



Middle–Upper Jurassic (Upper Callovian–Lower Kimmeridgian) stable isotope and elemental records of the Russian Platform: Indices of oceanographic and climatic changes



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ABSTRACT

New isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and elemental (Mg/Ca, Sr/Ca) data of well-preserved belemnite rostra, ammonite and gastropod shells from the Middle Oxfordian–Lower Kimmeridgian (Densiplicatum–Kitchini zones) of the Russian Platform are presented. This record is supplemented with published data from the Upper Callovian–Lower Kimmeridgian interval (Athleta–Kitchini zones). Significant differences in average temperatures calculated from $\delta^{18}\text{O}$ values of particular fossil groups (5–15 °C) show the thermal gradient and the presence of cold bottom waters in the Middle Russian Sea during the Late Callovian–Middle Oxfordian. An Upper Oxfordian–lowermost Kimmeridgian decrease in $\delta^{18}\text{O}$ values and an increase in Sr/Ca ratios of cylindroteuthid belemnite rostra likely reflect a warming of the bottom waters of ca. 3.5 °C. The gradual Late Oxfordian–earliest Kimmeridgian warming is followed by an abrupt temperature rise of 3–6 °C that occurred at the transition of the Early Kimmeridgian Bauhini and Kitchini chrons.

The occurrences of cold bottom waters and of (Sub)Mediterranean ammonites and belemnites in the Middle Russian Sea at the Middle–Late Jurassic transition are regarded as a result of the opening of seaways during a sea level highstand. The bottom waters are considered to have been formed in the cool Boreal Sea. The subsequent retreats of the cold bottom waters and of the (Sub)Mediterranean cephalopods from the Middle Russian Sea in the Late Oxfordian are explained by the restriction of water circulation during a sea-level fall. The Early Kimmeridgian rise of bottom temperatures of the sea is linked to a global climate warming. The data presented do not support a major cooling of the Arctic and a consequent glaciation in this region at the Middle–Late Jurassic transition. Since occurrences of cold water masses are diachronous in different European basins, the observed variations in sea water temperatures are interpreted as a result of changes in marine currents and water circulation.

$\delta^{13}\text{C}$ values of belemnite rostra from the Russian Platform are scattered but show the long-term Upper Callovian–Middle Oxfordian positive excursion consistent with the previously published isotope records of the Boreal Realm and terrestrial organic matter.

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1. Introduction

Oxygen isotope records of biogenic carbonates from the Russian Platform and of tooth phosphates from Western Europe as well as migrations of ammonite fauna have been interpreted as an evidence of severe cooling at the Middle–Late Jurassic transition and subsequent warming (Dromart et al., 2003; Nunn et al., 2009; Price and Rogov, 2009; Donnadieu et al., 2011) or of prominent sea-level rise and changes in water circulation and salinity (Wierzbowski et al., 2009; Wierzbowski and Rogov, 2011). Major perturbations in the

carbonate carbon cycle have been observed at the Middle–Late Jurassic transition, with a decline of carbonate platforms during the Late Callovian–Early Oxfordian and a recovery of carbonate sedimentation starting from the Middle Oxfordian (Bartolini et al., 1996; Morettini et al., 2002; Dromart et al., 2003; Cecca et al., 2005). The perturbations in the carbonate carbon cycle were claimed to be a source of the low atmospheric CO_2 level in the Late Callovian–Early Oxfordian period followed by a rise in the atmospheric CO_2 content in the Middle Oxfordian (Louis-Schmid et al., 2007b; Donnadieu et al., 2011). The enhanced volcanic activity of the seafloor observed during the Middle–Late Jurassic transition was in turn suggested to have been a source of the increased CO_2 degassing from the lithosphere (Wierzbowski et al., 2009, 2012).

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Despite numerous studies climatic proxy data for the Middle–Upper Jurassic are still fragmentary. The theories presented are therefore of limited relevance for the understanding of the contentious nature of environmental changes during and after the Middle–Late Jurassic transition.

The paper presents a compilation of new and old isotope and elemental data from the Subboreal Province of the Russian Platform. The new and old datasets are precisely correlated stratigraphically with the Submediterranean ammonite zonation of Central Europe. The interpretation of the environmental changes in the Middle–Late Jurassic (Late Callovian–Early Kimmeridgian) is based on thorough analysis of geochemical and faunistic proxies. The aim of the present contribution is to unravel the causes of the prominent changes that occurred in the Middle Russian Sea during and after the Middle–Late Jurassic transition and to discuss the reasons for the migrations of marine faunas.

2. Paleogeography and paleobiogeography

Most of Europe was flooded by shallow, epicontinental seas during the Late Callovian–Early Kimmeridgian (Fig. 1). Non-depositional events occurred in central-European seas during the Late Callovian–Early Oxfordian, whereas calm carbonate sedimentation prevailed in the Middle–Late Oxfordian and the Early Kimmeridgian. North-eastern European basins including the huge Middle Russian Sea and its central part – the Volga basin were connected with both the Boreal Sea and the Tethys Ocean and surrounded by land-masses. The Middle–Upper Jurassic deposits of the north-eastern Europe basins consist predominantly of siliciclastics – they are often organic rich and calcareous. The Callovian–Oxfordian boundary sections of the north-European basins are generally more complete than are those of the Tethyan and peri-Tethyan areas.

The provincialism of Jurassic ammonite and belemnite fauna caused the development of two major biochoromas: the Boreal (Arctic) and the Mediterranean (Tethyan) realms. Transitory faunistic zones, including

the belemnite Boreal–Atlantic Subrealm (or Province) and the ammonite Subboreal and Submediterranean provinces, are also distinguished in Europe (Doyle, 1987; Westermann, 2000; Cecca and Westermann, 2003; Page, 2008; Page et al., 2009). Worth noting is the marked overlap of ammonite faunas observed in Europe during the latest Callovian–Early Oxfordian. This results in difficulties in the determination of province borders but has enabled common utilization of the standard Boreal ammonite zonation (Matyja and Wierzbowski, 1995; Page et al., 2009).

The Volga Basin was settled predominantly by Boreal–Subboreal ammonites (cardioceratids, kosmoceratids and aulacostephanids) and belemnites (cylindroteuthids) in the Late Callovian–Early Kimmeridgian. Other ammonites (aspidoceratids, perisphinctids and oppeliids) that usually inhabited Submediterranean and Mediterranean provinces, and Tethyan mesohibolitid (“belemnopsoid”) belemnites, were also present in this area (cf. Główniak et al., 2010).

3. Geological setting

Belemnites, ammonites and a few gastropods (*Bathrotomaria* sp.) were collected from the Middle Oxfordian–Lower Kimmeridgian succession of the Makar’yev (57° 54’ 21” N, 43° 49’ 44” E) and Mikhalenino (57° 59’ 56” N, 44° 0’ 23” E) outcrops located at the Unzha river (tributary of the Volga), in the Kostroma District of Russia (Fig. 2). The sediments exposed in the Makar’yev and Mikhalenino sections consist of gray calcareous clays containing a few glauconitic and phosphoric layers and one layer of calcareous concretions (Mesezhnikov, 1989; Hantzpergue et al., 1998; Bushnev et al., 2006; Rogov and Kiselev, 2007; Główniak et al., 2010). Two bituminous oil shale horizons occur in the Middle–lowermost Upper Oxfordian part of the succession (TOC contents of 5–15%; Hydrogen Index of 400–500; Hantzpergue et al., 1998; Bushnev et al., 2006). The clays that outcrop in the Makar’yev and Mikhalenino sections have a total thickness of ca. 11 m and are rich in well-preserved foraminifer, ostracod, gastropod, ammonite and

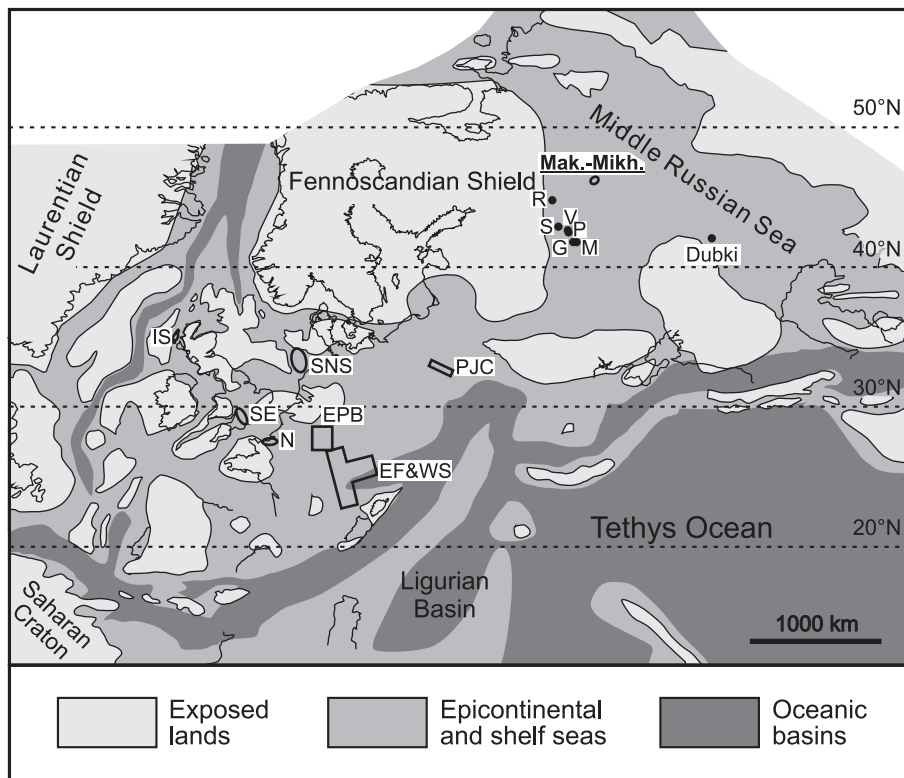


Fig. 1. Early Oxfordian paleogeography of Europe (after Wierzbowski and Rogov, 2011). Areas of paleoclimatic studies (referred in the text and figures): EPB – eastern Paris Basin; EF&WS – eastern France and western Switzerland; G – Gorenka; IS – Isle of Skye; M – Mikhalenino; Mak.-Mikh. – Makar’yev, Mikhalenino; N – Normandy; P – Peski; PJC – Polish Jura Chain; R – Rybnsk (Ioda River); S – Shchelkovo; SE – southern England; SNS – southern North Sea; V – Voskresensk.

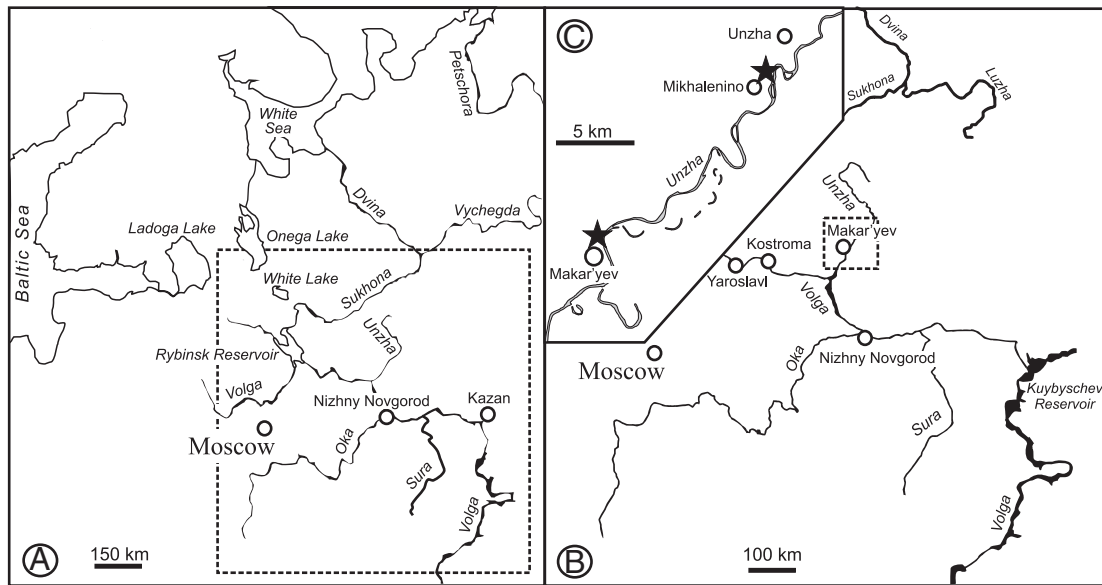


Fig. 2. Location of city of Makar'yev in Russia (A, B) and of Mikhalenino and Makar'yev outcrops (C).

belemnite faunas (cf. Azbel, 1989; Guzhov, 2004; Ustinova, 2009; Głowniak et al., 2010; Tesakova et al., 2012). The sediments were deposited in a calm off-shore environment as indicated by the lack of intercalations of coarser deposits and the presence of well-preserved fragile shells of open sea animals (cf. Mesezhnikov, 1989; Głowniak et al., 2010). The presence of a diversified assemblage of gastropods, benthic and planktonic foraminifers as well as (Sub)Mediterranean and Boreal ammonites and belemnites in the Middle Oxfordian and the lower part of the Upper Oxfordian indicates normal marine environmental settings and faunal migrations from Tethyan areas (cf. Azbel, 1989; Guzhov, 2004; Ustinova, 2009; Głowniak et al., 2010). The faunal assemblage becomes gradually more monotonous and dominated by local – (Sub)Boreal taxa in the Upper Oxfordian and the Lower Kimmeridgian (cf. Guzhov, 2004; Ustinova, 2009; Głowniak et al., 2010).

The ammonite stratigraphy of the Mikhalenino section comprising the Boreal Middle Oxfordian–Lower Kimmeridgian (Densiplicatum–Kitchini zones) was presented by Rogov and Kiselev (2007) and revised by Głowniak et al. (2010). Since the lowermost part of the Mikhalenino section was not accessible during field work in years 2009–2010 the nearby Makar'yev section was sampled for the Densiplicatum Zone of the Middle Oxfordian. Although the stratigraphy of the Makar'yev section was presented by Mesezhnikov (1989), the stratigraphy of its lower part has been revised for the purposes of the present study (Fig. 3). The revised stratigraphy of the Makar'yev section is based on newly collected cardioceratid ammonites. The Vertebrale Subzone of the Densiplicatum Zone is identified in the Makar'yev section between the oldest appearance of *Cardioceras* (*Vertebrioceras*) *vertebrale* (Sowerby) and the last representative of the *C. (Plasmatoceras)* *tenuicostatum* group (cf. Sykes and Callomon, 1979). The Maltonense Subzone of the Densiplicatum Zone is recognized there between the first appearance of the subgenus *Maltonioceras* and the first appearance of the subgenus *Mitcardioceras* (cf. Sykes and Callomon, 1979). It comprises the Lower Black Shale (LBS) layer. The first representatives of subgenus *Mitcardioceras* indicative of the younger Tenuiserratum Zone (cf. Sykes and Callomon, 1979) were found 60 cm below the Upper Black Shale (UBS). No ammonites were found from the interval located 0–45 cm below the UBS. From the same interval of the Makar'yev section Mesezhnikov (1989) mentioned *C. (Mitcardioceras)* *tenuiserratum* (Oppel) and *C. (Mitcardioceras?) zietenii* Rouillier characteristic of the Tenuiserratum Zone. The oldest *Amoeboceras* fauna

consisting of *Amoeboceras ilovaiskii* (Sokolov) and *A. newbridgense* Sykes and Callomon indicative of the Ilovaiskii Subzone of the Glosense Zone of the Upper Oxfordian (cf. Sykes and Callomon, 1979) was found in the UBS. The same interval is exposed at Mikhalenino (cf. Głowniak et al., 2010).

The co-occurrence of Boreal (cardioceratids) and (Sub)Mediterranean (perispinctids, oppeliids and aspidoceratids) ammonites in the Mikhalenino section allowed the elaboration of a revised correlation scheme between the Boreal and Submediterranean ammonite zonation of Europe (cf. Głowniak et al., 2010). The correlation chart (Fig. 4) is adapted from Głowniak et al. (2010) and supplemented with unpublished data on the position of Submediterranean Plicatilis–Transversarium zone boundary found in the Makar'yev section (E. Głowniak, personal communication).

4. Methodology

Thin sections prepared from the belemnite rostra collected were studied by means of cold-cathode cathodoluminescence microscopy. Non-luminescent rostra were subsequently cleaned with a micro-drill to remove adherent sediment, apical line infillings and, if necessary, external, luminescent rims (Fig. 5). Whole-dimensional fragments of belemnite rostra were powdered and homogenized to get average isotope values. Aliquots of the carbonate powders were used for the trace element and the isotope analysis. Trace element contents (Ca, Mg, Sr, Mn, Fe) were determined using the ICP-OES method after dissolving the carbonate powders in 5% hydrochloric acid.

Powdered and homogenized parts of aragonitic shells (including fragments of external walls of adult portions of ammonite shells and fragments of a few gastropod shells) were screened for a potential contribution of diagenetic calcite using the X-ray diffraction method. 1–2 subsamples taken from each specimen were studied. Powdered samples were scanned from 25° to 75° 2 θ using a D8 Advance Bruker AXS diffractometer with CoK α radiation. X-ray diffractograms were examined for the strongest reflections of the calcite and aragonite phases. Quantitative estimation of the mineral phases was performed by Rietveld analysis using Topas software. The preservation state of the original microstructure of pure aragonitic (>99%) shells was examined with a scanning electron microscope.

Carbonate samples were reacted with 100% H₃PO₄ at 70 °C in an online, automated carbonate reaction device (Kiel IV) connected to

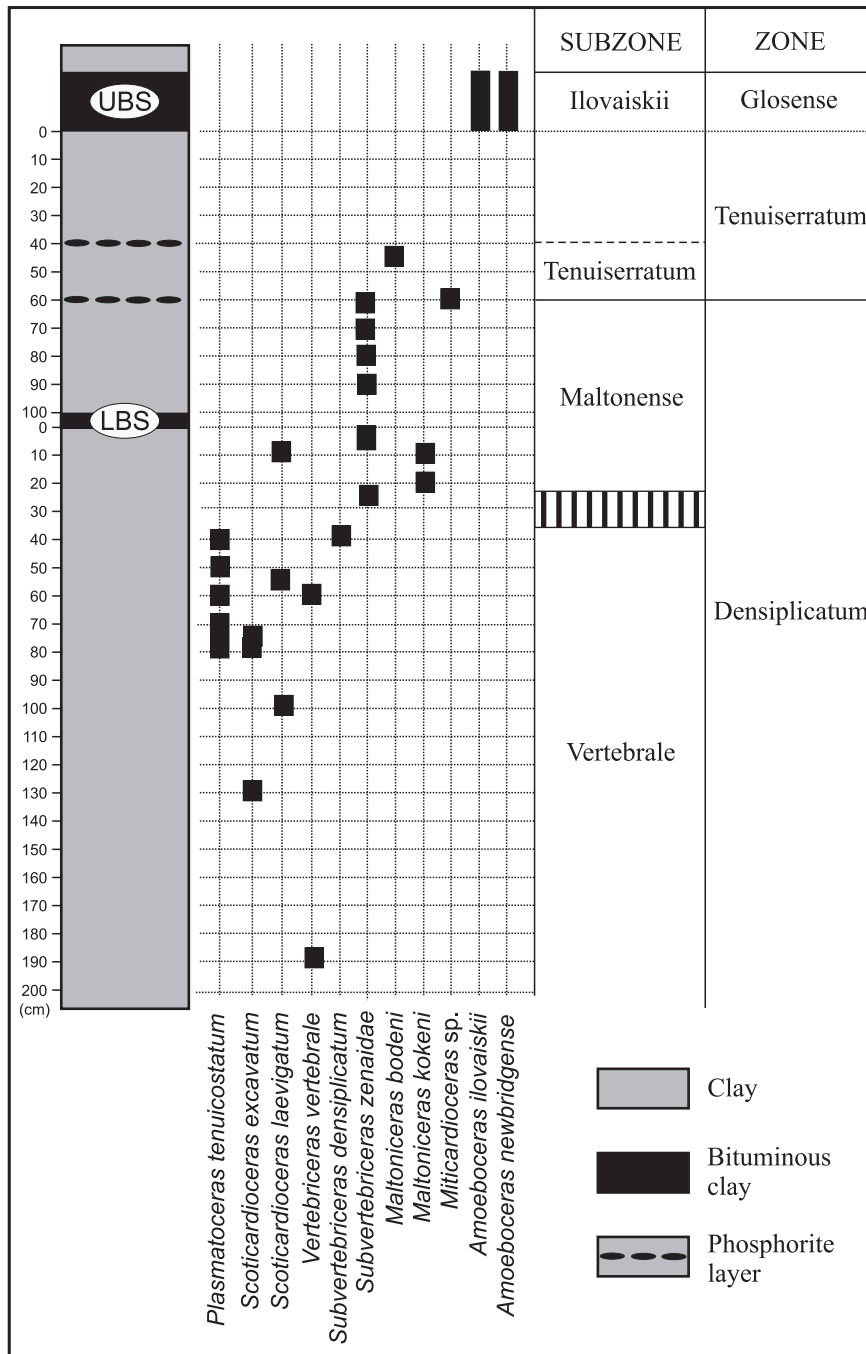


Fig. 3. Lithology, stratigraphy, and ammonite ranges in the Middle–lowermost Upper Oxfordian of the Makar'ev section. LBS – Lower black shale, UBS – upper black shale.

a Finnigan Mat Delta Plus mass spectrometer at the Institute of Geological Sciences, Polish Academy of Sciences in Warsaw. Isotopic ratios were referenced to NBS19 standard ($\delta^{13}\text{C} = 1.95\text{‰}$, $\delta^{18}\text{O} = -2.20\text{‰}$). The oxygen isotope composition of aragonite was calculated from the $\delta^{18}\text{O}$ value of evolved CO_2 using an acid fractionation factor of 1.00883, which is the estimated value of the conventional acid fractionation factor for aragonite at 70 °C (conventional $\alpha_{\text{CO}_2\text{-aragonite}}$ amounts to 1.01034 at 25 °C; see Friedman and O'Neil (1977)). Its estimated value for 70 °C was calculated using the temperature dependence of the factor given by Kim et al. (2007) although the absolute values of the factor reported by Kim et al. (2007) differ from conventional ones). All oxygen and carbon isotope results are reported in δ notation in per mil relative to the VPDB international standard. Reproducibility (1σ) of isotope

measurements was checked by replicate analysis ($n = 271$) of oxygen isotope composition of laboratory reference and was better than $\pm 0.05\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.17\text{‰}$ for $\delta^{18}\text{O}$.

Paleotemperatures were calculated from the oxygen isotope composition of calcitic belemnite rostra using Eq. (1) of O'Neil et al. (1969) modified by Friedman and O'Neil (1977) and SMOW to PDB scales conversion given by Friedman and O'Neil (1977)

$$10^3 \ln \alpha_{\text{calcite-water}} = 2.78 \cdot 10^6 / T^2 - 2.89 \tag{1}$$

where $\alpha_{\text{calcite-water}}$ is equilibrium fractionation factor between calcite and water, T is the temperature in Kelvin.

SUBMEDITERRANEAN PROVINCE				BOREAL PROVINCE			
Substage	Zone	Subzone	Position of the base (digital units)	Position of the base (digital units)	Subzone	Zone	Substage
Lower Kimmeridgian	Platynota	Guilherandense	25.5	24.5	Modestum	Kitchini	Lower Kimmeridgian
		Desmoides	24.5				
		Polygyratus	23.5	22.5	Subkitchini		
Upper Oxfordian	Planula	Galar	22.5			19	
		Planula	21				
	Bimammatum	Hauffianum	20				
		Bimammatum	19				
Upper Oxfordian	Bifurcatus	Hypselum	18	18	Rosenkrantzi	Upper Oxfordian	
		Grossouvrei	17	17.10	Serratum		
		Stenocycloides	16	16.73	Serratum		
		Wartae	15	16.33	Koldeweyense		
Middle Oxfordian	Transversarium	Elisabethae	14	14.44	Ilovaiskii	Middle Oxfordian	
		Buckmani	13	13.75	Blakei		
		Arkeili	12	13.50	Tenuiserratum		
	Plicatilis	Ouatius	11	10	Vertebrale		Densiplicatum
		Patturatensis	10				
Lower Oxfordian	Cordatum	Cordatum	9	9	Cordatum	Lower Oxfordian	
		Costicardia	8	8	Costicardia		
		Bukowskii	7	7	Bukowskii		
	Mariae	Praecordatum	6	6	Praecordatum		Mariae
		Scarburgense	5	5	Scarburgense		
Upper Callovian	Lamberti	Lamberti	4	4	Lamberti	Upper Callovian	
		Henrici	3	3	Henrici		
	Athleta	Spinosum	2	2	Spinosum		Athleta
		Proniae	1	1	Proniae		
		Phaeinum	0	0	Phaeinum		

Fig. 4. Correlation of the Submediterranean and Boreal ammonite zonal schemes (after Głowniak et al., 2010, and E. Głowniak – personal information).

Temperatures calculated for the measured range of $\delta^{18}\text{O}_{\text{calcite}}$ values using the equation of O'Neil et al. (1969) modified by Friedman and O'Neil (1977) are 0–1.5 °C lower than the temperatures calculated

using Eq. (2) of Epstein et al. (1953) corrected by Craig (1965) and modified by Anderson and Arthur (1983)

$$T(^{\circ}\text{C}) = 16.0 - 4.14 * (\delta_c - \delta_w) + 0.13 * (\delta_c - \delta_w)^2 \quad (2)$$

where δ_c is the oxygen isotope composition of carbonate in the PDB scale and δ_w is the oxygen isotope composition of water in the SMOW scale. Eq. (2) of Anderson and Arthur (1983), albeit frequently used for skeletal calcite, is based on aragonite–calcitic mollusc shells (see Epstein et al., 1953). Paleotemperatures calculated using Eq. (2) of Anderson and Arthur (1983) are shown on figures for comparison.

Paleotemperatures from aragonite fossils were calculated using the corrected version (3) of the equation of Grossman and Ku (1986) established for “molluscs”. The equation of Grossman and Ku (1986) for “molluscs” had to be standardized to the SMOW scale as the original $\delta^{18}\text{O}$ values of ambient water were reported vs. “average marine water” being 0.2‰ depleted in ^{18}O in comparison to the SMOW (cf. Grossman and Ku, 1986)

$$T(^{\circ}\text{C}) = 21.8 - 4.69 * (\delta^{18}\text{O}_{\text{aragonite}} - (\delta^{18}\text{O}_{\text{water}} - 0.2)) \quad (3)$$

where $\delta^{18}\text{O}_{\text{aragonite}}$ is the isotope composition of shell aragonite vs. PDB and $\delta^{18}\text{O}_{\text{water}}$ is the isotope composition of ambient water vs. SMOW.

Temperatures calculated for the measured range of $\delta^{18}\text{O}_{\text{aragonite}}$ values using the equation of Grossman and Ku (1986) established for

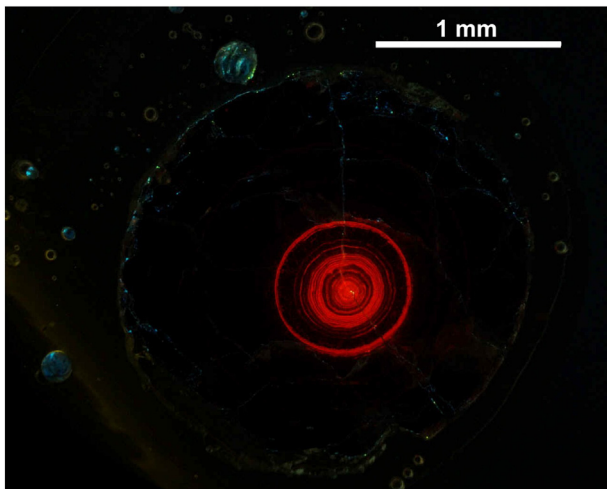


Fig. 5. Cathodoluminescence photomicrographs of non-luminescent *Hibolites cf. orlovi* rostrum with luminescent apical line area. Sample RM114, Maltonense Subzone, Densiplicatum Zone, Middle Oxfordian, Makar'yev section.

“molluscs” are 0.3–1.4 °C higher than the temperatures calculated using the Eq. (4) of Grossman and Ku (1986) for “all data”. The equation of Grossman and Ku (1986) for “all data” had been standardized to the SMOW scale

$$T(^{\circ}\text{C}) = 20.6 - 4.34 * (\delta^{18}\text{O}_{\text{aragonite}} - (\delta^{18}\text{O}_{\text{water}} - 0.2)) \quad (4)$$

where $\delta^{18}\text{O}_{\text{aragonite}}$ is the isotope composition of shell aragonite vs. PDB and $\delta^{18}\text{O}_{\text{water}}$ is the isotope composition of ambient water vs. SMOW. Paleotemperatures calculated using the Eq. (4) of Grossman and Ku (1986) for “all data” are shown on the figures for comparison.

Temperatures assessed tentatively on Mg/Ca ratios of cylindroteuthid belemnites were calculated from the relationship given by Nunn and Price (2010)

$$T(^{\circ}\text{C}) = \ln[(\text{Mg}/\text{Ca})/1.2]/0.11 \quad (5)$$

where Mg/Ca ratio of calcite is in mmol/mol.

All the data were correlated with both Boreal and the Submediterranean ammonite zonation (Fig. 4). The vertical scale of the presented diagrams is based on assumed equal duration of Submediterranean ammonite subchrons to enable correlations with Tethyan areas.

5. Diagenetic alteration

The oxygen and carbon isotope ratios of carbonate rocks are prone to diagenetic alteration. An assessment of the degree of diagenetic alteration of calcite can be made using trace element concentrations and cathodoluminescence studies. Diagenetic alteration often causes an increase in Fe and Mn contents in calcite and a decrease in its Sr contents as concentrations of these elements drastically differ between seawater and diagenetic fluids in reduced or freshwater environments (Veizer, 1974, 1983; Marshall, 1992). Mn^{2+} ions are also an activator of orange-red cathodoluminescence that is distinctive of diagenetically altered calcites (Marshall, 1992; Savard et al., 1995). Strict criteria were used for the selection of the best preserved material. The belemnite rostra used were non-luminescent (small luminescent rostra parts were sometimes removed before preparation, Fig. 5) and characterized by low Fe (<200) and Mn (<100 ppm) and high Sr concentrations (>800 ppm; Supplementary Table S2). Although slightly different threshold levels of element concentrations in well-preserved belemnite rostra were given by various authors, the reported values are commonly employed (cf. Veizer, 1974; Veizer et al., 1999; Price et al., 2000; Gröcke et al., 2003; Price and Rogov, 2009; Wierzbowski and Rogov, 2011).

Aragonite is metastable, therefore, aragonite shells are uncommon in Mesozoic deposits. Diagenetic alteration of the microstructure of pure aragonitic ammonite and bivalve shells has also been observed by various authors (Dauphin and Denis, 1990; Wierzbowski and Joachimski, 2007; Cochran et al., 2010; Wierzbowski and Rogov, 2011). All ammonoid and gastropod samples that contained minor traces of calcite (>1%) were excluded from further investigations. Investigated samples were characterized by well-defined nacreous tablets devoid of signs of re-crystallization and dissolution (Fig. 6A). Samples characterized by the alteration of the microstructure were excluded from isotope analyses (Fig. 6B).

6. Results

6.1. $\delta^{18}\text{O}$ values

Measured $\delta^{18}\text{O}$ values of Middle Oxfordian–Lower Kimmeridgian samples were supplemented with the Upper Callovian–Lower Oxfordian data of Wierzbowski and Rogov (2011) from the Dubki section (51° 40' 21" N, 46° 1' 17" E) and depicted in Fig. 7. $\delta^{18}\text{O}$ values of

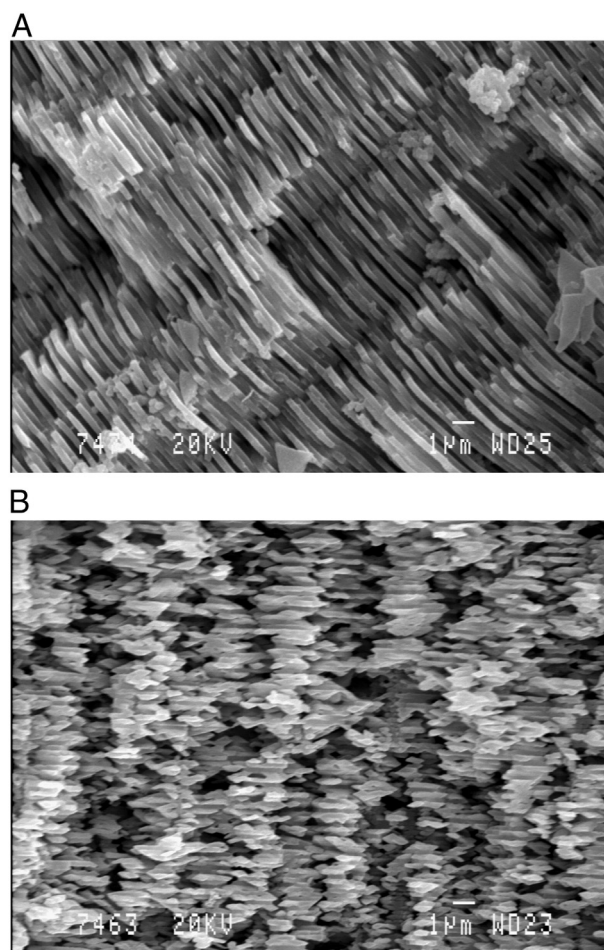


Fig. 6. SEM photomicrographs of nacreous layer of aragonite shells (>99% aragonite). (A) Well-preserved microstructure of the nacreous layer of *Amoeboceeras ilovaiskii*, sample RM65, Ilovaiskii Subzone, Glosense Zone, Upper Oxfordian, Mikhalenino section. (B) Dissolution and aggregation of nacreous tablets of an undetermined ammonite, Subkitchini Subzone, Kitchini Zone, Lower Kimmeridgian, Mikhalenino section.

cylindroteuthid belemnites range from –0.6 to 2.8‰ (mean of 1.6‰) in the Upper Callovian and Lower and the Middle Oxfordian (Lamberti to Tenuiserratum zones). $\delta^{18}\text{O}$ values of cylindroteuthid belemnites decrease gradually starting from the Upper Oxfordian Glosense Zone. Lowest cylindroteuthid $\delta^{18}\text{O}$ values of –1.3 to 0.0‰ (mean of –0.7‰) are noted in the Lower Kimmeridgian Kitchini Zone. $\delta^{18}\text{O}$ values of mesohibolitid belemnites range from –0.6 to 1.4‰ (mean of 0.8‰) in the Upper Callovian–lowermost Upper Oxfordian (Lamberti to Glosense zones). $\delta^{18}\text{O}$ values of mesohibolitid belemnites are a bit more scattered with two lower values (–0.6 and –0.4‰) in the upper part of the Middle Oxfordian Densiplicatum Zone. Mesohibolitid belemnites do not occur in strata younger than lowermost Upper Oxfordian (Glosense Zone).

$\delta^{18}\text{O}$ values of well-preserved ammonite shells range from –2.6 to 1.3‰ (mean of –0.3‰) in the interval from the Upper Callovian to the lowermost Upper Oxfordian (Lamberti to Glosense zones; Fig. 7). Well-preserved ammonite shells were not found in younger strata. Lowest ammonite $\delta^{18}\text{O}$ values (between –2.6 and –0.6‰, mean of –1.5‰) are observed at the Middle–Upper Oxfordian boundary (Blakei Subzone of the Tenuiserratum Zone and the Ilovaiskii Subzone of the Glosense Zone, within UBS and its proximity) and in the Vertebrales Subzone of the Densiplicatum Zone of the Middle Oxfordian. $\delta^{18}\text{O}$ values of three *Bathrotomaria* samples derived from the Densiplicatum Zone of the Middle Oxfordian range from 0.9 to 1.3‰ (mean of 1.1‰).

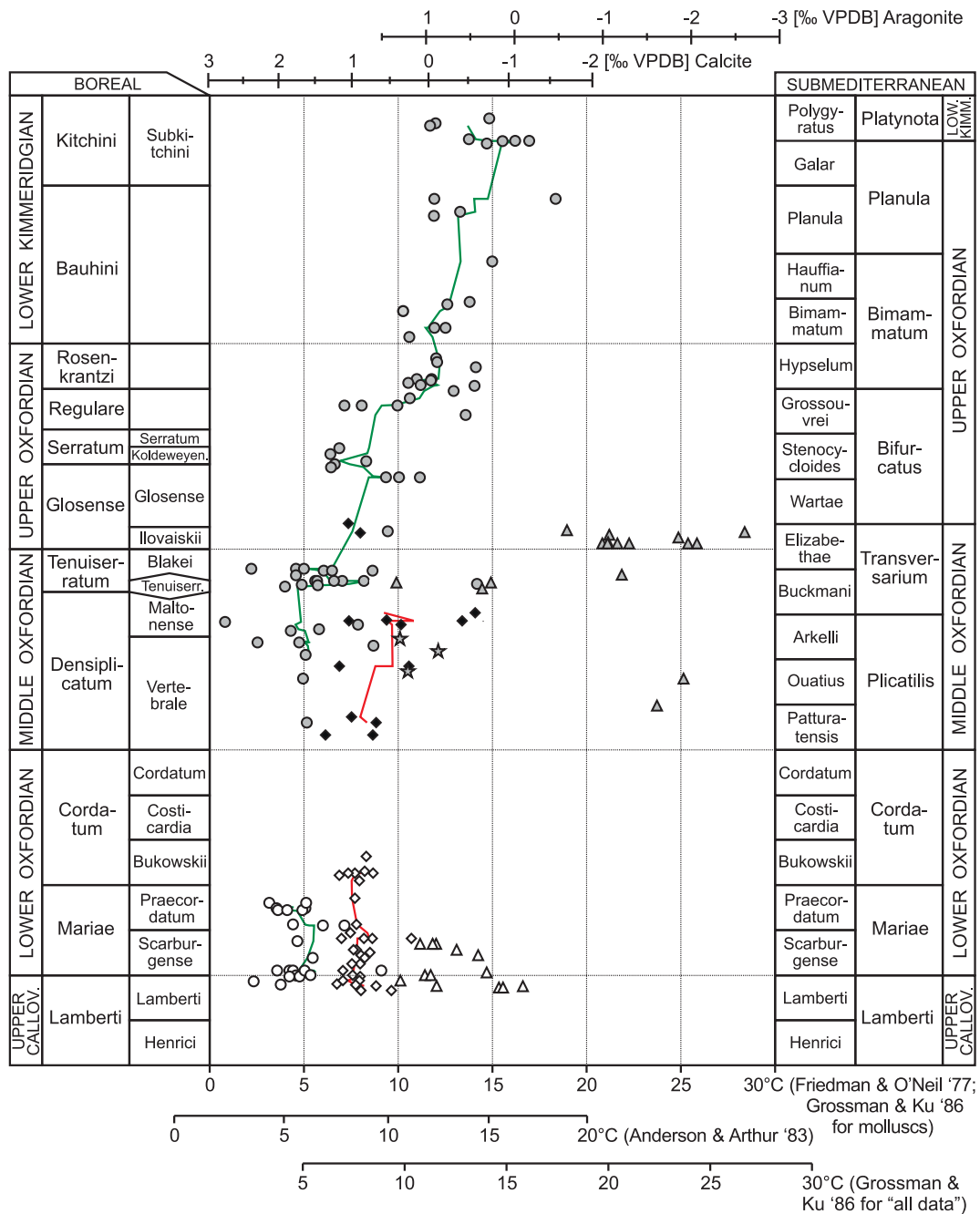


Fig. 7. Stratigraphy, $\delta^{18}\text{O}$ values and paleotemperatures calculated from $\delta^{18}\text{O}$ values of well-preserved belemnite rostra, ammonite and gastropod shells from the Dubki, Makar'yev and Mikhalevino sections. Filled symbols – data from the present study, open symbols – data from Wierzbowski and Rogov (2011). Circles – cylindroteuthid rostra, diamonds – mesohibolitid rostra, triangles – ammonite shells, stars – *Bathrotomaria* gastropod shells. Curves represent 5-point running averages for cylindroteuthid and mesohibolitid data.

6.2. Mg/Ca ratios

Measured Mg/Ca ratios of Middle Oxfordian–Lower Kimmeridgian belemnite rostra were supplemented with ratios calculated from the elemental contents of Upper Callovian–Lower Oxfordian rostra reported by Wierzbowski and Rogov (2011; see Supplementary Table S2). Mg/Ca ratios of cylindroteuthid belemnites, which are regarded as a valuable paleotemperature proxy, vary between 3.9 and 10.7 mmol/mol in the entire interval studied (Fig. 8). Most of Mg/Ca ratios of cylindroteuthid belemnite oscillate between 3.9 and 7.6 mmol/mol in the Upper Callovian, Oxfordian and lowermost Lower Kimmeridgian (lower part of the Bauhini Zone) forming an average trend of ca. 5.5 mmol/mol. An increase of the Mg/Ca ratios

of cylindroteuthid belemnites to 5.3–9.2 mmol/mol (mean of 7.1) is observed in the uppermost part of the Lower Kimmeridgian Bauhini Zone and in the Kitchini Zone.

6.3. Sr/Ca ratios

Sr/Ca ratios of cylindroteuthid belemnites supplemented with ratios calculated from the data of Wierzbowski and Rogov (2011; see Supplementary Table S2) show a clear temporal trend (Fig. 8). Sr/Ca ratios vary between 0.97 and 1.22 mmol/mol (mean of ca. 1.08 mmol/mol) in the Upper Callovian, Lower and the Middle Oxfordian (Lamberti, Mariae, Densiplacatum and Tenuiserratum zones). Sr/Ca ratios of cylindroteuthid belemnites rise gradually starting from the lowermost Upper Oxfordian

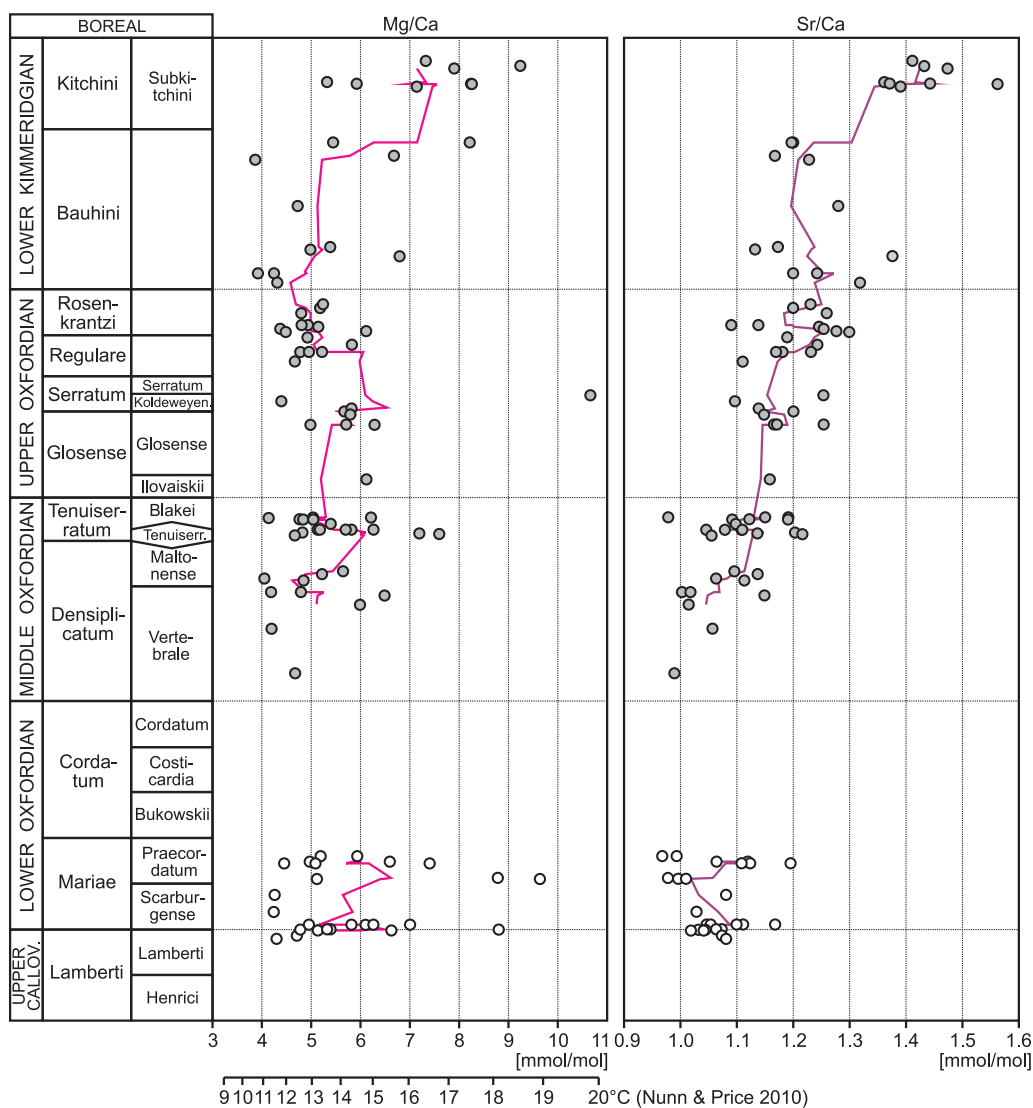


Fig. 8. Stratigraphy, Mg/Ca and Sr/Ca ratios values of well-preserved cylindroteuthid belemnite rostra from Dubki, Makar'yev and Mikhalenino sections. Symbols as in Fig. 7. Curves represent 5-point running averages for cylindroteuthid data.

Glosense Zone and reach a range of 1.13 to 1.38 mmol/mol (mean of 1.23 mmol/mol) in the Bauhini Zone of the Lower Kimmeridgian. Further rapid rise of cylindroteuthid Sr/Ca ratios to 1.36–1.56 mmol/mol (mean of 1.43 mmol/mol) is observed in the Kitchini Zone of the Lower Kimmeridgian.

6.4. $\delta^{13}\text{C}$ values

Cylindroteuthid and mesohibolitid $\delta^{13}\text{C}$ values (current data supplemented with the data of Wierzbowski and Rogov, 2011) are characterized by a wide scatter and vary between 1.0 and 3.8‰ in the whole interval investigated (Fig. 9). The highest belemnite $\delta^{13}\text{C}$ values are observed in the Upper Callovian and the Lower–Middle Oxfordian (Lamberti to Tenuiserratum zones; calculated running averages of 2.2 to 3.1‰), whereas a decrease to mean values of 1.7 to 2.5‰ is observed in the Upper Oxfordian and lowermost Lower Kimmeridgian (Glosense to the Bauhini Zone). In the upper part of the Bauhini Zone and in the lower part of the Kitchini Zone of the Lower Kimmeridgian a slight increase of the average $\delta^{13}\text{C}$ of belemnite rostra to 2.4–2.9‰ is observed. $\delta^{13}\text{C}$ values of well-preserved ammonite shells are characterized by significant scatter (up to 4.9‰; Supplementary Table S1) showing no temporal trend, therefore, they are not depicted.

6.5. Differences in δ values of various groups of fossils

$\delta^{18}\text{O}$ values of co-occurring cylindroteuthids and mesohibolitids show constant difference of ca. 0.7‰ with mesohibolitids characterized by lower values (Fig. 7).

Ammonite $\delta^{18}\text{O}$ values (current data supplemented with the data of Wierzbowski and Rogov, 2011) can be divided into two groups: one from the Upper Callovian–Lower Oxfordian boundary (the Lamberti and Mariae zones) and from the Tenuiserratum Subzone of the Tenuiserratum Zone with values of -0.1 to 1.3 ‰ (mean of 0.7 ‰) and another one from the Vertebrale Subzone of the Densipilatum Zone and the Middle–Late Oxfordian boundary (the Blakei Subzone of the Tenuiserratum Zone and the Ilovaiskii Subzone of the Glosense Zone) with much lower $\delta^{18}\text{O}$ values of -0.6 to -2.6 ‰ (mean of -1.5 ‰; Fig. 7).

$\delta^{13}\text{C}$ values of coeval mesohibolitids and cylindroteuthids are similar to each other (Fig. 9). No remarkable difference is also found among the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of co-occurring species of Middle Oxfordian cylindroteuthid belemnites (Fig. 10).

6.6. Variations in Mg/Ca and Sr/Ca ratios of belemnites

Mesohibolitid belemnites (genus *Hibolites*) show much higher Mg/Ca ratios (8.9 to 20.6 mmol/mol) compared to the ratios of

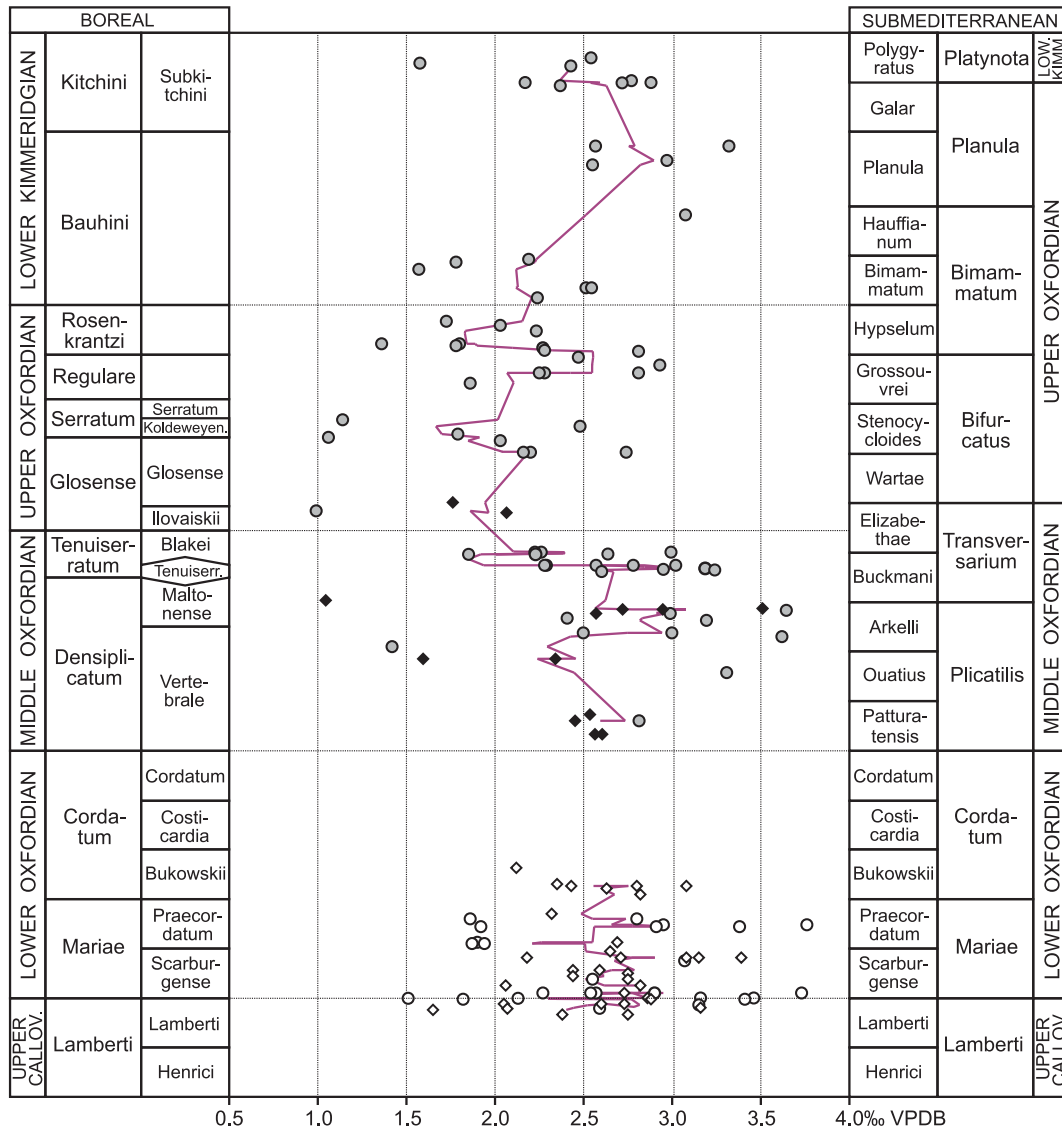


Fig. 9. $\delta^{13}\text{C}$ values of well-preserved belemnite rostra from the Dubki, Makar'yev and Mikhalenino sections. Symbols as in Fig. 7. The curve represent 5-point running averages for the entire dataset.

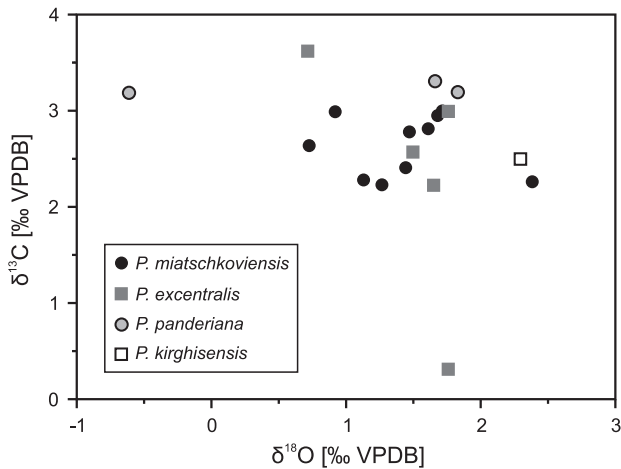


Fig. 10. $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ values of well-preserved Middle Oxfordian cyliodreuthid rostra (genus *Pachyteuthis*). No difference between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of various *Pachyteuthis* species is observed.

cyliodreuthids (3.9 to 10.7 mmol/mol; Supplementary Table S2). Sr/Ca ratios of mesohibolitic belemnites (1.2 to 1.7 mmol/mol) are slightly higher than cyliodreuthids (1.0 to 1.6 mmol/mol; Supplementary Table S2). No remarkable differences are found in Mg/Ca ratios of co-occurring species of Middle Oxfordian cyliodreuthid belemnites (Fig. 11). Sr/Ca ratios of Middle Oxfordian cyliodreuthid species *Pachyteuthis miatschkoviensis* despite overlapping with the Sr/Ca ratios of *P. excentralis* and *P. panderiana* show a somewhat lower average ratio (a difference in Sr/Ca ratio of 0.06 mmol/mol; Fig. 11). The Sr/Ca ratios of Upper Callovian–Lower Kimmeridgian cyliodreuthids correlate positively with their $\delta^{18}\text{O}$ values (Fig. 12).

7. Discussion

7.1. Oxygen isotopes and temperatures

Belemnites, ammonites and gastropods are considered to have precipitated calcium carbonate in oxygen isotope equilibrium with ambient seawater (Grossman and Ku, 1986; Wierzbowski, 2002; Lécuyer et al., 2004; Rosales et al., 2004; Wierzbowski and Joachimski, 2007; Price and Page, 2008; Nunn et al., 2009; Price and Rogov, 2009; Lukeneder et al., 2010; Nunn and Price, 2010; Wierzbowski and Rogov, 2011).

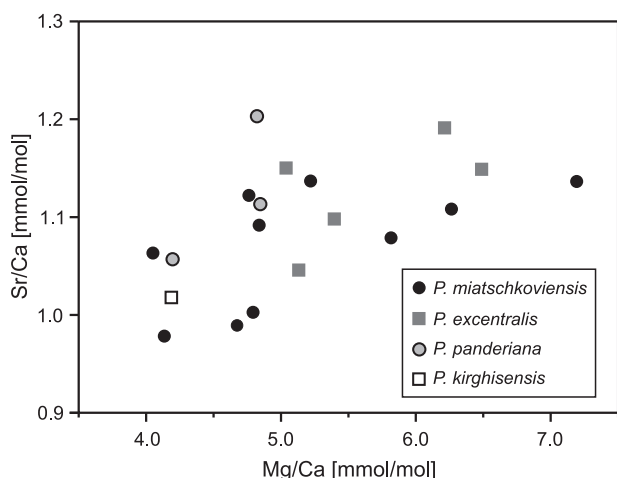


Fig. 11. Mg/Ca ratios versus Sr/Ca ratios of well-preserved Middle Oxfordian cyldroteuthid rostra (genus *Pachyteuthis*). No significant difference between Mg/Ca ratios versus Sr/Ca ratios of various *Pachyteuthis* species is observed.

Paleotemperatures were calculated from $\delta^{18}\text{O}$ values of well-preserved shells assuming normal marine salinity of the Middle Russian Sea and the commonly accepted $\delta^{18}\text{O}$ value of Jurassic seawater of -1‰ SMOW as distinctive of an ice-free world (Shackleton and Kennett, 1975). Temperatures calculated with the $\delta^{18}\text{O}$ values of Upper Callovian–Middle Oxfordian cyldroteuthid belemnites (average of ca. $5\text{ }^{\circ}\text{C}$; Fig. 7) are surprisingly low. High $\delta^{18}\text{O}$ cyldroteuthid values are compatible with the normal-marine or slightly increased salinity of ambient waters. The cyldroteuthid temperatures would increase a little if the temperature equation of Anderson and Arthur (1983) is employed (Fig. 7). Mesohibolitid belemnites (genus *Hibolites*) show higher temperatures (average of ca. $8.5\text{ }^{\circ}\text{C}$) than co-occurring cyldroteuthids. A minor increase in temperatures calculated from $\delta^{18}\text{O}$ values of youngest Middle Oxfordian mesohibolitid belemnites is additionally observed (Fig. 7). The highest temperatures are calculated from Upper Callovian–Middle Oxfordian ammonite $\delta^{18}\text{O}$ values (average of ca. $15\text{ }^{\circ}\text{C}$).

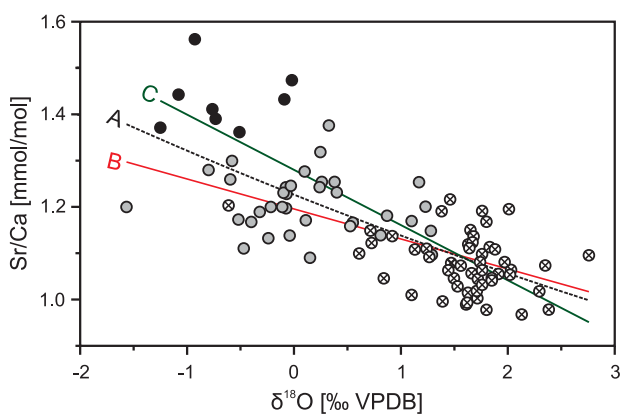


Fig. 12. Sr/Ca ratios versus $\delta^{18}\text{O}$ values of well-preserved cyldroteuthid rostra from the Upper Callovian–Lower Kimmeridgian (present data supplemented with ratios calculated from data of Wierzbowski and Rogov, 2011). Crossed circles – Upper Callovian and Lower–Middle Oxfordian data, gray circles – Upper Oxfordian and Lower Kimmeridgian Bauhini Zone data, black circles – Lower Kimmeridgian Kitchini Zone data. Trend A – relationship between all Sr/Ca ratios and $\delta^{18}\text{O}$ values, $R^2 = 0.55$, $\text{Sr/Ca} = 1.227 * \exp(-0.075 * \delta^{18}\text{O})$; Trend B – relationship between Sr/Ca ratios and $\delta^{18}\text{O}$ values from the Upper Callovian, Lower–Middle Oxfordian, Upper Oxfordian and Lower Kimmeridgian Bauhini Zone, $R^2 = 0.45$, $\text{Sr/Ca} = -0.065 * \delta^{18}\text{O} + 1.196$; Trend C – relationship between Sr/Ca ratios and $\delta^{18}\text{O}$ values from the Upper Callovian, Lower–Middle Oxfordian and the Lower Kimmeridgian Kitchini Zone, $R^2 = 0.67$, $\text{Sr/Ca} = -0.119 * \delta^{18}\text{O} + 1.128$.

A significant range of calculated paleotemperatures points to thermal stratification and to different depth habits of the studied animals. Cyldroteuthid belemnites are considered to have occupied the deepest and coldest environments, mesohibolitid belemnites a bit shallower depth, whereas ammonites seem to have lived in subsurface waters (cf. Wierzbowski and Rogov, 2011). It is worth noting that comparable pattern of depth segregation is observed for modern boreal and tropical squids in the shelf area of northwestern Africa (Arkhipkin and Laptikhovskiy, 2006).

Cyldroteuthid and mesohibolitid belemnites are interpreted to have been nektobenthic (Anderson et al., 1994; Wierzbowski, 2002; Wierzbowski and Joachimski, 2007; Price and Teece, 2010; Wierzbowski and Rogov, 2011) although mesohibolitids were also regarded as nektonic deep-water dwellers (Price and Page, 2008; Alberti et al., 2012a; Mutterlose et al., 2012). Both group of belemnites studied may be found in the same place despite inhabiting different depths or bottom niches, as a consequence of occasional migrations e.g. for spawning or as a result of predation. The nektobenthic life style of the belemnites studied is substantiated by similar temperatures calculated from three benthic *Bathrotomaria* gastropods and coeval *Hibolites* and the rarity of calcitic belemnite rostra in organic-rich black shale layers (LBS and UBS in the Maltonense Subzone of the Densiplicatum Zone and the Ilovaikii Subzone of the Glosense Zone), which were deposited under decreased oxygen content (cf. Bushnev et al., 2006). Only a few juvenile rostra were found in the black shales despite the presence of abundant nektonic ammonite fauna there and numerous findings of aragonitic belemnite rostra. The belemnite rostra differ from other belemnites in morphology and are regarded as slow-swimming forms inhabiting shallow depths (cf. Rogov and Bizikov, 2006).

Ammonite data from the Callovian–Oxfordian boundary and the Tenuiserratum Subzone of the Tenuiserratum Zone translates into temperatures of $10\text{--}16.5\text{ }^{\circ}\text{C}$ (average of $13\text{ }^{\circ}\text{C}$). Ammonite temperatures calculated using data from the Vertebrata Subzone of the Densiplicatum Zone and from the Middle–Upper Oxfordian boundary are much higher ($19\text{--}28.5\text{ }^{\circ}\text{C}$; average of $23\text{ }^{\circ}\text{C}$). Although the former group of ammonites consist of cardioceratids and oppellids and the latter predominantly of perisphinctids it is not clear if the difference in ammonite $\delta^{18}\text{O}$ values can be related to taxonomic factors (cf. Wierzbowski and Rogov, 2011; see also Supplementary Table S2). The temperatures of ca. $13\text{ }^{\circ}\text{C}$ may represent temperatures of the upper part of the water column of a cool basin. The temperatures of ca. $23\text{ }^{\circ}\text{C}$ may point to the existence of a large temperature gradient within the water column, although no isotope data from belemnites are derived from the interval with low ammonite $\delta^{18}\text{O}$ values. It is also possible that the latter temperatures may be overestimated due to the freshwater influx to surface waters. Most low ammonite $\delta^{18}\text{O}$ values derive from the black shale layer within the Ilovaikii Subzone or its proximity. It is likely that the organic-rich shale was deposited under a water stratification that favored the accumulation of organic matter (Hantzpergue et al., 1998; Bushnev et al., 2006). The lowermost Upper Oxfordian organic-rich shale layer has a regional extent and is known from the Moscow area (Hantzpergue et al., 1998). Its deposition may be linked to the enhanced influx of nutrients from neighboring land areas and an increase in surface water bioproductivity (cf. Shchepetova et al., 2011). The enhanced flux from lands may have been connected with the freshwater input. Ammonites might have preyed in fertile surface waters characterized by decreased salinity and $\delta^{18}\text{O}$ values avoiding deep waters below the halocline characterized by a diminished oxygen content. This model could explain the low $\delta^{18}\text{O}$ values of ammonites in the intervals rich in organic matter.

A range of average temperatures ($5\text{--}15\text{ }^{\circ}\text{C}$) calculated from $\delta^{18}\text{O}$ values of the Upper Callovian (Lamberti Zone) and the Lower–Middle Oxfordian (Cordatum, Densiplicatum, Tenuiserratum zones) cyldroteuthid and mesohibolitid rostra as well as ammonite shells (Fig. 7) points to a considerable vertical thermal gradient in the

water column and the presence of cold bottom waters in the Middle Russian Sea during the latest Callovian–Middle Oxfordian. Differences in the temperature regime of the sea may however have existed between the Late Callovian–Early Oxfordian and the Middle Oxfordian due to different paleolatitudes of Dubki and Makar'yev–Mikhailenino outcrops (Fig. 1).

The remarkable and constant $\delta^{18}\text{O}$ decrease (of ca. 2.3‰) of Upper Oxfordian and Lower Kimmeridgian cylindroteuthid belemnites from Mikhailenino (Fig. 7) may result from warming of the bottom waters. The decrease in the $\delta^{18}\text{O}$ values is not connected with changing occurrences of cylindroteuthid genera and species as no difference in the isotope composition of various cylindroteuthid taxa was found in the Upper Callovian–Middle Oxfordian (Fig. 10; see also Wierzbowski and Rogov, 2011). This interval is characterized by approximately constant δ values of cylindroteuthids, and therefore may be treated as reference level for the determination of potential differences in the isotope composition of their taxa. The Upper Oxfordian–Lower Kimmeridgian decrease in $\delta^{18}\text{O}$ values of cylindroteuthid belemnites, if treated solely as a result of a temperature increase, shows a warming of ca. 9.5 °C. The temperature rise may have resulted from climate warming or shallowing of the Volga basin during the Oxfordian sea-level fall (cf. Wierzbowski et al., 2009). It is also possible that the decrease in belemnite $\delta^{18}\text{O}$ values is partly caused by the increasing freshwater influx to the Volga basin during the Late Oxfordian and the Early Kimmeridgian. This question is irresolvable based solely on the oxygen isotope composition of fossils (see further discussion in Section 7.2.).

Oxygen isotope composition of cylindroteuthid belemnite rostra from the Russian Platform were reported previously from the Upper Callovian–Lower Kimmeridgian (Podlaha, 1995; Podlaha et al., 1998; Riboulleau et al., 1998; Barskov and Kiyashko, 2000). The previously published data were correlated with West-European ammonite zonation and given as evidence of severe cooling at the Callovian–Oxfordian boundary and subsequent warming in latest Early or the Middle Oxfordian (Dromart et al., 2003; Price and Rogov, 2009). We have re-correlated the available data from the Russian Platform based on revised correlation schemes (see Fig. 13). Moreover, we have corrected the position of some of the samples of Podlaha (1995) and Podlaha et al. (1998) based on the revised stratigraphy of the Peski (55° 12' 08" N, 38° 47' 20" E; after Smirnova et al., 1999) and the Rybinsk–Ioda river sections (57° 58' 45" N, 38° 53' 28" E; after Kiselev, 2003; see also Główniak et al., 2010). The published belemnite $\delta^{18}\text{O}$ data, despite being collected from various sections, are similar to our cylindroteuthid data in the Upper Callovian–Lower Oxfordian and partly similar, or partly lower, in the Middle Oxfordian–Lower Kimmeridgian interval (Fig. 13). The lower $\delta^{18}\text{O}$ values of some of the samples of Podlaha (1995), Podlaha et al. (1998) and Riboulleau et al. (1998) from the Voskresensk, Rybinsk–Ioda river and Makar'yev sections might result from unrecognized diagenetic alteration, as some of the samples of Podlaha (1995) and Podlaha et al. (1998) were characterized by elevated Fe contents (up to 1245 ppm) and decreased Sr concentrations (to 700 ppm), and data on the Mn and Fe concentrations in the samples of Riboulleau et al. (1998) are not available. The previously published data do nevertheless confirm the timing of the presence of cold bottom waters in the Middle Russian Sea. These very likely appeared at the beginning of the Late Callovian Lambert Chron and were present in the Volga Basin approximately till the end of the Boreal Middle Oxfordian i.e. the end of the Tenuiserratum Chron (unfortunately data are missing at the Tenuiserratum–Glosense zone boundary; Fig. 13). Likewise, the published data confirm the timing of a decrease in $\delta^{18}\text{O}$ values of Russian cylindroteuthid rostra starting from the Late Oxfordian Glosense Chron. The previous, erroneous timing of the decrease in the belemnite $\delta^{18}\text{O}$ values resulted from the incorrect correlation of the Boreal Alternoides Subzone of the Alternoides Zone (an equivalent of the Glosense Subzone of the Glosense Zone; Główniak et al., 2010) recognized in the Rybinsk–Ioda river section (cf. Podlaha, 1995; Podlaha et

al., 1998; Kiselev, 2003) with the Submediterranean Transversarium Zone (see Dromart et al., 2003). In addition, the revised stratigraphy of the Rybinsk–Ioda river section by Kiselev (2003) revealed a bigger thickness of the Serratium–Rosenkrantzi zones; see also the stratigraphic range of *A. ovale* (Quenstedt) and *A. tuberculatoalternans* (Nikitin) in Główniak et al. (2010). Data derived from the lowermost part of this interval, possibly comprising the Serratium Zone, were assigned to the Middle Oxfordian Transversarium Zone by Dromart et al. (2003). The data of Podlaha (1995) and Podlaha et al. (1998) from the Rybinsk–Ioda river section (described as Yaroslavl) were additionally incorrectly correlated with the Lower–Middle Oxfordian Cordatum and Plicatilis zones by Price and Rogov (2009).

7.2. Elemental ratios and temperatures

Mg/Ca and Sr/Ca ratios of belemnite rostra often correlate with their $\delta^{18}\text{O}$ values (McArthur et al., 2000, 2004, 2007a,b; Bailey et al., 2003; Rosales et al., 2004; Nunn and Price, 2010; Li et al., 2012). As the Mg/Ca ratios of calcitic foraminifers show exponential temperature dependence (Lea et al., 1999; Lear et al., 2002; Anand et al., 2003) similar dependence is suggested for belemnite rostra (Bailey et al., 2003; Nunn and Price, 2010). Despite the relation of the Sr/Ca ratio to metabolic activity and salinity in many biogenic low-Mg calcites (Klein et al., 1996; Lea et al., 1999; Stoll et al., 2007; Kısakürek et al., 2008), the Sr/Ca ratio was reported to be strongly temperature dependent in modern *Pecten* bivalves and some belemnite groups (Freitas et al., 2006; McArthur et al., 2007a; Li et al., 2012). Salinity is generally considered to have exerted a minor impact on the Mg/Ca ratios of biogenic calcites (Lea et al., 1999; Armendáriz et al., 2012). The temperature equations for belemnite Mg/Ca and Sr/Ca ratios were not given or have a speculative character (cf. Nunn and Price, 2010).

Interestingly, the Mg/Ca and Sr/Ca ratios of *Hibolites* show no temperature relation, or a weak one only (McArthur et al., 2004, 2007b; Bodin et al., 2009; Wierzbowski and Joachimski, 2009). The *Hibolites* rostra are interpreted to be characterized by different metabolic fractionation and higher Mg contents compared to the rostra of other co-occurring belemnites (McArthur et al., 2004, 2007b). This is confirmed by the results of the present study (see Supplementary Table S2). This restricts the utility of Mg/Ca and Sr/Ca ratios of *Hibolites* as a temperature proxy. For this reason, only Mg/Ca and Sr/Ca ratios of cylindroteuthid belemnites are presented and interpreted (Fig. 8).

The Mg/Ca ratios of cylindroteuthid rostra along with tentatively calculated temperatures are noisy in the whole studied interval. The mean cylindroteuthid Mg/Ca ratio, despite secondary oscillations, does not increase throughout the Upper Callovian–lowermost Lower Kimmeridgian. This might indicate relatively constant seawater temperatures. An increase of the mean cylindroteuthid Mg/Ca ratio of ca. 1.6 mmol/mol at the boundary of the Bauhini and the Kitchini zones of the Lower Kimmeridgian may be connected with a temperature rise of ca. 3 °C (Fig. 8). Similar temperatures rise is calculated in this interval from belemnite $\delta^{18}\text{O}$ values (Figs 7, 13).

Sr/Ca ratios of cylindroteuthid belemnites correlate with their $\delta^{18}\text{O}$ values (Figs 8, 12). It is likely that this indicates temperature dependence of the Sr/Ca ratio. The dependence of belemnite Sr/Ca ratios on $\delta^{18}\text{O}$ values was previously reported by McArthur et al. (2000), Bailey et al. (2003) and Li et al. (2012). A stepwise rise of the Sr/Ca ratio (of ca. 0.15 mmol/mol) of cylindroteuthids throughout the Middle–Upper Oxfordian and the lowermost Kimmeridgian (Fig. 8) may be linked to a gradual temperature increase. An abrupt rise of the cylindroteuthid Sr/Ca ratio of 0.2 mmol/mol in the Kitchi Zone of the Lower Kimmeridgian may be caused by sudden warming and correlates with the noticeable increase in Mg/Ca ratios (Fig. 8). The relationship between cylindroteuthid Sr/Ca ratios and $\delta^{18}\text{O}$ values is slightly different for “all data” (Fig. 12, line A), the data from the lower and the middle part of the section (devoid of Lower Kimmeridgian Kitchini Zone results, Fig. 12, line B) and the data

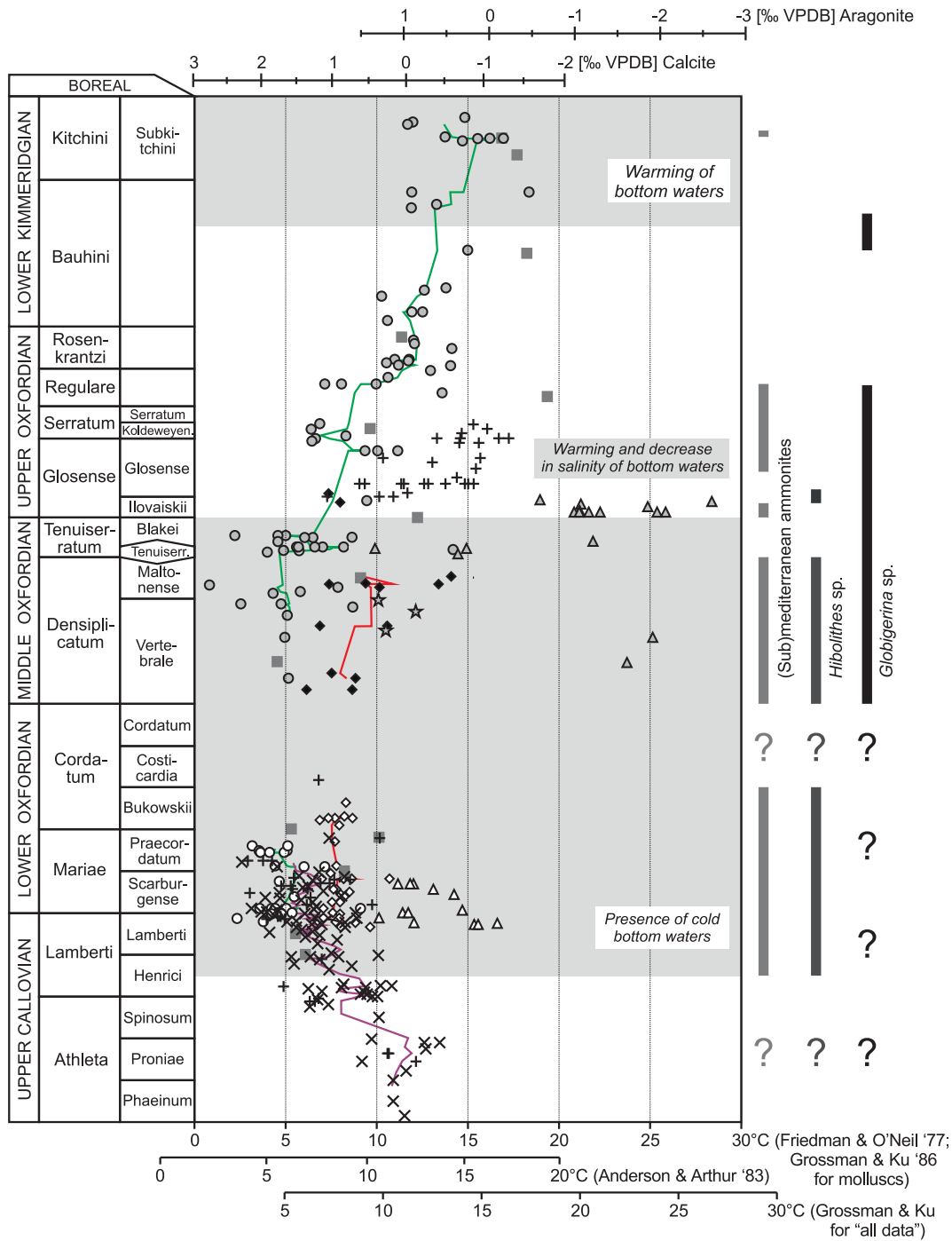


Fig. 13. Stratigraphy, faunistic ranges, $\delta^{18}O$ values and paleotemperatures calculated from new and published $\delta^{18}O$ values of well-preserved belemnite rostra, ammonite and gastropod shells from the Russian Platform. Symbols as in Fig. 7. Additional symbols: crosses – belemnite data of Podlaha (1995) and Podlaha et al. (1998; Peski, Rybinsk–Ioda river, Voskresensk); squares – belemnite data of Riboulleau et al. (1998; Makar'yev); Saint Andrew's crosses – belemnite data of Barskov and Kiyashko (2000; Mikhaylov, Gorenka and Shchelkovo). Curves represent 5-point running averages for the new cylindroteuthid and mesohibolitid data, the data of Wierzbowski and Rogov (2011) and the data of Barskov and Kiyashko (2000).

from the lower and uppermost part of the section (devoid of Upper Oxfordian and Lower Kimmeridgian Bauhini Zone results; Fig. 12, line C). The trend B may be affected by a decrease in salinity and water $\delta^{18}O$ values. The trend C, which only takes into account the abrupt Kitchini Zone Sr/Ca ratio increase, may represent the true temperature dependence of cylindroteuthid Sr/Ca ratio. The calculation of the effect of the freshwater on cylindroteuthid $\delta^{18}O$ values is possible using the difference in $\delta^{18}O$ values calculated from the equations of the trends B and C. The calculated freshwater effect on the cylindroteuthid $\delta^{18}O$ values during the Late Oxfordian–earliest

Kimmeridgian amounts to 0.7‰. This imposes a reduction of the temperature rise of bottom waters in the Late Oxfordian–earliest Kimmeridgian to 3.5 °C (compared to 6.5 °C calculated without the freshwater correction). The re-calculated temperature rise may have been followed by a return to normal marine salinity and a rapid warming of max. 6 °C at the Early Kimmeridgian Bauhini–Kitchini chron transition.

Mg/Ca and Sr/Ca ratios of cylindroteuthid belemnites are helpful in temperature reconstructions as an independent temperature proxy. It is likely that these indicate that the Late Oxfordian–earliest

Kimmeridgian temperature rise, which was calculated using belemnite $\delta^{18}\text{O}$ values from the Russian Platform, was lower, than previously assumed, due the freshwater influx. Abrupt warming is however noted at the transition of Early Kimmeridgian Bauhini and Kitchini chrons. The warming may have ranged between 3 and 6 °C as there is a slight discrepancy in calculations based on belemnite Mg/Ca and Sr/Ca ratios.

7.3. Faunistic changes

During the Late Callovian–earliest Middle Oxfordian Subboreal kosmoceratid and Boreal cardioceratid ammonites migrated southward and reached southern Europe, the northern Caucasus, Turkmenistan, Iran and the Western Interior of North America (Arkell, 1956; Hallam, 1971; Imlay, 1982; Callomon, 1985; Matyja and Wierzbowski, 1995; Majidifard, 2003; Page et al., 2009). The “Boreal spread” of ammonites (sensu Arkell, 1956) at the Middle–Late transition was linked to a global cooling (Dromart et al., 2003; Kiselev, 2004; Donnadieu et al., 2011). The “Boreal Spread” was however accompanied by the northern migration of (Sub)Mediterranean ammonites and marked faunal unification across Europe (Hallam, 1971; Callomon, 1985; Matyja and Wierzbowski, 1995; Cecca et al., 2005; Wierzbowski et al., 2009). This situation is apparent in the Upper Callovian–Middle Oxfordian of the Volga Basin in the Russian Platform where (Sub)Mediterranean ammonites (Aspidoceratidae, Perisphinctidae, Opelellidae) and belemnites are common to abundant (Fig. 13; see also Rogov, 2003; Matyja et al., 2009; Główniak et al., 2010; Wierzbowski and Rogov, 2011).

The migrations of Boreal and Tethyan ammonites in Europe during the Late Callovian–Early Middle Oxfordian are considered to be the result of a global sea-level rise and the opening of the land-locked Boreal Sea (Matyja and Wierzbowski, 1995; Cecca et al., 2005; Wierzbowski et al., 2009). The Early Oxfordian spread of planktonic foraminifers was also linked to a sea-level highstand (Brassier and Geleta, 1993; Oxford et al., 2002; Hudson et al., 2005). An apparent paradox of the co-occurrence of (Sub)Mediterranean ammonites and belemnites along with cold bottom waters may result from current activity and mixing of water masses in the Middle Russian Sea during the Late Callovian–Middle Oxfordian.

Occurrences of (Sub)Mediterranean ammonites in the Russian Platform become discontinuous at the Middle–Upper Oxfordian boundary, and they disappear in the Upper Oxfordian of this area (Rogov, 2003; Główniak et al., 2010). Tethyan mesohibolitid belemnites disappear a bit earlier – in the lowermost Upper Oxfordian of the Russian Platform (Fig. 13). Planktonic foraminifers also disappear in the Upper Oxfordian (Fig. 13; Azbel, 1989; Ustinova, 2009). Interestingly, this interval is characterized by increasing bottom temperatures as shown with $\delta^{18}\text{O}$ values, and Sr/Ca ratios of cylindroteuthid belemnites.

All Russian *Hibolites*, including the species known from Central and Southern Europe, are characterized by their small size (maximal diameter below 8 mm) compared to the much bigger *Hibolites* rostra found in (Sub)Mediterranean areas (cf. Gustomesov, 1976). The Upper Jurassic *Hibolites* belemnites are extremely rare in the Russian Platform north of the Unzha river (Gustomesov, 1976). This may indicate unfavorable conditions for their growth and breeding. The disappearance of Sub(Mediterranean) belemnites and ammonites from the Middle Russian Sea during the Late Oxfordian may thus be related to a restriction in marine connections that prevented migrations of Tethyan cephalopod juveniles – assuming that conditions for the growth of (Sub)Mediterranean taxa in the sea with increasingly warmer bottom waters did not change significantly. The increased provincialism of European ammonite faunas during the Late Oxfordian is shown by the re-emergence of the Subboreal Province with a new lineage of Aulacostephaninidae ammonites (Matyja and Wierzbowski, 1995; Główniak et al., 2010).

Ammonites of the (Sub)Mediterranean origin again invaded the Middle Russian Sea during the Kimmeridgian. Such an ammonite

immigration event is recognized in the Makar'yev section (oppeleids are present in Mesezhnikov's collection; Rogov and Kiselev, 2007), and in the Mikhalenino section, where aspidoceratids shortly re-appear near the Bauhini/Kitchini zonal boundary (Główniak et al., 2010). The re-appearance of planktonic foraminifers is noticed in the Lower Kimmeridgian (Fig. 13; see also Azbel, 1989; Ustinova, 2009). Boreal cardioceratids (genus *Amoeboceras*) migrated into the Submediterranean Province again during the latest Oxfordian–Early Kimmeridgian. This interval is also characterized by invasions of Mediterranean ataxioceratids and Subboreal aulacostephanids into the Submediterranean Province of Europe, which is related to a new transgressive pulse (Atrops and Meléndez, 1988; Matyja and Wierzbowski, 1995).

The Middle–Late Callovian sea-level increase and Early Oxfordian highstand conditions, despite some contradictory data (cf. Dromart et al., 2003), are well-documented in many areas (e.g. Norris and Hallam, 1995; Ardill et al., 1998; Jacquin et al., 1998; Ciszak et al., 1999; Burgess et al., 2000; Hallam, 2001; Wierzbowski et al., 2009). Sea-level variations in the areas of the Russian Platform and the West Siberia are considered to have been more complex with three major transgressions at the Callovian–Oxfordian boundary, in the Middle Oxfordian and the Lower Kimmeridgian (Sahagian et al., 1996; Shurygin et al., 1999). A short-term regression period (interpreted based on abundant stratigraphic gaps) is noted there at the Lower–Middle Oxfordian boundary and a long-term regression is assigned to the Upper Oxfordian (Sahagian et al., 1996; Shurygin et al., 1999). Despite some differences these data correspond well with the interpretation of faunistic changes in the Tethys and the Middle Russian Sea as caused by the opening of marine connections during the sea-level highstand in the Late Callovian–Middle Oxfordian, the restriction of marine connections during the Late Oxfordian and the establishing new links during the Early Kimmeridgian.

7.4. Oceanographic and climatic changes

Oxygen isotope and elemental data of marine fossils along with observed faunistic variations are an important proxy for the reconstruction of paleoenvironments and global climate change. The geologic record is however often restricted to areas or habitats affected by local factors like bathymetry changes, salinity variations or marine currents. The interpretation of the global climate change based on such data may be ambiguous.

The presence of cold bottom waters of normal marine salinity in the Middle Russian Sea (a slight increase in salinity cannot be also excluded) partly coincides with a cooling of ~4 °C observed in the oxygen isotope record of belemnite rostra from the Isle of Skye in Scotland in the Mariae Chron of the Early Oxfordian (Nunn et al., 2009) and a cooling inferred from sporomorph data from the southern North Sea in the Mariae and Cordatum chrons of the Early Oxfordian (Abbink et al., 2001). The fish tooth isotope record from southern England, Normandy, eastern France and western Switzerland shows in turn a temperature decrease of ~5 °C in the entire Oxfordian (Lécuyer et al., 2003). Belemnite isotope data from the Polish Jura Chain in central Poland point to a temperature decrease of ~2 °C in the Henrici Subchron of the Lamberti Chron and of ~3 °C at the transition of the Lamberti and Mariae chrons, but no cooling is inferred based on these data in the Lamberti Subchron of the Lamberti Chron and the Cordatum Chron (Wierzbowski et al., 2009, and unpublished data). Oyster isotope data from the eastern Paris Basin indicate, on the other hand, a cooling of ~7 °C in the Late Oxfordian (Brigaud et al., 2008). Relatively constant Late Callovian–Early Oxfordian temperatures calculated from $\delta^{18}\text{O}$ values of belemnites, brachiopods and oysters followed by a cooling of 3–4 °C in the Middle and earliest Late Oxfordian are also reported from the Kachchh Basin in India (Alberti et al., 2012a,b). The compilation of Jurassic isotope data by Dera et al. (2011) shows in turn the temperature minimum in the Late Callovian. The timing of the

cooling and the presence of cold waters is, as one can see, different in all cases. This suggests a strong paleocirculation and paleoceanographic control over the appearances and disappearances of cold water masses in different basins (see Fig. 1).

The cold water masses could have originated in cool Arctic. It is likely that they reached the Middle Russian Sea, Scotland, and peri-Tethyan basins at the Middle–Late Jurassic transition as a result of sea-level rise and opening of seaways. Cold waters characterized by normal-marine salinity would have sunk in the Boreal Sea and moved southward, penetrating the sea bottom. Such movement would have been associated with warmer superficial currents flowing northward from the Tethys. This is consistent with the acceleration of current activity postulated on the basis of the sedimentary record of the Middle–Upper Jurassic boundary of European basins (Dembicz and Praszkiel, 2003; Rais et al., 2007). The question arising is, however, how cool was the Arctic to have enabled the circulation of cold waters and whether it was colder during the Middle–Late Jurassic transition than previously. $\delta^{18}\text{O}$ values (0.5 to 1.5‰) of Middle Oxfordian cylindroteuthid belemnites from the Nordvik section in the Taymyr Peninsula located close to the North Pole in the Jurassic (Žak et al., 2011) are a bit lower than the data presented here from the Russian Platform. It is not clear if they have been affected by freshwater influx so their interpretation is ambiguous (Žak et al., 2011). The disappearance of glendonites from the Upper Callovian of Northern Siberia (cf. Kaplan, 1978; Rogov and Zakharov, 2010; Wierzbowski and Rogov, 2011), the occurrences of organodetrinitic and oolite limestones there, and the diversification of the Arctic bivalve assemblages in the Lamberti Chron of the latest Callovian, indicate a warming of the Boreal Sea in this time (Kaplan et al., 1979). The Late Callovian Boreal Sea warming may have been linked to its opening (due to sea-level rise) and the inflow of warmer waters, which subsequently cooled down and sank accelerating water circulation in the relatively stagnant Jurassic oceans. Such scenario is possible under open seaways and diminished freshwater influx to the Boreal Sea, as this basin might have been characterized by lowered salinity during periods of enhanced isolations (cf. Zhou et al., 2008), which may have prevented the process of sinking of cooled waters.

According to the recent theory of Donnadieu et al. (2011) the deceleration of the carbonate production rate in the oceans during the Late Callovian–Early Oxfordian may have resulted in a build-up of seawater alkalinity and a reduction in atmospheric CO_2 contents, which in turn generated a global cooling episode. Unfortunately, some assumptions of the model presented by Donnadieu et al. (2011), such as a global sea-level fall as a source of the demise of carbonate platform, or of a revision in the paleogeography of Northern Siberia and NE Asia, are not consistent with geologic evidences (for the correct paleogeography see Zakharov et al., 1983). The same applies to the results obtained from the modeling including the seawater alkalization, which is not documented (cf. Dromart, 1989; Donnadieu et al., 2011). There is also no evidence for the Late Callovian–Early Oxfordian cooling in the Arctic, given scenarios assuming major global cooling and glaciation are inconsistent with available geologic data (cf. Kaplan et al., 1979; Wierzbowski et al., 2009; Wierzbowski and Rogov, 2011; Alberti et al., 2012a,b). It is however possible that the deceleration of carbonate productivity at the Middle–Late Jurassic transition may have produced a decrease in atmospheric $p\text{CO}_2$ and a moderate, short-term cooling in the Early Oxfordian. Further investigations of the sedimentary record, especially in the Arctic, are therefore necessary to precisely document the global climatic pattern and variations. The current data show, nevertheless, the paramount effect of oceanic circulation that may have overprinted and obscured subtle to moderate climatic variations at the Middle–Late Jurassic transition. This is consistent with interpretations of Wierzbowski et al. (2009) and Wierzbowski and Rogov (2011).

The Late Oxfordian–earliest Kimmeridgian increase in calculated temperatures is partly linked to the increased freshwater influx and

the shallowing of the Middle Russian Sea (cf. Sahagian et al., 1996; Shurygin et al., 1999), although it may also be connected with global warming as a coeval decrease in belemnite $\delta^{18}\text{O}$ values is noted in Poland and Scotland (cf. Wierzbowski, 2002, 2004; Nunn et al., 2009). The data presented here show a marked warming of the Middle Russian Sea of 3–6 °C that occurred at the transition of the Early Kimmeridgian Bauhini and Kitchini chrons. The Early Kimmeridgian warming coincides with an increase in the oxygen isotope temperatures calculated from belemnite rostra from Scotland (Nunn et al., 2009) and North Siberia (Žak et al., 2011) as well as a temperature record of India (Alberti et al., 2012a,b). Likewise, it correlates with an inferred Early Kimmeridgian temperature rise based on sporomorph data from the North Sea (Abbink et al., 2001). As the Early Kimmeridgian was reported to be marked by another sea-level rise (cf. Sahagian et al., 1996; Shurygin et al., 1999; Hallam, 2001), the observed warming is suggested to be a global phenomenon. It may represent a part of a stepwise Middle–Late Jurassic warming that started at the Bathonian–Callovian boundary (cf. Brigaud et al., 2009; Wierzbowski et al., 2009; Dera et al., 2011) and continued further through the Kimmeridgian (cf. Abbink et al., 2001; Lécuyer et al., 2003; Price and Rogov, 2009; Nunn and Price, 2010; Dera et al., 2011; Žak et al., 2011). Progressive warming of the Arctic may have hampered process of cold bottom water formation in this region, as they are not noted in the Kimmeridgian isotope record (cf. Dera et al., 2011).

7.5. Carbon isotopes

The similarity between $\delta^{13}\text{C}$ values of mesohibolitid and cylindroteuthid rostra points to comparable biofractionation effects in both belemnite groups (Fig. 8; cf. Wierzbowski and Rogov, 2011). Oxfordian–Lower Kimmeridgian $\delta^{13}\text{C}$ values of belemnite rostra from the Russian Platform are characterized by a significant scatter (up to 2.5‰) and 1–2.5‰ higher values compared to coeval rostra from the Submediterranean Province of Europe (cf. Wierzbowski, 2002; Wierzbowski, 2004; Główniak and Wierzbowski, 2007; Wierzbowski and Rogov, 2011). The higher $\delta^{13}\text{C}$ values of belemnite rostra from the Russian Platform show regional enrichment of dissolved inorganic carbon (DIC) in the ^{13}C isotope. The regional enrichment of DIC in the ^{13}C isotope in partly restricted Boreal–Subboreal basins was linked to the high organic matter productivity and/or burial (Wierzbowski, 2004; Wierzbowski and Rogov, 2011). Absolute $\delta^{13}\text{C}$ values of Submediterranean and Boreal rostra partly overlap in the Upper Callovian (Wierzbowski and Rogov, 2011). This may indicate the unification of the isotope signal of oceanic DIC during this period.

The carbonate and organic matter $\delta^{13}\text{C}$ values from the Isle of Skye in Scotland show a pronounced and long-lasting positive excursion comprising the Upper Callovian–Middle Oxfordian (Nunn et al., 2009). The data presented derived from Russian belemnite rostra, which are characterized by high $\delta^{13}\text{C}$ values through the uppermost Callovian–Middle Oxfordian (Fig. 8), corroborate the timing of the positive carbonate excursion in the Boreal Realm. It is important to note that the carbonate carbon isotope record in the Western Tethys and peri-Tethys areas, including the Mediterranean and Submediterranean provinces of Europe, is different. It is characterized by the presence of two (Upper Callovian and Middle Oxfordian) positive carbon isotope excursions interleaved by a Lower Oxfordian interval characterized by decreased $\delta^{13}\text{C}$ values (see Bartolini et al., 1996; Morettini et al., 2002; Wierzbowski, 2002; Louis-Schmid et al., 2007a; Wierzbowski et al., 2009). This indicates that there was no single marine carbonate carbon isotope pool during the Middle–Late Jurassic transition, and that the available records are affected by local factors that influenced not only absolute $\delta^{13}\text{C}$ values but the patterns of secular trends. As terrestrial organic matter shows a long-term positive $\delta^{13}\text{C}$ excursion in the Upper Callovian–Middle Oxfordian (Nunn et al., 2009) the carbonate carbon isotope signal from the Boreal–Subboreal provinces is suggested to have recorded the global variations in the carbon cycle. The carbon isotope record of

the Lower Oxfordian of Western Tethys may be affected by local circulation changes such as the presence of upwelling, which may have carried waters enriched in ^{12}C isotope (cf. Wierzbowski, 2002). The presence of positive carbon isotope excursion(s) in the Upper Callovian–Middle Oxfordian may be linked to the global sea-level rise that resulted in the enhanced organic matter burial and diminished weathering carbon flux from partly drowned land areas (cf. Wierzbowski et al., 2009).

The less-pronounced rise of belemnite $\delta^{13}\text{C}$ values in the upper part of the Bauhini Zone and the Kitchini Zone of the Lower Kimmeridgian (Fig. 8) does not correlate with carbon isotope record of the Isle of Skye in Scotland (cf. Nunn et al., 2009). Although a hardly discernible increase in belemnite $\delta^{13}\text{C}$ values is noted in the coeval Planula Zone of the Submediterranean Upper Oxfordian of central Poland (Wierzbowski, 2002, 2004) it is not statistically significant. Therefore, the belemnite $\delta^{13}\text{C}$ values of the Russian Platform are considered to record local effects in this interval.

8. Conclusions

New belemnite and ammonite samples have been collected from stratigraphically well-dated Middle Oxfordian–Lower Kimmeridgian sections in the Mikhalenino and Makar'yev in the Russian Platform. The belemnite rostra and ammonite shells studied are found to be well-preserved based on cathodoluminescence studies, trace element analyses, X-ray studies and SEM observations.

The samples analyzed along with the published isotope data of Podlaha (1995), Podlaha et al. (1998), Riboulleau et al. (1998), Barskov and Kiyashko (2000) and Wierzbowski and Rogov (2011) show the presence of cold bottom waters (1–9 °C) in the Middle Russian Sea during the Late Callovian–Middle Oxfordian (Lamberti to Tenuiserratum chrons). Differentiation of the oxygen isotope composition within fossils (nektobenthic cylindroteuthid and mesohibolitid belemnites and nektonic ammonites) points to the presence of a thermal gradient in the water column (spread of average temperatures of 5–15 °C). The low $\delta^{18}\text{O}$ values (–2.6 to –0.6‰) of ammonite shells collected from black shales rich in organic matter are interpreted as a result of water stratification and the increased flux of freshwater to the surface waters of the basin. It is consistent with models of organic rich sedimentation in the Middle Russian Sea presented by Shchepetova et al. (2011).

$\delta^{18}\text{O}$ values and Mg/Ca and Sr/Ca ratios of cylindroteuthid rostra show a Late Oxfordian–earliest Kimmeridgian warming of 3.5 °C (the warming was corrected for the freshwater inflow based on a change in elemental ratios). The gradual Late Oxfordian–earliest Kimmeridgian warming is followed by an abrupt temperature rise (of 3–6 °C) that occurred at the transition of the Early Kimmeridgian Bauhini and Kitchini Chrons. The Late Oxfordian–Early Kimmeridgian temperature rise is interpreted as a result of bathymetry changes and of the global warming, which is discernible in the Early Kimmeridgian.

The Late Callovian–earliest Late Oxfordian spread of (Sub)Mediterranean ammonite and belemnite faunas in the Middle Russian Sea and their subsequent retreat are explained by changes in water circulations due to the sea level highstand at the Callovian–Oxfordian transition, and by the restriction in marine connections during the Late Oxfordian. The cold bottom waters are considered to have been formed in the Boreal Sea. The observed variations in temperatures recorded from different basins in the Callovian–Oxfordian are interpreted to have arisen primarily because of changes in water circulation. There is still insufficient data to document global climatic changes in the course of the Middle–Late Jurassic transition; the available data do not however support theories assuming major cooling and glaciation in this time period.

$\delta^{13}\text{C}$ values of belemnite rostra from the Russian Platform are noisy but show the Upper Callovian–Middle Oxfordian positive excursion to be consistent with the isotope record from the Isle of Skye in Scotland (see Nunn et al., 2009). Differences in absolute $\delta^{13}\text{C}$ values and carbon isotope trends between Submediterranean and Subboreal provinces

during the Oxfordian–Early Kimmeridgian are interpreted to have resulted from local factors including high organic matter production and burial as well as water circulation and upwelling.

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