

Norwegian University of Life Sciences

Master's Thesis 2024 45 ECTS MINA

The geochemistry of Lower Paleozoic shales in the Oslo Region (Norway): A reconnaissance study

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Abstract

This study includes the compilation and modification of a substantial whole-rock geochemical dataset containing Lower Paleozoic shale samples from northern Europe, including Norway, Sweden, Estonia, and Russia. The main purpose of this dataset is to (1) support future shale studies for northern Europe by making the compilation publicly available <u>here</u>, and for this study to (2) enhance current knowledge of the geological conditions under which the Lower Paleozoic shale was formed in the Oslo Region. These geological conditions were studied based on the Norwegian sample's geochemical composition, provenance, paleoweathering, paleosalinity, paleoproductivity, and paleoredox conditions. Lower Paleozoic black shale formations in Norway can have a detrimental impact on the natural environment because of their acid rock drainage (ARD) potential. The results of this study may be useful in obtaining a better understanding of this issue.

An extensive quality assessment was done for all compiled data, which determined that only the Oslo Region whole-rock data was credible enough for further analysis in this study. Key findings from the selected paleoenvironmental analyses include the following: (1) No significant paleoweathering changes were detected, suggesting that the regions paleoclimate remained relatively stable from Late Cambrian to Middle Ordovician. (2) The youngest analyzed shale formations (Early Ordovician, Middle Ordovician) showed signs of increased paleosalinity compared to the older formations (Late Cambrian, Early Ordovician). This is suspected to have affected the mobility and distribution of specific trace elements. (3) In this study, sedimentary mass accumulation rates for Ba, P and total organic carbon (TOC) were used as paleoproductivity proxies. Although the results from the three proxies are somewhat contradictory, a general trend of decreasing paleoproductivity from the Late Cambrian to the Early Ordovician is observed. (4) Paleoredox conditions were analyzed with Total Degree of Pyritization (DOP_T) and TOC vs. organic P ratios. The results indicate that the older formations were deposited under more reducing conditions, and that pyritization, particularly for the Early Ordovician, might be influenced by other factors (e.g. hydrothermal activity). (5) None of the analyzed paleoenvironmental conditions showed a direct correlation with the ARD potentials associated with the individual Norwegian shale formations (Appendix B4). This indicates that the development of severe ARD potential is influenced by a combination of paleoenvironmental conditions or by later processes, such as hydrothermal activity.

Acknowledgement

This study marks the end of a remarkable chapter of my life at NMBU and in Norway. The past five years have been influenced by many extraordinary individuals, opportunities and experiences, all of which have enriched me both academically and personally.

I would like to begin by thanking my thesis supervisor, Jan Marten Huizenga, for his exceptional guidance and collaboration. I am truly grateful for all the work we have accomplished together, and all the time and efforts dedicated to this project. My appreciation extends to guidance counselor Marte Lise Lægreid for her unwavering support and availability, and to my amazing study group and colleagues, whose passionate discussions and perspectives have elevated my time at NMBU. To NMBU I am thankful for the numerous opportunities made available for me both at the university and abroad, and for the opportunity to pursue a deeply personalized academic path.

Lastly, I want to express my sincere gratitude to my best friend and partner for his constant encouragement and patience, and to our families for their invaluable support throughout this journey.

(Julie Lunde Jepsen, 12.12.2024)

"Den aller beste håndteringen av skiferen er å la den ligge urørt!" – Norwegian Geotechnical institute

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1. Introduction

Lower Paleozoic black shale is widely exposed in northern Europe. These shales are of particular interest in southern Norway, where their acid producing nature can lead to corrosion of infrastructure and severely impact natural ecosystems through acidification, heavy metal contamination and biodiversity loss. Most studies in Norway have focused on geochemical classification and leaching experiments, to construct a prediction method for black shale acid producing potential. The current prediction methods used in Norway can results in false positives or negatives, which leads to incorrect handling of rock deposits and economical or environmental losses.

So far, not much research has been done to obtain a better understanding of the geological conditions under which the Lower Paleozoic shale was formed in the Oslo Region. Carbon-rich black shale is typically formed in very reduced environments, which increases the chances of pyrite formation during sedimentation. However, sulphide minerals can also form due to hydrothermal activity induced by post depositional tectonic activity, which if present, makes the prediction of acid producing potential significantly more complicated. This study is, to the author's knowledge, the first attempt to evaluate the depositional paleoenvironment of the Lower Paleozoic shale in the Oslo Region, based on major and trace element whole-rock geochemistry.

1.1 Purpose of this study

The primary objectives of this study are twofold. Firstly, compilation of a geochemical dataset for northern European Lower Paleozoic shale, with focus on Norwegian shale from the Oslo Region. Secondly, geochemical characterization of the Lower Paleozoic shale in the Oslo Region in order to identify the paleoenvironment during shale deposition.

1.2 Organization of this thesis

The following chapters include a literature review of the geological setting of Lower Paleozoic black shales in Norway and a review of publicly available whole-rock compositional datasets from northern Europe. Four existing datasets have been reviewed containing samples from Norway (Wærsted et al., 2021; Sæther et al., 2010; Gautneb and Sæther, 2009), Estonia, Sweden and Russia (Ofili et al., 2022). A big part of this study is the compilation and modification of these existing whole-rock compositional datasets for Lower Paleozoic shales. All reviewed data has been compiled in a user-friendly Excel spreadsheet, available as an electronic appendix through the provided link in Appendix A1.

Further assessments of the paleoenvironment during shale deposition were ultimately only done for a part of the Norwegian data (Wærsted et al., 2021) for reasons which are explained in the text. Conditions studied include whole-rock composition comparison with Upper Continental Crust (UCC) and Median Black Shale (MBS), provenance, paleoweathering, paleosalinity, paleoproductivity and paleoredox environments.

2. Geological setting of Lower Paleozoic shale in the Oslo Region

This chapter will give a brief overview of the regional geology of the Oslo Region in Norway (Fig. 1) as part of the then Baltica continental plate, focusing on the geological setting of the Lower Paleozoic sedimentary rocks (Fig. 2). Unless stated otherwise, the information in this chapter is derived from Nakrem and Worsley (2013) and references therein.

2.1. Background

The Oslo Region is well known for its highly variable geology, which includes: (1) Precambrian basement gneiss belonging to the Fennoscandian Shield, (2) Lower Paleozoic sedimentary shales, sandstones, and limestones (541-419 Ma), and (3) intrusive and extrusive igneous rocks associated with the development of the Oslo rift, such as larvikite, rhomb-porphyry, gabbro, basalt, and granite (290-250 Ma). The main tectonic events that have affected the region are the Caledonian deformation (folding and faulting) at 455-405 Ma, and the development of the Oslo rift (310-250 Ma).

2.1.1. Stratigraphy of the Lower Paleozoic sedimentary rocks

The Lower Paleozoic (Cambrian, Ordovician, and Silurian) sedimentary rock sequence in Norway, is subdivided into stratigraphic horizons with alphanumeric names (introduced in 1857 by Professor Theodor Kjerulf, University of Oslo). The total thickness of this sequence is ca. 2600 m (Fig. 2) but varies throughout the region.

2.1.2. Depositional environment of Lower Paleozoic sediments

At the start of the Paleozoic period (ca. 541 Ma), most of the abiotic continental plate had been eroded down to low-altitude plains of bare granitic bedrock. At that time, the global average temperature was 6-10°C higher than today's global average temperature of ca. 15°C (Scotese et al., 2021). Norway was located around 60° south of the equator, and the lowaltitude bedrock plains were intermittently flooded as the sea level increased during the Early Cambrian. These sea transgressions created large areas with shallow, warm seas, which, together with the evolution of shell producing organisms, resulted in a significant increase in aquatic bioactivity and sedimentation rate.

During the Middle and Late Cambrian, the sea was deep and stagnant. The seabed, therefore, became anaerobic, which decreased the decomposition rate of organic material. These conditions created black, carbon-rich shale beds that are enriched in sulfide-bearing minerals and heavy metals (horizon 1-2 in Fig. 2). Within a relatively short period of 100 My (Early Cambrian to Late Ordovician) Norway drifted 30° northwards. The drift caused the climate to shift, which is reflected in alternating beds of dominating shale and limestone (horizon 3-5 in Fig. 2), formed due to rhythmical variations in sea level during the Ordovician (485-443 Ma). During shallow sea level conditions, the temperature would increase, and circulation improve. This lowered the organic matter content and resulted in lighter colored, calcium-rich sediments (limestone beds).



Figure 1: Geological map and legend (on the following page) for the Oslo Region. Map modified by Jan Marten Huizenga (unpublished) from the Geological Survey of Norway (2021).

Igneous and sedimentary rocks associated with the Oslo rift [<i>320-250 Ma</i>] Conglomerate, sandstone, claystone [<i>280-250 Ma</i>]	Reverese fault / Normal fault / shear zone					
K-feldspar granite [280-255 Ma]	Sedimentary rocks [540-450 Ma]					
Granite, granodiorite [290-255 Ma]	Ta Limestone, slate, sandstone, conglomerate [440-420 Ma]					
Quartz-K-feldspar syenite to nepheline syenite [295-255 Ma]	⁸⁰ Slate, sandstone, limestone [470-450 Ma]					
Monzonite (larvikite), monzodiorite, syenite [300-265 Ma]	81 Limestone, slate, sandstone [485-470 Ma]					
Rhyolite to trachyte, latite, basalt [280-270 Ma]	Limestone, slate, alum shale, sandstone, conglomerate [540-470 Ma]					
Volcanic breccia, tuff, agglomerate, ignimbrite [300-250 Ma]						
10 Trachite [300-250 Ma]	Sedimentary rocks [750-520 Ma]					
11 Latite (rhomb porphyry), sedimentary rocks [300-280 Ma]	⁸³ Sandstone, quartzite, .slate, conglomerate [600-520 Ma]					
12 Basalt, sedimentary rocks [320-295 Ma]	Igneous and metamorphic rocks [1740-910 Ma]					
Rhomb porphyry, mafic dyke [320-250 Ma]	Precambrian basement rocks					

Figure 1: (Continued).

Deeper conditions would in turn lower the decomposition rate of organic matter and result in carbon-rich shale beds. From the Middle Ordovician onwards, sedimentation in the Oslo Region was subject to both local and regional variation. In the Late Ordovician (445-443 Ma) the sea was shallow, and some areas rose above sea level. The exposed areas were eroded down and freshwater channels cut through the previously deposited sediments, causing the sedimentation rate to increase and coarse sand to mix with the marine sediments. While only 600 m of sediments were deposited during Cambrian and Ordovician (100 My), nearly 2000 m were deposited in the following 25 My during the Silurian.

In the Early Silurian (440-435 Ma) the sea level increased once again. In the north, south, and west of the Oslo Region the Ca-rich sediments were covered with sand, while central Oslo was deep underwater and experienced black sludge sedimentation (horizon 6a-c in Fig. 2). Later, less detrital sediments were deposited (horizon 7 in Fig. 2), and calcium-rich sedimentation dominated again. In the Late Silurian (ca. 420 Ma), the Caledonian mountain range was formed west-northwest of the Oslo Region. These mountains were subsequently eroded, and river systems deposited large amounts of sand in the south-east ocean, which resulted in the deposition of a thick red sandstone formation (horizon 10 in Fig. 2).

2.1.3. Tectonic events affecting Lower Paleozoic sedimentary rocks

The Caledonian orogeny, i.e. the collision of the Baltica and Laurentia (later North America) continental plates, resulted in folding and (thrust) faulting of the Lower Paleozoic sedimentary rocks and mainly affected the northern part of the Oslo Region (Strand, 1960).

About 100 My after the Caledonian folding, the Baltica and Laurentia plates further collided and formed Pangea with the southern continental plate Gondwana (later South America and Africa). This collision resulted in a western pull of west Norway and an eastern pull of east Norway, hereby forming multiple north-south trending normal faults in the Oslo Region creating the Oslo rift valley (Hurum and Frøyland, 2004). The Oslo rift valley covers a 60 x 220 km nearly rectangular area (stretching from Langesund in the south



Figure 2: Stratigraphy of the Lower Paleozoic in the Oslo Region illustrating the variety in lithology and sedimentation patterns. Figure modified after Strand (1960) and Nakrem and Worsley (2013).

to Bermunddal in the north, Fig. 1) where erosion was limited. This led to better preservation of the areas Lower Paleozoic sedimentary rocks, than for those located in the surrounding regions. During rifting, extensive magmatism resulted in contact metamorphism of the sedimentary rocks, especially in the southern districts of the Oslo Region (Holmestrand, Skien, and Porsgrunn) (Hurum and Frøyland, 2004). Magmatic hydrothermal activity resulted in local sphalerite-pyrite mineralization (Jamtveit and Andersen, 1993).

2.2. Alum shale

The Alum Shale Formation (horizon 1a-3a β , Fig. 2) contains the oldest Lower Paleozoic sedimentary rocks in the Oslo Region. Figure 3 shows the original distribution of alum shale in Scandinavia and that they have been preserved in the Oslo Region. The Alum Shale Formation is ca. 75 m thick in the Oslo Region and is mainly comprised of organic-rich shale, limestone, and sandstone. The term alum shale was introduced hundreds of years ago when the alum salt, KAI(SO₄)₂·12H₂O (Fig. 4a), was used in e.g. the textile and paper industry, and for skin preservation. The alum shale is of particular interest in Norway due to its potential detrimental impact on the natural environment.



Figure 3: North European distribution of Lower Paleozoic sedimentary rocks. Map modified by Jan Marten Huizenga (unpublished) from Nielsen et al. (2018).



Figure 4: a) Salt precipitation associated with ARD on alum shale and b) alum shale unconformably overlying Precambrian basement granite stained by ARD. Picture from Slemmestad, Norway. Coordinates: 59.780202, 10.498429. Date: 21-04-2023.

Alum shales are rich in sulphide-bearing minerals (e.g. pyrite), organic matter and a variety of trace elements (e.g. V, Ni, Cu, Zn, As, Cd, Pb, and U) (Pabst et al., 2017). The alum shale sequence in Norway has a carbon content of 5-15 wt.% and is enriched in heavy metals like V and U (up to 6188 and 306 ppm, respectively). When exposed to atmospheric conditions the sulphide-bearing minerals in the rock oxidize and release protons, which generates an acidic solution. This process is referred to as acid rock drainage (ARD) (Pabst et al., 2017). If the exposure of sulphide minerals to the atmosphere is human induced (e.g. mining or infrastructure development), then this process is also referred to as acid mine drainage (AMD) (Warren, 2011). The impact of ARD can easily be recognized in the field by the typical redyellow staining of the rocks (Fig. 4b) and the precipitation of specific minerals associated with acid drainage (e.g. gypsum and jarosite).

The following equations describe the oxidation of pyrite (FeS_2) under circumneutral and below 4 pH (Chandra and Gerson, 2010; Singer and Stumm, 1970):

$2FeS_{2(S)} + 7O_{2} + 2H_{2}O \rightarrow 2Fe^{2+} + 4SO_{4}^{2-} + 4H^{+}$	Direct oxidation by O_2	(1)
$2Fe^{2+} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$	Fe(II) oxidation to Fe(III)	(2)
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3 (S)} + 3H^+$	Fe oxyhydroxide precipitation	(3)
$FeS_{2 (S)} + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2SO_4^{2-} + 16 H^+$	Indirect oxidation by Fe(III)	(4)

Acid rock drainage is O₂-driven (equation 1) at circumneutral pH. Here sulphide-bearing minerals, including pyrite, are dissolved through exposure to oxygen and water, releasing metals like Fe(II). Under these conditions Fe(II) further oxidizes to Fe(III) (equation 2) and is removed through Fe oxyhydroxide precipitation (equation 3). At pH below 4, Fe (III) is highly soluble and will no longer precipitate. Acid rock drainage generation at below 4 pH is therefore Fe(III)-driven (equation 4), causing oxidation of pyrite to happen faster and to generate more acid compared to the O₂-driven reaction. Therefore, ARD at below 4 pH can significantly accelerates chemical weathering of adjacent rock formations and metal contamination in the surrounding environment (Warren, 2011). The main recipients of ARD contamination are adjacent surface waters, groundwater and soils. Human exposure occurs through increased radioactivity and bioaccumulation of metals in crops from contaminated agricultural soil or water. Indirect effects occur through destabilization of ecosystems and potential loss of natural resources and ecosystem services (Parviainen and Loukola-Ruskeeniemi, 2019). Additionally, pyrite oxidation (reactions 1 and 4) is exothermal, which can lead to self-combustion (Gous and Genc, 2023).

The acid producing potential of alum shale is influenced by multiple factors including wholerock geochemical composition, minerology, contact with atmosphere, the adjacent rock types, and depositional and post-depositional conditions. Rocks with higher concentrations of sulphide-bearing minerals typically generate higher amounts of ARD, while adjacent rocks with a high natural acid neutralization capacity will decrease the ARD release. Contact with the atmosphere depends on sequence thickness, hydraulic properties of adjacent rocks, and natural and anthropogenic accelerated fractures and weathering (Parviainen and Loukola-Ruskeeniemi, 2019). Several deposition conditions are suggested to have an influence on the environmental impact of individual alum shale formations, e.g. redox conditions, the concentration of organic matter, the clay particles available for sorption with metals, metal source (seawater vs. later hydrothermal activity) and post-depositional metamorphic alteration (Parviainen and Loukola-Ruskeeniemi, 2019).

Incorrect classification with regards to the acid producing potential of shale can cause both environmental and economic issues and is often connected to the mining and construction industry. Today, Norwegian legislation classifies all disturbed acid producing rock as contaminating, which initiates strict and expensive landfill deposition (Wærsted et al., 2021). Permanent local deposition of excavated black shale can be applied for, as in the case of the excavation for the new Riksvei 4 tunnel near Gran, Norway (Fjermestad et al., 2018). However, approval for permanent local deposition is rare. It requires extensive examination of both the excavated materials and deposition location, which are highly time-consuming and expensive (Fjermestad et al., 2018). Therefore, the avoidance of unnecessary excavation remains the best practice for minimizing the detrimental effect of acid producing rocks on the natural environment in Norway. Appendix B4 gives an overview of the expected acid producing potential for each of the analyzed shale horizons (Wærsted et al., 2022; Kibsgaard et al., 2015).

3. Geochemical datasets

This chapter consists of detailed descriptions of four different datasets containing Lower Paleozoic shale samples from northern Europe. The descriptions include sample localities, stratigraphic positions, the analytical methods used, and the data use limitations. It will be explained why only the dataset published by Norwegian Geotechnical Institute (NGI) was used for further geochemical characterization, and an overview will be given of how the NGI data were modified for the purpose of this study.

3.1. Dataset introduction

One of the aims of this study is to compile a dataset of publicly available geochemical datasets containing Lower Paleozoic shales from northern Europe. An extensive literature search resulted in the identification of four geochemical datasets. These datasets include the whole-rock major and trace element geochemistry of Lower Paleozoic sedimentary rock samples from Norway, Estonia, Sweden and Russia. Table 1 provides an overview of these geochemical datasets, which were published by NGI (Wærsted et al., 2021), the Geological Survey of Norway (NGU) (Gautneb and Sæther, 2009; Sæther et al., 2010), and Ofili et al. (2022). The compiled and modified dataset is made available as an Excel spreadsheet (Appendix A1).

Dataset	Major elements as oxides	Trace elements	Trace elements Other	
NGI (Norway)	Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, Ba	Be, S, Sc, V, Cr, Co, Ni, Cu, Zn, As, K, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Ba, W, Hg, Pb, Th, U		<u>Appendix C</u> in <u>Wærsted et al.</u> (2021)
NGU 1 (Norway)	Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, Ba	V, Cr, Ni, Cu, Zn, Mo, Ba, Th, U	TOC, LOI, radioactivity measured as counts per second (cps)	Appendix 2 in Gautneb and Sæther (2009)
NGU 2* (Norway)	Li, Be, B, S, Sc, V, Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, Ba Li, Be, B, S, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, Ba, La, Ce, Pb, Th, U		Appendix 3 in <u>Sæther et al.</u> (2010)	
Ofili et al. (2022) (Estonia, Sweden and Russia)	ili et al. (2022) stonia, Sweden d Russia) Si, Al, Fe, Mn, Mg, Ca, Na, K, Ti, P, Ba Li, Sc, V, C Ni, Cu, Zn, Sr, Zr, Nb, Hf, Pb, Th,		LOI, S and TC data is notably absent	Supplementary material from Ofili et al. (2022)

Table 1: Overview of whole-rock geochemical datasets obtained from publicly available sources. *Samples from NGU 2 are included in the NGI dataset (further information on this can be found in section 3.1.2. and 3.3.5.). The references are hyperlinked to the relevant sources for convenience.

3.1.1. Norwegian Geotechnical Institute (NGI) dataset

The NGI dataset was used by Pabst et al. (2017) without publishing the dataset. The data were first published as an appendix in a 2021 NGI report (Appendix C in Wærsted et al., 2021). The dataset contains 332 sample analyses of sedimentary rock from the Oslo Region (i.e., Oslo, Slemmestad, Hønefoss, Hadeland, and Hamar) collected between 2010 and 2015 from different projects (Pabst et al., 2017). The stratigraphic position (Upper Cambrian, Lower Ordovician, Middle Ordovician) and age of the samples were determined using trace fossils and are available in Table 1 in Pabst et al. (2017). The exact location of where the samples were collected is not disclosed in any published material. The publication by Pabst et al. (2017) does, however, present a simplified geological map with approximate sample localities (Fig. 1 in Pabst et al., 2017), but it is not revealed which samples were taken from which localities (red dots in Fig. 5b). The authors were contacted to enquire about the exact localities, but unfortunately, no further information was provided. A hand specimen description of the analyzed samples, including mineralogy, is also not available.

3.1.2. Geological Survey of Norway (NGU) datasets

Two NGU reports have published datasets containing whole-rock analysis for Lower Paleozoic shale samples (Table 1). These datasets are referred to as NGU 1 (Appendix 2 in Gautneb and Sæther, 2009), and NGU 2 (Appendix 3 in Sæther et al., 2010). Upon thorough inspection of the datasets, it was discovered that all samples included in the NGU 2 dataset are also included in the NGI dataset (Wærsted et al., 2021). This fact is not disclosed by Wærsted et al. (2021).

NGU 1, dataset from Gautneb and Sæther (2009)

The first dataset (Appendix 2 in Gautneb and Sæther, 2009) contains older data used in an unpublished MSc thesis (University of Oslo) by Nyland and Teigland (1984). This thesis work is only available as a hard copy at the University of Oslo library. The dataset contains geochemical analyses for 235 samples from 20 different locations in the Oslo Region. A majority of the samples are derived from outcrops, while 49 samples are from drill cores. Additionally, the dataset includes stratigraphic position information (Lower Cambrian, Upper Cambrian, Lower Ordovician) and UTM coordinates (zone 32) of the sample localities (blue dots in Fig. 5b). Unlike the remaining datasets, this dataset provides lithological information including shale, siltstone, sandstone, conglomerate, and limestone. For the purpose of this study, only the shale samples (195 samples) were included. It should be noted that there are two apparent translation errors in the geochemical table included in this dataset. First, the samples that are supposed to be categorized as Lower Ordovician are erroneously indicated as U. Ordovician, suggesting Upper Ordovician. However, U. Ordovician stands for the Norwegian word "Under" (meaning Lower), in other words, U. Ordovician means Lower Ordovician. Second, the rock type shale is incorrectly translated as schist (a mistake that likely resulted from the incorrect English translation of the Norwegian word for shale, "skifer").



Figure 5: Sample locations for all countries (Pabst et al., 2017; Gautneb and Sæther, 2009; Ofili et al., 2022). (a) Overview map of north European shale and Paleozoic sediment distribution (modified from Nielsen, 2018). (b) Simplified map inset of Norwegian sample locations from NGI (red dots) and NGU 1 (blue dots). A more detailed map of the Norwegian sample locations is available in Appendix A1. Map insets illustrating sample locations from (c) Sweden, (d) Estonia and (e) Russia are modified from Figure 1 in Ofili et al. (2022). Note that scalebars in (c), (d) and (e) are corrected as they were inaccurate in the original publication.

NGU 2, dataset from Sæther et al. (2010)

The second NGU dataset (Appendix 3 in Sæther et al., 2010) contains geochemical data from 100 samples deposited during the Late Cambrian and Middle Ordovician. The outcrop and drill core samples were collected from two localities: Ankerskogen (Hamar) and Øvre Slottsgate (Oslo). The drill core samples from Ankerskogen (Middle Ordovician) were taken from a near-horizontal 25 m long borehole perpendicular to the strike. The samples from Øvre Slottsgate (Late Cambrian) are outcrop samples from an excavated basement. As previously mentioned all the samples in this dataset are also included in the NGI dataset described in section 3.1.1. (Appendix C in Wærsted et al., 2021). In the NGI dataset, these samples are labeled "ANK" in horizon 4aα and "*SLO*" in horizon 2d, indicate the locations Ankerskogen and Øvre Slottsgade, respectively. Neither the NGI report (Wærsted et al., 2021) nor the publication by Pabst et al. (2017) indicate the exact source of these samples, giving the false impression that the NGU 2

and NGI datasets are completely different. Only five trace elements (i.e. Be, Sc, As, Mo, and Cd) from the NGU 2 samples were not published in the NGI dataset. It was also decided not to include these trace elements in the modified dataset compilation, as a different method with very different results appears to have been utilized. For example, some trace elements (e.g. V) in the NGU 2 dataset are analyzed twice. The values for "V ppm" are included in the NGI dataset, while the values for "V" (like Be, Sc, As, Mo and Cd) were not included. Sample ANK1 in the NGU2 dataset has the values 66.2 and 213ppm for "V" and "V ppm", respectively.

3.1.3. Ofili et al. (2022) dataset

The publication by Ofili et al. (2022) includes a compilation of Lower Cambrian to Upper Ordovician shale samples from Estonia, Sweden and Russia (supplementary materials for Ofili et al., 2022). Information concerning the origin of the Sweden and Russia datasets is limited.

Estonia data

This dataset consists of 362 Lower Ordovician samples from 20 different locations (red dots in Fig. 5d) from the Türisalu Formation (Ofili et al., 2022). These samples were collected from 17 drill cores and three outcrops (Pakri, Saka and Nõmmeveski). The drill core samples were collected 30-40 years ago (Vind and Bauert, 2020). Samples from Pakri and Saka were collected in 2013 (Voolma et al., 2013), whereas sampling localities and collection year of the samples from the Nõmmeveski outcrop remains undetermined due to lack of data. The geochemical analyses of the Estonia samples were performed by multiple research groups.

Sweden data

This dataset consists of 53 outcrop samples from eight locations in southern Sweden (red dots in Fig. 5c). The samples represent the Alum Shale Formation deposited from Middle Cambrian to Early Ordovician (Ofili et al., 2022). Information regarding when the samples were collected is not available, but they were collected before 2014.

Russia data

This dataset consists of 266 samples from 34 drill cores collected in the St. Petersburg region of western Russia (red dots in Fig. 5e). The Early Ordovician samples are from the Koporye Formation (Ofili et al., 2022). Like for the Swedish samples, information regarding when samples were collected is not available, but they were collected before 2014.

3.2. Analytical methods

The four compiled datasets were originally assembled using different analytical methods. This section describes the analytical methods used for each dataset, with an overview in Table 2. The methodology description for the NGI and NGU 2 (Wærsted et al., 2021; Sæther et al., 2010) datasets have been combined, as the NGU 2 samples were found to be included in the NGI dataset. Meanwhile, the Estonia samples from Ofili et al. (2022) have undergone different methodology than the samples from Sweden and Russia from the same source. The Ofili et al. (2022) methodology is therefore divided in Table 2 accordingly.

Table 2: Overview of whole-rock geochemical methodology for each original dataset. The references are hyperlinked to the relevant sources for convenience.

Dataset	Major elements	Trace elements	Trace elements Other	
NGI and NGU 2 (Norway)	Inductively coupled plasma atomic emis- sion spectrometer (ICP-AES)	Inductively coupled plasma sector field mass spectrometer (ICP-SFMS)	TIC + TOC: Colorimetric method (ISO 10694 and BS EN 13137) LOI: Unknown	<u>Pabst et al.</u> (2017)
NGU 1 (Norway)	X-ray fluorescence spectrometry (XRF)	XRF	TOC, LOI and radioactivity: Unknown	<u>Gautneb and</u> Sæther (2009)
Ofili et al. (2022) (Estonia)	ICP-AES and XRF	ICP-AES and Inductively coupled plasma-mass spec- trometry (ICP-MS)	N/A	<u>Ofili et al.</u> (2022)
Ofili et al. (2022) (Sweden and Russia)	XRF	ICP-MS	N/A	<u>Ofili et al.</u> (2022)

3.2.1. Norwegian Geotechnical Institute (NGI) and Geological Survey of Norway (NGU 2)

Whole-rock analysis was done at the Australian Laboratory Services. Geochemical composition was analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-AES) for major elements and an inductively coupled plasma sector field mass spectrometer (ICP-SFMS) for trace element composition. Total organic and inorganic carbon content were both determined with a colorimetric method, based on the standards ISO 10694 and BS EN 13137 (Pabst et al., 2017).

3.2.2. Geological Survey of Norway (NGU 1)

Major and trace element whole-rock geochemical compositions were determined by X-ray fluorescence (XRF) spectrometry. Semi-quantitative mineralogical analyses were also performed using X-ray diffraction (XRD), but these data have been excluded as it is beyond the scope of this study. No information was provided about how the TOC was determined and how the radioactivity measurements (measured as counts per second) were done (Gautneb and Sæther, 2009). The geochemistry was analyzed at the Institute of Geology, Oslo University (Nyland and Teigland, 1984).

3.2.3. Ofili et al. (2022) dataset

Estonia data

The Estonian dataset is a compilation of multiple different analyses methods, divided into: (a) One outcrop (Nõmmeveski) and seven drill cores (F314, F326, F328, F338, F345, F347, F360), (b) Ten drill cores (F298, F330, F343, F344, F354, F355, F362, F366, F369, K14), and (c) the two outcrops Pakri and Saka. The major and trace element data from outcrop Nõmmeveski and the seven drill cores were originally obtained from a 2020 Geological Survey of Estonia report

(Vind and Bauert, 2020; Soesoo et al., 2020). Whole-rock major and trace element analyses for these samples was done with ICP-AES in Finland at the Australian Laboratory Services (Vind and Bauert, 2020). The ten drill cores from the Geological Survey of Estonia drill core repository were analyzed by XRF for their major element composition. Trace elements for six of these ten drillings (F354, F355, F362, F366, F369, K14) were determined with the procedure MA250 at Bureau Veritas in Canada (Ofili et al., 2022), whereas the trace element composition for the remaining four drillings were obtained from the before mentioned Geological Survey of Estonia report (Vind and Bauert, 2020). Major and trace element composition for the two outcrops Paki and Saka were analyzed using an XRF-spectrometer and inductively coupled plasma-mass spectrometry (ICP-MS) respectively. All geochemical analyses for the Paki and Saka outcrops were done at the Institute of Geology, Tallinn University (Voolma et al., 2013).

Sweden and Russia data

Fresh rock samples were analyzed at the Russian Geological Research Institute in St. Petersburg. Major elements were determined by XRF, whereas trace elements were analyzed using ICP-MS (Ofili et al., 2022).

3.3. Data use limitations

The use of the geochemical datasets is constrained by (1) the storage age of the samples, (2) when the geochemical analysis was done, (3) sample locality and descriptions, and (4) what elements and other chemical variables were included in the geochemical analysis. These aspects are discussed below in more detail. Ultimately, the quality assessment (5) based on these limitations concluded that only the NGI data was suitable for the purpose of this study.

3.3.1. Sample storage age

The dataset from Estonia (Ofili et al., 2022) partly contains recent geochemical analyses from samples that were collected 30-40 years ago (Vind and Bauert, 2020). It is highly likely that the older Estonian samples have undergone changes in material composition while stored. In particular, pyrite-rich samples could have undergone oxidation.

3.3.2. When was the geochemical analysis done?

The NGU 1 dataset (Gautneb and Sæther, 2009) contain geochemical analyses that are several decades old (1984), i.e. the methods used were likely less accurate and less precise (in particular for the trace elements) compared to the analyses that were done more recently.

3.3.3. Sample locality and sample description

Exact localities for the samples from the NGI report (Wærsted et al., 2021) are not publicly available, whereas localities for the remaining datasets are made available in the respective datasets as GPS coordinates. Furthermore, none of the publications in which the datasets are included present a geological context of the samples. For example, structural information such as deformation features, the presence of nearby faults, sills, or dykes, are not described.

The mineralogical composition of the samples is, except for the samples in the NGU 2 dataset (Sæther et al., 2010), not available. The NGU 2 dataset presents the qualitative mineralogical composition of the samples as determined by X-ray diffraction [see p. 125-128 in the Sæther et al. (2010) report]. All shale samples included in this report contain quartz, illite, and K-feldspar. Chlorite, pyrite, calcite, dolomite and ankerite are also present but not in all samples.

3.3.4. What is included in the geochemical analysis?

As shown in Table 1, the different datasets are not identical in terms of what has been analyzed for. Obviously, this limits the geochemical evaluation, as different methods for determining for example paleoclimate conditions, redox environment, and productivity require specific elements. Furthermore, to evaluate the geochemistry of black shale, certain elements are indispensable, including TOC and S which is only available for some of the datasets (see Table 1). Lastly, the loss on ignition (LOI) is of critical importance to determine the quality of the major element analysis. The total sum of all major elements (measured as oxides) including LOI should be 100% (e.g., Rollinson, 1993). Loss on ignition data is included in the Norwegian datasets, but is not included in the data from Estonia, Sweden and Russia.

3.3.5. Data quality assessment: What data to use?

Based on the limitations described above, it was decided that only the NGI dataset (Wærsted et al., 2021) was suitable for the further detailed geochemical evaluation of this study. The old geochemical data compiled and presented in the NGU 1 report by Gautneb and Sæther (2009) were analyzed by outdated analytical methods thereby introducing an uncertainty that is too large for reliable analysis. The data by Ofili et al. (2022) does not include LOI, which makes it impossible to do a quality check of the whole-rock major element geochemistry. In addition, these data do not include TOC and S data. As mentioned previously, all the geochemical analyses in the NGU 2 report by Sæther et al. (2010) are also available in the NGI dataset (Wærsted et al., 2021). The dataset obtained from Sæther et al. (2010) is therefore from this point forward considered a part of the NGI dataset.

Although the NGI dataset was determined to be suitable for further analysis, which will be presented in chapters 4 and 5, this dataset also has some limitations and uncertainties. For example, only 15 of the 23 trace elements included in the dataset are analyzed for the Late Cambrian horizons (2a and 2d). The lack of As data is particularly unfortunate, as this metalloid often is associated with pyrite formation, and these horizons are thought to have the greatest acid producing potential. Furthermore, the Early Ordovician horizons $3b\alpha$, $3b\beta$ and 3c contain little to no usable major elemental data (see Appendix C6). Limitations and modification of the dataset are further explained in section 3.4.

3.4. Data modification

3.4.1. Organization of the data spreadsheets

All data has been collected in a single Excel spreadsheet with worksheets for each of the Norwegian datasets (Wærsted et al., 2021; Gautneb and Sæther, 2009) and each country (Estonia, Sweden and Russia) included in Ofili et al. (2022). As the chemical composition data from the now three datasets were combined, certain modifications were done to make the datasets uniform. Modifications include: (1) Making all datasets follow the same layout, (2) reorganizing trace elements by atomic number, and (3) reorganizing samples by age instead of sample location. Organization by age was not possible for the Estonia, Sweden and Russia samples as they do not include sample specific age information. Further revision of the NGI dataset is described in the remaining part of section 3.4., with an overview available in Table 3 and as a detailed sample specific table in Appendix B1.

Table 3: Summary of excluded or rearranged NGI samples. (*1) Only major element data is excluded. (*2) Identical data originally included in both horizon 3a and $3b\alpha$, because the authors of the source publication could not decide where they belong. These data are now grouped separately as $3a/3b\alpha$ and were not used for further analyses in this study. (*3) Signifies "up to X samples". However, the number of remaining samples used for further analyses in this study is for some elements lower than indicated in this table. To ensure transparency, a detailed overview of sample counts and data gaps is available in Appendix C6.

Reason/Horizon	2a	2d	3a	3a/3bα	3bα	3bβ	3c	4aα	Total
Limestone	-4	-2	-3		-4	-2	-20	-7	-42
Duplicates moved into new transition horizon			→ -15*²	+15*2	← -15*²				
Uncertainty (sum range)*1	-3	-4	-23	-10	-21	-33	-5	-15	-114
Original sample count	50	24	62	0	45	40	25	86	332
Remaining samples used for major element analysis* ³	43	18	21	0	5	5	0	64	156
Remaining samples used for trace element analysis* ³	45	22	44	0	26	38	5	79	259
Total remaining samples in dataset	46	22	44	15	26	38	5	79	275

3.4.2. Duplicate samples in the NGI dataset

Fifteen samples were found to be duplicated in the NGI dataset within two different horizons (3a and 3b α). Erlend Sørmo, co-author of Pabst et al. (2017), confirmed by e-mail to the author of this study (02-04-2024) that the repetition occurred because the samples were collected from a transition zone, making horizon classification unclear. In the new compilation dataset, these samples have been placed in their own transition horizon grouping named 3a/3b α . This transition horizon is not considered to be a true horizon and is, therefore, excluded from any further geochemical evaluation in this study. Note that the original sample IDs for these 15

duplicates were slightly different in horizon 3a and $3b\alpha$, making them appear as unique samples, even though their geochemical compositions are identical (Appendix B1).

Another error was found for the sample ID BH4-03-5-60. This ID appears twice under NGI horizon $3b\beta$, but each sample has unique geochemical data. The two samples are now renamed BH4-03-5-60a and BH4-03-5-60b.

3.4.3. Incorrect horizon classification in the NGI dataset

Inconsistencies in horizon classification were found for 22 samples in the NGI dataset. As previously mentioned, these samples were originally published in the NGU 2 report by Sæther et al. (2010). In this NGU report the 22 samples were classified as horizon 2d, while they were classified as 2b in the NGI Excel data file. It is assumed that the horizon classification in the NGU 2 report is correct, as this is the original publication.

3.4.4. Exclusion of poor quality samples

Samples that were found to not represent shale samples or were associated with significant uncertainty have been excluded from the NGI dataset. A full overview of which samples were excluded is available in Appendix B1.

Limestone samples were identified by their low SiO_2 and their high CaO and TIC contents. Consequently, 42 NGI samples were identified as limestone and removed from the dataset. The remaining data was further classified using the SandClass System (Herron, 1988).



Figure 6: Template for the SandClass system for geochemical classification of terrigenous sandstones and shales, where all oxides are analyzed in wt.%. Numbers represent plotting coordinates for the field boundaries. Modified from Figure 2 and Appendix 1 in Herron (1988).

Samples associated with significant uncertainty were identified by calculating the total sum for all major elements to assess the quality of major element concentration determination (Rollinson, 1993). All samples with a total sum outside of the range of 97.5-102.5%, were excluded from further major element analysis (114 of the 275 NGI samples).

Notably, no samples from horizon 3c were found to fall within the set quality range, resulting in no major element analysis being done for this horizon. Furthermore, horizons $3b\alpha$ and $3b\beta$ only contain five samples each within the acceptable range. This low sample number increases the uncertainty for further geochemical characterization. It must be emphasized that these excluded samples were still used for trace element geochemical characterization, as analyses for major and trace elements were conducted separately.

3.5. Data addition

3.5.1. Data used for normalization

The UCC composition (major and trace elements) from Rudnick and Gao (2014) and the MBS composition (trace elements only) from Ketris and Yudovich (2009) were used for normalization purposes and are available in Appendix B2. These, and other compositions, are also included as an additional worksheet in the compiled and modified dataset (Appendix A1).

3.5.2. Major elements as cations

All major elements were originally analyzed as weight percent (wt.%) oxides. In the compilation dataset the major element composition is also represented as cations, which was calculated as follows (using Fe_2O_3 as an example):

$$Fe (wt.\%) = Fe_2O_3 (wt.\%) \times 2 \times M_{Fe} / [2 \times M_{Fe} + 3 \times M_O]$$
(5)

in which M_{Fe} and M_{O} denote the molar mass of Fe and O, respectively.

3.5.3. Total of major oxides

The total sum of the major element oxides was originally only available in the NGU dataset. It was calculated and added in the NGI dataset based on LOI data, but is not possible to calculate for the Estonia, Sweden and Russia samples, as the LOI data are not included for these samples.

3.5.4. Basic statistics

Basic statistical information has been calculated in the modified compilation dataset. An Excel worksheet was added for each Norwegian dataset and for each country (Estonia, Sweden and Russia) included in the Ofili et al. (2022) dataset.

4. Methodology for this study

This chapter describes the methods used to further geochemically characterize the Lower Paleozoic shales from the Oslo Region, using the modified NGI dataset as summarized in Table 3 and explained in the previous chapter. The samples from this dataset are divided into seven horizons (2a, 2d, 3a, 3b α , 3b β , 3c and 4a α), which have been compared to evaluate the geochemical variation of the Lower Paleozoic shales in the Oslo Region (Fig. 2).

4.1. Comparison of shale major and trace element composition with UCC and MBS

Upper Continental Crust (Rudnick and Gao, 2014) and the MBS (Ketris and Yudovich, 2009) compositions (Appendix B2) were used for normalized comparisons. This has been visualized in a similar manner as for, for example, Rare Earth Element (REE) or trace element spider diagrams (e.g. Rollinson, 1993). All parameters expressed as mass ratios.

4.2. Major element geochemistry

The major element concentrations have been used to determine the shales provenance, paleoweathering and paleosalinity. These methods are described in the following subsections.

4.2.1. Provenance

Provenance characterization is used to determine from which parent rock the shale was derived, and was here determined with M^+ , 4Si, and R^{2+} ternary diagrams (Fig. 7). This method was introduced by Meunier et al. (2013) and is defined as follows with mol.% units:

$$M^{+} = Na^{+} + K^{+} + 2Ca^{2+}$$
(6)

$$4Si = Si^{4+} / 4$$
 (7)

$$R^{2+} = Fe^{2+} + Mg^{2+} + Mn^{2+}$$
(8)



Figure 7: Template for ternary diagram describing provenance based on the chemical composition of main crust forming rock types. TTG: tonalite, trondihemite, granodiorite. Modified from Figure 1A and Table 1 in Meunier et al. (2013). Upper Continental Crust (UCC) is from Rudnick and Gao (2014). All parameters are expressed as mol.%.

4.2.2. Paleoweathering and paleoclimate

Paleoweathering and paleoclimate conditions can be assessed by analyzing the Chemical Index of Alteration (CIA), introduced by Nesbitt and Young (1982), and the Weathering Index (WIP), introduced by Parker (1970). Here, these methods have been combined as outlined by Garzanti et al. (2013) and shown in Figure 8 below. Strong weathering is indicated by high CIA and low WIP values. The credibility of the CIA method is further strengthened by evaluating the processes K-alteration, sediment recycling, and sediment sorting, as these processes can significantly influence the CIA values (Wang et al., 2022).



Figure 8: Template for paleoweathering diagram illustrating the relationship between the Chemical Index of Alteration (CIA) and the Weathering Index (WIP). The diagram is modified from Figure 9 in Garzanti et al. (2013). Upper Continental Crust (UCC) is from Rudnick and Gao (2014). All parameters expressed in molar ratios.

Chemical Index of Alteration (CIA)

Chemical weathering is primarily accelerated by enhanced moisture and temperature, which lead to the loss of mobile cations (e.g. Ca^{2+} , Na^+ , K^+) and, consequently, a high CIA value. Low CIA values indicate less chemical weathering which indicates cold or arid paleoclimate conditions (Fedo et al., 1995). The CIA is calculated as follows:

$$CIA = molar (Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O) \times 100$$
(9)

The CaO* value represents the CaO content that is present in silicate minerals, i.e. it requires a correction for the fraction of CaO in apatite and calcite (Fedo et al., 1995). This correction was done following the method proposed by McLennan (1993) and involves the following (note that all concentrations are in molar):

$$CaO' = CaO - (10/3) P_2O_5$$
 (10)
If $CaO' > Na_2O \rightarrow CaO^* = Na_2O$

If CaO' < Na₂O \rightarrow CaO* = CaO'

As previously mentioned, it is necessary to evaluate whether K-alteration, sediment recycling, or sediment sorting have altered the CIA values (Wang et al., 2022). All horizons that showed signs of significant influence from any of these three processes were removed from the final paleoweathering assessment.

Potassium alteration: Post-depositional K accumulation can occur in the rocks during hydrothermal activity (Wang et al., 2020). Considering the historic deformation and rift-related magmatism of the Oslo Region, K-alteration is a distinct possibility. Potassium alteration in sedimentary rocks can be assessed by plotting the molar ratio of Chemical Index of Weathering (CIW) against the CIA. When the CIW and the CIA parameters correlate, the sediments are not affected by K-alteration. The CIW is identical to the CIA except it's calculated without K_2O :

$$CIW = molar \left[Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O)\right] \times 100$$
(11)

Sediment recycling: Sediment recycling refers to the alteration of sediment composition by weathering and erosion, here assessed with Zr concentration. Low Zr concentration (< ca. 200 ppm) indicates minimal sediment recycling (Wang et al., 2022).

Sediment sorting: Sediment sorting indicates whether hydrodynamic processes have altered the shales mineral composition. Here, the Index of Compositional Variability (ICV), introduced by Cox et al. (1995), was used to assess sorting in the samples:

$$ICV = (Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2) / Al_2O_3$$
(12)

in which all the oxides are given in wt.%. Since clay minerals have high Al₂O₃ concentrations, an ICV value >1 suggests a significant fraction of non-clay minerals. A high fraction of non-clay minerals indicates poor sorting and suggests that sediments represent first sedimentary cycling and tectonic active settings. Sediment sorting evaluates the accuracy of the CIA based on the notion that poorly sorted sediments have undergone less physiochemical alteration.

Weathering Index (WIP)

Finally, the WIP can be plotted against CIA values (Fig. 8) for samples which are not affected by either K-alteration, sediment recycling or sediment sorting. The WIP is defined as follows:

in which all the oxides are given in mol.%, and the values 0.7, 0.35, 0.25, and 0.9 representing the bond strength of the individual major elements with oxygen. The WIP equation presented above differs slightly from those described by Parker (1970) and Garzanti et al. (2013). Parker (1970) focused on the weathering of silicate rocks and did therefore not correct for the CaO fraction in apatite (a phosphate mineral). Garzanti et al. (2013) addressed this by including P_2O_5 in the equation, assuming that P is solely present as apatite. In this study, the CaO content was further corrected for calcite, with CaO calculated as CaO* (equation 10). This adjustment makes the WIP equation more suitable for Norwegian shales, which commonly contain calcite.

4.2.3. Paleosalinity

Paleosalinity describes the salinity conditions in the depositional environment. High salinity environments have a higher chance of developing stratification in the water column, where layers of varying water density will limit circulation. Reduced water circulation limits the influx of oxygen from the surface, which promotes reducing bottom conditions and organic matter preservation (Deng et al., 2019). The paleosalinity has been determined by the ratio between $100 \times Mg/Al$ and the TOC/S_T ratio (Lei et al., 2002; Berner and Raiswell, 1984), with all parameters expressed as ppm. Lei et al. (2002) proposed that the values of $100 \times Mg/Al > 10$, 1-10, and < 1 indicate saline, brackish and freshwater conditions, respectively. Berner and Raiswell (1984) proposed that the TOC/S_T ratios of 0.5-5, 5-10 and >10 indicate saline, brackish and freshwater conditions respectively.



Figure 9: Paleosalinity diagram template modified from Xu et al. (2021). The darkest blue areas indicate freshwater conditions, while white areas indicate marine conditions. All remaining shades of blue indicate various brackish conditions. All parameters are expressed as ppm.

4.3. Trace element geochemistry

The trace elemental data have been used to determine paleoproductivity and paleoredox conditions during deposition. These methods are described in the following subsections.

4.3.1. Paleoproductivity

Paleoproductivity refers to the original level of biological productivity and is commonly estimated with the proxies TOC, organic P (P_{org}) and biogenic Ba (Ba_{bio}). Marine algal biomass is the primary source of sedimental TOC and P_{org} , whereas Ba_{bio} estimates productivity based on the relationship between barite mineral (authigenic barite) production and the decay of

organic matter in seawater. It is advised to estimate paleoproductivity with multiple proxies, since no single proxy is reliable under all conditions (Schoepfer et al., 2015).

The main conditions affecting the reliability of TOC, P_{org} and Ba_{bio} are redox conditions and sediment Bulk Accumulation Rate (BAR). Redox conditions are a particularly important preservation factor for TOC, where up to 30% of TOC is preserved in sediments under reducing conditions, while oxic conditions often preserve less than 1% due to increased microbial activity (Canfield, 1994). In contrast, oxic and suboxic conditions favor preservation of P_{org} and Ba_{bio}. Under these conditions barite is relatively insoluble, while P_{org} can, through a variety of P-trapping mechanisms, become saturated in porewater leading to precipitation of authigenic P minerals. Furthermore, the significance of redox conditions decreases as BAR increases (especially for TOC) due to reduced exposure of the sediments. However, increased BAR can also have a diluting effect depending on the amount of detrital input (Schoepfer et al., 2015).

The Babio fraction of Ba can be calculated as follows (Deng et al., 2019):

$$Ba_{bio} = Ba_{sample} - AI_{sample} \times (Ba / AI)_{detrital}$$
(14)

Typically, the $(Ba / AI)_{detrital}$ values are calculated using UCC values. However, as shown by Deng et al. (2019), it is more appropriate to use Ba vs. Al cross plots, following the method described by Rutsch et al. (1995). The lowest possible trendline is drawn in the cross plots, which signifies the detrital fraction, i.e. the slope of this trendline represents $(Ba / AI)_{detrital}$. Organic P is determined with the same method as Ba_{bio} . In this study, Ba_{bio} , P_{org} and TOC were corrected with BAR and used to determine the total productivity with the respective mass accumulation rates for Ba (BaAR), P (PAR) and TOC (TOCAR), as calculated by Hu et al. (2020). An example for Ba is provided below:

$$BaAR = Ba_{bio}/1000 \times BAR$$
(15)

Both BaAR and BAR are measured as $g/cm^2 \times kyr$. The BAR is calculated by multiplying the shale density (g/cm^3) with the Linear Sedimentation Rate (LSR, cm/kyr). The shale density was calculated as follows (Schoepfer et al., 2015):

Shale
$$\rho = 0.0794 \times \ln(age) + 0.65$$
 (16)

where age is the average horizon age in kyr. Linear Sedimentation rates and age data are provided in Figure 2 and Appendix B3.

4.3.2. Paleoredox

Paleoredox conditions are commonly evaluated based on elemental proxies. Multiple indicators exist such as different C-S-Fe-P systems, proxies based on trace elemental ratios, and proxies based on trace element Enrichment Factors (Algeo and Liu, 2020). Here, the indicators Total Degree of Pyritization (DOP_T) and TOC/P_{org} ratio were used as proxies to determine the paleoredox conditions.

Total Degree of Pyritization (DOP_T): True DOP as a redox proxy was first introduced by Raiswell et al. (1988), who utilized the effects of redox conditions on Fe speciation in sedimentary systems. The true DOP can be approximated with the redox proxy DOP_T. This proxy utilizes total S and total Fe, instead of highly reactive Fe species (Algeo and Liu, 2020). The formation of pyrite is dependent on the concentration of H₂S, which is greater under sulfidic and anoxic conditions. Greater DOP_T values, therefore, indicate anoxic conditions. The DOP_T is calculated as follows (Algeo and Li, 2020):

$$DOP_{T} = total S_{sample} (wt.\%) \times [M_{Fe} / (2 \times M_{S})] / total Fe_{sample} (wt.\%)$$
(17)

where M_{Fe} and M_S denote the molar mass of Fe and S. Note that the Fe and S contents in the NGI dataset represent total Fe and total S. The paleoredox threshold values for the DOP_T are shown in Table 4 below.

Ratio between TOC and organic P: The redox proxy TOC/P_{org} ratio was introduced by Algeo and Ingall (2007), in which the ratio is compared to the Redfield ratio (C/P=~106) in marine algae. As P is released by degradation near the sediment/water interface, the TOC/ P_{org} ratio will deviate from the Redfield ratio depending on the environment's redox conditions (Algeo and Li, 2020). Under anoxic conditions P is precipitated less, resulting in a higher ratio than the Redfield ratio. The TOC/P_{org} is calculated as follows (Algeo and Li, 2020):

$$TOC/P_{org} = [TOC (wt.\%) / M_C] / [P (wt.\%) / M_P]$$
 (18)

where M_C and M_P denote the molar mass of C and P. The paleored ox threshold values for the TOC/P_{org} are shown in Table 4.

Table 4: Threshold values for paleoredox indicators. Note that DOP_T thresholds are suspected to be formation specific and that TOC/P_{org} values range from 10-1000 (Algeo and Li, 2020).

Method	Redox conditions	Threshold (molar mass)	Method	Redox conditions	Threshold (molar ratio)
	Oxic	DOP _T < 0.25		Oxic	TOC/P _{org} < 50
DOPT	Suboxic	$0.25 < DOP_T < 0.60$	TOC/P _{org}	Suboxic	50 < TOC/P _{org} < 100
	Anoxic	$DOP_{T} > 0.60$		Anoxic	TOC/P _{org} > 100

5. Results and interpretation

Median values only, or 25th, 50th, and 75th percentile values (box plots), were used to visualize the geochemical variation of the different horizons in the various diagrams. This was done for easy visual comparison of the different horizons and to minimize the effect of outlier data. Outliers from box plots are instead listed as values in associated tables. As stated previously, the major elemental data from horizon 3c were excluded. Further transparency is given through an overview of all data gaps and sample counts in Appendix C6.

5.1. Lithological classification: The SandClass system

Four individual samples were classified as wacke (Appendix C1) but were retained in the dataset due to the similarities between wacke and shale, as well as the limitations of the method. All remaining samples reside in the shale or Fe-shale zones (Appendix C1).



Figure 10: The SandClass system showing the median composition of analyzed shale samples for each horizon, where all oxides were analyzed in wt.%. Modified from Figure 2 and Appendix 1 in Herron (1988).

Discussion of results

The SandClass system (Fig. 10) shows that, while there are some minor variations, the horizons have generally similar major element geochemistry. Additionally, it is confirmed that no obviously non-shale samples remain in the dataset. Combined with the other data selection methods applied, this ensures the dataset's reliability for further analysis.

5.2. Major and trace element composition of the different horizons

5.2.1 Horizon comparison for selected major and trace elements

The compositions for selected elements (i.e. S, TOC, V, U, As and Cd) are presented in Figure 11. It is noteworthy that all chemical elements show the same trend. The oldest horizons from 2a and 2d (Late Cambrian) and 3a (Early Ordovician) have the highest concentrations, whereas the youngest horizons 3b, 3c (Early Ordovician) and 4a α (Middle Ordovician) have lower concentrations. Note that a deviation is present for V, which has the highest concentration in 3a and not in 2d.



Figure 11: Box diagrams (25th, 50th, and 75th percentile) showing the composition for selected elements: (a) S, (b) TOC, (c) V, (d) U, (e) As, and (f) Cd for the analyzed horizons. Box values for each horizon are available in Table 5-7. Sample counts are available in Appendix C6.

	(a) S (wt.%)						wt.%) (b) TOC (wt.%)			
Horizon	Min	Q1	Median	Q3	max	Min	Q1	Median	Q3	Max
4aα	0.01	0.20	0.38	0.84	1.49	0.14	0.34	0.43	0.71	3.75
3c	0.17	0.18	0.21	0.22	0.22	0.21	0.28	0.42	0.72	0.99
3bβ	0.59	1.25	1.86	2.12	3.87	0.12	0.56	2.09	2.59	3.32
3bα	0.26	0.52	1.02	1.59	3.94	0.14	0.21	0.66	1.59	3.24
3a	1.37	2.97	3.40	4.00	7.17	1.70	3.58	3.87	4.50	5.97
2d	1.59	3.66	3.94	4.29	5.35	7.06	9.15	9.69	10.69	11.58
2a	1.04	2.38	3.11	3.56	6.05	1.78	7.68	8.73	9.87	12.97

 Table 5: Box values for (a) sulphur and (b) TOC as visualized in Fig. 11a and 11b, respectively.

 Table 6: Box values for (c) vanadium and (d) uranium as visualized in Fig. 11c and 11d, respectively.

			(c) V (ppm)				(d) U (ppm	ı)	
Horizon	Min	Q1	Median	Q3	max	Min	Q1	Median	Q3	Max
4aα	139	184	195	212	739	3	6	8	9	38
3c	155	159	171	233	250	4.2	4.7	6.5	6.9	7.0
3bβ	140	243	521	707	1130	2.3	11.5	28.3	35.5	42.8
3bα	173	204	434	625	973	1.5	7.6	13.9	20.4	26.0
3a	468	1410	1735	1928	2120	15.6	39.6	42.7	73.9	134
2d	472	585	623	803	894	123	138	162	186	264
2a	323	432	727	1080	6188	28	52	85	154	306

 Table 7: Box values for (e) arsenic and (f) cadmium as visualized in Fig. 11e and 11f, respectively.

	(e) As (ppm)							(f) Cd (ppn	n)	
Horizon	Min	Q1	Median	Q3	max	Min	Q1	Median	Q3	Max
4aα	2.9	3.2	6.0	8.5	10.4	0.03	0.03	0.04	0.04	0.04
3c	4.0	4.1	4.8	9.1	10.3	0.04	0.06	0.10	0.13	0.14
3bβ	2.9	12.7	24.0	31.3	47.8	0.03	0.51	1.20	2.49	4.81
3bα	2.6	8.3	11.7	18.6	23.2	0.05	0.12	0.30	0.38	7.98
3a	8.5	41.9	53.2	66.3	193	2.9	7.2	9.7	11.6	20.5
2d	-	-	-	-	-	-	-	-	-	-
2a	-	-	-	-	-	-	-	-	-	-

5.2.3. Comparison of shale major and trace element composition with UCC and MBS

Figure 12 shows the chemical composition of the horizons 2a, 2d, 3a, $3b\alpha$, $3b\beta$, 3c and $4a\alpha$ relative to the UCC (Rudnick and Gao, 2014) and MBS (Ketris and Yudovich, 2009) compositions. We see that certain elements tend to deviate from these standards. Standards are available in Appendix B2.

Upper Continental Crust (UCC)

The diagrams (Fig. 12a-m) show a general tendency of the horizons to be enriched with S, U, and As, whereas some horizons are also enriched in Mo, Cd, V and BaO. No significant depletion was found, but Na_2O and MnO compositions tend to be lower than the UCC values.

Median Black Shale (MBS)

Comparison with MBS is only possible for trace elemental data (Fig. 12g-m). Arsenic is here only enriched for horizon 3a, while data for the horizons 2a and 2d is unavailable. Uranium is enriched for horizons 2a, 2d, 3a and 3b β , while 3b α is equal to MBS values, and the youngest horizons 4a α and 3c are U depleted compared to MBS. A severe Cd- and Mo-depletion was found for horizon 4a α and 3c, while both elements are unavailable for horizon 2a and 2d.



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Figure 12: Major element (a-f) and trace element (g-m) compositions (note that the oldest horizons are at the bottom of the figure). Values >1 are enriched while <1 are depleted compared to UCC (red) or MBS (black). The UCC and MBS compositions are based on Rudnick and Gao (2014) and Ketris and Yudovich (2009), respectively. Grey areas signify elements with no available data, whereas additional sample counts are listed in Appendix C6. All parameters are shown as mass ratios.

Discussion of results

The general trend observed for the horizons (Fig. 11a-f) is that older horizons have higher values of S, TOC, V, U, As, and Cd compared to the younger horizons, indicating a positive correlation between the TOC and the other elements. The enrichment of S, V, U, As, Mo, and Cd in older horizons exceeds the UCC composition (Fig 12g-m). Unfortunately, data for As, Cd, and Mo are unavailable for the Late Cambrian horizons (2a and 2d).

New shale classification guidelines have recently been implemented based on trace elemental compositions from the original 332 NGI samples (Pabst et al., 2017; Wærsted et al., 2021). As shown in Table 3, a large portion of this data was found to be of poor quality, making it unsuitable as a foundation for national guidelines, while the method also requires an expensive and time-consuming full chemical analysis of shale samples. A scenario where fewer trace elements are necessary for shale deposit categorization could make classification possible with a calibrated handheld XRF. In this study, As, Cd, and Mo were found to indicate interesting yet inconclusive correlations (Fig. 12g-m). However, these trace elements were not included in Pabst et al. (2017). If future research finds that Late Cambrian (2a and 2d) samples typically are enriched by As and not significantly depleted in Cd and Mo (as is seen for horizons 3c and 4a α), then a handheld XRF calibrated for these three elements could potentially identify deposits derived from horizons 3c and 4a α in a faster and cost-effective fashion.

5.3. Major element geochemistry

5.3.1. Provenance

All median values are located within the mafic zone and were found to resemble the UCC composition (Fig. 13). Individual horizon provenance diagrams are available in Appendix C2 with sample counts.



Figure 13: Provenance analysis of the different horizons using median shale compositions. The ternary diagram describes the provenance compared to the chemical composition of main crust forming rock types. TTG: Tonalite, Trondihemite, Granodiorite. The figure is modified from Figure 1A and Table 1 in Meunier et al. (2013). The UCC composition is based on Rudnick and Gao (2014). All parameters are expressed as mol.%.

Discussion of results

The fact that the different horizons plot in close proximity to each other indicates little variation in the source rocks, but no clear indication of provenance is observed. According to Bjørlykke (1974), there is little evidence to suggest that large parts of the Precambrian shield surrounding the Oslo Region served as an important detrital sediment source, as exposure of these was limited. There is evidence, however, that suggests that weathered material was mainly transported from north of the Oslo Region (Bjørlykke, 1974). During the Cambrian, sea level increased leading to limited exposure of rock and little erosion, whereas the sea level decreased during the Ordovician period (Nakrem and Worsley, 2013). Sediment supply to the Oslo Region during Middle Ordovician is thought to have originated from volcanic ash fall (evidenced by bentonite beds), and erosion of exposed volcanic rocks (Bjørlykke, 1974). During the Late Ordovician (after the deposition of horizon 4a α), the sea level further decreased leading to sand being mixed with limestone and shale (Nakrem and Worsley, 2013). This sand contained clastic feldspar and might have originated from Precambrian rocks comprised mainly of mafic lithologies with some granitic rocks (Bjørlykke, 1974).

5.3.2. Paleoweathering and paleoclimate

The paleoweathering intensity is evaluated with the CIA vs. WIP cross plots (Fig. 15). As mentioned in section 4.2.2., the CIA can only be used if K-alteration (Fig. 14), sediment recycling (Table 8), and sediment sorting (Table 9) are all limited. The CIA values for horizons 4a α , 2d and 2a were found to be trustworthy, while horizon 3a showed signs of K-alteration

and was subsequently excluded from further weathering analysis. Horizons $3b\alpha$, $3b\beta$ and 3c were also excluded due to their limited sample size (< 10 samples).



Figure 14: Potassium alteration illustrated with Chemical Index of Alteration (CIA) vs. Chemical Index of Weathering (CIW) for horizons (a) $4a\alpha$, (b) 3a, (c) 2d and (d) 2a. A significant correlation ($R^2 > 0.7$) indicates the absence of any substantial K-metasomatism. Note that one outlier for horizon 3a (sample BØII-2,6) was removed. All parameters are expressed in molar ratios.

Table 8: Sediment recycling assessed with zircon (Zr) values. Values > 200 ppm indicate that the shale samples are influenced by sediment recycling.

Horizon	Min	Q1	Median	Q3	max	Sample count	Samples with > 200 ppm Zr
4aα	121	146	164	184	222	79	6
2d	128	138.75	146	153.25	162	22	0
2a	137	160	166	175	212	31	1

Table 9: Sediment sorting assessed with Index of Compositional Variability (ICV) values. An ICV < 1 indicates that the shale samples are influenced by sediment sorting.

Horizon	Min	Q1	Median	Q3	max	Sample count	Samples < 1 ICV
4aα	0.77	1.13	1.21	1.31	2.23	64	5
2d	1.08	1.21	1.28	1.43	2.12	18	0
2a	0.64	0.91	0.96	1.07	1.70	43	26



Figure 15: Paleoweathering presented as Chemical Index of Alteration (CIA) vs. Weathering Index (WIP) plots for horizons (a) $4a\alpha$, (b) 2d and (c) 2a. Red points indicate median values. Modified after Figure 9 in Garzanti et al. (2013). Upper Continental Crust (UCC) is from Rudnick and Gao (2014). All parameters are expressed in molar ratios.

Discussion of results

All three horizons were found to have an intermediate weathering intensity, indicating that Late Cambrian (horizons 2a and 2d) shales have similar weathering characteristics to Middle Ordovician (horizon $4a\alpha$) shales. It can therefore be concluded that the three horizons were deposited under similar climate conditions, as paleoweathering is predominantly controlled by temperature and humidity. Considering the similarities between the oldest and youngest horizons, it is likely that the remaining horizons experienced a similar weathering intensity.

5.3.3. Paleosalinity

Paleosalinity was examined by combining two proxies ($100 \times Mg/Al$ and TOC/S_T ratio described by Lei et al. (2002) and Berner and Raiswell (1984), respectively). Figure 16 indicates that the horizons were deposited in saline to slightly brackish water.



Figure 16: Paleosalinity diagram modified from Xu et al. (2021). The darkest blue indicates freshwater conditions and white indicates saline water conditions. All remaining shades of blue indicate various brackish water conditions. The figure shows median values for the analyzed horizons. All parameters are expressed in ppm.

The Mg/Al values (y-axis of Fig. 16) show the largest variation where older horizons were deposited in brackish water, whereas the TOC/S_T values (x-axis of Fig. 16) categorized all horizons as deposited in saline water. Interestingly, a general trend of increasing salinity with decreasing age is observed. Note that individual diagrams for each horizon are available in Appendix C3 with sample count.

Discussion of results

As discussed in chapter 2, the Early Paleozoic intermittently experienced areas with shallow warm seas, especially from the Ordovician period and onwards, while the continent also drifted closer to the equator (Nakrem and Worsley, 2013). A high paleosalinity is often associated with warm and arid climates where evaporation exceeds precipitation rates, e.g. in restricted marine basins. Figure 16 shows that the two oldest horizons (2a and 2d from Late Cambrian) are categorized as the least saline. These horizons are associated with the highest sea level (Nakrem and Worsley, 2013), where freshwater influxes or more open marine conditions might have decreased the salinity.

Trace metal concentrations often decrease with increasing salinity due to the influence of salt ions. For instance, the cation Cd becomes more soluble and precipitates less as salinity increases. This is due to the high affinity between Cd and Cl, and the sorption between competing cations (e.g. Mg and Ca) and organic matter (ANZECC and ARMCANZ, 2000). Figure 16 shows that paleosalinity is highest for the youngest horizon (4a α), while Figure 11f shows that the Cd concentration is lowest in the same horizon. This could suggest that Cd concentrations in shale samples are somewhat influenced by salinity. However, trace metal distribution is complex and depends on various factors, such as metal type, water quality parameters, sorption, complexation, and dissolved organic matter (ANZECC and ARMCANZ, 2000). In the case of Cd, it is possible that salinity has affected the chemical composition of the sediments. However, the change in TOC is expected to have a much bigger impact, as higher concentrations of TOC will adsorb more Cd (ANZECC and ARMCANZ, 2000). Furthermore, the data gaps in Figures 11 and 16 make it unreliable to fully assess the relationship between trace metal composition and paleosalinity. In the case of U (Fig. 11d), increasing salinity will decrease the sorption of U to particles and organic matter (van den Berg, 1993), while the trace metal is also strongly affected by redox conditions and pH (ANZECC and ARMCANZ, 2000). Though anion trace elements like As (Fig. 11e) behave differently than cations, As is also highly affected by increasing TOC concentrations, while its speciation and interaction with microorganisms are affected by salinity (ANZECC and ARMCANZ, 2000).

5.4. Trace element geochemistry

5.4.1. Paleoproductivity

Paleoproductivity was examined with Ba_{bio} and P_{org} (Fig. 17). Values were calculated through Ba/Al and P/Al cross plots to determine the fraction of detrital Ba and P (Appendix C4 and C5). Biogenic Ba, P_{org} and TOC were subsequently used to determine their respective mass acceleration rates (denoted as BaAR, PAR and TOCAR). The total paleoproductivity results from BaAR, PAR and TOCAR, are here all very different from each other (Fig. 18).



Figure 17: Box diagrams (25th, 50th, and 75th percentile) for paleoproductivity presented with (a) the biogenic Ba fraction and (b) organic P fraction. Note that only diagram (a) is presented on a logarithmic scale. Box values for each horizon are available in Table 10. Sample count is available in Appendix C6.



Figure 18: Box diagrams (25th, 50th, and 75th percentile) for total paleoproductivity expressed as mass accumulation rates for (a) biogenic Ba (BaAR), (b) organic P (PAR) and (c) TOC (TOCAR). Note that only diagram (a) is presented on a logarithmic scale. Box values for each horizon are available in Table 11. Sample count is available in Appendix C6.

			(a) Ba _{bio} (p	pm)		(b) P _{org} (ppm)					
Horizon	Min	Q1	Median	Q3	max	Min	Q1	Median	Q3	Max	
4aα	0	55	103	145	574	0	58	186	591	3029	
3c	-	-	-	-	-	-	-	-	-	-	
3bβ	0	91	755	1196	1394	0	251	897	1694	1788	
3bα	0	2175	34575	37996	38016	0	35	134	437	723	
3a	0	549	991	3385	19784	0	143	227	361	1683	
2d	0	149	214	334	527	0	238	428	561	1045	
2a	0	86	173	389	6849	0	105	240	422	3900	

Table 10: Box values for (a) Ba_{bio} and (b) P_{org} as visualized in Fig. 17a and 17b, respectively.

Table 11: Box values for the mass accumulation rates for (a) Ba_{bio} (BaAR), (b) P_{org} (PAR) and (c) TOC (TOCAR), visualized in Fig. 18a, 18b and 18c, respectively.

		(a)	BaAR (g/cm	n² × kyr)		(b) PAR (g/cm ² × kyr)				
Horizon	Min	Q1	Median	Q3	max	Min	Q1	Median	Q3	Max
4aα	0	0.07	0.13	0.18	0.71	0	0.07	0.23	0.73	3.73
3c	-	-	-	-	-	-	-	-	-	-
3bβ	0	0.03	0.21	0.33	0.39	0	0.07	0.25	0.47	0.50
3bα	0	0.61	9.63	10.58	10.59	0	0.01	0.04	0.12	0.20
3a	0	0.15	0.28	0.94	5.51	0	0.04	0.06	0.10	0.47
2d	0	0.03	0.05	0.07	0.08	0	0.05	0.09	0.12	0.22
2a	0	0.02	0.04	0.08	1.45	0	0.02	0.05	0.09	0.82

	(c) TOCAR (g/cm ² × kyr)											
Horizon	Min	Q1	Median	Q3	max							
4aα	1.72	4.24	5.23	8.71	46.11							
3c	0.58	0.78	1.17	1.99	2.77							
3bβ	0.34	1.57	5.81	7.21	9.25							
3bα	0.39	0.58	1.85	4.43	9.03							
3a	4.74	9.96	10.77	12.54	16.63							
2d	14.92	19.33	20.48	22.59	24.47							
2a	3.77	16.14	17.71	20.49	27.40							

Discussion of results

The credibility of the total paleoproductivity proxies is highly influenced by factors such as redox conditions, sedimentation rates and detrital input (Schoepfer et al., 2015).

The input of detrital material is expected to have remained relatively constant from the Late Cambrian to the Middle Ordovician, whereas sedimentation rates increased from 0.125 to 0.73 cm/kyr (Appendix B3). While the difference in sedimentation rate is minimal, it correlates with a noticeable enrichment for all mass accumulation rate proxies (TOCAR, BaAR and PAR, Fig. 18), when compared to the horizon profile diagrams for TOC (Fig. 11b), Ba_{bio}, and P_{org} (Fig. 17a-b). This enrichment is primarily observed for horizon $4a\alpha$, as the remaining horizons have similar sedimentation rates.

Despite the influence by sedimentation rate on horizon $4a\alpha$, redox conditions are believed to have a significant impact on the estimated total paleoproductivity proxies. Total organic carbon is typically better preserved under reducing conditions, whereas Ba_{bio} and P_{org} are more stable under oxic and suboxic conditions (Schoepfer et al., 2015). Therefore, paleoproductivity estimates based on Ba_{bio} and P_{org} are likely underestimated in reducing environments, while TOC proxies will be underestimated in oxic to suboxic environments. Consequently, it can be presumed that the TOCAR proxy (Fig. 18c) is most reliable for horizons deposited under reducing conditions (i.e. 2a, 2d, 3a and 3ba, Fig. 19a-b), whereas the proxies BaAR and PAR (Fig. 18a-b) are more reliable for the younger, more oxic horizons. Additionally, it should be noted that TOCAR and PAR have been described by Schoepfer et al. (2015) as reliable paleoproductivity proxies, while BaAR is only considered suitable for specific environments, such as the equatorial Pacific.

Considering these factors, the results suggest an increase in total paleoproductivity in the following order: $3b\alpha$, 3a, 2a and 2d (Fig. 18c). Paleoproductivity for the younger, more oxic horizons is less clear, although horizons $3b\beta$ and $4a\alpha$ appear to have similar productivity rates (Fig. 18a-b).

5.4.2. Paleoredox

The DOP_T and TOC/P_{org} ratio (Algeo and Liu, 2020; Algeo and Ingall, 2007) proxies have been used to examine the paleoredox conditions. Although older horizons are generally placed in the anoxic zone, the results (Fig. 19a-b) from each method depict very different redox patterns for the horizons. While a steady increase in reducing conditions from youngest to oldest horizon is seen with the TOC/P_{org} proxy (Fig. 19b), the DOP_T peaks in horizon 3a (Fig. 19a).



Figure 19: Box diagrams (25^{th} , 50^{th} , and 75^{th} percentile) for paleoredox conditions determined with (a) Total Degree of Pyritization (DOP_T) in wt.% and (b) TOC vs. organic P ratios as molar ratio. Both diagrams use the same grey scale for redox conditions. Box values for each horizon are available in Table 12. Sample count is available in Appendix C6.

		(a) DOP _T (wt.	.%)		(b) TOC/P _{org} (molar ratio)				
Horizon	Min	Q1	Median	Q3	max	Min	Q1	Median	Q3	Max
4aα	0.00	0.02	0.06	0.12	0.23	3	17	94	174	1747
3c	-	-	-	-	-	-	-	-	-	-
3bβ	0.18	0.19	0.20	0.33	0.38	7	8	9	11	12
3bα	0.35	0.36	0.55	0.66	0.71	11	49	284	10111	1200
3a	0.41	0.61	0.68	0.80	1.06	55	295	424	629	2916
2d	0.27	0.58	0.62	0.65	0.72	270	481	556	996	1602
2a	0.33	0.52	0.60	0.64	0.72	58	546	1023	2073	5908

Table 12: Box values for (a) DOP_T and (b) the TOC/P_{org} ratio, visualized in Fig. 19a and 19b, respectively.

Discussion of results

A general trend shows reducing conditions for older horizons and suboxic to oxic conditions for younger horizons. However, as was the case for paleoproductivity, the results derived from the analyzed proxies do not evolve similarly. Noteworthy are the relatively high DOP_T values for the Early Ordovician horizons 3a and $3b\alpha$, compared to the low TOC/P_{org} values. This indicates that pyrite is not solely associated with an anoxic depositional environment, implying post-sedimentary pyrite mineralization has occurred. The fact that horizon 3a was also affected by K-alteration (Fig. 14b) appears to support this hypothesis. Post-sedimentary processes that may be responsible for pyrite mineralization are most likely associated with the development of the Oslo Rift and may include magmatism-related hydrothermal alteration in the direct vicinity of the magmatic rocks or along fault structures.

6. Summary and conclusions

6.1. Compilation and modification of geochemical dataset

The geochemical whole-rock data from three datasets (Wærsted et al., 2021; Gautneb and Sæther, 2009; Ofili et al., 2022) have been compiled and modified for the purpose of this and future studies on Lower Paleozoic shales. Following an extensive data quality assessment, this study has only utilized data obtained from NGI (Wærsted et al., 2021) for further analysis of the Oslo Region's paleoenvironment. Future applications for the full dataset may include further investigation of the Lower Paleozoic climate and environmental conditions, and improvement of Norwegian shale-legislation.

6.2. Paleoenvironment of Lower Paleozoic shale formation in the Oslo Region

The following paleoenvironmental conditions for the Lower Paleozoic shales in the Oslo Region were identified in this study:

- *Provenance:* All horizons indicate similar provenance to each other and UCC. However, no specific rock type was identified as provenance for the horizons, which correlates well with the periods minimal detrital input.
- *Paleoweathering:* All horizons indicate similar intermediate paleoweathering (Fig. 15). This suggests that no severe changes in paleoclimate occurred between Late Cambrian and Middle Ordovician, and that the temperature and humidity stayed rather stable.
- Paleosalinity: The Late Cambrian horizons (2a and 2d) indicate deposition under lower salinity compared to younger horizons (Fig. 16). Horizon 4aα (Middle Ordovician) was deposited under the most saline conditions, which could contribute to the relatively low concentrations of some hazardous trace elements (e.g. Cd) in this horizon.
- Paleoproductivity: The influence by redox conditions on the acquired paleoproductivity results (Fig. 18), makes it impossible to compare the youngest horizons to the oldest. However, it is indicated that horizon 3bα (Early Ordovician) has a lower productivity than the horizons which were deposited prior (2a, 2d and 3a).
- Paleoredox conditions: Despite some inconsistencies between the analyzed proxies (DOP_T and TOC/P_{org}, Fig. 19), it is estimated that the oldest horizons (2a, 2d, 3a and 3b α) were deposited under reducing conditions. The younger horizons (3b β and 4a α) were deposited under oxic and suboxic conditions.

The potential environmental impact associated with Norwegian shale (Appendix B4), as determined in Wærsted et al. (2022) and Kibsgaard et al. (2015), does not show a direct correlation with any one specific paleoenvironmental condition. This suggests that the development of severe ARD is influenced by a combination of paleoenvironment conditions or by later processes, such as hydrothermal activity associated with the Oslo rift development. However, it is important to once again acknowledge that significant data gaps (Appendix C6) are limiting both the selection of suitable proxies and their reliability.

6.3. Recommendations for future research

As a reconnaissance study, this thesis naturally recommends various future research studies, which could significantly contribute to the understanding of Norwegian and north European Lower Paleozoic shales.

- Expansion of the dataset: It is advised to address data gaps with a general dataset expansion. Coincidentally, a substantial amount of additional data from a country-wide shale mapping program in Finland (Parviainen and Loukola-Ruskeeniemi, 2019) was discovered late in this study. This data could be included in future studies. However, a similar mapping program for Norway would be preferred, yielding a complete and publicly available geochemical database for Norwegian shale.
- Geochemical classification of shales for ARD: Norwegian shale classification guidelines are implemented to assess the acid producing potential of shale deposits (Pabst et al., 2017; Wærsted et al., 2021). The underlying data for these guidelines are the original 332 samples from the NGI dataset. However, this study has identified some issues with this NGI dataset, implying that the classification method requires re-evaluation. An additional problem with this shale classification (Pabst et al., 2017; Wærsted et al., 2021) is that the samples from which the geochemical data were obtained were not further analyzed with regards to mineralogy.
- Geochemical characterization of hydrothermal activity: Potassium alteration results, as discussed in section 5.3.2., suggest a hydrothermal influence in horizon 3a, which could have affected the observed peak for horizon 3a in DOP_T (Fig. 19a). Future research should focus on the geochemical and mineralogical characterization of hydrothermal activity in shale from the Oslo Region.
- Interaction between trace metal behavior and environmental conditions: The mobility of some trace elements is strongly affected by environmental conditions and water quality parameters (e.g. salinity, redox conditions, pH, dissolved organic matter, and clay concentrations). Future research on these interactions can potentially be used as paleo proxies and improve understanding of the underlying factors for trace element distribution (discussed in section 5.3.3.).
- Element Enrichment Factors: A more in-dept geochemical analysis could include analysis based on Enrichment Factors for specific elements, to study various paleoenvironmental conditions. Element Enrichment Factors are Al-normalized values (to correct for the detrital input), which is then compared with a reference material (e.g. UCC or MBS). The Enrichment Factors are included for various elements in the modified dataset but were not used for further analysis due to time constraints.

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Appendix A – Supplementary material

Material	Available as				
Compiled and modified dataset of whole-rock composition for north European shale.	Available as an	Excel spreadsheet			
	NGI	<u>Appendix C</u> in <u>Wærsted et al. (2021)</u>			
Publicly available whole-rock	NGU 1	Appendix 2 in Gautneb and Sæther (2009)			
geochemistry datasets used as basis for the modified	NGU 2	Appendix 3 in <u>Sæther et al. (2010)</u>			
compilation dataset.	Estonia, Sweden and Russia	<u>Supplementary material</u> from <u>Ofili et al. (2022)</u>			
Map of Norwegian sample locationsDetailed map of samples from NGI and NGU datasets, mod by Jan Maten Huizenga (unpublished).					

A1: Hyperlinks to pCloud for supplementary materials.

Appendix B – Method and standards

B1: Overview of NGI samples which were excluded or rearranged during data selection (section 3.4.).

Reason for exclusion	Horizon		NGI ID					
	2a	St12.1	St5.1	St48.1	St48.1	4		
	2d	SLO7	SLO20			2		
	3a	C8G-1,3	CØIV-1,3	BH4-10-4-70		3		
Limestone	3bα	BH2-10-4-40	BH2-13-2-20	BH3-07-3-40	BH3-08-2-60	4		
behalf of limestone	3bβ	BH1-14-3-50	BH1-14-4-20			2		
characteristics (The samples contained high values of TIC, high CaO or low SiO ₂)	3с	BH1-09-2-50 BH1-09-5-50 BH1-10-3-50 BH1-11-5-50 BH1-12-4-50	BH1-13-1-40 BH1-13-4-20 BH3-01-2-50 BH3-01-3-50 BH3-01-4-50	BH3-01-5-50 BH3-02-3-50 BH3-02-4-50 BH3-02-5-50 BH4-01-1-70	BH4-01-2-75 BH4-01-3-80 BH4-01-4-85 BH4-01-5-90 BH4-02-1-10	20		
	4aα	ANK25 ANK70	ANK74 BH1-02-4-50	BH1-03-4-40 BH1-03-5-60	BH1-08-3-50	7		
Total count:	1	1				42		
Duplicates Repeated data in horizon 3a and 3bα have been re-categorized as a	3a	BØII - 4,0 BØIII - 1,3 BØIII - 2,6 BØIV - 1,3	BØIV - 2,6 BVIII - 1,3 BVIII - 2,6 BVIII - Stov	BVIV - 1,3 BVIV - 2,6 CØII - 2,6 CØV - 1,3	VDIV - 1,0 VDIV - 2,0 VDIV - 3,0	15		
transition horizon named 3a/3bα (Note that ID names are slightly different)	3bα	BØ II~4 BØ III-1,3 BØ III-2,6 BØ IV-1,3	BØ IV 2,6 BV III-1,3 BV III-2,6 BV III-støv	BV IV-1,3 BV VI-2,6 CØ V-2,6 CØ V-1,3	VD III-1 VD IV-2 VD IV-3	15		
Total count:						15		
	2a	St15.1	St17.1	St36.1		3		
	2d	SLO5	SLO13	SLO16	SLO18	4		
Uncertainty Major element data excluded on behalf of total major oxide quality	За	BØI-2,6 BØI-6,6 BØI-8,3 BØII-1,3 BØII-6,5 BØIII-Rest	BVII-1,0 BVII-2,6 CI-6,5 C1+8-1,3 C1+8-2,6 C1+8-4,0	C1+8-Rest C8G Kolonne CØII-2,0 CØIII-1,3 VDI-2,0 VDIII-Samlat	BH4-07-2-70 BH4-07-3-80 BH4-07-4-50 BH4-07-4-90 BH4-08-5-90	23		
control. All data outside of the major element total sum range 97,5- 102,5 wt.% was	3a/3bα	BØII-4,0 BØIII-1,3 BØIV-1,3	BØIV-2,6 BVIII-Støv BVIV-1,3	BVIV-2,6 CØII-2,6 VDIV-2,0	VDIV-3,0	10		
excluded.	3bα	BH1-16-5-20 BH1-17-1-40 BH1-17-2-40 BH2-10-3-50 BH2-10-5-50 BH2-11-2-50	BH2-11-3-30 BH2-11-5-40 BH2-12-3-40 BH2-13-5-40 BH2-14-1-15 BH3-06-3-30	BH3-06-4-30 BH3-06-5-30 BH3-07-1-30 BH3-07-2-30 BH3-07-3-30 BH3-07-4-40	BH3-08-2-20 BH3-08-3-40 BH3-08-5-40	21		

B1 (Continued)

	BH1-13-5-40	BH3-03-4-50	BH3-05-4-50	BH4-02-4-10	33
	BH1-14-1-80	BH3-03-5-50	BH3-05-5-50	BH4-02-4-20	
	BH1-14-5-60	BH3-04-1-50	BH3-06-1-30	BH4-03-1-20	
	BH1-15-2-40	BH3-04-2-40	BH3-06-2-30	BH4-03-2-25	
3bβ	BH1-15-5-40	BH3-04-4-60	BH3-09-2-40	BH4-03-5-60b	
	BH1-16-2-40	BH3-04-5-50	BH3-09-4-50	BH4-04-3-30	
	BH1-16-3-40	BH3-05-1-50	BH3-10-1-50		
	BH3-03-1-50	BH3-05-2-50	BH3-10-3-40		
	BH3-03-2-50	BH3-05-3-50	BH4-02-3-10		
	BH1-10-5-30	BH3-01-1-50	BH3-02-2-50		5
30	BH1-11-2-50	BH3-02-1-50			
	ANK12	ANK18	ANK73	BH1-07-3-60	15
4.5.5	ANK13	ANK21	BH1-04-4-20	BH1-08-1-60	
4aα	ANK15	ANK47	BH1-05-4-40	BH1-08-5-40	
	ANK17	ANK50	BH1-06-3-50		
Total count:					114

B2: Upper Continental Crust (UCC) from Table 1 and 2 in Rudnick and Gao (2014) and MBS composition data by Ketris and Yudovich (2009), retrieved from Table 2 in Slack et al. (2020).

Major element oxides (wt.%)	SiO2	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na₂O	K ₂ O	TiO ₂	P ₂ O ₅	BaO
Upper Continental Crust	66.62	15.40	5.60	0.10	2.48	3.59	3.27	2.80	0.64	0.15	0.07
Median Black Shale	-	-	-	-	-	-	-	-	-	-	-

Trace element (ppm)	Ве	S	Sc	v	Cr	Со	Ni	Cu	Zn	As	Rb	Sr
Upper Continental Crust	2.1	621	14	97	92	17.3	47	28	67	1.4	84	320
Median Black Shale	2.4	-	14	200	100	17	84	100	140	27	93	200
Trace element (ppm)	Y	Zr	Nb	Мо	Cd	Sn	Ва	W	Hg	Pb	Th	U
Trace element (ppm) Upper Continental Crust	Y 21	Zr 193	Nb 12	Mo	Cd 0.09	Sn 2.1	Ba 624	W 1.9	Hg 0.05	Pb 17	Th 10.5	U 2.7

B3: Average horizon age, shale density and linear sedimentation rate for the analyzed Lower Paleozoic shale horizons. Information was used during paleoproductivity estimation.

Parameters	2a	2d	3a	3bα	3bβ	Зc	4aα	Source
Average horizon age (kyr)	491200	491200	477700	477700	477700	477700	464200	International Chronostratigraphic Chart (2023)
Shale density (g/cm ³)	1.69	1.69	1.69	1.69	1.69	1.69	1.69	Schoepfer et al. (2015)
Linear sedimentation rate (LSR, cm/kyr)	0.125	0.125	0.165	0.165	0.165	0.165	0.73	Figure 13 in Bjørlykke (1974)

B4: Expected ARD potential for the individual horizons. Table is modified from Wærsted et al. (2022) and Table 3 in Kibsgaard et al. (2015).

Horizon	Period	Formation	Properties	Expected ARD	Thickness	
4aα	Middle Ordovician	Elnes	Lime-rich. Contain some sulfides.	Very low	> 80 m	
3c	Early Ordovician	Huk	Divided in three layers with lime- stone on top and bottom with a Lime-rich shale layer in between.	None	Ca. 30 m	
Зbβ	Early Ordovician	Tøyen (Galgeberg)	Varying content of trace elements	Moderate – Iow	10-20 m	
3bα	Early Ordovician	Tøyen (Hagaberg)	Varying content of trace elements	Very low	5-10 m	
Заү	Early Ordovician	Alum shale (Bjørkåsholmen)	Lime-rich.	None	1-4 m	
3aα, 3aβ	Early Ordovician	Alum shale (3)	High to moderate concentration of trace elements. Possible radionuclide content.	High	5-20 m	
2a-2e	Late Cambrian	Alum shale (2)	Highest ARD potential. High concentration of trace elements. Possible radionuclide content.	High	60-80 m	
1	Early-Middle Cambrian	Alum shale (1)	Sandstone and shale mixture	None	-	

Appendix C - Results

C1: Rock classification made with the SandClass system (Herron, 1988), where all oxides were analyzed in wt.%. Blue points represent individual samples. Red points represent median value for the specific horizon.



C2: Provenance diagrams for the analyzed horizons, modified from Figure 1A and Table 1 in Meunier et al. (2013). Upper Continental Crust (UCC) is from Rudnick and Gao (2014). Blue points represent individual samples, while red points represent median value for the specific horizon. All parameters are expressed as mol.% and n signifies sample count.



n= 43

C3: Salinity diagrams modified from Xu et al. (2021). Darkest blue areas indicate freshwater conditions, while white areas indicate marine conditions. All remaining shades of blue indicate various brackish water conditions. X-axis: The TOC/S ratio indicates fresh, brackish and saline conditions at > 10, 5-10 and < 5, respectively. Y-axis: For 100 × Mg/Al indicates fresh, brackish and saline conditions at < 1, 1-10 and > 10, respectively. Blue points represent individual samples, while red points represent median value for the specific horizon. All parameters are expressed in ppm.



C4: Barium vs. Al cross plots used in paleoproductivity estimations. Cross plots divide detrital Ba from and the biogenic fraction. The lowest possible trendline indicates detrital fraction. All samples above the trendline represent Ba_{bio} . Method described by Rutsch et al. (1995). Grey area signifies Ba > 5000 ppm for easier comparison of the horizons.



C5: Phosphate vs. Al cross plots used in paleoproductivity estimation. Cross plots divide detrital P from the organic fraction. The lowest possible trendline indicates detrital fraction. All samples above the trendline represent P_{org} . Method described by Rutsch et al. (1995).



Horizon	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	BaO	тос
4aα	64	64	64	64	64	64	64	64	64	64	64	79
3c	-	-	-	-	-	-	-	-	-	-	-	5
3bβ	5	5	5	5	5	5	5	5	5	5	5	38
3bα	5	5	5	5	5	5	5	5	5	5	5	26
3a	21	21	21	21	21	21	21	21	21	21	21	44
2d	18	18	18	18	18	18	18	18	18	18	18	22
2a	43	43	43	43	43	43	43	43	43	43	42	46
	Ве	S	Sc	v	Cr	Со	Ni	Cu	Zn	As	Rb	Sr
4aα	6	79	6	79	79	79	79	79	79	6	73	79
3c	5	5	5	5	5	5	5	5	5	4	-	5
3bβ	38	38	38	38	38	38	38	38	38	38	-	38
3bα	26	26	26	26	26	26	26	25	26	22	-	26
3a	44	44	44	44	44	44	44	44	44	44	-	44
2d	-	22	-	22	22	22	22	22	22	-	22	22
2a	-	31	-	31	31	31	31	31	31	-	31	31
	Y	Zr	Nb	Мо	Cd	Sn	Ва	w	Hg	Pb	Th	U
4aα	79	79	79	3	3	6	79	6	-	79	79	79
3c	5	5	5	3	4	5	5	5	-	5	5	5
3bβ	38	38	38	36	38	38	38	38	33	38	38	38
3bα	26	26	26	23	25	26	26	26	24	26	26	26
3a	44	44	44	44	44	44	44	7	-	44	44	44
2d	22	22	22	-	-	-	22	-	-	22	22	22
2a	31	31	31	-		-	45	-	-	31	31	31
	BaAR		PAR			TOCAR		DOPT			TOC/P _{org}	
4aα	64		64			79		64			64	
3c	-		-			5		-			-	
3bβ	5		5			38		5			4	
3bα	5		5			26		5			4	
3a	21		21		_	44		21		_	20	
2d	18		1	18		22		18		_	17	
2a	42		43			46		29			42	

C6: Sample counts for major and trace elements, as well as the total paleoproductivity (BaAR, PAR and TOCAR, Fig. 18) and paleoredox proxies (DOP_T and TOC/P_{org}, Fig. 19). Red signifies a sample count < 10 and grey signifies no available data. Note that horizons are arranged from youngest to oldest in the table.



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