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ILLITIZATION OF EARLY PALEOZOIC K-BENTONITES IN THE BALTIC BASIN: DECOUPLING OF BURIAL- AND FLUID-DRIVEN PROCESSES

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Abstract—The mineralogical characteristics of Ordovician and Silurian K-bentonites in the Baltic Basin were investigated in order to understand better the diagenetic development of these sediments and to link illitization with the tectonothermal evolution of the Basin. The driving mechanisms of illitization in the Baltic Basin are still not fully understood. The organic material thermal alteration indices are in conflict with the illite content in mixed-layer minerals. The clay fraction of the bentonites is mainly characterized by mixed-layered illite-smectite and kaolinite except in the Upper Ordovician Katian K-bentonites where mixed-layer chlorite-smectite (corrensite) occurs. The variation in expandability plus other geological data suggest that the illitization of Ordovician and Silurian K-bentonites in the Baltic Basin was controlled by a combination of burial and fluid driven processes. The illitization in the south and southwest sectors of the basin was effected mainly by burial processes. The influence of the burial process decreases with decreasing maximum burial towards the central part of the basin. The advanced illitization of the shallow-buried succession in the north and northwest sectors of the basin was enhanced by the prolonged flushing of K-rich fluids in relation to the latest phase of development of the Scandinavian Caledonides ~420–400 Ma.

Key Words—Baltic Basin, Illite-smectite, Illitization, K-bentonite.

INTRODUCTION

Illitization of smectite is one of the most studied but still much debated clay mineral alteration processes and is widely considered to be a temperature-controlled reaction associated with diagenesis (*e.g.* Środoń, 1999). Various diagenetic and low-grade metamorphic environments show a contemporary increase in the burial depth (temperature) and the illite content in mixed-layer illite-smectite (I-S). The illitization, therefore, can be used as a tool for describing the development of sedimentary basins (Środoń and Eberl, 1984; Pollastro, 1993). The illitization of smectite-rich sediments at different burial settings can also be driven by the intrusion of hydrothermal fluids or diagenetic brines in relation to orogenic processes at the basin margins (*e.g.* Elliot and Aronson, 1987; Hay *et al.*, 1988) or due to the early diagenesis of carbonate-facies deposits in marine evaporitic settings (Sandler and Saar, 2007). Alternatively, illitization has been found to occur under surface conditions in saline-alkaline lakes (*e.g.* Deconinck *et al.*, 1988) where the illite-smectite 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). The reciprocal interplay of different diagenetic to hydrothermal conditions possibly driving the illitization process makes it difficult to recognize the mechanism of illitization and, thus, the diagenetic development of sedimentary sequences (*e.g.* Clauer, 2006).

The Baltic Basin is an old cratonic area that has existed under exceptionally stable tectonic conditions for the last 500 Ma (Hendriks *et al.*, 2007). The vertical and lateral trends of illitization within the Baltic Basin, however, are complex and are in some cases opposite to a normal burial trend (Somelar *et al.*, 2009), 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 by possible heat- and/or fluid-flow episodes. The Lower Paleozoic sedimentary sequence of Silurian and Ordovician carbonate rocks in the Baltic Basin contains numerous bentonites that are typically classified as K-bentonites (see Bergström *et al.*, 1992, 1995, 1998). The bentonites found in the Baltic Basin include the thickest and most widespread Paleozoic K-bentonite in northwestern Europe – the Kinnekulle bed, equivalent to the North American Millbrig K-bentonite (Bergström *et al.*, 2004). The aim of this contribution was to investigate the powder X-ray diffraction (XRD) characteristics of mixed-layer minerals in Lower Paleozoic bentonites in order to elucidate the illitization processes linked to the tectonic and thermal evolution of the Baltic Basin and to its marginal areas that have resulted in the controversial illitization patterns observed.

GEOLOGICAL BACKGROUND

The Baltic Basin (Figure 1) is an old stable epi- to pericratonic marine basin covering portions of the East

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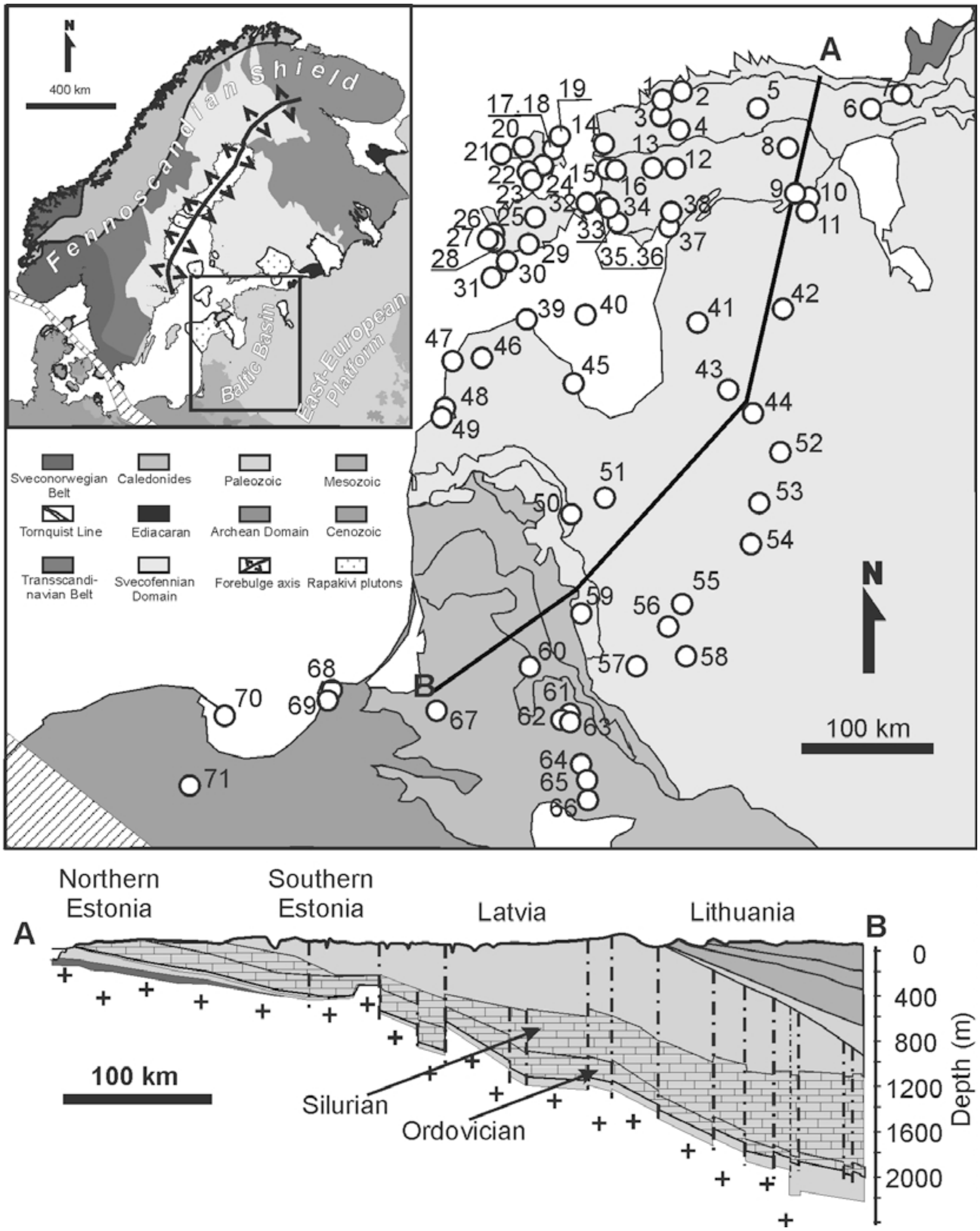

Figure 1. Simplified geological map of Fennoscandia and the Baltic Basin with the locations of the drill cores studied. Legend: (1) Keila-138; (2) Pääsküla; (3) Vasalemma; (4) F-306; (5) Pa. 37; (6) F-198; (7) F-639; (8) Oostriku; (9) Laeva-1; (10) Laeva-4; (11) Laeva-18; (12) Velise-99; (13) Velise-98; (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) Bliudiai; (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, and 71 are from Środoń *et al.* (2009); 8, 15, 16, 20, 51, 60, and 65 are from Rateev and Gradusov (1971); and 41, 44, 46, 49, 52, 53, 54, 55, 56, 57, 58, 61, 62, 63, 66, 67, 68, and 69 are from Kepežinskas *et al.* (1994).

European Platform in the Baltic region. The most complete and thickest (>2000 m) stratigraphic record extends from the latest Precambrian to the Cenozoic in the southwestern part of the basin, whereas in the northern part of basin only sediments of the Late Proterozoic and the Early Paleozoic are known (Nikishin *et al.*, 1996).

The Ordovician and Silurian sedimentary successions of the basin contain numerous bentonites, which occur in the form of thin but laterally continuous beds within siliciclastic or carbonate successions (*e.g.* Bergström *et al.*, 1992, 1995). Most of the bentonite beds are found in certain stratigraphic intervals where the beds commonly form distinct series composed of a number of closely spaced layers. In the Ordovician section, the bentonite successions are found in the Upper Ordovician Sandbyan and Katian stages and in the Silurian section in the Llandoverian Telchian and Wenlockian Sheinwoodian Stages (Bergström *et al.*, 1992, 1995, 1998) (Figure 2). Among these are two of the thickest and most widespread Paleozoic K-bentonites of northwestern Europe, the Ordovician Kinnekulle and the Silurian Osmundsberg K-bentonites, which have been traced across large areas in Baltoscandia and Britain (Bergström *et al.*, 1995, 1998).

The bentonite host rocks are dominated by normal marine carbonate rocks, the composition of which varies with respect to facies-zone changes from the northern part of the basin to the southwestern part of the basin next to the Tornquist-Teysseyre Zone. In the northern part of the basin the sediments are characterized by shallow marine limestones and argillaceous limestones, which are replaced by (kerogenous) shales, marlstones, and limestones in deep shelf facies in the southwestern part of the Baltic Basin.

The bentonites in the Baltic Basin are typically characterized by a clay matrix composed of mixed-layer illite-smectite with some kaolinite (Kiipli *et al.*, 2007; Hints *et al.*, 2008). The feldspathized bentonites, however, occur in the section (Kiipli *et al.*, 2007) and the bentonites of Upper Ordovician Katian age (Pirgu Regional Stage) are characterized by chlorite-smectite mixed-layer minerals (Hints *et al.*, 2006). The whole-rock composition of the bentonites can vary laterally in the profile. In the Kinnekulle K-bentonite, the K-feldspar-rich bentonite occurs in the northern part of the basin and is replaced by illite-smectite and then by an illite-smectite and kaolinite association towards the south-central part of the basin (Kiipli *et al.*, 2007).

MATERIAL AND METHODS

The material investigated came from 37 drillcores located in the Baltic Basin (Figure 1) with 77 samples analyzed in total. Of these, 48 samples were chosen from Ordovician and 29 samples from Silurian bentonite beds.

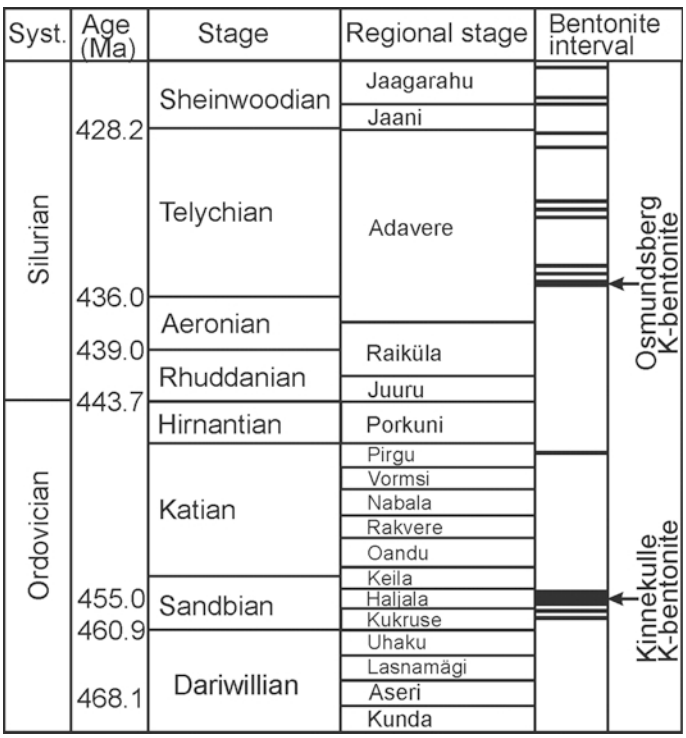

Figure 2. Stratigraphic scheme of Ordovician and Silurian bentonite intervals in the Baltic Basin.

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Both plastic and non-plastic (feldspathized) varieties of bentonite were sampled.

The bentonite clay was dispersed in distilled water with the help of ultrasonic treatment and the clay fraction (<2 μm) was obtained by standard sedimentation procedures. The Mg- or Ca-exchanged <2 μm size fractions were studied as oriented clay aggregates in both the air-dry and ethylene-glycol solvated (EG) state by means of XRD with a DRON-3M diffractometer using CuKα radiation.

The qualitative and quantitative estimation of illite, kaolinite, and smectite in mixed-layer illite-smectite (I-S), illite-smectite-vermiculite (I-S-V), and chlorite-smectite (corrensite) were modeled using the MLM2C and MLM3C codes of Plançon and Drits (2000). The experimental XRD profiles were compared to calculated structural models by a trial-and-error procedure until optimum fit was achieved. The profiles were fitted in the 2–50º2θ range, taking into account instrumental and experimental factors as well as the orientation factor, using the mass adsorption coefficient and structural layer compositions suggested by Moore and Reynolds (1997). The coherent stacking domain sizes (CSDS) were distributed log-normally.

The dataset analyzed was complemented with a selection of Baltic Basin Lower Paleozoic bentonite data from published mixed-layer mineral analyses by Rateev and Gradusov (1971), Kepežinskas *et al.* (1994), Somelar *et al.* (2009), and Środoń *et al.* (2009).

Mass-balance calculations for potassium losses and gains in the isochronous and easily traced Kinnekulle K-bentonite bed were made using the chemical mass-balance model developed by Brimhall and Dietrich (1987). The calculations were made on an anhydrous basis and presumed Al as an immobile element during devitrification of glass and smectite illitization (*e.g.* Huff *et al.*, 1996). The bulk chemical data for the Kinnekulle bed were adopted from Kepežinskas *et al.* (1994) and Kiipli *et al.* (2007), and the chemical composition of the parent rhyolitic glass and densities of the glass and Kinnekulle bentonite from Huff *et al.* (1996) were used.

RESULTS

The clay mineral compositions of Ordovician and Silurian bentonites from the Baltic Basin are characterized by mixed-layered illite-smectite and kaolinite except in the Katian bentonites of Pirgu age where mixed-layer chlorite-smectite (corrensite) occurs (Figure 3). The kaolinite content in the bentonite clay fractions varies considerably from 4 to 60%. The mixed-layered illite-smectite composition is particularly characteristic in the northern, shallow-facies, carbonate-dominated part of the basin, whereas the kaolinite content increases in the central and southern parts of the basin characterized by deep-water facies zones in transitional and central confacies sediments. Kaolinite is more frequent (in 39 of 128 samples) and more abundant (average 22%) in Silurian K-bentonite beds. In Ordovician K-bentonites, kaolinite occurs more rarely and mostly in the southern part of the basin.

The XRD analysis of mixed-layer mineral interstratification showed that in most samples the mixed-layer mineral is composed of illite (I) and low-charge smectite (S) or I, S, and high-charge smectite (V, vermiculite-like) components. In upper Katian bentonites the mixed-layer mineral is composed of regularly interstratified chlorite and low-charge smectite (corrensite) components.

The Ordovician K-bentonites (except the upper Katian bentonites) are characterized by a highly illitic mixed-layer I-S-V mineral with an illite content of 56–86% (Figure 4). The content of fully expandable (low-charge) smectite and the high-charge smectite (vermiculite) layers varies from 14 to 41 and 0 to 18, respectively. The structure of mixed-layer minerals is characterized by R1 type ordering with the vermiculite-vermiculite sequence probability varying from 0 to 0.4. At the northernmost margin of the basin, in the area where the bentonite beds crop out, the smectite content of the Ordovician bentonites ranges from 15 to 44%. The expandability increases with increasing depth of the southward dipping bentonites and can be traced to a depth of ~300–400 m where the smectite layers content varies from 20 to 40% (Figures 4, 5). Further to the south, in the deeper part of the basin (>400 m), the mixed-layer mineral expandability decreases gradually with increasing depth as would be expected from a normal burial trend. At >2000 m depth the expandability of Ordovician bentonites decreases to ~15–20% (Figure 5).

The diagenetic maturity variation in the Silurian bentonites within the Baltic Basin shows trends that are similar to the mixed-layer minerals in Ordovician beds. The expandability of the Silurian K-bentonites, however, is somewhat less compared to the Ordovician beds in the same depth range. The S% of the mixed-layer I-S and I-S-V minerals in shallow-buried Silurian K-bentonites varies from 15 to 41%. The expandability increases with increasing burial depth to ~40% at 280–300 m in the central part of the basin (Figure 4, 5). From this depth the expandability of the mixed-layer mineral decreases with increasing depth to ~25% at 500 m. Moreover, the most expandable mixed-layer minerals in Silurian K-bentonites are characterized by a two-component R1 ordered illite-smectite without high-charge smectite interlayers, whereas in the Ordovician bentonites the mixed-layer mineral was best described almost exclusively by assuming a three-component mixed-layering.

The clay mineral composition of Ordovician Katian K-bentonites, of Pirgu age, differ from other Ordovician and Silurian bentonites. The clay fraction of the Pirgu bentonite samples contains mixed-layer R1 ordered regular chlorite-smectite (corrensite) (Figure 3) together

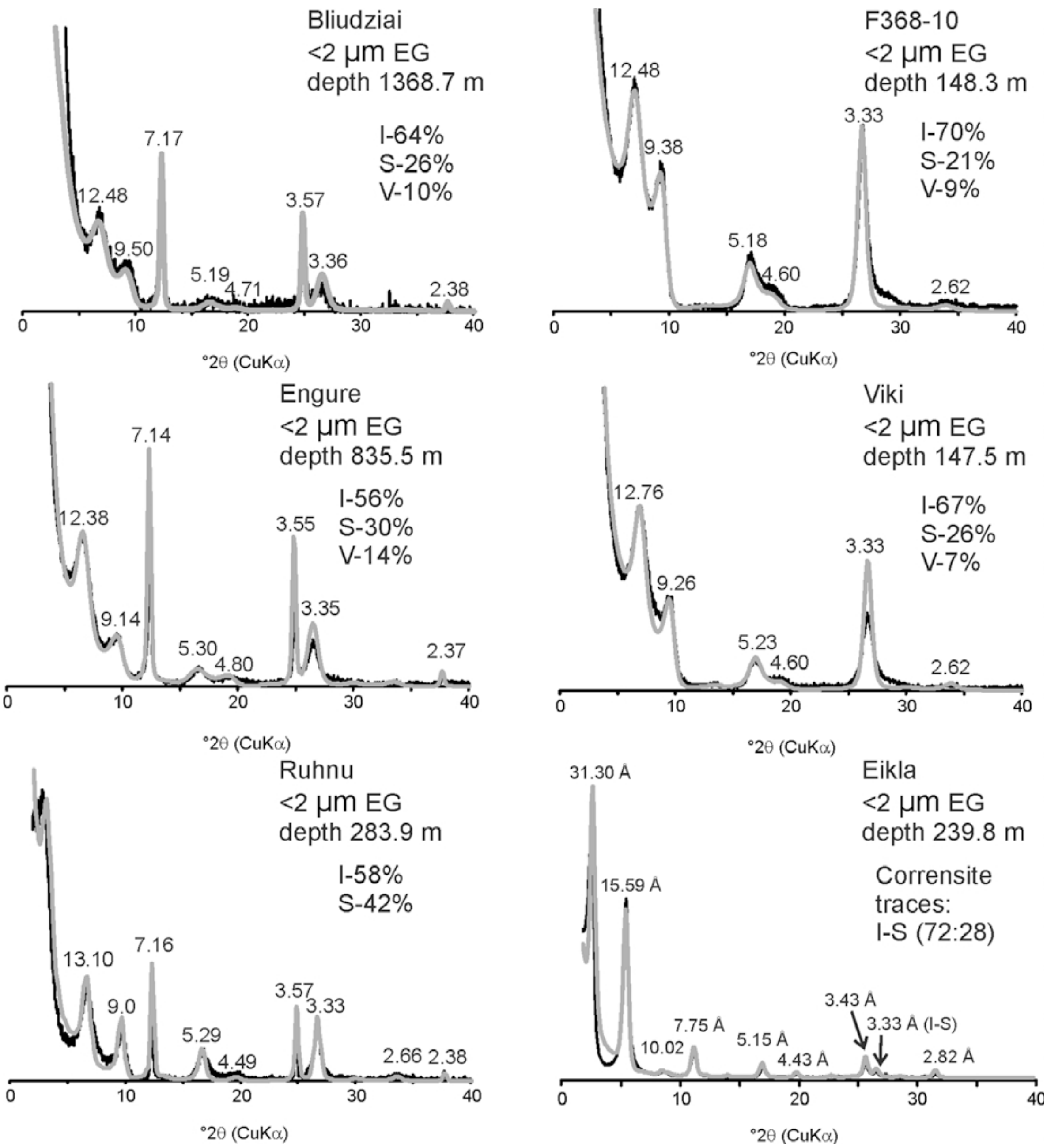

Figure 3. Comparison of the experimental and the calculated XRD profiles of selected Ordovician and Silurian bentonite <2 µm fractions in an EG-saturated state. The black lines show measured and gray lines calculated profiles.

with mixed-layer I-S and kaolinite. Corrensite is the most abundant clay mineral in most of the Pirgu samples and I-S dominates in a few. The mixed-layer illite-smectite in the Pirgu samples is similar to other Ordovician beds and is characterized by a three-component I-S-V composition. Hints *et al.* (2006) suggested that the corrensite in the Pirgu K-bentonites originated from early diagenesis in a marine evaporative sabkha-type environment where the flux of saline Mg-rich fluids through subaerially exposed rocks provided the large amount of Mg needed for the formation of saponite-type smectite and led to the consequent saponite-to-chlorite transformation. The chloritized bentonites are restricted to the Pirgu Stage, which was characterized by several relative sea-level drops and the formation of the large, shallow-water, supra-tidal sabkha environments along the northern margin of the basin (Hints *et al.*, 2006).

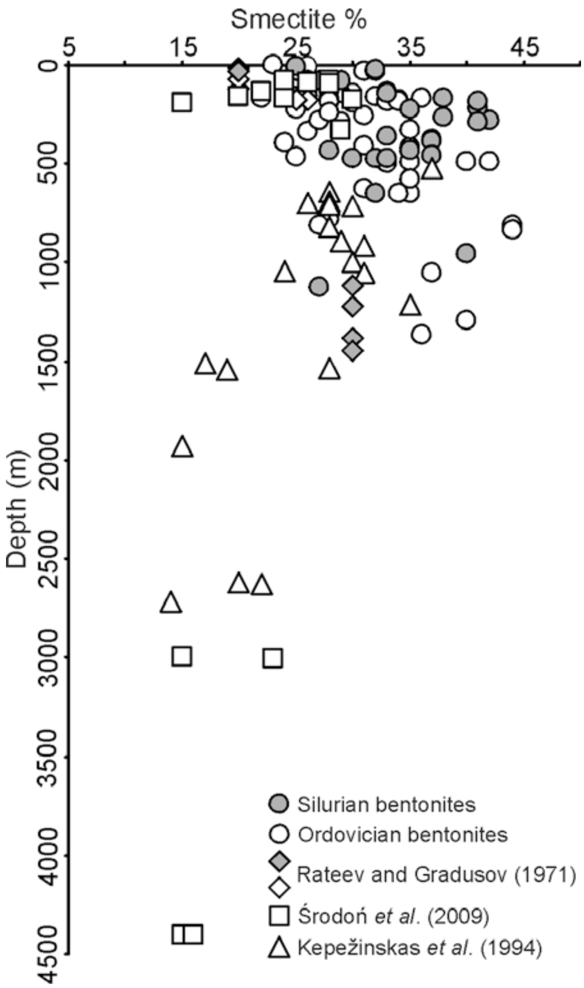

Figure 4. Smectite content in the mixed-layer mineral in relation to the present-day burial depth.

DISCUSSION AND CONCLUSIONS

The illitization of smectite has been shown to be principally controlled by temperature (Hower *et al.*, 1976, 1986; Pollastro, 1993). The onset of illitization in K-bentonites occurs at ~70ºC and the mixed-layer I-S structural ordering transition from R0 to R1 at 35%S at temperatures of ~150ºC (Šucha *et al.*, 1993). A similar burial-diagenesis mechanism of illitization in the Baltic Basin would require burial depths in all parts of the basin of >5 km, assuming normal cratonic geothermal gradients of 20–25ºCkm^{-1}. The organic thermal alteration indices within the basin suggest, however, a gradual increase of the maximum paleotemperatures towards the main depocenter in the southwestern part of the basin. The subsiding Silurian-Devonian basin developed following the collision of Baltica with Avalonia as a rapidly subsiding foredeep along the southwestern margin of Baltica (Torsvik and Rehnström, 2003). The sediments in the northern part of the basin (present day depths <1000 m) are thermally immature and the thermal maturity increases to immature/early mature in the central part of the basin (1000–2000 m). Peak maturity occurs in the southwestern part of the basin (>2000 m), with maximum estimated paleotemperatures of <50–80ºC up to ~150ºC, respectively (Zdanavièiûte, 1997; Grotek, 1999; Nehring-Lefeld *et al.*, 1997; Talyzina *et al.*, 2000).

In this sense the burial illitization model was feasible in the south and southwestern sectors of the Baltic Basin bordering the Tessiere-Tornquist Zone where the estimated diagenetic state of organic material and the illitic content in mixed layer I-S agree. Burial diagenesis in this part of the basin is supported by K-Ar ages (294–382 Ma) of the bentonite I-S fractions (Środoń and Clauer, 2001; Środoń *et al.*, 2009), which coincide with the period of maximum burial in Devonian–Carboniferous time (Kirsimäe and Jrgensen, 2000). The %S of I-S in the south to southwestern sector of the basin decreases towards the east and north in accordance with the tectonic subsidence development of a typical (flexural) foreland basin during the Silurian that resulted from an oblique collision of Baltica and Eastern Avalonia (Poprawa *et al.*, 1999). In the north and central cratonic parts of the basin, however, the organic thermal maturation values as well as the compilation of Fennoscandian apatite fission-track data (Hendriks *et al.*, 2007) shows no evidence of deep burial (>2–3 km) and the illitic I-S (<35%S) is in conflict with the digenetic grade of the sediments. Moreover, the mineral composition and the K_2O content of the K-bentonite whole rock in the basin shows a variable trend of increasing K_2O and authigenic K-feldspar content towards the shallower north and northwestern part of the basin where the K_2O content in the bulk bentonite reaches 7.5–13.8% compared to 6.0–7.5 to 4.1–6.0% in the central and southern parts of the basin, respectively (table 1 and figure 3 in Kiipli *et al.*, 2007). Such K_2O enrichment agrees with the illitization trend observed in the present study, suggesting a different illitization path, probably enhanced by episodic fluid flow.

The illitization and K-feldspar authigenesis of bentonites in the northern part of the Baltic Basin, yielding Late Silurian – Early-to-Middle Devonian ages (I-S 370–420 Ma, Somelar *et al.*, 2009; Środoń *et al.*, 2009; K-feldspar ~420 Ma, Środoń *et al.*, 2009), is at least 20–30 Ma older than the southern sector of the basin and was probably contemporaneous with the Scandian phase of the Caledonian continent-continent collision. Poprawa *et al.* (2006) showed, in the Baltic Basin, the presence of a system of syn-sedimentary reversed compression or transpression southwestern–northeastern faults, developed mainly in the late Silurian to Early Devonian (Lochkovian) and, thus, correlating in time with the Scandian orogenic phase in the Scandinavian Caledonides. The development of fault systems within the Paleozoic sequence of the Baltic Basin provided migration routes for fluids that could

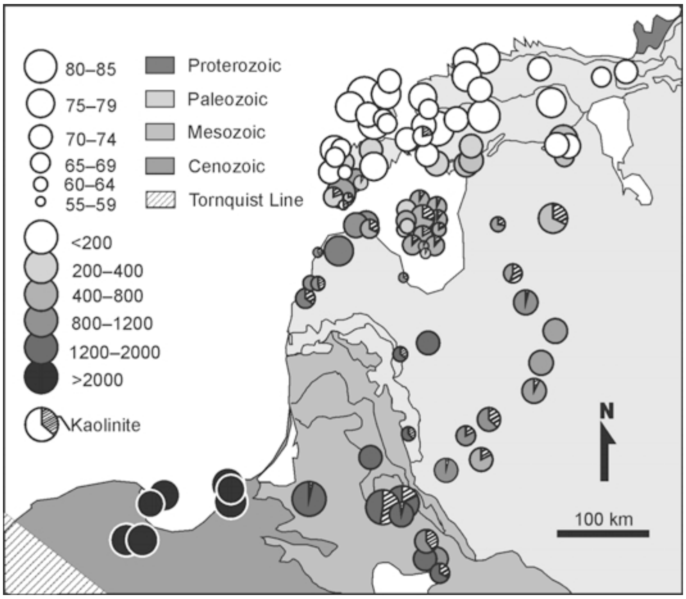

Figure 5. Lateral distribution of illite in mixed-layer illite-smectite and kaolinite in Ordovician and Silurian bentonites in the Baltic Basin.

have been either meteoric waters percolating by gravity-driven flow at topographic highs within the collision zones or deep-seated basinal brines driven by tectonic compression and geothermal gradients away from the thrust zone(s) toward the Caledonian foreland basin as suggested for the Scottish sector of the Laurentian margin during the Caledonian orogeny (Mark *et al.*, 2007).

At the beginning of the main illitization event in the Late-Silurian (~420 Ma), the northern sector of the basin became an uplifted, eroded, and by-pass area due to the propagation of the forebulge of the Scandinavian Caledonian foredeep basin, the axis of which was running along the present day Bothnian Gulf (*e.g.* Plink-Björklund and Björklund, 1999; Tullborg *et al.*, 1995). Furthermore, the extensional collapse and uplift in the Scandinavian Caledonides occurred in the late Early Devonian to early Middle Devonian (*e.g.* Rey *et al.*, 1997; Milnes *et al.*, 1997) causing the erosion of foredeep sediments and decay of the forbulge. The event was coeval with the end of K-bentonite illitization in the northern/central part of the basin and suggests that fluid flow was being induced in the uplifted forebulge area of the Caledonian foredeep by water percolating through the extensional fractures penetrating the Ediacaran–Lower Paleozoic sedimentary succession and the Paleoproterozoic crystalline basement. This interpretation is supported by the Lower Paleozoic radiogenic age of galena mineralization in Ediacaran and Lower Paleozoic successions in the northern Baltic Basin. The age suggests the presence, at least in a significant portion, of local, basement-derived fluids (Sundblad *et al.*, 1999) which were, based on the lack of high-temperature mineralogical and organic maturation indicators, of a low-temperature character (<100ºC).

Low-temperature fluid alone is inadequate to explain the observed illitization and K-feldspar authigenesis phenomena, since these reactions would require an elevated K^+ activity to promote in combination with increased pH the K-mineral diagenesis (*e.g.* Sandler *et al.*, 2004). The infiltrating fluids in the forebulge region could have produced this elevated K^+ concentration in their migration through the K-feldspar rich crystalline basement rocks underlying the Ediacara-Paleozoic sediments, and gained by this the elevated K^+ concentration. The Paleoproterozoic crystalline basement in northern Estonia and southern Finland as well as in the Finnish Gulf and the southern Gulf of Bothnia consists of Paleoproterozoic Svecofennian orogenic crust (1.90–1.80 Ga) composed of microcontinent-type terrains and island arc mosaics, with chiefly metavolcanic rocks and metasedimentary rocks as well as their anatectic products, late orogenic migmatite-forming S-type granitoids (Lehtinen *et al.*, 2005; Koistinen, 1996). During early Mesoproterozoic time, the crust was intruded by numerous plutons of anorogenic rapakivi granites cropping out now in the regions of Bothnia, the Finnish Gulfs, and the central Baltic Sea (Lehtinen *et al.*, 2005; Koistinen, 1996) (Figure 2). The rapakivi granites, as well as the late Svecofennian migmatite granites, exposed in the area of the Caledonian orogen forebulge are characterized by their large K-feldspar content (mostly 35–45 vol.%) and corresponding large K_2O content (5–6 wt.% on average) (Marmo, 1971;

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Koistinen, 1996; Kirs *et al.*, 2004; Lehtinen *et al.*, 2005). These are the likely source for enrichment of the migrating fluids with respect to K^+ through K-feldspar dissolution. Note that the anion hydrolysis of the feldspar consumes the H^+ and the reaction results in an elevated pH of the fluid, which is required for illitization and K-feldspar formation.

The external K flux to the bentonite beds in the northern and central parts of the basin is evident from a basin-wide mass balance calculation of K_2O losses and gains in the Kinnekulle bed (Figure 6) which indicates the consistent addition of K_2O compared to original rhyolitic glass towards the northern and northwestern parts of the basin. Note that the same level of illitization (80−85% I) in the southern part of the basin has not required external K-flux, which agrees with the data of Huff *et al.* (1996) suggesting that more than enough K is present in the parent glass to account for illitization under burial conditions. The migration of the K-rich fluid through the Ediacaran and Lower Paleozoic succession in the northern basin is also supported by the common presence of authigenic K-feldspar (including overgrowths on older grains) within the sandstone lithofacies rocks of Ediacaran, Cambrian, and Ordovician age (Valle Raidla and Kalle Kirsimäe, pers. comm., 2009), suggesting that fluids were saturated enough with respect to K, Al, and Si to induce the nucleation of authigenic K-feldspar and probably authigenic illite. Zeolites were probably formed in the bentonites flushed by K-rich alkaline fluids. Zeolites are the second most common alteration products of volcanics after smectite (Meunier, 2005) and zeolitic tephra beds are common in Cenozoic and Mesozoic deposits (*e.g.* Sheppard and Hay, 2001). Hints *et al.* (2008) discussed the formation of possible metastable zeolite phases in Baltic bentonites in order to explain the whole-rock mineral composition of these beds. However, zeolites are unstable under diagenetic conditions (Sheppard and Hay, 2001) and are not found in Paleozoic bentonites. Typically the potassic-sodic alkali zeolite species recrystallize into K-feldspar (*e.g.* Hay and Guldman, 1987) suggesting that at least part of the authigenic K-feldspar found in feldspathized varieties of the bentonite beds in the northern part of the Baltic Basin would have had alkali-feldspar precursor. The early formation of metastable K-bearing zeolites is also important in retaining K in the system, which can be used for illitization during the later stages of diagenesis (Christidis, 2001).

The same fluids resulting from the Caledonian tectonic reactivation of the Svcofennian basement were probably responsible for the Silurian-Devonian remagnetization recorded in the shear zones in southern Finland (Mertanen *et al.*, 2008) and Late Devonian–Mississippian remagnetization of Silurian dolomites in central Estonia (Plado *et al.*, 2008). The remagnetization behavior of the crystalline rocks in southern Finland (Mertanen *et al.*, 2008) and Ordovician and Silurian carbonate successions in the northern part of the Baltic Basin (Plado *et al.*, 2008, 2009) also point, however, toward a second remagnetization event in Permian to mid-Triassic time, and probably in the Cretaceous, that may be related to the Permian−Triassic uplift and extensive erosion over all of the Svecofennian domain and the Baltic Basin (*e.g.* Tullborg *et al.*, 1995).

The north (northwestern) to south (southwestern) variation pattern of illitization in the northern and central parts of the Baltic Basin accompanied by K-feldspar distribution (*sensu* Kiipli *et al.*, 2007) in K-bentonites would then reflect the fluid-flow direction along the topographic and/or geochemical gradient (Figure 7). The illitization and K-feldspar abundance trends, however, are in accord with the lithological pattern of the host rocks. Most illitic and K-feldspar-rich bentonites are seated in carbonate-dominated, shallow-shelf facies, whereas the I-S-dominated bentonite composition gradually replaces the K-feldspar-I-S association in deeper-shelf argillaceous carbonates. The I-S-kaolinite association occurs in the carbonate-rich shales of the deepest part of the shelf (Figure 5). This transition led Kiipli *et al.* (2007) to conclude that the syn-depositional to early diagenetic formation of K-feldspar, illite-smectite, and kaolinite was controlled by the regular variation of seawater pH, host-rock composition,

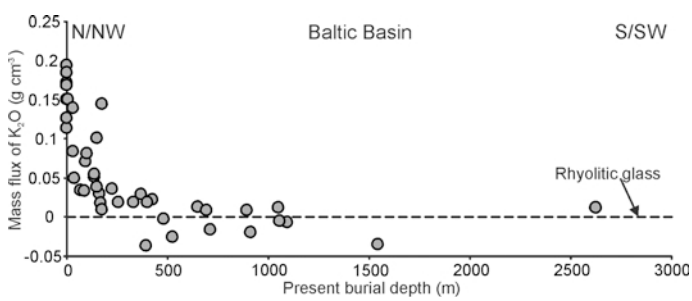

Figure 6. Calculated mass gain and loss (absolute mass change per unit volume of parent rock) of K_2O in the Kinnekulle bentonite in the Baltic Basin relative to parent rhyolitic glass. The composition of rhyolitic glass for Kinnekulle bentonite is according to Huff *et al*. (1996).

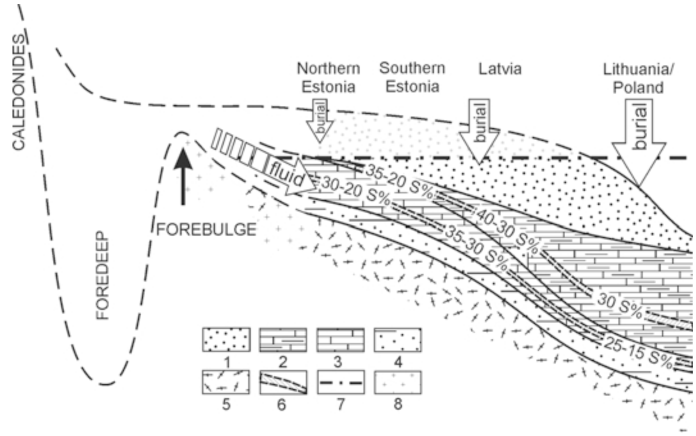

Figure 7. Schematic representation of the bentonite diagenesis in the Baltic Basin (not to scale). (1) Devonian, (2) Silurian, (3) Ordovician, (4) Cambrian, (5) crystalline basement, (6) bentonite, (7) present erosional surface, (8) K-rich rapakivi plutons.

and sedimentation rate along the facies profile in the Baltic Basin. The thermodynamic disequilibrium of I-S–K-feldspar–kaolinite assemblages (Hints *et al.*, 2008), however, does not support this interpretation. Also, the diagenetic ages of the K-feldspar and illite-smectite are >10 My younger than the depositional age (Somelar *et al.*, 2009; Środoń *et al.*, 2009). The host-rock composition and early diagenetic environment inevitably have influenced the formation of kaolinitic and chlorite-smectite bentonites (Hints *et al.*, 2006, 2008) and the possibility cannot be ruled out that the facies zonation corresponding to host-rock shale content within the basin has influenced the composition of K-rich fluids along the migration path by creating ion enrichment on the upflow side of the semi-permeable to impermeable shaley units due to ion hindrance (Kastner and Siever, 1979; Mark *et al.*, 2007).

In summary, the illitization of the Ordovician and Silurian K-bentonites in the Baltic Basin was probably controlled by a combination of burial- and fluid-driven processes that has resulted in variable illitization patterns throughout the basin. The burial process was dominant in the deeply buried south and southwestern sectors of the basin where the age of illitization corresponds to the period of maximum burial in the Silurian through Permian/Triassic, and has resulted in mixed-layer I-S minerals with 25–15% of expandable layers. The influence of the burial process decreases with the decreasing maximum burial toward the central part of the basin where the %S of the mixed-layer I/S mineral decreases to 40–30%. The advanced illitization of the shallow-buried succession in the north and northwestern sectors of the basin with <25% of expandable layers was enhanced by the prolonged flushing of K-rich fluids in relation to the latest phase of development of the Scandinavian Caledonides. The illitization of bentonites and the precipitation of authigenic K-feldspar in bentonites as well as in Lower Paleozoic sandstone successions were driven by waters enriched with respect to K^+ by leaching of the K-feldspar-rich rapakivi granites and migmatite granites of the Svecofennian crystalline basement in the uplifted forebulge of the Caledonian foredeep located at the north to northwestern margin of the Baltic Basin.

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