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Illitization of the lower Cambrian (Terreneuvian) Blue Clay in the northern Baltic Palaeobasin

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Abstract. The clay mineral composition of the lower Cambrian (Terreneuvian) Blue Clay (BC) in the northern Baltic Palaeobasin was studied. The proportion of illite in mixed-layer illite-smectite in the BC increases gradually from *ca* 85% in northern Estonia to *ca* 92% in central Latvia with the present burial depth increasing from a few hundred metres to *ca* 1000 m. The high level of illitization suggests a mature diagenetic grade of the sediments, which is typically achieved with burial at several kilometres. However, uncompact nature and thermally immature organic material suggest only shallow burial and maximum palaeotemperatures not exceeding 50 °C. The smectite-to-illite transformation in the BC was described using a kinetic modelling to assess the constraints on burial-driven illitization. Modelling results show that the present illitization level is possible to achieve by assuming burial during the Devonian to Permian prior to the erosion in the Mesozoic. The thickness of eroded sediments in the northern part of the basin was in this case only about 400–800 m. The smectite-to-illite transformation process in the BC in the northern Baltic Palaeobasin was controlled rather by time than by temperature.

Key words: illite-smectite, low-temperature illitization, Baltic Palaeobasin.

INTRODUCTION

Clay mineral evolution in sedimentary basins is principally controlled by temperature and time, but also by chemical variables. The most common process observed along with the advancing diagenesis is the smectite-to-illite transformation through a series of intermediate mixed-layer illite-smectite (I-S) minerals. The kinetic constraints for this reaction have been studied since the early works on illitization. Based on laboratory experiments, natural illitization trends and numerical models, several kinetic models have been proposed (Eberl & Hower 1976; Roberson & Lahann 1981; Whitney & Northrop 1988; Velde & Vasseur 1992; Huang et al. 1993; Cuadros & Linares 1996; Wei et al. 1996; Cuadros 2006). However, according to Ferrage et al. (2011), smectite illitization is a complex reaction involving multiple phases and the true meaning of the activation parameters describing the rate of the illitization reaction(s) are not fully understood. Nonetheless, progressive smectite-to-illite conversion has been used as an empirical geothermometer reflecting the diagenetic grade of the sediments (Pollastro 1993). Illitization ‘onset’ temperatures are estimated usually between 60 and 110 °C at burial depths over 2–3 km (Hoffman & Hower 1979). However, there is no strict correlation with depth and temperature (Freed & Peacor 1989, 1992), and illitization may occur at temperatures as low as 20–30 °C at depths of only 500 m (Schoonmaker et al. 1986; Buatier et al. 1992; Huggett & Cuadros 2005; Sandler & Saar 2007). Also, organic material maturation data (e.g. vitrinite reflectance), strongly correlating with temperature, show that illitization, which usually lags behind the organic material maturation, is more advanced than expected from temperatures in some ‘cold’ older basins (Velde & Espitalie 1989; Hillier et al. 1995).

The aim of this paper is to study the time-temperature constraints of the smectite-to-illite transformation in claystones (the Blue Clay (BC)) of early Cambrian (Terreneuvian) age in the northern part of the Baltic Palaeobasin (BP). These clays have retained, despite their high age, a natural plasticity and high water content (~20–30%) and the palaeotemperature in these sediments, estimated from the alteration of microfossils organic material and biomarker molecular characteristics, has probably not exceeded 50 °C (Hagenfeldt 1996; Talyzina 1998; Talyzina et al. 2000; Pehr et al. 2018). This and assumed burial depths of a few hundred metres are in conflict with the mature diagenetic grade of the sediments suggested by the low expandability of I-S of 10–20% (Chaudhuri et al. 1999; Kirsimäe et al. 1999a, 1999b; Kirsimäe & Jørgensen 2000; Clauer et al. 2003).

The diagenetic history of the BC has deserved close attention over decades, but the driving mechanisms behind illitization are yet to be understood. Gorokhov et al. (1994) proposed a multistage illite evolution owing to retrograde diagenesis of these sediments. Kirsimäe et al. (1999a) and Kirsimäe & Jørgensen (2000) suggested low-temperature and slow-rate illitization during a shallow burial, whereas Chaudhuri et al. (1999) and Clauer et al. (2003) associate smectite-to-illite transformation in the BC with short high-temperature heating events or the intrusion of high-temperature hydrothermal brines at some stage of basin evolution. Similarly, studying the diagenetic history of the altered Ordovician volcanic ash beds (K-bentonites), Somelar et al. (2009, 2010) suggested that the illitization of the Palaeozoic clay-rich sediments in the BP was driven by the combination of burial diagenesis and intrusion of low-temperature K-rich diagenetic fluids.

In this contribution we study different scenarios for a nearly complete illitization at a shallow burial and low average temperatures assuming only a burial- (i.e. temperature-) driven illitization. The modelling is based upon a tentative reconstruction of the burial and thermal history in the basin. We apply the kinetic modelling of the smectite-to-illite transformation that has been widely used to study the effect of the burial history and palaeothermal conditions upon illitization (Gharrabi & Velde 1995; Renac & Meunier 1995; Sachsenhofer et al. 1998; Cuadros 2006).

GEOLOGICAL SETTING

The BP (Fig. 1) is an old stable intracratonic sedimentary basin of the East European Platform where the complete stratigraphic record extends from the latest Precambrian to the Cenozoic Neogene period. The sedimentary column is the thickest (>2000 m) and complete in the southwestern part of the basin, whereas in the northern part of the basin deposits of only Neoproterozoic (Ediacaran) and lower Palaeozoic age are known (Nikishin et al. 1996; Šliaupa & Hoth 2011). Cambrian deposits are distributed throughout the BP. Lower Cambrian clayey deposits, in particular, occur in the northern and eastern parts of the basin (Rozanov & Łydka 1987). These clayey deposits, known as Blue Clay, outcrop at the present northern margin of the BP on the southern slope of the Fennoscandian (Baltic) Shield (Fig. 1). The burial depth of the BC increases gradually towards the south-southwest and reaches about 1000 m depths in central Latvia (Fig. 1). The thickness of the BC varies greatly, but it is about 60–100 m in North Estonia. The BC is in the study area stratigraphically divided into two formations (Mens & Pirrus 1997). The older Lontova Formation consists of pelagic marine greenish-grey and variegated clays with interbeds of coarse- to fine-grained sandstones in the lowermost and fine-grained sandstones in the uppermost part. Clayey sediments of the Lontova Formation are found in large areas on the East European Platform reaching the Moscow Basin, and they form an overall transgressive-regressive sedimentary cycle (Mens & Pirrus 1986). The Lontova Formation is transgressively succeeded by the Lükati Formation consisting of lithologically similar interbedded greenish-grey clays and very fine-grained sandstones or siltstones up to 10 m thick. Sediments of the Lükati Formation were probably deposited under alternating water energy conditions in a shallow-water gulf-like basin (Mens & Pirrus 1997). The BC sequence in the northern part of the basin is overlain by about 20–60 m of lower to middle Cambrian well-sorted sandstones and up to 400 m thick shallow-shelf Ordovician and Silurian limestones and dolomites. In the central part of the basin, the uppermost part of the sedimentary cover on top of the BC is composed of up to 800 m thick Devonian silt- and sandstones, and dolomites.

The pre-trilobitic Lontova Formation belongs to the Terreneuvian, Stage 2 (521–529 Ma), whereas the Lükati Formation belongs to the *Schmidtiellus mickwitzi* trilobite Zone of Series 2, Stage 3 (Meidla 2017) with an approximate age of 514–521 Ma (Geyer 2019). The provenance and original mineral composition of the BC is virtually unknown. The isotope age of the coarse-grained detrital mica and K-feldspar in the BC of 0.9–1.6 Ga (Chaudhuri et al. 1999; Kirsimäe et al. 1999b) suggests detritus derived from the weathering and erosion of mafic high-grade metamorphic rocks in the Proterozoic Sveconorwegian (0.9–1.1 Ga) and Svecofennian (1.5–1.8 Ga) terranes of the Baltic Shield. However, recent detrital zircon ages of a single sample from the Lontova Formation (Isozaki et al. 2014) show zircon ages clustering at 2900 Ma (Mesoarchaean), 1700–2000 Ma (Palaeoproterozoic) and 1300–1650 Ma (Palaeoproterozoic–Mesoproterozoic), whereas a sample from the overlying and lithologically similar Lükati Formation shows a zircon age spectrum represented in addition to Palaeo- and Mesoproterozoic grains by domains at 500–600, 850 and 1100–1200 Ma while Archaean grains are absent. Mixed detritus input from different sources particularly in the western part of the East European Platform is well demonstrated by a single grain dating of detrital zircon in the Cambrian of Central Poland (Valverde-Vaquero et al. 2000). Their U–Pb data show input from sources with ages of *ca* 530–700 Ma, 1.0–2.2 Ga and >2.5 Ga.

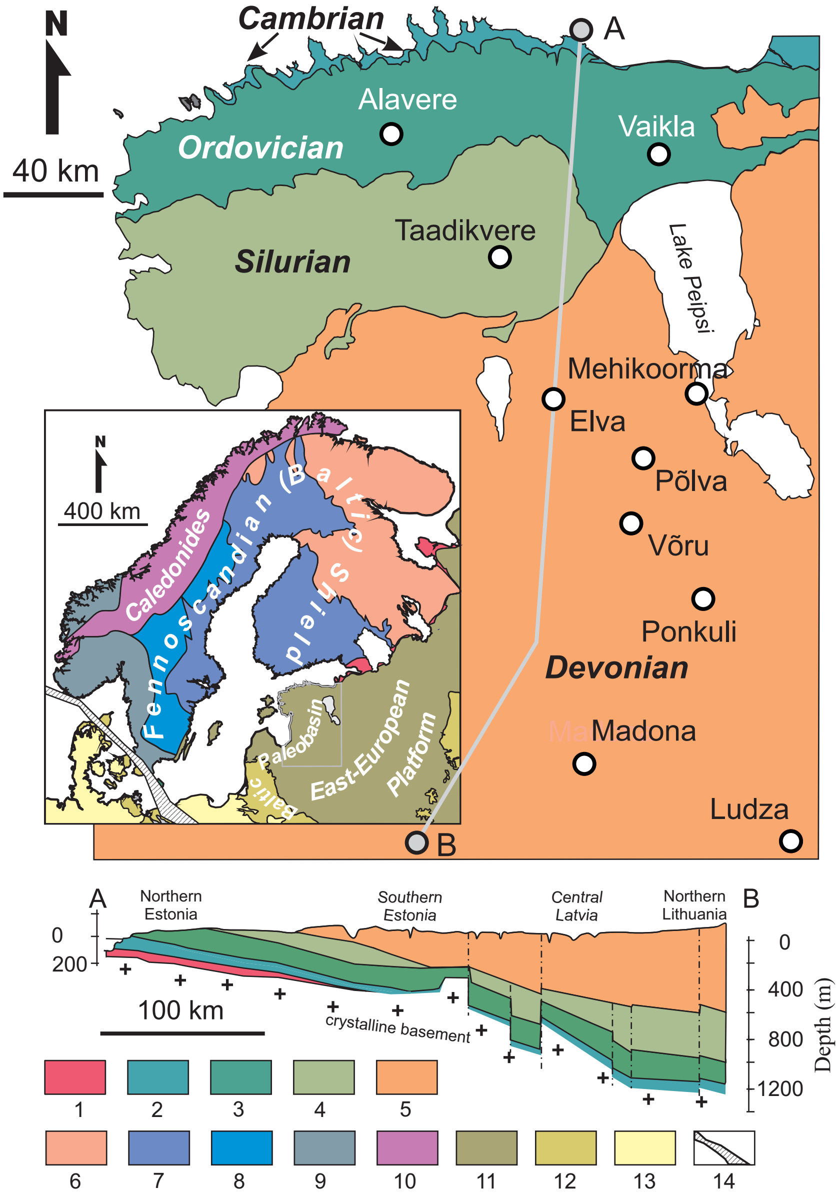

Fig. 1. Simplified geological map of Fennoscandia and the northern part of the Baltic Palaeobasin (BP) with locations of the studied drill core sections and geological profile through the northern part of the BP. 1, Neoproterozoic (Ediacaran); 2, Cambrian; 3, Ordovician; 4, Silurian; 5, Devonian; 6, Archaean Domain; 7, Svecofennian Domain; 8, Transscandinavian Belt; 9, Sveconorwegian Belt; 10, Caledonides; 11, Palaeozoic; 12, Mesozoic; 13, Cenozoic; 14, Tornquist lineament.

MATERIAL AND METHODS

The material investigated comes from ten drill cores located in the northern and central parts of the BP (Fig. 1). Altogether 63 samples were chosen from clayey sediments of the Lükati and Lontova formations. From two northernmost drill cores Vaikla and Alavere, with the thickest BC section, 36 and 9 samples were taken, respectively, to characterize the vertical variation through the 70–80 m BC section. In all drill cores only clay and clay-rich sand- and siltstone lithologies were sampled.

Air-dry samples were broken into about 0.5–1 cm^3 pieces and dispersed in distilled water with short ultrasonic treatment (2 min, 70 W). The samples were fractionated by standard sedimentation procedures and the <2 µm size fraction was flocculated and Sr^{2+} saturated with 0.1 M SrCl$_2$. Excess salt was removed after repeated rinsing with distilled water and ethanol. Oriented clay aggregates were made by smearing the clay pastes onto glass slides. X-ray diffraction (XRD) data were obtained using a 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. Scanning steps of 0.02 °2θ from 2 to 40 °2θ and a counting time of 3 s per step were used. The ambient relative humidity varied between 60% and 65%.

The XRD patterns were decomposed in the 5 to 11 °2θ region using the AXES code (Mändar et al. 1996) and criteria given by Lanson (1997) after stripping the Lorentz-polarization factor shape background. The wide low angle peaks of I-S and poorly crystalline illite (a mixed-layer mineral with <5% expandable layers) were fitted assuming a symmetrical Pearson 7 shape curve doublet with a maximized exponent (>10), which is equivalent to a Gaussian shape. Chlorite, well-crystalline illite and kaolinite were fitted assuming a symmetrical Pearson 7 shape with the exponent set to 1.0 (equivalent to a Lorentzian curve). For each peak the position, intensity, full width at half maximum and the integrated peak area were measured. The smectite percentage in mixed-layer I-S was estimated from low angle peak positions of I-S patterns calculated with the MLM2C code (Plancon & Drits 2000). Air-dry, R1-ordered I-S curves corresponding to a coherent stacking domain sizes (CSDS) distribution exponentially proportional to the mean defect free distance of seven layers in the range of $4 \leq N \geq 10$ layers were calculated assuming *d*(001) 9.98 Å for illite and *d*(001) 15 Å for smectite. In addition, selected patterns were modelled using the MLM2C and MLM3C codes (Plancon & Drits 2000) and multi-specimen fit approach assuming log-normally distributed CSDS (Sakharov et al. 1999) to estimate the illite, kaolinite, chlorite, I-S and illite-smectite-vermiculite type minerals qualitatively and quantitatively

The relative abundances of clay minerals in the <2 μm fraction were estimated semi-quantitatively from the fitted peak integral intensities of air-dry oriented clay aggregates, using correction factors of Kirsimäe et al. (1999b). The I-S *d*(001/002), poorly crystalline illite *d*(001) and well-crystalline illite *d*(001) peaks at ~11 Å, ~10.3 Å and 10 Å, respectively, were measured. The quantification of chlorite and kaolinite was based on the separation of the chlorite (004) and kaolinite (002) basal reflections with *d*-values at about 3.53 Å and 3.56 Å, respectively. The estimated accuracy is not better than ±10% for major phases and probably less for minor components.

The smectite-to-illite transformation was modelled assuming kinetic equations with a two-step reaction sequence (Velde & Vasseur 1992), which is in better agreement with the complex multistage illitization model (Ferrage et al. 2011) rather than a single-step solid-state transformation model (e.g., Cuadros 2006). The model proposed by Velde & Vasseur (1992) has been found to be the most effective in describing illitization in older basins (Elliott & Matisoff 1996). The first of these first-order Arrhenius-type reactions (1) is the formation of a random (R0) I-S phase with 100 to 50% expandable layers. The second reaction (2) is the R1-ordered I-S transformation from 50 to 0% expandable layers.

$$dS/dt = -k_1 S \quad \text{with} \quad \log(k_1) = \log(A_1) - E_1/RT, \quad (1)$$

$$dM/dt = k_1 S - k_2 M \quad \text{with} \quad \log(k_2) = \log(A_2) - E_2/RT, \quad (2)$$

where E – activation energy, A – pre-exponential factor, R – universal gas constant, T – absolute temperature.

The original set of the reaction parameters, pre-exponential factors (A) and activation energies (E) by Velde & Vasseur (1992) were evaluated by Renac & Meunier (1995), who showed that the given parameters cannot describe the changes in the I-S composition during the last stages of illitization and that the activation energy of the second reaction is lower than supposed by Velde & Vasseur (1992). However, Velde (1995) proposed a new set of kinetic reaction constants which give the best fitting with I-S evolution trends in relatively shallow and cold Early Mesozoic and Palaeozoic basins. The parameters given by Velde (1995) are used in this study. The pre-exponential factors and activation energies are $\log A_1$ = 24.4 My^{-1}, E_1 = 76.8 kJ mol^{-1} and $\log A_2$ = 3.6 My^{-1}, E_2 = 22.2 kJ mol^{-1} for the first and the second reaction, respectively.

RESULTS

Representative XRD patterns of the studied samples are shown in Fig. 2. The BC is illitic clay characterized by an illite(I-S)–kaolinite–chlorite clay mineral assemblage. The <2 μm fraction contain mostly illite, I-S, chlorite and kaolinite with small traces of quartz, K-feldspar, hematite/pyrite, albite and dolomite. Illite and I-S are the most abundant phases exceeding usually 75% of clay minerals (Fig. 3). The content of kaolinite and chlorite is commonly <20% and <10%, respectively. Occasionally, a higher kaolinite content (up to 32%) was found in samples of silty clay.

The *d*-values of I-S (001/002) peak shifts from 11.5 to 10.8 Å with increasing sampling depth that varied from ~100 m in northern Estonia to ~1000 m in Latvia (Fig. 4). The corresponding content of illitic layers in I-S increases regularly from ~85% to 90–91%, indicating slight difference in the diagenetic smectite-to-illite transformation progress in different parts of the basin. The structural

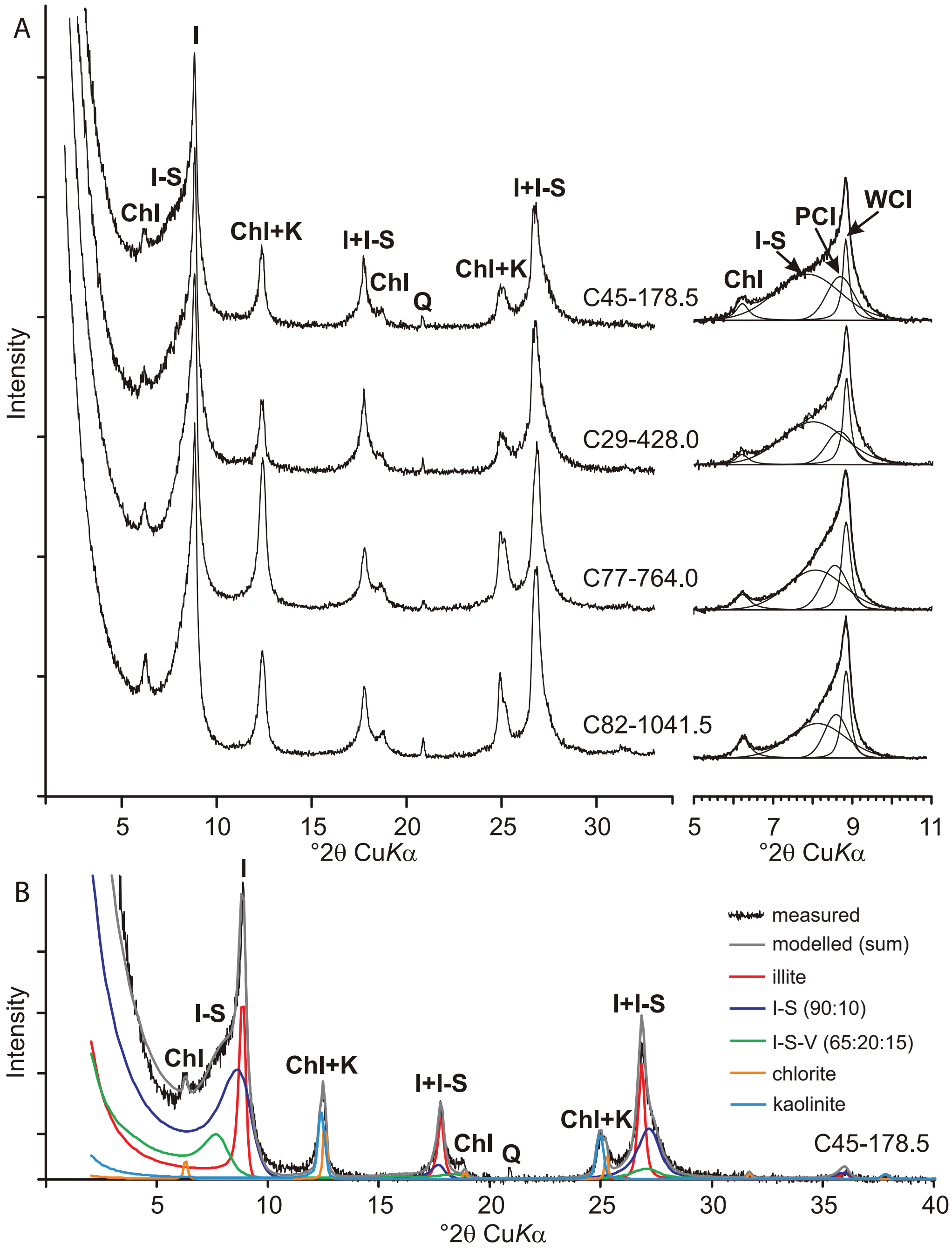

Fig. 2. Representative XRD patterns of the <2 μm fraction. **A**, in air-dry state, and the same patterns after background stripping and decomposition in the 5–11 °2θ (Cu$K\alpha$) region; **B**, MLM2C and MLM3C modelled clay mineral composition of C45 sample. Chl, chlorite; I, illite; I-S, illite-smectite mixed-layer mineral; I-S-V, 3-component illite-smectite-vermiculite mixed-layer mineral; K, kaolinite; PCI, poorly crystalline illite (illitic illite-smectite); Q, quartz; WCI, well-crystalline illite and/or detrital mica.

modelling of the mixed-layer clay mineral indicates that the most expandable I-S phase can be best described as a three-component illite-smectite-vermiculite mixed-layer mineral assuming 10–15% 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 0.3 (Fig. 2).

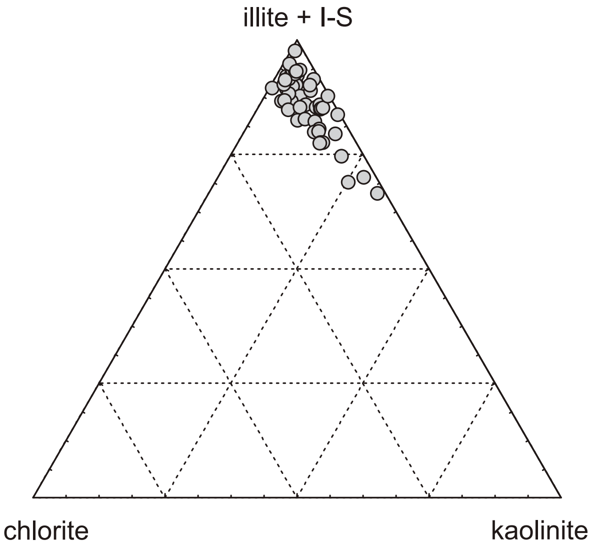

Fig. 3. Triangular diagram showing the semi-quantitative clay mineral composition of the <2 µm fraction of the Cambrian Blue Clay in the northern Baltic Palaeobasin.

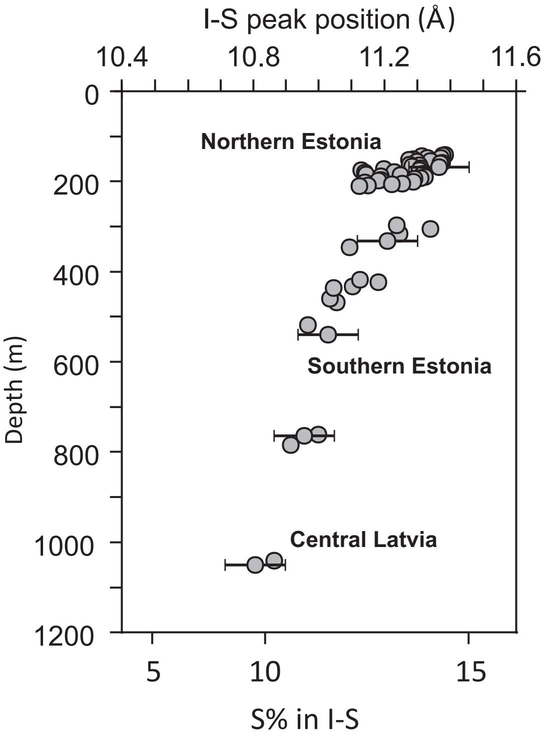

Fig. 4. Change in *d*-values with the sampling depth for the decomposed illite-smectite (I-S) mixed-layer mineral and the change in the content of smectitic layers (S%) in illite-smectite. The estimated standard deviation for the I-S peak position determination shown in the figure is in the range of 0.1–0.2 Å.

DISCUSSION

Palaeothermal and burial history reconstruction

The highly illitic nature of the mixed-layer mineral in the BC in the northern BP suggests an advanced diagenetic status of the sediments pointing to either deep burial diagenetic conditions during basin development or some other process leading to smectite recrystallization, and potassium uptake and fixation like in hydrothermal processes. The compilation of illitization data by Meunier & Velde (2004) to estimate maximum temperatures shows that R1-ordered I-S is attained at 90–100 °C for reaction times $>10^7$ years and at 130–150 °C for times of $<10^6$ years. Indeed, the time needed for a certain illitization level to be achieved, not considering other factors (e.g., pore fluid composition), depends clearly on temperature. As suggested in earlier studies (Chaudhuri et al. 1999; Kirsimäe & Jørgensen 2000), there is no evidence of deep burial (>2–3 km) throughout the Finnish–Estonian sector of the Fennoscandian Craton encompassing the northern part of the BP, and the geological evidence suggests that the burial depth has not exceeded 1–1.5 km. This is exemplified by the organic material thermal alteration index of acritarchs (TAI) at 1 that denotes maximum palaeotemperatures <50 °C for the BC since the deposition in the northern part of the BP (Talyzina 1998). The same is evident from biomarker parameters that are typically used for thermal maturity assessment of petroleum and source rocks. The BC acritarch organic material is characterized by $20S(20S + 20R)$ epimer ratios of C_{29} and C_{28} steranes of 0.137 and 0.306, respectively (Talyzina 1998). Also, the directly underlying Ediacaran sediments show low $T_{\max}$ values (average 426 °C) from Rock-Eval pyrolysis as well as the dominance of polycyclic biomarker alkanes over *n*-alkanes and survival of 17β,21β(H)-hopanes resolvable from the more abundant hopanes possessing stable 17β,21α(H)- and 17α,21β(H)-stereochemical configurations (Pehr et al. 2018), all plainly pointing to a thermally immature state of the BC. Consequently, judging from biomarker evidence, although the smectite percentage in I-S is about 10–20% and shows a clear tendency to decrease with increasing depth, these sediments were never very deeply buried and/or heated to temperatures typically associated with illitization in other well-studied basins (e.g., Gulf Coast). A similar phenomenon has been described by Gorokhov et al. (1997) for burial diagenesis of unmetamorphosed Mesoproterozoic (Lower Riphean) shales (1.45–1.49 Ga) from the Anabar Massif, northern Siberia, which were never heated above 60–70 °C.

The central and southern areas of the BP, however, are today and most probably were also in the geological past more deeply buried. This is at first instance indicated by the thermal maturation of organic material. If 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 <1, vitrinite reflectance R_0 ~0.5, mature biomarker indicators), then, on the contrary, the organic material alteration state is notably more mature (R_0 0.7–1) in the central (present-day depths 1000–1500 m) and southwestern (present-day depths >1500 m) parts of the basin. The estimated maximum palaeotemperatures were 50–80 °C and *ca* 150 °C in the central and southwestern parts of the basin, respectively (Nehring-Lefeld et al. 1997; Zdanavičiūtė 1997; Talyzina et al. 2000; Grotek 2006). In this sense the observed illitization trend with the smectite percentage decreasing in the mixed-layer mineral with increasing present-day burial depth from *ca* 100–150 m in northern Estonia to *ca* 1000 m in central Latvia would reflect the burial diagenetic trend.

The rate law presented by Bethke & Altaner (1986) predicts considerable illitization at shallow depths and/or low temperatures in slowly subsiding old basins, where the residence time at a given temperature is an important factor. The stratigraphic (depositional) age of the lower Cambrian claystones in the BP is between 515 and 530 Ma (Meidla 2017; Geyer 2019). However, the time factor alone is not sufficient for illitization at present depths and borehole temperatures in northern Estonia where the BC is found at a depth of a couple hundred metres. To account for burial-driven illitization, part of previously covering sediments must be missing in the present sedimentary record.

The sedimentary pile in the BP is composed of late Neoproterozoic to Early Palaeozoic (Ediacaran to Devonian) alternating clastic–carbonate succession in the northern part of the basin reaching *ca* 1000 m in thickness and Neoproterozoic to Mesozoic–Cenozoic deposits in the southern part of the basin with a maximum thickness reaching >2000 m (Nikishin et al. 1996; Šliaupa & Hoth 2011). The former is tied to the slowly subsiding (2–3 m $\mathrm{Myr^{-1}}$) depocentre in the central and eastern part of the basin and the latter to the depocentre in the Peri-Tornquist zone (Šliaupa & Hoth 2011; Tuuling 2019). It is generally assumed that the late Palaeozoic–Mesozoic marine deposition was limited to SW Latvia and Lithuania, whereas the northern part of the BP underwent denudation initiated in the Devonian–Carboniferous in relation to the compressional tectonic regime of the Caledonian orogeny (Paškevicius 1997; Šliaupa & Hoth 2011).

It has been speculated that during the Late Silurian and Devonian about 3–6 km thick clastic sediments were deposited in the Scandinavian Caledonian foreland basins (Zeck et al. 1988; Larson & Tullborg 1998; Larson et al. 1999). Sedimentary equivalents in the BP are of Middle to Late Devonian age and are represented by mainly mixed marine-terrestrial prograding delta silt- and sandstones alternating with lagoonal carbonate and clay interbeds (Kuršs 1992). Devonian sediments were, however, deposited at the backbulge of the Scandinavian Caledonian fold-and-thrust belt foredeep–forebulge system that migrated to the northwestern margin of the BP during the earliest Eifelian, as indicated by the lack of subsidence in the northern/northwestern margin during the early transgressive phase of the Devonian deposition in the northern BP (Tänavsuu-Milkeviciene et al. 2009). Instead, a denudation episode in the Late Silurian–Early Devonian caused an about 50–100 m deep erosion in NE Estonia (Puura et al. 1999). The sedimentation resumed by deltaic progradation in the Middle Devonian and was associated with the orogenic collapse and uplift in the Scandinavian Caledonides that caused the erosion of the foreland basin fill and the clastic sediment transport into the BP (Tänavsuu-Milkeviciene et al. 2009). The maximum thickness of Devonian deposits is more than 1000 m in the southwestern part of the basin (Brangulis et al. 1982). In the central and northern parts of the basin, however, the sedimentation rate was lower (10–15 m $\mathrm{Myr^{-1}}$) and the thickness of Devonian deposits did not exceed 500–700 m (Kuršs 1992). A similar conclusion can be derived from thermal history modelling studies using apatite fission track data for southern Finland that indicate an up to 0.5–1.5 km thick pile of clastic sediments derived from the Scandinavian Caledonides covering Finland and burial temperatures reaching up to 80 °C at the base of the sedimentary succession (Larson et al. 1999; Murrell & Andriessen 2004; Kohn et al. 2009). Sedimentation in the northern part of the basin terminated in the Carboniferous and probably only the earliest Carboniferous mixed terrestrial–lagoonal low-rate sedimentation (1–2 m $\mathrm{Myr^{-1}}$) took place in the central-northern part of the BP (Fig. 5).

Geomorphological (Lidmar-Bergstrom et al. 2013) and apatite fission track data (Japsen et al. 2016) suggest a series of regional exhumation/cooling events in southern-central Sweden. These events commenced with Middle Triassic uplift and erosion, followed by exhumation and deep weathering during the Middle Jurassic to Cretaceous (Oligocene) caused by epeirogenetic uplift during the breakup of Pangaea. However, the apatite fission track modelling suggests that in southern Finland moderate mid-Palaeozoic (350–400 Ma) heating followed a long slow cooling over 200 million years starting at about 300 Ma (Kohn et al. 2009). In the northern BP we can presume that the low-rate erosion started in the Permian possibly with the rifting in the Oslo area (Ziegler 1987) and lasted for about 150–200 Myr (Fig. 5). The last 80–100 Myr of this basin history are characterized by stable tectonic conditions with insignificant local sedimentation and erosion.

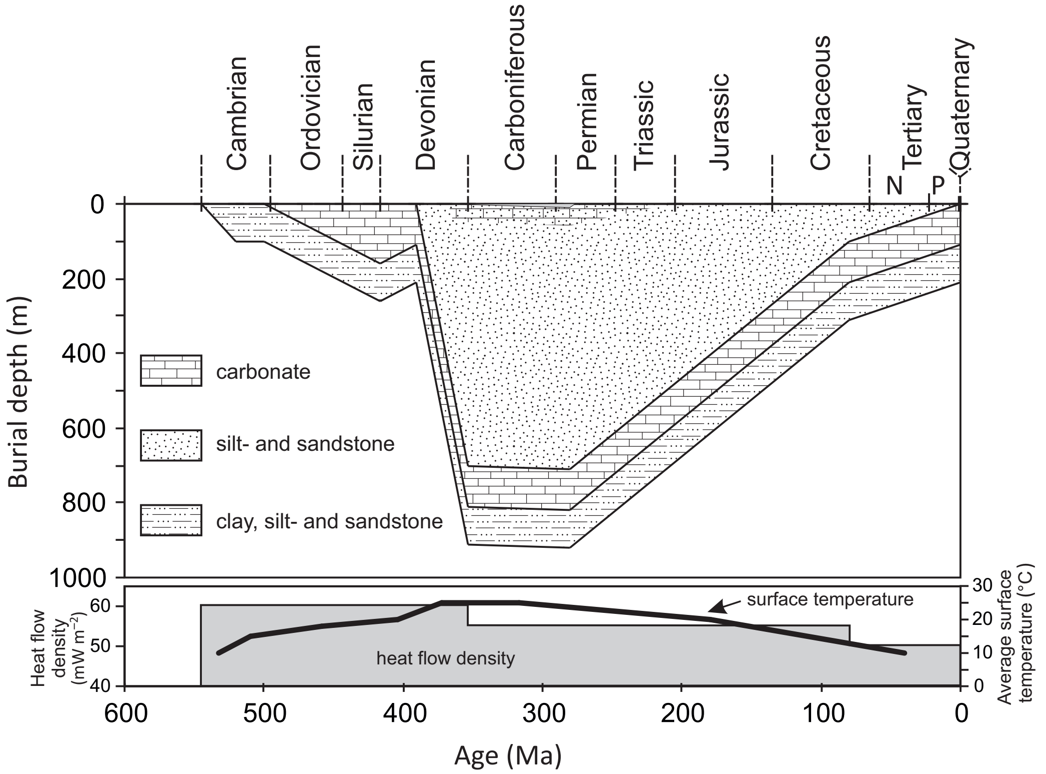

Fig. 5. Reconstruction of the burial history of the lower Cambrian Blue Clay in the northern Baltic Palaeobasin.

Another parameter to be considered for illitization modelling is the geothermal gradient. The present mean heat flow density in this area is *ca* 50 mW m^{-2} (Kukkonen & Jõeleht 1996). The use of such a low constant thermal gradient during the entire basin history is unrealistic though the gradient values cannot have been much higher in post-Cambrian time. The BP is situated in the interior part of an old craton, formed 1.8–1.9 Ga ago (Bogdanova et al. 2006). The last magmatic intrusions, post-orogenic rapakivi granite plutons, in this area were emplaced 1.58–1.63 Ga ago, whereas no major tectonic/volcanic activity has been recognized since the crust formation in the northern part of the BP (Kirs et al. 2009), suggesting that the lithosphere cooling since Cambrian times was negligible compared to the cooling during the first 1.0–1.3 Ga after the craton formation. Therefore, it is reasonable to assume an initial heat flow density of *ca* 60 mW m^{-2} (average gradient of 30 °C km^{-1}), decreasing in steps over the Mesozoic–Cenozoic to the present value of 50 mW m^{-2}. Variations in the mean surface temperature also become important when dealing with shallow sequences in which the burial temperatures have not exceeded 60 °C. The mean surface temperature will vary with palaeolatitudes, which can be reconstructed from continental drift, the global change between warm non-glacial and cold glacial climatic types as well as the water depth in marine basins. The Baltica microcontinent was, from Late Precambrian to Early Palaeozoic, located at high to intermediate southerly latitudes (30–50°). It drifted in general northwards, reaching equatorial latitudes by Middle Silurian times, northerly latitudes between 15° and 40° in the Permian, 50° latitude in the Late Cretaceous (Torsvik et al. 2012) and about 58° at present. Relying on these data, we can use an average sediment–water interface temperature, corrected for water depth, at 10 °C during the Cambrian and Early Ordovician and 15 °C during the Middle Ordovician and Silurian. For the next period, corresponding to the closure of the Iapetus ocean followed by the Caledonian overthrusting (orogeny) in Scandinavia, we assume the same high heat-flow density (60 mW m^{-2}) in the northern BP situated at some distance from tectonically active zones. Mean surface temperature for the Devonian terrestrial basins can be estimated at 20 °C at the beginning and 25 °C at the end of the period (Fig. 5).

Kinetic modelling

Our modelling results, using average sedimentation and erosion rates, suggest that the present illitization grade could be achieved if the thickness of eroded sediments was about 500–600 m (Fig. 6). This sedimentary pile consisted mostly of Devonian and Carboniferous deposits eroded during the Late Palaeozoic and Mesozoic. With this modelling the maximum palaeotemperature in the lower Cambrian sediments did not exceed 58 °C, which is in good agreement with the maximum temperature from thermal maturation estimates. Nevertheless, this burial model suffers from a poor determination of the post-Palaeozoic history and is based on many assumptions. So far the best estimate for necessary erosion would be in the range 400–1000 m. We found that the model is rather insensitive to heat flow density (50–60 mW m^{-2}), but is more sensitive to the relationships between the residence time at maximum burial, and the erosion rate and timing. If a short time is spent at maximum burial, a slower erosion is needed, and *vice versa*, a long time at critically higher temperatures must later be compensated by a high rate of erosion. The present knowledge of the burial and erosion history of the northern BP, however, does not support a short, intensive erosion event.

It is reasonable to assume that the minimum thickness of eroded sediments was not less than 300 m, otherwise unrealistically high heat flow density values (>70 mW m^{-2}) in a long perspective (>50 Ma) must have been in place. On the other hand, a generally low compaction level of the sediments shows that the maximum overburden cannot have been more than 1000–1500 m, setting the upper limit to the thickness of the sedimentary pile, whereas the estimated maximum temperature (50 °C) would have required an overburden of 2500 m or more if the lowest realistic gradient (20 °C km^{-1}) was used. In contrast to the

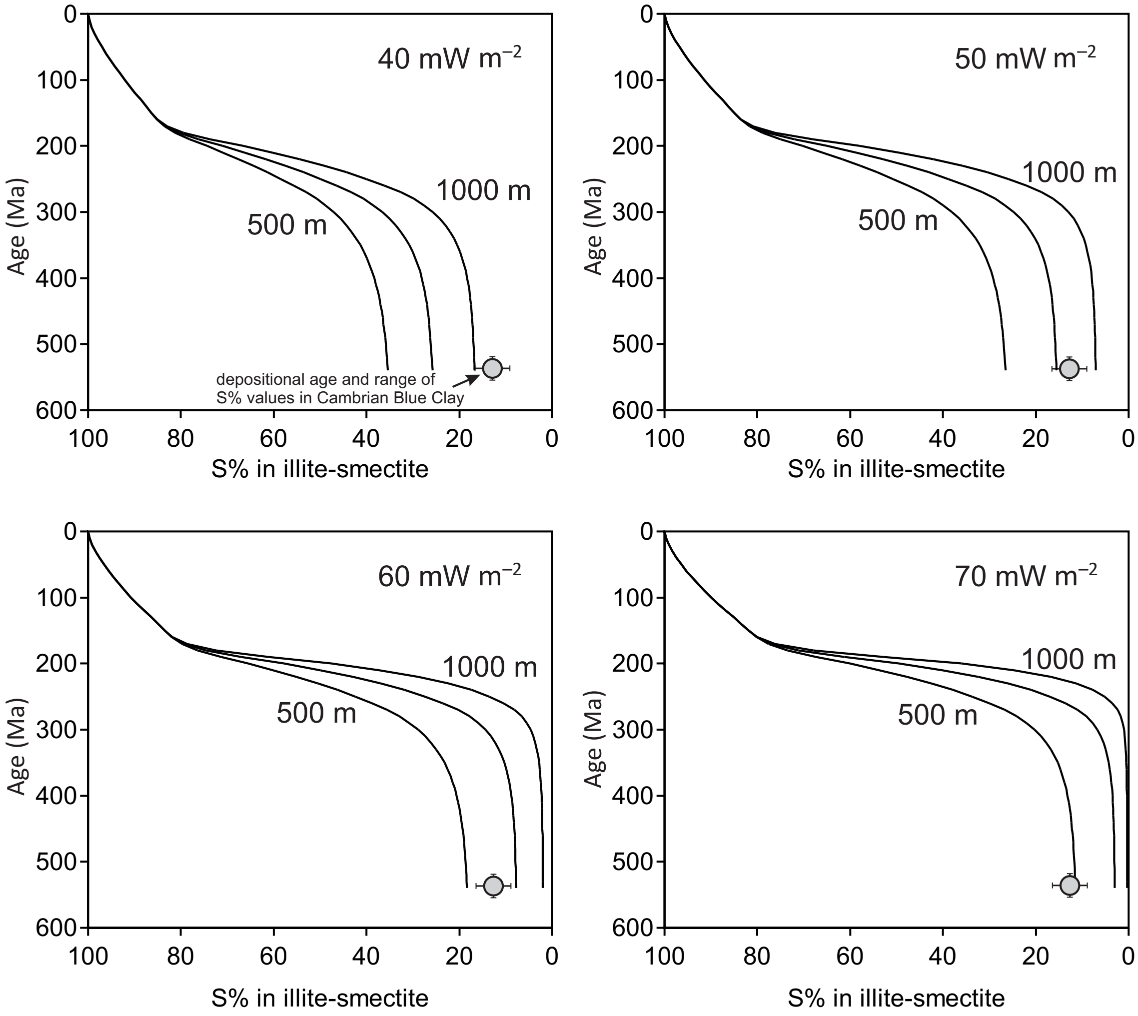

Fig. 6. Estimated increase in smectitic layers (S%) in smectite-to-illite evolution, modelled with a two-step reaction (Velde & Vasseur 1992) assuming different peak burial depths and heat flow densities.

residence time and erosion rates, the variation in starting smectite percentage in the mixed-layer mineral from 100% to 80% causes only a small (less than 100 m), reduction in the thickness of the eroded sediments, and consequently seems to be an insensitive factor in this time-dependent system.

The Rb/Sr isotope analyses of the BC (Kirsimäe & Jørgensen 2000) show that the isotope data even for the finest separated fraction (<0.06 μm) are highly scattered and geologically meaningful ages cannot be derived directly. Nevertheless, the diagenetic ages of I-S at about 327 Ma, interpreted from Rb–Sr model-ages (Kirsimäe & Jørgensen 2000) and at about 380 Ma, from alkylammonium treated fine-fraction K–Ar age (Chaudhuri et al. 1999), fall within the period of maximum burial in the Devonian–Carboniferous, supporting thus the illitization driven by burial diagenesis.

In contrast, Clauer et al. (2003) presented K–Ar data for the Estonian BC size fractions showing a range of ages from 580–625 Ma in coarse detrital illite fractions to 464–473 Ma in the finest (<0.1 μm) fraction. Using Ar diffusion modelling, they suggested that the BC in the Lontova Formation was heated to a temperature of 130–140 °C for a duration of 2–5 Myr or the temperature may have been as high as 170 °C during a shorter period of time (< 1 Myr), in relation to large-scale fluid migration and dolomitization in the Silurian–early Devonian. Indeed, recent studies (Eensaar et al. 2017a, 2017b; Gaškov et al. 2017) have shown evidence of hydrothermal activity in the northern BP and have delineated a Zn–Pb mineralization event driven by the intrusion of highly saline low- to moderate-temperature (60–200 °C) fluids, the maximum age of which can be constrained by cross-cutting relationships to the early Middle Devonian (Eifelian). However, this event is tied to thin cross-cutting sphalerite–(galena)–calcite veins and scattered fracture zones with no evidence of significant wall-rock alteration (Eensaar et al. 2017a). Moreover, the large scatter of Rb–Sr and K–Ar ages of the BC finest fractions excludes the possibility of short (<5 Myr) abnormal heat and/or hydrothermal pulses responsible for the BC illitization that would have not been registered in organic material maturation data but have been responsible for illitization, which in this case should be characterized by a well-defined isotope signal. In addition, the short regional high-temperature heat pulse and/or fluid intrusion should have resulted in high alteration gradients both between the margins and centres of clay units beds, and laterally. The BC succession in northern Estonia varies between 60 and 100 m in thickness and is stratigraphically bordered by loose Ediacaran sandstones below and Cambrian sandstones above, neither of which shows evidence of extensive high-temperature hydrothermal alteration/cementation. Most part of the BC succession is composed of homogenous variegated clay (Mahu and Kestla members) and is considered as a regional aquitard with low maximum hydraulic conductivity of 10^{-7}–10^{-5} m d^{-1} (Perens & Vallner 1997). The BC deposits do not show any significant variation in the illitization state or thermal maturity indicators neither laterally nor vertically through the succession (Kirsimäe et al. 1999a, 1999b; Kirsimäe & Jørgensen 2000). If the regional hydrothermal activity or heat-flow had increased drastically for a short time, the illitization state would show lateral/stratigraphic variation with high illitization at contacts to heat source/fluid conduits and less advanced illitization away from such contacts (Buhmann 1992; Drits et al. 2007; Kurnosov et al. 2016). However, there is no geological evidence for either case. From the above, we may conclude that the nearly complete illitization in lower Cambrian clayey sediments in the northern part of the BP could be attained during a shallow burial diagenesis at depths of <1500 m and temperatures about 50 °C in the course of a very long basin history from the early Cambrian.

Most intriguingly, several experimental studies have revealed that microbial activity can significantly promote the illitization (Kim et al. 2004; Zhang et al. 2007a, 2007b; Koo et al. 2016). It has been shown that microbial reduction of Fe(III) in detrital smectite occurred already at temperatures below 40 °C (Kim et al. 2004; Koo et al. 2016). Recently Ijiri et al. (2018) reported the illitization of smectite driven by microbial Fe-reduction in modern shallow sediments at temperatures well below 30 °C. The mixed-layer mineral in the BC is characterized by Fe–Mg-rich highly illitic I-S composition (Kirsimäe & Jørgensen 2000), whereas the ferric iron in these sediments is rather abundant as the sediment colour varies from greenish-grey to reddish-violet. The latter has been interpreted by Mens & Pirrus (1986) as the original sediment colour and the greenish colouring as resulting from microbial iron reduction. It is therefore possible that the illitization of the BC in the northern BP was also prompted by microbial processes taking place at shallow burial.

CONCLUSIONS

The illitic mixed-layer mineral in the lower Cambrian (Terreneuvian) Blue Clay (BC) in the northern Baltic Palaeobasin (PB) shows gradual increase in illitic layers from *ca* 85% in northern Estonia at present burial depths of a few hundred metres to *ca* 92% in central Latvia with the present burial depth of *ca* 1000 m. Despite the high level of illitization, the high porosity and indicators of thermal alteration of immature organic material suggest only a shallow burial and maximum palaeotemperatures below 50 °C. The kinetic modelling of smectite-to-illite transformation in the BC suggests that the observed illitization level could have been attained by assuming peak burial during the Devonian to early Permian, followed by a period of low-rate erosion that started by the end of the Permian and lasted through the Mesozoic. The thickness of the eroded Devonian (and possibly Carboniferous) sedimentary succession was in this case about 400–800 m. The smectite-to-illite transformation process in the BC in the northern BP was controlled rather by time than by temperature, though the illitization could have been promoted by microbial processes. Our study also suggests that the degree of illitization, estimated from the smectite–illite ratio in mixed-layer I-S, should not be used for geothermal applications if the burial and thermal history of the basin is not constrained.

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Alam-Kambriumi “sinisavi” illitiseerumine Balti paleobasseini põhjaosas

Kalle Kirsimäe, Peeter Somelar ja Argo Jõeleht

Savimineraalide diageneetilistest protsessidest on kõige olulisem ja levinum settelise smektiidi transformeerumine metastabiilsete vaheastete (illiit-smektiidi) kaudu mattumistingimustes stabiilseks illiidiks. Smektiidi illiidistumist kontrollivad temperatuur, fluidide ja algse smektiidi koostis, orgaaniliste ühendite juuresolek ning aeg. Seejuures on smektiidi illiidistumise ulatust laialdaselt kasutatud geotermomeetrina maksimaalsete paleotemperatuuride määramiseks. Käesolevas töös uuriti Balti paleobasseini paleosoilise läbilõike alumise osa, Alam-Kambriumi “sinisavide” illitseerumist. Illiidistumise metastabiilse vaheprodukti, illiit-smektiidi punduvus ehk smektiitsus on Kambriumi sinisavides 10–20% ja see väheneb uuritud läbilõigetes koos praeguse mattumissügavuse suurenemisega lõunasuunalisel profiilil Põhja-Eestist umbes 15(20)%-lt kuni 8–10%-ni basseini sügavalt (>1000 m) maetud keskosas. Illiidistumise kineetiline modelleerimine näitas, et smektiidi illiidistumine on võimalik madalatel temperatuuridel (~50 °C) ja mattumissügavustel (<1500 m), kuid arvestades väga pikka reaktsiooni kestust, mis eeldab, et Kambriumi “sinisavide” maksimaalne mattumissügavus saabus Devonis ning see kestis ligikaudu 100–150 miljonit aastat, enne kui käivitus erosioon Mesosoikumis, millega denudeeriti Balti paleobasseini põhjaosas ligikaudu 500–700 m valdavalt terrigeenseid Devoni setteid.