

# Instability in tropical Pacific sea-surface temperatures during the early Aptian

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## ABSTRACT

The Cretaceous has long been recognized as a time when greenhouse conditions were fueled by elevated atmospheric CO<sub>2</sub> and accompanied by perturbations of the global carbon cycle described as oceanic anoxic events (OAEs). Yet, the magnitude and frequency of temperature change during this interval of warm and equable climate are poorly constrained. Here we present a high-resolution record of sea-surface temperatures (SSTs) reconstructed using the TEX<sub>86</sub> paleothermometer for a sequence of early Aptian organic-rich sediments deposited during the first Cretaceous OAE (OAE1a) at Shatsky Rise in the tropical Pacific. SSTs range from ~30 to ~36 °C and include two prominent cooling episodes of ~4 °C. The cooler temperatures reflect significant temperature instability in the tropics likely triggered by changes in carbon cycling induced by enhanced burial of organic matter. SST instability recorded during the early Aptian in the Pacific is comparable to that reported for the late Albian–early Cenomanian in the Atlantic, suggesting that such climate perturbations may have occurred during the Cretaceous with concomitant consequences for biota and the marine environment.

**Keywords:** TEX<sub>86</sub> index, oceanic anoxic events, Cretaceous sediments, carbon isotopes.

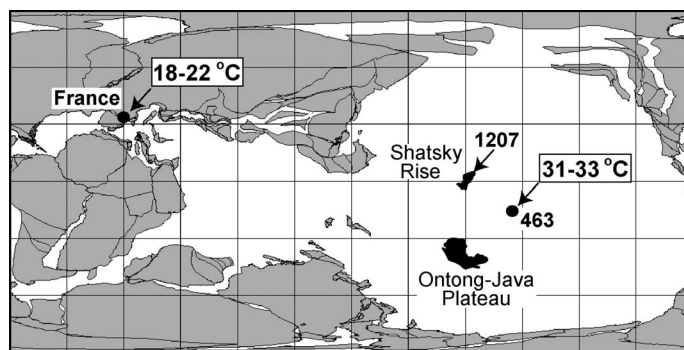
## INTRODUCTION

Elucidation of tropical sea-surface temperatures (SSTs) for the Cretaceous presents significant challenges. Critical progress in recent years has addressed issues of isotopic integrity of microfossils by determination of the δ<sup>18</sup>O composition of selected well-preserved substrates, namely, foraminifera, fish teeth, brachiopods, aragonitic rudists, and magnesian calcite cements (e.g., Huber et al., 1995; Wilson and Opdyke, 1996; Norris and Wilson, 1998; Price et al., 1998; Erbacher et al., 2001; Pearson et al., 2001; Wilson and Norris, 2001; Norris et al., 2002; Wilson et al., 2002; Pucéat et al., 2003; Voigt et al., 2004; Steuber et al., 2005). These studies have principally focused on the Cenomanian–Turonian, so Cretaceous temperature records including those for the early Aptian (Fig. 1) remain sparse, especially in the Pacific. Most are of low resolution, documenting time-averaged SST values that poorly constrain rates of cooling or warming. The scarcity of well-preserved foraminifera and other microfossils further precludes extensive use of oxygen isotope paleothermometry in Cretaceous sequences, a limitation heightened for organic-rich sediments deposited during oceanic anoxic events (OAEs). By contrast, such sediments are excellent candidates for determination of SST using the TEX<sub>86</sub> index, a molecular paleoclimate proxy based on the distribution of Crenarchaeota tetraether lipids (Schouten et al., 2002, 2003). Here, we assess paleotemperatures using TEX<sub>86</sub> for organic-rich sediments corresponding to the early Aptian oceanic anoxic event (OAE1a) from sediments deposited in the equatorial Pacific at Shatsky Rise. The SST record obtained reveals two cooling events that attest to significant variability in the tropical climate during the early Aptian.

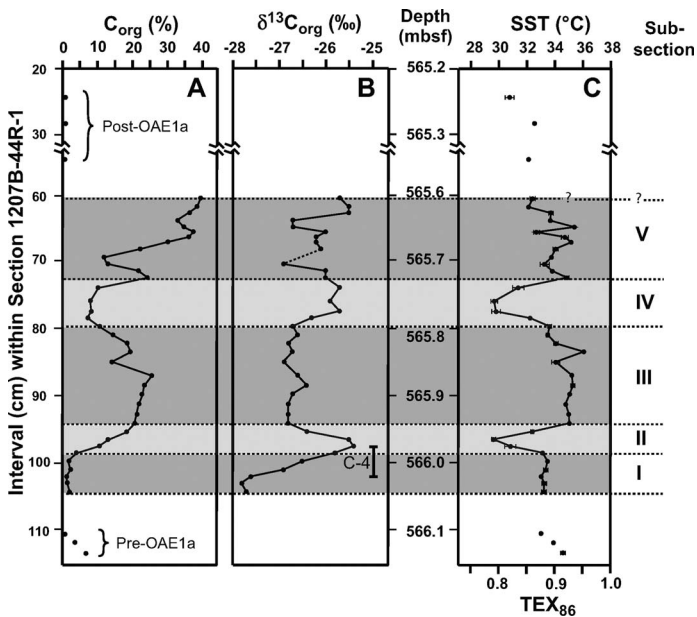
## EARLY APTIAN OCEANIC ANOXIC EVENT AT SHATSKY RISE

Cretaceous OAEs represent relatively short (≤1 m.y.) episodes of enhanced sequestration of organic matter (OM), and they record major perturbations of the ocean system and the carbon cycle (Schlanger and Jenkyns, 1976). OAE1a (ca. 120 Ma) is one of the two such events that has a global extent (Arthur et al., 1990; Leckie et al., 2002). OAE1a is characterized by (1) a decrease in <sup>87</sup>Sr/<sup>86</sup>Sr values attributed to a combination of enhanced hydrothermal activity, increased seafloor spreading, or submarine volcanism associated with emplacement of the Ontong-Java igneous province (Fig. 1), (2) high trace-metal concentrations indicative of increased hydrothermal activity, and (3) a major decline in the abundance of the nannoplankton group called nannocoinids (Erba, 1994, 2004; Bralower et al., 1997; Jones and Jenkyns, 2001; Leckie et al., 2002; Erba and Tremolada, 2004). OAE1a is also marked by an initial negative δ<sup>13</sup>C excursion attributed to dissociation of CH<sub>4</sub> hydrates (Jahren et al., 2001; Beerling et al., 2002), and followed by a positive δ<sup>13</sup>C excursion associated with accelerated burial of OM linked to enhanced productivity (Menegatti et al., 1998; Hochuli et al., 1999; Leckie et al., 2002). Molecular analyses suggest that nitrogen-fixing cyanobacteria were more prevalent among marine phytoplankton at this time (Kuypers et al., 2004; Dumitrescu and Brassell, 2005).

Early Aptian samples were obtained from Ocean Drilling Program (ODP) Site 1207 (ODP Leg 198; 37°47.433'N, 162°45.053'E; 3101 m water depth) on the northern high of Shatsky Rise (Fig. 1). Paleogeographic reconstructions place Site 1207 in the central equatorial Pacific in early Aptian time (Schettino and Scotese, 2000). A 45 cm continuous interval of finely laminated, dark brown radiolarian claystone rich in marine algal and bacterial OM (Dumitrescu and Brassell, 2005) was recovered at a depth of 565.60–566.05 meters below seafloor (mbsf) in Hole 1207B (1207B-44R-1, 60–105 cm; Bralower et al., 2002; Rob-



**Figure 1.** Paleogeographic map (after Schettino and Scotese, 2000) showing locations of early Aptian (ca. 120 Ma) sites for which temperature data are available (France: Pucéat et al., 2003; Deep Sea Drilling Project [DSDP] Site 463: Schouten et al., 2003). Range of temperatures from Site 463 excludes sample reported with temperature of 27 °C, a value now thought suspect because of maturity. Latitude and longitude are represented by 30° × 30° grids.



**Figure 2.** Depth profiles of biogeochemical (meters below seafloor [mbsf]) and paleotemperature data for oceanic anoxic event 1a (OAE1a) sequence recovered from Ocean Drilling Program (ODP) Site 1207. Recovered sequence corresponding to OAE1a is shaded, with subsections (I to V) discussed in text designated by intensity of shading. **A:** Organic carbon content (%). **B:** Carbon isotopic composition of organic matter (‰, Vienna PDB), with positive excursion assigned as C-4 (Dumitrescu and Brassell, 2006; Menegatti et al., 1998). **C:** Sea-surface temperatures (SSTs) based on  $TEX_{86}$  proxy.

inson et al., 2004). This interval represents ~40% of the estimated total thickness of OAE1a at Site 1207 (~1.2 m; Bralower et al., 2002; Robinson et al., 2004). Biostratigraphic analysis of calcareous nanofossils reveals that these sediments correspond to nanofossil zone NC6, which confirms that they are early Aptian, synchronous with OAE1a (Bralower et al., 2002).

#### ANALYTICAL METHODS

Early Aptian sediments were sampled at centimeter scale. Organic carbon ( $C_{org}$ ) contents were determined on acidified, powdered samples using an ELTRA CS-2000 instrument. Our  $\delta^{13}C_{org}$  values were determined using a ThermoFinnigan Delta Plus XP mass spectrometer connected online to a Costech elemental analyzer. The  $\delta^{13}C$  composition of the  $CO_2$  gas liberated was calibrated against an internal laboratory standard (acetanilide,  $\delta^{13}C_{org} = -29.85\text{‰}$ ), expressed relative to the Vienna Pee Dee belemnite (VPDB) international standard.

Powdered samples (~1–9 g) were extracted using an accelerated solvent extractor or by Soxhlet when  $C_{org}$  was  $\geq 21.7\%$ . Extracts were concentrated, reduced to dryness under  $N_2$ , and separated by silica gel column chromatography into aliphatic, aromatic, and polar fractions. Polar fractions were further separated by  $Al_2O_3$  column chromatography, yielding a fraction containing the glycerol dialkyl glycerol tetraethers (GDGTs), which were analyzed using published protocols (Schouten et al., 2002; Jenkyns et al., 2004).  $TEX_{86}$  values determined from relative GDGT peak areas were converted to SST values using equation B in Figure 2 of Schouten et al. (2003). Derivation of absolute temperature for Cretaceous samples required extrapolation of the established calibration line, which created uncertainty in such estimates. However, the range of  $TEX_{86}$  values at Site 1207 provides convincing evidence that this proxy records temperature changes that are significant. Moreover, the abundance of immature biomarkers in the samples (Dumitrescu and Brassell, 2005) confirms that tetraether distributions are unaffected by thermal degradation and, hence, attest to the veracity

of the  $TEX_{86}$  measurements. Replicate analyses have shown that the reproducibility of  $TEX_{86}$  values is commonly  $\leq 0.01$  or  $\leq 1^\circ C$ .

#### PALEOTEMPERATURE RECORD FOR THE TROPICAL EARLY APTIAN

At Site 1207,  $C_{org}$  contents vary markedly (~0.6%–40%) within OAE1a and exhibit a general trend of increasing values with decreasing depth (Dumitrescu and Brassell, 2006; Figure 2A). The negative  $\delta^{13}C$  excursion that is characteristic of the onset of OAE1a (Jahren et al., 2001; Beerling et al., 2002) and defines segment C-3 (Menegatti et al., 1998), was not retrieved (Dumitrescu and Brassell, 2006). However, the base of the recovered OAE1a interval records the subsequent positive  $\delta^{13}C$  shift (Fig. 2B; Dumitrescu and Brassell, 2006) that corresponds to segment C-4 from previous reports (Menegatti et al., 1998). Thus, the recovered interval derives from the basal portion of OAE1a, and is presumed to be the lower part of the ~1.2 m section of organic-rich sediments inferred from geophysical logs (Bralower et al., 2002; Robinson et al., 2004).

SSTs were determined using the  $TEX_{86}$  index, based on archaeal GDGT membrane lipids (Schouten et al., 2002, 2003; Jenkyns et al., 2004). This approach has advantages over oxygen isotope paleothermometry because it is unaffected by the calcification crisis that restricts calcareous organisms during OAE1a (Erba, 2004; Erba and Tremolada, 2004), and is not subject to uncertainties arising from differences in their textural preservation (Wilson and Opdyke, 1996; Norris and Wilson, 1998; Price, 2003), nor is it influenced by other factors that may cause changes in the  $\delta^{18}O$  of seawater. The high-resolution  $TEX_{86}$  record at Site 1207 yields SSTs for the early Aptian tropics that range from ~30 to ~36 °C (Fig. 2C), and it exhibits discrete variations that define and determine its division into five subsections (I to V, Fig. 2C). The data reveal two cooler episodes (98–94.7 cm, 79–73 cm; subsections II and IV) when temperatures decreased by ~4 °C to values less than 30 °C (Fig. 2C). The recurrence of such cooling events suggests temporal instability in tropical SST during the first global Cretaceous OAE (i.e., OAE1a) in the dominant Pacific Ocean. When coupled with complementary evidence for temperature change (~6 °C) on ~10 k.y. time scales in the tropical Atlantic during the late Albian–early Cenomanian (ca. 100 Ma; Wilson and Norris, 2001; Norris et al., 2002), these  $TEX_{86}$  data suggest that tropical SST instability may have been a persistent or a recurrent feature of Cretaceous oceans. SSTs values typical of Cretaceous greenhouse climate are also recorded prior to OAE1a (~33–35 °C, below 105 cm), at the base of OAE1a (~33 °C, 105–98 cm; subsection D), in the interval that separates the two cooling episodes (~34–36 °C, 94.7–79 cm; subsection III), and in the uppermost part of the recovered OAE1a interval (~32–35 °C, 73–60 cm; subsection V; Fig. 2C). Similar SSTs have been recorded from samples in a low-resolution study from a more southerly tropical location (~20°S) in the mid-Pacific Mountains (Deep Sea Drilling Project [DSDP] Site 463; Schouten et al., 2003) (Fig. 1). At Site 1207, temperatures decrease to ~31 °C after OAE1a, which is consistent with arguments for a cooler climate during either the late early Aptian (Hochuli et al., 1999) or the late Aptian (Weissert and Lini, 1991).

The observed fluctuations in tropical temperatures during the early Aptian prompt an evaluation of their time scales. The scarcity of preserved microfossils (Bralower et al., 2002) precludes estimations of the duration of the organic-rich interval recovered at Site 1207. Yet, OAE1a likely lasted ~500–750 k.y. (cf. Bralower et al., 1994; Leckie et al., 2002; Erba, 2004), which implies that the recovered interval at Site 1207 represents  $\sim 234 \pm 46$  k.y. (given a total thickness for OAE1a of 1.2 m; Bralower et al., 2002; Robinson et al., 2004). Assuming constant sedimentation rates, the cooling events (in subsections II and IV; Fig. 2C) recur on a time scale of  $102 \pm 23$  k.y., which suggests a possible relationship with Milankovitch orbital cycles, po-

tentially coupled to changes in solar insolation, as recognized elsewhere during Cretaceous OAEs (e.g., Wagner et al., 2004).

## IS TROPICAL SST INSTABILITY COUPLED TO ENVIRONMENTAL CHANGES?

The early Aptian is recognized as an interval of significant environmental change, including emplacement of the Ontong-Java igneous province, enhanced burial of OM, and a major biocalcification crisis (Erba, 1994, 2004; Erba and Tremolada, 2004; Weissert and Erba, 2004). Thus, it is pertinent to explore possible links between these changes and the observed tropical SST instability.

Emplacement of large igneous provinces such as the Ontong-Java Plateau has been proposed as a causal mechanism for raised atmospheric CO<sub>2</sub> levels and triggering of global warming (Larson and Erba, 1999; Weissert and Erba, 2004). Rapid warming at the onset of the OAE1a may have led to CH<sub>4</sub> hydrate dissociation (Jahren et al., 2001; Beerling et al., 2002), which could account for the negative  $\delta^{13}\text{C}_{\text{org}}$  excursion designated as C-3 (Menegatti et al., 1998). Emplacement of the Ontong-Java Plateau has also been proposed as a mechanism for increasing nutrient fluxes in the ocean (Larson and Erba, 1999). Increased nutrient availability may have supported high surface productivity leading to oxygen depletion in intermediate and deep waters, thereby enhancing sequestration of organic carbon in pelagic sequences (e.g., Site 1207; Fig. 2A). Increased burial of OM and, perhaps a waning of CH<sub>4</sub> release, may have triggered the cooling within subsection II (Fig. 2C). The  $\delta^{13}\text{C}_{\text{org}}$  values  $> -26\text{‰}$  associated with this cooling (Figs. 2B and 2C) can be interpreted as a response to the increase in OM burial. Such higher  $\delta^{13}\text{C}_{\text{org}}$  values are inconsistent with upwelling-induced cooling because upwelling waters supply <sup>13</sup>C-depleted CO<sub>2</sub>(aq), which would lower  $\delta^{13}\text{C}_{\text{org}}$ . The lag between the onset of the positive  $\delta^{13}\text{C}_{\text{org}}$  excursion and the subsection II cooling (Figs. 2B and 2C) suggests that the climate responded only after substantial quantities of OM had been buried. CH<sub>4</sub> hydrate dissociation could again explain the subsequent decrease in  $\delta^{13}\text{C}_{\text{org}}$  values, but it seems unlikely during cooler times. An increase in the intensity or frequency of volcanic activity would raise the atmospheric flux of <sup>13</sup>C-depleted CO<sub>2</sub>, which, in combination with faster recycling of OM, could induce the associated negative  $\delta^{13}\text{C}_{\text{org}}$  values observed above the C-4 segment (Fig. 2B) and the associated warming trend in subsection II. The minor fluctuations in  $\delta^{13}\text{C}_{\text{org}}$  concurrent with the warmer interval of subsection III (Figs. 2B and 2C) could have arisen from temporal changes in phytoplankton productivity or assemblages linked to variations in the flux of nutrients (Erba, 2004; Dumitrescu and Brassell, 2006). C<sub>org</sub> contents  $> 10\%$  in this warmer interval (subsection III) indicate that productivity remained at sufficiently high levels to sustain significant accumulation of OM, which in turn could have triggered the second episode of cooling (within subsection IV) and could explain the higher values of  $\delta^{13}\text{C}_{\text{org}}$  observed at 79–73 cm (Figs. 2B and 2C). These more positive  $\delta^{13}\text{C}_{\text{org}}$  values may also reflect a decrease of volcanic CO<sub>2</sub> emissions.

Volcanic activity has been invoked to explain the global biocalcification crisis during the early Aptian that caused a decline in specific nannoplankton—the so-called nannoconid crisis—and carbonate platform drowning, especially in the Tethys region (Erba, 1994, 2004; Föllmi et al., 1994; Weissert et al., 1998; Wissler et al., 2003; Erba and Tremolada, 2004; Weissert and Erba, 2004). The nannoconid crisis has been interpreted as a result of increased productivity and excess CO<sub>2</sub> (Leckie et al., 2002; Erba, 2004; Erba and Tremolada, 2004; Weissert and Erba, 2004), whereas the demise of carbonate platforms has been attributed to various environmental factors, notably extreme water temperatures and high nutrient levels (Weissert et al., 1998; Wilson et al., 1998; Jenkyns and Wilson, 1999; Wissler et al., 2003). Recognition of tropical SST instability at Shatsky Rise prompts consideration of its possible impact on biocalcification. Paleotemperatures of  $\sim 33\text{--}36\text{ °C}$

(Fig. 2C) during the early Aptian are thought to reflect increased CO<sub>2</sub> levels, which would lead to a decrease in calcium carbonate oversaturation, which, in turn, could reduce the calcification capability of calcareous nannoplankton and affect carbonate platform growth (Erba, 2004; Weissert and Erba, 2004). By contrast, the episodes with cooler paleotemperatures of  $\sim 30\text{--}32\text{ °C}$  (Fig. 2C) could have sustained Pacific carbonate platforms by maintaining favorable environmental conditions for the platform biota, thus facilitating their survival in the Pacific. These considerations illustrate the importance of temperature controls on carbon cycling, and their potential to trigger environmental change.

## CONCLUDING REMARKS

Assessment of SSTs using the TEX<sub>86</sub> proxy reveals significant temperature instability at Site 1207 on Shatsky Rise in the tropical Pacific during the early Aptian OAE1a. Two cooling events occurred within this interval of extreme warmth, and they appear to be related to changes in carbon cycling induced by enhanced burial of OM. In addition, the temperature variability may have contributed to changes in biocalcification, marked by the nannoconid crisis and carbonate platform drowning. In the Cretaceous, comparable SST variations have previously been documented in the tropical Atlantic during the late Albian–early Cenomanian (Wilson and Norris, 2001; Norris et al., 2002). Thus, the evidence for fluctuating temperatures during two distinct stages of the Cretaceous implies that tropical SST instability may have been persistent or recurrent during this era. Further determination of paleotemperatures using the TEX<sub>86</sub> proxy in the Pacific and elsewhere, especially at mid- and high latitudes, for the early Aptian and/or other OAEs should better constrain latitudinal temperature gradients, which, in turn, can enhance our understanding of both Pacific and global climates at times of critical changes in carbon cycling.

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