DISSERTATIONES GEOLOGICAE UNIVERSITATIS TARTUENSIS
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PEETER SOMELAR

Illitization of K-bentonites in the Baltic Basin

TARTU UNIVERSITY
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CONTENTS

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 **Somelar, P.,** Kirsimäe, K., Środoń, J. (2009). Mixed-layer illite-smectite in the Kinnekulle K-bentonite, northern Baltic Basin. Clay Minerals, accepted.

II **Somelar, P.,** Hints, R., Kirs, J., Kirsimäe, K. (2009). Illitization of the Early Palaeozoic bentonites in the Baltic Basin: decoupling of burial and fluid driven processes. Manuscript, submitted to Sedimentary Geology.

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.

IV 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.

Author's contribution in papers

Paper I: The author was primarily responsible for planning original research, X-ray diffraction and atomic-force microscope analysis, interpretation and synthesis of mineralogical and chemical analytical data and the writing of the manuscript.

Paper II: The author was primarily responsible for planning research, XRD mineralogical analysis and interpretation of analytical results, synthesis of different analytical results and the writing of the manuscript.

Paper III: The author was responsible for data collection, analysis and interpretation of clay fraction mineralogy, and for writing the manuscript in parts discussing the composition of clay fraction.

Paper IV: The author was responsible data collection, analysis and interpretation of clay fraction mineralogy, and to the writing of the manuscript in parts discussing the composition of clay fraction.

1. INTRODUCTION

Smectite is a typical product of surficial weathering of primary silicate materials. However, it is an unstable phase and tends to recrystallize into illite- or chlorite-type minerals under diagenetic and/or metamorphic/ metasomatic conditions (Meunier and Velde 2004). Consequently, illitization of smectite is one of the most common clay mineral diagenetic processes that has been extensively studied over the last fifty years (e.g. Burst 1959, 1969; Weaver 1959; Shutov et al. 1969; Perry and Hower 1970; Hower et al. 1976; Środoń 1979; Nadeau and Bain 1986; Velde et al. 1986; Sucha et al. 1993; Lindgreen et al. 2002; Lanson et al. 2009).

Illitization occurs in a wide variety of geological environments including burial diagenesis (Hower et al., 1976; Środoń 1984; Boles and Francks 1979), hydrothermal, metasomatic and (contact-)metamorphic alteration (Inoue et al. 1988; Velde and Brusewitz 1986; Drits et al. 2007).

Illitization of smectite is considered to proceed through mixed-layer illite-smectite (I/S) intermediates, which show a progressive mineralogical trend with an increase of non-expandable illite at the expense of expandable smectite (e.g. Altaner and Ylagan 1997). Reaction mechanisms for smectite illitization can be classified into two main categories: SST and DC. The SST mechanism (Shutov et al. 1969; Dunoyer de Segonzac 1970; Hower et al. 1976) involves illitization in the solid state, with gradual replacement of smectite by illite on a layer-by-layer basis. The charge of the smectite interlayer increases due to Al substitution in the neighbouring tetrahedra, potassium is fixed, and smectite converts to illite. In this process, which typically also involves fluids that can act as catalysts and transport media, the replacement of smectite by illite takes place in close topotactic contact (Lázaro 2007). The DC mechanism involves complete dissolution of smectite, followed by precipitation of I/S or illite. This process allows of major changes in the structure and texture to occur as illitization proceeds so that the structural memory of the precursor mineral is lost (Altaner and Ylagan 1997). The DC mechanism includes two main versions: (1) progressive dissolution of smectite in a reaction front on a very small scale with in situ precipitation of the new phase (Ahn and Peacor 1986) and (2) initial dissolution of smectite followed by progressive coarsening of illite governed by an Ostwald ripening process (Eberl and Środoń 1988; Eberl et al. 1990).

The range of physical conditions of illite formation at the expense of smectite varies from 20 °C in surface soils, up to 300 °C in hydrothermal or diagenetic/metamorphic environments (Meunier and Velde 2004). The illitization advance is regarded as a palaeogeothermometer (e.g. Pollastro 1993). However, illitization is limited not only by temperature, but also by chemical parameters, mainly the availability of potassium (e.g. Bauer and Velde 1999), fluid/rock ratio (Altaner and Ylagan 1997), composition of precursor phases (Drits et al. 2002), and the time factor (e.g. Velde and Vasseur 1992). Therefore, illitization can be influenced differently in each specific geological environment, and could provide valuable information on the diagenetic development of sedimentary basins and contribute to evaluation of their formational models (e.g. Środoń 1999).

Sedimentary basins, however, may have largely variable tectonothermal evolutionary paths in addition to a simple burial digenesis. Illitization can also be driven by the intrusion of high-temperature and/or K-rich hydrothermal fluids or diagenetic brines in relation to the orogenic processes at the basin margins (e.g. Elliot and Aronson 1987; Hay et al. 1988), and intrusion of magmatic rocks (e.g. Drits et al. 2007). Moreover, illitization can proceed at surface conditions and low temperatures in saline-alkaline lakes (e.g. Deconinck et al. 1988) or due to early diagenesis of carbonate facies deposits in marine evaporitic settings (Sandler and Saar 2007). Moreover, I/S formation at low temperatures can be significantly advanced by wetting-drying cycles (Eberl et al. 1986) and by increased pH (Bauer and Velde 1999; Bauer et al. 2006). This reciprocal interplay of different diagenetic to hydrothermal/metamorphic conditions, possibly driving the illitization process, makes difficult to recognize the mechanism of illitization and the diagenetic development of sedimentary sequences (e.g. Clauer 2006).

The Baltic Basin (BB) is an old cratonic area that has been stabilized under an exceptionally stable tectonic regime for the last 500 Ma (Hendriks et al. 2007). However, the vertical and lateral trends of illitization within the BB are complex and in some cases opposite to a normal burial trend (Somelar et al. 2009b – PAPER II), suggesting that the overall stable tectonic development of the basin has been masked either by variable subsidence and uplift histories in its different parts or possible heat and/or fluid flow episodes. Diagenetic history, particularly the illitization of the BB Lower Palaeozoic clayey sediments has deserved close attention in the last decades (Gorokhov et al. 1994; Chaudhuri et al. 1999; Kirsimäe et al. 1999, Kirsimäe and Jørgensen, 2000; Lindgreen et al. 2000; Środoń and Clauer 2001; Somelar et al. 2009a – PAPER I; Somelar et al. 2009b – PAPER II; Środoń et al. 2009). In particular, diagenesis of the Lower Cambrian claystones (Blue Clay) and Cambrian–Ordovician Black Shales in the northern part of the basin, and Ordovician–Silurian K-bentonites within the basin and across the Teysseyre–Tornquist tectonic zone at the south-western-most tip of the basin in Pomerania have been investigated. However, there is no consensus between diagenetic/palaeothermal reconstructions in these studies. The organic material thermal alteration indexes (CAI, TAI) of ≤1 (Nehring-Lefeld et al. 1997; Talyzina 1998) of sediments in the shallowly buried northern part of the basin (<500 m) suggest that this sedimentary sequence is thermally very immature, which does not agree with the illite-rich composition of I/S mixed-layer minerals (>65% of illite layers). In the central and southern parts of the basin where the burial depth increases over 1000 m, the organic material alteration suggest much higher maturity of the sediments. The mixed-layer mineral composition in the central part of the basin, however, shows less illite layers (60–70%), and only in the most deeply buried south–eastern part of the basin (~2000 m) the illitization advance is at the same level as in its northern part (Somelar et al. 2009b – PAPER II; Środoń et al. 2009). As a result, the driving mechanisms of illitization in the BB are not fully understood.

Typically, the clay mineral composition of shales is a physical mixture of detrital and diagenetic minerals. Significant diagenetic information (composition and the isotope age of mixed-layer I/S) can be obtained from such sediments only by controlled size separation because authigenic illite and I/S tend to be smaller in size than detrital mica/illite (e.g. Clauer et al. 1997; Chaudhuri et al. 1999). However, earlier studies in the BB have shown that even the fine grain-size fractions (<0.06 μm) of clay-rich sediments are not purely monomineralic (Kirsimäe and Jørgensen 2000).

Altered volcanic ash beds – K-bentonites – are, in this sense, of great value to diagenesis studies because they do not contain detrital dioctahedral micas but only pristine diagenetic illite and I/S. K-bentonite beds are frequent in the Ordovician and Silurian sequences of the BB (Bergström et al. 1992, 1995, 1998). The bentonites found in the BB include the thickest and most widespread Palaeozoic K-bentonite of north-western Europe, the Kinnekulle bed, equivalent to the North American Millbrig K-bentonite (Bergström et al. 2004).

The aim of this thesis is:

- first, to study the mineralogical characteristics and isotope age of the diagenetic I/S of the Ordovician and Silurian K-bentonites in order to understand the illitization and diagenetic development of these sediments in the BB;
- secondly, to link illitization with the tectonothermal evolution of the and its marginal areas.

2. GEOLOGICAL SETTING

The BB is a stable intercratonic sedimentary basin of the East-European Platform in the East Baltic between the Scandinavian and German–Polish branches of the Caledonian orogenic system. The complete stratigraphic record in total thickness of >2000 m extends from the latest Precambrian (Ediacaran) to the Cenozoic Neogene period in the south-western part of the basin, whereas in the northern and central parts of the basin (Estonia, north Latvia, north-western Russia) sediments of only Neoproterozoic and Lower Palaeozoic age are known (e.g. Nikishin et al. 1996). The Lower Palaeozoic sedimentary section of the northern BB in Estonia and northern Latvia is monoclinal, slightly dipping southwards (2–4 m per km) (Figure 1).

The Baltic Basin (BB) represents one of the most stable old cratonic areas of the world. The apatite fission tracks (AFT) in Finland, in the area of the East European Craton (EEC), show the oldest ages on Earth of 500–800 Ma (Hendriks et al. 2007) referring to a long stable geological history.

During the Late Palaeoproterozoic and early Mesoproterozoic a thick Svecofennian juvenile crust (1900–1800 Ma) was opened for extensive denudation, ending with the formation of sub-Cambrian peneplain. The internal block-and-fault structure of the Precambrian basement developed with the formation of Palaeo- to Mesoproterozoic rapakivi plutons, Jotnian and Post-Jotnian rift basins in the crust (1600–1000 Ma; Puura and Floden 2000) and subsequent large crustal depressions after the break-up of the Precambrian supercontinent Rodinia (Kumpulainen and Nystuen 1985). From the latest Neoproterozoic onwards the development of the passive margin of the Iapetus Ocean and Tornquist Sea the deformation and accumulation of the sedimentary cover, took place.

The Caledonian orogeny (the collision of the Baltica continent with Laurentia) occurred in the Late Silurian to Devonian about 350–420 Ma (Roberts and Gee 1985; Ziegler 1987; Torsvik and Rehnström 2001) This event was accompanied by the development of the North German–Polish Caledonides following the closure of the Tornquist Sea (Ziegler 1987).

Neoproterozoic to late Palaeozoic sedimentary deposits within the BB represent the fill-up of a slowly subsiding epicontinental sea and subsequent infill of the developing Caledonian foreland basin. In the northern and central parts of the basin the Late- and/or post-Palaeozoic deposits are missing and any sedimentary evidence for the last 300–400 Ma history is lacking.

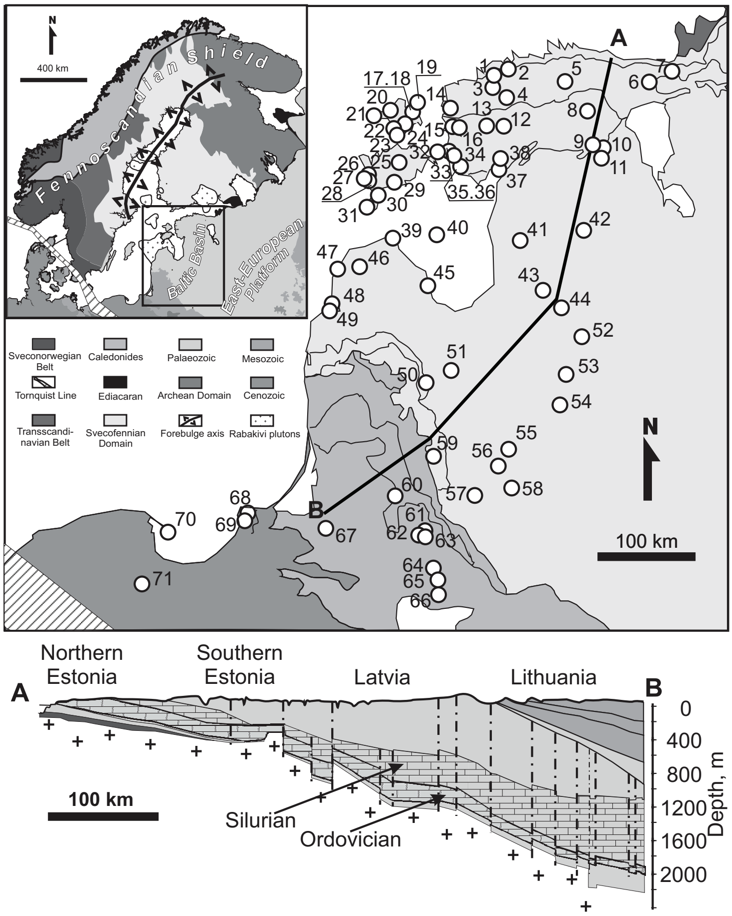

Figure 1. Simplified geological map of Fennoscandia and the Baltic Basin with the location of the drill cores studied. Legend: 1. Keila-138, 2. Pääsküla, 3. Vasalemma, 4. F-306, 5. Pa. 37, 6.F-198, 7. F-639, 8. Oostriku, 9.Laeva-1, 10. Laeva-4, 11. Laeva-18, 12. Velise-99, 13. Velise-98, 14.F-350, 15. Haapsalu, 16. Kirikuküla, 17. Kärdla-1,18. Kärdla 18, 19. F369, 20. Kõrgesaare, 21. F-356, 22.F-368, 23. F-363, 24. Vaemla, 25. Eikla, 26. Viki, 27. Pa. 871, 28. Kuusnõmme, 29. Kuressaare, 30. Kaugatoma, 31. Ohessaare, 32. Viirelaid, 33. Virtsu, 34. D-8, 35. Varbla, 36. Paatsalu, 37. Pärnu-6, 38. Are, 39. Kolka, 40.Ruhnu, 41. Puikule-42, 42. Valga, 43. Nitaure, 44. Taurupe, 45. Engure, 46. Piltene-1, 47. Venspils, 48. Aispute, 49. Vergale-49, 50. Bliudžiai, 51. Ligum, 52. Nagli-106, 53. Butkünai-241, 54. Svedasai-252, 55. Ledai-179, 56. Graudžai-105, 57. Sutkai-87, 58. M.Lapes-106, 59. Kunkojai, 60. Kybartai, 61. Gusev-3, 62. Gusev-9, 63. Gusev-6, 64. Virbalise, 65. Pajevonis, 66. Vištytis-17, 67. S.Krasnoborsk-3, 68. Y.Yagodnoe-2, 69. Putilovskaya, 70. Hel IG-1, 71. Koscierzyna.
Drillcores 5, 7, 12, 14, 19, 21, 23, 26, 70, 71 are from Środoń et al. (2009); 8, 15, 16, 20, 51, 60, 65 from Ratejev and Gradusov (1971) and 41, 44, 46, 49, 52, 53, 54, 55, 56, 57, 58, 61, 62, 63, 66, 67 ,68, 69 from Kepežinskas et al. (1994).

The Ordovician and Silurian sedimentary successions of the BB contain numerous altered volcanic ash beds – bentonites that are usually K-rich and can be referred to as K-bentonites. Normally those beds are thin (from a few mm up to 2 m) and laterally continuous within siliciclastic or carbonate successions (see for a review Bergström et al. 1992; 1995). They commonly form distinct series and are composed of a number of closely spaced layers, which can be found in certain stratigraphic intervals (e.g. Jürgenson 1958; Lapinskas 1965; Rateev and Gradusov 1971; Snäll 1976; Utsal and Jürgenson 1971; Bergström et al. 1992; 1995; Kepezhinskas et al. 1994; Kiipli et al. 1997, 2001).

In the Ordovician section the bentonite series are mostly found in the Upper Ordovician Sandbian and Katian stages, in the Silurian section in the Llandoverian Telychian Stage and Wenlockian Sheinwoodian Stage (Bergström et al. 1992; 1995; 1998; Figure 2). These include the two thickest and most widespread Palaeozoic K-bentonites of north-western Europe, the Ordovician Kinnekulle and Silurian Osmundsberg K-bentonites that have been traced across large areas in Baltoscandia and Britain (Bergström et al. 1995, 1998).

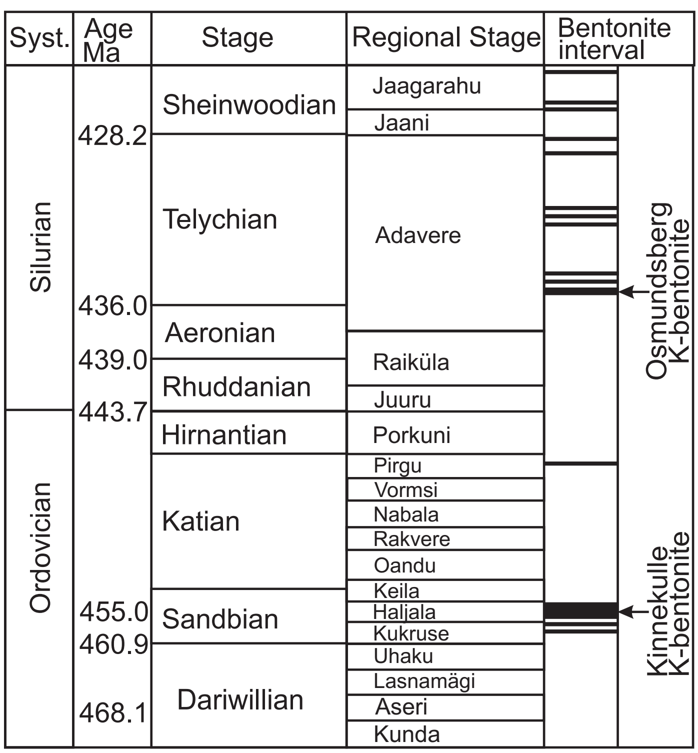

Figure 2. Stratigraphic scheme of Ordovician and Silurian bentonite intervals in Baltic Basin modified after Kiipli (2008).

The source ash in the BB was deposited into a shallow epicontinental basin where normal marine carbonate sedimentation occurred during the Ordovician and Silurian. The basin bathymetry of that time shows a broad shallow shelf in the north and a depression in the south, causing variation in the host rock composition connected with the respective change of facies zones from the northern part of the basin to its south-western part next to the Tornquist–Teisseyre Zone (Harris et al. 2004). In the northern part of the basin the sediments are represented by shallow marine limestones and argillaceous limestones, which are replaced by (kerogenous) shales, marlstones and limestones in the deep shelf facies in the south-western part of the BB.

The immobile geochemical signatures of bentonite composition as well as phenocrysts and melt inclusions in quartz (Huff et al. 1996; Kiipli and Kallaste 1996; Kiipli et al. 2008) suggest that the source magma of Ordovician and part of Silurian bentonites was of calc-alkaline type, predominantly rhyolitic or dacitic. The geochemical composition of several Silurian bentonites, however, is more alkaline (Bergström et al. 1992; Batchelor and Jeppson 1999), likely suggesting a different provenance. The potential tectonomagmatic setting might have been the Tornquist–Teisseyre Zone (Batchelor and Jeppsson 1999; Torsvik and Rehnström 2003), where the Tornquist Sea between Avalonia and Baltica was finally closed in the Silurian.

The composition of bentonite clay matrix in the BB is typically mixed-layer I/S what can occur with some amount of kaolinite (Kiipli et al. 2007 – PAPER III; Hints et al. 2008). However, strongly feldspathized bentonites occur in the section (Kiipli et al. 2007 – PAPER II) and the bentonites of Upper Ordovician Katian age (Pirgu Regional Stage) are characterized by chlorite-smectite type mixed–layer minerals (Hints et al. 2006 – PAPER IV). The whole-rock composition of bentonites can vary laterally as well as in vertical profile. In the Kinnekulle K-bentonite K-feldspar-rich variety occurs in the northern part of the basin and it is replaced by I/S and then I/S and kaolinite association towards the south-central part of the basin. Kiipli et al. (2007 – PAPER III) described this laterally changing whole- rock association with respect to facies zonation, which was interpreted due to environmental (pH, silica activity) conditions during initial devitrification of pyroclastics.

The Kinnekulle K-bentonite in north-Europe is the largest and most widespread bentonite bed. It covers an estimated area of 6.9×10^5 km^2 in north-western Europe and is today locally up to 1–2 m thick. The thickness of this bentonite bed in is up to 70 cm in the northwestern part and a few cm in the eastern and southern parts of the BB. The thickness and grain size of detrital pyroclastic minerals distribution increase from Estonia to southern Sweden and southern Norway, which indicates that the source material came from south–western Scandinavia (Huff et al. 1996). The formation of Kinnekulle bentonite bed is connected with the closure of the Iapetus Ocean that separated Baltica and Laurentia (Scotese and McKerrow 1991; Huff et al. 1996). The subduction/ collision against the south-eastern margin of Laurentia caused eruptive plinian and co-ignimbrite eruptions from the island arcs or microplates.

A possible common source of and transatlantic correlation between the Kinnekulle and Millbrig K-bentonite beds has been proposed by Huff et al.

(1992, 1996). However, Sampson et al. (1989) described different Sc and Yb compositions in zircons from the Millbrig and Kinnekulle beds. Haynes et al. (1995) detected differences in the composition of biotite phenocrystals and Min et al. (2001) found large age difference (~7 Myr) between volcanic phenocrysts in of these beds. They all concluded that the Millbrig and Kinnekulle beds represent separate eruptions. Nevertheless, Huff et al. (2004) argue that radiometric datings are in conflict with the well–defined biostratigraphical position of these beds and that one should also consider variations inside the bed. Huff et al. (2004) still suggested, that according to biostratigraphy and chemostratigraphy, both ash beds are closely similar, if not identical, in age, and at least parts of these huge ash deposits are also indistinguishable chemically and their geographic distribution patterns are in agreement with the idea that they originated from the same region and even shared the same source volcano(es). Some chemical heterogeneity of the Kinnekulle bed suggests that it is probably composed of complex or multiple eruptions, each contributing to a bentonite (Huff 2008). However, variation between these possible units is insignificant and they can be considered as a single unit.

3. MATERIAL AND METHODS

Altogether 77 K-bentonite samples, (48 samples from the Ordovician and 29 samples from the Silurian, from 37 drill cores across the Baltic Basin) were chosen for this study. The bentonite clay fractions were analysed by means of X-ray diffractometry (XRD), atomic-force scanning microscopy (AFM) and K-Ar dating methods. Bentonite samples represent in most cases the middle or lower homogenoeus parts of the beds. Thickness of these beds varied from 5 to 44 cm. Both plastic and non-plastic (feldspathized) varieties of bentonite were sampled.

The mineral composition of <0.2 μm, 0.2–2 μm and <2 μm clay fractions, saturated with Mg or Sr, was analysed with the DRON-3M diffractometer with Ni filtered Cu *K*α radiation, 0.5 mm divergence slit, 0.25 mm receiving slit and two 1.5° Söller slits. The scanning steps of 0.02 °2θ from 2 to 50 °2θ or 2 to 40 °2θ and a counting time of 3 s per step were used. The XRD data for oriented <0.2, 0.2–2 μm and <2 μm clay aggregates were obtained in air-dry and ethylene glycol (EG) solvated state.

The Newmod (Reynolds 1985), MLM2C and MLM3C codes (Plançon and Drits 2000) and multispecimen fit approach (Sakharov et al. 1999) were used to estimate the illite, kaolinite and smectite in mixed-layer illite/smectite (I/S), illite/smectite/vermiculite (I/S/V) and chlorite-smectite (corrensite)–type minerals qualitatively and quantitatively. The experimental XRD profiles were compared to calculated structural models by a trial-and-error procedure until an optimum fit was achieved. The profiles were fitted in the 2–50 °2θ range considering the given instrumental and experimental factors and orientation factor, mass adsorption coefficient and composition of structural layers suggested by Moore and Reynolds (1997). The coherent stacking domain sizes (CSDS) were distributed log-normally.

Polyvinylpyrrolidone (PVP-10) treatment was used to estimate the thickness of fundamental particles in mixed–layer mineral. Suspensions of <0.2 μm Na-saturated fractions of selected samples were mixed with PVP-10 in a proportion of 2 parts of PVP-10 to 1 part of clay and treated with ultrasound for 1–2 min according to Uhlik et al. (2000). The clay films were prepared on low background substrates and measured from 2 to 45 °2θ, with scanning steps of 0.02 °2θ and counting time of 5 s per step The area-weighted thickness of particles and respective distribution was calculated by the Bertaut–Warren–Averbach technique using the MudMaster code (Eberl et al. 1996).

Morphological analysis of I/S particles in the <0.2 μm fraction was performed by atomic force microscopy (AFM) in non-contact mode. The specimens were scanned under ambient humidity conditions. The AFM imaging window varied from 1x1 μm to 5x5 μm. Altogether six representative bentonite samples from different depths and locations were analysed. Na-saturated samples were dispersed by ultrasonic treatment in distilled water and one drop of the very diluted suspension was placed on a freshly cleaved mica surface that was warmed on a hot plate at about 60 °C (Blum 1994). The dimensions measured were length (the longest particle axis), width (the axis perpendicular to the length) and thickness. The dimensions of only completely separated particles were measured. Generally about 50 particles per sample were measured. For comparison with the XRD-PVP method the area-weighted thickness was calculated for each sample.

The K-Ar determinations were made for Sr-saturated <0.2 µm and 0.2–2 µm size fractions at the ING PAN laboratory in Kraków, Poland, following the technique described in detail by Środoń et al. (2006). The Ar measurements were controlled using the GLO standard and the K_2O measurements using two NIST standards: 70a and 76a. The K-Ar dates were calculated with the standard decay constants (Steiger and Jäger 1977).

4. RESULTS

4.1. X-ray diffractometry (XRD)

4.1.1. Mineral composition of the clay fraction

The XRD analysis of Ordovician and Silurian bentonites in EG-saturated and air-dried states characterize clay mineral composition mainly as mixed-layer I/S-type minerals and kaolinite (Somelar et al. 2009b – PAPER II), except for the Katian bentonites of Pirgu age where the mixed-layer mineral is composed of regularly interstratified chlorite and low-charge smectite components chlorite-smectite (corrensite) (Hints et al. 2006 – PAPER IV). Both Ordovician and Silurian bentonites show a variation in clay mineral composition with respect to facies zones – nearly monomineral I/S bentonites are are found in the shallow water facies, and the I/S and kaolinite assemblage occurs in the deep water facies (Somelar et al. 2009b – PAPER II; Kiipli et al. 2007 – PAPER III; Hints et al. 2008). Kaolinite was detected in 39 samples out of 128. Its content in kaolinite-bearing beds varies from 4 to 60%, being in kaolinte on average 22%. Kaolinite is more frequent and in Silurian bentonite beds and in Ordovician bentonites contain kaolinite more rarely, mostly in the southern part of the basin.

Ordovician Katian bentonites of Pirgu age are exceptional among the Ordovician and Silurian bentonite beds. The Pirgu bentonites contain a mixed-layer regular chlorite-smectite (corrensite) mineral with R1-ordering (Hints et al. 2006 – PAPER IV). Chlorite-smectite is typically accompanied with mixed-layer I/S and kaolinite. Corrensite is predominanting in most of the Pirgu samples but there are some exceptions where the I/S is the main clay mineral phase.

4.1.2. Mixed-layer minerals

The structural state of mixed-layer minerals was studied by comparison of experimentally measured XRD patterns with those calculated for two-dimensional lamellar clay structures using Newmod (Reynolds 1985), MLM2C and MLM3C codes (Plançon and Drits 2000).

The modelling suggests that the mixed-layer mineral in BB bentonites is typically an illitic R1-ordered I/S with 56–86% illite layers. However, simple two-component NEWMOD models gave only qualitative match in peak positions and large discrepancies were recorded in peak shapes and intensities between experimental and calculated patterns (Kiipli et al. 2007 – PAPER III). For better fit the models calculated with MLM2C and MLM3C codes were used. In most cases the MLM3C code assuming a three-component mixed-layer mineral proved to be the best for describing the measured patterns. Nevertheless, for some Silurian bentonite samples the MLM2C two-component model with R1-ordering provided equivalent fit to the three-component model (Somelar et al. 2009b – PAPER II; Hints et al. 2008). In such cases a two-component model was preferred.

The best fit with three-component models was achieved by assuming 5–11% high-charge smectite (vermiculite-like) layers in addition to fully expandable low-charge smectitic layers in R1-ordered lamellar structure with the probability of a vermiculite-vermiculite sequence varying from 0 to 0.4.

During modelling using MLM2C and MLM3C codes also two alternative models assuming (1) a simple two-component composition of mixed-layer minerals with R1–R2-ordering and (2) a physical mixture of two mixed-layer phases (I/S – I/V and I/S – I/S) were tested (e.g. Sakharov et al. 1999). However, neither the simple two-component model or physical mixtures of two-component I/S and I/V, and I/S and I/S models could provide satisfactory fit for both EG and air-dry patterns (Somelar et al. 2009a – PAPER I, Figure 3).

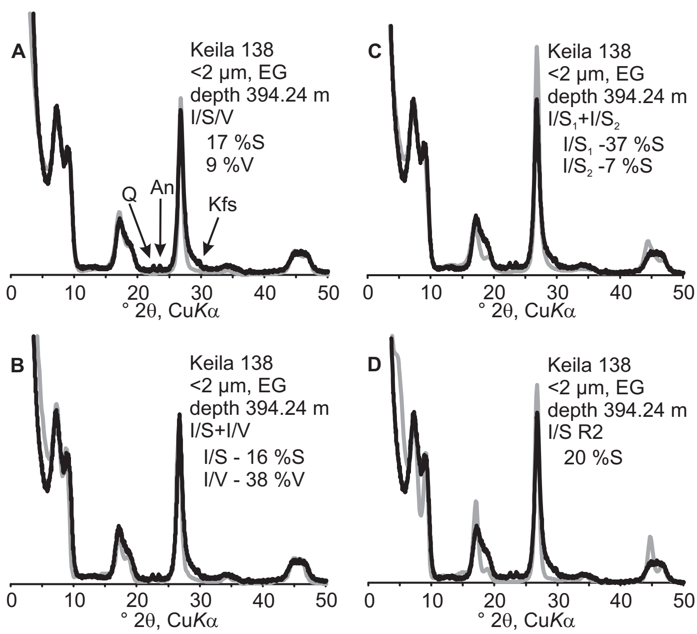

Figure 3. Comparison of the experimental and calculated XRD profiles. (A) three-component illite-smectite-vermiculite, (B) physical mixture of two mixed-layer phases illite-smectite and illite-vermiculite, (C) physical mixture of two mixed-layer illite-smectite phases (I/S_1 and I/S_2), (D) simple two-component mixed-layer mineral with R2 ordering. Black line – experimental profile, grey – calculated profile. Q – quartz, An – anatase, Kfs – K-feldspar

The closest fit for two-component models was obtained assuming a nearly maximum possible degree of ordering for R2 I/S mineral with *p*SII varying between 0.6 and 0.9. However, the intensities and peak shapes of the measured and modelled patters deviated significantly in the area between peaks at ~12.3 Å and ~9.5 Å (*001/1* and *001/2*, respectively) and at peaks at ~4.8 Å and ~5.18 Å. The peak positions were overlapping for glycolated samples, but it was impossible to get satisfactory fit neither for peak positions nor shapes for air-dry patterns.

The best fit for a mixture of I/S and I/V phases was found assuming I/S with 15–20% illite and I/V with 55–65% vermiculite layers, and for mixtures of two different I/S phases (R1 mineral 50–60 I% and R2 mineral 90–95 I%). For glycolated samples one of the phases in the mixture produced strong peaks at 9.6–9.8 Å and 5.1–5.2 Å, and the second phase showed peaks at 12.2–12.6 Å and 4.8–4.9 Å. The modelled peak intensities and the position of the peak at ~9.5 Å, however, were not matched and therefore three-component models were preferred (Figure 3).

The expandability of mixed-layer minerals shows a regular variation with respect to the position within the basin (Somelar et al. 2009a,b – PAPERS I, II). The expandability of I/S in Ordovician bentonites in the northernmost part of the basin ranges from 15 to 30%. Towards the southern part of the basin the expandability and depth increase until the ~300–400 m depth is reached, where the expandability varies from 20 to 40%. After 400 m (in the deeper part of the basin) the expandability starts to decrease gradually with the increasing depth as it would be expected from the normal burial trend, and decreases to about 15–20% at a depth of >2000 m.

Interestingly, also the Newmod models of mixed-layer minerals in the Kinnekulle K-bentonite (Kiipli et al. 2007 – PAPER III), which were discarded from further study, suggested different long-range probability ordering type stacking-sequences (PSII.I) of I/S mineral for different facies zones. The deep-shelf zone samples showed PSII.I of 0.10–0.25, the transition zone PSII.I 0.50–0.57 and the shallow facies samples had the highest PSII.I probability values of 0.60–0.77, which agrees with the higher illitic composition of mixed-layer mineral in the northern, shallow part of the basin.

Silurian bentonites in the BB follow similar trends to Ordovician bentonites. However, in the same depth range the expandability of Silurian bentonites is somewhat less compared to the Ordovician beds. The smectite (S)% of mixed-layer I/S and I/S/V minerals in shallowly buried Silurian K-bentonites varies from 15 to 41% (Somelar et al. 2009b – PAPER II). The expandability increases with increasing burial depth to about 40% at 280–300 m depth in the central part of the basin, but decreases from this depth forwards to ~25% at 500 m. Importantly, the Silurian mixed-layer minerals with the highest expandability are characterized by two-component R1-ordered I/S without high-charge smectite interlayers. In Ordovician bentonites the mixed-layer mineral was best described almost exclusively by assuming a three-component mixed-layering (Somelar et al. 2009b – PAPER II)

The mixed-layer layer I/S mineral in chlorite-smectite dominated Katian bentonites of Pirgu age is similar to the other Ordovician beds and is characterized by three-component I/S/V composition with 27–29% of expandability (Hints et al. 2006 – PAPER IV).

4.1.3. XRD – the thickness of illite fundamental particles

The PVP-XRD analysis of selected samples with 69–78%I shows thin fundamental particles (coherent stacking domains) with the area-weighted mean thickness varying from 1.9 to 3.6 nm ('best-mean' according to Eberl et al. 1996; Somelar et al. 2009a – PAPER I). The PVP-XRD indicate lognormal distributions for all studied samples with α and β^2 varying within 0.7–1.24 and 0.08–0.14, respectively. These samples scatter at the α vs. β^2 plot on the conjunction of two crystal growth mechanisms (Eberl et al. 1998), suggesting the initial stage of the surface–controlled growth of illite crystals.

4.2. Atomic force microscopy

Atomic force microscopy (AFM) analysis of <0.2 μm fractions shows that the samples contain regular lath-shaped and euhedral to nearly isometrical particles with particle edges at 60º or 120º (Somelar et al. 2009a – PAPER I). The width of lath-shape particles is 30–70 nm and length 80–200 nm. Euhedral particles are 45–165 nm wide and 70–225 nm long. Euhedral particles with the width/ length aspect ratio of 1.2–2 are predominanting in all studied samples. The lath-shaped particles, however, with aspect ratio higher than 4 are more frequent in less illitic samples. In both cases the measured thickness of particles is about 3±1.5 nm increases slightly with the increasing illite content in the mixed-layer mineral. Comparison of the AFM data with PVP-XRD analysis of selected samples showed similar thin fundamental particles (coherent stacking domain sizes). As expected, the particles measured by the AFM method were thicker than those measured by the PVP-XRD method whereas only illite fundamental particles were detected in the latter analysis.

4.3. K-Ar dating

The K-Ar dating of Kinnekulle K-bentonite samples (Somelar et al. 2009a – PAPER I) shows that the apparent isotope age of 0.2–2 μm and <0.2 μm fractions is significantly lower than the stratigraphic age of the Kinnekulle bentonite, which is 454.8±2.0 Ma (Min et al. 2001). The ages of 0.2–2 μm and <0.2 μm fractions vary within 319.1–418.6 Ma and 371.1–418.6 Ma, respectively. The shallowly buried mixed-layer minerals in the northern part of the basin are generally isotopically younger, which correlates with their overall higher illite content in I/S. However, the deepest measured bentonite in the Aizpute core is much younger, but less illitic. The K-Ar dates for most samples increase with decreasing particle size, with the exception two samples taken from the same 44-cm thick bed (Somelar et al. 2009a – PAPER I).

5. DISCUSSION

Transformation from smectite to illite is mainly controlled by temperature. Advanced illitization in a sedimentary basin should reflect either deep burial diagenetic conditions during basin development or alteration due to intrusion of hydrothermal fluids. As indicated by earlier investigations (e.g. Chaudhuri et al. 1999; Kirsimäe et al. 1999) and confirmed by the recent compilation of apatite fission track (AFT) data (Hendriks et al. 2007), there is no evidence of deep burial throughout the Fennoscandian Craton encompassing the northern part of the BB, the burial depth of which has not exceeded 1–1.5 km (Kirsimäe and Jørgensen 2000). The central and southern areas of the basin, however, are today and were in the geological past most probably more deeply buried. This is indicated by the thermal maturation of organic material. The shallow burial and low temperatures in the northern part of the basin (present-day depths <1000 m) are strongly supported by the thermally immature state of the organic material (TAI, CAI <1, R_0 ~0.5). On the contrary, the organic material alteration state in sediments is more mature (R_0 0.7–1) in the central (present-day depths 1000–1500 m) and south-western parts (present day depths >1500 m) of the basin with maximum estimated palaeotemperatures of <50–80 °C up to ~150°C, respectively (Zdanavièiûte 1997; Nehring-Lefeld et al. 1997; Grotek 1999; Talyzina et al. 2000).

However, mixed-layer minerals in K-bentonites of the BB contain small number of smectite interlayers (<35%S), which would suggest considerably higher burial temperatures than expected form alteration of organic material. Illitization of smectite in bentonites is considered to begin at ~70 °C and the mixed-layer I/S structural ordering transition from R0 to R1 at 35%S occurs at temperatures ~150 °C (Šucha et al. 1993). If this was the case in the BB, the observed illitization of Ordovician and Silurian bentonites with illite content of 70–75%, 65–70% and 75–85% in the northern, central and south-western parts of the basin, respectively, would require burial depth in all parts of the basin in excess of 5 km assuming a normal cratonic geothermal gradient of 20–25°C · km^{-1}. The AFT data show that the temperatures in southern Finland next to the northern margin of the BB have not been higher than 125 ºC during the last 600–700 Myr (Hendricks et al. 2007). This excludes deep burial at least in the northern part of the basin.

Nevertheless, the organic material alteration indexes that are gradually increasing towards the central and south-western parts of the basin suggest that a thick sedimentary pile developed after the Baltica collision with Avalonia in a rapidly subsiding foredeep along the SW margin of Baltica (Torsvik and Rehnström 2003) causing increase in sediment temperatures. It seems that in southern and south-western sector of the BB bordering the Teissyere-Tornquist Zone the bentonite transformation is characterized by burial illitization.

A simple burial diagenesis model in the southern and south-western parts of the BB is supported by K-Ar ages (294–382 Ma) of the bentonite I/S fractions (Środoń and Clauer 2001; Środoń et al. 2009), which agree with the period of the most rapid sedimentary accumulation in the Devonian and Carboniferous. Moreover, the %S of I/S in the S–SW sector of the BB decreases towards the central part of the basin in the east and north (Somelar et al. 2009b – PAPER II). The gradual S% decrease from the central part of the basin towards the deeply buried southern part would then correspond to the increasing burial of beds in accordance with the development of tectonic subsidence of a typical (flexural) foreland basin during the Silurian which resulted from oblique collision of Baltica and Eastern Avalonia (Poprawa et al. 1999). The K-Ar data of I/S by Środoń et al. (2009) suggest that the illitization started in Early-Devonian after the Lochkovian tectonic event when deep burial conditions were created in central and southern part of the basin. The peak illitization in S and SW part of the BB developed under the maximum cover of Devonian and Carboniferous sediments that occurred about 305–325 Myr ago (Ulmishek 1990). Illitization was terminated by major erosion in the end of Carboniferous (Środoń et al.2009).

The digenetic history of sediments in the northern part of the basin is more complicated. Principally, the mixed-layer I/S formation in surface conditions (e.g. in saline-alkaline lakes) has been described by several earlier authors, e.g. Singer and Stoffers (1980), Deconinck et al. (1988), Turner and Fishman (1991). Illite-smectite formation can be also advanced at low temperatures by wetting-drying cycles and increased pH (Eberl et al. 1986; Bauer and Velde 1999). Similarly, Sandler et al. (2004), Sandler and Harlavan (2006) and Sandler and Saar (2007) explained the early formation of ordered illitic mixed-layer I/S, as well as of authigenic K-feldspar, in shallow marine carbonate sediments and at near surface temperatures by the interaction of sediment with K-enriched brines formed by the evaporation of seawater and precipitation of calcite or dolomite. The residual solution left after such precipitation had increased pH and K concentrations that promoted the illitization of original smectite and initiated authigenic K-feldspar formation. Indeed, Hints et al. (2006 – PAPER IV) explained the formation of mixed-layer chloritic phases in Katian bentonites by early diagenetic transformation of volcanic ash to saponite-type smectite in response to the reflux of hypersaline solutions in sabkha-type environment, consequently transforming into a regularly interstratified chloritic mixed-layer mineral. However, the expandability of mixed-layer I/S accompanying the chlorite-smectite in these bentonites does not differ from that recorded in the other Ordovician or Silurian beds in the basin (Somelar et al. 2009b – PAPER II). Moreover, the illitization driven by early diagenetic fluids would result in K-Ar dates of K-feldspar and I/S coincident (within 10 Myr) with the sedimentation age (e.g. Sandler and Harlavan 2006). The K-Ar dates of I/S and authigenic feldspar in the BB bentonites, however, are much younger than the stratigraphic age and do not support such an interpretation (Środoń et al. 2009; Somelar et al. 2009a – PAPER I). They do not exclude a possible effect of surface-temperature illitization, but imply at least an overprint of a younger illitization episode, which points to a Palaeozoic thermal and/or fluid intrusion episode at shallow depths.

Diagenetic-hydrothermal fluid activity in the Fennoscandian Craton in relation to the Caledonian orogeny (390–430 Ma), which generally agrees with the reported K-Ar ages of the I/S and K-feldspar, has been reported by many authors. Högdal et al. (2001) concluded from low pressure-temperature resetting of U-rich zircons in central Sweden that the basement regions east of the Caledonian front have been affected by saline fluids with the temperature of ~150 °C. Considering data on noble gases and halogens, Kendrick et al. (2005) suggested a Caledonian mineralization event, caused by mixing of two or more, long-lived, hydrothermal basinal brines and pore fluids to explain the Cambrian sandstone hosted Pb-Zn ores in Scandinavia. The high-resolution UV laser microprobe Ar/Ar dating of the zoned K-feldspar overgrowths from the same sandstone-hosted Pb-Zn bodies also suggests two discrete events – early burial diagenesis (528–567 Ma) and a later tectonically induced fluid flow event related to the collapse of the Caledonian orogeny (400–425 Ma) (Sherlock et al. 2005). The Pb/Pb data on calcite, fluorite and galena veins and U/Pb data from Sweden and southern Finland, as well as Nd model ages of the fluorite-bearing veins, suggest, although with a large error, the Caledonian age of mineralization (~400 Ma; Alm et al. 2005; K. Sundblad personal communication 2007). Clauer et al. (2003) proposed that the illitization of Lower Cambrian clays in the BB was triggered by a short-lived thermal pulse reaching 130–140°C with the duration of 2–5 Ma at about 485 Ma, or even later.

The age of possible hydrothermal event(-s) proposed in these reports generally agrees with the K-Ar ages of mixed-layer mineral in bentonites, suggesting the main illitization event at 370–420 Ma. Nevertheless, compared to the mineralization at the Caledonian front (e.g. Lindblom 1986), the hydrothermal activity in the BB seems to be 5–20 Ma younger. This age difference, noticed also for Sm-Nd ages of fluorite and galena- bearing veins suggests that the fluids were not directly derived from the Caledonian front, but were probably related to the migration of the forebulge at the front of the Caledonian continent-continent collision zone, causing a fracturing and fluid flow due to an extensional tectonic regime in the BB (Alm et al. 2005).

The fluids reaching the BB were considerably cooler (<100 ºC) than the hydrothermal fluids recorded in the Caledonian zone. Low temperatures have been concluded for fluorite, galena and calcite veins in southern Finland (Alm et al. 2005). Also stable isotope geothermometry of vein/fracture fillings and cements in siliciclastic sediments with late carbonate minerals (dolomite/calcite) in Estonia suggest maximum temperatures of 50–70 ºC (Kalle Kirsimäe and Valle Raidla unpublished data 2009). The geochemical signatures of remagnetization of Silurian dolomites in the northern BB, showing weak remagnetization in Late Devonian-Mississippian (Plado et al. 2008), suggest mainly oxidized fluid species, which does not agree with the deep and high-temperature origin. There is no doubt that hydrothermal fluids with sulphide mineralization existed at the Caledonian front, but it seems that the fluids that reached the BB had already considerably cooled down.

The isotope composition of galena-dominated Pb(±Zn) mineralization in Ediacaran and Lower Palaeozoic successions in the northern BB suggests local basement-derived origin of low-temperature fluids (<100 °C, Sundblad et al. 1999). Most probably the fluid flow was induced somewhere in the uplifted forebulge area of the Caledonian foredeep. The fluid was transported through the extensional fractures penetrating the Ediacaran – Lower Palaeozoic sedimentary succession and the Palaeoproterozoic crystalline basement. At the beginning of the main illitization event in the Late-Silurian (~420 Ma) the northern part of the BB was uplifted and the forebulge of the Scandinavian Caledonian foredeep basin, which axis was running along the present-day Gulf of Bothnia, was opened to erosion (e.g. Tullborg et al. 1995; Plink-Björklund and Björklund 1999). In the early Middle Devonian to Late-Devonian the extensional collapse and uplift in the Scandinavian Caledonides (e.g. Milnes 1997; Rey et al. 1997) led to erosion of foredeep sediments. By that time forebulge was eroded and simultaneously with the decay of the forebulge the illitization of K-bentonites in the northern part of the BB ended.

The low-temperature fluids penetrating the section must have been enriched with K^+, which, combined with increased pH, significantly promotes K-mineral diagenesis (e.g. Sandler et al. 2004; Bauer et al. 2006; Sandler and Saar 2007). We suggest that the elevated K concentration of infiltrating fluids was achieved by migration through K-feldspar-rich crystalline basement rocks exposed under the Ediacaran–Palaeozoic sediments. The Palaeoproterozoic crystalline basement in northern Estonia and southern Finland, as well as in the Gulf of Finland and southern Gulf of Bothnia, consists of the Palaeoproterozoic Svecofennian orogenic crust intruded by numerous plutons of anorogenic rapakivi granites outcropping now in the regions of the Gulfs of Bothnia and Finland and central Baltic Sea (Koistinen 1996; Lehtinen et. al. 2005). The rapakivi granites, also the late Svecofennian migmatite granites are characterised by a high content of potassium feldspar (35–45 vol%).

High K^+ activity of diagenetic fluids is strongly supported by common feldspathisation of bentonites, especially in the northern part of the basin (Kiipli et al. 2009 – PAPER III). The K-feldspar distribution and the N(NW) to S(SE) variation pattern of illitization in K-bentonites in the northern and central parts of the BB (Kiipli et al. 2007 – PAPER III; Somelar et al. 2009b – PAPER II) would then reflect the fluid flow direction along the topographic and/or geochemical gradient. However, we must note that the illitization and K-feldspar abundance trends are concordant with the lithological pattern of the host rocks. Most illitic and K-feldspar-rich bentonites are seated in carbonate-dominated shallow shelf facies rocks, whereas the I/S-dominated bentonite composition gradually replaces the K-feldspar–I/S association in deeper shelf argillaceous carbonates and the I/S–kaolinite association occurs in the carbonate-rich shales of the deepest part of the shelf. Kiipli et al. (2007 – PAPER III) interpreted this transition as an evidence of syn-depositional to early diagenetic formation of K-feldspar, I/S and kaolinite, which was controlled by regular variation in the seawater pH, host rock composition and the sedimentation rate along the facies profile in the BB. The diagenetic ages of K-feldspar and I/S are >10 Myr younger than the depositional age (Somelar et al. 2009; Środoń et al. 2009) and the thermodynamic disequilibrium of I/S – K-feldspar – kaolinite assemblages (Hints et al. 2008), however, does not support our earlier interpretation.

Nevertheless, the host rock composition and early diagenetic environment has inevitably influenced the formation of kaolinitic and chlorite-smectite bentonites (Hints et al. 2006 – PAPER IV; Hints et al. 2008) and we cannot rule out that the increasing shaleness of the host rock along the deepening facies profile has influenced the composition of K-rich fluid along the migration path by creating ion enrichment on the upflow side of the semipermeable to impermeable shaly units due to ion hindrance (Kastner and Siever 1979; Mark et al. 2007).

5.1. Illitization mechanism

Generally, smectite illitization has been considered to proceed according to two general mechanisms: solid-state transformation (SST) and dissolution and crystallization (DC). Usually the SST mechanism has been proposed for materials with low permeability such as bentonite (Altaner et al. 1984; Środoń et al. 1986; Inoue et al. 1990; Elliott et al. 1991), shale and bentonite (Bell 1986), and mudstone (Lindgreen and Hansen 1991; Lindgreen et al. 1991). The DP mechanism has been proposed for environments of higher permeability, such as hydrothermal systems (Inoue 1986; Yau et al. 1987; Inoue et al. 1988; Kitagawa et al. 1994; Inoue and Kitagawa 1994).

The structural composition, isotope data and morphological parameters of I/S in Ordovician and Silurian bentonites of the BB seem to indicate a mixed dissolution-crystallization (DC) and solid-state-transformation (SST) mechanism. The SST mechanism would be suggested form clay particles of very low and rather constant thicknesses at about 3±1.5 nm, whereas the particle thickness increases only slightly with the increasing illite content in a mixed-layer mineral. Also, the formation of the high-charge crystal interfaces (vermiculite-type layers) from the original low-charge montmorillonite points towards the SST mechanism.

On the other hand, regular euhedral-lath-shaped particles and morphological evolution along with the structural rearrangement would indicate the DC mechanism. At the same, the K-Ar ages of bentonite fractions show that a coarser fraction (0.2–2 μm) exhibits lower K-Ar age than a fine-sized clay fraction (<0.2 μm). This results typically from a ripening process in which the finest particles are older and are continuously dissolved while coarser particles grow continuously (Meunier and Velde 2004). This variation in the K-Ar ages between different size fractions suggests that if the illitization of smectite in bentonites at the northern margin of the basin was triggered by K-rich fluid activity, it must have occurred over a prolonged period instead of a short single hydrothermal event that would have resulted in equal K-Ar ages for all sizes of

I/S particles (Środoń et al. 2002). Moreover, the ripening type of crystal growth in K-bentonites is also supported by AFM data that show gradual increase in average thickness and lateral dimensions (area) with increasing content of illite layers in mixed- layer minerals. On the base of these arguments we would suggest that illitization mechanism in these bentonites is mainly controlled by the SST mechanism but this evolution has been overprinted by the DC–type process.

6. CONCLUSIONS

The clay fraction of the studied Silurian and Ordovician K-bentonites from the BB is dominated by three-component mixed-layer I/S/V mineral with the illitic layer content varying from 54 to 85%. The variation of clay mineral composition is related to the change of facies zones. Nearly monomineral I/S/V and rarely I/S bentonites are found in shallow-water facies and the I/S/V(I/S)–kaolinite association occurs in deep water facies host rocks. The Katian bentonites of Pirgu age are exceptional among other Silurian and Ordovician K-bentonite beds due to their mixed-layer regular chlorite-smectite (corrensite) and I/S/V composition. The bentonites in the northern part of the basin are frequently feldspathized.

The northern margin of the BB (present day burial depths <300 m) is characterized by mixed-layer I/S/V with the expandability of 15–30%. At the depth of ~300–400 m the expandability varies at 20–40% and does not change before the 1400 m depth is reached in the south-central part of the BB. Further to the south the expandability starts to decrease and reaches the minimum at depths exceeding 2000 m where the expandability of Ordovician K-bentonites is 15–20%. In the same depth range the expandability of the Silurian K-bentonites is somewhat less than that of Ordovician beds.

The K-Ar data from the southern and south-western parts of the BB shows ages of 294 to 382 Ma (Środoń et al. 2009), which suggest illitization coinciding with the maximum burial that developed in Devonian-Carboniferous. The illitization was terminated in the Carboniferous when major erosion in southern part of the BB started. The K-Ar ages of the mixed-layer mineral from the northern and central parts of the BB suggest a somewhat earlier illitization age of 370 to 420 Ma that agrees with the extensional collapse of the Scandinavian Caledonides.

The illitization in the Ordovician and Silurian K-bentonite beds in the BB is evidently controlled by a combination of burial and fluid–driven processes. The burial process predominated in the deeply buried southern and south-western part of the BB where the illitization period corresponds to the maximum burial in the Silurian–Carboniferous. The influence of the burial diagenesis decreases with the decreasing burial depth from the southern part of the BB towards the central part of the basin. We suggest that illitization in the northern and north-western part of the BB was triggered by the prolonged flushing of K-rich fluids in relation to the latest phase of the development of the Scandinavian Caledonides about 420–400 Ma. The K-rich fluids were probably derived by the leaching of the K-feldspar containing rapakivi granites and migmatite granites of the Svecofennian crystalline basement, which were uplifted in the forebulge area of the Caledonian foredeep just at the northern and northwestern margin of the BB.

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SUMMARY IN ESTONIAN

Ordoviitsiumi ja Siluri bentoniitide varadiageneetiline areng Balti Basseinis

Illiit-smektiit on looduses levinuim segakihiline savimineraal, mis esineb nii murenemiskoorikutes(muldades), merelistes kui ka kontinentaalsetes setetes ja hüdrotermaalsetes muutumistsoonides. Illit-smektiit on kvaasistabiilne faas, mis kujutab endast muutuva koostisega üleminekulist vaheastet kahe teise laialt levinud savimineraali – smektiidi ja illiidi vahel. Smektiidi diageneetilist transformeerumist illiidiks nimetatakse illitiseerumiseks ning see on savimineraalide diageneetilistest protsessidest olulisim ja levinuim. Smektiidi illitiseerumine on mitmeastmeline protsess mida kontrollivad keskkonna temperatuur, settes liikuvate fluidide ja algse smektiidi koostis, orgaaniliste ühendite juuresolek ning (reaktsiooni) kestus. Seega peaks illitiseerumise diageneetiline areng setetes peegeldama settebasseini tektoonilis-termaalset arengut, sealhulgas basseini eksisteerimise vältel esinenud soojusvoo lokaalseid muutusi. Tüüpilistel illitiseerumistemperatuuridel (70–150°C) toimub ka setetesse maetud orgaanilise ainese termokatalüütiline lagunemine ning nafta ja maagaasi formeerumine. Seepärast on illitiseerumisuuringud kõrvuti mineraalide transformeerumisprotsesside üldise tundmaõppimisega esmatähtsad reservuaarikivimite nafta- ja gaasipotentsiaali hindamiseks. Siiski, kuigi illitiseerumist on intensiivselt uuritud viimase viie kümnendi jooksul nii looduslikes settebasseinides kui ka laboratoorselt, ei ole selle nähtuse toimemehhanismid ja arenguteed veel lõpuni selged.

Balti Bassein, eriti selle põhjapoolse osa (tänapäevane Eesti ja Läti ala), paleosoilist kuni kaasaegset geoloogilist evolutsiooni iseloomustab äärmiselt stabiilne tektoonilis-termaalne režiim. Siinsed Vara-Paleosoikumi terrigeensed setted ei ole kunagi sügavalt maetud ja on seetõttu praktiliselt litifitseerumata. Madalale diageneesiastmele viitab ka orgaanilise ainese muutumisaste, mis näitab, et paleotemperatuurid nendes setetes on ulatunud maksimaalselt kuni 50–80°C-ni. Vaatamata sellele on Balti Basseini settekivimite I/S kõrge illiitsusega (illiidi kihtide sisaldus >65%), mis peaks iseloomustama kaugele arenenud illitiseerumist. Seda ebakõla illitiseerumise ja setete termaalse arenguküpsuse vahel on varem selgitatud madalatemperatuurilise ajafaktori poolt kontrollitud illitiseerumisega või lühiajaliste termaalsete impulsside mõjuga.

Balti Basseini Alam-Palesoikumi Siluri ja Ordoviitsiumi karbonaatsetes kivimites esineb arvukalt bentoniidi (ümberkristalliseerunud püroklastilise materjali) kihte, millede savimineraalses koostises on ainult autigeensed faasid. Neid kunagisi vulkaanilise tuha kihte klassifitseeritakse tavaliselt kui K-bentoniite, mis märgib nende kõrgenenud kaaliumi sisaldust. Balti Basseini K-bentoniitide savifraktsioon (<2 μm) koosneb enamjaolt segakihilisest kolmekomponendilisest illiit-smektiit-vermikuliidi tüüpi mineraalist ja kaoliniidist. Erandiks on Ülem-Ordoviitsiumi Katiani (Pirgu lade) bentoniidid mille savifraktsiooni domineerivaks mineraaliks on kloriit-smektiidi (korrensiidi) tüüpi savimineraal, mis esineb koos illiit-smektiidi ja harvem kaoliniidiga.

Käesoleva töö eesmärgiks oli, esiteks, selgitada Ordoviitsiumi ja Siluri K-bentoniitide savimineraalide koostis, struktuurne seisund ja isotoopvanused ning nende parameetrite varieerumine Balti Basseinis. Teiseks töö eesmärgiks oli Balti Basseini setetendite tektono-termaalse arenguloo rekonstrueerimine tuginedes illitiseerumise seaduspärasustele. Balti Basseini väikestest mattumissügavustest ja stabiilsest tektoonilisest arengust tulenev diageneesikeskkond ja seda määranud parameetrid erinevad teistest sügavatest paleosoilistest, mesosoilistest ja kainosoilistest settebasseinidest, kus smektiidi illitiseerumist on siiani uuritud.

Uuritud K-bentoniitide savifraktsioonis domineerib illiit-smektiit-vermikuliidi (I/S/V) tüüpi segakihiline faas milles on illiitsete kihtide sisaldus vahemikus 54–85%. Kõrvuti segakihilise faasiga esineb bentoniitides autigeenne kaoliniit, mille sisaldus varieerub 4 kuni 60% (keskmiselt 22%). Basseini madalaveelise faatsiese valdavalt karbonaatsele põhjaosale (tänapäevane mattumissügavus <300m) on iseloomulik monomineraalne segakihiline I/S/V, kus illiitsete kihtide sisaldus on 70–85%. Illiitsete kihtide sisaldus väheneb umbes 60–80%-ni 300–400 m sügavusel ja ei muutu kuni sügavuseni 1400 m basseini kesk ja lõunaosas. Liikudes basseini keskosast järjest enam lõunasse kasvab illiidikihtide sisaldus K-bentoniitide segakihilises mineraalis kuni saavutab maksimaalselt 80–85% >2000 m sügavustel. Seejuures on Siluri K-bentoniitide illiidi sisaldus võrreldes Ordoviitsiumi kihtidega samal sügavusel pisut madalam. Kaoliniidi sisaldus suureneb basseini kesk- ja lõunaosa suunas ja selle mineraali esinemine iseloomustab peamiselt sügavaveelise faatsiese savikaid ümbriskivimeid.

Savifraktsiooni K-Ar dateeringute vanused (294-382 Ma) basseini lõuna- ja edelaosast viitavad sellele, et intensiivseim illitiseerumine rööbistub ajas setete maksimaalse mattuvusperioodiga, mis algas Devonis, ning mis basseini lõuna- ja edelaosas lõppes suureulatusliku erosiooniga Karbonis. Erinevalt basseini lõunaosast on segakihilise mineraali monomineraalsete fraktsioonide K-Ar dateeringud BB põhja- ja keskosast oluliselt nooremad (370–420 Ma) ja langevad kokku Skandinaavia Kaledoniidide mäestikutekke lõppfaasiga.

Segakihiliste mineraalide koostise, morfoloogia ja isotoopvanuste ruumiline varieerumine näitab, et Balti Basseini Ordoviitsiumi ja Siluri K-bentoniitide savimineraalide diageneesi on kontrollinud mattumisdiageneesi ja fluidi-protsesside kombinatsioon. Mattumisdiageneesi (st temperatuuri) kontrollitud illitiseerumine on domineeriv sügavalt maetud basseini lõuna- ja edelaosas, kus illitiseerumise vanus langeb kokku maksimaalse mattumisperioodiga Siluris-Karbonis. Mattumisdiageneesi protsesside osatähtus väheneb liikudes basseini lõunaosast basseini keskosa suunas koos bentoniidikihtide sügavuse vähenemisega. Peamiseks illitiseerumist mõjutavaks protsessiks Balti Basseini põhja- ja loodeosas on pikaajaline K-rikaste fluidide sissevool, mis on seotud Skandinaavia Kaledoniidide arenguga (~420–400 Ma tagasi). Fluid rikastus K-ga tõenäoliselt meteoorsete vete liikumisel läbi Svekofennia kristalliinse aluskorra K-päevakivi rikaste, rabakivi ja migmatiit graniitide, mis paiknesid Kaledoniidide eelsügaviku eelkerke (*forebulge*) alal.

PUBLICATIONS

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