

## Centimetre-scale variability of redox-sensitive elements in Tremadocian black shales from the eastern Baltic Palaeobasin

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**Abstract.** The high-resolution study of vertical geochemical variability of shallow-water Tremadocian black shales of the Türisalu Formation targeted two drill core sections from Suur-Pakri Island, NW Estonia. Altogether 374 samples from 4.6 m thick shale were analysed by XRF. The metalliferous and organic-rich black shales revealed significant centimetre-scale variation in the concentration of redox-sensitive trace metals – U, Mo and V. The V profiles show cyclic variations in half a metre- to metre-scale and the strongest correlation with loss on ignition (LOI) 500 °C (interpreted to reflect organic matter abundance). The abundance of Mo presents high values near the lower and upper contacts of black shale and otherwise moderate covariance with LOI. The distribution of U is not coupled with LOI, being characterized by irregular local enrichment anomalies in the profiles of both sections. This suggests that sequestration of U may have been time-dependent and possibly favoured by dissimilatory U-reduction at the sediment–water interface under iron-reducing conditions. Significant depositional variability of the studied organic-rich muds apparently supported dynamic physicochemical and biological microenvironments at the sediment–water interface and thus temporally and spatially diversified the paths and efficiency of synsedimentary redox-sensitive trace element enrichment.

**Key words:** black shale, geochemistry, redox-sensitive elements, Tremadocian, Baltica.

### INTRODUCTION

Organic-rich deposits ranging from shallow estuarine to ocean floor varieties act as a significant sink for a number of redox-sensitive elements (e.g. Calvert & Pedersen 1993; Morford & Emerson 1999). The distribution of redox-sensitive elements in ancient organic-rich deposits have shown to be useful proxies for interpreting the redox-structure of palaeoseawater, primary productivity and palaeohydrography (e.g. Algeo & Maynard 2004; Algeo & Lyons 2006; Brumsack 2006; März et al. 2008; Algeo & Tribovillard 2009). The interpretations rely on enrichment models compiled mostly on the basis of data from anoxic deposits from relatively deep-water settings. Nevertheless, black shales can also be found in shallow-water proximal sedimentary environments (Schieber 1994; Hints et al. 2014). The high-resolution case studies of such assemblages help to test the usefulness of trace-metal proxies for palaeoenvironments that are likely prone to a much higher influence of short-term (including annual oscillations) environmental changes compared to deep-water settings. Furthermore, such investigations are essential for providing new insights into the set of palaeoenvironment conditions, which could support the development of proximal black shales, including some rather metalliferous varieties (e.g. Coveney et al. 1991).

The Tremadocian black shales of the Türisalu Formation (Fm.) make up a laterally extensive organic-rich siliceous mudstone bed in northern Estonia, eastern part of the Baltic Palaeobasin. Characterized by a high content of U, Mo, V and some chalcophile elements, the complex is a potential resource of a variety of metals (Hade & Soesoo 2014). Recent findings suggest that the Türisalu Fm. exemplifies transgressive, but rather shallow-water reducing marine muds with spatially heterogeneous properties (Voolma et al. 2013; Hints et al. 2014). According to biostratigraphic data, the unit is diachronous and varies in thickness from less than half a metre in northeast Estonia to more than 6 m in northwest Estonia (Heinsalu et al. 2003) (Fig. 1). The average distribution of enriched redox-sensitive elements shows significant lateral variations in the Türisalu Fm. (Pukkonen & Rammo 1992). However, the genetic factors behind the documented spatial and temporal trace metal heterogeneity are not well understood. Based on the biostratigraphic framework and a recent time scale calibration (Cooper & Sadler 2012), one could argue that the primary muds of the Türisalu Fm. should have been deposited within a maximum time frame of ~5 My (Hints et al. 2014). Whereas the long-term accumulation rates apparently stayed very low during sedimentation of the primary organic-rich muds of the Türisalu Fm., the sedimentary fabrics in the black shales suggest dynamic deposition,

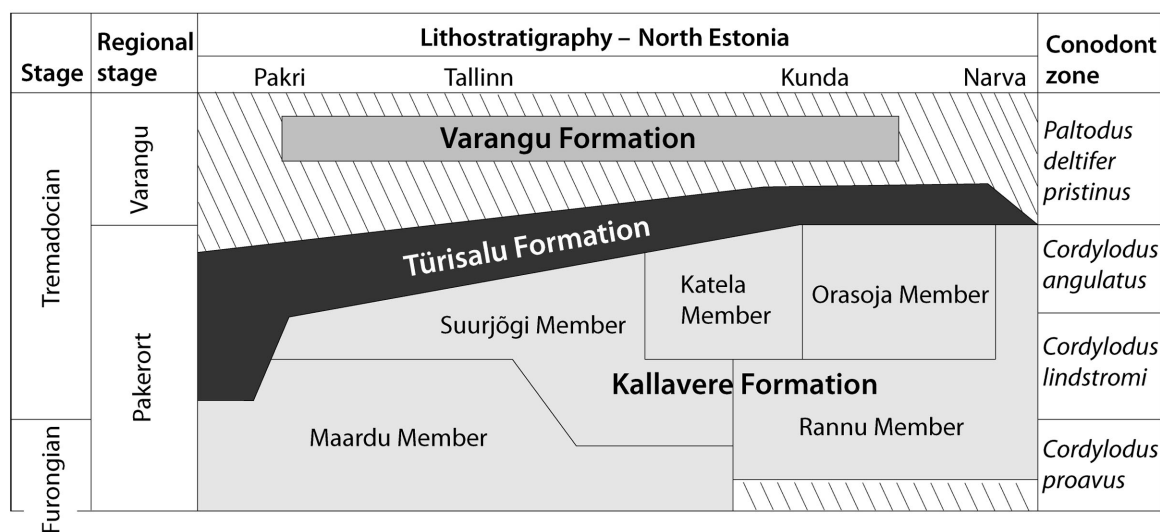


Fig. 1. Stratigraphic position of the Türisalu Fm. (modified after Heinsalu et al. 2003).

frequent reworking of sea bottom and changes in deposition rates (Hints et al. 2014). The studies of modern organic-rich muds have revealed usefulness of high-resolution sampling within a limited geographic range (e.g. Algeo & Lyons 2006), allowing more reliable distinction between possible driving factors behind the synsedimentary trace metal sequestration and more consistent environmental interpretations.

In this paper we report the first results of a centimetre-scale study of redox-sensitive trace metal distribution in the Tremadocian black shales in two closely spaced drill core sections from NW Estonia, Baltica. The study was carried out in order to record and interpret detailed enrichment patterns of redox-sensitive elements in the Türisalu Fm.

## MATERIAL AND METHODS

The study material comes from two drill cores from Suur-Pakri Island, NW Estonia, located less than a kilometre apart: SP2 (59°20'13.07"N, 23°53'54.74"E, WGS84) and SP3 (59°20'15.33"N, 23°54'33.8"E, WGS84). The ca 4.6 m thick black shale successions show high lithological variability, including the presence of finely laminated, ripple laminated, graded, massive, biolaminated, bioturbated fabrics and small-scale synsedimentary faulting. The dominant fabric types and thickness of individual beds vary as well.

A quarter of the black shale in both drill cores was sampled and analysed by 2-cm intervals. Siliciclastic beds belonging to the Kallavere Fm. and the Varangu Fm. near the lower and upper contacts of the Türisalu Fm.

were also sampled. Altogether 374 homogenized samples were analysed for major and trace element composition with Bruker S4 PIONEER XRF spectrometer (X-ray tube with a rhodium anode, operated at 3 kW) at the Institute of Geology at Tallinn University of Technology. The samples were measured with a manufacturer's standard as MultiRes modification. In-house standard ES-2 ('Dictyonema Shale') was used as a reference sample (Kipli et al. 2000).

In the current overview we focus on the results of vertical variability of enriched redox-sensitive elements in the studied sections. Other trace element data will be published elsewhere. From all samples loss of ignition at 500 °C (LOI 500 °C) was determined from 1 g of sample material and used as an indicator of organic matter abundance (except in case of sulphide-rich samples).

## RESULTS

The studied black shales of the Türisalu Fm. revealed a remarkably homogeneous major element composition of mineral matter. The average values of major elements and redox-sensitive trace elements are summarized in Table 1. The recorded high content of Si and K are typical features of the black shales of the Türisalu Fm., where silt-size particles dominate over clay fraction and which contains abundant authigenic K-feldspar (Loog et al. 2001). Aluminium content shows low variability, being on average smallest in the middle part of the sections. Furthermore, Ti/Al ratios, commonly interpreted to reflect changes in terrigenous input and provenance

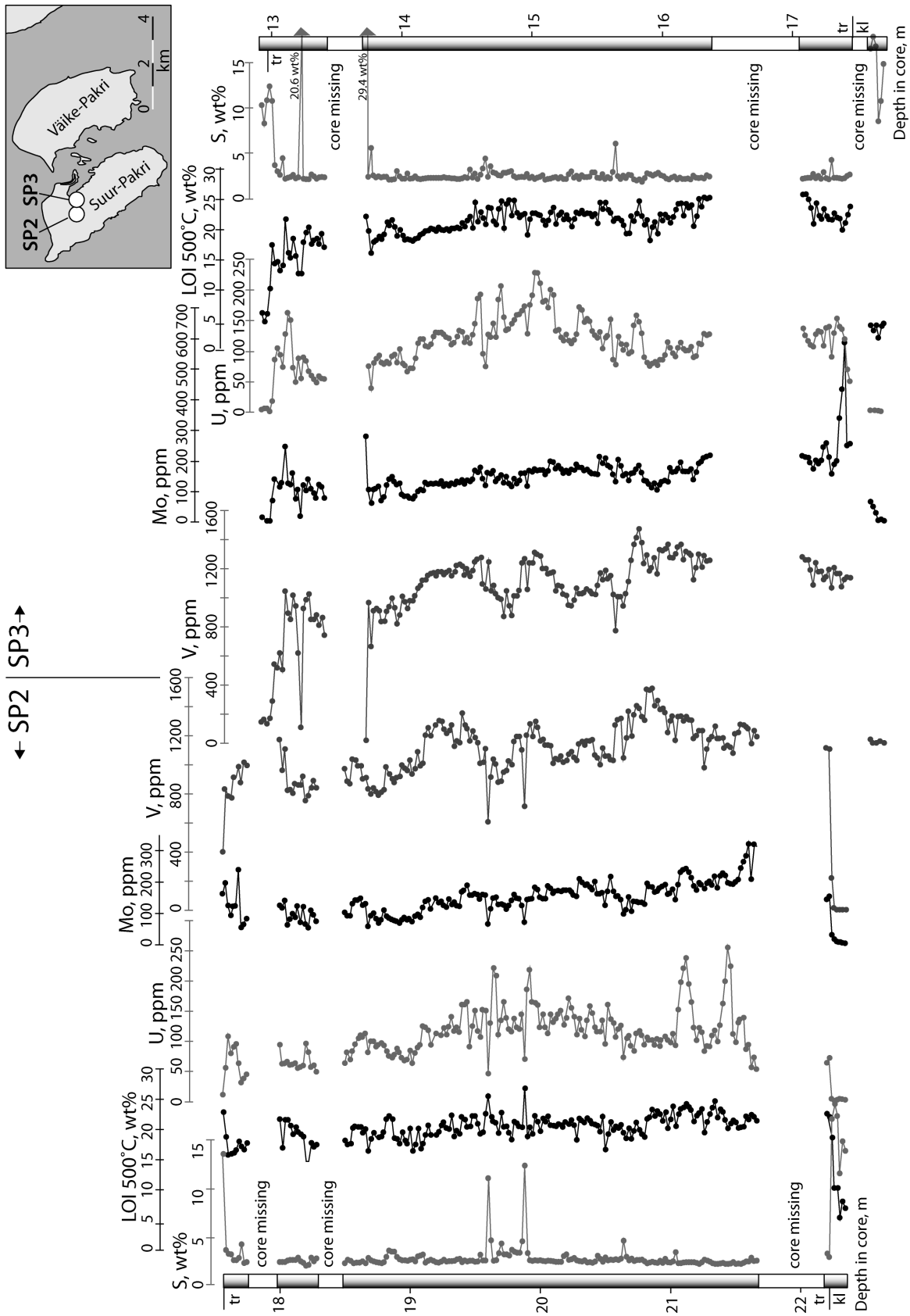
**Table 1.** Summarized results of XRF analyses of major elements (wt%) and redox-sensitive elements (ppm), recorded loss on ignition values (wt%) and calculated Ti/Al molar ratios of the black shales of the Türisalu Fm. from SP2 and SP3 drill cores

Component	SP2 <i>n</i> = 183				SP3 <i>n</i> = 168			
	Mean	SD	Max	Min	Mean	SD	Max	Min
SiO <sub>2</sub>	49.82	1.48	54.47	46.35	50.36	1.49	54.29	47.08
TiO <sub>2</sub>	0.75	0.03	0.86	0.67	0.74	0.03	0.81	0.63
Al <sub>2</sub> O <sub>3</sub>	12.90	0.32	14.06	11.93	13.21	0.35	13.90	11.84
Fe <sub>2</sub> O <sub>3</sub>	5.27	0.77	9.22	4.54	5.05	0.77	10.93	4.29
MnO	0.020	0.001	0.022	0.016	0.020	0.004	0.066	0.014
MgO	1.20	0.05	1.34	1.03	1.25	0.11	2.20	1.05
CaO	0.24	0.09	1.05	0.16	0.30	0.42	4.45	0.16
Na <sub>2</sub> O	0.07	0.01	0.09	0.02	0.07	0.01	0.11	0.01
K <sub>2</sub> O	7.75	0.20	8.56	7.11	7.70	0.23	8.31	6.86
P <sub>2</sub> O <sub>5</sub>	0.14	0.07	0.72	0.07	0.16	0.12	1.00	0.09
S	2.76	0.45	4.76	2.05	2.51	0.42	5.63	1.94
LOI 500°C	20.628	1.887	24.9	15.05	21.183	2.48	25.874	12.67
100Al/Ti	3.74	0.11	4.166	3.478	3.58	0.09	3.78	3.302
Mo	151	51	323	55	156	58	589	62
U	114	40	257	33	118	36	229	40
V	1101	172	1520	752	1097	175	1474	508

areas (e.g. Boyle 1983), showed invariable patterns in both of the studied cores. The average recorded LOI 500°C value in the shale samples is ca 21 wt%, decreasing slightly in the upper parts of both sections (Table 1, Fig. 2). The LOI 500°C variations, which could in most part be interpreted in terms of organic matter abundance in organic-rich deposits, are, however, dependent on other additional processes such as decomposition of sulphides and carbonates and dehydration of clays. The gathered compositional data agree with the rather low carbonate content and uniform clay mineral abundance in the studied profiles. Therefore, those components have apparently a minor role in the observed mass loss. On the other hand, the analyses indicate the occurrence of a few highly sulphidic samples ( $S > 5$  wt%), mostly close to the upper and lower contacts of the formation. Such samples were excluded from the dataset used to calculate descriptive statistics for the black shale geochemistry. The calculated determination coefficient for S and LOI ( $r^2 = 0.05$ ,  $n = 351$ ) for samples with  $S < 5$  wt% does not indicate covariance between those variables, thus likely no general strong linear relationship exists between LOI and sulphide content in the black shale samples. The recorded distribution trends of Fe in the studied black shales largely mimic that of S, suggesting that the higher abundance of the metal could largely be attributed to the elevated content of pyrite.

In contrast to the major components, the studied enriched redox-sensitive trace elements show rather

heterogeneous centimetre-scale vertical distribution patterns (Fig. 2). The average estimated content of V is 1100 ppm, Mo 150 ppm and U 115 ppm. According to these values, the studied sections represent the less-enriched area of the Türisalu Fm. (cf. Pukkonen & Rammo 1992). However, the concentration of the considered redox-sensitive elements is markedly elevated in the samples from the Türisalu Fm. compared to the underlying and overlying siltstones. To minimize the effect of terrigenous dilution, the trace element contents of marine deposits are commonly presented as ratios of the trace element to Al. However, normalization was not used in this study due to rather low variability of Al content and to avoid possible appearance of spurious correlations between variables (Van der Weijden 2002). Whereas in general the recorded V and Mo show positive covariance with LOI 500°C (and supposedly organic matter content), the behaviour of each redox-sensitive trace element is rather distinct in detail. Vanadium shows moderate positive covariance with LOI 500°C ( $r^2 = 0.42$ ,  $n = 351$ ) and cyclic variations in half a metre- to metre-scale in both of the studied cores. Considerably similar V distribution patterns in the middle part of the two sections may serve as a basis for chemostratigraphic correlation. Distribution profiles of Mo exhibit weak covariance with LOI 500°C ( $r^2 = 0.28$ ,  $n = 351$ ) and are characterized by enrichment peaks near the upper and lower contacts of the black shale in close vicinity of sulphide-rich beds. The average Mo content shows slight



**Fig. 2.** Vertical distribution profiles of U, V, Mo, LOI 500°C and S in the black shales of the Türisalu Fm. and under- and overlying siliciclastic complexes from drill cores SP2 and SP3, Suur-Pakri Island, NW Estonia. tr – Türisalu Fm.; kl – Kallavere Fm.

decrease towards the upper part in both of the studied profiles. Uranium displays no obvious covariance with LOI 500°C ( $r^2 = 0.19$ ,  $n = 351$ ). Its average content tends to be the highest in the middle part of the successions. However, U distribution is characterized by irregular enrichment peaks, which mostly do not coincide with peak V and Mo values, nor does U show clear covariance with the distribution of S. Furthermore, the enrichment peaks of U, which show sharp centimetre-scale deviations from general distribution trends of the element, appear to be local in character, as there is no good match between such U peaks in the two studied localities. This suggests that some local factor(s) affected the speciation and enrichment process of uranium, in addition to the changing redox state of seawater or organic matter input.

## DISCUSSION AND CONCLUSIONS

Redox-sensitive metals tend to form mobile species under oxic conditions and immobile species in reducing environments, therefore typically accumulating in sediments near redox boundaries. However, several recent investigations suggest that the reduction and sequestration of U, Mo and V occurs via various speciation pathways and thus parallel assessment of the behaviour of different redox-sensitive elements might potentially give a much more detailed picture of primary environments than single-element-based approaches (e.g. Algeo & Maynard 2004; Tribovillard et al. 2006). According to Gill et al. (2011), widespread euxinia characterized the Late Cambrian oceans. The ocean redox structure at the beginning of the Tremadocian is nevertheless poorly known, as is the redox structure in the shallow-water proximal part of the vast epicontinental Baltic Palaeobasin, where primary organic-rich muds of the Türisalu Fm. deposited. Based on the high content of redox-sensitive metals and organic matter in the Türisalu Fm., Pukkonen & Rammo (1992) suggested that kerogenous muds in northwestern Estonia were once deposited under a stagnant, stratified and permanently euxinic water column. However, bioturbation, which could be fairly intensive in some intervals of the studied sections (e.g. SP2 between 14.1 and 14.5 m, note rather homogeneous abundance of redox-sensitive elements there), favours a more complex syndepositional environment with free oxygen present at the sediment–water interface (SWI) more or less regularly. The general positive covariance of V and Mo with that of organic matter in the studied drill cores from Suur-Pakri Island confirms that the sequestration process of metals from seawater was in general controlled by metal reduction triggered by oxygen depleted seawater or anoxia below the SWI

and closely coupled with organic matter degradation, whereas organic–metal complexation could have acted as a major pathway for metal enrichment (cf. Algeo & Maynard 2004). The herein documented complex distribution patterns of elements imply that other factors besides redox should be considered as potential sources of variance, including the influence of the presence of free HS<sup>-</sup>, possible role of particulate shuttles, position and stability of the chemocline in the enrichment environment, influence of microbial mediation, bioturbation and redeposition. For example, Mo enrichment near the formation boundaries, which is not coupled with enhanced U and V abundances, may indicate that euxinic conditions favourable for activation of thiomolybdate switch (Helz et al. 1996) quickly turned prevailing in the lower water column during the start of organic-rich mud accumulation, facilitating sequestration of Mo via sulphide formation. The recorded Mo-enrichment may as well reflect an episode of more efficient scavenging of the metal by Mn–Fe-oxyhydroxide under intermittent redox conditions and fluctuating chemocline (Algeo & Tribovillard 2009) during the initial phases of transgression. Early diagenetic enrichment of Mo cannot be excluded either, as elevated abundances of the element appear near black shale contacts with more permeability siltstones. The Mo/U ratio for the studied profiles, whose variations could potentially indicate restriction of palaeoseawater masses (Algeo & Tribovillard 2009), does not suggest draw-down of aqueous concentration of Mo during organic-rich mud deposition. Slight decrease in the average Mo/U ratio in the upper part of the sections is interpreted to reflect somewhat less reducing conditions at the SWI rather than depletion of an aqueous Mo reservoir. Accordingly, open to semi-restricted marine conditions likely prevailed during most of the organic-rich mud accumulation period.

The forcing mechanisms behind the observed cyclic distribution patterns of V, whose reduction could start under slightly less reducing conditions than that of U and Mo (Algeo & Maynard 2004), are far from clear. The data presented here indicate low variability in terrigenous influx and thus lack of major terrigenous control (e.g. due to climatic or eustatic changes) over V sequestration. The cyclicity of V abundance might be linked to factors such as alteration of thermohaline circulation or water depth fluctuations and related cyclic changes in dissolved oxygen availability near the sea bottom. On the other hand, Hints et al. (2014) suggested that high primary productivity rates driven by phosphate loading and effective recycling in the shallow water column (sea bottom within the photic zone) characterized the accumulation of the muds of the Türisalu Fm. The recorded V pattern might thus be connected to cyclic changes in nutrient loading and palaeoproductivity.

Nevertheless, a more consistent interpretation of the triggering forces behind V behaviour requires considering additional datasets.

Unlike that of Mo and V, which could be reduced both within the marine water column and in sediments, U reduction is known to occur only within sediments (e.g. Algeo & Maynard 2004). Based on shoreward increase in U in the Cambrian Alum Shales in Scandinavia, Schovsbo (2002) suggested that synsedimentary U enrichment had been controlled by a more efficient advective transport of U in those settings. Both sections of the Türisalu Fm. studied herein show sedimentary features indicative of deposition under a hydrodynamically active water column, and thus the dominance of advective rather than diffusive transport of elements to the SWI is likely. Furthermore, the average thickness of shale beds and Al content drops in the middle part of the studied black shale sections, while the abundance of bioclastic fragments increases, generally coinciding with a high U content. Those changes could have favoured more efficient element exchange over the SWI and the longevity of the SWI. We hypothesize that under such conditions the U enrichment anomalies could record enhanced efficiency of local U reduction at the SWI, possibly favoured by the dominance of an iron-reducing rather than H<sub>2</sub>S-enriched environment and microbially controlled processes within pore waters of the upper sediment layer. Numerous recent studies of the modern aquatic system and experimental works (e.g. Komlos et al. 2008) have indicated that efficient U-trapping through microbially mediated dissimilatory metal reduction could occur simultaneously with Fe(III)–Fe(II) transition under iron-reducing conditions. It is noteworthy that the middle parts of the studied black shale successions, which show the highest U abundances, also contain common remains of probable microbial mats.

In summary, the two sections of the Türisalu Fm. studied are characterized by high centimetre-scale vertical variability of V, Mo and U. Significant depositional heterogeneity of shallow-water kerogenous muds likely favoured dynamic physicochemical and biological micro-environments at the SWI and thus spatially and temporally diversified pathways and efficiency of synsedimentary enrichment of Mo and especially U, even in rather closely set localities. Due to considerable influence of local enrichment factors, the application of redox-sensitive elements as indicators of palaeoredox conditions of seawater is limited in the Türisalu Fm.

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