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Use of immobile trace elements for the correlation of Telychian bentonites on Saaremaa Island, Estonia, and mapping of volcanic ash clouds

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Abstract. Thirty suspected altered volcanic ash (bentonite) samples from the Nässumaa-825 and Orissaare-859 sections were analysed by the X-ray fluorescence method. Twenty of these samples revealed chemical signs of pure volcanogenic material, one was of mixed terrigenous–volcanogenic origin, and nine were classified as terrigenous claystones. Twenty of the bentonites were correlated, with variable confidence, with bentonites from earlier studied sections; one sample represents a formerly unknown eruption. New and earlier published bentonite correlations were used for tracing the diachronous nature of the Rumba–Velise formations boundary and for composing new isopach schemes of six Telychian bentonites.

Key words: bentonites, K-bentonites, Telychian, correlation, isopach schemes, East Baltic.

INTRODUCTION

Altered volcanic ash beds (bentonites, K-bentonites, metabentonites, tonsteins, feldspathites) in sedimentary sections provide an important proxy for ancient volcanic activity on a scale of hundreds, and sometimes thousands of kilometres (Fisher & Schmincke 1984). Volcanic ashes, deposited almost instantly in a geological sense, may serve as perfect, chronologically fixed marker horizons for stratigraphy (Thorslund 1945; Batchelor & Jeppsson 1994; Bergström et al. 1995, 1998; Batchelor & Evans 2000; Kiipli & Kallaste 2006; E. Kiipli et al. 2006; Kiipli et al. 2007a, 2008). To reconstruct the volcanic history of a region, the stratigraphic distribution of numerous ash beds must be identified in different sections. Using well-preserved phenocrysts (sanidine, biotite, apatite, zircon, quartz, etc.) is advantageous compared to the bulk bentonite composition (Kiipli & Kallaste 2002; Kallaste & Kiipli 2006), although in some cases immobile trace elements can also serve as a good basis for correlation (Kiipli et al. 2001). Use of immobile trace elements is especially important in regions where metamorphism has destroyed primary magmatic phenocrysts, e.g. western Scandinavia. In this paper a range of immobile trace elements (TiO_2, Zr, Nb, Th) determined by the X-ray fluorescence method is used to demonstrate correlations between sections. New and earlier studied sections (Kiipli & Kallaste 2002; Kallaste & Kiipli 2006) are used to trace the diachroneity of the boundary between the Rumba and Velise formations and to construct isopach maps to illustrate the distribution of ash beds.

STRATIGRAPHY

The stratigraphic position of the studied samples is in the Adavere Stage and the lower part of the Jaani Stage (Fig. 1). The lower part of the Adavere Stage consists of nodular limestones (Rumba Formation), while the upper part consists of shaly marlstones (Velise Formation). The carbonate content increases gradually in the lower part of the Jaani Stage (Mustjala Formation), where the rocks are represented by carbonate marlstones. Conodont and chitinozoan biozonation and scolecodont distribution in the Paatsalu section is described in O. Hints et al. (2006), while conodont zonation in the Viirelaid and Nässumaa sections is available in Kiipli et al. (2001). Telychian bentonites have also been correlated with graptolite zonation (Kiipli et al. 2007a). The boundary between the Adavere and Jaani stages is marked by the uppermost bentonite in a section of rocks with a high frequency of bentonites (Aaloe 1960). In terms of new bentonite stratigraphy, it is the level of the Kirikuküla Bentonite (ID 457) (Kallaste & Kiipli 2006), lying very close to the lower boundary of the *Pterospathodus a. amorphognathoides* conodont Zone (Kiipli et al. 2001).

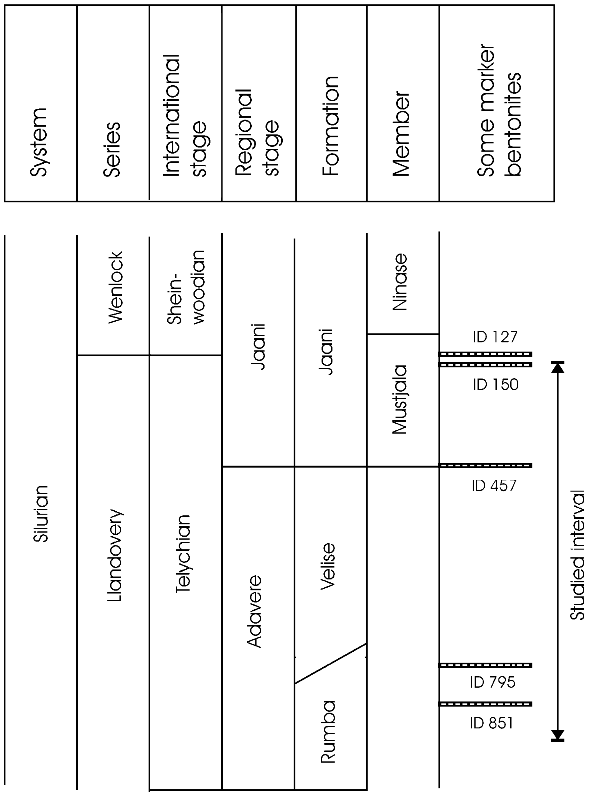

Fig. 1. Stratigraphic chart modified from Nestor (1997) with indication of the studied interval. The Llandovery–Wenlock boundary is given according to Kiipli et al. (2008). ID 127, Ireviken Bentonite; ID 150, Lusklint Bentonite; ID 457, Kirikuküla Bentonite; ID 795, Mustjala Bentonite; ID 851, Osmundsberg Bentonite.

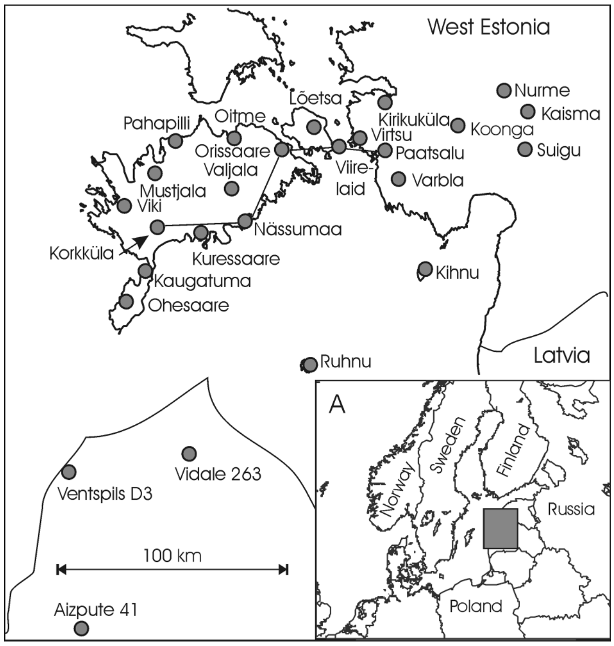

Fig. 2. Location of boreholes where bentonites were studied during 1998–2007. Note: The Korkküla-863 drill core (drill-core database of the Geological Survey of Estonia) is erroneously named the Tehumardi core in Kiipli & Kallaste (2002) and E. Kiipli et al. (2006).

In terms of graptolite stratigraphy, the boundary between the Adavere and Jaani stages, which is marked by the Kirikuküla Bentonite, is close to the *spiralis–lapworthi* boundary (Kiipli et al. 2007a). Bentonite names and ID numbers used herein are from Kallaste & Kiipli (2006). The same ID numbers and names were used also in Kiipli et al. (2007a, 2007c).

MATERIAL

In 2006, 16 clay-rich and feldspathic potential bentonite samples were collected from the Nässumaa-825 drill core. These include five bentonites that have been studied earlier by Kiipli et al. (2001) and Kiipli & Kallaste (2002). From the Orissaare-859 drill core 14 samples were collected, which have not been studied previously. The Nässumaa section is located in the southeastern part and Orissaare in the eastern end of Saaremaa Island (Fig. 2). Both cores are stored in the Geological Survey of Estonia.

In addition to the original material of this contribution, correlations based on the sanidine compositions from Kiipli & Kallaste (2002) and Kallaste & Kiipli (2006) were used for isopach schemes and study of the Rumba–Velise formations boundary.

LABORATORY METHODS

Standard X-ray fluorescence (XRF) techniques, using a VRA-30 at the Institute of Geology at Tallinn University of Technology, were employed for trace and major element analyses of sample material. Samples were powdered and mixed in a ball mill and small aliquots were used to make pressed powder pellets for analyses. Feldspathite powders required the addition of some drops of 5% MOWIOL solution. No binding material was used for pressing pellets of clay material. Empirical coefficients were used to account matrix corrections and overlapping X-ray spectral lines. Corrected total intensities of characteristic peaks were used to calibrate major element concentrations, while peak to background ratios were used for calibration of trace element concentrations. In a complicated range of the spectrum, with many overlapping peaks (e.g. Mo Kα to Pb Lβ), the background was modelled and element intensities were calculated using a theoretical idealized spectrum. The measurements were calibrated using well characterized reference materials from France (Govindaraju 1995), Geological Survey of Japan, and Estonia (Kiipli et al. 2000; Kiipli 2005), and intercalibration samples of the International Association of Geoanalysts (IAG) (www.geoanalyst.org). Participation in IAG controlled proficiency testing over many years has verified the reliability and accuracy of the laboratory and its methods (Fig. 3).

IDENTIFICATION OF VOLCANIC ASH BEDS

Previous works (R. Hints et al. 2006; Kiipli et al. 2008) have used X-ray diffractometry measurements to identify samples of volcanogenic origin. Good criteria are the occurrence of illite-smectite, authigenic K-feldspar, kaolinite and/or chlorite-smectite, together with low concentrations or absence of quartz. Bentonites can also be identified visually by colour variation and/or abundance of biotite flakes. Bentonite clays are often much softer than the host sediments. Feldspathites are similar to siltstones in appearance and have yellowish white colour. Herein we use XRF analyses for the identification of volcanic origin.

Pure terrigenous claystones are not common in Telychian sections of Estonia. Most rocks contain some carbonate material and few weight per cent of CaO. In contrast, volcanic ash layers typically contain <1 wt% CaO (see Kiipli et al. 2007c). Therefore low CaO concentrations constitute a preliminary indicator of the presence of volcanic ash layers in sections dominated by carbonate rock and marlstone. Higher abundance of carbonates and quartz in the host rock, as opposed to altered volcanic ashes, reduce the proportions of clay minerals, and consequently of the elements typical of clays and authigenic feldspar, such as Al_2O_3 and K_2O. Therefore, the most useful monitor for bentonite identification is a binary chart of these two components. The samples from the Nässumaa and Orissaare cores were compared with altered volcanic ashes, terrigenous and carbonate rocks from Estonia and Latvia (Fig. 4). Terrigenous sediments are characterized by relatively low contents of Al_2O_3 (<20%) and K_2O (<7%), while altered volcanic ashes show higher concentrations of these elements. Most bentonites can be described as K-rich, containing 5–12% K_2O and 19–26% Al_2O_3. Deep sea facies sediments of South Estonia and Latvia are characterized by kaolinite-rich bentonites and K_2O contents of 2–5%. Similar kaolinite-rich bentonites, often referred to as tonsteins, are known from coal formations (Bohor & Triplehorn 1993) and have very high Al_2O_3 contents (26–34%). Many altered volcanic ashes in Estonia and North America (Hay et al. 1988) contain >50% authigenic potassium feldspar (referred to as feldspathites; Kiipli et al. 2001, 2007b) and 12–16% K_2O. Chlorite-smectite-rich bentonites, such as those found in the Pirgu Stage in Estonia (R. Hints et al. 2006), are particularly rich in MgO (6–15 wt%) and may be referred to as Mg-rich bentonites.

Twenty of the studied samples (Tables 1–3) lie in the fields of K-rich bentonites and feldspathites, one is a mixed feldspathite/terrigenous rock, and nine are in the field of terrigenous rocks. Some samples of the last group can contain a portion of volcanogenic material as far as fields of terrigenous rocks and mixed rocks are partly overlapping.

CORRELATION OF BENTONITES

To correlate bentonites from the Nässumaa and Orissaare sections with previously described sections, Zr and TiO_2 concentrations were compared with the nearby Viirelaid and Paatsalu sections (Fig. 5) and provisional correlations were established. Then, using ratios of immobile elements (Table 4, Fig. 6), provisional correlations were checked. Geochemical correlation is based on the XRF analyses published in Kiipli et al. (2007c).

Five known bentonites occur in the Mustjala Formation (Kallaste & Kiipli 2006). Taking into consideration the stratigraphic position of the bentonites and comparing their compositions, the bentonites found at 55.3 and 58.8 m in the Orissaare section (Fig. 4) can be correlated with the Lusklint (ID 150) and Ohesaare (ID 210) bentonites, respectively, but not with the Ireviken (ID 127), Storbrut (ID 139), and Aizpute (ID 311) bentonites. The Aizpute Bentonite has notably higher Nb and Th and lower Sr contents; the Ireviken Bentonite has lower Sr and higher P_2O_5 contents; while the Storbrut Bentonite has lower Zr and Th contents. Sr contents vary in ID 150 and 210 from 108 to 236 ppm, in ID 127 from 69 to 94 ppm, and in ID 311 from 102 to 125 ppm. The P_2O_5 contents vary in ID 150 and 210 from 0.03 to 0.12%, in ID 127 from 0.14 to 0.42%, and in ID 311 from 0.12 to 0.18% (Kiipli et al. 2007c).

Five bentonites occur in the upper part of the Velise Formation, corresponding to the upper half of the *Pterospathodus a. lithuanicus* and the lowermost

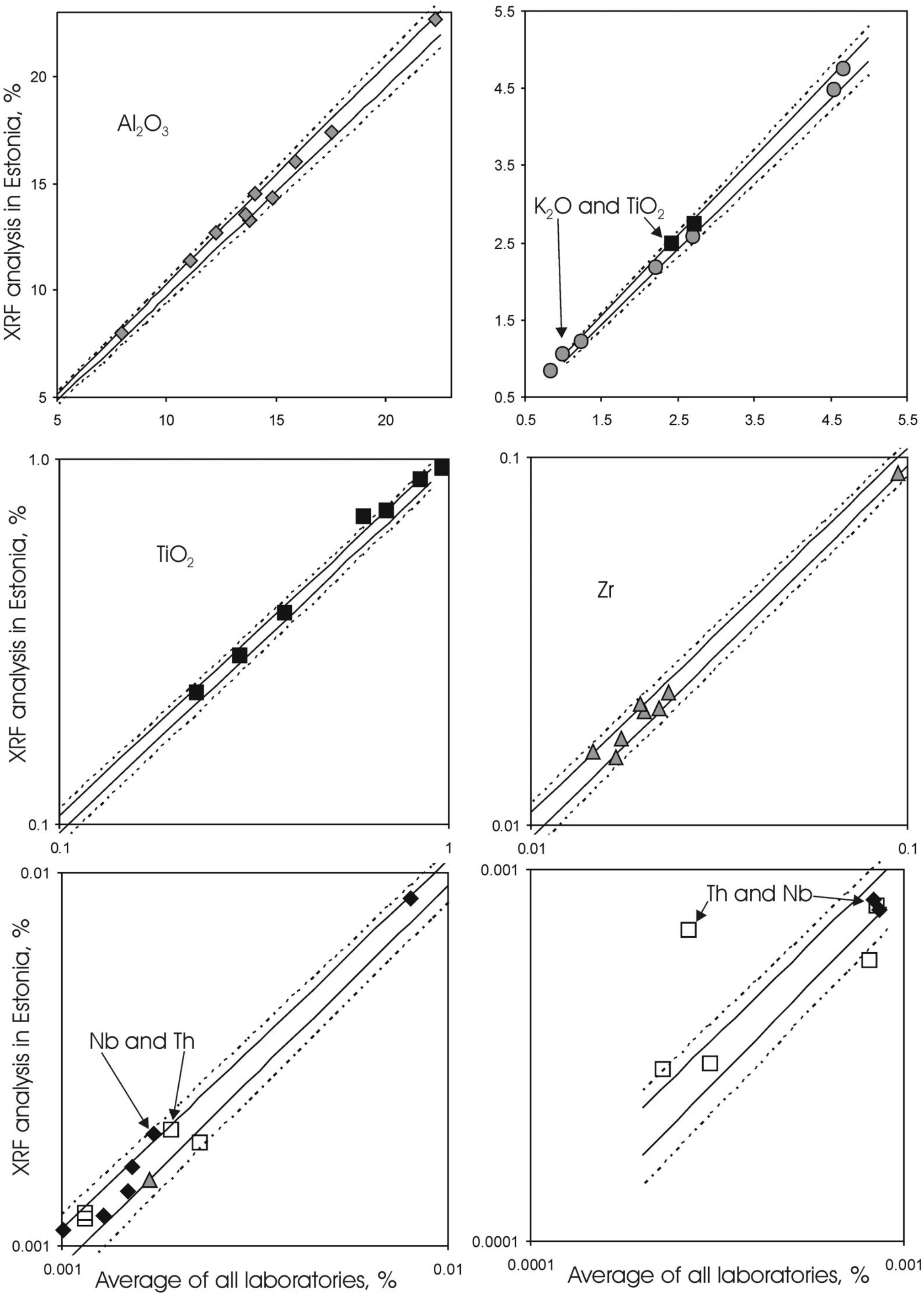

Fig. 3. Comparison of XRF analyses of Al_2O_3, K_2O, TiO_2, Zr, Nb, and Th in the Institute of Geology at Tallinn University of Technology with the results of the proficiency tests of the International Association of Geoanalysts (IAG) in the years 1998–2007. In these tests 77 laboratories were involved. Solid lines embrace deviation from the average allowed for research quality and dotted lines embrace deviation allowed for applied geochemistry. For the definition of the allowed deviation limits see the website: www.geoanalyst.org. The figure shows that concentrations above 0.001% (10 ppm) were predominantly analysed with research or applied geochemistry quality (only one TiO_2 determination exceeds slightly the permitted limit of deviation). Concentrations between 0.0001 and 0.001% were determined semiquantitatively, with deviation from the average often exceeding the value allowed by the IAG.

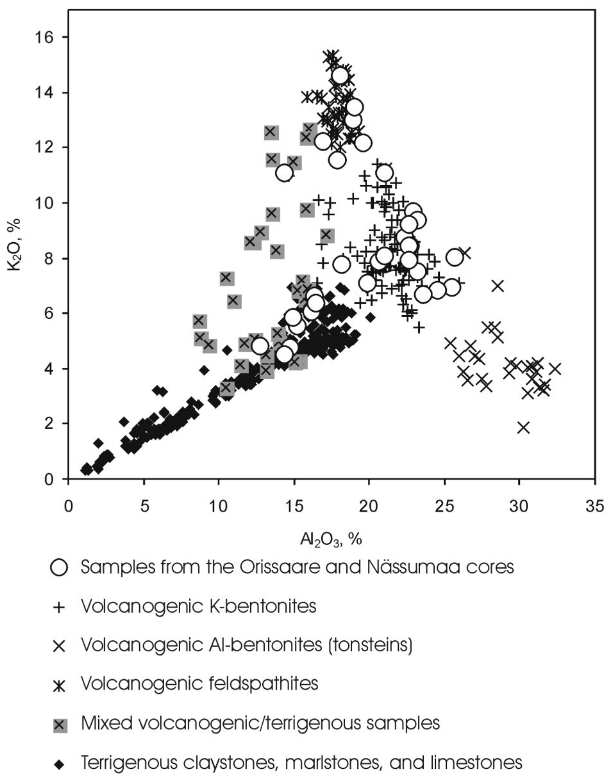

Fig. 4. Comparison of Al_2O_3 and K_2O contents of Nässumaa and Orissaare samples with the database of XRF analyses in the Institute of Geology. Data on terrigenous and carbonate rocks are from the unpublished database of E. Kiipli. XRF analyses of more than 200 bentonites expressed in the figure are available in Kiipli et al. (2007c).

P. a. amorphognathoides conodont biozones (Kiipli et al. 2001) (Fig. 5). The bentonites at 201.8 and 199.7 m in the Nässumaa core correlated with the Ruhnu (ID 494) and Kirikuküla (ID 457) bentonites by sanidine composition (Kiipli & Kallaste 2002). This is confirmed also by the results of geochemical analyses herein (Table 4 and Fig. 6).

The compositions of bentonites at 200.7 m in the Nässumaa core and 69.9 m in the Orissaare core are very similar, and cluster near the data for the Viki (ID 475) and Kaugatuma (ID 480) bentonites (Fig. 6). The Viki and Kaugatuma bentonites may be distinguished by their contrasting sanidine compositions (Kallaste & Kiipli 2006). In addition, the Kaugatuma Bentonite has a considerable thickness (0.5–1.5 cm) only in cores of western Saaremaa. Consequently, the bentonites at 200.7 m in the Nässumaa core and at 69.9 m in the Orissaare core are positively correlated with the Viki Bentonite (ID 475).

The interval from the lower half of the *P. a. lithuanicus* conodont Biozone to the *P. a. angulatus* Biozone contains four significant bentonites (ID 518, 520, 521, 568). They are all geochemically similar and are characterized by high TiO_2, Sr (182–320 ppm), and Ba (226–837 ppm) contents. Zr, Nb, and Th occur in lower concentrations. Bentonites ID 520 and ID 568 are characterized by elevated phosphorus (ID 520, 0.56–1.65%; ID 568, 0.05–0.36%) contents; ID 520 has also quite a high Y (59–80 ppm) content. From these data it can be suggested that the bentonites at 72.4 and 73.1 m in the Orissaare core are identical to ID 518 and ID 521. Meanwhile, the bentonites at 208.2 m in the Nässumaa core and at 76.8 m in the Orissaare core can be correlated with ID 568. The bentonite at 204.9 m in the Nässumaa core has similar geochemical features to both ID 518 and ID 521, but there is insufficient data to distinguish between the two.

In the section of the Velise Formation, equivalent to the *Pterospathodus eopennatus* ssp. n. 2 conodont Zone, using analogous arguments based on the composition, it is possible to correlate the bentonites at 219.4 m in the Nässumaa core and at 84.0 m in the Orissaare core with ID 696. A connection between ID 696 and the Nässumaa 219.4 m bentonite has also been suggested on the basis of sanidine composition (Kiipli & Kallaste 2002). Following similar arguments, and moving down the core, a number of other correlations between bentonites in the Korkküla-863, Viirelaid, and Paatsalu cores and bentonites from Orissaare and Nässumaa can be identified. The bentonites at 86.8 and 87.2 m in the Orissaare core can be positively correlated with ID 731 and ID 744. Meanwhile, the bentonite at 224.1 m in the Nässumaa core and at 87.2 m in the Orissaare core can be correlated with one another, as well as with ID 755. A positive correlation between the bentonite at 226.7 m in Nässumaa and ID 777 can also be drawn. The bentonite clay identified at 91.5 m in the Orissaare core does not correlate positively with any other samples studied here or in previous works.

At 93.9 m in the Orissaare core (in the Rumba Formation) there is a bentonite with anomalously high (3.7%) Ba content and a possible graphic correlation with the bentonite at 83.0 m in the Viirelaid core (ID 843) exists. The high Ba content is probably caused by authigenic accumulation of barite, although the source for authigenic accumulation of the element could be primary volcanic ash. The sample collected at 95.4 m in the Orissaare core can be confidently correlated with ID 851, which is also recognized as the Osmundsberg

Table 1. XRF analyses of altered volcanic ash beds in the Nässumaa core

	Depth of the bed, m									Determin-ation limit
	199.7	200.7	201.8	204.9	208.2	219.4	224.1	226.7	235.0	
Thickness, cm	3	4	4	0.1	2.5	2.5	4	2.5	8	
ID	457	475	494	521?	568	696	755	777?	851	
Content of major elements, %										
SiO_2	55.2	54.5	59.4	54.6	54.4	56.3	53.0	55.4	61.4	0.07
TiO_2	0.766	0.863	0.345	1.30	1.01	0.455	0.998	0.655	0.385	0.003
Al_2O_3	16.9	25.0	23.1	17.9	22.4	21.9	19.9	18.2	18.9	0.08
Fe_2O_3 total	0.81	1.98	1.54	4.48	3.64	4.04	8.52	5.90	1.29	0.004
MnO	0.014	0.006	0.005	0.006	0.008	0.020	0.019	0.061	0.013	0.002
MgO	1.05	3.16	2.89	1.33	2.52	3.16	3.35	3.51	1.67	0.2
CaO	5.08	0.95	0.41	1.10	0.84	0.78	1.01	2.31	0.74	0.06
K_2O	12.2	6.89	9.55	11.6	8.75	7.72	7.07	7.79	13.0	0.004
P_2O_5	0.17	0.07	0.04	0.27	0.27	0.07	0.11	0.07	0.14	0.02
BaO	0.46	0.02	0.01	0.03	0.02	0.02	0.01	0.03	0.05	0.01
S	0.22	0.12	0.10	1.76	0.09	0.05	0.01	0.00	0.47	0.01
LOI 920 ºC	4.30	5.96	3.98	4.20	4.20	4.80	5.10	5.60	1.60	0.01
Content of trace elements, ppm										
As	10	6	6	17	9	5	1	5	7	8
Bi	<8	<8	<8	<8	<8	<8	<8	<8	<8	8
Br	<3	<3	<3	<3	3.2	2.2	<3	<3	<3	3
Ce	120	184	<60	63	99	54	148	142	<60	60
Ga	3	17	13	7	14	21	19	19	15	3
La	<40	55	<40	<40	<40	30	70	39	<40	40
Mo	<3	<3	<3	<3	<3	<3	<3	<3	<3	3
Nb	13	37	38	18	22	17	21	18	11	3
Pb	9	10	5	21	16	7	11	7	4	7
Rb	59	83	91	64	82	128	96	113	74	3
Se	<4	<4	<4	<4	<4	<4	<4	<4	<4	4
Sr	208	92	59	225	159	72	77	81	75	3
Th	16	30	36	22	24	18	27	19	23	8
Tl	<12	<12	<12	<12	<12	<12	<12	<12	<12	12
U	6	9	<8	7	7	<8	<8	<8	<8	8
Y	20	36	3	19	33	25	27	29	2	3
Zr	219	710	339	243	335	205	428	276	177	10

Bentonite (Bergström et al. 1998), found at several locations across Baltoscandia (Fig. 5).

DIACHRONEITY OF THE RUMBA–VELISE FORMATIONS BOUNDARY

Correlation of limestones of the Rumba Formation in Estonia with shales of the Degole Beds in Latvia has been demonstrated by the correlation of the Osmundsberg Bentonite through different facies zones (E. Kiipli et al. 2006). Einasto et al. (1972) argued that the boundary of the Rumba and Velise formations is synchronous in southwestern Estonia. Here we intend to show the diachronous nature of the Rumba–Velise boundary in Estonia (Fig. 5). The Rumba Formation consists of nodular limestones. The percentage of limestone nodules and marlstone interbeds varies, with the rock being in general more argillaceous in sections of western and southwestern Saaremaa and more carbonate in eastern sections. In the Korkküla, Nässumaa, and Orissaare sections there is a sharp boundary between nodular limestones of the Rumba Formation and homogeneous marlstones of the Velise Formation. The Viirelaid and Paatsalu sections include a 1.5–2 m thick transition interval with abundant limestone nodules in marlstone. Limestone nodules are

Table 2. XRF analyses of altered volcanic ash beds in the Orissaare core

	Depth of the bed, m												Determin-ation limit
	55.3	58.8	69.9	72.4	73.1	76.8	84.0	86.8	87.2	87.6	93.9	95.4	
Thickness, cm	4	6	3	1	1	1.5	6	3	1	7	1	10	
ID	150	210	475	518	521	568	696	731	744	755	843?	851	
Content of major elements, %													
SiO_2	51.4	57.2	57.2	60.2	58.1	56.6	57.3	57.3	57.6	55.1	51.4	61.1	0.07
TiO_2	0.915	0.590	0.849	1.12	1.12	1.00	0.454	0.450	0.500	0.979	0.484	0.404	0.003
Al_2O_3	23.6	25.6	22.7	19.0	19.6	21.0	22.6	22.6	21.0	22.6	15.3	18.3	0.08
Fe_2O_3 total	4.63	1.12	1.92	1.16	1.72	1.62	3.16	2.45	3.32	3.37	0.61	1.18	0.004
MnO	0.006	0.005	0.007	0.012	0.006	0.007	0.019	0.004	0.009	0.002	0.008	0.014	0.002
MgO	3.06	3.25	3.29	1.07	1.53	2.07	3.20	3.73	3.60	3.59	0.93	0.92	0.2
CaO	0.97	0.82	1.04	1.17	1.08	0.95	0.57	0.47	0.64	0.54	6.90	0.45	0.06
K_2O	6.69	8.01	8.43	13.5	12.2	11.1	9.21	8.43	8.08	7.93	11.1	14.6	0.004
P_2O_5	0.06	0.05	0.06	0.28	0.22	0.36	0.08	0.07	0.07	0.09	0.06	0.22	0.02
BaO	0.03	0.02	0.02	0.05	0.04	0.04	0.03	0.02	0.02	0.00	3.70	0.04	0.01
S	2.47	0.13	0.17	0.25	0.88	0.84	0.13	0.06	0.08	0.13	1.17	0.30	0.01
LOI 920 ºC	7.90	5.00	5.00	1.50	2.80	3.20	3.60	4.60	4.40	5.00	5.30	0.60	0.01
Content of trace elements, ppm													
As	30	8	5	9	21	33	7	3	5	1	6	6	8
Bi	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	8
Br	2.0	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	3
Ce	<60	<60	<60	<60	<60	88	<60	168	<60	173	250?	<60	60
Ga	12	15	15	7	9	11	20	23	21	19	2	12	3
La	<40	<40	30	<40	39	<40	39	75	36	56	<40	<40	40
Mo	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	3
Nb	31	25	33	17	18	18	17	34	32	23	13	8	3
Pb	36	11	5	9	30	43	12	4	4	6	4	10	7
Rb	65	75	91	78	69	66	126	95	109	92	43	65	3
Se	<4	<4	<4	<4	<4	<4	<4	<4	<4	<4	<4	<4	4
Sr	236	137	85	270	222	236	68	92	86	88	364	62	3
Th	34	26	25	18	18	17	21	28	25	27	12	18	8
Tl	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	<12	12
U	9	7	9	7	9	9	<8	7	<8	6	<8	6	8
Y	38	23	32	15	22	22	37	22	10	20	9	5	3
Zr	570	459	626	240	309	290	268	392	254	498	175	191	10

Table 3. XRF analyses of terrigenous claystones and mixed clays with altered volcanic ashes in the Nässumaa and Orissaare cores

	Nässumaa, m							Orissaare, m		Determination limit
	201.6	208.2	224.3	224.6	224.8	229.5	229.5	78.9	91.5	
Thickness, cm	0.2	2.5	1	2	2	5	5	1	5	
ID	488	568								
Content of major elements, %										
SiO_2	51.7	52.8	53.6	56.7	55.8	42.6	51.2	48.2	55.9	0.07
TiO_2	0.729	0.606	0.861	0.939	0.924	0.626	0.805	0.729	0.895	0.003
Al_2O_3	14.7	16.4	15.2	16.2	16.2	12.7	15.0	14.4	16.5	0.08
Fe_2O_3 total	4.64	4.21	8.47	8.81	6.02	5.56	7.19	4.39	5.18	0.004
MnO	0.050	0.037	0.063	0.045	0.051	0.129	0.094	0.049	0.040	0.002
MgO	4.19	3.37	4.01	3.90	3.98	3.29	4.12	4.21	4.19	0.2
CaO	7.98	6.59	4.16	1.26	3.90	15.86	6.37	11.37	4.00	0.06
K_2O	4.77	6.64	5.53	6.12	6.07	4.84	5.83	4.52	6.37	0.004
P_2O_5	0.06	0.08	0.05	0.05	0.03	0.06	0.04	0.07	0.02	0.02
BaO	0.03	0.03	0.04	0.04	0.04	0.03	0.03	0.04	0.03	0.01
S	0.13	0.04	0.01	0.01	0.00	0.01	0.01	0.24	0.39	0.01
LOI 920 ºC	11.80	9.00	8.00	5.10	7.30	16.60	9.50	13.70	6.70	0.01
Content of trace elements, ppm										
As	5	7	12	10	4	5	3	4	4	8
Bi	<8	<8	<8	<8	<8	<8	<8	<8	<8	8
Br	3.7	<3	<3	<3	<3	<3	<3	<3	<3	3
Ce	69	57	64	92	70	51	<60	46	<60	60
Ga	14	14	18	18	17	12	19	17	19	3
La	38	<40	<40	60	31	<40	37	35	<40	40
Mo	<3	<3	<3	<3	<3	<3	<3	<3	<3	3
Nb	16	12	16	16	16	12	13	14	16	3
Pb	2	9	10	10	5	5	7	0	9	7
Rb	129	119	141	150	142	96	131	120	137	3
Se	<4	<4	<4	<4	<4	<4	<4	<4	<4	4
Sr	106	127	103	69	103	133	96	131	80	3
Th	11	10	17	15	16	11	15	11	18	8
Tl	<12	<12	<12	<12	<12	<12	<12	<12	<12	12
U	<8	6	<8	<8	<8	<8	<8	<8	6	8
Y	21	25	25	27	28	22	20	22	18	3
Zr	179	172	177	184	187	138	172	161	192	10

abundant in the lower part of the Velise Formation also in the Varbla, Seliste, and Ikla sections (Einasto et al. 1972). Interestingly, by bentonites this transition interval of the Paatsalu section correlates confidently with the lower part of the Velise Formation in the Viirelaid core without limestones and with the even higher part of the Velise Formation in the Orissaare, Nässumaa, and Korkküla sections (Fig. 5). The Mustjala Bentonite (ID 795) in the Rumba Formation at 83.9 m in the Paatsalu core correlates with the 80.9 m level in the Viirelaid core (transition interval) and with 190.3 m in the Korkküla core, being without doubt within the lower part of the Velise Formation. Therefore, bentonite correlations show in detail the diachronous nature of the lithological boundary within a small distance of about 20–70 km.

THICKNESS DISTRIBUTION OF BENTONITES

When combined with stratigraphy, thickness distribution maps for volcanic ash beds are a useful tool for predicting the occurrence of particular ash beds. They can also be used to predict the geographic location of source volcanoes. The distribution patterns in Fig. 7 indicate that volcanic ash clouds arrived from the west (Viki, Kaugatuma, and Nässumaa bentonites), northwest

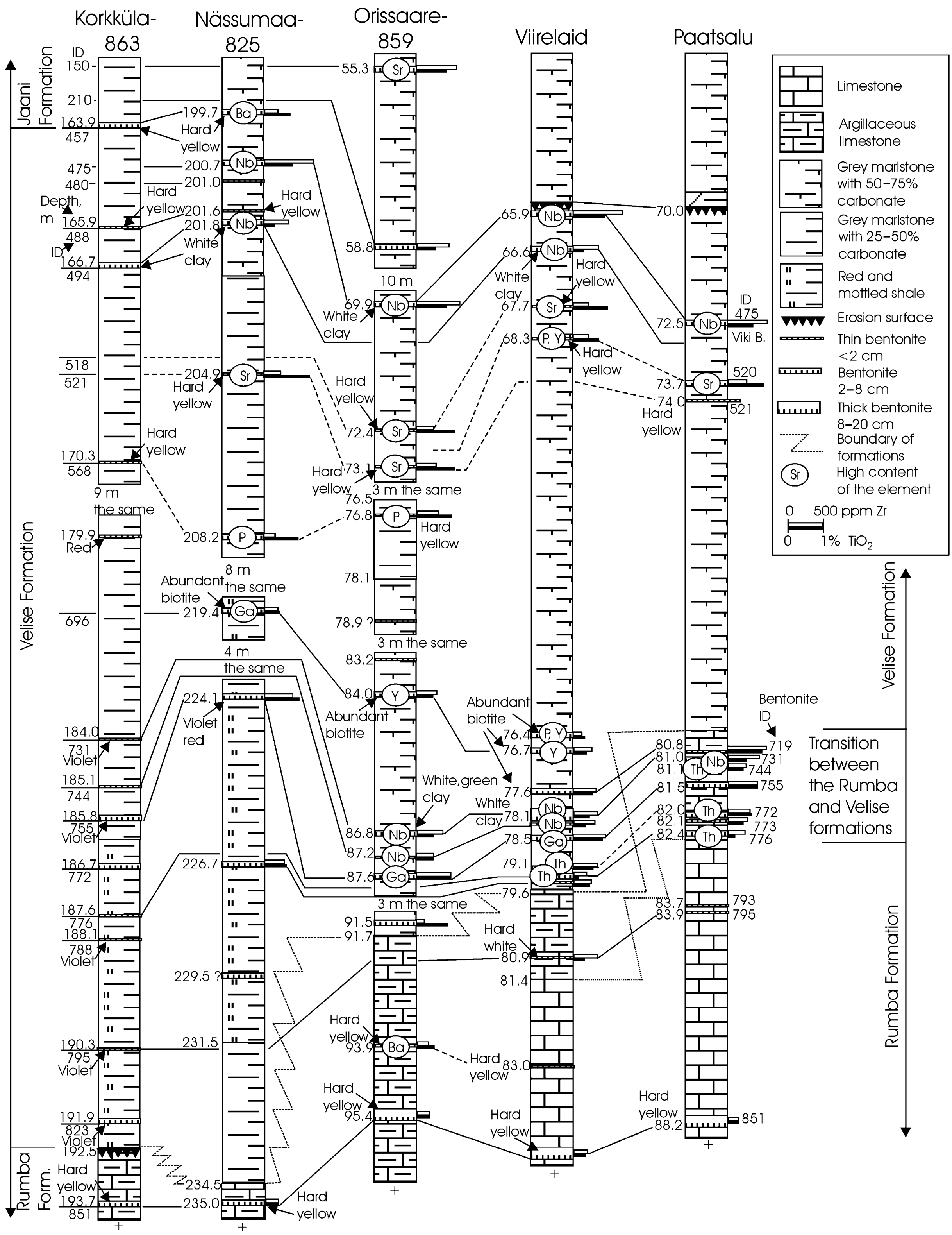

Fig. 5. Correlation of bentonites in different sections. ID numbers and names of bentonites according to Kallaste & Kiipli (2006). ID 150, Lusklint Bentonite; ID 210, Ohesaare Bentonite; ID 457, Kirikuküla Bentonite; ID 475, Viki Bentonite; ID 480, Kaugatuma Bentonite; ID 488, Kuressaare Bentonite; ID 494, Ruhnu Bentonite; ID 518, Viirelaid Bentonite; ID 696, Nässumaa Bentonite; ID 719, Virtsu Bentonite; ID 731, Nurme Bentonite; ID 744, Tehumardi Bentonite; ID 755, Paatsalu Bentonite; ID 772, Pahapilli Bentonite; ID 795, Mustjala Bentonite; ID 851, Osmundsberg Bentonite.

Table 4. Geochemical comparison of bentonites from the Orissaare (O) and Nässumaa (N) sections with the database of XRF analyses (Kiipli et al. 2007c). ID, identification number of bentonites; No., number of analyses; Avg, average; Std, standard deviation; Ter, terrigenous sediments

ID		Zr/TiO_2	Nb/TiO_2	Th/TiO_2
127	No.	3	3	3
	Avg	0.0467	0.00373	0.00361
	Std	0.0067	0.00042	0.00065
139	No.	1	1	1
	Avg	0.036	0.00282	0.00235
150	No.	6	6	6
	Avg	0.0541	0.00306	0.00361
	Std	0.0098	0.00059	0.00041
	O-55.3	0.0626	0.00345	0.00370
210	No.	6	6	4
	Avg	0.0655	0.00342	0.00426
	Std	0.0109	0.00051	0.00042
	O-58.8	0.0778	0.00419	0.00444
311	No.	3	3	3
	Avg	0.0610	0.00458	0.00569
	Std	0.0049	0.00042	0.00006
457	No.	5	5	4
	Avg	0.0338	0.00171	0.00213
	Std	0.0046	0.00015	0.00012
	N-199.7	0.0284	0.00170	0.00213
475	No.	9	9	6
	Avg	0.0772	0.00435	0.00333
	Std	0.0067	0.00048	0.00040
	N-200.7	0.0803	0.00429	0.00337
	O-69.9	0.0736	0.00391	0.00293
480	No.	3	3	3
	Avg	0.0717	0.00429	0.00371
	Std	0.0077	0.00015	0.00041
488	No.	6	6	5
	Avg	0.0199	0.00121	0.00151
	Std	0.0028	0.00007	0.00029
494	No.	10	10	6
	Avg	0.0967	0.01119	0.01061
	Std	0.0056	0.00082	0.00121
	N-201.8	0.0975	0.01094	0.01075
518	No.	5	5	4
	Avg	0.0245	0.00148	0.00168
	Std	0.0041	0.00007	0.00008
	O-72.4	0.0214	0.00151	0.00158
520	No.	5	5	3
	Avg	0.0294	0.00159	0.00220
	Std	0.0026	0.00010	0.00056
521	No.	4	4	3
	Avg	0.0235	0.00149	0.00155
	Std	0.0037	0.00012	0.00015
	N-204.9	0.0187	0.00142	0.00168
	O-73.1	0.0276	0.00160	0.00157
568	No.	5	5	4
	Avg	0.0282	0.00161	0.00178
	Std	0.0044	0.00037	0.00041
	N-208.2	0.0332	0.00217	0.00233
	O-76.8	0.0290	0.00178	0.00171
658	No.	1	1	1
	Avg	0.0939	0.00705	0.00690
693	No.	1	1	1
	Avg	0.0410	0.00449	0.00449
696	No.	10	10	7
	Avg	0.0550	0.00331	0.00419
	Std	0.0115	0.00068	0.00106
	N-219.4	0.0457	0.00368	0.00398
	O-84.0	0.0596	0.00382	0.00478
705	No.	1	1	1
	Avg	0.0920	0.00808	0.00693
719	No.	5	5	3
	Avg	0.0657	0.00364	0.00424
	Std	0.0122	0.00071	0.00093
720	No.	1	1	1
	Avg	0.1154	0.00963	0.02573
722	No.	1	1	1
	Avg	0.0253	0.00184	0.00230
731	No.	11	11	8
	Avg	0.0849	0.00777	0.00709
	Std	0.0104	0.00081	0.00072
	O-86.8	0.0871	0.00747	0.00613
744	No.	7	7	6
	Avg	0.0590	0.00746	0.00800
	Std	0.0103	0.00126	0.00196
	O-87.2	0.0508	0.00646	0.00490
750	No.	1	1	1
	Avg	0.0354	0.00312	0.00502
755	No.	8	8	6
	Avg	0.0476	0.00228	0.00289
	Std	0.0068	0.00040	0.00035
	N-224.1	0.0428	0.00211	0.00270
	O-87.6	0.0508	0.00240	0.00274
772	No.	6	6	5
	Avg	0.0560	0.00381	0.00663
	Std	0.0123	0.00071	0.00164
773	No.	1	1	1
	Avg	0.0653	0.00324	0.00588
774	No.	1	1	1
	Avg	0.0949	0.00552	0.00424
776	No.	4	4	4
	Avg	0.1005	0.00951	0.02080
	Std	0.0212	0.00352	0.00405
777	No.	4	4	4
	Avg	0.0453	0.00277	0.00314
	Std	0.0080	0.00051	0.00030
	N-226.7	0.0425	0.00269	0.00295
788	No.	1	1	1
	Avg	0.0584	0.00365	0.00291

Table 4. *Continued*

ID		Zr/TiO_2	Nb/TiO_2	Th/TiO_2	ID		Zr/TiO_2	Nb/TiO_2	Th/TiO_2
795	No.	3	3	3	851	No.	11	11	8
	Avg	0.0864	0.00489	0.00668		Avg	0.0483	0.00228	0.00492
	Std	0.0139	0.00197	0.00071		Std	0.0039	0.00048	0.00082
818	No.	1	1	1		N-235.0	0.0479	0.00328	0.00605
	Avg	0.0346	0.00205	0.00000		O-95.4	0.0478	0.00210	0.00445
823	No.	3	3	2	870	No.	1	1	1
	Avg	0.1006	0.00525	0.00481		Avg	0.0132	0.00079	0.00054
	Std	0.0092	0.00069	0.00167	880	No.	2	2	2
843	No.	2	2	2		Avg	0.0264	0.00149	0.00214
	Avg	0.0335	0.00315	0.00242		Std	0.0084	0.00046	0.00095
	Std	0.0041	0.00051	0.00011	Ter	No.	8	8	8
	O-93.9	0.0365	0.00279	0.00250		Avg	0.0219	0.00182	0.00175
						Std	0.0027	0.00013	0.00016

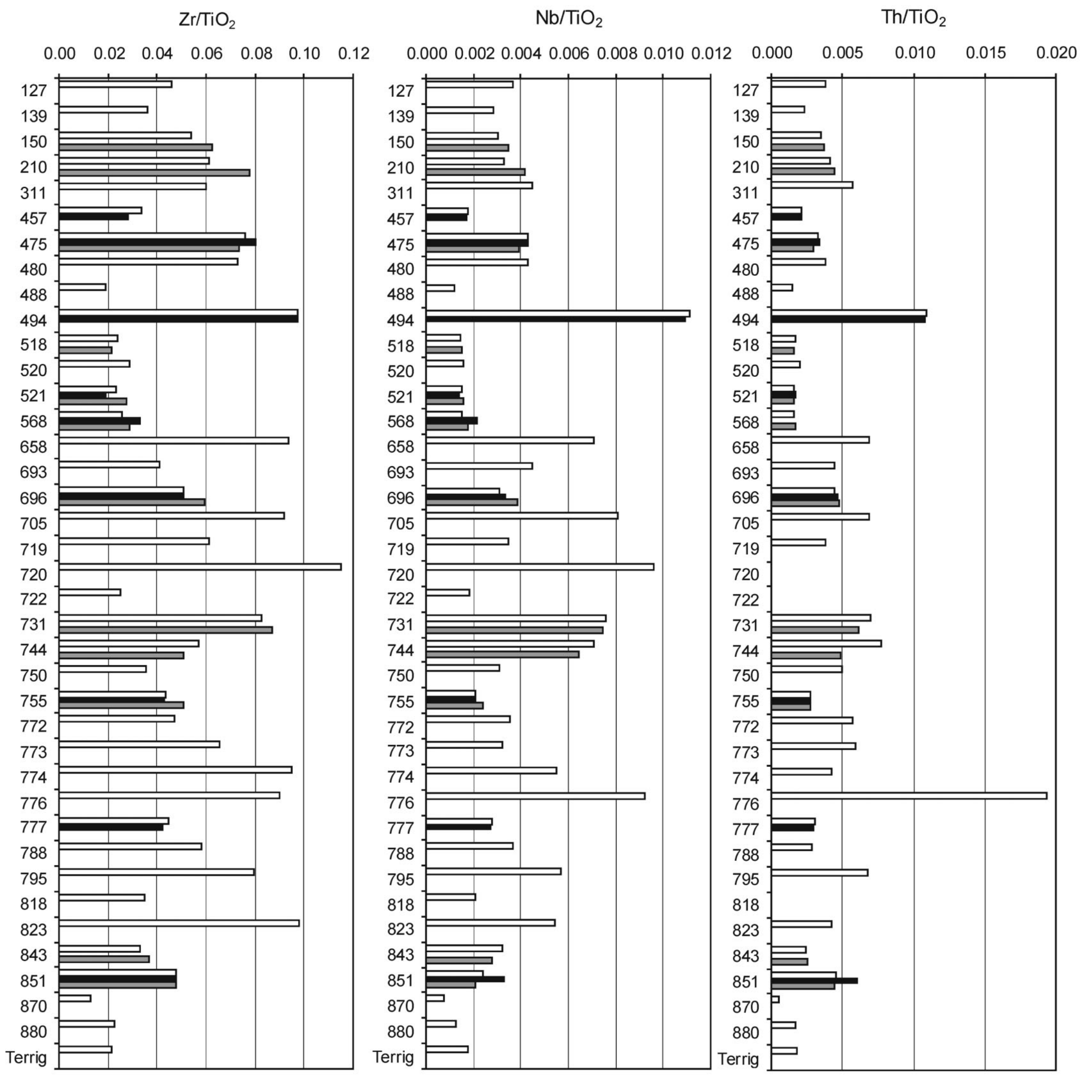

Fig. 6. Geochemical comparison of bentonites of the Orissaare (grey bars) and Nässumaa (black bars) cores with the average (white bars) calculated from the complete database of XRF analyses (Kiipli et al. 2007c). ID numbers of bentonites on the left arrange bentonites in the order of successive eruptions. Terrig = terrigenous clay.

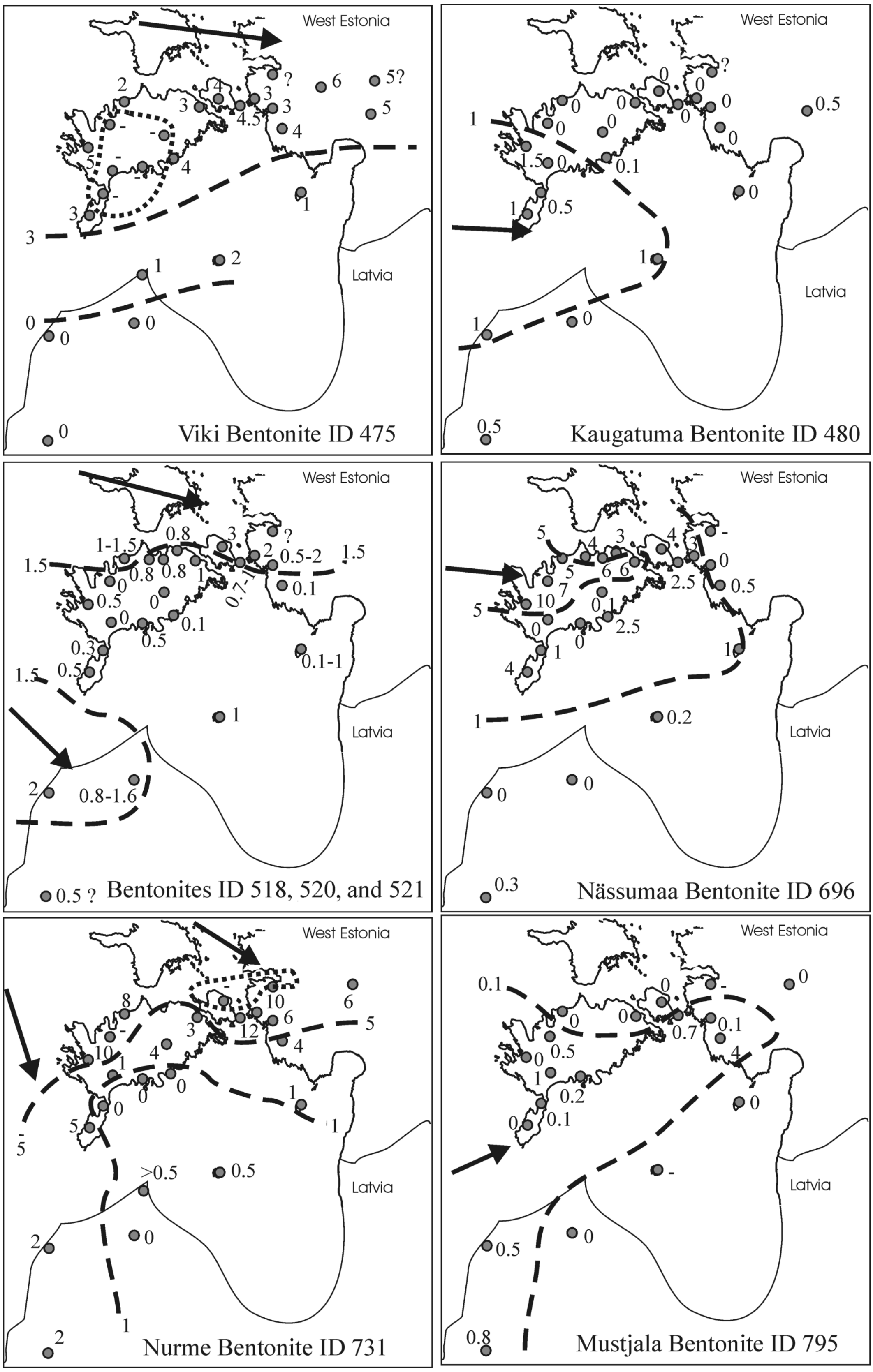

Fig. 7. Thickness (cm) distribution patterns of some Telychian bentonites. Dashed lines – thickness isolines of bentonites, dotted lines – supposed hiatuses in sedimentation, arrows – provisional movement direction of the volcanic ash cloud.

(bentonites ID 518, 520, 521, and 731) or southwest (Mustjala Bentonite). The distribution pattern of the Nurme Bentonite indicates a change in the wind direction during long-lasting eruption. Two ash cloud directions are indicated also on the composite isopach scheme of bentonites ID 518, 520, and 521. It is natural that all these eruptions had different ash cloud distributions and therefore two ash cloud movement directions are normal. Some other thickness distribution patterns of Silurian bentonites in the East Baltic and Scandinavia were published in Bergström et al. (1998), Kallaste & Kiipli (2006), E. Kiipli et al. (2006), Kiipli & Kallaste (2007), and Kiipli et al. (2007c, 2008).

CONCLUSIONS

Immobile trace elements Ti, Zr, Th, and Nb in combination with other geochemical signatures can be successfully used for correlation of bentonites in the Telychian of Estonia. Correlation potential of other trace elements needs to be studied carefully before using, because the mobility of many elements in the Earth's surface conditions can be expected from general geochemical considerations. Bentonite correlations show clear diachroneity of the Rumba–Velise formations boundary in Estonia. Thickness distribution patterns of bentonites indicate volcanic sources in the northwest, west or southwest.

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Immobiilsete mikroelementide kasutamine Telychi bentoniitide korrelatsiooniks Saaremaal ja vulkaaniliste tuhapilvede kaardistamine

Tarmo Kiipli, Kiira Orlova, Enli Kiipli ja Toivo Kallaste

Röntgenfluorestsentsmeetodil on analüüsitud kolmekümmet oletatavat vulkaanilise tuha (bentoniidi) proovi Nässumaa-825 ja Orissaare-859 puursüdamikest. Selle tulemusel on selgunud, et 20 neist on puhtad vulkanogeensed setted, üks vulkanogeense ja terrigeense materjali segu ning üheksa terrigeensed savid. Bentoniitidest 20 korreleeruvad varem teada olnud vulkaaniliste kihtidega; üks uuritud bentoniitidest (Orissaare 91,5 m) esindab uut, varem mitte teada olnud vulkaanipurset. Uusi ja varem avaldatud korrelatsioone on kasutatud Rumba ja Velise kihistu piiri diakroonsuse jälgimiseks ning bentoniitide leviku ja paksuse skeemide koostamiseks.