes based on the benthic foraminiferal boron-to-calcium ratio (B/Ca) and their links to global carbon reorganization since the last ice age. Existing deep ocean [CO$_3^{2-}$] reconstructions are consistent with changes in the biological pump, in ocean stratification, and in the associated oceanic alkalinity inventory as key mechanisms for modulating atmospheric CO$_2$ on glacial-interglacial time scales. We find that the global mean deep ocean [CO$_3^{2-}$] was roughly similar between the Last Glacial Maximum (LGM; 18,000–22,000 years ago) and the Late Holocene (0–5,000 years ago). In view of elevated glacial surface [CO$_3^{2-}$], this indicates enhanced storage of respiratory carbon in a more alkaline deep ocean during the LGM. During early deglaciation, rising [CO$_3^{2-}$] at three locations in the deep ocean suggests a release of deep-sea CO$_2$ to the atmosphere, probably via the Southern Ocean. Both increased late deglacial carbonate burial in deep-sea sediments due to elevated [CO$_3^{2-}$] and Holocene expansion of coral reefs on newly flooded continental shelves depleted global ocean alkalinity, which reduced CO$_2$ solubility in seawater and contributed to atmospheric CO$_2$ rises at these times.
INTRODUCTION
One of the most intriguing findings in paleoclimate research concerns systematic glacial-interglacial atmospheric CO₂ variations, as revealed by measurements of air bubbles trapped in ice cores from Antarctica. During the last 800,000 years, atmospheric CO₂ fluctuations have been highly correlated with climate on millennial time scales (Figure 1; Lisiecki and Raymo, 2005; Jouzel et al., 2007; Lüthi et al., 2008). Because CO₂ is a greenhouse gas, atmospheric CO₂ fluctuations likely caused, or at least amplified, the climatic changes. Thus, resolving the reasons for glacial-interglacial atmospheric CO₂ fluctuations is essential for improved understanding of the mechanisms that control the global climate system.

Despite intensive research, the mechanisms for past atmospheric CO₂ changes remain elusive. Because the ocean is the largest carbon reservoir that equilibrates with the atmosphere on a ~1,000 year time scale, Broecker (1982) argued that the ocean must have played a critical role in modulating past atmospheric CO₂ variations. Changes in physical conditions, including temperature, salinity, and ocean volume (due to waxing and waning of ice sheets; Figure 1), have opposing effects, resulting in a net decrease in atmospheric CO₂ by ~15 ppm during glacial transitions (Sigman and Boyle, 2000; Brovkin et al., 2007). This decrease is barely enough to counter the atmospheric CO₂ rise that is due to the transport of ~500 Gt (1 Gt = 10¹⁵ g) of carbon from the land biosphere to the ocean during interglacial to glacial transitions (Bird et al., 1994; Ciais et al., 2012). To explain up to ~100 ppm glacial-interglacial atmospheric CO₂ fluctuations requires more complex ocean processes. Existing evidence suggests that biogeochemistry and physical circulation changes, especially in the Southern Ocean, are critical (Sigman and Boyle, 2000; Stephens and Keeling, 2000; Toggweiler et al., 2006; Anderson et al., 2009; Sigman et al., 2010).

Deepwater carbonate ion concentration, [CO₃²⁻], is a critical parameter in investigations of carbon reorganization in the climate system. To a first approximation, [CO₃²⁻] = ALK – DIC (Zeebe and Wolf-Gladrow, 2001), where ALK is alkalinity and DIC is dissolved inorganic carbon (DIC = [CO₂] + [HCO₃⁻] + [CO₃²⁻]), both of which affect atmospheric CO₂ (Figure 2). ALK represents the excess base that affects deprotonation of aqueous CO₂ into bicarbonate ion (HCO₃⁻) and CO₃²⁻. Everything else being equal, an increase in ALK causes more DIC to take the form of CO₃²⁻ and less of it to be aqueous CO₂, lowering CO₂ partial pressure (Figure 2B) and effectively increasing CO₂ solubility in seawater and decreasing atmospheric CO₂. Deepwater [CO₃²⁻] determines seawater carbonate saturation, affecting dissolution/preservation of CaCO₃ on the seafloor and, hence, the global oceanic ALK inventory. Reconstruction of deep ocean [CO₃²⁻] chemistry changes therefore can elucidate critical processes and mechanisms in the past global carbon cycle. We review recent progress in such reconstructions since the last ice age, along with the impacts on atmospheric CO₂ changes.

MODERN OCEAN [CO₃²⁻] VARIABILITY
We first summarize variations in [CO₃²⁻] and factors controlling them in the modern ocean (Figure 3; Key et al., 2004). In general, surface-ocean [CO₃²⁻] is elevated relative to the deep ocean. Temperature and salinity changes have small effects on seawater [CO₃²⁻], with sensitivities of 0.5 µmol kg⁻¹ per °C and ~0.5 µmol kg⁻¹ per ‰, respectively (Yu et al., 2008). The elevated surface [CO₃²⁻] is predominantly caused by conversion of DIC and ALK into biological particles during phytoplankton photosynthesis in the euphotic zone (less than ~150 m). At a rain ratio
(C\textsubscript{organic}:C\textsubscript{CaCO\textsubscript{3}}) of 4:1 (Broecker and Peng, 1982), photosynthesis consumes seawater DIC and ALK at a ratio of 3.58:1 (Yu et al., 2008) and leads to an increase in seawater [CO\textsubscript{2−3}] (Figure 2A). Different from other regions, the Southern Ocean exhibits reduced surface-deep water [CO\textsubscript{2−3}] contrast (Figure 3A), due to intensive upwelling of very deep waters and inefficient nutrient utilization (Broecker et al., 1998).

Sinking and subsequent decomposition of biological matter decreases [CO\textsubscript{2−3}] in the deep ocean (Figure 2A), but different water masses bear distinctive values that reflect their different histories (Figure 3). The well-ventilated North Atlantic Deep Water (NADW) has the highest [CO\textsubscript{2−3}], ~120 µmol kg\textsuperscript{−1}, and the poorly ventilated North Pacific Deep Water (NPDW) has the lowest [CO\textsubscript{2−3}], ~50 µmol kg\textsuperscript{−1}. Lower Circumpolar Deep Water (LCDW) and Antarctic Intermediate Water (AAIW), both formed in the Southern Ocean, have intermediate [CO\textsubscript{2−3}] values of ~80 µmol kg\textsuperscript{−1}. The [CO\textsubscript{2−3}] gradient along the deepwater pathway from the North Atlantic to the North Pacific reflects gradual accumulation of remineralized biological matter, which is also indicated by higher DIC in the deep equatorial Pacific, by ~170 µmol kg\textsuperscript{−1}, than in the deep equatorial Atlantic Ocean (Figure 3C). Ocean circulation imposes secondary features on the general decrease in [CO\textsubscript{2−3}] with increasing water depth. For example, northward penetration of AAIW produces a [CO\textsubscript{2−3}] minimum at ~850 m in the equatorial Atlantic Ocean, while southward advection of low-[CO\textsubscript{2−3}] NPDW leads to a [CO\textsubscript{2−3}] minimum at ~700 m in the equatorial Pacific Ocean (Figure 3B).

Although less obvious, deep water [CO\textsubscript{2−3}] is also significantly affected by ALK changes associated with CaCO\textsubscript{3} dissolution on the seafloor, especially in the Pacific Ocean. In the equatorial Pacific Ocean, waters below ~2.5 km are mainly sourced from the Southern Ocean. Compared to waters at ~5 km water depth, the southward return flow at ~3 km has stayed in the deep ocean for a longer time and, hence, has accumulated more remineralized DIC and ALK (Schmitz, 1996). As a consequence, DIC is ~50 µmol kg\textsuperscript{−1} higher at 3 km water depth than at 5 km water depth in the equatorial Pacific (Figure 3C). Were this DIC increase solely due to remineralization of biological particles sinking from the surface, then ALK would be expected to rise by ~15 µmol kg\textsuperscript{−1}, which is less than the observed increase of ~40 µmol kg\textsuperscript{−1}. This discrepancy suggests an introduction of ALK into deep waters by CaCO\textsubscript{3} dissolution on the seafloor. Compared to the deep equatorial Atlantic Ocean, the observed ~25 µmol kg\textsuperscript{−1} decrease in deep equatorial Pacific [CO\textsubscript{2−3}] corresponds to shoaling of the calcite saturation horizon by ~1.3 km (Figure 3B), deterioration of the calcite saturation degree, and promotion of CaCO\textsubscript{3} dissolution in the Pacific Ocean. As a consequence, the calcite lysoclone—the depth where CaCO\textsubscript{3} dissolution intensifies...
in sediments, which is highly coupled with the calcite saturation horizon in the modern ocean (Broecker and Takahashi, 1978)—is ~ 1 km shallower in the Pacific Ocean than in the Atlantic Ocean. CaCO₃ dissolution adds ALK and DIC to seawater at a ratio of 2:1 and increases seawater [CO₃²⁻] (Figure 2A). In a sense, CaCO₃ dissolution in the deep Pacific Ocean serves as a buffering mechanism to reduce decreases in [CO₂] and pH caused by the remineralization of sinking biological matter.

**BENTHIC B/CA AS A PROXY FOR DEEPWATER [CO₃²⁻]**

Because of its sensitivity to deepwater saturation degree, CaCO₃ preservation in sediments has been used to estimate deepwater [CO₃²⁻] (e.g., Crowley, 1983; Farrell and Prell, 1989; Le and Shackleton, 1992; Anderson and Archer, 2002). However, estimates of CaCO₃ dissolution-based proxies are mostly qualitative and are complicated by factors such as dissolution in pore waters and surface water condition changes (Archer and Maier-Reimer, 1994; Barker and Elderfield, 2002), and they become insensitive at shallow water depths where seawater is generally supersaturated and carbonate dissolution is minimal. Recent core-top studies show that boron isotope ratios (δ¹¹B) in some benthic foraminiferal species are useful for reconstructing deepwater pH and [CO₃²⁻], but down-core δ¹¹B measurements are of low temporal resolution and limited to a few locations, partially due to the relatively large sample size requirement for analyses (Hönisch et al., 2008; Yu et al., 2010b; Rae et al., 2011). Some empirical approaches have also been developed to quantify deepwater [CO₃²⁻]. For example, the partitioning of Zn into benthic foraminiferal carbonates appears to be correlated with the degree of deepwater calcite saturation (∆[CO₂], defined by ∆[CO₂] = [CO₂]_{in situ} - [CO₂]_{sat}, where [CO₂]_{sat} is [CO₂] for CaCO₃ saturation at in situ temperature and pressure) at ∆[CO₂] values below ~ 25 µmol kg⁻¹. However, the prerequisite to knowing past seawater [Zn], which is nontrivial, makes application of this method a challenge (Marchitto et al., 2000).

![Figure 3](image-url)  
*Figure 3. (A) Distribution of seawater [CO₃²⁻] in the global modern ocean. Four water masses are indicated: NADW = North Atlantic Deep Water, AAIW = Antarctic Intermediate Water, LCDW = Lower Circumpolar Deep Water, and NPDW = North Pacific Deep Water. Inset shows the locations of hydrographic sites used for the [CO₃²⁻] section. circles and diamonds show, respectively, the locations of cores for deep and surface water [CO₃²⁻] reconstructions displayed in Figure 6. Vertical dashed lines indicate locations of hydrographic sites for depth profiles shown in (B–D). (B) Bathymetric profile of [CO₃²⁻] with salinity normalized to account for effects of mixing and evaporation-precipitation. (C) and (D) Bathymetric profiles, respectively, of DIC and ALK in the equatorial Atlantic and Pacific Oceans. (B) also shows calcite saturation [CO₃²⁻] and the saturation horizons in equatorial Atlantic and Pacific Oceans. The saturation horizon is defined as the depth where in situ [CO₂] equals the saturation [CO₂] (which is largely determined by pressure or water depth). Above the saturation horizon, seawater is saturated and CaCO₃ tends to be preserved, whereas below the saturation horizon, seawater is undersaturated and CaCO₃ has the potential to dissolve. Panel (A) is generated using Ocean Data View (Schlitzer, 2006). Data are from the GLObal Ocean Data Analysis Project (GLODAP) data set (Key et al., 2004).*
2013a; Rickaby et al., 2010; Raitzsch et al., 2011). As Figure 4 shows, B/Ca in the species *Cibicidoides wuellerstorfi* and *Cibicidoides mundulus* shows clear linear relationships with deepwater $\Delta [\text{CO}_3^{2-}]$, and there appears to be no threshold in the B/Ca-$\Delta [\text{CO}_3^{2-}]$ sensitivity at high $\Delta [\text{CO}_3^{2-}]$, allowing reconstructions using shallow sites. Both *C. wuellerstorfi* and *C. mundulus* are epifaunal species, with a habitat above the sediment-seawater interface (Lutze and Thiel, 1989), which minimizes complications in B/Ca due to pore water chemistry. Because B is conservative in seawater, changes in the B concentration or inventory over time scales of 14–20 million years (Lemarchand et al., 2001), which would increase B/Ca in benthic foraminiferal carbonates and lead to a positive correlation between $\text{CO}_3^{2-}$ and B/Ca. However, the relationships considered here concern benthic B/Ca against $\Delta [\text{CO}_3^{2-}]$ (Figure 4), which includes both in situ $[\text{CO}_3^{2-}]$ and $[\text{CO}_3^{2-}]_{\text{sat}}$ (a pressure effect). In addition, the foraminiferal calcification rate, which is partially affected by seawater $\Delta [\text{CO}_3^{2-}]$, may impose some influence on B/Ca. Different B/Ca ranges and B/Ca-$\Delta [\text{CO}_3^{2-}]$ sensitivities between *C. wuellerstorfi* and *C. mundulus* also suggest biological influences on B incorporation into benthic foraminiferal carbonate. Despite incomplete understanding of the mechanisms, a down-core comparison between benthic B/Ca and $\delta^{11}$B (Yu et al., 2010b) strongly supports the feasibility of the core-top calibrations for past deepwater $[\text{CO}_3^{2-}]$ reconstructions as shown in Figure 4. Currently, calibrations are only available for a few species, and B/Ca in other benthic species remains to be explored.

![Figure 4](image_url)  
Figure 4. Benthic foraminiferal B/Ca proxy for deepwater $[\text{CO}_3^{2-}]$ (Yu and Elderfield, 2007; Brown et al., 2011; Rae et al., 2011; Raitzsch et al., 2011; Yu et al., 2013a). In seawater, $\Delta [\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_{\text{sat}} - [\text{CO}_3^{2-}]_{\text{sat}}$, where $[\text{CO}_3^{2-}]_{\text{sat}}$ represents saturation $[\text{CO}_3^{2-}]$ and remains roughly stable on glacial-interglacial time scales. Benthic B/Ca can be converted into $\Delta [\text{CO}_3^{2-}]$ using the calibrations shown in this figure. Deepwater $[\text{CO}_3^{2-}]$ is then calculated by $[\text{CO}_3^{2-}] = \Delta [\text{CO}_3^{2-}] + [\text{CO}_3^{2-}]_{\text{sat}}$. The images show morphologies of umbilical sides of the two species (Rae et al., 2011). See http://www.foraminifera.eu for more species images.

![Figure 5](image_url)  
Figure 5. Bathymetric distribution of seawater $[\text{CO}_3^{2-}]$ in the North Atlantic and Indo-Pacific Oceans during the Late Holocene (0–5,000 years ago) and the Last Glacial Maximum (LGM; 18,000–22,000 years ago) (Yu et al., 2013a).
**DOWN-CORE [CO$_3^{2-}$]**

**RECONSTRUCTIONS AND IMPLICATIONS FOR PAST ATMOSPHERIC CO$_2$ CHANGES**

**Last Glacial Maximum**

Figure 5 shows bathymetric distributions of benthic B/Ca-derived deepwater [CO$_3^{2-}$] in the North Atlantic and Indo-Pacific Oceans during the Last Glacial Maximum (LGM; 18,000–22,000 years ago) and Late Holocene (0–5,000 years ago) (Yu et al., 2013a). The large LGM-to-Holocene [CO$_3^{2-}$] changes from about +20 to −35 µmol kg$^{-1}$ in the North Atlantic Ocean are consistent with substantial changes in the geometry of Atlantic Meridional Ocean Circulation. During the LGM, Glacial North Atlantic Intermediate Water (GNAIW) was characterized by low nutrient content, high δ$^{13}$C, and high [CO$_3^{2-}$] values, and sank to ~2.5 km in the North Atlantic (Boyle and Keigwin, 1987; Curry and Oppo, 2005; Yu et al., 2008). Below GNAIW were Antarctic-derived waters with high-nutrient, low-δ$^{13}$C, and low-[CO$_3^{2-}$] properties (Figures 3a and 5). During the LGM, elevated [CO$_3^{2-}$] at the mid-depth range likely resulted from high surface preformed [CO$_3^{2-}$] in the North Atlantic (Figure 6a,b) (Henehan et al., 2013; Yu et al., 2013b), while decreased [CO$_3^{2-}$] in the deep North Atlantic is consistent with a greater penetration of low-[CO$_3^{2-}$] deep waters from the Southern Ocean (Figure 3a; Curry and Oppo, 2005).

Because (1) the Atlantic is relatively small in volume (~25% of the global ocean), and (2) opposite changes in [CO$_3^{2-}$] at shallow and deep water masses tend to cancel each other, changes in Atlantic [CO$_3^{2-}$] have negligible impacts on the global mean deep ocean [CO$_3^{2-}$]. In contrast, LGM-to-Holocene [CO$_3^{2-}$] changes in the deep Indo-Pacific Oceans (accounting for ~75% of the global deep-sea volume) are within about ±5 µmol kg$^{-1}$, implying efficient buffering of deepwater pH by deep-sea CaCO$_3$ dissolution in these basins (Anderson and Archer, 2002). Our reconstructions are different from the large [CO$_3^{2-}$] changes inferred in an early study using δ$^{11}$B (Sanyal et al., 1995), which were likely compromised due to the use of mixed benthic foraminiferal species.

Supported by foraminiferal assemblage changes and a modest change in calcite lysocline depth in the Pacific Ocean (Catibug et al., 1998; Anderson and Archer, 2002), the small LGM-to-Holocene [CO$_3^{2-}$] contrast in the deep Indian and Pacific Oceans (Yu et al., 2013a) suggests comparable global mean deep ocean [CO$_3^{2-}$] between the LGM and the Late Holocene. This places...
important constraints on factors influencing the global carbon cycle and low atmospheric CO$_2$ during glacials.

During the LGM, atmospheric CO$_2$ was ~ 90 ppm lower than during the pre-industrial period (Figure 6G; Lüthi et al., 2008). Assuming equilibrium between the surface ocean and the atmosphere, surface water [CO$_2^-$] during the LGM would have been ~ 60 µmol kg$^{-1}$ higher than at pre-industrial times (a rule of thumb: seawater $p$CO$_2$ and [CO$_2^-$] are inversely correlated; Figure 2), which is supported by surface water reconstructions in the tropical and polar North Atlantic Ocean (Figure 6A,B; Henehan et al., 2013; Yu et al., 2013b). Although not yet fully established, it is therefore reasonable to expect that the surface source waters for newly formed deep waters had a substantially higher preformed [CO$_2^-$] during the LGM than today (pre-industrial). Similarity of deepwater [CO$_2^-$] values between the LGM and the Late Holocene then suggests an enhanced surface-to-deep [CO$_2^-$] gradient in the LGM ocean. This requires a larger amount of respiratory CO$_2$ stored in the deep sea during the LGM due to remineralization of biogenic matter, which titrated the higher preformed [CO$_2^-$] surface waters to deepwater [CO$_2^-$] values that were similar to those observed in the modern deep sea (Figure 2A). Increased respiratory CO$_2$ in the glacial deep sea is consistent with reduced dissolved O$_2$ concentrations in the glacial deep Pacific Ocean (Galbraith et al., 2007; Bradtmiller et al., 2010; Iaccard and Galbraith, 2012). It also agrees with inferences of increased biological pump efficiency and enhanced stratification in the glacial ocean (Kumar et al., 1995; Lund et al., 2011; Burke and Robinson, 2012), which would have facilitated a buildup of CO$_2$ in the deep ocean and contributed to reduced glacial atmospheric CO$_2$ levels (Sigman and Boyle, 2000; Sigman et al., 2010).

During the LGM, the carbon lost from the atmosphere (~ 200 GtC) and the terrestrial biosphere (~ 500 GtC) must have been stored as DIC in the deep ocean (Broecker, 1982), assuming there were no significant changes in the ocean-atmosphere carbon inventory. Given the observed minor change in global mean deep ocean [CO$_2^-$] (Figure 5), deep ocean ALK (=[CO$_2^-$]+DIC) must have been substantially higher during the LGM than today. Elevated glacial oceanic ALK likely resulted from decreased CaCO$_3$ burial. Sequestration of excess respiratory CO$_2$ into the deep ocean during the transition from the last interglacial to the last ice age as a result of iron fertilization would have lowered deepwater [CO$_2^-$] (Figure 2A) and resulted in shoaling of the saturation horizon, which increased CaCO$_3$ dissolution on the seafloor. In addition, the replacement of NADW with GNAIW allowed more corrosive Southern-sourced deep waters (Figure 3A) to occupy the deep Atlantic, further strengthening CaCO$_3$ dissolution there (Figure 6D). Moreover, reduced coral growth during glacial times due to substantial shrinkage of shelf areas caused by ~ 120 m sea level drop (e.g., Grant et al., 2012) reduced the removal of ALK by reef aragonite on continental shelves (Opdyke and Walker, 1992). Assuming stable ALK input from rivers and unchanged pelagic CaCO$_3$ production, reduced CaCO$_3$ accumulation in deepsea sediments and on shelves would upset the oceanic ALK balance between riverine input and marine burial. This activates carbonate compensation, a negative feedback to bring the ocean carbonate system back to a new steady state (Broecker and Peng, 1987). Reduced CaCO$_3$ burial introduces ALK and DIC in a 2:1 ratio into the ocean, causing oceanic [CO$_2^-$] to rise (Figure 2A) until the ALK balance is restored on a time scale of ~ 5,000 years (Broecker and Peng, 1987). A net ALK gain occurred during glaciations. By increasing CO$_2$ solubility in seawater, increased ocean ALK helps to further lower atmospheric CO$_2$ during glaciations (Figure 2B; Broecker and Peng, 1987; Boyle, 1988).

The Last Deglaciation
Figure 6 shows benthic B/Ca-derived deepwater [CO$_2^-$] at four locations from the global deep ocean (middle panel), together with some surface water [CO$_2^-$] (top panel) and atmospheric CO$_2$ and Antarctic temperature changes (bottom panel) during the last 25,000 years. During the early deglaciation (17,500–14,500 years ago), [CO$_2^-$] rose by about 10 µmol kg$^{-1}$ in the deep Atlantic, Indian, and equatorial Pacific Oceans (Figure 6D–F). This cannot
be explained by changes in preformed $[\text{CO}_3^{2-}]$ because surface $[\text{CO}_3^{2-}]$ declined during this time interval (Figure 6A,B). Because increasing deepwater $[\text{CO}_3^{2-}]$ would promote deep-sea $\text{CaCO}_3$ preservation and thus deplete the oceanic ALK inventory, a $[\text{CO}_3^{2-}]$ rise likely reflects a decrease in DIC (Yu et al., 2010a). Therefore, these deepwater $[\text{CO}_3^{2-}]$ increases during the early deglaciation are consistent with transfer of CO$_2$ from deep ocean basins into intermediate water depths (as indicated by a $[\text{CO}_3^{2-}]$ decline at mid-depth in the North Atlantic [Figure 6C]) and into the atmosphere (Figure 6G). Release of deep-sea CO$_2$ may have occurred by increased "leakage" of CO$_2$ in the Southern Ocean due to (1) reduced nutrient consumption caused by a decline in dust deposition in the Subantarctic Zone (Broecker and Henderson, 1998; Martinez-Garcia et al., 2011), (2) breakdown of ocean stratification in the Southern Ocean as suggested by opal flux and radiocarbon results (Anderson et al., 2009; Burke and Robinson, 2012), and (3) melting of sea ice, a physical barrier to sequestration of CO$_2$ in the ocean, induced by rapid warming around Antarctica (Figure 6H; Stephens and Keeling, 2000; Jouzel et al., 2007). The release of deep-sea CO$_2$ is suspected to be responsible for a ∼ 50 ppm rise in atmospheric CO$_2$ and a ∼ 190% decline in atmospheric radiocarbon during the early deglaciation (Broecker and Barker, 2007; Lüthi et al., 2008).

During the late deglaciation (14,000–10,000 years ago), the global deep ocean had elevated $[\text{CO}_3^{2-}]$ relative to the LGM, and Indo-Pacific records show plateaus in deepwater $[\text{CO}_3^{2-}]$ (Figure 6C,D). The little $[\text{CO}_3^{2-}]$ change in the deep Indo-Pacific at this time is counterintuitive, given continued transfer of carbon amounting to ∼ 450 GtC from the deep sea to the atmosphere and terrestrial biosphere as deduced from benthic $\delta^{13}$C and atmospheric CO$_2$ (Lüthi et al., 2008; Yu et al., 2010a), which ought to drive up deepwater $[\text{CO}_3^{2-}]$ by decreasing DIC in deep ocean basins (Figure 2A). The absence of a rise in deep Indo-Pacific $[\text{CO}_3^{2-}]$ likely indicates an ALK decrease possibly associated with carbonate compensation (Broecker and Peng, 1987). The initial deepwater $[\text{CO}_3^{2-}]$ increase due to CO$_2$ release during the early deglaciation would promote the preservation and burial of $\text{CaCO}_3$ in sediments, which is observed at many locations worldwide from 14,000–10,000 years ago (Berger, 1977; Farrell and Prell, 1989, 1991; Hodell et al., 2001; Anderson et al., 2008; Yu et al., 2010a). Improved $\text{CaCO}_3$ preservation during the last deglaciation in turn decreased the oceanic ALK inventory and, hence, lowered oceanic $[\text{CO}_3^{2-}]$ (Figure 2A). Thus, the late deglacial $[\text{CO}_3^{2-}]$ plateau in the Indo-Pacific suggests a strong carbonate compensation effect that counteracted the rise in deepwater $[\text{CO}_3^{2-}]$ driven by CO$_2$ degassing. By reducing whole ocean alkalinity, carbonate compensation helps to release additional CO$_2$ from the deep ocean during deglaciations (Figure 2B).

The Holocene

Deepwater $[\text{CO}_3^{2-}]$ in the deep Indian and Pacific Oceans declined by 5–15 μmol kg$^{-1}$ during the Holocene (0–10,000 years ago; Figure 6E,F). Ocean circulation changes may account for different magnitudes in this $[\text{CO}_3^{2-}]$ decline, as well as for the opposite $[\text{CO}_3^{2-}]$ changes observed in the Atlantic Ocean (Figure 6C,D). Because benthic $\delta^{13}$C (which is sensitive to biological respiration) has remained roughly constant (e.g., Yu et al., 2010a), the Holocene $[\text{CO}_3^{2-}]$ decline in the deep Indo-Pacific Oceans likely resulted from a depletion in oceanic ALK. This inferred ALK decrease is consistent with continued carbonate compensation in response to the carbon reorganization that occurred during the last deglaciation. Additionally, coral reef buildup on shelves due to an increase in the area of shallow water environments at high sea level stand may have contributed to the removal of ALK and resulted in a decrease in whole ocean $[\text{CO}_3^{2-}]$ (Opdyke and Walker, 1992). By reducing CO$_2$ solubility in the ocean, the decrease in the whole ocean ALK inventory drives up atmospheric CO$_2$ (Figure 2B) and contributes to the 20 ppm rise in atmospheric CO$_2$ since ∼ 8,000 years ago (Figure 6G), as demonstrated by modeling (Ridgwell et al., 2003; Menviel and Joos, 2012).

**SUMMARY**

Deep-ocean $[\text{CO}_3^{2-}]$ is tightly linked to processes that affect carbon reorganization in the ocean and thus serves as a valuable tracer for investigations of the global carbon cycle. Reconstructions based on benthic foraminiferal B/Ca are consistent with a stronger biological pump, increased ocean stratification, and elevated global ocean alkalinity during the LGM, all of which contributed to reduced atmospheric CO$_2$ levels during ice ages. The synchronicity of an important early deglacial deep-sea $[\text{CO}_3^{2-}]$ increase and various events in the Southern Ocean (including reduced dust deposition and biological pump efficiency in the sub-Antarctic, a breakdown of polar Antarctic stratification, and sea ice retreat) has suggested to many that Southern Ocean processes are critical to carbon release from the deep ocean during glacial terminations. The deep
ocean [CO$_2$]$_3$] history also highlights the importance of changes in the whole ocean alkalinity inventory (associated with carbonate compensation and coral reef buildup) on carbon reorganization in the ocean-atmosphere-land biosphere system. Existing deep ocean [CO$_2$]$_3$] reconstructions are short and limited to a few locations. Development of high-resolution records since the last glacial and of reconstructions that span several glacial-interglacial cycles will improve and quantify our understanding of the role of deep ocean carbonate chemistry in past atmospheric CO$_2$ changes.

ACKNOWLEDGEMENT
We thank Samuel Jaccard and an anonymous reviewer for constructive comments. JY is supported by ARC DP140101393.

REFERENCES


