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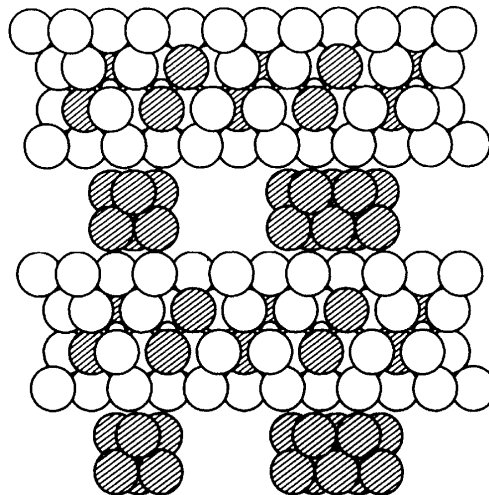

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MSc thesis at the Department of Forest Soils, SLU

Effects of Ammonium Oxalate Treatment on Inter-layer Materials in 2:1 Layer Silicates From a Podzol

Effekter av behandling med ammoniumoxalat på mellanskiktsmaterial hos 2:1-skiktsilikater i en podsol

Ylva Hedstrand

PREFACE

This thesis is made as a 20 credit points individual course and fulfils all the requirements for a Master of Science thesis in Soil Science at the department of Forest Soils at the Swedish University of Agricultural Sciences. The study has been conducted as an integrated part of the departments research on the properties of podzols.

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Erik Karltun, supervisor

CONTENTS

SUMMARY. In an ongoing study it was found that ammonium oxalate treatment in the dark (NH$_4$Ox-D) reduced the permanent charges considerably in the Bh horizon and to a lesser degree in the Bs1 and Bs2 horizon in a podzolised soil. The aim of this study was to evaluate if the loss of permanent charge can be explained by removal of partial hydroxy-Al interlayer material by the NH$_4$Ox-D treatment, resulting in a collapse of the interlayer space. The clay fraction from NH$_4$Ox-D treated and untreated samples from the three horizons were separated. The samples were K-saturated, parallel oriented and analysed by X-ray diffraction at 25°C, 300°C and 500°C.

The broad and less intense peaks at ~13 Å, at 25°C, in both of the samples from the Bh horizon indicated that the minerals were partially interlayered. Comparison between the NH$_4$Ox-D treated sample and the untreated sample, at 25°C, showed a more pronounced peak at 10 Å after NH$_4$Ox-D treatment indicating a lower degree of interlayer filling. Both of the samples completely collapsed to 10 Å after heating to 300°C. The low resistance to heating showed that the interlayer material was less stable and that may also be a result of partial interlayering in the mineral. The lower degree of interlayer filling in the minerals in the NH$_4$Ox-D treated sample may be a result of the treatment but the effect was not large enough to explain the large loss of permanent charges in the horizon.

The higher degree of interlayer material in the mineral in the Bs1 and Bs2 horizons were resistant against the NH$_4$Ox-D treatment showed by the 14 Å peak at 25°C that did not shift to 10 Å after heating to 300°C and 500°C.

Keywords: interlayer, ammonium oxalate, vermiculite, smectite, podzol, clay, surface charge

SAMMANFATTNING. I en pågående studie visade det sig att ammoniumoxalatbehandling i mörker (NH$_4$Ox-D) betydligt minskade de permanenta laddningarna i Bh horisonten och till en lägre grad även i Bs1 och Bs2 horisonten, i en podsol. Syftet med den här studien var att utvärdera om minskningen av permanenta laddningar kan förklaras med att NH$_4$Ox-D behandlingen avlägsnat det delvis fyllda Al-hydroxyl mellanskiktsmaterialet och därmed resulterat i kollaps av mellanskiktet. Lerfraktionen från NH$_4$Ox-D behandlat och obehandlat prov separerades. Proven K-mättades, parallelorienterades och analyserades med röntgendiffraktion vid 25°C, 300°C och 500°C.

Båda proven från Bh horisonten resulterade i en bred topp med låg intensitet vid ~13 Å, vid 25°C, vilkat indikerar att mineralens mellanskikt var delvis fyllda. Jämförelse mellan det behandlade och det obehandlade provet visade en tydligare topp vid 10 Å i det NH$_4$Ox-D behandlade provet, vilket indikerar en lägre grad av fyllning i mellanskiktet. Mellanskiktet i båda proven kollapsade till 10 Å redan efter uppvärmning till 300°C. Den låga motståndskraften mot uppvärmning visar att mellanskiktsmaterialet förmodligen var mindre stabilt. Det kan också vara en effekt av att mineralens mellanskikt var delvis fyllda. Den lägre graden av fyllning i mellanskikten i det NH$_4$Ox-D behandlade provet kan vara ett resultat av behandlingen men effekten kan inte förklara den stora minskningen av permanenta laddningar i horisonten.

Den höga graden av fyllning av mellanskiktsmaterial i mineralen i Bs1 och Bs2 horisonterna gjorde mellanskikten motståndskraftiga mot NH$_4$Ox-D behandlingen, vilket visades med att 14 Å toppen vid 25°C inte flyttades till 10 Å efter uppvärmning till 300°C och 500°C.

Sökord: mellanskikt, ammoniumoxalat, vermikulit, smektit, podsol, lermineral, ytladdning

INTRODUCTION

Layer-silicate clay minerals with high permanent (structural) charge, such as vermiculite, smectite, hydroxy-Al interlayered vermiculite and hydroxy-Al interlayered smectite are important sources of negative surface charge in soils. The structural negative charge gives rise to cation exchange capacity (CEC) (Barnhisel & Bertsch, 1989; Borchardt, 1989; Douglas, 1989). The clay contribution to the CEC of the soil varies in magnitude with clay content but may also depend on the nature of the clay minerals.

Hydroxy-Al interlayered vermiculite and smectite can be considered to form a solid-solution series, with vermiculite or smectite, without hydroxy-Al interlayering, as one end-member and pedogenic or aluminous chlorite as the other end member. In between the end-members there is a range of structures from weakly interlayered to extensive and well-developed interlayered minerals. There is a range of CECs reported for hydroxy-Al interlayered vermiculite and smectite, depending on the degree of hydroxy filling in the interlayer space (Barnhisel & Bertsch, 1989). Thus, the degree of interlayering may be an important factor determining the clay contribution to CEC in podzols.

Occurrence

Hydroxy-Al interlayered vermiculite and smectite exists in several soil orders and have a wide geographic distribution, although they are most abundant in Ultisols and Alfisols in humid-warm and temperate regions (Barnhisel & Bertsch, 1989; Karathanasis et al., 1983; Soil Survey Staff, 1975). In Swedish podzols, vermiculite and hydroxy-Al interlayered vermiculite occurs in B and upper C horizons (Lång & Stevens, 1996; Olsson & Melkerud, 1989; Sjöström & Lin, 1996). In Scandinavia, smectite without hydroxy-Al interlayering is commonly found in the E horizons of Orthic Podzols (Melkerud, 1984). Vermiculite, without hydroxy-Al interlayering, may also occur in the E horizon (Lång & Stevens, 1996; Olsson & Melkerud, 1989). The presence of hydroxy-Al interlayered smectite in soils is well described by several authors (Barnhisel & Bertsch, 1989; Borchardt, 1989; Goh & Huang, 1984; Karathanasis, 1988; Lou & Huang, 1994; Singer & Huang, 1993) but the occurrence of the mineral is not well documented in Swedish podzols. A possible explanation is that concentration of soluble Al is low in the E horizon of Swedish podzols. In general, hydroxy-Al interlayering of the minerals decrease with depth and surface horizons have a higher degree of interlayering than subsoil horizons (Karathanasis et al., 1983; Law et al., 1991; Lång & Stevens, 1996). Hydroxy-Al interlayered vermiculite and smectite are found both in the coarse clay fraction (2-0.2μm) and in the fine clay fraction (<0.2μm) (Barnhisel & Bertsch, 1989; Karathanasis, 1988). However, the minerals occur to a greater extent in the fine clay fraction.

The structure of the minerals and the interlayer material

Vermiculite and smectite consists of a 2:1 layer structure and contains exchangeable cations in the interlayer. The minerals exist in dioctahedral (weathered from muscovite) and trioctahedral (weathered from biotite) forms (Douglas, 1989; Schultz, 1989). Smectite comprise a group of minerals. The dioctahedral montmorillonite and beidellite are supposed to be the most important smectite minerals in the soil environment (Borchardt, 1989). However, in many cases a 14 Å mineral with swelling properties has been called soil smectite (Melkerud, 1984) and soil smectite has been called montmorillonite (Borchardt, 1989).

Both vermiculite and smectite have negative, permanent charge in the layers. The permanent charge is a result of isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet or/and divalent cations such as Mg^{2+} and Fe^{2+} for trivalent cations such as Al^{3+} and Fe^{3+} in the octahedral sheet (Borchardt, 1989; McBride, 1994). Vermiculite from soils developed from silica rich rocks have a higher negative charge in the tetrahedral sheet compared to vermiculite found in soils developed from mica-free silica poor rocks (Douglas, 1989). Vermiculite has a layer charge of ~0.9-0.6 charges per formula unit. As a comparison, micas (muscovite and biotite) have a layer charge of ~ 1 charge per formula unit and have therefore non-exchangeable K in interlayer positions. Smectite has a lower layer charge than vermiculite, ~0.6-0.25 charges per formula unit (Schulze, 1989). As a consequence, vermiculite has a higher CEC than smectite. Smectite shrink upon drying and swell upon wetting because the relatively low layer charge density in the octahedral sheet allows the layers to separate and expand to larger dimensions in water. Vermiculite do not swell in water because the higher negative layer charge density in the tetrahedral sheet enables the positive counter ions to electrostatically pull the layers together more energetically and limit the extent of layer separation (McBride, 1994). Investigators have debated the possibility that a continuum exists between vermiculite and smectite. However, even if the minerals are differentiated from each other because of differing expansion properties, the

ranges of total charge of the two minerals overlap. Deviating forms of the two mineral groups have been called high-charge smectite, when the charge is > 0.6 per formula unit and low-charge vermiculite, when the charge is < 0.6 per formula unit (Douglas, 1989).

Hydroxy-Al interlayered minerals form when Al ions, released during weathering, undergoes hydrolysis and polymerises to lager polycations in the interlayers of vermiculite and smectite (Schulze, 1989). The layer structures of hydroxy-interlayered vermiculite and smectite minerals vary depending on the degree of interlayer filling and the chemical composition of the hydroxy materials found within the interlayer. The difficulty in identifying the presence and layer structure of hydroxy- interlayered forms of clay minerals in soils has resulted in wide range of terms used in the literature denoting different phases in these clays (Barnhisel & Bertsch, 1989). The interlayer material in hydroxy-interlayered clays is suggested to be a six-membered ring structure, $Al_6(OH)_{15}^{3+}$ (Hsu & Rich, 1960). The six-membered ring structure is perhaps the smallest polymer that may exist in clays without being subjected to exchange by other cations (Barnhisel & Bertsch, 1989). Jackson (1963) proposed a larger and more complex polymer of hydroxy-Al as an interlayer species. Progressive filling of the interlayer space by hydroxy-Al polymers may take place either by adding more polymer units in form of a six-membered ring structure or by progressive building of larger, more polymerised structures, that finally may form complete layers (Harsh & Doner, 1984).

Karathanasis et al. (1983) presented an average formula for hydroxy-Al interlayered vermiculite:

$$K_{0.24}Ca_{0.08}(Si_{3.24}Al_{0.76})(Al_{1.56}Fe_{0.24}Mg_{0.20})$$
$$[Al_{1.45}(OH)_{3.79}]O_{10}(OH)_2$$
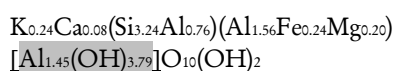
where the hydroxy-Al interlayer component is shadowed.

It has been suggested that moderately acidic conditions are optimal for hydroxy-Al interlayering of vermiculite and montmorillonite (smectite). The pH optimum for interlayer formation in montmorillonite and vermiculite is 5.0-6.0 and 4.5-5.0, respectively (Rich, 1968). Small hydroxy-ions are most likely produced at low pH (Ruff & Tyree, 1955 cited in Rich, 1960). A lower pH might be necessary for interlayer formation in vermiculite because of the high charge density that makes the distance shorter between adjacent silicate sheets. Therefore only hydroxy-Al species of a smaller polymer size can penetrate into the interlayers (Rich, 1968; Ruff & Tyree, 1955 cited in Rich, 1960). The shorter distance between the sheets contribute to a slower diffusion within the interlayer space and therefore slower interlayer formation in vermiculite than in smectite (Rich, 1960). Furthermore, Borchardt (1989) suggested that a decrease in pH in the soil environment can make smectite unstable. The H_3O^+-ions may destroy part of the smectite structure (Coleman & Harward, 1953 citied in Borchardt, 1989). However, other authors found that acidic conditions favour soil smectite formation (Melkerud, 1984) and limit vermiculite interlayering (Lång & Stevens, 1996). The hydrolysis of Al in pure water occurs at a pH above 5 (McBride, 1994). Rich (1960) found that pH stabilised at 5.70, in an Al-vermiculite suspension. A slow change in pH indicates a slow reaction of interlayer-Al in the mineral and a stable pH indicates that there is little hydrolysis-reaction going on in the suspension (Rich, 1960). However, fixation of Al in the interlayer space may occur at a lower pH (Low, 1955 cited in Rich, 1960) but if a soil is extremely acid the hydroxy-Al polymer formation will not occur because all Al in solution will be in the form of Al^{3+}-ions. Furthermore, when pH approaches 7.0 hydroxy-Al interlayering may not occur because Al would more likely be in the form of $Al(OH)_3$ and precipitate outside the interlayer space (Rich, 1968). Hydrolysis may proceed either in the interlayer space or in an external solution. Because of the strong affinity with which Al^{3+} ions are held by clays, their hydrolysis is normally limited (Low, 1955 cited in Rich, 1960), but the hydrolysis may be promoted by the addition of other cations that compete with Al^{3+} ions for exchange sites. Furthermore, low organic matter content, oxidizing conditions, and frequent wetting and drying cycles are conditions that favour formation of hydroxy-Al interlayer (Rich, 1968).

It is common that smectites and vermiculites in acidic soils and sediments are partially interlayered. Completely interlayered clays are very rare (Rich, 1968). The interlayer can be a complex material and may include other components than hydroxy-Al. In a study of interlayer material of partially interlayered vermiculite it was found that the interlayer materials consisted of polymeric hydroxy-Al cations bonded with silicate anions. It seems like silicate anions are incorporated with interlayer hydroxy-Al cations during their formation by hydrolysis of exchangeable Al (Matsue & Wada, 1988). Law et al., (1991) suggested that the partial hydroxy-interlayers of natural clays in acidic environments in temperate and subtropical regions might be siliceous in nature, depending on the Si level in soil solutions. Si and Al concentrations in soil solution can vary considerably in acidic environments. The concen-

tration is influenced by many factors e.g. pH and the nature and concentration of organic and mineral matters. The common range for soluble Si in acidic temperate soils is 0.04 to 1 mM, and that of soluble Al is 0.02 to 0.2 mM (Karathanasis, 1988). According to Lou & Huang (1994) Si was adsorbed to the interlayer space of montmorillonite in form of HAS-ions (polymeric hydroxy-aluminosilicate ions). The adsorption of Si occurred only when $Si(OH)_4$ concentration was high enough (>0.066 mM) to allow the formation of HAS ions. At lower concentrations they observed that Si was released from montmorillonite. Adsorption of Al occurred at much lower concentration (2.9 µM) than that of Si. The HAS ions have a lower proportion of positive charge per Al atom than do the hydroxy-Al ions formed under similar conditions (Wada & Wada, 1980). As a consequence, the negatively layer charge in smectite has a lower affinity for HAS compared to hydroxy-Al ions. Unlike Si, adsorption of Al does not depend on the formation of HAS ions. At low Si concentrations Al can be adsorbed as Al^{3+} or hydroxy-Al ions (Lou & Huang, 1994).

Humic acid (HA) may form hydroxy-Al-HA complexes and perturb the hydroxy-Al interlayering in montmorillonite (Singer & Huang, 1993). However, the perturbation of hydroxy-Al interlayering in montmorillonite was only evident at high levels of HA and when montmorillonite was added last to the system. Goh & Huang (1984) observed the effect of citric acid on the formation of hydroxy-Al-montmorillonite complexes. The effect depended on the initial citrate/Al molar ratio. A low citrate/Al ratio of 0.1 did not significantly affect the hydroxy-Al-montmorillonite complexes but at a citrate/Al ratio of 1.0, most of the Al was prevented from being adsorbed by montmorillonite.

Weathering of hydroxy interlayered minerals

Hydroxy-Al interlayered smectite and vermiculite are thought to occur in soils as weathering products derived from chlorite weathering where the hydroxy-interlayered component is an intermediate mineral in the weathering sequence,

chlorite → secondary chlorite → hydroxy-Al interlayered vermiculite → vermiculite

(Ross et al. 1982). However, in most acidic environments hydroxy-Al interlayered vermiculite and smectite are weathering products of micas (biotite and muscovite) (Barnhisel and Bertsch, 1989),

mica → illite → vermiculite → hydroxy-Al interlayered vermiculite → kaolinite

or

mica → illite → vermiculite → smectite → hydroxy-Al interlayered smectite → kaolinite.

Both hydroxy-Al interlayered vermiculite and trioctahedral vermiculite or smectite are probably formed by alteration of biotite (Law et al., 1991; Schulze, 1989). Dioctahedral vermiculite or smectite is weathered from muscovite (Schulze, 1989). Harris et al. (1988) found no vermiculite but an abundance of hydroxy-Al interlayered vermiculite, even in soils containing mica. This suggests that vermiculite may be an unstable intermediate in these soils. In fact, hydroxy-Al interlayered vermiculite seems to be weathered more or less directly from mica (biotite). The rapid conversion may be possible because K occurs within residual, occluded mica zones. Another possibility is that the incursion of hydroxy-Al polymers into interlayers of weathering mica may be fast enough to trap some K and protect it from subsequent exchange by hydrated cations.

Hydroxy-Al interlayered vermiculite may persist in association with kaolinite and gibbsite (Karathanasis et al., 1983). Karathanasis et al. 1983 suggested that dioctahedral hydroxy-Al interlayered vermiculite might dissolve at a lower rate than kaolinite in undersaturated soil solutions. The study indicated a possible equilibrium coexistence of the two minerals with a hydroxy-Al vermiculite stability field below or above that of soil kaolinite, depending on the degree of hydroxy-Al interlayering. They found that surface-soil clays were generally dominated by hydroxy-Al vermiculite, with kaolinite being the second abundant mineral. Kaolinite was dominant in Bt horizon at the expense of hydroxy-Al interlayered vermiculite. Harris et al. (1980) suggested that hydroxy-Al interlayered vermiculite can be more stable in acid environments compared to kaolinite. They found that the amount of chloritized vermiculite (hydroxy-Al interlayered vermiculite) increased with age relative to kaolinite in surface soils. They also found an increase in kaolinite content with depth. They proposed that kaolinite forms more readily in the subsoil and that the conditions for formation of minerals in the surface soil are less favourable for kaolinite than for hydroxy-Al vermiculite.

The formation of hydroxy-Al interlayers may be at the expense of gibbsite formation. The interlayer precipitation of aluminium prevent the solubility product of $Al(OH)_3$ (i.e. gibbsite) from being reached in the soil solution. The latter has been called an "antigibbsitic effect" in weathering (Jackson, 1963).

Permanent charge, CEC and ion fixation

The structural (permanent) charge arises from substitution of Al^{3+} for Si^{4+} in tetrahedral sheets and substitution of divalent cations such as Mg^{2+} and Fe^{2+} for trivalent cations such as Al^{3+} and Fe^{3+} in the octahedral sheets (Borchardt, 1989). Cation exchange capacity (CEC) is the quantity of cations reversibly adsorbed per unit weight of mineral (e.g. $cmol_c$ kg^{-1}, centimoles of negative charge per kilogram). The permanent charges and the CEC are not always equal in magnitude, because some portion of the permanently charge sites may be inaccessible (McBride, 1994).

The permanent, negative charge per formula unit of vermiculite is ~0.6 to 0.9 and that of smectite ~0.6-0.25 (Schulze, 1989). The proportion of the charge is different within the tetrahedral and the octahedral sheet. According to McBride (1994) the permanent charge of "representative" vermiculite is –0.85 in the tetrahedral and +0.23 in the octahedral sheet and for "representative" montmorillonite 0 in the tetrahedral and –0.33 in the octahedral sheet. In hydroxy-Al interlayered vermiculite, the variation of Al isomorphous substitution is ranging from 0.10 to 0.83 and in hydroxy-Al interlayered smectite from 0.06 to 0.93 moles negative charge per formula weight (Karathanasis, 1988). He found that there was a tendency for a higher degree of isomorphous substitution in hydroxy-Al interlayered vermiculite than hydroxy-Al interlayered smectite structures. The presence of extra Al was also favoured in octahedral and interlayer positions of the hydroxy-Al interlayered structures.

There is a wide range of cation exchange capacities (CEC) for hydroxy-interlayered forms of vermiculite and smectite, which reflects the continuum between aluminous chlorite and the vermiculite and smectite end-members (Barnhisel & Bertsch, 1989). The major mechanisms proposed for charge reduction in hydroxy-interlayered clays compared to the noninterlayered end-members are precipitation of Al on surfaces and/or into interlayer spaces, blocking exchange sites, and adsorption of positively charged hydroxy-Al polymers that are non-exchangeable (Barnhisel & Bertsch, 1989). The CEC decrease with increasing degree of non-exchangeable hydroxy-Al interlayering and the reduction of CEC in vermiculite is almost linear with the amount of Al adsorbed in the interlayer (Lång & Stevens, 1996; Schulze, 1989).

The average CEC value of trioctahedral vermiculite is 159 $cmol_c$ kg^{-1}, whereof 145 $cmol_c$ kg^{-1} are in the interlayers sites and 5 $cmol_c$ kg^{-1} on external surfaces (Alexiades & Jackson, 1965). The CEC of dioctahedral vermiculite is difficult to calculate because of the difficulty in obtaining pure samples of the mineral (Douglas, 1989). Different calculations give varying estimates ranging from between 144 and 207 $cmol_c$ kg^{-1} (Barshad & Kishk, 1969 cited in Douglas, 1989), up to 250 $cmol_c$ kg^{-1} (Cook & Rich, 1963 cited in Douglas, 1989). Soil smectite has a CEC about 110 $cmol_c$ kg^{-1} (Alexiades & Jackson, 1966 cited in Douglas, 1989). The CEC for ideal, nonferruginous montmorillonite is 135 $cmol_c$ kg^{-1}. However, since all soil smectite contain a significant amount of Fe and it will result in a lower degree of isomorphous substitution and therefore a lower CEC (Borchardt, 1989) the CEC for smectite is probably lower than 135 $cmol_c$ kg^{-1}. Karathansis (1988) reported that hydroxy-Al interlayered vermiculite was more extensively hydroxyinterlayered than hydroxy-Al interlayered smectite, i.e. hydroxy-Al interlayered vermiculite has more hydroxy-Al components in the interlayer space. Consequently, hydroxy-Al interlayered vermiculite has lower CEC than hydroxy-Al interlayered smectite. The hydroxy-Al components occupied about 68 % of the total layer charge in hydroxy-Al interlayered vermiculite compared to only 22% in hydroxy-Al interlayered smectite. The average CEC for hydroxy-Al interlayered vermiculite was 29.6 $cmol_c kg^{-1}$ compared to 60.5 $cmol_c kg^{-1}$ for hydroxy-Al interlayered smectite (Karathansis, 1988).

Cations with low hydration energies and the appropriate size such as K^+, NH_4^+, Rb^+ and Cs^+, can be fixed and thereby non-exchangeable in the interlayer position, (Douglas, 1989; Barnhisel & Bertsch, 1989). Hydroxy-Al interlayers can significantly influence the ion exchange behaviour of these ions. The hydroxy-Al interlayers can prevent fixation, since the hydroxy-Al interlayer groups act as "props" inhibiting layer collapse. If the layer collapses, the CEC decrease significantly because the K^+, NH_4^+, Rb^+ and Cs^+ get "locked in" and their migration becomes restricted (Barnhisel & Bertsch, 1989). The increased cation exchange selectivity associated with hydroxy-Al interlayers can also been explained by the existence of wedge zones between "propped" layers stabilized by the hydroxy-Al polymers, and collapsed zones where the ions are fixed within the ditrigonal cavities. The wedge zones selectively adsorb ions with small hydrated radii, since large hydrated cations, e.g. Ca^{2+}, Mg^{2+} and Sr^{2+}, are too large to access the sites (Le Roux et al., 1970). The K^+ fixation (non-exchangeable K) is nearly eliminated by the hydroxy-Al interlayer formation (Barnhisel & Bertsch, 1989). Cations with high hydration energy, such as Ca^{2+}, Mg^{2+} and Sr^{2+}, produce hydrated, expanded interlayers, and easily migrate during exchange reactions (Douglas,

1989). Vermiculite exhibits preferential adsorption of Mg^{2+} over Ca^{2+} (Levy & Shainberg, 1972), while the lower-charge montmorillonite exhibits preferential adsorption of Ca^{2+} over Mg^{2+} (Borchardt, 1989).

The presence of humic acids (HA) may also influence CEC. Singer & Huang (1993) found that the exchange capacities of smectite increased when HA was adsorbed to the interlayer hydroxy-Al material. The CEC increased, especially at a high level of added HA, because of the suppression of hydroxy-Al interlayers and the dissociation of functional groups of HA bound to hydroxy-Al.

Identification by X-ray Diffraction (XRD)

X-ray diffraction properties of hydroxy-Al interlayered clay mineral forms are intermediate between those of the end-members, and are dependent on the degree of interlayer filling and/or the thermal stability of the interlayer component (Barnhisel & Bertsch, 1989). X-ray patterns from Mg-saturated glycerol or ethylene glycol-treated samples of hydroxy-interlayered minerals are similar to those for vermiculite and chlorite. Thus, this treatment is not useful except perhaps to differentiate chlorite from smectite and swelling chlorite. The response to heat treatment of K-saturated samples is the most useful XRD criterion to indicate the presence of hydroxy-interlayered forms. However, as the filling of the interlayer space with hydroxy polymers approaches completeness, it becomes increasingly more difficult to differentiate this mineral from Al-chlorite. Similar problems exist when only a few polymers occupy the interlayer space, as XRD patterns then become similar to those of vermiculite or smectite (Barnhisel & Bertsch, 1989).

Mg-saturated samples of vermiculite without interlayering have diagnostic peaks at 14.3 Å and do not expand after glycerol treatment. Typically for vermiculite is that the 14.3 Å peak collapses to 10.2 Å upon K-saturation, at 25°C, 110°C, 300°C and 550°C (Douglas, 1989; Whittig & Allardice, 1986). According to Borchardt (1989) all smectites without interlayering do produce a 15 Å peak after Mg saturation. Montmorillonite expands to 18 Å after Mg-glycerol-treatment and to 17 Å after Mg-ethylene-glycol treatment. Whittig & Allardice (1986) suggested that the diffraction peak for smectites is at 14-15 Å after Mg-saturation and at 17.7-18 Å after Mg-glycerol-treatment. K-saturated smectite produces a 12.5 Å peak, at 25°C, and a 10 Å peak upon heating to 110°C, 300°C and 550°C (Borchardt, 1989; Whittig & Allardice, 1986).

K-saturated hydroxy-interlayered minerals have a 14 Å peak that collapses towards 10 Å, after heating to 110°C, 300°C or 550°C (Barnhisel & Bertsch, 1989; Whittig & Allardice, 1986). The shift of the 14 Å peak towards 10 Å after heating to 550°C differs in magnitude depending on the degree of the interlayer filling. If the 10 Å peak is pronounced the interlayer filling is low or absent but if there is a shoulder present on the low-angle side of the peak or if the peak is broad that indicates the presence of partial hydroxy interlayering (Barnhisel & Bertsch, 1989; Sjöström & Lin, 1996). Enhanced background intensity indicates also the presence of interlayering (Sjöström & Lin, 1996). The temperature required to collapse (or partial collapse) the 14 Å peak towards 10 Å may be used to estimate the relative degree of filling. The higher the temperature needed to obtain a shift of the 14 Å peak is, the larger the degree of filling. Even with low levels of hydroxy interlayering, a collapse to exactly 10 Å upon heating between 500°C to 550°C is not usually obtained, and the d-spacing is in the range of 10.2 to 10.5 Å. Therefore, the magnitude of the shift in d-spacing upon K-saturation and heating to 500°C is a measure of the degree of filling – small changes from 14 Å indicate large amounts of filling (Barnhisel & Bertsch, 1989).

In addition to the degree of filling, the chemical composition of the hydroxy interlayer component can also influence shifts in d-spacing at K-saturation and after heating (Barnhisel & Bertsch, 1989). When the interlayer material in montmorillonite consists of polymeric hydroxy-aluminosilicate ions (HAS) the d-spacing change depend on the concentration of HAS ions. The d-spacing increased from 11.8 Å when HAS ions were absent to 12.2 Å to 12.6 Å when HAS ions occurred in low concentration and to 16.8 Å when the concentration of HAS ions were rather high (K-saturated, at 25°C) (Lou & Huang, 1994). The low d-spacing was apparently a result of partial interlayering of HAS fragments. The partial interlayering materials were less stable as indicated by the decrease in their basal spacing after heating at 110° C, whereas the heating had little affect on those with a higher degree of interlayer filling. The partial interlayers were largely destroyed after heating at 350°C due to the dehydroxylation (Lou & Huang, 1994). Singer & Huang (1993) suggested that humic acid (HA) interfered with the ordered interlayering of Al polymers in the montmorillonite structure. An experiment showed that when hydroxy-Al-HA-montmorillonite complexes were formed, a distinct XRD peak at 18.4 Å followed by a weak peak at 13.2 Å was present in the X-ray diffraction patters (at 25°C). On heating to 300°C, the 18.4 Å peak was no longer present in any of the samples.

There was a weak peak at 9.9 Å after heating to 300°C and 520°C (Singer & Huang, 1993).

Different treatments can remove variable amounts of interlayer material from the interlayer space depending on their stability, degree of development (Iyengar et al., 1981), and the composition of the interlayer material (Rich, 1968; Lou & Huang, 1994; Singer & Huang, 1993). Monitoring of the change in shape and shift of the "ideal" 14 Å peak towards 10 Å in K saturated samples at 25°C and after subsequent heating to 300°C and thereafter to 500°C, is one method to measure the effect of the treatment.

Solubility of the interlayer material

Iyengar et al. (1981) made a study of the effects of Na-citrate-dithionite (NaCD), ammonium oxalate in the dark (NH4Ox-D) at pH 3.5, and ammonium oxalate combined with photolytic reaction under ultraviolet radiation (NH4Ox-P) at pH 3.25 on interlayers in clay fractions (<2-μm). The NH4Ox-P treatment produced considerable degradation of hydroxy-interlayered vermiculites in these clays, as evidenced by a shift of the 14 Å X-ray peaks to a lower spacing after heating the sample. The NH4Ox-D and NaCD treatments, on the other hand, resulted in no X-ray diffraction detectable alterations. The study indicated that in addition to iron oxides, NH4Ox-P treatment removed considerable amounts of hydroxy-Al material from the interlayer region of 2:1 phyllosilicates. NH4Ox-D treatment had a minimal effect on the mineralogy of these soils, indicating that the method can be safely used to estimate amorphous oxides in soils (Iyengar et al., 1981). In another experiment with a soil clay containing chloritised vermiculite, the interlayer was removed by treatment with dilute NaOH at pH 10 but the hydroxy-Al interlayer material was redeposited when the pH decreased. The Ca/Mg CEC increased from 33 to 169 $cmol_c kg^{-1}$ at pH 10 but when the sample was ageing for 12 days at low pH the Ca/Mg CEC decreased (Lietzke & Mortland, 1973). Hodges & Zelazny (1980) compared NH4Ox-D with NaOH treatment and found that <1 % of a trioctahedral vermiculite dissolved during 2-hr NH4Ox-D treatment. They recommended NH4Ox-D treatment as an extractant of amorphous components.

The NaCD extraction dissolved crystalline iron oxides (McKeague et al., 1971), as well as much of the amorphous materials (McKeague & Day, 1966). The NH4Ox-D treatment, commonly referred to as Tamm`s reagent (Pawluk, 1972; Iyengar et al., 1981), is suggested as a method for the measurement of amorphous iron content in podzolic B horizons (Pawluk, 1972). McKeague & Day (1966) modified Tamm`s method and their study was based on a considerable number of controlled experiments and validated by a number of tests on a variety of Canadian soils. They found that the NH4Ox-D treatment dissolved the iron and aluminium from the amorphous material but that it dissolved very little of the crystalline oxides. On the other hand, NH4Ox-P extractions remove both crystalline and noncrystalline oxides from soils (DeEndredy, 1963 cited in Iyengar et al., 1981).

There are conflicting reports as to the susceptibility of clay minerals to NH4Ox-D treatment. Iyengar et al., (1981) found that hydroxy-interlayered vermiculite is susceptible to dissolution by extractants employed to remove Fe-oxides i.e. NH4Ox-D treatment, depending on the degree of development and stability of hydroxy-Al "islands" in the interlayered region of vermiculite. Arshad et al. (1972) found that NH4Ox-D treatment extracted Fe, Al and Mg from biotite and chlorite but not from illite. The study showed that the release of cations by NH4Ox-D treatment increased with decreasing particle sizes. They used the same procedure for the oxalate extraction as McKeague & Day (1966). McKeague & Day (1966) reported that NH4Ox-D treatment had little effect on kaolinite, montmorillonite, and illite and that interlayer materials of natural Al-chloritized clays were only slightly affected and that some interlayer Al was removed from artificially prepared Al-chloritized bentonite (smectite). Pawluk (1972) observed that prolonged extraction with NH4Ox-D treatment resulted in slight dissolution of hydrous mica (illite) and trioctahedral chlorite and Hodges & Zelazny (1980) did find that some of the trioctahedral vermiculite dissolved during a 2-hr NH4Ox-D treatment.

It has been suggested that interlayer materials, in hydroxy-Al interlayered vermiculite and smectite, contain not only Al but also Si (Matsue & Wada, 1988; Lou & Huang, 1994). Matsue & Wada (1988) made a study to provide information on the interlayer material of partially interlayered vermiculite (PIV) in Dystrochrepts derived from Tertiary sediments. The interlayer material was analysed by dissolution with oxalate treatment (0.15 M oxalate-oxalic acid, at pH 3.5 or 3.0, performed in the dark at 25° C for 4 and 24 h) and citrate treatment (hot 1/3 M sodium citrate 1, 2 and 4 h). The soil samples were analysed by XRD. The 4-h oxalate treatment extracted a large amount of Al but only a small amount of Si, and there was almost no indication of interlayer collapse. The 4-h oxalate treatment was followed by a 24 h citrate treatment that dissolved both Al and Si and completely or nearly completely collapsed the interlayer. This and further comparisons be-

tween the oxalate and the citrate treatment made Matsue & Wada (1988) suggest that the interlayer materials contain both Al and Si and that the dissolved Si had contributed to the inhibition of interlayer collapse in association with the interlayer Al. They suggested that silicate anions could be incorporated with interlayer hydroxy-Al cations during the formation of exchangeable Al by hydrolysis. There was a good correlation between the dissolution of Al and the extent of interlayering, which indicates that it would not be any Al dissolution without interlayering. The dissolution of Si did not show such correlation and the molar Si/Al ratio of the dissolved material decreased from 0.72 to 0.24 with increasing interlayering. The result indicated that the dissolved Al largely originated from the interlayer materials, but the source of the dissolved Si remained indeterminate. The formation of hydroxy-aluminosilicate cations (HAS cations) has also been observed by Wada & Wada (1980). They suggested that orthosilicic acid react with hydrolysed polymer Al ions.

Aim

In an ongoing study (Karltun, unpublished data) on the contribution of surface charge by soil minerals in podzolised soils it was found that an acid oxalate treatment in the dark (NH_4Ox-D) reduced the permanent surface charge considerably in some soil horizons but to a much lesser degree in others. A possible explanation for this observation is that all or some of the partially filled hydroxy interlayers were removed by the oxalate treatment (Arshad et al., 1972; Hodges & Zelazny, 1980; Iyengar, 1981; Pawluk, 1972). The objective of this study was to examine if the ammonium oxalate (NH_4Ox-D) treatment significantly altered the hydroxy-Al interlayered vermiculite and smectite in order to evaluate if the effects of the treatment could explain the loss of permanent charge from the clay minerals.

MATERIALS & METHODS

Study site and soil profiles

The analysis of soil samples in this study was made on stored soil samples. The site information presented here is taken from Olsson and Melkerud (1989). The site, Skånes Värsjö, is located in southern Sweden (56° 40′N and 13° 30′E) and an altitude of 130 m.a.s.l. Climate is of the cool-temperature type with a mean annual temperature of 6.5°C and a monthly average temperature for the warmest month (July) at 16.5°C. Mean annual precipitation is 725 mm.

The parent till material is locally derived. The texture of the till is loamy sand to sandy loam. Clasts of the Precambrian basement of the vicinity predominate in the till. Proportions are 20% reddish, coarse-grained granites, 32% reddish fine- to medium-grained granites, 4% reddish gneisses, 43% greyish gneisses and 1% greenstones and mica schists. The studied soil is freely drained. The soil is classified as an Orthic Podzol (Olsson & Melkerud, 1989). The parent material contains quartz, feldspar, amphiboles, chlorite and accessories such as illite and mixed layer minerals.

The tree stand consists of Norway spruce (*Picea abies*) in monoculture. The field layer is dominated by dwarf shrubs (*Vaccinium myrtillus*) and grass (*Deschampsia flexuosa*). In the bottom layer mosses (*Pleurozium schreberi* and *Hylocomium splendens*) are most common. The area has previously been used for crop production and grazing.

Sample preparation

Soil samples from three depths in the B horizon (Bh, (B/A) Bs1, Bs2) were used in this experiment. The soil samples were wet-sieved through a 50 μm mesh and sub-sequently freeze-dried. Two sub-samples, 20 g each, from each horizon were taken out from the dried soil sample. One of the sub-samples was treated with acid ammonium oxalate. 2000 ml of 0.2 M ammonium oxalate (pH 3.0) solution (AO) was added to 20 g of soil sample. The suspension was shaken in the dark for 4 h, centrifuged and washed with de-ionised water. The resulting samples are hereafter referred to as Bh-Ao, Bs1-Ao and Bs2-Ao. The untreated samples are referred to as Bh-U, Bs1-U and Bs2-U.

The six samples were pre-treated with 35% H_2O_2 to remove organic matter, washed with 100 ml 1.0 M NaOAc (pH 7) to remove released cations and Na saturate the soil to facilitate dispersion. A single wash with 100 ml 50% ethanol was done to remove the bulk of the Na-ions.

The sample was dispersed by adding 400 ml pH 9.5 of Na_2CO_3 solution to the suspension and stirred by a propeller-mixer to disperse the clay. After that, the suspension was treated with an ultrasonic probe, for 2 × 2 min, to further disperse the clay fraction. The suspension was diluted to 1 L with a Na_2CO_3 solution (pH 9.5). The samples were siphoned to a depth of 31 cm after 24 h sedimentation to separate the < 2 μm fractions and the procedure was repeated five times. For the samples Bs1-U and Bs2-U a shorter sedimentation time (6 hrs) was used to separate the < 4 μm fraction of the soil. The latter modification was made in order to obtain enough sample material for preparing the clay X-ray specimens.

The pH of the clay suspensions was adjusted to pH 5 with HCl and 7.2 g $MgCl_2 \cdot (H_2O)_6$ per liter suspension was added and left overnight until the clay fraction had flocculated. The supernatant was thereafter removed by siphoning and centrifuging.

The suspension was K-saturated by addition of 10 ml 1.0 M KCl, shaken for 15 min and thereafter centrifuged at 3000 rpm for 5 min. The procedure was repeated four times. Finally, the suspension was washed free from salt with deionised water.

Parallel oriented samples of the K-saturated clay suspensions were prepared for X-ray powder diffraction (XRD) analysis by depositing 10 ml of sample on a 0.45 μm filter (Millipore). The moist filter was placed clay-side down on a glass slide and transferred with a rolling pressure of a glass rod (Drever, 1973). The K-saturated samples were analysed by XRD, after air-drying, at 25°C, 300°C and 500°C. The XRD samples were analysed on two different XRD equipments because one of the equipments was taken out of operation due renovation of the laboratory. A Philips 1710 diffractometer was used for XRD analysis of the Bs1-Ao and Bs2-Ao samples and a Siemens 5000 diffractometer was used for XRD analysis of the Bh-Ao, Bh-U, Bs1-U and Bs2-U samples. Both diffractometers were equipped with a $CuK\alpha$ radiation tubes. The radiation in the Philips 1710 diffractometer was generated at 40 kV and 24mA and in the Siemens 5000 diffractometer at 40 kV and 40 mA. Scans were run from 2°-40° (2-theta) in the Philips 1710 diffractometer and from 2°-35° (2-theta) in the Siemens 5000 diffractometer, with step size 0.02° (2-theta) and counting time 1 s step[-1] in both diffractometers. The analyses were performed with a fixed 1° divergence and a 2 mm receiving slit. The XRD raw files from the Siemens 5000 diffractometer were taken up in the Bruker/Siemens DIFFRAC[PLUS] software (version 2.2), and evaluated in the programme EVA. The minerals were identified by means of the PDF (1994) computer database.

RESULTS

Hydroxy-Al interlayered vermiculite and smectite in the Bh horizon

The X-ray diffractogram from the Bh-Ao sample, at 25°C, resulted in two broad peaks, one around 13.0 Å and the other one between 10.0 Å to around 11.0 Å (Figure 1). The broad and less marked shape of the both peaks and the shoulder at the low-angel side on the 10.0 Å to 11.0 Å reflection indicates partial or low degree of interlayer filling in the minerals. The peak at 13.0 Å indicated that the interlayered minerals could be vermiculite or maybe smectite but the peak at ~11.0 Å to 10.0 Å is probably only a result from interlayered vermiculite. The 10.0 Å reflection also indicates the possible presence of vermiculite without interlayer. Furthermore, there is a possibility that the broad peaks from ~11.0 Å to 10.0 Å, and the peak at 13.0 Å, may partially arise from mixed-layer illite-montmorillonite.

The X-ray diffractogram from the Bh-U sample, at 25°C (Figure 2), showed a similar pattern as the diffractogam from the Bh-Ao sample. The result showed a broad peak from ~13.0 Å to 10.0 Å with two maxima at 12.8 Å and 11.0 Å. They were less clearly distinguished from each other compared to the two broad peaks in the diffractogram from the Bh-Ao sample. The area around

~11.0 Å to 10.0 Å from the Bh-U sample were also less intense and because of the remaining Fe-oxides in the untreated sample the background intensity was higher.

The XRD diffractograms from the Bh-Ao and Bh-U sample showed an intense and well-pronounced peak at 10 Å after heating to 300°C and 500°C (Figure 1 and 2). The complete collapse to 10 Å already at 300°C indicate that the minerals are partially interlayered and therefore less stable. Furthermore, the weak 5.0 Å peak at 300°C that was enhanced after heating to 500°C is the 2nd order reflection of the 10.0 Å peak.

The result may have been affected by changes in relative humidity in the Bh-Ao sample at 25°C. The preparation was therefore analysed at different levels of relative humidity (RH). The same preparation were analysed after wetting to almost 100 % RH (diffractogram a in Figure 3) and after drying with warm air (diffractogram b in Figure 3). A further preparation from the Bh-Ao sample were analysed after drying over night in a room where the relative humidity was 53 % (diffractogram c in Figure 3). The change in relative humidity did result in small changes in the XRD patterns in the area around 10 Å to 14 Å. The changes may indicate the presence of smectite in the Bh horizon.
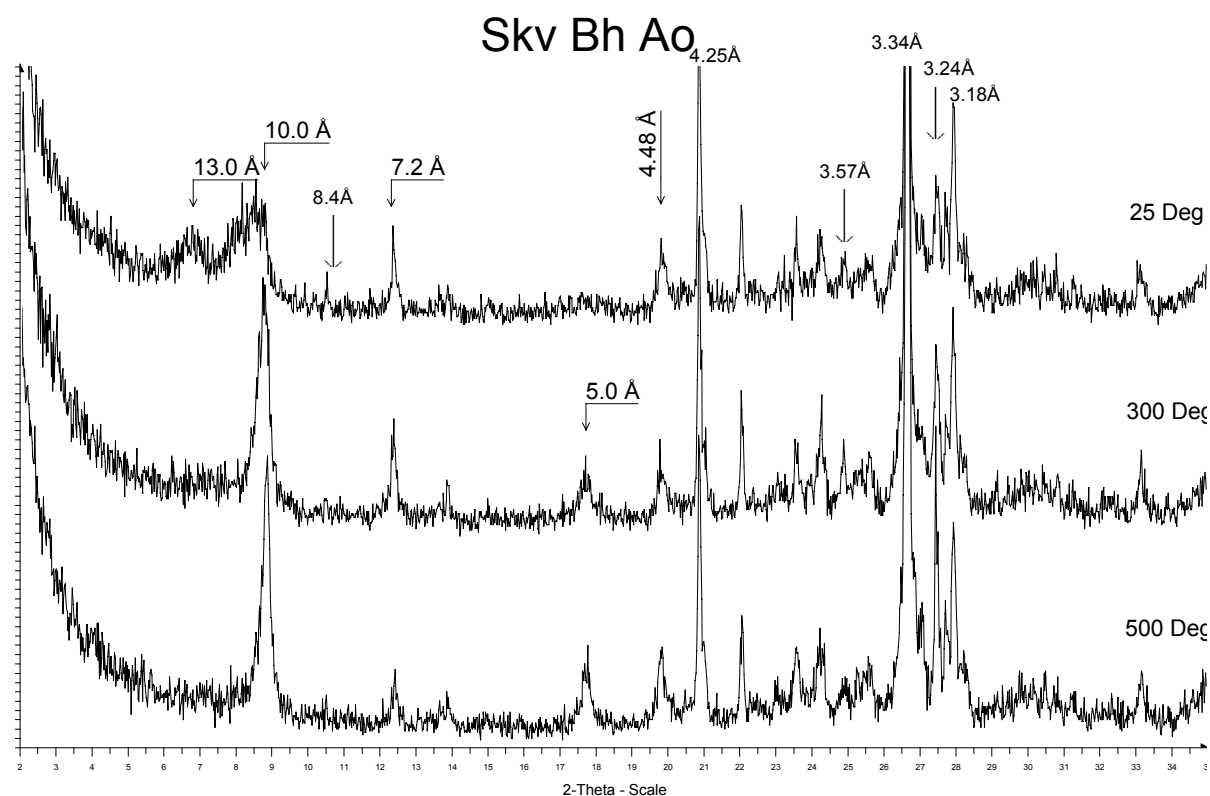

Figure 1. X-ray diffractograms of K-saturated and ammonium oxalate treated sample (Bh-Ao) from the Bh horiazon at 25ºC, 300ºC and 500ºC (Y-axis: counts per second (cps), X-axis: º2).
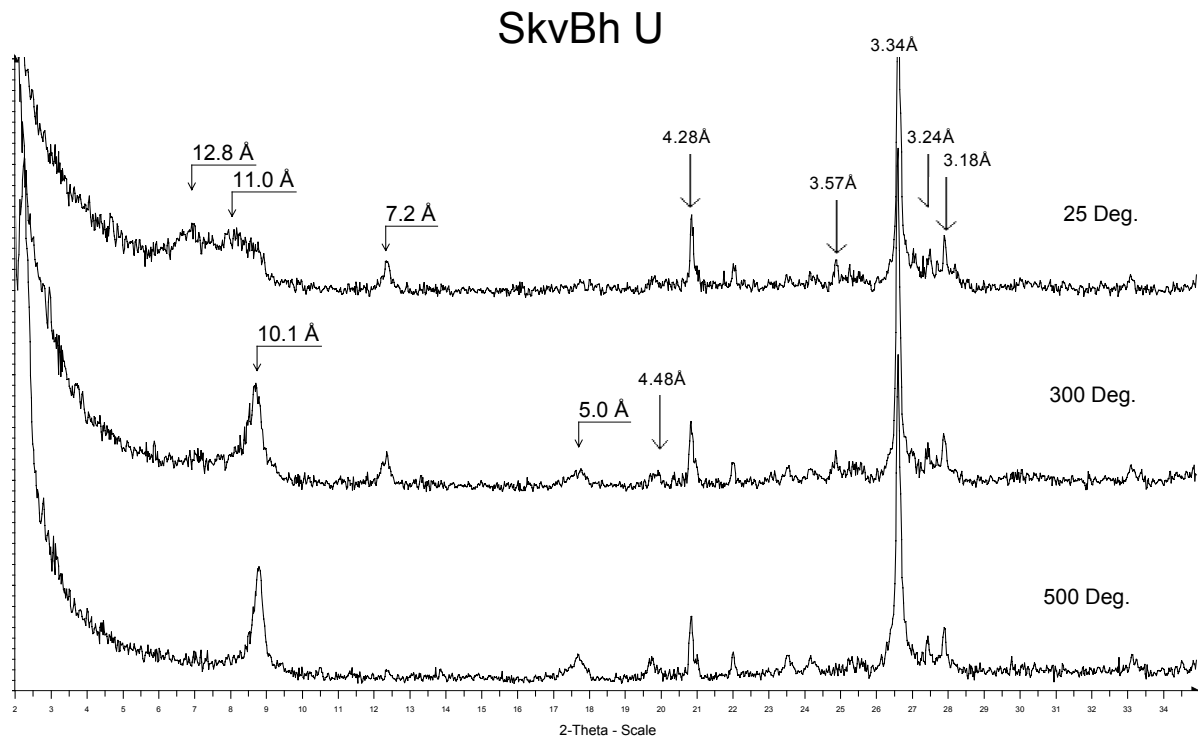
SkvBh U

Figure 2. X-ray diffractograms of K-saturated and untreated sample (Bh-U) from the Bh horizon at 25ºC, 300ºC and 500ºC (Y-axis: counts per second (cps), X-axis: º2).
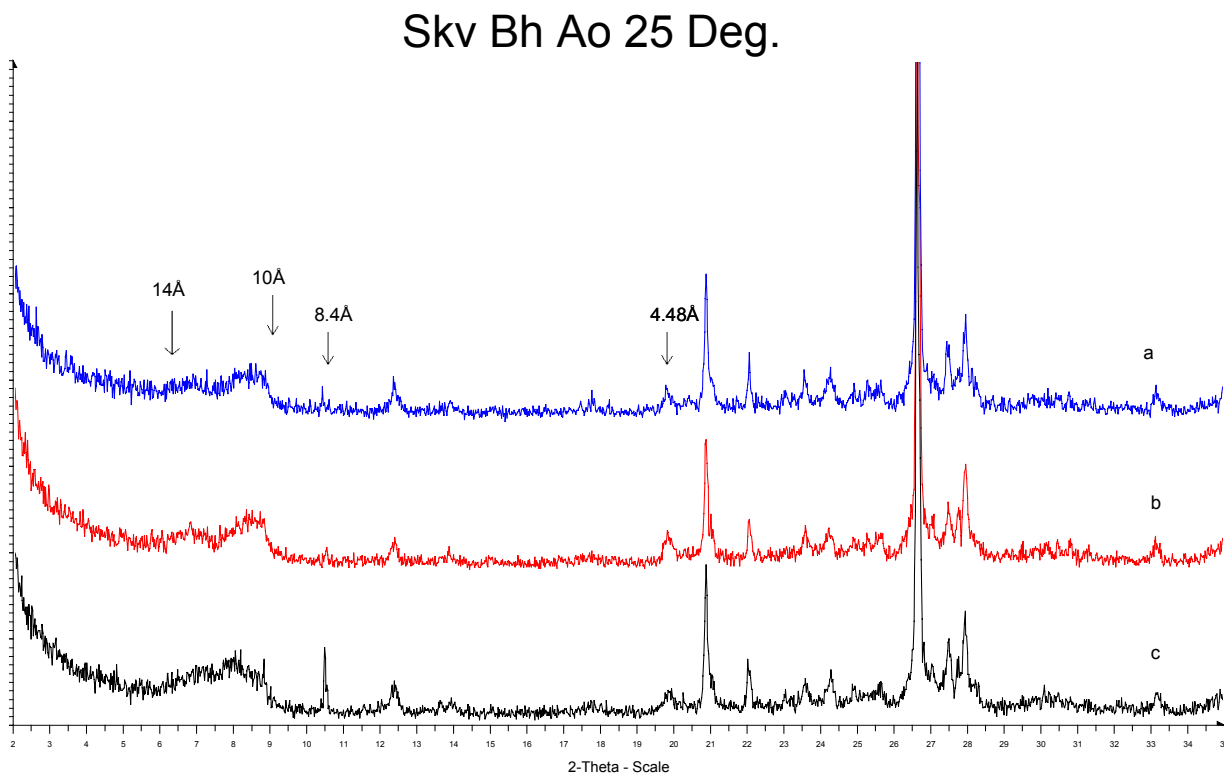
Skv Bh Ao 25 Deg.

Figure 3. X-ray diffractograms of K-saturated and ammonium oxalate treated sample (Bh-Ao) from the Bh horizon at 25ºC and at different RH, (a) ∼100% RH, (b) dried with warm air and (c) ∼53% RH (Y-axis: counts per second (cps), X-axis: º2).

Hydroxy-Al interlayered vermiculite in the Bs1 and Bs2 horizons

The X-ray diffractograms, at 25°C, from the Ao-treated (Figure 4 and 5) and the untreated (Figure 6 and 7) samples in both the Bs1 and Bs2 horizon showed similar patterns with a marked and well pronounced peak at ~14 Å. After heating to 300°C and 500°C the peaks shifted towards 10.0 Å but the 14 Å peak did not completely collapse to 10.0 Å. The incomplete collapse even after heating to 500°C indicated the presence of a high degree of interlayer filling in the mineral and/or a more stable chemical structure of the interlayer material.

The 14 Å peak, in the Bs1-Ao sample (Figure 4), shifted to a broad and less distinguished peak between 12.6 Å and 10.0 Å after heating to 300°C. On further heating to 500°C the peak was more pronounced around 10.5 Å, compared to the peak at 300°C, but the peak was still broad. The 14 Å peak, in the Bs2-Ao sample (Figure 5), shifted to a less intense and broader peak at 12.6 Å after heating to 300°C. After heating to 500°C the peak was more pronounced around 11.2 Å, with a small "side-peak" at ~10 Å indicating a slightly higher resistance to collapse and therefore probably a higher degree of interlayer filling of the mineral compared to the Bs1-Ao sample.

The untreated sample showed the same resistance to complete collapse to 10.0 Å upon heating to 300°C and 500°C (Figure 6 and 7). The less intense peaks in the untreated samples are due to the enhanced background caused by the Fe-oxides and the coarse fraction (>2 μm and <4 μm) in the sample. Comparison between the Ao-treated and the untreated samples in the Bs1 and Bs2 horizon indicated that the untreated sample had a higher degree of interlayer filling of the mineral in the Bs1-horizon. The 14.3 Å peak shifted to a broad peak around ~11.3 Å in the Bs1-U sample whereas the 14 Å peak shifted to ~10.5 Å in the Bs1-Ao sample, after heating to 500°C. In the Ao-treated sample from the Bs2-horizon the peak shifted from ~14 Å to 11.2 Å with a small peak at ~10 Å and the untreated sample shifted from 14.2 Å to a broad peak around ~11.3 Å, indicating a similar degree of interlayer filling of the minerals in the Ao-treated and the untreated samples.
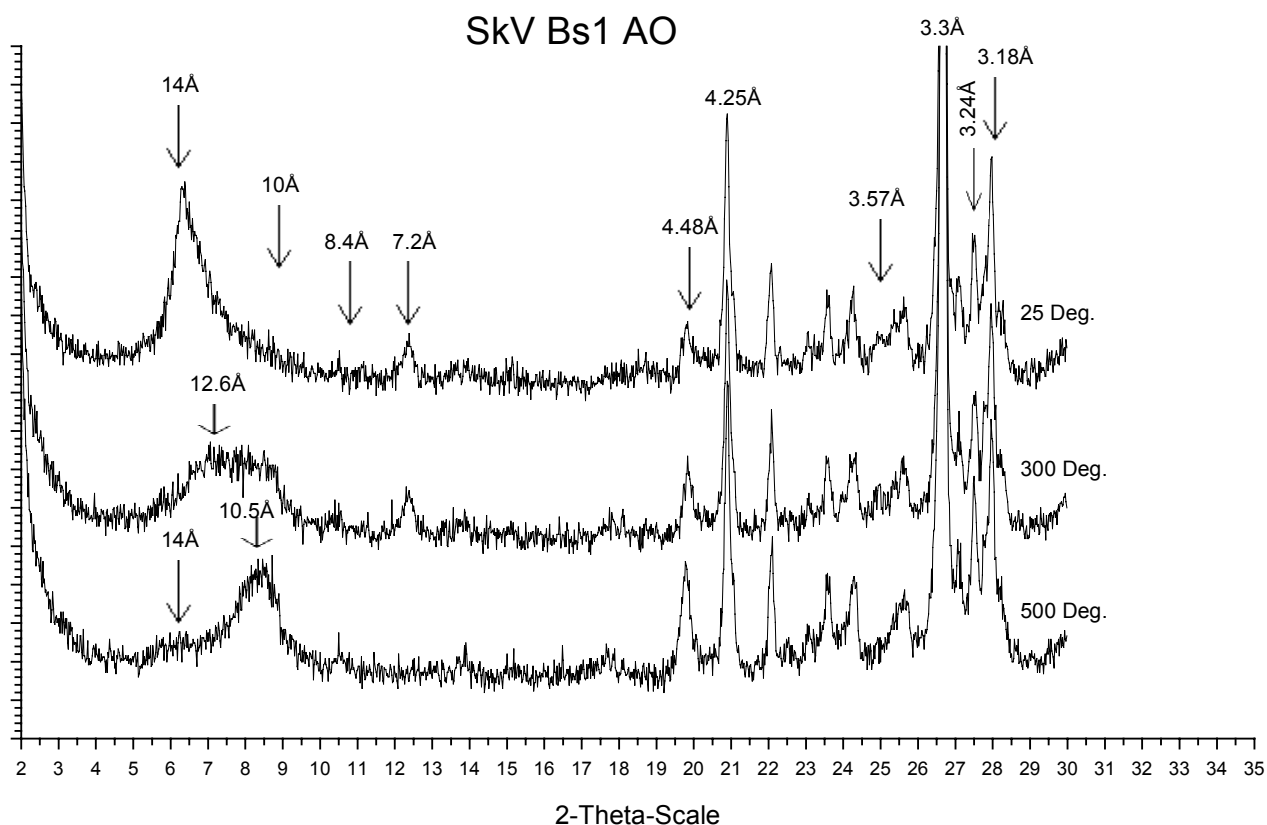

Figure 4. X-ray diffractograms of K-saturated and ammonium oxalate treated sample (Bs1-Ao) from the Bs1 horiazon at 25ºC, 300ºC and 500ºC. (Y-axis: counts per second (cps), X-axis: º2).
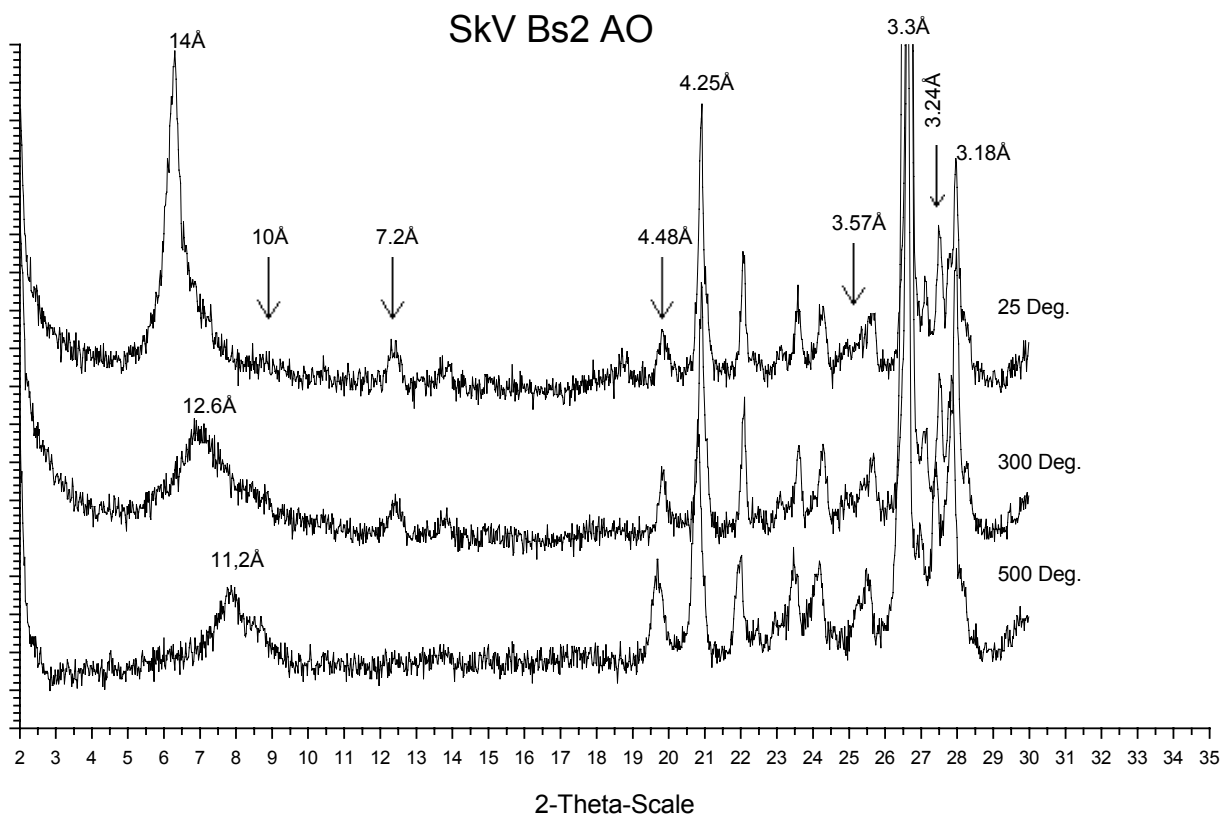
Figure 5. X-ray diffractograms of K-saturated and ammonium oxalate treated sample (Bs2-Ao) from the Bs2 horiazon at 25°C, 300°C and 500°C. (Y-axis: counts per second (cps), X-axis: °2).
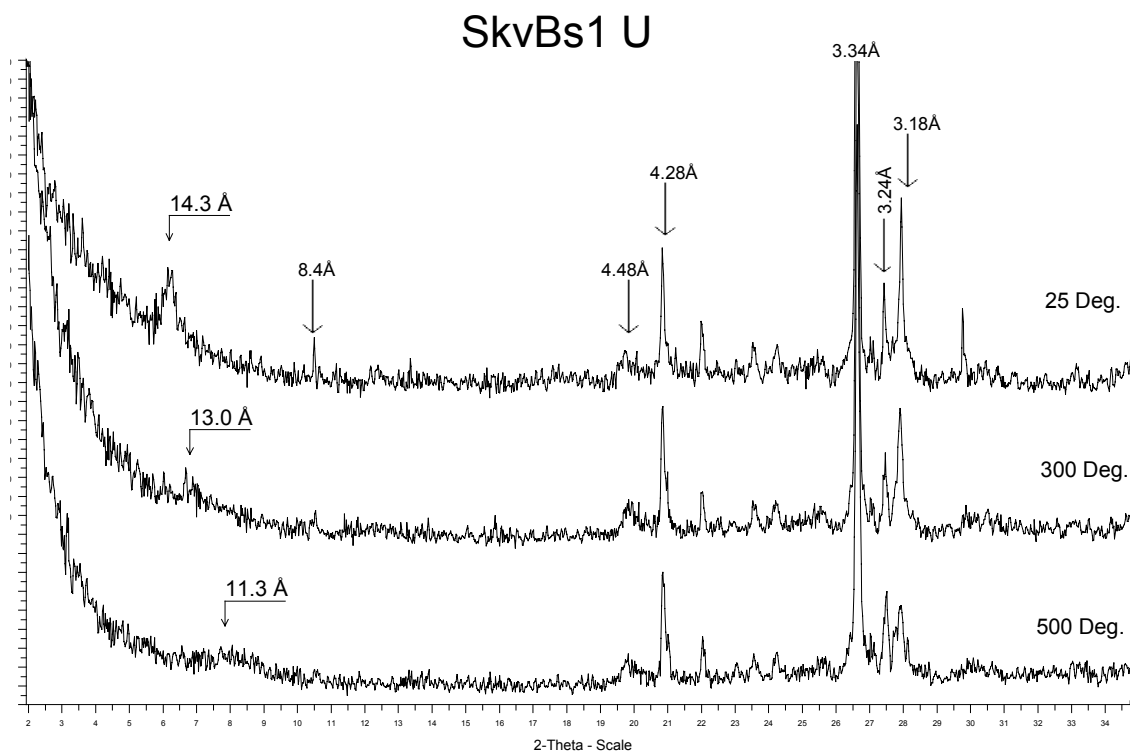

Figure 6. X-ray diffractograms of K-saturated and untreated sample (Bs1-U) from the Bs1 horiazon at 25°C, 300°C and 500°C
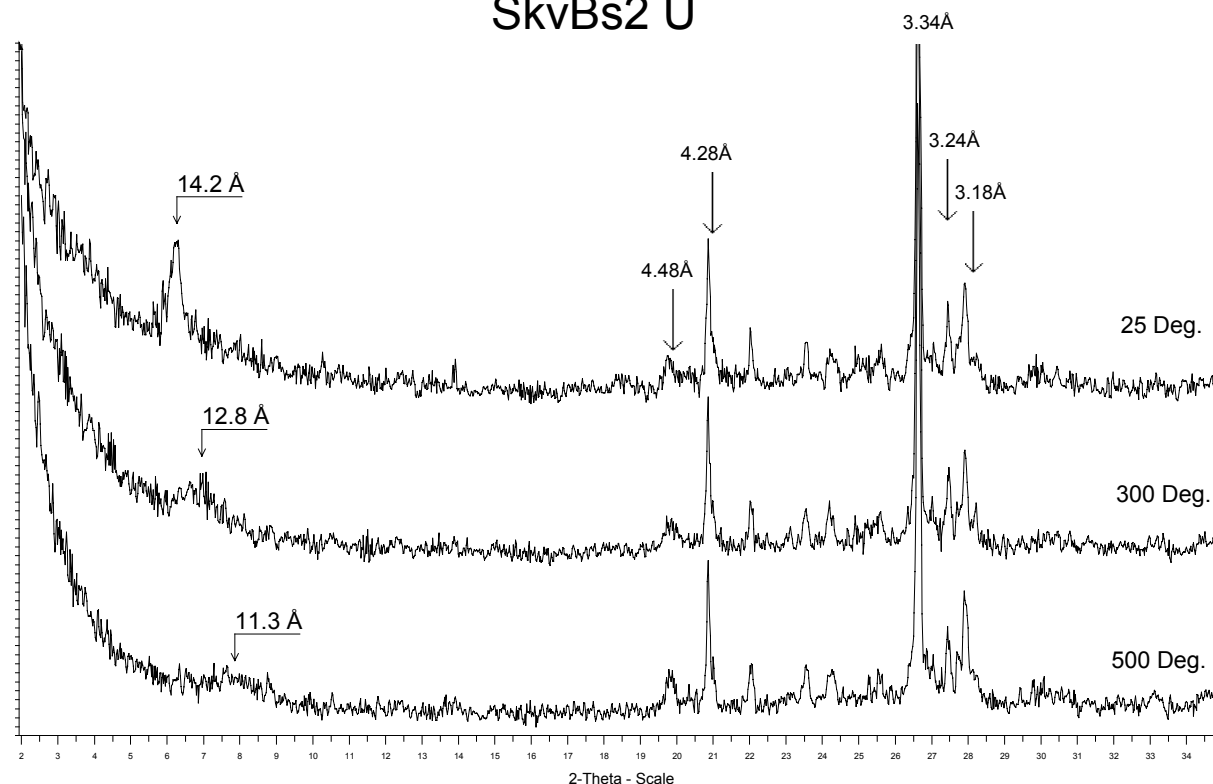
SkvBs2 U

Figure 7. X-ray diffractograms of K-saturated and untreated sample (Bs2-U) from the Bs2 horiazon at 25°C, 300°C and 500°C (Y-axis: counts per second (cps), X-axis: °2).

Other minerals in the Bh, Bs1 and Bs2 horizons

Small amounts of kaolinite were present in the Bh-U, Bs1-Ao and Bs2-Ao sample identified by peaks at 7.2 Å and 3.57 Å at 25°C and 300°C that disappeared after heating to 500°C (Olsson & Melkerud, 1989). The 7.2 Å and 3.57 Å peaks were present in the Bh-Ao sample at 25°C and 300°C as well but the peaks did not disappear after heating to 500°C, indicating presence of chlorite. However, chlorite was not definitely detected in any of the samples, because of the absence of a 14 Å peak remaining unaltered after heating to 300°C and 500°C. The absence of the 7.2 Å and 3.57 Å peaks in the Bs1-U and Bs2-U sample may be due to the enhanced background intensity or the coarser grain size (<4 μm) in the samples. The 5.0 Å peak in the Bh-Ao and Bh-U sample that was enhanced after heating to 300°C and 500°C is the 2nd order reflection of the 10.0 Å peak caused by vermiculite without interlayering. Quartz was identified in all of the samples by peaks at 4.25 Å and 3.3 Å. Potassium-feldspar and plagioclase were present in all the samples and identified by peaks at 3.24 Å and 3.18 Å, respectively. The origin of the 4.48 Å peak that was present in all of the samples is not clear. However,

the 4.48 Å peak may arise from disordered kaolinite or poorly crystalline dioctahedral micas. The 8.4 Å peak in the Bh-Ao, Bs1-Ao, Bs1-U samples indicates the presence of hornblende. The changes in intensity of the 8.4 Å peak in Figure 3c may be that crystals have been differently oriented under different conditions during the diffraction analysis.

DISCUSSION

Both the Bh-Ao and the Bh-U sample had broad peaks between 13.0 Å and 10.0 Å. As all of the soil samples in this study were only K-saturated a well-pronounced peak at 14.0 Å indicates high degree of interlayer filling and a well-pronounced peak at 10.0 Å indicates absence of interlayer filling in the mineral. The broad, low-intensity peak with a shoulder on the low-angle side indicates the presence of low or partial degree of interlayer filling in the mineral (Barnhisel & Bertsch, 1989; Sjöström & Lin, 1996). Both the Bh-Ao and the Bh-U sample required a low temperature (300°C) to shift the broad peaks completely to 10 Å, which also indicated low or partial degree of interlayer filling. The enhanced background intensity in the area between 13.0 Å to 10.0 Å indicates the presence of interlayering in the mineral

19

(Sjöström & Lin, 1996). The chemical composition and structure of the interlayer material can affect their stability (Barnhisel & Bertsch, 1989) as well as the strength with which the interlayer material is bound in the mineral. However, there were some differences in the XRD patters for the Bh-Ao and the Bh-U sample. In the Bh-Ao sample, the broad peak was divided in two peaks and the peak ~10.0 Å was more intense compared to the peak at ~13.0 Å. The result from the Bh-U sample did also show two peaks, but they were less sharp and the intensity of the peak at ~11.0 Å were lower compared to the peak at ~12.8 Å. The result may indicate that the ammonium oxalate treatment had some effect on the degree of interlayer filling. The mineral in the Bh-Ao sample had a lower or more partial degree of interlayer filling reflected by the more pronounced peak at ~10.0 Å compared with the broad, less intense peak at ~11.0 Å in the result from the Bh-U sample. However, the comparison between the results from the two samples is complicated by the presence of the Fe-oxides in the untreated sample. The Fe-oxides enhance the background and might influence the shape of the peaks. Furthermore, other factors that influence intensities are concentration of the minerals, particle size, crystal perfection, chemical composition, variations in sample packing and crystal orientation (Jackson, 1969 cited in Whittig and Allardice, 1986).

Whether the interlayered mineral is vermiculite or smectite may also influence the degree of interlayer filling and the effect of the ammonium oxalate treatment. The forested area where the soil samples were collected has previously been used for crop production. The cultivation of the originally podzolized soil makes it possible that the E horizon, containing smectite, has been mixed with the Bh horizon and that the smectite subsequently has become interlayered in the Bh horizon. K-saturated vermiculite, without interlayering, has a peak at 10 Å at 25°C (Douglas, 1989; Whittig & Allardice, 1986). Hydroxy-Al interlayered vermiculites may therefore vary between >10 Å to 14 Å. However, according to Barnhisel (1965 cited in Douglas, 1989) does hydroxy-Al vermiculite not collapse to 10 Å, rather to 11-11.5 Å. K-saturated smectite, without interlayering, has a peak at ~12 Å at 25°C (Borchardt, 1989; Whittig & Allardice, 1986). Thus, reflections of hydroxy-Al interlayered smectites vary between just above 12 Å with low or absent of interlayer filling to 14 Å with high degree of filling. However, smectite can occur as a mixed-layer mineral of illite-montmorillonite with varying degree of interlayer filling in the montmorillonite component (Reynolds & Hower, 1979). The interval between ~12

Å to 10 Å may therefore include reflections of the mixed mineral, if illite-montmorillonite is present in the Bh horizon.

The larger distance between the sheets may make the interlayer material easier to remove in smectite compared to vermiculite. Furthermore, a change to an acid pH makes smectite unstable (Borchardt, 1989) because the H_3O^+-ions may destroy part of the smectite structure (Coleman & Harward, 1953 cited in Borchardt, 1989). During part of the preparation of the soil sample the pH were acid. The pH was 3.0 during the ammonium oxalate treatment. Measurement of the pH before the H_2O_2 treatment showed that the pH were 4.8 in the Bh-Ao sample and 4.1 in the Bh-U sample. After two additions of H_2O_2 the pH had decreased to 3.8 in the Bh-Ao sample and it was as low as 2.32 in the Bh-U sample.

The expansive characteristics of smectite might affect the result of XRD analyses of the mineral. Smectite is sensitive to the change of the relative humidity (RH) in the room were the soil sample is analysed by the XRD diffractometer. Relative humidity must be carefully controlled for proper identification (Borchardt, 1989). The diagnostic peak for K-saturated smectite, at 25°C, is ~12 Å at 54 % RH (Borchardt, 1989) or air-dried (Whittig and Allardice, 1986). The "air-dried" sample may have a relative humidity above 54 % on a rainy day and that may affect the result. The small variation in the area from 10 Å to 13 Å, between the Bh-Ao and the Bh-U samples, may be due to variable spacing of smectite layers in the interstratified minerals at different levels of humidity.

If the soil sample is not well dispersed the sample will not be perfect parallel oriented. The change in intensity of the 8.4 Å peak in the Bh-Ao sample (Figure 3c) and the small variation in the area from 10 Å to 13 Å, between the Bh-Ao and the Bh-U samples, may arise from changes in orientation of crystals that were not perfect parallel oriented. Parallel oriented samples result in an enhancement of basal (00*l*) diffraction maxima. This often allows detection of small quantities of phyllosilicate species that might otherwise be obscured among more crystalline or more perfect diffracting species in the sample. The parallel oriented sample has the advantage that variations in basal spacing may be examined more critically and minor variations more easily detected (Whittig and Allardice, 1986).

The XRD analyses from the Bs1 and Bs2 horizon indicated a high degree of interlayer filling in the mineral. The ammonium oxalate treatment did not remove the interlayer or affect the degree of interlayer filling. The factors discussed above that may influence the XRD diffractogram did not affect the result because of the high degree of interlayer filling.

The interlayered mineral was most likely vermiculite because smectite has not been detected in the Bs1 and Bs2 horizon.

CONCLUSIONS

The ammonium oxalate treatment may have had some effect on the hydroxy-Al interlayered mineral in the Bh horizon but the effect was not large enough to explain the large loss of permanent charges from the clay minerals in the horizon. An alternative explanation for the loss of permanent charges may instead be complete dissolution of the finer clay particles by the acid oxalate treatment but more studies need to be done to confirm that. The ammonium oxalate treatment did not affect the hydroxy-Al interlayered mineral in the Bs1 and Bs2 horizon. There is a possibility that the hydroxy-Al interlayered mineral in the Bh horizon consisted of both hydroxy-Al interlayered smectite and hydroxy-Al interlayered vermiculite but smectite may have been dissolved during the pre-treatment of the soil sample. The hydroxy-Al interlayered mineral in the Bs1 and Bs2 horizons was most likely vermiculite.

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