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Version: Version of Record

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http://dx.doi.org/doi:10.1130/G35806.1

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Geology 2014;42;1003-1006
doi: 10.1130/G35806.1
Enhanced carbon dioxide outgassing from the eastern equatorial Atlantic during the last glacial

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ABSTRACT

Biological productivity and carbon export in the equatorial Atlantic are thought to have been dramatically higher during the last glacial period than during the Holocene. Here we reconstruct the pH and CO₂ content of surface waters from the eastern equatorial Atlantic Ocean over the past ~30 k.y. using the boron isotope composition of Globigerinoides ruber (a mixed-layer–dwelling planktic foraminifera). Our new record, combined with previously published data, indicates that during the last glacial, in contrast to today, a strong west to east gradient existed in the extent of air:sea equilibrium with respect to (a mixed-layer–dwelling planktic foraminifera). Our new record, combined with previously published data, indicates that during the last glacial, in contrast to today, a strong west to east gradient existed in the extent of air:sea equilibrium with respect to pCO₂ (∆pCO₂), with the eastern equatorial Atlantic acting as a significant source of CO₂ (+100 µatm) while the western Atlantic remained close to equilibrium (+25 µatm). This pattern suggests that a five-fold increase in the upwelling rate of deeper waters drove increased Atlantic productivity and large-scale regional cooling during the last glacial, but the higher than modern ∆pCO₂ in the east indicates that export production did not keep up with enhanced upwelling of nutrients. However, the downstream decline of ∆pCO₂ provides evidence that the unused nutrients from the east were eventually used for biologic carbon export, thereby effectively negating the impact of changes in upwelling on atmospheric CO₂ levels. Our findings indicate that the equatorial Atlantic exerted a minimal role in contributing to lower glacial-age atmospheric CO₂.

INTRODUCTION

Over at least the past 800 k.y., the CO₂ content of the atmosphere has shifted from ~240–280 ppm during the warm interglacial periods to 180–200 ppm during the cold glacial periods (Petit et al., 1999; Lüthi et al., 2008); most attention has been focused on the amount of carbon stored in the deep ocean during glacials to explain these CO₂ changes (e.g., Sigman et al., 2010). One important mechanism in this regard is the biological pump: biomass produced in the surface ocean sinks to depth and decomposes, thereby pumping both nutrients and organic carbon into the deep ocean, where the carbon is sequestered away from the atmosphere and the nutrients are temporarily unavailable to fuel new biological production. Given their importance today in terms of oceanic primary production (Fig. 1B), attention has long focused on the equatorial oceans to at least partially explain the lower glacial CO₂ levels (e.g., Mix, 1989).

A small proportion of the equatorial regions is termed high-nitrate, low-chlorophyll (HNLC; e.g., the eastern equatorial Pacific Ocean), where the plentiful supply of macronutrients (N, P) from upwelling of cold (Fig. 1A), nutrient-rich (Fig. 1C) and high-CO₂ (Fig. 1D) water is often underutilized because of the relative paucity of essential macronutrients such as Fe (Moore et al., 2013). The incomplete utilization of macronutrients in HNLC regions gives rise to outgassing of excess CO₂ to the atmosphere (Fig. 1D). Changing the efficiency of nutrient utilization (e.g., through enhanced productivity via dust fertilization of Fe-limited areas; Martin, 1990) clearly has the potential to lower the pCO₂(sw) (sw is seawater) in these regions. However, most areas of the equatorial and low-latitude oceans are non-HNLC regions, where productivity is not micronutrient limited (e.g., by Fe), and organisms are eventually able to fully utilize all the available macronutrients (N, P; Fig. 1C) with correspondingly lower quantities (5–30 µatm) of excess CO₂ (defined herein as ∆pCO₂ = pCO₂(sw) – pCO₂ atm; e.g., the eastern equatorial Atlantic; Fig. 1D). As a result, across the low-latitude non-HNLC regions macronutrient (as opposed to micronutrient) limitation currently exists (Moore et al., 2013). In these regions, there is more limited scope to decrease pCO₂ atm by enhanced nutrient utilization, since most of the nutrients are already nearly fully utilized.

Despite the apparent potential for changing pCO₂ atm in either HNLC or non-HNLC regions via alleviation of macronutrient or micronutrient limitation, it has been hypothesized that their role in glacial-interglacial CO₂ change should have been minor (Sigman et al., 2010; Hain et al., 2014), because of the following:

(1) Nutrients supplied to the low-latitude surface from below are all eventually consumed by productivity as the nutrient-rich water flows away from the site of upwelling before the water is able to sink into the ocean interior (Sigman and Haug, 2003). Even if an increase in on-axis (where axis refers to the longitudinally extensive zone of upwelling) consumption of nutrients occurred in an equatorial upwelling region

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METHODOLOGY

Samples from ca. 30 ka to 10 ka were selected from Site GeoB1105-4 (R/V Meteor cruise M9/4; herein GeoB1105) from the eastern equatorial Atlantic (Fig. 1), located near the center of modern upwelling. Age models for the studied period were discussed by Henrich et al. (2013) for Ocean Drilling Program (ODP) Site 999 and Site GeoB1523, and based on ¹⁴C dating for GeoB1105 (Bickert and Mackensen, 2003). Our new data, combined with published ³⁶Cl data for G. ruber from ODP Site 999A
(herein ODP 999) and Site GeoB1523-1 (herein GeoB1523) from the Caribbean and western equatorial Atlantic, respectively (Foster, 2008; Henegan et al., 2013), allow us to examine zonal gradients in surface ocean carbonate chemistry (Fig. 1). All boron isotopic measurements presented here were performed by multicolonlector–inductively coupled plasma–mass spectrometry at the University of Bristol (UK), closely following the methodologies in Foster (2008) and Rae et al. (2011). The basis for the boron isotope–pH proxy was discussed extensively elsewhere (e.g., Foster, 2008; Rae et al., 2011), and we use the new δ11B–pH calibration for this species (Henegan et al., 2013). We also generated sea-surface temperature (SST) records for the same samples using Mg/Ca ratio of *G. ruber* and the calibration of Anand et al. (2003). See the GSA Data Repository1 for more details of the methodologies used to calculate pH and pCO2 from δ11B; the relevant data are in Table DR1.

RESULTS

Figure 2 shows data from the three sites in the eastern Atlantic Ocean (blue), western Atlantic (black), and Caribbean (red). Our Mg/Ca-derived SST records reveal a persistent pattern throughout the past 30 k.y. of an eastward decrease in SST (i.e., SST GeoB1523 > SST GeoB1105, > SST GeoB1105-1, Fig. 2), but with larger differences between the sites before ca. 18 ka and the greatest extent of glacial-aged cooling at our easternmost site (GeoB1105; Fig. 2A). δ11B values of *G. ruber* and the calculated surface-water pH exhibit similar values across the three sites during Marine Isotope Stage 1 (MIS 1; Figs. 2B and 2C), consistent with the absence of a major pH gradient in the Atlantic today. However, δ11B and calculated pH diverge during MIS 2 (Figs. 2B and 2C). From these δ11B and pH records, we calculate that surface water in the Caribbean and western Atlantic (ODP 999 and GeoB1523) remained close to equilibrium with the atmosphere (purple line in Fig. 2D) with respect to CO2 for the past 30 k.y., albeit with a minor and consistent offset comparable to that observed today at both sites (20–30 µatm; Figs. 1D and 2D). This contrasts with GeoB1105 in the eastern equatorial Atlantic, where we reconstruct a significant excess of pCO2 compared to the contemporaneous atmosphere (by >100 µatm), indicating that this region was a strong source of CO2 to the atmosphere during MIS 2 and MIS 3. Therefore, in marked contrast to MIS 1 (Fig. 2), a significant east to west gradient in ΔpCO2 existed during the last glacial that was well correlated with the contemporaneous SST gradient (Figs. 2, 3A, and 3B). Notably, this strong cross-basin gradient in calculated pCO2 is also evident in δ11B alone, as reflected in the large differences between δ11B of *G. ruber* (to 1.5‰) from the three sites during the last glacial (e.g., ODP 999 versus GeoB1105; Fig. 2B) in comparison to correspondingly small δ11B gradients during MIS 1.

Figure 1. Surface water of the modern equatorial Atlantic, Indian, and Pacific Oceans constructed using Ocean Data View software (R. Schlitzer, 2014, http://odv.awi.de). EQ—equator. A: Mean annual sea-surface temperature (Locarnini et al., 2006). Sites used in this study are shown (see text). B: Mean primary productivity (MPP). Data were derived from satellite data available at http://oceancolor.gsfc.nasa.gov and http://pathfinder.nodc.noaa.gov/ using the vertically generalized productivity model of Behrenfeld and Falkowski (1997). C: Mean annual phosphate (Garcia et al., 2006). D: Mean annual ΔpCO2 (Takahashi et al., 2009). Note that ΔpCO2 in eastern equatorial Atlantic during some seasons can locally be 80–100 µatm (Bakker et al., 2001).

Figure 2. Data from three sites in the eastern Atlantic Ocean. Ocean Drilling Program (ODP) Site 999 is shown by red squares, Site GeoB1523 (R/V Meteor cruise M16/2), is shown by black triangles, and Site GeoB1105 (R/V Meteor cruise M16/4) is shown by blue circles; vertical lines denote the boundaries for the marine isotope stages. A: Mg/Ca based sea-surface temperature (SST, with 1σ uncertainty band ±0.75 °C); modern SSTs for each site are shown as open colored symbols. B: δ11B for *Globigerinoides ruber* with analytical uncertainty shown as a band (±0.25‰; 2a). C: Mixed-layer pH (error band is ±10 as dark band, ±20 as light band). D: pCO2 (sw—seawater) calculated using an assumed constant total alkalinity of 2300 µmol/kg (solid line); error band is as for pH. Dotted lines are pCO2 calculated using a total alkalinity that scales with salinity (for more details, see the Data Repository [see footnote 1]). Modern pCO2 at these locations (from Takahashi et al., 2008) are shown as open colored symbols. Purple line is atmospheric CO2 from ice cores (Monnin et al., 2001; Petit et al., 1999). E: δ18O for *G. ruber* from Schmidt et al. (2004), Schneider et al. (1996), and Mulitza et al. (1998) for ODP Site 999, Site GeoB1523, and Site GeoB1105, respectively.

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1GSA Data Repository item 2014351, data table, details of methods, and a figure showing phosphate concentration over the past 30 k.y. at GeoB1105, is available online at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
DISCUSSION

Our SST reconstruction across the equatorial Atlantic (Fig. 2A) shows a glacial-age cooling that was stronger in the east (3–4 °C) than the west (1–2 °C) (e.g., MARGO Project Members, 2009; Pflaumann et al., 2003), likely attributable to enhanced eastern upwelling of cold water owing to stronger glacial-age southeast trade winds (Mix and Morey, 1996; Wolff et al., 1999; MARGO Project Members, 2009). Intensified glacial upwelling in the east is also consistent with an increased east to west tilt in the equatorial Atlantic thermocline (Fig. 3D; Wolff et al., 1999), a shallow nutricline in the east (Molfino et al., 1999), and opal fluxes (not shown; Bradtmiller et al., 2003), a shallow nutricline in the eastern Atlantic Ocean. Ocean Drilling Program (ODP) Site 999 is shown in red, Site GeoB1523 (R/V Meteor cruise M162/2), is shown in black, and Site GeoB1105 (R/V Meteor cruise M9/4) is shown in blue; vertical lines denote the boundaries for the marine isotope stages. A: Boron isotope-derived ∆CO₂ (sea-air) for Ocean Drilling Program (ODP) Site 999, Site GeoB1105, and Site GeoB1523. Modern mean annual disequilibrium is shown as open symbols (ODP 999 = +21 µatm, GeoB1523 = +29 µatm, GeoB1105 = +30 µatm). B: Zonal sea-surface temperature (∆SST) gradient between Sites GeoB1105 and ODP 999 (red) and GeoB1105 and GeoB1523 (black). Error band is a quadratic addition of ±0.75 °C for each record; modern SST gradient is shown by open symbols. C: Paleo–primary productivity (PP; as g/m²/yr of carbon export) for GeoB1105 (Schmidt et al., 2003) and GeoB1523 (Rühlemann et al., 1996). D: Thermocline depth from foraminiferal transfer functions for GeoB1523 and GeoB1105 (Wolff et al., 1999). E: δ¹⁸O for Globigerinoides ruber from Schmidt et al. (2004), Schneid er et al. (1996), and Mulitza et al. (1998) for Sites ODP 999, GeoB1523, and GeoB1105, respectively.

As the CO₂-rich surface waters in the east were advected westward during the last glacial toward the western (GeoB1523) equatorial Atlantic and Caribbean (ODP 999), ∆CO₂ rapidly decreased (to ~20–30 µatm; Fig. 3A), probably through biological utilization of CO₂, as in the modern equatorial Pacific (Quay, 1997). While primary productivity at GeoB1523 was not higher during MIS 2 (Fig. 3C), it is apparent from the regional compilations of Kohfeld et al. (2005) and Bradtmiller et al. (2007) that export production was enhanced throughout much of the eastern and western equatorial Atlantic (Bradtmiller et al., 2007, their figure 2c). We therefore conclude that the enhanced biological productivity in the equatorial Atlantic during the last glacial (e.g., 3× higher rates of Cₑₑ, burial and primary productivity during MIS 2 compared to MIS 1; Fig. 3C) was primarily driven by enhanced upwelling in the eastern part of the basin (e.g., Schmidt et al., 2003) and the lateral transport of unused nutrient from the site of enhanced upwelling (and incomplete nutrient consumption) toward the central and western equatorial Atlantic. Our data from the eastern Atlantic demonstrate that this enhanced upwelling (and the presumed incomplete consumption of nutrients) increased the excess CO₂ in the eastern Atlantic surface, thereby enhancing local CO₂ outgassing. However, by analogy with the modern Pacific equatorial upwelling system, our data from the western equatorial Atlantic and Caribbean (Fig. 3A) suggest that the excess CO₂ upwelled in the east was ultimately consumed by intensified downstream biological carbon export, fuelled by the unused nutrients that were laterally advected alongside the excess CO₂. For this reason, the coupled intensification of upwelling in the east and a stronger biological pump in the wider equatorial Atlantic region likely had little or no effect on glacial atmospheric CO₂ levels.

CONCLUSIONS

By reconstructing the patterns of pCO₂ atm across the equatorial Atlantic over the past 30
k.y. we demonstrate that the equatorial Atlantic underwent an at least fivefold increase in the rate of upwelling. Although this upwelling intensified regional productivity (Kohfeld et al., 2005; Schmidt et al., 2003), our reconstructed higher than modern ΔpCO₂ for the eastern equatorial Atlantic indicates that export production did not keep pace with the strengthened upwelling of nutrients, giving rise to significant CO₂ outgassing (Fig. 3A). We thus find that the low-latitude Atlantic was not a significant contributor to the drawdown of atmospheric CO₂ concentrations during the last glacial, providing support for the dominance of high-latitude processes in glacial-interglacial CO₂ change.

ACKNOWLEDGMENTS

This work was supported by Natural Environment Research Council (NERC) grant NE/D008765/X2 to Foster and NERC grant NE/I006346/1 to Sexton and Foster. We thank Richard Fairbanks for maintaining the mass spectrometers at the University of Bristol (UK) and James Rae and Mathis Hain for discussion on an earlier draft of this manuscript. We also thank Stephanie Henson for producing panel B of Figure 1, Barbara Donner for supplying samples for site GeoB1105, and Karen Kohfeld, Jimin Yu, and two anonymous reviewers for thorough reviews that significantly improved the manuscript.

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