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Correlation of upper Llandovery–lower Wenlock bentonites in the När (Gotland, Sweden) and Ventspils (Latvia) drill cores: role of volcanic ash clouds and shelf sea currents in determining areal distribution of bentonite

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Abstract. Study of volcanic ash beds using biostratigraphy, sanidine composition and immobile elements within bentonites has manifested several well-established and some provisional correlations between Gotland and East Baltic sections. Energy dispersive X-ray fluorescence microanalysis of phenocrysts has revealed bentonites containing Mg-rich or Fe-rich biotite. Sanidine phenocrysts contain, in addition to a major Na and K component, often a few per cent of Ca and Ba. On the basis of new correlations the mapping of the distribution areas of bentonites has been extended from the East Baltic to Gotland. The bentonite distribution can be separated into two parts in North Latvia–South Estonia, indicating the existence of shelf sea currents in the Baltic Silurian Basin.

Key words: correlation, bentonites, K-bentonites, sea currents, Silurian, East Baltic, Gotland.

INTRODUCTION

Volcanic ash beds in sedimentary sections have been used as time markers for refining stratigraphy (Rubel et al. 2007; Kiipli et al. 2011). Sometimes large eruptions have caused significant environmental changes followed by extinction of marine biota (Hints et al. 2003). Thin altered volcanic ashes (bentonites, K-bentonites), providing evidence for volcanism at nearby plate margins, have been detected in Baltoscandia, from the lower Silurian (e.g. Bergström et al. 1992; Batchelor et al. 1995; Batchelor & Jeppsson 1999; Hetherington et al. 2011) to the lower part of the upper Silurian (Snäll 1977). Many Silurian bentonites have been recorded also in England (e.g. Ray 2007; Ray et al. 2011) and Scotland (e.g. Batchelor & Weir 1988; Batchelor 2009). In the East Baltic area ash beds from a total of 51 volcanic eruptions have been identified in the Telychian (Kiipli et al. 2008b, 2008c, 2008d, 2010b) and 55 in the Wenlock (Kiipli et al. 2010a). Several ash beds are known in the lower Ludlow (Kiipli et al. 2011), but these are very rare in younger sedimentary rocks.

With the aim of extending the correlation of volcanic ash layers, we have studied the Llandovery–lower Wenlock of the Ventspils-D3 core section of Latvia and the När core section of Gotland (Sweden). New correlations are used for interpreting ash clouds and shelf sea currents in the Silurian Baltic Basin.

MATERIAL AND METHODS

Thirty-one bentonite samples were taken from the Llandovery and lower Wenlock of the Ventspils-D3 and När cores (Fig. 1). The thickness of the ash beds varies from 1 mm to 4 cm, which is generally less than in Estonia, where ash beds frequently reach a thickness of 5–10 cm. An additional complication with the När core was that as a result of previous studies only half of the core was preserved and we were able to find only some

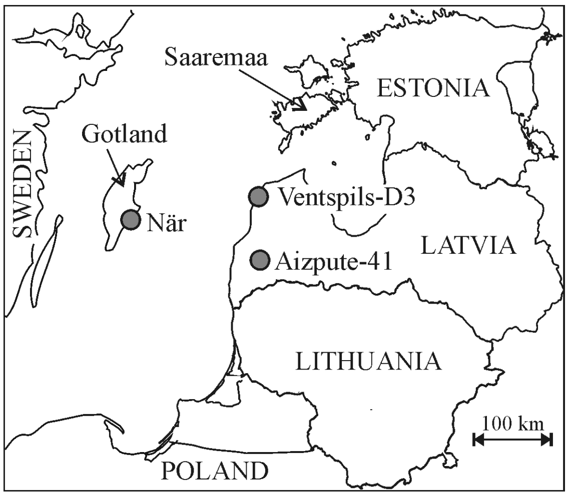


Fig. 1. Location of the studied sections.

of the ash beds recorded by Snäll (1977) in the fresh core. The stratigraphical position of the ash beds was established using chitinozoan and graptolite biozonation (Gailite et al. 1987; Nestor 1994; Grahn 1995; Loydell & Nestor 2005; Fig. 2). The composition of sanidine phenocrysts in bentonites was used for correlation with the biostratigraphically well studied Aizpute-41 section (Loydell et al. 2003). The samples were analysed by X-ray diffractometry (XRD) for identifying major minerals and determination of magmatic sanidine phenocryst composition. The XRD spectra of sanidine in Telychian and lower Sheinwoodian bentonites are available online at http://sarv.gi.ee/reference.php?id=2533. The authors have applied the same methods in their previous works (Kiipli & Kallaste 2002, 2006; Kiipli et al. 2010a, 2011). The composition of volcanic phenocrysts in the bentonites of the När section was studied also by energy dispersive X-ray fluorescence (EDS) microanalysis in five samples. Samples of sufficient size (at least 2 g) were subjected to standard X-ray fluorescence (XRF) analysis for major and trace elements. The results are available in the database at http://geokogud.info/git/reference.php?id=1586 (Kiipli et al. 2011). Table 1 describes the concentrations of immobile and other useful elements for chemical fingerprinting as follows: high concentration of elements – $Al_2O_3 > 26\%$ and $TiO_2 > 1.2\%$; Zr > 510, Nb > 37, Th > 40, Sr > 190, Ba > 320, La > 48, Ce > 140 and Y > 50 ppm; low concentrations of elements – $Al_2O_3 < 20\%$ and $TiO_2 < 0.66\%$; Zr < 320, Nb < 22, Th < 29, Sr < 110, Ba < 190, La < 18, Ce < 35 and Y < 27 ppm. These values were derived by dividing all available analyses of bentonites from the Baltic Silurian deep shelf area into three equal groups – high, average and low concentrations for each element. Geochemical analyses were carried out in the Institute of Geology at Tallinn University of Technology.

RESULTS

Major minerals in altered volcanic ashes

Bentonites in Estonia are composed mainly of highly illitic illite-smectite and authigenic potassium feldspar (Kiipli et al. 2008b), with kaolinite present only in the sections near the southern border. In Latvia and Gotland, however, kaolinite is a common major component in addition to illite-smectite, while K-feldspar is relatively rare and occurs in lower concentrations (Table 1). This areal difference has been studied in the Ordovician Kinnekulle ash bed (Kiipli et al. 2007) and probably originates from differences in sedimentary facies. During the Early Palaeozoic Era, Latvia and Gotland were located on the deep shelf and Estonia mainly in the shallow shelf area. By contrast, Hints et al. (2008) proposed a late diagenetic origin for potassium feldspar in bentonites. Kaolinite-rich ash beds have lost much more silica and other major components during the conversion of ash to clay than illite-smectite- and feldspar-rich bentonites in Estonia (Kiipli et al. 2006). Consequently, the expected concentrations of immobile elements used for chemical fingerprinting are significantly higher in Latvia and Gotland than in the correlative beds in Estonia (Kiipli et al. 2008d). Ratios of immobile elements can still be used for chemical identification of eruption layers. Authigenic pyrite and its weathering products (gypsum and jarosite) in drill core boxes are frequent in bentonite beds. Pyroclastic quartz occurs in almost all bentonites in a concentration of ca 1%. Reflections of anatase appear on XRD patterns, starting from TiO_2 concentrations of ca 1%.

Aeronian (Llandovery) bentonites

Snäll (1977) recorded nine thin bentonites in the När core within the interval 363.0–371.8 m containing *Conochitina iklaensis*, which Grahn (1995) assigned to the lower Aeronian *Coronograptus gregarius* graptolite Biozone (= *Demirastrites triangulatus–Pribylograptus leptotheca* biozones). Due to the poor state of the core, we found material from only two bentonites. The attempts to analyse sanidine composition revealed no XRD reflection (369.8 m) or only a weak reflection (367.8 m). Wide sanidine reflections were established in two bentonites from the Dobele Formation of the Aizpute-41 section. No ash bed correlations can be suggested on the basis of the data available at present.

Bentonites in the *Spirograptus turriculatus–Streptograptus crispus* Biozone interval (Telychian, Llandovery)

In terms of chitinozoan biozonation, this interval belongs to the lower part of the *Eisenackitina dolioliformis* Biozone. Eight bentonites were found in the Ventspils

Fig. 2. Correlation of the Llandovery–lower Wenlock sections between Gotland (Sweden) and Latvia. Biostratigraphy of the När core is from Grahn (1995), Aizpute from Loydell et al. (2003) and Ventspils from Nestor (1994), Gailite et al. (1987) and Loydell & Nestor (2005). *Streptograptus wimani* in the Ventspils core indicates the lower part of the *lapworthi* Biozone. The interpretations of the depth interval ca 920–935 m of the Aizpute core by Loydell et al. (2003) differ ca 2 m from the depths used for bentonites. For the correct position of bentonites relative to samples studied by Loydell et al. (2003) see Kiipli & Kallaste (2006).

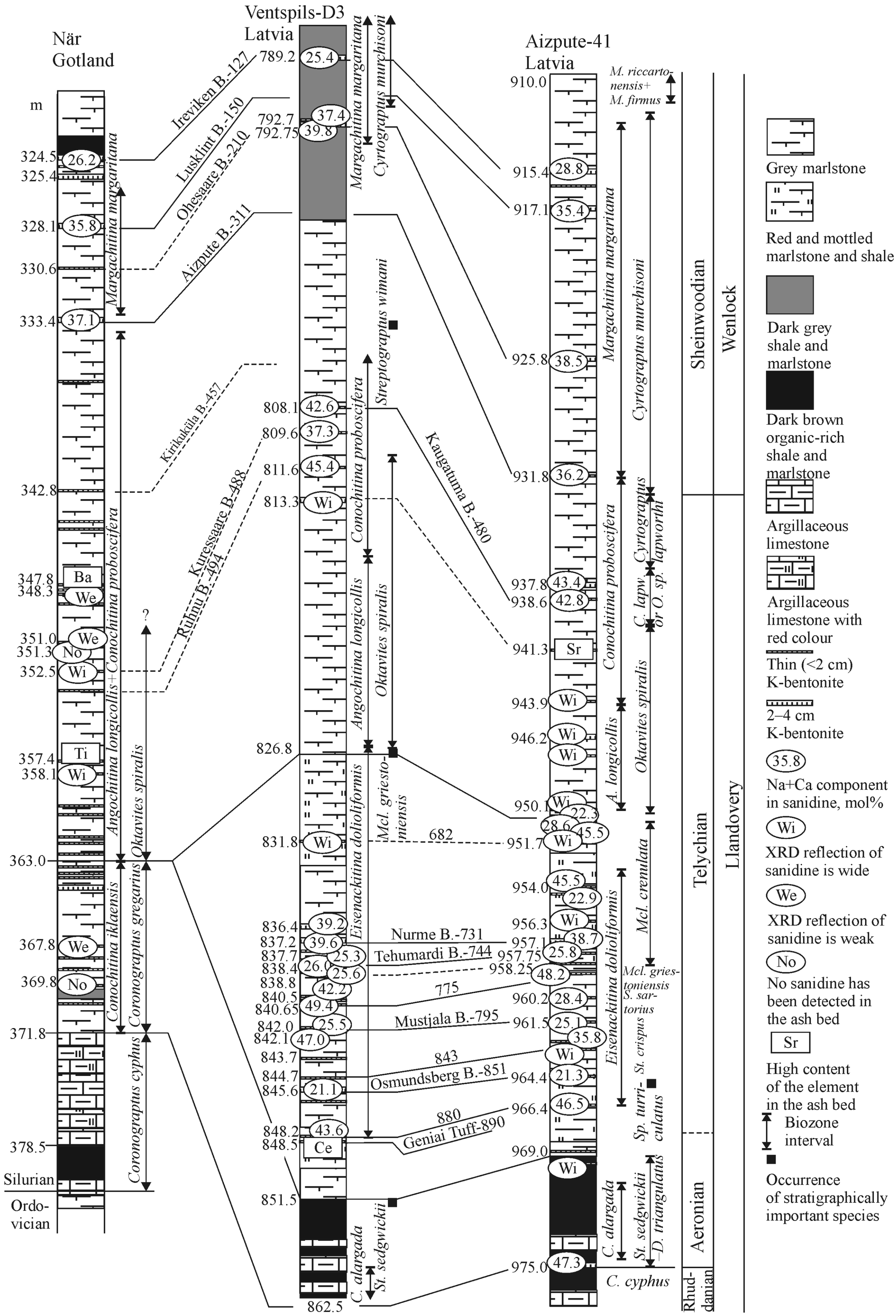

När
Gotland
Ventspils-D3
Latvia
Aizpute-41
Latvia
m
Ireviken B.-127
Lusklint B.-150
Ohesaare B.-210
Aizpute B.-311
Kirikuküla B.-457
Kuressaare B.-488
Ruhnu B.-494
Kaugatuma B.-480
682
Nurme B.-731
Tehumardi B.-744
775
Mustjala B.-795
843
Osmundsberg B.-851
880
Geniai Tuff-890
Margachitina margaritana
Cyrtograptus murchisoni
Streptograptus wimani
Conochitina proboscifera
Angochitina longicollis
Angochitina longicollis+Conochitina proboscifera
Oktavites spiralis
Conochitina iklaensis
Coronograptus gregarius
Coronograptus cyphus
Eisenackitina dolioliformis
Mcl. griestoniensis
C. alargada
St. sedgwickii
M. riccartonensis+
M. firmus
A. longicollis
C. lapw. Cyrtograptus
or O. sp. lapworthi
Mcl. crenulata
Mcl. griestoniensis
S. sartorius
St. crispus
Sp. turriculatus
St. sedgwickii
–D. triangulatus
C. cyphus
Silurian
Ordovician
Sheinwoodian
Wenlock
Telychian
Llandovery
Aeronian
Rhuddanian
Grey marlstone
Red and mottled marlstone and shale
Dark grey shale and marlstone
Dark brown organic-rich shale and marlstone
Argillaceous limestone
Argillaceous limestone with red colour
Thin (<2 cm) K-bentonite
2–4 cm K-bentonite
35.8
Na+Ca component in sanidine, mol%
Wi
XRD reflection of sanidine is wide
We
XRD reflection of sanidine is weak
No
No sanidine has been detected in the ash bed
Sr
High content of the element in the ash bed
Biozone interval
Occurrence of stratigraphically important species

Table 1. Analytical data of the studied bentonites

Depth, m	Thickness, cm	Stratigraphy	Sanidine properties			Biotite abundance	XRD mineralogy of bulk sample	XRF, trace elements		Correlations	
			Na + Ca modal component, mol%	Width of the reflection	Remarks			Low content	High content	Bentonite ID	Bentonite name
När core											
324.5	2.0	Sheinwoodian	26.2	0.12	Weak	+++	I/S,kaol,biot	Ba,Ce,La,Sr,Y	Al	127	Ireviken
325.4	4.0	Sheinwoodian					Kaol,K-fsp,I/S,qu,gyp,pyr			139?	Storbrut?
328.1	2.0	Sheinwoodian	35.8	0.18		++	Kaol,I/S,K-fsp,goyazite/ florencite,qu		Al,Ce,La,Sr,Y,Zr	150	Lusklint
333.4	2.0	Sheinwoodian	37.1	0.09		++	I/S,kaol,K-fsp,qu,Na-K-san, biot	Ce,La	Al,Nb,Th,Zr	311	Aizpute
342.8	0.7	Telychian					K-fsp,I/S,kaol,qu,anatase		Ti,(Sr),Y,Zr	457?	Kirikuküla?
347.8	0.4	Telychian					K-fsp,I/S,kaol,anatase	Nb,Th	Ti,Ba,Ce,La,Sr,Y		New
348.3	0.5	Telychian	33.4	0.16	Weak	++	I/S,kaol,qu(traces)	Ti,Ba,	Al,Nb,Th,Zr		New
348.9	0.2	Telychian					I/S,qu(traces)				New
351.0	0.2	Telychian			Very weak	+	I/S	Ba,Ce,La	Y,Zr		New
351.3		Telychian			No	++(+)	I/S,biot,kaol(traces)	Ti,Ba,Ce,La,Nb,Th,Zr			New
352.5	0.9	Telychian			Wide	++	K-fsp,I/S,kaol,qu,anatase	La	Al,Ti,Ba,Sr	488?	Kuressaare
353.6	0.2	Telychian					K-fsp,I/S,kaol,anatase, terrig(traces)			?	
357.4	0.3	Telychian					K-fsp,I/S,kaol(traces), anatase,qu,pyr,jar,gyp	Al,La,Y	Ti,Ba,Sr		New
358.1	0.5	Telychian			Wide	–	I/S,kaol,K-fsp,anatase		Al,Ti,Ce,Th,Y,Zr		New
367.8	2.0	Aeronian	27.4	0.21	Weak	++	I/S,calcite,kaol,anatase				
369.8	1.0	Aeronian			No	++	I/S,terrig,calcite				
Ventspils-D3 core											
789.2	3.5	Sheinwoodian	25.9	0.29		+++	Kaol,I/S,biot,qu	Ti,Ba,Ce,Nb,Sr,Y	Al	127	Ireviken
792.7	0.2	Sheinwoodian	37.4	0.13		+	I/S,kaol,K-fsp,qu,gyp,pyr				New
792.75	3.0	Sheinwoodian	39.8	0.27		+	I/S,kaol,K-fsp,qu,pyr,jar,gyp	Ti,Ba	Al,Ce,La,Y	210	Ohesaare
808.1	1.0	Telychian	42.6	0.24		++	Kaol,I/S,K-fsp,qu,anatase, biot,gyp	Ba,Sr	Al,Ti,Ce,La,Nb,Th,Y, Zr	480	Kaugatuma
809.6	0.2	Telychian	37.3	0.26		?	Kaol,I/S,K-fsp,anatase,biot, qu,gyp			488?	Kuressaare?

Table 1. *Continued*

Depth, m	Thick-ness, cm	Stratigraphy	Sanidine properties			Biotite abun-dance	XRD mineralogy of bulk sample	XRF, trace elements		Correlations	
			Na + Ca modal component, mol%	Width of the reflection	Remarks			Low content	High content	Bento-nite ID	Bentonite name
811.6	1.0	Telychian	45.8	0.09		++	I/S,kaol,qu,Na-K-san?	Ti,Ba,Sr	Al,Nb,Th,Zr	494	Ruhnu
813.3	2.0	Telychian	38.2	0.32	Wide	+	K-fsp,kaol,I/S,anatase,qu,pyr	Th	Al,Ce,La	518?	Viirelaid?
831.8	0.3	Telychian	28.8	0.32	Very wide	+	K-fsp,I/S,kaol,qu,anatase, chalc?,hematite,biot			682	
836.2		Telychian					I/S,kaol,K-fsp?,qu	Ba,Sr	Al,Ce,La,Nb,Th,Zr		New
836.4	3.0	Telychian	39.3	0.08		++	I/S,kaol,K-fsp,qu,Na-K-san?	Ti	Al,Ce,La,Nb,Th,Y,Zr		New
837.2	2.0	Telychian	39.6	0.11		++	I/S,kaol,K-fsp,qu	Ti	Al,Ce,La,Nb,Th,Y,Zr	731	Nurme
837.7	1.0	Telychian	25.3	0.15		?	I/S,K-fsp,kaol,qu,Na-K-san, hematite, chalc?	Ti,Ba,Ce,La,Y,Zr			New
838.4	3.0	Telychian	26	0.10		++	I/S,kaol,K-fsp,qu,biot,Na-K-san, hematite	Ti,Ba,Sr,Y,Zr		744	Tehumardi
838.8	0.7	Telychian	25.6	0.29		+	I/S,kaol,K-fsp,qu,anatase	Ba,Sr	Al,Ti,Ce,La,Th,Y,Zr	755	Paatsalu
840.5	0.3	Telychian	42.2	0.20		+++	I/S, terrig		Ti,Ba,Nb,Y,Zr	773	
840.55	0.2	Telychian	46.2	0.15		++	I/S,kaol,K-fsp,qu			774	
840.65	0.2	Telychian	49.4	0.09		++	I/S, terrig	Al,La,Zr		775	
842.0	0.5	Telychian	25.5	0.06		+++	Kaol,I/S,K-fsp,qu,qyp,biot,pyr	Sr	Al,Th,Zr	795	Mustjala
842.1	0.2	Telychian	47	0.14		++	I/S,kaol,K-fsp,qu?,anatase,qyp		Al,Ti,Ba,Ce,La,Nb, Th,Zr	800	
843.7	0.3	Telychian	32.4	0.32	Wide	+	Terrig,I/S,gyp	Al,Nb,Th,Zr	Sr	818	
844.7	0.4	Telychian	31.2	0.34	Very wide	++	Terrig,I/S,calcite,dolomite	Al,Th		843	
845.6	3.0	Telychian	21.1	0.06		++	Grey: kaol,I/S,K-fsp,biot,qu?, Na-K-san	Ce,La,Nb,Y,Zr	Al,Ba	851	Osmundsberg
846.0	0.2	Telychian					I/S,k-fsp,kaol,qu,anatase				New
848.2	1.5	Telychian					I/S,k-fsp,kaol,apatite,anatase	Nb,Th	Ti,Ba,Ce,La,Sr,Y	880	
848.5	1.0	Telychian					K-fsp,kaol,I/S,goyazite/ florencite,apatite,anatase		Ti,Ba,Ce,La,Sr,Y	890	Geniai

Terrig = illite + chlorite + quartz, kaol = kaolinite, I/S = illite-smectite, K-fsp = potassium feldspar, qu = quartz, gyp = gypsum, pyr = pyrite, chalc = chalcopyrite, biot = biotite, san = sanidine, jar = jarosite.

core in this interval, four of which can be correlated with bentonites from the Aizpute section on the basis of sanidine composition and Ti and Nb (Figs 2 and 3). Among these, a bed at 845.6 m is correlative with the well-known and widespread Osmundsberg Bentonite (ID851) (Kiipli et al. 2006, 2008b; Inanli et al. 2009). In Ventspils the Osmundsberg Bentonite consists of a grey and a red part, both revealing identical sanidine composition, but the concentrations of immobile elements are significantly lower in the red part than in the grey part (Fig. 3). A thin bed at 842.1 m in the Ventspils core reveals very high Zr, Th, Nb and Ti concentrations (Fig. 3), excluding (together with its position in the section) correlation with ash beds known in Estonia and the Aizpute-41 section in Latvia. A unique 1 cm thick hard tuff layer (the Geniai Tuff) occurs at 848.5 m containing La, Ce, Nd, Sr and P at the level of major components. We have suggested a source magma of carbonatite composition for this bed (Kiipli et al. 2012). In the När core this interval is in a stratigraphical gap, which, according to Grahn (1995), encompasses much of the Aeronian and the Telychian up to the *Oktavites spiralis* graptolite Biozone.

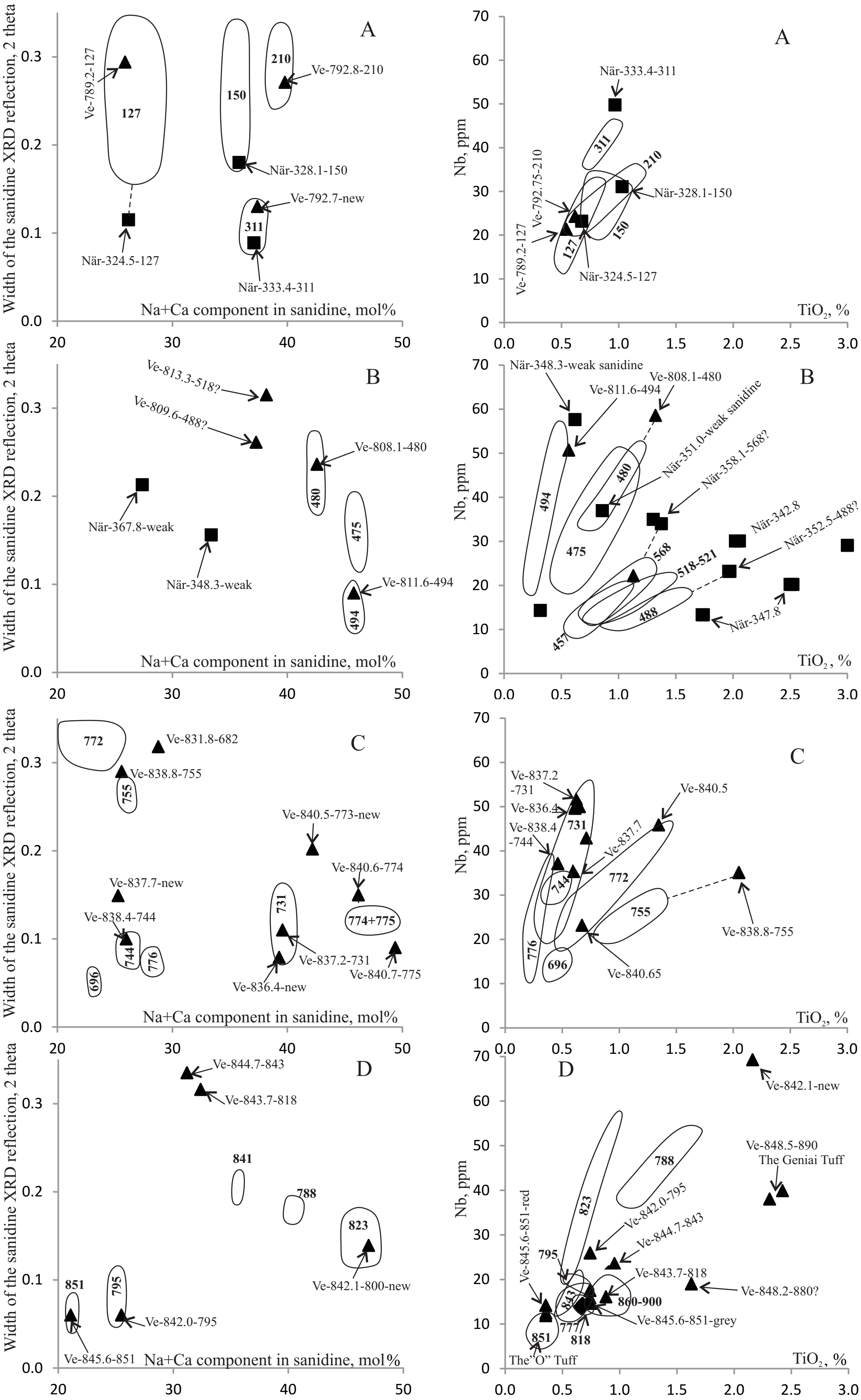
Bentonites in the *Streptograptus sartorius–Monoclimacis crenulata* Biozone interval (Telychian, Llandovery)

In terms of chitinozoan biozonation, this interval belongs to the upper part of the *Eisenackitina dolioliformis* Biozone. In the Ventspils core ten bentonites have been found in this interval, two of which (at depths 840.65 m and 838.4 m) can be firmly correlated on the basis of their sanidine composition with the Aizpute section and sections in Estonia (Figs 3, 4, Table 1). The Nurme Bentonite (ID 731), which is in the *Monoclimacis crenulata* Biozone in the Aizpute core (Fig. 2), has two correlation possibilities in the Ventspils section differing by only 0.8 m in depth (836.4 m and 837.2 m). An identical composition of sanidine, immobile trace elements and close stratigraphical position in the section permit of both correlations. At the same time these compositional signatures confidently distinguish these ash beds from others in this interval. Evidently both ash layers originate from the same volcanic source and the short time span between the eruptions did not allow noticeable evolution of the magma composition. Provisionally, the Nurme Bentonite has been correlated with the bentonite at 837.2 m depth, and the bentonite at 836.4 m depth is considered as new. The bentonite at 837.7 m depth is also new, having no counterparts in previously studied sections. This bed is characterized by a low concentration of all immobile elements and potassium-rich sanidine similar to the Mustjala Bentonite occurring 2.3 m lower in the core. In the När core this interval is still within the stratigraphical gap (Fig. 2).

Bentonites in the *Oktavites spiralis–Cyrtograptus lapworthi* Biozone interval (Telychian, Llandovery)

In terms of chitinozoan biozonation, this interval belongs to the *Angochitina longicollis* and *Conochitina proboscifera* biozones. A bentonite in the Ventspils core at 808.1 m depth correlates, on the basis of its distinctive sanidine composition (42.6 mol% of $(Na + Ca)AlSi_3O_8$ in the modal component) and high content of Nb and Zr, with a bentonite at 938.6 m depth in the Aizpute core and with the Kaugatuma Bentonite (ID 480) in Estonia. Similarly, a bentonite in the Ventspils core at 811.6 m depth correlates perfectly (45.8 mol% of the $(Na + Ca)AlSi_3O_8$ in the modal component and sharp XRD reflection) with the Ruhnu Bentonite (ID 494) in Estonia. In the När core, according to Snäll (1977), 19 ash beds occur in the 334–363 m interval. From 11 of these we found some material for laboratory study. These ash beds are mostly characterized by wide or weak sanidine XRD reflections and a high content of P, Ti, Sr, Ba, La and Ce. In Estonia six ash beds have a similar geochemical type. The wide sanidine reflection does not enable unequivocal correlations. Some provisional correlations can be proposed based on the TiO_2–Nb chart (Fig. 3). One variant of these provisional correlations is expressed in Fig. 2, but clearly this is not the only one possible. According to this correlation variant, at least nine ash beds of this type occur in Latvia and Gotland and two of the Estonian ash beds (ID 520 and 521) do not extend to these areas. Two ash beds in the När section at depths of 348.3 m and 351.0 m belong to another geochemical type characterized by a high content of Nb, Zr and Th (Fig. 3). By contrast with Nb-, Zr- and Th-rich ashes in Estonia, these beds do not exhibit a strong and sharp sanidine reflection and consequently most probably are the product of other eruptions. The ash beds of these two geochemical types were first distinguished by Batchelor

Fig. 3. Sanidine composition (left column) and TiO_2/Nb ratio (right column) in the studied bentonites compared with the bentonites from Estonia (oval contours). ID numbers of Estonian bentonites are in bold font. Ve – Ventspils-D3, Ve-838.8-755 – core-depth (m)-ID number of the bentonite. A – *murchisoni* Biozone interval, B – *spiralis–lapworthi* Biozone interval, C – *sartorius–crenulata* Biozone interval, D – *turriculatus–crispus* Biozone interval. Broken lines indicate correlations.



Width of the sanidine XRD reflection, 2 theta
Na+Ca component in sanidine, mol%
Nb, ppm
TiO2, %
A
Ve-789.2-127
Ve-792.8-210
När-328.1-150
Ve-792.7-new
När-324.5-127
När-333.4-311
Ve-792.75-210
B
Ve-813.3-518?
Ve-809.6-488?
Ve-808.1-480
När-367.8-weak
När-348.3-weak
Ve-811.6-494
När-348.3-weak sanidine
När-351.0-weak sanidine
När-358.1-568?
När-342.8
När-352.5-488?
När-347.8
518-521
C
Ve-831.8-682
Ve-838.8-755
Ve-840.5-773-new
Ve-840.6-774
Ve-837.7-new
Ve-838.4-744
774+775
Ve-837.2-731
Ve-836.4-new
Ve-840.7-775
Ve-837.2
-731
Ve-836.4
Ve-838.4
-744
Ve-837.7
Ve-840.5
Ve-840.65
D
Ve-844.7-843
Ve-843.7-818
Ve-842.1-800-new
Ve-842.0-795
Ve-845.6-851
Ve-842.1-new
Ve-848.5-890
The Geniai Tuff
Ve-845.6-851-red
Ve-843.7-818
Ve-848.2-880?
860-900
Ve-845.6-851-grey
The "O" Tuff

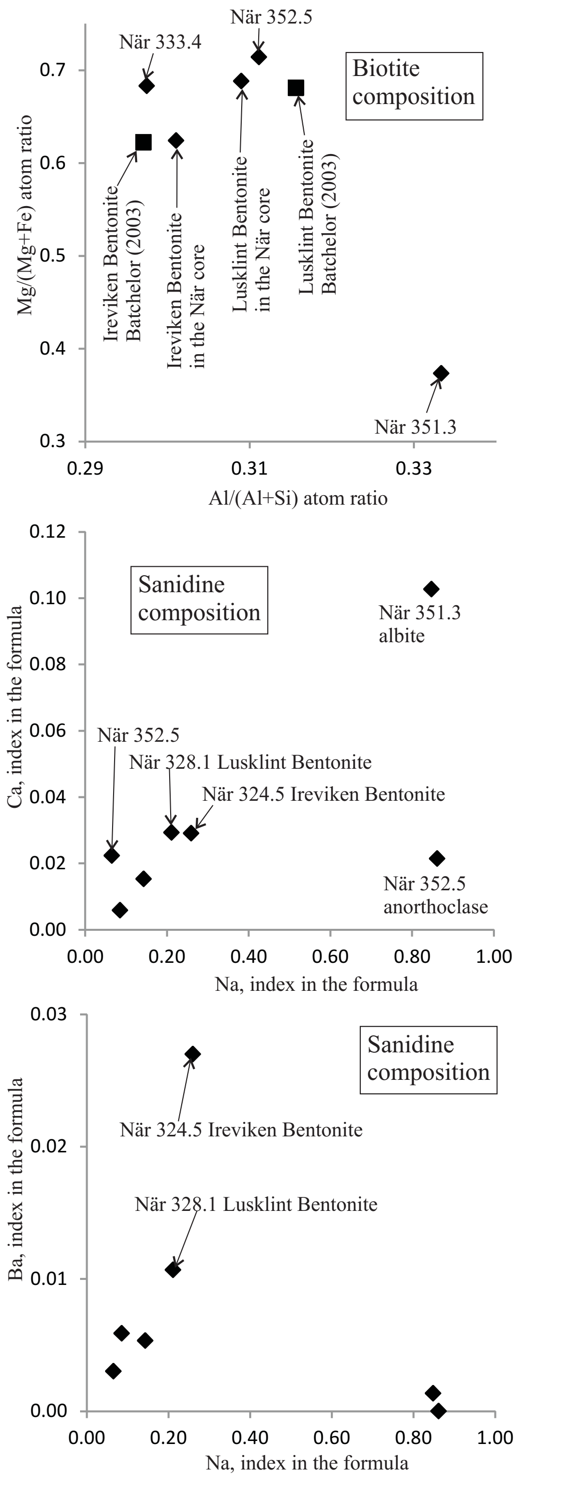


Fig. 4. Composition of biotite and sanidine phenocrysts according to the EDS microanalyses.

et al. (1995) in the Garntangen section in Norway correlating with this level (Kiipli et al. 2001). In total, probably seven studied ash beds within this interval in the När section are new (at depths 358.1, 357.4, 351.3, 351.0, 348.9, 348.3 and 347.8 m), i.e. not known from previously studied sections.

Bentonites in the *Cyrtograptus murchisoni* Biozone interval (Sheinwoodian, Wenlock)

In terms of chitinozoan biozonation, this interval belongs to the *Margachitina margaritana* Biozone (Fig. 2). The Aizpute Bentonite is distinct from others in this interval in its sharp sanidine reflection with 37 mol% of Na + Ca component and high Nb, Zr and Th contents. In the När core the Lusklint and Ireviken bentonites, in the Ventspils core the Ohesaare and Ireviken bentonites are found as well (Figs 2 and 3). The Ireviken Bentonite marks Ireviken Event Datum 2 (Jeppsson & Männik 1993). Kiipli et al. (2008a) showed that this level correlates to a level within the upper part of the *C. murchisoni* graptolite Biozone. The occurrence of the Ireviken Bentonite in the Ventspils section (Fig. 2) also within the *C. murchisoni* Biozone supports that correlation. A new ash bed occurs in the Ventspils core at a depth of 792.7 m, having a sharp sanidine reflection not found in other sections at this stratigraphical level.

Composition of volcanic phenocrysts according to EDS microanalysis

Five samples from the När core where enough grain material was available were subjected to EDS microanalysis. In each sample 30–70 grains were measured. Reference glass material BBM-1 distributed by the International Association of Geoanalysts was analysed together with the samples under study and corrections to the results of a few per cent of the concentration were derived from the reference sample analysis. The results are presented in Table 2 and Fig. 4.

Among the phenocrysts, quartz dominates in the Ireviken, Lusklint and När-351.3 m bentonites and sanidine in the Aizpute and När-352.5 m bentonites. Biotite is present in all studied samples in variable concentrations. A few grains of authigenic kaolinite, pyrite, barite and illite are found as well. An especially rich assemblage of minerals was detected in the När-351.3 m bentonite, represented by several magmatic (magnetite, Ti-oxide, albite) and authigenic (pyrite, strontianite, goyazite-florencite, kaolinite and illite) grains.

Biotite composition was calculated according to the idealized half-cell chemical formula with eight cations: $(K,Na)_1(Mg,Fe,Ti,Mn,Ca,Sr,Ba)_3(Al,Si,P)_4O_{10}(OH,F)_2$. The average of 5–9 grains is represented in Table 2 and in Fig. 4. Four of the studied ashes contain Mg-rich biotites and one (När-351.3 m) contains Fe-rich biotite. The same two groups of biotite were found in the Telychian of the Viirelaid core (Estonia), although

Table 2. Composition of phenocrysts in ash beds of the När core

	Ireviken B. När 324.5	Lusklint B. När 328.1	Aizpute B. När 333.4	När 351.3	När 352.5
Quartz, %	63	54	17	67	7
Sanidine, %	13	35	56	19	76
Biotite, %	24	10	28	14	17
Other minerals	Kaolinite, pyrite	Kaolinite, apatite in sanidine	Kaolinite, barite, illite	Magnetite, Ti-oxide, pyrite, strontianite, goyazite-florencite, albite, kaolinite, illite	Anorthoclase, barite, illite
Composition of biotite, atoms per chemical formula					
Na	0.08	0.11	0.10	0.13	0.13
K	0.92	0.89	0.90	0.87	0.87
Mg	1.65	1.79	1.79	0.99	1.87
Fe	1.00	0.81	0.83	1.65	0.75
Ti	0.29	0.31	0.34	0.30	0.30
Mn	0.016	0.026	0.019	0.019	0.016
Ca	0.007	0.002	0.005	0.019	0.011
Sr	0.005	0.004	0.002	0.006	0.011
Ba	0.030	0.055	0.022	0.019	0.042
Al	1.20	1.24	1.19	1.33	1.24
Si	2.80	2.76	2.81	2.66	2.75
P	0.001	0.000	0.000	0.011	0.003
Composition of sanidine, atoms per chemical formula					
Na	0.26	0.21	0.14	0.09	0.06
K	0.68	0.74	0.83	0.90	0.91
Ca	0.029	0.029	0.015	0.006	0.022
Sr	0.002	0.005	0.002	0.001	0.002
Ba	0.027	0.011	0.005	0.006	0.003
Al	1.00	0.93	1.03	1.00	1.01
Si	2.93	3.05	2.94	2.99	2.96
Ti	0.011	0.005	0.021	0.003	0.006
Mn	0.000	0.002	0.001	0.001	0.001
Fe	0.065	0.008	0.014	0.004	0.023

Fe-rich biotites occurred stratigraphically at a somewhat lower level in the Telychian *crispus–crenulata* graptolite biozones (Kiipli et al. 2008d). Comparison with biotite analyses from Batchelor (2003) shows similar results for the Ireviken and Lusklint bentonites from outcrops on Gotland and from the När core (present study), confirming the correlation based on sanidine composition.

Sanidine composition was calculated according to the idealized chemical formula with five cations: $(K,Na,Ca,Ba,Sr)_1(Al,Si,Ti,Mn,Fe)_4O_8$. An average of 6–31 grains is represented in Table 2 and Fig. 4. The average content of the Na + Ca component is generally lower according to EDS analysis than the modal component according to XRD analysis. The reason is the presence of other components than modal, predominantly with a lower content of the Na + Ca component. The difference may arise in part also from the smaller number of grains, and consequently the less reliable result analysed by EDS (6–31 grains) compared to XRD (simultaneous average of ca 2000 grains). An interesting result from EDS analysis, not accessible by XRD, is the concentration of other cations than sodium and potassium in sanidine. Relatively high (2–3 mol%) content of the $CaAl_2Si_2O_8$ component in sanidine was established in the Ireviken, Lusklint and När-352.5 m bentonites. Sanidine in the Ireviken and Lusklint bentonites is remarkable for the high content (1–2.5 mol%) of $BaAl_2Si_2O_8$. The Sr, Ti, Mn and Fe concentrations in sanidine were too low for reliable calculation of the index in the chemical formula (Table 2).

Areal distribution of bentonites

The areal distribution of bentonites depends on the ancient volcanic ash clouds and the distribution maps can reveal the directions from which the ashes were transported. The distribution areas composed by Kiipli et al. (2008b, 2008c, 2008d, 2010b) for ca 20 bentonites in the eastern Baltic indicate ash transport from the northwest in terms of the present-day orientation of Europe. Correlation with the När section enables extension of the bentonite distribution areas for the Ireviken, Lusklint, Ohesaare and Aizpute bentonites (Fig. 5). These areas confirm ash transport from the Iapetus Ocean, closing between Baltica and Laurentia. Judging from these maps, the bentonites in Jämtland and Dalarna in Sweden should be significantly thicker than in Estonia and Latvia. This conclusion is confirmed by the occurrence of the 1 m thick Osmundsberg Bentonite in Dalarna (Inanli et al. 2009). In southern Sweden and in the Oslo region we can expect these volcanic ashes to have similar thicknesses as in the eastern Baltic, e.g. in the range of milli- and centimetres.

Sea currents, too, can modify the areal extent of individual bentonites, redistributing and sorting the material by grain size. This has happened with an ash bed in recent sediments near the coast of Chile (Fisher & Schmincke 1984), where an oceanward current separates the volcanic ash area into two parts. Examining the distribution of bentonites in the Baltic Silurian (Fig. 5; Kiipli et al. 2008b, 2008c, 2008d, 2010b), we notice that the bentonite distribution areas are often similarly separated into two parts. There are two possible explanations: the influence of sea currents or a change in wind direction during a long-lasting eruption. As the separation occurs in a specific part of the Silurian basin, in present-day North Latvia and South Estonia, a sea current is a more likely reason. In the same area gaps or condensed sequences often occur in Silurian sections (Fig. 2; Loydell et al. 2003; Kiipli et al. 2011, 2012). In terms of basin depth, this area belongs to the transition between shallow shelf and deep shelf regions. An oceanic current coming from the southeast was interpreted from the kaolinite admixture in deep shelf sedimentary rocks by Kiipli et al. (2009) for Telychian time. Separation of the distribution areas of Silurian bentonites into two provides further support for the existence of this current. Figure 6 displays the shelf sea branch of the oceanic current in accordance with the bentonite distribution areas. It is not clear how closed the ocean within the Caledonian collision zone was during the Telychian–early Wenlock: possibly the shelf sea branch of the current returned to the Rheic Ocean (Fig. 6), but alternatively there could also have been a passage to a remnant of the Iapetus Ocean. Worsley et al. (2011) measured the direction of ripple and tool marks on bedding planes in the Telychian of the Oslo Region and established the dominant direction of currents from northwest to southeast, i.e. opposite to the direction we have proposed. A reasonable explanation could be that a

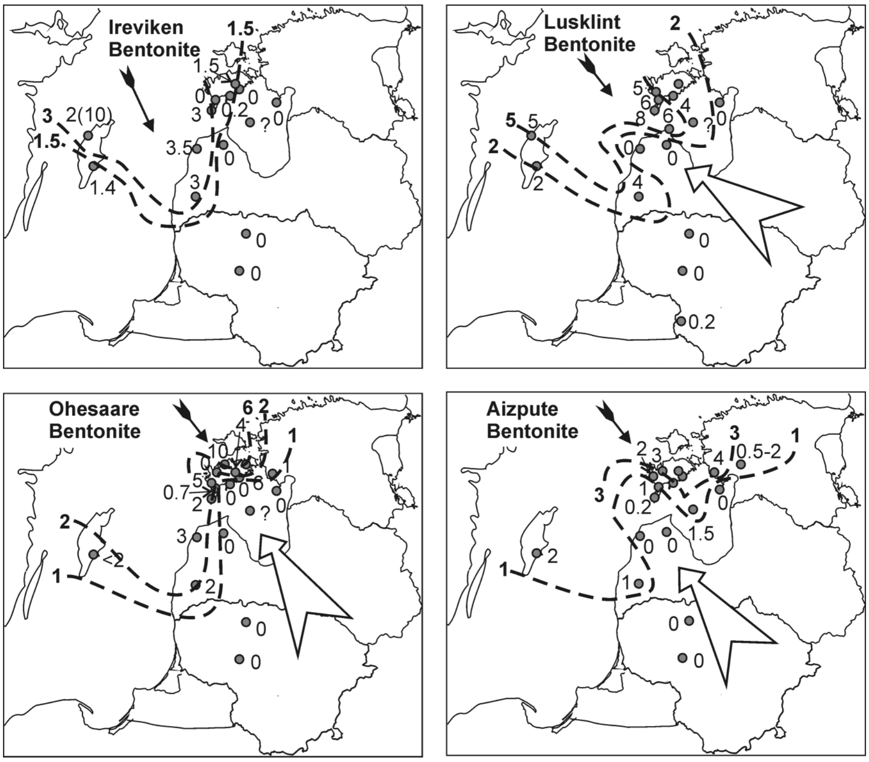


Fig. 5. Distribution maps of the four bentonites from the Sheinwoodian (lower Wenlock). Details of the distribution in Estonia and names and numbers of all drill cores can be found in Kiipli et al. (2008b, 2008d, 2010b).

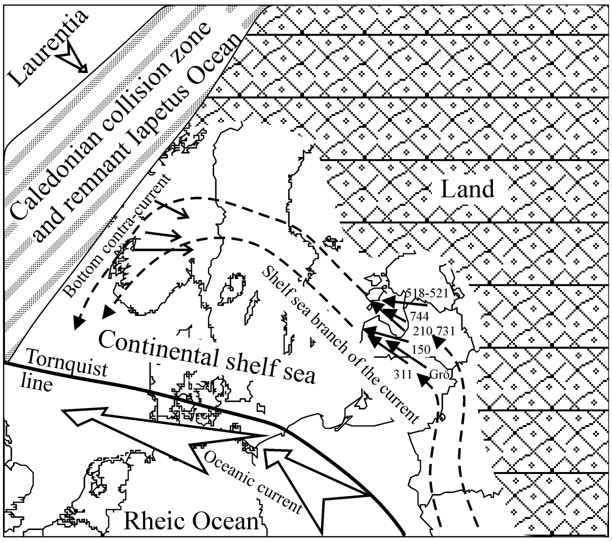


Fig. 6. Silurian shelf sea in Baltoscandia with interpreted shelf sea currents (arrows with broken lines). Arrows with solid lines indicate currents which separate the volcanic ash distribution areas into two parts. The ID numbers of the bentonite are near the arrows. The oceanic current is shown according to Kiipli et al. (2009). Arrows indicating coastal contracurrent direction are from Worsley et al. (2011).

shelf sea current flowing from the southeast and striking the coast formed by the rising Caledonian mountains rebounded as a contra-current along the sea bottom.

CONCLUSIONS

Correlation of volcanic ash beds using biostratigraphy, phenocryst composition and immobile elements within bentonites has revealed several well-established and a number of provisional correlations between the Gotland and East Baltic sections. The occurrence of the Aizpute Bentonite in the subsurface of Gotland together with the Lusklint and Ireviken bentonites increases the confidence that the correlation of exposed sections on Gotland, based on volcanic ash beds, with the graptolite biozonation at the level of the Ireviken Event (Kiipli et al. 2008a) is reliable. Approximately twelve new ash beds were discovered and geochemically characterized. These characterizations could be used for demonstrating correlations in future studies. New correlations enabled extension of the mapping of the distribution areas of bentonites from the East Baltic to Gotland. These extended maps point more reliably than previous studies to the volcanic source areas in the closing Iapetus Ocean. Separation of the bentonite distribution areas into two parts in North Latvia–South Estonia indicates the existence of a shelf sea current in the Baltic Silurian Basin coming from the southeast in terms of the present-day orientation.

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Ülem-Llandovery – Alam-Wenlocki bentoniitide korrelatsioon Näri (Gotland, Rootsi) ja Ventspilsi (Läti) puursüdamike vahel: vulkaanilise tuha pilvede ning merehoovuste roll bentoniidi levikuala tekkel

Tarmo Kiipli, Toivo Kallaste ja Viiu Nestor

Biostratigraafia, sanidiini koostis ja immobiilsed elemendid bentoniitides võimaldasid kindlaks teha mitu kindlat ning mõned esialgsed korrelatsioonid Gotlandi ja Ida-Baltikumi vahel. Fenokristallide mikroanalüüs näitas, et bentoniitides esineb Mg- või Fe-rikast biotiiti. Sanidiini fenokristallid sisaldavad peale K- ja Na-komponendi ka mõni protsent Ca- ning Ba-komponenti. Uued korrelatsioonid võimaldasid laiendada bentoniitide leviku skeeme Gotlandini. Bentoniitide levikualad jagunevad Põhja-Lätis – Lõuna-Eestis kaheks, osutades hoovusele Balti Siluri šelfimeres, mis jaotas vulkaanilise tuha osakesi ringi.