Early Eocene to Late Miocene Variations in the South Atlantic CCD: Constraints from the Walvis Ridge Depth-Transect (ODP Leg 208)

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INTRODUCTION

Carbonate saturation profiles are complex and dynamic products of processes operating on spatiotemporal scales from the "short-term local" (e.g., carbonate export production, carbonate ion concentration) to the "long-term global" (e.g., carbonate-silicate weathering, shelf:basin carbonate partitioning). For example, in the modern ocean, the carbonate saturation profile typical of our current interglacial is predicted to shoal drastically as a result of the anthropogenic flux of CO_2 from fossil fuels to the ocean-atmosphere system. Thus, a refined history of carbonate saturation may provide insight on global carbon-cycle dynamics. An established, if crude, proxy for reconstructing carbonate saturation is the wt% carbonate content of pelagic sediments, where <20 wt% is ascribed to deposition below the carbonate compensation depth (CCD). A number of classic works (Figures 1 and 2) established first-order and presumably global CCD fluctuations, and largely attributed these fluctuations to shelf:basin partitioning via glacioeustatic sea level variations through the Cenozoic.

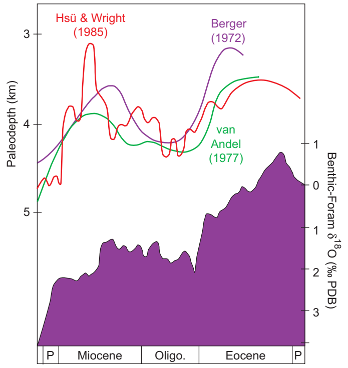


Figure 1. South Atlantic paleoCCD reconstructions and global benthic-foram $\delta^{18}O$ record (after Berger and Wefer, 1996).

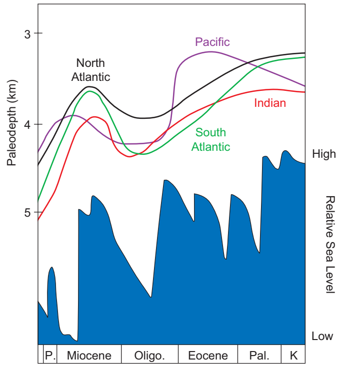


Figure 2. PaleoCCD reconstructions for various ocean basins and relative global sea level estimate (after van Andel, 1979).

STUDY LOCATION

The Walvis Ridge depth-transect of ODP Leg 208 represents an excellent opportunity to refine our understanding of the South Atlantic Cenozoic CCD (Figure 3). Six sites were drilled on the northwestern flank of the ridge, and this study focuses on Site 1267 and expands to the shallower Site 1266 and deeper Site 1262. While such closely spaced sites on a subsiding ridge would appear ideal for such studies, one potential caveat is the potential for downslope transport and reworking, and evidence exists for such processes at Site 1267 based on benthic foraminifer and calcareous nannoplankoton biostratigraphy (see Leg 208 Initial Report, 2003).

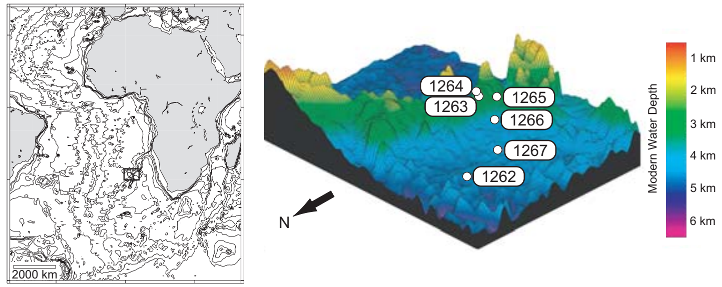


Figure 3. Drill sites of ODP Leg 208 on the South Atlantic Walvis Ridge
(Left map view from GMT; Right map is northwest 3-D view modified from Leg 208 Initial Results Volume)

METHODS AND RESULTS – SITE 1267

Wt% $CaCO_3$ is typically determined by spectrophotometric coulometry. For this study, we explored the fidelity of this evolved CO_2-based method with a dissolved [Ca]-based method using Inductively Coupled Plasma - Optical Emission Spectrophotomery (ICP-OES). For the ICP-OES method, a dry powered bulk-sediment split of known mass was acidified with a known volume of 0.5 M HNO_3 solution, a solution aliquot was analyzed by ICP-OES to determine [Ca], and wt% $CaCO_3$ was stoichiometrically calculated by assuming that $CaCO_3$ was the sole source of dissolved Ca.

Resultant wt% $CaCO_3$ values from the two methods for 92 Site 1267 samples are significantly correlated ($r^2 = 0.998$, $p < 0.001$; Figure 3), with a slope not significantly different from unity and a slightly (<1%) elevated y-intercept, perhaps due to minor non-$CaCO_3$-derived calcium. Therefore, the ICP-OES cation-based method was applied to a suite of 298 bulk sediment samples from Site 1267, with the resultant wt% $CaCO_3$ estimates plotted in the time-domain using the shipboard age-model (Figure 5, green circles).

These wt% $CaCO_3$ values are significantly correlated with their associated Natural Gamma Ray (NGR) values ($r^2 = 0.92$, $p < 0.001$; Figure 4), and this relationship was capitalized upon to synthesize a more continuous (~2.5-cm resolution) NGR-based wt% $CaCO_3$ record (Figure 5, green line). This synthetic record agrees well with the actual wt% $CaCO_3$ values (green circles; n = 298; unsurprising given their relationship) as well as 47 independent wt% $CaCO_3$ values from shipboard analyses (green triangles; n = 47). The presence of "negative" wt% $CaCO_3$ values in the synthetic record likely reflects (1) a failure to capture extremely high NGR end-member values in the calibration data set (i.e., Figure 4) and (2) locally elevated NGR values for the unsampled Middle Miocene interval at Site 1267.

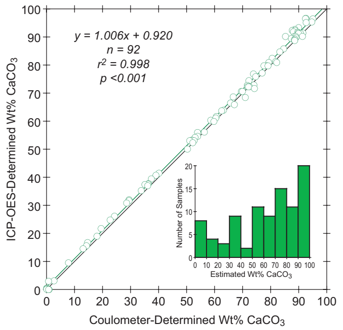


Figure 3. Comparison of ICP-OES cation-based and coulometry spectrophotometry-based methods for determining wt% $CaCO_3$.

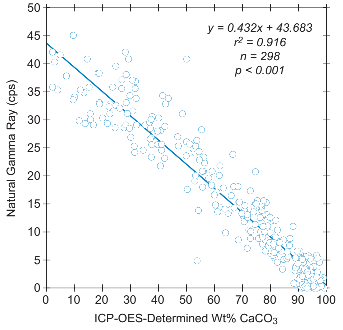


Figure 4. Correlation of natural gamma ray and ICP-OES-determined wt% $CaCO_3$.

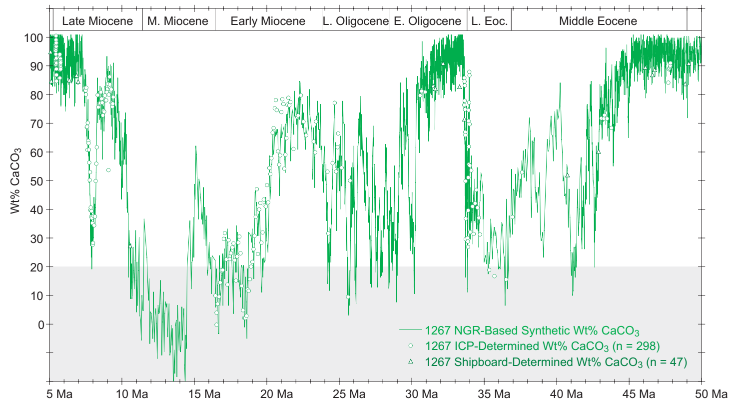
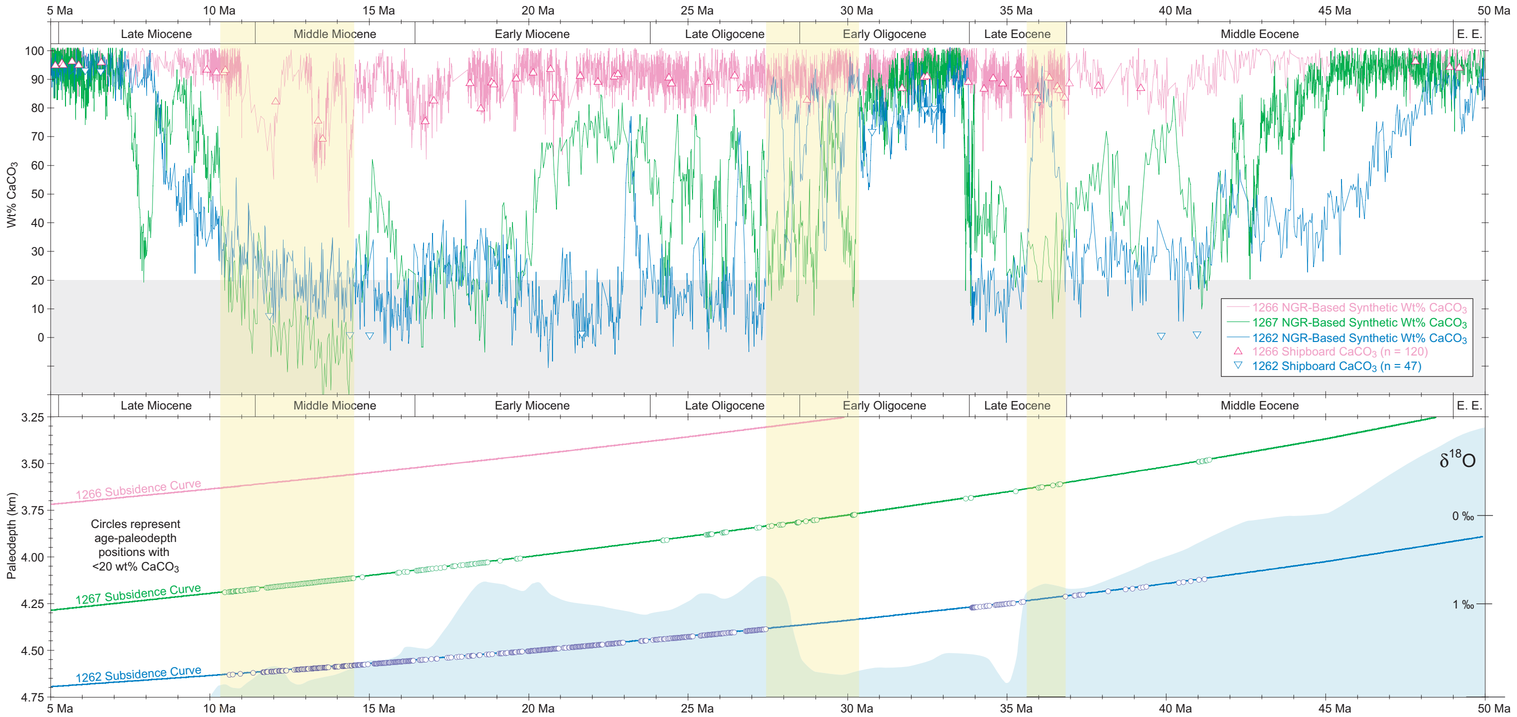


Figure 5. NGR-based wt% $CaCO_3$ record synthesized from the application of NGR–wt% $CaCO_3$ calibration (Figure 4) to the spliced ~2.5-cm-resolution NGR record for Site 1267. Circles and triangles are ICP-OES-determined and shipboard-determined wt% $CaCO_3$, respectively.

APPLICATION OF SITE 1267 NGR–WT% $CaCO_3$ CALIBRATION TO ~0.6 KM SHALLOWER SITE 1266 AND ~0.4 KM DEEPER SITE 1262 AND CONVERSION TO TIME–PALEODEPTH DOMAIN



APPLICATION OF SITE 1267 CALIBRATION TO OTHER SITES AND PALEODEPTH ESTIMATION

The upper panel above shows a preliminary attempt to constrain depth variation in the CCD through time by applying the Site 1267 NGR-wt% $CaCO_3$ calibration to the NGR records at the ~0.6 km shallower Site 1266 (red line) and ~0.4 km deeper Site 1262 (blue line) to produce analogous synthetic wt% $CaCO_3$ records. Site 1266 shipboard wt% $CaCO_3$ values (n = 120) shows good correspondence to its synthetic curve, whereas the more limited Site 1262 shipboard wt% $CaCO_3$ values (n = 47) appear to show slighly lower values compared to its synthetic curve at very low carbonate concentrations.

The lower panel above shows the calculated paleodepth through time for the three sites (lines) based on standard crustal subsidence equation corrected for sediment accumulation. Circles on each subsidence curve indicate time–paleodepth coordinates where sediments contained < 20 wt% $CaCO_3$. The Zachos et al. (2003) global benthic foram $\delta^{18}O$ curve is shown as a light blue backdrop.

OBSERVATIONS, INTERPRETATIONS, AND CAVEATS FOR PALEOCCD RECONSTRUCTION

In the Early Eocene, all three sites show high wt% $CaCO_3$, followed by a decreasing trend first in the deeper Site 1262 and then the intermediate Site 1267 through the early Middle Miocene. The paleoCCD appears to oscillate about Site 1262 paleodepths (~4.1-4.3 km) through the later Middle and Late Eocene, with a major "reversal" in expected 1267–1262 wt% $CaCO_3$ values (i.e., higher values at deeper site) during the early Late Eocene (yellow band). At the Eocene–Oligocene boundary, the paleoCCD rapidly deepens below Site 1262 (>4.3 km). A second "reversal" during the middle Oligocene (yellow band) is followed by paleoCCD shoaling above Site 1262 (>4.4 km) and perhaps transiently above Site 1267 (>3.8 km). By the middle Early Miocene, the paleoCCD rises above Site 1267 (>4.0 km), with marked transient decreases to 40-60 wt% $CaCO_3$ at the shallowest Site 1266, and remains above Site 1267 until rapidly deepening to below ~4.6 km in the early Late Miocene. A third "reversal" occurs during the late Middle Miocene through early Late Miocene (yellow band). These three "reversals" in expected 1267–1262 wt% $CaCO_3$ values may be due to reworking and downslope transport, minor intersite age-model offsets, and intersite errors in applying the Site 1267 calibration.

PRELIMINARY CONCLUSIONS

- ICP-OES cation-based and coulometry-based methods produce comparable wt% $CaCO_3$ values.
- NGR appears to be an excellent proxy for wt% $CaCO_3$ at Site 1267 and shows good potential for site-specific calibration at the other sites.
- Although some time intervals show a reversal in expected wt% $CaCO_3$ depth relations, temporal variations in the paleoCCD show good correspondence with benthic foraminifer $\delta^{18}O$, supporting glacioeustacy as a major driver of carbonate saturation variations.

ONGOING AND FUTURE WORK

- Site-specific NGR–wt% $CaCO_3$ calibration for Sites 1262 and 1266.
- Evaluation of reworking and downslope transport for "reversed wt% $CaCO_3$" intervals.
- Refinement of age-models via ongoing biostratigraphic and cyclostratigraphic research.
- Conversion of wt% $CaCO_3$ data to carbonate mass acccumulation rates.
- Estimation of lysocline variations through selected intervals by planktonic foram fragmentation, etc.

ACKNOWLEDGEMENTS

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