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A deeper respired carbon pool in the glacial equatorial Pacific Ocean

L.I. Bradtmiller [a,*], R.F. Anderson [b,c], J.P. Sachs [d], M.Q. Fleisher [b]

[a] *Department of Environmental Studies, Macalester College, Saint Paul, MN, 55105, USA*
[b] *The Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, USA*
[c] *Department of Earth and Environmental Sciences, Columbia University, New York, NY, USA*
[d] *School of Oceanography, University of Washington, Seattle, WA, USA*

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ABSTRACT

Atmospheric pCO_2 was approximately 80 ppm lower during the last glacial period than during pre-industrial times. Identifying the fate of that carbon has been one of the great challenges in paleoceanography. We present evidence from ten equatorial Pacific Ocean sediment cores to show that the deep Pacific Ocean likely stored more carbon during the last glacial period than the Holocene. The concentration of the redox-sensitive metal uranium (U) in sediments was systematically greater during the last glacial period than during the Holocene, indicating more reducing conditions in glacial-age sediments. Reconstructions of biogenic opal flux indicate that changes in U distribution were not the result of changes in biological productivity and the ensuing rain of organic carbon to the sea floor, which also affects the redox conditions of the sediments. Together, these results lead to the interpretation that bottom water in the equatorial Pacific during the glacial period had significantly lower oxygen concentration than during the Holocene, and a correspondingly greater level of respired CO_2. This conclusion is supported by evidence for greater preservation of brassicasterol, a biomarker produced by diatoms, in glacial-age sediments of the eastern equatorial Pacific. The presence of additional respired CO_2 in the glacial deep ocean would have lowered atmospheric pCO_2 by 1) increasing the total storage of CO_2 in the glacial ocean and 2) increasing ocean alkalinity following a transient carbonate dissolution event. Our results are consistent with recently published data from the North Pacific Ocean; this suggests that increased carbon storage in the glacial deep Pacific Ocean was a basin-wide phenomenon, consistent with a large-scale transfer of carbon to the deep ocean during glacial periods.

1. Introduction

The concentration of CO_2 in the atmosphere was approximately 80 ppm lower during the last glacial period than during pre-industrial times (Petit et al., 1999), but efforts to definitively identify where that carbon was stored during the glacial period have so far been unsuccessful. Because of the large size of the deep ocean carbon reservoir (relative to the size of the atmospheric carbon reservoir) and its rapid rate of exchange with the atmosphere (relative to glacial–interglacial timescales), the deep ocean has long been central to the search for this missing glacial carbon (Broecker, 1982). While previous approaches to this problem have focused on reconstructing the distribution of carbon or other nutrients in the glacial ocean (Boyle, 1988, 1992), we focus here on reconstructing the redox conditions imposed by respiration of the hypothesized additional carbon. Using proxies for redox conditions, the rain of organic matter from the surface ocean, and the preservation of organic material on the seafloor, we show that the deep Pacific Ocean was likely the repository for a large portion of the carbon removed from the atmosphere during the glacial period.

Meridional overturning circulation is largely responsible for the distribution of dissolved oxygen and remineralized nutrients in the ocean. Deep water forms in the North Atlantic and accumulates the regenerated products of sinking organic material as it flows through the Southern Ocean and into the North Pacific (Broecker et al., 1998). As this organic matter is respired, deep water becomes increasingly depleted in oxygen and enriched in nutrients and dissolved inorganic carbon, resulting in the presence of low-oxygen, high-nutrient water throughout the deep North Pacific (Key et al., 2004). This process is also reflected in the carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{(DIC)}$) throughout the ocean. Observed $\delta^{13}C_{(DIC)}$ in modern North Atlantic surface water is about 1.5‰, and as this water sinks and flows southward as North Atlantic Deep Water (NADW) the addition of isotopically light remineralized carbon drives this value lower throughout its transit through the Southern Ocean (0.5‰) towards the north Pacific (−0.5‰) (Kroopnick, 1985).

The $\delta^{13}C_{(DIC)}$ has been widely used to compare modern and paleo-circulation, often with the goal of identifying changes in the deep ocean carbon pool as they relate to changes in the concentration of atmospheric CO_2. Several studies have shown that glacial Pacific deep

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[*] Corresponding author.
E-mail address: lbradtmi@macalester.edu (L.I. Bradtmiller).

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water (below 2000–2500 m) was enriched in nutrients (depleted in $\delta^{13}C_{(DIC)}$) relative to the Holocene, while the opposite was true in intermediate waters (e.g. Keigwin, 1998; Matsumoto et al., 2002). This is consistent with data from the Atlantic (Curry and Oppo, 2005; Duplessy et al., 1988; Sarnthein et al., 1994), Indian (Duplessy et al., 1988; McCorkle et al., 1998) and Southern Oceans (Hodell et al., 2003; Ninnemann and Charles, 2002), all of which indicate the presence of a strong nutrient gradient at similar water depths. These data support the idea of "nutrient deepening" as proposed by Boyle (1988), which suggests that a transfer of nutrients from intermediate depths to the larger-volume deep water reservoir stored more carbon in the glacial ocean, drawing down atmospheric CO_2.

Proxy reconstructions of dissolved O_2 and phosphate (PO_4) concentrations appear to contradict the nutrient deepening hypothesis. If the glacial deep Pacific Ocean was filled with respired carbon, dissolved O_2 concentrations should have decreased significantly. While redox-sensitive metals suggest that deep water O_2 concentrations were slightly reduced in all ocean basins (Francois et al., 1997; Mangini et al., 2001; Pattan and Pearce, 2009; Sarkar et al., 1993; Thomson et al., 1990), including the north Pacific (Galbraith et al., 2007), the abundance of aerobic benthic foraminifera in the glacial north Pacific (Calvert and Pedersen, 1993) limits this to a smaller decrease than would be expected from a large addition of respired carbon.

If the glacial deep Pacific contained relatively more respired carbon than today, it would also likely have contained increased concentrations of other remineralized nutrients. The cadmium:calcium ratio (Cd/Ca) is often used to reconstruct past concentrations of the nutrient phosphate based on the correlation between dissolved Cd and PO_4 in the modern ocean (Boyle, 1992; Boyle et al., 1976). However, Cd/Ca measurements of benthic foraminifera suggest that there was little change in PO_4 concentration in the deep north Pacific from the last glacial period through the present (Boyle, 1992; Boyle and Rosenthal, 1996; Ohkouchi et al., 1994).

In a recent paper, Jaccard et al. (2009) sought to reconcile records of $\delta^{13}C_{(DIC)}$, Cd/Ca and redox-sensitive metals in the glacial north Pacific Ocean. Using redox-sensitive metals to infer redox conditions in sediments and biogenic Ba and opal measurements to constrain organic carbon export, the authors showed that glacial North Pacific deep waters were oxygen-depleted but not anoxic, consistent with the storage of more dissolved inorganic carbon (DIC) in the glacial ocean relative to the present. In order to reconcile these results with Cd/Ca records, the authors suggest a variant of Boyle's hypothesis (Boyle, 1988), which they term the "respired-carbon deepening hypothesis". Jaccard et al. (2009) proposed that during the glacial period, the deep Pacific contained a higher ratio of remineralized: preformed nutrients. This distinction is important, since nutrients can enter deep water either associated with carbon as sinking organic material (remineralized) or without sequestering any carbon at all, as when unused nutrients in surface waters are subducted directly into deeper waters (preformed). The global average ratio of remineralized: preformed nutrients is the master variable characterizing the efficiency of the ocean's biological pump and its regulation of atmospheric CO_2 concentrations (Sigman and Boyle, 2000). Therefore, an increase in the ratio of remineralized:preformed nutrients could have increased the DIC concentration of the glacial deep Pacific, simultaneously lowering dissolved O_2 content, without increasing the total concentration of PO_4 (or other nutrients). Because Cd/Ca reflects total PO_4 (remineralized + preformed), simply changing the ratio of remineralized:preformed PO_4 would not be expected to change the Cd/Ca ratio, consistent with the available data (Boyle, 1992; Boyle and Rosenthal, 1996; Ohkouchi et al., 1994).

In this paper we present results to show that the deep equatorial Pacific Ocean was also less oxygenated during the LGM than at present. We show that the concentration of the redox-sensitive metal uranium (U) in sediments was greater during the last glacial period than during the Holocene, implying a more reducing environment. Reconstructions of biogenic opal flux using ^{230}Th normalization show that changes in U distribution are not likely the result of changes in biological productivity and the ensuing rain of organic carbon to the sea floor, which also affects the redox conditions of the sediments. Instead, these results lead to the interpretation that bottom water in the equatorial Pacific during the glacial period had significantly lower oxygen concentration than during the Holocene, a conclusion that is further supported by evidence for greater preservation of organic biomarkers in glacial-age sediments. Lower oxygen in deep Pacific waters, in turn, indicates the presence of a correspondingly greater level of respired CO_2. Our findings provide renewed evidence for a large-scale transfer of carbon from the atmosphere to the deep ocean during the last glacial period, and when combined with data from the North Pacific (Jaccard et al., 2009), imply that this phenomenon was basin-wide.

2. Proxies

Uranium is well mixed in the ocean, and behaves conservatively in oxygenated sea water as U(VI) within the highly soluble uranyl carbonate complex ($UO_2(CO_3)_3^{4-}$) (Langmuir, 1978). The primary mechanism of U addition to the ocean is through the weathering of continents, while one of the main mechanisms of removal is through diffusion into reducing surface sediments (Klinkhammer and Palmer, 1991). Suboxic conditions reduce soluble U(VI) to insoluble U(IV), which precipitates as uraninite (UO_2) (Morford and Emerson, 1999) and thereby reduces pore water [U], resulting in a concentration gradient between bottom water and sediment pore water. Dissolved U then diffuses into sediments along the concentration gradient, and the sustained precipitation of this diffusive flux leads to an enrichment of U in reducing sediments. This excess or precipitated U is referred to as authigenic U (aU).

There are two major controls on the redox state of sediment: the rain of organic material from the surface ocean, which consumes dissolved oxygen as it is respired, and the oxygen content of bottom water masses. In order to reconstruct changes in both factors over time we employ two proxies used by the Jaccard et al. (2009) study, ^{230}Th normalized opal fluxes and the concentration of aU. Authigenic U provides information about the overall redox state of the sediment, while opal fluxes provide information about the vertical rain of organic material from the surface ocean. If sediments become more reducing with no observed increase in opal flux (i.e. no increased oxygen demand due to the respiration of organic material), it can be inferred that the change in redox state is due to a decrease in bottom water oxygen concentration. It is important to note that aU precipitation is non-linear with respect to the sediment redox state, and also the rain rate of organic matter from the surface ocean. Specifically, below the threshold flux of organic carbon required to create anoxia in sediments, little or no deposition of aU occurs; above this threshold, there is a non-linear positive relationship between aU deposition and organic carbon flux (Kumar et al., 1995).

Opal fluxes cannot be used as a quantitative proxy for organic carbon delivery to the seafloor, but they have been shown to reflect spatial patterns of primary productivity in the equatorial Pacific (Bradtmiller et al., 2006). Opal forms as the siliceous frustules of diatoms and shells of radiolaria, and is therefore directly related to export productivity. While the majority of opal produced in the surface ocean is dissolved before reaching the seafloor, a study in the eastern equatorial Pacific Ocean concluded that there has been little change in opal preservation over the last glacial cycle (Warnock et al., 2007), which suggests that it is appropriate to compare glacial and Holocene opal fluxes from this region as a qualitative proxy for changes in export productivity. It is also possible to identify core sections that have been affected by post-depositional opal dissolution using the $^{231}Pa/^{230}Th$ ratio in sediments, and those data are available for all new cores presented here (Bradtmiller et al., 2006).

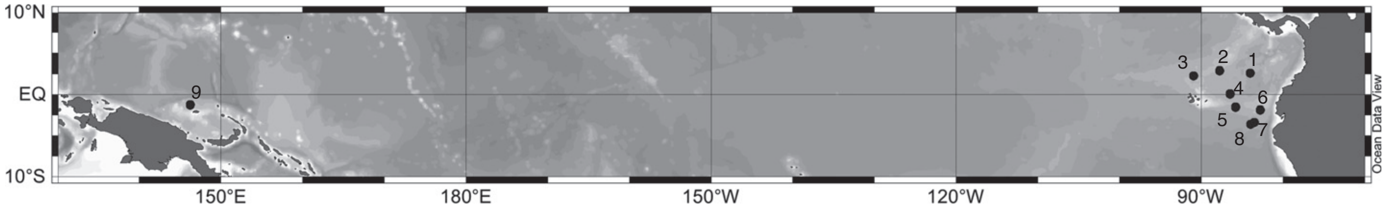

Fig. 1. Locations of cores from this study, Kienast et al. (2007) and Yang et al. (1995). 1. P7; 2. RC13-140; 3. TR163-19P; 4. ME0005-24JC, Y69-71P; 5. RC11-238; 6. ME0005-27JC; 7. V19-30; 8. TR163-31P; 9. MD97-2138. Additional information about these cores is provided in Table 1.

Opal flux is linked to the rain of particulate organic carbon (POC) to the sea floor. Although early statistical analyses identified a global correlation between the fluxes of POC and of $CaCO_3$ (Francois et al., 2002; Klaas and Archer, 2002), more detailed studies indicate a stronger mechanistic relationship between diatom productivity and the flux of POC to the deep sea. This relationship exists primarily because the fraction of net primary production that is exported from the euphotic zone is strongly correlated with the abundance of large phytoplankton taxa, especially diatoms (Buesseler, 1998; Buesseler et al., 2007; Guidi et al., 2009; Honda and Watanabe, 2010). A secondary but significant contributing factor is that opal also serves as an effective ballast to enhance the transfer of POC to the deep sea (Boyd and Trull, 2007; Honda and Watanabe, 2010). Consequently, while we cannot correlate preserved opal flux in sediments quantitatively with the rain of POC, we can have some confidence in the qualitative relationship that allows the sense of a trend in POC rain to be inferred from the contemporary trend in opal flux. Specifically, as shown below, when we find that the opal flux in glacial sediments was less than the opal flux at the same locations during the Holocene we can infer that the POC rain was also less during the glacial period.

Additional information can be gained by measuring concentrations of brassicasterol (24-methylcholesta-5,22E-dien-3b-ol), a common lipid biomarker for diatoms (Pourmand et al., 2007; Werne et al., 2000). Keeping in mind that the preservation of opal in eastern equatorial Pacific (EEP) sediments has remained approximately constant since the Last Glacial Maximum (LGM) (Warnock et al., 2007), downcore variability in brassicasterol/opal ratios can be interpreted to reflect changes in brassicasterol preservation if the brassicasterol/opal ratio exported from surface waters has also remained relatively uniform. Preservation of brassicasterol, in turn, can be linked to changes in bottom water oxygen concentrations (Zonneveld et al., 2010), thereby providing a crosscheck on interpretations based on authigenic uranium and opal flux.

3. Methods

We present new results from four cores in the equatorial Pacific Ocean. Three cores were recovered from the EEP, and one core was recovered from the western equatorial Pacific (WEP) (Fig. 1). Cores V19-30 and RC11-238 come from the region of high biological productivity in the modern EEP, while core RC13-140 comes from farther north, in an area of slightly lower modern productivity. Core MD97-2138 sits in the modern Western Pacific Warm Pool, in the shallower waters to the north of Papua New Guinea. In addition, we show aU concentrations in six cores derived from data published by Kienast et al. (2007). Table 1 describes core locations, length, depth, age control and data sources.

Uranium (^{238}U, ^{234}U) and thorium (^{232}Th, ^{230}Th) concentrations were determined by inductively coupled plasma mass spectrometry after sediment dissolution (HNO_3, HF and $HClO_4$ treatment) and anion resin column chemistry to separate the Pa fraction and U/Th fraction (Anderson and Fleer, 1982; Fleisher and Anderson, 2003). The authigenic fraction of U was determined by subtracting the detrital fraction of ^{238}U from the total ^{238}U present. The detrital fraction of ^{238}U was calculated assuming a detrital source for all ^{232}Th, and a detrital ^{238}U:^{232}Th activity ratio of 0.7. The average 2σ error on aU concentration was 3.5%, which includes measurement error as well as uncertainty due to the age model.

Percent biogenic opal was measured by alkaline extraction after Mortlock and Froelich (1989). Average errors for this method range from 0.2 to 1.0%. Opal fluxes were calculated by normalizing to ^{230}Th to correct for lateral redistribution of sediments by deep-sea currents (Bacon, 1984; Francois et al., 1990, 2004; Frank et al., 1996). Thorium normalization works on the assumption that the flux of particulate ^{230}Th sinking to the ocean floor is approximately equal to its known rate of production from ^{234}U decay in the water column because the residence time of ^{230}Th in the water column is relatively short (on the order of a few decades) (Anderson et al., 1983) compared to the time scale for lateral mixing in deep ocean basins (Anderson et al., 1990). Where burial rates of ^{230}Th are found to exceed its production in the water column, this is attributed to the lateral redistribution of sediments by deep-sea currents. The ^{230}Th normalization method has been supported by findings from both modeling (Henderson et al., 1999) and sediment trap studies (Scholten et al., 2001, 2005; Yu et al., 2001).

Setting the vertical flux of ^{230}Th equal to its known production rate, fluxes of preserved material can be calculated as: $F_i = \frac{C_i \times \beta \times z}{xs^{230}Th_0}$ where F_i is the flux of a sedimentary constituent of interest, C_i is the concentration of that constituent in bulk sediment, β*z is equal to the production rate of ^{230}Th in the water column, z is the depth of the

Table 1
Core locations, depths, age control and data sources. Latitude is expressed in degrees N and Longitude is expressed in degrees E. The number in the second column (No.) refers to label number in Fig. 1.

Core	No.	Lat.	Long.	Water depth (m)	Age control	Age model source	Data source
V19-30	7	−83.52	−3.38	3091	$\delta^{18}O$	Shackleton et al (1983), N. Shackleton personal communication	This study
RC13-140	2	−87.75	2.87	2246	^{14}C	Koutavas and Lynch-Stieglitz (2003)	This study
RC11-238	5	−85.82	−1.52	2573	^{14}C	Koutavas and Lynch-Stieglitz (2003)	This study
MD97-2138	9	146.24	−1.25	1900	^{14}C and $\delta^{18}O$	Pichat et al., 2004	This study
ME0005-24JC	4	−86.46	0.02	2941	^{14}C	Kienast et al. (2007)	Kienast et al. (2007)
Y69-71P	4	−86.48	0.1	2740	^{14}C and $\delta^{18}O$	Kienast et al. (2007)	Kienast et al. (2007)
P7	1	−83.99	2.6	3085	^{14}C	Yang et al. (1995)	Yang et al. (1995)
ME0005-27JC	6	−82.79	−1.85	2203	^{14}C and $\delta^{18}O$	Kienast et al. (2007)	Kienast et al. (2007)
TR163-31P	8	−83.95	−3.6	3209	^{14}C and $\delta^{18}O$	Martin et al. (2002)	Kienast et al. (2007)
TR163-19P	3	−90.95	2.26	2348	$\delta^{18}O$	Lea et al. (2000), Spero and Lea (2002)	Kienast et al. (2007)

water column (cm) and $\beta = 2.63*10^{-5}$ dpm cm^{-3} kyr^{-1}), and xs^{230}Th$_0$ is equal to the decay-corrected concentration of Th in the sample (dpm/g) in excess of that supported by its parent, ^{234}U. The average 2σ error on ^{230}Th normalized fluxes was 5.5%, which includes measurement error as well as uncertainty due to the age model.

Concentrations of brassicasterol in samples from V19-30 were determined by gas chromatography with flame-ionization detection and co-injected standards, following identification by gas chromatography–mass spectrometry (Sachs and Anderson, 2003, 2005).

4. Results

Results will be described here in three sections. First, we will describe in some detail the new results from this study, for which both opal flux and aU data are available. These results are available as an electronic appendix to this study. We will then briefly describe aU data published elsewhere and included here for comparison. These results are available from the National Climatic Data Center at http://www.ncdc.noaa.gov/paleo/metadata/noaa-ocean-6414.html. Finally, new brassicasterol results from V19-30 will be presented in the third section.

4.1. Opal and aU results from this study

Opal fluxes in the three EEP cores all show slightly lower fluxes during the glacial period than during the late Holocene (Fig. 2a). In core V19-30, opal fluxes during the late glacial range from 0.16 g cm^{-2} kyr^{-1} to 0.29 g cm^{-2} kyr^{-1}, with an average late glacial (18 ka to 30 ka) value of 0.21 g cm^{-2} kyr^{-1}. Opal flux increases to a maximum of 0.35 g cm^{-2} kyr^{-1} by 14 ka, and remains at that level until 10 ka, after which opal flux decreases to values between 0.24 and 0.27 g cm^{-2} kyr^{-1}. RC11-238 shows a late glacial decrease in opal flux from 0.09 g cm^{-2} kyr^{-1} to a minimum of 0.02 g cm^{-2} kyr^{-1} at 21 ka, a quasi-linear increase to a maximum opal flux of 0.17 g cm^{-2} kyr^{-1} at 11 ka, and a steady decrease toward a late Holocene opal flux of 0.11 g cm^{-2} kyr^{-1}. RC13-140 also exhibits a slight glacial minimum in opal flux, but the range of variability in this core is much smaller than those in the other two cores—approximately 0.06 g cm^{-2} kyr^{-1}—and thus the relative glacial-Holocene differences are less pronounced.

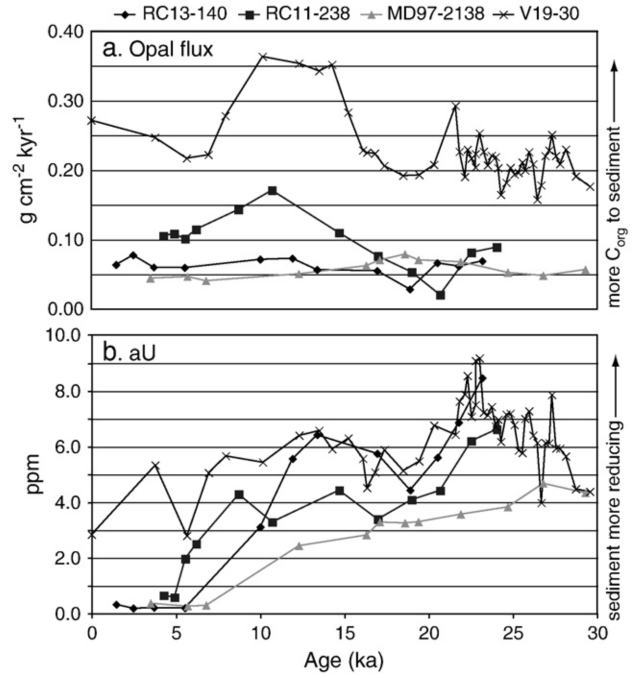

Fig. 2. Opal fluxes (a) and aU concentrations (b) in the four cores from this study.

The opal flux record in core MD97-2138 from the WEP shows the opposite trend to the three EEP cores. Opal fluxes at the LGM are greater (0.08–0.05 g cm^{-2} kyr^{-1} at ~19 ka) than late Holocene fluxes (0.04 g cm^{-2} kyr^{-1}), although the interval of maximum opal flux is relatively brief. In older sediments (ca. 24–30 ka) the opal flux is not significantly greater than during the Holocene.

All four cores exhibit similar trends in aU, as each core contains higher concentrations of aU during the glacial period than during the Holocene (Fig. 2b). Core V19-30 contains aU in concentrations as high as 6.8 ppm during the glacial period, while Holocene samples range from 2.8 to 5.3 ppm. The concentration of aU in core RC11-238 decreases from 6.6 to 3.4 ppm during the late glacial, then remains relatively stable (between 3.3 and 4.4 ppm) between 17 and 9 ka, followed by a steep decline into the late Holocene to a coretop value of 0.65 ppm. RC13-140 shows a similar pattern, with a late glacial decrease from 8.5 to 4.4 ppm followed by a slight increase in aU concentration to a peak of 6.4 ppm at 13 ka, again followed by a steep decrease to 0.20 ppm where concentrations remain steady throughout the late Holocene. MD97-2138 shows a slightly different pattern, in that the aU concentration steadily declines from 3.83 ppm at 25 ka to 0.29 ppm from 7 ka, where concentrations remain steady throughout the middle Holocene.

4.2. Results from previous studies

Concentrations of aU in the six other equatorial Pacific cores presented here were calculated from published data (Kienast et al., 2007; Yang et al., 1995), although the references cited did not discuss aU data in the published material. Of the six cores originally presented by Kienast et al. (2007) and Yang et al. (1995), five show higher concentrations of aU during the last glacial period than during the Holocene (Fig. 3). Core P7 contains similar concentrations of aU to the other cores during the glacial period (between 7 and 9 ppm), but unlike in the other cores aU concentration remains elevated throughout the record, with 8.0 and 5.9 ppm at 10 and 7 ka, respectively. Late Holocene data are not available for P7. Core TR163-31P shows aU concentrations between 6 and 9 ppm during the glacial period, and concentrations between 5.4 and 7.3 ppm through the remainder of the record. The remaining four cores (ME0005-24JC, Y69-71P, ME0005-27JC and TR 163-19P) share a similar pattern of temporal variability in aU concentration, with higher concentrations during the glacial period (between 4.0 and 9.5 ppm) and a gradual decline to late Holocene values between 0.7 and 2.9 ppm.

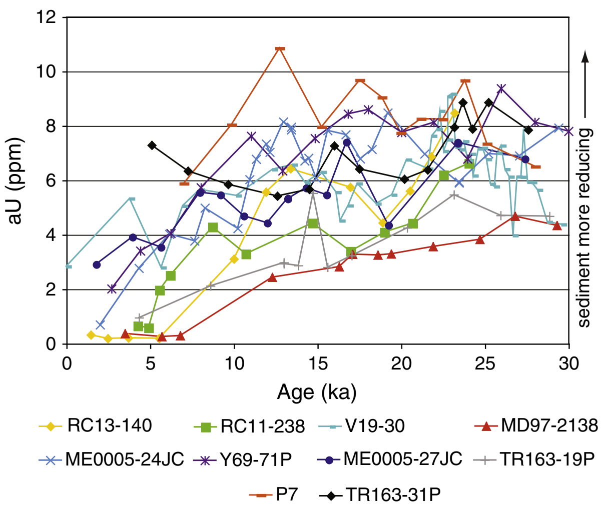

Fig. 3. Concentrations of aU in cores from this study and from the literature (Kienast et al., 2007; Yang et al., 1995). Most records show decreasing concentrations of aU during the Holocene.

4.3. Biomarker results from this study

Fluxes of the biomarker brassicasterol in core V19-30 were more than twice as great during the LGM than the Holocene (Fig. 4a). Values during the late glacial period range between 0.37 and 0.82 μg cm^{-2} kyr^{-1} before a peak of 0.89 μg cm^{-2} kyr^{-1} at 16 ka. Fluxes then decrease steadily until ~8 ka, and remain between 0.18 and 0.10 μg cm^{-2} kyr^{-1} from 8 ka to the present.

5. Discussion

5.1. Features common to the north and equatorial Pacific regions

In addition to the results presented here, there is other evidence that the rain rate of organic carbon in the equatorial Pacific Ocean was lower during the last glacial period than during the Holocene. Studies utilizing the ^{230}Th normalization technique have interpreted lower fluxes of calcite and opal as evidence that biological productivity in the glacial equatorial Pacific was less than that of the Holocene (Bradtmiller et al., 2006; Kienast et al., 2006; Loubere et al., 2004; Pichat et al., 2004). In contrast, studies that calculate linear sedimentation rates from core chronologies have interpreted increased calcite and barite mass accumulation rates (MARs) as evidence for increased glacial productivity (e.g. Lyle et al., 2002; Paytan et al., 1996). Proponents of MARs assert that ^{230}Th normalization overestimates the effects of sediment redistribution (as compared to seismic data), and therefore the observed decrease in ^{230}Th normalized fluxes since the LGM is an artifact (Lyle et al., 2005). However, two studies have shown that Holocene ^{230}Th normalized fluxes of opal and of organic carbon are consistent with observed modern primary productivity (Bradtmiller et al., 2006; Kienast et al., 2007), and that the differences in focusing factors predicted by ^{230}Th accumulation at two nearby sites are in fact consistent with predictions based on seismic data (Kienast et al., 2007). Other studies using the constant flux proxy ^{3}He (Marcantonio et al., 1996, 2001), sediment traps (Scholten et al., 2005; Yu et al., 2001) and model simulations (Henderson et al., 1999; Marchal et al., 2000) have also validated the ^{230}Th normalization approach. Furthermore, independent analyses using benthic foraminiferal transfer functions have also shown lower glacial than Holocene productivity in the EEP (Loubere, 1999, 2000, 2003). Therefore, we proceed under the assumption that reconstructions of paleo-productivity based on ^{230}Th normalized biogenic fluxes are valid, and that export productivity in the eastern equatorial Pacific Ocean was likely greater during the Holocene than during the last glacial period.

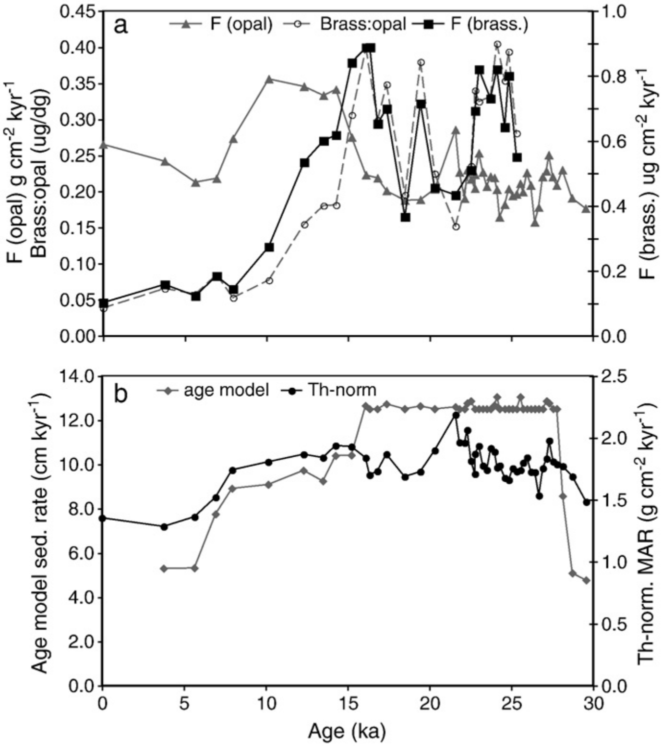

Fig. 4. ^{230}Th-normalized fluxes of opal and brassicasterol, and the brassicasterol:opal flux ratio in V19-30 (a). Note that the Brassicasterol:opal ratio is reported in units of μg/dg. Linear sediment accumulation rate of V19-30 derived from the published age model, and ^{230}Th-normalized mass accumulation rate (b).

All four equatorial Pacific cores for which new results are presented here contain higher concentrations of aU during the glacial period than during the Holocene, consistent with the findings of Jaccard et al. (2009) in the north Pacific. Furthermore, cores RC13-140, RC11-238 and V19-30 show lower glacial than Holocene opal fluxes, which implies that changes in sedimentary redox conditions were driven by changes in the oxygen content of overlying bottom waters rather than by changes in the rain of organic material from the surface ocean (see Section 2). This supports the findings and interpretations of Jaccard et al. (2009), who suggest that during the glacial period the deep Pacific Ocean contained a higher ratio of remineralized: preformed nutrients, which led to lower dissolved oxygen concentrations and greater total CO_2 storage than during the Holocene.

While its aU record looks similar to that of the other three cores, MD97-2138 differs from the eastern cores in that the trend in opal flux is similar to the trend in aU (i.e. both opal flux and aU are greater during the late glacial, at ~19 ka, than during the Holocene). This allows for the possibility that the aU record in this core partially reflects changes in organic carbon delivery to the sediment, perhaps in addition to changes in bottom water oxygen content. However, examining the full record of aU and opal flux in this core reveals that bottom water oxygen content must have played an important role in determining the redox state of sediment at this site. Opal fluxes (Fig. 2a) during the late Holocene (3–7 ka) were indistinguishable from those recorded in early MIS 2 (24–30 ka), from which we can infer that POC fluxes to the sea floor were also comparable during these two time periods. Despite comparable POC fluxes, the aU concentrations in sediments from 24 to 30 ka (~4 ppm) were much greater than during the Late Holocene (~0.3 ppm). Therefore, while the maximum in opal flux during the LGM limits our ability to reach firm conclusions about that specific time interval, the results from MD97-2138 are more broadly consistent with results from all other sites in indicating that bottom water oxygen levels must have been lower during the last glacial period than during the Holocene. Furthermore, the water depth of this core site (1900 m) suggests that in the equatorial region, the low O_2 carbon-rich water mass may have extended to much shallower depths than proposed by Jaccard et al. (2009) in the North Pacific (3000 m). This shallower depth is consistent with estimates from $\delta^{13}C_{(DIC)}$, which place the shallow boundary of the carbon-rich water mass at 2000–2500 m water depth in the Pacific Ocean (Keigwin, 1998; Matsumoto et al., 2002).

Combining the data presented here with aU data from the literature further confirms that there is a marked trend in aU concentrations in the equatorial Pacific Ocean, from higher concentrations during the glacial period to lower concentrations during the middle and late Holocene (Fig. 3). This again supports the idea that bottom water oxygen levels were lower during the glacial period than during the Holocene in this region, and it is consistent with the "respired-carbon deepening hypothesis" (Jaccard et al., 2009). It is difficult to identify a consistent temporal pattern in the aU data from these cores. The beginning of the transition from high concentrations of aU during the glacial period occurs between 18 and 13 ka in several cores, but is difficult to identify in some locations because of a stepwise decrease. Without accompanying opal flux data, it is not possible to definitively attribute these changes solely to changes in bottom water oxygen concentration or organic carbon export. However, these data help to illustrate a regional shift in sedimentary redox conditions from the last glacial period to the present. Given the similarity of the Kienast et al. (2007) records to the new records presented here, as well as their relative physical proximity, it seems reasonable to suggest that the same processes were responsible throughout the region.

5.2. Differences between the north and equatorial Pacific regions

The timing of changes in aU is internally consistent within the four new cores studied here, but differs from that reported by Jaccard et al. (2009). The Jaccard et al. (2009) record from the north Pacific shows a sharp increase in opal flux and a gradual decline in aU, both beginning at 14.7 ka. Our records all show high glacial values of aU followed by a decrease and a plateau during the deglaciation. Values then typically remain well above zero until the early Holocene, when they decline to near zero. The exception is V19-30, where aU values remain above zero throughout the Holocene, likely due to extremely high modern primary productivity at this site. The timing of the decrease to near-zero values occurs between 10 and 5 ka in the other three cores. Sample resolution does not allow us to be more specific with regard to the timing for cores MD97-2138 or RC13-140, but RC11-238 shows a sharp decline in aU concentration beginning at 8.7 ka and reaching a minimum at 4.9 ka. The difference in timing between the two regions implies that if changes in aU indeed reflect only changes in bottom water oxygen composition, then those changes were delayed in reaching the equatorial Pacific relative to the north Pacific. This is consistent with the modern pattern of deep water circulation in the north Pacific. Deep water enters from the South Pacific as a deep western boundary current, upwells in the north Pacific, and spreads to the south (e.g. Broecker et al., 1998). However, the amount of time elapsed between the changes seen in the north Pacific and near the equator is much greater than would be expected simply from being ‘farther along’ the conveyor belt, so something else must have contributed to the delayed reduction of aU content of EEP sediments.

Examining variability in eastern equatorial Pacific opal fluxes during the deglaciation can help to reconcile the delay in decreased aU concentrations relative to the north Pacific. Opal fluxes increase during this deglacial interval in all three EEP cores, and RC11-238 and V19-30 show peak fluxes during the early Holocene (10.7 ka and 10.1 ka, respectively) before decreasing slightly into the late Holocene. When combined with aU data, this suggests that as the bottom water oxygen concentration increased following 14.7 ka (as per Jaccard et al. (2009)), increased fluxes of organic material from the surface were sufficient to keep equatorial Pacific sediment pore waters in a reducing state for several thousand years. As opal fluxes decreased into the Holocene, and as bottom water oxygen content continued to increase, sediment pore waters eventually became less reducing, lowering the rate of aU deposition. This is consistent with the conclusions of Jaccard et al. (2009), in that it invokes differences in local productivity imposed upon a consistent change in bottom water oxygen content in north and equatorial Pacific deep waters.

5.3. Support from biomarker fluxes

Several factors influence the preservation and burial of organic matter in marine sediments (see review by Zonneveld et al., 2010). The amount of organic matter buried is first of all regulated by the amount produced by organisms in surface water, and by factors affecting the efficiency of export to depth, such as the size of the organisms and the availability of ballast to enhance sinking. Oxygen availability at the sea floor is a second major factor regulating the preservation of organic matter on the sea bed. Physical factors also influence organic matter preservation. For example, the rate of sediment accumulation has an indirect effect by controlling the duration of organic matter exposure to oxygen. Mineral surfaces may also help protect organic matter from degradation.

If other factors remain relatively constant, then changes in bottom water oxygen concentration impose a strong regulatory effect on organic matter preservation. Preservation seems to be most closely correlated with the duration of exposure to molecular oxygen (Hartnett et al., 1998; Hedges et al., 1999), which accounts for burial rate as well as bottom water oxygen concentration. Although biomarker preservation efficiency has not been calibrated quantitatively in terms of oxygen exposure time, some important benchmarks have been established. For example, in a study of Arabian Sea sediments Keil and Cowie (1999) found that a transition to much greater organic carbon to mineral surface area ratios occurred over a range of bottom water oxygen concentration between 15 and 35 μmol/kg. Prahl et al. (2001) noted that the preservation efficiency of C37 alkenones (produced by coccolithophorids) varies by as much as a factor of 40 over a range of sedimentary redox conditions.

Comparing brassicasterol and opal fluxes in V19-30 reveals substantially different patterns over the past 25 kyr (Fig. 4a). In particular, brassicasterol/opal ratios decrease by about a factor of five between 16 ka (4.0 μg/g) to 10 ka (0.77 μg/g). Increasing opal fluxes over this interval reflect the deglacial increase in biological productivity discussed above. The contemporary decline in brassicasterol flux must, therefore, reflect a substantial reduction in biomarker preservation. As noted in the preceding section, evidence from North Pacific sediments indicates a rise in deepwater oxygen concentration at ~14.7 ka. Brassicasterol/opal ratios in V19-30 drop most precipitously after ~15 ka (Fig. 4a). Within uncertainty of the respective age models, the drop in brassicasterol/opal ratio in V19-30 seems to be contemporary with the rise in deepwater oxygen levels inferred from North Pacific proxy records (Jaccard et al., 2009).

Varying sediment accumulation rate likely had little impact on brassicasterol preservation during deglaciation (Fig. 4b). Over the interval between 16 and 10 ka, ^{230}Th-normalized mass accumulation rates exhibited no detectable change, while sediment accumulation rates based on stratigraphic age control dropped by only about one third. With little influence from changes in sediment accumulation rate, we attribute the five-fold drop in brassicasterol/opal ratio in V19-30 to a rise in deepwater oxygen concentration between 16 and 10 ka, consistent with our interpretation derived by comparing aU and opal fluxes.

Brassicasterol is produced by some coccolithophorids (including *E. huxleyi*) as well as by diatoms, and it is therefore necessary to show that brassicasterol fluxes in V19-30 were produced by diatoms, and consequently that the comparison with opal flux is relevant to the questions posed here. Alkenones are long-chained ketones produced exclusively by certain haptophyte algae, predominantly *E. huxleyi* and *G. oceanica* in the open ocean (Herbert, 2001; Sachs et al., 2000). Thus, comparing alkenone and brassicasterol records can help to identify (dis)similar sources for the two lipids (Pourmand et al., 2007; Werne et al., 2000). Alkenone fluxes in V19-30 are greater during the last glacial period than the Holocene (Fig. 5) (Koutavas and Sachs, 2008), consistent with increased preservation of organic material during the glacial period. However, second-order features show that peak alkenone fluxes occur between 19 and 22 ka, while brassicasterol fluxes were low to moderate during this time. Conversely, brassicasterol fluxes peak between 15 and 16.5 ka, while alkenone fluxes simultaneously decrease. The lack of similarity in the second-order features of the two lipid records suggests that diatoms and not *E. huxleyi* likely produced the brassicasterol. In addition, a recent study (Krause et al., in press) has shown that diatoms are a significant source of primary productivity in the EEP, consistent with the presence of diatom-derived biomarkers in the sediment. Specifically, while diatoms account for 18% of overall primary productivity, diatoms >5 μm account for 18–44% of nitrate uptake using conservative estimates of ammonia uptake. Since the presence of large

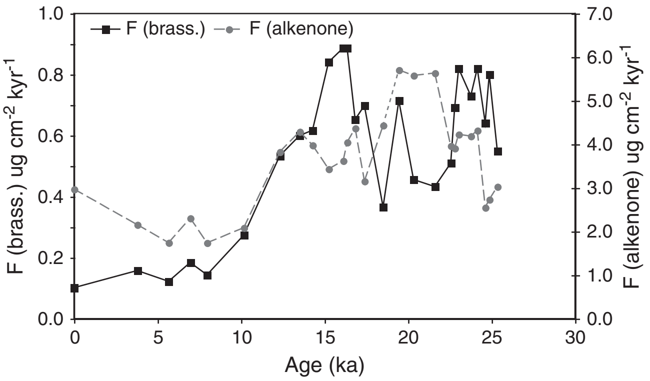

Fig. 5. ^{230}Th-normalized fluxes of brassicasterol and alkenones in V19-30. Alkenone concentrations come from Koutavas and Sachs (2008).

phytoplankton taxa (especially diatoms) is strongly correlated with the fraction of net primary production that is exported from the euphotic zone (Buesseler, 1998; Buesseler et al., 2007; Guidi et al., 2009; Honda and Watanabe, 2010), these data support the assertion that diatoms are an important source of primary productivity in the EEP, as well as an important source for organic material exported to EEP sediments.

6. Conclusions

The aU data presented here show that sediments in the deep equatorial Pacific Ocean were less oxygenated during the LGM than at present. Opal fluxes in each of four cores imply that this change in the sedimentary redox state was not caused by a change in the rain of organic carbon to the sea floor, but by a change in the dissolved oxygen content of overlying bottom waters. Preferential preservation of the organic biomarker brassicasterol during the LGM further supports our conclusion that the glacial deep Pacific Ocean was filled with a high DIC, low O_2 water mass, and therefore likely stored more carbon than the modern deep Pacific Ocean. Our results are also consistent with recently published data from the North Pacific (Jaccard et al., 2009), which suggests that increased carbon storage in the glacial deep Pacific Ocean was a basin-wide phenomenon (Fig. 6). This provides renewed evidence for a large-scale transfer of carbon from the atmosphere to the deep ocean during glacial periods.

Such a change would have had two effects on atmospheric $p\mathrm{CO}_2$. First, the shift of respired CO_2 into the deep ocean from intermediate waters would have resulted in increased total ocean storage of CO_2 during the glacial period, decreasing $p\mathrm{CO}_2$ in the atmosphere. The shift of respired carbon from intermediate to deep waters would also have resulted in a transient $CaCO_3$ dissolution event in the deep ocean, as discussed in the original "nutrient deepening" hypothesis by Boyle (1988). The gradual increase in ocean alkalinity due to enhanced $CaCO_3$ dissolution would have resulted in a further drawdown of CO_2 from the atmosphere. Quantitative estimates of deep water O_2 concentrations (and therefore dissolved inorganic carbon concentrations) are outside the scope of this paper. However, Jaccard et al. (2009) used their estimate of glacial bottom water O_2 concentration to calculate that the increase in total ocean storage of CO_2 and the increase in alkalinity resulted in decreases of atmospheric $p\mathrm{CO}_2$ of 60 ppm and 15-20 ppm, respectively. While these estimates depend on assumptions about 1) the ratio of remineralized:preformed PO_4 in the glacial ocean, 2) the ratio of O_2 uptake:PO_4 release during respiration, and 3) the volume of the ocean represented by redox proxy records, our results support the hypothesis that this mechanism was an important contributor to lower concentrations of atmospheric CO_2 during the last glacial period.

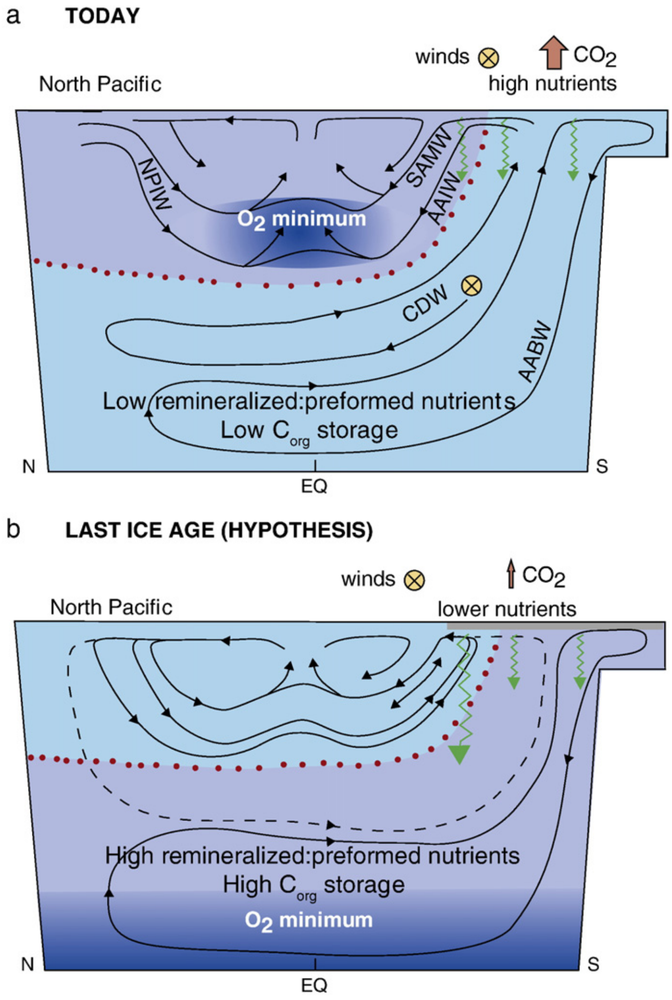

Fig. 6. A highly simplified illustration of circulation in the modern Pacific ocean (a), and hypothesized circulation in the glacial ocean (b), after Sigman and Boyle (2000) and modified with permission. The blue shading indicates changes in the intensity of circulation, with the lighter shade representing regions of more vigorous circulation. The oxygen minimum zone is indicated in each half of the figure, and shifts from its relatively shallow position in the modern ocean to fill much of the deep Pacific Ocean during the last glacial period. Biological productivity and the export of organic carbon to the seafloor in the Southern Ocean are represented by green arrows, which indicate a northward shift in the principal region of diatom productivity during the glacial period (Bradtmiller et al., 2009).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.epsl.2010.09.022.

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