# PROPERTIES AND QUANTITATIVE ESTIMATION OF POORLY CRYSTALLINE COMPONENTS IN SESQUIOXIDIC SOIL CLAYS*

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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 selective dissolution techniques. 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 0.5 N 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 2 hr shaking in the dark with 0.2 M 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. 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. 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 less than that of the poorly-crystalline, Al-substituted iron oxide component which is removed by deferration with citrate–dithionite–bicarbonate reagent.

## INTRODUCTION

Sesquioxidic soils may be regarded as those in which the oxides, hydroxides or oxyhydroxides of aluminium and iron have accumulated, either as discrete crystalline phases or as coatings on clay mineral surfaces to the extent that they exert a dominating influence on soil 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 group of allophane-rich volcanic ash soils known as Andosols.

Techniques for quantitative determination of the colloidal constituents, especially in these soils, have limitations. The biggest uncertainly lies in the quantitative determination of amorphous material. A procedure for the latter was proposed by de Villiers (1971), which 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 0.5 N NaOH should be expressed as such.

One problem is that 0.5 N NaOH treatment of clays is rather harsh and therefore not completely selective for amorphous material. An alternative would be to employ a milder dissolution treatment. However, the indications 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 objective of this paper is to examine the clay fractions of selected sesquioxidic soils by a number of chemical techniques. Particular attention is given to various methods for determination of the 'amorphous' component.

## MATERIALS AND METHODS

Six samples from Oxisols in Natal (Nos. 2–7), one each from Australia (No. 8) and Brazil (No. 18) and volcanic-ash soils from Japan (No. 11) and New Zealand (No. 17) were chosen for investigation. These are the same samples used in earlier papers by Fey and le Roux (1975, 1976). Previous work on similar Natal soils has indicated that the clay fraction consists mainly of kaolinite, pedogenic aluminous chlorite, gibbsite, amorphous aluminosilicates and poorly crystalline hydrous sesquioxides (le Roux, 1973). The Oxisols from Australia and Brazil were selected to represent material which has been subject to extreme weathering under humid, tropical conditions. The Andosols have formed under similar conditions of intensive leaching in relatively recent deposits of volcanic ash, with clay fractions dominated by allophane (Wada and Aomine, 1973; N.Z. Soil Bureau, 1968).

Natural clay fractions (<2 μm), minimally affected

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by chemical pretreatment, were separated following successive ultrasonic treatments. Three amorphous alumino silica gels were prepared by co-precipitation from sodium metasilicate and aluminium chloride solutions having compositions corresponding to 41, 53 and 65% $Al_2O_3/Al_2O_3 + SiO_2$, respectively (Fey and le Roux, 1975, 1976).

Freeze-dried, K-saturated natural clays and synthetic aluminosilica 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 0.1 M Na-pyrophosphate (pH 10.5) for 12 hr on an end-over-end shaker; (ii) 10 ml 0.2 M $NH_4$-oxalate (pH 3) for 2 hr on an end-over-end shaker in darkness; and (iii) 10 ml 0.3 M Na-citrate buffered with Na-bicarbonate plus 0.75 g Na-dithionite at 80°C. Clays deferrated according to extraction (iii) above, were treated with 5% $Na_2CO_3$ at 90°C for 2 hr 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 of Davenport (1949) after digestion of a suitable aliquot, taken to dryness by heating in a volumetric flask, with 1 ml concentrated $H_2SO_4$ until fuming, followed by 10 ml 30% $H_2O_2$ until a clear solution was obtained (Tokashiki and Wada, 1972).* Analysis for Si was by the method of Weaver et al. (1968). The procedure was modified for analysis of oxalate extracts to overcome interference arising from Mo complexation by oxalate (Fey and le Roux, 1975). Residues from all treatments were weighed after $NH_4$ saturation and heating at 110°C for 24 hr.

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* To a 10-ml aliquot in a 50-ml polypropylene beaker containing a maximum of 2.4 ml 0.2 M 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.

## RESULTS AND DISCUSSION

Some chemical properties of the soil collection are shown in Table 1. In the Natal Oxisols (samples 2–7), 1 N 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 measured net negative charge (No. 18) exhibit little difference in pH values measured in water and KCl, as would be expected (van Raij and Peech, 1972). Exchangeable Al is present only in 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. 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 1) may have been slightly higher (with accordingly higher net CEC) than that prevailing during 0.2 N $NH_4Cl$ 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 and 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. 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.

*'Amorphous' material by* NaOH *selective dissolution*

Results for NaOH dissolution of deferrated clays are presented in Table 2. Various possible sources

Table 1. Chemical properties and exchange data (mequiv/100 g) of the soil collection*

| Soil | Org. C (%) | Clay (%) | pH† (H₂O) | pH† (N KCl) | 0.2 N NH₄Cl exchangeable: Bases‡ | Al | Total | CEC | AEC | Net charge | pH§ of CEC, AEC determination |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 |

* Exchangeable Al was determined by successive 0.2 N $NH_4Cl$ extractions (Skeen and Sumner, 1965); exchangeable bases were estimated from five 0.2 N $NH_4Cl$ extractions; CEC and AEC were determined after 1 N KCl washings by the weighing technique using 0.05 N KCl with 1 N $(NH_4)_2SO_4$ as replacing electrolyte (Fey and le Roux, 1976).
† 1:2.5::soil:solution.
‡ Ca + Mg + Na + K.
§ 1:25::soil:0.05 N KCl.
‖ Wada and Aomine (1973).
¶ N.Z. Soil Bureau (1968).

Table 2. Possible sources of $SiO_2$ and $Al_2O_3$ dissolution from deferrated clays by boiling 0.5 N NaOH treatment

| Sample | Gibbsite (by DTA) (%) | Dissolved $SiO_2$ (%) | Dissolved $Al_2O_3$ (%) | | Molar ratios | | Amorphous* | Allophane† | 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) | | | 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 | — | — |
| 17 | 0.0 | 38.11 | 36.52 | 36.52 | 1.77 | 1.77 | 82.9 | 54.9 | 25.7 | — | — |

* 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.

of dissolved silica and alumina can be considered. Gibbsitic alumina (determined by DTA) is subtracted from total dissolved alumina, since the dissolution of this component is effectively complete (XRD of residues). 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 per cent amorphous material* (Alexiades and 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 powder diffraction and infrared spectroscopic data. 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 also were calculated according to the scheme of de Villiers (1971)† as allophane plus residual alumina (Table 2). 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). This is inconsistent with the relative magnitude of such properties as pH-dependent CEC observed for these materials (Fey and le Roux,

1976). It may be argued that allophane in the Oxisol clays conforms to the halloysitic variety (Jackson, 1964), and is therefore relatively inert physicochemically. 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 2) according to either equation (3) or (5) of Alexiades and Jackson (1966).‡ Residual alumina contents of the Oxisol clays (last column, Table 2) are relatively low.

### 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 and Jackson, 1960) and hot 5% sodium carbonate (Follett et al., 1965). The results of this comparative study are presented in Table 3 for natural clays and Table 4 for deferrated clays.

In addition, Table 5 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 and de Villiers, 1970) to their study as a means towards elucidating the nature and properties of allophane.

(1) Sodium pyrophosphate. Pyrophosphate appears to possess a specificity for Al extraction from the soil clays (Table 3), since relatively insignificant quantities of Fe and Si were dissolved by this treatment. The same can be said for the gel data (Table 5). 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

$$* \% \text{Amorphous} = \frac{\% SiO_2 + Al_2O_3}{0.9}$$

(division by 0.9 allocates 10% $H_2O$).

$$† \% \text{Allophane} = \frac{x + 0.384x}{0.89},$$

where $x = \% SiO_2$, and division by 0.89 allocates 11% $H_2O$.

‡ Equation (3):

$$\% \text{kaolinite + halloysite} = \frac{x}{0.465}$$

(when molar $SiO_2/Al_2O_3 < 2$).
Equation (5):

$$\% \text{kaolinite + halloysite} = \frac{x/0.465 + y/0.395}{2}$$

(when $2 \leqslant$ molar $SiO_2/Al_2O_3 < 3$),

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

Table 3. Dissolution of $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ from natural clays by various extractants

| Sample | 0.1 M Na-pyrophosphate (pH 10.5) | | | | % removed by: NH₄-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 4. Dissolution of $SiO_2$ and $Al_2O_3$ from deferrated clays by 5% $Na_2CO_3$ and acid $NH_4$-oxalate

| | | | | % removed by: | | | |
| | | Hot 5% $Na_2CO_3$ | | | $NH_4$-oxalate (pH 3) | | |
| Sample | $SiO_2$ | $Al_2O_3$ | $SiO_2/Al_2O_3$ (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 |

obtained. Since pyrophosphate also tends to peptize a certain amount of amorphous, inorganic colloid (Bascomb, 1968), extracted alumina is unlikely to be entirely of organic origin.

(2) *Acid ammonium oxalate*. Oxalate extracted large amounts of alumina and silica from the volcanic-ash soil clays (Tables 3 and 4). 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 5).

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 CDB-oxalate treatment and those by oxalate treatment alone (Table 7). This view is reinforced by the fact that the clay:solution ratio of the oxalate extraction which followed CDB treatment was about five times lower than that of the separate treatment with oxalate alone, the implication being that a particular component is being extracted highly specifically.

In this context, data in Table 3 tend to support the assumption made earlier (Table 2) that the bulk of boiling 0.5 N 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 and electron-optical evidence. Furthermore, negligible disso-

lution of alumina from samples 8 and 18 (Table 3) indicates that gibbsite (with which these clays are relatively enriched) 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 2). This evidence might suggest that the former extractant is not as efficient as the latter. On the other hand, the NaOH-soluble fraction also will represent variable dissolution from sources such as imogolite (Wada and Aomine, 1973; Yoshinaga *et al.*, 1973), chloritized 2:1 layer silicates and poorly-ordered kaolinite and halloysite. For these reasons, oxalate values are considered to be the most meaningful of the two in terms of amorphous material as such.

A significant advantage of oxalate over other commonly used extractants is its additional specificity for amorphous ('active') iron oxides (McKeague *et al.*, 1971; Schwertmann, 1973). Interestingly, oxalate-extractable iron in all the soil clays is relatively low (Table 3), despite indications (XRD and DTA evidence) that the iron oxide component in these clays is poorly crystalline.

(3) *Citrate–dithionite–bicarbonate*. CDB extraction data (Table 3) support the contention (Norrish and Taylor, 1961) that goethite should be recognized as an important source of the often large amounts of Al released by this treatment. The presence of goethite in most of the clays was established from random powder diffractograms, which display the peak broadening and lower $d$ spacing characteristics typical (Norrish and 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

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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 3) is considerably lower than that of the goethitic Kraznozem clay (No. 8).

Table 5. Effect of various chemical extractants on dissolution of synthetic amorphous aluminosilica gels

| | | | | % removed by: | | | |
| | $SiO_2/$ | Pyrophosphate | | Oxalate | | 5% $Na_2CO_3$ | |
| Gel Sample | $Al_2O_3$ (molar) | $SiO_2$* + $Al_2O_3$ (%) | $SiO_2/Al_2O_3$ (molar) | $SiO_2$* + $Al_2O_3$ (%) | $SiO_2/Al_2O_3$ (molar) | $SiO_2$† + $Al_2O_3$ (%) | $SiO_2/Al_2O_3$ (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 110°C. The oxalate extraction values merely represent complete solubilization of the gels by this treatment.

Table 6. Sesquioxidic components of the Oxisol clays

| | Organic $Al_2O_3$ (%) | Sesquioxide fraction | | | | | |
| | | Amorphous plus interlayer* | | Crystalline | | | |
| | | | | Monohydrate‡ | | Trihydrate | |
| Sample | | $(Al,Fe)_2OH_5$ (%) | Al/Al + Fe† | $(Al,Fe)OOH$ (%) | Al/Al + Fe† | $Al(OH)_3$ (%) | Total§ |
|---|---|---|---|---|---|---|---|
| 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 | 42.2‖ | 0.19 | 28.7 | 75.5 |

\* Based on higher of two values for natural deferrated clay.
† Al/Al + Fe = $Al_2(OH)_5/(Al,Fe)_2OH_5$ and $AlOOH/(Al,Fe)OOH$, respectively.
‡ Based on CDB-extractable Al and Fe after subtraction of oxalate-soluble Fe.
§ Excluding organic $Al_2O_3$.
‖ Probably a mixture of monohydrate and $(Al,Fe)_2O_3$. Calculation as either formula would make little difference quantitatively.

small amounts of oxalate-soluble iron (Table 3) suggest that the mixed sesquioxide monohydrate is not a significant source of oxalate-extractable Al.

Relative proportions of $SiO_2$ and $Al_2O_3$ extracted from the allophanic clays (11 and 17) indicate that CDB treatment (Table 3) removes fairly large amounts of amorphous alumina but that amorphous aluminosilicates are left largely intact. It is significant that 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.

(4) *Sodium carbonate*. Results for the synthetic gels (Table 5) 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 discrete amorphous alumina is the main source of dissolution, and that an amorphous aluminosilicate phase—or permutite (van Reeuwijk and de Villiers, 1970)—is little affected by one extraction. These results contrast with the complete solubility of the gels in acid ammonium oxalate (Table 5).

Dissolution of Oxisol clays by sodium carbonate is greater than by oxalate (Table 4). 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 $Na_2CO_3$ extraction is less specific than oxalate.

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

*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 not adequately meaningful.

(1) *Oxisol clays*. Results presented so far (Tables 2, 3 and 4) enable the differentiation of four types of sesquioxidic material in the Oxisol clays. These are presented in Table 6. 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, sample No. 18 excepted.

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 2.3–2.5 has been estimated for chloritized Canadian prairie soil clays (Huang and 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 precursor. On the other hand, amorphous hydroxy-Fe and some hydroxy-Al will intergrade with the mixed sesquioxide monohydrate (Table 6). Amounts of amorphous Fe are small compared to amorphous Al (Table 3). For convenience, both are considered to belong to a mixed amorphous sesquioxide system having an approximate average basicity of 2.5 (Table 6).

Whereas amorphous (oxalate-soluble) Fe was first subtracted before calculation of the mixed Al–Fe monohydrate (Table 6) 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 3 and 4). 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 6) was calculated from oxalate-soluble Fe values for natural clay (Table 3) and from the higher of the two oxalate-Al values obtained for natural and deferrated clay (Table 3 or 4). 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 6), beyond the fact that they range from 1.5 to 7%, 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 6) ranges from 30–40% in the Natal Oxisol clays, to 75% in the Kraznozem (No. 8) and Latosol Roxo (No. 18).

(2) *Allophanic clays.* Owing to uncertainties regarding the model system for allophane, allocation of constituents dissolved from samples 11 and 17 by oxalate to the de Villiers (1971) formula, as was done in Table 2, 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 and Swindale, 1969). The problem is then confined to that of allocating water content (Fey and le Roux, 1975).

In view of the similarities in behaviour which has 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 (Fey and le Roux, 1975). 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 7).

2. $H_2O$ content corresponding to % $Al_2O_3/Al_2O_3 + SiO_2$ was read from the ignition weight loss curve and allocated to the sum of $SiO_2$ and $Al_2O_3$ extraction values to give % allophane (Table 7).

Values for % $Al_2O_3/Al_2O_3 + SiO_2$ were 69.9 and 70.6, while $H_2O$ content was 21.8 and 22.6% for samples 11 and 17, respectively.

In Table 7, amorphous and crystalline Fe oxides have been assigned (for comparison) the same formulae as were applied for the Oxisol clays. The very small amount 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.

### 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

Table 7. Sesquioxide and amorphous aluminosilicate components of the volcanic-ash soil clays

| Sample | Organic $Al_2O_3$ (%) | Sum of CDB + oxalate (sequential) extraction (%) | | | Oxalate extraction from natural clay (%) | | | $Fe_2O_3$* difference as FeOOH (%) | Allophane† (%) | $SiO_2/Al_2O_3$ (molar) | 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.
‡ Excluding organic $Al_2O_3$.

Table 8. NaOH-CDB selective dissolution data: calculation of kaolinite plus halloysite content

| Sample | 0.5 N NaOH-soluble* $SiO_2$ (%) | 0.5 N NaOH-soluble* $Al_2O_3$ (%) | CDB-soluble† $Fe_2O_3$ (%) | $SiO_2/Al_2O_3$ (molar) | Kaolinite‡ + halloysite (%) | Residual $Al_2O_3$ (%) |
|---|---|---|---|---|---|---|
| 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 2) and after ignition at 550°C, 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).

meaningful quantitative estimation of the amorphous component, the assumption that 0.5 N NaOH extracts predominantly kaolinitic material prior to ignition of the Oxisol clays (last column, Table 2) is adhered to. Consequently, an estimate of kaolinite plus halloysite content can be obtained using the appropriate equation (Alexiades and Jackson, 1966), and values for $SiO_2$ and $Al_2O_3$ representing the sum of silica and alumina dissolved before and after ignition at 550°C, excluding gibbsitic alumina. These values are presented, along with corresponding $SiO_2/Al_2O_3$ ratios and kaolinite–halloysite contents, in Table 8.

Despite limitations, it is considered that kaolinite plus halloysite values (Table 8) represent more realistic estimates of this component than would otherwise have been obtained using conventional NaOH-SDA alone. The relatively large quantity of kaolinite (40–60%) in the Oxisol clays are certainly in better agreement with semi-quantitative XRD indications (Fey, 1975).

Mineralogical composition of natural clays is finally summarized in Table 9. Values obtained for deferrated clays were recalculated on the basis of weight of material removed during deferration. For the Oxisol clays, this was taken as % (Al, Fe) OOH (Table 6). 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 7) plus FeOOH (Table 7). Quartz and mica contents were determined

according to the method of Alexiades and Jackson (1966). Chlorite values were calculated by difference (le Roux, 1973). A 14 Å peak was observed in X-ray diffractograms of samples 11 and 17. However, chlorite values for these clays may be overestimated, due to probable interference from imogolite dehydroxylation above 400°C (Aomine and Mizota, 1972). Since the diffractogram of sample No. 3 does not show a 14 Å peak, chlorite probably is over-estimated in this clay. This is attributed to the fact that 15% TGA water for kaolinite in this sample is too low. For example, use of 17% $H_2O$ [theoretical halloysite water at 300°C is 16.3%; Alexiades and 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 reasonable accuracy. Determination by TGA requires the same assumption because of the correction factor involved. 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 powder diffraction.

*Chemical reactivity and charge characteristics*

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

Table 9. 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 |

mineralogical data, has been demonstrated for allophanes and synthetic amorphous aluminosilicates (Fey and le Roux, 1975). The Oxisol clays appear to constitute a relatively more complex reaction system, made up of small but probably highly-labile organic and amorphous Al and Fe fractions, as well as large amounts of variably-crystalline sesquioxide (Fey, 1975) which militates against the establishment of straightforward parameteric 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 0.5 N 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 (Fey, 1975). 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 0.5 N NaOH treatment (Fey and le Roux, 1975).

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 mainly are responsible for these properties (Fey and le Roux, 1976).

Evidence has been presented by Fey and le Roux (1975) in favor 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 hydroxy-alumina 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% $Al_2O_3/Al_2O_3 + SiO_2$. In nature, allophane probably forms under conditions somewhere between the dystrophic and eutrophic extremes of deficiency and saturation with basic cations. Hence the attainment of maximum Al for Si substitution in the aluminosilicate phase would correspond theoretically to a composition somewhere between 45 and 80 or 85% $Al_2O_3/Al_2O_3 + SiO_2$; the actual composition being unique to a specific environment. However, since this range presumably represents a condition of intermediate to advanced desilication, bases will be at least partially deficient in the weathering regime. As alumina content increases with further desilication, bases will also become progressively more deficient. Hence on the assumption that low $SiO_2/Al_2O_3$ ratios in allophane are caused primarily by leaching and desilication, it can be seen

that the maximum 1:1 Al for Si substitution in the aluminosilicate and the appearance of the crystalline hydrated aluminas (in soil, this corresponds to neutralization of the anti-gibbsite effect) will occur simultaneously (Fey and le Roux, 1975).

To a large extent, the incomplete substitution of Al in the aluminosilicate phase of allophane could explain why measured exchange charge is often at variance with that predicted on the basis of behavior of synthetic aluminosilica gels coprecipitated from solutions of simple inorganic salts.

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