

ment in the same manner as described above shows substantial loss of the martensite peak over a period of 9 h (after which the experiments were terminated), with no change in the height of the austenite peak (Fig. 1e). Although the procedure took longer to reduce the martensite peak substantially, we nevertheless observed a significant reduction, even after 3 h. The electrochemically induced removal of martensite clearly occurs to some significant depth beneath the metal surface, and is not confined to the surface atoms only. We estimate the depth of annealing after 9-h electrochemical treatment to be at least 8 μm .

Although the origins of electrochemical annealing are not yet clear, some aspects can be rationalized. In the cathodic part of the pulse, water is reduced by electrolysis to hydrogen. Hydrogen atoms entering the metal produce considerable strain within the lattice, causing microstructural changes as well as phase transformations. Previous work on cathodic charging gives conflicting information. Cathodic charging is reported to generate both the α' as well as the hexagonal ϵ phases of martensite^{10,12}. In contrast to this, it is also reported that only the α' phase, and not the ϵ phase, is generated for the same grade of stainless steel¹⁴. Okada *et al.*¹² show that ϵ and α' martensite are formed during cathodic charging of type 304 stainless steel, both of which persist after ageing, although type 310 stainless steel (a more highly alloyed material containing 20% Cr and 22% Ni) showed ϵ martensite during cathodic charging which subsequently decomposed during ageing. Our observations from pulse experiments differ substantially. The pulsed annealing treatment destroys the α' martensite phase, rather than generating it. No sign of ϵ phase (whose largest reflection would be observed¹⁰ at $2\theta = 46.96^\circ$; Fig. 1) was found, either during mechanical deformation, or after electrochemical treatment. The pulse treatment leaves the structure entirely austenitic, a phenomenon not before observed, to our knowledge. Kinetically, the hydrogen reaction could account for the observed changes. By assuming the rate-determining step to be diffusion within the metal phase, the minimum annealed depth of 8 μm estimated above gives a diffusion coefficient of about $2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. This corresponds quite well to the value of $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for thermally annealed 304 stainless steel obtained by extrapolating from high-temperature data¹⁷ to our experimental temperature of 80 °C. However, one cannot preclude possible synergistic effects of nitrogen produced by cathodic reduction of the electrolytic nitrite ion. Examination of the treated metal by energy dispersive X-ray analysis in a scanning electron microscope, and by energy loss spectroscopy in the transmission electron microscope (both methods *ex situ*) failed to reveal the presence of nitrogen. Nevertheless, we were unable to achieve electrochemical annealing in aqueous potassium carbonate solution using similar electrochemical surface treatment. Nitrite is certainly electrochemically reducible, at least to ammonia¹⁸, and reduction to atomic nitrogen is in principle possible.

In the anodic part of the potential pulse, the metal passivates by oxide film growth, in accordance with the classical behaviour of stainless steels. (Transpassive dissolution of the chromium component does not occur at the potentials imposed here.) Any reduced hydrogen and nitrogen generated in the previous cathodic pulse and dissolved into the metal matrix would also tend to be re-oxidized anodically and dissolve into the electrolyte. The defects generated by ingress of hydrogen (and perhaps nitrogen) would leave vacancies after re-oxidation and provide for surface relaxation of the metal atoms over very short range, giving the observed annealing. The defects that remain would then be available for penetration of further reduced atoms in the subsequent cathodic pulse. In this way a deeply affected layer could be induced. To our knowledge, this is the first time that such an annealing phase change procured by electrochemical means has been reported.

The present work paves the way for further development of new methods of electrochemical surface processing that could enhance the surface properties of metals, without altering their

bulk properties—in contrast to the action of heat treatment, which acts on both the surface and the bulk. □

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- Sumitomo, H. Investigation of the development of cold-rolling and annealing textures in SUS304 austenitic stainless steel. *J. Iron Steel Inst. Jpn* **77**, 558–565 (1991).
- Angel, T. Formation of martensite in austenitic stainless steel. *J. Iron Steel Inst.* **177**, 165–174 (1954).
- Ludwigson, D. C. & Berger, J. A. Plastic behaviour of metastable austenitic stainless steels. *J. Iron Steel Inst.* **207**, 63–69 (1969).
- Olson, G. B. & Cohen, M. Kinetics of strain-induced martensitic transformation. *Metall. Trans. A* **6**, 791–795 (1975).
- Olson, G. B. & Cohen, M. Stress-assisted isothermal martensitic transformation: application to TRIP steels. *Metall. Trans. A* **13**, 1907–1914 (1982).
- Huang, G. L., Matlock, D. K. & Krauss, G. Martensite formation, strain rate sensitivity and deformation behaviour of type 304 stainless steel sheet. *Metall. Trans. A* **20**, 1239–1246 (1989).
- Tomimura, K., Takaki, S. & Tokunaga, Y. Reversion mechanism from deformation induced martensite to austenite in metastable austenitic stainless steels. *ISIJ Int.* **31**, 1431–1437 (1991).
- Takaki, S., Tomimura, K. & Ueda, S. Effect of pre-cold-working on diffusional reversion of deformation induced martensite in metastable austenitic stainless steel. *ISIJ Int.* **34**, 522–527 (1994).
- Petersen, S. F., Mataya, M. C. & Matlock, D. K. The formability of austenitic stainless steels. *J. Mater.* **49**, 54–58 (1997).
- Bentley, A. P. & Smith, G. C. Phase transformation of austenitic stainless steels as a result of cathodic hydrogen charging. *Metall. Trans. A* **17**, 1593–1600 (1986).
- Tähtinen, S., Kivilahti, J. & Hanninen, H. Crystallography of hydrogen-induced surface cracking in a spheroidal austenitic stainless steel single crystal. *Scripta Metallurgica* **19**, 967–973 (1985).
- Okada, H., Hosoi, Y. & Abe, S. Formation of cracks in austenitic stainless steels cathodically charged with hydrogen. *Corrosion* **26**, 183–186 (1970).
- Ohtani, N., Asano, S., Fujishima, Y. & Yamamasu, Y. Hydrogen-induced transformation and embrittlement in 18-8 stainless steel. *J. Jpn Inst. Metals* **37**, 746–753 (1973).
- Narita, N., Altstetter, C. J. & Birnbaum, H. K. Hydrogen-related phase transformations in austenitic stainless steels. *Metall. Trans. A* **13**, 1355–1365 (1982).
- Szumner, A. & Janko, A. Hydride phases in austenitic stainless steels. *Corrosion* **35**, 461–464 (1979).
- Szumner, A. in *Hydrogen Degradation of Ferrous Metals* (eds Oriani, R. A., Hirth, J. P. & Smialowski, M.) 512–534 (Noyes Publications, Park Ridge, New Jersey, 1985).
- Perng, T. P. & Altstetter, C. J. Effects of deformation on hydrogen permeation in austenitic stainless steels. *Acta Metall.* **34**, 1771–1781 (1986).
- Newman, R. C. & Burstein, G. T. Anion effects in the stress-corrosion cracking of copper and brass. *J. Electrochem. Soc.* **127**, 2527 (1980).

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Cooler winters as a possible cause of mass extinctions at the Eocene/Oligocene boundary

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The Eocene/Oligocene boundary, at about 33.7 Myr ago, marks one of the largest extinctions of marine invertebrates in the Cenozoic period¹. For example, turnover of mollusc species in the US Gulf coastal plain was over 90% at this time^{2,3}. A temperature change across this boundary—from warm Eocene climates to cooler conditions in the Oligocene—has been suggested as a cause of this extinction event⁴, but climate reconstructions have not provided support for this hypothesis. Here we report stable oxygen isotope measurements of aragonite in fish otoliths—ear stones—collected across the Eocene/Oligocene boundary. Palaeotemperatures reconstructed from mean otolith oxygen isotope

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values show little change through this interval, in agreement with previous studies^{5,6}. From incremental microsampling of otoliths, however, we can resolve the seasonal variation in temperature, recorded as the otoliths continue to accrete new material over the life of the fish. These seasonal data suggest that winters became about 4 °C colder across the Eocene/Oligocene boundary. We suggest that temperature variability, rather than change in mean annual temperature, helped to cause faunal turnover during this transition.

The US Gulf coastal plain preserves one of the best-studied Palaeogene marine shelf sections in the world. The molluscan fossil record is especially well constrained owing to more than a century of intensive collecting and the compilation of a standardized taxonomy^{7–10}. Turnover at the Eocene/Oligocene (E/O) boundary is very high, with fewer than 10% of late Eocene species surviving into the Oligocene^{2,3}. Although temperature remains the most likely cause of this turnover^{4,11}, no studies to date have been able to demonstrate conclusively a temperature change specific to the boundary in this region. Temperatures derived from the $\delta^{18}\text{O}$ of planktonic foraminifers from the Gulf of Mexico, the Caribbean, and low-latitude North Atlantic Ocean show no change in temperature across the boundary⁵. Palynomorph (pollen and spores) assemblages from Gulf Coast sections suggest a progressive cooling and drying on land beginning in the late Eocene and continuing into the early Oligocene^{6,12}, but detailed palaeofloristic work could resolve no significant climate change at the boundary⁶. Conversely, calcareous nanoplankton assemblages suggest that cooling began only later in the early Oligocene, after the boundary extinctions¹³. If temperature is to remain a viable mechanism for extinction, it is necessary that data on temperature show some excursion at the boundary.

To test the hypothesis that temperature played a role in faunal turnover, and to shed light more broadly on environmental changes that may have occurred on the shelf during this interval of time, we sectioned and incrementally microsampled fish otoliths collected

across the E/O boundary in the Gulf Coast. Stable oxygen isotopic compositions of aragonite subsamples provide a proxy record for temperature during the lifetime of fish^{14–17}. Moreover, high-resolution analyses of accretionary otolith aragonite enable the approximation not only of mean annual temperature but also of the seasonal range of temperature variation. This technique provides an advantage over more traditional proxies of bulk carbonate or whole-shell (for example, foraminiferal) analyses because seasonality is a factor inaccessible from them but crucial in determining the biogeographic distributions of organisms today^{18,19}.

Mean $\delta^{18}\text{O}$ values of congrid and ophidiid otoliths (Fig. 1a) increase slightly ($\sim 0.4\text{‰}$) at the middle/late Eocene boundary and again by $\sim 0.6\text{‰}$ across the E/O boundary. Similar increases (although of a somewhat higher magnitude across the E/O boundary) have been observed in numerous records of benthic foraminifer $\delta^{18}\text{O}$ in the deep ocean^{5,20–22}. However, when mean palaeotemperatures are calculated (Fig. 1b), the data reveal little change from the middle Eocene into the Oligocene. A *t*-test between middle Eocene and late Eocene samples grouped by age is statistically insignificant (0.3 °C , $P = 0.613$, $n = 20$ otoliths). The difference between late Eocene and early Oligocene mean temperatures (1.1 °C) is also statistically insignificant ($P = 0.186$, $n = 12$ otoliths). The maximal

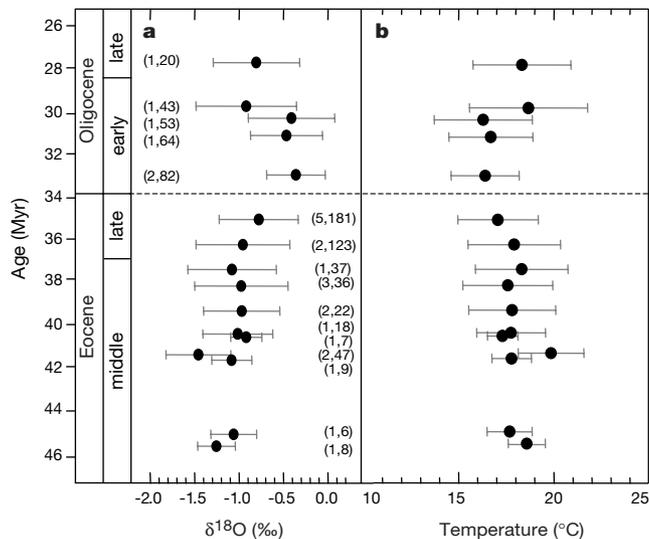


Figure 1 Results from isotopic analyses of microsampled otoliths. The figure shows mean annual $\delta^{18}\text{O}$ (a) and mean annual temperature (b) for the middle Eocene to the end of the Oligocene. Values plotted are means of all analyses from all otoliths from a given stratigraphic horizon, including both congrid and ophidiids; error bars are 1 standard deviation around the mean. Number of otoliths and total number of analyses per interval are given in parentheses; a total of 756 isotopic analyses on microsamples from 26 otoliths are reported. See text for values of Palaeogene seawater $\delta^{18}\text{O}$ used in temperature calculations. Timescale is from ref. 28. Ages of samples are the mean age of the formation/member from which they came, as interpolated from planktonic foraminifer zones given in refs 29 and 30. All $\delta^{18}\text{O}$ values are reported relative to VPDB.

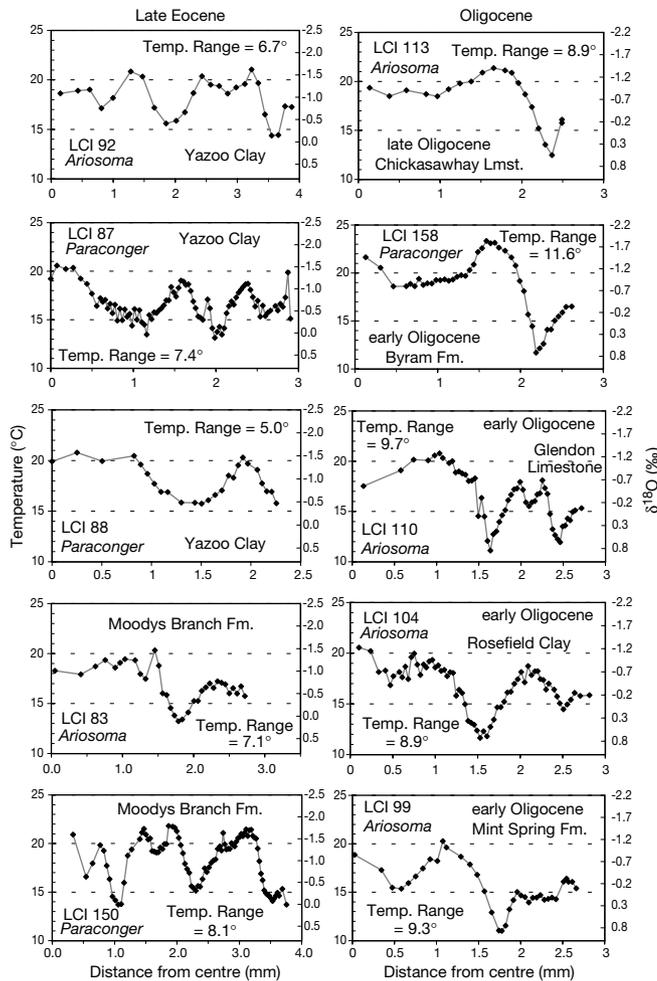


Figure 2 Individual temperature records from microsampled congrid otoliths. Records are shown from the late Eocene (left) and the early and late Oligocene (right). Sample number, genus, formation and seasonal range of temperature for each otolith are indicated on the plots. In each panel, temperature and $\delta^{18}\text{O}$ are shown on the left- and right-hand vertical axis, respectively. We note that the early Oligocene is more seasonal and has cooler winters than the late Eocene, yet summer temperatures do not differ appreciably.

change across the Eocene/Oligocene boundary as indicated by a comparison of latest Eocene and earliest Oligocene samples is 1.8 °C, but again is statistically insignificant ($P = 0.202$, $n = 7$ otoliths). The lack of substantial change in mean temperature across the Eocene/Oligocene boundary is consistent with earlier work in the Gulf Coast and with Mg/Ca ratios of deep-sea benthic foraminifers²³. Relative consistency in temperature through time might be expected in the Gulf Coast because cooling during the transition from early Eocene warmth to Oligocene glacial conditions was far more extreme at high latitudes than at low⁵. Our data suggest that if there was cooling in the Gulf from an early Eocene thermal maximum, the bulk of it must have occurred before the middle of the middle Eocene.

Beyond estimates of mean annual temperature, $\delta^{18}\text{O}$ values of individual serially microsampled otoliths also record the seasonal temperature variation experienced throughout the lifetimes of the fish. Figure 2 shows temperature profiles from ten late Eocene and early Oligocene congrid otoliths. The range of temperatures experienced in the late Eocene generally falls between 15 and 20 °C, with winter minima not extending below about 13.5 °C. The Oligocene congrids record similar warm month temperatures of around 20 °C, but winter temperatures consistently fall below those of the Eocene samples, with values as low as 11.0 °C. The scalloped nature of Oligocene curves also suggests that otolith growth may have slowed significantly or stopped during the coldest month(s)²⁴, indicating that winter temperatures may have been even colder than those recorded in the otolith carbonate. The trend in minimum and maximum temperatures from the late Eocene into the Oligocene is shown in Fig. 3a. A t -test of summer and winter temperatures recorded by late Eocene and Oligocene otoliths demonstrates no significant change in summer temperatures ($P = 0.800$, $n = 21$ summers in 12 otoliths), while Oligocene winters were colder than late Eocene winters ($P = 0.025$, $n = 21$ winters in 12 otoliths) by as much as 4 °C. Figure 3b compares the seasonal range of temperature variation in the late Eocene versus the Oligocene, and shows that seasonality increases significantly across the boundary.

These data suggest that while summer temperatures did not change appreciably over the Eocene/Oligocene transition, cold

month mean temperatures dropped by some 4 °C, or more if cold month extremes are not actually recorded. Such a decrease in winter minimum temperature on the shelf would have a significant effect on the biogeographic ranges of taxa, and could be responsible for the extinctions of stenothermal (unable to tolerate large fluctuations in temperature) tropical taxa in the Gulf. The pattern of a drop in winter temperatures without a concomitant change in summer temperatures may also help to discriminate between alternative explanations for Eocene/Oligocene cooling. A decrease in the concentration of greenhouse gases may be more likely to result in uniform degrees of cooling in summer and winter months, while changes in oceanographic and/or atmospheric circulation could produce more variable results.

Several caveats about these data and the conclusions drawn from them should be mentioned. First and perhaps most serious is the question of how representative of an interval of time encompassed by an individual sampling horizon (of the order of 10^3 – 10^4 years) is the record of seasonal variation preserved in one or several otoliths, from fish that lived for 2–3 years. Although this is a potential limitation, samples from different otoliths taken from different formations at different localities through the late Eocene and early Oligocene show a generally consistent pattern in the temperatures they generate; hence, the trend appears to be robust.

Other potential limitations are associated with interpreting seasonal ranges of temperature from discretely sampled carbonate. By necessity, the degree of annual temperature variation will correlate with sampling resolution. The more finely resolved the subsampling, the greater the range in inferred temperature; conversely, the coarser the sampling, the greater the amount of time averaged within each sample, and the more seasonal amplitudes will be reduced. As mentioned above, this may be a concern with the ophidiid otoliths. Sampling resolution does vary to some degree among the late Eocene and Oligocene congrid otoliths presented here, yet sampling intensity is always high enough to record a significant number of points from each seasonal cycle. As a result, it is unlikely that inferred seasonal ranges of variation are compromised.

Our data reflect temperature variations experienced at the bottom on a marine shelf. The palaeodepths of these samples are poorly constrained; however, the seasonal range of temperature variation in the northern Gulf at 50 m depth today is about 5 °C (ref. 25), roughly that observed in our data. Temperatures recorded at the sea bottom on the Atlantic shelf in 50 m water depth accurately reflect surface temperatures from November to May, when the water column is isothermic²⁶. Stratification during the summer months prevents maximum bottom-water temperatures from reaching those at the surface, but turnover in the autumn mixes warm surface water to the bottom. This suggests that while our warmest bottom temperatures may underestimate those reached at the surface, cold-month temperatures accurately record surface temperatures as long as Gulf waters experienced turnover.

Our estimates of palaeotemperature are based on assumptions about the $\delta^{18}\text{O}$ of the water from which the otoliths were precipitated (see Methods). Lear *et al.*²³ provide an alternative interpretation of $\delta^{18}\text{O}$ of sea water through time, and suggest that the shift in $\delta^{18}\text{O}$ of carbonate across the Eocene/Oligocene boundary is entirely due to changes in ice volume and hence seawater $\delta^{18}\text{O}$. Using their values for seawater composition inverts our results, suggesting that winter temperatures remained constant while summers became warmer. This is not consistent with the selective extinction of warm-water taxa, and hence we prefer the Zachos *et al.*⁵ estimates of $\delta^{18}\text{O}$ of sea water. It is conceivable that isotopically more negative freshwater runoff may have influenced the $\delta^{18}\text{O}$ of sea water in the early Oligocene due to regression and increasing proximity of the shoreline. However, the observed shift in $\delta^{18}\text{O}$ of carbonate is positive, the opposite direction to what would be expected from a salinity effect, and is consistent with the offset seen in the deep sea

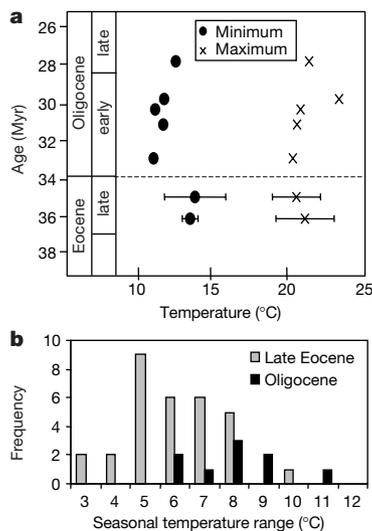


Figure 3 Eocene/Oligocene seasonal temperature change, as inferred from $\delta^{18}\text{O}$ of otoliths. **a**, Minimum and maximum temperatures for late Eocene and Oligocene otoliths from given sampling horizons. **b**, Frequency distribution of seasonal temperature ranges recorded by late Eocene and Oligocene otoliths. Values for range include every combination of local maximum minus local minimum temperature that could be unambiguously recognized as a seasonal peak within each otolith. The difference between late Eocene and Oligocene seasonal temperature range is highly significant ($P = 0.004$, $n = 40$ differences between summer and winter temperatures in 12 otoliths).

record²². Any damping of the magnitude of this shift by freshwater admixture would serve to decrease our estimate of mean temperature change across the boundary, and hence our values should be taken as minimum estimates of change. Nevertheless, consistency with earlier climate work in the Gulf and the lack of palaeontological evidence for reduced salinity suggest that any deviation from normal marine sea water was minimal if present at all. We emphasize that variations in $\delta^{18}\text{O}$ of sea water through time due to local changes in salinity or global changes in ice volume will affect only the absolute values of inferred palaeotemperatures, and will have no effect on our conclusions about the seasonal range of temperature variability.

The well-documented positive shift of roughly 1‰ in $\delta^{18}\text{O}$ of deep ocean foraminifers in the earliest Oligocene^{21,22} must record some combination of cooling and increasing ice volume near the Eocene/Oligocene boundary. That this shift is also manifest, if to a lesser degree, in the lower-latitude shelf waters of the Gulf Coast suggests that increasing ice volume and concomitant change in the $\delta^{18}\text{O}$ of the global ocean is more likely than temperature change alone. Minimal change in mean annual temperature across the boundary, as shown here, supports this contention. By the mid-late Oligocene, isotopic compositions in the Gulf once again approximated those of the late Eocene, suggesting either that the ice sheet was not long-lived and/or that temperatures warmed into the late Oligocene.

With the ability to reconstruct seasonal maximum and minimum temperatures, we find that warm-month temperatures do not change significantly across the Eocene/Oligocene boundary, but that early Oligocene winters were markedly cooler than those in the late Eocene. The drop in cold-month mean temperature and the associated increase in seasonality, rather than a drop in mean annual temperature, probably had a significant effect on the distributions of marine organisms in the Gulf, and may be the primary cause of the large faunal turnover associated with the boundary. □

Methods

Otoliths were collected from middle Eocene to Oligocene fossiliferous, glauconitic, marly sands deposited on an open marine shelf and exposed in western Alabama, Mississippi, Louisiana and east Texas. Additional samples were obtained from D. Nolf at the Institut Royal des Sciences Naturelles de Belgique in Brussels. To reconstruct Palaeogene shelf temperatures, we use otoliths from fish in the families Congridae (conger eels), and Ophidiidae (cusk eels). Modern adults in these groups are fully marine, crypto-benthic in relatively deep water, and non-migratory. All are desirable traits for recording temperatures experienced by the benthic shelf biota from which most of the fossil record comes. Modern congrids have a planktonic larval stage, but a clear signal of surface water conditions was difficult to detect in the data, suggesting little if any effect on resulting patterns. Species belonging to extant genera (*Ariosoma* and *Paraconger* in the congrids, *Lepophidium* in the ophidiids) were chosen to minimize concerns about assumptions of ecological consistency through time.

Otoliths were polished flat on one side, mounted on glass slides, and polished on the other to produce a thin layer through the centre. The outer edge, centre, and any obvious growth bands were digitized, and interpolated growth-line-parallel sampling paths calculated so that sample masses exceed roughly 20 µg. Micromilling was done on a computer-controlled three-dimensional positioning stage set under a fixed high-precision dental drill. Stable oxygen and carbon isotopic compositions of resulting powders were analysed on the Finnigan MAT 252 mass spectrometer at Syracuse University or the Finnigan MAT 251 at the University of Michigan, both coupled with automated carbonate preparation systems. This sampling methodology provides a high-resolution profile of isotopic variation recorded by the otolith throughout the lifetime of the animal, with individual microsamples representing as little as 1.5–2 weeks of growth.

Palaeotemperatures are calculated from the stable oxygen isotopic compositions of otolith aragonite using the experimentally determined otolith palaeotemperature equation in ref. 17. This equation is very close to thermodynamic equilibrium, the slope is indistinguishable from that given in ref. 27 for bivalve aragonite, and it describes data from freshwater and marine fishes equally well: hence we believe it to be robust. We use middle and late Eocene and Oligocene seawater $\delta^{18}\text{O}$ values of -0.9‰ , -0.8‰ and -0.5‰ , respectively (all relative to VSMOW; ref. 5; composition on an ice-free Earth is -1.0‰). The mean value of all analyses from all otoliths of a given age provides an approximation of mean annual temperature for that time. Calculated mean temperatures may be biased slightly toward temperatures in the season of fastest growth, but this offset should be consistent through time.

Palaeoseasonality can be estimated through a comparison of mean minimum and maximum temperature values for each time interval, and can be assessed with confidence for late Eocene and Oligocene congrid otoliths. Middle Eocene samples are dominated by

ophidiids, and while co-occurring congrids and ophidiids show equivalent mean $\delta^{18}\text{O}$ values, lower otolith precipitation rate by the ophidiids may increase time-averaging and lead to an underestimate of seasonal range. Reliable estimates of middle Eocene seasonal range are therefore unavailable at present. Calculated palaeotemperatures depend on the $\delta^{18}\text{O}$ value assumed for sea water. With revisions of these assumptions, absolute values for temperature will change, but the range of temperature variation within samples will not be affected.

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- Raup, D. M. & Sepkoski, J. J. Periodic extinction of families and genera. *Science* **231**, 833–836 (1986).
- Dockery, D. T. Punctuated succession of Paleogene mollusks in the Northern Gulf Coastal Plain. *Palaios* **1**, 582–589 (1986).
- Haasl, D. M. & Hansen, T. A. Timing of latest Eocene molluscan extinction patterns in Mississippi. *Palaios* **11**, 487–494 (1996).
- Hansen, T. A. Extinction of Late Eocene to Oligocene molluscs: Relationship to shelf area, temperature changes, and impact events. *Palaios* **2**, 69–75 (1987).
- Zachos, J. C., Stott, L. D. & Lohmann, K. C. Evolution of early Cenozoic marine temperatures. *Paleoceanography* **9**, 353–387 (1994).
- Oboh, F. E., Jaramillo, C. A. & Reeves-Morris, L. M. Late Eocene-Early Oligocene paleofloristic patterns in southern Mississippi and Alabama, US Gulf Coast. *Rev. Palaeobot. Palynol.* **91**, 23–34 (1996).
- Palmer, K. V. W. & Brann, D. C. Catalogue of the Paleocene and Eocene mollusca of the southern and eastern United States: Part I. Pelecypoda, Amphineura, Pteropoda, Scaphopoda, and Cephalopoda. *Bull. Am. Paleontol.* **48**, 1–443 (1965).
- Palmer, K. V. W. & Brann, D. C. Catalogue of the Paleocene and Eocene mollusca of the southern and eastern United States: Part II. Gastropoda. *Bull. Am. Paleontol.* **48**, 471–1027 (1966).
- Dockery, D. T. Lower Oligocene Bivalvia of the Vicksburg Group. *Mississippi Dept Natural Resour. Bur. Geol. Bull.* **123**, 1–261 (1982).
- MacNeil, F. S. & Dockery, D. T. Lower Oligocene Gastropoda, Scaphopoda, and Cephalopoda of the Vicksburg Group in Mississippi. *Mississippi Dept Natural Resour. Bur. Geol. Bull.* **124**, 1–415 (1984).
- Hansen, T. in *Eocene-Oligocene Climatic and Biotic Evolution* (eds Prothero, D. R. & Berggren, W. A.) 341–348 (Princeton Univ. Press, Princeton, New Jersey, 1992).
- Frederiksen, N. O. Sporomorph biostratigraphy, floral changes, and paleoclimatology, Eocene and Earliest Oligocene of the Eastern Gulf Coast. *US Geol. Surv. Prof. Pap.* **1448**, 1–68 (1988).
- Seisser, W. G. Paleogene sea levels and climates: U.S.A. Eastern Gulf Coastal Plain. *Paleogeogr. Paleoclimatol. Paleoecol.* **47**, 261–275 (1984).
- Kalish, J. M. ¹³C and ¹⁸O isotopic disequilibria in fish otoliths: metabolic and kinetic effects. *Mar. Ecol. Prog. Ser.* **75**, 191–203 (1991).
- Kalish, J. M. Oxygen and carbon stable isotopes in the otoliths of wild and laboratory-reared Australian salmon (*Atripis trutta*). *Mar. Biol.* **110**, 37–47 (1991).
- Iacumin, P., Bianucci, G. & Longinelli, A. Oxygen and carbon isotopic composition of fish otoliths. *Mar. Biol.* **113**, 537–542 (1992).
- Patterson, W. P., Smith, G. R. & Lohmann, K. C. in *Climate Change in Continental Isotopic Records* (eds Swart, P., Lohmann, K. C., McKenzie, J. & Savin, S.) 191–202 (AGU Monograph 78, American Geophysical Union, Washington DC, 1993).
- Valentine, J. W. *Evolutionary Paleocology of the Marine Biosphere* (Prentice-Hall, Englewood Cliffs, New Jersey, 1973).
- Vermeij, G. J. *Biogeography and Adaptation* (Harvard Univ. Press, Cambridge, Massachusetts, 1978).
- Miller, K. G. in *Eocene-Oligocene Climatic and Biotic Evolution* (eds Prothero, D. R. & Berggren, W. A.) 160–177 (Princeton Univ. Press, Princeton, New Jersey, 1992).
- Zachos, J. C., Breza, J. R. & Wise, S. W. Early Oligocene ice-sheet expansion on Antarctica: Stable isotope and sedimentological evidence from Kerguelen Plateau, southern Indian Ocean. *Geology* **20**, 569–573 (1992).
- Zachos, J. C., Lohmann, K. C., Walker, J. C. G. & Wise, S. W. Abrupt climate change and transient climates during the Paleogene: A marine perspective. *J. Geol.* **101**, 191–213 (1993).
- Lear, C. H., Elderfield, H. & Wilson, P. A. Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite. *Science* **287**, 269–272 (2000).
- Dettman, D. L. & Lohmann, K. C. in *Climate Change in Continental Isotopic Records* (eds Swart, P. K., Lohmann, K. C., McKenzie, J. & Savin, S.) 153–163 (AGU Monograph 78, American Geophysical Union, Washington DC, 1993).
- NOAA/PMEL *World Ocean Atlas* [online] (cited Nov. 1999) <http://ferret.wrc.noaa.gov/fbin/climate_server> (1994).
- Weidman, C. R., Jones, G. A. & Lohmann, K. C. The long-lived mollusc *Arctica islandica*: A new paleoceanographic tool for the reconstruction of bottom temperatures for the continental shelves of the Northern Atlantic Ocean. *J. Geophys. Res.* **99**, 18305–18314 (1994).
- Grossman, E. L. & Ku, T.-L. Oxygen and carbon isotope fractionation in biogenic aragonite: temperature effects. *Chem. Geol.* **59**, 59–74 (1986).
- Berggren, W. A., Kent, D. V., Swisher, C. C. I. & Aubry, M.-P. *A Revised Cenozoic Geochronology and Chronostratigraphy* 129–212 (Special Publication 54, SEPM, Tulsa, Oklahoma, 1995).
- Baum, J. S., Baum, G. R., Thompson, P. R. & Humphrey, J. D. Stable isotopic evidence for relative and eustatic sea-level changes in Eocene to Oligocene carbonates, Baldwin County, Alabama. *Geol. Soc. Am. Bull.* **106**, 824–839 (1994).
- Yancey, T. E. & Davidoff, A. J. *Paleogene Sequence Stratigraphy of the Brazos River Section, Texas* (Gulf Coast Association of Geological Societies, Austin, Texas, 1994).

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