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Upper Katian (Ordovician) bentonites in the East Baltic, Scandinavia and Scotland: geochemical correlation and volcanic source interpretation

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Abstract – Altered volcanic ash interbeds (bentonites) in the upper Katian of Baltoscandia indicate significant volcanic activity in neighbouring tectonically active areas. Katian bentonites in the East Baltic can be reliably correlated using sanidine phenocryst composition. Ratios of immobile trace elements TiO_2, Nb, Zr and Th to Al_2O_3 enable extension of the correlations to Scandinavia, where late diagenetic alterations could have caused recrystallization of sanidine phenocrysts. At least seven volcanic eruptions were recognized in Baltoscandian sections. Several bentonites found in deep-sea sediments are absent in shallow-sea sediments, indicating extensive breaks in sedimentation and erosion during late Katian and Hirnantian times. The areal distribution pattern of Katian bentonites in Baltoscandia indicates a volcanic source from the north or northwest (present-day orientation) from the margins of the Iapetus Palaeo-Ocean. Signatures of ultra-high-pressure metamorphism in the Seve Nappe (Central Sweden) and intrusions in the Helgeland Nappe Complex in Central Norway have been proposed as potential sources of the magmas that generated the volcanic ashes deposited in the East Baltic in Katian times. Geochemical similarities between Baltoscandian and Dob's Linn bentonites from southern Scotland suggest a common volcanic source in Katian times.

Keywords: K-bentonites, Mg-bentonites, Katian, Ordovician, volcanism, Iapetus, Baltica.

1. Introduction

Bentonites (altered volcanic ashes) in sedimentary sections carry information about tectonomagmatic processes in volcanic source areas (Huff *et al.* 1993; Batchelor & Evans 2000; Kiipli, Soesoo & Kallaste, 2014), directions to volcanic sources (Bergström *et al.* 1995; Kiipli *et al.* 2013), the diagenetic environments of sedimentary rocks (Hints *et al.* 2006, 2008; Somelar *et al.* 2010; Williams *et al.* 2013) and the isotopic ages of rocks (Bergström *et al.* 2008; Cramer *et al.* 2012; Sell, Ainsaar & Leslie, 2013). Recognizing the distinct chemical signatures of eruption layers can lead to exceptionally precise correlations of sections (Emerson *et al.* 2004; Inanli, Huff & Bergström, 2009; Kiipli, Kallaste & Nestor, 2010, 2012; Kiipli *et al.* 2010, 2011; Ray *et al.* 2011; Kiipli, Radzevicius & Kallaste, 2014).

While Ordovician Sandbian and Silurian bentonites in the Baltoscandian region have been described in several publications, Ordovician Katian bentonites have been less well studied. Some correlations in the East Baltic sections based on sanidine phenocryst compositions were described in the WOGOGOB conference abstract book (Kiipli, Kallaste & Kiipli, 2004). The unusual authigenic mineralogy of Katian bentonites represented by the frequent dominance of chlorite–smectite was discussed in Hints *et al.* (2006) and aspects of the source magma geochemistry in Kiipli, Soesoo & Kallaste (2014). Geochemical evidence indicates vast environmental changes in Late Ordovician time and palaeontological studies have shown strong extinction events (Brenchley, Carden & Marshall, 1995; Harper, Hammarlund & Rasmussen, 2013; Bergström *et al.* 2014). Therefore, intensive research during recent decades has been dedicated to this time interval, and data on volcanism and uniquely precise correlations enabled by volcanic ash beds are useful additions to these studies.

Herein, we update correlations in the East Baltic with new finds together with new Scandinavian material. In addition to the sanidine composition, immobile trace elements are applied to proving the correlations. The relationship of Katian bentonites to the magmatic activity in the Iapetus Palaeo-Ocean is also discussed.

2. Material and methods

Samples were collected from 21 drill core sections from Estonia, the Aizpute-41 core from Latvia, the När core from Gotland (Sweden), the Röstånga-1 core from southern Sweden and from natural exposures from the Jämtland and Västerbotten regions (Central Sweden) (Fig. 1). In the cores, all interbeds distinguished by an unusual appearance (e.g. pure clay or shaly interbeds

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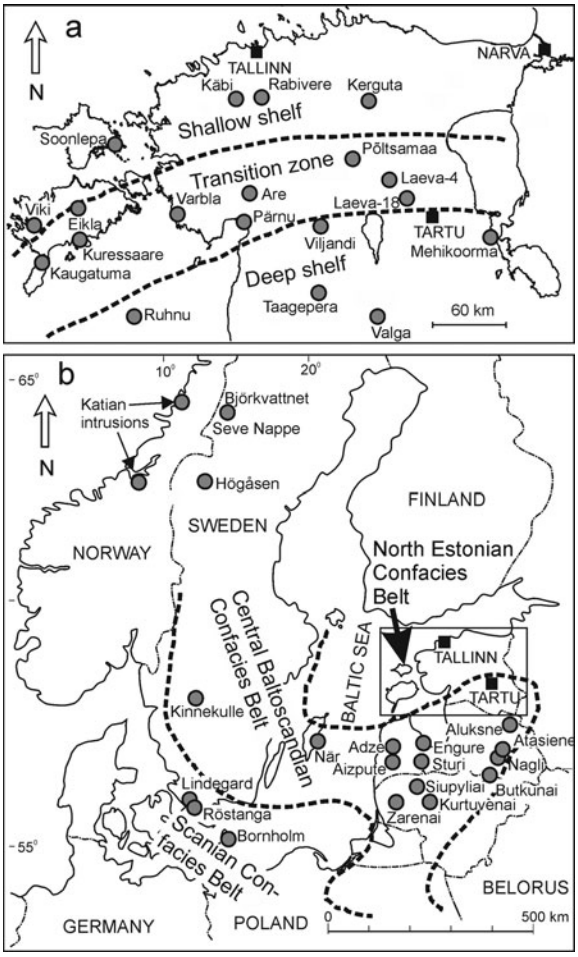

Figure 1. Location of sections studied and discussed in text. (a) Sections sampled from Estonia; (b) sections sampled or discussed from Sweden, Norway, Denmark, Latvia and Lithuania. Broken lines separate palaeoenvironmental zones and confacies belts.

in limestones and marls) were sampled. In the northernmost sections in Estonia (Soonlepa, Käbi and Rabivere), interbeds of hard feldspathic tuffs were found. In total, around 60 samples were studied by X-ray diffractometry (XRD), and the presence of volcanic material was established in 45 samples.

To identify major minerals in the sampled interbeds of supposed volcanic origin, bulk samples were analysed by XRD. An association of illite–smectite and chlorite–smectite as major minerals has been considered as a provisional indication of a volcanic origin for the interbeds. Pure end-member authigenic (Kastner, 1971) K-feldspar forms a major portion of the feldspathic tuffs in North Estonia.

Magmatic sanidine ($(K,Na,Ca)AlSi_3O_8$) phenocrysts were analysed by XRD from coarse fractions (0.04–0.1 mm) separated from 2 g of bentonite applying the calibration established in the experimental study by Orville (1967). A shift in the $20\bar{1}$ reflection enables the discrimination of small cations (Na + Ca) from large (K + Ba) cations. The method was described in detail in Kiipli, Kallaste & Nestor (2010) and Kiipli *et al*. (2011). All measured XRD spectra of sanidine in the upper Katian bentonites are available in the collections database of the Institute of Geology at Tallinn University of Technology at http://geokogud.info/reference/3841.

Major components and trace elements were analysed in 21 samples of pressed powders, where sufficient quantity (8 g) of material was available, by the X-ray fluorescence (XRF) method using an S-4 (Bruker AXS) analyser. The concentrations were calculated automatically by the manufacturer's software and corrected on the basis of reference materials (Govindaraju, 1995; Kiipli *et al*. 2000) and proficiency test samples distributed by the International Association of Geoanalysts (http://www.geoanalyst.org).

3. Geological background

3.a. Lithology and facies

Jaanusson (1995) distinguished the following facies areas in the Ordovician of Baltoscandia: North Estonian Confacies, Central Baltoscandian Confacies, Lithuanian Confacies and Scanian Confacies (Fig. 1). In Estonia, an additional transition zone between shallow- and deep-shelf palaeoenvironments was recognized by Põlma (1967). In the upper Katian Pirgu Stage the transition zone is especially notable with its specific facies, greater thicknesses and frequent breaks in sedimentation (Fig. 2). Rocks of the Pirgu Stage in the East Baltic were described in Hints, Oraspõld & Nõlvak (2005) and herein we briefly refer to this content.

In the North Estonian Confacies (shallow shelf sea in terms of palaeoenvironment), the rocks of the Pirgu Stage include two formations: (1) the Moe Formation (lower Pirgu): relatively pure coarsely nodular limestones, typically with interbeds of brownish organic-rich marl and frequent occurrences of the tubular algae *Dasyporella*; and (2) the Adila Formation (upper Pirgu): relatively argillaceous thin to medium nodular limestones with thin grey marl interbeds. Among the studied sections, a typical development is reflected in the Soonlepa core from Hiiumaa Island.

While the Pirgu Stage in the North Estonian Confacies (shallow shelf) and Central Baltoscandian Confacies (deep shelf) is characterized by a relatively simple and uniform lithology, the transition zone between these areas shows variable types of rocks, and this natural diversity has caused numerous discussions on correlations and the differentiation of stratigraphic units. Among the studied sections the Varbla section is considered to be the most representative, and the following formations (from the base) can be distinguished (Fig. 2): (1) the Jonstorp Formation: argillaceous red-coloured limestone; (2) the Tootsi Formation: finely nodular grey strongly argillaceous limestone with violet patches; (3) the Halliku Formation: marlstone with or without carbonate nodules and argillaceous limestone in the upper part; (4) the Oostriku Formation: relatively pure nodular limestone; and (5) the Kabala

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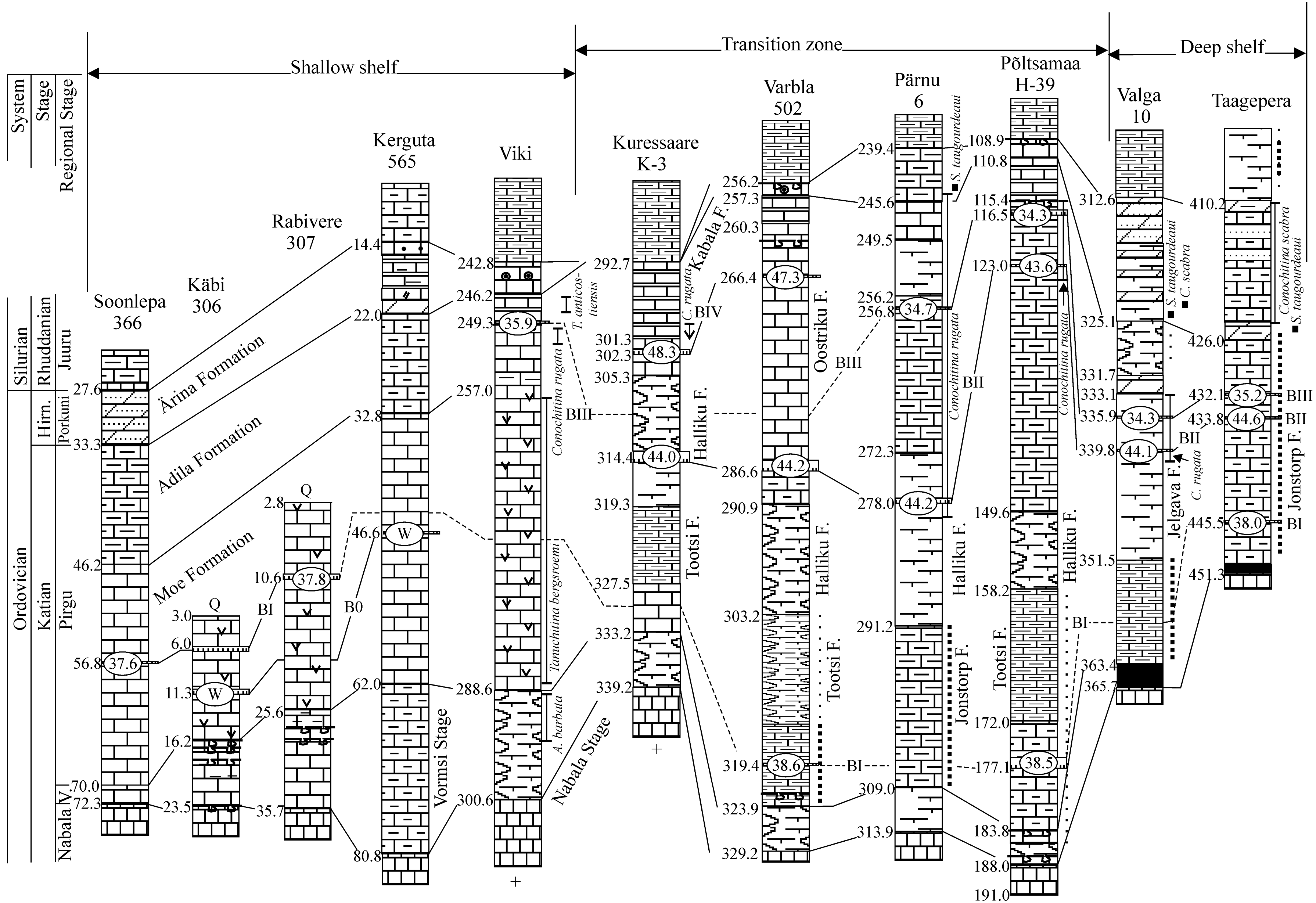

Figure 2. Correlation of Katian and Hirnantian sections in Estonia. For legend see Figure 3. B0, BI, BII, BIII and BIV are indexes of bentonites. Among the chitinozoans, only ranges of zonal forms are shown.

Formation: alternating thick (20–50 cm) limestone and marl layers of contrasting composition. In other sections transitional varieties often occur and thicknesses vary greatly.

In the Central Baltoscandian Confacies in Latvia and South Estonia, the Jonstorp Formation represented by red-coloured argillaceous limestones and marls composes the lower thicker part of the Pirgu Stage; upwards follow the Paroveja Formation (relatively pure nodular limestones) and the Kuili Beds (red-coloured marls and argillaceous limestones). Among the studied sections the Aizpute-41 core in Figure 3 is typical. In Central Sweden, Jaanusson (1963) distinguished the Lower Jonstorp Formation (grey-coloured finely nodular limestone and marl), the Upper Jonstorp Formation (red-coloured finely nodular limestone and marl) and between them the Öglunda Limestone (e.g. the När section in Fig. 3).

In the Scanian Confacies Belt the Pirgu Stage is represented by the Lindegård Mudstone, a section of grey marlstones (Fig. 3) (Glimberg, 1961; Bergström *et al*. 1999, 2014).

The sample from Jämtland is from the lower allochthonous unit the Kogsta Siltstone at the Högåsen locality (for more information see Dahlqvist, 2005). Thin greenish/grey laminae are seen in the otherwise dark shale/siltstone in the uppermost metres of the unit. The origin of these conspicuous beds has been discussed previously, and Cherns & Karis (1995) and Karis & Strömberg (1998) suggested they are of volcanic origin but no analysis has been made until this study. The Västerbotten sample was taken from an island shore section in Lake Björkvattnet. The sample is most probably from the uppermost part of the Vojtja Quartzite, close to the onset of carbonate production reflected in the development of the Slätdal Limestone (Kulling, 1933). The sample is from the Upper Allochthon (Köli Nappe), which is believed to have occupied an intra-Iapetus island arc setting during Ordovician time (Stephens, 1977; Stephens & Gee, 1985).

3.b. Chitinozoans

An obvious feature is the progressive decrease in chitinozoan diversity long before the Hirnantian glaciation. This low diversity and density of the main groups of microfossils is well visible in the diversity dynamics curves for the Pirgu Age, the prelude to the terminal Ordovician mass extinction (Kaljo, Nõlvak & Uutela, 1996; Brenchley *et al*. 2003; Kaljo *et al*. 2011). However, this study reports ages based on chitinozoans from limited sections. Bentonite layers BII, BIII and BIV (Fig. 2) of the upper Halliku and Adila formations span the *Conochitina rugata* chitinozoan zone (Nõlvak & Grahn, 1993; Nõlvak, Hints & Männik, 2006) and a little above indicating an age of late Pirgu (latest Katian). The lower bentonite beds (BO, BI; Fig. 3) are distributed mainly in the red-beds of the Jonstorp Formation, which are totally barren of all groups of acid-resistant organic-walled microfossils, and the timing of bentonite deposition in these sections remains unclear. In the North Estonian Confacies these two lower bentonites occur in the Moe Formation belonging to the *Tanuchitina bergstroemi* Zone (Hints, Oraspõld & Nõlvak, 2005).

3.c. Graptolites, brachiopods, carbon isotopes and isotopic age

In the Lindegård section the graptolites *D. complanatus*, *O. gracilis* and *D. anceps* were found in the lower part of the Lindegård Mudstone (Glimberg, 1961). In the Röstånga-1 section *N. persculptus* was identified in the upper part of the Hirnantian (Bergström *et al*. 1999). A carbon isotope positive excursion in the lower Hirnantian, established in many sections, in particular also in Röstånga-1, is correlated with the *N. extraordinarius* graptolite Biozone (Bergström *et al*. 2014), and it helps to establish the Katian/Hirnantian boundary. Below the Lindegård Mudstone, in the Fjäcka Shale, *D. clingani* has been recovered (Glimberg, 1961). Thus, the Pirgu Stage is correlated with graptolite biozones *complanatus* and *anceps* (Hints *et al*. 2010). According to the current time scale (Gradstein, Ogg & Hilgen, 2012), the Katian (including the Pirgu Stage in the upper part) corresponds to the time interval 445.2–453.0 Ma.

In Jämtland the uppermost Kogsta Siltstone is believed to be of latest Katian to earliest Hirnantian age (Dahlqvist, Harper & Wickström, 2010). The age determination of the sample from the Vojtja Quartzite from Västerbotten is unclear, but, close to the sampled interval, the overlying Slätdal Limestone has yielded the brachiopod *Holorynchus giganteus* (Kulling, 1933). *Holorynchus giganteus* is restricted in time to the upper Katian and to beds just below the Hirnantian carbon isotope event (Brenchley *et al*. 1997).

4. Results

4.a. Composition of the bentonites

According to XRD measurements, the Estonian bentonites of the Pirgu Stage contain variable amounts of three authigenic minerals: chlorite–smectite, illite–smectite and K-feldspar. According to Kastner (1971), pure end-member K-feldspars are of authigenic origin. In the shallow palaeoshelf area authigenic K-feldspar dominates, forming hard feldspathic tuffs; in the transition zone chlorite–smectite and illite–smectite dominate being equally abundant; and in the deep shelf area illite–smectite is the most abundant authigenic mineral. A similar distribution pattern (except the dominance of K-feldspar in the shallow shelf area) was revealed when studying the clay fraction of the bentonites (Hints *et al*. 2006). The major chemical components (Table 1; Fig. 4) display a continuous range of compositions from high-K_2O-containing feldspathic tuffs through K-bentonites of intermediate compositions to Mg-bentonites with high contents of MgO.

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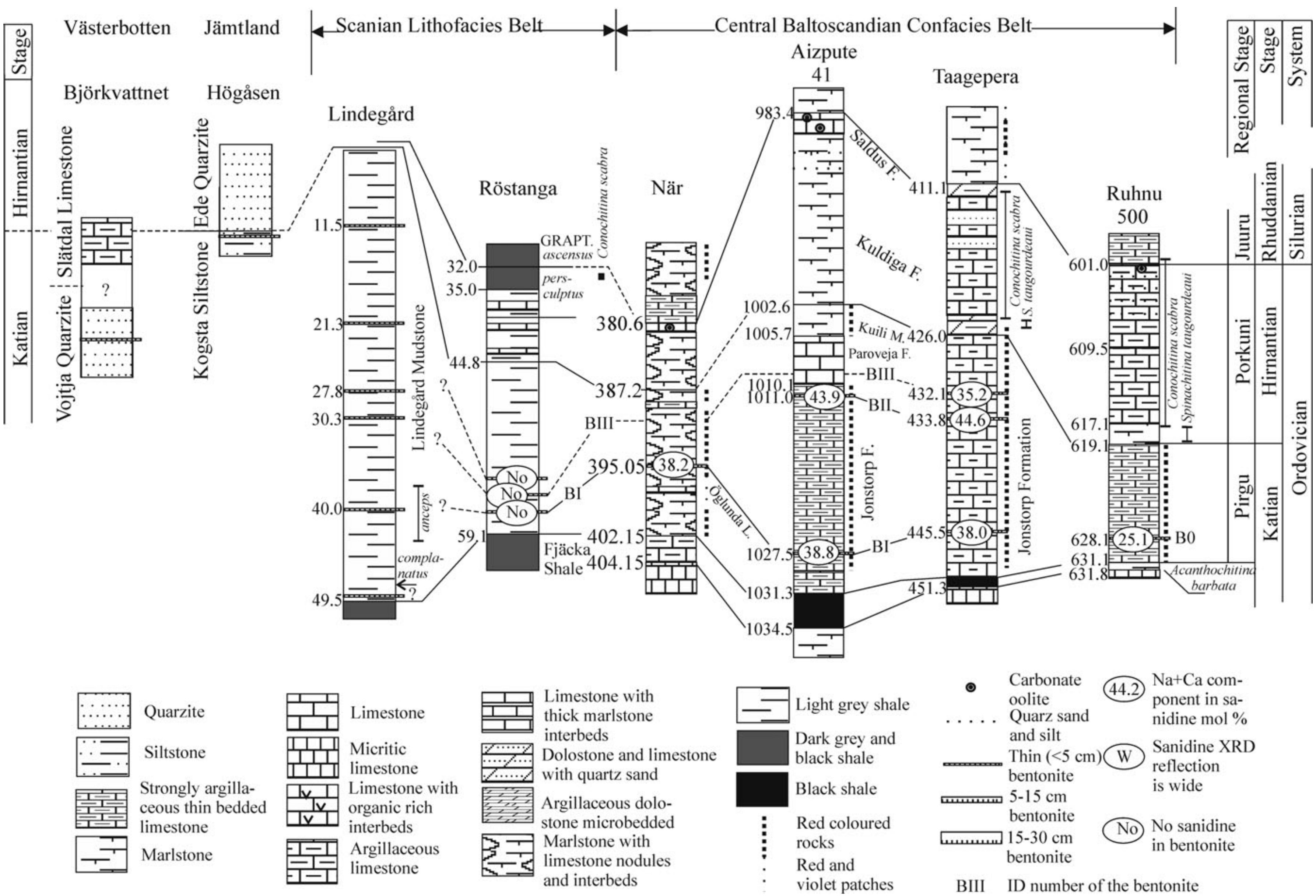

Figure 3. Correlation of Katian and Hirnantian sections of Sweden, Latvia and Estonia. Among the chitinozoans, only ranges of zonal forms are shown.

Table 1. Results of XRF analyses of upper Katian bentonites

Bentonite ID Locality	Högåsen	Björkvattnet	Röstånga	B III Röstånga	B I Röstånga	B IV Kuressaare	B IV Kuressaare	B IV Varbla	B III Põltsamaa	B III Taagepera	B II Eikla
Depth, m			upper	middle	lower	302.20	302.25	266.40	116.50	436.10	239.75
LOI_{920} (%)	4.3	5.1	24.6	11.2	8.0	11.6	8.1	14.9	9.3	17.5	5.6
SiO_2 (%)	57.5	49.5	26.9	46.1	48.9	44.9	48.8	40.4	46.4	40.6	56.4
TiO_2 (%)	1.18	1.29	0.41	0.51	0.33	0.41	0.38	0.42	0.24	0.32	0.22
Al_2O_3 (%)	21.8	25.2	15.2	21.4	25.7	14.0	15.5	13.0	10.6	12.6	15.4
Fe_2O_3 (%)	5.1	5.6	1.8	4.0	2.5	3.3	3.1	3.7	7.7	2.9	1.6
MnO (%)	0.01	0.00	1.79	0.64	0.31	0.02	0.01	0.02	0.01	0.23	0.01
MgO (%)	2.4	2.5	2.3	2.9	2.7	10.0	8.8	12.3	15.3	9.8	6.2
CaO (%)	0.12	0.06	22.8	7.04	2.84	5.33	2.71	7.32	3.75	9.8	2.91
Na_2O (%)	0.11	0.14	0.26	0.32	0.30	0.09	0.31	0.22	0.17	nd	0.18
K_2O (%)	7.4	10.8	4.1	6.1	7.4	8.1	9.6	6.4	4.0	5.0	11.5
P_2O_5 (%)	0.13	0.06	0.04	0.05	0.04	0.02	0.02	0.02	0.02	0.05	0.02
S (%)	0.02	0.01	0.10	0.04	0.01	0.36	0.39	0.48	0.86	nd	0.29
As (ppm)	6.8	15.6	32.2	1.0	0.4	8.9	9.7	10.2	8.2	nd	5.9
Ba (ppm)	889	1891	1454	2454	3344	147	121	124	136	nd	75
Ce (ppm)	102	263	65	69	44	34	8	5	4	nd	65
Cr (ppm)	98	83	12	68	8	37	25	38	46	nd	19
Cs (ppm)	7.4	10.6	9.9	16.0	15.5	1.1	2.2	− 0.9	2.5	nd	4.4
Cu (ppm)	7.1	6.2	13.4	15.1	94.7	7.8	7.1	6.9	3.1	nd	6.5
Ga (ppm)	28	35	11	20	24	15	16	12	12	nd	15
La (ppm)	46	119	25	27	21	15	9	6	1	nd	22
Mo (ppm)	<3	<3	0.6	0.6	0.7	1.5	2.7	2.4	5.1	<3	1.3
Nb (ppm)	24	26	8	21	22	38	35	22	12	16	27
Ni (ppm)	39	10	22	64	36	26	23	23	23	nd	18
Pb (ppm)	10	<10	321	4	7	20	22	24	12	10	22
Rb (ppm)	291	351	124	210	218	69	67	59	37	104	56
Sc (ppm)	19.0	18.6	<5	9.9	9.1	2.8	5.2	6.9	5.8	nd	3.9
Sn (ppm)	4.5	5.7	2.1	4.2	4.3	4.8	3.4	5.2	3.7	nd	5.8
Sr (ppm)	15	21	132	81	91	86	60	82	153	83	33
Th (ppm)	16	25	17	32	27	33	34	29	18	24	30
U (ppm)	5.2	5.6	4.8	3.5	4.7	8.5	5.5	3.5	2.6	<4	6.6
V (ppm)	178	120	58	149	94	40	30	40	20	nd	17
Y (ppm)	39	80	87	47	40	17	16	18	10	14	23
Zn (ppm)	56	105	888	631	42	29	22	23	17	nd	15
Zr (ppm)	256	448	200	229	270	205	236	210	144	148	244

All three samples from the Röstånga-1 core represent K-bentonites, as the main silicate component in all is highly illitic illite–smectite, quartz is absent as a major component, and the Al_2O_3 content ranges between 24 and 27 % and K_2O between 6.9 and 7.8 % in the silicate part. In the grain fractions, rare (frequent in lower sample) hexagonal biotite phenocrysts occur. All the bentonites contain calcite with a very high content of manganese. This is reflected in a shift of the calcite XRD 104 reflection and also in the high CaO and MnO content in the XRF results (Table 1). An especially high content of Mn-calcite is present in the upper bentonite sample from Röstånga.

According to the chemical composition, the samples from Jämtland (Högåsen) and Västerbotten (Björkvattnet) containing Al_2O_3 over 20 % and K_2O over 7 % are defined as K-bentonites (Table 1; Fig. 4). The high content of TiO_2, which is 1.5 times higher than is normal in terrigenous rocks (Table 1), is additional evidence for the volcanic origin of these layers. A few more samples from the Jämtland Kogsta Siltstone contained around 70 % SiO_2 and correspondingly less Al_2O_3 and K_2O, and have been assigned to metamorphosed terrigenous siltstones. As rocks in Jämtland and Västerbotten are metamorphosed, K-bentonites consist mostly of muscovite with a smaller addition of quartz and chlorite in the Högåsen sample.

In the East Baltic and in the När core of Gotland, volcanic sanidine was also found in several shaly interbeds not forming distinct bentonitic layers. Separation of the phenocryst material from the shaly interbeds was possible owing to the larger grain size of the phenocrysts (0.04–0.1 mm) compared with the terrigenous material (dominantly less than 0.04 mm). In some cases, separation of the volcanic material from the shaly interbeds was even easier than from the bentonites where an abundance of authigenic K-feldspar aggregates of a similar size often hampers this procedure.

4.b. Correlations based on sanidine phenocryst composition

Bentonites from five volcanic eruptions were distinguished in the East Baltic, all of them containing characteristic sanidine $(K,Na,Ca)AlSi_3O_8$ phenocrysts, the compositions of which enable trustworthy identification (Table 2; Fig. 5) and correlation (Figs 2, 3). Biotite contents are mostly low, exceeding ten flakes in the separated grain fraction frequently only in the two lower layers. The stratigraphic indexes BI, BII and BIII for the bentonites described in Kiipli, Kallaste & Kiipli (2004) were assigned by Hints, Oraspõld & Nõlvak (2005) and are adopted here. Additional indexes B0

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Table 1 (continued) Results of XRF analyses of upper Katian bentonites

Bentonite ID Locality	B II Pärnu	B II Põltsamaa	B II Varbla	B II Viljandi	B I Are	B I Põltsamaa	B I Rabivere	B I Rabivere	B I Soonlepa	B 0 Käbi
Depth, m	278.00	123.00	286.55	294.35	237.40	177.10	10.62	10.68	56.80	11.30
LOI_{920} (%)	4.7	7.7	5.7	7.0	8.2	7.6	4.2	nd	3.7	3.9
SiO_2 (%)	58.1	53.6	54.9	55.0	47.0	53.0	57.8	64.1	58.1	59.6
TiO_2 (%)	0.22	0.18	0.22	0.24	0.27	0.33	0.25	0.22	0.25	0.31
Al_2O_3 (%)	17.5	13.2	17.3	15.8	16.0	15.8	16.4	17.3	17.2	16.8
Fe_2O_3 (%)	1.3	2.3	2.5	1.6	7.6	4.5	1.5	1.4	1.4	2.6
MnO (%)	0.01	< 0.01	0.00	0.03	0.01	0.02	0.01	0.00	0.01	0.01
MgO (%)	5.0	12.6	9.6	3.7	16.2	8.8	1.4	0.6	1.8	3.3
CaO (%)	1.52	2.6	0.99	3.13	0.86	2.36	2.98	0.25	3.39	1.15
Na_2O (%)	0.35	nd	0.48	0.12	0.42	0.15	0.04	0.03	0.08	0.03
K_2O (%)	10.8	7.3	7.7	11.7	3.3	7.1	13.9	15.3	12.8	12.9
P_2O_5 (%)	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.01	0.02
S (%)	0.17	nd	0.19	0.05	0.07	0.11	0.48	0.59	0.49	0.75
As (ppm)	11.5	nd	4.1	0.3	− 0.9	1.5	9.2	11.8	6.5	12.0
Ba (ppm)	94	nd	70	61	78	127	136	138	129	162
Ce (ppm)	32	nd	27	13	3	35	13	10	6	1
Cr (ppm)	43	nd	18	10	4	73	11	7	21	24
Cs (ppm)	2.3	nd	5.1	2.7	1.9	1.0	2.4	2.1	0.8	1.1
Cu (ppm)	4.1	nd	6.5	2.9	0.2	4.9	6.5	4.4	5.2	8.3
Ga (ppm)	18	nd	20	13	15	17	12	12	13	10
La (ppm)	17	nd	6	11	10	6	4	6	3	0
Mo (ppm)	1.1	< 3	1.4	0.5	0.3	0.7	5.7	6.6	2.1	4.9
Nb (ppm)	29	22	31	27	17	19	15	14	15	11
Ni (ppm)	16	nd	20	13	78	47	12	8	13	22
Pb (ppm)	11	9	9	3	− 1	− 1	40	49	25	48
Rb (ppm)	93	42	93	68	58	93	50	50	71	62
Sc (ppm)	3.8	nd	5.8	0.6	7.6	7.1	3.6	5.6	3.3	3.4
Sn (ppm)	7.6	nd	6.2	5.0	4.2	6.3	4.2	4.5	4.6	5.3
Sr (ppm)	45	144	67	28	82	70	25	14	46	24
Th (ppm)	34	19	34	29	27	25	23	24	22	35
U (ppm)	8.7	<4	4.1	6.8	3.5	3.5	2.7	3.8	4.7	6.2
V (ppm)	14	nd	11	13	17	39	17	8	15	34
Y (ppm)	26	15	23	27	17	14	12	9	10	9
Zn (ppm)	7	nd	14	14	25	22	53	16	9	32
Zr (ppm)	267	210	269	240	189	190	179	158	172	178

and BIV are used here for the first time. The characterization of sanidine in the bentonites (from the base) is as follows:

(1) B0 is characterized by weak and wide sanidine XRD reflection. Commonly, sanidine cannot be characterized numerically in this bed. Only from the shaly interbed of the Ruhnu core (628.1 m) did we extract sufficient sanidine for XRD analysis and the result shows 25 mol % of the Na + Ca component. This composition is significantly more potassic than in other layers of volcanic origin in the Pirgu Stage. In contrast to other bentonites in the Pirgu Stage, B0 contains biotite in a notable amount.

(2) BI is characterized by sharp (less than 0.2 deg on the 2-theta scale) XRD reflection and 37.2–38.7 mol % of the Na + Ca component in the sanidine. Stratigraphically close, bentonites B0 and BI occur together in the Käbi core section (Fig. 2) indicating that B0 is older. Sanidine corresponding to the composition typical of BI was also established in the När core (Gotland, Sweden) in a shaly interbed at the depth of 395.05 m in the Upper Jonstorp Formation (Fig. 3). Commonly, slightly more than ten flakes of biotite occur among separated grains.

(3) BII is the thickest bentonite in the Pirgu Stage reaching 30 cm and is characterized by sharp sanidine reflection and 43.8–44.3 mol % of the Na + Ca component in the sanidine. Typically biotite is absent.

(4) BIII is characterized by sharp sanidine reflection and 34.3–36.2 mol % of the Na + Ca component in the sanidine phenocrysts.

(5) BIV is characterized by sanidine having the most sodium-rich composition (average 47–48 mol % of the Na + Ca component) among the bentonites of the Pirgu Stage. XRD reflection is wide and sometimes, like in the Kuressaare section at 302.25 m, two components of sanidine can be recognized. BIV is clearly higher than BII, but its relationship with BIII is not proven as BIII and BIV were not found together in any of the studied sections.

Bentonites from the Röstånga section did not reveal a sanidine XRD reflection. The most probable reason is that Ordovician rocks at Röstånga, although not strongly metamorphosed, were deformed (Bergström *et al.* 1999) and tectonic deformation was likely accompanied by some elevated temperatures accelerating recrystallization of sanidine. Similarly, we did not find sanidine in Silurian bentonites from the Garntangen section in the Oslo region. Rocks in the Garntangen section are deformed too, but not strongly metamorphosed (Bergström, 1980; Batchelor, Weir & Spjeldnaes, 1995). Separation of magmatic phenocrysts from the

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Table 2. Composition of sanidine phenocrysts and occurrence of biotite in studied samples

	Depth, m	Bentonite index	Thickness, cm	Na + Ca in sanidine, mol%	Width of the XRD reflection, 2-theta	Biotite
Varbla 502	266.40	BIV		47.3	0.22	0
Kuressaare K3	302.25	BIV	10	48.3	0.256	++
Põltsamaa H39	116.50	BIII	5	34.3	0.058	0
Taagepera 1	436.10	BIII	2	35.2	0.052	++
Valga	335.90	BIII		34.3	0.081	+
Pärnu 6	256.80	BIII	8	34.7	0.167	+
Kihnu 526	398.70	BIII		34.7	0.061	+
Viki	249.30	BIII	Terr + Bent	36.2	0.1	+
Põltsamaa H39	123.00	BII	1.5	43.6	0.106	0
Viljandi 91	294.40	BII	8	42.6	0.159	0
Eikla 508	239.80	BII	20	42.9	0.125	0
Varbla 502	286.32	BII	30	44.2	0.08	0
Varbla 502	286.55	BII	30	43.7	0.134	0
Varbla 502	286.60	BII	30	44.7	0.095	0
Laeva 4	166.01	BII		44.1	0.131	0
Laeva 18	185.60	BII		44.3	0.102	0
Valga	339.80	BII		44.1	0.102	0
Pärnu-6	278.00	BII	30	44.2	0.122	0
Aispute 41	1011.00	BII	Terr + Bent	43.9	0.057	+
Taagepera 1	437.80	BII	Terr + Bent	44.6	0.11	+
Kuressaare K3	314.40	BII	30	44.0	0.1	?
Kaugatuma 509	356.00	BII	20	43.8	0.094	?
Kaugatuma 509	356.20	BII	20	43.8	0.102	?
Aispute 41	1011.00	BII	Terr + Bent	43.9	0.06	?
Tartu 453	256.00	BII		42.6	0.156	?
Põltsamaa H39	177.10	BI	15	38.5	0.079	+
Are 171	237.40	BI	10	38.7	0.074	++
Aispute 41	1027.50	BI	Terr + Bent	38.8	0.122	+
Rabivere 307(3)	10.68	BI	10	37.2	0.116	+
Rabivere 307(4)	10.63	BI	10	38.2	0.062	++
Soonlepa 366	56.80	BI		37.6	0.098	++
Mehikoorma-421	251.80	BI	Terr + Bent	37.6	0.079	++
Varbla 502	319.40	BI		38.6	0.044	++
Taagepera 1	449.50	BI	Terr + Bent	34–38	0.03–0.1	+
När	395.05	BI	Terr + Bent	35.6–38.2	0.127–0.199	++
Ruhnu 500	628.05	B0	Terr + Bent	25.2	0.34	+++
Ruhnu 500	628.05	B0	Terr + Bent	25.0	0.26	++
Kerguta 565	46.60	B0	Terr + Bent		Weak	?
Käbi 306	11.30	B0	4		Weak	+

0 – no biotite in grain fraction; + – biotite is rare: 1 to 10 flakes in separated grain fraction; ++ – biotite is frequent: 11 to 100 flakes in separated grain fraction; +++ – biotite is abundant: more than 100 flakes in separated grain fraction; ? – biotite content was not estimated.

metamorphosed bentonites of the Jämtland Region was not attempted.

4.c. Correlations based on immobile trace elements

Following the approach of Kiipli *et al.* (2013) applied to Silurian bentonites, in Figure 6 TiO_2 (%), Nb (ppm), Zr (ppm) and Th (ppm) ratios to Al_2O_3 (%) are shown. These five elements have been proven to be immobile during the conversion of volcanic ash to authigenic silicates (Kiipli *et al.* 2008). To bring all the ratios numerically to the same scale, TiO_2/Al_2O_3 was multiplied by 50 and Zr/Al_2O_3 by 0.1. After arranging the samples according to previous correlations based on the sanidine compositions we can see the similarity of the trace element spectra between the samples from the same volcanic eruptions (Fig. 6). B0 is characterized by higher Th contents than the other layers, BI by a rise in element ratios from Ti to Th, BII by low Ti and high ratios of other elements, BIII by equally high Ti, Nb and Zr ratios and even higher Th, and BIV by high ratios of all elements, especially Nb and Th. The immobile trace elements perfectly confirm the correlations established by the sanidine phenocryst compositions.

Trace element spectra from Röstånga, where sanidine was likely recrystallized, allow a correlation with bentonites from Estonia. The middle bentonite from Röstånga shows a similar trace element spectrum to BIII and the lower sample to BI (Fig. 6). The upper sample from Röstånga appears to originate from a different volcanic eruption not found in Estonia.

Trace element spectra of bentonites from Jämtland and Västerbotten differ significantly from the Estonian and Röstånga bentonites by having higher TiO_2/Al_2O_3 ratios, but are quite similar to each other based on their trace element ratios (Fig. 6). In the trace element spectra some similarities with bentonites from Dob's Linn in Scotland can be observed (see Section 5).

5. Discussion

5.a. Bentonites and correlation of lithostratigraphic units in the East Baltic and Sweden

Despite the restricted amount of data about chitinozoan distribution from the described sections, it does

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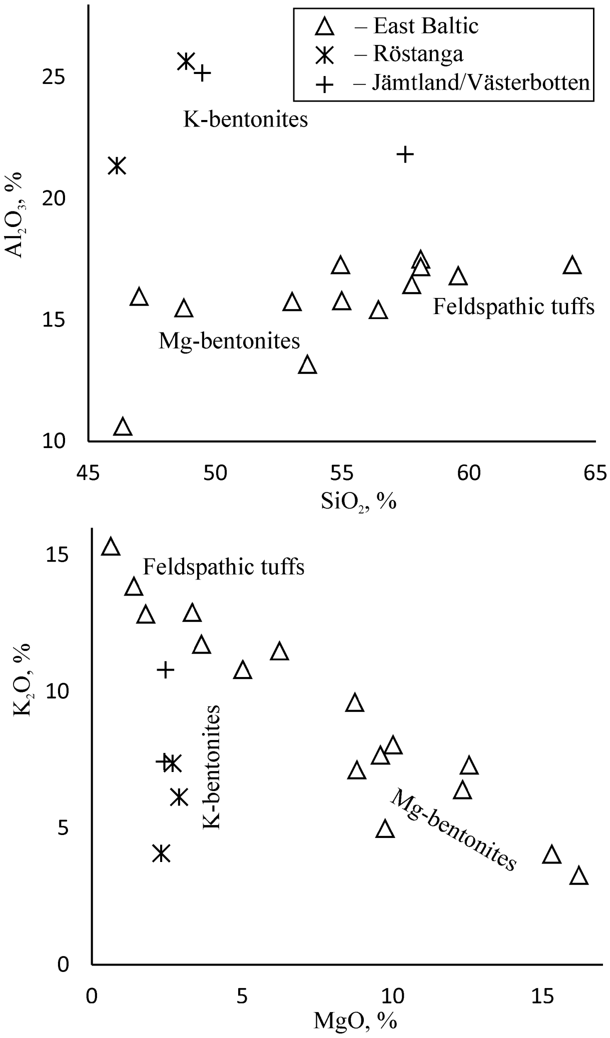

Figure 4. Composition of altered volcanic ashes of the Pirgu Stage.

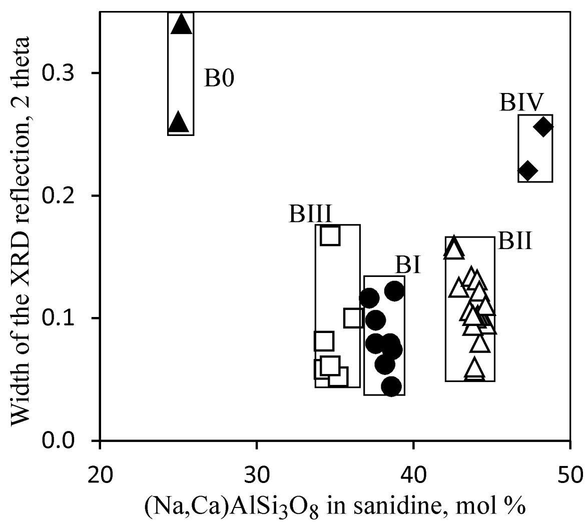

Figure 5. Composition of sanidine phenocrysts in the bentonites of the Pirgu Stage from the East Baltic according to XRD analysis. Frames embrace correlated bentonites shown by different symbols.

not contradict the age interpretation of the geochemically studied bentonite layers. Chemical fingerprints of the studied bentonite beds give an additional time control and precision to the correlation, especially in the East Baltic sections with limited biostratigraphic data (Fig. 7). Correlation of the B0 and BI bentonites from the middle of the Moe Formation in shallow-sea sections of North Estonia with bentonites in the Tootsi and Jonstorp formations in the transition zone and in the lower part of the Jonstorp Formation in deep shelf sections in South Estonia and Latvia confirms the correlation proposed by Oraspõld (1982) and Hints, Oraspõld & Nõlvak (2005). Finding of the BI bentonite in the När core above the Öglunda Limestone indicates correlation of the lower Pirgu Stage with the lower part of the Upper Jonstorp Formation as defined by Jaanusson (1963). The Lower Jonstorp Formation may correlate with the lower part of the Pirgu Stage or with the Vormsi Stage in the East Baltic. This new version of correlation must be considered preliminary and it needs confirmation by studying bentonites in more sections from Sweden.

Correlations of the BII and BIII bentonites from the middle and upper parts of the Halliku Formation in the transition zone with the upper part of the Jelgava Formation in the Valga section and the upper part of the Jonstorp Formation in the Taagepera and Aizpute sections and BIII from the Adila Formation of the Viki core from the southern part of the shallow palaeoshelf area indicate that these most-argillaceous parts of the middle of the Pirgu Stage are coeval.

Limestones of the Oostriku Formation as they occur in the Varbla and Kuressaare sections (Fig. 2) clearly occur higher than the BII bentonite and correlate with limestones of the Paroveja Formation in Latvia. The Oostriku Formation contains bentonite BIV. In the Põltsamaa, Pärnu and Laeva sections, in the transition zone, the Oostriku Formation probably correlates with the gap indicated by the pyrite-rich discontinuity surface between the Halliku and Kabala formations.

An absence of bentonites higher than BI in North Estonian sections may indicate a gap caused by late Katian to Hirnantian sea level fall(s) due to the glaciation in Gondwana and erosion of sediments (Bergström *et al.* 2014).

It is not surprising that bentonites which occur in lithologically variable sections of the East Baltic have only been sporadically preserved in drill cores. In general, this time interval is characterized by a regression cycle, temporary sea level low-stand periods and gaps in sedimentation, which are reflected in very complicated lithofacies schemes (Harris *et al.* 2004; Hints, Oraspõld & Nõlvak, 2005; Fig. 2), considerably differing from the situation in the sections of the uppermost Sandbian in the East Baltic area below and above the Kinnekulle Bentonite (Bergström *et al.* 1995). Such a difficult and complicated depositional situation is well revealed also in the distribution of bentonite layers in the sections included in this study (Figs 2, 3).

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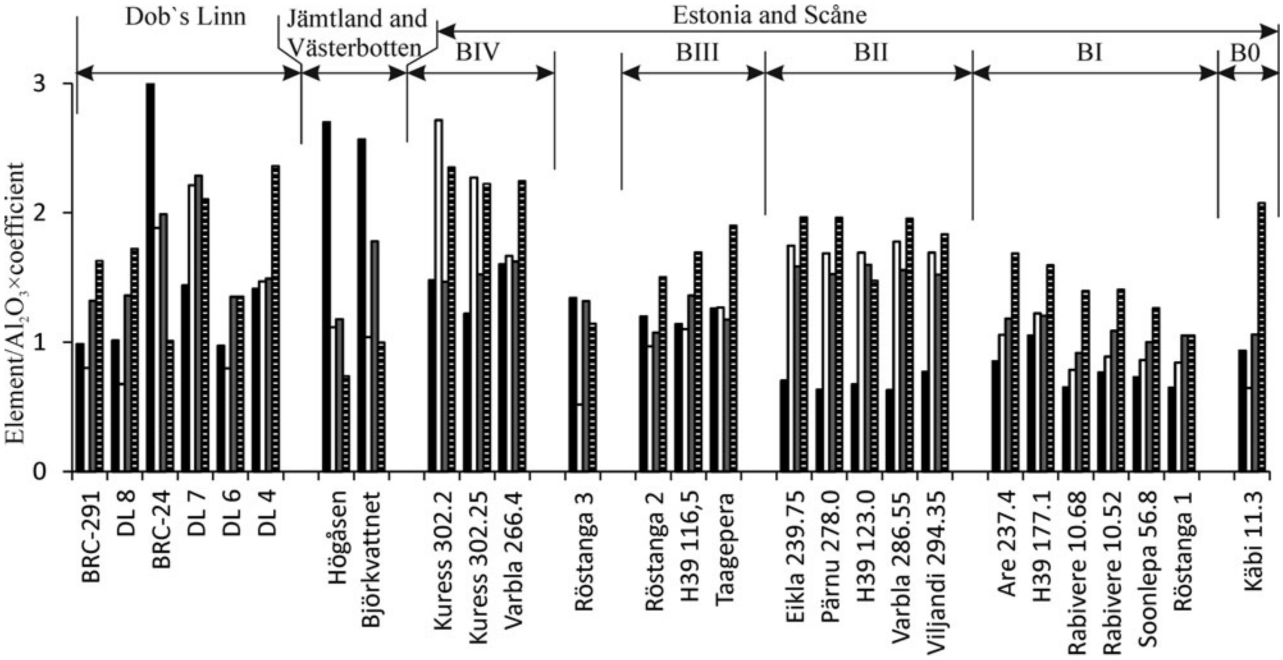

Figure 6. Ratios of immobile trace elements to Al_2O_3 in upper Katian bentonites. Bars from left to right: black – TiO_2(%)/Al_2O_3 (%) × 50; white – Nb(ppm)/Al_2O_3 (%); grey – Zr(ppm)/Al_2O_3 (%) × 0.1; banded – Th(ppm)/Al_2O_3 (%).

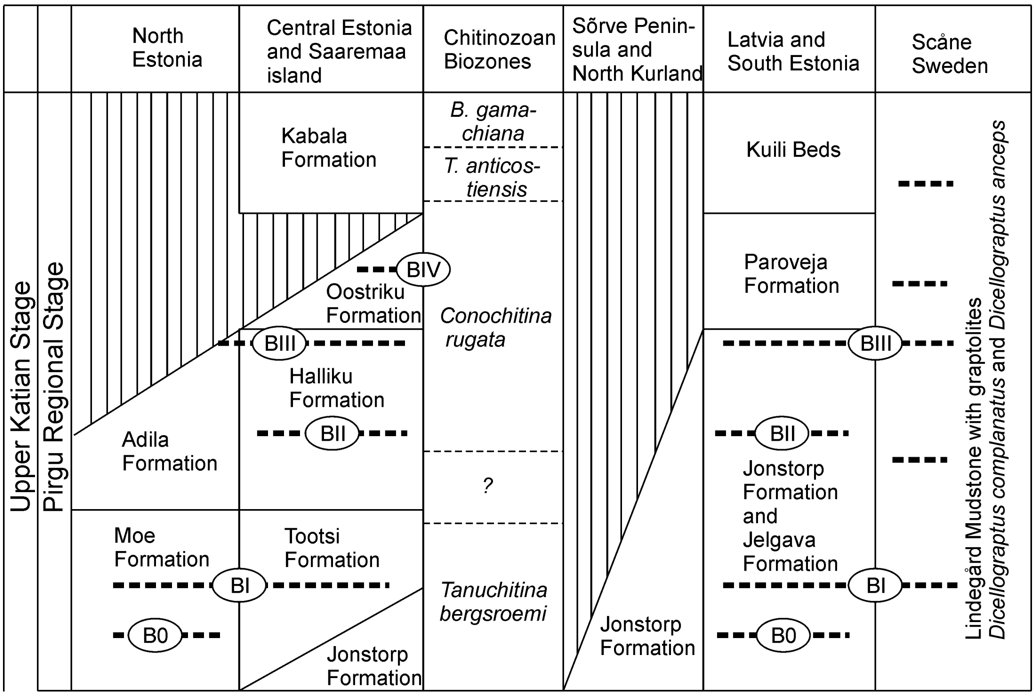

Figure 7. Summary stratigraphic chart of the upper Katian Pirgu Stage in the East Baltic and Scåne, Sweden.

5.b. Estimation of source magma composition

The source magmas of the Katian bentonites from the East Baltic have been interpreted as high-Th rhyolites (Kiipli, Soesoo & Kallaste, 2014). Moderate Nb contents indicate subalkaline source magmas (Table 1). TiO_2 contents below 0.5 % and moderately high Zr contents between 150 and 300 ppm in the East Baltic and Röstånga bentonites (Fig. 8) confirm that source magmas were evolved rhyolites. Lower Zr/TiO_2 ratios in the Jämtland and Västerbotten bentonites compared with those from the East Baltic and Röstanga (Fig. 8) indicate less-evolved dacitic or andesitic source magmas. Elevated Ga in the Jämtland and Västerbotten bentonites may hint at a slightly alkaline trachyandesitic composition. Higher Al_2O_3 contents (22–25 %) in the Jämtland, Västerbotten and Scottish bentonites compared with normal concentrations in an evolved source (12–16 %) indicate significant enrichment in Al and immobile trace elements compared with the source magma due to the alteration process which removed much of the SiO_2. Removal of SiO_2 is proven by frequent

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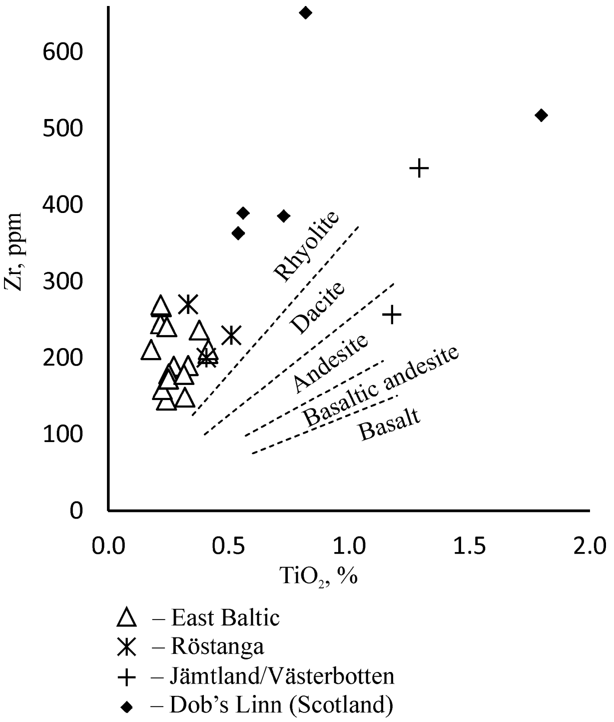

Figure 8. Estimation of source magma composition of the upper Katian bentonites.

chert in host rocks near the bentonites (e.g. Laufeld & Jeppsson, 1976). This enrichment is reflected by a shift of the Jämtland, Västerbotten and Scottish points on Figure 8 to the right and up compared with the East Baltic bentonites.

5.c. Interpretation of volcanic source area

In the East Baltic area, bentonites in the Pirgu Stage occur in recognizable thicknesses (up to 30 cm) in the northernmost area in Estonia. In Latvian and South Estonian sections, volcanic material has been extracted from shaly interbeds of terrigenous origin. In Latvian sections studied by Hints, Oraspõld & Nõlvak (2005) the thicknesses are not reported, and some bentonites from their article, not studied here, are marked with a plus sign in Figure 9 showing the distribution of the thickest BII bentonite. In the southernmost sections of Lithuania bentonites are not recorded (Hints, Oraspõld & Nõlvak, 2005). This distribution pattern suggests the arrival of a volcanic ash cloud from the north or northwest. Data from Sweden and Denmark suggest a similar distribution. Bentonites of Pirgu age are not recorded in Bornholm (Schovsbo *et al.* 2011); three bentonites with thicknesses around 1 cm occur in the Röstånga core (Bergström *et al.* 1999), and northwards, in the Lindegård core five bentonites less than 5 cm in thickness are known (Glimberg, 1961). Further to the north, in the Kinnekulle section in the Upper Jonstorp Formation, two bentonites have been found (Jaanusson, 1963).

Volcanic and plutonic rocks of Katian age are known in the Helgeland Nappe Complex in the Scandinavian Caledonides (Barnes *et al.* 2002, 2007). In the Seve

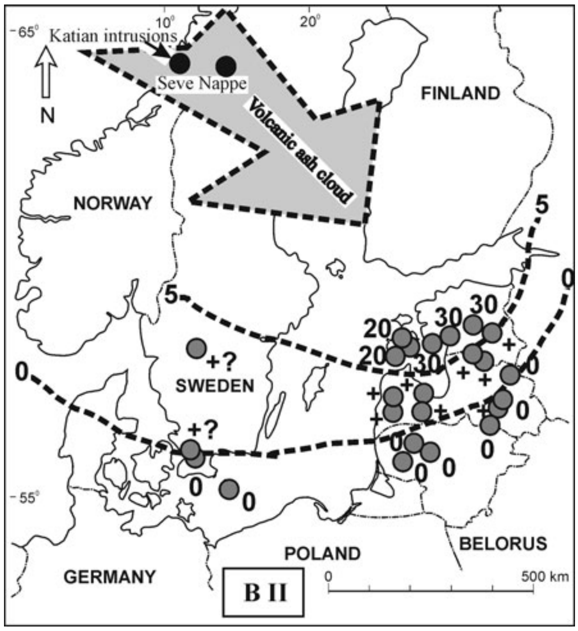

Figure 9. Distribution and thickness (cm) of the BII bentonite, plus marks showing where volcanic material was extracted from shaly interbeds or the thickness was not recorded.

Nappe in Jämtland, metamorphic minerals originated in ultra-high-pressure conditions with an age of 450 Ma, which indicates subduction of crustal rocks (Brueckner, Roermund & Pearson, 2004; Klonowska *et al.* 2014; Majka *et al.* 2014). We propose that intrusions in the Helgeland Nappe Complex (Kiipli, Soesoo & Kallaste, 2014) or the subduction process (Seve Nappe) accompanied by presently unknown magmatism could have supplied the Pirgu sediments in Baltoscandia with volcanic ash (Fig. 9). In reconstructing the volcanic source area it is important to mention that Caledonian rocks have been displaced up to 400 km eastward from their original location (Gee *et al.* 2010). Considering that the distance from Jämtland to Central Estonia is 800 km, we see that the volcanic eruptions during Pirgu time were very large, distributing ash to more than 1200 km from the source.

5.d. Comparison with bentonites from Dob's Linn, Scotland

Bentonites from the *complanatus* and *anceps* graptolite zones are known from the Dob's Linn section of southern Scotland (Batchelor & Weir, 1988, samples prefixed by DL; Merriman & Roberts, 1990; Huff *et al.* 1993, samples prefixed by BRC). Geochemical comparison of the Dob's Linn and Baltoscandian bentonites reveals remarkable similarities. The bentonites from Dob's Linn have high contents of Th reaching 60 ppm. DL4 has a quite similar immobile trace element spectrum to B0 in the East Baltic, BRC-291 and DL8 to BI and BIII, DL6 to Röstånga-3, and BRC-24 to the Jämtland and Västerbotten bentonites (Fig. 6), suggesting that some of these bentonites may correlate. On the TiO_2–Zr chart (Fig. 8) DL4, DL6, DL8 and BRC-291 plot close to

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the East Baltic and Röstånga bentonites. Higher Al_2O_3 concentrations (26–29 %) in Dob's Linn bentonites indicate greater residual enrichment with immobile elements than in the East Baltic and Röstånga bentonites, and accordingly, the original concentrations in the source magmas must have been very close in all these localities.

According to the palaeotectonic reconstructions (Leslie, Smith & Soper, 2008), the Southern Uplands of Scotland were located north of the Iapetus suture on the Laurentia side of the Iapetus Palaeo-Ocean. This interpretation suggests that in Late Ordovician time the Dob's Linn section was far away from the probable volcanic source of the Baltoscandian bentonites. But considering that the rocks from Dob's Linn are oceanic sediments containing abundant graptolites (Underwood *et al*. 1997; Grieg *et al*. 2005) it is possible that in Late Ordovician time the Southern Uplands of Scotland was located somewhere in the middle of the Iapetus Palaeo-Ocean and was attached to the Laurentian continent later, during the Scandian collision of Laurentia with Baltica. The geochemical similarity of the volcanic ashes in Baltoscandia and Dob's Linn, suggesting the same source, supports this interpretation. The same volcano could distribute ash in different directions: to Baltica or to Dob's Linn depending on weather conditions during the eruption. Considering that the ashes had been transported to the East Baltic from a distance of 1200 km, other eruptions of similar power could also reach more than 1000 km to the southwest where the sediments of the Southern Uplands formed at that time. Geochemical similarities between the bentonites in southern Scotland and Baltica for the Lower Silurian Osmundsberg Bentonite were noted by Inanli, Huff & Bergström (2009) and for the Ordovician Sandbian bentonites by Batchelor (in press).

6. Conclusions

(1) Katian bentonites in the East Baltic can be reliably correlated using the XRD analysis of the sanidine phenocryst composition. Volcanic phenocrysts can often be extracted, analysed and identified even from visually common terrigenous shaly interbeds. Bentonites from five volcanic eruptions have been established in the East Baltic.

(2) The absence of several bentonites in shallow-sea sediments found in a deep palaeo-sea area indicates extensive breaks in sedimentation and erosion during late Katian and Hirnantian sea level falls.

(3) Ratios of immobile trace elements TiO_2, Nb, Zr and Th to Al_2O_3 have enabled correlations to be extended to Scandinavia, where likely late diagenetic alterations have caused recrystallization of sanidine phenocrysts.

(4) The areal distribution pattern of Katian bentonites in Baltoscandia indicates a volcanic source from the north or northwest (present-day orientation). Signatures of ultra-high-pressure metamorphism in the Seve Nappe (Central Sweden) and intrusions in the Helgeland Nappe Complex in Central Norway have been proposed as potential sources for volcanic ashes deposited in the East Baltic during Katian times.

(5) The geochemical similarity between Baltoscandian and Dob's Linn bentonites from Scotland of Katian age suggests the same volcanic source. This hypothesis needs to reinterpret the location of the Southern Uplands of Scotland as being not close to Laurentia, but more likely in the middle of the Iapetus Palaeo-Ocean in Katian times.

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