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Early diagenesis
of Ordovician and Silurian Bentonites
in the Northern Baltic Palaeobasin

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LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following papers, in the text referred to by their Roman numerals. The papers are reprinted by kind permission of the publishers.

- I Hints, R.**, Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2008). Multi-phase Silurian bentonites in the Baltic Palaeobasin. *Sedimentary Geology*, 209, 69–79.
- II Hints, R.**, Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2006). Chloritization of Late Ordovician K-bentonites from the northern Baltic Palaeobasin – influence from source material or diagenetic environment? *Sedimentary Geology*, 191, 55–66.
- III Kiipli, T.**, Kiipli, E., Kallaste, T., **Hints, R.**, Somelar, P., Kirsimäe, K. (2007). Altered volcanic ash as an indicator of marine environment, reflecting pH and sedimentation rate – example from the Ordovician Kinnekulle bed of Baltoscandia. *Clays and Clay Minerals*, 55, 177–188.

AUTHOR'S CONTRIBUTION IN PAPERS

- Publication I: The author was primarily responsible for planning original research, bentonite whole-rock mineralogical analysis, interpretation and synthesis of analytical data and the writing of the manuscript.
- Publication II: The author was primarily responsible for planning research, mineralogical analysis and interpretation of analytical results, synthesis of different analytical results and the writing of the manuscript.
- Publication III: The author contributed to data collection and mineralogical analysis and to the writing of the manuscript.

I. INTRODUCTION

Bentonites are altered volcanic ash beds, which were deposited in aquatic environment and have gone through chemical and physical changes during diagenesis. The mineral and chemical composition of bentonites has been used to study different aspects of the evolution of tephra beds – from the type of the source magma (e.g. Batchelor, 2003) to late diagenetic *in situ* mineralization processes (e.g. Nadeau and Bain, 1986). Bentonites are widely used in industry and in different environmental technologies, e.g. production of drilling suspension and disposal of nuclear waste. The typical bentonites are homogeneous clayey beds consisting of authigenic dioctahedral clay minerals, such as discrete smectite or illite, or metastable mixed-layer illite-smectite (I/S) (Meunier, 2005). In geologically young beds smectite is the prevailing phase, but during progressive burial and diagenesis, smectite tends to transform into illite through a series of mixed-layer I/S phases.

The altered ash beds that have evolved to different levels of maturity are referred to using slightly different names. For the Palaeozoic bentonites of illitic or illitic-smectitic composition, the terms “metabentonites” (Ross and Hendricks, 1945) and “K-bentonites” (Weaver, 1953) have been employed to emphasize their difference from younger smectite-dominated ash beds.

Illitization of bentonites, one of the most studied, but still least understood transformations in old tephra beds, is conventionally regarded as a temperature-controlled process (Środoń, 1999). Various diagenetic and low-metamorphic settings demonstrate correlation between increase in burial depth, i.e. temperature, increase in illite layers in I/S and rise in the ordering of smectite and illite layers in I/S crystallites (e.g. Pollastro, 1993). Therefore I/S-rich beds such as bentonites are also promising for research of overall geothermal history and burial path of sedimentary complexes (e.g. Środoń *et al.*, 2006).

Bentonites are usually characterized by rather homogeneous smectite- and/or I/S-dominated composition (Meunier, 2005). However, their composition can be largely variable with a number of major phases (e.g. Christidis *et al.*, 1995) and the bentonite beds can exhibit chemical and mineralogical zonation (e.g. Altaner *et al.*, 1984). The occurrence of authigenic minerals such as zeolites, potassium feldspar, kaolinite, quartz, chlorite and chlorite mixed-layer phases has been reported from different altered ash settings. Kaolinite-dominated altered ash beds, or tonsteins, occur in terrestrial settings, particularly in coal basins (Bohor and Triplehorn, 1993). Authigenic kaolinite is also reported from the Silurian K-bentonites of British Isles and Scandinavia as a common minor authigenic phase (Huff *et al.*, 1998). K-feldspar-enriched assemblages are typical of beds formed from siliceous ashes deposited in alkaline environments (e.g. Hay and Guldman, 1987). Zeolites are among the most common products of alteration in terrestrial vitric pyroclastic beds (Hay, 1978). Chloritic mixed-layer phases occur in lacustrine and sabkha deposits, as well as in metasomatically changed pyroclastic beds (e.g. Chamley, 1989).

Various causes – different source material, composition of sea or interstitial water, character of host rock, bacterial activity and metasomatic transformation –

have been put forward to explain the appearance of these authigenic minerals from primary ash. However, the initial stages of the volcanic ash transformation into smectite-rich bentonite are still poorly understood (Meunier, 2005).

The source material of bentonites, vitric volcanic ash, is produced as a rule by plinian or co-ignimbrite type of volcanic eruptions of felsic composition (e.g. Huff *et al.*, 1996). The ash is thermodynamically unstable in the earth's surface environments and starts to devitrify and recrystallize during the initial stages of its burial. The recrystallization of original amorphous matter into new *in situ* early diagenetic minerals is accompanied by intensive leaching of mobile elements, leading to gradual modification of the initial composition of ash. The alteration of bentonite depends on interactions of volcanic ash with seawater, enclosing rocks/sediments, interstitial water and organic matter and on the activity of microorganisms (e.g. Bohor and Triplehorn, 1993; Compton *et al.*, 1999; Jeans *et al.*, 1997).

Clays, especially the detrital clay mineral assemblages, which reflect the type of continental weathering, are considered as consistent proxy indicators for palaeoclimatic as well as palaeoceanographic reconstructions (e.g. Singer, 1984; Chamley, 1989; Hillier, 1995; Środoń, 1999; Meunier, 2005). The authigenic clay mineral–feldspar–zeolite paragenesis of continental or marine sediments can also reflect the environmental conditions which prevailed during the deposition and early diagenetic evolution of these sequences (e.g. Kastner and Sievers, 1979; Kastner, 1981; Christidis *et al.*, 1995; Aoki and Kohyama, 1998; Karpoff *et al.*, 2002). Nevertheless, in geologically older tephra beds, like Palaeozoic K-bentonites, primary diagenetic mineral assemblages and textures of devitrified volcanic ash have been replaced in the course of progressive diagenesis, and their synsedimentary and early diagenetic transformation is therefore difficult to assess (e.g. Meunier, 2005).

The lower Palaeozoic sedimentary sequence of the Silurian and Ordovician carbonate rocks in the northern part of the Baltic Palaeobasin includes numerous unmetamorphosed K-bentonite beds (see for a review Bergström *et al.*, 1992, 1998) the composition of which varies largely in stratigraphic cross sections as well as laterally (Hints *et al.*, 2006 – Paper II; 2008 – Paper I; Kiipli *et al.*, 2007 – Paper III). The high compositional variability of these bentonites, containing kaolinite and K-feldspar besides smectite (montmorillonite)-type clay minerals, was noted and described already at the end of the 1950s (Jürgenson, 1958; Utsal and Jürgenson, 1971; Rateev and Gradusov, 1971).

Due to the overall tectonical stability of the northern Baltic area throughout the Phanerozoic, the burial-geothermal history of early Palaeozoic bentonites of the region is rather exceptional. The whole lower Palaeozoic complex has probably never been buried deeper than 2 km (Kirsimäe and Jørgensen, 2000) and the burial temperatures were kept, at least in long term, well below 100°C (Kirsimäe *et al.*, 1999). Compared to deep burial settings, much less is known about the behaviour of siliceous systems (e.g. bentonites) passing through long-term shallow burial diagenesis, whereas slow compaction is accomplished by sluggish reaction rates at low temperatures. If the evolution of bentonites was

driven at generally low temperatures and the bentonites were not overprinted by late diagenetic or low-grade metamorphism recrystallization, the final mineral assemblages have potentially preserved information of those factors which controlled early diagenetic pathways of ash transformation.

This thesis focuses on the mineral and geochemical composition of the early Palaeozoic bentonites from the northeastern part of the Baltic Palaeobasin, which are characterized by largely variable multiphase mineral assemblages (Fig. 1).

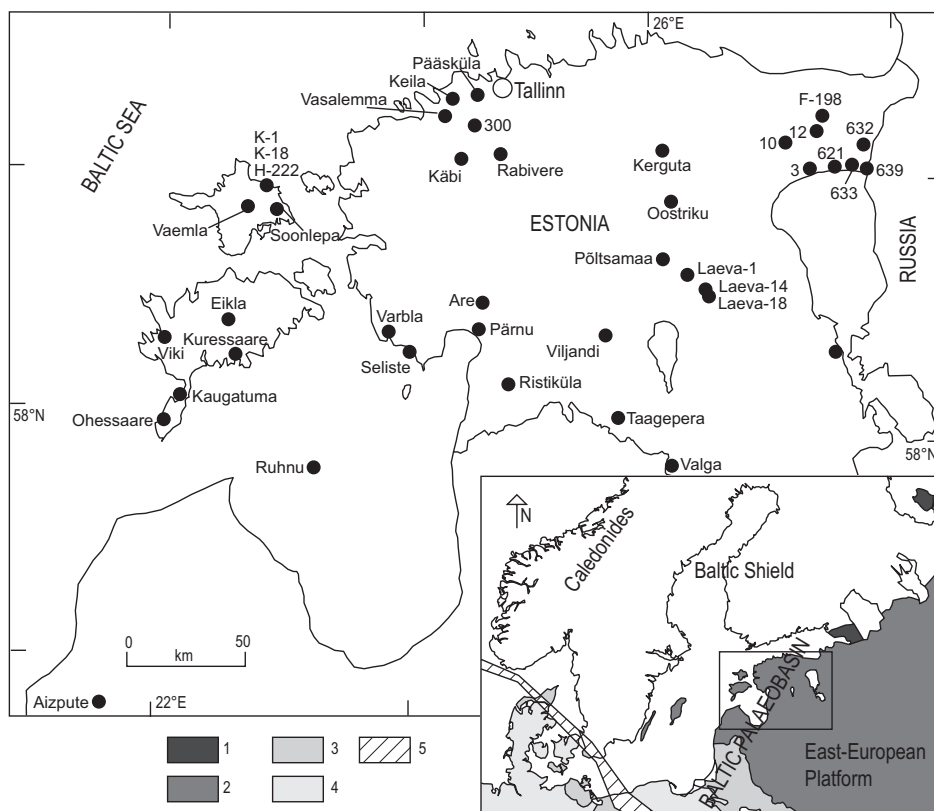


Figure 1. Schematic map of the study area showing location of the investigated drill cores and Pääsküla outcrop. 1 – Ediacaran sediments, 2 – Palaeozoic sediments, 3 – Mesozoic sediments, 4 – Cenozoic sediments; 5 – Tornquist lineament.

The aim of the study is:

- (1) to understand the processes controlling the whole rock compositional variability of these bentonites;
- (2) to reveal how the diagenetic evolution of the composition of bentonites is related to the original composition of the pyroclastic material and water–pyroclastics–host-rock (sediment) reactions at the time of deposition, during initial devitrification and early diagenesis.

2. GEOLOGICAL BACKGROUND

The study area lies within the limits of the Baltic Palaeobasin, which was a large epi- to pericratonic marine basin covering the areas of the East European Platform on the outskirts of the Baltica continent in the early Palaeozoic (Fig. 1). The sedimentary sequence of the Ordovician and Silurian deposits in the northern part of the Baltic Palaeobasin has been systematically studied and discussed in numerous works, e.g. Männil (1966), Kaljo (1970), Rõõmusoks (1970), Jaanusson (1976), Nestor and Einasto (1997 and references therein).

During the Ordovician and Silurian the main study area was a shallow-water peripheral part of the palaeobasin characterized by a slow sedimentation and subsidence rate. The sedimentary record is not continuous (Nestor and Einasto, 1997). The sediment succession in Estonia embraces unmetamorphosed Late Ediacaran to Late Devonian carbonate and siliciclastic deposits (Raukas and Teedumäe, 1997). The whole homoclinal section is gently tilted to the south and the thickness of the Palaeozoic sedimentary complex above the crystalline Proterozoic bedrock varies from 20 m in northwestern Estonia to 800 m in southern Estonia. Southwards, on the territory of Latvia, towards the eastern central part of the palaeobasin, the burial depth of the lower Palaeozoic complex increases further. The Palaeozoic complex in Estonia and northern Latvia is mainly covered by glacial Quaternary deposits of variable thickness.

Estonia is located on the southern flanks of the Baltic Shield – a stable Precambrian nucleus of the Baltica continent where major tectonical activity was largely diminished by the beginning of the Phanerozoic (Nikishin *et al.*, 1996). The extreme stability of the region is confirmed by the Fennoscandian apatite fission track data (Hendriks *et al.*, 2007). The shallow burial and low diagenetic temperatures for the Estonian Palaeozoic complex are indicated by finds of unaltered organic and phosphatic remains in sedimentary beds (Nehring-Lefeld *et al.*, 1997; Talyzina, 1998). The conodont alteration index (CAI) for Estonian lower Palaeozoic sediments is 1–1.5, suggesting maximum diagenetic temperatures from 50 to 80°C (Männik and Viira, 1990). The occurrence of very old (>500 My) unconsolidated plastic “Blue Clay” in the Lower Cambrian of Estonia also points to moderate diagenetic temperatures. According to Kirsimäe *et al.* (1999), these Cambrian rocks have undergone diagenetic alteration below 50°C, which suggests a maximum burial depth less than 1.5 km. The maximum burial depth was apparently achieved by the end of the Devonian or the beginning of the Carboniferous. The complex was stabilized under these conditions by the Permian (Kirsimäe *et al.*, 1999), when uplift started, presumably simultaneously with the extensional tectonic movements in the region (Puura *et al.*, 1999). During most of the Mesozoic and Cenozoic, Estonia was a stable terrestrial area with minimal erosion. In the Neogene, however, several ice ages occurred in Baltoscandia and glaciers removed the weathered upper part of Palaeozoic rocks.

The sedimentary succession of Estonia and the neighbouring areas in Baltoscandia contains numerous Ordovician and Silurian bentonites. These beds

are characterized by lateral persistency and limited vertical thickness (from a few millimetres up to 2 m) and mainly I/S-dominated composition. Bentonites are mostly connected with particular stratigraphic levels, where the beds commonly form distinct series composed of a number of closely set layers (e.g. Jürgenson, 1958; Lapinskas, 1965; Rateev and Gradusov, 1971; Utsal and Jürgenson, 1971; Snäll, 1976; Bergström *et al.*, 1992, 1995). Main bentonite series are found in the Upper Ordovician (Sandbian and Katian stages), Llandovery (Telychian Stage) and Wenlock (Sheinwoodian Stage) (Bergström *et al.*, 1992, 1995, 1998). Some of the most prominent beds, like the Kinnekulle Bed in the Upper Ordovician (Bergström *et al.*, 1995) and the Osmundsberg Bed in the Llandovery (Bergström *et al.*, 1998; Huff *et al.*, 1998), have been correlated across the sedimentary basin and serve as excellent chronostratigraphic markers for event-stratigraphic, palaeoecological and sedimentological studies. Moreover, Huff *et al.* (1992) proposed a transatlantic correlation for the Kinnekulle Bed with the Millbrig Bentonite in North America and suggested that the corresponding volcanic eruption and ash-fall had been one of the largest during the Phanerozoic.

The studies of the whole-rock trace element composition and phenocrysts of bentonites, and melt inclusions in quartz (Huff *et al.*, 1996) confirm that the source magma of the Baltoscandian Ordovician and part of the Silurian bentonites has apparently been of calc-alkaline type, predominantly rhyolitic or dacitic in composition. The character of magma points to the continental-crust-based, destructive plate margin setting (Huff *et al.*, 1992). The volcanic source area(s) of ash clouds were probably situated somewhere between the Baltica and Laurentia continents, inside the closing Iapetus Ocean. However, many Silurian bentonites in the region show a different thickness distribution pattern, diverse immobile trace element geochemistry (Bergström *et al.*, 1992) and more alkaline affinity (Batchelor and Jeppsson, 1999), likely suggesting a different provenance. The potential tectonomagmatic setting might have been the Tornquist–Teyseyre Zone (Batchelor and Jeppsson, 1999; Torsvik and Rehnström, 2003), where closure of the Tornquist Sea between Avalonia and Baltica was finalizing in the Silurian.

After their first description by Jaanusson (1948), the general lithological and chemical outlines and distribution of Estonian Ordovician and Silurian bentonites were discussed by Jürgenson (1958, 1964). Basinal-scale correlation of Estonian bentonite beds was first considered in detail by Männil (1958). Subsequently, the distribution pattern of bentonites and possible direction of source volcanoes as well as the mineral composition of Caradoc ash beds were studied by Vingisaar (1972). During the 2000s a number of papers have been published concerning the local and regional stratigraphic correlation of bentonite beds in Estonia, based on the chemical fingerprinting of trace elements and pyroclastic sanidine (Kiipli *et al.*, 2001; Kiipli and Kallaste, 2002, 2006; Kallaste and Kiipli 2006; Kiipli *et al.*, 2006; Kiipli *et al.*, 2008a, 2008b). The various aspects of the mineralogy and chemistry of Palaeozoic bentonites in the northern Baltic Palaeobasin have been addressed by Jürgenson (1958, 1964),

Rateev and Gradusov (1971), Utsal and Jürgenson (1971), Vingisaar and Murnikova (1973), Bergström *et al.* (1992, 1995), Huff *et al.* (1996, 1998), Kiipli and Kallaste (1996), Kiipli *et al.* (1997, 2001, 2007 – Paper III, 2008c), Kirsimäe *et al.* (2002), Hints *et al.* (2006 – Paper II, 2008 – Paper I).

The bentonite record in Estonia is not as complete as in the Scandinavian succession, probably because the shallow-water high-energy environment prevailed in this part of the basin and the sedimentary sequence contains many hiatuses (Kiipli and Kallaste, 2006). This could also be related to the palaeogeographic location of Estonian territory far from active volcanic settings (e.g. Bergström *et al.*, 1992; Huff *et al.*, 1996) and therefore possibly near the maximum lateral reach of distal ash clouds. The maximum thickness of the Ordovician bentonites in the northern part of the Baltic Palaeobasin has been recorded on Baltic Sea islands, west of the Estonian mainland. The thickness of the most prominent Ordovician ash bed, the Kinnekulle Bentonite, reaches up to 60 cm in the drill cores of NW Hiiumaa Island. In general, the overall thickness of Estonian Ordovician bentonites decreases eastwards and they disappear from sequences in Ingria (northwestern Russia) (Vingisaar, 1972; Bergström *et al.*, 1995).

The Silurian bentonites, however, show a more heterogeneous areal distribution (Jürgenson, 1964; Kiipli and Kallaste, 2006). The sequences with an extensive bentonite record are known only in Baltic Sea islands, and west-southwest of the Estonian mainland. The number of Silurian bentonites is highest in the Ohessaare core, on Saaremaa Island, where Jürgenson (1964) described more than 50 bentonite beds. In the other parts of the Estonian mainland the Silurian deposits are missing (northern Estonia) or the succession is discontinuous with gaps in bentonite record (central Estonia) (Kaljo, 1970). The outcrops of Ordovician and Silurian bentonites in Estonia are limited in number, however, the bentonite beds could be found in hundreds of drill cores penetrating the lower Palaeozoic deposits.

3. MATERIALS AND METHODS

The material investigated came from 40 drill cores and one outcrop penetrating the lower Palaeozoic sedimentary sequence in the northern and central part (Estonia and northern Latvia) of the Baltic Palaeobasin (Fig. 1). Altogether nearly 120 whole-rock samples from the Ordovician and Silurian bentonites were studied by means of X-ray fluorescence analyses (XRF), X-ray diffraction analyses (XRD) coupled with computer modelling and scanning electron microscopy (SEM).

The sampled beds and sequences were selected in order to give an overview of lateral as well as bed-to-bed variability of the lower Palaeozoic bentonites in the region. The lateral compositional variability of bentonites was studied in the Kinnekulle Bed and three bentonite beds in the Pirgu Stage. The Kinnekulle Bed was sampled besides drill cores also in the outcrop at Pääsküla, where the samples were taken through the vertical profile of the bed. Silurian bentonites were studied in the Ruhnu and Ohessaare drill cores (see Fig. 1 for locality map), presenting a most complete record of Silurian stratigraphy and bentonites in this part of the Baltic Palaeobasin. The bentonite samples involved both plastic and non-plastic (feldspathized) varieties of altered ash.

The bentonite whole-rock samples and clay fractions were studied for mineral composition by means of X-ray diffraction. The samples were fractionated by standard sedimentation procedures and the Sr-, Mg- or Ca-exchanged <2 µm size fractions were studied, as oriented clay aggregates, in air-dry and ethylene glycol solvated state. Unoriented mounts were made of powdered and homogenized representative whole-rock samples. The whole-rock and clay fraction composition of all samples was studied by means of powder X-ray diffraction, employing a DRON-3M and an HZG-8 diffractometer, using CuK α and CoK α radiation, respectively.

The quantitative mineral content of powdered and unoriented whole-rock preparations was measured using the Rietveld-based code Siroquant-2.5TM (Taylor, 1991). Qualitative and quantitative estimation of illite, kaolinite and smectite in mixed-layer I/S and chlorite-smectite (corrensite) mineral was modelled by the computer codes NEWMOD (Reynolds, 1985), and MLM2C and MLM3C (Plançon and Drits, 2000). The developed models were principally the same, but the best fit was observed in MLM2C/MLM3C models. The experimental XRD profiles were compared with the calculated structural models using the trial-and-error procedure until an optimum fit was achieved. The profiles were fitted in the 2–40°2 θ range considering given instrumental and experimental factors and the orientation factor, mass adsorption coefficient and composition of structural layers suggested by Moore and Reynolds (1997).

Scanning electron microscopy observation of freeze dried and gold coated bentonite samples was carried out with the instruments JEOL JSM-840A, Zeiss DSM940 SEM and LEO-EVO.

The chemical composition of main elements in selected whole-rock samples was analysed in Li-tetraborate fused pellets by the XRF method in the laboratory of the Institute of Geology, Tallinn University of Technology with the VRA-30 spectrometer equipped with a chromium X-ray tube. For calibration, CRPG reference materials (Govindaraju, 1995) were used.

4. RESULTS AND DISCUSSION

4.1. Chemical and mineral composition of bentonites

4.1.1. Whole-rock chemical composition

The chemical composition of the Ordovician and Silurian bentonites of the northern Baltic Palaeobasin is comparable with typical K-bentonites found in the well-studied Scandinavian localities (e.g. Huff *et al.*, 1996, 1998; Batchelor and Jeppsson, 1999). However, the variability of major element chemistry is much higher in Estonian and Latvian sequences. The greatest difference is the occurrence of varieties rich in potassium and silica but poor in aluminium, in the northern and central Estonian settings (Jürgenson, 1958, 1964; Kiipli *et al.*, 2007 – Paper III). Also, bentonites with a high Al/Si ratio were described from southern Estonia and northern Latvia, where Al-rich varieties are particularly abundant in upper Llandovery–lower Wenlock sequences (Hints *et al.*, 2008 – Paper I). The variation of major components of Ordovician and Silurian bentonites concurs with the changes in host-rock character in different facies zones (Kiipli *et al.*, 1997, 2007 – Paper III). The Kinnekulle Bed in northern and northwestern Estonia, hosted in normal marine shallow-shelf limestones, contains 7.5–13.8% K₂O. In argillaceous limestones of central and southern Estonia the same bed contains 6–7.5% K₂O, whereas in deep-shelf marlstones and shales of Latvia and Lithuania the bed has 4–6% K₂O (Kiipli *et al.*, 2007 – Paper III). The major element composition of bentonites varies markedly also between different closely lying beds (vertical distance <5 m). For instance, in the Adavere Stage of the Ohessaare core the K₂O content fluctuates from 4 to 13% (Hints *et al.*, 2008 – Paper I). Furthermore, a number of thicker beds, like the Kinnekulle Bed, exhibit vertical within-bed zonation (Kiipli *et al.*, 2007 – Paper III), with the potassium content generally decreasing from the periphery towards the centre of the beds. Moreover, the Ordovician bentonites of the Pirgu Stage in northern and central Estonia were found to be significantly enriched in magnesium (Hints *et al.*, 2006 – Paper II).

4.1.2. Whole-rock mineral composition

The studied lower Palaeozoic bentonites of the Baltic Palaeobasin are characterized by the authigenic mineral assemblage of I/S, K-feldspar and kaolinite. Usually these minerals make up more than 85% of crystalline phases, being clearly distinct from chlorite–illite–quartz–carbonates-dominated terrigenous clay associations found in host rocks (Jürgenson, 1988; Põlma, 1982). Mixed-layer I/S with about 55–80% of illite layers (Somelar *et al.*, 2009b) is the dominant mineral in most bentonite beds. The second most abundant phase is an authigenic orthoclase variety of K-feldspar, which occurs in the form of

euohedral microcrystalline aggregates. In its structural parameters, as well as chemical composition, the authigenic K-feldspar differs from pyroclastic K-feldspar (K–Na sanidine). The latter can be found as a minor accessory phase in most bentonite beds (Kiipli *et al.*, 2008). In addition, bentonites containing a considerable amount of kaolinite or, in some cases, kaolinite-dominated bentonite beds, were reported by Hints *et al.* (2008 – Paper I).

The altered ash beds differ largely from the terrigenous clays present in the Estonian Palaeozoic sequence. However, the elevated amount of typical terrigenous phases (esp. chlorite, illite, carbonates) in some thin bentonite beds probably reflects the mixing of primary ash with detrital material. Quartz, whose content in bentonites mainly stays below 10%, is mostly authigenic and/or pyroclastic in origin. Occasionally, the stratified silicification of host rock or authigenic quartz nodules is connected with bentonite beds. The majority of bentonite beds contain (macroscopic) biotite, which has been considered an indicator of volcanic origin. Among authigenic accessory phases pyrite and anatase are common (Jürgenson, 1958; Hints *et al.*, 2008 – Paper I).

The studied Palaeozoic sequence in the northern Baltic Palaeobasin contains some altered ash beds with rather atypical mineral composition. Hints *et al.* (2006 – Paper II) reported the mixed-layer chlorite-smectite (corrensite)-dominated bentonites in the Upper Ordovician Pirgu Regional Stage. These beds contain an authigenic mineral assemblage of corrensite, I/S and K-feldspar and the quantity of individual phases shows systematic areal variations with respect to facies zones.

The variation patterns of mineralogical as well as chemical composition of different bentonite beds (bed series) have great similarities in a lateral scale. The K-feldspar-rich bentonite varieties that in some cases contain more than 80% K-feldspar are found in shallow-water carbonate ramp settings (Kiipli *et al.*, 2007 – Paper III). In transition zone between shallow water ramp and deep shelf the I/S-rich varieties dominate, whereas kaolinite–I/S assemblage prevails in deep shelf settings. These changes are concordant with trends in the chemical composition: kaolinite-rich assemblages are rich in Al_2O_3 and depleted of silica and K_2O , whereas K-feldspar-rich assemblages show the highest K_2O and SiO_2 values. Similarly, in chloritic Pirgu bentonites corrensite is a prevailing mineral in the shallow-water part of the palaeobasin. Its proportion decreases towards the palaeobasin depression and mixed-layer chlorite minerals disappear in deeper shelf settings in southernmost Estonia, where the mineral assemblage is dominated by I/S (Hints *et al.*, 2006 – Paper II).

Another dimension of mineral variations is related to bed-to-bed variability of bentonites. The Silurian bentonite sequences of the Ruhnu and Ohessaare cores, both penetrating the deposits that formed within the transition zone, reveal high bed-to-bed variability (Hints *et al.*, 2008 – Paper I). In the Ohessaare core, within a series of closely spaced upper Llandoveryan bentonites, the K-feldspar-dominated beds were found to interfinger with kaolinite–I/S assemblages.

Variation may occur also in the vertical profiles of single thicker ash beds (e.g. distribution of certain pyroclastic minerals such as biotite or changes in authigenic assemblages). Hints *et al.* (1997) and Kiipli *et al.* (2007 – Paper III) described a vertical zonation in the Kinnekulle Bed in the Pääsküla outcrop, where the middle part of the 30 cm thick bed is composed of I/S, but near the upper and lower contacts a K-feldspar-rich variety dominates.

4.1.3. Clay mineral composition

The clay fraction (<2 µm) of the studied bentonites consists predominantly of mixed-layer I/S, although in the deep shelf zone the kaolinite–I/S assemblage is most common. Chloritic bentonites of the Pirgu Stage contain chlorite-smectite (Hints *et al.*, 2006 – Paper II, 2008 – Paper I). In K-feldspar-rich bentonites of the Estonian sequence the clay fraction may account for less than 10% of the whole-rock.

The I/S found in Estonian bentonites is a typical high-maturity I/S having approx. 55–80% illite layers and being characterized by R1–R1.5 ordering (Kirsimäe *et al.*, 2002; Huff *et al.*, 2002; Kiipli *et al.*, 2007 – Paper III; Hints *et al.*, 2008 – Paper I; Somelar *et al.*, 2009a, 2009b). The I/S in the Palaeozoic bentonites may contain a limited proportion of high-charged smectite (vermiculite-type) layers in addition to the fully expandable smectite layers and illitic component (Hints *et al.*, 2006 – Paper II, 2008 – Paper I; Kiipli *et al.*, 2007 – Paper III; Somelar *et al.*, 2009a, 2009b). For comparison, the Kinnekulle Bed in its type locality in Sweden has I/S with 45–65% illitic component (Brusewitz, 1986, 1988) while the same bentonite bed in Latvia and Lithuania contains 63–83% illite in I/S (Kepeshinskas *et al.*, 1994). The illitization of Palaeozoic bentonites in the Baltic Palaeobasin is discussed in detail by Somelar *et al.* (2009a, 2009b). The chloritic phases of Pirgu bentonites are represented by R1-ordered chlorite-smectite (corrensite)-type mineral having 0.5/0.5 chlorite and smectite layers (Hints *et al.*, 2006 – Paper II).

4.2. General factors controlling diagenetic alteration of bentonites

The transformation into bentonite of primary volcanic ash that deposited in marine environment results from the alteration of an open system during progressive diagenesis. This changes the overall composition of the tephra bed, enriching it in potassium and aluminium and decreasing the content of silica. The final bulk composition of bentonites is therefore different from that of normal eruptive volcanic material. Transformation of the ash starts as a rule with the formation of monomineralic (dioctahedral) smectite assemblages, which are replaced by metastable mixed-layer I/S and illite during later stages of diagenesis (e.g. Meunier, 2005).

The lower Palaeozoic bentonites of Scandinavia are typically regarded as I/S-dominated marine bentonites with only a few sporadic occurrences of particularly feldspathized and/or kaolinitic beds (e.g. Snäll, 1976; Bergström *et al.*, 1992, 1998; Kiipli *et al.*, 2007 – Paper III). However, the studies of Estonian bentonites (Hints *et al.*, 2006 – Paper II, 2008 – Paper I; Kiipli *et al.*, 2007 – Paper III) show that the whole-rock mineral composition of these altered ash beds is far more diverse and involves several authigenic minerals such as mixed-layer I/S, K-feldspar, kaolinite and mixed-layer chlorite-smectite. The observed mineral assemblages and their variation in sedimentary successions reflect either variation in source volcanics/source magma composition and/or environmental factors during the mineral formation and subsequent transformation of the deposited ash. The multiphase assemblages could have formed due to reciprocal interplay of several factors such as (1) differences in source ash material; (2) specific early diagenetic environments and (3) differential alteration under late diagenetic, metasomatic and/or early metamorphic processes.

4.3. Influence of primary ash composition on diagenetic alteration

The studies of modern sedimentary-volcanogenic sequences, as well as numerous experiments with natural tephtras, have demonstrated considerable influence of source material composition and type, size and structure of glass fragments on the subsequent alteration path of ash and on the character of authigenic phases (e.g. Bonatti, 1965; Hein and Scholl, 1978; Imbert and Desprairies, 1987; Christidis and Dunham, 1993, 1997). The volcanic ash of Estonian Palaeozoic bentonites is thought to be of rhyolitic to andesitic-trachyandesitic composition, originally containing 55–75% SiO₂ and being produced by volcanoes related to calc-alkaline magma series (Kiipli and Kallaste, 2003). However, while the majority of I/S-dominated bentonites show a similar trachyandesite–rhyolite–dacite composition, pointing to calc-alkaline source (e.g. Bergström *et al.*, 1992; Huff *et al.*, 1998), then the Wenlockian bentonites of the same region might have originated from alkaline-type volcanics (Batchelor and Jeppsson, 1999).

Different concentrations of K and Na in tephtras of alternating magma series might have caused the variation in the bentonite mineral composition from I/S-dominated to kaolinite dominated bentonite assemblages in Silurian bentonites of Estonia (Hints *et al.*, 2008 – Paper I). Similarly, Huff *et al.* (1998) noted that Silurian bentonites tend to be on average more kaolinite-rich than their Ordovician counterparts, which would reflect the development of the volcanics composition during the closure of the Iapetus Ocean. Despite small variations, the generally homogeneous composition of Baltoscandian Palaeozoic bentonites is likely to indicate homogenization of different starting materials in the course of diagenetic alteration. Thus the composition of the original ash has likely not

been the key variable determining the formation of multiphase and variable assemblages in the bentonites in the northern inshore settings of the palaeo-basin.

Similarly, the occurrence of exceptional mixed-layer chlorite-smectite bentonites of the Pirgu Stage (Katian Stage) (Hints *et al.*, 2006 – Paper II) could be related to basic source magmas, as far as chloritic phases and Fe-rich smectites (saponite) are common alteration products of basic igneous rocks and tephra beds in terrestrial settings. However, the distal position of the Baltic basin with respect to volcanic activity centres and limited potential of the volcanoes to produce widespread basic tephra clouds and respective beds, do not support this possibility (Hints *et al.*, 2006 – Paper II).

4.4. Early diagenetic alteration and formation of the smectite-kaolinite assemblage

The early transformation of modern marine tephra layers is accompanied with principal restructuring of the primary ash material, considerable leaching of various elements (e.g. K, Na, Ca, Si) depending on the particular alteration environment, and notable mass transfer between tephra and enclosing sediments (e.g. Imbert and Desprairies, 1987). The composition of the glass melt inclusions in primary quartz phenocrysts of the I/S dominated Kinnekulle Bentonite (Huff *et al.*, 1996) suggests that the conversion of ash to bentonites in this particular case resulted in a loss of total mass ~35%, mostly on account of Si and partly of Na and K.

The multiphase assemblage of Estonian Palaeozoic bentonites in a diagenetically very immature sedimentary sequence provides potentially an insight into the synsedimentary/early diagenetic processes of the ash transformation. Like other Palaeozoic bentonites, these beds do not contain volcanic glass or its amorphous derivatives, except as inclusions in volcanogenic phenocrysts (e.g. Huff *et al.*, 1996). Glass shards of ash are thermodynamically unstable and start to devitrify and re-crystallize after deposition, commonly via several labile silicate phases. The time gap between ash deposition and start of devitrification can be highly variable – syn-depositional to tens of million years. It depends on a number of factors such as rock permeability, fluid composition, etc. After studying rhyolitic-ash beds in the Bering Sea, Hein and Scholl (1978) concluded that 5–6 million years were required to convert primary ash beds to smectite-dominated bentonites. Furthermore, basaltic glass has been described from the Jurassic (170 Ma) deep ocean crust (Fisk and Kelley, 2002). In general, factors like higher content of silica and crystalline fragments, thickness of tephra beds, closed alteration environment, could seriously influence the early phase of devitrification. During early stages of alteration bentonites are usually thought to act as open chemical systems with respect to the surroundings and the transformation is controlled by reciprocal influence of the

composition of seawater and interstitial water. However, the different timing of devitrification can favour the dominance of one of these factors (Velde, 1985).

In marine environments, the formation and stability of authigenic silicates, like smectite, is primarily controlled by variations in pH, dissolved silica and alkali ion concentrations (Garrels and Christ, 1965; Helgeson and Mackenzie, 1970; Velde, 1985). The clay mineral assemblages of the studied Ordovician and Silurian bentonites of the northern Baltic Palaeobasin exhibit lateral zonation of principal components, I/S and kaolinite. These areal variations have been shown to correlate with sedimentary phase patterns of host rocks of bentonites (Kiipli *et al.*, 2007 – Paper III; Hints *et al.*, 2008 – Paper I). On the basis of mutual changes in the clay mineral assemblage and host rock character, Kiipli *et al.* (2007 – Paper III) concluded that the diversification of bentonite clay assemblages and formation of kaolinite-smectite occurred during early diagenetic alteration of ash, reflecting the existence of distinct geochemical environments in the palaeobasin. The formation of kaolinite during hydrolysis of volcanic ash is favoured at low pH (<7.5), low silica activity and low activity of alkali ions in the solution, whereas smectite formation requires high activity of silica and increased activity of K^+ (Velde, 1985). In the studied kaolinite-rich bentonite beds extensive leaching is suggested, based on covariance between kaolinite- and anatase (Hints *et al.*, 2008 – Paper I). Ti, like Al, is relatively immobile during low-temperature alteration and is, therefore, passively enriched during leaching. Similar kaolinite and anatase-rich bentonite varieties have been described from the contemporaneous Llandovery sequence in Gotland (Snäll, 1976). Large-scale conversion of tephra beds to kaolinite (tonsteins) is known from terrestrial volcanoclastic settings in connection with coal deposits, where low pH favourable for stabilization of kaolinite was induced by breakdown of organic matter in adjacent coal beds (e.g. Bohor and Triplehorn, 1993). The same transformation mechanism could be suggested for the kaolinitic bentonites observed in the Baltic Palaeobasin. The kaolinite-rich Silurian bentonites in the Ruhnu and Ohessaare cores occur within the sedimentary sequence containing bituminous host rocks (Hints *et al.*, 2008 – Paper I). Most of the kaolinitic beds are found within the upper Llandovery and lowermost Wenlock, characterized by a sea-level highstand that is possibly followed by a rapid regression episode (Johnson, 2006). The widespread occurrence of contemporaneous graptolitic shales in the basinal facies of the Baltic Palaeobasin (Kaljo, 1970), the position of Baltica in tropical latitudes (Torsvik and Rehnström, 2003), low atmospheric O_2 in the Silurian, and circulation models for Silurian oceans (Wilde, 1978) suggest a stratified water column with suboxic bottom waters within the palaeobasin – conditions that favour burial of organic matter. Organic matter has been regarded as a driving force in early diagenesis in marine sediments and its breakdown by primary or secondary oxidants produces carbonate acid and different organic acids, which might lead to local lowering of pH of internal solutions (Chester, 2003). Alternatively, the lower pH may have resulted from the combination of high surface productivity, strongly stratified water column and oxygen-depleted (sulphate-reducing condition) bottom waters. The bed-to-

bed variations in Silurian bentonites of the Ohessaare and Ruhnu cores show, however, that kaolinite-rich bentonite beds occurred not only within terrigenous shales, but also within marls. This indicates that the pH of seawater should have been high enough to support the formation and/or burial of carbonates. The extent of the pH decrease, induced by decay of organic matter inside the sediment column, and thus affecting the formation of authigenic silicates in ash, was apparently also related to the host rock type. Lime muds could efficiently neutralize the excess carbonate acid and support high silica activity needed for smectite formation from the primary ash (Kiipli *et al.*, 2007 – Paper III). In siliciclastic sediments, like shales, the organic matter breakdown likely induced considerable decrease in pore water pH. Additionally, enclosing silicates may also control the activity of dissolved $\text{SiO}_{(\text{aq})}$, keeping it below the quartz saturation limit and thus favouring kaolinite formation (Aagaard and Helgeson, 1982). In transitional facies sequences between carbonate ramp and deeper water settings (e.g. Ohessaare core, Hints *et al.*, 2008 – Paper I) early lithification of carbonates might have influenced the water exchange and diffusion pattern inside the early diagenetic zone of the sediment profile, causing increase in the heterogeneity of vertical interstitial water profiles. That would explain the occurrence of bentonites with contrasting clay mineral assemblages in closely spaced beds, as observed in the Ohessaare and Ruhnu drill cores (Hints *et al.*, 2008 – Paper I).

4.5. Mixed-layer chlorite-rich bentonites

Containing mixed-layer chloritic phases bentonites of the Late Ordovician Pirgu Stage are exceptional in the region (Hints *et al.*, 2006 – Paper II). Mixed-layer chloritic minerals are nevertheless found in a wide range of environments like low-grade regional metamorphic and hydrothermal systems, in lacustrine and marine evaporitic environments, mafic volcanoclastic settings and among weathering products of igneous assemblages (e.g. Inoue, 1995; Reynolds, 1988). Chloritic K-bentonites, including K-bentonites with mixed-layer chlorite-smectite, are occasionally found in the Ordovician and Silurian K-bentonites of North America, the British Isles and rarely in Baltoscandia (Huff and Morgan, 1990; Bergström *et al.*, 1992, 1998). In these beds the chloritic phases have probably formed as a result of alteration under low-grade metamorphic conditions (Krekeler and Huff, 1993). However, for Pirgu bentonites containing corrensite (regular interstratification of trioctahedral chlorite and trioctahedral smectite), metamorphic overprinting can be excluded, as far as various thermal maturity indices suggest very low maturity of the entire Palaeozoic complex in this part of the Baltic Palaeobasin (Hints *et al.*, 2006 – Paper II). On the other hand, corrensite, which is not common in modern sediments, can be found in numerous ancient marine and lacustrine beds, where its appearance is often connected with volcanogenic material (Chamley, 1989). In such settings corrensite has formed by either breakdown of Mg-rich mafic

detrital minerals or volcanics (Hillier, 1993; Chang *et al.*, 1986; Inoue and Utada, 1991; Son *et al.*, 2001), or crystallization of Mg-rich trioctahedral smectite (saponite) in response to the formation of solutions with a high activity ratio of $\text{Mg}^{2+}/\text{H}^{+}$ (Hover *et al.*, 1999). Saponite has been found in modern lacustrine, aeolian but also in dolomite-dominated sabkha-type evaporitic environments (Hover *et al.*, 1999). The Mg-rich precursor is transformed to R1-ordered mixed-layer chlorite phases as a result of diagenetic, hydrothermal, or metamorphic alteration of beds (Beaufort *et al.*, 1997).

The formation of corrensite in Pirguan bentonites from a mafic volcanic precursor can be regarded as unlikely due to the typical rhyolite–rhyolite-dacite and dacite–trachyandesite composition of parental magma for Baltoscandian bentonites (Bergström *et al.*, 1995; Huff *et al.*, 1996; Kiipli and Kallaste, 1996). The same magma source for Pirguan bentonites is indicated by their characteristically high Zr/TiO_2 ratio (0.06–0.12) (Hints *et al.*, 2006 – Paper II). According to Inoue and Utada (1991), corrensite can form directly from saponite under hydrothermal conditions at temperatures between 100°C and 200°C. Traces of (late) diagenetic dolomitization within the Estonian Palaeozoic complex apparently indicate circulation of magnesium-rich fluids during some stage of its evolution (e.g. Pichugin *et al.*, 1975). However, extensive regional dolomitization is observed only in northeastern Estonia or is related to certain stratigraphic boundaries, particularly near the lower contact of the Ordovician–Silurian carbonate complex and below Devonian siliciclastic deposits. The dolomitization of limestones of the Pirgu Stage is rather patchy, being mostly asymmetric with respect to the upper boundaries of limestone beds. Notably, the areal dolomitization pattern observed in Pirguan limestones does not match the lateral variation of corrensite in bentonites. However, corrensite variation shows strong correlation with facies distribution of Pirgu age (Hints *et al.*, 2006 – Paper II). The beds richest in corrensite occur in northern and northwestern localities; towards the south and southeast the content of corrensite decreases gradually. Close to the southern border of Estonia corrensite is missing and I/S is the dominant clay mineral (Hints *et al.*, 2006 – Paper II).

The covariance between corrensite distribution and host rock facies could reflect possible influence of synsedimentary or early diagenetic environment on mineral genesis. The Baltica continent had reached tropical latitudes by Katian time (Torsvik and Rehnström, 2003) and the end of Pirgu time was characterized by rapid sea-level changes, denudation and tectonic movements inside the palaeobasin (Harris *et al.*, 2004). These conditions are favourable for temporal formation of semiclosed evaporitic shallow-water environments like sabkhas in near-shore settings. Several regression–transgression cycles can be followed during the Katian, leading to gradual shallowing of sea level in limestone ramp settings, hosting corrensite-rich bentonites (Harris *et al.*, 2004). In the same stratigraphical interval probably microbially enhanced carbonate mounds are known in several places of Baltoscandia (the so-called Boda mounds; Hints and Meidla, 1997; Harris *et al.*, 2004). Even so, the sedimentary

sequence of the Pirgu Stage lacks clearly distinguishable evaporitic assemblages, such as gypsum or halite. However, dolomites of the Rõa Formation (the upper Pirgu–Lower Pokuni Stage) may have formed as a result of very early dolomitization of limestone beds, suggesting at least local reflux of early diagenetic Mg-rich fluids. Hints *et al.* (2006 – Paper II) argue, therefore, that corrensite in the Pirgu bentonites could have started as the response to Mg-rich solution reflux from the above-lying sabkha settings. This interpretation is supported by the occurrence of corrensite not only in bentonites, but also as minor admixture throughout the Pirguan sedimentary complex (Kalle Kirsimäe, pers. comm., 2006).

4.6. Formation of potassium-rich associations

Despite the major influence of early post-sedimentary transformation processes on ash alteration, these changes fail to provide adequate explanation to all aspects of mineral variability in bentonites, e.g. illitization and feldspathization within the studied beds. The latter processes are likely connected with ash transformation during progressive diagenesis.

Being characterized by shallow burial and a generally low thermal gradient throughout its Phanerozoic geological history, the lower Palaeozoic sedimentary complex in the northern part of the Baltic Palaeobasin represents a rather unique stable geothermal-tectonic evolutionary record. As indicated by the thermally immature state of organic matter in this part of the palaeobasin (Nehring-Lefeld *et al.*, 1997; Talyzina *et al.*, 2000), the temperatures achieved at maximum burial presumably stayed well below 100°C. The whole complex was stabilized at its maximum burial depth from late Devonian to Permian for nearly 100 million years (Kirsimäe *et al.*, 1999). However, if phase stability of the I/S–K-feldspar–kaolinite assemblage observed in Estonian bentonites is assessed in the framework of a simplified aqueous K–Si–Al system (e.g. Aagaard and Helgeson, 1982, Fig. 2), K-feldspar and kaolinite are not expected to stabilize together at temperatures below 100°C. Consequently, the authigenic assemblage present in the bentonites is thermodynamically unstable (Hints *et al.*, 2008 – Paper I) and phases like kaolinite and K-feldspar have apparently formed at different stages of the diagenetic development. The micromorphological scanning-electron microscope observation (Hints *et al.*, 2008 – Paper I) indicates that both K-feldspar and kaolinite are primary authigenic phases, without obvious signs of alteration, and K-feldspar can often be defined as the latest or coeval phase precipitated in the assemblage with I/S. Therefore, the coexistence of K-feldspar and kaolinite obviously reflects incomplete equilibration of the mineral assemblage during late diagenesis, whereas kaolinite, which had formed during the initial stage of ash alteration, apparently played a passive role in late diagenetic environments (Hints *et al.*, 2008 – Paper I).

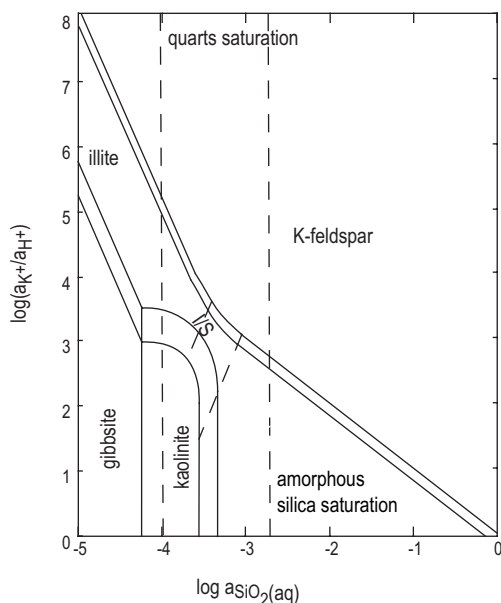


Figure 2. The activity diagram of the K^+ , H^+ and SiO_2 system after Aagaard and Helgeson (1982) with the stability boundaries for K-feldspar, smectite (illite and illite-smectite) and kaolinite. Note that K-feldspar and kaolinite cannot form a stable diagenetic paragenesis and are apparently stabilized at different diagenetic stages.

In general, smectite is the major primary alteration product of volcanic glass (e.g. Tomita *et al.*, 1993), which afterwards during progressive diagenesis evolves into a stable illite through a series of metastable I/S phases (Środoń, 1999). The formation of smectite from siliceous glass proceeds through removal of excess Si and alkali compounds and therefore smectite is a typical alteration product in open to half-opened systems. However, if sufficient Si and alkalis are retained in half-opened or closed systems, then zeolites and/or authigenic quartz polymorphs (opal, cristobalite) form and also K-feldspar may occur as a subordinate phase in these beds (Hay and Guldman, 1987). Zeolites, which are the second most common alteration products of pyroclastic material, may stabilize in low-burial environments rich in dissolved alkalis and silica (Velde, 1985). The experiments by Bernhard and Barth-Wirsching (2002) show that during recrystallization of amorphous volcanic matter in contact with aqueous solution at temperatures from 100°C to 200°C the zeolite formation almost invariably precedes appearance of K-feldspar. The sequence of crystallization is represented as follows: habazite/phillipsite → phillipsite+analcime → analcime+K-feldspar. However, it is notable, that while zeolitic tephra beds are ubiquitous in Cenozoic and common in Mesozoic deposits (e.g. Hay, 1978), primary zeolites have not been documented in Palaeozoic tephra beds and K-feldspar occurs there as the only major authigenic alkali framework silicate.

In closed environments low-temperature aqueous transformation and crystallization of highly disordered primary mixtures such as amorphous glasses would result in a phase with the highest entropy for the possible crystalline substances that can exist in different polymorphic forms. Thus, the system far from equilibrium (e.g. vitric ash) tends to transform into metastable phases (e.g.

smectite, zeolites) as the first steps of crystallization. Because of their high Gibbs free energy, high lattice disorder and large amount of water in structures, at long reaction times zeolites tend to recrystallize into phases with more stable structures according to the Ostwald step rule (e.g. Morse and Casey, 1988). A common end-member of recrystallization of potassic-sodic alkali zeolite species is K-feldspar (e.g. Hay, 1986). Hay and Guldman (1987) reported that in saline alkaline environment zeolites are recrystallized into K-feldspar already in 140 000 years. Nevertheless, in some cases K-feldspar can precipitate directly from dissolution of volcanics in alkaline lacustrine environments (e.g. Christidis, 1995)

The formation of zeolites during the initial phases of bentonite diagenesis would thus explain the K-feldspar–kaolinite association. Bowers and Burns (1990, Fig. 3) presented equilibrium activity diagrams for the K–Si–Al–H₂O system that characterizes relative stability limits of prominent alkali zeolites found in the Yucca Mountains. According to their findings, alkali zeolites (e.g. K-phillipsite) may equilibrate and coexist with kaolinite. Therefore we may forward a hypothesis that the initial crystallization of amorphous material of the examined altered lower Palaeozoic ash beds could produce metastable alkali zeolites (instead of K-feldspar) together with kaolinite. In the course of diagenesis, zeolites recrystallized into K-feldspar. Although there is no ubiquitous causal relationship between the type of source material and crystallizing zeolite species, the silicic vitric material has been reported to alter preferably into phillipsite and/or clinoptinolite (+smectite) (Hay, 1986), which further supports the above possibility.

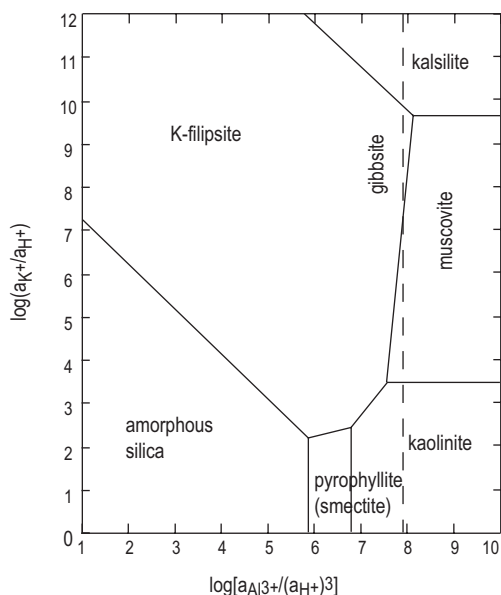


Figure 3. The activity diagram representing the stability limits for zeolite-pyrophyllite (smectite)–muscovite–kaolinite in the K⁺, Al³⁺ and H⁺ system (after Bowers and Burns, 1990). Note that unlike K-feldspars, zeolites form a stable/equilibrium assemblage with kaolinite.

It could then be argued that individual bentonite layers acted like half-opened microsystems during diagenesis, which with high sensitivity reacted to variations in local environment and probably in source material composition (e.g. Christidis, 2001). Diagenetic sequences of volcanic material transformation probably started with the formation of hydrated aluminosilicate gel and/or early smectite at the expense of glass. This process was followed by the formation of primary zeolites, initiated by elevated concentration of dissolved silica after smectite crystallization and by enhanced dissolution of glass (e.g. Hay and Guldman, 1987). Under nearly neutral or alkaline conditions the early evolution of the studied bentonites comprised at least two metastable phases, early smectite and zeolite, which in later stages were replaced by illite-smectite and K-feldspar, respectively (Fig. 4).

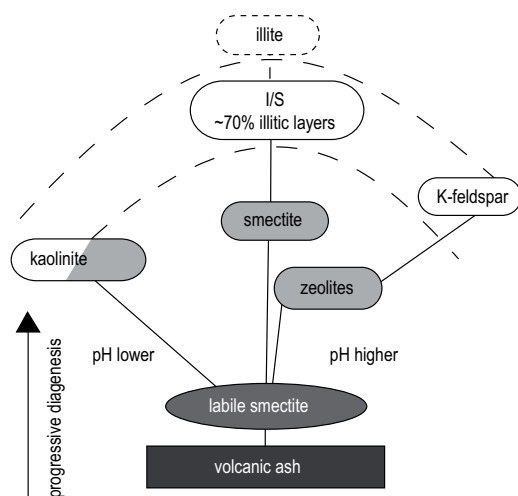


Figure 4. The diagenetic evolution model of bentonite transformation. Filled boxes show the early diagenetic metastable phases, replaced during progressive burial. Kaolinite formation in the system is pre-determined by variation in the sediment pore-water pH. Empty boxes represent the observed authigenic phases of bentonites.

Nevertheless, it is disputable whether such evolution could fully explain the occurrence of K-rich associations in bentonites. It is interesting enough that while the dissolution of K-feldspars in siliciclastic deposits has been regarded as the major source of K^+ for smectite illitization (e.g. Hower *et al.*, 1976), then the bentonites in the northern part of the Baltic Palaeobasin contain an assemblage of authigenic unaltered euhedral K-feldspar and illitic I/S (Somelar *et al.*, 2009a). Total K_2O content of strongly feldspathized bentonites reaches up to 14%, which is close to the K_2O content of pure stoichiometric K-feldspar (16.7%). Thus, external potassium was apparently needed during diagenesis to achieve nearly complete feldspathization. For comparison, the K_2O content of homogeneous I/S-dominated Palaeozoic bentonites varies within 1.5–6.5% in the Scandinavian region (e.g. Huff *et al.*, 1996, 1998), whereas rhyolitic glass melt from the Kinnekulle Bed yielded about 4% K_2O (e.g. Huff *et al.*, 1996). The high potassium content in bentonites of northern and central Estonia

correlates with the dominance of authigenic K-feldspar in assemblages. Also, I/S in Estonian bentonites is considerably K-rich, with 56–78% illite layers and showing R1 ordering of layer components (Hints *et al.*, 2008 – Paper I; Somelar *et al.*, 2009a, 2009b). Such an illite proportion in I/S is unexpectedly high and does not agree with the thermally immature state of organic matter in the Palaeozoic complex of the northern Baltic Palaeobasin. Instead it suggests illitization under the influence of low-temperature K-rich late diagenetic or hydrothermal fluids (Somelar *et al.*, 2009a, 2009b; Środoń *et al.*, 2009).

The late diagenetic origin of I/S and K-feldspar is strongly supported by the K–Ar isotope age of 385–410 Ma for I/S (Somelar *et al.*, 2009a) and 415–419 Ma for authigenic K-feldspar (Środoń *et al.*, 2009) in the Kinnekulle Bentonite, which is at least 44 million years younger for I/S and 35 million years younger for K-feldspar than the age of deposition. Somelar *et al.* (2009b) suggest that the illitization and K-feldspar formation in bentonites were connected with multiple or single prolonged events of low-temperature alkaline gravitationally driven hydrothermal fluid flows, which possibly originated in the forebulge region of the Caledonian orogeny and gained most of its dissolved K^+ during fluid migration through potassium-rich basement rocks and late Proterozoic–Cambrian siliciclastic assemblages.

In local scale, however, the K-feldspar formation in a distinct bentonite bed in response to the flux of basinal hydrothermal fluids could have been controlled by primary lithology of the ash bed as well as by the character of the enclosing rock. This would explain incoherent crystallization of K-feldspar in close-lying beds (Hints *et al.*, 2008 – Paper I). Authigenic K-feldspar occurring in bentonites with a moderate amount of K_2O was observed to form distinct coalesced patches within rather homogeneous clayey matrix. In highly feldspathized varieties, however, uniformly distributed discrete cryptocrystalline euhedral K-feldspar builds up a strong carcass with voluminous inter-crystal pore space, whereas the genetical relations between K-feldspar and clay phases stay unclear (Hints *et al.*, 2008 – Paper I). In the last case, the morphological features suggest metasomatic K-feldspar formation at the expense of a precursor phase rather than neoformation/crystallization in the available pore space, which supports the hypothesis of a precursor zeolite phase. Hay *et al.* (1988) studied the formation of authigenic K-feldspar-rich Ordovician tuffs in the Mississippi Valley and suggested metasomatic formation of K-feldspar at the expense of primary illite or I/S as a response to episodes of regional flow of basinal brines. K-feldspar in Estonian bentonites, however, is isotopically older than I/S (e.g. Somelar *et al.*, 2009a; Środoń *et al.*, 2009), which further strengthens the hypothesis, about precursor zeolite.

5. CONCLUSIONS

The lower Palaeozoic bentonites of the northern Baltic Palaeobasin are characterized by multiphase authigenic assemblages composed of I/S, K-feldspar, kaolinite with occasional mixed-layer chlorite-smectite (corrensite) in the Upper Ordovician Katian bentonites of the Pirgu Regional Stage.

The results suggest that the early diagenetic environment of ash alteration had a major effect on the development of secondary assemblages in the studied bentonites. The heterogeneous composition of the altered ash beds resulted from the combination of several factors, including the character of the enclosing sediments and the composition of interstitial solutions. In a more general scale bentonite formation was controlled by distinct sedimentary facies within the studied part of the Ordovician–Silurian palaeobasin, whereas each facies was characterized by a particular early diagenetic environment (pH, Eh, dissolved silica and alkali ion activities, etc.).

Kaolinite- and corrensite-rich bentonites also reflect specific early diagenetic environments. Kaolinite formation was controlled by pH decrease in diagenetic solutions, induced by the breakdown of buried organic matter in enclosing sediments. The formation of mixed-layer chloritic phases was primarily enhanced by early diagenetic transformation of ash to saponite-type smectite in response to the reflux of hypersaline solutions in sabkha-type environment.

Authigenic K-feldspar, which is abundant in bentonites of northern and central Estonian settings, could have formed at the expense of metastable alkali zeolites. The formation of zeolites instead of smectite during the initial stages of ash alteration might have been supported by high pH and silica activities in interstitial solutions in carbonate-dominated host rock. Alternatively, metasomatic K-feldspar formation could have been induced by one or several episode(s) of low-temperature hydrothermal K-rich alkaline fluid flow during the final stages of Caledonian orogeny, which was also responsible for illitization of smectite in bentonites.

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REFERENCES

- Aagaard, P., Helgeson, H.C. (1982). Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions-I. Theoretical considerations. *American Journal of Science*, 282, 237–285.
- Altaner, S.P., Hower, J., Whitney, G., Aronson, J.L. (1984). Model for K-bentonite formation; evidence from zoned K-bentonites in the Disturbed Belt, Montana. *Geology*, 12, 412–415.
- Aoki, S., Kohyama, N. (1998). Cenozoic sedimentation and clay mineralogy in the northern part of the Magellan Trough, Central Pacific Basin. *Marine Geology*, 148, 21–37.
- Batchelor, R.A. (2003). Geochemistry of biotite in metabentonites as an age discriminant, indicator of regional magma sources and potential correlating tool. *Mineralogical Magazine*, 67, 807–817.
- Batchelor, R.A., Jeppsson, L. (1999). Wenlock metabentonites from Gotland, Sweden: geochemistry, sources and potential as chemostratigraphic markers. *Geological Magazine*, 136, 661–669.
- Beaufort, D., Baronnet, A., Lanson, B., Meunier, A. (1997). Corrensite: A single phase or a mixed-layer phyllosilicate in the saponite-to-chlorite conversion series? A case study of Sancerre-Couy deep drilling hole (France). *American Mineralogist*, 82, 109–124.
- Bergström, S.M., Huff, W.D., Kolata, D.R., Bauert, H. (1992). Silurian K-bentonites in the Iapetus Region: A preliminary event-stratigraphic and tectonomagmatic assessment. *GFF*, 114, 327–334.
- Bergström, S.M., Huff, W.D., Kolata, D.R., Bauert, H. (1995). Nomenclature, stratigraphy, chemical fingerprinting and areal distribution of some Middle Ordovician K-bentonites in Baltoscandia. *GFF*, 117, 1–13.
- Bergström, S.M., Huff, W.D., Kolata, D.R. (1998). The Lower Silurian Osmundsberg K-bentonite. Part 1: Stratigraphic position, distribution and palaeogeographic significance. *Geological Magazine*, 135, 1–13.
- Bernhard, F., Barth-Wirsching, U. (2002). Zeolitization of a phonolitic ash flow by groundwater in the Laach Volcanic Area, Eifel, Germany. *Clays and Clay Minerals*, 50, 710–725.
- Bohor, B.F., Triplehorn, D.M. (1993). Tonsteins; altered volcanic ash layers in coal-bearing sequences. *Geological Society of America, Special Paper*, 285, 44 pp.
- Bonatti, E., 1965. Palagonite, hyaloclastites and alteration of volcanic glass in the ocean. *Bulletin of Volcanology*, 28, 251–269.
- Bowers, T.S., Burns, R.G. (1990). Activity diagrams for clinoptilolite: Suceptibility of this zeolite to further diagenetic reactions. *American Mineralogist*, 75, 601–619.
- Brusewitz, A.M. (1986). Chemical and physical properties of Paleozoic potassium bentonites from Kinnekulle, Sweden. *Clays and Clay Minerals*, 34, 442–454.
- Brusewitz, A.M. (1988). Asymmetric zonation of a thick Ordovician K-bentonite bed at Kinnekulle, Sweden. *Clays and Clay Minerals*, 36, 349–353.
- Chamley, H. (1989). *Clay Sedimentology*. Springer-Verlag, Berlin-Heidelberg, 623 pp.
- Chang, H.K., Mackenzie, F.T., Schoonmaker, J. (1986). Comparisons between the diagenesis of dioctahedral and trioctahedral smectite, Brazilian offshore basins. *Clays and Clay Minerals*, 34, 407–423.
- Chester, R. (2003). *Marine Geochemistry*. Blackwell Publishers, London, 520 pp.

- Christidis, G.E. (1995). Mechanism of illitization of bentonites in the geothermal field of Milos Island Greece: evidence based on mineralogy, chemistry, particle thickness and morphology. *Clays and Clay Minerals*, 43, 569–585.
- Christidis, G.E. (2001). Geochemical correlation of bentonites from Milos Island, Aegean, Greece. *Clay Minerals*, 36, 295–306.
- Christidis, G.E., Dunham, A.C. (1993). Compositional variations in smectites: part 1. Alteration of intermediate rocks. A case study from Milos Island, Greece. *Clay Minerals*, 28, 255–274.
- Christidis, G.E., Dunham, A.C. (1997). Compositional variations in smectites: Part II. Alteration of acidic precursors. A case study from Milos Island, Greece. *Clay Minerals*, 32, 253–270.
- Christidis, G.E., Scott, P.W., Markopoulos, T. (1995). Origin of the bentonite deposits of eastern Milos, Aegean, Greece – geological, mineralogical and geochemical evidence. *Clays and Clay Minerals*, 43, 63–77.
- Compton, J.S., Conrad, M.E., Vennemann, T.W. (1999). Stable isotope evolution of volcanic ash layers during diagenesis of the Miocene Monterey formation, California. *Clays and Clay Minerals*, 47, 84–95.
- Fisk, M.R., Kelley, K.A. (2002). Probing the Pacific's oldest MORB glass: mantle chemistry and melting conditions during the birth of the Pacific Plate. *Earth and Planetary Science Letters*, 202, 741–752.
- Garrels, R.M., Christ, C.L. (1965). *Solutions, Minerals and Equilibria*. Harper and Row, New York, 335 pp.
- Govindaraju, K. (1995). Working values with confidence limits for twenty-six CRPG, ANRT and IWG-GIT. *Geostandards Special Issue, Geostandards Newsletter*, 19, 1–32.
- Harris, M.T., Sheehan, P.M., Ainsaar, L., Hints, L., Männik, P., Nölvak, J., Rubel, M. (2004). Upper Ordovician sequences of western Estonia. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 210, 135–148.
- Hay, R.L. (1978). Geological occurrence of zeolites. In: L.B. Sand, F.A. Mumpton (eds.), *Natural zeolites: Occurrence, Properties, Use*. Pergamon Press, Oxford, pp. 135–143.
- Hay, R.L. (1986). Geological occurrence of zeolites and some associated minerals. *Pure and Applied Chemistry*, 58, 1339–1342.
- Hay, R.L., Guldman, S.G. (1987). Diagenetic alteration of silicic ash in Searles Lake, California. *Clays and Clay Minerals*, 35, 449–457.
- Hay, R.L., Lee, M., Kolata, D., Matthews, J.C., Morton, J.P. (1988). Episodic potassic diagenesis of Ordovician tuffs in the Mississippi Valley area. *Geology*, 16, 743–747.
- Hein, J.R., Scholl, D.W. (1978). Diagenesis and distribution of late Cenozoic volcanic sediment in the southern Bering Sea. *Geological Society of America Bulletin*, 89, 197–210.
- Helgeson, H.C., Mackenzie, F.T. (1970). Silicate – sea water equilibria in the ocean system. *Deep-sea Research*, 17, 877–892.
- Hendriks, B., Amdiessen, P., Huigen, Y., Leighton, C., Redfield, T., Murrell, G., Gallagher, K., Nielsen, S.B. (2007). A fission track data compilation for Fennoscandia. *The Norwegian Journal of Geology*, 87, 143–155.
- Hillier, S. (1993). Origin, Diagenesis, and Mineralogy of Chlorite Minerals in Devonian Lacustrine Mudrocks, Orcadian Basin, Scotland. *Clays and Clay Minerals*, 41, 240–259.

- Hillier, S. (1995). Erosion, sedimentation and sedimentology origin of clays. In: B. Velde (ed.), *Origin and Mineralogy of Clays*. Springer, Berlin, Heidelberg, New York, pp. 162–219.
- Hints, L., Meidla, T. (1997). Pirgu Stage. In: A. Raukas, A. Teedumäe (eds.), *Geology and Mineral Resources of Estonia*. Estonian Academy Publishers, Tallinn, pp. 82–85.
- Hints, O., Kallaste, T., Kiipli, T. (1997). Mineralogy and micropalaeontology of the Kinnekulle altered volcanic ash bed (Ordovician) at Pääsküla, North Estonia. *Proceedings of the Estonian Academy of Sciences. Geology*, 46, 107–118.
- Hints, R., Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2006). Chloritization of Late Ordovician K-bentonites from the northern Baltic Palaeobasin – influence from source material or diagenetic environment? *Sedimentary Geology*, 191, 55–66.
- Hints, R., Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2008). Multiphase Silurian bentonites in the Baltic Palaeobasin. *Sedimentary Geology*, 209, 69–79.
- Hover, V.C., Walter, L.M., Peacor, D.R., Martini, A.M. (1999). Mg-smectite authigenesis in a marine evaporative environment, Salina Ometepe, Baja California. *Clays and Clay Minerals*, 47, 252–268.
- Hower, R.J., Eslinger, E.V., Hower, M.E., Perry, E.A. (1976). Mechanisms of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence. *Geological Society of America Bulletin*, 87, 725–737.
- Huff, W.D., Morgan, D.J. (1990). Stratigraphy, mineralogy and tectonic setting of Silurian K-bentonites in Southern England and Wales. In: V.C. Farmer, Y. Tardy (eds.), *Proceedings of the 9th International Clay Conference*. Strasbourg, pp. 33–42.
- Huff, W.D., Bergström, S.R., Kolata, D.R. (1992). Gigantic Ordovician ash fall in North America and Europe: biological, tectonomagnetic, and event-stratigraphic significance. *Geology*, 20, 875–878.
- Huff, W.D., Kolata, D.R., Bergström, S.M., Zhang, Y.S. (1996). Large magnitude Middle Ordovician volcanic ash falls in North America and Europe – dimensions, emplacement and post-emplacement. *Journal of Volcanology and Geothermal Research*, 73, 285–301.
- Huff, W.D., Bergström, S.M., Kolata, D.R., Sun, H.P. (1998). The Lower Silurian Osmundsberg K-bentonite. Part II: Mineralogy, geochemistry, chemostratigraphy and tectonomagmatic significance. *Geological Magazine*, 135, 15–26.
- Huff, W.D., Bergström, S.M., Kolata, D.R., Kirsimäe, K. (2002). K-bentonite mineralogy and geochemistry. In: A. Põldvere (ed.), *Soovälja (K-1) drill core*. Estonian Geological Sections, Bulletin 4. Geological Survey of Estonia, Tallinn, pp. 12–17.
- Imbert, T., Desprairies, A. (1987). Neoformation of halloysite on volcanic glass in a marine environment. *Clay Minerals*, 22, 179–185.
- Inoue, A. (1995). Formation of clay minerals in hydrothermal environments. In: B. Velde (ed.), *Origin and Mineralogy of Clays*. Springer, Berlin, Heidelberg, New York, pp. 268–330.
- Inoue, A., Utada, M. (1991). Smectite-to-chlorite transformation in thermally metamorphosed volcanoclastic rocks in the Kamikita area, northern Honshu, Japan. *American Mineralogist*, 76, 628–640.
- Jaanusson, V. (1948). Traces of volcanic activity in Ordovician sedimentary rocks in western Baltoscandia. Estonia, Karlsruhe (in Estonian).
- Jaanusson, V. (1976). Faunal dynamics in the Middle Ordovician (Viruan) of Baltoscandia. In: M.G. Bassett (ed.), *The Ordovician*. Proceedings of a Palaeontological Association Symposium, Birmingham, 1974, pp. 301–326.

- Jeans, C.V. Fallick, A.E., Fisher, M.J., Merriman, R.J., Corfield, R.M., Manighetti, B., (1997). Clay- and zeolite-bearing Triassic sediments at Kaka Point, New Zealand: evidence of microbially influenced mineral formation from earliest diagenesis into lowest grade of metamorphism. *Clay Minerals*, 32, 373–423.
- Johnson, M.E. (2006). Relationship of Silurian sea-level fluctuations to oceanic episodes and events. *GFF*, 128, 115–121.
- Jürgenson, E.A. (1958). Metabentonites in Estonian SSR. *Proceedings of Institute of Geology of Estonian Academy of Sciences*, 2, 73–85 (in Russian).
- Jürgenson, E.A. (1964). Silurian metabentonites of Estonian SSR. In: S.S. Baukov (ed.), *Lithology of Palaeozoic deposits in Estonia*. Estonian Academy Publishers, Tallinn, pp. 87–100 (in Russian).
- Jürgenson, E. (1988). Deposition of the Silurian beds in the Baltic. Valgus Publishers, Tallinn, 175 pp. (in Russian with English summary).
- Kaljo, D.L. (1970). *Silurian of Estonia*. Valgus Publishers, Tallinn, 333 pp. (in Russian).
- Kallaste, T., Kiipli, T. (2006). New correlations of Telychian (Silurian) bentonites in Estonia. *Proceedings of the Estonian Academy of Sciences, Geology*, 55, 241–251.
- Karpoff, A.M., Destigneville, Chr., Bartier, D., Déjardin, P. (2002). Phyllosilicates and zeolite assemblages in the carbonate periplatform of the Great Bahama Bank: origin and relation to diagenetic processes (ODP Leg 166, Sites 1006 and 1007). *Marine Geology*, 185, 55–74.
- Kastner, M. (1981). Authigenic silicates in deep-sea sediments: formation and diagenesis. In: C. Emiliani (ed.), *The Sea*, 7. Wiley, New York, pp. 915–980.
- Kastner, M., Siever, R. (1979). Low temperature feldspars in sedimentary rocks. *American Journal of Science*, 279, 435–479.
- Kepeshinskas, K., Laškovas, J., Šimkevicius, P., 1994. The Ordovician metabentonites of the Baltic region as a reflection of volcanic activity in the Iapetus paleocean-Tornquist Sea. *Geologija*, 16, 34–42.
- Kiipli, E., Kallaste, T. (1996). Geochemical characterization of some Estonian metabentonites. *Proceedings of the Estonian Academy of Sciences, Geology*, 45, 68–77.
- Kiipli, E., Kiipli, T., Kallaste, T. (2006). Identification of the O-bentonite in the deep shelf sections with implication on stratigraphy and lithofacies, East Baltic Silurian. *Geologiska Föreningens i Stockholm Forhandlingar*, 128, 255–260.
- Kiipli, T., Kallaste, T. (2002). Correlation of Telychian sections from shallow to deep sea facies in Estonia and Latvia based on the sanidine composition of bentonites. *Proceedings of the Estonian Academy of Sciences, Geology*, 51, 143–156.
- Kiipli, T., Kallaste, T. (2003). Altered volcanic ash beds. In: A. Pöldvere (ed.), *Ruhnu (500) drill core*. Estonian Geological Sections, Bulletin 5. Geological Survey of Estonia, Tallinn, pp. 31–33.
- Kiipli, T., Kallaste, T. (2006). Wenlock and uppermost Llandovery bentonites as stratigraphic markers in Estonia, Latvia and Sweden. *GFF*, 128, 139–146.
- Kiipli, T., Kiipli, E., Kallaste, T. (1997). Metabentonite composition related to sedimentary facies in the lower Silurian of Estonia. *Proceedings of the Estonian Academy of Sciences, Geology*, 46, 93–104.
- Kiipli, T., Männik, P., Batchelor, R.A., Kiipli, E., Kallaste, T. Perens, H. (2001). Correlation of Telychian (Silurian) altered volcanic ash beds in Estonia, Sweden and Norway. *Norsk Geologisk Tidsskrift*, 81, 179–193.
- Kiipli, T., Kiipli, E., Kallaste, T., Hints, R., Somelar, P., Kirsimäe, K. (2007). Altered volcanic ash as an indicator of marine environment, reflecting pH and sedimentation

- rate - example from the Ordovician Kinnekulle bed of Baltoscandia. *Clays and Clay Minerals*, 55, 177–188.
- Kiipli, T., Jeppsson, L., Kallaste, T., Söderlund, U. (2008a). Correlation of Silurian bentonites from Gotland and the eastern Baltic using sanidine phenocryst composition and biostratigraphical consequences. *Journal of the Geological Society*, 165, 211–220.
- Kiipli, T., Radzevicius, S., Kallaste, T., Motuza, V., Jeppsson, L., Wickström, L. (2008b). Wenlock bentonites in Lithuania and correlation with bentonites from sections in Estonia, Sweden and Norway. *GFF*, 130, 203–210.
- Kiipli, T., Soesoo, A., Kallaste, T., Kiipli, E. (2008c). Geochemistry of Telichian (Silurian) K-bentonites in Estonia and Latvia. *Journal of Volcanology and Geothermal Research*, 171, 45–58.
- Kirsimäe, K., Jørgensen, P., Kalm, V. (1999). Low-temperature diagenetic illite-smectite in Lower Cambrian clays in North Estonia. *Clay Minerals*, 34, 151–163.
- Kirsimäe, K., Jørgensen, P. (2000). Mineralogical and Rb-Sr isotope studies of low-temperature diagenesis of Lower Cambrian clays of the Baltic Palaeobasin of North Estonia. *Clays and Clay Minerals*, 48, 95–105.
- Kirsimäe, K., Gorokhov, I., Kallaste, T., Kiipli, T., Kikas, R. (2002). Illite-smectite diagenesis of Ordovician K-bentonites of the Baltic basin: implications for basin development. In: J. Satkūnas, J. Lazauskienė (eds.), *The Fifth Baltic Stratigraphical Conference. Extended Abstracts*. Geological Survey of Lithuania, Vilnius, pp. 84–85.
- Krekeler, M.P.S., Huff, W.D. (1993). Occurrence of corrensite and ordered (R3) illite/smectite (I/S) in a VLGM Middle Ordovician K-bentonite from the Hamburg Klippe, central Pennsylvania. *Geological Society of America Abstracts with Programs*, 25, pp. 30.
- Lapinskas, P.P. (1965). Lower Silurian metabentonites in Lithuania. *Geology and oil reservoirs in Southern Baltics*, Institute of Geology, Vilnius, pp. 49–63 (in Russian).
- Männik, P., Viira, V. (1990). Conodonts. In: D. Kaljo, H. Nestor (eds.), *Field Meeting Estonia 1990. An Excursion Guidebook*. Estonian Academy Publishers, Tallinn, pp. 84–90.
- Männil, R. (1958). *Grundzüge der stratigraphie der Keila-stufe (Ordovizium, Estland)*. Estonian Academy Publishers. Tehnilise ja Füüsikalise-Matemaatiliste Teaduste Seeria, 7, 235–246 (in Russian with German summary).
- Männil, R. (1966). Evolution of the Baltic basin during the Ordovician. *Valgus Publishers*, Tallinn, 199 pp. (in Russian with English summary).
- Meunier, A. (2005). *Clays*. Springer, Heidelberg, 472 pp.
- Moore, D.M., Reynolds, R.C. Jr. (1997). *X-ray diffraction and the identification and analysis of clay minerals*. Oxford University Press, New York, 378 pp.
- Morse, J.W., Casey, W.H. (1988). Ostwald processes and mineral paragenesis in sediments. *American Journal of Science*, 288, 537–560.
- Nadeau, P.H., Bain, D.C. (1986). Composition of some smectites and diagenetic illitic clays and implications for their origin. *Clays and Clay Minerals*, 34, 455–464.
- Nehring-Lefeld, M., Modliński, Z., Swadowska, E. (1997). Thermal evolution of the Ordovician in the western margin of the East-European Platform: CAI and Ro data. *Geological Quarterly*, 41, 129–138.
- Nestor, H., Einasto, R. (1997). Ordovician and Silurian carbonate sedimentation basin. In: A. Raukas, A. Teedumäe (eds.), *Geology and Mineral Resources of Estonia*. Estonian Academy Publishers, Tallinn, pp. 192–204.

- Pichugin, M., Puura, V., Vingisaar, P., Erisalu, E. (1975). Regional metasomatic dolomitization associated with tectonic disturbances within the Lower Palaeozoic deposits in the northern Baltic region. *Soviet Geology*, 10, 78–90 (in Russian).
- Plançon, A., Drits, V.A. (2000). Phase analysis of clays using an expert system and calculation programs for X-ray diffraction by two- and three component mixed layer minerals. *Clays and Clay Minerals*, 48, 57–62.
- Pollastro, R. (1993). Considerations and applications of the illite/smectite geothermometer in hydrocarbon bearing rocks of Miocene to Mississippian age. *Clays and Clay Minerals*, 41, 119–133.
- Põlma, L. 1982. Comparative lithology of the Ordovician carbonate rocks in the Northern and Middle East Baltic. Valgus Publishers, Tallinn, 152 pp. (in Russian).
- Puura, V., Vaher, R., Tuuling, I. (1999). Pre-Devonian landscape of the Baltic Oil-Shale Basin, NW of the Russian platform. In: B.J Smith, W.B. Whalley, P.A. Warke (eds.), *Uplift, Erosion and Stability: Perspectives on Long-term Landscape Development*. Geological Society, London, Special Publications, 162, 75–83.
- Rateev, M.A., Gradusov, B.P. (1971). Types of mixed-layer varieties of mica-montmorillonitic series in Silurian-Ordovician metabenonites of the Baltic area. *Lithology and Mineral Resources*, 2, 74–83 (in Russian).
- Raukas, A., Teedumäe, A. (1997). *Geology and mineral resources of Estonia*. Estonian Academy Publishers, Tallinn, 436 pp.
- Reynolds, R.C., Jr. (1985). NEWMOD©, A computer program for the calculation of one-dimensional diffraction patterns of mixed-layer clays. In: Reynolds, R.C., Jr., 8 Brook Drive, Hanover, NH 03755.
- R.C. Reynolds, Jr. (1988). Mixed layer chlorite minerals. *Mineralogical Society of America, Reviews in Mineralogy*, 19, 601–629.
- Rõõmusoks, A. (1970). *Stratigraphy of the Viruan Series (Middle Ordovician) in Northern Estonia*. Valgus Publishers, Tallinn, 346 pp. (in Russian with English summary).
- Ross, C.S., Hendricks, S.B. (1945). Minerals of the montmorillonite group. *US Geological Survey Professional Paper*, 205-B, 23–79.
- Singer, A. (1984). The palaeoclimatic interpretation of clay minerals in sediments – a review. *Earth Science Reviews*, 21, 251–293.
- Snäll, S. (1976). Silurian and Ordovician bentonites of Gotland (Sweden). *Acta Universitat Stockholm*, 31, pp. 1–80.
- Somelar, P., Hints, R., Kirs, J., Kirsimäe, K. (2009a). Illitization of the Early Palaeozoic bentonites in Baltic Basin: decoupling of burial and fluid driven processes (submitted to *Sedimentary Geology*).
- Somelar, P., Kirsimäe, K., Šrodoň, J. (2009b). Mixed-layer illite-smectite in the Kinnekulle bentonite, northern Baltic Basin (submitted to *Clay Minerals*).
- Son, B.K., Yoshimura, T., Fukasawa, H. (2001). Diagenesis of dioctahedral and trioctahedral smectites from alternating beds in Miocene to Pleistocene rocks of the Niigata Basin, Japan. *Clays and Clay Minerals*, 49, 333–346.
- Šrodoň, J. (1999). Extracting K-Ar ages from shales: A theoretical test. *Clay Minerals*, 33, 375–378.
- Šrodoň, J., Kotarba, M., Biron, A., Such, P., Clauer, N., Wojtowicz, A. (2006). Diagenetic history of the Podhale-Orava Basin and the underlying Tatra sedimentary structural units (Western Carpathians): evidence from XRD and K-Ar of illite-smectite. *Clay Minerals*, 41, 751–774.
- Šrodoň, J., Clauer, N., Huff, W., Dudek, T., Banaś, M. (2009) K-Ar dating of Ordovician bentonites from the Baltic Basin and the Baltic Shield: implications for

- the role of temperature and time in the illitization of smectite (submitted to *Clay Minerals*).
- Talyzina, N.M. (1998). Fluorescence intensity in Early Cambrian acritarchs from Estonia. *Reviews in Paleobotany and Palynology*, 100, 99–108.
- Talyzina, N.M., Moldowan, J.M., Johannisson, A., Fago, F.J. (2000). Affinities of Early Cambrian acritarchs studied by using microscopy, fluorescence flow cytometry and biomarkers. *Review of Paleobotany and Palynology*, 108, 37–53.
- Taylor, J.C. (1991). Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. *Powder Diffraction*, 6, 2–9.
- Tomita, K., Yamane, H., Kawano, M. (1993). Synthesis of smectite from volcanic glass at low temperature. *Clays and Clay Minerals*, 41, 655–661.
- Torsvik, T.H., Rehnström, E.F. (2003). The Tornquist Sea and Baltica–Avalonia docking, *Tectonophysics*, 362, 67–82.
- Utsal, K.R., Jürgenson, E.A. (1971). Mineralogy of Estonian metabentonites. *Eesti NSV Teaduste Akadeemia Toimetised, Keemia, Geoloogia*, 20, 336–348 (in Russian).
- Velde, B. (1985). *Clay minerals. A Physico-Chemical Explanation of their Occurrence. Developments in Sedimentology* 40, Elsevier, Amsterdam, 425 pp.
- Vingisaar, P. (1972). On the distribution of the main metabentonite stratum (D; XXII) in the Middle Ordovician of Baltiscandia. *Eesti NSV Teaduste Akadeemia Toimetised, Keemia, Geoloogia*, 21, 62–70 (in Russian with English summary).
- Vingisaar, P., Murnikova, T. (1973). New data on the mineralogy of some Lower Caradocian metabentonites of Estonia. *Eesti NSV Teaduste Akadeemia Toimetised, Keemia, Geoloogia*, 22, 149–158 (in Russian).
- Weaver, C.E. (1953). Mineralogy and petrology of some Ordovician K-bentonites and related limestones. *Geological Society of America Bulletin*, 64, 921–944.
- Wilde, P. (1978). Model of progressive ventilation of the Late Precambrian-Early Paleozoic ocean. *American Journal of Science*, 287, 442–459.

SUMMARY IN ESTONIAN

Ordoviitsiumi ja Siluri bentoniitide varadiageneetiline areng Balti Paleobasseini põhjaosas

Bentoniidid on vulkaanilise päritoluga setendikihid, kus algne amorfne materjal (vulkaaniline tuhk) on devitrititseerunud ja diageneetiliselt transformeerunud valdavalt savimineraalideks. Bentoniitiga seonduv teadusprobleemide ring on äärmiselt lai, ulatudes paleogeograafiast ja stratigraafiast autigeensete savimineraalide tekke ja settekomplekside mattumislöö uurimiseni. Samas kasutatakse bentoniitideid savisid laialdaselt ka tööstuses ning erinevates keskkonnatehnoloogiates. Nii leiavad bentoniitide punduvad savid kasutust näiteks tuumajäätmete matmisel ja puurimislahuste valmistamisel.

Balti Paleobasseini Ordoviitsiumi ning Siluri settekompleks sisaldab enam kui 150 sellist bentoniidikihti. Tüüpilised paleosoilised bentoniidid on kaaliumirikkad ning suhteliselt monomineraalsed, koosnedes peamiselt segakihelistest savimineraalidest illiit-smektiidist ja illiidist. Eesti varapaleosoiliste bentoniitide mineraalkooslus on aga märksa mitmekesisem – illiit-smektiidi kõrval esinevad selles tüüpiliste autigeensete faasidena kaaliumpäevakivi ja kaoliniit. Käesolev uurimistöö keskendub Eesti Ordoviitsiumi ja Siluri bentoniitide autigeense mineraalkoosluse tekkemehhanismidele, pöörates eelkõige tähelepanu varadiageneetilistele muutustele, mis võisid mõjutada bentoniitide koostise pindalalise ja kihtidevahelise muutlikkuse kujunemist.

Uuritud materjal esindab Ordoviitsiumi Keila lademe Kinnekulle bentoniiti, kolme Pirgu lademe bentoniiti ja Siluri läbilõigete bentoniite Ohessaare (34 kihti) ja Ruhnu (18 kihti) puuraugust. Bentoniite kogukivimi ja savifraktsiooni proove uuriti mineraloogiliste ja geokeemiliste analüüsimeetoditega (XRD, XRF, SEM).

Eesti paleosoiliste bentoniitide illiit-smektiidist, K-päevakivist ja kaoliniidist koosnev autigeenne mineraalkooslus on, vaatamata nende märkimisväärsele geoloogilisele eale ja pikale diageneetilisele arengule, termodünaamiliselt ebastabiilne. Lisaks iseloomustab uuritud bentoniite mineraalse koostise suur varieeruvus. Kogukivimi proovidest leitud illite-smektiidi, K-päevakivi ja kaoliniidi sisaldused jäävad vastavalt 0–89%, 0–95% ja 0–45% piiridesse.

Bentoniitide savifraktsioonis valdavad R1 korrastatusega illiitne illiit-smektiit, mis sisaldab 56–78% illiitseid kihte, ja kaoliniit. Illiit-smektiidi ja kaoliniidi vahetõrje bentoniitides muutub koos bentoniitide ümbriskivimi tüübi ja paleobasseini setendite fatsiaalsete muutustega. Tõenäoliselt kontrollisid kaoliniidi ja smektiidi teket varadiageneetilistes protsessides ümbritsevate setendite orgaanilise ainese hulk ning silikaatsete ja karbonaatsete faaside suhtetõrje.

Eriladne autigeenne mineraalkooslus tuvastati Pirgu lademe muundunud tuhakihtidest. Viimaste savifraktsioonis domineerivad illiit-smektiidi kõrval segakihelised kloriitsed faasid (korrensiit), mille osakaal väheneb madalaveelistest settefaatsiitest paleobasseini süvaveelisema osa suunas. Ka korrensiidi

teke on ilmselt algselt olnud seotud bentoniitide varadiageneetilise arenguga, kui oletatavalt sabkha-laadses evaporiitses keskkonnas tekkinud Mg-rikkad fluidid löid tingimused saponiidi tüüpi smektiidi tekkeks. Hilisema diogeneesi käigus on primaarsed Mg-rikkad savifaasid transformeerunud kloriit-smektiidi tüüpi mineraaliks. Korrensiidi esinemine bentoniitides lubab pelgalt mineraloogiliste tunnuste põhjal rekonstrueerida settejärges mittedäälitud evaporiitseid faatsiesi.

Uuritud varapaleosoiliste bentoniitide üheks iseärasuseks on väga kaaliumirikaste erimite esinemine. Suur kaaliumi sisaldus korreleerub massilise autigeense kaaliumpäevakivi esinemisega tuhakihtides. Kõige sagedamini leidub taolisi päevakivirikaid bentoniite Põhja-Eestis ning nende osakaal väheneb järk-järgult lõuna suunas. Autigeenne kaaliumpäevakivi võib olla tekkinud varadiageneetiliste metastabiilsete Na-K tseoliitide arvel. Tseoliitide teket primaarsel tuha ümbekristaliseerumisel võisid soodustada lubimudade settesisest lahuste kõrge pH, ja lahustunud räni- ning leelismetallide ionide kõrge kontsentratsioon. Alternatiivse hüpoteesi järgi võis autigeenne kaaliumpäevakivi tekkida metasomaatilisel kaaliumirikaste ning madalatemperatuursete hüdrotermaalsete fluidide mõjul, samaaegselt Kaledoonia orogeneesi lõpufaasiga.

Saadud tulemused näitavad, et heterogeensete bentoniitide teke on olnud tihedalt seotud vulkaanilise tuha varadiageneetiliste muutustega, ning et uuritud bentoniitide autigeensed kooslused peegeldavad suuremal või vähemal määral settesiseseid keskkonnatingimusi tuhalasundite varases mattumisstaadiumis. Tegemist on ühe esimese hästi dokumenteeritud juhuga, kus leiab kinnitust varadiageneetiliste muutuste kriitiline mõju enam kui 400 miljoni aasta vanuste bentoniitide kujunemisele.

PAPERS I-III

CURRICULUM VITAE

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Career

Institution and position held

2002–... Estonian Museum of Natural History; head of department

Education

2001–... University of Tartu, PhD student geology

1998–2001 University of Tartu, master studies, geology, MSc 2001

1994–1998 University of Tartu, bachelor's studies, geology, BSc 1998

Administrative responsibilities

2008– ... Estonian Geological Society, council member

Research activity

Degree information

Rutt Hints, Master's Degree, 2001, (sup) Väino Puura, Pressure-temperature evolution of high-grade Svecofennian gneisses near Saaremaa Shear Zone (Pressure-temperature evolution of high-grade Svecofennian gneisses near Saaremaa Shear Zone), University of Tartu, Faculty of Biology and Geography, Institute of Geology.

Field of research

Mineralogy and geochemistry, diagenesis of bentonites, clay mineralogy, tectonic and thermal evolution of the Baltic Palaeobasin, high grade metamorphism

Current grants and projects

Evolution of volcanism at the margins of the Baltica plate and Ordovician and Silurian chemostratigraphy based on altered volcanic ash layers – ETF7605.

Evolution of the Fennoscandian-Baltic lithosphere: geochemistry, geochronology, paleoenvironments and mineral resources – SF0182533s03.

Honours and Awards

2002, 1st prize for written contributions by young researchers – Estonian Geological Society

Publications

Hints, L., Männik, P., Hints, O., **Hints, R.** (2008). Discovery of the Ordovician Kinnekulle K-bentonite at Põõsaspea cliff, NW Estonia. *Estonian Journal of Earth Sciences*, 57, 192–196.

Hints, O., Isakar, M., **Hints, R.** (2008). Eesti geoloogilised kollektsioonid [Geological collections in Estonia]. In: E. Parmasto, J. Viikberg (eds), Eesti humanitaar- ja loodusteaduslikud kogud. Seisund, kasutamine, andmebaasid. Tartu Ülikooli Kirjastus, Tartu, pp.181–200.

Hints, R., Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2008). Multiphase Silurian bentonites in the Baltic Palaeobasin. *Sedimentary Geology*, 209, 69–79.

Kiipli, T., Kiipli, E., Kallaste, T., **Hints, R.**, Somelar, P., Kirsimäe, K. (2007). Altered volcanic ash as an indicator of marine environment, reflecting pH and sedimentation rate – example from the Ordovician Kinnekulle bed of Baltoscandia. *Clays and Clay Minerals*, 55, 177–188.

Hints, R., Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2006). Chloritization of Late Ordovician K-bentonites from the northern Baltic Palaeobasin—influence from source material or diagenetic environment? *Sedimentary Geology*, 191, 55–66.

Puura, V., **Hints, R.**, Huhma, H., Klein, V., Konsa, M., Kuldkepp, R., Mänttari, I., Soesoo, A. (2004). Svecofennian metamorphic zones in the basement of Estonia. *Proceedings of the Estonian Academy of Sciences, Geology*, 53, 190–209.

Kirsimäe, K., **Hints, R.**, Kallaste, T., Kiipli, E., Kiipli, T. (2004). Chloritization of Upper Ordovician Pirgu bentonites – source material or diagenetic environment? In: O. Hints, L. Ainsaar (eds.), WOGOGOB-2004: 8th Meeting of the Working Group on the Ordovician Geology of Baltoscandia. Abstracts and field guidebook. Tartu University Press, Tartu, pp. 57–58.

- Hints, R.**, Kirsimäe, K., Kallaste, T., Kiipli, T. (2004). Early diagenetic control on Lower Paleozoic K-bentonite composition in Baltic Basin. *Geochimica et Cosmochimica Acta*, 68, A351–A351.
- Kirsimäe, K., Gorokhov, I., Kallaste, T., Kiipli, T., **Kikas, R.** (2002). Illite-smectite diagenesis of Ordovician K-bentonites of the Baltic basin: implications for basin development. In: J. Satkūnas, J. Lazauskienė (eds.), *The Fifth Baltic Stratigraphical Conference. Extended Abstracts*. Geological Survey of Lithuania, Vilnius, pp. 84–85.

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1998–2001 Tartu Ülikool, magistrantuur geoloogia ja mineraloogia
erialal, MSc 2001
1994–1998 Tartu Ülikool, bakalaureuseõpe geoloogia erialal, BSc
1998

Teadusorganisatsiooniline ja administratiivne tegevus

2008—... Eesti Geoloogia Selts, volikogu liige

Teadustegevus

Teaduskraadi info

Rutt Hints, magistrikraad (teaduskraad), 2001, (juh) Väino Puura, Pressure-temperature evolution of high-grade Svecofennian gneisses near Saaremaa Shear Zone, Tartu Ülikool, Bioloogiageograafiateaduskond, Geoloogia instituut.

Teadustöö põhisuunad

Mineraloogia ja geokeemia, K-bentoniitide diagenees, savimineraloogia, Balti Paleobasseini tektoonilis-termaalne areng, kõrgetemperatuuriline metamorphism.

Jooksvad projektid

Vulkanismi areng Baltika laami äärealadel ja sellel tuginev Ordoviitsiumi ja Siluri kemostratigraafia Baltoskandia regioonis – ETF7605.

Kontinentaalse maakoore ülaosa struktuurid, koostis ja evolutsioon – SF0182533s03.

Teaduspreemiad ja -tunnustused

2002, 1. koht Eesti Geoloogia Seltsi noorte geoloogide parimate uurimuste konkursil

Publikatsioonid

Hints, L., Männik, P., Hints, O., **Hints, R.** (2008). Discovery of the Ordovician Kinnekulle K-bentonite at Põõsaspea cliff, NW Estonia. *Estonian Journal of Earth Sciences*, 57, 192–196.

Hints, O., Isakar, M., **Hints, R.** (2008). Eesti geoloogilised kollektsioonid [Geological collections in Estonia]. Teoses: E. Parmasto, J. Viikberg (toim), Eesti humanitaar- ja loodusteaduslikud kogud. Seisund, kasutamine, andmebaasid. Tartu Ülikooli Kirjastus, Tartu, lk.181–200.

Hints, R., Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2008). Multiphase Silurian bentonites in the Baltic Palaeobasin. *Sedimentary Geology*, 209, 69–79.

Kiipli, T., Kiipli, E., Kallaste, T., **Hints, R.**, Somelar, P., Kirsimäe, K. (2007). Altered volcanic ash as an indicator of marine environment, reflecting pH and sedimentation rate – example from the Ordovician Kinnekulle bed of Baltoscandia. *Clays and Clay Minerals*, 55, 177–188.

Hints, R., Kirsimäe, K., Somelar, P., Kallaste, T., Kiipli, T. (2006). Chloritization of Late Ordovician K-bentonites from the northern Baltic Palaeobasin–influence from source material or diagenetic environment? *Sedimentary Geology*, 191, 55–66.

Puura, V., **Hints, R.**, Huhma, H., Klein, V., Konsa, M., Kuldkepp, R., Mänttari, I., Soesoo, A. (2004). Svecofennian metamorphic zones in the basement of Estonia. *Proceedings of the Estonian Academy of Sciences, Geology*, 53, 190–209.

Kirsimäe, K., **Hints, R.**, Kallaste, T., Kiipli, E., Kiipli, T. (2004). Chloritization of Upper Ordovician Pirgu bentonites – source material or diagenetic environment? O. Hints, L. Ainsaar (toim.), WOGOGOB-2004: 8th Meeting of the Working Group on the Ordovician Geology of Baltoscandia. Abstracts and field guidebook. Tartu University Press, Tartu, lk. 57–58.

- Hints, R.**, Kirsimäe, K., Kallaste, T., Kiipli, T. (2004). Early diagenetic control on Lower Paleozoic K-bentonite composition in Baltic Basin. *Geochimica et Cosmochimica Acta*, 68, A351–A351.
- Kirsimäe, K., Gorokhov, I., Kallaste, T., Kiipli, T., **Kikas, R.** (2002). Illite-smectite diagenesis of Ordovician K-bentonites of the Baltic basin: implications for basin development. In: J. Satkūnas, J. Lazauskienė (eds.), *The Fifth Baltic Stratigraphical Conference. Extended Abstracts*. Geological Survey of Lithuania, Vilnius, lk. 84–85.

DISSERTATIONES GEOLOGICAE UNIVERSITATIS TARTUENSIS

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