

# CLAY MINERALOGY OF ANDESITE SAPROLITE

*by*

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## ABSTRACT

CLAY mineral associations in saprolite of two andesites from the Cascade Range of northeastern California were determined. Sesquioxidic allophane with a high CEC delta value dominates the clay fraction of the least weathered saprolite in each series (47% and 37% in hypersthene andesite and olivine andesite saprolites, respectively). With further weathering, the content of amorphous clay remains high (over 30% in all cases) but the CEC delta value of the clay drops markedly. The amorphous material in the more weathered saprolite has the properties of halloysitic allophane. Halloysite, present in all saprolites, is highest in concentration (over 30%) in the more strongly weathered members of each of the saprolite series. Formation of sesquioxidic allophane during early stages of weathering and its transformation to halloysitic allophane and halloysite during later stages of weathering are supported by X-ray diffraction, electron microscopic, DTA, elemental analysis, and CEC delta value data.

## INTRODUCTION

GENESIS of specific clay mineral species and genetic relationship between species have long been subjects for intensive investigation. In search for explanations of weathering transformations, many investigations have focused attention in recent years on rock-saprolite régimes.

Recent studies of mineralogical and geochemical changes during weathering of andesite rock to saprolite at two locations in the Cascade Range of northeastern California (Hendricks and Whittig, 1967a; 1967b) have revealed significant relationships between primary mineral alteration, elemental losses and clay mineral weathering products. Relatively rapid weathering of plagioclase microlite and matrix glass in both a hypersthene andesite

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rock and an olivine andesite rock has been accompanied by pronounced loss of alkali and alkaline earth metals and moderate loss of Si and Al during early stages of weathering. An amorphous alkali-soluble component, judged to be allophane, appears in the early stages of weathering. In saprolite representing more advanced stages of weathering, halloysitic components increase relative to allophane.

In the present paper, clay extracted from saprolite samples is examined by X-ray diffraction, differential thermal, electron microscopic, and chemical methods. The allophane and halloysite\* components are identified, chemically characterized, quantitatively allocated, and correlated with degree of saprolite weathering.

## MATERIALS

Samples included in the present study were selected from two series of Pliocene andesite saprolite collected under acid soils in the Cascade Range of northeastern California. One saprolite series, at an elevation of 6550 ft, has developed by weathering hypersthene andesite. The second series, at 3700 ft elevation, has developed from olivine andesite. Petrology of the fresh andesite rocks and their saprolite have been described by Hendricks and Whittig (1967a).

The saprolite samples collected at each location represent several stages of weathering. The samples, taken from near the bottom of each profile pit, were selected according to degree of weathering and not necessarily with regard to depth. The saprolites are designated by number from 1 to 4 in the order of increasing degree of weathering, as ascertained by megascopic examination.

## METHODS

### *Preparation of Samples*

Saprolite samples, initially moistened with water, were gently crushed in a mortar with a rubber-tipped rod to limit breakdown of primary mineral particles. A pestle was required to crush the least weathered saprolite in each series, however. The crushed samples were subjected to dithionite-citrate-bicarbonate treatment (Mehra and Jackson, 1960) for removal of free iron oxides prior to separation of size fractions. Clay fractions were separated according to the method described by Jackson (1956). Coarse ( $2-0.2 \mu$ ) and fine ( $<0.2 \mu$ ) fractions were separated for X-ray diffraction analysis. Total clay ( $<2 \mu$ ) fractions were used for differential thermal, electron microscopic, elemental, CEC delta value, and selective dissolution analyses.

\* For simplicity, the term halloysite is used, henceforth, as the designation for halloysitic components without regard to state of hydration.

### *X-ray Diffraction*

Clay samples were prepared as oriented aggregates on porous ceramic plates. Suspended clay was sedimented on the plates by drawing the liquid through the plates with suction (modified procedure of Kinter and Diamond, 1956). The clays on the plates were subsequently saturated with Mg (Jackson, 1956) prior to analysis. Samples, while moist, after drying in air, and after heating at 110°C, were analyzed with a General Electric XRD-5 diffractometer using  $\text{CuK}\alpha$  radiation.

### *Differential Thermal Analysis*

Samples were Ca-saturated and air-dried prior to analysis. Differential thermal reactions within the samples (150 mg) were measured against powdered  $\text{Al}_2\text{O}_3$  as a reference. The heating rate was approximately 11°C per minute. A light beam, deflected by a reflecting galvanometer, was used to record photographically the DTA patterns.

### *Electron Microscopy*

Samples were prepared for examination by placing a drop of 0.005% clay suspension on a collodion-coated copper grid. After drying in a desiccator, the samples were examined and photographed with an RCA Model EMU-3G electron microscope by Mr. K. Miyano of the University of California Electron Microscope Laboratory.

### *Elemental Analysis*

Total Si was determined in NaOH-fused samples by the molybdenum blue method (Shapiro and Brannock, 1956). Al was determined after NaOH fusion by the method described by Hsu (1963). Total Fe was determined in separate samples, after  $\text{HF-HClO}_4$  dissolution (Riley, 1958) by the orthophenanthroline method (Shapiro and Brannock, 1956). Water content was measured as loss on ignition between 110° and 950°C.

### *Cation Exchange Capacity Delta Value*

The difference in cation exchange capacity as measured after pretreatment of samples with pH 3.5 acetate buffer and after treatment with pH 10.7  $\text{Na}_2\text{CO}_3$  (Aomine and Jackson, 1959) gave a distinctive method for differentiation of sesquioxidic and halloysitic allophanes. The delta value was used for quantitative estimation of sesquioxidic allophane in some samples.

### *Quantitative Determination of Allophane and Halloysite*

Si and Al dissolved by NaOH selective dissolution, first after heating samples to 110°C, then after heating to 550°C, were used to determine allophane and halloysite, respectively (Hashimoto and Jackson, 1960; Alexiades and Jackson, 1966). Allophane content was calculated from the

quantity of Si+Al dissolved and assuming an allophane water content of 10%. Si dissolved after dehydroxylation was used as the basis for calculation of halloysite content.

The criteria used for identification of allophane in this study are those described by Jackson (1965). Sesquioxidic allophane exhibits a CEC delta value of approximately 100 meq/100 g and has a relatively low  $\text{SiO}_2:\text{Al}_2\text{O}_3$  molar ratio. Halloysitic allophane has a CEC delta value of approximately 18 meq/100 g and a  $\text{SiO}_2:\text{Al}_2\text{O}_3$  molar ratio approaching 2.0. Both types of allophane are dissolved in boiling 0.5 N NaOH and are X-amorphous.

## RESULTS

Halloysite is the dominant crystalline species in both the coarse (2–0.2  $\mu$ ) and fine (<0.2  $\mu$ ) fractions of all saprolite samples examined. In no case were 2:1 layer silicates detected. Neither glycerol solvation nor K saturation effected any significant change in the X-ray patterns.

The halloysitic component in all samples appears to be composed largely, if not entirely, of a halloysite–metahalloysite complex (Figs. 1 and 2). In all cases, the area in the 7–10 Å region yields relatively high background scatter indicative of partially dehydrated halloysite. Diffraction maxima resolved for metahalloysite range between 7.2 and 7.6 Å and, in general, the peaks are asymmetrical, sloping more toward higher spacings.

The metahalloysite diffraction maxima (7 + Å) obtained from Mg-saturated, air-dried samples are of lower intensity and less clearly defined in the hypersthene andesite saprolite clay (Fig. 1) than in the olivine andesite saprolite clay (Fig. 2). From the hypersthene andesite saprolite, in fact, discrete metahalloysite peaks are evident in only the fine clay fractions of saprolites 2, 3, and 4 (saprolite 3 not shown) after Mg saturation and air drying. Halloysite, identified by its 10 Å spacing, is clearly resolved in only two of the Mg-saturated, air-dried samples of the hypersthene andesite saprolite series; the coarse clay fraction of saprolite 1 and the fine clay fraction of saprolite 4. The presence of hydrated halloysite is evidenced, however, by the intensification of 7 Å peaks upon heating the samples to 110°C. Both clay fractions of saprolite 1 resisted collapse to 7 Å upon heating, however.

All of the fine clay fractions of both saprolite series (except for hypersthene andesite saprolite 1) yielded more intense and clearly defined 7 Å spacings after air drying than when moist. This occurred despite the fact that the original samples had been stored in cardboard containers in the laboratory for several months prior to clay separation and had probably reached the air-dry state. There was no significant difference in any case, on the other hand, between moist and air-dried coarse clay fractions. This behavior indicates that the fine clay metahalloysite is susceptible to partial rehydration.

The halloysite–metahalloysite complex in the hypersthene andesite saprolite samples is present in noticeably higher concentrations in the fine clay

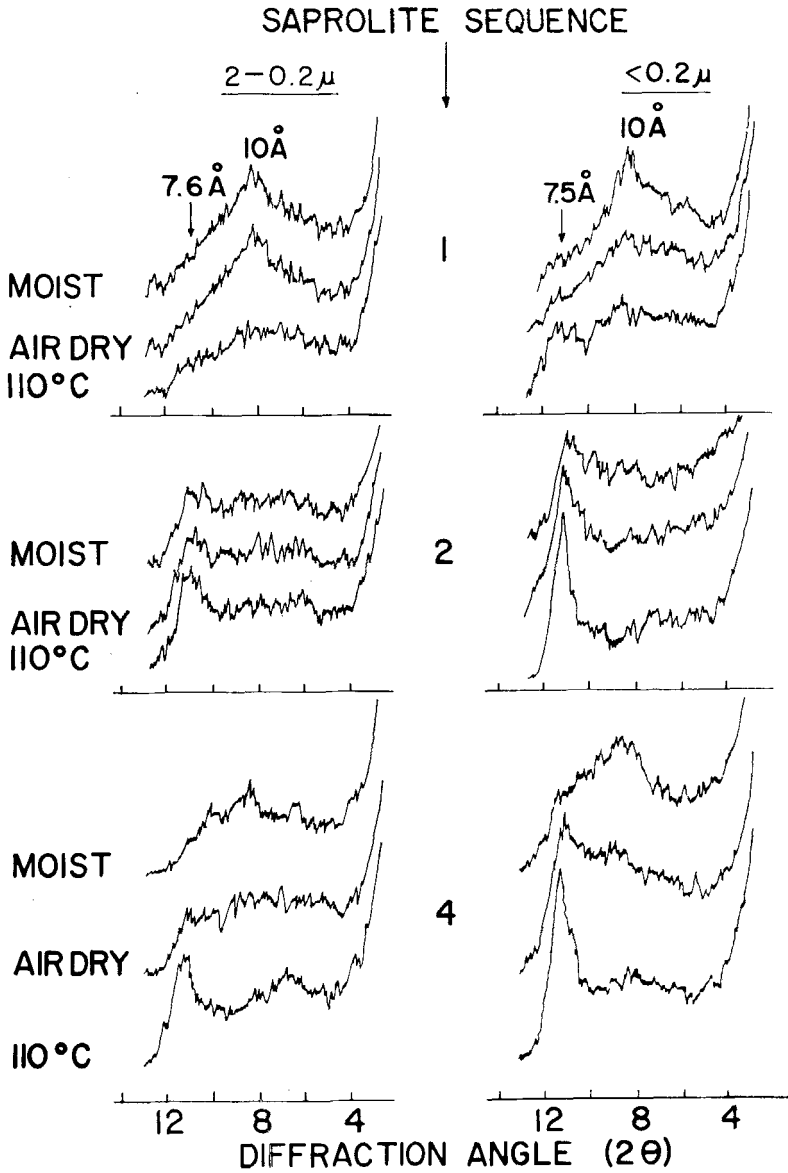


FIG. 1. X-ray diffraction patterns of Mg-saturated hypersthene andesite saprolite clays.

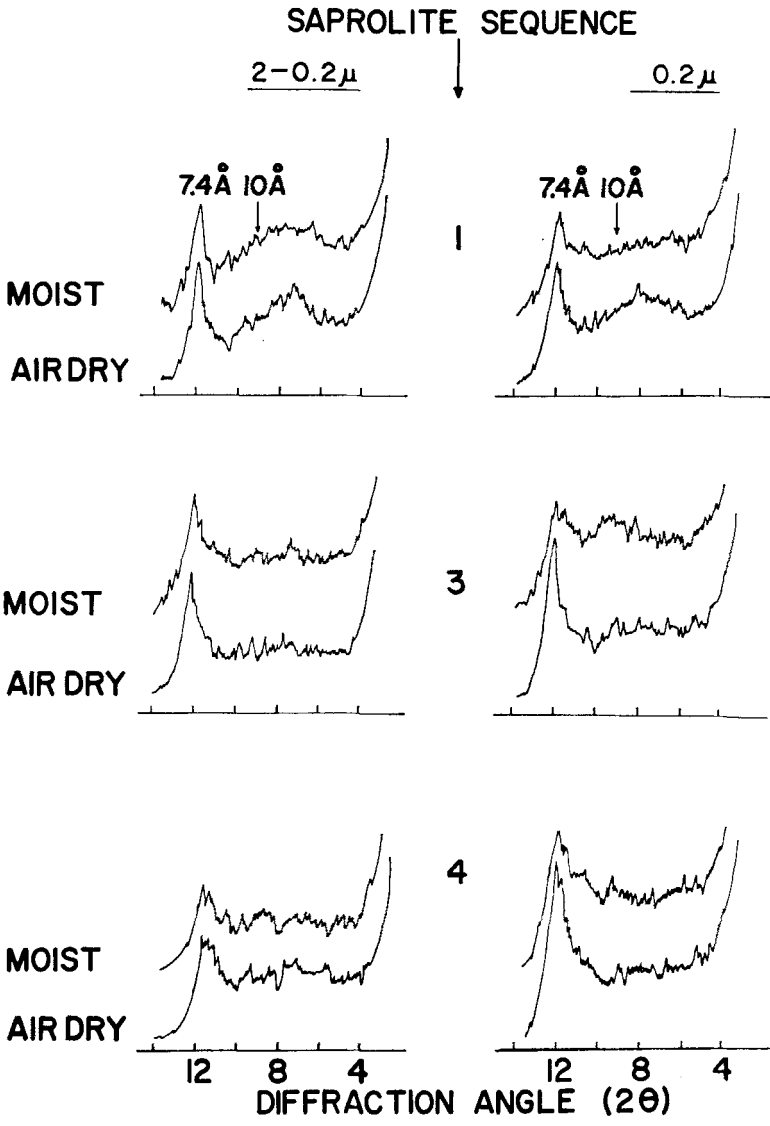


FIG. 2. X-ray diffraction patterns of Mg-saturated olivine andesite saprolite clays.

fraction than in the coarse clay fraction. The same general relationship holds for the olivine andesite saprolite samples, though the differences as exhibited by the diffraction patterns are less pronounced.

Differential thermal analysis provides further confirmation of the halloysitic nature of the saprolite clays (Figs. 3 and 4). The high-temperature endotherms at about 550°C and the low-temperature endotherms at about 120°C, indicative of halloysite, are of similar intensity and shape in corresponding samples of each saprolite series. In each series, the clay from the

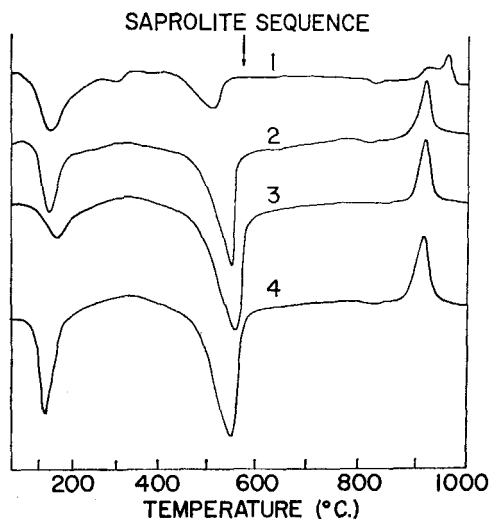


Fig. 3. Differential thermal analysis of hypersthene andesite saprolite clays ( $< 2 \mu$ ).

least-weathered saprolite yields low-intensity high-temperature endotherms. Endotherms obtained from the clays from succeeding saprolite samples are of greater, and approximately equal, intensity. The high-temperature endotherms in all cases are asymmetrical with a sharp slope on the recovery side. This characteristic has been suggested as a criterion for halloysite (Dean, 1947; Bramao *et al.*, 1952).

The low-temperature endotherms, though characteristic of halloysite, may have been contributed, at least in part, by allophane.

Further evidence of halloysite in the saprolite clays is afforded by electron micrographs of selected samples (Plate 1). The tubular forms characteristic of halloysite are much in evidence.

Electron micrographs of the hypersthene andesite saprolite clay show small spherical bodies (Plate 1*a*) similar to those described by Sudo (1954) and by Sudo and Takahashi (1956) and a few small irregular-shaped halloysite tubes (Plate 1*b*). Large, possibly amorphous, bodies, which for the most part have

irregular rounded edges, are a common constituent of the saprolite clays (Plate 1*b*). The small tubular bodies of the saprolite 2 and 4 clays are more rod-shaped like typical halloysite and they are more abundant than in the saprolite 1 clay. The spherical bodies in saprolite 2 and 4 have small protrusions which resemble halloysite tubes. These protrusions appear to be growing out of the spherical bodies. The large amorphous-appearing bodies that occur in saprolite 2 and 4 also appear to have halloysite tubes protruding from the edges. The possibility that these larger bodies may be agglomerates of halloysite cannot be discounted.

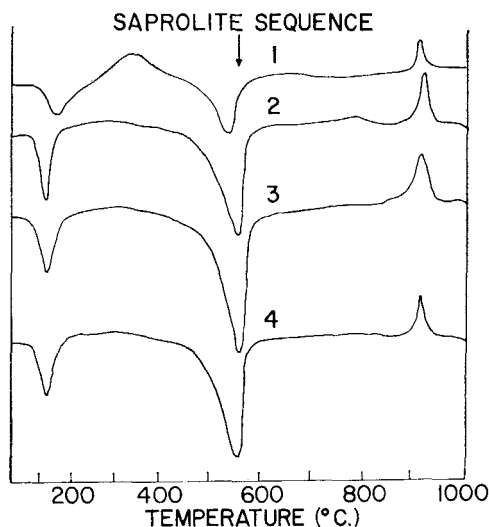


FIG. 4. Differential thermal analysis of olivine andesite saprolite clays ( $< 2 \mu$ ).

The olivine andesite saprolite clay appears similar to that of the hypersthene andesite saprolite clay, except that the small halloysite tubes are better formed and a little more abundant. Olivine andesite saprolite 3 clay (Plate 1*d*) has more small halloysite tubes than is evident in the saprolite 1 clay (Plate 1*c*). These tubes are longer and appear to be better formed than those in the hypersthene andesite saprolites. Bodies containing protruding halloysite tubes also occur in saprolite 3.

Quantitative chemical data, provided by partial elemental analysis, selective dissolution and CEC delta values, confirm the presence of halloysite and allophane in the saprolite samples. In addition, the chemical analyses confirm the presence of two different allophane components and signify trends in the relationship between the species as related to the degree of weathering within the saprolite series.

The partial elemental analysis of selected saprolite clays is presented in Table 1. It is significant, as will be discussed later, that the  $\text{SiO}_2:\text{Al}_2\text{O}_3$



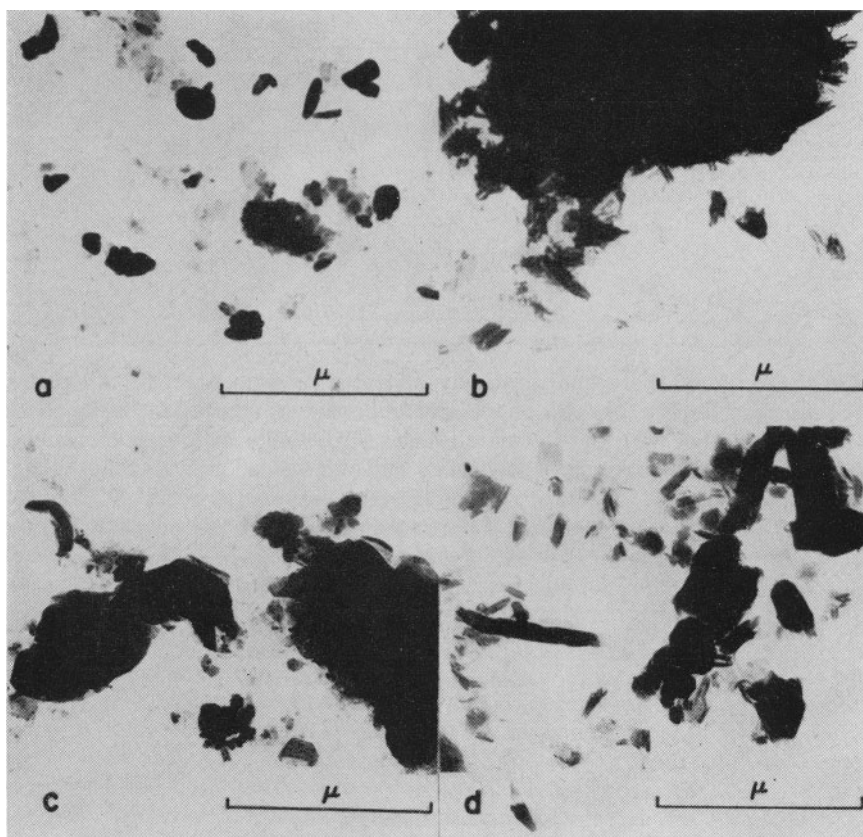


PLATE 1. Electron micrographs of saprolite clays.

- (a) Saprolite 2—hypersthene andesite
- (b) Saprolite 4—hypersthene andesite
- (c) Saprolite 1—olivine andesite
- (d) Saprolite 3—olivine andesite

molar ratios of the saprolite 1 clays in both series are less than 2. In the more weathered saprolites the ratio is greater than 2.

The  $\text{Fe}_2\text{O}_3$  reported in the analyses of these deferrated clay samples cannot be allocated to any particular species from data obtained in this study. It is interesting to speculate, however, that the iron may be incorporated within the structures of allophane and/or halloysite. Kunze and Bradley (1964) have indicated iron as a possible component in halloysite.

From data obtained by NaOH selective dissolution analysis, first after heating samples to  $110^\circ\text{C}$ , then after heating to  $550^\circ\text{C}$ , allophane and halloy-

TABLE 1.—ELEMENTAL ANALYSIS (% BY WEIGHT) OF SAPROLITE CLAYS (< 2  $\mu$ )

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	Molar SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
<i>Hypersthene andesite</i>					
1	37.2	37.0	2.7	18.3	1.79
2	42.0	34.9	3.4	15.1	2.04
3	45.1	35.3	3.5	15.4	2.17
4	41.4	33.7	4.2	15.1	2.08
<i>Olivine andesite</i>					
1	38.8	34.4	3.1	18.7	1.91
3	38.8	31.0	4.6	18.5	2.12

site, respectively, were quantitatively allocated as prescribed by Alexiades and Jackson (1966). The allophane and halloysite contents of the saprolite samples, together with the calculated SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> molar ratios as determined by the respective treatments, are shown in Table 2.

TABLE 2.—ALLOPHANE AND HALLOYSITE OF SAPROLITE CLAYS (< 2  $\mu$ )

Sample	Allophane		Halloysite	
	%	Molar SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>	%	Molar SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>
<i>Hypersthene andesite</i>				
1	47	1.28	10	1.31
2	38	1.65	33	1.64
3	37	1.71	35	1.67
4	36	1.73	34	1.81
<i>Olivine andesite</i>				
1	37	1.48	25	1.85
3	32	1.91	38	1.78

Allophane content is highest in the saprolite 1 samples in both series. Allophane decreases in the hypersthene andesite saprolite from a high of 47% in sample 1 to a low of 36% in sample 4. In the olivine andesite saprolite there is a moderate decrease in allophane from 37% in sample 1 to 32% in sample 3. The decrease in allophane is associated, in both series, with an increase in halloysite.

In addition to the quantitative changes in allophane content from the least weathered to the more highly weathered saprolites, there is a significant change in the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> molar ratios of the allophane. The ratio is 1.28 and 1.48 in the hypersthene and olivine andesite saprolite 1 samples, respectively. The ratios increase to values of 1.7 and 1.9 in the more weathered of the respective saprolites. It is of interest also that the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> molar

TABLE 3.—CEC DELTA VALUES (meq per 100 g)  
FOR SAPROLITE CLAYS (< 2  $\mu$ )

Sample	Na-acetate pH 3.5	Na <sub>2</sub> CO <sub>3</sub> pH 10.7	Delta value	Corrected* delta value
<i>Hypersthene andesite</i>				
1	59	107	48	46
2	40	49	9	3
4	32	48	17	10
<i>Olivine andesite</i>				
1	40	77	37	32
3	27	45	18	11

\* Value corrected for halloysite, assuming halloysite to have a cation exchange delta value of 18 meq per 100 g.

ratios of the halloysite approach, but do not reach, the theoretical value of 2 as would be expected in classic halloysite.

CEC delta values (Table 3) are highly significant in terms of the clay species present. The delta values are relatively high in both the saprolite 1 clays and relatively low in the other saprolite samples analyzed. According to Aomine and Jackson (1959) and Jackson (1965), the CEC delta value (taken as 100 meq per 100 g) can be used, as a first approximation, to determine the sesquioxidic allophane content of a sample. It is interesting to note in this regard that using the 100 meq per 100 g value, the CEC delta values for the saprolite 1 clays yield nearly the same allophane content as determined by selective dissolution analysis (Table 2). This does not hold true, however, for the other saprolite samples, which have allophane contents considerably higher than their CEC delta values would indicate. In the more weathered saprolites, the CEC delta values can be allocated, approximately, to the halloysite and the allophane if both the halloysite and the allophane are assumed to have a CEC delta value of 18 meq per 100 g.

The delta value data indicate that there are two types of allophane present in the saprolites. The allophane in the saprolite 1 clay of both series has low SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> molar ratio (1.3 to 1.5) and high CEC delta value (approximately 100 meq per 100 g). This fits the definition of sesquioxidic allophane (Jackson, 1965). The allophane in the clay of the other saprolite samples, on the other hand, has higher SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio (1.7 to 1.9) and lower CEC delta value that can be allocated to halloysite and to the allophane if it is assumed that this allophane has the same cation exchange delta value (18 meq per 100 g) as halloysite. This allophane conforms with the definition of halloysitic allophane (Jackson, 1965).

## DISCUSSION

Data obtained in this study support the conclusions that (1) there is a genetic relationship between sesquioxidic allophane, halloysitic allophane,

and halloysite in the andesite saprolite samples, and (2) sesquioxidic allophane, with a high CEC delta value and relatively low  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio, forms during the early stages of saprolite weathering.

Appearance of sesquioxidic allophane in the earliest stages of weathering, coupled with the observation (Hendricks and Whittig, 1967a) that plagioclase microlites and matrix glass are the first rock components to weather, suggests that the sesquioxidic allophane is a product of weathering of one or both of these rock components. Bates (1960) has suggested that the development of allophane is a logical stage in the weathering of the glass in the matrix of volcanic rocks. Aomine and Wada (1962) are of the opinion that both volcanic glass and feldspars weather directly to allophane as a step in the formation of halloysite.

Although a transformation apparently takes place between sesquioxidic allophane and halloysite and halloysitic allophane, mechanisms involved in this change cannot be established from this study. Some implications, however, can be made on the basis of the electron micrographs. In the least-weathered hypersthene andesite saprolite clay, small spherical bodies together with larger amorphous-appearing bodies exist. In the clay of the more weathered saprolite, similar bodies appear, except that halloysite-like tubes appear to be growing out of them. A similar situation exists in the olivine andesite clays, although a few small spherical bodies having tubular protrusions exist in the saprolite 1 sample as well. It is suggested that the growth of these halloysite tubes is a manifestation of the transformation from sesquioxidic allophane to halloysite. Even if the large bodies are agglomerates of halloysite tubes, rather than amorphous bodies, with tubes growing out of them, there must be some genetic relationship between the amorphous bodies without tubular protrusions and those with protrusions.

The relationship of allophane to halloysite is uncertain. A precise distinction between amorphous and crystalline clay materials is impossible because of the transitional nature of the boundary between the two, as has been pointed out by Jackson (1965). It is very likely that a complete structural gradation exists between allophane through poorly crystalline to well-crystallized halloysite. That which is determined by selective dissolution will include the allophane plus the poorly crystalline halloysite which is susceptible to attack by the NaOH treatment.

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