Variations in the Biological Pump through the Miocene: Evidence from organic carbon burial in Pacific Ocean sediments.

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Abstract. The biological pump, defined as the marine biological production and sedimentation of particulate organic carbon (POC), is a fundamental process to fix atmospheric carbon dioxide in the oceans, transfer carbon away from the atmosphere to the deep ocean, and maintain the CO_2 level of the atmosphere. The level of carbon sequestration by the biological pump has varied throughout the last 50 million years, from particularly weak in the warm Eocene to much stronger in the Holocene. However, persistently warm climates in the more recent past, e.g., the Miocene Climate Optimum (MCO; 17 million years ago [Ma] to 13.8 Ma) also have affected the biological sequestration of carbon. A series of scientific ocean drill sites from the equatorial Pacific contain very low sedimentary POC % in the period prior to 14 Ma but higher and much more variable POC % afterward. Although lower absolute productivity may have contributed to the lower POC burial at the MCO, higher relative POC degradation also occurred. Ratios of POC to other productivity indicators indicate higher relative loss of POC. Temperature records imply that the higher POC degradation occurred in the upper water column, and global cooling strengthened the biological pump but led to more variability in burial. Similar records of low POC at the MCO can be found in the North Pacific, which suggest this was a global—rather than regional—change. A weakened biological pump during warm climate intervals helps to sustain periods of global warmth.

1 Introduction

The sequestration of organic carbon in pelagic sediments sums all the biological, physical, and chemical processes; from carbon fixation by photosynthesis, water-column transport and degradation, to ultimate sea floor deposition and burial. Heterotrophic consumption as well as inorganic oxidation greatly reduces the total particulate organic carbon (POC) mass falling from the surface and its reactivity. POC that is eventually buried in pelagic sediments is protected from further attack because the remainder is relatively recalcitrant after all the water column degradation and because POC binds to sediments and is less accessible for further degradation (Hedges and Keil, 1995; Mayer, 1995). Buried organic matter represents a small fraction, less than 1%, of the original primary productivity in the pelagic realm (Suess, 1980, Muller and Suess, 1979; Martin et al., 1987). In the Pleistocene pelagic equatorial Pacific, POC content found in surface sediments is typically low, ~ 0.2% (Murray and Leinen, 1993) while ocean margin surface sediments contain much higher POC (between 1-2%). The difference results from lower primary productivity in the equatorial Pacific, deep waters (>4 km for the equatorial Pacific vs <1 km for the ocean margins), and much slower sedimentation rates that allow the POC to be exposed to oxygenated sea water for thousands of years.

There is evidence that during extended periods of global warmth POC degradation tends to be larger and occurs higher up in the water column (John et al, 2014; Boscolo-Golazzo et al, 2021). Upper water column POC degradation results in poorer sequestration of atmospheric CO_2, higher atmospheric CO_2 in dynamic equilibrium with the oceans, and higher nutrient levels in upwelled waters. Unlike the last century, where there is intense global warming in the surface above a cold ocean, there is not necessarily a strong oxygen minimum during stable warm periods. Long periods of warming deepen the permanent thermocline and weaken the pycnocline, allowing more extensive mixing of oxygen into the ocean in contrast to the modern condition, where surface warming strengthens the temperature and density contrast between the mixed layer and colder deeper waters. The resulting strong pycnocline in the modern ocean restricts mixing and oxygen transport downward. Higher dissolved oxygen and higher water temperatures found in long warm intervals thus intensifies POC degradation in surface waters and reduces burial rates. Nutrients and CO_2 resulting from POC degradation cycle back to the surface faster under warm earth conditions. Surface water that is subducted to shallow depths often reappears at the surface in decades rather than centuries for waters that are cycled to abyssal depths. Therefore, the biological pump weakens under longer intervals of global warming (Boyd, 2015). Indeed, a recent paper by Li et al (2023) estimated global POC burial in the Neogene and found much less POC burial than expected during the Miocene Climate Optimum (MCO) interval.

The hypothesis that POC degradation occurred much shallower in the water column during warm ocean conditions is supported by John et al. (2014). They measured ocean depth gradients in carbon isotopes measured on planktonic foraminifera compared to earth system model representations for the Paleocene-Eocene Thermal Maximum (PETM) and during the greenhouse Eocene to conclude that the Eocene had shallower POC degradation and recycling. Similarly, Boscolo-Galazzo et al (2021) examined the change in the abundance of planktonic foraminifera living at different depths in the ocean in the period from 15 to 0 Ma and used stable carbon isotope values of the foraminiferal tests, combined with earth system models, to monitor changes in carbon flux through the water column. When combined with modeling of temperature dependent POC degradation, their results were consistent with cooling having caused more particulate POC rain to penetrate deeper into the water column to affect a stronger biological pump.

The biological pump can also be studied by examining the POC buried in the sediments. The POC mass accumulation rate (MAR; burial flux) depends upon all the processes in the water column above the sediments and is the obverse of measurements that could be made in the water column because POC does not sprout from the sediments below. It is a measure of the integrated effectiveness of the biological pump. While high primary productivity increases the flow of particulate POC to the sea floor, increases in heterotrophic consumption by zooplankton and microbes, reduce the resulting downward flux. Because of the fundamental temperature dependence of metabolic activity (e.g., see Brown et al, 2004), higher water temperatures increases the rate of POC degradation by zooplankton and microbes, and decreases POC burial (e.g., Boscolo-Galazzo et al., 2018).

Preservation of POC in sediments can also be studied by comparing it to other paleoproductivity measures that are better preserved. For example, Biogenic barium (bio-Ba) deposition is strongly correlated to POC rain from the euphotic zone (Dymond and Collier, 1996) and is better and more consistently preserved at the sea floor under typical oxygenated conditions (Dehairs et al, 1980; Dymond et al., 1992; Ganeshram et al., 2003). Lyle and Baldauf (2015) studied relative $CaCO_3$ dissolution in this way, using ratios of $CaCO_3$ to Ba. Under warm earth conditions associated with early Cenozoic greenhouse conditions (Olivarez Lyle and Lyle, 2005, 2006, Lyle et al., 2005) buried POC % was extremely low (Eocene average of 0.03%). Olivarez Lyle and Lyle (2005, 2006) used bio-Ba burial to estimate an ‘expected’ POC MAR assuming modern conditions. All POC burial during the Eocene was much lower than modern POC burial relative to production, indicating much higher heterotrophic consumption of POC within the water column. The ratio of POC to Ba is thus an indicator of relative POC preservation.

We produced long-term, low-resolution POC and $CaCO_3$ data between 2008 and 2013 for drill sites extending into the Miocene in the Pacific Ocean (Fig 1, Table I). In this paper we report discrete POC measurements we have made on 3 scientific drill sites from the eastern and central equatorial Pacific (ODP Site 574, and IODP Sites U1337, and U1338) and combine them with data from the Ontong Java Plateau in the western equatorial Pacific (ODP Sites 806 and 807; Stax and Stein, 1993). We also report briefly on two sites from the northwest Pacific (Sites 884 and 1208) to show that changes in POC burial were not limited to the equatorial region. We use these data to study changes in the biological carbon pump from the MCO to the present by comparing the patterns of POC preservation through time and, where we have data, by comparing how POC survives relative to bio-Ba, a better preserved paleoproductivity indicator.

		N is +	E is +	water	5 Ma		10 Ma		15 Ma		20 Ma		Notes
Site	location	Latitude	Longitude	depth (m)	Latitude	Longitude	Latitude	Longitude	Latitude	Longitude	Latitude	Longitude	
U1338	E. equatorial Pacific	2.508	-117.969	4205	1.43	-113.79	0.49	-110.00	-0.37	-106.31	...	...	eq crossing at 13 Ma
U1337	E. equatorial Pacific	3.833	-123.206	4466	2.55	-119.07	1.50	-115.31	0.53	-111.63	-0.36	-107.93	eq crossing at 18 Ma
574	E. equatorial Pacific	4.209	-133.33	4571	2.60	-129.18	1.35	-125.41	0.21	-121.73	-0.86	-118.02	eq crossing at 16 Ma
806	W. equatorial Pacific	0.319	159.361	2521	-1.99	163.62	-3.41	167.39	-4.63	171.04	-5.90	174.69	eq crossing at <1 Ma
807	W. equatorial Pacific	3.607	159.625	2804	1.33	160.94	-0.05	164.76	-1.24	168.45	-2.48	172.13	eq crossing at 10 Ma
1208	N. Pacific, Shatsky Rise	36.127	158.208	3346	33.83	163.05	32.42	167.37	...	...	...	...	Hiatus to Paleocene >12 Ma
884	N. Pacific, Detroit Seamount	51.45	168.337	3827	49.05	173.09	47.52	177.48	46.19	-178.30	44.82	-174.21	eq crossing at 10 Ma

Table I: Locations of drill sites discussed in this paper and paleo-locations of the sites through the Miocene

Li et al. (2023) used a global set of mass accumulation rates to show that there was a global low in POC MAR during the MCO, with a primary objective of the paper to test the "Monterey hypothesis" that high $d^{13}C$ between 17 and 13 Ma resulted from higher POC burial. They found that the MCO interval had globally low POC burial and was not a cause for high $d^{13}C$ at that time. The objective in this paper is different. We chose to examine a focused region (the equatorial Pacific) and use additional sedimentary data to separate changes in production from changes in preservation in the ultimate POC record. We examine 4 hypotheses for the low POC burial at the MCO— (1) low primary productivity, (2) POC degradation in warmer deep waters, (3) POC degradation in warmer surface waters, and (4) a fundamental change in the proxy-POC relationship. We find that the low POC MAR in the equatorial Pacific results largely from better preservation of sedimentary POC as the earth cooled through lower degradation in the surface ocean.

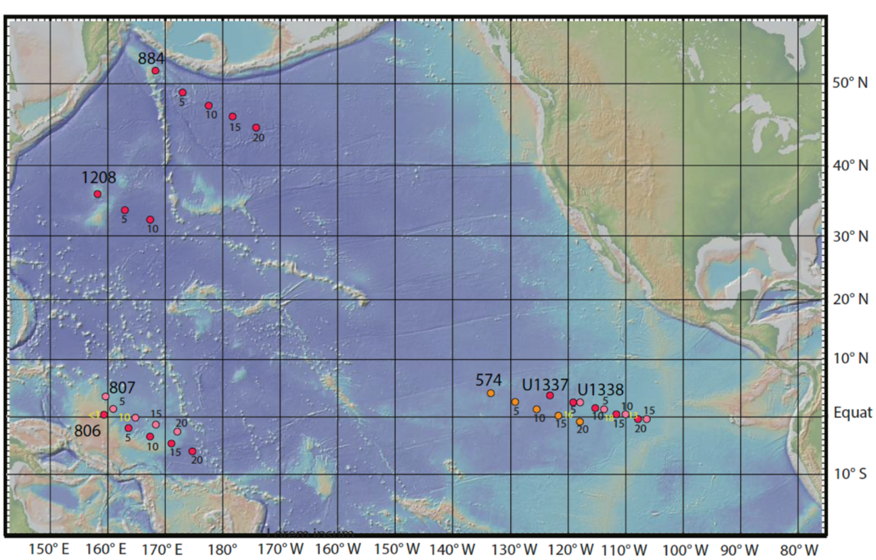

Figure 1: Drill site locations discussed in this paper. Paleo-locations for each site are shown at 5 Myr intervals, using a fixed hotspot rotation pole for the Pacific tectonic plate. The equatorial ODP drill sites 806 and 807 were drilled on ODP leg 130 (Stax and Stein, 1993. Sites U1337 and U1338 were drilled on IODP expedition 321 (Lyle et al, 2019; Pälike et al, 2010). Site 574 was drilled on DSDP Leg 85 (Mayer et al, 1985). Two other sites are briefly discussed—Site 1208 on the Shatsky Rise (Bralower et al., 2002) and Site 884 near Detroit Seamount at the northern end of the Hawaii-Emperor chain (Rea et al., 1993). Yellow numbers indicate the age of each site's equator crossing, a local high in primary productivity and sediment deposition.

2 Analytical Methods

We measured over 1,600 samples (1,215 presented here plus 388 previously published) for POC and $CaCO_3$, from 5 Sites of the Deep Sea Drilling Project, Ocean Drilling Program, and Integrated Ocean Drilling Program (Sites 574, 884, 1208, U1337, and U1338, see Fig. 1 and supplemental tables). Freeze-dried sediment samples were analyzed using coulometry and furnace methodologies presented in Lyle et al., (2000) which provide accurate POC values at very low levels.

First, Total carbon of the sediment sample was measured through combustion in a 1000°C furnace and analyzed using a coulometer. POC was determined by acidifying a second, larger aliquot of the sample to remove the $CaCO_3$-based CO_2, then analyzing the remaining sediment residue via combustion in pure oxygen at 1000°C via coulometry. From these two measurements, the $CaCO_3$ fraction is calculated based on the difference between the CO_2 measured for Total carbon and the organic carbon fraction. We found that this method is accurate for estimating $CaCO_3$ down to the <1% level and for POC at the 0.01% level (Olivarez Lyle and Lyle, 2005). We have checked for consistency of our carbon analyses, as described in Olivarez Lyle and Lyle (2005), by running an in-house sediment standard "Midway" with each carbon run and for which hundreds of analyses and summary statistics have been compiled ("Midway" standard: Total carbon = 2.64±0.02 wt %, n=523; POC = 0.85±0.01, n=570). We also repeated the analysis of every 4th unknown sample during each run day. We monitor both total carbon and organic carbon. The average absolute difference between repeated unknown samples for POC is <0.01 wt%, and if this difference exceeded 0.02 wt % we re-analyzed the sample. Data for Site 574 sediments older than 12 Ma are reported in Piela et al (2012). Site 574 POC and CaCO3 data spanning 12 to 2 Ma were analyzed later in our lab and are published here. For Sites U1337 and U1338, POC data are reported in Wilson (2014; PhD. Thesis) but were not discussed in Wilson's thesis.

POC and $CaCO_3$ data from Sites 884 and 1208 are also included. All the data for Site 1208 were analyzed in our lab with the same analytical methods as above. Site 884 has a mixture of our data and culled shipboard carbon data as marked in Supplemental Table S8. We added the shipboard data for depth intervals not analyzed in our lab, primarily those younger than 4.8 Ma. Typically, we do not use shipboard POC data from DSDP or ODP because their POC determination is a calculation, not measurement, based on the difference between measured Total carbon and measured $CaCO_3$. This is inaccurate at POC levels below 0.3% when in the presence of significant (>15 wt%) sedimentary $CaCO_3$ (Olivarez Lyle and Lyle, 2005). Hence, we used only shipboard POC and $CaCO_3$ data at Site 884 (Table S8) when $CaCO_3$ was less than 15 wt%. The error in POC of the shipboard method at this level of $CaCO_3$ is relatively small .

We include data from Stax and Stein (1993) for Sites 806 and 807. They measured POC by dissolving an unweighed split of the sample with HCl and measuring POC after dissolving the $CaCO_3$. They then corrected the split POC to that of the total sample by measuring total carbon on a separate split of the sample and calculating the relative proportion of POC. Using this method, they could dissolve a much larger split of sediment for POC, so that they were accurate at low POC contents while also being able to measure other POC properties.

The net deposition and preservation of POC at Sites U1337, U1338, and Site 574 is estimated from ratios to the barium content in the sediments. Extensive work has shown this element is precipitated in the water column as $BaSO_4$ via organic matter oxidation, is well-preserved, and importantly, is a good proxy for primary productivity (Dymond et al, 1992, Dymond and Collier, 1996; Ganeshram et al., 2003). Although barium sulfate can form through other processes, in equatorial Pacific sediments, the Ba content is primarily biogenic in origin and not diluted by other Ba-containing components, for example, by barium in terrigenous clays (Piela et al., 2012; Lyle and Baldauf, 2015)). We calibrated Ba measurements from X-ray fluorescence (XRF) (normalized median-scaled 'NMS', see Lyle et al, 2012) to discrete ICP-MS analyses for Sites U1337 and U1338 (Wilson, 2014). At Site 574 we used ICP-MS barium data from Piela et al. (2012) for sediments older than 12 Ma.

We use XRF-estimated total $BaSO_4$ to calculate ratios to other biogenic elements to investigate POC preservation. We did not partition total barium to remove non-biogenic sources, because the equatorial Pacific sediments at Sites U1337 and U1338 primarily consist of biogenic remains and contain minimal clay minerals (Lyle and Baldauf, 2015), so the majority of Ba is biogenic in origin. We further tested this assumption by making a normative estimate of terrigenous clay- and authigenic oxide-fixed Ba at Site U1338 using other XRF-measured elements (Al, Si, Ca, Mn, Fe, Ti) as well as discrete opal calibrations (Lyle and Baldauf, 2015). Assigning typical Ba contents to the normative sedimentary components, we found that biogenic $BaSO_4$ averaged 93% ±4% of total $BaSO_4$. The greatest potential error is in sections where the clay contents are highest, i.e., the younger sediments of each site. Here the POC/$BaSO_4$ is highest, and estimated POC preservation is best. Any bias based on total $BaSO_4$ would tend to reduce the ratio and apparent POC preservation. Therefore, the total $BaSO_4$ method we used is conservative.

3 Age Models and Mass Accumulation Rates (MAR)

For all sites we calculated POC mass accumulation rates (MAR), equivalent to POC burial flux, as another indication of the rate of POC deposition and burial. MAR has units of mass per unit area per unit time and typical reported as "grams /(cm^2 x 10^3yr)". For any component in a sedimentary mixture, calculating its mass accumulation rate eliminates artifacts in the resulting data profile over depth/time that are necessarily caused by variable deposition of the other sedimentary components. Converting weight % data to MAR is particularly important for evaluating changes in minor components such as POC because change is deposition of the major components can dominate and distort actual changes of the component of interest. However, MAR calculations are subject to errors (for example, sedimentation rates) that are primarily caused by an imprecise age model. This issue is addressed below.

We developed age models for all sites to calculate MAR to further study rates of burial. See the Supplemental Material for details and for data from each of the sites. MARs are developed by making an age model (age vs. depth profile) that is differentiated to calculate a sedimentation rate (thickness of sediment deposited per unit time; cm per kyr) over the time interval of interest. Sedimentation rate, multiplied by the Dry Bulk Density results in a bulk MAR (g solid/cm^2/kyr) for the sediment over a given age interval. Individual component MARs are calculated by multiplying the bulk MAR by the weight fraction (wt %/100) of the component in the dry sample.

3.1 Sites U1337, U1338

For Site U1337 (24 Ma crust) we used an astro-chronologically-tuned age model to 20 Ma by combining the Drury et al (2017, 2018) age model to 8.2 Ma and correlating the 20 Myr combined isotope record from Site U1337 (Holbourn et al., 2015; Tian et al., 2018) to the stable isotope stack from Westerhold et al (2020) to 20 Ma. For Site U1338 (18 Ma crust) we used the established age model to 8.2 Ma (Lyle et al., 2019). The U1338 ages greater than 8.2 Ma were derived by correlating the U1338 $CaCO_3$ profile to that from Site U1337, which is justified because $CaCO_3$ profiles are very similar across the central and eastern Pacific (Lyle et al, 2019; Mayer,1991).

3.2 Site 574

Site 574 (35 Ma crust) was drilled in 1985 during Leg 85 of the Deep Sea Drilling Project and lies about 1000 km west of Site U1337. It was one of the first sites to have hydraulically piston cored sediments. We XRF-scanned the upper 5 cores of Holes 574 and 574A and used these data and the GRA bulk density record in deeper sections to make a new splice to ~17.4 Ma (225 m composite depth, the base of Holes 574 and 574A) using the *Code for Ocean Drilling Data* software (CODD; https://www.codd-home.net/, last access: 08 August 2023). The new splice was then correlated to Site U1337 by a $CaCO_3$ profile produced by using the Site 574 GRA bulk density to estimate $CaCO_3$ content. In the eastern and central Pacific Ocean, the GRA bulk density is highly correlated with changes in $CaCO_3$ content (Mayer, 1991). The noncarbonate fraction in the equatorial Pacific is primarily low density, high porosity biogenic silica remains of diatoms. The GRA bulk density data is also much higher resolution than the discrete carbonate analyses used for calibration. The spliced GRA density record from Site 574 is in the supplemental tables with assigned ages (Supplemental Table S2), as well as the new splice developed for Site 574 (Supplemental Table S1).

3.3 Sites 806 and 807

We used polynomial fits to ages updated to the biostratigraphic ages used for Sites U1337 and U1338 (Expedition 320/321 scientists, 2010) for the biostratigraphic datum levels for Sites 806 and 807 reported in the Initial Reports volume (Kroenke et al., 1991). Such fits are less accurate than a direct correlation, but these sites do not have long stable isotope records, nor was it possible to correlate the carbonate records to the eastern Pacific. While not as accurate as the other age models, ages should still be good to ± 0.2 Ma or better. The major potential error is the spacing of biostratigraphic sampling, approximately every 3 m for foraminifera and every 4.5 m for calcareous nannofossils (Chaisson and Leckie, 1993; Takayama, 1993)

3.4 Sites 1208 and 884

Age-depth profiles for Sites 1208 (Shatsky Rise, to 12.4 Ma) and 884 (Detroit Seamount, at the north end of the Hawaii-Emperor seamount chain, to 19.7 Ma) were made using linear interpolations between magnetochrons. Magnetochrons were determined via shipboard pass-through magnetometry with shore-based further analysis. Shipboard magnetic measurements were made every 10 cm at Site 884, and every 5 cm at Site 1208. We used Evans (2006) for magnetochrons from Site 1208, and shipboard paleomagnetic data for Site 884 (Rea et al., 1993). All magnetochrons have updated ages based on Westerhold et al. (2020). Accuracy of ages should be better than 0.1 Ma. The profiles are listed in the supplemental material. Site 1208 was located on the Shatsky Rise itself and had an extreme slowdown in sedimentation from the middle Miocene through the late Cretaceous which may have affected the early part of the profile.

Bulk MAR for each site was calculated as the product of sedimentation rate (from the age/depth profiles) and the dry bulk density to yield the total mass of sediment deposited over a given age interval (bulk MAR). Dry bulk density was estimated by correlating discrete physical properties data from each drill site to the reported GRA wet bulk density data. We used the correlation to develop a higher resolution dry bulk density profile from the GRA data.

4 Results

4.1 Organic Carbon Variations:

There is a striking difference between the POC records from the Pacific equatorial sites older than ~13 Ma and the younger sections, as illustrated by Figure 2. Low sedimentary POC %, POC MAR, and POC:$BaSO_4$ within the MCO changes to higher and more scattered values between 14 and 12 Ma, after the MCO. POC wt.% was much lower in the older record as compared to the Pliocene and Pleistocene (Fig 2A). Within the MCO, between 17 and 14 Ma, POC wt% in these 5 sites averaged 0.043 ± 0.014 %, in contrast to a nearly 3-fold increase (0.124 ± 0.058 %) in the Pleistocene and Pliocene (0-4 Ma) and we note the MCO values are more similar to the average measured for Eocene equatorial Pacific (POC roughly 0.03 wt%, >34 Ma; Olivarez Lyle and Lyle, 2006). Both the concentration of sedimentary POC and the variability were much lower in the period prior to 14 Ma.

High dilution by other sedimentary components can lower POC %, but dilution in the equatorial Pacific requires higher preservation and burial of either biogenic $CaCO_3$ or biogenic SiO_2 relative to modern conditions. Nonetheless, this possibility can be evaluated by calculating the POC MAR which removes the dilution effect and is a measure of the actual burial flux. Fig 2B shows the POC MAR data for the 5 equatorial Pacific sites. We note a relatively low and consistent POC MAR between 18 and 14 Ma. Somewhat higher levels of POC MAR occur prior to 19 Ma and higher but very scattered MAR after 14 Ma.

4.2 Variations in Biogenic Barium

Ba was measured at 3 of the sites, all in the high-productivity region of the eastern Pacific. The POC:$BaSO_4$ ratio compares the burial of the more labile POC (<1% POC preserved) to that of the better-preserved biogenic Ba (~30% preservation, Dymond et al, 1992, Dymond and Lyle, 1994). Since Ba has a linear relationship with POC in the particulate rain of the modern equatorial Pacific Ocean (Dymond and Collier, 1996), changes in the POC:$BaSO_4$ ratio is interpreted to reflect the relative preservation of POC. Fig 2C shows that there was lower POC burial relative to Ba prior to 14 Ma than later in the records.

Ba was measured by ICPMS at Site 574 for the sediment column older than 12 Ma (Piela et al, 2012). Sites U1337 and U1338 have Ba measured by scanning XRF for the entire composite sediment column (Lyle et al., 2012; Wilson, 2014, Lyle and Baldauf, 2015). All have low POC:$BaSO_4$ ratios (poor POC preservation) prior to 14 Ma in the MCO, and higher ratios with much greater variation since then.

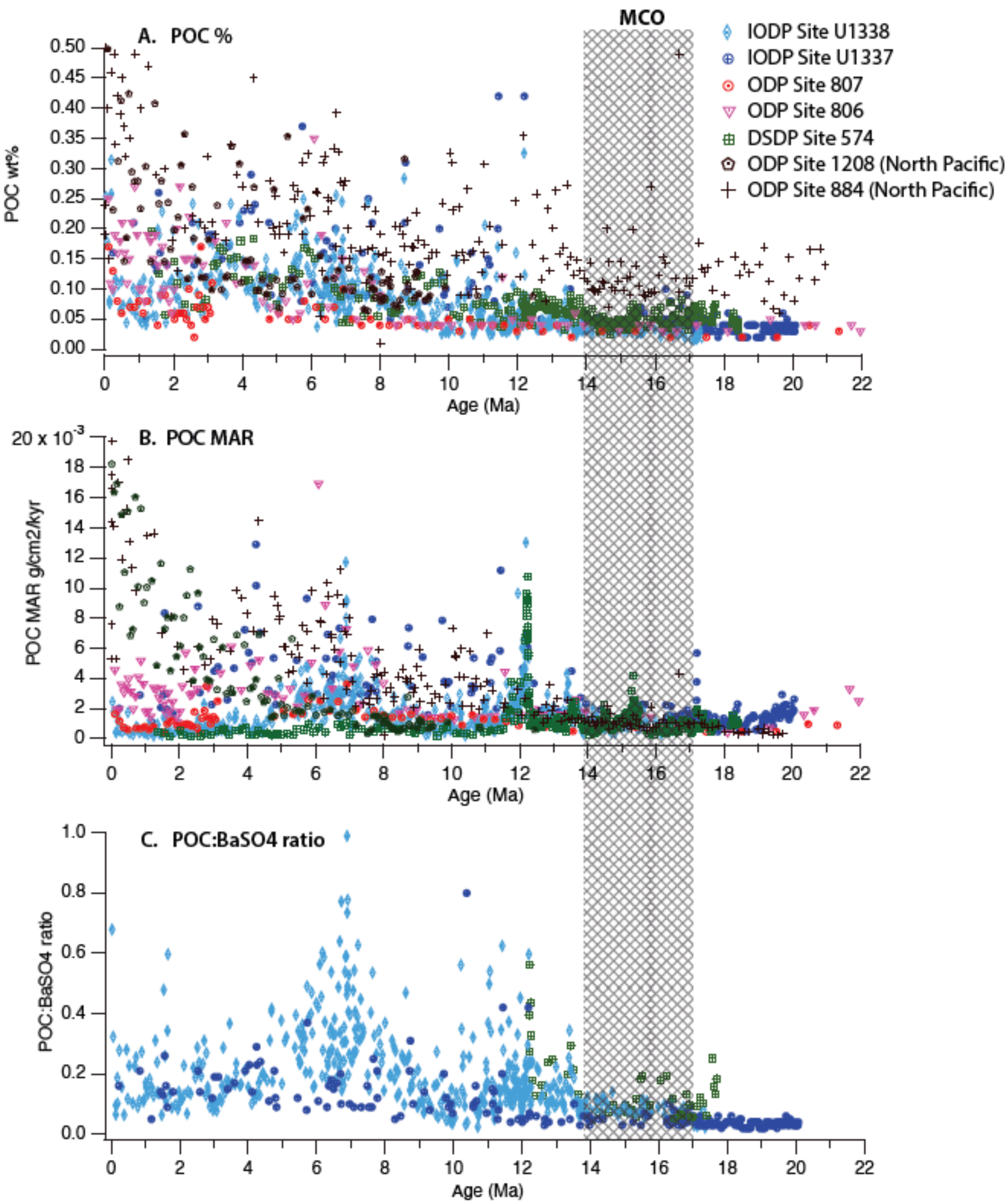

Figure 2: POC % (A) POC MAR (B) for the equatorial drill sites 574, 806, 807, U1337, and U338 with North Pacific Sites 1208 and 884. POC:$BaSO_4$ (C) is only available from Sites 574, U1337, and U1338. These records show evidence of low POC contents and poor POC preservation over the Miocene Climate Optimum (MCO, 17-13.8 Ma) and the early Miocene.

Low POC % during the MCO is not confined to the equatorial Pacific but also found in the north Pacific. We also analyzed two Sites from the North Pacific which show increased POC burial as the Miocene progressed. At Sites 1208 on the Shatsky Rise, and Site 884 on Detroit Seamount (Fig 1), POC MAR has increased strongly post MCO (Figure 2A,B; Supplemental tables S8 and S10) A straightforward interpretation of these records, however, is complicated by the fact that there is a major increase in sedimentation rate at Site 1208 after a Paleocene hiatus which in itself also causes increased POC MAR post 7.5 Ma. As such, it is unclear to what extent the local sedimentation regime played a role in the increase of POC MAR relative to regional levels of preservation. At Site 884, sedimentation rates increase in the early Miocene, leading to higher POC MAR after the MCO (see supplemental material Fig S5). There is no reason to suspect that the Site 884 record was strongly influenced by changes in the local sedimentary environment, however, there is overall much higher clay deposition here that might have affected POC burial. In summary, these two Sites suggest a general increase in POC MAR throughout the Pacific after the MCO, but more records need to be produced and evaluated to support the hypothesis. However, it is important to highlight the data from a recent study by Li et al (2023) who found surprisingly low POC burial across the MCO worldwide, in support of the hypothesis that a global slowdown in POC deposition occurred during the MCO.

Another important observation is that periods that have been identified previously in the late Miocene as high productivity also can have high relative burial of POC. The effect is most obvious at Site U1338, an eastern Pacific equatorial drill site (Fig 2, Fig 3). The late Miocene Biogenic Bloom (LMBB) has elevated POC MAR, and is a period of elevated POC:$BaSO_4$. Elevated POC MAR during the LMBB is also found at sites 806, 807 and Site 884. Similarly, there is significant POC MAR at around 12 Ma in an earlier interval that appears to be productivity related (Lyle and Baldauf, 2015). Not only are these intervals high in POC deposition, but also high with respect to POC:$BaSO_4$. It appears that under certain conditions of high productivity, both burial and preservation of POC is enhanced as shown by POC:$BaSO_4$. How apparent elevated productivity affects ultimate POC burial deserves further study.

5 Discussion and Implications

We expect variability in the deposition of biogenic particulate matter resulting from large scale tectonic-biogeographic processes and from global intervals of high productivity, as well as from regional variation in primary productivity. We note that POC depositional variability from 12 to 0 Ma is high, between 0.03 and 0.40 wt.%. The variation is partly caused by the geographic position of the site relative to the high equatorial productivity zone, and partly from the presence of high productivity intervals since the MCO. Some may also result from protection of POC by the deposition of other sedimentary components. Nevertheless, we note that more slowly accumulating sediments of the Pliocene and Pleistocene tend to have high POC % (Figs 3 and 4) but without corresponding high biogenic MARs. In other words, factors other than high productivity have caused better preservation of POC between 8 and 0 Ma since high POC % is not necessarily found with other indicators of high paleoproductivity. All records in the equatorial Pacific show evidence for low POC % and POC MAR during the MCO (Fig 2), while sediments from the Pliocene and Holocene have higher POC % even though many of the sites exhibit low POC MAR.

We investigated the possibility that bioturbation might bias the POC records, since POC remains in the 5-10 cm equatorial Pacific sedimentary mixed layer for thousands of years (Kadko and Heath, 1984; Broecker et al, 1991). It is possible that a change in sedimentation rate from fast to slow might enhance POC degradation by enhancing exposure to oxygenated bottom waters. We know that labile POC is degraded rapidly within the equatorial Pacific sediment mixed layer (Stephens et al., 1997) so perhaps more recalcitrant POC would be degraded if sedimentation rates slowed. If this were true, there should be a correlation between sedimentation rate and POC content, since high sedimentation rates should shorten the time that POC spends in the mixed layer. We checked and found no correlation.

We interpret the scatter of POC % to reflect the localized response to the timing of productivity drivers changing transport of POC from surface waters combined with better POC preservation in more recent times. There are 2 major productivity drivers in the equatorial Pacific: First, when the site is carried across the equatorial high productivity region by tectonic motion of the Pacific plate (line of high productivity for the Neogene; Lyle, 2003, Moore et al., 2004), and second, during high productivity intervals which typically are limited in both space and time. There is a well-documented global productivity interval between 8 and 4.5 Ma found globally as the "Late Miocene Biogenic Bloom", (LMBB) (Dickens and Owen, 1999; Diester-Haas et al, 2002; Lyle and Baldauf, 2015; Drury et al, 2017; Lyle et al, 2019; Karatsolis et al, 2022; Gastaldello et al., 2023). An earlier high productivity interval has been identified in the eastern equatorial Pacific between 13 and 10.5 Ma (Lyle and Baldauf, 2015) and extending to ~14 Ma (Holbourn et al., 2014).

5.1 Tectonic passage through the equatorial productivity zone and equatorial primary productivity

Modern studies of equatorial biological productivity, including direct measurements in the water column, MAR in surface sediments, and those based on interpretations of satellite color find that the particulate flux both at the surface and to sediments is highest at the equator and strongly decreases to the north and south (Wyrtki, 1981; Chavez and Barber, 1987; Dugdale et al., 1992; Murray and Leinen, 1993; Honjo et al., 1995; Behrenfeld et al, 2005). This pattern of high equatorial biogenic flux has been found throughout the Neogene (Moore et al., 2004, Berger, 1973). The records are strong evidence that the equatorial divergence and upwelling driven by the SE trade winds crossing the equator has been a persistent feature of the Cenozoic oceans that causes high primary productivity at the equator. The magnitude of equatorial productivity has not remained constant through time, however, but has waxed and waned along with global climate change. We expect to find a change to higher productivity and deposition of biogenic sediments as the movement of the Pacific Plate brings a drill site into position at the equator, and a decrease in biogenic MARs as the site is moved away from the equator.

For example, Piela et al (2012) found that high biogenic silica mass accumulation rate, bio-Si MAR, and barium mass accumulation rate, Ba MAR, occurred during the Site 574 paleo-equator crossing at 16.25 Ma, despite low POC MAR and low $CaCO_3$ MAR. They hypothesized that the dissolution of $CaCO_3$ exposed more POC in surface sediments to potential degradation and reduced POC with respect to other productivity signals. It could also represent preferential degradation of POC in surface waters.

At site U1338, high burial rates of biogenic components other than POC coincide with the period that Site U1338 was within ± 0.5° of the paleo-equator during the middle Miocene (= 55 km distance, 16-10 Ma, Fig 3). POC MAR, unlike the other biogenic components, was not as enhanced during the MCO. POC burial was minimized relative to other biogenic components during the MCO and immediately after. Also, at Site U1338, the high POC MAR and opal MAR at 12 Ma are roughly equivalent to modern MARs in surface sediments as reported by Murray and Leinen (1993). $CaCO_3$ MAR is not only affected by high productivity but also by changes in carbonate dissolution through time. Nevertheless, much of the variation in $CaCO_3$ at Site U1338 is common with variations in both opal and $BaSO_4$ MARs, indicating a strong productivity signal at the site.

The 15-20 Ma section of the site U1337 oxygen isotope record is part of the Westerhold et al. (2020) Cenozoic oxygen isotope splice and thus, along with Site U1338, represents the MCO interval in the equatorial Pacific. The sediments from Site U1337 (Fig 4) crossed the equator from the south-east to north-west at an earlier time than Site U1338 (from 21 to 15 Ma versus 16 to 10 Ma, respectively) and had relatively low biogenic MARs in the older sediments as compared to later in the U1337 section. This is in part caused by sediment focusing within the younger part of the record, especially in the intervals 6.2-5.4 Ma and 4.5-3 Ma (Lyle et al., 2019, and its supplemental material). The sediment focusing is shown by anomalously high Pleistocene and

Pliocene sedimentation rates compared to piston cores and other sites at this latitude. Furthermore, erosional channels to the northeast of the site were found in the site survey (Fig 5, Moore et al, 2007; Lyle et al, 2019). Nevertheless, sediment focusing has not affected the time interval spanning the MCO for which we find very low POC % and POC MAR. Such low values contrast with the expected pattern of higher biogenic sedimentation beneath the high productivity region of the paleo-equator. We also note that $BaSO_4$ MARs at Site 1337 are 3 times higher than at Site 1338 during the MCO, implying greater primary productivity and organic carbon production, yet a POC signal was not preserved in the sediments.

Sites 806 and 807, in the western Pacific on Ontong Java Plateau, crossed the equatorial region at <1 Ma and 10 Ma, respectively. In the modern ocean, the upwelling signal in the far western equatorial Pacific is not nearly as strong as in the eastern equatorial Pacific (Behrenfeld et al., 2005; Rousseaux and Gregg, 2017). Site 806 has its highest POC MAR in the Pleistocene as expected by its recent equator crossing. However, Site 807 shows little sign of its equator crossing in POC MAR at 10 Ma, although it and Site 806 have a high POC MAR resulting from the LMBB. However, both sites have low POC MAR during the warm MCO.

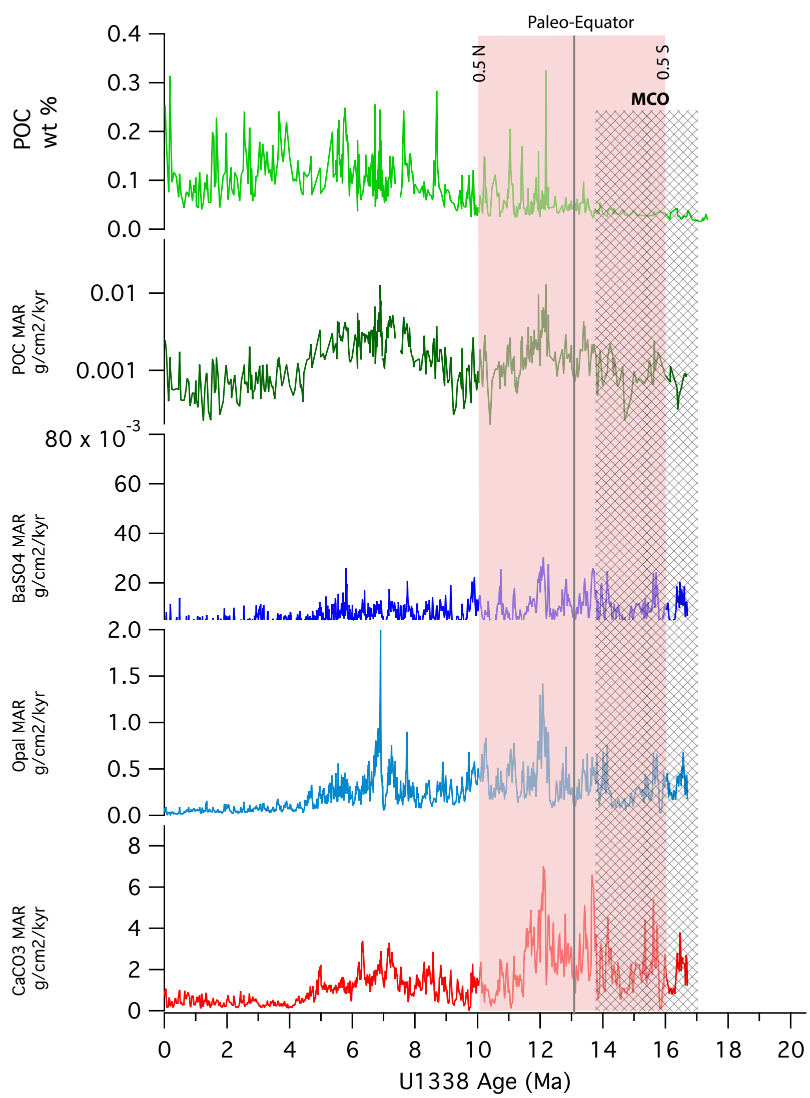

Figure 3: A) POC wt %, B) POC MAR, C) $BaSO_4$ MAR, D) Biogenic SiO_2 MAR, and E) $CaCO_3$ MAR time series for Site U1338, on ocean crust formed at 18 Ma.. High biogenic MARs are characteristic of later high productivity intervals. However, the MCO has low

POC contents and POC MAR, despite Site U1338 being relatively near the equator at that time. Paleo-equator line marks the time when plate tectonic movement aligned the site with the equator.

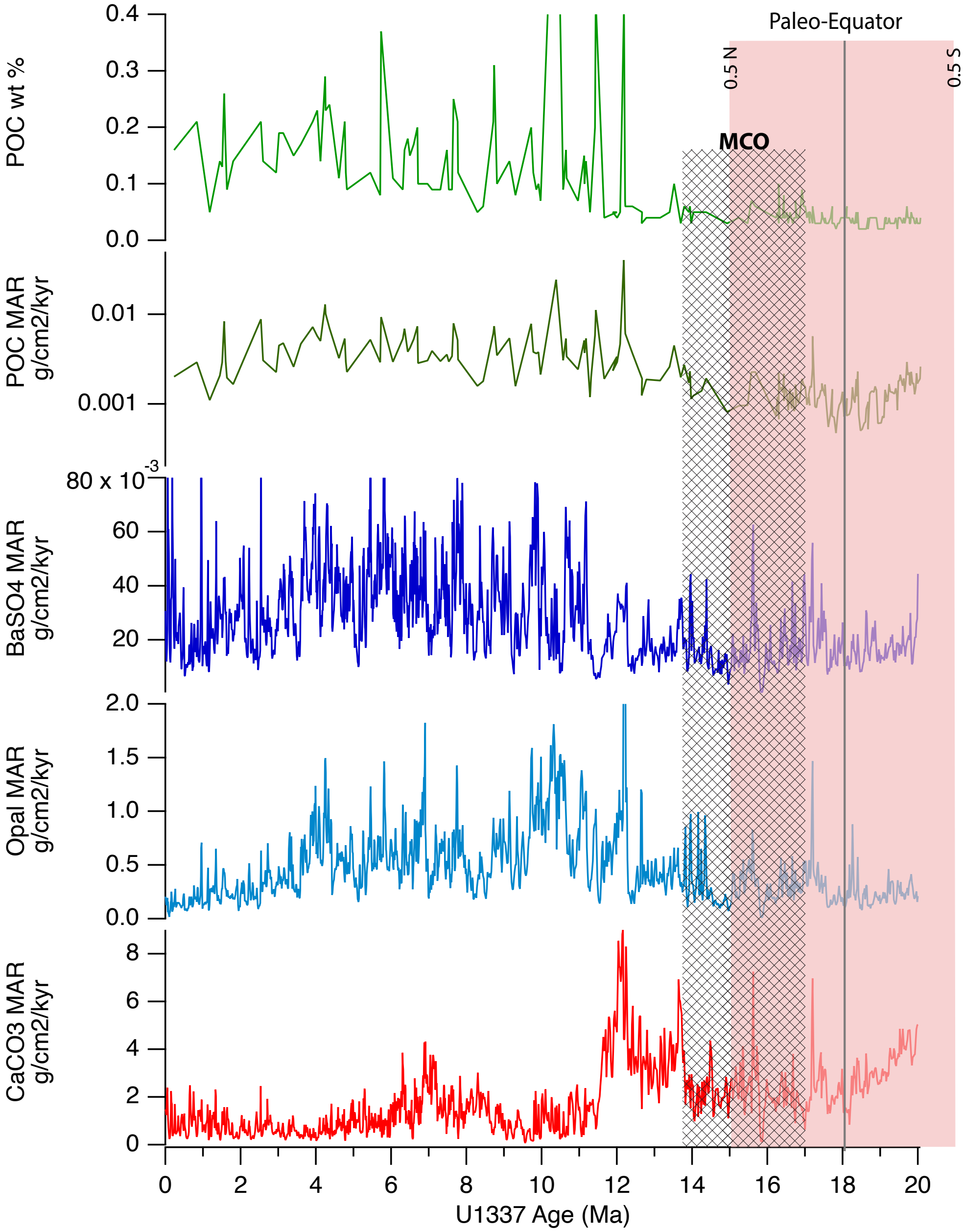

Figure 4: A) POC wt %, B) POC MAR, C) $BaSO_4$ MAR, D) Biogenic SiO_2 MAR, and E) $CaCO_3$ MAR time series for Site U1337, to the west of Site U1338, on 24 Myr ocean crust. The biogenic MAR time series are more complex here because of sediment focusing in the younger part of the record. However, the MCO has low POC contents and POC MAR, despite Site U1337 being relatively near the equator at that time. Paleo-equator marks the time when plate tectonic movement aligned the site with the equator.

5.2 Past high productivity intervals

Figure 3 shows the time series of all biogenic MAR's at Site U1338. All biogenic MAR's are elevated between ~14.5 Ma to 11.5 Ma , indicating high primary production despite low POC burial within the MCO. High productivity near 14 Ma at Site U1338 was first noted by Holbourn et al. (2014), who suggested that biogenic silica production was a factor ending the MCO by reducing high atmospheric CO_2.

Both episodes are clearly observed at Site U1338. At Site U1337, there are similar levels of biogenic Si MAR to Site U1338 during the older interval, but there is another interval filled with laminated diatom mats between 10 and 12 Ma (200-250 m CCSF) that might represent accumulation near the subduction boundary between the South Equatorial Current and North equatorial countercurrent (Exp 320/321 Scientific Party, 2010b). So, at Site U1337, the two separate higher productivity intervals are joined by a third interval of higher deposition. Both Sites 806 and 807 show elevated POC MAR associated with the LMBB indicating that these global high productivity intervals affect all sites in the equatorial Pacific.

5.3 Four Hypotheses to explain low POC burial at the MCO

We propose four working hypotheses for the cause of low levels of POC MAR along the Pacific equator during the MCO: (1) generally low primary productivity during the MCO, (2) warmer deep waters and increased POC degradation in the lower water column or sediment surface, (3) increased degradation of POC in surface waters; and (4) low apparent POC as an artifact of changing proxy relationships, e.g., Ba fixation in relation to POC fixation in particles. In only one hypothesis (1, low primary productivity) does the relationship between POC production, production of productivity proxies and their ultimate burial remain the same; the others assume a change in these relationships occurred during the MCO.

5.3.1 Hypothesis (1): Low productivity is the primary factor for low POC during the MCO

Under hypothesis (1), the observed low POC % during the MCO reflects low average productivity during the MCO interval. However, the data do not support this hypothesis. Each of the sites were in a different position relative to the equatorial high productivity zone at the time of the MCO. Those near the equator had as low a POC % and POC MAR as those farther away. Furthermore, there is no evidence of global low productivity during the MCO. Site U1338 which was in the equatorial zone late in the MCO, has increases in POC % and POC MAR at the end of the MCO. Since other paleoproductivity indicators tended to be high during the MCO it is apparent that low POC MAR is not a result from low MCO primary productivity.

In summary, while we find some evidence for somewhat lower productivity during the MCO, high primary productivity associated with drill site equator crossings are reflected in increased burial of other biogenic sediment components, but not for POC. Therefore, we conclude that additional factors caused the lower POC MAR during the MCO.

5.3.2 Hypothesis (2): warmer deep waters and more POC degradation in the lower water column or sediment surface led to low POC MAR during the MCO

Particulate matter falls through the oceans at a rate of ~50-150 m/day once they leave the surface ocean (Honjo et al, 1982; Berelson, 2001; McDonnell and Buessler, 2010); thus spending 7-10 days above 1000 m in the upper water column. Particles transiting the remaining 3km water column (assuming an average 4 km ocean water depth), require an additional 3 weeks to a month before reaching bottom. Afterwards, particulate organic carbon (POC) resides decades to centuries at the sediment surface before final burial. Provided the POC has survived passage through the upper water column, it is possible that temperatures or other processes in the lower water column have controlled burial of POC by temperature-dependent degradation of POC. If the change in POC degradation occurs primarily in the lower water column, one consequence is that the biological pump would still function, albeit at a somewhat lower rate.

There are two problems with the hypothesis for lower water column control of POC burial—first, most POC is re-mineralized in the upper water column in the modern oceans, so only the more recalcitrant or protected POC fractions survive to abyssal depths. Second, note that cooling of the abyssal Pacific occurs much later than the end of the MCO (Fig 5); thus, any temperature-linked degradation of POC in relatively warm deep waters should decrease after the deep waters cool. As Fig 5 illustrates, Pacific deep waters were only slightly warmer within the MCO than immediately after that period and stayed at a relatively constant temperature of 7° C until about 6 Ma (Lear et al, 2015). Only after 6 Ma did the deep waters cool to a modern temperature of about 2°Ç. Therefore, we expect a POC signal primarily caused by deep water cooling to have a much different signal than that observed.

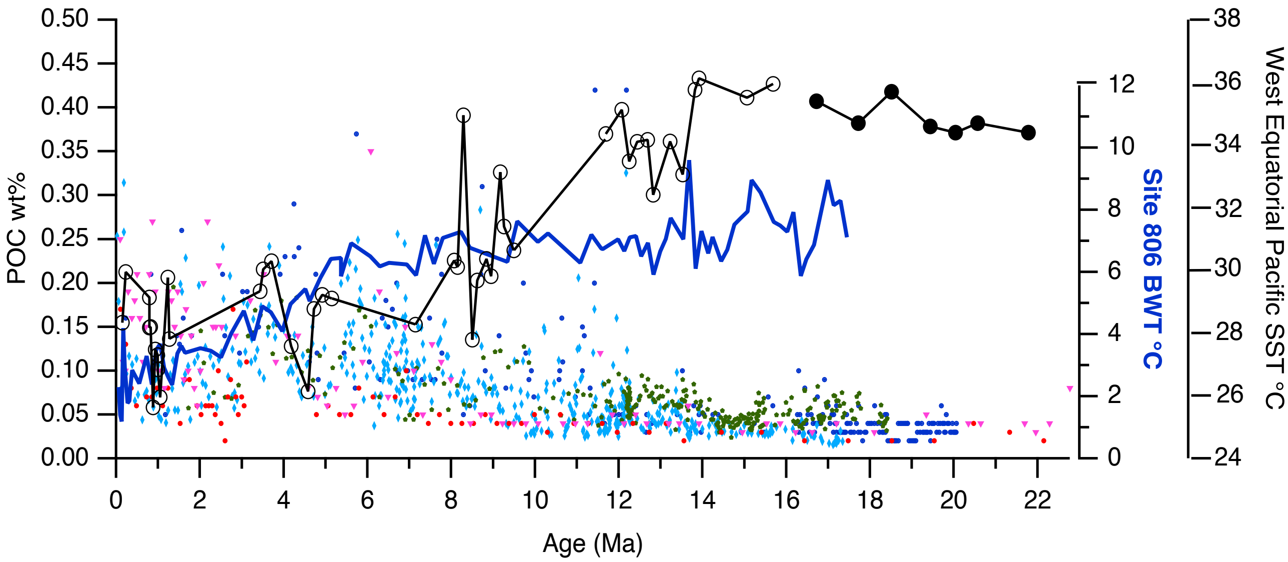

Figure 5: POC wt % time series in the equatorial Pacific (left axis) along with bottom water temperature (BWT, Lear et al, 2015, from Site 806) and a western equatorial Pacific sea surface temperature record (SST, Mg/Ca proxy, open circles Site 806; closed circles Site 872; Guillermic et al, 2022, with Site 872 data from Sosdian et al, 2018).. BWT in the Pacific did not change much until after 6 Ma, too late to affect POC degradation in the MCO, while SST was high until the end of the MCO. SST dropped about 3°Ç at the end of the MCO, followed by another ~3°C by 9 Ma.

The abyssal temperature change during the MCO is relatively small. Lear et al. (2015) data show that the MCO was 0.4°C warmer than the next 3 Myr of the temperature record at Site 806 (Fig 5). Kochann et al. (2017), in contrast, describe an abyssal temperature change of 1.7° at the end of the MCO at Site U1338 and 2.2°C at Site 1146 in the South China Sea. However, they did not observe consistently warm temperatures through the intervals in the MCO that they measured, in contrast to the consistently low POC contents. Kochann et al. (2017) noted a transient 2.6°C warming of bottom water temperatures at the onset of peak MCO warmth (15.5 Ma) at sites U1337 and U1338. However, both Lear et al (2015) and Kochann et al. (2017) found intermittent warming during the MCO, thus inconsistent with abyssal warmth being a driver of the low POC over the entire MCO.

A low percentage of particulate matter derived from total productivity reaches the sea floor, and sediment trap studies have shown that the particulate flux that reaches the sea floor is relatively rich in POC. The deepest sediment traps in the Joint Global Ocean Flux Study (JGOFS) tropical Pacific Experiment caught a particulate flux that contains around 5 wt % POC (Honjo et al., 1995; particulate rain from sediment traps between 2191 m and 3618 m depth within ± 5° of the equator), which, subsequently, must degrade down to the typical content found in surface equatorial sediments, around 0.2 to 0.3% (Murray and Leinen, 1993; Prahl et al, 1989). This order of magnitude loss of organic carbon, from the deepest waters to surface sediment, appears to be a consistent level of degradation in the pelagic equatorial Pacific, as is also shown by core top values of POC in the drill site data. Interestingly, the highest POC found in surface sediments, measured in the JGOFS transect by Murray and Leinen (1993), are in off-equatorial sites where clay is much more abundant, and sedimentation rates are much lower. The lower equatorial POC is partly a dilution effect by additional $CaCO_3$ compensated by higher sedimentation rates near the equator (Murray and Leinen, 1993).

5.3.3: Hypothesis (3): warmer surface waters and more POC degradation in the upper water column during the MCO

Here we discuss our preferred hypothesis based on the temperature-dependency of the biological pump; i.e., higher POC degradation in warmer surface waters prior to and during the MCO caused reduced POC burial via diminished rates of POC transferred to deep waters. This hypothesis requires that the converse is also true: i.e., cooling of surface waters post-MCO should also result in increased POC transfer to the abyss. Note that for all warm-cold or cold-warm transitions, the strength of the POC sedimentary signal ultimately preserved is partly dependent on the productivity regime over each drill site.

In Figure 5 we present a western equatorial Pacific sea surface temperature (SST) record using Mg/Ca SST proxies from Guillermic et al (2022), who combined Site 806 data with early Miocene data from the tropical guyot Site 872 (Sosdian et al., 2018). Sea surface temperatures in the early Miocene, prior to the MCO, were warm in the western equatorial region, between 34 and 36°C. Surface temperatures cooled quickly at the end of the MCO by about 3°C, and cooled again by ~3°C around 11 Ma. The cooling SST coincided with the increase in POC in our sedimentary record. Low POC in the period prior to the MCO (Fig 2), is further evidence that surface water warmth is an important factor in POC burial; i.e., low POC burial is not restricted to the MCO.

Modeling of carbon isotope distributions from foraminifera dwelling at different depths (see John et al., 2014 for the Eocene), and observations of plankton distribution suggest POC degradation occurs primarily within the surface ocean layer, above 1000 meters. Supplemental material from Boscolo-Galazzo et al. (2021) showed that there were much steeper $\delta^{13}C$ depth gradients in older time intervals, which model to a much shallower depths for POC degradation and a sharper O_2 minimum than in the Holocene. Using their temperature dependent model, the Holocene flux of particulate POC at equatorial Pacific Site U1338 was 3 to 4 times greater at 600 m in the Pleistocene relative to 15 Ma for the same level of primary productivity. Similarly, we observe a factor of 3 to 4 increase in POC sediment content over this same time interval at Site U1338. If this reflects degradation in the water column, a much smaller POC flux was sequestered in abyssal waters during the warm MCO climate relative to modern conditions. In other words, warm conditions caused a weaker biological pump.

In the modern ocean, however, POC content of particulate rain that arrives at the abyssal seafloor is significantly larger than the POC buried in the surface sediments, as noted previously from sediment trap studies. The particulate rain captured in deep sediment traps within the equatorial Pacific region (± 5° of the equator) contains about 5% POC (Table 5 of Honjo et al., 1995). This is an order-of-magnitude higher than surface sediments whose POC concentrations range between 0.23 and 0.33% (Murray and Leinen, 1993). Lower POC MAR away from the equator reflects the lower particulate rain rates away from the equator, and not the lower POC contents in the particulate rain. Differences in $CaCO_3$ rain versus bio-SiO_2 rain were observed but did not strongly affect the total POC preserved. In the Holocene, productivity apparently affects the rate of deposition of the particulate rain, but not so much its composition. We should be mindful of the role that the upper water column plays to determine both the magnitude of the biological pump and the level of POC content in sediments.

We note that after the MCO, our data show an overall increase in the ratio of POC to $BaSO_4$ and especially during periods previously identified as high productivity events. For example, at Site U1338 (Fig 2-C), where we have the best record, POC: $BaSO_4$ is greatest during the late Miocene Biogenic Bloom (Dickens and Owen; 1999; Diester-Haas et al, 2002; Lyle and Baldauf, 2015; Drury et al, 2017; Lyle et al, 2019; Karatsolis et al, 2022).

5.3.4 ***Hypothesis (4): A change in proxy relationships for productivity, changing estimates of paleoproductivity***

Another hypothesis worth considering is that during the MCO there is a change in the response of the proxy that varies from the expected modern response. For example, diatom deposition or POC: BaSO4 might behave differently with respect to POC production. Under these conditions there could be lower actual POC export to the interior ocean than that indicated by the proxy, minimizing the deposition of POC without indicating lower productivity. We believe that there is some likelihood that the relationship between export of particulate POC from the euphotic zone to other biogenic components may be somewhat different under warm earth conditions but propose that these differences result primarily from relative changes in POC consumption in the upper water column.

Dymond and Collier (1996) described how POC rained out of the modern equatorial Pacific relative to Ba. They found lower POC particulate rain away from the equator, corresponded to much lower ratio of POC to Ba (~30). In contrast, this ratio is ~150 near the equator where POC rain was high. The data suggests relatively rapid formation of Ba in microenvironments within particulate rain, followed by a loss of POC versus Ba. There is more complete consumption of POC in the surface ocean where the POC flux is lower. The sediment POC to Ba ratios found in sediments (Fig 2) are much lower because of the high degradation of POC at the sea floor relative to Ba (>20x reduction for POC vs ˜3x for Ba) before burial. However, the amount of Ba fixed in micro-environments depends on the Ba composition of seawater. In the modern ocean, Ba rain is significantly lower in the Atlantic than in the Pacific relative to POC because of the lower dissolved Ba in the Atlantic (Dymond and Collier, 1996).

If the modern observations across the equatorial region are consistent with changes that might occur in a warm interval like the MCO, we expect lower POC in the particulate rain relative to Ba. Conceivably then, the POC rain might slow even though the Ba flux did not. This could happen if dissolved Ba is fixed into barite ($BaSO_4$) relatively early in the rain of particulates, so that later degradation of POC only affects the POC: BaSO4 leaving surface waters (Fig 3). However, the POC MAR resembles the opal MAR to a certain extent after the end of the MCO, indicating that the POC MAR has a profile like a different proxy for productivity when surface waters cool. Perhaps the presence of diatoms causes a more effective transport of particulate POC to the sea floor.

In time series at Site U1338 we find significant, non-random changes in the ratio of POC to Ba, associated with apparent changes in productivity (Fig 3). Specifically: high POC: BaSO4 associated with the late Miocene Biogenic Bloom, and during a period around 12 Ma that shows high biogenic Si and $CaCO_3$ deposition as well. These time series show that the biogenic components have their individual processes that lead from creation to burial, so that care needs to be taken to quantitatively ascribe a certain level of primary productivity to the remains found in the sediments. Nevertheless, the lack of POC response during the MCO likely results from upper water column processes.

6 Conclusions

In earlier work we have found that warm earth conditions in the Eocene are marked by very low levels of POC burial (Olivarez Lyle and Lyle, 2005, 2006). In this study we also show that warm earth conditions during the early Miocene and Miocene Climate Optimum are also characterized by a low level of POC burial compared to the later sedimentary record. The low levels are represented in both the weight % POC and POC MAR's, and as low ratios of POC relative to other better preserved biogenic components like $BaSO_4$, despite relatively high deposition of other paleoproductivity proxies like biogenic silica. We formed 4 hypotheses to explain the low POC at the MCO: lower productivity, higher degradation in the lower water column, higher degradation in the upper water column, and a change in relationships between proxies, and rejected all except higher degradation the upper water column.

Our data suggest that POC is preferentially removed in the upper water column, an indication of a 'short circuit' in the biological pump under extreme global warmth once the ocean equilibrates. We observe that the average POC content of equatorial Pacific MCO sediments, the warmest Miocene interval, was about 0.04 % organic carbon, which is 5 times lower than modern surface sediment (0.2 to 0.3% POC; Murray and Leinen, 1993). POC in modern surface sediments is roughly proportional to the rain of POC that reaches the sea floor (near-bottom sediment traps). During the MCO it appears that ~5 times less POC reached the seafloor, likely caused by higher metabolic degradation in surface waters.

While the proportionality of POC particulate rain to burial is an oversimplification of early diagenesis in pelagic environments, it is an example of how the pelagic sedimentary environment responds to warm earth conditions. Better diagenetic models under low sedimentation rates and oxic conditions might improve our ability to hindcast particulate rain in the past. Clearly, though, there is a sedimentary response to these processes in the water column.

Author Contributions

Mitchell Lyle helped to collect the cores from Sites U1337 and U1338. He organized the XRF analyses along the continuous sediment sections (splices) and found funding for the discrete calibration carbon samples. He had primary responsibility for writing the paper. Annette Olivarez Lyle trained and supervised student analysts in both the bio-SiO_2 and the carbon analyses ($CaCO_3$ and POC) and was responsible for quality control of the resulting data. She also helped write and edit the paper.

Competing Interests

The authors declare that they have no conflict of interest.

Supplemental Material

Supplemental material for this paper are archived at Pangaea.de.

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