sites, one of which does not take part in the exchange process because a proton on this site protrudes into the sodalite cage, which is inaccessible to methane. For the remaining three accessible pathways, the proton affinity differences are 35 kJ mol^{-1} or higher. In combination with the appropriate Boltzmann factors for the proton occupancy of oxygen sites, this leads to a reduction of the exchange rate by a factor of 80 at 700 K compared with the molecular catalyst.

MFI has a more complex crystal structure with 12 different T-sites[23]. For each of these, we repeated the calculation outlined above. Between different T-sites, the exchange rate varied by two orders of magnitude (Fig. 3). The large activity differences corroborate empirical evidence that the acid sites are heterogeneous[24]. Assuming a random distribution of aluminium over all T-sites, the overall exchange rate in MFI is the average of these exchange rates, which at 700 K is a factor of 20 lower than that of the molecular catalyst and thus a factor 4 larger than in FAU. These reduction factors vary with temperature; the predicted reaction-rate dependencies are shown by dashed lines in Fig. 1.

The theoretical predictions of the relative rates for the two zeolites and their temperature dependence agree well with experiment. It should be mentioned that there is a 20 kJ mol^{-1} uncertainty in the absolute value of the barrier as predicted by quantum chemistry. But this uncertainty affects the predictions for all zeolites to the same extent, so the prediction of a factor of four difference in reactivity between zeolites FAU and MFI is not affected.

Our results show that heterogeneous catalysts can be understood at the atomic level, and that quantitative agreement between theory and experiment can be achieved. For the exchange reaction studied here, we have predicted the reaction path and established the relationship between acidity and catalytic activity. When combined with theoretical estimates for the proton affinity of the various oxygen sites within the zeolite, this gives an *ab initio* prediction of heterogeneous catalytic activity. Applying the argument in reverse, it gives a first, albeit indirect, experimental measure of the acidity differences in zeolites, which must be ~ 60 kJ mol^{-1} to explain satisfactorily the reactivity differences between FAU and MFI. □

Received 29 January; accepted 7 May 1993.

1. Thomas, J. M. *Scient. Am.*, **266** (IV), 82–88 (1992).
2. Maxwell, I. E. & Stork, W. H. J. in *Introduction to Zeolite Science and Practice*, (eds van Bekkum, H. *et al.*) 571–630 (Elsevier, Amsterdam, 1991).
3. Jacobs, P. A. & Martens, J. A. in *Introduction to Zeolite Science and Practice*, (eds van Bekkum, H. *et al.*) 445–496 (Elsevier, Amsterdam, 1991).
4. Abbot, J. & Wojciechowski, B. W. *J. Catal.* **115**, 1–15 (1989).
5. Stefanidis, C., Gates, B. C. & Haag, W. O. *J. Molec. Catal.* **67**, 363–367 (1991).
6. Sauer, J., Kölmel, C. M., Hill, J. R. & Ahlrichs, R. *Chem. Phys. Lett.* **164**, 193–198 (1989).
7. Sauer, J., Horn, H., Häser, M. & Ahlrichs, R. *Chem. Phys. Lett.* **173**, 26–32 (1990).
8. Dubsky, J. Beran, S. & Bosáček, V. *J. Molec. Catal.* **6**, 321–326 (1979).
9. Schröder, K.-P., Sauer, J., Leslie, M., Catlow, R. C. A. & Thomas, J. M. *Chem. Phys. Lett.* **188**, 320–325 (1992).
10. Schröder, K.-P., Sauer, J., Leslie, M. & Catlow, R. C. A. *Zeolites* **12**, 20–23 (1992).
11. Kramer, G. J. & van Santen, R. A. *J. Am. chem. Soc.* **115**, 2887–2897 (1993).
12. Kramer, G. J., de Man, A. J. M. & van Santen, R. A. *J. Am. chem. Soc.* **113**, 6435–6441 (1991).
13. Sauer, J. *chem. Rev.* **89**, 199–255 (1989).
14. Dupuis, M., Sprangler, D. & Wendolowski, D. *NRCC Software Catalog 1*, Program No. QG01, GAMESS (1980).
15. Szabo, A. & Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Macmillan, New York, 1982).
16. Rice, O. K. *Statistical Mechanics, Thermodynamics and Kinetics* (Freeman, San Francisco, 1966).
17. Thruhlar, D. G. & Gordon, M. S. *Science* **249**, 491–497 (1990).
18. Gilbert, R. G. & Smith, S. C. *Theory of Unimolecular and Recombination Reactions* (Blackwell, Oxford, 1990).
19. Barrer, R. M., & Sutherland, J. W. *Proc. R. Soc.* **A237**, 439–450 (1956).
20. Papp, H., Hinsen, W., Do, N. T. & Baerns, M., *Thermochim. Acta* **82**, 137–148 (1984).
21. Yashonath, S., Thomas, J. M., Nowak, A. K. & Cheetham, A. K. *Nature* **331**, 601–604 (1988).
22. Johnston, H. S. *Gas Phase Reaction Rate Theory* (Ronald, New York, 1966).
23. Meier, W. M. & Olson, D. H. *Atlas of Zeolite Structure Types*, 2nd edn (Butterworth, Cambridge, 1987).
24. Lombardo, E. A., Sill, G. A. & Hall, W. K. *J. Catal.* **119**, 426–440 (1989).

ACKNOWLEDGEMENTS: We thank B. J. Milan for help in the experimental work.

Milankovitch theory viewed from Devils Hole

J. Imbrie*, A. C. Mix† & D. G. Martinson‡

*Department of Geological Sciences, Brown University, Providence, Rhode Island 02912, USA
†College of Oceanography, Oregon State University, Corvallis, Oregon, 97331, USA
‡Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York 10964, USA

VARIATIONS in the oxygen isotope content ($\delta^{18}O$) of late Quaternary deep-sea sediments mainly reflect changes in continental ice mass[1], and hence provide important information about the timing of past ice ages. Because these sediments cannot yet be dated directly beyond the range of radiocarbon dating (40-50 kyr), ages for the $\delta^{18}O$ record have been generated[2,3] by matching the phase of the changes in $\delta^{18}O$ to that of variations in the Earth's precession and obliquity. Adopting this timescale yields a close correspondence between the time-varying amplitudes of these orbital variations and those of a wide range of climate proxies[4], lending support to the Milankovitch theory that the Earth's glacial-interglacial cycles are driven by orbital variations. Recently Winograd *et al.*[5] reported a record of $\delta^{18}O$ variations in a fresh-water carbonate sequence from Devils Hole, Nevada, dated by U–Th disequilibrium[6]. They concluded that the timing of several of the features in the record, which reflects changes in the temperature of precipitation over Nevada as well as changes in the isotopic composition of the moisture source[5,7], showed significant deviations from that predicted by Milankovitch theory. Here we demonstrate that applying the Devils Hole chronology to ocean cores requires physically implausible changes in sedimentation rate. Moreover, spectral analysis of the Devils Hole record shows clear evidence of orbital influence. We therefore conclude that transfer of the Devils Hole chronology to the marine record is inappropriate, and that the evidence in favour of Milankovitch theory remains strong.

The Devils Hole $\delta^{18}O$ record was obtained from a 36-cm core (DH-11) drilled in a layer of calcite lining a water-filled cavern in southern Nevada. Ground water here originates as snow and rain in the surrounding mountains[5]. The time resolution of the $\delta^{18}O$ record is comparable to that in deep-sea records and contains 21 precise radiometric dates[6] from the ^{230}Th method[8]. The general resemblance of the Devils Hole $\delta^{18}O$ record to that of the ocean is striking (Fig. 1). Indeed, the coherency is so high that it is tempting to overlook how different the physics underlying each record must be and jump to the conclusion that they are in fact synchronous. The SPECMAP marine $\delta^{18}O$ stack is an average of many open-ocean records in which values become heavier during glacial intervals, mainly because of storage of fresh water as ice. In contrast, the $\delta^{18}O$ data in DH-11 reflect the isotopic distillation of atmospheric moisture, a process linked to local precipitation temperature[5]. Values in this record therefore become lighter during glacial intervals. But to interpret these data properly as an air temperature signal, one must make assumptions not only about the isotopic composition of the oceanic moisture source (which changes over a glacial cycle), but also about air-parcel trajectories at the relevant seasons[7]. Winograd *et al.*[5] address some, but not all, of these complex issues.

A convenient way of comparing the DH-11 and SPECMAP chronologies is to examine a mapping function[9] that adjusts the ages in one curve to give the best match with $\delta^{18}O$ variations in the other (Fig. 2). Overall, the similarity between these physically very different records is remarkable (r=0.85). But we focus here on two glacial intervals, stages 6 and 10, in which the DH-11 ages are significantly older.

We consider three possible explanations for these differences: (1) that the $\delta^{18}O$ events recorded in these groundwater and oceanic records are synchronous, and the DH-11 chronology is wrong; (2) that the events are synchronous, and the SPECMAP chronology is wrong; or (3) that the events are not synchronous, and both chronologies are right. The first possibility has been examined in two recent papers that ask if Devils Hole ages could be biased by the incorporation of ^{230}Th during calcite growth[10,11]. Although some avenues of research remain to be explored, in the absence of compelling evidence for such a bias we will assume that there is nothing wrong with the chronology of DH-11.

To test the second possibility, we examine the geological consequences of applying the DH-11 chronology to the oceanic $\delta^{18}O$ record (Fig. 1*b*). We do this by transferring the Devils Hole chronology to a set of four deep-sea cores (Fig. 3). The records chosen come from widely separated locations away from continental margins, at sites (in the eastern[12] and western[1] tropical Pacific, equatorial Atlantic[13], and Subantarctic[14] oceans) where sediments accumulate at different average rates, in very different oceanographic settings and with different histories of surface and deep-water masses. Radiocarbon studies constrain models of sedimentation across the stage 2–1 transition at these sites. For V28-238 and V30-40, published dates are available[15,16]. For the other two cores there are nearby records with accelerator mass spectrometry ^{14}C dating[17,18]. During late glacial time, sedimentation rates (converted to calendar years) were 30% lower than post-glacial rates in V28-238; 40% higher near RC13-110; a factor of 5 lower near RC11-120; and essentially unchanged in V30-40.

The one thing we would not expect to find during glacial maxima is a synchronous increase in sedimentation rates at all four sites. Yet this is what application of the DH-11 chronology implies for stage 6. Large anomalies in sedimentation rates in stage 6 are produced in all four cores, with anomalously high rates followed immediately by anomalously low rates (varying by a factor of 5 or 6). No similar excursions measured at this resolution have been detected in these cores over the past 300 kyr on either chronology, and these cores lack lithological changes that would be expected to accompany such excursions. In contrast, sedimentation-rate variations implied by the SPECMAP age model are small, spread rather evenly through the depth of each core, and are not similar at all sites. Similar arguments apply to the stage 10 anomaly.

We therefore reject the second hypothesis (that $\delta^{18}O$ events in DH-11 and the ocean are synchronous) and reaffirm our earlier conclusion, based on detailed investigations of relative accumulation rates[19,20], that the SPECMAP chronology (ref. 2, with modification in the older section in refs 21–23, and higher resolution provided in ref. 3) is a suitable age framework for Quaternary deep-sea sediments. Certainly the absolute chronology of this common temporal framework can be improved[24]. For the stage 6–5 transition, we expect that improvements will come from dates on unaltered corals tied directly to early portions of the sea-level rise in stage 6 (ref. 25) rather than from dates, however accurate they may be, that fix the timing of events on land. As yet, such dates are not available. Meanwhile, we note that the most reliable coral dates (those with modern values of initial $^{234}U/^{238}U$ on essentially pure aragonite samples of the reef-crest coral *Acropora palmata*) for the highest stand of sea level in Barbados, Haiti and the Bahamas (122 to 126 kyr before present) seem to support this part of the SPECMAP chronology[25,26].

For the present, therefore, we will assume that both the SPECMAP and the Devils Hole chronologies are right when applied to their respective records, and we ask whether the Devils Hole record, displayed on its own timescale, is "inconsistent with the Milankovitch hypothesis that orbitally controlled variation in solar insolation plays a direct role in Pleistocene climate change"[5]. To address this problem convincingly in the time domain, we require two models that are not yet available: (1) a time-dependent model of processes governing the response of the climate system to Milankovitch forcing, including those in

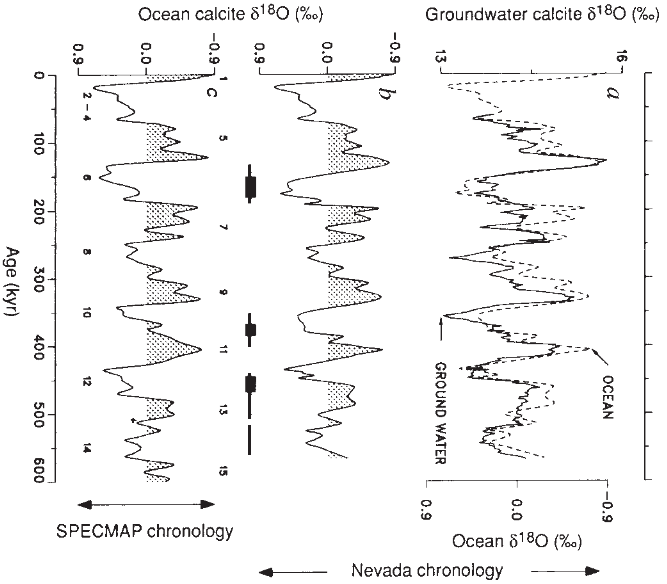

FIG. 1 A stacked $\delta^{18}O$ record[2] from ocean calcite (*a*, *b*, *c*) compared with the $\delta^{18}O$ record from groundwater calcite at Devils Hole, Nevada[5] (*a*) on two different chronologies. No effort is made to eliminate the temperature effect in the oceanic ($\delta^{18}O$) record of sea level, or the $\delta^{18}O$ moisture-source effect in the groundwater record of atmospheric temperature[7]. In *a* and *b*, the SPECMAP oceanic chronology (*c*) has been adjusted[9] to maximize the correlation between the two records. Shaded portions designate interglacial stages in the standard sequence of numbered marine $\delta^{18}O$ stages[20]. The stage 6–5 transition in the DH-11 chronology (*b*) occurs much more slowly, relative to the 2–1 transition, than in the SPECMAP chronology (a pattern that conflicts with inferences drawn from multiple sediment records normalized in the depth domain to obtain a relative chronology[19,20]). Black bars show where the two chronologies differ by more than 10 kyr (narrow bars) and 20 kyr (wide bars).

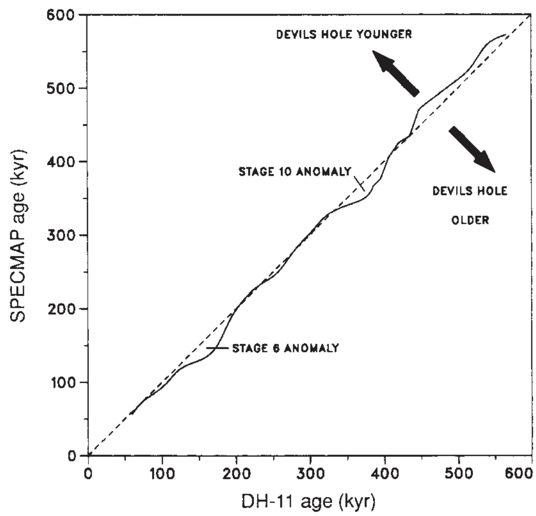

FIG. 2 Mapping function[9] used to optimize the correlation between the oceanic and groundwater $\delta^{18}O$ curves in Fig. 1*a*. Mapping functions and the oceanic data used in this paper are available in digital form as SPECMAP Archives 2 and 3 at the National Center for Atmospheric Research and at the National Geophysical Data Center, both in Boulder, Colorado.

the atmosphere over Nevada and in ground waters of the Great Basin; and (2) a model that will isolate the local temperature component of the DH-11 record. But knowing that large ice sheets have time constants of the order of 15 kyr (refs 27, 28), we can still make one confident prediction: during the transition to an interglacial state, some part of the atmosphere must warm substantially before ice sheets melt and lower the fraction of ^{18}O in the ocean.

Lacking the desired models, we can make some progress by expressing the data as a spectrum (Fig. 4), thus breaking a difficult problem into simpler parts. In particular, we can look for evidence of linear responses to orbital forcing near 23 and 41 kyr (ref. 4), where virtually all the insolation change occurs, and consider these mechanisms separately from those which drive the broader-band, 100-kyr cycle (in which the response to any forcing, whether internal or external, must involve strong nonlinearities). As in the marine data, the spectrum of the Devils Hole data reveals three main concentrations of variance (Fig. 4*a*). Could these reflect orbital influence? Peaks in the DH-11 spectrum occur at 91 kyr and 42 kyr, with two adjacent peaks at 27 kyr and 23 kyr, rather than in bands centred at the periods of the orbital forcing (100 kyr, 40 kyr and 23 kyr) during this interval as in the marine spectrum. Still, considering the bandwidth of our analysis, the existence of discrete, coherent concentrations of variance at or near orbital periods in both records suggests orbital influence. This suggestion seems to be confirmed by the observation that the DH-11 record is strongly coherent ($r > 0.94$) with the two dominant cycles of insolation at 23 kyr and 40 kyr (Fig. 4*b*). The peak near 27 kyr could reflect the same nonlinear interaction tone between orbital frequencies (~29 kyr) that is found in records of the trade winds[29,30].

Thus even when we assume that the Devils Hole record is a well-dated and simple measure of climate, we find evidence of orbital influence. We therefore reject the notion that this record as a whole is inconsistent with modern versions of the Milankovitch theory (see, for example refs 31–33). Looking beyond Devils Hole to other parts of the late Pleistocene world[4], and much farther back in time [21, 23, 34-37], we find compelling evidence in favour of the Milankovitch theory. □

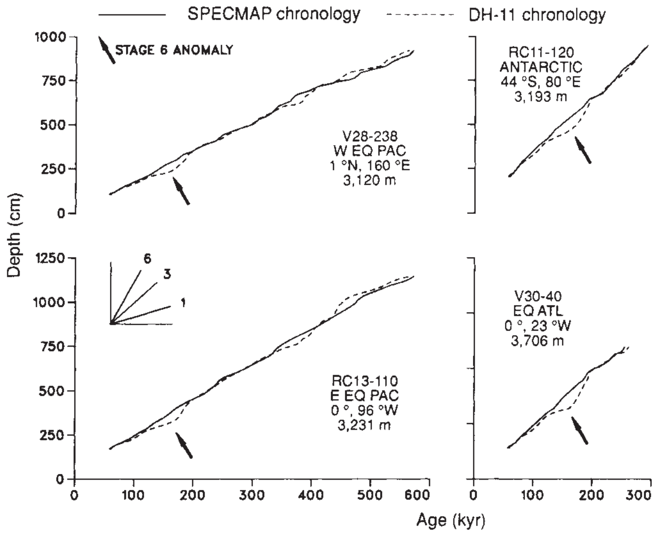

FIG. 3 Depth against age in four deep-sea cores[1,12–14] according to the oceanic (SPECMAP) and Nevada (DH-11) chronologies. Slopes in the insert (lower left) show accumulation rates in cm kyr^{-1}. Large and physically implausible changes in sedimentation rate in stages 6 and 10 are implied by the application of the DH chronology to these cores.

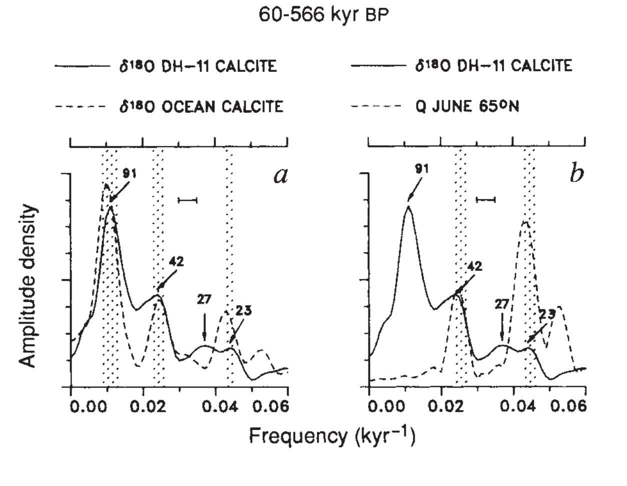

FIG. 4 Spectra of $\delta^{18}O$ records in calcite from DH-11 (Nevada) and the ocean calculated[4,38] at a bandwidth of 0.005 kyr^{-1} on the assumption that the chronology developed for each record is correct. *a*, Comparison of $\delta^{18}O$ spectra. Dominant periods in the DH-11 record are indicated in kyr; in the ocean record, they are 100,41 and 23 kyr. *b*, Comparison of DH-11 and radiation[39] spectra. Dominant periods in radiation are 40 and 23 kyr. For *a* and *b*, record pairs are significantly coherent at the 80% level in the frequency bands with shading.

Received 23 December 1992; accepted 27 April 1993.

1. Shackleton, N. J. & Opdyke, N. D. *Quat. Res.* **3**, 39-55 (1973)
2. Imbrie, J. *et al.* in Milankovitch and Climate, Part 1 (eds Berger, A. L., Imbrie, J., Hays, J., Kukla, G. & Saltzman, B.) 269-305 (Reidel, Dordrecht, 1984).
3. Martinson, D. G. *et al. Quat. Res.* **27**, 1-30 (1987)
4. Imbrie, J. *et al. Paleoceanography* **7**, 701-738 (1992)
5. Winograd, I. J. *et al. Science* **258**, 255-260 (1992)
6. Ludwig, K. R. *et al Science* **258**, 284-287 (1992)
7. Benson, L. & Klieforth, H. in *Aspects of Climate Variability in the Pacific and the Western Americas* (ed. Peterson, D. H.) 41-59 (Am. geophys. Un. Geophys. Monogr. 55, Washington DC, 1989).
8. Edwards, R. L., Chen, J. H. & Wasserburg, G. J. *Earth planet. Sci. Lett.* **81**, 175-192 (1986).
9. Martinson, D. G., Menke, W. & Stoffa, P. *J. geophys. Res.* **87**,4807-4818 (1982).
10. Edwards, R. L. & Gallup, C. D.*Science* **259,** 1626 (1993).
11. Shackleton, N. J. *Nature* **362**, 596 (1993).
12. Mix, A. C. *et al. Paleoceanography* **6**, 205-226 (1991)
13. Mix, A. C. in *The Last Interglacial/Glacial Transition in North America* (eds Clark, P. U. & Lea, P. D.) 19-30 (Geol. Soc. Am., Spec. Pap. 270, Boulder, 1992).
14. Hays, J. D., Imbrie, J. & Shackleton, N. J. *Science* **194**, 1121-1132 (1976).
15. Mix, A. C. & Ruddiman, W. F. *Quat. Sci. Rev.* **4**, 59-108 (1985).
16. Broecker, W. S. *et al. Radiocarbon* **30**, 261-295 (1988).
17. Shackleton, N. J. *et al. Nature* **335**, 708-711 (1988).
18. Bard, E. *et al.* in *Geological History of the Polar Oceans: Arctic versus Antarctic* (eds Bleil, U. & Thiede, J.) 405-416 (Kluwer, Dordrecht, 1990).
19. Pisias, N. G. *et al. Mar. Geol.* **56,** 119-136 (1984).
20. Prell, W. L. *et al. Paleoceanography* **1,** 137-162 (1986).
21. Ruddiman, W. F., Raymo, M. E., Martinson, D. G., Clement, B. M. & Backman, J. *Paleoceanography* **4**, 353-412 (1989)
22. Johnson, R. G. *Quat. Res.* **17,** 135-147 (1982).
23. Shackleton, N. J., Berger, A. & Peltier, W. R. *Trans. R. Soc. Edin: Earth Sci.* **81,** 251-261 (1990).
24. Pisias, N. G., Mix, A. C. & Zahn, R. *Paleoceanography* **5,** 147-160 (1990)
25. Hamelin, B., Bard, E., Zindler, A. & Fairbanks, R. G. *Earth planet. Sci. Lett.* **106,** 169-180 (1991).
26. Chen, J. H., Curran, H. A., White, B. & Wasserburg, G. J. *Geol. Soc. Am. Bull.* **103,** 82-97 (1991).
27. Weertman, J. *J. Glaciol.* **5.** 145-158 (1964).
28. Fairbanks, R. G. *Nature* **342,** 637-642 (1989)
29. Pisias, N. G. & Rea, D. K. *Paleoceanography* **3,** 21-37 (1988).
30. Clemens, S. C. & Prell, W. L. *J. geophys. Res.* **96,** 22683-22700 (1991).
31. Maasch, K. A. & Saltzman, B. *J. geophys. Res.* **95,** 1955-1963 (1990).
32. Short, D. A., Mengel, J. G., Crowley, T. J., Hyde, W. T. & North, G. R. *Quat. Res.* **35,** 157-173 (1991).
33. Gallée, H.*et al J. geophys. Res.* **97,** 15713-15740 (1992).
34. Arthur, M. A. & Garrison, R. E. (eds) *Paleoceanography* **1,** 369-586 (1986).
35. Hilgen, F. J. *Earth Planet. Sci. Lett.* **104,** 226-244 (1991).
36. Baksi, A. K., Hsu, V., McWilliams, M. O. & Farrar, E. *Science* **256,** 356-357 (1992).
37. Tauxe, L., Deino, A. D., Behrensmeyer, A. K. & Potts, R. *Earth planet. Sci. Lett.* **109,** 561-572 (1992).
38. Jenkins, G. M. & Watts, D. G. *Spectral Analysis and Its Applications* (Holden-Day, San Francisco, 1968).
39. Berger, A. & Loutre, M. F. *Quat. Sci. Rev.* **10,** 297-317 (1991).

ACKNOWLEDGEMENTS. This work was supported by the NSF. We thank S. Clemens, R. Fairbanks, J. M. Landwehr, N. Shackleton and I. J Winograd for comments on an earlier draft, and N. G. Pisias, W. Prell, and J. R. Toggweiler for discussions. A Duffy made the calculations required to transfer the Devils Hole chronology.