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## DIAGENESIS OF LOWER CRETACEOUS PELAGIC CARBONATES, NORTH ATLANTIC: PALEOCEANOGRAPHIC SIGNALS OBSCURED

TRACY D. FRANK<sup>1</sup>, MICHAEL A. ARTHUR<sup>2</sup>, AND WALTER E. DEAN<sup>3</sup>

### ABSTRACT

The stable isotope and minor element geochemistry of Neocomian (Lower Cretaceous) pelagic carbonates of the North Atlantic Basin (Deep Sea Drilling Project Sites 105, 367, 387, 391, and 603) was examined to develop a diagenetic model for pelagic limestones. In particular, we hoped to test the fidelity of whole-rock geochemical records as paleoceanographic indicators for pelagic deposits of pre-Aptian age, in which individual microfossils are not available for analysis. Data indicate that in addition to depth of burial, rhythmic variations in primary carbonate content have strongly controlled diagenetic patterns and associated geochemical signatures in these Neocomian sequences. Samples become increasingly depleted in Sr and <sup>18</sup>O with increasing CaCO<sub>3</sub> content. Within individual sedimentary sections, substantial decreases in Sr/Ca ratios and δ<sup>18</sup>O values are evident over a range of 4 to 98% CaCO<sub>3</sub>. However, even over a relatively narrow range of 50 to 98% CaCO<sub>3</sub>, a 2.5‰ variation in δ<sup>18</sup>O values and a change of a factor of 1.7 in Sr/Ca ratios are observed. Carbon isotope compositions do not vary as extensively with CaCO<sub>3</sub> content, but carbonate-rich intervals tend to be relatively depleted in <sup>13</sup>C. Petrographic analysis reveals that these geochemical patterns are related to the transfer of CaCO<sub>3</sub> from carbonate-poor intervals (calcareous shales and marlstones) to adjacent carbonate-rich intervals (limestones) during burial compaction and pressure solution. This process results in the addition of diagenetic cement to carbonate-rich intervals to produce a bulk composition that is relatively depleted in Sr and <sup>18</sup>O and, at the same time, enables the retention of more-or-less primary carbonate that is relatively enriched in Sr and <sup>18</sup>O in adjacent carbonate-poor intervals. Thus, although cyclic variations in CaCO<sub>3</sub> content are primary in the Neocomian sequences examined, measured variations in Sr/Ca ratios and δ<sup>18</sup>O values are not and, as such, do not provide reliable proxies for past variations in climate, oceanographic conditions, or global ice volume.

### INTRODUCTION

Pelagic carbonate sequences have major potential as integrators of global chemical and climate signals. For paleoceanographers, a major objective is to understand and interpret these signals. Unfortunately, whole-rock geochemical signatures derived from deep-sea sediments can be variably affected by recrystallization and burial diagenesis, variations in vital effects, and local partitioning among ma-

rine geochemical reservoirs. Thus, paleoceanographic interpretations based on geochemical proxies are typically determined from analyses of well-preserved, monospecific planktonic and benthic foraminifera. In deep-sea sequences older than the Aptian, however, planktonic foraminifera (and other faunal components suitable for such geochemical analyses) are extremely small and usually altered. Geochemically based paleoceanographic reconstructions for these time intervals must therefore rely upon records derived from the analysis of whole-rock samples. Previous workers have suggested that burial diagenetic effects on the oxygen isotope compositions of bulk pelagic carbonate can be quantified, such that δ<sup>18</sup>O records can be corrected for diagenetic overprints (Schrag and others, 1992, 1995). On the basis of such models, it has been suggested that fluctuations in whole-rock δ<sup>18</sup>O and Sr records derived from Neocomian pelagic sequences in the North Atlantic reflect changes in global ice volume (Stoll and Schrag, 1996). This interpretation contradicts the long-held notion that the Cretaceous climate was too warm for extensive buildup of continental ice (e.g., Barron and others, 1985).

The goal of the present study is to test the accuracy of whole-rock geochemical records from Neocomian pelagic sedimentary sequences of the North Atlantic as paleoceanographic indicators. Rather than generating continuous geochemical records from individual sites, we focus in detail on short sedimentary intervals recovered at Deep Sea Drilling Project (DSDP) Sites 105, 387, 391, and 603 in the western basin and Site 367 in the eastern basin of the North Atlantic (Fig. 1). Sampled intervals have undergone variable amounts of burial and exhibit a range of carbonate contents (Fig. 2). This sampling strategy allowed us to evaluate the impacts of carbonate content and burial depth on geochemical signatures derived from whole-rock analyses of these sequences.

### GEOLOGIC SETTING

Neocomian pelagic carbonate sequences of the North Atlantic are characterized by cyclic interbeds of laminated, dark-olive to black marlstone and laminated to bioturbated, light-gray to white limestone (Fig. 3). The stratigraphic unit comprising these rocks has been called the Blake-Bahama Formation by Jansa and others (1979), and is equivalent to the upper Tithonian to Aptian Maiolica (or Biancone) Formation of Garrison (1967) that crops out in the Tethyan regions of the Mediterranean (Bernoulli, 1972; Jansa and others, 1979), to thick limestone sequences of the Vocontian Trough in France (e.g., Cotillon, 1984), and to sediments recovered at DSDP Site 535 in the Gulf of Mexico (Buffer and others, 1984; Cotillon and Rio, 1984). This lithologic unit represents the widespread deposition of biogenic carbonate over much of the deeper North Atlantic and Tethyan seafloor during a time of overall low sea level and a deep carbonate compensation depth (CCD; e.g., Tucholke and

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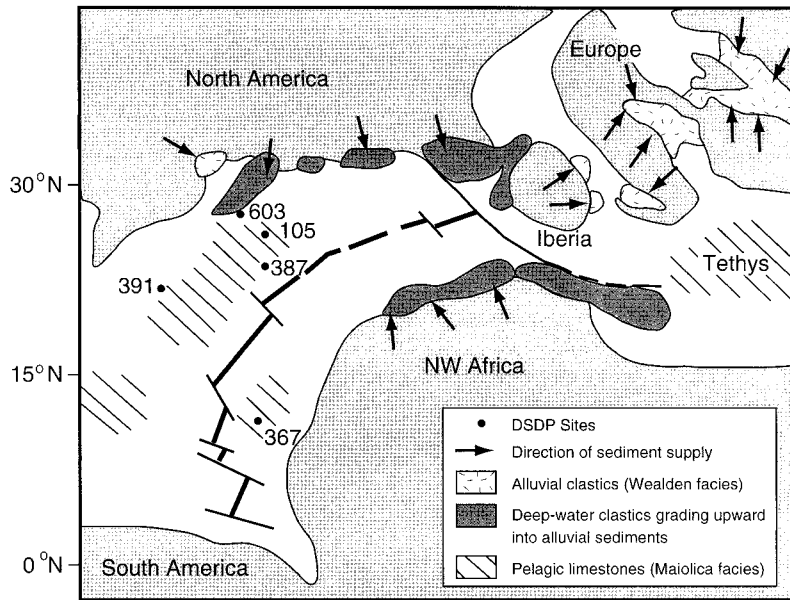


FIGURE 1. Neocomian paleogeographic reconstruction of the North Atlantic basin showing sediment sources and locations of DSDP sites examined (after Dean and Arthur, 1999).

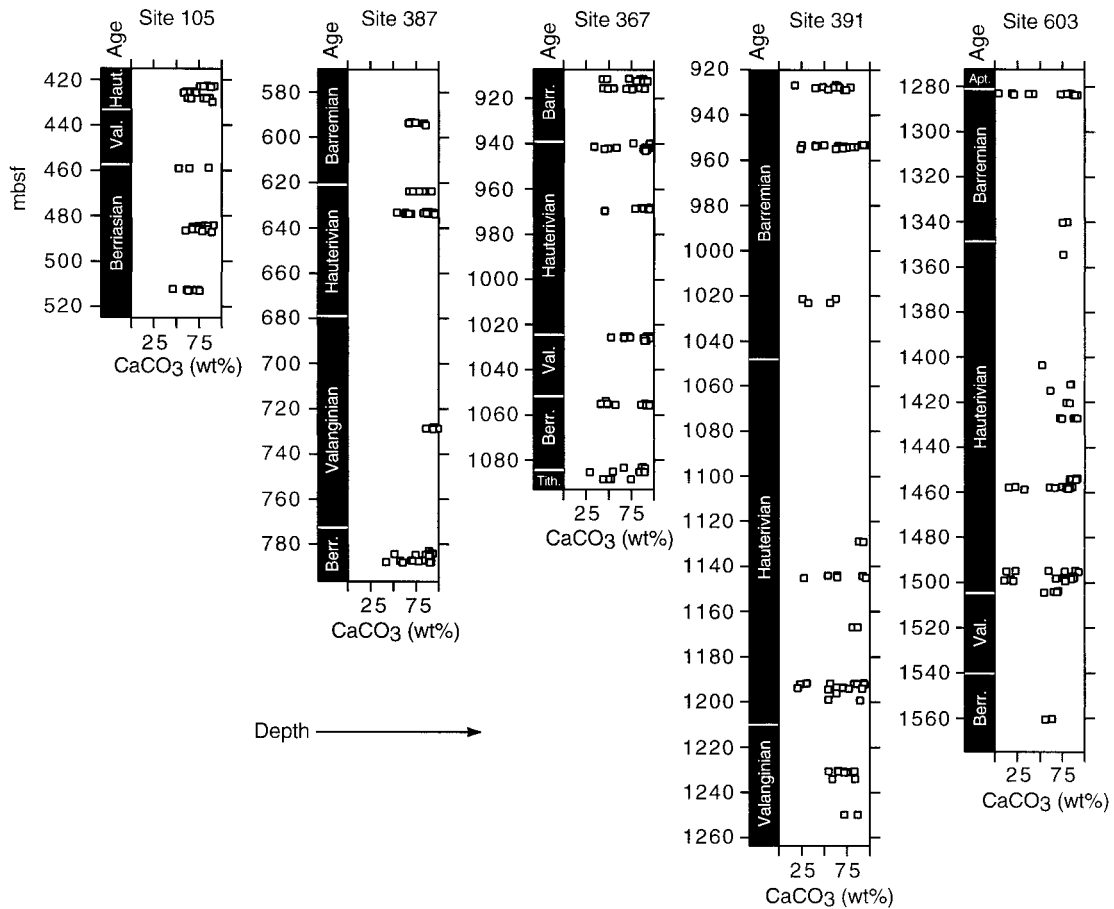


FIGURE 2. Site and depth distribution versus CaCO<sub>3</sub> content of samples examined in the present study. Reported depths of stage boundaries are based on biostratigraphic information provided in DSDP reports.

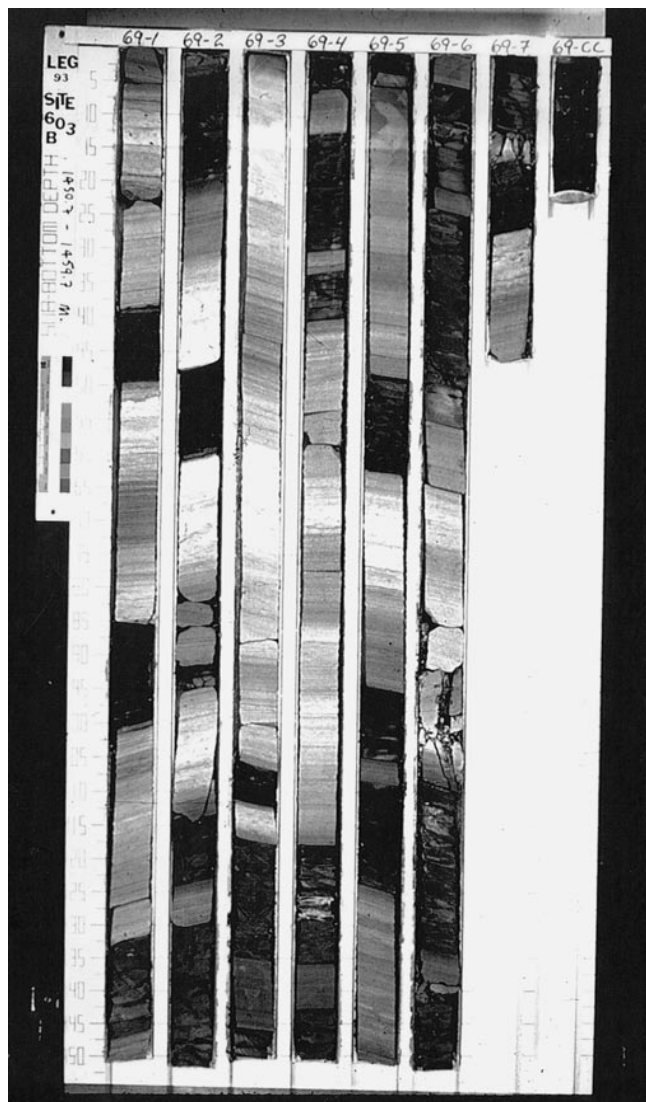


FIGURE 3. Photograph of Deep Sea Drilling Project Core 93-603B-69 illustrating the cyclic nature of the Blake-Bahama Formation in the North Atlantic basin. Scale on the left side of the photograph is in cm. Numbers across the top of the photograph refer to sections; top of core is at upper left (Section 69-1), base of core is at right (Section 69-CC). Sub-bottom depth is 1450.7-1459.7 m; age of core is Hauterivian.

Vogt, 1979; Thierstein, 1979; Dean and Arthur, 1986). The widely developed cyclicality of bioturbated and laminated pelagic sediments of Neocomian age has intrigued many workers (Dean and others, 1978; Weissert and others, 1979; Cotillon, 1984; Arthur and others, 1984; Cotillon and Rio, 1984; Herbert, 93) because the estimated 20–50 ky duration of the cycles suggests that they may be related to insolation variations caused by changes in the Earth's orbital parameters.

Four lithologic types are present in the Neocomian pelagic sequences of the North Atlantic basin (Fig. 3; see also Dean and Arthur, 1999). These lithologies include (1) bioturbated white to light gray limestone and marly limestone, (2) finely to coarsely laminated, streaked or microburrowed brown to light gray marlstone and marly limestone, (3) dark brown to black homogeneous claystone and calcareous clay-

stone, and (4) gray to tan, graded to massive siltstone and sandstone (not considered here). The relative proportion of each lithologic type varies with depth: interbedded laminated and bioturbated limestones dominate in the lower part of the sequence (Berriasian-Valanginian) and the abundance of terrigenous clastic sediment increases upsection. At all sites, background sedimentation is represented by cyclic interbeds of laminated marlstone and bioturbated limestone; in general, it appears that laminated beds predominate over bioturbated limestones throughout most of the unit. In the western North Atlantic basin, these cyclic sequences contain beds of black, homogenous claystone, which have been interpreted to reflect episodic input of turbiditic muds derived from the adjacent continental margin (von Rad and Sarti, 1986; Dean and Arthur, 1999). The present study focuses on marlstone and limestone interbeds.

Although the lithologic expression of cyclic sedimentation is generally uniform throughout the extent of the Blake-Bahama Formation and its equivalents, contrasts in the composition of the non-carbonate fraction in marlstone interbeds in the eastern versus western basins of the North Atlantic provide evidence of the variable impact of orbital insolation on oceanographic variables and resulting pelagic sedimentation (Arthur and others, 1984; Dean and Arthur, 1987, 1999). At sites in the western North Atlantic basin, laminated marlstones contain reworked terrigenous detritus mixed with normal pelagic material. In this region, the laminated/bioturbated limestone cycles have been interpreted to reflect a combination of periodic dilution and restructuring of sediment by bottom currents (Dean and Arthur, 1999). Eastern North Atlantic basin cycles contrast somewhat with those in the western basin in that the dark-colored marlstone intervals at Site 367 are more finely laminated, have higher organic carbon contents, and better-preserved organic matter. Although calcareous nannofossil abundance varies across cycles, preservation in marlstone beds is generally as good or better than that in the limestone interbeds (e.g., Thierstein and Roth, 1991). Therefore, it is unlikely that the cycles at Site 367 are simple dissolution cycles. Rather, cycles in this region probably reflect variations in carbonate productivity, with periods of low productivity characterized by more sluggish deep-water circulation and the development of anoxic conditions that ultimately resulted in enhanced preservation of organic carbon. Dilution cannot be ruled out, but the dark marlstone beds at Site 367 are generally thinner than the interbedded limestones, suggesting decreased supply of carbonate rather than increased supply of terrigenous material as the cause of lithologic variations (Arthur and Dean, 1991; Dean and Arthur, 1999).

## METHODS

All analyses were performed on samples that were air-dried and ground to pass through a 149  $\mu\text{m}$  sieve. Splits of samples were digested in hydrofluoric acid and analyzed for 40 major, minor and trace elements by induction-coupled argon-plasma emission spectrometry (ICP); only Sr/Ca ratios are reported here. Sr and Ca concentrations were also determined on the carbonate fraction of select samples by inductively coupled atomic emission spectrometry (ICP-AES). The carbonate fraction of these samples was isolated



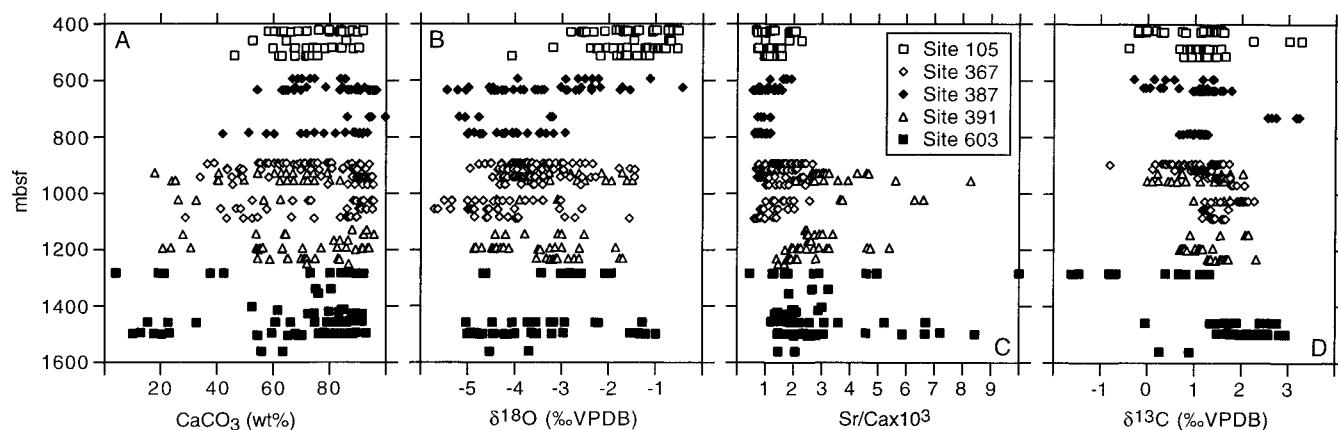


FIGURE 4. (A)  $\text{CaCO}_3$  content, (B) Sr/Ca ratios, (C)  $\delta^{18}\text{O}$  values, and (D)  $\delta^{13}\text{C}$  values versus burial depth (meters below seafloor; mbsf) for Neocomian pelagic carbonates from DSDP sites 105, 367, 387, 391, and 603.

through digestion of samples in a buffered acetic acid solution and removal of insoluble material by filtration. Analysis of samples using both methods revealed no significant differences in Sr/Ca ratios. Total carbon (TC) was determined by combustion using a Coulometrics Coulometer System 140. Organic carbon (OC) was determined on subsamples that were acidified with 2N HCl (Engleman and others, 1985). Precision of the coulometric technique is better than 2% for both TC and OC. Inorganic carbon (IC) was determined by difference between TC and OC. Percent carbonate (as  $\text{CaCO}_3$ ) was calculated by dividing percent IC by 0.12, the fraction of carbon in  $\text{CaCO}_3$ . Stable carbon and oxygen isotope analyses were performed at the University of Rhode Island using a Delta 602E mass spectrometer and at Pennsylvania State University using a Finnigan-MAT 252 mass spectrometer. At both institutions, samples were reacted with anhydrous phosphoric acid in a common acid bath coupled to the mass spectrometer. Isotopic ratios were corrected for  $^{17}\text{O}$  contribution (i.e., Craig, 1957) and are reported in permil (‰) relative to the Vienna Pee Dee belemnite (VPDB) standard. Precision is better than 0.10‰ for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values and was monitored through multiple analyses of National Bureau of Standards (NBS) 19 and other powdered calcite standards. Duplicate analyses revealed no interlaboratory differences in measured compositions. The geochemical data described in this paper and in Dean and Arthur (1999) are available electronically at the World Data Center-A for Paleoclimatology, NOAA/NGDC, 325 Broadway, Boulder, CO 80303 (e-mail: paleo@mail.ngdc.noaa.gov; URL: <http://www.ngdc.noaa.gov/paleo/contrib-list.html>; Contribution number 1999-031).

#### PATTERNS IN GEOCHEMICAL DATA

Neocomian pelagic sequences of the North Atlantic exhibit large variations in  $\text{CaCO}_3$  content (Fig. 4A). The degree of variability in carbonate content appears to reflect largely site location and proximity to sources of terrigenous influx (Fig. 1; Dean and Arthur, 1999). For example, carbonate contents at Sites 105 and 387, located on the Hatteras abyssal plain, vary between ~40 and 95%, whereas contents range from 4–95% at Site 603, located adjacent to the North American continental margin. Large variations in  $\text{CaCO}_3$

(30–95%) at Site 367 have been related to fluctuations in carbonate productivity, with periods of low productivity accompanied by the development of anoxic conditions (Dean and Arthur, 1999).

Samples exhibit an overall depletion in  $^{18}\text{O}$  with increasing depth over the range of 400 to 800 meters below seafloor (mbsf; Fig. 4B). We interpret the gradual decrease in  $\delta^{18}\text{O}$  values to reflect the progressive addition of diagenetic cement and the effect of increasing temperature with burial depth on the distribution of oxygen isotopes between water and diagenetic calcite (Friedman and O'Neil, 1977). Such temperature effects explain why  $\delta^{18}\text{O}$  values at Site 105, where sediments have undergone the least amount of burial, are generally higher than values at other sites (Fig. 4B). The relative constancy in the range of  $\delta^{18}\text{O}$  values below ~800 m suggests that little cement has been added to these successions below this depth. No clear depth-related trends are evident in either Sr/Ca ratios or  $\delta^{13}\text{C}$  values. In general, Sr/Ca ratios lie between  $0.5 \times 10^{-3}$  and  $3.0 \times 10^{-3}$  (Fig. 4C), although higher values (up to  $10.0 \times 10^{-3}$ ) were measured in a number of carbonate-poor samples from sites adjacent to the North American continental margin (Sites 391 and 603). Higher values in these samples may reflect proximity to sources of terrigenous influx. Carbon isotope compositions exhibit no apparent relationship with site location (Fig. 4D). Within and among sites, Sr/Ca ratios and  $\delta^{18}\text{O}$  values decrease with increasing  $\text{CaCO}_3$  content. Over a range of 4–98%  $\text{CaCO}_3$ ,  $\delta^{18}\text{O}$  values decrease by nearly 4‰ (Fig. 5A). The decrease in Sr/Ca ratios over the same range of  $\text{CaCO}_3$  contents is nearly exponential (Fig. 5B): Sr/Ca ratios decrease by a factor of 3–4 over a range of 4–50%  $\text{CaCO}_3$  and decrease by a factor of ~1.7 over the range of 50 to 98%  $\text{CaCO}_3$ . Carbon isotope compositions, on the other hand, do not exhibit any significant relationship with  $\text{CaCO}_3$  content (Fig. 5C).

The ranges in  $\delta^{18}\text{O}$  values (2–4‰) and Sr/Ca ratios (factor of 1.5–5) from each site are generally too large to be readily related to primary oceanographic processes such as fluctuations in temperature, salinity, or global ice volume (sea level). Given that the variations in these parameters are not solely reflecting primary processes, it follows that these signals, at least in part, must reflect diagenetic effects.

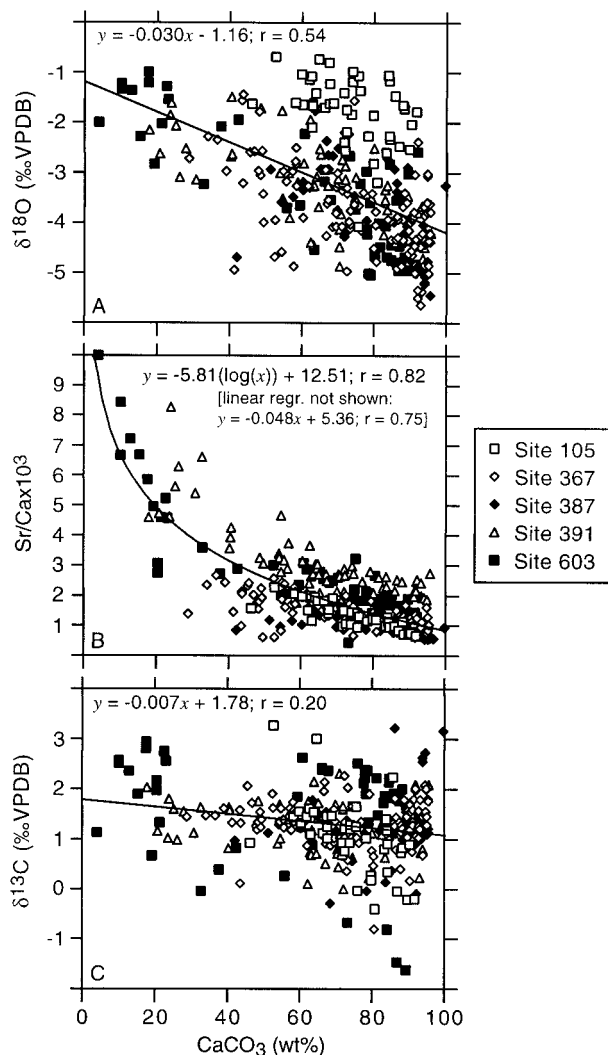


FIGURE 5. (A) Sr/Ca ratios, (B)  $\delta^{18}\text{O}$  values, and (C)  $\delta^{13}\text{C}$  values versus  $\text{CaCO}_3$  content for Neocomian pelagic carbonates from DSDP sites 105, 367, 387, 391, and 603.

Trends of decreasing Sr/Ca ratios and  $\delta^{18}\text{O}$  values with increasing carbonate content (Fig. 5A, B) suggest that the rhythmic variations in lithology that characterize the Neocomian pelagic successions examined in this study played a role in governing processes of burial diagenesis.

Linear regression of the relationship between  $\delta^{18}\text{O}$  values and carbonate content (4–98 wt%  $\text{CaCO}_3$ ) reveals that the slope of this relationship is similar among sites (Table 1). Moreover, the slopes calculated for each site are comparable to the slope of the regression for the entire data set (Fig. 5A). Although the  $r$  values for linear regression equations for  $\text{CaCO}_3$  and  $\delta^{18}\text{O}$  are between 0.37 and 0.53, we argue on the basis of the large number of observations that the trends are significant; for  $n = 50$ , an  $r$  value of 0.27 is statistically significant at the 95th percentile confidence level. The consistent relationship between  $\delta^{18}\text{O}$  values and  $\text{CaCO}_3$  content provides further evidence that the trend of decreasing  $\delta^{18}\text{O}$  values with increasing  $\text{CaCO}_3$  content cannot be attributed solely to sample- or site-dependent parameters such as age, location, or burial depth. Rather, these

TABLE 1.

Site 105	$\delta^{18}\text{O} = -0.023_{(\pm 0.009)} \times \% \text{CaCO}_3 - 0.032_{(\pm 0.695)}$ ; $r = 0.37$ ( $\text{Sr}/\text{Ca} \times 10^3$ ) = $-0.036_{(\pm 0.003)} \times \% \text{CaCO}_3 + 4.033_{(\pm 0.258)}$ ; $r = 0.87$
Site 387	$\delta^{18}\text{O} = -0.038_{(\pm 0.108)} \times \% \text{CaCO}_3 - 0.676_{(\pm 0.581)}$ ; $r = 0.53$ ( $\text{Sr}/\text{Ca} \times 10^3$ ) = $-0.020_{(\pm 0.002)} \times \% \text{CaCO}_3 + 2.614_{(\pm 0.199)}$ ; $r = 0.75$
Site 367	$\delta^{18}\text{O} = -0.021_{(\pm 0.005)} \times \% \text{CaCO}_3 - 2.210_{(\pm 0.439)}$ ; $r = 0.39$ ( $\text{Sr}/\text{Ca} \times 10^3$ ) = $-0.023_{(\pm 0.002)} \times \% \text{CaCO}_3 + 3.163_{(\pm 0.216)}$ ; $r = 0.68$
Site 391	$\delta^{18}\text{O} = -0.022_{(\pm 0.005)} \times \% \text{CaCO}_3 - 1.908_{(\pm 0.369)}$ ; $r = 0.47$ ( $\text{Sr}/\text{Ca} \times 10^3$ ) = $-0.027_{(\pm 0.005)} \times \% \text{CaCO}_3 + 4.515_{(\pm 0.363)}$ ; $r = 0.59$
Site 603	$\delta^{18}\text{O} = -0.024_{(\pm 0.005)} \times \% \text{CaCO}_3 - 2.614_{(\pm 0.367)}$ ; $r = 0.49$ ( $\text{Sr}/\text{Ca} \times 10^3$ ) = $-0.032_{(\pm 0.006)} \times \% \text{CaCO}_3 + 4.432_{(\pm 0.452)}$ ; $r = 0.62$

Relationship between  $\delta^{18}\text{O}$  and  $\% \text{CaCO}_3$  determined for the range of 10–98 wt%  $\text{CaCO}_3$ ; relationship between  $\text{Sr}/\text{Ca} \times 10^3$  and  $\% \text{CaCO}_3$  determined for >50 wt%  $\text{CaCO}_3$ .

similarities suggest that present variations in oxygen isotope compositions have been controlled to a large degree by factors that are common to all sites examined, namely primary variations in carbonate content and burial diagenetic processes.

Although regression analysis reveals that the linear relationship between Sr/Ca ratios and  $\text{CaCO}_3$  contents is also statistically significant (Table 1), the overall trend defined by these parameters is perhaps better described logarithmically (Fig. 5B). Unfortunately, the relatively limited range of  $\text{CaCO}_3$  contents at Sites 105, 367, and 387 make it difficult to statistically compare trends among sites over the full range of  $\text{CaCO}_3$  concentrations measured. This is because the slope of the relationship at each site is strongly dependent upon Sr/Ca ratios associated with lower carbonate contents. For comparative purposes we therefore restricted our examination of the linear relationship between Sr/Ca ratios and  $\text{CaCO}_3$  among sites to samples containing >50 wt%  $\text{CaCO}_3$ . Results reveal that the relationship between these parameters is statistically significant at each site and that the slope describing the relationship is similar among sites (Table 1). As with trends in  $\delta^{18}\text{O}$  values and  $\text{CaCO}_3$ , the consistent nature of the relationship between Sr/Ca ratios and  $\text{CaCO}_3$  content provides further evidence that rhythmic variations in lithology that characterize Neocomian pelagic carbonates of the North Atlantic have exerted a strong control on patterns of burial diagenesis and resulting geochemical signatures. Potentially, the relationships described above can be used to quantify the effect of primary variations in carbonate content on measured  $\delta^{18}\text{O}$  values and Sr/Ca ratios in the sequences examined. This possibility is considered below.

## DIAGENETIC PROCESSES

Given that diagenetic carbonates in pelagic sequences are generally depleted in Sr and  $^{18}\text{O}$  relative to primary phases (e.g., Matter and others, 1975; Renard and others, 1978; Baker and others, 1982), it stands to reason that geochemical signatures related to primary oceanographic processes should be more closely preserved in carbonate-poor lithol-

ologies (calcareous shales and marlstones). By contrast, the geochemical characteristics of carbonate-rich, bioturbated limestones should contain signatures expected to result from burial diagenesis. As such, relationships between Sr/Ca ratios and  $\delta^{18}\text{O}$  values and  $\text{CaCO}_3$  suggest that primary variations in carbonate content imparted differences on the susceptibility of calcareous components in adjacent cyclic interbeds to alteration during burial (e.g., Scholle, 1974; Brennecke, 1977; Thierstein and Roth, 1991). Lower Sr/Ca ratios and  $\delta^{18}\text{O}$  values indicate that bioturbated limestones were more altered during burial diagenesis. By contrast, higher Sr/Ca ratios and  $\delta^{18}\text{O}$  values in carbonate-poor intervals suggest that carbonate components in calcareous shales and laminated marlstones were significantly less altered during burial.

Sedimentologic and petrographic observations are consistent with this interpretation. Burrows and other primary sedimentary structures are commonly well-preserved in limestones of the Blake Bahama Formation (Fig. 3). The preservation of such features suggests that carbonate-rich intervals have undergone some degree of early lithification. Bioturbation structures in adjacent laminated marlstones, on the other hand, are often flattened, indicating that early lithification in these intervals was relatively minor (i.e., Figures 24, 25 in Sheridan and others, 1983; Figure 7 in Haggerty, 1987; Figure 7 in Ogg and others, 1987). In some instances, compaction processes in laminated marlstones have led to the development of dissolution seams and anastomosing stylolites (i.e., Figure 26 in Sheridan and others, 1983; Figure 5 in Robertson and Bliefnick, 1983). Examination under the scanning electron microscope (SEM) reveals that carbonate-rich intervals of bioturbated limestone are characterized by an abundance of intact coccolithophores (Fig. 6A), calcitic overgrowths on coccolith elements, and an abundance of secondary cement with individual crystals reaching 10  $\mu\text{m}$  in diameter (Fig. 6B). By contrast, no intact coccolithophores were observed in laminated marlstones and diagenetic cement consists almost entirely of microcrystalline carbonate with individual crystals less than 5  $\mu\text{m}$  in diameter (Fig. 6C). In these carbonate-poor intervals, coccolith elements are commonly fragmented and slightly etched and, in some cases, grain edges appear rounded (see also Baltuck, 1987).

Numerous studies have demonstrated that pressure solution provides enough  $\text{CaCO}_3$  to account for all of the cement precipitated during the progressive transformation of carbonate ooze to limestone during burial diagenesis (e.g., Lancelot and others, 1972; Schlanger and Douglas, 1974; van der Lingen and Packham, 1975). In the case of the Neocomian sequences examined in the present study, this process of autolithification (*sensu* Matter, 1974) appears to be controlled chiefly by variations in primary sediment composition rather than by burial depth, such that processes of dissolution and cementation are not distributed evenly through the section. Rather, it appears that diagenetic cement is added preferentially to initially carbonate-rich intervals (bioturbated limestones), whereas original carbonate is preferentially dissolved in adjacent carbonate-poor intervals (laminated marlstones and calcareous shales). Considered in a context of mass balance, these relationships suggest that carbonate liberated by dissolution in calcareous shales and

marlstones has been transported over tens of centimeters to sites of nucleation in adjacent bioturbated limestones.

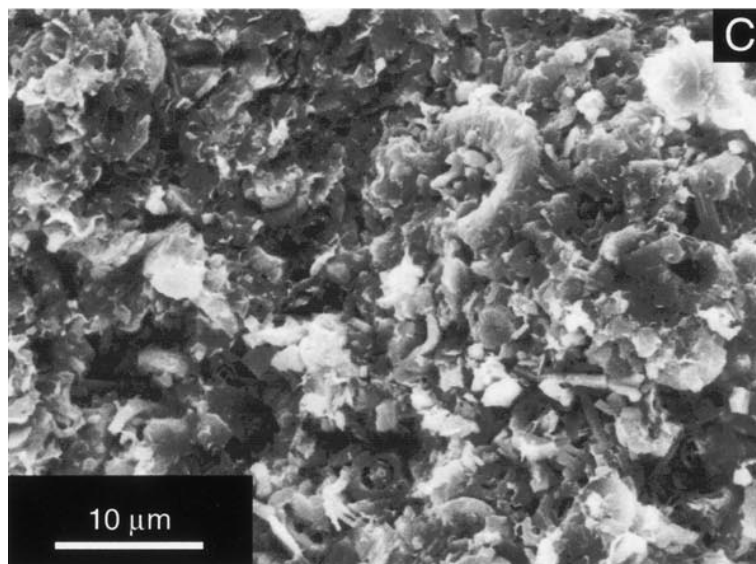
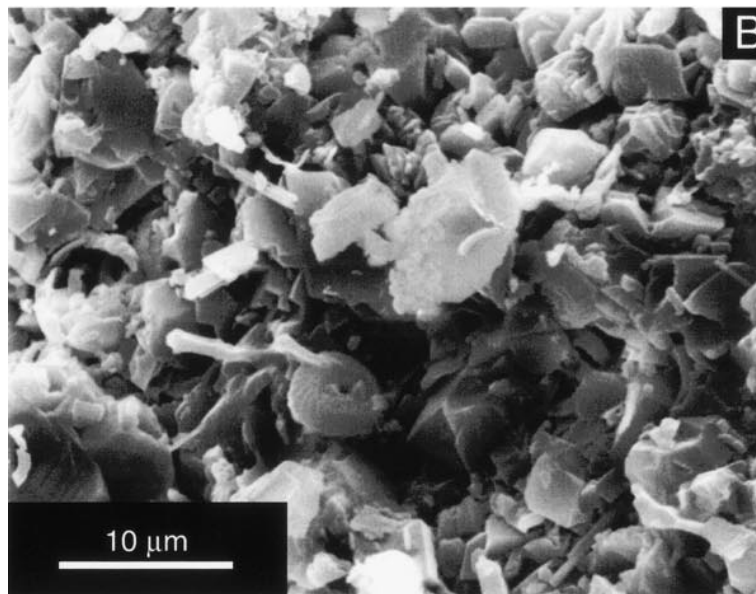
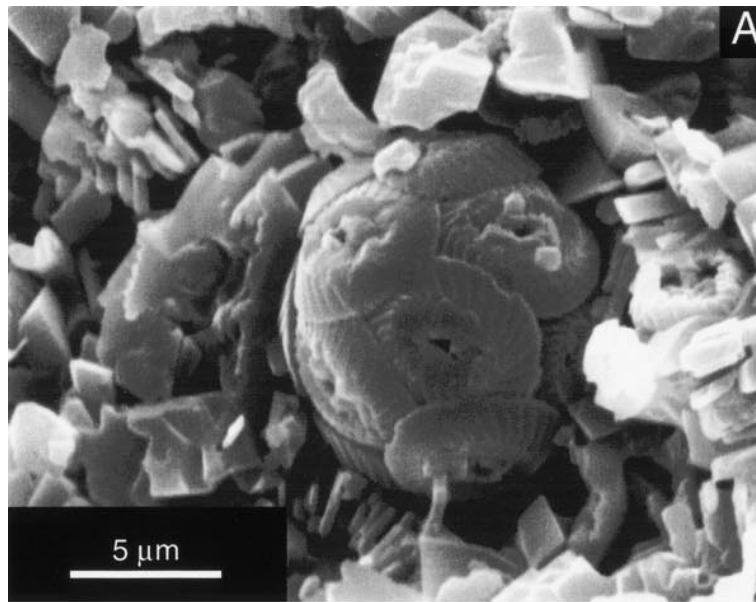
A diagenetic process involving the transfer of carbonate across primary depositional cycles in Neocomian pelagic carbonates is consistent with observed patterns in geochemical data. On the basis of the observations outlined above, we therefore propose the following diagenetic model. Assuming that cyclic variations in the carbonate content in the sequences examined reflect either periodic dilution (western North Atlantic) or variations in productivity (eastern North Atlantic; Dean and Arthur and others), it is likely that intervals of carbonate ooze were initially characterized by similar or slightly higher Sr/Ca ratios and  $\delta^{18}\text{O}$  values relative to adjacent marls (Fig. 7A). During burial, removal of  $\text{CaCO}_3$  from calcareous shales and marlstones and the progressive precipitation of this material as cement in adjacent carbonate-rich intervals led to gradual changes in the bulk compositions of cyclic interbeds (Fig. 7B). Owing to the relatively Sr- and  $^{18}\text{O}$ -depleted nature of diagenetic carbonate, the progressive addition of cement resulted in a gradual decrease in bulk Sr/Ca ratios and  $\delta^{18}\text{O}$  values of carbonate-rich intervals. By contrast, little secondary material was added to carbonate-poor intervals. Thus, with the possible exception of minor differences in composition that might reflect the preferential dissolution of slightly more reactive carbonate, the bulk geochemical compositions of marlstones remained virtually unaltered (Fig. 7B). As such, differential cementation and dissolution during burial diagenesis enhanced primary lithologic differences and, ultimately, reversed and then exaggerated initial variations in Sr/Ca and  $\delta^{18}\text{O}$  among cyclic interbeds (Fig. 7B). Carbon isotope compositions typically exhibit only minor ( $\pm 0.2\%$ ) variations across carbonate cycles and do not appear to be significantly altered during diagenesis. We attribute the retention of primary  $\delta^{13}\text{C}$  values across cycles to the buffering effect of carbonate carbon on the diagenetic system and the minor influence of temperature on the distribution of carbon isotopes between DIC and carbonate (Friedman and O'Neil, 1977).

## IMPLICATIONS

### CORRECTION TO PRIMARY VALUES?

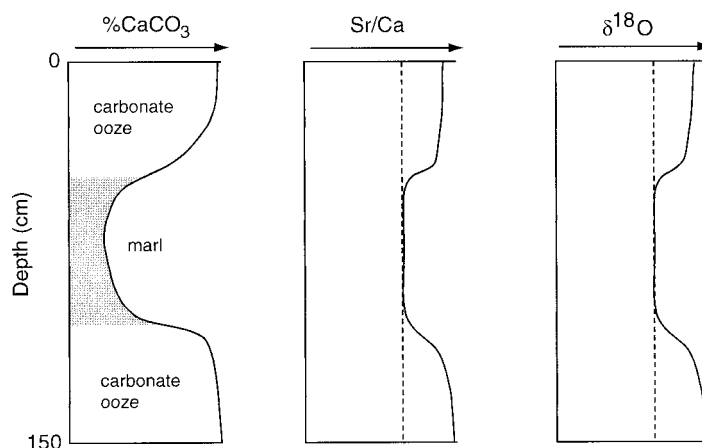
Because burial diagenesis has a significant effect on the Sr content and oxygen isotope composition of the Neocomian pelagic carbonates, it is difficult if not impossible to ascertain initial compositions in order to make paleoceanographic interpretations from the data. Some previous workers (e.g., Schrag and others, 1992; 1995) have suggested that  $\delta^{18}\text{O}$  values of Cenozoic whole-rock carbonate can be corrected for diagenetic overprints, such that paleotemperature information can be extracted. Testing the efficacy of numerical models for such corrections, however, requires some knowledge of surface-to-deep water temperature gradients, sedimentation rates (and corresponding thermal gradients upon burial),  $\delta^{18}\text{O}$ -depth gradients in pore fluids, as well as corresponding records derived from carbonate components (i.e., planktonic and benthic foraminifers) with which whole-rock results can be compared. Unfortunately, the Neocomian record offers none of these parameters and the extent of burial diagenesis is greater (e.g., to complete re-







## A. PRIMARY LITHOLOGIC AND GEOCHEMICAL VARIATIONS



## B. LITHOLOGIC AND GEOCHEMICAL VARIATIONS AFTER BURIAL DIAGENESIS

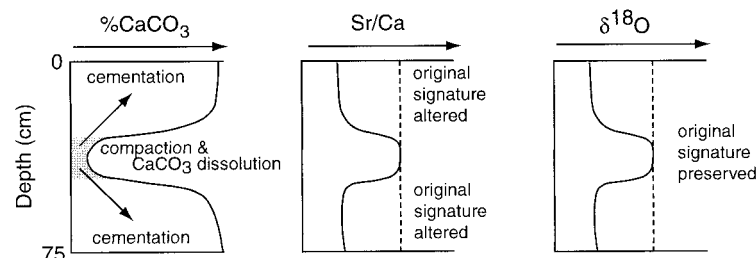


FIGURE 7. Schematic diagram illustrating the effects of mass transfer of carbonate across primary carbonate cycles on geochemical signatures in pelagic sequences consisting of interbeds of varying carbonate content. Primary variations in Sr/Ca ratios and  $\delta^{18}\text{O}$  values (A) are reversed and exaggerated (B) during burial diagenesis.

duction of porosity) than for most of the Cenozoic sequences studied previously.

For the Neocomian pelagic carbonates, however,  $\delta^{18}\text{O}$  values and Sr/Ca ratios covary as a function of  $\text{CaCO}_3$  content (Fig. 5), at least after imposition of the diagenetic overprint, such that much of the variation in composition can be accounted for. The consistent relationship between these variables provides a possible means by which  $\delta^{18}\text{O}$  and Sr/Ca values can be adjusted to account for differential diagenetic alteration resulting from variation in  $\text{CaCO}_3$ . In this "correction" procedure, all measured geochemical values are adjusted using the slopes of the relationships between  $\delta^{18}\text{O}$  and  $\text{CaCO}_3$  and Sr/Ca and  $\text{CaCO}_3$  (Table 1). Using these relationships, an "initial" carbonate-corrected  $\delta^{18}\text{O}$  value can be calculated, wherein  $m$  is the slope of the relationship:

$$m = (\delta^{18}\text{O}_{\text{meas}} - \delta^{18}\text{O}_{\text{initial}}) / (\text{CaCO}_{3\text{meas}} - \text{CaCO}_{3\text{initial}});$$

$$\delta^{18}\text{O}_{\text{initial}} = \delta^{18}\text{O}_{\text{meas}} - (m(\text{CaCO}_{3\text{meas}} - \text{CaCO}_{3\text{initial}}))$$

A similar relationship is developed for Sr/Ca vs.  $\text{CaCO}_3$  (for  $>50$  wt%  $\text{CaCO}_3$ ). Assuming a constant value of  $\text{CaCO}_3$

"initial" for each site ( $=x\%$ ), the  $\text{CaCO}_3$  effect can be removed. This method may allow estimation of the degree of original variation in  $\delta^{18}\text{O}$  (independent of  $\text{CaCO}_3$  content). Although small-scale compositional heterogeneities may have promoted differential dissolution of primary carbonate components during burial, a key assumption in this model is that much of the original oxygen isotope and Sr/Ca signal has been retained in relatively carbonate-poor intervals.

Adjusting the data in this way results in much less apparent variation over a sampling interval spanning several carbonate cycles (Fig. 8). However, this procedure does not account for additional differential depth-related diagenetic effects on Sr/Ca ratios and  $\delta^{18}\text{O}$  values. Some of the depth-related trends may be embodied in the  $\delta^{18}\text{O}$  and Sr/Ca vs.  $\text{CaCO}_3$  trends, although it is clear that carbonates buried to greater depths have lower  $\delta^{18}\text{O}$  values and higher Sr/Ca ratios than those of equivalent age at shallower burial depths (Fig. 4). We attempted to correct for burial depth as well, but the "corrected"  $\delta^{18}\text{O}$  values then appear to be too high relative to those expected for nanofossil carbonate in the subtropics. Given the good preservation of burrow mor-

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FIGURE 6. Scanning electron photomicrographs showing petrographic characteristics of samples with varying  $\text{CaCO}_3$  content. (A) Intact coccolithosphere in Sample 41-367-30-1, 60-62 cm (sub-bottom depth 1025.10 m); sample contains 95 wt%  $\text{CaCO}_3$ . (B) Pore-filling cement in Sample 41-367-30-1, 60-62 cm (sub-bottom depth 1025.10 m); sample contains 95 wt%  $\text{CaCO}_3$ . (C) Disaggregated and etched coccoliths in Sample 41-391-31-1, 135-137 cm (sub-bottom depth 1191.85 m); sample contains 56 wt%  $\text{CaCO}_3$ .

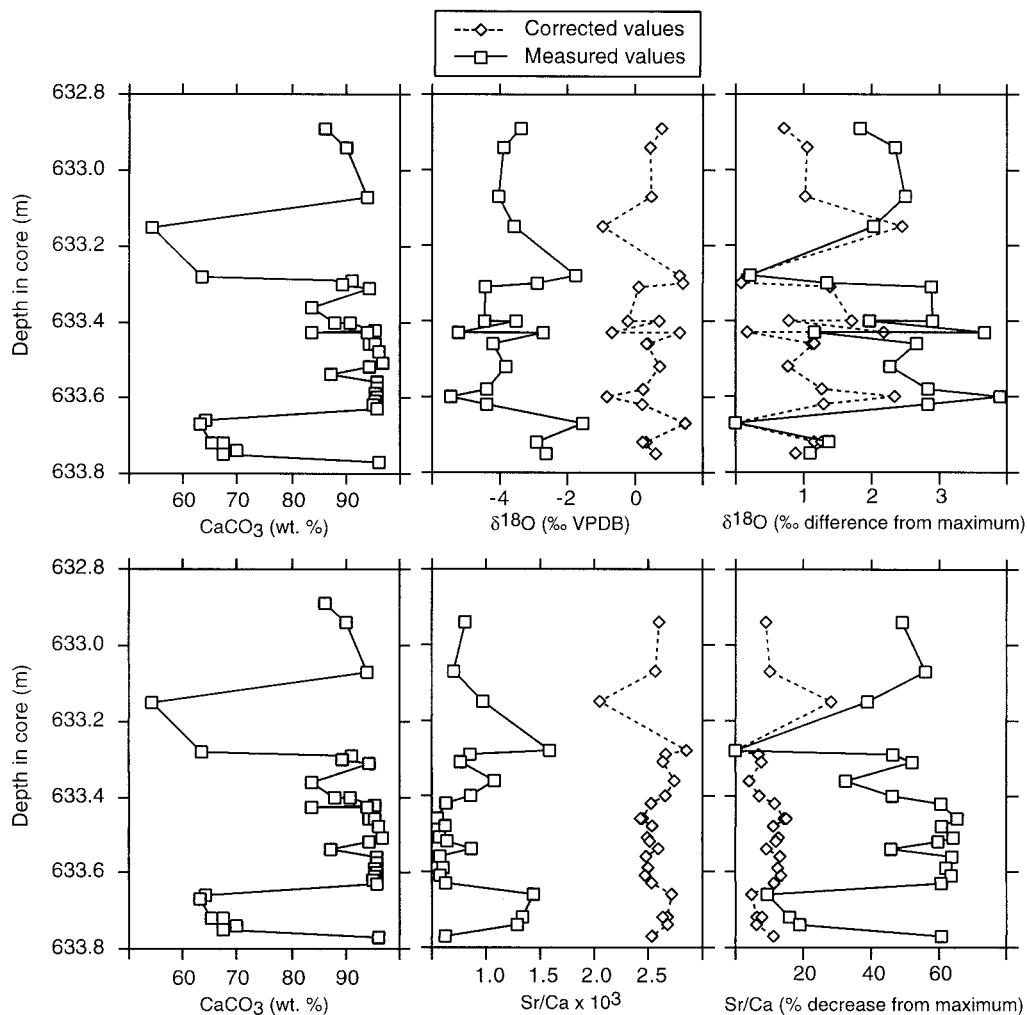


FIGURE 8. Measured and  $\text{CaCO}_3$ -corrected Sr/Ca ratios and  $\delta^{18}\text{O}$  values over a one-meter interval at Site 387. Shown are carbonate content (upper, lower left), measured and corrected  $\delta^{18}\text{O}$  values (upper middle) and Sr/Ca ratios (lower middle), and deviation of measured and corrected  $\delta^{18}\text{O}$  values (upper right) and Sr/Ca ratios (lower right) from maximum.

phologies in bioturbated limestones (Fig. 3), it is possible higher than expected  $\delta^{18}\text{O}$  values reflect some amount of recrystallization/lithification at shallow burial depths and in the presence of cold seawater (e.g., Baker and others, 1982). The degree to which such processes may have affected original oxygen isotope compositions, however, is not readily quantifiable. We therefore urge caution in interpreting the results of such corrections, but some general interpretive considerations merit further discussion below.

#### PALEOCEANOGRAPHIC INTERPRETATION

One of the interesting questions that has arisen regarding the Neocomian (Berriasian-Barremian) is whether this interval is characterized by warmer "greenhouse" climates that have been inferred to prevail for the middle and Late Cretaceous (e.g., Weissert, 1989; Lini and others, 1992; Channell and others, 1993), or whether there may also be significant intervals of cooler prevailing climate (e.g., Kemper, 1983, 1986), perhaps even culminating in the development of substantial ice sheets on Antarctica (e.g., Stoll and Schrag, 1996). In this context, the Neocomian pelagic

record has potential as an indicator of regional and global climatic conditions. As discussed above and in Dean and Arthur (1989), however, diagenetic overprints have compromised the stable isotopic and geochemical signals in these strata.

In a stimulating paper, Stoll and Schrag (1996) manipulated geochemical data from Neocomian successions at DSDP Sites 391, 534, and 603 in the western North Atlantic in an attempt to extract primary variations  $\delta^{18}\text{O}$  values and Sr/Ca ratios. They argued that the Neocomian pelagic carbonates with carbonate contents greater than 50% retain a record of relative primary differences (not initial values) between adjacent samples. In other words, they treated any geochemical variation as primary, in contrast to our hypothesis that initial carbonate content plays a major role in determining the extent to which primary compositions are retained. Their diagenetic model assumed that adjacent samples were shifted equally to more  $^{18}\text{O}$ -depleted compositions during burial diagenesis and that the extent of the depletion was solely a function of burial depth. In order to determine the amplitude of primary variations in  $\delta^{18}\text{O}$  values and Sr/

Ca ratios, Stoll and Schrag (1996) subtracted a smoothed baseline function and normalized all  $\delta^{18}\text{O}$  values for each site to the resulting minimum (trend-corrected) value at that site. Their model ignores any initial differences in diagenetic potential between adjacent beds, adopting the assumption of Richter and DePaolo (1987; 1988) and Richter and Liang (1993) that the curve of recrystallization rate as a function of age is a smooth function for any given location. This generalization, of course, ignores the significant variation in bulk density, porosity, and lithification from bed to bed over any given depth interval in less deeply buried pelagic carbonate sequences (e.g., Schlanger and Douglas, 1974; Borre and Fabricius, 1998), as well as observations of differences in the volume of secondary cement between adjacent limestone and marlstone beds in the Neocomian sequences studied here (see also Robertson and Bliefnick, 1983; Baltuck, 1987; Thierstein and Roth, 1991).

The consequence of the Stoll and Schrag (1996) diagenetic model is that they obtain estimates for primary, high-frequency variations in  $\delta^{18}\text{O}$  values and Sr/Ca ratios that are substantially larger than those obtained in the present study; the amplitude of their modeled variation in  $\delta^{18}\text{O}$  values is as large as 1.8‰ and that of their estimated variation in Sr/Ca ratios is as much as 1.7 times the minimum value. In general, decreases in  $\delta^{18}\text{O}$  values correspond to decreased Sr/Ca ratios, as also would be expected from differential diagenesis. Stoll and Schrag (1996), however, relate these geochemical variations to high-amplitude sea level fluctuations apparent in the sea level curve of Haq and others (1987). Increases in strontium concentration are interpreted to record the rapid release of Sr into the oceans as Sr-rich aragonite inverted to Sr-poor calcite during episodic exposure of continental shelves. On the basis of corresponding increases in  $\delta^{18}\text{O}$  values, the large and rapid changes in sea level necessary to account for the periodic exposure of continental shelves are attributed to the growth of continental ice sheets on Antarctica.

In the context of evidence that overall climatic conditions during the Early Cretaceous were too warm for extensive accumulation of continental ice (e.g., Barron and others, 1984), an alternative explanation for apparent high-amplitude sea level variations is that the sequence stratigraphic data that form the basis for the Haq and others (1997) eustatic curve are recording relative sea level changes caused by regional tectonic activity (Hallam, 1992). In this regard, we would argue that variations in  $\text{CaCO}_3$  content in the North Atlantic records examined both in the present study and by Stoll and Schrag (1996), at least in part, reflect basin-scale sea level fluctuations (i.e., increased terrigenous dilution during sea level lowstands). Given that the extent to which primary compositions are altered during diagenesis is largely determined by initial carbonate content, substantial variations in Sr/Ca ratios and  $\delta^{18}\text{O}$  values would be produced during burial even without any significant initial variation in these geochemical parameters as a function of  $\text{CaCO}_3$  content. Therefore, although an intrabasinal correlation of Sr/Ca ratios,  $\delta^{18}\text{O}$  values, and  $\text{CaCO}_3$  concentrations might be expected to correlate with sea level variations, neither the relative nor the absolute values of these parameters would have meaning in terms of primary processes.

## CONCLUSIONS

A detailed study of the textures and geochemistry of Lower Cretaceous pelagic carbonate sequences recovered from North Atlantic Deep Sea Drilling Project sites reveals that primary variations in carbonate content and depth of burial are the main factors that influence the extent of diagenesis and overprinting of primary geochemical compositions. Although cyclic variations in  $\text{CaCO}_3$  content are primary, measured Sr/Ca ratios and  $\delta^{18}\text{O}$  values are not and cannot be readily interpreted in terms of paleoceanographic or paleoclimatic variations. In fact, burial diagenesis has reversed and then exaggerated initial variations in Sr/Ca ratios and  $\delta^{18}\text{O}$  values in the sequences examined. Limestones have lower  $\delta^{18}\text{O}$  values and Sr/Ca ratios than adjacent marlstones. The  $\delta^{13}\text{C}$  values in both lithologies, however, are not significantly altered during diagenesis and, at the same time, exhibit very minor ( $\pm 0.2\text{‰}$ ) primary variation across decimeter-scale carbonate cycles. The  $\delta^{18}\text{O}$  values decrease with increasing burial depth for strata of equivalent age.

The diagenesis of these carbonate sequences involves the progressive transfer of carbonate from carbonate-poor intervals (calcareous shales and marlstones) to relatively high-porosity, carbonate-rich intervals (limestones) over tens of centimeters during burial compaction and pressure solution. As a result, the initially carbonate-poor intervals are more likely to preserve primary geochemical signals without addition of significant amounts of carbonate cement. By contrast, the addition of abundant pore-filling cement and overgrowths on coccolith elements in initially carbonate-rich intervals results in an overall decrease in bulk Sr concentrations and  $\delta^{18}\text{O}$  values. We attempted to correct for variations in diagenetic overprinting that resulted from primary differences in carbonate content. However, the resulting  $\delta^{18}\text{O}$  values remain difficult to interpret, primarily because we have not yet found a satisfactory method for correcting for additional, depth-related diagenesis in these sediments. One possible method involves subtracting baseline trends related to depth of burial (e.g., Richter and DePaolo, 1987; 1988; Richter and Liang, 1993), but this technique may remove some vestige of primary geochemical variation that should be retained. In any case, petrographic and geochemical relationships indicate that drawing any detailed paleoceanographic inferences from the carbonate geochemistry of Neocomian North Atlantic pelagic sequences is hampered by differential diagenetic overprinting during burial. We suggest that recent arguments concerning the effects of glaciation and sea level change on the geochemistry of Neocomian pelagic carbonates are highly speculative and not supported by new data and inferences regarding diagenesis.

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