

ALTERED VOLCANIC ASH AS AN INDICATOR OF MARINE ENVIRONMENT, REFLECTING pH AND SEDIMENTATION RATE – EXAMPLE FROM THE ORDOVICIAN KINNEKULLE BED OF BALTOSCANDIA

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Abstract—The composition of altered volcanic ash of the Late Ordovician Kinnekulle bed was studied in geological sections of the Baltic Paleobasin. The composition of altered ash varies with paleosea depth from northern Estonia to Lithuania. The ash bed in shallow shelf limestones contains an association of illite-smectite (I-S) and K-feldspar, with the K₂O content ranging from 7.5 to 15.3%. The limestone in the transition zone between shallow- and deep-shelf environments contains I-S-dominated ash with K₂O content from 6.0 to 7.5%. In the deep-shelf marlstone and shale, the volcanic ash bed consists of I-S and kaolinite with a K₂O content ranging from 4.1 to 6.0%. This shows that authigenic silicates from volcanic ash were formed during the early sedimentary-diagenetic processes. The composition of the altered volcanic ash can be used as a paleoenvironmental indicator showing the pH of the seawater or porewater in sediments as well as the sedimentation rate.

Key Words—Baltoscandia, K-bentonite, Kinnekulle, Marine Environment, Ordovician, pH, Sedimentation Rate, Volcanic Ash.

INTRODUCTION

The alteration of volcanic ash in sedimentary environments has resulted in a variety of authigenic minerals. In the Cenozoic and Mesozoic, bentonites consisting mostly of smectite were widely developed (Grim and Güven, 1978). In the Paleozoic, K-bentonites dominate with illite-smectite (I-S) as the main authigenic mineral. In coal formations, volcanic beds, referred to as tonsteins, have altered to kaolinite (Bohor and Triplehorn, 1993). Volcanic materials deposited in saline alkaline lakes of arid regions are altered to zeolite and K-feldspar (Sheppard and Gude, 1968, 1973). Illite and chlorite are common in slightly metamorphosed volcanic ashes. However, unmetamorphosed, chloritic (chlorite-smectite mixed-layered mineral) bentonites have been found, probably denoting a specific early diagenetic environment (Hints *et al.*, 2006). Different mechanisms have been put forward, accounting for variations in the mineral composition of the altered ashes: composition of source magma, climate and sedimentary conditions at the time of eruption, diagenetic processes and later metamorphism (Grim and Güven, 1978; Chamley, 1994). In complicated geological situations and due to late diagenetic and/or metamorphic overprinting it is usually difficult to restore the diagenetic history of mineral transformations in all individual cases.

The purpose of this contribution is to study the alteration of silicate phases in a single and well-correlated Kinnekulle volcanic bed (Bergström *et al.*, 1995) extending through different depositional environments from shallow- to deep-sea facies.

The Lower Paleozoic sedimentary section of the northern Baltic Paleobasin in Estonia and northern Latvia (Figure 1) is monoclinical, slightly southward dipping (2–4 m per km), unmetamorphosed, and contains well preserved fossils indicative of minimal late diagenetic overprinting. The conodont alteration index is 1–1.5, suggesting temperatures of no more than 50–80°C (Männik and Viira, 1990). Kirsimäe *et al.* (1999) estimated maximum paleotemperatures of even less than 50°C. The present-day depths of the Kinnekulle bed range from outcrops in northern Estonia and Sweden to >1000 m in Latvia and to 2400 m in Lithuania (Lashkovas, 2000). Host rocks range from normal marine shallow shelf limestone in northern and central Estonia to deep-shelf shale and marlstone in southern Estonia, Latvia and western Lithuania. Constraining the study to a single bed makes the influence of source material variation and weather conditions at the time of eruptions nearly constant, therefore reducing considerably the number of the factors affecting the early diagenetic alteration of the pyroclastic materials.

STRATIGRAPHY AND CORRELATION

The Kinnekulle volcanic ash bed belongs to the Upper Ordovician Sandbyan Stage (Caradoc in previous stratigraphic schemes) (Nölvak *et al.*, 2006). It is remarkable for its thickness, reaching 70 cm in the

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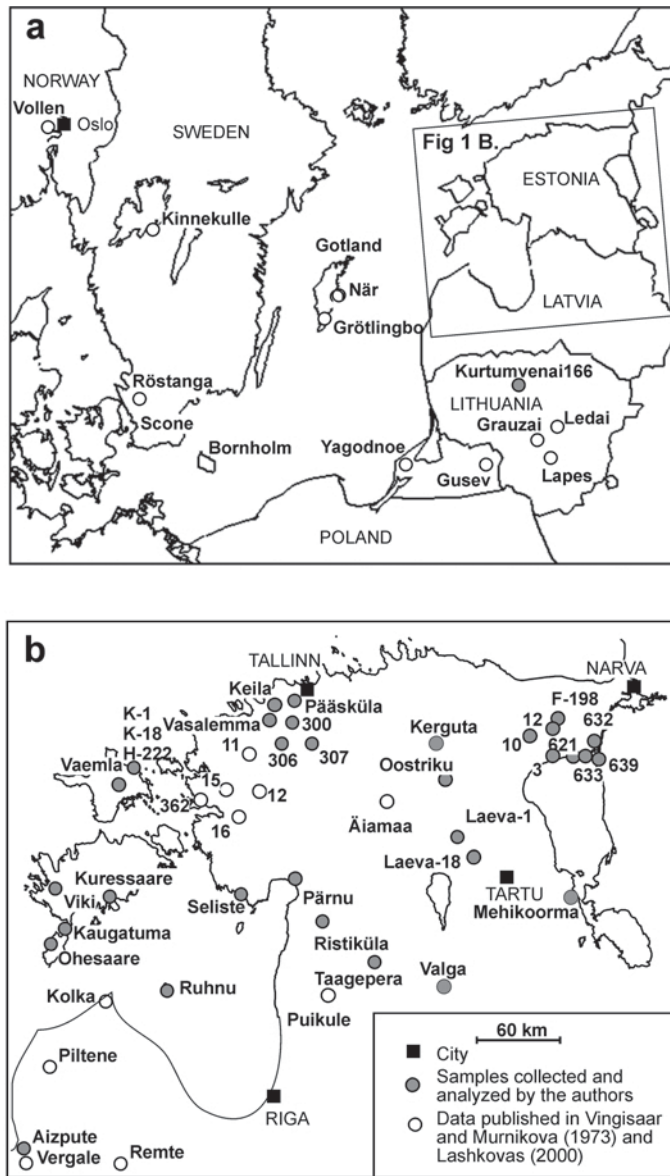


Figure 1. Locations of boreholes and outcrops: (a) area from both sides of Baltic Sea with localities discussed in the text; (b) locations of boreholes in Estonia and northern Latvia.

Baltic region and ~2 m in southern Sweden, exceeding all other Paleozoic volcanic intercalations. Based on thickness, paleontological and geochemical data, this bed has been correlated over northern and central Estonia, Sweden and Norway (Bergström *et al.*, 1995). The Ordovician sedimentary basin of the Baltic Paleobasin is divided into the North Estonian Confacies, the Lithuanian Confacies, the Central Baltoscandian Confacies and the Scanian Lithofacies (Jaanusson, 1995). A confacies includes various lithofacies. The North Estonian Confacies, represented by limestones and argillaceous limestones, contains fossil assemblages indicative of a shallow sea. The Central

Baltoscandian Confacies, represented by shales, marlstones and limestones, contains fossils of the deep sea. A transition zone between these two confacies was distinguished by Põlma (1982) (Figures 2, 3). The Kinnekulle bed can be found and stratigraphically correlated through all these confacies.

In the present study, correlation of the Kinnekulle bed is also confirmed by the composition of pyroclastic K-Na-sanidine. The $\text{NaAlSi}_3\text{O}_8$ content of the magmatic sanidine from the Kinnekulle bed is remarkably stable, ranging between 24.2 and 26.4 mol.%. The sanidine composition measured by X-ray diffraction (XRD) fits well with the earlier results of chemical analysis of

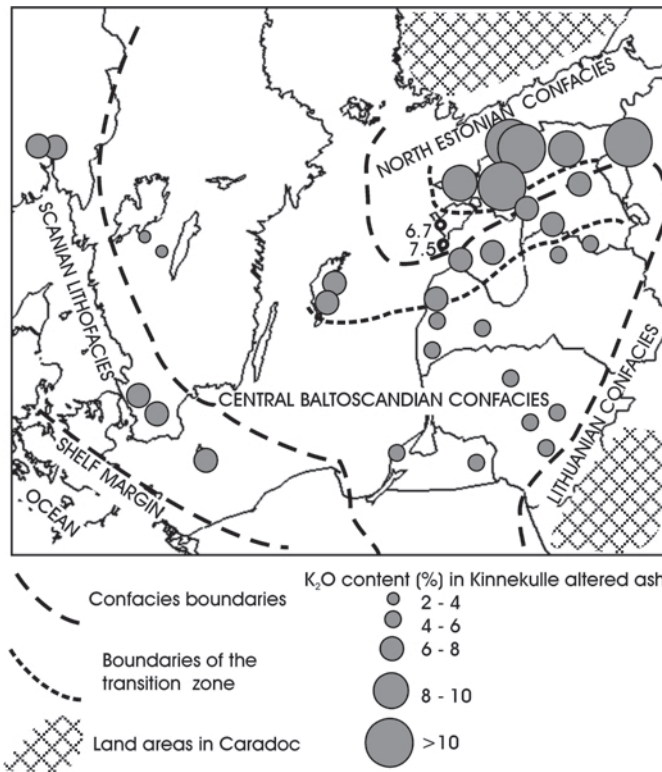


Figure 2. K₂O content of the Kinnekulle altered volcanic ash bed in Baltoscandia. Confacies borders after Jaanusson (1995).

pyroclastic sanidine from the Kinnekulle type locality in Sweden (26.0 mol.%, Byström, 1956). The composition of magmatic sanidine in the Kinnekulle ash bed is clearly distinct from that of other Caradocian volcanic beds that are characterized mostly by a weak and wide

20 $\bar{1}$ reflection indicating large compositional variations in the sanidine (Kiipli and Kallaste, 2002b). The Caradocian altered volcanic ash beds of Lithuania, Latvia and the Kaliningrad area, used in the present study (Lashkovas, 2000), were not precisely correlated

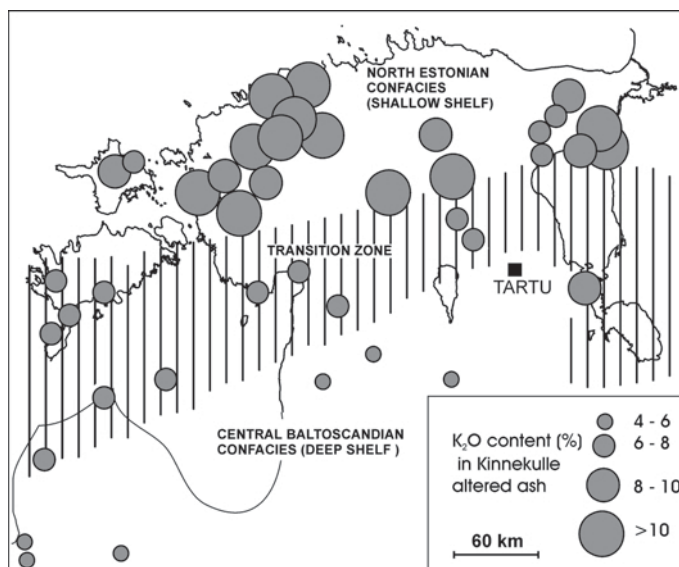


Figure 3. Lateral changes in the K₂O content of the Kinnekulle altered volcanic ash bed from shallow to deep paleoshelf in Estonia and northern Latvia. The hatched area is the transition zone according to Põlma (1982).

with volcanic beds in Estonia and Scandinavia. However, published $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios for these Caradocian bentonites from the southern Baltic area (Lashkovas, 2000) vary from 0.0085 to 0.0218 which is comparable with the samples of the Kinnekulle bed studied in this paper (0.0099 to 0.0190) and published data (0.0085 to 0.0215, Huff *et al.*, 1996) and it does not contradict the correlation. Most of the other Caradocian K-bentonites have greater $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios, up to 0.0856 (Kiipli and Kallaste, 2002b), and only a few others have ratios within this range.

Some chemical heterogeneity of the Kinnekulle bed suggests that it is probably composed of complex or multiple eruptions each contributing to a bentonite (Huff *et al.*, 1999). However, the variation between these possible units is insignificant and Min *et al.* (2001) argued that the duration of such complex deposition would not be resolvable with isotopic methods and it can be considered as a single unit.

MATERIAL AND METHODS

A total of 36 samples of the Kinnekulle volcanic ash bed were studied from drill-cores and outcrops of Estonia, Latvia, Lithuania and Norway (Figure 1). Samples were taken mostly from the middle part of the bed, but in sections with thin volcanic ashes the bed was sampled to its full thickness. The bed is exposed in the walls and roof of abandoned underground military tunnels at Pääsküla (Tallinn, Estonia) to a thickness of ~27 cm (Hints *et al.*, 1997), where a vertical profile through the Kinnekulle altered ash bed was sampled. The K_2O distribution map was compiled using previously published data (Bergström *et al.*, 1997; Brusewitz, 1986; Snäll, 1977; Thorslund, 1947; Vingisaar and Murnikova, 1973).

The main elements (Table 1) in whole-rock samples were analyzed by X-ray fluorescence (XRF) in the laboratory of the Institute of Geology at the Tallinn University of Technology. Samples were powdered in an agate mortar, diluted 1:5 with Li tetraborate and fused at 1200°C. Measurements were carried out using a VRA-30 spectrometer equipped with Cr X-ray tube at 25 mA and 30 kV. For calibration, CRPG reference materials (Govindaraju, 1995) from France were used. In 15 of the samples, Na_2O , P_2O_5 and MnO were also analyzed, but their concentrations were less than the detection limits of the method: $\text{Na}_2\text{O} < 0.7\%$, $\text{P}_2\text{O}_5 < 0.2\%$ and $\text{MnO} < 0.02\%$. An exception is the sample from the Vollen (Norway) outcrop, containing 0.05% MnO.

The whole-rock samples and clay fractions of selected representative samples were studied for mineral composition by means of powder XRD using a DRON-3M diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation, 0.5 mm divergence slit, 0.25 mm receiving slit and two 1.5° Söller slits. Scanning steps of $0.02^\circ 2\theta$ from 2 to $40^\circ 2\theta$ and a counting time of 3 s per step were used for

clay slides and 2 to $50^\circ 2\theta$ and 5 s for unoriented preparations. A quantitative mineral content of powdered and unoriented whole-rock preparations was measured using Rietveld-based code, Siroquant-2.5TM (Taylor, 1991).

The XRD data for oriented $<2 \mu\text{m}$ and $<0.2 \mu\text{m}$ clay aggregates were obtained in air-dried and ethylene glycol-solvated (EG) state. Qualitative and quantitative estimations of illite and kaolinite, as well as proportions of smectite in mixed-layer I-S, were modeled using the computer programs Newmod (Reynolds, 1984) and MLM3C (Plançon and Drits, 2000). The experimental XRD profiles were compared to calculated structural models by trial-and-error until an optimum fit was achieved. The profiles were fitted in the $2\text{--}40^\circ 2\theta$ range using the instrumental and experimental factors, the orientation factor and the mass adsorption coefficients and structural layer compositions suggested by Moore and Reynolds (1997). The coherent stacking domain sizes were distributed log-normally.

The composition of pyroclastic high-sanidine was analyzed from coarse fractions (0.04–0.1 mm) by XRD measurement of the $20\bar{1}$ peak position according to Orville (1967) on HZG-4 (VEB Freiburger Präzisionsmechanik). Curve fitting was applied to differentiate the $20\bar{1}$ peak of the pyroclastic high-sanidine from authigenic low-sanidine and quartz. The details of the method were described by Kiipli and Kallaste (2002a).

RESULTS

XRF

The K_2O content of bulk-rock samples of the Kinnekulle bed varies from 4.1 to 13.8% and the composition of the altered volcanic ash shows a clear trend in relation to the confacies zones (Figures 2 and 3). The highest K_2O content is found in the bed within shallow shelf sediments (7.5–13.8%) and the content decreases towards deeper shelf sediments in the Central Confacies zone. Within the same bed a vertical zonation in chemical composition often occurs in an ash bed (Hints *et al.*, 1997) (Figure 4).

The altered ash bed within limestone and argillaceous limestone of the transition zone contains from 6.0 to 7.5% K_2O . In deep-shelf marlstone and shale of SE Estonia, Latvia and Lithuania (Central Confacies), the K_2O content varies in the volcanic ash bed from 4.1 to 6.0%.

In the Gotland sections the K_2O content varies from 6.0 to 6.2%, which corresponds to the transition zone. Much lower K_2O levels, from 2.4 to 4.0%, have been recorded from the mainland of Sweden at Kinnekulle type localities (Brusewitz, 1986). At the ocean side of Baltic Paleobasin in Scåne, the Oslo region, and the island of Bornholm, the K_2O values range from 6.2 to 7.3%.

The other main components – LOI, SiO_2 , Al_2O_3 , Fe_2O_3 , CaO and MgO – also show changes controlled

Table 1. Chemical composition of Caradocian altered volcanic ash samples (%) and content of illite layers in illite-smectite (%). Composition of illite-smectite in Estonian drill-cores after Kirsimäe *et al.* (2002).

Locality	Depth (m)	Thickness (cm)	Stratigraphy	L.O.I.	SiO ₂	Al ₂ O ₃	MgO	CaO	K ₂ O	Fe ₂ O ₃ T	TiO ₂	I in I-S
Pääsküla outcrop												
Pääsküla, Es-15	0.20	27	O ₂ Kin	1.54	63.0	18.0	0.76	0.29	14.9	0.89	0.200	87
Pääsküla	0.225	27	O ₂ Kin	3.18	60.3	16.5	0.84	2.29	14.90	0.92	0.220	
Pääsküla	0.185	27	O ₂ Kin	1.91	61.7	17.6	1.44	0.31	15.32	0.75	0.195	78
Pääsküla	0.155	27	O ₂ Kin	2.46	60.9	17.8	2.67	0.47	14.55	0.92	0.205	
Pääsküla	0.14	27	O ₂ Kin	3.06	61.6	18.7	2.76	0.68	11.88	0.93	0.211	77
Pääsküla	0.09	27	O ₂ Kin	3.1	60.1	18.4	3.28	0.78	12.48	1.00	0.220	75
Pääsküla	0.045	27	O ₂ Kin	2.31	61.7	18.1	2.26	0.43	13.70	1.09	0.219	76
Pääsküla	0.003	27	O ₂ Kin	1.85	62.1	17.9	0.92	1.27	13.47	2.06	0.313	
Samples from Estonian drillcores												
Keila	7.05	8	O ₂ Kin	1.96	62.2	18.2	1.14	0.64	13.81	1.48	0.339	72
300	32.60	35	O ₂ Kin	2.77	60.2	18.6	2.80	0.38	13.42	1.05	0.202	
Oostriku	175.30	1	O ₂ Gri	2.88	61.0	17.7	1.55	0.97	13.18	2.09	0.397	74
Oostriku	177.70	5	O ₂ Kin	2.93	61.5	18.0	1.24	1.79	13.27	1.18	0.193	75
632			O ₂ Kin	3.15	61.0	19.3	2.03	0.61	12.60	1.45	0.192	
Vasalemma	31.10	31	O ₂ Kin	3.40	61.6	18.9	4.35	0.57	10.13	1.47	0.204	75
306	92.25	30	O ₂ Kin	4.15	59.9	20.2	3.86	0.43	10.00	2.18	0.209	
307	102.15	10	O ₂ Kin	4.87	57.5	18.9	4.10	0.41	9.97	3.12	0.200	
Vaemla	139.20		O ₂ Kin	3.60	61.4	20.1	4.20	0.55	8.65	2.90	0.261	
F-198	35.01	2	O ₂ Kin	6.79	54.6	19.2	3.62	1.22	8.11	3.96	0.219	71
3	68.70		O ₂ Kin	5.76	56.1	21.2	4.88	0.65	7.87	2.41	0.215	
H-222	87.80	70	O ₂ Kin	4.97	59.4	21.0	4.91	0.78	7.73	2.88	0.205	
Laeval	226.60	12	O ₂ Kin	4.47	57.8	19.9	5.01	0.53	7.50	3.64	0.230	81
D-8	163.95	20	O ₂ Kin	4.47	57.7	20.8	4.62	0.53	7.43	2.63	0.225	76
Kuressaare	368.50	40	O ₂ Kin	5.61	57.7	20.7	4.71	0.59	7.35	2.51	0.257	
Kärdla18	166.90	50	O ₂ Kin	5.19	57.7	21.9	4.71	0.69	6.97	2.51	0.229	
Ruhnu	650.00	20	O ₂ Kin	5.28	55.6	22.1	4.17	0.49	6.65	4.33	0.263	
Kärdla01	173.10	40	O ₂ Kin	6.04	58.0	22.4	5.14	0.69	6.52	2.70	0.198	
Laeval8	255.45	20	O ₂ Kin	4.45	59.3	21.5	4.37	0.52	6.91	3.45	0.227	75
Ristiküla174	424.40	30	O ₂ Kin	6.34	56.1	20.5	4.45	0.85	6.84	3.92	0.250	
Seliste173	398.00		O ₂ Kin	5.70	56.9	21.1	4.38	0.58	6.80	3.15	0.240	
Viki	329.95	50	O ₂ Kin	5.11	58.7	20.8	5.50	0.63	6.71	2.23	0.215	76
Taagepera	482.20	10	O ₂ Kin	6.49	54.8	23.9	3.47	0.54	6.01	3.10	0.33	
Valga	394.25	2	O ₂ Kin	8.76	51.5	29.7	2.18	0.72	4.10	2.74	0.471	
Samples from Latvia and Lithuania												
Kurtuvenai166	1092.70	?	O ₂ Kin?	6.00	54.5	24.5	3.5	0.52	5.77	4.45	0.370	
Aizpute41	1055.00	?	O ₂ Sin?	6.00	57.9	21.1	3.75	1.46	5.26	3.30	0.566	82
Aizpute41	1056.30	3	O ₂ Gre?	3.32	58.8	17.5	0.78	3.07	12.13	1.00	2.300	84
Vollen outcrop in Norway												
Vollen	Outcrop	95	O ₂ Kin	7.03	49.5	21.9	4.30	4.64	6.76	4.00	0.285	
Published data (Lashkovas, 2000; Thorslund, 1947; Bergström <i>et al.</i> , 1997)												
Piltene	1047.00	10	Caradoc	9.52	51.3	22.5	2.83	1.55	6.71	4.80	0.430	76
Kolka	693.00	10	Caradoc	9.77	50.1	20.8	2.99	3.28	5.95	4.20	0.190	72
Remte	1041.20		Caradoc	11.48	51.4	23.5	1.91	2.23	4.54	6.20	0.330	
Gusev	1542.50		Caradoc	11.71	48.1	28.5	1.06	2.86	4.08	3.80	0.330	81
Kinnekulle	Outcrop	180	O ₂ Kin	7.39	59.8	20.0	4.19	2.46	2.65	2.89	0.150	46–65
Röstanga	Outcrop	50	O ₂ Kin		53.6	25.1	2.80	0.70	6.35	1.74	0.440	85
Source magma composition from melt inclusions in quartz (Huff <i>et al.</i> , 1996)												
			O ₂ Kin		78.35	12.99	0.07	0.77	4.04		0.11	Na ₂ O (%) 2.27

by the sedimentary-facies distribution (Table 1). The SiO₂ contents are >60% in the shallow-shelf feldspar-rich varieties, decreasing to 50% in kaolinite-containing ash beds of the deep shelf, whereas Al₂O₃ behaves contrary to SiO₂. The Fe and Ca contents are relatively high in ash beds from the deep-shelf area, probably due to the small thickness of volcanic ash, which favors mixing with host sediments by bioturbation.

Interestingly, the CaO content is also greater in the Kinnekulle section (Sweden), probably because of the greater expandability of I-S than in other areas (Brusewitz, 1986, 1988).

XRD – whole-rock

The whole-rock mineralogical composition of the Kinnekulle bed agrees with the chemical variations. The

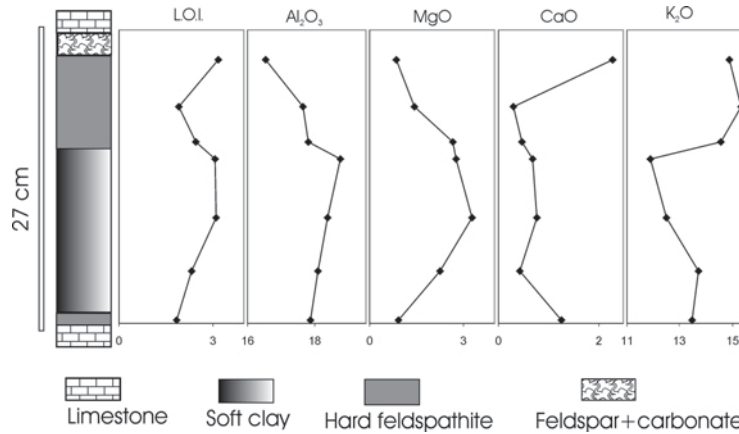


Figure 4. Vertical distribution of chemical components in the Kinnekulle altered volcanic ash section from Pääsküla.

composition of bentonite in shallow-shelf limestones is characterized by assemblages of I-S and K-feldspar (Figure 5). The K-feldspar content in feldspathized beds can be as much as 95% (upper portion of hard feldspathite in Pääsküla outcrop) but varies on average from 30 to 70% in Northern Confacies zone (Figure 6). The transition zone is characterized by mixed-layer I-S dominated assemblages with subdued K-feldspar (average 10–20% of the whole rock). In the deep-shelf zone (Central Confacies), with the lowest K_2O content, the bentonite whole-rock is of mixed-layer I-S and kaolinite composition with minor K-feldspar (<5%). The transition to kaolinitic (tonstein-like) composition is rather sharp, right at the transition–central zone boundary and in most cases the kaolinite appears in considerable amounts (>30%, Figure 6).

XRD – clay mineralogy

The composition of Kinnekulle bentonite is dominated by a nearly monomineral mixed-layered I-S mineral in the northern and transition zone, and by an I-S and kaolinite assemblage in the Central Confacies zone (Figure 7). The I-S in the studied samples is characterized by a highly illitic mixed-layer mineral with an illitic content of 69–77%. Bruswitz (1986, 1988) studied the composition of the I-S of the 1.8 m thick Kinnekulle bed at the Kinnekulle site in Sweden, and she established 45–65% illite layers in I-S. In Latvia and Lithuania, I-S of Caradocian bentonites contains 63–83% illitic layers (Lashkovas, 2000).

Most of the studied samples are of the same diagenetic maturity regardless of their position within the confacies zones, but there are differences in

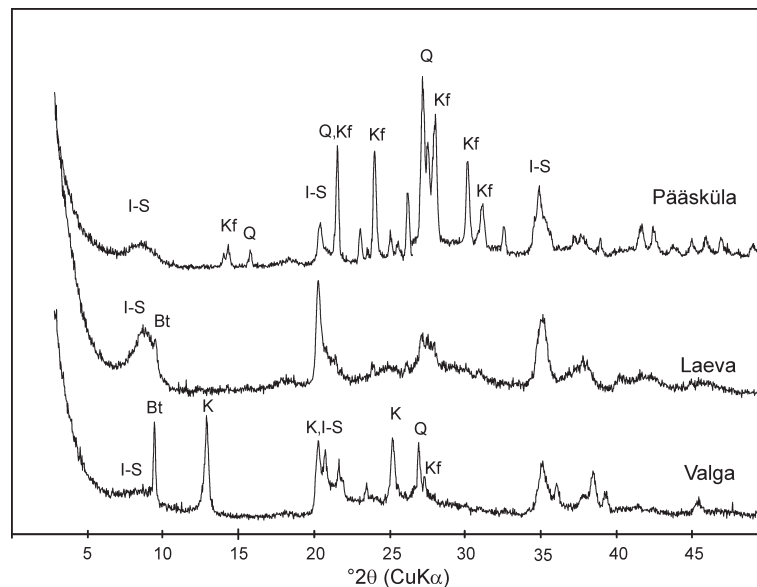


Figure 5. Whole-rock XRD patterns of Kinnekulle altered volcanic ash from different facies zones. The Pääsküla represents feldspathized bentonite in the northern Estonian Confacies. The Laeva represents I-S-dominated bentonite from the transition zone. The Valga sample represents a deep paleoshelf area in southern Estonia. For the sample locations, see Figure 1, and for the chemical compositions, see Table 1. Legend: I-S – illite-smectite, Kf – K-feldspar, Q – quartz, K – kaolinite, Bt – biotite.

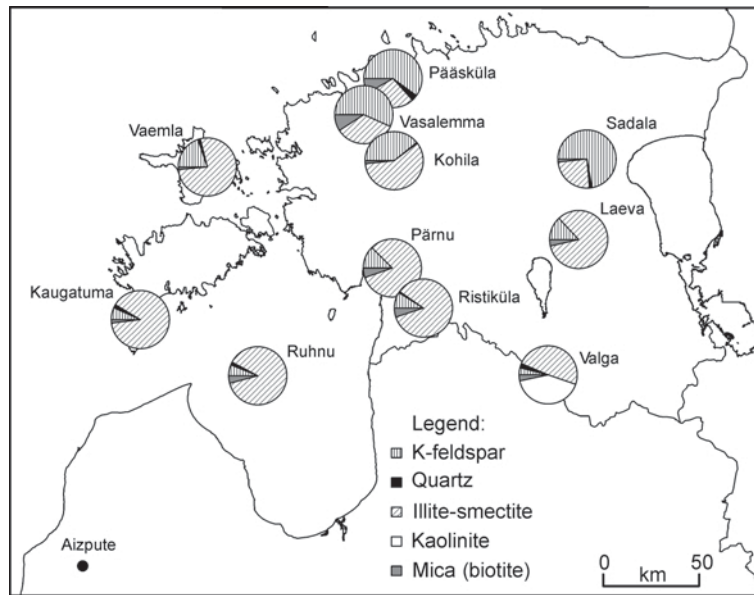


Figure 6. Whole-rock mineral composition of Kinnekulle altered volcanic ash through sedimentary facies.

structural arrangement of the smectitic and illitic layers in the mixed-layer mineral. According to the mixed-layer mineral models given by the Newmod program (Reynolds, 1984), the deep-shelf zone samples are characterized by mixed layering with the probability of long-range ordering type stacking-sequences (PSII.I) of 0.10–0.25, whereas the transition zone Kinnekulle

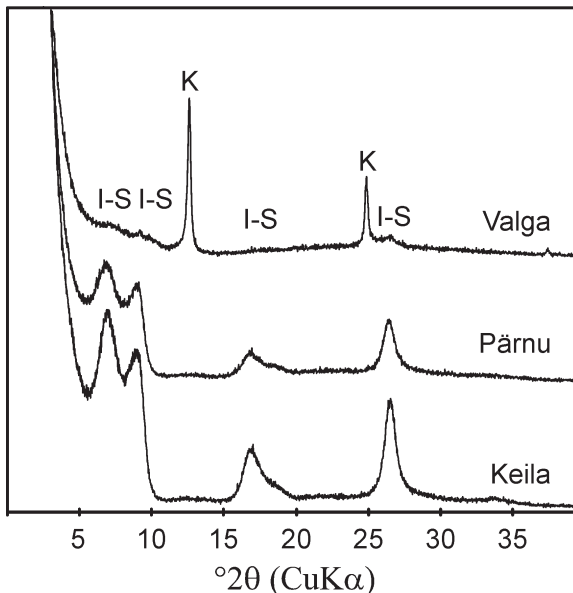


Figure 7. XRD patterns of the $<0.2 \mu\text{m}$ clay fractions (in an ethylene glycol-solvated state) from the Kinnekulle bed. The Keila sample is a feldspathized bentonite in the northern Estonian Confacies. The Pärnu sample is from the transition zone and the Valga sample represents a kaolinite-dominated deep paleoshelf. Legend: I-S – illite-smectite, K – kaolinite.

bentonite samples show PSII.I of 0.50–0.57. In the Northern Confacies the I-S shows the greatest probability of PSII.I type sequences of 0.60–0.77.

The simple two-component Newmod models, however, match experimental patterns only qualitatively and there are large discrepancies in peak shapes and intensities between experimental and calculated patterns (Figure 8). Indeed, a much better fit was obtained by assuming a three-component mixed-layer mineral using the MLM3C program (Plançon and Drits, 2000) (Figure 8). Compared to the Newmod models, the share of illitic layers in three-component minerals is about the same (70–78%), but the best fit was achieved by assuming 5–11% of high-charge smectite (vermiculite-like) layers in addition to fully expandable smectitic layers assuming R1-type ordering with the probability of a vermiculite-vermiculite sequence varying from 0.1 to 0.5.

There is no clear relationship with present burial depth and I-S diagenetic maturity. However, the kaolinitic samples show a somewhat greater content of illite layers in the mixed-layered mineral.

Petrography of magmatic phenocrysts

Coarse fractions (0.04–0.1 mm) rich in pyroclastic phenocrysts amount to a few per cent of Estonian K-bentonites. Petrographic observations show that most of the phenocrysts are fragmentary quartz, broken or hexagonal sanidine and biotite crystals. No visual signs of dissolution or recrystallization of these minerals are observed in Estonian I-S and authigenic feldspar-dominated ash beds. The XRD measurements revealed a $20\bar{1}$ reflection of K-Na-sanidine providing evidence of good preservation of this metastable mineral (Kiipli and Kallaste, 2002a). However, the sanidine was not

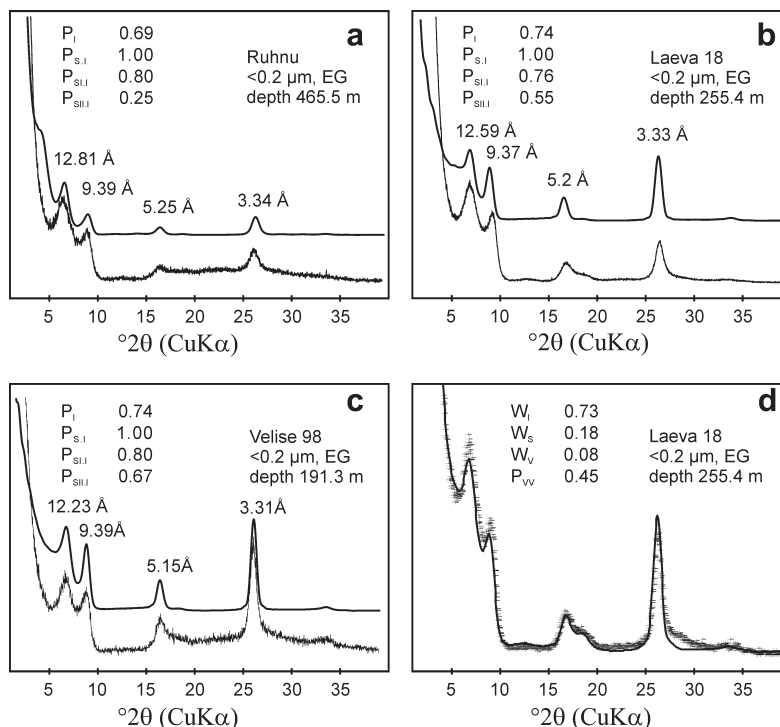


Figure 8. I-S experimental (lower traces) and calculated (upper traces) XRD patterns: (a,b,c) calculated using Newmod assuming two-component models and d (the same pattern as in b) using MLM3C assuming a three-component illite-smectite-vermiculite mineral. Note the considerably better fit of the three-component model between peak shapes and intensities compared to the two-component model.

preserved in the Oslo and Bornholm sections which have been influenced by elevated temperatures in late diagenesis (authors' unpublished observation).

Biotite from the Kinnekulle ash bed in Estonia was studied by Huff *et al.* (2002), and from the Silurian in Estonia by the present authors (unpublished). Both studies showed high K_2O contents 8.2–9.0% and 8.9–9.9%, respectively, indicating good preservation of that mineral.

Plagioclase, which is a common phenocryst in fresh volcanic rocks, has not been recorded in altered volcanic ash beds in the Baltic Paleobasin. If it was present initially it evidently was dissolved and/or recrystallized into authigenic K-feldspar and clay minerals.

In deep-shelf kaolinite-containing bentonites of Lithuania (Lapinskas, 1965) and Gotland (Snäll, 1977), biotite and feldspar have been partially or completely replaced by kaolinite. In K-bentonites from Bornholm, biotite has been replaced by chlorite (authors' observation).

DISCUSSION AND CONCLUSIONS

The changes in the bulk composition of altered volcanic ash in concordance with sedimentary facies in the Baltic Paleobasin suggests the early formation of the main authigenic silicate assemblages controlled by environmental variables and host-rock composition at

the time of deposition and during shallow burial in the sediments. The pyroclastic material deposited in a carbonate-dominated (normal) shallow shelf (Northern Confacies zone) were predominantly transformed into an association of K-feldspar and clay (smectite-to-illite transformation series). In transition and central zones, where shallow-shelf, normal, argillaceous carbonate facies are gradually changed to carbonate-rich shales, the volcanic glasses were replaced by clay minerals. The transition zone is characterized by dominant illitic I-S mixed-layer material and the deepest-shelf zone by I-S and kaolinite assemblages.

In the marine environment, the formation and stability of authigenic silicates is primarily controlled by variation in pH and dissolved silica activity (Garrels and Christ, 1965; Helgeson and Mackenzie, 1970; Velde, 1985). In the upper 1000 m of the ocean, the pH varies from 8.4 at the surface to 7.4 in an organic matter remineralization zone at >200 m deep (Park, 1968; Bearman, 2001). However, greater values in surface waters can result from intensive primary bioproduction removing CO_2 from water. Also, in shallow waters, dissolution of unstable fresh carbonates consumes H^+ from sediment pore-waters raising the pH and accordingly the K^+/H^+ ratio, favoring incorporation of cations into silicates. Below the mixing zone in the oceans, the pH of seawater is reduced to 7.4 due to the release of CO_2 *via* remineralization of reducing organic matter.

Within these pH ranges the other important variable is the activity of dissolved silica, which in geochemical systems controls the feldspar and/or clay mineral nucleation during devitrification of volcanic glass (Kastner and Siever, 1979) whereas the K-feldspar nucleation is favored at high pH and silica activities. Huff *et al.* (1996) analyzed Kinnekulle source magma composition from glass inclusions in pyroclastic quartz (Table 1) and their calculations of gains and losses during the devitrification of volcanic glass showed 50% loss of silica, which suggests sufficient silica source from volcanics. On the other hand, the pelagic clay can efficiently adsorb the dissolved silica depending on pH, ionic strength of pore fluid and mineral composition of the clay (Siever and Woodford, 1973), thus lowering the silica activity below the K-feldspar nucleation limit.

The observed compositional variation of the Kinnekulle bed between different facies zones corresponds well to the water depth within the Baltic Paleobasin (see Figures 1, 2). In limestones deposited in a shallow shelf at relatively high pore-water pH and silica activity, the pyroclastic material was devitrified and recrystallized preferentially into a feldspar-type phase. The increased pelagic clay content in host rocks towards deeper parts of the shelf and presumably the lower pH have resulted in clay-dominated devitrification products. The feldspathization of the pyroclastic beds can be also controlled at high silica concentrations by precipitation of kinetically preferred amorphous silica (opal-CT) (Kastner *et al.*, 1977). This is well demonstrated by frequent records of chertification below thick ash beds (Grim and Güven, 1978) and which is also established below the Kinnekulle bed in sections on west Estonian islands which are dominantly of I-S composition. The common occurrence of chert below and rarely above ash beds points to the early dissolution and recrystallization of volcanic ash on the seafloor before the burial.

The kaolinite formation in clay-rich altered beds is probably controlled by pH variation due to decomposition of falling organic matter in the water column and in deep-shelf, fine-grained terrigenous mud, which reduces the pH, favoring the formation of kaolinite over smectitic-illitic phases. The deepest parts of the wide Paleozoic shelf seas could have been some hundreds of meters deep, which was sufficient for the formation of relatively low-pH bottom waters. In contemporary oceans, low pH, accompanied by a low oxygen zone, occurs in the upper part of the continental slope where sediments are spread only sporadically. Berry *et al.* (1989) and Railsback *et al.* (1990) proposed the concept of anoxic salinity-stratified Paleozoic oceans, therefore some differences in the chemistry of the contemporary and Paleozoic oceans cannot be excluded either (Lowenstein *et al.*, 2003). Moreover, in the deep-shelf area we can expect long-lasting contact with open seawater, as the sedimentation rate of the host sediment is low. This further promotes loss of silica and the formation of kaolinite. A model for volcanic ash alteration in submarine weathering on the seafloor, depending on environmental variables during sedimentation and early diagenesis is presented in Figure 9.

Authigenic K-feldspar is a common accessory mineral in carbonates, preferably in association with illite and chlorite instead of other clay minerals (Kastner, 1971). Authigenic K-feldspar is also a typical low-temperature alteration product, formed after volcanic ash in terrestrial and marine environments (Sheppard and Gude, 1968, 1973; Kastner, 1971). The formation of K-feldspar is thermodynamically feasible at low temperature from seawater and interstitial waters similar in composition to seawater whereas at high pH the seawater can be considered as the main source of K for the formation of K-feldspar (Kastner and Siever, 1979). Also, acidic magmas contain enough K to form highly

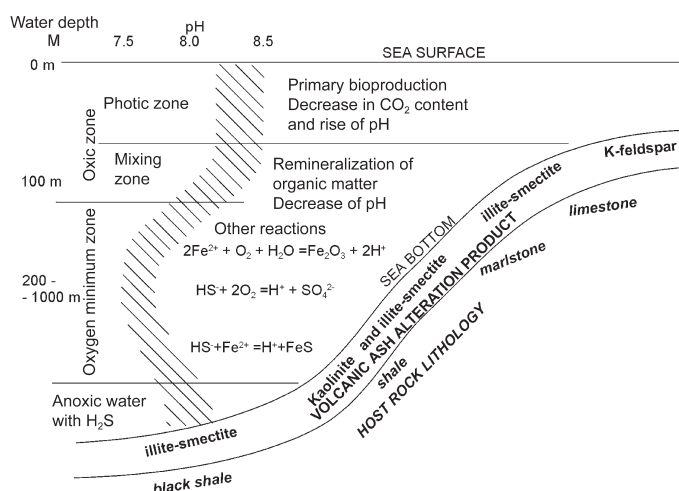


Figure 9. Model explaining the formation of authigenic silicates from volcanic ash by submarine weathering in the Ordovician shelf sea. The dashed area represents pH changes in the vertical water column.

illitic I-S after a large loss of silica (Huff *et al.*, 1996) and volcanic glass can be considered as a significant source of K for K-feldspar as well.

The feldspathite layer of even thickness from the lower part of the ash bed at the Pääsküla site suggests that the contact of ash with carbonate sediment below stimulates the formation of K-feldspar instead of I-S. The upper feldspathite layer of uneven thickness points to a variable chemical environment within the upper part of the bed at the time of feldspar formation. The patchy sedimentation of the overlying lime mud layer probably created a contact with lime material earlier in some locations and later in others. We can assume that fresh carbonate sediment overlying the bed is chemically more active than the underlying older sediment, increasing the pH of pore waters through dissolution of aragonite particles. This could explain locally more intensive feldspar formation in the upper part of the ash bed. Interestingly, the feldspar-rich altered ashes occur most frequently in the north-western part of the shallow shelf ramp, where the sedimentation rate was the greatest in the studied area, as indicated by sediment thickness variation between K-bentonite layer complexes (Nemliher and Ainsaar, 2002).

Unusually K-rich Ordovician K-bentonites and feldspathized bentonite beds are known in the Mississippi Valley area, USA (Hay *et al.*, 1988). However, Hay *et al.* (1988) associated feldspathization and illitization of these beds by three episodes of short-lived intrusion of hot saline brines in early Devonian to Permian. Similarly, Elliot and Aronson (1987) explained the illitization of highly illitic, but shallowly buried K-bentonites in the southern Appalachian Basin by hot fluid expulsion coincident with the Alleghanian orogeny in late Carboniferous to Permian.

The low thermal maturity of the organic material in the Baltic Paleobasin suggests only shallow burial of the sediments and excludes heating by large-scale hot brine intrusion. Moreover, the compositional variation of Caradoc and Llandovery altered ash beds occurring closely in sections in the Aizpute and Ruhnu drill-cores shows that in the Caradoc section, both the feldspathite and clay-type K-bentonites are lying at a vertical distance of 1.5 to 3 m, whereas the carbonate host rock contains feldspathite and the argillaceous carbonate host rock clayey K-bentonite. In the Llandovery of the Ruhnu core, I-S, kaolinite- and feldspar-rich bentonite beds occur within an interval of 5 m, which does not support bentonite alteration by intrusion of secondary fluids that should have resulted in uniform or similar composition of the beds. Also, selective feldspathization of these bentonites due to different host-rock permeability seems improbable here due to the low porosity (1–4%) of host limestones. The argillaceous limestone (wackestone with micritic matrix of 60–70%) of the Caradoc in the Northern Confacies zone is considered as a local aquitard. The Ordovician and Silurian carbonate rocks

in Baltic Paleobasin are modified by late diagenetic dolomitization (Vingisaar and Taalman, 1974; Kiipli, 1983). However, on the regional scale, the limestones are converted to cavernous dolomites near the lower and upper contacts of carbonate rocks with Lower Ordovician sandstones below and Middle Devonian sandstones above. The thickness of the dolomitized contact zone varies from a few meters to 15 m at the lower contact and to 30 m at the upper contact (Vingisaar and Taalman, 1974). Dolomitization also occurs in vertical, tectonically crushed zones. The width of these zones is up to some hundreds of meters. The studied Kinnekulle ash bed lies 40–70 m above the lower contact of carbonates and sandstones, being well out of the reach of the dolomitizing fluids. Our sample set from the Kinnekulle bed does not include altered ashes hosted by dolomites. The influence of late diagenetic processes including intrusion of hot fluids cannot be excluded at the western margin of the basin in Scandinavia in the vicinity of the Caledonian thrusts and Permian intrusives in the Scane-Oslo belt where we observe the increase in the K₂O content in the bentonite beds.

The isotopic age of K-feldspar in these beds is not known. The K-Ar ages of I-S fine clay fractions (<0.2 µm) of the Kinnekulle bed in the northern Baltic Paleobasin scatter from late Silurian to early Carboniferous, 420–357 Ma (Kirsimäe *et al.*, 2002; K. Kirsimäe and P. Somelar, unpublished data, 2006), which coincides with the maximum burial period (maximum up to 1–1.5 km) of these sediments. The large scatter of K-Ar ages in the northern part of the basin suggests a slow, long-lasting conversion of smectite to I-S at relatively low diagenetic temperatures from the Ordovician to the present, as suggested by Kirsimäe *et al.* (2002), rather than in a short illitization episode. The K-Ar ages of I-S in Silurian and Ordovician bentonites in the deeply (>2 km) buried southern extension of the Baltic Paleobasin in Pomerania, northern Poland are 366–368 Ma and 370–389 Ma, respectively (Środoń and Clauer, 2001). The illitization occurred there in much less time, but the difference in ages of Silurian and Ordovician beds there does not support illitization by intrusion of short-lived, basin-wide brines.

From the relationships described, we conclude that altered volcanic ash, represented by a laterally changing association of K-feldspar, I-S and kaolinite in well preserved marine Ordovician sediments of Baltic States and Scandinavia is a sensitive environmental indicator reflecting variations in pH, host-rock composition and the sedimentation rate during its deposition and initial transformation. The principal silicate composition of the bentonite is determined by environmental conditions during initial devitrification of pyroclastics and the bentonites preserve it through diagenetic processes (*e.g.* smectite-to-illite transformation) and the compositional

variations can be used for paleogeographic reconstruction of ancient environments. The depths of the Ordovician sea in the Central Baltoscandian Confacies reached at least a few hundred meters allowing the distribution of pH and oxygen minimum zones in the deep waters of shelf. For correct use of altered ash in the reconstruction of paleoenvironmental conditions, all possible factors must be distinguished: magmatic, sedimentary, early and late diagenetic processes, potentially influencing the formation of the chemical and mineralogical composition.

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