**Biogenic sediment regimes in the Neogene equatorial Pacific,
IODP Site U1338: Burial, production, and diatom community**

*26 March 2015 resubmission to Palaeo*³

Mitchell Lyle^{1,2} (Corresponding Author, e-mail: mlyle@coas.oregonstate.edu)

Jack Baldauf¹ (e-mail: jbaldauf@tamu.edu)

¹Dept of Oceanography, Texas A and M University, TAMU 3146, College Station TX
77840

²College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, 104
CEOAS Admin Bldg, Corvallis OR 97331

1.0 Abstract

The equatorial Pacific experienced significant changes in productivity and microfossil assemblage since 16 million years ago (Ma). We compiled a record of those changes from IODP Site U1338 using a reconnaissance of diatom assemblages and high-resolution XRF-scan chemical profiles (1-2 kyr spacing). Productivity and CaCO_3 dissolution intervals are defined by sediment component ratios, in particular opal/clay opal/ BaSO_4 and $\text{CaCO}_3/\text{BaSO}_4$ or $\text{CaCO}_3/\text{clay}$. There are large abrupt changes in export production in the Miocene, especially compared to the Pleistocene and Pliocene and average levels of export production are higher throughout the Miocene compared to the Pliocene and Pleistocene. Using diatom assemblages and bulk sediment composition, the U1338 sediment record is divided into several distinct deposition regimes: (1) a Middle Miocene regime >13.2 Ma marked by low diatom numbers and a few short-lived productivity intervals, (2) a Carbonate Crash regime distinguished by an older substage (13.2 -10.2 Ma) with relatively high abundances of productivity-related diatoms and common productivity-related depositional intervals interspersed with CaCO_3 dissolution intervals and a younger carbonate crash substage (10.2-8.0 Ma) with weaker brief productivity intervals, high CaCO_3 dissolution, and moderately high numbers of upwelling diatom species, (3) the Biogenic Bloom regime (8.0-4.5 Ma) marked by extended periods of high opal and CaCO_3 deposition with a maximum between 7.0 and 6.4 Ma, and (4) a Pliocene-Modern regime (4.5-0 Ma) with lower productivity and high cyclic CaCO_3 dissolution. Changes in production and dissolution result from reorganizations of nutrient supply to the equatorial Pacific, not by higher wind-driven upwelling. We propose that nutrients were more accessible in the Miocene because of a combination of factors including higher organic matter degradation in the upper water column and deep-intermediate nutrient pathways that efficiently recycled nutrients to

upwelling zones. Closure of the Central American Seaway was likely a prime cause of the Biogenic Bloom.

Keywords:

Export productivity, paleoproductivity, Neogene, equatorial Pacific, IODP, Site U1338, diatom assemblage, XRF scanning

2.0 Introduction

It has long been known that the equatorial Pacific, one of the largest regions of high primary productivity on the planet, has had multiple million-year intervals where oceanographic conditions were altered significantly from the modern equatorial system (Berger, 1973; van Andel et al., 1975; Farrell et al., 1995). Changes in both biogenic sediment production and carbonate dissolution reflect changes in oceanographic conditions and are recorded in the sediment record from the Cenozoic equatorial Pacific.

Studies of paleoproductivity have been hampered by a lack of good data on sediment chemical composition. Because CaCO_3 is easily measured and is the major biogenic sediment in the equatorial Pacific, most studies have attempted to understand the CaCO_3 record and changes in its sedimentary mass accumulation rate (MAR) over time even though it was well known that bathyal CaCO_3 dissolution strongly affected the CaCO_3 record (Berger, 1973; van Andel et al., 1975). Other biogenic sediment components, biogenic SiO_2 (opal), C_{org} , and biogenic Ba (bio-Ba) have been suggested as ways to gauge productivity (Leinen, 1979; Lyle et al., 1988; Dymond et al., 1992; Paytan and Kastner, 1996) but their analyses have proven relatively time-consuming. Understanding biogenic records other than CaCO_3 in the equatorial Pacific has also required a reasonable age model in order to reconstruct MAR, since changes in CaCO_3

dissolution strongly affect the sediment composition. In high CaCO₃ sediments like those of the equatorial Pacific, the weight % of minor elements measured in bulk sediments is inversely proportional to the preserved CaCO₃ flux because of changes in dilution by carbonates (van Andel et al., 1975).

A new way to study changes in biogenic sedimentation results from the use of X-ray fluorescence (XRF) scanning, where both major and minor element sediment composition can be analyzed with reasonable accuracy and speed. These and improved Neogene age models are producing new ways to understand changes in equatorial Pacific productivity (Holbourn et al., 2014).

Another perspective on paleoproductivity can be fashioned by analyzing the distribution of biosiliceous sediments and microfossil assemblages preserved in the sediments. For example, Lisitzin (1972) found that the distribution of biosiliceous surface marine sediments reflects overlying surface water productivity and occurs beneath regions of high surface water productivity. Since the world oceans are undersaturated with respect to biogenic silica there must be high export production for incorporation of the biogenic silica into the sedimentary record. Baldauf and Barron (1990) and Cortese et al., (2004), among others, have related the shifts in biosiliceous sedimentation patterns to oceanic reorganization and climate variability.

Diatom assemblages and specific species are other tools that continue to be used as indicators of increased surface water productivity. High productivity indicator species typically include forms such as *Chaetoceros*, *Thalassiothrix longissima*, and *Thalassionema nitzschioides* (e.g., Sancetta, 1983, 1995; Lopes et al., 2006; Romero and Armand, 2010). In this paper, we make use of both the sediment composition approach and microfossil assemblages to examine depositional variability in the period from 16 to 0 Ma. We use the record from International

Ocean Discovery Program (IODP) Site U1338 (Figure 1) because most of the sediment record at Site U1338 was deposited within the Pacific equatorial zone ($\pm 2^\circ$ N or S of the equator) and thus reflects production changes related to the equatorial zone.

2.1 Importance of the eastern equatorial Pacific in global biogeochemical cycles

The equatorial Pacific is one of the earth's major climate-driven biogeochemical systems, huge in scale and with a strongly coherent response to climate perturbations. In the Holocene a major proportion of global ocean new production occurs here (20-60%, Chavez and Barber, 1987), as well as ~40% of global CaCO_3 production (Dunne et al., 2012). About 2/3 of ocean efflux of CO_2 to the atmosphere also comes out of the equatorial Pacific (Takahashi et al., 2009). The equatorial Pacific is also Fe-limited (Martin et al., 1994) so that minor changes in trace nutrients can potentially produce a large response by atmospheric CO_2 from changing the efficiency of the biological carbon pump (Takeda, 1998; Pichevin et al., 2009; Pichevin et al., 2014). Understanding the production and burial of biogenic sediment in the equatorial Pacific is critical to understanding the global carbon cycle. Because of the large scale of the equatorial Pacific and its coherent response to the evolution of Neogene climate the evolution of the productivity system also can be studied with relatively few records.

From the East Pacific Rise westward ($>100^\circ\text{W}$), the equatorial productivity zone is primarily zonal in nature and responds to large-scale climate patterns (Chavez et al., 1996; Chavez et al., 2003). East of the Galapagos ($<90^\circ\text{W}$), productivity patterns also reflect interactions between climate and the geography of the American continents (Messie and Chavez, 2011, 2012). Closure of the Central American Seaway (CAS) has had strong effects on patterns of biogenic deposition near the Americas but weaker effects away from it (Farrell et al., 1995; Lyle et al., 1995). Hagelberg et al. (1995) used Ocean Drilling Program (ODP) Leg 138 data to

show that there is a coherent response of equatorial CaCO_3 deposition centered at the equator for the last 6 million years (Myr), as expected if changes in CaCO_3 production are a major factor in its burial at the sea floor. Opal MAR patterns (Farrell et al., 1995) are more complicated, with equatorially-centered upwelling west of the East Pacific Rise (100°W) but a switch around 7 Ma from relatively low opal deposition to much higher deposition east of 100°W , presumably associated with the Panama uplift.

2.2 Site Location

Site U1338 ($2^\circ 30.469'\text{N}$, $117^\circ 58.178'\text{W}$; 4200 m water depth) was one of the eight sites occupied during IODP Expedition 320/321 to form the Pacific Equatorial Age Transect (Figure 1; Pälike et al, 2010a). Site U1338 was cored on 18 Ma basalt crust just north of the Galapagos Fracture Zone to obtain a continuous sedimentary sequence to basement. Four holes were completed resulting in the recovery of a nearly complete 415-m-thick sequence of lower Miocene to Holocene sediments. The recovered sediments consist of diatom-rich nannofossil ooze and chalk. Lower sedimentation rates were found near the base of sediments, typical of initial sediment accumulation on basaltic crust (Expedition 320/321 Scientists, 2010a). Unknown fractions of added hydrothermal sediments and mild opal diagenesis near the base of the sediment column resulting from hydrothermal fluids percolating upward from basement (Moore, 2008) make the basal sediments difficult to interpret. We therefore present data from 16 Ma to the present, not reporting data from the bottom 25 m of the sediment column.

In the Holocene Site U1338 is positioned beneath equatorial tropical surface waters and is in the transition zone between the nutrient-poor North Equatorial Countercurrent coming from the western Pacific and the more nutrient-rich South Equatorial Current coming from the east (Figure 1; Fiedler and Talley, 2006), and is situated at the northern edge of the Equatorial Cold

Tongue. The Equatorial Cold Tongue is produced by equatorial upwelling, advection of cold waters in the South Equatorial Current from Peru, and feedback from growth of high-albedo stratus clouds over cold waters (Philander et al., 1996). West of 100° W productivity is centered at the equator in response to upwelling there (Chavez et al., 1996), biogenic particulate rain is highest at the equator (Honjo et al., 1995), and so is biogenic sediment burial (Murray et al., 2000). High biogenic deposition at the equator is a feature of the equatorial system for all of the Neogene (Hagelberg et al., 1995; Lyle, 2003; Moore et al., 2004). Using the plate tectonic change of Site U1138 paleoposition (Figure 1, Pälike et al., 2010b) Site U1338 was initially positioned southeast of its current location (~1°S, 105°W at 16 Ma) and migrated northwest with the Pacific plate to cross the equator between 12 and 11 Ma en route to its present location.

3.0 Assessing equatorial Pacific Productivity

Many types of data have been proposed to indicate changes in equatorial Pacific productivity including changes in biogenic sediment MAR, primarily opal, C_{org}, or bio-Ba (van Andel et al., 1975; Lyle et al., 1988; Paytan et al., 1996; Murray and Leinen, 1993), changes in ratios of biogenic components to other components with relatively stable deposition, like clay minerals, e.g. Ba/Ti (Murray et al., 2000) or opal/Ti (Holbourn et al., 2014), and also excess accumulation of dissolved trace elements that can be scavenged by particulate rain, e.g. Al/Ti (Murray and Leinen, 1996; Dymond et al., 1997) or even ²¹⁰Pb (Moore and Dymond, 1988). Micropaleontologists have often used the microfossil assemblage as an indicator of productivity based on assemblages typically found in high productivity regions (i.e. Ren et al. 2014, Katsuki et al., 2003). For each of these proxies a correlation has been found between some aspect of productivity and the change in a measured property. However, C_{org} also has a strong preservation signal overprinted, and among the hypothesized factors is ocean temperature and sedimentation

rate (Olivarez Lyle and Lyle, 2006; Piela et al., 2012). C_{org} data will not be discussed further in this paper.

3.1 Sediment traps and sediment burial fluxes—proxy calibrations

Equatorial Pacific biogenic sediments are composed of biogenic carbonates (~ 75% of the sediment), biogenic silica (opal, ~20%), bio-Ba (~0.5%, primarily barite; Dymond et al., 1992, Griffith and Paytan, 2012), and organic carbon (C_{org} , ~ 0.1%). Typically, clay contents are ~5% (Murray et al., 2000; Piela et al., 2012; Wilson, 2014). Of the biogenic sediments, variable levels of $CaCO_3$ dissolution at the sea floor affect the burial of carbonate relative to other biogenic components and cause changes in the carbonate compensation depth (CCD) over time (Farrell and Prell, 1989, 1991; Lyle, 2003; Pälike et al., 2012). Here we present data on the biogeochemical fluxes to the sea floor (the particulate rain) of biogenic minerals to better understand how production may affect the resulting sediment composition.

3.1.1 Production and preservation of biogenic opal and carbonate

Two factors set the level of $CaCO_3$ and opal burial in equatorial Pacific sediments: the ratio of $CaCO_3$ to opal in the particulate rain to the sea floor and the differential dissolution of these two biogenic sediments after they touch bottom. Figure 2 shows the particulate fluxes through the water column ('rain') in tropical environments, using JGOFS equatorial Pacific and Arabian Sea sediment trap data (Honjo et al., 1995; 1999) to serve as modern analogs to past environments. We use data confined to the 2000-2500 m range because this is a depth range where upper water column transformations of the fluxes have ended and dissolution in the deep water column becomes more important (Walsh et al., 1988; Dymond and Lyle, 1994).

In Figure 2a, both CaCO_3 and opal (bio- SiO_2) rain increase as the export rain of C_{org} (the biogeochemically significant measure of productivity) increases. In other words, as productivity increases in surface waters and drives a higher rain of particulate C_{org} to the deep ocean, both CaCO_3 and opal fluxes also increase—competition between opal (diatom) production with that by calcareous phytoplankton may slow the increase of CaCO_3 rain but evidently does not reduce it in magnitude. Both opal rain and CaCO_3 rain increase with increased C_{org} rain. As an aside, there is no evidence of ballasting of the particulate C_{org} flux in these data (Klaas and Archer, 2002). If ballasting were a major cause to change export C_{org} flux, C_{org} flux would be more highly correlated with CaCO_3 flux, since CaCO_3 is >20% more dense than opal.

Opal rain increases slightly faster than the C_{org} rain and causes a concave upward trend. In contrast, the CaCO_3 rain increases more slowly and has a concave downward trend (Figure 2a). As primary production becomes iron limited, the biological pump becomes less efficient and the opal/ C_{org} ratio increases (Hutchins and Bruland, 1998; Pichevin et al., 2009; Pichevin et al., 2014). The slight increase in opal flux relative to C_{org} is probably an indicator of the change in pump efficiency. Since the Arabian Sea receives roughly 100 times the dust and Fe flux as the equatorial Pacific (Mahowald et al., 2009, dust fluxes from sediment trap Al fluxes in Honjo et al., 1995, 1999) the relative efficiency change may be subdued in the combined data set. The highest opal to C_{org} rain ratio occurs in the northwest Pacific (Honjo et al., 2008) where there are high nutrients and moderate dust fluxes and thus opportunities for Fe-limiting conditions to appear (Han et al., 2011).

If both CaCO_3 and opal rain are summed, the combined flux is linear with respect to C_{org} ($r^2=0.91$) so the proportion of opal to CaCO_3 increases at higher flux times relative to low flux ones (Figure 2b). Under high productivity regimes the initial percentage of CaCO_3 in particulate

rain that reaches the sea floor is lower than in low flux regimes, before any subsequent dissolution.

At the sea floor, particularly when the sediment surface is below the lysocline, dissolution also strongly impacts the CaCO_3 record. For CaCO_3 , both the ambient $[\text{CO}_3]^-$ content in the deep waters and the high flux of C_{org} to the sediments may enhance dissolution (Emerson and Bender, 1981). Opal dissolution depends on sedimentation rate because opal is always undersaturated in the ocean and gets preserved only when buried (Broecker and Peng, 1982; Dymond and Lyle, 1994; Ragueneau et al., 2000). Opal preservation increases from ~5% of the particulate rain for sediments deposited at 1-2 cm/kyr to ~25% at ~10 cm/kyr (Ragueneau et al., 2000). At higher particulate fluxes on seafloor beneath the lysocline, CaCO_3 dissolution is high because of corrosive bottom water and because of metabolic CO_2 production as C_{org} degrades within the surface sediments. In contrast, opal dissolution tends to decrease because sedimentation rates increase as biogenic rain increases, so sediment with low CaCO_3 content is formed because of both a higher initial opal/ CaCO_3 in particulate rain and better opal preservation under higher sedimentation rates. Relationships among opal, C_{org} , and CaCO_3 found in the equatorial Pacific appear continuous with those from higher tropical productivity regimes in the Indian Ocean (Figure 2) defining a continuum in biogenic component relationships in the tropical oceans. Higher surface productivity should lead to higher opal relative to carbonate in sediments both from the production side as well as from the preservation side.

The change in CaCO_3 MAR in relation to productivity change is complicated by dissolution within the benthic boundary layer which can change significantly irrespective of a change in productivity. Changes in deep dissolved inorganic carbon (DIC) storage or exposure to water masses with different DIC can strongly affect preservation in the deep oceans below 3.5

km. In the late Pleistocene, glacial-interglacial deep-water changes cause prominent glacial-interglacial CaCO_3 cycles (Hays et al., 1969; Farrell and Prell, 1989). Without additional information beyond opal and CaCO_3 contents it is impossible to distinguish between an opal % increase caused by an increase in production versus one caused by the heightened dissolution of CaCO_3 alone. However, additional geochemical data from XRF-scanning can potentially be very useful to distinguish productivity and preservation.

3.1.2 Bio-Ba and elemental ratios to constrain production and dissolution

X-ray fluorescence (XRF) can measure Ba and the clay-forming elements Al, K, and Ti. Of these, Ba is a good measure of bio-Ba where aluminosilicate fluxes are small and porewater sulfate gradients are weak (Dymond et al., 1992; von Breyman et al., 1990; Torres et al., 2002; Piela et al., 2012). Ti is the best of the XRF elements to estimate clays, because, unlike Al, it fluoresces X-rays strongly and the fluoresced X-ray energy is sufficiently high to minimize absorption by air or water before reaching the detector. In addition, there is good evidence within the equatorial Pacific that high particle fluxes scavenge dissolved aluminum from the water column (Murray and Leinen, 1996; Dymond et al., 1997), forming a peak in the Al/Ti ratio at the equator.

3.1.2.1 Bio-Ba systematics

About 75% of the total particulate bio-Ba is fixed above 1200 m, and the remaining 25% is fixed as the particles transit the remainder of the distance to the sea floor (Dymond and Collier, 1996). High-Ba seawater reacts with C_{org} and organic-sulfur-rich particulate rain to form barite in the falling particles. Ba flux correlates with C_{org} flux but in the equatorial Pacific observed Ba fluxes taper off at higher C_{org} fluxes (Figure 3a; Dymond and Collier, 1996). At the

same C_{org} rain, less Ba is fixed in the Atlantic than in the Pacific, because dissolved Ba contents in Atlantic waters are lower than those in the Pacific.

Ba is well preserved in sediments where sedimentary sulfate reduction is not prevalent (~30% preservation, Dymond et al., 1992; Eagle et al., 2003; Griffith and Paytan, 2012) because much of the Ba is in the form of barite in the sediments, and barite is difficult to dissolve in oxic and suboxic geochemical environments. High levels of Ba preservation in sediments and a good correlation with C_{org} flux make bio-Ba a robust indicator of C_{org} export flux (Eagle et al., 2003). Because barite is more difficult to dissolve than either opal or $CaCO_3$, enhanced barite levels can be found at the fringes of productive regions, what Dymond (1981) termed as the ‘dissolution residue’. Near continents total Ba may mostly be from clays rather than from water column production (Dymond et al., 1992), but in the equatorial Pacific where clay contents are 5% or less, the clay correction is small and can be neglected (Piela et al., 2012). For the average Ba of 3898 ppm in the U1338 sediments, the aluminosilicate correction is under 50 ppm.

3.1.2.2 XRF $BaSO_4/TiO_2$ or $BaSO_4/Clay$ and paleoproductivity

In the absence of detailed MAR data, one way to calculate high deposition of Ba is to use the sediment ratio of Ba to Ti (Goldberg and Arrhenius, 1958; Murray et al., 2000), or in the case of XRF components, $BaSO_4/TiO_2$. Goldberg and Arrhenius (1958) showed that there was a peak in Ba/Ti in the Pacific at the equator. If the flux of aeolian clays is relatively constant, the variation of $BaSO_4/TiO_2$ (or $BaSO_4/clay$) should be caused primarily by changes in water column export production. The assumption of relatively constant flux of clay is a good first approximation of windblown clay deposition to the equatorial Pacific. Dust sources to Site U1338, since it always is south of the Intertropical Convergence Zone, are primarily South American deserts more than 5000 km away (Xie and Marcantonio, 2012). Fluxes to the

equatorial Pacific are estimated to be some of the lowest Ba fluxes in the world (Mahowald et al., 2009). Clay MARs trend lower by about 30% for the period from 16 Ma to the present, as Site U1338 moves away from the South American dust source. The constant clay flux assumption should cause an underestimate of productivity relative to MAR in the middle and late Miocene because of the inverse proportionality in the ‘constant clay’ approximation. In the Pleistocene, fluxes will be biased low during dusty glacials (Winckler et al., 2008).

3.1.2.3 XRF CaCO₃/ BaSO₄ or CaCO₃/Clay and CaCO₃ dissolution

CaCO₃ flux has a scattered but linear relationship with Ba in the JGOFS equatorial Pacific sediment trap data (Figure 3b; Dymond and Collier, 1996). Because the two elements are fixed by production in the water column, the higher and more consistent preservation of bio-Ba potentially allows the CaCO₃/ BaSO₄ ratio to be used to scale dissolution. Similarly, if clay deposition is relatively constant, CaCO₃/clay can be another measure.

The scatter between CaCO₃ rain and Ba rain probably represents real seasonal variability in their respective production and transport cycles. While the CaCO₃/BaSO₄ ranges between 160 and 1400 over the measurement year, much of the variability results from the change in particle rain with latitude. The CaCO₃/BaSO₄ ratio (partitioning all Ba as BaSO₄) for the JGOFS 0°N sediment trap is 425±261 over the 1992-1993 trapping period, while the CaCO₃/BaSO₄ ratio at 9°N is 143±78.

For the time series that will be shown later, high production should produce an initially high CaCO₃/BaSO₄ in the particulate rain that is subsequently lowered by seafloor dissolution. Ba dissolution (assuming ~30% preserved) in the absence of CaCO₃ dissolution raises the rain ratio by a factor of 3, while CaCO₃ dissolution will lower it again. Because the ratio changes

with average production, high production should cause higher $\text{CaCO}_3/\text{BaSO}_4$ ratios than low production, even when the same dissolution is imposed.

Once particles are deposited at the sea floor, CaCO_3 dissolution will decrease the $\text{CaCO}_3/\text{BaSO}_4$ or $\text{CaCO}_3/\text{clay}$ ratio by a variable amount. If there were only loss of BaSO_4 and no CaCO_3 dissolution, the $\text{CaCO}_3/\text{BaSO}_4$ should be ~1200 at the latitude of Site U1338; the Holocene measured $\text{CaCO}_3/\text{BaSO}_4$ ratio in the surface sediments at Site U1338 is ~400, indicating a preservation of roughly 1/3 of the CaCO_3 rain. This level of preservation is similar to that measured at a similar water depth at MANOP Site C, where 1/3 of the CaCO_3 rain is preserved, estimated by comparing sediment trap CaCO_3 rain to surface sediment CaCO_3 MAR (Dymond and Lyle, 1994).

3.1.2.4 XRF opal/ BaSO_4 and paleoproductivity

Another indicator of high production is opal/ BaSO_4 . In this case, the ratio varies with respect to export C_{org} flux because opal rain increases at a faster rate than the C_{org} rain (Figure 2), while Ba may increase more slowly than C_{org} at higher fluxes (Figure 3a). The net result is that as C_{org} rain increases, the opal/ BaSO_4 ratio also increases. It is unclear whether the change in ratio represents a change in biological carbon pump efficiency at higher production or an artifact of how the proxies record fluxes. In the late Pleistocene, the sedimentary opal/ BaSO_4 at U1338 averages about 10 and fluctuates between 0 and 20, versus a sediment trap ratio of about 150. Compensating for a 30% preservation of BaSO_4 , only about 2% of the opal is also preserved in the late Pleistocene. Dymond and Lyle (1994) found 11% opal preservation at 1°N (MANOP Site C) and 4% at 8°N on the East Pacific Rise (MANOP Site M), so the opal/ BaSO_4 estimate of preservation appears to be somewhat low.

3.1.2.5 XRF opal/clay or $\text{Al}_2\text{O}_3/\text{TiO}_2$ and paleoproductivity

Opal/ TiO_2 can also be used to identify intervals of high opal production using XRF (Holbourn et al., 2014). XRF opal/ TiO_2 or normative opal/clay used in this paper shows intervals within the sediment section with excess Si relative to the aluminosilicate flux. If the flux of clay is relatively constant, changes in the ratio should represent changes in opal deposition. Another paleoproductivity proxy ratio that can be measured via XRF scanning is Al/Ti (Murray and Leinen, 1996; Dymond et al., 1997), reported in this paper as $\text{Al}_2\text{O}_3/\text{TiO}_2$. Within the JGOFS transect the Al/Ti ratio tracked particle flux, and apparently dissolved Al is scavenged by particle flux, possibly binding to opal (Dymond et al., 1997). Comparison between these ratios will provide a test of their consistency as paleoproduction indices.

3.2 Diatom assemblages and paleoproductivity

The abundance and variation of diatom composition have often been linked to specific water masses and used as indicators of productivity both in the surface waters and the sedimentary record. As examples, Romero and Armand (2010) provide an overview of the use of diatoms as indicators of oceanographic conditions. Kobayashi and Takahashi (2002) analyzed diatoms from western and central Pacific surface waters to determine the distribution, abundance and composition of taxa. In doing so, they determined that the diatom distribution was aligned to specific water masses including the Western Pacific Warm Pool and the equatorial upwelling region. Sancetta (1995) used variation in flux patterns and taxonomic composition in the Gulf of California to assess the pattern of seasonal diatom production. Ren et al. (2014) mapped the distribution of the diatom assemblage from North Pacific surface sediments to overlying water masses.

Within the eastern equatorial Pacific sedimentary sequences diatom analysis for paleoceanographic reconstruction typically relied on variation in the relative abundance or percentage data of the diatom assemblage (Baldauf, 1985; Barron, 1985a; Schrader et al., 1993). There are exceptions, for example Schrader and Sorknes (1990) determined absolute diatom abundance for sediment cores from ODP Leg 112 along the Peru margin and Romero et al. (2011) generate absolute numbers of diatom abundance during the last glacial cycle for piston core MD02-2529 in the coastal Panama Basin.

Several species are commonly used as proxies for surface water conditions within the equatorial Pacific. *Thalassiothrix longissima* accumulates in surface sediments beneath regions of upwelling and biological productivity including the equatorial Pacific (Sancetta, 1983). The skeletal remains of this species often comprise laminated mat deposits in Neogene equatorial Pacific sediments (Kemp et al., 1995). *Thalassionema nitzschioides* has been used in the equatorial Pacific sedimentary record as a proxy for intensified upwelling and increased productivity (Margalef, 1978; Romero et al., 2009). *Thalassionema nitzschioides* var. *parva* is associated with warmer surface waters (Schrader and Sorknes, 1990; Romero et al., 1999) and high salinity (Schrader et al., 1993). *Azpeitia nodulifera* is associated with tropical surface waters (Schrader et al., 1993; Schrader and Sorknes, 1990) and equatorial upwelling (Cooke-Poerl et al., 1975; Baldauf, 1985).

The combination of diatom census data and bulk sediment chemistry allows a comparison of two distinct proxies to understand the evolution of the equatorial Pacific upwelling system. Diatoms give information about surface water masses and ecosystem response, while the bulk sediment chemistry gives information about the biogeochemical consequences of surface water changes.

4.0 Methods

Three types of data are incorporated into this paper: (1) bulk sediment chemical composition from calibrated XRF scans, (2) quantitative diatom census data from discrete samples along the U1338 splice were combined with (3) an updated age model for U1338 so that MAR could be studied and changes in productivity and assemblage could be evaluated via burial rates.

4.1 XRF Scans and data processing for bulk sediment chemical composition

XRF scanning was done using the TAMU ODASES XRF scanner at the IODP Gulf Coast Repository (<http://odases.tamu.edu/index.php/xrf-scanner>), a third generation Avaatech XRF scanner with a Canberra X-PIPS SDD, Model SXD 15C-150-500 150 eV resolution X-ray detector. The XRF scanner is configured to analyze split sediment core halves for elements between Al and U in the periodic table (Richter et al., 2006, Lyle et al., 2012). XRF parameters used for the Site U1338 XRF scans can be found in Lyle et al. (2012). Core sections along the U1338 splice were measured at 2.5 cm intervals, at 10 kV for the elements Al, Si, S, Cl, K, Ca, Ti, Mn, and Fe, and at 50 kV for Ba.

XRF data were processed and calibrated using the methods described in Lyle et al. (2012) and Lyle and Backman (2013). First the XRF data were median-scaled, i.e., the median of the raw peak areas for each element was set to the oxide composition of a model average sediment composition. In the case of U1338, we used the median of the ICP-MS bulk sediment analyses for each element as the model composition. For example, the median Al peak area measured was set to equal a model Al_2O_3 composition of 0.375%. The components of the model composition used are 0.375% Al_2O_3 for a median Al peak area, 15.5% SiO_2 for total Si, 0.123% K_2O for K,

76.25% CaCO₃ for Ca, 0.003% TiO₂ for Ti, 0.188% MnO for Mn, 1.089% Fe₂O₃ for Fe, and 0.396% BaSO₄ for Ba.

Elemental peak areas were then converted to a median-scaled composition (S_e) by the following:

$$S_e = \text{Model \% Med}_e \times (\text{PeakArea}_e / \text{PeakArea}_{e,\text{med}})$$

Typical sums of these raw median-scaled components will often not equal 100% because of differences in porosity (where water replaces the sediment elements that fluoresce X-rays) or cracks and an uneven sediment surface changing the volume illuminated. Normalizing the sum of raw median-scaled components to 100% eliminates the problem caused by different masses of sediment under X-ray illumination and produces the normalized median-scaled data (NMS, Lyle et al., 2012), ready for calibration.

The NMS data is calibrated with independent bulk sediment analyses (Lyle et al., 2012; Lyle and Backman, 2013) and both the NMS and calibrated data are contained in Supplemental Table 1. Calibration was achieved by analyzing a set of discrete samples for bulk sediment analysis by ICP-MS and separately for CaCO₃ and opal. For the ICP-MS analysis the samples were dissolved with trace metal grade perchloric acid, nitric acid, and hydrofluoric acid in Teflon beakers, following the procedure outlined in Piela et al. (2012) and analyzed for Al, Ca, Ti, Mn, Fe, and Ba. SiO₂ was not analyzed because the trace element clean HNO₃ was contaminated with SiO₂ when it was distilled in glass stills. CaCO₃ was analyzed separately by acidification (Lyle and Backman, 2013) and was used to calibrate the XRF CaCO₃ estimate. Opal was also analyzed on a split from the sample calibration set, using the molybdate blue colorimetric technique using 1M KOH for opal dissolution as in Piela et al. (2012). Clay-bound SiO₂ was

estimated by multiplying the calibrated TiO_2 by the upper crustal Si/Ti ratio from Taylor and McClennan (1995), and total SiO_2 used for the calibration was calculated by summing the clay-bound SiO_2 to the opal SiO_2 that was directly measured. Estimated clay-bound SiO_2 averaged $10 \pm 6\%$ of the total SiO_2 and was a minor but significant addition to the total SiO_2 content. XRF-estimated opal content was subsequently estimated by subtracting the estimated clay-bound SiO_2 fraction from total SiO_2 .

4.2 Age Model

Figure 4 presents the age depth model for Site U1338 used in this paper, based on the Backman and Baldauf (personal communication, 2010) linear age model produced after drilling and the Mix et al. (1995) Site 849 age model for 0-5.3 Ma. The Backman-Baldauf age model uses a cleaned data set of 33 paleomagnetic, 33 calcareous nannofossil and 72 diatoms events ages assigned by the event chronology presented by the Expedition 320/321 Scientists (2010b). For 0-5.3 Ma we have correlated the CaCO_3 profile from Site U1338 to that of ODP Site 849 and used the Mix et al (1995) age model for Site 849. CaCO_3 contents for Site 849 sediments were estimated from the wet bulk density GRA measurements using the method outlined in Hagelberg et al. (1995). At Site 849 Mix et al. (1995) developed an orbitally tuned chronology with benthic stable isotopes. CaCO_3 profiles provide a simple and apparently accurate chronostratigraphy in the equatorial Pacific (Farrell and Prell, 1991). The ages were matched between the two sets at 5.3 Ma, and are linear below this depth.

In Figure 4 it is difficult to see the results of correlation of the U1338 carbonate record of the 5-0 Ma interval to the orbitally tuned record of Site 849 because the net age-depth result is nearly linear. In the 4.5-0 Ma interval, sedimentation rates at Site U1338 average 16 ± 6 m/Myr

with variability at Milankovitch periods. For the period from 16.2-4.5 Ma, the sedimentation rate is nearly double, 27 ± 10 m/Myr.

The depth shown in Figure 4 is the compressed meters composite depth (CMCD using the CCSF-B method). A continuous sediment column was reassembled by splicing together sections from holes about 20 m apart across gaps between cores to form the mcd or meters composite depth (Wilkens et al., 2013). Then the depth was compressed by the coring stretch factor observed by comparing the mcd depth to the drillers depth (1.107, Figure F44 in Exp320/321 Scientists [2010]). Dry sediment density (ρ_{dry}) needed for MAR calculations was determined by a linear correlation ($R^2 = 0.95$) of discrete shipboard dry density to the scanned GRA (Gamma Ray Attenuation) wet bulk density data. Dry bulk density in g/cm^3 was then estimated from GRA along the spliced sediment column using the following equation:

$$(2) \rho_{\text{dry}} = 1.403(\text{GRA}) - 1.379$$

The dry bulk density multiplied by the sedimentation rate in cm/kyr yields the bulk MAR in $\text{g/cm}^2/\text{kyr}$; MARs for individual components result from multiplying the bulk MAR by the sediment fraction of the component (component % divided by 100). Microfossil AR are calculated by multiplying the quantitative counts (specimens/g sediment) by the bulk MAR. The MAR data are found in supplemental Tables 2 and 4.

4.3 Biota

A total of 418 samples were examined from Holes U321-1338A through U1338C for siliceous microfossils (Supplemental Table 3; Baldauf, 2013). The meter composite depth scales (CCSF-A) follows the Wilkens et al. (2013) revised splice. After processing we found out that we had not received samples from certain intervals and thus had a sampling gap between 10.5 to 9.3 Ma.

Samples from Site U1338 were processed for quantitative analysis using a variation of the method described by Scherer (1994) processing a nominal 0.1 g of dry sediment. The primary difference was to neutralize the residue in the same vial, thereby eliminating potential residue loss. The total number of diatoms, radiolarians, and silicoflagellates was tabulated for 50 fields of view or the first 600 diatoms encountered. The number of valves/skeletons per gram sediment was calculated following Scherer (1994). Samples were examined at 500x using a Zeiss Axio Imager A2 microscope. Species identifications were completed at 1250x. The counting techniques of Schrader and Gersonde (1978) were used. See Baldauf (2013) for a complete tabulation of species occurrences. Supplemental Table 3 provides the total valves per grams for *A. nodulifera*, *T. longissima*, *T. nitzschioides*, and *T. nitzschioides* var. *parva*. For the purpose of this specific manuscript other diatom taxa were not tabulated separately.

Ratios were developed for each species/variety based on variations in abundance of each species/variety relative to the entire diatom assemblage to compare with each other and the geochemical proxies. A species ratio differs from a percentage in that the ratio is the abundance (valves per g sediment) of the species divided by the sum of the abundance of the other diatom species, not divided by the total diatom abundance.

5.0 Results

There are 4 distinct regimes with different modes of production and dissolution identified here and from past work: a pre-13.2 regime (termed “Middle Miocene”), a 13.2 -8 Ma regime split at 10.2 Ma (“Carbonate Crash” regime, divided into an early high opal production substage and a later high CaCO₃ dissolution substage), a “Biogenic Bloom” regime (8- 4.5 Ma), and post 4.5 Ma regime (“Pliocene-Modern”). We identified the regimes based on previous observations as well as on the character of both the XRF and diatom profiles, discussed below. We will first

describe the data that we used to divide the record into regimes and then we will describe the regimes in more detail at the end of the section.

The Middle Miocene Regime contains the ‘silica switch’ transition at ~15 Ma where sediments with high diatom numbers disappeared from the North Atlantic and diatom-rich sediments appeared in the North Pacific (Keller and Barron, 1983). The Carbonate Crash Regime includes older low-CaCO₃ intervals found on both sides of the Isthmus of Panama (Roth et al., 2000) and the later carbonate crash CaCO₃ minimum found only on the Pacific side (Lyle et al., 1995; Nathan and Leckie, 2009). The Biogenic Bloom Regime was first defined by Farrell et al. (1995) and is marked by several major high production intervals with the most prominent at 7 Ma. Finally, the Pliocene-Modern Regime is the relatively low biogenic MAR regime that is found after 4.5 Ma at U1338, and all sites of the Leg 138 110°W transect (Farrell et al., 1995; Hagelberg et al., 1995). There is a shift of biogenic sediment deposition initiated at the beginning of the Pliocene-Modern Regime from the equatorial Pacific west of the East Pacific Rise toward South America, presumably because of the effective closure of the CAS (Farrell et al., 1995; Cortese et al., 2004).

5.1 Geochemical Profiles

XRF scanning adds data about bulk sediment composition that is important for understanding biogenic production and its effects upon the U1338 sediment column. Percentage data alone has limited usefulness because of the effects of variable CaCO₃ dilution upon the percentages of other sediment fractions. Component ratios or MAR data are more useful to understand how biogenic sedimentation changes. While XRF scans continue to the base of the sediment section (Supplemental Table 1, see also Wilson, 2014), only the data younger than 16 Ma are shown. Sediments in the 17.9-16 Ma age range reside in the basal 25 m of sediment

above basalt. Other sites from Exp 320/321, in particular Site U1337 (Shackford et al., 2014; Wilson, 2014; Holbourn et al., 2015), have better lower Miocene records than Site U1338 and are being used to explore that period.

5.1.1 Description of biogenic components

Figure 5 contains profiles of percentage data for different biogenic sediment components in U1338 from 16 Ma to the present, along with representative benthic oxygen isotope data mostly from the Pacific (top profile, Figure 5). CaCO_3 (2nd from the top, Figure 5) forms the bulk of the sediment except for occasional major CaCO_3 lows, with several prominent ones at ~14 Ma, between 11 and 9 Ma, between 8 and 6 Ma, and between 4 and 3 Ma. These CaCO_3 lows are responsible for the regional seismic reflection horizons found in the equatorial Pacific region (Mayer et al., 1986; Bloomer and Mayer, 1997; Tominaga et al., 2011)

Opal % mirrors CaCO_3 % (Figure 5; negative linear correlation to CaCO_3 with $r^2=0.89$). Opal and CaCO_3 are the only two major sediment components; therefore in percentage data, if CaCO_3 percentage decreases opal % must increase and vice versa. MAR data is ideal to distinguish between a loss of CaCO_3 versus addition of opal as a factor to change the sediment percentages, but the age model used in this paper is not of sufficiently high resolution to distinguish intervals shorter than ~500 kyr prior to 5.2 Ma. MAR will be discussed later in the paper. Minor elements and ratios to minor elements can help to distinguish CaCO_3 dissolution intervals from production ones at a high resolution since the XRF data have a resolution <2 kyr and can easily resolve orbital variability.

Minor sediment components, as illustrated by BaSO_4 and clay calculated by multiplying the measured $\text{TiO}_2\%$ by the TiO_2 in average upper continental crust ('clay' = $199.8 \times \text{TiO}_2$;

Taylor and McClennan, 1995), are mostly an inverse signal to the CaCO_3 . Important deviations from the inverse correlation reflect changes in deposition and are best explored via ratios (next section). Both BaSO_4 and clay increase when there is major CaCO_3 and opal dissolution, leaving behind the more refractory barite-rich dissolution residue and clays (Dymond, 1981). In Figure 5, there is an increase in both clay and BaSO_4 within the Carbonate Crash Regime and in the Pliocene-Modern Regime after 4.5 Ma. The Pliocene-Modern Regime is an interval of significantly lower sedimentation rate (Figure 5) and lower burial for both opal and CaCO_3 . CaCO_3 contents also are highly cyclic associated with the Pleistocene glacial cycles in sediments younger than 2 Ma. The lower sedimentation rate in the 4.5-0 Ma regime is partly because Site U1338 is traversing out of the equatorial upwelling zone by this time, passing 1.5°N at ~ 4.5 Ma. More importantly, there is a region-wide decrease in CaCO_3 and opal burial since 4.5 Ma (Farrell et al., 1995; Hagelberg et al., 1995).

There is little evidence for an increase in clay deposition in the 4.5-0 Ma regime. Site U1338 always remains south of the intertropical convergence zone (ITCZ) and mainly receives dust from a South America source similar to Site 851 at the same latitude but 500 km to the east (Xie and Marcantonio, 2012). TiO_2 MAR decreases by about 30% since 16 Ma (Supplemental 2); the increase in clay percentage within the 4.5-0 Ma regime is caused by slowdown in sedimentation rates and higher dissolution of opal and CaCO_3 . The high cyclicity in the Pleistocene of clay primarily reflects cyclicity in dissolution with minor synchronous changes in CaCO_3 production.

5.2 Geochemical ratios of production and dissolution and biogenic deposition at Site U1338

In the absence of a robust high-resolution age model, the use of geochemical ratios is an excellent way to investigate changes in production and dissolution in pelagic sediments. These

ratios are important to identify regimes that tend toward different styles of biogenic production and/or higher CaCO_3 dissolution. In section 3.1 we developed the rationale behind the application of the biogenic production ratios opal/clay (or TiO_2), opal/ BaSO_4 , $\text{BaSO}_4/\text{TiO}_2$, and $\text{Al}_2\text{O}_3/\text{TiO}_2$, as well as the use of $\text{CaCO}_3/\text{BaSO}_4$ to examine a combination of production and dissolution, and $\text{CaCO}_3/\text{Clay}$ to examine CaCO_3 dissolution. All ratios that depend on clay or TiO_2 assume that the aeolian clay deposition is relatively constant or that it varies much less than that of the biogenic component, while the opal/ BaSO_4 ratio makes use of the faster increase of opal rain relative to the fixing of BaSO_4 , related to the C_{org} rain, as shown by the change in opal/ BaSO_4 with latitude in the 1992 JGOFS sediment trap experiment (Honjo et al., 1995; Dymond and Collier, 1996), from 55 at 9°N to 116 at the equator.

The $\text{U1338 CaCO}_3\%$ profile is at the top of Figure 6 while underneath are the 4 proxies for paleoproductivity. While there are differences in detail among the different proxies, they all basically agree on intervals where high productivity occurs, or at least high biogenic deposition. Most of the production intervals last less than 100 kyr in duration and probably have a component of the signal modulated by orbital variations. However, the spacing between high production intervals is often large and is apparently irregular. If orbital forcing contributes to the amplitude of production there must be a relatively high threshold before a high production interval is initiated. Only a few optimal orbital configurations apparently result in high production.

Much of the record older than 4.5 Ma have higher proxy ratios than the 4.5-0 Ma interval. The average opal/clay is 6.7 in the older sediments compared with an average opal/clay of 1.7 in the younger interval. Even comparing the low baselines, the average low production is about 2-3 times higher prior to 4.5 Ma than after this time.

Only three intervals had sustained high production longer than 100 kyr: 7.1-6.4 Ma during the Biogenic Bloom (700 kyr) and two intervals during the early Carbonate Crash, 10.5-10.2 Ma (300 kyr), and 10.9-10.7 Ma (200 kyr). Superimposed on these long high-productivity intervals is a set of shorter but sometimes similarly intense intervals. The relative amplitude and duration of the productivity intervals helps to refine the regimes presented earlier.

XRF bulk chemical data can be used to study CaCO_3 dissolution and possibly CaCO_3 production as well. Figure 7 has profiles of CaCO_3 and two indicators of relative rate of CaCO_3 burial, $\text{CaCO}_3/\text{BaSO}_4$ and $\text{CaCO}_3/\text{clay}$. Figure 7 also delineates intervals of apparent strong dissolution ($\text{CaCO}_3/\text{clay} < 10$) in tan and intervals of high opal production in lavender, from high opal/clay in Figure 6. The Pliocene-Modern Regime is most consistently marked by dissolution, followed by the Carbonate Crash Regime, particularly between 11 and 7.8 Ma. Like opal production, maximum CaCO_3 dissolution rarely lasted longer than a 100 kyr eccentricity cycle, suggesting that orbital variability intermittently accentuated CaCO_3 dissolution. Only in the Pleistocene are the CaCO_3 cycles and orbital variations consistently varying together (Farrell and Prell, 1989). Three significant CaCO_3 dissolution intervals mark the record, at 9.8- 9.7 Ma, 4.1-3.9 Ma, and 3.2- 3 Ma. They are imbedded in larger-scale periods with frequent dissolution intervals from 11 to 7.8 Ma and from 4.5 Ma to the present. The combination suggests that there are long periods within the deep Pacific where higher average levels of DIC relative to alkalinity occurred, presumably by added deep Pacific carbon storage, that bias the Pacific toward higher CaCO_3 dissolution. Relatively short CaCO_3 dissolution intervals appear because of orbitally driven variability in abyssal carbon chemistry, as has been demonstrated repeatedly in the Pleistocene (e.g., Arrhenius, 1952; Farrell and Prell, 1989). In contrast, there are also long intervals where dissolution is uncommon, e.g. 7.6-4.6 Ma in the Biogenic Bloom Regime.

Within the Carbonate Crash Regime high opal production intervals are interbedded within high CaCO_3 dissolution which combined led to lower CaCO_3 % in the U1338 profile between 10.5 and 10.2 Ma.

Besides periods of high CaCO_3 dissolution, there are also high periods of high CaCO_3 deposition and preservation. These periods overlap but do not completely coincide with levels of high opal burial. Prior to 13.2 Ma, there are short intervals of high opal production (opal/clay) that also have high CaCO_3 /clay and a more muted response in CaCO_3 / BaSO_4 . This is a response expected from moderate increases in surface production, in which both opal and CaCO_3 deposition increase. The 2 largest events, peaking at 14.1 and 14.0 Ma in this paper's linear age model (versus 14.0 and 13.9 with the orbitally tuned age model in Holbourn, 2014), are lows in CaCO_3 % and CaCO_3 / BaSO_4 , but are highs in CaCO_3 /clay. The best explanation for these ratios is higher relative production of opal than CaCO_3 with some CaCO_3 dissolution, but also with higher CaCO_3 production and deposition relative to surrounding intervals.

The situation is more complex for the sequence younger than 13.2 Ma. There are two relatively long highs in both CaCO_3 / BaSO_4 and CaCO_3 /clay at about 12.5 and 11.3 Ma, and further ones at 7.2 and 6.4 Ma. All these coincide with high CaCO_3 contents in the U1338 CaCO_3 % profile. However, they are offset from the high opal/clay peaks (Figure 6). For example, in the time window between 7.2 and 6.4 Ma (peak Biogenic Bloom), the highest diatom production as indicated by opal/clay is at 7.0 Ma, accompanied by a small peak in CaCO_3 /clay as well. Two large peaks found in both CaCO_3 /clay and CaCO_3 / BaSO_4 occur at either edge of the high opal/clay interval. The highs in the CaCO_3 ratios are caused either by a significant change in production of CaCO_3 relative to opal or by a large relative change in CaCO_3 preservation at the sea floor. Low CaCO_3 dissolution is probably the principal cause of the peaks,

since production of CaCO_3 and opal are well-correlated in the modern tropical oceans even at production levels well beyond those typical in the equatorial Pacific (Figure 2). With data from U1338 and other sites it should be possible to quantitatively make an estimate of CaCO_3 dissolution, making use of the zonal pattern of equatorial productivity and the depth dependence of CaCO_3 dissolution. This exercise awaits additional analyses on a geographic spread of Neogene records.

5.3 microfossil Profiles

Total biosiliceous microfossil numbers range from 0 to 2.8×10^9 specimens per gram sediment (s/gs) at Site U1338 (Figures 8 and 9). Diatoms dominate the biogenic composition averaging 77.5% of the overall biosiliceous component and attain values as high as 96.3 % of the total specimens per g (264.09 cmcd; 11.7 Ma). Silicoflagellates and radiolarians comprise a much smaller fraction of the siliceous microfossil composition. Silicoflagellates average 8.6% and attain values as high as 31.9% (175.38 cmcd; 8.54 Ma). Radiolarians average 9.4% and attain values as high as 36.2% (48.95 m cmcd; 3.9 Ma). Average diatom percentage is lowest in the intervals that have high CaCO_3 dissolution, <5.0 Ma and 10.7-8 Ma, indicating a link between CaCO_3 dissolution and diatom preservation.

The total siliceous microfossil abundance averages 5.5×10^8 s/gs throughout the 16-0 Ma interval and is typically lowest in samples from the >13.2 Ma interval (avg. 2.1×10^8 s/gs). Numerous samples older than 13.2 Ma either have no biosiliceous microfossils or have limited numbers. Average biosiliceous microfossil numbers in the stratigraphic sequence increase in two steps, 13.2-8.0 Ma (avg. 5.5×10^8 s/gs) and 8.0-4.5 Ma (avg. 8.7×10^8 s/gs), with the highest average values occurring in the 8.0-4.5 Ma Biogenic Bloom regime. Siliceous microfossil numbers decline in the Pliocene-Modern regime (<4.5 Ma, avg. 3.8×10^8 s/gs).

The abundance of diatom frustules varies significantly from 0 to 2.25×10^9 valves per gram sediment (v/gs) throughout the sediment column. Overall, diatoms average 4.5×10^8 v/gs. The Middle Miocene Regime (>13.2 Ma) contains the lowest overall average diatom concentration (1.8×10^8 v/gs). Diatoms were not always found in samples within this regime due to poor preservation and diatoms average 83.1% of the total biosiliceous microfossils. Diatom abundance increases first at 13.2 Ma and again at 8.0 Ma with the greatest diatom abundance (avg. 7.2×10^8 v/gs) occurring in the 8.0-4.5 Ma Biogenic Bloom regime. Diatom abundance declines (avg. 2.9×10^8 v/gs.) in the <4.5 Ma regime.

The abundance of silicoflagellates also varies throughout the stratigraphic record, averaging 5.4×10^7 s/gs but ranging from 0 to a maximum of 3.9×10^8 s/gs (Figure 8)..There is a distinct maximum between 8.5-6.0 Ma. Silicoflagellates are typically present only in low abundance in sediments older and younger than 8.5-6.0 Ma. Note that the high variability observed with the diatom abundance is also observed in the silicoflagellate abundance.

Radiolarians average 4.5×10^7 s/gs (Figure 8). The abundance distribution can be subdivided into two intervals, a lower unit >10.6 Ma (225.62 cmcd; 10.6 Ma) with fewer radiolarians and an upper unit <10.6 Ma with more. Radiolarians average 2.8×10^7 s/gs and attain a maximum abundance of 8.6×10^7 s/gs in the lower unit. In sediments younger than 10.6 Ma Radiolarians are on average twice as abundant (5.6×10^7 s/gs) and attain a maximum abundance of 1.8×10^8 s/gs (48.95 cmcd; 3.9 Ma) associated with a prominent CaCO_3 dissolution interval (Figure 7).

5.4 Diatom flora characteristic

113 diatom species, forms and varieties were recorded from the 446 m Miocene to Holocene stratigraphic sequence recovered from Site U1338 (Baldauf, 2013). The assemblage is composed of typical equatorial Pacific species of that were previously described by Barron (1985a, 1985b), Baldauf (1985), and Schrader et al., (1993), among others. Forty-two species and varieties comprise the majority of the assemblage, while the remaining 71 species are a minor component. The overall diatom assemblage is dominated by *T. longissima*, *T. nitzschioides*, and *T. nitzschioides* var. *parva* whose abundances are listed in Supplemental Table 3. These three forms occur throughout the sequence. Although there is significant variability, the three forms total an average 2.0×10^8 v/gs and average about 38% of the entire diatom assemblage. Note that other species such as *Denticulopsis simonsenii* and *Crucidenticula nicobarica* also contribute significantly to the overall diatom assemblage in the older sequence (see Supplemental Table 3; Baldauf, 2013), but are not discussed here given that both species are extinct and have limited modern analogs in the equatorial Pacific.

Thalassionema longissima averages 7.0×10^7 v/gs and 14.1% of the diatom assemblage through the entire sequence and attains values as high as 62.4% of the assemblage (122.49 cmcd, 6.8 Ma). The overall *T. longissima* abundance is subdivided into three units. The lowermost unit (> 12.3 Ma or >284.30 cmcd) typically has low but variable occurrences of *T. longissima*. Abundance within this interval averages 3.6×10^8 v/gs and *T. longissima* averages 13.4% of the assemblage. The intermediate unit (12.3-4.5 Ma ;284.30-56.11 cmcd) reflects the greatest abundance of *T. longissima* with average values of 1.0×10^8 v/gs and with a peak abundance of 8.0×10^8 v/gs (127.55 cmcd). *T. longissima* averages 57.8% of the assemblage in this unit. The upper unit (<4.5 Ma; <56.11 cmcd) has a decline in the abundance of *T. longissima*, averaging

670 2.2×10^7 v/gs and 7.0% of the assemblage. However, values as high as 1.7×10^8 representing
671 27.5 % of the diatom assemblage were occasionally observed.

672 *Thalassionema nitzschioides* averages 7.3×10^7 v/gs and averages 13.6% of the overall diatom
673 assemblage throughout the sequence. Similar to *T. longissima*, the overall abundance of *T.*
674 *nitzschioides* is also separated into three units. >9.3 Ma (191.64 cmcd), 9.3-5.1 Ma (191.64 -
675 69.45 cmcd), and <5.1 Ma (<69.45 cmcd). The 9.3 Ma break is poorly constrained because of the
676 lack of samples in the surrounding intervals. In the >9.3 Ma unit, *T. nitzschioides* has an average
677 abundance of 2.1×10^7 v/gs or 5.4% of the diatom assemblage. Distinct spikes in abundance
678 occur within the uppermost portion of this unit, up to 2.2×10^8 v/gs. The intermediate unit (9.3-
679 5.1 Ma) has significantly higher *T. nitzschioides* abundance with an average of 1.7×10^8 v/gs.,
680 more than double the lower unit numbers. *T. nitzschioides* also averages 27.3% of the diatom
681 component, but is variable with a peak abundance of 8.0×10^8 v/gs at 6.1 Ma (96.36 cmcd,
682 45.7% of the diatom flora) . The upper unit (<5.1 Ma) has lower abundance than the middle
683 interval, averaging 2.9×10^7 v/gs and 8.8 % of the overall diatom component.

684 *Thalassionema nitzschioides* var. *parva* averages 5.3×10^7 v/gs and 11.3% of the overall
685 diatom abundance. The abundance of *T. nitzschioides* var. *parva* is bimodal having two peak
686 abundances centered at about 11.1 Ma (244.56 cmcd) and at 5.8 Ma (88.94 cmcd). This bimodal
687 distribution allows the overall abundance to be subdivided into the following units (>12.0 Ma
688 (272.49 cmcd), 12.0-10.7 Ma (272.49-232.13 cmcd), 10.7-6.8 Ma (232.13-122.49 cmcd), 6.8-5.0
689 Ma (122.49-68.41 cmcd), and <5.0 Ma (<68.41 cmcd). The lowermost unit (>12.0 Ma) has the
690 lowest average abundance of *T. nitzschioides* var. *parva*, with 1.2×10^7 v/gs and 3.5% of the
691 overall diatom assemblage. The 12.0-10.7 Ma unit has ten times higher abundance, averaging 1.3

692 $\times 10^8$ v/gs and 27.1 % of the diatom flora with a peak occurrence of 5.2×10^8 v/gs at 241.81
693 cmcd.

694 The abundance of *T. nitzschioides* var. *parva* decreases in the 10.7-6.8 Ma interval,
695 averaging 3.7×10^7 v/gs. However, distinct peaks as high as 4.7×10^8 v/gs (131.44 cmcd, 7.1 Ma)
696 are observed in this unit. A secondary peak abundance marks the unit from 6.8-5.0 Ma where *T.*
697 *nitzschioides* var. *parva* averages 1.4×10^8 v/gs and 20.5% of the diatom component but attains
698 values as high as 4.3×10^8 v/gs (71.45 cmcd, 5.2 Ma) or 59.8% of the diatom assemblage. The
699 youngest unit (<5.0 Ma) has significantly lower values of *T. nitzschioides* var. *parva*, 3.2×10^7
700 v/gs and 10.7% of the diatom component.

701 The species-specific ratios (specific diatom abundance/total other diatoms) for *T.*
702 *longissima*, *T. nitzschioides*, *T. nitzschioides* var. *parva*, and *A. nodulifera* are shown in
703 Figure 9. Each species has its own distribution pattern through the sequence. Ratios are shown
704 because they eliminate an artifact of percentage data where changes become smaller when
705 diatom reaches high abundances. Ratios instead show the numbers relative to the numbers of all
706 the other species and give a better sense of the magnitude that one species dominates.

707 *T. longissima* ratios are variable throughout the stratigraphic sequence and typically range
708 between 0 and 0.6. However, distinct peaks (>1.5) are found throughout its range correlating in
709 time with diatom mat intervals in the eastern equatorial Pacific (see below). *T. longissima* ratios
710 decline distinctly in the < 4.5 Ma regime.

711 In contrast, *T. nitzschioides* ratios typically are less than 0.5, but values increase
712 significantly in the ~9-6 Ma interval attaining values >1.5 where overall diatom numbers are low
713 to moderate (Figure 9). *T. nitzschioides* var. *parva* values are typically <0.5, but the diatom is in

abundance during two distinct intervals (12-10.5 and 6-5.5 Ma), with peak values >1.0, i.e., where *T. nitzschioides* var. *parva* is more than half the total diatom assemblage. A single peak occurrence of *T. nitzschioides* var. *parva* also occurs in the 1-0.5 Ma interval. *A. nodulifera* values are typically < 0.5 and increases from very low values to higher ones typical of the upper sequence around 8 and 6 Ma. Significant peak values approaching 1.0 occur in the upper sequence.

The variation in abundance and dominance of *T. longissima*, *T. nitzschioides*, *T. nitzschioides* var. *parva*, and *A. nodulifera* throughout the U1338 sedimentary sequence reflects changing oceanographic and sedimentary conditions. Preservation is problematic in the >13.2 Ma regime with occasional samples that are barren of diatoms. However, the <13.2 Ma sequence contains a typical diatom assemblage that includes finely silicified forms and suggests that the assemblage is reflecting response to oceanographic conditions rather than post depositional changes.

T. longissima typically dominates the diatom assemblage and is characterized by high amplitude peaks of short duration (Figure 9). The occurrence of *T. longissima* at Site U1338 is interpreted to reflect a broad scale response of the equatorial Pacific region. For example the decline in the magnitude of the peaks in *T. longissima* in the 4.5 Ma to the present may reflect a shift of nutrient availability to the easternmost equatorial Pacific and the southern ocean (Farrell et al., 1995) . The significant peak of *T. longissima* at ~7.0 Ma corresponds to a times when *T. longissima* comprise significant mat deposits within the sedimentary record elsewhere in the eastern equatorial Pacific (see Kemp et al., 1995; Kemp and Baldauf, 1993) including IODP Site U1337 (Expedition 320/321 Scientists, 2010c).

T. longissima has been recognized as an indicator of high surface water productivity (Sancetta 1983; Kemp et al., 1995). Within the eastern equatorial Pacific the *T. longissima* mat deposits are interpreted to reflect increased concentration associated with a sharp frontal boundary between the cooler South Equatorial Current and warmer waters of the North Equatorial Current (Kemp et al., 1995; Kemp et al., 2006). A modern-analog would be the *Rhizosolenia* mats observed during the EqPac JGOFS program (Yoder et al., 1994; Kemp et al., 1995). Berger et al. (2002) postulated that the *Thalassiothrix antarctica* mat deposits found in upper Pliocene sediments recovered during ODP Leg 175 along the Benguela current corresponded to a frontal boundary between cooler upwelling waters and the warmer South Atlantic surface waters. The absence of mat deposits in the U1338 sedimentary sequence suggest that the frontal system in the U1338 site vicinity was not as well developed over this site.

T. nitzschioides increases in abundance and dominance in the 8-4.5 Ma regime representing an increase in surface water nutrients and productivity. *T. nitzschioides* is typically associated with coastal and open ocean upwelling (Romero and Armand, 2010). Based on analysis of surface sediments from the eastern equatorial Pacific Schrader et al. (1993), Schuette and Schrader (1979), and Cooke-Poerl et al. (1975) associated *T. nitzschioides* with the Peru Current. Romero et al. (2009) indicated that *T. nitzschioides* represented 22 to 29% of the flux assemblage from the mid November samples from the Cariaco Basin in the Caribbean. They equated this abundance with the E-NE trade winds upwelling season.

Within the sedimentary record Burckle et al. (1982) suggested that an increase the abundance of *T. nitzschioides* at Deep Sea Drilling Project (DSDP) Site 158 reflect an increase influence of the cooler Peru Current in the equatorial region. Barron (1985b) likewise linked an increase of *T. nitzschioides* with subtropical and equatorial upwelling at DSDP Site 77 resulting

from cooling. Barron (1985b) associated increases in abundance with isotope peaks and interpreted these abundance peaks to reflect increase cooling in the equatorial Pacific and the Peru Current. Baldauf (1985) suggested that increased abundance at DSDP Site 503 was associated with upwelling of the equatorial undercurrent.

The two peak occurrences of *T. nitzschioides* var. *parva* dominate the assemblage between 12-10.5 Ma and 6-5 Ma (Figure 9). *T. nitzschioides* var. *parva* is associated by Schrader et al. (1993) with subtropical surface waters having variable temperatures and high ($>36^{0/00}$) salinity. They included this variety as a key component of their southern subtropical assemblage representing 23% of the overall diatom assemblage. Schrader et al. (1993) indicated that *T. nitzschioides* var. *parva* peak abundance ($>30\%$) occurs in surface sediments west of 100°W and south of the equator. Others such as Schrader and Sorknes (1990), Romero et al. (2011), and Romero et al. (1999) all identify this form as indicative of warmer pelagic waters suggesting less influence of the cold tongue, and or weaker upwelling and possible greater influence of the equatorial Pacific warm pool at times of its peak occurrences at Site U1338.

The increase of *A. nodulifera* at 8.0 Ma corresponds to the start of the Biogenic Bloom regime. *A. nodulifera* is associated with the northern subtropical assemblage of Schrader et al. (1993) characterized by tropical surface waters and accounts for typically 35% of the diatom assemblage north of 5° . Schrader and Sorknes (1990) included this species as a member of their warm-water group. Cooke-Poerl et al. (1975) associated this species with equatorial upwelling. However, Sancetta (1995) identified *A. nodulifera* as the dominate species of her factor 4 scores of sediment traps samples from the Gulf of California reflecting the influence of tropical Pacific waters in the Gulf of California during ENSO-like conditions

5.4 Microfossil and Geochemical Accumulation Rates

Geochemical MAR and diatom species AR provide data for different types of environmental factors that led to high production in the equatorial Pacific. As might be expected, the relationships between the geochemical expression of production and the species expression of high productivity evolved through the Miocene.

5.4.1 Diatom AR and opal MAR

Figure 10 compares Opal MAR with accumulation rates for the total diatom abundance, *T. longissima*, *T. nitzschioides*, *T. nitzschioides* var. *parva*, and *A. nodulifera* for 16-0 Ma (Supplemental Tables 2 and 4). Below about 13.4 Ma there is lower biosiliceous preservation that limits detailed interpretation of the lowermost U1338 sequence. Both the Opal MAR and the diatom AR exhibit similar trends with highs associated with the 13.2- 10 Ma and 8.0- 4.5 Ma intervals and lows associated with the 10.0-8.0 Ma and 4.5-0 Ma intervals. Most noticeable is the low in both Opal MAR and diatom AR in the 4.5-0 Ma regime compared to that for the older sediments. The accumulation rates for individual species also vary. The 13.2-10.0 Ma high in diatom AR reflects high *T. longissima* AR and *T. nitzschioides* var. *parva* AR and the 8.0-4.5 Ma high reflects high AR's for *T. nitzschioides*, *T. longissima*, *A. nodulifera*, and *T. nitzschioides* var. *parva*.

Obviously the individual diatom species had different times in which they were a significant part of diatom deposition. *T. nitzschioides* and *A. nodulifera* both are in high abundance in the biogenic bloom interval between 8.0 and 6.0 Ma, where peak total diatom ARs occur and *T. longissima* and *T. nitzschioides* var. *parva* are most abundant in the earlier diatom interval (and highest opal MAR interval) between 11.0 and 9.8 Ma (Supplemental Tables 3 and 4). The variation in the diatom assemblage reflected by the opal MAR and species AR indicates

that the variation in the MAR reflects a complex environmental depositional history, and not just the same response repeated many times. Variations in the species specific AR suggest that each species/variety is responding to changing ecological/depositional conditions.

T. longissima, has a much more spiky record than other species, indicating geologically brief intervals in which conditions are optimal for its growth. The peak Biogenic Bloom at 7.0 Ma is the strongest of these high *T. longissima* intervals (Figure 9) and corresponds to the *T. longissima* mat-forming interval found at 110°W by Kemp and Baldauf (1993) and tracked by PEAT drilling further west (Pälike et al., 2010b). *T. nitzschioides* has a significant AR high in the 8-4.5 Ma Biogenic Bloom Regime relative to the other regimes. Above and below this regime *T. nitzschioides* is a consistent, but limited contributor to the sediment composition. *T. nitzschioides* var. *parva* has two AR highs that tend to flank the highest opal MAR deposition intervals. The oldest AR high occurs between 12.0 and 10.5 Ma and the youngest AR high occurs after the peak biogenic bloom deposition, peaking between 6.0 and 5.0 Ma. *A. nodulifera* has a single AR high from 8.0 to 5.5 Ma corresponding to the early portion of the biogenic bloom regime.

5.4.2 *CaCO₃ MAR and carbonate dissolution*

CaCO_3 MAR and the ratios $\text{CaCO}_3/\text{BaSO}_4$ and $\text{CaCO}_3/\text{clay}$ change both by production and dissolution. Low ratios are an indication of dissolution, especially of $\text{CaCO}_3/\text{BaSO}_4$. Both CaCO_3 MAR and the ratios are high prior to 11 Ma and between 8-4.5 Ma, and would appear to represent changes in dissolution through time (Figure 11). While low CaCO_3 MAR and the ratios $\text{CaCO}_3/\text{BaSO}_4$ and $\text{CaCO}_3/\text{clay}$ clearly must be caused by dissolution, it is unclear whether highs result more from better preservation or higher production of CaCO_3 .

Change in production of CaCO_3 and BaSO_4 are not linear and the ratio of CaCO_3 to BaSO_4 increases at higher C_{org} production levels (Dymond and Collier, 1996; Figure 3c). If the production ratio were constant, then changes in $\text{CaCO}_3/\text{BaSO}_4$ could be treated purely as a dissolution indicator. However, the $\text{CaCO}_3/\text{BaSO}_4$ ratio in particulate rain increases as C_{org} rain increases, pointing to a change caused by changing production. The median $\text{CaCO}_3/\text{BaSO}_4$ ratio in the JGOFS equatorial Pacific trap experiment increases from 143 at a C_{org} rain of 60 $\text{mg}/\text{cm}^2/\text{kyr}$ at the 9°N deployment to a $\text{CaCO}_3/\text{BaSO}_4$ ratio of 431 at a median C_{org} rain of 156 $\text{mg}/\text{cm}^2/\text{kyr}$ at the equator (Figure 3c). Nearly tripling the C_{org} rain results in nearly a tripling in the $\text{CaCO}_3/\text{BaSO}_4$ ratio, and is shown by the curvature expressed in the fluxes in Figure 3. Ba rain increases most rapidly at the lower end of the C_{org} or CaCO_3 rain spectrum (Figure 3a and 3b), and increases more slowly relative to C_{org} at higher production levels. The curvature may be driven by the rapid rise in new production (the fraction of C_{org} flux which escapes recycling in the euphotic zone, Eppley and Peterson, 1979) as primary productivity rises. Bio-Ba should therefore rise rapidly as the efficiency of recycling decreases, and level off as the percent of new production to total productivity stabilizes at higher productivity values. Both CaCO_3 and opal rain remain more linear with respect to C_{org} rain so that $\text{CaCO}_3/\text{BaSO}_4$ and opal/ BaSO_4 start low and increase at higher production levels.

For the CaCO_3 records we observe significant changes in MAR as well as changes in the $\text{CaCO}_3/\text{BaSO}_4$ and $\text{CaCO}_3/\text{clay}$ ratios that help to define the biogenic sediment regimes. However, these changes don't completely align with the paleoproductivity proxies shown in Figure 6. For example, higher burial of CaCO_3 occurs at the edges of the peak Biogenic Bloom interval defined by high opal/clay between 7.0 and 6.4 Ma. Highest $\text{CaCO}_3/\text{clay}$ or $\text{CaCO}_3/\text{BaSO}_4$ occurs at 7.2 Ma and at 6.2 Ma, immediately before and after the most opal-rich

interval. The higher CaCO_3 burial at the edges could represent elevated CaCO_3 dissolution at peak opal deposition from water mass changes or elevated C_{org} degradation at the sea floor, or it could result from a change in the linkage between CaCO_3 and opal production in the surface ocean. More records are needed to sort dissolution from production signals.

5.5 Age divisions for biogenic deposition regimes

Geochemical and diatom assemblage trends can be used to define time frames for different biogenic deposition regimes building upon earlier work. The regimes each have different levels of CaCO_3 dissolution and have different frequency and strength of high opal production intervals. They also have different responses by the diatom community. While the high opal production intervals often appear short when viewed on a 16-Myr graph like Figure 7, most lasted for tens of thousands of years. They apparently represent average upwelling conditions that have lasted for long periods of time, not events as we typically think of them for the Pleistocene.

5.5.1 Middle Miocene (>13.2 Ma)

The Middle Miocene Regime has consistent CaCO_3 burial with few swings in either $\text{CaCO}_3/\text{BaSO}_4$ or $\text{CaCO}_3/\text{clay}$. Opal production intervals are typically small, relatively short, and infrequent. The opal intervals are associated with higher relative CaCO_3 burial as indicated by $\text{CaCO}_3/\text{clay}$. The two largest events are associated with the middle Miocene Climate Transition (MMCT) and were previously reported by Holbourn et al. (2014). Diatom abundance is significantly lower during this regime than later. This is the interval of the silica switch, when opal deposition dropped in the North Atlantic and increased in the Pacific (Keller and Barron, 1983; Cortese et al., 2004). However, at Site U1338, the low diatom abundances may have been driven in part by near-basement silica dissolution (Moore, 2008).

5.5.2 Carbonate Crash (13.2 to 8.0 Ma: early [13.2-10.2Ma],late[10.2 -8.0 Ma])

The beginning of the Carbonate Crash Regime was chosen based on a significant increase in the number of diatom frustules found in the sediment after 13.2 Ma. The end is marked increased opal/clay beginning at 8.0 Ma. CaCO_3 is better preserved than at the peak crash, but there is one significant dissolution interval between 8.0 and 7.8 Ma. The carbonate crash regime is divided into two substages. The early carbonate crash substage (13.2-10.2 Ma) has few moderate opal/clay intervals that increase in magnitude and duration to finish with 3 major production events, 10.9-10.7 Ma, 10.5-10.4 Ma, and 10.35-10.15 Ma. The early Carbonate Crash substage also has high abundance of *T. nitzschioides* var *parva*. High CaCO_3 /clay and high opal/clay coincide throughout in production events in both Carbonate Crash substages, indicating higher CaCO_3 production as well as diatom productivity both occurred in the production intervals in a background of high CaCO_3 dissolution. CaCO_3 dissolution intervals are interspersed between the production intervals, beginning about 11 Ma.

In the late Carbonate Crash substage (10.2-8.0 Ma), the CaCO_3 dissolution intervals persist and get stronger, while the production intervals weaken and get shorter. Because we did not have diatom samples from the late Carbonate Crash substage, the diatom response is poorly defined between 10.5 and 9.3 Ma. The period between 9.3 and 8.0 Ma has a high *T. nitzschioides* ratio and moderate *T. nitzschioides* AR.

5.5.3 Biogenic Bloom (8.0 to 4.5 Ma)

The Biogenic Bloom Regime has higher average production indices than the Pliocene-Modern, and is also punctuated by important long-lasting production intervals. CaCO_3 burial is high, and the dissolution indicators $\text{CaCO}_3/\text{BaSO}_4$ and $\text{CaCO}_3/\text{clay}$ stay high, indicating low dissolution throughout the interval, varying with a long-period beat. The Biogenic Bloom

894 Regime has the highest sedimentation rates and MAR of the U1338 record. CaCO₃ burial, as
895 indicated by CaCO₃/clay, has a broad high throughout the period, with highest levels of
896 CaCO₃/clay at 7.2 Ma, immediately before the opal/clay peak interval and 6.2 Ma, immediately
897 after it. Low CaCO₃ at 7 Ma results from high dilution of CaCO₃ by high opal deposition and
898 perhaps higher CaCO₃ dissolution.

899 Diatom production as indicated by opal/clay is also high throughout The Biogenic Bloom
900 Regime; periods of high production are extended in time, beginning with smaller events, then an
901 extended moderate interval between 7.6 and 7.2 Ma, and culminating in the high production
902 between 7.1 and 6.4 Ma. The regime ends with periodic moderate high-productivity intervals
903 every 200-300 kyr, and the final moderate production interval is found between 4.8 and 4.6 Ma.

904 All diatom species AR are high through the interval, but there is significant structure. *T.*
905 *longissima* responds most strongly to the peak bloom interval at 7 Ma (Figures 9 and 10) and has
906 a minor peak in the final production interval at 4.6-4.8 Ma. *T. nitzschioides* and *A. nodulifera*
907 have high AR during 5.75-7.75 Ma, and *T. nitzschioides* var. *parva* AR increases from the
908 beginning to the end of the biogenic bloom, peaking around 5.2 Ma.

909 **5.5.4 Pliocene-Modern (4.5 to 0 Ma)**

910 The Pliocene-Modern Regime includes the Holocene equatorial Pacific. At Site U1338
911 there are low levels of biogenic production relative to the earlier record, and relatively high
912 levels of CaCO₃ dissolution. From 2 Ma to the Holocene, CaCO₃ dissolution intervals are
913 associated with interglacials, resulting in the familiar Pleistocene carbonate cycles (Hays et al.,
914 1969; Farrell and Prell, 1989). There is probably higher biogenic production in the glacials, but
915 the glacial-interglacial change in production is not large (Lyle et al., 1988; Murray et al., 2000).

The low production signal found at Site U1338 is in part aided by the site's movement away from the equator during this time period, moving from 1.5 to 2.5°N, but similar decreases in biogenic deposition are found near the equator at 110°W (Sites 849, 850, and 851; Farrell et al., 1995; Schroeder et al, 1997) in the interval younger than 4.5 Ma . The Pliocene-Modern Regime begins with 2 major dissolution intervals at 4 Ma and 3.2 Ma. Because of the relatively high dissolution throughout the regime, sediments are enriched in clay and other dissolution resistant components, like barite.

6.0 Discussion: Neogene change in equatorial Pacific biogenic production

Nutrient availability in the equatorial Pacific in the Neogene has consistently been forced by easterly trade winds causing upwelling as indicated by high productivity near the equator since the Eocene (Moore et al., 2004) despite the lack of an E-W temperature gradient and Walker circulation feedback for much of the Neogene. Superimposed on the common pattern are enigmatic high-production transients common to the Miocene are difficult to explain without radical changes in subsurface nutrient delivery. Why these intervals appear and then gradually disappear is a challenge to paleoceanography. Overprinting the ocean-atmospheric influence is the oceanographic response to tectonic changes in ocean circulation: e.g., restriction of the CAS by the tectonic uplift of the Isthmus of Panama. Changes in nutrient delivery to the oceans by enhanced weathering of phosphorus from the continents (Filipelli and Delaney, 1994; Filipelli, 1997) may have also contributed to changes in primary productivity.

The Neogene exhibits a surprising variety of responses since 16 Ma. We will discuss two especially interesting intervals: (1) the middle/late Miocene before 10.2 Ma where high production transients lasted 50-200 kyr and opal burial was an order of magnitude higher than baseline production and (2) the peak production interval in the Biogenic Bloom regime where

sustained high production occurred in addition to periodic fluctuations of opal production and burial. In contrast, the diatom flora responded partly with respect to these high-production intervals and partly in response to changing surface conditions unrelated to nutrient delivery.

6.1 ENSO, El Padre, and high productivity in the warm Miocene equatorial Pacific

It is important to understand how biogenic production in the time frame after 4.5 Ma differs from earlier in the Neogene. Production and sea surface temperature (SST) were decoupled during the Miocene and early Pliocene in the eastern equatorial Pacific. The eastern Pacific had both higher biogenic production but also significantly higher SST than is found in the late Pleistocene (Zhang et al., 2014; Ravelo et al., 2014). At site U1338, for example, alkenone-estimated SST ranged between 26 and 28°C prior to 4 Ma, versus 24°C for the modern ocean (Rouselle et al., 2013). The eastern equatorial Pacific only cooled after ~2.5 Ma (Wara et al., 2005); previously there was only a weak E-W SST gradient across the Pacific and presumably weak Walker circulation (Etourneau et al., 2010). The warm east Pacific and small meridional SST gradient are reminiscent of an ENSO event, and has been described as a “permanent el Niño” (Wara et al., 2005, Federov et al., 2006). The lack of SST gradient has also been referred to as “el Padre” (Ravelo et al., 2014) to avoid confusing the lack of a Pliocene temperature gradient with the presence of modern ENSO dynamics, where trade winds are suppressed and upwelling is weak. Instead, there is good evidence that subsurface waters were warmer but also nutrient-rich so that upwelling had a much subdued temperature signal but also high production. For example, Dekens et al. (2007) found that high productivity was decoupled from cold temperature in upwelling systems worldwide prior to 3 Ma.

Our data show vigorous biogenic production in the equatorial Pacific during the warm Miocene and early Pliocene. With a true ENSO, there would be low productivity at the equator

associated with warm temperatures, and production with low opal/CaCO₃ (Dymond and Collier, 1988; Honjo et al., 1995). Gradual cooling of SST in the eastern Pacific began around 4 Ma, so following the hypothesis that the cooling may actually represent reduced numbers of ENSO events (Wunsch, 2009), production should have gradually increased after 4 Ma as the Walker Circulation was reinforced. Similarly, if the slow decrease in SST at Site U1338 (Rouselle et al., 2013) reflects higher upwelling of cold subsurface waters, there should be an increase of production toward the Pleistocene.

Instead significantly higher productivity is found before 4.5 Ma as compared to after then (higher diatom AR, higher opal MAR, higher CaCO₃ MAR, higher productivity ratios). In other words, warm temperatures do not equate with low productivity, except in the Holocene and perhaps the Pleistocene. Even in the Pleistocene there is an offset between coolest equatorial SST and highest organic carbon burial, showing some decoupling between upwelling and SST (Lyle et al., 1992).

Plate tectonic movement of Site U1338 may have contributed to the drop in biogenic production at 4.5 Ma. However, this same drop in biogenic sedimentation is found at sites at the equator at the same time (ODP Sites 851, 850, and 849; Farrell et al., 1995; Schroeder et al., 1997). The decrease in production after 4.5 Ma is true of the entire equatorial Pacific region between the longitude of Hawaii and the East Pacific Rise. Nearer the South American continent, however, opal production increased (Site 846, Farrell et al., 1995).

Regional deposition patterns based on all the equatorial Pacific drilling imply that trade winds were sufficiently strong under warm equatorial conditions to maintain a strong equatorial divergence.. Not only do records from individual drill sites show higher biogenic deposition in

the equatorial region, but also patterns of deposition centered at the equator have been maintained through the Neogene (Lyle, 2003; Moore et al., 2004). Strengthening of trade winds with developing Walker Circulation can be eliminated as a primary driver of Neogene changes in biogenic production.

6.2 Differences between Fluxes in the Pliocene-Modern Regime, the Biogenic Bloom, and the early Carbonate Crash substage

Both the strength and length of high production intervals changed dramatically since 16 Ma, as illustrated in Figure 12, showing CaCO_3 % and opal/clay for selected 1.5 Myr intervals in the U1338 record. A 1.5 Myr record is sufficiently short so that both longer period and shorter period milankovitch cyclicity can be observed and length of production intervals can be studied. The relationship CaCO_3 to diatom production, represented by opal/clay, can be better seen in these shorter time slices as well. We have overlain the eccentricity signal in light gray on each time slice so orbital pacing can be gauged. Obliquity has a periodicity roughly 2.5 times more frequent than the eccentricity cycle, and precession has 5 times the number of cycles.

The contrast between the Pleistocene (1.5-0 Ma, Figure 12, top panel) and the other production intervals is striking. The opal/clay variation for the 1.5-0 Ma interval (top) is an order of magnitude smaller than in the other two intervals (note the scale change for opal/clay on the top panel). The distinctive Pleistocene 100-kyr CaCO_3 cycles (Farrell and Prell, 1989) are easily observed in the 1.5-0 Ma CaCO_3 % record, but CaCO_3 content in the earlier records are more strongly influenced by opal dilution. The Pleistocene opal/clay cycles are small (factor of 2 change), periodic, and align with the 100-kyr high CaCO_3 glacials, as has previously been observed for opal MAR in the Pleistocene (Lyle et al., 1988; Murray et al., 2000).

6.3 Productivity tipping points prior to 10 Ma?

The early part of the U1338 record, as exemplified by the 11.5-10 Ma time slice (Figure 12, bottom panel), has infrequent abrupt high production intervals that last for 50-200 kyr. The high production intervals are apparently clusters of shorter high intensity production events during a period where conditions for high productivity were optimal. The high opal/clay intervals appear every 200-400 kyr, above a baseline opal/clay ratio that is similar to that of the Pleistocene. The strongest Miocene high-production intervals have 20 times the opal deposition as the surrounding low opal intervals. In the Pleistocene only factor of two changes occur between glacials and interglacials (Figure 12, top).

The production intervals in the early Carbonate Crash substage and Middle Miocene Regime are problematic to understand because of their odd periodicity, large and rapid beginnings, and long extent of high productivity relative to climate forcing. High production intervals begin rapidly, doubling in deposition in less than 10 kyr. They last for up to 200 kyr, and then abruptly end. The timing and structure suggests that thresholds are important to trigger the high production interval, causing a relatively rapid switch between low and high production.

Holbourn et al. (2014) have already suggested that there was a linkage between the brief high production intervals near 14 Ma to Antarctic cooling. Since diatom productivity is strongly associated with availability of dissolved Si (Dugdale et al., 2002), such a link to the Antarctic causing delivery of Si periodically to the equatorial Pacific could explain these intervals presumably resulting from cooling. If this is true, there is an unstable link between nutrients in the equatorial Pacific and a rich nutrient pool near the Antarctic.

Many but apparently not all of the high production intervals are associated with significantly higher deposition of *T. longissima*, a mat-forming pennate diatom associated with oceanic convergences. Surface water convergences then focus the deposition of biogenic hard parts into a relatively narrow depositional band, at the expense of deposition elsewhere. Instability waves in the modern equatorial Pacific produce subduction and focusing of particles near 2°N (Yoder et al., 1994; Smith et al., 1996; Walsh et al., 1997) that concentrate and increase fluxes to the bottom (Boden and Backman, 1996; Kemp et al., 2006). Such a process could conceivably magnify a change in production. If the convergence moves north and south with the seasons or with decadal/centennial climate change, the band of high deposition will be spread out in latitude.

It is likely that the main fronts were to the north of Site U1338, since U1338 was essentially at the equator during the 10-12 Ma time frame, and because much more intense diatom deposition occurred in this interval at Site U1337, 1.3° to the north (Expedition 320/321 Scientists, 2010c). However, high opal deposition was also found both north and south of the paleo-equator for the 10.2-10.35 Ma high-productivity interval (e.g., Sites 849, 1.5°S and 851, 1°N, Kemp and Baldauf, 1993), indicating that mat-forming diatoms were buried over a relatively broad region rather than at a strict frontal zone. We have little earlier information from Leg 138, since the base of sediments along the Leg 138 110°W transect is at about 11 Ma.

Because we can't identify a specific convergence zone, we view the *T. longissima* signal to indicate generally high biogenic production in the Miocene intervals, and recommend further study to understand the details of its deposition. More detailed analysis from transects of sites across the equatorial band (e.g., additional studies on U1335 and U1337, and perhaps studies of basal sediments from Leg 138) will help to quantify the convergence process in the future.

Separation of production from dissolution in the CaCO_3 record is still problematic but potentially useful to understand high production intervals. Using ratios like $\text{CaCO}_3/\text{clay}$, it is possible to observe relative changes in burial without needing detailed age models to reconstruct CaCO_3 MAR in detail. Even with ratios it is difficult to separate the contribution by dissolution from the contribution by increased production (Figure 11). Nevertheless, high $\text{CaCO}_3/\text{clay}$ is typically found in most of the high production intervals in both the Middle Miocene Regime and the early Carbonate Crash substage. If CaCO_3 dissolution was not important, the opal/clay (Figure 6) and $\text{CaCO}_3/\text{clay}$ (Figure 7) should be coherent in timing as well as amplitude. However, there are intervals, e.g., 12.45-12.7 Ma, with high $\text{CaCO}_3/\text{clay}$ but no opal/clay signal suggesting a period of low dissolution. The data from JGOFS on upper water column production in the tropics (section 3.1) finds a good relationship between CaCO_3 rain and opal rain. The offset between peaks in opal/clay and $\text{CaCO}_3/\text{clay}$ is then a good indication that CaCO_3 dissolution is variable and is driven by different processes.

6.4 Stable high production in the Biogenic Bloom Regime

In contrast to the older section, the peak Biogenic Bloom Regime (7.5-6 Ma, Figure 12 middle panel), has relatively weak high-production intervals in the beginning, but then maintains an opal/clay above 10 (5 times more than the 0-1.5 Ma average) for the 300-kyr interval between 7.0 and 6.7 Ma. This long high production interval also includes variations that are of the right periodicities to potentially be associated with changes in obliquity. Roughly 2.5 cycles occur in every 100 kyr eccentricity cycle shown in Figure 12.

The biogenic bloom has a sawtooth pattern, with very high biogenic production developing quickly just older than 7.0 Ma, followed by slowly declining oscillations, the last of which occurs between 4.6 and 4.8 Ma. Such a long pattern with slow decay suggests a tectonic

influence, in which gateway changes are influencing the flow of nutrients around the oceans and their re-emergence into the euphotic zone. For this reason, we have proposed a tectonic hypothesis for the Biogenic Bloom interval, to be discussed soon. Nevertheless, the large variability along with the abrupt changes in biogenic deposition invite further dynamic hypotheses.

Opal MAR over the 7.5-6.0 Ma interval is nearly 6 times higher than in the 1.5-0 Ma interval (Figure 10, Supplemental Table 2), CaCO_3 MAR is about 3 times higher (Figure 11), but BaSO_4 MAR is only 2 times higher. Sustained higher transport of nutrient and Si-rich water to the surface equatorial Pacific must have been in place to maintain the biogeochemical fluxes buried in the sediments. The difference in burial of BaSO_4 (a C_{org} rain proxy) and opal is an evidence that the biogeochemical carbon pump was less efficient and perhaps an indicator that organic matter was recycled rapidly and effectively in the upper water column versus opal (Figure 6, opal/ BaSO_4).

6.5 The Biogenic Bloom Regime and CAS closure?

The coincident timing of the Biogenic Bloom and the closure of the CAS implies that there may be a relationship between the two. The end of high biogenic deposition after 4.6 Ma clearly fits in timing with the effective closure of the CAS and separation of Caribbean and Pacific by (Haug and Tiedemann, 1998; Chaisson and Ravelo, 2000). The beginnings of the Biogenic Bloom match with a major late Miocene decrease in global benthic $\delta^{13}\text{C}$ (Billups et al, 2002; Hodell and Venz-Curtis, 2006; Poore et al., 2006; Nathan and Leckie, 2009).

Nathan and Leckie (2009) proposed that productivity in the western Pacific (Ontong Java Plateau) declined after 7.2 Ma as the Biogenic Bloom appeared in the eastern Pacific. They

1095 proposed that ocean conditions at that time switched from El Niño-like to La Niña-like at about
1096 that time, which would shallow the thermocline in the eastern Pacific as the thermocline deepens
1097 in the west. The ENSO analogy has problems, as we have already discussed, although the
1098 observation is important. As an alternative, as CAS closes a nutrient trap forms in the eastern
1099 Pacific and shifts the locus of opal deposition to the east of the East Pacific Rise (Farrell et al.,
1100 1995; Cortese, 2004) and diverts nutrients from other upwelling regions.

1101 Another idea worth exploring is that the process of closure enhanced vertical transport of
1102 nutrients into surface waters of the eastern Pacific. The modeling of Butzin et al. (2011)
1103 suggests that vertical transport of nutrients into the eastern equatorial Pacific is enhanced when
1104 critical CAS sill depths are passed, between ~1000 and 500 m depth. Relatively shallow CAS sill
1105 depths enhance westward flow of near-surface water into the Pacific but cause strong eastward
1106 flow for subthermocline waters through the CAS into the Atlantic. This circulation also enhances
1107 Pacific meridional overturning, bringing subsurface water (and presumably nutrients) up from
1108 depth into waters that could potentially be upwelled. We hypothesize that the extended high
1109 production associated with the Biogenic Bloom results from the enhanced transport of nutrients
1110 into the eastern equatorial Pacific by CAS closure both by transport of subthermocline waters
1111 through the region to the Atlantic and by net upwelling from deep sources.

1112 Other factors may also have contributed to the Biogenic Bloom. Subsurface waters were
1113 probably warmer in the late Miocene, since they cooled in conjunction with the final closure of
1114 the CAS (Ford et al., 2012), and it is likely that nutrients were more enriched in the warm more
1115 buoyant subsurface waters than in waters of similar density today (Dekens et al., 2007). Less
1116 wind stress is needed, therefore, to bring more nutrients to the euphotic zone. , Dissolved Si
1117 transport may have also been enhanced by the development of Antarctic sea ice, reducing

1118 nutrient utilization in Antarctic waters and lowering the $\delta^{13}\text{C}$ of global deep water during the 8-6
1119 Ma time interval (Butzin et al., 2011).

1120 **6.6 A Global Biogenic Bloom?**

1121 Others have suggested that the Biogenic Bloom is the Pacific manifestation of a global
1122 high productivity interval in the late Miocene (Filipelli, 1997; Dickens and Owen, 1999, Diester-
1123 Haass et al., 2004). Dickens and Owen (1999) suggest a change in ocean circulation that upwells
1124 more nutrients into the Indo-Pacific tropics while Dister-Haass et al. (2004) link high production
1125 in the Biogenic Bloom interval to lowered sea level along the South African margin, and thus to
1126 an Antarctic driver. Filipelli (1997) proposed that the initiation of the Asian monsoon might have
1127 caused synchronous late Miocene high primary production by increased weathering of P to the
1128 oceans. The level of synchronicity is still under debate, because there has yet to be a systematic
1129 global synthesis using the most recent age models. Nevertheless, there is abundant evidence that
1130 late Miocene production was significantly higher than modern in most oceans.

1131 Weathering of nutrients could potentially produce synchronous changes in production.
1132 Both Si and P residence times in the oceans are sufficiently short that changes in weathering
1133 could rapidly change ocean nutrient content (Si: 10 kyr, Treguer and De La Rocha, 2013;
1134 phosphorus: 30-50 kyr, Delaney, 1998). Tectonic forces that may result in increased weathering,
1135 however, like the uplift of the Himalayas combined with the initiation of the monsoon, are
1136 relatively slow in progression and are the primary limit on the rate that the system will change.
1137 Weathering changes should result in slow productivity change unless there are major nonlinear
1138 thresholds in the scale of Himalayan monsoon rainfall. In addition, weathering nutrient delivery
1139 would have to increase and then decrease by the early Pliocene.

6.7 Regional redistribution of nutrients in the Pacific during the Biogenic Bloom

While there is some evidence that the late Miocene and early Pliocene were globally periods of higher productivity, evidence around the Pacific suggests that there was strong regionality to the pattern of production. The western Pacific (Site 806) is interpreted to have somewhat lower productivity during the critical 7.0-6.4 Ma time frame (Nathan and Leckie, 2009), for example. In the North Pacific, in a record that begins at 6 Ma (Site 882, Haug et al., 1999), opal deposition continued to increase after 5.0 Ma up to the precipitous drop at 2.7 Ma associated with the initiation of northern hemisphere glaciation. While equatorial Pacific productivity dropped at 4.6 Ma, productivity increased in the subarctic Pacific. Opal deposition along the California margin is also apparently inverse to that from the equatorial Pacific (Sites 1010 and 1021, Barron et al., 2002), with high deposition in the period between 10.0 and 7.6 Ma, and lower deposition in the 7.6 to 6.5 Ma interval (peak Biogenic Bloom). Barron et al (2002) also find that opal burial along the California margin increased in onshore sections within the Monterey formation in the 10.0-7.6 Ma period, indicating that the changes were related to changes in the upwelling cell. Nevertheless, biogenic sedimentation along the California margin nearly disappeared in the period between 4.6 and 3.5 Ma, similar to the drop in production in the eastern equatorial Pacific. Barron et al. (2002) interpreted the Pliocene drop in opal accumulation along the California margin to result from a focusing of nutrients to the subarctic northwest Pacific. More work to understand the timing of productivity change is clearly needed.

The evidence suggests significant reorganization of subsurface nutrient reservoirs throughout the Miocene Pacific, perhaps superimposed on larger global changes in nutrients, and a general decrease in production in the Pliocene and Pleistocene. In the eastern equatorial Pacific and California margin, productivity was strongly reduced in the period from 4.6 to 2.7 Ma, and

1163 in the North Pacific opal deposition was high up until 2.7 Ma. The pattern suggests a
1164 competition for nutrients as deep or intermediate water is mixed into the critical near-surface
1165 regions. We propose that the enhanced subthermocline flow through a shallowing CAS into the
1166 Atlantic focused nutrients into the eastern equatorial Pacific during the Biogenic Bloom regime.
1167 High Miocene productivity was probably also enhanced by higher overall levels of nutrients in
1168 the Miocene shallow subsurface.

1169 **6.8 Trade winds and periodic high productivity**

1170 The cyclic behavior and low amplitude of high production intervals within the
1171 Pleistocene 1.5-0 Ma interval fits a hypothesis where production is driven by higher trade winds
1172 in the glacials lifting more nutrient-rich waters to the surface and potentially being fertilized by
1173 higher dust deposition (Lyle et al., 1992; Winckler et al., 2008; Murray et al., 2012).
1174 Incidentally, the higher glacial dust fluxes potentially reduce the amplitude of glacial/interglacial
1175 opal/clay variation by increasing the clay MAR in addition to the opal MAR during glacials. If
1176 winds and dust result in a factor of two changes in opal production in the Pleistocene, is it
1177 possible that high trade winds cause the high Miocene high production intervals? .

1178 The evidence suggests that higher trade winds could not be a leading cause of the large
1179 Miocene high-production intervals because: (1) intervals of high production are long with respect
1180 to atmospheric and even ocean dynamics, so the hypothesis begs the question of why the winds
1181 might suddenly increase, remain high for 50 kyr or more, and then slow again. And (2) the
1182 strengthening of the winds needs to be very large to pump sufficient nutrients into the euphotic
1183 zone.

In the Pleistocene, there is evidence that there were increases in glacial wind speeds based on the grain size of dust that accumulated. Janecek and Rea (1985), for example, estimated that glacial trade wind intensity at Site 503 (eastern equatorial Pacific) was 36% higher than the interglacials, based on changes in aeolian grain size. Since wind stress on the oceans is proportional to the square of the wind velocity (Smith, 1988), such a change in wind velocity nearly doubles the wind stress, which should potentially be sufficient to double the nutrient delivery to the euphotic zone during glacials.

In the Miocene, an order of magnitude increase in productivity resulting from Ekman divergence requires increases in wind speeds of a factor of 3 for tens of thousands of years. Typical modern trade winds have wind speeds of ~5-10 m/s. In order to pump up ~10 times the nutrients, hypothetical Miocene trade winds would have been near tropical storm force, too strong under any circumstances especially in the absence of a SST feedback from upon the Walker cell.

6.9 The microfossil expression of regimes and paleoproductivity

Comparing the AR and v/gs of total diatoms and specific species for the depositional regimes indicates significant variability in the diatom assemblage and therefore the ecological/depositional conditions at Site U1338 (Figures 9 and 10). The most distinct elements of the U1138 record is the significant increase of total diatoms during the Biogenic Bloom regime (8-4.5 Ma) and the decline in diatoms during the pre-modern regime (<4.5 Ma.)

The Biogenic Bloom regime recognized in the opal/clay record is also observed in the total diatom v/gs. The Biogenic Bloom reflects an increase in accumulation rates of multiple species, not just one (Figure 10) suggesting a more complex productivity/depositional history than a signal driven purely by variability in upwelling. In fact, the increase in multiple species at different times suggests both local and regional environmental influences.

1207 The opal MAR maximum (8.2-5.8 Ma, figure 10) mostly overlaps with the *T.*
1208 *nitzschioides* AR high from 7.8 to about 5.8 Ma but is offset from it. The association of *T.*
1209 *nitzschioides* with coastal and ocean upwelling (section 5.1) is evidence that there is high
1210 nutrient flow to the euphotic zone during the Biogenic Bloom regime. The magnitude of the
1211 increase relative to the other regimes and continuity in duration lasting several Myr is significant.
1212 The coincidence in time for shallowing and closure of the CAS (as discussed above) seems a
1213 likely mechanism for increase nutrients resulting from upwelling from intermediate or deeper
1214 water sources. The influence of the Peru Current and the Equatorial Cold Tongue in the U1338
1215 region may also be a factor increasing productivity, but should be associated with greater
1216 variability, because they are wind-driven, and should appear later in time as the Cold Tongue
1217 develops. The Biogenic Bloom occurs before temperatures cool at Site U1338 and the Cold
1218 Tongue forms (Rouselle et al., 2013), so the signal must relate to the relative supply of nutrients.

1219 Increases in AR for *T. longissima*, *T. nitzschioides* var. *parva*, and *A. nodulifer* at the start
1220 of the Biogenic Bloom regime (7.8 Ma) points to other factors contributing to the AR increase in
1221 addition to the closure of the CAS that need further study. For example, the five-fold increase in
1222 the *T. longissima* AR centered around 7 Ma suggests a response to oceanic front(s) resulting
1223 from large scale-oceanographic changes (Kemp and Baldauf; 1993; Kemp et al., 2006, among
1224 others), similar to that described for *Rhizosolenia* blooms by Yoder et al. (1994) during the
1225 equatorial Pacific JGOFS study. Note, however, that although there is a significant increase in *T.*
1226 *longissima* AR, diatom mat layers are not found at Site U1338. Instead, these *T. longissima*
1227 intervals are dispersed within the typical calcareous nannofossil matrix (Expedition 320/321
1228 Scientists, 2010a), suggesting that U1338 may be only on the fringe of the frontal system.

1229 Dickens and Barron (1997) recorded upper Miocene and lower Pliocene diatom ooze and
1230 laminae composed of *Thalassionema* and *Thalassiothrix* species from ODP Sites 885/886 in the
1231 North Pacific. The site position beneath the northern polar frontal boundary suggests that these
1232 deposits may result from intensification of the frontal system similar to that described for the
1233 equatorial Pacific. Given the apparent synchronicity of these deposits with *T. longissima* mats
1234 from the equatorial Pacific, Dickens and Barron (1997) suggest that, if these deposits are related,
1235 they reflect large-scale processes such as the intensification of frontal boundaries throughout the
1236 subtropical gyre system as a result of changes in ocean atmospheric dynamics.

1237 Unraveling the forcing mechanisms for the Biogenic Bloom regime is made more
1238 complicated by the increases in AR for both *T. nitzschioides* var. *parva* and *A. nodulifera*. The
1239 AR for *T. nitzschioides* var. *parva* shows a gradual 4-fold increase commencing at 8.2 Ma and
1240 continuing until 5.0 Ma. The *T. nitzschioides* var. *parva* AR then abruptly declines to Pliocene-
1241 Modern regime values after 5.0 Ma, prior to the final production interval of the Biogenic Bloom
1242 (Figure 10).

1243 The AR values for *A. nodulifera* also have a ~3-fold increase from 7.8 to about 5.8 Ma
1244 followed by a decline to pre-modern regime values. The pattern of *A. nodulifera* AR mimics the
1245 *T. nitzschioides* AR high, whereas the gradual increase in *T. nitzschioides* var. *parva* achieves its
1246 high (6.2-5.0 Ma) after the declines in the AR peaks of *A. nodulifera*, and *T. nitzschioides*. Since
1247 *A. nodulifera* is associated with warm, more nutrient poor subtropical waters, the increased
1248 deposition may indicate periodic incursions of warmer waters. Higher resolution diatom
1249 assemblage studies are needed to understand the signal.

1250 The occurrence and gradual increase of *T. nitzschioides* var. *parva* suggests that the mode
1251 of nutrient supply to the Site U1338 region varies, with possible different modes, intensities and
1252 source waters. *T. nitzschioides* var. *parva* AR increase suggests that towards the end of the
1253 Biogenic Bloom regime there may be a change in mode of open ocean upwelling and possible
1254 weakening influence Peru Current advection to a warmer subtropical influence since *T.*
1255 *nitzschioides* var. *parva* is associated with warmer waters off Peru in the late Pleistocene
1256 (Schrader and Sjørknes, 1990) . The high AR of *A. nodulifera* during this period also is
1257 suggestive of a more subtropical influence (see discussion 5.1) inferring a possible greater
1258 influence of the North Equatorial Current/Warm Water Pool as Site U1338 moved northward on
1259 the Pacific plate. Clearly a greater understanding of the environmental limiting factors for these
1260 proxies is required.

1261 The significant decline in total diatom AR during the Pliocene-Modern regime at Site
1262 U1338 corresponds to a focusing of opal deposition to the easternmost equatorial Pacific and
1263 Galapagos Basin from the equatorial Pacific region between 100 and 150°W (Hawaii to the East
1264 Pacific Rise). Farrell et al. (1995) and Cortese et al. (2004) document the opal depocenter change
1265 in the equatorial Pacific. Opal contents decline to nearly zero following the biogenic bloom at
1266 ODP Site 850 (110°W), but remaining high at ODP Site 846 (90°W, Cortese et al., 2004).

1267 Both *T. longissima* and *T. nitzschioides* var. *parva* are prevalent taxa within the older
1268 U1338 regime (13.2-8 Ma). *T. longissima* AR shows variability with occasional spikes (i.e. 10
1269 and 12 Ma). *T. nitzschioides* var. *parva* AR has a 4 fold increase centered around 11 Ma. The
1270 increase in *T. nitzschioides* var. *parva* is suggestive of influence of subtropical surface waters
1271 (see section 5.1), but additional analysis is necessary to explain causal mechanisms.

The occasional samples without diatoms in the Middle Miocene Regime (>13.2 Ma) prevents a meaningful interpretation of the diatoms representing this regime. Note also that the 4 species/varieties discussed in detail comprise about 60% of the overall diatom assemblage in the interval younger than 9.5 Ma and up to ~40% of the diatom assemblage >9.5 Ma. The diatom assemblages in the two older regimes (13.2-8.0 Ma and >13.2 Ma) also have prevalent pre-modern forms such as *Denticulopsis simonsenii* and *Crucidentricula nicobarica*, (see supplement Table 3; Baldauf, 2013). The absence of modern analogs for these pre-modern species presents a challenge for paleoenvironmental reconstruction. However, increases in the relative abundance of both species have previously been related to polar cooling. Barron (1985b) demonstrated a positive correlation of the abundance of *C. nicobarica* at DSDP Sites 574 and 575 to the benthic foraminiferal oxygen-isotope curves for Sites 289 and 574. He also noted that this correlation was overprinted by other factors such as a decline in abundance commencing at 13.5 Ma (time scale of Berggren et al., 1985) resulting from diatom species turnover and possible reorganization of equatorial Pacific water masses. Barron (1985b) attributed *D. hustedtii* (= *Denticulopsis simonsenii*) to cool, low salinity water characteristic for the middle to high latitudes where this species is common during the middle and late Miocene. He indicated that excursions of this species (and other cold-water diatoms) in to the low latitudes was tied to cooling of equatorial surface resulting from polar cooling and the strength of the eastern boundary currents.

7.0 Conclusions

Combined studies of total silica microfossils, diatom species assemblages and bulk sediment composition for Site U1338 have shown an intricate pattern of change in biogenic production and surface ecosystem since the Miocene Climate Optimum. We have documented

1295 that the changes reflect variability in the equatorial Pacific of nutrients and temperature, but also
1296 show that biogenic burial is subject to major production thresholds and is overprinted by
1297 carbonate dissolution. We have found that different biogeochemical ratios for productivity
1298 (opal/clay, opal/BaSO₄, BaSO₄/TiO₂, and Al₂O₃/TiO₂) all give similar patterns for high opal
1299 production intervals, although with some significant differences. We have used these ratios to
1300 define high production intervals within the equatorial Pacific for the last 16 Myr.

1301 Some high production intervals like the 7-6.4 Ma main Biogenic Bloom can be related to
1302 tectonic changes in nutrient exchange. However, other very large changes in burial are
1303 problematic because of their abrupt appearance, stability for time periods ranging from 50 to 200
1304 kyr, and abrupt disappearance. Because of the presence of mat-forming *T. longissima* associated
1305 with many of these intervals, frontal convergence may help to amplify the signals by
1306 concentrating production over a wide latitude band to be deposited at one spot. However, higher
1307 *T. longissima* deposition has been found in the same time intervals at Site U1337 to the north and
1308 in the Leg 138 transect to the east. The pattern of deposition does not fit with an expected
1309 convergence and this explanation also begs the question about why such strong convergences
1310 appear and disappear. The Miocene high production intervals probably had significant changes
1311 in subsurface nutrient availability, but it is unclear from where the nutrients are sourced.

1312 CaCO₃ burial is intriguingly offset from opal burial. Since production of both biogenic
1313 components is linked by surface productivity, offsets are evidence for significant variability of
1314 CaCO₃ dissolution. CaCO₃ dissolution, being an indicator of DIC accumulation in the deep
1315 Pacific, thus shows offsets from processes that deliver nutrients to the surface equatorial Pacific.
1316 Potentially signals from multiple equatorial Pacific sites can take advantage of the high spatial
1317 correlation of production, along with the pressure-dependent change of CaCO₃ dissolution with

water depth to better quantify the scale of both CaCO_3 production and dissolution in the Neogene. Our understanding would be highly improved by further sediment trap studies within the tropical upwelling systems, almost 25 years since the JGOFS studies were completed.

High production intervals in the Miocene are much stronger than those from the Pliocene-Modern (4.5-0 Ma), and orbital climate variability seems to be a secondary driver for for Miocene productivity variability. Both long-term and orbital-scale intervals are found in the record, but without a strong pattern of cyclicity. The change in relative abundance of different diatom species implies an evolution of temperatures, nutrients, and seasonality to drive change in the equatorial Pacific system that needs to be further studied.

The lack of simple repeating patterns between changes in the diatom assemblage and opal production events implies that nutrient upwelling is only one driver of the diatom assemblage, and also implies that there is no simple model of diatom production in response to nutrient delivery. As the diatom ecosystem changes, deposition shifts to new species to produce a depositional response that changes subtly through time. Bloom intervals that have high opal production may thus result from multiple causes.

.Acknowledgments

This research used samples and data provided by the Integrated Ocean Drilling Program (IODP). IODP is a sponsored by the U.S. National Science Foundation (NSF) and participating countries under the management of International Management Incorporated. Support for data acquisition and analysis was from the National Science Foundation grant OCE-0962184, the Wenner-Gren Foundation, Stockholm University, and Texas A&M University. The author (JB)

1339 thanks Jan Backman for hosting is stay at Stockholm University where a portion of this research
1340 was completed.

1341 8.0 References

- 1342 Arrhenius, G.O.S., 1952. Sediment cores from the east Pacific, *Reports of the Swedish Deep Sea*
1343 *Expedition, 1947-1948*, 5, 1-228.
- 1344 Baldauf, J.G., 1985. A high resolution Late Miocene-Pliocene diatom biostratigraphy for the
1345 eastern equatorial Pacific. Mayer, L., Theyer, F., et al., Init. Repts, DSDP, 85:
1346 Washington (U.S. Govt. Printing Office), 457-475.
- 1347 Baldauf, J.G., 2013. Data report: diatoms from Sites U1334 and U1338, Expedition 320/321. In
1348 Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition
1349 320/321 Scientists, Proc. IODP, 320/321: Tokyo (Integrated Ocean Drilling Program
1350 Management International, Inc.). doi:10.2204/iodp.proc.320321.215.2013.
- 1351 Baldauf, J.G., and Barron, J.A., 1990. Evolution of biosiliceous sedimentation patterns-Eocene
1352 through Quaternary: Paleooceanographic response to polar cooling, in *Geological History*
1353 *of the Polar Oceans: Arctic versus Antarctic*, edited by Bleil, U, Thiede, T., Kluwer
1354 Academic Publishers, 575-607.
- 1355 Barron, J.A., 1985a. Late Eocene to Holocene diatom biostratigraphy of the equatorial pacific
1356 ocean, Deep Sea Drilling Project Leg 85. Mayer, L., Theyer, F., et al., Init. Repts, DSDP,
1357 85: Washington (U.S. Govt. Printing Office), 413-456.
- 1358 Barron, J.A., 1985b. Diatom paleoceanography and paleoclimatology of the central and eastern
1359 equatorial Pacific between 18 and 6.2 Ma. Mayer, L., Theyer, F., et al., Init. Repts,
1360 DSDP, 85: Washington (U.S. Govt. Printing Office), 935 – 945.
- 1361 Barron, J., Lyle, M., Koizumi, I., 2002. Late Miocene and early Pliocene biosiliceous
1362 sedimentation along the California margin. *Revista Mexicana de Ciencias Geologicas* 19
1363 (3), 161-169.
- 1364 Berger, W.H., 1973. Cenozoic sedimentation in the eastern tropical Pacific, *Geological Society*
1365 *of America Bulletin*, 84, 1941-1954.
- 1366 Berger, W.H., Lange, C.B., and Perez, M.E., 2002. The early Matuyama diatom maximum off
1367 SW Africa: a conceptual model. *Marine Geology* 180, 105-116.
- 1368 Berggren, W. A., D. V. Kent, J. J. Flynn, and J. A. Van Couvering, 1985. Cenozoic
1369 geochronology, *Geological Society of America Bulletin*, 96, 1407-1418.
- 1370 Billups, K., J. E. T. Channell, and J. Zachos, 2002. Late Oligocene to early Miocene
1371 geochronology and paleoceanography from the subantarctic South Atlantic,
1372 *Paleoceanography*, 17, doi: 10.1029/2000PA000568.
- 1373 Bloomer, S. F., and L. A. Mayer, 1997. Core-log-seismic integration as a framework for
1374 determining the basin-wide significance of regional reflectors in the eastern equatorial
1375 Pacific, *Geophysical Research Letters*, 24(3), 321-334.
- 1376 Boden, P., and J. Backman, 1996. A laminated sediment sequence from the northern North
1377 Atlantic Ocean and its climatic record, *Geology*, 24, 507-510.
- 1378 Broecker, W. S., and T.-H. Peng, 1982. *Tracers in the Sea*, Eldigio Press, Lamont-Doherty Geol.
1379 Obs, NY.
- 1380 Burckle, L.H., Keigwin, L., and Opdyke, N.D., 1982. Middle and Late Miocene stable isotope

1381 stratigraphy: correlation to the paleomagnetic reversal record. *Micropaleontology*, 28, 4,
1382 329-334.

1383 Butzin, M., G. Lohmann, and T. Bickert, 2011. Miocene ocean circulation inferred from marine
1384 carbon cycle modeling combined with benthic isotope records, *Paleoceanography*, 26,
1385 PA1203, 1219 pp.

1386 Chaisson, W. P., and A. C. Ravelo, 2000. Pliocene development of the east-west hydrographic
1387 gradient in the equatorial Pacific, *Paleoceanography*, 15(5), 497-505.

1388 Chavez, F.P., and R.T. Barber, 1987. An estimate of new production in the equatorial Pacific,
1389 *Deep-Sea Research*, 34, 1229-1243.

1390 Chavez, F.P., K.R. Buck, S.K. Service, J. Newton, and R.T. Barber, 1996. Phytoplankton
1391 variability in the central and eastern tropical Pacific, *Deep Sea Research II*, 43(4-6), 835-
1392 870.

1393 Chavez, F.P., Ryan, J., Lluch-Cota, S.E., and Niquen, M., 2003. From anchovies to sardines and
1394 back: multidecadal change in the Pacific Ocean, *Science*, 299, 217-221,
1395 doi:10.1126/science.1075880.

1396 Cooke-Poferl, K., Burckle, L.H., and Riley, S., 1975. Diatom evidence bearing on the late
1397 Pleistocene climate change in the equatorial Pacific. *Geol. Soc. Amer. Abstr. Prog.* 7,
1398 1038-1039.

1399 Cortese, G., Gersonde, R., Hillenbrand, C-D., and Kuhn, G., 2004. Opal sedimentation shifts in
1400 the world ocean over the last 15 myr. *Earth and Planetary Sciences Letters*, 224, 509-
1401 527.

1402 Delaney, M. L., 1998. Phosphorus accumulation in marine sediments and the oceanic
1403 phosphorus cycle, *Global Biogeochemical Cycles*, 12(4), 563-572.

1404 Dickens, G.R., and Barron, J.A., 1997. A rapidly deposited pennate diatom ooze in upper
1405 Miocene-Lower Pliocene sediment beneath the North Pacific polar front. *Marine*
1406 *Micropaleontology*, 31, 177-182.

1407 Dickens, G.R. and Owen, R., 1999. The latest Miocene-early Pliocene biogenic bloom: a
1408 Revised Indian Ocean perspective. *Marine Geology* 161, 75-91.

1409 Diester-Haass, L., Meyers, P.A., and Bickert, T., 2004. Carbonate crash and biogenic bloom in the
1410 late Miocene: evidence from ODP Sites 1085, and 1087 in the Cape Basin, southwest
1411 Atlantic Ocean. *Paleoceanography*, 19, PA1007, doi:10.29/2003PA000933.

1412 Dugdale, R.C., Wischmeyer, A.G., Wilkerson, F.P., Barber, R.T., Chai, F., Jiang, M.S., and H.
1413 Peng, T.H., 2002. Meridional asymmetry of source nutrients to the equatorial Pacific
1414 upwelling ecosystem and its potential impact on ocean-atmosphere CO₂ flux; a data and
1415 modeling approach, *Deep Sea Research part II*, 49, 2513-2531.

1416 Dunne, J.P., Hales, B., and Toggweiler, J.R., 2012. Global calcite cycling constrained by
1417 sediment preservation controls, *Global Biogeochemical Cycles*, 26, GB3023, 14 pp.

1418 Dymond, J., 1981. Geochemistry of Nazca plate surface sediments: an evaluation of
1419 hydrothermal, biogenic, detrital, and hydrogenous sources, *Geological Society of America*
1420 *Memoir* 154, 133-173.

1421 Dymond, J., and R. Collier, 1988. Biogenic particle fluxes in the equatorial Pacific: Evidence for
1422 both high and low productivity during the 1982-1983 El Niño, *Global Biogeochemical*
1423 *Cycles*, 2(2), 129-139.

1424 Dymond, J., Suess, E., and M. Lyle, M., 1992. Barium in deep-sea sediment: A geochemical
1425 proxy for paleoproductivity, *Paleoceanography*, 7(2), 163-181.

1426 Dymond, J., and Lyle, M., 1994. Particle fluxes in the ocean and implications for sources and

- preservation of ocean sediments. In Hay, W.W. (Ed.), *Material Fluxes on the Surface of the Earth*: Washington D.C. (National Academy of Science), 125–143.
- Suess, and M. Lyle (1992), Barium in deep-sea sediment: A geochemical proxy for paleoproductivity, *Paleoceanography*, 7(2), 163-181.
- Dymond, J. and Collier, R., 1996. Particulate barium fluxes and their relationships to biological productivity, *Deep Sea Research, Part II*, 43, 1283-1308
- Dymond, J.R. Collier, R., and McManus, J., 1997. Can the aluminum and titanium contents of ocean sediments be used to determine the paleoproductivity of the oceans?, *Paleoceanography*, 12(4), 585-593.
- Eagle, M. Paytan, A., Arrigo, K.R., van Dijken, G., and Murray, R.W., 2003. A comparison between excess barium and barite as indicators of carbon export, *Paleoceanography*, 18(1), doi: 10.1029/2002PA000793.
- Emerson, S., and Bender, M., 1981. Carbon fluxes at the sediment-water interface of the deep-sea: calcium carbonate preservation, *Journal of Marine Research*, 39, 139-162.
- Eppley, R. W., and B. J. Peterson, 1979. Particulate organic matter flux and planktonic new production in the deep ocean, *Nature*, 282, 677-680.
- Etourneau, J., Schneider, R., Blanz, T., Martinez, P., 2010. Intensification of the Walker and Hadley atmospheric circulations during the Pliocene-Pleistocene climate transition. *Earth and Planetary Science Letters* 297, 103-110.
- Expedition 320/321 Scientists, 2010a. Site U1338. In Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition 320/321 Scientists, Proc. IODP, 320/321: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.320321.110.2010
- Expedition 320/321 Scientists, 2010b. Methods. In Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition 320/321 Scientists, Proc. IODP, 320/321: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.320321.102.2010
- Expedition 320/321 Scientists, 2010c. Site U1337. In Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition 320/321 Scientists, Proc. IODP, 320/321: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.320321.109.2010
- Farrell, J.W., Raffi, I., Janecek, T.R., Murray D.W., Levitan, M., Dadey, K.A., Emeis, K.C., Lyle, L., Flores, J.A., and Hovan, S., 1995. Late Neogene sedimentation patterns in the eastern equatorial Pacific Ocean, in *Proceedings of the Ocean Drilling Program, Scientific Results*, edited by Pisias, N.G., Mayer, L.A., Janecek, T.R., Palmer-Julson, A., and van Andel, T.H., vol, 138., Ocean Drilling Program, College Station, Texas, 717-756
- Farrell, J.W., and Prell, W.L., 1989. Climatic change and CaCO₃ preservation: an 800,000 year bathymetric reconstruction from the central equatorial Pacific Ocean, *Paleoceanography*, 4(4), 447-466.
- Farrell, J.W. and Prell, W.L., 1991. Pacific CaCO₃ preservation and $\delta^{18}\text{O}$ since 4 Ma: paleoceanic and paleoclimatic implications. *Paleoceanography*, 6, 485-498.
- Fiedler, P.C., and Talley, L.D., 2006. Hydrography of the eastern tropical Pacific: A review. *Progress in Oceanography*, 69, 143-180.
- Filipelli, G.M., and Delaney, M.L., 1994. The ocean phosphorus cycle and continental weathering during the Neogene, *Paleoceanography*, 9(5), 643-652.
- Filipelli, G.M., 1997. Intensification of the Asian monsoon and a chemical weathering event in

- the late Miocene-early Pliocene: Implications for late Neogene climate change, *Geology*, 25, 27-30, doi:10.1130/0091-7613(1997)025<0027:IOTAMA>2.3.CO.
- Ford, H.L., Ravelo, A.C., Hovan, S., 2012. A deep eastern equatorial Pacific thermocline during the early Pliocene warm period. *Earth and Planetary Science Letters* 355-356, 152-161.
- Goldberg, E.D., and Arhenius, G., 1958. Chemistry of Pacific pelagic sediments. *Geochimica et Cosmochimica Acta*, 13, 153-212.
- Griffith, E., and Paytan, A., 2012. Barite in the Ocean - Occurrence, Geochemistry, and Palaeoceanographic Applications. *Sedimentology*, 59, 1817-1835, DOI: 10.1111/j.1365-3091.2012.01327.x
- Hagelberg, T.K., Pisias, N.G., Mayer, L.A., Shackleton, N.J., and Mix., A.C., 1995. Spatial and temporal variability of late Neogene equatorial Pacific Carbonate: Leg 138, in *Proceedings of the Ocean Drilling Program, Scientific Results, 138*, edited by N. G. Pisias, L. A. Mayer, T. R. Janecek, A. Palmer-Julson and T. H. van Andel, Ocean Drilling Program, College Station, TX., pp. 321-336,
- Han, Y., T. Zhao, L. Song, X. Fang, Y. Yin, Z. Deng, S. Wang, and S. Fan, 2011. A linkage between Asian dust, dissolved iron and marine export production in the deep ocean, *Atmospheric Environment*, 45, 4291-4298.
- Haug, G. H., and R. Tiedemann, 1998. Effect of the formation of the Isthmus of Panama on Atlantic Ocean thermohaline circulation, *Nature*, 393(18 June), 673-676.
- Haug, G.H., Sigman, D.M., Tiedemann, R., Pedersen, T.F., Sarnthein, M., 1999. Onset of permanent stratification in the subarctic Pacific Ocean. *Nature*, 401, 779-782.
- Hays, J. D., Saito, T., Opdyke, N.D., and Burckle, L.H., 1969. Pliocene-Pleistocene sediments of the equatorial Pacific: Their paleomagnetic, biostratigraphic, and climatic record, *Geological Society of America Bulletin*, 80, 1481-1514.
- Hodell, D. A., and K. A. Venz-Curtis, 2006. Late Neogene history of deepwater ventilation in the Southern Ocean, *Geochemistry, Geophysics, Geosystems*, 7(9). DOI:10.1029/2005GC001211
- Holbourn, A., Kuhnt, W.; Lyle, M., Schneider, L., Romero, O.E., Andersen, N., 2014. Middle Miocene climate cooling linked to intensification of eastern equatorial Pacific upwelling. *Geology*, 42(1), 19-22.
- Holbourn, A., Kuhnt, W., Kochhann, K.G.D., Andersen, N., Meier, K.J.S., 2015. Global perturbation of the carbon cycle at the onset of the Miocene Climate Optimum. *Geology* 43, 123-126.
- Honjo, S., Dymond, J., Collier, R., and Manganin, S.J., 1995. Export production of particles to the interior of the equatorial Pacific Ocean during the 1992 Eq.Pac. experiment, *Deep-Sea Research*, 42(2-3), 831-870.
- Honjo, S., Dymond, J., Prell, W.L., and Ittekkot, V., 1999. Monsoon-controlled export fluxes to the interior of the Arabian Sea, *Deep Sea Research II*, 46, 1859-1902.
- Honjo, S., Manganini, S.J., Krishfield, R.A., Francois, R., 2008. Particulate organic carbon fluxes to the ocean interior and factors controlling the biological pump: a synthesis of global sediment trap programs since 1983. *Progress in Oceanography* 76, 217-285.
- Hutchins, D.A. and Bruland, K.W., 1998. Iron-limited diatom growth and Si:N uptake ratios in a coastal regime, *Nature* 393, 561-564.
- Janecek, T.R., Rea, D.K., 1985. Quaternary fluctuations in the northern hemisphere trade winds and westerlies. *Quaternary Research* 24, 150-163.
- Katsuki, K., K. Takahashi, and M. Okada, 2003. Diatom assemblage and productivity changes

- during the last 340,000 years in the subarctic Pacific, *Journal of Oceanography*, 59, 695-707.
- Keller, G., and Barron, J.A., 1983. Paleooceanographic implications of Miocene deep-sea hiatuses, *Geological Society of America Bulletin*, 94, 590-613.
- Kemp, A.E.S., and Baldauf, J.G., 1993. Vast Neogene laminated diatom mat deposits from the eastern equatorial Pacific Ocean. *Nature*, 362,141-144.
- Kemp, E.S., Baldauf, J.G., and Pearce, R.B, 1995. Origins and paleoceanographic significance of laminated diatom ooze from the eastern equatorial Pacific. Pisias, N.G., Mayer, L.A., Janecek, T.R., Palmer-Julson, A., and van Andel, T.H. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results*, 138, 641-645.
- Kemp, E.S., Pearce, R., Grigorov, I., Rance, J., Lange, C., Quilty, P., and Salter, I., 2006. The production of giant marine diatoms and their export at oceanic frontal zones: implications for Si and C flux in stratified oceans. *Global Biogeochemical Cycles*,23,pp GB4S04.
- Klaas, C. and Archer, D.E., 2002. Association of sinking organic matter with various types of mineral ballast in the deep sea: implications for the rain ratio. *Global biogeochemical cycles*, 16, 1116, doi:10.1029/2001GB001765,2002.
- Kobayashi, F. and Takahashi K., 2002. Distribution of diatoms along the equatorial transect in the western and central Pacific during the 1999 La Niña conditions. *Deep Sea Research Part II: Topical Studies in Oceanography*. 49(13-14), 2801-2821.
- Leinen, M., 1979. Biogenic silica accumulation in the central equatorial Pacific and its implications for Cenozoic paleoceanography: Summary., *Geological Society of America Bulletin, PartI*, 90, 801-803; 1310-1375.
- Lisitzyn, A.P.,1972. Sedimentation in the world ocean, Special Publication 17, Soc Econ. Paleont .Miner.Tulsa, 218p.
- Lopes, C., Mix, A., and Abrantes, F. 2006. Diatoms in northeast Pacific surface sediments as paleoceanographic proxies. *Marine Micropaleontology* 60, 45–65.
- Lyle, M., Murray, D., Finney, B.P., Dymond, D., Robbins, J.M., and Brooksforce, K., 1988. The record of late Pleistocene biogenic sedimentation in the eastern tropical Pacific ocean, *Paleoceanography*, 3(1), 39-59.
- Lyle, M.W., Prahl, F.G., and Sparrow, M.A., 1992. Upwelling and productivity changes inferred from a temperature record in the central equatorial Pacific, *Nature*, 355, 812-815.
- Lyle, M., Dadey, M., Farrell, J., 1995. The late Miocene (11-8 Ma) eastern Pacific carbonate crash evidence for reorganization of deep-water circulation by the closure of the Panama gateway. Pisias, N.G., Mayer, L.A., Janecek, T.R., Palmer-Julson, A., and van Andel, T.H. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results*, 138, 821-838.
- Lyle, M., 1997. Reconstructed geographic positions and water depths for Leg 167 drill sites *In* Lyle, M., Koizumi, I., Richter, C., et al., Proc. ODP, Init. Repts., 167: College Station, TX (Ocean Drilling Program), 41–46. doi:10.2973/odp.proc.ir.167.103.1997
- Lyle, M., 2003. Neogene carbonate burial in the Pacific Ocean, *Paleoceanography*,18(3), DOI 10.1029/2002PA000777.
- Lyle, M., Olivarez Lyle, A., Gorgas, T., Holbourn, A., Westerhold, T., Hathorne, E., Kimoto, K., and Yamamoto, S., 2012. Data report: raw and normalized elemental data along the Site U1338 splice from X-ray fluorescence scanning. *In* Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition 320/321 Scientists, *Proc. IODP*, 320/321: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). [doi:10.2204/](https://doi.org/10.2204/)

- iodp.proc.320321.203.2012
- Lyle, M., and Backman, J., 2013. Data report: calibration of XRF-estimated CaCO₃ along the Site U1338 splice. In Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition 320/321 Scientists, *Proc. IODP*, 320/321: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). [doi:10.2204/iodp.proc.320321.205.2013](https://doi.org/10.2204/iodp.proc.320321.205.2013)
- Mahowald, N. M., et al., 2009. Atmospheric iron deposition: Global distribution, variability, and human perturbations, *Annual Review of Marine Science*, 245-278.
- Margalef, R., 1978. Life-forms of phytoplankton as survival alternatives in an unstable environment. *Oceanologica Acta* 1 (4), 493–508.
- Martin, J. H., et al. .1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean., *Nature*, 371, 123-129.
- Mayer, L. A., Shipley, T.H.,and Winterer, E.L.,1986. Equatorial Pacific seismic reflectors as indicators of global oceanographic events, *Science*, 233, 761-764.
- Messie, M., and Chavez, F.P., 2011, Global modes of sea surface temperature variability in relation to regional climate indices, *Journal of Climate*, 24, 4314-4331, [doi:10.1175/2011JCLI3941.1](https://doi.org/10.1175/2011JCLI3941.1).
- Messie, M., and Chavez, F.P., 2012. A global analysis of ENSO synchrony: the oceans' biological response to physical forcing, *Journal of Geophysical Research*, C117, C09001 09019pp, [doi:10.1029/2012JC007938](https://doi.org/10.1029/2012JC007938).
- Mix, A. C., Pisias, N.G., Rugh, W., Wilson, J., Morey, A., and Hagelberg, T.K.,1995. Benthic foraminifer stable isotope record from Site 849 (0-5 Ma): local and global climate changes, *Proceedings of the Ocean Drilling Program, Scientific Results*, 138, 371-413.
- Moore, W.S., and Dymond, J., 1988. Correlation of ²¹⁰Pb removal with organic carbon fluxes in the Pacific Ocean, *Nature*, 331, 339-341.
- Moore, T.C., jr., Backman, J., Raffi, I., Nigrini, C.A., Sanfilippo, A., Pälike, H., and Lyle, M., 2004. The Paleogene tropical Pacific: clues to circulation, productivity and plate motion, *Paleoceanography*, 19, [doi:10.1029/2003PA000998](https://doi.org/10.1029/2003PA000998).
- Moore, T.C. jr. , 2008. Chert in the Pacific: Biogenic silica and hydrothermal circulation, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 261, 87-99.
- Murray, R.W., and Leinen, M., 1993. Chemical transport to the seafloor of the equatorial Pacific Ocean across a latitudinal transect at 135°W: tracking sedimentary major, trace, and rare earth element fluxes at the equator and the Intertropical Convergence Zone, *Geochimica et Cosmochimica Acta*, 57, 4141-4163.
- Murray, R.W., and Leinen, M., 1996. Scavenged excess aluminum and its relationship to bulk titanium in biogenic sediment from the central equatorial Pacific Ocean, *Geochimica et Cosmochimica Acta*, 60(20), 3869-3878.
- Murray, R.W., Knowlton, C., Leinen, M., Mix, A.C., and Polsky, C.H., 2000. Export production and terrigenous matter in the Central Equatorial Pacific Ocean during interglacial oxygen isotope Stage 11, *Global and Planetary Change*, 24, 59-78.
- Murray, R.W., Leinen, M., and Knowlton, C.W., 2012. Links between iron input and opal deposition in the Pleistocene equatorial Pacific Ocean, *Nature Geoscience*, 5, 270-274.
- Nathan, S. A., and Leckie, R.L., 2009. Early history of the Western Pacific Warm Pool during the middle to late Miocene (~13.2-5.8 Ma): Role of sea-level change and implications for equatorial circulation, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 274, 140-159.

- Pälike, H., Nishi, H., Lyle, M., Raffi, I., Gamage, K., and Klaus, A., and the Expedition 320/321 Scientists, 2010a. Proceedings of the IODP, 320/321, Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.320321.2010.
- Pälike, H., Nishi, H., Lyle, M., Raffi, I., Gamage, K., and Klaus, A., and the Expedition 320/321 Scientists, 2010b. Expedition 320/321 summary. In Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition 320/321 Scientists, *Proc. IODP*, 320/321: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.320321.101.2010.
- Pälike, H., et al., 2012. A Cenozoic record of the equatorial Pacific carbonate compensation depth, *Nature*, 488, 609-614.
- Paytan, A., and Kastner, M., 1996. Benthic Ba fluxes in the central equatorial Pacific, implications for the oceanic Ba cycle, *Earth and Planetary Science Letters*, 142, 439-450.
- Philander, S. G. H., D. Gu, D. Halpern, G. Lambert, N.-C. Lau, T. Li, and R. C. Pacanowski, 1996. Why the ITCZ is mostly north of the equator, *Journal of Climate*, 9, 2958-2972.
- Pichevin, L. E., B. C. Reynolds, R. S. Ganeshram, I. Cacho, L. Pena, K. Keefe, and R. M. Ellam, 2009. Enhanced carbon pump inferred from relaxation of nutrient limitation in the glacial ocean, *Nature*, 459, 1114-1117.
- Pichevin, L.E., Ganeshram, R.S., Geibert, W., Thunell, R., and Hinton, R., 2014. Silica burial enhanced by iron limitation in oceanic upwelling margins, *Nature Geoscience*, 7, 541-546.
- Piela, C., Lyle, M., Marcantonio, F., Baldauf, J.G., and Olivarez Lyle, A., 2012. Biogenic sedimentation in the equatorial Pacific: Carbon Cycling and paleoproduction, 12-24Ma., *Paleoceanography*, vol. 27, PA2204, doi:10.1029/2011PA002236
- Poore, H. R., R. Samworth, N. J. White, S. M. Jones, and I. N. McCave, 2006. Neogene overflow of Northern Component Water at the Greenland-Scotia Ridge, *Geochemistry, Geophysics, Geosystems*, 7(6), Q06010, 06024pp.
- Ragueneau, O., et al., 2000. A review of the Si cycle in the modern ocean; recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy, *Global and Planetary Change*, 26(4), 317-365.
- Ravelo, A. C., P. S. Dekens, and M. D. McCarthy, 2006. Evidence for El Niño-like conditions during the Pliocene, *GSA Today*, 16(3), 4-11.
- Ravelo, A.C., Lawrence, K.T., Federov, A., Ford, H.L., 2014. Comment on "A 12-million-year temperature history of the tropical Pacific Ocean". *Science*, 346, 1467a.
- Ren, J., Gersonde, R., Esper, O., and Sancetta, C., 2014. Diatom distributions in northern North Pacific surface sediments and their relationship to modern environmental variables. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 402, 81-103.
- Richter, T.O., van der Gaast, S., Koster, B., Vaars, A., Gieles, R., de Stigter, H.C., De Haas, H., and van Weering T.C.E., 2006. The Avaatech XRF core scanner: technical description and applications to NE Atlantic sediments, in *New Techniques in Sediment Core Analysis*, edited by R. G. Rothwell, pp. 39-50, *Geological Society, Special Publications*, 267, London.
- Romero, O.E. and Armand, L.K., 2010. The Diatoms: Applications for the Environmental and Earth Sciences, 2nd Edition, eds. John P. Smol and Eugene F. Stoermer. Cambridge University Press. Cambridge University Press, 373-400.
- Romero, O.E., Lange, C.B., Fisher, G. Treppke, U.F., Wefer, G., 1999. Variability in export production documented by downward fluxes and species composition of marine planktic

- diatoms: observations from the tropical and equatorial Atlantic, *In* Fisher, G., Wefer, G., *Use of proxies in paleoceanography, examples from the South Atlantic*, Springer-Verlag, Berlin, Heidelberg, 365-392.
- Romero, O.E., Ledue, G., Vidal, L., and Fischer, G., 2011. Millennial variability and long-term changes of the diatom production in the eastern equatorial Pacific during the last glacial cycle. *Paleoceanography* 26, PA2212, doi:10.1029/2010PA002099, 1-11.
- Romero, O.E., Thunell, R.C., Astor, Y., and Varela, R. 2009. Seasonal and interannual dynamics in diatom production in the Cariaco Basin, Venezuela. *Deep-Sea Research I*, 56, 571-581, doi:10.1016/j.dsr.2008.12.005.
- Roth, J. M., A. W. Droxler, and K. Kameo, 2000. The Caribbean carbonate crash at the middle to late Miocene transition: linkage to the establishment of the modern global ocean conveyor, in *Proceedings of the Ocean Drilling Program, Scientific Results*, 165, edited by R. M. Leckie, H. Sigurdsson, G. D. Acton and G. Draper, pp. 249-273, Ocean Drilling Program, College Station, TX.
- Sancetta, C., 1983. Biostratigraphy and paleoceanographic events in the eastern equatorial Pacific: Results of Deep Sea Drilling Project Leg 69 Cann, J.R., Langseth, M.G., Von Herzen, R.P., White, S.M. et al., Init. Repts., DSDP 69, Washington, (U.S.Govt. Printing Office), 311-320.
- Sancetta, C., 1995. Diatoms in the Gulf of California: Seasonal flux patterns and the sediment record for the last 15,000 years *Paleoceanography*, 10, 67-84.
- Scherer, R. P., 1994. A new method for the determination of absolute abundance of diatoms and other silt-size sedimentary particles. *Journal of Paleolimnology* 12, 171-179.
- Schrader, H.J., and Gersonde, R., 1978. Diatoms and Silicoflagellates. In Zachariasse, W.J., et. al., (Eds.) Micropaleontology counting methods and techniques: An exercise of an eight metres section of the lower Pliocene of Cap Rossello, Sicily. *Utrecht Micropaleontology Bull.*, 17, 129-176.
- Schrader, H., and Sorknes, R., 1990. Spatial and temporal variation of Peruvian coastal upwelling during the latest Quaternary. *In* Suess, E., von Huene, R., et al., *Proc. ODP, Sci. Results*, 112: College Station, TX (Ocean Drilling Program), 391–406. doi:10.2973/odp.proc.sr.112.188.1990.
- Schrader, H.S., Swanberg, N., Katrine Lycke, A., Paetzel, M., and Schrader, T. 1993. Diatom-inferred productivity changes in the eastern equatorial Pacific: The Quaternary record of ODP Legt 111, Site 677. H von Dami (ed.) Twelfth International Diatom Symposium, Kluwer Academic Publishers. *Hydrobiologia* 269/270, 137-151.
- Schroeder, J. O., Murray, R.W., Leinen, M., Pflaum, R.C., and Janecek, TR., 1997. Barium in equatorial Pacific carbonate sediment: Terrigenous, oxide, and biogenic associations, *Paleoceanography*, 12(1), 125-146.
- Schuette and Schrader, H.J., 1979. Diatom taphocoenoses in the coastal upwelling area off western South America. *Nova Hedwigia*, 64, 359-378.
- Shackford, J.K., Lyle, M., Wilkens, R., and Tian, J., 2014. Data report: raw and normalized elemental data along the Site U1335, U1336, and U1337 splices from X-ray fluorescence scanning. *In* Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and the Expedition 320/321 Scientists, *Proc. IODP*, 320/321: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). doi:10.2204/iodp.proc.320321.216.2014
- Shackleton, N. J., M. A. Hall, and D. Pate, 1995. Pliocene stable isotope stratigraphy of Site 846, *Proceedings of the Ocean Drilling Program, Scientific Results*, 138, 337-355.

- Smith, C. R., D. J. Hoover, S. E. Doan, R. H. Pope, D. J. DeMaster, F. C. Dobbs, and M. A. Altabet, 1996. Phytodetritus at the abyssal seafloor across 10° of latitude in the central equatorial Pacific, *Deep Sea Research II*, 43(4-6), 1309-1338.
- Smith, S.D., 1988. Coefficients for sea surface wind stress, heat flux, and wind profiles as a function of wind speed and temperature. *Journal of Geophysical Research, Oceans*, 93, 15467-15472.
- Steph, S., R. Tiedemann, M. Prange, J. Groeneveld, M. Schulz, A. Timmerman, D. Nürnberg, C. Rühlemann, C. Saukel, and G. H. Haug, 2010. Early Pliocene increase in thermohaline overturning: a precondition for the development of the modern equatorial Pacific cold tongue, *Paleoceanography*, 25, doi: 10.1029/2008PA001645
- Takeda, S., 1998. Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters, *Nature*, 395, 774-777.
- Takahashi, T., et al., 2009. Climatological mean and decadal change in surface ocean pCO₂, and net sea-air CO₂ flux over the global oceans, *Deep Sea Research II*, 56, 554-577.
- Taylor, S. R., and McLennan, S.M., 1995. The geochemical evolution of the continental crust, *Reviews of Geophysics*, 33(2), 241-265.
- Tominaga, M., Lyle, M., and Mitchell, N.C., 2011. Seismic interpretation of pelagic sedimentation regimes in the 18–53 Ma eastern equatorial Pacific: Basin-scale sedimentation and infilling of abyssal valleys, *Geochemistry, Geophysics, Geosystems*, 12(3), Q03004, 03022p.
- Torres, M. E., McManus, J., and Huh, C.A., 2002. Fluid seepage along the San Clemente Fault scarp: basin-wide impact on barium cycling, *Earth and Planetary Science Letters*, 203, 181-194.
- Tréguer, P. J., and C. L. De La Rocha, 2013. The world ocean silica cycle, *Annual Review of Marine Science*, 5, 5.1–5.25.
- van Andel, T.H., Heath, G.R., and Moore, T.C.jr., 1975. *Cenozoic History and Paleooceanography of the central equatorial Pacific Ocean*, *GSA Memoir 143*, 133 pp., Geological Society of America.
- Von Breymann, M. T., Emeis, K.C., and Camerlenghi, A., 1990. Geochemistry of sediments from the Peru upwelling area: Results from Sites 680, 682, 685, and 688, in Suess, E, von Huene, R, et al, *Proceedings of the Ocean Drilling Program, Scientific Results*, 112, 491-503.
- Walsh, I., Dymond, J., and Collier, R.B., 1988. Rates of recycling of biogenic components of settling particles in the ocean derived from sediment trap experiments, *Deep-Sea Research*, 35, 43-58.
- Walsh, I.D., Gardner, W.D., Richardson, M.J., Chung, S.P., Plattner, C.A., and Asper, V.L., 1997. Particle dynamics as controlled by the flow field of the eastern equatorial Pacific, *Deep Sea Research II*, 44, 2025-2047.
- Westerhold, T., T. Bickert, and U. Röhl, 2005. Middle to late Miocene oxygen isotope stratigraphy of ODP site 1085 (SE Atlantic): new constraints on Miocene climate variability and sea-level fluctuations, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 217, 205-222, doi:10.1016/j.palaeo.2004.12.001.
- Wilkens R., Dickens, G.R., Tian, J, and Backman, J., 2013. Data Report: Revised composite depth scales for Sites U1336, U1337 and U1338. In: Pälike, H, Lyle, M, Nishi, H, Raffi, I, Gamage, K, Klaus, A, and the Expedition 320/ 321 Scientists, *Proc. IODP 320/321 Tokyo* (Integrated Ocean Drilling Program Management International Inc), pp 1-158.

- doi:10.2204/iodp.proc.320321.209.2013
- Wilson, J.K., 2014. Early Miocene carbonate dissolution in the eastern equatorial Pacific. PhD thesis, Texas A&M University, College Station TX.
- Winckler, G., R. F. Anderson, M. Q. Fleisher, D. McGee, and N. Mahowald, 2008. Covariant glacial-interglacial dust fluxes in the equatorial Pacific and Antarctica., *Science*, 320, 93-96
- Wunsch, C., 2009. A perpetually running ENSO in the Pliocene? *Journal of Climate*, 22, 3506-3510.
- Xie, R.C., and Marcantonio, F., 2012. Deglacial dust provenance changes in the Eastern Equatorial Pacific and implications for ITCZ movement. *Earth and Planetary Science Letters* 317-318, 386-395.
- Yoder, J. A., S. G. Ackleson, R. T. Barber, P. Flament, and W. M. Balch, 1994. A line in the sea, *Nature*, 371, 689-692.
- Zhang, X., et al., 2012. Changes in equatorial Pacific thermocline depth in response to Panamanian closure: Insights from a multi-model study, *Earth and Planetary Science Letters*, 317-318, 76-84.
- Zhang, Y.G., Pagani, M., Liu, Z., 2014. A 12-million-year temperature history of the tropical Pacific Ocean. *Science*, 344, 84-87.

Figures

Figure 1. Location of IODP site U1338 in the eastern equatorial Pacific with a hotspot reference site backtrack for the Pacific plate (Lyle, 1997) and with bathymetry from GeoMapApp (Geomapapp.org). Other plate motion models leave U1338 within 0.5° of the equator at 11 Ma.

Figure 2: Comparison of biogenic fluxes from JGOFS tropical sediment trap experiments from sediment traps in the 2000-2500 m range. Data from Honjo et al (1995, 1999). All fluxes are in mg/cm²/kyr. (a) CaCO₃ particulate rain (reds) and bio-SiO₂ (opal) in purples vs C_{org} rain (export production to 2000 m). Opal fluxes increase more rapidly than the export flux of C_{org}, while CaCO₃ fluxes increase slightly less. The result is that initially the particulate rain is carbonate-rich and gradually switches to be opal rich. (b) CaCO₃ particulate rain vs bio-SiO₂ particulate rain. There is a positive but nonlinear correlation between them.

Figure 3: Ba particulate rain in the equatorial Pacific compared to other biogenic fluxes, in sediment traps from 2000 m from the JGOFS equatorial Pacific study (Honjo et al, 1995; Dymond and Collier, 1996). Open circles are data from individual 17-day trap cups, while large closed circles mark median mooring values for the 1992 deployment. (a) Ba vs C_{org} particulate rain, showing a strong but nonlinear relationship between the two. (b) CaCO₃ vs Ba particulate rain, indicating a scattered but positive correlation. (c) CaCO₃/BaSO₄ ratio (assuming all Ba is BaSO₄) against C_{org} particulate rain. If the ratio were relatively constant, then there would be a simple transformation from Ba burial to initial CaCO₃ deposition at the sea floor. However, high export production (C_{org} rain)

correlates with higher $\text{CaCO}_3/\text{BaSO}_4$

Figure 4: The age depth model for Site U1338 used in this paper, based on the Backman and Baldauf (personal communication) piecewise linear age model produced after drilling by correlating the upper U1338 CaCO_3 profile to ODP Site 849 to use the Mix et al (1995) age model for 0-5.25 Ma. The Backman-Baldauf age model is a piecewise linear age model using a cleaned set of 33 paleomagnetic, 33 calcareous nannofossil, and 72 diatom event ages assigned by the event chronology presented by IODP 320/321 Scientists (2010 b). Shown in this figure are all the chronostratigraphic data from Site U1338 (IODP 320/321 Scientists (2010 a). See text for more details.

Figure 5: Benthic oxygen isotope records for the Neogene (top), compared to Site U1338 bulk chemical profiles for 16-0 Ma. Benthic isotopes are from from Mix et al (1995; Site 849), Shackleton et al, (1995, Site 846), Westerhold et al, (2005, Site 1085), and Holbourn et al. (2014, Site U1338). Below the isotope records are the percentages of $\text{CaCO}_3\%$ (red, 2nd from top), Opal% (blue, 3rd from top), $\text{BaSO}_4\%$ (green, 4th from top), and Clay% (grey, bottom). The background shading marks the depositional regimes discussed in the text.

Figure 6: Comparison of the Site U1338 16-0 Ma $\text{CaCO}_3\%$ profile (red, top), with 4 proxies for paleoproductivity: Opal/Clay (blue, 2nd from top) Opal/ BaSO_4 (purple, 3rd from top), $\text{BaSO}_4/\text{TiO}_2$ (green, 4th from top), and $\text{Al}_2\text{O}_3/\text{TiO}_2$ (black, bottom). The background shading reflects the >13.2 Ma, 13.2-8 Ma, 8-4.5 Ma, and <4.5 Ma depositional regimes discussed in this paper. The different paleoproductivity proxies typically agree when high production occurred.

Figure 7: Comparison of the Site U1338 16-0 Ma $\text{CaCO}_3\%$ profile (red, top), to $\text{CaCO}_3/\text{BaSO}_4$ (purple, middle), and $\text{CaCO}_3/\text{clay}$ (brown, bottom). Intervals of production based on opal/clay are indicated in vertical purple bars. Intervals of dissolution, where $\text{CaCO}_3/\text{clay}$ is <10, are indicated by light brown vertical bars. High opal production intervals, where opal/clay >8 (Figure 6) have been marked by lavender bars. Two small intervals that have both CaCO_3 dissolution and high opal production are marked by light blue. Most of the dissolution intervals are concentrated in the late Carbonate Crash substage and the Pliocene-Modern Regime..

Figure 8: Comparison of the U1338 16-0 Ma Opal% profile (light blue, top), with the opal/clay production proxy (dark blue, 2nd from top), total diatom valves per gram sediment (purple, 3rd from top), Radiolarians specimens per gram sediment (red, 4th from top), and Silicoflagellates specimens per gram sediment (gray, bottom). Highest diatom radiolarian and silicoflagellate numbers are found during the Biogenic Bloom regime.

Figure 9: Comparison for the 16-0 Ma at Site U1338 of the opal/clay profile (dark blue, top) to total diatoms (valves per gram sediment (purple, 2nd from top) with individual species ratios. A ratio is the valves of the species divided by the total other diatom valves. The ratios for *T. longissima* (green, 3rd from top), *T. nitzschoides* (brown, 4th from top), *T. nitzschoides* var. *parva* (purple, 4th from top), and *A. nodulifera* (red, bottom) differs from a percentage in that it is the abundance (valves/g sediment) of the species divided by the

sum of the abundance of the other diatom species, not divided by the total diatom abundance.

Figure 10: Comparison of Opal mass accumulation rates (MAR) (mg/cm²/kyr [black]) with accumulation rates (AR) for total diatoms (diatom AR #/cm²/kyr) (olive), and the diatom species/varieties *A. nodulifera* (red), *T. nitzschioides* var. *parva* (purple), *T. nitzschioides* (green), and *T. longissima* (brown) for 16-0 Ma at Site U1338.

Figure 11: Comparison of 16-0 Ma profiles at Site U1338 of CaCO₃% (red, top), CaCO₃ MAR (mg/cm²/kyr; maroon, 2nd from top), CaCO₃/clay (orange, 3rd from top), and CaCO₃/BaSO₄ (purple, bottom). Dissolution is apparent with low ratios and MAR in the late Carbonate Crash substage and in the Pliocene-Modern Regime.

Figure 12: Comparison of three 1.5 Myr time slices from the U1338 record. Top panel is from 0-1.5 Ma (Pliocene-Modern Regime), while middle panel is from 6-7.5 Ma from the Biogenic Bloom Regime. The bottom panel is the time interval 10-11.5 Ma from the early Carbonate Crash substage. In each panel CaCO₃% is the red curve and Opal/Clay is the dark green profile. The eccentricity change (light gray) is also shown in each panel to illustrate orbital pacing. Opal production as illustrated by opal/clay is in synchrony with the CaCO₃ cycles in the 0-1.5 Ma panel. In contrast, high opal production dilutes CaCO₃ in the two older intervals.

Lyle and Baldauf Figure 1. Location of IODP site U1338 in the eastern equatorial Pacific with a hotspot reference site backtrack for the Pacific plate (Lyle, 1997) and with bathymetry from GeoMapApp (Geomapapp.org). Other plate motion models leave U1338 within 0.5° of the equator at 11 Ma.

Lyle and Baldauf Figure 2: Comparison of biogenic fluxes from JGOFS tropical sediment trap experiments from sediment traps in the 2000-2500 m range. Data from Honjo et al (1995, 1999). All fluxes are in mg/cm²/kyr. (a) CaCO₃ particulate rain (reds) and bio-SiO₂ (opal) in purples vs Corg rain (export production to 2000 m). Opal fluxes increase more rapidly than the export flux of Corg, while CaCO₃ fluxes increase slightly less. The result is that initially the particulate rain is carbonate-rich and gradually switches to be opal rich. (b) CaCO₃ particulate rain vs bio-SiO₂ particulate rain. There is a positive but nonlinear correlation between them.

Lyle and Baldauf Figure 3: Ba particulate rain in the equatorial Pacific compared to other biogenic fluxes, in sediment traps from 2000 m from the JGOFS equatorial Pacific study (Honjo et al, 1995; Dymond and Collier, 1996). Open circles are data from individual 17-day trap cups, while large closed circles mark median mooring values for the 1992 deployment. (a) Ba vs C_{org} particulate rain, showing a strong but nonlinear relationship between the two. (b) CaCO₃ vs Ba particulate rain, indicating a scattered but positive correlation. (c) CaCO₃/BaSO₄ ratio (assuming all Ba is BaSO₄) against C_{org} particulate rain. If the ratio were relatively constant, then there would be a simple transformation from Ba burial to initial CaCO₃ deposition at the sea floor. However, high export production (C_{org} rain) correlates with higher CaCO₃/BaSO₄

Lyle and Baldauf Figure 4: The age depth model for Site U1338 used in this paper, based on the Backman and Baldauf (personal communication) piecewise linear age model produced after drilling by correlating the upper U1338 CaCO₃ profile to ODP Site 849 to use the Mix et al (1995) age model for 0-5.25 Ma. The Backman-Baldauf age model is a piecewise linear age model using a cleaned set of 33 paleomagnetic, 33 calcareous nannofossil, and 72 diatom event ages assigned by the event chronology presented by IODP 320/321 Scientists (2010 b). Shown in this figure are all the chronostratigraphic data from Site U1338 (IODP 320/321 Scientists (2010 a). See text for more details.

Lyle and Baldauf Figure 5: Benthic oxygen isotope records for the Neogene (top), compared to Site U1338 bulk chemical profiles for 16-0 Ma. Benthic isotopes are from from Mix et al (1995; Site 849), Shackleton et al, (1995, Site 846), Westerhold et al, (2005, Site 1085), and Holboun et al. (2013, Site U1338). Below the isotope records are the percentages of CaCO₃% (red, 2nd from top), Opal% (blue, 3rd from top), BaSO₄% (green, 4th from top), and Clay% (grey, bottom). The background shading marks the depositional regimes discussed in the text

Lyle and Baldauf Figure 6: Comparison of the Site U1338 16-0 Ma CaCO₃% profile (red, top), with 4 proxies for paleoproductivity: Opal/Clay (blue, 2nd from top) Opal/BaSO₄ (purple, 3rd from top), BaSO₄/TiO₂ (green, 4th from top), and AL₂O₃/TiO₂ (black, bottom). The background shading reflects the >13.2 Ma, 13.2-8 Ma, 8-4.5 Ma, and <4.5 Ma depositional regimes discussed in this paper. The different paleoproductivity proxies typically agree when high production occurred.

Lyle and Baldauf Figure 7: Comparison of the Site U1338 16-0 Ma $\text{CaCO}_3\%$ profile (red, top), to $\text{CaCO}_3/\text{BaSO}_4$ (purple, middle), and $\text{CaCO}_3/\text{clay}$ (brown, bottom). Intervals of production based on opal/clay are indicated in vertical purple bars. Intervals of dissolution, where $\text{CaCO}_3/\text{clay}$ is < 10 , are indicated by light brown vertical bars. High opal production intervals, where opal/clay > 8 (Figure 6) have been marked by lavender bars. Two small intervals that have both CaCO_3 dissolution and high opal production are marked by light blue. Most of the dissolution intervals are concentrated in the late Carbonate Crash substage and the Pre-Modern Ocean Regime..

Lyle and Baldauf Figure 8: Comparison of the U1338 16-0 Ma Opal% profile (light blue, top), with the opal/clay production proxy (dark blue, 2nd from top), total diatom valves per gram sediment (purple, 3rd from top), Radiolarians specimens per gram sediment (red, 4th from top), and Silicoflagellates specimens per gram sediment (gray, bottom). Highest diatom radiolarian and silicoflagellate numbers are found during the Biogenic Bloom regime.

Lyle and Baldauf Figure 9: Comparison for the 16-0 Ma at Site U1338 of the opal/clay profile (dark blue, top) to total diatoms (valves per gram sediment (purple, 2nd from top) with individual species ratios. A ratio is the valves of the species divided by the total other diatom valves. The ratios for *T. longissima* (green, 3rd from top), *T. nitzschoides* (brown, 4th from top), *T. nitzschoides* var. *parva* (purple, 4th from top), and *A. nodulifera* (red, bottom) differs from a percentage in that it is the abundance (valves/g sediment) of the species divided by the sum of the abundance of the other diatom species, not divided by the total diatom abundance.

Lyle and Baldauf Figure 10: Comparison of Opal mass accumulation rates (MAR) (mg/cm²/kyr [black]) with accumulation rates (AR) for total diatoms (diatom AR #/cm²/kyr) (olive), and the diatom species/varieties *A. nodulifera* (red), *T. nitzschoides* var. *parva* (purple), *T. nitzschoides* (green), and *T. longissima* (brown) for 16-0 Ma at Site U1338.

Lyle and Baldauf Figure 11: Comparison of 16-0 Ma profiles at Site U1338 of CaCO₃% (red, top), CaCO₃ MAR (mg/cm²/kyr; maroon, 2nd from top), CaCO₃/clay (orange, 3rd from top), and CaCO₃/BaSO₄ (purple, bottom). Dissolution is apparent with low ratios and MAR in the late Carbonate Crash substage and in the Pre-Modern Ocean Regime.

Lyle and Baldauf Figure 12: Comparison of three 1.5 Myr time slices from the U1338 record. Top panel is from 0-1.5 Ma (Pliocene-Modern Regime), while middle panel is from 6-7.5 Ma from the Biogenic Bloom Regime. The bottom panel is the time interval 10-11.5 Ma from the early Carbonate Crash substage. In each panel $\text{CaCO}_3\%$ is the red curve and Opal/Clay is the dark green profile. The eccentricity change (light gray) is also shown in each panel to illustrate orbital pacing. Opal production as illustrated by opal/clay is in synchrony with the CaCO_3 cycles in the 0-1.5 Ma panel. In contrast, high opal production dilutes CaCO_3 in the two older intervals.