



# Glacial deep ocean sequestration of CO<sub>2</sub> driven by the eastern equatorial Pacific biologic pump



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## ARTICLE INFO

### Article history:

Received 13 February 2013  
Received in revised form 29 June 2013  
Accepted 9 July 2013  
Available online 25 August 2013  
Editor: J. Lynch-Stieglitz

### Keywords:

Panama Basin  
B/Ca  
last glacial period  
carbon storage  
carbonate saturation state  
paleoproductivity

## ABSTRACT

The potential influence of low latitude ocean primary productivity on glacial atmospheric carbon dioxide levels has proven challenging to deduce using mass accumulation rates (MARs) of biogenic particulates in deep sea sediment cores. Benthic foraminiferal B/Ca serves as a proxy for past seawater calcite saturation state, and thereby provides a fresh perspective on this outstanding paleoceanographic problem. Here we employ *Cibicidoides wuellerstorfi* B/Ca in the Panama Basin region of the eastern equatorial Pacific (EEP) to investigate the nature of deep tropical Pacific carbon storage over the past 50 ka BP. We present evidence for persistently lower deep Panama Basin calcite saturation state, reflecting an increase in total carbon dioxide storage, during the last ice age relative to the Holocene. These results reflect the modification of inflowing deep waters by overlying export productivity, and support the concept of an invigorated glacial EEP soft-tissue pump possibly driven by oceanic nutrient (iron and silica) redistribution. Benthic *Cibicidoides* spp. carbon-13 is consistent with this conclusion by exhibiting substantially lighter values during glacial time, reflecting the accumulation of metabolic carbon dioxide in the deep tropical Pacific. Counterintuitively, downcore application of the Globorotalia menardii calcite fragmentation index (MFI) reveals enhanced glacial sedimentary calcite preservation in the Panama Basin. Together these results point towards a systematic decoupling of bottom water chemistry from biogenic burial fluxes: the crux of the aforementioned traditional paleoproductivity problem.

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## 1. Introduction

The ocean's "biological pump" exerts control over atmospheric carbon dioxide concentrations (CO<sub>2</sub>) by removing carbon from the surface ocean via photosynthetic fixation and sequestering it in the deep ocean via respiration of sinking particles. Understanding how marine primary production influenced the past distribution of carbon between these reservoirs is prerequisite to a full explanation for the late Pleistocene atmospheric carbon dioxide (CO<sub>2</sub>) fluctuations recorded by Antarctic ice cores (Siegenthaler et al., 2005; Lüthi et al., 2008). Motivated by the observed 30% decrease in CO<sub>2</sub> levels during glacial maxima – "the glacial CO<sub>2</sub> problem" – most researchers have identified the deep ocean reservoir as the main repository of excess atmospheric carbon (see Sigman and Boyle, 2000, for a review). It is likely that increased deep ocean storage of respired CO<sub>2</sub> (Boyle, 1988; Keir, 1988; Toggweiler, 1999), hereafter "CO<sub>2</sub> deepening," was accompanied by decreased communication between deep waters and the atmosphere (Sigman et al., 2010). Due to the synergistic nature of the physical and biogeochemical processes which likely contributed to oceanic uptake of CO<sub>2</sub> (Hain et al., 2010), it is difficult to deconvolve the relative contribution

of each component. The role of the low latitude biological pump in sustaining a portion of CO<sub>2</sub> deepening remains poorly understood.

The eastern equatorial Pacific Ocean (EEP) is currently responsible for ~2/3 of the global CO<sub>2</sub> efflux from the ocean to the atmosphere (Takahashi et al., 2002), in part because the heavy load of dissolved CO<sub>2</sub> and macronutrients supplied by upwelling is not efficiently utilized by primary producers (Barber and Chavez, 1991). Logic dictates that a more efficient biological pump may have worked to lower surface ocean pCO<sub>2</sub> and stem this particular deep ocean carbon leak to the atmosphere during glacial intervals. However numerical models demonstrate that net glacial atmospheric CO<sub>2</sub> drawdown cannot be achieved by simply staunching the outgassing of CO<sub>2</sub> in the EEP, e.g. by increasing nutrient utilization, since this would rob surrounding regions of nutrients and thereby suppress the extratropical biological pump (Sigman et al., 2010). In addition, low latitude primary production is typically associated with calcifying organisms and the "carbonate counter-pump," which itself works to increase surface ocean pCO<sub>2</sub> through removal of alkalinity (Sigman et al., 1998). In fact, early hypotheses to explain the glacial CO<sub>2</sub> problem called upon a more efficient global biological pump (Broecker, 1982), but attention was predominantly given to Southern Ocean biogeochemical processes, in part because the large deep ocean reservoir communicates with the atmosphere there (Knox and McElroy, 1984;

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Sarmiento and Toggweiler, 1984). The mid-high latitude Southern Ocean is currently dominated by silica-secreting diatom production and is thus considered an important nexus between the soft-tissue pump, deep ocean ventilation, and atmospheric CO<sub>2</sub> (Sigman et al., 2010).

However, evidence for a more efficient glacial Southern Ocean biological pump does not preclude a supporting role for tropical ocean diatom productivity in facilitating a portion of the glacial atmospheric CO<sub>2</sub> drawdown (Sarmiento et al., 2004). The spatial pattern of limiting nutrients in the glacial Pacific Ocean is thought to have been fundamentally different than present-day. The atmospheric supply of dust-borne iron (Fe) to the glacial Southern Ocean may have stimulated organic matter production while at the same time reducing the silica (Si) requirements of opal-secreting diatoms, such that even under the condition of more complete nutrient consumption, silicic acid “leaked” through intermediate water pathways from high southern latitudes to the tropical oceans (Matsumoto et al., 2002; Brzezinski et al., 2002). This would in turn relax silica limitation in the EEP and promote diatom production over coccolithophores, thereby inhibiting the carbonate counter-pump (Dugdale and Wilkerson, 1998; Leynaert et al., 2001; Moore et al., 2004; Brzezinski et al., 2011). Similarly, it has been proposed that natural wind-driven Fe-fertilization over the EEP itself triggered an analogous cascade-effect whereby dissolved Si leaked out of the EEP and stimulated subtropical diatom production (Pichevin et al., 2009). These and other effects (see Section 4.5) that increase the efficiency of organic carbon export could have made the EEP an important locus of CO<sub>2</sub> deepening during glacial time, thereby contributing to its sequestration away from the atmosphere.

Past levels of primary productivity, in particular the production ratio of C<sub>org</sub> to CaCO<sub>3</sub> required to test the aforementioned hypotheses, are notoriously difficult to reconstruct in the EEP using records of biogenic sedimentation. Mass accumulation rates (MARs) of C<sub>org</sub>, opal, and CaCO<sub>3</sub> are conventionally interpreted as mechanistic proxies for biologically mediated surface-to-deep ocean carbon transfer and shape the current understanding (or lack thereof) of Last Glacial Maximum (LGM) primary productivity (summarized in Loubere, 1999; Singh et al., 2011). There remains considerable discrepancy between the absolute magnitude of vertical flux estimates derived from <sup>14</sup>C age-model MARs versus <sup>230</sup>Th normalized MARs. However, there is an emerging overall picture in the EEP of: (1) higher Marine Isotope Stage (MIS) 2 C<sub>org</sub> flux relative to the Holocene with a deglacial peak (Pedersen, 1983; Lyle, 1988; Kienast et al., 2007; Pichevin et al., 2009); (2) lower MIS 2 opal flux relative to the Holocene with a deglacial peak (Bradtmiller et al., 2006, 2010; Kienast et al., 2006; Warnock et al., 2007; Pichevin et al., 2009; Dubois et al., 2010; Calvo et al., 2011); and (3) constant or lower absolute MIS 2 CaCO<sub>3</sub> flux relative to the Holocene with a slight deglacial peak and better MIS 2 preservation (Loubere, 2004; Loubere and Richaud, 2007; Richaud et al., 2007; Mekik et al., 2012). High MIS 2 C<sub>org</sub> may be reconciled with low opal if Fe-fertilization decreased the diatom utilization ratio of Si:C and/or increased the solubility of frustules (Watson et al., 2000; Warnock et al., 2007; Pichevin et al., 2009; Dubois et al., 2010).

Ultimately, sediment-based biogenic fluxes represent the fraction of carbon that exits the ocean/atmosphere system. Of equal or greater relevance is the storage of dissolved inorganic carbon (DIC) in the deep sea at the expense of the upper ocean and atmosphere (Sigman et al., 2010). Recent work has found that B/Ca in benthic foraminiferal calcite is strongly and quantifiably influenced by ΔCO<sub>3</sub><sup>2-</sup> with respect to calcite (ΔCO<sub>3</sub><sup>2-</sup> = [CO<sub>3</sub><sup>2-</sup>]<sub>in situ</sub> - [CO<sub>3</sub><sup>2-</sup>]<sub>saturation</sub>) and thus provides a good measure of DIC speciation (Yu and Elderfield, 2007). Speciation of the DIC pool accommodates changes in seawater conservative alkalinity (ALK) and DIC to maintain charge balance, whereby an increase

(decrease) in ALK: DIC increases (decreases) [CO<sub>3</sub><sup>2-</sup>]<sub>in situ</sub>. All else being equal, an increase in deep EEP DIC storage due to a stronger soft-tissue pump would be reflected by lower ΔCO<sub>3</sub><sup>2-</sup>. However, the predicted signal of ΔCO<sub>3</sub><sup>2-</sup> in any given deep EEP core in response to CO<sub>2</sub> deepening may be attenuated over timescales of several thousand years by “CaCO<sub>3</sub> compensation,” which acts to restore [CO<sub>3</sub><sup>2-</sup>]<sub>in situ</sub> to global ocean steady-state conditions that balance weathering with CaCO<sub>3</sub> burial (Broecker and Peng, 1987; Boyle, 1988; Marchitto et al., 2005).

The compensation feedback (dissolution of seafloor CaCO<sub>3</sub>) adds excess alkalinity to the deep ocean, reversing the initial ΔCO<sub>3</sub><sup>2-</sup> drop. The timescale of this return to a global steady state is controlled by dissolution kinetics and the average mixing time of the ocean (~10<sup>3</sup> yr), so that it can be difficult to identify the presence of excess respired CO<sub>2</sub> from a deep Pacific glacial ΔCO<sub>3</sub><sup>2-</sup> reconstruction where sedimentation rates are typically low (Marchitto et al., 2005). Even if a stronger glacial low latitude soft-tissue pump imposed a persistently steeper vertical DIC gradient, we might not expect to detect much LGM-Holocene difference in baseline ΔCO<sub>3</sub><sup>2-</sup>, a complication that is in fact supported by the ensemble of Pacific proxy data (Anderson and Archer, 2002; Zeebe and Marchitto, 2010). For this reason, most studies hoping to elucidate glacial-interglacial carbon rearrangement focus on the deglacial interval, where the compressed timescale of CO<sub>2</sub> removal from the deep sea to the atmosphere results in a larger predicted ΔCO<sub>3</sub><sup>2-</sup> signal. Previous downcore application of B/Ca and Zn/Ca-based ΔCO<sub>3</sub><sup>2-</sup> proxies have identified a deep tropical Pacific ΔCO<sub>3</sub><sup>2-</sup> spike on the order of 5–30 μmol kg<sup>-1</sup> as evidence for wholesale carbon removal from the deep Pacific (>2.3 km) during Termination I (Marchitto et al., 2005; Yu et al., 2010). However, it is unclear whether this represents a vertical signal (relaxation of the low latitude soft-tissue pump) or was dominated instead by a far-field horizontal influence (altered modes of deepwater formation that reallocated the volumetric importance of water masses with different preformed [CO<sub>3</sub><sup>2-</sup>]<sub>in situ</sub>).

The Panama Basin has been described as a “mini-ocean basin” (Moore et al., 1973) and is frequently targeted for paleo-oceanographic research due to its uniquely isolated location within the vast EEP. The relatively shallow (~2.3 km) bounding ridges work to preserve local patterns of deep-sea sedimentation apart from basin-wide horizontal influences. A common theme amongst several decades of Panama Basin research is the quest to characterize past levels of primary productivity (e.g. Pedersen, 1983; Pedersen et al., 1991; Mix et al., 1995a, 1995b; Loubere, 2003; Martínez et al., 2006; Kienast et al., 2007), as the basin underlies the highly productive, yet iron-limited, eastern equatorial divergence zone (Barber and Chavez, 1991; Moore et al., 2004). Circumventing the disagreement between sedimentary component accumulation rates, we employ B/Ca-based ΔCO<sub>3</sub><sup>2-</sup> reconstructions to test the hypothesis of an invigorated soft-tissue pump during the LGM. Bathymetric barriers would have largely isolated the basin from hypothetical far-field changes in deep ocean carbon storage, which appear to have been limited to depths below the basin’s sill as inferred from existing [CO<sub>3</sub><sup>2-</sup>]<sub>in situ</sub> reconstructions (Yu et al., 2010). As such, our cores are well suited to deconvolve the regional vertical (biologic) component of CO<sub>2</sub> deepening from basin-wide circulation change. Furthermore the first-order expectation of the CaCO<sub>3</sub> compensation hypothesis, that deep sea ΔCO<sub>3</sub><sup>2-</sup> will return to a steady state that allows for global ocean CaCO<sub>3</sub> burial to balance weathering over multi-millennial timescales (Broecker and Peng, 1987), holds no particular ΔCO<sub>3</sub><sup>2-</sup> requirement for semi-isolated regions such as Panama Basin. Hence the Panama Basin ΔCO<sub>3</sub><sup>2-</sup> history may have been shielded from the masking effect of global compensation.

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