



Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate

Heather M. Stoll

Department of Geology, Universidad de Oviedo, Oviedo, Asturias 33005, Spain (heather.stoll@asturias.geol.uniovi.es)

Daniel P. Schrag

Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, Massachusetts 02138

[1] **Abstract:** Polyspecific coccolith separates from core top sediments in the eastern equatorial Pacific show variations of $\sim 15\%$ in Sr/Ca ratios across the equatorial upwelling zone, with Sr/Ca highest at the equator and decreasing off-axis. These variations cannot be due to changes in the Sr/Ca of seawater, which varies by less than 2% in the surface ocean. Variations in Sr/Ca of coccolith sediments are similar to variations in primary productivity and alkenone-estimated coccolithophorid growth rates in overlying surface waters and to CaCO_3 rain rates measured in sediment traps. Because of these relationships and because calcification rate exerts a strong control on Sr/Ca in abiogenic calcites, we suggest that the observed Sr/Ca variations in coccoliths may be strongly controlled by coccolithophorid growth and calcification rates, although temperature may also influence coccolith Sr/Ca to a lesser degree. Changes in dissolution intensity and coccolith assemblages appear to exert a minor influence, if any, on coccolith Sr/Ca in these sediment core tops. If further work confirms relationships between coccolith Sr/Ca and coccolithophorid productivity, Sr/Ca records of past changes in coccolithophorid productivity may be useful in reconstructing past variations in the rain ratio of organic to carbonate carbon, an important control on deep ocean pH and partitioning of CO_2 between the atmosphere and ocean. In addition, coccolith Sr/Ca might provide an independent record of past changes in coccolithophorid growth rates, which in combination with data on the carbon isotopic fractionation in coccolithophorid organic matter may permit more reliable calculations of past dissolved CO_2 in the surface ocean.

Keywords: Geochemistry; carbonate; Sr/Ca; coccoliths; carbon cycle; strontium.

Received September 16, 1999; **Revised** February 21, 2000; **Accepted** March 10, 2000; **Published** May 30, 2000.

Stoll, H. M., and D. P. Schrag, 2000. Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate *Geochem. Geophys. Geosyst.*, vol.1, Paper number 1999GC000015 [12,215 words, 12 figures, 2 tables]. May 30, 2000.

1. Introduction

[2] Although the minor and trace element chemistry of biogenic carbonates is widely applied to infer past oceanographic conditions, most of the work has focused on the chemistry of foraminifera and, more recently,

that of corals. Ironically, the very abundant calcite produced by coccolithophorids has not been previously utilized in minor element studies. The minor element chemistry of coccoliths, external plates of calcite produced by coccolithophorids, may provide a unique perspective on past changes in climate and

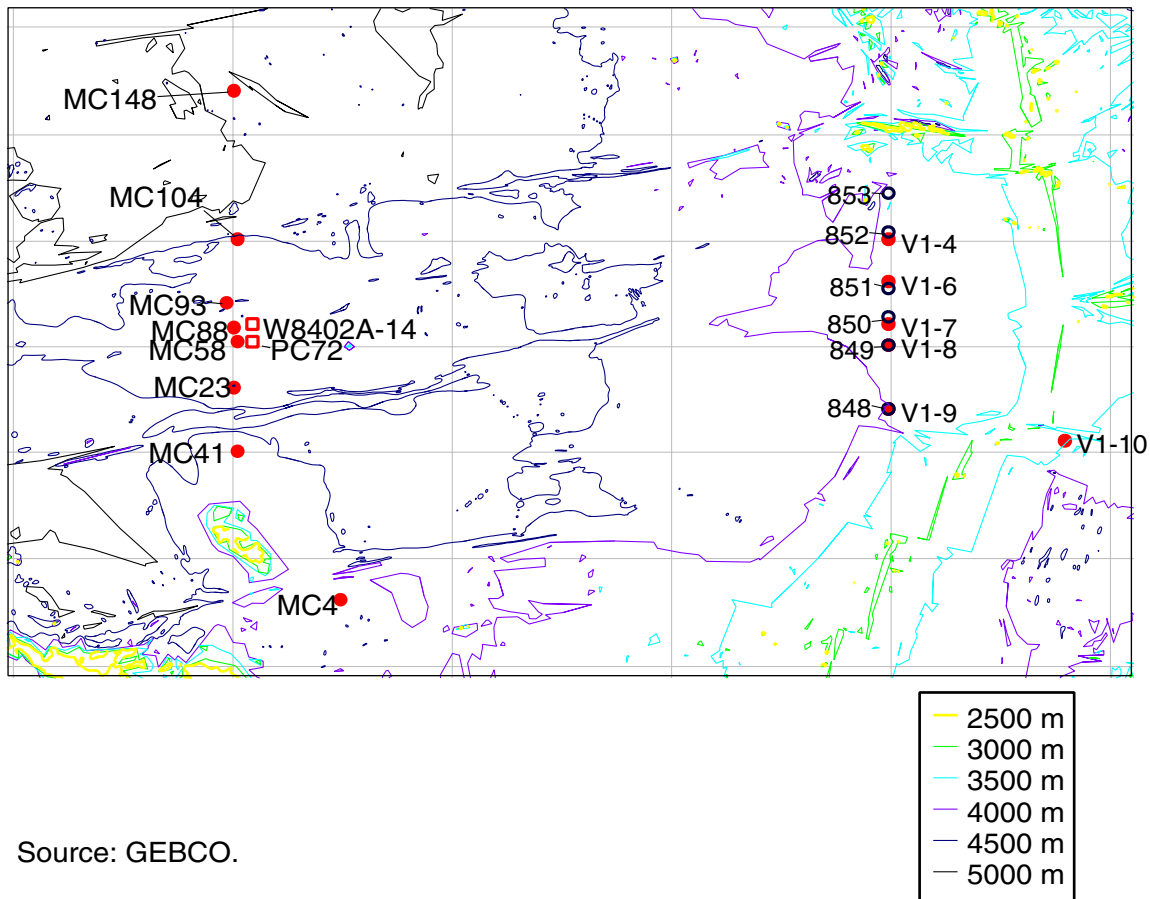


the carbon. This is because the coccolithophorids (marine algae class *Prymnesiophyceae*) are primary producers and play key roles in the global carbonate and carbon cycles [Westbroeck *et al.*, 1993]. Coccoliths are a major component of calcareous sediments in the open ocean, contributing up to 80% of the CaCO_3 in some locations [Fabry, 1989; Deuser and Ross, 1989; Honjo, 1978]. As coccolithophorids are the only widely distributed primary producers that preserve a fossil record, they may provide critical information on past variations in primary productivity and carbon and carbonate fluxes.

[3] Sr may be a particularly useful geochemical characteristic in coccolith carbonate. The Sr/Ca ratio of biogenic carbonate depends on the Sr/Ca ratio of the seawater and the Sr partitioning coefficient of the carbonate. Variations in carbonate Sr/Ca greater than 2% must be due to varying Sr partitioning. This is because Sr/Ca in surface water varies by less than 2% [de Villiers *et al.*, 1994; de Villiers, 1999] in the modern ocean, and likely varied by less than 3% over the last several hundred thousand years [Stoll and Schrag, 1998; Stoll *et al.*, 1999]. In abiogenic calcites, Sr partitioning is strongly controlled by precipitation rate [Lorenz, 1981; Tesoriero and Pankow, 1996]. In coccolithophorids the rate of calcite production varies widely [e.g., Balch *et al.*, 1996; Nimer and Merrett, 1993] and is frequently correlated with coccolithophorid growth rates [e.g., Balch *et al.*, 1996; Nimer and Merrett, 1993]. If, as in abiogenic calcites, Sr partitioning in coccolith carbonate is strongly controlled by calcite precipitation rates, coccolith Sr/Ca may record variations in coccolithophorid productivity. If postdepositional effects and changing coccolith components do not bias coccolith Sr/Ca in the sediment record, they might be used to extract records of past variations in coccolith productivity and CaCO_3 production. Such

proxies are important in evaluating model scenarios proposed for changes in atmospheric CO_2 over glacial cycles [e.g., Archer and Maier-Reimer, 1994; Archer *et al.*, 2000]. In addition, if the Sr/Ca ratio of coccoliths was to track past variations in coccolithophorid growth rates, it might be possible to use coccolith Sr/Ca ratios in combination with the carbon isotopic fractionation in alkenones to estimate past dissolved CO_2 concentrations in surface waters. This would improve our understanding of changes in oceanic sources and sinks of CO_2 which are likely to have contributed to past CO_2 and thus climatic variability of glacial/interglacial timescales.

[4] In this study, we examine Sr/Ca ratios in coccoliths from core top and downcore sediments to establish whether or not there are important variations in Sr partitioning in coccolith carbonate and how the Sr/Ca variations of coccolith carbonate relate to Sr/Ca variations in foraminiferal and bulk carbonate. We also seek to assess the evidence for relationships between coccolith Sr/Ca and coccolith productivity (growth and/or calcification rate) and other environmental parameters. Using a recently developed inductively coupled plasma-atomic emission spectroscopy (ICP-AES) technique [Schrag, 1999], we obtained high-precision (0.4% *rsd*) measurements of Sr/Ca in mixed coccolith assemblages from core tops along two transects from $\sim 10^\circ\text{S}$ to 5°N at 140° and 110°W in the eastern Pacific. In this region, upwelling brings cool nutrient- and CO_2 -rich waters to the surface in a narrow band at the equator, leading to large latitudinal gradients in biological productivity, sea surface temperatures, and surface nutrient and dissolved CO_2 concentrations. In the 140°W transect where data are available, estimated coccolithophorid growth and calcification rates also vary latitudinally. Relationships between Sr/Ca and changes in species assemblages and



Source: GEBCO.

Figure 1. Location of core top (solid red circles) and downcore (open red squares) samples used in this study. Core top samples from the 140°W transect are multicores from the TT013 cruise. Downcore piston core PC-72 is also from the TT013 cruise. Core top samples from the 110°W transect are from the VNTR01 cruise. Nearby ODP sites, used for additional information on sediments, are indicated by open black circles.

the relative flux of coccoliths to foraminifera across core top transects are also investigated. This approach may not provide definitive evidence on controls of Sr partitioning in coccoliths, in part because of limited modern surface-water measurements. Nevertheless, it can demonstrate systematic trends and suggest important factors meriting further investigation, perhaps through culture studies and plankton experiments where coccolith chemistry and biological and environmental factors can be more reliably linked.

2. Sediments

2.1. Location of Samples

[5] Core top sediment samples were obtained from two transects across the equator in the eastern Pacific, from 12°S to 5°N at 140°W and from 5°S to 5°N at 110°W (Figure 1). Core top depths average 4300 m for the 140°W transect and 3600 m for the 110°W transect. Sediments are high in carbonate (75–90% [Murray and Leinen, 1996]) within



5°–6° of the equator, but on the flanks of biogenic sediment pile away from the equator, the seafloor is beneath the carbonate compensation depth, and carbonate preservation decreases significantly to CaCO₃ of 55% at 12°S. Biogenic opal and terrigenous detritus are the primary noncarbonate components in the 140°W transect. In the 110°W transect, hydrothermal precipitates, especially fine Mn and Fe oxides, are also present due to the proximity of the Galapagos spreading ridge [Mayer *et al.*, 1992]. For the 140°W transect, radiocarbon dates available for core tops between 5°N and 5°S all yield late Holocene ages; no radiocarbon dates are available for the 12°S core [DeMaster *et al.*, 1996]. Oxygen isotope stratigraphy for the 110°W transect indicates that all core top samples are Holocene in age (A. Mix, personal communication, 1999).

[6] Downcore sediment samples were obtained from two sites within the main zone of equatorial upwelling. From site TT013-PC72 (0°06'N, 139°24'W, depth 4298 m) we studied samples covering the last 150 ka, and in core W8402A-14GC at the MANOP-C site (0°57.2'N, 138°57.3'W, depth 4287 m), we studied samples covering the last 250 ka. Age models for the downcore sites are based on correlation of benthic foraminiferal $\delta^{18}\text{O}$ records with the SPECMAP “stacked” benthic foraminiferal $\delta^{18}\text{O}$ timescale of Martinson *et al.* [1987]. In site TT013-PC72, age models are from Murray *et al.* [1995] and in MANOP-C from Jasper *et al.* [1994].

2.2. Separation of Coccolith and Foraminiferal Fractions

[7] In all core top samples we measured Sr/Ca in bulk sediment, the foraminiferal fraction (>63 μm) and the coccolith fraction (<12 μm); for the 140°W transect we also measured Sr/Ca in monospecific samples of foraminifera

Globorotalia tumida. Our method for separating coccolith calcite is based on observations of Paull *et al.* [1988] on the distribution of carbonate particles in the <38 μm fraction of sediments. Particle size distributions have a mode centered around 4 μm equivalent spherical diameter, corresponding to coccolith-sized particles, and a secondary mode in the range of 10–25 μm equivalent spherical diameter, corresponding to fragments of foraminifera and calcareous dinoflagellate cysts. We sought to minimize noncoccolith carbonate by separating the <12 μm size fraction from bulk sediments. Bulk carbonate was sieved to obtain the <63 μm fraction. Ethanol was used for sieving to prevent dissolution [e.g., Pingitore *et al.*, 1993]. The 12–63 μm size fraction was then removed by settling the suspension in ethanol for 10 min. Particle size analysis with a Coulter Counter indicates that the material remaining in suspension contains particles of up to 12 μm in equivalent spherical diameter, with maximum frequency of particles around 3–5 μm equivalent spherical diameter. We extract the suspension, allow this fraction to settle overnight, and siphon off the ethanol.

[8] To obtain a carbonate fraction dominated by foraminifera, the > 63 μm size fraction was crushed and sonicated repeatedly in ethanol to remove all adhered fine carbonate and noncarbonate material. This sonication was apparently more efficiently applied to the samples from the 140°W transect than the 110°W transect, since upon dissolution some fine noncarbonate material remained in the latter samples (implying that some fine coccolith carbonate may have been present as well).

2.3. Characterization of Coccolith Assemblages in Coccolith Fraction

[9] We used scanning electron microscope (SEM) images from smear slides at a magnification of 1500 times to identify coccolith



assemblages in the separated coccolith fraction. Our goal was to identify major changes in the coccolith assemblages and not to precisely determine relative abundances of all species in the samples. We recorded the number of intact coccoliths from the 6 most common taxa in 10 fields of view, counting on average 200 specimens per sample in the 110°W core top transect, 114 specimens per sample in the 140°W transect, and 272 specimens per sample from six depths in the MANOP-C downcore record. In the case of *C. leptoporus*, many of the distal and proximal shields were separated, and from some views it was not possible to determine if the shields were intact or if only one shield was present, complicating estimation of the relative contribution of this species to the sample. Because examples of clearly separated shields were nearly as abundant as intact shields in ambiguous views, we assumed that 50% of all counted specimens of *C. leptoporus* represented single shields and weighted the counts by 0.66 when calculating the relative contribution of *C. leptoporus* to the sample. *Florisphaera profunda* is also present in these sediments, but its small size prohibited reliable counts in our smear slide preparations. Likewise, the smallest *Gephyrocapsa* (<2 μm) were not counted.

[10] Counts were used to estimate the relative abundance of different taxa and the relative contribution of calcite from each species. The percent calcite from each species was calculated by estimating the average weights of coccoliths from each species by measuring the average coccolith diameter in our samples and using the diameter/volume relationships for each species established by *Young and Ziveri* [2000]. This calculation does not include *F. profunda*, which is assumed to be an insignificant source of calcite in these samples. Furthermore, it assumes that the species present as fragments of coccoliths

(which were not counted) are present in the same relative abundance as the intact coccoliths. However, selective breaking of more fragile species may lead to their underrepresentation in counts of intact coccoliths. In these samples, the weight contribution of the less abundant species is so minimal that their underrepresentation by a factor of 2–4 would not significantly affect the results.

3. Cleaning Techniques and Sr/Ca Analysis

3.1. Sample Cleaning and Sr/Ca Analysis

[11] Although carbonate is the dominant source of both Sr and Ca in our marine sediments, both ions may be present in contaminant phases such as Fe and Mn oxyhydroxides [Apitz, 1991]. In addition, the contribution of scavenged and adsorbed Sr and Ca may be significant, especially in the coccolith fraction where it is not possible to physically separate coccoliths from fine aluminosilicate detritus. To evaluate the influence of noncarbonate Sr and Ca on our measurements, we compared several methods for the preparation of coccolith samples for analysis. All samples were rinsed in ethanol. Some samples were shaken 30 min with ion exchange solutions, either 3 mL of 1 N NH₄Cl/4 mg sediment or 6 mL of 2% NH₄OH/4 mg sediment, followed by rinsing in distilled water. Others were shaken 4 hours with reducing solutions (25 g NH₂OH:HCl, 200 mL concentrated NH₄OH, in 300 mL distilled water; to reduce iron and manganese oxyhydroxides) followed by ion exchange and distilled water rinses. Following the precleaning procedures, ~0.5–1.0 mg of calcite was dissolved in 5 mL of ultrapure 2% HNO₃. However, splits of several samples were dissolved in 0.1 M ammonium acetate/acetic acid buffer to minimize the influence of acid strength on release of noncarbonate Sr during dissolution. Bulk carbo-



nate and the $>63 \mu\text{m}$ fraction were analyzed with no additional cleaning other than ethanol rinsing during the separation of the $>63 \mu\text{m}$ fraction. Monospecific samples of the foraminifera *Globorotalia tumida* from the 140 transect were analyzed following reducing and ion exchange cleaning steps. Results of all cleaning experiments are reported in Table 1.

[12] A potential drawback of some of these cleaning procedures is that they can partially dissolve the sample (e.g., NH_4Cl) or alter the chemistry of the calcite (e.g., hydroxide solutions). Treatment of pure, abiogenic aragonites with hydroxide solutions results in replacement of CaCO_3 by $\text{Ca}(\text{OH})_2$ [Pingiatiore *et al.*, 1993] and may decrease Sr/Ca ratios by 5% [Love and Woronow, 1991]. We discuss these complications in detail in a section 3.2.

[13] Sr/Ca ratios were determined by inductively coupled plasma-emission spectroscopy (ICP-ES) on a Jobin-Yvon simultaneous instrument, model 46-P. Sr/Ca ratios were corrected for a small effect of the concentration of Ca on the measured ratio following Schrag [1999]. Resulting precision is $>0.4\%$ (1σ) based on replicate analyses of the same sample at different dilutions over the course of several days. This precision is slightly worse than that reported by Schrag [1999] because there is greater variability in Sr/Ca ratios of foraminifera and coccoliths compared to corals. Since the concentration effect depends on the Sr/Ca ratio, the correction is less precise when applied to samples with a range of Sr/Ca ratios.

3.2. Effect of Adsorbed Cations

[14] Adsorbed Sr and Ca are potentially important contributors to the Sr/Ca ratio measured in the coccolith fraction, since components with high cation exchange capacity (alumino sili-

cates in silt and clay fraction) cannot be separated physically from the coccolith fraction. The coccolith fraction of TT013 MC148 (which contains $<1\%$ CaCO_3) releases ~ 5000 ppm Ca from noncarbonate sources when exposed to strong acid (2% HNO_3). The Sr/Ca ratio of this exchangeable fraction is 10.9 mmol/mol, consistent with Sr/Ca ratios measured in pore fluids at the sediment/water interface in equatorial Pacific sediments [Delaney and Linn, 1993]. Simple mass balance calculations indicate that for sediments with high- CaCO_3 content, the contribution of exchangeable Sr and Ca will be minor. For example, exchangeable Sr and Ca would increase the Sr/Ca ratio by only 1% for coccolith fractions comprised of 80% carbonate and 20% noncarbonate material (assuming noncarbonate material similar to that of MC148). However, exchangeable Sr and Ca may elevate the Sr/Ca ratio by 15% in coccolith fractions comprised of 20% carbonate and 80% noncarbonate material similar to that of MC148.

[15] For the 140°W transect, removal of exchangeable cations is likely responsible for much of the decreases in Sr/Ca observed with reducing (MNX) and ion exchange (IONX) cleaning procedures (Table 1 and Figure 2). There is no additional decrease in Sr/Ca with the use of reducing techniques compared to ion exchange treatments alone, comparing samples with strong acid dissolution. The variable decrease in Sr/Ca for different samples correlates with geochemical indicators of the contribution of terrigenous material and scavenging, such as ppm Al (Figure 2b) [Murray and Leinen, 1996]. However, the Sr/Ca reduction in the 12°S site is much lower than expected from the very high detrital component and low CaCO_3 percent. This may indicate incomplete removal of exchangeable cations from noncarbonate phases in this sample and/or that Sr and Ca are released from other noncarbonate sites upon acidification with 2% HNO_3 for carbo-



Table 1. Location of Sr/Ca Data From Different Core Top Sediment Fractions and Different Cleaning Procedures

| Cleaning steps Method name Ethanol rinse Reducing step Ion exchange Dissolution | Site | Longitude, deg | Latitude, deg | Depth, m | Coccolith Fraction, <12 um | | | | | | >63 um Sr/Ca | G. tumida Sr/Ca | Bulk Sr/Ca |
|------------------------------------------------------------------------------------------------|-------|-------------------|------------------|----------|----------------------------|--------------------|-----------------------|--------|-------|--------|-----------------|--------------------|---------------|
| | | | | | Sr/Ca | Sr/Ca | Sr/Ca | Sr/Ca | Sr/Ca | Sr/Ca* | | | |
| | | | | | ETH | IONX | APITZ | APITZ* | ETH | ETH | ETH | ETH | |
| | | | | | x | x | x | x | x | x | x | x | |
| | | | | | - | - | 2x | - | - | - | - | - | |
| | | | | | - | NH ₄ Cl | NH ₄ OH 2x | - | - | - | - | - | |
| | | | | | HNO3 | HNO3 | acetate | HNO3 | HNO3 | HNO3 | HNO3 | HNO3 | |
| <i>Samples</i> | | | | | | | | | | | | | |
| TT013 | MC148 | -140 | 12 | 4900 | 10.9 | | | | | | | | |
| TT013 | MC104 | -140 | 5 | 4416 | 2.18 | 2.04 | 1.95 | 2.04 | 1.30 | 1.23 | 1.63 | | |
| TT013 | MC93 | -140 | 2 | 4413 | 2.33 | 2.25 | | | 1.30 | 1.23 | 1.85 | | |
| TT013 | MC88 | -140 | 0.82 | 4415 | 2.35 | 2.27 | | | 1.31 | 1.22 | 2.10 | | |
| TT013 | MC58 | -140 | 0.11 | 4307 | 2.36 | 2.33 | 2.25 | 2.34 | 1.32 | 1.24 | 1.90 | | |
| TT013 | MC23 | -140 | -2 | 4365 | 2.26 | 2.23 | | | 1.32 | 1.22 | 1.88 | | |
| TT013 | MC41 | -140 | -5 | 4269 | 2.24 | 2.21 | | | 1.32 | 1.24 | 1.73 | | |
| TT013 | MC4 | -135 | -12 | 4280 | 2.58 | 2.46 | 2.24 | 2.33 | 1.35 | 1.29 | 2.10 | | |
| VNTRO1 | 4 | -110 | 5 | 3848 | 2.47 | 2.25 | 2.15 | 2.24 | 1.29 | 1.29 | 1.92 | | |
| VNTRO1 | 6 | -110 | 3 | 3765 | 2.16 | 2.07 | | | 1.38 | 1.57 | 1.57 | | |
| VNTRO1 | 7 | -110 | 1 | 3722 | 2.39 | 2.27 | | | 1.36 | 2.05 | 2.05 | | |
| VNTRO1 | 8 | -110 | 0 | 3791 | 2.36 | 2.29 | 2.21 | 2.30 | 1.59 | 1.97 | 1.97 | | |
| VNTRO1 | 9 | -110 | -3 | 3860 | 2.22 | 2.13 | | | 1.32 | 1.85 | 1.85 | | |
| VNTRO1 | 10 | -102 | -4.5 | 3405 | 2.20 | 2.06 | | | 1.33 | 1.80 | 1.80 | | |

^aFor the Sr/Ca data, a checklist of the cleaning steps (listed on the left-hand margin) used in the preparation of samples is given at the top of each column. A dash indicates that the cleaning step was not used in preparing Sr/Ca results for analysis. The cross denotes that the procedure was applied. The asterisk denotes correction of Sr/Ca data for inferred changes in the calcite chemistry during cleaning, as described in text.

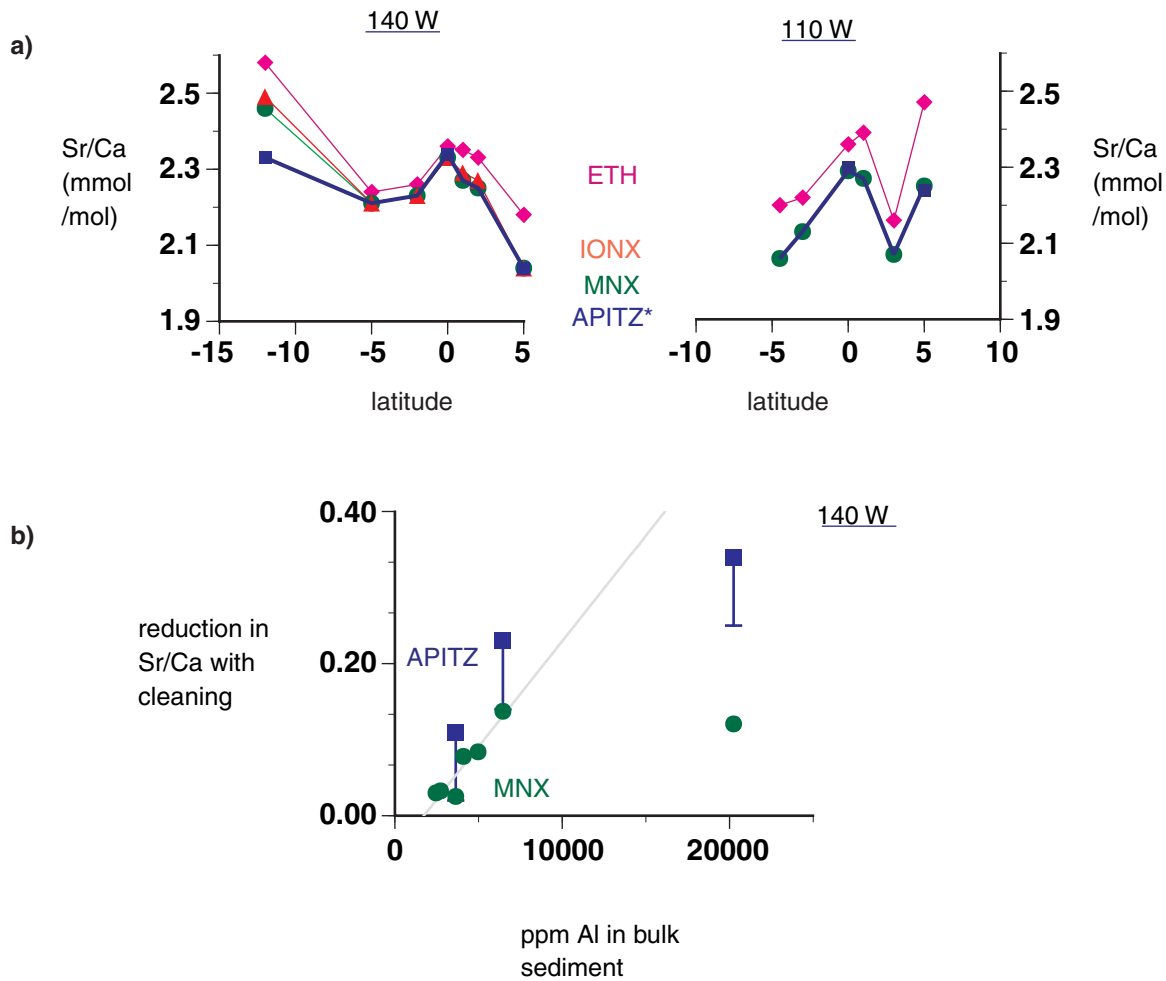


Figure 2. Sr/Ca ratios in the coccolith fraction with different cleaning treatments. (a) Variation in coccolith Sr/Ca for cleaning treatments ETH (ethanol rinse), IONX (ion exchange), MNX (reducing and ion exchange), and APITZ* (reducing and ion exchange with dissolution in buffered acetic acid), corrected as described in text and denoted in Table 1. (b) Difference (in mmol/mol) in sediment Sr/Ca ratios with ETH and MNX or APITZ (uncorrected) cleaning treatments, compared with bulk ppm Al [Murray and Leinen, 1996], an indicator of detrital input and scavenging. Error bars on the APITZ measurements indicate inferred changes in carbonate chemistry from hydroxide exposure during cleaning.

nate dissolution. The analyzed coccolith fraction for 12°S consisted of at most 30% carbonate and 70% noncarbonate material likely similar to that of MC148. Mass balance considerations indicate that exchangeable cations should elevate the Sr/Ca ratio by at least 9%, implying coccolith carbonate Sr/Ca ratio of 3.34 mmol/mol or less.

[16] More intense ion exchange and reducing steps (doubling the amount of reagent per mg of sediment) followed by dissolution in acetic acid/ammonium acetate buffer may minimize the contribution of noncarbonate Sr and Ca [e.g., Apitz, 1991] (procedure abbreviated “APITZ”). However, the increased exposure to hydroxide solutions may also decrease the

Table 2. Age Data and Sr/Ca Measurements of Downcore Sampling^a

| Core Depth, cm | Age, ky | Coccolith Fraction | |
|-------------------------------|---------|--------------------|------------|
| | | Sr/Ca; ETH | Sr/Ca; MNX |
| <i>Cruise TT013 Site PC72</i> | | | |
| 1 | 0 | 2.29 | 2.29 |
| 8 | 4 | 2.29 | 2.29 |
| 12 | 7 | 2.30 | 2.27 |
| 19 | 10.5 | 2.28 | 2.27 |
| 25 | 13.5 | 2.29 | 2.28 |
| 31 | 16.3 | | 2.24 |
| 37 | 19.1 | 2.17 | 2.15 |
| 44 | 22.4 | 2.20 | 2.20 |
| 50 | 25.5 | 2.20 | 2.19 |
| 55 | 28.4 | 2.20 | 2.20 |
| 64 | 33.6 | 2.26 | 2.26 |
| 70 | 37.2 | 2.24 | 2.23 |
| 80 | 43 | 2.22 | 2.22 |
| 90 | 48.9 | 2.22 | 2.23 |
| 100 | 54.7 | 2.24 | 2.24 |
| 105 | 57.3 | 2.23 | 2.22 |
| 115 | 63.5 | 2.23 | 2.19 |
| 122 | 68.4 | | 2.19 |
| 128 | 72.9 | 2.20 | 2.15 |
| 132 | 75.8 | 2.20 | 2.12 |
| 139 | 81.2 | 2.11 | 2.00 |
| 145 | 85.8 | | 2.07 |
| 151 | 91.9 | 2.18 | 2.15 |
| 161 | 108.1 | 2.14 | 2.12 |
| 171 | 122.9 | 2.25 | 2.21 |
| 181 | 129.7 | 2.23 | 2.24 |
| 195 | 139.8 | 2.11 | 2.12 |
| 202 | 144.3 | 2.12 | 2.15 |
| 211 | 150.1 | 2.20 | 2.18 |
| 218 | 155.8 | 2.16 | 2.16 |
| 224 | 161 | 2.21 | 2.19 |
| 230 | 166.5 | 2.25 | 2.24 |
| 235 | 170.1 | 2.28 | 2.28 |
| 244 | 176 | 2.27 | 2.27 |
| 250 | 179.7 | 2.44 | 2.28 |
| 256 | 183.9 | 2.33 | 2.31 |
| 260 | 194 | 2.39 | 2.36 |
| 267 | 200 | 2.37 | 2.38 |
| 275 | 208.5 | 2.35 | 2.33 |
| 285 | 219.6 | | 2.34 |
| 290 | 223.6 | 2.33 | 2.30 |
| 295 | 227.6 | 2.30 | 2.29 |
| 305 | 234.3 | 2.30 | 2.34 |
| 321 | 249 | 2.25 | 2.27 |
| 325 | 252.8 | 2.28 | 2.31 |

Table 2. (continued)

| Core Depth, cm | Age, ky | Coccolith Fraction | |
|-------------------------------|---------|--------------------|------------|
| | | Sr/Ca; ETH | Sr/Ca; MNX |
| <i>Cruise TT013 Site PC72</i> | | | |
| 9 | 0 | 2.28 | 2.27 |
| 19 | 5.11 | 2.31 | 2.32 |
| 29 | 9.13 | 2.34 | 2.32 |
| 39 | 12.61 | 2.34 | 2.33 |
| 49 | 15.8 | 2.25 | 2.26 |
| 59 | 18.9 | 2.28 | 2.26 |
| 69 | 22.12 | 2.28 | 2.25 |
| 79 | 25.74 | 2.31 | 2.27 |
| 89 | 30.32 | 2.26 | 2.24 |
| 99 | 36.62 | 2.23 | 2.21 |
| 109 | 43.5 | 2.27 | 2.26 |
| 119 | 50.15 | 2.27 | 2.26 |
| 129 | 55.16 | 2.31 | 2.33 |
| 139 | 59.49 | 2.3 | 2.29 |
| 149 | 63.74 | 2.3 | 2.3 |
| 159 | 68.36 | 2.32 | 2.32 |
| 169 | 73.88 | 2.32 | 2.34 |
| 179 | 80.89 | 2.18 | 2.21 |
| 189 | 89.54 | 2.21 | 2.25 |
| 199 | 99.15 | 2.29 | 2.3 |
| 209 | 108.3 | 2.27 | 2.29 |
| 219 | 116 | 2.37 | 2.38 |
| 229 | 122.4 | 2.29 | 2.3 |
| 239 | 128.4 | 2.25 | 2.26 |
| 249 | 134.4 | 2.19 | 2.19 |
| 269 | 144.4 | 2.16 | 2.16 |
| 279 | 149.1 | 2.14 | 2.15 |

^aCleaning steps for each technique are delineated in Table 1 and are described in detail in the text.

Sr/Ca of the carbonate. With the exception of MC4, this treatment decreases the Sr/Ca ratio of coccolith fractions by 3–4% compared to MNX, maintaining a trend parallel to that of MNX treatments for 140°W samples in Figure 2b. We believe that the 3–4% reduction may be due to changes in calcite chemistry and not to removal of exchangeable cations, whereas the larger reduction in MC4 (9%) is in part due to additional removal of exchangeable cations. If this 4% effect is removed from all analyses, the final Sr/Ca ratio of MC4 is 3.33 mmol/mol, very similar to the maximum ratio calculated from mass balance considerations. It is possible that the Sr/Ca ratios of coccolith carbonate may be lower, but additional MNX and IONX

cleaning procedures are likely to incur additional changes in the calcite chemistry. Consequently, extracting true Sr/Ca ratios of coccolith calcite in low-carbonate sediments may be difficult and may require further refinement of cleaning techniques. To reflect the greater uncertainty of estimating coccolith Sr/Ca in these sediments, we distinguish this measurement with a different symbol in subsequent graphs. There is little difference (<1%) in Sr/Ca between the treated and untreated fractions for the downcore coccolith samples (Table 2), consistent with the very high CaCO₃ and low detrital components in these equatorial sites.

3.3. Effect of Sr and Ca in Mn and Fe Hydroxides in Coccolith Fraction

[17] In the 110°W transect we did not analyze samples with ion-exchange treatments alone. Consequently, it is more difficult to separate the effects of ion exchange and reduction of Fe and Mn oxides. The effects of ion exchange may be comparable to those in the 140°W transect; however, there is likely an additional effect of removing Sr present in Mn and Fe oxides, which may explain the greater average reduction in Sr/Ca with cleaning in the 110°W transect (5 versus 3%). The sites of the 110°W transect lie close to the Galapagos spreading ridge (Figure 1) and may be influenced by hydrothermal plumes. Hydrothermal Fe and Mn oxides can elevate the Sr/Ca ratio of sediments by up to 20% [Apitz, 1991]. The largest reduction in Sr/Ca occurs at the 5°N sample, where the reducing and ion exchange treatment lowers Sr/Ca ratios by 9%. This location also has the highest magnetic susceptibility (indicative of fine terrigenous or metaliferous particles) of the Ocean Drilling Program (ODP) sites coinciding with our transect and was the only ODP site where abundant Mn and Fe oxide particles were identified in smear slides [Mayer *et al.*, 1992]. It is difficult

to assess whether all Sr and Ca associated with Mn and Fe oxides were removed during the APITZ cleaning treatment. It is possible that the Sr/Ca ratios of coccolith carbonate may be lower, but as discussed previously in section 3, additional MNX and IONX cleaning procedures are likely to incur additional changes in the calcite chemistry. Extracting reliable Sr/Ca ratios of coccoliths in sediments with abundant Mn and Fe oxides may be difficult. To reflect the greater uncertainty of estimating coccolith Sr/Ca in this site, we distinguish this measurement with a different symbol in subsequent graphs.

3.4. Selective Dissolution in the Coccolith Fraction

[18] We compared the change in Sr/Ca with partial dissolution of two carbonate-rich samples and one carbonate-poor sample upon exposure to varying amounts of 0.001 N HNO₃. When we dissolve <50% of the sample, Sr/Ca ratios of the remaining carbonate (dissolved in 2% HNO₃) are only slightly affected and are intermediate between those of ethanol-rinsed samples and those cleaned with reducing and ion-exchange steps (Figure 3). However, extreme partial dissolution of the samples (>50% dissolved) results in increased Sr/Ca ratios, possibly due to increasing influence of non-carbonate Sr and Ca relative to carbonate Sr and Ca.

[19] Treatment of samples with 1 M NH₄Cl to remove exchangeable Sr also results in partial dissolution of carbonates when larger volumes of NH₄Cl are used. In this example of partial dissolution, exchangeable Sr should be partially removed. For carbonate-rich samples, extreme partial dissolution (>50%) does not lead to a large increase in Sr/Ca ratios. This suggests that the increase in Sr/Ca ratios with extreme partial dissolution in 0.001 N HNO₃ was caused by exchangeable Sr. Although there

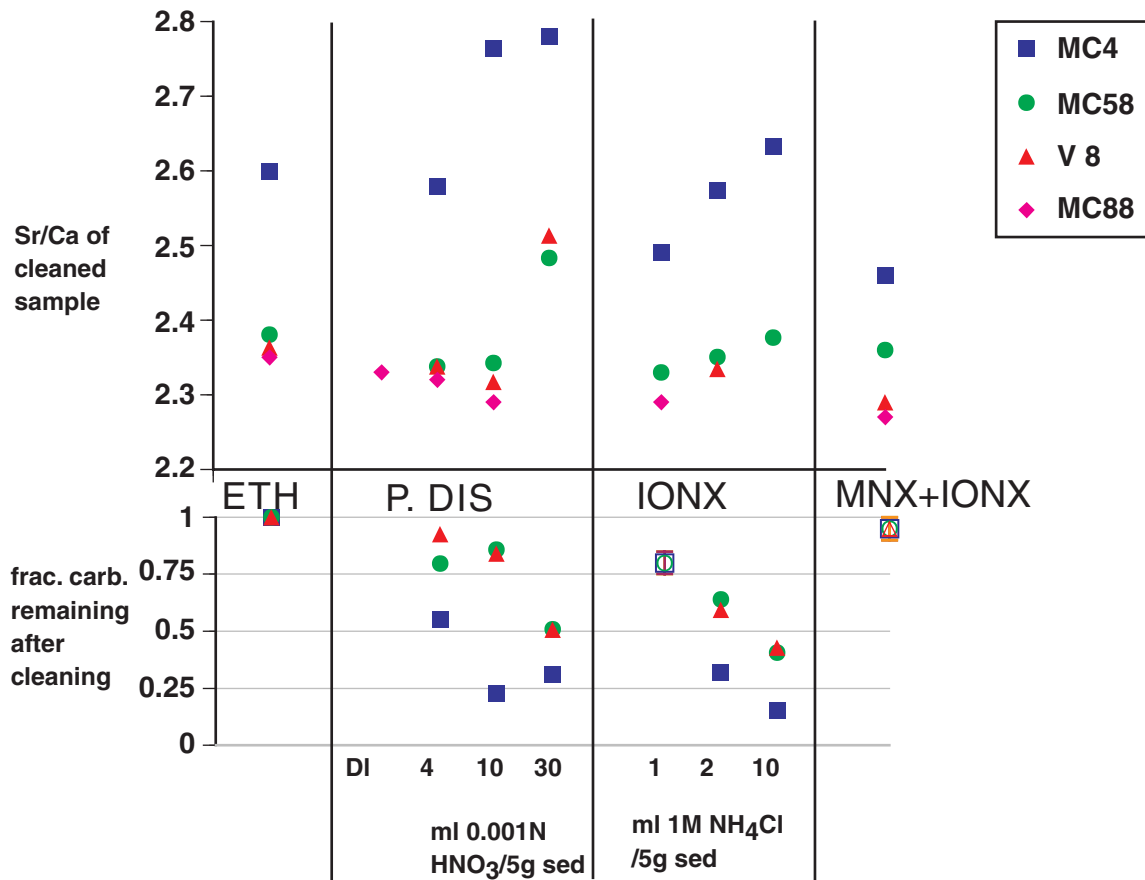


Figure 3. Results of partial dissolution experiments. (top) Sr/Ca ratios of sediments after different extents of partial dissolution. (bottom) Fraction of carbonate remaining after treatment. Open symbols are estimates based on prior experiments; solid symbols represent measurements made in this experiment. ETH, samples rinsed in ethanol (no partial dissolution); PDIS, samples partially dissolved with different amounts of 0.001 N HNO₃; IONX, samples treated with different amounts of 1 M NH₄Cl; and MNX, samples treated with reducing and ion exchange solution as described in the text. After cleaning, all samples were dissolved in 2% HNO₃ for analysis.

is still a significant ascent of Sr/Ca ratios for the low-carbonate sample with increasing dissolution, the Sr/Ca increase is much lower for comparable levels of partial dissolution. These results suggest that while partial dissolution may affect sediment Sr/Ca by altering the proportion of cations from carbonate and non-carbonate sources, the carbonate Sr/Ca of these coccolith fractions is relatively insensitive to partial dissolution. The constancy of coccolith Sr/Ca with moderate to extreme dissolution

suggests that partial dissolution is not responsible for the latitudinal trends in Sr/Ca observed in the equatorial Pacific transect.

3.5. Implications for Sr/Ca of Other Carbonate Fractions

[20] Since noncarbonate sources may contribute appreciable Sr and Ca to the carbonate fraction, these sources must also influence the Sr/Ca ratio of bulk sediment. Consequently,



the Sr/Ca ratio of bulk carbonate is likely to be much lower than that of bulk sediment measured in sites MC4 (140°W, 12°S) and VNTR014 (110°W, 5°N) and somewhat lower than bulk sediment in MC104 (140°W, 5°N). For subsequent discussions (e.g., Figure 4), we estimate a likely range of bulk carbonate Sr/Ca for these samples, on the basis of the effect on noncarbonate Sr and Ca in the coccolith fraction. Noncarbonate Sr and Ca are likely to have much smaller effects on the Sr/Ca ratios of the foraminiferal fraction because most noncarbonate components (clay/silt and fine Fe or Mn oxides) have been physically removed from the foraminifera during picking and separation.

4. Sr/Ca in Core Top and Downcore Carbonates

4.1. Sr/Ca in Core Top Carbonates

[21] The Sr/Ca ratio of coccolith carbonate is much higher than that of bulk carbonate or foraminiferal carbonate (Figure 4a). Coccolith Sr/Ca across the core top transects ranges from 2.04 to 2.33, much larger than the Sr/Ca variation in the >63 μm foraminiferal fraction or in the monospecific *G. tumida* foraminiferal record. This large variation (~15%) in coccolith Sr/Ca exceeds the <2% variation in Sr/Ca observed in modern seawater and must be due to variations in Sr partitioning in coccolith carbonate.

[22] Both coccolith and bulk carbonate show maxima in Sr/Ca at the equator in both transects. However, the variation in bulk carbonate Sr/Ca is larger than that of coccolith carbonate and must be driven both by changes in coccolith Sr/Ca and by changes in the relative proportion of coccolith versus foraminiferal carbonate across the transect, as calculated in Figure 4b. Coccoliths contribute the greatest fraction of carbonate at the equator.

4.2. Sr/Ca and Composition of Coccolith Carbonate

[23] We compare variations in the Sr/Ca ratio of coccolith carbonate across the transects with the species composition of the coccolith fraction to see if changing species composition is responsible for the Sr/Ca variations. The <12 μm fraction from the core top samples consists of intact coccoliths, fragments of coccoliths, and fragments of diatom opal. We do not observe any small foraminifera in our samples and estimate that fragments of foraminifera are not significant contributors to the calcite since many of the calcite fragments present can be identified as fragments of coccoliths. The coccolith assemblages in all samples consist of *Calcidiscus leptoporus*, *Gephyrocapsa oceanica*, *Emiliana huxleyi*, *Umbilicosphaera sibogae*, *Helicosphaera* spp., and *Gladiolithus flabellatus* (Figure 5b). *C. leptoporus* and *G. oceanica* are the most abundant taxa in all core top samples, together contributing 50–90% of the whole coccoliths (Figure 5b). There are slight variations in the relative abundance of different coccolithophorid taxa across the transects. In the 140°W transect, the relative abundance of *E. huxleyi* increases slightly around the equator while that of *C. leptoporus* decreases. In the 110°W transect, the relative abundance of *E. huxleyi* and *G. flabellatus* increases at 5°S and 3°N at the expense of *C. leptoporus* and *G. oceanica*.

[24] According to our estimates, nearly all of the calcite in the coccolith fraction of the core top samples derives from *C. leptoporus* (50–80%) and *G. oceanica* (5–45%, Figure 5c). The contribution of calcite from *C. leptoporus* versus *G. oceanica* shows no consistent relationship with the Sr/Ca variations (Figure 5a). In general, there is no consistent correlation between the coccolith assemblage and the Sr/Ca of the coccolith fraction. This suggests that the variations in coccolith Sr/Ca across our core

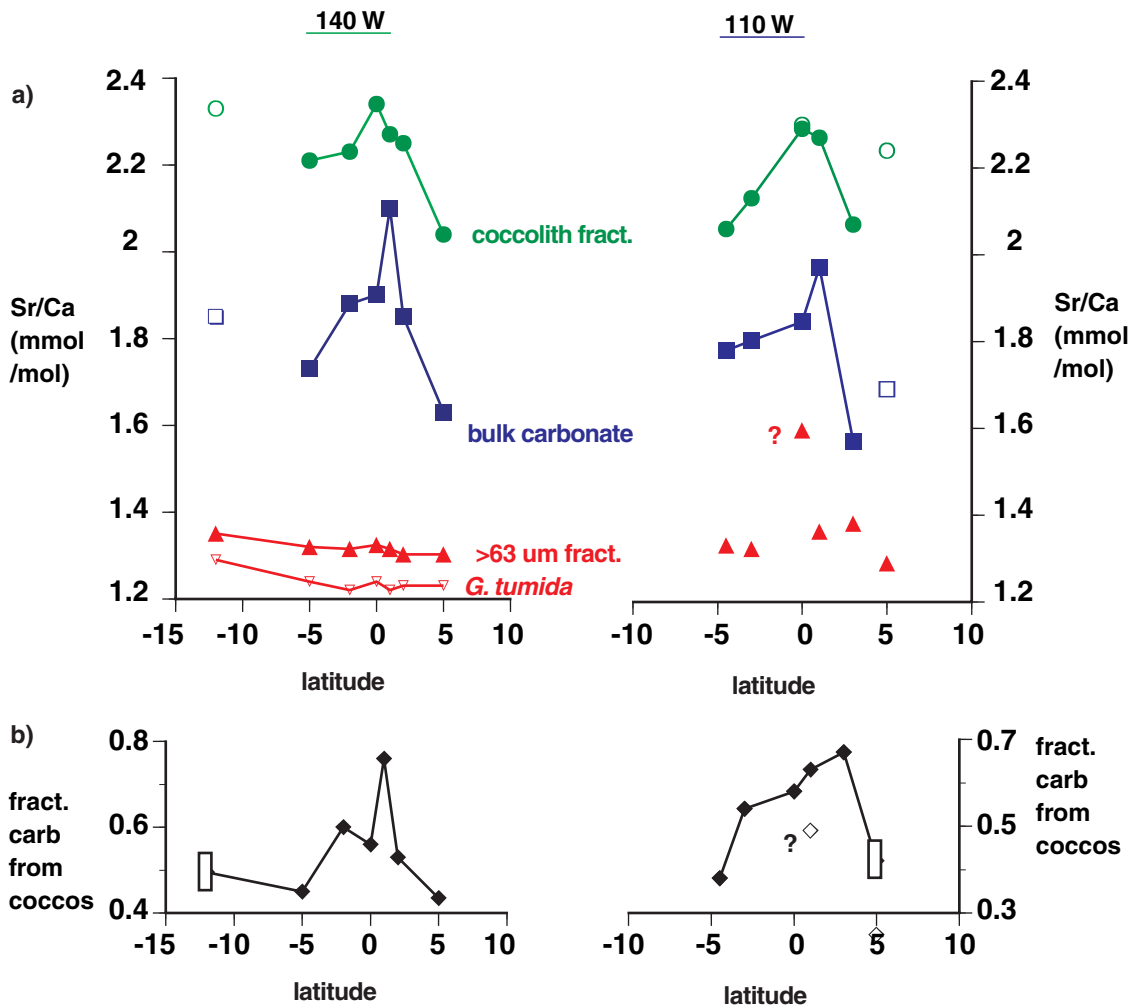


Figure 4. (a) Sr/Ca ratios of coccolith carbonate (green circles) compared with Sr/Ca of bulk carbonate (blue squares) and Sr/Ca of the $>63 \mu\text{m}$ foraminiferal fraction (red solid triangles) and Sr/Ca of foraminifera *G. tumida* (red open triangles) for 140° and 110°W transects. Open circles and open squares denote coccolith fraction and bulk carbonate sediments, respectively, with high Sr and Ca contribution from noncarbonate fractions as discussed in the text. (b) Fraction of carbonate from coccoliths, calculated as described in the text.

top transects are not primarily controlled by variations in the components of the coccolith assemblage.

4.3. Sr/Ca in Downcore Carbonates

[25] In downcore records from the equatorial Pacific, Sr/Ca in the coccolith fraction varies by

nearly 20% over the last 250 ka with identical trends for the MNX cleaned and ethanol-rinsed samples (Table 2 and Figure 6b). For the 150 ky overlap between records at TT013-PC72 and MANOP-C, Sr/Ca variations show similar minima at 18, 80, and 140–150 ka which correspond to maxima in the composite benthic $\delta^{18}\text{O}$ curve [Martinson *et al*, 1987]. Variations

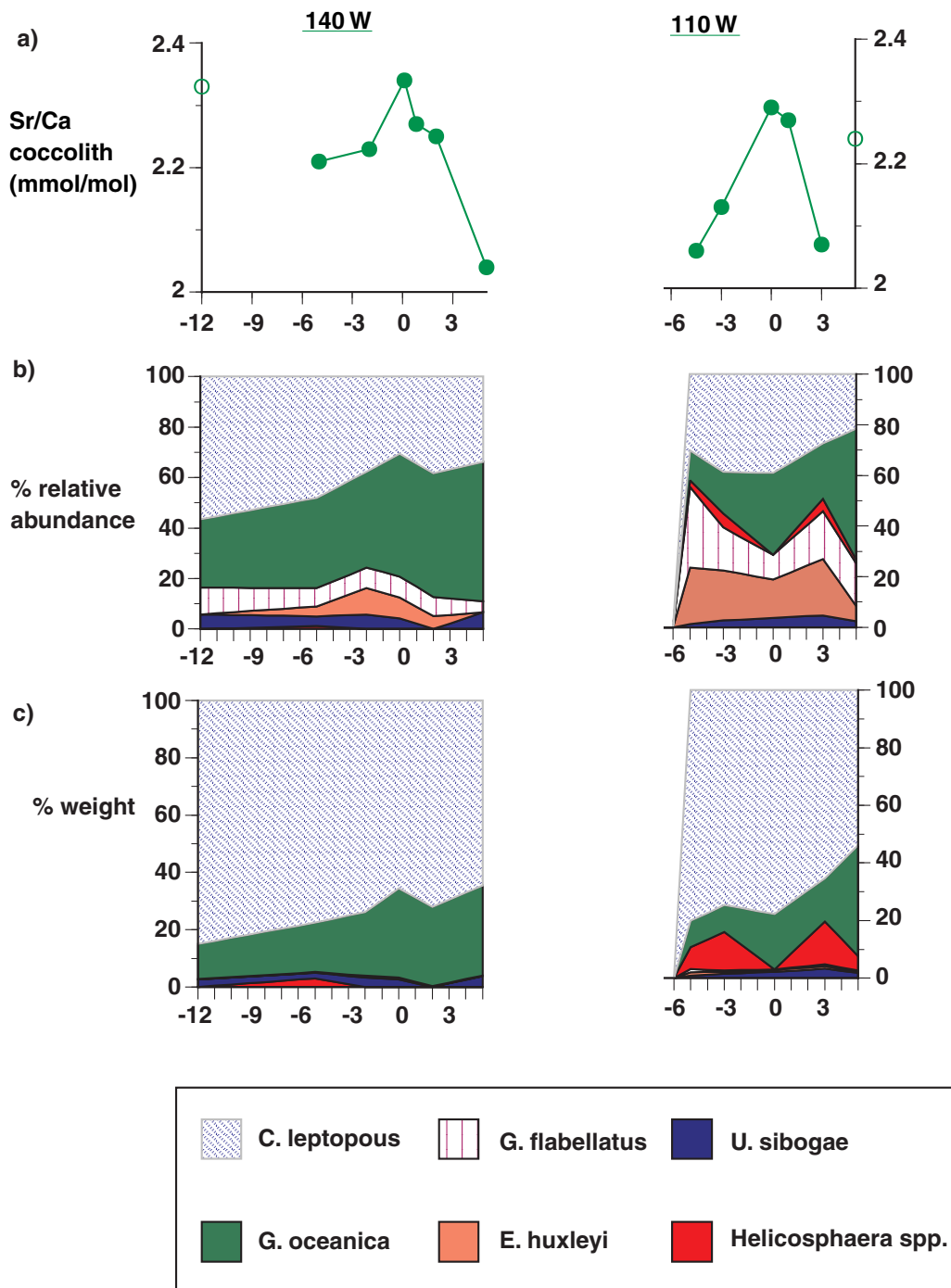


Figure 5. Sr/Ca of coccolith fraction and species composition data for core tops. (a) Sr/Ca data for coccolith carbonate. Symbols same as in Figure 4. (b) Relative abundance of species among intact coccoliths. (c) Percent of calcite contributed by each species, calculated as described in the text.

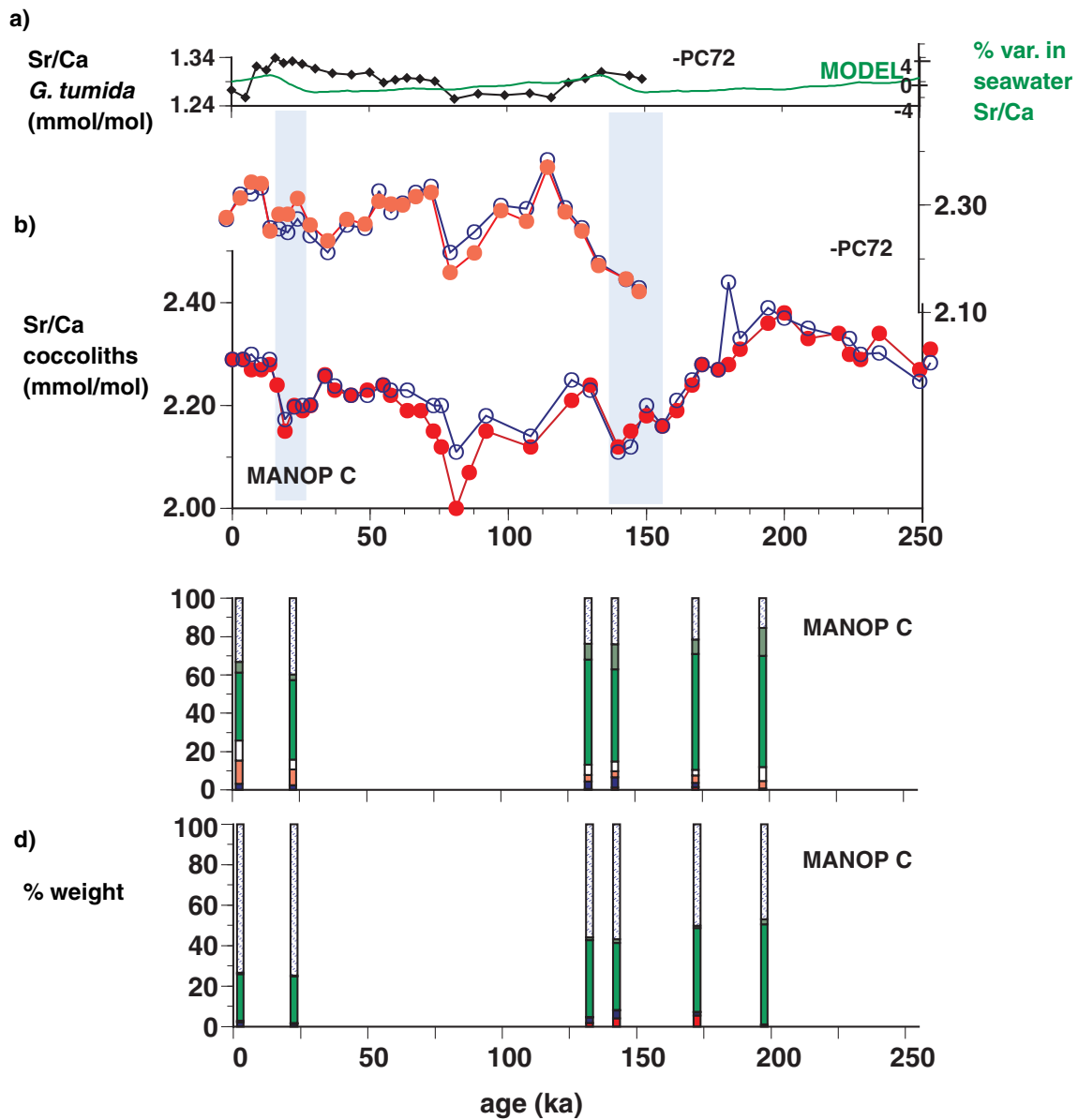


Figure 6. Sr/Ca and species composition data for downcore records. (a) Sr/Ca data of *G. tumida* from site PC72 in black symbols [Stoll *et al.*, 1999]. Green curve is maximum variation in seawater Sr/Ca predicted by models of Stoll and Schrag [1998]. (b) Sr/Ca of coccolith carbonate; blue circles for ethanol rinse and red circles for reducing and ion exchange (“MNX”) cleaning. (c, d) Relative abundance of species and percent carbonate contribution by each species among intact coccoliths from selected samples in MANOP-C. Legend same as in Figure 5. Stippled pattern shows glacial maxima as defined by benthic $\delta^{18}\text{O}$ record for MANOP-C [from Jasper *et al.*, 1994].



in coccolith Sr/Ca are much larger than those of foraminifer *G. tumida* from TT013-PC72, and coccolith Sr/Ca does not covary with *G. tumida* Sr/Ca (Figure 6a) [Stoll *et al.*, 1999].

[26] To assess whether the rapid shifts in coccolith Sr/Ca might be due to changes in the coccolith assemblage, we analyzed the species composition of six downcore samples spanning large shifts in coccolith Sr/Ca. The species composition of the six analyzed downcore samples is similar to that of core top samples in the 140°W transect (Figures 6c and 6d). *C. leptoporus* and *G. oceanica* are the most abundant taxa and contribute the majority of the calcite. No significant changes in the coccolith assemblages accompany the short-term Sr/Ca variations between 0 and 18 ka, 129 and 139 ka, and 170 and 195 ka. However, *G. oceanica* contributes a larger fraction of calcite in the older sediments (59%) than in the most recent sediments (29%). The older (>170 ka) sediments also exhibit the highest Sr/Ca ratios of the time series. Consequently, changes in species composition may contribute to longer-term changes in coccolith Sr/Ca. Alternatively, higher productivity may favor higher abundances of *G. oceanica*.

5. Interpretation of Variations in Coccolith Sr/Ca

5.1. Relation to Variations in Productivity

[27] Coccolith Sr/Ca in core top sediments generally covaries with modern measurements of primary productivity in the overlying surface waters in both transects (Figure 7), although higher coccolith Sr/Ca contrasts with low productivity at 12°S in the 140°W transect and 5°N in the 110°W transect. While primary productivity at these sites is dominated by picoplankton [Murray *et al.*, 1994], growth rates for alkenone-producing haptophytes parallel primary productivity in the 140°W trans-

ect where alkenone data are available (Figure 7b) [Bidigare *et al.*, 1997]. While not all coccolithophorids produce alkenones and other noncoccolithophorid haptophytes may contribute alkenones, the alkenone-estimated growth rates provide the best available approximation of coccolithophorid growth rates in field samples. These data suggest a possible relationship between coccolith Sr/Ca and coccolithophorid growth rate. The divergence of this relationship farther from the equator may be due to complications in the measurement of coccolith Sr/Ca in these two sediments due to contributions from noncarbonate sources, as discussed previously. Alternatively, or perhaps in addition, this divergence may indicate that coccolith Sr/Ca is additionally influenced by other factors.

[28] One complication in relating the chemistry of coccoliths in sediments to overlying surface water chemistry is that the coccolith assemblages may be significantly modified during deposition. For example, the coccolith assemblages in sediment core tops consist largely of dissolution-resistant species [Roth, 1994], and the relative abundance of species is different from that observed in shallow sediment traps from the same region. Sediment traps from 5°S at 140°W (1216 m) and from 12°S at 135°W (1292 m) are dominated by *G. flabellatus* (≈50%) with *G. oceanica* and *F. profunda* also contributing significantly to the assemblage (greater than ≈10% each [Broerse, 2000]). However, calculations of the amount of calcite contributed by each species indicate that *G. oceanica* contributed 42 and 30% of calcite at 12° and 5°S, respectively, while *C. leptoporus* contributes 7 and 14%, respectively. Extensive dissolution of fragile *G. flabellatus* has likely occurred in the sediments. Although there are no assemblage data for living plankton for the 140° or 110°W transects, a transect at 155°W was characterized by higher abundances of *E. huxleyi* and *Gephyrocapsa* spp. and much lower abundances of *G. flabellatus* around the

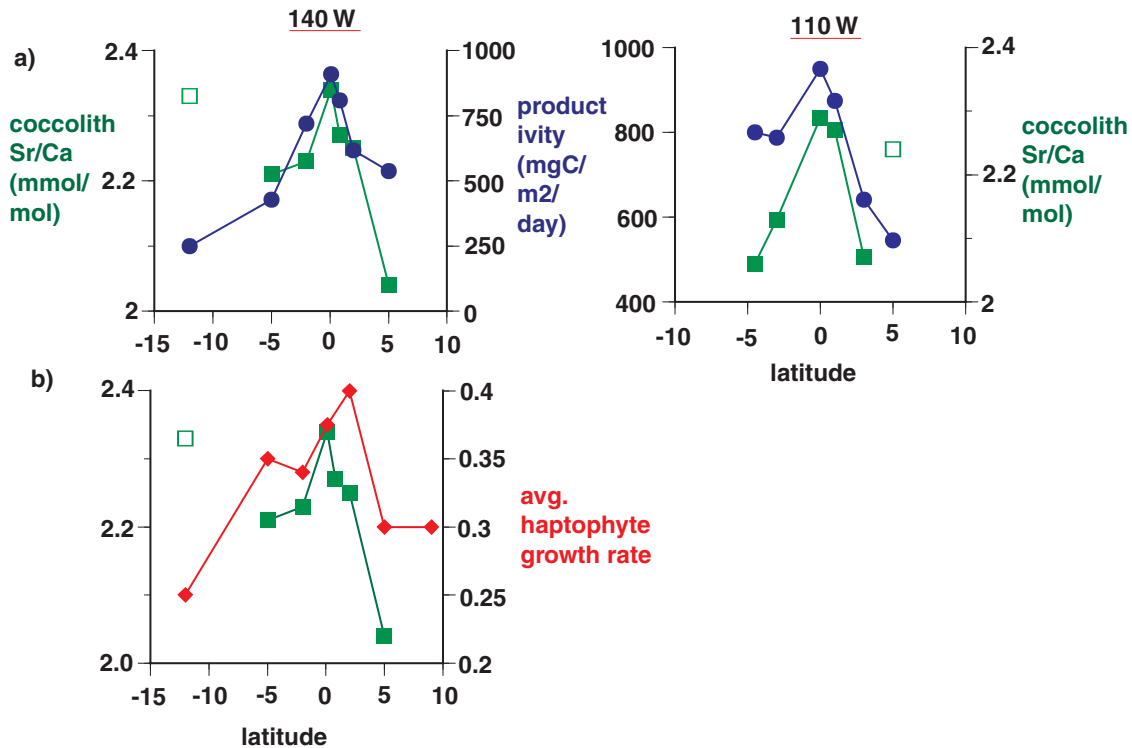


Figure 7. (a) Coccolith Sr/Ca from core top sediments (green squares) and long-term average productivity (blue circles; data from Chavez *et al.* [1990], Barber *et al.* [1991], and Chavez *et al.* [1998]) versus latitude. (b) Coccolith Sr/Ca (green squares) and alkenone-estimated coccolithophorid growth rates (red diamonds) versus latitude [Bidigare *et al.*, 1997]. Open symbols denote sediments with high Sr and Ca contribution from noncarbonate fractions as discussed in the text.

equator, and a sharp transition to abundant *Umbellosphaera* spp. around 10S [Honjo and Okada, 1974]. It is unclear if this difference reflects spatial variations in the Pacific or selective dissolution between the photic zone and the 1200 m sediment traps.

[29] Selective dissolution of coccoliths has enriched the core top sediments in the alkenone-producer *G. oceanica*. However, calcite is dominantly from *C. leptoporus*, which does not produce alkenones (H. Kinkel, personal communication, 2000). Nonetheless, *C. leptoporus* is likely to follow the same growth rate maximizing *r* selector strategy of alkenone producers *E. huxleyi* and *G. oceanica* and is likely to

show similar growth rate variations across the upwelling zone [Young, 1994]. In addition, the export production of *C. leptoporus* covaries with that of *E. huxleyi* and *G. oceanica* in both the Gulf of California and San Pedro upwelling systems [Ziveri *et al.*, 1995a, b; Ziveri and Thunnell, 2000]. Consequently, the core top Sr/Ca measurements for these sediments likely register the behavior of alkenone-producing coccolithophorids whose growth rates are estimated in the modern 140°W transect.

5.2. Relation to Variations in Calcification

[30] Several estimates of calcite production rates are available for the 140°W transect as a result of the Joint Global Ocean Flux Study

Equatorial Pacific process study carried out in 1992. In equatorial Pacific surface waters, coccolithophorids dominate carbonate production; counts of foraminifera and measurements of foraminiferal carbon in CTD casts [Stoecker *et al.*, 1996] indicate that foraminifera did not contribute appreciable calcite to the particulate inorganic carbon (PIC) measurement at any of the stations. We compare coccolith Sr/Ca from core top sediments with the CaCO₃ rain rate at 4000 m sediment traps and with estimated calcification rates in surface waters.

[31] The rain rate of CaCO₃ recorded in sediment traps is one indicator of the rate of CaCO₃ production by coccolithophorids in the equatorial Pacific. At 4000 m, the average CaCO₃ rain rate was highest at the equator and decreased away from the equator, similar to the trends in coccolith Sr/Ca (Figure 8a). This suggests a possible relationship between coccolithophorid calcite production and coccolith Sr/Ca, although, as in the previous cases, the curves diverge at 12°S.

[32] Calcification rates were measured in August–September 1992 from 12°S to 12°N at depths of 0–120 m at 140°W via in situ and simulated in situ ¹⁴C incubation experiments [Balch and Kilpatrick, 1996]. Calcification rates derived from incubation experiments have high uncertainties: the correlation coefficient between simulated in situ and in situ measurements for each station is only 0.2. PIC and coccolithophorid surface area were also measured [Balch and Kilpatrick, 1996] and in combination with alkenone-estimated coccolithophorid growth rates [Bidigare *et al.*, 1997] provide an additional estimate of calcification rate, assuming that growth rates for all calcifying species follow those of alkenone producers. Since sediments integrate calcification rates from all depths in the photic zone, we calculate the average calcification rate for each

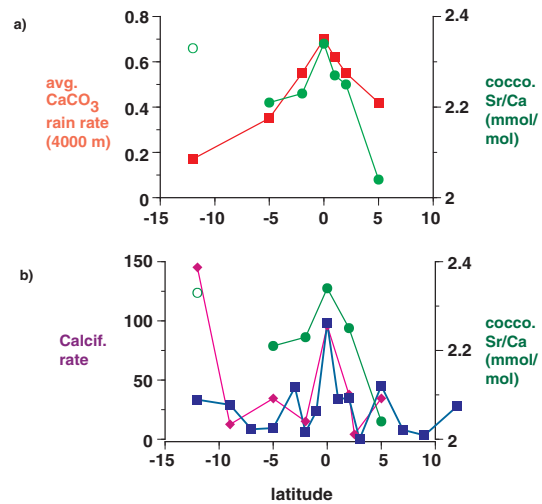


Figure 8. Estimated growth and calcification rates in the 140°W transect. (a) Coccolith Sr/Ca (green circles) and average 1992 CaCO₃ rain rate [Honjo *et al.*, 1995] (red squares) in 4000 m sediment traps. (b) Coccolith Sr/Ca (green circles) and estimated calcification rates from incubation experiments (blue squares) and PIC measurements (violet diamonds) based on data Balch and Kilpatrick [1996]. Units for calcification rate are g calcite C/m² coccosphere surface area/day. Open symbols denote sediments with high Sr and Ca contribution from noncarbonate fractions as discussed in the text.

station, weighting the calcification rate/cell surface area for each depth by the fraction of calcite produced at that depth. Estimates derived from incubation and PIC data both show high calcification rates at the equator, decreasing away from the equator (Figure 8b). These trends are broadly similar to those in coccolith Sr/Ca, although there is more local variability in the calcification estimates, and the PIC estimate indicates high calcification rates per cell surface area at 12°S. The sediment Sr/Ca record may be slightly smoothed by lateral transport of carbonate rain or sediments and by seasonal migrations of the zone of most intense upwelling and maximum calcification rates. In addition, the calcification rate estimates may be noisy as indicated by the low



reproducibility of the incubation measurements.

5.3. Relation to Environmental Data

[33] The variations in primary productivity and coccolithophorid productivity observed across the equatorial Pacific result from upwelling-driven variations in availability of macronutrients and micronutrients, CO₂, temperature, and other environmental factors. Consequently, it can be difficult to distinguish whether variations in coccolith Sr/Ca result directly from the environmental variations or from the biological responses of coccolithophorids (e.g., varying growth rates) to these environmental variations. Here, we compare coccolith Sr/Ca with long-term averages of sea surface temperature (SST), surface nutrient concentrations, and dissolved CO₂ concentrations (Figure 9).

[34] In the 140°W transect, trends in coccolith Sr/Ca are generally inversely correlated with temperature and broadly covary with surface nutrient and dissolved CO₂ concentrations. In the 110°W transect, there is no clear correlation between Sr/Ca and SST, nutrient concentrations, or dissolved CO₂ concentrations.

[35] Temperature is an important control on Mg/Ca and Sr/Ca ratios in other biogenic calcites [e.g., Nurnberg *et al.*, 1996; Beck *et al.*, 1992; Cooper *et al.*, 1999]. However, culture experiments indicate a direct, rather than inverse, relationship between temperature and Sr partitioning in calcite of planktonic foraminifera [Lea *et al.*, 1999] and coccolithophorids (H. Stoll, unpublished data, 1997). An inverse relationship is observed in the Sr/Ca ratios of coccoliths from core tops at 140°W: Sr/Ca ratios are high at the equator where sea surface temperatures are depressed by upwelling of cold subsurface waters. Consequently, temperature cannot be the primary factor controlling coccolith Sr/Ca in core top sediments.

Temperature may exert a secondary influence on coccolith Sr/Ca in our transects, partially attenuating the observed correlation between coccolith Sr/Ca and productivity near the equator. Elevated temperatures away from the upwelling zone may contribute to the higher Sr/Ca ratios at 12°S in the 140°W transect and at 5°N in the 110°W transect. Consequently, temperature may be an important influence on coccolith Sr/Ca and needs to be further investigated in culture studies. Although variations in nutrient and dissolved CO₂ concentrations covary with Sr/Ca near the equator in the 140°W transect, the lack of relation in the 110°W transect suggests that these are not important direct controls on coccolith Sr/Ca ratios.

5.4. Controls of Sr Partitioning in Coccoliths

[36] In abiogenic experiments, increasing the precipitation rate over 2 orders of magnitude results in a fivefold difference in the effective Sr partitioning coefficient (Figure 10) [Lorens, 1981; Tesoriero and Pankow, 1996] due to surface enrichment effects [Watson, 1996] or surface reaction kinetics in general [Morse and Bender, 1990]. Although coccolithophorids exert a high degree of control over the timing and location of calcification [e.g., Young *et al.*, 1992], similar thermodynamic and kinetic effects may occur. Coccolith Sr/Ca shows coherent trends across the equatorial Pacific upwelling zone which are similar to variations in the growth rates and calcite production of coccolithophorids in overlying surface waters. Growth and calcification rates of coccolithophorids are frequently correlated [Westbroek *et al.*, 1993]. This observation, along with the strong dependence of Sr partitioning on calcification in abiogenic calcites, suggests that coccolithophorid growth (and calcification) rates may be an important control on Sr/Ca variations in coccoliths from core top sedi-

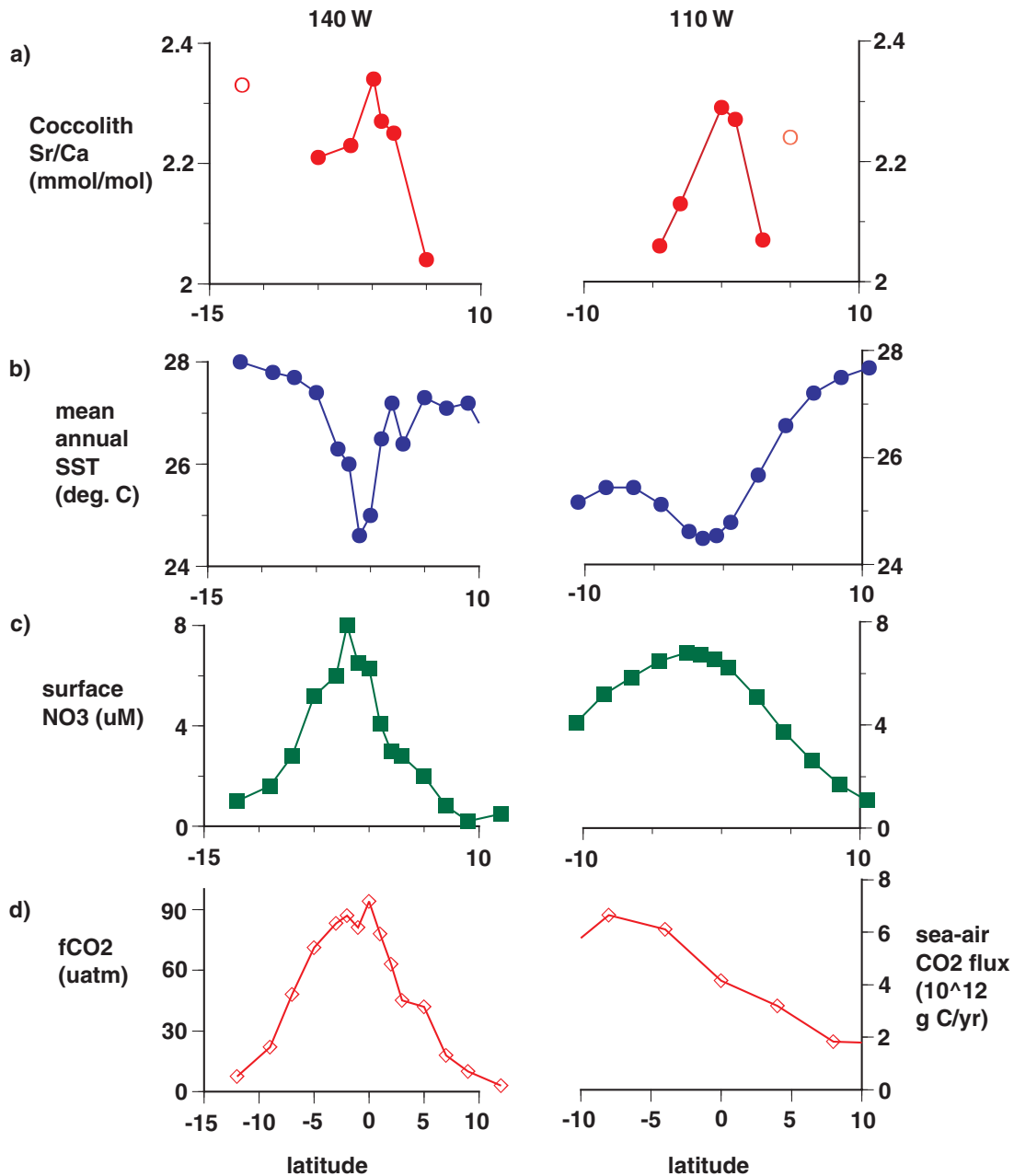


Figure 9. Coccolith Sr/Ca from core tops compared with variations in chemistry of overlying waters. (a) Sr/Ca in coccoliths, symbols same as in Figure 4. (b) Annual average SST. (c) Long-term average surface NO₃. (d) Long-term average *f*CO₂ (140°W) and sea-air CO₂ flux in 1990 (110°W). Temperature, nutrient, and *f*CO₂ for 140°W from Barber and Chavez [1991]; temperature and nutrient from 110°W from Levitus et al. [1994]. Sea-air CO₂ flux for 110°W from Takahashi et al. [1997].

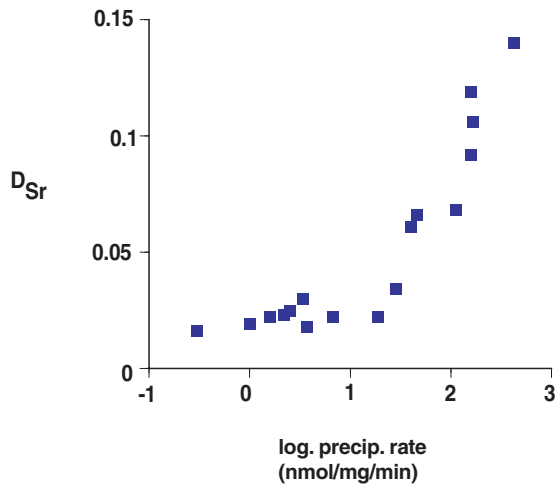


Figure 10. Partitioning coefficient of Sr in abiogenic calcite (D_{Sr}) as a function of calcite precipitation rate (nmol calcite/mg calcite seed/minute). Data from Tesoriero and Pankow [1996].

ments. This interpretation can be tested through culture studies where calcification, growth rate, temperature, and other factors can be reliably determined and compared with coccolith Sr/Ca ratios. Culture studies also will provide opportunities to investigate the extent to which the highly regulated biomineralization processes of coccolithophorids affects Sr partitioning differently from abiogenic calcite crystallization.

6. Possible Paleooceanographic Applications

6.1. Coccolith Sr/Ca to Track Past Variations in Coccolithophorid Productivity and $CaCO_3$ Rain Rate

[37] The relative production rates of carbonate-producing and noncarbonate-producing (frequently siliceous) organisms are important in setting the pH of the deep ocean and consequently the ocean-atmosphere partitioning of CO_2 . Extensive modeling experiments indicate that changes in the rain ratio of carbonate to

organic carbon remains one of the “front-runners” in explaining glacial/interglacial atmospheric PCO_2 cycles [Archer *et al.*, 2000]. However, rigorous evaluation of this hypothesis has been limited by difficulties in modeling ecological partitioning of carbonate versus silica-producing phytoplankton in the ocean and by lack of proxy data for past variations in the productivity of these groups. Because the partitioning of planktonic functional types in the ocean is poorly understood, it is difficult to model how their distributions and relative productivities may have varied in response to changing environmental conditions over glacial cycles. If a reliable proxy for past variations in coccolithophorid productivity were identified, it could contribute significantly to the resolution of this dilemma.

[38] If coccolithophorid growth and calcification rates are the predominant control on coccolith Sr/Ca ratios, downcore Sr/Ca ratios might be used to infer past changes in coccolithophorid productivity. The trends in equatorial Pacific core tops suggest a relationship between coccolith Sr/Ca and coccolithophorid productivity, but culture experiments and a wider survey of coccolith Sr/Ca in other regions are needed to confirm these relationships. In particular, more work is needed to assess the extent to which temperature may also affect Sr partitioning in coccolith calcite. In addition, to be a reliable proxy of past coccolithophorid productivity, downcore coccolith Sr/Ca records must not be significantly biased by variations in dissolution intensity over time, either through selective dissolution effects on a constant species assemblage or changes in the species assemblage. Changes in the coccolith assemblages, including changes in the dominance of different phenotypes, must be minor or the effects of these changes must be well understood. Finally, it is important to consider potential variations in the Sr/Ca ratio of seawater. Fortunately, the long

residence times of Sr and Ca in the ocean greatly attenuate variations in seawater Sr/Ca over glacial/interglacial timescales. Numerous modeling experiments indicate that Sr/Ca likely varies by <3% over Quaternary glacial cycles [Stoll and Schrag, 1998; Stoll et al., 1999].

[39] If the relationships between coccolithophorid productivity and coccolith Sr/Ca in equatorial Pacific core tops are general and temperature variations do not overwhelm the signal, then our downcore Sr/Ca records may reflect past variations in coccolithophorid productivity. In these records, coccolith Sr/Ca does not covary with changes in dissolution intensity calculated as the composite preservation index at an adjacent site (WEC8803B-GC51 [LaMontagne et al., 1996]). We have shown that the rapid shifts in coccolith Sr/Ca are not due to changes in the coccolith assemblage. However, it is possible that the long-term decrease in the dominance of *C. leptoporus* relative to *G. oceanica* influences long-term trends in Sr/Ca, although there is no consistent relationship between coccolith Sr/Ca and the relative abundances of these two taxa in the core top transects. Downcore Sr/Ca variations of 20% significantly exceed predicted changes of 1–3% in the Sr/Ca ratio of seawater over the last 250,000 years. Consequently, the downcore coccolith Sr/Ca records from the equatorial Pacific may indicate times of low coccolithophorid productivity during glacial maxima and around 80 ka (Figure 6). In contrast, accumulation rates of organic carbon, opal, and barite all suggest higher overall productivity in the equatorial Pacific during glacial maxima [Lyle et al., 1988; Paytan et al., 1996], although these estimates may be variably biased by errors in accumulation rates caused by carbonate dissolution cycles and sediment focusing. Nonetheless, if the organic carbon accumulation data from the equatorial Pacific are not biased by preserva-

tion or problems in the calculation of accumulation rates, then lower coccolith Sr/Ca ratios may suggest that during the last two glacial maxima high organic carbon production combined with decreased calcification led to an increased $C_{org}:C_{inorg}$ particle flux in this region.

[40] Relationships between coccolith Sr/Ca and coccolithophorid productivity may also be useful on longer timescales, for investigating the response of this important group of primary producers to major environmental changes in the past. In the Cretaceous, for example, Sr/Ca ratios of coccolith-dominated carbonates appear to respond to environmental changes resulting from major pulses of volcanic activity [e.g., Stoll and Schrag, 1999; H. M. Stoll and D. P. Schrag, Sr/Ca variations in Cretaceous carbonates: Relation to productivity and sea level changes, submitted to *Palaeogeography Palaeoclimatology Palaeoecology*, 1999]. However, for longer-term studies, the possibility of changes in seawater Sr/Ca ratios must also be considered.

6.2. Coccolith Sr/Ca to Correct for Growth Rate Contribution to ϵ_p for Estimating Paleo- pCO_2 (aq)

[41] Estimation of past concentrations of dissolved CO_2 in the ocean is another approach used to understand past changes in the carbon cycle. To study the role of the ocean in glacial/interglacial atmospheric PCO_2 variations, workers attempt to estimate past air-sea CO_2 fluxes in different regions and then surmise about the underlying processes which control changes in these fluxes over glacial cycles [e.g., Jasper et al., 1994]. On longer timescales, workers have also attempted to estimate atmospheric PCO_2 from calculations of dissolved CO_2 for regions of the ocean presumed to be in equilibrium with the atmosphere [e.g., Pagani et al., 1999]. Estimates of



past dissolved PCO_2 are made from measurements of carbon isotopic fractionation in algal organic matter, which depends on dissolved CO_2 concentrations, along with algal growth rate and cell geometry [Popp *et al.*, 1998]. Through the use of taxon-specific biomarkers, it is possible to measure fractionation in compounds derived from a single cell geometry, although the precise surface area/volume relationship may vary with cell size. However, the lack of an independent proxy for past variations in algal growth rates has limited estimation of past dissolved CO_2 concentrations using this approach.

[42] If coccolith Sr/Ca varies with coccolithophorid growth rates, then coccolith Sr/Ca would be particularly suited for correcting growth rate effects on carbon isotope fractionation in alkenones because coccoliths and alkenones both derive from the same group of organisms. As discussed in section 6.1, the relationships between coccolith Sr/Ca and growth rate need to be confirmed through a broader survey of coccolith Sr/Ca in core tops and ideally through culture experiments where both coccolith Sr/Ca and ϵ_p (isotopic fractionation between coccolithophorid biomass and dissolved CO_2) are monitored. The influence of temperature on Sr partitioning in coccoliths also must be assessed. Likewise, in downcore records the potential biases of selective dissolution and changing species assemblages must be addressed. Because there are strong evolutionary variations within coccolithophorids [e.g., Bollmann, 1997; Knappertsbusch *et al.*, 1997] the relationship between Sr/Ca and growth rates may change through time, even within the same species. However, such changes may also affect the relationship between carbon isotopic fractionation and dissolved CO_2 . A further caveat is that the organic biomarkers derive from *E. huxleyi* and *Gephyrocapsa* which are not the only contributors to coccoliths in the sediments.

[43] In the case of the downcore records from the equatorial Pacific, alkenone producer *G. oceanica* is a major contributor of coccolith calcite, and the other important species, *C. leptoporus*, has a similar ecology in the modern ocean. It is difficult to evaluate the significance of changing relative proportions of these species on the coccolith Sr/Ca record. The downcore increase in *G. oceanica* may partly drive the slight downcore increase in Sr/Ca, or environmental conditions favoring higher coccolithophorid productivity (and higher coccolith Sr/Ca) further back in the past may also have favored a higher abundance of *G. oceanica*. These factors complicate the interpretation of the equatorial Pacific coccolith Sr/Ca records in terms of coccolithophorid growth rates. However, as an exercise, we consider the effect of a Sr/Ca-based growth rate correction on calculated dissolved CO_2 concentrations from the equatorial Pacific for the last 250,000 years.

[44] We use the downcore Sr/Ca record from MANOP-C site and the alkenone carbon isotopic fractionations measured in the same core by Jasper *et al.* [1994]. We roughly calibrated the relationship between coccolith Sr/Ca and coccolithophorid growth rate using two approaches. In the first approach, we compared estimated average cell-specific growth rates of modern alkenone-producing haptophytes from 5°N to 5°S in the 140°W transect (data from Bidigare *et al.*, [1997]) with Sr/Ca of core top coccoliths from the same latitude (Figure 11, top). A second approach used to calibrate the relation between Sr/Ca and growth rate takes advantage of a strong correlation observed between PO_4 concentrations and the slope of the relationship between ϵ_p which presumably reflects variations in coccolithophorid growth rate [Bidigare *et al.*, 1997]. We compare PO_4 data from 1992 JGOFS surveys (C. Garside, personal communication, 1999) in the 140°W

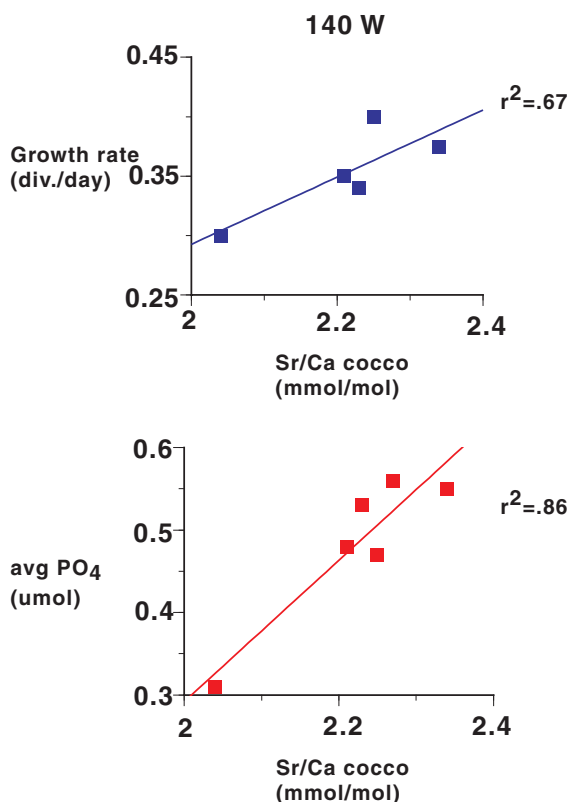


Figure 11. (top) Correlation between coccolith Sr/Ca and alkenone-estimated growth rates [Bidigare *et al.*, 1997] between 5°S and 5°N in 140°W transect. (bottom) Correlation between coccolith Sr/Ca and average surface PO₄ [from Bidigare *et al.*, 1997] between 5°S and 5°N in 140°W transect.

transect with core top Sr/Ca from the same latitude (data from 5°N to 5°S only; Figure 11, bottom). Because there are a small number of data points, and only a single point at low growth rates and PO₄ concentrations, there is considerable uncertainty to these calibrations. More stable calibrations must be extracted from other regions and culture studies for more reliable inference of past variations in coccolithophorid growth rates.

[45] For the growth rate calibration, we apply the relation:

$$\epsilon_p = 24.6 - 137.9(\mu_{\text{cell}}/\text{Ce})$$

from culture experiments by Bidigare *et al.* [1997]. For the PO₄ calibration, we use the relationships from Bidigare *et al.* [1997]:

$$b = 38 + 160(\text{PO}_4/\mu\text{mol})$$

$$b = (25 - \epsilon_p)\text{Ce}$$

[46] Following Jasper *et al.* [1994], we assumed that variations in the $\delta^{13}\text{C}$ of DIC followed those of *Neogloboquadrina dutertrei*. Spero *et al.* [1997] have shown that carbon isotope fractionation in foraminiferal calcite depends on the carbonate ion concentration of seawater. However, we calculate that the predicted variation in $\delta^{13}\text{C}$ of *N. dutertrei* due to the carbonate ion effect ($\delta^{13}\text{C}$ shifts 0.3–0.8 permil for constant $\delta^{13}\text{C}$ of DIC) has a negligible effect on the calculated paleo- $p\text{CO}_2$ (aq). Likewise, the small changes in seawater Sr/Ca ratios over glacial cycles [Stoll and Schrag, 1998] also have a negligible effect on coccolith Sr/Ca ratios and on calculated paleo- $p\text{CO}_2$ (aq). Paleo- $p\text{CO}_2$ (aq) calculated with both growth rate and phosphate calibrations are similar, although $p\text{CO}_2$ (aq) calculated with the growth rate calculation are consistently 50 ppm higher. These results are compared with the paleo- $p\text{CO}_2$ (aq) calculated using the approach of Jasper *et al.* [1994] assuming constant algal growth rates (Figure 12).

[47] There are small but significant differences between the paleo- $p\text{CO}_2$ (aq) records calculated assuming constant algal growth rates and those calculated using Sr/Ca to correct for likely changes in algal growth rates (Figure 12). The correlation coefficient (Spearman) of the two records is 0.71, which is statistically different from zero at the $p=0.000$ level. Differences between the two records are greatest between 60 and 120 ka and 170–250 ka. During the latter interval, the $p\text{CO}_2$ (aq) estimates exceed those of any other interval for the growth-rate-corrected record, whereas the estimates in the uncor-

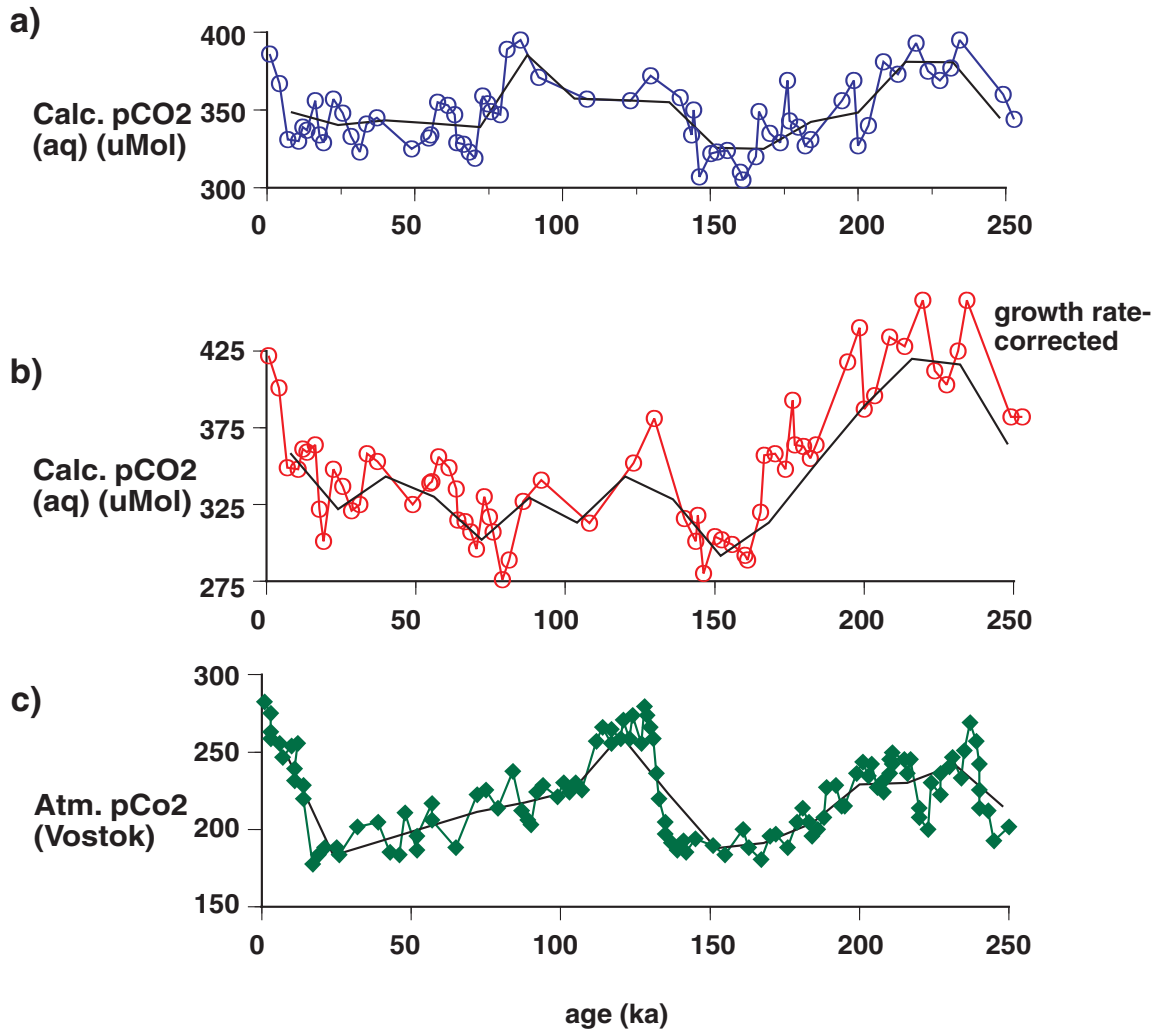


Figure 12. Calculated dissolved CO₂ concentrations for MANOP-C site for last 250 ka. (a) Calculation of Jasper *et al.* [1994] assuming constant algal growth rates. (b) Calculation correcting for variations in algal growth rates using Sr/Ca variations. (c) Atmospheric CO₂ record from Vostok ice core [Petit *et al.*, 1999]. Black lines indicate data smoothed at 16 ka intervals.

rected record are comparable with those of other interglacial intervals. The higher calculated $p\text{CO}_2$ (aq) in this older part of the record may be due to a shift in the Sr/Ca versus growth rate relation or the influence of temperature changes on coccolith Sr/Ca. It is also possible that algal growth rates were indeed higher but that average cell size of alkenone producers was smaller, leading to

overestimation of $p\text{CO}_2$ (aq) from the ε_p relation (H. Kinkel, personal communication.). Detailed study of changes in coccolithophorid assemblages in nearby Deep Sea Drilling Program site 573 (0.5°N, 133.3°W [Pujos, 1985]) indicates that prior to 150 ka, the small *Gephyrocapsa protohuxleyi* and *G. aperta* were more abundant than the medium size *G. oceanica*. This change in the size of



alkenone-producing cells may lead to an overestimation of $p\text{CO}_2$ (aq) from ε_p . If growth rates were higher during this interval, as suggested by Sr/Ca, the overestimate of $p\text{CO}_2$ (aq) from ε_p would have been partially compensated by the assumption of constant growth rates.

[48] By comparing calculated records of $p\text{CO}_2$ (aq) with the Vostok record of atmospheric PCO_2 variations, it is theoretically possible to evaluate changes in the air-sea CO_2 flux from the equatorial Pacific. However, differences in the resolution of the two types of records and uncertainties in their correlation complicate this process. Overall, both records of Pacific $p\text{CO}_2$ (aq) show elements of the ~ 100 ka cyclic variation in atmospheric PCO_2 , indicating some covariation between Pacific $p\text{CO}_2$ (aq) and atmospheric PCO_2 . The growth-rate-corrected $p\text{CO}_2$ (aq) calculation matches the timing of interglacial PCO_2 maxima in the Vostok atmospheric PCO_2 curve at with local maxima at 0, ~ 130 , and ~ 240 ka [Petit *et al.*, 1999], whereas the uncorrected curve places the stage 5 maximum at ~ 80 ka instead of ~ 130 ka. However, it is difficult to statistically discern which record is more correlated with the Vostok curve and whether the implied air-sea CO_2 disequilibria are meaningful. For curves with 16 ka smoothings which minimizes problems of age correlation, the correlation coefficient of the uncorrected $p\text{CO}_2$ (aq) curve with the Vostok curve ($r=0.60$) is statistically indistinguishable ($p \gg 0.1$) from the correlation coefficient of the corrected curve ($r=0.55$).

[49] In order to fully utilize the potential of coccolith Sr/Ca to produce more reliable records of past $p\text{CO}_2$ (aq) from ε_p , the relationships between coccolith Sr/Ca and growth rate need to be confirmed through a broader survey of coccolith Sr/Ca in core tops and ideally through culture experiments where both coccolith Sr/Ca and ε_p are monitored.

7. Conclusions

[50] 1. Sr/Ca ratios of polyspecific fractions of coccolith carbonate separated from core tops in the equatorial Pacific vary by 15% across the equatorial upwelling front. These variations are much larger than the very limited ($< 2\%$) variations in the Sr/Ca ratio of modern seawater and must reflect variations in Sr partitioning in coccolith calcite. Sr/Ca ratios of coccolith fractions from the equatorial Pacific are much higher and more variable than Sr/Ca ratios of planktonic foraminifera.

[51] 2. Coccolith Sr/Ca covaries with primary productivity near the equator in both the 110°W and 140°W transects studied. In the 140°W transect where data are available, variations in coccolith Sr/Ca are similar to those of alkenone-estimated growth rates of coccolithophorids in overlying surface waters and variations in the CaCO_3 rain rate in deep sediment traps. These relationships suggest that coccolith Sr/Ca in these core tops may depend primarily on coccolithophorid growth and calcification rates, which are commonly linked in coccolithophorids. However, temperature may also influence Sr partitioning in coccoliths, partially attenuating the relationships between coccolith Sr/Ca and coccolithophorid productivity.

[52] 3. In this case, changing species composition was not likely to be the dominant influence on coccolith Sr/Ca. Dissolution strongly modified the composition of the species assemblage and selected for dissolution-resistant species across both transects, resulting in similar sediment assemblages. However, in shallower sediments and those with higher coccolith diversity, changes in coccolith species assemblages may exert a larger influence on coccolith Sr/Ca. In addition, in most of our samples, noncarbonate contributions of Sr and Ca were insignificant. However, samples with a high detrital or hydrothermal content may require additional in-



vestigation of cleaning procedures to yield meaningful data on the Sr/Ca of coccolith carbonate.

[53] 4. The relationships between coccolith Sr/Ca and coccolithophorid growth and calcification rates suggest that coccolith Sr/Ca may be a valuable tool for investigating past changes in coccolithophorid productivity which may provide key data on changes in the carbon and carbonate cycles in the past. One advantage of coccolith Sr/Ca records is that unlike most other paleoproductivity proxies, their application in paleoproductivity studies does not require estimation of sediment accumulation rates, advantageous because accumulation rates are difficult to measure precisely and may be biased by sediment focusing. While coccolith Sr/Ca may provide information only about past variations in coccolithophorid productivity, such information may have important applications both in the determination of past variations in the rain ratio of organic to inorganic carbon [e.g., *Archer and Meier-Reimer*, 1994; *Archer et al.*, 2000] and in improving estimates of past CO₂ (aq) from carbon isotope fractionation in coccolithophorid biomarkers [e.g., *Jasper et al.*, 1994].

[54] 5. Culture studies are needed to confirm the relationships suggested by this study and optimize possible paleoceanographic applications. In cultures the relationships between coccolith Sr/Ca and coccolithophorid calcification and growth rates and the effect of temperature on Sr partitioning can be reliably measured. Sr partitioning can also be investigated in different species.

Acknowledgments

[55] This material is based upon work supported by the North Atlantic Treaty Organization under a Grant awarded in 1998 (DGE-98-04555 to H.M.S.) and by the II Plan Regional de Investigacion del Principado de Asturias (H.M.S.). Critical and insightful readings by

Hanno Kinkel, Jeremy Young, and Patrizia Ziveri greatly improved this manuscript. We thank David Lea and an anonymous reviewer for numerous suggestions. We thank Ricardo Anadon and Rick Murray for useful discussions Markus Geison, and Patrizia Ziveri for useful discussions and assistance with the taxonomy and ecology of coccolithophorids. We appreciate the skillful management of the Harvard ICP-ES provided by Ethan Goddard and acknowledge the Servicio Comun de Estadistica of the University of Oviedo for advice on statistical analyses of time series. Samples were provided by repositories at the University of Rhode Island Graduate School of Oceanography (OCE-9711464) and Oregon State University (OCE-97-12024).

References

- Apitz, S. E., The lithification of ridge flank basal carbonates: Characterization and implications for Sr/Ca and Mg/Ca in marine chalks and limestones, Ph.D. thesis Univ. of Calif., San Diego, 1991.
- Archer, D., and E. Maier-Reimer, Effect of deep-sea sedimentary calcite preservation on atmospheric CO₂ concentration, *Nature*, **367**, 260–263, 1994.
- Archer, D., A. Winguth, D. Lea, and N. Mahowald, What caused the glacial/interglacial pCO₂ cycles?, *Rev. Geophys.*, in press, 2000.
- Balch, W. M. and K. Kilpatrick, Calcification rates in the equatorial Pacific along 140 W, *Deep Sea Res., Part II*, **43**, 971–993, 1996.
- Balch, W. M., J. Fritz, and E. Fernandez, Decoupling of calcification and photosynthesis in the coccolithophorid *Emiliana huxleyi* under steady-state light limited growth, *Mar. Ecol. Prog. Ser.*, **142**, 87–97, 1996.
- Barber, R. T., and F. P. Chavez, Regulation of primary productivity rate in the equatorial Pacific, *Limnol. Oceanogr.*, **36**, 1803–1825, 1991.
- Barber, R. T., J. W. Murray, and J. J. McCarthy, Biogeochemical interactions in the equatorial Pacific, *Ambio*, **23**, 62–66, 1991.
- Beck J. W., R. L. Edwards, E. Ito, F. W. Taylor, J. Recy, F. Rougerie, F. Joannot, and C. Henin, Sea-surface temperature from coral skeletal strontium/calcium ratios, *Science*, **257**, 644–647, 1992.
- Bidigare, R., et al., Consistent fractionation of ¹³C in nature and in the laboratory: Growth-rate effects in some haptophyte algae, *Global Biogeochem. Cycles*, **11**, 279–292, 1997.
- Bollman, J., Morphology and biogeography of Gephyrocapsa coccoliths in Holocene sediments, *Mar. Micropaleontol.*, **29**, 319–350, 1997.
- Broerse, A. T. C., Coccolithophore export production in selected ocean environments: Seasonality, biogeography



- and carbonate production. Ph.D. dissertation, Vrije Univ., Amsterdam, 2000.
- Chavez, F. P., K. R. Buck, and R. T. Barber, Phytoplankton taxa in relation to primary production in the equatorial Pacific, *Deep Sea Res.*, **37**, 1733–1750, 1990.
- Chavez, F. P., K. R. Buck, S. K. Service, J. Newton, and R. T. Barber, Phytoplankton variability in central and eastern tropical Pacific, *Deep Sea Res., Part II*, **43**, 835–870, 1998.
- Cooper, M., H. Elderfield, M. Vautravers, and N. Shackleton, Multi-species investigation of Mg/Ca and Sr/Ca in planktonic foraminiferal calcite, *J. Conf. Abstr.*, **4**(1), 199, 1999.
- Delaney, M. L., and L. J. Linn, Interstitial water and bulk calcite chemistry, Leg 130, and calcite recrystallization, *Proc. Ocean Drill. Program Sci. Results*, **130**, 561–572, 1993.
- DeMaster, D. J., R. H. Pope, O. Ragueneau, and C. R. Smith, Burial rates of biogenic material along the EQ-PAC transect: Holocene variability and paleoflux indicators, *Eos Trans. AGU*, **76**, Ocean Sci. Meet. Suppl., OS187, 1996.
- Deuser, W. G., and E. H. Ross, Seasonally abundant planktonic foraminifera of the Sargasso Sea: Succession, deep-water fluxes, isotopic compositions, and paleoceanographic implications, *J. Foraminiferal Res.*, **19**, 268–293, 1989.
- de Villiers, S., Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans, *Earth Planet. Sci. Lett.*, **171**, 623–634, 1999.
- de Villiers, S., G. T. Shen, and B. K. Nelson, The Sr/Ca temperature relationship in coralline aragonite: Influence of variability in Sr/Ca seawater and skeletal growth parameters, *Geochim. Cosmochim. Acta*, **58**, 197–208, 1994.
- Fabry, V. J., Aragonite production by pteropod mollusks in the subantarctic Pacific, *Deep Sea Res.*, **36**, 1735–1751, 1989.
- Honjo, S., Sedimentation of materials in the Sargasso Sea at a 5,367 m deep station, *J. Mar. Res.*, **36**, 469–492, 1978.
- Honjo, S., and H. Okada, Community structure of coccolithophores in the photic layer of the mid-Pacific, *Micro-paleontology*, **20**, 209–230, 1974.
- Honjo, S., J. Dymond, R. Collier, and S. Manganini, Export production of particles to the interior of the equatorial Pacific Ocean during the 1992 EqPac experiment, *Deep Sea Res.*, **43**, 831–870, 1995.
- Jasper, J. P., J. M. Hayes, A. C. Mix, and F. G. Prahl, Photosynthetic fractionation of ¹³C and concentrations of dissolved CO₂ in the central equatorial Pacific during the last 255,000 years, *Paleoceanography*, **9**, 781–798, 1994.
- Knappertsbusch, M., M. Cortes, and H. Thierstein, Morphologic variability of the coccolithophorid *Calcidiscus leptoporus* in the plankton, surface sediments, and from the Early Pleistocene, *Mar. Micropaleontol.*, **30**, 293–317, 1997.
- LaMontagne, R. W., R. W. Murray, K.-Y. Wei, M. Leinen, and C.-H. Wang, Decoupling of carbonate preservation, carbonate concentration, and biogenic accumulation: A 400-kyr record from the central equatorial Pacific Ocean, *Paleoceanography*, **11**, 553–562, 1996.
- Lea, D. W., T. A. Mashiotta, and H. J. Spero, Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, *Geochim. Cosmochim. Acta*, **63**, 2369–2379, 1999.
- Levitus, S., R. Burgett, and T. Boyer, *World Ocean Atlas 1994, NOAA Atlas NEDIS*, U.S. Dept. of Commer., Washington D.C., 1994.
- Lorens, R. B., Sr, Cd, Mn, and Co distribution coefficients in calcite as a function of calcite precipitation rate, *Geochim. Cosmochim. Acta*, **45**, 553–561, 1981.
- Love, K. M. and A. Woronow, Chemical changes induced in aragonite using treatments for the destruction of organic material, *Chem. Geol.*, **93**, 291–301, 1991.
- Lyle, M., D. W. Murray, B. P. Finney, J. Dymond, J. M. Robbins, and K. Brokksforce, The record of late Pleistocene biogenic sedimentation in the eastern tropical Pacific Ocean, *Paleoceanography*, **3**, 39–59, 1988.
- Martinson, D. G., N. G. Pisias, J. D. Hays, J. Imbrie, T. C. J. Moore, and N. J. Shackleton, Age dating and the orbital theory of the ice ages: Development of a high-resolution 0 to 300,000 year chronostratigraphy, *Quat. Res.*, **27**, 1–29, 1987.
- Mayer, L., et al., *Proceedings of the Ocean Drilling Program, Initial Rep. 138*, Ocean Drill. Program, College Station, Tex., 1992.
- Morse, J. W., and M. L. Bender, Partition coefficients in calcite: Examination of factors influencing the validity of experimental results and their application to natural systems, *Chem. Geol.*, **82**, 265–277, 1990.
- Murray, J. W., R. T. Barber, M. R. Roman, M. P. Bacon, and R. A. Freely, Physical and biological controls on carbon cycling in the equatorial Pacific, *Science*, **266**, 58–65, 1994.
- Murray, R. W., and M. Leinen, Scavenged excess aluminum and its relationship to bulk titanium in biogenic sediment from the central equatorial Pacific Ocean, *Geochim. Cosmochim. Acta*, **60**, 3869–3878, 1996.
- Murray, R. W., M. Leinen, D. W. Murray, A. C. Mix, and C. W. Knowlton, Terrigenous Fe input and biogenic sedimentation in the glacial and interglacial equatorial Pacific Ocean, *Global Biogeochem. Cycles*, **9**, 667–684, 1995.
- Nimer, N. A., and M. J. Merrett, Calcification rate in



- Emiliania huxleyi Lohmann in response to light, nitrate, and availability of inorganic carbon, *New Phytol.*, **123**, 673–677, 1993.
- Nurnberg, D., J. Buma, and C. Hemleben, Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. Cosmochim. Acta*, **60**, 803–814, 1996.
- Pagani, M., K. H. Freeman, and M. A. Arthur, Late Miocene atmospheric CO₂ concentrations and the expansion of C₄ grasses, *Science*, **285**, 876–879, 1999.
- Paull, C. K., S. J. Hills, and H. R. Thierstein, Progressive dissolution of fine carbonate particles in pelagic sediments, *Mar. Geol.*, **81**, 27–40, 1988.
- Paytan, A., M. Kastner, and F. P. Chavez, Glacial to interglacial fluctuations in productivity in the equatorial Pacific as indicated by marine barite, *Science*, **274**, 1355–1357, 1996.
- Petit, J. R., et al., Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature*, **399**, 429–436, 1999.
- Pingitore, N. E., S. B. Fretzdorf, B. Seitz, L. Estrada, P. Borrego, G. Crawford, and K. Love, Dissolution kinetics of CaCO₃ in common laboratory solvents, *J. Sed. Petrol.*, **63**, 641–645, 1993.
- Popp, B. N., E. A. Laws, R. R. Bidigare, J. E. Dore, K. L. Hanson, and S. G. Wakeham, Effect of phytoplankton cell geometry on carbon isotopic fractionation, *Geochim. Cosmochim. Acta*, **62**, 69–77, 1998.
- Pujos, A., Nannofossils from Quaternary deposits in the high-productivity area of the central equatorial Pacific, Deep Sea Drilling Project Leg 85, in *Proceedings of the DSDP Scientific Results Leg. 85*, edited by L. Mayer et al., pp. 553±579, U.S. Govt. Print. Off., Washington, D.C., 1985.
- Roth, P. H., Distribution of coccoliths in oceanic sediments, in *Coccolithophorids*, edited by A. Winter and W. G. Siesser, pp. 199–218, Cambridge Univ. Press, New York, 1994.
- Schrag, D. P., Rapid analysis of high precision Sr/Ca ratios in corals and other marine carbonates, *Paleoceanography*, **14**, 97–102, 1999.
- Spero, H. J., J. Bijma, D. W. Lea, and B. Bemis, Effect of seawater carbonate chemistry on planktonic foraminiferal carbon and oxygen isotope values, *Nature*, **390**, 497–500, 1997.
- Stoecker, D. K., D. E. Gustafson, and P. G. Verity, Micro- and mesoprotozooplankton at 140 degrees W in the equatorial Pacific: Heterotrophs and mixotrophs, *Aquat. Microbial Ecol.*, **10**, 273–282, 1996.
- Stoll, H. M., and D. P. Schrag, Effects of Quaternary sea level changes on strontium in seawater, *Geochim. Cosmochim. Acta*, **62**, 1107–1118, 1998.
- Stoll, H. M., and D. P. Schrag, Coccolith Sr/Ca as an indicator of marine paleoproductivity, *J. Conf. Abstr.*, **4**(1), 206, 1999.
- Stoll, H. M., D. P. Schrag, and S. C. Clemens, Are seawater Sr/Ca variations preserved in Quaternary foraminifera?, *Geochim. Cosmochim. Acta*, **63**, 3535–3547, 1999.
- Takahashi, T., et al., Global air-sea flux of CO₂: An estimate based on measurement of sea-air pCO₂ difference, *Proc. Natl. Acad. Sci. U.S.A.*, **94**, 8299–8929, 1997.
- Tesoriero, A. J., and J. F. Pankow, Solid solution partitioning of Sr²⁺, Ba²⁺, and Cd²⁺ to calcite, *Geochim. Cosmochim. Acta*, **60**, 1053–1063, 1996.
- Watson, E. B., Surface enrichment and trace-element uptake during crystal growth, *Geochim. Cosmochim. Acta*, **60**, 5013–5020, 1996.
- Westbroek, P., et al., A model system approach to biological climate forcing: The example of *Emiliania huxleyi*, *Global Planet. Change*, **8**, 27–46, 1993.
- Young, J. R., Functions of coccoliths, in *Coccolithophorids*, edited by A. Winter and W. Siesser, pp. 63–82, Cambridge Univ. Press, New York, 1994.
- Young, J. R., J. M. Didymus, P. R. Bown, B. Prins, and S. Mann, Crystal assembly and phylogenetic evolution in heterococcoliths, *Nature*, **356**, 516–518, 1992.
- Young, J. R., and P. Ziveri, Calculation of coccolith volume and its use in calibration of carbonate flux estimates, *Deep Sea Res.*, in press, 2000.
- Ziveri, P., and R. C. Thunnell, Coccolithophore export production in Guaymas Basin, Gulf of California: Response to climate forcing, *Deep Sea Res., Part II*, in press, 2000.
- Ziveri, P., R. C. Thunnell, and D. Rio, Seasonal changes in coccolithophore densities in the Southern California Bight during 1991–1992 El Niño Event. *Deep Sea Res., Part I*, **42**, 1881–1903, 1995a.
- Ziveri, P., R. C. Thunnell, and E. Rio, Export production of coccolithophores in an upwelling region: Results from San Pedro Basin, Southern California Bight, *Mar. Micropaleontol.*, **24**, 335–358, 1995b.