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Master's Thesis

Geochemical Peculiarities of Sandy Sediments from the Late Pleistocene and Holocene of Lithuania

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I dedicate this thesis to my family, whose support and encouragement have been instrumental in my academic journey. Your love, understanding, and belief in me have been a constant source of motivation. This accomplishment would not have been possible without you. Thank you for always being there for me.

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INTRODUCTION

Rare Earth Elements (REE) constitute a group of 17 chemically similar elements that play a critical role in modern technology, including electronics, renewable energy systems, and advanced materials. Despite their name, rare earth elements (REE) are not truly rare; rather, they are unevenly distributed in the Earth's crust, making their geochemical characteristics and patterns a topic of significant interest in earth sciences (Taylor & McLennan, 1985). In sedimentary systems, REEs serve as tracers of geological processes, such as weathering, transport, and deposition. This provides valuable insights into sediment provenance and environmental conditions (McLennan, 1989). Furthermore, their distribution patterns can reflect the influence of glacial and interglacial processes, rendering them particularly pertinent for the study of Quaternary sediments.

The Quaternary period, which spans the last 2.6 million years, is distinguished by considerable climatic variability, characterized by alternating glacial and interglacial periods. During the glacial periods, extensive areas of the Earth's surface were covered by ice sheets, which exerted a profound influence on the landscape through processes such as erosion, transportation, and the deposition of sediments. In contrast, interglacial periods were characterized by warmer climates, which led to the retreat of ice sheets and the re-establishment of fluvial and aeolian systems (Ehlers & Gibbard, 2007). In the late Pleistocene, glaciers from the Scandinavian ice sheet covered the Lithuanian territory and formed the largest part of Quaternary deposits in Lithuania (Guobytė, 2023). These cycles had a profound impact on the composition and distribution of sediments, particularly in glaciated regions. Sediments derived from glacial processes are often rich in fine-grained material sourced from the erosion of bedrock, while interglacial sediments may reflect more localized depositional environments. The Baltic region, including Lithuania, lies at the intersection of several major glacial advances, making it a key area for studying the geological imprints of Quaternary processes. Quaternary sediments constitute an invaluable archive of past environmental, geological, and climatic conditions. The composition of these sediments reflects the complex interplay between glacial dynamics, bedrock geology, and subsequent post-glacial processes. An REE analysis of these sediments can provide insights into their provenance, degree of weathering, and depositional environments (Gaigalas, 2001). Furthermore, anomalies in REE distributions, such as those observed in the concentrations of elements such as europium (Eu) or cerium (Ce), can provide insights into the redox conditions and the processes of sedimentary recycling.

Lithuania, situated in the eastern Baltic region, has a complex Quaternary history shaped by multiple glaciations and interglacial periods. The region's sediments provide a distinctive opportunity to examine the impact of glacial erosion and transport on REE composition, as well as the influence of post-glacial weathering and fluvial processes. Despite the considerable Quaternary sedimentary record in Lithuania, the REE composition of these sediments remains relatively underexplored, resulting in gaps in our understanding of regional geochemical processes.

The Quaternary sediments of Lithuania were deposited under the influence of the Scandinavian ice sheet, which advanced and retreated on multiple occasions during the Pleistocene. The glaciation left behind a diverse array of sediments, including till, outwash plains, and lacustrine deposits. The sediments range from clay-rich tills deposited directly by the glaciers to well-sorted sands and gravels deposited by meltwater streams and rivers. It is known that rare earth element (REE) distribution in sediments depends on their content in the parent rocks and their distribution in the mineral phases; the ability of secondary minerals formed during the reactions to accommodate REE (Kaminskas et al., 2013). Thus, quantities of REEs may vary depending on transportation and sedimentation. Sources of REE could be of various origins: suspended river runoff, aeolian dust, glacier runoff, etc. The principal objective of this thesis was to undertake an analysis of the rare earth element (REE) composition of Quaternary sandy sediments in Lithuania, with a view to identifying any distinctive features that may be attributable to potential environmental influences. In order to achieve this, the study addresses the following objectives:

- To characterize REE distributions in Quaternary sediments using geochemical normalization techniques, including the Chondrite, European Shale (EUS), and North American Shale Composite (NASC).
- The influence of glacial and post-glacial processes on REE patterns is evaluated in order to identify sediment provenance and depositional environments.
- Furthermore, REE peculiarities under varying environmental conditions are compared; these include redox-sensitive anomalies (e.g., cerium or europium anomalies).
- Finally, basic descriptive statistics and correlation analysis were employed for better interpretation.

1. LITERATURE REVIEW

Rare Earth Elements (REE) have long been acknowledged as crucial geochemical tracers due to their predictable behavior during geological and sedimentary processes (Taylor & McLennan, 1985). The distribution of these elements in sediments is reflective of a number of processes, including weathering, transportation, deposition, and diagenesis (McLennan, 1989). The study of REE in sedimentary environments frequently concentrates on the patterns of enrichment, the fractionation between light and heavy REE, and anomalies such as Eu or Ce, which indicate specific geochemical conditions (Henderson, 1984). Earlier studies showed that during weathering, REE become mobile and fractionate (Nesbit, 1979).

REE studies have demonstrated their utility in deciphering sediment provenance and assessing environmental influences on a global scale. For example, research on glacial sediments has demonstrated that REE can effectively trace contributions from distinct bedrock sources (Goldstein & Jacobsen, 1988). Similarly, REE anomalies in lacustrine and marine sediments have provided insights into redox conditions and depositional environments (Cullers et al., 1987; Cullers, 1994).

The Quaternary period, which was characterized by repeated glaciations and interglacial periods, has resulted in the formation of extensive deposits of sediments with diverse compositions. Glacial sediments are particularly susceptible to intense physical weathering and the mechanical transport of material from a range of bedrock sources. These processes exert an influence on the REE signatures of sediments, rendering them a valuable instrument for elucidating the dynamics of glaciers and sedimentary processes (Ehlers & Gibbard, 2007).

The study of Quaternary sediments in glaciated regions, including Scandinavia and North America, has revealed distinctive REE patterns associated with glacial erosion and depositional environments. Nevertheless, only a limited number of studies have concentrated on the Baltic region, where multiple glaciations have resulted in a highly complex record of sedimentation. Gaigalas (2001) emphasized the importance of Lithuania's Quaternary deposits but also highlighted the lack of geochemical research conducted on these sediments.

The majority of research conducted on the Quaternary geology of the Baltic region has concentrated on sediment stratigraphy, glacial history, and depositional processes (Satkūnas et al., 2003). Nevertheless, detailed geochemical investigations, particularly those focusing on rare earth element (REE) composition, remain scarce. A limited number of studies have examined the distribution of rare earth elements (REE) in glacial sediments from Scandinavia, identifying distinctive patterns of enrichment and anomalies associated with regional bedrock sources (Johannesson et al., 1999). These studies highlight the potential of rare earth elements (REE) as a means of tracing sediment provenance and inferring environmental conditions in glaciated terrains.

In Lithuania, research into Quaternary sediments has primarily concentrated on stratigraphic and lithological analyses, with relatively little attention devoted to their geochemical characteristics. While studies such as those by Guobytė and Satkūnas(2011), and Satkūnas et al. (2009) have provided valuable insights into the region's glacial history, they have not explored the REE composition of these sediments. This gap in the literature emphasizes the necessity for comprehensive REE analysis to facilitate a deeper comprehension of the geochemical processes that have shaped Lithuania's Quaternary deposits.

The analysis of rare earth elements (REE) typically employs the use of inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES), which provide precise measurements of REE concentrations. To facilitate the interpretation of REE data, normalization techniques are frequently employed, with Chondrite (McDonough & Sun, 1995), European Shale (EUS) (Baua et al., 2018), and North American Shale Composite (NASC) (McLennan, 1989), being the most commonly utilized standards. These methods assist in the identification of patterns such as LREE-HREE fractionation and anomalies, thereby providing insights into geochemical processes.

The lithological features of these sites could be characterized using the Si and Al oxide ratio, which infers the clay content in sediments. For it is known that the clay content directly influences the distribution and quantities of REE in sediments (Kaminskas et al., 2013). Meanwhile, quartz is said to contain no REE and acts solely as a dilution factor for REE in sediments (Taylor and McLennan, 1985).

The application of statistical techniques, such as Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA), has also demonstrated efficacy in the interpretation of REE data, particularly in the identification of sediment provenance and the differentiation between depositional environments (Skurzyński et al., 2024). These methods permit researchers to establish a correlation between REE patterns and environmental and geological factors, thereby facilitating a comprehensive understanding of sedimentary processes.

In conclusion, while considerable advancement has been achieved in the comprehension of REE distributions in glacial and sedimentary settings, crucial knowledge gaps persist.

i. There is a paucity of studies that have focused on the REE composition of Quaternary sediments in the Baltic region, particularly in Lithuania.
ii. There is a dearth of investigations that have explored the influence of environmental factors, such as redox conditions and post-glacial processes, on REE patterns in these sediments.
iii. The application of multivariate statistical techniques to REE data in this context is underexplored, offering potential for new insights.

2. STRATIGRAPHY AND LITHOLOGY

Lithuania's rocks are mostly made up of deposits from the last 2.6 million years, which were shaped by glaciers and the periods between them (Guobytė, 2023). The Last Glaciation (Weichselian) left a significant imprint on the region's geological record, which is characterized by a sequence of glacial advances, retreats, and associated sedimentary formations. The thickness of Quaternary sediments (deposits of soil, rock, and other materials) in Lithuania varies significantly. In the north, the deposits are as thin as a few meters. In upland areas, the thickness can exceed 200 meters. The maximum thickness recorded was 314.2 meters near Vembūtai in the Žemaitija Highland. Morainic Ridges and Highlands: These were formed by glacial accumulation and tectonic activity. The country's highest point is Aukštojas Hill, which is 293.8 meters above sea level. Fluvial and Lacustrine Plains: These areas were shaped by meltwaters during the last ice age and are full of sediments left by glaciers and lakes. Aeolian Features: Post-glacial wind activity led to the formation of dunes in certain regions.

Lithuania's bedrock is mainly made up of Precambrian crystalline basement, which is overlain by sedimentary sequences from the Paleozoic, Mesozoic, and Cenozoic eras. Lithological investigations reveal that the Quaternary deposits of Lithuania are dominated by a variety of glacial sediments, including tills, glaciolacustrine clays, sands, and organic-rich interlayers. These sediments help in understanding the processes of glaciation, deglaciation and the associated climatic conditions. A notable example is the Buivydžiai outcrop in eastern Lithuania, which exhibits a 70-80 m thick sequence that is characteristic of the maximum extent of the Last Glaciation. This section includes sands, silts with humus, clay, and gyttja, which indicate diverse depositional environments ranging from glacial to interglacial settings (Seiriene, 2012; Seiriene et al., 2015). These older formations include sandstone, limestone, dolomite, and shale, which were made in different places and at different times.

The carbonate component constitutes a substantial proportion of Pleistocene tills (Rudnickaitė E., 2016). The content of carbonates in tills is contingent on a number of factors, including the assimilation of carbonaceous rocks by advancing glacier beds, the appearance of new carbonate minerals in till strata during the stages of transition and early genesis of glacial debris, the formation of carbonate minerals under hypergenetic conditions, and so forth. The carbonate content of tills is closely related to the glacial relief and composition of rocks. Furthermore, analysis of the carbonate content in paleolacustrine sediments from the Venta River valley in northwestern Lithuania highlights the variation in lithological composition across three distinct paleoclimatic cycles. These cycles correspond to glacial and interglacial phases, with the carbonate content reflecting temperature fluctuations and environmental changes (Rudnickaite, 2012). Of particular interest is the formation of kame terraces and glaciolacustrine deposits, which provide evidence of the interaction between active ice lobes and areas of dead ice. This challenges the traditional view of ice-marginal retreat during the Late Weichselian (Bitinas, 2012).

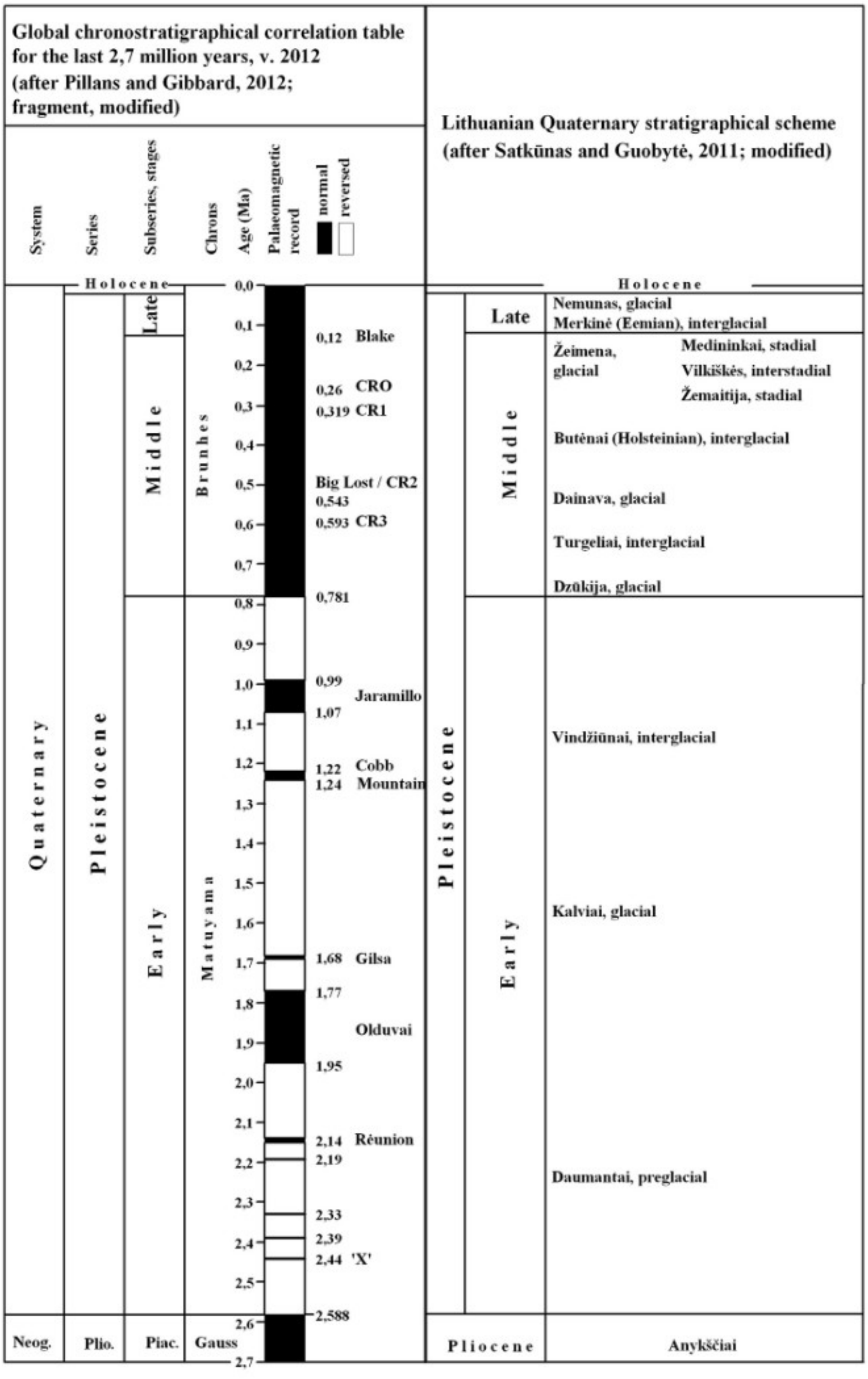

Fig. 1. Stratigraphic scheme of the Lithuanian Quaternary and its correlation with the paleomagnetic scale (after Pillan and Gibbard, 2012).

The Quaternary Period in Lithuania is characterized by alternating glacial and interglacial stages, leading to a complex record of layers:

•Pleistocene Epoch: There were many times when glaciers advanced over Lithuania, leaving behind lots of glacial sediments. These deposits are called tills and are a mixture of clay, silt, sand, gravel, and boulders, showing the different types of rock they are made of. Between these glaciations, there were times when the land was wet and formed lakes, rivers, and swamps. This led to the build-up of sands, silts, clay, and organic-rich sediments like peat. In the Quaternary succession, glaciogenic sediments (including glacial, glaciofluvial, and glaciolacustrine deposits) dominate, whereas interglacial sediments (such as alluvial, lacustrine and biogenic formations) are less common. Lithuania hosts extensive glacial formations from the Late Mid-Pleistocene (LMP) period, with thickness varying from 80 to 150 m, or sometimes even more in paleo-incisions and upland areas. In contrast, glaciolacustrine and glaciofluvial deposits are significantly thinner. Interglacial and interstadial sediments are primarily concentrated in the northern and southeastern regions of the country (Seiriene and Bitinas, 2023).

• Holocene Epoch: After the last ice age, warmer climates became the norm, leading to the creation of large peat bogs, alluvial plains, and the development of soils. Coastal processes during this time contributed to the formation of features like the Curonian Spit. The Last Glaciation, recognized in this region as the Late Nemunas Glaciation, attained its maximum extent in the southeastern part of Lithuania approximately 21-22 Ka (Guobyte, 2012). This glaciation is subdivided into two major stadials: the Grida Stadial (older) and the Baltija Stadial (younger). The differentiation of these stadials is based on lithostratigraphic criteria. Cosmogenic beryllium-10 dating (10Be) indicates that the retreat of the Grida ice margin began no later than 18.3 ± 0.8 Ka, while the Baltija moraine dates to approximately 14.0 ± 0.4 Ka (Guobyte, 2012). Three additional ice-marginal zones to the northwest of the Baltija Uplands record successive phases of ice retreat: the South Lithuanian Phase (13.1 ± 0.5 Ka), the Mid-Lithuanian Phase (13.5 ± 0.6 Ka), and the North Lithuanian Phase (13.3 ± 0.7 Ka). These phases are believed to have been caused by the rapid advance of ice lobes into areas of stagnant, decaying ice (Guobyte, 2012).

The Buivydžiai outcrop also contains evidence of an older interglacial period, which was previously attributed to the Snaigupėlė Interglacial (MIS 7). However, recent investigations have called into question the independence of this interglacial, suggesting instead similarities to the Eemian (Merkinė) Interglacial. Pollen analysis indicates a dominance of coniferous trees, with a slight increase in broad-leaved species, while the diatom assemblages point to oligotrophic-eutrophic conditions in a gradually infilling paleobasin (Seiriene, 2012; Kabailienė, 2006).

Freshwater malacofauna from interglacial deposits in Lithuania provide additional insights into the region's stratigraphic record. Archaic species such as Parafossarulus crassitesta and Fagotia wuesti are characteristic of the Augustovian Interglacial, corresponding to the Bavelian Stage in Western Europe. The appearance of subtropical immigrant species, such as Corbicula fluminalis, during the Holsteinian Interglacial further delineates interglacial periods (Sanko, 2012; Seiriene et al., 2015).

During the Eemian Interglacial, the Atlantic mollusc Belgrandia marginata moved into the Baltic region, while the species Dreissena polymorpha shows that there was a connection between the Pre-Dnepr basin and modern-day Lithuania through water. This shows how climate change and human activity can affect where animals and plants live (Sanko, 2012).

Recent studies suggest a new understanding of the Scandinavian Ice Sheet (SIS) dynamics during the last glaciation. Traditional models of the layers of ice are being questioned because there is evidence of the ice moving and also of areas of dead ice. This shows that the ice in many areas at the same time was melting, rather than the ice at the edge of the ice sheet moving back slowly (Bitinas, 2012). Dating shows that before the Younger Dryas (YD) re-advance, the ice sheet was much bigger, covering a huge area from the Middle Lithuanian Phase to the Gulf of Finland, and it eventually melted between 13,500–13,000 years ago. (Bitinas, 2012). The Younger Dryas (12,600–11,500 cal. yr BP) is well-preserved in sediments from the Lopaičiai hollow in northwestern Lithuania. This site shows the change from the warmer Allerød conditions to the colder, drier conditions of the Younger Dryas. Pollen data show a change from pine and birch forests to grasslands, including species like Selaginella selaginoides, which can be found in harsh environments like tundras. (Kabailiene, 2006)

In this study, the chronostratigraphic record of all three sites (Krokšlys, Dengtiltis outcrop, and Šventoji-46766 borehole) displays absolute ages ranging from the Mid-Late Pleistocene to the Holocene Epoch. The Krokšlys outcrop shows samples with thermoluminescence (TL) ages of 9,600 ± 2000 a BP at a level of 0.75 m depth, 11,100 ± 2000 a BP at 1.25 m depth, 11,700 ± 2000 a BP at 1.55 m depth, and 25,800 ± 4000 a BP at 1.6 m depth (Andronikov et al., 2015). This section is composed of sandy-silty and loamy deposits, with evidence of stratified glaciofluvial materials in the lower portion. The upper layers contain fine-grained sands and loess-like sediments, indicative of aeolian and fluvial reworking. The Dengtiltis sample from the level of 4 m displays a TL age of 11,200 ± 1300 a BP, a sample from the level of 4.5 m an age of 14,100 ± 1500 a BP, and a sample from the level of 5.3 m an age of 16,600 ± 1700 a BP (Andronikov et al., 2015; Rudnickaite et al., 2012). Radiocarbon dating ages were also obtained in this study for samples at the level of 1.61 m and 2.39 m, dated at 14C 220 ± 100 a BP and 14C 855 ± 100 a BP, respectively. The lithology of the Dengtiltis section is characterized by the presence of yellow to brown sands, siltstone, and silty layers, exhibiting clear stratification. The upper units comprise organic-rich soils, which are indicative of Holocene soil formation processes. In contrast, the deeper layers are characterized by the presence of coarse sands and silts, reflecting glaciofluvial deposition under cold-climate conditions. Lastly, ages from the Šventoji borehole by the Baltic Sea section were based on optically stimulated luminescence (OSL). The dates range between 43.7 ± 4.0 Ka and 48.4 ± 4.5 Ka to 48.8 ± 6.2 Ka (Bitinas et al., 2022) for depths between 5 and 6 m, suggesting that these deposits were formed in the middle of the Nemunas glaciation. The lithology of this site is characterized by glaciogenic sediments. The lower layers consist of sands and gravels that are poorly sorted, indicating deposition under subglacial or proglacial conditions. The uppermost strata, by contrast, transition to finer-grained sands and silts, indicative of post-glacial reworking. This transition is presumed to be associated with rising sea levels and increased sedimentation within a coastal or near-shore environment.

In summary, the stratigraphical subdivision of the Neogene and Quaternary transition zone sediments is challenging due to the limited applicability of dating methods to this time span (Pillans and Gibbard, 2012). Given the lithological composition of the sediments (which renders them unsuitable for dating using isotopic methods) and in view of the results of previous research, paleomagnetic investigations were identified as the most suitable method. It is noteworthy that paleomagnetic investigations were previously attempted several decades ago (Pevzner and Gaigalas, 1976). However, these proved to be unsuccessful due to the resulting low measurement accuracy. The stratigraphical scheme of the Lithuanian Quaternary and its correlation with the paleomagnetic scale are illustrated in Table 1 (Pillans and Gibbard, 2012; from Bitinas et al., 2015).

3. MATERIALS AND METHODS

3.1 Material

Quaternary sediments were collected from three sites in Lithuania. The Krokšlys outcrop is located close to Varėna, the Dengtiltis outcrop is located near Šiauliai, and the Šventoji-46776 well is located in Šventoji (Fig. 2).

Fig. 2. A map showing the location of the studied sedimentary sequences in Lithuania (black asterisks): Dt - Dengtiltis outcrop; Sv - Šventoji - 46776 drilling site; Kr - Krokšlys outcrop.

3.2 Methods

3.2.1 *Chemical Analysis*

A total of 129 samples from three sites, i.e., Krokšlys (64), Dengtiltis (26), and Šventoji (39), were analyzed at ACME Labs Ltd., Canada. Major elements (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO) and minor elements (Sc, V, Cr_2O_3, Ba, Be, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, W, Zr, Cu, Pb, Zn, Ni, As, Sb, Au, Tl) were analyzed by ICP emission spectrometry following a lithium metaborate/tetraborate fusion and dilute nitric digestion. The detection limit was 0.01%. Rare earth elements were determined by ICP mass spectrometry following a lithium metaborate/tetraborate fusion and nitric acid digestion of 0.2 g. Detection limits for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were 0.1, 0.1, 0.02, 0.3, 0.06, 0.02, 0.06, 0.01, 0.06, 0.02, 0.03, 0.01, 0.06, and 0.01 ppm, respectively.

3.2.2 *Normalization Techniques*

REE are normalized to study their variations in hypergene processes. There are two different types of materials widely used for REE normalization: chondrite as a representative of bulk earth (i.e., CI chondritic meteorite; e.g., McDonough and Sun, 1995; Barrat et al., 2012; Anders and Grevesse, 1989) and shale as a representative of the average composition of post-Archean upper continental crust.

Chondrite normalization values from McDonough and Sun (1995) were applied. This normalization was used to examine some geochemical processes like fractionation between light REE (LREE) and heavy REE (HREE).

The REE data was also normalized using European Shale (EUS) (Baua et al., 2018) and North American Shale Composite (NASC) (McLennan, 1989). The EUS normalization provides a regional baseline for comparing the Quaternary sedimentary composition in Lithuania, given their proximity to European sedimentary systems. Normalization to NASC enables comparison with global sedimentary data. The normalized REE concentrations will be visualized using logarithmic distribution plots.

Among the REE patterns, Ce and Eu can develop anomalies. This pattern can show either a depletion (negative anomaly) or an enrichment (positive anomaly) of the element. Eu anomalies are commonly considered to be inherited from source rocks, while Ce anomalies are generated post- or during deposition (McLennan, 1989; Jin et al., 2006; Pourret et al., 2008). Ce anomalies (Ce_{SN}/Ce^*_{SN}) are traditionally calculated by comparing the normalized concentration of Ce with its neighboring REE. A more appropriate way to calculate Ce anomalies, avoiding comparison with La, was proposed by Lawrence et al., (2006) and has been used throughout this study: Ce_{sn}/Ce^*_{sn}= $[Ce]_{sn}/([Pr]_{sn})2/[Nd]_{sn}$ – where sn – shale normalized. Eu anomaly was calculated using the following formula: Eu_{sn}/Eu^*_{sn}= $2[Eu]_{sn}/([Pr]_{sn}+[Nd]_{sn})$ – where sn – shale normalized. Zirconium (Zr) could be enriched in heavy minerals and is commonly associated with the relatively coarse-grained fraction of siliciclastic sediments. The amounts of Rb may be used as a measure of amounts of fine-grained, siliciclastic material present when comparing sediments from the same depositional basin (Fralick and Kronberg, 1997). The ratio of light to heavy REE is represented as La_N/Yb_N (Prudencio et al., 2022).

3.2.3 *Geochemical Indices*

In the field of geochemistry, elemental ratio proxies serve as a compelling instrument in the reconstruction of past environmental conditions (Syaeful H., et al., 2024). The climate-sensitive trace elements strontium (Sr) and copper (Cu) in paleoclimate analysis have been shown to reflect paleoclimate conditions. The Sr/Cu ratio has been demonstrated to be a valuable tool for evaluating paleoclimate conditions, with a Sr/Cu ratio greater than 5 indicating dry and hot climates and a ratio between 1 and 5 suggesting warm and humid climates (Zhang et al., 2021).

The elemental ratio of titanium (Ti) and aluminum (Al) is used as a weathering intensity proxy in addition to the Chemical Index of Alteration (CIA), which is the measure of the ratio of original primary minerals and secondary products such as clay minerals. This is because Ti and Al are both considered immobile during weathering and diagenesis. In a glaciofluvial setting where there is minimal weathering intensity, Al is constant, while Ti is variable. During extreme weathering conditions, Al tends to be translocated in place of Ti. Therefore, higher Ti/Al values indicate extreme weathering, and lower values indicate low weathering (Nesbitt and Young 1998). The europium anomaly can also be used as a weathering index, since it is influenced by the weathering of feldspar, where values below <1 signify increased weathering because of the fractionation of feldspar (Tostevin et al., 2016) and higher values >1 indicate the accumulation of primary feldspar in reducing environments due to sediment sorting or low chemical weathering conditions.

In the context of paleo-redox analysis, the redox-sensitive elements vanadium (V), uranium (U), iron (Fe), manganese (Mn), cobalt (Co), chromium (Cr), and nickel (Ni) serve as indicators of the redox characteristics of the depositional environment. This is because these elements remain static after deposition and burial. This characteristic renders them a highly suitable proxy for interpreting paleo-redox conditions within sedimentary rocks. The Cu/Zn ratio has been shown to define the paleo-redox environment, with high Cu/Zn ratios reflecting reducing depositional conditions and low Cu/Zn values indicating oxidizing depositional conditions (Omietimi et al., 2022; Li et al., 2021). The Cerium anomaly also serves as an index for redox conditions, with values greater than >1 implying reduced environment and vice versa. The Cu/Zn ratio is another redox condition index; a lower ratio indicates more anoxic conditions. Specifically, a Cu/Zn ratio less than 0.5 signifies an anoxic environment, and a Cu/Zn ratio greater than 0.5 signifies a relatively oxic environment (Syaeful H., et al., 2024; Wei et al, 2021).

In the context of paleohydrodynamics and grain size analysis, a lower Zr/Rb ratio is indicative of increased water depth and diminished hydrodynamic pressure. Conversely, a high Zr/Rb ratio is indicative of shallow water and strong hydrodynamic pressure. A Zr/Rb ratio of less than 1.25 is commonly associated with a weak paleohydrodynamic regime, while a ratio between 1.25 and 4.76 is indicative of intermediate to strong hydrodynamic pressure, and ratios greater than 4.76 are associated with a strong hydrodynamic regime (Omietimi et al., 2022).

Other elemental ratio proxies such as (Zr+Rb)/(Ca+Mg) and (Si+Al+K+Ti+Na)/(Ca+Mg) are used to infer siliciclastic:carbonate dominance. Regarding carbonates, the ratio between Ca and Mg may give insights on the calcite:dolomite content, but not limited to this, it could also give insights on feldspar content.

4. RESULTS

4.1 Geochemical Indices

4.1.1 Krokšlys

A total of 64 samples were analyzed from the depth interval ranging from 1 to 9.95 meters from the river surface. The analysis revealed the presence of anomalous concentrations of Ba and Zr (except for K1, K3, and K5). With the exception of these anomalous elements, Sr, Rb, V, Zn, Ni, and Cu were identified as the most concentrated trace elements at this site. With regard to rare-earth elements (REE), cerium (Ce) was found to be the most abundant, followed by neodymium (Nd), lanthanum (La), and yttrium (Y). The samples from this outcrop are from the Late Pleistocene and Holocene epochs, with the boundary at 1.55 m (K12), where TL dates were recorded (Andronikov et al., 2015).

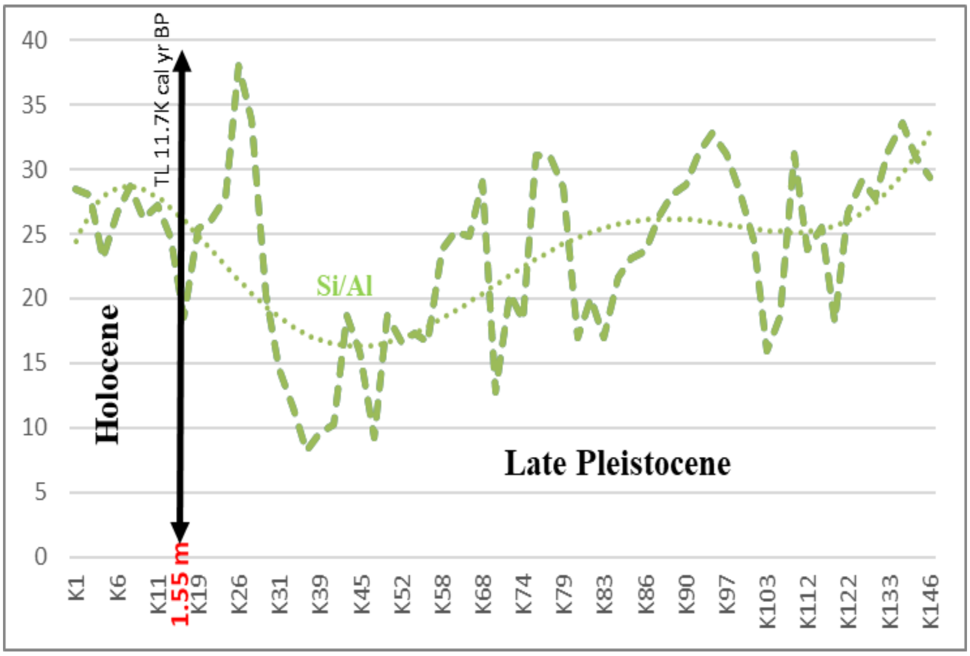

Fig. 3. Diagram showing the distribution of SiO_2/Al_2O_3 throughout the Krokšlys outcrop.

The Si/Al relationship, as illustrated in Figure 3, exhibits an initial rise during the Holocene, followed by a decline at the onset of the Late Pleistocene, and a subsequent rebound. Due to the rough nature of the plot with several peaks and troughs, a polynomial line was inserted in order to make it more comprehensive and smooth.

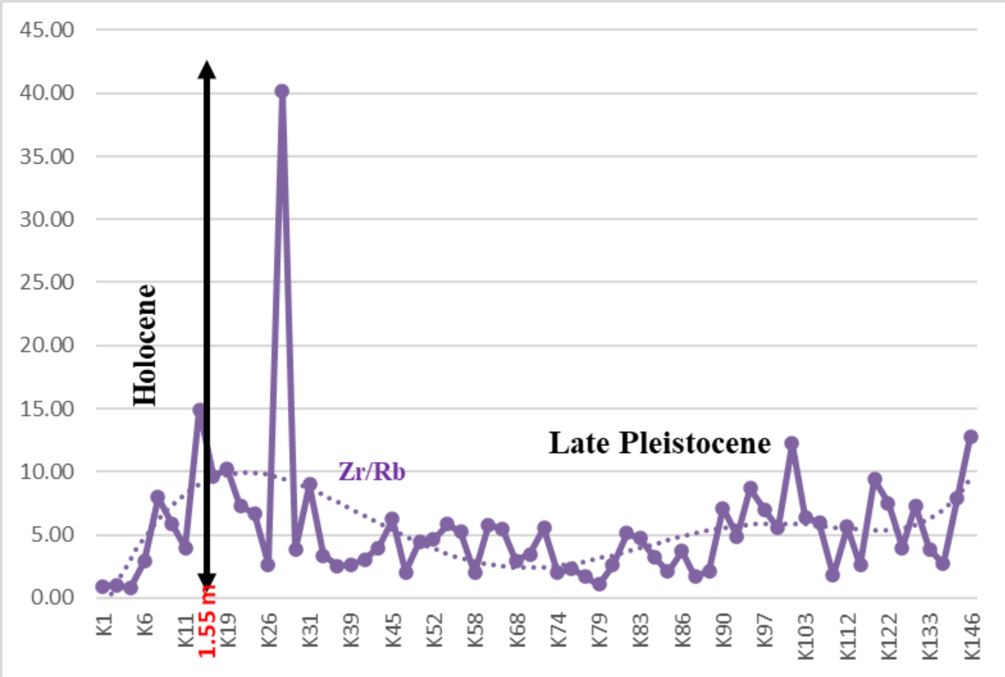

Fig. 4. Diagram showing grain-size sorting in Krokšlys calculated using the Zr/Rb ratio proxy.

The grain-size and paleo-hydrodynamics plot (Fig. 4) demonstrates a general upward trend, accompanied by minor fluctuations in the size of the samples during the Late Pleistocene. There is a very significant peak at K28 (3.05-3.10 m) compared to all other samples in this outcrop.

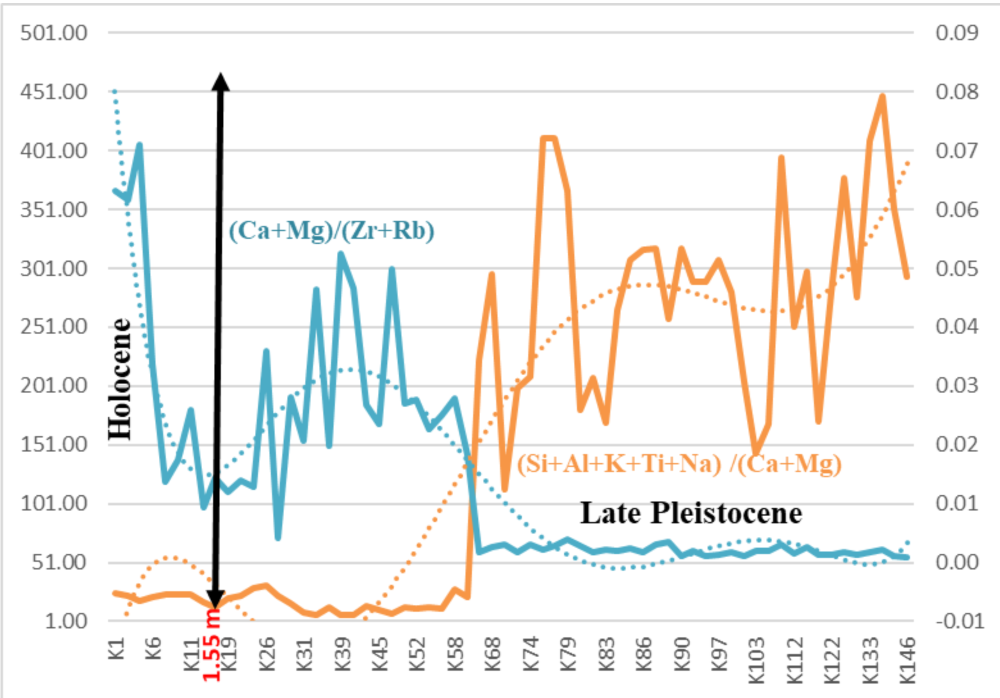

Fig. 5. Diagram showing the relationship between siliciclastic and carbonate in Krokšlys using two different proxies. (Si+Al+K+Ti+Na)/(Ca+Mg) is on the left axis and (Ca+Mg)/(Zr+Rb) on the right axis.

The ratio of siliciclastic to carbonates from both geochemical proxies employed in Fig. 5 demonstrate an inverse proportional relationship, with the Ca-Mg fraction predominating (K1-K58). At the conclusion of the Late Pleistocene epoch, the siliciclastic fraction assumes dominance. But we also notice that the values of (Ca+Mg)/(Zr+Rb) are extremely low, very much closer to zero.

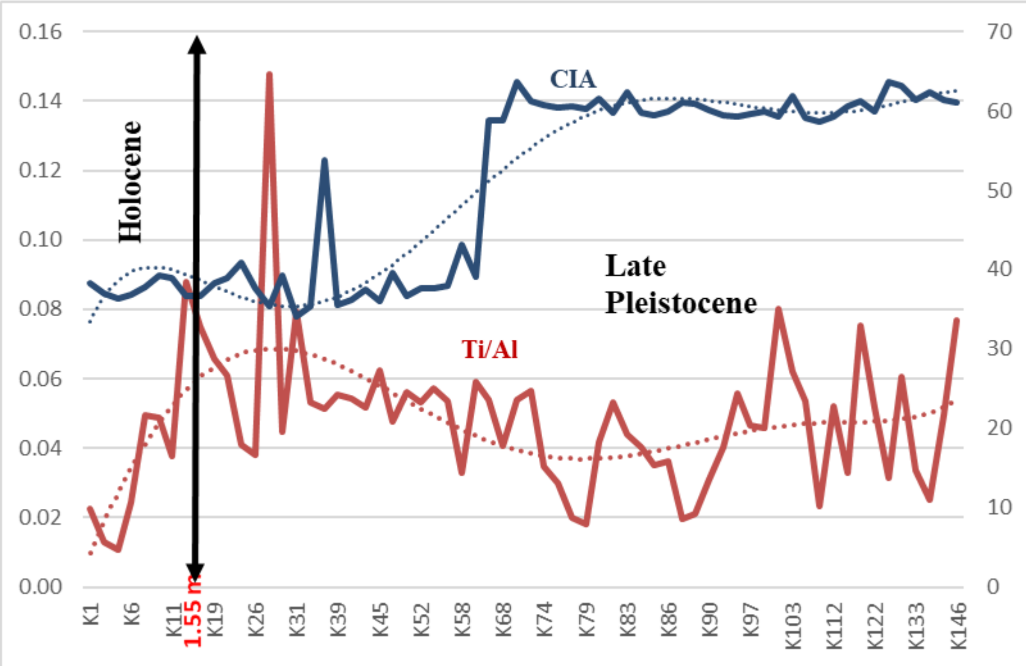

Fig. 6. Diagram showing chemical weathering intensities in Krokšlys using CIA (right axis) and Ti/Al ratio (left axis).

In Fig. 6, the Ti/Al ratio and CIA are presented as chemical weathering proxies. The CIA values range from 34 to 64, with an increasing trend from the Holocene to the Late Pleistocene, while the Ti/Al ratio displays very low values with a gradual increase-decrease trend throughout the samples. The highest Ti/Al value (0.15) is found on K28. Also, at a depth of 4.50-4.55 m (K60) marks the shift to intermediate values of the CIA index.

4.1.2 Dengtiltis

A total of 26 samples were retrieved from the depth interval ranging from 0.90 to 5.50 meters below the river's surface. The analysis revealed the presence of anomalous concentrations of Ba and Zr in all samples. With the exception of these elements, Sr, Rb, Cu, Ni, V, Zn, Pb, and Hf were identified as the most concentrated trace elements at this site. About rare-earth elements (REE), cerium (Ce) was found to be the most abundant, followed by neodymium (Nd), yttrium (Y), and lanthanum (La). The samples from this outcrop are from the Late Pleistocene and Holocene epochs, with the boundary at 4.15 m (DT42), where TL dates were recorded (A.V. Andronikov et al, 2015; Rudnickaite et al., 2012).

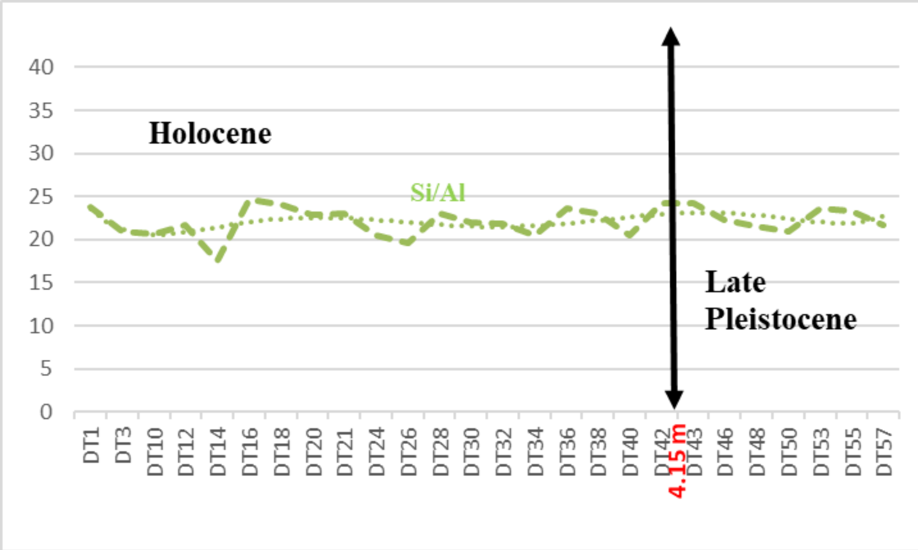

Fig. 7. Diagram showing the distribution of SiO_2/Al_2O_3 throughout the Dengtiltis Outcrop.

The Si/Al relationship, as illustrated in Fig. 7, exhibits no significant variation throughout the samples. The polynomial trendline is almost flat in this outcrop, thus not providing adequate information on clay content.

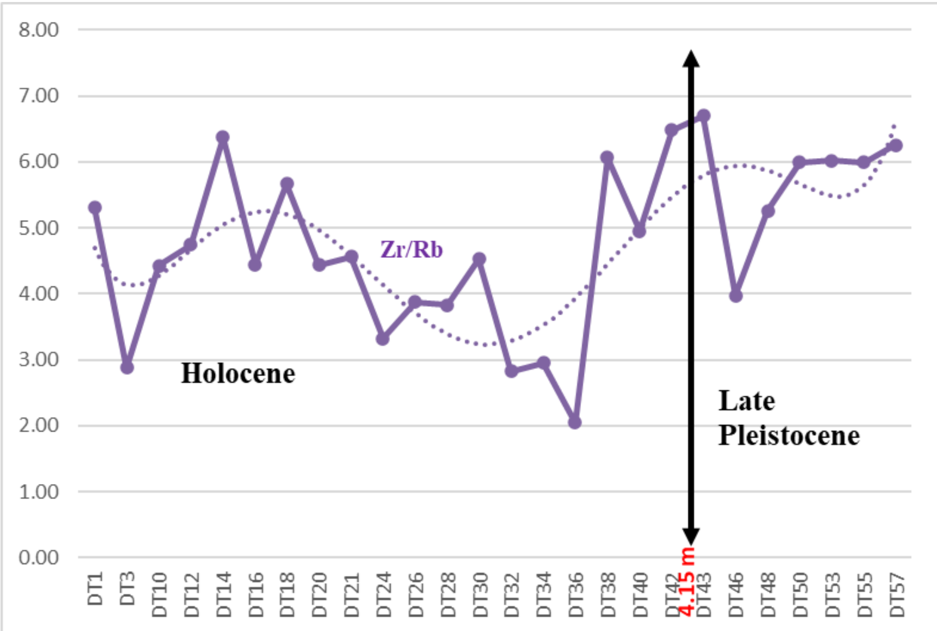

Fig. 8. Diagram showing grain-size sorting in Dengtiltis calculated using Zr/Rb ratio proxy.

The grain size and paleo-hydrodynamics plot (Fig. 8) demonstrates a comparatively rising trend with minor fluctuations in the size of the samples. A noticeable fall in grain size is seen at K46 right after the stratigraphic boundary, then a rise afterwards.

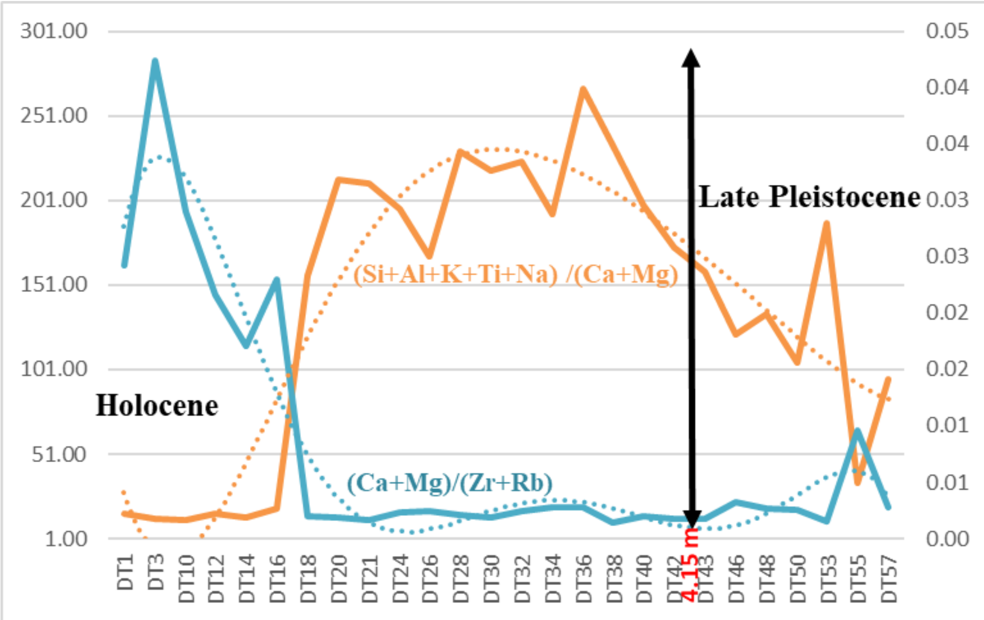

Fig. 9. Diagram showing the relationship between siliciclastic and carbonate in Dengtiltis using two different proxies. (Si+Al+K+Ti+Na)/(Ca+Mg) is on the left axis and (Ca+Mg)/(Zr+Rb) on the right axis.

The ratio of siliciclastic to carbonates, as demonstrated in Figure 9, exhibits an inverse proportional relationship, with the Ca-Mg fraction predominating (DT1 – DT16) and a subsequent transition to siliciclastic dominance (DT18 – DT42). In the Late Pleistocene epoch, the siliciclastic fraction commences a decline. A reminder is set on the difference in range between both proxies.

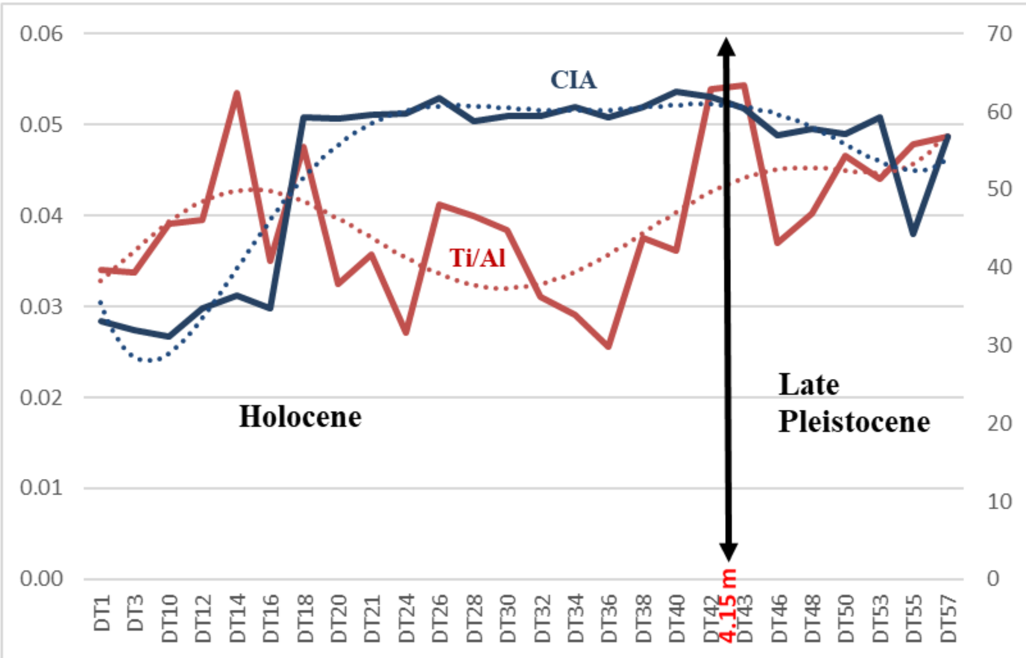

Fig. 10. Diagram showing chemical weathering intensities in Krokšlys using CIA (right axis) and Ti/Al ratio (left axis).

Fig. 10 reflects the Ti/Al ratio and CIA as chemical weathering proxies. The CIA values range from 31 to 62, with an increasing trend from the Holocene to the Late Pleistocene, while the Ti/Al ratio displays very low values with a gradual increase-decrease trend throughout the samples. The CIA values begin to increase at a depth of 1.55-1.70 m (DT18), and between DT40 and DT46 we notice a positive shift in the Ti/Al ratio.

4.1.3 Šventoji-46766 Borehole

Thirty-nine samples were analyzed from the depth interval of 2.7-7.0 m between 0 to -20 m above sea level (a.s.l.) of the Šventoji-46766 borehole. It was found that all samples exhibited anomalous concentrations of Ba and Zr (except for SV7, SV8, and SV10). With the exception of these anomalous elements, Sr, V, Rb, Zn, and Ni were identified as the most concentrated trace elements at this site. Regarding rare-earth elements (REE), cerium (Ce) is the most abundant, followed by neodymium (Nd), lanthanum (La), and yttrium (Y). All samples from this borehole belong to the Middle and Late Pleistocene epoch, and the boundary is placed at 6 m (SV56), where optically stimulated luminescence (OSL) dates were recorded (Bitinas et al., 2022).

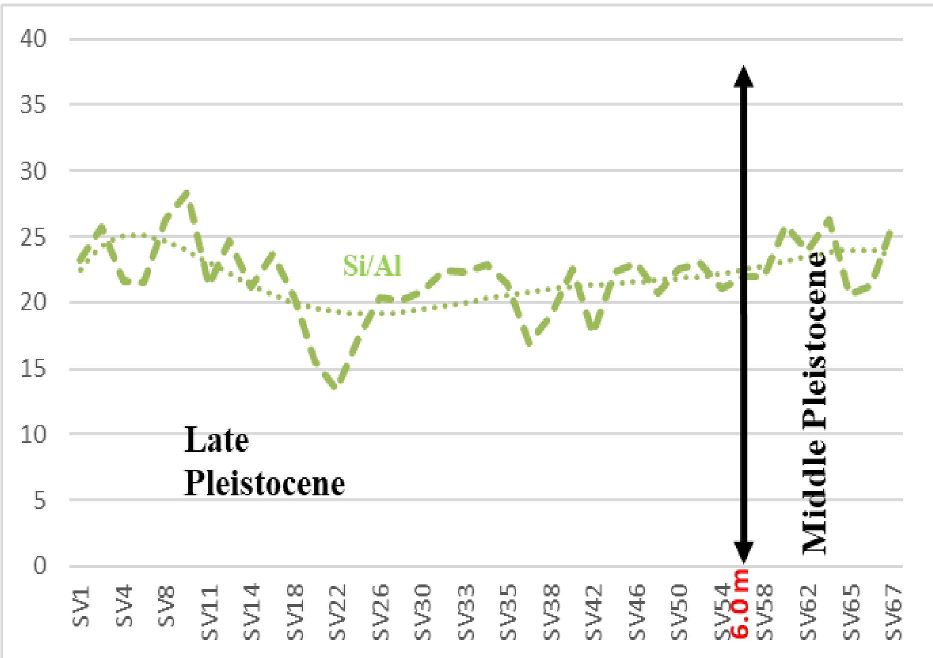

Fig. 11. Diagram showing the distribution of SiO_2/Al_2O_3 in the Šventoji-46766 borehole.

The Si/Al relationship, as depicted in Fig. 11, exhibits no significant variation among the samples; however, a slight decrease is observed in the middle of the Late Pleistocene epoch at 4.0-4.2 m (SV20-SV24), despite the overall increasing trend.

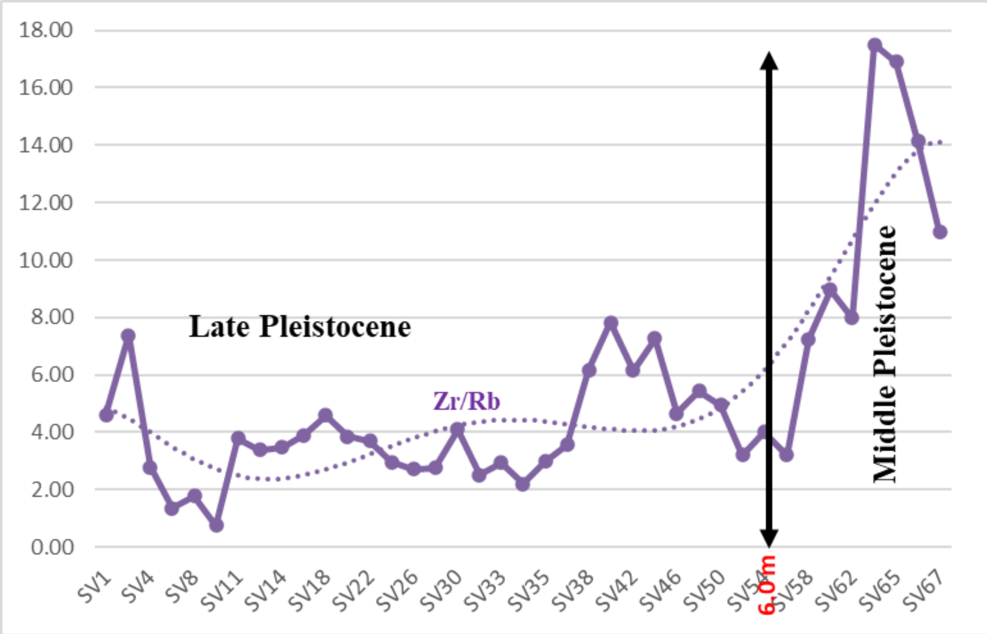

Fig. 12. Diagram showing grain-size sorting in Šventoji-46766 borehole calculated using the Zr/Rb ratio proxy.

As demonstrated in Figure 12, the grain-size and paleo-hydrodynamics plot exhibit a general upward trend, accompanied by minor variations in the dimensions of the samples during the Late Pleistocene epoch. In the Middle Pleistocene we witness a peak at SV62 compared to all other samples.

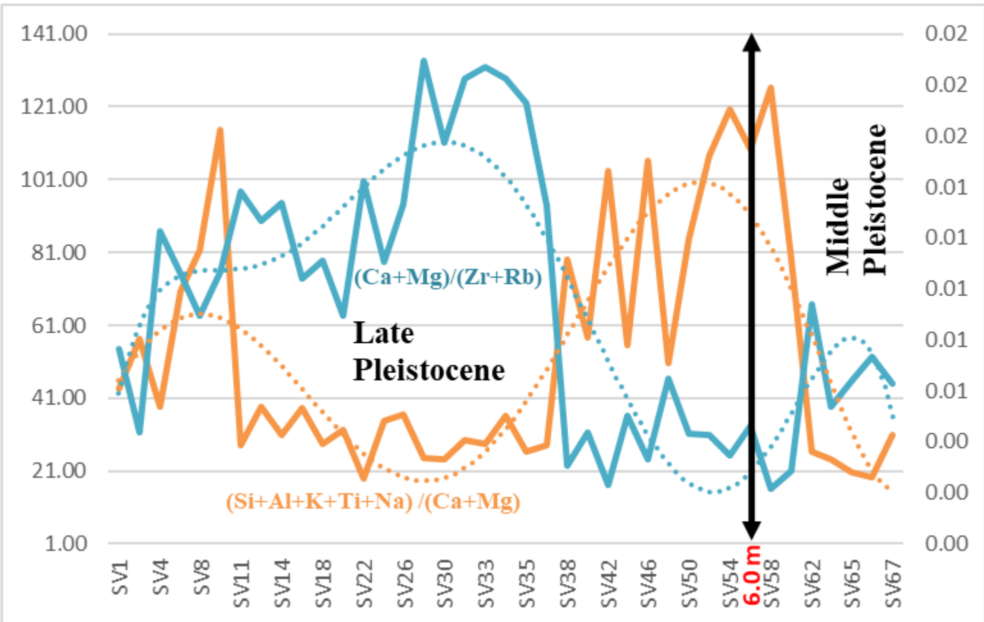

Fig. 13. Diagram showing the relationship between siliciclastic and carbonate in the Šventoji-46766 borehole using two different proxies. (Si+Al+K+Ti+Na)/(Ca+Mg) is on the left axis and (Ca+Mg)/(Zr+Rb) on the right axis.

The ratio of siliciclastic to carbonates from both geochemical proxies employed in Fig. 13 demonstrates an inverse proportional relationship, with the Ca-Mg fraction predominating (SV1-SV38). Conversely, at the conclusion of the Late Pleistocene epoch, the siliciclastic fraction assumes dominance. Emphases is laid on the difference in range between both proxies.

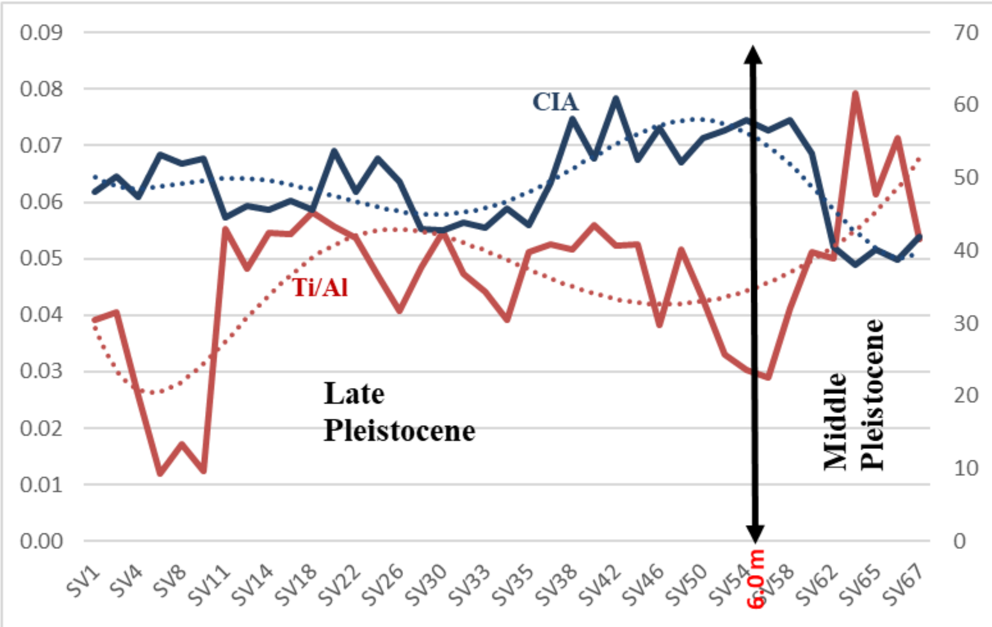

Fig. 14. Diagram showing chemical weathering intensities in the Šventoji-46766 borehole using CIA (right axis) and Ti/Al ratio (left axis).

The Ti/Al ratio and CIA are presented as chemical weathering proxies in Fig. 14. The CIA values range from 39 to 61, with an increasing trend from the Late to the Middle Pleistocene, while the Ti/Al ratio displays very low values with a gradual increase-decrease trend throughout the samples. We also observe that the upper part of the Late Pleistocene (SV4-SV10), at a depth ranging from 2.93-3.4 m, exhibits lower Ti/Al values compared to all other samples.

The appendices provide further details on the use of Sr/Cu and Cu/Zn proxies, which were employed to analyze paleoclimate and paleo-redox environments, respectively. The Sr/Cu diagram (Appendix 3) reflects a dry and hot climate for values greater than 5. Nevertheless, in this research, the threshold was taken at 25 because of the anomalous concentration of Sr compared to Cu. Meanwhile, the baseline for Cu/Zn (Appendix 3) is 0.5, where values above this baseline indicate an oxic environment and vice versa (see Appendix 3). The Cerium (Ce) anomaly was also calculated as a paleo redox proxy, and the results can be found in Table S1 (see Appendix 2). Though we have terrigenous sediments, this is to ascertain the results gotten from the Cu/Zn ratio proxy.

4.2 Europium (Eu) anomaly

Rare earth elements from all sites were normalized following three standards: European Shale (EUS) (Baua et al., 2018), North American Shale Composite (NASC) (McLennan, 1989), and CI-Chondrite (McDonough & Sun, 1995) (see supplementary material). The distribution pattern, and anomalies of these elements were evaluated, and in this study, only the Eu anomaly is considered.

In Krokšlys, the EUS and NASC normalization demonstrate broadly analogous patterns throughout the outcrop from the Late Pleistocene to the Holocene. Conversely, the chondrite normalization exhibited a substantially diminished trend, thereby signifying Eu behavior in relation to primitive mantle values (Fig. 15). Most of the samples (EUS and NASC) from this outcrop display Eu/Eu* values ranging between 1.0 and 1.3, with some notable peaks (above 1.40) during the Holocene. Concurrently, other samples manifest a pronounced decline in Eu/Eu*, as evidenced by K28 and K146.

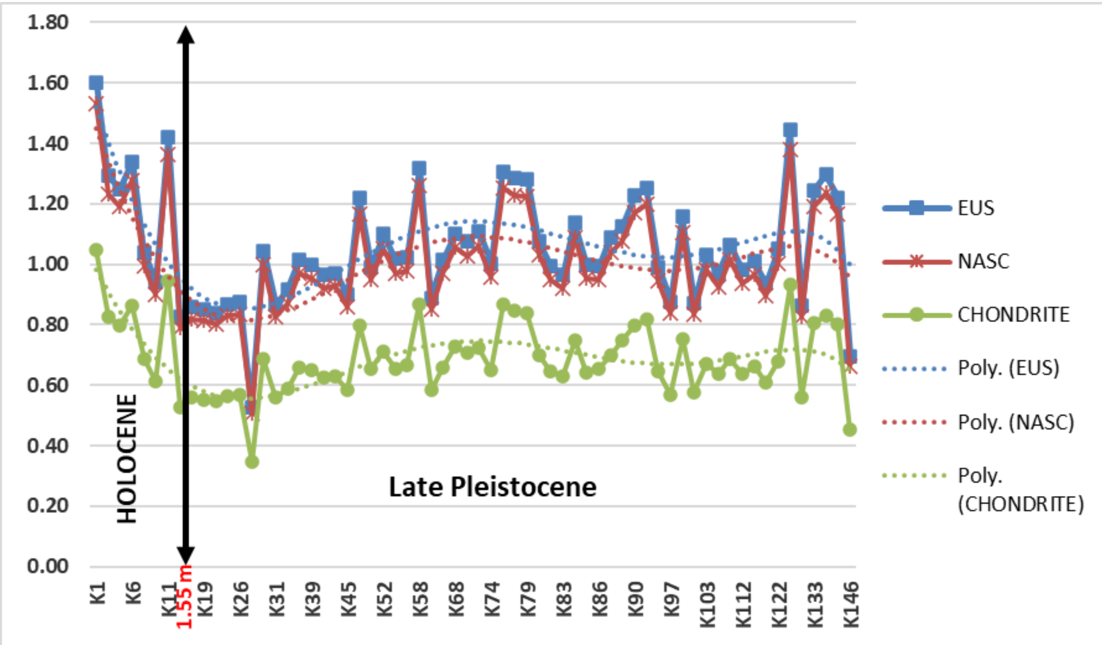

Fig. 15. Diagram showing the Eu anomaly trends in sediments from Krokšlys outcrop, normalized to EUS, NASC, and chondrite values. Polynomial trendlines display overall patterns in each normalization scheme.

In a manner analogous to that observed in Krokšlys, the Dengtiltis outcrop also demonstrates the same patterns between the EUS and NASC normalization, with chondritic values exhibiting a relatively lower frequency throughout the samples (Fig. 16). Most samples from the EUS and NASC demonstrate values ranging from 1.0 to 1.20. However, a precipitous decline is evident in sample DT42, which delineates the stratigraphic boundary between the Holocene and Late Pleistocene layers at depths of 4.15-4.20 m.

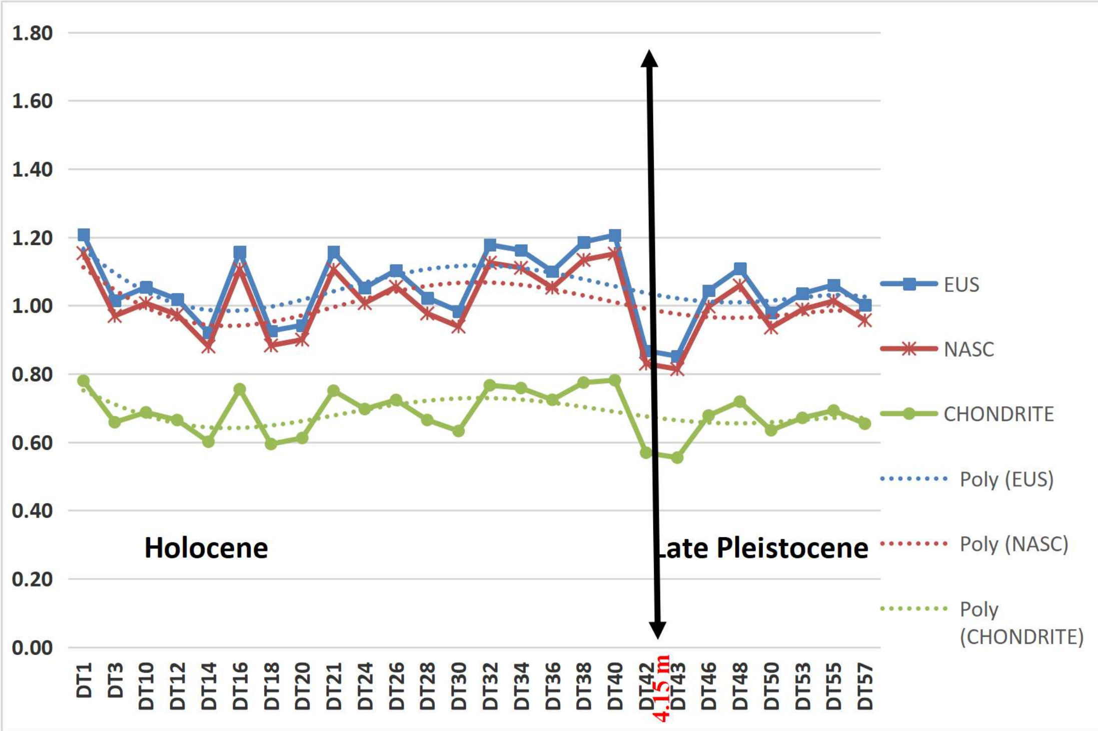

Fig. 16. Diagram showing the Eu anomaly trends in sediments from Dengtiltis outcrop, normalized to EUS, NASC, and chondrite values. Polynomial trendlines display overall patterns in each normalization scheme.

As illustrated in Figure 17, the normalized Eu/Eu* values of EUS and NASC exhibit fluctuations between 1.0 and 1.4, with two prominent peaks at 1.4. The chondrite-normalized values are consistently low, with an average below 0.8 in the Late Pleistocene. While no extreme anomalies are observed, a notable spike is evident at a depth of 6.0 m (SV56), marking the boundary between the Late and Middle Pleistocene periods (EUS & NASC), followed by a swift decline prior to a period of stabilization. At this same point, an increase is also marked on the Chondrite-normalized curve, though not to the same extent as previously noted.

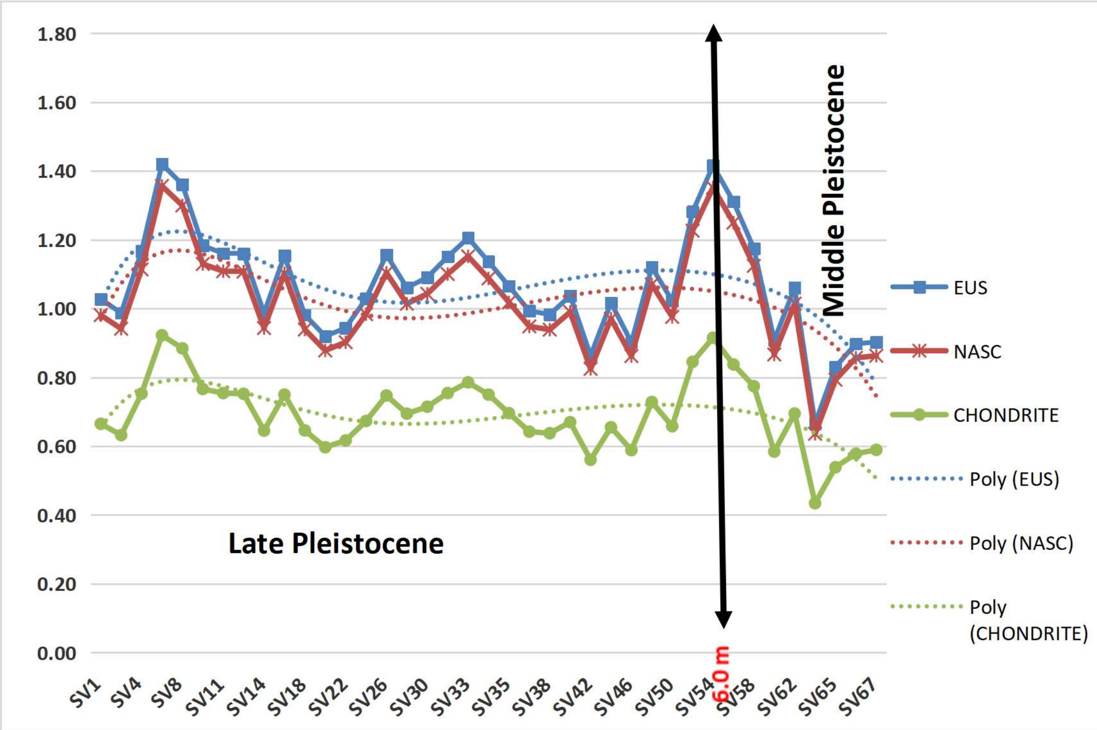

Fig. 17. Diagram showing the Eu anomaly trends in sediments from the Šventoji 46766 borehole, normalized to EUS, NASC, and chondrite values. Polynomial trendlines display overall patterns in each normalization scheme.

5. DISCUSSION AND INTERPRETATION

5.1 Geochemical Indices

The use of major and minor elements as ratio proxies aids in giving ideas to the presence or absence of some mineralogies, such as clay content, and determining the paleoenvironmental conditions in which the sediments occurred. The geochemical composition of sediments from the Krokšlys, Dengtiltis, and Šventoji-46766 sites demonstrates a consistent presence of trace elements such as Sr, Rb, V, Zn, Ni, and Cu, with Ba and Zr appearing in anomalous concentrations in most samples (Table S1- see Appendix 2). These therefore suggest or point toward a felsic continental crustal provenance, as felsic rocks are typically enriched in light rare earth elements (LREE) and in large lithophile elements (LILE). The dominance of some REE, such as Ce, Nd, La, and Y, in the REE suite across all sites also supports this interpretation.

Moreover, the Si/Al oxide ratio gives an idea about clay content. "Since quartz (SiO_2) is known to contain no REE and acts solely as a dilution factor for REE in sediments and the clay content directly influences the distribution and quantities of REE in sediments" (Kaminskas et al., 2013), it is therefore important to evaluate the presence of clay in each sequence. The observed Si/Al oxide ratios (Fig. 3, 7 & 11) indicate a great siliciclastic input, which is consistent with detrital quartz and feldspar derived from upper continental crust rocks.

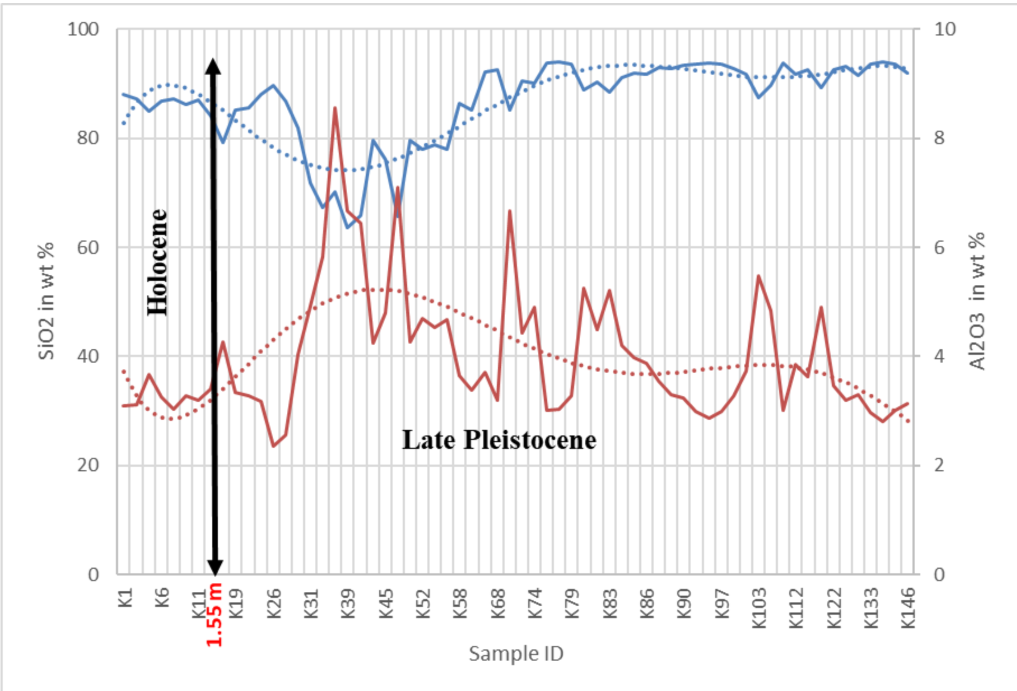

Fig. 18. Diagram showing variability of SiO_2 and Al_2O_3 in wt.% from Krokšlys (SiO_2 on the left axis and Al_2O_3 on the right axis).

Further analysis was done in comparing the correlation between SiO_2 and Al_2O_3 to aid in the lithological classification of these sediments, as seen in Figs. 18, 19, & 20 (see also Appendix 1). In summary, the correlation defines sediments from the Krokšlys outcrop to be heterogeneous with a strong negative correlation (-0.73): that is, having contrasting lithologies alternating with one another. These could possibly be sands, silt, or clayey layers and a mixture of materials. Dengtiltis is seen to be much more homogeneous with a slightly positive correlation (+0.25), showing little or no variation, and could mostly be made up of clayey or feldspathic sands. The Šventoji borehole-46766 also has a moderate negative correlation (-0.61) and is most likely made up of stratified silica-rich rocks and a few layers of silty or clayey material. In short, these sediments are of terrigenous origin.

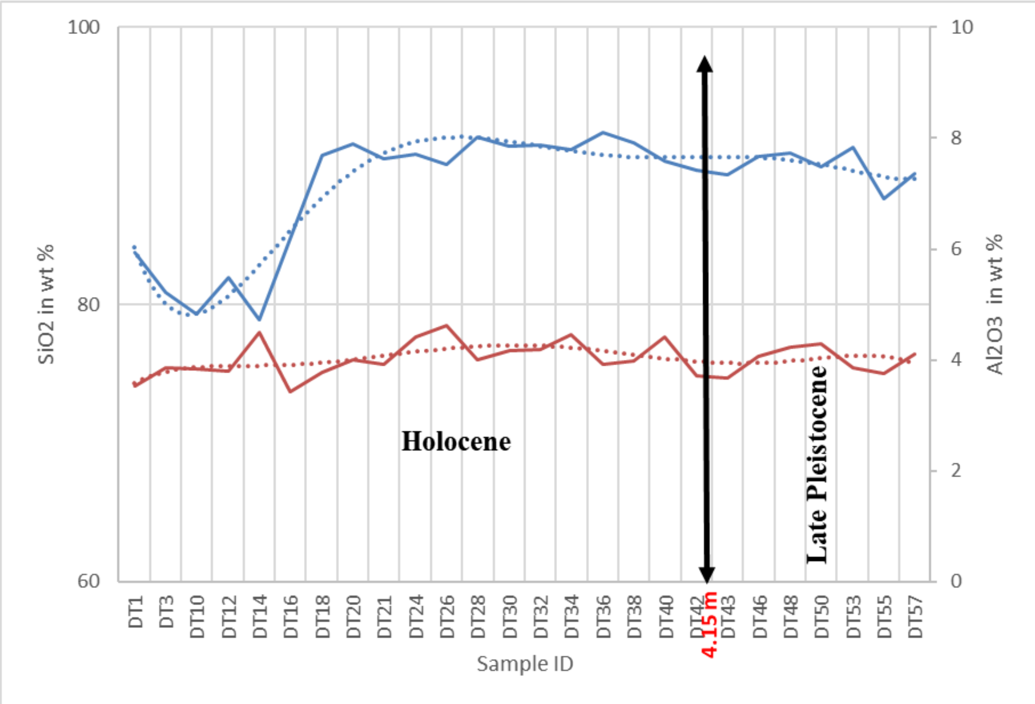

Fig. 19. Diagram showing variability of SiO_2 and Al_2O_3 in wt.% from Dengtiltis, (SiO_2 on the left axis and Al_2O_3 on the right axis).

Grain size was calculated using the ratio Zr:Rb [the baseline is taken at 10 instead of 1 because of the anomalous concentrations of zirconium (Zr) compared to rubidium (Rb)], where values greater than one (>10) indicate the coarser fraction and values less than one (<10) the finer fraction. This is because zirconium is primarily concentrated in the mineral zircon ($ZrSiO_4$), which is a very resistant and dense mineral. Zircon grains tend to be concentrated in coarser, sand-sized fractions of sediments due to their high density and resistance to weathering, whereas Rb is mostly included in fine-grained clays (e.g., Beil et al., 2018; Calvert and Pedersen, 2007; Dypvik and Harris, 2001; Kylander et al., 2011; F.A. Trentin et al., 2025).

The grain-size and paleo-hydrodynamic proxies reveal a general increasing trend during the Late Pleistocene in all profiles (Figs. 4, 8 & 12), suggesting a gradual increase in depositional energy and thus an increase in grain size over time. This could be reflected during enhanced fluvial activity in the Late Pleistocene, possibly related to glacial melting or increased seasonal runoff. But a general weak correlation between grain size (Zr/Rb) and mineralogical composition (SiO_2 & Al_2O_3) implies that zircon-heavy sediments are not consistently sand-rich and vary independently, probably due to post-depositional alterations or variable source provenance.(see Appendix 1)

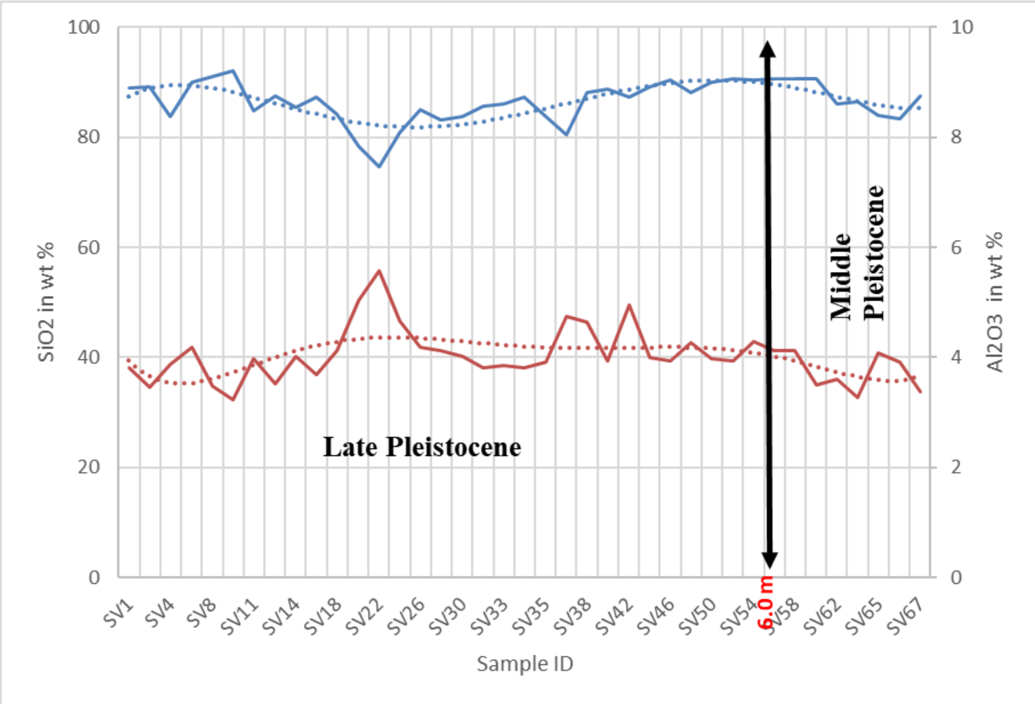

Fig. 20. Diagram showing variability of SiO_2 and Al_2O_3 in wt.% from Šventoji-46766 (SiO_2 on the left axis and Al_2O_3 on the right axis).

The inverse relationship between the (Ca+Mg)/(Zr+Rb) and (Si+Al+K+Ti+Na) /(Ca+Mg) ratios reflects the transition from carbonate-rich to siliciclastic-dominated environments across all three sites (Fig. 5, 9 & 13). The upper sections (carbonate-rich) indicate a change from low-energy, chemically precipitated environments (e.g., lakes or floodplains) to dynamic or higher-energy, detrital environments (e.g., fluvial input or glacial outwash) typical of deglacial or periglacial phases. The calcium and magnesium ratio (Ca:Mg) may not necessarily serve as a carbonate indicator in this study because the Ca/Mg values are way too low (Table S1-see Appendix 2). Nevertheless, this Ca:Mg could aid in corroborating the idea of feldspathic mineral sources.

As demonstrated in a number of studies (Schmidt 1963; McLennan et al. 1979; Sugisaki et al., 1982; Sreenivas and Srinivasan, 1994), the ratio between the oxides of Ti and Al (hereafter referred to as the Ti/Al ratio) has been utilized as an indicator of provenance. However, Ti and Al are generally regarded as being among the more immobile elements during the processes of weathering and diagenesis (Sugisaki, 1978; Law et al., 1991; Nesbitt and Wilson, 1992). Consequently, instead of merely examining their proportions in sedimentary rocks, Nesbitt and Young, in 1996, did a study of glacial deposits derived from crystalline bedrock demonstrated that the effects of chemical weathering are negligible. “It is only by investigating the behavior of Ti and Al in weathering profiles in sediments under such "controlled" conditions that the effects of physical and chemical weathering can be separated and evaluated with confidence. As weathering becomes extreme, it shows a marked increase in the Ti/Al ratio. This was reported by Maynard (1992, in his fig. 2A), who suggested that changes in Ti:Al ratio (generally increased ratios) may be due to either chemical or physical removal of Al" (Nesbitt and Young, 1998).

In order to chart the behavior of specific elements in weathering profiles, it is necessary to quantify the degree of chemical alteration (weathering) that individual samples have undergone. Nesbitt and Young (1982, 1984) proposed a methodology for the quantification of the degree of weathering to which rocks have been subjected. The chemical index of alteration (CIA) is calculated using the following formula: $[Al_2O_3/ (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$.

In this context, values are expressed as molar proportions, and CaO* represents CaO in silicate minerals exclusively. The details of the CIA calculation can be found in Nesbitt and Young (1982, 1984) and Fedo et al. (1995). The CIA provides a measure of the ratio of primary minerals and secondary products, including clay minerals. This parameter can be expressed as a dimensionless number, which typically ranges from approximately 50 for fresh rocks to 100 for completely weathered rocks composed entirely of secondary minerals such as kaolinite and gibbsite.Some CIA values to estimate the degrees of weathering:

★ < 50 to 60 initial stages of weathering,
★ 60 to 80 intermediate degrees,
★ 80 to 100 extreme degrees.

In this study, the chemical weathering intensity (Figs. 6, 10 & 14) therefore ranges from weak to moderate degree. The CIA values generally range from 31 to 64 across all three sites, showing an upward trend of weathering intensity from the Holocene to the Late Pleistocene, suggesting that older sediments have undergone more intense chemical weathering either before or post burial. This could imply longer exposure to subaerial conditions, possibly due to reduced sedimentation rates or maybe more intense glacial-interglacial cycling. In addition, the lower Ti/Al oxide (<1) ratios reinforce this proposition (low weathering intensity) and as well strengthen the idea that felsic source materials dominate throughout the sediment profiles.

5.2 Europium (Eu) Anomaly

The Eu anomaly provides us with valuable information regarding sediment source rock type since it is considered to be inherited from the parent rock. Generally, across all three sites, the EUS and NASC normalized values range mostly from 1.0-1.4, and this indicates a relatively stable source with little or no plagioclase removal. Thus, reinforcing a felsic upper continental crustal source where Eu anomalies are relatively mild or slightly positive. The chondrite-normalized values, on the other hand, are significantly lower, often below <0.8, affirming that the sediments are more differentiated from a primitive mantle composition. This in turn promotes the idea that continental crust-derived materials dominate in these regions.

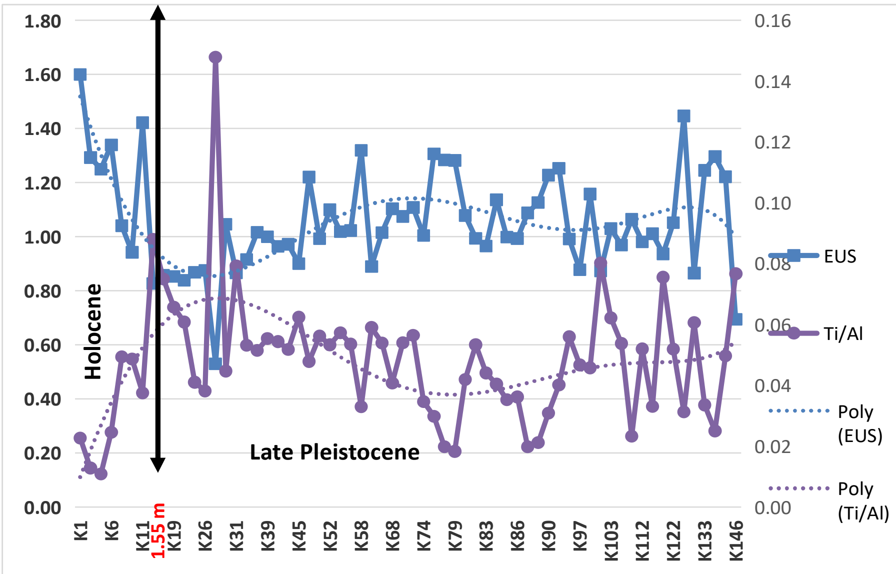

Fig. 21. Diagram showing the relation between Eu/Eu* (normalized to EUS) on the left axis and the Ti/Al oxide ratio on the right axis in the Krokšlys outcrop.

Krokšlys displays the highest peak (at 1.6 from sample K1), with other moderate positive anomalies between 1.0-1.4 (Fig. 15), likely related to episodic influxes of primary plagioclase-rich material or reduced weathering conditions during the Holocene. Two troughs are seen at K28 and K146, suggesting potential depletion through chemical weathering or sediment sorting. Subsequently, Dengtiltis shows similar normalization patterns with a sharp drop at DT42-DT43(4.15 m depth), which marks the Holocene/Late Pleistocene boundary (Fig. 16) and may indicate a sudden shift in sediment source or weathering regime, possibly due to some climatic change or glacial input. A notable spike in Eu/Eu* at SV56 (6.0 m depth) in the Šventoji-46766 borehole aligns with the Middle/Late Pleistocene boundary (Fig. 17), implying a significant sedimentary event, where glacial advancement delivered fresh, primary plagioclase-rich material, and the quick decline afterward suggests a return to more weathered sediment input.

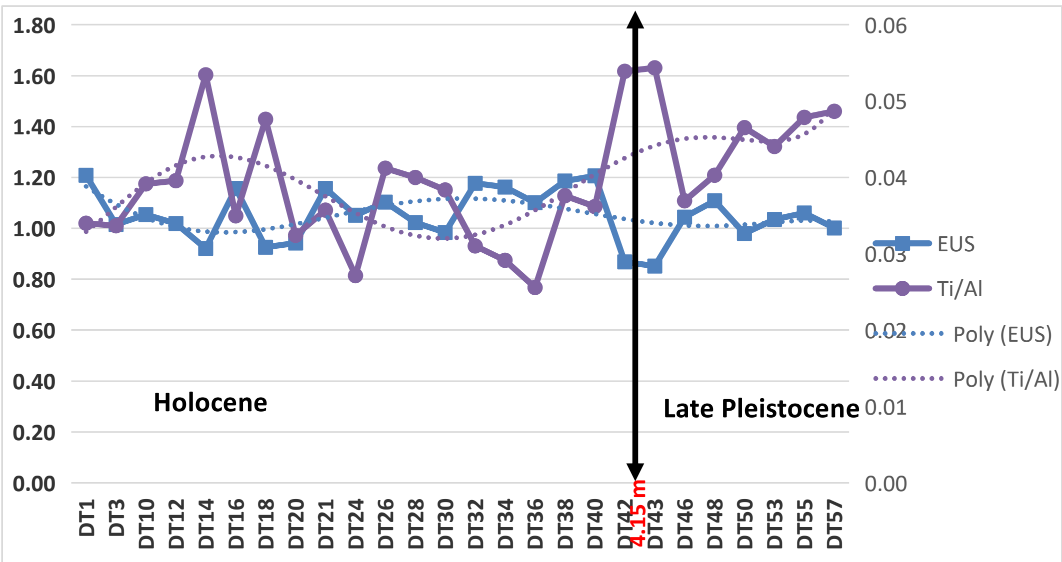

Fig. 22. Diagram showing the relation between Eu/Eu* (normalized to EUS) on the left axis and the Ti/Al oxide ratio on the right axis in the Dengtiltis outcrop.

To ascertain the above information, the Eu anomaly normalized to EUS was plotted alongside the Ti/Al oxide ratio for each site and used to determine the weathering intensity and climate regime (Figs. 21, 22 & 23). In essence, the inverse relationship between the Eu/Eu* and Ti/Al oxide attests to the above-mentioned interpretation, which states that the Holocene experienced less chemical weathering than the Late Pleistocene in the Krokšlys outcrop (Fig. 21), and the Dengtiltis outcrop experienced more weathering with a greater removal of Al, hence high Ti/Al ratio values. Possibly due to the last glaciation (Nemunas) during the Late Pleistocene, we observe in Fig. 23 a probable glacial advancement (SV1-SV11) bringing forth an accumulation of feldspathic or clayey-rich minerals. This phenomenon is also observed on the boundary between the Late and Middle Pleistocene (SV54-SV56), then followed by a retreat causing an increase in weathered material.

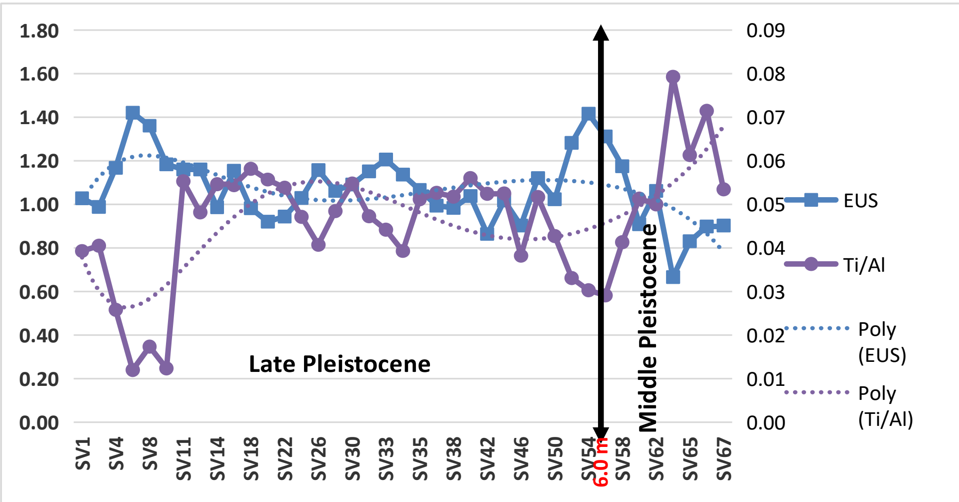

Fig. 23. Diagram showing the relation between Eu/Eu* (normalized to EUS) on the left axis and the Ti/Al oxide ratio on the right axis in the Šventoji-46766 borehole.

The transition from carbonates to siliciclastic dominance and the increasing trend of Zr/Rb as well as Eu/Eu* together suggest that sediments became coarser and more energetic over time between glacial and interglacial periods. For example, on the Šventoji-46766 borehole at 6.0 m depth, there is an increase in grain size and in Eu anomaly, alluding to a glacial advancement event introducing coarser and less weathered sediments, meanwhile a retreat follows during the interglacial phase, depositing more altered sediments in the area.

In addition, the paleo redox and paleoclimatic proxies (that is, Cu/Zn and Sr/Cu, respectively) give us a general idea about the depositional and climatic conditions that influenced these samples. Krokšlys and Dengtiltis demonstrate a drier and hotter climate with anoxic conditions during the Holocene period and then transitions to oxic conditions in a warm and humid climate during the Late Pleistocene, thus an increase in weathering intensity. Unlike Krokšlys and Dengtiltis, the Šventoji-46766 borehole displays more anoxic conditions during the Late to Middle Pleistocene, with a dry and hot climate prevailing. (see Appendix 3)

CONCLUSION

1. The studied Quaternary sequences from the Krokšlys outcrop, Dengtiltis outcrop, and Šventoji borehole-46766 reveal distinct stratigraphic divisions that correspond to the Middle to Late Pleistocene and the Holocene with varying sediment types such as periglacial sands, siltstone, and clays to organic-rich soils in Krokšlys and Dengtiltis exhibiting post-glacial warming.
2. Geochemical ratio proxies such as SiO_2/Al_2O_3, Zr/Rb, and siliciclastic to carbonate ratios indicate a mixture of sediment sources and shifts in depositional environment with fluctuating carbonate-dominated conditions to siliciclastic regimes most likely in response to glacial-interglacial dynamics..
3. The CIA (31 – 64) and very low TiO_2/Al_2O_3 (0 – 0.15) ratio values point to a low to moderate chemical weathering intensity from the Holocene to Pleistocene and sediment recycling under changing paleoclimatic conditions.
4. All samples from the three locations demonstrate LREE enrichment over HREE and noticeable positive and negative Eu anomalies. This suggests a possible input from felsic source rocks with some plagioclase fractionation indicating weathering conditions.
5. The REE patterns and geochemical characteristics of this study demonstrate consistency with other Quaternary sediments in the Baltic region, thereby supporting the hypothesis of a primarily felsic source with minor mafic input. However, the presence of localized variability in depth, as observed through the spatial and temporal resolution of the data set, suggests the existence of more complex depositional histories.
6. Evidence of the pronounced Eu anomaly at SV56 (Fig. 10) indicates a short-term yet substantial alteration in environmental conditions or source material, a phenomenon that has not been previously documented in extant studies.

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S U M M A R Y

JESSICA CINDY SAME FAKAM

Geochemical peculiarities of sandy sediments from the Late Pleistocene and Holocene of Lithuania

This master's thesis explored the geochemical composition of Late Pleistocene to Holocene sediments from two outcrops (Krokšlys and Dengtiltis) and one borehole (Šventoji-46766) in Lithuania. The analysis revealed a consistent light rare earth element (LREE) composition, with variable Europium (Eu) anomalies ranging from moderately negative (0.5) to strongly positive (1.60) signifying differences in source material and feldspar weathering. Geochemical indices such as Si/Al, Zr/Rb, Ti/Al and Chemical Index of Alteration (CIA) highlighted shifts in grain size and weathering intensity across stratigraphic layers. The results suggest that the sediments were primarily derived from felsic continental crust that has been altered by glacial processes and changing environmental conditions. The presence of Eu anomalies is indicative of mineral input or localized sedimentary events, which in turn demonstrate paleoclimatic dynamics. This study demonstrates the value of combining elemental ratio proxies with REE patterns in reconstructing sediment provenance and palaeoenvironmental conditions. Furthermore, it provides a fundamental geochemical framework for future palaeoenvironmental research in glaciated regions of the Baltic.

S A N T R A U K A

JESSICA CINDY SAME FAKAM

Lietuvos vėlyvojo pleistoceno ir holoceno smėlingų nuosėdų geocheminiai ypatumai

Šiame magistro darbe buvo tiriama vėlyvojo pleistoceno ir holoceno nuosėdų iš dviejų atodangų (Krokšlio ir Dengtilčio) ir vieno gręžinio (Šventosios-46766) Lietuvoje geocheminė sudėtis. Analizė atskleidė nuoseklią lengvųjų retųjų žemių elementų (LRŽ) sudėtį, su kintančiomis europio (Eu) anomalijomis: nuo vidutiniškai neigiamų (0,5) iki stipriai teigiamų (1,60). Geocheminiai rodikliai, tokie kaip Si/Al, Zr/Rb, Ti/Al ir cheminio pakitimo indeksas (CIA), išryškino granuliometrinės sudėties ir dūlėjimo intensyvumo pokyčius vėlyvajame pleistocene ir holocene. Rezultatai rodo, kad nuosėdos daugiausia susidarė iš ardomos felzinės kontinentinės plutos, kurią pakeitė ledynmečio procesai ir besikeičiančios aplinkos sąlygos. Europio anomalijų buvimas rodo mineralų patekimą arba lokalius nuosėdų susidarymo įvykius, kurie savo ruožtu rodo paleoklimatinę dinamiką. Šis tyrimas parodo, kaip vertinga derinti elementų santykio tarpinius rodiklius su RŽE modeliais rekonstruojant nuosėdų kilmę ir paleoaplinkos sąlygas. Be to, jis suteikia pagrindinį geocheminį pagrindą būsimiems paleoaplinkos tyrimams Baltijos apledėjusiuose regionuose.

APPENDICES

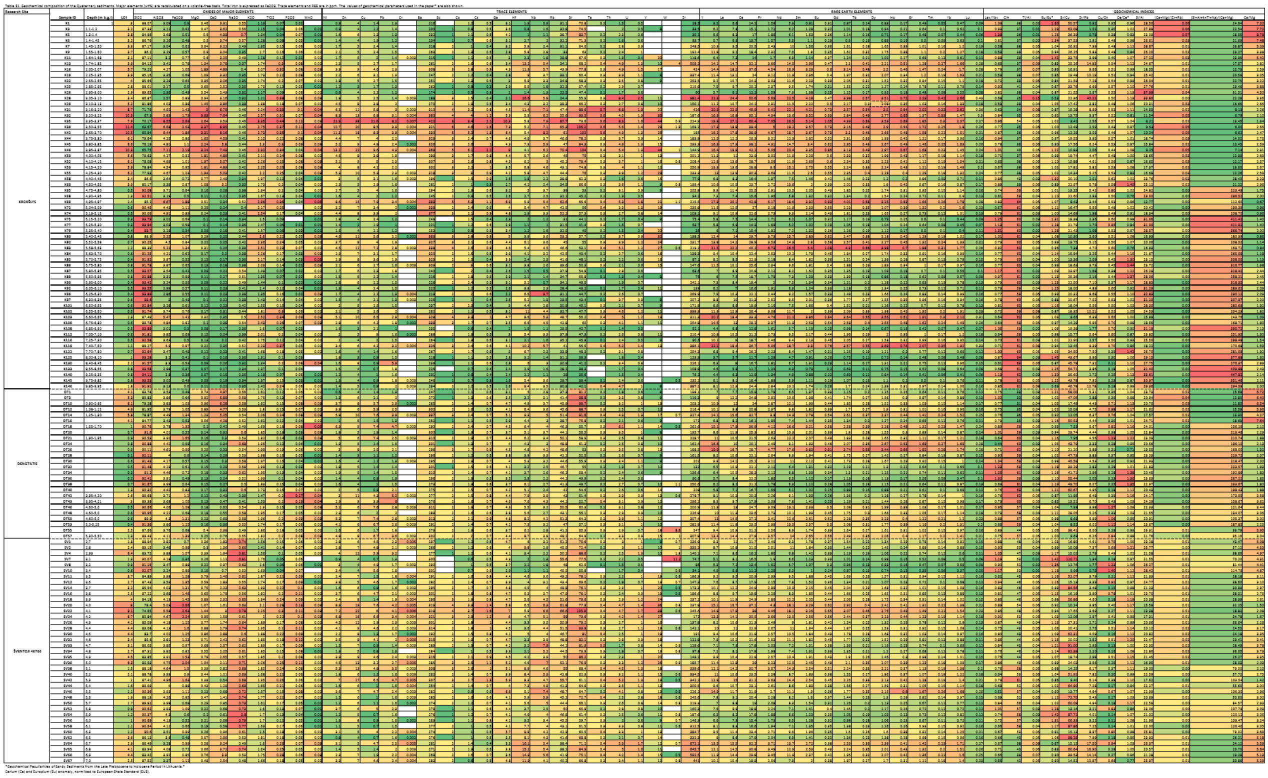
APPENDIX 1-1

PEARSON'S CORRELATION TABLE

Krokslys	Zr/Rb	SiO2	Al2O3	Dengtiltis	Zr/Rb	SiO2	Al2O3	Sventoji	Zr/Rb	SiO2	Al2O3
Zr/Rb	1			Zr/Rb	1			Zr/Rb	1		
SiO2	0.03	1		SiO2	-0.11	1		SiO2	-0.01	1	
Al2O3	-0.20	-0.73	1	Al2O3	-0.22	0.25	1	Al2O3	-0.21	-0.61	1

Table 1. Correlation Analysis: Relationship between grain size (Zr/Rb) and mineral composition (SiO_2/Al_2O_3) in Krokšlys, Dengtiltis and Šventoji-46766.

SUPPLEMENTARY TABLE



The color scale was developed using the Conditional Formatting function of MS Excel - the red-yellow-green color scale indicates the position of a given value in the entire range of values in a given column, including all main and supplementary research sites (red = high values, green = low values).

Table S1. Geochemical composition of the Late Pleistocene to Holocene sandy sediments. Major elements (wt%) are recalculated on a volatile-free basis. Total iron is expressed as Fe2O3. Trace elements and REE are in ppm. The values of geochemical indices used in the paper* are also shown. (Readable as supplementary material at https://eu.docworkspace.com/d/sII73vryKAbSavMEG)

APPENDIX 3-1

SCATTER PLOT CHARTS
KROKŠLYS OUTCROP

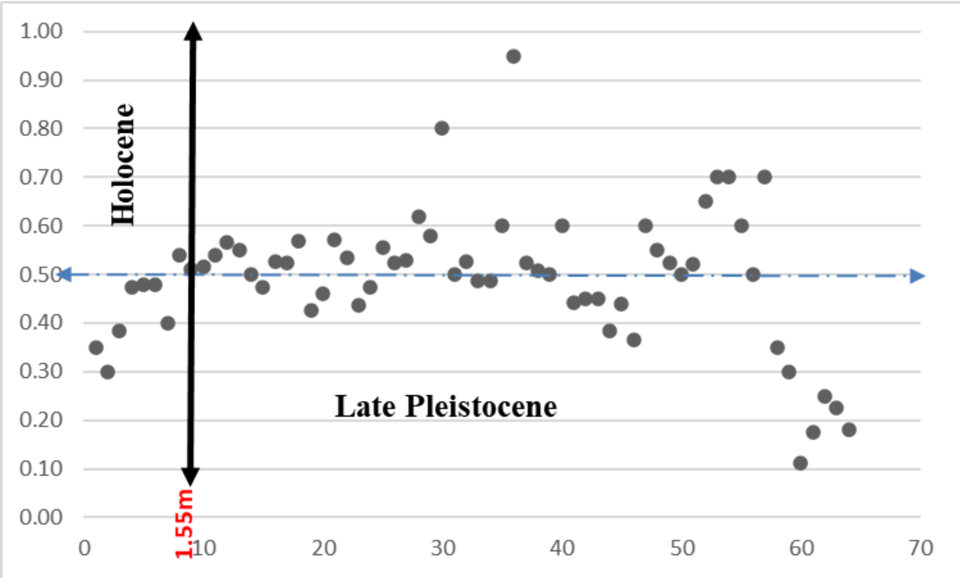


Fig. 1. Scatter plot from Krokšlys, showing the paleo redox (**referred here as Cu/Zn**) behaviour of samples. The baseline (blue dashed line) is at 0.5, where values above this signifies an oxic environment and below signifies an anoxic environment.

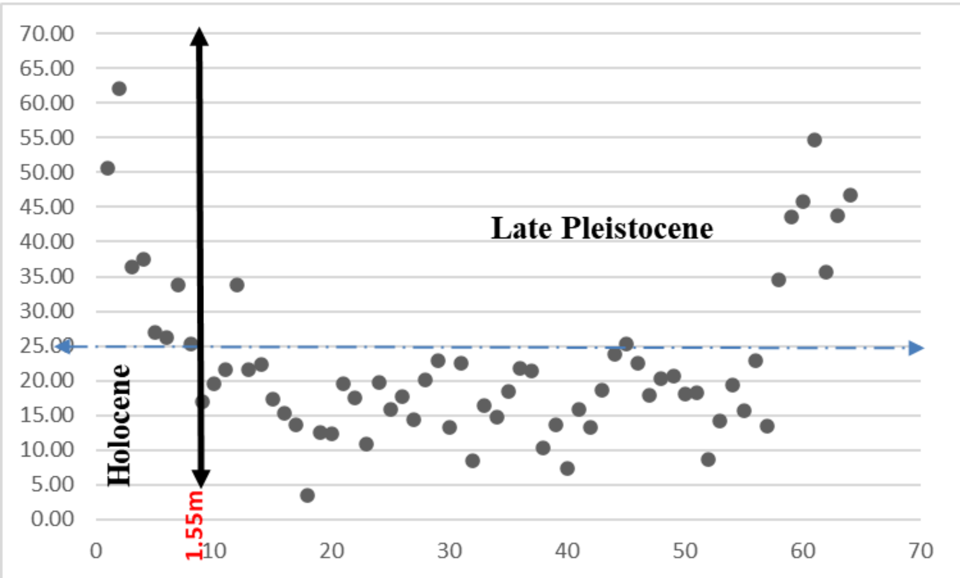


Fig. 2. Scatter plot from Krokšlys, showing the paleoclimatic (**referred here as Sr/Cu**) behaviour of samples. The baseline (blue dashed line) is at 25, where values above this signifies a dry and hot climate and below signifies a warm and humid climate.

APPENDIX 3-2

SCATTER PLOT CHARTS
DENGTILTIS OUTCROP

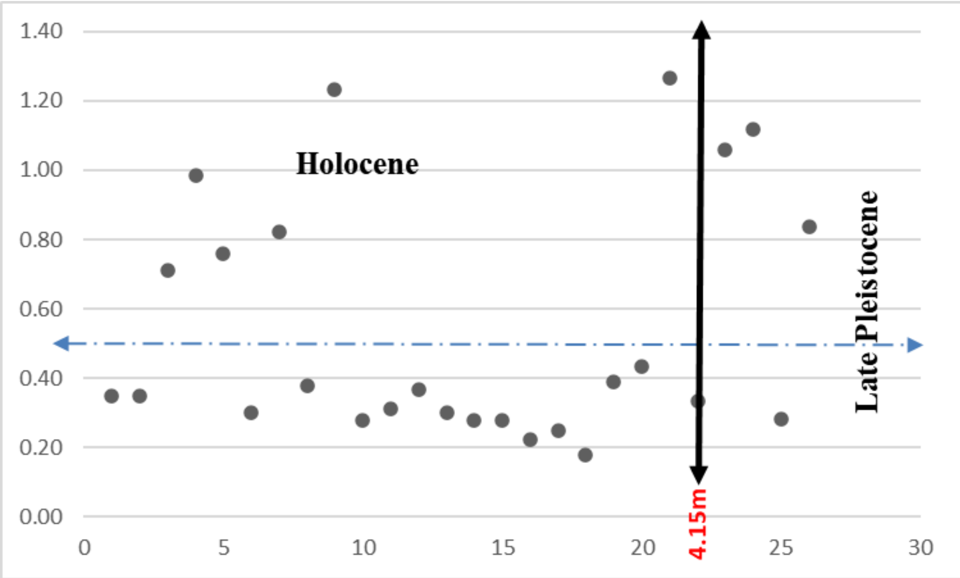


Fig. 3. Scatter plot from Dengtiltis, showing the paleo redox (**referred here as Cu/Zn**) behaviour of samples. The baseline (blue dashed line) is at 0.5, where values above this signifies an oxic environment and below signifies an anoxic environment.

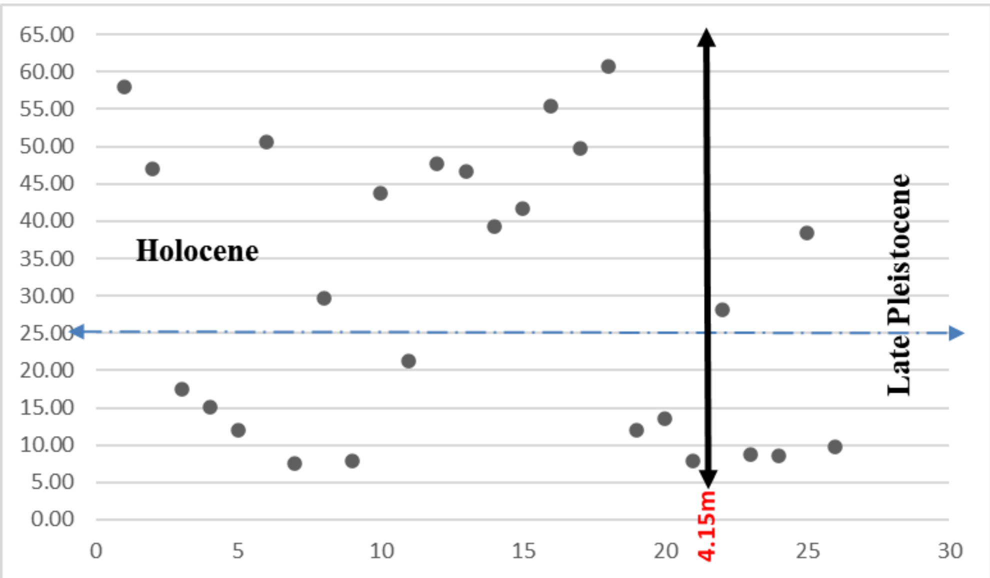


Fig. 4. Scatter plot from Dengtiltis, showing the paleoclimatic (**referred here as Sr/Cu**) behaviour of samples. The baseline (blue dashed line) is at 25, where values above this signifies a dry and hot climate and below signifies a warm and humid climate.

SCATTER PLOT CHARTS
ŠVENTOJI-46766 BOREHOLE

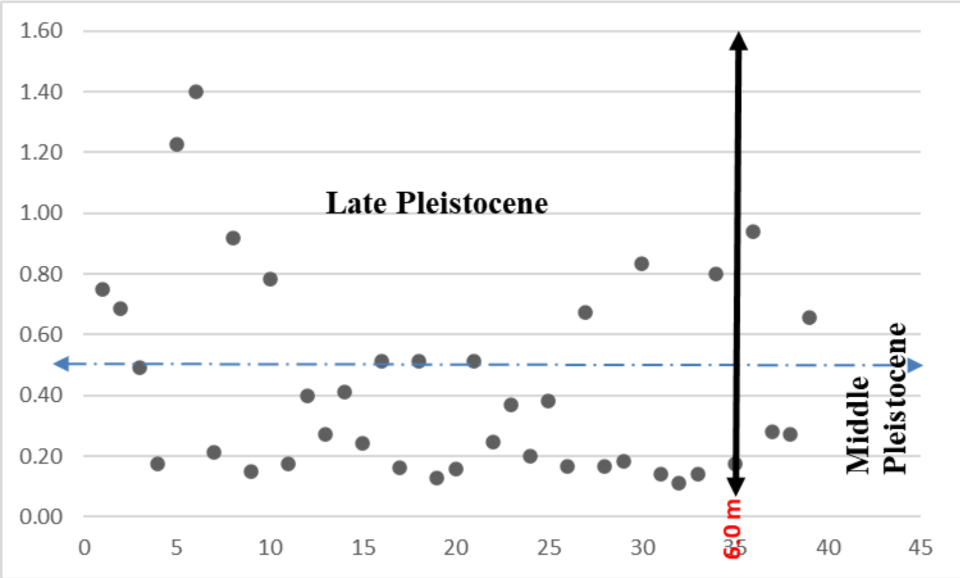


Fig. 5. Scatter plot from Šventoji-46766, showing the paleo redox (**referred here as Cu/Zn**) behaviour of samples. The baseline (blue dashed line) is at 0.5, where values above this signifies an oxic environment and below signifies an anoxic environment.

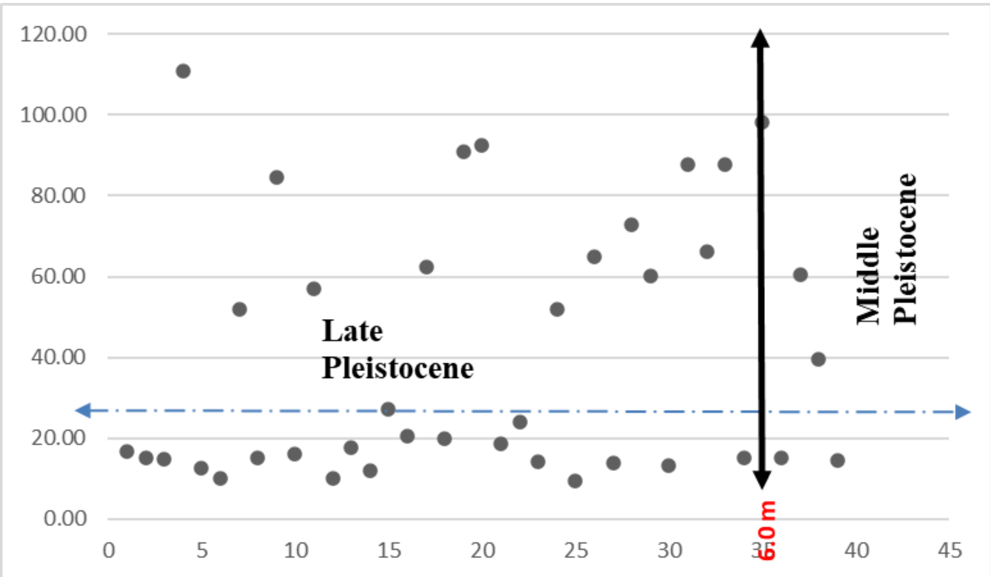


Fig. 6. Scatter plot from Šventoji-46766, showing the paleoclimatic (**referred here as Sr/Cu**) behaviour of samples. The baseline (blue dashed line) is at 25, where values above this signifies a dry and hot climate and below signifies a warm and humid climate.