Drilling and Dating New Jersey Oligocene-Miocene Sequences: Ice Volume, Global Sea Level, and Exxon Records

Kenneth G. Miller,* Gregory S. Mountain, the Leg 150 Shipboard Party, and Members of the New Jersey Coastal Plain Drilling Project

Oligocene to middle Miocene sequence boundaries on the New Jersey coastal plain (Ocean Drilling Project Leg 150X) and continental slope (Ocean Drilling Project Leg 150) were dated by integrating strontium isotopic stratigraphy, magnetostratigraphy, and biostratigraphy (planktonic foraminifera, nannofossils, dinocysts, and diatoms). The ages of coastal plain unconformities and slope seismic reflectors (unconformities or stratal breaks with no discernible hiatuses) match the ages of global $\delta^{18}O$ increases (inferred glacioeustatic lowerings) measured in deep-sea sites. These correlations confirm a causal link between coastal plain and slope sequence boundaries: both formed during global sea-level lowerings. The ages of New Jersey sequence boundaries and global $\delta^{18}O$ increases also correlate well with the Exxon Production Research sea-level records of Haq *et al*. and Vail *et al*., validating and refining their compilations.

Eustatic (global sea level) changes exert one of the primary controls on the stratigraphic record (*1*, *2*), although controversy surrounds the age, magnitude, and mechanism of these changes (*3*). Vail *et al.* (*4*) and Haq *et al.* (*5*) reconstructed eustatic history by applying sequence stratigraphy to a global array of proprietary Exxon Production Research (EPR) data comprising seismic profiles, wells, and outcrops. Previously released EPR seismic data demonstrated that Oligocene to Recent sequences are well defined beneath the New Jersey shelf, although the age control on these sequences was poor (±1 million years or worse) (*6*). To improve understanding of sea-level change, we collected additional multichannel seismic data (cruise Ew9009) and traced seismic sequences from the New Jersey shelf to the slope (*7*). These sequences were dated at four slope sites drilled during Ocean Drilling Project (ODP) Leg 150 (*8*) (Fig. 1). Drilling onshore at Island Beach, Atlantic City, and Cape May, New Jersey (ODP Leg 150X; Fig. 1), provided additional ages and facies of these same sequences in much shallower paleodepths (*9*). This report synthesizes Leg 150 and Leg 150X chronologic studies of Oligocene to middle Miocene sequences that are preserved onshore and have the clearly visible seismic reflection terminations offshore. We compare the stratigraphic record of the New Jersey sequence with published $\delta^{18}O$ records (Figs. 1 and 2) and with the inferred eustatic record of Haq *et al.* (*5*).

Deep-sea $\delta^{18}O$ records provide a proxy for ice volume and sea-level (glacioeustatic) changes during the Oligocene to Recent "Icehouse World" (*10*, *11*). Glaciomarine sediments near Antarctica and deep-sea oxygen isotopic records (*10*, *11*) indicate that large ice sheets have existed in Antarctica since the earliest Oligocene [~35 million years ago (Ma) (*12*)]. Because ice preferentially sequesters light oxygen isotopes, fluctuations in ice volume cause changes in global seawater $\delta^{18}O$ (δ_w). These global δ_w changes are recorded by benthic and planktonic foraminifera along with variations in seawater temperature and local isotopic composition. Comparisons of benthic and low-latitude (nonupwelling) planktonic foraminiferal $\delta^{18}O$ records can be used to isolate ice volume effects from local isotopic and temperature changes (*13*). Using this strategy, Miller *et al.* (*10*) and Wright and Miller (*14*) identified 12 Oligocene to Miocene benthic foraminiferal $\delta^{18}O$ increases (all >0.5 per mil); these increases culminated in $\delta^{18}O$ maxima that were used to define zones Oi1 to Oi2b and Mi1 to Mi7 (Figs. 1 and 2 and Table 1). Six of the $\delta^{18}O$ increases are also recorded by tropical or subtropical planktonic foraminifera; the other six lack suitable low-latitude isotopic records. Miller *et al.* (*10*) interpreted coeval increases in benthic and planktonic $\delta^{18}O$ records as the consequence of glacioeustatic lowerings of ~30 to 80 m. On the basis of the ODP Site 747 $\delta^{18}O$ record (Fig. 1), we suggest that the Mi3 increase (13.4 to 14 Ma; Table 1) can be split into two increases (Mi3a and Mi3b). We assume that all 13 Oligocene to early-to-late Miocene $\delta^{18}O$ increases (Figs. 1 and 2) reflect million-year scale increases in ice

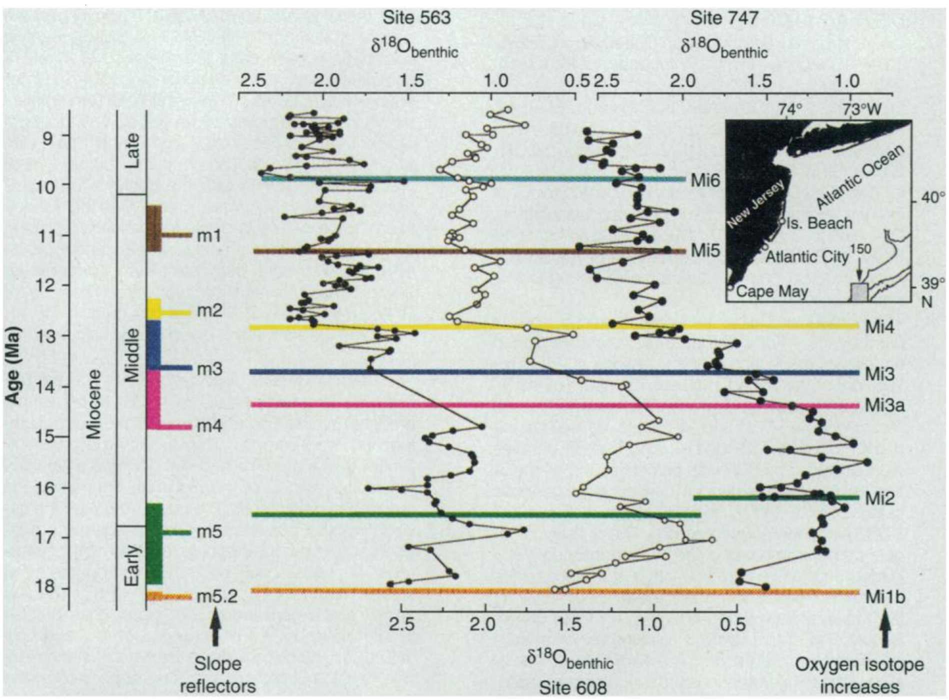

Fig. 1. Comparison of the timing of middle Miocene reflectors on the New Jersey slope with three benthic foraminiferal $\delta^{18}O$ records (units are per mil). Zones Mi1b to Mi6 are oxygen isotopic zones associated with the $\delta^{18}O$ increases. Reflectors m5.2 to m1 are dated on the New Jersey slope. Two independently dated sets of stippled lines are shown: (i) lines are drawn through inflections in the $\delta^{18}O$ records; (ii) ages of the reflectors are shown as best estimates (lines) and error bars (boxes) (Table 1). Oxygen isotope data for ODP sites 563 (western North Atlantic), 608 (eastern North Atlantic), and 747 (Indian sector, Southern Ocean) are generated on *Cibicidoides* spp. after Wright and Miller (*14*). Inset map shows locations of the onshore and offshore drilling sites.

K. G. Miller, Department of Geological Sciences, Rutgers University, Piscataway, NJ 08855, USA, and Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA.
G. S. Mountain, Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY 10964, USA.
The members of the Leg 150 shipboard party and the New Jersey Coastal Plain Drilling Project are listed (*33*).

*To whom correspondence should be addressed.

volume, although additional low-latitude planktonic foraminiferal $\delta^{18}O$ data are needed to confirm this (*15*).

Oligocene to Recent seismic reflections beneath the New Jersey shelf exhibit erosional truncation, onlap, downlap, and toplap and are thus objectively identified as sequence boundaries (*4*, *6*, *8*). We traced these sequence boundaries from the shelf to the slope, using both EPR and Ew9009 multichannel seismic data including Red, Tuscan, Yellow-2, Pink-2, and Green (*6*) plus Ochre, Sand, True Blue, Pink-3, and Green-2 (*8*). To simplify the nomenclature and incorporate reflections restricted to the slope, we use a unified alpha-numeric scheme (o1, m6; Figs. 1 and 2 and Table 1) based on the results of ODP Leg 150 (*8*).

We derived time-depth relations for correlating seismic profiles to the boreholes from three sources: the velocity log from the Continental Offshore Stratigraphic Test (COST) B-3 well, semblance velocities from analysis of Ew9009 Common Depth Point (CDP) stacks on the adjacent shelf, and sonobuoy data from the continental rise (*8*). Synthetic seismograms derived from log (*8*) and core physical properties data (*16*) were used to evaluate these correlations. The sedimentary expression of sequence boundaries on the slope is muted because of relatively uniform Oligocene to Miocene lithologies (silty clays) (*8*), and several reflectors are associated with a correlative conformity (*17*). Still, many sequence boundaries are associated with hiatuses or increased sand content immediately above the boundary, both of which yield impedance contrasts (*8*) and consequently seismic reflections.

We developed the Oligocene to middle Miocene chronology on the slope by integrating Sr isotopic stratigraphy (*17*) and magnetostratigraphy (*18*) with planktonic foraminiferal (*19*), nannofossil (*20*), dinocyst (*21*), and diatom (*22*) biostratigraphy (Table 1). We do not discuss late Miocene to Recent history here because (i) the chronology of the upper Miocene slope sections is still uncertain, (ii) Pliocene strata are poorly represented in the slope boreholes, and (iii) the recovered Quaternary sections were restricted to the middle Pleistocene (stages 15 to 5.5) and Recent (*23*).

Onshore boreholes recovered fossiliferous Oligocene to middle Miocene strata; younger strata were mostly unfossiliferous and undateable (*9*, *24*). We identified unconformities (sequence boundaries) in the onshore boreholes using physical stratigraphy, including erosional contacts, reworking, bioturbation, major facies changes, gamma-ray peaks, and paraconformities inferred from biostratigraphic and Sr isotopic age breaks. Onshore sequences consist of basal transgressive deposits (Transgressive Systems Tracts; glauconitic in the Oligocene; occasionally shelly in the Miocene) that progressively shallow upsection to medial silts and upper sands (High-Stand Systems Tracts); low-stand deposits are not found on the coastal plain but are restricted to beneath the shelf and slope (*6*). Miocene onshore sequences were named Kw0 to Kw-Cohansey (*9*, *25*), whereas Oligocene sequences were termed O1 to O6 (*26*). Age control for the Miocene onshore sections relies primarily on Sr isotopic stratigraphy with an age resolution of ± 0.4 million years for the early Miocene and ± 0.9 million years for the middle Miocene (*27*). Diatom and planktonic foraminiferal biostratigraphy supplements Miocene onshore control (*9*, *25*). We derived age control for Oligocene onshore sections by integrating magnetostratigraphy, biostratigraphy (planktonic foraminifera and nannofossil), and Sr isotopic stratigraphy, with a resulting stratigraphic resolution of better than ± 0.5 million years in most cases.

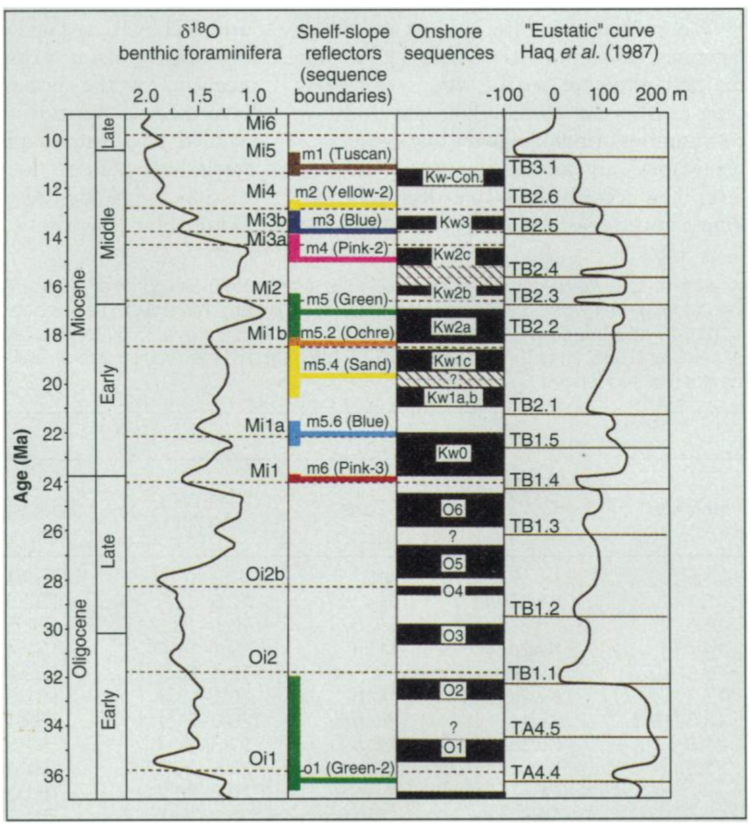

Fig. 2. Comparison of the timing of Oligocene to middle Miocene reflectors on the New Jersey slope with a benthic foraminiferal $\delta^{18}O$ record, a summary of onshore sequences, and the inferred eustatic record of Haq *et al.* (*5*). The $\delta^{18}O$ record is a stacked composite of *Cibicidoides* spp. from several sites that has been smoothed to remove all periods longer than ~1 million years (*32*); Oi1 to Mi6 are $\delta^{18}O$ maxima; dashed lines indicate inflections in the $\delta^{18}O$ records immediately before the maxima. Reflectors o1 to m1 are dated on the New Jersey slope and are shown with best age estimates indicated with thin lines and error bars indicated with boxes (Table 1). Onshore sequences are indicated by dark boxes; the white areas in between are hiatuses. Sequences O1 to O6 are Oligocene, and Kw0 to Kw-Cohansey (Coh) are Miocene onshore New Jersey sequences; cross-hatched areas indicate uncertain ages. Sequences TA4.4 to TB3.1 are from Haq *et al.* (*5*), and arrows are drawn at the inflection points in their inferred eustatic record.

There is excellent correlation between the timing of the major Oligocene to middle Miocene slope reflectors dated at the Leg 150 slope sites and glacioeustatic lowerings inferred from the $\delta^{18}O$ record (Figs. 1 and 2 and Table 1). Reflectors o1, m6, m5.6, m5.2, m5, m4, m3, m2, and m1 correlate with the Oi1, Mi1, Mi1a, Mi1b, Mi2, Mi3a, Mi3b, Mi4, and Mi5 $\delta^{18}O$ increases, respectively (Figs. 1 and 2 and Table 1). This similarity confirms a link between sequence boundaries traced from the shelf and glacioeustatic changes. Of the reflectors, only m5.4 does not appear to have a corresponding $\delta^{18}O$ increase. Of the $\delta^{18}O$ increases, only Oi2b and Oi2 fail to have equivalent reflectors because Oligocene seismic resolution is limited by the thin section and concatenated reflections on the slope (Fig. 2).

Detailed comparison of the ages of slope reflectors and their corresponding error estimates with three of the middle Miocene benthic foraminiferal $\delta^{18}O$ records used to define the Mi zones (Fig. 1) shows remarkably similar ages for the $\delta^{18}O$ inflections and reflectors. This comparison indicates that the sequence boundaries formed during intervals of rapid glacioeustatic fall, as predicted by various models (*28*).

This link between offshore New Jersey sequences and $\delta^{18}O$ records is further strengthened if one compares the slope sequences with their correlative onshore counterparts (Fig. 2). Early to middle Miocene onshore sequence boundaries correlate well with major $\delta^{18}O$ increases (*24, 25*) (Fig. 2 and Table 1), indicating that these unconformities were formed by global sea-level lowerings. Oligocene Oi1, Oi2, and Oi2b $\delta^{18}O$ increases also correlate with onshore sequences O1, O3, and O5, respectively (*26*). Sequence boundaries O2, O4, and O6 may correlate with minor $\delta^{18}O$ increases noted in recently published records (*29*).

The onshore and offshore sequences compare well with each other and with the $\delta^{18}O$ record. The exceptions are as follows: (i) The Kw1c sequence boundary correlates with the m5.4 slope reflector but with no $\delta^{18}O$ change within 1 million years. Either Kw1c or m5.4 sequences are the result of a local lowering of base level, or they may correlate with a minor $\delta^{18}O$ increase at about 21 Ma (*14*). (ii) The Kw2c sequence boundary has no definite offshore counterpart. We are uncertain of the significance of this sequence boundary onshore because it has been recovered at only one borehole (Cape May). (iii) The Oligocene onshore boreholes record sequences not resolved on slope seismic profiles because of slope sediment starvation.

Although the record of Haq *et al.* (*5*) has come under criticism as a reliable indicator of eustatic change (*3*), there is excellent correlation between the record of Haq *et al.* and the New Jersey records in both the number and ages of Oligocene to middle Miocene sequences (Fig. 2 and Table 1). Comparison of the ages of the two independent sets of sequences shows the following essentially identical ages: TB2.6 and m2 sequences (~12.6 Ma); TB2.5 and m3 (~13.6 Ma); TB2.3 and m5 (16.5 to 16.9 Ma); and TB1.5 and m5.6 (22 Ma). The ages of the Oligocene TB1.4 and m6, TB1.3 and O6, TB1.2 and O5, TB1.2 and O3, TB4.5 and O2, and TB4.4 and O1 sequences are similar when they are corrected for differences in the time scale used in each study (*30*). The record of Haq *et al.* (*5*) also compares well with the $\delta^{18}O$ increases (Table 1). However, on the basis of our correlation to the New Jersey sequences and $\delta^{18}O$ records, there are differences compared to the ages of several other of the Miocene sequences of Haq *et al.* (Table 1). It appears that TB3.1 (10.5 Ma), TB2.4 (15.5 Ma), and TB2.2 (17.5 Ma) correlate with ~11-Ma, 14.8-Ma, and 18.5-Ma slope reflectors and with the ~11.4-Ma, 14.4-Ma, and 18.5-Ma $\delta^{18}O$ increases, respectively (Table 1). The minor differences in age (Table 1) among the sequences of Haq *et al.*, New Jersey slope reflectors, and the $\delta^{18}O$ increases are generally within the errors in dating the margin sequences. For example, differences in age between the $\delta^{18}O$ inflections and the New Jersey sequences are less than 0.6 million years in all cases but one (Table 1); differences with the record of Haq *et al.* are larger because the latter relied on well cuttings [particularly on the New Jersey margin (*6*)] and not on continuously cored boreholes.

We suggest that the ages of the $\delta^{18}O$ increases (inflections on Table 1) provide the best estimates on the timing of Oligocene to Miocene eustatic falls and that unconformities (including seismic sequence boundaries) are formed during falls in sea level. Our records show that deposition resumed in the coastal plain by the time of the lowest low stand (maximum $\delta^{18}O$ values; Fig. 2). Our margin chronologic resolution is insufficient to evaluate small leads and lags (<1/4 of a cycle or a resolution of better than 0.25 to 0.5 million years) between eustatic falls and the timing of unconformities or hiatuses on the New Jersey margin. Reynolds *et al.* (*31*) used forward models to predict that the unconformities begin to form on old, slowly subsiding margins such as New Jersey early in the fall of sea level (before the inflection and the maximum rate of fall). We cannot yet evaluate at what point in a eustatic fall the unconformities begin to form on this margin.

Although it is not possible to evaluate fully the age errors in the EPR records, ours can be specified. Stratigraphic resolution is coarse in some intervals (for example, reflectors m5 and m5.4 have age uncertainties of at least ±0.9 and ±1.1 million years, respectively; Table 1), whereas others are well dated by integrating Sr isotopic, magnetostratigraphic, and biostratigraphic data. For example, the small uncertainty in the age of reflector m6 (23.8 ± 0.2 Ma) allows a precise and unequivocal correlation with the Mi1 oxygen isotopic increase (inflection at 23.8 Ma; Fig. 2).

Given that some reflectors and sequences have age errors of greater than 0.5 million years, one could argue that the correlations shown on Figs. 1 and 2 are at best fortuitous and, at worse, are beyond the precision of the geochronology that we have used. Using this argument, Miall (*3*) claimed that stratigraphic resolution may not be sufficient to document precise correlation and causal links between sequences and the global synthesis of Haq *et al.* (*5*). In

Table 1. Comparison of Sr isotope–based age estimates of Oligocene–middle Miocene seismic reflectors, New Jersey continental slope with onshore sequences (*24, 26*), oxygen isotopic increases (*10, 14*), and the sequences of Haq *et al.* (*5*). The column labeled Best uses the older (1985) time scale, whereas the column labeled BKSA95 provides the ages of sequences using the new (1996) time scale of Berggren *et al.* (*12*). We obtained corrected ages of Haq *et al.* (*5*) by linearly interpolating ages between TB1.4 corrected for time scale differences (24.2 versus 25.5 Ma), the revised age of the TB1.1 sequence of 32.2 Ma (*30*), and the revised age of TA4.4 of 35.9 Ma (*30*).

Slope reflector	Age estimate (Ma)		Onshore sequence	$\delta^{18}O$		Haq *et al.*	
	Best (error)	BKSA95		Zone	Maximum inflection	Sequence	Age/corrected age
m1 (Tuscan)	~11 (10.5–11.3)	~11.5		Mi5	11.3–11.4	TB3.1	10.5
m2 (Yellow-2)	12.5 (12.5–12.6)	12.7	Kw-Coh?	Mi4	12.6–12.8	TB2.6	12.5
m3 (Blue)	13.6 (12.8–13.6)	13.6	Kw3	Mi3b	13.5–13.6	TB2.5	13.8
m4 (Pink-2)	14.8 (13.8–15.0)	14.7	Kw2c	Mi3a	14.1–14.4*	TB2.4	15.5
m5 (Green)	~16.9 (16.3–18.0)	~16.6	Kw2b	Mi2	16.1–16.3	TB2.3	16.5
m5.2 (Ochre)	18.2 (18.0–18.4)	17.7	Kw2a	Mi1b	18.1–18.5	TB2.2	17.5
m5.4 (Sand)	19–20 (18.4–20.6)	18.8–19.8	Kw1c	?minor	?20.6–21.1*	TB2.1	21.0
m5.6 (True blue)	~22 (21.5–22.5)	21.8	Kw1a,b	Mi1a	21.8–22.4	TB1.5	22.0
m6 (Pink-3)	23.8 (23.6–24.0)	23.8	Kw0	Mi1	23.5–23.8	TB1.4	25.5/24.2
			O6	?minor	26.0–26.2*	TB1.3	26.5/26.3
			O5	Oi2b	28.0/28.2	TB1.2	28.4/29.4
			O4	?minor	?		
			O3	Oi2	31.5–32.0	TB1.1	30.0/32.2
			O2	?minor	?	TB4.5	33.0/34.4
o1 (Green)	35.8–36.7 (32–36.7)		O1	Oi1	35.8–36.0	TA4.4	36.0/35.9

*Not a formal isotopic zone.

contrast, we propose that it is unnecessary to demonstrate that every event correlates with a resolution of better than 0.5 million years. We have anchored key stratigraphic levels (such as reflectors m1 to m4 and m6) to a precise chronology and report a similar number of events in both the margin and $\delta^{18}O$ records, indicating that unconformities (sequence boundaries) correlate with glacioeustatic lowerings. By firmly dating the sequences and providing error estimates for these ages, we provide a template of Oligocene to Miocene sequences that will be compared with records from other margins.

REFERENCES AND NOTES

1. L. L. Sloss, *Geol. Soc. Am. Bull.* **74**, 93 (1963).
2. J. Imbrie *et al.*, *Report on the Second Conference on Scientific Ocean Drilling* (European Science Foundation, Strasbourg, France, 1988).
3. A. D. Miall, *J. Sediment. Petrol.* **61**, 497 (1991).
4. P. R. Vail *et al.*, *Mem. Am. Assoc. Pet. Geol.* **26**, 49 (1977).
5. B. U. Haq, J. Hardenbol, P. R. Vail, *Science* **235**, 1156 (1987).
6. S. M. Greenlee, W. J. Devlin, K. G. Miller, G. S. Mountain, P. B. Flemings, *Geol. Soc. Am. Bull.* **104**, 1403 (1992).
7. K. G. Miller and G. S. Mountain, *Proc. Ocean Drilling Program Init. Rep.* **150**, 11 (1994).
8. G. S. Mountain *et al.*, Eds., *ibid.*, p. 1.
9. K. G. Miller *et al.*, *ibid.* **150X**, 5 (1994); K. G. Miller *et al.*, *Proc. Ocean Drilling Program Sci. Results*, in press.
10. K. G. Miller, J. D. Wright, R. G. Fairbanks, *J. Geophys. Res.* **96**, 6829 (1991); K. G. Miller, R. G. Fairbanks, G. S. Mountain, *Paleoceanography* **2**, 1 (1987).
11. J. C. Zachos, L. D. Stott, K. C. Lohmann, *Paleoceanography* **9**, 353 (1994).
12. W. A. Berggren, D. V. Kent, J. J. Flynn, J. A. van Couvering, *Geol. Soc. Am. Bull.* **96**, 1407 (1985). We use this time scale throughout, except as noted on Table 1. Although the revised time scale of W. A. Berggren, D. V. Kent, C. C. Swisher, and M. P. Aubry [in *Geochronology, Time Scales, and Global Stratigraphic Correlation* (SEPM Special Publ. **54**, Society for Sedimentary Geology, Tulsa, OK, in press)] dramatically revises the Oligocene ages (with minor changes in the Miocene), we report the Leg 150 studies using the older scale to maintain consistency among all leg results.
13. N. J. Shackleton and N. D. Opdyke, *Quat. Res.* **3**, 39 (1973).
14. J. D. Wright and K. G. Miller, *Proc. Ocean Drilling Program Sci. Results* **120**, 855 (1992).
15. There are higher frequency (10^4 to 10^5 years, "Milankovitch scale") $\delta^{18}O$ and sea-level variations embedded within the longer term (10^6 years) changes (Figs. 1 and 2) that we do not address.
16. J. M. Lorenzo and S. P. Hesselbo, *Proc. Ocean Drilling Program Sci. Results*, in press.
17. K. G. Miller, C. Liu, M. Feigenson, *ibid.*, in press.
18. M. Van Fossen and M. Urbat, *ibid.*, in press.
19. S. W. Snyder, K. G. Miller, E. Saperson, *ibid.*, in press.
20. M.-P. Aubry, *ibid.*, in press.
21. L. de Verteuil, *ibid.*, in press.
22. L. H. Burckle, *ibid.*, in press.
23. B. A Christensen, B. Hoppie, R. Thunell, K. G. Miller, L. Burckle, *ibid.*, in press.
24. K. G. Miller and P. J. Sugarman, *Geology* **23**, 747 (1995).
25. P. J. Sugarman, K. G. Miller, J. P. Owens, M. D. Feigenson, *Geol. Soc. Am. Bull.* **105**, 423 (1993).
26. S. F. Pekar, thesis, Rutgers University (1995); ______ and K. G. Miller, unpublished manuscript.
27. J. S. Oslick, K. G. Miller, M. D. Feigenson, J. D. Wright, *Paleoceanography* **9**, 427 (1994).
28. W. C. Pitman, *Geol. Soc. Am. Bull.* **89**, 1389 (1978).
29. E. Barrera, J. Baldauf, K. C. Lohmann, *Proc. Ocean Drilling Program Sci. Results* **130**, 269 (1993).
30. See also K. G. Miller, P. R. Thompson, and D. V. Kent [*Paleoceanography* **8**, 313 (1993)] for discussion of this in Alabama boreholes.
31. D. J. Reynolds, M. S. Steckler, B. J. Coakley, *J. Geophys. Res.* **96**, 6931 (1991).
32. J. D. Wright, K. G. Miller, *Antarct. Res. Ser.* **60**, 1 (1994).
33. The Leg 150 shipboard party includes K. G. Miller and G. S. Mountain; P. Blum and S. Gartner, Texas A&M University, College Station, TX 77845, USA; P.-G. Alm, University of Lund, S-221 00 Lund, Sweden; M.-P. Aubry, Institut des Sciences de l'Evolution, Montpellier Cedex 5, France; L. H. Burckle, G. Guerin, M. E. Katz, Lamont-Doherty Earth Observatory; B. A. Christensen, University of South Carolina, Columbia, SC 29208, USA; J. Compton, University of South Florida, St. Petersburg, FL 33701, USA; J. E. Damuth, University of Texas, Arlington, TX 76019, USA; J.-F. Deconinck, Universite de Lille, 59655 Villeneuve D'Asq Cedex, France; L. de Verteuil, University of Toronto, Ontario M5S 3B1, Canada; C. S. Fulthorpe, University of Texas, Austin, TX 78759, USA; S. P. Hesselbo, University of Oxford, Oxford OX1 3PR, UK; B. Hoppie, University of California, Santa Cruz, CA 95064, USA; N. Kotake, Chiba University, Chiba 263, Japan; J. M. Lorenzo, Louisiana State University, Baton Rouge, LA 70803, USA; S. McCracken, University of Western Australia, Nederlands, 6009 Australia; C. M. McHugh, Queen College, Flushing, NY 11367, USA; W. C. Quayle, University of Newcastle, Newcastle on Tyne, NE1 7RU UK; Y. Saito, Geological Survey of Japan, Higashi 1-1-3, Tsukuba, Ibaraki 305, Japan; S. W. Snyder, East Carolina State University, Greenville, NC 27858, USA; W. G. ten Kate, Free University, Amsterdam, The Netherlands; M. Urbat, Universitat zur Koln, 500 Koln, Germany; M. C. Van Fossen, Rutgers University; and A. Vecsei, Geologisches Institut der Universitat, 79104 Freiburg i. Br., Germany. The New Jersey Coastal Plain Drilling Project includes K. G. Miller; P. J. Sugarman and L. Mullikin, New Jersey Geological Survey, Trenton, NJ 08625, USA; S. Pekar, J. V. Browning, C. Liu, M. C. Van Fossen, M. D. Feigenson, M. Goss, D. Gwynn, Rutgers University; D. V. Kent and L. H. Burckle, Lamont-Doherty Earth Observatory; M.-P. Aubry, Institut des Sciences de l'Evolution; D. Queen, D. Powars, T. Heibel, U.S. Geological Survey, Reston, VA 22092, USA; and D. Bukry, U. S. Geological Survey, Menlo Park, CA 94025, USA.

34. We thank three anonymous reviewers for comments. Supported by NSF grants OCE89-11810, OCE92-03282, and EAR92-18210 and by the Joint Oceanographic Institute of the U.S. Science Advisory Council. This is Lamont-Doherty Earth Observatory contribution 5456.

29 September 1995; accepted 21 December 1995

Self-Assembling Dendrimers

Steven C. Zimmerman,* Fanwen Zeng, David E. C. Reichert, Sergei V. Kolotuchin

Hydrogen bond–mediated self-assembly is a powerful strategy for generating large structures from smaller subunits. The synthesis of molecules containing two isophthalic acid units covalently attached to a rigid aromatic spacer is described. By normal pairing of carboxylic acids into hydrogen-bonded dimers, these molecules self-assemble in organic solvents to form either a series of linear aggregates or a cyclic hexamer. These molecules were linked to the core of a family of polyether dendrimers, which caused the hexamer to be formed preferentially. The stability of the hexamer depended on the generation number of the dendrimer. The largest of these hydrogen-bonded macromolecular assemblies is roughly disk-shaped with a 9-nanometer diameter and a 2-nanometer thickness. Its size and molecular mass (34,000 daltons) are comparable to that of small proteins.

One of the hallmarks of biological organization is the noncovalent assembly of large structures from smaller subunits. The self-assembly strategy not only minimizes the energy invested in synthesis, it maximizes the accuracy with which the subunits can be produced, and therefore better guarantees the structural fidelity of the ultimate assembly. The same reasoning and principles have been applied recently to the construction of abiotic structures, where the chemical synthesis of compounds with nanometer dimensions remains a formidable challenge (*1*). Among the most notable nanoscale compounds synthesized to date are the dendrimers, a group of highly branched macromolecules emanating from a central core to a periphery that becomes more dense with increasing generation number (*2–5*). A wide range of dendrimers have been prepared through iterative synthesis.

Dendrimers can be made in multigram quantities, and their large size and controllable peripheral functionality make them ideal building blocks for assembling larger nano- and mesoscopic structures in solution (*2*). For example, amphiphilic compounds wherein a hydrophobic dendrimer resides at one end of a hydrophilic polyethyleneoxide polymer aggregate in aqueous solution (*4*) and act as surfactants (*6*). Likewise, the hydrophobic linker in dumbbell-shaped arborols stack to form rod-shaped assemblies, resulting in gel formation in aqueous solution (*7*). Meijer and co-workers recently reported that dendritic block copolymers with amphiphilic character self-assemble to

Department of Chemistry, 600 South Mathews Avenue, University of Illinois, Urbana, IL 61801, USA.

*To whom correspondence should be addressed.