Rare-earth element geochemistry of Ordovician and Silurian shales in Lithuania: A provenance study

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Šliaupa S. Rare-earth element geochemistry of Ordovician and Silurian shales in Lithuania: a provenance study. *Geologija*. Vilnius. 2002. N. 37. P. 3–19. ISSN 1392–110X.

The Baltic basin is a part of the Dniepr–Baltic system of marginal basins established in Vendian – Early Palaeozoic time due to continent breaking along the Baltica margin. The Vendian – Middle Ordovician evolution of the basin is described in terms of passive continental margin. In Late Ordovician–Silurian time the subsidence of the basin drastically increased; that is related to the docking of Eastern Avalonia to the western margin of Baltica, associated with a gradual increase in terrigenous supply to the basin. The Ordovician and the former part of the Silurian are described in terms of starved basin which evolved into an overfilled foreland basin by the end of the Silurian – Earliest Devonian. Deep water graptolithic shales dominate over the western and central parts of the basin. In the east they grade into shallow-water carbonates. Close to the North German–Polish Caledonides (NGRC) siltstones were deposited since Llandovery and Wenlock.

The previous lithofacies studies suggest the domination of the eastern (platform) provenance during the Ordovician and the former part of the Silurian, while the western (orogenic) area supplied the major part of terrigens in the middle and late Silurian. Seeking to map the spatial distribution of differently sourced shales and to reveal the temporal trends in the provenance, rare-earth and trace elements were studied in shale and marlstone sampled in one Ordovician section and three representative Silurian wells located in eastern, central and western Lithuania, thus examining the three major lithofacies belts recognised in the central and eastern parts of the Baltic basin. Because REE are not easily fractionated during sedimentation, sedimentary REE patterns provide an index to the average composition of the provenance.

Ordovician and Silurian shales show different REE patterns, pointing to different sources. The Silurian shows a strong similarity of all samples, thus pointing to the domination of one source during the Silurian. Comparison with sediments of different tectonic setting indicates the strongest affinity to source rocks deposited on the passive continental margins. This might be alternatively interpreted as an indication of (1) dominating influx of terrigens from the eastern Sarmatia–Fennoscandia platform or (2) recycled orogen type of the western Caledonides. The similarity of the REE patterns for all samples points to a domination of one terrigenic source in the territory of Lithuania during the Silurian. Yet, a miserable addition of the mafic component in the late Silurian, recognised in the western and central lithofacies, is likely to reflect the advancement of mafic sources. Also, Archean-sourced-like shales were reported from the easternmost part of the basin from Ludlow and Pridoli rocks, which strongly suggests an increased influx from the east in the latter part of the Silurian, which is explained in terms of the basin regression and advancement of the eastern shore line.

Keywords: Silurian, Ordovician, provenance, REE, foreland, geochemistry

Received 18 February 2002, accepted 30 February 2002

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INTRODUCTION

Ordovician sediments are only a few hundred meters thick, while Silurian deposits represent the main bulk of the sedimentary pile of the Baltic basin. The thickness of Silurian sediments increases to the south-west, towards the edge of the East European Craton, while Ordovician sediments show an opposite trend referred to non-compensated sedimentation. Close to the Tornquist Zone the thickness of Silurian deposits exceeds 3.5 km (Grigelis, 1994), and palaeoreconstructions indicate an originally thicker

Silurian pile (Vejbaeck, 1994). In the Fjerritslev trough located close to the Starslund-Tornquist zone, the preserved Lower Palaeozoic sediments are suggested to be as thick as 6–7 km (Lie, Andersson, 1998). The backstripping showed a drastic acceleration of the subsidence during the Silurian, preceded by a slow Late Cambrian–Ordovician subsidence (respectively more than 100 m/Ma and 2–3 m/Ma). This was related to the onset of the collision regime along the south-western margin of the Baltica continent due to docking of Eastern Avalonia to the western margin of the Baltica continent, which earlier presented a passive continental margin (Sliaupa et al., 1997; Poprawa et al., 1997). The overthrusting of the North German–Polish Caledonides onto the craton margin evoked the subsidence of the marginal Baltic basin. Obduction of orogenic wedges onto the platform was confirmed by commercial seismic data (Hoffman, Franke, 1997) and DSS profiling (Krawchik et al., 1999; Abramovitz et al., 1998). A concave shape of backstripped curves indicating acceleration of the basin subsidence is thought to be related to the advancement of the accretionary wedge and to an increasing orogenic load onto the craton margin during the Silurian (Sliaupa et al., 1997; Poprawa et al., 1997). This is in accordance with the sedimentation trend, indicating the starvation stage of the Baltic basin in the beginning of the Silurian (Lapinskas, 1987) to its overfilling in the beginning of the Devonian (Suveizdis, Sliaupa, 1999). The lithofacies distribution suggests the prevalence of the eastern source during the Ordovician and the former part of the Silurian time, whereas the western provenance became dominant since late Wenlock (Lapinskas, 1987; Laškovas, 2001). The role of the western sources is advocated by sedimentation of siltstones since the Llandovery and Wenlock close to the deformation front of the North German–Polish Caledonides (McCann, 1992). Also, there are indications of western sourcing in the Late Ordovician, evidenced by occurrence of siltstones in the westernmost part of the Baltic basin. The dominant clastic sedimentation started in the German sector of the foreland; *e.g.*, siltstones, sandstones and mudstones constitute the Llandovery section of the G14-1/86 well (Maletz, 1997), and gradually progressed to the south and south-east relating to the oblique convergence of Eastern Avalonia (Jaworowski, 2000). Beier et al. (1999) interpreted these facts in terms of the domination of the terrigenic influx from the Avalonian orogen to the foreland. Still, the fine-grained composition of Silurian sediments in the Baltic foreland implies a rather low topography of the adjacent Caledonides which provided terrigens into the basin. The soft docking of Avalonia to the Baltica continent implied from the structural evolution in the foreland also suggests a rather low-topography orogen (Sliaupa, 1999).

In this way, both geodynamic reconstructions and lithological studies imply a strong correlation of the geological evolution of the Silurian Baltic basin to the build-up of the adjacent Caledonides, while the Ordovician passive margin sedimentation was linked to the adjacent platform. It is still not clear to what extent the western (Avalonian) provenance influenced the sedimentation processes in the basin competing with the eastern sources during the Silurian (Fig. 1) and in what time exactly the redistribution in provenances took place. Furthermore, the Scandinavian Caledonides might have been the third partner, as is indicated by occurrence of Burgsvik sandstones in the Gotland area (Kershaw, 1993), probably transported from the Scandinavian provenance. However, its contribution should not have been very extensive, taking into consideration the onset of the Silurian forebulge separating the Scandinavian foreland from the Baltic depression (Baarly, 1990).

Both palaeontological (*e.g.*, Cocks et al., 1997) and palaeomagnetic data (Torsvik, 1998) suggest a considerable attenuation of the Tornquist Sea separating the Baltica margin from the East Avalonian microplate by the Late Ordovician. However, the age of the Caledonian deformation and consequently the growth of the topography of the provenance are still questionable. South of the Ringkobing-Fyn High the low-metamorphic rocks yielded 440 Ma (Frost et al., 1981), which was interpreted as an evidence of the Caledonian deformation. Maletz et al. (1997), by studying the Lower Palaeozoic sediments of the Danish–Rügen area, dated the first phases of the deformation along the North German – Polish CDF as the Llanvirnian. Following these authors, the overthrusting of the accretional wedges led to downwarping of the Baltica margin, which resulted in a suppression of sedimentation in the foreland. McCann and Negendank (1997) suggested that tectonic activity in the German Caledonides as well as in its foreland increased significantly in the Ordovician. The succeeding strong overthrusting event triggered the fast overfilling of the foreland basin in the Llandovery (Maletz et al., 1997). This process continued into the Wenlock, what is indicated by an extensive deposition of shallow-water clastics in the Rügen–Danish area. In Western Pomerania, undeformed Pridoli shales and siltstones rest on the strongly tectonised older Silurian sediments (Milaczewski, Modlinski, 1998). Giese et al. (1997) documented Silurian tectonic structures in the Rügen Island, indicating an overthrusting of the northern margin of the Avalonian wedges onto the marginal foredeep lithofacies. Isotope studies from the Rügen Island point to the onset of deformations in the

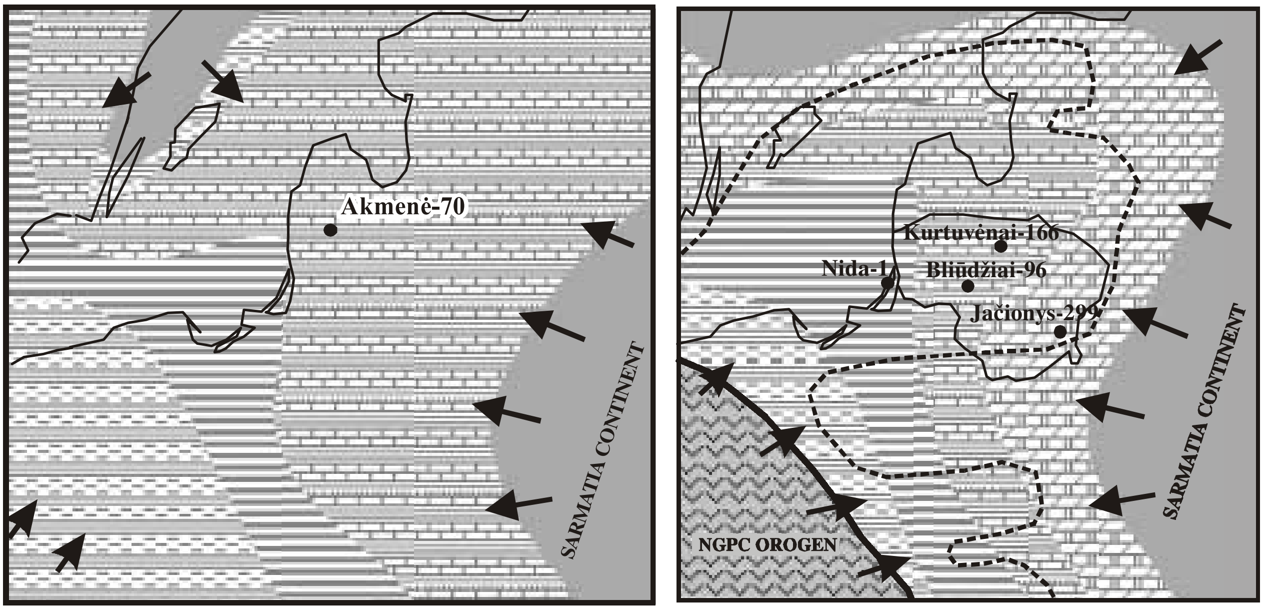

Fig. 1. Ordovician (left) and Silurian (right) lithofacies distribution in the western margin of East European Platform, following from the east to the west: carbonate, mixed carbonate and shale, shale, silty lithofacies. Arrows indicate sourcing of terrigens from different provenances. Broken line marks recent distribution of Silurian sediments. Locations of studied wells are indicated

1 pav. Ordoviko (kairėje) ir silūro (dešinėje) litofacijų pasiskirstymas vakariniame Rytų Europos platformos pakraštyje einant iš rytų į vakarus: karbonatinės, karbonatinės molingos, molingos, aleuritingos. Rodyklės rodo terigeninės medžiagos prinešimą iš skirtingų šaltinių. Punktyrinė linija žymi dabartinio silūro uolienų paplitimo ribą. Pažymėti tirti gręžiniai

Early Silurian (Giese et al., 1995). In the G14-1/86 well the whole section of Silurian deposits shows evidences of compressional deformation, thus implying collisional processes during the Silurian, still the intensity of deformation decreases up the section (Beier, Katzung, 1997). In the foredeep the Silurian igneous activity was just minor (Berthelsen, 1992).

The intensity of deposition and lithology of the foreland infill depends much on the distance to the deformation front and topography of the fold-belt. A most drastic change in the orogen topography occurs while accretional wedges straddle the continental slope of the foreland. For a long time the boundary between Baltica and Eastern Avalonia was considered to be confined to the Caledonian Defomation Front (CDF), which was encountered in wells in Denmark, NE Germany, NW Poland. However, since EUGENO-S deep seismic survey in the eighties it has been clearly realised that the major tectonic boundary between the two plates is located further to the south and west. This was supported by DSS studies BABEL (Meissner et al., 1994), DEKORP (Krawzhik et al., 1999), MONA LIZA (MONA LIZA Working Group, 1998; Abramovitz et al., 1998). Furthermore, the major suture has been suggested to be related to the Elbe Zone (Abramowitz et al., 1998; Kind et al., 1999), which is located 200–300 km west and south of the CDF, thus conflicting with the original idea of Cocks and Fortey (1982) relating the Baltic margin to the Tornquist lineament. Some palaeontological studies are also in favour of the Elbe zone as the major lineament separating the Baltica continent from Eastern Avalonia (McKerrow, van Staal, 1997). Other investigators place the major line inbetween these two, *e.g.*, the Starslund-Anklam Fault passing to the Schleswig-Holstein Fault (Hoffman, Franke, 1997).

Only scarce information is available on the CDF lithologies, which is important in provenance studies. Ordovician deep water rift-related sediments were preserved only in the NE German basin, whereas Silurian deposits were likely deposited and later eroded (McCann, 1996; Giese et al., 1994). Strongly deformed Middle Ordovician–Silurian rocks were drilled in Western Pomerania, west of the CDF (Milaczewski, Modlinski, 1998). Caradocian sediments are represented here by siltstones with some sandstones and piroclasts. Siltstones and shales dominate the Silurian succession.

The recent provenance studies consider just the westernmost part of the Caledonian foreland. It was shown that the deep water Ordovician sediments of the Rügen Island were derived from a volcanic provenance. The ophiolitic and volcanic arc sources are evidenced by sediment lithologies, and this was interpreted as the indicator of the southern polarity of the subduction which later on changed into the northern one (Franke et al., 1996). The greywackes provide information on the source lithologies, as they are least subjected to chemical weathering. Mineralogical studies in the Rügen area revealed ophiolitic sources of the Ordovician sediments (Giese, Katzung, Walter, 1994). Isotopic studies indicate that sediments of the Rügen Caledonides and the adjacent foredeep were sourced from different provenances (Tschernoster et al., 1997), having respectively Gondvana and Baltica affinities. A mixture of two sources took place in the Late Ordovician, suggesting a considerable narrowing of the Tornquist Sea.

The present study is aimed at the inspection of the REE and trace-element geochemistry of the Ordovician and Silurian shales of Lithuania to trace the major trends in the provenance. REE is a rather useful tool in studying shale provenance lithologies, because they may provide an information on the average composition of the exposed terranes supplying sediments to the sedimentary basin (McLennan et al., 1980; Bhatia and Taylor, 1981; Andre et al., 1986, etc.; Cullers, Podkovyrov, 2000; Nath et al., 2000). Despite some fractionation of REE during weathering, transportation and sorting, it is believed that the element contents is a function of the provenance lithologies (Bhatia, Taylor, 1981; Andre et al., 1986; McLennan, 1990; Condie, 1991; Johnsson, 2000). REE are characterised by low solubility during weathering, they have short residence times (<1 ka) in seawater (McLennan, 1982), consequently REE abundances in low temperature surface water are exceedingly low (McLennan, 1989). Furthermore, REE are relatively immobile during most post-depositional processes such as diagenesis and metamorphism.

The most important factors that determine the REE content in shales are source rocks geochemistry (Andre et al., 1986), and it is less controlled by weathering conditions (Brown et al., 1955; Duddy, 1980; Ronov et al., 1967), depositional environment (Tlig, Steinberg, 1982), diagenesis (Lev et al., 1999). It is well established that REE are carried mostly as suspended loads rather than in dissolved form (McLennan, 1989). Therefore, they may be transported almost in bulk from the parent rock to the basin. Some mobility of rare-earth elements during weathering processes were reported by Ronov et al. (1967), Roaldset (1973), etc. Following Schieber (1986), weathering conditions as well as conditions of deposition influence the REE patterns in shales. This can help in stratigraphic correlation of different basin lithofacies.

REE abundances were studied in the Ordovician shale and Silurian shales (Figs. 1, 2) seeking to obtain the evolutionary trend in the provenance areas, as well as to determine the tectonic scenario in the Silurian Baltic basin, since the tectonic setting of a sedimentary basin and the surrounding source area strongly imprint the REE patterns of the terrigens. Sediments deposited in the passive margin setting commonly show more differentiated rare-earth element patterns than those deposited near young volcanic arcs (McLennan, 1989). Bhatia and Taylor (1981) have studied REE differences in arc-derived and continental margin sediments in Australia, *i.e.* an attempt has been undertaken to examine the relationship between REE patterns and the tectonic setting of sediments. Totten and Weaver (2000) analysed the geochemical features of shales, seeking to identify their tectonic setting. Following J. Murphy

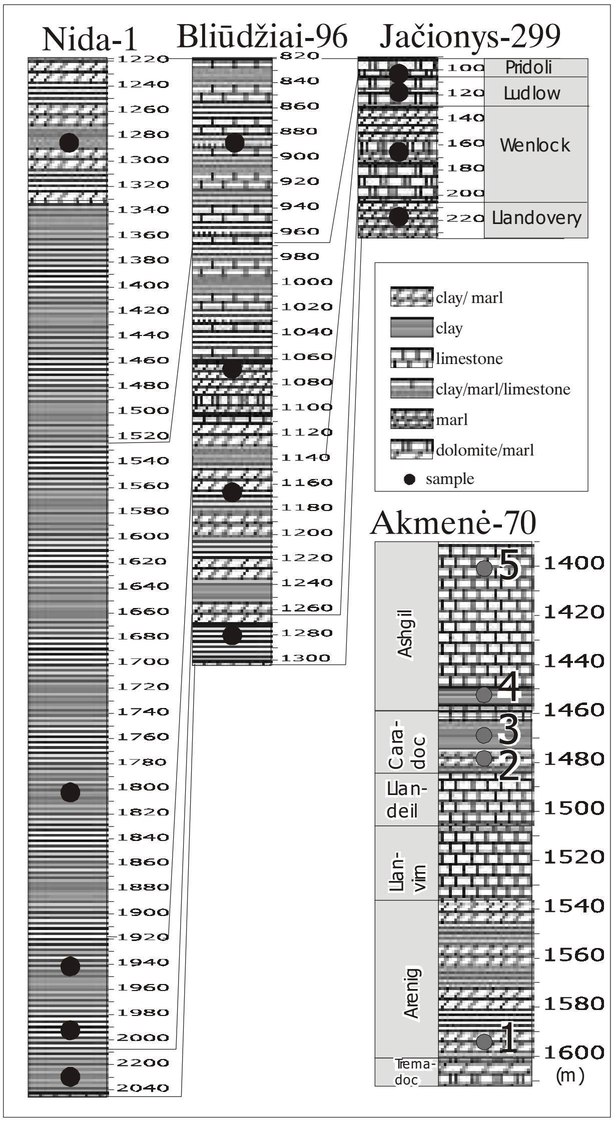

Fig. 2. Lithostratigraphy and sampling scheme of the wells studied

2 pav. Tirtų gręžinių litostratigrafinės kolonėlės, nurodyti bandinių paėmimo gyliai

(2000), gechemical signatures of clastic sediments hardly reveal the tectonic environment of the accumulating basin, showing rather the tectonic setting of the provenance.

1. ORDOVICIAN AND SILURIAN STRATIGRAPHY OF THE BALTIC BASIN

The thickness of Ordovician deposits ranges from 40 m in paleouplifts to 260 m in the deepest Jelgava depression. They are represented by carbonates (limestones, dolomites) intercalating with shales. All Ordovician stages are present in the succession of the Baltic basin. Breaks of sedimentation were rather short-term and restricted mainly to the marginal parts of the basin (Laškovas, 2001), indicating a persistent though low-rate subsidence of the Ordovician basin. Carbonates are more abundant on the basin flanks, while shales dominate the central and western portions of the Baltic basin.

The thickness of the Silurian succession increases westward, exceeding 3.5 km close to the Pomeranian CDF. Compared to the underlying Ordovician succession, the rate of deposition during the Silurian was one-two orders higher, indicating a drastically increased subsidence and an influx of fine clastics to the basin. The sedimentation was rather persistent in the Baltic basin during the Silurian, resulting in stratigraphic completeness, with no basin-wide hiatuses recognised. Breaks in the sedimentation are documented only on the periphery of the basin due to low-amplitude tectonic movements and sea level oscillations. The rate of sedimentation increased in the course of the Silurian. The thickness of the Llandovery does not exceed 60 m across the basin, whereas the Wenlock sediments are as thick as 600 m close to the Tornquist Zone (Лапинскас, 1987). The overlying Ludlow sediments are up to 2400 m thick. The Pridoli does not exceed 700 m in the west, and the original thickness was much larger.

The sedimentation environment of the Silurian basin deepened towards the western margin of Baltica (Пашкявичюс, 1982). Graptolite shales dominate the western and central parts of the Silurian basin (Лапинскас, 1987). They gradually give way to marlstones, limestones and dolomites in the east. Closest to the NGPC, deposition of siltstones started since the Llandovery to the middle Wenlock. The Llandovery – middle Wenlock sedimentation is considered in terms of a starvation stage, which was followed by compensated deposition during the Late Silurian. Increase in the terrigenous supply, inferred from the sediment thickness, is associated with a gradual shallowing of the depositional environment (Lapinskas 1996). This is associated with an increase in carbonate deposition (Musteikis, Kaminskas, 1996).

2. SAMPLING STRATEGY

The Ordovician samples were obtained from the Akmenė-70 well located in NW Lituhania, on the southern flank of the Jelgava depression, which resulted in abundance of shaly lithologies (Fig. 1). Five shale samples were collected from the Arenig, Johvi, Mossen, Fjacka and Porkuni stratigraphic levels (Fig. 2). The aim of the study was to recognise temporal changes in terrigen sourcing during the Ordovician and to compare them to Silurian provenance signatures.

Thirteen samples were collected from three representative wells (Jačionys-299, Bliūdžiai-96 and Nida-1) located respectively in eastern, middle and western Lithuania (Figs. 1, 2). These wells represent three major lithofacies zones of the Silurian basin (Fig. 1). The Jačionys-299 well penetrated marginal lithofacies composed of shallow-water shales, marlstones, limestones, dolomites, with domination of the latter two. Sediments were deposited in open shallow marine and lagoonal environments. Four samples were obtained from the Llandovery shale, Wenlock, Ludlow and Pridoli dolomitic marlstones (Fig. 2). The Bliūdžiai-96 well is located within the transition zone separating shallow-water carbonates in the east and deep shelf shales in the west. As compared to the Jačionys-299 well, the succession is of a more clayey composition, the Lower Silurian is dominated by graptolitic shales, whereas the Upper Silurian is largely composed of marlstones with limestones increasing upward. Four samples were collected from the Bliūdžiai-96 well, representing Llandovery and Wenlock shales, Ludlow and Pridoli marlstones (Fig. 2). The westernmost well Nida-1 penetrated deep-shelf graptolitic shales. Each stage was characterized by one sample, except Wenlock shales represented by two samples obtained from the lower and upper portions (Fig. 2) in order to register the geochemical trends associated with the most dramatic changes in the sediment supply to the basin. Six samples were collected for bulk chemistry analysis from the Kurtuvėnai-166 well located in central Lithuania. One sample represents Llandovery graptolitic shale, two samples were obtained from Wenlock clayey marlstone, two samples characterise Ludlow marlstone, one sample was taken from Pridoli.

3. RESULTS

3.1. Ordovician

Concentration of REE in Ordovician rocks from the Akmenė-70 well ranges from 134 to 174 ppm, while maximum abundance was documented in Porkuni shale, which is characterized by a minimum content of carbonates (LOI is only 6%, while other samples show 12–22%). The pattern of chondrite-normalised REE is rather similar in all samples (Fig. 5), showing enrichment in LREE and only miserable differentiation of HREE. The La_n/Sm_n ratio is 3.5–4.4 (minimum in Mossen shale and maximum in Fjacka shale). Gd_n/Yb_n ratio, which describes HREE differentiation, ranges in the order 1.14–1.65. The LREE / HREE ratio expressed as La_n/Yb_n varies from 7.2 to 10.5. The Eu/Eu* anomaly is around 0.7, which is close to the "standard" shales, except Fjacka shale (0.55). The REE patterns normalised to standard shales (NASC) show similar trends, with a characteristic positive Pr-to-Eu anomaly (Fig. 7). The main differences are related to background levels, relating to carbonate dillution. The Johvi shale shows some higher concentration of HREE. The Fjacka shale stays apart from the other Ordovician samples, indicating a gradual decrease in relative concentration from LREE to HREE. This possibly indicates different sourcing during Fjacka time.

Table 1. **REE concentrations (ppm) in Silurian shaly rocks, Lithuania. Indicatory ratios and abundances (%) of major elements are given bellow**
1 lentelė. **RŽE kiekis (ppm) silūro molingose uolienose (Lietuva). Toliau pateikti indikatoriniai elementų santykiai ir pagrindinių elementų koncentracija (%)**

Elements	Nida-1					Bliūdžiai-96				Jačionys-299			
	1	2	3	4	5	6	7	8	9	10	11	12	13
ppm													
La	32.3	31.9	33.1	33.1	37.6	28.2	28.9	28.2	37.3	13	5.8	20.9	29.8
Ce	60	68	66.7	66.6	74.3	53.1	53.7	55	73.3	26.1	12	44.6	60
Pr	8.01	9.23	8.91	8.5	10.33	6.75	7.13	7.63	10.29	3.56	1.7	6.17	7.91
Nd	28.5	32.5	31	30.9	36.7	24.2	25.8	26.5	36.4	12.4	6.5	22.1	27.5
Sm	5.2	6.9	6.0	5.9	7.0	4.6	5.0	5.3	6.7	2.3	1.1	4.5	5.2
Eu	1.2	1.44	1.35	1.31	1.55	1.06	1.12	1.25	1.5	0.61	0.44	1.01	1.17
Gd	5.58	6.61	6.09	5.96	7.28	4.65	4.97	5.61	6.72	2.38	1.47	4.52	5.05
Tb	0.82	1.06	0.94	0.92	1.16	0.71	0.77	0.84	1.02	0.34	0.20	0.63	0.79
Dy	4.18	5.21	4.73	4.39	5.94	3.61	3.79	4.18	5.13	1.74	1.04	3.13	3.89
Ho	0.87	1.05	1.00	0.89	1.19	0.75	0.78	0.87	1.04	0.36	0.20	0.66	0.84
Er	2.45	3.08	2.90	2.74	3.42	2.30	2.42	2.46	3.11	1.06	0.63	1.77	2.48
Tm	0.38	0.45	0.43	0.42	0.54	0.39	0.37	0.36	0.50	0.15	0.07	0.26	0.40
Yb	2.21	2.69	2.43	2.46	3.05	2.22	2.118	2.23	2.62	0.79	0.46	1.61	2.37
Lu	0.38	0.46	0.43	0.39	0.52	0.37	0.37	0.38	0.47	0.15	0.07	0.26	0.40
ΣREE	152	171	166	164	191	133	137	141	186	65	32	112	148
La_n/Yb_n	9.77	7.93	9.11	9.00	8.24	8.49	8.86	8.46	9.52	11.00	8.43	8.68	8.41
La_n/Sm_n	3.83	2.85	3.40	3.46	3.31	3.78	3.57	3.28	3.44	3.49	3.25	2.87	3.54
Gd_n/Yb_n	2.01	1.96	2.00	1.93	1.90	1.67	1.82	2.01	2.04	2.40	2.55	2.24	1.70
Eu/Eu*	0.685	0.655	0.687	0.679	0.667	0.705	0.691	0.705	0.687	0.801	1.06	0.688	0.702
Ta/Ta*	0.26	0.23	0.23	0.25	0.23	0.26	0.23	0.24	0.21	0.23	0.13	0.23	0.22
La/Th	2.86	2.80	2.93	3.15	2.96	2.71	2.49	3.00	3.06	3.02	5.27	2.94	2.87
%													
Ca	2.66	4.12	4.43	3.78	2.82	4.12	4.99	7.90	2.79	13.31	19.04	9.95	5.41
Mg	2.85	1.98	2.47	2.40	2.25	3.06	3.10	3.00	2.39	7.97	9.86	6.49	3.57
Fe	4.77	3.93	3.76	3.47	3.94	4.02	3.26	2.87	3.44	1.39	0.71	2.20	3.06
Ti	0.38	0.32	0.35	0.32	0.39	0.36	0.33	0.28	0.40	0.13	0.05	0.21	0.32
Al	8.15	6.78	7.06	6.41	7.04	7.37	5.75	5.49	7.23	2.83	1.10	4.07	5.27
Na	0.62	0.60	0.62	0.45	0.41	0.25	0.58	0.54	0.51	0.06	0.04	0.10	0.09
K	3.71	2.72	3.01	2.74	2.96	3.90	3.30	2.72	3.16	1.61	0.75	2.60	3.55
P	0.036	0.06	0.032	0.037	0.037	0.023	0.028	0.038	0.039	0.020	0.005	0.038	0.008

Samples: well Nida-1: *1* – 1286 m (S2pr); *2* – 1797 m (S2ld); *3* – 1940 m (S1w); *4* – 1992 m (S1w); *5* – 2030 m (S1lnd); well Blūdžiai-96: *6* – 889 m (S2pr); *7* – 1069 m (S2ld); *8* – 1165 m (S1w); *9* – 1274 m (S1lnd); well Jačionys-299: *10* – 99 m (S2pr); *11* – 118 m (S2ld); *12* – 165 m (S1w); *13* – 223 m (S1lnd)

3.2. Silurian

A content of rare-earth elements in Silurian samples vary in a wide range (from 32 to 190 ppm) (Table 1). A trend of REE increase from the shallow-water lithofacies of the Jačionys-299 well in the east to the deep-shelf shales of the Nida-1 well in the west is distinct. An average content of REE in Silurian shales of the Nida-1 well, estimated for 5 samples, is 168 ppm, whereas shales and marlstones of the Bliūdžiai-96 well average to 149 ppm and to only 89 ppm in Jačionys-299. Moreover, an upward decrease of REE abundances is reported from all the wells. These trends are explained in terms of carbonate dilution effect. Carbonate sediments typically have substantially lower total REE abundances than do clastic sediments (McLennan, 1989). Therefore, admixture of dolomite and calcite results in a lower content of REE in the rock. It is seen in Fig. 3 that contents of Ca and Mg sistematically increase from Nida-1 to Jačionys-299. The vertical trends are more complex, though the general upward increase is quite obvious. Figure 4 illustrates this strong invert correlation of REE to Ma and Ca (–0.96 and –0.94, respectively), which are the constituents of the carbonate admixture in Silurian shales. Clay minerals contain the major bulk of REE, as is seen in REE *vs*. aluminium and REE *vs*. potassium diagrams (Fig. 4). The lowest content of REE (32 ppm) was registered in the sample taken from the Ludlow dolomitic marsltone in the Jačionys-299 well, which shows the highest admixture of Ca and Mg (Fig. 4). The highest value was measured in the Llandovery shale in the Nida-1 well (190 ppm). Furthermore, the Llandovery shales are most enriched in REE in all the wells (147–190 ppm). The Wenlock deposits contain remarkably lower amounts of REE (112–164 ppm), which are slightly higher than those reported from Ludlow (32–171 ppm) and Pridoli (65–152 ppm).

Normalised to chondrite, REE abundances indicate that despite considerable variations in contents, the samples studied have striking similarities in REE patterns (Fig. 5). They show a steep LREE slope and a rather flat HREE trend. The La_n/Sm_n ratio, indicating the fractionation of light REE, is fairly uniform for all samples, ranging from 2.85 to 3.83. No regular trend has been stated for both lateral and vertical variations. The Bliūdžiai-96 and Jačionys-299 wells show similar La_n/Sm_n patterns with a minimum in Wenlock rocks and increasing ratios through the Ludlow to Pridoli. Pridoli shows the maximum ratio in all the wells. Heavy REE are much less fractionated, as is indicated by low ratios of Gd_n/Yb_n varying from 1.67 to 2.55. The LREE / / HREE ratios expressed as La_n/Yb_n are quite variable (8.24–11.0). The highest values were obtained from the Pridoli shales of the Nida-1 and Jačionys-299 wells. No regular trends were recognised.

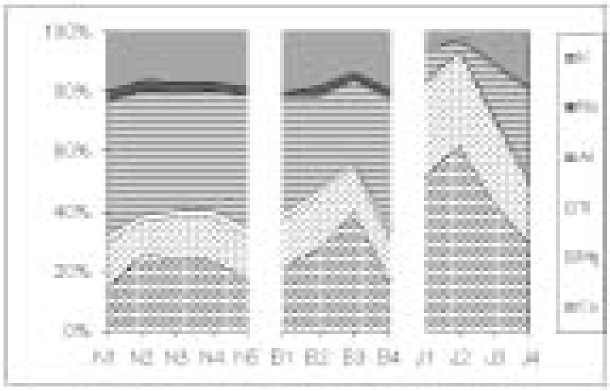

Fig. 3. Bulk chemical composition of Silurian samples (see Table 1 for sample numbering)
3 pav. Silūro bandinių pagrindinių elemetų procentinė sudėtis (bandinių numeracija nurodyta 1 lentelėje)

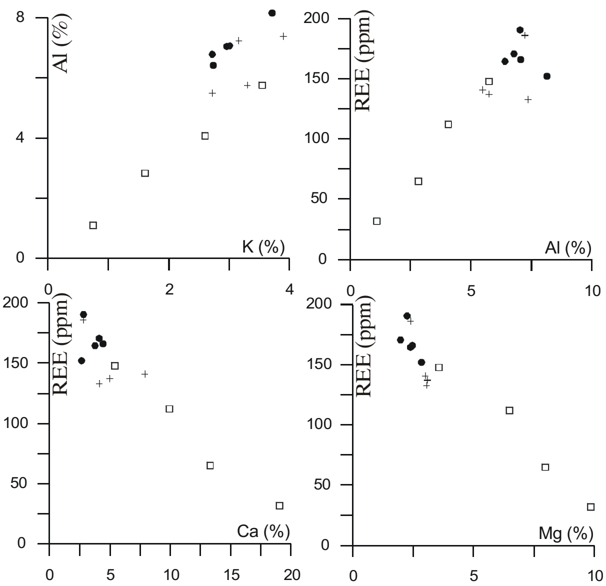

Fig. 4. Correlation of bulk and rare-earth elements in Silurian rocks
4 pav. Silūro uolienų pagrindinių ir retųjų žemės elemetų diagramos

The most distinct feature recorded in the chondrite-normalised REE patterns is the Eu anomaly, distinct in all Silurian samples studied, except Ludlow and Pridoli of the Jačionys-299 well (Fig. 5). This fact might reflect the geochemical signatures of the parental rocks in the provenance. Various factors control the distribution of Eu in igneous rocks. Eu anomalies are generated during melting events at fairly shallow depths (McLennan, 1982). Here feldspar, particularly plagioclase, is of primary importance. Liquids that have formed where pla-

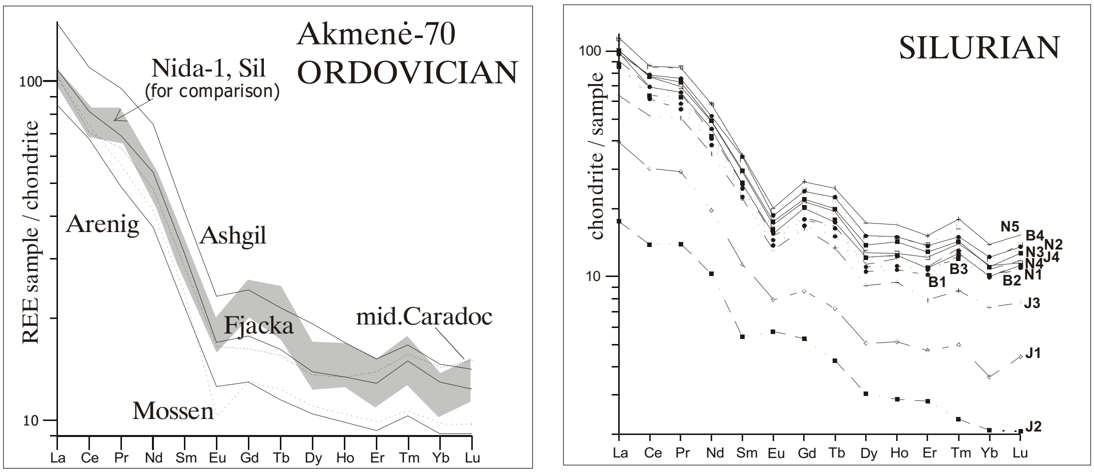

Fig. 5. Chondrite normalised REE patterns of Orodovician (left) and Silurian (right) shales and marlstones
5 pav. Chondrito normalizuoto RŽE kiekio pasiskirstymas ordoviko (kairėje) ir silūro (dešinėje) molyje ir mergelyje

gioclase is a stabile residual phase, or from which plagioclase is crystallised and lost, will tend to be depleted in Eu. The fact that there is no correlation between either Al or Zr and Eu/Eu* (correlation is respectively –0.24 and –0.19) indicates that neither clays nor zircon are solely responsible for Eu anomalies in shales. It is likely that detritus is thoroughly mixed during sediment transport. The samples indicate the ratios of 0.65–0.7, *i.e.* comparable to most shales worldwide, typically showing 0.6–0.7. Two contrasting maximums recognised in the Jačionys-299 Pridoli and Ludlow dolomitic marlstone are interpreted as an indication of a significant change in the provenance.

Because of a great difference of REE contents in sediments *vs*. chondrites, interpretation of REE distribution is somewhat better aided by normalisation to shales. Normalisation of samples to standard shales makes chemical features more obvious. For this purpose different standards are used, *e.g.*, NASC and PAAS (North American Shale Composite, Post-Archean Australian Average Shale – McLennan, 1989), Sco-1 shale (Jarvis, Jarvis, 1985). The general trends of chondrite-normalised NASC, PAAN and Nida-1 shales (other Lithuanian samples were not compared because of carbonate dillution effect) are rather uniform, showing the same steep LREE slope and low HREE differentiation (Fig. 6). Actually, most post-Archean sedimentary rocks have fairly uniform REE patterns with $(La/Yb)_n < 15$ and Gd/Yb within the range of 1–2 (McLennan, 1989). Strong Eu and Tm anomalies are defined in all the curves, while negative Ce and positive Gd and Tb anomalies are a peculiar feature of the Nida-1 shales. These anomalies are recognised in all Lithunian samples when normalised to NASC shale (Fig. 7). The shape of the curves is strikingly similar, only the rock/NASC ratios are controlled by carbonate dilution. The REE abundances of the Nida-1 rocks are compatible to standard shales, while Bliūdžiai and Jačionys rocks are depleted in REE contents (influence of carbonates). The Ce negative anomaly is a characteristic feature of Lithuanian samples (Figs. 5, 7). Tlig and Steinberg (1982) reported three types of REE patterns in terrigens with regard to cerium, which are: (1) no Ce anomaly, (2) negative Ce anomaly, (3) Ce enriched in sediments such as manganese nodules. The negative anomaly is thought to be related to authigenic phases, because Ce is strongly depleted in seawater relative to other REE. If carbonate minerals precipitate in equilibrium with seawater, they typically possess a negative Ce ano-

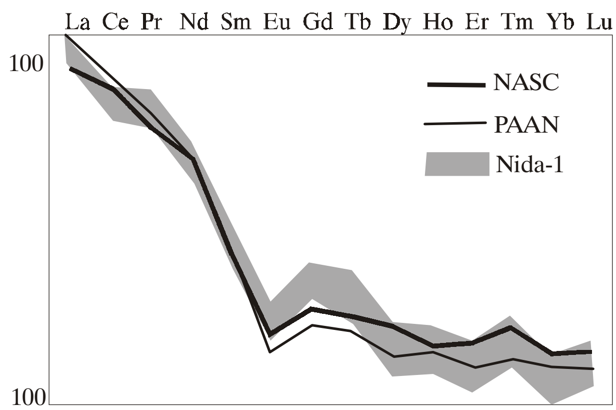

Fig. 6. Comparison of chondrite-normalised REE patterns of Nida-1 shales with standard NASC and PAAN shales
6 pav. Chondrito normalizuoto RŽE kiekio Nidos-1 gręžinio molyje palyginimas su standartiniu Šiaurės Amerikos ir Australijos moliu

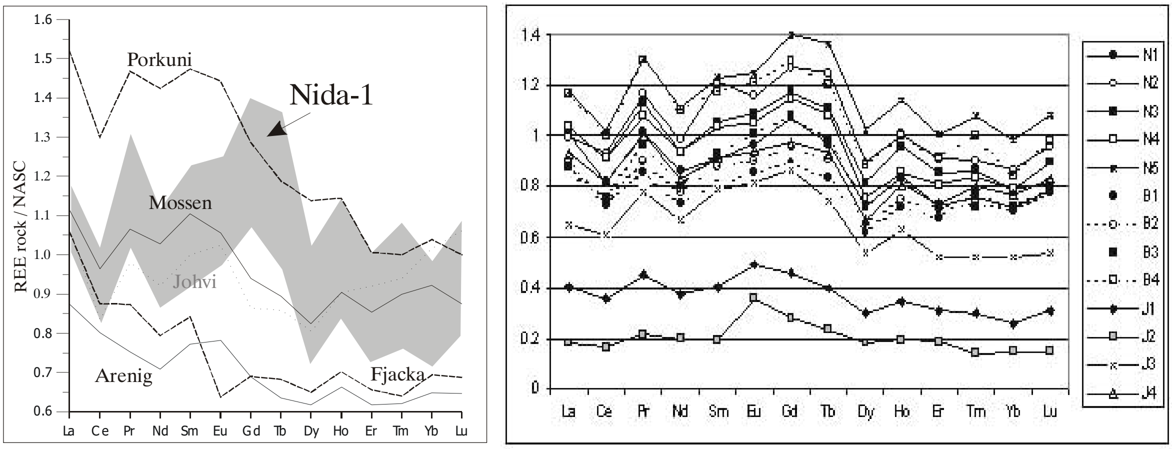

Fig. 7. NASC-normalised REE patterns of Ordovician (left) and Silurian (right) shales and marlstones
7 pav. NASC normalizuotas RŽE kiekis ordoviko (kairėje) ir silūro (dešinėje) molyje ir mergelyje

maly (McLennan, 1989). Ce is more or less depleted in calcareous organisms (Tlig, Steinberg, 1982). Yet, the mineralogical composition of clays is also of importance. A large proportion of smectite may lead to Ce enrichment.

A comparison of Silurian and Ordovician REE patterns normalised to NASC indicates that they compose two different groups (Fig. 7). The characteristic feature of Silurian shales is enrichment in MREE, while Ordovician clayey rocks show a maximum enrichment in LREE. This points to differences in sourcing of the Baltic basin during the Ordovician and Silurian times.

Similarly to REE contents, the diluting effect of carbonates in Silurian clayey sediments is obvious with regard of other trace elements. Almost all trace elements measured (Table 2) indicate decreased abundances from the west to the east. Commonly, Lower Silurian sediments are more enriched than the Upper Silurian clayey rocks. It should be concluded that most of trace elements were transported to the Silurian basin with terrigenous material. Still, the influence of the sedimentation environment must not be neglected. The low content of Ga reported from Lithuanian samples (11–16 ppm) points to a normal salinity of the marine water. This is in ac-

Table 2. **Trace element concentrations (ppm) in Silurian shaly rocks, Lithuania**
2 Lentelė. **Retųjų elementų kiekis (ppm) silūro molingose uolienose (Lietuva)**

Elements	Nida-1					Bliūdžiai-96				Jačionys-299			
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
Mo	0.5	3	7	15	4	0.5	0.5	6	0.5	0.5	0.5	0.5	0.5
Cu	37	47	37	43	141	25	21	29	82	10	43	7	13
Pb	4	19	28	33	18	5	4	28	9	2	2	2	2
Zn	62	69	65	156	394	52	51	39	113	27	10	23	37
Ni	57	55	52	58	49	56	34	35	54	12	5	19	32
Co	17.7	19.6	16.3	16.7	13.9	16.9	13.0	11.2	12.2	6.2	3.1	7.0	14.3
Mn	558	368	382	345	341	386	342	358	321	244	323	328	405
As	5	15	10	16	12	3	3	7	3	2	1	1	11
Cr	103	75	73	71	78	81	67	51	86	28	12	37	56
Ba	392	480	406	327	325	371	444	335	352	170	52	205	313
Be	2	2	2	2	2	2	2	1	2	1	0.5	1	2
Sc	11	9	9	9	10	10	8	7	10	4	1	5	8
Cd	0.1	0.6	0.3	0.7	2.4	0.1	0.1	0.1	0.5	0.1	1	0.1	0.1
Sb	0.4	1	0.9	3.2	1.8	1.6	3.4	2.5	3	3.2	2	4.6	2.4
Cs	6.7	5	4.8	5.3	5.9	6.2	5.1	4.5	6	2.4	0.5	3.7	5.7
Ga	16	15.6	13.9	13	14.6	15.2	13.9	11.5	14.4	6.7	1.5	8.6	12.7

Table 2 (continue)
2 lentelės tęsinys

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
Hf	4.1	4.9	5	4.3	5.4	4.2	4.3	4.1	5.4	1.6	0.4	2.7	5.1
Nb	11.28	11.72	11.3	10.46	12.05	10.82	10.62	10.07	12.15	4.48	1.11	6.86	10.81
Rb	148	131	128	120	131	148	132	108	132	64	15	97	128
Sn	2.6	1.8	2.3	8.9	2.2	2.1	2.1	2	2.5	1	0.4	1.4	1.6
Sr	119	152	168	114	116	118	106	277	110	83	102	73	86
Ta	0.9	0.8	0.8	0.8	0.9	0.8	0.8	0.7	0.8	0.3	0.05	0.5	0.7
Th	11.3	11.4	11.3	10.5	12.7	10.4	11.6	9.4	12.2	4.3	1.1	7.1	10.4
U	2.3	4.6	6.3	8.1	6.2	2.7	3.7	3.7	4.7	1.6	0.6	1.4	2.3
V	98	134	159	157	187	96	76	99	111	42	16	53	86
W	1.5	1.3	1.1	1.2	1.5	1.3	1.2	0.9	1.3	17.3	0.04	0.7	1.4
Zr	120	158	155	133	178	125	132	131	244	33	0.4	77	172
Y	19.3	24.6	23.3	22.2	27.9	17.6	18.8	20.7	23.9	8.6	5.8	15	19.9
Yb	2.21	2.69	2.43	2.46	3.05	2.22	2.18	2.23	2.62	0.79	0.46	1.61	2.37
Th/U	4.91	2.48	1.79	1.30	2.05	3.85	3.14	2.54	2.60	2.69	1.83	5.07	4.52
Cr/V	0.93	0.57	0.45	0.38	0.39	0.82	0.84	0.54	0.69	0.74	0.71	0.77	0.67
Zr/Y	5.47	4.39	5.63	5.12	5.32	6.17	6.54	4.88	5.89	4.83	2.60	4.67	6.43
Ba/Co	23.8	40.1	25.2	21.4	25.3	21.4	40.6	35.6	36.6	33.5	61.0	67.0	19.8

Samples: well Nida-1: *1* – 1286 m (S2pr); *2* – 1797 m (S2ld); *3* – 1940 m (S1w); *4* – 1992 m (S1w); *5* – 2030 m (S1lnd); well Blūdžiai-96: *6* – 889 m (S2pr); *7* – 1069 m (S2ld); *8* – 1165 m (S1w); *9* – 1274 m (S1lnd); well Jačionys-299: *10* – 99 m (S2pr); *11* – 118 m (S2ld); *12* – 165 m (S1w); *13* – 223 m (S1lnd)

cordance with assumptions made by Wigforss-Lange and Buchardt (1997) based on the carbon and oxygen isotope studies of Ludlow-Pridoli rocks in Scania. A pronounced attenuation of Ga content in the Jačionys-299 well (1.5–8.6 ppm) mirrors a lagoonal sedimentation environment inferred from lithofacies. Also, organic matter influences the trace elements abundance in shaly rocks. Clay minerals are capable of adsorbing large quantities of trace elements on cation exchange sites (*ca*. 150 meq/100 g), but trace elements are more readily adsorbed by organic matter due to the higher cation exchange capacity of organic matter (500 meq/100 g) (Kelepertsis, 1981). Ag, Mo, Zn, Ni, Cu, Cr, V, U, Zn, Hg, As are usually enhanced in organic-rich shales (Leventhal, Hosterman, 1982; Glikson et al., 1985). In Lithuanian samples this process is most pronounced for Cu, Ni, V, U, Zn.

4. DISCUSSION

The Ordovician succession is represented by carbonates and shales, while the Silurian one is dominated by clayey lithologies. It is rather amazing that a huge amount of fine clastic sediments was provided in a short time as is the Silurian period. Felsic rocks, containing a high proportion of quartz, usually produce significantly more sand and mafic rocks generate significantly more mud (Cox, Lowe, 1995), which might be a case in the Baltic basin. Still, Silurian sediments may represent recycled sedimentary material accumulated in the foreland.

Clay minerals act as collectors and concentrators of many trace elements, which may be either sorbed onto their surfaces or included in interlayer cation sites. Insoluble trace elements remain associated with clays and transported from the outcrop by mechanical processes. As a result, their abundance in mudrocks generally reflects the composition of the source rocks (Cox, Lowe, 1995). REE are essentially not easily fractionated during sedimentation, therefore sedimentary REE patterns provide the most reliable index to the average composition of a provenance (McLennan, 1989). The investigated REE abundances in the Ordovician and Silurian shales may provide also important information on the tectonic setting of the basin and its surroundings. Sediments deposited in different tectonic settings commonly show different REE and trace element patterns (*e.g.*, McLennan, 1989; Bhatia, 1985) than do volcanic rocks (*e.g.*, Deng, Yang, 1996). Sediments of the basins developed on the passive margin consist of recycled deposits and igneous/metamorphic rocks, and REE patterns are similar to those of

PAAS, while active margin sediments show strong similarities to undifferentiated volcanic arc rocks, they have lower REE abundances, La/Sm and La/Yb ratios and are devoid of Eu-anomaly (McLennan, 1989). However, quite often active margin deposits show REE patterns intermediate between a low-differentiated arc pattern and PAAS, the Eu/Eu* ratio ranging from 0.60 to 1.0, which points to a mixture of sediments derived from an old cratonic crust and younger volcanic arc-related rocks.

A comparison of REE patterns obtained from the Nida-1 well (other Silurian samples were not used for comparison because of a strong dilution effect) to those reported from sediments deposited in the basins of different tectonic setting indicates a strongest resemblance to the passive margin turbidates (Fig. 8), though the difference from the active margin sediments is not significant. At large, it suggests a miserable amount of low-differentiated mafic rocks in the source area that provided sediments into the Baltic basin.

As was mentioned, no distinct trend in LREE slope evolution was recognised in Silurian samples either in vertical or horizontal scales, as otherwise should be expected assuming the change in the provenance from the old Precambrian platform to younger volcanic arcs. The La_n/Yb_n of the Silurian sediments studied is in the range of 7.9–11 characteristic of felsic rocks, which is comparable, for instance, to Ordovician sediments of the Brabant massif (8.9–13.9) supplied from an exposed Precambrian felsic crust (Andre et al., 1986). Th and La abundances are also rather high, respectively 10–12 and 28–37 ppm, *i.e.* much higher than those in sediments with a considerable mafic input. The La/Th ratio is 2.8–3.1, and this is just slightly less than the La/Th ratio registered for most post-Archean sedimentary rocks from Australia (2.7) (McLennan, 1982). Following Condy and Martell (1983), sediments derived from a granitic source have a low La/Th ratio (1.5–3.5), while mafic rocks show higher ratios (4.5–10). Arc-derived sediments usually show the La/Th of 6–7, while granitoid-dominated derived deposits 2.6, and recycled sediments show the lowest value (2.5) (Bathia, Taylor, 1981). The uranium content in Lithuanian samples (2.3–8.1 ppm, and it is less in eastern carbonate-diluted samples) is also more typical for a passive margin setting. Arc-derived sediments contain low levels of U (0.52 ppm), whereas sediments of the passive continental margin setting are more "mature" (U = 3.4 ppm) mirroring higher levels in granitic and sedimentary source rocks. The Hf content in Lithuanian shales (1.6–5 ppm) is inbetween of typical granites (4–10 ppm) and mafic rocks (0–3.5 ppm), and it is slightly less than in recycled sediments (5 ppm) (Condy, Maretel, 1983; Bathia, Taylor, 1981). The Hf maximum is confined to Llandovery shales, and its minimum levels are found in the Pridoli samples. Ta also provides valuable information on provenance composition. The deepening of Ta negative anomaly is usually related to an increasing granitic component in the source area. Also, Ta depletion is typical of subduction-related igneous rocks (Totten, Weaver, 2000). In Lithuanian samples Ta is strongly depleted relative to Th and La, the estimated Ta/Ta* ratio is 0.21–0.26 ppm, *i.e.* much less than in mafic-sourced deposits (Andre et al., 1986). However, a slight maximum is recognised in Pridoli deposits in all the three wells studied, while the lowest values are reported from the Llandovery samples. This might point to some increase of the mafic

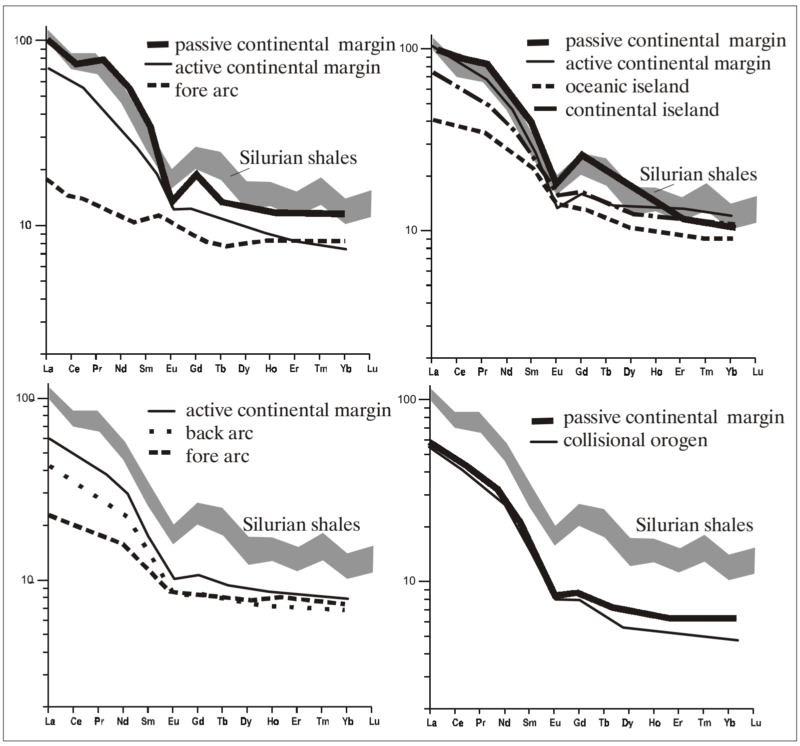

Fig. 8. Chondrite-normalised REE patterns of various geotectonic settings (Guldenpfennig, 1998) in comparison with the REE distribution of Nida-1 Silurian shales

8 pav. Skirtingoje tektoninėje aplinkoje susidariusių uolienų chondrito normalizuoto RŽE kiekio palyginimas su Nidos-1 gręžinio silūro molio RŽE pasiskirstymu

portion in the provenance from the Early to Late Silurian. It is in accordance with aforementioned Hf trend. The contents of U and Th also decrease from the Lower Silurian to Upper Silurian shales and marlstones, what might be interpreted in terms of an increasing influence of the mafic source. The Th/ /Sc, Th/Sr, Ti/Zr ratios which reflect source rock composition (Lahtinen, 1996) also support this suggestion. Figure 9 illustrates a sharp increase of Ti/ /Zr in Pridoli samples, associated with a drastic decrease of Th/Sc and Th/Sr. These trends strongly suggest an increase in mafic component in the provenance in the latest Silurian. The shapes of curves are identical for all the samples, except two Upper Silurian samples from the Jačionys-299 well, showing a drastic decrease of Th/Sc and Th/Sr in Ludlow rocks and an increase in Pridoli marlstone.

Europium is stable under diagenetic conditions and is not fractionated relative to the other REE. Eu/Eu* values for mudrocks would therefore not change as a consequence of recycling (Cox, Lowe, 1995). Felsic igneous rocks generally have smaller values of Eu/Eu* than mafic rocks. Eu anomaly is strongly negative in Silurian shales. Samples indicate the ratios 0.65–0.7, *i.e.* comparable to shales worldwide, sourced from post-Archean provenances. Still, Pridoli and Ludlow dolomitic marlstones of Jačionys-299 contrast the general Eu trend, the Eu/Eu* of the Ludlow is higher than that of the Lower

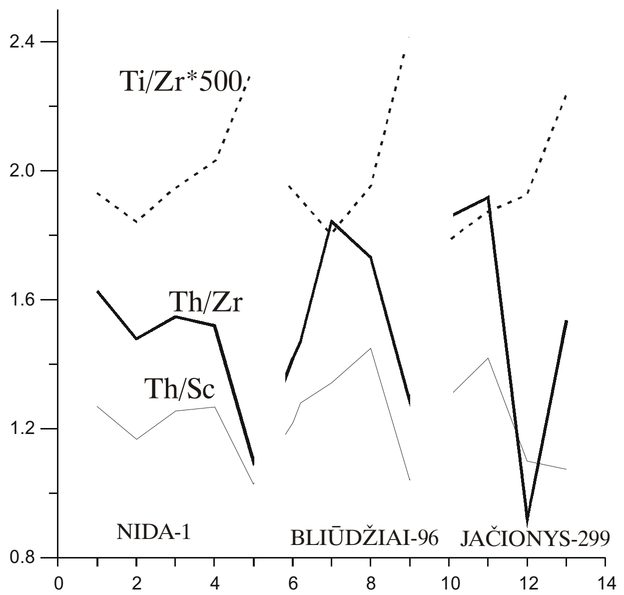

Fig. 9. Th/Sc, Th/Zr and Ti/Zr ratios in Silurian shales, Nida-1, Bliūdžiai-96, Jačionys-299 wells (see Table 1 for sample numbering)
9 pav. Th/Sc, Th/Zr and Ti/Zr santykiai Nidos-1, Bliūdžių-96 ir Jačionių-299 gręžinių molingose uolienose (pavyzdžių numeriai nurodyti 1 lentelėje)

Silurian, and the ratio in the Pridoli is >1, implying a possible input of the cratonic Archean material during the Late Silurian. This comes in agreement with the affore-described trends of Th/Sc, Th/Sr, Ti/ /Zr in the Jačionys-299 well. For instance, a similar Eu/Eu* ratio close to 1 was confirmed by Samson et al. (2000) for recent sediments derived from the SW Indian Archean craton.

The other trace elements might be of help in decoding the source lithologies. It should be kept in mind, however, that clay minerals go through a complex history of transportation, deposition, diagenetic transformations, and in each stage the new environment exerts an influence on the trace-element budget of clays, which partly obliterates the records of previous chemical events. The Sn concentration in clays can be used to determine parent rocks (Mosser, 1983). This element has a strong affinity to octahedral or tetrahedral sites of clay minerals and is less prone to ionic exchange. Its content in Silurian shales (2–2.5 ppm) is higher than in average clay (1.5 ppm), pointing to a sialic provenance. On the other hand, Cr, Co and Ni concentrations are rather high, inferring a possible input of mafic lithologies (70–100, 12–18, 50–65 ppm) (Tottten, Weaver, 2000). The Zr/Y, Ba/Co ratios, which are least susceptible to modification by secondary processes (Zhang et al., 1998), are inbetween mafites and granites, though closer to the latter.

Analysis of bulk chemical elements measured for Silurian shales of the Kurtuvėnai-166 well also support the aforementioned implications. The calculated discriminant coefficients indicate a sourcing from either sedimentary rocks or felsic igneous province (Fig. 10). The Al_2O_3 *vs*. TiO_2 diagram also indicates a high chemical maturity of the parent rocks (Fig. 10). Similar trends were recorded also for Ordovician samples from the Akmenė-70 well (Fig. 10). The Th–La–Sc plot (Fig. 11) indicates that the average composition of Ordovician and Silurian source rocks was close to that of granodiorites. The average felsic source is indicated also by the Hf–La/Th plot (Fig. 11). The Ordovician samples are slightly shifted towards a more mafic provenance. The differences in Ordovician and Silurian provenances are well reflected in the Th/Sc–La/Sc diagram showing that Silurian shales are of more felsic composition that those Ordovician. This is in accordance with data obtained from the G-14 well (Rügen sector), showing that the composition of Rügen Ordovician shales is close to that of Akmenė-70 clayey deposits, while Silurian shales in the Rügen sector indicate an extremely acid composition of the provenance (Šliaupa et al., 2000). The "acidity" of Rügen Silurian shales is much higher than of Lithuanian

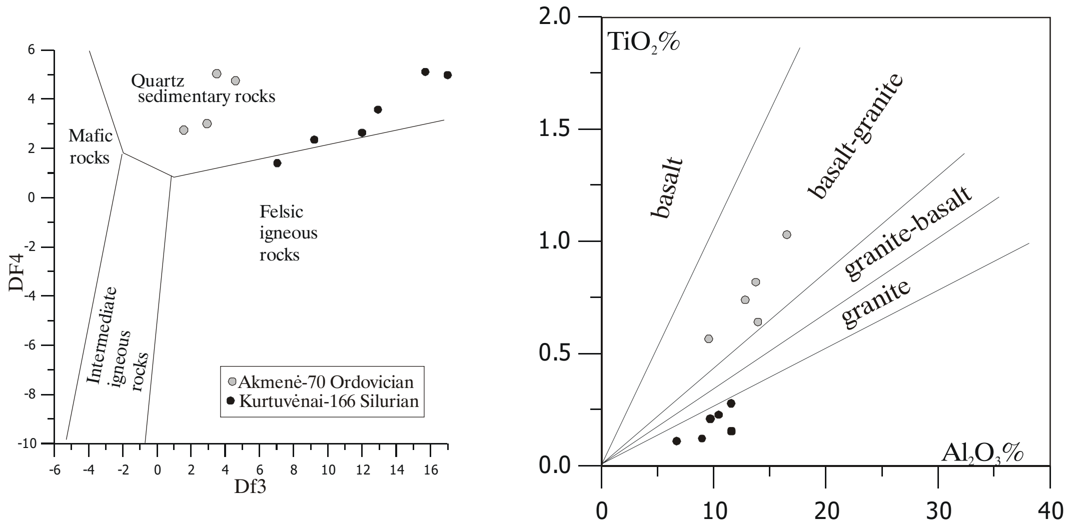

Fig. 10. Provenance lithologies of Ordovician and Silurian clayey rocks
Left: DF3-DF4 plot. Coefficients after Roser & Korsch (1988). DF3 = [30.638 TiO_2 – 12.541 Fe_2O_3 (total) + 7.32MgO + + 12.031 Na_2O + 35.402 K_2O] / Al_2O_3 – 6.382. DF4 = [56.50 TiO_2 – 10.879 Fe_2O_3 (total) + 30.875 MgO – 5.404 Na_2O + + 11.112 K_2O] / Al_2O_3 – 3.89.
Right: Al_2O_3 / TiO_2 binary plot. Fields for source rocks according to Amajor (1987).
10 pav. Silūro ir ordoviko molingų uolienų denudacinės zonos diskriminantinės diagramos.
Kairėje: DF3-DF4 diagrama. Koeficientai DF3, DF4 pagal Roser & Korsch (1988).
Dešinėje: Al_2O_3 / TiO_2 diagrama. Denudacinės medžiagos šaltinių laukai pagal Amajor (1987)

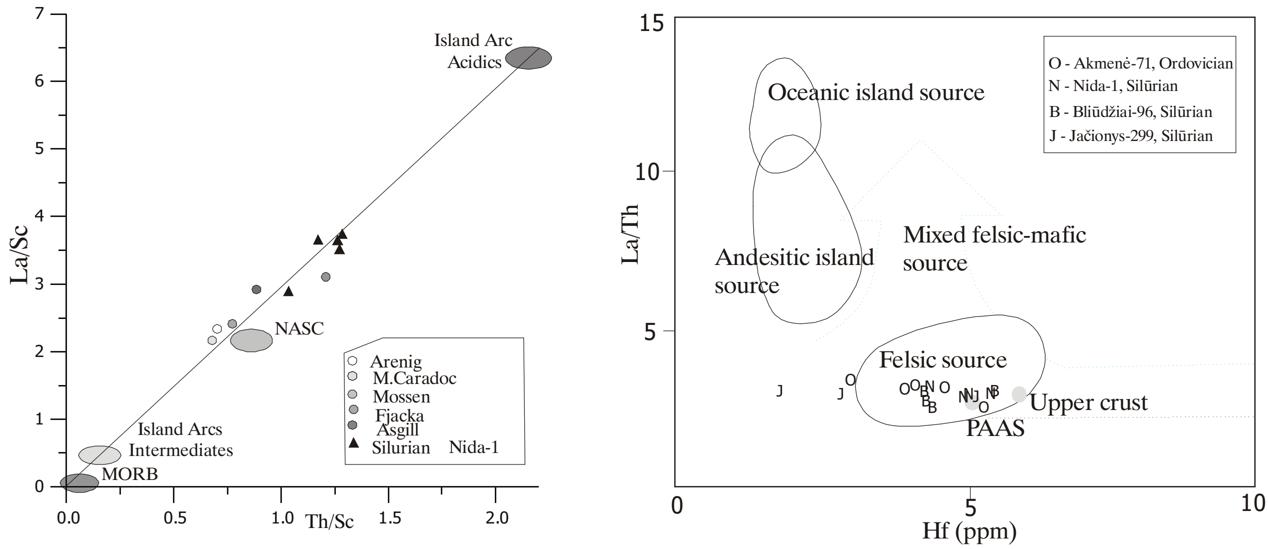

Fig. 11. Provenance discrimination of Ordovician and Silurian clayey rocks. La/Sc–Th/Sc, Hf–La/Th, Th–La–Sc plots
11 pav. Ordoviko ir silūro molingų uolienų denudacinių šaltinių diskriminantinės diagramos La/Sc–Th/Sc, Hf–La/Th, Th–La–Sc

samples, still the common trend of Silurian rocks growing more acid both in the western and central parts of the Baltic basin is evident, pointing to a common tectonic-sedimentary scenario.

CONCLUSIONS

Based on the study of the REE and trace elements, a significant rearrangement in provenance providing clastic material to the eastern and central parts of the Baltic basin seems to have taken place at the transition from the Ordovician to Silurian times. This change is a few million years younger than the drastic change registered close to the German Caledonides in Rügen sector (Šliaupa et al., 2000), which indicates a progressing advancement of orogenic build-up to the east, the erosional products first affecting the westernmost part of the basin and further expanding to the east. Still, the REE trends in the western and central parts of the Baltic basin are very different, implying that the western (German) sources might have influenced the central and eastern parts of the basin only partly, while the bulk of the terrigens were received from other sources. There are two alternatives regarding these sources: (*i*) the influence of the eastern (platform) provenance increased during the Silurian, and (*ii*) clastic material was transported to the east from the Pomeranian Caledonides which were of different composition than German orogen. The latter supposition is rather convincing, taking into consideration recent paleontological studies in the Pomeranian foredeep. Jachowicz (2000) reported Lower Ordovician acritarchs of Mediterranean provincialism from the Pomeranian Silurian shales, which indicates that the foredeep has accumulated denudation products of the Pomeranian orogen containing Ordovician sedimentary rocks. By contrast, the G-14 well Silurian shale geochemistry points to domination of felsic igneous rocks in German Caledonian orogen. Therefore, the Silurian shales of the central part of the Baltic basin might be a result of a mixture of these two provenances (German Igneous and Pomeranian Sedimentary).

Alternatively, Lithuanian Silurian shales might be a product of the terrigens transported from the eastern platform. The Baltic basin regressed during the Silurian, and it was more narrow in the east than during the Ordovician time. This regression might have led to exposure of the Precambrian (Archean) crust and of the overlying Vendian–Cambrian deposits in the east.

Both Ordovician and Silurian sediments show affinity to average granodiorite. Ordovician shales represent recycled sediments, while Lithuanian Silurian shales verge between recycled sediments and igneous rocks. The possible candidates of the Ordovician provenance are the Fennoscandian Shield and the Belarus Height, both composed of Early Proterozoic metamorphic and igneous rocks covered by pre-Ordovician sediments. These two tectonic provinces were covered by the marine basin during the Silurian, while the vast area of Archean craton was exposed to denudaton in the east. Amazingly, no significant changes in the lithology of the provenance in the course of Silurian sedimentation (*i.e.* no significant redistribution in the sourcing) were recorded, except some hint recognised in the Upper Silurian easternmost lithofacies. Similarity of the REE patterns of all samples points to a domination of one terrigenic source in the territory of Lithuania during the Silurian. Yet, a miserable addition of the mafic component in the late Silurian, most distinct in the western and central lithofacies, is likely to reflect the advancement of mafic sources. By contrast, the Archean-sourced-like shales were reported from the easternmost part of the basin in Ludlow and climaxed in Pridoli rocks, strongly suggesting an increasing influx from the east in the latest Silurian, which is explained in terms of the basin regression and an advancement of the eastern shoreline and an associated active influx from the Archean Sarmatian platform in the east.

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ORDOVIKO IR SILŪRO MOLINGŲ UOLIENŲ RETŲJŲ ŽEMIŲ ELEMENTŲ GEOCHEMINIAI YPATUMAI LIETUVOJE: DENUDACINĖS ZONOS TYRIMAS

S a n t r a u k a

Baltijos sedimentacinis baseinas yra Dniepro–Baltijos pakraštinių baseinų sistemos dalis, kuri susiformavo suskilus žemynui vendo–kambro metu. Ordovike Baltijos baseinas buvo pasyvaus žemyno pakraščio tipo struktūra. Silūre grimzdimo greitis baseine gerokai paspartėjo, ir tai siejama su Rytų Avalonijos ir Baltikos žemynų kolizija, o šis laikotarpis apibrėžiamas kaip konvergentinio žemyno pakraščio baseino stadija. Grimzdimo greitėjimą lydėjo suintensyvėjęs nuogulų prinešimas į baseiną. Ordoviko laikotarpis ir pirmoji silūro pusė apibrėžiama kaip „badaujančio" baseino stadija, antrojoje pusėje įsivyravo kompensuotos ir perpildymo sedimentacijos sąlygos. Baseine ordoviko ir silūro metu klostėsi molis ir karbonatai, pastarieji vyravo baseino rytinėje dalyje.

Remiantis litofacijų analize, ordoviko metu ir silūro pradžioje Baltijos regione vyravo terigeninės medžiagos prinešimas iš rytų, tuo tarpu antrojoje silūro pusėje pagausėjo prinešimas iš gretimų kaledonidų vakaruose. Siekiant nustatyti terigeninės medžiagos šaltinių tendencijas bei išryškinti denudacinės zonos raidą ordoviko ir silūro metu, buvo tirti retieji ir retieji žemės (RŽE) elementai molyje ir mergelyje keturiuose Lietuvos gręžiniuose: Akmenės-70, Jačionių-299, Bliūdžių-96 ir Nidos-1; trys iš jų atstovauja 3 pagrindinėms silūro baseino litofacinėms zonoms (rytinė ir centrinė Baltijos baseino dalys). Kadangi RŽE sunkiai frakcionuoja sedimentacijos metu, jų pasiskirstymas leidžia atkurti denudacinės zonos litologiją.

Ordoviko ir silūro geocheminiai trendai labai skiriasi, ir tai rodo nemažus pokyčius denudacinėje zonoje ordoviko–silūro riboje. Vidutinė denudacinės zonos sudėtis buvo artima granodioritui, ordoviko moliui būdingas kiek padidėjęs bazingumas. Pagal pagrindinių cheminių elementų pasiskirstymą molis susidarė irstant anksčiau susiklosčiusioms nuosėdinėms uolienoms.

RŽE kiekis tirtuose silūro pavyzdžiuose gerokai skiriasi, tačiau normalizuotos (chondritas ir NASC molis) jų kreivės labai panašios, ir tai rodo mažai kaičią denudacinės zonos litologiją, t. y. nebuvo ryškesnio šaltinių persiskirstymo silūro metu. Galimos kelios terigeninio prinešimo į rytinę ir centrinę Baltijos baseino dalį silūro metu alternatyvos: 1) Sarmatijos-Fenoskandijos platforminio šaltinio vyravimas silūro sedimentacijoje; 2) vakariniai kaledonidai yra perdirbto (perklostyto) tipo, jų įtaka rytinei prieškalnės baseino pusei galėjo būti dalinė. Pažymėtinos tik nedidelės geocheminės variacijos, kurios leidžia numanyti neryškų bazinio komponento padidėjimą vėlyvajame silūre vakarinėse ir centrinėse litofacijose (o tai reikštų kalnų priartėjimą), tačiau šis padidėjimas yra labai nedidelis. Kitas svarbus požymis – archėjinės komponentės atsiradimas viršutinio silūro rytinėse litofacijose yra siejamas su baseino regresija, rytinės kranto linijos priartėjimu ir platforminės medžiagos prinešimo pagausėjimu rytuose.

Саулюс Шляупа

ОСОБЕННОСТИ РЕДКОЗЕМЕЛЬНОГО СОСТАВА ОРДОВИКСКИХ И СИЛУРИЙСКИХ ГЛИНИСТЫХ ПОРОД ЛИТВЫ: РЕКОНСТРУКЦИЯ ДЕНУДАЦИОННОЙ ЗОНЫ

Р е з ю м е

Балтийский бассейн является составной частью Днепровско-Балтийской системы перикратонных бассейнов. В ордовикское время Балтийский бассейн представлял собой пассивную континентальную окраину. В силуре погружение бассейна резко увеличилось, что связывается с коллизией континентов Восточной Авалонии и Балтики. Этот период характеризуется как этап конвергентной континентальной окраины. Увеличение прогибания земной коры ассоциировало с увеличением привноса глинистого материала в бассейн. Ордовикский–раннесилурийский этап описывается как этап некомпенсированного осадконакопления, тогда как второй половине силура свойствено компенсированное осадконакопление. Карбонаты доминируют в восточной части бассейна, глинистые породы составляют разрез западной, более глубоководной, половины бассейна.

По данным литофациального анализа, глинистый материал привносился с восточной платформы в ордовикское время и в первой половине силура. В позднем силуре резко увеличился привнос глинистых осадков с западных каледонидов.

Редкоземельный состав глинистых пород изучался в ордовикских и силурийских породах Литвы для выявления эволюции денудационных зон во время ордовика и силура. Скв. Акмяне-70, Ячёнис-299, Блюджяй-96, Нида-1 представляют разные литофациальные зоны Балтийского бассейна. Так как редкоземельные элементы (РЗЭ) незначительно фракционируют во время седиментации, они являются хорошим индикатором литологического состава денудированных пород.

Выявленные геохимические тренды ордовикских и силурийских пород ощутимо различаются, что указывает на значительные изменения в денудационной зоне на рубеже ордовика и силура. Средний состав денудируемых пород был близок к гранодиоритам, для ордовикских глин отмечается несколько увеличенная основность. Судя по составу породообразующих элементов, глины образовались при переотложении осадочных пород.

Концентрация РЗЭ значительно варьирует в силурийских глинах, но кривые (нормализованные по хондриту и стандартной НАСК-глине) имеют те же характеристики, это указывает на то, что литологический состав зоны денудации мало изменился. Делается вывод, что не было значительного перераспределения в источнике глинистого материала во время силура. Возможны несколько объяснений в отношении источника глинистого материала:

(1) Сарматско-Фенноскандский источник доминировал во время силура;

(2) Западные каледониды представляют собой переотложенный тип. Выявлен слабый сигнал увеличения основности химического состава во время силурийского осадконакопления, что, возможно, указывает на приближение вулканических дуг к окраине Балтики. Вторая выявленная особенность – появление „архейских“ компонентов в геохимическом составе восточных глин верхнего силура, что интерпретируется как обнажение архейских блоков или рифейско-вендских отложений на востоке.