Short-term anoxia coinciding with rotaliporid extinctions during the Cenomanian–Turonian transition in the middle-neritic eastern North Atlantic inferred from organic compounds

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METHODS

For organic geochemical study, twenty-three mudstone or marl samples were collected from the 24-m-thick sedimentary sequence (Fig. 2). Approximately 200 g of hand-sized specimens were powdered for each sample after removal of apparent surface contaminations. The powdered samples (130–220 g) were extracted with a benzene and methanol solvent mixture (6:4, v/v) by homogenization for 15 min, allowing for re-extraction of residue after centrifugation and recovery of the supernatant. The supernatants of the first extraction and the following two re-extractions were combined.

We chromatographically separated out the major compounds using a silica gel column (1 g of pre-activated silica, 63–200 mesh). Four fractions were obtained by elution with the following solvents: 2 ml of *n*-hexane (Fraction 1), 2 ml of *n*-hexane/benzene 3:1 v/v (Fraction 2), 3 ml of benzene (Fraction 3), and 3 ml of benzene/methanol 4:1 v/v (Fraction 4). Fraction 2 (aromatic hydrocarbon) was analyzed by gas chromatography–mass spectrometry.

Identification of the hydrocarbons was performed using an Agilent 6893 gas chromatograph interfaced to an Agilent 5973 mass selective detector (MSD), operated with an ionizing–electron energy of 70 eV and scanned from m/z 50 to 550 with a scan time of 0.34 s. A fused silica HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness) was used with helium as the carrier gas. Samples were injected at 50°C and held at that temperature for 1.0 min; the temperature was then raised to 120°C at a rate of 30°C/min and to 310°C at a rate of 5°C/min, and finally held constant for 20 min.

The abundance of dibenzothiophenes was quantified by gas chromatography-mass spectrometry analysis relative to an external standard for C_0-C_2 dibenzothiophenes. 2,3,6-Trimethylarylisoprenoids were identified by comparing their retention times and mass spectra with those reported by Summons and Powell (1987). Quantification of these arylisoprenoids was based on the comparison of the peak area on the mass chromatogram with that of isorenieratane, a precursor of arylisoprenoids, as quantified through gas chromatography-flame ionization detection analysis.

The carbon isotope ratios of the bulk carbonates (41 samples) and the brachiopod shells (10 samples, collected at outcrop) were analyzed using a Finnigan Mat Delta-S mass spectrometer. The overall analytical reproducibility during this study was estimated to be 0.05‰ or better. The overall uncertainties of $\delta^{13}C$ are within 0.2‰. All isotopic values are reported relative to the Peedee belemnite (PDB) standard.

TOC content of the sediment was determined by Carlo-Erba Elemental Analyzer (EA1108). The powdered samples (3 g) were decarbonated in 6 N HCl at 70°C for 24 hours. Acid-treated samples were washed by ultrapure water for a few times for neutralization. Approximately 10 mg of dried residual powder sample free from carbonate was packed into a tin capsule and introduced to the EA1108. Corrections of carbon contents were made for the weight loss incurred at acid treatment. The limits of detection for this analytical method are approximately 0.01 wt % for carbon. The reproducibility of the carbon concentrations is better than 0.01 wt %.

AGE MODEL

The base of Bed 16 is the bottom of the measured section in this study. The last occurrence (LO) of the planktonic foraminifer *Rotalipora greenhornensis*, with an estimated age of 93.95 Ma (Keller et al., 2004), is at about –7.1 m, at the top of Bed 2. The LO of *Rotalipora cushmani*, with an estimated age of 93.90 Ma (Hardenbol et al., 1998), is at 0.03 m. The first occurrence (FO) of the calcareous nannofossil *Quadrum gartneri* (93.2 Ma; Erba et al., 1995) is at about 9 m, in the middle of the planktonic foraminiferal *Whiteinella archaeocretacea* Zone, and at or near the C–T boundary (Tsikos et al., 2004).

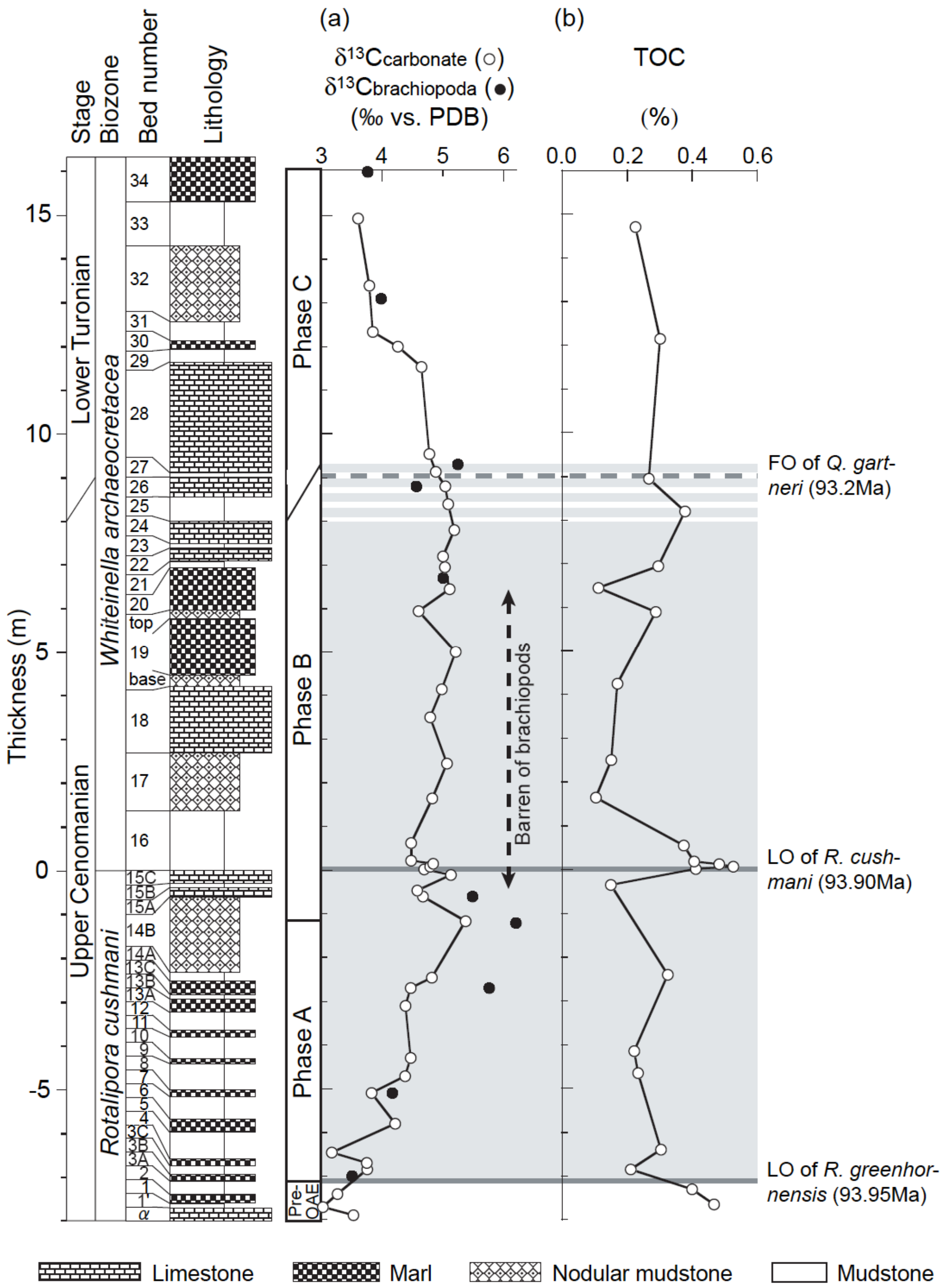

Figure DR1. Schematic stratigraphic column of the Cenomanian–Turonian outcrop of the Arobes section. (a) Profile of $\delta^{13}C$ values (vs. PDB) of carbonates and brachiopod shells. (b) TOC content.

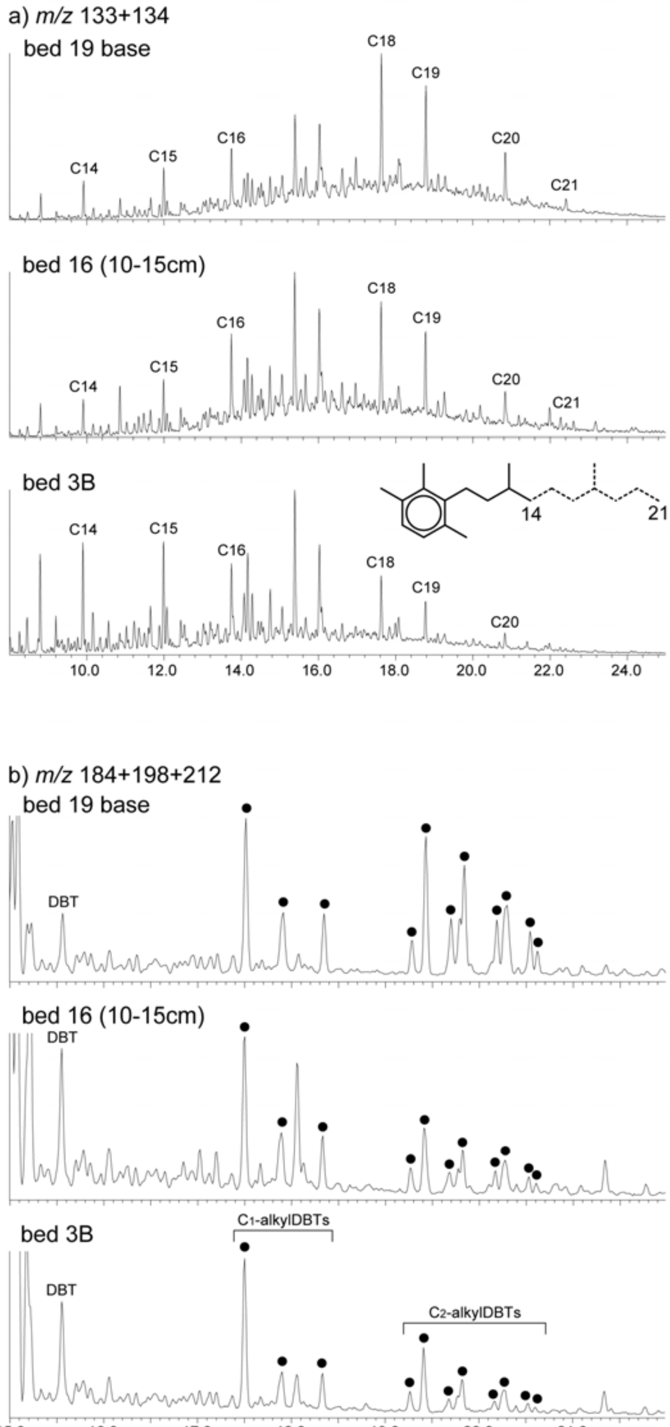

Figure DR2. Mass chromatograms of *m/z* 133+134 and *m/z* 184+198+212 showing a homologous series of 2,3,6-trimethylarylisoprenoids (numbers represent the number of carbon atoms in individual homologs) and C_0-C_2 dibenzothiophenes (DBTs), respectively, in samples from Bed 3B, 16 (0-15cm) and 19base of the Arobes section.

Table DR1. The stratigraphic distribution of benthic foraminifers (>63 µm)

Samples	Height (m)	Benthic foraminifera (>63 µm)/%																				
		Lenticulina rotulata	*Dentalina* sp.A	*Textularia chapmani*	*Haplophragmoides* sp.A	*Tritaxia tricarinata*	*Dorothia* sp.A	*Pravoslavlevia* sp.	*Bathysiphon* spp.	*Reophax* sp.A	*Psilocitharella* sp.A	*Haplophragmoides* sp.B	*Spiroplectammina* sp.A	*Fursenkoina* sp.A	*Praebulimina* sp.A	*Nodosaria* sp.	*Bolivina* sp.A	*Trochammina* sp.A	*Cibicides*	*Gyroidinoides praestanse*	*Dentalina* spp.	*Rosalina* sp.A
33	14.94									1.2												98.8
31	12.34		100.0																			
29	11.94		4.8											38.1								57.1
28 top	11.54																					
28	9.54																					
25	8.39	1.4	7.1				2.8							22.2								66.6
23	7.54	2.8			6.0	3.6	29.3							29.1								29.1
22	7.20						2.5							29.7								67.8
21	6.95	0.5			0.8	0.0	22.2							40.9	7.6							27.9
20 B(top)	6.45	1.6			0.2	1.2	5.2			0.3				25.2	6.9		18.3					41.2
19 A(top)	5.94						28.4		0.4													71.1
19 base	4.14	0.6			0.1									99.4								
17 E	2.44	0.6		38.4															3.5			57.5
17 D	2.09																					
17 C	1.79	0.0		9.0	0.0									3.5	5.2							82.3
17 B	1.64	0.0	0.0	27.7										6.0	5.3							60.8
17 A	1.44	0.3		28.3		0.0		0.3						5.2	10.4		1.2			0.3		54.0
16/100-110	1.19																					
16/90-100	1.06	0.5		4.0	0.2					1.5					2.6				1.3			89.9
16/80-90	0.94	0.0		0.7	0.2					1.9					34.7					2.1		60.4
16/70-80	0.84																					
16/60-70	0.73	0.0		0.6	0.0					1.2	0.0	0.2			20.8					3.0		74.1
16/50-60	0.62	0.0		1.7	1.7					1.7		0.1			1.6				0.8	4.9		87.2
16/40-50	0.51	0.3		4.8	1.8					5.6								0.4	1.6	3.2		82.3
16/30-40	0.40	0.0		6.6	0.1					3.1		1.1			15.8			0.3		15.0		57.8
16/23-30	0.31	0.2		4.2	0.3					2.3		1.3						0.7	0.7	20.0	0.0	70.3
16/15-23	0.22																					
16/10-15	0.15	0.8		1.5	1.0					3.1								0.3	8.1	22.8	0.3	62.1
16/4-10	0.08	1.8		3.0	2.0					1.5		2.3			28.9				1.1	1.5		57.8
16/0-4	0.02	0.7	0.0	38.3	0.0	0.3								4.7	9.9		3.0			2.2		40.8
15 C	-0.11																					
15 B	-0.46																					
14,3	-1.16	0.4	0.4	10.8	0.0			5.1	0.0	0.2				64.4	6.5		2.8					9.3
14,1	-2.46		1.0		0.2					0.1		0.3		24.6	32.8				10.3			30.8
13 B	-2.91											1.8						40.0		29.1		29.1
12	-3.41											100.0										
10	-4.21											1.5			3.3	0.4		62.2		3.0		29.6
8	-4.71									10.0		90.0										
6	-5.41									10.5		9.3	80.2									
4	-6.46											0.2		5.4						8.1		86.3
3B	-6.85																					
2	-7.41									4.1									1.6	1.6		92.7
1	-7.71													100.0								

Table DR2. The stratigraphic distribution of planktonic foraminifers (>125 µm)

Samples	Height (m)	Planktonic foraminifera (>125 µm)																								
		Rotalipora greenhornensis	*Rotalipora cushmani*	*Rotalipora brotzeni*	*Rotalipora montsalvensis*	*Rotalipora* sp.	*Dicarinella algeriana*	*Dicarinella difformis*	*Dicarinella hilalensis*	*Dicarinella indica*	*Dicarinella* spp.	*Preglobotruncana delrioensis*	*Preglobotruncana gibba*	*Preglobotruncana inornata*	*Preglobotruncana stephani*	*Preglobotruncana* spp.	*Whiteinella aprica*	*Whiteinella archaecretacea*	*Whiteinella baltica*	*Whiteinella paradubia*	*Whiteinella praehelvetica*	*Whiteinella* spp.	*Favusella washitensis*	*Marginotruncana* sp.	*Hedbergella postdawnensis*	*Falsotruncana* sp.
33	14.94							X		X							X			X						
31	12.34										X					X						X				
29	11.94						X	X	X		X		X		X	X	X		X			X				
28 top	11.54																									
28	9.54																									
25	8.39							X			X				X	X	X					X				
23	7.54																									
22	7.20																									
21	6.95							X		X					X		X		X		X				X	X
20 B(top)	6.45																									
19 A(top)	5.94																									
19 base	4.14																									
17 E	2.44																									
17 D	2.09																									
17 C	1.79																									
17 B	1.64																									
17 A	1.44																									
16/100-110	1.19																									
16/90-100	1.06																									
16/80-90	0.94																									
16/70-80	0.84																									
16/60-70	0.73																									
16/50-60	0.62																									
16/40-50	0.51																									
16/30-40	0.40																									
16/23-30	0.31																									
16/15-23	0.22																									
16/10-15	0.15																									
16/4-10	0.08																									
16/0-4	0.02		X					X			X						X	X						X		
15 C	-0.11																									
15 B	-0.46																									
14,3	-1.16		X	X	X	X	X	X					X	X	X									X		
14,1	-2.46		X	X			X								X											
13 B	-2.91																									
12	-3.41																									
10	-4.21																									
8	-4.71																									
6	-5.41			X											X				X				X			
4	-6.46																									
3B	-6.85																									
2	-7.41	X	X	X			X	X				X			X											
1	-7.71						X																			