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Eocene seasonality and seawater alkaline earth reconstruction using shallow-dwelling large benthic foraminifera

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ABSTRACT

Intra-test variability in Mg/Ca and other (trace) elements within large benthic foraminifera (LBF) of the family Nummulitidae have been investigated using laser-ablation inductively-coupled plasma mass spectrometry (LA-ICPMS). These foraminifera have a longevity and size facilitating seasonal proxy retrieval and a depth distribution similar to 'surface-dwelling' planktic foraminifera. Coupled with their abundance in climatically important periods such as the Paleogene, this means that this family of foraminifera are an important but under-utilised source of palaeoclimatic information. We have calibrated the relationship between Mg/Ca and temperature in modern *Operculina ammonoides* and observe a $\sim 2\%$ increase in Mg/Ca $^\circ C^{-1}$. *O. ammonoides* is the nearest living relative of the abundant Eocene genus *Nummulites*, enabling us to reconstruct mid-Eocene tropical sea surface temperature seasonality by applying our calibration to fossil *Nummulites djokdjokartae* from Java. Our results indicate a 5–6 °C annual temperature range, implying greater than modern seasonality in the mid-Eocene (Bartonian). This is consistent with seasonal surface ocean cooling facilitated by enhanced Eocene tropical cyclone-induced upper ocean mixing, as suggested by recent modelling results. Analyses of fossil *N. djokdjokartae* and *Operculina* sp. from the same stratigraphic interval demonstrate that environmental controls on proxy distribution coefficients are the same for these two genera, within error. Using previously published test–seawater alkaline earth metal distribution coefficients derived from an LBF of the same family (Raitzsch et al., 2010) and inorganic calcite, with appropriate correction systematics for secular Mg/Ca_{sw} variation (Evans and Müller, 2012), we use our fossil data to produce a more accurate foraminifera-based Mg/Ca_{sw} reconstruction and an estimate of seawater Sr/Ca. We demonstrate that mid-Eocene Mg/Ca_{sw} was $\lesssim 2$ mol mol^{-1}, which is in contrast to the model most commonly used to correct deep-time Mg/Ca data from foraminifera, but in agreement with most other Paleogene proxy and model data. This indicates that Mg/Ca_{sw} has undergone a substantial (3–4×) rise over the last ~ 40 Ma.

1. Introduction

The trace element chemistry of foraminifera tests is increasingly being used as a palaeoceanic reconstruction tool. Many potential proxies linking test chemistry to palaeoenvironmental information have been developed (see e.g. Katz et al., 2010), which are most commonly applied in the fossil record to either planktic or deep benthic foraminifera (where deep is used here to distinguish these foraminifera from the shallow-dwelling large benthic species under consideration in this study) (e.g. Tripati et al., 2011; Bohaty et al., 2012; Lear et al., 2000). The abundance of foraminifera in sediment cores, along with the widespread distribution of some species (Fraile et al., 2008) has resulted in this group of organisms becoming one of the key sources of palaeoceanic proxy information available (Pearson, 2012).

A disadvantage with the use of planktic foraminifera for palaeoceanic reconstruction is that they are relatively short lived, mineralising over days or weeks (Anderson and Faber, 1984), thus providing a short temporal record of changes in (e.g.) sea surface temperature (SST) (but see Wit et al., 2010). This may be further complicated by migration through the water column during the lifespan of some foraminifera (Eggins et al., 2003) or seasonal bias in biomineralisation (e.g. Jonkers et al., 2010). Seasonality is increasingly being recognised as a key component of climate change (Hollis et al., 2012; Denton et al., 2005; Crowley et al., 1986), although there are a limited amount of studies that have attempted to reconstruct seasonality from periods such as the Paleogene, potentially one of the most important time intervals with respect to similarity to predicted future pCO_2 (Zachos et al., 2008). Much of

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what is currently known is derived from $\delta^{18}O$ measurements in bivalves (e.g. Ivany et al., 2004; Andreasson and Schmitz, 2000; Dutton et al., 2002; Kobashi et al., 2004), which – whilst being an almost unique source of Paleogene ocean seasonality reconstruction – may suffer from biases resulting from freshwater-modified seawater $\delta^{18}O$ in near-coastal environments. Clumped isotope data may offer a solution to this problem (Keating-Bitonti et al., 2011), particularly with improved precision of such measurements.

Reconstructing seawater Mg/Ca (Mg/Ca_{sw}) is of great importance as fossil Mg/Ca data must be corrected for secular changes in this ratio when applying Mg/Ca–temperature calibrations derived from samples grown in or collected from modern seawater. The Cenozoic evolution of Mg/Ca_{sw} has been the subject of considerable debate (e.g. Coggon et al., 2011; Broecker and Yu, 2011; Lear et al., 2002), some of which is the result of uncertainties regarding the appropriate methodology for the correction of foraminiferal Mg/Ca data (summarised in Evans and Müller, 2012). It is clear that in order for the Mg/Ca palaeothermometer to produce accurate pre-Pleistocene palaeotemperatures, further reconstructions of palaeo-Mg/Ca_{sw} are required.

In order to (1) provide a method of seasonality reconstruction other than mollusc $\delta^{18}O$ and (2) produce an accurate foraminifera-derived Mg/Ca_{sw} reconstruction, we have investigated trace element heterogeneity in the tests of large benthic foraminifera (LBF). We utilise laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICPMS) as a highly spatially-resolved technique capable of identifying µm-scale heterogeneity whilst simultaneously assessing sample preservation. LBF are an informal group that typically exceed 3 mm^3 in volume (Ross, 1974) and have photosymbiotic algae (Hallock, 1984), inhabiting the photic zone. We present data from LBF of the family Nummulitidae, with focus on the Eocene genus *Nummulites*, as well as its nearest living relative *Operculina*, which was also present in the Eocene. Our data are primarily derived from *Nummulites* because they are more abundant than *Operculina* and form far larger tests, implying growth over a longer time period, therefore *Nummulites* have greater potential as tools for seasonal palaeoenvironment reconstruction. By comparing Recent *O. ammonoides* and *O. complanata* from seven modern locations to fossil samples of both *Operculina* sp. and *N. djokdjokartae* from the Eocene Nanggulan Formation of Central Java, we demonstrate how these foraminifera can be used as a palaeoceanic reconstruction tool. The size, abundance and (sub)tropical distribution of LBF such as the nummulitids make them a hitherto under-utilised source of proxy information from a climatically critical region of the oceans – the low latitudes – of which our knowledge of palaeocean temperatures is currently limited.

1.1. Ecology and biology of the nummulitids

The main morphological features of the nummulitids (order: Rotaliida) referred to in the text are shown in Fig. 1. The nummulitids are defined by the presence of a marginal cord (Fig. 1), the thickened margin of the shell exposed in an equatorial section (Loeblich and Tappan, 1987). This serves as a method of communication and transport between chambers, as well as playing an important role during sexual reproduction (Röttger et al., 1984). These foraminifera initially construct their chambers with walls consisting of two layers of calcite formed on either side of a primary organic membrane (Reiss, 1958). The test is hyaline, giving well-preserved calcite a glassy appearance.

LBF have a complex reproductive cycle resulting in morphologically distinct generations. Those with a large proloculus and a small number of chambers are known as the macrospheric generation, or A-forms. These reproduce sexually to form a microspheric generation (B-form) with a small proloculus and a large number of chambers (Dettmering et al., 1998; Kuile and Erez, 1991). This generation undergoes multiple fission, producing A-forms. Through this reproductive cycle at least two morphologically distinct generations of the same species are produced.

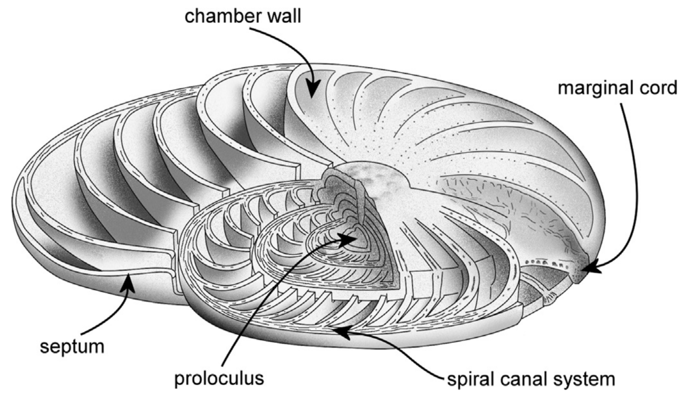

Fig. 1. Cutaway diagram of *O. ammonoides* with features referred to in the text labelled. Re-drawn from Carpenter et al. (1862). Although there are morphological differences between Recent *O. ammonoides* and Eocene *N. djokdjokartae*, all features labelled are present in both genera.

O. ammonoides are epifaunal, prefer sandy substrates and have a peak abundance range of 10–35 m water depth (Renema, 2008, 2006; Renema and Troelstra, 2001) but may live as deep as 130 m in the northernmost Red Sea (Reiss and Hottinger, 1984). This depth range may be related to the less turbid waters of the Gulf of Eilat; the nummulitids are sensitive to high light intensity and live at shallower depths if suspended sediment reduces the extent of the photic zone (Reiss and Hottinger, 1984). *O. complanata* prefers lower light intensities and occurs slightly deeper than *O. ammonoides* (Renema, 2003). Although temperature at the peak abundance depth of *O. ammonoides* may be 1–2 °C below SST, planktic foraminifera such as *Globigerinoides ruber* that are routinely considered to be surface dwelling inhabit a similar range (Anand et al., 2003). Hence, results derived from these LBF can be considered comparable to surface-dwelling planktic foraminifera, with respect to the extent to which these results relate to surface ocean conditions. *O. ammonoides* are limited to areas with minimum SST > 18 °C and are currently found in the Indian and west Pacific Oceans (Langer and Hottinger, 2000).

1.2. Previous LBF proxy development and application

Given the abundance of LBF in geologically and palaeoclimatologically important periods such as the Paleogene it is surprising that there has been relatively little work investigating their use as palaeoenvironmental archives. Wefer and Berger (1980) investigated intra-test stable isotope variability in the Recent LBF *Marginopora vertebralis* and *Cyclorbiculina compressa*. $\delta^{18}O$ microsampled from these foraminifera showed seasonal variation matching instrumental records in both species, demonstrating that these organisms record seasonality along their test growth axis. Recent *O. ammonoides* from the Red Sea precipitate calcite slightly lighter than expected for inorganic calcite (Fermont et al., 1983), although using the *Cibicidoides* $\delta^{18}O$–temperature calibration of Lynch-Stieglitz et al. (1999) and the local $\delta^{18}O_{sw}$ value (1.9‰) yields mean reconstructed temperature virtually identical to measured sea surface temperature (SST). Brasier and Green (1993) and Purton and Brasier (1999) were the first to apply mean $\delta^{18}O$ and stable isotope heterogeneity data from fossil LBF to reconstruct palaeoseasonality and temperature respectively. This work, based on well-preserved Eocene *Nummulites* revealed what the authors interpreted to be seasonal cycles, demonstrating the potential of these organisms for palaeoseasonality reconstruction.

Table 1
Sample site details. MAT is the mean annual sample site temperature with half of the seasonal range in temperature given as an error, with the exception of the Gulf of Eilat for which the November–April mean was used (specimens were collected in early May and have a test size implying growth over ∼ 6 months). The number of specimens analysed from each sample site is also given.

Location	Sample prefix	*n*	Co-ordinates	Water depth (m)	MAT (°C)	Mean Mg/Ca ($mmol\,mol^{-1}$)	Notes
Recent							
Great Barrier Reef	SS07613	5	19.73°S, 150.22°E	74	24.7 ± 0.8	141.5 ± 7.0	
Spermonde Shelf,	BTE27	5	5.053°S, 119.332°E	27	28.0 ± 0.8	153.1 ± 6.2	See Renema and Troelstra (2001)
SW Sulawesi	KKE30	5	5.106°S, 119.290°E	30	28.0 ± 0.4	151.7 ± 6.3	
Celebes Sea,	BBx25C	2	2.057°N, 118.441°E	53	27.4 ± 0.4	150.3 ± 2.5	See Renema (2006)
NE Kalimantan	BBx49A	4	1.388°N, 118.819°E	48	27.5 ± 0.5	147.9 ± 3.7	
Kepulauan Seribu,	SER	6	5.51–6.00°S,	14–24	29.0 ± 0.5;	155.4 ± 7.9;	See Renema (2008)
Jakarta			106.56–106.83°E		28.9 ± 0.5	153.5 ± 7.3	
Gulf of Eilat, Red Sea	Eil12	8	29.543°N, 34.972°E	10–15	21.9 ± 0.8	136.7 ± 9.3	
Eocene							
Nanggulan, Central Java	KW	26	–	–	–	–	See Lelono (2000)

Even less is known about trace element variation in LBF. Using electron microprobe analysis, Raja et al. (2005) produced the first (and only previous) Mg/Ca–temperature calibration for an LBF species, namely *Marginopora kudakajimaensis*. A Mg/Ca increase of $\sim 3\%\,°C^{-1}$ was observed, validating the Mg/Ca palaeothermometer in LBF. Raja et al. (2007) demonstrated the need for spatially-resolved analytical techniques when studying LBF; whole test Mg/Ca showed no relationship with temperature.

These studies demonstrate the potential of LBF as palaeoceanic archives and provide a basis for more detailed investigations into intra-test geochemical variability in the nummulitids, with the particular goal of assessing the use of such material in palaeoclimate reconstruction. With this aim we present highly spatially-resolved LA-ICPMS-derived element/Ca maps and profiles of both Eocene and Recent *Nummulites* and *Operculina*.

2. Materials and methods

Recent *O. ammonoides* were hand sampled live from reefs from five locations in Indonesia, the Great Barrier Reef (GBR) and the Gulf of Eilat (see Table 1 for details). In order to assess possible geochemical differences between different nummulitids, *O. complanata* was also collected from one of the sample sites (sample BBx49A from offshore northeast Kalimantan). Temperature data for the purposes of calibration were taken from the nearest available location in the World Ocean Atlas 2009 (Locarnini et al., 2010), with the exception of those from the Gulf of Eilat for which daily SST monitoring was available from the Interuniversity Institute for Marine Sciences in Eilat (http://www.iui-eilat.ac.il). The depth that matched the sampling depth most closely was used. With the exception of the Gulf of Eilat, sample site seasonality is small (maximum 1.6 °C) and therefore the mean annual temperature for each location was used to assess trace element–temperature relationships. For the Gulf of Eilat, the November–April mean was used (see Section 3.2.3).

Eocene *N. djokdjokartae* and *Operculina* sp. were collected from four stratigraphic levels within the Nanggulan Formation, Central Java. The Nanggulan Formation is a sequence of overall deepening upwards marine mudstones, sandstones and conglomeratic sandstones. At the top of the sampled interval the presence of abundant large *Discocyclina* indicates that this stratigraphic level correlates with the middle Bartonian Ta–Tb boundary (see Renema, 2007). Based on this, the samples are considered to be early Bartonian (38–40 Ma). During the mid-Eocene, the palaeolatitude of Central Java was 6°S (Hall, 2002). *N. djokdjokartae* were recovered from sandy beds from all four intervals, *Operculina* from only the lowest of these levels.

N. djokdjokartae were sectioned along the equatorial plane, mounted in epoxy resin and polished to expose the marginal cord. *Operculina* specimens were smaller and were embedded into epoxy without prior sectioning. All samples were cleaned prior to laser-ablation analysis (see the supplementary material for details). The LA-ICPMS system at RHUL features the RESOlution M-50 prototype laser-ablation system (193 nm ArF) coupled to an Agilent 7500ce ICPMS (Müller et al., 2009). Methodology and LA-ICPMS parameters different from those described in Müller et al. (2009) are given in Table S1. Monitored masses were ^{11}B, ^{24}Mg, ^{25}Mg, ^{27}Al, ^{43}Ca, ^{55}Mn, ^{66}Zn, ^{88}Sr, ^{89}Y, ^{138}Ba, ^{139}La, ^{140}Ce and ^{238}U. Eocene marginal cord profiles and mean marginal cord measurements of the Recent samples were obtained by profiling along the exposed marginal cord using a 44 μm laser spot (effective resolution was 120 μm because the 99% cell washout time is ∼ 1.5 s). In order to investigate intra-test trace element variability in greater detail, element maps were created for three Recent *O. ammonoides* from the Gulf of Eilat. The methodology for the production of LA-ICPMS elemental images of these foraminifera is detailed in Evans and Müller (2013).

Eocene seasonal temperature change was reconstructed using the magnitude of long-period Mg/Ca variability along the marginal cord profiles. Because there is considerable fine-scale Mg/Ca heterogeneity in both Eocene and Recent material, the magnitude of Mg/Ca variability was measured from a 20-point running mean, equivalent to an average of 430 μm of marginal cord calcite at a laser scan speed of $50\ \mu m\,s^{-1}$ and an ICPMS total dwell time of 0.43 s.

3. Results

3.1. Visual preservation

The tests of Eocene *N. djokdjokartae* appear glassy under optical microscopy. Comparative SEM images of Recent and Eocene material show that the fossil material is not recrystallised, has no secondary calcite overgrowths and that the pores are not infilled (Fig. 2). Features such as the spiral canal system (Figs. 1, 2) are clearly visible in the fossil material, demonstrating that significant recrystallisation of the tests cannot have taken place.

3.2. Geochemistry

Analytical data are available in Tables S3 and S4. Representative comparative Recent *O. ammonoides* and Eocene *N. djokdjokartae* example LA-ICPMS profiles are shown in Fig. 3. Measured element/Ca ratios not plotted are typically homogeneous within the marginal cord, where they are not modified by μm-scale diagenetic alteration.

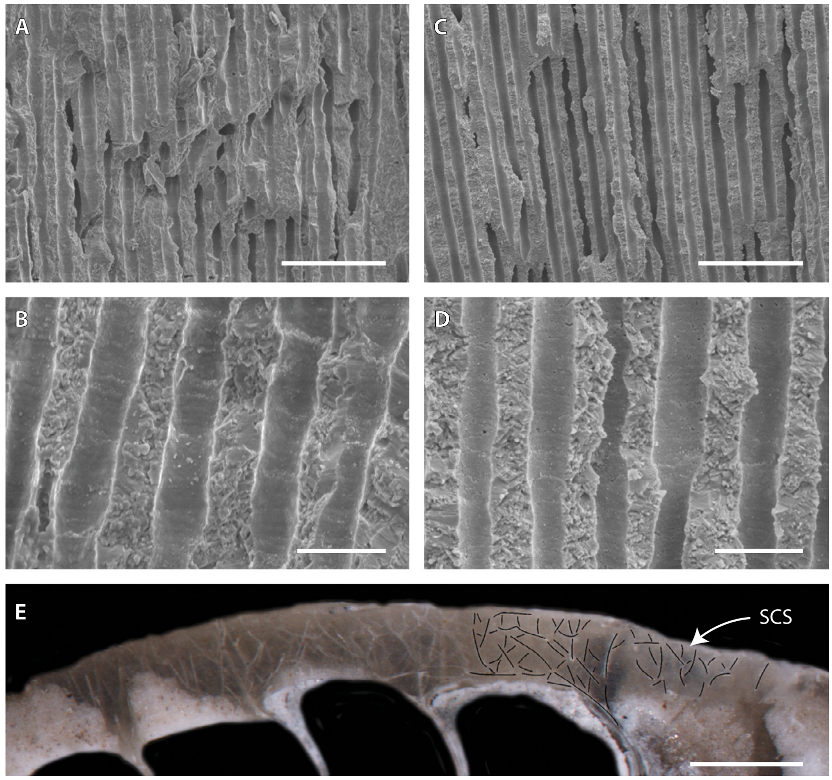

Fig. 2. Comparative SEM images of broken chamber walls of Recent *O. ammonoides* (A, B) and *N. djokdjokartae* (C, D). There is no evidence of secondary calcite overgrowths or recrystallisation of the fossil material. (E) Optical image of part of the marginal chord of an Eocene *N. djokdjokartae* specimen, with the spiral canal system (SCS) clearly visible (overlain with black lines on the right of the image). This demonstrates that significant recrystallisation cannot have taken place. Scale bars 20 μm (A, C), 5 μm (B, D), 500 μm (E).

3.2.1. *Geochemical preservation*

Certain element/Ca ratios were analysed specifically in order to identify poorly preserved samples, or less well-preserved areas of the tests of visually exceptionally-preserved samples. Al/Ca was used to assess the presence of clay minerals, Mn/Ca, Y/Ca and two rare earth element/Ca (REE/Ca) ratios – La/Ca and Ce/Ca – were used to identify areas affected by secondary calcite mineralisation; secondary calcite is generally expected to have higher Mn/Ca and REE/Ca ratios than the primary foraminiferal calcite (Scherer and Seitz, 1980; Pena et al., 2005). Mean Mn/Ca ratios in the fossil material are 220 $\mu mol\,mol^{-1}$, compared to 4–100 $\mu mol\,mol^{-1}$ in Recent *O. ammonoides*, depending on sample site (Fig. S3). Y/Ca and REE/Ca ratios are also 5–10× higher in the fossil material. Al/Ca ratios are comparable in Recent and fossil material, suggesting no clay-mineral contamination.

Occasional portions of approximately half the Recent and Eocene profiles have elevated Al/Ca and Mn/Ca (e.g. Fig. 3, top). These areas (Al–Mn/Ca >1 $mmol\,mol^{-1}$) were excluded for the purposes of mean specimen X/Ca calculation and error propagation. Exclusion of small amounts of data in this way does not affect our results which are based on numerous specimens.

3.2.2. *Nummulitid Mg/Ca–temperature relationship*

Our data demonstrate that, like other foraminifera, Mg/Ca responds systematically to temperature in *O. ammonoides* (Fig. 4). Sample site temperature ranges between 22 °C during winter/spring in the northernmost Gulf of Eilat to 29 °C north of Jakarta Bay.

The resulting Mg/Ca–temperature relationship with 95% confidence intervals is ($n = 32$):

$$\ln(\mathrm{Mg/Ca}) = 0.0198 \pm 0.0012T + 4.47 \pm 0.03 \quad (1)$$

or in linear form:

$$\mathrm{Mg/Ca} = 2.86 \pm 0.44T + 71.4 \pm 11.8 \quad (2)$$

This calibration is based on the mean of all analyses for each of the seven sample sites (see the supplementary information), each analysis itself representing the mean of all data collected from a laser-ablation track following the entirety of the marginal cord of an individual specimen. There are eight data points in Fig. 4 because samples were collected from more than one depth from Kepulauan Seribu, Jakarta. Mg/Ca error bars are ±2SD of the mean of all analyses from each sample site. These error bars are relatively larger than those typical of measurements produced by the bulk analysis (typically ICP-AES) of multiple individuals, because the analysis of whole dissolved tests masks natural sample variability. We report 2SD errors in order to show the degree of individual sample variability but highlight that the error in the slope of our calibration is smaller as it assumes that the mean of each sample set is well known. It is necessary to analyse at least five individual foraminifera using the technique outlined here in order to obtain a representative mean. There is no difference between a linear and exponential approximation of the Mg/Ca data in terms of goodness of fit ($R^2 = 0.977$ and 0.980 respectively), both regressions have gradients amounting to a ∼ 1.9% increase in Mg/Ca $°C^{-1}$.

3.2.3. *Recent material intra-test and inter-site variability*

Of the sampled locations, the Gulf of Eilat has the largest seasonal temperature variation and therefore these samples are expected to show the greatest potential for seasonally varying trace element concentrations. Corresponding element/Ca maps (Fig. 5) show intra-test Mg/Ca variation of ∼ 25 $mmol\,mol^{-1}$. There is no co-variation between the distribution of this Mg/Ca variation and heterogeneity in any other element/Ca ratio (with the exception of Ba/Ca), negating differential cleaning as the product of the observed Mg/Ca variability. These samples were collected in early May and have higher Mg/Ca ratios in the centre, decreasing towards the outer whorls. In the Gulf of Eilat, maximum

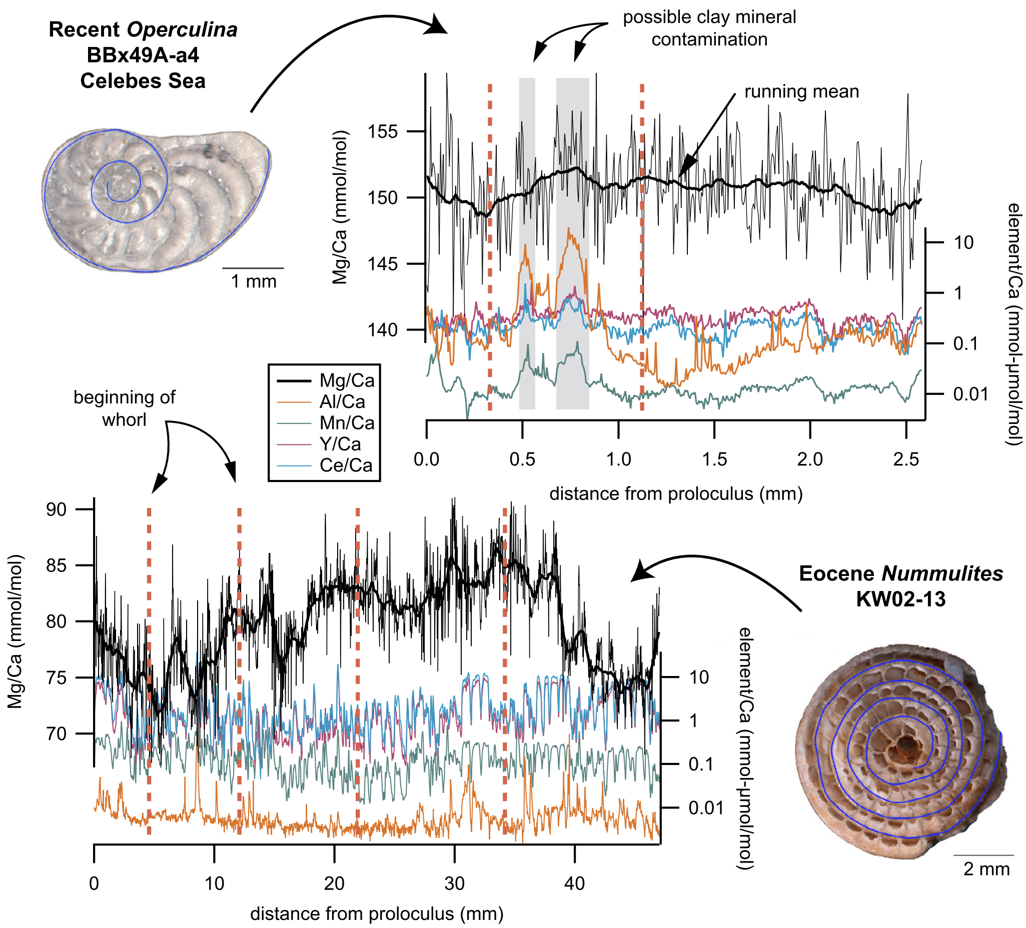

Fig. 3. Representative Mg/Ca (linear scale) and trace element profiles (log scale) of Recent *O. ammonoides* (top) and Eocene *N. djokdjokartae* (bottom). Specimens sectioned for analysis are shown alongside, with ablation paths overlain in blue. Eocene *N. djokdjokartae* show significant long term changes in Mg/Ca (solid black lines) interpreted as being the result of seasonal temperature variation. Trace element ratios used to identify artefacts from the preparation procedure (Al/Ca) or areas affected by diagenesis (Mn–Y–Ce/Ca) are shown.

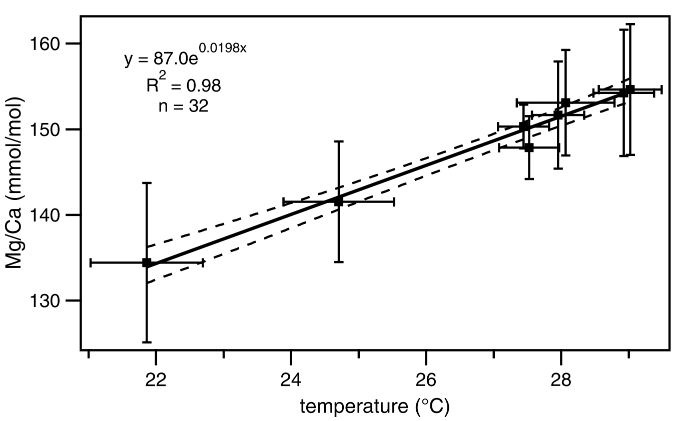

Fig. 4. Mg/Ca–temperature field calibration for *O. ammonoides*. Mg/Ca data are the mean ±2SD of all analyses from each sample location. These errors provide an estimate of uncertainty if only one single specimen were to be analysed. Temperature errors are 2SD of all mean monthly data from the World Ocean Atlas.

summer temperature (∼27 °C) occurs during late August, decreasing steadily until the end of the year where temperature remains within 1 °C of 21 °C until May. Assuming a mean growth rate of one chamber per 3–4 days, these specimens lived for up to six months and therefore exhibit intra-test Mg/Ca variability that matches the observed temperature variation remarkably well, providing evidence that seasonal temperature change is recorded via the Mg/Ca ratio of modern LBF tests.

Excluding the Gulf of Eilat, maximum sample site seasonality is 1.6 °C on the Spermonde Shelf (WOA 2009, Locarnini et al., 2010); seasonal Mg/Ca shifts are not expected to be resolvable within these samples. Mg/Ca fluctuation is observed (Fig. 3), although on a scale too fine for temperature to be a viable control of this heterogeneity. The mean Mg/Ca RSD of a single specimen is 5.6%, similar to that reported elsewhere for LBF (Raitzsch et al., 2010). Given the magnitude of this variability, statistically significant long-period Mg/Ca shifts of <5 mmol mol^{-1} are not identifiable and therefore it is not possible to accurately reconstruct seasonal temperature changes of less than 3 °C. With the exception of trace element ratios used to identify diagenesis or contamination, there is little coherent variation within the tests from all locations in any of the other 'proxy' element/Ca ratios. An exception to this is Ba/Ca, which is elevated in samples from the Gulf of Eilat compared to the other Recent sample sites, and appears to be anti-correlated with Mg/Ca (Fig. 5).

3.2.4. Eocene intra- and inter-test variability

Fine-scale trace element heterogeneity, assessed by single specimen standard deviations, are similar in Eocene and Recent material. *N. djokdjokartae* fine-scale Mg/Ca heterogeneity is within the range observed in Recent *O. ammonoides* precluding this being a diagenetic feature. A plot of the mean of all proxy element/Ca measurements from coexisting Eocene *N. djokdjokartae* and *Operculina* sp. shows no significant deviation from a 1:1 line for B, Mg, Zn and Sr (Fig. S4), suggesting that the distribution coefficients for

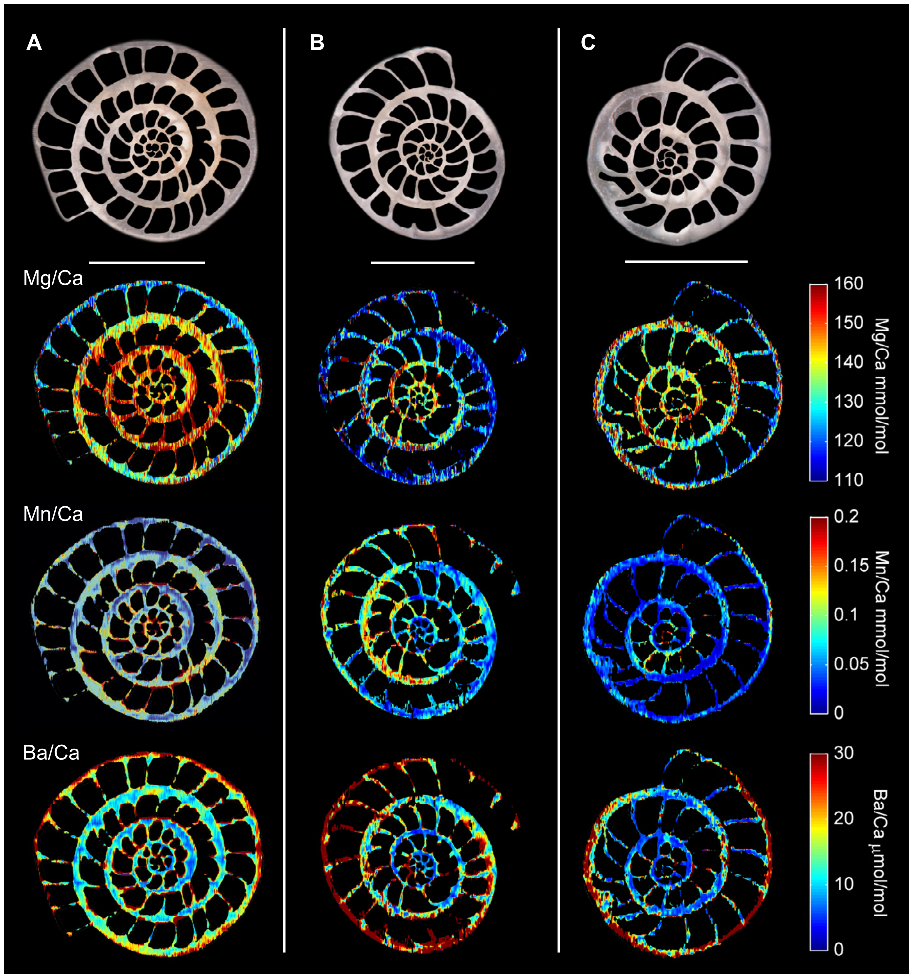

Fig. 5. LA-ICPMS maps for three modern *O. ammonoides* specimens from the Gulf of Eilat (top). All specimens show consistent and coherent Mg/Ca variability, implying first chamber growth beginning during a warmer period with subsequent chambers mineralised as temperature decreased, consistent with the date of collection (see text for details). Ba/Ca is anti-correlated with Mg/Ca, possibly as a result of winter upwelling. Scale bars 1 mm.

the trace elements under discussion here are the same or similar in both foraminifera.

Eocene samples have substantially lower Mg/Ca than Recent LBF. *N. djokdjokartae* and *Operculina* sp. have mean ±2SD Mg/Ca ratios of 86.4 ± 13.2 ($n = 20$) and 82.3 ± 4.8 ($n = 6$) respectively. Given the excellent preservation of these samples, the lower ratios are most parsimoniously explained as being a function of lower Eocene seawater Mg/Ca (Mg/Ca_{sw}), which exerts a control on foraminifera Mg/Ca at least as great as temperature (Evans and Müller, 2012; Segev and Erez, 2006), see Section 4.2. Eocene *N. djokdjokartae* specimens are characterised by the presence of significant long-period changes in Mg/Ca, manifest as 10 $mmol\,mol^{-1}$ shifts in marginal cord laser-ablation profiles and present in the majority of the specimens analysed. Typical profiles are shown in Fig. 6. The period of these approximately sinusoidal curves is consistent between specimens and is the same for both A- and B-forms.

N. djokdjokartae are not perfectly flat in the equatorial plane; the shape of these foraminifera is more appropriately described as a parabolic hyperboloid. Consequently it is very difficult to produce an equatorial section that exposes only the marginal cord. The example Eocene profile of Fig. 3 shows rapid fluctuations in Mn–Y–Ce/Ca (and to a lesser extent Al/Ca) by an order of magnitude, particularly between 30–40 mm. Such areas are those where the marginal cord is not exposed, the rapid changes represent the difference between the non-porous septal calcite and the perforate chamber wall, which have higher and lower Mn/Ca and Y–Ce/Ca ratios respectively. This is not observed in Mg, B or Sr, which demonstrates that our mean marginal cord measurements are not biased by this unavoidable sample preparation problem. However, it is possible that switching between the marginal cord, septa and chamber wall may explain some of the minor irregularities in the Mg/Ca profiles, as these three parts of the test are likely to have calcified at slightly different times and therefore at potentially different temperatures.

Sr/Ca and Ba/Ca are similar between Eocene *N. djokdjokartae* and Recent *O. ammonoides*. Comparative means of all analyses are 2.39 ± 0.39 and 2.44 ± 0.27 $mmol\,mol^{-1}$ respectively for Sr/Ca and 2.90 ± 0.37 and 3.06 ± 1.1 for Ba/Ca.

4. Discussion

The 1.9% increase in Mg/Ca per degree temperature change found here is comparable to the 3.1% observed by Raja et al. (2005) for the LBF *Marginopora kudakajimaensis* insofar as both species are characterised by a far smaller gradient than planktic species (typically ∼ 10%). The exponential component of this calibration is almost identical to that for inorganic calcite (Mucci, 1987; Burton and Walter, 1991) and the slope is similar to the Mg/Ca–temperature calibration of Burton and Walter (1991) at modern (late 20th century) pCO_2 ($1.7\%\,^{\circ}C^{-1}$). Whilst both linear and exponential regressions are equally applicable over the

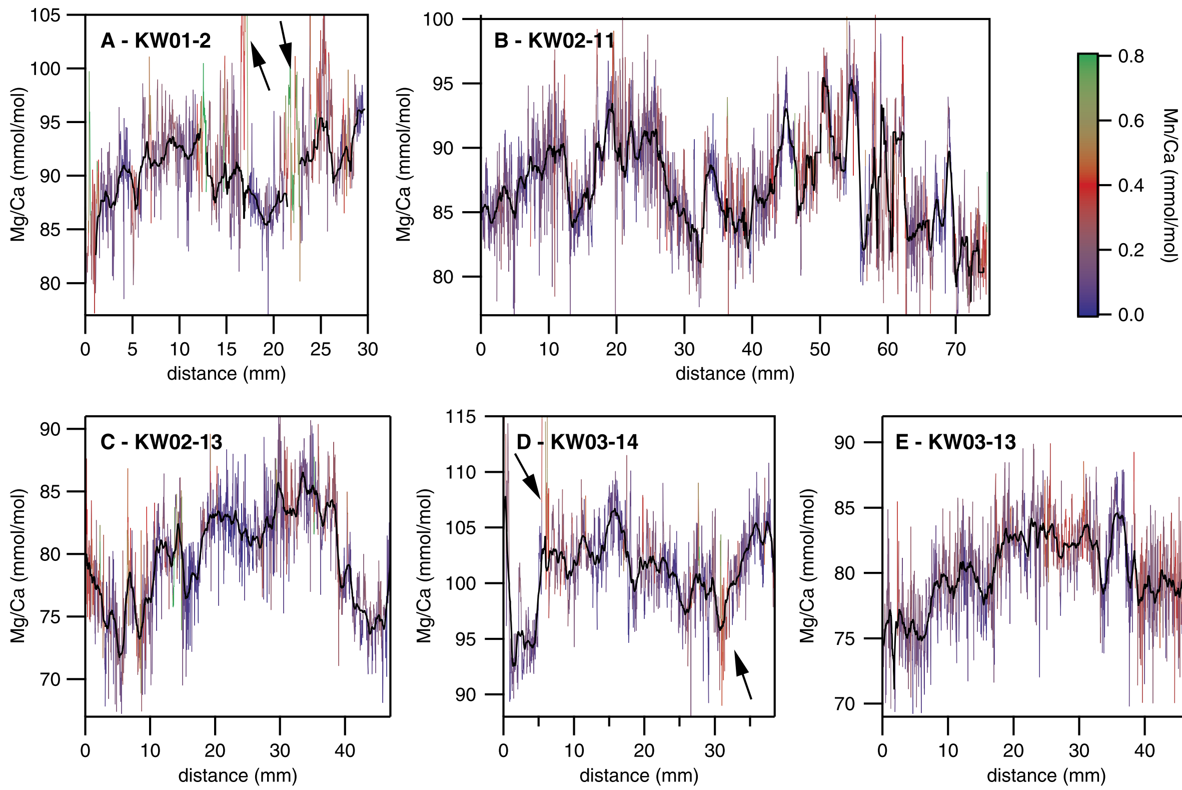

Fig. 6. Representative Eocene *N. djokdjokartae* Mg/Ca marginal cord profiles showing significant quasi-periodic shifts. Thick black lines are 40-point running means. Unsmoothed data colour is shown as a function of Mn/Ca, demonstrating that anomalous or noisy portions of the Mg/Ca profiles are explicable by minor diagenesis, highlighted with arrows.

sampled temperature range, we base our further discussions on the exponential best-fit only because it is not possible to calculate palaeoseasonality using a linear calibration without prior knowledge of Mg/Ca_{sw}. This is because, unlike an exponential relationship between temperature and Mg/Ca, the difference between two Mg/Ca-derived temperature reconstructions (i.e. those derived from maximum and minimum Mg/Ca_{test}) is not constant as Mg/Ca_{sw} varies (see the supplementary material).

The relationship between Mg/Ca and temperature reported here is biased towards sample sites with mean annual SST in the range 27–29 °C. However, four geographically distinct sample sites (BTE27, KKE30, BBx25C, BBx49A – see Table 1) exhibit a temperature range of just 0.6 °C but are otherwise hydrographically different (e.g. in terms of seasonal salinity variation). Therefore these samples provide a good test of Mg/Ca repeatability when environmental factors other than temperature are not the same. The mean of all measurements of samples from these locations exhibit a Mg/Ca range of 3.5%, of which one third is explicable as a result of temperature, leaving a residual variation of just 2.3%, which is similar to the achievable precision of these measurements (1.6%). This consistency of results implies that our data accurately represent the shape of the Mg/Ca–temperature curve and demonstrates that the addition of further temperature points is unlikely to significantly alter the shape of the curve over the studied temperature range, because the mean of all measurements from these four samples are essentially identical even though they are from waters with different physical (and possibly chemical) properties. Furthermore, because the nummulitids have a lower temperature tolerance of ∼ 18 °C, and are therefore applicable as environmental indicators to the palaeo low-mid latitudes, the temperature range covered here provides a basis for palaeoenvironment reconstruction in the (sub)tropics.

4.1. Eocene seasonality

Palaeoseasonality can be estimated using the fraction difference between the minimum and maximum Mg/Ca ratios in the Eocene *N. djokdjokartae*, coupled with the gradient of Eq. (1). The Mg/Ca curves are consistent in that virtually all show amplitudes of ∼ 10 $mmol\,mol^{-1}$, which is equivalent to a seasonality of 5–6 °C. Present day seasonality on the southeast Java coast is 4 °C due to August to October upwelling associated with a temperature drop to 26.5 °C from a summer maximum of 30.5 °C when the Indonesian throughflow dominates SST (Hendiarti et al., 2004). Reconstructed Eocene palaeoseasonality is greater than any open ocean tropical seasonality at the present day and 50% greater than upwelling-induced seasonal temperature change on the modern Java coast, either implying enhanced middle-Eocene temperature seasonality or a greater degree of seasonal upwelling at this location. The lower Ba/Ca of the Eocene samples compared to Recent *O. ammonoides* from the Gulf of Eilat may imply that enhanced upwelling cannot explain the greater than modern seasonality reconstruction, given that elevated seawater Ba/Ca is associated with upwelling (e.g. Lea et al., 1989) and seawater Ba/Ca is recorded in foraminiferal calcite (Hönisch et al., 2011), which is also suggested by our laser-ablation Ba/Ca maps (Fig. 5).

The amplitude of reconstructed seasonality from these Mg/Ca profiles is (to an extent) dependent upon the degree of smoothing applied (Fig. S6). We use a 40-point running mean (Fig. 6) as this was found to remove outliers and artificial variation from the fine-scale Mg/Ca variability present in both Recent and Eocene nummulitids (±5 $mmol\,mol^{-1}$), without dampening temperature-controlled Mg/Ca variation.

Seasonal temperature variation decreases with water depth, therefore it is possible that our reconstruction is an under-estimate of seasonality if the habitat of *N. djokdjokartae* is towards the lower extreme of that of Recent *O. ammonoides*. In the modern Gulf of

Eilat, seasonal temperature range decreases approximately linearly at the rate of 1 °C 40 m^{-1} over the top 100 m of the water-column. However, the relatively coarse grain size of the sampled stratigraphic horizons (see the supplementary information) suggests high palaeo-turbidity, implying (by analogy to their nearest living relative) a shallow peak abundance depth for these fossil samples and therefore a representative estimate of the surface annual amplitude of temperature variation.

Some of the profiles in Fig. 6 show (occasional) sharp jumps in Mg/Ca (e.g. profile B at ~ 35 mm; profile D at ~ 7 mm) that may suggest discontinuous growth in some specimens. Whilst this potentially accounts for the deviation of some of these profiles from a sinusoidal Mg/Ca curve, it seems improbable that seasonality reconstructions are biased by growth cessation as there is no coherent pattern in the position of these features; they do not all occur at Mg/Ca minima. Instead, it is more likely that these shifts are the combined result of minor μm-scale diagenesis (e.g. profile A at ~ 23 mm) and the precise positioning of the laser-ablation tracks. The trace element images of Recent *O. ammonoides* (Fig. 5) also show occasional sharp changes in Mg/Ca, despite overall coherence in Mg incorporation.

The elevated Mn–REE/Ca ratios of the fossil material is unlikely to bias our seasonality reconstruction or any of the fossil proxy trace element data. There is no correlation between any of the diagenesis indicators and proxy trace element ratios with the exception of U/Ca–Y/Ca (Fig. S3), both within and between specimens. Furthermore, there is no correlation between any of the diagenesis indicators and proxy trace element ratios and all ratios measured for purposes other than to assess diagenesis are within the range of those in Recent *O. ammonoides*, with the exception of Zn/Ca. If all of the excess Mn in the fossil samples is attributed to kutnahorite ($Ca(Mn,Mg,Fe)(CO_3)_2$, an identified secondary carbonate contaminant phase in foraminifera, see Pena et al., 2005), then simple mass-balance calculations would indicate that the resulting worst case Mg/Ca bias would be 0.9%, which is non-resolvable given that analytical accuracy is $\sim 2\%$.

A further feature of these profiles is that there is a relatively large range in mean test Mg/Ca. For example, profiles A and B (Fig. 6) have mean Mg/Ca ≈ 90 $mmol\,mol^{-1}$ whereas C and E have mean Mg/Ca ≈ 80 $mmol\,mol^{-1}$. Similar natural variation is observed within the Recent *O. ammonoides* populations (e.g. samples from the Gulf of Eilat have a range in mean marginal cord Mg/Ca values of 129–142 $mmol\,mol^{-1}$), therefore this feature of the fossil data is not unexpected and analysis of several individuals ($\geqslant 5$) is necessary in order to produce a representative mean (see also Sadekov et al., 2008). However, the magnitude of long period intra-test Mg/Ca variability is consistent between all samples.

Our seasonality estimate is similar to previous Eocene reconstructions from both the Gulf of Guinea (Andreasson and Schmitz, 1998) and Panama (Tripati and Zachos, 2002), to our knowledge the only other estimates of early-mid Cenozoic tropical palaeoseasonality. Andreasson and Schmitz (1998) invoked upwelling as the reason for large $\delta^{18}O$ shifts in molluscan aragonite, whereas the $^{87}Sr/^{86}Sr$ data of Tripati and Zachos (2002) (also micro-sampled mollusc-derived) suggest some bias by freshwater input. It is important to understand the extent to which our seasonality estimate is controlled by other factors, given that there is no current estimate of Eocene palaeoseasonality unequivocally from an area unaffected by coastal processes. The concentration of Mg and Ca in seawater is substantially higher than average global river water; consequently it is not possible to modify seawater Mg/Ca by mixing with freshwater within the salinity tolerance of foraminifera (mixing 60% freshwater with 40% seawater results in a $< 5\%$ decrease in solution Mg/Ca but a $\sim 20‰$ salinity reduction, depending on exact freshwater composition). This is in contrast to seawater $\delta^{18}O$ which can be easily modified in coastal proximal environments. Therefore, our estimate does not suffer from this potential bias. Whilst it has been shown that high salinity environments can modify foraminifera Mg/Ca (e.g. Arbuszewski et al., 2010; Hoogakker et al., 2009), there is no palaeogeographic evidence that this should be the case for our fossil samples which lived in an open shallow sea to the south of a landmass comprising present day west Borneo, northwest Java and Sumatra (Hall, 2009).

Our seasonality reconstruction implies that at least one surface ocean location was characterised by higher magnitude seasonal temperature changes during the mid-Eocene compared to the present. Whilst recent clumped isotope measurements of palaeosols and molluscs suggest that Eocene continental interiors were not as equable as previously thought (Snell et al., 2013), there is limited proxy evidence that would imply a greater than present day surface ocean seasonality. Interpretation of our data is dependent upon the cause of the greater reconstructed seasonality; more vigorous Eocene upwelling on the southernmost Sunda Shelf would require a different mechanism to increased seasonality related to (for example) seasonal shifts in the position of ocean currents. We therefore discuss our results both with and without increased upwelling as the fundamental cause of the greater than present reconstructed annual temperature shift.

Whilst our Eocene Ba/Ca analyses do not provide evidence for upwelling at this fossil site, it is possible that it is not evident in our data. Analysis of coeval bivalves could provide a method of testing this, as Ba/Ca in some bivalve shells has been shown to be a sensitive indicator of chlorophyll concentration which may in turn relate to seasonal upwelling (Elliot et al., 2009). Reduced Eocene equator to pole SST temperature gradients may have resulted in broadly weaker Hadley Cell circulation and lower zonal wind speed (Sloan and Rea, 1995; Vecchi and Soden, 2007), which may result in a decrease in the vigour and frequency of tropical upwelling. However, there is strong proxy and model evidence for a link between increased atmospheric CO_2 and the intensity of tropical cyclones (e.g. Schmitz and Pujalte, 2007; Oouchi et al., 2006) which also has the effect of reducing SST through thermocline mixing (Price, 1981; Sriver and Huber, 2007). Furthermore, slow-moving hurricanes may directly cause coastal upwelling (Shi and Wang, 2007). Both of these closely related mechanisms can explain our greater than present day seasonality estimate, particularly because the depth over which modelled hurricane-forced upper ocean mixing occurs significantly increases at higher atmospheric CO_2 (Korty et al., 2008), which in turn leads to greater surface ocean cooling during any given event. If this was the case for southeast Asia during the mid-Eocene, these relatively sudden events may also explain the deviation of our Mg/Ca profiles from smooth curves.

Alternative explanations for increased Eocene seasonality that do not invoke upwelling may come from seasonal shifts in ocean currents. There is recent model evidence for anticyclonic gyres in the Eocene Indian Ocean during the northern hemisphere winter, which would result in seaward directed ocean mass transport on the southern Asian shelf (Huber and Goldner, 2012; Winguth et al., 2010). This was not observed during the northern hemisphere summer and may provide a mechanism for greater Eocene seasonal temperature change in this region if this current carried cooler water, or itself induced upwelling in the region. Finally, a smaller mid-Eocene obliquity compared to the present day would result in greater seasonally variable incoming shortwave radiation (Heinemann et al., 2009), however this cannot account for seasonal temperature shifts of the magnitude which we reconstruct.

Deep-time surface ocean seasonality reconstructions are of insufficient spatial coverage to place accurate constraints on Eocene climate dynamics. However, given that there is evidence for increased seasonality during periods of global cooling (e.g. Ivany et al., 2000), it seems more likely that the explanation for our reconstructed seasonality lies in dynamic events such as cyclone-induced thermocline mixing rather than resulting from an implied link between higher temperature (and/or pCO_2), and tropical ocean seasonality. Whilst our Eocene Ba/Ca data do not prove that upwelling was an important process at this time, mixing of the upper ∼ 200 m of the water column (as implied by Winguth et al., 2010) may not necessarily result in greatly increased surface seawater Ba/Ca.

4.2. Implications for palaeoseawater Mg/Ca and Sr/Ca

Previous studies attempting to reconstruct Mg/Ca_{sw} using foraminifera have produced results that are in poor agreement with virtually all other proxy evidence and model-derived results (Coggon et al., 2011). This is a consequence of assuming a linear relationship between test and seawater Mg/Ca; laboratory culture calibrations have demonstrated that Mg/Ca_{test} variation with Mg/Ca_{sw} is best described by a power regression (summarised in Evans and Müller, 2012). An appropriate equation to use when reconstructing palaeo-Mg/Ca_{sw} is:

$$Mg/Ca_{sw}^{t=t} = \sqrt[H]{\frac{Mg/Ca_{test}^{t=t} \times Mg/Ca_{sw}^{t=0\,H}}{B \exp^{AT}}} \qquad (3)$$

where $t = 0$ is the present day and $t = t$ is some point in the past. H is the power component of a seawater-test Mg/Ca calibration (Ries, 2004; Hasiuk and Lohmann, 2010; Evans and Müller, 2012) and B and A are constants to be defined for a specific species or group of species.

In order to reconstruct seawater Mg/Ca from fossil data, the power relationship between test and seawater Mg/Ca (H) must be known. We provide a reconstruction based on (1) the inorganic calibration of Mucci and Morse (1983) and (2) the relationship between test and seawater Mg/Ca which has been calibrated in *Heterostegina depressa*, a closely related nummulitid (Raitzsch et al., 2010). Because our fossil *N. djokdjokartae* and *Operculina* sp. have, within error, identical proxy X/Ca ratios the Mg/Ca–temperature and test–seawater Mg–Sr/Ca relationships of the two genera must be similar, as it would be highly coincidental if the hypothetically different Mg/Ca–temperature responses of the two species crossed at the palaeotemperature of the fossil sample site. The application of calibrations based on Recent *O. ammonoides* to measurements of fossil *N. djokdjokartae* is therefore justified. The value of H that Raitzsch et al. (2010) derive for *H. depressa* may be more applicable, given that we demonstrate above that trace element distribution coefficients are the same within error for all nummulitids analysed, however this calibration was carried out over a narrow range of Mg/Ca_{sw} values and is not well constrained between 1–3 $mol\,mol^{-1}$. The inorganic value of H may be appropriate when reconstructing Mg/Ca_{sw} utilising these samples because of the similarity between our Mg/Ca–temperature calibration and those of inorganic calcite. Whichever value of H is used, we use an appropriate correction technique with defined test–seawater chemistry relationships and our data therefore yield a more reliable estimate of alkaline earth palaeoseawater chemistry based on foraminifera.

In order to reconstruct Mg/Ca_{sw} using Eq. (3) some constraint of palaeotemperature is required (or vice versa). In order to demonstrate the extent to which foraminifera-derived Mg/Ca_{sw} has previously been over-estimated, we plot a range of potential values based on a temperature range of 25–35 °C, equivalent to assuming the palaeotemperature of the sample site is similar to or greater than present day tropical ocean temperatures, with an upper bound defined by the addition of a realistic error to the maximum reconstructed Eocene $\delta^{18}O$-derived temperature (Pearson et al., 2007). Reconstructed Mg/Ca_{sw} (Fig. 7) ranges from 1.0–1.8 $mol\,mol^{-1}$ based on the value of H for *H. depressa* (Raitzsch et al., 2010) or 1.6–2.2 $mol\,mol^{-1}$ based on that of inorganic calcite (Mucci and Morse, 1983). This range includes uncertainty in the mean *N. djokdjokartae* Mg/Ca_{test} value over the entire temperature range. We thereby demonstrate that Mg/Ca_{sw} at ∼ 39 Ma was below or close to 2 $mol\,mol^{-1}$, in good agreement with the majority of model and proxy evidence suggesting relatively low Paleogene values (e.g. Stanley and Hardie, 1998; Coggon et al., 2010). This contrasts previous foraminifera-based constraints of palaeo-Mg/Ca_{sw} (Broecker and Yu, 2011; Lear et al., 2002), which are inaccurate because they are based on the assumption that Mg/Ca_{test} varies linearly with Mg/Ca_{sw} (Evans and Müller, 2012). Based on this, it seems probable that Mg/Ca_{sw} has undergone a 2.5–4× increase over the last 40 Ma, although the question regarding the mechanisms for such a relatively large change remains.

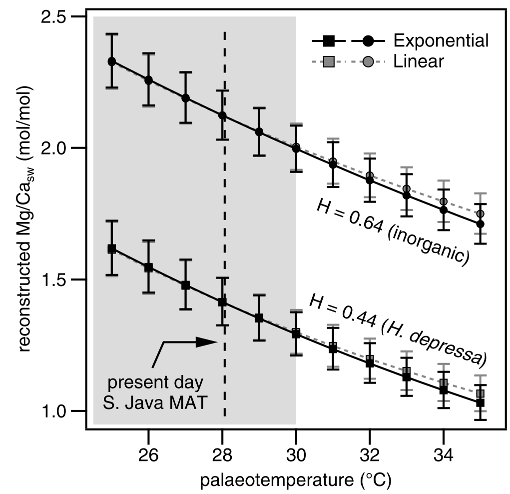

Fig. 7. Mg/Ca_{sw} reconstruction based on the calibrated relationship between Mg/Ca and temperature given in this study and the Mg/Ca_{sw}–Mg/Ca_{test} calibrations of Raitzsch et al. (2010) and Mucci and Morse (1983), for a range of palaeotemperature assumptions for Java at 39 Ma. The present range of modern tropical mean annual sea surface temperature (MASST) (shaded region) and the current MASST off the south Java coast are shown for comparison. The exponential and linear series relate to the format of the Mg/Ca–temperature regression.

Reconstruction of Sr/Ca_{sw} is in some respects less complicated than Mg/Ca_{sw} because the Sr distribution coefficient (D_{Sr}) does not vary with Sr/Ca_{sw} (Raitzsch et al., 2010). However, a $Mg/Ca_{calcite}$ control on $Sr/Ca_{calcite}$ has been demonstrated by Mucci and Morse (1983), which must be taken into account when reconstructing Sr/Ca_{sw} using LBF as these foraminifera exhibit a large range in test Mg/Ca. Mucci and Morse (1983) find a linear relationship between Sr/Ca and Mg/Ca (at constant solution [Sr]), amounting to a 0.010 $mmol\,mol^{-1}$ increase in Sr/Ca per 1 $mmol\,mol^{-1}$ increase in Mg/Ca. We apply this correction to our fossil data (characterised by Mg/Ca_{test} ∼ 60 $mmol\,mol^{-1}$ lower than our Recent samples), which amounts to an upwards shift of our measured Eocene Sr/Ca ratios by 0.67 $mmol\,mol^{-1}$. This method assumes that the inorganic calcite calibration of Mucci and Morse (1983) is applicable to the nummulitids, which may be reasonable given similar Mg incorporation in nummulitid and inorganic calcite.

The D_{Sr} of *O. ammonoides* is 0.26 derived from our data, which is in close agreement with that of *H. depressa*, ($D_{Sr} = 0.28$, Raitzsch et al., 2010). Using our value for D_{Sr} results in reconstructed Sr/Ca_{sw} at 39 Ma of 10.4 and 10.9 $mmol\,mol^{-1}$ derived from Eocene *N. djokdjokartae* and *O. ammonoides* respectively, compared to a modern day ratio of 8.5 $mmol\,mol^{-1}$. This estimate would be 1.5 $mmol\,mol^{-1}$ lower if no correction is applied for the difference between Eocene and Recent Mg/Ca_{test}.

There is significant disagreement between previous Sr/Ca_{sw} reconstructions. Data from ridge-flank vein carbonates suggests Cenozoic values as low as ~ 2 mmol mol^{-1} (Coggon et al., 2010) whereas analyses of deep benthic foraminifera broadly suggest a slight (1–2 mmol mol^{-1}) increase over the last 50 Ma (Lear et al., 2003). Tripati et al. (2009) and Sosdian et al. (2012) reconstructed Sr/Ca_{sw} in the range 11–18 mmol mol^{-1} and 10–14 mmol mol^{-1} for the period 38–64 and 0–40 Ma respectively, based on gastropod aragonite. An in-depth discussion of the reasons for the differences between these studies is beyond the scope of this contribution (see Sosdian et al., 2012 for a recent synthesis). However our reconstruction is in broad agreement with the studies of Sosdian et al. (2012), Lear et al. (2003) and Tripati et al. (2009) for samples of an equivalent age. Support for a middle Eocene value in this range (7.2–7.9 mmol mol^{-1} for 47–51 Ma) is also provided by Balter et al. (2011), who analysed the Sr/Ca ratio of shark and ray tooth enamel. Coupled with the data presented here, these independent Sr/Ca_{sw} reconstructions based on a variety of organisms converge on a mid-Eocene value within $\sim \pm 20\%$ of present day.

5. Conclusion

Large benthic foraminifera are an important and widespread component of shallow marine ecosystems. The abundance of large genera in climatically important periods such as the early-mid Paleogene means that this group of foraminifera have excellent potential for palaeoceanic reconstruction. Mean Mg/Ca measurements of sectioned Recent foraminifera of the genus *Operculina* demonstrate a systematic relationship with temperature. Laser-ablation-derived element/Ca maps show that intra-test variation in Mg/Ca responds as expected to seasonal sample site temperature variation, demonstrating that this group of organisms can be used as an alternative to molluscs for palaeoseasonality reconstruction. We apply this technique to fossil *N. djokdjokartae* from a mid-Eocene succession in Java and show that this site was characterised by 5–6 °C seasonal temperature shifts, $> 2\,^{\circ}$C higher than the equivalent present day location. The fossil sample site contains coeval *Operculina* sp., enabling us to demonstrate that different nummulitids have equivalent alkaline earth/Ca ratios, validating the application of *O. ammonoides*-derived calibrations to Paleogene *Nummulites*.

Furthermore, because a calibration between seawater Mg/Ca and test Mg/Ca has already been carried out for a foraminifer from the same family (Raitzsch et al., 2010), coupled with an improved understanding of foraminiferal Mg/Ca systematics (Evans and Müller, 2012) our fossil Mg/Ca data enable us to produce a more accurate estimate of palaeoseawater Mg/Ca using foraminifera. We demonstrate that Mg/Ca_{sw} at ~ 39 Ma was close to or below 2 mol mol^{-1}, in agreement with most other proxy and model estimates for the Paleogene but in contrast to the relatively high values implied by the model of Wilkinson and Algeo (1989). This is important because this model has most commonly been applied to fossil samples when correcting for secular change in Mg/Ca_{sw}. The reconciliation of foraminiferal Mg/Ca with other lines of Mg/Ca_{sw} proxy evidence should mark a shift in the debate regarding the chemical evolution of the oceans and the use of proxy Mg/Ca_{sw} data in the production of more accurate Mg/Ca-derived pre-Pleistocene palaeotemperatures.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2013.08.035.

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