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Geochemistry and correlation of volcanic ash beds from the Rootsiküla Stage (Wenlock–Ludlow) in the eastern Baltic

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Abstract. Nine altered volcanic ash samples from the shoal and lagoonal sediments of the Rootsiküla Stage (Wenlock–Ludlow boundary interval, Estonia) were analysed, compared and correlated with five samples of deep sea environments from Latvia. Volcanic ash correlations indicate that the Wenlock–Ludlow boundary correlates with the boundary of the Viita and Kuusnõmme beds, i.e., it is significantly lower than proposed earlier. The distribution of chitinozoans supports this new correlation. Geochemical data indicate subalkaline source magma of volcanic ashes with potassium dominating over sodium.

Key words: bentonites, K-bentonites, Wenlock, Ludlow, Silurian, chitinozoans, volcanism.

INTRODUCTION

Volcanic ash beds altered to clay (bentonites, K-bentonites) in Silurian sections have been successfully applied in stratigraphy as perfect time markers for correlation (Batchelor 2009; Inanli et al. 2009; Kallaste & Kiipli 2006; Kiipli & Kallaste 2006; Kiipli et al. 2006, 2008a, 2010b). For identification of a particular eruption bed the composition of apatite (Ray 2007; Carey et al. 2009), biotite (Batchelor 2003) and sanidine phenocrysts (Kiipli & Kallaste 2002), the specific shape of phenocrysts (Kiipli et al. 2009) and immobile trace elements (Huff et al. 1998; Kiipli et al. 2008b) have been used. The phenocryst and bulk geochemistry of bentonites provides also an opportunity to interpret magma geochemistry and evolution of tectonomagmatic processes in source areas (Histon et al. 2007; Kiipli et al. 2008d, 2010a). Volcanic ash beds in sedimentary sections represent valuable material for isotopic dating (Huff 2008).

The volcanic ash beds from the Wenlock–Ludlow boundary interval in northern Europe have been studied by Batchelor & Jeppsson (1999), Hetherington et al. (2004), Kiipli et al. (2008a, 2008c) and Ray et al. (2011). The Homerian Stage shows significant extinction of marine fauna, called the Mulde Event when characterized by conodonts (Jeppsson & Calner 2003; Calner et al. 2006) or the Lundgreni Event in graptolite studies (Koren 1987; Porebska et al. 2004). The extinction of marine life was followed by the positive excursion of the carbon isotope ratio in marine sediments (Kaljo et al. 1997) and global sea level fall (Johnson 2009; Kiipli et al. 2010c). Precise correlation of sections is important for establishing a detailed succession and causes of these environmental events.

The aim of the present study is to report new geochemical data of volcanic ash beds in the Wenlock–Ludlow boundary interval and to use ash beds for refinement of correlation between deep-sea and shallow-water sections. The interpretation of the source magma type is also proposed.

MATERIAL AND METHODS

Fourteen samples from interbeds of supposedly volcanic origin were collected from six drill cores from Saaremaa Island, Estonia, and two cores from Latvia (Fig. 1). Additionally seven samples from the Grötlingbo Bentonite studied by Kiipli et al. (2008c) were reanalysed by standard X-ray fluorescence (XRF) spectrometry in order to create the best comparison with new data. Twenty-one samples were taken from the Vidale-263 core for palaeontological study. Saaremaa cores, except the Ohesaare core, are stored at the Geological Survey of Estonia, Latvian cores at the Latvian Agency of Environment, Meteorology and Geology. The Ohesaare core is held at the Institute of Geology at Tallinn University of Technology.

Bulk mineralogy of the samples was determined from randomly oriented samples by X-ray diffractometry

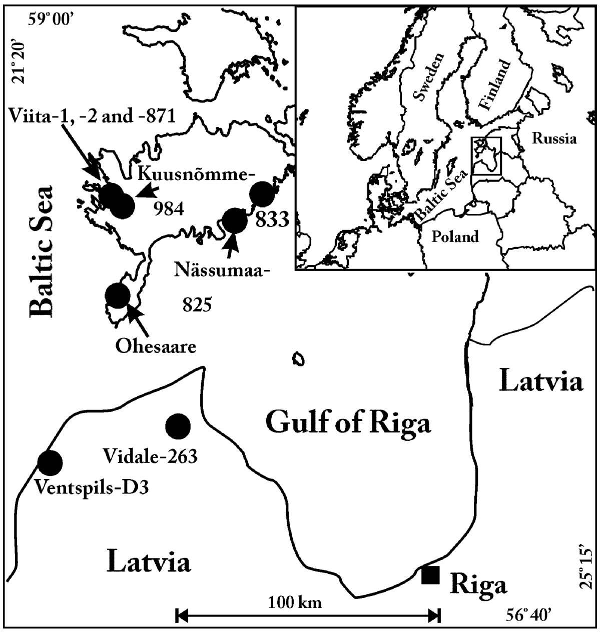

Fig. 1. Location of the studied drill core sections.

(XRD). An association of mixed-layer illite-smectite and kaolinite as major minerals has been considered as the indicator of the volcanic origin of these beds (Hints et al. 2008). Host shales are composed of different associations of terrigenous minerals including illite, quartz, chlorite and minor K-feldspar.

Magmatic sanidine phenocrysts $(K,Na,Ca)AlSi_3O_8$ were analysed from coarse fractions (0.04–0.1 mm) separated from 2 g of bentonite. The fraction 0.04–0.1 mm makes up a few per cent of the bulk bentonite. Sanidine dominates among phenocrysts, with biotite and quartz being subordinate. The $20\overline{1}$ reflection of sanidine was measured in the range from 23.5 to 26.0 °2θ, using Fe filtered Co Kα radiation. From the position of the $20\overline{1}$ reflection, the $(Na,Ca)AlSi_3O_8$ content in $(K,Na,Ca)AlSi_3O_8$ solid solution (sanidine) was calculated according to Orville (1967), using linear relationship between K-sanidine (d = 4.233 Å) and albite (d = 4.033 Å). The position of the magmatic sanidine XRD reflections was refined, using quartz (d = 4.255 Å) or authigenic K-feldspar (d = 4.233 Å) naturally occurring in samples. In favourable cases (sharp reflection and low content of authigenic potassium feldspar) the precision of the method was ±1%. In less favourable cases the precision was ±2%. Small amounts of Ca substituted for Na can influence the position of the sanidine $20\overline{1}$ reflection and thus the Na + Ca component (mol%) can be determined. Considering this effect as minor, in our previous works (Kiipli & Kallaste 2002) sanidine composition was expressed in units of Na-component concentration in $(K,Na)AlSi_3O_8$. The numerical values presented herein are still strictly comparable with those of our previous publications. The integral width of the sanidine reflection (without the instrumental component) was calculated as the reflection surface area divided by height. Large variations in the width of the sanidine reflection are probably caused by the heterogeneous composition of the crystals commonly occurring as zonation in phenocrysts (Ginibre et al. 2004). Small sizes of crystallites can also influece the width of the reflection. The terms 'wide reflection' and 'sharp reflection' through the text indicate reflections wider and sharper than 0.15°. All measured XRD spectra are available in the collections database of the Institute of Geology at Tallinn University of Technology (http://geokogud.info/git/reference.php?id=1586).

Samples of sufficient size, at least 8 g, were analysed by XRF from pressed powders for major and trace elements by applying empirical correction coefficients. The analyses were performed with the Bruker AS S-4 spectrometer in the Institute of Geology at Tallinn University of Technology. The precision of the method was mostly better than ±5% of the concentration and for trace elements in the range 10–30 ppm better than ±10%. For calibration and quality control reference materials from France (Govindaraju 1995) and Estonia (Kiipli et al. 2000) were used. The accuracy of the method is described in Kiipli et al. (2008b).

LITHOLOGY AND STRATIGRAPHY

The Rootsiküla Stage in Saaremaa consists of shallow-water sediments: finely laminated lagoonal dolomites with *Eurypterus*, bioturbated dolomites, laminated stromatolites, biomorphic and coarse-grained limestones. Beds with *Eurypterus* (now the Rootsiküla Stage) were first distinguished as a separate stratigraphical unit by Schmidt (1891) and were correlated with the lower part of the Ludlow. Einasto (1970) described in detail the internal structure and boundaries of the stage, based on the cyclic nature of sedimentation. He established four sedimentary cycles starting from grainstones and biomorphic limestones affected by strong wave action and ending with lagoonal dolomites of quiet-water environment. These cycles were named (from bottom to top) the Viita, Kuusnõmme, Vesiku and Soeginina beds (Fig. 2). Later Viira & Einasto (2003) distinguished the Anikaitse Beds between the Vesiku and Soeginina beds. The Wenlock–Ludlow boundary has been supposed to correlate with some level within the Rootsiküla Stage (Einasto 1970), or due to lack of more precise information, has been considered formally to coincide with the boundary of the Rootsiküla and Paadla stages (Nestor & Nestor 1991; Nestor 1997). Viira & Einasto (2003) assigned the Soeginina Beds to the Paadla Stage and lower Ludlow.

<table>
<tr><th>Cyclostratigraphy in Saaremaa (Einasto 1970; Viira & Einasto 2003; +present study)</th><th>Einasto (1970)</th><th>Nestor (1997)</th><th>Combined from Kaljo et al. (1997), Viira & Einasto (2003)</th><th>Present study</th></tr>
<tr><td>Sauvere Beds K_2S</td><td>Paadla Stage K_2</td><td>Paadla Stage K_2</td><td rowspan="2">Paadla Stage K_2</td><td rowspan="5">Ludlow</td></tr>
<tr><td>Soeginina Beds K_2Sn</td><td rowspan="5">Rootsiküla Stage K_1</td><td rowspan="6">Rootsiküla Stage K_1</td></tr>
<tr><td>Anikaitse Beds K_1A</td><td rowspan="5">Rootsiküla Stage K_1</td></tr>
<tr><td>Vesiku Beds K_1Vs</td></tr>
<tr><td>Kuusnõmme Beds K_1Kn</td></tr>
<tr><td>Viita Beds K_1Vt</td><td rowspan="3">Wenlock</td></tr>
<tr><td>Iide Beds K_1I</td><td rowspan="2">Jaagarahu Stage J_2</td></tr>
<tr><td>Tagavere Beds J_2T</td><td>Jaagarahu Stage J_2</td><td>Jaagarahu Stage J_2</td></tr>
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Fig. 2. Stratigraphy of the Rootsiküla Stage.

The lower boundary of the Rootsiküla Stage is quite clear in the main part of Saaremaa and coincides with the upper boundary of lagoonal bioturbated dolomites of the Tagavere Beds. Additional beds characterized by a positive carbon isotope excursion occur only in the Ohesaare core in the depth interval 150.5–161.5 m (Kaljo et al. 1997). These beds are represented by marlstones and limestones with coarse-grained carbonate detritus. The Ruhnu core contains also carbonate oolites in a correlative level. These beds include also the 25 cm thick Grötlingbo Bentonite (Figs 3 and 4). The significant positive carbon isotope excursion indicates changes in the natural carbon cycle at that time. Lack of the positive carbon isotope excursion in the Viki core at this level in the main northern part of Saaremaa (Kaljo et al. 2003) suggests a major hiatus in sedimentation. Jeppsson & Calner (2003) estimated a sea level fall in the late Wenlock due to the glaciation in polar areas in a range from 22 to 58 m. A larger sea level fall of ca 100 ± 30 m at that time was interpreted from the geochemical data of the Priekule core (Kiipli et al. 2010c). The layers in the Ohesaare core between 150.5 and 161.5 m represent the first rise of sea after the lowest level, which is still in gap in Ohesaare (depth 161.5 m), and are represented by microbedded limestone of the Ančia Member in the deep shelf area. These layers occur between the LAD of *Conochitina cribrosa* and the FAD of *Ctenognathodus murchisoni* and correspond approximately to the *Gothograptus nassa* graptolite Zone (Figs 3 and 4). Figure 3 presents a detailed lithology of these layers lying between the Sõrve Formation of the Jaagarahu Stage and the well recognizable Viita Beds of the Rootsiküla Stage. We propose to name these layers as the Iide Beds after a village on the Sõrve Peninsula in Saaremaa. On Gotland the Halla/Mulde Beds (Manten 1971) or Halla Formation (Calner & Jeppsson 2003; Calner et al. 2006) correspond to this interval. In terms of conodont zonation this interval in the Ohesaare core can be correlated with the *Ozarkodina bohemica longa* Zone and the *Kockelella ortus absidata* Zone (Jeppsson & Calner 2003). In the Ohesaare core this interval was previously assigned to the Jaagarahu Stage (Einasto 1970), divided between the Jaagarahu and Rootsiküla stages (Nestor 1997), or assigned to the Rootsiküla Stage (Kaljo et al. 1997). This interval is probably in hiatus also in the Vidale-263 core as the positive carbon isotope excursion was not found there. All $\delta^{13}C$ values between the depths of 495.1 and 525.5 m in the Vidale-263 core range from –2.8‰ to –0.8‰ without any positive peak.

DISTRIBUTION OF CHITINOZOANS

The distribution of chitinozoans in the uppermost Wenlock sequence has earlier been studied in five East Baltic drill cores: Ohesaare, Kolka, Ventspils-D3, Pavilosta and Gussev-1 (Nestor 2007), as well as in the Ruhnu (Nestor 2003) and Viki (Nestor 2010) cores. In the last two cores the chitinozoans were extremely rare or absent in the upper Wenlock samples.

Chitinozoans were studied in 21 samples from the interval of about 40 m of the Vidale-263 drill core. They represent a typical upper Wenlock assemblage of chitinozoan species (Fig. 5). The lowermost two samples

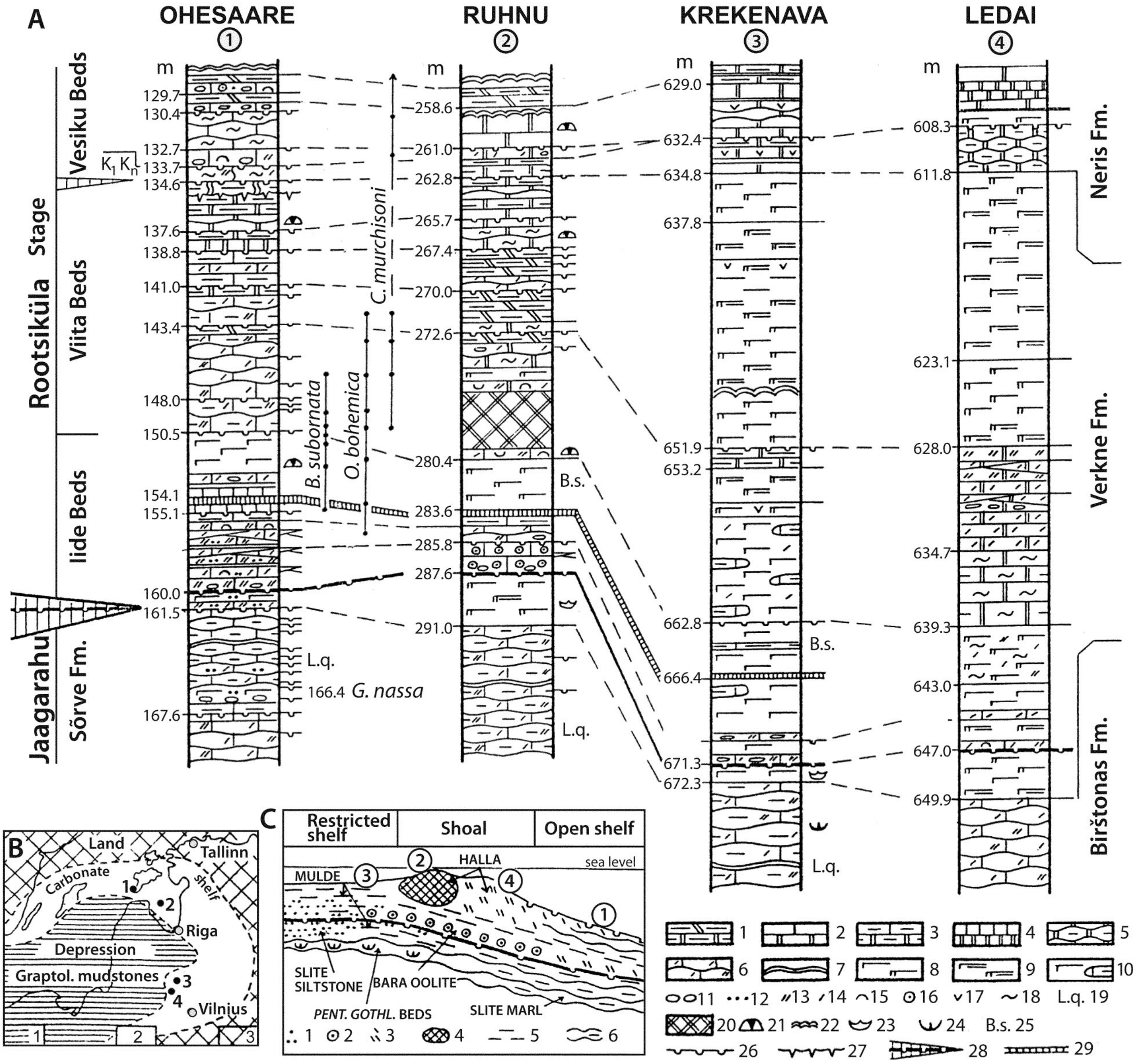

Fig. 3. A, Lithology and stratigraphy of the upper Jaagarahu and lower Rootsiküla rocks in the transition zone between shallow and deep shelf, East Baltic area: 1, argillaceous laminated lagoonal dolostones with *Eurypterus*; 2, limestones and diagenetic dolostones; 3, argillaceous lime- and dolostones; 4, micritic lime- and dolostones; 5, argillaceous nodular dolostones; 6, nodular wackestones; 7, wave-bedded marlstone interbeds; 8, calcareous or dolomitic marls; 9, shaly marls; 10, marl with limestone nodules; 11, pebbles and conglomerates; 12, admixture of sand and silt; 13, coarse grainstones; 14, fine grainstones; 15, shells; 16, oolites; 17, gypsum; 18, bioturbation tracks; 19, ostracodes *Leptobolbina quadricuspidata*; 20, dolomitized bioherm; 21, corals; 22, stromatolites; 23, lingulid shells; 24, *Pentamerus gothlandicus*; 25, ostracodes *Beyrichia subornata*; 26, hardgrounds; 27, mudcracks; 28, significant hiatus in the outcrop area; 29, Grötlingbo Bentonite. **B**, Palaeogeography of the Late Wenlock Baltic Basin and location of drill core sections: 1, Ohesaare; 2, Ruhnu; 3, Krekenava; 4, Ledai. **C**, Facies model of the Slite and Halla/Mulde boundary beds in Gotland with the approximate facies position of the sections from part A of the figure: 1, siltstone; 2, oolites; 3, carbonate grainstone; 4, reefs; 5, shale and marlstone; 6, marlstone with carbonate nodules. Compiled by R. Einasto.

(from 536.80 and 535.80 m) contain only transitional species from the lower–middle Wenlock.

Conochitina cribrosa Nestor and *Eisenackitina* sp. occur and disappear in the interval 513.10–528.50 m in the Vidale-263 drill core, like also in the uppermost part of the Sõrve Formation in the Ohesaare core and in the uppermost part of the Riga Formation in the Ventspils-D3 core (Nestor 2007). *Cingulochitina cingulata* (Eisenack) as well disappears at the level of 513.10 m in the Vidale-263 core, correlating with the middle of the

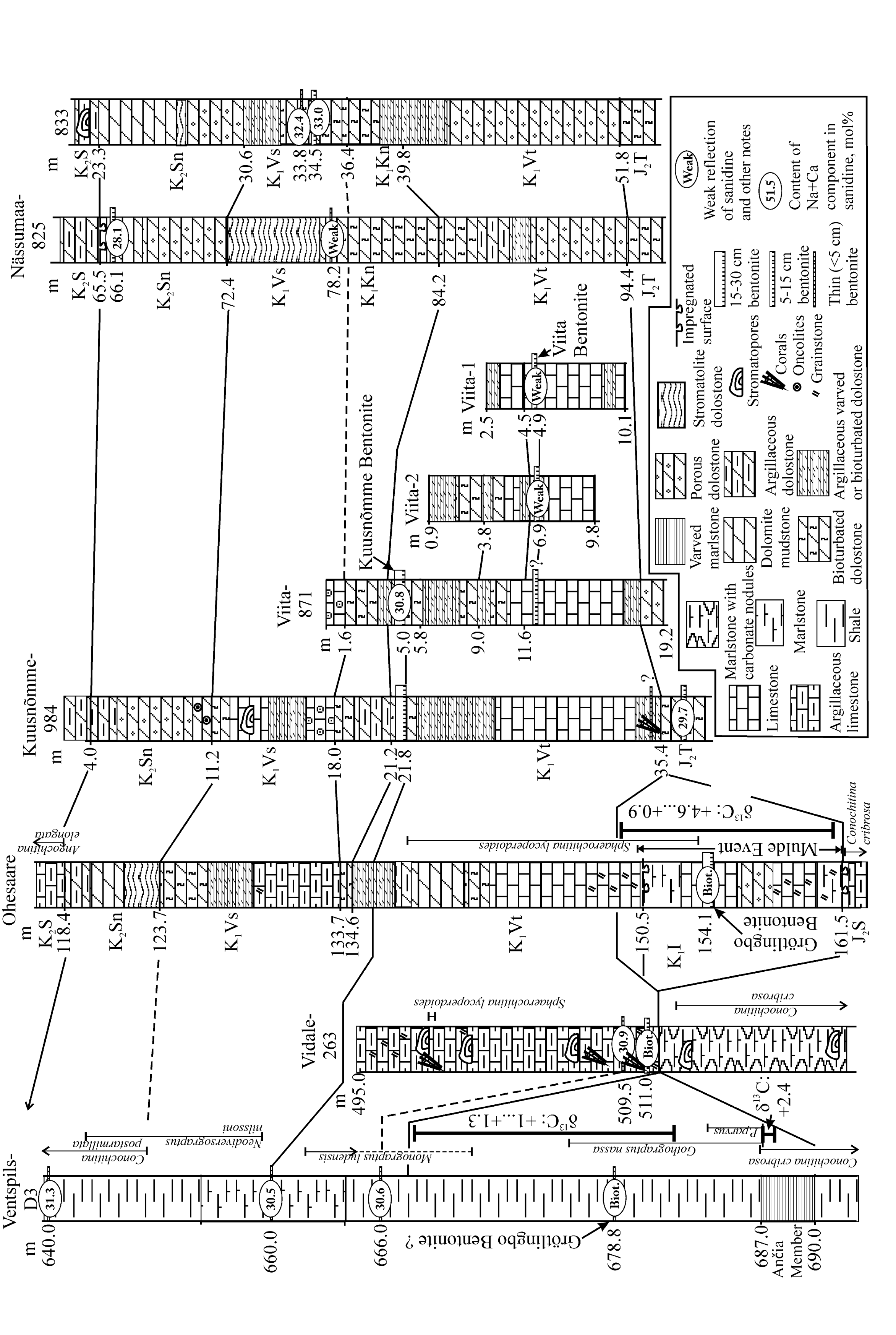

Fig. 4. Correlation of sections with the position of studied volcanic ash beds. Intervals of the carbon isotope positive excursions are from Kaljo et al. (1997, 1998). The Mulde Event interval is according to Jeppsson & Calner (2003). The distribution of graptolites is from Gailite et al. (1987). See Fig. 2 for indices of beds. J_2S, Sõrve Formation of the Jaagarahu Stage.

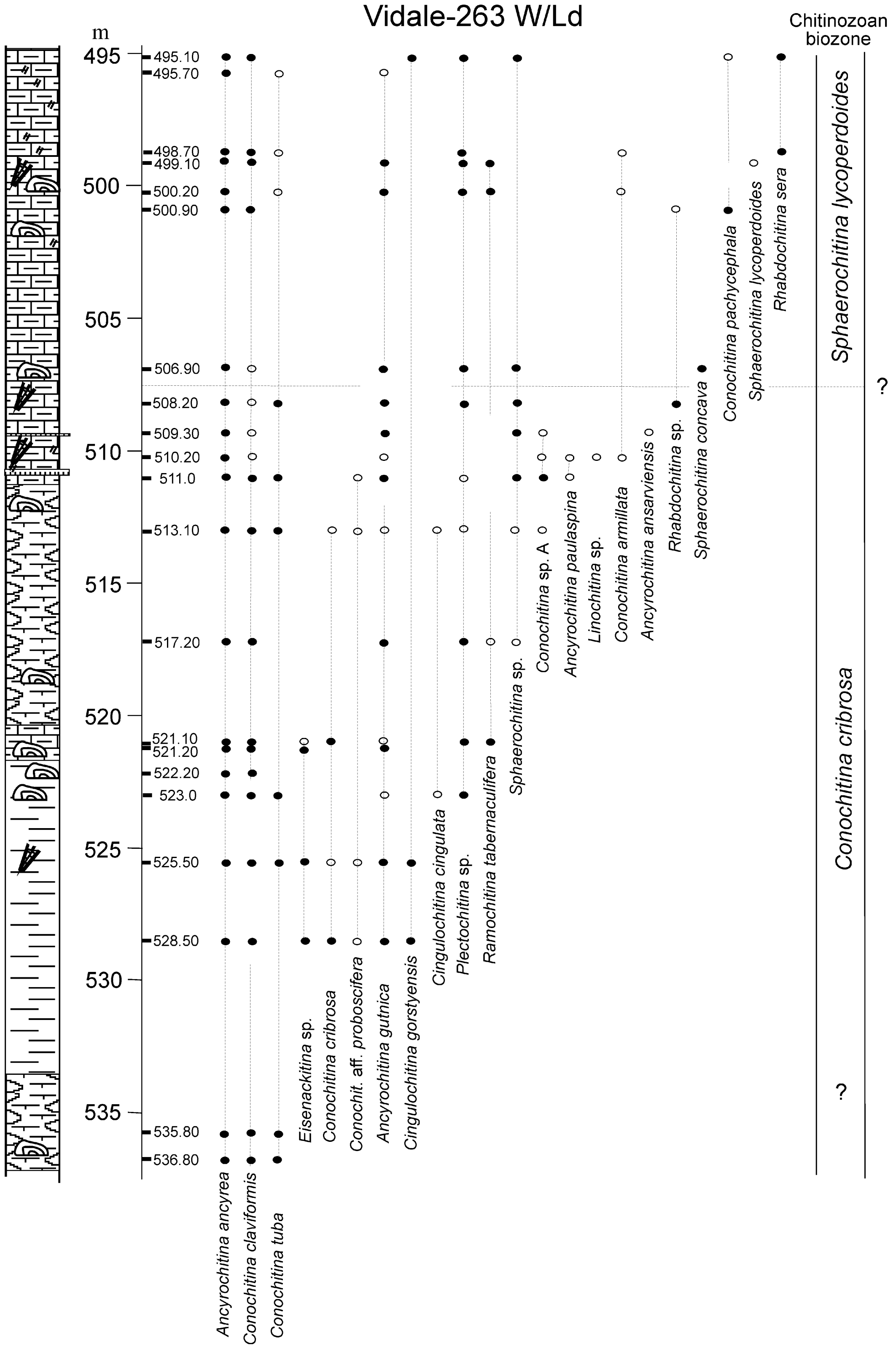

Fig. 5. Distribution of chitinozoans in the Vidale-263 section. Dark ring – reliable identification, empty ring – problematic identification. For legend see Fig. 4.

Iide Beds in the Ohesaare core (158.15 m). *Conochitina* aff. *proboscifera* Eisenack ranges up to a depth of 511.10 m in the Vidale-263 drill core but disappears in the upper parts of the Sõrve and Riga formations, respectively, in the Ohesaare and Ventspils cores. *Ramochitina tabernaculifera* (Laufeld) is also characteristic of the upper Wenlock, occurring in the interval 499.10–521.10 m in the Vidale-263 core. In the Ohesaare core it ranges up to the level of 143.80 m in the Viita Beds of the Rootsiküla Formation.

Ancyrochitina ansarviensis Laufeld, *Sphaerochitina concava* Laufeld and *Sphaerochitina lycoperdoides* Laufeld appear in the Ohesaare drill core at 152.9–153 m, in the lowermost part of the Viita Beds of the Rootsiküla Stage, above the Grötlingbo Bentonite and the Mulde Event (see Jeppsson & Calner 2003; Nestor 2007). The same level is recognized also in the Vidale-263 core, where these species appear in the interval 499.10–509.30 m (Fig. 5). The appearance level of *Rhabdochitina sera* Nestor of 498.70 m in the Vidale-263 drill core and 667 m in the Ventspils-D3 core seems to be a good correlative level for these sections, although the index species *Sphaerochitina lycoperdoides* has not been found in the Ventspils-D3 core (Nestor 2007).

Thus, according to Nestor (2007), most part or the whole interval of the Mulde Event, formerly established in the Ohesaare and Ventspils-D3 cores, is missing in the Vidale-263 drill core (Fig. 4).

In the Kolka, Ventspils-D3, Pavilosta and Gussev-1 drill cores the *Conochitina postarmillata* Biozone, corresponding to the lowermost Ludlow *nilssoni* graptolite Zone, has been distinguished above the *Sphaerochitina lycoperdoides* Biozone and the range of the chitinozoan species *Rhabdochitina sera* (Nestor 2007). In the Ohesaare core the *S. lycoperdoides* Biozone corresponds to the Viita Beds of the Rootsiküla Stage; thus, the Wenlock–Ludlow boundary very likely can be correlated with the boundary between the Viita and Kuusnõmme beds of the Rootsiküla Stage at 137.6 m.

VOLCANIC ASH BEDS IN THE ROOTSIKÜLA STAGE

Volcanic ash layers in shallow-water sediments of the Rootsiküla Stage (Fig. 4) occur sporadically in drill cores, probably due to wave activity dispersing fine-grained volcanic ash particles and due to discontinuous sedimentary record only partly covering the whole time span (Viira & Einasto 2003). Anyhow, volcanic ashes in these sediments often reach a great thickness of 10–30 cm (Table 1). The Kuusnõmme Bentonite, with a total thickness of 30 cm (Fig. 6), contains besides the volcanic component also significant amounts of carbonate and terrigenous shaly material. The same mixing is evident

Table 1. Stratigraphy and mineralogy of pyroclastic material from the studied bentonites. See Fig. 2 for indices of beds

Core	Depth, m	Bentonite name	Thick-ness, cm	Beds	Chitinozoans	Graptolites	Width of the sanidine reflection, deg	Notes	Content of the Na + Ca component, mol%	Biotite abun-dance
Ventspils-D3	640.0		0.1		*postarmillata*	*nilssoni*	0.060		31.3	+++
Nässumaa-825	66.1		10	K_2Sn			0.161		28.1	+
833	33.8		1	K_1Vs			0.192		32.4	+
833	34.5		5	K_1Vs			0.117		33.0	No
Nässumaa-825	78.2		4	K_1Vs? or K_1Kn			0.173	Weak	29.1	No
Ventspils-D3	660.0	Kuusnõmme	0.4			*ludensis/nilssoni*	0.096		30.5	++
Viita-871	4.9	Kuusnõmme	30	K_1Vt			0.104		30.8	++
Viita-1	4.9	Viita	10	K_1Vt				Very wide		+
Viita-2	6.9	Viita	10	K_1Vt				Weak		No
Ventspils-D3	666.0		1			*ludensis*	0.087	Strong	30.6	++
Vidale-263	509.5		1				0.053	Terrigenous	30.9	++
Vidale-263	511.0		8				0.197		29.0	+++
Ohesaare	154.1	Grötlingbo	25	K_1I	*cribrosa*			Weak		+++
Ventspils-D3	678.8	Grötlingbo?	?			*nassa*				+++
Kuusnõmme-984	36.6		20	J_2T			0.089		29.7	+

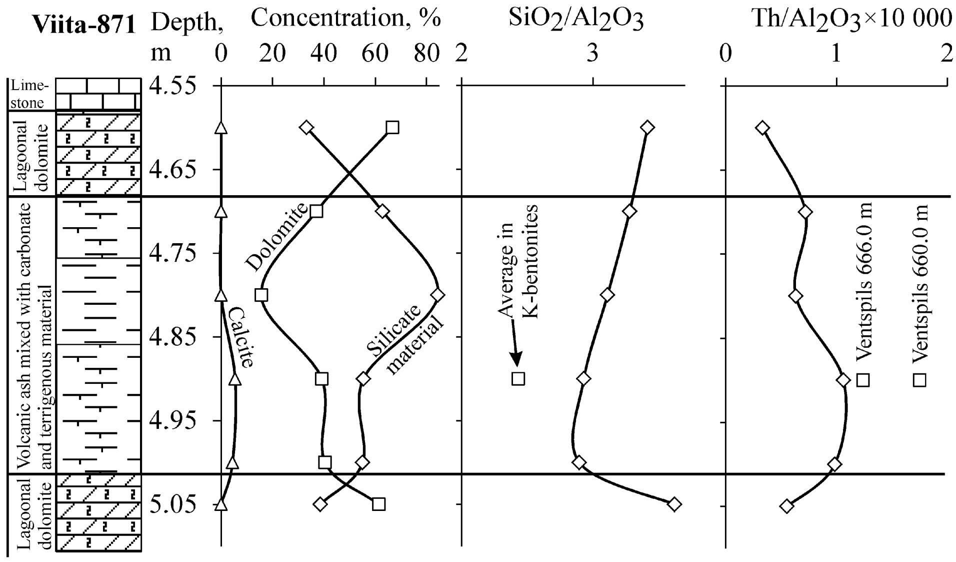

Fig. 6. Composition of the Kuusnõmme Bentonite in the Viita-871 core. Major components calcite, dolomite and silicate material are calculated from XRF data. The SiO_2/Al_2O_3 ratio in the ash bed, compared with pure K-bentonites and pure terrigenous material from below the bentonite, indicates that even the silicate part of the Kuusnõmme Bentonite contains 40–60% terrigenous admixture. The Th/Al_2O_3 ratio in the Kuusnõmme Bentonite is between the pure terrigenous material and pure bentonites from the Ventspils core.

in several other beds, but the volcanic component can be identified by the occurrence of illite-smectite in XRD traces, and the presence of biotite and sanidine in coarse fraction confirms the volcanic origin. The Kuusnõmme Bentonite occurring within lagoonal dolomites contains ca 50% of dolomite and even the silicate part of the bed contains 40–60% of terrigenous shaly material (Fig. 6). Kaolinite-rich volcanic ashes are found in the Latvian Ventspils-D3 section.

CORRELATION OF VOLCANIC ASHES BETWEEN GRAPTOLITE FACIES AND THE ROOTSIKÜLA STAGE

In the Ventspils-D3 core, where graptolites are well studied, four bentonites occur close to the Wenlock–Ludlow boundary (Fig. 4). The Wenlock–Ludlow boundary, defined as the beginning of the *Neodiversograptus nilssoni* graptolite zone (Holland 1982), lies between depths of 662.1 m (LAD of *Monograptus ludensis*) and 659.6 m (FAD of *N. nilssoni*) (Gailite et al. 1987).

Comparison of the Ventspils 678.8 m and Vidale 511.0 m bentonites with the Grötlingbo Bentonite

Bentonite at a depth of 678.8 m in the Ventspils-D3 core was recorded among others in the description by E. Jürgenson in 1975 (stored in the Institute of Geology at Tallinn University of Geology collections database). This bed is distinguished by the abundance of biotite. The ash bed occurs within the second peak of the positive carbon isotope excursion (Kaljo et al. 1998). These arguments suggest a correlation with the Grötlingbo Bentonite. Unfortunately, at the time of our field studies in 2005 the bed was absent in the core, probably due to previous samplings, and therefore we have no geochemical data for further proof of the correlation.

The bentonite at 511.0 m in the Vidale-263 core has also an abundance of biotite similarly to the Grötlingbo Bentonite, but the positive carbon isotope excursion was not detected at this level. The comparison of the geochemical composition of the Vidale 511.0 m bentonite with that of the Grötlingbo Bentonite (Kiipli et al. 2008c) reveals differences in the concentration of P, Nb, Ba, Cr and Ni up to about two times, indicating that the bentonite at 511.0 m in the Vidale-263 core is related to a different volcanic eruption.

Comparison of the Vidale 509.5 m and 511.0 m bentonites with the Djupvik bentonites from Gotland

Two terrigenous shale interbeds from the Djupvik exposure in Gotland (upper part of the Halla Formation) revealed some content of pyroclastic phenocrysts (Batchelor & Jeppsson 1999; Kiipli et al. 2008a). Both beds are rich in biotite and due to the high content of terrigenous quartz exhibited only weak sanidine XRD reflections. The same signatures characterize also the bentonites at 509.5 and 511.0 m in the Vidale-263 core, belonging to the lowermost layers of the Viita Beds according to the correlations in Fig. 4. Therefore, at the level of present knowledge it cannot be excluded that these bentonites occurring within close stratigraphic levels are related to the same two or three eruptions.

Comparison of the Ventspils 666.0 m and 660.0 m bentonites with bentonites in shallow-water sections

Both bentonites in the Ventspils-D3 core revealed sharp sanidine reflection and an identical content of the Na + Ca component (30.5–30.6 mol%) in sanidine (Table 1, Fig. 7). A significant difference was observed in the grain size of pyroclastic material. The bentonite at 666.0 m contains abundantly grains larger than 100 μm, while that at 660.0 m contains mostly pyroclasts within the range of 40–100 μm and only a small portion of larger grains. Also the sanidine $20\overline{1}$ reflection of the 666.0 m bentonite is uniquely strong. In shallow-water sediments only the bentonite in the Viita-871 core at a depth of 4.9 m (Kuusnõmme Bentonite) revealed a similar sanidine composition with a sharp reflection. Pyroclastic grains are within the range 40–100 μm and sanidine reflection is not notably strong. Thus, the study of pyroclastic fraction suggests a potential correlation of the Kuusnõmme Bentonite with the Ventspils 660.0 m bentonite.

As the Kuusnõmme Bentonite in the Viita-871 core contains much of carbonate and terrigenous shale admixture, the comparison of trace element contents is difficult. In Fig. 8 trace elements from the Ventspils

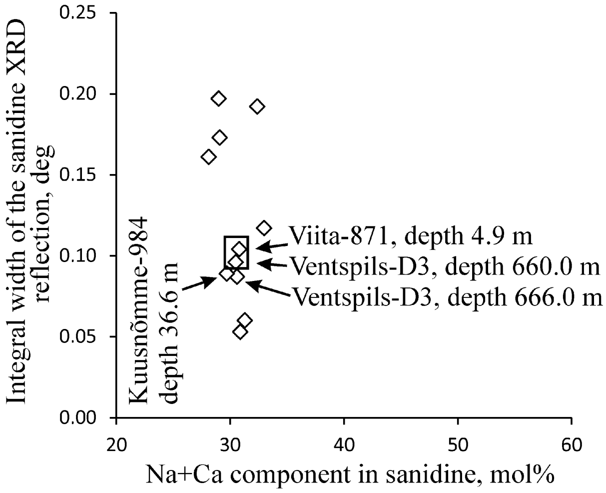

Fig. 7. Composition of sanidine in the studied bentonites. The frame embraces the proposed correlation between Viita-871, depth 4.9 m and Ventspils-D3, depth 660.0 m. Correlation with the bentonite from the Kuusnõmme-984 core can be excluded because of its significantly different stratigraphical position (upper part of the Jaagarahu Stage). Correlation of Viita-871 with depth 666.0 m of the Ventspils-D3 core was abandoned for several reasons (see discussion in text). Ranges of chart axes represent a full compositional range of sanidine from the East Baltic Silurian bentonites. Measurements were made using Co Kα radiation. Precision of the determination of the Na + Ca component is ±1% in case of sharp reflection (integral width is less than 0.15°) and ±2% for wider reflections.

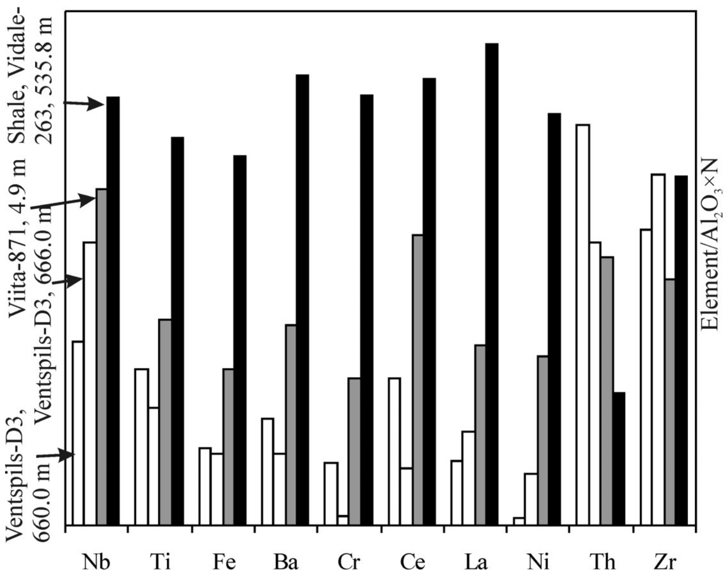

Fig. 8. Comparison of pure bentonites from the depths of 660.0 and 666.0 m in the Ventspils-D3 core with mixed bentonite-terrigenous material from the Viita-871 core, depth 4.9 m and terrigenous shale from a depth of 535.8 m in the Vidale-263 core. On the vertical scale aluminium normalized concentrations of elements are multiplied by variable coefficients in order to bring all element ratios numerically to the same range. The figure shows that all element ratios in the Viita-871 bentonite are between terrigenous shale and pure bentonites from the Ventspils-D3 core, allowing both correlations. Analytical data see at http://geokogud.info/git/reference.php?id=1586

666.0 and 660.0 m bentonites are compared with the bentonite at 4.9 m in the Viita-871 core and terrigenous shale at 535.8 m in the Vidale-263 core. The concentrations of trace elements in the Kuusnõmme Bentonite from the Viita-871 core are mostly between pure Ventspils bentonites and terrigenous shale from Vidale, indicating that the correlation with both Ventspils bentonites is possible.

The bentonite at 666.0 m in the Ventspils-D3 core occurs only 1.5 m above the end of the positive carbon isotope excursion, suggesting correlation with the lower part of the Viita Beds in the Ohesaare section. For the Ventspils 666.0 m bentonite possible correlation exists with the 509.5 m level in Vidale, where the mostly terrigenous interbed contains some volcanic sanidine grains with the same composition as in the Ventspils 666.0 m bentonite.

These arguments (similarity of the sanidine composition, grain size of pyroclastic material and the position of these ash beds relative to the carbon isotope positive excursion (Fig. 4)) indicate that most probably the Ventspils 660.0 m bentonite correlates with the Viita 4.9 m bentonite and thus the Wenlock–Ludlow boundary (0.4 m above the bentonite at 660.0 m in Ventspils) correlates with the boundary of the Viita and Kuusnõmme beds in Saaremaa. The distribution of chitinozoans supports this correlation (Figs 4, 5).

The bentonite at a depth of 640.0 m in the Ventspils-D3 core probably does not have a correlatable bed in shallow-water sediments. Although the sanidine composition in the Ventspils 640.0 m bentonite is very similar to sanidine at 33.8 m depth in drill core 833 from eastern Saaremaa (Fig. 4, Table 1), the content of biotite is much different, making correlation unlikely.

INTERPRETATION OF SOURCE MAGMA

Using Zr/TiO_2 as the magma fractionation index (Winchester & Floyd 1977), Al_2O_3 normalized Nb as the alkalinity index and Italian volcanic rocks (Peccerillo 2005) for background information, we estimated source magma types (Fig. 9). XRF analyses of studied samples are available at the website http://geokogud.info/git/reference.php?id=1586 (record Nos 361–388, 430–445, 607–627, 637–642). Most of the studied volcanic ashes show the best fit with source magma of dacitic composition. The Grötlingbo Bentonite and the Ventspils 666.0 m bentonite originated most probably from the rhyolitic source magma. Low Nb concentrations in our samples indicate subalkaline magmas. Subalkaline magmatism recorded in the East Baltic bentonites is also typical of the earlier times in

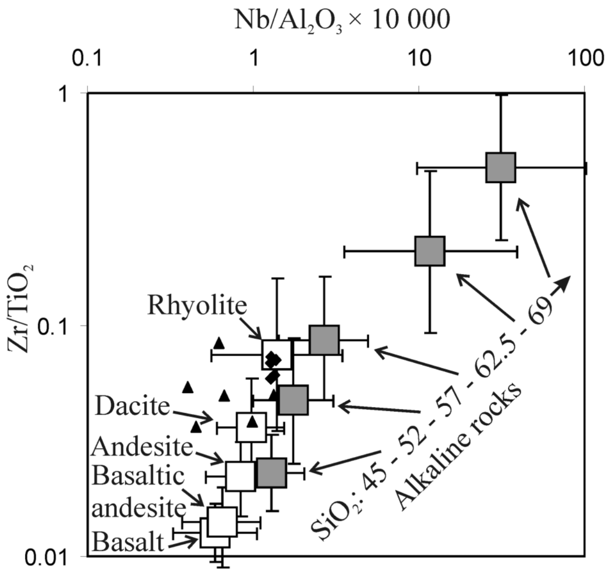

Fig. 9. The studied bentonites (black triangles – Rootsiküla Stage and black diamonds – Grötlingbo Bentonite), in the frame of Zr/TiO_2 (fractionation index) and Nb/Al_2O_3 (alkalinity index). For comparison analytical data of ca 1500 Italian volcanic rocks are used from Peccerillo (2005). Empty quadrangles – Italian subalkaline rocks, grey quadrangles – Italian alkaline rocks. Bars represent standard deviation. The chart indicates subalkaline nature of the late Wenlock–early Ludlow volcanism supplying ashes to Estonia and Latvia.

the Silurian (Kiipli et al. 2010a). On the basis of the composition of apatite phenocrysts Batchelor & Jeppsson (1999) suggested alkaline source magma for some upper Wenlock bentonites of Gotland. Hetherington et al. (in press) studied K-bentonite of Wenlock age from southern Norway with the Nb content as high as 72 ppm. Such a high Nb content indicates certainly at least mildly alkaline source magma. Our data show that these rare occurrences of possibly alkaline volcanism are exceptions among the dominating subalkaline type of volcanism.

Sanidine composition in all studied bentonites is characterized by small variation in the Na + Ca component between 28 and 33 mol%, indicating probably potassium-dominated source magmas (Fig. 7). Lack of sodium-dominated source magmas, which were frequent during earlier times in the Silurian (Kiipli et al. 2010a), is a significant evolutionary change in the geochemistry of volcanic source magma. Small variation in the composition of phenocrysts probably refers to a single source volcano for most of the studied ash beds. The Grötlingbo and Viita bentonites, characterized by weak and wide sanidine XRD reflections, possibly originated from another source.

DISCUSSION ON PALAEOGEOGRAPHY AND TECTONICS

At the time of the Wenlock–Ludlow transition around 423 Ma ago the Baltica, Avalonia and Laurentia continents had already collided (McKerrow et al. 1991) and the Iapetus Ocean between these continents was most probably closed. Fossen et al. (2008) estimated that the collision of continents was nearing a relative acme and was forming tectonic nappes ca 425 Ma ago. Several microcontinents approaching Baltica from the south were accompanied by magmatic activity (Timmerman 2008). Both regions could potentially supply the Baltic sedimentary basin with volcanic ash. Considering that volcanic ashes of upper Wenlock–lower Ludlow age reach great thickness of 10–30 cm in Estonia (Table 1), much less (0.1–8 cm) in Latvia, and that in Lithuania no other bentonites have been recorded besides the Grötlingbo Bentonite (Kiipli et al. 2008c), the probable direction for ash transport was from the collision zone between Baltica and Laurentia.

The dominance of subalkaline volcanism and only rare occurrence of possibly alkaline volcanic ashes indicate that volcanic activity is related to the collision stage. Extensional tectonics, causing alkaline Nb-rich volcanism like around the Tyrrenian Sea in Italy, was not inherent to the tectonism between Baltica and Laurentia at that time.

CONCLUSIONS

Shoal and lagoonal sediments of the Rootsiküla Stage in Estonia are characterized by sporadic occurrence of bentonites often having significant thickness between 10 and 30 cm. These volcanic ashes are mostly of similar composition and originate probably from a single source area. Source magma for all ashes was subalkaline, ranging from dacite to rhyolite. Sanidine composition indicates potassium-dominated source magmas. Subalkaline source magma and decrease in ash thicknesses to the south suggest the origin of ashes from the collision zone between Baltica and Laurentia.

Correlation of bentonites and chitinozoans between deep-sea graptolite facies and shallow-sea Rootsiküla Stage sediments showed that the Wenlock–Ludlow boundary most probably correlates with the boundary of the Viita and Kuusnõmme beds in Saaremaa.

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Rootsiküla lademe vulkaaniliste kihtide geokeemia ja korrelatsioon Ida-Baltikumis

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On analüüsitud üheksa muutunud vulkaanilise tuha kihti Siluri ladestu Rootsiküla lademest (Wenlocki-Ludlow' piiriintervall) ja võrreldud viie vulkaanilise tuha prooviga Läti sügavaveelistest läbilõigetest. Tulemused näitavad, et Wenlocki-Ludlow' piir (graptoliiditsooni *Neodiversograptus nilssoni* algus) korreleerub Viita ja Kuusnõmme kihtide piiriga, mis on märgatavalt allpool, kui varem oletati. Kitiinikute levik lubab seda uut korrelatsiooni. Geokeemilised andmed osutavad, et vulkaanilised kihid pärinesid normaalrea magmast, milles kaaliumit oli rohkem kui naatriumit.