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Carbon and oxygen isotope composition of Oxfordian–Early Kimmeridgian belemnite rostra: palaeoenvironmental implications for Late Jurassic seas

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Abstract

Stable isotope analyses have been undertaken on Oxfordian–Early Kimmeridgian belemnite rostra derived from three palaeogeographic provinces of Europe: (1) the Boreal–Subboreal Province (Isle of Skye in Scotland); (2) the Submediterranean Province (central Poland and southern Germany); and (3) the Mediterranean Province (Pieniny Klippen Belt in the Western Carpathians). The samples have been screened for possible diagenetic alteration by using cathodoluminescence and trace element analyses and have been found to be largely well-preserved. Calculated palaeotemperatures (10–15°C) and analyses of belemnite habitats suggest that the Boreal–Subboreal belemnites were living in a relatively shallow sea (not deeper than 100–150 m) while the other belemnites possibly inhabited deeper neritic environments. Despite the influence of a vital effect, the $\delta^{13}\text{C}$ values of belemnite rostra are interpreted to reflect primary variations in the oceanic carbon isotope signal. The fairly uniform Submediterranean $\delta^{13}\text{C}$ values indicate a similar isotope composition of dissolved inorganic carbon (DIC) in the area of sedimentation of sponge megafacies in the deep Tethyan shelves. The slightly lowered $\delta^{13}\text{C}$ values of some Mediterranean belemnites might occur due to upwelling providing ^{12}C enriched bottom waters onto the area of the Czorsztyn Ridge in the Oxfordian. The discernibly more positive (1–2.5‰) $\delta^{13}\text{C}$ values of Boreal–Subboreal belemnites are related to a high biologic productivity and a high organic matter burial in the partly isolated Boreal Sea. The stated differentiation in carbonate $\delta^{13}\text{C}$ values distinctly exceeds present-day differences in isotope composition of seawater DIC.

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Keywords: stable isotopes; belemnites; Oxfordian–Early Kimmeridgian; Boreal–Subboreal Province; Submediterranean Province; Mediterranean Province

1. Introduction

Marine carbonates are a valuable source of in-

formation on ancient seawater chemistry. The carbonate $\delta^{13}\text{C}$ values record secular variations in isotopic composition of oceanic dissolved inorganic carbon (DIC). Carbon isotope fractionation between calcium carbonate and HCO_3^- ions is constant in a wide temperature range resulting in the enrichment of the calcium carbonate in ^{13}C averaging 1‰ in the case of calcite and

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2.7‰ in the case of aragonite (Romanek et al., 1992). Due to a slight discrepancy between isotopic composition of bicarbonate ions and DIC, calcium carbonate–DIC ^{13}C enrichment factors are greater by around 0.3‰ (Grossman, 1984).

The carbonate $\delta^{13}\text{C}$ record of the Phanerozoic is characterised by numerous short-lived excursions towards more positive values, so-called carbon isotope events. The interpretation of these events often remains controversial but they are normally accepted to represent fluctuation in the global carbon cycle. In addition, it is usually believed that the carbon isotope record characterises the entire oceanic carbon reservoir. In fact, the isotopic composition of DIC is distributed uniformly (in approximation) in the modern ocean averaging 0–1‰ Vienna PeeDee Belemnite (VPDB) except the sea surface layer, where carbon isotope composition up to +2‰ VPDB is measured, due to preferential fixation of ^{12}C by phytoplankton (Kroopnick, 1985). Differentiation of isotope composition of DIC between surface and bottom waters can be traced in the geological record of planktonic and benthic foraminifera which typically amounts to 1‰ for the whole Cenozoic (Berger and Vincent, 1986). The surface ocean-to-deep ocean carbon isotope gradient is indicated to reach around 1.5‰ in the latest Cretaceous (Zachos et al., 1989).

Minor local deviations in isotope signatures of DIC up to –4‰ VPDB occur in the area of some modern carbonate platforms as a result of long residence time of water masses (Patterson and Walter, 1994). A similar effect is possibly recognised from the Pennsylvanian carbonate platform of northwestern Spain (Immenhauser et al., 2002). Besides, very negative $\delta^{13}\text{C}$ values characterise methane-seep carbonates documented from both modern seas and the geological record (e.g. Peckmann et al., 1999; Díaz-del-Río et al., 2003).

Analysis of carbon isotope composition of ancient pelagic limestones is a powerful tool of chemostratigraphy. The isotope stratigraphy of bulk-carbonates, however, concentrates on characteristics of isotope trends rather than on absolute $\delta^{13}\text{C}$ values. The uniform composition and genesis of detrital matrix-micrite is generally assumed for studied sections. Common occurrence of non-

equilibrium fractionation of carbon isotopes in calcareous skeletons of many marine organisms, including foraminifera and coccolithophorids, may bias bulk-carbonate $\delta^{13}\text{C}$ values, away from the $\delta^{13}\text{C}$ values of DIC (Berger and Vincent, 1986; Wefer and Berger, 1991; Ripperdan, 2001). Additional difficulty exists in the case of the Jurassic due to the still debatable origin of various marine carbonates (cf. Dercourt et al., 1994; Kaźmierczak et al., 1996). Moreover, the origin and the aragonite-to-calcite ratio of oceanic limestone mud should have varied both vertically and laterally in ancient seas. Bulk-carbonates cannot be, therefore, a fully reliable proxy for differentiation of the $\delta^{13}\text{C}$ values of DIC in the Jurassic Ocean.

The present study deals with isotope composition of belemnite rostra of Oxfordian to Early Kimmeridgian age (Late Jurassic) in order to obtain spatial records of the $\delta^{13}\text{C}$ values of seawater DIC and to calculate seawater temperature. Belemnite rostra are considered reliable indicators of variations in the isotopic composition of seawater DIC despite the influence of a vital effect, which produces a constant isotopic offset between belemnite and brachiopod $\delta^{13}\text{C}$ values (Wierzbowski, 2002). It appears, on the other hand, that belemnites, like modern cephalopods, do not exert vital effects in oxygen isotope composition of the skeleton (see discussion in Section 5.2). Hence, they can be used for palaeotemperature determinations. An additional advantage of using belemnites is their wide geographic distribution in the Late Jurassic seas, which has been especially important in the case of the Boreal Sea where carbonate sedimentation did not occur. The regional approach to the $\delta^{13}\text{C}$ values of belemnite guards has indicated that the differentiation of isotope composition of DIC in the Jurassic Ocean was larger than nowadays. The current paper also provides new interesting $\delta^{18}\text{O}$ data, which allow comparison of seawater temperatures among different palaeobiogeographic provinces.

2. Geological settings

Samples of Oxfordian to Lower Kimmeridgian

belemnites were collected from several regions belonging to different palaeoclimatic zones of European seas: (1) Isle of Skye in Scotland; (2) Kujawy area in north-central Poland; (3) Polish Jura Chain in south-central Poland; (4) Swabian Alb in southern Germany; and (5) Pieniny Klippen Belt in Polish Western Carpathians (Fig. 1).

The shallow-sea siliciclastic sediments of the Isle of Skye, which are typical of the Jurassic Boreal Province, belong to the Staffin Shale Formation and are subdivided into several members, e.g. the Glashvin Silt Member, Digg Siltstone Member and Flodigarry Shale Member (Sykes, 1975). The Oxfordian–Lower Kimmeridgian sediments reach a total thickness of around 80 m. A rapid facies change from siltstones to bituminous shaly clays takes place close to the Middle–Upper Oxfordian boundary at the base of the Flodigarry Shale Member. Clastic sediments of the Isle of Skye were deposited below the fair-weather wave base, but the presence of thin sandstones depos-

ited during storm events indicates a relatively shallow water environment (Morton and Hudson, 1995). It seems that the maximal water depths of about 100–150 m could be reasonably accepted for the Oxfordian Sea in this area. Investigated rocks yield numerous Boreal–Subboreal belemnites and ammonites, the latter precisely stratigraphically interpreted by Sykes and Callomon (1979) and Wright (1989); see also Morton and Hudson (1995). The Middle Oxfordian to the Lower Kimmeridgian zonation, like the position of the Oxfordian–Kimmeridgian boundary based on Boreal–Subboreal ammonites, differs significantly from that based on the Mediterranean–Submediterranean ammonites of Central and Southern Europe. The detailed stratigraphic correlation of the discussed zonations accepted in the paper is that of Matyja and Wierzbowski (1997, 1998) (see also Figs. 4 and 5).

Studied marly-limestone rocks from the area of Kujawy and the Polish Jura Chain in central Po-

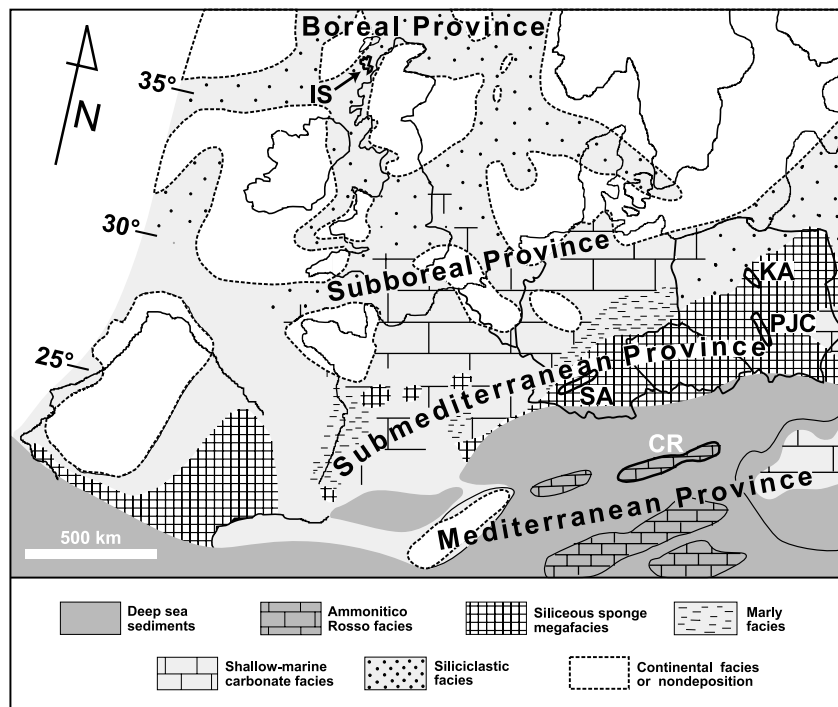


Fig. 1. Palaeogeography and main facies distribution during the Oxfordian in Europe. Abbreviations: IS, Isle of Skye; KA, Kujawy area; PJC, Polish Jura Chain; SA, Swabian Alb; CR, Czorsztyń Ridge. Map modified after Matyja and Wierzbowski, 1995, using data of Thierry et al., 2000, and Golonka et al., 2000.

land as well as carbonate rocks from the Swabian Alb in southern Germany belong to the so-called siliceous sponge megafacies, which is widely distributed in the peri-Tethyan part of Oxfordian open shelves of the Submediterranean ammonite province in Europe (Matyja and Wierzbowski, 1996). These deposits are characterised by various thicknesses occurring due to different carbonate productivity. Furthermore, growth of the microbial-sponge bioherms sometimes resulted in marked differentiation of sea-bottom relief. A few hundred metres deep-water setting is generally postulated for the siliceous sponge biofacies (Pisera, 1997). More precise data for the Late Oxfordian in the Polish Jura Chain imply a water depth between 240 and 400 m in isotopically investigated interbiohermal areas and extremely high sea-bottom relief attaining 160–200 m (Matyja and Wierzbowski, 1996). The belemnite carbon and oxygen isotope record of the Oxfordian from the Polish Jura Chain has been previously investigated (Wierzbowski, 2002). Additional belemnite samples derived from the Kujawy area of Poland (a part of Bielawy–Wapienno section of early Middle Oxfordian age) and Swabian Alb

(Plettenberg section of Late Oxfordian age) are examined for the first time in this study. The ammonite stratigraphy of the lower part of the Bielawy–Wapienno section from the Kujawy area is based on the study of Matyja et al. (1985), and B.A. Matyja's unpublished data. The stratigraphy of the Plettenberg section from the Swabian Alb is based on the data of Schweigert and Callomon (1997).

The Stankowa Skała section from the Pieniny Klippen Belt in the Polish Western Carpathians consists of deep marine carbonate rocks of the Czorsztyn Limestone Formation (Ammonitico Rosso type facies). The deposits are highly condensed, as the whole Oxfordian in the section is about 0.6 m thick (Jaworska, 2000). The studied rocks were deposited in the Czorsztyn Ridge within the Mediterranean ammonite province of Europe (Tethys Ocean). The precise biostratigraphical zonation of the Stankowa Skała section is hampered by the scarcity of a well-preserved ammonite fauna. Nevertheless, the data of Jaworska (2000) and additional recognition for this study allowed division of these strata to the substage or zone levels (see Fig. 2).

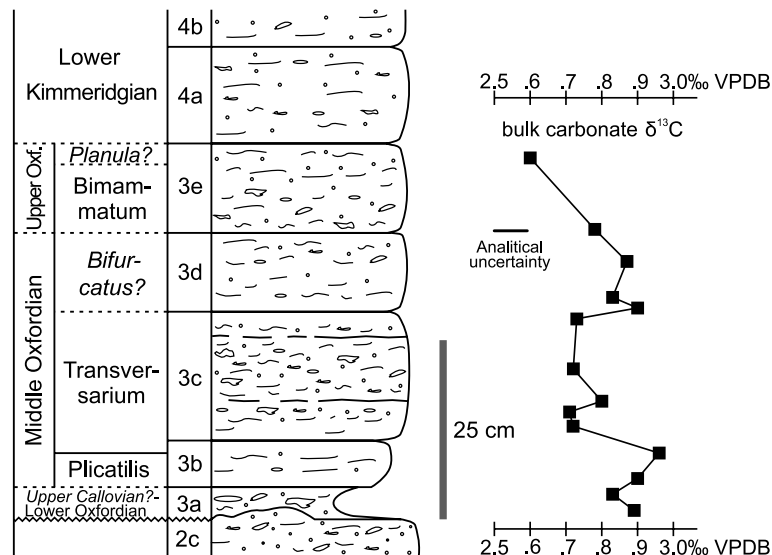


Fig. 2. Stratigraphy of the Stankowa Skała section from the Pieniny Klippen Belt in the Polish Western Carpathians (after A. Wierzbowski in Jaworska 2000, modified). The bulk-carbonate $\delta^{13}C$ trend is recognised for the present study. The transition between the Plicatilis and Transversarium zones corresponds to the mid-Oxfordian $\delta^{13}C$ peak (cf. Wierzbowski, 2002).

Table 1
Isotopic and chemical data for belemnites

Taxa	Bed	(Sub)zone	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Mn	Fe	Sr	Na
<i>Isle of Sky, Scotland (bed numbers after Sykes and Callomon, 1979; Wright, 1989)</i>								
<i>Cylindroteuthis</i> sp.	45	Cymodoce	1.30	0.08	73	207	1031	1223
<i>Cylindroteuthis</i> sp.	45	Cymodoce	2.34	−1.26	81	184	1180	1559
<i>Cylindroteuthis</i> sp.	43	Cymodoce	2.41	−0.41	37	112	1137	1313
<i>Pachyteuthis</i> sp.	41	Baylei	1.46	−0.61	52	225	1105	1715
<i>Pachyteuthis</i> sp.	37	Baylei	1.82	−1.88	90	205	1120	1640
<i>Pachyteuthis</i> sp.	37	Baylei	0.62	−0.17	96	167	1164	1336
<i>Pachyteuthis</i> sp.	37	Baylei	1.13	−0.07	60	161	1087	1390
<i>Pachyteuthis</i> sp.	35	Baylei	1.72	0.03	30	175	1200	1335
<i>Pachyteuthis</i> sp.	35	Baylei	1.07	−0.51	85	171	1076	1277
<i>Pachyteuthis</i> sp.	35	Baylei	1.26	−0.57	25	200	1100	1215
<i>Pachyteuthis</i> sp.	35	Baylei	1.10	−0.14	6	40	1370	1675
<i>Pachyteuthis</i> sp.	35	Baylei–Rosenkranzi boundary	2.07	0.04	25	86	1109	1337
<i>Pachyteuthis</i> sp.	33	Regulare	1.55	−1.39	145*	305*	1270	1680
<i>Cylindroteuthis</i> sp.	32	Serratum	3.00	0.21	60	156	1130	1396
<i>Pachyteuthis</i> sp.	31	Glosense–Tenuiserratum boundary	2.22	0.81	16	70	1015	1325
<i>Pachyteuthis</i> sp.	24/25	Tenuiserratum	2.99	0.03	14	75	1105	1633
<i>Pachyteuthis</i> sp.	23	Tenuiserratum	2.99	−0.61	5	40	1045	1677
<i>Pachyteuthis</i> sp.	23	Tenuiserratum	3.50	−0.62	15	90	1014	1281
<i>Pachyteuthis</i> sp.	21	Densiplicatum	3.02	0.24	34	83	813	1211
<i>Pachyteuthis</i> sp.	21	Densiplicatum	3.74	−0.64	10	51	1150	1410
<i>Pachyteuthis</i> sp.	21	Densiplicatum	3.98	0.11	5	25	1100	1410
<i>Pachyteuthis</i> sp.	21	Densiplicatum	2.97	0.67	12	45	1185	1700
<i>Pachyteuthis</i> sp.	21	Densiplicatum	4.69	−0.27	10	45	1150	1430
<i>Bielawy–Wapienno section, Kujawy area, Poland (unit numbers after Matyja et al., 1985)</i>								
<i>Hibolithes/Belemnopsis</i> sp.	unit B ₁	Tenuicostatum	0.67	−0.40	20	89	1523	1596
<i>Hibolithes/Belemnopsis</i> sp.	unit B ₁	Tenuicostatum	0.92	0.46	30	134	1509	1630
<i>Hibolithes/Belemnopsis</i> sp.	unit B ₁	Tenuicostatum	0.82	0.81	27	37	956	1486
<i>Hibolithes/Belemnopsis</i> sp.	unit A	Tenuicostatum	0.11	−0.05	27	27	1086	1643
<i>Plettenberg section, Swabian Alb, Germany (bed numbers after Schweigert and Callomon, 1997)</i>								
<i>Hibolithes/Belemnopsis</i> sp.	30	Planula	−0.08	−0.53	6	61	1093	1881
<i>Hibolithes/Belemnopsis</i> sp.	27	Planula	0.10	−0.02	6	6	1395	1752
<i>Hibolithes/Belemnopsis</i> sp.	26	Planula–Hauffianum boundary	0.39	−0.33	9	27	1003	1702
<i>Hibolithes/Belemnopsis</i> sp.	23	Hauffianum	−0.18	−0.86	16	76	1092	2007
<i>Hibolithes/Belemnopsis</i> sp.	22	Hauffianum	−0.09	−0.39	11	26	1257	1918
<i>Hibolithes/Belemnopsis</i> sp.	22	Hauffianum	0.54	−0.59	17	104	939	2027
<i>Stankowa Skala section, Piwny Klippen Belt, Polish Western Carpathians (bed numbers after Jaworska, 2000; see also Fig. 2)</i>								
<i>Hibolithes/Belemnopsis</i> sp.	4a	Lower Kimmeridgian	1.17	−0.75	119*	22	1540	1610
<i>Hibolithes/Belemnopsis</i> sp.	3e	Bimammatum	0.53	−0.79	70	13	1590	1430
<i>Hibolithes/Belemnopsis</i> sp.	3d	Bifurcatus?	0.69	0.12	30	55	1550	1420
<i>Hibolithes/Belemnopsis</i> sp.	3d	Bifurcatus?	−0.5	−0.07	67	24	964	1332
<i>Hibolithes/Belemnopsis</i> sp.	3d	Bifurcatus?	−0.31	0.00	40	71	1430	1219
<i>Hibolithes/Belemnopsis</i> sp.	3d	Bifurcatus?	0.04	0.25	50	30	1080	1357
<i>Hibolithes/Belemnopsis</i> sp.	3c	Transversarium	−0.59	0.04	45	17	1380	1540
<i>Hibolithes/Belemnopsis</i> sp.	3c	Transversarium	0.77	−0.34	50	17	1500	1450
<i>Hibolithes/Belemnopsis</i> sp.	3c	Transversarium	0.07	0.03	30	13	1450	1530
<i>Hibolithes/Belemnopsis</i> sp.	3b	Plicatilis	0.50	−0.10	85	10	853	1254
<i>Hibolithes/Belemnopsis</i> sp.	3b	Plicatilis	−0.87	0.43	83	26	997	1350
<i>Hibolithes/Belemnopsis</i> sp.	3b	Plicatilis	−0.45	0.01	85	15	901	1252
<i>Hibolithes/Belemnopsis</i> sp.	3b	Plicatilis	0.43	−0.49	36	20	1126	1370
<i>Hibolithes/Belemnopsis</i> sp.	3b	Plicatilis	−0.30	0.02	46	5	1051	1224
<i>Hibolithes/Belemnopsis</i> sp.	3a	Lower Oxfordian–Upper Callovian?	−0.27	0.09	25	17	1250	1440
<i>Hibolithes/Belemnopsis</i> sp.	3a	Lower Oxfordian–Upper Callovian?	0.62	−0.17	99	10	1042	1366

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are in ‰ vs. VPDB; the trace element ratios are in ppm.

3. Materials and methods

The collected belemnites originate from two different families: (1) the Mediterranean–Submediterranean family Belemnopseidae, belemnites from Poland and Germany, and (2) the Boreal–Subboreal family Cylindroteuthidae, belemnites from Scotland. The belemnopseid belemnites belong to two very closely related genera: *Hibolithes* and *Belemnopsis* albeit their determination without thorough preparation of entire specimens from hard rock samples has been impossible. Hence, they are not specified in Table 1. Boreal belemnites of the family Cylindroteuthidae belong to two different genera: a more massive *Pachyteuthis* and a more elongated *Cylindroteuthis*, both of which are identified in Table 1.

Only well-preserved, dark-coloured belemnites were selected for the study. A few centimetres long, whole-dimensional or half-dimensional fragments of belemnite rostra derived from solid parts of the guards situated behind the phragmocone were taken for analyses. Some polished belemnite chips were used for cathodoluminescence studies. All samples were subsequently carefully cleaned from surrounding sediments and apical canal diagenetic infillings by means of diamond dental drill. The specimens were ground and homogenised in order to avoid seasonal variations in iso-

topic composition. The preparation procedure was the same as in the isotope study of belemnite rostra from the Polish Jura Chain (Wierzbowski, 2002).

Trace element concentrations were determined on 100 mg subsamples, analysed using an AAS–30 Carl Zeiss Jena atomic absorption spectrophotometer. The samples were dissolved in 3% HCl according to the technique described by Brand and Veizer (1980). The results of Mn, Fe, Sr, Na content are reported in Table 1.

Cathodoluminescence studies were carried out with Cold Cathode Luminescence Cambridge Image Technology 8200 mk III device coupled with a Jenapol microscope. Operating conditions were an accelerating potential of 15–20 kV at beam current of 300–400 μ A and beam size 4×2 mm.

About 10 mg of powdered samples were used for isotope analyses (see Table 1). The samples were reacted overnight in sealed vessels with 100% orthophosphoric acid ($d = 1.92 \text{ g/cm}^3$) at 25°C. Extracted CO_2 was analysed by using a Finnigan Mat Delta Plus mass spectrometer at the Institute of Geological Sciences and Institute of Palaeobiology, Polish Academy of Sciences in Warsaw. The internal laboratory standard was Carrara marble calibrated vs. VPDB by using NBS 19. The overall reproducibility for the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values was close to 0.1‰.

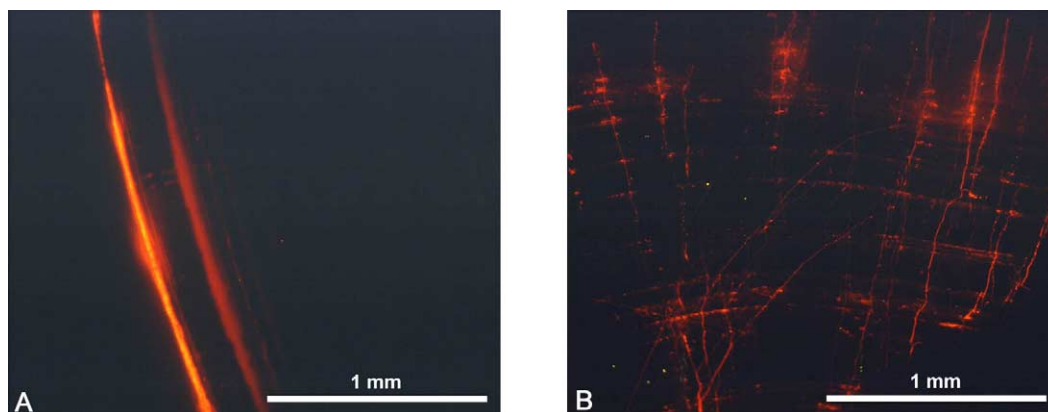


Fig. 3. Cathodoluminescence microphotographs of the belemnite rostra. (A) The non-luminescent rostrum from the Isle of Skye in Scotland. The rostrum edge indicates bright luminescence. (B) The slightly luminescent rostrum from the Pieniny Klippen Belt in the Polish Western Carpathians. Note the luminescence of microfractures and the dull luminescence of some growth rings.

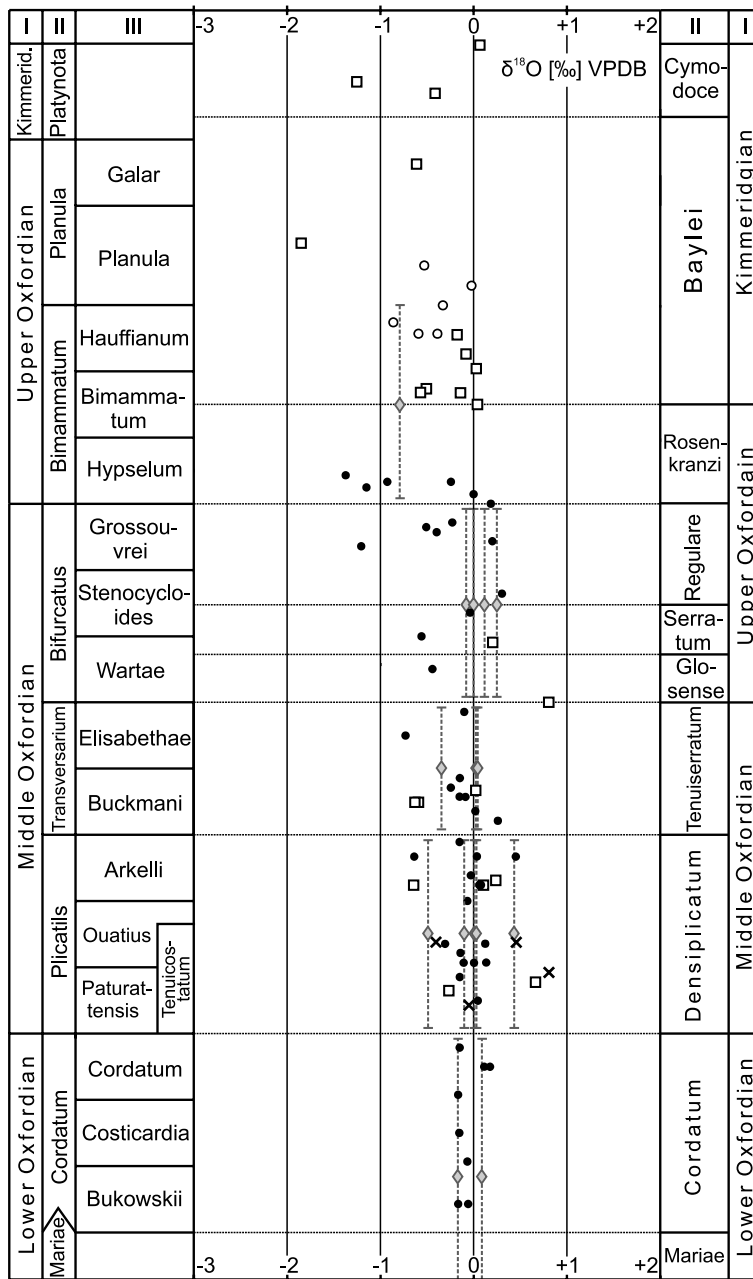


Fig. 4. The $\delta^{18}\text{O}$ values of the Oxfordian belemnite rostra. Symbols: filled dots, Submediterranean belemnites from the Polish Jura Chain (record after Wierzbowski, 2002); crosses, Submediterranean belemnites from the Kujawy area in Poland; open dots, Submediterranean belemnites from the Swabian Alb in Germany; diamonds, Mediterranean belemnites from the Pieniny Klippen Belt in Polish Western Carpathians; open squares, Boreal–Subboreal belemnites from the Isle of Skye in Scotland; I, (sub)stages; II, zones; III, subzones. The ranges of possible datings are indicated in the case of the Mediterranean samples.

4. Results

Results of the trace element analyses exhibit the low Mn (< 100 ppm) and Fe (< 250 ppm) contents of all but two belemnite samples (Table 1).

The rostra have Sr concentrations which vary from 800 to 1600 ppm. The Na contents of the rostra are rather high and oscillate between 1200 and 2000 ppm (Table 1).

The belemnite rostra were, in general, non-lu-

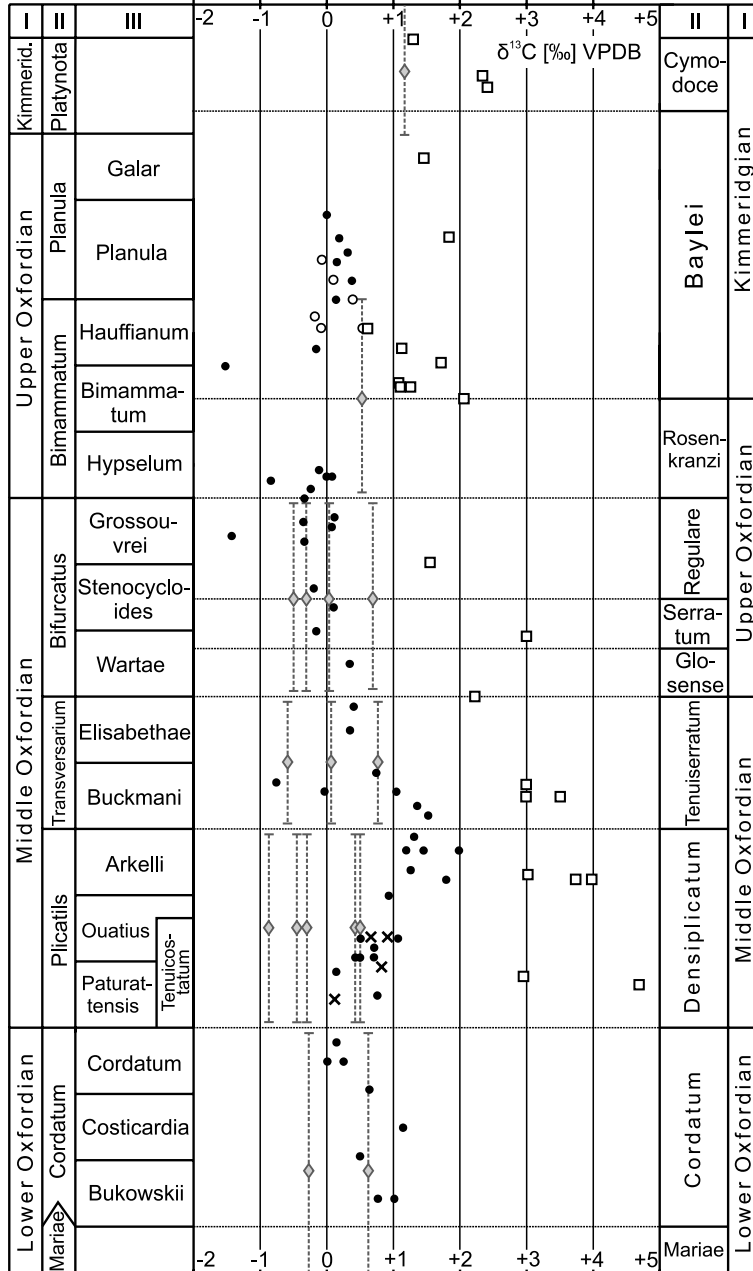


Fig. 5. The δ¹³C values of the Oxfordian belemnite rostra. Symbols as in Fig. 4

minescent under cathodoluminescope showing the good preservation of the internal structures. Only apical line areas, radial microfractures as well as some growth rings, especially in the external part of the guard, indicated different luminescence intensity (Fig. 3).

The $\delta^{18}\text{O}$ values of several belemnite rostra, derived from the Submediterranean Province in the Kujawy area of Poland and the Swabian Alb of Germany, are similar to each other, ranging from about -0.9‰ to $+0.8\text{‰}$ VPDB (Fig. 4). These data resemble likewise the $\delta^{18}\text{O}$ values of well-preserved Oxfordian belemnite rostra and brachiopod shells from Submediterranean sections in the Polish Jura Chain (cf. Wierzbowski, 2002 and Fig. 4).

Belemnite guards from the Mediterranean Province in the Stankowa Skała section of the Czorsztyn Ridge have $\delta^{18}\text{O}$ values, which range from -0.8 to $+0.4\text{‰}$ VPDB (Fig. 4). The $\delta^{18}\text{O}$ values of northern belemnites from Scotland are similar as well and range from -1.9‰ to $+0.8\text{‰}$ VPDB at the mean value of around -0.25‰ VPDB (Fig. 4).

The $\delta^{13}\text{C}$ values of belemnite rostra from sponge sediments in the Kujawy area and the Swabian Alb are placed exactly within an Oxfordian temporal trend obtained from the Polish Jura Chain area (Fig. 5).

The $\delta^{13}\text{C}$ values of all but one Mediterranean belemnite derived from the Pieniny Klippen Belt (Czorsztyn Ridge) in the Western Carpathians are similar, partly lowered up to around 1‰ , when compared with the Submediterranean data (Fig. 5). Unfortunately, the fairly large age ranges of these samples do not allow comparison below the zone level.

The $\delta^{13}\text{C}$ values of Boreal–Subboreal belemnite rostra from the Isle of Skye are $1\text{--}2.5\text{‰}$ higher than the values of their Submediterranean counterparts (Fig. 5). The Scottish $\delta^{13}\text{C}$ values also are more scattered but do resemble roughly the Oxfordian carbon isotope trend obtained from Submediterranean belemnites. An isotopic offset between both groups of values seems to be most pronounced during the mid-Oxfordian $\delta^{13}\text{C}$ maximum (Fig. 5).

5. Discussion

5.1. Diagenetic alteration

Belemnite rostra are built of a low-Mg calcite, which is the most stable component during limestone diagenesis (see Marshall, 1992). In addition, a circulation of diagenetic fluids is hindered by the large cylindrical shape of the guards.

Some authors postulate that the rostra were originally slightly porous and could become cemented during percolation of early diagenetic fluids (Veizer, 1974; Spaeth, 1975). However, one should notice that the carbon isotope composition considered to be the main subject of the present study is not very susceptible to diagenetic alteration. As proved by Banner and Hanson (1990), the diagenetic fluid:solid phase ratio, which is necessary to alter isotopic composition of carbon in calcium carbonate minerals, is several times greater than in the event of oxygen isotopes. For this reason many porous carbonate samples, whose $\delta^{18}\text{O}$ values are diagenetically lowered, maintain original $\delta^{13}\text{C}$ values providing a focus for isotope research.

The recrystallisation and exchange processes with diagenetic fluids should normally alter both the isotopic composition and the trace element contents of the fossils (Veizer, 1974; Marshall, 1992). Revealed manganese and iron concentrations are typical of well-preserved belemnite guards (cf. Price and Sellwood, 1997; Price et al., 2000). Two samples with slightly higher Fe and/or Mn contents were excluded from the set of $\delta^{18}\text{O}$ values.

Further evidence of good preservation of the samples is their high Na concentrations and high Sr concentrations (between 800 and 1600 ppm), which are close to the predicted equilibrium contents for marine carbonates (Veizer, 1974).

Small cathodoluminescent bands, which reflect seasonal shell growth, are typical of some modern organisms like *Nautilus* (Barbin et al., 1995). Therefore, slight cathodoluminescence effects of the investigated belemnite material cannot be used as evidence for diagenetic alterations. Summarising, the investigated samples meet accepted

criteria for the retention of both carbon and oxygen original isotopic values.

5.2. Palaeotemperatures and depth habits of belemnites

Belemnites are traditionally regarded to secrete oxygen in their skeletons in isotopic equilibrium with ambient seawater (e.g. Lowenstam and Epstein, 1954; Sælen et al., 1996; Price and Sellwood, 1997). This assumption can be supported by the fact that $\delta^{18}\text{O}$ values of modern cephalopod shells, including *Sepia*, which seems to be a close relative of belemnites, are close to equilibrium fractionation (Wefer and Berger, 1991; Bettencourt and Guerra, 1999). Moreover, comparison between belemnite and brachiopod isotope compositions from the Oxfordian in the Polish Jura Chain reveals similar $\delta^{18}\text{O}$ values of both groups of fossils, suggesting near-isotopic equilibrium precipitation of oxygen isotopes within belemnite rostra, and a nektobenthic habitat of these animals (Wierzbowski, 2002).

Due to a significant water depth and open marine environment, which occurred in the area of sedimentation of sponge megafacies, one can assume constant salinity and $\delta^{18}\text{O}$ values of Oxfordian seawater to have been -1.0‰ Vienna Standard Mean Ocean Water (VSMOW) as characteristic of an icecap-free world (Shackleton and Kennet, 1975). Accordingly, palaeotemperatures that are calculated by using the equation of Anderson and Arthur (1983) for Submediterranean belemnites derived from the Kujawy and Swabian Alb vary between $+9^\circ\text{C}$ and $+15.6^\circ\text{C}$ (mean value $+12.7^\circ\text{C}$). These temperatures are close to the temperatures ($+12$ and $+14.3^\circ\text{C}$) which were identically calculated using Oxfordian belemnites from the Polish Jura Chain (Wierzbowski, 2002). They suggest the existence of similar palaeoecological conditions and nektobenthic habitats of all Submediterranean belemnites which lived in the area of the siliceous sponge megafacies during the Oxfordian. The comparison between an ancient fauna of siliceous sponges with the recent one, which prefers deep-waters of the tropical zones, indicates that the temperatures of around $10\text{--}15^\circ\text{C}$ could be reasonably

accepted for bottom waters of the Oxfordian Sea (Pisera, 1997).

The $\delta^{18}\text{O}$ values of Mediterranean belemnites from the Stankowa Skała section in the Czorsztyn Ridge imply temperatures of around $+12.5 \pm 2^\circ\text{C}$. However, the Ammonitico Rosso facies represents a deep marine carbonate sediment, which was deposited near a lysocline. Therefore, a possible increase in water temperature in the area of the Mediterranean Tethys might have been negligible if the local belemnites had been deep-ocean dwellers. Unfortunately, there is no agreement among authors on the life habits of belemnites. It has been suggested that belemnites may have migrated vertically in the water column like modern cephalopods and may have had neritic or neritic–pelagic habitats (Stevens and Clayton, 1971; Doyle and Bennett, 1995). On the other hand, a nektobenthic life style of belemnites is indicated by Anderson et al. (1994) on the basis of isotope data. This conclusion has been confirmed by Martill et al. (1994), who note a late appearance of belemnites in the transgressive succession after an appearance of bivalves, echinoderms and ammonites. The opposite situation is observed in the Kimmeridgian of the Holy Cross Mountains in central Poland. Siliceous sponge sediments in this region are gradually replaced by a shallow-sea carbonate platform. Despite common findings of ammonites, belemnites disappear totally along with the disappearance of deep neritic sponges (Matyja et al., 1989 and unpublished data).

Nevertheless, the construction of the belemnite phragmocone imposes a habitat depth limit because of the possibility of implosion from hydrostatic pressure. For two species of *Hibolithes* the habitat depth limit is calculated at around 215 m (Westermann, 1973; Hewitt, 2000). According to the data of these authors, other belemnites should have had a lower depth limit averaging 150 m, similar to the depth limit of a majority of ammonites. A differentiation of depth limit is, however, possibly recognised within the genus *Cylindroteuthis* (Westermann 1973; Hewitt et al., 1999). Similarly, the large differentiation of depth limit is observed for modern *Sepia*; particular *Sepia* species differing in the shell size and septal thickness inhabit either shallow or deep waters (Sherrard,

2000). For these reasons the calculations of the depth habitat of belemnites seem not to be very exact.

The Upper Oxfordian interbiohermal sediments from the Polish Jura Chain were formed somewhere between 240 and 400 m depth according to the data of Matyja and Wierzbowski (1996). The collected rock samples were, however, derived from shallower zones of interbiohermal areas as a consequence of the vicinity of the outcrops to biohermal complexes. Taking into account the inferred nectobenthic habitat of the Submediterranean belemnites, it appears that these cephalopods were able to live up to a depth of at least 240 m. Consequently, rather low temperatures, which were calculated for two palaeogeographic provinces, and the possible depth limit of belemnites justify the acceptance of a similar depth habitat of the Mediterranean belemnites from the Stankowa Skala outcrop in the Pieniny Klippen Belt. The temperature gradient between the Submediterranean Province and the Mediterranean Province at a depth of around 200 m might have been not significant. Furthermore, the occurrence of cold upwelling in the Czorsztyn Ridge area (see Section 5.3) might have been responsible for a slight lessening of seawater temperature. Nevertheless, the Mediterranean belemnites seem to be derived from shallower zones of the Czorsztyn Ridge and to be deposited after death in deep-sea Ammonitico Rosso sediments.

Because of the vicinity of landmass (see Fig. 1) and the possible riverine runoff, the Boreal seawater at the Isle of Skye may have been characterised by a lower salinity and decreased $\delta^{18}\text{O}$ values. However, a relatively abundant stenohaline fauna of belemnites and ammonites as well as a diverse palynoflora indicate an open marine depositional setting (Morton and Hudson, 1995; Riding and Thomas, 1997). Thus, the predicted marine environment may be characterised, if any, by only a slight decrease in salinity. Although modern *Sepia* is occasionally caught in water of 29‰ salinity (Schäfer, 1972), the extant and ancient cephalopods are generally regarded to tolerate salinity not lower than 30‰ (Wright, 1987). Accepting the normal sea salinity of an ice-free Earth to have been 34.3‰ (Wright,

1987), one can assess the possible depletion in salinity for the Boreal Ocean to have been not higher than ca. 4.3‰. Due to the palaeolatitude of the Isle of Skye close to 37°N (Thierry et al., 2000), the $\delta^{18}\text{O}$ values of freshwater input of -7‰ VSMOW may be estimated (see Sælen et al., 1996). Accordingly, a 4.3‰ decrease in salinity would result in a $\delta^{18}\text{O}$ shift from -1‰ VSMOW of normal salinity water to around -1.75‰ VSMOW of lower salinity water. Consequently, the temperature calculated from the mean belemnite $\delta^{18}\text{O}$ value amounts to +13°C in the case of normal salinity and +10.1°C in the case of lowered salinity. Both temperatures are again very similar to previously provided temperatures for Submediterranean and Mediterranean belemnites.

Due to the lower equator-to-pole temperature gradient of the Mesozoic, some authors claim that the temperatures of tropical bottom waters and polar surface waters have been equal (Kitchell and Clark, 1982; Oschmann, 1988). This temperature effect is likely responsible for the similarity of all temperatures which were calculated on the basis of the isotope composition of belemnite guards. The sediments from the Isle of Skye were deposited in a shallow sea not deeper than 100–150 m. The surface waters in this area may have been characterised by a lowered temperature similar to a temperature of deep-shelf waters of the Tethys Ocean.

5.3. Carbon isotope composition

Analysis of Oxfordian belemnites from the Polish Jura Chain revealed a compact $\delta^{13}\text{C}$ temporal trend characterised by 2.5–3‰ lower values when compared with coeval brachiopod data (Wierzbowski, 2002). This may be assigned to a vital effect of belemnites since modern brachiopods of the same groups secrete their shells in near-isotopic equilibrium with seawater (cf. Carpenter and Lohmann, 1995). In addition, vital effects in carbon isotope composition of the shells appear to be distinctive of modern cephalopods (Wefer and Berger, 1991; Bettencourt and Guerra, 1999).

So-called metabolic vital effects in exclusively carbon isotope composition rely on the incorpo-

ration of an isotopically lighter, respired CO_2 into the shell carbonate (McConnaughey et al., 1997). Metabolic effects characterise particular animal groups and depend on the ratio of environmental CO_2 to respired CO_2 within an organic tissue. Comparable metabolic rates may be assumed for all investigated belemnites because they have precipitated calcium carbonate in similar temperatures, which has been calculated using $\delta^{18}\text{O}$ values. All Mediterranean and Submediterranean belemnites also belong to the same taxa. On the other hand, Boreal cylindroteuthid belemnites are sometimes found together with Mediterranean–Submediterranean *Hibolites* in the area of the Russian Platform. In Callovian and Oxfordian strata both belemnites have similar $\delta^{13}\text{C}$ values (Podlaha et al., 1998). This rules out the possibility of the occurrence of a different intensity of vital effect within these two belemnite groups. Thus, the $\delta^{13}\text{C}$ values of all belemnites are regarded to represent a trustworthy proxy for differentiation of the isotope composition of DIC in Oxfordian seas.

The unsurprising resemblance in $\delta^{13}\text{C}$ values of all Submediterranean belemnites clearly demonstrates similar palaeoenvironmental conditions and a similar isotope composition of DIC in the area of siliceous sponge sedimentation during the Oxfordian in Europe.

Slightly lowered $\delta^{13}\text{C}$ signatures of some Mediterranean belemnites might be because of upwelling providing deep-ocean waters, which were rich in isotopically light carbon derived from the decomposition of organic matter. Palaeoclimatic modelling suggests that the prevailing wind direction during the Jurassic may have induced upwelling at the southeastern margin of the Czorsztyn Ridge (Golonka and Krobicki, 2001). Lifted nutrient-rich waters appear to be responsible for the growth of abundant and diverse faunal assemblages associated with the ridge during the Jurassic (Birkenmajer, 1986; Golonka and Krobicki 2001).

High $\delta^{13}\text{C}$ values of northern belemnites could be linked to specific Boreal water chemistry. For example, changes in carbonate concentration induced by changes in alkalinity of seawater may affect $\delta^{13}\text{C}$ ratios of carbonates. A decrease in

seawater $[\text{CO}_3^{2-}]$ concentration at lower alkalinity is inferred by Spero et al. (1997) to increase $\delta^{13}\text{C}$ values of calcium carbonate secreting organisms.

However, the carbonate-concentration effect is recognised in foraminiferal shells and it is also suggested for other calcareous species, which display $\delta^{18}\text{O}:\delta^{13}\text{C}$ covariance connected with simultaneous depletion in heavy isotopes (Spero et al., 1997). This covariance corresponds to kinetic isotope effects described by McConnaughey (1989). Belemnites do not display such a covariance (Podlaha et al., 1998; Wierzbowski, 2002). In addition, widespread carbonate precipitation might have decreased alkalinity of the Tethys Ocean. Hence, the carbonate-concentration effect is not expected to be involved in a positive carbon isotope shift of Boreal–Subboreal belemnite rostra.

Despite the shallower water environment (100–150 m) and the possibly greater influence of a surface carbon isotope gradient, the high Boreal–Subboreal $\delta^{13}\text{C}$ values distinctly indicate regional enrichment of DIC in ^{13}C . This may be due to high organic matter productivity and burial, which was also manifested by abundant occurrences of organic-rich sediments within the partly isolated Boreal basins.

The Upper Oxfordian Flodigarry Shale Member in the Isle of Skye section is organic-rich. Other organic-rich sediments of Late Jurassic age are commonly found in different Boreal Sea areas from Arctic Canada to the Barents Sea and the English Channel (e.g. Smelror et al., 2001). A proposed model of organic-rich sedimentation in the Boreal Sea based on the presence of a pycnocline and fresh water inflow (Tyson et al., 1979) is inconsistent with geological evidence (Smelror et al., 2001). The presence of a stable pycnocline and bottom water anoxia in the case of the Flodigarry Shale Member seems also to be excluded due to the occurrence of numerous beds rich in epifaunal benthos. The anoxic conditions occurred then mainly beneath the sediment–water interface (Morton and Hudson, 1995). The temporal variations in biologic productivity of the Boreal Sea may be responsible for the scattered $\delta^{13}\text{C}$ results of northern belemnites.

It is difficult to correlate the data obtained in this study with previously published $\delta^{13}\text{C}$ values

due to the scarcity of well-dated samples of Oxfordian–Early Kimmeridgian belemnites. Nevertheless, a comparison between the belemnite data from the Callovian–Lower Kimmeridgian on the Russian Platform (Barskov and Kiyashko, 2000; Riboulleau et al., 1998; for detailed stratigraphy see Hantzpergue et al., 1998) and roughly dated belemnite samples from the Callovian–Lower Tithonian on the Falkland Plateau (Price and Gröcke, 2002) is worthy of attention. Lower Oxfordian $\delta^{13}\text{C}$ results from the Russian Platform being part of the Boreal realm are scattered from +1‰ to +4‰ VPDB, attaining high mean values between +2.5‰ to +3‰ VPDB (Barskov and Kiyashko, 2000). The $\delta^{13}\text{C}$ values of Oxfordian–Early Kimmeridgian belemnites from this area range from +0.9‰ to +3.5‰ VPDB (Riboulleau et al., 1998). Temporal variation of these results assigned to particular levels of the Oxfordian and the Early Kimmeridgian (see Table 2) roughly resembles the $\delta^{13}\text{C}$ trend obtained herein from the Boreal–Subboreal belemnites of Scotland. It is also of interest that the $\delta^{13}\text{C}$ values of many Oxfordian belemnites from the Russian Platform presented by Podlaha et al. (1998) are positive and scattered similarly to the Scottish data revealed in this study.

Conversely, the belemnite $\delta^{13}\text{C}$ values from the Falkland Plateau oscillate around 0–1‰ VPDB except for one sample which has a slightly more positive value (Price and Gröcke, 2002). These

values most likely characterised the carbon isotope composition of the global ocean being similar to the data from the Submediterranean Province of Europe. All of these facts lead to the conclusion that restricted Boreal basins were characterised by an isotope composition of DIC different from the global ocean. Due to strong influences of local fractionation on the isotopic values of DIC, the Boreal Sea and partly the Czorsztyn Ridge area do not appear to represent good locations for the recognition of global carbon isotope trends.

Differences in the $\delta^{13}\text{C}$ values of European belemnites ranged from 2 to 5‰ in particular levels of the Oxfordian (Fig. 5). It is more than the differentiation of the $\delta^{13}\text{C}$ values of DIC in the modern ocean. Regional differences in the carbon isotope composition of bulk-carbonates and brachiopod shells have been revealed so far in the uppermost Ordovician and the Silurian (Wenzel, 1997; Salzman, 2001) as well as in the Toarcian Stage of the Lower Jurassic (Jenkyns and Clayton, 1997). Abnormally high $\delta^{13}\text{C}$ values of limestones have also been indicated in the Carboniferous–Permian Sverdrup Basin of northern Canada (Beauchamp et al., 1987). In all of these cases, like in the present study, the local enrichment in ^{13}C is related to enhanced bioproductivity and/or organic matter storage in restricted sea areas. The relatively large differentiation of isotope composition of seawater DIC during the ma-

Table 2

Oxfordian and Lower Kimmeridgian belemnite $\delta^{13}\text{C}$ values from the Russian Platform presented by Riboulleau et al. (1998) and ammonite stratigraphy after Hantzpergue et al. (1998)

Level	$\delta^{13}\text{C}$ (‰ VPDB)	Zone	Stage
Mk 0	2.40	Cymodoce	Kimmeridgian
Mk 2-2	2.28	Cymodoce	Kimmeridgian
Mk 2-3	0.94	Cymodoce	Kimmeridgian
Mk 8c	1.11	Baylei	Kimmeridgian
Mk 8d 1	1.21	Rosenkranzi–Regulare	Oxfordian
Mk 10a	0.98	Rosenkranzi–Regulare	Oxfordian
Mk 11d	1.52	Serratum	Oxfordian
Mk 15 top	1.51	Tenuiserratum–Densiplicatum, (top)	Oxfordian
Mk 15-3	3.21	Tenuiserratum–Densiplicatum	Oxfordian
Mk15-7	2.68	Tenuiserratum–Densiplicatum	Oxfordian
Mk 16-15	3.49	Cordatium	Oxfordian
Mk 16-1	1.60	Cordatium	Oxfordian
Mk 16 middle	2.33	Cordatium	Oxfordian

for parts of the Palaeozoic and the Mesozoic was likely enabled by a generally weaker than nowadays oceanic water circulation.

6. Conclusions

(1) Seawater palaeotemperatures provided by belemnites derived from different palaeogeographic provinces range between 10 and 15°C. Regional climatic variations appear to be partially obscured by inferred different depth habits of the studied belemnites.

(2) The belemnite $\delta^{13}\text{C}$ record is believed to reflect secular variations in the isotope composition of DIC in the upper layer of the global ocean. The latter assumption arises from the habitat depth limit of belemnites.

(3) Comparable $\delta^{13}\text{C}$ values of all Submediterranean belemnite rostra prove the existence of the uniform isotopic composition of DIC in the deepneritic environment of the northern Tethyan shelves during the Oxfordian.

(4) Slightly lower $\delta^{13}\text{C}$ values of some Mediterranean belemnites, when compared with coeval Submediterranean data, might be caused by upwelling providing ^{12}C enriched bottom waters.

(5) 1–2.5‰ higher (than Submediterranean) $\delta^{13}\text{C}$ values of Boreal–Subboreal belemnites may be linked to high organic matter productivity and burial in the partly isolated Boreal seas. Because of the scattered $\delta^{13}\text{C}$ values obtained in this study, the Boreal basins do not seem to be a good place for recognition of secular $\delta^{13}\text{C}$ carbonate curves.

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