Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs

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Climate models with increased levels of carbon dioxide predict that global warming causes heating in the tropics, but investigations of ancient climates based on palaeodata have generally indicated cool tropical temperatures during supposed greenhouse episodes. For example, in the Late Cretaceous and Eocene epochs there is abundant geological evidence for warm, mostly ice-free poles, but tropical sea surface temperatures are generally estimated to be only 15–23 °C, based on oxygen isotope palaeothermometry of surface-dwelling planktonic foraminifer shells. Here we question the validity of most such data on the grounds of poor preservation and diagenetic alteration. We present new data from exceptionally well preserved foraminifer shells extracted from impermeable clay-rich sediments, which indicate that for the intervals studied, tropical sea surface temperatures were at least 28–32 °C. These warm temperatures are more in line with our understanding of the geographical distributions of temperature-sensitive fossil organisms and the results of climate models with increased CO_2 levels.

Since the discovery that the oxygen isotope ratio ($\delta^{18}O$) of calcite is dependent on the temperature of the water from which it is precipitated[1,2], many studies have used the technique as a thermometer for the ancient oceans by analysing the shells of fossil planktonic foraminifera and other organisms. As has been widely debated[3,4], in order to produce quantitative temperature estimates it is necessary to consider factors such as isotope fractionation by the organism, the oxygen isotopic composition of ocean water, global ice volume, the evaporative, precipitation and mixing history of the local water mass, and variations of pH and alkalinity. It is also necessary to assume that the original shell $\delta^{18}O$ does not change over time, but this is difficult to assess and strict preservational criteria have seldom been applied. The quality of preservation generally declines with geological age and burial depth in the cored pelagic oozes and chalks that are the principal resource for palaeoceanographic studies[5,6]. Most workers have accepted estimates of sea surface temperature (SST) from samples in which clear species differences are preserved between surface, deeper-dwelling and benthic taxa, and, for time-ordered data sets, in which reasonable values—and trends and events that can be correlated—are observed[3,7]. Unfortunately, this does not guarantee unaltered isotopic compositions because the possibility of a component of diagenetic calcite cannot be excluded.

After the first phase of ocean drilling, it became evident that the oxygen isotope technique predicted surprisingly cool Eocene tropical SSTs from planktonic foraminifera, while at the same time indicating relatively warm SSTs at higher latitudes and warm deep-water temperatures (based on analysis of benthic foraminifera)[7–9]. This led to the suggestion that more efficient poleward heat transport might have occurred in the past, perhaps due to a fundamentally different mode of ocean circulation[7,10,11]. In this way it might even be possible to warm the poles sufficiently to prevent ice build-up without invoking a higher global heat budget. However, it has been calculated that an excessive heat flux would be required to flatten latitudinal gradients sufficiently[12], and all climate

models to date—using modern or ancient reconstructed ocean basin geometries[13–17]—have failed to simulate such a climate regime. Although ocean circulation no doubt has an important influence on global climate through albedo-related feedbacks, it seems evident that an increased solar constant or enhanced greenhouse-gas concentrations are required to heat the poles to the required degree, and tropical warming has always attended such models.

The mismatch between data and models has become more acute as further tropical deep-sea carbonates have been drilled and analysed for $\delta^{18}O$ (refs 18, 19). A very similar pattern has also emerged for the Late Cretaceous epoch[20,21] and, in more general terms, for oxygen isotope measurements of carbonate sediments from warm climates spanning the past 500 Myr (refs 22, 23). This has led some authors to question the primary role of carbon dioxide in determining global temperatures[22], while others have maintained that the $\delta^{18}O$ measurements may be biased toward positive values because of early diagenesis in the cold sea-floor environment[5,6,24,25].

A recent detailed evaluation of the diagenetic problem concluded that overgrowth and infilling of foraminifer shells by calcite could reduce apparent temperatures by a maximum of 5 °C and by probably only 1–2 °C for a typical sample[3], which is far short of the values necessary to resolve the discrepancy. Although microscopic recrystallization is also widely recognized as a possible problem, its effect is more difficult to quantify[3]. The most persuasive argument in support of the cool temperature interpretation of planktonic foraminiferal $\delta^{18}O$ follows from the expectation that the carbon isotopic composition ($\delta^{13}C$) of diagenetic calcite should be around +3% (a typical bulk sediment value), which is within the range of reported inter-species values for planktonic foraminifera. Hence, although additional diagenetic calcite might plausibly displace $\delta^{18}O$ measurements to more positive values while retaining most of the inter-species differentials, the $\delta^{13}C$ differentials would be expected to rapidly collapse if such overprinting occurred[3].

A representative example of a recrystallized Middle Eocene

multi-species data array[26] is shown in Fig. 1, along with an interpretative model for the depth habitats of the respective species. Significant oxygen and carbon isotope differentials between the species are observed, which are explained by their different ecologies. These differentials are consistent with many other sites in which the same species have been analysed. Furthermore, species-specific relationships between carbon isotope compositions and size are also observed in surface-dwelling taxa in this and similar samples[26]. Data such as these have led most authors to conclude that substantial diagenetic overprinting of the isotopic ratios is unlikely, even when the microstructural preservation is acknowledged as imperfect[3,26].

However, while the vast majority of $\delta^{18}O$ estimates have supported the cool tropics view, occasional studies of exceptionally well preserved mollusc shells[25,27], early diagenetic cements[25], and phosphates[28] have indicated considerably warmer temperatures approaching 30 °C. In addition, recent studies[29,30] of exceptionally well preserved planktonic foraminifera have indicated similar warm temperatures in the Middle Cretaceous. These results have prompted us to collect rare, exceptionally well preserved assemblages from the Late Cretaceous and Eocene of Tanzania and elsewhere, to further test the validity of planktonic foraminiferal SST estimates for these periods.

Shell construction and diagenesis in foraminifera

The primary shell wall in planktonic foraminifera is constructed from aggregates of morphologically discontinuous microgranules or plaques of sub-micrometre size that are originally precipitated intra-cellularly close to the site of chamber formation[31]. The microgranules are then fused or bound together by further calcite growth creating a smooth surface, often with finely sculpted features such as pores, hexagonal pore-pits, surface pustules and radiating spines (Fig. 2a–f). Planktonic shells appear to have substantial microscopic porosity between the microgranules, whereas benthic foraminifera tend to have denser, more robust shells. The relatively low-density shell structures of planktonic foraminifera may be an adaptation for maintaining buoyancy.

High-resolution scanning electron microscope (SEM) images[31] show that planktonic foraminifer microgranules have irregular shapes and consequently high surface areas, making them prone

to diagenetic recrystallization. In this way, a shell may become thoroughly recrystallized on a micrometre scale without obliterating structures such as wall pores, internal shell layering features and surface ornament. Our observations of many Cretaceous and Palaeogene samples suggests that this kind of diagenesis is ubiquitous in the pelagic oozes and chalks that are commonly used in palaeoceanographic studies, even when preservation has been described as good or excellent (Fig. 2g–i). We emphasize that this process is distinct from a more obvious mode of alteration that involves the precipitation of euhedral inorganic calcite crystals from solution on the inner and outer surfaces of the shells, sometimes resulting in substantial infillings or overgrowths. Such overgrowths are also very common in more deeply buried chalk and limestone samples, but have generally been avoided in previous isotopic work.

Pristine planktonic foraminifer shells of small modern non-encrusting species or juveniles are translucent and appear 'glassy' under the light microscope. This kind of preservation is rare in ancient material. 'Glassy' preservation does, however, occur in some impermeable clay-rich sediments that have escaped significant burial[29,30]. The reason for this appears to be that clay-rich sediments have very low porosity and permeability, so that carbonate fossils are effectively sealed within the sediment and quickly equilibrate with their accompanying fluids.

Certain localities have been prized by micropalaeontologists for their exceptional preservation but have not previously been targeted in isotopic work. In particular, outcrops of Cretaceous and Palaeogene silty clays in southern coastal Tanzania have long been known to yield excellently preserved material from a wide range of ages[32,33]. We re-collected these sites with a view to conducting new stable isotope studies and testing what has become known[20] as the 'cool tropic paradox'. We also analysed three other exceptionally well preserved Eocene assemblages from Mexico, Alabama and the Adriatic Sea, allowing us to examine other tropical to mid-latitude sites. Details of the localities, their geological setting and micropalaeontological characterization are available; see Supplementary Information.

Stable isotope results

We selected samples for analysis in which there is no significant overgrowth or infilling of diagenetic calcite, and in which
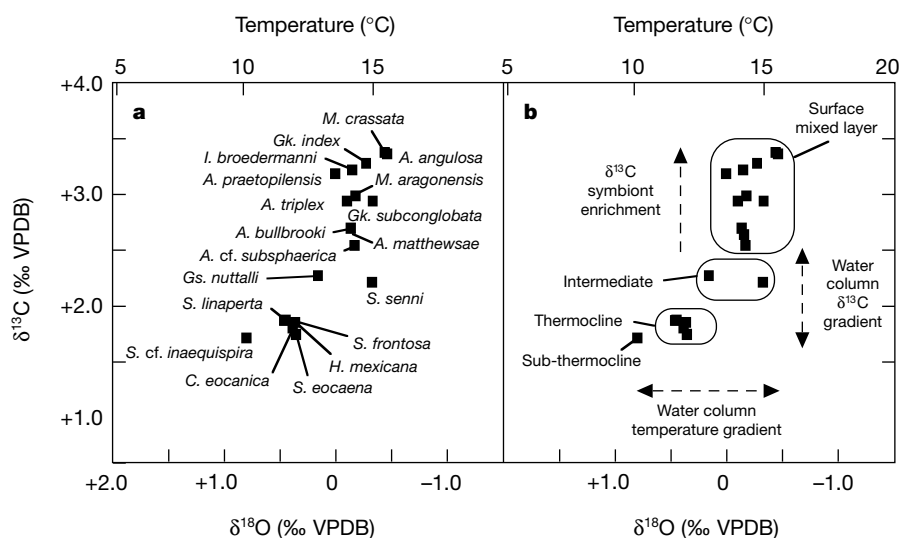
Figure 1 Multi-species stable isotope array from a typical recrystallized planktonic foraminifer assemblage from the Middle Eocene (DSDP Site 523, Angola basin, South Atlantic Ocean, modified from ref. 26). **a**, Cross-plot of mean oxygen (scale reversed) and carbon isotope ratios of each species. Note the retention of substantial carbon isotope differentials despite diagenesis. **b**, Interpretative model for the respective depth-habitats of the different species. Burial depth is 150–180 m. Absolute temperature estimates and $\delta^{13}C$ values are affected by diagenesis. $\delta^{18}O = [(^{18}O/^{16}O)_{sample} / (^{18}O/^{16}O)_{standard}] - 1$, $\delta^{13}C = [(^{13}C/^{12}C)_{sample} / (^{13}C/^{12}C)_{standard}] - 1$, VPDB standard in both cases. *M. Morozovella*; *A. Acarinina*; *Gk. Globigerinatheka*; *S. Subbotina*; *H. Hantkenina*; *C. Clavigerinella*; *Gs. Guembelitrioides*; *I. Igorina*.

preservation of foraminiferal shells appears excellent on a micrometre scale. Each clay sample was washed and sieved and monospecific splits were prepared, typically of 5–10 adult individuals but more in the case of smaller species. Shells were ultrasonically cleaned, and treated with hydrogen peroxide to remove organic matter. Stable isotope analyses were conducted on a VG Prism mass spectrometer with a minimum analytical precision of ±0.08‰ for oxygen and ±0.06‰ for carbon. All data are available as Supplementary Information.

Multi-species results for each sample are given in Fig. 3. We have chosen not to apply a latitude-based 'correction' for seawater $\delta^{18}O$ by analogy with the modern ocean[34] because the precise form of the correction depends on unknown climatic factors[17,35], and because the outer continental shelf environments represented in this study were probably affected by boundary currents, making $\delta^{18}O$ values measured there unrepresentative of open-ocean values at the same latitudes. Because even un-encrusted planktonic foraminifera dwelling in the surface mixed-layer can precipitate some calcite in slightly deeper conditions, we take the most negative $\delta^{18}O$ value in the assemblage as representative of the seasonal maximum SST. Note that the benthic foraminifera in these samples reflect bottom-water temperatures on the continental shelf, and therefore are not comparable to coeval temperatures in deep-sea environments.

A possible objection to a stable isotope study in an outer-shelf environment is that it may be affected by freshwater inputs from large rivers, biasing the $\delta^{18}O$ measurements towards light ('warm') values. We do not consider this a significant problem for the Cretaceous and Middle Eocene samples analysed in this study for several reasons. The setting is a deep-water hemipelagic environment. Palaeogeographic reconstructions[36,37] suggest a shoreline approximately 30–50 km inland of the present coastal localities

and, as today, an absence of large rivers. Trace fossils of the deep-water *Nereites* assemblage are common in parts of the succession[37] and planktonic microfossils are fully diverse, unlike modern environments affected by plumes of river water. Modern offshore Tanzania has normal marine salinities and temperatures due to the southward-flowing Somali current, which brings equatorial Indian Ocean water on to the narrow shelf, and similar circulation patterns and salinities have probably occurred since at least the Late Cretaceous[15]. The distribution of isotopic values is indicative of a well stratified open-ocean environment with no anomalous data as might be evident from a freshwater plume. Finally, freshwater runoff in tropical environments generally has an isotopic composition closer to that of sea water than in the middle and high latitudes, making it difficult to greatly affect the $\delta^{18}O$ without a very large freshwater influence. Despite this, we acknowledge that the Late Eocene samples from Tanzania and Alabama probably represent relatively shallower-water environments on account of the lower planktonic:benthic ratios and less diverse plankton assemblages, and so might be more likely to be affected by low salinities.

A single data set from a Late Cretaceous sample (sample LIN 99-100, *Abathomphalos mayaroensis* Zone, Maastrichtian age, 67 ± 2 Myr ago) is presented in Fig. 3a. Species have not been divided *a priori* into depth habitats because too little is known of Late Cretaceous planktonic foraminifer ecology. Nevertheless, our data are generally consistent with previous isotopic rankings[20,21] in that small species belonging to the genera *Rugoglobigerina* and *Rugotruncana* and species with serially arranged chambers generally yield the more negative $\delta^{18}O$ values, whereas the larger, more ornate forms give more positive values. Two notable exceptions to this are *A. mayaroensis* which elsewhere[21] has been recorded as a 'deep dweller' but has relatively negative $\delta^{18}O$ in our study, and *Rugoglobigerina rugosa* which has more positive isotopic ratios
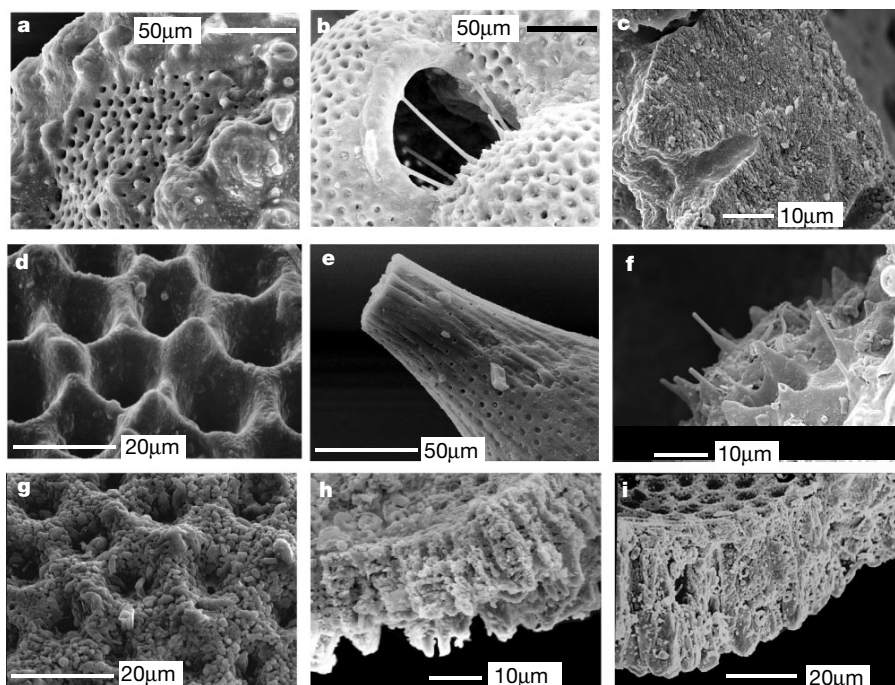
Figure 2 Scanning electron micrographs of planktonic foraminifera, contrasting well preserved (**a**–**f**) and poorly preserved (**g**–**i**) shell textures. **a**, *Globotruncanita stuarti*, Maastrichtian, sample LIN 99-100, Lindi, Tanzania. **b**, *Globigerinatheka index* with preserved spines, Middle Eocene, sample LIN 99-17, Kitunda, Tanzania. **c**, *Globoquadrina tripartita*, Middle Eocene, cross-section of wall showing microgranular texture, sample LIN 99-17, Kitunda, Tanzania. **d**, *Globoquadrina tapuriensis*, holotype, lowermost Oligocene, detail of hexagonal pore-pits, sample FCRM-1645, Kitunda, Tanzania. **e**, *Hantkenina lehneri*, Middle Eocene, detail of tubulospine base, type section of Guayabal formation,

Vera Cruz, Mexico. **f**, *Guembelitrioides nuttalli*, Middle Eocene, spine bases, 1,170 m below sea floor, Hole IM-5, Adriatic Sea, Middle Eocene. **g**, *Globoquadrina tripartita*, Late Eocene, detail of recrystallized pore-pits, ODP sample 1052B, 10H-2, 133–135 cm in core section, western North Atlantic. **h**, *Acarinina praetopilensis*, Middle Eocene, cross-section of wall with coarse recrystallization, ODP Hole 865B, Pacific Ocean. **i**, *Morozovella aragonensis*, Middle Eocene, cross-section of recrystallized wall, DSDP Site 523, sample 49-2, 38–40 cm in core section.

than expected. We note that the relatively positive $\delta^{13}C$ of *Hedbergella holmdelensis* may indicate an association with symbiotic dinoflagellates. The most negative $\delta^{18}O$ in the assemblage is given by *Pseudotextularia elegans*, which has previously been recognized as a marker for surface-water conditions[21].

The 'isotopic niches' of Middle Eocene species (Fig. 3b–f) are better known, and most species in the Tanzanian, Mexican and Adriatic samples plot in approximately their expected relative positions in comparison to earlier work[26,38,39]. We note that the more encrusted mixed-layer species in the genera *Morozovella*, *Acarinina* and *Globigerinatheka* tend to have more positive $\delta^{18}O$ values than do the more weakly ornamented acarininids, suggesting that a component of deeper water calcite added at gametogenesis is

present in those forms. We also note the unusual but consistent isotopic characteristics of the little-studied planispiral species *Pseudohastigerina micra*. We interpret this species as a mixed-layer calcifier that exhibits a large negative $\delta^{13}C$ vital effect, possibly because of incorporation of some metabolic CO_2 into the shell. More surprising was the relatively light $\delta^{18}O$ values of *Subbotina eocaena* in sample KIL 99-41, which suggests that not all Middle Eocene subbotinids were deep dwellers—as has sometimes been assumed[18].

The Late Eocene assemblages (Fig. 3g–i) show smaller isotopic differentials between species, especially in $\delta^{13}C$, as has frequently been observed in other studies[38]. Surface-water conditions seem to be indicated by the genera *Pseudohastigerina*, *Globigerinatheka* and
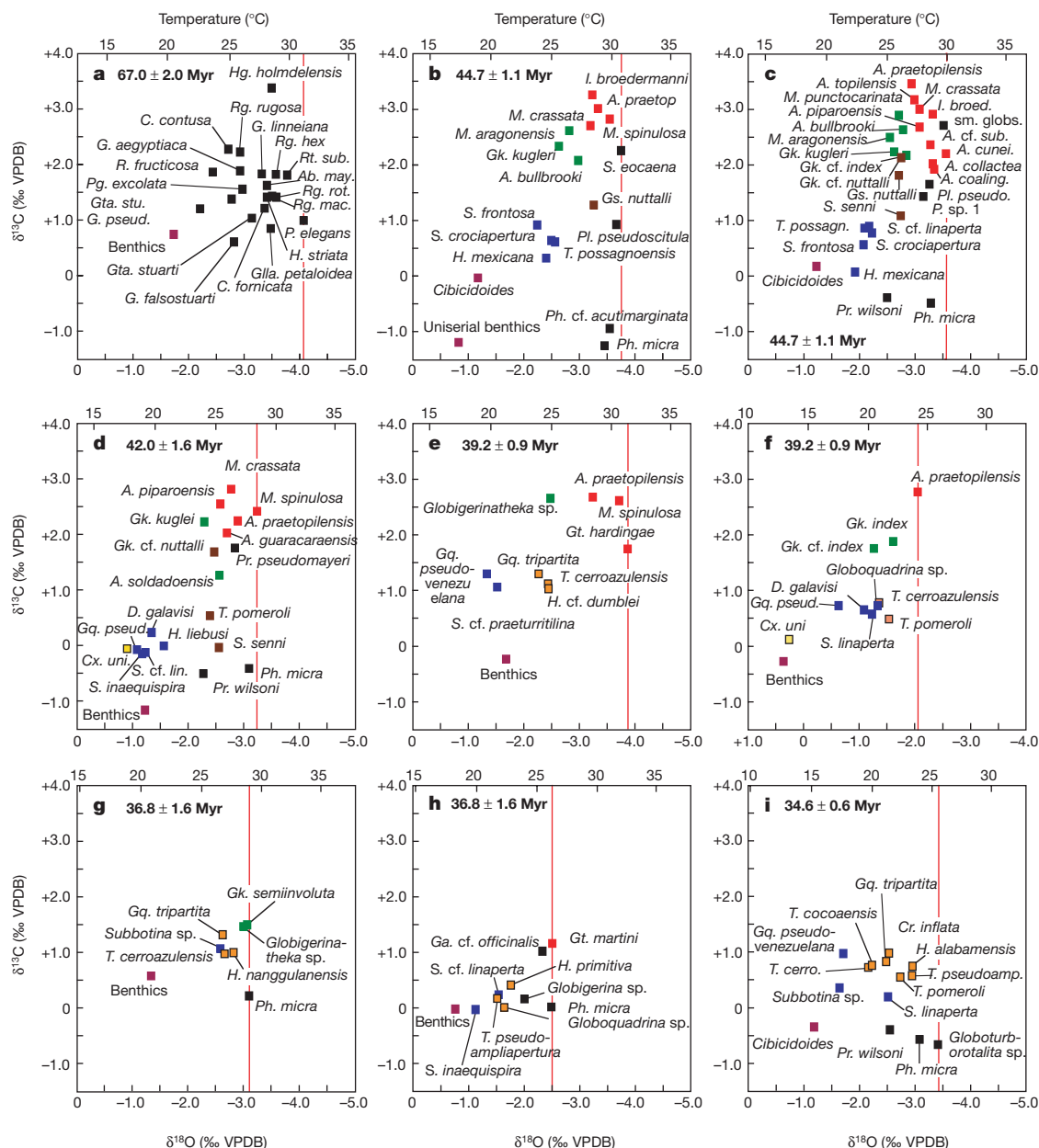
Figure 3 Multi-species stable isotope arrays for a variety of exceptionally well preserved samples. Vertical red lines indicate the most negative $\delta^{18}O$ of each assemblage, indicating inferred sea surface temperature. The temperature scale is calculated using the equation of ref. 50, and includes an ice-volume correction to seawater $\delta^{18}O$ of $-1.00‰$ for the Late Cretaceous, $-0.75‰$ for the Middle Eocene, and $-0.5‰$ for the Late Eocene. Samples are dated to within one planktonic foraminifer biozone. Coloured squares indicate habitat as follows: red, mixed-layer symbiotic; green, encrusted mixed-layer

symbiotic; brown, intermediate habitat; blue, thermocline; yellow, sub-thermocline; black, planktonic, habitat uncertain; purple, benthic. See Supplementary Information for biostratigraphy and full Linnaean binomials of foraminifer species. **a**, Sample LIN 99-100, Lindi, Tanzania. **b**, Sample KIL 99-41, Kilwa Masoko, Tanzania. **c**, Sample RAS 99-17, Ras Mtama, Tanzania. **d**, Guayabal formation, Mexico. **e**, Sample LIN 99-17, Lindi, Tanzania. **f**, Istra-more 5 well, Adriatic Sea. **g**, Sample PP98-L11, Lindi, Tanzania. **h**, Cocoa Sands formation, Alabama. **i**, Sample NAM 99-01, Namadingura, Tanzania.

the small globular genus *Globoturborotalita* which was probably ancestral to many modern mixed-layer species.

Diagenesis reconsidered

Although the relative positions of the various species in our sample are generally as expected from earlier work, a greater range of values is observed in both stable isotopes, and the $\delta^{18}O$ data are considerably more negative than has generally been reported. These discrepancies can be resolved if we interpret our exceptionally well preserved material as representing the true, warm, SSTs, whereas other more recrystallized material has been 'overprinted' by a component of diagenetic calcite precipitated in cold bottom waters. This accords with the fact that $\delta^{18}O$ values are expected to be altered toward more positive values in early marine diagenesis[3,5,6], which is the reverse of the more normal trend towards negative values in meteoric and high-temperature diagenesis.

To explore this possibility, particularly with regard to the problem that carbon isotope differentials between species are apparently retained to some extent during diagenesis[3], we have plotted (Fig. 4) the data from a representative sample from our study (RAS 99-17) on the same scale as the DSDP Site 523 data from Fig. 1 (which is approximately the same age). A total of 11 species are common to both data sets, and are joined by lines for clarity. The burial depth of the Site 523 samples is approximately 200 m, within the zone at which diagenesis is expected to cause a shift towards positive $\delta^{18}O$ (ref. 5). We have plotted on Fig. 4 the expected isotopic composition of diagenetic calcite at shallow burial depths[3]. We note a clear convergence of the lines towards this composition, which at face value would indicate a likely component of 50% diagenetic calcite and 50% original calcite in the Site 523 data, and a reduction of apparent palaeotemperature of nearly 15 °C.

However, we acknowledge that the RAS 99-17 temperatures may not be representative of the Site 523 assemblage before diagenesis. The Tanzanian data set (palaeolatitude ~19° S) probably existed in a warm boundary current, whereas the Site 523 data are from a higher sub-tropical palaeolatitude (~32° S) and may have been influenced by a colder northward proto-Benguela current. If the RAS 99-17 data were shifted by several degrees to cooler values to compensate, the data would still yield a plausible set of 'mixing lines', still indicating a substantial overprint (~50% by volume) in both $\delta^{18}O$ and $\delta^{13}C$, but converging on warmer bottom-water temperatures. That interpretation would in fact be more in line with benthic foraminifer stable isotope data from the Middle

Eocene that indicate bottom-water temperatures nearer 10 °C (ref. 40).

We infer from this that most planktonic foraminifer stable isotope data from carbonate oozes and chalks are 'suspect', and may represent a roughly equal combination of surface- and bottom-water signals. The effect probably varies in degree between sites according to their burial depths and diagenetic histories. Samples from more clay-rich sites and horizons are probably less altered than more carbonate-rich sites. This result would have profound importance for palaeoceanography in general, including studies of the long-term evolution of global climate and the interpretation of transient climate events which may involve changes in both surface- and bottom-water conditions.

The 'broad warm tropics' orthodoxy?

In Fig. 5 we show oxygen isotope data from mixed-layer and deeper-dwelling foraminifera from a variety of locations plotted as a function of latitude, with the new data from excellently preserved carbonates highlighted in red. The contrast between the new and old data is evident, in both the absolute values and the surface-to-thermocline differentials.

A corollary of our interpretations is that diagenesis would be expected not only to decrease the measured temperatures and inter-species differentials, but also to reduce the apparent meridional temperature gradients inferred from recrystallized material. This is because deep-sea temperatures and early diagenetic conditions are expected to be fairly homogeneous at any given time, regardless of latitude. We therefore propose that meridional gradients were probably steeper than previously thought in the Late Cretaceous and Eocene epochs. This is supported by a comparison of the tropical data with the higher-latitude sample from the Adriatic, which indicates markedly cooler temperatures for the same species. However, we highlight the need for more data from excellently preserved material from a variety of latitudes to test this proposition.

Present-day SSTs rarely exceed 30 °C (except in isolated basins), leading some to suggest that negative feedbacks involving cloud cover[41], evaporation or changes in circulation patterns[42] limit open ocean temperatures. Several of our estimates are above 30 °C, and it is unlikely that we have sampled the warmest parts of the oceans. So although we acknowledge multiple uncertainties in estimating temperatures for distant time periods, our data would appear to contradict the existence of a strict homeostatic limit to tropical SSTs in greenhouse conditions.

Low-latitude temperatures have a significant effect on wind strengths, monsoons, oceanic upwelling intensities and zonal patterns of precipitation and evaporation. A recent comparison[35] of Eocene climate simulations with cool and warm (>30 °C) tropical SSTs suggests that a broad warm tropical belt produces a realistic simulation of Eocene climate that is consistent with most geological evidence[35]. It has also been pointed out[17] that even moderately higher tropical temperatures than today (+2 °C) would markedly increase evaporation rates and hence latent heat transport by the atmosphere, helping to explain the inferred polar warmth of past warm climate phases.

The warm tropics view is also supported by the geographical distributions of temperature-sensitive organisms such as larger foraminifera, corals, mangroves, palms and reptiles. All of these organisms have present-day minimum temperature requirements that have previously been argued as contradicting the cool tropics view[43–45]. Unfortunately, it is more difficult to place a precise upper bound on the likely temperatures given the distributions of fossil organisms, and the question has received less attention[46]. Symbiotic corals may be the most sensitive of these groups to high temperatures, and it is interesting that they were apparently less common and diverse in Cretaceous and Palaeogene times than they are today[46]. It has been suggested that Pacific carbonate platforms
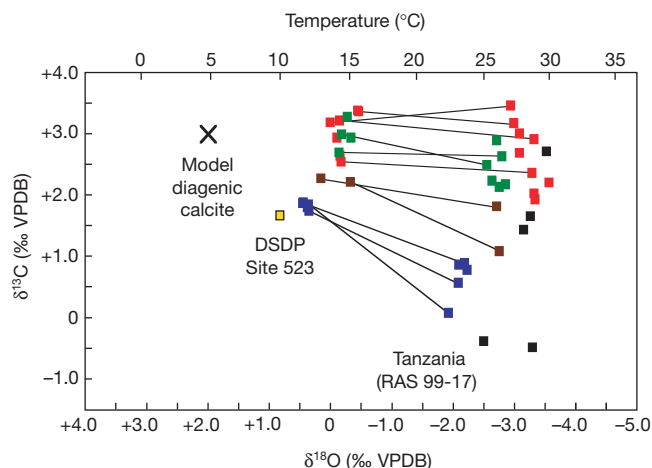
Figure 4 Comparison of stable isotope data from a typical recrystallized sample (DSDP Site 523, data as in Fig. 1) with a representative sample from this study of approximately the same age (sample RAS 99-17). Lines join species that are common to the two data sets. The approximate composition of diagenetic calcite is from ref. 3. Colours as in Fig. 3.
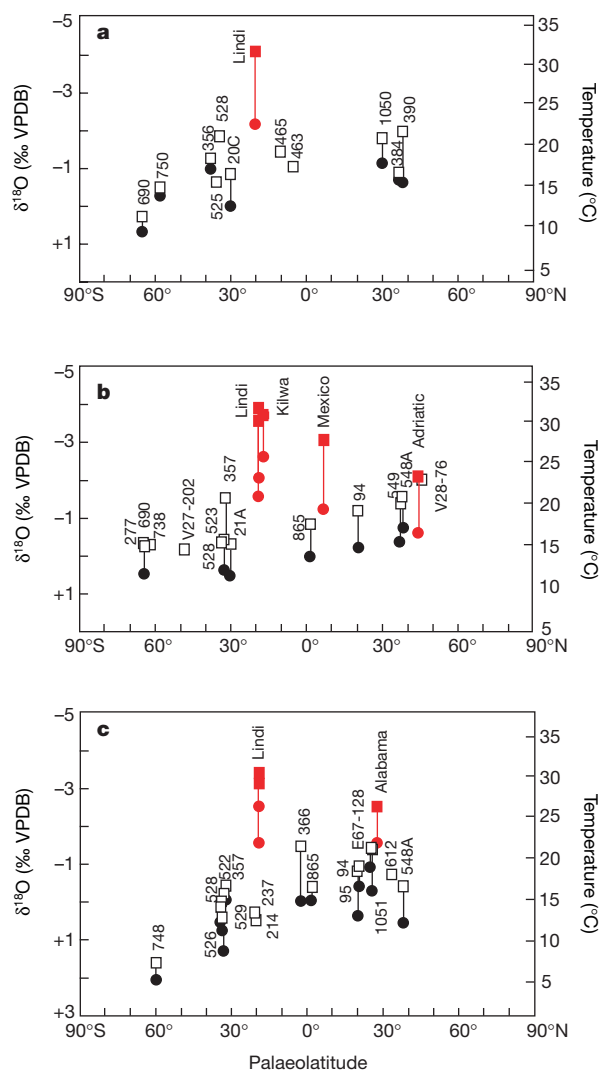
Figure 5 Zonal profiles of planktonic foraminifer δ^{18}O as a function of palaeolatitude. **a**, *A. mayaroensis* zone, Late Cretaceous epoch; **b**, zone P11–P14, Middle Eocene; **c**, zone P15–P16, Late Eocene. Squares, mixed-layer-dwelling species; circles, deeper-dwelling species. Data from this study are highlighted in red. Ice-volume corrections for seawater δ^{18}O are the same as in Fig. 2.

that moved on the plate tectonic conveyor into the tropics during these times often died, possibly as a result of high temperatures[47]. Also suggestive is that organisms such as crocodilians, which peak in diversity in the modern equatorial region, had sub-tropical diversity peaks in both hemispheres during greenhouse periods[45], possibly because they were excluded from the equator by unfavourable climate conditions.

Discussion

Our analysis of planktonic foraminifer shells from hemipelagic clays suggests that, for those parts of the Late Cretaceous and Eocene epochs that we have sampled, tropical temperatures were at least as warm as today, and probably several degrees warmer. This result is in line with known patterns of biotic distribution and the predictions of climate models, and allows us to dispose of the 'cool tropic paradox' that has bedevilled the study of past warm climates. The new evidence also removes a significant impediment[22] to the view that high levels of greenhouse gases contributed to global warming during these periods[48,49].

We contend that most previous workers, including ourselves, have been misled to some extent by fine-scale recrystallization of

planktonic foraminifer shells, which occurs at shallow burial depths in open ocean pelagic oozes and chalks. This process introduces a much larger component of diagenetic calcite than has generally been recognized, making such shells unsuitable for sea surface palaeo-temperature analysis. However, we acknowledge that even if a recrystallized shell is a roughly equal mixture of sea-surface and early diagenetic calcite, much work can still be done, within a modified interpretative framework, in the study of long-term climate change and also in the study of Milankovitch-scale variation and transient events. Also, we stress that benthic foraminifer shells are probably not affected by diagenesis to the same degree, so the classic deep-sea δ^{18}O record of the Cenozoic era[40] remains a valuable benchmark for long-term palaeoclimate research. As scientific ocean drilling enters a new phase, we hope that our data will act as a spur for the targeting of hemipelagic muds of Cretaceous and Palaeogene age from a variety of latitudes that are likely to contain exceptionally well preserved planktonic foraminiferal shells. □

1. Urey, H. C. The thermodynamic properties of isotopic substances. *J. Chem. Soc.* **1947,** 562–581 (1947).
2. Emiliani, C. Depth habitats of some species of pelagic foraminifera as indicated by oxygen isotope ratios. *Am. J. Sci.* **252,** 149–158 (1954).
3. Crowley, T. J. & Zachos, J. C. in *Warm Climates in Earth History* (eds Huber, B. T., MacLeod, K. S. & Wing, S. C.) 50–76 (Cambridge Univ. Press, Cambridge, 2000).
4. Spero, H. J., Bijma, J., Lea, J. W. & Bemis, B. E. Effect of seawater carbonate chemistry on planktonic foraminiferal carbon and oxygen isotope values. *Nature* **390,** 497–500 (1997).
5. Schrag, D. P., DePaolo, D. J. & Richter, F. M. Reconstructing past sea surface temperatures: Correcting for diagenesis of bulk marine carbonate. *Geochim. Cosmochim. Acta* **59,** 2265–2278 (1995).
6. Schrag, D. P. Effects of diagenesis on the isotopic record of late Paleogene tropical sea surface temperatures. *Chem. Geol.* **161,** 215–244 (1999).
7. Shackleton, N. J. & Boersma, A. The climate of the Eocene ocean. *J. Geol. Soc. Lond.* **138,** 153–157 (1981).
8. Savin, S. M. The history of earth's surface temperature during the past 100 million years. *Annu. Rev. Earth Planet. Sci.* **5,** 319–355 (1977).
9. Shackleton, N. J. in *Fossils and Climate* (ed. Brenchley, P.) 27–34 (Wiley, Chichester, 1984).
10. Barron, E. J. Eocene equator-to-pole surface ocean temperatures: a significant climate problem? *Paleoceanography* **2,** 729–739 (1987).
11. Rind, D. & Chandler, M. Increased ocean heat transports and warmer climate. *J. Geophys. Res.* **96,** 7437–7461 (1991).
12. Horrell, M. A. Energy balance constraints on [18]O based paleo-sea surface temperature estimates. *Paleoceanography* **5,** 339–348 (1990).
13. Manabe, S. & Bryan, K. CO_2-induced change in a coupled ocean-atmosphere model and its paleoclimatic implications. *J. Geophys. Res.* **90,** 11689–11708 (1985).
14. Sloan, L. C. & Rea, D. K. Atmospheric carbon dioxide and early Eocene climate: A general circulation model sensitivity study. *Palaeogeogr., Palaeoclimatol. Palaeoecol.* **119,** 275–292 (1995).
15. Bush, A. B. G. & Philander, S. G. H. The late Cretaceous: Simulation with a coupled atmosphere-ocean general circulation model. *Paleoceanography* **12,** 495–516 (1997).
16. Rind, D. Latitudinal temperature gradients and climate change. *J. Geophys. Res.* **103,** 5943–5971 (1998).
17. Bice, K. L., Scotese, C. R., Seidov, D. & Barron, E. J. Quantifying the role of geographic change in Cenozoic ocean heat transport using uncoupled atmosphere and ocean models. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **161,** 295–310 (2000).
18. Bralower, T. *et al.* Late Paleocene to Eocene paleoceanography of the equatorial Pacific Ocean: Stable isotopes recorded at Ocean Drilling Program Site 865, Allison Guyot. *Paleoceanography* **10,** 841–865 (1995).
19. Wade, B. in *Western North Atlantic Palaeogene and Cretaceous Palaeoceanography* (eds Kroon, D., Norris, R. D & Klaus, A.). 273–291 (Spec. Publ. 183, Geological Society, London, 2001).
20. D'Hondt, S. & Arthur, M. A. Late Cretaceous oceans and the cool tropic paradox. *Science* **271,** 1838–1841 (1996).
21. D'Hondt, S. & Arthur, M. A. Interspecies variation in stable isotopic signals of Maastrichtian planktonic foraminifera. *Paleoceanography* **10,** 123–125 (1995).
22. Veizer, J., Godderis, Y. & François, L. M. Evidence for decoupling of atmospheric CO_2 and global climate during the Phanerozoic eon. *Nature* **408,** 698–701 (2000).
23. Crowley, T. J. & Berner, R. A. CO_2 and climate change. *Science* **292,** 870–872 (2001).
24. Killingley, J. S. Effects of diagenetic recrystallization on ^{18}O/^{16}O values of deep-sea sediments. *Nature* **301,** 594–597 (1983).
25. Wilson, P. A. & Opdyke, B. N. Equatorial sea surface temperatures for the Maastrichtian revealed through remarkable preservation of metastable carbonate. *Geology,* **24,** 555–558 (1996).
26. Pearson, P. N., Shackleton, N. J. & Hall, M. A. Stable isotope paleoecology of middle Eocene planktonic foraminifera and multi-species isotope stratigraphy, DSDP Site 523, South Atlantic. *J. Foram. Res.* **23,** 123–140 (1993).
27. Andreasson, F. P. & Schmitz, B. Tropical Atlantic seasonal dynamics in the early middle Eocene from stable oxygen and carbon isotope profiles of mollusk shells. *Paleoceanography,* **13,** 183–192 (1998).
28. Kolodny, Y. & Raab, M. Oxygen isotopes in phosphatic fish remains from Israel: paleothermometry of tropical Cretaceous and Tertiary shelf waters. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **64,** 59–67 (1988).
29. Norris, R. D. & Wilson, P. A. Low-latitude sea-surface temperatures for the mid-Cretaceous and the evolution of planktic foraminifera. *Geology* **26,** 823–826 (1998).

30. Wilson, P. A. & Norris, R. D. Warm tropical ocean surface and global anoxia during the mid-Cretaceous period. *Nature* **412,** 425–429 (1991).

31. Hemleben, C., Spindler, M. & Anderson, O. R. *Modern Planktonic Foraminifera* (Springer, New York, 1989).

32. Blow, W. H. & Banner, F. T. in *Fundamentals of Mid-Tertiary Stratigraphical Correlation* (ed. Eames, F. T.). 61–151 (Cambridge Univ. Press, Cambridge, 1962).

33. Blow, W. H. *The Cainozoic Globigerinida: a Study of the Morphology, Taxonomy and Evolutionary Relationships and the Stratigraphical Distribution of some Globigerinida (mainly Globigerinacea)* Vols 1–3 (Brill, Leiden, 1979).

34. Zachos, J. C., Stott, L. D. & Lohmann, K. C. Evolution of early Cenozoic marine temperatures. *Paleoceanography* **9,** 353–387 (1994).

35. Huber, M. & Sloan, L. C. Climatic response to tropical sea surface temperature changes on a 'greenhouse' Earth. *Paleoceanography* **15,** 443–450 (2000).

36. Kent, P. E., Hunt, M. A. & Johnstone, M. A. *The Geology and Geophysics of Coastal Tanzania.* (Natural Environment Research Council Geophysical Paper no. 6, HMSO, London, 1971).

37. Schluter, T. *Geology of East Africa* 239 (Borntraeger, Stuttgart, 1997).

38. Boermsa, A., Premoli Silva, I. & Shackleton, N. J. Atlantic Eocene planktonic foraminiferal paleohydrographic indicators and stable isotope paleoceanography. *Paleoceanography* **2,** 287–331 (1987).

39. Coxall, H. K., Pearson, P. N., Shackleton, N. J. & Hall, M. A. Hantkeninid depth adaptation: an evolving life strategy in a changing ocean. *Geology* **28,** 87–90 (2000).

40. Zachos, J., Pagani, M., Sloan, L., Thomas, E. & Billups, K. Trends, rhythms, and aberrations in global climate 65Ma to present. *Science* **292,** 686–693 (2001).

41. Ramanathan, V. & Collins, W. Thermodynamic regulation of ocean warming by cirrus clouds deduced from satellite observations of the 1987 El Niño. *Nature* **351,** 27–32 (1991).

42. Waliser, D. E. Some considerations on the thermostat hypothesis. *Bull Am. Meteorol. Soc.* **77,** 357–360 (1996).

43. Adams, C. G., Lee, D. E. & Rosen, B. R. Conflicting isotopic and biotic evidence for tropical sea-surface temperatures during the Tertiary. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **77,** 289–313 (1990).

44. Graham, A. Neotropical Eocene coastal floras and ^{18}O/^{16}O-estimated warmer vs. cooler equatorial waters. *Am. J. Bot.* **81,** 301–306 (1994).

45. Markwick, P. Fossil crocodilians as indicators of Late Cretaceous and Cenozoic climates: implications for using palaeontological data in reconstructing palaeoclimate. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **137,** 207–271 (1998).

46. Barron, E. J. in *Effects of Past Global Change on Life* 108–117 (National Academy Press, Washington D.C., 1995).

47. Wilson, P. A., Jenkyns, H. C., Elderfield, H. & Larson, R. L. The paradox of drowned carbonate platforms and the origin of Cretaceous Pacific guyots. *Nature* **392,** 889–894 (1998).

48. Pearson, P. N. & Palmer, M. R. Atmospheric carbon dioxide concentrations over the past 60 million years. *Nature* **406,** 695–699 (2000).

49. Retallack, G. J. A 300-million-year record of atmospheric carbon dioxide from fossil plant cuticles. *Nature* **411,** 287–290 (2001).

50. Erez, B. & Luz, J. Experimental paleotemperature equation for planktonic foraminifera. *Geochim. Cosmochim. Acta* **47,** 1025–1031 (1983).

letters to nature

addendum

An efficient room-temperature silicon-based light-emitting diode

Wai Lek Ng, M. A. Lourenço, R. M. Gwilliam, S. Ledain, G. Shao & K. P. Homewood

Nature **410,** 192–194 (2001).

Silicon light-emitting diodes (LED) show light emission at the bandgap energy of silicon with efficiencies approaching those of standard III–V emitters: 0.1% for planar devices (our Letter) and about 1% when total internal reflection is minimized by surface texturing[1]. We point out here an additional example of a silicon device also showing light emission at the bandgap[2]. The authors described devices made by the SACMOS-3 process and focus the bulk of the paper on visible emission under reverse bias. However, they also report briefly on a device operated under forward bias giving efficiencies of around 0.01%, although no explanation of the mechanism is given. It is now becoming clear that crystalline silicon, when appropriately engineered, is capable of supporting efficient light emission, opening up many significant applications. □

1. Green, M. A., Shao, J., Wang, A., Reece, P. J. & Gal, M. Efficient silicon light-emitting diodes. *Nature* **412,** 805–808 (2001).
2. Kramer, J. *et al.* Light-emitting devices in industrial CMOS technology. *Sensors Actuators* **A37–A38,** 527–533 (1993).

erratum

Warm tropical sea surface temperatures in the Late Cretaceous and Eocene epochs

Paul N. Pearson, Peter W. Ditchfield, Joyce Singano, Katherine G. Harcourt-Brown, Christopher J. Nicholas, Richard K. Olsson, Nicholas J. Shackleton & Mike A. Hall

Nature **413,** 481–487 (2001).

In this Article, the temperature scale in Figure 3i should have been the same as in Figure 3g. □

corrections

Self-assembled monolayer organic field-effect transistors

Jan Hendrik Schön, Hong Meng & Zhenan Bao

Nature **413,** 713–716 (2001).

The values of the transconductance in Table 1 and in the text (page 715, second paragraph) are incorrect. The values should be divided by ten. The data plotted in Figs 2 and 3 are correct and the conclusions are not affected. □

Ordered nanoporous arrays of carbon supporting high dispersions of platinum nanoparticles

Sang Hoon Joo, Seong Jae Choi, Ilwhan Oh, Juhyoun Kwak, Zheng Liu, Osamu Terasaki & Ryong Ryoo

Nature **412,** 169–172 (2001).

We inadvertently omitted to cite an earlier reference alongside ref. 8 (G. Che, B. Lakshmi, E. R. Fisher and C. R. Martin *Nature* **393,** 346–349; 1998), which was published in 1995 (and not 2000 as printed). Also, our suggestion that using the pores in a microporous material as templates could be a way in which to produce nanoscale materials has been discussed before (see, for example, C. R. Martin *Science* **266,** 1961–1966 (1994) and J. C. Hulteen & C. R. Martin *J. Mater. Chem.* **7,** 1075–1087 (1997)). □

The timing of the last deglaciation in North Atlantic climate records

Claire Waelbroeck, Jean-Claude Duplessy, Elisabeth Michel, Laurent Labeyrie, Didier Paillard & Josette Duprat

Nature **412,** 724–727 (2001).

We directly used the observed leads of sea surface temperature with respect to air temperature (dated in calendar years), whereas the air temperature calendar ages should have been converted into ^{14}C ages, with reservoir ages computed as the difference between marine and atmospheric ^{14}C ages. Taking this into consideration, apparent surface-water ages are $1,180 \pm 630$ to $1,880 \pm 750$ years at the end of the Heinrich 1 surge event (14,500 years BP) and 930 ± 250 to $1,050 \pm 230$ years at the end of the Younger Dryas cold episode. This does not change the discussion and conclusions. □