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245 CHARACTERISTICS OF SESQUIOXIDIC SOILS

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ABSTRACT

Sesquioxidic soil clays from Oxisols in South Africa, Australia and Brazil, and two clays from Andosols in Japan and New Zealand, were investigated by XRD, DTA, IR, EM and quantitative mineralogical analysis. The volcanic-ash soil clays are dominated by allophane; clays from Natal are dominated by kaolin (30 - 45%) and free iron oxides (20 - 25%), with smaller amounts of gibbsite (0 - 12%) and pedogenic chlorite (less than 20%); Oxisol clays from Australia and Brazil contain free iron oxides (40 - 50%), gibbsite and kaolin (both about 25%).

Acid ammonium oxalate (pH 3) was found to be superior to currently popular alkaline reagents for extracting amorphous aluminosilicates and alumina from these clays. Boiling 0,5N NaOH dissolved large amounts of finely-divided kaolinite and halloysite, while hot 5% Na_2CO_3 reaction was too slow (partial dissolution of synthetic amorphous aluminosilicates with one extraction) and insufficiently selective (gibbsite and kaolin of poor crystallinity dissolve to a variable extent). On the other hand, synthetic gels (molar SiO_2/Al_2O_3 ranging from 0,91 to 2,55) dissolved completely after 2h shaking in the dark with 0,2M acid ammonium oxalate (0,2 ml/mg). Specificity of oxalate for natural allophane was indicated by removal of similar quantities of silica and alumina using different clay : solution ratios.

Oxalate extraction data indicated that allophane is absent in Oxisol clays, which are characterized by small quantities of amorphous, Al-rich sesquioxide (1,5 to 7%), some of which may originate in interlayers of 2 : 1 phyllosilicate structures. Allophane was determined quantitatively in volcanic-ash soil clays by allocating hydroxyl water content to oxalate-soluble silica plus alumina on the basis of an ignition weight loss/chemical composition function for synthetic amorphous aluminosilicates. Both SiO_2/Al_2O_3 ratios and quantities of allophane were found to be lower than those obtained using boiling 0,5N NaOH, in agreement with the interpretation that the latter treatment attacks crystalline aluminosilicates.

Parameters of chemical reactivity and distribution of electric charges following various chemical pretreatments of allophane were found to correspond closely to those predicted on the basis of synthetic gel behaviour. Results for Oxisol clays suggested that the role of amorphous (oxalate-soluble) alumina in governing physicochemical properties is generally subdominant to that of the poorly-crystalline, Al-substituted iron oxide component which is removed by deferration with citrate-dithionite-bicarbonate reagent.

Hysteretic pH-dependent net negative exchange charge was shown to arise from hysteresis of positive exchange charge, while CEC is fully reversible by titration with strong acid. A mechanism is postulated to account for this observation.

Levels of silica in the soil solution of Natal Oxisols are higher than those of more strongly-weathered soils from Australia and Brazil, and may be sufficiently high to exert a favourable effect on plant-available P following phosphate fertilization. Although soluble silica levels are also relatively high in volcanic-ash soils, a similar effect is not likely to manifest itself significantly owing to the very high P adsorption capacity of allophane.

A study of soil solution equilibria indicated that in terms of silica and aluminium hydroxide potentials, kaolinite is the most stable mineral in all the soils. Allophane persists as a partial metastable equilibrium state in volcanic-ash soils while gibbsite formation in Oxisols is contingent upon periodic, non-equilibrium leaching conditions. The role of clay mineral suite in governing levels of exchangeable aluminium in acid soils is examined.

A revised model system for allophane is proposed in which tetrahedral substitution of Al for Si may reach a maximum of 1 : 1 in an aluminosilicate phase. Additional alumina takes the form of discreet amorphous or crystalline material. The composition of allophane corresponding to maximum Al for Si substitution will depend upon the availability of basic cations for charge balancing during neogenesis of the amorphous aluminosilicate.

INTRODUCTION

Sesquioxidic soils may be regarded as those in which the oxides, hydroxides or oxyhydroxides of aluminium and iron have accumulated, either as discreet crystalline phases or as coatings on clay mineral surfaces, to the extent that they exert a dominant influence on soil properties.

Oxisols, in which this accumulative process has reached an advanced stage, occur extensively in the Highlands and Midlands Mistbelt of Natal. By virtue of the climate with which they are associated as well as their very favourable physical properties, these soils possess a high potential for intensive agriculture.

Exploitation of this potential has, until relatively recently, been impeded by natural infertility associated with properties such as high phosphate fixing capacity, the presence of toxic levels of exchangeable aluminium, and low cation exchange capacity. For this reason, a large proportion of local research effort has centred on these acid, highly-weathered soils. By and large, some of the major problems have been identified, and agricultural production has received a considerable boost from the consequent more rational use of fertilizer and ameliorant.

Much of this progress can be attributed to research of a relatively fundamental nature. Clay mineralogical investigation, for example, has provided a better understanding of soil genesis, and has consequently permitted more meaningful comparison with similar soils elsewhere. In this way it has often been possible to predict soil behaviour in response to a particular set of conditions without having to resort to more than a cursory search for the possible causal relationships involved.

The present study was undertaken with a view to following up previous work on the mineralogy and chemical properties of the colloidal fraction in Natal Oxisols. The primary objective was to carry out detailed clay mineralogical analysis on a limited number of samples in order to assess the nature of the relationships which exist between chemical properties and soil clay mineralogy. The importance, in this context, of the amorphous or poorly-ordered component of soil clay is widely acknowledged. It was therefore considered that particular emphasis on the characterization of such material was required.

At the same time it was realized that the results of such an investigation would have more general significance if the sample collection included, from elsewhere, a selected number of soils having a similarly acid, highly-weathered

nature, containing large amounts of sesquioxides/sesquioxidic amorphous material, and which have been relatively well-studied and characterized in other laboratories. The study is therefore in certain respects a comparative one. As such, it serves to pinpoint some of the unique attributes of highly-weathered soils in Natal. Conversely, such comparison helps to establish those properties which are common to all acid soils characterized by substantial accumulations of sesquioxidic material.

CHAPTER I

CLAY MINERALOGICAL INVESTIGATION

1.1 Introduction

The clay mineralogy of acid, sesquioxidic soils in Natal has been studied fairly extensively (de Villiers, 1969; le Roux, 1973), resulting in a considerably enhanced appreciation of both pedogenesis and problems associated with soil fertility. Definitive aspects of local soil classification (van der Eyk, MacVicar & de Villiers, 1969) have benefited from such knowledge. The established predominance of hydrous sesquioxides, kaolin and pedogenic chlorite in the clay fraction of these soils has helped to explain many of their characteristic properties. These properties are common to most soil materials which have undergone a high degree of acid weathering in the humid tropics and subtropics, and are probably most strongly expressed in the widely-distributed group of allophane-rich volcanic ash soils known as Andosols.

Techniques for quantitative determination of the colloidal constituents of soils have limitations. Despite a number of more recent refinements, the analytical approach developed by M. L. Jackson and co-workers (Alexiades & Jackson, 1966) still contains a number of uncertainties.

For example, the quantitative determination of montmorillonite based on CEC measurements assumes negligible CEC of sesquioxidic amorphous material, even though chemical pretreatments for dispersion and deferration may expose some pH-dependent CEC associated with such material, as well as with pedogenic chlorite (de Villiers & Jackson, 1967a).

The biggest uncertainty lies in the quantitative determination of amorphous material. A greatly improved procedure was recently proposed by de Villiers (1971), and evidence of its use is beginning to appear (Taylor, 1972; Griffith, 1974; Warkentin & Maeda, 1974). Based on a model system for allophane (van Reeuwijk & de Villiers, 1970), the procedure assumes that allophane itself constitutes an aluminosilicate phase having a molar SiO_2/Al_2O_3 ratio of 6, so that any additional alumina dissolved by boiling 0,5N NaOH (Hashimoto & Jackson, 1960) should be expressed as such. Correction for gibbsite dissolution using a separate value determined by DTA (Dixon, 1966) is made prior to allocating dissolved constituents to the allophane formula.

One problem is that 0,5N NaOH treatment of clays is rather harsh and therefore not completely selective for amorphous material. Dissolution of

iron-rich phyllosilicates can be corrected for (Briner & Jackson, 1970; El-Attar & Jackson, 1973) by measuring released iron in the residue (Mehra & Jackson, 1960) and by assuming a molar SiO_2/Al_2O_3 of 4 for this material. Partial dissolution of poorly-ordered kaolinite (Langston & Jenne, 1964) and halloysite (Askenasy, Dixon & McKee, 1973) has also been reported. The possibility of using quantitative DTA correction for kaolinite dissolution similar to that for gibbsite merits some attention.

An alternative would be to employ a milder dissolution treatment. The effects of successive extractions with cold and hot 5% Na_2CO_3 solutions have been examined by Follett, McHardy, Mitchell and Smith (1965) and by Jørgensen, Birnie, Smith and Mitchell (1970). To effect the complete removal of gibbsite, as many as three successive hot sodium carbonate treatments are needed, while usually only one boiling NaOH treatment is required. The indications from this work are that different extraction procedures will merely make correspondingly different inroads into the continuum which exists between truly amorphous and highly crystalline material in soil.

The use of acidified ammonium oxalate as an extractant for amorphous Al and Fe from soils (Tamm, 1922) is becoming increasingly popular. One extraction in darkness serves as a useful measure of the quantity of amorphous or 'active' iron oxides in soil (Schwertmann, 1973). Large quantities of oxalate-soluble Al and Fe have been measured in clay from a Podzol having properties closely resembling those of allophane (Brydon & Shimoda, 1972). In contrast to alkali dissolution procedures, there is little interference from partial solubilization of crystalline material besides that of magnetite (Baril & Bitton, 1969) and trioctahedral layer silicates (Arshad, St Arnaud & Huang, 1972), both of which are rarely present as major constituents of soil clay.

In this chapter, the clay fractions of selected sesquioxidic soils are examined by a number of physical and chemical techniques. Particular attention is given to various methods for determination of the amorphous component.

1.2 Materials

Ten samples from Oxisols in Natal, Australia and Brazil and from volcanic-ash soils in New Zealand and Japan were chosen for investigation (Table 1). Soil profile descriptions and other information are given in Appendix I.

The Natal soils are clay-rich, dystrophic members of the Griffin and Hutton soil forms (Soil Classification Working Group, 1974). They occupy a

TABLE 1 Sample collection*

Sample no.	Soil	Horizon	Depth (cm)	Parent rock	Locality
			OXISOLS		
2	Farmhill	B21	22-60	basalt	Highmoor Forest Reserve, Natal
3		B22	60-78		
4	Farmhill	B21	20-75	shale	Donnybrook, Natal
5	Balmoral	B23	150-230	dolerite	
6	Farningham	A1	0-15	dolerite & shale	Thabamhlope Expt. Sta., Natal
7		B21	45-60		
8	Kraznozem	B2	210-240	basalt	Gregory Falls, Australia
18	Latosol Roxo	B22	120-200	diabase	Ribeirão Preto, Brazil
			ANDOSOLS		
11	Kodonbaru	B22	-	volcanic ash	Kyushu, Japan
17	Tirau Silt Loam	B2	33-51		Tirau, New Zealand

* Acknowledgement is due, for sample material, to R. J. Isbell (Australia), A. C. Moniz and P. de Souza Santos (Brazil), S. Aomine and K. Wada (Japan) and M. L. Leamy and R. J. Furkert (New Zealand).

significant portion of the landscape in humid, subtropical Natal. Previous work (de Villiers & Jackson, 1967a; de Villiers, 1969; le Roux, 1973) has indicated that the clay fraction consists mainly of kaolinite, pedogenic aluminous chlorite, gibbsite, amorphous aluminosilicates and poorly-crystalline hydrous sesquioxides.

The Oxisols from Australia and Brazil were selected to represent material which has been subjected to extreme weathering under humid, tropical conditions.

The Andosols have formed under similar conditions of intensive leaching in relatively recent deposits of volcanic ash. Their clay fractions are dominated by allophane (Wada & Aomine, 1973; N.Z. Soil Bureau, 1968).

1.3 Methods

1.3.1 Preparation of samples for mineralogical analysis

(i) Deferrated clay fraction. Air dried soil samples, crushed to pass a 2 mm screen, were digested on a steam bath with 30 percent H_2O_2/1N NaOAc (pH 5) for removal of organic matter (Jackson, 1956), and dispersed at pH 8 with NaOH (pH 4 with HCl was required for efficient dispersion of the volcanic ash soils). The clay fraction (particles with limiting diameter of less than 2 µm) was separated by centrifuge sedimentation (Jackson, 1956), then deferrated, after flocculation with NaCl, by citrate-dithionite-bicarbonate (CDB) treatment (Mehra & Jackson, 1960). The clay was then centrifuged-washed sequentially with water, methanol and acetone until free of entrained salt (negative $AgNO_3$ test for chloride), and stored in Na-saturated suspension. For some analyses, a portion of the suspension was K-saturated, washed free of salt as before, and freeze-dried (Appendix II).

(ii) Natural clay fraction. Clay affected as little as possible by chemical pretreatments (hereinafter referred to as natural clay) was separated as follows: soil samples (< 2 mm) in 1 : 5 :: soil : distilled water were given successive ultrasonic treatments and the clay (< 2µm) removed by centrifuge sedimentation. Prior saturation with KCl (sample no. 3), NaCl (nos. 5, 7 and 17) or LiCl (no. 18) was required before these soils would disperse significantly. Clays were then K-saturated, washed salt-free, and freeze-dried (Appendix II).

(iii) Size fractionation of deferrated clay. Coarse clay (2 - 0,2 µm) was sedimented from the original Na-suspensions in 100 ml tubes using an International No. 2 centrifuge after the procedure given by Jackson (1956; p. 140). The < 2 µm cut was separated into medium (0,2 - 0,08 µm) and fine (< 0,08 µm) clay fractions using a Sorvall centrifuge with fixed-angle, GSA rotor and a method (Appendix III) based on principles outlined by Jackson (1956, pp. 127 & 146). Sodium carbonate solution (pH 9,5) was used as dispersant, except for the volcanic-ash soil clays (samples 11 and 17) which required HCl

(Jackson, 1956, p. 153) for effective removal of < 0,2 μm clay. Owing to low yield of this fraction, further separation of fine clay was not attempted for samples 11 and 17. The various separates were stored as Na-saturated suspensions, portions of which were K-saturated, washed free of excess salt, and freeze-dried (Appendix II).

(iv) Synthetic gels. Three amorphous aluminosilica gels were prepared by the method of van Reeuwijk and de Villiers (1970), having proportions of silica and alumina corresponding to 41% (gel II), 53% (gel III) and 65% (gel IV) $Al_2O_3/Al_2O_3 + SiO_2$. Composition was checked by chemical analysis. After equilibration at pH 6, the gels were K-saturated and freeze-dried.

1.3.2 X-ray diffraction analysis

A Phillips X-ray diffractometer with CoKα radiation was used. For routine analysis of deferrated clays (Whittig, 1965), 25 to 30 mg clay orientated on a glass slide was examined after Mg or K saturation and various solvation or heat treatments.

Dimethyl sulphoxide (DMSO) solvated clays (Gonzalez-Garcia & Sanchez-Camazano, 1968) were prepared by refluxing 50 mg clay with 5 ml DMSO in an Al foil-covered glass tube in a water bath at 90C for 8 h. Two ml of suspension was pipetted onto a glass slide which was carefully warmed to remove the free liquid surface.

Coarse, medium and fine clays (deferrated) were examined after Mg-saturation and glycerol solvation.

Natural clays were examined as random powders mounted in rectangular aluminium frames.

Clay residues from a variety of selective chemical dissolution treatments were analysed as orientated specimens.

1.3.3 Thermal analysis

Differential thermal analysis was carried out using a Leeds and Northrup assembly with a furnace similar to that employed by Webb (1958). Potassium-saturated, freeze-dried sample (300 mg) was mixed with 900 mg calcined alumina, then equilibrated at 56% relative humidity over saturated $Mg(NO_3)_2.6H_2O$ solution *in vacuo* for 4 days or longer. The mixture was sandwiched between layers of similarly equilibrated alumina in the sample holder such that the thermocouple tip was located centrally within the sample, the whole being hard-packed with a glass rod during filling.

Gibbsite and kaolinite standards were diluted with calcined alumina to give a range representing 0 to 50 percent in a sample (maximum of 150 mg thermally active material) using standard Georgia kaolinite and a pure synthetic gibbsite* respectively. All samples were heated in an atmosphere of flowing nitrogen (approximately 200 ml/min).

Thermogravimetric analysis (TGA) was carried out on K-saturated samples heated in tared Pt crucibles to 110, 300 and 950C (Alexiadee & Jackson, 1967).

1.3.4 Infrared spectroscopy

IR spectra were recorded using a Perkin Elmer Model 457 grating infrared spectrophotometer. Discs 5 mm in diameter were prepared from mortar mixtures of K-saturated, freeze-dried clay and KBr in a ratio 1 to 200, dried overnight at 70C.

1.3.5 Electron microscopy

Selected freeze-dried clays were dispersed ultrasonically in distilled water and a drop of each suspension was placed on collodion-coated 200-mesh copper grids for viewing with a Hitachi HU 11E Electron Microscope. Surface replicas of material were prepared by shadowing orientated specimens on glass slides with Pt/carbon at an angle of 20° (Bradley, 1965), followed by vertical shadowing with carbon. The resultant replica was floated off in 9N HF/1N HCl solution, allowed to stand overnight, then washed in 50% ethanol before being mounted on a 200-mesh copper grid for examination.

1.3.6 Surface area determination

Approximately 0,5 g freeze-dried clay was Ca-saturated and specific surface area estimated from ethylene glycol monoethyl ether (EGME) adsorption (Carter, Heilman & Gonzalez, 1965), using the modified method of Eltantawy and Arnold (1973) which incorporates a free liquid surface of EGME and dry $CaCl_2$ as separate phases in the evacuating chamber. In keeping with recommendations of the latter authors, samples were dried at 110C for 24 h prior to solvation.

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* Prepared and supplied by C. I. Rich (Virginia Polytechnic Institute, U.S.A.)

1.3.7 Quantitative mineralogical analysis

Analyses were made for the following clay minerals: quartz plus feldspar by $Na_2S_2O_7$ - HCl - NaOH selective dissolution analysis (SDA), with an approximate estimate of the quartz/feldspar ratio by X-ray diffraction (Kiely & Jackson, 1965); mica by analysis for dissolved K after HF dissolution (Kiely & Jackson, 1965); vermiculite and montmorillonite by K fixation and CEC analysis (Alexiades & Jackson, 1965); amorphous material plus gibbsite, and kaolinite plus halloysite by NaOH-thermal SDA (Alexiades & Jackson, 1966), kaolinite and gibbsite also being estimated by DTA; and chlorite by thermogravimetric analysis (Alexiades & Jackson, 1967).

1.3.8 Fractionation of sesquioxides and amorphous material

Freeze-dried, K-saturated natural clays and synthetic alumino-silica gels were subjected to a number of further selective dissolution procedures. Subsamples, equivalent to 50 mg oven-dry clay or gel, were extracted with (i) 10 ml 0,1M Na-pyrophosphate (pH 10,5) for 12 h on an end-over-end shaker; (ii) 10 ml 0,2M NH_4-oxalate (pH 3) for 2 h on an end-over-end shaker in darkness; and (iii) 10 ml 0,3M Na-citrate buffered with Na-bicarbonate plus 0,75 g Na-dithionite at 80C (Mehra & Jackson, 1960). Clays deferrated according to extraction (iii) above, were treated with 5% Na_2CO_3 at 90C for 2 h on a water bath, and with acid NH_4-oxalate as in (ii), both the latter treatments being carried out using a clay : solution ratio of 40 mg/50 ml.

Analysis of Fe and Al in the centrifuged extracts was made by the ferron method after digestion with H_2SO_4-H_2O_2 (Tokashiki & Wada, 1972; Appendix IV). Si was analysed by the method of Weaver, Syers and Jackson (1968). The latter procedure was modified (Appendix IV) for analysis of oxalate extracts to overcome interference arising from Mo complexation by oxalate. Residues from all treatments were weighed after NH_4-saturation and heating at 110C for 24 h.

1.4 Results and discussion

1.4.1 X-ray diffraction analysis

Diffraction patterns for the deferrated soil clays and their size-subfractions are presented in Figures 1 to 5*, while powder diffractograms of natural clays are shown in Figure 6. In agreement with the findings of previous studies on these soils (Verster, 1964; de Villiers & Jackson, 1967a;

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* Late receipt of the Latosol Roxo sample (no. 18) accounts for the absence here and in places elsewhere, of a full complement of results for this material.

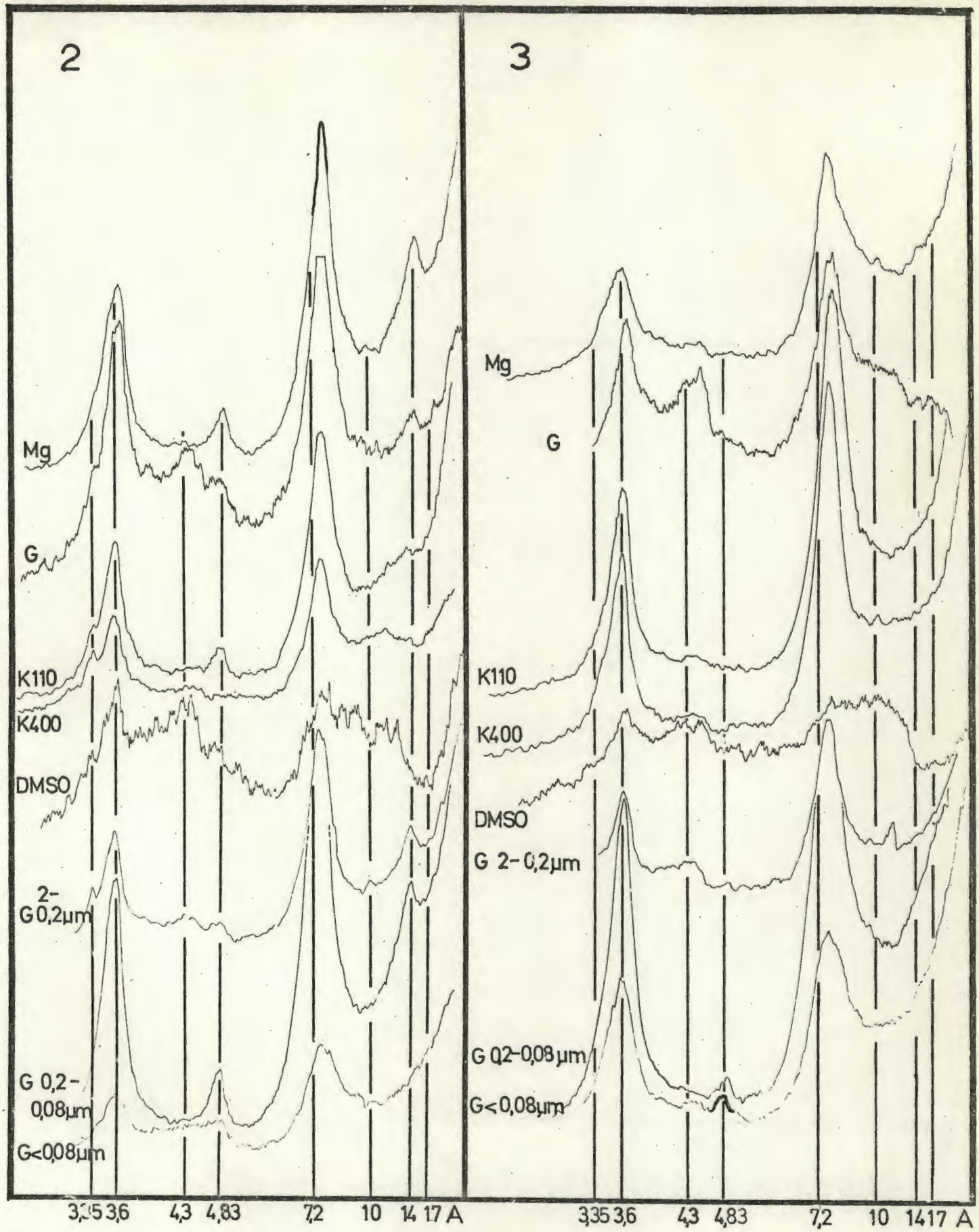

FIGURE 1. X-ray diffractograms of deferrated clay from samples 2 and 3 (Mg : Mg-saturated, air-dried; G: Mg-saturated, glycerol-solvated; K 110, 400, 500: K-saturated and preheated to indicated temperature (C); DMSO: dimethyl sulphoxide intersalated; clays < 2 µm unless otherwise indicated)

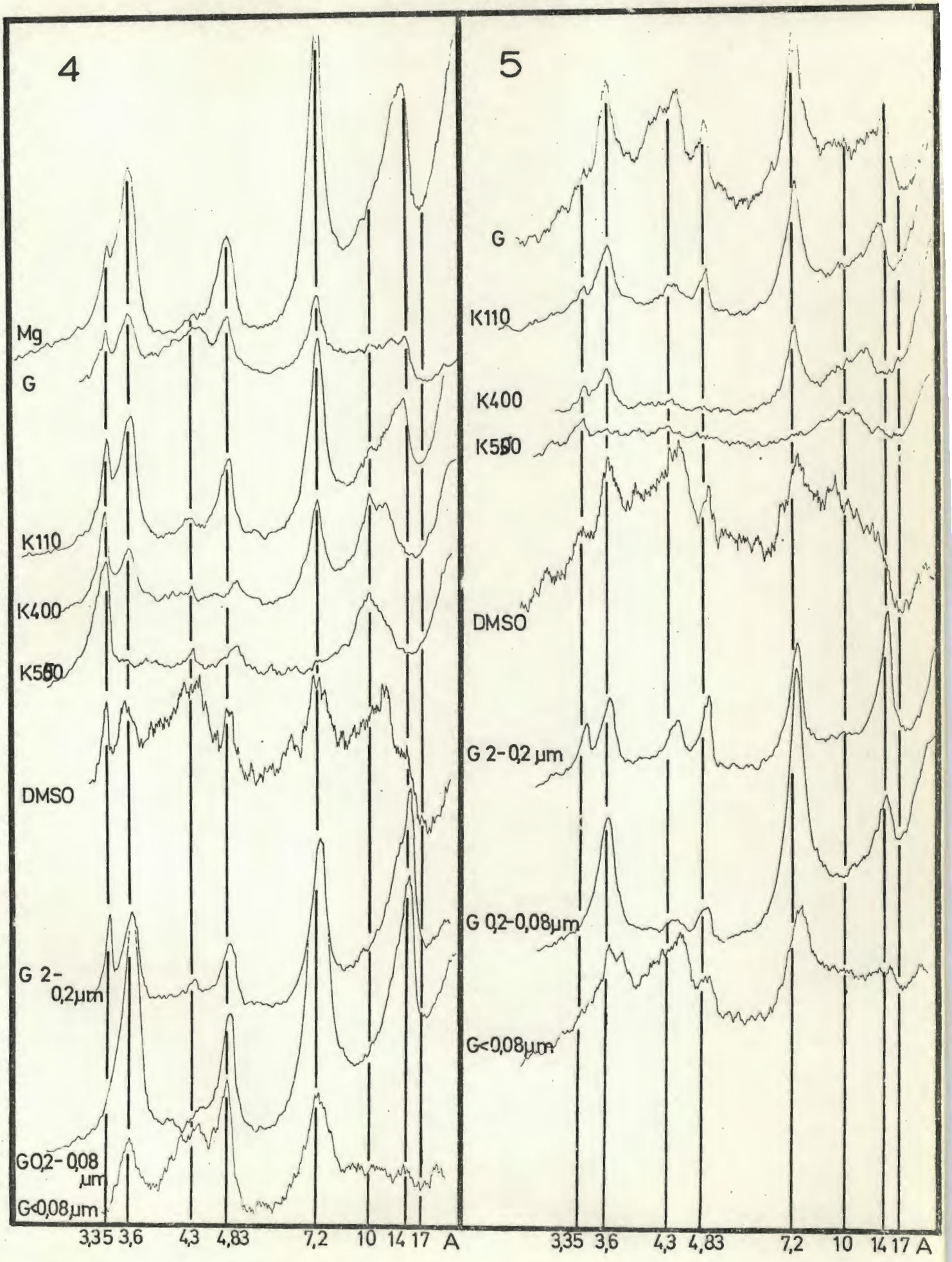

FIGURE 2. X-ray diffractograms of deferrated clay from samples 4 and 5 (legend as for Fig. 1)

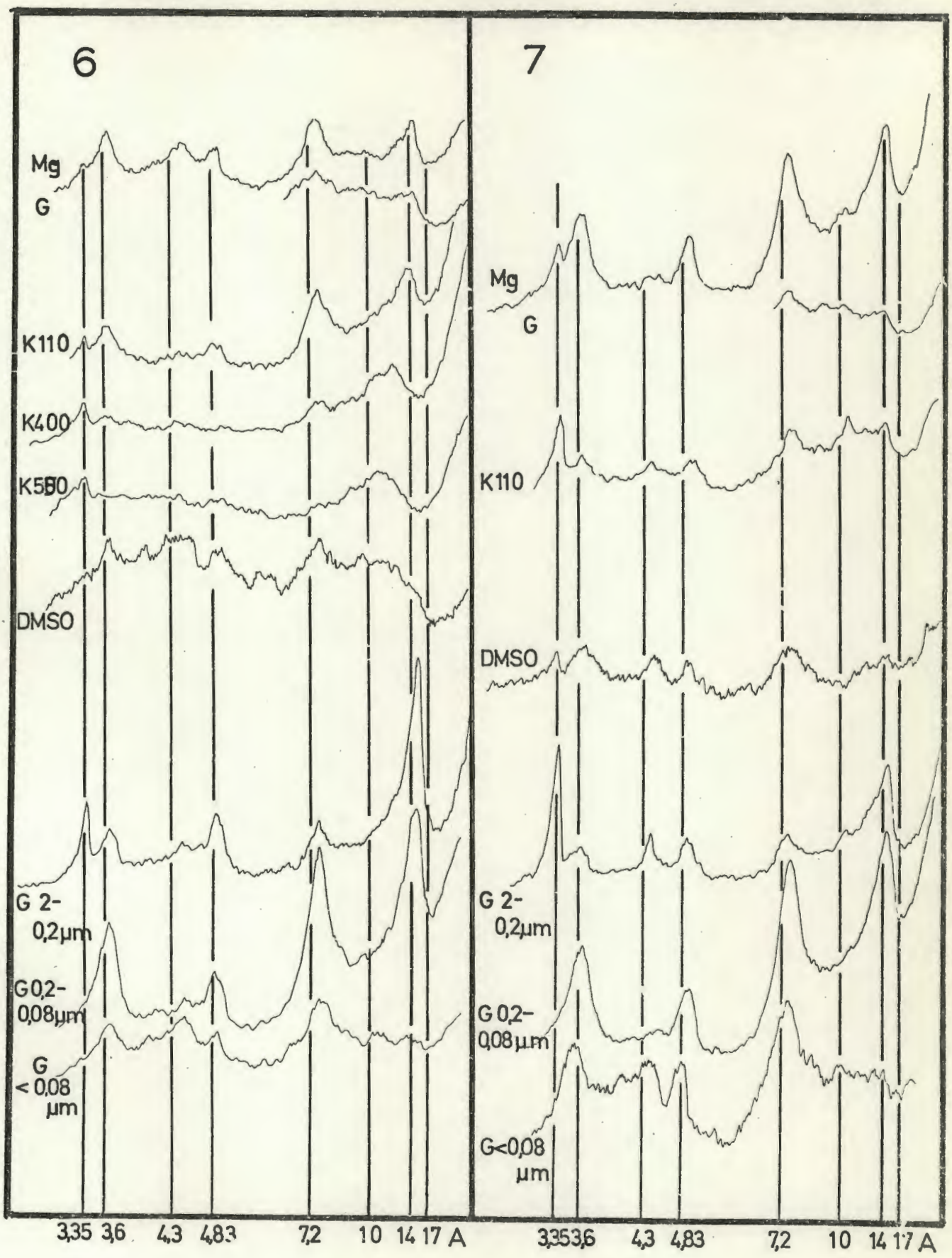

FIGURE 3. X-ray diffractograms of deferrated clay from samples 6 and 7 (legend as for fig. 1)

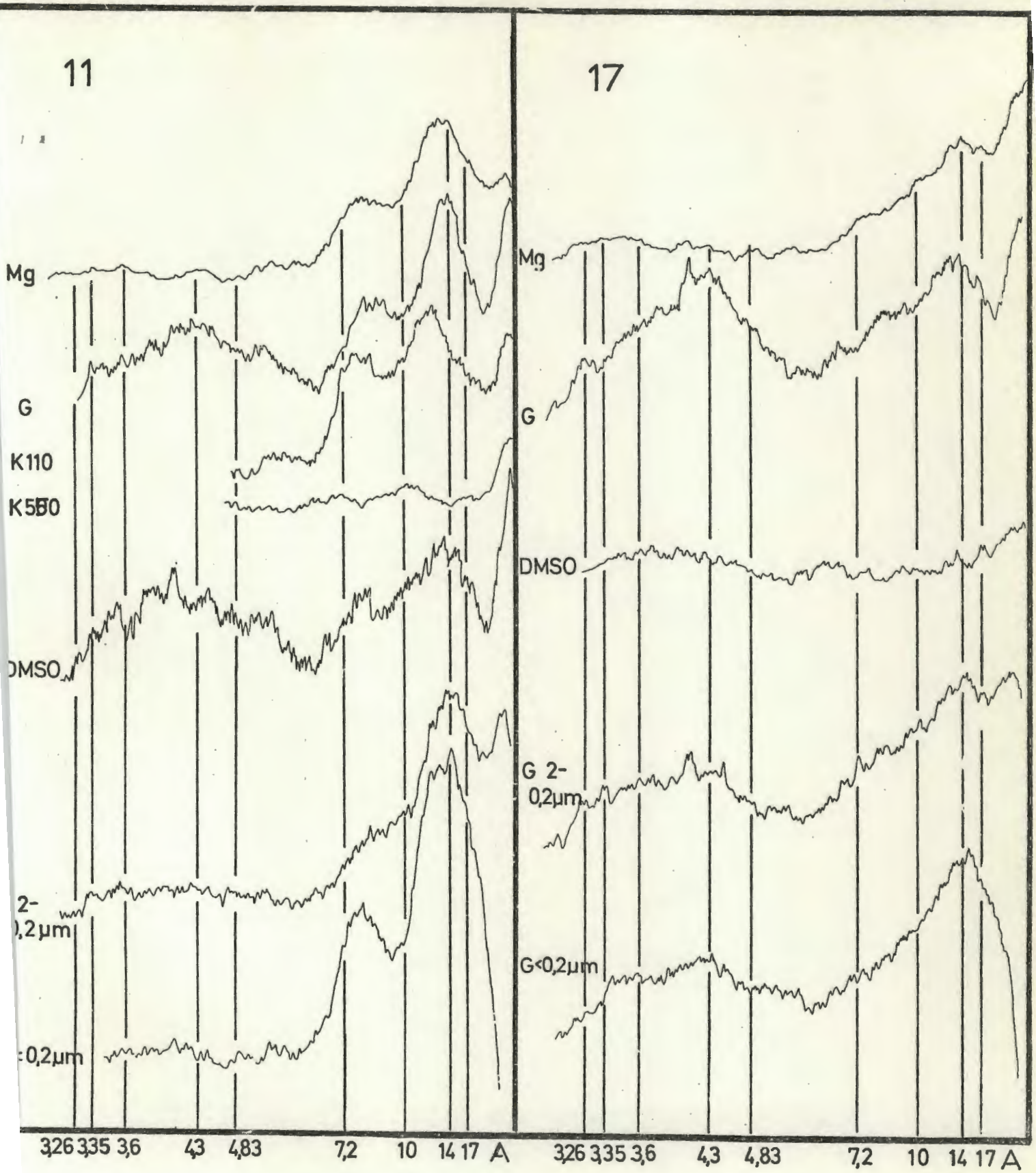

FIGURE 4. X-ray diffractograms of deferrated clay from samples 11 and 17 (legend as for Fig. 1)

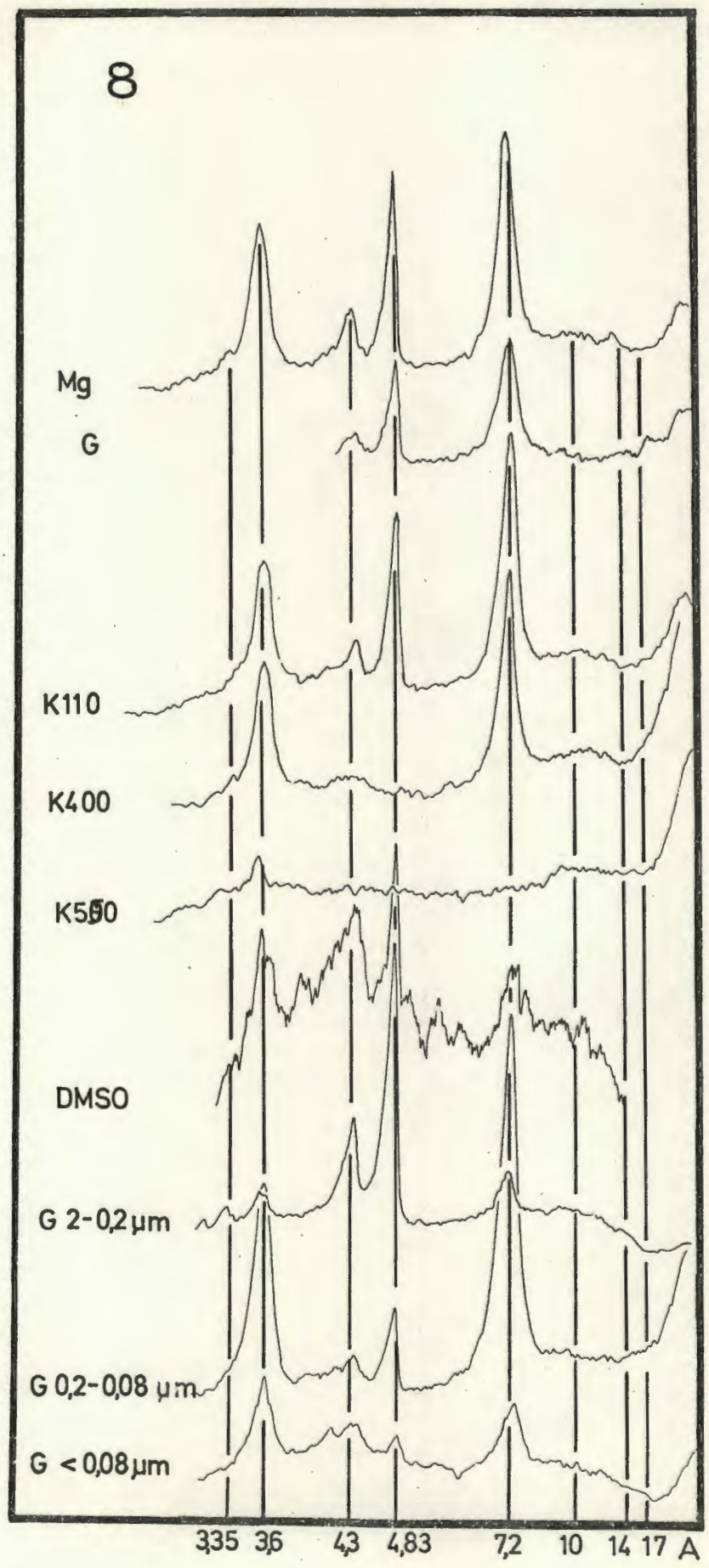

FIGURE 5. X-ray diffractograms of deferrated clay from sample 8 (legend as for Fig. 1)

le Roux, 1973), clay fractions of the Natal Oxisols (Figs. 1 - 3) contain mainly kaolinite and pedogenic aluminous chlorite, with smaller amounts of gibbsite and accessory amounts of quartz and mica.

The presence of chlorite in Natal Oxisol clays is confirmed by a 14A peak which is stable after K-saturation and heating to 110C, and which collapses, after heating at 550C, to a broad, rather diffuse 10A peak exhibiting asymmetry in the 14A direction. At 400C only partial collapse is observed, indicating only partial dehydroxylation of interlayer material at this temperature. The thermal stability of this chloritic component appears to be somewhat variable. For example, the Balmoral and Kranskop soil clays studied by de Villiers and Jackson (1967a) contained a relatively stable chlorite which displayed, even at 550C, a negligible tendency to collapse. On the other hand, chlorites synthesized from Kenya vermiculite by Brydon and Turner (1972) displayed thermal characteristics similar to those encountered here, with dehydroxylation of Al interlayers occurring somewhere between 400C and 550C. No chloritic material was identified in the Kraznozem (Fig. 5) or in the lower B horizon of the Farmhill derived from basalt (Fig. 1). In the latter, a lithological discontinuity exists between the upper (yellow) and lower (red) B horizons (samples 2 and 3 respectively), with the possibility that some sandstone-derived material may have become admixed with the upper part of the solum. This may explain why chlorite and quartz (3,35A) are present in sample no. 2 but not in no. 3. The allophanic clays (Fig. 4) also display relatively strong, somewhat broad 14A reflections, in agreement with the reported frequent occurrence of chlorite and vermiculite-chlorite intergrades in the clay fraction of volcanic ash soils (Wada & Aomine, 1973; Chichester, Youngberg & Harward, 1969).

Formation of chlorite via hydroxyinterlayering of weathered mica (le Roux, 1973) would explain the predominance of chlorite in soil clays derived from micaceous shales (e.g. sample no. 4) and would account for its decreasing abundance with particle size, as indicated by diffractograms for coarse, medium and fine clays of the Natal Oxisols (Fig. 1 - 3). However, it is difficult to explain this trend for the Balmoral clay (Fig. 2) which is thought to have formed from dolerite (Appendix I). Kantor and Schwertmann (1974) have established that smectite neogenesis can occur in close proximity to weathering basic rock within an otherwise strongly-leached pedological environment. Smectite thus formed rapidly disappears with acid weathering in the surrounding soil. In the Balmoral, it is possible that, although fine smectite may have weathered rapidly, larger neoformed particles may have had greater metastability and hence sufficiently protracted residence in the solum to effect

interlayering with hydroxyalumina, with consequent resistance to acid weathering. The contention that pedogenic Al-chlorite may, in this respect, be more stable than kaolin (de Villiers, 1965), appears to be contradicted by the absence of the former and presence of the latter, along with some gibbsite (4,83A), in the fine clay fraction. However, it is possible that the 2 : 1 layer silicate structure may retain its relatively greater susceptibility to acid attack to an extent inversely proportional to the degree of hydroxyinterlayering, which, as the data for K-saturated clays in Figures 1 - 3 indicate, is by no means complete. It is interesting to note that the 14A peak is more pronounced in diffractograms of medium plus fine clay than in those of coarse clay of the volcanic ash soils (Fig. 4). This may point to a neogenetic origin of chlorite, as suggested by Wada and Aomine (1973) for soils formed from andesitic ash.

Certain evidence points to the presence of halloysite, together with kaolinite, in some of the Natal soils. In samples 2 and 3, a d spacing of 7,4A is evident, as opposed to 7,2A for pure kaolinite. In the other Natal samples there is a shift of the (001) maximum from 7,2A toward 7,3A and higher spacings as particle size decreases - that is, most of the fine clays are halloysitic. The relatively broad nature and low intensity of kaolin peaks in the < 0,08 µm fraction suggest that this material, in addition to being halloysitic, is of comparatively short-range order and poor crystallinity. The actual quantity of such material in the clay fraction as a whole can be gauged from the relative proportions of coarse, medium and fine clay shown in Table 2: with the exception of the Kraznozem (no. 8), fairly large amounts are present. Partial dehydroxylation of kaolin in sample no. 6 (Fig. 3) at 400C, as indicated by a marked reduction in intensity of diffraction maxima at this temperature, is also indicative of halloysite-like material. Electron microscopy (dealt with later) has confirmed these observations. Of interest is the fact that in all cases, the 1 : 1 layer silicate component is concentrated in the 0,2 - 0,08 µm clay. In cases where abundant chlorite was present, intersalation with DMSO provided positive identification of kaolin (11,18A), although it appears as though intersalation was probably not always complete (Figs. 1 - 5).

Gibbsite (4,83A) is present in all the Oxisols, being most abundant in the Kraznozem (no. 8). Surprisingly, the relative decrease of this component with particle size in the Kraznozem clay is not found in some of the Natal clays, where the reverse is true. For example, in sample no. 3 (red B horizon from basalt), it was only possible to identify gibbsite by separate examination of medium and fine clay separates.

TABLE 2 Relative proportions of size-subfractions in deferrated soil clays*

Sample	Coarse clay (2 - 0,2 μm)	Medium clay (0,2 - 0,08 μm)	Fine clay (< 0,08 μm)
	%		
2	36	46	18
3	64	26	10
4	38	42	20
5	28	57	15
6	23	54	23
7	26	57	17
8	33	64	3
11	59	41†	
17	49	51†	

* Estimated on the basis of oven dry weight after NH_4-saturation.

† Medium plus fine clay.

Diffractograms of glycerol-solvated fine clays indicate that there is little or no montmorillonite present in any of the samples studied. Quartz (3,35A) is a common constituent of most of the clays (see also section 1.4.5.3). Its distribution is confined to the coarse clay fraction and it is probably of inherited origin. The absence of any pronounced 10A reflections indicates that quantities of mica are insignificant.

Random powder diffraction patterns of natural clays (Fig. 6) indicate that goethite (4,15A) is probably the major form of occurrence of free iron oxide in the Natal Oxisols and the Kraznozem, while the Latosol Roxo* from Brazil is dominated by a mixture of one or more of hematite, maghemite and ilmenite. Small goethite reflections are also apparent in diffractograms of the volcanic-ash soil clays (11 and 17). It is considered that, because of the relatively large amounts of alumina associated with CDB-extractable iron oxide (Table 3), the goethite in these clays is probably highly Al-substituted, and therefore of relatively poor crystallinity (Norrish & Taylor, 1961). This would account for the rather weak goethite diffraction maxima generally observed in Fig. 6. The random powder patterns also enable the identification of imogolite (3,26A - Wada, 1967) in both the volcanic-ash soil clays. Interestingly, imogolite was reported in volcanic ash soils from New Zealand for the first

* A strong gibbsite reflection (4,83A) is also evident.

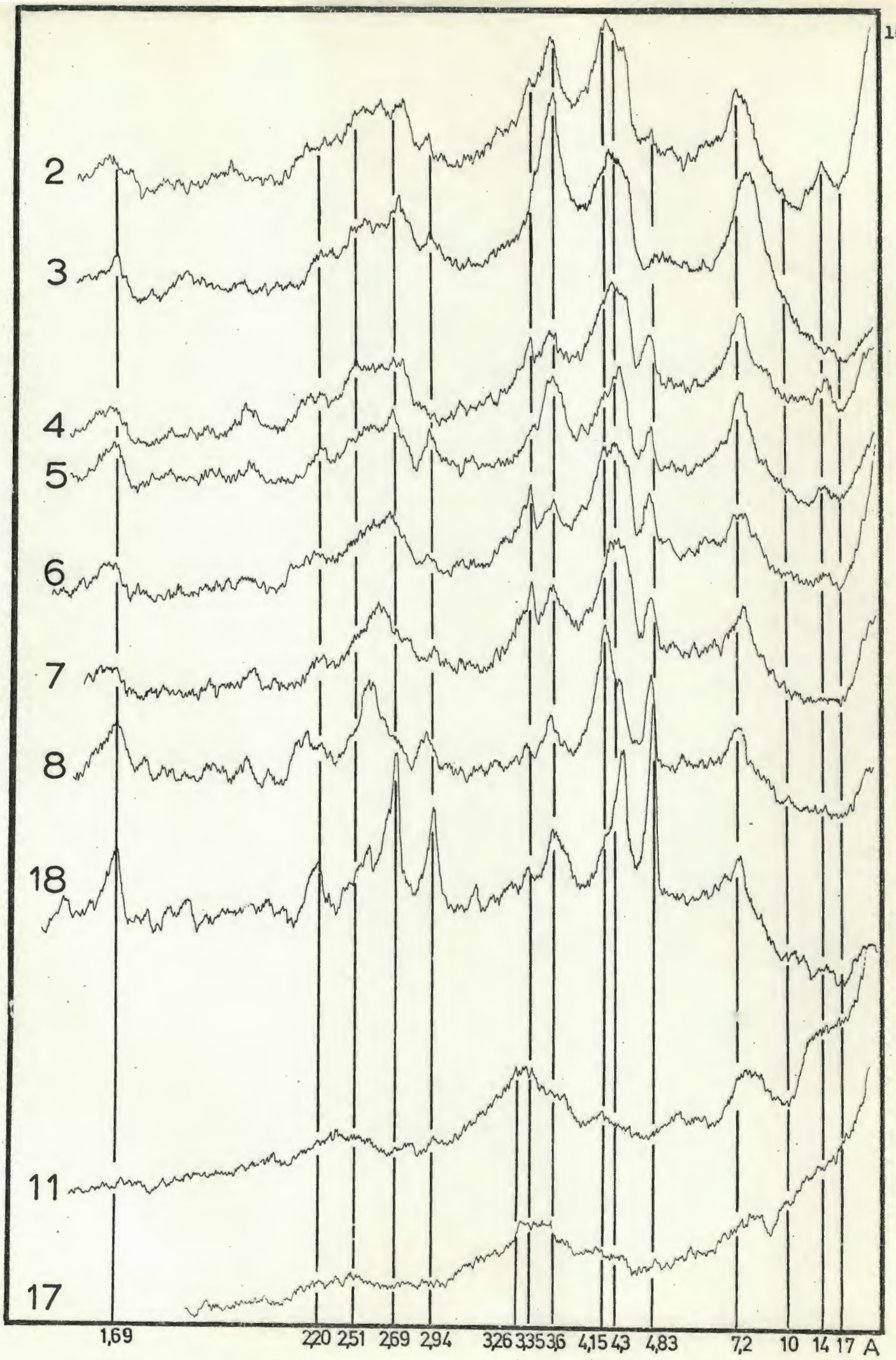

FIGURE 6. X-ray powder diffractograms of K-saturated, freeze-dried natural

TABLE 3 Quantities of CDB-extractable iron oxide and alumina in the soil clays*

Sample	— % Extracted —	
	Fe_2O_3	Al_2O_3
2	13,6	7,0
3	18,7	3,8
4	10,8	7,6
5	18,3	4,5
6	12,3	7,8
7	14,7	7,6
8	33,0	11,2
18	30,6	7,0
11	4,9	15,7
17	3,1	10,9

* See also section 1.4.5.

time recently (Yoshinaga, Tait & Soong, 1973). One of these soils was Tirau Silt Loam, from which sample no. 17 originates (Table 1). Imogolite is known to be present in sample no. 11 (Wada & Aomine, 1973 - their sample 905).

1.4.2 Thermal analysis and surface area

Differential thermograms of H_2O_2-treated, deferrated clays and natural clays are presented in Figures 7 and 8 respectively. Areas of major endotherms are given in Table 4, and were measured by the triangulation method of Dixon (1966), with a modification in the case of the low-temperature endotherm involving the baseline extrapolation technique used by Webb (1958), which eliminates difficulties associated with baseline drift following dehydration.

The thermograms confirm the presence, indicated by X-ray diffractometry, of gibbsite (which dehydroxylates at about 300C) and kaolinite-halloysite (endotherm in the region of 500C) in the Oxisols. The volcanic-ash soil clays exhibit thermal behaviour typical of allophane, with a large low-temperature dehydration endotherm, and a high-temperature exotherm, while a mid-range endotherm around 500C is absent. Low-temperature endotherms of the Oxisols are all relatively large, indicating the presence of hydrated amorphous material, halloysite, or both.

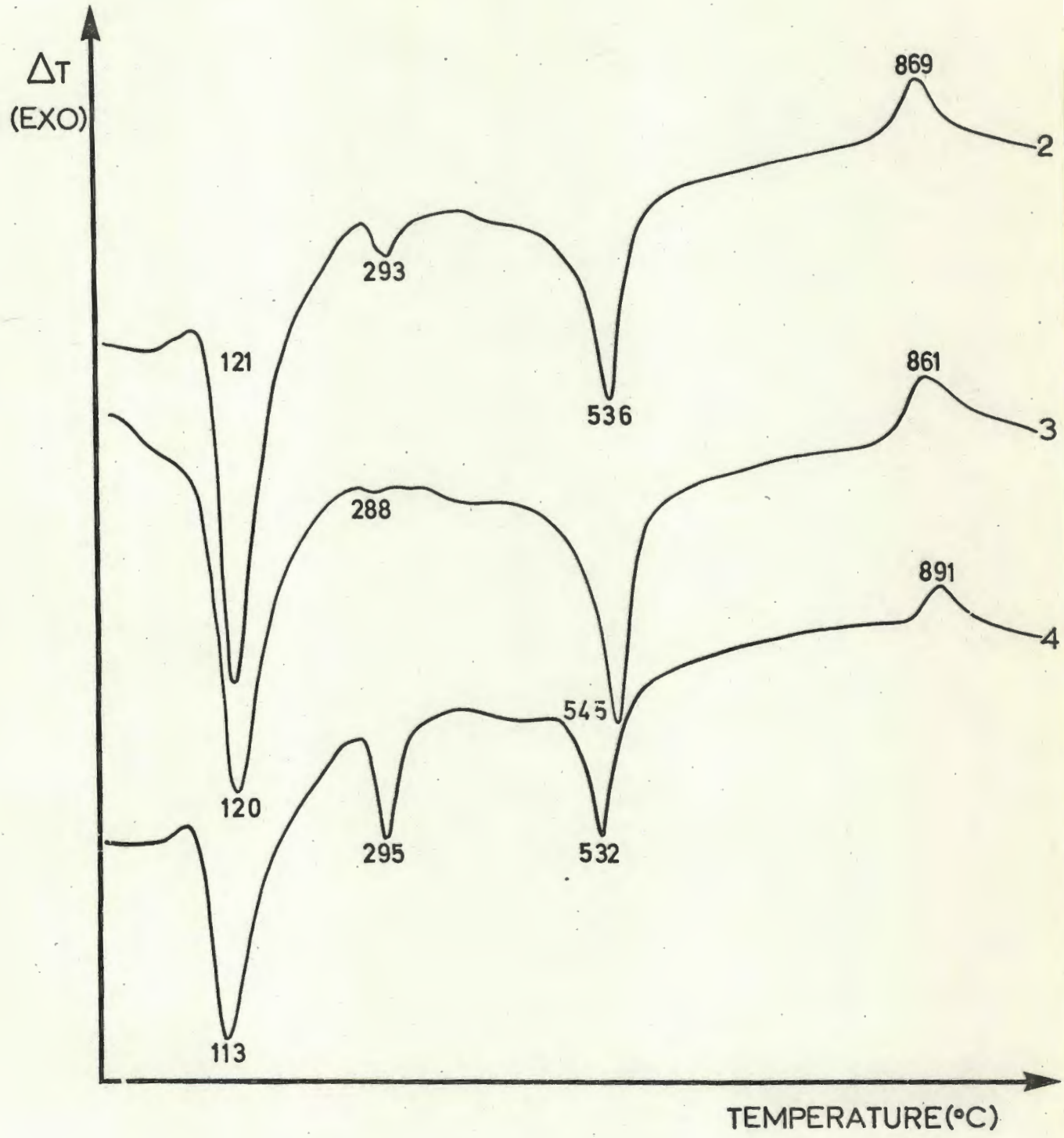

FIGURE 7a. Differential thermograms of H_2O_2-treated, deferrated Natal Oxisol clays (samples 2, 3 & 4)

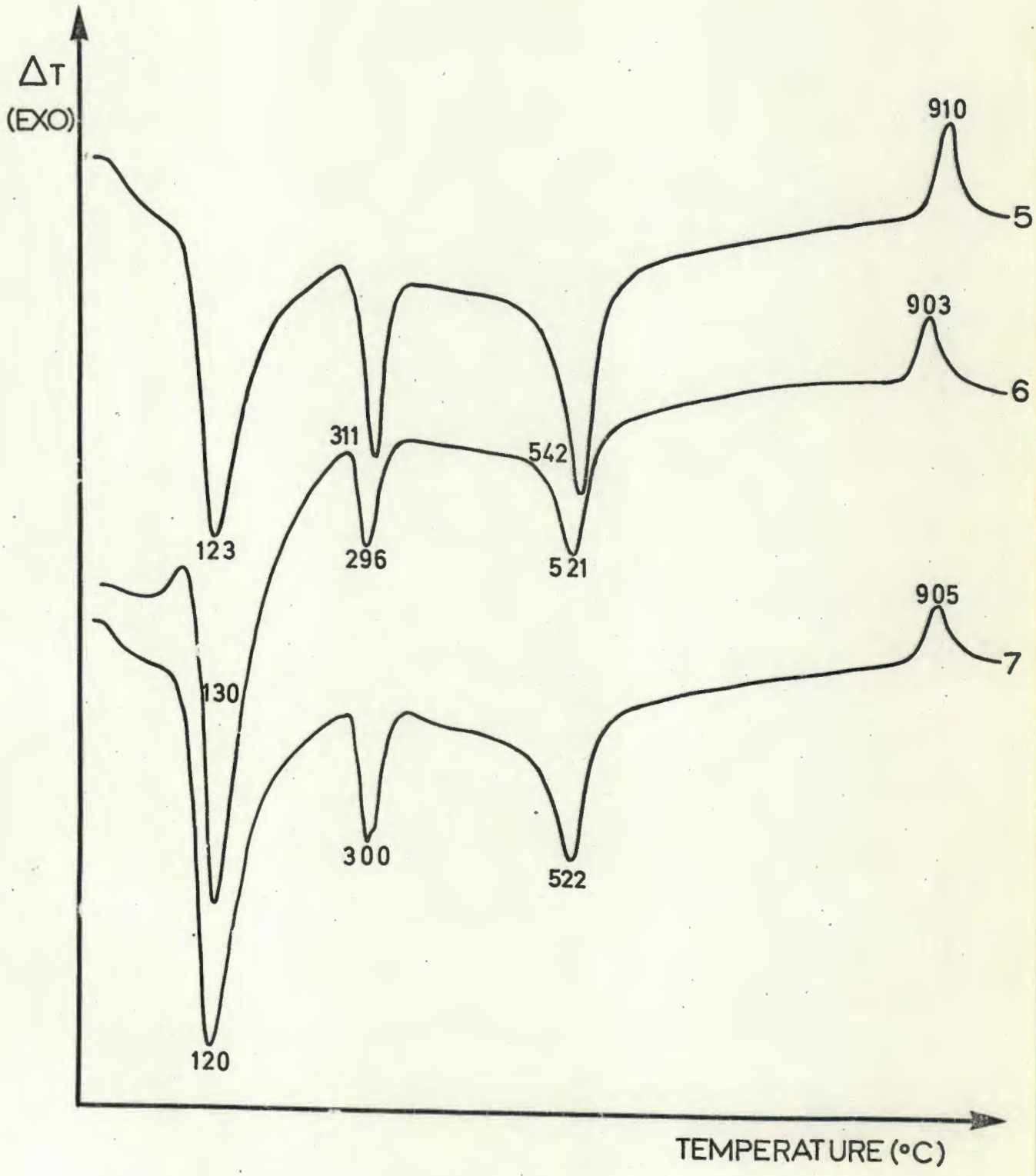

FIGURE 7b. Differential thermograms of H_2O_2-treated, deferrated Natal Oxisol clays (samples 5, 6 & 7)

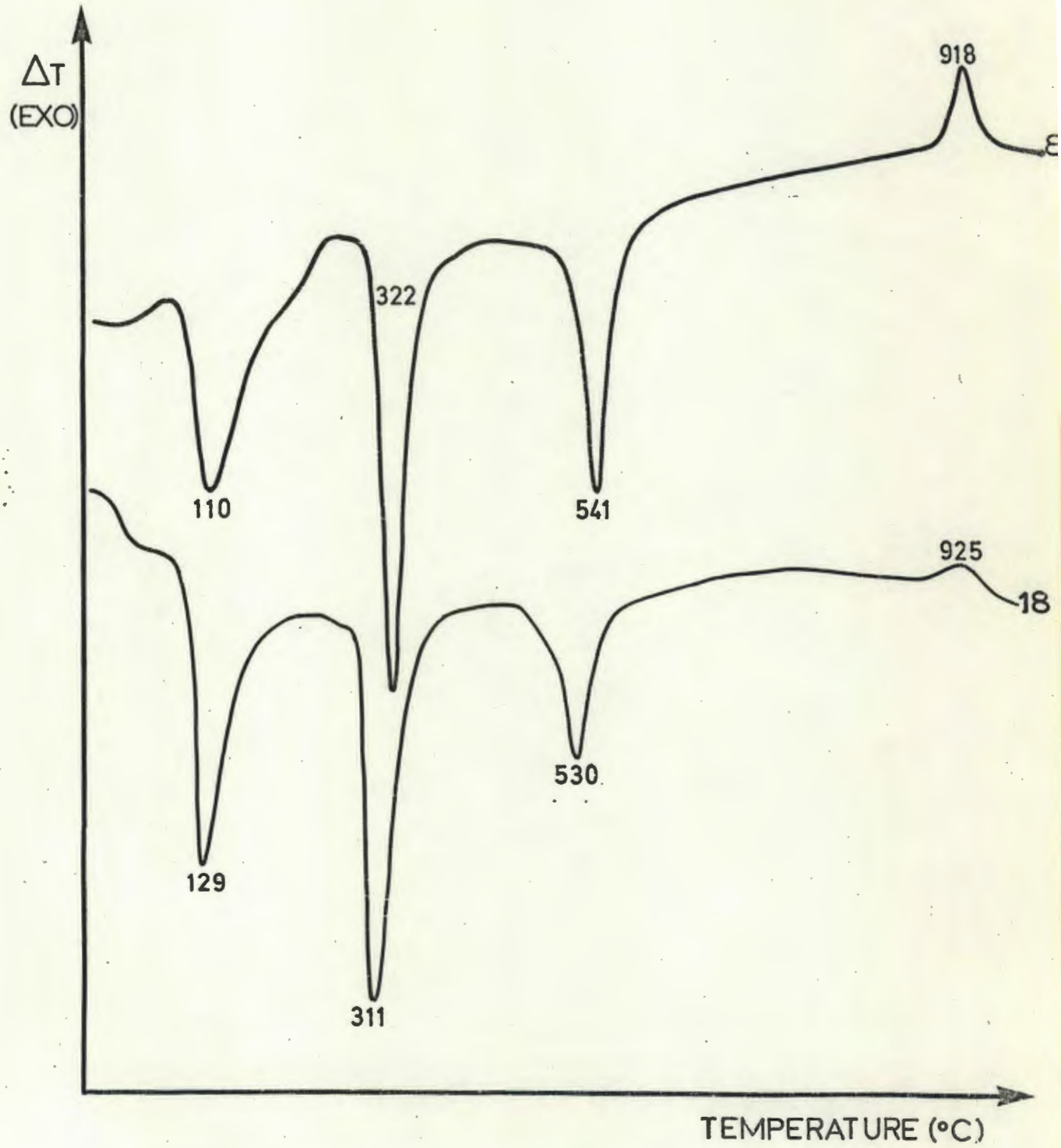

FIGURE 7c. Differential thermograms of H_2O_2-treated, deferrated Kraznozem and Latosol Roxo clays (samples 8 & 18)

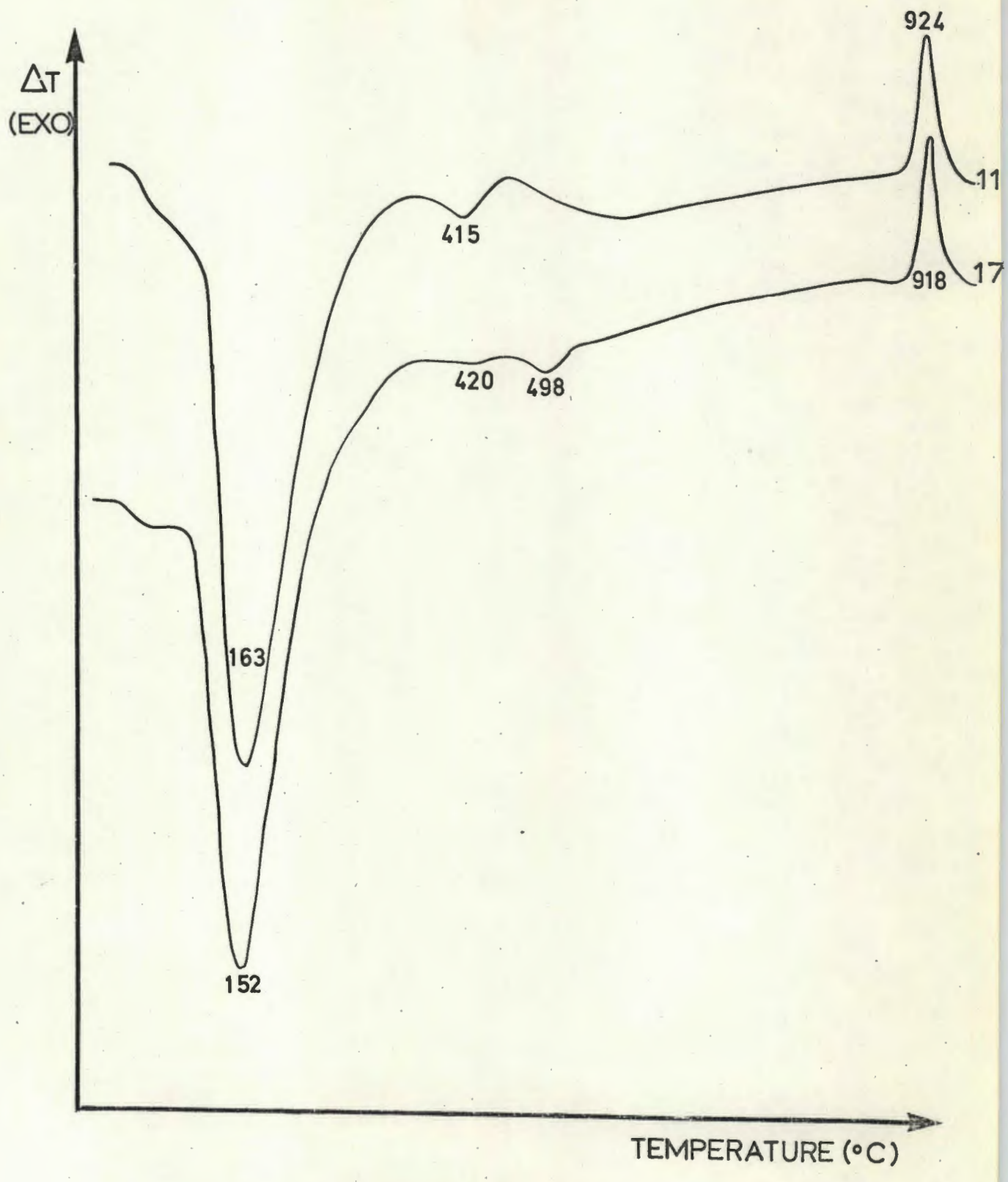

FIGURE 7d. Differential thermograms of H_2O_2-treated, deferrated volcanic ash soil clays: Kodonbaru and Tirau (samples 11 & 17)

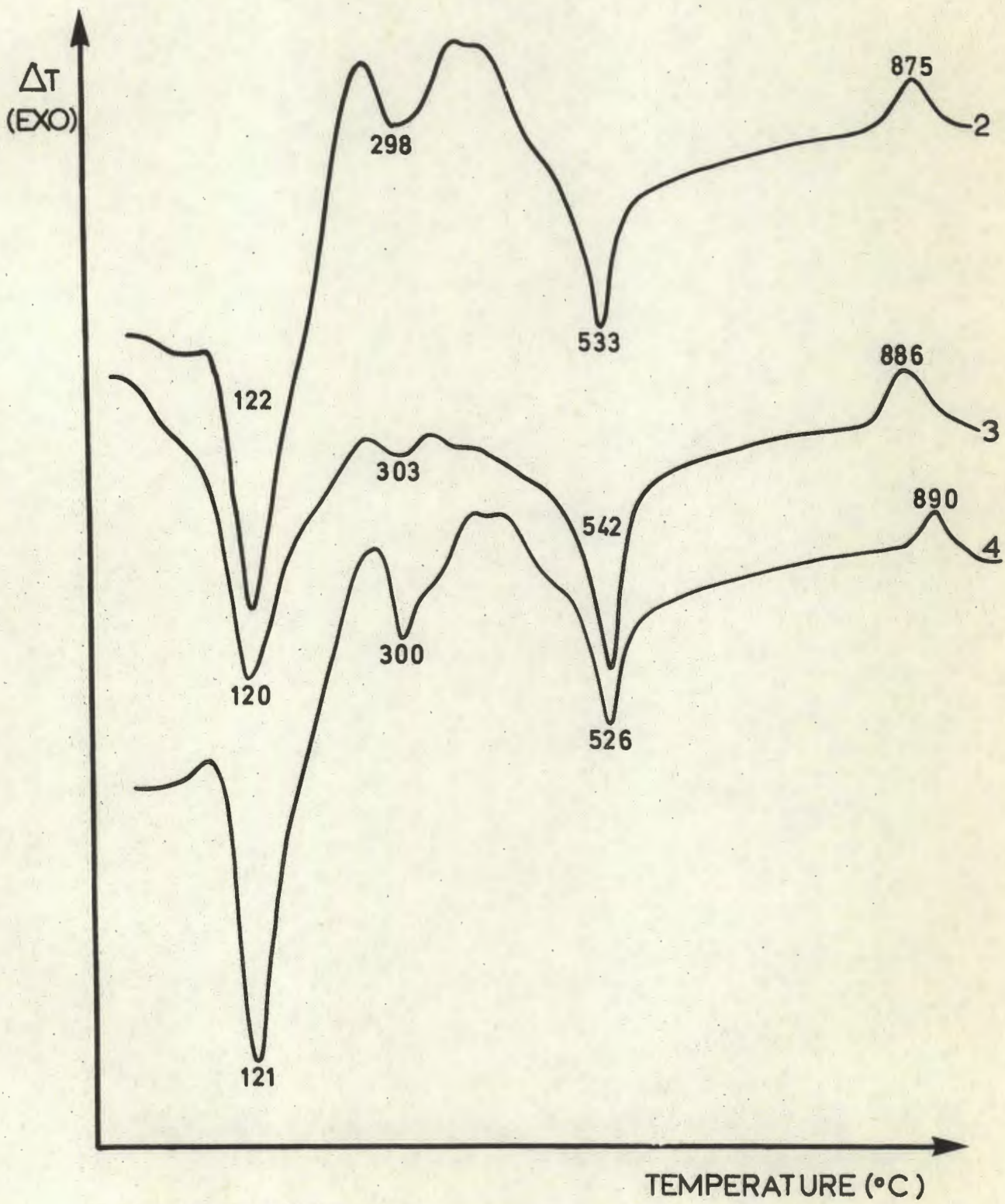

FIGURE 8a. Differential thermograms of natural clay from Natal Oxisols (samples 2, 3 & 4)

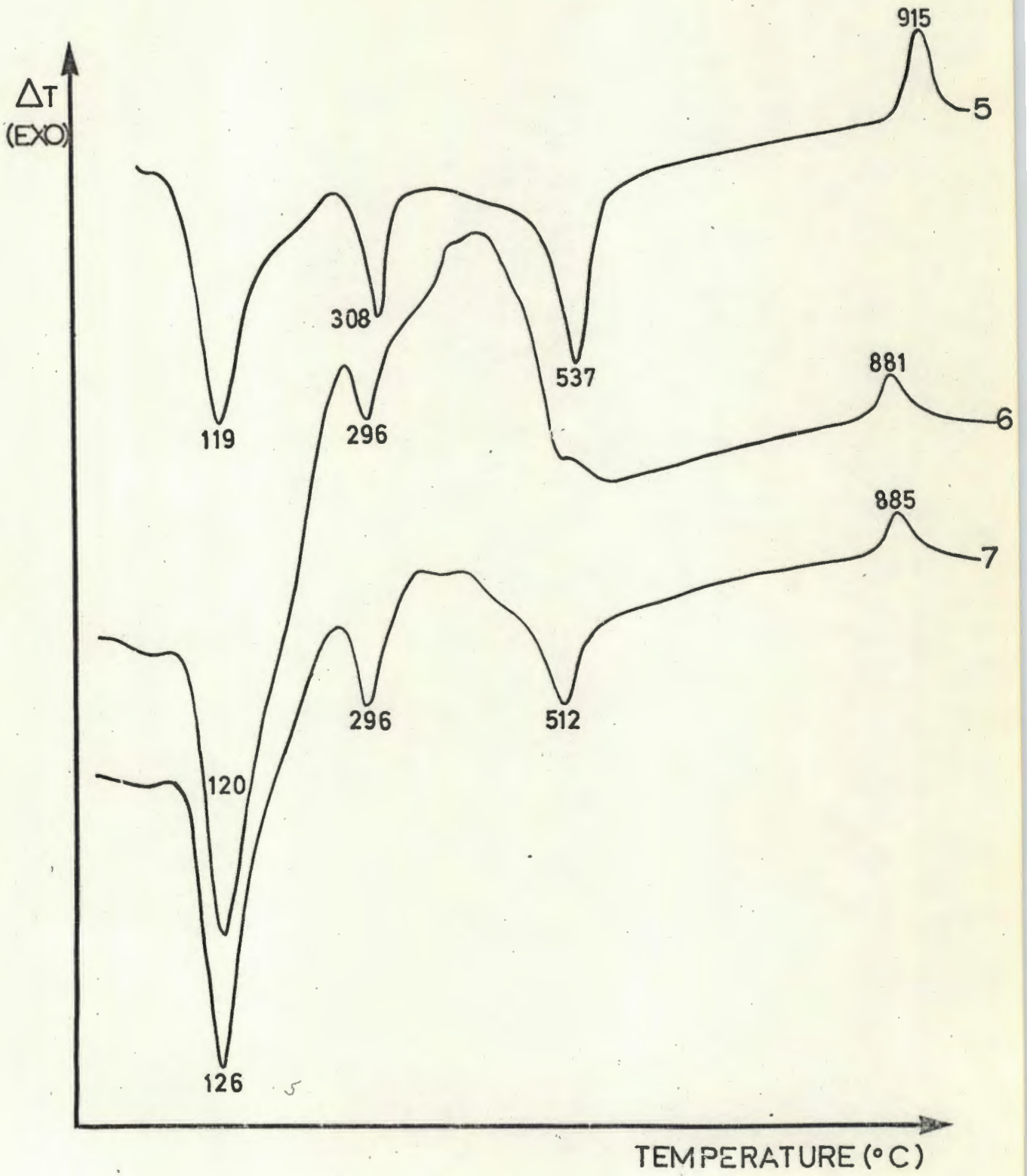

FIGURE 8b. Differential thermograms of natural clay from Natal Oxisols (samples 5, 6 & 7)

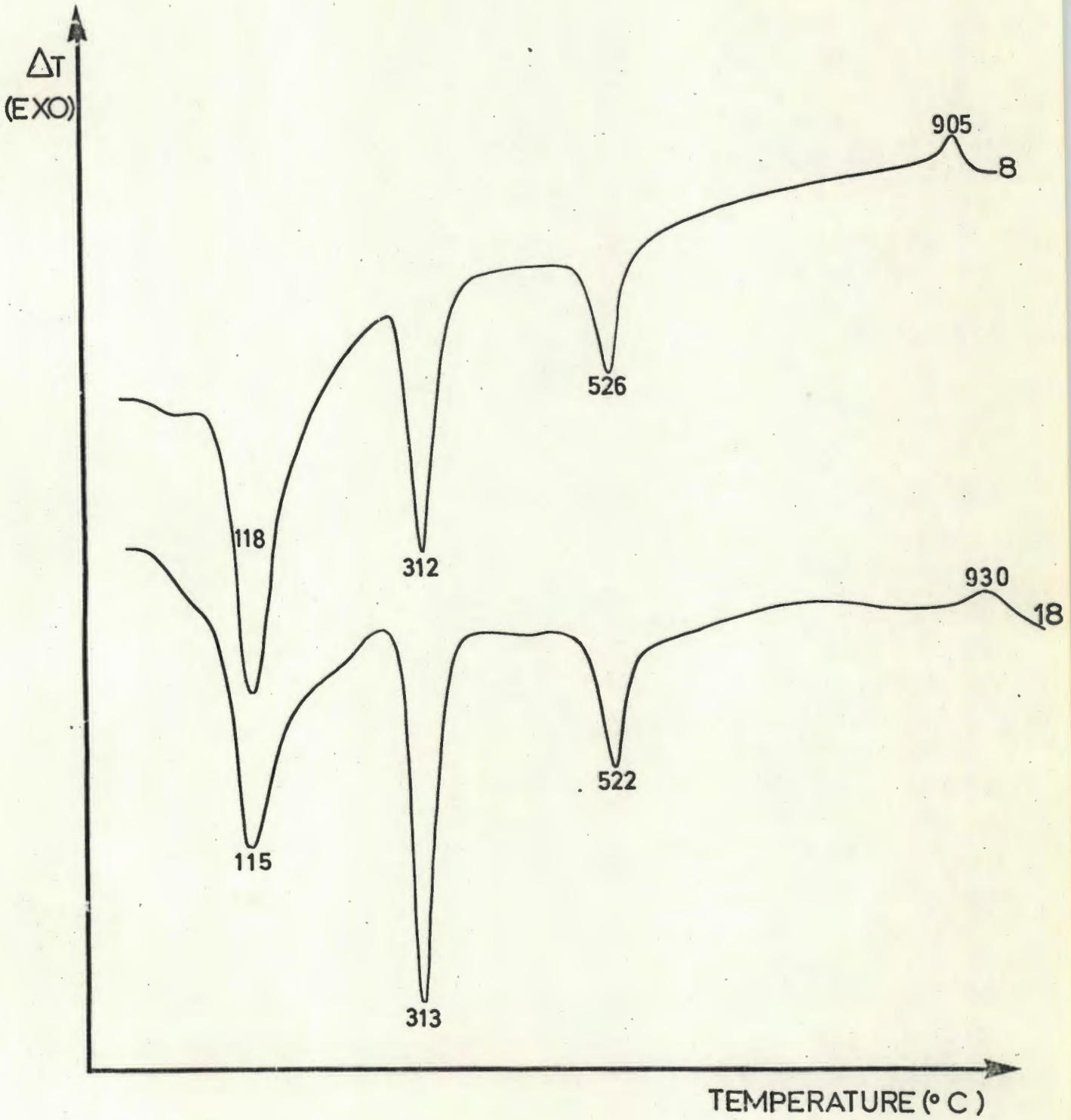

FIGURE 8c. Differential thermogram of Kraznozem and Latosol Roxo natural clays (samples 8 & 18)

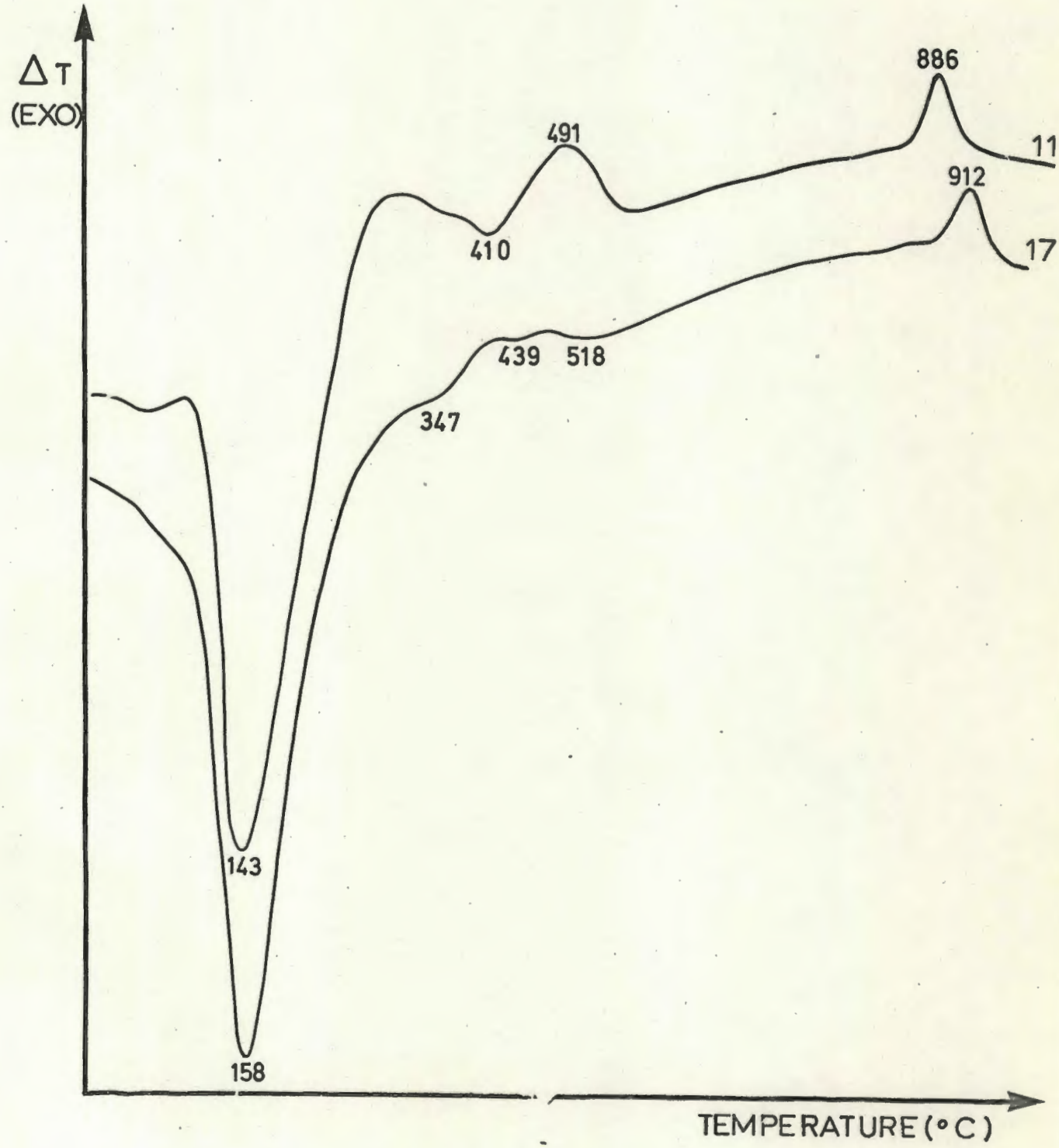

FIGURE 8d. Differential thermograms of natural clay from volcanic ash soils: Kodonbaru and Tirau (samples 11 & 17)

It has already been shown by X-ray diffractometry that little or no montmorillonite exists in these clays. The hydration index (Table 4), calculated as the ratio of the low-temperature endotherm area to the combined area of the two mid-range dehydroxylation endotherms, was derived in an attempt to obtain some meaningful measure which might relate to the quantity of amorphous material present. Although there is no close relationship between either the low-temperature endotherm area or the hydration index and surface area values, the hydration index in particular seems to differentiate fairly clearly the three groups of materials, namely the Natal soil clays, the Oxisol clays from Australia and Brazil, and the amorphous, highly hydrated volcanic-ash soil clays from Japan and New Zealand.

TABLE 4 Quantitative differential thermal data and specific surface area of natural and deferrated soil clays

Sample	Endotherm area (cm^2)			Hydration index*	Specific surface area (m^2/g)
	Low temp. 100-200C	300C	500C		
H_2O_2-CDB treated clay					
2	70,2	0,9	33,3	2,1	292
3	83,5	0,5	38,1	2,2	256
4	46,4	12,6	16,7	1,6	199
5	80,9	20,8	39,7	1,3	261
6	61,9	11,6	19,8	2,0	349
7	105,9	17,1	23,2	2,6	307
8	49,0	63,6	35,7	0,5	117
18	67,5	65,5	25,2	0,7	105
11	223,8	8,1**	-	27,6	509
17	174,8	4,8**	-	36,4	538
Natural Clay					
2	62,3	24,2	16,5	1,5	284
3	79,2	3,6	32,1	2,8	246
4	67,3	15,3	19,6	1,9	223
5	77,4	15,5	28,2	1,8	313
6	74,4	8,1	†	-	240
7	69,3	10,7	17,5	2,5	325
8	64,3	36,1	15,7	1,2	265
18	67,5	53,7	20,8	0,9	139
11	185,3	†	-	-	441
17	219,0	-	-	-	473

* Ratio of areas of low temp./300C + 500C endotherms.

** Endotherms at about 400C due to dehydroxylation of imogolite and/or halloysite.

† Endotherm obscured by combustion of organic matter.

There appears to be no consistent effect of peroxide treatment and deferration on surface area values (Table 4). This can be attributed to the fact that, on the one hand, cementing agents are removed, giving rise to an increase in specific surface, while on the other, a certain amount of amorphous and poorly-crystalline material will be removed, which would be expected to cause a decrease in surface area. The relatively high surface area values of the Natal Oxisol clays after H_2O_2-CDB treatment reflect the presence of a significant quantity (Table 2) of finely-divided, poorly-ordered, halloysitic kaolin (see X-ray diffraction data for < 0,08 µm clays). Hydration index (Table 4) varies accordingly.

Interestingly, DTA appears to be a very poor diagnostic tool for clays high in chlorite. Meyers and Ahlrichs (1972) showed that the technique is poorly sensitive even to fully Al-hydroxyinterlayered montmorillonite, recording rather shallow endotherms at 359C and 462C corresponding to dehydroxylation of interlayer material. Close inspection of the thermograms in Figures 7 and 8 reveals a subtle though consistent asymmetry of the 500C kaolinite endotherm which might correspond to dehydroxylation of chlorite interlayers between 350 and 500C. In some cases (e.g. no. 4, Fig. 7a) there is even a separate, very weakly expressed endothermic effect around 400C. The much larger endotherms in this temperature range displayed by the allophanic clays (Fig. 7d) are therefore probably not due to a chloritic component (the presence of which is indicated by XRD analysis), but rather to imogolite and/or halloysite. The former has been found to dehydroxylate at around 420C when subjected to a heating rate of 20C/min (Aomine & Mizota, 1972).

Despite a flowing N_2 atmosphere, organic matter in the natural clays burnt off to produce a variable exothermic effect between 200 and 500C (Fig. 8) which to some extent eliminates any useful comparison of the 300C endotherms for natural and deferrated clays. Nevertheless, the fact (Table 4) that in some cases (samples 2, 3 and 4 - Fig. 8a) the 300C endotherm was larger for the natural clay than for its deferrated residue, while in the remaining Oxisols (Figs. 8b, c) it was larger than would be expected were its relative size to be dictated merely by a physical dilution effect of CDB-extractable material, points to the dehydroxylation in this temperature region of another component besides gibbsite. This component is likely to be goethite, which is envisaged as being extensively Al-substituted (Table 3) owing to its relatively low dehydroxylation temperature (the typical temperature for pure goethite is around 380C - MacKenzie & Berggren, 1970).

The 300C endotherm areas of deferrated clays (Table 4) were used to estimate quantitatively the amounts of gibbsite present (Table 5).

TABLE 5 DTA estimates of gibbsite and kaolin contents of the deferrated clays

Sample	Gibbsite	Kaolin
	%	
2	2,6	39,4
3	0,4	45,1
4	9,4	19,8
5	15,6	47,0
6	8,8	23,4
7	12,8	27,5
8	47,7	42,2
18	49,6	30,0
11	0,0	0,0
17	0,0	5,7

Attempts to similarly estimate kaolinite plus halloysite content were less successful. Calibration was not as good as that for gibbsite, while it was suspected, after comparison with values obtained by selective dissolution analysis, that kaolinite-halloysite contents (Table 5) were generally underestimated by this method. This may point to the association of a smaller energy change with dehydroxylation of poorly-ordered kaolinite and halloysite than with that of well-crystallized kaolinite. (Georgia kaolinite was used as a standard while X-ray indications that many of the clays contain halloysite were confirmed by electron microscopy.) Quantitative gibbsite values are dealt with later.

TABLE 6 Thermogravimetric data for the deferrated clays

Sample	WT. LOSS (%)		
	110C	110 - 300C	300 - 950C
2	4,5	4,5	10,3
3	4,2	2,4	11,0
4	3,7	6,6	8,8
5	3,4	6,5	12,3
6	5,0	6,3	10,6
7	4,8	6,6	10,1
8	1,4	11,2	11,2
11	18,7	11,9	11,4
17	17,9	11,0	7,4

The results of thermogravimetric analysis are shown in Table 6. Weight loss after heating to 110C is expressed on the basis of original weight of the K-saturated clay equilibrated at 56% RH, that between 110 and 300C is based on oven-dry (110C) weight, and ignition loss above 300C is based on the weight of clay after heating at 300C (Alexiades & Jackson, 1967). As would be expected, there is a close correspondence between weight loss at 110C (Table 6) and hydration index (Table 4). Whereas the weight loss of Oxisol clays between 110 and 300C appears to be governed to a large extent by dehydroxylation of gibbsite (note correspondence with gibbsite values in Table 5), the large weight loss of samples 11 and 17 must arise from dehydroxylation of allophane. DTA appears to be unable to differentiate between adsorbed H_2O and structural OH. There may in fact be a gradation between the two. It has been established from infrared spectroscopic evidence (Wada, 1966) that all the OH groups of allophane are located at the surface. It is also generally thought that the functional group typically responsible for the reactivity of amorphous sesquioxides in soil takes the form $-OH_2^{\frac{1}{2}+}$ (de Villiers & Jackson, 1967a), and is readily deprotonated to -OH if the pH is raised sufficiently. Hydroxyls in allophane are probably therefore intimately associated with adsorbed water. Sample no. 11 retains a larger quantity of water at 300C than does no. 17, which corresponds more closely to the value of 8% for allophane suggested by Alexiades and Jackson (1967). Dehydroxylation of halloysite, imogolite, and pedogenic chlorite may account for this higher value. Calculation of chlorite contents from data for ignition weight loss above 300C (Table 6) is dealt with later.

1.4.3 Infrared spectroscopy

Although amorphous substances give more featureless spectra than do well crystallized minerals, they absorb as strongly, so that their presence in admixture with crystalline clays is less likely to be overlooked than in examination using other techniques (Farmer, 1968). Previous studies on the clay mineralogy of Natal Oxisols have pointed to the presence of a fairly considerable quantity of amorphous (alkali-extractable) silica and alumina (de Villiers & Jackson, 1967a; le Roux, 1973). As yet infrared spectroscopy has not been used for the investigation of these soil clays.

IR spectra of natural clays, deferrated clays, and selected deferrated fine (< 0,08 µm) clays are presented in Figures 9, 10 and 11 respectively. Absorption bands in the OH stretching vibration region indicate the presence of kaolinite-halloysite (3700 and 3620 cm^{-1}), gibbsite (3520, 3450 and - smaller - 3380 cm^{-1}) and goethite (3200 cm^{-1}) in clay fractions of the

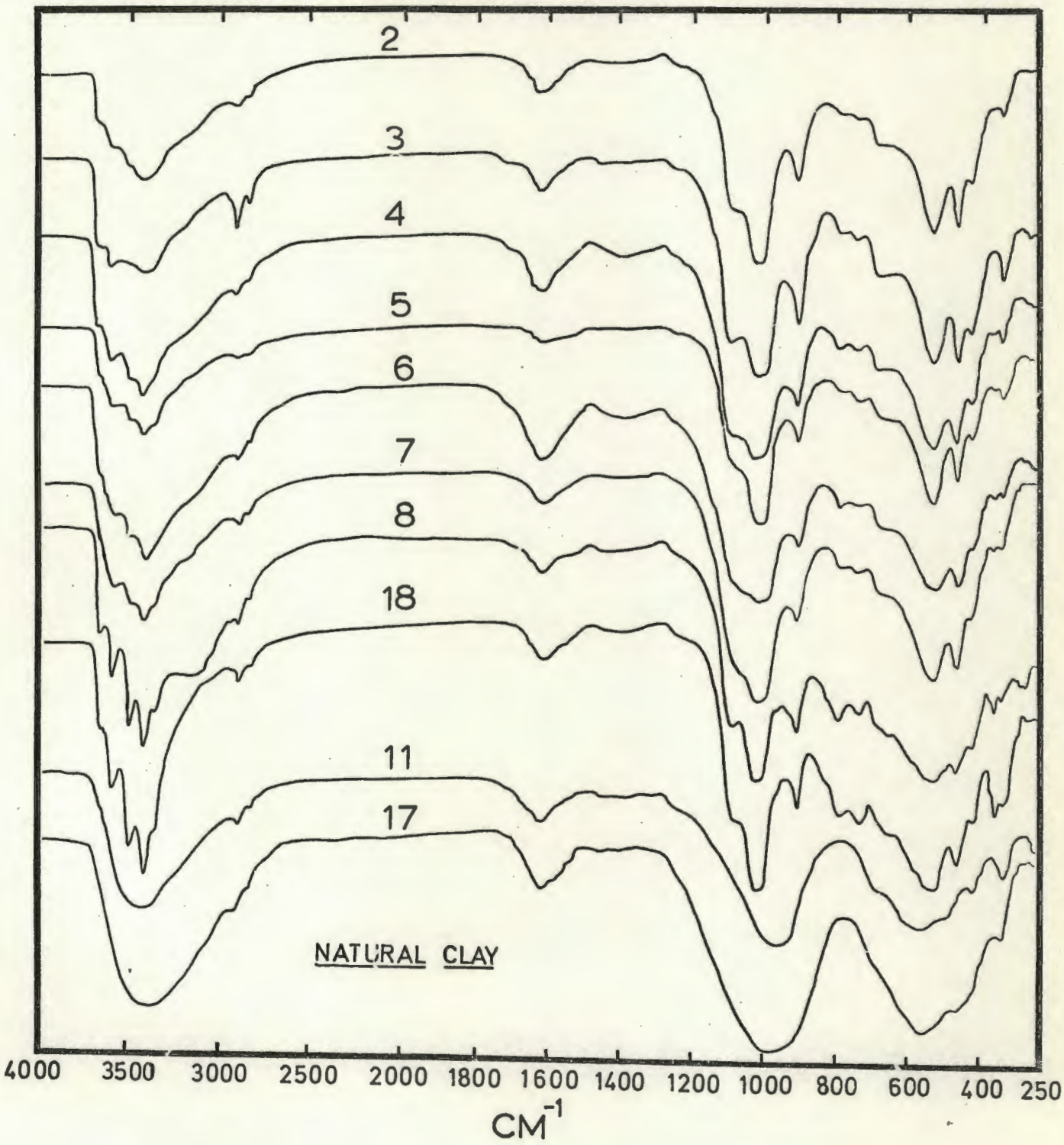

FIGURE 9. Infrared spectra of natural clays (< 2 μm)

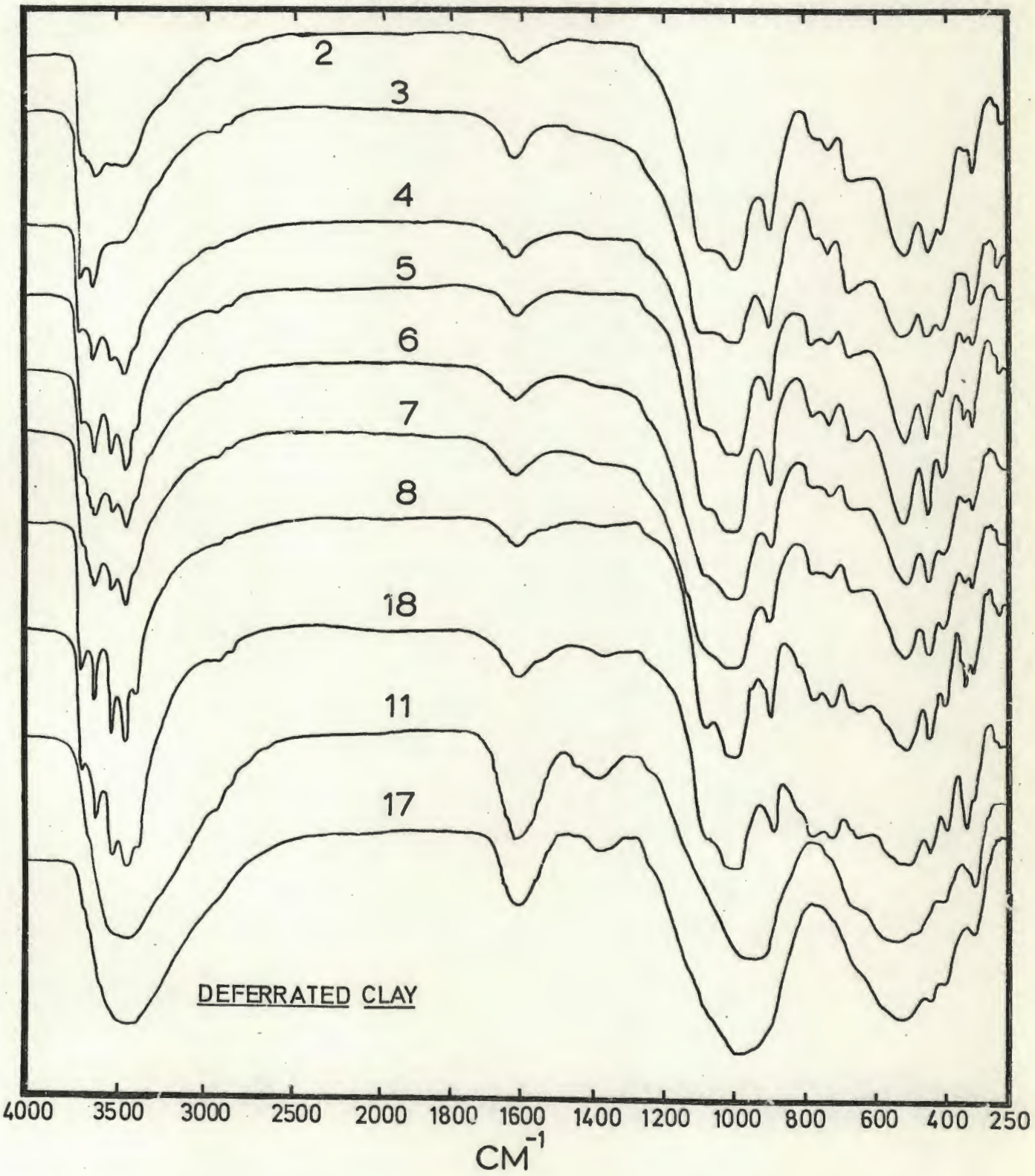

FIGURE 10. Infrared spectra of deferrated clays (< 2μm)

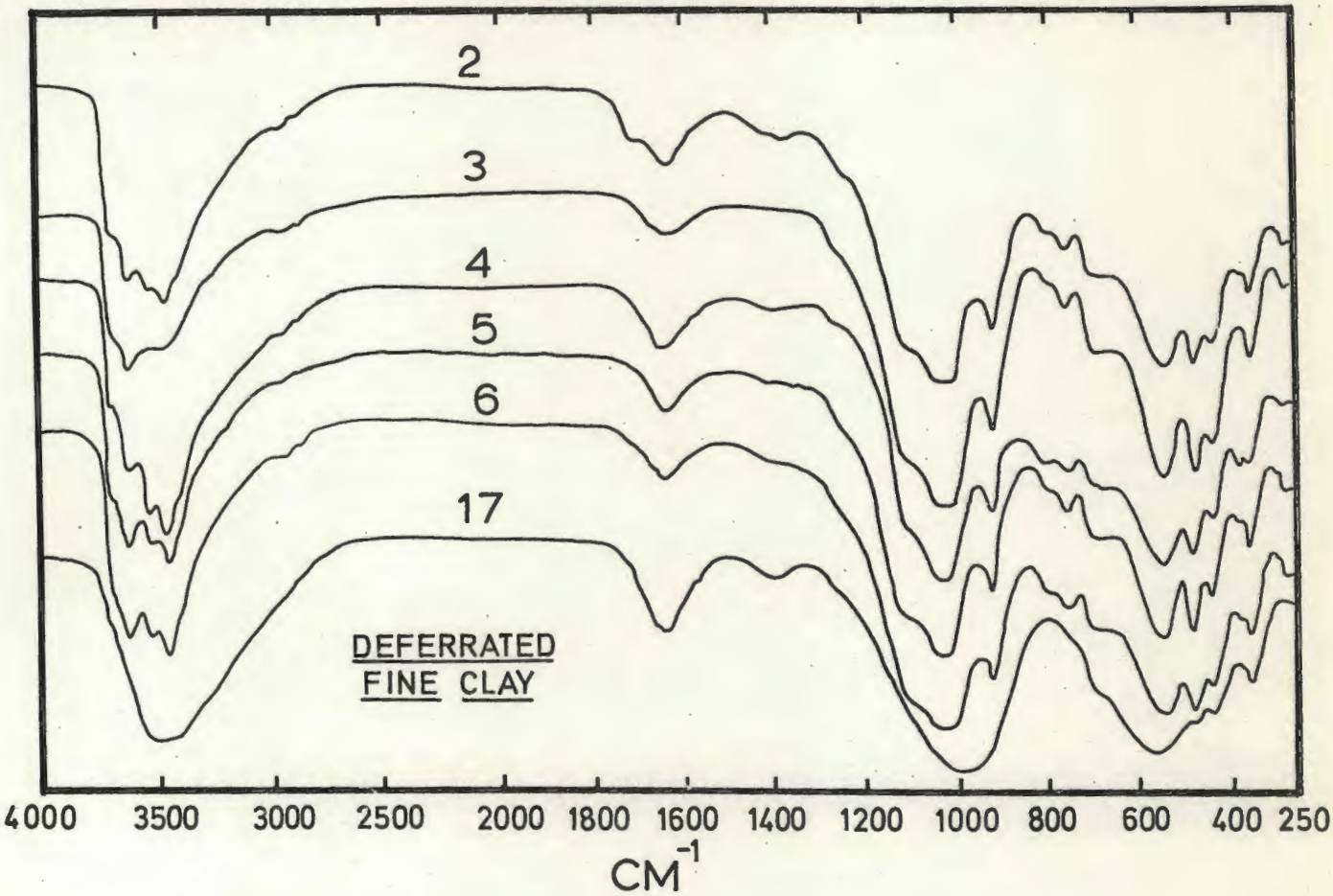

FIGURE 11. Infrared spectra of selected, deferrated fine clays (< 0,08 µm)

Oxisols. The goethite band (Fig. 9) is broad and very weak except in the spectrum of the Kraznozem clay (no. 8), which is consistent with X-ray powder diffractometric evidence (Fig. 6). Interlayer hydroxyls of aluminous chlorite absorb in the same region as those of kaolinite (Meyers & Ahlrichs, 1972), so that IR cannot be used to differentiate admixtures of these two minerals. The broad diffuse bands (3800 - 3000 cm^{-1} region) in spectra of the volcanic-ash soil clays (11 and 17) are typical of allophane (Mitchell, Farmer & McHardy, 1964). An interesting feature common to almost all the spectra in Figures 9, 10 and 11 is a pair of absorption bands at 2850 and 2920 cm^{-1}, which bear no apparent relation to the strength of other absorption bands elsewhere in the spectra. This doublet appears in spectra published by Greenland, Wada and Hamblin (1969), Brydon and Shimoda (1972) and Parfitt (1972), although none of these authors account for its presence. Apparently this absorption behaviour is indicative of the presence of hydrogen-bonded hydroxyl (Davis, Thompson, Taylor & Holdridge, 1970). This would explain why diaspore (β-AlOOH) absorbs at 2900 ± 20 cm^{-1} (Frederickson, 1954). If, as has been suggested earlier, there is extensive Al substitution for Fe of goethite in these clays, then a diaspore-like alumina monohydrate structure could be present. The resistance of such material to CDB-extraction (Norrish & Taylor, 1961) would account for its persistence in the deferrated clays (Figs. 10 and 11). Despite the fact that these considerations might constitute further evidence for the existence of an X-ray amorphous, alkali-soluble alumina monohydrate in certain sesquioxidic soil clays as proposed by de Villiers (1969), there is another possible source of this IR absorption behaviour which must be considered. Wells and Furkert (1972), in a study of the bonding of water to allophane using IR and vacuum DTA, established the presence of three types of adsorbed water in field-moist allophanic soils. The most resistant of these to thermal expulsion was water existing as hydrogen-bonded clusters of H_2O molecules sited in micropores. Despite prior K-saturation, spectra in Figures 9, 10 and 11 all display a fairly pronounced HOH angle deformation band (1640 cm^{-1}) indicative of adsorbed water retained at 70C (the sample pretreatment temperature), which could therefore constitute, in terms of what has been discussed above, an alternative source of H-bonded hydroxyl.

As indicated by spectra for allophanes the degree of diffuseness of absorption in the hydroxyl stretching region is a function of the abundance of amorphous material in the sample (Mitchell, et al., 1964). Comparison of spectra in Figures 9 and 10 shows that deferration (CDB treatment) of the Natal Oxisol clays in particular, leaves a residue with considerably enhanced

crystallinity. This increased sharpness of absorption cannot be accounted for by a decrease in the content of adsorbed water, since there is little difference in the sizes of the corresponding 1640 cm^{-1} bands. This, coupled with the fact that the goethite band (3200 cm^{-1}, Fig. 9) is very weak in spectra of the Natal Oxisol clays, suggests that material removed by CDB treatment (10 - 20% Fe_2O_3 plus up to 8% Al_2O_3) is mainly of an amorphous or poorly-crystalline nature. Likewise, comparison of spectra for Oxisol clays in Figures 10 and 11 point to the poor crystallinity of the deferrated fine clay fractions. As already shown by X-ray diffractometry, the latter clays consist mainly of poorly-ordered kaolinite-halloysite and gibbsite.

A further indication of the relatively poor crystallinity of the fine clays is provided by differences (Figs. 10 and 11) in strength of the two major kaolinite hydroxyl stretching bands. According to Farmer and Russell (1967), it has been conclusively established (Ledoux & White, 1964) that the 3620 cm^{-1} band arises from the inner hydroxyl of the kaolin structure, while the other major band at 3700 cm^{-1} arises from surface hydroxyls. The almost complete disappearance of the latter band in the fine clay spectra points to a rather disorganized surface of the kaolinite (halloysite) particles, and supports the idea (Follett _et al._, 1965; de Villiers, 1969) of there being a continuum between amorphous and crystalline components of soil clay.

The strong Si-O stretching vibration band in the 1000 cm^{-1} region has been used in the past for assessing the SiO_2/Al_2O_3 ratio of the amorphous fraction (Lai & Swindale, 1969; Mitchell _et al._, 1964). However, in the presence of substantial quantities of crystalline phyllosilicates this approach is likely to be of little value in characterizing the amorphous fraction. For this reason, a relatively large amount of sample was used for recording the IR spectra in Figures 9, 10 and 11, thus suppressing the Si-O stretching maximum (Beer's law) in favour of improved resolution and sensitivity over the remainder of the spectrum. It will be noticed that allophane-rich clays again absorb rather diffusely in this region. Maxima for samples 11 and 17 at frequencies of 950 to 980 cm^{-1} indicate that they consist of sesquioxidic allophane (Lai & Swindale, 1969). A slight band shift to higher frequencies after CDB treatment corresponds to the removal of an alumina-rich component (Wada & Greenland, 1970) leaving a relatively more siliceous residue (between 5 and 8 times more Al_2O_3 than SiO_2 were extracted from samples 11 and 17 by CDB treatment). Sharper Si-O stretching bands at higher frequencies (greater than 1000 cm^{-1}) confirm the abundance of kaolin or kaolin and pedogenic chlorite in the Oxisol clays.

At frequencies below 1000 cm^{-1}, a number of Al-OH and Fe-OH bending vibrations, together with further vibrations of the silicate anion (Farmer & Russell, 1967) make this region of the spectra rather more complex and therefore less open to straightforward interpretation. For example, although Parfitt (1972) attributes bands at 800 and 900 cm^{-1} to goethite, their persistence in spectra of deferrated clays implies that they probably arise jointly from Al-OH and Fe-OH bending vibrations. A reduction in intensity of the 740 cm^{-1} band relative to the 795 cm^{-1} band of the Kraznozem clay (no. 8 - Figs. 9 and 10) suggests that Fe-OH vibration contributes to absorption in the 740 cm^{-1} region. The 370 cm^{-1} band is probably due entirely to Al-OH bending vibrations in gibbsite; this is inferred from its absence in spectra of samples 3, 11 and 17, which contain little or no gibbsite, and its relatively large size in spectra of samples 8 and 18, high in gibbsite. The 345 cm^{-1} band is present in all spectra, and may arise from Al-OH bending in aluminosilicate structures generally, irrespective of degree of crystallinity.

In most of the spectra CDB treatment of soil clay results in the appearance of an absorption band at 270 cm. Published mineral spectra seldom, if ever, extend beyond 400 cm^{-1} so that the cause of this absorption is uncertain. However, the absence of this feature in spectra of the allophanes (11 and 17, Fig. 10) suggests that it arises from OH bending or Si-O vibrations in crystalline clay. The allophanic clays exhibit, in addition to those in the OH- and SiO-stretching regions, another broad maximum below 800 cm^{-1}. IR studies of amorphous aluminosilica gels (Mitchell _et al._, 1964) have shown this band to be characteristic of pure alumina gels. For soil clays such a feature would imply the presence of free amorphous alumina.

Finally, an attempt was made to further characterize the amorphous component by selective deuteration. Initially, the method used by Meyers and Ahlrichs (1972) was adopted, but was found to effect not more than a trace of OH-OD exchange. Consequently, the following method was tried: after running the spectrum of a clay sample in an atmosphere of dry nitrogen, the die containing the pellet was placed in a heating mantle and D_2O vapour (dry N_2 as carrier) was flushed through the die continuously for 1 h at 100C. The resulting spectra, recorded immediately in an atmosphere of dry N_2, showed a noticeable shift to the OD stretching region (2700 - 2300 cm^{-1}). For illustration, spectra of the Kraznozem clay before and after deuteration are shown in Figure 12. It is inferred from the absence of an adsorbed D_2O band at 1200 cm^{-1}, that the broad OD stretching band (2530 cm^{-1}, with a shoulder at 2320 cm^{-1}) arises from exchange for structural hydroxyl at clay surfaces. The broadness and low intensity of the OD band may indicate that exchange has taken place

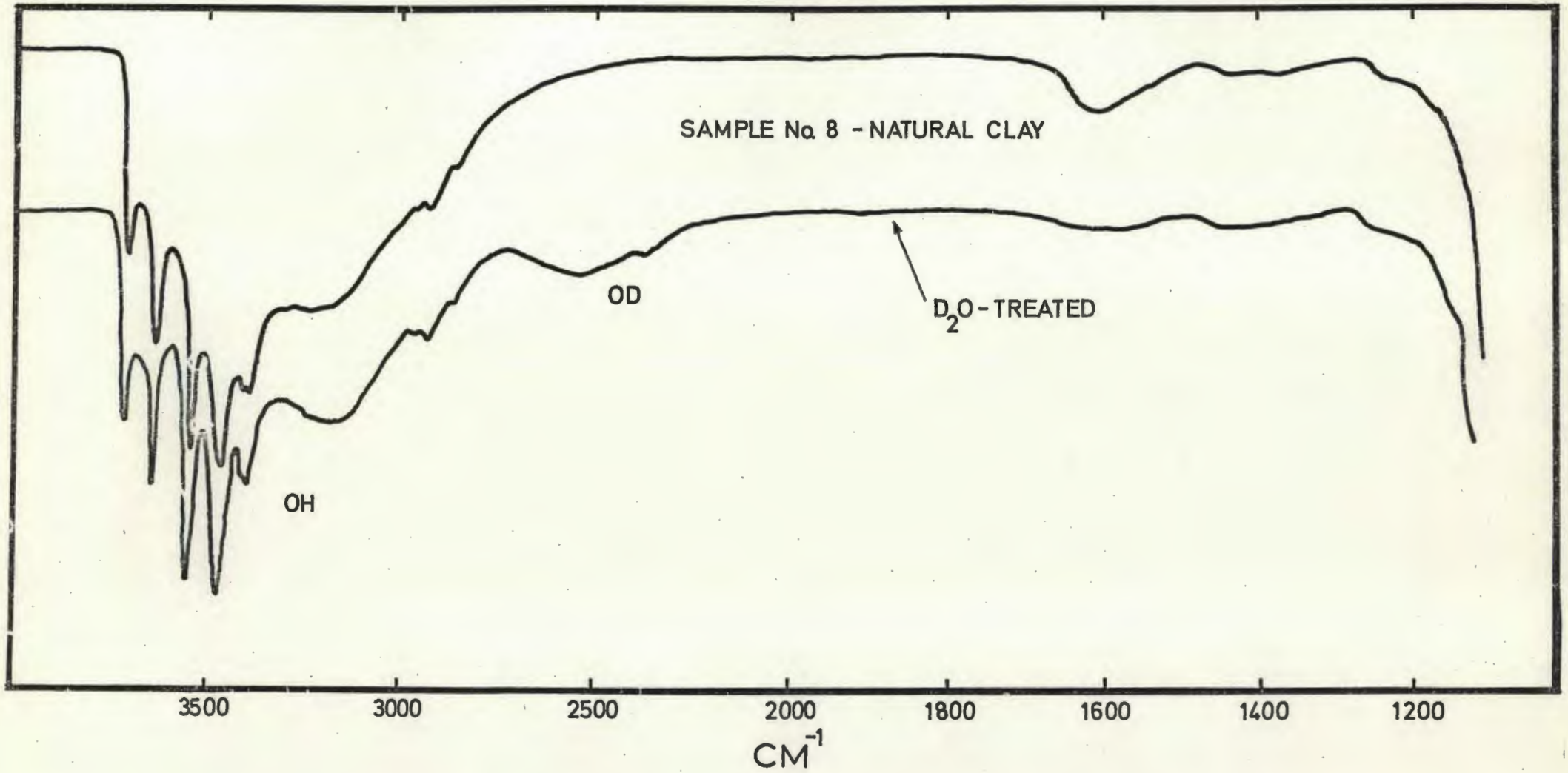

FIGURE 12. IR spectra of natural clay from sample no. 8 recorded before and after flushing the KBr pellet with D_2O vapour at 100C for 1 hour

mainly with goethite hydroxyls. However, the residual intensity of the goethite band at 3200 cm^{-1} (which is actually enhanced by the treatment, as are gibbsite and kaolin bands, due to thermal removal of adsorbed H_2O) shows that only partial exchange has taken place. Similarly it was found that the technique used here did not effect more than a partial shift of allophane hydroxyls in the volcanic ash soil clays, so that for a study of this nature it appears that anything less vigorous than the D_2O washing-film drying technique used by Wada (1966) is unsatisfactory*.

1.4.4 Electron microscopy

One of the main purposes for inclusion of electron-optical investigation in this study was to establish conclusively the presence of halloysite in the Natal Oxisols. Results reported so far, particularly those of X-ray diffractometry, as well as the findings of an earlier study (Verster, 1964), have pointed to the presence of halloysite in the clay fraction of these soils. Seven selected electron micrographs of the soil clays are reported here (Plates 1 - 7).

Plates 1, 2, 4 and 6 show examples of the association of varying amounts of halloysite† (tubular particles) with poorly-ordered kaolinite, and in one case (Plate 6) with an amorphous, gel-like mass. Indications from XRD analysis that the red Farmhill B horizon clay derived from basalt (sample no. 3) is particularly rich in halloysitic material are confirmed here (Plates 1 and 2). Halloysite particles in Plate 1 exhibit a condition of fragmentation suggestive of poor crystallinity, although this appearance may have been caused by ultrasonic treatment for dispersion. Plate 1 also shows smaller halloysite particles in mutual aggregation with what is probably very finely divided sesquioxidic material (small arrows). The discreet, granular clusters of more electron-dense material (large arrows) could not be observed in deferrated specimens of this clay (Plate 2 and others not shown) and are similar to the 'blackberries' of discreet iron oxides observed by Greenland, Oades and Sherwin (1968). The absence of a characteristic spiky goethite morphology (Beutelspacher & van der Marel, 1968) is consistent with the indication (Table 3) that the iron oxide component in all these clays is extensively Al-substituted. Deferration

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* Use of fluoride reactivity and other chemical techniques for characterizing clay surfaces (Chapters II and III) were opted for in preference to further attempts to assess proportions of amorphous-hydroxyl through complete, yet still selective, deuteration.

† It should be emphasized that the mineral present in these soils is actually metahalloysite, with 7,4A spacing as opposed to 10A for hydrated halloysite (Sieffermann & Millot, 1969). In view of the absence of the latter, the term halloysite will be retained for convenience.

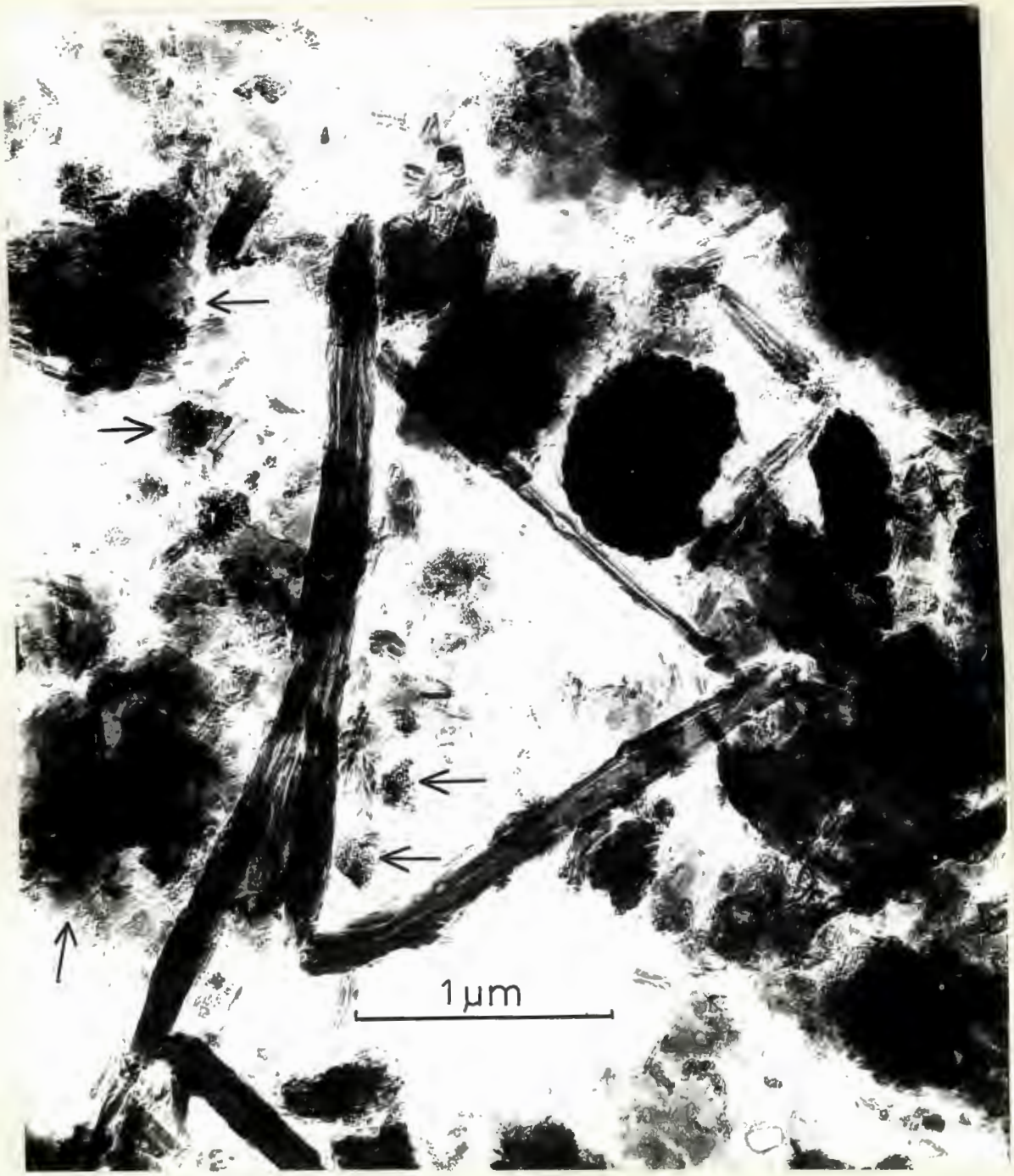

PLATE 1. Electron micrograph of natural clay (< 2 µm) from sample no. 3 (X 40 000)

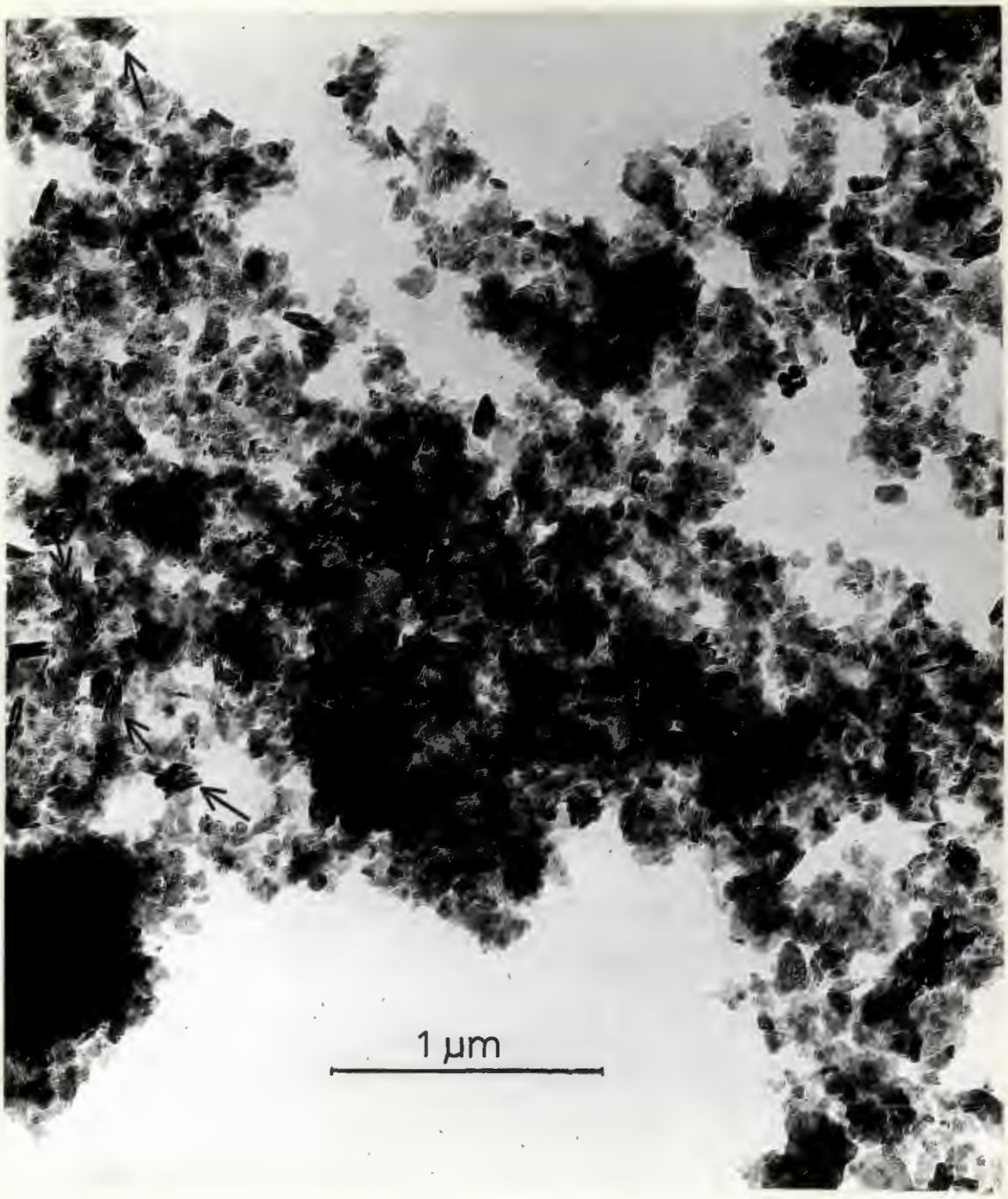

PLATE 2. Electron micrograph of deferrated fine clay (< 0,08 µm) from sample no. 3 (X 40 000)

treatment results in improved dispersion (Plate 2 - deferrated < 0,08 μm fraction of no. 3), although pH 9,5 Na_2CO_3 washings for fine clay fractionation may have been chiefly responsible for this. Improved dispersion would account for the fact that, while deferration removes over 20% Al_2O_3 plus Fe_2O_3 from this sample (Table 3), specific surface area decreases from 256 m^2/g to only 246 m^2/g (Table 4).

Plate 2 indicates, in addition to fine halloysite, the presence of flaky, pseudohexagonal particles with irregular outline, which are probably poorly-ordered kaolinite (XRD evidence indicates that some gibbsite of short range order is also present in this sample). There appears to be a certain degree of intergradation between flakes and tubular particles (marked by arrows). Beutelspacher and van der Marel (1968, p. 46) mention this as a characteristic phenomenon, the tubular habit being acquired through the presence of interlayer water which produces distortion by inducing OH-OH bonding on octahedral layer surfaces (Nagasawa, 1969).

One must inquire whether the postulated transformation of halloysite to kaolinite (which is essentially a dehydration reaction) in basaltic soils (Eswaran & De Coninck, 1971) can occur in the reverse direction. Hydration of kaolinite, as well as rehydration of dehydrated halloysite, has been performed through prior intersalation with compounds such as hydrazine (Range, Range & Weiss, 1969). However, the possibility that an analogous mechanism might operate under natural conditions seems rather remote.

Another interesting feature of Plate 2 is the random spotted pattern on faces of many of the particles, reminiscent of active points arising from crystal imperfections (Beutelspacher & van der Marel, 1968, p. 256). This is seen more clearly at higher magnification (Plate 3) on particles of fine deferrated clay from sample no. 4, comprising poorly-ordered kaolinite and gibbsite (see X-ray diffraction pattern - Fig. 2). The dappled effect may have resulted from patchy attack during various chemical pretreatments (alkaline dispersion, peroxidation, deferration). On the other hand the spots may represent surface appendages in view of their resemblance to discreet, relatively electron-transparent particles at lower left.

The very rounded appearance of the kaolinite particles in Plate 3 attests to their poor crystallinity, and to the possible presence of gel coatings (marked by arrows), which explains the virtual absence of a well-defined surface hydroxyl stretching band at 3700 cm^{-1} in IR spectra of this and other fine clay fractions examined (Fig. 11).

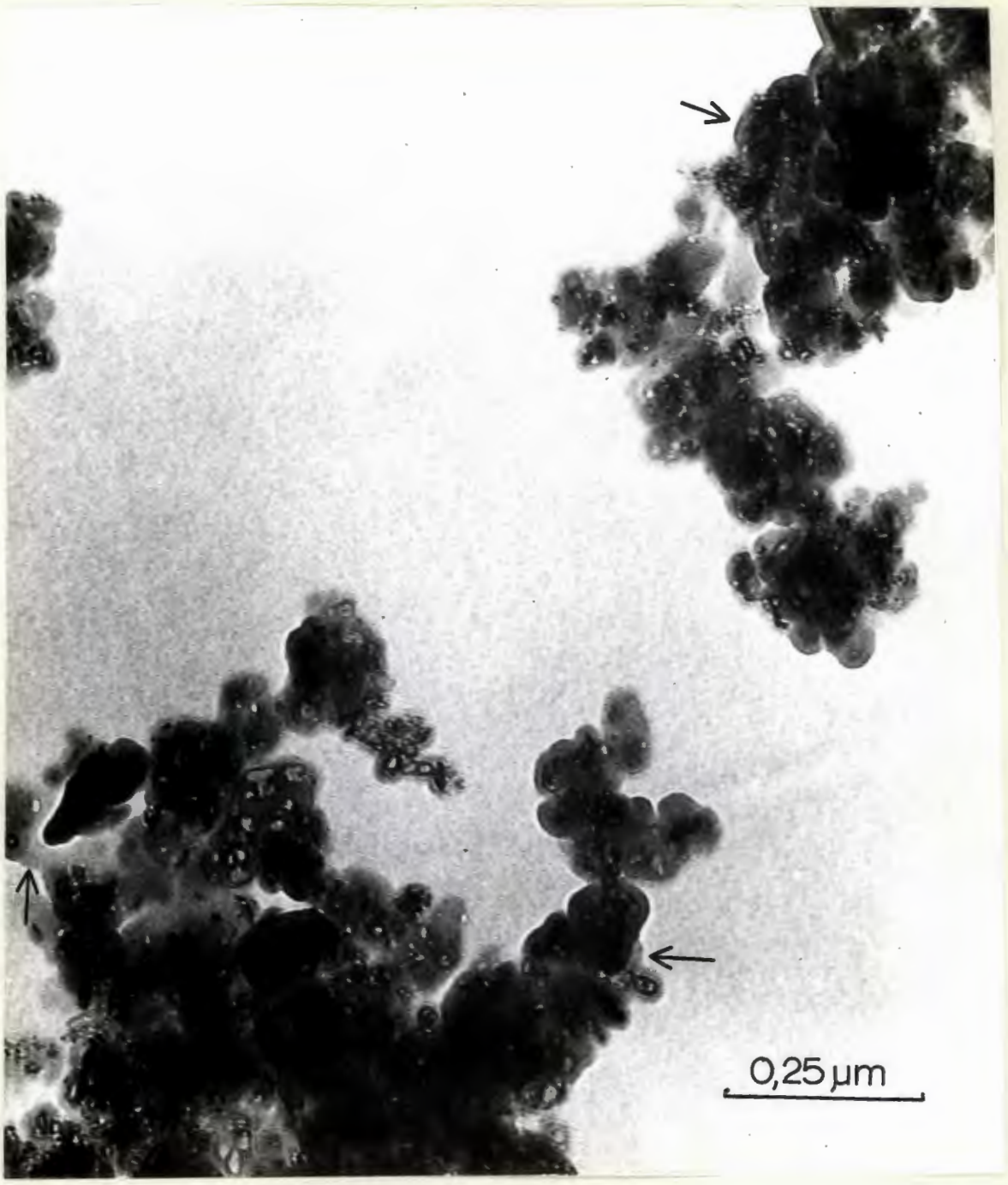

PLATE 3. Electron micrograph of deferrated fine clay (< 0,08 µm) from sample no. 4 (X 120 000)

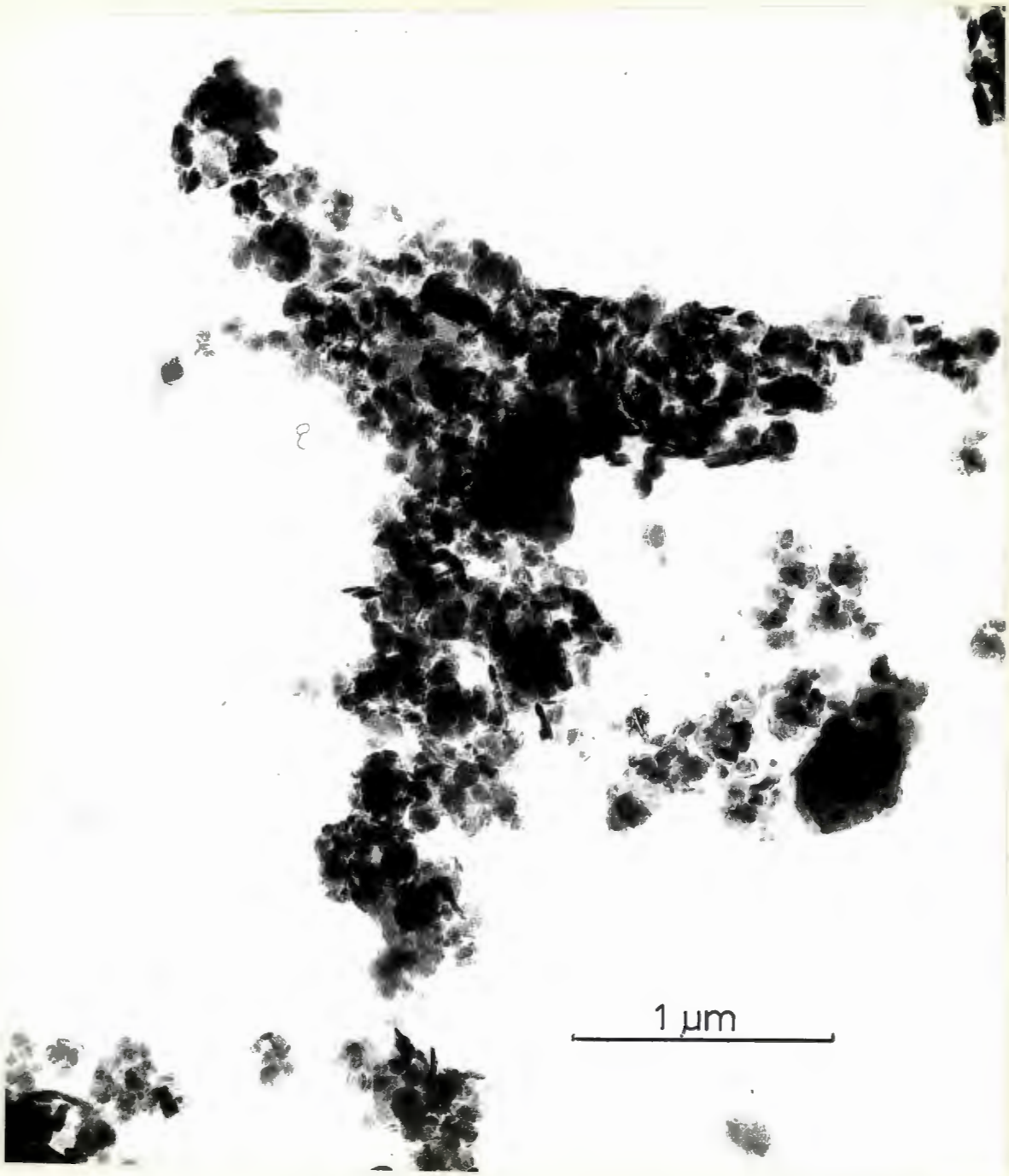

PLATE 4. Electron micrograph of deferrated clay (< 2 µm) from sample no. 5 (X 40 000)

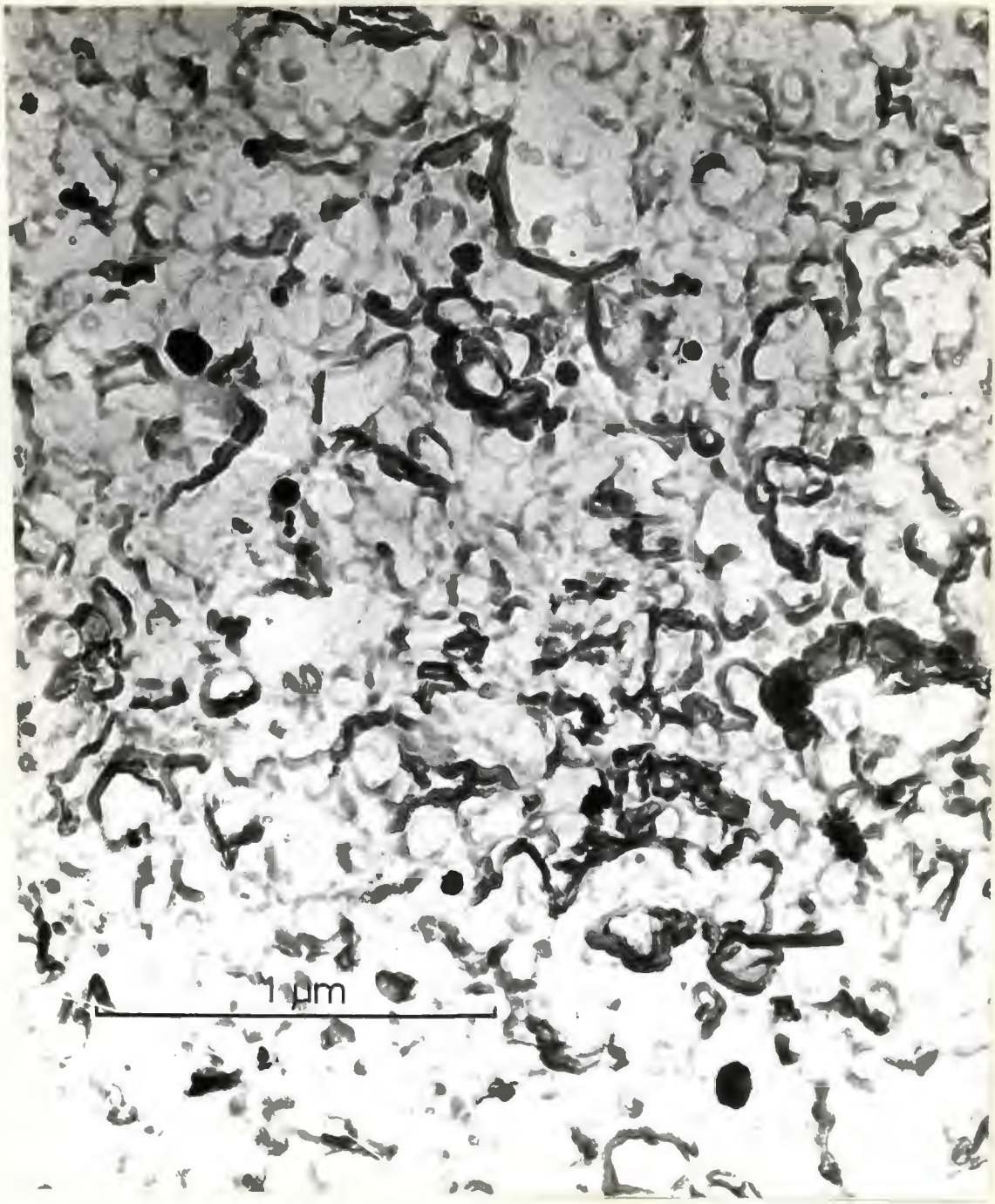

PLATE 5. Electron micrograph of Pt/carbon replica of deferrated clay (< 2 µm) from sample no. 5 (X 60 000)

PLATE 6. Electron micrograph of natural clay (< 2 µm) from sample no. 6 (X 40 000)

PLATE 7. Electron micrograph of deferrated clay (< 2 µm) from sample no. 11 (X 60 000)

Particles in Plate 4 (deferrated clay from no. 5, containing kaolin, chlorite, gibbsite and some quartz) appear to be relatively well-ordered. Some halloysite-like particles are present (lower left) as well as some electron-dense lath-shaped particles which may be rutile (Raman & Jackson, 1965) since they were also observed adhering to some HF-treated carbon replicas of this clay. A representative carbon replica of deferrated clay is shown in Plate 5 and the hexagonal shape of kaolinite particles is discernible.

Plate 6 is an electron micrograph of natural clay from the topsoil (sample no. 6) of the Farningham profile, and shows the rather striking feature of tubular particles (halloysite) embedded in a gel matrix, conveying the impression of a diagenetic link between the two phases (Sieffermann & Millot, 1969; Eswaran & De Coninck, 1971). Large aggregates of similar gel-like material were observed throughout this specimen in contrast to other samples examined which have very much less organic matter, suggesting that the gel may be of an organo-sesquioxidic nature.

Finally, Plate 7 shows deferrated allophane in the Kodonbaru clay (no. 11) with a typical, spongy convoluted appearance (Mitchell, et al., 1964). Despite the known presence of imogolite (Wada & Aomine, 1973) none was observed in this specimen. A possible reason for this is that clay separation was performed by acid dispersion which, according to Russell, McHardy and Frazer (1969), tends to cause imogolite coagulation.

1.4.5 Quantitative mineralogical analysis

1.4.5.1 Amorphous material by NaOH selective dissolution analysis

At an early stage in this study, it was realized that quantities of alkali-soluble amorphous material in the Oxisol clays were much larger than could be accounted for by relative measures of chemical reactivity. At the same time, quantitative values for kaolinite-halloysite seemed somewhat lower than those indicated by XRD, IR and DTA evidence. In the Alexiades and Jackson (1966) procedure, kaolinite plus halloysite is determined by subtraction of 'amorphous' silica and alumina dissolved prior to ignition from that which is removed after ignition by boiling 0,5N NaOH solution. It was suspected that, as has been found previously (Langston & Jenne, 1964; Askenasy, et al., 1973), a relatively large proportion of kaolin may have been removed by NaOH treatment without requiring prior structural collapse through ignition at 550C.

Results for NaOH dissolution of deferrated clays are presented in Table 7. Various possible sources of dissolved silica and alumina are considered.

TABLE 7. Possible sources of SiO_2 and Al_2O_3 dissolution from deferrated clays by boiling 0,5N NaOH treatment

Sample	%				Molar Ratios		%				
	Gibbsite (by DTA)	Dissolved SiO_2	Dissolved Al_2O_3				Dissolved SiO_2 and Al_2O_3 (2) calculated as:				
			(1) Total	(2) non-gibbsitic	SiO_2/Al_2O_3 (1)	SiO_2/Al_2O_3 (2)	Amorphous*	Allophane**	Residual Al_2O_3	Kaolinite‡ + halloysite	Residual Al_2O_3
2	2,6	12,80	22,70	21,00	0,96	1,03	37,6	18,5	17,4	27,5	10,1
3	0,4	13,98	14,57	14,31	1,63	1,66	31,4	20,2	10,4	30,1	2,4
4	9,4	10,64	21,18	15,03	0,85	1,20	28,5	15,3	12,0	22,9	6,0
5	15,6	16,69	30,66	20,46	0,92	1,38	41,3	24,1	15,7	35,9	6,3
6	8,8	15,50	24,23	18,47	1,09	1,42	37,7	22,3	14,1	33,3	5,3
7	12,8	18,27	26,71	18,34	0,93	1,69	40,7	26,3	13,2	39,3	2,8
8	47,7	10,99	40,35	9,15	0,46	2,04	22,4	15,8	6,0	23,4	0,0
18	49,6	7,11	38,33	5,89	0,31	2,05	14,4	10,2	3,9	15,1	0,0
11	0,0	31,60	42,94	42,94	1,25	1,25	82,8	45,6	34,0	68,0	16,1
17	0,0	38,11	36,52	36,52	1,77	1,77	82,9	54,9	25,7	82,0	4,2

* Alexiades and Jackson (1966).

** de Villiers (1971).

‡ Kaolinite + halloysite as specified by Alexiades and Jackson (1966), according to molar SiO_2/Al_2O_3 ratio.

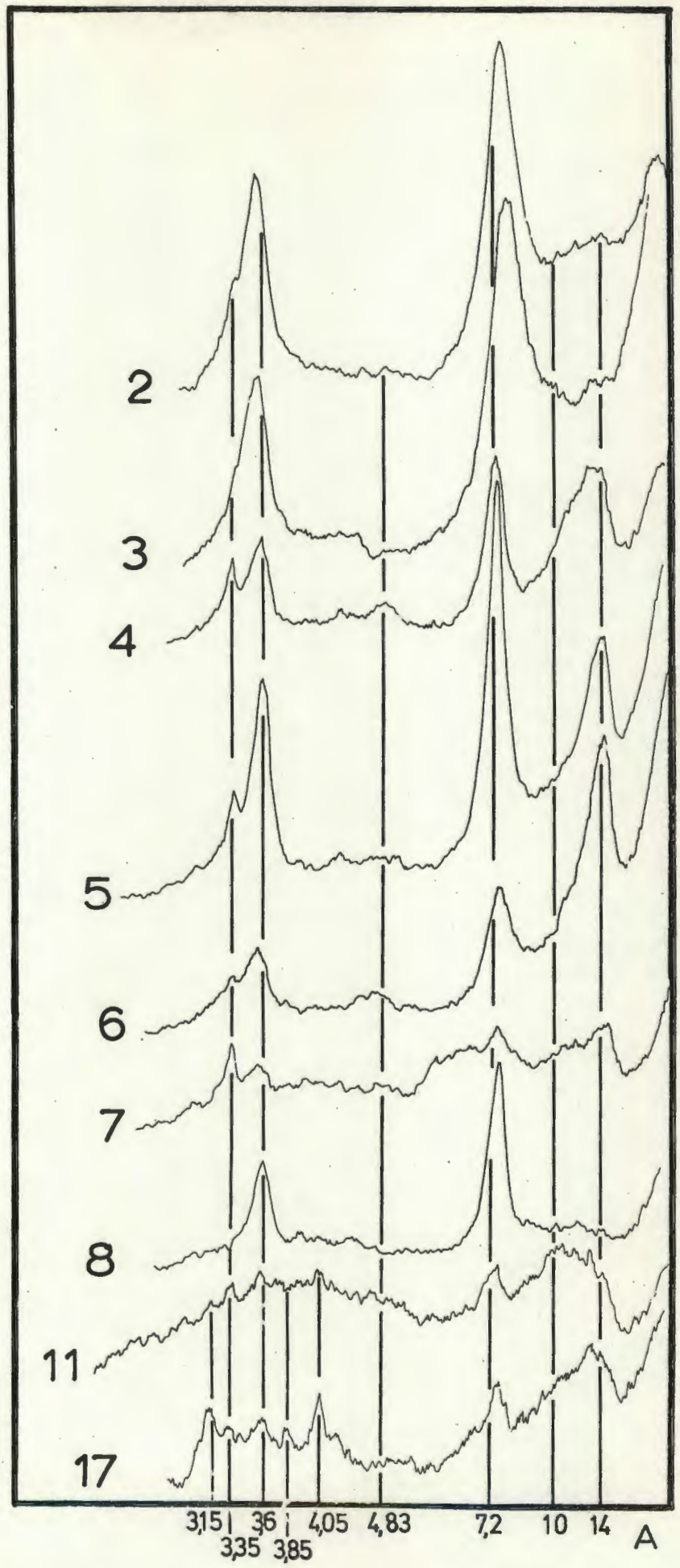

FIGURE 13. X-ray diffractograms of deferrated clay residues following treatment with boiling 0,5N NaOH

Firstly, gibbsitic alumina (determined by DTA - Table 5) is subtracted from total dissolved alumina, since the dissolution of this component is effectively complete (XRD of residues - Figure 13). Subsequent molar SiO_2/Al_2O_3 ratios range between values of 1 and 2, which confirms the sesquioxidic nature of these clays. When amounts of dissolved silica and alumina (excluding that from gibbsite) are used to calculate percent amorphous material* (Alexiades & Jackson, 1966), values for the Oxisol clays - the Natal samples particularly - seem somewhat high when considered in terms of the large crystalline component indicated by X-ray diffractometric and IR spectroscopic data (Figs. 1-3, 5, 6, 9 & 10). On the other hand, values for the allophanes (samples 11 and 17) fall within expectations: Wada and Aomine (1973) report a value of 86% NaOH soluble amorphous material for sample no. 11 (their sample 905).

Dissolved constituents were also calculated according to the scheme of de Villiers (1971)† as allophane plus residual alumina (Table 7). In this case it is found that quantities of allophane (allocated a composition corresponding to 22% $Al_2O_3/Al_2O_3 + SiO_2$) in the Oxisol clays are as much as half those calculated for the allophane-rich volcanic-ash soil clays (samples 11 and 17). As will be seen from results reported later, this is inconsistent with the relative magnitude of such properties as pH-dependent CEC observed for these materials. It may be argued that allophane in the Oxisol clays conforms to the halloysitic variety (Jackson, 1964), and is therefore relatively inert physiochemically. Such an assumption would, however, contradict the theoretical basis of allophane calculation following the scheme of de Villiers (1971).

Alternatively, the possibility must be considered that the bulk of alkali-soluble silica and alumina arises from dissolution of finely-divided kaolinite plus halloysite. Assuming this to be the case (and grounds for this assumption are more fully substantiated by later results), dissolved silica and alumina were allocated to the formula for kaolinite plus halloysite (Table 7) according to either equation 3 or equation 5 of Alexiades and Jackson (1966)‡. Residual

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* $\% \text{ Amorphous} = \dfrac{\% SiO_2 + \% Al_2O_3}{0{,}9}$ (division by 0,9 allocates 10% H_2O).

† $\% \text{ Allophane} = \dfrac{x + 0{,}283x}{0{,}89}$

where $x = \% SiO_2$, and division by 0,89 allocates 11% H_2O .

‡ Equation 3: $\% \text{ kaolinite + halloysite} = \dfrac{x}{0{,}465}$ (when molar $SiO_2/Al_2O_3 < 2$).

Equation 5: $\% \text{ kaolinite + halloysite} = \dfrac{x/0{,}465 + y/0{,}395}{2}$ (when $2 \leq$ molar $SiO_2/Al_2O_3 < 3$).

where $x = \% SiO_2$ and $y = \% Al_2O_3$.

alumina contents of the Oxisol clays (last column - Table 7) are relatively low. Owing to their predominantly amorphous nature, no significance is attached to corresponding values for samples 11 and 17. The implications of this approach are considered later.

1.4.5.2 Selective dissolution by other reagents

The amorphous component was subsequently investigated, in both natural and deferrated clays, by extraction with reagents such as sodium pyrophosphate, which has high specificity for organically-bound sesquioxides (McKeague, 1967; Bascomb, 1968), acid ammonium oxalate (Tamm, 1922; Schwertmann, 1973), citrate-dithionite-bicarbonate (Mehra & Jackson, 1960) and hot 5% sodium carbonate (Follett et al., 1965). The results of this comparative study are presented in Table 8 for natural clays and Table 9 for deferrated clays.

In addition, Table 10 summarizes the effect of these dissolution procedures on three synthetic amorphous aluminosilica gels (prepared as described earlier). These gels were included for investigation because of the importance which has previously been attached (Cloos et al., 1969; van Reeuwijk & de Villiers, 1970) to their study as a means towards elucidating the nature and properties of allophane.

(i) Sodium pyrophosphate. Pyrophosphate appears to possess a specificity for Al extraction from the soil clays (Table 8), since relatively insignificant quantities of Fe and Si were dissolved by this treatment. The same can be said for the gel data (Table 10). The high specificity of this extractant for organically-bound sesquioxides is confirmed by correlation of extracted alumina with organic carbon contents (in parentheses) of the soils from which these natural clays were obtained. Since pyrophosphate also tends to peptize a certain amount of amorphous, inorganic colloid (Bascomb, 1968; Table 10), extracted alumina (Table 7) is unlikely to be entirely of organic origin.

(ii) Acid ammonium oxalate. Oxalate extracted large amounts of alumina and silica from the volcanic-ash soil clays (Tables 8 and 9). On the other hand, relatively small quantities (< 5%) were dissolved from the Oxisol clays. At the same time, oxalate treatment brought about complete dissolution of the synthetic gels (Table 10).

That this procedure holds promise as a means of quantitatively extracting amorphous material is suggested by the very close correspondence between values for silica and alumina dissolved from the allophanic clays by sequential

TABLE 8. Dissolution of SiO_2 , Al_2O_3 and Fe_2O_3 from natural clays by various extractants

Sample	% removed by:											
	0,1M Na-pyrophosphate (pH 10,5)				NH_4-oxalate (pH 3,0)				Citrate-dithionite-bicarbonate			
	SiO_2	Al_2O_3	Fe_2O_3	Total	SiO_2	Al_2O_3	Fe_2O_3	Total	SiO_2	Al_2O_3	Fe_2O_3	Total
2	0,0047	1,51 (1,65)*	0,02	1,53	0,0820	2,08	0,64	2,23	0,0070	6,96	13,62	20,59
3	0,0217	0,01 (0,18)	0,00	0,03	0,0914	4,42	0,71	4,58	0,0071	3,76	18,74	22,51
4	0,0029	1,91 (1,32)	0,01	1,92	0,0416	1,47	0,11	1,62	0,0186	7,61	10,84	18,47
5	0,0015	0,01 (0,12)	0,00	0,01	0,0989	1,04	0,53	1,19	0,0033	4,50	18,30	22,80
6	0,0075	1,86 (3,06)	0,02	1,89	0,0845	1,98	0,77	2,83	0,0057	7,78	12,28	20,07
7	0,0023	1,13 (0,61)	0,00	1,14	0,1083	2,44	0,93	3,48	0,0027	7,60	14,67	22,27
8	0,0014	0,05 (0,49)	0,00	0,05	0,1321	1,00	0,13	1,26	0,0174	11,17	33,01	44,20
18	0,0052	0,01 (0,57)	0,00	0,02	0,0323	1,29	0,37	1,69	0,0016	7,01	30,56	37,57
11	0,0058	1,37 (1,24)	0,01	1,38	19,35	44,49	0,57	64,41	1,94	15,71	4,87	22,52
17	0,0067	1,16 (1,10)	0,00	1,17	13,27	35,83	0,46	49,57	1,89	10,85	3,08	15,82

* Organic carbon (%C) contents of the soils are included in parentheses for comparison.

TABLE 9. Dissolution of SiO_2 and Al_2O_3 from deferrated clays by 5% Na_2CO_3 and acid NH_4-oxalate

Sample	% removed by:					
	Hot 5% Na_2CO_3			NH_4-oxalate (pH 3)		
	SiO_2	Al_2O_3	SiO_2/Al_2O_3 (molar)	SiO_2	Al_2O_3	SiO_2/Al_2O_3 (molar)
2	3,34	7,25	0,78	0,305	4,17	0,12
3	3,91	4,35	1,53	0,216	1,30	0,28
4	2,35	13,01	0,31	0,111	3,91	0,05
5	3,20	5,35	1,02	0,177	1,50	0,20
6	3,54	10,57	0,57	0,160	4,32	0,06
7	2,78	9,55	0,49	0,172	3,75	0,08
8	1,06	12,33	0,15	0,133	0,59	0,38
18	0,69	13,55	0,09	0,083	2,21	0,06
11	5,06	18,15	0,47	21,39	35,83	1,01
17	7,02	10,84	1,10	16,07	27,03	1,01

TABLE 10. Effect of various chemical extractants on dissolution of synthetic amorphous aluminosilica gels

Gel Sample	SiO_2/Al_2O_3 (molar)	% removed by:					
		Pyrophosphate		Oxalate		5% Na_2CO_3	
		SiO_2* $+Al_2O_3$ (%)	SiO_2/Al_2O_3 (molar)	SiO_2* $+Al_2O_3$ (%)	SiO_2/Al_2O_3 (molar)	SiO_2* $+Al_2O_3$ (%)	SiO_2/Al_2O_3 (molar)
II	2,44	0,53	0,069	100	2,44	14,01	2,29
III	1,50	2,66	0,006	100	1,50	19,02	0,89
IV	0,91	5,02	0,002	100	0,91	19,67	0,31

* No account was taken of water content retained at 110C. The oxalate extraction values merely represent complete solubilization of the gels by this treatment.

CDB-oxalate treatment and those by oxalate treatment alone (Table 12). This view is reinforced by the fact that the clay : solution of the oxalate extraction which followed CDB treatment was about five times lower than that of the separate treatment with oxalate alone (section 1.3.8), the implication being that a particular component is being extracted highly specifically.

In this context, data in Table 8 tend to support the assumption made earlier (Table 7) that the bulk of boiling 0,5N NaOH-soluble material in the Oxisol clays is not amorphous *per se*, but is more likely to be finely-divided (and probably poorly-ordered) kaolinite-halloysite, in agreement with XRD, IR and electronoptical evidence already presented.

Furthermore, negligible dissolution of alumina from samples 8 and 18 (Table 8) indicates that gibbsite (with which these clays are relatively enriched - Tables 5 and 7) is resistant to oxalate treatment.

Amounts of silica and alumina dissolved by oxalate from the allophanic clays (11 and 17) are somewhat lower than those removed by NaOH (Table 7). This evidence might suggest that the former extractant is not as efficient as the latter. On the other hand, the NaOH-soluble fraction will also represent variable dissolution from sources such as imogolite (Wada & Aomine, 1973; Yoshinaga, *et al.*, 1973), chloritized 2 : 1 layer silicates and poorly-ordered kaolinite and halloysite (as indicated by maxima at about 7,4A in diffractograms of both NaOH residues - Fig. 13). For these reasons, oxalate values are considered to be the most meaningful of the two in terms of amorphous material as such.

In cases where the quantity of amorphous material being extracted is large (samples 11 and 17), the effect of CDB-pretreatment upon the subsequent extracting power of oxalate is negligible (Table 12). The corresponding effect for Oxisol clays is variable (Tables 8 and 9). In this case crystalline sesquioxides may impede oxalate dissolution of further sources of alumina such as that located in interlayers of pedogenic chlorite. As with CDB influence on surface area (Table 4), the variable effect is attributed to increased particle dispersion (exposure of new surfaces) on the one hand, and prior removal by CDB of some amorphous (high specific surface) material on the other.

A significant advantage of oxalate over other commonly used extractants is its additional specificity for amorphous ('active') iron oxides (McKeague, Brydon & Miles, 1971; Schwertmann, 1973). Interestingly, oxalate-extractable iron in all the soil clays is relatively low (Table 8), despite indications (XRD, IR and DTA evidence - Figs. 6 - 9) that the iron oxide component in these clays is poorly-crystalline.

(iii) Citrate-dithionite-bicarbonate. CDB extraction data (Table 8) support the contention (Norrish & Taylor, 1961) that goethite should be recognised as an important source of the often large amounts of Al released by this treatment. The presence of goethite in most of the clays has already been established from random powder diffractograms (Fig. 6), which display the peak broadening and lower d spacing characteristics typical (Norrish & Taylor, 1961) of finely-divided, Al-substituted goethite*. The fact that alumina removed by CDB treatment is in most cases considerably higher than that dissolved by oxalate is a strong indication of its origin in a crystalline matrix. Conversely, the small amounts of oxalate-soluble iron (Table 8) suggest that the mixed sesquioxide monohydrate is not a significant source of oxalate-extractable Al (Table 8).

Relative proportions of SiO_2 and Al_2O_3 extracted from the allophanic clays (11 and 17) indicate that CDB treatment (Table 8) removes fairly large amounts of amorphous alumina but that amorphous aluminosilicates are left largely intact. It is significant that most of the iron oxide in the volcanic-ash soils is also crystalline (inasmuch as oxalate extracts the equivalent of about a tenth of the iron removed by CDB), which implies that allophane as such consists essentially of hydrated silica and alumina. It is assumed (on the basis of the humid environment of these soil clays and their distinctly yellow chromas) that the iron in samples 11 and 17 has monohydrate (i.e. goethite) character.

(iv) Sodium carbonate. Results for the synthetic gels (Table 10) suggest that hot 5% Na_2CO_3 is a relatively poor extractant for amorphous aluminosilicates†. The low SiO_2/Al_2O_3 ratios of dissolved material suggest that discreet amorphous alumina is the main source of dissolution, and that an amorphous aluminosilicate phase - or permutite (van Reeuwijk & de Villiers, 1970) - is little affected by one extraction. These results contrast with the complete solubility of the gels in acid ammonium oxalate (Table 10).

Dissolution of Oxisol clays by sodium carbonate is greater than by oxalate (Table 9). The reverse is the case for the allophanic clays. This evidence suggests that while sodium carbonate is a relatively inefficient extractant for amorphous material (gel data), it is still capable of dissolving small quantities of poorly-ordered aluminosilicates and gibbsite, the implication being that

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* Although sample no. 18 is probably dominated by hematite and/or maghemite rather than goethite, these minerals could also contain some Al in isomorphous substitution. However, the Al_2O_3/Fe_2O_3 ratio (Table 8) is considerably lower than that of the goethitic Kraznozem clay (no. 8).

† Although other investigators (for example, Jørgensen, et al., 1970) have demonstrated the complete dissolution of gibbsite if a number of extractions are made on the same sample.

Na_2CO_3 extraction is less specific than oxalate.

(v) General comment. It is concluded that acid ammonium oxalate (pH 3; one extraction in darkness) is more efficient and selective as an extractant for both allophane and amorphous hydrous sesquioxides than are other reagents currently available for this purpose. To quote de Villiers (1971):

"Selective dissolution procedures for amorphous materials exploit the fact that reaction rate varies widely according to specific surface area, extent of structural order, and chemical bond strength, and is accordingly higher or much higher for amorphous than for most crystalline materials." In this context, the factor which, in the writer's opinion, provides oxalate with such superior selectivity for amorphous aluminosilicates and sesquioxides is undoubtedly the strong complexing power of its carboxyls for aluminium (or iron) associated with material having a high degree of structural randomness*. Reaction rate is probably enhanced by acid conditions (pH 3). That acid attack alone is insufficient was demonstrated by van Reeuwijk (1967), who found that synthetic aluminosilica gels of composition corresponding to 45% $Al_2O_3/Al_2O_3 + SiO_2$ or lower, resisted acid (1N HCl) attack to an extent which increased with increasing silica content†. Whether oxalate attack will be met with similar resistance by gels of higher silica content is not known. However, since soil allophane is generally of a sesquioxidic nature - high molar SiO_2/Al_2O_3 ratios (> 3) measured even for alkali-soluble material are normally regarded as an indication of smectite dissolution (Alexiades & Jackson, 1966) - such a possibility would be of little practical significance in terms of quantitative SDA.

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* In this connection, the relatively high susceptibility of magnetite to oxalate dissolution (Baril & Bitton, 1969) is envisaged as being due to its spinel structure, whereby the difference between ferrous and ferric ionic radii gives rise to inherently low structural stability.

† In terms of the model system for allophane (van Reeuwijk & de Villiers, 1970), the chemical status of silica in the amorphous aluminosilica gel system is unchanged above a composition corresponding to 22% $Al_2O_3/Al_2O_3 + SiO_2$, since the tetrahedral silica framework is maximally-occupied by Al at this composition. Any further Al_2O_3 takes the form of discreet, polymeric, charge-balancing cations. This aspect of the model is contradicted by the acid dissolution observations of van Reeuwijk (1967), who found, in addition, that a 60% $Al_2O_3/Al_2O_3 + SiO_2$ gel was completely dissolved in 1N HCl. On the other hand, if further tetrahedral substitution of Al in the silica framework could take place up to compositions corresponding to about 45% $Al_2O_3/Al_2O_3 + SiO_2$, the resistance of the aluminosilicate (permutite) phase to acid dissolution would decrease accordingly, until, at a composition equivalent to 60% $Al_2O_3/Al_2O_3 + SiO_2$, the aluminosilicate phase (containing at least 1 : 1 Al substitution for Si) would be completely acid-soluble. Such a situation would be more consistent with actual observations, and is supported by evidence reported later.

1.4.5.3 Sesquioxide* type and allocation of water content

For realistic quantitative mineralogical analysis it is important to evaluate the actual proportion (by weight) of the clay fraction which is occupied by amorphous and crystalline sesquioxides and allophane. Expression of these components merely as dissolved oxides of Al, Fe and Si is insufficiently meaningful.

(i) Oxisol clays. Results presented so far (Tables 7, 8 and 9) enable the differentiation of four types of sesquioxidic material in the Oxisol clays. These are presented in Table 11. Pyrophosphate extraction provides a measure of organically-bound sesquioxide, which is essentially aluminous. Amorphous (oxalate-soluble) sesquioxide is also predominantly aluminous, but the proportion of amorphous iron is sufficiently high to require consideration. Crystalline sesquioxides include gibbsite and iron oxides. The latter contain relatively large amounts of isomorphously-substituted Al, and there is sufficient evidence to permit the assignment of a monohydrate formula (i.e. goethite) to this component†.

Realistic allocation of water content to amorphous sesquioxide is more difficult. It is assumed that a certain proportion of oxalate-soluble alumina originates in interlayers of 2 : 1 phyllosilicate structures. Because gibbsite is present in all the Oxisol clays, it is feasible to assume that negatively-charged phyllosilicate surfaces are more or less completely saturated with polymeric hydroxyalumina to the extent that any anti-gibbsite effect (Jackson, 1963) is effectively neutralized. Most of the amorphous hydroxy-Al is therefore envisaged as being in a relatively advanced stage of polymerization, that is, its basicity (OH/Al) probably approaches that of the crystalline end product, gibbsite.

The basicity of interlayer hydroxyalumina appears, for optimum retention by clay minerals, to range between 2,5 and 2,7 in synthetic systems (Turner, 1965; Hsu, 1968), while a range of 2,3 to 2,5 has been estimated for chloritized Canadian prairie soil clays (Huang & Lee, 1969). Based on these findings it would seem reasonable, as an approximation, to assume an average basicity of 2,5 for amorphous hydroxyalumina in the Oxisol clays. This status is represented by the empirical formula $Al_2(OH)_5$. Basicities between 2,5 and 3 would be consistent with the role (considered above) of amorphous alumina as gibbsite

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* The term sesquioxide is used in a broad sense (de Villiers, 1969), and refers to discreet compounds of Al or Fe without specifying degree of crystallinity or hydration state.

† Sample no. 18 excepted (see section 1.4.5.2, part (iii)).

TABLE 11. Sesquioxidic components of the Oxisol clays

Sample	Sesquioxide fraction						
	Organic Al_2O_3 (%)	Amorphous plus interlayer*		Crystalline			Total‡
				Monohydrate**		Trihydrate	
		$(Al,Fe)_2OH_5$ (%)	Al/Al + Fe†	(Al,Fe)OOH (%)	Al/Al + Fe†	$Al(OH)_3$ (%)	
2	1,51	5,2	0,85	22,6	0,29	2,0	29,8
3	0,01	6,9	0,87	25,2	0,18	0,3	32,4
4	1,91	4,4	0,97	21,0	0,43	7,4	32,8
5	0,01	2,4	0,73	25,6	0,21	11,6	39,6
6	1,86	6,3	0,85	22,8	0,40	6,8	35,9
7	1,13	5,7	0,80	25,3	0,36	9,6	40,6
8	0,05	1,5	0,90	49,8	0,27	23,9	75,2
18	0,01	4,6	0,90	42,2ϟ	0,19	28,7	75,5

* Based on higher of two values for natural and deferrated clay.

** Based on CDB-extractable Al and Fe after subtraction of oxalate-soluble Fe.

† Al/Al + Fe = $Al_2(OH)_5/(Al,Fe)_2OH_5$ and AlOOH/(Al,Fe)OOH, respectively.

‡ Excluding organic Al_2O_3 .

ϟ Probably a mixture of the monohydrate and $(Al,Fe)_2O_3$. Calculation as either formula would make little difference quantitatively.

precursor. On the other hand, amorphous hydroxy-Fe and some hydroxy-Al will intergrade with the mixed sesquioxide monohydrate (Table 11). Amounts of amorphous Fe are small compared to amorphous Al (Table 8). For convenience, both are considered to belong to a mixed amorphous sesquioxide system having an approximate average basicity of 2,5 (Table 11).

Whereas amorphous (oxalate-soluble) Fe was first subtracted before calculation of the mixed Al-Fe monohydrate (Table 11) using CDB extraction data, the same was not done in the case of amorphous Al. This step was based on the fact that oxalate-soluble Al in deferrated clays was of the same order as, and sometimes higher than that extracted by oxalate from corresponding natural clays (Tables 8 and 9). While dithionite-citrate will solubilize both amorphous and crystalline Fe, the removal of amorphous Al will only be partial, to an extent dependent upon the complexing power of citrate for Al. The latter, judging from results for citrate treatment of aluminosilica gels presented by van Reeuwijk (1967), is considerably lower than the complexing power of oxalate for Al.

Amorphous plus interlayer sesquioxide (Table 11) was calculated from oxalate-soluble Fe values for natural clay (Table 8) and (for reasons outlined in section 1.4.5.2 (ii)) from the higher of the two oxalate-Al values obtained for natural and deferrated clay (Table 8 or 9). For example, while some amorphous Al may be removed during CDB pretreatment, the latter may at the same time expose new surfaces (interlayers in particular) to oxalate attack. It is assumed that interlayer hydroxyalumina of pedogenic chlorite is partially, although probably incompletely, dissolved by oxalate*. Only minimal significance can therefore be attached to quantitative values for amorphous plus interlayer sesquioxide (Table 11), beyond the fact that they range from 1,5 to 7 per cent, indicating (and this is important) that amorphous material is, on a weight basis, a relatively insignificant component of the Oxisol clays.

Finally, description of these clays as sesquioxidic is justified in all cases, since total sesquioxide (last column - Table 11) ranges from 30 - 40% in the Natal Oxisol clays, to 75% in the Kraznozem (no. 8) and Latosol Roxo (no. 18).

(ii) Allophanic clays. Owing to uncertainties regarding the model system for allophane (see footnote earlier), allocation of constituents dissolved from samples 11 and 17 by oxalate to the de Villiers (1971) formula, as was done in

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* Citrate, which is a similar, though milder, complexing reagent has been used in the past for extracting Al-hydroxyinterlayer material (Rich, 1968). It is therefore likely that a relatively large proportion of interlayer Al is removed by oxalate treatment.

TABLE 12. Sesquioxide and amorphous aluminosilicate components of the volcanic-ash soil clays

Sample	%									SiO_2/Al_2O_3 (molar)	%	
	Organic Al_2O_3	Sum of CDB + oxalate (sequential) extraction			Oxalate extraction from natural clay			Fe_2O_3* difference as FeOOH	Allophane**		Amorphous iron $Fe_2(OH)_5$	Total†
		SiO_2	Al_2O_3	Fe_2O_3	SiO_2	Al_2O_3	Fe_2O_3					
11	1,37	18,51	43,47	4,87	19,35	44,49	0,57	4,8	80,4	0,73	0,7	85,9
17	1,16	15,42	33,60	3,08	13,27	35,83	0,46	2,9	63,4	0,70	0,6	66,9

* $(CDB - oxalate)_{Fe}$ for natural clay.

** Based on average SiO_2 and Al_2O_3 dissolved by CBD + oxalate and oxalate alone; water content from curve 3, Fig. 14.

† Excluding organic Al_2O_3 .

Table 7, would be too arbitrary. Instead, it becomes necessary at this stage to revert to an earlier definition of allophane as a hydrated, amorphous aluminosilicate mineral (Lai & Swindale, 1969). The problem is then confined to that of allocating water content.

Thermogravimetric data for synthetic amorphous aluminosilicates obtained by Cloos et al. (1969), by van Reeuwijk (1967) and in the present study, are summarized in Figure 14.

Firstly, comparison of ignition weight loss curves of Cloos et al. (1969) - curve 1 - and van Reeuwijk (1967) - curve 2 - points to a difference between these two synthetic gel systems. Curve 2 terminates at a level consistent with the theoretical ignition weight loss of $Al(OH)_3$, in agreement with the observed demixing, in this system, of a crystalline bayerite phase at high alumina contents. The contrasting tail-off in weight loss exhibited by curve 1 corresponds to the appearance, as recorded by Cloos et al. (1969), of a mixed monohydrate-trihydrate crystalline phase. Consistently higher weight losses recorded by the latter authors over the remainder of the gel composition range could be explained by the earlier appearance (with increasing alumina content), of discreet, charge-balancing hydroxyalumina in their salt-free system. Part of the difference could also be attributed to the fact that curve 1 represents water retained at 100C whereas curve 2 represents ignition weight loss above 105C.

Results of the present study (curve 3) represent weight loss above 110C (Alexiades & Jackson, 1967). The extrapolation of curve 3 terminates (approximately) at the theoretical $Al(OH)_3$ weight loss value. This divergence of curves 2 and 3 with decreasing alumina content in the gel system is attributed to the use by van Reeuwijk (1967) of Na-saturated gels, whereas the present study employed K-saturated samples. The use of Na introduces a high cation-associated water content into the weight basis, whereas K does not (Alexiades & Jackson, 1966). The effect will be magnified by high CEC, which increases as alumina content decreases (van Reeuwijk & de Villiers, 1970).

In view of the similarities in behaviour which have been observed in the past between allophane and synthetic amorphous aluminosilicates containing similar proportions of silica and alumina, it was decided that the best approximation of allophane water content could be made from an ignition weight loss-chemical composition function for synthetic gels. Under present circumstances, curve 3 (Fig. 14) is the most suitable, since the weight basis is the same as that used for the soil clays, viz. 110C-heated, K-saturated samples.

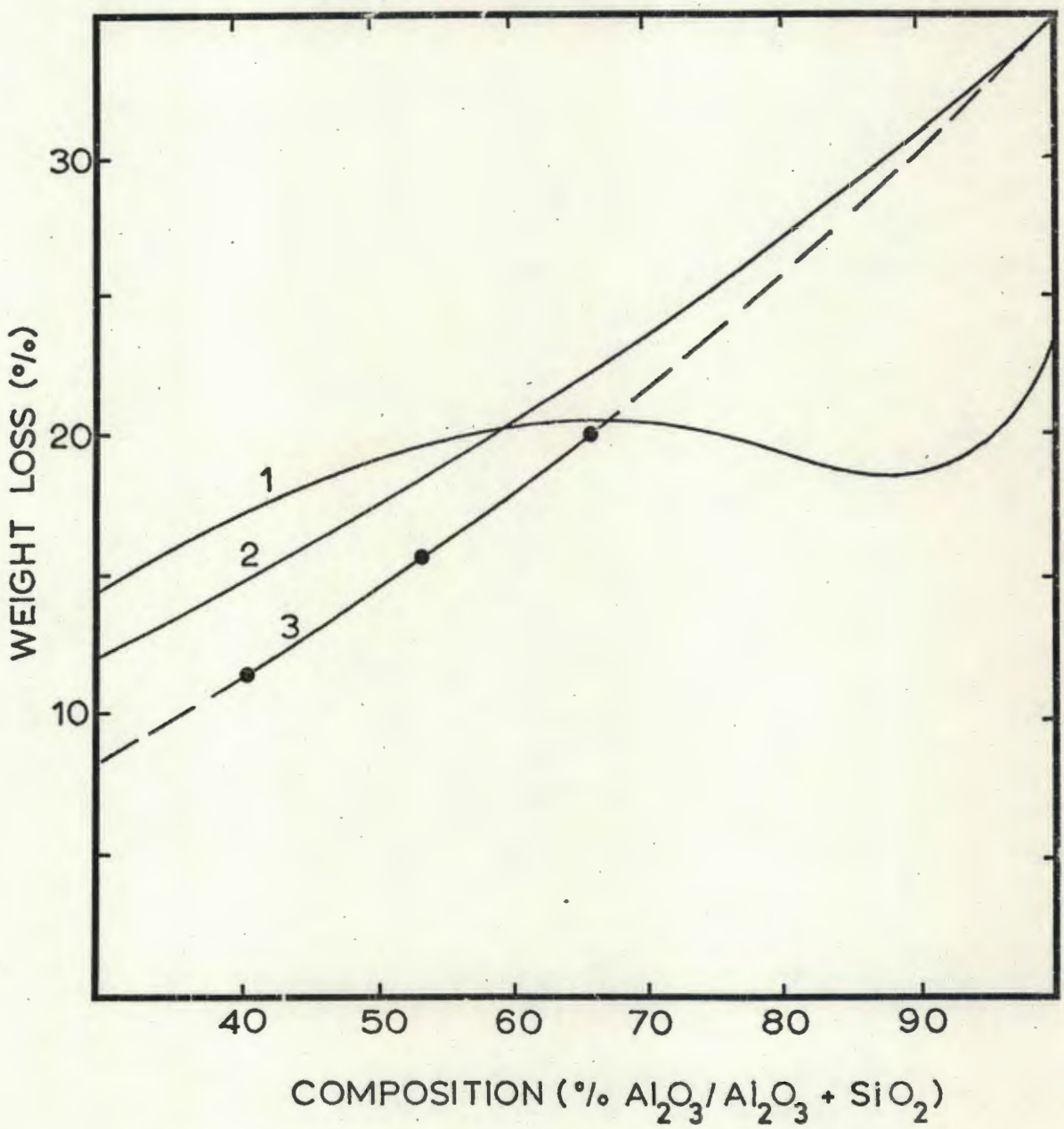

FIGURE 14. Ignition weight loss of synthetic aluminosilica gels as a function of chemical composition (1: Cloos et al., 1969; 2: van Reeuwijk, 1967; 3: present study)

Consequently, allophane content of samples 11 and 17 was calculated as follows:

1. Amorphous (oxalate-soluble) SiO_2 and Al_2O_3 values were calculated as the average of those obtained by sequential CDB-oxalate extraction and by oxalate alone, since these two sets of values correspond very closely (Table 12).
2. H_2O content corresponding to % $Al_2O_3/Al_2O_3 + SiO_2$ was read from curve 3, Figure 14, and allocated to the sum of SiO_2 and Al_2O_3 extraction values to give % allophane (Table 12).

Values for % $Al_2O_3/Al_2O_3 + SiO_2$ were 69,9 and 70,7 , while H_2O content was 21,8 and 22,6% for samples 11 and 17 respectively.

In Table 12, amorphous and crystalline Fe oxides have been assigned (for comparison) the same formulae as were applied for the Oxisol clays. The very small amounts of amorphous Fe present in samples 11 and 17 confirm that allophane is essentially an aluminosilicate mineral. Again, use of the term sesquioxidic in describing these clays is justified by the low molar SiO_2/Al_2O_3 ratio (0,7) of their dominant allophanic component.

1.4.5.4 Estimation of kaolinite plus halloysite

Since it has been demonstrated (specifically, on the basis of selective dissolution analyses for allophanic clays and synthetic aluminosilica gels) that acid ammonium oxalate extraction provides the most meaningful quantitative estimation of the amorphous component, the assumption that 0,5N NaOH extracts predominantly kaolinitic material prior to ignition of the Oxisol clays (last column - Table 7) is adhered to.

Consequently, an estimate of kaolinite plus halloysite content can be obtained using the appropriate equation (Alexiades & Jackson, 1966), and values for SiO_2 and Al_2O_3 representing the sum of silica and alumina dissolved before and after ignition at 550C, excluding gibbsitic alumina. These values are presented, along with corresponding SiO_2/Al_2O_3 ratios and kaolinite-halloysite contents, in Table 13. Silica and alumina values for sample no. 17 represent dissolution after ignition only. Insufficient residue was available for ignition-SDA of sample no. 11.

For the Oxisol clays, oxalate-soluble silica values are very low (Table 9), so that the possibility of estimating dissolved alumina twice - once as amorphous Al and once as kaolinite plus halloysite - is avoided, since

TABLE 13. NaOH-CDB selective dissolution data: calculation of kaolinite plus halloysite content

Sample	%				%	
	0,5N NaOH-soluble*		CDB-soluble†	SiO_2/Al_2O_3 (molar)	Kaolinite + halloysite‡	Residual
	SiO_2	Al_2O_3	Fe_2O_3			Al_2O_3
2	27,24	33,63	6,53	1,37	58,6	10,5
3	28,25	26,27	1,18	1,82	60,8	2,3
4	18,95	23,39	2,95	1,37	40,8	7,3
5	27,27	30,98	1,24	1,49	58,6	7,8
6	24,07	27,06	2,06	1,51	51,7	6,6
7	25,15	24,51	1,22	1,74	54,1	2,8
8	21,88	20,07	2,12	1,85	47,1	1,5
18	20,34	18,73	3,10	1,84	43,7	1,5
17	2,83	2,31	0,82	2,08	6,1	0,0

* Sum of SiO_2 and Al_2O_3 extracted before (Table 7) and after ignition at 550C, excluding gibbsitic Al_2O_3. No. 17 after ignition only.

† Extracted from ignited residue following NaOH treatment.

‡ By equation 3 (Oxisol clays) or 5 (sample 17) of Alexiades and Jackson (1966).

SiO_2/Al_2O_3 ratios (Table 13) are such that kaolinite plus halloysite content is computed on the basis of NaOH-soluble silica (equation 3 of Alexiades & Jackson, 1966).

There are nevertheless some uncertainties attached to the determination of kaolinite plus halloysite:

(i) SiO_2/Al_2O_3 molar ratios lower than 2 (Table 13) reflect the dissolution of amorphous Al (gibbsitic Al has already been subtracted). Calculated residual alumina (over and above that allocated to a kaolin formula) is, however, generally higher than amorphous (oxalate-soluble) alumina (Table 9). The additional NaOH-soluble alumina may come from halloysitic material of SiO_2/Al_2O_3 molar ratio < 2, since the possibility has been recognised (Jackson, 1963) that halloysite may contain some Al tetrahedrally substituted for Si in addition to that of its octahedral layer.

(ii) CDB extracts relatively large amounts of Fe_2O_3 from the ignited residues following NaOH treatment (Table 13). The most probable source of this iron is crystalline Al-substituted sesquioxide resistant to CDB treatment. Norrish and

Taylor (1961) demonstrated the resistance of finely-divided, Al-substituted goethite to removal by dithionite. Furthermore, following size-fractionation of deferrated clay in the present study it was observed that, while coarse and medium size separates retained a relatively bleached appearance, some fine clays (< 0,08 µm) had a pale yellowish colour. This was particularly evident in samples 2, 4, 6 and 8 (size-fractionation was not performed for sample 18), which release significantly more Fe than the other clays (Table 13). Because resistance to dithionite removal seems to be related to degree of Al-substitution, persistent sesquioxide may also have contributed to residual alumina values in Table 13*.

(iii) A kaolinite plus halloysite value of 6,1 per cent for sample no. 17 may represent an underestimation, since partial dissolution will have occurred in the extraction prior to ignition. The presence of imogolite in both 11 and 17 (Wada & Aomine, 1973; Yoshinaga, et al., 1973) complicates the quantitative estimation of a separate kaolin component (cf. diffraction maxima at 7,3 - 7,4A, Fig. 13). The possibility that sesquential oxalate-NaOH-ignition NaOH-SDA may be of some use in determining allophane, imogolite and kaolinite plus halloysite separately, warrants further investigation.

Despite these limitations, it is considered that kaolinite plus halloysite values (Table 13) represent more realistic estimates of this component than would otherwise have been obtained using conventional NaOH-SDA alone. The relatively large quantities of kaolin (40 - 60 per cent) in the Oxisol clays are certainly in better agreement with semi-quantitative XRD and IR spectroscopic indications.

1.4.5.5 Vermiculite and montmorillonite

In line with more recent developments (El-Attar & Jackson, 1973), CEC measurements for vermiculite and montmorillonite determination were made using a weighing technique which eliminates an intermediate alcohol-washing step for removal of excess cation prior to replacement†. In this case, 0,06N $CaCl_2$ and 0,05N KCl were employed as saturating solutions. Otherwise CEC (Ca//Mg) and CEC (K//NH_4) were determined in the usual way after H_2O_2-NaOAc (pH 7) pretreatment of 200 mg deferrated clay (Alexiades & Jackson, 1965; 1966).

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* De Villiers and van Rooyen (1967) found that the alumina of synthetic Al-substituted lepidocrocite preparations is removed during digestion with NaOH.

† The reader is referred to Chapter III for a more detailed account of the principles which form the basis of this technique.

TABLE 14. CaEC and KEC of deferrated clays in relation to vermiculite and montmorillonite calculation

Sample	CEC (Ca//Mg)	CEC (K//NH_4)	'Vermiculite' CEC	CEC (K//NH_4) -5	'Montmorillonite'
	me/100g				%
2	16,4	24,5	-8,1	19,5	18,6
3	21,0	27,6	-6,1	22,6	21,5
4	13,6	15,0	-1,4	10,0	9,5
5	14,9	17,9	-3,0	12,9	12,3
6	20,4	23,4	-3,0	18,4	17,5
7	20,3	23,2	-2,9	18,2	17,3
8	7,4	7,8	-0,4	2,8	2,7
18	n.d.	n.d.	0,0*	-	0,0*
11	22,5	24,5	-2,0	19,5	18,6
17	17,5	23,7	-6,2	18,7	17,8

* Moniz and de Oliveira (1974 - in press).

n.d. Not determined.

Results are present in Table 14. CEC (Ca//Mg) is consistently lower than CEC (K//NH_4), giving negative values for vermiculite CEC. Wada and Harada (1969) have shown that halloysite exhibits a particular tendency towards non-Coulombic adsorption of K and NH_4 salts. This intersalation effect (which may have been enhanced by pH 7 NaOAc washings given prior to saturation) is unlikely, according to results of the latter authors, to have been large, but could well have introduced an error term of the order of 1 or 2 me/100g. Any further difference could well be accounted for by the fact that all water retained by the clay does not necessarily act as solvent (Wada & Harada, 1969). The latter authors found the effect to be most pronounced for Ca-halloysite and Ca-allophane systems. In the present case, Ca ions introduce a much larger quantity of cation-associated, non-solvent water than K ions. Since X-ray diffraction data indicate the presence of little or no vermiculite (stable 14A peak, where present, at 110C after K-saturation), this mineral is assumed to be absent in the soil clays.

Owing to the large pH-dependent component of CEC in these clays (see Chapter III), determination of montmorillonite will depend to a large extent on clay pretreatment. Retention of citrate, and probably acetate as well,

against unbuffered salt washings by sesquioxidic functional groups results in CEC increase (chemisorbed negative charge - Chapter III), while pH 7 NaOAc pretreatment will also give rise to the measurement of some pH-dependent CEC in these naturally acid clays. Such factors are likely to be responsible for the artificially high montmorillonite values for most of the clays (Table 14). Since glycerol-solvated fine clay X-ray diffractograms failed to reveal the presence of a swelling 2 : 1 layer silicate, montmorillonite is also assumed to be absent in these clays.

1.4.5.6 Other minerals

Results for quartz plus feldspar, mica and chlorite determinations are presented in Table 15. X-ray diffraction analysis of pyrosulphate residues (not presented) indicated the absence of feldspar in the Oxisol clays, while the volcanic-ash soil clays contain crystoballite (no. 11) and crystoballite, quartz and some feldspar (no. 17).

TABLE 15. Quantities of quartz + feldspar, mica, and chlorite in deferrated clays

Sample	%		
	Quartz + feldspar	Mica*	Chlorite†
2	2,6	3,9	5,9
3	0,9	2,5	11,6
4	4,7	14,1	10,2
5	2,0	2,3	20,9
6	3,3	6,5	13,6
7	8,2	7,3	7,1
8	0,2	1,4	21,9
18	0,0‡	0,5‡	n.d.
11	1,5	1,6	39,1
17	7,4	6,9	12,2

* Based on 10% K_2O in dioctahedral micas (Alexiades & Jackson, 1967).

† By TGA (Alexiades & Jackson, 1966).

‡ Moniz and de Oliveira (1974 - in press).

Mica contents were generally low (Table 15) except that of the Farmhill clay (no. 4) derived from Beaufort shale high in mica (le Roux, 1973). The pronounced heat stable 14A peak for this clay (Fig. 2) suggests development of chlorite by hydroxyinterlayering of weathered mica. The absence of a corresponding 10A peak in such cases has been attributed to the existence of mica as unweathered cores concealed by extensive scrolling of weathered edges (le Roux, 1973).

Chlorite was determined by TGA (300 - 950C ignition weight loss) after subtraction of 4,5% water for mica, 15% for kaolin (approximate average of kaolinite and halloysite water), 2% for gibbsite and 8% for amorphous material (Jackson, 1956; Alexiades & Jackson, 1967). In this case amorphous material was oxalate-extractable alumina (allocated a basicity of 2,5) or allophane (hydration state allocated using curve 3, Fig. 14) of deferrated clays (Table 9). The reliability of the TGA method for chlorite determination is questionable, since chlorite values (Table 15) bear little relationship to amounts indicated semi-quantitatively by X-ray diffractometry. For example, no 14A peak was observed in diffractograms of samples 3 and 8. Previous investigations (Huang & Lee, 1969; El-Attar & Jackson, 1973) have tended to allow for a certain amount of leeway in chlorite values obtained by this method.

Mineralogical composition of natural clays is finally summarized in Table 16. Values obtained for deferrated clays were recalculated on the basis of weight of material removed during deferration*. Chlorite values, in view of the uncertainties mentioned above, were calculated by difference (le Roux, 1973). A 14A peak was observed in X-ray diffractograms of samples 11 and 17. However, chlorite values for these clays may be overestimated, due to probable underestimation of kaolin (mentioned earlier) and to interference from imogolite dehydroxylation above 400C (Aomine & Mizota, 1972). Since the diffractogram of sample no. 3 does not show a 14A peak (Fig. 1), chlorite is probably overestimated in this clay. This is attributed to the fact that 15% TGA water for kaolin in this sample is too low. For example, use of 17% H_2O (theoretical halloysite water at 300C is 16,3% - Alexiades & Jackson, 1967) would reduce the calculated chlorite value to about 2%. Reliable estimation of chlorite by difference depends, of course, on the assumption that all other mineral components present have been estimated with reasonably accuracy. Determination by TGA requires the same assumption because of the correction factor involved.

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* For the Oxisol clays, this was taken as % (Al,Fe)OOH (Table 11). For the volcanic-ash soil clays, weight of material removed by CDB was estimated as the sum of allophane (calculated from SiO_2 and Al_2O_3 removed as for % allophane in Table 12) plus FeOOH (Table 12).

TABLE 16. Summarized clay mineralogical composition of natural clays*

Sample		%							
		Allophane	Amorphous $(Al,Fe)_2(OH)_5$	Crystalline (Al,Fe)OOH	Quartz	Mica	Kaolinite plus halloysite	Gibbsite	Chlorite**
Farmhill	2	0,0	5,2	22,6	2,0	3,0	45,4	2,0	19,8
Farmhill	3	0,0	6,9	25,2	0,7	1,9	45,5	0,3	19,5
Farmhill	4	0,0	4,4	21,0	3,7	11,1	32,2	7,4	20,2
Balmoral	5	0,0	2,4	25,6	1,5	1,7	43,6	11,6	13,6
Farningham	6	0,0	6,3	22,8	2,5	5,0	39,9	6,8	16,7
Farningham	7	0,0	5,7	25,3	6,1	5,5	40,4	9,6	7,4
Kraznozem	8	0,0	1,5	49,8	0,1	0,7	23,6	23,9	0,4
Latosol Roxo	18	0,0	4,6	42,2	0,0	0,3	25,3	28,7	0,0
Kodonbaru	11	80,4	0,7	4,8	1,0	1,1	n.d.	0,0	12,0
Tirau	17	63,4	0,6	2,9	5,9	5,5	4,8	0,0	16,9

* From Tables 11, 12, 13 and 15.

** By difference (100% - other minerals).

In the presence of large amounts of kaolinite or halloysite, accurate determination of chlorite will depend to a large extent upon the reliability of kaolinite plus halloysite estimation. In such cases it is important to supplement results with X-ray diffractometry.

1.5 General discussion

Using a variety of instrumental and chemical techniques it has been shown that kaolin, pedogenic chlorite and crystalline hydrous sesquioxides are the major constituents in the clay fraction of some representative samples of Natal Oxisols. Accessory material includes quartz, mica and relatively small amounts of amorphous, Al-rich sesquioxide (2 - 7%). Clay from soils representative of extreme weathering conditions in Australia and Brazil both differ from the Natal soil clays in that pedogenic chlorite is absent, there is less quartz and mica present, while enrichment with crystalline sesquioxides is considerably greater. Amounts of amorphous alumina are of the same order as those found in the Natal soil clays.

Although acid ammonium oxalate reagent has been in use for some time as an extractant for amorphous iron and aluminium from soils, the demonstration here of its superiority over conventional alkaline selective dissolution treatments for the determination of amorphous aluminosilicate material in soil clays is considered to be of great significance. That it extracts slightly smaller quantities of silica and alumina than are removed by boiling 0,5N sodium hydroxide from soil clays known to consist predominantly of allophane, attests to its greater specificity for amorphous material as such. Poorly-ordered kaolinite-halloysite and gibbsite resist oxalate attack, and future investigation may show that even imogolite, a recently discovered filiform mineral often found associated with allophane, is relatively unscathed by the oxalate reaction.

Allophane was determined in the clay fraction of two volcanic-ash soils from Japan and New Zealand by allocating, to oxalate-soluble silica and alumina, a water content derived from an ignition weight loss/composition function for synthetic amorphous silicoaluminas similar to those derived previously by other investigators, but modified to include K-saturation prior to ignition. Water content of both allophanes was found to be in the region of 22 per cent, while molar SiO_2/Al_2O_3 ratios were 0,73 for the Japanese allophane and 0,70 for the New Zealand sample, in contrast to values of 0,93 (calculated from data of Wada & Aomine, 1973 - their Table 3) and 2,2 (N.Z. Soil Bureau, 1968; p. 81) respectively. Dissolution of imogolite (SiO_2/Al_2O_3 close to 1,0) and some

halloysitic material by more harsh alkaline extractants is considered to be the reason for these higher values reported in the literature.

The highly sesquioxidic nature of these allophanes eliminates chemical composition as a basis for arguing that imogolite probably represents an intermediate phase in the transformation from allophane to gibbsite (Wada & Aomine, 1973). Since it is generally recognised that imogolite forms from, or at least in the presence of allophane, transformation could only take place following an influx of silica. This is consistent with the statement by Wada and Aomine (1973) that imogolite formation is usually connected with relatively thin overburden deposition (fresh ash), and with ample porosity within the deposit. Presumably, heavier deposits of ash and/or stagnant moisture regime inhibit imogolite formation, that is, it occurs in situations where the overall SiO_2/Al_2O_3 ratio is still relatively low. Its formation therefore probably coincides with mild rather than intense resilication of allophane. This interpretation contradicts the assumption (Aomine & Mizota, 1972; Wada, Henmi, Yoshinaga & Patterson, 1972) that a mobile aluminium phase is a prerequisite to the formation of imogolite.

The absence of allophane in the Oxisol clays is noteworthy. The high phosphate fixing capacity of such soils is probably as much due to the presence of large amounts of Al-substituted, poorly crystalline goethite as it is to the relatively smaller quantities of amorphous alumina. However, the latter is likely to account for other reactive properties such as pH-dependent CEC and strong buffer capacity. Some of this alumina is present in interlayer positions of 2 : 1 expanded phyllosilicates, the significance of which has been dealt with previously (de Villiers & Jackson, 1967a). The hypothesis (de Villiers, 1965) that pedogenic aluminous chlorite may have greater weathering stability than kaolin is questionable in the light of results obtained in the present study. In Natal Oxisols, chlorite extinction is observed with decreasing particle size (even when the possible effects of crystallinity on relative intensities of X-ray diffraction maxima are taken into account) while kaolin persists, along with gibbsite, in the fine (< 0,08 µm) fraction. Further, soil clays from Australia and Brazil which have been subjected to far more severe weathering contain no chlorite at all. It may be argued that the 2 : 1 layer silicate matrix of pedogenic chlorite is lithological. This would most certainly seem to be the case in the Farmhill soil (no. 4) derived from mica-rich shale, but is more doubtful in the case of the Balmoral (no. 5) which, from field evidence, has formed from deeply weathered dolerite and was sampled at considerable depth.

The subject of yellow subsoil colours in Natal Oxisols is of some interest. Previously the source of this distinctive property has been attributed to the

presence of a poorly crystalline mixed iron-aluminium oxide with a lepidocrocite structure (van der Eyk et al., 1969; p. 52) although recent work (Fitzpatrick, 1974) has cast some doubt on the investigation which forms the basis of this statement. On the other hand, the present study points to the presence of a goethite rather than a lepidocrocite structure. Otherwise the interpretation remains unchanged. Thus red subsoil clays (samples 3 and 5) contain goethite with considerably lower Al content (as measured by citrate-dithionite extraction) than the yellow clays (samples 2, 4, 6 (after H_2O_2 digestion) and 7*). Furthermore, organic Al content is low (0,1%) in the red clays and considerably higher (up to 2%) in the yellow clays. This may point to an organometallic precursorship to formation of the mixed Al-Fe monohydrate as suggested by de Villiers (1969), and would support the observation (van der Eyk et al., 1969; p. 53) that a plentiful supply and rapid turnover of organic matter may be a prerequisite to the formation of yellow subsoil horizons in Natal.

It is important to consider the conditions which favour the formation and persistence of random-structured aluminosilicates in soil. Fieldes (1966) suggests that formation primarily requires either rapid precipitation of dissolved solutes or the weathering of primary aluminosilicates, such as volcanic glasses, which themselves lack ordered structure. Persistence is governed either by the continued presence of a weathering source, or by conditions that are permanently moist, the latter maintaining a high degree of hydration which prevents shrinkage, and hence further cross-linking to form a more ordered structure. The relatively short life of allophane, imogolite and allophane-like constituents in an open, leaching soil environment has been recently established from ^{14}C age data (Wada & Aomine, 1973). It would therefore seem that this short period is governed in turn by the life-time of random-structured weathering sources, the extinction of which leads to the rapid appearance of halloysite, gibbsite and chloritic intergrades as culminating crystalline phases of pedogenesis.

Recent micromorphological evidence (Eswaran & De Coninck, 1971) for the direct transformation of feldspar to kaolinite in saprolite zones of basalt weathering under humid tropical conditions, suggests that clay nucleation (Jackson, 1965a) is an important factor dictating the pathway of clay mineral neogenesis in soils. The absence of allophane in Natal Oxisols could be explained by their age alone. Periodic deposition of ash or other pyroclastic

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* Sample no. 7 is actually yellowish-red. The soil from which it was sampled might be classified, more appropriately, as a Farningham-Griffin intergrade (i.e., its properties should be intermediate between those of red and yellow apedal B horizons). With respect to organic carbon content and organically-bound Al, this sample belongs to the yellow rather than the red group of sesquioxidic materials.

materials, necessary for the maintenance of an early weathering stage, has not influenced Quaternary pedogenesis in this humid subtropical region. The additional influence of crystalline nuclei, such as feldspar in igneous rocks or admixtures of clay-size phyllosilicates in soil parent materials of sedimentary origin, in dictating the preferential development of an essentially crystalline clay mineral suite, could well be significant.

On the other hand, clay mineralogical differences between the Natal Oxisols and those from Australia and Brazil are considered to largely reflect corresponding differences in weathering intensity, along lines proposed by Jackson (1968). Thus the Natal Oxisols are essentially at stage 10 (kaolinite maximum), with incipient gibbsite formation (stage 11), while the Australian and Brazilian soils represent stages 11 and 12 (gibbsite and iron oxides) of the weathering sequence of clay-size minerals in soils (Jackson, 1968). In a study of basaltic Queensland soils, Simonett (1961) observed that kaolinite content is at a maximum under a rainfall of 1000 mm per annum, while under higher rainfall, gibbsite content increases at the expense of kaolinite. Although the controlling factor is essentially effective rainfall, it must be realized that cooler conditions which favour a higher effective rainfall, and hence more rapid desilication, will be counteracted by the effects of slower weathering (influence of temperature on reaction rate). The rainfall under which the Natal Oxisols have formed is in the region of 1000 mm, while that of the Kraznozem and Latosol Roxo is considerably higher (Appendix I). In this context, clay mineral data for these soils conform to Simonett's observations.

The fact that amorphous, hydrated sesquioxide occurs in similar quantities in both groups of Oxisols might suggest a limitation in determining this component by oxalate extraction. The simultaneous presence of much larger amounts of Al-substituted, crystalline iron oxides in the Kraznozem and Latosol Roxo may be responsible for a large proportion of the Al removed by oxalate. However, the point to be emphasized is that amorphous material in these soils is considerably lower than would have been estimated by conventional alkali dissolution analysis. The significance of oxalate-soluble material in terms of physicochemical properties is indicated by results reported in subsequent chapters.

Although kaolin in the Natal Oxisols has been shown to consist of an admixture of kaolinite and metahalloysite, the same cannot be said with certainty for the other Oxisols. The only evidence in this respect is that the Kraznozem clay exhibited a shift in the (001) diffraction maximum to higher d spacings with decreasing particle size. However, the small amount of fine clay in this material would suggest that halloysite, if present, occurs in negligible quantities. The point has already been made that Natal Oxisols represent

an earlier weathering stage than that of the Australian and Brazilian soils. Electronoptical evidence has suggested an intergradation, in one specimen, between kaolinite and metahalloysite particles. It could therefore be inferred that metahalloysite is a precursor to kaolinite formation, although this cannot be established with any certainty.

In conclusion, the present clay mineralogical investigation has focussed mainly on the quantitative determination of amorphous material in sesquioxidic soil clays. Since the data obtained differ in important respects from those of previous studies employing more conventional techniques on similar materials, they require testing with respect to their significance in terms of the physico-chemical properties of the component which they represent. In particular, such testing will determine whether acid ammonium oxalate extraction is more specific for the reactive amorphous component of soils than are other procedures commonly employed for this purpose.

CHAPTER II

PHOSPHATE ADSORPTION AND CHEMICAL REACTIVITY

2.1 Introduction

Research on highly weathered soils of Natal has established that one of the major factors limiting crop yields is their high capacity for immobilizing phosphate. This property is generally attributed to the presence of amorphous or 'active' Al and Fe compounds, while the fixation mechanism appears to be essentially one of chemisorption (Smith, 1965; Hsu, 1965; Easton, 1970; Reeve & Sumner, 1970; Habibullah, 1972).

In the previous chapter, quantitative clay mineralogical analysis of a variety of sesquioxidic soils was carried out. Use of a wide range of techniques and procedures enabled, in many respects, a thorough differentiation of various sesquioxidic components present in these materials. It was therefore considered important to investigate the extent to which this more detailed analysis alters interpretations concerning the source of chemical reactivity in these soils and the extent to which this is expressed.

Two procedures have recently been developed which show promise as means of evaluating the chemical reactivity of soil clays. The action of fluoride appears to provide, through monitoring of hydroxyl as a reaction product, a relatively meaningful measure of the quantity of amorphous or 'active' material (sesquioxides, allophane) present in a sample (Huang & Jackson, 1965; Fieldes & Perrott, 1966; Bracewell, Campbell & Mitchell, 1970). Estimation of reactive Al by titration of its double hydroxide formed with Mg in the buffer range pH 8,2 to 8,5 gives an index of reactivity which has been found to correlate well with soil properties such as phosphate-fixing capacity (Schalscha, Pratt & Gonzalez, 1972a).

The objective of this chapter is to present and discuss results obtained from the use of these two techniques (with some modifications) for estimating the reactivity of a selection of sesquioxidic soil clays in relation to their capacities for immobilizing phosphate. Such an evaluation is essentially relative rather than absolute, and affords the opportunity of establishing the existence of possible relationships between chemical reactivity and mineralogical composition.

2.2 Materials and methods

Freeze-dried, K-saturated natural clays and synthetic aluminosilica gels were used (Chapter I; Appendix I).

Phosphate adsorption. The equivalent of 50 mg oven-dry (110C) material was equilibrated with 10 ml of KH_2PO_4 solutions having concentrations corresponding to 1,10 and 100 ppm P in 20 ml glass centrifuge tubes with rubber stoppers on an end-over-end shaker at room temperature (23C) for 24 h. Equilibrium P concentration in the centrifuged supernatants was measured by the ascorbic acid method of Watanabe and Olsen (1965).

Fluoride reactivity. In principle, the technique employed was based on that developed by Bracewell et al. (1970), but was modified with respect to fluoride salt, reaction time, and initial fluoride/sample ratio. A Radiometer automatic titration assembly was used to continuously monitor OH released by the reaction of a 25 mg sample with 10 ml 1N KF solution, maintained with vigorous stirring at a constant pH of 6,8 with HCl as titrant. Concentration of the latter was such that no more than 0,5 ml was required for the full reaction period, which was terminated once OH release rate (recorded graphically) was found to be essentially constant (after approximately 25 - 40 min).

Reactive Al. This determination is based on the stoichiometric relationship between Al and the equivalents of base required to titrate the double hydroxide formed in the presence of excess Mg ions over the pH interval 8,2 to 8,5 (Schalscha et al., 1972a). The latter authors obtained a value for equivalents of base from a discontinuous plot of pH vs. volume of base added serially to a large number of soil samples. The procedure employed in the present investigation was as follows: using a Radiometer automatic titration assembly in pH-stat mode, a 25 mg sample suspended in 15 ml 0,5N $MgCl_2$ was titrated to, and maintained at pH 8,2 with 0,050N NaOH for 30 min, or until the titration rate required to maintain this pH was constant. The operation was then repeated at pH 8,5. Titration rate functions were recorded graphically.

2.3 Results and discussion

2.3.1 General considerations

Phosphate adsorption by the clays and gels (Table 17) is, in the case of the 1 and 10 ppm levels, almost equivalent to the total amount added (20 and 200 mg P/100 g respectively) to some samples (the allophanes and gel IV particularly). Consequently, adsorption data at the 100 ppm P level (equivalent to the addition of 2000 mg P/100 g sample) are the most significant when

comparing relative adsorption capacities. The allophanes and gel IV adsorb from four to sixteen times as much P as the Oxisol clays. Lower P adsorption by gels II and III is in agreement with previous observations (Takahashi, 1964; Saunders, 1965; Cloos, Herbillon & Echeverria, 1968) that Si in allophane and synthetic amorphous silicoaluminas inhibits reaction with P.

Reactive Al (Table 18) was calculated as one-half of the total milliequivalents of NaOH consumed in the pH interval 8,2 to 8,5 (Schalscha et al., 1972a). The latter was derived graphically as shown in Figure 15; the linear portions of the titration curves at pH 8,2 and 8,5 were interpolated to zero reaction time to obtain volumes of titrant which represent the neutralization of highly reactive buffering at each pH level (effectively, weak buffering represented by the linear portion of each curve is subtracted by this operation).

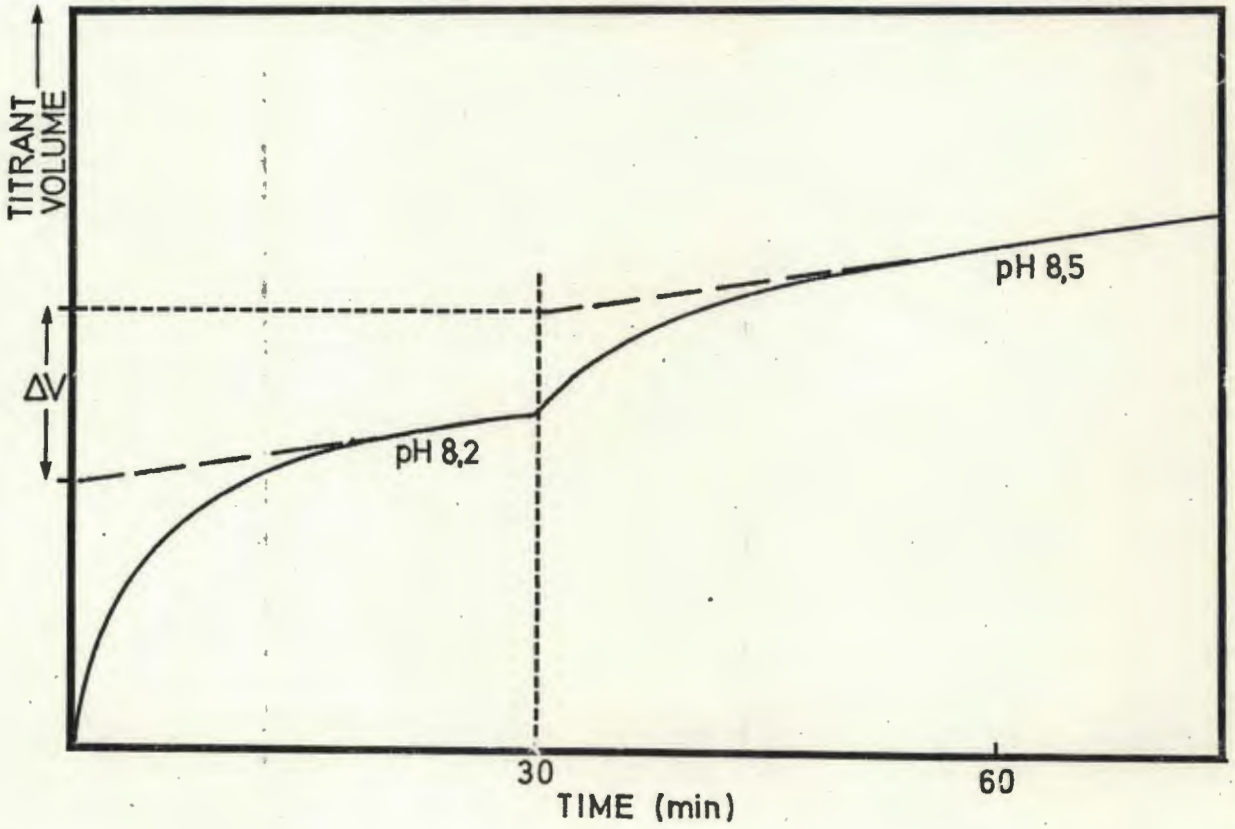

FIGURE 15. Diagrammatic presentation of procedure used to determine volume of titrant (ΔV) required to titrate the Mg-Al double hydroxide in the pH interval 6,2 to 8,5

The volume of titrant neutralized by the Mg-Al double hydroxide was then obtained by difference (ΔV, Fig. 15). The same procedure was used to derive values for hydroxyl released from HCl titration curves of fluoride-treated

TABLE 17. Phosphate adsorption capacity of sesquioxidic soil clays and synthetic aluminosilica gels.

Sample	mg/100g P retained by 50 mg from 10 ml KH_2PO_4 of concentration:		
	1 ppm P	10 ppm P	100 ppm P
2	18,9	154	307
3	19,1	126	175
4	19,0	119	115
5	19,3	166	298
6	17,5	103	185
7	19,2	167	315
8	18,8	197	474
18	18,6	141	145
11	19,2	197	1632
17	19,0	198	1547
Gel II	15,1	90	593
Gel III	18,9	156	975
Gel IV	19,1	198	1856

TABLE 18. Reactive Al and OH of sesquioxidic soil clays and synthetic aluminosilica gels in relation to specific surface area

Sample	Reactive Al	Reactive OH	OH/Al*	Specific† surface area (m^2/g)
	me/100g			
2	20	102	5,1	284
3	15	57	3,8	246
4	22	68	3,2	223
5	12	61	5,2	313
6	28	103	3,7	240
7	20	108	5,5	325
8	15	66	4,3	265
18	12	44	3,6	139
11	36	1819	50,5	441
17	35	980	28,2	473
Gel II	20	3220	161,0	496
Gel III	24	2610	108,8	490
Gel IV	31	805	26,0	432

* Reactive OH/reactive Al. † EGME method (Chapter I).

clays and gels (reactive OH, Table 18). Values obtained in this way are more meaningful than those obtained by volume measurement after a standard titration time* (e.g. Bracewell et al., 1970, based fluoride reactivity measurements on a 25 min. reaction period).

There appears to be no simple direct relationship between reactive Al, reactive OH, the resultant OH/Al ratio, or surface area (Table 18) and P fixing capacity at the 100 ppm P level (Table 17). Two factors are most likely to be responsible for this. Firstly, because P adsorption depends to a large extent on equilibrium rather than initial P concentration, comparison of P fixing capacities should properly be made for a specific equilibrium P concentration. Only a few of the Oxisol clays with relatively low P retention capacity are likely to have their adsorption sites effectively saturated with P by the 100 ppm treatment. Secondly, the sesquioxide fraction in these materials is a multi-component system (Chapter I) comprising amorphous alumina and/or aluminosilicates, as well as variable quantities of gibbsite and iron oxides. Variable degrees of Al for Fe substitution in the latter will result in corresponding variations in chemical reactivity. A small, organic-associated quantity of Al is also present in some of the clays, and is probably a highly labile constituent. Despite these factors, there are some relationships which deserve particular attention.

2.3.2 Similarities between allophane and synthetic aluminosilica gels

Relationships between P adsorption, reactive Al, OH/Al ratio, and chemical composition are plotted graphically for the allophanic clays (samples 11 & 17) and the synthetic aluminosilica gels in Figures 16 and 17. In all cases the natural allophanes exhibit a degree of behaviour which is remarkably close to that which would have been predicted on the basis of the various chemical composition functions for synthetic amorphous aluminosilicates. This close matching of behaviour vindicates a number of previous attempts

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* In this connection it should be emphasized that neither approach obviates an important limitation to both these techniques. It was observed that the slope of the linear section of the titration curve was variable, being relatively shallow for the Oxisol clays and considerably steeper for the allophanes and gels. In general, the steepness of the slope was a function of initial reactivity of the material (as measured by interpolation). The following explanation is put forward to account for these observations: in the Oxisol clays, a relatively small amount of amorphous material (Chapter I) would, if it existed as coatings on crystalline clay surfaces, account for the low residual reactivity following a rapid initial reaction; on the other hand, in the allophanes and gels, the bulk of the solid phase is amorphous and would therefore be expected to produce a relatively much larger residual surface reactivity.

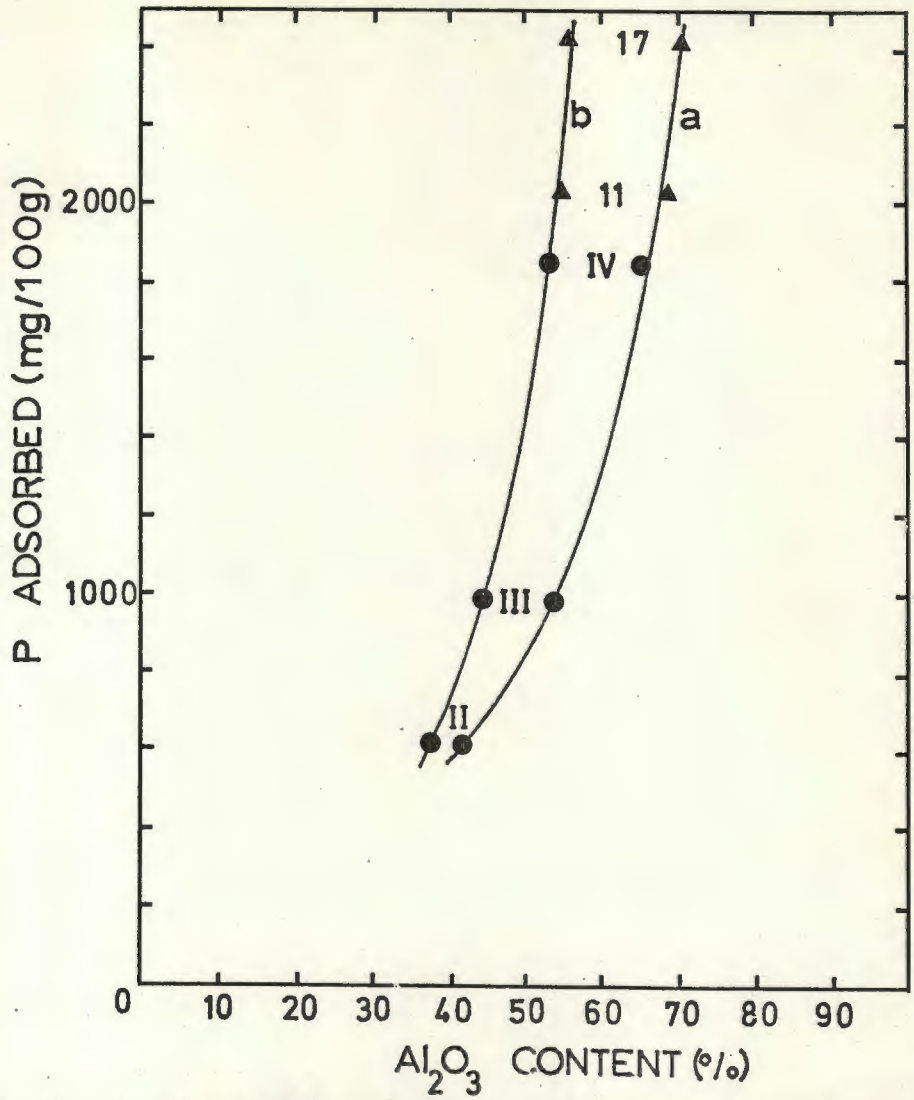

FIGURE 16. P adsorption by allophanes (▲) and aluminosilica gels (●) as a function of Al_2O_3 content, expressed as (a) $Al_2O_3/Al_2O_3 + SiO_2$ or (b) $Al_2O_3/Al_2O_3 + SiO_2 + H_2O$, where H_2O = % water retained at 110C (Fig. 14). P adsorption by samples 11 & 17 calculated as mg P/100g allophane (Table 16)

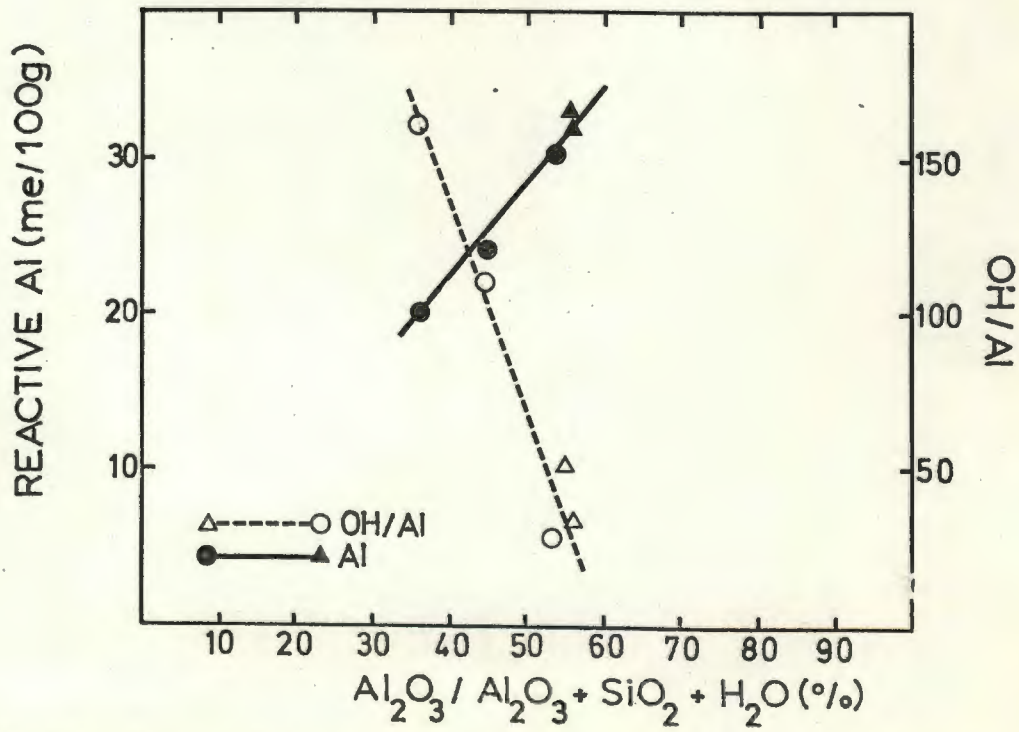

FIGURE 17. Relationship of reactive Al and OH/Al ratio (Table 18) to composition (as in b, Fig. 16) of allophanes (▲,△) and aluminosilica gels (●,○)

(Mitchell et al., 1964; de Villiers & Jackson, 1967a; Cloos et al., 1968, 1969; van Reeuwijk & de Villiers, 1970) to elucidate the nature of allophane via models based on studies of simple, synthetic co-precipitates of silica and alumina.

Evidence supporting the suggestion by Cloos et al. (1968) and others that structural silica blocks P adsorption can be deduced from Figure 16. Calculation of P adsorption by samples 11 and 17 on the basis of their allophane content (actual adsorption is in the region of 1600 mg P/100g - Table 17) requires the assumption that complementary material is relatively crystalline and accordingly fairly inert with respect to reaction with phosphate. The close matching of P adsorption values calculated in this way with those that would be theoretically predicted by extrapolation, lends considerable support to the selectivity of acid ammonium oxalate as an extractant for allophane (Chapter I), in contrast to boiling 0,5N NaOH which dissolves material from both clays having composition corresponding to approximately 55% $Al_2O_3/Al_2O_3 + SiO_2$ (Table 7, Chapter I), or about 45% $Al_2O_3/Al_2O_3 + SiO_2 + H_2O$. The same inference can be drawn from Figure 17.

The relationships of P adsorption capacity (Table 17), and reactive Al and OH/Al ratio (Table 18) to chemical composition of the allophanes and gels (Figs. 16 & 17) indicate that, while there appears to be a direct relationship between P adsorption and reactive Al, adsorption of phosphate is inversely related to OH/Al ratio. An inverse relationship between P adsorption and fluoride reactivity itself is unlikely, since the mechanism of reaction of highly electronegative anions such as phosphate and fluoride with hydroxyalumina is probably very similar. It is therefore inferred that, whereas an anion penetration mechanism (Bailar, 1956; Jackson, 1963) may account for much of the P adsorption by gels II and III (high levels of fluoride-displaced OH, (Table 18), it clearly becomes less significant in the case of gel IV and the allophanes. In the latter, it is considered that a lower proportion of Al-O-Si bonds has permitted Al dissolution and its subsequent precipitation as taranakite (Wada, 1959) or variscite (Gebhardt & Coleman, 1974b). The surface basicity of hydroxyalumina (insofar as OH/Al ratios are a measure of this*) may even inhibit, through hydroxyl blocking, the degree of covalent bonding between Al and oxyanions such as phosphate.

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* TGA weight loss data (Chapter I) indicate that basicity increases, rather than decreases, with Al_2O_3 content, reaching a maximum of 3 (alumina trihydrate). Fluoride-displaced OH data therefore suggest either (i) that the proportion of surface-to inner-hydroxyls decreases with increasing Al_2O_3 content in the system, or (ii) that hydrolysis (surface water splitting) is involved in the adsorption mechanism.

Evidence has been presented elsewhere (Easton, 1970; de Villiers, 1969), suggesting that terminal-OH_2 sites, rather than ligand-OH (anion penetration) positions, are the most reactive to the presence of phosphate. This evidence was based on two observations. Firstly, P adsorption and pH are inversely related. Secondly, sorption of P by a synthetic hydroxyalumina and by the hydroxyl-Al of two synthetic amorphous aluminosilicates was found to decrease with Al_2O_3 content. In both cases the effect was attributed to the degree of polymerization (and hence proportions of ligand-OH and terminal-OH_2 positions) of the hydroxalumina, as affected either by pH or by the amount of polymerization inhibitor (negatively-charged permutite core containing 22% $Al_2O_3/Al_2O_3 + SiO_2$) associated with the hydroxy-Al. Some comment on these findings is necessary.

Firstly, proton consumption associated with P adsorption (Gebhardt & Coleman, 1974b) could explain the pH effect (an increase in pH would constitute an additional, competitive proton sink which would presumably inhibit P adsorption). Furthermore, reduced specific surface arising from pH-induced polymerization could equally account for the observed reduction in P adsorption.

Secondly, the results obtained by Easton (1970), and on which the arguments of de Villiers (1969) are based, conflict with those of the present study, since, even when P adsorption data for the gels (Table 17) are calculated in the basis of Al_2O_3 in excess of that allocated to a permutite core containing 22% Al_2O_3, adsorption still increases with total alumina content of the system (from 14 470 mg/100 g for gel II to 28 580 mg/100 g for gel IV). A probable explanation for this is that Easton (1970) employed an 11 day equilibration period (as opposed to 24h in the present investigation), so that despite the fact that total P added was higher (maximum of 10 000 compared with 2000 mg/100 g respectively), reaction with the solid phase was essentially complete (close to 100% adsorption - Table 3 of Easton, 1970). Subsequent adsorption values, calculated on the basis of excess hydroxy-Al therefore have dubious significance, since any calculated decrease in adsorbed P with increasing Al_2O_3 content will be an arithmetic one. Hence the present study provides additional evidence suggesting that the model for allophane proposed by van Reeuwijk and de Villiers (1970) requires revision.

2.3.3 Reactivity of Oxisol clays

Results presented in Tables 17 and 18 indicate that reactivity of the Oxisol clays is considerably lower than that of the allophanes and synthetic gels. It is also much lower than that which might have been predicted on the basis of the relatively large amounts of 'amorphous' silica and alumina

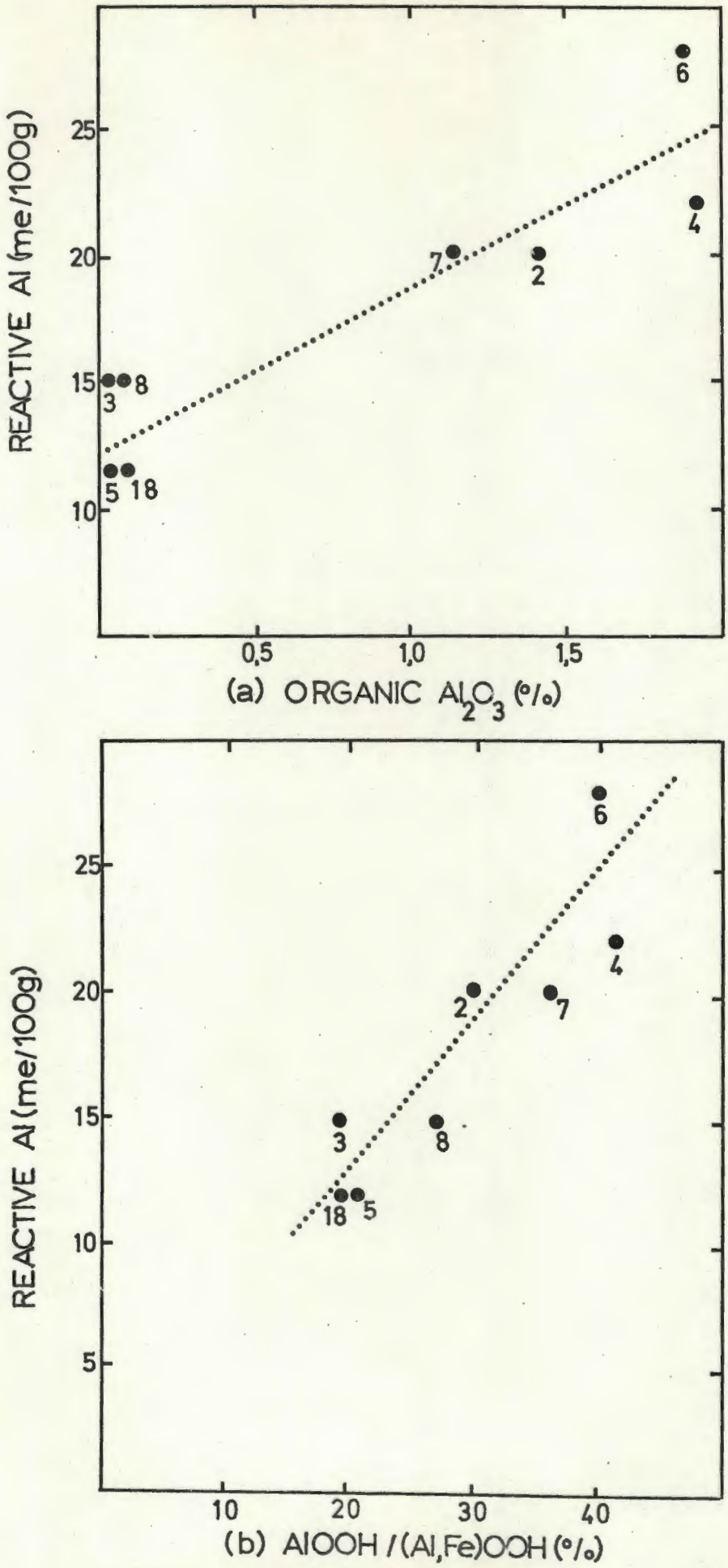

FIGURE 18. Relationship of reactive Al in Oxisol clays to (a) organic (pyrophosphate-extractable) alumina and (b) degree of Al substitution in the iron oxide (CDB-extractable) component (Table 11)

removed by boiling 0,5N NaOH* (Table 7 - Chapter I). That the determination of amorphous material by oxalate extraction is more meaningful, is indicated by the corresponding values for allophane or amorphous sesquioxide (Table 16 - Chapter I) and P adsorption (Table 17). Saunders (1965) and Ballard and Fiskell (1974) have established significant correlations between oxalate-Al and P retention. However, in view of the relatively small amounts of amorphous (oxalate-soluble) alumina measured in the Oxisol clays, it might be expected that the much larger quantities of Al-substituted iron oxides present will contribute significantly to both P adsorption and to other parameters of reactivity (Tables 17 & 18). This is confirmed by the fact that the Kraznozem clay (no. 8), which contains in the region of 50 per cent aluminous goethite ($Al_2O_3/Al_2O_3 + Fe_2O_3 = 0,23$), retains considerably more P than the Natal Oxisol clays, which have less (Al,Fe)OOH but more amorphous sesquioxide (Table 16). Lower P adsorption by the Latosol Roxo clay, which also contains about 50 per cent iron oxides, is attributed to the less reactive nature of the latter (mainly hematite and/or maghemite with lower degree of Al-substitution - Chapter I).

Some idea of the source of reactive Al in the Oxisol clays is provided by the correlation of the latter with both organic (pyrophosphate-extractable) alumina and with degree of Al substitution in the goethitic component (Fig. 18). On the other hand, reactive Al bears no apparent relationship to amorphous (oxalate-soluble) alumina (Tables 8 & 18). In Chapter I, attention was drawn to the probable role (as suggested by de Villiers, 1969) of organically-bound Al as precursor to formation of the mixed Al-Fe monohydrate. Hence either or both these components could govern levels of reactive Al.

The fact that there is not a corresponding relationship between reactive Al or OH and P adsorption indicates that reactivity parameters determined in this way are meaningful up to a certain point only. A direct relationship between P adsorption and reactive Al, for example, would imply that there is, in turn, a relationship between the accessibility of reactive Al sites to phosphate anions on the one hand, and to Mg and OH ions on the other. Such a condition is probably met by the allophanes and gels (section 2.3.2) where the abundance of highly-reactive amorphous hydroxyalumina effectively constitutes a homogeneous reaction system. On the other hand, reactive sesquioxidic material in the Oxisol clays has multicomponent character and reaction with phosphate,

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* In addition to sesquioxidic allophane, Jackson (1964) has recognised the existence of so-called halloysitic allophane (molar SiO_2/Al_2O_3 ratio of about 2) which is relatively much more stable and inert than the sesquioxidic variety. The present investigation suggests that such material is not allophane but finely-divided, kaolinite-halloysite or relatively poor crystallinity.

fluoride and magnesium hydroxide is correspondingly less simple and direct.

2.4 Conclusions

The suitability of fluoride reaction and Mg-Al double hydroxide titration as techniques for obtaining parameters of reactivity which bear distinct relationships to P adsorption capacity and quantitative mineralogical data, has been demonstrated for allophanes and synthetic amorphous aluminosilicates. The relatively more complex reaction system of the Oxisol clays, containing small but probably highly-labile organic and amorphous Al and Fe fractions, as well as large amounts of variably-crystalline sesquioxide, militates against the establishment of straighforward parametric relationships.

In general, values for oxalate-extractable amorphous material are in better agreement with relative P adsorption capacities of Oxisol and volcanic-ash soil clays than those obtained by 0,5N NaOH dissolution analysis. However, because of the relatively small amorphous component in the Oxisol clays, its role in governing colloidal reactivity is subdominant to that of crystalline sesquioxides having relatively short-range order as a result of extensive isomorphous substitution. On the other hand, relationships between reactivity parameters and chemical composition of allophanic clays and synthetic aluminosilica gels suggest that oxalate removes the amorphous (reactive) component far more specifically than 0,5N NaOH treatment.

The close matching of actual chemical reactivity and that predicted for natural allophanes on the basis of similar behaviour of synthetic amorphous coprecipitates, points to the importance of studying the latter as a way to better characterization and understanding of the behaviour and genesis of their natural analogues. So far, the indications have been that the model system for allophane proposed by van Reeuwijk and de Villiers (1970) requires revision, specifically with respect to the content of tetrahedral Al in the structure. Further evidence in favour of such revision is presented in the next chapter.

P adsorption by allophanes and synthetic gels was found to be inversely related to hydroxyl release during contact with fluoride solution. This suggests that an anion penetration mechanism (adsorption *via* replacement of structural-OH) is of limited significance in the P adsorption process.

The reaction of phosphate with amorphous hydroxyalumina of allophane is an understandably rapid one, leading, within a relatively short period of time, to decomposition followed by reprecipitation of crystalline Al-phosphate (Wada, 1959; Gebhardt & Coleman, 1974b). The reaction with crystalline clays

(Kittrick & Jackson, 1956) is slower, but proceeds along an essentially similar pathway. Hence no soil clay system will be in equilibrium with added P until the matrix solution becomes supersaturated with respect to neoformed phosphosesquioxide products (Blanchar & Scrivner, 1972; Gebhardt & Coleman, 1974b). Factors such as quantity of added P and time of contact are therefore of crucial significance to any study of this nature. The conditions used in this investigation permitted comparison of P immobilizing capacities on a relative basis, thus satisfying objectives. From an applied (agronomic) point-of-view, kinetic studies of P reaction with sesquioxidic soils, insofar as these relate to rate of plant uptake/rate of immobilization balance, would appear to be a more promising aspect warranting further investigation.

CHAPTER III

ELECTRIC CHARGES ON SESQUIOXIDIC SOIL CLAYS

3.1 Introduction and literature review

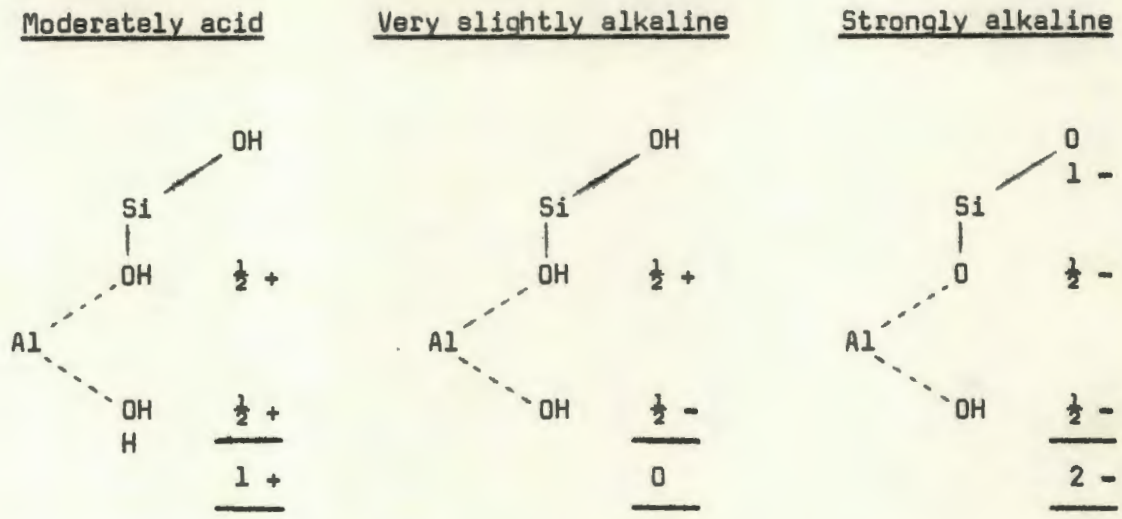
3.1.1 General perspective

The study of electric charges on soil colloids is of fundamental importance to soil fertility. This is particularly so in the case of acid, strongly-leached soils of the humid tropics and subtropics. These soils often contain substantial accumulations of free sesquioxides associated with a clay mineral suite characteristically dominated by 1 : 1 layer silicates. The latter possess a relatively small isomorphous substitutional negative charge which interacts with positive charge associated with surfaces of free sesquioxides to produce a low net electric charge. The resulting capacity of such soils to retain plant nutrient cations is therefore very poor (Schofield, 1939). Furthermore, interaction of positive and negative charges is an important factor governing colloid stability and hence favourable soil structure (Sumner, 1961).

Attempts to lime these highly-weathered, sesquioxidic soils to near neutrality according to procedures used in temperate regions have very often failed (Kamprath, 1970; Reeve & Sumner, 1970b) owing to an exceptionally high buffer capacity. The latter has been shown (de Villiers & Jackson, 1967a) to be stoichiometrically equivalent to pH-dependent CEC, that is, to the CEC which develops following an increase in soil pH.

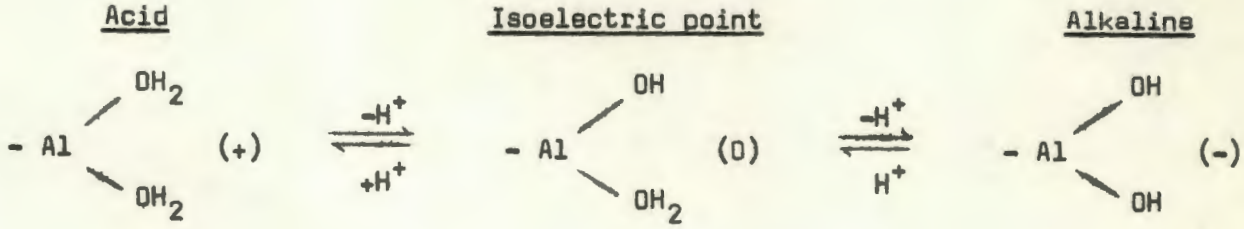
Schofield (1949) established that this variable component of CEC, which he distinguished from so-called 'permanent' CEC arising from isomorphous substitution, was due initially (in the pH range of about 5 to 7) to the neutralization of positive charges, and later (above about pH 6), to the development of negative charge additional to that already present. The source of positive charge was taken to be mainly hydrous ferric oxides.

It was also believed that broken edge faces of layer silicates could contribute to variable charge in soils. Schofield and Sampson (1953) illustrated the effect for kaolinite edges as follows:



Deprotonation of silanol, Al-OH and Al-OH_2 groups progresses in the presence of an increasingly strong proton sink (hydroxyl ions) with a resultant loss of positive charge. Later, Sumner (1961) and Sumner and Reeve (1966) showed that the presence of small amounts of sesquioxide impurities (removed upon deferration) could equally account for the measured positive charge and pH-dependent CEC behaviour of kaolinite.

Jackson (1963) suggested that deprotonation of edge hydronium (Al-OH_2) is a more feasible source of pH-dependent CEC than the dissociation of hydroxyl (silanol) groups. He proposed the existence of a so-called 'isoelectric edge' consisting of hydrogen-bonded pairs (OH_2 ... OH) to account for the balancing of broken-edge charges (0,5 - per edge hydroxyl and 0,5 + per edge alumino-hydronium), and for pH-dependent CEC as follows (Sumner, 1961, presented a similar scheme for iron oxide edges):



That a relatively small contribution is likely to come from silanol groups has been demonstrated for common layer silicates (de Villiers & Jackson, 1967a) and on the basis of the relatively low pH-dependent CEC found for amorphous silica (van Reeuwijk & de Villiers, 1970).

Another rather unique source of pH-dependent CEC was proposed by Fieldes and Schofield (1960) as arising from tetrahedral Al at broken edge sites in allophane and feldspars. Water molecules co-ordinated at such sites would deprotonate, with increasing pH, in the usual way.

The marked pH-dependent CEC behaviour of allophane-rich volcanic ash soils (Aomine & Jackson, 1959; Fieldes & Schofield, 1960) and of Oxisols (le Roux & de Villiers, 1966) has been attributed (de Villiers & Jackson, 1967a) to deprotonation of positively-charged, polymeric hydroxyalumina, either surface-associated with a negatively-charged, amorphous aluminosilicate phase (in allophane) or with interlayers of expanded 2 : 1 phyllosilicate structures (pedogenic aluminous chlorite). A notable feature of both these materials is that a high proportion of the pH-dependent CEC is hysteretic (Jackson, 1968). This property, termed 'CEC delta value' (Aomine & Jackson, 1959) has been exploited for the quantitative estimation of allophane in soil clays (Jackson, 1965b).

3.1.2 Chemical pretreatments

Much of the present knowledge concerning the nature of electric charges in soil has come from studying the effects of pretreating colloid surfaces with various chemical reagents.

Phosphate adsorption is accompanied by the neutralization of positive charge as well as an increase in total negative charge (de Haan, 1965; van Reeuwijk, 1967; Griffith, 1974). Pyrophosphate (Cashen, 1959) and hexa-metaphosphate (Sumner & Reeve, 1966) presumably have a similar effect.

Extraction with acid ammonium oxalate in sunlight was used by Schofield (1949) to deduce the ferruginous nature of positively-charged material in a Rothamsted subsoil. On the other hand, the use of this extractant in the dark, currently popular for estimating amorphous or 'active' sesquioxides (McKeague, Brydon & Miles, 1971; Schwertmann, 1973), may extract considerably more Al than Fe (Chapter I). Significant correlations have been obtained between oxalate-extractable Al and pH-dependent CEC (Clark, Green & Nichol, 1967; Pritchard, 1971).

Pretreatment of sesquioxidic soils with 0,5M $CaCl_2$ (pH 1,5) was found by Tweneboah, Greenland and Oades (1967) to reduce the positive charge developed at low pH and to extract relatively much larger amounts of Al than Fe or Si, while negative charge was little affected by the treatment. These authors concluded that the positive charges present were mostly due to active alumina.

Deferration (dithionite treatment) has been used to indicate the contribution of free iron oxides to positive charges in soil (Sumner, 1962; Davidtz & Sumner, 1965). Since dithionite extraction usually removes variable but sometimes large amounts of alumina as well, it is not always possible to establish which constituent is the major source of positive charge (Habibullah, 1972; Moshi, Wild & Greenland, 1974).

Alkaline extractants have also found use in elucidating the nature and source of pH-dependent CEC (de Villiers & Jackson, 1967a).

3.1.3 Choice of technique

The method of measuring electric charges on soil colloids is crucial to subsequent interpretations concerning the mechanism of pH-dependent CEC and the actual status of charges under field conditions.

The conventional approach has been to saturate exchange sites with an index electrolyte, remove excess salt by washing with alcohol (the low dielectric constant minimizes effects such as double layer overlap, hydrolysis and dispersion), and then to measure the quantity of index ions exchanged by a replacing electrolyte solution. An alternative approach eliminates the washing step by making a weight correction for the excess salt present before replacement (Ensminger, 1944; Schofield, 1949; Wada & Harada, 1969; El-Attar & Jackson, 1973).

Schofield (1949) argued for the use of 0,2N NH_4Cl as saturating electrolyte since this was sufficiently dilute for purposes of accuracy, and at the same time sufficiently concentrated to guarantee the simultaneous measurement of discreet positive and negative charges (electric double layer overlap and size of ionic atmosphere both increase with electrolyte dilution). Any method incorporating an alcohol washing step will therefore result in the measurement of lower electric charges (Sumner, 1963).

Wada and Harada (1969) have shown that measured CEC and AEC can be strongly dependent on both concentration and type of electrolyte used. A salt concentration of 0,05N was found to be the optimum at which the opposing effects of hydrolysis in more dilute solutions, and non-Coulombic adsorption at higher concentrations, were smallest. Since the latter effect was largest for small hydrated cations (K and NH_4), these authors proposed that an intersalation mechanism was operative.

In view of the stereospecificity which soil clay constituents such as vermiculite (Alexiades & Jackson, 1965) and allophane-like material (van Reeuwijk & de Villiers, 1968; Raman & Mortland, 1969; Wada & Harada, 1969) display towards cations in solution, it seems that the use of K or NH_4 would be preferable to that of cations such as Na, Ca or Mg with larger ionic radii. At least, ionic radii of saturating and replacing cations should be of the same order. For measurement of positive charge, chloride or nitrate are preferable because of the minimal specificity with which these anions are adsorbed (Gebhardt & Coleman, 1974a).

3.1.4 Objectives

An investigation of positive and negative charges is a logical consequence of the mineralogical and chemical reactivity studies presented in Chapters I and II.

The objectives of the present chapter are:

(i) to study the variation of electric charges in sesquioxidic soil clays and synthetic aluminosilica gels in response to pH changes and to a variety of chemical pretreatments;

(ii) to re-examine the basis of ion exchange behaviour used by van Reeuwijk and de Villiers (1970) in formulating a model system for allophane; and

(iii) to investigate the phenomenon of, and the factors which give rise to, pH-dependent exchange charge hysteresis.

3.2 Materials and methods

Freeze-dried, KCl-saturated natural clays and synthetic gels were used (Chapter I). No pH adjustment was employed for separation of natural clays. The synthetic gels had been adjusted to pH 6 prior to washing and drying (van Reeuwijk & de Villiers, 1970).

Variation of electric charges with pH was measured as follows: 200 mg samples were weighed into 100 ml beakers, 50 ml 1N KCl added, and the pH adjusted to 4,7 or 10 with HCl or KOH. Readjustment was made after two hours and once more following overnight equilibration. The suspensions were then transferred quantitatively to tared 20 ml glass centrifuge tubes, and centrifuge-washed five times with 0,05N KCl adjusted to the appropriate pH. An equilibration period of 30 min was allowed for the final washing. The pH of the final supernatant was measured and the tube plus contents weighed immediately after decantation. Suspensions were then washed five times (including two overnight equilibrations) with neutral 1N $(NH_4)_2SO_4$. K and Cl were analysed in the combined washings made up to 100 ml with 1N $(NH_4)_2SO_4$ by flame emission and with an Aminco-Cotlove chloride titrator, respectively. KEC and ClEC were calculated after correction for occluded salt. The determination was performed in duplicate.

To test for hysteresis, the soil clays which had been adjusted to pH 10 were washed three times with 1N KCl, readjusted to pH 4, and the above procedure was repeated.

Separate 50 - 100 mg subsamples were given the following pretreatments:

(i) 10 ml KH_2PO_4 solution containing 100 ppm P for 24h (as in Chapter II); (ii) 10 ml 0,1M sodium pyrophosphate (pH 10,5) for 12h; (iii) 10 ml 0,2M ammonium oxalate (pH 3) for 2h in the dark; (iv) 10 ml citrate-bicarbonate solution plus 0,75 g sodium dithionite at 80C; and (v) on a duplicate, deferrated sample, 15 ml 5% Na_2CO_3 for 2h at 90C in a water bath (treatments (ii) - (v) as in Chapter I). Residues from all treatments were centrifuge-washed three times with 1N KCl, then five times with 0,05N KCl. The pH of the final washing (30 min equilibration) was measured and CEC and AEC were determined by $(NH_4)_2SO_4$ extraction as outlined above. Results were expressed on the basis of final weights of residues washed free of salt and dried at 110C.

3.3 Results and discussion

The results of pH adjustment and chemical pretreatment on the distribution of electric charges (CEC and AEC) are presented in Figures 19, 20 and 21.

3.3.1 Variation of electric charges with pH

Clays from the Natal Oxisols possess a large pH-dependent component of CEC and a smaller amount of AEC which is also pH-dependent (Fig. 19). None of the clays have an isoelectric point above pH 4. Clays from the Kraznozem (no. 8) and Latosol Roxo (no. 18) possess considerably lower CEC, a smaller pH-dependent component, and relatively large amounts of positive charge (Fig. 20). They have isoelectric points at pH 7,0 and 5,9 respectively. The allophanes (samples 11 and 17) display typically large pH-dependent CEC (Aomine & Jackson, 1959; Fieldes & Schofield, 1960), as well as substantial positive charge (Fig. 20). They are isoelectric at pH 6,9 and 5,6 respectively, in agreement with the finding that B horizon allophanic colloids generally have net positive charge at field pH (Aomine & Egashira, 1968). Variation of electric charges of the aluminosilica gels with pH is plotted as a function of chemical composition (Fig. 21). As would be expected on the basis of previous comparisons (Chapter II), gel IV exhibits properties remarkably similar to those of the allophanes.

In all but one case (sample no. 8, Fig. 20), the increase in CEC with pH is considerably larger than the corresponding decrement of positive charge. This indicates that pH-dependent net negative charge does not arise merely through neutralization of positive charge which blocks 'permanent' or isomorphous substitutional negative charge at acid pH levels (de Villiers & Jackson,

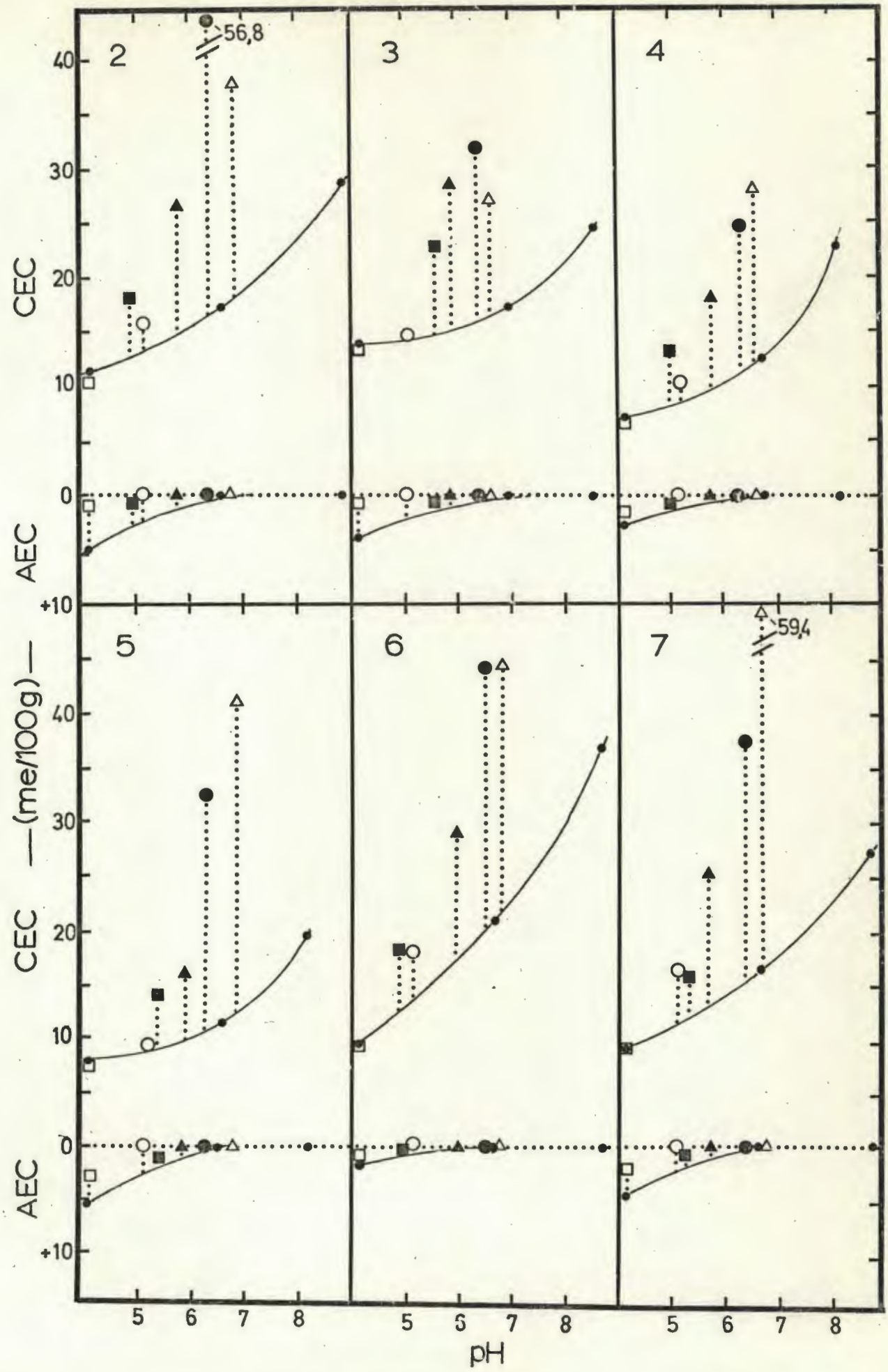


FIGURE 19. Influence of pH and chemical pretreatments on CEC and AEC of natural clays from Natal Oxisols. (Legend: ●—● variation with pH; □ pH 10 pretreatment; ■ pretreatment with 2000 mg P/100g; △ pyrophosphate; ▲ CDB; ○ Oxalate; ● CDB + Na_2CO_3)

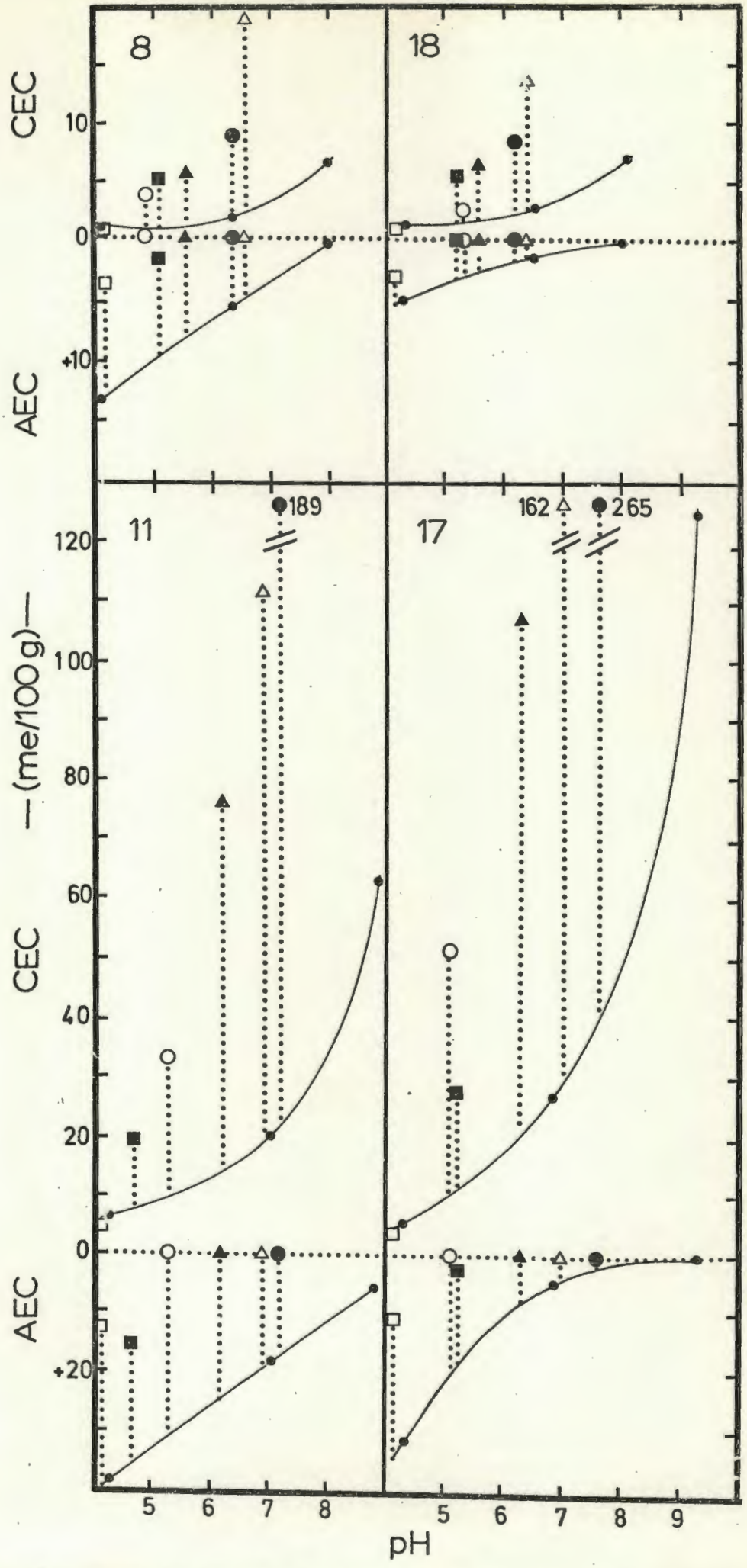


FIGURE 20. Influence of pH and chemical pretreatments on CEC and AEC of natural clays (samples 8, 18, 11 & 17). Legend as for Figure 19

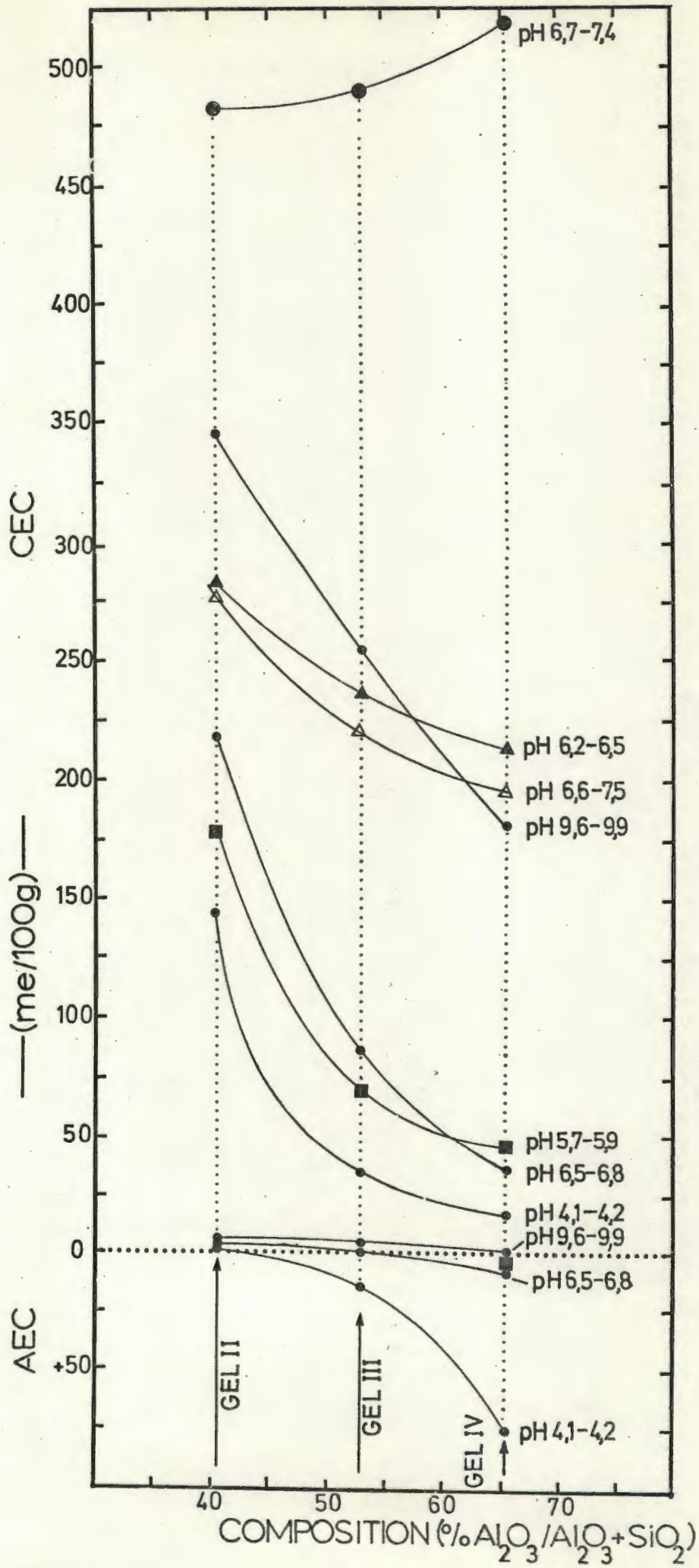


FIGURE 21. CEC and AEC variation with pH and chemical pretreatments in relation to composition of synthetic aluminosilica gels. (Legend as for Fig. 19; indicated pH ranges refer to those

1967a, b). The present results confirm the conclusion by Schofield (1949) that negative charge additional to that already present develops under alkaline conditions, and can be explained by charge reversal on edge (Al,Fe)-OH_2 functional groups (Sumner, 1961; Jackson, 1963; Parks, 1967).

Large positive charge of the allophanes and gel IV under acid conditions is attributed to the presence of aluminohydronium groups (Jackson, 1963) on polymeric hydroxyalumina. On the other hand, amorphous (oxalate-soluble) alumina content is of the same order in all the Oxisol clays, which suggests that (in sample no. 8 at least) much of the positive charge is located on surfaces of crystalline iron oxides (Chapter I). The presence of aluminated 2 : 1 layer silicate structures in the Natal Oxisol clays and the absence thereof in samples 8 and 18 (Chapter I) would account for the much higher permanent and pH-dependent CEC of the former group (de Villiers & Jackson, 1967a). Halloysite, which is relatively more abundant in the Natal soil clays, could also give rise to their higher negative exchange charge in view of the possibility (Jackson, 1963) that Al for Si substitution is a characteristic feature of this mineral.

Sample no. 8 is unique in that pH-dependent CEC is not greater than the corresponding reduction in AEC over the same pH range. Persistence of positive charge above pH 7 may explain this, if it is assumed that surface charge reversal (which has been taken above to be responsible for the development of negative charge additional to that already present) is only initiated following the complete neutralization of positive charge. This assumption is energetically feasible when viewed in the context of the deprotonation mechanism by which charge variation with pH takes place. A similar explanation could account for the fact that sample no. 11 develops only half as much negative charge, at high pH, as the mineralogically similar sample no. 17: at pH 9, about 5 me of positive charge/100g persists in the former, whereas in the latter positive charge is neutralized somewhere between pH 7 and pH 8,5.

The effect of pretreatment at pH 10 on electric charges at pH 4 is also shown in Figures 19 and 20 (this feature was not examined in the synthetic gels). In all cases there is a pronounced positive charge hysteresis while negative charge is not significantly affected. Griffith (1974) measured the dissolution of not more than 1,5 me Al/100g by similar treatment of Chilean Dystrandepts (which compare mineralogically with samples 11 and 17), so that removal of positively charged hydroxyalumina is likely to account for very little of the positive charge reduction measured here. The absence of pH-dependent, hysteretic negative charge as measured by the present technique conflicts with the findings of de Villiers and Jackson (1967a), who measured CEC by a technique which incorporated an alcohol washing step. Electrolyte dilution during the

latter was shown by Sumner (1963) to effect the reduction of measured positive and negative charges in approximately equal amounts, signifying mutual charge neutralization through expansion of oppositely-charged electric double layers. Hence any (hysteretic) reduction in positive charge would result in a corresponding increase in measured CEC, to an extent dependent on the degree of mutual charge neutralization during washing. The fact that hysteresis is due exclusively to reduction in positive charge has not, to the best of the author's knowledge, been previously established. A mechanism to account for this behaviour is proposed later.

Measured exchange charge of the gels (Fig. 21) also depends to a large extent on technique. Van Reeuwijk and de Villiers (1970), while measuring simultaneous CEC and AEC for a natural allophane, only recorded either a positive or negative charge (depending on pH and chemical composition) for similar synthetic aluminosilica gels. The technique used by these authors involved an alcohol washing step following saturation with KCl, after which replacement was effected with $CaCl_2$. Specific retention effects (van Reeuwijk & de Villiers, 1968) and mutual neutralization of some positive and negative charge (Sumner, 1961) would account for the very much lower CEC values which they measured than those determined here (Fig. 21).

It has been suggested* that a distance parameter is operative in determining the extent to which positive and negative charges can be measured separately. Calculation of the average distance between charges at different pH levels (Table 19) reveals that, under the majority of conditions, interaction between surface charges of opposite sign will be greater in the synthetic gels than in the natural allophanes, and very much greater than in the Oxisol clays. For example, the presence of a small amount of positive charge in gel II (41% $Al_2O_3/Al_2O_3 + SiO_2$) might escape detection (through Coulombic attraction of Cl ions) owing to interaction with crowded negative surface charges. The latter, in addition, effect a slight negative adsorption of chloride (up to 5 me/100g - Fig. 21)†, which to a large extent will also be governed by the magnitude of negative surface charge density. It is interesting to note that average spatial separation of surface charges (Table 19) appears to be a good criterion for differentiating the groups of colloidal materials under study herein.

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* M. E. Sumner - personal communication.

† At high pH values, negative adsorption of Cl by the soil clays was also observed (seldom exceeding 0,5 me/100g). However, since ion exchange capacity values are based on oven-dry (110C) weights of the exchanger, some of the measured negative adsorption may well arise through error involved in the assumption that adsorbed water, driven off by drying, participates as normal solvent water during the exchange process (Wada & Harada, 1969; see also section 1.4.5.5). For this reason little attention has been paid to negative adsorption values.

TABLE 19. Calculated average distance between surface charges at different pH values*

Sample		pH 4			pH 7	pH 8 - 10
		Negative charges	Positive charges	All charges	Negative charges	Negative charges
		Average separation (A)				
Natal Oxisol clays	2	21	39	18	16	13
	3	17	29	15	16	13
	4	23	36	19	17	13
	5	25	30	19	21	16
	6	21	46	19	13	10
	7	24	33	20	18	14
Kraznozem	8	75	18	18	39	25
Latosol Roxo	18	35	22	18	24	18
Allophanes	11	36	14	13	19	11
	17	39	15	14	17	8
Aluminosilica gels	II	8	-	8	6	5
	III	16	24	13	10	6
	IV	20	10	9	12	6

* Based on surface charge density (surface area by EGME adsorption - Chapter I).
Average distance between charges $= \sqrt{\frac{167}{x}}$ A ,

where x = surface charge density (me/cm^2) ,
taking 1 me = 6×10^{20} units of charge.

3.3.2 Effect of chemical pretreatments

It was possible to normalize the effects of chemical pretreatments with respect to pH by measuring the pH of the final 0,05N KCl wash and plotting measured positive and negative charges in relation to those, at the same pH, which had not been affected by any of the pretreatments concerned (Figs. 19 & 20). For the gels, pretreatment effects are plotted as a function of chemical composition (Fig. 21).

Pretreatment with phosphate (2000 mg P as KH_2PO_4/100g) results in (i) a substantial neutralization of positive charge and (ii) the development of a considerably larger component of negative charge. The increase in CEC following P treatment is a well-known phenomenon (de Haan, 1965; van Reeuwijk, 1967; Schalscha, Pratt, Kinjo & Amar A. 1972b; Griffith, 1974). It would account for the molecular adsorption mechanism (Wada, 1959; Cloos et al., 1968)

suggested to explain the simultaneous uptake of large amounts of K following P adsorption from KH_2PO_4 solutions. The increase in net negative charge following P adsorption implies that phosphate is chemisorbed by the solid phase irrespective of positive surface charge density, although where the latter is large the effect will be correspondingly greater.

Pyrophosphate treatment results in neutralization of positive charge and a dramatic increase in negative charge. Despite the loss of up to 2% organic-complexed alumina (Chapter I) a net gain in weight was measured for some of the clays (results not shown), indicating chemisorption of highly charged pyrophosphate anions. This would account for the effectiveness of pyrophosphate as a soil dispersant.

Removal of amorphous sesquioxide from the Oxisol clays (2 to 7% - Chapter I) eliminates positive charge but does not alter CEC greatly (chemisorption of oxalate anions would account for increased CEC), which suggests that charge interaction under the conditions of measurement is minimal. A relatively much higher CEC increase in samples 11 and 17 corresponds with the quantitative removal of sesquioxidic allophane (the synthetic gels were completely dissolved by this treatment) leaving a highly-charged residue. The elimination of large positive charge, and hence interaction effects, may also have contributed to the higher CEC measured.

CDB reagent dissolved the positively-charged sesquioxidic component. The net increase in negative charge over and above that which may have arisen from elimination of charge neutralization effects is again attributed to chemisorption, in this case of citrate and possibly also of $S_2O_4^{=}$.

Sesquential CDB - Na_2CO_3 treatment results in a CEC increase of similar magnitude to that induced by pyrophosphate in the Oxisol clays. In many cases the effect is little greater than that brought about by CDB alone. On the other hand, the net effect of 5% Na_2CO_3 treatment of the allophanes and gels is considerably greater than that of any other pretreatment. The reason for this behaviour is not clear. It is possible that whereas CDB pretreatment leaves a crystalline phyllosilicate residue in the Oxisol clays, there is sufficient residual amorphous hydroxyalumina in the allophanes and gels to cause additional CEC increase either through charge reversal on aluminohydroxyhydronium edge groups (discussed earlier), or through chemisorption of carbonate anions. However, the former effect has been shown to be fully reversible (section 4.3.1). The most likely factor responsible for CEC increase after CDB-Na_2CO_3 treatment is the removal of large amounts of relatively sesquioxidic material, leaving a residue with high negative charge (see Table 20). The implications of this are discussed below.

3.3.3 Similarities between allophane and aluminosilica gels

Recent proposals for a model system for allophane (Cloos et al., 1969; van Reeuwijk & de Villiers, 1970) have been based on the similarity in behaviour between natural allophanes and synthetic amorphous coprecipitates of silica and alumina. De Villiers (1971) has outlined the essential differences between the two systems, which arise mainly from the method of gel preparation. The two models are identical in their salient features, namely, that the CEC of allophane arises through isomorphous substitution of Al for Si in a tetrahedral framework, and that discreet positively-charged coatings of polymeric hydroxy-Al in octahedral co-ordination perform a charge balancing function, through Coulombic association with the negatively charged aluminosilicate surface. At high alumina contents (greater than about 80% $Al_2O_3/Al_2O_3 + SiO_2$) a demixing of alumina to form a separate crystalline phase (trihydrate, or monohydrate plus trihydrate) takes place.

Van Reeuwijk and de Villiers (1970) proposed, on the basis of CEC evidence, a maximum of one ^{IV}Al to every 3 Si in tetrahedral co-ordination. However, Cloos et al. (1969) showed, using X-ray fluorescence measurements, that the $^{IV}Al/Si$ ratio increases with total alumina content to a maximum value of about 1,0 at a composition corresponding to that at which a crystalline phase demixes (in the vicinity of 80% $Al_2O_3/Al_2O_3 + SiO_2$). This corresponds to 50 per cent Al for Si substitution in a tetrahedral framework, which apparently (Eitel, 1964; p. 20) is also possible in feldspar. According to Lai and Swindale (1969), other workers (Houng, Uehara & Sherman, 1966) have found a CEC maximum for aluminosilica gels to occur at 42% $Al_2O_3/Al_2O_3 + SiO_2$, while it was suggested that the amount of tetrahedral Al can be as high as 62% Al_2O_3.

Implicit in the model proposed by van Reeuwijk and de Villiers (1970) is that once the maximum tetrahedral Al content of the gel series has been reached, additional alumina takes the form of positively-charged coatings on the aluminosilicate surface. Assuming, for the technique used here, that (i) full resolution of measured positive and negative charge is obtained, and (ii) that maximum positive charge is developed at pH 4 (i.e. no further conversion of hydroxyl to aluminohydronium groups is possible), then it could be inferred from Figure 21 that maximum tetrahedral Al content occurs at a composition corresponding to 45% $Al_2O_3/Al_2O_3 + SiO_2$, after which development of positive charge corresponds to the appearance of a separate hydroxyalumina phase. In the salt-rich environment in which these gels were synthesized, positively-charged hydroxyalumina would not be required in a charge-balancing capacity, so that all the Al up to this point would presumably take on fourfold co-ordination in combination with silica.

As a result of these considerations, the maximally substituted aluminosilicate phase has the empirical formula, $K^{+}\left[SiAlO_4\right]^{-}.H_2O^{*}$, which has a calculated theoretical CEC of 565 me/100g, and corresponds to the maximum $^{IV}Al/Si$ ratio of 1,0 measured by Cloos et al. (1969). By following the same line of argument as that used by de Villiers (1971), it can be shown that in the system studied by Cloos et al. (1969) maximum 1 : 1 substitution of Al for Si will only occur at a composition corresponding to 90% $Al_2O_3/Al_2O_3 + SiO_2$, if the average charge per polymer Al is unity and protons are not available for charge-balancing. Significantly, X-ray fluorescence measurements by the latter authors indicated that this stage was reached for $Al_2O_3/Al_2O_3 + SiO_2$ = 80%. A slightly lower positive charge per unit Al and/or the presence of some protons in a charge-balancing role would lead to a closer matching of the observed results with those predicted here.

Gel II (41% $Al_2O_3/Al_2O_3 + SiO_2$) has a CEC close to 350 me/100g at pH 10 (Fig. 21), which is considerably higher than that predicted by the model of van Reeuwijk and de Villiers (1970). On the other hand, corresponding interpolated CEC of a 45% gel (Fig. 21) would be 310 me/100g, which is much lower than the theoretical value of 565 me/100g predicted for the situation (above) whereby all the Al is in fourfold co-ordination.

TABLE 20. Dissolution of SiO_2 and Al_2O_3 from allophanes and aluminosilica gels by sequential CDB-5% Na_2CO_3 treatment‡

Sample		Initial composition $Al_2O_3/Al_2O_3 + SiO_2$ (%)	Fraction removed		Residue composition $Al_2O_3/Al_2O_3 + SiO_2$ (%)
			$SiO_2 + Al_2O_3$ (%)	SiO_2/Al_2O_3 (molar)	
Allophanes	11	70	51*	0,35	45†
	17	71	49*	0,30	48†
Gels	II	41	25	1,07	33
	III	53	40	0,43	29
	IV	65	45	0,22	35

* Based on allophane content (80 and 63% in 11 and 17 respectively).

† Composition of residual allophane.

‡ Calculated from data in Chapter I.

However, sequential CDB-Na_2CO_3 treatment of the gels leaves residues having CEC between 480 and 520 me/100g (Fig. 21). The treatment

* Allocation of one H_2O is supported by a TGA weight loss of 13% (Fig. 14 - Chapter I) which corresponds to H_2O = 1,1 in this formula.

dissolves a large amount of material of relatively low molar SiO_2/Al_2O_3 ratio, while residue composition ranges from 29 to 35% $Al_2O_3/Al_2O_3 + SiO_2$ (Table 20). These results are consistent with the partial dissolution of an aluminosilicate phase and therefore with a concomitant loss of negative charge. Viewed in this context, a CEC_{max} of 565 me/100g (for the formula $K^+[SiAlO_4]^-.H_2O$) would not seem unrealistic.

It is not certain why conventional pH adjustment does not permit measurement of CEC approaching this value in magnitude. Harsh alkaline treatment may result in further deprotonation of hydroxyl groups (oxalation - Bailar, 1956) which would generate considerable additional negative charge. Another uncertainty arises from the fact that at pH 4,7 and 10, negative charge of gel II exceeds that (albeit through interpolation) of the 45% gel. A possible explanation may be in the differential susceptibility of silanol, Al-OH and Al-OH_2 groups, and of ^{IV}Al-OH_2 type sites (Fieldes & Schofield, 1960), to deprotonation. Clearly, the situation demands further investigation.

TABLE 21. Comparison of predicted and measured CEC and AEC of allophane in volcanic ash soil clays (samples 11 and 17)

Pretreatment	Sample	me/100g			
		Predicted*		Measured†	
		CEC	AEC	CEC	AEC
pH 4	11 17	16	80	8 9	48 50
pH 7	11 17	30	12	25 43	24 6
pH 10	11 17	160	0	80 198	9 0
2000 mg P/100g	11 17	45	0	25 44	0
Pyrophosphate	11 17	190	0	140 257	0
CDB	11 17	210	0	95 171	0
CDB + 5% Na_2CO_3	11 17	500	0	236 420	0

* From Fig. 21, on the basis of a composition corresponding to 70% $Al_2O_3/Al_2O_3 + SiO_2$.

† Calculated as me/100g allophane (80% & 63% in samples 11 and 17 respectively)

In view of the similarities observed in Chapter II between the chemical behaviour of the allophanes and that predicted from reactivity functions for the aluminosilica gels, it was decided to extend the basis for comparison to surface charge characteristics. In Table 21, approximate CEC and AEC predicted from Figure 21 for samples 11 and 17 are compared with values actually measured, the latter being recalculated on the basis of allophane content (Chapter I). There is a good correlation between predicted and measured values, particularly in the case of sample no. 17. A possible reason why the measured CEC of sample no. 11 is consistently lower than that predicted may be that it has a relatively high isolectric point (section 4.3.1). Further, the "non-allophanic" component in these clays will contribute, either positively or by dilution, to the actual charges measured. The most important constituents in this respect are organic matter (Aomine & Egashira, 1968), chloritized 2 : 1 layer silicates (Chichester, Harward & Youngberg, 1970; Chapter II) and imogolite (Jenne, 1972). It is not known to what extent imogolite is dissolved by acid ammonium oxalate during quantitative extraction of allophane. Another important factor militating against close matching is the difficulty of normalizing the comparison with respect to pH. Considering these limitations, predicted and measured exchange charges in Table 21 are of surprisingly similar order.

3.3.4 Proposed mechanism for exchange charge hysteresis

Earlier it was noted that hysteretic (i.e. incompletely reversible) pH-dependent net negative charge arises exclusively through alteration of the status of positive charge, while negative exchange charge <u>per se</u> is unaffected when subjected to cyclic pH changes. Pretreatment with KH_2PO_4 , on the other hand, reduced AEC and simultaneously increased CEC. In terms of the mechanism outlined below, the difference between these two effects is considered to be one of degree rather than kind.

A two-part mechanism is proposed for pH-dependent, positive exchange charge hysteresis:

(i) Increasing pH induces deprotonation of positively charged sites of the $M\text{-}OH_2^{0,5+}$ type (M = Al or Fe), resulting in reduction of positive charge and an increase in negative charge. The latter will exceed the decrease in AEC to an extent governed by the proportion of positively-charged sites which are of sufficiently close separation from negatively-charged sites as to escape detection by measurement of anion exchange capacity (c.f. distance parameter considerations - section 4.3.1). This means that pH-dependent CEC arises both from unblocking of permanent negative

charge and through charge reversal of the type $M\text{-}OH_2^{0,5+} \longrightarrow M\text{-}OH^{0,5-}$. When the pH is lowered, Coulombic attraction between protons and negatively charged sites induces the preferential reprotonation of neutralized functional groups closely associated with these sites, i.e. those groups which, at acid pH, were responsible for the non-measurable component of positive charge and for the blocking of permanent negative charge. Functional groups at a greater distance from negatively charged sites are envisaged as being relatively poorer proton acceptors, owing to the absence of the Coulombic induction required for complete reprotonation within a relatively short period of equilibration. This will result in AEC hysteresis.

(ii) Sites with large positive charge per unit Al (or Fe) of reactive sesquioxide may Coulombically adsorb OH ions as the pH is raised, i.e. charge variation may arise through hydroxyl adsorption rather than by depronation. At high pH, edge sites with low positive charge may also take up hydroxyl ions in a similar manner. However, at the latter sites a net negative charge will result. A reduction in pH would favour rapid desorption of OH from sites of low positive charge, whereas some OH ions at the former sites will remain fixed by strong Coulombic attraction. This would account for full reversibility of pH-dependent negative charge and only partial (or slowly reversible) positive charge.

In the presence of dilute electrolyte (0,05N KCl), the competitive effects of Cl would probably reduce the significance of the second mechanism, although de Haan (1965) has suggested the possibility of OH uptake at high pH in a manner similar to the adsorption of silicate or phosphate.

The much stronger affinity of phosphate for edge Al sites would account for the simultaneous increase in CEC due to minimal desorption from sites at which net negative charge has developed. Acid buffer washings of the kind used by de Villiers and Jackson (1967a) for pH adjustment will accelerate the reversibility of both processes (i) and (ii). Both are considered to be reaction rate phenomena, implying that pH-dependent exchange charge hysteresis does not constitute a permanent modification of sesquioxidic soil clay surfaces.

3.4 Conclusions

Under the dystrophic conditions commonly prevailing in acid soils, a dilute matrix solution will result in the mutual neutralization of large amounts of positive and negative charge. Consequently the capacity of such soils to retain cationic plant nutrients is severely curtailed.

Measurement of electric charges by ion exchange has limitations. Use of dilute (0,05N) concentrations of index ions may result in some residual interaction between positive and negative charges which will consequently escape detection as exchange charge. However, higher index ion concentrations often give rise to non-Coulombic adsorption effects and hence overestimation of exchange charge. Further experimentation with technique is therefore warranted.

Although positive charge and large pH-dependent net negative charge in allophanic clays can be attributed to the presence, in large amounts, of polymeric hydroxyalumina associated with a negatively-charged amorphous aluminosilicate phase, in Oxisols hydroxy-Fe compounds may also be responsible for these properties.

Variation of net negative charge with pH arising through deprotonation of edge-hydronium groups comprises unblocking of permanent negative charge as well as charge sign reversal through the conversion of hydronium to edge-hydroxyl. Hysteretic effects are considered to originate at sites lacking Coulombic induction from negatively-charged sites for complete reprotonation of hydroxyls. There is also the possibility that OH ion adsorption at sites of low positive surface charge density contribute to pH functional negative charge, while strong retention at high positive charge density sites gives rise to AEC hysteresis. CEC is fully reversible during cyclic pH adjustment by titration with strong acid or base.

Evidence is presented in favour of a model system for allophane in which a maximum tetrahedral Al content in the aluminosilicate phase is possible for a composition corresponding to 45% $Al_2O_3/Al_2O_3 + SiO_2$, provided that there is a sufficiency of basic cations for charge-balancing during synthesis (neogenesis). In the absence of the latter, positively-charged polymeric hydroxyalumina cations balance negative charge developed through incorporation of tetrahedral Al into the aluminosilicate phase, and maximum substitution of 1 Al : 1 Si is only attained at a composition corresponding to about 80% $Al_2O_3/Al_2O_3 + SiO_2$. Formation of allophane in nature probably proceeds along a pathway intermediate between these two extremes. To a large extent this would explain why measured exchange charge is often at variance with that predicted on the basis of behaviour of synthetic aluminosilica gels coprecipitated from solutions of simple inorganic salts.

The effect of chemical pretreatments on exchange charge provides a simple explanation for the efficiency of citrate, oxalate, phosphatic and alkaline solutions as soil dispersants. The presence of large net positive charge at acid pH values would explain why allophanic soils are very often more efficiently dispersed by lowering rather than raising the pH (Jackson, 1956; Russell, McHardy & Frazer, 1969). It would also account for the high yield of water-dispersible clay obtained (Chapter I) from the Kraznozem (sample no. 8), which has large net positive charge under field conditions. On the other hand, the well-known physical stability (low erosion hazard, high permeability and porosity) of Natal Oxisol B horizons can be attributed to the presence of approximately equivalent amounts of interacting positive and negative charges under field conditions, resulting in a flocculated, well-aggregated colloidal fraction. Heavy dressings of lime, phosphate or organic manures are therefore likely to be detrimental to soil structure.

CHAPTER IV

SOIL SOLUTION COMPOSITION IN SESQUIOXIDIC SOILS

4.1 Introduction

The mineralogical nature and surface characteristics of soil colloids will influence soil-plant chemical relationships indirectly, through control of soil solution composition. At the same time, a knowledge of soil solution composition under conditions of equilibrium provides useful indications of prevailing pedogenetic processes.

A characteristically high capacity for immobilizing applied phosphate, and the common presence of toxic levels of exchangeable aluminium, are two properties of acid, highly-weathered Natal soils which have received considerable attention in the past (le Roux & de Villiers, 1965; Skeen & Sumner, 1965; Easton, 1970; Reeve & Sumner, 1970a & b, 1971; Dekkers, 1971; Thompson, 1972).

Phosphorus adsorption by sesquioxidic soils is a well-known and reasonably well-understood phenomenon (Chapter II). One particularly interesting aspect is that a reciprocal relationship appears to exist between soluble silica and soluble phosphorus in soils, that is, silica and phosphate compete for adsorption sites (de Haan, 1965; Roy, 1969; Easton, 1970; Griffith, 1974). According to D'Hoore and Coulter (1972), the nature of this interaction, which is often erroneously attributed to anion exchange, is not well known, except that it probably takes place at adsorption sites on free sesquioxides. Some earlier conclusions (McKeague & Cline, 1963) indicated little or no relationship between soluble silica and clay mineral suite, and that the behaviour of silica in soils is controlled by a pH-dependent adsorption mechanism (Beckwith & Reeve, 1963; Jones and Handreck, 1963). However, more recent work (Kittrick, 1969; Weaver, Jackson & Syers, 1971) has established the important extent to which clay mineral type governs the level of silica concentration in the soil solution.

The nature of the relationship between soluble or exchangeable aluminium and other soil properties is not exactly clear. Nevertheless, a first prerequisite to the existence of exchangeable Al in soils seems to be an acid pH - usually less than 5,0 to 5,6 (Ayres, Hagihara & Stanford, 1965; Pionke & Corey, 1967; Kamprath, 1972). Thereafter the role of pH in governing levels of exchangeable Al appears to become secondary to that of net CEC and degree of base saturation (Reeve & Sumner, 1971). Net CEC, insofar as this is affected by the extent of interaction between oppositely-charged electric double layers,

will depend to a large degree on soil solution composition (Chapter III). The latter will also govern the extent to which the exchange complex is occupied by basic cations. Furthermore, clay mineral type can exert a significant influence on soil pH (van Breemen & Wielemaker, 1974a & b).

The present study was motivated by the knowledge that clay minerals in soil exert a strong influence on soil solution composition (Garrels & Christ, 1965; Kittrick, 1969).

In view of these considerations, the possibility exists that soil properties such as phosphorus adsorption (insofar as this is affected by phosphorus-silicon interaction) and Al toxicity can be related, indirectly, to the mineralogical nature of soil colloids. The thermodynamic approach to mineral solubility (Garrels & Christ, 1965; Kittrick, 1969; Weaver, Jackson & Syers, 1971) is particularly valuable for establishing such relationships. Basically, it embodies the concept that soil solution composition will be governed, under conditions of chemical equilibrium, by the mineralogical nature of the solid phase and vice versa. The system can be described in terms of thermodynamic parameters pertaining to the various solid-solution reactions which take place. Application of this approach to soil studies can be performed in a relatively simple fashion in the laboratory (Weaver et al., 1971).

The objective of this chapter is therefore to examine possible relationships between the clay mineralogy of sesquioxidic soils and soil solution composition, insofar as the latter relates to exchangeable Al status and phosphorus-silicon interaction. The implications which soil-solution equilibria have for interpretations of pedogenesis are also considered.

4.2 Materials and methods

Soils investigated were the same as those on which clay mineralogical analyses were carried out (Chapter I). Samples were air-dried and ground to pass a 2 mm screen. Three synthetic aluminosilica gels (K-saturated and freeze-dried - Chapter I) of composition corresponding to 22%, 41% and 65% $Al_2O_3/Al_2O_3 + SiO_2$ (hereinafter referred to as gels I, II and IV respectively) were included for comparison in one experiment.

Organic carbon content was estimated by wet oxidation (Walkley, 1947). Mechanical analysis was conducted by hydrometer method after H_2O_2-treatment and NaOH dispersion. Soil pH was determined with a glass electrode immersed in the supernatant of a suspension (soil : solution :: 1 : 2,5) of soil in distilled water or 1N KCl equilibrated for one hour.

Exchangeable Al was determined by successive 0,2N NH_4Cl extractions (Skeen & Sumner, 1965). Exchangeable bases were estimated from five 0,2N NH_4Cl extractions. CEC and AEC were determined after 3 1N KCl washings by the weighing technique using 0,05N KCl with 1N NH_4SO_4 as replacing electrolyte (Chapter III). The pH of the final 0,05N KCl washing solution was measured at a soil : solution ratio of 1 : 25 after 30 min equilibration. Al was determined by the ferron method* (Davenport, 1949), Ca and Mg by atomic absorption, K and Na by emission flame photometry and Cl using an Aminco-Cotlove chloride titrator.

Adsorption of P and Si was measured by equilibrating 2 g soil samples with 50 ml of sodium metasilicate or KH_2PO_4 solutions in polypropylene centrifuge tubes on an end-over-end shaker for 24h at room temperature. Solutions of P and Si were made 0,001M with respect to $CaCl_2$. The effect of Si pretreatment on P adsorption was tested by sequential equilibrations with Si then P solutions performed in the same manner. A control washing with 0,001M $CaCl_2$ was used to estimate water-soluble silica. P and Si were measured in the supernatants after centrifugation at 2200 r.p.m. for 30 min by method I of Jackson (1958; p. 141) and by the molybdenum blue method (Weaver et al., 1968), respectively.

The composition of matrix solutions equilibrated with selected soils and gels was determined as follows: 20 g air-dry samples (10 g gel) were equilibrated with 200 ml (100 ml for gels) of distilled, deionized water in 200 ml polypropylene conical flasks at 25 ± 1C for 40 days†. The suspensions were periodically flushed with moist air to minimize anaerobic raductive processes (Weaver et al., 1971). A 50 ml aliquot from each suspension was then centrifuged at 14 000 r.p.m. for 25 min. Supernatants were analysed for Al, Si, Ca, Mg, Na and K‡, and pH was measured in the original suspension. The activity of H_4SiO_4 was taken to be equal to concentration (Siever, 1957). Activities of other ions were calculated using the Debye-Hückel expression, with constants given by Garrels and Christ (1965; pp. 61 - 62). Ionic strengths were calculated on the assumption that only HCO_3^- and/or Cl^- were present in significant concentrations (Weaver et al., 1971).

The same suspensions were then equilibrated for a further 40 days, after volume adjustment and acidification with HCl to about pH 3, and the analyses repeated.

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* Absorbance was measured in 4 cm cuvettes to improve sensitivity.

† Weaver et al. (1971) observed no significant change in similar matrix solution compositions after 30 days equilibration.

‡ No Fe was detected in either original or acidified matrix solutions by ferron colorimetric analysis.

4.3 Results and discussion

4.3.1 Factors governing levels of exchangeable aluminium

Some chemical properties of the soil collection are shown in Table 22. In the Natal Oxisols (samples 2 - 7), 1N KCl substantially depresses pH relative to that measured in water, which is consistent with the presence of net negative charge. Soils with net positive charge (samples 8, 11, 17) or very low net negative charge (no. 18) exhibit little difference in pH values measured in water and KCl, as would be expected (van Raij & Peech, 1972). The Natal soil with the lowest net negative charge (no. 7) exhibits the smallest difference between the two pH values.

Exchangeable Al is present only in the Natal Oxisols. Its absence in the volcanic-ash soils and the Oxisols from Australia and Brazil can be attributed to the higher pH of the latter group, as measured in KCl* (Table 22). The sum of exchangeable Al and exchangeable bases is very close to the value for net CEC, in agreement with the findings of le Roux and de Villiers (1966) and Reeve and Sumner (1971). That net CEC values are consistently slightly higher than total exchangeable cations does not necessarily indicate that the balance of net negative exchange charge is occupied by hydrogen ions, since the pH at which CEC and AEC were measured (last column, Table 22) may have been slightly higher (with accordingly higher net CEC - Chapter III) than that prevailing during 0,2N NH_4Cl extraction.

The very high level of exchangeable Al in sample no. 3 is related to the high net CEC of this soil, and confirms the hypothesis (Reeve & Sumner, 1971) that net CEC is a dominant factor in controlling exchangeable Al levels in acid soils. The much higher CEC of this soil relative to those of the other Natal Oxisols could well be due to the abundance of halloysite in the clay fraction (Chapter I). Jackson (1963) has suggested that tetrahedral Al substitution may be common in halloysite. This would result in a higher negative charge than is generally encountered in minerals of the kaolin group.

Distribution of charges in samples 8, 18, 11 and 17 is generally consistent with that found for natural clay fractions (Chapter III), although comparison is limited owing to variable clay content and to the fact that such soils are generally difficult to disperse efficiently using conventional treatments for

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* Surprisingly, pH (H_2O) values failed to provide a similar indication. A possible explanation for this may lie in the variable influence which positive and negative charges present in these soils will exert on liquid junction potential, manifested through the suspension effect (Woodruff, 1965). The latter effect is eliminated by measuring pH in an electrolyte (e.g. KCl) suspension.

TABLE 22. Chemical properties of the soil collection

Soil	%		pH*		me/100g						pH** of CEC, AEC determination
	Organic C	Clay	H_2O	N KCl	0,2N NH_4Cl exchangeable:			CEC	AEC	Net charge	
					Bases†	Al	Total cations				
Farmhill 2	1,65	58	5,7	4,2	1,0	3,2	4,2	7,1	1,8	-5,3	4,8
Farmhill 3	0,18	60	5,3	4,1	1,9	11,1	13,0	15,5	1,9	-13,6	4,8
Farmhill 4	1,32	62	5,7	4,3	1,4	1,1	2,5	4,5	0,8	-3,7	4,8
Balmoral 5	0,12	68	5,6	4,2	0,8	1,8	2,6	6,1	2,4	-3,7	4,8
Farningham 6	3,06	35	4,7	4,0	1,3	1,9	3,2	5,7	0,2	-5,5	4,9
Farningham 7	0,61	47	4,5	4,3	0,8	0,8	1,6	3,9	1,3	-2,6	4,9
Kraznozem 8	0,49	55	5,7	5,6	0,5	0,0 ♭	0,5	0,7	4,9	+4,2	5,1
Latosol Roxo 18	0,57	50	5,6	5,9	1,3	0,0 ♭	1,3	3,0	1,5	-1,5	5,4
Kodonbaru 11	1,24	15‡	5,6	5,5	0,7	0,0 ♭	0,7	5,3	5,9	+0,6	5,1
Tirau 17	0,50	20♮	5,5	5,3	0,9	0,0 ♭	0,9	2,0	8,9	+6,9	5,9

* 1 : 2,5 :: soil : solution. ** 1 : 25 :: soil : 0,05N KCl. † Ca + Mg + Na + K.

‡ Wada and Aomine (1973). ♮ N.Z. Soil Bureau (1968).

♭ It should be noted that small (less than 0,01 me/100g) and relatively constant amounts of Al were removed with each 0,2N NH_4Cl extraction. However, by definition (Skeen & Sumner, 1965) this is not exchangeable Al.

this purpose. The net positive charge of the allophanic soils (11 and 17), measured in unbuffered electrolyte, is in agreement with previous findings (Fieldes & Schofield, 1960; Aomine & Egashira, 1968) for similar soils. It would certainly account (along with pH) for the absence of exchangeable Al. Interestingly, where there is net positive charge (samples 8, 11, 17), total exchangeable cations do not exceed a level of 0,9 me/100g. The latter figure provides an indirect measure of the extent to which positive and negative charges interact under field conditions.

4.3.2 Phosphorus-silicon relationships

Results presented in Table 23 show that P is adsorbed considerably more strongly than silica. A relative measure of P adsorption capacity of the clay fraction of these soils has already been obtained (Chapter II). It is noteworthy that silica adsorption capacity is greatest in sample no. 8, which has the lowest soluble silica level. Relatively low Si adsorption by the volcanic-ash soils (comparable to that by the Natal Oxisols) corresponds to their high soluble silica levels. Complexation of sesquioxide adsorption sites in sample no. 6 by organic matter (Table 22) probably accounts for the very low Si adsorption (and lower P retention) by this soil (Moshi, Wild & Greenland, 1974).

Displacement of Si by increasing P applications is shown in Figure 22 (correction was first made for removal of soluble silica). Silica release by the Oxisols is effectively linear with respect to P addition up to the highest level of added P, whereas in the volcanic-ash soils (11 and 17) the quantity of labile (or easily displaced) silica appears to be limited to about 70 µg/g. The reason for this is not clear, since it would be expected that the presence of an amorphous aluminosilicate phase (Chapter I) constitutes a ready source of labile silica. On the other hand, a relatively large amount of silica in samples 3, 5 and 7 is removed by P treatment. Silica is probably adsorbed less strongly at sesquioxide sites in these soils than in the volcanic-ash soils. Complexation of adsorption sites in samples 2, 4 and 6 by organic matter (Table 22; Moshi _et al._, 1974) may account for their low levels of P-replaceable silica. The Kraznozem (no. 8) is considerably more weathered than any of the Natal soils (Chapter I) and a silica deficiency would therefore be expected. It is noteworthy that samples 3, 5 and 7 have reddish chromas while samples 2, 4, 6 (after H_2O_2-treatment), and 8 are yellow (Appendix I)*. Easton (1970)

* In terms of silica status (Fig. 22) sample no. 7 again occupies a position intermediate between the red and yellow soil materials, confirming the view expressed earlier (footnote - p. 71) that this soil is essentially a Griffin-Farningham intergrade.

TABLE 23. Soluble silica and relative response of soils to silica and phosphate added in solution

Soil*	Soluble silica	Si adsorbed		P adsorbed		Effect of Si pretreatment** (625 µg/g)	
		125 µg added/g	625 µg added/g	125 µg added/g	625 µg added/g	Reduction in P adsorption (%)	Increase in equilibrium P concentration (%)
		µg/g					
2	16,3	61,1	385,4	124,5	623,6	0,33	146
3	29,5	47,5	409,7	124,9	623,7	0,10	46
4	16,0	50,9	453,5	124,1	622,1	0,82	176
5	47,9	25,2	453,1	124,9	624,5	0,34	453
6	34,6	2,1	242,4	123,5	608,5	0,78	29
7	28,2	49,8	454,9	123,7	621,0	1,25	169
8	6,3	108,0	578,5	124,9	624,1	0,16	108
11	61,1	53,3	514,2	124,9	624,8	0,01	11
17	68,8	46,3	526,1	124,8	624,5	0,09	20

* Sample no. 18 (Table 22) was not procured until after the completion of this study.

** Si-pretreated soils were centrifuge-washed once with 0,001M $CaCl_2$ prior to equilibration with 50 ml of 25 ppm P solution.

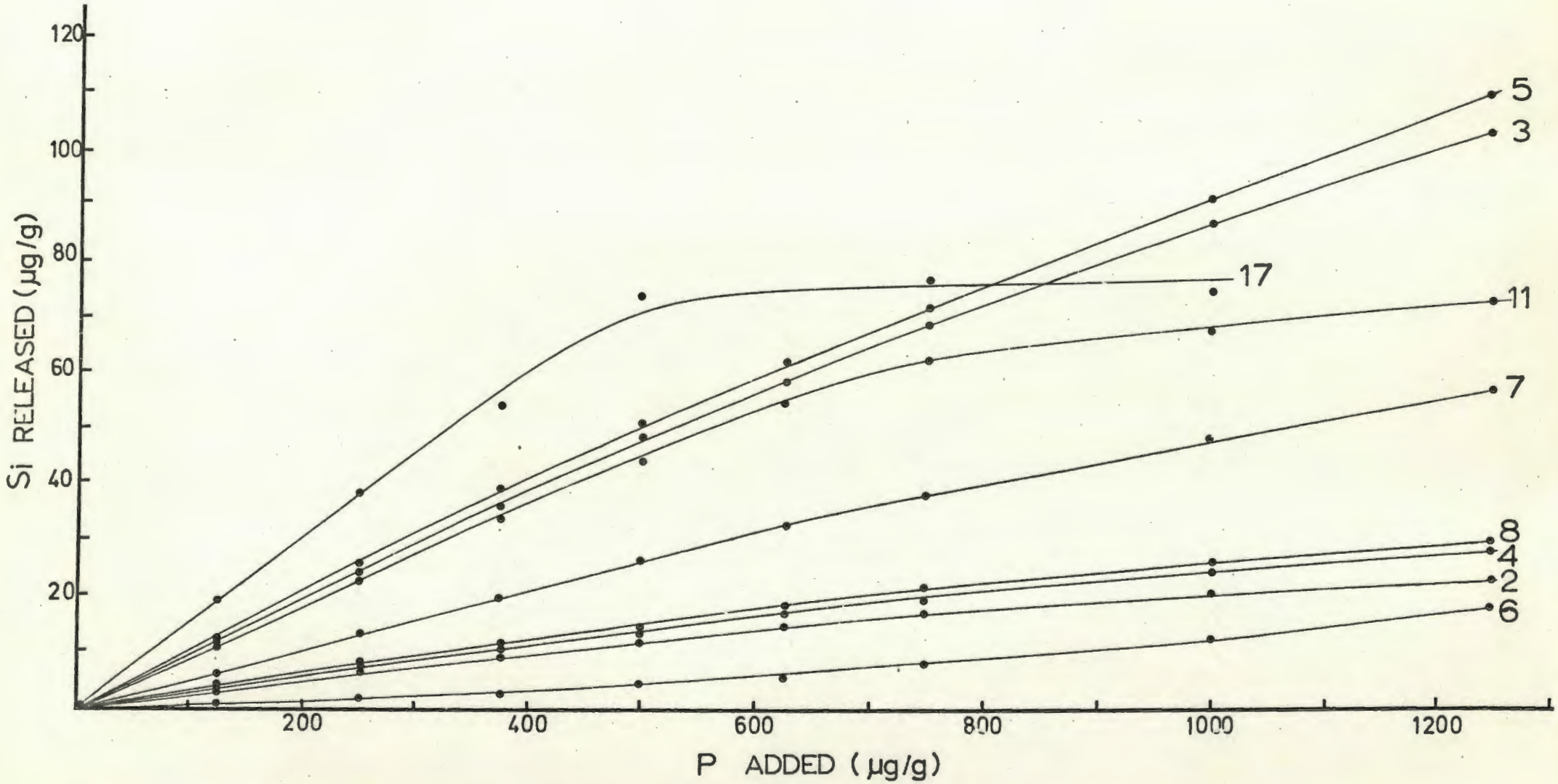

FIGURE 22. Si released by shaking 2 g subsamples of soil with 50 ml KH_2PO_4 solutions of different concentrations. Water-soluble Si values (Table 23) have been subtracted from measured Si values in equilibrated supernatants

found that the yellow B horizon of a Farmhill soil retained significantly more P than the underlying red horizon. Thus differences in Si release following P treatment (Figure 22) may arise from variation in the binding energy with which Si is adsorbed to sesquioxide surfaces.

P adsorption is not reduced significantly by pretreatment with monomeric silica (Table 23). This finding contrasts with that of Easton (1970), who observed a 20 - 100% decrease in P retention following silica pretreatment. The present results can be attributed to a milder Si treatment (25 ppm Si solution), and to the fact that soils were washed with 0,001M $CaCl_2$ prior to equilibration with P. An advantage of mild pretreatment is that its effect will provide some indication of the extent to which naturally soluble silica is likely to compete for P adsorption sites under field conditions. The generally large percentage increase in equilibrium P concentration following Si pretreatment (Table 23) is of more significance for soil-plant relationships than values for reduction in P retention. Very high P adsorption capacity of samples 11 and 17 (Chapter III) would account for the minimal influence of Si pretreatment on P retention by these two soils. In the other soils, added silica did not exceed naturally soluble silica by a factor of more than 10, and a large proportion was probably removed during 0,001M $CaCl_2$ washing. It is therefore inferred that soluble silica levels in the Natal soils are high enough to result in larger concentrations of P in the soil solution than would otherwise be the case after the addition of phosphate. In the Kraznozem and the volcanic-ash soils, levels of naturally soluble silica are unlikely to be high enough to have a similar effect on levels of dissolved P.

4.3.3 Soil solution composition in relation to clay mineralogy

Initially, in order to test for a relationship between soil solution composition and clay mineralogy, the approach of Kittrick (1969, 1971) was adopted. This involves the simultaneous consideration of gibbsite, kaolinite, montmorillonite, and amorphous silica in an aqueous system. The only other colloidal constituents likely to be present in significant quantities are allophane, amorphous hydroxyalumina, free iron oxides, pedogenic aluminous chlorite and halloysite (Chapter I). No iron was detected in equilibrated matrix solutions and its influence on solution composition at equilibrium can be ignored (Kittrick, 1971). Fully-interlayered aluminous chlorite will have a composition corresponding essentially to that of kaolinite. Halloysite is metastable relative to kaolinite (Kittrick, 1969). Hence apart from the minerals considered by Kittrick (1971), only allophane and amorphous alumina require further attention.

The hydrolysis reaction for allophane

$$Al_2O_3.2SiO_2.nH_2O + 6H^+ \rightleftharpoons 2Al^{3+} + 2H_4SiO_4 + (n - 1)H_2O \qquad (1)$$

has a pK value of -10,1 (Reesman & Keller, 1968). Since this formula for allophane corresponds closely to the empirical formula $2\left[AlSiO_4.H_2O\right]^-$ proposed in Chapter III, equation (1) was used to locate the solubility line of allophane with reference to the ordinates $pH - \frac{1}{3}pAl^{3+}$ and pH_4SiO_4 as follows: from equation (1),

$$2 \log Al^{3+} + 2 \log H_4SiO_4 - 6 \log H^+ = \log K = 10,1$$

$$\text{so that} \qquad pH - \tfrac{1}{3}pAl^{3+} = \tfrac{1}{3}pH_4SiO_4 + 1,68 \ . \qquad (2)$$

Equation (2) has the same slope as kaolinite ahd halloysite solubility lines except that the latter have intercepts of 1,1 and 1,7 respectively (Kittrick, 1969). Like halloysite, allophane will therefore be metastable relative to kaolinite.

In practice, the stability of allophane is likely to be modified by the presence of associated amorphous, polymeric hydroxyalumina. Amorphous $Al(OH)_3$ has a solubility line which is described by the equation (Kittrick, 1969)

$$pH - \tfrac{1}{3}pAl^{3+} = 3,2 \ . \qquad (3)$$

However, the basicity of polymeric hydroxyalumina in most sesquoxidic soils is likely to be closer to 2,5 (Chapter I). The value of log K for the reaction

$$Al_6(OH)_{15}^{3+} + 15H^+ \rightleftharpoons 6Al^{3+} + 15H_2O \qquad (4)$$

has been estimated as -36,0 (Richburg & Adams, 1970). Although the hexamer $Al_6(OH)_{15}^{3+}$, which has a basicity of 2,5 , has been considered as a dissolved species (van Breemen & Wielemaker, 1974a), it will be associated Coulombically with negatively-charged aluminosilicate surfaces. Hence as part of the solid phase its activity can be assumed to be unity, so that from equation (4),

$$\log K = 15 \log H^+ - 6 \log Al^{3+} = -36,0$$

$$\text{and} \qquad pH - 0,4pAl^{3+} = 2,4 \ . \qquad (5)$$

This can be compared with the equation for gibbsite,

$$pH - \tfrac{1}{3}pAl^{3+} = 2,7 \ . \qquad (6)$$

While solubility lines represented by (5) and (6) cannot be plotted on the same ordinates, at a fixed pH and pH_4SiO_4 , gibbsite will nevertheless support a higher pAl^{3+} than will $Al_6(OH)_{15}^{3+}$, which means that the hexamer will be less stable than gibbsite*. Mineral stability in the Al_2O_3-SiO_2-H_2O system is therefore not modified by simultaneous consideration of either allophane or amorphous hydroxyalumina.

Analyses of soil matrix solutions are given in Appendix V. Measured pH values after equilibration are given in Table 24. Calculated composition points are plotted relative to mineral solubility lines in a composite stability diagram (Fig. 23). Where a given mineral is the most stable of the group, its solubility line is shown solid. A broken line represents the metastable solubility line of the indicated mineral phase.

Composition points obtained from equilibration of soils† and gels with distilled water (open circles) are somewhat more scattered and remote from expected stability areas than those pertaining to acid equilibrium (solid triangles). This is attributed to three factors: (i) Al concentrations in the former solutions were very low and therefore difficult to measure accurately, (ii) the requirement that pH should be below 5, and preferably between 3 and 4, so as to enable a reliable measurement of soluble Al as monomeric Al^{3+} (Kittrick, 1971) is not met (Table 24), and (iii) the level of dissolved CO_2 will be lower (due to periodic aeration) than that occurring under natural conditions. A reduction in P_{CO_2} increases the equilibrium pH subtended by soil minerals (van Breemen & Wielemaker, 1974b - their Table 1). Acidified suspensions were not aerated during equilibration (the acidity was considered to sufficiently inhibit microbial activity) and dissolved CO_2 levels were therefore probably higher.

For these reasons the discussion will be confined to acidified matrix solution compositions. The montmorillonite stability line (Fig. 23) is based

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* Persistence of the hexamer (or amorphous, polymeric hydroxyalumina in general) as a metastable phase will be governed by a number of colloidal interactions which inhibit crystallization in the pedosphere (de Villiers, 1969). The relative stability of gibbsite is illustrated in practice by the rapidity with which a synthetic hydroxy-Al precipitate transforms to a crystalline product.

† Six soils were selected for this experiment. The Latosol Roxo (no. 18) and Kraznozem (no. 8) are mineralogically very similar (Table 16, Chapter I) and would be expected to subtend similar matrix solution compositions at equilibrium.

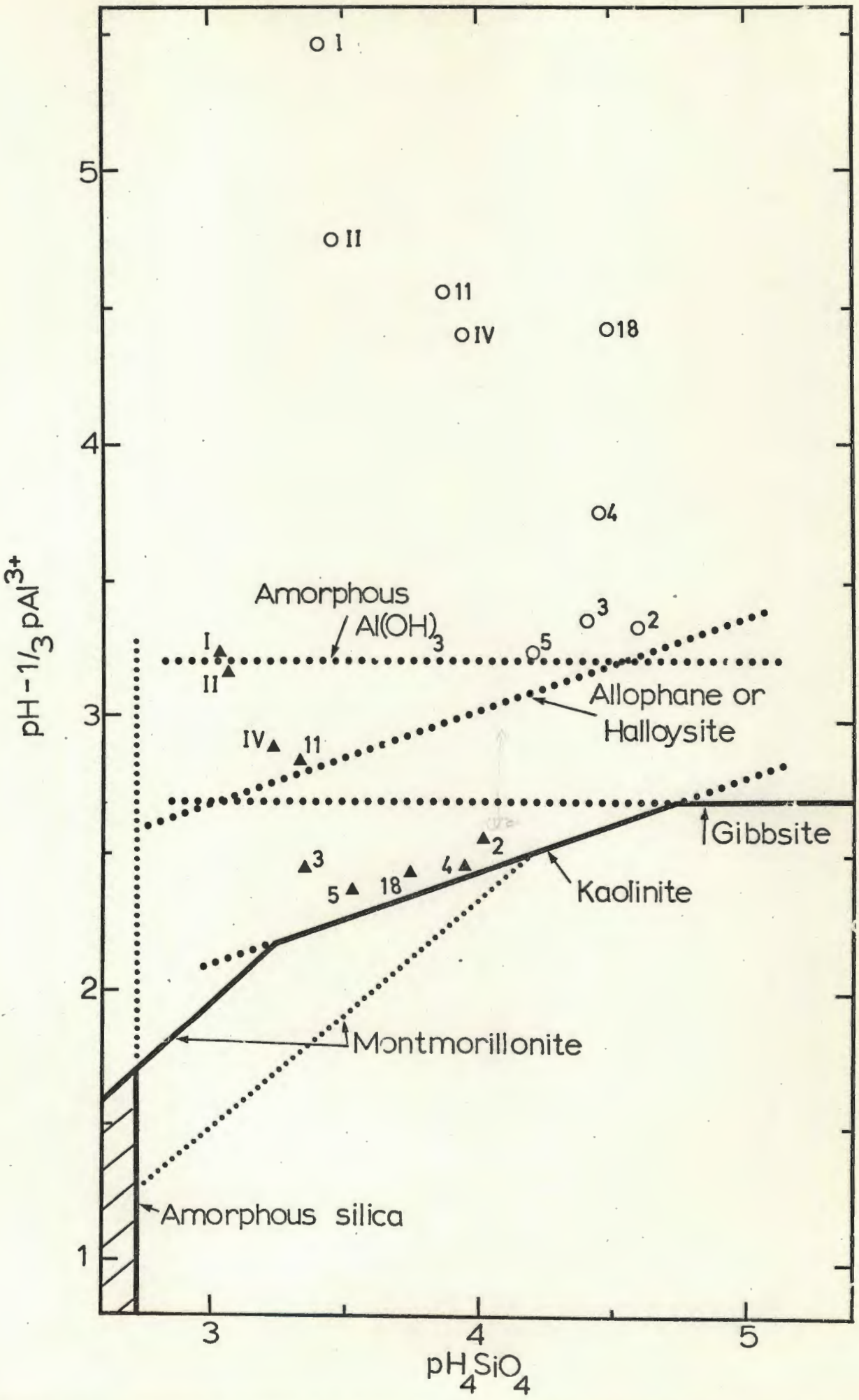

FIGURE 23. Composite stability diagram for selected minerals in the Al_2O_3-SiO_2-H_2O system at 25C and 1 atm, showing composition points for equilibrated soil matrix solutions (O not acidified; ▲acidified)

TABLE 24. Measured pH of soil matrix solutions equilibrated before and after acidification with HCl

Sample		pH after 40 days	
		Water equilibration	Acid equilibration
SOILS	2	5.70	3,59
	3	5,72	3,50
	4	5,68	3,50
	5	5,40	3,43
	11	6,01	3,86
	18	6,12	3,51
GELS	I	7,11	5,00
	II	6,48	4,78
	IV	5,93	4,28

on Kittrick's (1971) Belle Fourche montmorillonite, but with intercept adjustment using a pH of 3,50 and an average pMg^{2+} of 2,25 (as opposed to values of 6 and 3,7 respectively), based on analyses of the soil matrix solutions (Table 24; Appendix V).

Composition points for the Oxisols all lie close to the kaolinite solubility line. The relatively high silica potential of samples 3 and 5 is consistent with their silica status compared with the other soils as indicated in section 4.3.2. Since all these samples contain a mixture of kaolinite and gibbsite, their pH_4SiO_4 values would be expected (Kittrick, 1969) to fall closer to the point at which the respective solubility lines intersect. That they do not indicates that gibbsite in these soils is unstable under conditions of solid-solution equilibrium.

The interpretations for pedogenesis are as follows: a seasonal rainfall fluctuation will result in alternating conditions under which either the soil solution will be supersaturated in silica with respect to gibbsite, or desilication through leaching will push the pH_4SiO_4 beyond a value of 4,73 (Fig. 23) and thus permit gibbsite formation. Nevertheless, it is unlikely that true equilibrium is reached within a period of 40 days, so that with further equilibration a shift of composition points (particularly that of sample 18 which is high in gibbsite) along the kaolinite solubility line towards the kaolinite-gibbsite phase join would be expected.

Evidence for the halloysitic, poorly-crystalline character of the clay fraction in soil no. 3 (Chapter I) is supported by the position of its composition point closer to the halloysite metastability line and further from the kaolinite line than other Oxisol composition points. Conversely, XRD and IR evidence (Chapter I) points to a more crystalline clay fraction in samples 4 and 18. Their composition points occupy a correspondingly closer position to the solubility line for well-crystallized kaolinite (Kittrick, 1969).

The extent to which Oxisol composition points are controlled by polymeric hydroxyalumina is difficult to establish. However, calculated pH - 0,4 pAl^{3+} values for these samples range from 2,17 to 2,34, and so are very close to the metastable line for $Al_6(OH)_{15}^{3+}$ defined by pH - 0,4pAl^{3+} = 2,4. The possible influence of amorphous hydroxyalumina in governing equilibrium aluminium hydroxide potential can therefore not be ruled out.

Composition points for the volcanic-ash soil (no. 11) and the three alumino-silica gels are close to the metastable solubility lines of amorphous $Al(OH)_3$ and allophane-halloysite (Fig. 23). The small difference in composition between gel IV and the allophane of sample no. 11 (Chapter I) is reflected by the close separation of their composition points. They subtend a pH_4SiO_4 at which kaolinite is the most stable mineral of the group. The location of their matrix solution composition points near the allophane-halloysite line is indicative of a partial, metastable equilibrium state (Helgeson, 1968), the persistence of which is governed by kinetic factors. The arguments outlined above to account for ultimate formation of gibbsite in the weathering environment apply equally to this case. It should be noted that gel IV and the clay fraction of soil no. 11 are far more sesquioxidic than the allophane for which the metastable solubility line in Figure 23 was developed. Again, influence of amorphous polymeric hydroxy-alumina is indicated by calculated pH - 0,4 pAl^{3+} values of 2,61 and 2,68, which are close to the value of 2,4 dictated by $Al_6(OH)_{15}^{3+}$ (equation (5)).

The more siliceous gels I and II subtend silica potentials fairly close to that at which amorphous silica precipitates. Their higher equilibrium pH values (Table 24) have probably resulted in a less reliable estimate of aluminium hydroxide potential (for reasons outlined earlier), and no significance is attached to the proximity of their composition points to the metastable amorphous $Al(OH)_3$ solubility line.

4.4 Conclusions

The presence of exchangeable Al in Natal Oxisols and its absence in the Latosol Roxo, Kraznozem and volcanic-ash soils is attributed to two factors. Firstly, in the Natal soils, net CEC is higher at field pH. In the other soils, net positive exchange charge and very low CEC under natural conditions precludes the possibility of Al existing in monomeric, salt-exchangeable form. Secondly, it has been shown elsewhere (van Breemen & Wielemaker, 1974b) that predominance of kaolinite in acid soils results in a more acid (pH 4,5 - 5,5) equilibrium pH value than in soils dominated by gibbsite or allophane, for which maximum buffer intensities commonly lie between pH 5,5 and 6,5. Hence exchangeable Al can be regarded as a transient soil property, depending, for its presence, upon the pH at which the soil mineral assemblage buffers the soil solution, and for its magnitude of expression, upon the distribution of electric charges and the amounts of exchangeable bases present in the soil solution. The latter two factors will also be indirectly governed, to a large extent, by mineralogical composition.

Levels of soluble silica in the Natal Oxisols are probably high enough to exert a favourable control on concentrations of added phosphorus in the soil solution. Higher P retention in volcanic-ash soils and more strongly-weathered Oxisols precludes the possibility of such natural ameliorative effects.

Under conditions of dynamic moisture regime and hence fluctuating silica potential, sesquioxide adsorption sites are likely to be the major factor dictating soluble silica status of sesquioxidic soils at a given point in time. On the other hand, under conditions of, or approaching, chemical equilibrium between the soil solution and the solid phase, control of silica potential by sesquioxidic surfaces will be superseded by the net effect of mineral dissolution reactions.

At equilibrium, kaolinite is the indicated stable mineral (i.e., that which supports the lowest aluminium hydroxide potential at a given silica potential) in matrix solutions of all the soils studied. Persistence of halloysite, allophane and amorphous polymeric hydroxyalumina as partial, metastable equilibrium states is governed by kinetic factors which are beyond the scope of normal laboratory investigation. Where any one of these three phases is present, soil solution composition corresponds closely to that which is predicted theoretically. Formation of gibbsite is contingent upon a seasonal fluctuation in silica potential which alternately favours kaolinite and gibbsite stability. Weathering has proceeded beyond the stage where creation of a stagnant moisture regime would permit the stability of montmorillonite. However, to a large

extent the latter will depend on prevailing concentrations of dissolved CO_2. The importance of P_{CO_2} control in soil-solution equilibria studies of this nature cannot be overemphasized.

GENERAL DISCUSSION

Acid ammonium oxalate is superior to commonly-used alkaline reagents as an extractant for allophane and amorphous sesquioxides in soil clays. This has important consequences.

Firstly, it appears that the commonly large amounts of alkali-extractable 'amorphous' aluminosilicates in Natal Oxisol clays are in fact finely-divided, poorly-crystalline kaolinite and halloysite. Amorphous material as such is present in small quantities (2 - 7%) and would appear to consist mainly of hydroxyalumina in the form of coatings on clay particles and interlayer surfaces of pedogenic aluminous chlorite. In the past, two kinds of allophane have been recognised. The sesquioxidic variety is characterized by a relatively low SiO_2/Al_2O_3 ratio and a high degree of chemical reactivity. Halloysitic allophane has higher SiO_2/Al_2O_3 ratio (similar to that of kandite minerals) and is relatively inert physicochemically. Alkali-extractable aluminosilicates in Natal Oxisols conform to the latter description. The term halloysitic allophane should therefore be considered redundant insofar as it refers to a distinct mineralogical entity in soil.

Secondly, allophane in volcanic-ash soils is more sesquioxidic than it was previously thought to be on the basis of NaOH selective dissolution analysis. Consequently it becomes necessary to revise some existing concepts of clay mineral genesis in volcanic-ash soils. For example, imogolite can no longer be considered as an intermediate phase in the transformation of allophane to gibbsite. On the contrary, formation of imogolite is more likely to proceed following mild resilication of allophane in well-drained environments as a result of thin overburden deposition of fresh ash.

The absence of amorphous aluminosilicates in the clay fraction of Oxisols may be attributed to two factors. Firstly, because of the short-lived existence of allophane in a leaching environment, its persistence is contingent upon the continued presence of random-structured weathering sources such as volcanic glass. Periodic deposition of ash or other pyroclastic materials, necessary for the maintenance of an early weathering stage, has not influenced formation of these soils. Secondly, it is considered that parent materials containing predominantly crystalline weathering sources (feldspars, layer silicates) will dictate, through nucleation, the formation of a predominantly crystalline clay mineral suite.

The presence of gibbsite in Natal Oxisols is indicative of an advanced stage of chemical weathering. Desilication, and hence accumulation of aluminium

in the weathering environment, has reached a stage at which an anti-gibbsite effect (i.e. the maintenance of amorphous hydroxyalumina in a relatively depolymerized state by negatively-charged aluminosilicate surfaces) no longer has functional significance. Relatively small amounts of amorphous alumina correspond to a limited area of negatively-charged surfaces available for adsorption (and hence persistence) of amorphous sesquioxides. The stage during weathering at which amorphous alumina demixes to form a crystalline gibbsite phase will depend to a large extent on negative surface charge density. Thus incipient gibbsite formation in allophane-rich soils would be indicative of a more advanced degree of weathering than in Natal Oxisols. Similarly, the large amounts of gibbsite in the Oxisols from Australia and Brazil can be related to the very low permanent negative charge of these soils. Hence during weathering, two factors are conducive to the appearance of gibbsite: firstly, a relative accumulation of alumina, and secondly, the hydrolytic erosion of negatively-charged aluminosilicate clays (amorphous or crystalline) which function as inhibitors of gibbsite formation.

Because quantities of amorphous (oxalate-soluble) iron are considerably lower than amorphous alumina, it can be inferred that a mechanism analogous to the anti-gibbsite effect is more or less inoperative during pedogenetic iron transformations. This may be due to preferential adsorption of hydroxyalumina at negatively-charged aluminosilicate surfaces, a phenomenon which in turn probably arises from a difference between the amount of positive charge per unit Al or Fe in amorphous hydroxysesquioxides. Such a situation is also reflected by the relatively much larger accumulation of Fe relative to Al as a culminating crystalline phase of pedogenesis in the Oxisol clays. A corrolary of this observation is that Fe-hydroxyinterlayering of expanded 2 : 1 phyllosilicates is probably negligible in environments characterized by a high turnover of polymeric hydroxyalumina material.

It is relatively easy to envisage the presence of pedogenic aluminous chlorite in acid sesquioxidic soils which derive from sediments containing 2 : 1 layer silicates (such as dioctahedral mica). Absence of pedogenic chlorite in soils derived from basalt or diabase can be accounted for by the fact that a lithologically inherited 2 : 1 layer silicate matrix is lacking. The presence of chlorite in the Balmoral could therefore indicate an admixtural shale influence in formation of this doleritic soil. However, smectite neogenesis during an early weathering stage, followed by interlayer alumination (and hence stabilization) under acid leaching, is a possible pathway of chlorite formation which cannot be dismissed.

The use of oxalate extraction in preference to NaOH selective dissolution analysis for quantitative determination of amorphous material results in values for the latter which correlate well with physicochemical parameters. However, whereas the behaviour of allophane-rich clays is fairly predictable because of the dominating reactivity of abundant, amorphous hydroxyalumina, the response of Oxisol clays to induced changes in chemical environment is somewhat more complex. It appears, for example, that much of the reactivity of Al in these soils can be related to an organically-bound fraction. At the same time, although hydrous iron oxides are almost entirely crystalline (chiefly goethite), extensive isomorphous substitution of Al for Fe reduces particle size and crystallinity. In the presence of relatively much smaller amounts of amorphous hydroxyalumina, this component exerts a major influence on electric charge distribution, P retention, and control of silica levels in the soil solution. A yellowish colouration also appears to be a function of the extent of isomorphous substitution by Al. Hence more silica is released from red sesquioxidic materials following P adsorption than from yellow materials.

Natal Oxisols possess a larger component of pH-dependent negative exchange charge than the more strongly-weathered soils from Australia and Brazil. To some extent this can be attributed to the presence of pedogenic aluminous chlorite in the Natal soils. However, the latter also have a relatively higher content of kaolin which has been shown to consist, in most cases, of an admixture of kaolinite, much of which is poorly-crystalline and finely-divided, and metahalloysite. Evidence from the literature indicates that tetrahedral substitution of Al for Si may be a common feature of halloysite. Thus the halloysitic character of fine clay in Natal Oxisols could also contribute to their relatively much larger pH-dependent CEC. While amorphous, polymeric hydroxyalumina consistutes an important source of positive exchange charge in acid, sesquioxidic soils, there is nevertheless evidence to suggest that in the severely weathered Oxisols from Australia and Brazil, the Al-substituted iron oxide component, which constitutes approximately half of the clay fraction by weight, is also a major source of positive charge.

Net CEC hysteresis arising from cyclic pH adjustment is due solely to positive charge hysteresis, while CEC as such is fully reversible by titration with strong acid. On the basis of additional observations on the effect of pretreating clays with different chemical reagents, a mechanism has been postulated to account for pH-dependent, positive exchange charge hysteresis involving chemisorption of hydroxyl ions and/or the operation of a Coulombic induction factor favouring reprotonation of functional groups closely separated from sites of permanent negative charge. Because hysteresis of this nature is probably

npt permanent (i.e. full reversibility of positive charge is governed by kinetics), the phenomenon may not be of much direct significance to soil fertilization practices. It nevertheless provides a better understanding of the nature of CEC variation with pH in sesquioxidic soils.

Measurement of electric charges in soils and clays will depend heavily upon the technique employed. The dilute field solution of acid, sesquioxidic soils will induce extensive, if not maximal, overlap and mutual neutralization of oppositely-charged electric double layers. If such conditions are simulated during measurement, large proportions of positive and negative exchange charge will not be detected. On the other hand, determination of exchange charge in the presence of relatively concentrated electrolyte, while affording optimum resolution of discreet sites of positive and negative charge, may give rise to non-Coulombic adsorption (species-dependent intersalation) of cations, and may also induce replacement of structural hydroxyl by anions which at lower salt concentrations are adsorbed non-specifically (i.e. only Coulombically). More work is needed to ascertain whether maximum electric charge resolution can be achieved at salt concentrations low enough to obviate these effects.

A prerequisite to the existence of exchangeable aluminium in soils is an acid pH (usually below a value of about 5,5). Thereafter, quantities of exchangeable Al present are governed by electric charge distribution and by concentration of bases in the soil solution. Current theory indicates that soil clays dominated by kaolin will subtend a more acid pH than clays enriched with gibbsite or allophane. Furthermore, the simultaneous presence of amorphous, polymeric hydroxyalumina tends to shift equilibrium pH to higher values. These considerations help to explain why Natal Oxisols invariably contain exchangeable aluminium in quantities which are often toxic to plants, while no exchangeable aluminium can be detected either in gibbsitic Oxisols from Australia and Brazil, or in volcanic-ash soils containing large amounts of sesquioxidic allophane. It is certainly important to dispel any notion that exchangeable aluminium levels are controlled by an equilibrium relationship with a labile pool of polymeric, non-exchangeable hydroxyalumina adsorbed on surfaces of silicate clays.

Phosphate and silica in solution compete for adsorption at sesquioxide surfaces. There is evidence to suggest that levels of soluble silica in Natal Oxisols are sufficient to cause significantly higher concentrations of P in the soil solution after equilibration with added phosphate than would otherwise be the case. Natural ameliorative action of this nature is unlikely to manifest itself either in more strongly-weathered, silica-depleted Oxisols, or in volcanic-ash soils which contain sesquioxidic allophane with a very high capacity for phosphorus retention.

Investigation of soil-solution equilibria in relation to clay mineralogy has confirmed known limitations in attempts at predicting clay mineral stability from soil solution composition. For example, while the silica potential of allophanic soil dictates kaolinite stability, soil solution composition under conditions of, or closely approaching, equilibrium with the solid phase, points to the existence of allophane as a partial metastable equilibrium state, the persistence of which is governed by kinetic factors. Similarly, kaolinite is the indicated stable mineral in Oxisols, despite the presence of associated gibbsite. In reality, silica potential fluctuates in response to variations in moisture regime and leaching rate, periodically favouring kaolinite dissolution and gibbsite formation.

Recent work has indicated that synthetic, amorphous co-precipitates of silica and alumina can be used to formulate fairly successful structural and behavioural models for natural allophane. The present study has shown that the physicochemical behaviour of allophane is strikingly similar to that which is predicted on the basis of compositional variation in chemical properties displayed by synthetic analogues. Much of the success of this comparison can be attributed to the development of an improved method for quantitative determination of allophane involving (i) the use of acid ammonium oxalate as an extractant, and (ii) allocation of water content on the basis of an ignition weight loss-composition function determined for synthetic gels, normalized with respect to saturating cation.

Evidence based mainly on ion exchange data and on previous observations reported in the literature, suggests that in media characterized by relatively high concentrations of basic cations, allophane formation proceeds through tetrahedral substitution of Al for Si in an aluminosilicate phase until a maximum substitution is reached at a composition corresponding to 45% $Al_2O_3/Al_2O_3 + SiO_2$. Any additional alumina takes the form of positively-charged, polymeric hydroxy-alumina surface-associated with the negatively-charged aluminosilicate phase. In systems deficient in basic cations, the necessity for charge-balancing by some alumina means that the corresponding maximum tetrahedral Al content will only occur at a composition corresponding to 80 - 90% $Al_2O_3/Al_2O_3 + SiO_2$. Formation of allophane in nature probably occurs under conditions intermediate between these two extremes. Procedures developed in this study should facilitate further testing of the revised model against natural materials.

APPENDIX I

PROFILE DESCRIPTIONS AND SAMPLE INFORMATION

Samples 2 and 3

SOIL FORM:*	Griffin	SOIL SERIES:*	Farmhill
LOCALITY:	Highmoor Forest Reserve	SITE:	3% grade; convex, North-facing, lower mid-slope
ELEVATION:	2010m	MEAN ANNUAL RAINFALL:	1250mm
VEGETATION:	Highland Sourveld: *Themeda* sp.	PARENT MATERIAL:	Basalt colluvium on weathered basalt (Stormberg series)

Sample	Horizon	Depth (cm)	Description
	Orthic A1	0 - 22	Moist, dark brown (7.5YR3/2) clay loam; weak, coarse, subangular blocky; friable; abundant roots; a few small gritty basalt fragments and very few, large, partly-weathered basalt stones. Gradual smooth transition.
2	Yellow-brown apedal B21	22 - 60	Moist, strong brown (7.5YR4/6) clay; apedal, massive; friable; very few roots; common small and medium partly-weathered basalt fragments, increasing in abundance towards stoneline at lower boundary; few roots; clear smooth transition.
3	Red apedal II B22	60 - 78	Moist, red to yellowish-red (2.5YR- to 5YR 4/8) clay; apedal, massive; friable; porous; few, small, bluish-white, brittle agate fragments; roots rare; diffuse smooth transition.
	IIC	78 - 190N	Moist, reddish-brown (5YR4/6) highly-weathered friable vesicular basalt with red, black and grey streaks along horizontal cleavage planes; many small agate inclusions, mostly preserved, or partly decomposed to soft black clay-textured material (probably Mn oxide).

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* Soil Classification Working Group (1974).

Sample 4

SOIL FORM:	Griffin	SOIL SERIES:	Farmhill
LOCALITY:	Donnybrook	SITE:	8% grade; convex, West-facing mid-slope
ELEVATION:	1230m	MEAN ANNUAL RAINFALL:	1000mm
VEGETATION:	Highland Sourveld: *Themeda*, *Eragrostis* spp.	PARENT MATERIAL:	Highly-weathered, mixed dolerite-shale colluvium (underlying material Beaufort shale; dolerite dike 30m upslope from profile)

Sample	Horizon	Depth (cm)	Description
	Orthic A1	0 - 20	Moist; very dark greyish-brown (10YR3/2) clay loam; moderate to strong medium sub-angular blocky; firm; abundant roots; gradual smooth transition.
4	Yellow-brown apedal B21	20 - 75	Moist, dark yellowish-brown (10YR4/4) clay; apedal, massive, friable; very few fine indurated iron-manganese nodules and small yellow shale fragments; very few roots; diffuse smooth transition.
	Red apedal B22	75 - 110	Moist, yellowish-red (5YR5/6) clay; apedal; massive; friable; very few, fine, indurated iron-manganese nodules and small shale fragments; gradual undulating transition.
	B3	110 - 160N	Moist, yellowish-brown (10YR5/6) clay, apedal; massive; firm and distinctly more dense than overlying horizons; very few small shale fragments.

Sample 5

SOIL FORM:	Hutton	SOIL SERIES:	Balmoral
LOCALITY:	Donnybrook	SITE:	5% grade; convex, N-E-facing, lower midslope
ELEVATION:	1260m	MEAN ANNUAL RAINFALL:	1000mm
VEGETATION:	Highland Sourveld: *Eragrostis*, *Themeda*, *Hyparrhenia*, *Leonotis*, and *Watsonia* spp.	PARENT MATERIAL:	Karroo dolerite

Sample	Horizon	Depth (cm)	Description
	Orthic A1	0 - 38	Dry, dark reddish-brown (5YR3/2) - 5YR2.5/2 when moist - sandy clay loam; moderate coarse subangular blocky; hard; abundant roots; gradual smooth transition.
	Red apedal B21	38 - 80	Moist, dark reddish-brown (2.5YR3/4) gritty clay; apedal; massive; friable; porous; few, fine, indurated Fe-Mn nodules; common roots; diffuse smooth transition.
	B22	80 - 150	Moist, dark red (2.5YR3/6) clay; apedal; massive; friable; porous; few roots; very few, fine, indurated Fe-Mn nodules; diffuse smooth transition.
5	B23	150 - 230N	Moist, dark red (2.5YR3/6) clay; apedal; massive; very friable and highly porous; common, faint, red clayskins in root channels and pores; few, fine, distinct, black manganese (?) streaks and flecks; occasional roots extend to lower limit of the profile.

Sample 8

Kraznozem Gn 3.11 (Profile No. T84, Gregory Falls Survey)*

LOCALITY:	Gregory Falls, Australia	SITE:	Moderate slope on undulating topography
ELEVATION:	240m	MEAN ANNUAL RAINFALL:	3000mm with 2 - 3 month dry season
VEGETATION:	Rain forest	PARENT MATERIAL:	Olivine basalt

Sample	Depth (cm)	Description
	+2	Layer of leaf litter, small twigs and bark fragments, some fresh, some partly decomposed.
	0 - 10	Dark reddish-brown (5YR3/4) clay loam, strong medium granular, friable, many fine roots.
	10 - 20	Dark red (5YR3/6), as above.
	20 - 60	Dark red (2.5YR3/6) clay loam, moderate sub-angular blocky tending massive, friable, some tree roots.
	60 - 90	As above light clay.
	90 - 180	Yellowish-red (5YR4/6) medium clay, strong fine polyhedral structure with many denser clay nodules of tubular form, friable.
8 (210-240 cm)	180 - 390	Reddish-brown (5YR4/4) medium clay, as above.
	390 - 450	Dark reddish-brown (5YR3/4), as above.
	450 - 570	Dark brown (7.5YR4/4) as above, occasional 2 cm ironstone nodules.
	570 - 690	As above with trace of soft weathered basalt.
	690 - 810	Dark brown (7.5YR4/4) medium clay with much soft weathered basalt.
	810 - 840	Soft weathered basalt with small amounts of dark brown clay.

* With acknowledgement to R. J. Isbell.

Other samples

Samples 6 and 7 were taken from a profile in virgin headlands on Thabamhlope Experiment Station, Natal. The soil is classified as Farningham series (described by van der Eyk *et al.*, 1969; p. 160), and occurs in intimate association with Griffin series (J. le Roux - personal communication).

Sample 18 (Latosol Roxo; Typic Haplorthox) was taken from profile no. 1107 of A. C. Moniz and J. Bertoldo de Oliveira (Instituto Agronômico, São Paulo, Brazil). No description is available.

Experimental data for sample 11 (otherwise known as '905', Uemura or Kodonbaru) are summarized by Wada and Aomine, (1973).

Sample 17 was taken from a site adjacent to that of the reference soil profile, Tirau silt loam, described in N.Z. Soil Bureau Bull. (1968).

APPENDIX II

FREEZE-DRYING PROCEDURE

Samples of clay or gel were K-saturated, and excess salt was removed by centrifuge-washing with water, methanol and methanol-acetone. Water was added to the sediment which was then transferred as a slurry to a wide-mouthed, round-bottomed flask (Pyrex; 250 or 500 ml capacity). Residual organic solvent was evaporated off at about 40C under vacuum by attaching the flask to a Büchi Rotavapor R rotary evaporation unit. These conditions permitted selective removal of organic solvent and obviated partial encrustation associated with evaporation of water at higher temperatures.

The slurry was then frozen rapidly by immersing the flask in solid CO_2-saturated acetone. Rotation ensured an even spread of material over the inner wall of the flask.

The sample was then dried by connecting the flask to a vacuum pump fitted with a refrigerated trap.

APPENDIX III

SEPARATION MEDIUM AND FINE CLAY FRACTIONS

Clay < 0,2 μm suspended in pH 9,5 Na_2CO_3 solution was separated into medium (0,2 - 0,08 μm) and fine (< 0,08 μm) fractions by centrifugation in 250 ml polypropylene bottles filled to the 200 ml mark using a Sorvall centrifuge fitted with a fixed-angle, GSA rotor. Allowing for approximately 1 cm sediment thickness, R and S (Jackson, 1956; p. 146) have values of 13,5 and 6,5 cm, respectively. Svedberg and Nichols'* integrated form of Stokes Law gives time for sedimentation as

$$t(\text{sec}) = \frac{\eta \log_{10} R/S}{3{,}81\ N^2 r^2 \Delta s} ,$$

where N = r.p.s. ;

r = particle radius (cm);

η = viscosity (poise) at the existing temperature; and

Δs = difference in S.G. between the solvated particle and the suspension liquid.

More conveniently,

$$t(\text{min}) = \frac{63 \times 10^8\ \eta \log_{10} R/S}{(\text{r.p.m.})^2 (\text{particle diameter in } \mu\text{m})^2 \Delta s} \qquad \text{(Jackson, 1956).}$$

To sediment particles > 0,08 μm and retain particles < 0,08 μm with SG (hydrated) = 1,52† in suspension at an operating r.p.m. of 8600 and a mean temperature of 14C (giving η = 0,01169p‡),

$$t(\text{min}) = 94 ,$$

which includes a correction of - 1 min for the net effect of speed-up and slow-down periods on sedimentation (estimated by graphical integration of r.p.m.-time curves).

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* J. Am. Chem. Soc. 45: 2910 (1923).

† Jackson (1956).

‡ CRC Handbook of Chem. and Physics 50th Ed. 1969 - 70, p. F-36.

APPENDIX IV

CHEMICAL ANALYSES

Determination of Al and Fe

The ferron colorimetric method was used to determine Al and Fe in the same solution by measuring absorbance at 370 and 600 mμ, respectively (Davenport, 1949; Tokashiki & Wada, 1972). Extracts containing complexing anions such as citrate or oxalate were digested prior to analysis by evaporation of an aliquot in a 50 ml volumetric flask to dryness on a sand-bath, carbonization by heating with 1 ml c.H_2SO_4 , then digestion with 10 ml 30% H_2O_2 (Tokashiki & Wada, 1972). The contribution of Fe to absorbance at 370 mμ is subtracted to give absorbance of the Al-ferron complex. As with the aluminon method, titanium has been found to interfere with the Al determination (Fitzpatrick, 1974).

Determination of Si

Silicon in various extracts was measured by the method of Weaver, Syers & Jackson (1968). The procedure is designed to eliminate Mo complexation by citrate in CDB extracts through addition of an excess of molybdate reagent.

Modification was required for analysis of Si in oxalate extracts to overcome similar complexation by oxalate. To a 10 ml aliquot in a 50 ml polypropylene beaker containing a maximum of 2,4 ml 0,2M ammonium oxalate (pH 3), 10 ml H_2SO_4 , 10 ml molybdate reagent, 5 ml tartrate and 1 ml amino acid reductant solution were added respectively. This procedure eliminates interference from up to 2 mmol oxalate in a total volume of 36 ml.

APPENDIX V

ANALYSES OF EQUILIBRATED SOIL MATRIX SOLUTIONS

Water equilibration

Sample	H_4SiO_4 moles/l x 10^{-6}	Cations (moles/l x 10^{-6})						Total cations	Ionic* strength x 10^{-4}
		H^+	Al^{3+}	Ca^{2+}	Mg^{2+}	Na^+	K^+		
2	26	2,0	0,1	2,2	1,7	16	9,2	31	0,34
3	40	1,9	0,1	1,0	1,5	24	3,6	32	0,35
4	37	2,1	2,0	2,0	6,5	24	7,1	43	0,70
5	67	4,0	0,3	3,6	1,0	74	7,6	90	1,00
11	135	1,0	69	4,5	2,2	34	12	123	4,10
18	34	0,8	10	2,3	6,2	26	9,8	55	1,10
I	349	0,1	29	0,0	0,0	174	5 563	5 766	58,5
II	348	0,3	21	0,0	0,0	416	14 450	14 887	150
IV	115	1,1	58	0,0	0,0	553	56 904	58 128	581

Acid equilibration

Sample	H_4SiO_4 moles/l x 10^{-6}	Cations (moles/l x 10^{-5})						Total cations	Ionic* strength x 10^{-4}
		H^+	Al^{3+}	Ca^{2+}	Mg^{2+}	Na^+	K^+		
2	89	26	229	12	15	15	15	311	127
3	440	32	172	32	0,4	44	7,2	287	103
4	112	32	232	13	0,1	2,2	9,5	288	124
5	293	37	202	7,2	4,5	7,0	10,7	306	112
11	454	14	236	4,3	1,6	1,7	6,6	278	123
18	182	31	192	48	0,1	8,7	4,3	284	113
I	857	1,3	3,0	0,0	0,0	62	4704	4770	479
II	852	1,7	8,3	0,0	0,0	111	5370	5491	553
IV	617	5,3	205	0,0	0,0	41	2864	3115	394

* $I = \frac{1}{2}\sum m_i z_i^2$ where m = concentration (moles/l) of the ith ion of valency z, assuming anions to be monovalent.

Calculations

$$pH_4SiO_4 = -\log C_{H_4SiO_4}$$

since activity is equal to concentration (Siever, 1957).

$$pAl = -\log a_{Al} ,$$

where $a_{Al} = \gamma_{Al} . C_{Al}$, and the activity coefficient γ_{Al} is obtained from the Debye-Hückel expression:

$$-\log \gamma_{Al} = \frac{Az^2_{Al}\sqrt{I}}{1 + \overset{o}{a}_{Al}B\sqrt{I}} .$$

Substituting values for the constants A, B and $\overset{o}{a}_{Al}$ of 0,5085 , 0,3281 x 10^{-8} and 9 x 10^{-8} respectively (Garrels & Christ, 1965; pp. 61 - 2), this expression reduces to the form

$$\log \gamma_{Al} = \frac{-4,5\sqrt{I}}{1 + 2,95\sqrt{I}} .$$

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