

Energy-dispersive X-ray analysis on thin sections and unimpregnated soil material

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Summary

A combination of scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXRA) was used in the study of soil materials. The investigation in situ of components in thin sections was used to estimate chemical elements with atomic numbers 11 upwards, from sodium on. EDXRA could detect chemical elements up to magnifications of $\times 10\,000$. The composition of amorphous and micro-crystalline materials cannot be estimated in thin sections by light microscopy but by this technique was clearly displayed. Composition of loose soil material can also be investigated. The material that could be studied by SEM-EDXRA did not need high polishing of the thin section, and the plastic used for impregnation of the soil material was not affected by the investigation.

Identification of chemical elements in situ, high resolution of the topographic image and relatively short testing times for the elements make this combination of techniques useful for soil research.

Introduction

Micromorphology of soils is the microscopic study of undisturbed soil samples. Thin sections are prepared from plastic-hardened soil samples. Our preparations are about 15×8 cm large and $15\ \mu\text{m}$ thick (Jongerius & Heintzberger, 1963). This thickness of the section is necessary to enable light to pass through the sample and to study soil characteristics by light microscopy. Many crystalline and amorphous materials, fabrics and other micromorphological features can be identified. A difficulty is that the resolution of the light microscope is limited: certain particles are too small to investigate as separate entities. Consequently other techniques must be used to identify these fine materials. By chemical analysis, X-ray diffraction and transmission electron microscopy, we can identify and characterize most of the submicroscopic soil components. Considerable information about clay minerals has been gathered in this way. These techniques are, however, mainly used with loose and disturbed soil material. For the study of submicroscopic and larger fractions in undisturbed state, other instruments are required.

Bocquier & Nalovic (1972) give a detailed account of the literature on instruments and methods for the characterization in situ of soil material. Two instruments which are in common use are the scanning electron microscope (SEM), which can be equipped with a system for analysing chemical elements (WDXRA or EDXRA) and the electron microprobe analyzer (EMA). The EMA operates with a wavelength-dispersive X-ray analysis system (WDXRA). These instruments have been used in previous research by several workers (Bocquier & Nalovic, 1972; Cescas et al., 1968; Delvigne & Martin, 1970; Gillespie & Elrick, 1968; Gillespie & Protz, 1972; Hill & Sawney, 1971; Innes & Pluth, 1970; Jeanson, 1966, 1969; Leroux et al., 1970; Quershi et al., 1969; Rutherford, 1969; Sawney, 1968; Sweatmann & Long, 1969; Veen & Maaskant, 1971).

For our purpose a combination of energy-dispersive X-ray analysis (EDXRA) and SEM was found to be more suited. This method has been used by McCrone & Delly (1973) to analyse loose minerals and industrial materials. The first results with SEM-EDXRA in soil micromorphology were presented at the 'First EDAX European Users Meeting' at Liège, Belgium (Henstra et al., 1973).

The SEM-EDXRA method has the following advantages over SEM-WDXRA or EMA:

- All peaks representing the elements Na to U can be displayed simultaneously. That allows a quick comparison between various samples and of spots within a sample;
- There is less beam damage, which is important for the study of plastic-impregnated thin sections;
- Rough surfaces can be studied.

Disadvantages are:

- Light elements (lower than Na) cannot be detected. There are, however, at present windowless detectors on the market which can also measure some of these light elements;
- The energy resolution is lower, so that peaks which are close to each other cannot be separated. See the section on instruments for details.

Instruments

The study used a Jeol-JSM-U₃ scanning electron microscope with an EDAX system consisting of a Si (Li) detector with a 707A-type multichannel analyzer (Fig. 1). The construction of the SEM is similar to that of the EMA and is based on the principles of Knoll (1935) and Von Ardenne (1938). The EMA was marketed in 1959 and the SEM in 1964. In both instruments a specimen is scanned by an electron beam and the following signals are emitted at the point of impact of the primary electron beam (Fig. 2):

- emitted electrons: secondary electrons with an energy of ≤ 50 eV and back-scattered electrons with an energy of > 50 eV;
- X-rays: a continuous spectrum (Bremsstrahlung) and characteristic X-rays (line spectra);
- ultraviolet, visible and infrared radiation.

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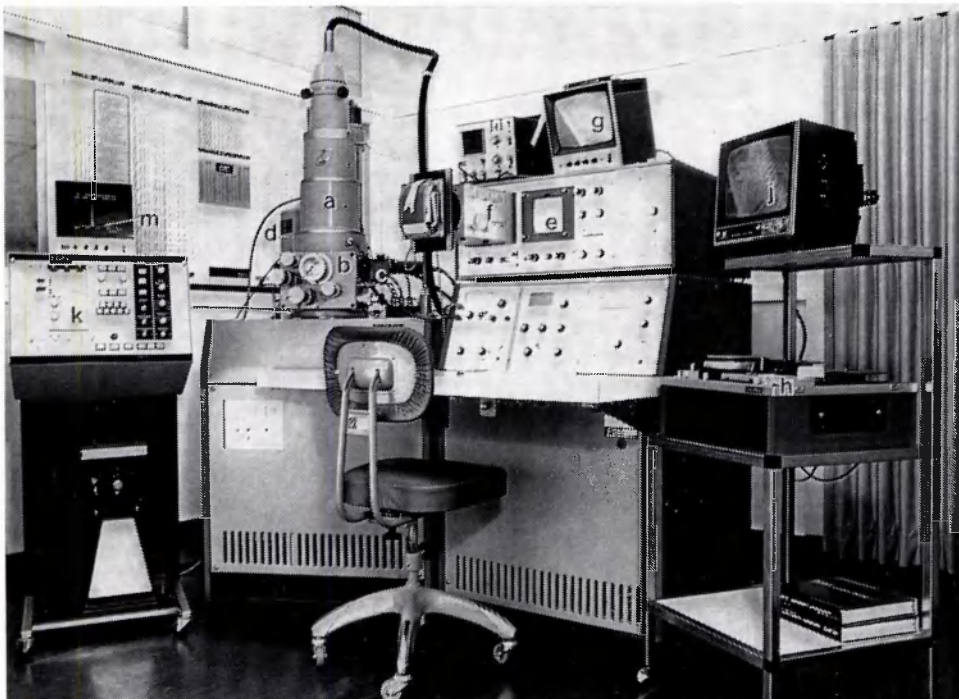


Fig. 1. Description of instruments.

In this case, a scanning electron microscope (SEM) from Jeol, type JSM-U₃, was equipped with an EDXRA system from EDAX consisting of a 707A multichannel analyzer and a Si (Li) detector with 169 eV resolution. The main unit of the SEM contains the electron optical column (a), the specimen chamber (b) and the detector for secondary electrons (c) and X-rays (d). The specimen is inserted in the specimen chamber by an airlock system.

The secondary electron signal is amplified and can be used to modulate the brightness of the electron beam within the 2 cathode ray tubes with a small screen. The right screen is used for display (e) and the left one, obscured by the camera (f), for photography.

If the specimen is scanned at TV speed, we get a continuous image on the large screen of a TV monitor (g). This method facilitates quick positioning of the desired area. A recording of this TV image can be made on a video recorder (h), which is provided with a monitor (j).

The X-ray signal is detected by a solid-state detector, a lithium-drifted silicon crystal, and the various wavelengths are separated according to their energies by electronic discrimination (EDXRA). Usually a multichannel analyzer (k) is used for recording the whole spectrum of pulses and the result is displayed simultaneously on the monitor (m). Part of the spectrum can be used to produce X-ray images of various elements. These images can be displayed on the cathode ray tubes of the SEM (e).

These signals can be used to form an image on the screen of a cathode ray tube (CRT) (Fig. 1, e) by the synchronous displacement of the CRT beam, the brightness of which is modulated by one of these signals. If the secondary or back-scattered electrons are used, we get a topographic image of the specimen. This is possible both by SEM and EMA.

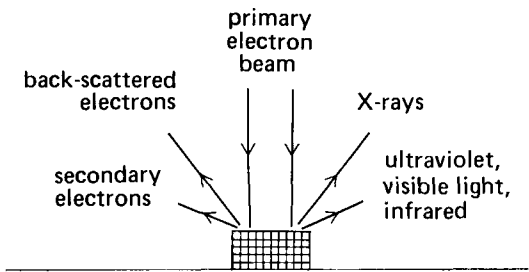


Fig. 2. Types of radiation produced by electron bombardment.

The X-ray spectrum consists of X-rays of different wavelength and energy, a continuous spectrum (Bremsstrahlung). There are, however, also characteristic X-rays with a definite energy or wavelength. Electrons of high energy can remove electrons from the inner shells of atoms. If an electron of the K shell is removed and is filled up by an electron of the L shell, a definite amount of energy is emitted as K_{α} radiation with characteristic parameters. If this new electron comes from the M shell, it is called K_{β} radiation. The energy of K_{β} rays is higher than of the K_{α} rays. The probability, however, that electrons are going from the M to the K shell is much lower than from the L shell to the K shell. Therefore K_{β} peaks are always lower than K_{α} peaks.

In the EMA, an instrument constructed for analysis, the sample is scanned by an electron beam with a minimum diameter of the order of $0.1 \mu\text{m}$. The importance of this instrument lies in the emitted X-rays which are detected by a wavelength-dispersive spectrometer. The nature of the element is determined by the wavelength of the radiation according to the Bragg equation,

$$n \lambda = 2d \sin \theta$$

where n is an integer, λ the X-ray wavelength, d the interplanar spacing and θ the diffraction angle.

The current of the electron beam lies between 10^{-6} and 10^{-8} A. Two or more spectrometers can be installed, working simultaneously. All the elements from boron ($Z = 5$) on can be analysed. If we use the secondary or back-scattered electrons to produce a topographic image, the resolution is poor because of the probe size.

The SEM is constructed as a microscope to produce topographic images of high resolution. This high resolution is obtained by the much smaller probe size, which is about 10 nm or less. For the detection of X-rays, this instrument can be equipped with either an EDXRA system or one or more WDXRA spectrometers, and in some types a combination of these two. The detector of the EDXRA is much more sensitive than the gas-flow counter used for WDXRA. The current of the electron beam on the specimen is about 10^{-11} A for EDXRA and 10^{-7} A for WDXRA. This higher current of the electron beam can damage temperature-sensitive mate-

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Table 1. Comparison of EDXRA and WDXRA systems.

	EDXRA	WDXRA
Current of electron beam (A)	10 ⁻¹¹	10 ⁻⁷
Surface of specimen	rough	polished
Topographic image	high resolution	poor
Energy resolution (eV)	> 150	< 20
Detection limit	Na . . . U (with a windowless detector, the lower limit is Z = 6 (carbon))	B . . . U

rials. Each system has its own merits and disadvantages, as listed in Table 1. Detailed technical information is given by several authors (e.g. Birks, 1971; Malissa, 1966; McCrone & Delly, 1973; Seiler, 1974; and Anon., 1972).

If the combination of SEM and EDXRA is used, all the images, except the energy peaks, are displayed on the CRT of the SEM (Fig. 1,e). These images are a secondary electron image, an X-ray image and a line scan.

X-ray images are produced with part of the energy spectrum, e.g. K_α radiation of a certain element, to modulate the intensity of the beam in the CRT. This peak can be selected from the entire spectrum with a 'window'.

The line scan gives the distribution of an element along a certain straight line. Energy peaks are displayed on the monitor (Fig. 1,m) and represent the chemical composition of an area or point of the sample.

Procedures for identification of soil components

SEM-EDXRA methods can be used for thin-section investigation where no reliable identification of soil components is possible by light microscopy. Such a problematic part of the exposed thin section is coated with a layer of carbon thick enough to make the thin section conductive and thin enough to keep absorption of X-rays as low as possible. A thickness of about 50 nm has proved suitable. A SEM picture is then made of the surface and the area found for analysis.

The lowest magnification of SEM is about ×20 and it can frequently be used for soil samples up to about ×10 000. Exceptionally a magnification of ×30 000 could be achieved. This instrument gives a secondary electron image of the surface of the thin section, so that height differences and roughness of the surface can be seen on SEM pictures. This information cannot be obtained with the light microscope.

The height differences and the roughness of the surface are, of course, differently expressed in SEM photographs of unimpregnated undisturbed soil materials and those from thin sections. Thin sections can be polished or studied directly after the grinding procedure. Height differences are always rather poorly expressed. SEM photographs of cohesive soil materials not impregnated with plastic show differences in height and roughness associated with the natural surfaces.

The instrument used for identification *in situ* is the EDXRA. It can detect chemical elements from sodium ($Z = 11$) on. Consequently H, He, Li, Be, B, C, N, O, F and Ne cannot be detected with our instrument. At present, however, instruments are being introduced to the market that can also detect elements with low atomic numbers, with non-destructive and destructive methods. The destructive method allows for the gradual and continuous removal downwards of the material in a certain point in the thin section. The destructive methods of the 'ion microprobe analyzer' (IMA) (McCrone & Delly, 1973), and SEM combined with laser beam (Magee et al., 1974), allow testing of subsequent levels in the thin section.

EDXRA measurements of the surface of thin sections start with a display of the peaks for elements on the monitor screen (Fig. 1,m). The height of the peaks gives a rough estimate of the amount of the elements present: small, moderate and large amounts of chemical elements.

We used the following procedure.

– The first step was to find out which chemical elements were present in the area displayed on the screen of the SEM (Fig. 1,e). The peaks of these elements were given on the monitor screen (Fig. 1,m).

– The next step is to find the position of the various elements in the area (Fig. 1,e). The SEM photograph is replaced by an X-ray image of the same area. White dots of the X-ray image indicate the position and amount of a particular element. For instance, four elements require four X-ray images, each representing the position and distribution of one element. A high density of white dots indicates a large amount of an element in the area. For small amounts, no X-ray image can be obtained.

– This problem can often be overcome by point analysis, which can indicate minute amounts of elements at a certain spot. Peaks of the elements present at such a spot can be read on the monitor screen (Fig. 1,m). The point being tested is visible on the screen (Fig. 1,e).

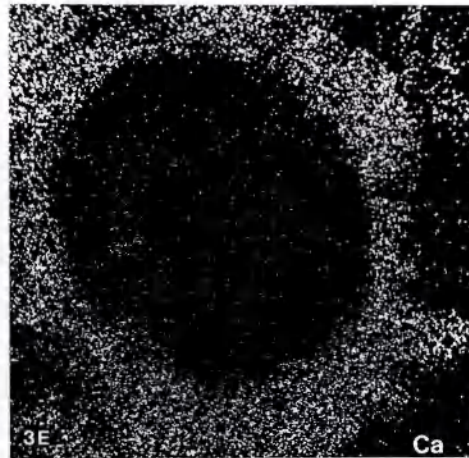
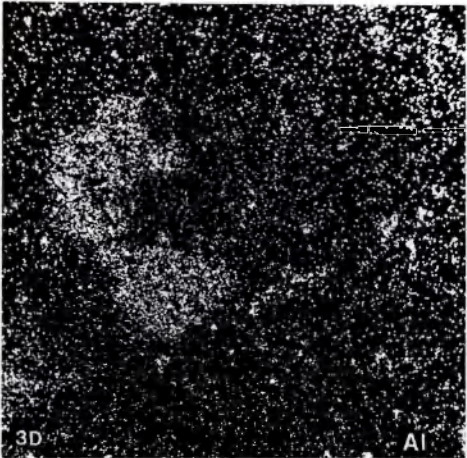
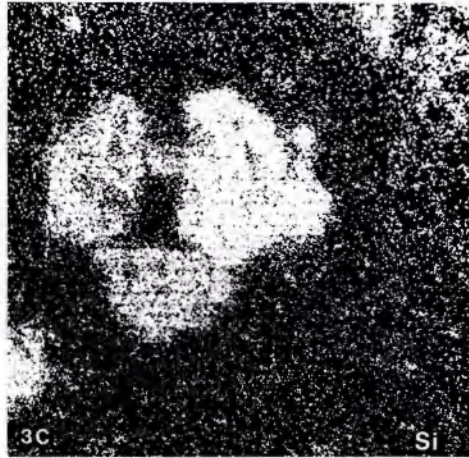
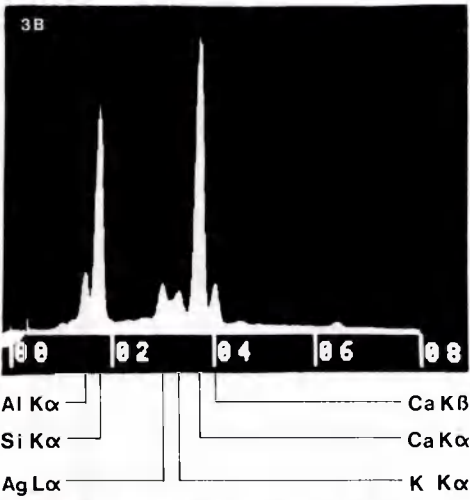
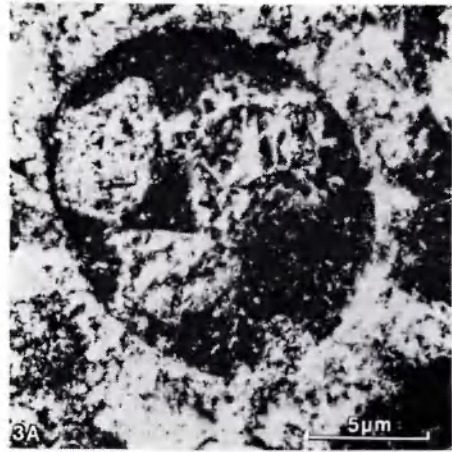
– A fourth possibility is the line scan, which is displayed on the CRT of the SEM (Fig. 1,e). It gives the distribution diagram of a certain element along a line.

Combination of SEM and EDXRA is applicable for research on amorphous and crystalline materials in thin sections. The techniques can also be used for unconsolidated soil materials. In such samples, point analysis is in general the only possible EDXRA test. X-ray images and line scans are frequently impossible because of the rough surface of the unconsolidated material. SEM photographs of loose material are, however, better than those of thin sections because of the difference between natural and polished surfaces.

Combination of SEM and EDXRA with light microscopy of thin sections is possible because SEM-EDXRA instruments can start at $\times 20$: an area of a thin section can be studied at similar magnifications with the light microscope and SEM-EDXRA. In general, a problematic field is photographed with the light microscope, which is thereafter used to recover the same area on the screen of the SEM (Fig. 1, e). Thereafter the magnification of the field can be increased beyond that possible with the light microscope: EDXRA could work to $\times 10\,000$ and SEM alone to $\times 30\,000$ for soil research.

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Fig. 3. SEM-EDXRA techniques with a thin section of a Gley soil, near Bathmen, Netherlands. A. Secondary electron image of three 'grains' in a root channel. B. Indication that Al, Si, K and Ca are present in the sample. Ag was used to attach the thin section to the specimen stub. Three 'grains' contain Si (Fig. 3C), two Al (Fig. 3D) and the root itself is surrounded by Ca (Fig. 3E).



Examples of the methods

An example of SEM-EDXRA with thin sections is given in Fig. 3A–E : a Gley soil or Humaquept (Anon., 1973) near Bathmen, Netherlands. The secondary electron image of the surface of the thin section shows three 'grains' inside a root channel. Under the light microscope, one of the 'grains' in the root channel proved to be quartz, whereas the other two 'grains' gave the impression of consisting of clay. The material that surrounded the root channel consisted of carbonate, whose particle size was too small for measurement with the light microscope.

The secondary electron image of the area is shown in Fig. 3A; a display of the energy peaks (representing the chemical elements) on the monitor screen (Fig. 1,m) is given in Fig. 3B; a Si – K_{α} image in Fig. 3C; an Al – K_{α} image in Fig. 3D; and a Ca – K_{α} image in Fig. 3E. Silver was measured (Fig. 3B), because it was used to attach the thin section to the specimen stub.

Aluminium is present in two grains in the root channel (Fig. 3D). Silicon was found in all three grains (Fig. 3C), but one of them had more. Because aluminium is absent in this grain, it must be the quartz grain identified with the light microscope. These data show that two grains consist of clayey material (both Al and Si) and that the third grain consists of silica. This result is in good agreement with light microscopy. To determine the nature of the clayey material, the EDXRA method would have to be combined with X-ray diffraction.

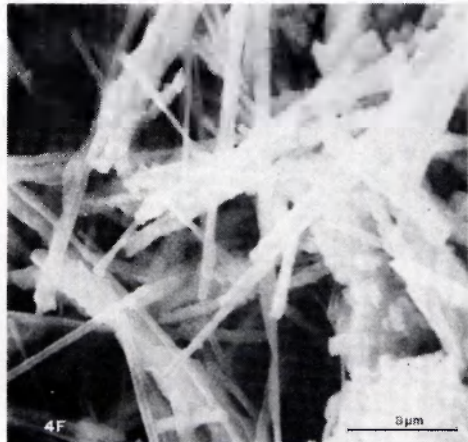
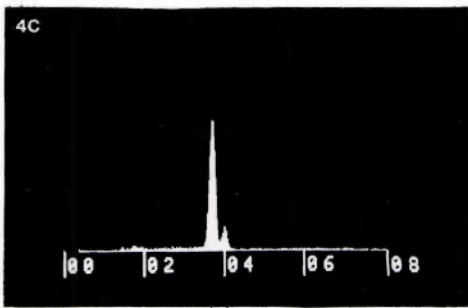
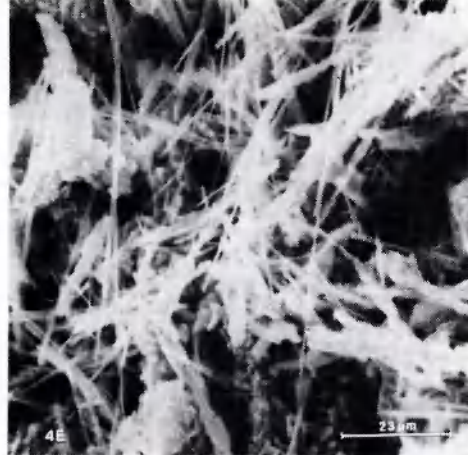
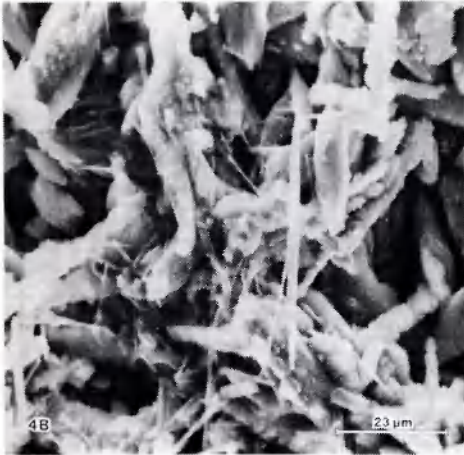
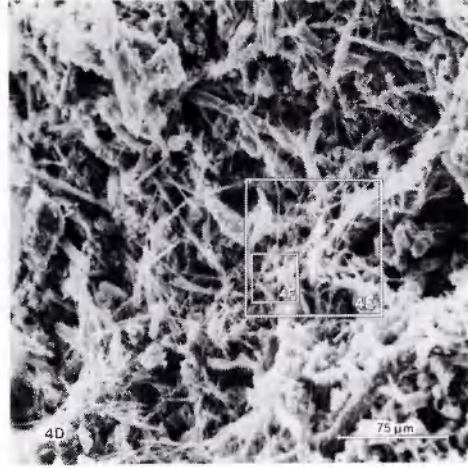
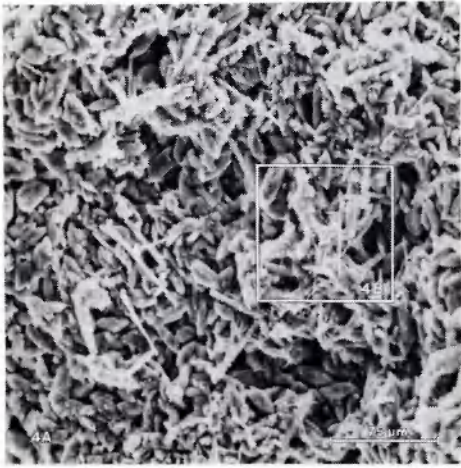
The material around the root channel contained calcium. Though carbon and oxygen cannot be detected with EDXRA in CaCO_3 , because of their low atomic numbers, light microscopy showed that the material was carbonate. Therefore it consisted of pure calcite.

The next examples are with loose soil material. The first sample is from a Red Mediterranean soil, a Rhodoxeralf (Anon., 1973) near Mérida, Spain. In Fig. 4A, needle-shaped carbonate is present amongst scalenohedro-rhombohedral calcite crystals, whereas in Fig. 4D of the same sample and with the same magnification needle-shaped crystals predominate. Details of the morphology of these needles are given in Fig. 4B, 4E and 4F. With EDXRA (Fig. 4C), only Ca could be detected, so that these needles (sometimes called lublinites) could be identified in situ as calcite. They would be difficult to separate for X-ray diffraction.

The second example of loose material is the mineral vivianite ($\text{Fe}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$) in a peat soil, a Histosol (Anon., 1973) in the Province of Drente, Netherlands. Of these elements, Fe and P can be measured (Fig. 5A). The intention was to investigate the morphology of the mineral, which is generally described as prismatic. SEM pictures (Fig. 5B, 5C and 5D) show that several cleavage directions can be seen. The larger magnifications show that a certain curvature exists in the fibers of the mineral, which seem to be inside the prisms. Very fine threads are dis-

Fig. 4. SEM-EDXRA of loose material from a Red Mediterranean soil near Mérida, Spain. A, B. Some needle-shaped carbonate and scalenohedro-rhombohedral calcite crystals. C. Calcium is the only measurable component in the needles. D, E, F. Needles predominate.

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Ca K α Ca K β

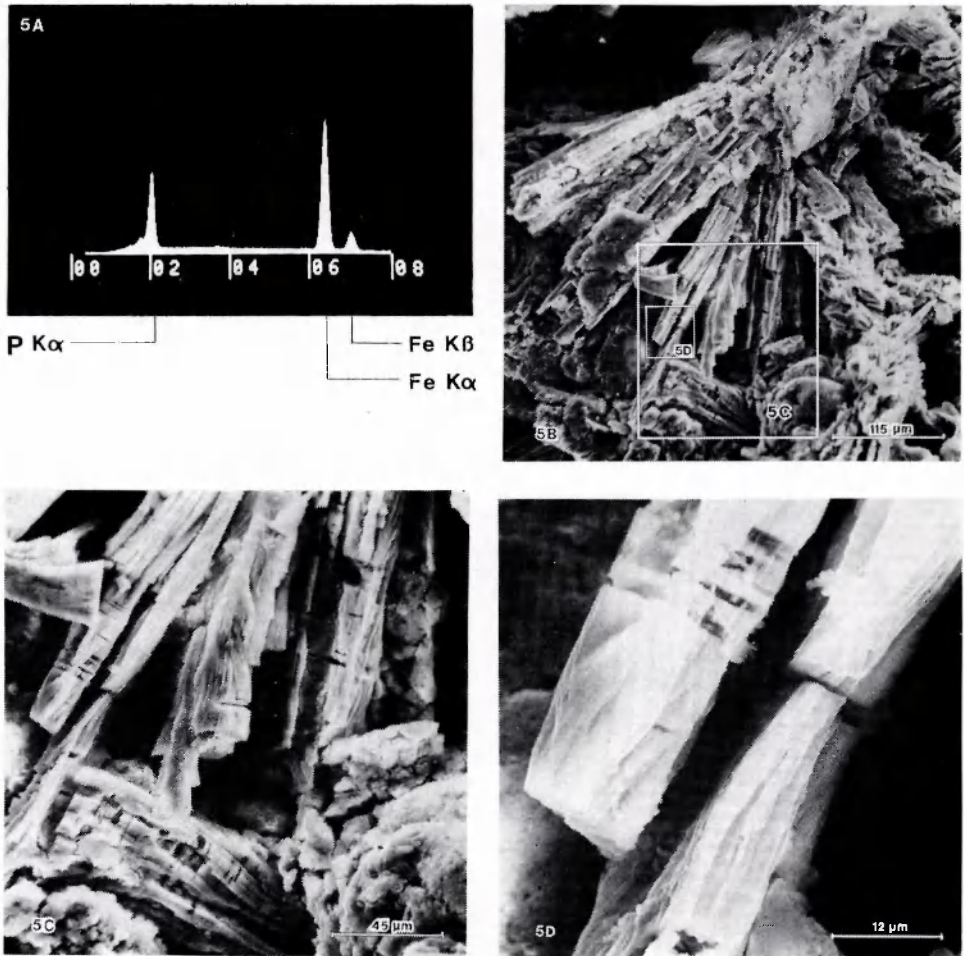
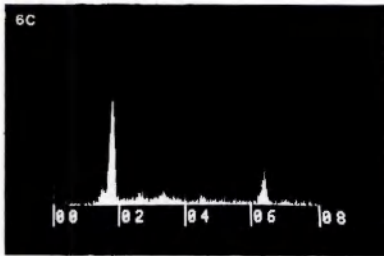
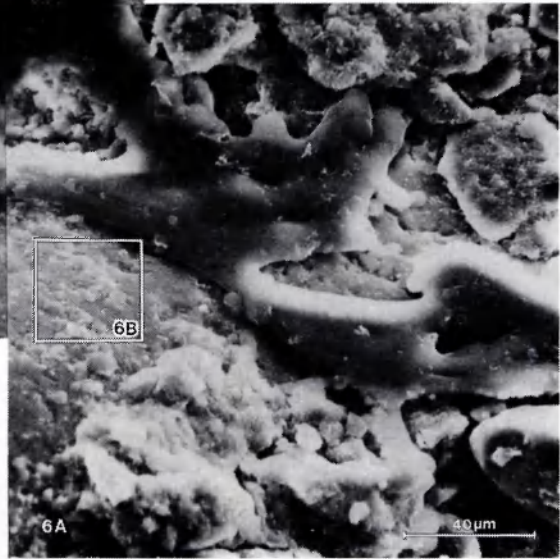
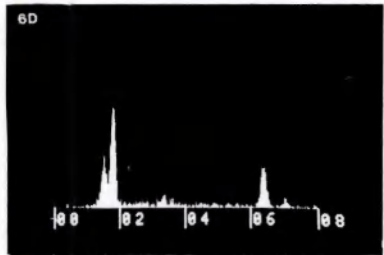


Fig. 5. Loose vivianite in a peat soil in the Province of Drente, Netherlands (B). Fig. 5A shows P and Fe in the mineral. Fig. 5C and 5D are magnifications.

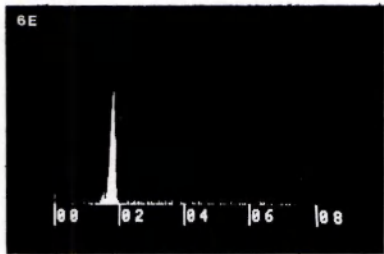
Fig. 6. 'Lava flow' of secondary silica on top of primary quartz grain (A) in a palaeosol (Red Yellow Podzolic) in the Province of Limburg, Netherlands. Disk-shaped secondary silica is also present on the primary quartz grain (Fig. 6B). Figure 6C is an analysis of the 'lava flow' of Fig. 6A. Here Si with some Fe contamination is measured. Fig. 6D shows Al, Si, Fe and some K in clayey material and Fig. 6E that the disk shapes contain only Si.



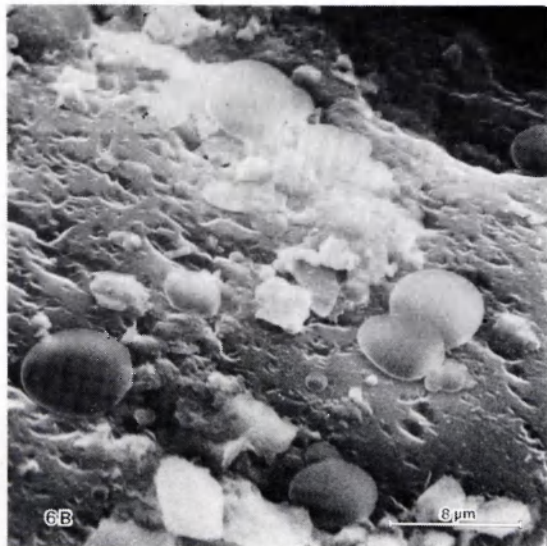
Si Kα ————— Fe Kα



Al Kα ————— Fe Kβ
Si Kα ————— K Kα ————— Fe Kα



————— Si Kα



tinguishable at points where the mineral is nearly broken (Fig. 5D). They form a type of bridge over the developing crack in the mineral.

The last example of cohesive but loose material is from the Province of Limburg, Netherlands. It is a Tertiary palaeosol, and can be classified as a Red-Yellow Podzolic. Secondary silica, which shows a pallasade type of orientation under crossed nicols, is the subject of study. Fig. 6A shows a type of 'lava flow' on a primary quartz grain. A detail of the material at the surface of the quartz grain is given in Fig. 6B. EDXRA analysis reveals that the 'lava flow' consists of silicon which is slightly contaminated with iron (Fig. 6C). Two analyses have been made of the material on the surface of the primary quartz grain outside the lava flow (Fig. 6D and 6E). One concerns the botryoidal aggregation at the lower right of Fig. 6A. This material contains Al, Si, Fe and a very small amount of K (Fig. 6D). The morphology of this material and its compositions indicate that it is probably clay. Figure 6B represents an area to the left of the clay concentration. EDXRA analysis revealed that the disk-shaped forms visible in the picture consist of pure silica (Fig. 6E). These results show that two morphologically different forms of secondary silica occur in this sample.

Acknowledgment

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