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Diagenesis-related differences in isotopic and elemental composition of late Campanian and early Maastrichtian inoceramids and belemnites from NE Belgium: palaeoenvironmental implications

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Abstract

Late Campanian and early Maastrichtian inoceramid bivalves and belemnite rostra from three sections in the Liège and Limburg provinces (Belgium) are analysed petrologically and geochemically. Oxygen isotope ratios indicate that the early Maastrichtian material has been more affected by diagenesis than the late Campanian specimens, but data for belemnites do support the cooling trend from the late Campanian to the early Maastrichtian. Late Campanian and early Maastrichtian mean palaeotemperatures are deduced to have been lower than 12.5 and 11.3 °C, respectively. Enrichment and depletion of elements, including rare-earth elements, and the generalised bright red-yellowish cathodoluminescence colour indicate cation-sensitive mobilisation processes during diagenesis.

Introduction and geographical-stratigraphical setting

The present paper aims to point out geochemical features of inoceramid bivalve shells and belemnite rostra from stratigraphical levels within the Late Cretaceous of Liège and Limburg (NE Belgium). Both types of fossils occur commonly in the chalk facies of late Campanian and early Maastrichtian age in the area. Attention is paid to two main aspects:

- the petrological and geochemical response of these molluscan shells in relation to the burial diagenesis which affected them;
- the original palaeoenvironmental geochemical signal, which, although modified by diagenesis, can still retain some of the primary chemical differences between inoceramid shells, belemnite rostra and the chalk matrix. If the shells were not chemically homogenised during diagenesis, a comparison with the geochemical features and trends of shells from other localities remains a viable method for palaeoenvironmental interpretation.

The inoceramid and belemnite material analysed for the present paper was collected from three outcrops in the type area of the Maastrichtian Stage, west and east of the River Meuse (Figure 1). One of these, the quarry of Ciments Portland Liégeois SA (CPL) at Haccourt-Oupeye, is one of three key sections in the area, exposing early Campanian to late Maastrichtian deposits. From this quarry, late Campanian samples were investigated.

Nearby, also investigated quarry of Heure-le-Romein, only the Zeven Wegen Member (Gulpen Formation) of Late Campanian age is currently worked.

Early and early late Maastrichtian strata in the are included in the Vijlen Member (Gulpen Fm., Felder 1975; Figure 2). East of the River Meuse, in the type area of the member (c. 20 km east of Maastricht; Felder & Bless 1994) and in the nearby 's-Gravenvoeren area (Belgium), several outcrops expose the early Maastrichtian portion of the member. The third section here investigated is exposed near Altembroeck castle and has recently been remeasured and sampled (Jagt et al. 1995). West of the Meuse, the early Maastrichtian portion of the member is almost completely eroded, whilst the early late portion is present. However, reworked specimens of early Maastrichtian index coleoid cephalopods are occasionally found in bur-

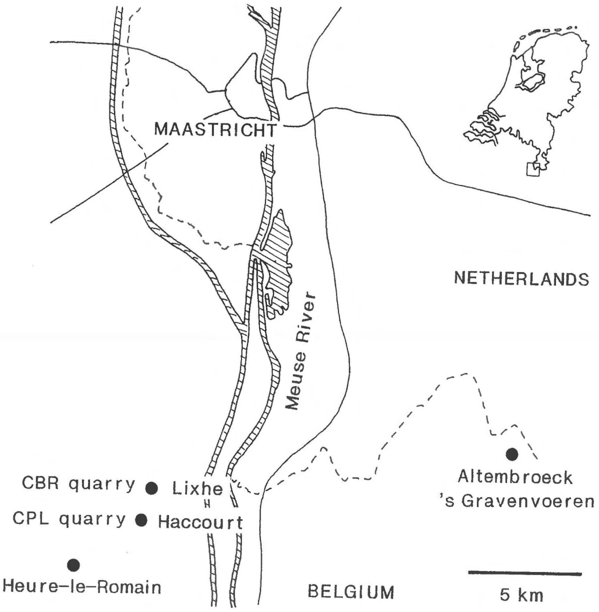

Figure 1. Map of the area south of Maastricht showing location of sections referred to in the text.

	Member	Zone	Age
Gulpen Formation	Lanaye Lixhe 3 Lixhe 2 Lixhe 1	*junior* auct.	Late Maastrichtian
	Vijlen	*cimbrica* *sumensis* *obtusa*	Early Maastrichtian
	Beutenaken	*'langei'*	Late Campanian
	Zeven Wegen	*roemeri* *basiplana/spiniger* *conica/mucronata*	

Figure 2. Lithostratigraphy, macrofossil biozonation and chronostratigraphy of the Gulpen Formation (sensu Felder 1975) as exposed in southern Limburg (the Netherlands) and contiguous areas.

rows in the chalkstone underlying the Froidmont Hardground. This hardground separates the Vijlen Member from the Zeven Wegen Member west of the river. Belemnites of the *cimbrica* Zone (upper part of early Maastrichtian) have been recorded from the basal part of the Vijlen Member as exposed in the CBR quarry at Lixhe.

Late Campanian

The Zeven Wegen Member as exposed in the Haccourt-Lixhe area reaches a thickness of some 30 m and comprises rather coarse-grained calcisiltites and calcilutites with scattered small flints, locally forming indistinct horizons. Recent logging has led to a preliminary macrofossil zonation, which is currently worked out in detail (J. Reynders in prep.).

Villain (1977, p. 7) concluded that the sedimentary environment for the 'Craie blanche' (= Zeven Wegen Mbr) up to and including the 'Craie tigrée' (= Lixhe Mbr) of the Gulpen Formation represented 'an environment open to oceanic influences (coccoliths, planktonic foraminifera), which represents the site of deposition of mainly fine particles [...]; the palynological spectrum does not change horizontally [...] over distances in the order of kilometres [...] and thus testifies to the absence of transportation or of horizontal currents, thus also of reworking. In this tranquil platform setting of muddy bottoms and depths of 80–150 m a possibly very agitated episode intercalates [...] during the depositional break at the top of the Craie blanche [...]' (translated by J.W.M. Jagt).

However, Bless (1989) provided arguments in favour of a shallower depositional environment for the Zeven Wegen Member. He recorded ostracod taxa indicative of a shallow, (sub)tropical setting, and related the change in ostracod faunas to an increase in water temperature rather than to a significant increase in depth.

Correlatives of the Zeven Wegen Member have been recorded from the Hautes Fagnes area (Ardennes), and the eastern Brabant Massif in Belgium (Bless et al. 1991a, b, respectively) and from the Kunrade area in the Netherlands (Bless et al. 1987, Felder & Bless 1989).

Early Maastrichtian

On account of major changes in the lateral and vertical composition of bioclast and microfossil contents, the Vijlen Member has presented many correlation problems. The unit comprises coarse-grained glauconitic calcisiltites, which in the type area reach a maximum thickness of some 65 to 70 m. Felder & Bless (1994) documented deposition of this member under relatively high-energy (shallow nearshore facies) as well as low-energy (more offshore facies) conditions in the type area. The bioclast content of the latter facies is echinoderm-dominated.

The section at Altembroeck has recently been sampled extensively for nanno-, micro- and macrofossil analyses. In a preliminary report (Jagt et al. 1995) the entire *sumensis* Zone of the NW-German scheme has been documented. Amongst the bivalves, at least five species of inoceramids, most of them long-ranging, have been recognised. Studies of ammonites, (micromorphic) brachiopods and other taxa of correlative value, are under way.

Methods

Several thin sections of inoceramid and belemnite samples were prepared for standard transmitted-light petrography, cathodoluminescence and carbonate staining with Alizarin Red S and potassium ferricyanide (following Adams et al. 1984). All luminescence work employed a Technosyn Cold Cathode Luminescence, model 8200 Mk II, mounted on an Olympus triocular research microscope with a maximum magnification capacity of 400 × and utilising universal stage objectives. Standard operating conditions were an accelerating potential of 12kV at 0.5–0.6 mA beam current with a focused beam diameter of approximately 5 mm.

Inoceramid shells, belemnite rostra and bulk-rock samples were powdered in a tungsten-carbide mill. Major elements (wt%) and Sc (ppm) were determined by ICP-Emission Spectrometry. Sample splits for trace and rare-earth elements (REE) analysis (ppm) were fused with ultrapure lithium metaborate flux, dissolved while molten in HNO_3, and analysed on a VG PlasmaQuad PQ22 inductively coupled plasma source mass spectrometer (ICP-MS) at the Centre de Recherches Pétrographiques et Géochimiques (Nancy, France), following techniques described by Govindaraju & Mevelle (1987).

The stable isotope ratios $^{18}O/^{16}O$ and $^{13}C/^{12}C$ of inoceramids, belemnites and bulk rock (chalk) were determined using a VG SIRA-9 mass spectrometer at the Universidad de Salamanca (Spain). Extraction of CO_2 from carbonates was carried out along the lines described by McCrea (1950). The results are expressed in δ notation in ‰ relative to the Pee Dee Belemnite (PDB) standard. Calcite palaeotemperature values were calculated by using Craig's (1965) equation

$$t^\circ\, C = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2,$$

where $\delta_c = \delta^{18}O$ of CO_2 generated by reaction of the carbonate with H_3PO_4 at 25 °C (PDB), and $\delta_w = \delta^{18}O$ of the water relative to standard mean ocean water (SMOW). A value of –1.0‰ was taken for non-glacial Cretaceous sea water as assumed by Lowenstam (1964) and Carson (1987), equivalent to –1.2‰ PDB for the above equation.

Results

Heure-le-Romain (late Campanian)

Thick-shelled inoceramids (complete shells and fragments of >100 mm overall length) and belemnite rostra occur in the white chalk facies of the Zeven Wegen Member exposed at Heure-le-Romain. The inoceramid shell thickness ranges from 1 to 3 mm. Under the microscope, we observed the characteristic coarsely prismatic calcitic ostracum microstructure. Each prism corresponds to a single crystal and is about 0.1 mm wide and 0.3 to 1 mm long.

Under cathodoluminescence (CL), the calcite prisms show a bright red-yellowish colour, interrupted only by silicified zones that consist of quartzine-lutecite (length-slow chalcedony) spherules together with small bands of the same composition covering the extremities of the shell fragments (Figures 3A, B). The shells show a uniform CL colour and probably have been chemically homogenised, as will be discussed below (see 'Discussion'). For this reason, it is difficult to see the very thin luminescent intercalated lines corresponding to the boundaries between prisms, unlike in specimens from the Basque-Cantabrian region in northern Spain, where these lines may have been the most favourable paths for diagenetic fluid advance (Elorza & García-Garmilla 1996).

We have not observed the inner aragonitic nacreous shell layer described by other authors from different deposits (Wright 1987, Whittaker et al. 1987, Pirrie & Marshall 1990a). The chalk host rock contains abundant broken and individualised inoceramid prisms, generated by compaction, which are also all luminescent. The biological growth lines, nearly parallel to the shell surface, usually detected in inoceramids from the Basque-Cantabrian region (Elorza & García-Garmilla 1996) are more difficult to distinguish under plane-polarised light than under CL.

The belemnite calcitic rostra are, in general, non-luminescent. Only calcite infilling the alveolus and some radial fracture lines, generated by compaction, have an intense red CL colour. Some specimens show irregular luminescent small zones in the most external part of the skeleton, as well as luminescent growth bands of variable width (Figures 3C, D). Silicified areas exhibit dark greenish CL colours, like the silica replacing inoceramid shells.

A dozen samples were analysed for $\delta^{18}O$ and $\delta^{13}C$ stable isotopes (2 from the chalk host rock, 8 from belemnite rostra and 2 from inoceramid shells, Table

Table 1. Isotopic data and palaeotemperatures obtained (including diagenetic effect) for inoceramid shells, belemnite rostra and chalk host rock of Heure-le-Romain, Haccourt and Altembroeck.

Sample	composition	$\delta^{18}O$‰ (PDB)	$\delta^{13}C$‰ (PDB)	t(°C)
Heure-le-Romain section (late Campanian)				
Inoceramid shells				
CPL-2	calcite	−0.46	1.96	13.7
CPL-4	calcite	−0.57	2.01	14.2
Mean value of inoceramid shells		−0.51 ± 0.07	1.98 ± 0.3	13.9
Belemnite rostra				
Bel-1	calcite	−0.43	2.20	13.6
Bel-2	calcite	−0.02	2.02	11.8
Bel-3	calcite	−0.04	2.22	11.9
Bel-4	calcite	−0.15	1.82	12.3
Bel-5	calcite	−0.10	1.78	12.1
Bel-6	calcite	−0.27	2.09	12.9
Bel-7	calcite	−0.40	1.57	13.5
Bel-8	calcite	−0.02	1.81	11.8
Mean value of belemnite rostra		−0.18 ± 0.17	1.94 ± 0.23	12.5
Chalk associated with inoceramid shells				
CPL-1	chalk	−1.45	1.96	17.9
CPL-3	chalk	−1.67	2.00	18.9
Mean value of chalk		−1.56 ± 0.15	1.98 ± 0.02	18.4
CPL Quarry, Haccourt (late Campanian)				
HACC-1	chalk	−0.84	1.58	15.4
HACC-2	calcite (inocer.)	−0.55	1.74	14.1
Altembroeck section (early Maastrichtian)				
Chalk associated with inoceramid shells				
ALTE-1	chalk	−2.65	0.65	22.7
ALTE-3	chalk	−2.15	0.58	20.8
ALTE-5	chalk	−2.22	0.75	21.0
Mean value of chalk		−2.34 ± 0.27	0.66 ± 0.08	21.5
Inoceramid shells				
ALTE-2	calcite	−2.92	1.14	23.7
ALTE-4	calcite	−2.37	1.48	21.6
ALTE-6	calcite	−3.79	0.98	26.9
Mean value of inoceramid shells		−3.03 ± 0.72	1.20 ± 0.25	24.1
Belemnite rostra				
ALTE-7	calcite	0.33	−0.10	10.2
ALTE-8	calcite	0.42	0.48	9.7
ALTE-9	calcite	0.29	1.33	10.3
ALTE-10	calcite	−0.85	1.08	15.4
ALTE-11	calcite	0.40	1.25	9.9
ALTE-12	calcite	−0.01	0.90	11.7
Mean value of belemnite rostra		0.09 ± 0.5	0.82 ± 0.5	11.3

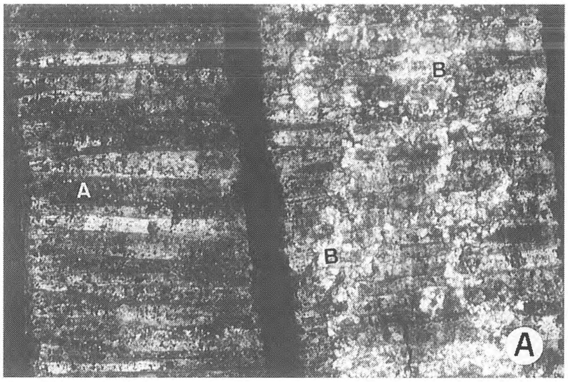

Figure 3A. Photomicrograph of two inoceramid shells from Heure–le–Romain, showing prismatic microstructure without silicification (A) and with partial silicification (B) by fibrous quartz (quartzine–lutecite). XPL. Photo width is 2.6 mm (sample Heur–1).

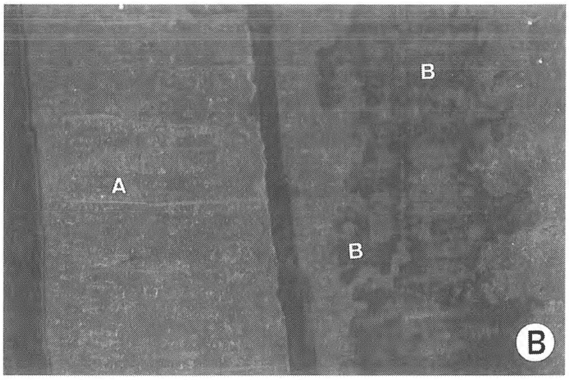

Figure 3B. The same view under CL. Part A was entirely affected by diagenesis resulting in an intense red–yellowish luminescent colour, whereas in part B the silicification resulted in non–luminescence.

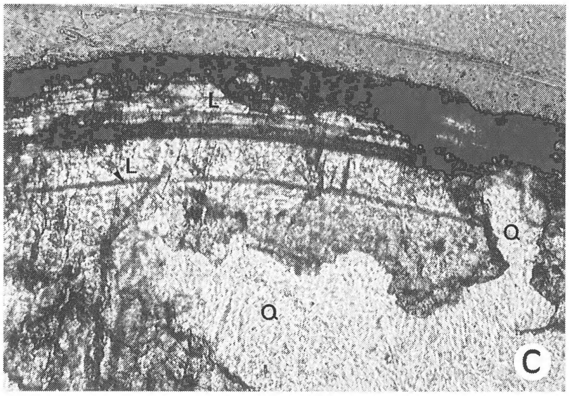

Figure 3C. Partial view of a belemnite calcitic rostrum from Heure–le–Romain showing well–preserved natural growth lines (L) and partial replacement by fibrous quartz (Q). PPL, Photo width is 1.3 mm (sample Bel–2).

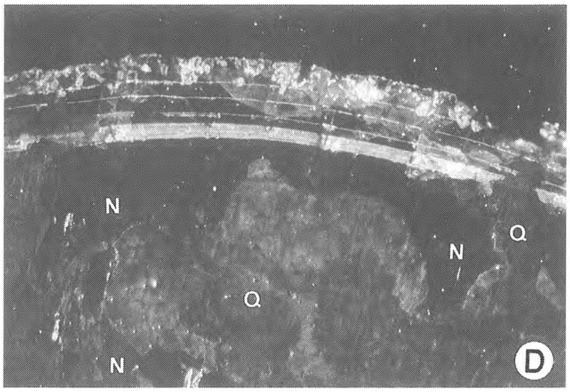

Figure 3D. The same view under CL. The luminescence is controlled by the external growth lines, whereas the calcitic inner part (N) appears non– luminescent. The silicified area (Q) here has a greenish luminescence colour and thus differs from that in Figure 3B.

Figure 3E. Detail of a complete inoceramid shell (I) and of a partial section of another inoceramid shell at the bottom (I∗), from Haccourt. Silicification by fibrous quartz (Q) appears at the central parts of both shells. XPL. Photo width is 2.6 mm (sample Hacc–1).

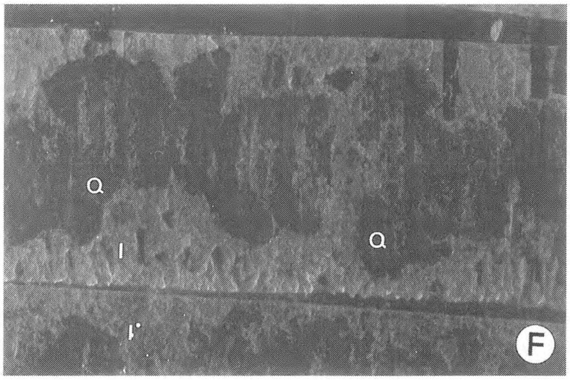

Figure 3F. The same view under CL. An intense red–yellowish luminescence is observed in the calcite prisms (I, I∗), whereas the silicified areas (Q) are non–luminescent.

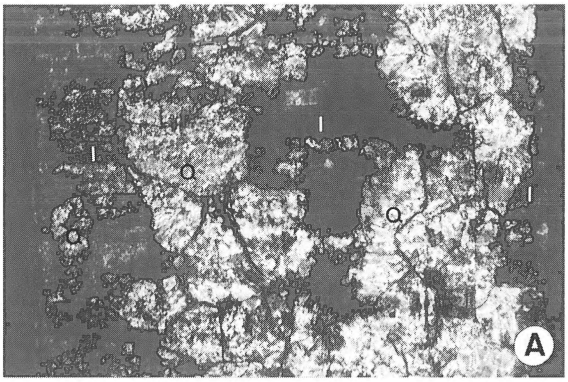

Figure 4A. Partial view of inoceramid shell microstructure from Altembroeck, similar to that in Figure 3E, and showing important silicification by spherulitic fibrous quartz (Q). The carbonate prismatic area remains at the central part of the shell as a relict (I). XPL. Photo width is 1.3 mm (sample Alte–2).

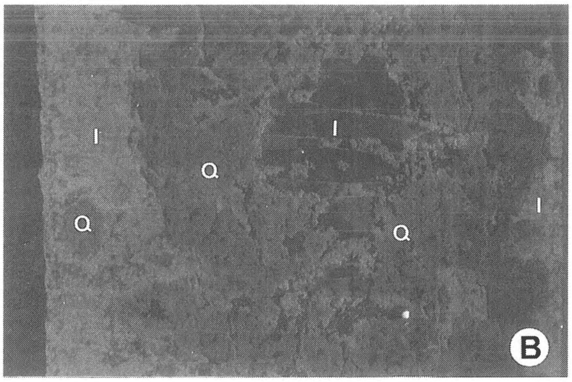

Figure 4B. The same view under CL exhibits an intense red–yellowish luminescence similar to that observed in Figures 3B and F. In spite of the oxygen isotopic differences (near to –2.5‰ PDB), with relation to the Heure–le–Romain and Haccourt sections, the similarity in luminescence colours should be noted.

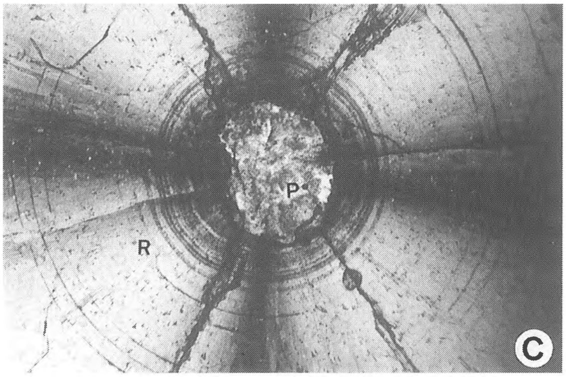

Figure 4C. Central view of a belemnite calcitic rostrum from Altembroeck showing well–preserved natural growth lines (R) and sparry calcitic filling of the alveolus (P). XPL. Photo width is 1.3 mm (sample Alte–10).

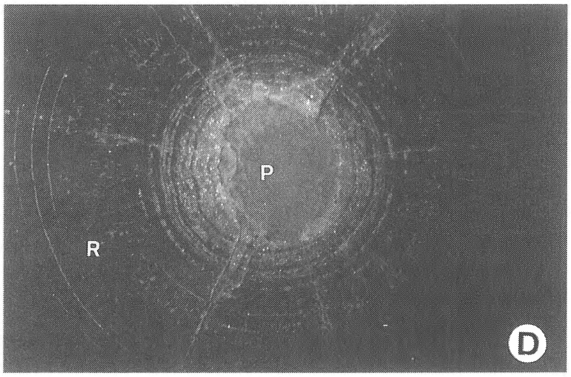

Figure 4D. The same view under CL. The luminescence is closely controlled by the growth lines and radial fractures. Luminescent sparry calcite (P) fills the alveolus, whereas most of the rostrum (R) appears non–luminescent.

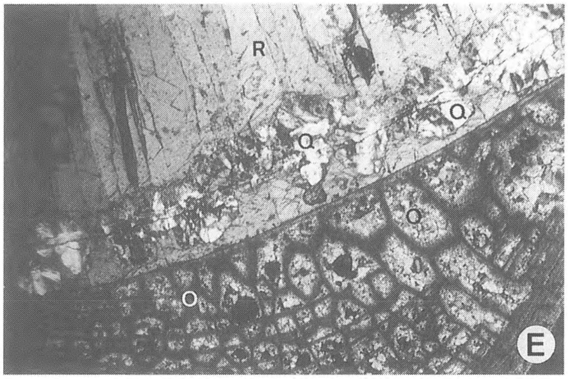

Figure 4E. Partial view of a belemnite calcitic rostrum (R) affected by silicification with quartzine–lutecite spherules (Q) together with an attached oyster shell section with vesicular and lamellar microstructures (O). XPL. Photo width is 1.3 mm (sample Alte–11).

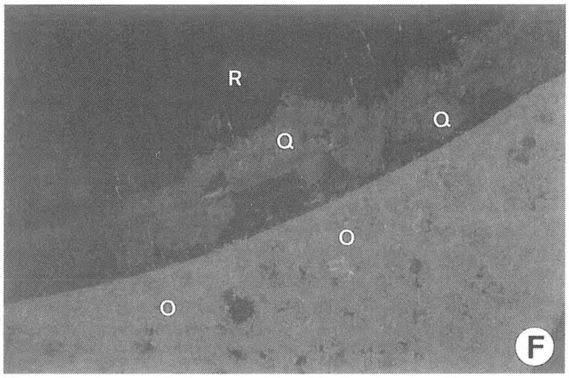

Figure 4F. The same view under CL. The oyster section (O) shows an intense red–yellowish colour. The silicified area (Q) is red–greenish, whereas most of the rostrum (R) appears non–luminescent.

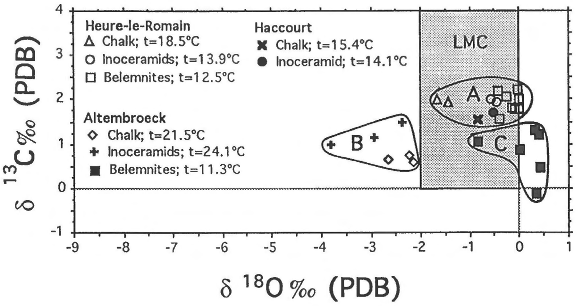

Figure 5. Carbon and oxygen isotope compositions of inoceramid shells, belemnite rostra and chalk matrixes from Heure–le–Romain, Haccourt and Altembroeck. The shaded LMC (low–magnesium calcite) area defines the lower and higher limits for calcium carbonate precipitated in isotopic equilibrium with ambient seawater under most near–surface conditions (Morrison & Brand 1986). Three clusters can be distinguished: cluster A is within the LMC area and corresponds to inoceramid shells, belemnite rostra and chalk from Heure–le–Romain and Haccourt; cluster B includes inoceramids and chalk from Altembroeck, while cluster C comprises belemnites from Altembroeck. Of note is the lack of isotopic continuity between clusters B and C (see text). Mean palaeotemperatures from inoceramids, belemnites and chalk of each section are included.

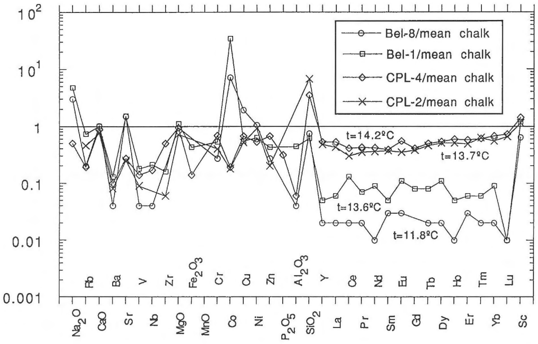

Figure 6. Analytical geochemical results of the most (CPL-4: $\delta^{18}O$ = −0.57‰ PDB) and the least (CPL–2: $\delta^{18}O$ = −0.46‰ PDB) diagenetically altered inoceramid shell in comparison to the mean value (unity) for whole rock (chalk) of Heure-le-Romain. The same comparison is made for the belemnite calcitic rostra: the most (Bel-1: $\delta^{18}O$ = −0.43‰ PDB) and the least (Bel-8: $\delta^{18}O$ = −0.02‰ PDB) diagenetically altered rostrum vs. the mean value of the whole rock.

1). Mean palaeotemperatures obtained by application of the equation of Craig (1965) are 13.9 °C (inoceramids) and 12.5 °C (belemnites).

The diagram $\delta^{18}O$ vs. $\delta^{13}C$ (Figure 5) shows how all values obtained from inoceramids, belemnites and chalk matrix lie within the inorganic low-magnesium calcite (LMC) area. This rectangular field defines the lower and higher limits (0.0 to –2.0‰; 0.0 to +4.0‰ $\delta^{13}C$) for calcium carbonate precipitated in isotopic equilibrium with ambient seawater under most near-water-surface conditions (Morrison & Brand 1986).

Whole-rock geochemical analysis of two chalk host rock samples (CPL-1 and 3), two inoceramid shells (CPL-2 and 4) and two belemnite rostra (Bel-1 and 8), was carried out using ICP and ICP-MS. The contents in 21 elements and 14 REE were determined (Table 2). The ratios of inoceramid and belemnite over chalk mean elemental content were also established (Figure 6).

Haccourt (late Campanian)

In order to confirm the above isotopic results, we collected a single sample of chalk matrix as well as an inoceramid shell from the Zeven Wegen Member at Haccourt (CPL quarry). The results suggest a palaeotemperature of 14.1 °C, a value very close to that obtained for Heure-le-Romain (Table 1). Figure 5 shows the isotopic values for both localities to be included within the LMC area (cluster A), which suggests a common origin.

The Haccourt inoceramid shells exhibit under CL an intense red-yellowish homogeneous luminescence except in their silicified areas (Figures 3E, F).

Altembroeck (early Maastrichtian)

Under CL, the inoceramid shells from Altembroeck, exhibit a strong red-yellowish, homogeneous colour like that in Haccourt. Silicification of the shells is common and appears as non-luminescent quartzine-lutecite spherules (Figures 4A, B), which constitute the clearest evidence of diagenetic modification. However, the belemnite rostra sections show a different pattern. Luminescence is restricted to the alveolus area, which was filled by sparry calcite, as well as to concrete concentric growth bands and radial fractures (Figures 4C, D). Luminescent concentric growth bands are frequent near the calcite-filled alveolus and gradually diminish in number towards the rostrum exterior. The luminescent radial fractures acted as paths for diagenetic fluids from the alveolus to the surrounding guard. Like the inoceramid shells, the external zones of the belemnite rostra were clearly affected by silicification. Silicified areas appear practically non-luminescent, unlike the intense red CL colour of the oyster shells attached to the external rostrum (Figures 4E, F). Cathodoluminescence of such oyster shells reveals an almost complete homogenisation of both the slightly brighter thin walls of oyster vesicles and the calcite filling these vesicles.

Table 2. Results of geochemical elemental analyses for inoceramid, belemnite and chalk-host rock samples of Heure-le-Romain (traces are below ICP–MS detection limit).

Sample Rock/Fossil	CPL-3 Chalk	CPL-1 Chalk	Mean Chalk	CPL-4 Inoceramid	CPL-2 Inoceramid	Bel-1 Belemnite	Bel-8 Belemnite
$\delta^{18}O$‰ (PDB)	– 1.67	– 1.45	– 1.56	– 0.57	– 0.46	– 0.43	– 0.02
Na_2O%	0.05	0.03	0.04	0.02	traces	0.19	0.12
Rb (ppm)	4.93	2.35	3.64	0.69	1.67	2.64	0.73
CaO%	53.14	52.51	52.83	47.3	39.88	53.56	53.77
Ba (ppm)	48.2	33	40.60	4.08	3.18	5.38	1.43
Sr (ppm)	783	807	795	215	202	1.204	1.184
V (ppm)	7.81	6.1	6.96	0.94	0.62	1.23	0.3
Nb (ppm)	0.54	0.42	0.48	0.08	traces	0.1	0.02
Zr (ppm)	9.89	6.87	8.38	4.2	0.54	1.32	traces
MgO%	0.32	0.29	0.31	0.29	0.22	0.34	0.29
Fe_2O_3%	0.16	0.12	0.14	0.02	traces	0.06	traces
MnO%	traces	traces	traces	traces	traces	traces	traces
Cr (ppm)	5.17	3.46	4.32	2.96	1.74	2.28	1.18
Co (ppm)	2.4	0.9	1.65	0.32	0.29	56.2	11.9
Cu (ppm)	9.74	12.7	11.22	7.48	5.82	6.13	21.6
Ni (ppm)	9.3	15.8	12.55	6.71	11.6	7.92	13.3
Zn (ppm)	12.1	13.7	12.90	8.61	2.6	5.6	3.5
P_2O_5%	0.1	0.03	0.07	0.02	traces	traces	traces
Al_2O_3%	0.57	0.42	0.50	0.03	traces	0.22	0.02
SiO_2%	3.01	5.5	4.26	14.82	28.89	2.61	3.17
Y (ppm)	7.39	6.84	7.12	3.79	3.4	0.37	0.16
La (ppm)	7.12	6.61	6.87	3.67	2.93	0.41	0.129
Ce (ppm)	5.59	4.47	5.03	2.07	1.52	0.64	0.111
Pr (ppm)	1.25	1.14	1.20	0.51	0.42	0.08	0.021
Nd (ppm)	5.11	4.19	4.65	1.95	1.66	0.4	0.047
Sm (ppm)	0.98	0.78	0.88	0.34	0.327	0.04	0.026
Eu (ppm)	0.2	0.162	0.18	0.1	0.063	0.02	0.006
Gd (ppm)	0.84	0.907	0.87	0.36	0.332	0.07	traces
Tb (ppm)	0.13	0.112	0.12	0.06	0.056	0.01	0.002
Dy (ppm)	0.84	0.73	0.79	0.42	0.4	0.09	0.018
Ho (ppm)	0.2	0.169	0.18	0.11	0.095	0.01	0.001
Er (ppm)	0.47	0.49	0.48	0.28	0.24	0.03	0.012
Tm (ppm)	0.06	0.071	0.07	0.04	0.041	0.004	0.001
Yb (ppm)	0.44	0.47	0.45	0.31	0.25	0.04	0.011
Lu (ppm)	0.07	0.067	0.07	0.05	0.045	0.001	0.001
Sc (ppm)	7.00	4.00	5.50	7.80	6.30	6.60	3.50

Twelve samples were analysed for stable isotopes (3 of chalk host rock, 3 of inoceramid shells and 6 of belemnite rostra, Table 1). The mean palaeotemperature obtained from inoceramid shells through Craig's (1965) equation is 24.1 °C, denoting clearly the modification undergone by the shells in relation to the Heure-le-Romain inoceramids. On the contrary, the mean value deduced from belemnite rostra is considerably lower: 11.3 °C. Figure 5 illustrates the lack of isotopic continuity between i) the inoceramid shells and chalk matrix (cluster B) and ii) the belemnite rostra (cluster C).

Discussion

Since the chalk in our material underwent such diagenetic processes as silicification (the origin of flint nodules was recently treated by Zijlstra 1995) and carbonate cementation leading to light $\delta^{18}O$‰ PDB values, our next objective was to determine how burial diagenesis affected the inoceramid shells (benthic organisms) and calcitic belemnite rostra (nektonic organisms).

By interpreting geochemical analyses, several palaeoenvironmental and palaeogeographical features may be deduced, which, however, have undoubtedly been modified by burial diagenesis. Luminescence can be used as an effective indicator of neomorphic calcite and as a first test for shell preservation. In general, primary biogenic carbonate does not show luminescence, whereas luminescent bioclasts reflect diagenetic alteration (Czerniakowski et al. 1984, Popp et al. 1986, Mason 1987, Middleton et al. 1991, Grossman et al. 1993).

The inoceramid shell sections of late Campanian specimens collected at Heure-le-Romain and Haccourt, and those from the early Maastrichtian at Altembroeck show a homogeneous red-yellowish CL colour. This suggests that diagenesis completely and homogeneously affected these shells (Figures 3B, F, 4B). Nevertheless, when plotted on a diagram $\delta^{18}O$ vs. $\delta^{13}C$ PDB, the $\delta^{18}O$ values for late Campanian specimens lie within the LMC area for calcium carbonate precipitated in isotopic equilibrium with ambient seawater (cluster A), whereas those of the early Maastrichtian inoceramids lie outside that field (Table 1; Figure 5).

This difference in oxygen isotopic ratios can be interpreted in two ways:

- If the diagenesis intensity was similar in the Campanian and the Maastrichtian rocks, then the isotopic difference may have resulted from different original palaeoenvironmental chemical and biochemical conditions. Following this assumption, late Campanian inoceramids from Heure-le-Romain and Haccourt, lived at lower temperatures (14 °C, including diagenetic effect) than those from the early Maastrichtian at Altembroeck (24.1 °C, including diagenetic effect). It is evident under this assumption that, although diagenesis made the isotopic signal lighter, it has not completely homogenised the original oxygen isotopic values.
- If diagenesis intensity varied with time, diagenetic alteration was more severe in the early Maastrichtian shells and chalk host rock at Altembroeck. In fact, the lighter isotopic mean value of the shells ($\delta^{18}O$ = –3.03‰ PDB) vs. that of the chalk host rock ($\delta^{18}O$ = –2.34‰ PDB) is an unusual feature that suggests that skeletal carbonates strongly recrystallised during diagenesis, as suggested by Haggerty (1987) and other authors, and that they possibly were enriched in light (meteoric) oxygen. More data are needed to investigate this aspect.

We determined the isotopic values of belemnite rostra from both Heure-le-Romain and Altembroeck in order to determine which of the above interpretations is correct. The rostra from Heure-le-Romain appear to be more resistant to diagenesis than the inoceramid shells, as inferred both from CL observations (Figure 3D) and isotopic data (Table 1, Figure 5). In fact, the most external growth lines and the calcite filling of the alveolus are the only luminescent parts of the rostra. In spite of the fact that belemnites lived in shallower and presumably warmer waters than inoceramids, the mean palaeotemperature isotopically obtained for belemnites is 12.5 °C, which is 1.5 °C lower than the mean value seen for inoceramid shells. However, this apparently warmer 'inoceramid' water should be taken with caution. Inoceramids lived in a continental sea whose bottom could have been above the thermocline under a well-mixed water mass. The confirmation of this would lie in a parallelism between the inoceramid-shell and the chalk-host rock isotope fluctuations. Inoceramid shells may well preserve the bottom-water isotopic signal and the chalk, consisting of coccolith debris, the shallow-water isotopic signal, as pointed out by Schönfeld et al. (1991) for the Lägerdorf-Kronsmoor section in NW Germany.

That the belemnite rostra are more resistant to diagenetic alteration than inoceramid shells is confirmed by data from the Altembroeck section. Belemnites from that section have an intense red CL colour in both the calcite fill of the alveolus and the attached oyster shells (Figures 4D, F), whereas their skeletal calcite is in general non-luminescent. The $\delta^{18}O$ mean value is 0.09‰ PDB, which suggests a palaeotemperature of 11.3 °C, including diagenetic alteration. When comparing the Altembroeck lighter $\delta^{18}O$ mean values (–3.03‰ PDB for inoceramid shells, equivalent to 24.1 °C; and –2.34‰ PDB for the chalk host rock) with those of Heure-le-Romain (–0.51‰ PDB for inoceramid shells, equivalent to 13.9 °C; and –1.56‰ PDB for the chalk host rock), it seems obvious that the Altembroeck sediments underwent a more intense diagenesis than those of Heure-le-Romain. However, in view of the resistance of belemnite rostra, their isotopic values suggest a cooling of sea water from the late Campanian (< 12.5 °C) to the early Maastrichtian (< 11.3 °C). In fact, in other latitudes Barrera et al. (1987), Parrish & Spicer (1988), Pirrie & Marshall (1990b) and Schönfeld et al. (1991) also assumed a general cooling trend in marine waters from the late Campanian to the early Maastrichtian.

Palaeotemperatures deduced from well-preserved inoceramid shells from several chalk sections, e.g. Lägerdorf-Kronsmoor, show values from 12 to 19 °C (mean value 16 °C) for the late Campanian to early Maastrichtian. The maximum value was recorded from latest Campanian specimens (*grimmensis*/*granulosus* Zone). The palaeotemperature decreases higher in the section in the early Maastrichtian (Schönfeld et al. 1991).

Parrish & Spicer (1988) and Spicer & Parrish (1990) observed from vegetational evidence a similar palaeotemperature trend. Mean annual temperatures estimated were about 10 °C near the North Pole during the mid-Cretaceous, dropping to 5 °C in the latest Cretaceous.

Jenkyns et al. (1994) deduced high palaeotemperatures for the English Chalk at the Cenomanian-Turonian boundary ($\leq$ 28 °C), followed by a general climatic decline from the Turonian onwards, stating that 'such determinations are essentially 'naïve' in that they derive from a mixture of planktonic and benthonic components to which a variable amount of diagenetic cement has been added.'

That temperatures declined towards the Maastrichtian becomes clear from geochemical data from various macrofossils collected at high palaeolatitudes in the southern hemisphere, e.g. at James Ross Island (Antarctica). Temperatures there range from a mean value of 13.6 °C during the Santonian-Campanian to 11.7 °C during the Maastrichtian (Pirrie & Marshall 1990b, Barrera et al. 1987).

We deduced palaeotemperatures around 14 °C from our late Campanian inoceramid shells. This value is very close to that estimated by Schönfeld et al. (1991) for coeval material from NW Germany. Our late Campanian palaeotemperatures from inoceramid shells and belemnite rostra (14 and 12.5 °C, respectively) do not differ significantly. By contrast, the respective values for the early Maastrichtian (24 and 11 °C) differ considerably. Thus we consider inoceramid shells not to be good palaeoenviromental indicators since they did not preserve the original isotopic signal during severe diagenesis.

Inoceramid shells and belemnite rostra from Heure-le-Romain have a relatively heavy carbon isotopic composition (1.98 and 1.94‰ PDB, respectively), which is close to that of the chalk host rock (1.98‰ PDB). For this reason, the hypothesis of a 'vital effect' upon the final composition of shells and rostra is unlikely, following Marshall (1992). However, the values obtained from the Altembroeck specimens are lighter and show differences between inoceramid shells (1.20‰ PDB), belemnite rostra (0.82‰) and the chalk host rock (0.66‰). The decrease in carbon isotopic composition of chalk may be explained, at least in part, by changes in the carbon cycle that can be linked to changes in oceanic productivity, basin shallowing and atmospheric greenhouse gases (Marshall 1992).

We analysed inoceramid shells and belemnite rostra from Heure-le-Romain in order to see if diagenesis produced similar changes in the oxygen isotopic composition and elemental contents. Isotopically heavier (CPL-2) and lighter (CPL-4) inoceramid shells and heavier (Bel-8) and lighter (Bel-1) belemnite rostra were geochemically analysed and compared with the chalk mean composition (Table 2, Figure 6).

Belemnite rostra show Na_2O, Sr, and Co values higher than the chalk mean value, considering the latter as unity (1). CaO and MgO values are close to unity and the remaining values are lower than 1. When comparing the different elements, the highest ratios are in the belemnite having the lighter oxygen isotopic value (Bel-1). This more intensely diagenetically altered specimen is closer to the chalk values than the less diagenetically altered and heavier specimen (Bel-8). REE values exhibit a similar trend; in spite of minimal isotopic differences, the more intensely altered rostrum is richer in REEs.

With regard to the relation inoceramid shell/mean chalk host rock, all obtained values are lower than 1, with the exception of that of SiO_2. The values of the more intensely diagenetically altered shell (CPL-4) are close to unity, particularly the REE values. For this reason, we may assume the different elements to have migrated into the shells during diagenesis. Despite the low diagenesis temperatures, the more strongly altered shell shows stronger enrichments of elements.

Conclusions

In spite of the fact that the original inoceramid shell architecture is visible and well-preserved, cathodoluminescence and geochemical data (isotopes, elements including REE) indicate diagenetic modification. This modification in inoceramid shells is less in Heure-le-Romain and Haccourt (late Campanian), and larger in Altembroeck (early Maastrichtian). This matches earlier sedimentological observations (Buurman 1971; Buurman & Van der Plas, 1971). The belemnite calcitic rostra from Heure-le-Romain and Altembroeck are diagenetically less altered than the inoceramid shells, and thus retain better the original isotopic signal.

The comparison of oxygen isotopic ratios of inoceramid shells, belemnite rostra and chalk host rock clearly shows that the investigated early Maastrichtian deposits were more intensely affected by diagenesis than those of late Campanian age. In spite of the diagenetic modification, the data from belemnite rostra support the cooling trend from late Campanian to early Maastrichtian marine waters.

All inoceramid shells collected from Heure-le-Romain, Haccourt and Altembroeck have their red-yellowish luminescence colour homogenised by diagenesis, and do not allow recognition of the paths for diagenetic fluids. Once a certain diagenetic degree is reached, the inoceramid sections have a completely homogenised bright red-yellowish CL colour, and it is thus impossible to determine, with this method, the degree of diagenetic intensity.

When diagenesis is mild, the oxygen isotopic values of inoceramid shells and belemnite rostra are relatively close, and the same may be stated for the deduced palaeotemperatures (13.9 vs. 12.5 °C, respectively). The isotopic differences strongly increase with intense diagenesis, and consequently the differences in derived temperatures become greater (24.1 °C for inoceramids vs. 11.3 °C for belemnites). In the latter case, the temperature values obtained from inoceramids cannot be taken into consideration for palaeoenvironmental interpretations.

Enrichment and depletion of elements, including REE, are considered to be the result of cation-sensitive, essentially diagenetic mobilisation processes. The Heure-le-Romain and Haccourt sections are the least affected by diagenesis. They are promising for the study of the palaeoenvironments prevailing during the deposition of the late Campanian Zeven Wegen Member in the Maastrichtian type area.

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