High-resolution record of export production in the eastern equatorial Pacific across the Eocene-Oligocene transition and relationships to global climatic records

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[1] Understanding changes in export production through time provides insight into the response of the biological pump to global climate change, particularly during periods of rapid climate change. In this study we consider what role changes in export production may have had on carbon sequestration and how this may have contributed to the onset of the Eocene-Oligocene transition (EOT). In addition, we consider if these export production variations are dominantly controlled by orbitally driven climate variability. To accomplish these objectives, we report changes in export production in the Eastern Equatorial Pacific (EEP) from Site U1333 across the EOT reconstructed from a high-resolution record of marine barite accumulation rates (BAR). BAR fluctuations suggest synchronous declines in export production associated with the two-step increases in oxygen isotopes that define the transition. The reduction in productivity across the EOT suggests that the biological pump did not contribute to carbon sequestration and the cooling over this transition. We also report a previously undocumented peak in EEP export productivity before the EOT onset. This peak is consistent with export production proxies from the Southern Ocean, potentially implying a global driver for this precursor event. We propose that this enhanced export production and the associated carbon sequestration in the late Eocene may have contributed to the pCO2 drawdown at the onset of Antarctic glaciation.

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1. Introduction

[2] The Eocene Oligocene transition (EOT) represents a time where a dramatic change from “greenhouse” to “icehouse” conditions occurred [Zachos et al., 2001; Cramer et al., 2009] with the onset of sustained Antarctic glaciation as evidenced by the shifts in benthic foraminifera oxygen isotope records [Miller et al., 1987; Miller et al., 2005; Zachos et al., 2001; Cramer et al., 2009]. The oxygen isotope record, along with Mg/Ca data, also indicates cooler deep water and surface water temperatures during the early Oligocene compared to the late Eocene [Coxall et al., 2005; Lear et al., 2008; Bohaty et al., 2012]. Additional changes including deepening of the calcite compensation depth (CCD) [Coxall et al., 2005; Rea and Lyle, 2005; Lyle et al., 2005; Lyle et al., 2008], changes in ocean circulation [Huber and Nof, 2006], aridification of continents [Dupont-Nivet et al., 2007], changes in weathering intensity [Ravizza and Peucker-Ehrenbrink, 2003], and major ecosystem shifts [Nilsen et al., 2003; Falkowski et al., 2004; Coxall et al., 2005; Zachos and Kump, 2005; Merico et al., 2008]. Changes in ocean productivity [Diester-Haass, 1995; Diester-Haass and Zahn, 2001; Diester-Haass and Zachos, 2003; Schumacher and Lazarus, 2004; Anderson and Delaney, 2005; Coxall and Wilson, 2011], export production [Diester-Haass and Zahn, 1996; Salamy and Zachos, 1999; Latimer and Filippelli, 2002; Griffith et al., 2010] and the organic to inorganic carbon burial ratio [Griffith et al., 2010] have also been observed at this time interval.

[3] Oxygen and carbon isotope records in foraminifera and high-resolution orbitally tuned stratigraphy indicate that the transition from Eocene greenhouse conditions to Oligocene icehouse conditions occurred as two distinct steps [Coxall et al., 2005; Katz et al., 2008]. The first major isotopic shift, a −0.6‰ δ18O positive excursion, started at 34 Ma (EOT-1), and took place over ~200 kyr [Katz et al., 2008; Coxall and Wilson, 2011]. The second major shift,
Katz et al. (2008) noted that temperature declines with little ice growth and a sea level drop of 50 m. Coxall and Wilson (2011) have postulated as a carbon sequestration mechanism across potential associated increases in export production, has also been widely used to reconstruct changes in export production and ecosystem structure across the globe [Dunkley Jones et al., 2008; Katz et al., 2008] and continental shelf environments [Katz et al., 2008] and is also observed in CCD records [Coxall et al., 2005; Coxall and Wilson, 2011].

The first isotopic shift, EOT-1, was driven primarily by temperature declines with little ice growth [Lear et al., 2008; Katz et al., 2008] culminating in a 20 m sea level drop [Houben et al., 2012]. The second shift, Eo-1, represents rapid and lasting ice growth in Antarctica [Zachos et al., 1999; Zachos et al., 2001; Ivany et al., 2006; Coxall and Pearson, 2007] and a sea level drop of 50–60 m. It has been suggested that the sea level drop exposed fresh rocks, the erosion of which reduced pCO2 providing a positive feedback to the cooling [Merico et al., 2008]. In addition, orbital parameters were favorable at this time for ice formation [Coxall et al., 2005; Merico et al., 2008].

The above observations, as well as a 1% positive excursion in benthic δ13C [Coxall et al., 2005; Coxall and Wilson, 2011] and a possible decrease in atmospheric pCO2 [Pearson et al., 2009; see also Pagani et al., 2011] at this time interval suggest that the carbon system played an important role in the transition. Indeed, modeling studies have proposed CO2 changes as a driver for Antarctic glaciation [Deconto et al., 2008; Liu et al., 2009; Tiggelaar et al., 2010]. However, the exact mechanisms linking specific C cycle responses and feedbacks to the observed climatic changes are still enigmatic and several processes and links have been suggested. These include changes in silicate weathering [Ravizza and Peucker-Ehrenbrink, 2003] and river inputs [Salamy and Zachos, 1999; Rea and Lyle, 2005; Merico et al., 2008], changes in deposition loci of carbonates [Coxall et al., 2005; Merico et al., 2008], changes in ocean ventilation [Miller et al., 2009], changes in the terrestrial biosphere [Salamy and Zachos, 1999], and changes in ecosystem structure and marine organic matter export and burial [Ravizza and Paquay, 2008; Miller et al., 2009]. Enhanced productivity, and the potential associated increases in export production, has also been postulated as a carbon sequestration mechanism across this transition [Schier and Martin, 2006, 2008; Pearson et al., 2009; Coxall and Wilson, 2011].

When considering these changes within the larger context of the Late Eocene, we see additional events of changing ocean chemistry and export productivity. Carbonate accumulation events (CAEs) represent periods of intermittently higher rates of carbonate accumulation resulting from changes in the CCD [Lyle et al., 2005]. These events, while smaller and not permanent as the changes during the EOT, also illustrate the climatically dynamic nature of this period.

Changes in ocean productivity, ecosystem structure, and export production can precipitate from changes in temperature, CO2, nutrient availability, and nutrient stoichiometry related to climate conditions, atmospheric composition, and climatically induced circulation changes [Sarmiento and Toggweiler, 1984; Broecker and Henderson, 1998]. In turn, changes in upwelling and export production can serve as feedbacks to the climate system by increasing the efflux of sequestration of C, respectively [Archer et al., 2000; Diester-Haass and Zahn, 2001; Takahashi et al., 2009]. Many studies have documented the response of the oceanic biosphere to changes across the EOT; changes in primary production, export production, and ecosystem structure have been documented but most records are not of high resolution and interpretations based on different proxies are inconsistent.

The purpose of this study is to determine what, if any, role changes in export production may have played in the drawdown of carbon and the potential contribution of increased export production to the climate changes observed at the EOT. In addition, we examine if changes in export production are driven by orbitally based climate cycles or if other drivers may be contributing to these changes. To more closely relate climate changes reflected in the oxygen isotope record and marine export production records in the Eastern Equatorial Pacific (EEP), we obtain BAR records over <8 million years bunding the EOT (39.59–31.78 Ma) with high-resolution sampling between 35 and 32 Ma to emphasize changes during the cooling and glaciation events (EOT-1 and Eo-1).

## 2. Methods

### 2.1. Sample Location and Collection

Samples from IODP Site U1333, Expedition 320 Pacific Equatorial Age Transect [Pälike et al., 2009] were used for this study. This site (10°31'N, 138°25'W, 4853 m modern water depth) (Figure 1) was at a paleo latitude of ~3°N during the EOT, placing it at the edge of the present day equatorial high-productivity zone. Three holes were drilled at this location, allowing for a record with no significant gaps or hiatuses. Samples used for this study are listed in Table S1 in the supplemental materials.

### 2.2. Barite Separation

Marine barite (BaSO4), a common, albeit minor, component of marine sediments, is abundant in sediments underlying areas of high productivity [e.g., Church, 1970; Paytan and Griffith, 2007]. A strong correlation between BAR and organic C export has been observed in core top sediments [Paytan et al., 1996; Eagle et al., 2003]. Assuming the processes that govern barite formation and preservation remained similar through time, changes in BAR reflect variations in export production. Indeed, BAR and excess Ba have been widely used to reconstruct changes in export production through time [Schnitz, 1987; Rutsch et al., 1995; Paytan et al., 1996; Dean et al., 1997; Nürnberg et al., 1997; Bonn et al., 1998; Bains et al., 2000; Martinez-Ruiz et al., 2003; Averyt and Paytan, 2004; Jaccard et al., 2005; Oliwére Lyle and Lyle, 2006; Griffith et al., 2010].

Approximately 20 grams of dry, homogenized sediment was used for barite separation. A sequential leaching procedure [Paytan et al., 1996] was employed to remove all sedimentary fractions except barite and a small amount of other resistant minerals. Barite recovery for this process is typically better than 90% [Eagle et al., 2003] and the consistency of stratigraphically closely spaced samples reinforces the vigor of this method. All samples were screened using a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDAX) to verify sample purity, with all but three samples in this study being >99% pure barite.
2.3. Age Models and Accumulation Rates

The generation of barite accumulation rates from raw percent barite data is achieved by multiplying barite contents by mass accumulation rates. Accumulation rate fluxes in turn require linear sedimentation rates and dry bulk densities as input parameters. Thus a carefully constructed age model is important, as it determines the linear sedimentation rates. While awaiting a pending astronomical age calibration for Site U1333, we have applied the following strategy to generate two age model versions for U1333. First, we apply a paleomagnetic age model to Site U1333 based on shipboard paleomagnetic reversals and corresponding ages that were developed as part of IODP Expeditions 320 and 321 [Pälike et al., 2010]. These paleomagnetic reversal ages are based on those derived from ODP Sites 1218 and 1219 by astronomical tuning and stratigraphic correlation [Pälike et al., 2006] but are linearly interpolated between magnetic reversals. We put physical property data from Sites 1218 and U1333 on a common age model by using the detailed stratigraphic site-to-site correlation developed by Westerhold et al. [2012]. The work of Westerhold et al. [2012] places Site U1333 and Site 1218 on a common depth scale, allowing for comparison between the two records at decimeter resolution. In addition, we apply the detailed orbital age calibration previously provided for Site 1218 [Coxall et al., 2005; Coxall and Wilson, 2011; Pälike et al., 2006] to Site U1333 using this correlation, allowing for comparison of a lower-resolution paleomagnetic age model and one that is orbitally calibrated for the late Eocene and Oligocene. Accumulation rates were calculated using linear sedimentation rates based on the above age models and shipboard measured dry bulk densities (Table S1). This sedimentation rate was smoothed between major climate shifts to minimize the potential of sharp sedimentation rate changes generating artificial peaks in the BAR record. Figure S1 in the supplemental materials shows a comparison of linear sedimentation rates, barite content, and barite accumulation rates for these two age model versions. Since BAR is a direct function of linear sedimentation rates and thus the chosen age model (as well as bulk densities), it is important to evaluate the potential influence of age model choice. We note that barite content (which is independent from the age model chosen) tends to be higher when sedimentation rates are lower and vice versa. This observation suggests that the resulting BAR variations are not amplified or muted by changes in the sedimentation rate used.

2.4. Spectral Analysis

To determine the temporal relationships between the BAR record and global orbitally controlled climatic changes, the BAR record was analyzed for orbital periodicity. In addition, this record was compared for coherency and phase relationships with magnetic susceptibility and density records from the same core, which have been suggested to vary with orbital frequency [Hovan et al., 1989; Barthes et al., 1999]. We also compare the record to time equivalent δ18O and δ13C records from Site 1218. Site 1218 was used because analysis of benthic foraminifera data from Site U1333 is not yet completed. To deconstruct time-dependent variability in spectral characteristics, we applied cross-spectral wavelet analysis techniques [Torrence and Compo, 1998; Maraun et al., 2007]. This method requires resampling of the BAR record onto the higher-resolution δ18O record from Site 1218.

Throughout the entire record, sample spacing allows us to identify potential 405 kyr cycles (or any longer time frame periodicity), and this observation should be robust even with an age model based on paleomagnetic reversals. The concentration of sampling in the time period surrounding the EOT (5–20 kyr spacing from 32 to 36 Ma) also enables resolving the possibility for 96 and 126 kyr and potentially 41 kyr cycles at select time periods (i.e., the earliest Oligocene). Higher-resolution cycles currently cannot be resolved at the sampling resolution. As a result, the focus of the analysis is on eccentricity cycles and their relation to BAR.

3. Results

Our data is generally consistent with previous observations of BAR in the EEP [Griffith et al., 2010, Figure 2]
showing overall higher BAR in the late Eocene (39.59–33.8 Ma average 1.0 mg cm⁻² kyr⁻¹) compared to the early Oligocene (33.8–31.78 Ma average 0.49 mg cm⁻² kyr⁻¹). However, our higher-resolution data provides considerably more detail and reveals previously unrecognized features (Figures 2 and 3), specifically a close correspondence between BAR and existing proxy records observed across the E/O transition is observed.

[16] Between 39.59 and 35 Ma the BAR record oscillates between 0.17 and 1.9 mg cm⁻² kyr⁻¹. Just prior to the EOT, between 35 and 34.2 Ma, BAR fluctuate between 0.6 and 1.3 mg cm⁻² kyr⁻¹ with an average of 0.9 mg cm⁻² kyr⁻¹. However, at 34.20 Ma, a relatively rapid increase in BAR taking place over ~90 kyr is observed. This increase peaks at 34.11 Ma (e.g., prior to EOT-1) with a BAR of 2.08 mg cm⁻² kyr⁻¹ (double pre-excursion). The high BAR is maintained for ~38 kyr before it declines over 75 kyr and returns to pre-peak values of ~0.88 mg cm⁻² kyr⁻¹. This BAR event from the start of the increase to return to pre-peak values spans ~200 kyr and terminates during EOT-1 (34.0 Ma). A small increase in BAR from 0.9 to 1.23 mg cm⁻² kyr⁻¹ is observed right after EOT-1 and throughout the 300 kyr between EOT-1 and Oi-1 BAR fluctuates between 0.51 and 1.36 mg cm⁻² kyr⁻¹. A pronounced drop to 0.06 mg cm⁻² kyr⁻¹ is seen at Oi-1 (33.7 Ma) after which BAR is maintained at low values (0.05–0.48 mg cm⁻² kyr⁻¹) until 33.44 Ma. BAR slightly increases to 0.90 mg cm⁻² kyr⁻¹ at Oi-1b, declining to 0.07 mg cm⁻² kyr⁻¹ by 33.2 Ma. The BAR remains lower in the early Oligocene compared to the late Eocene, averaging 0.58 mg cm⁻² kyr⁻¹, about half the average late Eocene BAR. These BAR values correspond to export production rates varying between a low of 13 gC m⁻² yr⁻¹ in the early Oligocene to and a peak of 16 gC m⁻² yr⁻¹ during the late Eocene based on present day core top calibrations obtained from this region [Paytan et al., 1996; Eagle et al., 2003] (Figure 2).

[17] Wavelet analysis of the BAR data (Figures 4a and 5a) allows identification of orbital signals, particularly at the ~100 kyr and ~405 kyr orbital eccentricity periods, but also at the obliquity (~41 kyr) period where the sample spacing is high enough (e.g., the earliest Oligocene). Throughout the record, the BAR shows power at the 405 kyr long-term eccentricity cycle, along with intermittent power in the 96 and 126 kyr shorter-term eccentricity cycles during periods of sufficient sampling frequency (Figure 4a). These shorter-term eccentricity cycles are observed between 38.2 and 39.5 Ma, 35.7 and 37 Ma, and 32 and 34.5 Ma. Obliquity (41 kyr) cycles are also alluded to during these intervals, though with less power than the longer period cycles. Overall, the 405-kyr cycle is the dominant driver throughout the record in both strength and continuity. In addition, the periodicity extends into longer period cycles (e.g., ~750 kyr) not directly related to defined orbital cycles.

[16] While these trends, in particular the eccentricity cycles, are strongest during time periods of highest sample resolution, i.e., 33–35 Ma, they are present throughout the record. This leads us to conclude that sampling resolution is not driving their presence or absence during this period. Since the sampling resolution during the lower resolution sections of the core averages 75 kyr while the high-resolution sections average 5–10 kyr, the 405 kyr cycles are significant throughout the record while cycles with periods of 41 kyr are only captured during high sampling resolution intervals.

[19] The 405 kyr and longer cycles are also seen in the bulk density and magnetic susceptibility records reported by Pälike et al. [2009] (Figure 4), though these signals are not as dominant as in the BAR records. The bulk density and magnetic susceptibility records can be used as proxies for carbonate content [Ortiz et al., 1999], and the comparison with the BAR allows us to identify relationships with carbonate content and compensation depth and related changes in the carbon cycle. In addition, since these records are all from the same set of cores, a direct comparison can be made for the entire data set without the correlation problems inherent in a comparison between samples from different locations.

[20] Overall trends and the coherence between BAR and the bulk density and magnetic susceptibility records were evaluated. When considering these data sets temporally, we see relatively stable values for density and magnetic susceptibility from ~38 Ma to ~34 Ma with the two sharp changes at EOT-1 and Oi-1 clearly captured. In addition, both bulk density and magnetic susceptibility are coherent with the BAR
at the 405 kyr power between ~34.5 Ma and 33.5 Ma, after the Oi-1 boundary (Figure 4b). Throughout the reminder of the record, coherency is only observed intermittently at the ~100 kyr shorter-term eccentricity cycles. The BAR and bulk density records are strongly in phase during all coherent periods from 40 Ma until 33.5 Ma, while the BAR and magnetic susceptibility show more variability (Figure 4c). The interval between 35 and 33.7 Ma corresponds to the section with higher data resolution in the BAR record and it is possible that the limited coherence outside this interval is a consequence of the lower sampling resolution. In addition, the high degree of coherence during this interval is likely tied to the predominance of the large stepwise shifts in both records at the EOT-1 and Oi-1. The reduction in cyclicity in the magnetic susceptibility records outside of this time period is another potential influence limiting coherency.

[21] A strong relationship between BAR and the oxygen and carbon isotopes records from site 1218 is observed at both long and short time scales (Figure 3 and Figure 5). Overall, the major isotope shifts marking the EOT-1 and Oi-1 are clearly observed in the barite record. The positive shifts in the isotope records, associated with cooling and glaciations, correspond to reductions in BAR. This relationship is best illustrated at Oi-1, where the $\delta^{18}O$ undergoes a 1% increase and BAR is reduced by 95% from ~1 mg cm$^{-2}$ kyr$^{-1}$ to ~0.05 mg cm$^{-2}$ kyr$^{-1}$.

[22] A clear peak is observed in the BAR record prior to the EOT, corresponding to a period of potentially large shifts in pCO$_2$. When compared to the Pearson et al. [2009] pCO$_2$ reconstruction, the peak in pCO$_2$ observed just prior to the EOT, roughly corresponds to the rise and decline in BAR. The Pagani et al. [2011] record, however, does not show the pre-EOT pCO$_2$ peak. The resolution of the pCO$_2$ data sets is very coarse, and differences between the two records may reflect the capture of smaller-scale changes or age model differences. While the low-resolution...
nature of these two records does not allow for a direct comparison to the shifts observed in the BAR record, it is clear that the EOT is a time of large changes in global climate and the carbon cycle potentially impacting global and regional ocean productivity.

Since accurate calculation of accumulation rates is a critical component to this record, BAR was calculated using two age models, Site U1333 paleomagnetism ages and Site 1218 tuned ages from Coxall and Wilson [2011] (supplemental material). BAR calculated using each of these age models show very similar features, with all significant peaks and declines represented. The absolute ages of the transitions are slightly different between the model, with the decline at EOT-1 beginning ~100 kyr later using the 1218 age model and occurring over a longer time frame. The initiations of the export production peak preceding EOT-1, and the transition at Oi-1, occur at the same time regardless of the age model and associated sedimentation rate used. Since each independent age model results in the same overall character for the BAR record, we do not believe that age model related errors and uncertainties are driving the observed features.

4. Discussion

One of the mechanisms proposed as contributing to the cooling and glaciation observed at the EOT is an increase in export production, sequestering C and reducing atmospheric pCO₂ [Scher and Martin, 2006]. Previous studies exploring productivity and export production across the EOT have utilized a variety of proxies including changes in diatom assemblages [Falkowski et al., 2004; Finkel et al., 2005; Finkel et al., 2007], benthic foraminifera accumulation rates (BFAR) [Coxall and Wilson, 2011], opal accumulation rates [Salamy and Zachos, 1999], P/Ti ratios [Latimer and Filippelli, 2002], and barium-based proxies such as Ba/Ti ratios [Latimer and Filippelli, 2002] and excess Ba [Anderson and Delaney, 2005]. These studies have generally shown productivity increases across the EOT in the equatorial Atlantic [Diester-Haass and Zachos, 2003], South Atlantic [Hartlet al., 1995], NW Australia [Diester-Haass and Zahn, 2001], and in some continental margin locations [Ravizza and Paquay, 2008]. In the Southern Ocean increased productivity at the EOT is evidenced by a rapid diversification of diatoms [Falkowski et al., 2004; Finkel et al., 2005, 2007], high opal accumulation rates [Salamy and Zachos, 1999], high P/Ti and Ba/Ti ratios [Latimer and Filippelli, 2002], and high Ba excess [Anderson and Delaney, 2005]. The exact timing of productivity increase varies depending on the site investigated and proxy used. For example, opal concentration increases only after Oi-1, while P/Ti and Ba excess increase gradually starting before EOT-1 [Latimer and Filippelli, 2002; Anderson and Delaney, 2005] (Figure 3).
Postulated causes for the increase in productivity include increased wind driven upwelling and/or increased input of dissolved nutrients during initial glaciation through erosion or eolian deposition [Diester-Haass and Zahn, 1996; Salamy and Zachos, 1999; Latimer and Filippelli, 2002; Miller et al., 2009]. Our BAR record from the EEP suggest considerable fluctuations in export production over the sampled time interval, particularly between 35 and 32 Ma. However, in contrast to records from the Atlantic and Southern Ocean our record shows a general decline in export production across the EOT, consistent with other BAR records for the Pacific [Griffith et al., 2010] (Figure 2).

In the present day ocean export production varies considerably spatially throughout the ocean, and it is not surprising that trends in export production at different ocean basins are decoupled. A potential mechanism to explain this decoupling calls for basin-specific changes in ocean circulation and mixing and the redistribution of the oceanic nutrient inventory among ocean basins rather than an overall global driver. Regional changes in ecosystem structure related to circulation induced nutrient availability and temperature changes would also result in changes in export production. Specifically, the establishment of deep mixing in the Southern Ocean and formation of intermediate and deep water sources originating in the Southern Ocean at the EOT can result in reorganization and redistribution of nutrient (and C) inventories and associated changes in export production may differ spatially in the ocean.

It is important to note that the Pacific is the largest ocean basin and the EEP in particular supports a significant proportion of export production (at present) and it is also responsible for a large fraction of the CO₂ efflux from the ocean to the atmosphere [Chavez and Toggweiler, 1995; Takahashi et al., 2009]; thus changes in export production in this basin may have a proportionally larger global impact. Accordingly, any estimate of global C cycle responses and feedbacks related to the EOT should take into account export production changes in the Pacific basin.

### 4.1. The Late Eocene: Priming the System

Export production at our site in the Late Eocene varied between 13 and 16 gC m⁻² y⁻¹, with an average of 14.4 gC m⁻². These values are at the lower range of export production observed in the modern equatorial Pacific Ocean. One potential explanation for these lower values is that the upwelling and high productivity belt along the equator was shifted southward at that time. This is consistent with the latitudinal gradient in BAR observed across the equator; BAR at Site U1333 located at ~3°C is up to approximately threefold lower than at Site 1218, located at 2°C, and up to approximately tenfold lower than at Site 574, located at paleo 1.3°C [Griffith et al., 2010; Moore and Kamikuri, 2012] (Figure 2).

BAR fluctuates between 0.5 and 1.5 mg cm⁻² kyr⁻¹ in the Late Eocene period until ~34.5 Ma, with a tendency toward higher BAR (increased export productivity) corresponding to warmer intervals as seen in the correlation with the oxygen isotope record (Figure 3). The oscillations in the BAR record correspond to the long-term (405 kyr) eccentricity cycle, implying that climatic drivers are impacting export production (our sampling resolution from 40 to 35 Ma is intermittently insufficient to capture higher-frequency cycles). In addition, long-term cycles at ~700 kyr are observed, though these are not directly tied to a particular known orbital oscillation.

The pronounced rise in BAR (from 0.8 to 2.1 mg cm⁻² kyr⁻¹) in the very latest Eocene, just before the onset of EOT-1 (between 34.2 and 34 Ma), suggests an increase in...
export production in the EEP. This increase corresponds to a time when the P/Ti and excess Ba records of the Southern Ocean (proxies of nutrient availability and export production, respectively) also show an increase [Latiner and Filippelli, 2002; Anderson and Delaney, 2005]. These concurrent increases in export productivity at both the Southern Ocean and the EEP suggest a common, possibly global, driving mechanism such as pCO2 or global temperature changes.

While the existing pCO2 record is data limited, the rise in pCO2 observed by Pearson et al. [2009] is roughly concurrent with the peak in BAR (Figure 3). However, this pCO2 peak is not observed in the Pagani et al. [2011] record until after EOT-1 a time when BAR drops. Since both pCO2 records are of relatively low resolution, it is difficult to directly link these smaller-scale shifts directly to productivity changes. Overall, however, the greater export production observed in the Eocene compared to the Oligocene in both the EEP BAR record and the Site 1090 Southern Ocean proxies [Anderson and Delaney, 2005] may relate to the overall higher pCO2 and higher temperatures during this interval. It has been suggested that high pCO2 could increase primary production [Doney et al., 2009] and impact ecosystem structure [Fabry et al., 2008; Hall-Spencer et al., 2008] and the warmer temperatures associated with this high pCO2 would enhance bacterial activity and degradation of organic matter to form marine barite.

The late Eocene export productivity peak is not captured in the benthic foraminifera accumulation rate记录 (BFAR) at nearby Site 1218. This discrepancy may result from selective preservation of foraminifera due to a shallow CCD with CaCO3 preservation of less than 75%, influencing the BFAR [Coxall and Wilson, 2011]. In addition, while dissolution horizons at Site 1218 impede a complete comparison, the peak in BAR (and potentially pCO2) does not correspond to any pronounced changes in the benthic foraminifera oxygen isotope record from Site 1218 or in the global benthic isotope compilation [Zachos et al., 2008] during this time (Figure 3). If anything, a small increase in δ18O (cooling) is seen despite the high pCO2, which would presumably induce a warming effect. This may indicate lower sensitivity of ocean temperatures to changing pCO2 in the Late Eocene prior to Antarctic glaciation compared to the present. The carbon isotopic record at Site 1218 changes toward more negative values during this interval, though the change in δ13C does not start until BAR has already peaked and the rate of the δ13C record following the BAR peak is obscured by the dissolution horizon. This relationship may indicate that BAR in the EEP (and the Southern Ocean) is responding to more global changes in the carbon system that impact the δ13C of the global ocean such as circulation and upwelling intensity changes [Scher and Martin, 2008; Thomas et al., 2008; Cramer et al., 2009; Pusz et al., 2011].

The Late Eocene peak in BAR, in conjunction with proxies from the Southern Ocean, is indicative of an increase in export production before the onset of EOT-1 and may have served as a feedback mechanism, reducing pCO2 and thus contributing to the conditions that precipitated the onset of the Oligocene glaciation. The high export production in both the EEP and the Southern Ocean together may have been sufficient to sequester enough C via the biological pump to be one of the many factors influencing pCO2. An increase in BAR from 0.8 to 2.1 mg cm^-2 kyr^-1 (corresponding to an increase in burial of 2.2 g C m^-2 d^-1) persisting over 200 krys in the equatorial Pacific high productivity region (area of 1.1 x 10^11 m^2) could account for the sequestration of ~2200 gigatons of carbon.

4.2. The Eocene Oligocene Transition and Early Oligocene Glaciation

Marine barite accumulation rates rapidly decline at the EOT and follow trends seen in the oxygen isotope record that is used to define EOT-1 and Oi-1. The two sharp declines in BAR are concurrent with the changes in the isotope and CCD records, indicating that BAR is responding directly or indirectly to the same climatic events that impacted the isotope and CCD records. The decline in export productivity at the EOT may be related to climatically induced changes in circulation at the onset of the Oligocene. Neodymium and C isotope records from the Southern Ocean indicate that with the onset of glaciation, deep mixing, and increased ventilation have developed [van de Flierdt et al., 2004; Via and Thomas, 2006; Scher and Martin, 2008; Thomas et al., 2008; Cramer et al., 2009; Pusz et al., 2011]. These circulation changes may have resulted in higher productivity and nutrient consumption in the Southern Ocean and low nutrient waters arriving to the EEP. In addition, the lower temperatures of subsurface waters that originated from the Southern Ocean may have increased stratification and reduced upwelling rates in the EEP, decreasing the delivery of nutrients to the surface waters and decreasing productivity [Miller et al., 2009]. Changes in nutrient stoichiometry may have also occurred inducing ecosystem changes impacting export production with relatively little change in net primary production [Boyd and Newton, 1999]. Finally, the lower temperatures at intermediate depths, where much of the organic matter is regenerated, may have lowered bacterial induced organic matter degradation and barite formation. This could increase the fraction of organic matter arriving at the sediment water interface.

Indeed, model results suggest that the uptake of nutrients in southern latitudes will limit available nutrient transport north, impacting productivity and export production at the EEP [Sarmiento et al., 2004]. This process is consistent with the observed latitudinal gradient in BAR (decreasing toward the north) [Griffiths et al., 2010]. Maximum BAR during EOT-1 is 0.2 mg cm^-2 kyr^-1 at Site 1209 (paleo 15°N), -2.5 mg cm^-2 kyr^-1 for Site U1333 (paleo 3°N), 3.5 mg cm^-2 kyr^-1 for Site 1218 (paleo 2°N), and 6.5 mg cm^-2 kyr^-1 for Site 574 (paleo 1.3°S) and, based on excess Ba, could be up to ~5 mg cm^-2 kyr^-1 in the Southern Ocean (Site 1090) [Anderson and Delaney, 2005].

In contrast to the decrease in export production implied by BAR during this transition, BFAR increases by twofold to threefold, suggesting an increase in the food supply to the sediment water interface [Coxall and Wilson, 2011]. However, as the BFAR prior to the EOT-1 is not reliable, it is hard to draw any conclusions about direction of change compared to the Late Eocene (the reported BFAR increase is in comparison to baseline Oligocene values after Oi-1). Moreover, the seeming lack of correspondence in trends between the records (e.g., BAR and BFAR) may not actually represent a disagreement among these proxies, since the proxies respond to different parameters. While BFAR corresponds to food or organic C input to the sediment water interface BAR represents the amount of C exported out of...
the surface layer and oxidized in the “twilight” zone (between 500 and 1500 m depth). If bacterial activity, responsible for organic matter degradation and barite formation in the water column during particle sinking, is less effective (due to cooling), it is conceivable that more organic matter actually arrives at the sediment water interface, resulting in a response of the benthic foraminifera. Alternatively, it is possible that the pool of organic matter that accumulated in the sediment during the high export productivity period in the Late Eocene was accessible to and supported the benthic foraminifera at least for some time following the decrease in export. It has also been suggested that the mode of transport of food to benthic foraminifera and the degree of benthic-pelagic coupling has changed at that time, complicating interpretation of the observed trends [Thomas and Gooday, 1996]. The low organic C accumulation rate in the sediment at that time is, however, consistent with low export production and low C burial [Pälike et al., 2009]. A general reduction in bulk sedimentation rates [Schmacher and Lazarus, 2004; Vanden Berg and Jarraud, 2004] also supports the observation of little to no increase in export production in the Equatorial and North Pacific across the EOT.

The low export production between 33.2 Ma and 33.7 Ma, spanning the period of cooling and glaciation, indicates that C sequestration by the oceanic biological pump did not contribute to lowering pCO2 at this time. This is consistent with the suggestion by Pagani et al. [2011] that changes in silicate weathering are required to explain the sustained reduction in pCO2 through the Oligocene.

After the EOT in the early Oligocene, low BAR implies sustained reductions in export production compared to the Eocene. Within this time period, the two glacial maxima associated with Oi-1a and Oi-1b may be differentiated and resolved in the BAR record, with Oi-1a representing the lowest BAR recorded during this study interval. While the variability increases after 33.2 Ma, export production remains low and does not return to the levels of the late Eocene. This change in the average rate of export production between the Eocene and Oligocene is consistent with a major long-lasting change in ocean biogeochemistry linked to the climatically induced oceanographic changes. This includes global temperature changes, changes in ocean circulation, and possibly changes in atmospheric greenhouse gas concentrations as well.

4.3. Relationships Between BAR and Climate Records

It is accepted that variations in the Earth’s orbit exert a profound influence on climate [Imbrie et al., 1992, 1993]. These changes have been previously captured in records of magnetic susceptibility and dry bulk density [Zachos et al., 2001] and are clearly shown in oxygen isotopic records [Coxall et al., 2005]. The 405-kyr long-term eccentricity cycles predominate in carbon isotopic records due to the long residence time of carbon in the oceans [Pälike et al., 2006] and commonly occur during times of unipolar glaciation in the pre-Pliocene [Woodruff and Savin, 1991; Flower and Kennett, 1993]. The ~100 kyr cycles predominate during glacial periods in the Pleistocene, responding specifically to Northern Hemisphere glaciation, and appear more sensitive to high-latitude variability [Ruddiman, 2006]. These eccentricity cycles are known to modulate the higher-frequency precessional cycles. While the effect of these changes in solar insulation on climate should be relatively insignificant [Berger et al., 1992], nonlinear responses can amplify the impact. These nonlinear responses can include internal feedbacks to the carbon cycle, ice sheet growth, and circulation [Imbrie et al., 1993].

Obliquity cycles (41 kyr) are prominent in benthic δ18O records from the early Oligocene and early Miocene [Pisias et al., 1985; Zachos et al., 1996], consistent with high-latitude controls on climate variability [Berger and Loutre, 1991; Paul et al., 2000]. These higher-resolution cycles, particularly obliquity (41 kyr) and precession (20 kyr) cycles, also modulate climate but are difficult to identify in paleoceanographic records without exceptionally high sedimentation rates and sampling frequencies not commonly found in pre-Pleistocene records. To determine the relationship between BAR and climate forcing, we analyzed each data set for orbital frequency and the relationships between BAR, magnetic susceptibility, bulk density, and time-matched oxygen and carbon isotopes (from Site 1218).

The 405 kyr eccentricity cycle is strongly observed in the BAR record (both in the low-resolution 40–35 Ma and higher-resolution 35–32 Ma parts of the record). This is consistent with the strength of the 405 kyr cycle observed through the Oligocene [Pälike et al., 2006]. The 126 and 96 kyr shorter-term eccentricity cycles are observed intermittently and are most clearly detected between 38.2 and 39.5 Ma, 35.7 and 37 Ma, and 32 and 34.5 Ma (Figure 4a). This strong orbital pacing indicates an overarching climatic control on the BAR and thus export productivity. This is consistent with other records showing climatically driven BAR variability [Paytan et al., 1996; Paytan and Griffith, 2007] and the reliance of productivity on climate influenced circulation and nutrient supplies, water column temperature changes, and greenhouse gas levels, though reliable records of the latter are not currently available to evaluate this. Finally, the variability in the barite record (order of magnitude changes) is stronger and more prevalent than that observed in the magnetic susceptibility and density records, which are both coarse proxies for carbonate weight percent. This indicates that barite is more sensitive than these records and is able to record climatic changes at locations where CCD variations are not observed.

Since the sampling frequency for magnetic susceptibility and density is high throughout the study interval, these records provide context for the BAR record, particularly between 34.5 and 40 Ma where the BAR record is of lower resolution. The dominant trends observed in the magnetic susceptibility and density records are the sharp changes at EOT-1 and Oi-1, along with the dramatic differences between the Eocene and Oligocene sections (Figure 4). This is consistent with known changes in the CCD over this time period [Lyle et al., 2005]. The magnetic susceptibility and density records also provide context for the high level of variability observed in the BAR record during carbonate accumulation event CAE-4. Swings in the BAR record may be driven by the same forces controlling the oscillations in the carbonate record through this interval. This is illustrated by the high level of coherence these records have during this time, particularly in the 96 kyr, 126 kyr, and 405 kyr frequencies (Figure 4b). In addition, phase relationship analysis through this interval (Figure 4c) shows that these covarying changes between the
density and BAR records are dominantly in-phase, implying a common driver.

[45] This enhanced coherence also appears during the remaining CAEs. All three records are coherent at a 96-kyr frequency during CAE-6 and appear in phase, while only the magnetic susceptibility and BAR results are coherent during CAE-5. While the sampling resolution throughout the record is high enough to observe the 405-kyr cycles, the higher sedimentation rates during these CAE events may contribute to the identification of these 96- and 126-kyr cycles. Finally, all three records are strongly coherent across the two major climatic steps, EOT-1 and Oi-1. This is likely driven by the magnitude of the shifts in each record, combined with the enhanced sampling frequency and high sedimentation rates as the record enters the Eocene. Phase relationships allow us to observe that the shifts in these data sets are contemporaneous, with BAR responding to the large climatic changes. The close relationship between BAR and carbonate proxies suggest that when carbonate is high BAR is also high, consistent with increases in productivity not only preservation or dilution impacts.

[46] Comparison of the BAR record of Site U1333 to the benthic foraminifera isotopic records of Site 1218 [Coxall and Wilson, 2011] provides more direct climate relationships during the time surrounding the EOT (Figure 5). While high-resolution relationships are more precarious when comparing cores of different locations, significant efforts in cross-correlation [Westerhold et al., 2012] provide confidence in these comparisons. Each of these records shows strong cyclicity at the 405-kyr frequency, especially across the EOT (Figure 5a). As a result, these records are coherent at the 405-kyr frequency throughout much of the highest resolution sampling interval between 33.4 and 34.5 Ma (Figure 5b). We observe some evidence of an increase in the shorter-term eccentricity cycles (96 and 126 kyr) directly after Oi-1. This could indicate a change in climate sensitivity, though it may also reflect the higher sedimentation rates and resulting sampling resolution across this interval. Coherency is not significant outside of these periods, implying that smaller-scale variations in BAR and oxygen are not in sync.

[47] Since the BAR and $\delta^{18}O$ records show strong statistically significant coherency, power, and an in-phase relationship at Oi-1 (Figures 5b and 5c), the BAR is likely dominantly controlled by the glacial onset indicated by the $\delta^{18}O$ record. Specifically, BAR sharply declines as $\delta^{18}O$ increases at the onset of glaciation. The comparison with the $\delta^{13}C$ also shows coherence at this time interval. Coxall et al. [2005] show that the $\delta^{13}C$ record lags the $\delta^{18}O$ record at the Oi-1 step. Therefore it is not surprising to see that the BAR, which is in phase with $\delta^{18}O$, is also out of phase with the $\delta^{13}C$ record at the shorter-term, and more sensitive, eccentricity and obliquity cycles. This suggests that the sharp decline in BAR at Oi-1 is controlled by glaciation-induced circulation changes at this time as recorded in the $\delta^{18}O$ record and not by global C cycle perturbations such as changes in vegetation, organic C burial, or atmospheric pCO$_2$. Finally, the data gap in the 1218 record preceding EOT-1 makes it difficult to definitively determine any relationships between BAR and the isotopic tracers during this gap period.

[48] To consider the temporal relations between export production and climate on a global scale, we compared BAR at Site U1333 to productivity records from Site 1218 in the EEP, Site 744 in the Indian sector of the Southern Ocean, and Site 1090 in the Atlantic sector of the Southern Ocean (Figure 3). While preservation issues limit comparisons of Site 1218 BFAR and Site 744 opal accumulation rates to the time period after Oi-1, Site 1090 provides a robust record throughout the study interval. We observe that multiple proxies, including Ba excess, opal accumulation rates, reactive P, and P/Ti ratios all suggest a rise in export production just before the onset of EOT-1. A gradual increase in export production initiates at 34.7 Ma, approximately 500 kyr before the rise in the Site U1333 BAR record. The increase intensifies with a sharp rise in the Southern Ocean export production proxies at 34.3 Ma, nearly contemporaneous with the BAR rise at 34.2 Ma and within the potential error of comparing two uncorrelated cores with different age models. This supports the conclusion of a global change in ocean chemistry potentially related to changes in pCO$_2$, increases in temperature, and/or circulation changes. This would provide more nutrients to these high productivity regions occurring in the latest Eocene. Overall, we see that the BAR record of export production at this time interval is supported by trends in other ocean basins and may correlate to global climatic cycles.

5. Conclusions

[49] Overall, we see that changes in export production proxies relate to changes in both climate and the carbon cycle across the study interval. The BAR record is responding to many of the major climatic shifts, particularly EOT-1 and Oi-1, that occur during this time period. We observe a strong 405-kyr long-term eccentricity cycle in the BAR record and intermittently observe shorter-term 125- and 96-kyr eccentricity cycles. This suggests that direct climatically driven changes such as temperature and pCO$_2$ and indirect changes such as circulation have impacted nutrient delivery and ecosystem structure in the EEP. Specifically, in the latest Eocene prior to EOT-1 a large peak in BAR is observed, consistent with Southern Ocean export production records. We believe that multiple occurrences of this export production increase point toward global forcing such as changes in temperature and/or pCO$_2$. We speculate that this peak in export productivity may have played a role in the greater carbon cycle through carbon sequestration, assisting in the drawdown of CO$_2$ thought to prime the system for EOT-1.

[50] When considering the larger record, we see evidence that regional circulation changes may have impacted nutrient fluxes and the resulting export production. We observe lower BAR in the more northern Site U1333 (3°N) than at Site 574 south of the Equator (1.3°S) throughout the record, implying a south to north transport and utilization of nutrients. In addition, Southern Ocean proxies show a larger and earlier increase in export production than the EEP. We propose that the well-documented circulation changes occurring across this time period [Scher and Martin, 2008; Thomas et al., 2008; Cramer et al., 2009; Pusz et al., 2011] may have impacted the regional transport of nutrients and influenced export production during the EOT.

[51] Overall, a combination of changes in both global climate and regional processes appear to impact export production in the EEP. Future work providing better constraint on the global pCO$_2$ record may allow us to discern causal relationships with export production, while additional records of
productivity and circulation in the Pacific Ocean may highlight interplay between these variables. Export production in the EEP appears to be sensitive to major climatic changes and continues to be an important tracer of ocean dynamics, particularly during periods of rapid climate change.

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