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SYLVESTER IKENNA OFILI

Geochemistry and depositional environments of two black shale formations: the Baltoscandian Cambrian-Ordovician Alum Shale and the Cretaceous Lokpanta Oil Shale

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Department of Geology, Institute of Ecology and Earth Sciences, Faculty of Science and Technology, University of Tartu, Estonia.

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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers. These papers are referred to in the text by their respective Roman numerals.

I. Ofili, S., Soesoo, A., Panova, E.G., Hints, R., Hade, S. and Ainsaar, L., 2022. Geochemical reconstruction of the provenance, tectonic setting and paleo-weathering of lower paleozoic black shales from northern Europe. *Minerals*, *12*(5), p. 602. https://doi.org/10.3390/min12050602

II. Vind, J., Ofili, S., Mänd, K., Soesoo, A. and Kirsimäe, K., 2023. Redox-sensitive trace metal hyper-enrichment in Tremadocian Alum Shale (graptolite argillite) in northwestern Estonia, Baltic Palaeobasin. *Chemical Geology*, *640*, p. 121746. https://doi.org/10.1016/j.chemgeo.2023.121746

III. Ofili, S. and Soesoo, A., 2021. General geology and geochemistry of the Lokpanta Formation oil shale, Nigeria. *Oil Shale*, *38*(1), pp. 1–25. https://doi.org/10.3176/oil.2021.1.01

The author's contribution:

Paper I: The author was primarily responsible for planning the original research, data acquisition, geochemical data analysis and interpretation, and writing the manuscript.

Paper II: The author was responsible for XRD analysis, and contributed to planning the original research, data collection, and writing the manuscript.

Paper III: The author was primarily responsible for planning the original research, mineralogical and geochemical analysis, interpretation and synthesis of analytical results, and writing the manuscript.

1. INTRODUCTION

Organic-rich black shales are common in geological records and occur in all continents of the world. Their chemistry is dependent on several factors, including depositional environment, redox condition, sedimentation rate, and seawater composition; hence they are useful as an archive of past climate, and in understanding geodynamic events in Earth's history (Bhatia and Crook, 1986; Zhao et al., 1990; Hayashi et al., 1997). In addition, some black shale may have economic interest as metal and hydrocarbon resources.

The formation of black shales is often associated with periods of widespread seawater column anoxia. In the early Palaeozoic, increased global marine anoxia is evidenced by the widespread distribution of Cambrian-Ordovician organic-rich black shale formation in the Baltic Paleobasin, widely known as the Alum Shale (Schovbo 2001; Dahl et al., 2010; Saltzman et al., 2015). Similarly, in the late Cretaceous and Jurassic periods, the globally distributed recurring organic-rich black shale intervals are often referred to as ocean anoxic events (OAEs) (Schlanger and Jenkyns, 1976). A notable example of black shale deposition in such anoxic events is the Cenomanian – Turonian Lokpanta Oil Shale in the Lower Benue Trough of Nigeria, potentially corresponding to OAE2 (Ekweozor and Unomah, 1990).

The Baltoscandian Alum Shale has deserved considerable attention over the years due to its high content of redox-sensitive elements such as U, V, Mo, and organic matter, making it a potential source of metals and hydrocarbons (Andersson et al., 1983; Voolma et al., 2013; Vind and Bauert, 2020). However, the depositional environment and redox state, as well as the source, distribution, and enrichment mechanism of metals in the black shale have not been fully resolved. Some studies have suggested that metal enrichments were sourced by diffusion from seawater or by dissolution of detrital minerals as suggested for uranium in the Alum Shale (Schovsbo, 2002; Schulz et al., 2019). Others have suggested redox element enrichments originating from hydrothermal activity, and the reactions of basaltic volcanic rocks with anoxic water (Berry et al., 1986; Vyalov et al., 2013).

The distribution of redox(-sensitive) elements in the Alum Shale is heterogeneous, reflecting variations in depositional settings (Voolma et al., 2013). Although most of the paleoenvironmental studies concentrate on syngenetically enriched metal assemblages, the variance of the primary clastic material has not been sufficiently studied, and its influence on metal enrichment in the black shale remains poorly understood (Schulz et al., 2019).

Owing to high Mo and V contents in the Alum Shale, the palaeoredox condition during the black shale formation has been interpreted as permanently euxinic (Bian et al., 2021; Bian et al., 2022). However, the black shale is rich in benthic fossil fauna (e.g. trilobites, graptolites), indicating episodic bottom water oxygenation and dynamic ocean redox conditions (Schovsbo, 2001; Dahl et al., 2019).

The Lokpanta Oil Shale has attracted the attention of several researchers mainly because of its potential to serve as a source of hydrocarbon (Ekweozor and Unomah, 1990; Akande et al., 2012; Abubaka, 2014). However, the depositional environment, redox condition, and metal geochemistry of the Lokpanta shale as well as its possible correlation with the global Cretaceous Oceanic Anoxic Event (OAE 2; Ehinola et al., 2010) are insufficiently studied. Previous studies have suggested that despite temporal differences, the enrichment trends of trace elements in the Lokpanta Oil Shale are similar to those of the Alum Shale, although in most cases, the trace element contents are higher in the latter (Amajor, 1987; Sonibare et al., 2011; Voolma et al., 2013). Additionally, having been deposited in anoxic basins, both the Alum Shale and the Lokpanta Oil Shale may share similarities in their depositional environment.

This thesis addresses the depositional environment and geochemistry of the Fennoscandian Cambrian-Ordovician black shale formation in Sweden, Estonia, and Russia, and the Lokpanta Oil Shale in Nigeria to model their trace element enrichment controls. It also counterpoints to recent theories that attribute the deposition of the Alum Shale to a restricted euxinic basin.

The objectives of the thesis are:

- To provide geochemical characterization of the Lower Paleozoic Cambrian-Ordovician Alum Shale and the Cenomanian-Turonian Lokpanta Oil Shale.
- To reconstruct the paleo-depositional conditions of the Alum Shale, and to compare them with those of the Nigerian Lokpanta Oil Shale formation to assess their control on trace element enrichment.
- To model the redox-sensitive metal distribution and accumulation mechanisms of the Alum Shale to better constrain redox and depositional environments in the Baltic Palaeobasin.

This thesis aims to test the following hypothesis:

1. Similarities in depositional settings between the Alum Shale and Lokpanta Oil Shale may account for the observed similarity in trace element enrichment patterns.
2. Mineral and geochemical composition of the siliciclastic components of the black shales has been controlled by climatic type of weathering in the provenance areas.
3. Despite hyper-enrichment of Mo and V in the Alum Shale, significant redox variability controlled by the sedimentary environment have been existed within the Baltic Paleobasin.

2. GEOLOGICAL SETTINGS OF THE ALUM SHALE AND THE LOKPANTA OIL SHALE FORMATION

2.1. Baltica paleocontinent

The Baltic Paleobasin existed during the Cambrian-Silurian period on the Baltica paleocontinent and was surrounded by the Fennoscandian and Sarmatian oldlands (Figure 1 a). The development of Baltica started in the Precambrian with the collision of Fennoscandian, Sarmatian and Volgo-Uralian blocks (Cocks and Torsvik, 2005). Since its development, Baltica has made a rotation, losing and gaining terranes in the process. Its geographical position (distance from the equator, hydrodynamic conditions) was one of the main factors that affected the type of sediments deposited. During the early Cambrian time, Baltica was located at 35–60º South of the equator, in a warm temperate climate (Willden, 1980; Torsvik and Cocks, 2013). In the late Cambrian to early Ordovician, Baltica had begun to drift northwards and was situated at about 40–50º in the Southern Hemisphere (Corks and Torsvik, 2005).

Deposition of the Lower Paleozoic black shales, which are widespread in the Baltoscandian region, extending from Oslo in Norway to NW Russia and covering an area of over 800,000 km^2, began when Baltica was situated at about 40–50º south of the equator (Corks and Torsvik, 2005; Nielsen and Schovsbo, 2011). Due to its vast lateral extent, the black shale bears different stratigraphic names in countries where it occurs. It is commonly referred to as Alum Shale in Sweden, Graptolite Argillite (GA) in Estonia and Dictyonema Shale in Russia. It is an organic-rich mudstone, with total organic matter between 10 to 25 wt% (Andersson et al., 1985). It was deposited in the Baltoscandian paleobasin, a large, shallow epicontinental sea that covered a substantial part of Baltica during the middle Cambrian to early Ordovician period (Andersson et al., 1985). This period was characterized by globally high sea levels, a likely occurrence of global anoxic conditions and a low rate of deposition in the Baltoscandian Basin (Nielsen and Schovsbo, 2015). Sediment deposition commenced in Sweden in the middle Cambrian (Miaolingian) and progressively became younger eastward (Nielsen and Schovsbo, 2007). In Estonia and NW-Russia, the age of the black shale is assigned to the early Ordovician (Tremadocian) (Nielsen and Schovsbo, 2007).

Stratigraphically, the Alum Shale in Estonia belongs to the Tremadocian Türisalu Formation, which overlies the phosphatic sandstone of the Furongian Kallavere Formation (Vind and Bauert, 2020). In western Estonia, the Türisalu Formation belongs to the Pakerort Regional Stage, whereas in Eastern Estonia and northwestern Russia, it has been assigned to the younger Varangu Regional Stage (Kaljo and Viira, 1989). In Norway, Denmark and Sweden, the basal parts of the Alum Shale, respectively represented by the Bjorkasholmen, Bjorkasho and Djupvik formations, are of Miolingian age (Bian et al., 2021).

Alum Shale deposition in Sweden formed in the deeper part of the epicontinental basin, whereas, in Estonia and NW-Russia, it has been placed within the proximal areas of the epicontinental sea (Schovsbo, 2002). The thickness of the Alum Shale reaches up to 180 m in Denmark compared to less than 0.5 m in NW Russia (Schovsbo et al., 2014; Vyalov et al., 2017). The main lithological difference between the Cambrian and Tremadocian succession is the lower proportion of carbonate concretions in the Tremadocian sediments (Schovsbo, 2002).

Alum Shale is characterized by high to very high concentrations of V, U, Mo, Ni, and other trace metals, making it a potential metal resource for Europe (Berry et al., 1986; Pukkonen and Rammo, 1992; Voolma et al., 2013). In Sweden and Estonia, the Alum Shale contains uranium between 50 and 215 ppm, molybdenum between 80 and 230 ppm, and vanadium between 800 and 2800 ppm (Sundblad and Gee, 1985; Voolma et al., 2013; Vind, 2018). In addition to its elevated metal content, the Alum Shale distribution is considered one of the best examples of shallow marine Cambrian to early Ordovician deposits, providing a ca. 16 Myr-long record of ocean chemistry and redox conditions, capturing a critical transition from the Cambrian to Ordovician (Kaljo, 1986; Zhao et al., 2022).

2.2. The Lower Benue Trough – the Lokpanta Formation

The Lokpanta Oil Shale occurs in the Lower Benue Trough of Nigeria and covers an area of 72.7 km^2 (Figure 1 b). The Benue Trough is one of the seven sedimentary basins in Nigeria. It is a NE-SW oriented basin, believed to have formed from the failed arm of a rift system that developed because of the separation of African and South American plates, and the consequent opening of the South Atlantic Ocean during the Early Cretaceous (Olade, 1975). It is part of the West and Central Africa Rift System (WCARS), and geographically subdivided into the Upper, Middle, and Lower Benue troughs Schull, 1988; Keller et al., 1995; Akande, 1999). Sedimentation in the trough was controlled by eustatic sea level change and basin tectonics (Nwachukwu, 1985). The Benue trough was subjected to four sedimentation cycles, leading to the deposition of approximately 6000 m of Cretaceous sediments (Wozny and Kogbe, 1983; Reyment and Dingle, 1987; Akande, 1999). The first sedimentation cycle took place in the Mid to Late Albian, and resulted in the deposition of the Asu River Group which are mainly arkosic sandstones, volcaniclastics, marine shales, siltstone and limestone. Unconformably overlying the Asu River Group is the approximately 1000 m thick Upper Cenomanian to Middle Turonian Ezeaku Formation, consisting predominantly marine shales, calcareous siltstones, limestones and marl, and representing the second depositional phase. The Lokpanta Oil Shale is commonly referred to as a facies of the Ezeaku Formation (Ekweozor and Unomah, 1989). The third (Upper Turonian to Lower Santonian) and fourth (Campanian to Maastritchian) cycles led to the deposition of the Awgu Shale and Nkporo shale/Owelli sandstone respectively (Petters, 1978).

Based on foraminiferal and ostracod biostratigraphy, the Lokpanta Oil Shale is believed to have been deposited on the outer shelf to the bathyal environment and is assigned to the Late Cenomanian to the Early Turonian age (Ehinola, 2010). The oil shale is a characteristically dark grey, laminated and fissile calcareous marlstone with inoceramus moulds (Ekweozor and Unomah, 1989). Provenance studies suggest that the granitoid and basaltic rocks of the Oban and Cameroon basement massifs served as the source of the sediments (Amajor, 1987). Organic geochemical assessment indicates that the oil shale has high total organic carbon content, occasionally greater than 7% and is of type II kerogen composition (Ekweozor and Unomah, 1990).

3. MATERIALS AND METHODS

3.1. Sample locations

Major (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_2, MnO, P_2O_5) and trace (As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Re, Sr, Th, U, V, Zn) element content of representative drill cores, outcrop samples and additional data of Alum Shale in Estonia, Sweden, Russia, and Lokpanta Oil Shale in Nigeria were studied to characterize the geochemistry, and reconstruct the paleodepositional environment and redox condition of the black shale (Figures 1 a & b).

In Estonia, samples from ten drill cores (F298, F330, F343, F344, F369, F362, F355, K14, F366, F354) provided by the Geological Survey of Estonia were analyzed for major and trace elements while four out of these (F298, F330, F343, F344) were analyzed for mineralogy. The samples were taken at 20 cm intervals where possible. Major and trace element data for an additional seven drill cores (F314, F326, F328, F338, F345, F347, F360) and one outcrop (Nõmmeveski) were collected from the report of the Geological Survey of Estonia (Vind and Bauert, 2020) and Soesoo et al. (2020). Geochemical data from two additional outcrops (Pakri and Saka) (Voolma et al., 2013) were also included in the study.

Major and trace element data of samples from eight outcrops in southern Sweden (Kvantorp, Latorp, Kinnekule, Billingen, Holleberg, Hunneberg, Billingen Tim, Öland; data provided by Panova) and 34 drill cores from western Russia (drill core 1, 4, 5 11, 11-2, 12, 13-1, 15, 21-1, 22-2, 23, 23-1, 30-2, 33, 34, 40, 42, 44, 47, 50, 51-1, 61, 63, 67, 70, 77, 81, D-11, D-21, D-24, D-30, D-36, D-37, D-44) were also collected and utilized for this study (Vyalov et al., 2014). In most outcrops of Sweden, the Upper Cambrian interval of the black shale was sampled layer by layer from bottom upward. Only in the Billingen section, the Middle Cambrian interval was sampled in addition to the Upper Cambrian interval.

Eighteen samples from three drill cores (CH1, CH2, CH3), and seven outcrop samples (LK-7, LK-8, LK-15, LK-19, LK-25, LK-28, LK-30) of Lokpanta Oil Shale in Nigeria were studied to characterize the oil shale.

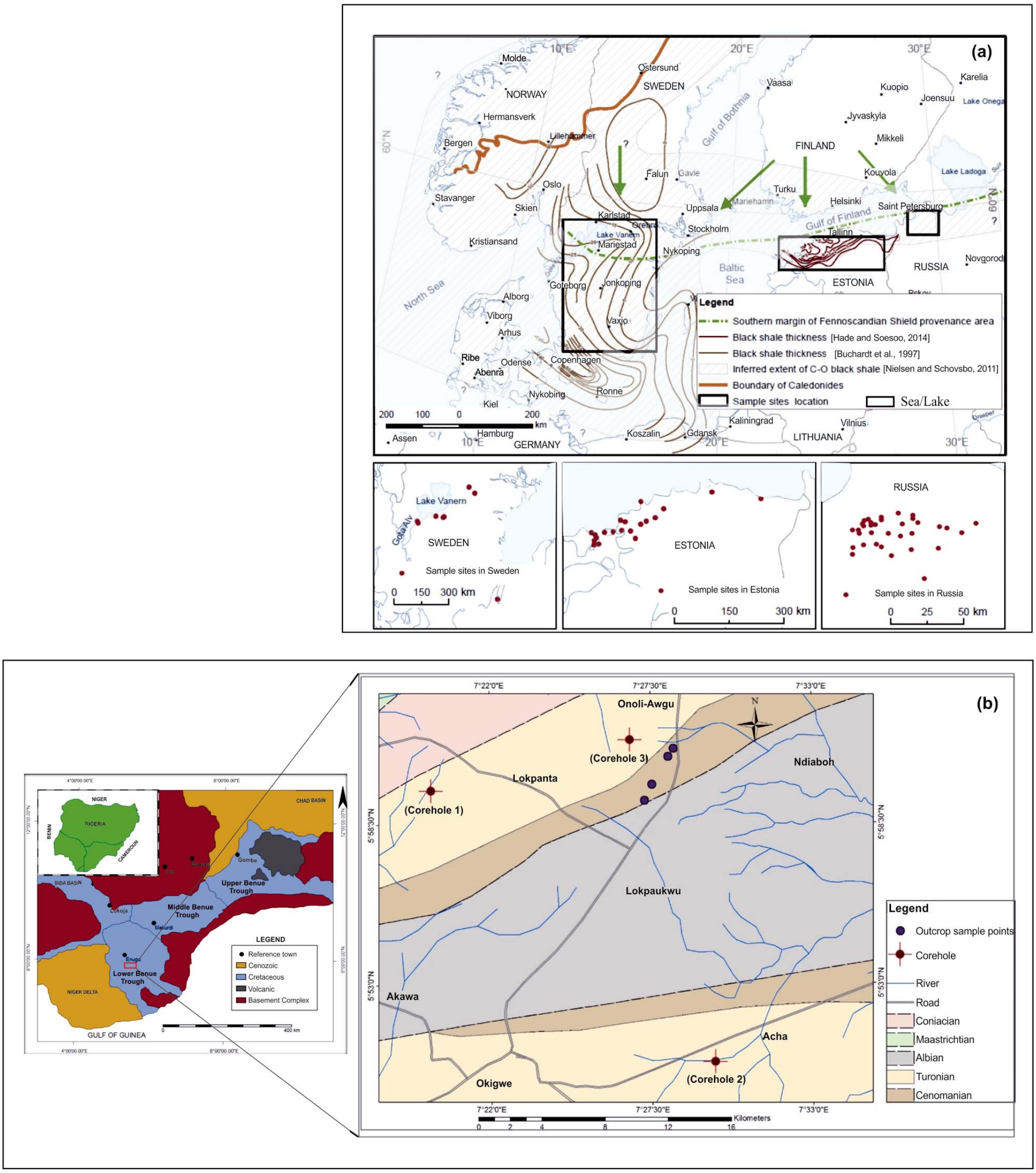

Figure 1. Map of Alum Shale (A) and Lokpanta Oil Shale (B) area showing sampling points after Nielsen and Schovsbo (2011), Soesoo et al. (2020), and Ehinola, (2010). The green arrows in (A) represent possible directions of sediment provenance, while dotted green lines represent the southern Fennoscandian landmass between the middle Cambrian to middle Ordovician periods, constructed according to Nikishin et al. (1996). The map insert represents the geological map of the Benue Trough modified from Obaje et al. (1999).

3.2. Laboratory methods

3.2.1. Estonian Samples

The mineralogical, and major and trace element composition of 95 samples from four drill cores in western Estonia (F298, F330, F343 and F344) were studied using X-ray diffractometry and inductively coupled plasma optical emission/ mass-spectroscopy (ICP-OES/ICP-MS) respectively. For mineralogy, unoriented powder preparations were measured with a Bruker D8 Advance diffractometer with CuKα radiation and a LynxEye positive sensitive detector in a 2–70° 2θ range. The semi-quantitative mineralogical composition was modelled and interpreted using the Rietveld-algorithm-based Topaz 4 software by Bruker.

Major and trace elemental compositions of pulverized samples were determined by inductively coupled plasma optical emission and mass-spectroscopy (ICP-OES/ICP-MS) from aliquots fused into $LiBO_2$ beads at ALS Minerals Loughrea in Ireland. Trace elements were digested using a mix of HNO_3, $HClO_4$ and HF and analysed via ICP-MS. Total organic carbon (TOC) and Sulfur data were obtained by using a high-frequency LECO elemental analyzer.

Trace element analysis was also done on a second set of 41 samples from drill cores (F369, F362, F355, K14, F366, F354) at Bureau Veritas, Canada, using multi-acid dissolution in a mixture of HNO_3, $HClO_4$, HF, and HCl.

3.2.2. Russian and Swedish Samples

The major and trace element concentrations of selected Alum Shale samples from Sweden and Russia were studied using ICP-MS at the Russian Geological Research Institute (Vyalov et al., 2014; Report). The samples were crushed to 74 μm sizes before analysis and were dissolved in a mixture of HNO_3, HF, and HCl. The analysis of the prepared solutions was carried out on Agilent 7700 and ELAN-6100 DRC devices. Major element concentrations were studied using the Rigaku Miniflex II X-ray fluorescence spectrometer.

3.2.3. Lokpanta Oil Shale Samples

The chemical and mineralogical composition of samples were analyzed at the University of Tartu.

For major elements, the Rigaku wavelength dispersive X-ray fluorescence spectrometer ZSX Primus II was used with semi-quantitative SQX Analysis method for quantification. For trace element concentration measurements, the samples were dissolved in the Anton Paar Multiwave PRO microwave digestion system in a mixture of HNO_3, HCl and 40% HF. The analyzes were performed using the Agilent 8800 ICP-MS.

The mineralogical composition of two samples (CH2-7.5 and CH3-28.3) was studied by XRD using the Bruker D8 Advance diffractometer with CuKα radiation and a LynxEye positive sensitive detector in 3–60° 2θ range. The semi-quantitative mineralogical composition was modelled and interpreted using the Rietveld-algorithm-based Topaz 4 software by Bruker.

The degree of chemical weathering was estimated using the Chemical Index of Alteration (CIA) (Nesbit and Young, 1982), and Chemical Index of Weathering (CIW) (Harnois, 1988). The indices were calculated using the equation:

$$CIA = [Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$$

$$CIW = [Al_2O_3/(Al_2O_3 + CaO + Na_2O)] \times 100$$

In the above equation, all values are in molecular proportion, and CaO* represents the amount of CaO incorporated into the silicate fraction of the rock.

4. RESULTS AND DISCUSSION

4.1. Mineralogical and whole rock geochemical composition of the Alum Shale

The mineralogical assemblage of Alum Shale (graptolite argillite) in Estonia is dominated by uniform quartz, K-feldspar and K-mica/illite minerals (Loog et al., 2001; Kaljuvee et al., 2022; Vind et al., 2023 – Paper II). The mineral concentration varied between 27–41, 15–29, and 21–31 wt% for K-feldspar, quartz, and K-mica/illite, respectively. The sum of these minerals makes up between 80–95 wt% of the total mineral composition in the black shale. Pyrite and carbonates (mainly dolomite) make up 4–10 wt% and 2 wt% of the mineral assemblage respectively. In the studied drill cores from western Estonia, there is no significant lateral or vertical variation in the mineralogy except for quartz content which showed a slight increase moving up of the studied successions (see supplementary Fig. S1 in Paper II).

The chemical analysis of major elements in the Palaeozoic black shale shows a fairly uniform concentration in the studied regions (Sweden, Estonia, and western Russia). The order of abundance is SiO_2, Al_2O_3, Fe_2O_3, and K_2O. The highest average concentration of 58 wt% for SiO_2 was recorded in samples from western Russia. As Al_2O_3 is associated with finer fractions (clay), these samples correspondingly recorded the lowest Al_2O_3 concentration suggesting a more silica-rich sediment source for the Alum Shale in Russia (Paper I).

In the studied outcrop samples from Sweden, the average SiO_2 concentration is 52 wt%, lower than that of samples from Russia. The average content of Al_2O_3 and Fe_2O_3 are 11 and 5 wt%, and 8 and 6 wt% for samples from Sweden and Russia respectively.

Samples from Estonia show SiO_2 content in the range of 35–72 wt% (with an average of 47 wt%), apart from 3 samples that had concentrations less than 35 wt%. The average values of Al_2O_3 and Fe_2O_3 in the black shale samples from Estonia are approximately 12 and 5 wt% respectively while K_2O and TiO_2 ranged between 5 to 8.5 wt% and 0.5–0.8 wt% respectively. The P_2O_5 content is usually lower than 0.3 wt%, except in a few apatite-rich samples where the concentration reaches up to 2.6 wt%. Similarly, CaO and MgO concentrations are typically lower than 1 wt% throughout the black shale succession in Estonia, except in some glendonite-bearing samples where it reaches up to 5.2 and 1.2 wt% respectively.

The total organic carbon (TOC) content recorded from samples from NW-Estonia varies between 7–13 wt% with an average concentration of 10 wt%. The TOC was observed to be typically higher in the lower part of the succession (see Figure 2 in paper II).

The trace element composition of the Alum Shale shows significant variation in redox-sensitive elements. Mo content varies widely, being 2–562 ppm in Russia (average 142 ppm), 6–1844 ppm in Estonia (average 189 ppm), and 2–411 in samples from Sweden (average 175 ppm). The concentration of U is lowest in the samples from Sweden, with an average content of 82 ppm, but twice as high in samples from Russia, with an average value of 169 ppm. In Estonia, the average U concentration is 105 ppm.

Drill cores from NW-Estonia show a higher concentration in V, Mo and U in the lower half of the successions where they typically are higher than 1100 ppm, 200 ppm and 100 ppm, respectively. There is a decrease in V, Mo, U in the easternmost cores where the average concentrations are 647, 82, and 58 ppm respectively. Zinc and As contents are usually 50–70 ppm, but occasionally reaches 1410 and 160 ppm in samples with pyrite and sphalerite intervals.

In comparison with average shale (Taylor and McLennan, 1985), the Alum Shale is highly enriched in V, Mo and U (Figure 2). Pb is also highly enriched in samples from Estonia and Russia, but slightly enriched in samples from Sweden. Similarly, there is a 10 and 3-fold enrichment of Zn in samples from Russia and Estonia respectively, but a depletion in Zn concentration in samples from Sweden.

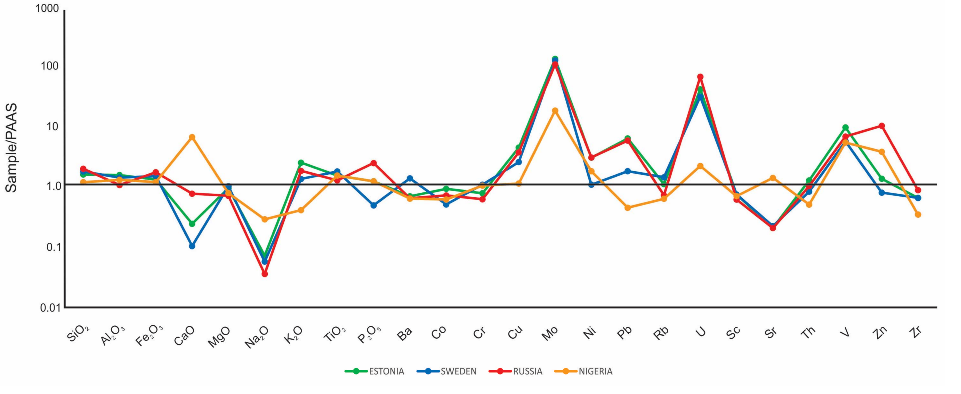

Figure 2. Major and trace element concentrations of Alum Shale and Lokpanta Oil Shale, normalized against Post Archean Australian Shale (Taylor and McLennan, 1993)

4.2. Mineralogical and geochemical composition of the Lokpanta Oil Shale

Mineralogically the Lokpanta Oil Shale is composed of carbonates, quartz, clay minerals, sulfides, feldspars, and trace amounts of anatase (Paper III). Illite/smectite (average 12 wt%), kaolinite (average 11 wt%), and halloysite (average 1.5 wt%) make up the clay mineral composition. The studied samples have a high content of carbonates with an average calcite composition of 32 wt%. In one of the two samples analyzed for mineralogy, dolomite (24.2 wt%) was found to be present. Pyrite (average 0.75 wt%) is present in the studied samples as the only sulfur/sulfade bearing primary phase mineral. The SiO_2 content ranges from 23 to 55 wt% with an average concentration of 35 wt%. The oil shale is enriched in CaO with contents ranging from 11–33 wt% in all but one sample. In comparison with the Estonian GA, the Lokpanta Oil Shale is calcareous, highly enriched in CaO, and depleted in K_2O. The Fe_2O_3 content is between 2.3 and 7.3 wt% and mostly shows scattering. Similarly, Na_2O and K_2O are scattered, with their concentrations being commonly low, up to 0.9 and 1.8 wt%, respectively. The content of Al_2O_3 varied from 6.3–16 wt% and showed a weak positive correlation with SiO_2.

Lokpanta Oil Shale shows significant variation in concentrations of Mo (4–66 ppm), Cu (15–41 ppm), Zn (19–768 ppm), As (4–29 ppm), U (3–10 ppm), and V (60–1635 ppm). When plotted against SiO_2, most trace elements exhibit highly scattered concentrations. Compared with other drill cores, Sr concentration is highest in the westernmost drill core (drill hole 1; Paper III). This may be associated with higher calcite content in the drill core.

When normalized to average shale (Taylor and McLennan, 1985), the heavy rare earth elements (HREE) content in the Lokpanta Oil Shale is much lower than that of average shale and Alum Shale (see Fig 4 in paper III). Middle REEs seem to be slightly enriched in the Lokpanta Oil Shale than in Alum Shale. The Lokpanta Oil Shale is generally depleted in major compounds (except CaO which shows high enrichment), Ba, Rb, and heavy REEs, and enriched in Zn, Sr (except in core hole 2), Mo, V, and U. However, the enrichment in redox-sensitive trace elements (Mo, V, U) is much lower than that of the Alum Shale (Figure 2).

4.3. Depositional conditions of the Alum Shale and Lokpanta Oil Shale

4.3.1. Provenance and tectonic setting

Provenance interpretation from several geochemical signatures for the studied Alum Shale suggests that the clastic input was generally derived from intermediate to felsic rocks and recycled sediments (Figure 3; see also Figure 4a in paper I). On the Th/Sc vs. Zr/Sc plot (Figure 4 a in paper I), the samples from the studied regions plot in the felsic field, but samples from Estonia and Russia show a trend in the direction of Zr addition. This suggests that recycled sediments in addition to felsic materials make up the clastic materials of the black shale. This interpretation is supported by the relatively higher ratios of Zr/Sc and K_2O/Na_2O in samples from Estonia and Russia.

The studied samples have Al_2O_3/TiO_2 ratios in the range of 9–39, with average ratio of 17, 18, and 15 for samples from Sweden, Estonia and Russia, respectively (Figure 3). This ratio suggests an intermediate to felsic provenance for the black shale.

According to Cambrian-Ordovician reconstructions of Baltoscandia, continental landmasses existed in the north and northwest of the black shale area (Figure 1 a). Thus, the likely provenance region was the Paleoproterozoic igneous and metamorphic basement of southern central and southern Finland, which consists predominantly of felsic to intermediate metamorphic (acidic to intermediate gneisses, felsic volcanics, microcline granites and migmatites) and igneous rocks (small granitic intrusions and large rapakivi granite intrusions), and reworked older Ediacaran and Lower Cambrian sediments (Mikkola et al., 2018).

Similarly, the Lokpanta Oil Shale samples plot within the intermediate and felsic rock composition region, suggesting that the source of its primary clastic material is from intermediate to felsic rock composition (Figure 3). It is generally believed that the basement granitoid rocks of the Oban and Cameroon massifs, east of the Benue trough, supplied the detritus of the Nigerian oil shale (Hoque,1977). However, other studies have shown that older Albian sequences of shales, limestones, and sandstones of the Asu River Group sediments uplifted by Cenomanian deformation, may also have supplied sediments to the Turonian Sea (Amajor, 1985).

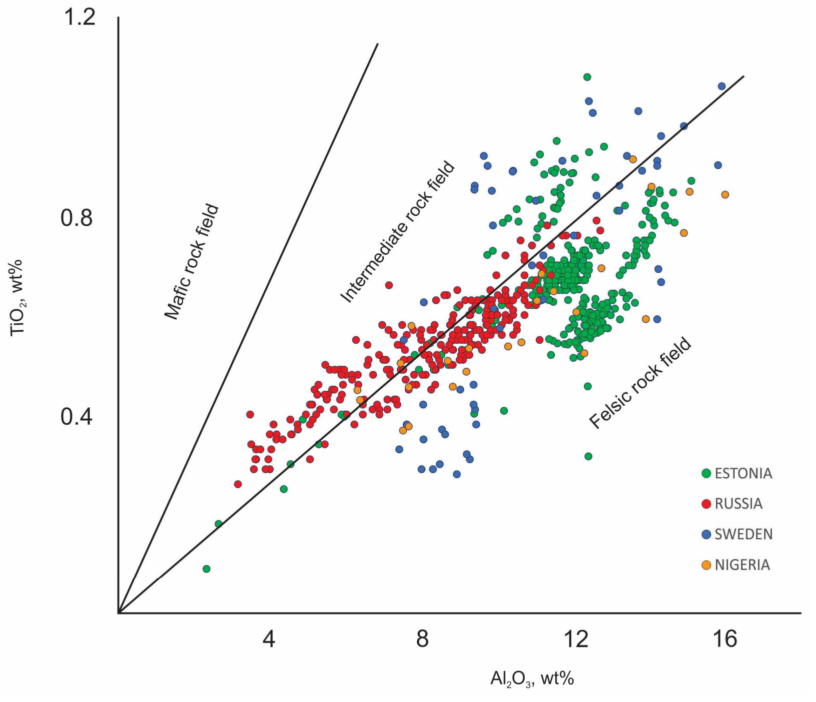

Figure 3. Provenance determination diagram for Alum Shale and Lokpanta Oil Shale (Hayashi et al., 1997)

Black shale samples from Russia exhibit a significantly more felsic provenance on Zr vs. TiO_2 plot where it plots equally on the intermediate and felsic composition fields, whereas samples from Estonia and Sweden plot almost entirely on the intermediate field (see Figure 4c in paper I). Samples from Russia also show a relative decrease in V and Sc, which suggests a more felsic provenance (Bhatia and Crook, 1986). This difference may represent the heterogeneity of rock types in southern and south-central Finland and may be attributed to the large rapakivi granite intrusion (Vyborg pluton) in south-eastern Finland, which served as a major provenance for the black shale area in Russia.

Tectonic setting reconstruction for the Alum Shale suggests a passive margin setting. Sediments of the passive margin setting are quartz-rich, but depleted in

CaO and Na_2O, and were deposited in plate interiors at stable continental margins. On the SiO_2 versus K_2O/Na_2O plot (Roser and Korsch, 1986), all samples (excluding 3 samples from Estonia) plot in the passive margin field (Figure 4).

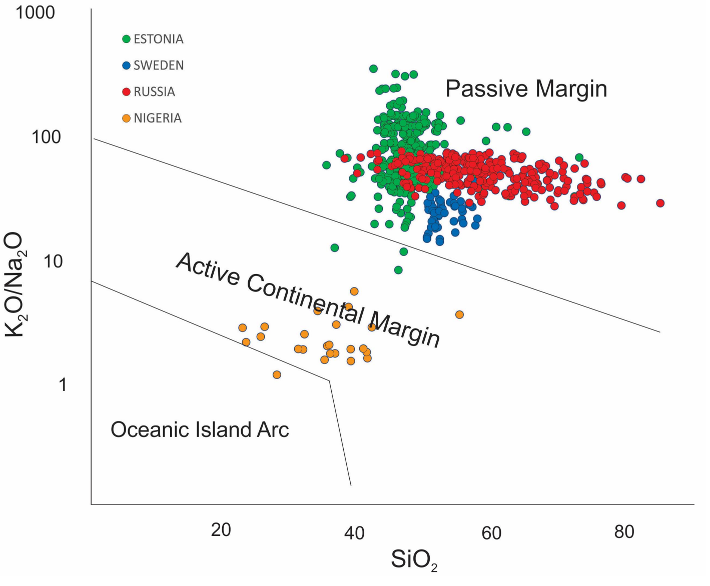

Figure 4. K_2O/Na_2O vs. SiO_2 cross plot for tectonic setting determination (Roser and Korsch, 1986)

The passive margin setting for the black shale is further supported by the result from the method of Verma and Armstrong-Altrin (2016) for tectonic setting determination. It uses either major elements (SiO_2 to P_2O_5) data only, or a combination of major and trace elements (Cr, Nb, Ni, V, Y and Zr). The samples also plot in the passive margin setting field with 99% confidence rate (see Figure 5b in paper I). This interpretation agrees with the knowledge of Baltoscandian geotectonic settings during the Lower Paleozoic era (Cocks and Torsvik, 2005).

The Lokpanta Oil Shale samples plot in the active continental margin field (ACM) in Figure 4. It's important to note, though, that this does not necessarily mean that the tectonic setting of the Lokpanta Oil Shale is an active continental margin. As demonstrated by Armstrong-Altrin and Verma (2005), sediments from passive margins can also fall within the ACM field on Roser and Korsch's 1986 diagram.

The relationship between TiO_2 and Fe_2O_3 +MgO content in the Lokpanta Oil Shale was also studied to understand the tectonic setting (Bhatia, 1983). None of the samples plotted within the ACM field, whereas four samples fell within the passive margin (see paper III). From the knowledge of the regional geology, the Benue Trough is part of a passive continental margin formed due to a series of extensional events that commenced during the Lower Cretaceous period, coinciding with the initiation of the South Atlantic's opening (Browne and Fairhead, 1983). A passive margin setting is therefore suggested for the Lokpanta Oil Shale.

4.3.2. Paleoweathering

The Chemical Index of Alteration (CIA) and Chemical Index of Weathering (CIW) were used to infer the degree of chemical weathering of the Alum Shale and Lokpanta Oil Shale (Harnois, 1988; Nesbitt and Young, 1989). CIA and CIW are measures of the degree of alteration of feldspars to clay minerals. The higher the values of CIA and CIW, the higher the degree of weathering. Typically, CIA ranges from 75 for muscovite to about 80 for illite and smectite and to 100 for chlorite and kaolinite (Nesbitt and Young, 1989). On the CIA plot, Alum Shale samples show a trend in the Al_2O_3-K_2O compositional line, which represents an advanced stage of weathering (see Figure 6 in paper I). However, the CIA values did not reflect an intense degree of weathering. CIA values ranged from 53 to 80. Alum Shale samples from Sweden have the highest values of 61–80, whereas Estonia and Russia samples have values in the range of 54–65 and 53–63 respectively (Figure 5). These lower CIA values may suggest that secondary processes may have resulted in the potassium metasomatism (Somelar et al., 2010). This is also corroborated by the scattered nature of the sample points (points not falling on a pre-defined weathering trend) on the CIA plot (see Figure 6 in paper I). In this case, where potassium alteration is believed to be affecting CIA values, it is helpful to evaluate the degree of weathering using the CIW. The average CIW values for the Alum Shale in Estonia, Sweden and Russia are similar, at 97, 96, and 95 respectively, thus indicating an intense degree of weathering of the source material of the black shale (Figure 5). This is a strong indication that secondary K-enrichment has overprinted the CIA values of the primary mineral matter. Indeed, a high degree of weathering is expected of the Baltoscandian shale as temperatures were high in the Tremadocian stage when it formed (Trotter et al., 2008).

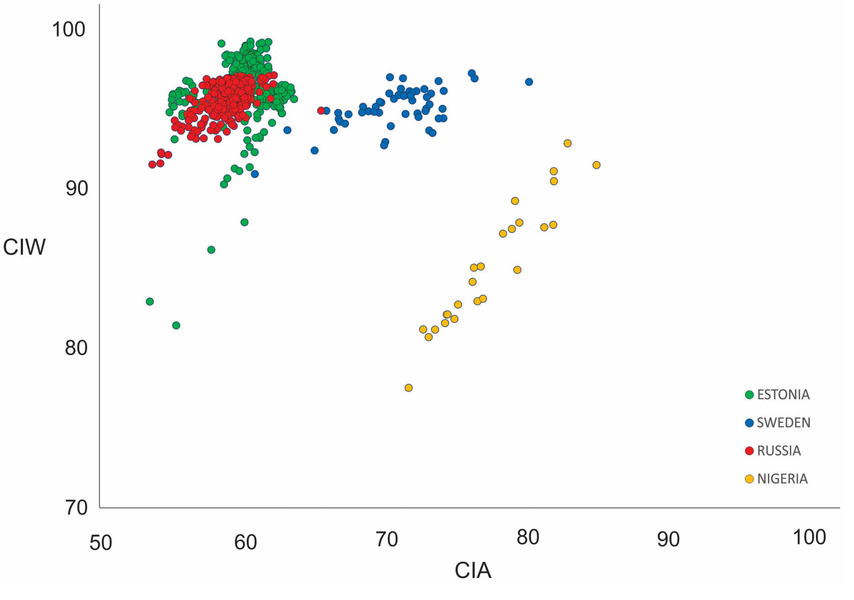

Figure 5. CIA vs CIW plot showing the degree of chemical weathering of source material (Nesbitt and Young, 1989; Harnois, 1988)

The origin and timing of possible secondary K-enrichment in Alum Shale remains unknown. Some studies have suggested that the K-enrichment may have resulted of volcanic ash input into the Baltic paleobasin (Kiipli et al., 2014). Other possible K-sources could be from late diagenetic K-rich fluids driven by the development of the Scandinavian Caledonides, or from the erosion of felsic high potassium granitoids and granitic gneisses in Southern and Central Finland (Somelar et al., 2010, Mikkola et al., 2018).

The CIA and CIW values of the Lokpanta Oil Shale are typically in the range of 72–87 and 82–92, indicative of a moderate to high degree of weathering in a warm and humid climate (Figure 5).

4.3.3. Paleoredox and basinal conditions

Owing to the high concentration of Mo and V, which is a strong indicator of the year-round presence of hydrogen sulfide in the water column (Scott and Lyons, 2012; Scott et al., 2017), the redox condition of the Cambrian-Ordovician black shale has been interpreted by previous workers as permanently euxinic and restricted (Bian et al., 2021; Bian et al., 2022). Nevertheless, Algeo and Lyons (2006) pointed out that there is no systematic relationship between Mo and dissolved sulfide concentration within euxinic basin, and Kunert et al. (2020) argue that hyper-sulfidic conditions are not prerequisite for V hyper-enrichment. Hence, using Mo and V alone as paleoredox tracers may be unreliable, given that they can be enriched in various depositional environments. A more reliable approach to reconstructing redox conditions would be to use coupled Mo, U and V data since their enrichment combinations are unique to sediments in various modern redox environments (Bennett and Canfield, 2020).

Under oxygenated conditions, U exists as U(VI). However, in anoxic environments, it is reduced to the thermodynamically favored U(IV), leading to U enrichment in sediments (Morford et al., 2001; Tribovillard et al., 2006). Similarly, under anoxic (sulfidic) condition, Mo is converted from molybdate anion (MoO_4^{2-}) to thiomolybdate specie ($MoO_{4-x}S_x^{2-}$) and sequestered in sediments (Sweere et al., 2018). Mo enrichment thresholds of <25 mg/kg, 25–100 mg/kg and >100 mg/kg has been proposed as indicative of anoxic, intermittently euxinic and permanently euxinic conditions, respectively (Scott and Lyons, 2012). Vanadium accumulation in sediments on the other hand involves two-stage process: first, unreactive V(V) is reduced to V(IV) in anoxic settings and then to V(III) under strongly anoxic, sulfidic conditions, leading to its accumulation in sediments (Algeo and Maynard, 2004; Bian et al., 2022).

The studied Alum Shale samples plot mostly within the perennial-oxygen minimum zone (P-OMZ) of V/Al vs. U/Al and V/Al vs. Mo/Al plots (Figure 6 a and b). This suggests a non-sulfidic, unrestricted anoxic redox setting at the time of the black shale deposition.

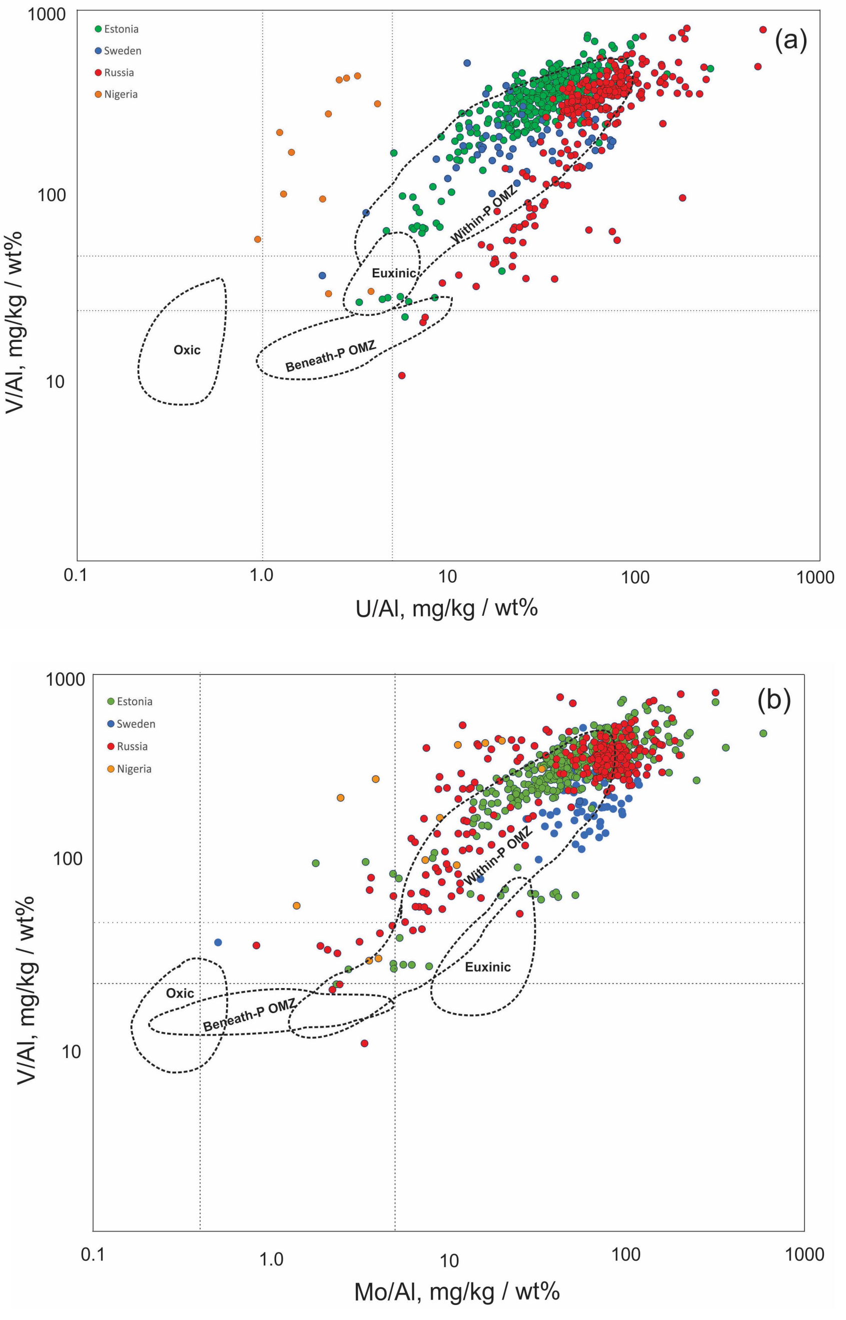

Figure 6. Cross plot of V enrichments against (a) U and (b) Mo enrichments in the studied shales. Fields of modern analogues of organic-rich sediments in oxic and euxinic basins and continental margin settings within and beneath P-OMZ are sourced from Bennett and Canfield (2020). The dashed lines represent trace metal enrichment thresholds suggested for different environmental settings by Bennett and Canfield (2020).

The P-OMZ is characterized by persistently low levels of oxygen, where V, U, and Mo concentrations are typically greater than 46, 5, and 5 mg/kg/wt%, respectively (Bennet and Canfield, 2020). However, the Alum Shale samples contain significantly higher V, U, and Mo content than those suggested by Bennet and Canfield (2020). One possible explanation for higher levels of Mo enrichment for instance, in this zone compared to euxinic zones, could be attributed to substantial input of organic matter and rapid sulfate reduction in shallow sediment layers. These conditions lead to increased concentrations of dissolved sulfide in the sediments, which efficiently scavenges Mo, even when there is no free sulfide in the overlying water. Additionally, the nature of the basin, which is unrestricted, allows for a high rate of Mo replenishment (Brüchert et al.,2003; Bennet and Canfield, 2020).

Modern sediments at highly productive continental margins with upwelling current are characterized by preferential Cd uptake with TOC relative to Mo and upwelling waters depleted in Co and Mn (Sweere et al., 2016). On the other hand, restricted basins with euxinic bottom waters exhibit higher Mo concentrations and lower primary production rates, resulting in Cd/Mo ratios of <0.1 and higher Co and Mn contents (Sweere et al., 2016).

Alum Shale typically has Co × Mn values below 0.4 mg/kg × wt% and Cd/Mo ratios well below 0.1 (often <0.02). These patterns somewhat differ from trends seen in modern sediments in productive upwelling regions (Sweere et al., 2016). Moreover, the studied Alum Shale samples mostly fall outside the ranges observed in modern basins (Figure 7). However, it's important to note that the redox thresholds established in modern systems for these elements may not directly apply to ancient oceans (Algeo and Li, 2020). Nonetheless, the low Co and Mn contents in the Alum Shale suggest, in agreement with Bian et al. (2023), that the black shale formed in a relatively open marine setting influenced by upwelling.

Additionally, paleontological evidence – the abundance of well-preserved graptolite rhabdosomes, also points to an unrestricted continental margin depositional setting for the Estonian black shale. Similar fossil occurrences in the Great Basin shales in the United States have been interpreted as indicating continental-margin upwelling zones within the oxygen minimum zones (Finney and Berry, 1997). This interpretation agrees with the regional geology of Baltoscandia. It has been suggested that there was an unrestricted connection of the Baltic paleobasin to the Iapetus Ocean by the Cambrian and Tremadocian (Sturesson et al., 2005; Nielsen et al., 2018; Gill et al., 2021).

Paleo redox indicators suggest that the Lokpanta Oil Shale was deposited in a suboxic/anoxic condition. On the V/Al vs. Mo/Al plot (Figure 6 a), the oil shale samples group closely with the Alum Shale, in and around the P-OMZ field. Whereas in the V/Al vs. U/Al plot, it groups outside (but close to) the P-OMZ field. Nevertheless, the high V and lower U content, and with an average Ni/Co ratio of 8, are consistent with suboxic/anoxic setting (Jones and Manning, 1994; Bennet and Canfield, 2020). The unrestricted nature of the Benue trough during the Cenomanian-Turonian period may have resulted in replenishment with oxygen-rich waters. Benthic fauna, such as species of Reophax and Haplophragmoids, which are commonly found in the Lokpanta Oil Shale, have also been recognized from Western Central Sinai of Egypt and other locations, suggesting a possible connection with the Tethys Sea and the world ocean (Eicher, 1967; Haig, 1979; Ehinola, 2002).

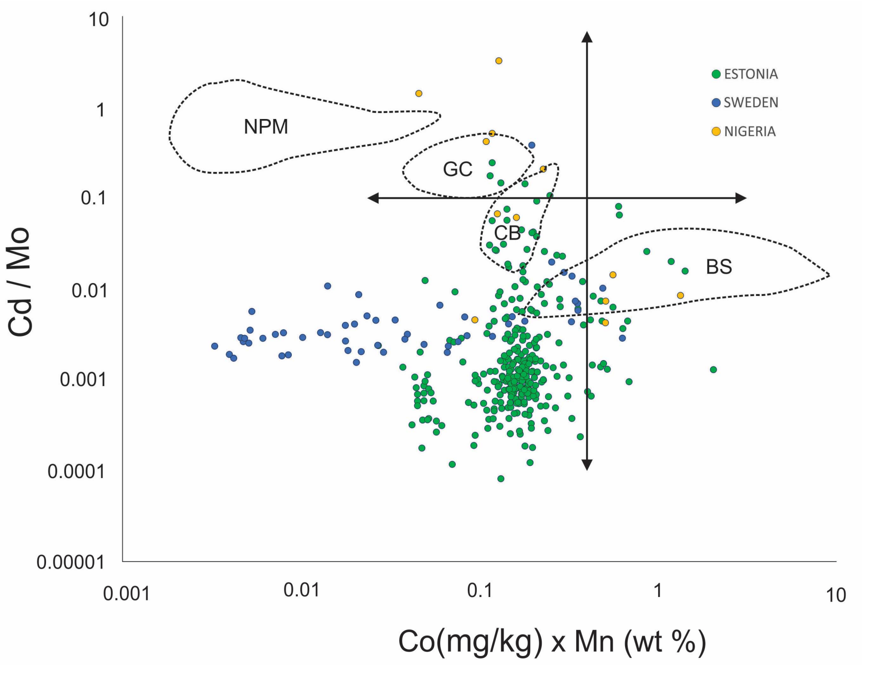

Figure 7. Cross plot of Co x Mn vs. Cd/Mo ratio in the studied black shales (Cd data is unavailable for samples from NW-Russia). Modified from Sweere et al. (2016). NPM – Namibian and Peruvian margin; GC – Gulf of California; CB – Cariaco Basin; BS – Black Sea.

4.3.4. Redox-sensitive trace metal distribution and enrichment mechanism in the Alum Shale

The concentration of redox-sensitive trace elements in the Alum Shale samples from NW-Estonia varies systematically. In the lower section of the black shale sequence, the highest enrichment of Mo V, U, and Re occurs (see Figures 2 and 6 in paper II). This enrichment generally decreases towards the upper section of the sequence. It is worth noting that a similar enrichment trend has been previously reported in coeval black shale intervals in Sweden (Schovsbo, 2001). Such an enrichment trend is indicative of varying redox controls and/or sedimentation rates. In the most eastern drill core in Estonia (F298), there is a relatively lower trace metal enrichment which may be explained by its younger stratigraphic position and consequent overlap with only the upper part of the other more westerly drill cores.

Despite the trace element hyper-enrichment in the Alum Shale, the driving mechanisms of element accumulation are yet to be resolved (Bian et al., 2022). Schovsbo (2002) have suggested a higher degree of bottom water circulation as the driving mechanism for uranium enrichment in the Alum Shale, and Nielsen and Schovsbo (2015) inferred that the Alum Shale deposition environment (sea) had an uncommon water mass composition, locally amplified by silled basinal conditions.

The deposition of the Alum Shale is believed to have occurred at an exceptionally slow rate (1–5 mm/kyr) in predominantly anoxic conditions (Andersson et al., 1985; Buchardt et al., 1997). Klinkhammer and Palmer (1991), and Liu and Algeo (2020) have shown with a diffusion-reaction model that the first-order control of U and Mo enrichment in anoxic basins is the sedimentation rate. The observed U and Mo enrichment in the Alum Shale aligns well with this model, suggesting that the trace element enrichment in the Alum Shale was controlled by extremely low sedimentation rates, combined with the prevailing anoxic conditions of the bottom water (see Figures 11 a and b in paper II) (Andersson et al. 1985; Buchardt et al. 1997; Nielsen and Schovsbo, 2015; Nielsen et al., 2018). Therefore, the declining trace element enrichment trends towards the upper part of the Estonian GA succession could be interpreted as a gradual increase in sedimentation rate.

In contrast, the sedimentation rate for the Lokpanta Oil Shale in the Lower Benue trough of Nigeria is believed to have been rapid (Nwachukwu, 1972). A similar interpretation has been made for the Mamfe Formation in Cameroon, which can be correlated with Albian – Cenomanian sediments of the adjoining Lower Benue Trough (Bassey et al., 2013).

Indeed, there is moderate to strong similarities in the depositional environment (sediment provenance, tectonic setting, paleoweathering, redox condition) between the Lokpanta Oil Shale and Alum Shale. However, the degree of redox trace element enrichment is higher in the Alum Shale. This suggests that other basinal differences such as sedimentation rate and seawater composition may have exerted more controls on redox trace element enrichment.

5. CONCLUSION

The geochemical study of two organic-rich black shales – Alum Shale of Baltoscandia and Lokpanta Oil Shale, have been undertaken to evaluate their depositional environment, redox condition, and metal accumulation and distribution. The conclusions are as follows:

1. The mineralogy of the Alum Shale is dominated by uniform content of quartz, K-feldspar and K-mica/illite minerals, accounting for up to 95% of its mineral composition. On the other hand, the Lokpanta Oil Shale has a lower K-feldspar but a much higher carbonate content than the Alum Shale, with calcite and dolomite making up about half of the mineral content. Illite/smectite and kaolinite have uniform proportion of about 12%, while quartz accounts for about 18% of the mineralogical composition of the Lokpanta Oil Shale.
2. The Alum Shale and Lokpanta Oil Shale exhibit similar trace element enrichment trends, being enriched in U, Mo and V, in comparison with average shale. However, the degree of enrichment is much higher in the Alum Shale.
3. Redox sensitive trace elements U, V, Mo, and Re vary systematically in the Alum Shale, with element content reaching up to hyper-enrichment at the base, followed by a declining trend towards the upper part of the succession.
4. Diffusion-controlled uptake owing to the slow sedimentation rate of the Alum Shale has been suggested as the driving mechanism of element enrichment, while temporal changes in sedimentation rate controlled the observed trace element trend.
5. Both the Baltoscandian Alum Shale and Nigerian Lokpanta Oil Shale were deposited on a passive margin setting. Provenance study indicates that the primary material of the Alum Shale and Lokpanta Oil Shale were of intermediate to felsic rock composition and recycled sediments. In the case of the Alum Shale, the likely provenance region was the intermediate to felsic Palaeoproterozoic igneous and metamorphic basement of southern central and southern Finland and reworked older Ediacarian and Lower Cambrian sediments. On the other hand, the basement granitoid rocks of the Oban massifs, east of the Benue trough in addition to older Albian sediments of the Asu River Group may have supplied the sediments of the Lokpanta Oil Shale.
6. The chemical index of weathering (CIW) indicates an intense degree of weathering for the Alum Shale. Chemical index of Alteration (CIA) cannot be reliably applied to Alum Shale because K-enrichment has overprinted the CIA values of the primary mineral matter. On the other hand, the CIA and CIW values of the Lokpanta Oil Shale are indicative of a moderate to high degree of weathering in warm and humid climate.

7. Paleoredox indicators suggest a similar, non-euxinic, relatively open anoxic depositional environment within a perennial oxygen minimum zone for the Alum Shale and Lokpanta Oil Shale. This study presents a contrasting viewpoint to recent theories that attribute the deposition of the Alum Shale in a restricted euxinic basin. Instead, it highlights the potential for notable redox variability within the Baltic Palaeobasin and the need to consider lateral controls in paleoredox assessments and the importance of using multiple independent proxies to accurately determine redox conditions. Our findings are significant for understanding potential connections between oceanic redox states and biotic events, such as the Cambrian Explosion and subsequent extinction and recovery events, much of which has relied on proxy data from the Alum Shale.

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SUMMARY IN ESTONIAN

Kambriumi-Ordoviitsiumi vanusega Baltoskandia Alum-kilt ja Kriidi vanusega Nigeeria Lokpanta põlevkivi: kahe musta kilda geokeemia ja tekkekeskkond

Orgaanikarikkad mustad kildad on laialt levinud settekivimid, mida leidub kõigil mandritel ja mille teke on tavaliselt seotud selliste perioodidega, kui merevees lahustunud hapniku vaesed keskkonnad on laiemalt levinud. Nende kivimite keemilist koostist mõjutavad settimisaegne keskkond, selle hapnikurežiim, settimiskiirus ja merevee koostis, mistõttu on neid võimalik uurida kui Maa geoloogilise ajaloo allikaid ja mineviku kliimatingimuste indikaatoreid. Fennoskandia piirkonnas leviv Paleosoiline Alum-kilt ja Nigeerias Benue alangus Kriidi ajastul tekkinud Lokpanta põlevkivi on näited sellistest orgaanikarikastest mustadest kiltadest.

Redoks-tundlike elementide uraani, molübdeeni, vanaadiumi ja orgaanilise aine kõrge sisaldus mõlemas põlevkivis on pälvinud märkimisväärset tähelepanu geoloogilistes uuringutes potentsiaalse majandusliku tähtsuse tõttu. Lõpuni selged pole siiski nende kivimite tekkekeskkonna küsimused, sealhulgas hapnikurežiimi ja metallidest rikastumise mehhanismid. Baltoskandia musta kilda tekketingimuste ning metallidega rikastumise selgitamiseks tehti geokeemilised analüüsid kümnest Eesti puursüdamikust, lisaks uuriti kaheksa Lõuna-Rootsi paljandi ja 34 Loode-Venemaa puursüdamiku geokeemiat ning tutvuti põhjalikult varasemate aruannete ja artiklite uuringute andmetega. Nigeeria Lokpanta põlevkivist võeti proove kolmest puursüdamikust ja seitsmest paljandist ning neid uuriti sarnaste meetoditega.

Alum-kilt (Eestis graptoliit-argilliit) koosneb Eesti alal K-päevakivist, kvartsist ja K-vilgu/illiidi savimineraalidest, mille sisaldused varieeruvad vastavalt 27–41, 15–29 ja 21–31 massiprotsendi piires. Lisanditena esineb vähesel määral püriiti ja karbonaatseid mineraale. Keemiline analüüs näitab põhielementide suhteliselt ühtlaseid sisaldusi uuritud Eesti läbilõigetes, kus kõige valdavam komponent on SiO_2 (35–72%) ja järgnevad Al_2O_3 (keskmiselt 12%), Fe_2O_3 (5%) ja K_2O. Orgaanilise süsiniku (TOC) kogusisaldus jääb vahemikku 7–13%, kusjuures kõrgemad sisaldused on tavaliselt kihi alumises osas. Alum-kilt on Loode-Venemaa läbilõigetes Eesti omadega võrreldes kõrgema ning Rootsi läbilõigetes madalama SiO_2 sisaldusega, viimastes on samas kõrgem Al_2O_3 sisaldus. Alum-kilda mikroelementide koostis varieerub oluliselt redoks-tundlike elementide osas, olles märkimisväärselt rikastunud vanaadiumist, molübdeenist, uraanist ja pliist võrreldes maakoore kiltade keskmise koostisega. Loode-Eestist pärit proovid näitavad V, Mo ja U kõrgemat kontsentratsiooni kihi alumises osas, kus nende elementide sisaldused ületavad vastavalt 1100 ppm, 200 ppm ja 100 ppm.

Lokpanta põlevkivi koosneb mineraloogiliselt karbonaatidest, kvartsist, savimineraalidest, sulfiididest, päevakividest ja väikestest kogustest anataasist. Illiit/smektiit, kaoliniit ja halluasiit moodustavad saviosakeste mineraalse koostise.

Karbonaate, peamiselt kaltsiiti, leidub suhteliselt suures koguses, kuni 32%, SiO_2 sisaldus jääb vahemikku 23–55%. Võrreldes maakoore kiltade keskmise koostisega on Lokpanta põlevkivi madalamate põhikomponentide (v.a. CaO) ja mitmete jälgelementide (Ba, Rb) ning raskete haruldaste muldmetallide sisaldustega, kuid kõrgemate Zn, Sr, Mo, V ja U sisaldustega. Selles põlevkivis on redoks-tundlike mikroelementide (Mo, V, U) rikastumine olnud siiski palju madalam kui Baltoskandia Alum-kildas.

Baltoskandia Alum-kilda purdmineraalide koostis näitab, et nende päritolu allikaks on happelised tard- ja moondekivimid ning ümbersetitatud settekivimite materjal. Baltoskandia piirkonna paleogeograafiliste rekonstruktsioonide järgi paiknesid mandrilised alad Kambriumis ja Ordoviitsiumis musta kilda tekkealast põhja- ja loode pool. Seega on kilda purdmaterjal tõenäoliselt pärit Lõuna-Soome Paleoproterosoikumi vanusega kristalse aluskorra kivimitest ning ümbersettinud vanematest Kambriumi ja Ediacara setetest.

Sarnaselt viitab ka Lokpanta põlevkivi purdmaterjal happeliste ja keskmise koostisega lähtekivimitele. Lokpanta põlevkivi purdosakesed pärinevad tõenäoliselt Obani ja Kameruni granitoidsetelt massiividelt või on ümber setitatud vanematest Kriidi (Alba) vanusega Asu River kompleksi settekivimitest. Sellise settematerjali sissekanne sobib seniste teadmistega mõlema piirkonna geoloogiast, sest nii Baltoskandia kui ka Benue alangu piirkond on asunud mustade kiltade kujunemise perioodil geotektooniliselt passiivsel kontinendi äärealal.

Alum-kilda ja Lokpanta põlevkivi murenemisastme hindamiseks kasutati keemilise koostise muutumisindeksit (CIA) ja keemilise murenemise indeksit (CIW). Alum-kilda CIA indeksi väärtused viitavad suhteliselt intensiivsele murenemisele. Eesti, Rootsi ja Venemaa musta kilda keskmised CIW väärtused (95–97) toetavad samuti seisukohta, et nende kivimite lähtematerjal on allunud algselt intensiivsele murenemisele. Lokpanta põlevkivi CIA ja CIW väärtused jäävad tavaliselt vahemikku vastavalt 72–87 ja 82–92, mis viitavad mõõdukale kuni intensiivsele murenemisele soojas ja niiskes kliimas.

Alum-kilda ja Lokpanta põlevkivi tekkeaegseid redokstingimusi analüüsiti mitme indikaatori abil. Molübdeeni ja vanaadiumi kontsentratsioone settekivimites seostatakse tavaliselt sulfiidsete tingimuste indikaatoritega, samas on nende usaldusväärsus redokstingimuste peegeldajana kahtluse alla seatud, eeskätt nende võimaliku rikastumise tõttu erinevate setteprotsesside käigus. Selle asemel soovitatakse redokstingimuste täpsemal hindamisel kasutada omavahel kombineeritud Mo, U ja V andmeid, kuna nende rikastumise kombinatsioonid on ainulaadsed erinevates redokskeskkondades olevate setete jaoks. Tuginedes V/Al vs. U/Al ja V/Al vs. Mo/Al vahekordade analüüsile näitavad Alum-kilda proovid püsiva hapnikusisalduse miinimumtsooni (P-OMZ) levikut, mida iseloomustavad mittesulfiidsed anoksilised redokstingimused avatud basseinis. Alum-kilda kujunemise hinnangut avatud kontinentaalse settebasseini äärealal toetavad ka paleontoloogilised tõendid, nagu hästi säilinud graptoliitide rabdosoomide rohkus.

Lokpanta põlevkivi proovid rühmituvad tihedalt koos Alum-kildaga P-OMZ väljale V/Al vs. Mo/Al graafikul. Samas U/Al graafikul rühmituvad need proovid veidi väljapoole P-OMZ välja. Sellegipoolest on kõrge V ja madalam U sisaldus ning keskmine Ni/Co suhe (8) kooskõlas suboksiliste/anoksiliste tingimustega, mida võis mõjutada Benue alangus olnud settebasseini avatus Cenomani-Turoni ajal. Sellele avatusele viitab ka põlevkivist leitud põhjaloomastiku sarnasus Tethyse ookeani elustikuga.

Redoks-tundlike jälgelementide kontsentratsioon Loode-Eesti graptoliit-argilliidi proovides varieerub üsna reeglipäraselt, suurim rikastumine Mo V, U ja Re osas toimub argilliidikihi alumises osas ja väheneb järk-järgult kihi ülemise osa suunas. Selline trend viitab ajas muutunud redoks-keskkonna tingimustele ja/või settimiskiirusele. Uuringuala kõige idapoolsemates läbilõigetes (Tallinnast edelas) on jälgelementide sisaldused graptoliit-argilliidis madalamad, mis on seletatav selle kihikompleksi osa noorema stratigraafilise vanusega ja selle korreleerumisega sama kompleksi ülemise osaga läänepoolsetes läbilõigetes. Alum-kilta moodustanud orgaanikarikka muda settimine toimus valdavalt hapnikuvaestes tingimustes, tõenäoliselt erakordselt aeglaselt, tekitades keskmiselt umbes 1–5 mm paksuse kiltja argilliidi kihi tuhande aasta jooksul. Uuringud on näidanud, et anoksilistes settekeskkondades kontrollib settimiskiirus hästi U ja Mo rikastumist. Uraani ja molübdeeni levik Alum-kildas ühtib hästi selle mudeliga, näidates, et jälgelementide rikastumist kontrollisid aeglased settimiskiirused ja anoksilised, veekogu põhjalähedased tingimused. Jälgelementide sisalduste vähenemine Eesti graptoliit-argilliidi kihi ülemises osas võib viidata settimiskiiruse järk-järgulisele suurenemisele.

Lokpanta põlevkivi settimise kiirus Nigeeria Alam-Benue alangus on olnud arvatavasti suhteliselt kiire. Sarnane tõlgendus on tehtud ka Kamerunis asuva Mamfe kihistu kohta, mida saab korreleerida külgneva Alam-Benue alangu kihtidega. Kokkuvõttes on siiski Lokpanta põlevkivi ja Alum-kilda ladestumise keskkonnas mitmeid sarnasusi setete päritolu, tektoonilise olukorra, murenemise ajaloo ja redoks-tingimuste osas. Samas on Alum-kildas redoks-tundlike jälgelementide rikastumise aste kõrgem, mis viitab sellele, et erinevused settimise kiiruses ja merevee koostises võisid nende elementide rikastumist oluliselt kontrollida.

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Publikatsioonid:

Ofili, S. and Soesoo, A., 2021. General geology and geochemistry of the Lokpanta Formation oil shale, Nigeria. *Oil Shale*, *38*(1), pp. 1–25. https://doi.org/10.3176/oil.2021.1.01

Ofili, S., Soesoo, A., Panova, E.G., Hints, R., Hade, S. and Ainsaar, L., 2022. Geochemical reconstruction of the provenance, tectonic setting and paleoweathering of lower Paleozoic black shales from northern Europe. *Minerals*, *12*(5), p. 602. https://doi.org/10.3390/min12050602

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