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NITROGEN ISOTOPES IN KUKERSITE AND BLACK SHALE IMPLYING ORDOVICIAN-SILURIAN SEAWATER REDOX CONDITIONS

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Abstract. *For the first time data on nitrogen isotopes from the Ordovician-Silurian sedimentary rocks of the Baltic Basin are reported. Supplementary samples come from several regions worldwide. The data reveal the existence of different primary bioproductivity pathways in the Ordovician-Silurian. During the formation of black shale surface waters were oxygen-poor and maintained* N_2*-fixing primary production indicated by* $\delta^{15}N$ *–0.3‰ on average. The average* $\delta^{15}N$ *of kukersite oil shale is +7.4‰. The positive* $\delta^{15}N$ *values are in accordance with the formation of kukersite in oxic waters, showing that Gloeocapsomorpha prisca was a nitrate-using not* N_2*-fixing cyanobacterium-like organism. The black shale samples from the deep shelf suggest that seawater, including the photic zone, often suffered from deficiency of oxygen.*

Keywords: *nitrogen isotopes, black shale, kukersite, Ordovician, Silurian, redox conditions.*

1. Introduction

The Palaeozoic ocean has been considered to be with an oxic surface water layer and increasingly anoxic deep water [1, 2]. The nitrogen isotopes of an organic matter-containing sedimentary rock indirectly indicate redox conditions in the photic zone, and can complement the existing conception. The oxic waters are rich in nitrates. In the present-day seas the isotopic value of nitrates, $\delta^{15}N$, is around +6‰ [3]. In photosynthesis the algae use nitrates for their growth. The positive $\delta^{15}N$ found in sediments suggest that the organic matter originates from nitrate-using algae whose environment of growth was an oxygen-rich photic zone. In anoxic conditions nitrates are lacking and the nitrogen demand is compensated for *via* fixation of the atmospheric N_2 gas dissolved in seawater. Mainly cyanobacteria use the photosynthetic pathway of N_2-fixation. The N_2-fixation converts unreactive

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N_2 into reactive nitrogen, such as ammonium. In the presence of oxygen the ammonium transforms into nitrates and other oxygen-containing nitrogen compounds [4]. The N_2-fixation commonly produces organic material with average $\delta^{15}N$ values around 0‰, ranging from –3 to +1 [3]. Consequently, the sedimentary organic matter with near-zero $\delta^{15}N$ indicates N_2-fixation in the photic zone and anoxic nitrate-poor waters.

The term 'anoxia' is used here conditionally referring to environments with a very low content of free oxygen. Normal seawater has a free oxygen content of 5 ml/l on average, the environment with the free oxygen content of from 1.5 to 0.1 ml/l is considered as denitrifying, and below 0.1 sulphate reducing. In low-oxygen waters denitrification occurs. This process destroys nitrates, the oxygen of nitrates is used for organic carbon consumption by bacteria, and nitrogen gas moves back to the atmosphere [4]. In oxic seawaters the nitrate-users outcompete N_2-fixers as N_2 fixation demands much energy to break up the strong triple bond of N_2 [5]. Also, Mo and Fe availability is important for N_2-fixers [6]. The organic matter produced by nitrate-users and N_2-fixers in the photic zone of seawater may alternate seasonally, resulting in the weighted average of $\delta^{15}N$ of a sediment sample [7]. In the initial stages of denitrification in the water column the residual nitrate of the uppermost water layer may become enriched in ^{15}N. The $\delta^{15}N$ of residual nitrates may rise up to 19‰, as the lighter isotope, ^{14}N, is preferentially utilised by denitrifying bacteria in the lower water layers [3]. The high $\delta^{15}N$ of the sedimentary organic matter may reflect enrichment of this kind pointing to denitrification in the water column. When reconstructing the past redox conditions the diagenetic change of the isotope ratio must be considered. The diagenetic changes may vary in the range of several per mills [8, 9]. In the presence of anoxic bottom waters the diagenetic alteration is smaller than in oxic conditions [10, 11].

The present-day ocean is mostly well mixed and ventilated. Most of the primary organic matter is produced on the basis of recycling nitrate. Anoxia and denitrification maintaining N_2-fixation occur in limited regions. The well-known anoxic basins, e.g. the Cariaco of Venezuela, Santa Barbara of US, Black Sea, Baltic Sea, eastern Mediterranean areas, and several fjords, are restricted by sills. Anoxia also occurs in upwelling regions, such as the Arab Sea, Peru coast and West African coast. In the Proterozoic seas the N_2-fixers prevailed as the atmospheric oxygen content was low [12, 4]. From the Proterozoic onward the oxygenation of the ocean improved, but the trend was not steady. In the Ordovician-Silurian the primary bioproductivity pathway alternated between dinitrogen-fixing and nitrate-using [13]. Based on given considerations and measurements of the $\delta^{15}N$ of the organic matter-rich sedimentary rocks we try to refine the redox conditions of the Ordovician-Silurian Baltic Basin, particularly in the uppermost photic zone of the sea. Samples from distant basins, such as Dob's Linn and Lake District, both UK, may indicate the oceanic conditions. The $\delta^{15}N$ values of kukersite oil shale and black shale as organic carbon-rich rocks with different pathways of photosynthesis and environmental conditions are compared.

2. Materials and methods

The nitrogen content, $\delta^{15}N$ and $\delta^{13}C_{org}$ of samples were measured in the Isotope Laboratory of the Cornell University, US. The $\delta^{15}N$ and $\delta^{13}C_{org}$ values are expressed as $^{15}N/^{14}N$ and $^{13}C/^{12}C$ difference from the standards, atmospheric N_2 and PDB, respectively. A ThermoFinnigan Delta Plus mass spectrometer (SIS, US) plumbed into a Carlo Erba NC2500 elemental analyser (Carlo Erba, Italy) was used. In-house laboratory standards verified against international reference materials guaranteed the calibration. In the $\delta^{13}C_{org}$ analysis the inorganic carbon was removed via acid fumigation. For a closer description of methods and laboratory techniques, as well as additional data see http://sarv.gi.ee/reference.php?id=2539. Two types of organic carbon-rich material were analysed – black shale and kukersite** oil shale (Fig. 1). The black shale is a finely laminated dark claystone with the

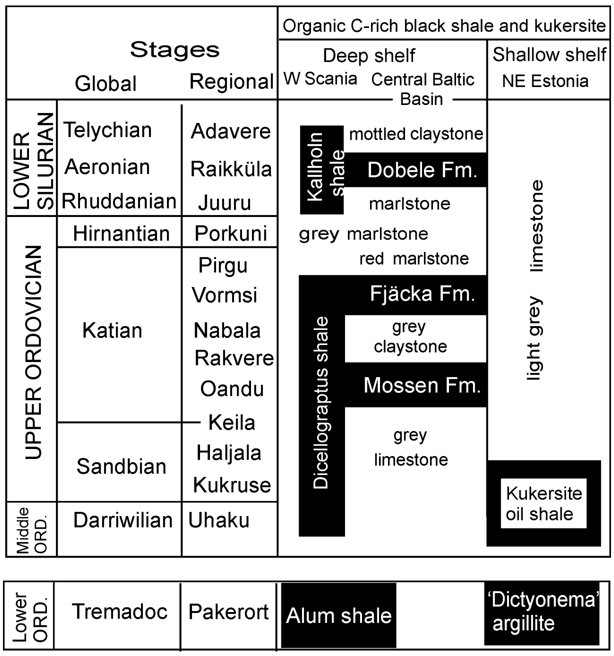


Fig. 1. Stratigraphic scheme of organic carbon-rich rock of the Baltic Basin.

** The use of the term "kukersite" by the authors is not traditional. The Editorial Board of the journal considers it reasonable to use the term only in its historial meaning, according to which "kukersite is a local name of Ordovician oil shale in Estonian and Leningrad deposits, which contains remains of alga Gloeocapsomorpha prisca Zalessky. The name is derived from the Kukruse (Kuckers in German) manor in North-East Estonia, where it was first described."

The editors are of the opinion that other varieties of oil shales may be classified as "kukersite-like" or "kukersitic" in case their lithologic and genetic similarity to kukersite has been scientifically proved.

organic content of around 10–20%, containing also transitional metals more than the shale on average [14]. The kukersite oil shale [15] is a light-brown rock containing up to 50–60% of organic material, carbonates, siliciclastics, and a low amount of transitional trace metals. The oil shale samples of the Sandbian, Katian and Darriwilian ages come from Estonian and Russian cores and mining quarries (Table 1, Fig. 2). Three Canadian and two Australian kukersites of the Ordovician age are analysed as well (Table 1). The kukersite oil shale is of shallow shelf origin. The deep shelf black shale samples come from the Upper Ordovician Mossen and Fjäcka formations and Lower Silurian Dobele Formation (Fm.) of the Latvian Aizpute-41 core (Fig. 2). The grey marlstone-claystone interval between Mossen and Fjäcka is analysed as well. One sample comes from the Tremadocian graptolite-argillite, the Dictyonema shale or argillite, as it was called in the earlier literature (for the change of the name see [16]), from a shallow shelf setting. This sample is an in-house standard Es-2 of the XRF Laboratory of the Institute of Geology at Tallinn University of Technology, whose elemental chemical composition has repeatedly been analysed [17]. Now it gets a measured $\delta^{15}N$ value as well. Several Ordovician-Silurian dark and black shales from Bornholm (Denmark), the Lake District and Dob's Linn (both UK) are involved as well.

Table 1. Nitrogen content, nitrogen and carbon isotope of shale and kukersite

Stratigraphy	Location	Sample ID	N, %	$\delta^{15}N$, ‰	$\delta^{13}C_{org}$, ‰	Lithology
		Silurian				
Aeronian, Dobele Fm.	Aizpute-41 core, W Latvia	968.8	0.02	1.9	nd	grey marl-stone
	(depth in m)	969.05	0.04	2.2	nd	grey clay-stone
"	"	969.15	0.58	–0.3	–30.1	black shale
"	"	969.45	0.79	–0.3	–29.2	"
"	"	969.8	0.18	–1.0	nd	calcareous black shale
"	"	970.5	0.05	1.6	nd	"
"	"	970.52	0.36	–0.7	–29.7	black shale
"	"	970.7	0.31	–1.1	–30.3	"
"	"	971	0.41	–0.9	–30.3	"
"	"	971.5	0.57	–0.2	–29.9	"
"	"	972	0.41	–0.8	–30.3	"
"	"	972.7	0.42	–0.8	–30.3	"
"	"	973.8	0.41	–0.6	–29.5	"
"	"	974.75	0.39	–0.9	–29.0	"
"	"	975.4	0.34	–0.6	–30.6	"

Stratigraphy	Location	Sample ID	N, %	$\delta^{15}N$, ‰	$\delta^{13}C_{org}$, ‰	Lithology
"	"	975.8	0.4	–0.4	–30.2	"
"	"	976.3	0.23	–1.1	–29.9	"
"	"	977.8	0.09	0.1	nd	calcareous grey shale
"	"	978.8	0.04	0.8	nd	"
	Ordovician					
Vormsi St.	"	1029.3	0.02	3.6	nd	grey marlstone
Vormsi St. Fjäcka Fm.	"	1031.4	0.18	–0.4	–30.8	black shale
"	"	1031.9	0.17	–0.3	–30.6	"
"	"	1032.4	0.29	–0.4	–30.4	"
"	"	1032.9	0.11	0.2	–30.1	"
"	"	1033.4	0.21	–0.4	–30.7	"
"	"	1034	0.34	–0.2	–31.1	"
"	"	1034.4	0.23	0.1	–31.0	"
Rakvere-Nabala St.	"	1035.3	0.05	2.2	nd	grey calcareous claystone
"	"	1037.3	0.01	1.2	nd	"
"	"	1038.3	0.04	1.9	nd	"
"	"	1040.5	0.03	3.1	nd	"
"	"	1041.5	0.03	4.0	nd	"
Oandu St. Mossen Fm.	"	1042.6	0.12	0.8	–29.8	black shale
"	"	1043.2	0.15	0.8	–30.3	"
"	"	1043.8	0.12	1.8	–30.0	"
"	"	1044.1	0.08	2.4	–29.6	"
"	"	1044.8	0.14	1.0	–30.1	"
"	"	1045.2	0.17	1.4	–30.2	"
"	"	1046	0.17	0.5	–29.7	"
Keila St. Blidene Fm.	"	1046.3	0.06	3.8	nd	grey claystone
"	"	1047.45	0.04	5.0	nd	"
"	"	1048.2	0.04	5.3	nd	"
Tremadoc, Pakerort St., Türisalu Fm.	Estonia, Tallinn	Es-2	0.22	–2.0	nd	black "Dictyo-nema" argillite
Ordovician-Silurian black shales from distant regions						
Katian, *clingani*	Scotland	Dob's Linn 1	0.14	–1.9	nd	black shale
Katian, *complanatus*	"	Dob's Linn 2	0.08	0.2	nd	"
Llandovery, *triangulatus*	"	Dob's Linn 3	0.08	–1.0	nd	"
Hirnantian, *persculptus*	England	Lake District 1	0.07	–0.8	nd	"
Hirnantian, *persculptus*	"	Lake District 2	0.05	–1.1	nd	"

Stratigraphy	Location	Sample ID	N, %	$\delta^{15}N$, ‰	$\delta^{13}C_{org}$, ‰	Lithology
Aeronian	"	Lake District 3	0.04	–1.4	nd	"
Rhuddanian	"	Lake District 4	0.07	0.3	nd	"
Oandu St. Mossen Fm.	Bornholm island	Bornholm 6	0.25	–0.5	nd	"
Llandovery, Raikküla St.	"	B-5, Olea brook	0.11	0.8	nd	"
Llandovery, Juuru St.	"	B-4, Olea brook	0.08	0.8	nd	"
Katian, Pirgu St.	"	B-3, Laesa brook	0.06	0.3	nd	"
Katian, Nabala-Vormsi St.	"	B-2, Laesa brook	0.16	–0.3	nd	"
Darriwilian, Kunda St. Komstad Fm.	"	B-1, Laesa brook	0.02	–2.4	nd	black limestone
Ordovician kukersite oil shales						
Katian Keila St.	NW Russia	Apraksin core	0.03	6.1	nd	kukersite
"	"	Andrejevo core	0.02	8.6	nd	"
Sandbian Jõhvi or Keila Stage?	"	Prebug core	0.05	3.8	nd	"
Sandbian Kukruse St.	NE Estonia	Viru mine	0.07	8.7	nd	"
"	"	Kiviõli quarry, E layer	0.09	9.5	nd	"
"	"	Kerguta core, III layer	0.08	12.0	nd	"
"	"	Kerguta core, C layer	0.08	6.3	nd	"
"	"	Kerguta core, upper	0.05	9.1	nd	"
"	"	Ervita core, IV layer	0.09	7.3	nd	"
"	"	Küttejõu quarry	0.07	8.5	nd	"
"	NW Russia	Tregubovo core	0.02	5.2	nd	"
"	"	Osmino core	0.12	7.5	nd	"
"	NE Estonia	Kohtla-7 core 28 m	0.12	4.4	nd	"
"	"	Kohtla-7 core 27.6 m	0.09	8.7	nd	"
"	"	Kohtla-7 core 26.4 m	0.08	8.0	nd	"
"	"	Kohtla-7 core 25.6 m	0.07	6.8	nd	"
Idavere or Kukruse Stage?	NW Russia	Nikol core	0.06	7.7	nd	"
Darriwilian Kunda St.	NE Estonia	Kauste core	0.02	4.7	nd	"
Yeoman Fm., Upper Ordovician	Canada	Saskatchewan WLS Froute	0.02	3.9	nd	"
Yeoman Fm., Upper Ordovician	"	Saskatchewan Midale 2578,32	0.04	4.0	nd	"
Yeoman Fm., Upper Ordovician	"	Saskatchewan Hornung 5683,3	0.13	7.3	nd	"
Goldwyer Fm. Mid-Ordovician	Australia	Canning Basin, Santalum 340083	0.06	7.4	nd	"
Goldwyer Fm. Mid-Ordovician	"	Canning Basin, Santalum 340082	0.05	4.2	nd	"

nd – not determined
Fm. – Formation
St. – Stage

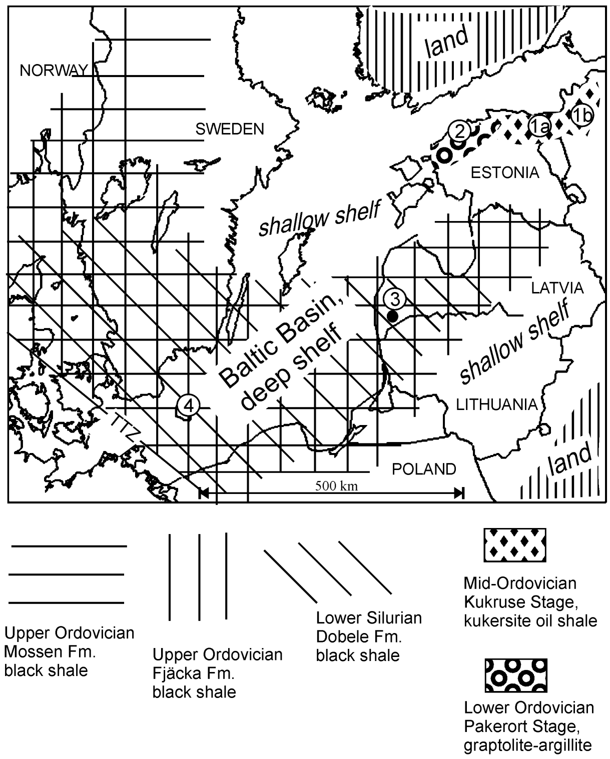


Fig. 2. Sketch-map of facies setting in the Palaeozoic Baltic Basin. Samples: kukersite 1a, NE Estonia; 1b, NW Russia; 2, Tremadocian graptolite-argillite, Tallinn; 3, black shale, Aizpute-41 core; 4, black shale, Bornholm.

3. Geological background

The epicontinental Ordovician Baltic Basin was opened to the Iapetus Ocean in its western, and to the Tornquist Ocean in the southern side. During the Ordovician both oceans narrowed, and closed in the Silurian. In the Silurian the area of the Baltic Basin diminished. The black shale was permanently present in the SW deepest part of the Baltic Basin. The rest of the Basin was covered with grey and red **c**layey and calcareous sediments. Episodically, in the Katian and Mid-Llandovery, the black shales of the Ordovician Mossen and Fjäcka formations, and Silurian Dobele Formation occupied the deep shelf (Fig. 2). The convergence of Baltica with the Avalonia microcontinent started in the Late Ordovician and might have affected the water exchange of the Baltic Basin with the ocean. The Ordovician-Silurian black shale of Dob’s Linn was deposited in the ocean ‘a long distance offshore from Avalonia’, whereas the Lake District represents a deep sea close to the Avalonia microcontinent [18]. The Estonian graptolite-argillite of the Tremadocian age (the ‘Dictyonema’ shale) formed in near-coastal stagnant waters was separated by sandy sills from the open sea [19].

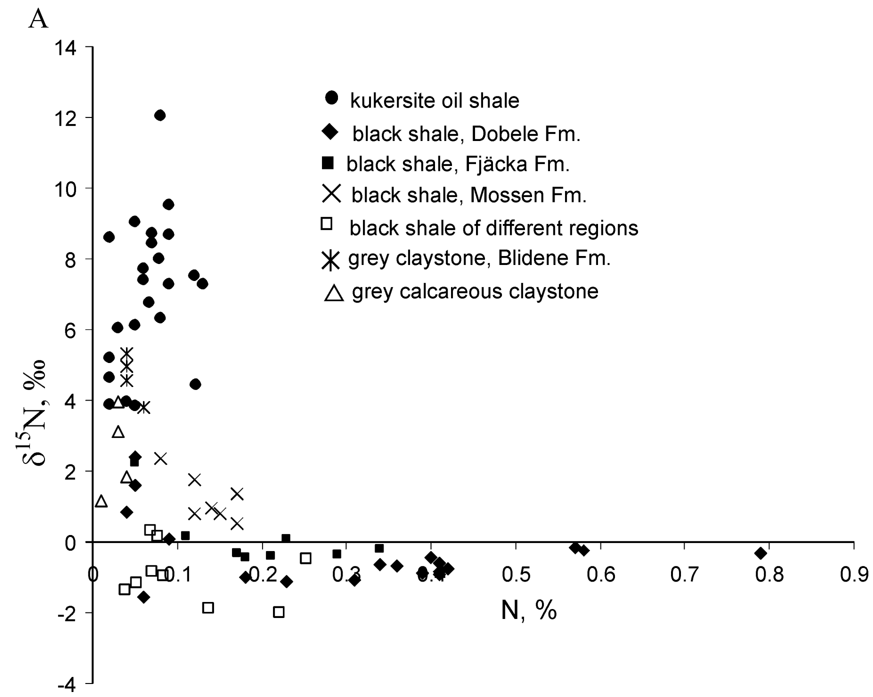
The kukersite oil shale was deposited in the East Baltic open shallow shelf. Single kukersite seams are found in the Lower Ordovician Kunda Stage. The occurrence of kukersite interlayers within limestone deposits increases in the Middle Ordovician Uhaku Stage. The Upper Ordovician Kukruse Stage is rich in kukersite beds [20]. The kukersite consists of remains of the extinct photosynthetic organism *Gloeocapsomorpha prisca*, either similar to the extant cyanobacterium *Entophysalis major* [21, 22] or green alga *Botryococcus braunii* [23]. The Mid- and Upper Ordovician kukersite consisting of *G. prisca* has a wide geography. Besides Estonia and NW Russia kukersite is recorded in Australia [24, 25], Canada [26, 27] and USA [28]. In the geological sections of the East Baltic Basin the *G. prisca* oil shale occurs sporadically from the lower Darriwilian to uppermost Katian. The Sandbian Kukruse Stage deposit of Estonia and NW Russia has industrial value – it is used as a mineral resource for power and chemical industries.

4. Results

The measurements revealed the difference between black shale and kukersite oil shale (Table 1). The $\delta^{15}N$ values of black shale converge near zero, those of kukersite oil shale are positive, on average +7.4‰ (Fig. 3A). The wide scatter, from +3.8 to +12.0‰, characterises the $\delta^{15}N$ of Baltic oil shale samples. Kukersite samples from Canada (the Hornung, Midale and Froute cores of the Saskatchewan) and Australia (Santalum 1A core of the Canning Basin) have the respective values between +3.9 and +7.4‰ (Table 1). Kukersite contains some N – on average 0.066% (Table 2). The carbon isotope ratios ($\delta^{13}C_{org}$) of Estonian kukersite range between –33.2‰ and –31.5‰ according to two samples [23].

The nitrogen content of black shale is on average 0.23% according to 41 samples, varying from 0.02 to 0.79%; the average $\delta^{15}N$ is –0.3‰, varying between –2.4 and +2.4‰ (Table 1). Nitrogen content is in positive correlation with organic content expressed as % of loss of weight on ignition at 450 ^{o}C (Fig. 3B). In the present work, the loss on ignition is not determined for kukersite samples. A previous research reports the organic content of from 30 to 70% [29].

The black shale of the Dobele, Fjäcka and Mossen formations of the Aizpute-41 core shows values of nitrogen isotope ratios from –1.1 to +2.4‰ (Fig. 4). The average $\delta^{15}N$ of the Dobele Fm. is –0.5‰, that of the Fjäcka Fm. –0.2‰ and of the Mossen Fm. +1.2‰. The N contents are diminishing in the same order: in the Dobele 0.37%, Fjäcka 0.22% and Mossen 0.14% (Table 2). The grey claystone-marlstone interval between the Mossen and Fjäcka black shales reveal $\delta^{15}N$ from +1.2 to +4.0‰. The average $\delta^{13}C_{org}$ value is –29.9, –30.7 and –30‰ for the Dobele, Fjäcka and Mossen black shale, respectively (Table 2). In the Dobele Fm. there are two intervals with



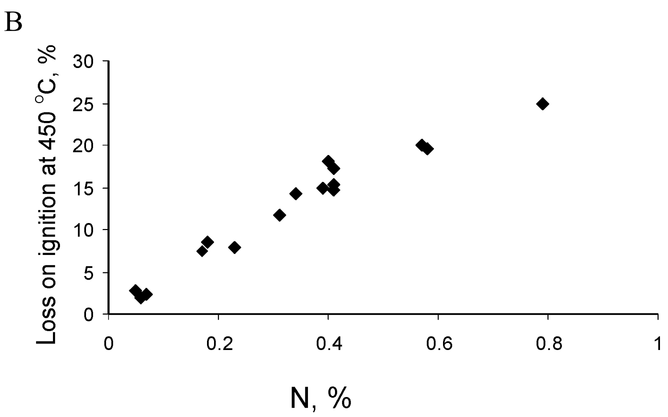


Fig. 3. Plot A – nitrogen content (%) *vs*. $\delta^{15}N$ (‰); B – loss on ignition at 450 °C (%) *vs*. nitrogen content (%).

+1‰ excursions of $\delta^{13}C_{org}$, in the *sedgwickii* and *triangulatus* graptolite zones (Fig. 4) [30]. Also, the *sedgwickii* excursion has been found in Dob's Linn (UK) and Cornwallis island (Canada) [31]. The excursion in the *triangulatus* zone correlates with the excursion of $\delta^{13}C_{carb}$ recorded in the calcareous sections of Estonia [32]. Carbon isotope positive excursions are often contemporaneous worldwide and reflect changes in carbon cycling and oceanic overturns mainly related to ice ages.

Table 2. Average nitrogen content, $\delta^{15}N$ and $\delta^{13}C_{org}$ of the black shale of the Aizpute-41 core and kukersite oil shale (from Table 1)

Average	Dobele Formation	Fjäcka Formation	Mossen Formation	Kukersite oil shale
N, %	0.37 (16)	0.22 (7)	0.14 (7)	0.066 (23)
$\delta^{15}N$, ‰	–0.5 (16)	–0.2 (7)	1.2 (7)	6.9 (23)
$\delta^{13}C_{org}$, ‰	–29.9 (14)	–30.7 (7)	–30 (7)	nd

* The number in parentheses indicates the number of analysed samples.
nd – not determined.

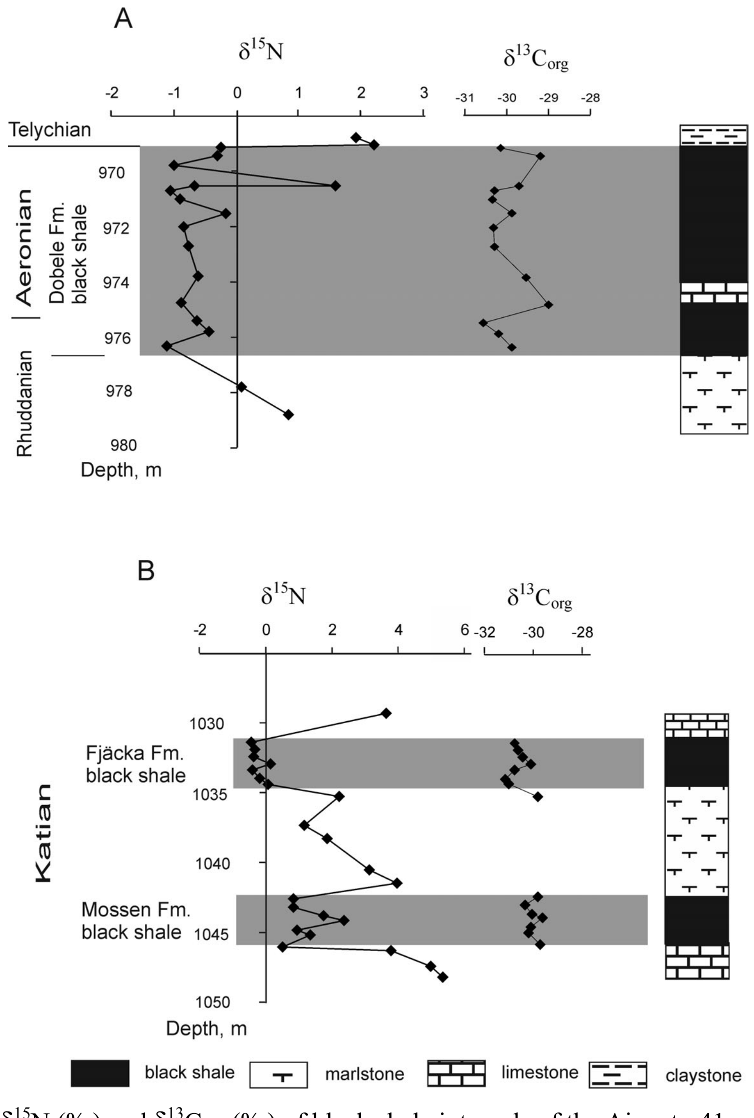


Fig. 4. $\delta^{15}N$ (‰) and $\delta^{13}C_{org}$ (‰) of black shale intervals of the Aizpute-41 core; A – Lower Silurian Dobele Formation. Graptolite zonation from [30]; B – Upper Ordovician Mossen and Fjäcka formations.

5. Discussion

5.1. Kukersite

Kukersite has very low N and P contents [20] compared to carbon, more than ten times lower than the Redfield value 106:16:1 (the atomic C:N:P ratio of an average marine photosynthetic organic matter). This suggests diagenetic changes. Phosphorus, nitrogen and easily degradable organic carbon were utilised by bacteria, whereas the refractory organic carbon was preserved [33]. The wide scatter of $\delta^{15}N$, from 3.8 to 12.0‰, also points to diagenetic changes alternating in different localities. A lot of calcareous faunal debris, such as brachiopods, trilobites, bryozoans, gastropods and bivalvia, occur in the Estonian kukersite oil shale. The richness of fossil fauna indicates oxygen-rich normal marine waters. The low content of transitional trace metals in kukersite oil shale evidences oxic conditions as well. Thereby, the *G. prisca* grew and was subjected to the early diagenesis in oxic waters. Only after burial the diagenesis continued in the anoxic sedimentary environment shown by the oil shale pyrite content, which is about a couple of percent [20]. The oxic waters contain nitrates and promote nitrate-using primary productivity suggesting that the *G. prisca* was a nitrate-using organism with an initial positive $\delta^{15}N$, not an N_2-fixer. The scatter of $\delta^{15}N$ indicates spatially varying diagenetic changes related to bacterial activity. As the bacteria in the sediment preferentially use a light isotope, ^{14}N, the rest of the nitrogen is enriched in ^{15}N, seen in the $\delta^{15}N$ values amounting to 9‰ and more. The kukersite oil shale from Canada and Australia reveal nitrogen content and $\delta^{15}N$ values in the same range as the Baltic oil shale (Table 1) signifying that the growth and diagenesis of *G. prisca* took place in similar environmental conditions. The formation of a high amount of kukersite organic matter needed a lot of P and N. A recent investigation of the East Baltic cores has revealed a probable link between kukersite and increased phosphorus content recorded in the sedimentary rock of the transitional zone between the shallow and deep shelf [34].

5.2. Black shale

The black shale intervals of the deep shelf Aizpute-41 core formed in anoxic conditions. The high content of organic matter and transitional trace metals signify sulphate-reducing conditions of the near-bottom water [35, 36]. The fine lamination of sediment points to the lack of bioturbation due to the anoxic stagnant water. The near-zero or slightly negative $\delta^{15}N$ values of the Dobele and Fjäcka black shales are indicative of a cyanobacterial N_2-fixing and photic zone oxygen deficiency. Consequently, not only the basin bottom waters were anoxic, but also the whole water column was poor in free oxygen. The black shale of the Mossen Fm. has a lower nitrogen content than that of the Fjäcka and Dobele formations (Table 2), suggesting a less reducing environment in deep waters and the upper water column. The positive $\delta^{15}N$ values of from +1 to +2‰ indicate that the primary bioproductivity coming from the N_2-fixation was supplemented by nitrate-using algae. The fractions of N_2-fixing $\delta^{15}N$ and nitrate-based $\delta^{15}N$ sum up and give a slightly positive average for the Mossen shale (Fig. 4, Table 2). For the Mossen Formation the alternation of seasonal oxic and anoxic conditions in the photic zone, similar to the modern-day Gotland Deep of the Baltic Sea [37], is likely.

5.3. Reasons for anoxia in the Baltic Basin

The anoxic conditions in the basins develop when water exchange stops and oxygen content drops. Sills hindering the water exchange, expansion of oxygen-poor waters from the ocean side, high productivity exhausting the oxygen ability to decompose organic matter, and/or temperature rise diminishing the oxygen dissolution can cause the basin water anoxia. For the Silurian Dobele Fm. the rise in bioproductivity resulting from the upwelling of the nutrient-rich but oxygen-depleted oceanic water was suggested [38]. The Ordovician Mossen and Fjäcka black shales and contemporaneous shallow shelf sediments do not reveal signs of increased bioproductivity, such as chert concretions and barite found in the limestone of the Raikküla Stage correlative with the Dobele Formation. Thereby, either the water stagnation due to basin restriction by sills or expansion of anoxic waters from the ocean side is most likely for the Mossen and Fjäcka formations. The emergence of islands during the approach of Avalonia to Baltica in the Late Ordovician is probable, as causing a temporary restriction of the Baltic Basin. The expansion of oxygen-deficient waters from the ocean facilitated by transgression, upwelling, tectonic submergence of the Basin floor, or an intensified anoxia of the ocean is another possibility. Near the continental slope in the SW Baltic Basin the black shale formed during most of the Cambrian and Ordovician indicating stagnant conditions of the adjacent ocean. The black shale samples from Bornholm in the vicinity of the ocean reveal near-zero or negative $\delta^{15}N$ values similar to Dob's Linn's or the Lake District's, pointing to N_2-fixing primary bioproductivity and oxygen-poor photic zone of the ocean. Probably, in the ocean the areas of stagnant waters alternated laterally with oxygenated areas of wind-driven oceanic gyres. The continuations of these oxic oceanic currents crossed the Baltic Basin episodically, and red-coloured facies in the central Basin mark the pathway of oxic currents [39]. The redox conditions of the ocean varied not only spatially but also temporally. In the westernmost Baltic Basin the dark organic C-rich sediments disappeared and were replaced by greyish sediments in the Late Katian and Hirnantian [19], showing that oceanic waters became better ventilated at the end-Ordovician. The role of temperature increase as promoting anoxia in the Baltic Basin has not been investigated, but is worth of considering.

6. Conclusion

The first data on nitrogen isotopes from the East Baltic Ordovician-Silurian sediments reveal the divergence in $\delta^{15}N$ values between black shale and kukersite, suggesting different primary bioproductivity pathways. The growth of *G. prisca* in oxic waters and high $\delta^{15}N$ values show that the *G. prisca* was a nitrate-using, not an N_2-fixing cyanobacterial organism. During the times of grey sediment formation the photic zone of the Baltic Basin was nitrate-rich as well. In the times of black shale formation the surface waters of the deep shelf became oxygen-poor and maintained N_2-fixing primary production. The sea water stagnation due to basin restriction and emergence of sills might have occurred episodically during the Baltica-Avalonia docking in the Late Ordovician. Alternatively, anoxic water expansion from the ocean to the Baltic shelf can be considered. The near-zero $\delta^{15}N$ values of pelagic sediments reveal that temporarily large parts of the Ordovician and Silurian oceans, including the photic zone, were denitrifying.

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