

THE INVESTIGATION OF CLAY MINERALS IN SOIL
THIN-SECTIONS

by

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INTRODUCTION

Being both mobile and reactive, the clay mineral fraction of soils plays an important role both in pedogenesis and plant nutrition. A method of identifying clay mineral species in situ within soil fabric would therefore be of value in soil studies. Normal methods of identification involve the separation of the clay fraction from the bulk soil and its homogenisation: its analysis is subsequently out of context with respect to its distribution within soil fabric. On the other hand, identification in soil thin-sections is difficult by normal optical microscopic methods since individual grains lie beyond the limit of optical resolution. (i. e. $\ll 1 \mu\text{m}$).

In this paper we report on an investigation into the potential of selected techniques in the identification of clay minerals in soil thin-sections. These include staining with U-V. fluorescent dyes, and the differential adsorption of radioisotopes and heavy metals and their subsequent detection by autoradiography and electron probe micro-analysis respectively. These techniques were initially evaluated on the following six reference clay minerals:

Kaolinite	A. P. I. No 17
Hydrous mica	A. P. I. No 35 ("Illite").
Chlorite	Separated from Silurian shale, Wales (Rezk 1975)
Vermiculite	Separated from altered dolerite, Bangor, U.K.

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Smectite	A. P. I. No 27
Attapulgite	A. P. I. No. 44

Subsequently, they were tried on a range of thin-sections selected from appropriate soil profiles.

CHEMICAL PRETREATMENT & U-V FLUORESECENT STAINING.

The use of chemical stains to identify clay minerals in aqueous suspension is a well-established, simple and inexpensive technique (c. f. Grim 1968) but it does not appear to have been applied to soil thin-sections. Application can be complicated by the presence of such pigmenting components as free iron oxides and organic matter and methods were therefore developed for their prior removal. Removal of free iron-oxides was achieved using the technique of Mehta & Jackson (1960). Dithionite, dissolved in citrate buffer solution preheated to 80° C, was added dropwise to the tilted surface of an uncovered thin-section; bleaching was usually evident after 20-30 drops whereupon the section was washed with distilled water; a similar procedure has been reported by Bullock et al. (1975). Although convenient and successful this procedure sometimes tended to damage sections by weakening adhesion to the slide and causing corrugation. These difficulties could be overcome by treating instead the surface of the polished block of resin impregnated soil from which undistorted sections of the bleached soil could subsequently be prepared (e. g. Fig. 1). Similar results were obtained for the removal of organic matter from the soil fabric using sodium hypochlorite (buffered at pH 9.5; Anderson 1963; Babel 1964). In this case the destruction of fresh organic matter could also be followed by the progressive decrease in autofluorescence observed with reflected U-V light.

Staining clay minerals with fluorescent dyes (Fahn &

Gennrich 1955) was first investigated with respect to the six reference clay minerals and six dyes (Acridine yellow; acridine orange ; auramine-O; berberine sulphate ; rhodamine-B; thioflavine-T). A stack of six orientated films, approximately 1 mm thick for each clay mineral, was prepared and impregnated under vacuum with resin, and transverse thin-sections produced in the normal way. Staining with a 0.1 % aqueous solution of each dye was carried out both on the initial clay samples prior to formation of the orientated films, and also on the polished surface of the uncovered thin-sections. When the sections were examined by transmitted U-V fluorescence microscopy using Leitz equipment (5 mm BG. 12 + BG. 38, & K530 filters) it was found that both sample preparations proved equally effective : the more convenient direct staining of the sections was therefore adopted. Intensity of fluorescence was least for kaolinite and most for the smectite : however, minerals did not show sufficient specificity towards any of the dyes for their differentiation, the only exception being Rhodamine-B which showed a strong preferential adsorption onto smectite.

Three procedures for staining clay minerals within soil fabric were tested. Soil blocks were leached with dye solutions prior to resin impregnation, dye solutions were applied to the polished surface of the resin impregnated block prior to the preparation of thin-sections, and were also applied to the surface of the uncovered thin-section. It was found that the leaching of the soil blocks (encased in a rubber jacket and connected to glass tubing above and below) proved impractical due to the length of time required to saturate and wash the soil (4-8 weeks) and the resulting tendency to structural derangement, whilst application to the soil thin-section, although convenient, again tended to distort the section. Treatment of the surface of the resin impregnated soil, however, proved to be as ef-

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fective as the leaching of unimpregnated soil, and enabled undistorted thin-sections to be prepared. Furthermore, staining could be preceded by the treatments described above to remove organic matter and free iron oxides if so desired.

Application of this staining procedure proved of value in following the general distribution of clay minerals within the soil fabric, revealing details which were otherwise hidden (Fig. 2). The most useful dyes in this respect proved to be acridine yellow and orange. However, clay mineral species could not be differentiated except for smectite, the presence of which was revealed by Rhodamine-B. By this means it was possible, for example, to show that in an aquic paleudalf smectite was present as thin seams within thick argillans, although undetectable in the soil matrix.

AUTORADIOGRAPHY

Autoradiography in soil thin sections involves the selective adsorption of a radioisotope within the soil fabric and its subsequent localisation as an image induced in photographic emulsion. For the present purpose the isotopes Ca^{45} (β -emitter; 0.25 MeV; $T_{1/2}$ -165 days) and Ni^{63} (β -emitter; 0.067 MeV; $T_{1/2}$ -120 years) were selected as being readily available tracers with suitably low energies of emission and long half lives. It was anticipated, that the former should follow the pattern of exchange sites in the soil generally, whilst the latter, due to similarity of the properties of Ni^{+2} (I. R. O. 69 Å), to those of Mg^{+2} (I. R. O. 66 Å) might follow more specifically the distribution of Mg in, for example, vermiculites and smectite.

As in the staining experiments, labelling with the radioactive tracers was attempted both by leaching soil blocks prior to impregnation (50 μ C in 100 ml), and by applying the tracer (0.5 μ C in 1 ml. for 2 hours) directly to the uncovered thin-sections. Both procedures were found

to be equally effective in the adsorption of the tracer on to the soil fabric. Successful autoradiographs were obtained from these samples by exposing them to Kodak Industrex MX film for 4-6 weeks: stripping techniques were not successful.

Differential adsorption was evident in the autoradiographs obtained with both tracers. This is illustrated in Fig. 3 where Ni^{63} occurs in higher concentrations within argillans peripheral to voids. As in the case of chemical staining this technique reveals, though somewhat laboriously, general patterns of clay mineral distribution, but does not at this stage offer much promise of differentiating individual clay mineral species.

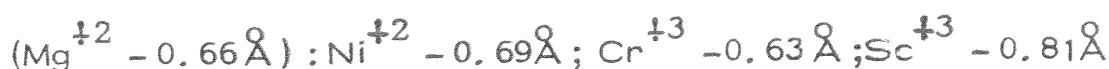
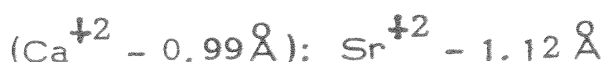
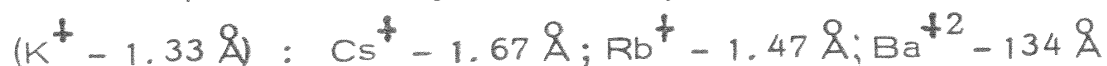
ELECTRON PROBE MICROANALYSIS

Electron probe microanalysis offers the possibility of elemental analysis at the level of individual clay mineral particles in situ within soil fabric. In this instrument a selected area of the order of $1\ \mu\text{m}^2$ on the surface of a thin-section is bombarded with a high energy electron beam; this causes X-ray emission from those elements present in the excited area, the wavelengths and intensities reflecting presence and concentrations respectively. Quantitative analysis can be made by point counts with a static beam, after suitable corrections, whilst one and two dimensional scans of the electron beam give qualitative indications of variations in element concentrations along selected lines or over selected areas.

The instrument was used in two different but simultaneous approaches to clay mineral studies. Identification was attempted, firstly, from the ratios of the X-ray responses from the major constituent elements (Si, Al, Fe, Mg, K & Na) : (c.f. Espinoza et al. 1975; Si/Al). Secondly, X-ray response ratios of differentially adsorbed trace metals were investigated: selective adsorption

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of cations by clay minerals has been discussed by Sawhney (Cs & Rb; 1.972) and by Murdock & Rich (Rb & Sr, 1.972) and applied to soil thin sections by Hill & Sawhney (Cs; 1.969). The following ions were selected for testing on the basis of their abilities to follow the distribution of particular major elements,



These techniques were tested on thin-sections of both the standard clay minerals (prepared as for the U-V dye tests) and of selected soils. On assessing the same three procedures as for the adsorption of radiotracers, it was again demonstrated that direct application of 1N metal solutions to the thin section was as effective as leaching of the soil core and far less time consuming; this procedure was therefore adopted for subsequent studies.

Areas to be investigated in the thin-sections were located and photographed with a Leitz Ortholux-pol system to facilitate their recognition through the optical system of the electron probe microanalyser. The low take off angle (20°) of the instrument used (JEOL JXA 3A) required a highly polished specimen surface (1, $\frac{1}{2}$ & $\frac{1}{4}$ μ m diamond) which was coated with carbon to ensure thermal and electrical conductance; this was further enhanced by encircling the selected areas (c. 1mm^2) with silver paste earthed to the specimen block. A small drop of the relevant trace metal solution was evaporated onto the

slide to enable to spectrometers to be peaked up on the appropriate 2θ angles. Normal operating conditions involved an accelerating voltage of 15 KV, and a specimen current adjusted to within the range 0.15 - 0.18_m A.. Suitable areas for point count analysis were selected by means of adsorbed electron images and both 2D and line scan modes of X-ray image, and replicate 50 sec. counts recorded for two elements simultaneously, the instrument being fitted twin spectrometers.

Since the aim was identification of clay mineral species rather than quantitative analysis, relative values only were sought, so avoiding complex correction procedures. Results are therefore given (Table I (i)), directly in terms of X-ray response ratios, Si being chosen as the common denominator. As anticipated, the particular mineral species analysed are adequately characterised by the following ranges of major element ratios, ($100 \times M/Si$) :

i. e. Kaolinite	Al/Si	> 40	
Hydrous mica	K/Si	> 5	
Chlorite	Fe/Si & Mg/Si	> 20	
Vermiculite	Fe/Si & Mg/Si	< 20 & > 8	
Smectite	Fe/Si & Mg/Si	8; K/Si < 1	
Attapulgite	Na/Si	> 5	

Adsorption was detectable for all trace metals except Ga. Differential adsorption from solutions of individual metals, again expressed as X-ray response ratios relative to Si, is evident in the results in Table 1- (ii). From these it can be seen that chlorite, vermiculite and smectite can be readily distinguished by the use of Sr, vermiculite and smectite by Cs, smectite by Ba, and hydrous mica by Rb, whilst kaolinite alone does not ad-

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sorb detectable Sc or Cr. Differential adsorption from mixtures of trace metals could also prove useful, as in the case of Cs Rb, and it is hoped to investigate this possibility further. From the present study, however, it would appear that the use of Sr in conjunction with major element analysis may prove adequate to distinguish most clay minerals. Applying the combined major and trace element analyses to selected soil thin sections, examples of close correspondence (i. e. differences insignificant at the 5 % level) of element ratios were obtained, with each of the individual reference clay minerals. In some instances it proved difficult to discriminate between smectite and vermiculite, but this could well reflect the presence of interstratified minerals in the particular soil examined.

There are clearly limitations to this analytical technique. At an instrumental level, problems can be caused by any slight (i. e. micron) drift of the beam from the desired point between successive analyses for different elements. It is also difficult to define precisely which mineral particle (s) lies within the volume excited by the electron beam. In particular the presence of Si, Al or Fe in either amorphous or crystalline (e. g. quartz, goethite, etc.) form would confuse or even invalidate the use of elemental ratios : this is probably the reason for the anomalous values more commonly found for Fe/Si, and this ratio was therefore used with caution. Clay mineral compositions also vary considerably about those of the particular specimens chosen as standards for this study (e. g. octahedral Al/Mg/Fe, and tetrahedral Al/Si) and this could blur the distinctions between the individual mineral species. Nevertheless, given homogeneity and relative purity of clay mineral composition over areas of several square microns, and also the availability of relevant standards, clay mineral species can be identified.

CONCLUSIONS

Three techniques have been evaluated for their ability to identify clay minerals in soil thin-sections. In developing suitable procedures, it has been demonstrated experimentally that the more convenient direct application of dye, radioisotope or trace metal solutions to the polished surfaces of resin-impregnated soil blocks or thin sections is as effective as the leaching of soil cores prior to impregnation; techniques for the preliminary removal of organic matter and iron oxides have also been developed. Of the three techniques, sorption of fluorescent dyes and radioisotopes, as observed by U-V fluorescence microscopy and autoradiography respectively, are of value in revealing the distribution of clay minerals generally within the soil fabric, but they cannot resolve individual clay size grains, nor do they offer at this stage much hope of identifying the different clay mineral species other than perhaps smectite. By contrast, the relatively simple and quick (though more expensive) technique of electron probe microanalysis may allow clay mineral species to be distinguished at the micron level within soil fabric on the basis of constituent major element ratios; identification can be further aided by the differential adsorption of such ions as Sr^{+2} .

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Table 1: X-ray count ratios (100 x M/Si) for reference clay minerals obtained by electron-probe micro-analysis.

M	Kaol.	H.mica	Chlor.	Verm.	Smect.	Attap.
(i) major component elements.						
Al	44 (2.0) [*]	19 (0.4)	33(1.1)	16(0.5)	20 (0.6)	8.2
Fe	3.8	5.8	50(1.1)	10(0.6)	4.8(0.4)	4.6
Mg	<	<	25(1.7)	16(1.0)	6.5(0.3)	<
K	<	7.1(0.3)	<	<	<	<
Na	<	<	<	<	<	7.9
(ii) added metal ions (individually : 1N)						
Cs	3.3	9.9	5.0	28	47	-
Rb	2.2	6.2	1.5	3.0	4.3	-
Ni	<	<	3.7	9.4	7.1	-
Cr	<	2.6	3.2	4.9	11	-
Ba	2.1	7.1	1.8	6.9	210	-
Sr	<	<	1.4	4.7	33	-
Sc	<	2.5	2.5	3.3	4.5	-
(iii) Rb & Cs added jointly (1N)						
Cs	2.9	10	4.2	24	29	-
Rb	2.1	5.3	2.3	2.9	4.4	-

^{*}(Standard Deviations) - from 11 analyses

< Ratio < 1, i.e. element not detectable; - no data

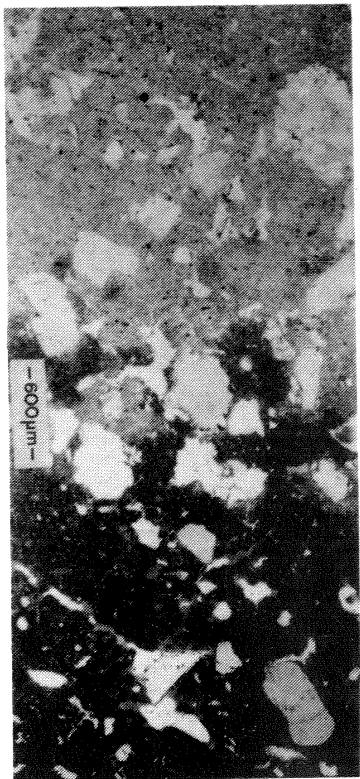


Fig. 1

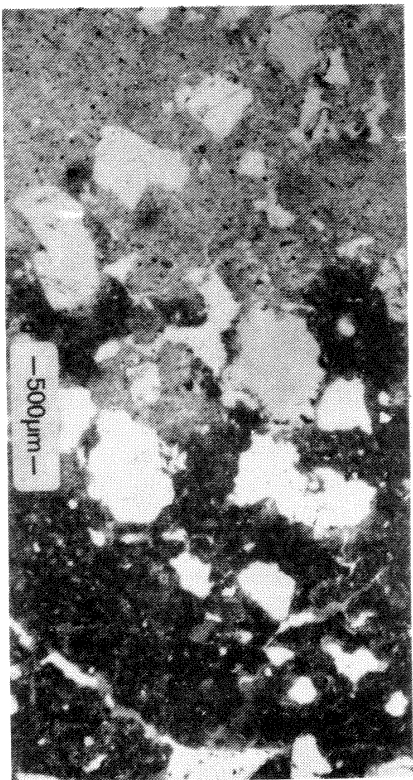


Fig. 2-a

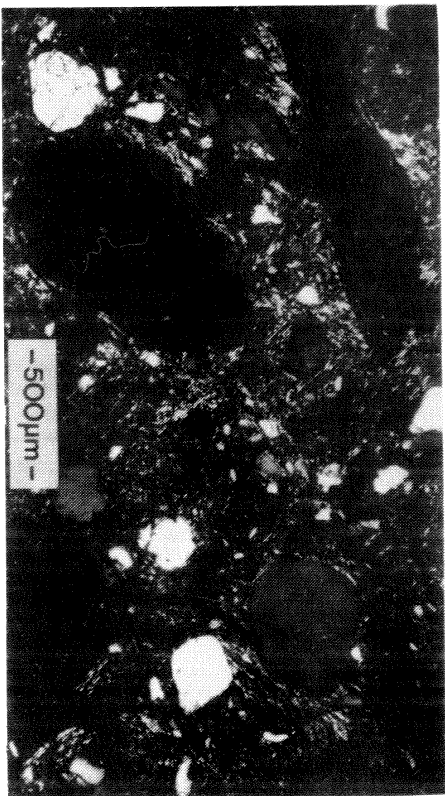


Fig. 2-b



Fig. 2-c

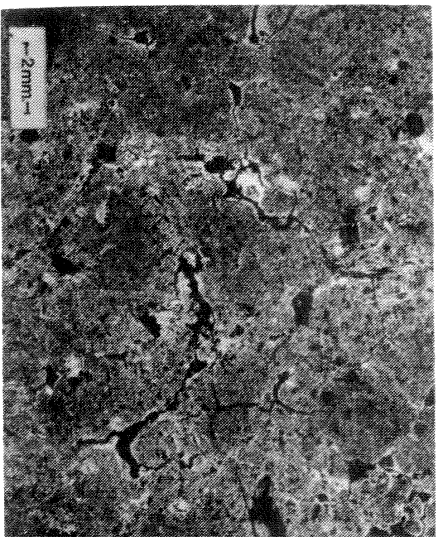


Fig-3

LEGENDS TO FIGURES

- Fig. 1 Removal of free iron oxides from half of a thin section of an oxisol (Buganda Series).
- Fig. 2 Clay mineral distribution within the fabric of an ochraqualf (Salop Series : Btg) stained with acridine orange (a) plane polarised light, (b), crossed polars, (c) transmitted U-V fluorescence (Leitz BG12-5mm † BG38 K530).
- Fig. 3 Autoradiographs of a hapludalf (Batcombe Series : Btg treated with Ni⁶³).

SUMMARY

Normal methods of clay mineral analysis do not provide information about the distribution of clay mineral species within the soil fabric, a factor which is of significance in soil-plant and pedogenic studies. Nor is it possible to identify easily grains of clay minerals in soil thin sections since their size places them beyond the limit of resolution of optical microscopes. This paper reports an investigation into techniques involving treatment with UV-fluorescent dyes, radio-isotopes, and metal cations, combined with electron probe microanalysis and autoradiography, which can supplement the information obtained by normal microscopic examination of soil thin-sections.

UV-fluorescent dyes, such as acridine orange, and yellow, rhodamine-B, etc., are detectable at low concentrations and are differentially adsorbed onto clay minerals. Direct staining of clay minerals in surfaces of resin-impregnated soil was shown to be equally effective and comparable to the staining in sections prepared from unimpregnated soil cores that had been leached with the dyes; it also proved to be very much more rapid and convenient, and allowed iron oxides and organic matter to

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be removed from the section prior to staining if so desired. Subsequent examination of the thin-sections by UV-fluorescence microscopy revealed the detailed distribution of clay minerals within the soil fabric, but it has so far only proved possible to distinguish smectites by this procedure.

Electron probe microanalysis proves useful both by semi-quantitative analysis for the major elements (Si, Al, Fe, Mg & K) and also by analysis for various metal ions absorbed onto the clay minerals. Direct absorption onto soil thin-sections of such ions as Cs^+ , Rb^+ , Ni^{+2} , Ba^{+2} , Sc^{+3} , and Cr^{+3} was again shown to be comparable to the absorption on leaching a soil core, and also far less time consuming. Similarly radio-isotopes such as ^{63}Ni and ^{45}Ca can be conveniently absorbed directly onto resin-impregnated soil surfaces from which autoradiographs can then be made. Such techniques have been tested on thin-sections prepared from standard clay minerals, and have subsequently been applied with varying success to the study of clay mineral distribution within the fabric of selected soil profiles.

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