

**COCCOLITH SR/CA RECORDS OF PRODUCTIVITY DURING THE  
PALEOCENE-EOCENE THERMAL MAXIMUM FROM THE  
WEDDELL SEA**

**Heather M. Stoll**

Geoscience Department, Williams College, Williamstown MA 01267, USA

**Santo Bains**

Department of Earth Sciences, University of Oxford, Oxford, OX1 3PR, UK

Submitted to *Paleoceanography* December 20, 2002

Accepted for publication on March 31, 2003

*The following statement is required by AGU Copyright policy: "Accepted for publication in  
Paleoceanography. Copyright 2003 American Geophysical Union. Further reproduction or  
electronic distribution is not permitted."*

## Abstract

A major perturbation of the global carbon cycle ~55 million years ago, believed to result from release of 1000-2000 Gt of C from methane hydrates, correlates with an intense but transient greenhouse warming event known as the Paleocene Eocene Thermal Maximum (PETM). The rapid ( $10^5$  yr) recovery of global temperatures reflects important negative feedbacks in the climate system and carbon cycle. Enhanced marine productivity may be one important feedback, but indicators for productivity changes have yielded conflicting results. Here we use a new independent indicator, Sr/Ca in coccolith carbonate which covaries with the productivity of coccolithophorid algae, to investigate the biotic response in the most complete PETM deep sea record which was recovered at ODP Site 690 in the Weddell Sea. In the dominant coccolithophorid genus *Toweius*, a large (40%) Sr/Ca increase immediately after the gas hydrate release signals a dramatic productivity increase. Productivity levels remained high for 60,000 years but decreased to pre-event levels by 120,000 years after the gas hydrate release. Productivity levels during the PETM are higher than observed at any other time in our -400,000 year record. Other coccolithophorid genera *Chiasmolithus* and *Discoaster* show a brief, modest (25% Sr/Ca increase) increase in productivity that lags behind the methane event by 50,000 years and is within the range of productivity variation elsewhere in the record. The timing of the *Toweius* productivity increase agrees well with Os isotope records of globally increased weathering intensity, which may have provided higher nutrient fluxes to stimulate algal productivity. If this type of productivity response occurred globally, it would also be consistent with the timing of C drawdown that may have returned temperatures to near pre-event levels.

## 1. Introduction

The Paleocene/Eocene (P-E) boundary is marked by widespread environmental changes including a dramatic warming (5-7° C) of the high latitudes and deep oceans (Kennett and Stott, 1991; Zachos et al., 1993) termed the Paleocene Eocene Thermal Maximum (PETM), extinction of numerous deep-sea fauna (Thomas and Shackleton, 1996), and a dramatic radiation of several mammalian orders (eg. Koch et al., 1992). This event is accompanied by a prominent large(3-4 permil) negative carbon isotope excursion (CIE) in marine and terrestrial reservoirs which likely reflects addition of 1000-3000 Gt of isotopically depleted carbon from dissociation of seafloor methane hydrates ( $\delta^{13}\text{C} = -60\text{‰}$ ). Most of the carbon addition occurred in less than 20,000 years, and the amount of carbon added is comparable to that predicted for anthropogenic C inputs (e.g. Dickens et al., 1995, 1997; Koch et al., 1995; Bains et al., 1999).

Available records suggest that within 100,000 years after the initial methane hydrate release of the PETM event, temperatures had cooled to within a few degrees of their pre-event temperatures, and much of the isotopically light carbon had been removed from the ocean/atmosphere system (Kennett and Stott, 1991; Bains et al., 1999). This rapid recovery requires enhanced removal of carbon from the ocean atmosphere system. One mechanism that has been proposed is climatically-enhanced continental weathering rates which provide nutrients to increase marine productivity and enhance carbon removal in marine sediments (eg. Dickens et al., 2001; Bains et al., 2000). Increased osmium isotopic ( $^{187}\text{Os}/^{186}\text{Os}$ ) ratios of seawater suggest elevated average global chemical weathering rates during the PETM (Ravizza et al., 2001). However, efforts to

confirm or refute a productivity feedback have been hampered by conflicting interpretations of paleoproductivity from different indicators, even at the same site.

The most expanded and complete PETM record examined to date is Ocean Drilling Program (ODP) Site 690 from the Weddell Sea. Bralower (2002) has interpreted calcareous nannofossil assemblages in Site 690 to indicate a shift from colder, more productive surface waters to warmer, more oligotrophic conditions during the PETM. However, given the large sea surface temperature changes in this site, temperature, rather than fertility, may have exerted the dominant influence over nanoplankton communities. Higher barite accumulation rates across the PETM at Site 690 were interpreted as evidence for increased productivity (Bains et al., 2000). However, Dickens et al. (in press) suggest instead that widespread barite enrichment in PETM sediments may result from improved barite preservation as excess dissolved barium was released from seafloor gas hydrate reservoirs. Consequently, even at this critical, well-preserved and expanded site there is no consensus on whether productivity increased or decreased during the PETM.

To elucidate productivity variations at this key Weddell Sea site, we use a new productivity indicator, the Sr/Ca ratio of coccolith carbonate which reflects nutrient-stimulated changes in coccolithophorid growth rates and productivity (Stoll et al., 2002b; Rickaby et al., 2002). Coccolithophorid algae are key players in the ocean's carbonate and organic carbon cycles. They are the dominant carbonate producers in the open ocean. While they are not the dominant primary producers of organic carbon in most oceanographic settings, they strongly influence the organic carbon cycle because the carbonate rain rate controls the transfer efficiency of organic matter from the photic zone

to the deep ocean (Francois et al., in press). Faster growth and calcification rates of the coccolithophorids alter cell physiology and biochemistry in ways that increase Sr incorporation in coccolith calcite (Stoll et al., 2002b; Rickaby et al., 2002). Sediment core-top calibration studies have demonstrated that the Sr/Ca ratio of coccoliths increases by up to 50% with increases in productivity and nutrient contents across modern productivity gradients (Stoll et al., 2002b). Coccolith Sr/Ca ratios also faithfully record known Quaternary paleoproductivity variations accompanying Mediterranean sapropel deposition (Stoll, unpub. data).

The coccolith Sr/Ca proxy overcomes several limitations of traditional productivity indicators. Unlike other geochemical productivity proxies, coccolith Sr/Ca is not based on calculating sediment mass accumulation rates, which may be biased by sediment focusing and are difficult to calculate in older sediments where precise age control is limited. Unlike paleontological proxies, which assume that a certain species is an indicator of high or low productivity conditions, coccolith Sr/Ca can profile the productivity response of individual species. Consequently, coccolith Sr/Ca records might be used to establish not only the sign of productivity change at the PETM and its magnitude compared to pre-event variations in this key site, but also the nature of the biotic response in ecologically diverse species.

Identification of productivity signals from coccolith Sr/Ca requires that other sources of variation in coccoliths Sr/Ca be constrained. In addition to productivity, coccolith Sr/Ca can be affected by changes in seawater Sr/Ca ratios, changes in coccolith species assemblages, and changes in sea surface temperatures, as well as post-depositional alteration. Fortunately the long ( $>10^6$  yr) residence times of Sr and Ca in the

ocean, and their similar behavior during weathering, preclude significant (>5%) variation in seawater Sr/Ca ratios during rapid events like the PETM (Stoll and Schrag, 2001). To minimize the influence of changing species assemblages, we apply new separation techniques that permit measurement of Sr/Ca of a single species or group of closely related species (Stoll and Ziveri, 2002; Minoletti et al., 2001). Estimates of changing sea surface temperatures during the PETM (Kennett and Stott, 1991) and culture calibrations of the temperature effect on coccolith Sr/Ca (Stoll et al., 2002b) allow us to calculate the temperature contributions to observed coccolith Sr/Ca variations. While Sr loss during diagenesis may slightly shift absolute Sr/Ca ratios of all carbonate fractions, if diagenetic alteration is uniform, primary relative changes in Sr/Ca are conserved, although partly attenuated (Schrag et al, 1995). We interpret only relative changes in Sr/Ca coccolith records.

By documenting large variations in Sr/Ca in different coccolith species, which cannot be explained by temperature or diagenetic effects, we demonstrate the potential of this new indicator to resolve productivity variations during the PETM and other transient climate events.

## **2. Samples and Methods**

### **2.1 Separation of coccolith fractions**

Latest Paleocene and earliest Eocene sediments at ODP Site 690 are composed of carbonate-rich (70-90% CaCO<sub>3</sub>) nannofossil ooze. The sediment is dominated by coccoliths of the genus *Toweius*, which contribute about half of the carbonate, while

other coccoliths contribute most of the remaining carbonate (Bralower, 2002). Twenty-one samples were processed from core depths of 173.8 to 167.9 mbsf in Hole 690B.

For each sample, compositionally distinct coccolith subfractions were obtained by a combination of microfiltering (Minoletti et al., 2001) and repeated decanting methods with settling times modified from Stoll and Ziveri (2002) for the larger coccoliths in the Paleocene material. Initial test separations of coccoliths into coarse, intermediate, and fine fractions showed that the intermediate size fraction was a mixture of many species and for subsequent samples only coarse and fine fractions were recovered for analysis. Nannofossil assemblages in all fractions were counted by scanning electron microscopy. Counts and size measurements were converted into carbonate contribution of each species using the approach of Young and Ziveri (2000), with shape factors adapted from modern morphologically similar species given in Young and Ziveri (2000).

The  $>20\ \mu\text{m}$  fraction dominated by foraminiferal fragments was reserved and cleaned of adhered fine carbonate by repeated cycles of rinsing and ultrasonication. There was not sufficient core material remaining for this interval of Hole 690B to permit picking individual species of foraminifera for analysis.

## **2.2 Cleaning and analysis**

Carbonates were cleaned with oxidizing, reducing, and ion exchange treatments to remove noncarbonate Sr and Ca as summarized in Stoll and Ziveri (2002). Samples were then dissolved in 0.1M acetic acid/ammonium acetate buffer and Sr/Ca ratios were measured via Inductively Coupled Argon Plasma Spectrometry in axial mode (Thermo Elemental model IRIS 1000 DUO at Middlebury College) with precision  $< 1\%$  (r.s.d).

### 3. Results

Nannofossil assemblage counts indicate that in the fine coccolith fraction most carbonate is from *Toweius* (typically 70-90% of the carbonate; Figure 1a). Minor carbonate is contributed by *Chiasmolithus* and *Zygrhablithus* (Figure 2a). In the coarse coccolith fraction, *Chiasmolithus* dominates in the lower part of the record and *Discoaster* and *Zygrhablithus* dominate in the upper part of the record (Figure 1b, 2b). *Toweius* is occasionally a minor component in the coarse coccolith fraction. Noncoccolith carbonate comprises less than a few percent of the carbonate in separated fractions, and variations in the amount of noncoccolith carbonate are not correlated with geochemical variations.

There are large (>40%) variations in Sr/Ca in both coccolith fractions (Figure 2). Sr/Ca ratios of the fine coccolith fraction (1.21 to 1.75 mmol/mol) are higher than those of the coarse coccolith fraction (0.97 to 1.39 mmol/mol). Sr/Ca ratios of both fractions decreased slightly and gradually in the lower part of the record then recovered shortly before the CIE onset (Fig. 2c). Comparison with high-resolution records of CaCO<sub>3</sub> and Fe (Rohl et al., 2000) shows that this trend of a gradual decline and recovery does not result from aliasing over precessional cycles. The Sr/Ca of the fine coccolith fraction continued to increase rapidly at the onset of the CIE, while that of the coarse coccolith fraction remained constant during the first part of the carbon isotope decrease and then increased. In both fractions, maximum Sr/Ca ratios were reached during the carbon isotope minimum and Sr/Ca values fell as carbon isotopic ratios rose to pre-excursion values.

## 4. Discussion

Several lines of evidence suggest that changes in coccolith Sr/Ca ratios during the PETM reflect primary variations in Sr incorporation in coccoliths which are not exclusively controlled by temperature effects nor changing species composition in the fine and coarse fractions. Thus, a large component of the observed variations in Sr/Ca reflects changing coccolithophorid productivity.

### 4.1 Constraining non-productivity influences on the coccolith Sr/Ca records

#### *4.1.1 Can the trends be explained by changing seawater Sr/Ca or postdepositional alteration?*

Models of the seawater Sr and Ca cycles suggest that over long time scales of several millions of years, seawater Sr/Ca can change by several tens of percent (Stoll and Schrag, 2001). However, the long ( $>10^6$  yr) residence times of Sr and Ca in the ocean and their similar behavior during weathering preclude significant ( $>5\%$ ) variation in seawater Sr/Ca ratios on timescales of 100,000 years or less (Stoll and Schrag, 2001; Stoll and Schrag, 1998). The constancy of Sr/Ca in the foraminiferal fraction ( $>20\ \mu\text{m}$ ) further suggests that changes in seawater Sr/Ca ratios are not responsible for the major Sr/Ca variation in the coccolith fraction. Foraminiferal Sr/Ca ratios respond to changing seawater Sr/Ca ratios (Delaney et al., 1985). Consequently, an increase in seawater Sr/Ca ratios by 40% over the Paleocene would have been recorded by a comparably large change in foraminiferal Sr/Ca ratios. Since the nonequilibrium effects on Sr partitioning in modern foraminiferal calcite are much smaller than in modern coccolith calcite (Stoll

and Schrag, 2001), it is unlikely the effect of such a large change in seawater Sr/Ca could be obscured by an equal and opposite effect on Sr partitioning in foraminiferal calcite.

The PETM is characterized by a shallowing lysocline and strong dissolution event (Thomas et al., 1999). At Site 690 this is expressed as a decrease in CaCO<sub>3</sub> from 90 to 70%. In microfossils with Sr and Mg distributed heterogeneously, as is the case for modern foraminifera possessing calcite produced during different life stages, partial dissolution preferentially removes the more soluble Sr, Mg-rich calcite and reduces Sr/Ca and Mg/Ca ratios (Brown and Elderfield, 1996; Rosenthal et al., 2000). Consequently, enhanced dissolution during the PETM might be expected to reduce Sr/Ca ratios of carbonate fractions with Sr and Mg distributed heterogeneously. However, this pattern of reduced Sr/Ca during the PETM is the opposite of what is observed in the coccolith records. Furthermore, each coccolith is a single crystal, and partial dissolution experiments confirm that Sr is distributed homogeneously so Sr/Ca ratios are not affected by partial dissolution (Stoll and Schrag, 2000).

Sr is lost during slow diagenetic recrystallization of buried biogenic carbonates (Richter and Liang, 1993). Uniform diagenetic alteration reduces absolute Sr/Ca ratios of carbonates and may partially attenuate primary Sr/Ca variations. However, it does not generate excursions in Sr/Ca ratios. Diagenesis can generate Sr/Ca excursions only when some sediment horizons recrystallize more, and lose more Sr, than others. A major shift in the amount of diagenetic recrystallization would be required to alter coccolith Sr/Ca ratios by 40%. This is inconsistent with the observation that nannofossil preservation is moderate to good throughout the section and does not vary significantly between samples

(Bralower, 2002). A major shift in the extent of diagenetic recrystallization would also have significantly affected Sr/Ca ratios of foraminiferal carbonate, which is not observed.

These observations and model constraints suggest that the variations in coccolith Sr/Ca are primary and are not artifacts of changing seawater Sr/Ca ratios.

#### *4.1.2 Do variations in coccolith Sr/Ca result from changing coccolith assemblages?*

Since absolute Sr/Ca ratios vary slightly among different species in ways that do not necessarily reflect their different relative productivities (eg. Stoll et al., 2002b), shifts in species assemblages can alter the Sr/Ca of a mixed coccolith assemblage independent of productivity changes. The PETM was characterized by an increase in the abundance of *Fasiculithus* and *Discoaster*, although *Toweius* remained the most abundant coccolith throughout the late Paleocene and Early Eocene at Site 690 (Bralower, 2002). In our separations, most of the *Fasiculithus* go into the intermediate size fraction that we have not analyzed. Both qualitative and quantitative evaluation of the assemblage and Sr/Ca records suggest that changes in assemblages are not responsible for the major variations in Sr/Ca.

In the coccolith fine fraction dominated by *Toweius*, the major change in Sr/Ca during the PETM does not coincide with changes in the relative contribution or assemblages of minor species in this fraction. This lack of correlation suggests that, to a first order, the major changes in Sr/Ca in this fraction are not artifacts of changing species assemblages.

In the coccolith coarse fraction dominated initially by *Chiasmolithus*, there is a shift to significant *Discoaster* carbonate at the start of the PETM that does not coincide

with a change in Sr/Ca. Either *Discoaster* has similar Sr/Ca ratios to *Chiasmolithus* and does not affect the Sr/Ca of the assemblage, or its higher or lower Sr/Ca is masked by decrease or increase in the Sr/Ca of *Chiasmolithus* during this time interval. From the second half of the PETM on, the *Discoaster* contribution is replaced by increased *Zygrhablithus*, coincident with an increase, then decrease, in Sr/Ca of the assemblage. These latter changes in Sr/Ca in this fraction are not artifacts of changing species assemblages since *Zygrhablithus* is abundant during both the ascent and decline in Sr/Ca.

While the major Sr/Ca shifts are independent of changes in species assemblages in our separated fractions, changing relative contributions of minor species may influence the small structure of Sr/Ca variations in both records. It is possible to constrain the magnitude and sign of these effects by estimating endmember compositions of the different species. If the fine and coarse fractions were mixtures of only two species, with the fine fraction dominated by *Toweius* and containing some *Chiasmolithus*, and the coarse fraction dominated by *Chiasmolithus* and containing some *Toweius*, it would be possible to uniquely solve for the endmember compositions of each species at every sample level. Since there are other contributing species, it is important to assess how the Sr/Ca ratios of these other species differ from those of *Toweius* and *Chiasmolithus*.

Constraints on the endmember Sr/Ca ratios of species are provided by Sr/Ca measurements on five different fractions produced for two sample levels (171.25 mbsf, and 170.49 mbsf; Figure 3). Since there is a wide range in abundance of *Toweius* and *Chiasmolithus* across these fractions, the high Sr/Ca ratios of *Toweius* and the lower Sr/Ca ratios of *Chiasmolithus* can be estimated with high precision. *Zygrhablithus* consistently shows Sr/Ca ratios as low as or lower than those of *Chiasmolithus*. At

170.49 mbsf, Sr/Ca ratios of *Discoaster* are comparable to those of *Chiasmolithus*, whereas Sr/Ca ratios of *Fasiculithus* are comparable to those of *Toweius*.

If we assume that species with similar Sr/Ca ratios (*Zygrhablithus*, *Chiasmolithus*, and *Discoaster*; *Fasiculithus* and *Toweius*) at 171.25 and 170.49 mbsf also have similar Sr/Ca ratios throughout the record, we can estimate the influence of changing assemblages on the trends in Sr/Ca in each fraction. To a first order, the continuously higher Sr/Ca ratio of the finer *Toweius* dominated fraction relative to the *Discoaster/Chiasmolithus*-dominated fraction supports this assumption. This approach permits treatment of the coarse and fine fractions as mixtures of two groups of species for which two endmember compositions may be calculated at each depth. The resulting estimation (Figure 4) is highly robust for *Toweius* since the fine fraction is typically 70 to 90% carbonate from *Toweius* and the Sr/Ca of minor carbonate from *Chiasmolithus* is well-constrained. The estimation for *Chiasmolithus* in the coarse fraction is less certain because *Chiasmolithus* does not dominate the coarse fraction throughout the record, and in addition to the well-constrained *Toweius* there is significant carbonate from other species whose Sr/Ca are not as well constrained. In particular, the Sr/Ca of *Zygrhablithus* may be overestimated in this calculation, which would underestimate the Sr/Ca of *Chiasmolithus* for the final part of the record (gray squares in Figure 4).

Consequently, we are highly confident that *Toweius* experienced a pronounced (40%) increase in Sr/Ca ratios during the PETM, followed by a decrease to pre-excursion values. We are moderately confident that *Chiasmolithus* and *Discoaster* experienced smaller increases (~25%) in Sr/Ca in the latest part of the PETM.

#### *4.1.3 What part of the observed variation is attributable to temperature changes?*

Increasing temperature elevates the Sr/Ca ratio in all species of coccoliths by about 1% per degree C in culture experiments (Stoll et al., 2002a,b). Because this temperature effect is indistinguishable from that observed in cultured planktonic foraminifera (Lea et al., 1999) and abiogenic calcite (Malone and Baker, 1999) we believe that it reflects a ubiquitous thermodynamic response which should be the same for extinct coccolith species. Evidence for a small effect of temperature on coccolith Sr/Ca is also supported by the positive covariation of coccolith Sr/Ca with upwelling intensity and productivity in core top sediments despite depressed temperatures in upwelling zones (Stoll et al., 2002b; Stoll and Schrag, 2000). This field data confirms that the productivity response may dominate over the temperature effect on coccolith Sr/Ca.

Both culture and recent sediment records suggest that the 6 °C warming of Site 690 surface waters during the PETM (inferred from planktonic foraminifera  $\delta^{18}\text{O}$  record of Kennett and Stott, 1991) would have increased coccolith Sr/Ca by no more than 10%. Thus, we believe that temperature change is directly responsible for only a small fraction of the observed Sr/Ca variations in the coccolith records (Figure 4). In the 200,000 years prior to the PETM, planktonic foraminiferal temperatures varied by less than 2 degrees, suggesting that the longer term trends in Sr/Ca cannot be attributed entirely to temperature changes.

#### **4.2 The record of changing coccolithophorid productivity at Site 690**

The balance of evidence suggests that the excursion to higher coccolith Sr/Ca ratios during the PETM results primarily from an increase in coccolithophorid

productivity (Figure 5). For *Toweius*, the increase in productivity began around 40,000 years prior to the onset of the CIE and productivity continued to increase rapidly at the onset of the CIE, reaching a maximum between 50,000 and 75,000 years after the CIE onset. As temperatures cooled and  $\delta^{13}\text{C}$  began to rise 70,000 to 120,000 years after the CIE onset, productivity of *Toweius* decreased rapidly to pre-excursion values. The productivity of *Toweius* during the PETM was much higher than at any other time in the ~350,000 year record analyzed from Site 690. The local maximum of Sr/Ca in the more complicated coarse fraction record provides additional data supporting the increase in productivity documented in the more robust *Toweius* record.

Higher temperatures and atmospheric  $\text{CO}_2$  during the PETM may have contributed to faster algal growth rates, but nutrient availability typically limits productivity. Increased nutrient fluxes during the PETM may have been the most important stimulus for algal productivity in the Weddell Sea area. Increased  $^{187}\text{Os}/^{186}\text{Os}$  ratios of seawater during the PETM suggest that average global chemical weathering rates were 20-30% higher (Ravizza et al., 2001), perhaps due to climatic enhancement of continental weathering. Enhancement of continental weathering during the PETM is consistent with climate models of increased precipitation over land surfaces (Sloan and Thomas, 1998) and warmer temperatures and higher  $\text{CO}_2$  contents which could also accelerate weathering. High latitude precipitation is particularly increased in models of hydrological response to increased greenhouse forcing (Manabe, 1996).

Regionally, an increase in continental weathering rates and an increase in clastic supply from Antarctica preceded the CIE onset by ~10,000 years (Robert and Kennett,

1994) and may have caused the initial increase in productivity of *Toweius* which preceded the CIE. The continued steep rise in the productivity of *Toweius*, the dominant coccolithophorid in the assemblage, closely paralleled the global average increase in continental weathering flux inferred from Os isotopes (Figure 5).

### **4.3 Tracking changes in the carbon cycle during the PETM**

The identification of a large increase in productivity in the dominant coccolithophorid *Toweius* at ODP Site 690 indicates that coccolith Sr/Ca has the potential to resolve the kinds of large, rapid changes in productivity that might be part of global feedbacks in the carbon cycle during the PETM. Productivity changes might influence both short and long term shifts in the carbon cycle by strengthening the biological pump and increasing carbon burial. If increased primary productivity led to regionally or globally higher export of carbon to the deep ocean, then the strengthened biological pump might have decreased atmospheric CO<sub>2</sub>. Coccolithophorid productivity records provide an elegant way to link primary productivity and deep export of carbon, since the transfer efficiency of organic carbon to the deep ocean is largely controlled by the carbonate rain rate (Francois et al., 2002) which is set by coccolithophorid carbonate production. Atmospheric CO<sub>2</sub> may have been highly sensitive to the strength of the biological pump in the Southern Ocean (Broecker et al., 1999), if the Southern Ocean were a source of deep water in the Late Paleocene, as it is today.

Long term recovery of the carbon cycle, and return to pre-event carbon isotopic ratios, would have required burial of the additional hydrate-derived carbon in sediment reservoirs of carbonate or organic carbon. Much of the organic carbon burial may have occurred in continental margin sediments, the locus of most organic carbon burial today

(Hedges and Kiel, 1995). Our record at Site 690 documents productivity response in a near-continent site which is synchronous with both locally and globally enhanced weathering intensity (Robert and Kennett, 1994; Ravizza et al., 2001) and might reflect the productivity response of similar environments worldwide.

Further application of the coccolith Sr/Ca indicator in other sites can test whether coccolithophorid productivity increased globally during the PETM. In some areas, benthic foraminiferal assemblages (Thomas, 1998) and phosphorus accumulation rates (Schmitz et al., 1997) provide evidence for increased organic carbon fluxes to the deep ocean; dinoflagellate assemblages (Crouch, 2001) indicate warmer temperature or elevated productivity in marginal seas. However, in some of these same areas, nannofossil (Bralower, 2002) and planktic foraminiferal assemblages (Kelly et al., 1996) are interpreted as indicating increased stratification and oligotrophy. Integrating data on coccolithophorid productivity with these other records may help resolve the true nature of changes in surface and deep ocean conditions that have given rise to these apparently conflicting interpretations.

Currently, time-resolved application of coccolith Sr/Ca is limited because there are few carbonate-bearing ODP sites that encompass the PETM interval and of these many are either very condensed or have hiatuses through the PETM interval. Even ODP site 1051 in the Western Atlantic, the first PETM record to be placed on an orbitally tuned timescale (Norris and Rohl, 1999), is now believed to have a minor or possibly major hiatus (Rohl et al. 2000; Farley and Eltgroth, in press). Analysis of coccolith Sr/Ca in 1051 is precluded by the abundance of non-coccolith carbonate, which exceeds 50% of the carbonate in some separated fractions and probably reflects disturbance and/or

red deposition of upslope sediments at this site (eg. Katz et al., 1999) Fortunately, recent ODP Legs at Shatsky Rise (Bralower et al., 2002) and upcoming legs at Demerara Rise (2003) and Walvis Ridge (2003) have the potential to provide new carbonate-rich PETM age material for high-resolution study.

In addition to assessing whether there was a global change in productivity, time-resolved records of coccolith Sr/Ca will be useful to evaluate the timing of this response and constrain possible models of feedbacks in the carbon cycle. Dickens (2001) used mass balance equations to compare the  $\delta^{13}\text{C}$  of the combined ocean-atmosphere-biosphere with the  $\delta^{13}\text{C}$  record of ODP site 1051. He concluded that accelerated carbon removal would have been required to match the rapid rate of  $\delta^{13}\text{C}$  recovery following the PETM perturbation. One possibility proposed by Dickens (2001) is that accelerated carbon burial scaled linearly with the amount of carbon in the exogenic reservoir, increasing rapidly upon carbon addition at the PETM and decreasing slowly thereafter (Figure 6A curve A). The form of this accelerated carbon removal differs slightly from the form of increased local productivity observed in the Site 690 record and from the global Os isotope weathering intensity record. If indicative of global trends in carbon burial, these Os and Sr/Ca records would imply carbon removal which peaked sooner after the CIE onset and dropped sharply back to pre-event levels more quickly (Figure 6 curve B). With the revised age scale proposed for Sites 1051 and 690 (Rohl et al., 2000),  $\delta^{13}\text{C}$  variations are no longer diagnostic of accelerated or constant C removal during the PETM, nor the form of any accelerated C removal.

If the warming during the PETM and subsequent climatic recovery were strongly influenced by changes in the carbon cycle, then records of temperature change might

offer a second indicator of feedbacks in the carbon cycle. Recent studies confirm that a significant part of the temperature change was synchronous with or post-dated the initial carbon isotope excursion and that methane reached the atmosphere prior to oxidation (Bains et al., 1999; Thomas et al., 2002), suggesting that greenhouse forcing was an important control over temperature changes. If the Site 690 oxygen isotopic record were broadly representative of the global temperature trends, then the recovery of sea surface temperatures after the PETM is more closely simulated by accelerated carbon removal which both peaks and falls off rapidly (Figure 6c). A wider distribution of high resolution coccolith Sr/Ca productivity records, as well as temperature records, will be needed to show if either of these potential forms of accelerated carbon removal occurred in marine sediments during the PETM.

The detailed timing of carbon removal and its relation to productivity will continue to be sensitive to refinements in the timescale of the PETM. Emerging work with  $^3\text{He}$  chronometry has suggested a dramatic increase in sedimentation rate coincident with the return of climate indicators to pre-event values (Farley and Eltgroth, in press). Consequently, recovery from the PETM may have occurred much more rapidly (30 ky) than inferred from the cyclostratigraphic timescale (60-150 ky; Rohl et al., 2000). If climate recovery was indeed so rapid, it would alter the details of our mass balance calculations on the carbon cycle, and would require accelerated removal of isotopically light carbon, either in organic matter or methane hydrates, to match the carbon isotopic record. As timescales and climate indicators are refined with data from new sites, it will be important to consider how possible carbon removal scenarios match the temperature record, as well as the carbon isotopic record.

## 5. Summary

Large (>40%) variations in coccolith Sr/Ca ratios in multiple species of coccoliths in late Paleocene sediments from ODP Site 690 are best explained by changing Sr incorporation in coccoliths driven by changing coccolithophorid productivity. The productivity of the dominant coccolithophorid genera *Toweius* increased significantly during the PETM, closely following a global increase in continental weathering intensity inferred from Os isotope records and local increase in weathering intensity inferred from clay mineralogy in Site 690 sediments. Nannofossil assemblage changes, previously interpreted as reflecting more oligotrophic conditions at Site 690 during the PETM, may reflect the large change in sea surface temperatures at the site, rather than changes in fertility. Temperature is the dominant control over coccolithophorid biogeography at modern high latitude sites (McIntyre et al., 1970; Molfino et al., 1982). Application of coccolith Sr/Ca at other complete marine PETM sections can confirm whether the Site 690 productivity response is representative of global trends and whether productivity served as an important negative feedback in the carbon cycle.

## Acknowledgements

Ray Coish generously provided instrument time on the ICAP at Middlebury College. We thank Jerry Dickens for discussions of his Paleogene carbon model and providing a preprint of work on the Ba cycle, Tim Bralower for assistance with coccolith identifications, and both for extensive critical comments on an earlier version of this work. Greg Ravizza and an anonymous reviewer provided thoughtful suggestions which

significantly improved this manuscript. This project was supported by startup funding at Williams College.

## References Cited

- Bains, S., Corfield, R., and Norris, R.D., Mechanisms of climate warming at the end of the Paleocene: *Science*, 285, 724-727, 1999.
- Bains, S., Norris, R.D., Corfield, R. M., and Faul, K., Termination of global warmth at the Palaeocene/Eocene boundary through productivity feedback: *Nature*, 407, 171-173, 2000.
- Bralower, T., Evidence for surface water oligotrophy during the Late Paleocene Thermal Maximum: nannofossil assemblage data from Ocean Drilling Program Site 690B, Maud Rise, Weddell Sea: *Paleoceanography*, 17: 2001PA000662, 2002.
- Bralower, T.J., Premoli Silva, I., Malone, M.J., et al., 2002. Proc. ODP, Init. Repts., 198 [Online]. Available from World Wide Web:  
[http://www-odp.tamu.edu/publications/198\\_IR/198ir.htm](http://www-odp.tamu.edu/publications/198_IR/198ir.htm). [Cited 2002-12-12]
- Broecker, W., Lynch-Stieglitz, J., Archer, D., Hofmann, M., Maier-Reimer, E., Marchal, O., Stocker, T., and Gruber, N., How strong is the Harvardton-Bear constraint? *Global Biogeochemical Cycles*, 13, 817-820, 1999.
- Brown, S. J., and Elderfield, H., Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: Evidence of shallow Mg-dependent dissolution. *Paleoceanography*, 11, 543-551, 1996.
- Crouch, E.M., Clausen, C.H., Brinkhus, H., Morgans, H., Rogers, K., Egger, H., and Schmitz, B. Global dinoflagellate event associated with the late Paleocene thermal maximum. *Geology*, 29, 315-318, 2001.

- Delaney, M.L., Be, A.W.H., and Boyle, E.A. Li, Sr, Mg, and Na in foraminiferal calcite shells from laboratory culture, sediment traps, and sediment cores. *Geochemica et Cosmochimica Acta*, 49, 1327-1341, 1985.
- Dickens, G.R., T. Fewless, E. Thomas & T.J. Bralower, Excess barite accumulation during the Paleocene/Eocene thermal maximum: Massive input of dissolved barium from seafloor gas hydrate reservoirs, in *Causes and Consequences of Globally Warm Climates in the Early Paleogene*: Geological Society of America Special Publication, in press.
- Dickens, G. R., Carbon addition and removal during the Late Palaeocene Thermal Maximum: basic theory with a preliminary treatment of the isotope record at ODP Site 1051, Blake Nose, in Kroon, D., Norris, R.D., and Klaus, A., eds., *Western North Atlantic Palaeogene and Cretaceous Paleoceanography*: Geological Society of London Spec. Pub., 183, 293-305, 2001.
- Dickens, G.R., O'Neil, J.R., Rea, D.K., and Owen, R.M., Dissociation of oceanic methane as a cause of the carbon isotope excursion at the end of the Paleocene: *Paleoceanography*, 10, 865-971, 1995.
- Dickens, G.R., Castillo, M.M., and Walker, J.C.G. A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology*, 25, 259-262, 1997.
- Farley, K. and Eltgroth, S., An alternative age model for the Paleocene-Eocene thermal maximum using extraterrestrial <sup>3</sup>He. *Earth and Planetary Science Letters*, in press.
- Francois, R., Honjo, S., Krishfield, R., and Manganini, S. Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean. *Global Biogeochemical Cycles*.
- Hedges, J., and Keil, R.G., Sedimentary organic -matter preservation – An assessment and speculative synthesis. *Mar. Chem.*, 49, 81-115, 1995.

- Katz, M.E., Pak, D.K., Dickens, G.R., and Miller, K.G., The source and fate of massive carbon input during the latest Paleocene Thermal Maximum. *Science*, 286, 1531-1533, 1999.
- Kennett, J.P. and Stott, L.D., 1991, Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene: *Nature*, 358, 225-229, in press.
- Kelly, D.C., Bralower, T.J., Zachos, J.C., Permolli Silva, I., and Thomas, E. Rapid diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the late Paleocene thermal maximum: *Geology*, 24, 423-426.
- Koch, P. L., Zachos, J.C., and Gingerich, P.D. Correlation between isotope records in marine and continental carbon reservoirs near the Palaeocene/Eocene boundary: *Nature*, 358, 319-322, 1992.
- Koch, P.L., Zachos, J.C., and Dettman, D.L., Stable isotope stratigraphy and paleoclimatology of the Paleogene Bighorn Basin (Wyoming, USA). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 115, 61-89, 1995.
- Lea, D.W, Mashiotta, T.A., and Spero, H.J. Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, *Geochimica et Cosmochimica Acta*, 63, 2369-2379, 1999.
- Malone, M.J. and Baker, P.A. Temperature dependence of the strontium distribution coefficient in calcite: an experimental study from 40° to 200° C and application to natural diagenetic calcites. *Journal of Sedimentary Research*, 69, 216-223, 1999.
- Manabe, S., Early development in the study of greenhouse warming: The emergence of climate models. *Ambio*, 26, 47-51, 1996.
- McIntyre, A., Be, A.W.H., Roche, B. Modern Pacific coccolithophorida: a paleontological thermometer. *N.Y. Acad. Sci. Trans. Ser. II* 32, 720-731, 1970.

- Minoletti, F., Gardin, S., Nicot, E., Renard, M., and Spezzaferri, S. Mise au point d'un protocole experimental de separaton granulometrique d'assemblages de nannofossiles calcaires; applications paleoecologiques et geochimiques: *Bulletin Societe Geologique France*, 172, 437-446, 2001.
- Molfinio, B., Kipp, N.G., and Morley, J. Comparison of Foraminiferal, Coccolithophorid, and Radiolarian Paleotemperature Equations: Assemblage Coherency and Estimate Concordancy. *Quaternary Research*, 17, 279-313, 1982.
- Richter, F. M., and Liang, Y., The rate and consequences of Sr diagenesis in deep-sea carbonates: *Earth and Planetary Science Letters*, 117, 553-565, 1993.
- Rickaby, R.E.M., Schrag, D.P., Zonzervan, I., and Riebesell, U. Growth rate dependence of Sr incorporation during calcification of *Emiliana huxleyi*. *Global Biogeochemical Cycles* 16, 1-8, 2002.
- Robert, C. and Kennett, J.P. Antarctic subtropical humid episode at the Paleocene-Eocene boundary: Clay-mineral evidence: *Geology*, 22, p 211-214, 1994.
- Ravizza, G., Norris, R.N., Blusztajn, J., and Aubry, M.-P. An osmium isotope excursion associated with the late Paleocene thermal maximum: Evidence of intensified chemical weathering: *Paleoceanography*, 16, 155-163, 2001.
- Rohl, U., Bralower, T.J., Norris, R.D., and Wefer, G., New chronology for the late Paleocene thermal maximum and its environmental implications: *Geology*, 28, 927-930, 2000.
- Rosenthal, Y., Lohman, G.P., Lohman, K.C., Sherrell, R.M., Incorporation and preservation of Mg in Globigerinoides sacculifer; implications for reconstructing the temperature and  $^{18}\text{O}/^{16}\text{O}$  of seawater. *Paleoceanography* 15, 135-145, 2000.
- Schrag, D. P., DePaolo, D. J., and Richter, F. M., Reconstructing past sea surface temperatures: correcting for diagenesis of bulk marine carbonate: *Geochimica et Cosmochimica Acta*, 59, 2265-2278, 1995.

- Schmitz, G., Charisi, S.D., Thompson, E.I., and Speijer, R.P. Barium, SiO<sub>2</sub> (excess) and P<sub>2</sub>O<sub>5</sub> as proxies of biological productivity in the Middle East during the Paleocene and latest Paleocene benthic extinction event. *Terra Nova*, 9, 95-99, 1997.
- Shipboard Scientific Party, 1998. Site 1051. In Norris, R.D., Kroon, D., Klaus, A., et al., Proc. ODP, Init. Repts., 171B, 171–240 [Online]. Available from World Wide Web:  
[http://www-odp.tamu.edu/publications/171B\\_IR/CHAP\\_03.PDF](http://www-odp.tamu.edu/publications/171B_IR/CHAP_03.PDF).  
[Cited 2002-10-10]
- Sloan, L.C. and Thomas, E., Global climate of the late Paleocene epoch: Modeling the circumstances associated with a climatic “event,” in Aubry, M.P. et al., eds., *Late Paleocene-Early Eocene Climatic and Biotic Events in the Marine and Terrestrial Records*: New York, Columbia Univ. Press, New York, 138-157, 1998.
- Stoll, H. and Ziveri, P., Methods for separation of monospecific coccolith samples from sediments: *Marine Micropaleontology*, 46, 209-221, 2002.
- Stoll, H.M., Rosenthal, Y., and Falkowski, P. Climate proxies from Sr/Ca of coccolith calcite: calibrations from continuous culture of *Emiliana huxleyi*. *Geochim. Cosmochim. Acta*, 66, 927-936, 2002a.
- Stoll, H.M., Ziveri, P., Geisen, M., Probert, I., and Young, J.R., Potential and limitations of Sr/Ca ratios in coccolith carbonate: new perspectives from cultures and monospecific samples from sediments: *Phil. Trans. Roy. Soc. of London, A* 360, 719-747, 2002b.
- Stoll, H.M. and Schrag, D.P. Sr/Ca variations in Cretaceous carbonates: relation to productivity and sea level changes. *Palaeogeography, Palaeoclimatology, Palaeoecology* 168, 311-336, 2001.

- Stoll, H. M., and Schrag, D. P., Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate: *Geochemistry Geophysics Geosystems* paper 1999GC000015, 2000.
- Stoll, H. M. and D. P. Schrag, Effect of Quaternary sea level cycles on the Sr budget of the ocean. *Geochimica et Cosmochimica Acta*, 62, 1107-1118, 1998.
- Thomas, D.J., Bralower, T.J., and Zachos, J., New evidence for subtropical warming during the late Paleocene thermal maximum: Stable isotopes from Deep Sea Drilling Project Site 527, Walvis Ridge. *Paleoceanography*, 14, 561-570, 1999.
- Thomas, D.J., Zachos, J., Bralower, T.J., Thomas, E., and Bohaty, S., Warming the fuel for the fire: Evidence for the thermal dissociation of methane hydrate during the Paleocene-Eocene thermal maximum. *Geology*, 30, 1067-1070, 2002.
- Thomas, E., and Shackleton, N.J., The Paleocene-Eocene benthic foraminiferal extinction and stable isotope anomalies, in *Correlation of the Early Paleogene in Northwest Europe*: Geol. Soc. Spec. Publ., 101, 401-441, 1996.
- Thomas, E. Biogeography of the Late Paleocene Benthic Foraminiferal Extinction. In Aubry, M.P., Lucas, S.G., and Berggren, W.A., eds. *Late Paleocene-Early Eocene Climatic and Biotic Events in the Marine and Terrestrial Records*. New York: Columbia University Press, 1998.
- Young, J.R., and Ziveri, P. Calculation of Coccolith Volume and its use in Calibration of Carbonate Flux Estimates. *Deep Sea Research Part II: Topical Studies In Oceanography* 47, 1679-1700, 2000.

Zachos, J.C., Lohmann, K.C., Walker, J.G.C., and Wise, S.W. Abrupt climate changes and transient climates during the Palaeogene: A marine perspective: *J. Geol.*, 101, p 193-213, 1993.

## Figure captions

Figure 1. Scanning electron micrographs of coccoliths from separated fractions. Left frame shows fine (3-5  $\mu\text{m}$ , from 170.05 m) and right frame shows coarse (8-12  $\mu\text{m}$  from 172.4 m) subfractions of sediment from Site 690 dominated by *Toweius spp* and *Chiasmolithus bidens*, respectively. Note that some etching of the specimens has occurred during sample cleaning and is not indicative of the preservation state of the coccoliths.

Figure 2. Species composition and Sr/Ca ratios of a) fine and b) coarse coccolith fractions separated from Site 690 sediments, along with c) Sr/Ca of the foraminiferal fraction and bulk carbonate  $\delta^{13}\text{C}$ . The weight abundance of different coccolith species in separated fractions is estimated from light microscope and scanning electron microscope counts and size measurements of species in separated fractions. Coccolith volume was calculated following Young and Ziveri (2000) using shape factors for morphologically similar extant species. Note that the x-axis of sample depth is a category scale, not a linear scale of depth.

Figure 3. Species assemblages and measured Sr/Ca ratios in multiple separated fractions constrain end member Sr/Ca for each species. a-b) Multiple fractions from 171.25 and 170.49 mbsf, showing relative carbonate contributions from each species and measured Sr/Ca of each fraction. c-d) Estimated endmember compositions. Symbol indicates optimum solution and the length of the error bars indicates the relative precision of the

estimated endmember compositions for each species for each sample depth. Error bars represent the maximum and minimum endmember compositions where the sum of squared errors is <0.4% in a sensitivity test where all other endmember compositions are set to optimum values (sum of squared errors for the optimum solution is 0.1% for 171.25 mbsf and 0.17% for 170.49 mbsf). Dashed lines show potential treatment of the fractions as mixtures of two groups of species with similar low Sr/Ca ratios (*Zygrhablithus*, *Chiasmolithus*, and *Discoaster*) and high Sr/Ca ratios (*Fasciculithus* and *Toweius*).

Figure 4. Estimated Sr/Ca ratios in *Toweius* and *Chiasmolithus/Discoaster*. The onset of the carbon isotope event (CIE) is used as the zero age for the time scale based on chronology of Rohl et al (2001). a) Symbols indicate Sr/Ca calculated for hypothetical pure endmembers *Toweius* and *Chiasmolithus/Discoaster*, calculated as described in section 4.1.2 of the text. For *Toweius* and *Chiasmolithus/Discoaster*, vertical bars extend to the measured Sr/Ca ratio of the fine and coarse coccolith fractions, respectively. Error bars illustrate the magnitude of the correction for changing species assemblages but not uncertainties in the abundance estimates of different species. For *Toweius* the calculated Sr/Ca is higher than the fine fraction because both minor contributors, *Chiasmolithus* and *Zygrhablithus*, have lower Sr/Ca ratios. For *Chiasmolithus* the calculated Sr/Ca is higher than the coarse fraction because minor contributor *Toweius* has higher Sr/Ca ratios. The timing of changing carbonate contributions for the coarse fraction are indicated: *Chiasmolithus* (65-90%; solid black squares), *Chiasmolithus* and *Discoaster* (30% each; black square with white cross), *Chiasmolithus* and *Zygrhablithus* (30% each; gray filled

squares). Small open circles show the magnitude of change in Sr/Ca expected if temperature were the only effect on coccolith Sr/Ca ratios. Changes in temperatures of surface waters at Site 690 were calculated from the planktic foraminiferal  $\delta^{18}\text{O}$  record (Kennett and Stott, 1991); the direct effect of temperature on Sr/Ca is taken from culture and field studies as described in section 4.1.3.

Figure 5. Estimated productivity-driven variation in Sr/Ca of *Toweius* (shaded band) compared with carbon isotopic and  $\text{CaCO}_3$  records from Site 690 and the global composite Os isotope record (Ravizza et al., 2001). The effects of temperature on *Toweius* Sr/Ca have been removed. Shaded band illustrates effect of uncertainties in the slope of the Sr/Ca vs. temperature relation (1 vs. 2% per degree C) and slight differences in temperature estimates from foraminiferal (Kennett and Stott, 1991) and bulk carbonate (Bains et al., 1999) records, as well as uncertainties estimating *Toweius* endmember Sr/Ca from the Sr/Ca record of the fine coccolith separated fraction. Bulk carbonate  $\delta^{13}\text{C}$  and weight fraction  $\text{CaCO}_3\%$  from Bains et al., (1999); Os isotope data from Ravizza et al. (2001).

Figure 6. Modeled variations in the exogenic carbon cycle over the PETM excursion. a) Rate of carbon removal in sediments. Scenario A (thin line) assumes carbon removal as a function of total carbon in the exogenic carbon reservoir (calculated as in Dickens, 2001); Scenario B (thick line) uses the timing of the Os record of weathering intensity to constrain the timing of changes in carbon burial rate; the amount of carbon burial is specified to match the recovery. Scenario C (gray thick line) assumes constant carbon

removal. We used the Paleogene carbon cycle parameterizations of Dickens, except that rate and amount of methane hydrate input was adjusted to match the bulk  $\delta^{13}\text{C}$  record of Site 690 with its new chronology. Small circles show changes in *Toweius* Sr/Ca as in Figure 5. b) Changes in  $\delta^{13}\text{C}$  of exogenic carbon reservoir according to scenarios A,B, and C (lines as in 5a). Small diamond symbols indicate Site 690  $\delta^{13}\text{C}$  from bulk carbonate (Bains et al., 1999). c) Mass of carbon in the exogenic carbon reservoir according to scenarios A, B, and C (lines as in 5a). Small diamond symbols indicate Site 690 sea surface temperatures calculated from bulk carbonate  $\delta^{18}\text{O}$  records (Bains et al., 1999), which show the same timing and degree of temperature change as planktic foraminiferal  $\delta^{18}\text{O}$  (Kennett and Stott, 1991) but provide a longer record.

Figure 1

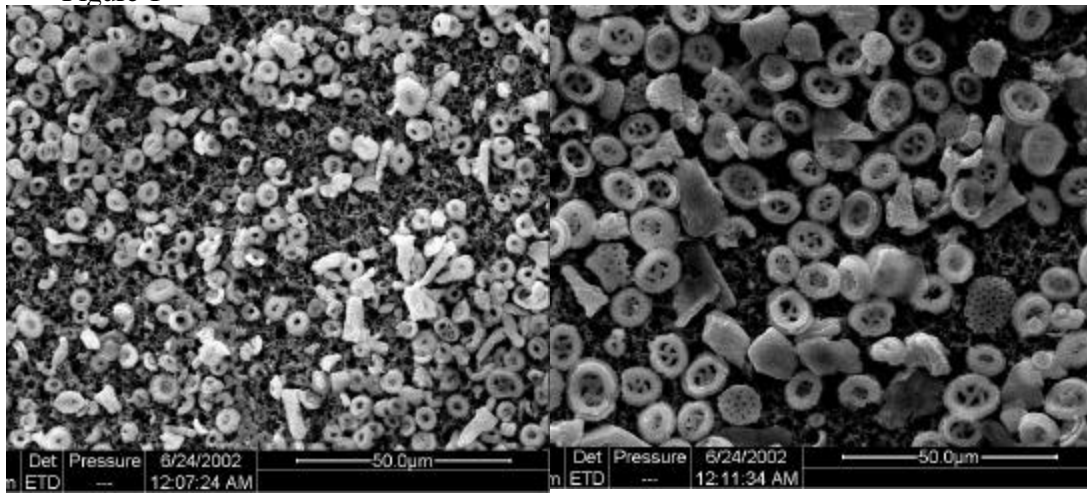


Figure 2

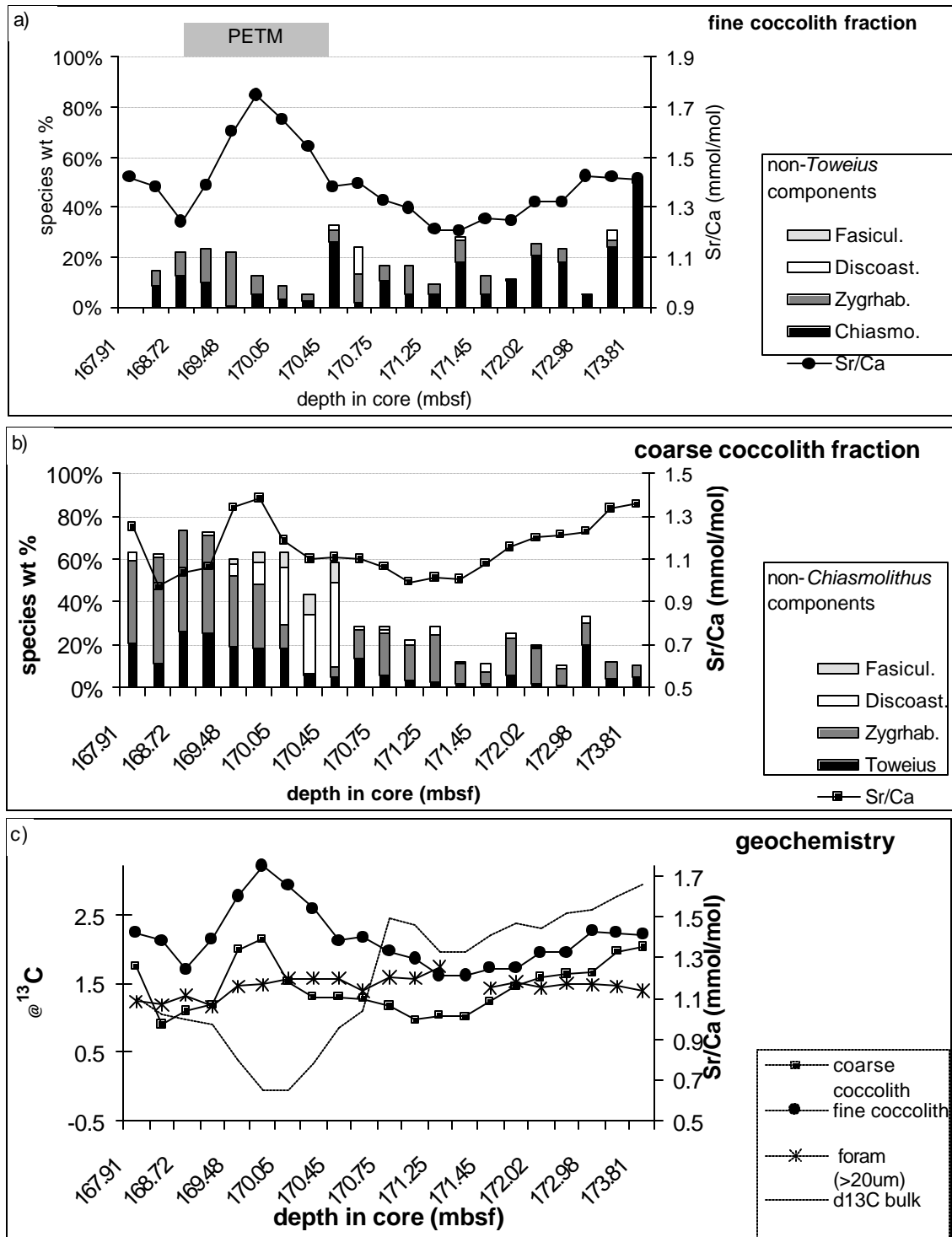


Figure 3

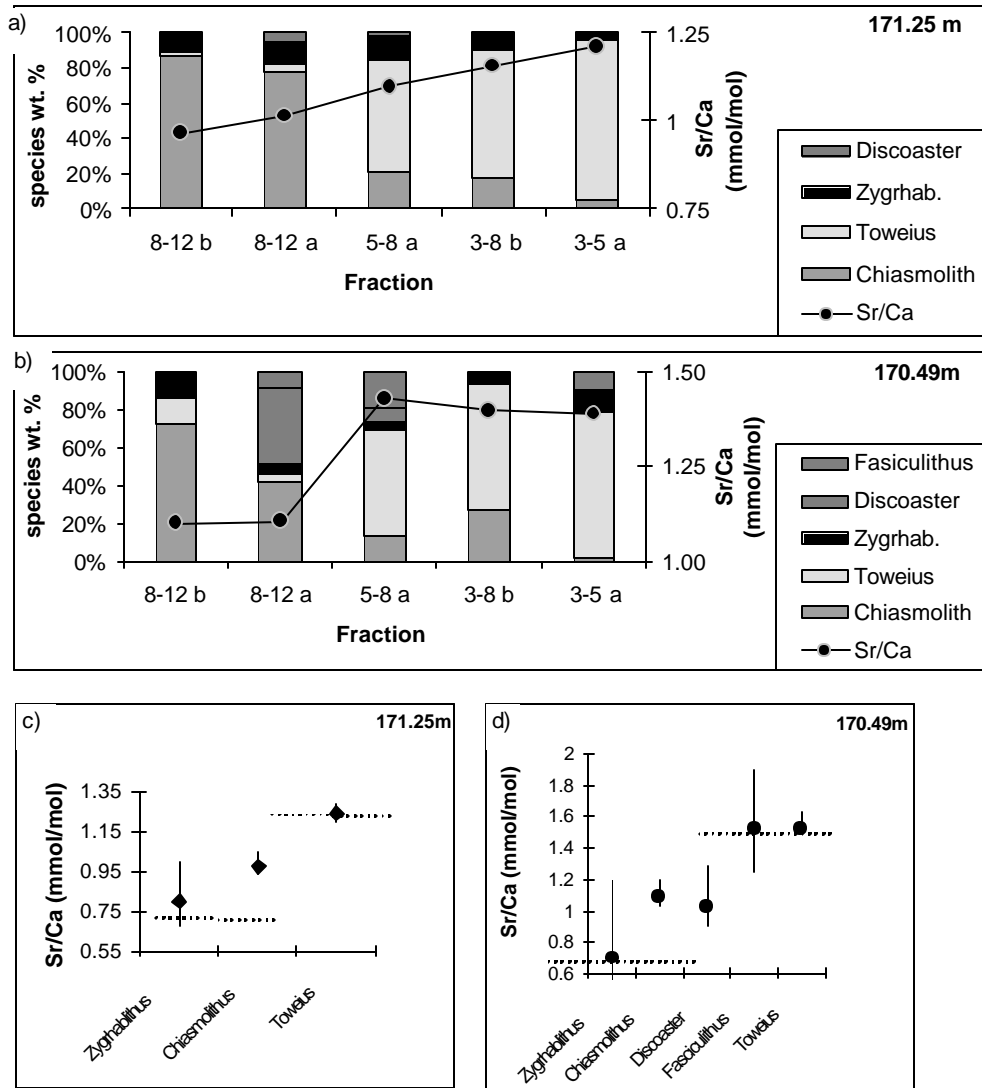


Figure 4

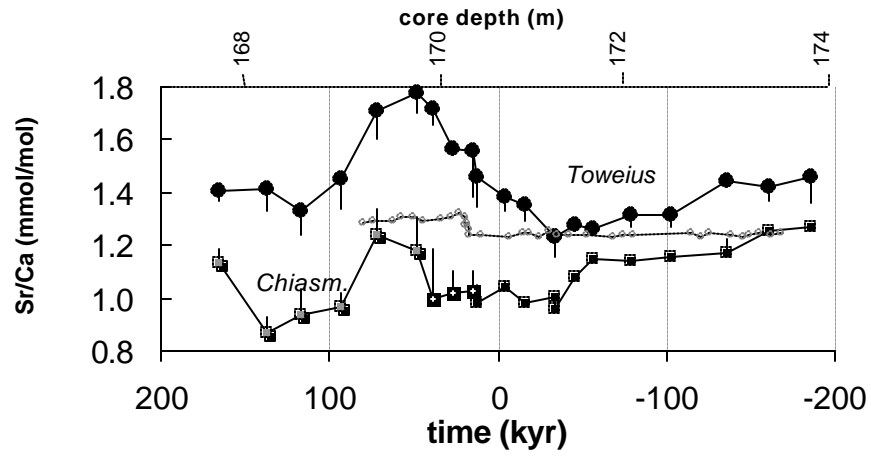


Figure 5

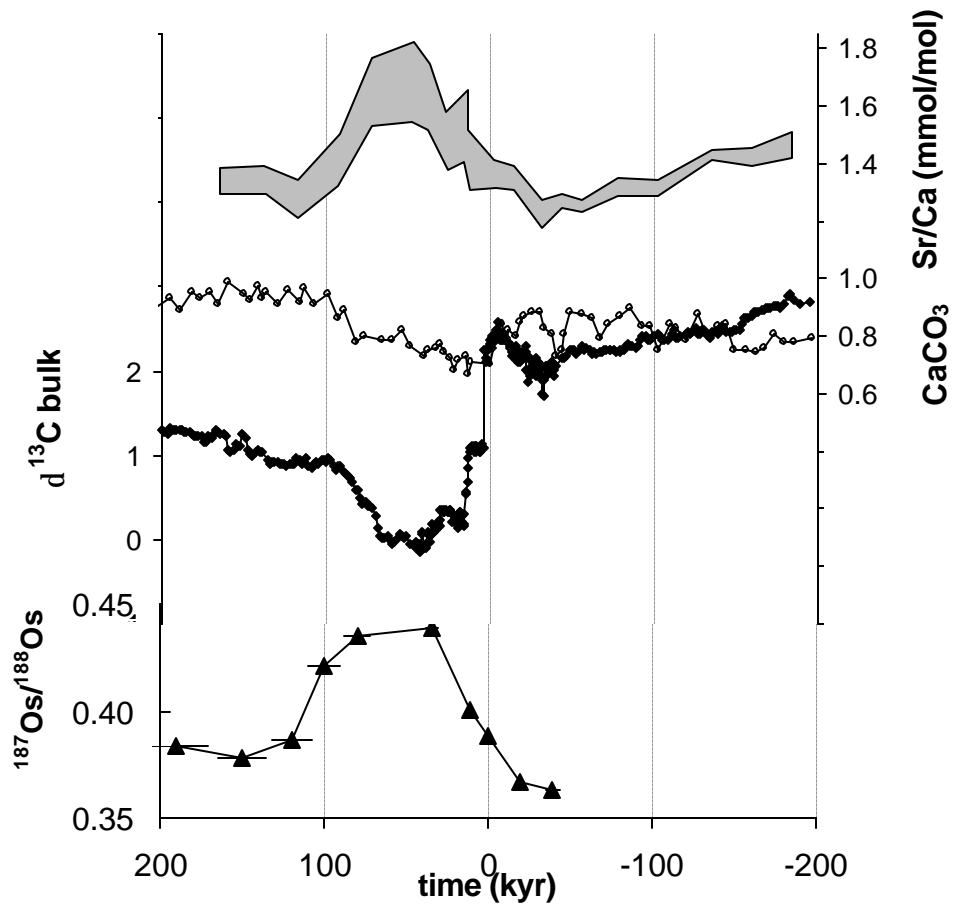


Figure 6

