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#### Notes

# Blake Nose stable isotopic evidence against the mid-Cenomanian glaciation hypothesis

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## ABSTRACT

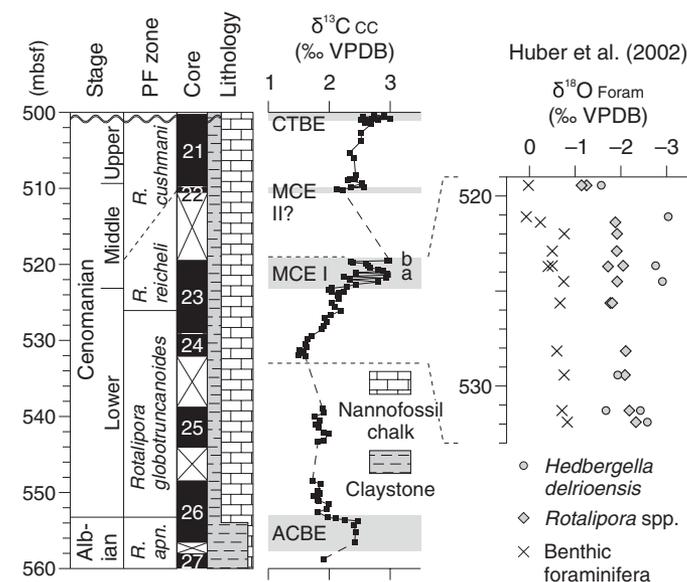
Detailed multitaxon stable isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) data from Blake Nose (western North Atlantic) argue against a mid-Cenomanian glaciation event during the mid-Cretaceous greenhouse. Results generated are precisely correlated to sea-level changes inferred from European sequence stratigraphy using the twin  $\delta^{13}\text{C}$  excursions mid-Cenomanian event (MCE) Ia and MCE Ib. Microfossils analyzed (surface-dwelling to deep-dwelling planktonic foraminifera, benthic foraminifera, coccoliths) show remarkably consistent intertaxon  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  offsets; comparative scanning electron microscope and Sr/Ca analyses allow some  $\delta^{18}\text{O}$  data to be eliminated because of selective diagenesis. Across MCE Ia, the proposed interval of major glacioeustatic regression, the planktonic  $\delta^{18}\text{O}$  values are constant for each taxon. The absence of a mean seawater  $\delta^{18}\text{O}$  shift contradicts predictions for the mid-Cenomanian glaciation episode. The benthic  $\delta^{18}\text{O}$  records show significant fluctuations during MCE I, implying short-term variability in North Atlantic intermediate-water and deep-water circulation patterns and/or sources at that time.

## INTRODUCTION

An ongoing debate in paleoclimatic research has centered on the occurrence of short-term cooling events during the mid-Cretaceous, and their possible link to the growth of continental ice sheets during greenhouse phases of the global climate. While supporting extreme warmth across the Cenomanian-Turonian (C-T) boundary (e.g., Huber et al., 2002; Wilson et al., 2002), the latest paleothermometry using  $\delta^{18}\text{O}$  and  $\text{TEX}_{86}$  proxies has highlighted the existence of four cooling pulses through the C-T interval (Voigt et al., 2004; Forster et al., 2007; Bornemann et al., 2008). Of these, the mid-Cenomanian (early Middle Cenomanian, ca. 96 Ma) is particularly well documented as a cool climate mode, supported by the appearance of a central Russian nektonic-benthic pulse fauna in western Europe (e.g., Voigt et al., 2004; Wilmsen et al., 2007). It is further distinguished from other C-T cooling events by possessing Milankovitch-paced short (100 k.y.) and long (400 k.y.) eccentricity cycles in marl-chalk successions (e.g., Gale et al., 1999) and by globally synchronous formation of depositional sequences (Gale et al., 2008), both of which potentially indicate glacioeustasy. The growth of short-lived mid-Cenomanian ice sheets, at least at the Antarctic high altitudes, was advanced by Stoll and Schrag (2000) and Miller et al. (2003, 2005), based on sequence stratigraphic evidence for high-amplitude sea-level falls (>25 m within 1 m.y.) that has been linked with bulk carbonate and benthic foraminiferal  $\delta^{18}\text{O}$  shifts. Moriya et al. (2007), however, argued against the glaciation hypothesis based on essentially invariant  $\delta^{18}\text{O}$  signals of planktonic foraminifera as well as the absence of planktonic-benthic  $\delta^{18}\text{O}$  covariation across the mid-Cenomanian interval at Demerara Rise in the equatorial Atlantic (Ocean Drilling Program [ODP] Site 1258). A pressing need has therefore

arisen to constrain more comprehensively the nature of the hypothesized mid-Cenomanian glaciation.

In this study we revisit the stable isotope record at ODP Site 1050, Blake Nose, western North Atlantic. Site 1050 is the only known section yielding abundant, well-preserved, diverse foraminifera of Middle Cenomanian age (Bellier and Moullade, 2002), allowing geochemical data acquisition from a typical open-ocean assemblage. Previous Site 1050 foraminiferal  $\delta^{18}\text{O}$  data (Huber et al., 2002; Fig. 1 herein) were cited in support of a glaciation event (Miller et al., 2003, 2005), but this interpretation has been called into question because it was based only on the sparse data from benthic foraminifera of questionable preservation (Moriya et al., 2007). Thus, the  $\delta^{18}\text{O}$  record from Blake Nose must be more carefully scrutinized in order to provide robust constraints on the mid-Cenomanian glaciation hypothesis. This study greatly increases the stratigraphic resolution of the isotope data from multiple calcareous microfossil taxa and adds scanning electron microscopic (SEM) and geochemical (Sr/Ca) observations to assess foraminiferal preservation and potential diagenetic artifacts.



**Figure 1. Cenomanian carbon isotope stratigraphy of coccolith fraction (CC) at Ocean Drilling Program Site 1050, Blake Nose, western North Atlantic. Planktonic foraminiferal (PF) zonation is from this study. Shaded intervals indicate correlative  $\delta^{13}\text{C}$  events with those named in European reference  $\delta^{13}\text{C}$  curves (ACBE—Albian-Cenomanian boundary event; MCE—mid-Cenomanian event; CTBE—Cenomanian-Turonian boundary event). Also shown are previous  $\delta^{18}\text{O}$  data of Huber et al. (2002) from target interval of this study. *R. apn.*—*Rotalipora appenninica*; mbsf—meters below seafloor; VPDB—Vienna Peedee belemnite.**

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## MATERIAL AND METHODS

Site 1050 was drilled off northern Florida (30°06.00'N, 76°14.10'W; water depth 2300 m) during ODP Leg 171B in 1997. Paleomagnetic study indicates that this site occupied a paleolatitude of ~25°N from the mid-Cretaceous through Eocene (Ogg and Bardot, 2001).

Chalk samples were taken with <50 cm spacing from the entire Cenomanian interval (cores 21–27 [part]). They were treated with dilute H<sub>2</sub>O<sub>2</sub> solution, sonicated, and wet sieved at 63 μm. The coccolith fraction (<63 μm) was separated from the wash water by settling and decantation. Well-preserved foraminifera were carefully selected from a narrow (212–300 μm) sieve fraction of core 23–24 samples. Their appearance under the stereomicroscope is more or less “frosty” (sensu Sexton et al., 2006). For stable isotope analyses of planktonic foraminifera, the dominant four species—*Praeglobotruncana stephani*, *Rotalipora globotruncanoides*, *Rotalipora montsalvensis*, and *Rotalipora reicheli*—were picked and typically 4–6 specimens were included in each analysis. For benthic foraminifera, each isolate comprised a single calcareous trochospiral group, but two species or more were combined when sample size was insufficient.

Stable oxygen and carbon isotope analyses were performed using a Thermo Finnigan DeltaPlus mass spectrometer at the Biogeochemistry Isotope Laboratory, University of Missouri. Data were reported relative to the Vienna Peedee belemnite (VPDB) standard after normalization based on the difference between the within-run average of NBS 19 and its recommended value ( $\delta^{18}\text{O} = 2.20\text{‰}$ ;  $\delta^{13}\text{C} = -1.95\text{‰}$ ). Replicate measurements of NBS 19 yielded long-term precision (1 standard deviation [SD]) better than  $\pm 0.06\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 0.03\text{‰}$  for  $\delta^{13}\text{C}$ . As a practical means of evaluating burial diagenesis, Ca and Sr concentrations were measured simultaneously on 0.1M acetic acid leachate of the coccolith fraction (20–25 mg) by using a Shimadzu ICPS7500 inductively coupled plasma-atomic emission spectrometer at Research Reactor Institute, Kyoto University (1 SD =  $\pm 1\%$  for Sr/Ca;  $n = 7$ ). Numerical data are provided in Table DR1 in the GSA Data Repository.<sup>1</sup>

## RESULTS

### Carbon Isotope Stratigraphy

A new Cenomanian  $\delta^{13}\text{C}$  profile from the coccolith fraction at Site 1050 (Fig. 1) essentially conforms to the reference  $\delta^{13}\text{C}$  curves from European hemipelagic sections in terms of both absolute values (1.5‰–3.0‰) and stratigraphic patterns (Mitchell et al., 1996; Jarvis et al., 2006). This observation is in line with the empirically established fundamentals of carbon isotope stratigraphy based on hemipelagic and pelagic carbonates; i.e., a globally correlative  $\delta^{13}\text{C}$  curve can be generated through bulk analysis of polyspecific coccolith calcite despite the diagenetic effects in chalk and limestone lithologies.

At least three well-known  $\delta^{13}\text{C}$  events (amplitude  $>+0.5\text{‰}$ ) are recognized: the Albian-Cenomanian boundary event; mid-Cenomanian event (MCE I); and the C-T boundary event (Jarvis et al., 2006). The assignments of the Albian-Cenomanian and C-T boundary events are definitive, considering their stratigraphic relationships with the first occurrence of *R. globotruncanoides* and the last occurrence of *R. cushmani*, respectively. On the other hand, there is some uncertainty in correlation of MCE I due to apparent interregional differences in the duration of the *R. reicheli* zone (cf. Coccioni and Galeotti, 2003). However, the fact that the  $\delta^{13}\text{C}$  profile registers the diagnostic twin peaks, Ia and Ib (Mitchell et al., 1996), unambiguously supports our assignment of MCE I at Site 1050.

<sup>1</sup>GSA Data Repository item 2009111, Figure DR1 (supplement to Fig. 2), Figure DR2 (SEM images) and Table DR1 (stable isotope and Sr/Ca data), is available online at [www.geosociety.org/pubs/ft2009.htm](http://www.geosociety.org/pubs/ft2009.htm), or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Recognition of MCE Ia and Ib allows high-resolution correlation of the Site 1050 data with the contemporary fossil and sedimentary records in western Europe, as summarized in Figure 2A. In European sequence stratigraphy, a consensus has been reached for placing the major sequence boundary (SB Ce III) near the base of the middle Cenomanian substage. From SB Ce III upward is the lowstand systems tract, followed by the transgressive systems tract. Based on compilation of available information, MCE Ia corresponds to the maximum sea-level fall, which is deemed by some to have been paced by eustasy (e.g., Gale et al., 2008).

### Multitaxon Isotopic Trends

Remarkably coherent  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  trends with small intraspecific variations and systematic interspecies offsets are present across the mid-Cenomanian interval (Fig. 2). Foraminiferal  $\delta^{13}\text{C}$  values consistently track the coccolith fraction  $\delta^{13}\text{C}$  curve. Regarding foraminiferal  $\delta^{18}\text{O}$  data, values for each planktonic species are uniform from pre-MCE I to MCE Ia, followed by a positive excursion of as much as +1.0‰ at MCE Ib. The benthic  $\delta^{18}\text{O}$  trend is remarkably constant in the pre-MCE I interval as well, whereas high-amplitude fluctuations are evident during MCE I. This  $\delta^{18}\text{O}$  variability is illustrated by a single taxon (*Gyroidinoides* spp.) and hence is not an artifact of benthic microhabitat differences (e.g., Friedrich et al., 2006). The coccolith  $\delta^{18}\text{O}$  trend correlates well with the planktonic foraminiferal records, with a systematic offset due to the coccolithophorid vital effect (e.g., Ennyu et al., 2002).

The marked and consistent planktonic-benthic  $\delta^{18}\text{O}$  gradient (as large as ~3‰) represents preservation of primary paleoecological information, namely planktonic foraminiferal depth stratification (e.g., Sexton et al., 2006) (see  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  cross plots in Fig. 2A and GSA Data Repository Fig. DR1). The low  $\delta^{18}\text{O}$  and high  $\delta^{13}\text{C}$  values observed for *P. stephani* suggest its shallow habitat, while the high  $\delta^{18}\text{O}$  and low  $\delta^{13}\text{C}$  values of *R. montsalvensis* and *R. reicheli* suggest their deeper habitats. It is interesting that *R. globotruncanoides* delineates the isotopic signal between both end members, implying a hitherto unknown intrageneric variation in the depth ecology of *Rotalipora*.

### Diagenetic Assessment

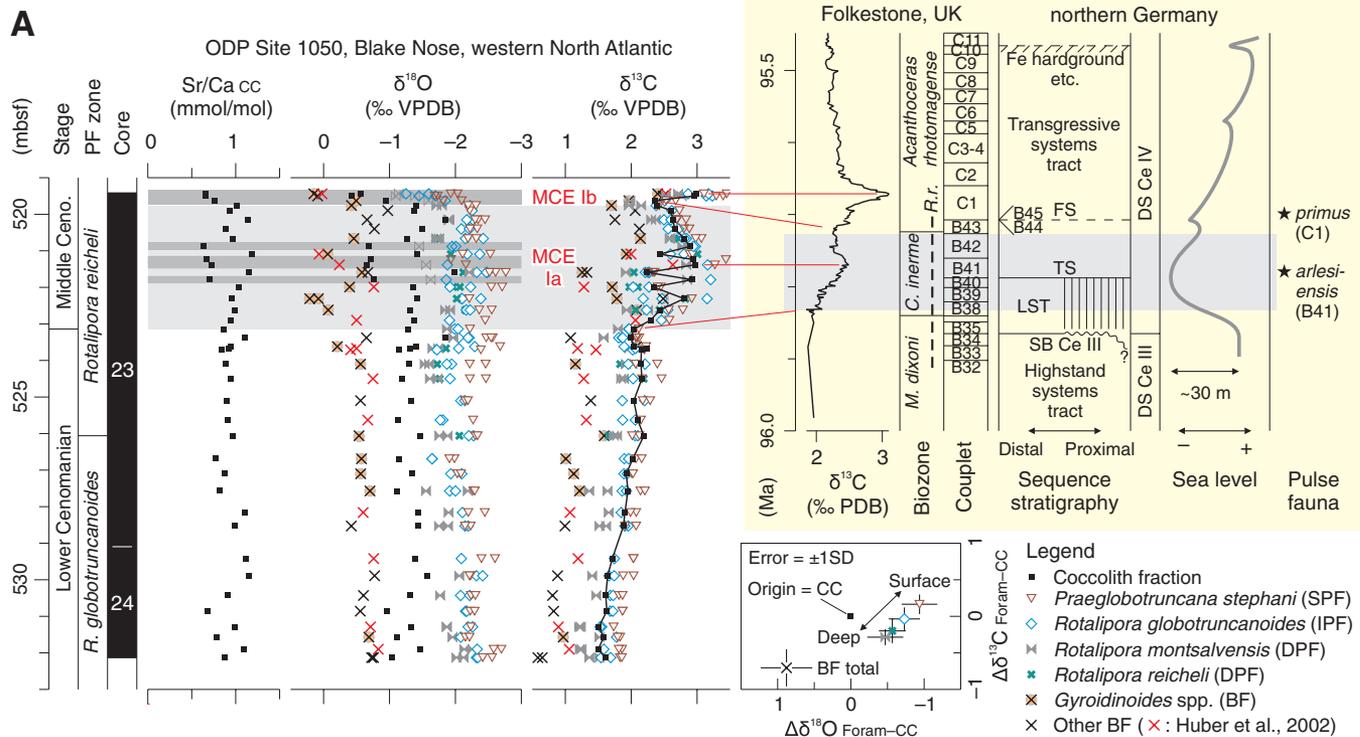
Significant correlation exists between Sr/Ca ratios and  $\delta^{18}\text{O}$  values in the coccolith fraction ( $R^2 = 0.80$ ) (Figs. 2A and DR1). Such strong Sr/Ca– $\delta^{18}\text{O}$  covariation is most likely a result of burial diagenesis (i.e., recrystallization), because secondary inorganic calcite is characterized by low Sr concentrations (e.g., Marshall, 1992; Ando et al., 2006) and by higher  $\delta^{18}\text{O}$  values through interaction with colder bottom and/or interstitial waters (Schrag et al., 1995; Sexton et al., 2006). However, an alternative paleoceanographic explanation may be possible for the observed correlation, such that coccolithophorid paleoproductivity (reflected in Sr/Ca; Stoll and Bains, 2003) and sea surface temperatures and/or salinity (reflected in  $\delta^{18}\text{O}$ ) covaried at this site.

SEM study illustrates good correspondence between Sr/Ca ratios and foraminiferal preservation (Figs. DR1 and DR2). Samples with lower Sr/Ca ratios exhibit a greater extent of secondary calcite development than those with higher Sr/Ca ratios (see Fig. DR2 caption for detailed explanation). Thus, the Sr/Ca– $\delta^{18}\text{O}$  covariation, including the remarkable multitaxon  $\delta^{18}\text{O}$  shift at MCE Ib, is best explained as an artifact of selective diagenesis. Considering that the Sr/Ca ratios as low as 0.7–0.8 are below the known range of ancient coccoliths (Stoll and Bains, 2003), data from those samples should be eliminated from further discussion.

## DISCUSSION AND IMPLICATIONS

### Evidence Against Glaciation Hypothesis

The updated Blake Nose isotopic record does not support the mid-Cenomanian glaciation hypothesis. If the major sea-level fall, as deduced



**Figure 2. A: Multitaxon  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data and coccolith fraction (CC) Sr/Ca data from across mid-Cenomanian interval at Ocean Drilling Program (ODP) Site 1050, and their chronostratigraphic integration (red line) with European reference chronostratigraphy and sequence stratigraphy. Cross plot of all foraminiferal  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  data is also shown with values after standardization with respect to coccolith fraction ( $=\Delta\delta_{\text{Foram-CC}}$ ). SPF, IPF, and DPF—surface-dwelling, intermediate-dwelling, and deep-dwelling planktonic foraminifera, respectively; BF—benthic foraminifera; VPDB—Vienna Pee Dee belemnite. Thick gray band marks mid-Cenomanian event (MCE) Ia interval. Thin dark gray shadings at Site 1050 highlight levels of selective diagenesis in MCE I based on Sr/Ca- $\delta^{18}\text{O}$  covariation (see text). Folkstone  $\delta^{13}\text{C}$  curve is from Jarvis et al. (2006), and biozone and marl-chalk couplet are from Paul et al. (1994) recalibrated against numerical ages of three ammonite datums (base *Mantelliceras dixonii* zone [97.39 Ma]; base *Cunningtoniceras inerme* zone [95.84 Ma]; base *Calycoceras guerangeri* zone [94.71 Ma]). Thick broken line denotes range of planktonic foraminifera *Rotalipora reicheli* (*R.r.*) (Mitchell and Carr, 1998). Sequence stratigraphy (shelf transect in northern Germany) and resultant sea-level curve are from**

**Wilmsen (2003, 2007), depicted to conform to Folkstone couplet scale. Additional two couplets (B44, B45) in northern Germany suggest ~80 k.y. hiatus at Folkstone (Gale et al., 1999). Placement of sequence boundary (SB) Ce III is relative to distinct facies change at B34-B35 boundary (Mitchell and Carr, 1998); this horizon is B33-B34 boundary at different areas (Gale, 1995; Wilmsen, 2007). LST—lowstand systems tract; DS—depositional sequence; TS—transgressive surface; FS—flooding surface. B: Diagenetically screened  $\delta^{18}\text{O}$  records in *R. reicheli* zone shown separately for each taxonomic group along with Sr/Ca data (see also Fig. DR1 [see footnote 1]).**

from sequence stratigraphy, actually resulted from the development of an Antarctic ice sheet, a pronounced positive  $\delta^{18}\text{O}$  shift should be present at MCE Ia in all taxa examined. However, as shown in Figure 2B, the planktonic  $\delta^{18}\text{O}$  record is constant and/or slightly shifted toward more negative values across this critical interval (e.g., *R. globotruncanoides*: pre-MCE I =  $-2.04\text{‰} \pm 0.18\text{‰}$  [mean  $\pm 1$  SD,  $n = 15$ ]; MCE Ia =  $-2.20 \pm 0.16\text{‰}$  [ $n = 23$ ]). Even if the expected foraminiferal  $\delta^{18}\text{O}$  shift associated with the hypothetical glaciation is small ( $0.43\text{‰}$ – $0.63\text{‰}$  for a 22 m sea-level fall with a 70% temperature component; Moriya et al., 2007), the isotopic signal should have been captured in our data set because the intraspecific variations are very small.

Our results validate those reported from Demerara Rise by Moriya et al. (2007). High-resolution  $\delta^{18}\text{O}$  analysis of “glassy” foraminifera notwithstanding, their Demerara Rise data set is still ambiguous as a global paleoceanographic signal because of limited age control and dependence

on the opportunistic taxon *Hedbergella delrioensis* with low  $\delta^{13}\text{C}$  values ( $\sim 1\text{‰}$  on average) for Cenomanian pelagic carbonates. Thus, with our new Blake Nose record, isotopic testing of the mid-Cenomanian glaciation hypothesis is more robust and conclusively negative.

### Benthic $\delta^{18}\text{O}$ Variation During MCE I

In contrast to the case of planktonic foraminifera, the diagenetic  $\delta^{18}\text{O}$  shift in benthic foraminifera is generally small because the tests are relatively robust, and secondary calcite forming through recrystallization would have  $\delta^{18}\text{O}$  values similar to those of the unaltered test (e.g., Schrag et al., 1995). Thus, the observed threefold positive  $\delta^{18}\text{O}$  fluctuations during MCE I can be interpreted as reflecting primary paleoceanographic variation. Note that the single positive benthic  $\delta^{18}\text{O}$  shift reported in Huber et al. (2002), which was employed to validate the mid-Cretaceous glaciation hypothesis (Miller et al., 2003, 2005), is no longer supported by the new  $\delta^{18}\text{O}$  data set (Figs. 1 and 2).

During the benthic  $\delta^{18}\text{O}$  excursions in MCE I, the planktonic-benthic  $\delta^{13}\text{C}$  difference is generally reduced (Fig. 2A), implying a less stratified ocean structure over Blake Nose, presumably due to strengthened upwelling or downwelling. If this observation can be extended to a basin-wide shift in deeper water circulation, then a physical paleoceanographic control (not cooling) may be possible for the pulse fauna in western Europe (Mitchell, 2005). Alternatively, such benthic  $\delta^{18}\text{O}$  fluctuations show some resemblance to those deciphered from Demerara Rise, for which regional incursion of high  $\delta^{18}\text{O}$  saline waters has been postulated (Friedrich et al., 2008). Further efforts are anticipated to elucidate the nature of short-term instability in North Atlantic intermediate-water and deep-water properties at the time of MCE I, and we expect that neodymium isotopes would be suitable tracers to address this issue (MacLeod et al., 2008).

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