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The effect of ocean alkalinity and carbon transfer on deep-sea carbonate ion concentration during the past five glacial cycles

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ABSTRACT

Glacial–interglacial deep Indo-Pacific carbonate ion concentration ($[CO_3^{2-}]$) changes were mainly driven by two mechanisms that operated on different timescales: 1) a long-term increase during glaciation caused by a carbonate deposition reduction on shelves (i.e., the coral reef hypothesis), and 2) transient carbonate compensation responses to deep ocean carbon storage changes. To investigate these mechanisms, we have used benthic foraminiferal B/Ca to reconstruct deep-water $[CO_3^{2-}]$ in cores from the deep Indian and Equatorial Pacific Oceans during the past five glacial cycles. Based on our reconstructions, we suggest that the shelf-to-basin shift of carbonate deposition raised deep-water $[CO_3^{2-}]$, on average, by 7.3 ± 0.5 (SE) μmol/kg during glaciations. Oceanic carbon reorganisations during major climatic transitions caused deep-water $[CO_3^{2-}]$ deviations away from the long-term trend, and carbonate compensation processes subsequently acted to restore the ocean carbonate system to new steady state conditions. Deep-water $[CO_3^{2-}]$ showed similar patterns to sediment carbonate content (%$CaCO_3$) records on glacial–interglacial timescales, suggesting that past seafloor %$CaCO_3$ variations were dominated by deep-water carbonate preservation changes at our studied sites.

1. Introduction

The deep ocean is the lead candidate to store additional carbon lost from the atmosphere during glacial times. This is because it holds ~60 fold greater carbon reservoir than the atmosphere and turns over at rates comparable to those of the atmospheric pCO_2 fluctuations. A panoply of mechanisms has been proposed to account for the glacially enhanced deep ocean storage of carbon, most of which invoke carbonate compensation as an amplifying feedback on carbon sequestration (Boyle, 1988; Broecker and Peng, 1989). The seawater carbonate system and sediment carbonate act as buffers to limit pH changes on different timescales. The seawater carbonate system opposes pH changes by altering the proportions of the abundant weak acid species including bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}), when relatively small amounts of acid or base are added into the ocean. On timescales on the order of 10s of kyrs, seawater pH is also buffered by reactions with carbonate sediments via a process called carbonate compensation (Boyle, 1988; Broecker and Peng, 1989).

When CO_2 dissolves in seawater, it speciates amongst $CO_{2(aq)}$, HCO_3^-, and CO_3^{2-}, the sum of which is defined as dissolved inorganic carbon (DIC). A constraint on the relative proportions of carbonate species is derived from the charge balance of ions in solution. The sum of the charge from the non-conservative ions in seawater, which to a first order can be approximated as $HCO_3^- + 2CO_3^{2-}$, must balance the net charge of conservative cations and anions (called alkalinity, ALK). In seawater, the relationship among $[CO_3^{2-}]$, DIC and ALK may be described by $[CO_3^{2-}] \approx 0.6 \times (ALK - DIC)$ (Yu et al., 2016).

The average ocean $[CO_3^{2-}]$ is regulated by the global alkalinity cycle (Broecker and Peng, 1982). Production of carbonate in the surface ocean exceeds the supply flux of alkalinity from rivers, so in order for the alkalinity fluxes to balance, only a fraction of carbonate production can be removed from the ocean by burial. The burial in the deep ocean is controlled by the saturation horizon depth, where seawater $\Delta[CO_3^{2-}]$ (defined as the difference between *in-situ* $[CO_3^{2-}]$ and saturation $[CO_3^{2-}]$: $\Delta[CO_3^{2-}] = [CO_3^{2-}] - [CO_3^{2-}]_{sat}$) is zero.

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Due to the pH dependence of carbon speciation, a draw-down in atmospheric pCO_2 during glacial periods should have been accompanied by an increase, at least, in surface ocean $[CO_3^{2-}]$. For the deep ocean which is not in direct contact with the atmosphere, its $[CO_3^{2-}]$ history is affected by multi-factors. However, since glacial deep ocean DIC likely increased, any increase in deep ocean $[CO_3^{2-}]$ would be driven by an increase in ocean alkalinity.

The ocean ALK inventory is influenced by the balance between carbonate–silicate weathering on land and marine $CaCO_3$ burial (Milliman et al., 1974). Fluxes of $CaCO_3$ burial are dictated by coral reef growth on continental shelves and marine plankton deposition in the deep ocean. As a result, modifications of neritic (e.g., due to continental shelf area variations) and pelagic (e.g., driven by biological export production rate or composition changes) carbonate depositions would have a profound effect on the whole ocean ALK budget and, by implication, glacial oceanic carbon sequestration. Past $CaCO_3$ deposition changes have spawned hypotheses for the ALK driven deep ocean carbon storage over glacial–interglacial cycles (Archer and Maier-Reimer, 1994; Berger, 1982; Opdyke and Walker, 1992). These hypotheses, however, had previously been dismissed, because despite a significant deepening of calcite saturation horizon in the glacial Pacific Ocean, it shoaled in the glacial Atlantic Ocean (Catubig et al., 1998). Recent deep-water $[CO_3^{2-}]$ reconstructions suggest that global ALK was increased in the glacial ocean (Rickaby et al., 2010; Yu et al., 2013), reviving the idea that a glacial ALK increase played a pivotal role in reducing atmospheric pCO_2. Nevertheless, debate surrounds the driving mechanism(s) and magnitude of the glacial ALK increase (Rickaby et al., 2010; Yu et al., 2013).

The global ALK inventory might have been changed by sequestration of additional DIC in the glacial deep ocean. Given a constant ALK, a DIC increase would have shifted DIC speciation away from carbonate ion and lowered seawater $[CO_3^{2-}]$. Because saturation $[CO_3^{2-}]$ ($[CO_3^{2-}]_{sat}$) remains roughly constant on glacial–interglacial timescales (Yu et al., 2008), this would have decreased deep-water $\Delta[CO_3^{2-}]$ ($= [CO_3^{2-}] - [CO_3^{2-}]_{sat}$) and hence shoaled the calcite saturation horizon. The resultant enhanced seafloor $CaCO_3$ dissolution would have disrupted the ALK balance between riverine inputs and seafloor burial. This would have led to an oceanic ALK gain until, via shifting deep-water $[CO_3^{2-}]$ and hence saturation horizon depth, carbonate burial matched the weathering supply. During this carbonate compensation, the global ocean ALK increase would have boosted carbon sequestration, further lowering surface-water and atmospheric pCO_2 (Boyle, 1988; Broecker and Peng, 1989).

In this work, we present three $[CO_3^{2-}]$ records from the deep Indian and Pacific Oceans. The modern Pacific and Indian Oceans are relatively homogeneous with respect to deep water $[CO_3^{2-}]$, because at depth C_{org}:$CaCO_3$ re-mineralise at about a 1:1 ratio, yielding a relatively weak water-mass aging effect on $[CO_3^{2-}]$ (Broecker and Sutherland, 2000). Therefore, glacial–interglacial $[CO_3^{2-}]$ changes in the deep Indo-Pacific Ocean should have been more sensitive to whole ocean carbonate system changes than those in the Atlantic where past water-mass reorganisation influences are thought to have been strong (e.g., Curry and Oppo, 2005; Yu et al., 2008). Coupled with benthic $\delta^{13}C$ and sediment carbonate contents (%$CaCO_3$), our $[CO_3^{2-}]$ records place important constraints on how the global carbon cycle changed over glacial–interglacial cycles. We show two records that are sufficiently well resolved to define how $[CO_3^{2-}]$ shifted through five glacial–interglacial cycles, and one high-resolution record that allows confident assessment of carbonate compensation processes over the last full glacial cycle. Together, these afford a robust insight into the mechanisms that drove deep ocean $[CO_3^{2-}]$ on glacial–interglacial timescales.

2. Core locations and methods

2.1. Core locations

Site WIND 28K is located at 4.2 km water depth in the Western Indian Ocean Mascarene Basin (Fig. 1, Table 1). Guided by prominent seafloor bathymetry, southern sourced Circumpolar Deep Water (CDW) ventilates the deep Western Indian Ocean (Toole and Warren, 1993). The Weddell Sea contributes to the densest waters found in the western basin, and above this, deep and intermediate waters enter from both the south and north.

Site TT013-PC72 is situated in the deep Equatorial Pacific Ocean at 4.3 km water depth, and site ODP 806 is located at 2.5 km water depth on the northeast margin of the Ontong Java Plateau (Fig. 1, Table 1). The latter core is located above the modern ocean calcite saturation horizon which lies at ∼3 km water depth. The Ontong Java Plateau straddles the equator in the Western Pacific Ocean, covering an area of 1000 km by 1500 km, and rises to shallow depths of ∼1.7 km.

2.2. Methods

Sediment samples of ∼10 cm^3, from 2 cm segments, were disaggregated in deionized water and wet sieved through 63 μm sieves. Since no size effect on B/Ca was found (Supplementary Material 1), we picked pristine *Cibicidoides wuellerstorfi* tests from all size fractions ranging from 180 to 500 μm. Shells were crushed between two glass plates and cleaned according to Barker et al. (2003). The reductive cleaning step was not included, due to the negligible difference between cleaning methods (Yu and Elderfield, 2007). Details of age models and sedimentation rates are shown in Supplementary Material 2 and Fig. S2.

Trace element ratios of cleaned foraminifera shells were determined by Quadrupole ICP-MS or Thermo® Element XR HR-ICP-MS at the University of Cambridge, according to Yu et al. (2005) and Misra et al. (2014), respectively. The long-term precision of B/Ca measured using in-house solution standards by Quadrupole ICP-MS is 153.3 ± 7.6 μmol/mol or 4.9% (2σ, $n = 88$), and by HR-ICP-MS is 198.6 ± 7.0 μmol/mol or 3.5% (2σ, $n = 144$). Full details of sample preparation and analytical methods are given in Supplementary Material 3.

Deep water $[CO_3^{2-}]$ was reconstructed from B/Ca changes relative to core-top values assuming that pre-industrial $[CO_3^{2-}]$ was recorded by core-top B/Ca measurements. This method of calculation eliminated the requirement for an intercept value, which due to the scatter around the B/Ca-$\Delta[CO_3^{2-}]$ regression line (Yu and Elderfield, 2007), can cause an offset between core-top and pre-industrial $\Delta[CO_3^{2-}]$ values. This approach was first implemented by Yu et al. (2008) and later discussed in detail by Yu et al. (2016). The widely applied linear sensitivity of *C. wuellerstorfi* B/Ca to $\Delta[CO_3^{2-}]$ of Yu and Elderfield (2007) was adjusted to account for systematic offsets based on measurements of internal laboratory standards (Supplementary Material 4):

$$\Delta\left[CO_3^{2-}\right]_{downcore} = \Delta\left[CO_3^{2-}\right]_{pre\text{-}industrial} + \Delta B/Ca/1.25$$

Here the $\Delta[CO_3^{2-}]_{pre\text{-}industrial}$ was calculated by removing the anthropogenic CO_2 influence on $\Delta[CO_3^{2-}]$ using the GLODAP dataset (Key et al., 2004), and $\Delta B/Ca$ represents the deviation of downcore B/Ca from the core-top value. Note that this slope modification had a negligible effect on previous deep-water $[CO_3^{2-}]$ reconstructions, as both core-top and downcore samples were measured by the same set of calibration standards (Yu and Elderfield, 2007; Yu et al., 2010a, 2010b; Rickaby et al., 2010). Changes in $[CO_3^{2-}]_{sat}$ were primarily driven by pressure (Mucci, 1983), with little influence from temperature and salinity changes. As a result, $[CO_3^{2-}]_{sat}$