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Insights on coccolith chemistry from a new ion probe method for analysis of individually picked coccoliths

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[1] The elemental chemistry of calcareous nannofossils may provide valuable information on past ocean conditions and coccolithophorid physiology, but artifacts from noncoccolith particles and from changing nannofossil assemblages may bias geochemical records from coccolith size fractions. We describe the first method for picking individual coccoliths using a tungsten needle in micromanipulator. Epoxy-mounted individuals and populations of coccoliths can be analyzed by secondary ion mass spectrometry (SIMS). For Paleocene sediments the technique distinguishes the high Sr/Ca ratios of coccoliths (0.3 to 2.8 mmol/mol) from low ratios in abiogenic calcite blades (0.1 mmol/mol). The large heterogeneity of Sr/Ca ratios among different genera suggests that primary geochemical differences have not been homogenized by diagenetic overgrowth and the thick massive coccoliths of the late Paleocene are a primary feature of biomineralization. Sr/Ca ratios for modern genera are on average higher than those of Paleogene genera but exhibit a comparable level of variability.

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1. Introduction

[2] There is emerging interest in measuring coccolith elemental chemistry since coccolith Sr/Ca ratios may reflect productivity of coccolithophorid algae [*Rickaby et al.*, 2002; *Stoll et al.*, 2002a, 2002b, 2007a; *Stoll and Schrag*, 2000]. To date, in natural material, coccolith Sr/Ca ratio has been

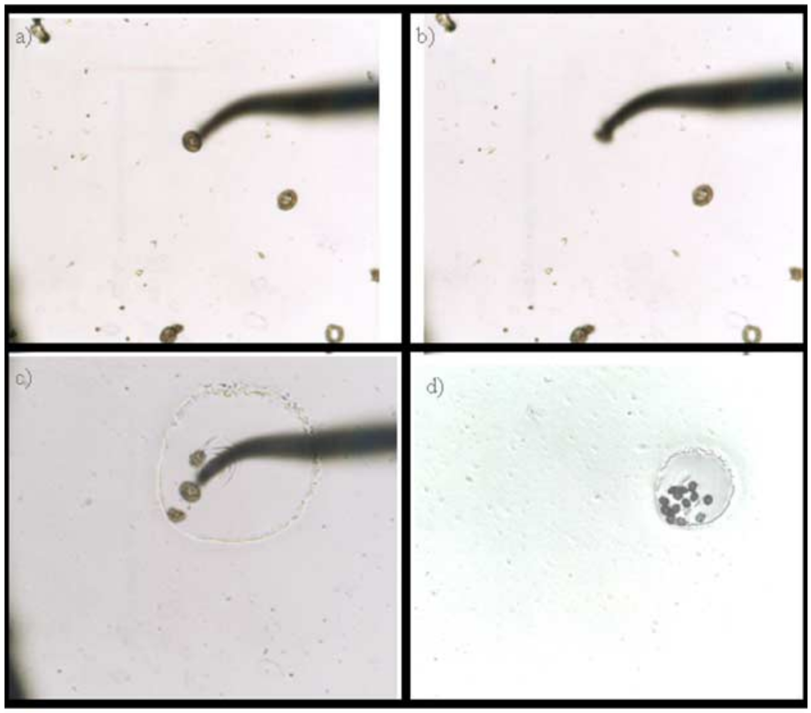

Figure 1. Schematic of picking sequence using the inverted microscope with transmitted light. (a) Tungsten needle approaches the desired coccolith, a late Paleocene *Chiasmolithus.* (b) The coccolith has been picked up by the tungsten needle. (c) The coccolith is deposited in the Tacky Dot well. (d) Population of picked coccoliths. Diameter of Tacky Dot is 75 μm.

analyzed either on coccolith-dominated bulk carbonate [*Stoll and Schrag*, 2001; *Billups et al.*, 2004], a coccolith fraction like <12 or <20μm [*Rickaby et al.*, 2007; *Stoll and Schrag*, 2000], or size separated coccolith fractions [*Stoll and Bains*, 2003; *Stoll and Ziveri*, 2002]. This contrasts with the standard approach for foraminifera, in which individuals are picked from a given species for geochemical analysis. Here we describe a new approach for analyzing coccolith elemental chemistry which allows picking of individual coccoliths and their elemental analysis by secondary ion mass spectrometry (SIMS) ion probe methods. Ion probe techniques have been successfully applied to other biogenic carbonates like corals and foraminifera [*Allison and Austin*, 2003; *Hart and Cohen*, 1996]. For analysis of coccoliths, this method has several advantages. (1) It permits analysis of selected, well preserved individuals from a single species. (2) It allows separation of coccoliths from other similarly sized, diagenetic or detrital carbonate particles. (3) It permits analysis of coccoliths where material is too limited or diversity too high to permit any conventional coccolith species separation as is the case for many sediment traps. Application of this method to Paleocene sediments and modern sediment traps has elucidated the primary coccolith geochemical signals.

2. Ion Probe Method

2.1. Picking and Mounting Coccoliths

[3] Individual microfossils are picked using a tungsten needle mounted in a micromanipulator. A dilute suspension of the sediment in ethanol is pipetted onto a glass slide and smeared across the slide with the pipet tip. Nannofossil coverage on the smear slide must be sparse enough that distance between nannofossils is approximately twice the length of the nannofossils. The slide is then placed under an inverted microscope (Nikon Diaphot 300) with x−y moveable stage and a Narishige micromanipulator (250 μm for 360° rotation). A tungsten needle, sharpened with a sodium nitrite stick in an alcohol flame, is mounted in the micromanipulator and centered. The microscope stage is then moved to center the desired coccolith under the crosshairs, and the tungsten needle is lowered to gently touch and pick up the coccolith (Figure 1). The tungsten needle is then raised, the sediment slide is removed

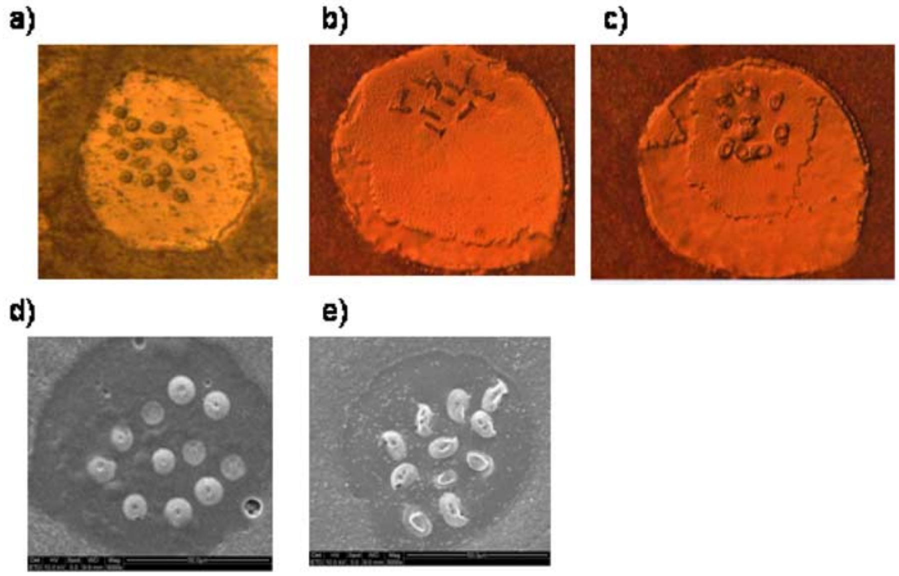

Figure 2. Images of picked assemblages (a–c) under reflected light after gold coating and (d and e) under scanning electron microscope. (a) Late Paleocene *Toweius*, (b) modern *Rhabdosphaera claviger*, (c) modern *Helicosphaera carteri*, (e) modern *Calcidiscus leptoporus*, and (f) modern *Helicosphaera carteri*. Diameter of Tacky Dot is 75 μm for Figures 2a–2c and 50 μm for Figures 2d and 2e.

and a Tacky Dot (SPI Corp.) slide is placed under the microscope. The tungsten needle is then lowered to deposit the coccolith into a selected Tacky Dot well. The process is repeated until a population of 12–20 coccoliths is assembled in a single Tacky Dot, with coccoliths packed as closely as possible (Figure 2). Although picking must be completed under transmitted light to see the tungsten needle, the polarizer can be inserted to verify nannofossil identifications. When the desired coccolith genera is abundant in the field of view, and the tungsten needle is adequately sharp, a population of 15 coccoliths can usually be picked in 30–60 minutes. Small and fragile coccoliths like *Emiliania huxleyi* require longer picking time because these fragile forms often break on contact with the tungsten needle. The large Paleocene nannofossils, and certain large modern coccoliths like *Helicosphaera,* are comparatively easy to pick.

[4] When picking is complete, epoxy (Buehler Epoxide) is poured into an aluminum mount on the Tacky Dot slide. When epoxy has cured the Tacky Dot slide is removed from the epoxy using ethanol to dissolve the Tacky Dot polymer coating. Samples are further exposed by abrasion on an ethanol-wetted felt pad. Further confirmation of nannofossil identification can be completed by imaging of the exposed coccoliths using scanning electron microscopy. Samples are gold coated for SIMS analysis to reduce charging.

2.2. Ion Probe Sr/Ca Analysis

[5] Sr/Ca ratios were measured on a Cameca IMS3f secondary ion mass spectrometer at the Northeast National Ion Microprobe Facility at Woods Hole. The SIMS analytical method used here is based on previous studies of trace elements in marine carbonates [*Hart and Cohen*, 1996]. A beam of negatively charged oxygen ions with a current of 2 nA was focused to 20μm beam and rastered across a 50μm square area. With a less intense beam focused to 5μm it is also possible to measure Sr/Ca ratios on individual coccoliths. However, we are interested in changes in the mean Sr/Ca ratio of coccolith populations, and not the interspecimen variability in Sr/Ca ratios, so it is more efficient to measure aggregate Sr/Ca ratios of populations by rastering. An energy offset of −90 v was used for suppressing interferences of molecular ions. We use a standard reference calcite from the Oka carbonatite complex, Quebec (OKA-C). The standard is run multiple times using the same analytical protocol as the samples at the onset of each daily session, and these values are used to calibrate for differential ionization efficiency of different elements. In 12 sessions over a two year period the measured 88/40 ratios of the OKA-C

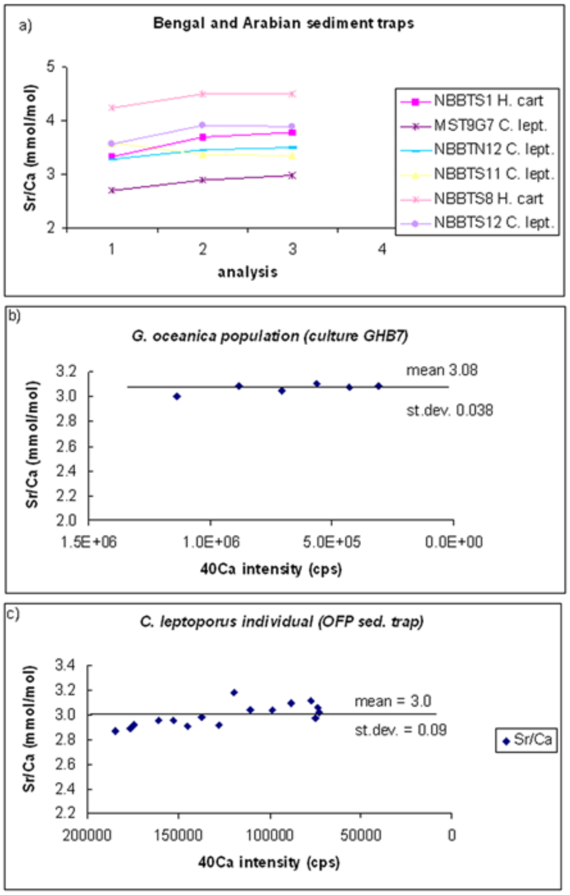

Figure 3. Sr/Ca ratios (all mmol/mol) of (a) typical analyses of coccoliths from sediment traps showing lower Sr/Ca in first analysis, (b) population of *Gephyrocapsa oceanica* from culture subjected to continuous rastering over 40 minutes, and (c) an individual *Calcidiscus leptoporus* from Ocean Flux Program (OFP) sediment traps subjected to continuous ablation by a focused beam for 2 hours.

standard had a relative standard deviation of 1.7% (1σ).

[6] Data were collected in three consecutive analyses of five cyclic scans of the magnetic field covering ^{24}Mg to ^{88}Sr, with typical counting errors of 1% or better for ^{88}Sr. For each cycle, we measure background at mass 23.5 for 10 seconds, at ^{24}Mg 10 seconds, ^{40}Ca 5 seconds, and ^{88}Sr 10 seconds, for a total cycle time of 35 seconds. Thus each analysis requires approximately three minutes for total data collection of 9 minutes. For samples, we rastered for several minutes prior to collecting data until the Ca intensity reached a plateau (“pre-data burn”). The mounted coccoliths are discrete particles which may be at slightly differing heights between and within samples and require a variable amount of pre-data burn time for exposing the sample and attaining a stable plasma. Consequently, it is not always possible to know when optimal stable conditions are reached for data collection for a given sample except by running successive analyses and evaluating reproducibility. In many cases in the first analysis, Sr/Ca ratios average 8% lower than for subsequent analyses which likely results from incomplete beam stabilization, or possibly a small degree of sample heterogeneity. In this case we discard this first low Sr/Ca analysis and collect data in at least two successive analyses in which Sr/Ca ratios typically vary by about 2% (Figure 3a). If in the first and second analyses Sr/Ca ratios agree within 3% we collect only these two analyses. For most analyses of modern and Paleocene coccoliths, except for the very small coccoliths of *E. huxleyi*, Ca intensity changes by less than 20%, usually less than 10%, over the course of the 2–3 successive analyses used for data collection. With continued rastering, we observe minimal change in Sr/Ca ratios of populations (range of 3.6%, relative standard deviation of 1%) even as Ca intensity falls by a factor of 3–4 (Figure 3b). Very long duration (2 hour) successive analysis of a single individual among the population, with a more focused and less intense beam, show only small variations in Sr/Ca ratios which may in part reflect charging effects (Figure 3c) which would not be encountered in a routine analysis. The intensity of counts in the epoxy mounting resin is less than 0.2% of the typical intensities for coccolith samples both for ^{88}Sr and ^{40}Ca.

[7] Sr/Ca ratios measured by ion probe on a population of *Helicosphaera carteri* grown in culture agreed to within 2% of the ratios measured on the culture sample by ICP-AES. The variation of Sr/Ca on replicate picked populations of coccoliths analyzed months apart constrains the reproducibility. This variability may reflect interspecimen heterogeneity and any analytical artifacts not corrected for with the standardization technique. Analyses of replicate populations of *Chiasmolithus* and *Toweius* coccoliths from the same sample picked and analyzed several months apart yield Sr/Ca ratios which differ by 8% and 1%, respectively. Analyses of replicate populations of 15 individuals of *Zygrhablithus* analyzed the same day yield Sr/Ca ratios which differ by 4%. For *Zygrhablithus* we also examined 8 sub-populations each containing 3–4 liths; as expected the variability was slightly higher, with a relative standard deviation of 9%. These results reaffirm the advantage of

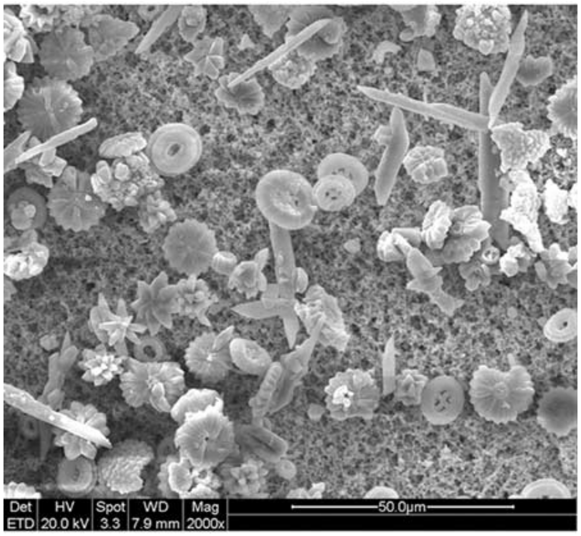

Figure 4. SEM image of 8–12 μm size fraction from ODP 1209 showing abiogenic calcite blades and nannofossils, including abundant *Discoasters*.

analyzing a modest population of individuals (e.g., 12–15 for coccoliths) as is standard practice in elemental or stable isotopic analysis of foraminifera.

3. Examples

3.1. Distinguishing Abiogenic and Coccolith Signals in Latest Paleocene Sediments

[8] Sediments at Ocean Drilling Program (ODP) Site 1209 contain a record of the Paleocene Eocene Thermal Maximum (PETM) from the tropical Pacific. Sediments containing the PETM contain abundant carbonate blades in the coccolith size range. Fourier Transform Infrared (FTIR) microscopy confirms that these blades are calcite and they are presumed of abiogenic origin. Because the abiogenic calcite blades are present in the same size fraction as the calcareous nannofossils, they cannot be physically separated from the nannofossil fractions through microfiltering and differential settling techniques as employed in previous sediments [*Stoll and Bains*, 2003] (Figure 4). Since equilibrium partitioning of Sr in abiogenic carbonate is an order of magnitude lower than in modern coccoliths and foraminifera [*Lorens*, 1981; *Tesoriero and Pankow*, 1996], these abiogenic particles can significantly affect the geochemical records. Indeed the Sr/Ca ratio of coccolith size fractions drops significantly over the PETM coinciding with the interval in which abiogenic calcite blades become abundant (Figure 5a). Although there are uncertainties in estimating the mass of the blades due to their variable thickness, counts of nannofossil and abiogenic components in size separated fractions indicate that up to 30% of the carbonate mass may arise from the abiogenic particles which could cause most or all of the observed drop in Sr/Ca in coccolith fractions.

[9] Ion probe data for individually picked nannofossils separated from these sediments show a range of Sr/Ca ratios which is much greater than the contrast observed among the size fractions (Figure 5b), probably because the size fractions each mix numerous species (Figure 6). Sr/Ca of all nannofossils is higher than that of the abiogenic blades. The genera with largest surface area/volume ratio, placoliths *Toweius* and *Chiasmolithus*, exhibit the highest Sr/Ca ratios, suggesting that the different Sr/Ca ratios among different genera are not due to differing proportions of overgrowth by low Sr calcite.

[10] Comparison of ion probe and size fraction data suggest that the Sr/Ca trends in the 5–8 μm size fraction are driven primarily by changes in the abundance of abiogenic calcite blades (Figure 5). Sr/Ca ratios of the most abundant coccoliths, *Coccolithus* and *Toweius,* decrease at the PETM onset, but in several aspects their trends are distinct from that of the abiogenic calcite-bearing 5–8 μm size fraction in which these genera occur. Sr/Ca of *Coccolithus* and *Toweius* decreases by 197.24 meters below seafloor (mbsf) and does not decrease further at 197.10 mbsf. In contrast the major decrease in Sr/Ca of the 5–8 μm size fraction does not occur until 197.10 mbsf where abiogenic blades become most abundant. The drop in Sr/Ca of the 5–8 μm size fraction is unique in the duration of the record here, whereas the variation in *Coccolithus* is not. *Discoaster multiradiatus* shows minimal change in Sr/Ca ratios through the PETM, whereas *Zygrhablithus* shows a major peak in the early part of the event; neither of these could contribute to the dramatic drop in Sr/Ca in the 5–8 μm size fraction. The significance of temporal Sr/Ca variations in the coccolith populations analyzed by the ion probe technique is discussed elsewhere [*Stoll et al.*, 2007b].

[11] If the abiogenic blades represent calcite produced under near-equilibrium conditions, then their Sr/Ca ratio might be used to infer seawater Sr/Ca ratios for the latest Paleocene. Assuming an equilibrium partitioning coefficient of 0.03 [*Lorens*, 1981; *Tesoriero and Pankow*, 1996], the measured ratio of 0.13 mmol/mol suggests seawater Sr/Ca ratios of 4.3 mmol/mol, about half the current

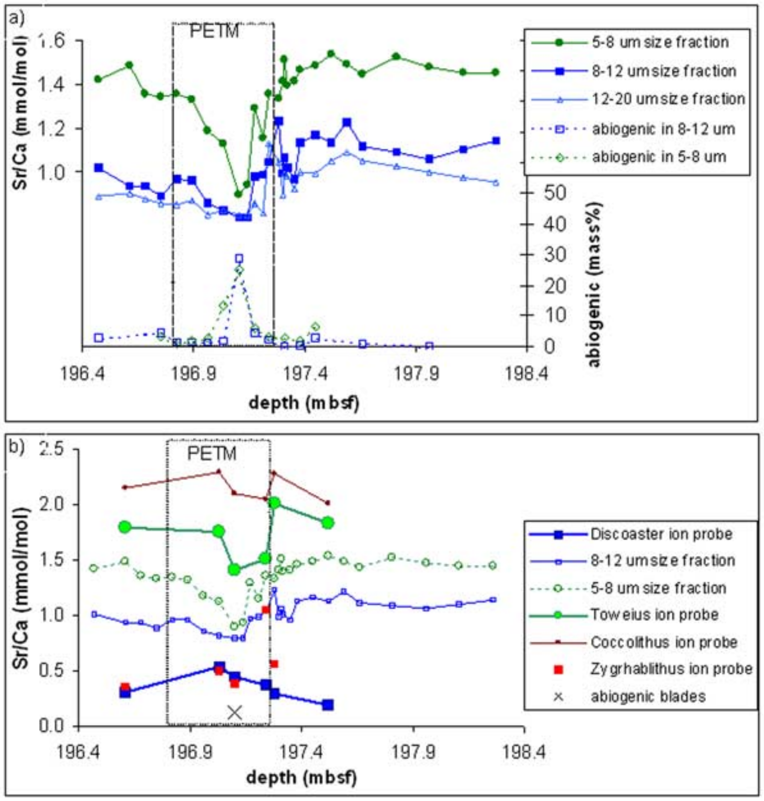

Figure 5. (a) Sr/Ca results for three size fractions from Ocean Drilling Program (ODP) 1209 (solid symbols) compared with calculations of the mass percent of calcite contributed by abiogenic blades for the 5–8 and 8–12 μm size fractions (open symbols), plotted versus depth in core (mbsf, meters below seafloor). The two dashed lines show the interval corresponding to the PETM. Mass contributions of nannofossils and abiogenic blades are calculated from census counts using nannofossil weights as calculated by *Stoll* [2005]. (b) Sr/Ca analysis determined by SIMS ion probe (solid symbols) compared with Sr/Ca on size fractions (open symbols) for ODP 1209.

value. This contrasts with seawater Sr/Ca estimates from benthic foraminiferal Sr/Ca which infer near present values for the latest Paleocene [*Lear et al.*, 2003]. Either Sr partitioning coefficients <0.03 characterized the precipitation of the abiogenic calcite blades, or Sr partitioning coefficients in benthic foraminifera were different in the Paleocene compared to modern. If abiogenic calcites were precipitated at fast growth rates, with higher partitioning coefficients [*Gabitov and Watson*, 2006], they imply even lower seawater Sr/Ca ratios for the Paleocene.

3.2. Comparing Sr/Ca in Modern and Paleocene Coccoliths

[12] Sr/Ca ratios in coccoliths from sediment traps and recent sediments show higher average Sr/Ca ratios than Paleocene genera, but comparable degree of variability in the Sr/Ca ratio of a given species under different conditions (Figure 7). A single modern *Thoracosphaera* had a Sr/Ca ratio twice that of the Paleocene *Thoracosphaera*. If Sr partitioning were constant in this genera over time, and the single individuals measured are representative, then this result could be consistent with

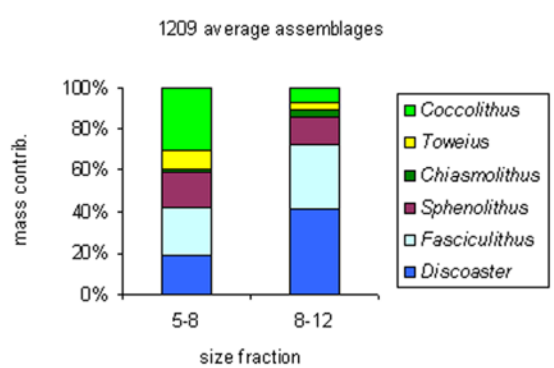

Figure 6. Average calcite contribution by different nannofossil genera in the 5–8 and 8–12 μm size fractions. Mass contributions of nannofossils are calculated from census counts using nannofossil weights as calculated by *Stoll* [2005].

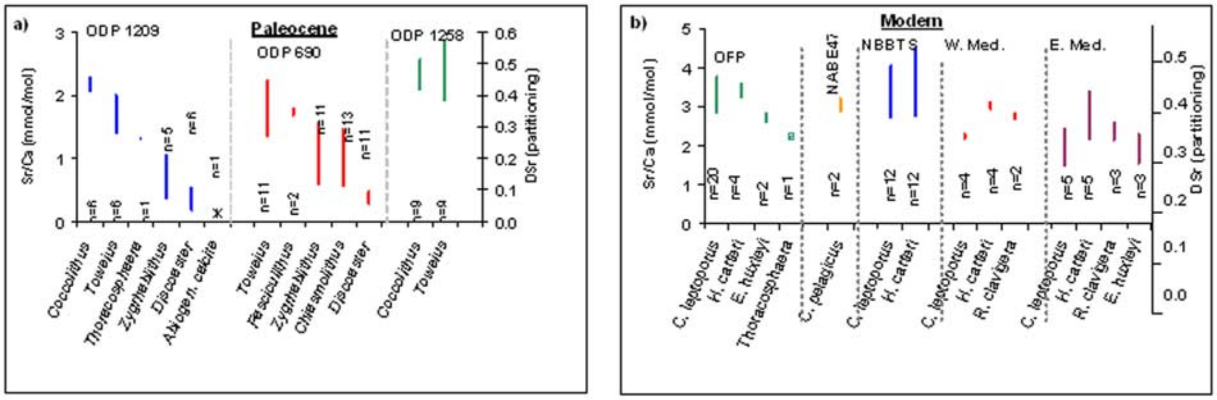

Figure 7. (a) Range of Sr/Ca ratios among different species of Latest Paleocene nannofossils compared with (b) range of Sr/Ca ratios among different species of modern nannofossils. Paleocene data from multiple sites summarized from *Stoll et al.* [2007b] and new data here. OFP, OFP sediment trap in Sargasso Sea, 2004 series. NABE47 traps from North Atlantic Bloom Experiment station (47°N 21°W). NBBTS, Bay of Bengal sediment trap in northern bay (15.5°N, 89.5°E), 1994 annual series. Early Holocene and modern coccoliths from 274G in western Mediterranean (37°16′N, 3°W), and BC07 (33°37′N, 24°2′E) eastern Mediterranean.

Paleocene seawater Sr/Ca ratios being lower by a factor of two. In contrast, modern *Coccolithus pelagicus* have Sr/Ca only slightly higher than Paleocene *Coccolithus pelagicus*.

[13] The origin of different absolute ratios in modern or ancient species is not known [*Stoll and Ziveri*, 2004]. Still, the preservation of large heterogeneity in Sr/Ca ratios among different Paleocene genera provides strong support that the Sr/Ca ratios are primary rather than diagenetic (Figure 7). Significant overgrowth of nannofossils by diagenetic calcite would reduce or eliminate the geochemical differences among different genera. The differences in Sr/Ca ratios among different Paleocene nannofossil genera appear to reflect primary differences in biomineralization processes. These differences are consistent among several locations [*Stoll et al.*, 2007b] (Figure 7).

[14] Paleocene nannofossils are thicker than their modern counterparts. For example, typical Paleocene 5 μm placolith *Toweius* has estimated mass of 47 pg/coccolith [*Stoll*, 2005]. In contrast, typical 5 μm placolith *Gephyrocapsa oceanica* has estimated mass of 17 pg/coccolith [*Young and Ziveri*, 2000]. The ion probe data demonstrate that the Paleocene forms represent primary calcite and their greater thickness cannot be due to diagenetic overgrowth. Hence the thickness of Paleocene nannofossils is a primary feature of Paleocene biomineralization. While culture experiments suggest that low pH and high CO_2 produce thinner coccoliths in some placolith species [*Riebesell et al.*, 2000], other factors such as high alkalinity must have driven a high level of calcification in the late Paleocene despite the inferred low seawater pH and high atmospheric CO_2 [*Pagani et al.*, 2005; *Pearson and Palmer*, 2000]. Some models suggest higher surface ocean carbonate saturation in the Paleocene compared to modern [*Ridgwell*, 2005] which may contribute to the thicker coccoliths.

4. Summary

[15] We have developed a technique to pick individual coccoliths for analysis of Sr/Ca using SIMS ion probe. The technique has precision and accuracy sufficient for distinguishing variations in mean Sr/Ca ratios of coccolith populations both among different genera and in a given genera through time. Sr/Ca distributions in coccoliths appear significantly homogeneous to permit precise determinations of mean Sr/Ca ratios of coccolith populations.

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