

Silurian bentonites in Lithuania: correlations based on sanidine phenocryst composition and graptolite biozonation – interpretation of volcanic source regions

Tarmo Kiipli^a, Sigita Radzevičius^b and Toivo Kallaste^a

^a Institute of Geology at Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; tarmo.kiipli@ttu.ee, toivo.kallaste@ttu.ee

^b Department of Geology and Mineralogy, Vilnius University, M. K. Čiurlionio 21/27, LT03101, Vilnius, Lithuania; sigita.radzevicius@gf.vu.lt

Received 10 October 2012, accepted 22 October 2013

Abstract. Integrated correlation of bentonites (altered volcanic ashes) and graptolite biozonation is presented. Detailed study of two Lithuanian drill core sections extended previous knowledge of the occurrence and composition of bentonites to the south. Identification of graptolite species allowed bentonites to be assigned their proper stratigraphical position. Silurian bentonites in Lithuania are mostly characterized by wide and very wide XRD 20 $\bar{1}$ reflections of the main component of sanidine phenocrysts. Only fourteen of the 69 samples studied contained sanidine with a sharp reflection, which gave the best correlation potential. In the Lithuanian sections one bentonite was found in the Rhuddanian, five bentonites were recognized in the Aeronian, 17 bentonites in the Telychian, 26 in the Sheinwoodian, 10 in the Homerian and six in the Ludlow. All bentonites found in Lithuania are characterized by the main component of sanidine. A large number of Lithuanian bentonites are not known in Latvia and Estonia, indicating that volcanic ashes reached the East Baltic area from two source regions – the Central European and Norwegian Caledonides.

Key words: Silurian, bentonites, sanidine, graptolites, correlation, East Baltic.

INTRODUCTION

Volcanic ashes occurring in palaeontologically well-characterized sedimentary sections offer a unique possibility of detailed correlations between different environments (Kiipli & Kallaste 2002; Kiipli et al. 2006, 2008a, 2009, 2010b, 2011, 2012a, 2012b). The mentioned studies used magmatic sanidine composition of bentonites (altered volcanic ashes) analysed by X-ray diffractometry as a correlation criterion. The good precision of that method, up to $\pm 1\%$ in favourable cases (Kiipli et al. 2011), enables discrimination of bentonites of quite similar composition. This is an important property, because successive eruptions from the same volcanic source can be characterized by very similar geochemical and mineralogical signatures (Kiipli et al. 2010a). Other methods, e.g. palaeontological, used in combination with sanidine composition of bentonites, provide the most reliable correlation. A negative aspect of using sanidine composition for fingerprinting bentonites is that magmatic sanidine is unstable at Earth's surface temperatures. Elevated diagenetic or metamorphic temperatures accelerate recrystallization significantly and Early Palaeozoic sanidine is often not preserved in some other regions. Sanidine may also be absent in source magma. To avoid these

shortcomings, researchers have used the composition of apatite phenocrysts (Batchelor 2009; Carey et al. 2009; Ray et al. 2011) or trace elements for proving correlations (Huff et al. 1998; Kiipli et al. 2008b, 2013a); Inanli et al. 2009; Hetherington et al. 2011. Up to now we have studied mostly Estonian and Latvian sections (Kiipli & Kallaste 2006; Kiipli et al. 2010a, 2011, 2012a). Some Silurian bentonites of Lithuania have been studied by Kiipli et al. (2008c) using the same methods. The occurrence of bentonites in the Silurian of Lithuania is also described in Lapinskas (1965, 2000) and Motuza et al. (2002). The areal distribution schemes of ca 20 bentonites from Estonia, Latvia and Scandinavia indicate volcanic sources from the Iapetus Palaeo-Ocean in the Telychian and Lower Sheinwoodian (Kiipli et al. 2008b, 2008d, 2010b, 2012a, 2013a). Several other researchers discuss a possible Central European source for ash beds (Batchelor & Jeppsson 1999; Böhnke & Katzung 2001; Hetherington et al. 2011). Thick bentonites and massive volcanic rocks of Silurian age are known from Belgium (Andre et al. 1986) and Poland (Timmerman 2008). So, according to the geological data, two source regions, the Central European and Norwegian Caledonides, were possible and Lithuania is in a key position for discriminating between these sources. The distribution of

graptolites in Lithuanian sections has been studied by Paškevičius (1982, 1997), Radzevičius (2006), Radzevičius & Paškevičius (2000, 2005) and Radzevičius et al. (2008). The correlation of graptolite biozones applied in different regions of the world is given in Loydell (2012). We studied in detail two Lithuanian drill core sections. Our aim was to extend bentonite correlations to the south and better recognize volcanic sources from the margins of the Iapetus and Rheic Palaeo-Oceans.

MATERIAL AND METHODS

Forty-six bentonite samples were collected from the Šiupyliai-69 and Kurtuvėnai-166 drill cores (Fig. 1). Twenty-three bentonites from other Lithuanian cores, seven of which have been published in Kiipli et al. (2008c), are also included in the present report (Table 1). Bentonites in predominantly grey Silurian shales were recognized by their yellowish or bluish colour. They are very thin, mostly only a few millimetres and rarely up to a few centimetres thick.

Biostratigraphy is based on over 200 rock samples taken from the Llandovery–Ludlow interval of the Viduklė-61 (Kiipli et al. 2008c), Šiupyliai-69 and

Kurtuvėnai-161 (Radzevičius & Paškevičius 2000, 2005; Motuza et al. 2002; Kaminskas et al. 2006) drill cores for the study of graptolites. Sampling density increased near the ash layers. Rhabdosomes were extracted from samples using HCl or HF acids. Graptolites were examined under a light microscope in Vilnius University.

To identify major minerals in the sampled interbeds of supposed volcanic origin, bulk samples were analysed by X-ray diffractometry (XRD). An association of illite-smectite and kaolinite as major minerals has been considered to indicate the volcanic origin of the interbeds (Kiipli & Kallaste 2002; Hints et al. 2008). Authigenic K-feldspar forms a significant portion of some bentonites. Host shales are composed of a different association of terrigenous minerals, including illite, quartz, chlorite and minor K-feldspar.

Magmatic sanidine phenocrysts $(K,Na,Ca)AlSi_3O_8$ were analysed in coarse fractions (0.04–0.1 mm) separated from 2 g of bentonite using the method described in detail in Kiipli et al. (2011). Various examples of sanidine XRD spectra are published in Kiipli & Kallaste (2006) and Kiipli et al. (2006, 2010a). All measured XRD spectra of sanidine in Lithuanian bentonites are available in the collections database of the Institute of Geology at Tallinn University of Technology at <http://sarv.gi.ee/reference.php?id=2544>.

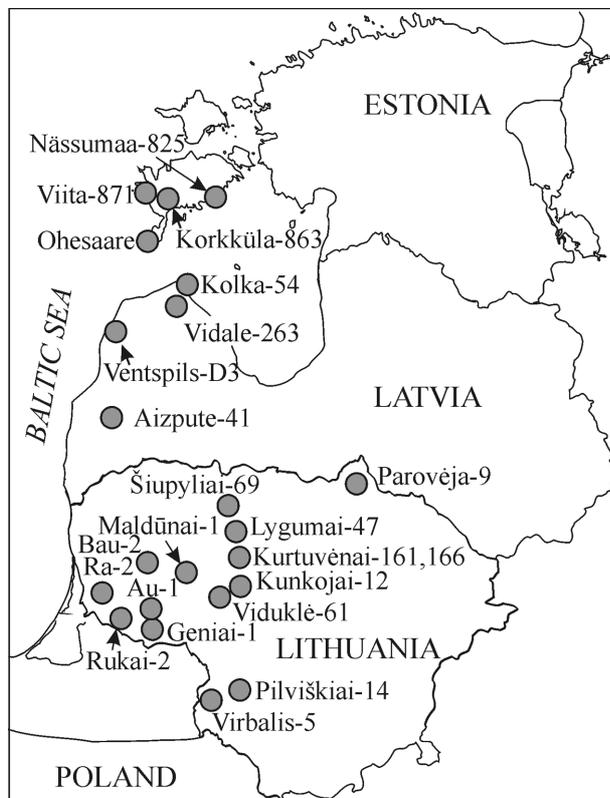


Fig. 1. Location of the studied drill core sections. Ra-2 = Ramučiai-2, Au-1 = Aukštupiai-1, Bau-2 = Baubliai-2.

RESULTS

Bulk bentonite mineralogy

Kaolinite is a common major component besides illite-smectite, whereas K-feldspar is relatively rare and occurs in lower concentrations. Pyroclastic quartz is present in almost all bentonites in ca 1% concentration. Reflections of anatase appear on XRD patterns starting from TiO_2 concentrations of ca 1%. Authigenic pyrite and its weathering products gypsum and jarosite are frequent in bentonites. Complete weathering of pyrite in bentonites and exceptional abundance of gypsum and jarosite is remarkable in the Šiupyliai-69 section. This feature facilitates separation of the pyroclastic material, as the grain fraction does not require treatment with nitric acid for removal of pyrite.

Sanidine composition

Silurian bentonites of Lithuanian cores are mostly characterized by wide and very wide XRD $20\bar{1}$ reflections of the main sanidine component (Table 1, Fig. 2). Only 14 of the 59 samples studied contain sanidine with sharp reflection having the best correlation value. Besides the sanidine main component, also other less abundant components are present in samples. These are mostly

Table 1. Bentonites in Lithuanian sections: biostratigraphy, sanidine properties and correlations

Stratigraphy	Graptolite zone	Core	Depth, m	Thickness, cm	Width of the sanidine reflection, deg	Na + Ca component in modal sanidine, mol%	Biotite	Correlations	Source
Ludfordian	<i>balticus?</i>	Geniai-1	1493.1	nd	No		+		Present study
Gorstian	<i>scanicus</i>	Pilviškiai-142	707.7	nd	0.211	27.4	+	Ventspils-D3 603.0	Present study
Gorstian	<i>scanicus-progenitor</i>	Viduklė-61	1232.8	nd	No		++		Present study
Gorstian	<i>progenitor</i>	Baubliai-2	1638.5	nd	No		-		Present study
Gorstian	<i>nilssoni</i>	Viduklė-61	1269.1	nd	Wide		+		Present study
Homerian	<i>parvus</i>	Viduklė-61	1308.0	7.0	No		+		Kiipli et al. 2008c
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	892.1	0.1	No		+++		Present study
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	898.0	3.0	0.206	48.1	+		Present study
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	901.8	1.0	0.213	48.7	+	Vidale-263 634.1?	Present study
Homerian	<i>lundgreni</i>	Šiupyliai-69	1017.0	0.4	0.081	34.4	-	Ventspils-D3 709.5	Present study
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	906.2	0.1+	0.098	35.9	+	Ventspils-D3 709.5	Present study
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	906.3	0.1	0.157	44.2	++	Šiupyliai-69 1032.3?	Present study
Homerian	<i>lundgreni</i>	Šiupyliai-69	1032.3	0.1?	0.246	40.8	-	Kurtuvėnai-166 906.3?	Kiipli et al. 2008c
Homerian	<i>lundgreni</i>	Šiupyliai-69	1035.0	2.0	0.388	36.4	-	Šiupyliai-69 1032.3	Present study
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	906.8	1.0	0.145	49.2	++	Ventspils-D3 714.1	Present study
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	909.0	2.0	0.274	50.0	+	Vidale-263 646.8	Present study
Homerian	<i>lundgreni</i>	Šiupyliai-69	1047.6	0.1	0.269	42.9	+	Ventspils-D3 718.7?	Present study
Homerian	<i>lundgreni</i>	Kurtuvėnai-166	924.8	0.5	0.086	22.9	+++	Rūhnu 337.5	Present study
Homerian	<i>lundgreni</i>	Šiupyliai-69	1052.0	0.1	0.066	23.4	++	Oheasaare 215.7	Present study
Sheinwoodian	<i>perneri-radians</i>	Šiupyliai-69	1076.0	0.1?	0.262	30.4	+	Ventspils-D3 738.6	Present study
Sheinwoodian	<i>perneri-radians</i>	Kurtuvėnai-166	933.8	0.2	0.399	34.6	++	Šiupyliai-69 1076.0	Present study
Sheinwoodian	<i>perneri-radians</i>	Šiupyliai-69	1081.5	1.0	0.269	26.6	+	Ventspils-D3 745.4	Present study
Sheinwoodian	<i>perneri-radians</i>	Kurtuvėnai-166	937.4	0.1	0.333	35.4	++		Present study
Sheinwoodian	<i>belophorus</i>	Šiupyliai-69	1096.5	0.3	0.317	21.2	-	Kurtuvėnai-166 944.0	Present study
Sheinwoodian	<i>belophorus</i>	Kurtuvėnai-166	944.0	0.1	0.358	17.9	+	Oheasaare 287.8	Present study
Sheinwoodian	<i>belophorus</i>	Kunkojai-12	1289.7	6.0	0.06	30.5	++	Oheasaare 288.4	Kiipli et al. 2008c
Sheinwoodian	<i>belophorus</i>	Kurtuvėnai-166	944.5	2.0	0.185	30.9	+	Oheasaare 288.4	Present study
Sheinwoodian	<i>belophorus</i>	Kurtuvėnai-166	946.7	0.5	0.143	32.9	+		Present study
Sheinwoodian	<i>belophorus</i>	Kunkojai-12	1296.0	5.0	0.22	35.0	+		Kiipli et al. 2008c
Sheinwoodian	<i>belophorus</i>	Kurtuvėnai-166	950.5	0.5	0.105	39.9	+		Present study
Sheinwoodian	<i>belophorus</i>	Lygumai-47	1343.0	nd	Very weak		-		Kiipli et al. 2008c
Sheinwoodian	<i>belophorus</i>	Lygumai-47	1343.4	nd	0.32	26.7	-	Viduklė-61 1385.6	Kiipli et al. 2008c
Sheinwoodian	<i>belophorus</i>	Viduklė-61	1385.6	1.0	0.3	26.5	-	Lygumai-47 1343.4	Kiipli et al. 2008c
Sheinwoodian	<i>antennularius</i>	Kurtuvėnai-166	953.0	4.0	0.371	30.4	+		Present study
Sheinwoodian	<i>antennularius</i>	Kurtuvėnai-166	955.0	0.1	0.258	30.5	+		Present study
Sheinwoodian	<i>antennularius</i>	Šiupyliai-69	1107.0	0.5	0.062	28.1	++	Vattenfalllet Bentonite	Present study

Table 1. Continued

Stratigraphy	Graptolite zone	Core	Depth, m	Thickness, cm	Width of the sandstone reflection, deg	Na + Ca component in modal sandstone, mol%	Biotite	Correlations	Source
Sheinwoodian	<i>antennularius</i>	Šiupyliai-69	1109.0	0.1	0.095	23.8	+++		Present study
Sheinwoodian	<i>riccartonensis</i>	Kurtuvėnai-166	958.8	1.0	0.3	27.8	+	Šiupyliai-69 1111.0	Present study
Sheinwoodian	<i>riccartonensis</i>	Šiupyliai-69	1111.0	1.0	0.316	26.2	-	Kurtuvėnai-166 958.8	Present study
Sheinwoodian	<i>riccartonensis</i>	Kurtuvėnai-166	959.8	0.2	No		+++		Present study
Sheinwoodian	<i>riccartonensis</i>	Kurtuvėnai-166	960.5	1.5	ca 0.3	ca 28	-		Present study
Sheinwoodian	<i>riccartonensis</i>	Kurtuvėnai-166	960.7	1.5	ca 0.3	ca 31	-		Present study
Sheinwoodian	<i>murchisoni</i>	Kurtuvėnai-166	971.2	1.0	0.214	30.3	+++	Ireviken Bentonite?	Present study
Sheinwoodian	<i>murchisoni</i>	Kurtuvėnai-166	971.7	3.0	0.207	30.0	+	Storbrut Bentonite?	Present study
Sheinwoodian	<i>murchisoni</i>	Virbalis-5	1122.4	0.2	0.24	35.0	+	Lusklint Bentonite ID150	Present study
Telychian	<i>lapworthi</i>	Šiupyliai-69	1125.0	1.0	Weak		+		Present study
Telychian	<i>lapworthi</i>	Šiupyliai-69	1127.8	3.0	0.306	27.9	+		Present study
Telychian	<i>spiralis-lapworthi</i>	Šiupyliai-69	1128.5	0.5	0.311	25.3	++		Present study
Telychian	<i>spiralis-lapworthi</i>	Šiupyliai-69	1130.0	0.5	Weak		++		Present study
Telychian	<i>spiralis</i>	Viduklė-61	1418.8	nd	0.3	29.4	+		Present study
Telychian	<i>spiralis</i>	Lygumai-47	1383.7	nd	0.395	26.5	+		Present study
Telychian	<i>crenulata</i>	Kurtuvėnai-166	985.2	1.0	0.25	27.4	++		Present study
Telychian	<i>crenulata</i>	Kurtuvėnai-166	987.4	0.1	0.355	22.1	+		Present study
Telychian	<i>griestoniensis</i>	Kurtuvėnai-166	991.0	0.3	0.316	27.1	++	Paatsalu Bentonite ID755	Present study
Telychian	<i>crispus</i>	Kurtuvėnai-166	992.5	0.2	0.117	24.7	++	Musfjala Bentonite ID795	Present study
Telychian	<i>crispus</i>	Kurtuvėnai-166	992.5	0.2	0.156	44.2	++	Ventspils-D3 842.1	Present study
Telychian	<i>crispus</i>	Ramučiai-2	1993.8	nd	No		-		Present study
Telychian	<i>crispus</i>	Rukai-2	1876.2	nd	0.425	24.8	+++		Present study
Telychian	<i>turriculatus</i>	Kurtuvėnai-161	1466.7	1.0	0.075	21.2	+	Osmundsberg B. ID851	Present study
Telychian	<i>linnaei-turriculatus</i>	Geniai-1	1751.0	1.0	0.441	23.1	-		Present study
Telychian	<i>linnaei-turriculatus</i>	Kurtuvėnai-166	1002.2	0.2	0.229	44.0	++	Aizpute-41 966.4 ID880	Present study
Telychian	<i>linnaei-turriculatus</i>	Kurtuvėnai-166	1002.2	0.5	0.242	41.9	+		Present study
Telychian	<i>linnaei-turriculatus</i>	Geniai-1	1752.1	1.0	No		nd	Geniai Tuff ID890	Present study
Aeronian	<i>sedgwickii</i>	Maldūnai-1	1692.2	nd	0.406	26.1	-		Present study
Aeronian	<i>sedgwickii</i>	Maldūnai-1	1692.3	nd	0.452	20.0	-		Present study
Aeronian	<i>sedgwickii</i>	Parovėja-9	714.2	nd	Wide		-		Present study
Aeronian	<i>sedgwickii</i>	Kurtuvėnai-166	1003.2	1.2	ca 0.45	ca 35	-	Aizpute-41 969.4 ID920	Present study
Aeronian	<i>sedgwickii</i>	Kurtuvėnai-166	1004.5	0.8	ca 0.35	ca 41	+		Present study
Rhuddanian	<i>cyphus</i>	Aukštupiai-1	1788.0	nd	Weak		+		Present study

Biotite abundance: - no biotite, + 1-10 flakes, ++ 10-100 flakes, +++ more flakes in the fraction of >0.04 mm separated from 2 g of bentonite; nd, not determined. Thickness of some beds not determined (nd). ID numbers of bentonites according to Kallaste & Kiipli (2006).

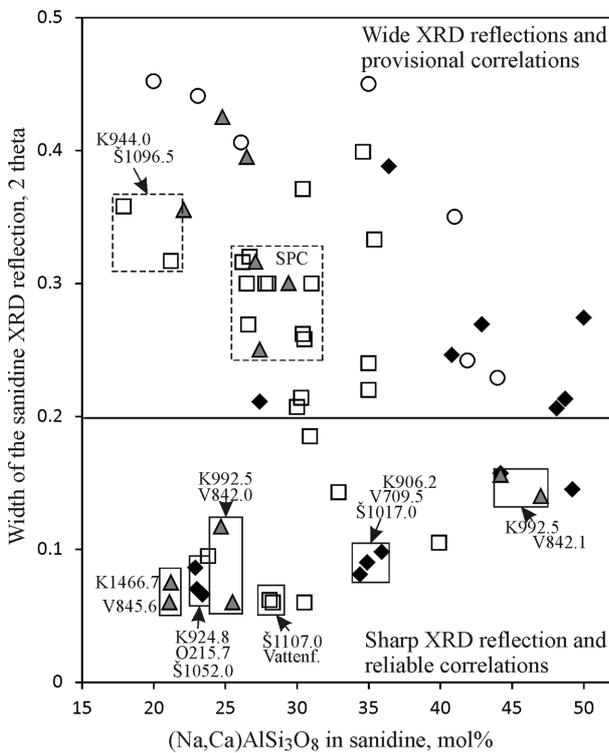


Fig. 2. Results of XRD measurements of sanidine composition on the binary chart: composition versus width of the XRD reflection. Width of the XRD reflection indicates homogeneity (sharp reflection) and heterogeneity (wide reflections) of sanidine crystals. Solid frames denote reliable correlations, broken line frames provisional correlations. K, Kurtuvėnai; Š, Šiupyliai; V, Ventspils; O, Ohesaare; Vattenf., Vattenfallet; SPC, several provisional correlations. Empty rings mark Aeronian, grey triangles – Telychian, empty quadrangles – Sheinwoodian, black diamonds – Homerian. Thirteen studied samples from Lithuania are absent from this figure, as they did not contain sanidine.

more potassic than the main component, but sometimes also more sodic like in the Y-bentonite known from Gotland (Kiipli et al. 2008a). The combination of the main and less frequent components often forms a unique shape of the 20 $\bar{1}$ reflection, which can be used for identification of the eruption layers.

Graptolites

Graptolite studies started in Lithuania in the middle of the 20th century (Paškevičius & Radzevičius 2006). Earlier overall results of graptolite biozonation are available in Paškevičius (1982, 1997). Later research has focused on certain intervals, e.g. the Wenlock–Ludlow boundary (Radzevičius 2006; Radzevičius et al. 2008). New data allowed revision of the Silurian graptolite biostratigraphy of Lithuania (see Fig. 3). However, the graptolite strati-

System	Series	Stage	Reg. stage	Lithuanian graptolite biozones (Paškevičius 1997; Radzevičius 2006)
SILURIAN	Ludlow	Ludfordian	Pagėgiai	<i>Formosograptus formosus</i>
				<i>Monograptus balticus</i>
				<i>Pseudomonoclimacis tauragensis</i>
				<i>Lobograptus scanicus</i>
				<i>Lobograptus progenitor</i>
				<i>Neodiversograptus nilssoni</i>
		Gorsian	Dubysa	<i>Colonograptus ludensis</i>
				<i>Colonograptus deubeli</i>
				<i>Colonograptus praedeubeli</i>
				<i>Gothograptus nassa</i>
				<i>Pristiograptus parvus</i>
				<i>Cyrtograptus lundgreni</i>
				<i>Cyrtograptus perneri</i>
	Wenlock	Homerian	Gėluva	<i>Monograptus belophorus</i>
				<i>Streptograptus antennularius</i>
				<i>Monograptus riccartonensis</i>
				<i>Cyrtograptus murchisoni</i>
				<i>Cyrtograptus centrifugus</i>
		Sheinwoodian	Jaagarahu	<i>Cyrtograptus lapworthi</i>
				<i>Oktavites spiralis</i>
				<i>Monoclimacis crenulata</i>
				<i>Monoclimacis griestonensis</i>
				<i>Streptograptus crispus</i>
	Llandovery	Telychian	Adavere	<i>Spirograptus turriculatus</i>
				<i>Rastrites linnaei</i>
				<i>Stimulograptus sedgwickii</i>
				<i>Lituigraptus convolutus</i>
				<i>Campograptus millepeda</i>
		Aeronian	Raiktila	<i>Demirastrites pectinatus</i>
				<i>Demirastrites triangulatus</i>
				<i>Coronograptus cyphus</i>
				?
				?

Fig. 3. List of Lithuanian graptolite biozones mentioned in text and in figures.

graphic scale presented in Fig. 3 is not accurate. It has some shortcomings that will be discussed below.

Graptolites near the Aeronian–Telychian boundary need revision. The appearance of *Rastrites linnaei* (Barrande) is marked by the lower boundary of the Telychian in Lithuania. According to Loydell (2012), the base of the *linnaei* Biozone does not conform to the base of the Telychian, since *R. linnaei* appears in the upper part of the Aeronian. So, he recommended that the *Stimulograptus halli* Biozone should be included in the upper part of the Aeronian, the *Spirograptus guerichi* Biozone in the lower part of the Telychian and the *linnaei* Biozone rejected.

Another problematic interval, which should further be investigated in Lithuania, is the upper part of the *lapworthi* Biozone in the upper Llandovery. According to Loydell (2012), the *Cyrtograptus insectus* Biozone

occurs between the *lapworthi* and *centrifugus* biozones. The *insectus* Biozone has not been defined in Lithuania, because no findings of *Cyrtograptus insectus* Bouček are known in that region and therefore this biozone is tentatively included into the *lapworthi* Biozone. The *insectus* Biozone is distinguished in the Kaliningrad district (Suyarkova 2012).

The third problematic interval is near the Gorstian–Ludfordian boundary. The interval from the upper boundary of the *scanicus* Biozone to the lower boundary of the *balticus* Biozone has been called the *Pseudomonoclimacis tauragensis* Biozone (Paškevičius 1997). The base of the *tauragensis* Biozone is marked by the appearance of *P. tauragensis* (Paškevičius). The identification of this biozone is not very reliable, because (1) *Pseudomonoclimacis tauragensis* has long biostratigraphical range, (2) *P. tauragensis* is hardly distinguishable from *P. haupti* (Kühne), (3) it is impossible to trace the Gorstian and Ludfordian boundary using *P. tauragensis*, (4) there exist better biozonal index species such as *Saetograptus leintwardinensis*, *S. linearis*, *Bohemograptus bohemicus tenuis* and others with short biostratigraphical ranges. So, this interval as well needs detailed study in future.

Stratigraphical distribution and correlation of bentonites

Only one bentonite has been found in the Rhuddanian of Lithuania and another is known from the Ohesaare core in Estonia (Kiipli & Kallaste 1996). The Aeronian, however, shows signs of remarkable volcanic activity. Five bentonites were established in the Aeronian part of the Dobeles Formation in Lithuania. Most of these bentonites are characterized by a wide or weak sanidine reflection (Figs 2, 4, Table 1), while in some bentonites sanidine is absent at all. This type of sanidine does not allow well-proved correlations by the XRD method. The ca 1 cm thick Geniai Tuff, characterized by an unusually high content of REE elements up to 3%, occurs near the Aeronian–Telychian boundary in the Geniai-1 core (Kiipli et al. 2012b).

Seventeen bentonites are found in the Telychian in Lithuanian sections. This number is significantly less than in Latvia and Estonia where bentonites from ca 50 eruptions have been described and correlated (Kiipli et al. 2010b). Two bentonites from the Kurtuvėnai-166 core (depths 971.2 and 971.7 m) may also belong to the upper Telychian. However, as graptolite finds from this level are not sufficiently complete and geochemical data allow correlations with lower Sheinwoodian bentonites, we attributed these layers provisionally to the Sheinwoodian. On the basis of the characteristic XRD reflections of the sanidine and graptolite zonation, three Lithuanian bentonites can be correlated with Estonian and Lithuanian

ones (Figs 2, 4, Table 1). These include the ash bed at a depth of 1466.7 m in the Kurtuvėnai-166 core correlating with the Osmundsberg Bentonite. The bentonite at 992.5 m in the Kurtuvėnai-161 core interestingly reveals two sharp sanidine reflections, hinting at the mixture of two eruptions. These eruptions can be correlated with 842.0 and 842.1 m bentonites in the Ventspils-D3 core. Sanidine in other bentonites is characterized by wide or weak XRD reflections or shows no reflection at all.

Twenty-six bentonites, representing 22 eruption layers, were found in the Sheinwoodian part of the section in Lithuania. Six of these bentonites were already described in Kiipli et al. (2008c), but are included also in Table 1. The volcanic record starts with three bentonites (Virbalis-5, 1122.4 m; Kurtuvėnai-166, 971.7 m; Kurtuvėnai-166, 971.2 m), which can be provisionally correlated with the Lusklint, Storbrut and Ireviken bentonites in Gotland, Latvia and Estonia. Finds of graptolites are not conclusive at this level, therefore these correlations are not finally proved.

The *riccartonensis* to *belophorus* graptolite biozones include mostly bentonites with wide and very wide sanidine reflections and correlations are therefore often provisional (Fig. 5). Still, very wide reflections can be differentiated from wide reflections with certainty and used for correlations. Some of Lithuanian bentonites contain a specific type of sanidine giving a wide reflection with the modal value of the Na + Ca component between 26 and 30 mol%. Some bentonites in Lithuania (e.g. at 944.5 and 946.7 m in the Kurtuvėnai-166 core) revealed a sharp sanidine reflection and can be correlated with bentonites in Latvia and Estonia (Fig. 5). The Šiupyliai-69 1107.0 m bentonite in the *antennularius* Biozone showed a sharp reflection with 28 mol% of the Na + Ca component and can be correlated with the Vattenfallet Bentonite from the exposure in the town of Visby on Gotland (Kiipli et al. 2008a).

Only four bentonites were found in the upper part of the Sheinwoodian in Lithuania. Among these the Šiupyliai-69 1076.0 m bentonite can be correlated with Latvian sections according to the sharp sanidine reflection and Na + Ca component of 30.4 mol%. The Ventspils-D3 and Vidale-263 sections of Latvia contain a large number of bentonites at this level (Kiipli et al. 2010a), while in Estonian sections bentonites are again relatively rare in this interval. Y-bentonite from the Slite Formation of Gotland (Batchelor & Jeppsson 1999) can be correlated by sanidine of specific shape (Kiipli et al. 2008a, 2013a) with bentonites in Estonian (Ohesaare, 275.3 m) and Latvian (Ventspils-D3, 736.4 m) sections (Fig. 5).

A 0.1 cm thick bentonite with a very strong and sharp sanidine reflection and the Na + Ca component 23.4 mol% was found in the lower part of the *lundgreni* Biozone at the beginning of the Homeric Stage at a

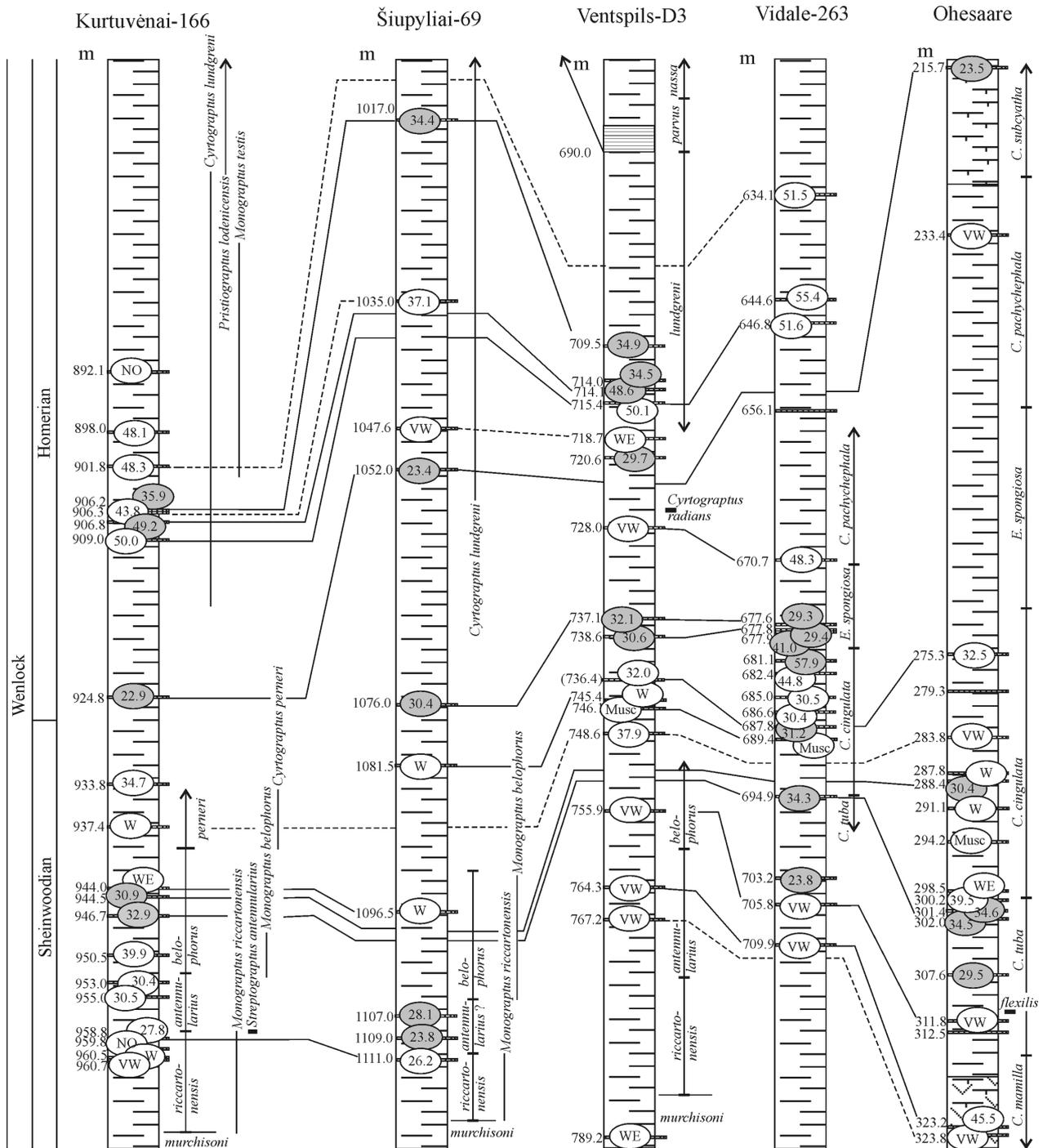


Fig. 5. Correlation of bentonites in the upper Sheinwoodian and lower Homerian. Distribution of graptolites in the Ventspils-D3 core from Gailite et al. (1987) and of chitinozoans from Kiipli et al. (2010a). For legend see Fig. 4.

partly correlating with the Lithuanian ash beds, and six bentonites are known from the Ohesaare core in Estonia. Considering correlations, up to 18 eruption layers can be counted in the *lundgreni* graptolite Biozone. Sanidines in these bentonites form two clusters according to the

XRD reflections: (1) with sharp reflections and the Na + Ca component between 31 and 36 mol% and (2) with wide reflections with the Na + Ca component 43–56 mol%. Several well-proved correlations occur between Lithuanian and Latvian sections (Fig. 5).

Higher in the Homerian, in the interval from *parvus* to *ludensis* graptolite biozones, volcanic ashes were not found in the Kurtuvėnai-166 and Šiupyliai-69 sections.

The Ludlow part has not been studied in detail in Lithuanian sections. We collected five bentonite samples, one of which, from 707.7 m in the Pilviškiai-142 section, belongs to the upper *scanicus* Biozone, possibly correlating with the Ventspils-D3 603.0 m bentonite.

DISCUSSION

The number of Aeronian bentonites increases to the southwest from the East Baltic area. For example, Bergström et al. (1999) recorded ten bentonites in the Röstanga core, southern Sweden, and Bjerreskov (1975) found eight bentonites in Bornholm. This refers to volcanic sources in the Central European Caledonides from the collision zone of the Avalonia and Baltica plates (Kiipli et al. 2013a, 2013b). A large number of Rhuddanian and Aeronian bentonites are known from the Southern Uplands of Scotland (Batchelor & Weir 1988). This area was in the Laurentian side of the Iapetus Ocean, indicating subduction of the ocean floor and volcanism near the Laurentian margin. Wide sanidine reflections in Telychian bentonites probably indicate other volcanic sources than for ash beds of that age in Estonia and Latvia, many of which are characterized by sharp sanidine XRD reflections. Central European sources from the collision zone of Avalonia and Baltica can be supposed. This result confirms that Telychian volcanic ashes, forming a number of the Estonian–Latvian bentonites which are not found in Lithuania, reached the East Baltic area from the north-western direction (present-day orientation) – from the margins of the Iapetus Ocean (Kiipli et al. 2008b, 2008c, 2010b, 2012a, 2013a). Scarcity of bentonites in the upper Homerian and Lower Ludlow of Lithuania and their frequent occurrence in Latvian and Estonian sections indicate a source from the northwest in terms of present-day orientation.

The Šiupyliai-69 1052.0 m bentonite with very distinctive sanidine composition can be used as a marker horizon for tracing the lower boundary of the *lundgreni* Biozone. In the Ohesaare section this bentonite belongs to the upper part of the Jamaja Formation and in the Ruhnu section to the lower part of the Sörve Formation (Kiipli & Kallaste 2006) in the middle of the *Conochitina subcyatha* chitinozoan Biozone (Kiipli et al. 2010a). This result confirms the correlation by Nestor (1994) where the lower boundary of the *testis* graptolite Biozone (roughly corresponding to the *lundgreni* graptolite Biozone) was correlated with the middle of the *C. subcyatha* chitinozoan Biozone. We propose the stratigraphic name

‘the Šiupyliai Bentonite’ for this marker horizon. This bentonite has not been found in the Ventspils-D3 and Vidale-263 cores, possibly because the sea current (Kiipli et al. 2012a, 2013a) has washed small ash falls away.

The Grötlingbo Bentonite occurs within the Mulde Event in the Homerian Stage (Calner et al. 2006; Dahlquist et al. 2012). Previously we studied a 7 cm thick bentonite in the *parvus* Biozone from the Viduklė-61 drill core (depth 1308 m) and correlated it with the Grötlingbo Bentonite (Kiipli et al. 2008c; Dahlquist et al. 2012). Now doubts have risen about that correlation. This bentonite occurs closely above the lithologically easily recognizable Ančia Member (finely laminated limestone), e.g. in the *parvus* graptolite Zone and within the lower carbon isotope positive excursion. The only unexplained fact is that the bentonite at 1308.0 m in the Viduklė-61 core did not contain biotite, which is typically abundant in the Grötlingbo Bentonite in other locations (Dahlquist et al. 2012). This correlation was followed by Cramer et al. (2012). Later Kiipli et al. (2010c) assigned the 10 cm thick bentonite, occurring 10 m above the Ančia Beds in the Priekule core, within the second carbon isotope positive excursion in the *nassa* graptolite Zone, to the Grötlingbo Bentonite. The reasons were significant thickness of the ash bed and abundance of biotite mentioned in core description. Kiipli et al. (2011) provisionally correlated the Grötlingbo Bentonite with the biotite-rich bentonite in the Ventspils-D3 core, 8 m higher than the Ančia Beds in the *nassa* Biozone. Thus, there are two ways of correlating the Grötlingbo Bentonite with graptolite zonation.

SUMMARY AND CONCLUSIONS

Study of Silurian bentonites in Lithuanian sections enabled us to extend correlations to the south. A wider study area allows better discrimination of volcanic sources from the Laurentia–Baltica and Avalonia–Baltica collision zones. Volcanic sources from the Avalonia–Baltica collision were significant in the Aeronian. In the Telychian this zone yielded ashes with a wide sanidine reflection to Lithuania, but the northern and central Baltic area was reached by a number of ashes from the Laurentia–Baltica collision area. Both sources were active also in the Sheinwoodian, but in the early Homerian the main source direction shifted to the west or northwest (in present-day orientation). Only a northwestern source can be recognized in the late Homerian and Early Ludlow. Volcanic activity almost ended in the Late Ludlow. Only a few ash beds are known in the latest Silurian of Lithuania, indicating again a possible southern volcanic source.

Correlation of the 1107.0 m bentonite of the Šiupyliai-69 core in the *antennularius* Biozone with the Vattenfallet Bentonite on Gotland shows correlation of the Höglint Formation on Gotland with the *antennularius* Zone. At the lower boundary of the Homeric Stage (lower *lundgreni* Zone) a new marker layer, the Šiupyliai Bentonite, indicates correlation with the Jamaja (Ohesaare core) and Sörve (Ruhnu core) formations in Estonia. This integrated bio- and chemostratigraphical study can serve as reference in future correlation works in the region.

Acknowledgements. This study was financed by the Estonian Science Foundation (grant 8963) and targeted financing project SF0140016s09. Sigitas Radzevičius was supported by the Science Council of Lithuania (project No. MIP-034/2012). The authors thank R. A. Batchelor and an anonymous reviewer for useful comments and suggestions. This research is a contribution to IGCP project 591.

REFERENCES

- Andre, L., Hertogen, J. & Deutsch, S. 1986. Ordovician–Silurian magmatic provinces in Belgium and the Caledonian orogeny in middle Europe. *Geology*, **14**, 879–882.
- Batchelor, R. A. 2009 (for 2008). Geochemical ‘Golden Spike’ for Lower Palaeozoic metabentonites. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, **99**, 177–187.
- Batchelor, R. A. & Jeppsson, L. 1999. Wenlock metabentonites from Gotland, Sweden: geochemistry, sources and potential as chemostratigraphic markers. *Geological Magazine*, **136**, 661–669.
- Batchelor, R. A. & Weir, J. A. 1988. Metabentonite geochemistry: magmatic cycles and graptolite extinctions at Dob’s Linn, southern Scotland. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **79**, 19–41.
- Bergström, S. M., Huff, W. D., Koren, T., Larsson, K., Ahlberg, P. & Kolata, D. R. 1999. The 1997 core drilling through Ordovician and Silurian strata at Röstånga, S. Sweden: preliminary stratigraphic assessment and regional comparison. *GFF*, **121**, 127–135.
- Bjerreskov, M. 1975. Llandoveryan and Wenlockian graptolites from Bornholm. *Fossils and Strata*, **8**, 1–93.
- Böhnke, A. & Katzung, G. 2001. The Middle Silurian from Bornholm (Denmark) – sedimentology, petrology and age. *Neues Jahrbuch für Geologie und Paläontologie*, **222**, 161–191.
- Calner, M., Kozłowska, A., Masiak, M. & Schmitz, B. 2006. A shoreline to deep basin correlation chart for the middle Silurian coupled extinction-stable isotopic event. *GFF*, **128**, 79–84.
- Carey, A., Samson, S. D. & Sell, B. 2009. Utility and limitations of apatite phenocryst chemistry for continent-scale correlation of Ordovician K-bentonites. *Journal of Geology*, **117**, 1–14.
- Cramer, B. D., Condon, D. J., Söderlund, U., Marshall, C., Worton, G. J., Thomas, A. T., Calner, M., Ray, D. C., Perrier, V., Boomer, I., Patchett, P. J. & Jeppsson, L. 2012. U–Pb (zircon) age constraints on the timing and duration of Wenlock (Silurian) paleocommunity collapse and recovery during the ‘Big Crisis’. *Geological Society of America Bulletin*, **124**, 1841–1857.
- Dahlquist, P., Calner, M., Kallaste, T., Kiipli, T. & Siir, S. 2012. Geochemical variations within the mid-Silurian Grötlingbo Bentonite of Sweden and the East Baltic area – discriminating between magmatic composition, ash transport fractionation and diagenetic effects. *GFF*, **134**, 273–282.
- Gailite, L. K., Ulst, R. J. & Yakovleva, V. I. 1987. *Stratotipicheskie i tipovye razrezy Silura Latvii* [Stratotype and Type Sections of the Silurian of Latvia]. Zinatne, Riga, 183 pp. [in Russian].
- Hetherington, C. J., Nakrem, H. A. & Potel, S. 2011. Note on the composition and mineralogy of Wenlock Silurian bentonites from the Ringerike District: implications for local and regional stratigraphic correlation and sedimentary environments. *Norwegian Journal of Geology*, **91**, 181–192.
- Hints, R., Kirsimäe, K., Somelar, P., Kallaste, T. & Kiipli, T. 2008. Multiphase Silurian bentonites in the Baltic Palaeobasin. *Sedimentary Geology*, **209**, 69–79.
- Huff, W. D., Bergström, S. M., Kolata, D. R. & Sun, H. 1998. The Lower Silurian Osmundsberg K-bentonite. Part II: mineralogy, geochemistry, chemostratigraphy and tectono-magmatic significance. *Geological Magazine*, **135**, 15–26.
- Inanli, F. Ö., Huff, W. D. & Bergström, S. M. 2009. The Lower Silurian (Llandovery) Osmundsberg K-bentonite in Baltoscandia and the British Isles: chemical fingerprinting and regional correlation. *GFF*, **131**, 269–279.
- Kallaste, T. & Kiipli, T. 2006. New correlations of Telychian (Silurian) bentonites in Estonia. *Proceedings of the Estonian Academy of Sciences, Geology*, **55**, 241–251.
- Kaminskas, D., Paškevičius, J. & Radzevičius, S. 2006. Graptolite biostratigraphy and peculiarities of depositional environments during Late Llandovery and Wenlock according to geochemical data from Kurtuvėnai-161 borehole (NW Lithuania). *Geologija (Vilnius)*, **53**, 1–7 [in Lithuanian].
- Kiipli, E. & Kallaste, T. 1996. Geochemical characterization of some Estonian metabentonites. *Proceedings of the Estonian Academy of Sciences, Geology*, **45**, 68–77.
- Kiipli, E., Kiipli, T. & Kallaste, T. 2006. Identification of the O-bentonite in the deep shelf sections with implication on stratigraphy and lithofacies, East Baltic Silurian. *GFF*, **128**, 255–260.
- Kiipli, T. & Kallaste, T. 2002. Correlation of Telychian sections from shallow to deep sea facies in Estonia and Latvia based on the sanidine composition of bentonites. *Proceedings of the Estonian Academy of Sciences, Geology*, **51**, 143–156.
- Kiipli, T. & Kallaste, T. 2006. Wenlock and uppermost Llandovery bentonites as stratigraphic markers in Estonia, Latvia and Sweden. *GFF*, **128**, 139–146.
- Kiipli, T., Jeppsson, L., Kallaste, T. & Söderlund, U. 2008a. Correlation of Silurian bentonites from Gotland and the East Baltic using sanidine phenocryst composition, and biostratigraphical consequences. *Journal of the Geological Society*, **165**, 211–220.

- Kiipli, T., Orlova, K., Kiipli, E. & Kallaste, T. 2008b. Use of immobile trace elements for the correlation of Telychian bentonites on Saaremaa Island, Estonia, and mapping of volcanic ash clouds. *Estonian Journal of Earth Sciences*, **57**, 39–52.
- Kiipli, T., Radzevičius, S., Kallaste, T., Motuza, V., Jeppsson, L. & Wickström, L. 2008c. Wenlock bentonites in Lithuania and correlation with bentonites from sections in Estonia, Sweden and Norway. *GFF*, **130**, 203–210.
- Kiipli, T., Soesoo, A., Kallaste, T. & Kiipli, E. 2008d. Geochemistry of Telychian (Silurian) K-bentonites in Estonia and Latvia. *Journal of Volcanology and Geothermal Research*, **171**, 45–58.
- Kiipli, T., Kallaste, T., Kleesment, A. & Nielsen, A. 2009. Corroded hydrothermal quartz in Ordovician altered volcanic ash beds of the Baltoscandian Region. *Estonian Journal of Earth Sciences*, **58**, 268–272.
- Kiipli, T., Kallaste, T. & Nestor, V. 2010a. Composition and correlation of volcanic ash beds of Silurian age from the eastern Baltic. *Geological Magazine*, **147**, 895–909.
- Kiipli, T., Kallaste, T., Nestor, V. & Loydell, D. K. 2010b. Integrated Telychian (Silurian) K-bentonite chemostratigraphy and biostratigraphy in Estonia and Latvia. *Lethaia*, **43**, 32–44.
- Kiipli, T., Kiipli, E. & Kaljo, D. 2010c. Silurian sea level variations estimated using $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios in the Priekule drill core section, Latvia. *Bollettino della Societa Paleontologica Italiana*, **49**, 55–63.
- Kiipli, T., Einasto, R., Kallaste, T., Nestor, V., Perens, H. & Siir, S. 2011. Geochemistry and correlation of volcanic ash beds from the Rootsiküla Stage (Wenlock–Ludlow) in the eastern Baltic. *Estonian Journal of Earth Sciences*, **60**, 207–219.
- Kiipli, T., Kallaste, T. & Nestor, V. 2012a. Correlation of upper Llandovery–lower Wenlock bentonites in the När (Gotland, Sweden) and Ventpils (Latvia) drill cores: role of volcanic ash clouds and shelf sea currents in determining areal distribution of bentonites. *Estonian Journal of Earth Sciences*, **61**, 295–306.
- Kiipli, T., Radzevičius, S., Kallaste, T., Kiipli, E., Siir, S., Soesoo, A. & Voolma, M. 2012b. The Geniai Tuff in the southern East Baltic area – a new correlation tool near the Aeronian/Telychian stage boundary, Llandovery, Silurian. *Bulletin of Geosciences*, **87**, 695–704.
- Kiipli, T., Kallaste, T., Kiipli, E. & Radzevičius, S. 2013a. Correlation of Silurian bentonites based on the immobile elements in the East Baltic and Scandinavia. *GFF*, **135**, 152–161.
- Kiipli, T., Soesoo, A. & Kallaste, T. 2013b. Geochemical evolution of Caledonian volcanism recorded in the sedimentary rocks of the eastern Baltic region. In *New Perspectives on the Caledonides of Scandinavia and Related Areas* (Corfu, F., Gasser, D. & Chew, D. M., eds), *Geological Society of London Special Publications*, **390**, <http://dx.doi.org/10.1144/SP390.5>
- Lapinskas, P. P. 1965. Metabentonitė nįzhnego silura Litvy [Lower Silurian metabentonites of Lithuania]. In *Geologiya i neftenosnos't paleozoya yuzhnoj Pribaltiki* [Geology and Oil Content of the Southern East Baltic Area] (Suveizdis, P. I., ed.), *Gosudarstvennyj Geologicheskij Komitet SSR, Institut Geologii, Trudy*, **1**, 49–63 [in Russian].
- Lapinskas, P. 2000. *Structure and Petroliferosity of the Silurian in Lithuania*. Institute of Geology, Vilnius, 203 pp.
- Loydell, D. K. 2012. Graptolite biozone correlation charts. *Geological Magazine*, **149**, 124–132.
- Loydell, D. K., Männik, P. & Nestor, V. 2003. Integrated biostratigraphy of the lower Silurian of the Aizpute-41 core, Latvia. *Geological Magazine*, **140**, 205–229.
- Motuza, V., Radzevičius, S. & Paškevičius, J. 2002. Influence of Caledonic volcanic activity for marine paleoenvironment: evidence from the Llandoveryan graptolites of Baltic Sedimentary Basin. In *The Fifth Baltic Stratigraphical Conference "Basin Stratigraphy – Modern Methods and Problems"* (Satkūnas, J. & Lazauskienė, J., eds), pp. 132–124. Vilnius.
- Nestor, V. 1994. Early Silurian chitinozoans in Estonia and North Latvia. *Academia*, **4**, 1–163.
- Paškevičius, J. 1982. Some questions on the distribution, development conditions and correlation of the Silurian fauna in Lithuania and the neighbouring countries. *Geologija (Vilnius)*, **3**, 17–51 [in Russian].
- Paškevičius, J. 1997. *The Geology of the Baltic Republics*. Geological Survey of Lithuania, Vilnius, 387 pp.
- Paškevičius, J. & Radzevičius, S. 2006. Rytinių baltijos kraštų silūro graptolitų tyrimų istorija ir jų zoninė skalė [The history of investigation of the Silurian graptolites and their zonal scale in the Eastern Baltic countries]. In *Science in the Nature Science Faculty: Fourth Scientific Conference on 23–24 November 2006, the Presentations* (Rukšėnas, O., ed.), pp. 194–209. Vilniaus universiteto leidykla, Vilnius [in Lithuanian, with English summary].
- Radzevičius, S. 2006. Late Wenlock biostratigraphy and the *Pristiograptus virbalensis* group (Graptolithina) in Lithuania and the Holy Cross Mountains. *Geological Quarterly*, **50**, 333–344.
- Radzevičius, S. & Paškevičius, J. 2000. Pristiograptids (Graptolites) and their adaptive types of the Wenlock (Silurian) in Lithuania. *Geologija (Vilnius)*, **32**, 88–109.
- Radzevičius, S. & Paškevičius, J. 2005. *Pristiograptus* (Graptoloidea) from the Upper Wenlock of the Baltic Countries. *Stratigraphy and Geological Correlation*, **13**, 159–169.
- Radzevičius, S., Paškevičius, J. & Meidla, T. 2008. Kai kurių silūro graptolitų evoliucija ir filogenija [Evolution and phylogenesis of some Silurian graptolites]. *Geologijos akiračiai*, **2**, 35–42 [in Lithuanian, with English summary].
- Ray, D. C., Collings, A. V. J., Worton, G. J. & Jones, G. 2011. Upper Wenlock bentonites from Wren's Nest Hill, Dudley; comparisons with prominent bentonites along Wenlock Edge, Shropshire, England. *Geological Magazine*, **148**, 670–681.
- Suyarkova, A. 2012. Biostratigrafiya pogranichnykh otlozhenij llandovery–venloka Kaliningradskoj oblasti po graptolitam [Biostratigraphy of the Llandovery–Wenlock boundary deposits of Kaliningrad District based on graptolites]. *Regional'naya Geologiya i Metallogeniya*, **52**, 15–20 [in Russian].
- Timmerman, M. J. 2008. Palaeozoic magmatism. In *The Geology of Central Europe. Volume 1: Precambrian and Palaeozoic* (McCann, T., ed.), pp. 665–748. Geological Society, London.

Siluri bentoniidid Leedus: korrelatsioonid sanidiini fenokristallide koostise ja graptoliitide biotsonaalsuse järgi – vulkaanipursete piirkondade interpretatsioon

Tarmo Kiipli, Sigitas Radzevičius ja Toivo Kallaste

On käsitletud Leedu bentoniitide (muutunud vulkaanilised tuhad) korrelatsiooni sanidiini koostise ja graptoliititsoonide alusel. Detailselt on uuritud bentoniitide esinemist kahes Leedu puursüdamikus ja tulemuste alusel on varasemaid korrelatsioone laiendatud lõuna suunas. Graptoliidiliikide identifitseerimine võimaldas tuvastada bentoniitide stratigraafilise asendi. Siluri bentoniitidele Leedus on iseloomulik sanidiini põhikomponendi lai või väga lai röntgendifraktsiooni $20\bar{1}$ refleks. Ainult 14 bentoniiti 69-st sisaldasid terava $20\bar{1}$ refleksiga sanidiini, mida saab efektiivselt kasutada kihtide korrelatsioonikriteeriumina. Leedu läbilõigetel leiti 1 bentoniit Rhuddanianis, 5 kihti Aeronis, 17 bentoniiti Telychis, 26 Sheinwoodis, 10 Homeris ja 6 Ludlow's. Vulkaanilise tuha kihid Ida-Baltikumis, mis olid bentoniitide lähtematerjaliks, pärinesid vähemalt 150 purskest Siluris. Suuremal osal Leedust leitud purskekihtidest ei ole Lätis ja Eestis korreleeruvat vastet. See näitab, et vulkaanilised kihid pärinesid kahest vulkaanilisest piirkonnast: Kesk-Euroopa ja Norra Kaledoniididest.