

# Recognition of alkenones in a lower Aptian porcellanite from the west-central Pacific

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## Abstract

ODP Leg 198 drilling on Shatsky Rise recovered a lower Aptian porcellanite (~120.5 Ma) deposited during oceanic anoxic event (OAE) 1a that contains C<sub>36</sub>–C<sub>39</sub> alkadienones: C<sub>37:2</sub> and C<sub>39:2</sub> alkadien-2-ones and C<sub>36:2</sub> and C<sub>38:2</sub> alkadien-3-ones. This alkenone distribution differs from that typical of contemporary sediments and haptophyte algae, but resembles that of Cretaceous sediments from the Blake-Bahama basin. The discovery of alkenones in the early Aptian extends their sedimentary record by 15 M.y. to 120.5 M.y. and demonstrates the potential for long-term survival of these diagnostic functional lipids under favorable depositional conditions and subsequent shallow burial. It also contributes to the understanding and reconstruction of evolutionary developments in alkenone distributions and biosynthesis over geologic time.

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## 1. Introduction

Among sedimentary biomarkers, alkenones perhaps provide the best direct connection of specific molecules to defined biological sources. The distinctive and diagnostic structural elements of alkenones are their long-carbon chains (C<sub>36</sub>–C<sub>41</sub>) and unsaturation at C<sub>7</sub> spacing with Z rather than E configuration (Brassell, 1993). The biosynthesis of alkenones is restricted to a few extant species of the Haptophyta, primarily *Emiliania huxleyi* and *Gephyrocapsa oceanica* (reviewed in Conte et al.,

1994; Volkman, 2000). Series of related alkenes and alkyl alkenoates also occur in these organisms and in sediments (Volkman et al., 1980; Marlowe et al., 1984, 1990; Brassell, 1993). The only organism known to contain similar lipids is *Chloroflexus*, which produces alkenes (C<sub>37:3</sub>) of comparable chain length with identical positions ( $\Delta^{8,15,22}$ ) of unsaturation, albeit with the biosynthetically prevalent E configuration (Shiea et al., 1991; Zeng et al., 1992; van der Meer et al., 1999).

An understanding of the origins of alkenone biosynthesis requires further evidence of temporal patterns of alkenone occurrences. Alkenone phylogeny has been explored by assessment of their co-occurrence with calcareous nannoplankton, a consistency in these associations prompted the supposition that alkenones were biosynthesized by species of *Reticulofenestra* during the Tertiary (Marlowe et al., 1990). The search for alkenones in ancient sediments that exhibit exceptional preservation of biolipids provides the best opportunity to achieve this objective, especially where the concentrations of functional lipids significantly exceed those of hydrocarbons.

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Mid-Cretaceous black shales recovered by the Ocean Drilling Program (ODP) and its predecessor the Deep Sea Drilling Project (DSDP) have often provided a valuable resource for recognition and elucidation of the structural characteristics of novel biomarkers (e.g. Hussler et al., 1981; Hussler and Albrecht, 1983; Brassell et al., 1983; Peakman et al., 1986), interpretation of their varied biological sources (Brassell and Eglinton, 1983; Simoneit, 1986) and assessment of the pathways of early diagenesis (Brassell et al., 1984). In addition these sediments have helped in the recognition of the earliest occurrences of several biomarkers, including alkenones (Farrimond et al., 1986), and thereby contributed significantly to the elucidation of the progression of evolutionary changes in molecules over time (Brassell et al., 1987; Brassell, 1984). Analysis of well-preserved organic-rich sediments, such as those from the early Aptian oceanic anoxic event 1a (OAE 1a) from Shatsky Rise in the west-central Pacific recovered during ODP Leg 198 (Bralower et al., 2002a,b), therefore, offers the possibility to extend the temporal ranges of biomarkers and merits examination as excellent candidates for investigation of alkenones in the mid-Cretaceous.

## 2. Methods

### 2.1. Carbon, carbonate and elemental analysis

Shipboard determination of elemental compositions of sediment samples utilized a Carlo Erba 1500 CNS analyzer. The amount of organic carbon ( $C_{\text{org}}$ ) was calculated as total carbon from CNS analysis minus the carbonate content quantified by coulometry.

### 2.2. Extraction and fractionation procedures

Selected samples (~2 g) were lyophilized, and extracted ultrasonically using  $\text{CH}_2\text{Cl}_2$  (10 ml) for 30 min. The extract was reduced to dryness under  $\text{N}_2$  and eluted through silica in a Pasteur pipette using hexane (4 ml) and  $\text{CH}_2\text{Cl}_2$  (5 ml) as eluates to collect fractions dominated by hydrocarbon and ketone constituents, respectively. Each eluant was taken to near dryness under  $\text{N}_2$  and dissolved in hexane (50  $\mu\text{l}$ ) for analysis by GC/MSD.

### 2.3. Biomarker analysis, identification and carbon isotope determinations

Shipboard analyses employed a Hewlett-Packard 6973 GC/MSD system consisting of a HP 6890 GC with a Mass Selective Detector (MSD) and a HP 7683 Automatic Liquid Sampler (ALS). The GC is equipped

with an EPC split-splitless injector and an HP capillary column (5% phenyl methyl siloxane; 30 m $\times$ 0.25 mm) programmed from 40 to 130 °C at 20 °C/min, then at 4 °C/min to 320 °C, and held isothermally at 320 °C for 20 min. Helium was used as the carrier gas. The transfer line was set at 280 °C and the source of the MS at 230 °C. The MSD was scanned from  $m/z$  27–550. An HP MS Chemstation was used for data acquisition and processing. The identity of individual components was determined from their mass spectral characteristics and retention times by comparison with the literature (e.g. de Leeuw et al., 1980; Volkman et al., 1980; Marlowe et al., 1984). Confirmatory shorebased GC–MS analyses used a Finnigan TSQ700 coupled to a HP 5890 GC equipped with an on-column injector and a Restek Rtx-1 capillary column (60 m $\times$ 0.32 mm) programmed from 60 to 320 °C at 2.5 °C/min, and held isothermally at 320 °C for 80 min. Helium is used as the carrier gas. The transfer line was set at 320 °C and the mass spectrometer was scanned from  $m/z$  50–600 in 0.8 s.

Carbon isotope compositions of alkenones and other compounds were determined by irmGC-MS (Hayes et al., 1990) using a Finnigan MAT 252 instrument coupled to a HP 5890 GC via a continuous-flow combustion interface that combusted and oxidized compounds to  $\text{CO}_2$ . The GC was equipped with an on-column injector and a Chrompack CP-Sil 8 CB capillary column (50 m $\times$ 0.32 mm) programmed from 60 to 320 °C at 3 °C/min, and held isothermally at 320 °C for 140 min. The mass spectrometer measured  $m/z$  44, 45 and 46 and was calibrated with both external and internal standards using deuterated *n*-alkanes and  $\text{CO}_2$  peaks of known isotopic composition, respectively.

## 3. Results

### 3.1. Organic-rich intervals

At Site 1213 on the southern high of Shatsky Rise in the west-central Pacific (31°34.649'N 157°17.861'E; 3883 m water depth), carbon and carbonate analyses during ODP Leg 198 (Bralower et al., 2002a,b) revealed five organic-rich samples (>1%  $C_{\text{org}}$ ; Table 1) within the Lower Cretaceous. The organic carbon content of these samples ranges from 2.5 to 25.2 wt.%, markedly higher than other samples from this stratigraphic interval (Table 1). The five samples corresponding to these carbonaceous intervals were the focus of study for extraction and biomarker analysis.

### 3.2. Stratigraphic framework

Sediment ages were constrained by biostratigraphy, based on calcareous nannofossils, planktic foraminifera,

Table 1  
Carbon and carbonate contents of lower cretaceous sediments from hole 1213B, Shatsky Rise

Sample	Interval (cm)	Lithology	Age	Inorg. C (%)	Org. C (%)
8R-1	47–48	Porcellanite	early Aptian	0.50	10.23
8R-1	63–64	Porcellanite	early Aptian	0.75	25.20
8R-1	96–97	Porcellanite	early Aptian	0.42	2.87
11R-1	61–62	Nannofossil chalk with clay	Hauterivian	67.89	0.41
14R-1	29–30	Chalk	Valanginian	82.55	n.d.
15R-1	9–10	Radiolarite with chalk/clay	Valanginian	49.06	2.54
19R-1	10–11	Clayey nannofossil chalk	Berriasian	91.96	n.d.
19R-1	110–111	Chalk with chert nodules	Berriasian	56.06	n.d.
19R-1	112–113	Nannofossil chalk/claystone	Berriasian	60.56	3.13
20R-1	31–32	Clayey nannofossil chalk	Berriasian	58.14	0.11
20R-1	67–68	Clayey nannofossil chalk	Berriasian	82.22	n.d.
21R-1	29–30	Clayey nannofossil chalk	Berriasian	83.72	n.d.
22R-1	24–25	Nannofossil chalk	Berriasian	96.46	n.d.
22R-1	116–117	Nannofossil chalk with clay	Berriasian	78.80	0.03
26R-1	16–17	Nannofossil chalk with clay	Berriasian	66.47	0.00

Notes: n.d. = not determined.

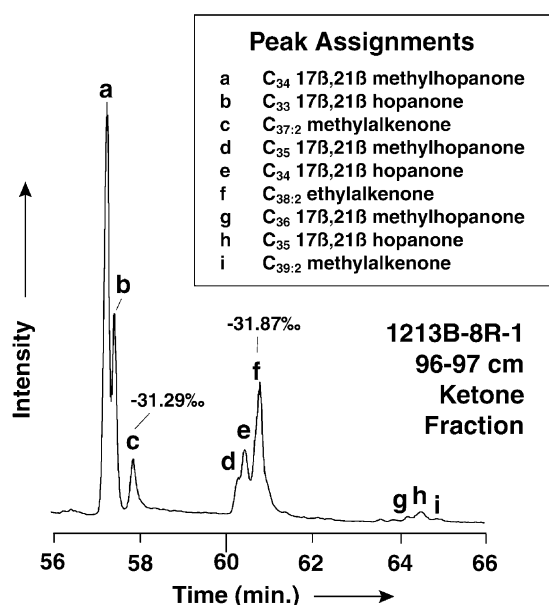


Fig. 1. Distributions and compound assignments of alkenones and hopanones in the lower Aptian porcellanite.  $\delta^{13}\text{C}$  values for the  $\text{C}_{37:2}$  and  $\text{C}_{38:2}$  alkenones are also given.

and radiolarians (Bralower et al., 2002a). A carbonate layer in Sample 1213B-8R-1, 3 cm yielded the lowest occurrence of *Eprolithus floralis* (Bralower et al., 2002a) denoting the base of Zone NC7 (early Aptian). The underlying organic-rich interval in Section 1213B-8R-1 therefore corresponds to the lower Aptian OAE 1a (Bralower et al., 2002a). The two deeper organic-rich intervals in sections 1213B-15R-1 and 1213B-19R-1 are both calcareous, and are assigned as Valanginian and Berriasian, respectively (Table 1), based on biostratigraphy.

### 3.3. Alkenone identification

The dominant components of the  $\text{CH}_2\text{Cl}_2$  eluate from all five of the organic-rich intervals are suites of steroidal ketones (principally  $5\alpha(\text{H})$ -stanones and  $\Delta^4$ -stanones) and various hopanones and 2-methylhopanones. Series of tocopherols (Brassell et al., 1983; Goossens et al., 1984) are also minor constituents of all the samples.

One of the lower Aptian samples (1213B-8R-1 96–97 cm), a carbonaceous porcellanite (2.9 wt.%  $\text{C}_{\text{org}}$ ), contained two components (Fig. 1) identified as alkenones ( $\text{C}_{37:2}$  Me and  $\text{C}_{38:2}$  Et) from their mass spectra, which included diagnostic fragment ions and molecular ions at  $m/z$  530 and 544, respectively. The presence of a third alkenone ( $\text{C}_{39:2}$  Me) in trace amounts was tentatively assigned (Fig. 1) by mass chromatography ( $m/z$  96) during shipboard analysis and confirmed in shorebased GC–MS studies, which also revealed the presence of the  $\text{C}_{36:2}$  Et alkenone previously identified in Black Sea sediments (Xu et al., 2001) and in both *G. oceanica* and suspended particulate organic matter from the Mediterranean (Rontani et al., 2001). The concentration of the  $\text{C}_{37:2}$  Me alkenone was estimated as approximately 0.2–0.5  $\mu\text{g/g}$  of dry sediment based on the comparative GC–MSD response of an  $n$ - $\text{C}_{36}$  alkane standard.

The single previous report of alkenones of Cretaceous age found them in two samples from the Blake-Bahama Basin (Farrimond et al., 1986). They occurred as the  $\text{C}_{37}$ – $\text{C}_{41}$  series of odd-numbered diunsaturated methyl ketones (alkadien-2-ones) and even numbered ethyl ketones (alkadien-3-ones). The distribution of alkenones in this lower Aptian sample resembles that of a Cenomanian interval containing alkenones from the Blake-Bahama basin (DSDP Sample 76-534-28-1), except that it does not extend to the higher carbon

numbers ( $C_{40:2}$  Et,  $C_{41:2}$  Me and perhaps  $C_{42:2}$  Et) identified in the Cenomanian sample (Farrimond et al., 1986). Shipboard analyses did not detect alkenones in any other organic-rich intervals within the lower Aptian from Shatsky Rise.

#### 4. Discussion

##### 4.1. Organic-rich intervals

The occurrence of organic-rich intervals in the early Aptian at Shatsky Rise is consistent with the global records that define OAE 1a as an episode of organic carbon enrichment associated with excursions in the  $\delta^{13}C$  values of carbonates and organic matter (e.g. Sliter, 1989; Arthur et al., 1990; Bralower et al., 1994; Menegatti et al., 1998; Jahren et al., 2001; Ando et al., 2002). Hole 1213B provides the first pelagic sequence of OAE 1a from the Pacific.

Age constraints on the Valanginian organic-rich interval based on initial shipboard results preclude determination of possible temporal affinities with  $\delta^{13}C$  excursions in the Tethyan realm (Channell et al., 1993; Gröcke, 2001) or organic-rich intervals in the Vocontian Basin (Mattioli et al., 2000) and the Southern Alps (Bersezio et al., 2002), that are assigned as Valanginian. However, the recognition of organic-rich intervals in the Pacific at this time is unprecedented, and may imply that global-scale perturbations of the carbon cycle related to climatic and environmental change extend into the Valanginian stage.

The varied lithologies of the organic-rich intervals, namely porcellanite, radiolarite with chalk and clay, and nannofossil chalk/claystone, serve to demonstrate the independence between the primary material of the sediment matrix and organic carbon accumulation.

##### 4.2. Alkenone abundance, distribution and survival

The significant concentrations of alkadienones in the lower Aptian porcellanite effectively preclude the possibility that co-occurring alkatrienones have been completely degraded by diagenetic processes. Moreover, the prevalence of labile components in the sample (concentrations  $> 2 \mu\text{g/g}$  dry sediment), such as  $\Delta^4$ -stenones, further attests to the limited extent of lipid alteration in these sediments. Such preservation is consistent with the shallow burial of these sediments, recovered at a depth of approximately 257 m (below sea floor). The abundance of alkenones in this sample far exceeds their concentrations in sediments where diagenetic loss of alkatrienones is reported (cf. Prahl et al., 1989, 2003; Hoefs et al., 1998; Pagani et al., 1999; Grimalt et al., 2001). It can therefore be argued convincingly that alkatrienones would likely have survived in the lower

Aptian sample if they had been produced in the original depositional setting. Thus, the veracity of alkenone unsaturation in this sample does not appear to be compromised by diagenetic processes, which leads to the conclusion that alkatrienones were never present. The apparent absence of any alkenones in the other lower Aptian samples from Site 1213B (8R-1, 47-48 and 8R-1, 63-64; Table 1) that contain markedly higher  $C_{\text{org}}$  contents also suggests that the primary control on their occurrence is production rather than preservation.

##### 4.3. Alkenones as paleotemperature proxies

The temperatures of surface waters where the alkenones were synthesized can be assessed using the alkenone unsaturation index ( $U_{37}^K$ ; Brassell et al., 1986), assuming that the calibration principles employed in assessment of contemporary characteristics (Prahl et al., 1988; Müller et al., 1998) are equally valid as a paleotemperature proxy for the mid-Cretaceous. This approach suggests warm surface waters at the site ( $> 28^\circ\text{C}$ ; cf. Prahl et al., 1988), which is consistent with expectations for tropical temperatures at that time (Wilson and Norris, 1991; Norris and Wilson, 1998). However, use of alkenones as paleotemperature proxies in the mid-Cretaceous is clearly a presumptive and unjustified extension of the temporal range of their validity that demands substantiation.

##### 4.4. Carbon isotope composition of alkenones

Two of the alkenones were present in concentrations sufficient to enable determination of their carbon isotope composition. The  $\delta^{13}C$  values are significantly lower ( $-31.29\text{‰}$  for  $C_{37:2}$  Me;  $-31.87\text{‰}$  for  $C_{38:2}$  Et) than those reported in modern environments, with the exceptions of Antarctic lake sediments (as low as  $-36.1\text{‰}$ ; Schouten et al., 2001) and particulate organic matter from the Black Sea (lowest value  $-32.7\text{‰}$ ; Freeman and Wakeham, 1992). However, alkenones in sediments from the Eocene/Oligocene boundary possess distinctly lower  $\delta^{13}C$  values ( $< -30\text{‰}$ ; Pagani, 2002) than those of modern and Miocene marine sediments whose minimum value is  $-28.8\text{‰}$  (Pagani et al., 1999; Pagani, 2002). These low  $\delta^{13}C$  values are consistent with  $\text{CO}_2$  concentrations perhaps 2–5 times modern levels (Pagani, 2002). Recognition of alkenones with comparably low  $\delta^{13}C$  values in the Cretaceous is therefore consistent with similar elevated levels of  $p\text{CO}_2$ .

##### 4.5. Stratigraphic and spatial range of alkenones

The earliest reported global occurrence of alkenones is in the Albian ( $\sim 105$  Ma) from the Blake-Bahama basin (Farrimond et al., 1986). In the Pacific, the oldest documented first occurrence of alkenones is in Eocene



C<sub>36:2</sub> alken-3-one in the early Aptian confirms the longevity of the biosynthetic pathways that produce ethyl alken-3-ones, even though this compounds was only recently recognized (Xu et al., 2001; Rontani et al., 2001).

The consistent absence of the alkatrienones at Shatsky Rise, and in other Cretaceous, Paleocene and early Eocene sediments (Farrimond et al., 1986; Yamamoto et al., 1996; Marlowe et al., 1990), may reflect the fact that these sediments predate the evolutionary development of alkatrienone biosynthesis. This interpretation is consistent with evidence that alkatrienones appear to be produced by desaturation of alkadienones (Volkman et al., 1980), which implies that the latter components are both the biosynthetic and ancestral precursors.

The observation that the earliest occurrence of alkatrienones is in the Eocene at high latitudes (Marlowe et al., 1990) prompts the suggestion that temperature controls on alkenone unsaturation may represent a biological response triggered by global cooling in the Paleogene. The discrepancies observed between the carbon number distributions of alken-2-ones and alken-3-ones in contemporary lakes and the oceans (Table 2) is consistent with the idea of past changes in the pathways or controls on their biosynthesis, presumably related to phytoplankton evolution. Thus, it seems likely that developments in the distributions of alkenones produced by marine calcareous nannoplankton were affected by external factors linked to climatic and environmental change, with global cooling perhaps acting as a dominant influence.

## 5. Conclusions

The ability to identify distinctive molecular traits in ancient sediments benefits the reconstruction of evolutionary records of biochemical pathways. Recognition of alkadienones in a lower Aptian sediment from Shatsky Rise extends the advent of this biosynthetic innovation to ~120.5 Ma. It also demonstrates the opportunity for lengthening the temporal range of biomarkers where depositional conditions have aided exceptional preservation of organic matter, and the possibility of using alkenone  $\delta^{13}\text{C}$  values to assess pCO<sub>2</sub> levels in the Cretaceous.

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