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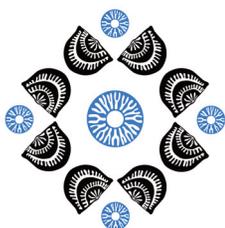
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Corresponding author:

Mawo Ndiaye
mawo.ndiaye@taltech.ee

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Nitrogen and organic carbon isotope record in Tremadocian highly metalliferous black shales from Baltica

Mawo Ndiaye, Merlin Liiv, Toivo Kallaste, Sophie Graul and
Rutt Hints

Department of Geology, Tallinn University of Technology, Ehitajate 5, 19086 Tallinn, Estonia

ABSTRACT

Tremadocian highly metalliferous black shales and associated grey shales from the Aseri PH012B drill core (NE Estonia) in the innermost part of the Baltic Palaeobasin were targeted to record their nitrogen and organic carbon isotope variance combined with the total organic carbon and total nitrogen record. The obtained molar C/N ratios of black shales from 26 to 52 indicate a considerable loss of N compared to primary biomass. The recorded $\delta^{15}\text{N}$ values from -2.5 to 0.2% likely evolved due to isotopic fractionation related to N_2 fixation by primary producers, superimposed by later anoxic ammonium oxidation processes within the uppermost sediments. The high net primary productivity, which controlled the accumulation of organic-rich shallow-water complexes, was fuelled by the internal cycling of P in the sea basin and combined with intensive N exchange between marine and atmospheric pools.

Introduction

An interval from the middle Cambrian to the Early Ordovician, represented by vast black shale complexes in the Baltic Palaeobasin, is recognized as a period of major environmental and biodiversity changes. The accumulation of organic-rich sediment throughout the outer and inner shelf of the palaeobasin has been attributed to elevated nutrient input, enhanced bioproduction, and prevailing anoxia in the lower water column, the latter likely disrupted by short-lived oxygenation events (Dahl et al. 2019). However, many fundamental questions remain regarding their genesis. Herein, we present coupled nitrogen ($\delta^{15}\text{N}_{\text{tot}}$) and carbon ($\delta^{13}\text{C}_{\text{org}}$) isotope records from the highly V-, U-, and Mo-enriched Tremadocian black shales and related metal-poor black and grey shales (*Cordylodus angulatus*–*Paltodus deltifer pristinus* biozones) from the inner shelf of the palaeobasin to decipher possible interrelated changes in the nutrient cycle, primary productivity, and redox conditions during their accumulation.

The dynamics of the deep-time biogeochemical cycle of N can be derived from the isotopic composition of the deposits. The cycle is closely tied to the redox state of the ocean and the atmosphere, and the N isotope values that are preserved in organic matter (OM) can reflect the redox state of the water column, as well as metabolic processes and pathways (Algeo et al. 2014). Nitrogen plays a crucial role in the biogeochemical cycling of C and other nutrients in the oceans (Stüeken et al. 2016). It can exist in different forms, including the diatomic molecule (N_2), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and dissolved organic nitrogen (DON). Autotrophs in the marine system can fix atmospheric N_2 ($\delta^{15}\text{N} = 0\%$) into OM with minimal isotopic fractionation ($\epsilon_{\text{org-N}_2}$ is ~ -3 to $+1\%$) (Zerkle et al. 2008; Valley and Cole 2001). The decomposing OM first undergoes ammonification, which also involves little isotopic alteration. Further, under oxic conditions, nitrification converts NH_4^+ to dissolved NO_3^- . The process potentially has a large net isotope fraction effect in settings where incomplete nitrification is favoured (Deutsch et al. 2007). However, it has minor importance in well-oxygenated seawater, where all generated NH_4^+ is effectively oxidized to NO_3^- . Under suboxic conditions, part of the N can escape from the nitrate pool through denitrification, with a potentially large isotopic effect (Valley and Cole 2019). Such an effect is, however, suppressed if quantitative denitrification takes place (Sigman and Fripiat 2001). In the anoxic seawater and sediment column,

N-loss could be further promoted by mineralization of OM through processes such as anoxic ammonium oxidation (anammox) with nitrates or alternative electron acceptors. The N mineralization pathways in anoxic sediments are still poorly understood. Importantly, depletion of bioavailable N-compounds in the water column supports the growth of diazotrophs if other nutrients are available. Interpretations of ancient sedimentary records exhibiting near-zero $\delta^{15}\text{N}_{\text{tot}}$ values, untypical of modern settings, have conventionally assumed that N_2 -fixation should have dominated as the main source of N, thus pointing to the nitrate-poor oxygen-depleted photic zone. For the Tremadocian black shales from the inner part of Baltica a single previously reported $\delta^{15}\text{N}$ value of $\sim -2\text{‰}$ is in the aforementioned range (Kiipli and Kiipli 2013).

Our research aimed at better understanding the distribution of $\delta^{15}\text{N}_{\text{tot}}$, $\delta^{13}\text{C}_{\text{org}}$, total organic carbon (TOC) and total nitrogen (TN) in those palaeoenvironments. We hypothesized that significant changes in the local nitrogen cycle would coincide with changes in the preservation of OM and the enrichment of redox-sensitive elements (RSE) in the black shales.

Geological setting

The analysed samples come from the Aseri PH012B (59.426053, 26.755267) drill core. During the Tremadocian period, the study area was the innermost shallowest part of the Baltic Palaeobasin. The thin complex of black shales of the Türisalu Formation (~ 1.1 m) deposited during the transgressive phase above the coastal and shallow-marine bio- and siliciclastic complexes of the Kallavere Formation. The latter is rich in phosphatic brachiopod detritus, but also shows cyclic alteration of black shale interbeds and siltstones in its uppermost part. The Türisalu Formation is overlain by grey shales of the Varangu Formation. The mineral matrix of the organic-rich black shales consists of K-feldspars, quartz, illite/mica, and illite/smectite, while pyrite content varies from 4 to 6%. Also, the presence of thin cyclic biosilica and sulphidic silty interlayers as well as glendonite-like carbonate concretions is characteristic of the study area. The OM of the Türisalu Formation is thermally immature (Schovsbo et al. 2012), purely marine in origin, largely amorphous, and compliant with Type-II kerogen with an average atomic H/C ratio of 1.24 and O/C ratio of 0.16 (Veski and Palu 2003). Lille (2003) suggested that its primary biomass could have been produced by cyanobacteria and possibly by green sulphur bacteria. Very high enrichment of RSE, with maximum content of V ~ 2300 ppm, U ~ 500 ppm, and Mo ~ 2700 ppm, has been documented in the basal and middle part of the Türisalu Formation in the Aseri PH012B section using the same sample set (Ndiaye et al. in press).

Materials and methods

To determine TOC and TN content, 186 samples of the Türisalu Formation and adjacent strata were analysed using combustion in a FLASH 2000 organic elemental analyser.

Each sample was approximately 1 cm thick, and 4–15 mg of powdered sediment was used depending on loss-on-ignition values. The samples were pretreated with 10% HCl, dried, and then wrapped into granules before being packed into Sn containers for combustion. Cystine was used as the standard, and organic carbon-rich sediment was used as the reference material.

Selected samples ($n = 26$) were analysed for $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{tot}}$. Approximately 1 g of sample powder was treated with 10% HCl, rinsed, and dried. The C isotopic ratios were measured using a FlashEA 1112 and a Delta V Advantage isotope ratio mass spectrometer. The results were expressed as relative deviations from V-PDB. Standards from the IAEA and IVA Analysentechnik were used for precision and calibration.

For $\delta^{15}\text{N}_{\text{tot}}$ analysis, 7 to 20 mg of sample powder was weighed into Sn capsules. The N isotopic ratios of the samples were measured using a FlashEA 1112, coupled via a ConFlo IV to a Delta V Advantage isotope ratio mass spectrometer. The $\delta^{15}\text{N}_{\text{tot}}$ values are expressed as the relative deviations from the measured $^{15}\text{N}/^{14}\text{N}$ ratio and with respect to atmospheric N_2 . Sample precision and data calibration were performed using IAEA standards IAEA-N-1 (+0.43‰) and IAEA-N-2 (+20.41‰) and IVA Analysentechnik Urea Isotopic Working Standard (−0.32‰).

Results and discussion

The TOC content was consistently high in the black shale samples from Kallavere and Türisalu formations, ranging between 8 and 15% ($n = 108$) and low $<1\%$ ($n = 16$) in the Varangu Formation (Fig. 1). TN values varied accordingly from 0 to 0.66% and $<0.07\%$, presenting strong positive covariance with TOC distribution ($R^2 = 0.89$, $n = 26$; Fig. 2). This suggests that most of the N resides in OM (note, however, that same samples also present consistent covariance between TOC, TN, and clay fraction indices). The average C/N atomic ratios from black shale of the Türisalu Formation, black shale interbeds from the Kallavere Formation, and grey shales from the Varangu Formation were ~ 37 ($n = 108$), ~ 29 ($n = 60$), and ~ 15 ($n = 16$), respectively. The $\delta^{13}\text{C}_{\text{org}}$ values of the black shales generally showed low variability ranging between -29.8 and -29.0‰ ($n = 35$), matching the values reported from Tremadocian complexes from the deeper part of the basin (Terfelt et al. 2014). Heavier $\delta^{13}\text{C}_{\text{org}}$ values (as high as -27.3‰) were detected in the organic-poor samples of the Varangu Formation and in a few intervals of coarse-grained black shales, with $\delta^{13}\text{C}_{\text{org}}$ increasing in phase with TOC, TN, and decreasing in C/N. The black shale samples characteristically showed $\delta^{15}\text{N}_{\text{tot}} \sim 0\text{‰}$, with an average value for the Türisalu Formation -0.7‰ ($n = 24$) and for the Kallavere Formation -1.8‰ ($n = 8$). The $\delta^{15}\text{N}_{\text{tot}}$ signal range from the uppermost metal-poor part of the Türisalu Formation was similar to that observed for the Kallavere Formation. The total $\delta^{15}\text{N}_{\text{tot}}$ variance from -2.5 to 0.2‰ is in the same range with typical organic-rich black shales, including those from the Baltic Palaeobasin (Kiipli and Kiipli 2013; Hammer and Svensen 2017). A distinctly different

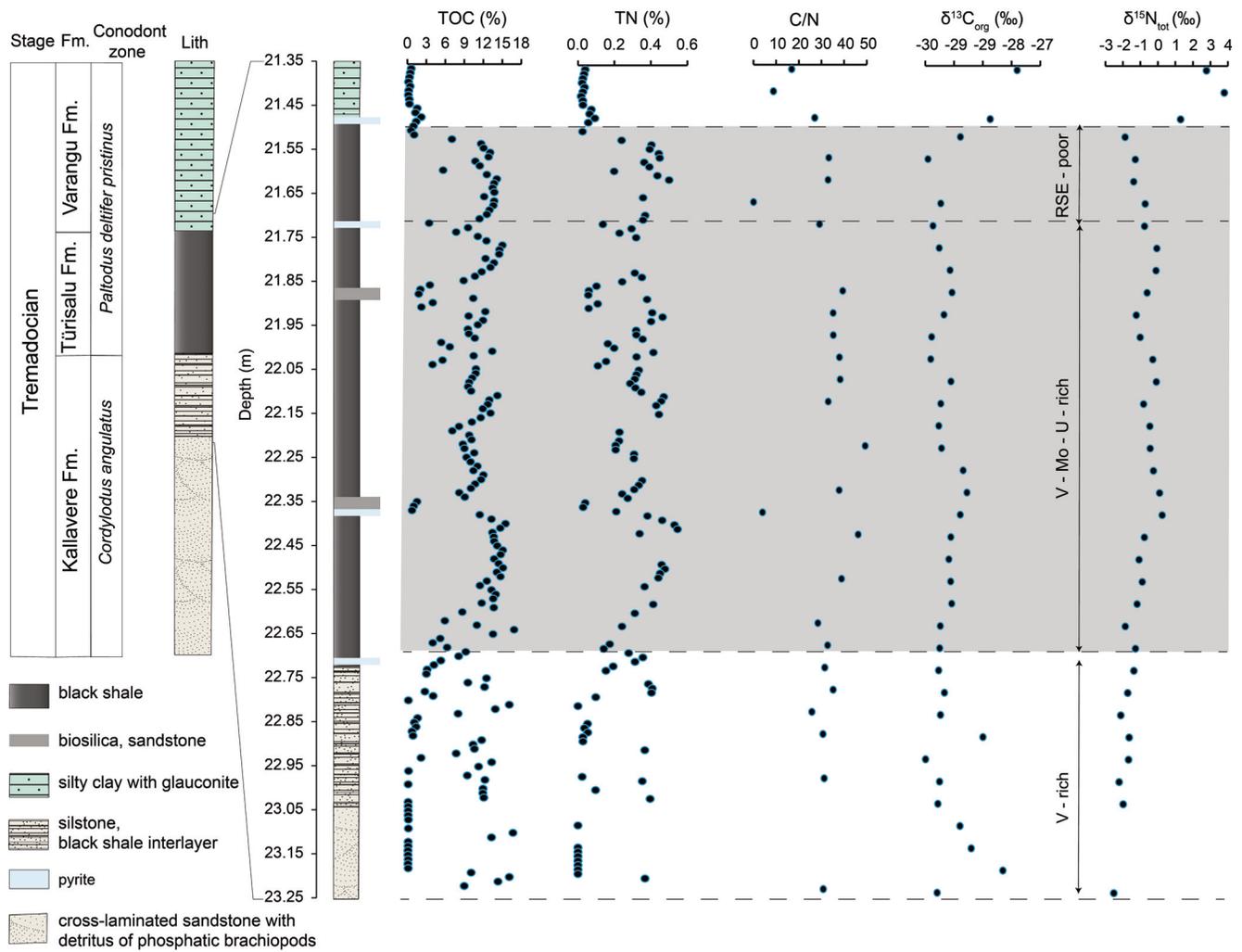


Fig. 1. Distribution of TOC, TN, molar C/N ratios, $\delta^{13}C_{org}$ and $\delta^{15}N_{tot}$ in the Aseri PH012B drill core. Abbreviations: Fm. – Formation, Lith – Lithology. Biozone boundaries after Heinsalu et al. (2003).

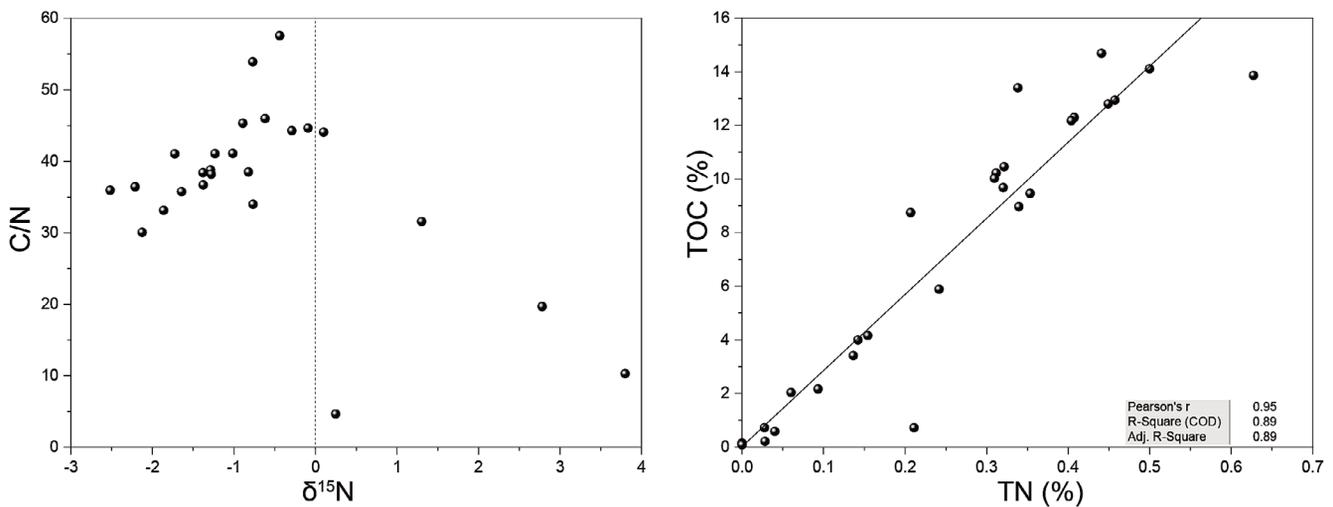


Fig. 2. Scatterplots of C/N ratios versus $\delta^{15}N$ and TOC versus TN for samples from the Aseri PH012B drill core. Abbreviation: Adj. – Adjusted.

$\delta^{15}N_{tot}$ range, between 1 and 4‰, was found in three samples from the Varangu Formation. No clear covariance was detected between TOC and $\delta^{13}C_{org}$ and between TOC and $\delta^{15}N_{tot}$. The distribution of $\delta^{15}N_{tot}$ versus C/N demonstrates that the loss of N from the black shale organic matter (assuming that primary biomass had a Redfield-like stoichiometry C:N \approx 16:106) is accompanied by a shift of

$\delta^{15}N_{tot}$ signal towards atmosphere-like unfractionated values.

We suggest, based on the observed variance, that N_2 fixation functioned as the dominant source of N for phytoplankton, helping to maintain a very high net primary production. The low negative $\delta^{15}N_{tot}$ values of the primary biomass (ranging from \sim -2.5 to -1‰) can be explained by

efficient biomass transfer to the sea bottom due to a shallow oxygen-depleted water column in which quantitative denitrification processes dominated. The following release of N near the sediment-water interface via OM mineralization by conventional or sulphate-reducing anammox, combined with decreased net sediment rates, controlled the modification of the sediment N isotope composition and led to a small positive shift ($\sim 1\%$) in $\delta^{15}\text{N}_{\text{tot}}$ (Hammer and Svensen 2017). Alternatively, the lower $\delta^{15}\text{N}_{\text{tot}}$ values in the Kallavere Formation and the RSE-poor part of the Türisalu Formation could be explained simply by a switch to alternative nitrogenase-using species due to Mo-limitation (Zhang et al. 2014) or a switch to another ^{15}N -depleted source of N. Nevertheless, the co-occurring decrease in the C/N ratios and $\delta^{15}\text{N}_{\text{tot}}$ suggests that the loss of N was most likely the reason behind the observed isotopic variance. The beginning of the accumulation of grey mud in the Varangu Formation marked the principal rearrangement in the nutrient cycle and redox architecture in the considered shallow shelf areas, establishing new equilibria in which NO_3^- assimilation became the major source of N for primary producers in a better oxygenated water column.

Conclusions

The relatively low $\delta^{15}\text{N}$ values of -2.5 to 0.2% , combined with high C/N, suggest that bioproduction during the deposition of organic-rich muds was likely nitrogen-limited. N_2 -fixation, as well as N_2 -outgassing through denitrification and anoxic mineralization of OM in sediments, played a significant role in the biochemical cycling of nitrogen. The mineralization of OM in anoxic sediments slightly shifted the $\delta^{15}\text{N}_{\text{tot}}$ of the remaining OM towards heavier isotopic compositions. The principal transition in the local cycle of N in the considered inner shelf settings of Baltica occurred with the start of sediment accumulation in the Varangu Formation with a likely switch from diazotrophic-dependent to nitrate-based primary production, as evidenced by a shift towards positive $\delta^{15}\text{N}_{\text{tot}}$ values.

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