# Cenozoic pelagic Sr/Ca records: Exploring a link to paleoproductivity

K. Billups

College of Marine Sciences, University of Delaware, Lewes, Delaware, USA

R. E. M. Rickaby

Department of Earth Sciences, University of Oxford, Oxford, UK

D. P. Schrag

Laboratory for Geochemical Oceanography, Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

[1]   Recent studies have revealed that Sr/Ca ratios of coccolithophores may be affected by productivity. Here we compile published Sr/Ca data from bulk carbonate, fine fraction sediment, and planktonic foraminiferal Sr/Ca records that span the past 60 Myr and attempt to place these records into a paleoceanographic framework. We account for changes in seawater Sr/Ca ratios using the curve of *Lear et al.* [2003] and discuss our observations with respect to changes in the partitioning coefficient of Sr through time. We discuss limitations associated with postburial processes, temporal changes in the coccolith/planktonic foraminiferal rain ratio, and the coccolith species composition of the sediment. Despite these caveats, we are able to show that in the bulk and fine fraction carbonate records there are two broad periods of enhanced partitioning of Sr relative to today, the Oligocene, and the middle to late Miocene/early Pliocene. Because these are two intervals for which we can cite evidence for a relatively productive ocean on the regional or global scale, we believe that the Sr/Ca ratios of bulk carbonate can be explained, at least in part, by the effects of oceanic nutrient levels on Sr uptake during calcification of coccoliths, which make up the vast majority of these sediments. Within the limits of the inferred seawater Sr/Ca record the results of this study contribute a geologic perspective to recent laboratory and field studies that have raised the possibility that Sr incorporation into biogenic calcite is controlled by biogeochemical processes.   *INDEX TERMS:* 1050 Geochemistry: Marine geochemistry (4835, 4850); 1615 Global Change: Biogeochemical processes (4805); 4267 Oceanography: General: Paleoceanography; *KEYWORDS:* coccoliths, foraminifera, Sr/Ca ratios, paleoproductivity, Cenozoic

## 1.  Introduction

[2]  This work is inspired by recent studies that suggest that coccolith Sr/Ca ratios may provide a new proxy for paleoproductivity. We set out to compile Sr/Ca records from the literature to investigate whether long-term trends exist in these records that can be placed into a common paleoceanographic framework. These Sr/Ca records were measured on different sediment components (bulk and fine fraction), span all major ocean basins, and different water and burial depths (Figure 1; Table 1). Despite these differences, there are common features in these records. Changes in nutrient content, either whole ocean or regional, which we cannot distinguish, is our favored explanation, although other factors such as changing coccolith species assemblages cannot be ruled out. We emphasize that it is not our goal to reconstruct paleoproductivity per se; we simply propose that productivity is a plausible explanation for the observed temporal Sr/Ca pattern in the bulk and fine fraction sediment.[1]

## 2.  Background

[3]  Sr/Ca ratios of oceanic biogenic carbonates depend on two factors: the Sr/Ca ratio in the ocean and the partitioning of Sr into the biogenic carbonate. Calibration studies of calcitic microfossils from oceanic sediments suggest that there is a large array of environmental influences on the Sr partitioning into biominerals. For instance, the partition coefficient ($D_{Sr}$) for benthic foraminifera varies with water depth [*Elderfield et al.*, 1996; *McCorkle et al.*, 1995; *Rosenthal et al.*, 1997]. The $D_{Sr}$ of planktonic foraminifera shows a complex relationship with test size and growth rate, while temperature appears to be the dominant influence on the $D_{Sr}$ of some deeper-dwelling species [*Elderfield et al.*, 2000]. Spatial variations in coccolithophorid Sr/Ca ratios

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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/pa/2004PA001011.
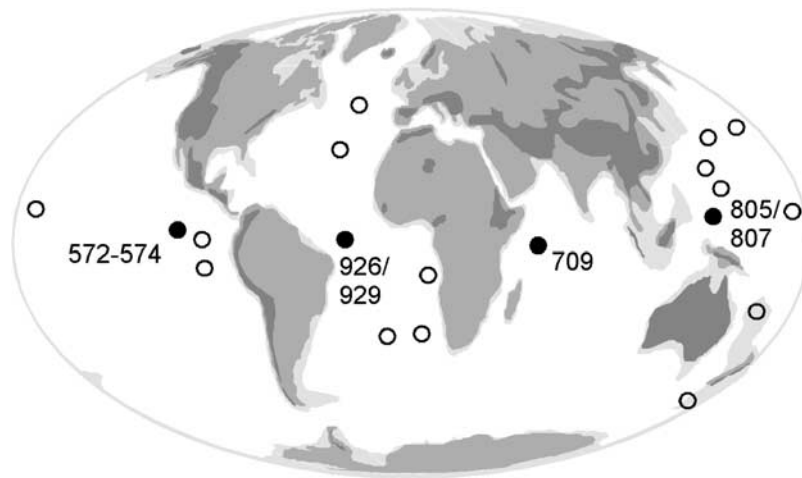
**Figure 1.** Locations of the Ocean Drilling Program (ODP) and Deep Sea Drilling Project (DSDP) sites compiled in this study. Sites used for the composite planktonic foraminiferal Sr/Ca record of *Graham et al.* [1982] are indicated as open circles but are not labeled. See Table 1 for a summary of information pertaining to exact location, water depth, sedimentation rates, and citation.

**Table 1.** Location of Sites

| Site | Longitude | Latitude | Sedimentation Rates, m/Myr | Paleodepth, m | Record Type[a] | Reference[b] |
|---|---|---|---|---|---|---|
| ODP 925 | 43.5°W | 4.2°N | 11–40 | 3042 | BS | 1 |
| ODP 927 | 44.5°W | 5.5°N | 12–46 | 3315 | BS | 1 |
| ODP 926 | 42.9°W | 3.7°N | 12–35 | 3598 | BS | 1 |
| ODP 928 | 43.7°W | 5.5°N | 7–36 | 4018 | BS | 1 |
| ODP 929 | 44°W | 6°N | 3–41 | 4356 | BS | 1 |
| ODP 805 | 161°E | 1.5°N | 12–39 | 3188 | BS | 2 |
| ODP 806 | 159.5°E | 0.5°N | 19–43 | 2520 | BS | 2 |
| ODP 807 | 157°E | 4°N | 14–41 | 2805 | BS | 2 |
| ODP 709 | 61°E | 2°S | 7–8 | 3041 | FF | 3 |
| DSDP 572 | 113°W | 1.5°N | 4–50 | 3893 | BS | 4 |
| DSDP 573 | 133°W | 0.5°N | 4–50 | 4301 | BS | 4 |
| DSDP 574 | 133°W | 14°N | 4–50 | 4555 | BS | 4 |
| DSDP 44 | 169°W | 19°N | N/A | 1478 | PF | 5 |
| DSDP 47.2 | 158°E | 32.5°N | N/A | 2689 | PF | 5 |
| DSDP 55 | 142.5°E | 9°N | N/A | 2850 | PF | 5 |
| DSDP 157 | 86°W | 2°S | N/A | 1591 | PF | 5 |
| DSDP 158 | 85°W | 6.5°N | N/A | 1953 | PF | 5 |
| DSDP 167 | 177°W | 7°N | N/A | 3176 | PF | 5 |
| DSDP 171 | 169.5°W | 19°N | N/A | 2290 | PF | 5 |
| DSDP 208 | 161°W | 26°S | N/A | 1545 | PF | 5 |
| DSDP 277 | 166°E | 52°S | N/A | 1232 | PF | 5 |
| DSDP 305 | 158°E | 32°N | N/A | 2903 | PF | 5 |
| DSDP 310 | 177°E | 33°N | N/A | 3516 | PF | 5 |
| DSDP 15 | 18°W | 31°S | N/A | 3927 | PF | 5 |
| DSDP 16 | 16°W | 30.5°S | N/A | 3527 | PF | 5 |
| DSDP 21 | 30.5°W | 28.5°S | N/A | 2113 | PF | 5 |
| DSDP 31 | 72°W | 15°N | N/A | 3369 | PF | 5 |
| V22-51 | 29°W | 28.5°S | N/A | 933 | PF | 5 |
| V22-54 | 29°W | 28.5°S | N/A | 37.81 | PF | 5 |
| V22-145 | 2°E | 32.5°S | N/A | 2056 | PF | 5 |
| V22-149 | 2°E | 31.5°S | N/A | 4012 | PF | 5 |
| V26-19 | 40°W | 26°N | N/A | 4548 | PF | 5 |
| V26-65 | 28°W | 26.5°S | N/A | 4510 | PF | 5 |
| V27-134 | 12°W | 48°N | N/A | 3350 | PF | 5 |
| V29-124 | 3°E | 28°S | N/A | 3063 | PF | 5 |
| V29-129 | 6°E | 26°S | N/A | 1068 | PF | 5 |
| V129-30 | 6.5°E | 24.5°S | N/A | 1075 | PF | 5 |
| V129-131 | 6.3°E | 24.5°S | N/A | 1068 | PF | 5 |
| V29-134 | 7.5°E | 24°S | N/A | 3804 | PF | 5 |

[a]BF, benthic foraminifera; BS, bulk sediments; PF, planktonic foraminifera.
[b]Number code is as follows: 1, *Hampt and Delaney* [1997]; 2, *Delaney and Linn* [1993]; 3, *Baker et al.* [1990]; 4, *Stout* [1985]; 5, *Graham et al.* [1982].

have been linked to changes in surface water productivity [*Stoll and Schrag*, 2000], and down-core changes in Cretaceous bulk carbonate can be explained by temporal changes in coccolithophorid productivity [*Stoll and Schrag*, 2001]. Culture experiments on planktonic foraminifera illustrate that Sr/Ca ratios increase with pH, suggesting a positive relationship between calcification rates and test chemistry [*Lea et al.*, 1999], but such a relationship does not appear to exist in coccolithophores [*Stoll et al.*, 2002a]. Rather, culture experiments using coccolithophorids demonstrate that the $D_{Sr}$ is positively correlated with rates of organic carbon fixation and calcification [*Rickaby et al.*, 2002; *Stoll et al.*, 2002a, 2002b]. These studies suggest that on short timescales relative to the residence times of Sr and Ca in the ocean (5 and 1 Myr, respectively) [*Broecker and Peng*, 1982], the Sr/Ca ratios in pelagic carbonates may provide an indicator of past changes in growth or calcification rate. Calcification rate and cell growth rate are closely related logically, but there are instances that would decouple the two rates such as changing surface water carbonate ion concentration or pH [*Barker and Elderfield*, 2002; *Riebesell et al.*, 2000].

## 3. Approach

### 3.1. Compiling the Data

[4] We have compiled Sr/Ca data from the literature keeping with the originally published age models (see section 3.2). Table 1 summarizes location, sedimentation rates, and water depth and provides the citation for each record. The records include Sr/Ca measurements from a depth transect on Ceara Rise in the western tropical Atlantic [*Hampt and Delaney*, 1997] (Figure 2a), as well as data from depth transects in the western and eastern equatorial Pacific from *Delaney and Linn* [1993] and *Stout* [1985], respectively (Figures 2b and 2c, respectively). *Baker et al.* [1990] separated fine fraction from bulk sediments from an intermediate water depth site, Ocean Drilling Program (ODP) Site 709C in the equatorial Indian Ocean (Figure 2d), noting that there is a slump that disturbs its sedimentary record between 13 and 17.5 Ma. Smoothing the data minimizes the effect of the disturbance on the data interpretations. We also show the mixed species planktonic foraminiferal Sr/Ca records generated by *Graham et al.* [1982] from a number of sites in the Atlantic and Pacific Ocean (Figure 2e).

[5] We smooth the data from each region using a negative exponential with a 10% sampling portion. For this purpose we combine records from different water depths because no consistent Sr/Ca trends with water depth can be discerned, which is evident in Figure 2 (all smoothed data are provided in the electronic archive). Diagenesis is thought to affect samples from different burial depths and sediment carbonate content [*Stout*, 1985; *Hampt and Delaney*, 1997; *Hampt-Andreasen and Delaney*, 2000a]. By smoothing the records from each region, we minimize diagenetic effects on our data interpretations. These smoothed data provide the basis for comparison of long-term trends and calculations of the partitioning coefficient of bulk and fine fraction sediment and the planktonic foraminifera.

[6] Temporal changes in seawater Sr/Ca ratios would introduce common trends into Sr/Ca records regardless of the sediment producer. We can quantitatively minimize the effect of seawater Sr/Ca by reporting our results in terms of the $D_{Sr}$ in bulk sediment, fine fraction, and planktonic foraminiferal records (Figures 3a and 3b). Seawater Sr/Ca ratios have been constrained by *Lear et al.* [2003] using benthic foraminiferal Sr/Ca records. To calculate the $D_{Sr}$, we first smooth the seawater Sr/Ca record using the same negative exponential with a 10% sampling portion function as above (Figure 3c). We then interpolate the seawater ratios to correspond to the ages of the smoothed bulk, fine fraction and planktonic foraminiferal Sr/Ca records. We calculate the $D_{Sr}$ using the following relationship:

$$D_{Sr} = Sr/Ca_{carbonate} \times Sr/Ca_{seawater}^{-1}. \tag{1}$$

### 3.2. Age Model

[7] A common timescale is not available for all records. Ages of the seawater Sr/Ca curve are reported on the timescale of *Berggren et al.* [1995] [*Lear et al.*, 2003]. Unfortunately, age models of the published bulk and fine fraction sediment and planktonic foraminiferal Sr/Ca records are not consistent with the *Berggren et al.* [1995] timescale. Only the bulk records from Ceara Rise [*Hampt and Delaney*, 1997] reflect this age scale. However, because of the generally low temporal resolution of the records, we focus on long-term trends, and age model discrepancies become a relatively minor uncertainty.

## 4. Results

### 4.1. Pelagic Sr/Ca Records

[8] The comparison of the published Sr/Ca records (smoothed) illustrates that a general trend of increasing ratios toward present-day characterizes all Sr/Ca curves regardless of the sediment fraction or carbonate producer (Figures 3a and 3b). This underlying trend likely reflects an increase in seawater Sr/Ca ratios over the course of the Cenozoic (Figure 3c) [*Lear et al.*, 2003]. Superimposed on the long-term trend, there are distinct Sr/Ca variations in the bulk and fine fraction sediments (Figure 3a). Common features among these are a steep rise during the early Eocene, generally increasing or high ratios during the Oligocene (~34–23 Ma), decreasing ratios toward an early Miocene minimum (between ~14 and 18 Ma), increasing ratios during the middle Miocene (12–14 Ma), and another minimum during the late Miocene (8–10 Ma). The Ceara Rise and Indian Ocean sites show further maxima during the Pliocene. During the Pleistocene, sediment Sr/Ca ratios decrease in all but the Ontong Java Plateau record. We note that the timing of maxima and mimima can differ among records by as much as ~2–4 Myr. For example, a second late Oligocene maximum in the Indian Ocean predates a second maxima recorded by the other records by ~ 2 Myr (Figure 3a). These discrepancies are too large to arise from age control; more likely, they reflect the importance of regional processes.

[9] Planktonic foraminiferal Sr/Ca ratios are lower than bulk and fine fraction ratios, and the variability is strongly
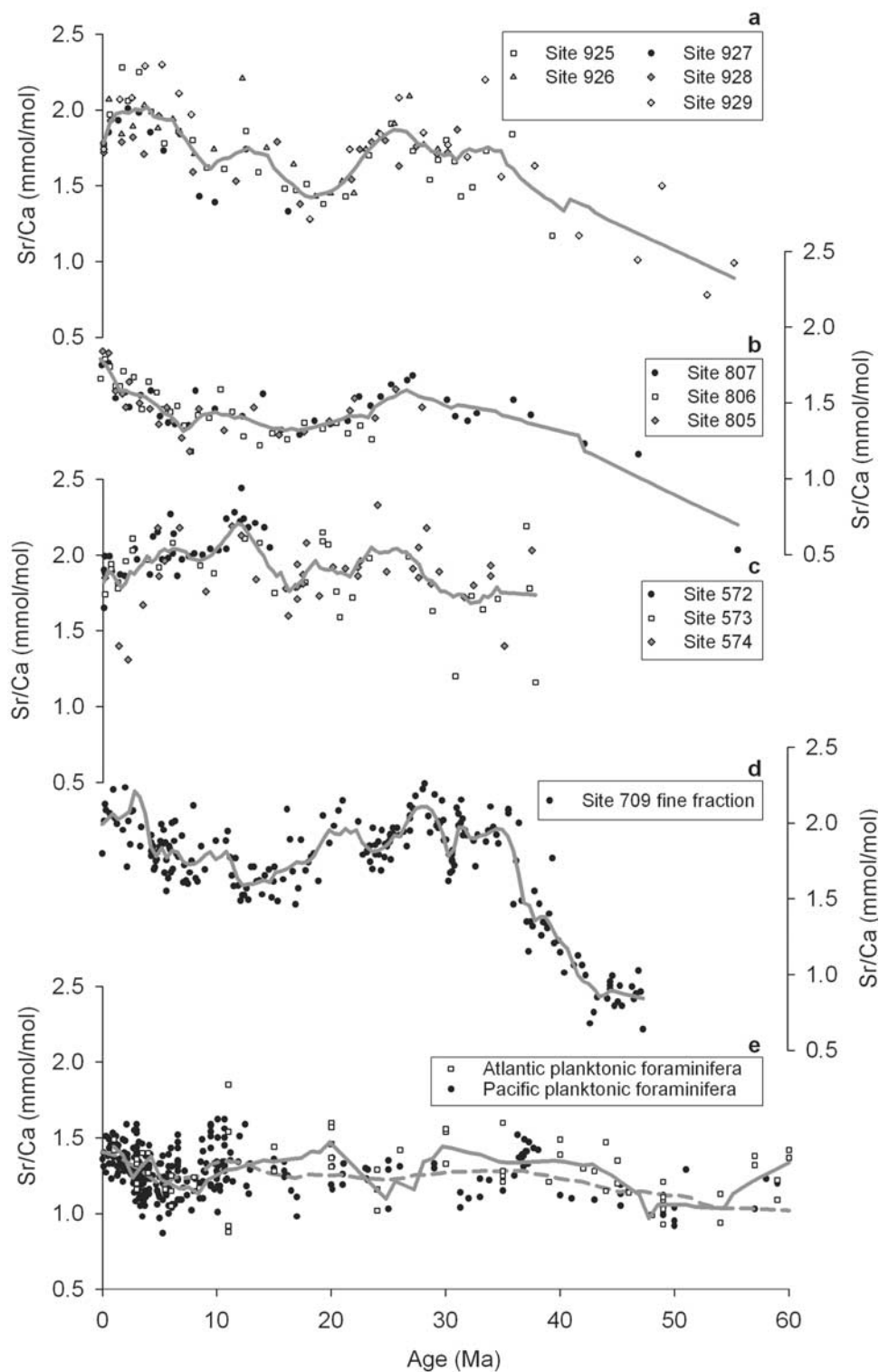
**Figure 2.** (a) Compilation of published bulk sediment Sr/Ca records from the western equatorial Atlantic [*Hampt and Delaney*, 1997]; (b) bulk sediment from the western equatorial Pacific [*Delaney and Linn*, 1993]; (c) fine fraction record from equatorial Indian Ocean Site 709 [*Baker et al.*, 1990]; (d) bulk sediment from the eastern equatorial Pacific [*Stout*, 1985]; and (e) planktonic foraminiferal records from the Atlantic and Pacific [*Graham et al.*, 1982]. The shaded curves represent a Gaussian smoothing function with a 10% sampling portion.
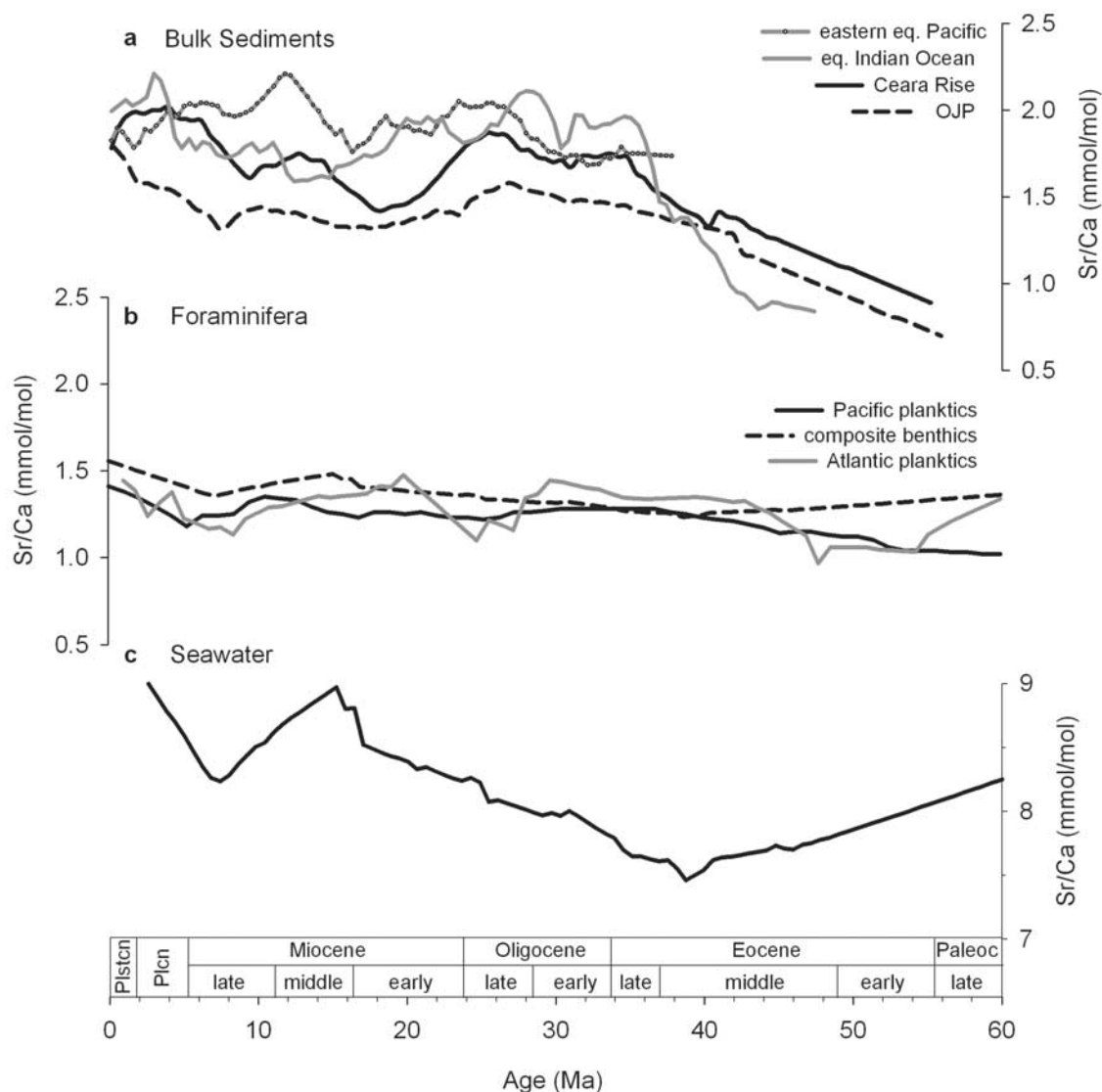
**Figure 3.** (a) Comparison of the smoothed published bulk carbonate and fine fraction Sr/Ca records from the eastern and western equatorial Pacific, the western equatorial Atlantic, and the equatorial Indian Ocean. (b) Comparison of the smoothed published planktonic [*Graham et al.*, 1982] and benthic [*Lear et al.*, 2003] foraminiferal Sr/Ca ratios. (c) Benthic foraminiferal Sr/Ca provides the basis for calculating seawater Sr/Ca ratios using a partitioning coefficient of 0.165 (see text and *Lear et al.* [2003]).

attenuated (Figure 3b). However, in general agreement with the bulk and fine fraction records, there is an, albeit subtle, increase during the middle Eocene, ratios tend to be slightly higher during the Oligocene, and we are able to discern a broad middle Miocene maximum between early Miocene and late Miocene minima. Lower foraminiferal Sr/Ca ratios and amplitude of variability are due to the small $D_{Sr}$ in planktonic foraminifera in comparison to coccolithophorid calcite [e.g., *Baker et al.*, 1982; *Stout*, 1985; *Hampt-Andreasen and Delaney*, 2000a, 2000b]. The comparison illustrates that this relationship has held since the early Cenozoic.

[10] Features contained in all records may reflect, in part, changes in the Sr/Ca ratios of seawater. In fact, seawater ratios show a distinct middle Miocene maximum

and late Miocene minimum at about the same time as the other records (Figure 3c). However, seawater ratios also display a middle Eocene minimum, a feature that is not apparent in any of the foraminiferal or carbonate records. In addition, during the relatively steep increase in sediment Sr/Ca ratios during the Eocene, seawater ratios decrease.

[11] The derivation of the seawater Sr/Ca curve and its implications with respect to Cenozoic cycling of Sr and Ca are discussed in detail by *Lear et al.* [2003]. Here we point out that this record does not indicate a change in seawater Sr/Ca ratios at the Eocene/Oligocene boundary; rather, Sr/Ca ratios increase continuously from a late Eocene minimum toward a middle Miocene maximum (Figure 3c). The apparent lack of a seawater Sr/Ca response to one of the
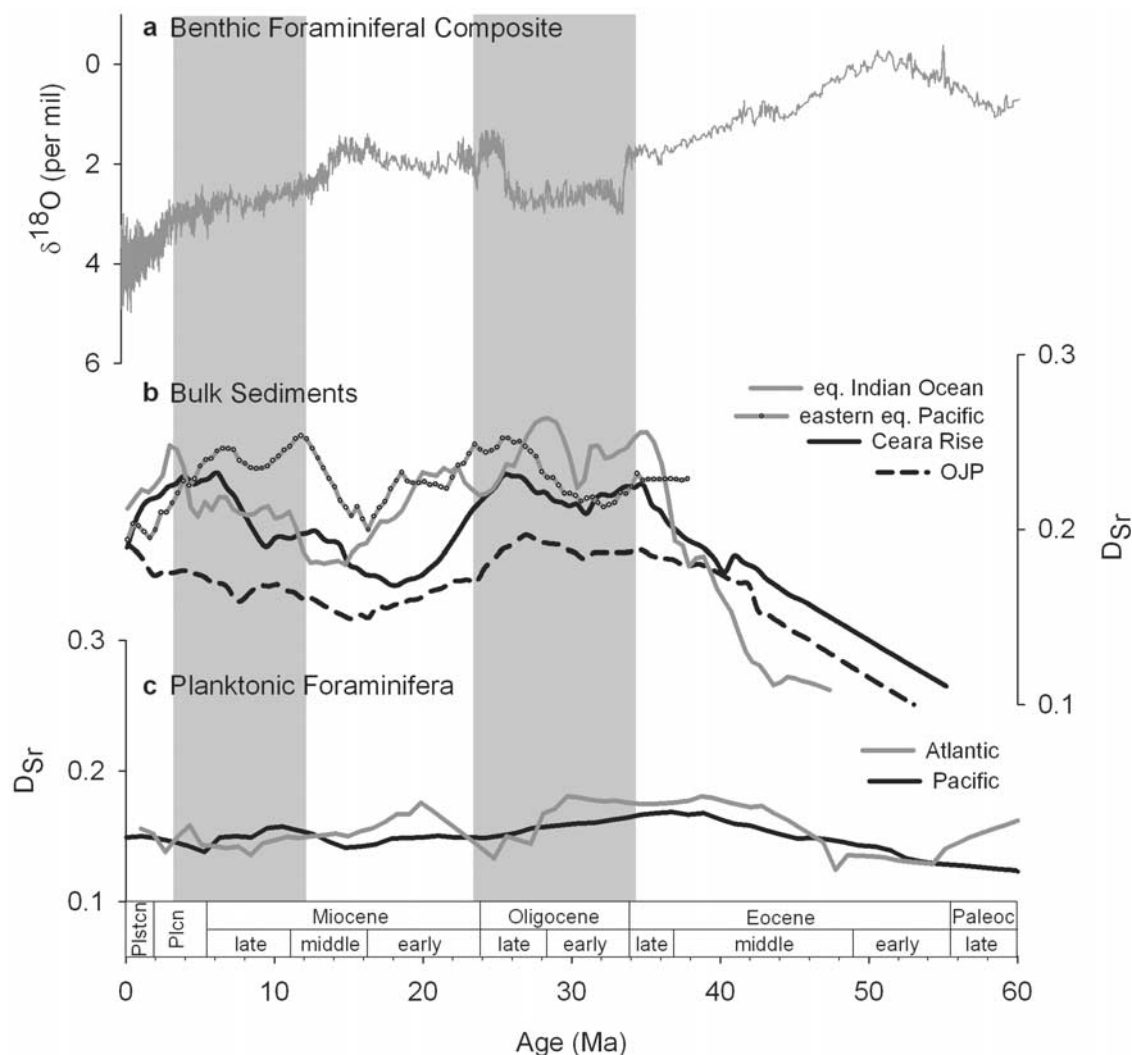
**Figure 4.**   (a) Comparison of the composite benthic foraminiferal $\delta^{18}O$ record of *Zachos et al.* [2001] to the (b) calculated $D_{Sr}$ for bulk carbonate and fine fraction and (c) planktonic foraminiferal Sr/Ca ratios. There are two intervals of time characterized by enhanced Sr partitioning in bulk and fine fraction sediment (shading), the Oligocene, and the late Miocene/Pliocene. These are intervals of time for which we can cite evidence from the literature for enhanced surface water productivity.

most rapid transitions in global climate [*Zachos et al.*, 1994, 1999, 2001] defined by the first major expansion of Antarctic ice and an associated drop in eustatic sea level [e.g., *Miller et al.*, 1998] may be explained by the fact that shelf carbonates exposed during the late Eocene/early Oligocene are of Cretaceous age. During the Cretaceous, dominant shelf carbonate producing corals were calcitic rather than aragonitic in mineralogy [*Stanley and Hardie*, 1998, and references therein]. Hence erosion and recrystallization of Cretaceous shelf carbonate should not have as large an effect on oceanic Sr/Ca ratios as during the Quaternary [*Stoll and Schrag*, 1998; *Stoll et al.*, 1999; *Martin et al.*, 1999].

## 4.2.   Sr Partitioning Over the Cenozoic

[12] Calculating the $D_{Sr}$ for each record (using equation (1)) highlights the overall agreement among the records

(Figure 4). The agreement is particularly good during the Eocene, when the three long records show a steep increase in Sr partitioning (Figure 4b). During the Oligocene, the $D_{Sr}$ remains high in all records and decreases during the early Miocene. The agreement is not as good thereafter; the timing of the Miocene minima differs as well as the character of the individual records during the late Miocene. However, the records do have in common that Sr partitioning begins to increase again during the middle to late Miocene. The Plio/Pleistocene sees a decrease in Sr partitioning in all records but those from the Ontong Java Plateau.

[13] Only some aspects of the long-term trends apparent in the bulk and fine fraction records are also noticeable in the foraminifera (Figure 4c). The foraminifera from both ocean basins show an increase in Sr partitioning during the early through middle Eocene, and values decrease toward a

middle Miocene minimum. At the finer scale, however, the two planktonic foraminiferal records show different trends, and a comparison to the bulk and fine fraction records is difficult. We note that the $D_{Sr}$ remains smaller than that derived from the bulk and fine fraction records, in agreement with modern differences among foraminifera and coccolithophores.

## 5.   Discussion

[14]   We observe common trends from records measured on different sedimentary components (bulk versus fine fraction), from different hydrographic regimes (e.g., western and eastern ocean basins), and different water and burial depths. These patterns cannot be explained entirely by sediment composition and postdepositional artifacts. Thus we believe that there may be a paleoceanographic significance to the bulk and fine fraction Sr/Ca variations over these long, Cenozoic, timescales.

[15]   The middle Eocene was a time of gradual global cooling culminating in the first major ice growth event on Antarctica at the Eocene/Oligocene boundary [e.g., *Miller et al.*, 1987; *Zachos et al.*, 2001]. The Oligocene remained relatively cool with ice volume perhaps half of the modern [*Zachos et al.*, 1994]. The early Miocene, however, is generally thought of as a time of relative warmth leading to a climate optimum at ∼15–16 Ma [e.g., *Kennett*, 1986; *Flower and Kennett*, 1993]. The mid-Miocene experienced the second major pulse of Antarctic ice advance [e.g., *Kennett*, 1986; *Flower and Kennett*, 1993]. The overall agreement between these large-scale climatic changes and the fine fraction Sr/Ca record from the Indian Ocean led *Baker et al.* [1990] to suggest that coccolith Sr/Ca ratios reflect basin to shelf fractionation of seawater Sr linked to glacioeustatic sea level changes. Because these trends prevail in the $D_{Sr}$ of this record (as well as the $D_{Sr}$ from the bulk sediment records), another mechanism must be sought.

[16]   A number of factors can explain variations in the $D_{Sr}$ in the bulk sediment and fine fraction records. We ultimately argue that coccolithophore Sr/Ca is most likely related to productivity variations, at least in part, but first we shall address potential complicating factors. Work by *Delaney and Linn* [1993], *Hampt and Delaney* [1997], and later by *Hampt-Andreasen and Delaney* [2000a, 2000b] reviews and discusses how recrystallization and the rain ratio of coccolith/planktonic foraminifera affect bulk sediment Sr/Ca ratios. Carbonate preservation could affect the Sr/Ca ratios in two ways, either directly because of increased dissolution susceptibility with increasing impurities in the calcite lattice, or indirectly because of differential dissolution susceptibility of nannofossil and foraminifera. Another complicating factor may be that coccolithophorid Sr/Ca ratios may be species specific, or at least associated with the size of the dominant sediment producers [*Stoll and Ziveri*, 2002; *Stoll and Bains*, 2003]. In addition, it may be that seawater temperature and carbon chemistry affect coccolithophorid growth rates, complicating interpretations with respect to paleoenvironmental significance. Below we

discuss each of these factors in turn, being able to constrain some, but not all of these effects on the observed trends in the $D_{Sr}$ in the bulk sediment and fine fraction records.

### 5.1.   $D_{Sr}$ and Temperature

[17]   While the impact of temperature on partitioning of trace metals is increasingly recognized [e.g., *Lea et al.*, 1999, *Rickaby and Elderfield*, 1999], low-latitude sea surface temperature variations seem an unlikely explanation for the variation in $D_{Sr}$. Culture studies resolve a positive Sr/Ca temperature relationship in coccolithophores [*Stoll et al.*, 2002a, 200b] and foraminifera [*Lea et al.*, 1999], and the observed trends are opposite of what we know about Cenozoic climate change. The early Eocene is generally thought of as the warmest interval of the Cenozoic, but the $D_{Sr}$ in the bulk and fine fraction records are at their minima. Furthermore, there is no evidence to support periods of warming during the Oligocene, an interval of time generally thought of as a period of globally cooler climate. In contrast, the early Miocene is probably one of the warmer intervals of the Cenozoic [e.g., *Shackleton and Kennett*, 1975], and if a temperature effect were present, we would expect it to cause an increase in Sr partitioning rather than the observed decrease. Thus we do not think that the observed variations in the $D_{Sr}$ of bulk sediment and fine fraction are a function of sea surface temperature changes.

### 5.2.   $D_{Sr}$ and Seawater Chemistry

[18]   Laboratory and field studies suggest that there may be a calcification rate effect on planktonic foraminiferal Sr/Ca ratios [*Lea et al.*, 1999; *Elderfield et al.*, 2002]. *Lea et al.* [1999] in particular illustrate that foraminiferal Sr/Ca ratios increase with pH of the culture water perhaps reflective of a pH dependency of calcification rates. We observe that the $D_{Sr}$ of planktonic foraminifera increases gradually during the Eocene, which may be consistent with evidence for increasing surface water pH during this time [*Pearson and Palmer*, 2000]. The limited coccolithophorid cultures that are available to illuminate this issue, however, do not show an increase in $D_{Sr}$ with culture water pH [*Stoll et al.*, 2002b]. In fact, over the proposed range in Eocene pH from 7.25 to 8.25, which is the largest change during the Cenozoic [*Pearson and Palmer*, 2000], the $D_{Sr}$ in cultured coccolithophores decreases by a very small amount [*Stoll et al.*, 2002b]. Presently, there is insufficient evidence to suggest that the steep increase in bulk and fine fraction $D_{Sr}$ during the middle Eocene reflects enhanced calcification rates due to surface water carbon chemistry.

[19]   Alternatively, increasing Sr/Ca ratios during the Eocene could reflect an increase in deep water carbonate ion concentration and thus enhanced preservation. The calcium carbonate compensation depth dropped by over a kilometer during the middle to late Eocene [*Sclater et al.*, 1979; *van Andel*, 1975]. However, as laboratory culture experiments demonstrate, coccolith Sr/Ca ratios are not sensitive to partial dissolution because Sr is homogenously distributed in the calcite platelet [*Stoll et al.*, 2002b]. Our results support the laboratory study; the sites compiled here come from different water depths (Table 1) and show similar trends. Likewise, for the post-Eocene, Sr/Ca

measurements along depth transects do not show consistent differences in the Sr/Ca ratios [e.g., *Hampt and Delaney*, 1997; *Stout*, 1985] (Figure 2). Thus we do not believe that the degree of preservation can account for the observed trends in the $D_{Sr}$.

### 5.3. $D_{Sr}$ and Diagenesis

[20] The records compiled here were constructed initially with the aim to assess calcite recrystallization in deep sea sediments. Recrystallization in the sediment column adds Sr-depleted calcite in the more deeply buried samples [*Hampt-Andreasen and Delaney*, 2000a, 2000b], increasingly attenuating the primary signal with core depth. Carbonate diagenesis appears to have a larger effect on samples from relatively carbonate-rich sites in comparison to samples from carbonate-poorer sites [*Stout*, 1985; *Hampt-Andreasen and Delaney*, 2000a]. Specifically, the western equatorial Pacific sites have the highest carbonate contents, ranging between ∼80 and 90%, throughout the Cenozoic and are hence most susceptible to diagenesis [*Hampt-Andreasen and Delaney*, 2000b]. The shallower Ceara Rise Sites 925–928 have consistently higher carbonate contents than the deeper Site 929 (∼50–80% versus ∼20–60%, respectively [*Hampt-Andreasen and Delaney*, 2000b]). In addition, among the eastern equatorial Pacific sites, Site 572 has the highest carbonate content and highest Sr/Ca ratios [*Stout*, 1985]. Thus calcite recrystallization may well explain the relatively small Sr/Ca variability in the western equatorial Pacific where carbonate content is highest in comparison to the other sites (Figures 3a and 4b). However, the common temporal trends despite these differences in water and burial depth are more likely to be indicative of paleoenvironmental conditions.

### 5.4. $D_{Sr}$ and Sediment Composition

[21] Importantly, changes through time in the rain ratio of nannofossil to planktonic foraminifera must affect the observed bulk sediment Sr/Ca records. Because the $D_{Sr}$ in coccolith calcite is ∼1.5 times greater than for planktonic foraminifera, an increase in the relative contribution of planktonic foraminiferal to the deep sea sediments will decrease the bulk sediment Sr/Ca ratio [*Hampt-Andreasen and Delaney*, 2000a, 2000b]. Changes in the sediment producers may be brought about by differential production at the sea surface or preferential dissolution on the ocean floor. The most cogent argument against changes in nannofossil/foraminiferal ratios in the sediment as an explanation of the variability in the $D_{Sr}$ is the observation that the long-term trends are also apparent in the fine fraction record, which, being the sediment fraction <63 microns, excludes foraminifera. Thus we also rule out that the large-scale common trends reflect changes in the ratio of nannofossils to foraminifera.

### 5.5. Nannofossil Species Effects

[22] Pioneering work by *Stoll and Ziveri* [2002] and *Stoll and Bains* [2003] illustrates that Paleocene coccolith Sr/Ca ratios are species specific. *Stoll and Bains* [2003] show that in Paleocene sediments, coccoliths belonging to larger size fractions (8–12 μm) have lower Sr/Ca ratios than smaller taxa (3–5 μm). Thus temporal changes in species

assemblages, and in particular, extinction and evolution of major sediment producing taxa may well have affected the trends observed in the bulk and fine fraction records.

[23] We do not have enough information to relate the observed changes in Cenozoic Sr/Ca ratios at each site with changing nannofossil species assemblages. However, we can offer a few observations that demonstrate the complexity of this issue. Nannofossil species abundances are linked to environmental conditions, water transparency in particular, with highest species diversity in an oligotrophic and lowest diversity in a eutrophic photic zone [*Aubry*, 1998]. *Florisphaera profunda* abundances, for example, have been used to reconstruct the depth of the photic zone and nutricline on Pleistocene timescales [*McIntyre and Molfino*, 1996; *Molfino and McIntyre*, 1990]. *Gibbs et al.* [2004] demonstrate that western tropical Atlantic nannofossil assemblages change on orbital timescales, likely linked to changes in regional productivity and/or water column turbidity (due to the proximity of the Amazon River). At the extreme the Oligocene is a time of extinction of many genera, while the Miocene is a time of evolution of new ones [*Aubry*, 1998]. If the now-extinct species had consistently higher ratios and the incoming taxa lower ratios, then at least the Oligocene/Miocene pattern may be in part the result of species effects. We can, however, cite one specific example that would provide an exception: *Chiasmolithus* becomes extinct during the late Oligocene [*Aubry*, 1998], and this is a small genus with low Sr/Ca ratios [*Stoll and Bains*, 2003].

[24] Our sites come from eastern and western ocean basins with presumably different photic zone characteristics through time. We are inclined to conclude that it is not likely that common large-scale trends at all sites reflect solely the assemblage pattern of the dominant species through time. However, we do admit that changing species assemblages provide an indisputable caveat in our discussion of a possible link between coccolith Sr/Ca ratios and productivity.

### 5.6. $D_{Sr}$ and Paleoproductivity

[25] In summary, we are relatively confident that the common trends in the $D_{Sr}$ derived from bulk and fine fraction Sr/Ca records are not a function of low-latitude sea surface temperatures, postburial processes including diagenesis and dissolution, or the nannofossil/foraminiferal rain ratio. We do not have evidence to support that the patterns are driven by seawater carbon chemistry. In regard to species effects, there is not enough information about the nannofossil assemblage changes through time at each site to discuss the extent to which the records may have been affected by changes in species assemblages.

[26] We proceed to discuss geologic evidence to link coccolith Sr partitioning and general changes in nutrient levels and surface water productivity. Starting with the early Cenozoic, we find no evidence to support an increase in productivity owing to an increase in ocean wide nutrient levels to explain increasing Sr partitioning. The seawater Sr/Ca curve reflects a decrease in river flux of Sr during the middle Eocene, suggesting that there was no increase in global weathering rates at this time [*Lear et al.*, 2003] and

by extension nutrient delivery to the ocean. Other records indicative of continental weathering are equivocal for this interval of time [*Peucker-Ehrenbrink et al.*, 1995]. However, the steeply increasing Sr partitioning may still reflect an increase in paleoproductivity stimulated by an increase in the regional nutrient availability. A more vigorous ocean circulation, perhaps driven by stronger winds as global climate cooled since the early Eocene climatic maximum, could have enhanced regional surface water nutrient availability.

[27] The Oligocene was a time of globally cooler climate with evidence for regional and perhaps global increases in nutrient levels. Oceanic nutrient levels and carbon burial increased in the Southern Ocean [e.g., *Diester-Haass and Zahn*, 1996; *Salamy and Zachos*, 1999]. Furthermore, in Oligocene-age pelagic sediments of the South and North Atlantic, the presence of chalky layers consisting almost exclusively of the coccoliths of *Braarudosphaera* has been interpreted as an expansion of midocean upwelling regions perhaps related to increased vigor of surface ocean circulation [*Kelly et al.*, 2003, and references therein]. The Sr/Ca seawater curve provides evidence for enhanced river fluxes of Sr to the ocean between the late Eocene and middle Miocene [*Lear et al.*, 2003], which may imply an increased flux of nutrients to the ocean stimulating primary productivity worldwide. Thus we have evidence to support that Oligocene maxima in all the $D_{Sr}$ may be related to either regional increases in surface ocean nutrient availability or global increases in oceanic nutrient levels.

[28] During the early Miocene, climate warmed culminating in the early Miocene climatic optimum at ~16 Ma [e.g., *Shackleton and Kennett*, 1975]. During this time, oceanic nutrient levels may have been relatively low in comparison to those of the late Miocene, as indicated by foraminiferal Cd/Ca ratios [*Delaney and Boyle*, 1987; *Delaney*, 1990] and small to nonexistent interocean $\delta^{13}C$ gradients [*Wright and Miller*, 1992; *Billups et al.*, 2002]. Thus the early Miocene decrease in $D_{Sr}$ (Figure 4b) would be consistent with other proxies that suggest lower oceanic nutrient levels. By extension, although not supported by evidence, we cannot rule out regional decease in nutrient availability perhaps related to a less vigorous surface ocean circulation.

[29] The $D_{Sr}$ increase again after 16 Ma, which corresponds in time to the middle Miocene episode of major Antarctica ice growth. During the later middle Miocene, extensive organic rich deposits form in the Pacific Ocean, which have been ascribed to an increase in coastal upwelling and oceanic nutrient levels, perhaps brought about by strengthened ocean circulation associated with global climate cooling [*Vincent and Berger*, 1985; *Flower and Kennett*, 1993, 1994]. During the late Miocene, increases in the uplift rate of the Himalayan-Tibetan Plateau [*Molnar et al.*, 1993] may have led to increased weathering rates and nutrient input to the ocean stimulating primary productivity, as evidenced by increased phosphorous and organic carbon burial [*Filippelli*, 1997]. There is further evidence for an increase in primary productivity associated with the Benguela Current upwelling system during the late Miocene [*Diester-Haass et al.*, 2002]. In addition, blooms occurred in otherwise low-productivity regions of the Atlantic and Indian Oceans at about this time [*Hermoyian and Owen*, 2001; *Dickens and Owen*, 1999]. Thus on a regional or global scale, increased nutrient availability to the coccolithophores may explain the generally enhanced Sr partitioning during the late middle Miocene through early Pliocene.

[30] We are limited in this discussion by the low resolution of the Sr/Ca records and associated uncertainties in the precise timing of Sr/Ca maxima, together with the difficulty of finding robust paleoproductivity records at individual core sites. Therefore a more detailed comparison between Sr/Ca ratios of surface dwellers and regional surface ocean paleoproductivity events awaits further study. For now we are satisfied that paleoproductivity perhaps provides the most plausible mechanism to explain the common long-term trends in the bulk sediment and fine fraction Sr/Ca records.

## 6. Speculations About Biomineralization

[31] Of all the ions that substitute for calcium in the calcite lattice, Sr is the most chemically similar to calcium. Nonetheless, experimental determination of the inorganic equilibrium partitioning of Sr into precipitating calcite predicts that there is a considerable discrimination between the larger Sr ions and Ca [e.g., *Lorens*, 1981; *Tesoriero and Pankow*, 1996]. If all biogenic carbonates were analogous to inorganic precipitates and discriminated Sr to the same degree, we would expect to obtain identical records of Sr/Ca from contemporaneous measurements of benthic and planktonic foraminifera and coccolithophores (or bulk sediments), from which we could derive the history of seawater Sr/Ca by applying a constant $D_{Sr}$. Instead, there are significant offsets among the Sr/Ca records derived from planktonic foraminifera versus bulk and fine fraction sediments (e.g., Figures 3b and 3c). The absolute value of Sr/Ca in bulk and fine fraction sediment is consistently higher than the foraminiferal calcite and varies over a three times greater range. These observations support prior studies that have elucidated the importance of biogeochemical processes on Sr incorporation during hard part formation.

[32] We believe that the foregoing discussion provides a platform for the hypothesis that the Sr/Ca ratios of bulk and fine fraction carbonate (primarily coccoliths) reflects the effects of increasing oceanic productivity on Sr partitioning into biominerals. A growth rate dependence of Sr/Ca in coccoliths has been observed in culture [*Rickaby et al.*, 2002; *Stoll et al.*, 2002a, 2002b] and in the field [*Stoll and Schrag*, 2000]. The underlying mechanism probably arises from a rate-dependent biological discrimination between the similarly sized ions during the calcium transport for calcification [*Rickaby et al.*, 2002]. This physiological model for Sr and Ca discrimination due to selectivity at Ca pumps is further supported by the different absolute values and sensitivity of $D_{Sr}$ for planktic foraminifera compared to bulk carbonate (coccoliths) (e.g., Figure 4).

[33] Three different explanations for these observations emerge from the Ca pump model. First, the totally intracellular process of calcification in a coccolithophore imprints a

larger biological signature on the Sr/Ca of the calcite than in the foraminifera, which calcifies by engulfing a seawater pool [*Elderfield et al.*, 1996]. Second, the foraminiferal Ca pumps are more able to differentiate between Sr and Ca than those of the coccolithophore. Third, the small coccolithophores have higher metabolic rates and rates of calcification than the larger foraminifera and at these faster rates are less able to discriminate against transport of the larger Sr. We intend to test these ideas by constructing parallel records of coccolithophorid and planktonic foraminiferal Sr/Ca ratios in regions of the ocean for which we have good evidence that changes in paleoproductivity occurred.

## 7.  Summary and Conclusions

[34] We are motivated by recent studies that have illustrated a relationship between coccolithophorid calcification rates and the Sr/Ca ratios of the calcitic coccoliths. We observe that published bulk sediment and fine fraction Sr/Ca records from the equatorial Atlantic Ocean, Indian Ocean, and the western and eastern Pacific display common trends. Over the past 60 Myr, there were two broad periods of enhanced partitioning of Sr in planktonic carbonate producers relative to today, the Oligocene, and the late Miocene/early Pliocene. Because these are two intervals for which we can cite evidence for a relative rise in oceanic nutrient levels, we conclude that the Sr/Ca ratios of bulk carbonate (and planktonic foraminiferal tests) reflect at least in part the effects of regional or global nutrient levels on Sr uptake. More detailed interpretations of the pelagic Sr/Ca records are limited by primarily postdepositional processes and more importantly by changing coccolithophorid species assemblages in the sediments. One other important aspect is the potential decoupling of growth rates linked to enhanced nutrient uptake from calcification rates linked to seawater carbon chemistry. However, presently there is not enough evidence to argue that seawater carbon chemistry affects coccolith Sr/Ca ratios. Thus we believe that the results of this study contribute a geologic perspective to recent laboratory and field studies that have raised the possibility that Sr incorporation into biogenic calcite is controlled by biogeochemical processes.

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K. Billups, College of Marine Sciences, University of Delaware, 700 Pilottown Road, Lewes, DE 19958, USA. (kbillups@udel.edu)

R. E. M. Rickaby, Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, UK. (rosr@earth.ox.ac.uk)

D. P. Schrag, Laboratory for Geochemical Oceanography, Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA 02138, USA. (schrag@eps.harvard.edu)