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Chloritization of Late Ordovician K-bentonites from the northern Baltic Palaeobasin–influence from source material or diagenetic environment?

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Abstract

The Baltic Ordovician–Silurian sedimentary succession embodies numerous altered volcanic ash beds that are illite–smectite dominated. Only a few beds rich in chlorite–smectite are known from the Upper Ordovician Pirgu Stage of Estonia. Mixed-layer chlorite–smectite occurs commonly in low-grade metamorphic and hydrothermal environments. However, chloritic K-bentonites of the Pirgu Stage have never been buried deeply and lack signs of metamorphic overprinting.

In order to understand the origin of chloritization, three distinct beds were sampled in 14 drillcores from Estonia and Latvia and analysed by means of XRD and SEM. The principal authigenic assemblage of the bulk samples consists of chlorite–smectite (corrensite) together with illite–smectite and K-feldspar. The actual mineral composition of K-bentonites though varies from sample to sample. The clay mineral assemblages range from virtually pure chlorite–smectite to illite–smectite dominated assemblages with minor or no chlorite–smectite. The proportion of chlorite–smectite in K-bentonites shows systematic lateral variations: the share of chloritic phases is highest in the shallower-water part of the palaeobasin and decreases towards the deeper part of the basin. Such regular lateral variations suggest a possible link between chloritization and the configuration of ancient palaeobasin. The present study suggests that the chloritization of primary felsic ashes occurred during early diagenesis and that it was caused by an influx of Mg-rich water probably from a marine sabkha-type environment.
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Keywords: K-bentonite; Diagenesis; Chlorite–smectite; Paleozoic; Baltic Palaeobasin; Pirgu

1. Introduction

The Paleozoic sedimentary succession of the Baltic Palaeobasin contains numerous K-bentonite layers, the diagenetic composition of which is dominated by an illite–smectite–K-feldspar–kaolinite mineral assemblage. The proportion of these minerals varies between individual layers as well as laterally from almost pure mixed-layer illite–smectite to K-feldspar and/or kaolinite end-member compositions, but the principal assemblage remains the same (e.g., Snäll, 1976; Bergström et al., 1992, 1998).

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The Upper Ordovician K-bentonites found in the Pirgu Regional Stage are in this respect exceptional in the Baltic Palaeobasin. The clay mineral composition of these beds is characterized by a mixed-layer chlorite–smectite and illite–smectite assemblage. Chlorite–smectite is a trioctahedral Mg-rich clay mineral, typically found in early metamorphic or hydrothermal environments and also in some evaporitic and volcano-clastic successions (e.g., Inoue, 1995; Reynolds, 1988). Chloritic K-bentonites, including K-bentonites with chlorite–smectite, are occasionally found among Ordovician and Silurian K-bentonites in North America, the British Isles and rarely in Baltoscandia (Huff and Morgan, 1990; Bergström et al., 1992, 1998). In these beds the chloritic phases of K-bentonite beds have been obviously formed during alteration under low-grade metamorphic conditions (Krekeler and Huff, 1993). The Paleozoic sedimentary succession of the northern part of Baltic Palaeobasin is, however, devoid of metamorphic overprinting and the organic material maturation indices there suggest very low temperatures (<100 °C; Talyzina, 1998) for early-to-late diagenesis. Therefore the formation of chloritic phases of Pirgu K-bentonites was likely related to processes other than metamorphic alteration.

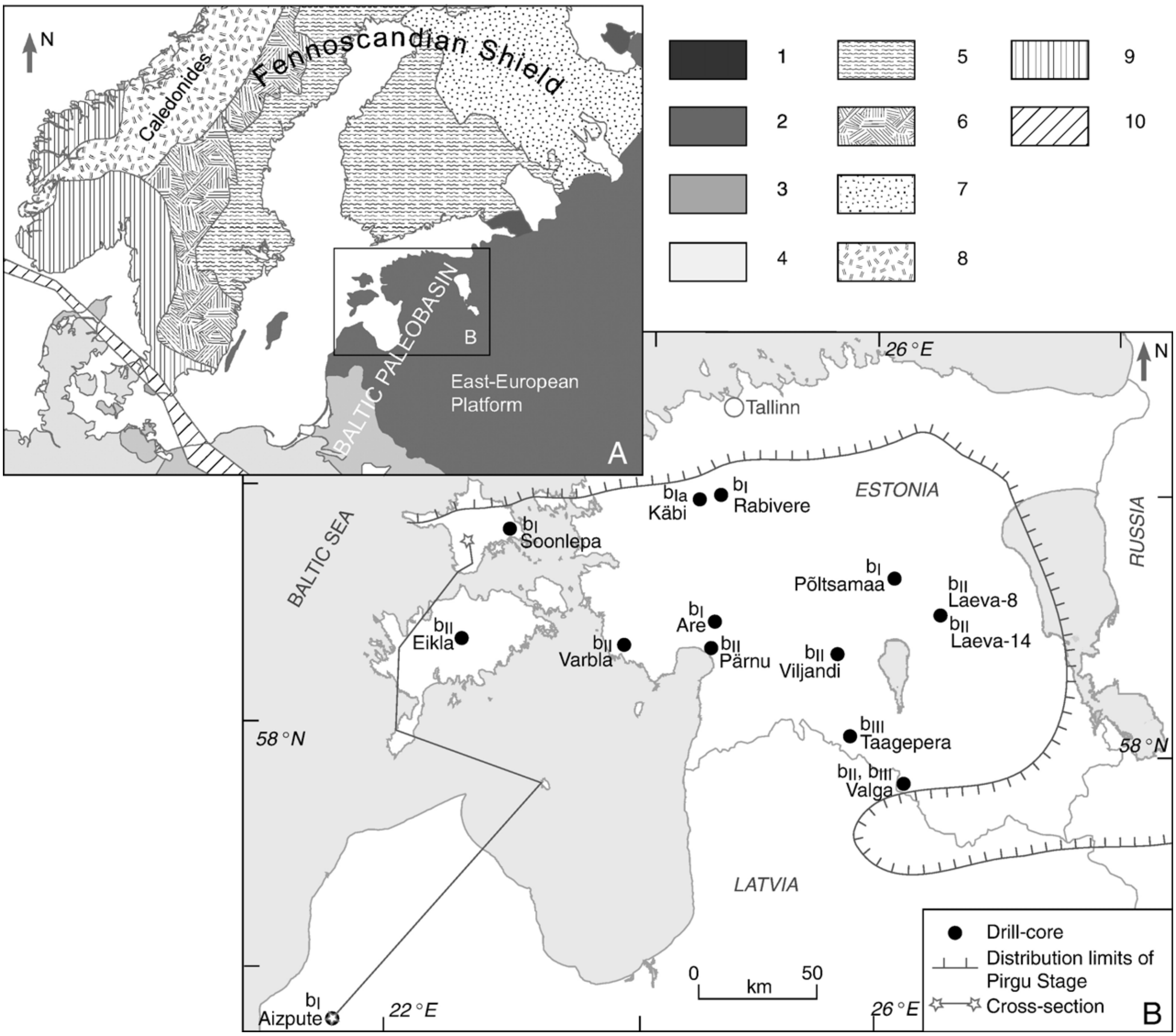

Fig. 1. (A) Simplified geological scheme of northern part of Baltic Palaeobasin and adjacent areas. 1 – Upper Precambrian sediments, 2 – Paleozoic sediments, 3 – Mesozoic sediments, 4 – Cenozoic sediments, 5 – Svecofennian Domain, 6 – Transscandinavian Belt, 7 – Archaean Domain, 8 – Caledonides, 9 – Sveconorwegian Belt, 10 – Tornquist lineament. (B) Sketch map with positions of studied drillcores and distribution limits of the Upper Ordovician Pirgu Stage. b_I, b_{II}, b_{III} and b_{Ia} mark sampled K-bentonite beds of the Pirgu Stage. Cross-section of the Pirgu Stage along the line is shown in Fig. 2.

This contribution focuses on different possible sources of chloritization, such as atypical source materials and special early diagenetic environments.

2. Geological setting

The Baltic Palaeobasin is an old stable pericratonic sedimentary basin of the East European Platform where the most complete stratigraphic record extends from the latest Precambrian to the Cenozoic (Fig. 1A). The sedimentary column is the thickest (>2000 m) and most complete in the southwestern (recent configuration) part of the basin, whereas in the northern part of the basin, only sediments of the Late Proterozoic and the Early Paleozoic are known (Nikishin et al., 1996).

The Lower Paleozoic sedimentary succession of the palaeobasin contains many altered pyroclastic beds known as K-bentonites, which occur in a form of thin but laterally continuous beds within siliciclastic or carbonate successions. These beds originate from single or multiple fallouts of volcanic ashes, erupted mostly from trachyandesitic-to-rhyolitic-type sources and transported through the atmosphere hundreds to thousands kilometers away from the source area before settling on the sea-bottom (Huff et al., 1996). During burial, the original mineral and chemical composition of the primary ashes was largely reworked resulting in specific diagenetic assemblages in the altered ash layers. In the northern part of the Baltic Palaeobasin – in Sweden, Norway, Latvia and Estonia as well as in the northwestern Russia – numerous K-bentonites occur within the Ordovician and Silurian intervals (e.g., Bergström et al., 1992, 1995). The thickest and most widespread Paleozoic K-bentonites of the northwestern

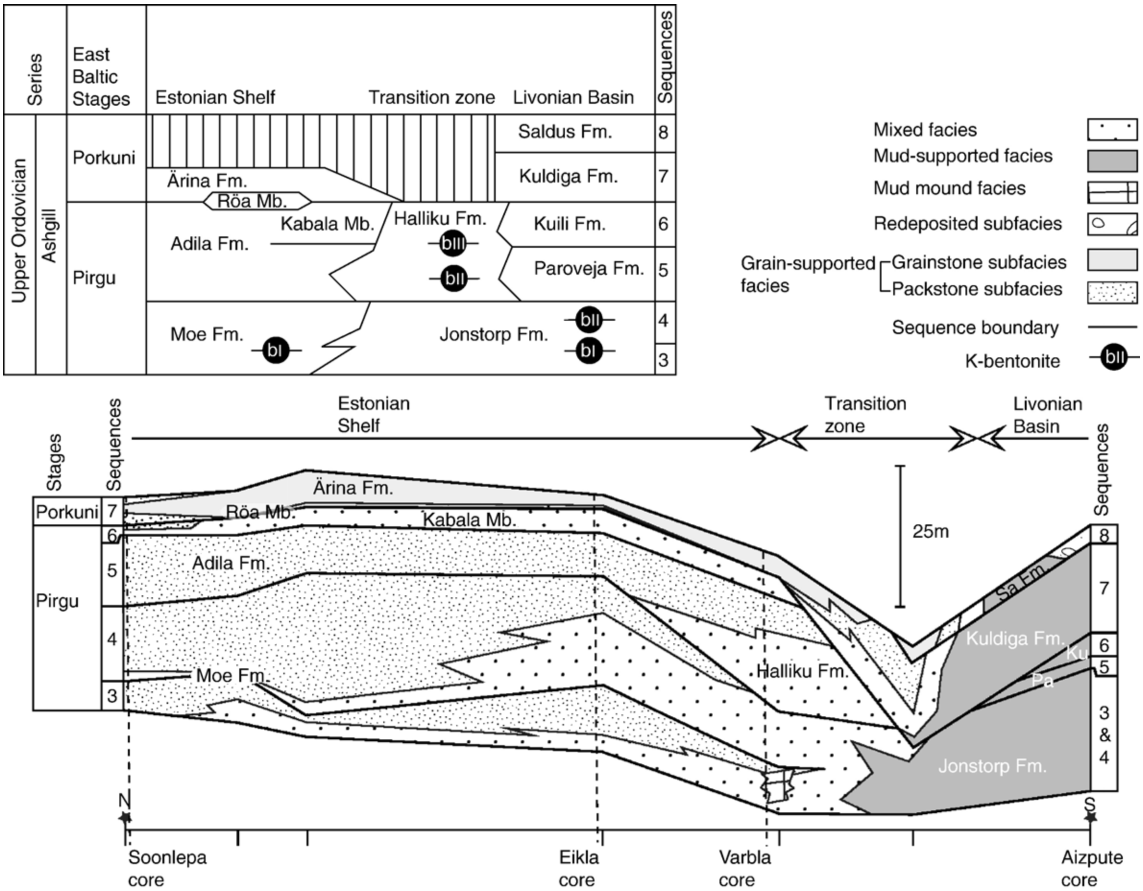

Fig. 2. Stratigraphic scheme and cross-section of the Pirgu Stage (see Fig. 1 for location) after Harris et al. (2004) with stratigraphic intervals of the studied K-bentonite beds (b_I, b_{II}, b_{III}). Note that the K-bentonite bed b_{II} is set within different sequences at the Estonian Shelf and Livonian Basin. The Soonlepa, Eikla and Varbla drill-core (located next to the actual cross-section line, however, their detailed stratigraphic successions are not fully compatible with these on the cross-section) are marked on cross-section line in order to illustrate their relative position on facies scheme. Distances between the cores are scaled except for the distance between two southernmost cross-section points. Abbreviated formation names: Ku – Kuili, Pa – Paroveja, Sa – Saldus.

Europe, the Middle Ordovician Kinnekulle bed and the Llandoverian Osmundsberg bed, have been traced across large areas in Baltoscandia and Britain (Bergström et al., 1995, 1998). Moreover, for the Kinnekulle bed a transatlantic correlation with North American Millbrig K-bentonite bed has been proposed (Huff et al., 1996). The occurrence of the K-bentonites in the Baltoscandian, British and eastern North American successions is apparently related to the eruptive volcanic activity from the island arcs or microplates undergoing subduction/collision against the southeastern margin of Laurentia, resulting in closure of the Iapetus Ocean that separated Baltica and Laurentia (Scotese and McKerrow, 1991). These Lower Paleozoic altered ash beds are characterized by a clay matrix, which consists chiefly of illite–smectite with lesser amounts of kaolinite (Kolata et al., 1996; Huff et al., 1998). The altered ash beds of the Upper Ordovician Pirgu Stage of Estonia are exceptions to this regularity since they contain significant amounts of chloritic phases.

The Pirgu Stage spread in the northeastern part of the Baltic Palaeobasin is a considerably thick unit, which consists of variable sedimentary rocks of marine origin (Fig. 2). In the Late Ordovician, the northeastern part of the palaeobasin was characterised by a well-developed facies zonation (Nestor, 1990), with a broad shallow shelf in the north and a deep central depression, cited as the Livonian Basin, in the south, together with a transitional belt in between (Harris et al., 2004) (Fig. 7). Within the shallow shelf facies of the Pirgu Stage, packstones predominate. The transitional facies successions in central Estonia are characterized by the interfingering of packstone–wackstone, whereas inside the deep basin belt red- or grey-coloured mudstones dominate (Hints and Meidla, 1997). The accumulation of a wide range of sediments as well as significant thickness variations of the stage have been obviously caused by eustatic sea-level changes, local tectonic movements and the formation of mud mounds inside the palaeobasin during the Pirgu Age (Hints and Meidla, 1997).

The Pirgu Stage contains at least three, distinct K-bentonite beds (Kiipli et al., 2004). The lateral extension and bed-to-bed correlation of individual beds is somewhat unclear, as most of the sections of the Pirgu Stage contain only one or two beds at the time. Based on pyroclastic sanidine composition of the K-bentonites, Kiipli et al. (2004) suggested correlations for the Pirgu beds. In this contribution the correlation proposed by Kiipli et al. (2004) is adopted and combined with the stratigraphical scheme of the Pirgu Stage by Harris et al. (2004).

The stratigraphically lowermost K-bentonite of the Pirgu Stage (b_I) occurs in the Moe and Jonstorp formations (Fig. 2). The two other beds examined in this contribution (b_{II} and b_{III}) are found in the Halliku and Jelgava formations, the last is distributed in the east of the Halliku Formation, within shelf facies and a transition zone. Inside of the Livonian basin, these beds are set in the Jonstorp or Jelgava formations. One K-bentonite bed from the Moe Formation in the Käbi core (b_{Ia}) exhibits a unique pyroclastic sanidine composition that might indicate an origin from a distinct fallout (Kiipli et al., 2004).

3. Materials and methods

The material investigated came from 14 drillcores located in the northern part (Estonia and northern Latvia) of the Baltic Palaeobasin (Fig. 1B). Altogether, 17 samples were chosen from the Pirgu K-bentonite beds. Both plastic and non-plastic feldspathised varieties of altered ash beds rich in detrital mica/biotite flakes were sampled.

The K-bentonite whole-rock samples and clay fractions were studied for mineral composition by means of powder X-ray diffraction (XRD). The samples were fractionated by standard sedimentation procedures and the <2 μm size fraction was flocculated and Sr^{2+} saturated with 0.1 M $SrCl_2$. Excess salt was removed after repeated rinsing with distilled water and ethanol. Oriented clay aggregates were made by smearing the clay pastes onto glass slides. Unoriented mounts were made of powdered and homogenised representative whole rock samples. XRD data of oriented air-dry and ethylene glycol solvated (EG) preparations and unoriented mounts were obtained using a DRON-3M diffractometer with Ni-filtered Cu$K\alpha$ radiation, 0.5 mm divergence slit, 0.25 mm receiving slit and two 1.5° Söller slits. Scanning steps of 0.02° 2θ from 2° to 40° 2θ and a counting time of 3 s per step were used for clay slides and 2° to 50° 2θ and 5 s for unoriented preparations. The ambient relative humidity varied from 60% to 65%.

Qualitative and quantitative estimations of illite and kaolinite, as well as proportions of smectite in mixed-layer illite–smectite and chlorite–smectite/corrensite, were modelled by the computer program 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 to calculated structural models by trial-and-error procedure until optimum fit was achieved. The

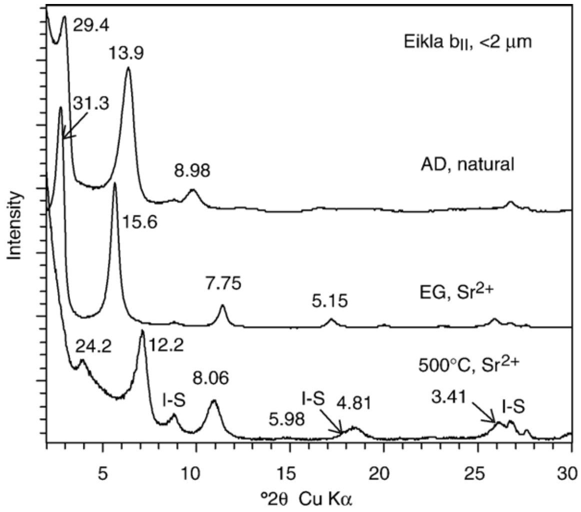

Fig. 3. XRD patterns of Corr-dominated <2 μm fraction of K-bentonite (b_{II}) from the Eikla core. The patterns are obtained from a single sample in air-dry, ethylene glycol solvated and heated state. Note the occurrence of Corr superstructure peak at 29.4 Å in air-dry state and 31.3 Å in ethylene glycol-solvated state.

profiles were fitted in the 2°–40° 2θ range using the instrumental and experimental factors, the orientation factor and the mass adsorption coefficients and structural layer compositions suggested by Moore and Reynolds (1997). The coherent stacking domain sizes were distributed log-normally assuming the extent of the scattering domains on the mean defect-free distance proposed by Ergun (1970). The mean thicknesses of coherent stacking domains were experimentally determined following the method of Drits et al. (1997).

The SEM studies of selected K-bentonite whole-rock samples were carried out on a LEO–EVO scanning electron microscope in the Estonian Agricultural University. The samples were coated with gold prior to analysis.

4. Results

The clay fraction (<2 μm) of 17 K-bentonite samples contains mixed-layer R1 ordered chlorite–smectite (corrensite)-type phases together with mixed-layer illite–smectite, discrete kaolinite, and probably discrete illite plus a 3-component mixed layer illite–vermiculite–smectite mineral. The chloritic phases are the most abundant clay minerals in the most samples, but also the illite–smectite may dominate in some mixtures with minor corrensite, while in some illite–smectite-rich samples, corrensite is absent.

The occurrence of corrensite, which is R1 ordered 0.5/0.5 interlayered chlorite and smectite mineral, is

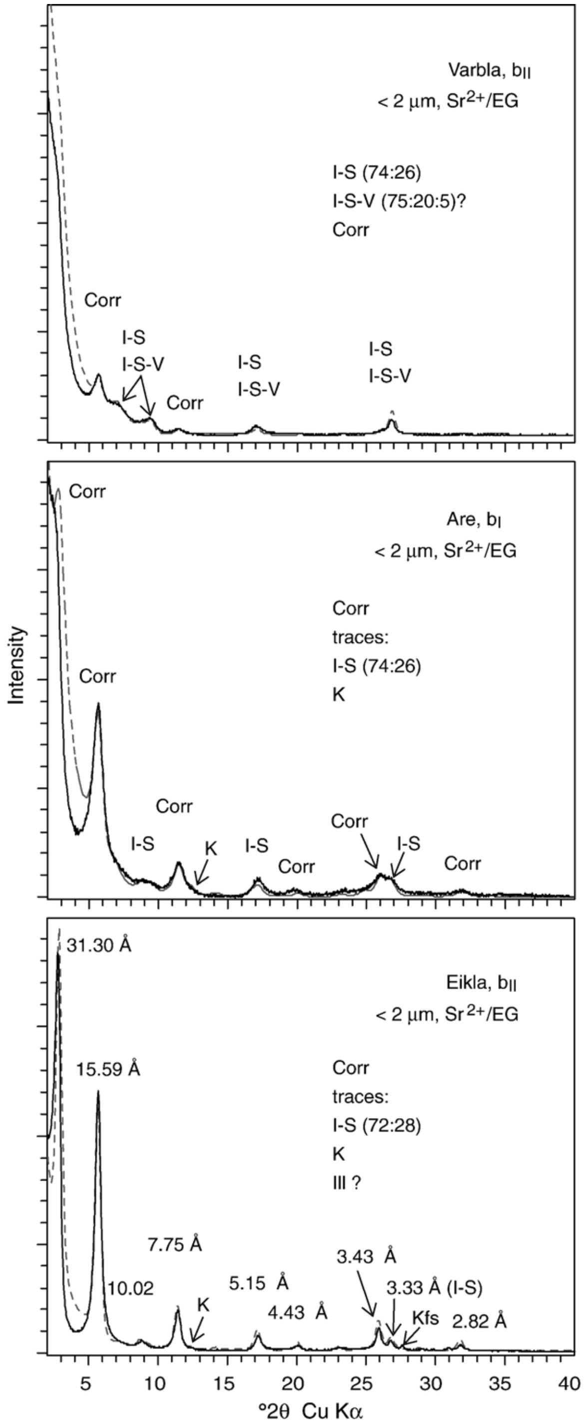

Fig. 4. Representative measured XRD patterns of oriented ethylene glycol solvated <2 μm fractions of K-bentonites and modelled diffraction patterns. Black solid line is the measured and grey dashed line the modeled pattern. Principal mineral assemblage of <2 μm fraction starting with the most abundant phase is presented in the figure. Abbreviated mineral names: I–S–V – illite–smectite–vermiculite, Corr – corrensite, I–S – illite–smectite, K – kaolinite.

suggested by the structure expansion and collapse by EG solvation and heating, respectively. Specifically, the corrensite-type phase is identified by the superstructure $d(001)$ spacing expansion from 29 Å in the air-dried state to 31 Å and a nearly harmonic series of peaks in the EG saturated state (Fig. 3). Some deviation from strict harmonicity of corrensite peaks series may indicate the possible interstratification effects of layers having different thicknesses (Calarge et al., 2003). Heating of the corrensite-rich sample at 500 °C for 1 h caused the spacing to collapse to 24 Å. The comparison of experimental and calculated profiles confirms the presence of corrensite-type mixed-layer phase (Fig. 4) in mixture with mixed-layer illite–smectite, kaolinite and discrete illite. The smectite layers content estimated by modelling in mixed layer illite–smectite varies between 71% and 74%. However, in some samples (e.g., Varbla, Fig. 4), the satisfactory agreement between experimental and calculated profiles was achieved only if some amount of three-component illite–smectite–vermiculite phase was assumed in addition to illite and smectite components. The layer proportions for illite–smectite–vermiculite were found 75 : 20 : 5, respectively.

The whole rock assemblage of the Pirgu K-bentonites consists of chlorite–smectite, illite–smectite, kaolinite and K-feldspar with some amounts of quartz, detrital mica/biotite and minor dolomite (Fig. 5). The samples present large compositional variations from nearly pure chlorite–smectite–K-feldspar to illite–smectite–K-feldspar composition. The change from chlorite–smectite to illite–smectite is gradual but shows systematic lateral variations from chlorite–smectite-rich beds in the northwestern and northern sections to illite–smectite beds in the south. Chloritic mixed-layer phases are found in both plastic and strongly feldspathised varieties of the Pirgu K-bentonites (Fig. 5, samples from the Are and Eikla core). The SEM observations of bulk samples of chlorite-rich K-bentonites indicate a boxwork pattern orientation of the anhedral-to-subhedral large (2–5 μm) chlorite–smectite flakes, especially in the pore space of the feldspathised matrix (Fig. 6A, B, C). In the clay-rich matrix/areas of the K-bentonite, the pattern shows parallel arrangement of folded subhedral-to-euhedral platy crystals of smaller particle size (Fig. 6D).

The systematic compositional variations are also evident in the clay fraction of the K-bentonites (Fig. 4). The mineral composition of the clay fraction varies significantly between distinctive K-bentonite beds from a single section, as well as laterally from section to section (Fig. 7). Chlorite mixed-layer phases occur in the bed b_{I} and b_{II}. In bed b_{III}, studied only in three

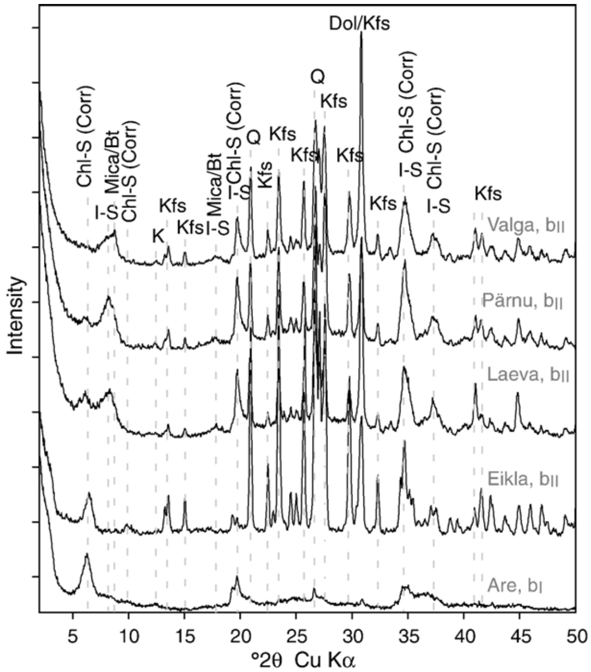

Fig. 5. XRD patterns of investigated K-bentonite whole rock samples and qualitative mineral composition of K-bentonites. Note that K-bentonite sample from the Are core is composed of almost pure Chl–S (Corr) and relative proportion of this phase in K-bentonite samples decreases in upward direction. Abbreviated mineral names: Chl–S – chlorite–smectite, Corr – corrensite, I–S – illite–smectite, Bt – biotite, K – kaolinite, Kfs – potassium feldspar, Q – quarts, Dol – dolomite.

sections from the Livonian Basin, chlorite–smectite (corrensite) is not detected. The most remarkable lateral variation of clay mineral composition of the K-bentonites is the gradual change of chlorite–smectite (corrensite)/illite–smectite ratio. The K-bentonites with abundant interstratfied chloritic phases are found in the northwestern localities, whereas in the southeast, in the deeper shelf and partly in the transition zone, illite–smectite and chlorite–smectite (corrensite) assemblages become dominant. The K-bentonites from southeastern Estonia contain only minor amounts of chloritic minerals and the clay assemblage there is made up predominantly of illite–smectite. In the Livonian Basin, mixed-layer chloritic phases are missing and the clay fraction of K-bentonites consists of illite–smectite with some kaolinite (Fig. 7). Chlorite mixed-layer phases were not detected in the sample from the Soonlepa core, which is one of the northernmost sampling localities. Local variations in the K-bentonites clay mineral composition are observed in the Varbla core, where within a single nearly 30-cm thick bed both chlorite–smectite (corrensite)-rich variety and illite–smectite-rich variety with minor chlorite–smectite (corrensite)

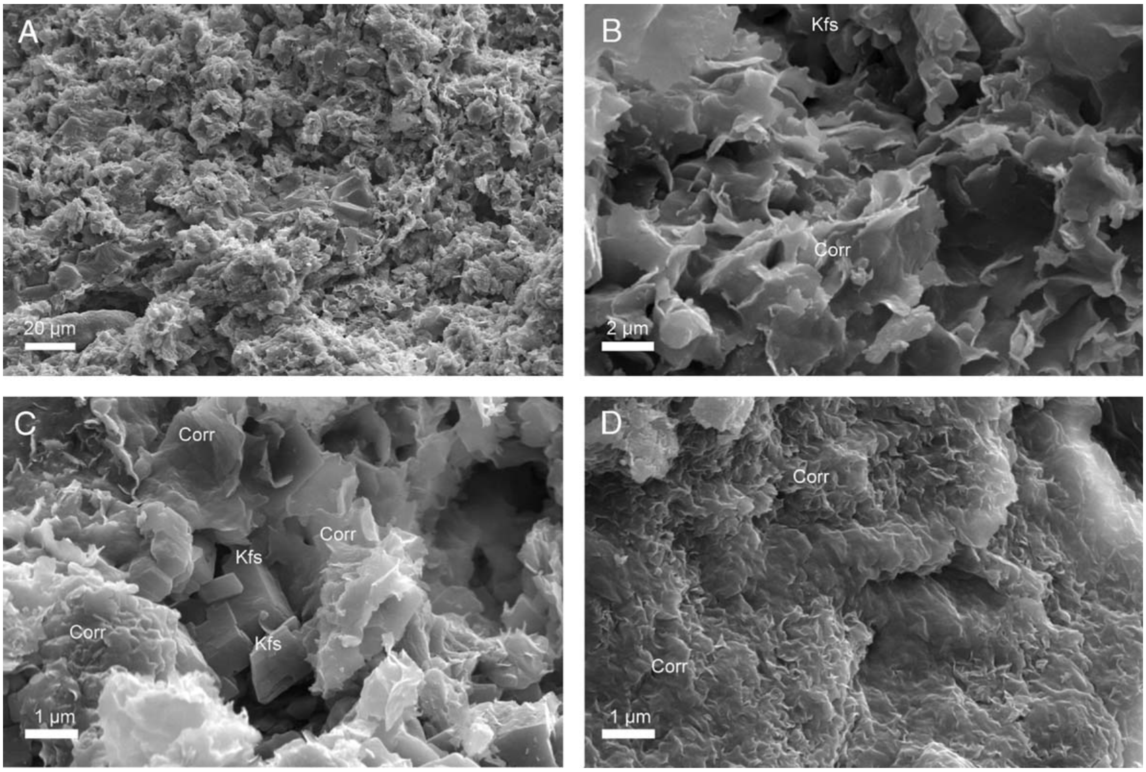

Fig. 6. SEM images of strongly feldspathised K-bentonite b_{II} from the Eikla core (A, B and C) and clay-rich K-bentonite b_I from the Are core (D). (A) Kfs-dominated matrix of K-bentonite is characterized large pore-space volume partly occupied by Chl–S (Corr). (B) Boxwork pattern established by large anhedral-to-subhedral flakes of Chl–S (Corr). (C) Small euhedral crystals of authigenic Kfs. (D) The folded subhedral-to-euhedral platy Chl–S (Corr) crystals wit orientation parallel to bedding plane. Note that the Chl–S (Corr) crystals have considerably smaller particle size than the same phases in Kfs-rich K-bentonite from the Eikla core. See Fig. 5 for abbreviated mineral names.

occur. Two samples collected near the lower boundary of the bed are characterized by the illite–smectite assemblage, whereas in the sample from the upper part of the bed the chlorite–smectite dominates.

5. Discussion

Chlorite–smectite and corrensite are widespread minerals in sub-greenschist grade metamorphic rocks and hydrothermal alteration environments, but they are found in various evaporitic and volcanoclastic sedimentary-diagenetic settings as well (e.g., Inoue, 1995; Reynolds, 1988). In sedimentary marine and lacustrine environments corrensite, which is not found in modern sediments (Chamley, 1989), is considered to result either from a moderate diagenetic evolution of detrital mafic minerals (Hillier, 1993) or the diagenetic evolution of smectite that has initially settled in carbonate (dolomite) dominated lagoonal or low-to-moderate energetic conditions in offshore areas (Han et al., 2000). In the Late Jurassic shallow-marine sandstones, the authigenic chlorite minerals corrensite, discrete chlorite and mixed-layer berthienite–corrensite were formed during burial diagenesis (90–120 °C) from precursor minerals, from odinite in the case of mixed-layer berthienite–corrensite and from saponite in the case of corrensite and discrete chlorite (Ryan and Hillier, 2002). Mg-rich smectite (saponite), which is thought to be the common precursor of diagenetic corrensite and chlorite, is commonly found in evaporative lacustrine and aeolian sediments (Chamley, 1989), but it is described also in modern marine-evaporative environments (Hover et al., 1999). In alternating pyroclastic-sedimentary beds the formation of dioctahedral smectite and subsequent smectite-to-illite conversion is related to acidic volcanic materials, while the formation of trioctahedral smectite (saponite) and transformation of smectite-to-chlorite occurs specifically at the expense of the mafic volcanics (e.g., Son et al., 2001).

A smectite-to-chlorite transformation is typical in the development of Mg–Fe-rich rocks and sediments. It begins usually with the formation of saponite-type smectite at the expense of Mg-rich volcanics or basic detrital minerals, which then in progressive diagenesis

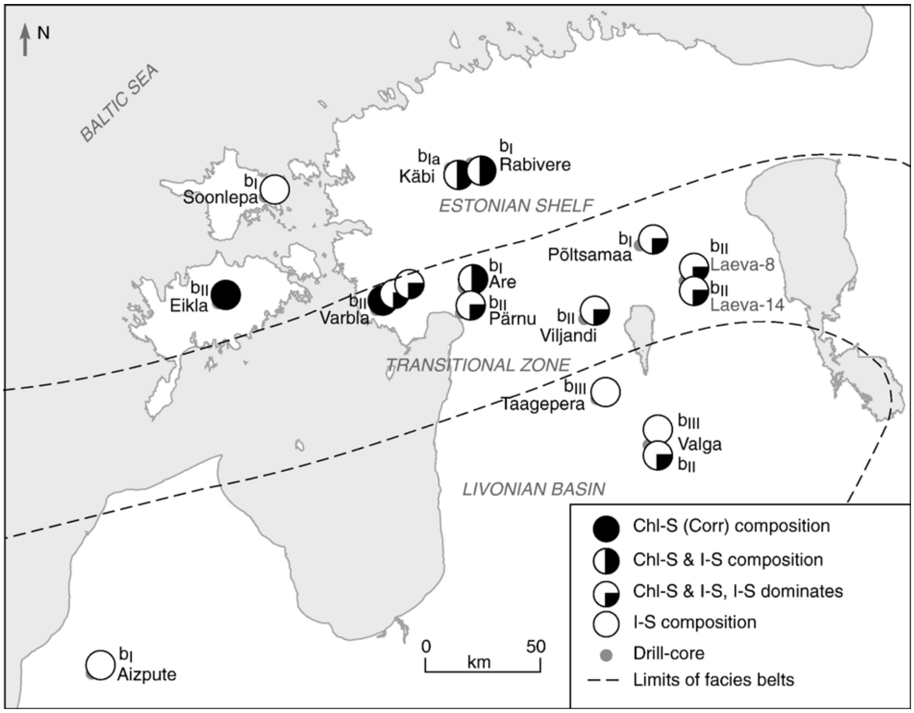

Fig. 7. Lateral distribution of Chl–S (Corr) in the K-bentonites of the Pirgu Stage on bases of clay fraction data. Chl–S (Corr) phases are most abundant in the northern and northeastern part of study area and decrease gradual south- and southeastward. The limits of facies belts of the Baltic Palaeobasin after Harris et al. (2004). See Fig. 5 for abbreviated mineral names.

or hydrothermal alteration transforms into corrensite (Reynolds, 1988). The chloritization in corrensite-to-chlorite conversion proceeds with the growth of chlorite layers in corrensite to form discrete chlorite domains in a corrensite matrix (Beaufort et al., 1997). In geothermal systems, the transformation from smectite to chlorite proceeds via three contrasting reaction pathways involving (a) a continuous mixed-layer chlorite–smectite series, (b) a discontinuous smectite–corrensite–chlorite series and (c) a direct smectite-to-chlorite transition. This suggests disequilibrium in a kinetically controlled reaction mineral series which depends upon fluid/rock ratios and/or a contrast between advective and diffusive fluid transport (Robinson et al., 2002). Also, corrensite can form directly from saponite under hydrothermal conditions at temperatures between ~100 and 200 °C (Inoue and Utada, 1991).

Considering different possible pathways for chloritization of the Pirgu K-bentonites the chloritic phases could have resulted, firstly, from metamorphic–hydrothermal environment, secondly, from the alteration of mafic source material and, thirdly, from a specific diagenetic environment.

The Paleozoic sedimentary succession in the northern Baltic Palaeobasin does not show any signs of deep late-diagenesis or metamorphic alteration (Kirsimäe and Jørgensen, 2000). Consequently, a metamorphic origin of the studied Pirgu K-bentonite beds can be excluded and the clay mineral composition of the beds has been likely controlled by original pyroclastic material composition or by a specific early diagenetic environment during the volcanic glass devitrification, both of which must have provided high Mg for saponite-type smectite formation and for subsequent saponite-to-chlorite transformation.

The trace element composition of whole rock and glass melt inclusions of the Baltoscandian Ordovician–Silurian K-bentonites suggest the parental magma of rhyolite–rhyolite–dacite and dacite–trachyandesite composition (Bergström et al., 1995; Huff et al., 1996; Kiipli and Kallaste, 1996), which implies that the magmas have been at least partly derived from melting of continental crustal rocks (Delano et al., 1990). The same is indicated by the relatively high Zr/TiO_2 ratio (0.06–0.12) of Pirgu K-bentonites. The ratio of these incompatible elements is frequently used to discriminate the source magmas of volcanic rocks (Winchester and Floyd, 1977). Since Zr and Ti are considered to be rather immobile under diagenetic conditions they can be used for the distinction of old diagenetically altered tephra layers (e.g. Batchelor and Jeppsson, 1999). The high Zr/TiO_2 ratios are characteristic for the rocks formed from more evolved magmas, which have undergone an extensive crystallization differentiation and/or assimilated a significant amount of continental crust material during their formation.

The saponite-to-chlorite series, on the contrary, are typically found to alter diagenetically or hydrothermally from more mafic-type andesitic pyroclastics (Chang et al., 1986; Inoue and Utada, 1991; Son et al., 2001). The hypothetical original mafic composition of the Pirgu altered ash beds conflicts also with the assumed transport distance of probably co-ignimbritic ash clouds in the range of several thousands of kilometers (Huff et al., 1996). The volcanic vents associated with active subduction zones of the closing Iapetus Ocean in the Ordovician–Silurian time were most likely situated at the Laurentian side of the ocean on an island arc or microplate that collided with Laurentia during the Ordovician (Huff et al., 1996) (Fig. 8). The mafic (andesitic) eruptions there could not have produced enough ash for the observed lateral distribution of pyroclastics all over the eastern North America, Baltoscandia and British Island. Moreover, the single fallout of mafic pyroclastics would not explain the lateral variation of the K-bentonite clay mineral composition.

The spatial distribution of the chloritic minerals in Pirgu bentonites suggests a relationship to depositional facies and/or specific diagenetic environment. The chloritic mixed-layer composition of K-bentonite beds occurs in the Eikla, Are, Rabivere and Pärnu drillcores, which are located within the most shallow water part of Estonian shelf (Fig. 7), whereas the K-bentonites in

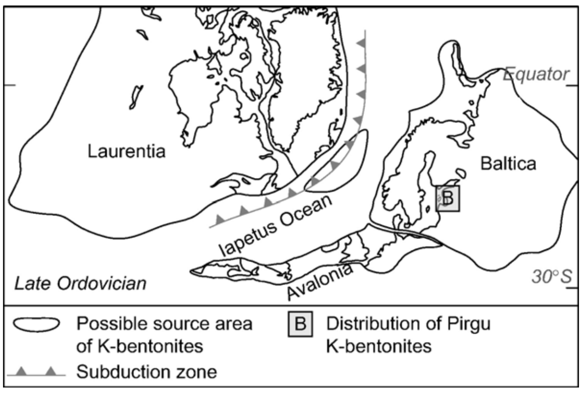

Fig. 8. Paleogeography of Baltica, Laurentia and Avalonia in the Late Ordovician with the major tectonic settings and probable source area of volcanic ashes of the Ordovician altered ash beds of the northern Baltic Palaeobasin (after Huff et al., 1996).

drillcores in more deeper transitional zone are dominated by illite–smectite and contain minor chlorite–smectite (corrensite). The K-bentonites in the Taagepera, Valga and Aizpute drillcores located in the Livonian Basin are characterized by illite–smectite mixed-layer minerals. Interestingly, one of the northernmost (the most nearshore located) sampling locality reveals a K-bentonite bed of purely illite–smectite composition.

The precursor trioctahedral Mg–smectite and following diagenetic chlorite–smectite (corrensite) formation in the Pirgu K-bentonites could have been controlled by high externally promoted pH and/or Mg^{2+} activity in shallow shelf area, which may have shifted the activity ratio of Mg^{2+}/H^{+} inside of ash layer sufficiently to precipitate the authigenic trioctahedral Mg–smectite at the expense of devitrification of felsic volcanic glass or initial Al–smectite (Hover et al., 1999), or to initiate directly the growth of brucite-like interlayers in precursor Al–smectite (Hillier, 1993). The high Mg influx, for example, can be attained by the fluids common to secondary dolomitization. Interestingly, Hover et al. (1999) report the formation of authigenic trioctahedral K-rich Mg–smectite in modern marine evaporative environments during very early diagenesis in a large supratidal evaporative sabkha complex near the mouth of the Colorado River (Baja, CA), where the authigenesis of Mg-clay was controlled by the sediment pore waters exceptionally rich in Mg^{2+} due to suppressed sulfate reduction which, in turn, inhibited the carbonate (dolomite) precipitation.

It is not very likely that the corrensite in the Pirgu K-bentonites is of lacustrine-evaporative or late dolomitization origin because of the lack of any direct sedimentological evidence of lacustrine-evaporative facies sediments or either regional secondary dolomitization in the Pirguan rocks. On the other hand, the end of Pirgu time was characterized by rapid seal-level changes, denudation and tectonic movements, which were accompanied by deposition of probably microbially enhanced carbonate mounds found at this time in several places of Baltoscandia (the so called Boda mounds; Hints and Meidla, 1997; Harris et al., 2004). This suggests that the Mg-clay-rich K-bentonites in the Pirgu Stage could have possibly originated during the early diagenesis in the (marine) evaporative sabkha-type environment. Harris et al. (2004) subdivide the Pirgu Stage into four sequences that exhibit shallowing-upward facies patterns on the Estonian Shelf and grade laterally through the transitional zone into mud-supported facies in the Livonian Basin (Fig. 7). The upper boundary of the Pirgu Stage is marked by a hiatus on the shelf and transition zone. As the result of several relative sea-level drops in the Pirgu Age the large shallow-water areas probably appeared on the Estonian Shelf and on the upper part of transition zone, whereas water exchange with the rest of the basin might have been more or less restricted due to uneven sea bottom topography. Furthermore, by the Late Ordovician, the Baltica had drifted to the vicinity of the Equator (Fig. 8) and high evaporation rates there might have favoured the development of abnormal salinity in semi-enclosed settings. Such sabkha-type environments would have provided the flux of saline Mg-rich aqueous fluids through subaerally exposed carbonate rocks and the K-bentonite beds. At these environmental conditions the additional (but evidently not sufficient) Mg-source could have come from the subaerial weathering of detrital pyroclastic biotite. Biotite phenocrysts are abundant in Ordovician K-bentonites (Haynes, 1994) and are macroscopically and microscopically observed in the Pirgu K-bentonite samples. The shallow-water, probably supratidal or tidally influenced lagoonal depositional environment attained at the boundary of the Pirgu and next younger Porkuni time is marked by the occurrence of very early diagenetic dolomitic beds of the Röa Formation (Hints and Meidla, 1997). The biostratigraphic position of the Röa Formation is unclear and it might denote both the very beginning of Porkuni time or the very end of Pirgu time (Fig. 2). Local early diagenetic dolomitization is also suggested by the occurrence of asymmetrical dolomitized zones within the Pirgu shelf deposits. The deposits were originally limestone because they contain lots of skeletal grains. These dolomitized zones provide evidence of early exposure-related dolomitizing fluids since they are found only below boundaries (Mark Harris, personal communication 2005).

If the interpretation of the formation of chlorite–smectite-rich beds in an evaporative sabkha-type environment is correct, then the absence of the chloritic phases in the Soonlepa core, which is the most nearshore located sampling locality, would suggest a rather substantial sea-level drop at the time of saponite formation, leaving this area outside the limits of supratidal/sabkha-like zone.

The occurrence of chloritic mixed-layer minerals in different mineral assemblages such as almost pure corrensite assemblage, potassium feldspar-rich K-bentonite and illite–smectite-dominated assemblage implies that stabilization of Mg clays was not restricted to one specific geochemical environment but could take place under a range of pH and silica activities provided that enough Mg was available from external source.

The extent to which the Mg-rich pore waters in the sabkha-like environment have influenced the clay mineral composition and diagenesis appears to be much wider than only K-bentonites, because the clay component in the Pirgu Stage host rocks is also found to contain some amount of chlorite–smectite.

6. Conclusions

The clay mineral composition of the Upper Ordovician Ashgill (the Pirgu Stage) K-bentonites in the Baltic Palaeobasin differs from other known Ordovician and Silurian K-bentonites in the area by the occurrence of the clay mineral chlorite–smectite (corrensite). Abundance of these chloritic phases shows regular variation with the host rock facies zones. The chloritic mixed-layer minerals prevail in the clay mineral assemblage of the altered volcanic ashes deposited in the broad shallow shelf facies zone (Estonian shelf) and their share gradually decreases within the transitional belt until disappearance in the deep central depression of Livonian Basin where the clay fraction of K-bentonites is composed of illite–smectite and some kaolinite. The present study suggests that chlorite–smectite (corrensite) in the Pirgu K-bentonites originates from early diagenesis in the marine evaporative sabkha-type environment where the flux of saline Mg-rich fluids through subaerally exposed rocks provided high Mg needed for saponite-type smectite formation and lead to consequent saponite-to-chlorite transformation.

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References

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. Geologiska Föreningens i Stockholm Förhandlingar 117, 1–13.

Bergström, S.M., Huff, W.D., Kolata, D.R., 1998. The Lower Silurian Osmundsberg K-bentonite: Part I. Stratigraphic position, distribution, and paleogeographic significance. Geological Magazine 135, 1–13.

Calarge, L., Lanson, B., Meunier, A., Formoso, M.L., 2003. The smectitic minerals in a bentonite deposit from Melo (Uruguay). Clay Minerals 38, 25–34.

Chamley, H., 1989. Clay Sedimentology. Springer-Verlag, Berlin.

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.

Delano, J.W., Schirnick, C., Bock, B., Kidd, W., Heizler, M., Putnam, G., De Long, S., Ohr, M., 1990. Petrology And geochemistry of Ordovician K-bentonites in New York state; constraints on the nature of a volcanic arc. Journal of Geology 98, 157–170.

Drits, V.A., Srodon, J., Eberl, D.D., 1997. XRD measurement of mean crystallite thickness of illite and illite/smectite: reappraisal of the Kübler index and the Scherrer equation. Clays and Clay Minerals 45, 461–475.

Ergun, S., 1970. Calculation of profiles of two-dimensional X-ray reflections from layered structures. Journal of Applied Crystallography 3, 153–156.

Han, G., Preat, A., Chamley, H., Deconinck, J.-F., Mansy, J.-L., 2000. Paleozoic clay mineral sedimentation and diagenesis in the Dinant and Avesnes Basins (Belgium, France): relationships with Variscan tectonism. Sedimentary Geology 136, 217–238.

Harris, M.T., Sheehan, P.M., Ainsaar, L., Hints, L., Männik, P., Nõlvak, J., Rubel, M., 2004. Upper Ordovician sequences of western Estonia. Palaeogeography, Palaeoclimatology, Palaeoecology 210, 135–148.

Haynes, J.T., 1994. The Ordovician Deicke and Millbrig K-bentonite beds of the Cincinnati Arch and Southern Valley and Ridge Province. Special Paper-Geological Society of America 290, 1–84.

Hillier, S., 1993. Origin, Diagenesis, and Mineralogy of Chlorite Minerals in Devonian Lacustrine Mudrocks, Orcadian Basin, Scotland. Clays and Clay Minerals 41, 240–259.

Hints, L., Meidla, T., 1997. Pirgu Stage. In: Raukas, A., Teedumäe, A. (Eds.), Geology and Mineral Resources of Estonia. Estonian Academy Publishers, Tallinn, pp. 82–85.

Hover, V.C., Walter, L.M., Peacor, D.R., Martini, A.M., 1999. Mg–smectite authigenesis in a marine evaporative environment, Salina Ometepec, Baja California. Clays and Clay Minerals 47, 252–268.

Huff, W.D., Morgan, D.J., 1990. Stratigraphy, mineralogy and tectonic setting of Silurian K-bentonites in southern England and Wales. Ninth International Clay Conference, Strasbourg, 1989. Proceedings. Sciences Géologiques Mémoires 88, 33–42.

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 characteristics. Journal of Volcanology and Geothermal Research 73, 285–301.

Huff, W.D., Bergström, S.M., Kolata, D.R., Sun, H., 1998. The Lower Silurian Osmundsberg K-bentonite: Part II. Mineralogy, geochemistry, chemostratigraphy, and tectonomagmatic significance. Geological Magazine 135, 15–26.

Inoue, A., 1995. Formation of clay minerals in hydrothermal environments. In: Velde, B. (Ed.), Origin and Mineralogy of Clays. Springer-Verlag, Berlin, 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.

Kiipli, E., Kallaste, T., 1996. Geochemical characterization of some Estonian metabentonites. Proceedings of the Estonian Academy of Sciences. Geology 45, 68–77.

Kiipli, E., Kallaste, T., Kiipli, T., 2004. Metabentonites of the Pirgu Stage (Ashgill, Upper Ordovician) of the East Baltic. In: Hints, O., Ainsaar, L. (Eds.), WOGOGOB-2004: Conference Materials. Abstracts and Field Guide Book. Tartu University Press, Tartu, p. 53.

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.

Kolata, D.R., Huff, W.D., Bergstrom, S.M., 1996. Ordovician K-bentonites of eastern North America. Special Paper-Geological Society of America 313, 1–84.

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. Abstracts with Programs-Geological Society of America 25, 30.

Moore, D.M., Reynolds Jr., R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd edition. Oxford University Press, Oxford.

Nestor, H., 1990. Basin development and facies models. In: Kaljo, D., Nestor, H. (Eds.), Field Meeting in Estonia 1990. An Excursion Guidebook. Estonian Academy of Science, Tallinn, pp. 33–36.

Nikishin, A.M., Ziegler, P.A., Stephenson, R.A., Cloetingh, S.A.P.L., Furne, A.V., Fokin, P.A., Ershov, A.V., Bolotov, S.N., Korotaev, M.V., Alekseev, A.S., Gorbachev, V.I., Shipilov, E.V., Lankreijer, A., Bembinova, E.Yu., Shalimov, I.V., 1996. Late Precambrian to Triassic history of the East-European craton: dynamics of sedimentary basin evolution. Tectonophysics 268, 23–63.

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.

Reynolds Jr., R.C., 1985. NEWMOD©, A computer program for the calculation of one-dimensional diffraction patterns of mixed-layer clays. In: Reynolds Jr., R.C., 8 Brook Drive, Hanover, NH 03755.

Reynolds Jr., R.C., 1988. Mixed layer chlorite minerals. Mineralogical Society of America Reviews in Mineralogy 19, 601–629.

Robinson, D., Schmidt, S.T., de Zamora, A.S., 2002. Reaction pathways and reaction progress for the smectite-to-chlorite transformation: evidence from hydrothermally altered metabasites. Journal of Metamorphic Geology 20, 167–174.

Ryan, P.C., Hillier, S., 2002. Berthierine/chamosite, corrensite, and discrete chlorite from evolved verdine and evaporite-associated facies in the Jurassic Sundance Formation, Wyoming. American Mineralogist 87, 1607–1615.

Scotese, C.R., McKerrow, W.S., 1991. Ordovician plate tectonic reconstructions. In: Barnes, C.R., Williams, S.H. (Eds.), Advances in Ordovician Geology. Geological Survey of Canada, Paper, vol. 90-9, pp. 271–282.

Snäll, S., 1976. Silurian and Ordovician bentonites of Gotland (Sweden). Acta Universitatis Stockholmiensis 31, 1–80.
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.
Talyzina, N.M., 1998. Fluorescence intensity in Early Cambrian acritarchs from Estonia. Review of Palaeobotany and Palynology 100, 99–108.
Winchester, J.A., Floyd, P.A., 1977. Geochemical discrimination of different magma series and their differentiation products using immobile elements. Chemical Geology 20, 325–343.