Clay minerals of clayey subsoils of Weichselian Age in the Zealand-Funen area, Denmark

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The distribution of clay mineral constituents of clay-size particles (<2 µm) from weathered and unweathered clayey subsoils of Weichselian age were studied at 8 sites within the Zealand-Funen area, Denmark. At a large regional scale, four classes (C1 to C4) of clay mineral assemblages of unweathered grey $CaCO_3$-rich till and melt-water clay were identified. The regional distribution of each of these classes revealed a close association with the movement of the glaciers during the Weichselian glaciation. Post-depositional processes (oxidation and leaching) had formed two weathering zones; an upper brownish $CaCO_3$-free zone down to depths of 1–3.5 m, and a lower brownish $CaCO_3$-rich zone down to 3–6.5 m. The composition of the clay minerals of weathered $CaCO_3$-rich clayey subsoils studied at a regional scale suggested a total-transformation process of chlorite, illite, and illite-smectite to smectite and vermiculite. The diversity of clay minerals, typically 5, impeded a more thorough characterization of the transformation of individual clay mineral constituents. Nevertheless, at the Havrebjerg site separate phases of the chlorite transformation were identified within a 0.6 m wide weathering sequence: lowest, a grey zone with unaltered inherited chlorite, followed by a greyish brown zone with slightly transformed chlorite, a brown zone with hydroxy-interlayered vermiculite/smectite, and a yellowish brown coloured zone with hydroxy-interlayered vermiculite/smectite and vermiculite/smectite (but no chlorite). Also, the weathering sequence reflected changes in the cation exchange capacities of the clay fraction and ratio of structural Fe(II) in clay minerals to total Fe.

Key words: Clay minerals, clay transformation, clayey till, meltwater-clay, subsoil, weathered, unweathered, Weichselian

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During the last few decades the environmental pressure on the soil medium has increased dramatically in most parts of the world. Increasing amounts of natural and anthropogenic compounds have been added to the soil surface, and below the root zone the fate of these compounds is determined by physical, chemical, and biological, but also mineralogical properties of the subsoils. Special attention should be given to the role of clay mineral constituents in controlling the adsorption, desorption, fixation, and redox properties of clayey subsoils.

In Denmark most information on clay mineral constituents present are on soil horizons, that have been investigated as a part of the ongoing research on soil formation, chosen to represent differences in geology,

morphology, and climatic conditions. Characteristics of clayey tills of Weichselian age have been reported by Fobian (1966), Faizy (1973), Møberg (1975), Lindgreen (1976), Møberg and Nielsen (1986), Møberg et al. (1988), Møberg (1990), Møberg (1991), and Møberg (1994). Information on clay mineral constituents of deeper Danish subsoils of Weichselian age is limited and obtained from studies of very different subjects, such as soil formation (Fobian 1966), mapping the stratigraphy of Røjle cliff (Graff-Petersen 1957; Graff-Petersen 1958), of Rislinge cliff (Sjørring et al. 1982), and the Kattegat Till Formation (Hegel 1992), for prospecting purposes in the Limfjord area (Ditlefsen 1988), and in environmental issues on distribution and transformation of nitrate (Ernstsen and
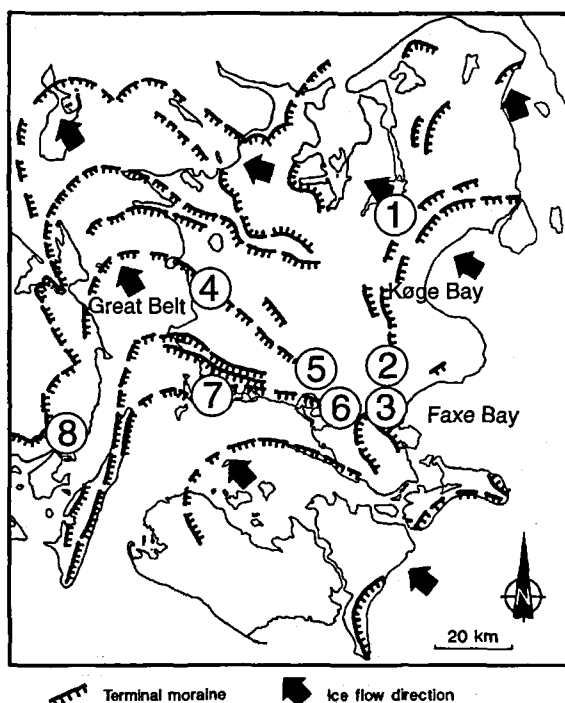
Fig. 1. Generalized ice flow directions and terminal moraines related to the final Weichselian glaciation of the Zealand-Funen area, Denmark (after Jensen, 1992). Field sites: 1) Syv bæk, 2) Denderup Vænge, 3) Sparresholm, 4) Havrebjerg, 5) Herlufmagle, 6) Ravnsbjerg Løjed, 7) Borreby, and 8) Lillebæk.

Geological setting and field sites

Throughout Denmark, the unconsolidated surface is composed almost entirely of glacial sediments. The country was covered by glaciers several times during the Pleistocene period and by lobes from different directions. In the latest event, the Zealand-Funen area was covered by ice when the Belthav Readvance (Weichselian glaciation, 14–15 Ka B.P.) invaded from an easterly direction over the Baltic Sea (Houmark-Nielsen 1987) (Fig. 1).

The glaciers took up older sediments developed under warmer and more humid climactic conditions as well as bedrock (Ringberg 1976), and deposited them at varying distances from the sources (Vortisch 1982). Therefore most of the clay minerals introduced into Danish glacial deposits have been derived from older pre-weathered clay deposits (Graff-Petersen 1958; Rosenqvist 1961; Vortisch 1982).

Free of ice (13–14 Ka BP), the Zealand-Funen area was covered by a deep regolith with a light colored surface which was sparsely vegetated. Post-depositional weathering processes have changed the original grey colors of the deposits. At the 8 sites chosen for this study two zones of alteration were recognized: (i) an upper brownish, oxidized $CaCO_3$-free zone to depths of 1–3.5 m; and (ii) a brownish, oxidized $CaCO_3$-rich zone to depths of 2.6–6.5 m. Below the weathered zones a grey $CaCO_3$-rich unweathered zone occurred (Table 1).

Analytical procedures

Sediment samples were collected and stored frozen until mineralogical analysis. The matrix colors were described following the Munsell Soil Color Chart system (Munsell Color Company 1976). For mineralogical analyses, the sediment samples were pretreated with sodium acetate at pH 5 to remove carbonates, washed free of excess salts using deionized water, and separated into a coarse (>20 µm) and a fine fraction (<20 µm) by the siphon principle. The fine fraction was further separated into clay (<2 µm) and silt (2–20 mm) fractions in a centrifuge.

The mineralogical composition of the fractions were determined by X-ray diffraction from oriented mounts prepared by the pipette methods (10–20 mg/cm²) using a Philips X-ray instrument equipped with a Philips 1050 goniometer and CoKa radiation generated at 40 kV and 30 mA. Series of a minimum of 4 slides of each clay sample were prepared by the following treatments: Mg-saturation and drying at room temperature (Mg_{AD}), Mg-saturation and addition of 1 drop of 10 % glycerol (Mg_{GLY}); K-saturation and drying at room temperature (K_{AD}), and K-saturation and heating at 300°C for one hour (K_{300}). For some samples K-saturated slides heated at 550EC also were included.

Semi-quantitative determination of different clay

Lindgreen 1985; Ernstsen 1991; Ernstsen 1996), pesticides (Jørgensen and Fredericia 1992) and radon (Gravesen et al. 1996).

So far the present knowledge of mineralogical constituents of different clayey deposits of Quaternary age has been based on data covering differences with respect to the methods of analysis, geographical observation density, and observation depth (soil horizons and geological deposits). These differences make it very difficult, or sometimes impossible, to compile all available data into one picture of the mineralogical composition of clayey soils and the deeper subsoils within Denmark. To meet the growing interest of natural clay minerals as essential solid phases controlling the fate of different natural and anthropogenic compounds, the present study was designed to produce comparable data on clayey subsoils at regional and site levels. The regional pattern of clay mineral composition of clay-sized particles (<2 µm) from grey unweathered and brown weathered clayey subsoils of Weichselian age was studied at 8 sites within the Zealand-Funen area. Additional observations on the weathering processes were obtained by a higher vertical sample density at two sites.
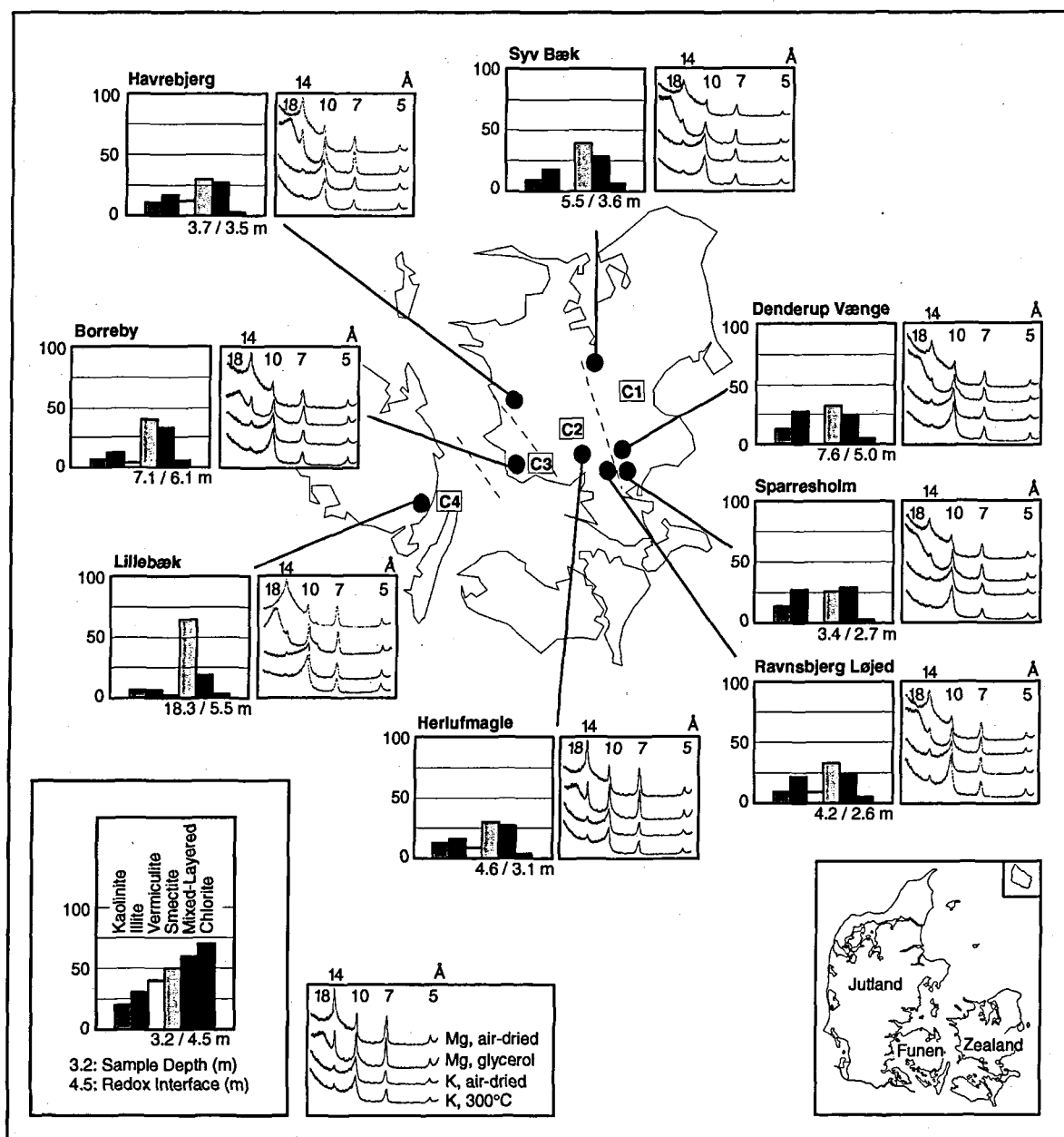
Fig. 2. Clay mineral constituents of unweathered clayey deposits of Weichselian age in the Zealand-Funen area, Denmark, and regional distribution of proposed clay classes; C1, C2, C3, and C4.

minerals were calculated from X-ray diffraction peak areas (partly after Biscaye 1965). Identification of the different clay mineral constituents was as follows: Mg_{AD}, 14Å, smectite, vermiculite and chlorite; Mg_{AD}, 10Å, illite; and Mg_{AD}, 7Å, kaolinite and chlorite. The Mg_{AD}, 14Å intensity of chlorite was estimated at 50% of the Mg_{AD}, 7Å intensity (the average of densities of Mg- and Fe-rich chlorite) (Brown and Brindley 1980), and the intensity of vermiculite at Mg_{AD}, 14Å peak area was calculated proportional to the Mg_{GLY}, 14Å peak where smectite was assumed to make up the remaining part of the Mg_{AD}, 14Å peak. The calculation of different peak areas was relative to the 7Å peaks which was proven constant after different Mg- and K- treatments (except for K-saturated samples heated at 550°C). The clay mineral compositions were calculated by relative reflection intensities; the total clay reflection area was normalized to 100%.

The cation exchange capacity ($CEC_{pH8.2}$) of the clay was calculated based on the sodium concentrations measured in the supernatant after ammonium saturation at pH 8,2, after first sodium saturation at pH 8.2, and after removal of excess salts using 96% ethanol. The elements present in the Na-saturated fractions were detected on pressed, carbon coated powder discs using a Philips Energy Dispersive X-ray Spectrometer, and calculated as the average of 3 measurements per disc. The oxidation state of iron in clay samples was measured by [57]Fe Mössbauer spectroscopy at 77K or by the photochemical phenanthroline method according to Komadel & Stucki (1988).

Mineralogical composition of clay of unweathered deposits

The regional pattern of clay minerals of clay-particle size (< 2 µm) from the grey unweathered (in the literature also described as unaltered, unoxidized or reduced) zone, revealed the presence of 5 to 6 different clay mineral constituents (Fig. 2). At the Denderup Vænge and Sparresholm sites the clay constituents were kaolinite, chlorite, illite, smectite and illite-smectite. The latter 3 were the most common occurring. The illite-smectite was identified from the Mg_{AD} and Mg_{GLY} X-ray patterns, where a raised baseline between the 10Å-peak and the 14Å-peak after Mg_{AD} treatment, but not after Mg_{GLY} treatment, was related to the presence of illite-smectite minerals. The composition of the clays at the Syv bæk site was similar to those at the Denderup Vænge and Sparresholm sites, though somewhat higher in the amounts of smectite and lower in the amount of illite.

In a region west of Syv bæk and Sparresholm, at the Havrebjerg, Herlufmagle, and Ravnsbjerg Løjed sites, small amounts of vermiculite and a total of 6 clay mineral constituents were present. More vermiculite was indicated by larger Mg_{GLY}, 14Å peak areas con-

current with unchanged Mg_{GLY}, 7Å peak areas. Except for the vermiculite, only minor changes in the frequency of other clay minerals also mentioned were observed for the Denderup Vænge, Sparresholm, and Syv bæk sites.

West of the Havrebjerg and Herlufmagle sites, at the Borreby site, smectite and illite-smectite were very commonly occurring, with less amounts of kaolinite, illite, vermiculite, and chlorite.

At the Lillebæk site the clay mineral composition of the unweathered clays was different from the other 7 sites. Here smectite was the dominating clay mineral and together with the illite-smectite represented more than 75% of the total clay. Only minor amounts of kaolinite, vermiculite, and chlorite occurred at the Lillebæk site.

Mineralogical composition of clay of weathered deposits

The clay sample of the Denderup Vænge site (forest) was from the lower part of the oxidized $CaCO_3$-depleted zone, but the samples from the other 7 sites (cultivated land) were from the oxidized $CaCO_3$-rich zone (Table 1). The samples were collected at different depths below the surface but also at different distances above the unweathered clayey zone, and showed various degrees of weathering. Nevertheless, the data of these 8 sites indicated the presence of 5 clay minerals in the assemblage; kaolinite, illite, vermiculite, smectite, and illite-smectite (Fig. 3). Most common were smectite (32–68%) and illite-smectite type minerals (15–27%) with smaller amounts of kaolinite (6–12%), illite (6–16%), and vermiculite (4–14%). Vermiculite was more common in the weathered zone than in the unweathered zone, as seen by larger Mg_{GLY}, 14Å peak areas in proportion to the Mg_{GLY}, 10Å peak areas. Chlorite was not identified in samples from the weathered zone (Fig. 3).

Clay mineral constituents and local geological heterogeneity: the Lillebæk site

As already mentioned, smectite was the dominating clay mineral of the unweathered, but also of the weathered zone, at the Lillebæk site. Additionally, samples of both zones (all $CaCO_3$-rich) confirmed the presence of a clay assemblage with high amounts of smectite (64–75%), illite-smectite (10–20%), and only low amounts (<10%) of kaolinite, illite, and vermiculite, except for the sample from 7.25 m (Fig. 4). Vermiculite was more common (3–6%) in the weathered zone than in the unweathered zone (2%), and chlorite (<5%) was present in the unoxidized zone, only. However, a weak peak at K_{300}, 14 Å and distinct peaks at

Table 1. Land use, lithology, presence (+) or absence (−) of CaCO$_3$, and subsoil matrix colors of samples from weathered and unweathered deposits at 8 sites within the Zealand-Funen study area.

Field site *Land use*	Lithology	CaCO$_3$	Matrix Color
Borreby *Cultivated*	0–15 m clayey till	− − + +	0.0–1.6 m brown 1.6–2.5 m yellowish brown 2.5–6.1 m yellowish brown 6.1–15.0 m grey
Denderup Vænge *Forest*	0–2 m clayey till 2–13 m melt-water clay	− + + + +	0.0–3.5 m yellowish brown 3.5–5.0 m yellowish brown 5.0–5.8 m greyish brown 5.8–6.5 m brownish grey 6.5–13.0 m grey
Havrebjerg *Cultivated*	0–5 m clayey till	− + + + +	0.0–2.0 m yellowish brown 2.0–3.3 m yellowish brown 3.3–3.5 m brown 3.5–3.7 m greyish brown 3.7–5.0 m grey
Herlufmagle *Cultivated*	0–7.5 m clayey till	− + +	0.0–2.0 m brown 2.0–3.1 m brown 3.1–7.5 m grey
Lillebæk *Cultivated*	0–9 m clayey till 9–17 m melt-water sand 17–20 m clayey till	− + + + + + +	0.0–2.0 m yellowish brown 2.0–5.5 m yellowish brown 5.5–7.0 m grey 7.0–7.5 m grey – reddish hue 7.5–9.0 m grey 9.0–12.0 m brown 12.0–20.0 m grey
Ravnsbjerg Løjed *Cultivated*	0–8.5 m clayey till	− + +	0.0–1.5 m yellowish brown 1.5–2.6 m yellowish brown 2.6–8.5 m grey
Sparresholm *Cultivated*	0–8.5 m clayey till	− + +	0.0–1.0 m brown 1.0–2.7 m brown 2.7–8.5 m grey
Syv bæk *Cultivated*	0–15 m clayey till	− + +	0.0–1.0 m yellowish brown 1.0–3.6 m yellowish brown 3.6–15.0 m grey

3.54 Å and 4.73 Å at a depth of 5.25 m (0.25 m above the redox interface) indicated that some chlorite was present in the oxidized zone also.

A distinctly different color at 7.25 m was the first sign of geological heterogeneity, caused by uneven mixing of the materials incorporated by the glaciers. The matrix color of this layer was "grey with reddish hue" (10YR 5/1, moist), whereas the adjacent tills above and below were grey colored (5Y 5/1, moist) (Fig. 4). The clay mineral assemblage of the off-colored zone here was different from the general regional pattern in having considerably higher contents of kaolinite (10 %), illite (8%), mixed-layered clay (34%), and chlorite (8%) (3.54Å and 4.71Å); much lower contents of smectite (<10%), but without any significant differences in the contents of quartz, K-feldspars, and plagioclase compared with other parts of the profile. The different clay mineral assemblage at 7.25 m was also reflected in lower values of CEC$_{pH8.2}$ (0.18 meq. g^{-1}) than typical for this profile (0.29–0.49 meq. g^{-1}), as well as greater amounts of structural Fe(II) in the clay minerals (53% Fe) than found in the unweathered zone (31–42%) (Fig. 4). The content of structural Fe(II) in clay minerals of the weathered zone was less than 20% to total Fe.
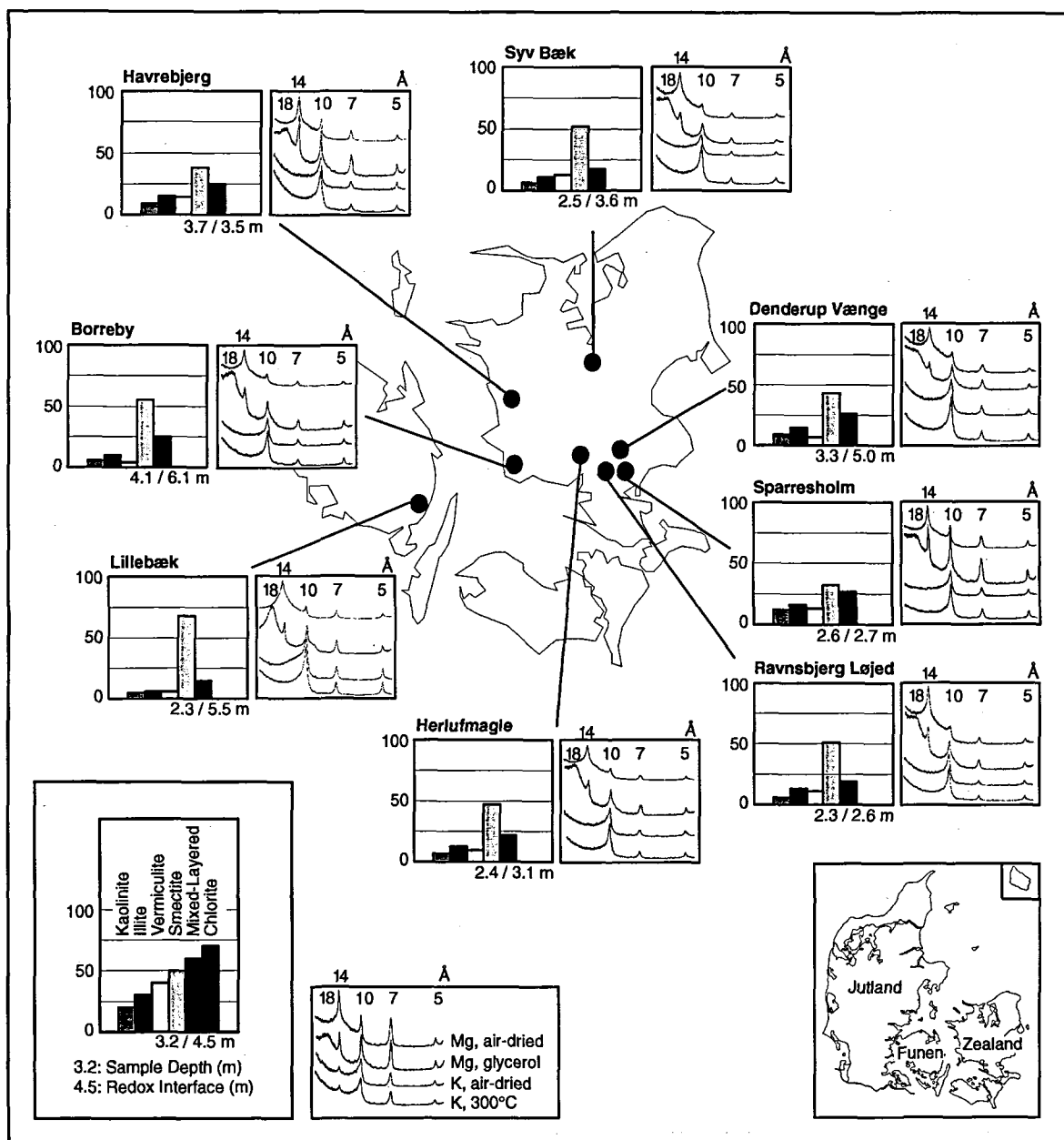
Fig. 3. Clay mineral constituents of weathered clayey deposits of Weichelian age in the Zealand-Funen area, Denmark. All samples were taken from the CaCO$_3$-rich zone, except the Denderup sample, which was taken from the lower part of the weathered CaCO$_3$-rich zone (Table 1).

Post-depositional alterations of clay minerals: the Havrebjerg site

Post-depositional weathering processes resulting in changes in the inherited clay assemblages were studied in a narrow $CaCO_3$-rich zone (3.12 to 3.83 m) encompassing the redox interface at the Havrebjerg site. Oxidation processes had resulted in a change of the original matrix color from grey (5Y 5/1) to yellowish brown (10YR 5/4, moist) down to a depth of 3.27 m; to brown (10YR 5/3, moist) down to 3.45 m; and greyish brown (10YR 5/2, moist) down to 3.71 m, where the unweathered till with the inherent grey colour appeared (Table 1).

The brownish colors revealed a weathering sequence that was closely related to the mineralogical composition of the clay fraction (Fig. 5). Most common was smectite that made up about 40% in the yellowish brown and brown upper zones and 25–32% in the greyish brown and grey lower zones. Illite-smectite made up 21–26% of the two brownish zones (down to 3.45 m) and increased to 28–32% in the greyish brown and grey zones (>3.45 m). The amount of vermiculite was significantly higher (13–18%) in the yellowish brown zone than in the deeper brown zone (11–12%) and greyish-grey zones (7–11%). The amount of illite was slightly lower in the two weathered brownish zones (12–15%) than in the two greyish zones (15–19%) below. The contents of kaolinite were approximately of the same size throughout the different weathering zones. Low contents (about 5%) of chlorite (K,14Å) occurred in both the minimally weathered greyish brown zone and the unweathered zone as indicated by broad peaks at K,14Å after heat-treatment to 300°C and 550°C. In the brown, more weathered zone (3.33 and 3.36 m) the intensity at K_{300}, 14Å after heat-treatment to 300°C became weak. After heat-treatment to 550°C no peak could be identified, and the instability of the 14Å peak was likely due to hydroxy-interlayered vermiculite/smectite. No chlorite was identified in samples from the yellowish brown zone (3.12–3.24 m) where small amounts of hydroxy-interlayered clays (indicated by weak 4.73Å and 3.54Å peaks) and increasing amounts of vermiculite and smectite were observed.

Changes in clay mineral constituents were mirrored by only small changes in values of $CEC_{pH8.2}$, from about 0.30 meq g^{-1} in the yellowish brown and brown zones to about 0.25 meq g^{-1} of the brownish grey and grey zones (Fig. 5) and only minor if any changes in the content of major elements, SiO_2, Al_2O_3, Fe_2O_3, MgO, and K_2O (Fig. 5).

Classes of clay mineral assemblages in unweathered deposits

On the basis of the variations in the compositions of clays from unoxidized (or unweathered) clayey subsoils within the Zealand-Funen area, the clay mineral assemblages could be separated into four classes (Fig. 2). Class C1 includes the Syv bæk, Denderup Vænge, and Sparresholm sites; all sites without a vermiculite constituent in the clay fraction but with about equal contents of illite, smectite, and illite-smectite, and containing only small contents of kaolinite and chlorite. Minerals of class C1 are located in the eastern part of Zealand a geographical region that corresponds well with the part of Zealand that, most recently had been covered during the Belthav Readvance (14–15 Ka BP) (Houmark-Nielsen 1987) by glaciers, that according to Jensen (1992) had flow directions of Køge Bay and Fakse Bay (Fig. 1). Class C2 includes the Havrebjerg, Herlufmagle, and Ravnsbjerg Løjed sites. The clay mineral constituents of this class has some similarity with those of class C1, but the vermiculite contents are high enough for X-ray identification. Class C2 clay minerals are located in the central and western part of Zealand, that correspond to the eastern remote parts of the Belthav Readvance of a southeasterly direction advancing through the Great Belt. Class C3 is only represented by the Borreby site and the clay mineral composition of this region was dominated by smectite and illite-smectite, but also with some vermiculite. Class 3 is thought to be a transition between the classes C2 and C4. Class C3 is located in the central part of the Belthav Readvance complex. The clay assemblage of class C4 was strongly dominated by smectite as described for the Lillebæk site. This region corresponds to the western part of the Belt Readvance.

A regional coverage of different clay mineral classes closely connected to the glaciation pattern has not been described before for clayey subsoils of Denmark, but has been known from other regions, e.g., the northern part of Germany (Vortisch 1982) and the State of Illinois (Glass and Killey 1986). From a study on the Kattegat formation (Weichselian age) based on constituents in clayey samples collected from 13 Danish cliffs, Hegel (1992) reported a less pronounced relation between the geographical pattern and the composition of the clay minerals. Most likely because both oxidized (and transformed) and unoxidized (stable and unchanged) clay minerals were included in this study (Hegel 1992).

Considering the methical principles here suggested, a regional classification system on clay minerals, as the one here introduced, can be useful in environmental studies and in mapping the distribution and fate of different pollutants in clayey subsoils, where both physical and chemical properties are highly dependent on the clay minerals present. It is obvious that this classification system represents the first step
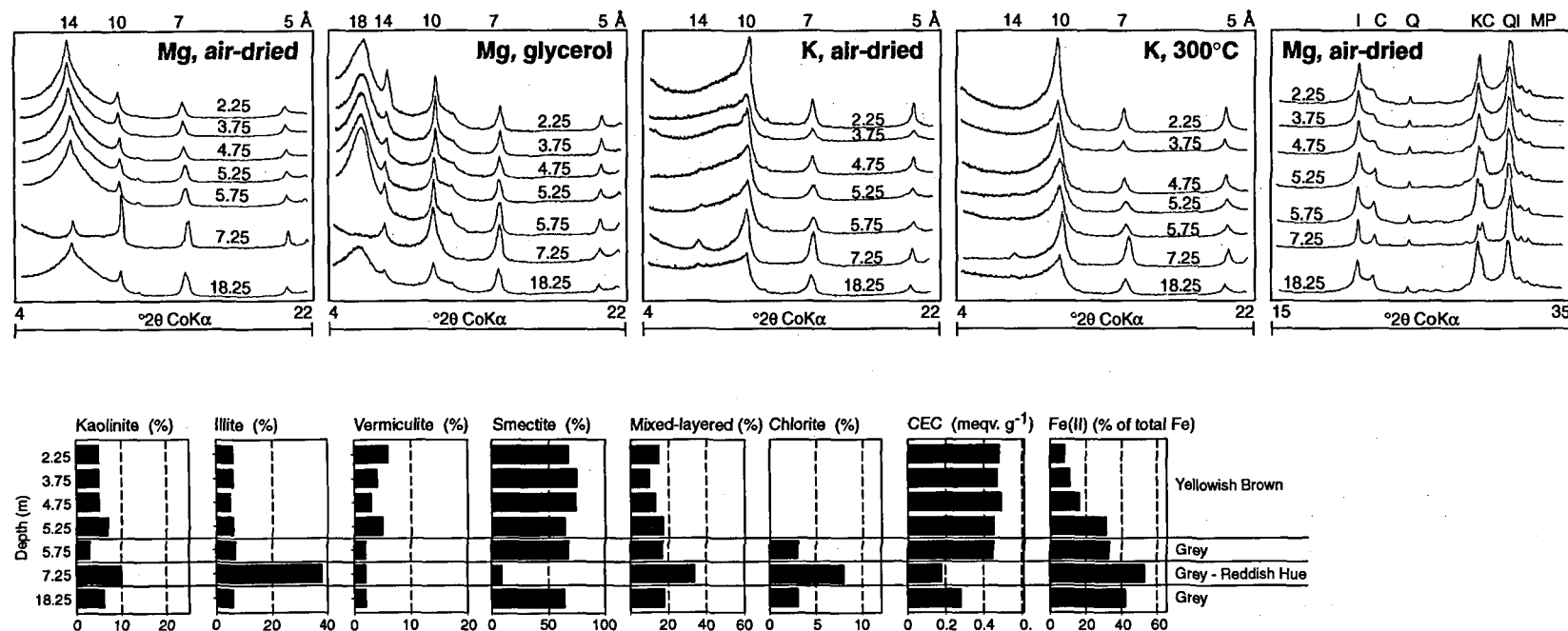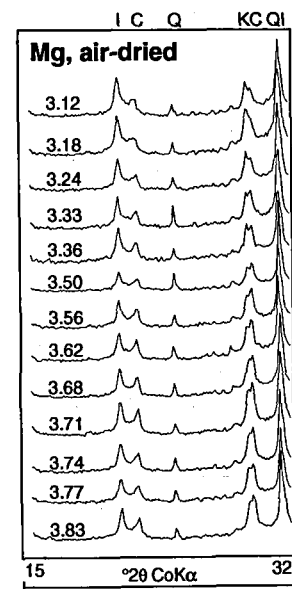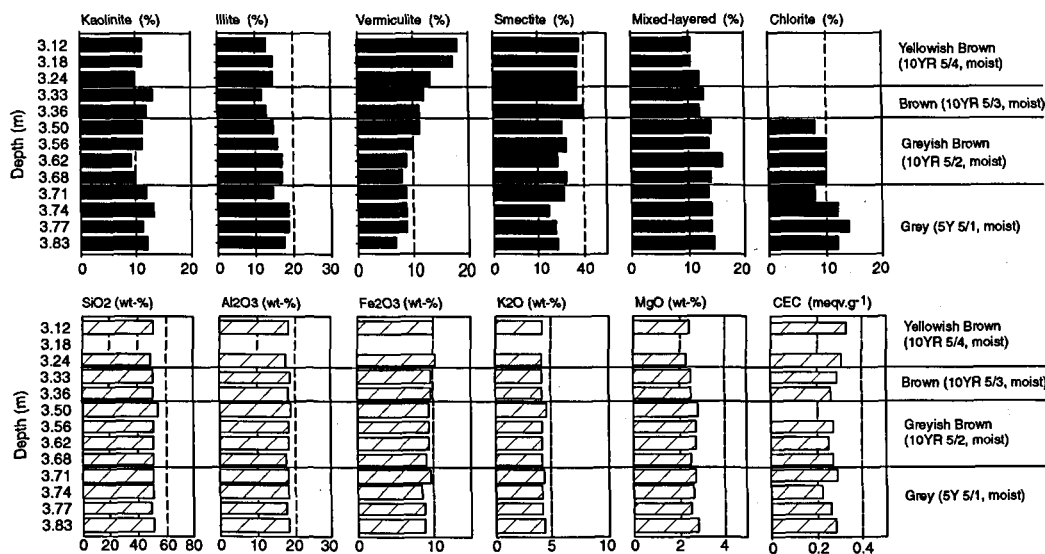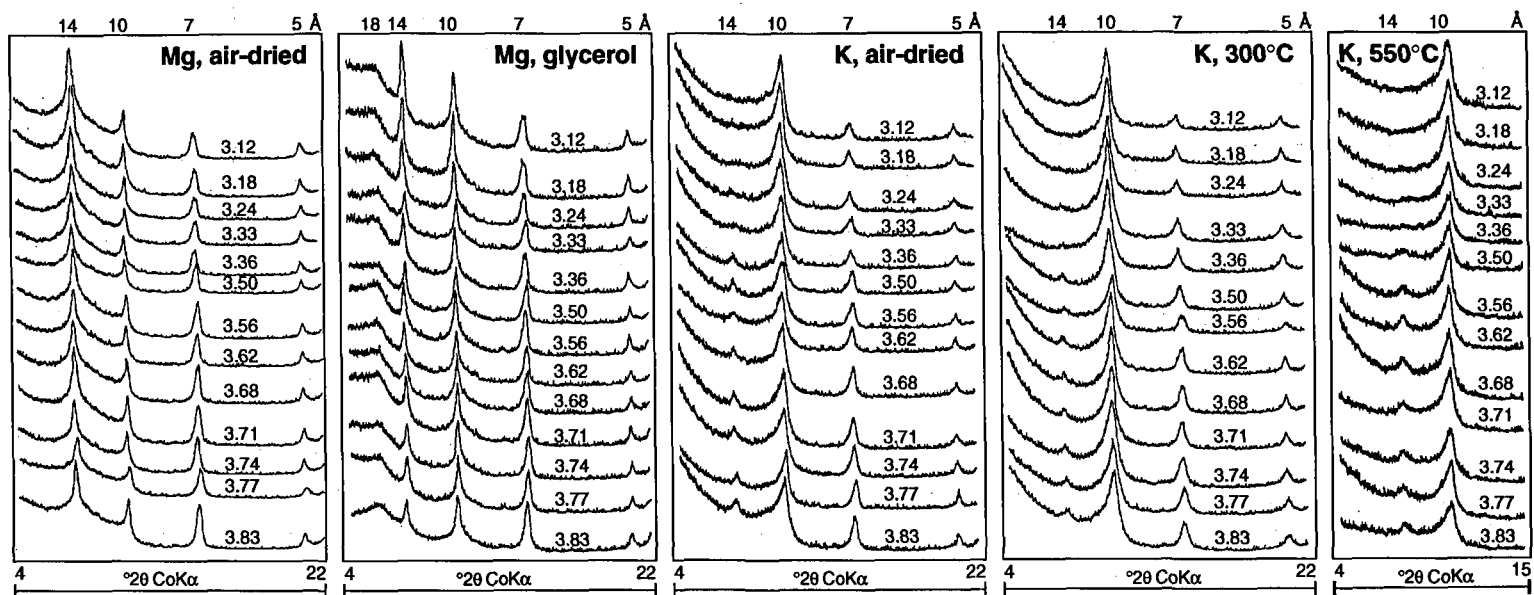
Fig. 4. X-ray patterns of clay (<2 μm) samples, mineral constituents, $CEC_{pH8.2}$, and structural Fe(II)-ratio in clay minerals to total Fe vs. depth in the Lillebæk profile. The off-colored geological heterogeniety was at 7.25 m. I: illite (3.33 Å and 4.98 Å); C: chlorite (3.54Å and 4.78Å); Q: quartz (3.34 Å and 4.26 Å and ; K: kaolinite (3.58 Å); M: K-felspar (3.25Å), and P: plagioclase (3.19Å).

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Fig. 5. X-ray patterns of clay (<2 μm) samples, mineral constituents, major elements, and $CEC_{pH8.2}$ of a yellowish brown/brown/greyish brown/grey weathering sequence at the Havrebjerg site. Major elements were measured on Na-saturated clay. I: illite; C: samples from 3.12–3.50 m, hydroxy-interlayered smectite/vermiculite, and samples from 3.50–3.83 m chlorite; Q: quartz; K: kaolinite (3.58 Å).

in a more systematic way for mapping the naturally occurring clay minerals in Denmark, and that additional data may be useful in both future descriptions of clay mineral classes and for a more accurate geographical mapping of the classes. More data would also allow distinguishing between less mixed clay mineral constituents of geological heterogeneities from local sources and thoroughly mixed minerals from remote sources.

Mineralogical assemblages and geochemical environments in weathered deposits

Owing to post-depositional oxidation processes, a sequence of brown colors formed in the originally unweathered greyish colored deposits. The brown colors which are representative for an *in situ* neoformation of free iron oxides (Dixon 1991; Ernstsen 1991) progressed within the Zealand-Funen area to depths of 2.6 m (the Ravnsbjerg Løjed site) to 6.1 m (the Borreby site), and variations were due to site specific differences, e.g., hydrological conditions, texture, and availability of structural Fe(II) in clay minerals. Studies of clayey glacial sediments from Zealand (Ernstsen and Lindgreen 1985; Ernstsen 1991; Ernstsen 1996) and from southern Sweden (Ringberg 1976) revealed oxidized zones as deep as 10 m; deepest in areas with sand and sandy deposits. Concurrent with the downward progress of oxidation, inherited $CaCO_3$ also leached from the upper 1-2 m. Thus, division into two major geochemical environments is proposed for the further description of mineralogical changes within the studied profile; an oxidized $CaCO_3$-free zone (pH <8) where both oxidation and acidification are active weathering processes, and an oxidized $CaCO_3$-rich zone (pH >8) where oxidation is the major process in the transformation of clay minerals.

The regional distribution of clay mineral constituents of the weathered oxidized zones (all, except Denderup Vænge were $CaCO_3$-rich) reflected only to some extent the inherited mineralogical pattern already given for unweathered deposits. However, due to post-depositional transformations of, e.g., chlorite into vermiculite, a division into class C1 (without vermiculite) and class C2 (with vermiculite) was not possible, and greater amounts of smectite in samples of class C3 and C4 sites also erased the inherited differences in clays in these regions. The data revealed for all sites that the oxidative and $CaCO_3$-rich geochemical environment in the weathered zone was favourable for transformations of clay minerals. In addition, the data revealed that only the clay mineral composition in the unoxidized zone was stable. Due to ongoing weathering processes and the erasure of important inherited differences in the original clay minerals, a classification system of the clay mineral assemblages in the oxidized zone, like that of the unweathered zone in the Zealand-Funen area, is both difficult and complex.

Post-depositional changes of the clay mineral assemblages

The regional clay mineral constituent pattern of the Zealand-Funen area suggested an alteration pattern that include illite and chlorite to smectite and vermiculite, in agreement agreed with other well-documented transformation processes (e.g., Møberg 1975; Melkerud 1984; Senkayi et al. 1981; Møberg et al. 1988; Barnhisel & Bertsch 1989; Fanning et al. 1989). Additionally, results from the Lillebæk site indicated that the total transformation in a $CaCO_3$-rich environment also should include the change of illite-smectite into smectite (Fig. 4), as indicated by an increase in the peak-widths (Mg_{AD}, 14Å) with depth through the weathered zone. But the diversity in clay minerals make separation of changes within each clay mineral constituent difficult. Also mineralogical transformation processes in particle size fractions >2 μm may contribute to the mineralogical composition of the clay fraction.

Different steps in the transformation of chlorite into vermiculite/smectite were identified at the Havrebjerg site in a narrow (0.6 m) weathering sequence located immediately above the redox interface. In samples from the yellowish brown zone (to a depth of 3.24 meter) no chlorite (no K_{AD}, 14Å and K_{300}, 14Å peaks) was present, but weak intensities at both 3.54Å and 4.73Å suggested the presence of hydroxy-interlayered vermiculite/smectite (Barnhisel & Bertsch 1989), which combine the formation of these minerals with a non-acid geochemical environment (Dixon 1991). In addition, some formation of vermiculite and/or smectite from chlorite may have taken place as indicated by a more frequent occurrence (Fig. 5). In samples of the brown zone (from 3.33 to 3.50 m) weak peaks were present at K_{AD}, 14Å and K_{300}, 14Å, but the peaks disappeared after further heat-treatment to 550°C. The heat-labile behavior of the samples and distinct peaks at 4.73Å and 3.54Å suggested the presence of hydroxy-interlayered vermiculite/smectite rather than chlorite under these geochemical conditions. In the X-ray patterns of samples from the underlying greyish brown zone (from 3.50 to 3.68 m), small peaks at K_{AD}, 14Å and K_{300}, 14Å were slightly more intense after heat-treatment to 550°C, and this together with distinct peaks at 4.73Å and 3.54Å, suggested that slightly transformed chlorite was present. A better heat stability of the 14Å peaks of samples from the grey zone indicated the presence of chlorite (Barnhisel & Bertsch 1989), that has remained unaltered since deposition. The kaolinite peak at 3.58Å was more intense than the chlorite peak at 3.54Å in

the yellowish brown zone, about the same height in the brown zone, but lower than chlorite in the greyish zones (Fig. 5). As kaolinite has been reported as unaffected by weathering processes in young tills (Faizy 1973; Nehmdahl & Møberg 1992), the transformation of chlorite as well, in terms of peak-height ratios for kaolinite and chlorite, strengthen the argument that chlorite transformation took place. The last step in the transformation of chlorite into either smectite or vermiculite could only be recognized by increasing occurrence. Transformation of chlorite into vermiculite or smectite is well-known from laboratory experiments (Leighton & MacClintock 1962; Ross 1975; Ross & Kodama 1976; Senkayi et al. 1981) and other studies of glacial tills (Quigley & Ogunbadejo 1976). Thus, it is reasonable to assume that chlorite to smectite/vermiculite transformation occurs since the yellowish brown zone had significantly more vermiculite and smectite than deeper parts of the oxidative weathering sequence (Fig. 5). A similar trend in the distribution of these minerals was also found at the Lillebæk site (Fig. 4.). Chlorite as a sensitive indicator of oxidative weathering has also been reported by among others, Willmann et al. (1966), Dixon (1991), and Ernstsen (1996).

At both the Lillebæk and the Havrebjerg sites the weathering processes and changes in clay mineral constituents were reflected in 5–15% increases in $CEC_{pH8.2}$, at the Lillebæk site (to 0.47–49 meq g^{-1}) and at the Havrebjerg site (to 0.26–0.33 meq g^{-1}), due to greater values of vermiculite (1.5–2.0 meq g^{-1}) and smectite (0.7–1.3 meq g^{-1}) than of chlorite (0.1–0.4 meq g^{-1}) and illite (0.2–0.5 meq g^{-1}) (Schachtschabel et al. 1989). The overall greater $CEC_{pH8.2}$ at the Lillebæk than the Havrebjerg site was due to more smectite at the Lillebæk site (Figs 4 and 5).

Concurrent with the oxidative weathering processes structural Fe(II) in the clay minerals has been oxidized. At the Lillebæk site only 8% Fe(II) remained in the upper part of the brownish zone, but 42% Fe(II) was found in the unweathered zone. At the Havrebjerg site the content of structural Fe(II) in clay minerals increased from 33% in the yellowish brown zone to 51% in the grey zone over a distance of only 0.6 m (Ernstsen et al. in press).

Conclusions

Four classes (C1, C2, C3 and C4) reflecting different assemblages of 6 clay mineral constituents in unweathered $CaCO_3$-rich grey till were identified within the Zealand-Funen area, and the regional distribution of these classes revealed a close association to the ice flow directions of glaciers during the Belthav Readvance (14–15 Ka BP). Post-depositional weathering processes (oxidation and leaching) formed two significantly different zones: an upper $CaCO_3$-free zone

with oxidation and acidification as important weathering processes to depths of 1–3.5 m and a $CaCO_3$-rich zone with oxidation as important weathering process to depths of 3–6.5 m. The composition of clay minerals of the weathered $CaCO_3$-rich zone had changed compared with that of the deeper, unweathered grey $CaCO_3$-rich zone. Even though the diversity of clay minerals made it difficult to follow changes in the individual groups of minerals, the data obtained at regional scale and at more detailed site levels permitted the observation of a general total-transformation of clay minerals in the weathered zone as a transformation of chlorite, illite, and illite-smectite into vermiculite and smectite. The steps in the oxidative transformation of chlorite were closely correlated to a 0.6 m yellowish brown-brown-greyish brown colored weathering sequence above the unweathered zone: where inherited chlorite was present in the unweathered zone; slightly changed chlorite in the greyish brown zone; hydroxy-interlayered vermiculite/smectite in the brown zone; and hydroxy-interlayered vermiculite/smectite with some vermiculite/smectite, but no chlorite in the yellowish brown zone. The mineralogical changes were parallelled by increasing cation exchange capacities and decreasing contents of structural Fe(II) in clay minerals of the total Fe, but without significant changes in contents of major elements.

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Dansk sammendrag

Kendskabet til sammensætningen af lermineraler i dybere danske kvartære aflejringer er meget sparsomt, og de eksisterende data kan kun meget vanskeligt sammenlignes på grund af bl.a. forskelle i valget af analysemetoder. Nærværende undersøgelse følger princippet om en analytisk enkel procedure og omfatter prøver fra otte sjællandske og fynske lokaliteter domineret af moræneler og/eller smeltevandsler. Prøverne indgår i en beskrivelse af såvel regionale som lokale forskelle i lermineralogien, hvor specielt den geologiske variation i det aflejrede materiale og postglaciale forvitringsprocesser har været afgørende for sidstnævnte lokale forskelle. Den regionale variation beskrives bedst ved sammensætningen af lermineraler

i den grå uforvitrede zone, hvor fordelingen af typisk seks forskellige typer lermineraler markerer tilstedeværelsen af fire forskellige klasser (C1–C4) inden for undersøgelsesområdet. På lokal skala har post-glaciale processer (iltning af oprindeligt reducerede forbindelser og udvaskning af bl.a. kalk) resulteret i dannelse af to forskellige (forvitrede) geokemisk miljøer; en øvre 1 til 3.5 meter brunfarvet og kalkfri zone, der efterfølges af en brunfarvet og kalkholdig zone ned til en dybde af 3 til 6.5 meter. Sammensætningen af lermineraler i den kalkrige brunfarvede og forvitrede zone er ændret sammenlignet med mineralogien i den underliggende kalkrige grå og uforvitrede zone. Omdannelsen af chlorit, illit og veksellags-mineralet illit-smectit til smectit og vermikulit udgør de vigtigste transformationer i forvitringsprocessen. Detaljerede undersøgelser i en profil af en kun 0.6 meter bred overgangszone, mellem den forvitrede og uforvitrede zone, i moræneler viser således fire faser i omdannelsen af chlorit; nederst den grå zone med det oprindelige indhold af chlorit, herover en gråbrun zone med svagt ændrede chlorit, efterfulgt af en brun zone med vermikulit/smectit veksellagsmineraler og øverst en gulbrun zone indeholdende hydroxy-interlayered vermikulit/smectit og vermikulit/smectit mineraler – men uden chlorit. Samtidig med den ændrede lermineralogiske sammensætning indtræder ændringer i lerfraktionens egenskaber, f.eks. kationombytningskapacitet og indholdet af strukturelt bundet ferrojern i lermineralerne. Lokalt kan forskelle i sammensætningen af det aflejrede materiale ligeledes give anledning til markante forskelle inden for gaske korte afstande i såvel sammensætningen af lermineraler som i co-variable egenskaber.

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