GEOLOGIJA. 2013. Vol. 55. No. 1(81). P. 1–7

Rare earth elements of Holocene sediments in the South-Eastern Baltic Region (Nida VI borehole, Lithuania)

Donatas Kaminskas,

Albertas Bitinas

Kaminskas D, Bitinas A. Rare earth elements of Holocene sediments in the South-Eastern Baltic Region (Nida VI borehole, Lithuania). *Geologija*. Vilnius. 2013. Vol. 55. No. 1(81). P. 1–7. ISSN 1392-110X.

Rare earth elements in three groups of Nida-VI borehole sediments were determined. Obtained data could be employed for more detailed further studies of the south-eastern Baltic Holocene deposits. Si and Al were the main criteria for categorization of the cross-section. The North American Shale Composite shale-normalized along with supplemented original analytical data is presented in the article. Possible relationship of the rare earth elements distribution to the origin of the sediments is discussed briefly.

Key words: geochemistry, rare earth elements, Holocene, south-eastern Baltics

Received 20 May 2013, accepted 25 June 2013

Donatas Kaminskas. Department of Geology and Mineralogy, Vilnius University, 21/27 M. K. Čiurlionio Street, LT-03101 Vilnius, Lithuania. E-mail: donatas.kaminskas@gf.vu.lt
Albertas Bitinas. Coastal Research and Planning Institute, Department of Geophysical Sciences, Klaipėda University, 84 H. Manto Street, LT-92294 Klaipėda, Lithuania. E-mail: albertas.bitinas@corpi.ku.lt

INTRODUCTION

The Curonian Lagoon was an object of many previous studies. The results of earlier studies were summarized in Kabailienė's articles (1967, 1995, 1997). The pollen and diatom composition was the primary target. The reconstruction of the geological history and paleogeographic changes in the Lithuanian Maritime Region during the Late Glacial and Holocene was done by Bitinas et al. (2002), Bitinas and Damušytė (2004) and Damušytė (2011). New geochemical data from the Curonian Lagoon was obtained during the state funded project entitled "Palaeogeographic Changes in Lithuania throughout the Postglacial Time under the Baltic Sea and Land Interaction" in the years 2010–2011. It is well known that rare earth element (REE) distribution in the sediment depends on their contents in the parent rocks and their distribution in the mineral phases; the ability of secondary minerals formed during the reactions to accommodate REE. Early studies showed that during weathering REEs were mobile and fractionate (Nesbit, 1979). Thus, quantities of REEs may vary depending on transportation and sedimentation. Sources of REEs could be of various origins: suspended river runoff, aeolian dust, glacier runoff, etc. Lithological or mineralogical control over REE distribution is observed in the Nida-VI borehole cross-section. This preliminary study aims to report newly obtained geochemical data on Holocene sediments data from Lithuania.

DATA AND ANALYTICAL METHODS

The Holocene sediments of the Nida VI borehole (Fig. 1) in the present study have been categorized into three groups according to the Si and Al oxides ratio (Fig. 2). The ratio of Si and Al was assumed to reflect the clay content of the sediment. It is known that the clay content directly influences the distribution and quantities of REEs in sediments. On the

Fig. 1. Location of the Nida VI borehole
1 pav. Nidos VI gręžinio vieta

other hand, quartz is generally thought to contain almost no REEs and act solely as a dilution factor for REE in sediments (Taylor, McLennan, 1985). All three (A, B and C) established groups at some extent represent sediments of different origin: aeolian sand (Group A), lagoon sediments (Group B) and glaciofluvial-fluvial sediments (Group C). Group A mainly consists of fine grained quartz dominated sand, Group B is composed of the so called “lagoon marl” containing elevated contents of silt, carbonate and organic material, Group C is dominated by mixed in grain size sand of quartz with admixture of feldspars (Table 1).

The normalization of REE to shale is applied to study their variations in hypergene processes. The Post-Archean Australian Shale (PAAS) or North American Shale Composite (NASC) is commonly used for normalization. The REEs in this study were normalized using the North American Shale Composite.

Sixty samples from the Nida VI borehole were analysed by ACME Labs Ltd. Major elements SiO_2 and Al_2O_3 were analyzed by ICP emission spectrometry following a lithium metaborate / tetraborate fusion and dilute nitric digestion. The de-

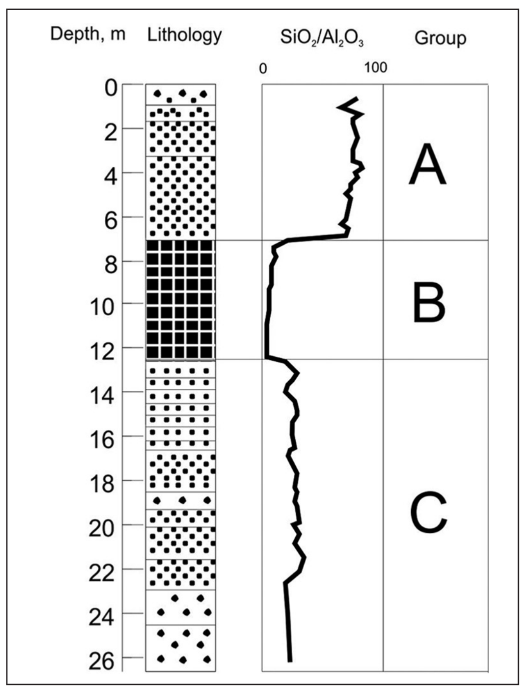

Fig. 2. Simplified lithological column, SiO_2/Al_2O_3 ratio and groups of sediments of the Nida VI borehole. See Table 1 for details
2 pav. Supaprastinta Nidos VI gręžinio litologinė kolonėlė, SiO_2 ir Al_2O_3 santykis bei nuosėdų grupės. Žr. 1 lentelę

Table 1. **Lithological description of the Nida VI borehole**

1 lentelė. **Litologinis Nidos VI gręžinio aprašymas**

Group	Description
A	Sand, fine-grained, greenish- or yellowish-grey and grey, composed of feldspar-quartz.
B	"Lagoon marl" (mixture of silt, fine sand, carbonates and organic matter), grey, massive, in the lowermost part – black-grey and patched, carbonaceous, with abundance of very small remnants of fossil mollusc shells, wood, fish bones, etc.
C	Layering of sand: from various grained (prevailed medium-grained) in the lowermost part of the section to fine-grained in the middle and upper ones. Sand, generally yellowish-grey, composed of carbonates-feldspar-quartz.

tection 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. The original data is presented in Table 2.

RESULTS AND DISCUSSION

Not only Si and Al oxides ratio but all REE averages for the established groups of the sediments are different (Table 3). The highest average values of REEs are in Group B, while the lowest ones are in Group A. In all samples shale-normalized values of REE are below 1, which indicates that sediments are

Table 2. **REE elements in the Nida VI borehole (ppm)**

2 lentelė. **RŽE Nidos VI gręžinyje (ppm)**

Depth, m	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
0.65	3.5	7.60	0.8	3.30	0.57	0.15	0.51	0.09	0.56	0.10	0.29	0.05	0.21	0.04
0.95	4.1	7.10	0.9	2.70	0.66	0.15	0.46	0.07	0.31	0.09	0.20	0.04	0.41	0.03
1.05	5.5	10.90	1.2	4.70	0.81	0.17	0.84	0.11	0.57	0.13	0.28	0.06	0.39	0.06
1.35	4.9	10.20	1.1	4.40	0.89	0.21	0.77	0.12	0.62	0.13	0.38	0.06	0.52	0.07
1.60	8	17.20	2.0	8.10	1.33	0.23	1.08	0.16	0.78	0.18	0.44	0.08	0.43	0.08
1.80	5.7	12.00	1.5	5.10	1.07	0.22	0.93	0.15	0.88	0.16	0.59	0.09	0.58	0.11
2.45	5.5	11.30	1.2	5.30	0.88	0.19	0.86	0.15	0.68	0.15	0.44	0.07	0.35	0.07
3.00	4.1	9.20	1.0	4.20	0.69	0.20	0.67	0.11	0.61	0.12	0.30	0.06	0.34	0.06
3.45	4.8	10.00	1.1	4.30	0.84	0.20	0.80	0.13	0.60	0.13	0.32	0.06	0.27	0.07
3.60	4.2	8.50	1.0	3.90	0.72	0.19	0.67	0.11	0.57	0.11	0.33	0.05	0.31	0.06
3.80	4.3	9.00	1.0	3.90	0.72	0.13	0.64	0.10	0.61	0.11	0.34	0.06	0.33	0.06
4.00	4.9	10.00	1.1	4.40	0.86	0.17	0.69	0.10	0.58	0.10	0.30	0.05	0.35	0.06
4.20	3.9	7.70	0.9	3.00	0.64	0.16	0.62	0.10	0.48	0.10	0.31	0.05	0.32	0.06
4.50	5.9	11.20	1.4	4.30	1.04	0.16	0.85	0.13	0.65	0.15	0.33	0.05	0.35	0.06
4.80	4.1	8.10	0.9	3.80	0.63	0.17	0.60	0.09	0.45	0.08	0.29	0.05	0.24	0.05
5.00	4.6	9.40	1.1	4.20	0.72	0.18	0.70	0.12	0.56	0.12	0.37	0.05	0.35	0.05
5.20	3.8	7.80	0.9	3.50	0.65	0.15	0.53	0.09	0.51	0.11	0.28	0.04	0.23	0.05
6.15	4	7.70	1.0	3.90	0.61	0.15	0.60	0.10	0.52	0.09	0.32	0.04	0.27	0.06
6.35	3.9	7.90	0.9	3.30	0.61	0.16	0.55	0.09	0.47	0.09	0.31	0.05	0.26	0.05
6.60	4.2	8.60	1.0	4.00	0.73	0.16	0.66	0.11	0.53	0.10	0.29	0.06	0.31	0.05
6.85	4.2	8.20	1.0	3.50	0.70	0.15	0.55	0.10	0.52	0.08	0.24	0.04	0.30	0.05
7.40	17.1	34.20	4.2	15.90	3.20	0.60	2.99	0.45	2.87	0.53	1.61	0.26	1.66	0.27
7.65	15.8	30.60	3.7	14.70	2.84	0.52	2.36	0.42	2.22	0.48	1.40	0.22	1.31	0.20
7.85	16.2	33.60	4.2	14.50	3.10	0.54	2.62	0.43	2.45	0.51	1.47	0.23	1.60	0.25
8.25	17.2	33.90	4.1	15.40	3.02	0.54	2.67	0.44	2.67	0.50	1.67	0.23	1.52	0.25
8.60	17.4	35.40	4.2	17.00	3.16	0.61	2.80	0.46	2.70	0.56	1.55	0.25	1.56	0.24

Table 2 **(continued)**
2 lentelė **(tęsinys)**

9.10	17.3	35.70	4.3	15.90	2.99	0.61	2.76	0.44	2.73	0.50	1.59	0.23	1.80	0.26
9.35	18.2	37.00	4.4	16.40	3.19	0.65	2.95	0.49	2.98	0.57	1.49	0.25	1.45	0.24
9.90	19.6	40.30	4.9	17.80	3.57	0.68	3.25	0.49	2.91	0.56	1.67	0.24	1.72	0.23
10.30	22.6	47.80	5.6	20.50	4.19	0.79	3.71	0.57	3.39	0.70	2.04	0.30	2.05	0.31
10.90	23.6	47.90	5.8	20.90	4.10	0.76	3.77	0.59	3.56	0.65	1.87	0.26	2.02	0.28
11.30	22.8	46.90	5.6	21.60	4.05	0.78	3.51	0.55	3.39	0.66	2.00	0.27	1.86	0.29
11.75	26.9	54.70	6.6	26.10	4.65	0.89	4.22	0.64	3.81	0.68	2.03	0.31	2.18	0.32
12.35	27.2	54.30	6.4	24.40	4.35	0.86	4.10	0.63	3.82	0.69	2.08	0.32	2.15	0.32
12.80	20.3	41.90	5.1	18.50	3.66	0.69	3.01	0.49	3.04	0.58	1.72	0.26	1.71	0.25
13.15	8.4	16.50	1.9	7.00	1.36	0.29	1.15	0.21	1.04	0.25	0.58	0.14	0.80	0.14
13.40	7.8	15.90	1.8	7.60	1.29	0.33	1.13	0.20	1.16	0.23	0.63	0.12	0.78	0.11
13.65	9.6	20.00	2.3	8.80	1.65	0.36	1.47	0.27	1.40	0.33	0.86	0.14	0.86	0.15
14.00	8.3	16.60	2.0	7.20	1.57	0.35	1.31	0.24	1.46	0.27	0.93	0.14	0.90	0.15
14.35	8.4	16.90	1.9	7.50	1.40	0.32	1.16	0.20	1.18	0.23	0.67	0.11	0.63	0.13
14.80	7.4	14.70	1.7	6.80	1.30	0.29	1.00	0.19	0.97	0.26	0.66	0.12	0.63	0.12
15.05	7.5	14.60	1.7	6.70	1.26	0.27	0.99	0.20	1.03	0.21	0.79	0.12	0.61	0.12
15.30	8.7	17.80	2.2	8.10	1.54	0.37	1.60	0.29	1.62	0.39	1.09	0.17	1.10	0.21
16.50	8	16.50	1.9	6.80	1.39	0.31	1.11	0.20	1.09	0.25	0.54	0.10	0.63	0.11
16.70	10.9	21.90	2.5	9.10	1.77	0.39	1.65	0.28	1.63	0.33	1.02	0.16	0.94	0.16
16.85	12.7	26.90	3.1	11.40	2.23	0.46	2.02	0.35	1.95	0.43	1.31	0.20	1.21	0.20
17.70	6.7	13.70	1.6	6.10	1.14	0.30	0.99	0.16	0.85	0.17	0.58	0.09	0.58	0.10
18.35	7.2	14.10	1.6	5.80	1.20	0.26	1.19	0.22	1.49	0.31	1.01	0.17	1.00	0.17
18.55	7.1	14.80	1.6	6.20	1.14	0.29	0.98	0.16	0.88	0.21	0.53	0.07	0.48	0.10
18.90	7.3	13.20	1.7	6.40	1.23	0.31	1.14	0.18	1.07	0.22	0.69	0.10	0.68	0.10
19.15	6.6	13.10	1.6	5.20	1.11	0.29	0.97	0.16	0.90	0.15	0.52	0.08	0.50	0.09
19.85	7.6	15.30	1.7	6.30	1.19	0.31	1.02	0.16	0.97	0.19	0.61	0.09	0.50	0.09
20.10	11.7	25.00	2.7	10.20	2.00	0.38	1.72	0.31	1.71	0.35	1.14	0.16	1.08	0.17
20.45	6.7	12.90	1.5	4.90	1.07	0.31	0.92	0.14	0.81	0.13	0.48	0.06	0.59	0.07
20.90	7.1	14.50	1.7	5.80	1.03	0.30	0.96	0.16	0.75	0.19	0.49	0.08	0.55	0.07
21.50	6	12.00	1.4	5.70	0.95	0.26	0.88	0.16	0.78	0.15	0.52	0.08	0.45	0.08
22.10	6.3	12.20	1.4	5.60	1.03	0.26	0.91	0.15	0.74	0.14	0.43	0.06	0.42	0.07
22.60	11.1	22.60	2.5	9.30	1.95	0.43	1.64	0.32	1.74	0.39	1.20	0.18	1.04	0.20
24.00	11.5	24.00	2.8	10.50	2.07	0.33	1.58	0.25	1.10	0.23	0.58	0.08	0.55	0.08
26.20	7.9	15.10	1.7	6.70	1.22	0.30	1.17	0.18	0.87	0.22	0.70	0.09	0.54	0.08

depleted in REE if compared to NASC (Table 4). In general, all three groups are different in averages of shale-normalized REE values. The fractionation curves of REEs of goups A and B, B and C are quite different (Fig. 3). Such a difference is determined by different lithology and mineralogical composition of the sediments. The shape of REE curves of A and C group sediments is quite similar (Fig. 3). It is hard to judge what factor is the most influencing, aeolian transport or influence of shoreline currents, but possibly both are responsible. A brief description of the established groups of sediments is presented below.

Group C

Group C represents a complex of freshwater basin sediments starting from glaciofluvial sand deposited in the Baltic Ice Lake during relatively cold climate conditions (at the lowermost part of the sediment complex) until sandy sediments deposited during a warm climate episode of Early Atlantic, probably during the initial phase of the Litorina Sea lagoon formation (middle and upper parts of the sediment complex). The primary source of the Litorina Sea sediments was the same glacigenic sediments, only re-deposited in the new basin. The fluvioglacial sediments contain more feldspars but

Table 3. **The averages of SiO_2/Al_2O_3 and REE contents (ppm) in Nida VI borehole sediments**
3 lentelė. **SiO_2/Al_2O_3 vidurkiai ir RŽE kiekiai (ppm) Nidos VI gręžinio nuosėdose**

Group	SiO_2/Al_2O_3	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
A	73.91	4.67	9.50	1.09	4.18	0.78	0.17	0.69	0.11	0.57	0.12	0.33	0.06	0.34	0.06
B	7.67	20.16	41.01	4.93	18.54	3.58	0.68	3.19	0.51	3.04	0.58	1.73	0.26	1.76	0.27
C	26.26	8.34	16.83	1.95	7.27	1.40	0.32	1.23	0.21	1.17	0.25	0.74	0.12	0.72	0.12

Table 4. **The averages of shale-normalized REE contents in Nida VI borehole sediments**
4 lentelė. **Normalizuotų RŽE kiekių vidurkiai Nidos VI gręžinio nuosėdose**

Group	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
A	0.15	0.13	0.14	0.13	0.14	0.14	0.13	0.13	0.11	0.11	0.10	0.11	0.11	0.12
B	0.63	0.56	0.62	0.56	0.63	0.55	0.61	0.60	0.58	0.56	0.51	0.52	0.57	0.55
C	0.26	0.23	0.25	0.22	0.25	0.26	0.24	0.25	0.22	0.24	0.22	0.23	0.23	0.26

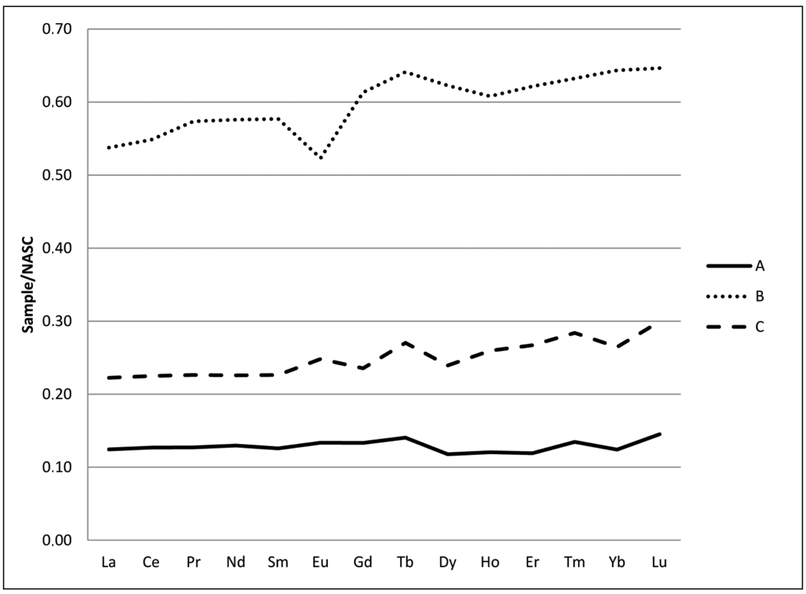

Fig. 3. Shale-normalized REE distribution diagram for averages of A, B and C sediments from the Nida VI borehole. For A, B and C explanation see the text
3 pav. Nidos VI gręžinio nuosėdų A, B ir C grupių normalizuotų RŽE vidurkių pasiskirstymo diagrama. A, B ir C išaiškinimą žr. tekste

less quartz, organic matter, carbonates if compared to Group A. The main source of the REEs in this unit is feldspars in sand and silt fraction.

Group B
The sediments of Group B have been deposited in a closed freshwater lagoon of the Litorina Sea during the late Atlantic and SubBoreal and is represented by the so-called "lagoon marl". The "lagoon marl" according to lithological and mineralogical data is a mixture of silt, fine sand, carbonates and organic matter. The lagoon was very shallow with an unstable water level: in the so called "lagoon marl" sedimentalogical gaps with eroded surfaces were observed (Damušytė, 2011). The average of Si/Al of this group of sediments is the lowest (7) if compared to groups A and C, 74 and 26, respectively. The REE shale-normalized average curve indicates depletion of Eu. In fact, this could be explained by the removal or absence of plagio-

clases (albite). Within the REE suite, Eu and Ce can develop anomalies (i. e. show different behavior from neighboring elements). Eu anomalies are generally considered to be inherited from source rocks while Ce anomalies are generated post-depositionally (McLennan, 1989; Jin et al., 2006; Pourret et al., 2008). No Ce anomalies, however, were observed. The average negative Eu anomaly (0.88) is observed in Group B, while in groups A and C positive anomalies are observed (1.06 and 1.10, respectively). The positive Eu anomaly in groups A and C is likely due to feldspar becoming a major REE contributing phase. The Ce anomaly was calculated using the following formula: $2Ce/Ce^{NASC}/(La/La^{NASC}+Pr/Pr^{NASC})$, while the Eu anomaly is calculated as follows: $2Eu/Eu^{NASC}/(Sm/Sm^{NASC}+Gd/Gd^{NASC})$.

Group A

The sediments of Group A are supposed to be mostly of aeolian origin. It is supposed that Group A sand could be transported by wind and deposited directly in the lagoon near shore, or it could be derived from eroded "aeolian horns" and sand was redistributed by circulating currents along the lagoon coast. The high (74) Si and Al ratio, XRD and visual inspection of the sediment confirms that quartz is the main constituent. Indeed, both averages and shale-normalized REE averages of Group A are the most depleted if compared to the sediments of groups B and C. The shape of the REE curve shows that in Group A HREE is slightly depleted compared to LREE. It could be an indication of aeolian influence when heavy fraction mostly as a source of HREEs diminishes.

The chemical weathering and fluvial process of sorting should be responsible for REE variation in the sediments of Group C. The well pronounced Eu negative anomaly in Group B of sediments is probably the result of increase in weathering of feldspar which is the main source of Eu. The ratio of LREE (La to Gd) and HREE (Tb to Lu) of groups B and C is 0.92 and 0.93, respectively. The mentioned ratio of Group A is 1.03. This is again in favor of aeolian origin of the latter group of sediments. The HREEs are mostly related to the minerals like garnet, titanite, rutile, zircon which are commonly depleted in aeolian origin of sediments. The main carrier of LREE is related to feldspar. Since the patterns of REEs of groups A and C are quite similar it could be concluded that the sediments source was the same. However, it is still unclear whether the sands were deposited by wind or sea shoreline currents. The inherited REEs pattern, abundant quartz, depleted REE quantities rather suggest that mainly it was deposited by wind.

ACKNOWLEDGEMENTS

This research was funded by a grant (No. LEK-10005) from the Research Council of Lithuania.

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Donatas Kaminskas, Albertas Bitinas

RETIEJI ŽEMĖS ELEMENTAI PIETRYČIŲ BALTIJOS HOLOCENO NUOSĖDOSE (NIDOS VI GRĘŽINYS, LIETUVA)

Santrauka

Trijose nuosėdų grupėse iš Nidos gręžinio buvo nustatyti retųjų žemių elementų kiekiai. Gauti duomenys gali būti naudojami tolesniuose Pietryčių Baltijos holoceno nuosėdų tyrimuose. Silicio ir aliuminio kiekiai buvo pagrindiniai kriterijai skaidant pjūvį. Straipsnyje pateikiami pagal Šiaurės Amerikos skalūno kompozitą normalizuoti ir pirminiai analitiniai duomenys. Trumpai aptariamas galimas ryšys tarp retųjų žemių elementų paplitimo ir nuosėdų kilmės.

Raktažodžiai: geochemija, retieji žemės elementai, holocenas, Pietryčių Baltija