SEM-EDXRA AND/OR IMMA ANALYSIS OF CUTANS, AN INDURATED HORIZON AND CLAYIFIED ROOTS IN THIN SECTIONS OF SOME DUTCH SOILS

by

E.B.A. Bisdom(1) & A. Jongerius(1)

1.- Introduction.-

During the past years a series of experiments have been carried out to complement in situ microchemical analysis of thin sections made possible with the EMA, electron microprobe analyzer (Bisdom et al., 1.975, 1.976, 1.977). Chemical elements of atomic number $\geqslant 5$ can be analysed by EMA with a magnification up to about x500. Our work was concentrated on SEM-EDXRA (Scanning electron microscope-Energy dispersive X-ray analysis) and IMMA. (Ion microprobe mass analyzer).

SEM-EDXRA.-

The scanning electron microscope (SEM) produces seemingly three-dimensional images using secondary electrons emitted from the surface of a sample after bombardment with a primary electron beam. SEM alone is not able to measure chemical elements but this can be done by combination of SEM with either an energy dispersive X-ray analyzer (EDXRA) or crystal spectrometers. Initial results of this work were presented at the "First EDAX European Users Meeting" at Liège, Belgium (Henstra et al. 1.973), and a description of the methods of analysis with different applications was treated in a later publication (Bisdom et al, 1.975).

Only heavier elements ($Z \geqslant 11$) can be analyzed using SEM-EDXRA. However, unlike EMA, analyses can be ma

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(1) Soil Survey Institute, Wageningen, Netherlands.

de on both polished surfaces and loose soil material at magnifications from x20 to x10 000, with simultaneous measurement of all elements.

EMA and SEM-EDXRA.-

Tests were carried out with EMA and SEM-EDXRA, to compare the performance of both instruments on the same material (Bisdom et al. 1.976). One of the samples tested consisted of organic matter, excrements, mineral grains and clay sized material. It appeared that heavy elements could be better analyzed with SEM-EDXRA in this type of material, whereas light element detection with EMA was only possible for oxygen in this case. C could not be measured with EMA because the surface of the insulating soil material was covered previously with C for analysis with SEM-EDXRA, and N could not be detected. In a tested iron-manganese nodule, however, EMA measurements of heavy elements were better than those obtained with SEM-EDXRA (Bisdom et al., 1.976).

IMMA .-

The ion microprobe mass analyzer accomplishes the analysis of a microvolume in a thin section of a soil by bombarding the surface with a high energy beam of ions which causes the atoms at the surface of the sample to be sputtered away. A fraction of the sputtered particles is electrostatically charged and these sputtered ions (secondary ions) are collected and analyzed according to their mass to charge ratio in a mass spectrometer. This general idea was introduced by Castaing and Slodzian (1.962), resulting in the development of a direct imaging secondary ion microscope with a non-focussed stationary ion beam as described by Rouberol et al. (1.968) and Socha(1.971).

IMMA was introduced in soil micromorphology (Bisdom et al., 1.977) because it can offer six features (Liebel, 1.975) which to a large extent can not be performed by either EMA or SEM-EDXRA, viz.:

- elemental analysis (all elements of the periodic system can be measured).
- trace concentrations (ppm and frequently even ppb concentrations can be detected in the thin section).
- trace amounts (as little as 10^{-8}g of sample material can yield a measurable mass peak).
- depth concentration profiling (determination of concentrations as a function of depth with a resolution of 50 Å while the sample is continuously eroded under ion bombardment, giving three dimensional information on the sample).
- isotopic analysis (isotopic abundance ratios can be measured with high accuracy without influence of any matrix effect).
- compound analysis (a number of compounds have been measured so far with this technique).

Some examples of SEM-EDXRA and IMMA measurements on soil material are presented in this paper. The examples are treated separately and at the end of each subject conclusions are given. For obvious reasons only a very small nomber of figures and data can be included.

2.- Homogeneity of fine grained soil materials in cutans and intergranular braces.-

Introduction .

Light microscope studies of fine grained materials in cutans and intergranular braces frequently show certain uniformity. To investigate whether this homogeneity really exists examples of such soil materials were investigated submicroscopically, i.e. with SEM-EDXRA. The samples are taken from B horizons of three soils which are respectively (Soil Survey Staff, 1.975) a Haplohumod near Lochem, a Humaquept near Horst, and a Haplaquod near Groenlo. In the Dutch soil classification (de Bakker and

Schelling, 1.966) the first soil is termed "Haar" podzol and the latter two "Veld" podzol.

SEM-EDXRA analysis.

a. Haplohumod

The B horizon of this soil is characterized by light brownish fine grained and homogeneous cutans and infillings between coarser mineral grains. In this material Si, Al and Fe were dominant, whereas K and Ti occurred in small quantities. Point analyses along traverses were made which revealed true homogeneity of the material because of a constancy in the measured element-spectra. It is possible, however, that humus is not homogeneously distributed throughout the cutanic material, but this cannot be checked with SEM-EDXRA as lighter elements cannot be measured.

b. Humaquept.

In this soil material most quartz grains are covered with oriented brownish-red fine clay-sized cutans, whereas intergranular braces of similar colour consist of clay-sized material and some silt-sized grains. Cutans of the same composition as the latter occur on a part of the quartz grains. In Fig. 1A an example is given in which a cutan is seen on the left quartz grain.

Si and Fe were found in cutans consisting of clay-sized material, together with some Al and K and sometimes Ti (fig. 1B). The clay-sized material of the intergranular brace had a similar composition, except that the quantity of Fe was somewhat higher and in some point analyses Ca was found. Similar results were obtained along other traverses.

c. Haplaquod.

A number of dark brown cutans exhibit homogeneity with the light microscope. In reality however, organic ma tter may veil the occurrence of clayey materials and often mineral compounds. The result is that light microscopic studies of these types of cutans are subject to conjecture.

SEM-EDXRA point analyses were made on a number of traverses. Al, Si and Fe were the principle elements with smaller quantities of K, Ca and Ti. Considerable differences in the height of the peaks representing elements in the spectra were found throughout the cutans.

Conclusions.

Three examples of cutans from B horizons of a Haplohumod, a Humaquept and a Haplaquod, showing a homogeneous appearence in the light microscope have been investigated with SEM-EDXRA. The cutan in the Haplohumod was homogeneous, exhibiting identical spectra of chemical elements (Al, Si, K, Ti and Fe) at all analyzed points.

The clay-sized cutans in the Humaquept appeared also to be homogeneous as did the intergranular braces although the latter have a slightly different composition (somewhat higher Fe and in some parts Ca).

The third example was an ↕ examination of a cutan which under the light microscope gave the impression of consisting of humic material. SEM-EDXRA measurements indicated, however, with relative certainty, that clayey material and iron compounds were also present in various ratios throughout the cutan.

3. - High Al-concentrations in a Haplaquod -

Introduction

Conventional chemical analysis of loose soil material demonstrated high Al concentrations in a Haplaquod ("Veld" podzol) near Groenlo, Netherlands. The B-horizon of this soil is strongly indurated a feature assumed to be caused by the excess of Al in the soil. If Al was responsible for the induration, high concentrations of it would be expected in the intergranular braces.

SEM-EDXRA AND/OR IMMA ANALYSIS OF CUTANS

SEM-EDXRA measurements on thin sections of this soil material demonstrated that Al, Si, K and Fe were present in the intergranular braces, but the quantities were not very high. However, preliminary analyses pointed to a dominant role of organic matter in the concentration of high Al contents in the Haplaquod.

Knowing this, the following types of materials occurring in the profile, were analyzed:

- The organic matter in the O_2 horizon.
- Organic matter in root mats.
- dark brown free grain cutans and infillings of intergranular spaces.
- reddish free grain cutans, predominantly consisting of amorphous humus.

O_2 horizon

Some humified plant remains, fungal fruiting bodies and faecal pellets were analyzed with SEM-EDXRA. Al and Si were the main elements, Ca was found in small amounts, whereas Fe occurred sporadically in very small quantities. Half of the points analyzed showed a higher than normal Al concentration.

Organic matter in root mats.

Several of such predominantly strongly humified root mats are present in the B horizon of the investigated profile. SEM-EDXRA analysis performed o several mats between 15 and 50 cm depth revealed that the Al concentration was high, with peaks over three times the height of those of Si (Fig. 2A), whereas Al normally has a peak height twice that of Si (Fig. 2B) in this material. The lowest Al concentrations found were those in which peak heights for Al and Si were the same (Fig. 2C).

It should be noted that high Al concentrations were not found (except in one point analysis) in the strongly humified root remnants occurring in the A_2 horizon.

Dark brown free grain cutans and infillings of intergranular spaces.-

This is the type of material described in section 2c where the homogeneity of dark brown cutans was discussed. Al concentrations are again much higher than normal, i.e. usually at least equal peak heights for Al and Si (Fig. 2C), and in occasional points Al peaks double the height of those of Si.

Reddish free-grain cutans, predominantly consisting of amorphous humus.-

SEM-EDXRA analyses of the fine soil material exhibit normal peak heights for Al, viz. half those of Si (Fig. 2D), varying quantities of Fe, some K and sometimes Ca or Ti in very small amounts.

Conclusions.

The analyses show that Al is concentrated mainly in the strongly humified root mats. Significant amounts of Al are also found in the dark brown cutans and infillings but these occur only locally. By contrast, the Al content is normal in the thin reddish free grain cutans which envelop nearly all skeleton grains. From these facts it may be concluded that Al is not the indurating agent in the B horizon of the Haplaquod.

4.- Clayified roots.-

Introduction.

The concept of clayified root was introduced in soil micromorphology by Parfeñova et al, (1.964). According to these authors the phenomenon was rare and probably caused by a more complex process than a simple infilling of the root with material moved from other parts of the profile. They envisaged reactions between colloidal solutions -introduced into the root tissue without disturbing its ana tomical structure - and decomposition products of the decayed root itself, leading to the formation of secondary clay minerals inside the root.

The mechanism enabling the formation of this "biogenic" or "organic clay" was suggested by Polynov (1.956), and Kononova (1.961). In this model adsorptive compounds were formed by combination of organo-mineral (Al, Fe, Si) complexes and clay minerals. The adsorptive compounds were named "argyllite" by Kononova (1.961) and considered to be of biogenic origin by Parfenova et al,. (1.964).

Description of clayified roots in a Dutch humaquept

Clayified alder roots were found in a Humaquept near Bathmen, Netherlands. The roots consist of humified remnants of the original tissue and yellow to brown rather homogeneous fine grained material (Fig. 3A). In the latter oriented clayey substance could be discerned at several places (Fig. 3B).

SEM-EDXRA and IMMA analyses.

Initial analyses of clayified roots were made with SEM-EDXRA. All point analyses showed Al, Si, K, Ca, Ti and Fe, whereas about half gave S and Cl in addition. Al and Si were the main components and Si the principal one. Fe was present in small or moderate amounts, whereas S, Cl, K, Ca and Ti were found in small or very small amounts. These data thus provided information on the nature and distribution of heavier elements in the clayified root, but no light elements specific for organic matter could be measured with this instrumentation. After comparison of SEM-EDXRA and EMA measurements (Bisdom et al,. 1.975), IMMA was used for analysis of organic material in thin sections (Bisdom et al., 1.977). For technical information the reader is referred to the papers quoted in the introduction.

Analogue ion spectra and ion images.

IMMA analogue ion spectra were made from points and ion images from areas in the clayified root. Positive ion spectra demonstrated H, Li, B, C, N (with some CH_2), O, Na, Mg, Al, Si, P, S (with some O_2), K, Ca, Ti, V, Cr, Fe, Mn and Ni whereas the negative secondary ion spectra exhibited H, C, O, F, Cl, as well as molecular ions of OH, CH, C_2H, CN (with some C_2H_2) and CO (Bisdom et al,. 1.977).

Positive ion images were made of ^{1}H(*) (Fig. 4), ^{12}C, ^{14}N, ^{16}O, ^{23}Na, ^{24}Mg, ^{27}Al, ^{28}Si, ^{31}P, ^{39}K, ^{40}Ca, ^{48}Ti, ^{52}Cr, ^{55}Mn and ^{56}Fe, and negative ion images from ^{1}H, ^{12}C, ^{24}C, ^{13}CH, ^{16}O, ^{19}F and ^{35}Cl. The digits refer to mass numbers.

Conclusions.

The following conclusions can be drawn from these IMMA, SEM-EDXRA and light microscipic data.

Light microscopic observations showed in situ formation of clayey material at some sites in the alder root. So far no X-ray diffraction studies could be made of the material in the root. Analyses with IMMA indicated a rather homogeneous distribution of elements throughout the clayified root, independent of measurements done in areas with newly formed clayey material or sites with rather high percentages of decayed root tissue. This possibly indicates that organic compounds, apart from the few pieces of visible organic matter, are also present in areas with newly formed clay. This agrees with the hypothesis of Parfenova et al., (1.964) which suggests that organic matter may play a role during the formation of secondary clay minerals. It remains an open question, however, whether this is an active role leading to the formation of biogenic clay (Parfenova et al, 1.964), or a passive one whereby the organic components only represent one of the factoros in an environ

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*) Hydrogen is measurable with IMMa but not with SEM-EDXRA and EMA

ment favourable for the formation of secondary clay minerals.

SUMMARY

Cutanic material often has a homogeneous appearance when examined with the light microscope. SEM-EXDRA measurements reveal, however, that if organic matter is present it may conceal heterogeneous distribution of other compounds.

SEM-EXDRA showed also that induration of the B horizon of a Haplaquod is not causes by the high Al content present in this soil. This Al appeared to be mainly concentrated in the strongly humified root mats occurring in this soil.

Light microscope investigations of clayified roots showed evidence of newformation of clayey material. IMMA and SEM-EXDRA analyses of the fine grained brownish substances occurring in these roots revealed that organic compounds are present together with a large number of heavier elements. This suggests that organic compounds can play a role during newformation of clayey material.

Figures

Fig. 1 SEM-EDXRA techniques applied to a thin section of a Humaquept, near Horst, Netherlands. (A). Cutan on quartz grain with adjoining intergranular braces. (B). Al, Si, K, Ti and Fe measured in the cutan.

Fig. 2 SEM-EDXRA analysis of a Haplaquod, near Groenlo, Netherlands. This soil exhibits various degres of Al concentrations (A-D). (A). Al-peak over three times as high as that of Si. (B). Al-peak about twice as high as Si. (C). Al and Si peaks are equally high. (D). Al-peak height half of that of Si (compare text).

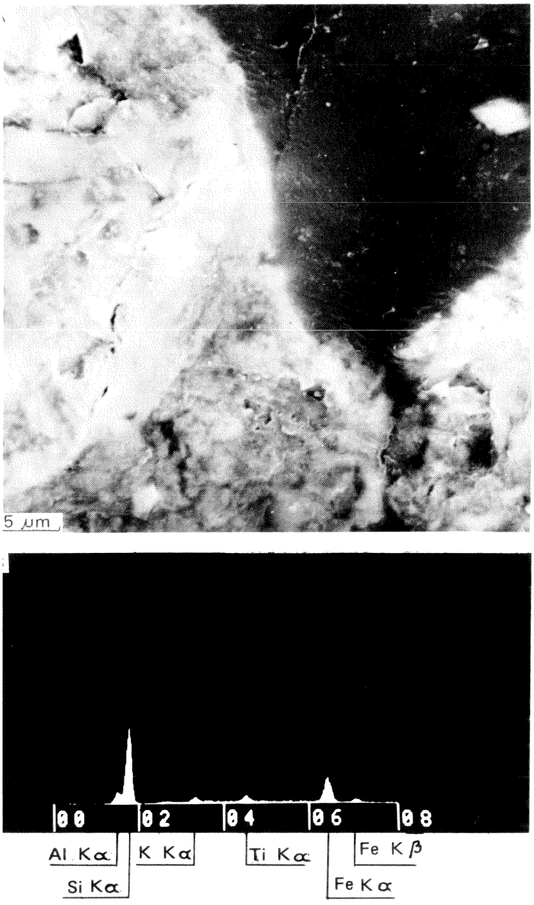
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Fig. 1

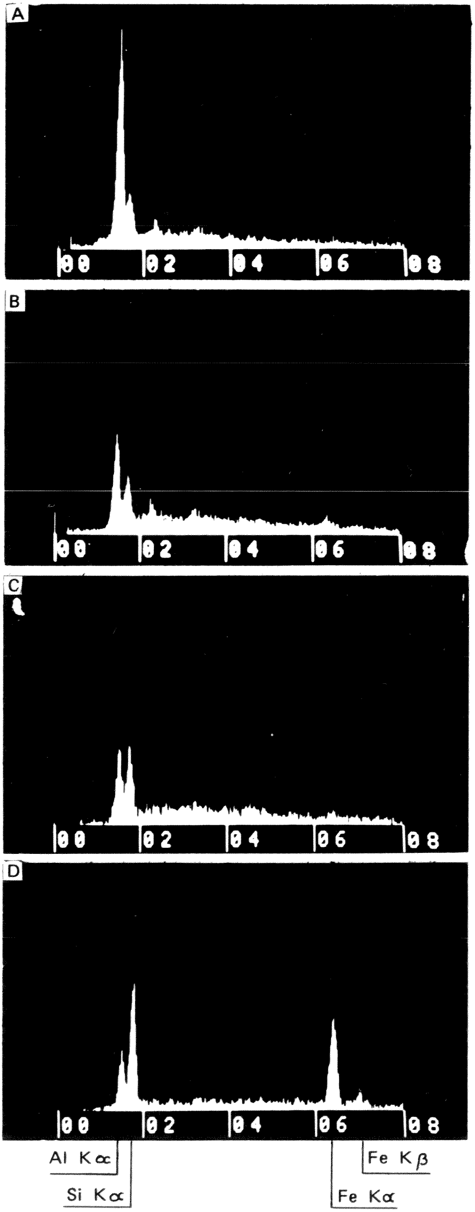
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Fig. 2

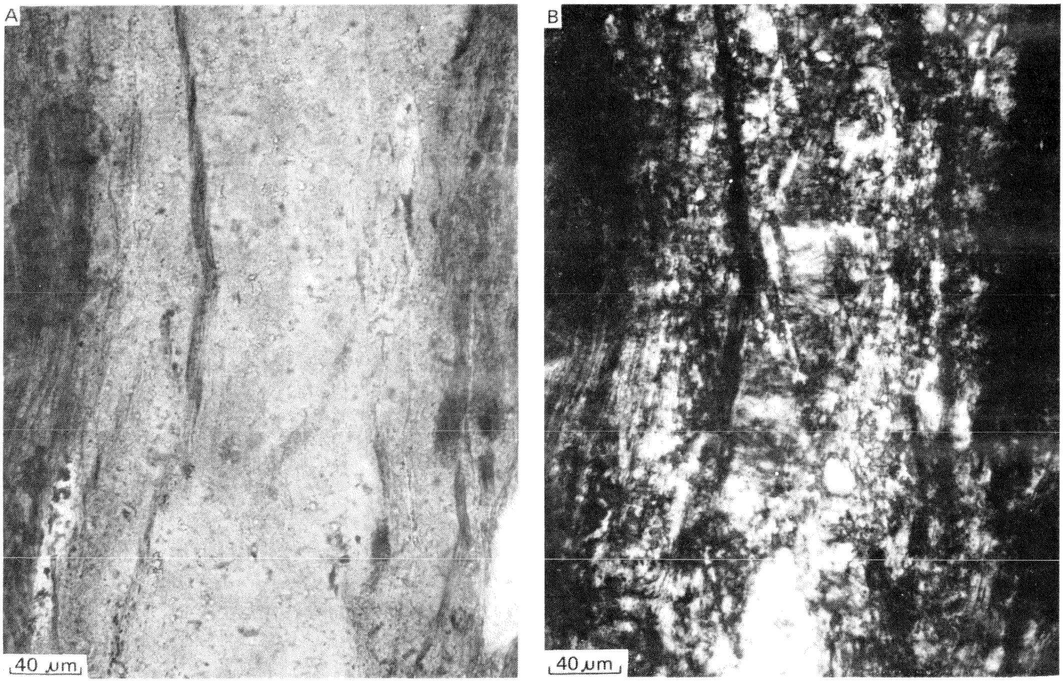

Fig. 3

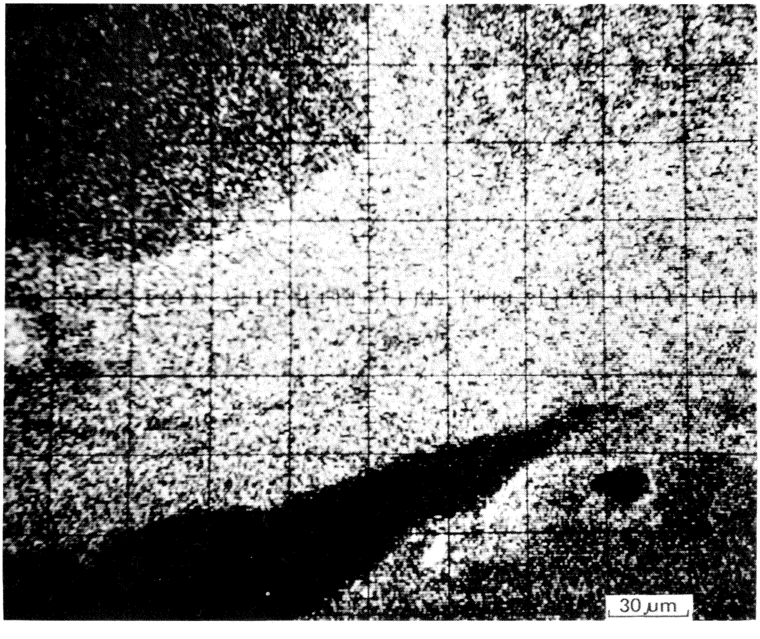

Fig. 4

Fig. 3 Clayified root in Hymaquept, near Bathmen, Netherlands. (A). Fine grained material in normal transmitted light. (B). The same image under crossed nicols, exhibiting booklets of newly formed clayey material.

Fig. 4 IMMA ion image of H^+ in the clayified alder root.

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