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Stable oxygen isotope chemostratigraphy and paleotemperature regime of mosasaurs at Bentiaba, Angola

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Abstract

Stable oxygen isotope values of inoceramid marine bivalve shells recovered from Bentiaba, Angola, are utilised as a proxy for paleotemperatures during the Late Cretaceous development of the African margin of the South Atlantic Ocean. The $\delta^{18}\text{O}$ values derived from inoceramids show a long-term increase from -3.2‰ in the Late Turonian to values between -0.8 and -1.8‰ in the Late Campanian. Assuming a constant oceanic $\delta^{18}\text{O}$ value, an $\sim 2\text{‰}$ increase may reflect cooling of the shallow marine environment at Bentiaba by approximately 10° . Bentiaba values are offset by about $+1\text{‰}$ from published records for bathyal *Inoceramus* at Walvis Ridge. This offset in $\delta^{18}\text{O}$ values suggests a temperature difference of $\sim 5^\circ$ between coastal and deeper water offshore Angola. Cooler temperatures implied by the $\delta^{18}\text{O}$ curve at Bentiaba coincide with the stratigraphic distribution of diverse marine amniotes, including mosasaurs, at Bentiaba.

Keywords: Cretaceous, South Atlantic Ocean, oxygen, paleotemperature, inoceramid

Introduction

We present a temporally calibrated, shallow marine $\delta^{18}\text{O}$ chemostratigraphic curve for Bentiaba, southern Angola (Fig. 1), relating stable oxygen isotopes of this portion of the southern hemisphere to values from the Walvis Ridge offshore Angola and elsewhere around the globe. The presented $\delta^{18}\text{O}$ values are used to estimate the paleotemperature regime in which mosasaurs and other marine amniotes along this portion of southwest Africa lived throughout much of the Late Cretaceous.

Mosasaurs have a fossil record extending from the Cenomanian, approximately 98 Ma, to their extinction at the end of the Cretaceous at 66 Ma (Jacobs et al., 2005a,b; Polcyn et al., 1999, 2014). Since 2005 our team, Projecto PaleoAngola, has conducted field expeditions in Cretaceous and younger rocks of coastal Angola, greatly improving the fossil record of

vertebrates from the eastern South Atlantic (Jacobs et al., 2006). The oldest mosasaurs known from the South Atlantic Ocean, *Angolasaurus bocagei* and *Tylosaurus iembeensis*, are found at Iembe, north of the capital Luanda, in Late Turonian nearshore deposits that also produced the sauropod dinosaur *Angolatitan adamastor* (Mateus et al., 2011). Marine amniote remains known from Iembe also include halisaurine vertebrae and a marine turtle, *Angolachely mbaxi* (Mateus et al., 2009, 2012; Polcyn et al., 2012).

The greatest concentration of mosasaurs in Angola comes from Upper Campanian–Maastrichtian sediments at Bentiaba (Strganac et al., 2014b), but there are significant exposures below the fossil-bearing horizons, which range in age from Cenomanian to Santonian. The chronological context for Bentiaba is provided by the magnetostratigraphy and a $\delta^{13}\text{C}$ chemostratigraphic framework anchored by an 84.5 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ whole-rock

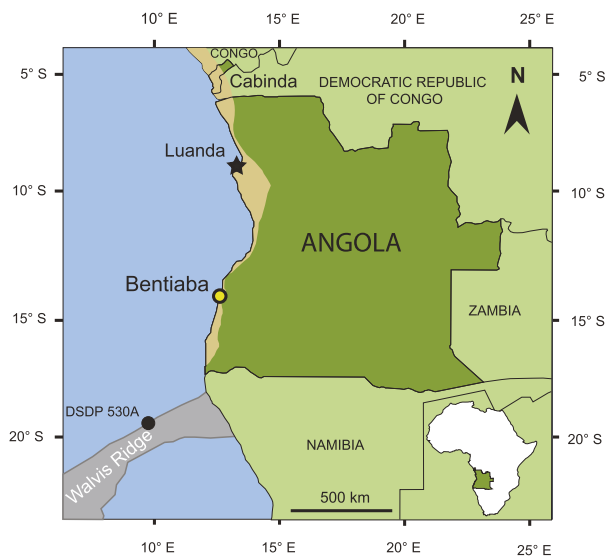


Fig. 1. Location map of Bentiaba, Angola. Inset shows location of Angola within Africa, offshore basins labelled in capital letters. Note location of DSDP Hole 530A, which is discussed in the text. Modified from Strganac et al. (2014a).

radiometric date on an intercalated basalt of the Ombe Formation, which is consistent with ammonite biostratigraphy (Strganac et al., 2014a). The Bentiaba $\delta^{18}\text{O}$ curve presented here was constructed as a complement to the $\delta^{13}\text{C}$ record presented by Strganac et al. (2014a).

The mosasaur fauna of the Campanian Baba Formation is fragmentary and includes both rüsselosaurians and mosasaurines, while that of the overlying Maastrichtian Mocuio Formation is predominately mosasaurine (Strganac et al., 2014b). Within the Mocuio Formation, the mid-Maastrichtian (approximately 71.5 Ma) Bench 19 fauna is particularly rich (Schulp et al., 2006, 2008, 2013; Polcyn et al., 2010, 2014; Mateus et al., 2012), and it is the subject of a paleoecological analysis (Strganac et al., 2014b). The paleogeographic context of Angolan vertebrates was initially examined in Jacobs et al. (2009, 2011) and Polcyn et al. (2010), and their paleoecology was examined initially in Robbins et al. (2008) and Polcyn et al. (2010, 2014).

Little paleotemperature research relevant to this study has been conducted in Africa. An analysis of paleosols in the Samba drill core from the Congo Basin (Cahen et al., 1959), representing the interior of Gondwana prior to the opening of the South Atlantic, indicates Jurassic average annual soil temperatures between 25 and $40 \pm 3^\circ\text{C}$, with an average of 33°C , $\sigma = 7.6^\circ\text{C}$ (Myers et al., 2011), accompanied by low biological productivity (Myers et al., 2012). Myers et al. (2011) also presented a Lower Cretaceous soil temperature estimate of $23 \pm 3^\circ\text{C}$.

Temperature tolerances for mosasaurs of Cenomanian age, near the time of origin for the group, were considered by Jacobs et al. (2005b). Kolodny & Luz (1991) reported the $\delta^{18}\text{O}$ value of the Cenomanian shark *Cretolamna appendiculata* from Angola, included by Puc at et al. (2007) in their study of Cretaceous

latitudinal temperature gradients. The current study provides temperature estimates of shallow marine environments, below wave base, for much of Late Cretaceous time as the South Atlantic was growing and was inhabited by diverse assemblages of marine amniotes.

Cretaceous $\delta^{18}\text{O}$ records have been used to elucidate changes in ocean circulation as well as temperature (Cramer et al., 2009; Friedrich et al., 2009, 2012). Most paleotemperature records utilise benthic foraminifera, whose $\delta^{18}\text{O}$ values reflect offshore deep marine environments with little to no influence by meteoric input or fluctuations in salinity (Grossman, 2012). These methods can be extended to shallow shelf setting unaffected by high freshwater influx (Sessa et al., 2012), which we assume to be the case at Bentiaba (Strganac et al., 2014b). The $\delta^{18}\text{O}$ curve from Bentiaba provides a shallow marine temperature curve that can be compared to the long-term benthic records to track broader temperature trends, to obtain indications of larger circulation patterns, and to provide a paleotemperature context for evolution in the marine realm.

The Late Cretaceous marks the transition from global high temperatures during the Late Cenomanian-Turonian climatic maximum and progressing through the cooler temperatures that characterise much of the Cenozoic. Cretaceous temperature trends coincide with significant paleoceanographic events, including Oceanic Anoxic Event 2 at the Cenomanian-Turonian Boundary, which is a widespread period of rapid burial of organic matter related to marine productivity and enhanced ocean stratification (Arthur et al., 1988; Erbacher et al., 2001, Forster et al., 2008; Friedrich et al., 2012; Strganac et al., 2014a). Connections between major ocean basins increased after the Turonian as a result of tectonic drift of continents, allowing cool waters derived from high latitudes to circulate equatorially, contributing to declining global temperature (Hay et al., 1999; Miller et al., 1999; Cramer et al., 2009; Robinson & Vance, 2012). The $\delta^{18}\text{O}$ stratigraphic curve presented here is a proxy for shallow marine temperature change at Bentiaba during the Late Cretaceous development of the South Atlantic.

The mosasaur-bearing portion of the Bentiaba section lies above the Ombe basalt in the Baba and Mocuio formations (Fig. 2). Carbonate cement creates benches in the Mocuio Formation, which are numbered in the section. Vertebrates occur throughout the Baba and Mocuio formations. The Campanian Baba Formation preserves a fragmentary but mixed rüsselosaurine-mosasaurine fauna extending into the lower part of the Mocuio Formation. In the Lower Maastrichtian part of the Mocuio Formation, the Bench 19 Fauna is dominated by mosasaurines. The highest levels of the Mocuio fauna, which we interpret as Upper Maastrichtian (Strganac et al., 2014a), preserve the globidensine *Carinodens* and a large, derived *Prognathodon* (Mateus et al., 2012; Schulp et al., 2013; Strganac et al., 2014b).

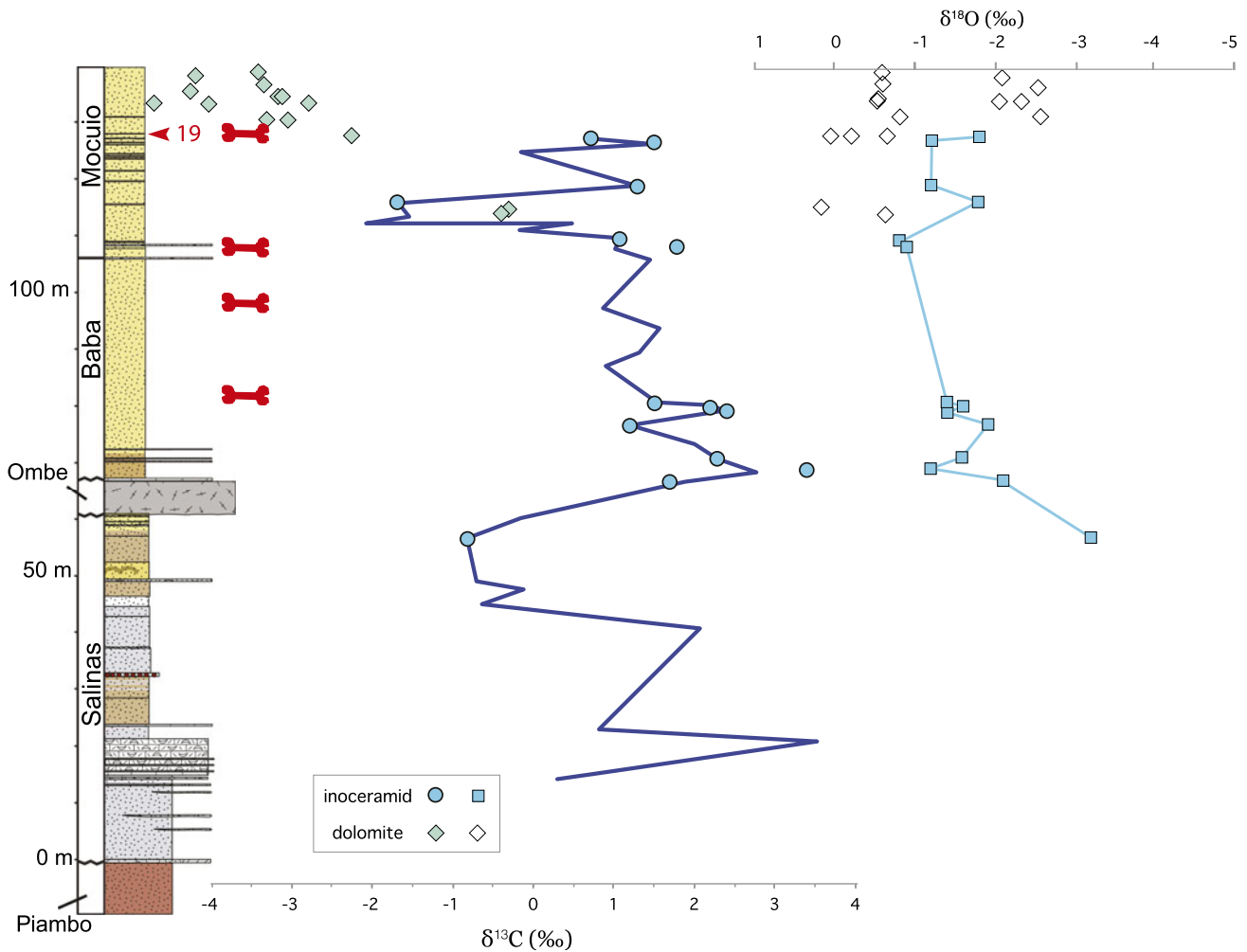


Fig. 2. Section at Bentiaba with $\delta^{13}C$ and inoceramid $\delta^{18}O$ stratigraphic curves. Red bones and '19' indicate marine amniote-bearing horizons and Bench 19. Note that the $\delta^{13}C$ curve is composite of inoceramid and other bivalve data in Strganac et al. (2014a).

Methods and materials

Stratigraphic $\delta^{18}O$ sampling

The inoceramid bivalves in this study represent a subset of data used in a $\delta^{13}C$ chemostratigraphic curve at Bentiaba (Strganac et al., 2014a). Marine bivalves throughout the section were sampled for stable isotope chemostratigraphy. Strganac et al. (2014a) tested inoceramid shells for diagenetic alteration by visual examination with binocular microscope and by scanning electron microscopy (SEM). Additional tests for alteration were performed by electron dispersive spectroscopy (EDS) and X-ray diffraction. Only samples of inoceramids with intact calcite prisms were used to estimate paleotemperatures in this study. Samples altered to dolomite were rejected, and stable oxygen isotope values from non-inoceramid bivalves were not used in this study, as these samples were not examined for diagenetic alteration in detail.

Twenty-four inoceramid shells were powdered with a carbide drill near the hinge where the shell is thickest to develop $\delta^{13}C$ and $\delta^{18}O$ chemostratigraphic curves. These powder samples

were vacuum-sealed in vessels and reacted with 100% orthophosphoric acid. Calcite reactions were performed in a 25°C bath for at least 4 hours and dolomite was reacted at 50°C for at least 24 hours. The resulting carbon dioxide gas was cryogenically purified and analysed in a Finnigan MAT 252 mass spectrometer with a precision of 0.1‰.

The $\delta^{18}O$ values were used to produce an oxygen isotope chemostratigraphic curve for Bentiaba that was then compared to $\delta^{18}O$ compilations from the South Atlantic at Walvis Ridge and from the Pacific Ocean (Friedrich et al., 2012). Paleotemperatures (T) were estimated using the calcite-temperature equation of Kim & O'Neil (1997):

$$1000\ln\alpha_{\text{calcite-water}} = 18.03(10^3 T^{-1}) - 32.42$$

where $\alpha_{\text{calcite-water}}$ represents the calcite-water fractionation factor.

Results

The results of the stable oxygen isotopic analysis for 14 calcite shells and 10 additional samples that were altered to dolomite

are shown in Table 1. The $\delta^{18}\text{O}$ values of calcite samples range between -3.2‰ and -0.8‰ , with an average value of -1.6‰ . These values and those for shells altered to dolomite are plotted in Fig. 2 against stratigraphy and the $\delta^{13}\text{C}$ chemostratigraphic and paleomagnetic data from Strganac et al. (2014a). The resulting pattern in stable oxygen isotopes of calcite shows a general trend of increasing $\delta^{18}\text{O}$ values up section. A positive $\sim 2\text{‰}$ excursion in the uppermost Salinas Formation to Lower Baba Formation results from values of -3.2‰ , -2.1‰ and -1.2‰ derived from shells recovered at 57, 67 and 69.5 m, respectively. Between 71 and 81 m, $\delta^{18}\text{O}$ values remain relatively constant, ranging between -1.4 and -1.9‰ . The maximum values of -0.8‰ and -0.9‰ are from shells collected at 108 m and 110.5 m. A positive 0.5‰ shift is observed in inoceramids recovered at the base of the Mocuio Formation, at 116 m, and remain between -1.2‰ and -1.8‰ to 128 m.

Discussion and conclusions

The pattern of $\delta^{18}\text{O}$ from inoceramids at Bentiaba is similar to those known from benthic foraminifera from the Pacific Ocean,

albeit with a negative $\sim 1\text{‰}$ offset (Fig. 3). This suggests that the oxygen isotope stratigraphy at Bentiaba tracks declining global temperatures beginning in the Late Turonian, concurrent with a deep ocean connection in the equatorial Atlantic. A $\delta^{18}\text{O}$ value of -3.2‰ derived from inoceramids at Bentiaba coincides with depleted values during the Late Turonian from benthic foraminifera in the Pacific and *Inoceramus* at Walvis Ridge. Values decrease $\sim 2\text{‰}$ by the Late Campanian, similar to the decrease observed at Walvis Ridge (Barron et al., 1984). In the Late Campanian, fluctuations of less than 1‰ in $\delta^{18}\text{O}$ at Bentiaba may reflect smaller variability in temperature or effects of salinity superimposed on a warming interval observed globally. Similar fluctuations in $\delta^{18}\text{O}$ values are also observed near the same time interval at the Walvis Ridge (Barron et al., 1984).

Bentiaba $\delta^{18}\text{O}$ values indicate a similar pattern to global values from the Turonian through the Late Campanian (Fig. 3) during a time when the shallow marine environment at Bentiaba became increasingly confined, possibly due to falling sea levels during the Campanian, indicated by dolomitisation of inoceramids at two stratigraphic levels in the Bentiaba section during the Late Campanian and Early Maastrichtian (Warren, 2000;

Table 1. Stable isotope values of inoceramid shells for the Bentiaba $\delta^{18}\text{O}$ stratigraphy. Paleotemperature calculated using calcite-temperature equation of Kim & O'Neil (1997).

Height (m)	Sample #	Taxon	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	T ($^{\circ}\text{C}$)
139.5	PA 457	Inoceramid*	-3.4	-0.6	-
138.5	PA 456	Inoceramid*	-4.2	-2.1	-
137.5	PA 458	Inoceramid*	-3.7	-0.6	-
136.5	PA 455	Inoceramid*	-4.3	-2.5	-
135.5	PA 454	Inoceramid*	-3.2	-0.6	-
134.5	PA 452	Inoceramid*	-4.7	-2.4	-
134.5	PA 451	Inoceramid*	-2.2	-0.2	-
134.5	PA 373	Inoceramid*	-4.0	-2.0	-
131.5	PA 372	Inoceramid*	-3.3	-2.6	-
129.0	PA 371	Inoceramid*	-2.2	-0.638	-
128	PA 386	Inoceramid*	0.7	-1.8	18.5
127	PA 370	Inoceramid*	1.5	-1.2	15.7
119	PA 383	Inoceramid*	1.3	-1.2	15.7
116	PA 382	Inoceramid*	-1.7	-1.8	18.5
110.5	PA 367	Inoceramid*	1.1	-0.8	13.9
108	PA 368	Inoceramid*	1.8	-0.9	14.4
81	PA 364	Inoceramid*	1.5	-1.4	16.7
80	PA 363	Inoceramid*	2.2	-1.6	17.6
79	PA 362	Inoceramid*	2.4	-1.4	16.7
77	PA 361	Inoceramid*	1.2	-1.9	19
71	PA 358	Inoceramid*	2.3	-1.6	17.6
69.5	PA 357	Inoceramid*	3.4	-1.2	15.7
67	PA 355	Inoceramid*	1.7	-2.1	20
57	PA 392	Inoceramid*	-0.8	-3.2	25.3

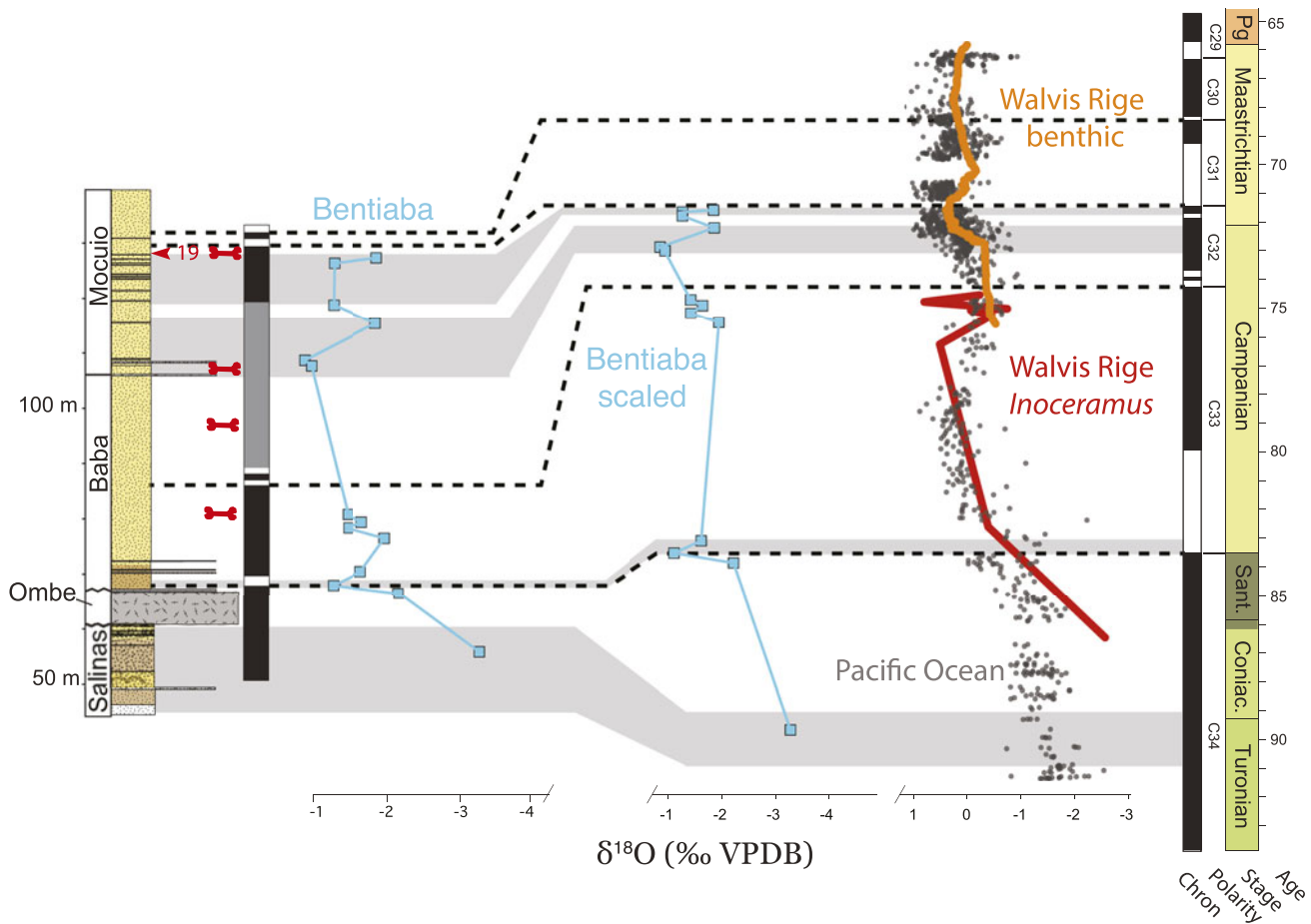


Fig. 3. Comparison of Bentiaba $\delta^{18}\text{O}$ stratigraphy to Inoceramus (Barron et al., 1984) and benthic foraminifera (Li & Keller, 1998; Friedrich et al., 2012) from Walvis Ridge and the Pacific Ocean compilation (Friedrich et al., 2012; their supplemental). Figure is as follows left to right: Bentiaba section with stable oxygen- and magnetostratigraphy, Bentiaba $\delta^{18}\text{O}$ curve calibrated with $\delta^{13}\text{C}$ (horizontal shaded areas) and paleomagnetic (dashed lines) correlations from Strganac et al. (2014a), Walvis Ridge and Pacific $\delta^{18}\text{O}$ curves.

Friedrich et al., 2009; Strganac et al., 2014a). While these conditions may seem to support higher evaporation rates and high salinities, the relatively depleted values at Bentiaba, offset by negative $\sim 1\text{‰}$ from deep ocean values, does not support this. Barron et al. (1984) predicted that the enrichment in $\delta^{18}\text{O}$ at Walvis Ridge in the Campanian was the result of dense saline waters originating from shallow seas from Africa, which our results also do not support. Depleted $\delta^{18}\text{O}$ values may result from meteoric input, but Bentiaba was within the arid latitudes ($\sim 24^\circ\text{S}$) and the sedimentary textures, mineralogy and sources suggest low meteoric input (Strganac et al., 2014b).

At Bentiaba, a Late Turonian paleotemperature estimate from calcite is $\sim 25^\circ\text{C}$. In the earliest Campanian the estimated paleotemperatures decrease to $15\text{--}18^\circ\text{C}$, similar to that estimated for the Australian Pacific (Friedrich et al., 2012). By the Late Campanian–earliest Maastrichtian, Bentiaba paleotemperatures remain approximately the same, $16\text{--}19^\circ\text{C}$, whereas temperatures in the Pacific and Walvis Ridge have decreased to $\sim 10^\circ\text{C}$. Assuming a constant ocean $\delta^{18}\text{O}$ value during the Cretaceous, the change in $\delta^{18}\text{O}$ values from -3.2 to -1.2‰ observed at

Bentiaba corresponds to a $\sim 10^\circ$ temperature decrease from the Late Turonian to Early Maastrichtian, similar to temperature changes inferred from oxygen isotopes derived from deep sea benthic foraminifera in the Pacific Ocean and Southern Ocean (Clarke & Jenkyns, 1999; Cramer et al., 2009; Friedrich et al., 2009, 2012).

Mosasaurs are known from Angola from the Late Turonian at Iembe to the Maastrichtian at Bentiaba (Fig. 1), during a trend of declining sea temperature implied by the Bentiaba stable oxygen isotope curve. During the Turonian, temperatures at Bentiaba ranged from ~ 22.4 to 25.3°C (Table 1). The temperature calculated from $\delta^{18}\text{O}$ values at the lowest amniote fossils at Bentiaba (Baba Formation, Chron C33n, approximately 75 Ma) is 16.7°C . The temperature estimate for Chron C32n2n (approximately 73 Ma), within the Baba Formation, which contains indeterminate rüsselosaurian and mosasaurine mosasaur fossils, is 19.0°C . The estimate for the mosasaurs and plesiosaurs in the Mocuio Formation, higher in Chron C32n2n at 72.8 Ma, is 13.9°C , reflecting a relatively rapid drop in temperature. The mosasaurine-dominated Bench 19 Fauna was recovered from

sediments dated to Chron C32n1n, about 71.5 Ma, which directly overlies a sampled interval that indicate temperatures of $\sim 18.5^\circ\text{C}$.

Examination of the $\delta^{13}\text{C}$ curve presented in Strganac et al. (2014a) shows declining, but relatively stable, values during deposition of the Baba Formation, but within the lower part of the Mocuio Formation a sharp negative excursion of $\sim 3\%$ in $\delta^{13}\text{C}$ values occurs with a recovery of equal magnitude coincident with the onset of the bench-forming depositional regime. This negative excursion is correlated with global patterns interpreted as the Campanian–Maastrichtian Boundary Events (tie points 9a and 8 *sensu* Voigt et al., 2012), but the precipitous recovery (tie point 7), coincident with the base of Bench 19, appears strongest in the South Atlantic Ocean observed in foraminifera from the Walvis Ridge and Bentiaba, and thus may reflect increased localised primary productivity for this time, which may account at least in part for the large number of marine amniotes in this part of the section.

Mosasaurus originated in relatively low latitudes during the high temperatures of the Cenomanian (Polcyn et al., 1999; Jacobs et al., 2005a,b; Bardet et al., 2008). Before the end of the Cretaceous they occupied waters from the Antarctic to the tropics and into the northern high temperate latitudes. Their dispersal across the globe is accompanied by an increase in size and morphological disparity (Polcyn et al., 2014), and by the acquisition and maintenance of high body temperature (Bernard et al., 2010), reasonably considered in this case as an adaptation to colder water temperatures, especially in high latitudes. In addition, skin pigmentation preserved in exceptional specimens indicates dark colouration, which has been suggested to be an aid in thermoregulation (Lindgren et al., 2014). In this study we have seen temperature decrease in waters throughout most of the Late Cretaceous Period in one region along the Angola coast continuously inhabited by mosasaurs.

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