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Southern high latitude warmth during the Jurassic–Cretaceous: New evidence from clumped isotope thermometry

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ABSTRACT

In order to understand the climate dynamics of the Mesozoic greenhouse world, it is vital to determine paleotemperatures from higher latitudes. For the Jurassic and Cretaceous climate, there are significant discrepancies between different proxies and between proxy data and climate models. We determined paleotemperatures from Late Jurassic and Early Cretaceous belemnites using the carbonate clumped isotope paleothermometer and compared these values to temperatures derived from TEX86 and other proxies. From our analyses, we infer an average temperature of ca. 25 °C for the upper part of the water column of the Southern Atlantic Ocean. Our data imply that for mid to high latitudes, climate models underestimate marine temperatures by >5 °C and, therefore, the amount of warming that would accompany an increase in atmospheric CO2 of more than 4x pre-industrial levels, as is projected for the near future.

INTRODUCTION

Modern anthropogenic CO2 production has resulted in rapid climate change, with near-surface air temperatures in the high latitude regions rising at ca. twice the global average rate (Screen and Simmonds, 2010). Predictions of how global and polar temperatures will change over
The next few decades in response to continued CO₂ release may be improved by studying past climate response to elevated CO₂ levels. The Late Jurassic to Early Cretaceous (164 to 100 million years ago) was characterized by extremely high but variable levels of atmospheric CO₂ (from ca. 2x to 8x pre-industrial levels; Wang et al., 2014; Foster et al., 2017), yet reconstructions of marine temperatures, particularly for the high latitudes, are contradictory (e.g., Huber et al., 1995; Price and Gröcke, 2002; Bice et al., 2003; Poulsen, 2004; Jenkyns et al., 2012; Price and Passey, 2013; O’Brien et al., 2017).

The stable oxygen isotope composition of the carbonate remains of marine organisms is the most extensively used temperature proxy, yet high-latitude sea-surface temperatures (SST) derived from independent organic geochemical paleothermometers, i.e., TEX86, may be ca. 10 °C warmer than δ¹⁸O-based temperature reconstructions (e.g., Mutterlose et al., 2010; O’Brien et al., 2012) and up to 6 °C warmer than general circulation model (GCM) predictions (Price and Passey, 2013). These differences have led some authors to suggest that the high TEX86 SST estimates are too warm (Hollis et al., 2009; Meyer et al., 2018), and there is an ongoing debate as to which calibration is appropriate for applications of the TEX86 proxy at specific regions and different intervals of the geologic record (Kim et al., 2012; Taylor et al., 2013). Conversely, δ¹⁸O-based paleotemperature reconstructions rely on several assumptions, among which is the oxygen isotope composition of the seawater (δ¹⁸O(sw; Huber et al., 1995; Price and Gröcke, 2002; Bice et al., 2003), and the accuracy of these assumptions still needs to be verified. If the interpretation of warm sub-polar paleo-ocean temperatures can be confirmed, they imply that past and future polar warming may be much greater (i.e., >5 °C) than indicated by climate models. Furthermore, such warm temperatures test the veracity of claims of Early to mid-Cretaceous polar ice, in particular from those studies deriving data from locations distal to the poles (Miller, 2009).
Deep Sea Drilling Project Site 511, on the Falkland Plateau (51°00.28'S, 46°58.30'W), is particularly well suited for studying Jurassic and Cretaceous climate due to its abundant, exceptionally preserved macrofossils, including belemnites (Jeletzky, 1983; Price and Sellwood, 1997; Price and Gröcke, 2002). The Falkland Plateau was located at approximately 53 °S during the Late Jurassic–Early Cretaceous (Scotese, 2014; Fig. 1). Mean annual temperatures derived from GCMs for the Late Jurassic and Early Cretaceous indicate that the temperatures of the Falkland Plateau region (avg. 10–22 °C) are representative of similar southern hemisphere paleolatitudes (Lunt et al., 2016). Earlier research at Site 511 used the TEX86H paleotemperature proxy to suggest that warm sea-surface conditions (26–35 °C) existed during the Late Jurassic–Early Cretaceous interval (Jenkyns et al., 2012). These paleotemperatures are consistently warmer than paleotemperature estimates based on δ18Obelemnite, assuming a δ18Osw of -1‰ SMOW (11–21 °C; Price and Gröcke, 2002). Another study, undertaken on Barremian to Aptian sediments from two outcrops in northern Germany, also shows that δ18Obelemnite-derived paleotemperatures (12–16 °C) are consistently cooler than TEX86-based estimates (26–32 °C; Mutterlose et al., 2010). Jenkyns et al. (2012) argue that the offset is due to TEX86 recording sea surface temperatures, whereas belemnites record temperatures from deeper water, possibly from below the thermocline.

In this study, we apply the carbonate clumped isotope paleothermometer to exceptionally well-preserved belemnite rostra from Site 511. This proxy provides seawater temperature estimates independent of δ18Osw (Price and Passey, 2013; Wierzbowski et al., 2018). In addition to constraining high latitude temperatures, we set out to resolve the uncertainties associated with previous δ18O-based belemnite temperature reconstructions.

**MATERIALS AND METHODS**

**Stratigraphy and samples**
The lithology of the sampled section of Site 511 consists of grey-black, thinly laminated mudstones and soft, grey claystones, which were deposited in a periodically anoxic, low-energy, shallow (< 400 m) basin (Basov and Krasheninnikov, 1983; Jeletzky, 1983). A geothermal gradient of 7.4 °C/100 m has been determined (Langseth and Ludwig, 1983) at Site 511, thus, for the samples analyzed in this study, we can estimate a maximum burial temperature of ca. 50 °C. At elevated temperatures, diffusion of carbon and oxygen isotopes in the carbonate mineral lattice may reset the initial bond-ordering (e.g., Henkes et al., 2014). However, theoretical calculations based on laboratory experiments provide evidence that solid-state diffusion, even in wet and high-pressure conditions, is insignificant below 100 °C burial temperatures on a timescale of 100–160 Ma (Passey and Henkes, 2012). Thus, it is unlikely that the belemnite rostra analyzed in this study were affected by solid-state reordering.

Eleven belemnites (*Belemnopsis* sp.) were selected for maximum stratigraphic coverage and were geochemically screened to include the best-preserved samples, as indicated by available trace element concentrations (i.e., low Fe and Mn; high Sr and Mg concentrations; Price and Gröcke, 2002; Supplemental Information) and cathodoluminescence analyses (Figure 5 of Price and Sellwood, 1997). Subsamples were derived avoiding the margins and apical zone, as these areas are much more susceptible to diagenetic overgrowth and cementation, respectively than the rest of the belemnite (e.g., Ullmann et al., 2015). In addition, we made electron backscatter diffraction (EBSD) analyses and secondary electron microscopy (SEM-BSE) images of selected rostra at the Goethe University Frankfurt (Supplemental Information).

### Clumped Isotope Analyses

Carbonate digestion (90 °C), CO₂ purification (cryotraps and GC) and subsequent measurement procedures (ThermoFisher MAT 253) are identical to the techniques described in Wierzbowski et al. (2018). Raw isotope values were calculated using the IUPAC isotopic
parameters, and are projected to the CO2 reference frame ($\Delta_{47}^{\text{RFAC}}$; Petersen et al., 2019). To verify the consistency and precision of the clumped isotope measurements, six carbonate standards (ETH1–4, MuStd, Carrara) were analyzed along the samples (Data S1). We used the in-house Wacker et al. (2014) calibration to convert $\Delta_{47}^{\text{RFAC}}$ values to temperatures (Supplemental Information; Petersen et al. 2019). Temperature uncertainties are based on external $1SE$ (including $t$-value) that is always larger than or identical to the best attainable internal precision as represented by the shot noise limit (0.004–0.005‰).

**RESULTS**

**Electron Microscopy**

All investigated rostra, excluding the areas adjacent to the apical line and the surface, are made up of optical calcite and the c-axis of the calcite grains point radially outwards (Figs. S1-S4). The distribution of the crystallographic a-axes also follows a pattern. This is analogous to pristinely preserved rostra (Stevens et al., 2017). Our EBSD and SEM-BSE analyses suggest that recrystallization, which would change the original orientation of the biogenic calcite grains, did not occur in the sampled areas.

**Clumped Isotope Analyses**

The $\Delta_{47}^{\text{RFAC}}$ values range between 0.690(±0.011)‰ and 0.707(±0.015)‰. The $1SE$ uncertainty for the clumped isotope measurements, calculated from 4–6 replicate analyses are between 0.004‰ and 0.015‰ (mean 0.010‰). The $\Delta_{47}^{\text{RFAC}}$ values yield seawater temperatures ranging between 21 °C and 28 °C (mean 25 °C) and show no significant stratigraphic trend (Fig. 2). The average uncertainty for the reconstructed temperatures is ±4 °C. Steeper-sloped calibrations yield indistinguishable temperatures within ±$1SE$ (Data S1).

**DISCUSSION**
The Δ47-derived temperature range (21–28 °C, mean 25 °C) for the entire section is higher than those temperatures reconstructed via stable oxygen isotope paleothermometry (11–19 °C, mean 16 °C, assuming δ18Osw = -1‰ SMOW; Price and Gröcke, 2002), and cooler, and rarely within error, of SST estimates derived from TEX86 (25–31 °C; Fig. 2; Jenkyns et al., 2012). In this study, as in Jenkyns et al. (2012), we calculate TEX86 temperatures using the TEX86H calibration (Kim et al., 2010). Given the shallow-water and high latitude setting of Site 511 TEX86H may yield maximum SST estimates (Schouten et al., 2013; Taylor et al., 2013). In contrast to TEX86H, the linear calibration used of O'Brien et al. (2017) yield ca. 2–3 °C warmer temperatures, whereas the calibrations that assume a non-surface export depth of GDGTs (Kim et al., 2012; Schouten et al., 2013) yield ca. 5–6 °C cooler estimates (Fig. 2). Although the TEX86H proxy is likely the most appropriate for a high latitude setting such as Site 511, there is ongoing discussion and revision of the various calibrations, and ongoing debate as to which calibration should be applied (e.g., Ho et al., 2014; Inglis et al., 2015). The difference between the TEX86H and the Δ47-derived temperatures for Site 511 may be partially resolved by considering a seasonal bias in either proxy. It has been postulated that belemnites, as nektonic cephalopods, reflect mean annual temperatures (MAT; Price and Sellwood, 1997; Mutterlose et al., 2010), while TEX86 may indicate summer temperatures, rather than MAT (Leider et al., 2010; Hollis et al., 2012). Nevertheless, our Δ47 temperatures suggest that belemnites were calcifying their rostra in the upper part of the water column (<200 m depth), and are broadly consistent with TEX86-derived SSTs, given the uncertainties listed above. Such an interpretation is in alignment with an assumed predator lifestyle in the photic zone for belemnites (Klug et al., 2016).

All three records from Site 511 show less than 7 °C variability across the entire Late Jurassic and Early Cretaceous interval, although the low sampling resolution means it is not possible to derive more detailed information on Jurassic and Cretaceous climate evolution. These
data confirm warm Late Jurassic–Early Cretaceous high latitude ocean temperatures, possibly precluding the likelihood of substantial land ice, and are consistent with estimated MATs from fossil plant assemblages from the Antarctic Peninsula (Francis and Poole, 2002). The most likely mechanism to account for such warmth observed at Site 511 is high atmospheric greenhouse gas concentrations and high polar heat transport. The shallow meridional temperature gradients of the past greenhouse climates pose a significant challenge to numerical climate models (Huber and Caballero, 2011), in that increased greenhouse gases may yield warm Polar Regions, but also overheat the Tropics. MATs for the Cretaceous derived from coupled ocean-atmosphere climate models provide estimates for 53 °S ranging from 12 °C to 21 °C (Zhou et al., 2008; Donnadieu et al., 2016). The higher of these estimates are generated with 2240 ppm $p$CO$_2$ (8 x pre-industrial levels; Donnadieu et al., 2016). These atmospheric CO$_2$ concentrations typically exceed estimates of Cretaceous $p$CO$_2$ derived from fossil leaf stomatal index measurements, isotope-based or geochemical model estimates (Wang et al., 2014; Foster et al., 2017). Furthermore, it is crucial to consider the magnitude of a non-CO$_2$ component of local climate change, before proxies from a single site are interpreted in a global context (Lunt et al., 2016). GCM output indicates warm conditions during the Cretaceous at Site 511 when compared to the Eocene (Lunt et al., 2016), with almost invariable modeled global mean temperatures over the same period, when $p$CO$_2$ is kept constant. This suggests that contributions from other processes (e.g., paleogeography) may account for some of the observed warmth. Despite these findings and those of others (Donnadieu et al., 2016), the role of paleogeography in regulating climate remains less than clear.

Such warm temperatures at Site 511 challenge our understanding of how the ocean-atmosphere system operated in the past (Poulsen, 2004) and may also have important implications for the prediction of future climates as they imply we may be underestimating future climate change.
in such regions (Spicer et al., 2008). Proposed mechanisms to increase the transfer of heat toward
the poles (Schmidt and Mysak, 1996), including sensible and latent heat transfer via the atmosphere
and heat transfer via the oceans (Hotinski and Toggweiler, 2003), are hence implied. As Site 511
was situated in a seaway open to the southwest (Fig. 1), increased heat transfer via warm ocean
currents can only be derived from the Pacific. Thus, other processes, including heat transfer via the
atmosphere, might also be important for this region.

These new warm Δ47-derived temperature reconstructions also have implications for basin-
scale hydrologies. In conjunction with the δ18Obelemnite data (Price and Sellwood, 1997; Price and
Gröcke, 2002), we can estimate δ18Osw, assuming the temperature dependence of oxygen isotope
fractionation between belemnite calcite and seawater corresponds to Kim and O’Neil (1997). The
δ18O–temperature equation of Kim and O’Neil (1997) indicates that δ18Osw may have averaged
+1.0‰ SMOW (1SE = 0.7‰; Fig. 2, Data S1), heavier than the global average for an ice-free world
(-1‰ SMOW; Shackleton and Kennett, 1975). This could suggest that the semi-enclosed basin in
which Site 511 was located was dominated by evaporation; alternatively, it is quite possible that the
Kim and O’Neil (1997) calcite equation is not applicable to belemnite calcite.

CONCLUSIONS

This proxy-to-proxy intercomparison reduces the uncertainty on temperature estimates for
the Mesozoic high southern latitudes. Our Δ47-derived temperatures, although slightly cooler, are
consistent with the TEX86H reconstructions for sea-surface temperatures. The new Δ47 data, in
conjunction with δ18Obelemnite data imply local δ18Osw values of ca. 1.0(±0.7)‰ SMOW, indicating a
strong role of evaporation on the Falkland Plateau, which was a semi-enclosed basin during the Late
Jurassic and Early Cretaceous. The warm reconstructed paleotemperatures, if extrapolated
poleward, reinforce evidence of temperate polar conditions and lack of polar ice. If these warm
ocean temperatures, occurring when pCO2 in Earth’s atmosphere were also high, prove accurate,
they may indicate that greenhouse gases could have heated the oceans during the Jurassic and Cretaceous more than currently accepted. This suggests that future warming from elevated atmospheric CO₂ concentrations may be much greater than that predicted by models.

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Figure 1. Paleogeographic setting of the Deep Sea Drilling Project Site 511. Early Cretaceous paleogeographic reconstruction after Scotese (2014).
Figure 2. Jurassic and Early Cretaceous temperatures and seawater δ¹⁸O from DSDP Site 511. (A) Clumped isotope seawater temperature reconstructions for Site 511 (this study) are compared to those based on δ¹⁸O belemnite (Price and Gröcke, 2002; Price and Sellwood, 1997; plotted using Kim and O’Neil, 1997, with an assumed δ¹⁸Osw of -1‰ SMOW) and TEX₈₆ (Jenkyns et al., 2012). Infilled green circles represent δ¹⁸O belemnite temperatures from Price and Gröcke (2002), hollow green circles are the belemnites that were also used for clumped isotopes analysis in this study. For TEX₈₆ temperatures, dotted lines used TEX₈₆H,₀⁻₂₀₀ (Kim et al. 2012, eq. 2), dashed used TEX₈₆-linear (O’Brien et al., 2017, eq. 4), and solid line and points used the TEX₈₆H calibration (Kim et al. 2010, eq.10). (B) Reconstructed δ¹⁸Osw values (this study) using the equation of Kim and O’Neil (1997). Error bars represent for δ¹⁸O belemnite and ∆₄⁷ the 1SE of multiple replicate analyses; for TEX₈₆H the calibration error; and for δ¹⁸Osw the 1SE corresponding to the ∆₄⁷ measurements. Age model construction is described in the Supplemental Information, whereas data for this figure can be found in Data S1.