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Low-temperature diagenetic illite-smectite in Lower Cambrian clays in North Estonia

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ABSTRACT: Early Cambrian sediments on the East European platform in North Estonia, represented mostly by clays and silty clays, were deposited under normal marine conditions. The sediments were never affected by significant tectonic or thermal events after sedimentation 530 Ma ago, and the clays still have high water contents. The clay fraction, divided into four sub-fractions, was studied using X-ray methods and Rb/Sr dating. Decomposition of the XRD curves was used to quantify the amounts of illitic minerals in the sub-fractions. Dating by Rb/Sr showed that the finest fraction ($<0.06 \mu\text{m}$) was formed 50–150 Ma after sedimentation. The coarser fractions also contain considerable amounts of diagenetically formed minerals. This shows that neoformation of illitic minerals in marine sediments with high water/sediment ratios is a very important process even at temperatures $<35^\circ\text{C}$.

Diagenetic formation of illite in argillaceous sediments has been an extensively studied phenomenon since the first observations by Burst (1959, 1969) and Perry & Hower (1970) from Gulf Coast basin sediments. The smectite to illite transition (Hower *et al.*, 1976; Boles & Franks, 1979) has often been used as an empirical tool describing the burial history and diagenesis of the thick Cenozoic, Mesozoic and Upper Palaeozoic sediments (e.g. Hoffman & Hower, 1979; Środoń, 1979; Glassman *et al.*, 1989; Eberl, 1993).

The diagenetic transitions of clay minerals in old (Lower Palaeozoic and Late Precambrian) intracratonic basins are not so well described. Besides the mainly temperature-dependent conversion through illite-smectite (I-S) intermediate phases, the pore-water chemistry and the duration of the process have been considered to play important roles (e.g. Essene & Peacor, 1995).

The Lower Cambrian clayey sediments in North Estonia provide a good opportunity to study the diagenetic changes of the clay mineral assemblages taking place at a very low temperature ($<35^\circ\text{C}$), with a small burial depth over a period of 500 million years. Different morphological types of

illitic particles in these sediments were described by Vikulova (1949, 1952) and Reier (1965a, 1965b). Firsov *et al.* (1971) and Gorokhov *et al.* (1994) distinguished three illitic generations based on their isotopic age and morphological features.

The purpose of the present study is to document mineral characteristics and the diagenetic I-S and illite formation in the Lower Cambrian sediments of North Estonia. The possible low rate transformation reactions are the functions of time, pore-water chemistry and the sediment permeability rather than of temperature. Thus, an important further objective of this study is to understand the diagenetic reaction mechanisms taking place under such conditions.

GEOLOGICAL SETTING AND STRATIGRAPHY

The sediments studied are located on the north-western part of the East European Platform on the southern slope of the Baltic (Fennoscandian) Shield (Fig. 1). During the Late Vendian and the Early Cambrian, clay, silty clay and silty sand, with a maximum thickness $>200 \text{ m}$, were deposited on this well-levelled crystalline basement. During the Early

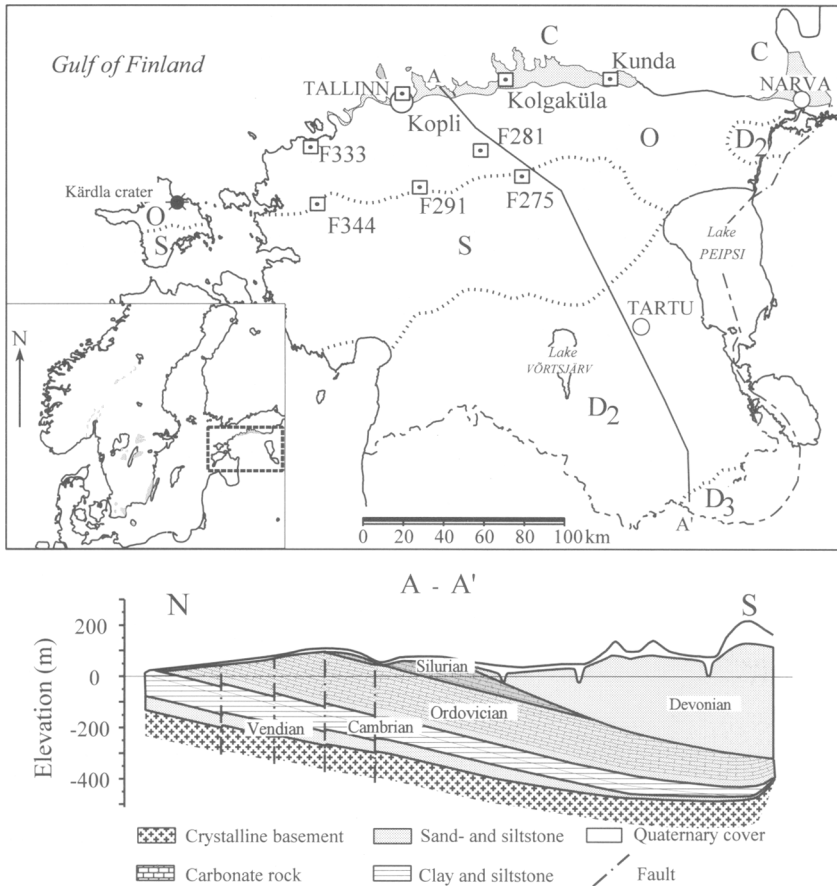


FIG. 1. Geological map of Estonia and the location of quarries and drillings studied. Outcropping areas of Cambrian sediments along the northern coast of Estonia and in Scandinavia are shown shaded.

Palaeozoic depositional subsidence of the Baltic Palaeobasin, the Vendian and Lower Palaeozoic beds became gently tilted ($2.5\text{--}3.5\text{ m km}^{-1}$) towards the south (Rõõmusoks, 1983). Consequently, the thickness of the sediments above the basement increases gradually from $\sim 200\text{ m}$ near the northern coast to $\sim 600\text{ m}$ at the border with Latvia (Fig. 1).

The Lower Cambrian sediments were probably formed under normal marine conditions (Mens & Pirrus, 1986) in a relatively shallow epicontinental basin of the Baltica microcontinent, which, from Late Precambrian to Early Palaeozoic times, was located as an individual continental unit in high to intermediate southerly latitudes ($50\text{--}30^\circ$), separated from the northern margin of Gondwana by the

Tornquist sea and from Laurentia by the Iapetus Ocean (Torsvik *et al.*, 1992).

The Lower Cambrian succession in North Estonia is represented by the clayey and silty sediments of the Lontova and Lükati Formations overlain by coarse-grained siltstones of the Tiskre Formation (Mens & Pirrus, 1977) (Fig. 2). In Western Estonia the Lontova Formation clays are replaced by shallow water siltstones and sandstones of the Voosi Formation (Mens *et al.*, 1990) (Fig. 2).

The erosion of the somewhat older Vendian terrigenous sediments as well as the igneous and metamorphic rocks of the Baltic Shield has been thought to supply the source material for the Lower Cambrian sediments (Mens, 1981; Pirrus, 1970). The lateral distribution of the facies patterns and

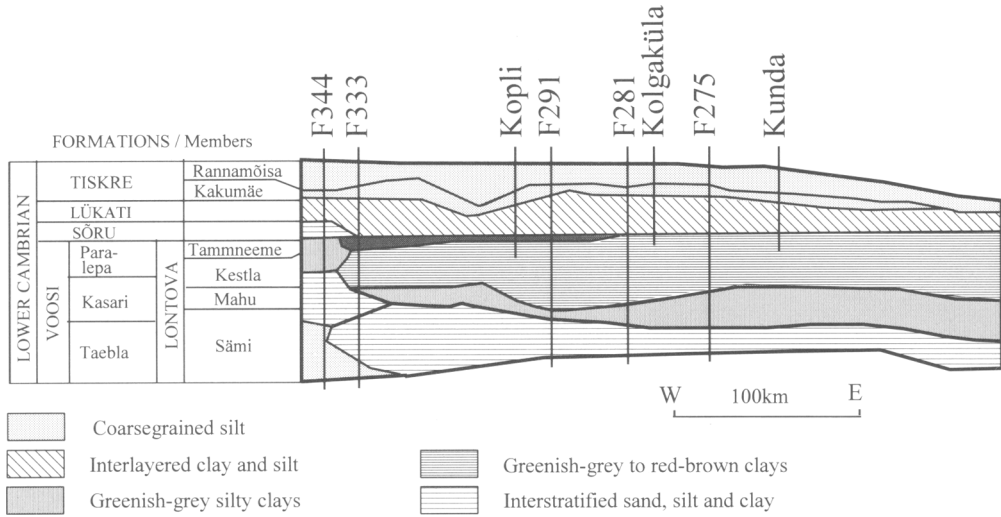


FIG. 2. Geological section and stratigraphy for the Lower Cambrian sediments along the northern coastline. Drillings and quarries are shown with vertical lines.

the clay minerals show that the main input was from northwest and west (Pirrus, 1983).

Burial

Lower Cambrian deposits in Baltoscandia have undergone different degrees of post-depositional change. In the Mjøsa region, Norway, there was strong deformation and maximum temperatures between 150 and 200°C during the Caledonian Orogeny. Shallow burial depth and thermal alteration well below 100°C took place in South-Central Sweden (Moczyłowska & Vidal, 1986).

A very good state of preservation of acritarch organic material (pale-transparent in appearance) in Estonian Lower Cambrian sediments (Ivo Paalits, pers. comm.) indicates, according to Moczyłowska & Vidal (1986), a temperature well below 100°C.

The thermal gradient in North Estonia, calculated from the present-day heat flow density (30–50 mW m⁻²) and assuming the thermal conductivity of sediments as 2.5–3.0 W m⁻¹ K⁻¹, was estimated to be 15–20°C km⁻¹ (Jõeleht, 1998). Thus, the previous maximum temperature and burial depth for the Lower Cambrian sediments in North Estonia can be estimated by adding the thickness of eroded strata since Devonian time to

the present-day situation (burial at 0–200 m, temperature 10–12°C measured in boreholes at 150 m).

The thickness of partly eroded Ordovician and Silurian strata in the area was ~300–400 m measured by considering the facies distribution (Männil, 1966; Kaljo, 1970). With the estimated extension and thickness of the completely eroded Devonian terrigenous sediments, the maximum thickness of the overlying strata could reach 800–1000 m. Therefore the maximum temperature in Lower Cambrian sediments has probably not exceeded 35°C.

MATERIAL AND METHODS

In total, 25 samples of clays and silty clays of the Lower Cambrian Lontova and Lükati Formations were collected from three quarries and five drill cores, all located in northern Estonia (Figs. 1,2).

The bulk samples were easily dispersed in distilled water by adding 4% sodium hexametaphosphate solution to prevent flocculation. Only gentle stirring and ultrasonic treatment were used.

The dispersed suspensions were fractionated by sieving and gravity sedimentation into the following fractions: <2, 2–6, 6–20, 20–63 and >63 µm.

Size-fractions of the $<2 \mu\text{m}$ fraction from 13 selected samples were obtained by centrifugation based on Stokes' formula. Using successive dispersion and centrifugation cycles, four fractions: 2–0.6, 0.6–0.2, 0.2–0.06 and $<0.06 \mu\text{m}$ were extracted and collected.

Oriented slides were prepared by sedimentation onto a porous porcelain plate under pressure or by smearing on a glass slide and subsequent drying at 54% relative humidity. Solvation in an ethylene glycol (EG) vapour (60°C, 48 h) and heat treatment (525°C, 2 h) were used to facilitate mineral identification. Occasional treatment with 10% HCl (80°C, 2 h) for kaolinite and chlorite distinction was used.

Mineral composition of the fine silt (2–6 μm), bulk clay ($<2 \mu\text{m}$) and four clay fractions (2–0.6, 0.6–0.2, 0.2–0.06, $<0.06 \mu\text{m}$) were studied by XRD. The composition of the bulk sediment and coarse fractions (6–20, 20–63 and $>63 \mu\text{m}$) were examined in only a few samples. Coarse fractions were crushed with distilled water in a micronizing mill before preparation of X-ray slides.

X-ray diffractograms were obtained at room temperature (20°C) using a Phillips 1710 diffractometer equipped with graphite monochromator (Cu- $K\alpha$ radiation) and a DRON 3M diffractometer with Ni-filtered Cu- $K\alpha$ radiation. Relative humidity was not controlled during the data collection. Digitally recorded XRD patterns, with step size of $0.02^\circ 2\theta$ and counting time of 3 or 4 s, were analysed using the computer programs PRXRD, written at the Agricultural University of Norway and AXES (Mändar *et al.*, 1996). Semiquantitative estimates of mineral proportions in <2 and 2–6 μm fractions were calculated from relative peak intensities corrected with the proportional factors adopted from Islam & Lotse (1986) and Pederstad & Jørgensen (1985).

The XRD profile decomposition technique (Lanson & Besson, 1992; Lanson & Velde, 1992) has been used as a reliable tool for describing the clay mineral evolution in multiphase systems (Lanson & Champion, 1991; Gharrabi & Velde, 1995; Lanson *et al.*, 1996). Decomposition of the 10 Å asymmetric illitic multiphase peak in the range $5\text{--}11^\circ 2\theta$ (Cu- $K\alpha$) was done with XRD curves of air-dried samples for the $<2 \mu\text{m}$ fraction and for all submicron fractions. Occasionally the ethylene glycol patterns were used to confirm the identification. Two decomposition programs, AXES (Mändar *et al.*, 1996) and WinFit (Krumm, 1994) were used.

Both programs gave similar results and little scattering. Because of its better graphical output, WinFit was used for the final presentation.

The Rb and Sr contents and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the $<2 \mu\text{m}$ sub-fractions of three samples were determined with a VG-354 mass spectrometer at the Laboratory of Isotope Geology, University of Oslo.

RESULTS AND DISCUSSION

Grain-size composition

The middle parts of the Lontova Formation (Kestla Member, Fig. 2), representing the maximum transgressive stage in the succession, are clays with $>45\%$ $<2 \mu\text{m}$. The rest is mainly fine (2–6 μm) and medium (6–20 μm) silt (Fig. 3, histogram A). The silty beds above (Tammneeme and Lükati Members) and below (Mahu Member) have a clear bimodal character with a maximum in the medium-coarse silt range. We believe that these sediments are mixtures of bedload and suspension load where the bedload contained almost no clay while the suspension load contained very little material coarser than 20 μm .

The $<2 \mu\text{m}$ fractionation shows a maximum between 0.2 and 0.6 μm (Fig. 3) while the amounts of coarse (2–0.6 μm) and fine clay (0.2–0.06 μm) are slightly smaller (20–30%). The content of the finest fraction ($<0.06 \mu\text{m}$) varies between 5 and 25% (of the clay fraction). As shown in Fig. 4, the relative content of this ultrafine clay fraction is highest in the most coarse grained sediments (silty clay and silt of the Lükati Formation and the Tammneeme Member). This relative enrichment of ultrafine clay in the coarse sediments can be a result of clay neof ormation.

Mineralogy

Mineralogical analysis of bulk sediments shows that the major components are 10 Å (illite) and 7 Å (chlorite, kaolinite) phyllosilicates, quartz and K-feldspar. Pyrite and hematite are common minor phases.

The $<2 \mu\text{m}$ fraction is characterized mineralogically by an assemblage of illite, illite-smectite, chlorite and kaolinite (Fig. 5), the illitic phases dominating, forming 65–80% of the fraction. The amounts of chlorite and kaolinite are normally between 7 and 15% and occasionally up to 30%, the remaining 10–20% is quartz, K-feldspar and

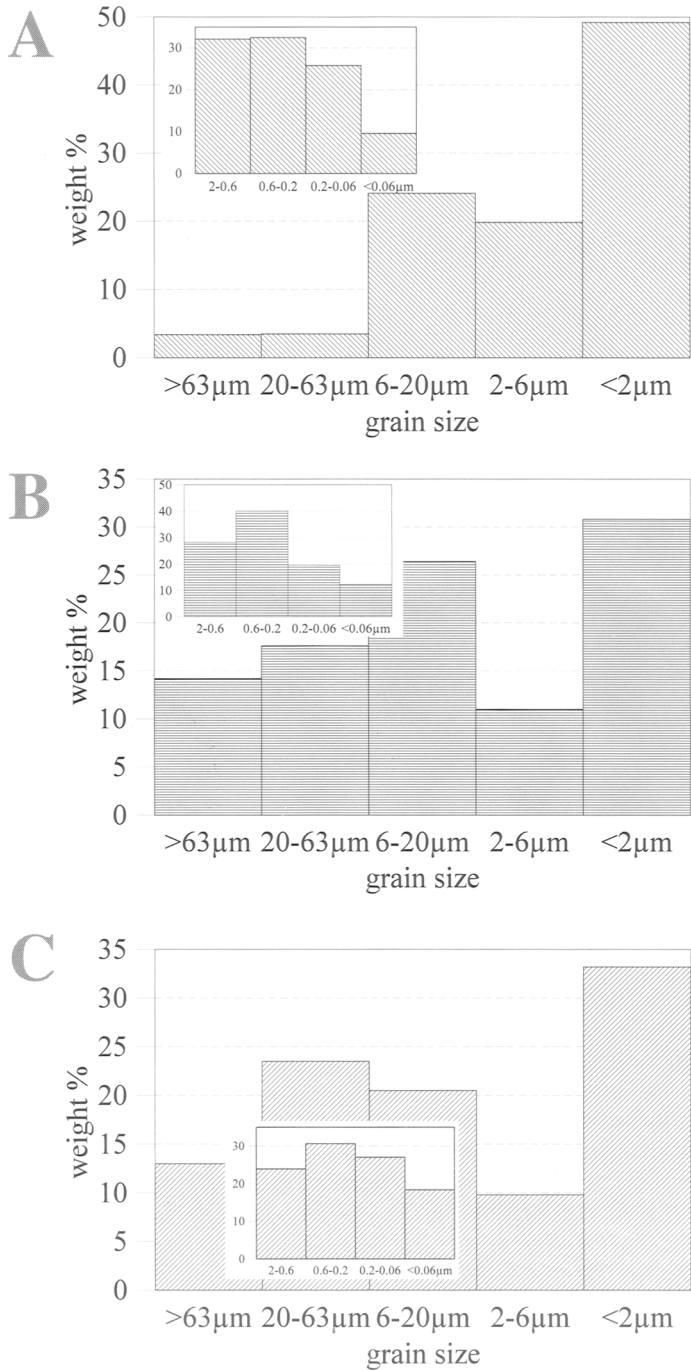


FIG. 3. Examples of grain-size distribution for Lower Cambrian sediments (A — Lontova F., Kestla Mb.; B — Lontova F., Tammneeme Mb.; C — Lükati F.). The grain-size composition of the <2 μm fraction, divided into four sub-fractions, is shown on the same figures.

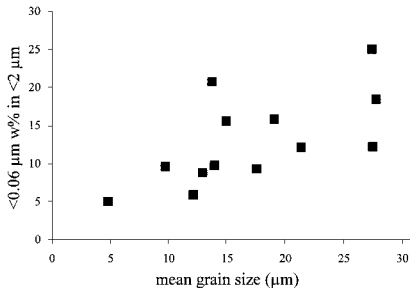


FIG. 4. Correlation between mean grain size of bulk sediment and wt% of $<0.06 \mu\text{m}$ in the clay ($<2 \mu\text{m}$) fractions.

hematite. As expected, the proportion of non-clay minerals increases rapidly with increasing particle size when the particle size is $>2 \mu\text{m}$. In the fraction

$2\text{--}6 \mu\text{m}$, the contents of illite and chlorite have been reduced to 15–25 and 1–3% respectively. Fractions $>6 \mu\text{m}$ contain mainly quartz, K-feldspar and minor amounts of pyrite and hematite, and occasionally some dolomite. The kaolinite content also normally decreases with increasing particle size but the decrease is less pronounced for the coarse sediments in the uppermost part of the sequence. The kaolinite content is also significantly greater in these sediments and this is related to the clear stratigraphic unconformity between Lontova and Lükati Formations (Mens *et al.*, 1990). The upper part of the Lontova Formation was to a great extent eroded during the Lükati Sea transgression and contributed significantly to the composition of the younger sediments. Indeed, in some areas there are partly preserved weathering crusts, with high contents of kaolinite, developed on the illitic claystones of the Lontova Formation (Brangulis *et al.*, 1978). This could explain the greater kaolinite content in the youngest sediments.

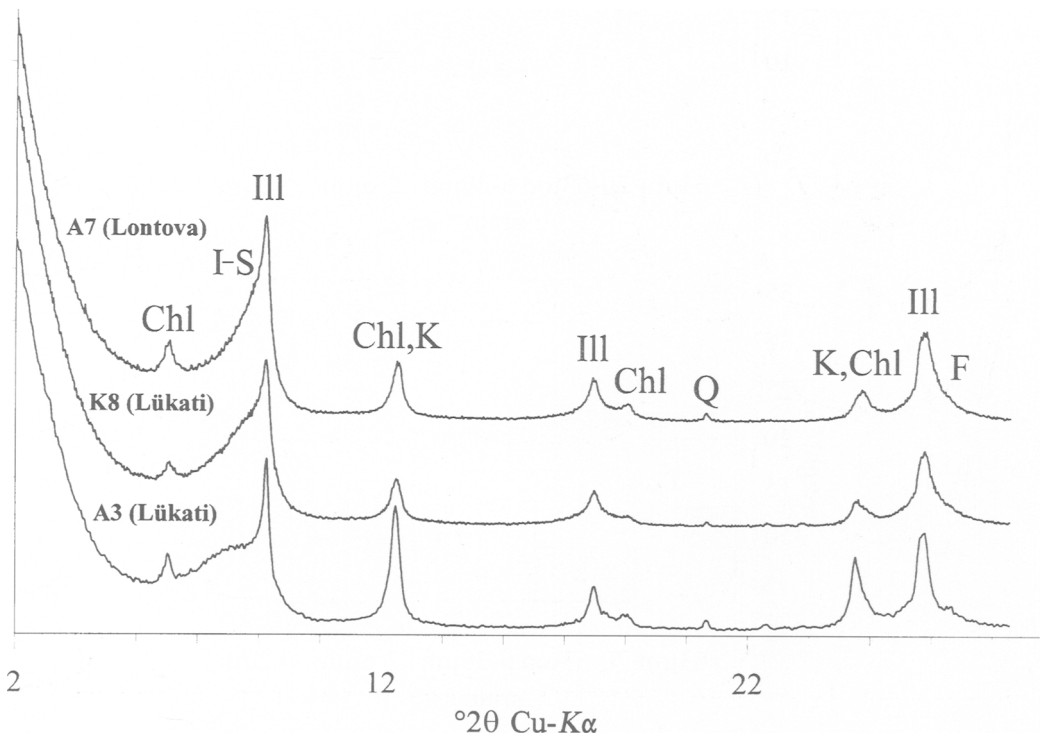


FIG. 5. Examples of XRD curves of oriented $<2 \mu\text{m}$ clay aggregates containing illite, I-S, kaolinite and chlorite. In addition there are traces of quartz and feldspars. Main peaks are labelled: Chl — chlorite, I-S — illite-smectite, Ill — illite, K — kaolinite, Q — quartz, F — K-feldspar.

Three types of illitic phases within the sub-fractions could be distinguished visually (Fig. 6). A micaceous illite (d_{001} 10.02 ± 0.04 Å) is prevailing in fractions 0.6–2 and 0.6–0.2 µm. The second type, a more fine-grained illite with an asymmetric peak, occurring in the 0.06–0.2 µm fraction, has the d_{001} value at 10.20 ± 0.05 Å. The finest, <0.06 µm fraction contains highly illitic (80–90%) I-S (Środoń, 1984) with a wide diffraction band (FWHM $>1.0^\circ 2\theta$) at 10.5 – 10.8 Å.

X-ray diffraction pattern decomposition according to Lanson & Besson (1992) and Lanson & Velde (1992) on the asymmetric 10 Å band of the <2 µm material is in general agreement with the XRD curves for the submicron fractions (Fig. 7). Two illite phases — one mica-like with d_{001} at 10.0 ± 0.03 Å and another, more fine-grained, at 10.13 ± 0.05 Å (<5% of smectite) — were found. In contrast to the sub-fractions, the I-S component in the <2 µm fraction is decomposed into two phases: one with a peak between 10.5 and 10.7 Å and another with a peak between 12.1 and 12.5 Å (in

some cases 11.7 Å), both having wide peaks indicating very small crystal thicknesses. The proportion of illitic layers in I-S was estimated, using modelled curves (Reynolds, 1985), to be 85–90% and 55–70%, respectively. The same two I-S peaks matched the asymmetric I-S diffraction peak in the <0.06 µm fraction curves (Fig. 8).

The well-crystallized mica-like phase (d_{100} 10.0 Å) is found only in the two coarser fractions (2–0.6 and 0.6–0.2 µm). These fractions also contain the 10.1 Å illitic phase as well as some I-S. The two finest fractions (0.2–0.06 and <0.06 µm) contain mainly I-S with 10.1 Å illite dominating in the coarser fraction. In the finest fraction (<0.06 µm) only I-S phases are recognized (Fig. 9).

Lanson & Besson (1992) showed that despite theoretical restrictions (Reynolds, 1989) the diffraction peaks of I-S phases are symmetrical even in the low-angle region and the Gaussian shape was found to give a good approximation for illite and I-S elementary peaks (Lanson & Besson, 1992; Lanson & Velde, 1992).

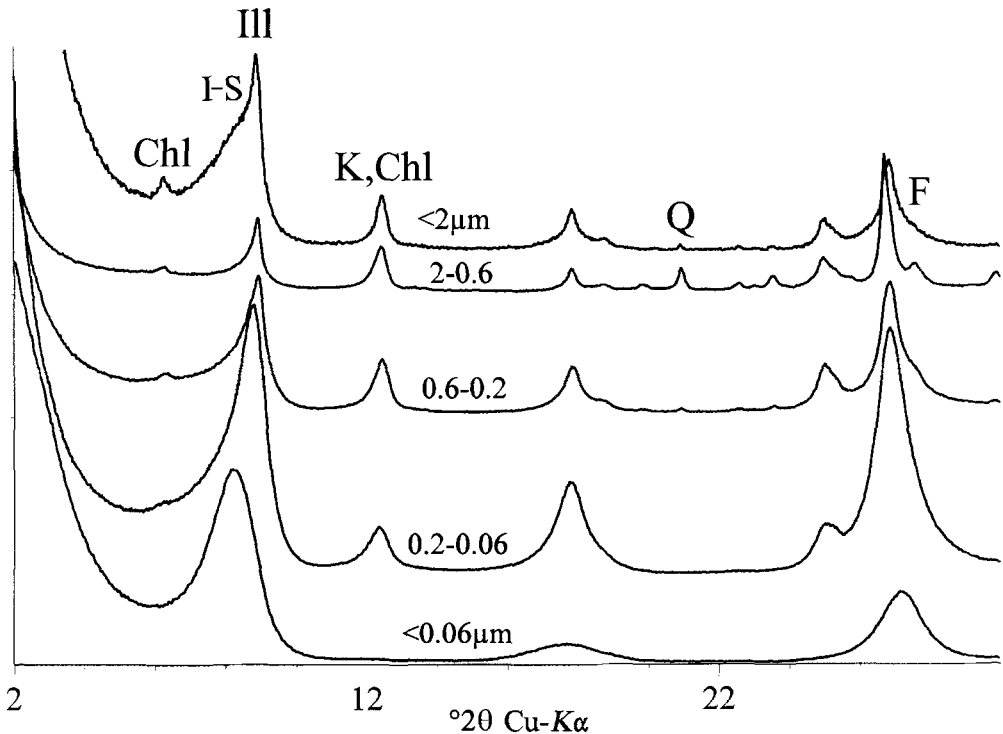


FIG. 6. XRD curves of <2 µm sub-fractions. In addition the XRD pattern of the <2 µm fraction of the same sample is shown above. Legend for labels ss in Fig. 5.

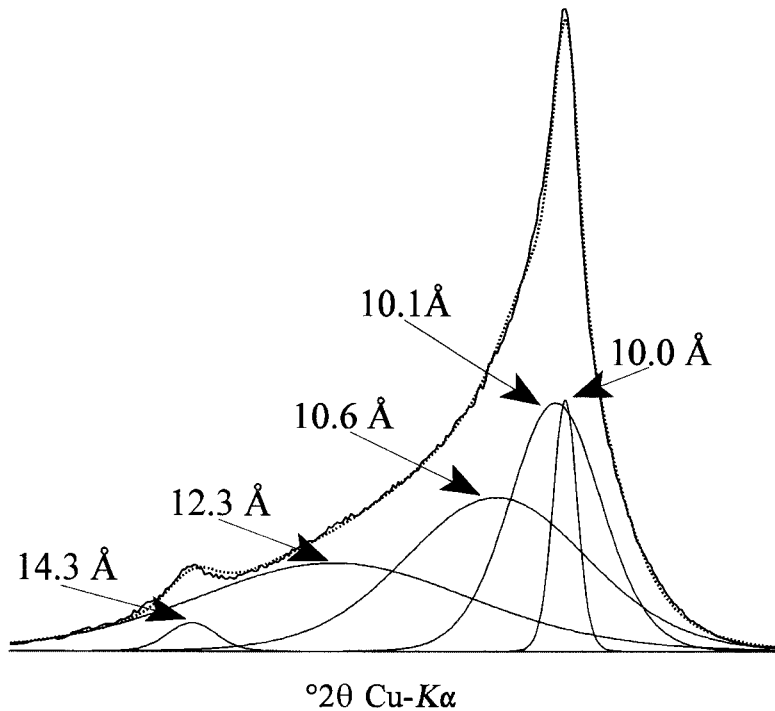


FIG. 7. Decomposed asymmetric 10 Å peak. The fitting was performed assuming a Gaussian shape of the elementary bands. The clay (<2 μm) fraction contains two illitic phases (10.0 and 10.1 Å) and two types of the I-S mineral (10.6 and 12.3 Å) which are the only phases in the <0.06 μm fraction. The 14.3 Å peak is due to chlorite.

However, the presence of two I-S phases fitting into an experimental XRD curve assuming Gaussian shape should be accepted with caution. The 12 Å peak may not have a physical meaning and the low-angle shoulder of the 10.6 Å I-S peak could represent the population of particles with gradually smaller CSDS. This could also explain the poorly defined consistency between decomposed XRD curves of the air-dry and EG solvated <0.06 μm clay (Fig. 8). Therefore in Fig. 9, illustrating the relative contents of the different illitic phases in the <2 μm fractions, the two I-S phases are not given separately, but as a sum.

Rb/Sr dating

The Rb/Sr isotope dating of the clay sub-fractions shows, in accordance with data from Gorokhov *et al.* (1994), that the apparent ages decrease with decreasing particle size from 860 to 456 ± 40 Ma (Fig. 10).

The interpretation of isotopic ages is rather complicated due to the presence of different impurities (e.g. kaolinite) and due to the mixing of the probable detrital and neoformed phases. A high content of detrital micaceous minerals from the Precambrian crystalline basement can explain the highest ages of the coarse fractions.

The Rb/Sr age at 860 Ma for the coarsest fraction (2–0.6 μm) gives an age close to the origin of the detrital micaceous material. The micaceous illite can be identified by electron diffraction (Gorokhov *et al.*, 1994) and unoriented XRD traces as the $2M_1$ polytype normally found in the metamorphic rocks. Metamorphic rocks with an age close to 900 Ma, formed during the Sveconorwegian Orogeny, which marked the closure of the Proto-Iapetus ocean, are known in southeastern Scandinavia (Gorbatshev & Bogdanova, 1993). This region can also be considered as one of the major sediment source areas during the Late Vendian and Early Cambrian (Puura *et al.*, 1987).

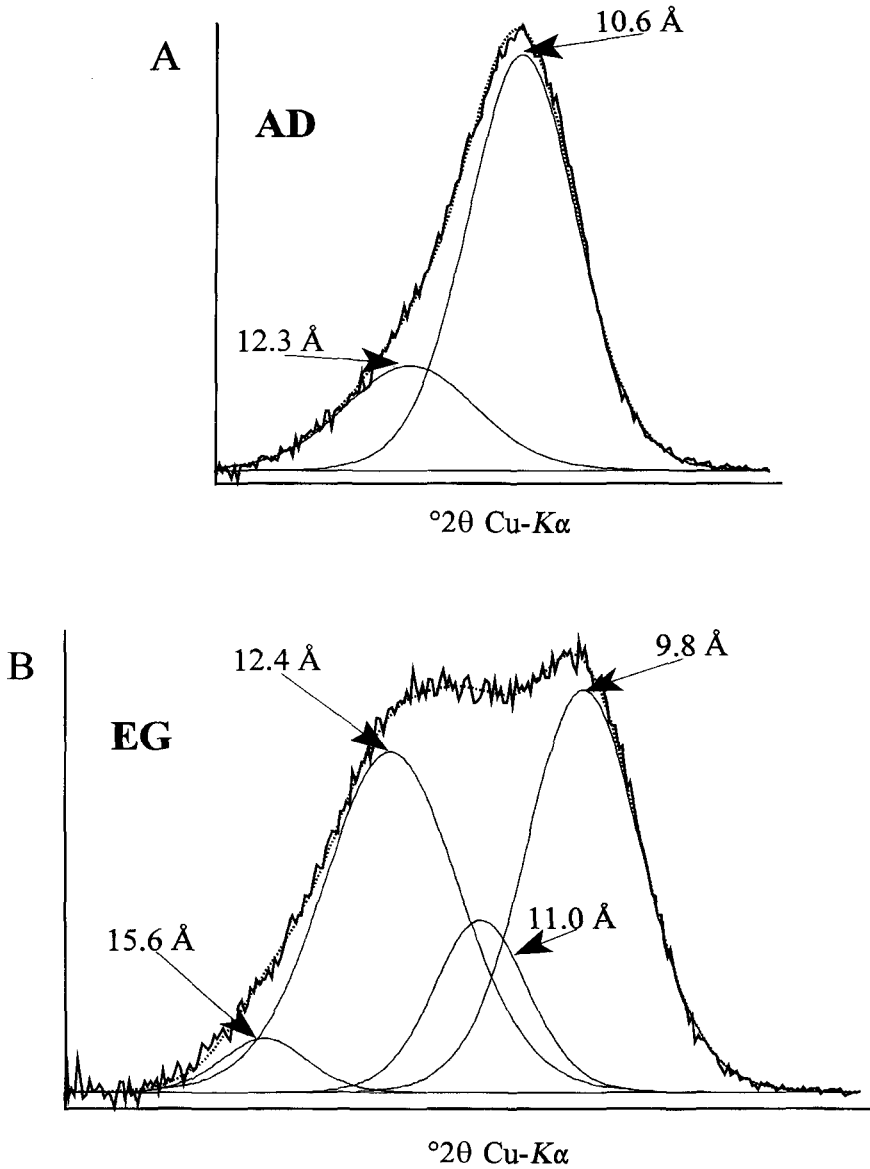


FIG. 8. Decomposition of XRD curves for A: air-dry (AD) and B: ethylene glycol (EG) treated $<0.06 \mu\text{m}$ fractions.

The initial sediment probably consisted of detrital (micaceous) illite and illite-smectite (smectite) with some chlorite and kaolinite derived from crystalline basement weathering crusts and older Vendian sediments. Since the sedimentation age of these Early Cambrian deposits is $\sim 530 \text{ Ma}$ (Bowring *et al.*, 1993) the finest fractions have apparent ages which are 50–150 million years younger than

deposition age (Fig. 10). This means that a major part of the I-S was formed diagenetically after deposition.

As the burial depth increased, diagenetic minerals began to form and the rate of formation increased with increasing temperature. At the same time 'old' minerals disappeared gradually in the finest fractions. Consequently there will be diagenetically

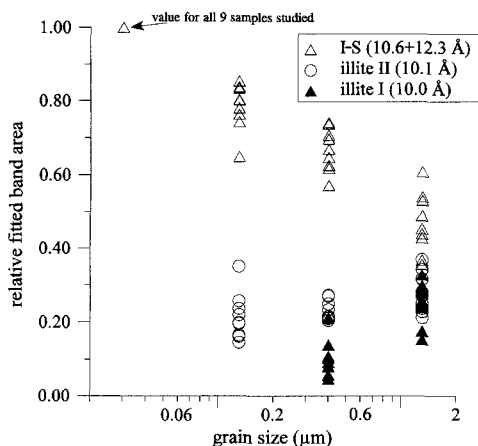


FIG. 9. Relative contents of the illitic phases in the $<2 \mu\text{m}$ sub-fractions. The proportion of each phase in the fraction is calculated as a quotient of the fitted band area of this phase and the sum of phases recognized. The I-S fitted band area is a sum of the 10.6 and 12.3 Å peak areas.

formed minerals with varying particle size and different average ages mixed with 'old' minerals in the different fractions. The apparent age for one fraction will be determined by the ratio of old and new Rb/Sr-carrying minerals, and by the average age for these mineral groups.

From our X-ray data we conclude that the finest fraction ($<0.06 \mu\text{m}$) contains no old Rb/Sr-minerals and the age $456 \pm 40 \text{ Ma}$ shows that the I-S in this fraction was formed 50–150 million years after sedimentation. Because of low gradients and low permeability there must have been a slow flow of water through these sediments where the pore-water could reach a state close to equilibrium with the reacting minerals. In other words, it was a partly open system where *in situ* processes were of great importance. The K needed for the I-S and illite must have come from dissolution of K-feldspar and micas present in sediments. Consequently, we picture a system where unstable minerals dissolved and illite/illite-smectite was formed from ionic solutions in the pore space. As a result the reaction rate was determined mainly by the temperature in the sediments, and the amount of minerals formed was determined by the burial temperature history from Early Cambrian to the present.

Mossmann *et al.* (1992) showed that illite and illite-rich I-S were formed at burial depths of $\sim 500 \text{ m}$ in normally subsiding Paris Basin Tertiary

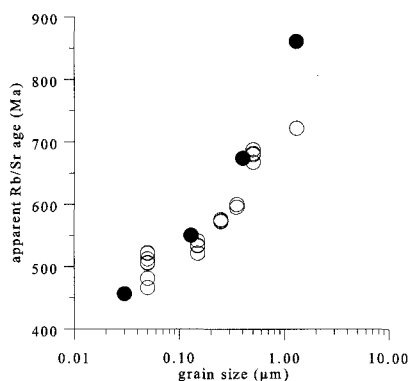


FIG. 10. Decrease of the Rb/Sr age of the fractions with decreasing grain size. The data for open circles after Gorokhov *et al.* (1994, Table 4).

sediments. This was explained by short periodical abnormal heat pulses coinciding with the widespread 'basement' tectono-hydrothermal activity of Liassic age (Mossmann *et al.*, 1992; Clauer *et al.*, 1995, 1996). Similarly, short-lived episodes of hot saline solution expulsions have been seen to trigger illitization regardless of the burial depth (Morton, 1985; Elliot & Aronson, 1987; Hay *et al.*, 1988).

No geological evidence of significant tectonic or hydrothermal activities during the Ordovician or Early Silurian has been reported from this area. It is possible that the heat flux was greater at the beginning of the basin development, but we believe that this old craton, formed $\sim 1.9\text{--}1.8 \text{ Ga}$ ago (Gorbatshev & Bogdanova, 1993), had already reached its thermal equilibrium during Cambrian times and the maximum burial temperature was probably reached with a maximum burial depth in Late Devonian. Besides, if we assume a significantly higher thermal regime, then the organic matter of microfossils would have been much more mature than observed.

However, it should be mentioned that Velde & Espitalié (1989) showed that clays in old shallow sediments are more evolved than the organic matter in same rocks and the less temperature-sensitive illitization proceeds at low temperatures indicating that important kinetic effects are involved (Velde & Vasseur, 1992). Since activation energies reported vary between 3 and 30 kcal mol^{-1} (Cuadros & Linares, 1996) for the transformation processes, it is not possible to calculate exactly the effect of

temperature upon these processes. For many reactions it has been found that the temperature coefficient k_{t+10}/k_t is between 2 and 3. If the temperature at maximum burial was 20°C greater than when the diagenesis started or 'ended', the transformation process was 4–9 times faster at maximum burial. This means that 50 million years at the maximum temperature has the same effect as 200–450 million years at the minimum temperature. Furthermore, Bethke & Altaner's (1986) solid-state transformation model predicts that illitization occurs at shallower depths and over smaller depth intervals in slowly subsiding basins. The northern part of the Baltic Palaeobasin serves as an extreme example of the very low average sedimentation rate of $<0.001 \text{ cm yr}^{-1}$ in Lower Palaeozoic, from Early Cambrian to Upper Devonian. This may explain the I-S and illite formation at shallow burial depth and at relatively low temperatures without the additional heat pulses and intrusion of saline brines. However, the important factors of pore-solution chemistry and pore-fluid migration cannot be rejected.

CONCLUSIONS

We suggest that there are two diagenetically formed illitic and I-S minerals present simultaneously with the detrital phases. The finest fraction, which is an almost pure diagenetic I-S phase, has an average age which is close to the period with maximum burial depth. There is no obvious evidence supporting external sources for abnormal heat pulses and highly ionic solutions. Therefore the most probable scenario is that upon burial, the dissolution of the most unstable detrital smectite (I-S) and dark Fe-Mg silicates started and precipitation of the illite-rich I-S occurred in a chemically partly-open system. The K^+ needed was incorporated from the dissolution of the fine-grained illite (mica) and other detrital phases such as abundant K-feldspar. As a result the old fine-grained phases (fine-grained detrital mica and detrital smectite-I-S) were destroyed and the younger, mostly fine grained ($<0.2 \mu\text{m}$) highly illitic phases were formed. The fine-grained illite or I-S with $<5\%$ smectite layers in the $0.06\text{--}0.2 \mu\text{m}$ fraction can be seen either as the most evolved I-S or as the diagenetically altered detrital illite, while the most coarse fractions, which apparently contain few or no diagenetically-formed minerals, must be representatives for minerals derived from the sediment source areas.

If the assumptions made are correct, it must be concluded that diagenetic formation of I-S minerals in marine sediments is a very important process even at low temperatures, $\sim 35^\circ\text{C}$, given enough time for the process. An important point for future work will be to establish more exactly the apparent age for the diagenetically-formed minerals by dating the finest fractions from more sediments.

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