Top down and bottom up:
Testing the fidelity of two paleoproductivity proxies in the context of the late Miocene to early Pliocene "biogenic bloom"

PI: Katharina Billups, University of Delaware

Funded by: American Chemical Society – Petroleum Research Fund, 2005

Top down and bottom up: Testing the fidelity of two paleoproductivity proxies in the context of the late Miocene to early Pliocene "biogenic bloom"

Abstract

I propose to compare two paleoproductivity indicators recording "opposite" aspects of primary productivity, organic carbon production at the sea surface (coccolith Sr/Ca ratios) and its consumption on the sea floor (benthic foraminiferal accumulation rates, BFAR). Calcification and growth rates of coccolithophores can be linked to particulate organic matter production in the photic zone (Balch and Kilpatrick, 1996). Benthic foraminifera feed on particulate organic matter and thus respond to the flux of organic carbon reaching the deep ocean (Berger and Wefer, 1990). If coccolith calcification rates are indicative of surface ocean productivity as recorded in coccolith Sr/Ca, and a significant amount of the particulate organic matter makes it to the sea floor as recorded by BFAR, then a relationship should exist between coccolith Sr/Ca ratios and benthic foraminiferal accumulation rates. I will construct down-core coccolith Sr/Ca records to parallel down-core BFAR during the late Miocene to early Pliocene "biogenic bloom" interval. I have chosen this interval because there is benthic foraminiferal evidence for an increase in paleoproductivity; hence there is a signal. Each proxy has its own set of biological and biogeochemical controls, and consequently uncertainties. This study will test the applicability of the two proxies to paleoproductivity reconstructions on longer time scales in the face of these uncertainties. Results of this study are important to the Petroleum Research Fund because an improved understanding of these paleoproductivity proxies will be valuable to the reconstructions of primary marine productivity, the ultimate determinant of potential hydrocarbon resources.

Goal

To explore the coherence of two paleoproductivity indicators: Coccolith Sr/Ca ratios as a measure of algal growth and calcification rates at the sea surface and benthic foraminiferal accumulation rates as a measure of organic carbon consumption on the sea floor (Figure 1)

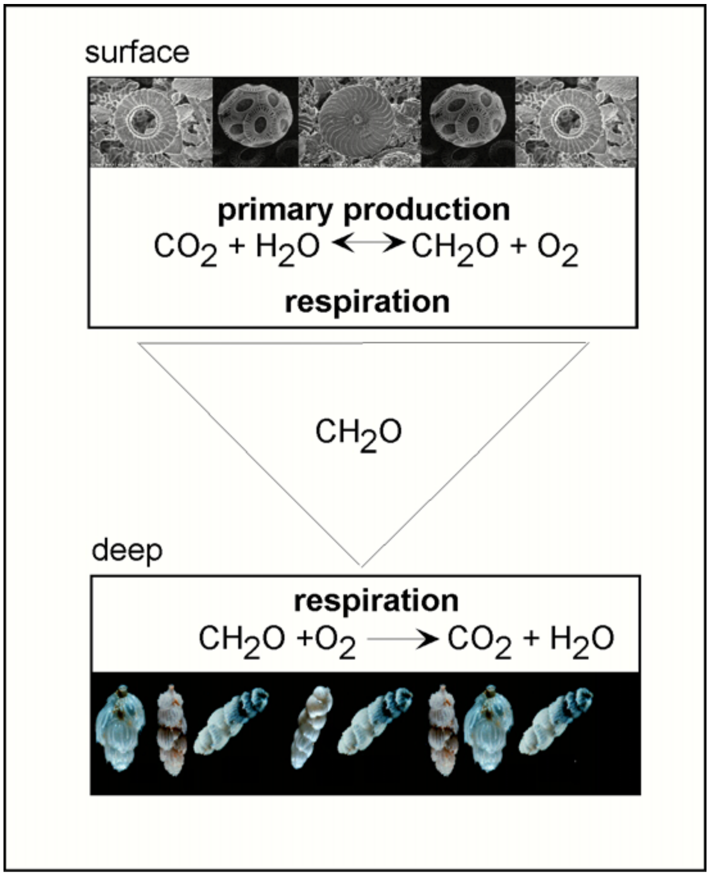


Figure 1. Cartoon to illustrate an oversimplified relationship between organic matter production (exemplified here by coccolithophores) and consumption at the sea surface (e.g., zooplankton respiration), continued consumption and transfer through the water column, and consumption on the ocean floor (e.g., by benthic foraminifera).

1. Introduction

1.1 Top Down:

Stoll's and Rickaby's research has shown that coccolith Sr/Ca ratios are in part a function of coccolithophorid calcification and growth rates. Coccolithophorid culture experiments demonstrate that the distribution coefficient of Sr (D_{Sr}) in coccolithophorid calcite is positively correlated with rates of organic carbon fixation and calcification (Stoll et al., 2000a; 200b; Rickaby and Schrag, 2002). Calcification and growth rates of coccolithophores can be linked to particulate organic matter production (Balch and Kilpatrick, 1996), thus coccolith Sr/Ca ratios should provide a proxy for primary productivity. This is supported by spatial variations of core-top coccolith Sr/Ca ratios in concert with primary productivity across the eastern equatorial Pacific (Stoll and Schrag, 2000) (Figure 2). In down-core studies, surface water productivity has been implicated to explain temporal variability in Cretaceous bulk sediment (primarily coccoliths) Sr/Ca ratios (Stoll and Schrag, 2001) and Paleocene/Eocene coccolith Sr/Ca data (Stoll and Bains, 2003). Over Cenozoic time scales, it is possible to relate common long-term trends in bulk sediment Sr/Ca ratios from various regions with what is known about large-scale productivity changes (Billups et al. 2004).

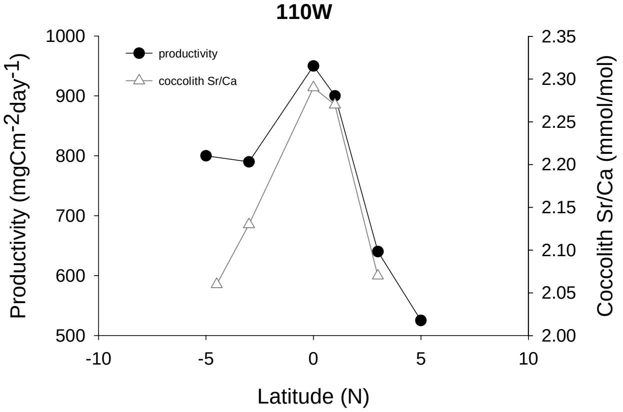


Figure 2. Relationship between primary productivity and coccolith Sr/Ca ratios in the eastern equatorial Pacific (data from Stoll and Schrag, 2000). Coccolith Sr/Ca ratios increase with surface ocean productivity, which is consistent with the positive correlation between the distribution coefficient of Sr in coccolith calcite and calcification rates (Stoll et al., 2002a; b; c; Rickaby and Schrag, 2002).

Although existing evidence suggests that coccolith Sr/Ca ratios provide a geologic perspective on the primary production of organic matter, there are uncertainties when applying this method to longer time scales. These include secular variations in seawater Sr/Ca (Lear et al., 2003), diagenesis (e.g., Hampt-Andreasen and Delaney, 2000), temperature effects on the coccolith Sr/Ca ratios (e.g., Stoll et al., 2000a), and species-specific Sr/Ca ratios (Stoll and Bains, 2003). Further concerns may arise from changes in surface and deep water carbon chemistry (pH effects on calcification rates and dissolution, respectively) as these are likely to change in response to primary productivity.

It is my objective in this study to constrain as many of these uncertainties as possible. As detailed in the **Research Strategy** seawater Sr/Ca variations can be accounted for by calculating the D_{Sr} from the coccolith Sr/Ca ratios and the seawater Sr/Ca curve (at least to the extent of which seawater Sr/Ca ratios are accurate). SEM imaging can be used to look for obvious signs of diagenetic overprinting of the individual coccoliths. Surface water temperatures can be constrained using planktonic foraminiferal Mg/Ca ratios. Species-specific Sr/Ca ratios can be limited by separating the samples into discrete size fractions. Down-core nannofossil assemblages can be monitored to obtain some measure of the extent of species-specific bias.

The geochemical concerns are more difficult to constrain. To date, there is no evidence for a relationship between coccolith Sr/Ca ratios and culture water pH (Stoll et al., 2002b). Thus, although productivity induced changes in pH may affect calcification rates, this mechanism may not drive coccolith Sr/Ca ratios. Regarding dissolution, unlike foraminiferal calcite, coccolith Sr/Ca ratios do not appear to be sensitive to partial dissolution because Sr is homogeneously distributed throughout the calcite platelet (Stoll et al., 2002b). In light of these biogeochemical and physiological controls, it is important to establish whether down-core changes in coccolith Sr/Ca ratios are dominated by a productivity signal.

1.2 Bottom up:

Benthic foraminifera feed on particulate organic matter settling from the photic zone and should therefore respond to export production, or rather, the flux of organic carbon reaching the deep ocean. Numerous studies from different regions have illustrated that there is an increase in benthic foraminiferal numbers with increased carbon flux to the sea floor (e.g., Berger and Wefer, 1990; Herguera and Berger, 1991; Nees, 1997; Schmiedl and Mackensen, 1997; Yasuda, 1997; van der Zwaan et al., 1999; Herguera, 2000; Diester-Haas et al., 2004). For a comprehensive review see the special issue of Marine Micropaleontology (2000) on *Foraminiferal Proxies and Paleoproductivity*). In this issue, Herguera (2000) illustrates that a well-defined relationship exists between benthic foraminiferal accumulation rates (BFAR) from core top sediments from the equatorial Pacific and Atlantic and the corresponding organic carbon flux (Figure 3).

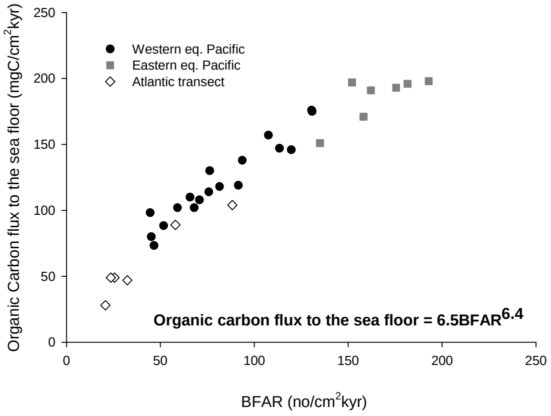


Figure 3. Relationship between core top benthic foraminiferal accumulation rates and organic carbon flux to the sea floor from Herguera (2000). The organic carbon flux numbers are derived from the regression between organic carbon flux, water depth and primary productivity of Berger and Wefer (1990). Herguera (2000) show how the BFAR can then be used to reconstruct paleo primary productivity (pPP) via the observed relationship between BFAR and water depth (Z): $pPP = 0.4*Z*BFAR^{0.5.}$ (eq. 1).

Berger and Wefer (1990) have established that there is a relationship between primary productivity at the sea surface and the organic carbon flux to the sea floor. Using this regression (not shown here), Herguera (2000) then derives a simple equation that relates “paleo” primary productivity to BFAR (equation 1):

$$pPP = 0.4*Z*BFAR^{0.5} \quad \text{(eq. 1)}$$

where pPP stands for paleo primary productivity, Z is the water depth of the sample, and BFAR are the benthic foraminiferal accumulation rates.

Modern ocean studies, however, indicate that the transfer of organic matter from the surface to the deep ocean is complex. The amount of export production of organic carbon out of the photic zone is not simply a function of the magnitude of primary productivity at the sea surface (Lampitt and Antia, 1997). Phytoplankton community structure is an important control on the amount of carbon leaving the photic zone (Boyd and Newton, 1999). For example, Francois et al. (2002) argue that carbonate producers provide a more efficient means to transfer carbon into the deep ocean owing to a “ballasting effect” of relatively heavy carbonate. Thus carbon in carbonate producing regions is transferred to deeper depths before it is remineralized than carbon in biogenic opal producing regions. These authors point out that while less organic carbon may be produced in the photic zone of an oligotrophic carbonate producing region than in a nutrient rich biogenic silica dominated region, a relatively larger fraction of it can make it to the sediment/water interface. Application of BFAR to reconstructions of paleoproductivity, which are calibrated to a few specific sites representing a specific environment, must assume that these factors remain constant through time.

Perhaps the largest source of uncertainty applying BFAR to paleoproductivity reconstruction arises from uncertainties associated with age control. Benthic foraminiferal accumulation rates are derived from mass accumulation rates and hence depend on sedimentation rates. Sedimentation rates are usually assumed linear between control points, which can be separated by as much as millions of years if based on biostratigraphy, or as little as a few thousand years if derived from astrochronology. However, age models are subject to change, which introduces unpredictable uncertainties in proxies dependent on sedimentation rates.

1.3 Top down and bottom up:

Coccolith Sr/Ca and benthic foraminifera offer two “opposite” views of primary productivity, production at the sea surface and consumption on the ocean floor. Each proxy has its own set of biological, biogeochemical, or geological controls, and hence uncertainties. Coupling coccolith Sr/Ca ratios with BFAR should present a coherent picture of paleo primary productivity if 1) coccolith Sr/Ca ratios are tightly coupled to changes in primary productivity regardless of the hydrographic setting, and 2) BFAR-based reconstruction of the deep ocean organic carbon flux faithfully tracks temporal changes in surface ocean productivity. In this project I propose to construct down-core records of coccolith Sr/Ca ratios from two sites for which corresponding BFAR data are available to test the extent to which it is possible to interpret these two different proxies in a common biogeochemical framework, primary productivity. A lack of a coherent picture would highlight the complex nature of productivity, carbon flux in the deep ocean, and the reconstruction thereof. Consistent trends, however, would strengthen the application of these proxies to paleoproductivity reconstructions. The results of this study will test our understanding of these two proxies.

2. Late Miocene/early Pliocene “Biogenic Bloom”

The late Miocene/early Pliocene “biogenic bloom“ interval (~7-3 Ma) provides an opportune time interval to examine the temporal relationship between coccolith Sr/Ca ratios and BFAR because a large body of evidence exists showing that during this interval of time an increase in primary productivity occurred at a number of sites in the Pacific and Indian Oceans (Petersen et al., 1992; Berger et al., 1993; Farrell et al., 1995; Dickens and Owen, 1994; Grant and Dickens, 2002) and the Atlantic (Diester-Haass et al., 2002; 2004; Diester-Haass et al., submitted). Thus a great opportunity now exists to test our understanding of the coccolith Sr/Ca and benthic fauna productivity proxies in the context of late Miocene through early Pliocene climate change. Causes of the "biogenic bloom" are being debated, but these are not the focus of this study (hence the lack of a more detailed review of the evidence here). What is important here is that a mechanism exists that, according to the conventional interpretation of the proxies, should change both coccolith Sr/Ca ratios and BFAR.

3. Detailed Objectives

- Construct size fraction specific records of coccolith Sr/Ca ratios from ODP Site 982 (North Atlantic) and from ODP Site 925 (western tropical Atlantic) using the same intervals as used for benthic foraminiferal accumulation rates (from Diester-Haass et al., submitted);
- Calculate the D_{Sr} from the Sr/Ca ratios and published seawater Sr/Ca ratios to account for secular changes in seawater Sr and Ca variations;
- Construct parallel records of planktonic foraminiferal Mg/Ca to monitor surface water temperature changes;
- Establish down-core patterns of nannofossil species assemblages at both sites;
- Compare the coccolith Sr/Ca records to the benthic foraminiferal accumulation rate/ paleoproductivity records from the same intervals;
- Evaluate if, to what degree, or which coccolith size fraction best parallels changes in benthic foraminiferal derived paleoproductivity at each site.

4. Research Strategy

My strategy falls into two catogories. In *4.1 Site Selection*, I justify the choice of the two sites. These include the availability of benthic foraminiferal data, sedimentological criteria, hydrographic regime and age control. In *4.2 Coccolith Sr/Ca Ratios,* I specify how I address caveats associated with the geochemical proxy, namely secular changes in seawater Sr/Ca ratios, temperature effects and changing coccolith species assemblages.

4.1 Site Selection

Paleoproductivity signal

I have chosen ODP Sites 982 (subpolar North Atlantic) and ODP Site 925 (western tropical Atlantic) (Figure 4) because counting of benthic foraminifera is complete indicating that an increase occured in paleoproductivity at both sites, confirming that a signal exists (see **Preliminary Results**, page 15). This provides the basis for the next step, and I have received the bulk sediments from each of the intervals to construct parallel records of coccolith Sr/Ca ratios.

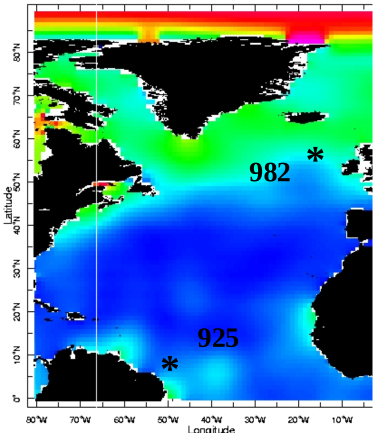
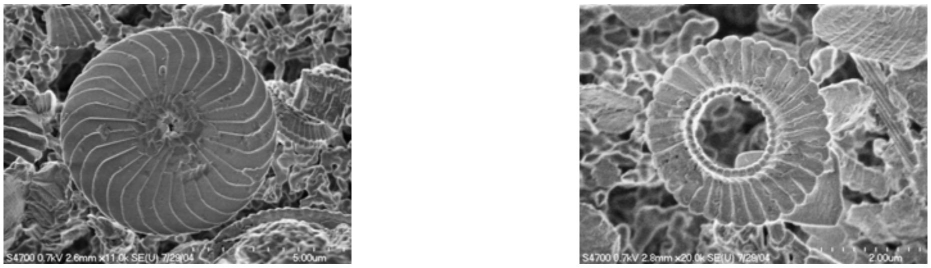


Figure 4. Location of ODP Site 925 (western tropical Atlantic, 3053 m water depth) and Site 982 (North Atlantic, 1134 m water depth). The shading reflects the annual average phosphate content, which I chose purely for illustrative purposes, ranging from 0.2 μmolar (dark gray) 0.4 μmolar (light gray). The map was generated using the Lamont Doherty data library.

Carbonate content and diagenesis

ODP Sites 982 and 925 have a high carbonate content (averaging ~90% and 80%, respectively Shipboard Scientific Party, 1996; 1995). This is important because Stoll and Schrag (2000) demonstrate that there can be an effect of adsorbed Sr and Ca cations from alumino silicates in the coccolith size fraction on the Sr/Ca ratio of the sample. By mass balance this effect decreases with increasing carbonate content (Stoll and Schrag, 2000). Thus high carbonate content (>80%) is critical for unambiguous results.

High carbonate content, however, is an environment conducive to carbonate diagenesis (e.g., Stout, 1985; Hampt-Andreasen and Delaney, 2000). It may not be possible to entirely rule out such effects, but SEM imaging of coccoliths from both sites does not show any obvious sign of diagenetic overprinting (Figure 5). Neither of the imaged samples shows evidence for euhedral calcite crystals that would indicate significant recrystallization.


Site 982

Site 925

Figure 5. Mid core examples of coccoliths from North Atlantic Site 982 (*Calcidiscus*) and western tropical Atlantic Site 925 (*Umbilicosphaera*). The calcite platelets are well preserved; there is no evidence of significant secondary calcification.

Hydrography

The two sites represent different hydrographic regimes (Figure 4), but only Site 925 lies within the BFAR-paleoproductivity calibration region of Herguera (2002). In the modern ocean large seasonal differences in primary productivity exist at subpolar Site 982 (0.1-0.65 gC/m^2/day), and at tropical Atlantic Site 925 primary productivity varies little throughout the year (0.2-0.35 gC/m^2/day) although the annual averages are similar (12.5 gC/m^2/day; Antoine et al., 1996). I do not propose to use the modern setting as an analog for the late Miocene/early Pliocene, but I can assume that the hydrographic regime differed from each other in the past simply because of their high versus low latitude locations. Thus, choice of these two sites tests the applicability of the BFAR based productivity proxy outside the environment for which it is calibrated.

Sites 982 and 925 come from different water depths (3053 m vs. ~1134m, respectively), which can be accounted for by applying the regression of Herguera (2000) and calculating paleoproductivity from BFAR (equation 1, page 5). However, the approach does assume that the water depth has remained constant through time. At both sites, the paleo water depth during the middle to late Miocene may have been shallower by 100-150 m than the modern water depth (Site 982: Andersson and Jansen, 2003; site 925: Shipboard Scientific Party, 1995). The water depth effect will introduce an uncertainty of about 4 % in the paleoproductivity estimates, which is not large enough to mask any longer-term trends.

Age control

Excellent age control exists at both sites, which is important for the calculation of sediment accumulation rates and hence BFAR from the number of benthic forams per gram sediment. At Site 982 the age model is based on tuning a benthic foraminiferal $\delta^{18}O$ record to obliquity (Hodell et al., 2001). Thus Site 982 age control points are denser (40 kyr) than the temporal resolution in this study (~50-80 kyr), and the assumption of constant sedimentation rates between control points is most likely a good one. At Site 925, the time scale is based on magnetic susceptibility tuned to Northern Hemisphere summer insolation (Shackleton and Crowhurst, 1997; Shackleton and Crowhurst, pers. communication). Again, age control points are denser than the sample spacing of this study and sedimentation accumulation rates can be assumed linear between control points.

4.2 Coccolith Sr/Ca Ratios

Seawater Sr/Ca ratios

Secular changes in seawater Sr/Ca ratios introduce a trend into the geochemical time series. There is evidence from benthic foraminiferal Sr/Ca ratios that seawater Sr/Ca ratios changed during the late Miocene to early Pliocene (Lear et al., 2003) (Figure 6). The long-term decrease toward 7 Ma and subsequent increase toward the present needs to be removed from the coccolith Sr/Ca time series. This will be achieved by calculating the distribution coefficient of Sr in coccoliths (equation 2) based on the measured coccolith Sr/Ca ratios and the benthic foram derived seawater Sr/Ca ratios of Lear et al. (2003):

$$D_{Sr} = [Sr/Ca_{coccolith}]*[Sr/Ca_{seawater}]^{-1} \qquad \text{(equation 2)}$$

Thus I will be comparing temporal changes in the D_{Sr} with benthic foraminiferal accumulation rates/paleoproductivity, not simply the coccolith Sr/Ca ratios.

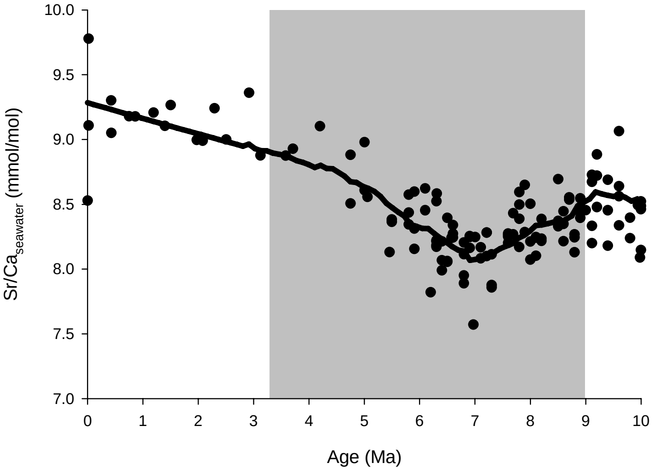


Figure 6. Seawater Sr/Ca ratios calculated from benthic foraminiferal Sr/Ca ratios using a benthic foraminiferal distribution coefficient of Sr of 0.165 (Lear et al., 2003). Benthic forams may be the best indicator of seawater ratios because the only known variable to affect the D_{Sr} is water depth, which has been accounted for in this study. Seawater Sr/Ca ratios change during the time interval under investigation (shaded) highlighting the importance of eliminating the long-term trend in the coccolith Sr/Ca records.

Temperature effects:

There is a temperature effect on Sr/Ca ratios of about 2 % $^{\circ}C^{-1}$ (Stoll et al., 2002b). In a tropical setting, such as Site 925, where even uppermost sea surface temperatures are comparatively stable (e.g., the modern seasonal range at 0 m water depth is only about 2ºC, Levitus and Boyer,

1994) this issue may be a minor concern (assuming that the hydrographic regime of the past is similar to today). At subpolar North Atlantic Site 982, on the other hand, the modern seasonal sea surface temperatures change is large, about 6ºC, which alone would introduce a ~12% change in Sr/Ca ratios. However, being photosynthetic, coccolithophores occupy the entire photic zone, thus the modern seasonal sea surface temperatures may be an overestimate of the photic zone temperature range. For example, at only 50 m water depth the seasonal temperature changes is strongly attenuated (~2ºC Levitus and Boyer, 1994).

Because it is difficult to argue that seasonal temperature changes are a quantitative analog for down-core variations, I will use planktonic foraminiferal Mg/Ca ratios to constrain the possibility of sea surface (or upper ocean) temperature changes that have affected the coccoliths Sr/Ca ratios. The temperature dependency of Mg incorporation into planktonic foraminiferal calcite has been well established and by now a number of species specific calibrations exist (e.g., Dekens et al., 2003; Anand et al., 2003). At western tropical Atlantic Site 925 I will use the abundant *Globigerinoides sacculifer,* a foraminifera that primarily occupies the mixed layer. At North Atlantic Site 982, I will use *Globigerina bulloides*, a mixed layer and thermocline dweller. The reconstructed temperature variability may overestimate the temperatures of the coccolithophorid calcification environment, particularly if the photic zone is deeper than the thermocline, but they will provide an important upper constraint.

In this context, secular changes in seawater Mg/Ca ratios need to be considered. However, although seawater Mg/Ca ratios may have been lower than today during the late Miocene/early Pliocene, no rapid changes occurred during this time interval (Wilkinson and Algeo, 1989; Stanley and Hardie, 1998). Thus, while the absolute temperature values may be affected by different seawater ratios, the variability in foraminiferal Mg/Ca ratios between sampling intervals, ~80 kyr, is due to temperature (the residence time of Mg and Ca being 13 Myr and 1 Myr, respectively). I believe that this aspect of the project is ideally suited for an undergraduate senior thesis.

Coccolith species effects

Stoll's recent work shows that there may be species-specific offsets in coccolith Sr/Ca ratios. Stoll and Bains (2003) illustrate that in Paleocene sediments, coccoliths belonging to larger size fractions (8-12 μm) have lower Sr/Ca ratios than smaller taxa (3-5 μm). Size division may split the nanno fossils broadly based on ecology with most of the cooler water/mesotrophic species in the small range, and the warm water/oligotrophic species in the larger size range (e.g., Gibbs et al., 2004). Thus temporal changes in species assemblages, perhaps in response to surface water paleoproductivity, will affect the interpretation of the Sr/Ca records.

We will separate the coccolith fraction into two size fractions by microfiltering at 8 μm. Although we cannot constrain species assemblage changes within each size faction, we will be able to eliminate bias due to changes in small versus large species, which may be brought about by environmental changes, throughout the study interval. Hence, Sr/Ca ratios within each size fraction more closely reflect the geochemical signal due to the kinetics of Sr incorporation.

In addition, we will prepare smear slides and record changes in coccolith species abundance in each of the intervals to be measured. Samantha Gibbs, currently at nearby Penn State, is an expert on nannofossil taxonomy and assemblages and has offered her expertise (see attached letter of support). Graduate student Amanda Waite, who is beginning this project for a Master's Thesis, has already visited Samantha Gibbs to learn coccolith identifications. The preliminary look tells us that there are comparatively few nannofossil species at North Atlantic Site 982 and that abundances are relatively constant. At tropical Atlantic Site 925, however, species diversity is high, and as demonstrated by the recent early Pliocene study of Gibbs et al (2004), assemblages change on orbital time scales. Thus, monitoring the down-core species assemblages will be particularly important at Site 925.

5. Preliminary Results

As noted above, BFAR have already been determined at both sites (Figure 7A). The results indicate that Site 982 BFAR are higher than those at Site 925, which is an example of the water depth effect (e.g., Herguera, 2000). Converting BFAR to paleoproductivity using equation 1 indicates more similar data averages (Figure 7B). The amplitude of the two major productivity peaks is comparable, although the timing differs (at 5 Ma and 6.5 Ma at sites 982 and 925, respectively).

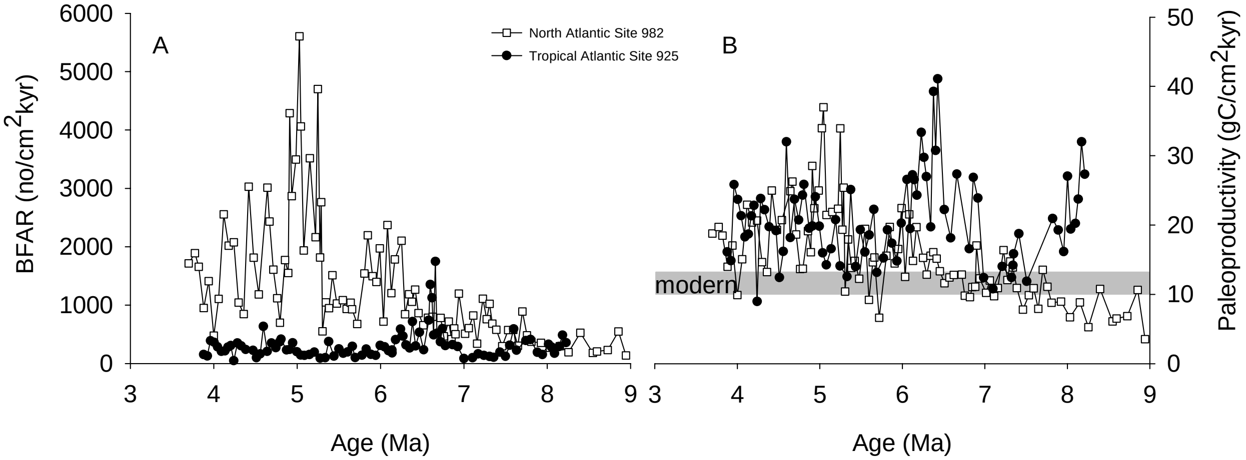


Figure 7. Benthic foraminiferal accumulation rates (BFAR) (A) and calculated paleoproductivity (B) from Sites 982 and 925 spanning the late Miocene to early Pliocene "biogenic bloom" interval (Diester-Haass et al., in preparation). Paleoproductivity is calculate using the relationship of Herguera (2000): paleoproductivity = 0.4 x water depth x BFAR$^{0.5}$. The gray horizontal bar in (B) outlines modern productivity in these regions (Antoine et al., 1996).

Preliminary low resolution Sr/Ca results using the entire coccolith size fraction (0-20μm) from North Atlantic Site 982 illustrate that there is encouraging agreement between the bottom up and top down perspective (Figure 8, next page). Site 982 coccolith Sr/Ca ratios increase from 9 to 5 Ma, the trend being paralleled by an overall increase the calculate paleoproductivity during this interval of time. With a few exceptions, the two proxies agree on the finer scale as well. Maxima in the paleoproductivity tend to be accompanied by maxima in the D_{Sr} (e.g., at 7.7 Ma, 6.9 Ma, 5.2 Ma, and 5.0 Ma, Figure 8). In fact, the relationship between the two records is quite good with a correlation coefficient of 0.46 (Figure 9); which is significantly different from zero at the 5% level. Interestingly, the magnitude as well as the timing of the single-point maximum in the D_{Sr} at 4 Ma recorded in the coccolith D_{Sr} agrees very well with the D_{Sr} maximum derived from fine fraction sediment in the Indian Ocean (e.g., Baker et al., 1982; Billups et al., 2004) suggesting an extra regional effect. These preliminary coccolith Sr/Ca data show much promise for interpreting the two proxies in the context of primary paleoproductivity.

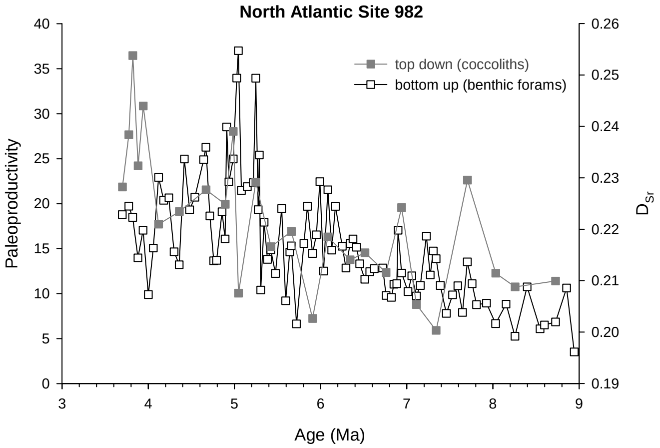


Figure 8. Comparison of Site 982 paleoproductivity derived from benthic foraminiferal accumulation rates with the D_{Sr} of coccoliths derived from coccolith Sr/Ca ratios (to account for changes in seawater Sr/Ca ratios). The agreement between the two proxies appears to be quite good both over the long term as well as in the peak-to-peak comparison.

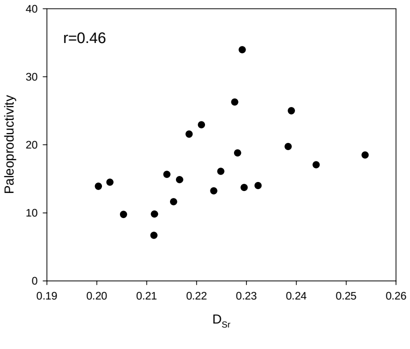


Figure 9. Scatter plot of the Site 982 D_{Sr} versus the benthic foraminiferal derived paleoproductivity. The correlation coefficient (r) is 0.46, which is significant at the 5% level (t-test: t=2.26; $t_{critical}$ at $\alpha_{0.025}$ =2.093).

6. Proposed Work (Table 1)

A total of 184 intervals (plus 10% duplicates) will be processed for coccolith Sr/Ca measurements from Sites 982 and 925 (Table 1). After cleaning, each sample will be microfiltered using 8 μm polycarbonate filter to separate the size fraction. We chose this particular size fraction in accord with Stoll's work, which shows significant differences in the 3-5 μm versus the 8-12 μm size fractions. Thus for each interval, two Sr/Ca measurements will be made. The coccolith Sr/Ca cleaning method has been published by Stoll and Schrag, 2000; and Stoll and Ziveri (2002). Stoll (pers. comm.) has kindly provided us with a very detailed step-by-step methodology that includes separating the sample into discrete size fractions, and, as the outside member of graduate student Amanda Waite's Thesis committee, is offering her continued support with this project. An outline of this method is summarized in Table 2.

For each interval, Mg/Ca ratios will be measured to monitor the extent to which surface water temperature changes may have affected the Sr/Ca ratios. Mg/Ca cleaning will follow the "Mg protocol" as outlined by Rosenthal et al. (2004), which includes several sonication steps to remove fine fraction material, an oxidating step using hot buffered peroxide to remove organic matter as well as an acid rinse. Dissolved samples will be sent for analysis using ICP-MS to the Oxford University (see attached letter from R. Rickaby).

Smear slides will be prepared for each interval to monitor the down core changes in species assemblages. To this end we will adopt the method of Backman and Shackleton (1982) and count the number of coccoliths belonging to the dominant species per mm^{-2} on the separated coccolith fraction on a smear slide. Graduate student A. Waite has already learned to prepare these slides and to identify the species. S. Gibbs (a former graduate student of N. Shackleton) will help in statistically quantifying the species counts (see attached letter of support from S. Gibbs).

I have all major equipment (e.g., a centrifuge, shaker, and a petrographic transmitting light microscope with 1000x magnification). The only piece of equipment that needs to be purchased is a laboratory counter for counting coccoliths to determine changes in species assemblages.

7. Significance

Coccolith Sr/Ca ratios are a relatively new proxy for paleoproductivity; benthic foraminiferal accumulation rates a comparatively well-established one. Each approach is limited by its own set of uncertainties. Together, however, the two proxies should yield a coherent picture of paleoproductivity if our understanding of each is adequate. This study explores whether a simple link can be made in the geologic record between surface ocean production of organic matter and deep ocean consumption, which would strengthen reconstructions of paleoproductivity. Preliminary results advocate such a simplistic link thereby lending support for the use of these proxies despite the many uncertainties.

The results from this study are important to the paleoceanographic community because they will advance our understanding of the coccolith Sr/Ca and BFAR proxies. If the preliminary results are confirmed by the proposed study, combining the two proxies will yield a powerful means to reconstruct paleoproductivity (coccolithophorid and other). This is important to the paleoclimatologist because primary productivity determines the partitioning of CO_2 between the atmospheric and oceanic reservoirs. It is important to the objectives of the Petroleum Research Fund because primary marine productivity is the source of potential hydrocarbon reservoirs.

Table 1. Summary of proposed work.

Site	temporal resolution	Number of intervals to be processed	*Number of Sr/Ca analyses (for two size fractions)	*Number of Mg/Ca analyses
982	50-80 kyr	96	211	105
925	50-80 myr	88	194	96
	Total	184	405	201

*Number includes 10% duplicate values

Table 2. Processing bulk sediments for coccolith Sr/Ca analysis (Stoll, pers. comm.)

Step	process
1	-wet sieve ~ 1 g bulk sediment through a 20μm sieve using ethanol to separate the foram and foram fragments from clay and coccolith fraction -pour into 15ml centrifuge tube -centrifuge or let settle overnight
2	-to the fine fraction, add 50% of 2% sodium hypochlorite and 30% hydrogen peroxide to oxidize the organic matter -react in a beaker for 1 hour, add 1 ml bleach and sonicate repeatedly. -recover the sediment using a vacuum filter (0.45 or 1 μm cellulose nitrate)
3	-to the fine fraction, add ~4ml of "MNX" (50g hydroxylamine hydrochloride in 400 ml NH_4OH and 600ml DDH_2O) to reduce Fe and Mn oxyhydroxides -shake for ~12 hours, centrifuge and siphon off the liquid
4	-to the fine fraction, add 4-10 ml "IONX" (65ml NH_4OH in 1 L DDH_2O) to remove exchangeable Sr -shake for ~2-24 hours, centrifuge and remove liquid
5	-rinse with DDH_2O, shake for 2 hours, centrifuge and siphon off the liquid
6	-microfilter using a 8 μm polycarbonate filter and retain both fractions.
7	-dissolve in 2% HNO_3, to ensure complete dissolution, centrifuge, siphon off the liquid and transfer into clean microcentrifuge tubes for analyses using ICP-AES.

References

Anand, P., H. Elderfield, and M. H. Conte, Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, 18, doi.: 10.1029/2002PA000846, 2003.

Andersson, C., and E. Jansen, A Miocene (8–12 Ma) intermediate water benthic stable isotope record from the northeastern Atlantic, ODP Site 982, *Paleoceanography*, 18, 10.1029/2001PA000657, 2003.

Antoine, D., J.-M. Andre, and A. Morel, Oceanic productivity, 2, Estimation at global scale from satellite (coastal zone color scanner) chlorophyll, *Global Biogeochemical Cycles*, 10, 57-70, 1996.

Backman, J., and N. J. Shackleton, Quantitative biochronology of Pliocene and early Pleistocene calcareous nannofossils from the Atlantic, Indian and Pacific Oceans, *Mar. Micropaleontol*. 8, 141-170, 1983.

Balch, W. M., and K. Kilpatrick, Calcification rates n the equatorial Pacific along 140°W, *Deep Sea Research II*, 43, 971-993, 1996.

Baker, P., J. M. Gieskes, and H. Elderfield, Diagenesis of carbonates in deep-sea sediments-evidence from Sr/Ca ratios and interstitial dissolved Sr data, *J. Sediment. Petrol*., 52, 71-82, 1982.

Berger, W., and G. Wefer, Export production: seasonality and intermittency, and paleoceanogrpahic reconsturction, *Palaeogeogr. Palaeoclimatol. Palaeoecol*. 89, 245-254, 1990.

Berger, W. H., R. M. Leckie, T. R. Janecek, R. Stax, and T. Takayama, Neogene carbonate sedimentation on Ontong Java Plateau: Highlights and open questions, *Proc. Ocean. Drill. Program Sci. Results, 130*, 711-744, 1993.

Billups, K., R. Rickaby, and D. P. Schrag, Cenozoic pelagic Sr/Ca records: Exploring a link to paleoproductivity, *Paleoceanography*, 19, doi.:10.1029/2004PA001011, 2004.

Boyd, P. W., and P. P. Newton, Does planktonic community structure determine downward particulate organic carbon flux in different oceanic provinces? *Deep-Sea Research I*, 46, 63-91, 1999.

Dekens, P. S., D. W. Lea, D. K. Pak, and H. J. Spero, Core top calibration of Mg/Ca in tropical foraminifera: Refining paleotemperature estimation, *Geochem. Geophys. Geosyst.*, 3, 1022, doi.: 10.1029/2001GC000200, 2002.

Dickens, G. R., and R. M. Owen, The latest Miocene-early Pliocene biogenic bloom: a revised Indian Ocean perspective, *Mar. Geol., 161*, 75-91, 1999.

Diester-Haass L, P.A. Meyers, L. Vidal, The late Miocene onset of high productivity in the Benguela Current upwelling system as part of a global pattern, *Marine Geology*, 180, 87-103, 2002.

Diester-Haass, L., P. A. Meyers, and T. Bickert, Carbonate Crash and Biogenic Bloom in the Late Miocene: Evidence from ODP Sites 1085, 1086 and 1087 in the Cape Basin, southeast Atlantic Ocean, *Paleoceanography*,19, PA1007 10.1029/2003PA000933, 2004.

Diester-Haass L., K. Billups, K. Emeis, In search of a global biogenic bloom, submitted to *Paleoceanography*.

Farrell, J.W., I. Raffi, T. R. Janecek, D. W. Murray, M. Levitan, K. A. Dadey, K.-C. Emeis, M. Lyle, J.-A. Flores, S. Hovan, 1995. Late Neogene sedimentation patterns in the eastern equatorial Pacific. In: *Proc. ODP, Sci. Res., 138*, College Station (TX), Ocean Drilling Program. 717-756.

Francois, R., S. Honjo, R. Krishfield, and S. Manganini, Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, *Global Biogeochemical Cycles*, 16, 1087-1097, 2002.

Gibbs, S., N. J. Shackleton, and J. Young, Orbitally forced signals in mid-Pliocene nannofossil assemblages, *Marine Micropaleontol.*, 51, 39-56, 2004.

Grant, K. M., and G.R. Dickens, Coupled productivity and carbon isotope records in the southwest Pacific Ocean during the late Miocene-early Pliocene biogenic bloom, *Palaeogeogr. Palaeoclimatol. Palaeoecol., 187,* 61-82, 2002.

Hampt-Andreasen, G., and M. L. Delaney, Lithologic controls on calcite recrystallization in Cenozoic deep-sea sediments, *Marine Geology*, 163, 109-124, 2000.

Herguera, J.C., and W. A. Berger, Paleoproductivity from benthic foraminifera abundance: glacial to postglacial change in the west-equatorial Pacific, *Geology, 19*, 1173-1176, 1991.

Herguera, J.C., Last glacial paleoproductivity patterns in the eastern equatorial Pacific: benthic foraminifera records, *Mar. Micropaleontol.*, 40, 259-275, 2000.

Hodell, D. A., J. H. Curtis, F. J. Sierro, and M. E. Raymo, Correlation of late Miocene to early Pliocene sequences between the Mediterranean and North Atlantic, *Paleoceanography*, 16, 155-163, 2001.

Lampit, R. S., and A. N. Antia, Particle flux in deep seas: regional characteristics and temporal variability, *Deep Sea Research I,* 44, 1377-1403, 1997.

Lear, C. H., H. Elderfield, P.A. Wilson, A Cenozoic seawater Sr/Ca record from benthic foraminiferal calcite and its application in determining global weathering fluxes, *EPSL,* 208, 69-84, 2003.

Levitus, S., and T. P. Boyer, World Ocean Atlas 1994, vol. 4, Temperature, NOAA Atlas NESDIS 4, 129 pp., Nat. Oceanic and Atmos. Admin., Silver Spring, Md., 1994.

Nees, S., Late Quaternary palaeoceanography of the Tasman Sea: the benthic foraminiferal view, *Palaeogeogr. Palaeoclimat. Palaeoecol.*, *131*, 365-389, 1997.

Peterson, L. C., D. W. Murray, W. U. Ehrmann, and P. Hempel, Cenozoic carbonate accumulation and compensation depth changes in the Indian Ocean, in *Synthesis of Results from Scientific Drilling in the Indian Ocean, Geophys. Monogr. Ser, 70*, pp. 311-333, AGU, Washington, D.C., 1992.

Rickaby, R. E. M., D. P. Schrag, I. Zondervan, and U. Riebesell, Growth-rate dependence of Sr incorporation during calcification of Emiliani huxleyi, *Global Biogeochemical Cycles*, 10.1029/2001GB001408, 2002.

Rosenthal, Y., S. et al., Inter-laboratory comparison study of Mg/Ca and Sr/Ca, measurements in planktonic foraminifera for paleoceanographic research, *Geochemistry, Geophysics, Geosystems*, 5 (4), 10.1029/2003GC000650, 2004.

Schmiedl, G., and A. Mackensen, Late Quaternary paleoproductivity and deep water circulation in the eastern South Atlantic Ocean: evidence from benthic foraminifera, *Paleogeogr. Paleoclimat. Paleoecol., 130*, 43-80, 1997.

Shackleton, N.J., and S. Crowhurst, Sediment fluxes based on orbitally tuned time scale 5 Ma to 14 Ma, site 926, In Shackelton, N. J., Curry, W. B., Richter, C., and Bralower, TJ., (Eds.) *Proc. ODP, Sci.. Results*:, 154, College Station, TX (Ocean Drilling Program), 1997.

Shipboard Scientific Party Leg 162, Site 982, *Proc. ODP, Init. Repts*., 162, College Station, TX (Ocean Drilling Program), 91-138, 1997.

Shipboard Scientific Party Leg 154, In Curry, W. B., Shackleton, N. J., Richter, C., wet al. (Eds.) *Proc. ODP, Init. Repts., 154*, College Station, TX (Ocean Drilling Program), 1995.

Stanley, S. M., and L. A. Hardie, Secular oscillations in the carbonate mineralogy or reef-building and sediment producing organisms driven by tectonically forced shifts in seawater chemistry, *Palaeogeography, Palaeoclimatology, Palaeoecology,* 144, 3-1, 1998.

Stoll, H.M., and S. Bains, Coccolith Sr/Ca records of productivity during the Paleocene-Eocene thermal Maximum from the Weddell Sea, *Paleoceanography*, 8, 10.1029/2002PA000875, 2003.

Stoll, M. H., Y. Rosenthal, and P. Falkowski, Climate proxies from Sr/Ca of coccolith calcite: Calibrations from continuous culture of Emiliani huxleyi, *Geochim. Cosmochim Acta*, 66, 927-936, 2002a.

Stoll, H. M., C. M. Klaas, I. Probert, J. R. Encinar, J. I. G. Alonso, Calcification rate and temperature effects on Sr partitioning in coccoliths of multiple species of coccolithophorids in culture, *Global and Planetary Change*, 34, 153-171, 2002b.

Stoll, H. M., P. Ziveri, M. Geisen, I. Probert, and J. R. Young, Potential and limitations of Sr/Ca ratios in coccolith carbonate: new perspectives from cultures and monospecific samples from sediments, *Phil. Trans. R. Soc. Lond. A.*, 360, 719-747, 2002c.

Stoll, H. M., and P. Ziveri, Separation of monospecific and restricted coccolith assemblages from sediments using differential settling velocity, *Mar. Micro*., 46, 209-221, 2002.

Stoll, H. M. and D. P. Schrag, Sr/Ca variations in Cretaceous carbonates: relation to productivity and sea level changes, *Palaeogeography, Palaeoclimatology, Palaeoecology*, 168, 311-336, 2001.

Stoll, H. M. and D. P. Schrag, Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate, *Geochemistry, Geophysics, Geosystems*, 1, 1999GC000015, 2000.

Stout, P. M., Interstitial water chemistry and diagenesis of biogenic sediments from the eastern equatorial Pacific, *Deep Sea Drilling Project Leg 85*, Mayer, L., P. Theyer, et al., *Init. Reports, DSDP*, 85, Washington DC, US Govt. Printing Office, 805-820, 1985.

van der Zwaan, G. J., I. A. P. Duijnstee, M. den Bulk, S. R. Ernst, N. T. Jannink, and T. J. Kouwenhoven, Benthic foraminifers: proxies or problems? A review of paleoecological concepts, *Earth Sci. Rev*., *46*, 213-236, 1999.

Wilkinson, B. H., and T. J. Algeo, Sedimentary carbonate record of calcium-magnesium cycling, *American Journal of Science*, 289, 1158-1194, 1989.

Yasuda, M., Berger, W.H., Wu, G., Burke, S., and Schmidt, H., Foraminifer preservation record for the last million years: Site 805, Ontong Java Plateau, *Proc. Ocean. Drill. Program Sci. Results*, *130*, 491-508, 1993.