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FORMED FROM MAZAMA TEPHRA

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Abstract approved _____

Soil samples from the Mazama tephra deposit were collected from the AC and C2 horizons at five different locations along the axis of the main depositional lobe. The clay fraction from the samples was recovered and studied by means of chemical, x-ray, DTA and electron microscopy methods in order to characterize the nature and properties of amorphous clays forming in this relatively homogeneous parent material of known age.

Dispersion of the amorphous clays from the pumice samples was found to be difficult unless samples were first pretreated to remove iron oxides and organic matter. The dithionite-citrate-bicarbonate (DCB) iron removal treatment, however, was found to significantly alter the morphology of a reference imogolite sample by leaving individual strands of mineral coated with a gel. The comparison of DTA data from the imogolite and synthetic allophanes before and after defferation treatment also shows that significant changes in

the amorphous clays resulted from the clean up treatment. Alternate methods for amorphous clay dispersion were tried on a variety of ando soil samples. None of the methods were found to be effective for dispersing all samples. Several washings in distilled water adjusted to pH 5.0 with HCl resulted in the dispersion of most samples and was used in this study to separate the amorphous clays from the Mazama tephra.

The clays removed from the pumice samples contained from 47 to 84 percent amorphous colloids. The molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ for all the samples was generally between 1 and 2.

The types of clays found at each site studied along the transect were rather varied. Halloysite was found at all locations except one and generally was more common near the base of the pumice profile. The mineral dominated the clay fraction at a poorly drained site near the source but was absent in another similar site about 400 km away. The latter contained abundant imogolite and allophane. This difference in secondary mineralogy from the same parent material under similar weathering regimes presents an enigma. One possible explanation is based on the observation that samples of undisturbed tephra at far distances from the source contain fewer feldspars than samples near the source. The halloysite is thought to be related to feldspar weathering. Samples from drier sites along the transect had clay fractions containing predominately allophane with some few

crystals of halloysite and some imogolite. All samples had appreciable quantities of clay size glass shards. Masses of silica bodies and oxides of iron in addition to halloysite and allophane were found in the C2 horizon at the driest site.

The cation exchange capacities of the clay samples were highly pH dependent. All samples had appreciable anion exchange capacities at pH 4.0. The DCB treated samples had CEC values much higher than non-treated samples. The magnitude of CEC for the synthetic gels depended on their composition and was highest when the molar $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio was about 4.0.

The clays sorbed large amounts of phosphate. The samples highest in the amorphous gels generally sorbed more phosphate than samples containing halloysite.

All the clays had weak acid buffering curves. Most samples had two distinct buffering ranges, one at low pH and one at high pH. The curves for the samples highest in halloysite were buffered at much higher pH values than samples containing mostly amorphous clays.

The nature and properties of the amorphous clays in the Mazama tephra were found to be similar to those reported by Japanese and New Zealand workers for other volcanic tephra deposits.

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Formed from Mazama Tephra

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THE NATURE AND PROPERTIES OF AMORPHOUS COLLOIDS FORMED FROM MAZAMA TEPHRA

I. INTRODUCTION

Vulcanism has been the major contributor of soil parent materials in the Pacific Northwest region of the United States. Eruptions have occurred sporadically throughout this sector since the paleocene epoch producing numerous cubic miles of pyroclastics (Baldwin, 1964). Consequently, most of the soils found in Oregon have been formed directly from volcanics or have had significant quantities of tephra added to them from showers of ash and lapilli. Furthermore, diagenesis of these pyroclastics in the pedosphere generally results in the production of copious quantities of colloidal amorphous alumino-silicates. The abundance of these non-crystalline clays in many of Oregon's soils imparts to them properties which are unique when compared to soils of non-volcanic parent materials. Therefore, the soils in this region of the United States have more in common with those of other circum-Pacific countries rather than more eastern parts of this country where volcanic parent materials are lacking.

During the past 20 years much work has been done to seek a better understanding of the complex amorphous clay system. Most of the effort has been concentrated in countries other than the United States, however. The clay mineral studies by American scientists

have been directed toward the identification of crystalline clays by x-ray diffraction techniques after the amorphous phases have been removed by selective dissolution in boiling 0.5 N NaOH (Jackson, 1956; Dudas and Harward, 1971). The method greatly improves x-ray patterns but does not yield much information about the amorphous clays. Recent studies indicate that amorphous clays compose up to 90% of the colloidal fraction in some Oregon soils (Chichester, 1967; Dudas, 1972). These reports do not disclose the types of amorphous clays found nor if they resemble those from New Zealand and Japan.

Since many of Oregon's soils contain significant quantities of amorphous clays, knowledge about the types present and their associated properties would seem desirable. The information gained would be of benefit in evaluating and predicting soil behavior when utilized for a variety of agricultural forestry and urban purposes. However, the study of this soil phase is not an easy task due to its highly reactive nature and its complex association with other soil components usually from mixed origins. On the other hand, the relatively homogeneous Mazama tephra deposit provides an ideal soil parent material to aid in the understanding of amorphous clays. It is the largest superficial geologic deposit in Oregon of known age and uniformity. Once the nature and types of amorphous clays in the Mazama tephra are understood it should be much easier to study those found in more complex soils.

A disquisition was initiated to seek more information on amorphous clays in the Mazama tephra with the following objectives:

1. To develop a method for obtaining amorphous clays in a form suitable for characterization studies.
2. To determine what types of amorphous clays are found in soils developed on the Mazama tephra and if they are morphologically similar to those reported in Japanese soils.
3. To assess some of the chemical properties of the Mazama Clays.

This dissertation will be organized in chapters discussing each of the above objectives.

II. PRELIMINARY STUDY: SEPARATION OF AMORPHOUS CLAYS FROM WEATHERED TEPHRA

Introduction

Separation of amorphous clays from soil in suitable form for characterization studies has not proven to be an easy task. Perusal of available data from different researchers indicate that the nature of amorphous clays can be greatly influenced by how a given sample was treated. For example, the cation exchange capacity of ando soils is abnormally subject to variations in index ion concentration and the kind, volume and water content of the washing solution (Birrell and Gradwell, 1956; Wada and Harada, 1969). Furthermore, treating samples of ando soil with pH 3.5 NaOAc or 2% Na_2CO_3 and subsequent determinations of cation exchange capacity resulted in over 100 meq/100 g difference in value. This procedure has been suggested as an indirect means of determining the presence of allophane (Aomine and Jackson, 1959). It has been observed that the temperature at which CEC measurements are made can cause more than a twofold difference in results (Wada and Harada, 1971). The peaks on a differential thermogram of amorphous clays will vary in magnitude and position depending on cation saturation (Miyachi and Aomine, 1966). Also changes in particle size, pH, and carbon content have been shown to significantly modify differential thermograms of

amorphous clays (Campbell, Mitchell and Bracewell, 1968). Peroxidation treatment for organic matter removal causes a near loss in the diagnostic high temperature exothermic peak of allophane. The same peak could be reduced in height and sharpness by decreasing the degree of hydrogen saturation on water dispersed clays. Restoration of the high temperature exothermic peak could be achieved by acid washing the previously alkaline treated clays. Consequently, pretreatments may be responsible for many of the anomalies reported for non-crystalline clays by different workers.

For the most part, clay mineralogy techniques have been somewhat standardized for crystalline clay analysis. On the other hand, standardized methods for amorphous clay studies are lacking and need to be implemented to facilitate data comparisons. It is the purpose of this chapter to determine what morphological changes occur in amorphous clays by some of the pretreatments used for separation and to develop a method of obtaining these colloids in a form suitable for measuring their "true" properties.

Review of Literature

Methods used to separate amorphous clays from soils vary considerably among researchers. In New Zealand Fields and Schofield (1960) have used pH 10.8 NaOH to effect dispersion and subsequent recovery of these colloids. Organic matter destruction

with peroxide followed by dilute NaOH dispersion was used by Birrell (1961a, b). Yoshinaga and Aomine (1962a, b) discovered that some soils contain both allophane and imogolite in the clay fraction and further proposed a method to separate the two phases for individual study. Their technique consisted of the following steps:

- A. Removal of organic matter with H_2O_2 ;
- B. Removal of amorphous iron with Dithionite-citrate-bi-carbonate treatment--DCB;
- C. Boiling in 2% Na_2CO_3 for five minutes followed by a differential dispersion first at pH 10.5 then 3.5.

The alkaline dispersed fraction contained only small amounts of imogolite as noted in their electron micrographs. On the other hand, x-ray diffraction data did not support their conclusion that imogolite would always be preferentially dispersed in pH 3.5 HCl. Later Aomine and Egashira (1968) outlined a flocculation method as a possible way of obtaining relatively pure allophane and imogolite from mixtures. Their data indicates that allophane remained flocculated while imogolite dispersed in dilute slightly acid NaCl. The technique, was not found to be successful for all soil samples. Other workers have tried ultrasonic vibration to disperse the clay fraction from soils. The technique seems to work well for all types of soils except those high in amorphous clays (Genrich and Bremner, 1972). The method has a disadvantage, in that sand and silt particles may be

reduced to clay size (Kanno and Arimura, 1967). The method was used by Russel et al. (1969) to obtain the <2 micron fraction from some Ando soil samples. They further attempted to concentrate the imogolite from the total clay of these samples by selective dissolution of the allophane phase with warm 0.5 N NaOH. Furthermore, they reported that allophane could be obtained in pure form by differential dispersion at pH 3.5. This procedure differs from that outlined by Yoshinaga and Aomine (1962a, b) in that they reported allophane dispersed only in pH 10.5 NaOH. Electron micrographs published with Russels paper show the allophane fraction to be a mixture containing much imogolite. The reason for this discrepancy between investigators is not apparent.

Another technique that has been employed to recover amorphous clays from soil samples makes use of a continuous particle electrophoretic cell (Park, 1969). His x-ray data shows that an amorphous and crystalline fraction could be separated from at least one soil. The amorphous phase recovered appeared to be allophane, but its purity was not ascertained. He concluded, however, that the amorphous material was a hydrolysis product of montmorillonite weathering. The sample studied had received both H₂O₂ and DCB pretreatments which may have influenced his results.

The techniques used to separate the amorphous clay have generally included some form of pretreatments to remove organic

matter and iron coatings. What affect these have on the amorphous clays has not been completely established. Nevertheless, dispersion of Ando soils is often difficult if some form of chemical treatment is not imposed. For many samples, dispersion occurs only after they have been treated with both H_2O_2 and DCB. Procedures for the separation of amorphous clay are not consistent among workers, but sample pretreatments with H_2O_2 and DCB, as an aid in dispersion, have been consistently employed.

Materials

Two soil samples and a synthetic gel were used to evaluate the effects of organic matter destruction with hydrogen peroxide and iron removal with DCB have upon amorphous clays. The first soil sample was from a site in Japan that is reported to be high in imogolite. The sample was collected by M. E. Harward on field trip F to Kyushu in conjunction with the 1969 International Clay Conference from an ash deposit previously studied by the Japanese. A slightly weathered sample of ash from the Mazama deposit in Oregon was used as another test sample. Synthetic gels of varying silica and aluminum compositions were used as known standards. The gels were prepared by the slow hydrolysis of tetraethylorthosilicate and aluminum isopropoxide as outlined in Chapter IV.

A variety of soil samples from Oregon, Hawaii, Japan and

Costa Rica were also used to determine the effectiveness of several conventional methods on clay dispersibility.

Methods

The samples used for the pretreatments study were divided into three equal parts, with the first being used as a check. The second subsample of each was treated with H_2O_2 on a hot plate overnight then dispersed in distilled water. All the clay fraction could not be removed from the samples receiving this treatment. Repeated washings up to about 20 times were needed to recover sufficient material for analysis. The third subsample was first treated with H_2O_2 followed by one defferation treatment using DCB as outlined by Jackson (1956). Samples treated in this fashion dispersed well in distilled water.

The electron microscope was used to observe morphological changes that occurred in the samples as a result of chemical pretreatment. The less than 53 micron fraction was placed on carbon coated grids for observation. Nine different fields of view were recorded for each sample using a Hitachi HU-11A electron microscope operated at 100 KV and 20 microamps beam current.

DTA patterns were run on the <2 micron fraction of each sample. The DCB extract from the synthetic standards was analyzed for Si and Al by atomic absorption. A dispersibility study using cold

dilute Na_2CO_3 , boiling 2% Na_2CO_3 , pH 3.5 HCl, ultrasonic vibration and distilled water was performed on subsamples of several ando soils. The effectiveness of a given method was ascertained by measuring the amount of clay recoverable after sample treatment.

Results

Pretreatment Effects on Amorphous Clays

Electron micrographs of the non-treated imogolite rich sample from Ksushu show an intricate mass of interwoven threads with a few grains of iron oxide (Plate 1). Individual strands of imogolite range in size from about 50 Å to 100 Å in diameter. Some large bundles of fibers are 600 Å or more across.

The peroxide treatment did not seem to drastically alter the imogolite morphology. On the other hand, small particles of iron oxide are more abundant here than in the non-treated sample and seem to be oriented along the imogolite strands (Plate 2). The oxides of iron have a similar morphology to those identified with the aid of an electron microprobe on other samples (unpublished data by R. C. Jones, University of Hawaii) and are similar to those reported by Beutelspacher (1968). It was not possible to determine if the association of iron oxide particles with imogolite strands was one of coincidence or whether some bonding was involved. Judging from their

Plate 1. Electron micrograph of the sample from Kyushu, Japan dispersed in slightly acid distilled water (top), and after the DCB treatment (bottom).

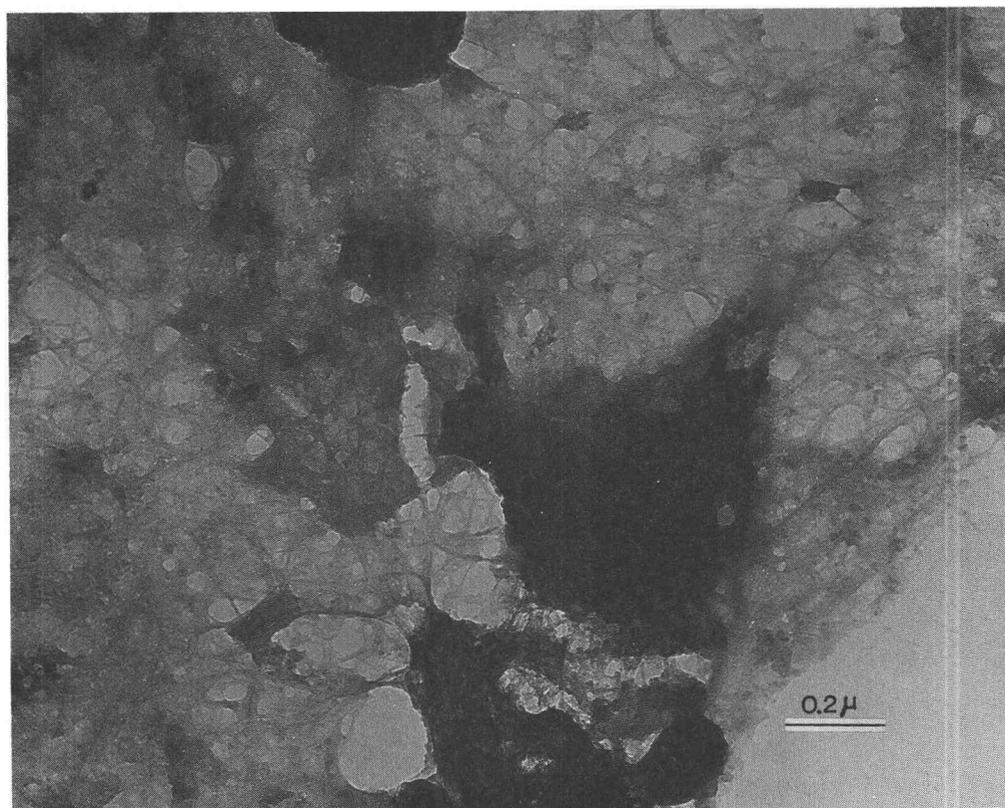
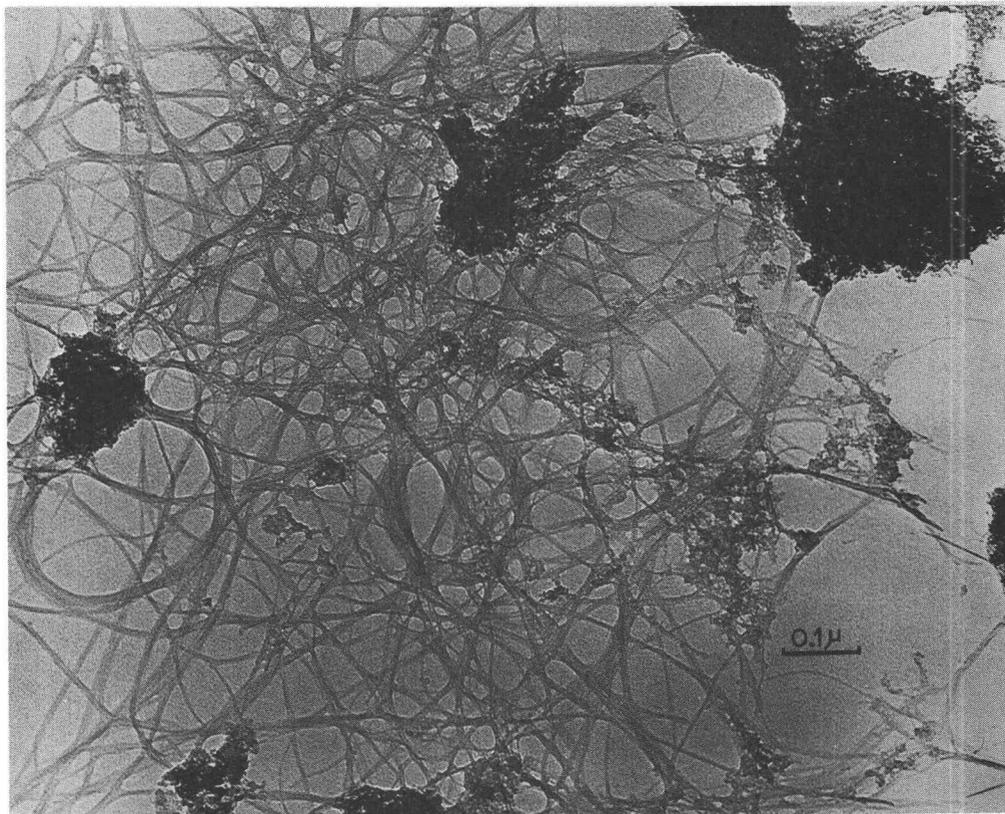


Plate 2. Electron micrographs of the Kyushu sample
treated with H_2O_2 .

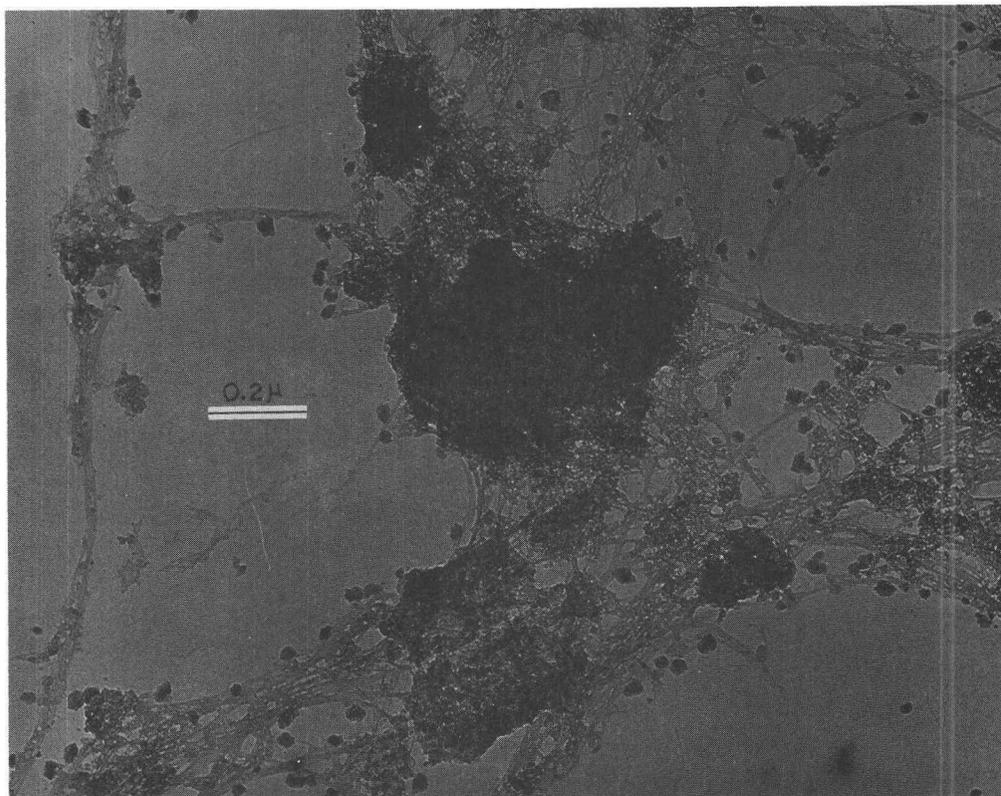
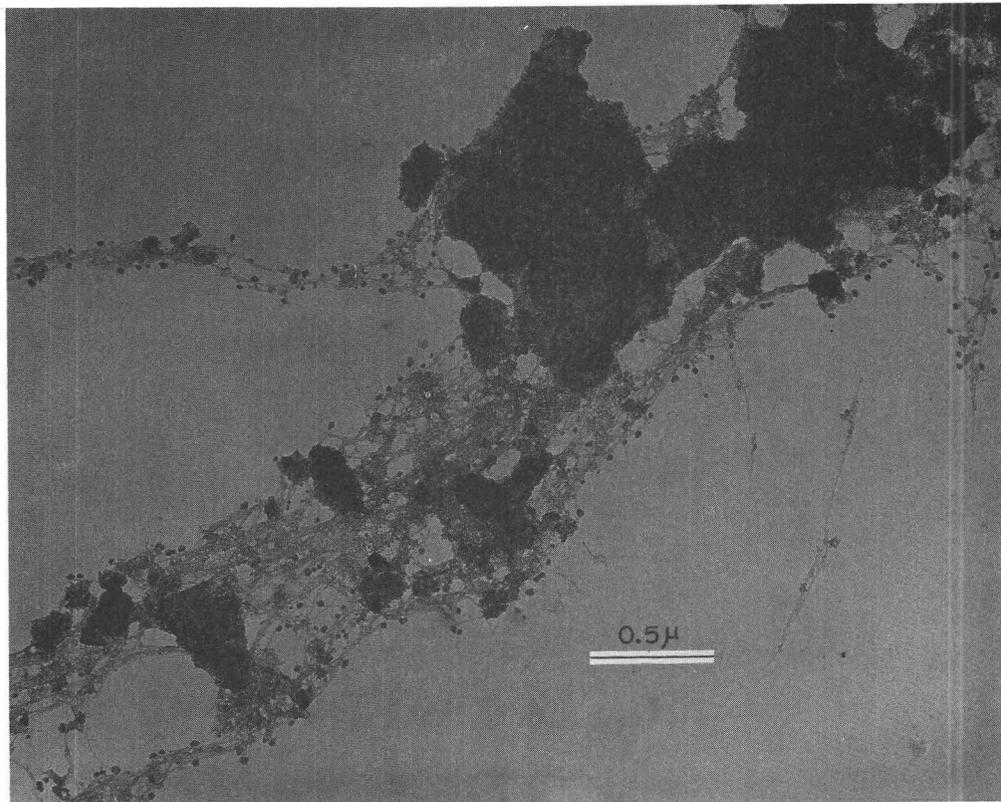
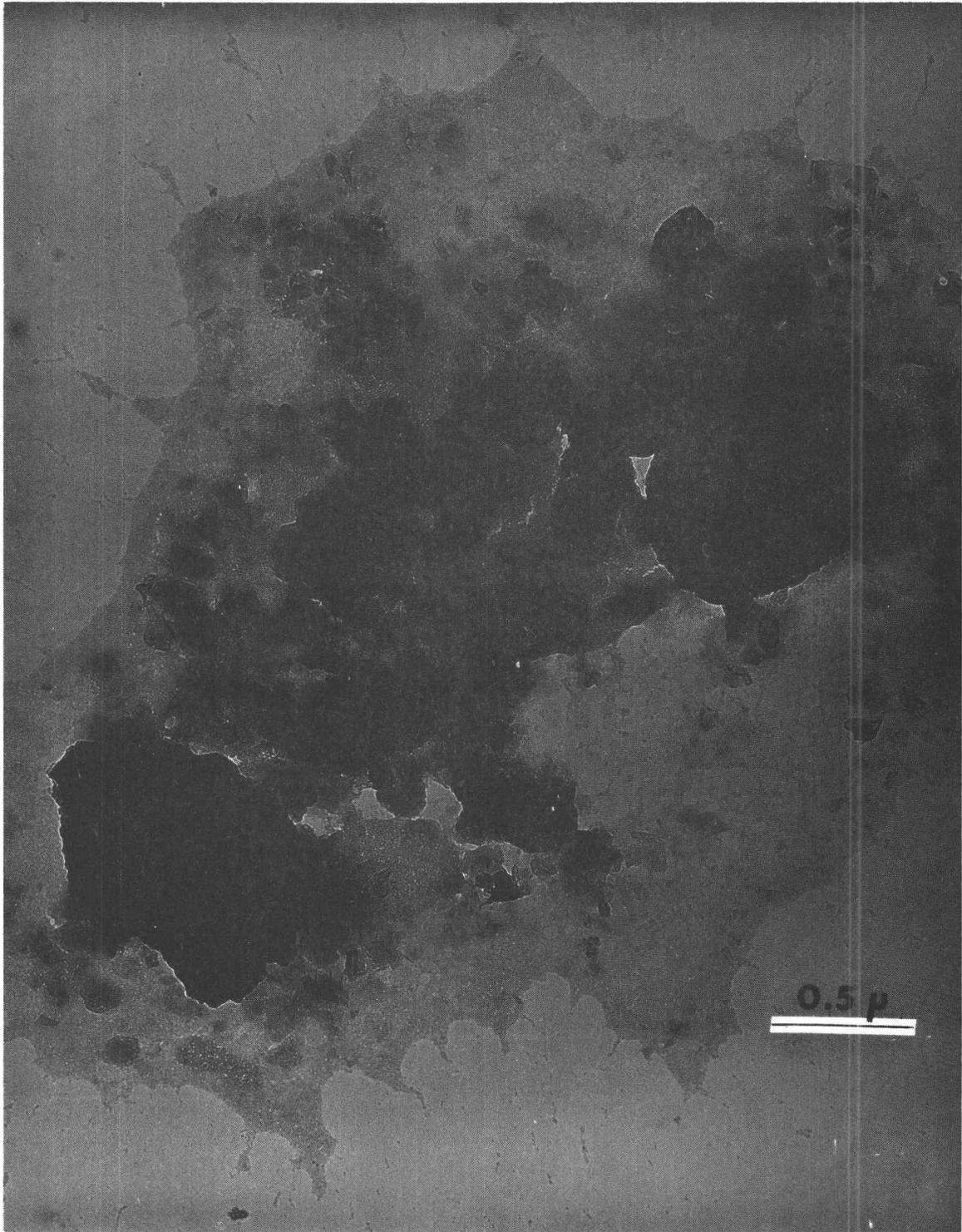


Plate 3. Electron micrograph of the Ochoco Butte sample
after treatment with H_2O_2 and DCB.



proximity and orientation to the strands the latter may be actually occurring.

The imogolite subsample receiving both H_2O_2 and DCB treatment was morphologically changed (Plate 1). Copious amounts of gel material seems to be formed from these chemical treatments.

The Mazama sample gave results which were generally similar to those on the Kyushu samples. The untreated sample contains some gel material. However, after the H_2O_2 and DCB treatment all particles seemed to be covered by even larger amounts of gel (Plate 3).

The synthetic allophane samples did not seem to change morphology as a result of the pretreatments but did lose significant amounts of aluminum as a result of the DCB extraction (Table 1). The gels were not destroyed by the treatment but did show significant changes in DTA curves (Figure 1). The most noticeable difference was the presence of an endotherm in all the treated samples between 457 and 504 degrees centigrade. The Kyushu imogolite sample, on the other hand, lost the intermediate DTA endotherm after treatment. The reason for the development of an intermediate endotherm in the gels after DCB treatment is not known but may have been due to further crystallization. The loss of the endotherm for the reference imogolite sample was probably due to the gel material obscuring the dehydroxylation.

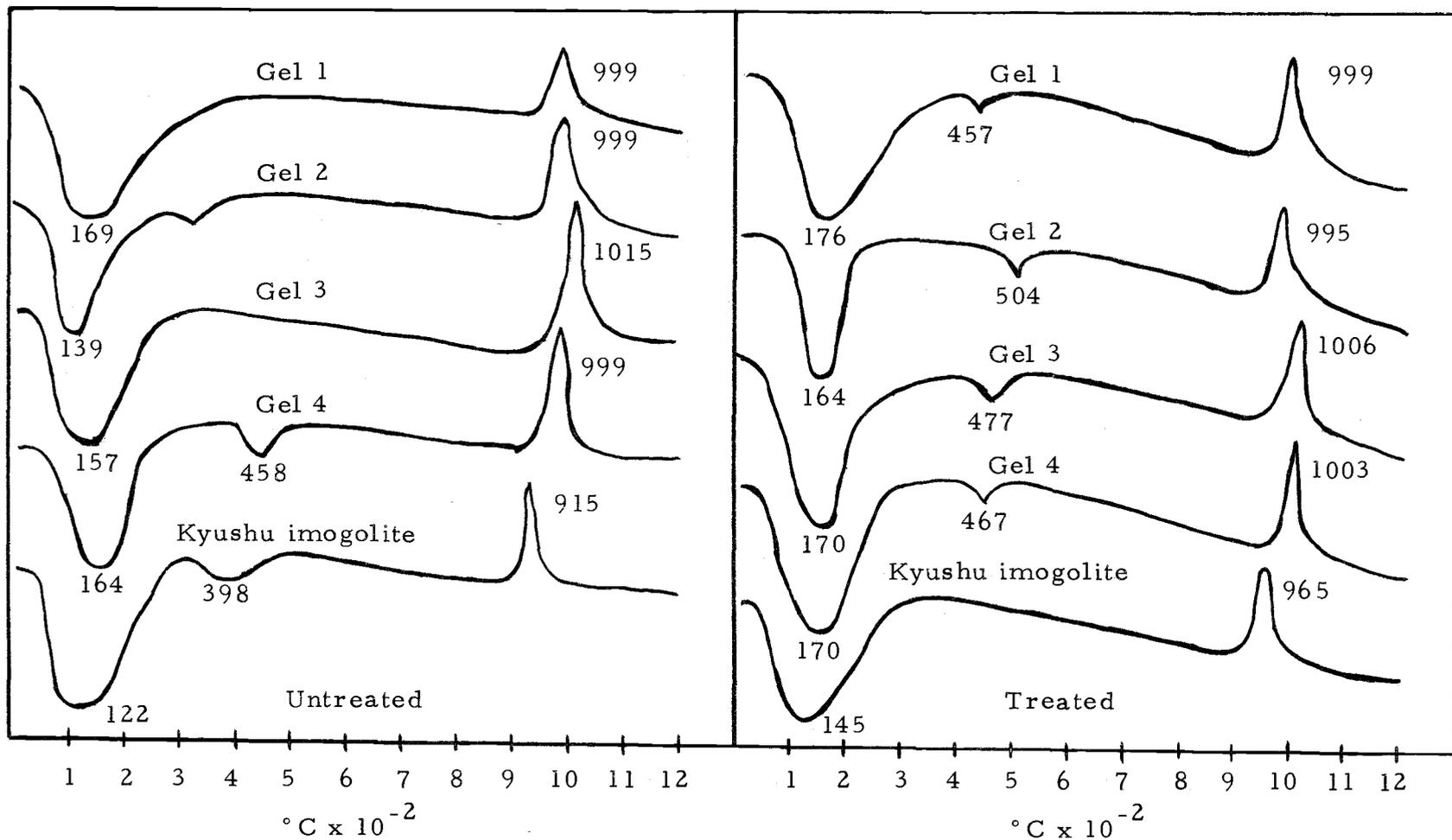


Figure 1. DTA curves of synthetic gels and Kyushu imogolite before and after one defferation treatment with DCB.

Table 1. The amounts of Si and Al removed from synthetic allophanes by one defferation treatment with DCB.

Gel	Composition		Extract Analysis		S/A
	% SiO ₂	% Al ₂ O ₃	mg/g Si	mg/g Al	
1	28.4	61.2	9.6	42.9	.22
2	45.3	44.7	6.2	26.2	.23
3	62.2	27.1	6.7	19.2	.35
4	80.1	10.6	8.3	24.3	.34

Dispersion Study Results

None of the dispersion methods were found to be effective for dispersing all the ando samples, although each procedure did result in the dissipation of some samples. Large floccules generally formed in each sample especially after vigorous stirring. Differences in DTA patterns were not observed for samples dispersed by two or more of the methods particularly when prepared identically for the analysis. The most effective method found for dispersing most of the ando samples was slightly acid distilled water. A supernatant pH between 5 and 6 was generally the most ideal. Even under these conditions vigorous stirring would cause flocculation in some samples. This acid medium was used on samples from all the Mazama sites studied and was effective in dispersing all except the Andies Prairie C2 horizon. This particular sample eventually formed a stable suspension after many repeated washings with gentle stirring.

Summary and Conclusions

Procedures used to obtain amorphous clays from Ando soils have involved various combinations of "clean up" treatments and differential dispersions. Electron micrographs indicate that the commonly used DCB iron removal treatment results in significant changes in the clay fraction of Ando soil samples. DTA patterns on both synthetic allophane and reference imogolite support these conclusions. The defferation treatment removed large amounts of aluminum from the synthetic allophane, although one treatment did not completely destroy the colloid.

When it is important to know more about the true nature of the amorphous colloids in a given sample, the DCB iron removal treatment should not be used. Alternate methods with less drastic effects on the amorphous clay need to be utilized. Ideally the procedure followed should meet the following requirements:

- a. It should be rapid,
- b. It should not induce changes in the morphology, composition, and properties of the amorphous clays.

Dispersion in pH 5.0 HCl may be the best way of separating amorphous clays from Ando soils with minimum alteration. Vigorous chemical pretreatments will have to be avoided if the "true" properties of the amorphous clays are to be studied.

III. AMORPHOUS CLAYS IN THE MAZAMA TEPHRA

Introduction

The Mazama pumice is the most extensive of all known tephra deposits in Oregon and provides a near ideal soil parent material for initial studies on amorphous clays. The pumice was deposited on at least two-thirds of the state and is found in various stages of weathering. Clay mineral studies on several soils formed from the tephra indicate that the <2 micron fraction is composed of up to 93% amorphous colloids (Chichester, 1967; Dudas, 1972). Their studies revealed that the crystalline clay fraction contained smectite, vermiculite-chlorite and hydrated halloysite. On the other hand, little is known about the variety of amorphous clays that dominate the colloidal phase of the deposit. This chapter will deal with the following questions. What morphological types of amorphous clays are found in the Mazama tephra? How do the amorphous colloids compare to those reported in the more classical allophanic soils of Japan?

Description of the Tephra and Sampling Sites

The distribution and composition of tephra from Mount Mazama has been described by Williams (1942). The deposit is classified mineralogically as a glassy, hypersthene-augite, dacite with accessory hornblende. Major element composition of unweathered tephra

is shown in Table 2. Trace element chemistry of glass and phenocryst fractions have been determined by Borchardt (1970) and Dudas (1972) for a host of locations throughout Oregon. Clay mineral studies by Chichester (1967) and Dudas (1972) show that amorphous alumino-silicates represent greater than 70% of the total clay based on dissolution by boiling 0.5 N NaOH. The 2:1 crystalline clays in the deposit can be accounted for as contaminants from either paleosol mixing or as part of the lithic fragments present (Dudas, 1972). The authigenic formation of hydrated halloysite in the deposit has been reported by Tidball (1965) and Dudas (1972). The amount of weathering taking place in well drained sites of the Mazama tephra is remarkably small when one considers that it was deposited about 6600 years before present as dated by Rubin and Alexander (1960).

In order to determine the nature of amorphous colloids forming in the Mazama tephra, an assortment of samples were selected from a range of weathering environments in Oregon containing relatively undisturbed pumice. Samples were taken along the northeastern transect from Crater Lake parallel to the axis of the main depositional lobe. The sites (Figure 2) selected were those used by Borchardt (1970), Rai (1971) and Dudas (1972) for other studies relating to the Mazama deposit. Specific locations for each soil profile studied is also given (Table 3).

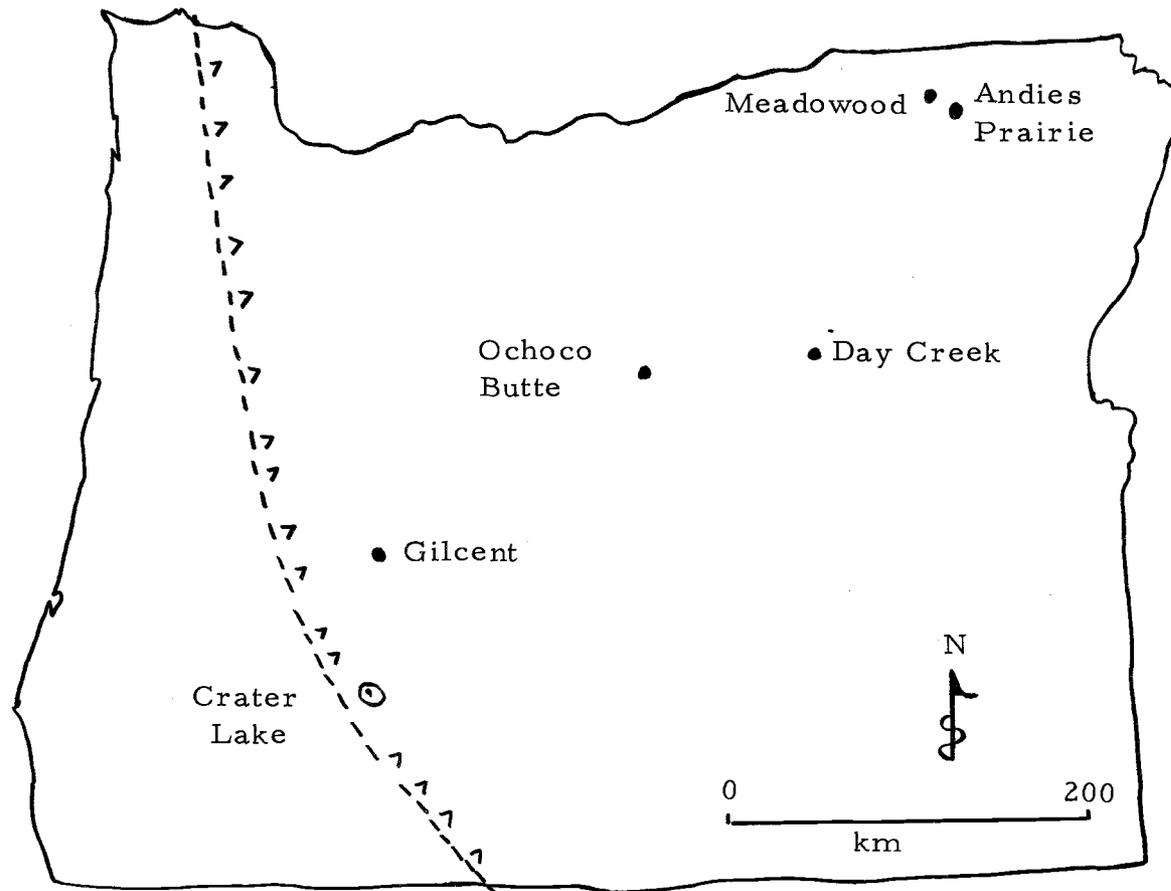


Figure 2. Site location and distribution of Mazama tephra in Oregon.

Gilcent GC¹

The Gilcent site is the most intensely weathered tephra profile along the transect. The pumice has filled an old broad abandoned stream channel of the Little Deschutes River and remains saturated with water throughout the year as a result of a high water table. The lapilli has retained much of its original shape but is easily deformed into fine slippery non-sticky gel like mass by gentle pressure between fingers. In contrast, adjacent well drained profiles contain little clay and show only small evidence of weathering near the soil surface. The tephra profile in the stream channel is thicker than adjacent ones but does not show much evidence of post depositional disturbances. The area receives about 48 cm of annual rainfall with most coming as snow during the winter months. The summers are very warm and dry from April through November (Johnsgard, 1963). The vegetation at this site as well as all others in this study is dominated by coniferous forest.

Ochoco Butte OB

This site is located in the Ochoco mountains east of Prineville, Oregon and 215 km from Crater Lake. The tephra is composed of

¹Two letter symbols will be used in the text to designate sites.

sand size and smaller particles. In this vicinity the ash is most often found in broad ridge tops or north facing slopes and associated with timbered ground cover (Rai, 1970). The ash is in a very early stage of weathering with most particles having some iron oxide stains. Most of the 48 cm of annual precipitation comes in winter as snow with summer being warm and dry from May to September (Johnsgard, 1963). A profile description of this site is given in the Appendix.

Day Creek DC

The Day Creek profile is very similar to Ochoco Butte, except that particle size has decreased at the greater distance. The area receives slightly less rainfall during winter but is much dryer than Ochoco Butte from April to October. The amount of weathering of these two sites should be minimal for soils developing in the Mazama Ash.

Meadowood MW

This site is located about 445 km from Crater Lake and is composed of very fine ash mixed with some loess. The area receives about 88 cm of precipitation with most coming as snowfall. The summers are warm and very dry during July and August. Even though more weathering has occurred here than at the DC and OB sites, soil horizonation is still only slight. A detailed soil description of this

site is in the Appendix.

Andies Prairie AP

The Andies Prairie profile is located about 5 km to the east of the MW site near the edge of a small bog and remains saturated with water throughout the year. The ash layer in the bog has been verified to be from Mt. Mazama (Borchardt, 1970). This site is the most weathered of any profiles found in the vicinity, and appears to be the least disturbed since deposition.

Materials

About five kilograms of tephra was carefully removed from both the AC horizon and from near the pumice paleosal contact at each site.² Samples were placed in plastic bags and stored at 5° C until used. A small amount of undisturbed air fall tephra was taken from each location for thin section study with the petrographic microscope.

Methods

The <2 micron fraction was separated from each sample by dispersion and centrifugation in distilled water adjusted to pH 5.0.

²The fine lower layer of material will be designated as C2 to distinguish it from the coarse surface C1 layer, to be consistent with the symbols used in other studies on the Mazama tephra.

The clays were sodium saturated, dried at 50° C and stored for subsequent analysis. The amount of amorphous clay in each sample was estimated by KOH dissolution procedure outlined by Dudas and Harward (1971). Carbon content was obtained with the aid of a Leco carbon analyser. DTA data were acquired with a Dupont 1200 thermal analyser equipped with micro-cup sample holders and matched platinum-platinum 13% rhodium thermocouples. The analyses were made on the <2 micron fraction using Al_2O_3 as a thermal reference and N_2 as an inert atmosphere. All samples were saturated with sodium and equilibrated at 54% relative humidity prior to analysis. X-ray diffractograms were obtained from a <53 micron random oriented fraction using a Phillips diffractometer and a curved crystal monochrometer.

Petrographic thin sections were made from samples of undisturbed air fall tephra at each location with the direction of orientation parallel to airfall. All sections were lapped to a 30 micron thickness. Constituent identifications were made using techniques outlined by Kerr (1959).

Samples used for observation with the TEM were prepared by first wet sieving at 53 microns.³ About 5 ml of this silt and clay fraction was adjusted to about 0.1% suspension in distilled water.

³ Transmission Electron Micrographs obtained with cooperation and courtesy of Dr. R. C. Jones, University of Hawaii. Soils Department.

This sol was placed in a clean glass de Vilbiss bulb connected to a nitrogen gas source by a rubber tube and flow regulator. Approximately two pounds flow pressure was used to atomize the suspension. Carbon coated grids were held in the fog from the atomizer to collect a random distribution of particles from each specimen. The carbon support films were prepared by first covering the copper grids with a colloidion film then depositing about a 100 Å thick layer of carbon on the plastic. The plastic film was then removed by dissolving in reagent grade acetone. The above method is similar to that suggested by Kay (1965). The grids were viewed with a Hatachi HU-11A TEM operated at 100 KV and 20 micro-amps beam current. Nine or ten random fields of view were recorded on glass plates for each sample. The beam was on a given field of view only long enough to obtain a photograph normally one minute or less. This was done in order to minimize sample contamination and heating by beam-sample interaction. Interpretations were made subsequently by examination of photographs.

Definitions and Criteria

The types of colloids in the Mazama transect soils are far more complex than had originally been suspected. In order to summarize the types of clays observed by the three different methods, it is necessary to consider the definitions and criteria used in the interpretations.

Allophane is considered to be the gels that have no recognizable structure as observed by the TEM analysis. Justification for this definition is based upon the following. To date a unique definitive criterion has not been established that unequivocally characterizes this material. The absence of x-ray diffraction maxima is not sufficient to establish that allophane is present because other components such as glass shards may show no diffraction. Infrared spectra may not indicate that allophane is present in a given sample since a small amount of well crystallized components having strong adsorption bands can obscure the more diffuse bands of more poorly ordered species, even though the latter may be the major part of the sample (Farmer, 1968). DTA data is not ideal either in that other components in the heterogeneous soil system may obscure diagnostic thermal patterns for allophane (McKenzie, 1955). Allophane in the presence of halloysite or imogolite is probably not detectable with DTA. Electron microscopy is not entirely diagnostic for allophane. The electron micrographs published by Grim (1968) and those of Beutelspacher (1968) of allophane have little resemblance to each other and may represent different soil components.

Several paradigms have been proposed for allophane since it was defined by Ross and Kerr (1934). These have included comparisons to silica-alumina petroleum cracking catalysts for aluminum coordination (Birrell, 1962) and charge properties. Measurements of

aluminum and silicon coordination number in synthetic amorphous silicoaluminas under controlled conditions revealed that all the aluminum was tetrahedrally coordinated when it made up less than 30% of the gel. Samples rich in aluminum on the other hand, had only octahedrally coordinated aluminum which became tetrahedrally coordinated upon dehydration (Leonard et al., 1964). Previously de Kempe et al. (1961) showed that negative charge was greatest in gels having 20 to 30 percent Al_2O_3 . The more basic the pH the greater the charge and more aluminum was found in tetrahedral coordination. Wada (1967) suggested the existence of two end members of allophane with chemical composition of $2\text{SiO}_2\text{-Al}_2\text{O}_3\text{-3H}_2\text{O}$ and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-xH}_2\text{O}$. He proposed a double chain structure in which the chains were composed of tetrahedral silica sharing corners with an aluminum octahedra. His model does not adequately explain the charge characteristics of allophane, especially its anion exchange property. He ascribes all CEC to pH dependent silanol and aluminol dissociation. This model may more nearly describe the mineral imogolite. The synthetic allophane prepared in this study (to be discussed in Chapter IV) resulted in essentially the same DTA patterns for gels having a wide range in composition. The homogeneity of the synthetics could not be determined and it is not known what other phases may have been present. Therefore assigning a definite composition to the gel may not be an ideal way to describe this soil component since it seems to

possess only short range order. Attributing a diagnostic morphology other than gel may not be meaningful at this time due to uncertainty of changes in the gel due to vacuum desiccation and electron beam interaction with this hydrous non-ordered alumino-silicate. For these reasons all the non-ordered gel material in these samples will be considered as allophane when the DTA pattern shows only a low temperature endotherm and a high temperature exotherm (Van Olphen, 1969). Imogolite will be used to describe the fiber morphology seen for a colloidal constituent of these soils. Specific x-ray and DTA data have been established for the mineral (Wada and Yoshinaga, 1969). Similar data could not be obtained from the small amount of fibers present in the Mazama samples.

The criteria used for the identification of halloysite have been well established (Brown, 1953; McKenzie, 1957; Grim, 1968). The mineral will collapse from 10 \AA to 7.4 \AA upon drying. DTA patterns show large endotherms at 130°C and 500°C with a sharp exotherm at 925°C . Electron micrographs show individual crystals to be rolled rods. Other crystals have a coiled disk shaped morphology (Sieffermann and Millot, 1969).

Results

Clay and Carbon Content

The amount of clay recovered from the Mazama samples by dispersion in slightly acid distilled water was generally less than six percent (Table 4). Two samples, GCAC and MWAC, were notable exceptions in that they had 16.2 and 9.1 percent clay respectively. Weight loss by dissolution in 1.0 N KOH ranged from 46 to 84 percent. The amount of carbon present in the clay fraction was always higher in the AC horizon at every site and ranged from 0.28% at the GC site to 10.8 at Andies Prairie. The C2 samples at all sites contained nearly 2.0 percent carbon regardless of depth.

Diffraction Analysis

The x-ray diffractograms of random oriented samples show that all sites contain some crystalline components (Figure 2). The patterns for Andies Prairie C2 and the Ochoco Butte AC horizon samples show quartz as the only crystalline phase present. All other patterns have reflections for quartz, feldspar and phyllosilicates. These components have been identified in other studies (Dudas, 1972) and will not be elaborated on here. All samples except those from the GC site exhibited a large increase in background scatter at angles corresponding to $<7 \text{ \AA}$ spacing. This increase in background scatter has

Table 4. Horizon, depth, carbon and clay content from selected Mazama sites.

Location	Horizon	Depth (cm)	Total Clay <2 μ %	Boiling KOH Weight Loss of Clay %	*Crystalline Clay % of Total	Carbon % of Clay
Gilcent	AC	6-10 cm	16.2	46	8.7	0.28
Ochoco Butte	A1	5-10 cm	5.1	84	0.81	4.91
	C2	90-104 cm	4.1	80	0.82	1.99
Day Creek	A1	5-15 cm	5.1	65	1.73	2.99
	C2	65-70 cm	6.2	81	1.17	1.42
Meadowood	A1	0-15 cm	9.1	66	3.09	4.61
	C2	60-70 cm	4.7	81	0.89	1.91
Andies Prairie	A1	1-10 cm	3.2	71	0.93	10.75
	C2	40-50 cm	3.0	56	1.32	1.90

*% residue x % total clay.

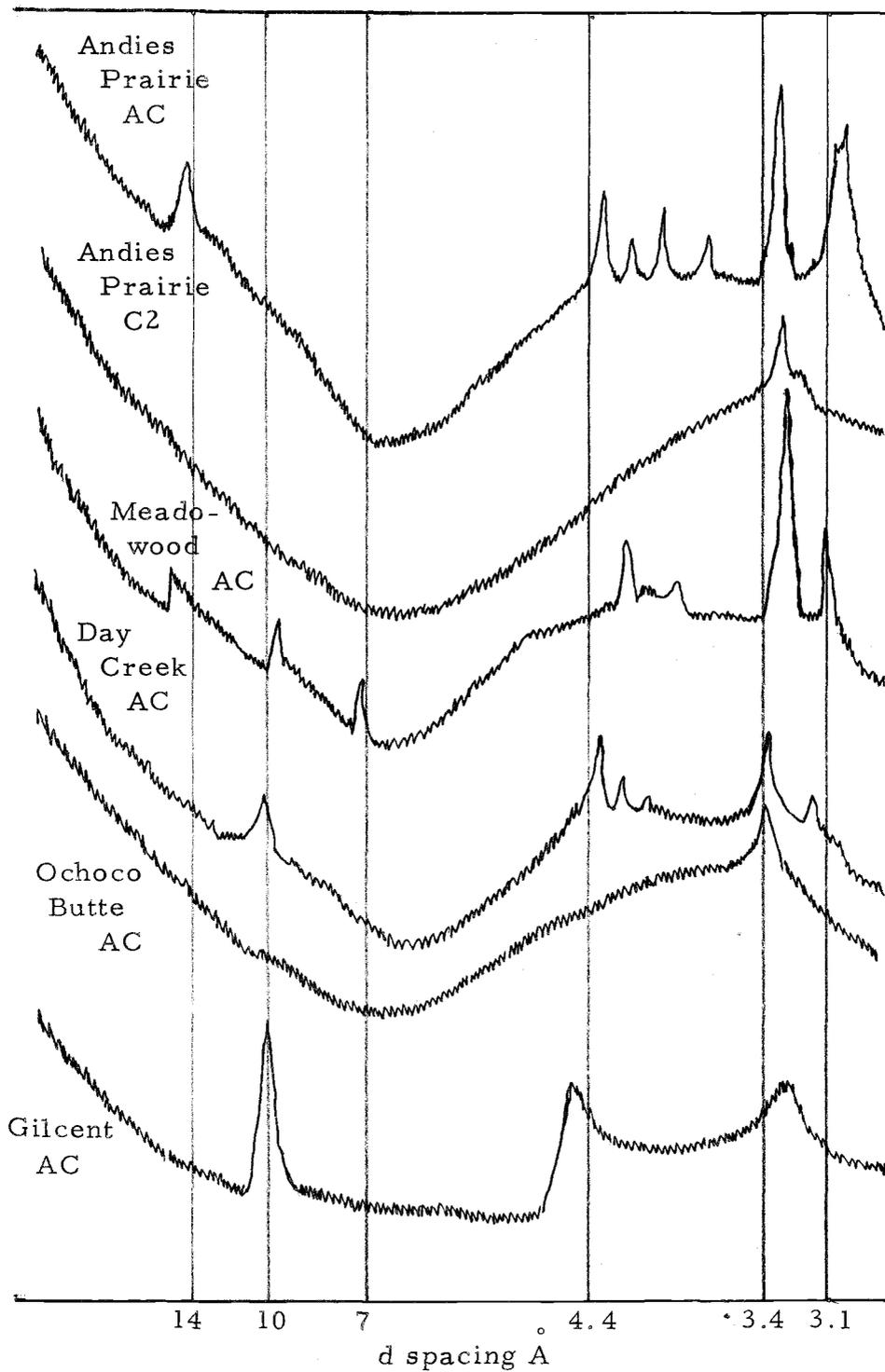


Figure 3. X-ray diffractograms on $<53\mu$ fraction of soils developed on Mazama pumice.

been reported as characteristic of material high in allophane (Ross and Kerr, 1934; Aomine and Jackson, 1959).

Thermal Analysis

DTA patterns for all the samples have a large low temperature endothermic peak characteristic of colloids that absorb large quantities of water. All patterns have an intermediate endotherm that corresponds to the loss of hydroxyl groups (Figures 4 and 5). All these patterns can be interpreted as indicative of halloysite (McKenzie, 1957) with the exception of Ochoco Butte AC and Andies Prairie AC and C2 samples. The Meadowood C2 pattern has a high temperature exotherm doublet indicating that more than one phase is present. The thermograms for the Ochoco Butte AC and Andies Prairie C2 samples suggest the presence of some imogolite. The dehydroxalation endotherm on these patterns is smaller and at lower temperatures than imogolite from Japanese soils (Yoshinaga and Aomine, 1962b). Even though DTA indicates that the Andies Prairie AC horizon is mostly amorphous, the x-ray pattern shows a 15 Å mineral to be present. This discrepancy is probably due to the difference in detection limits of the two methods. The 2:1 clays detected are not believed to be a weathering product of the ash but a post depositional contaminative. Dudas (1972) has calculated that significant quantities of non-pumice paleosol have been added to the ash by tree throw processes.

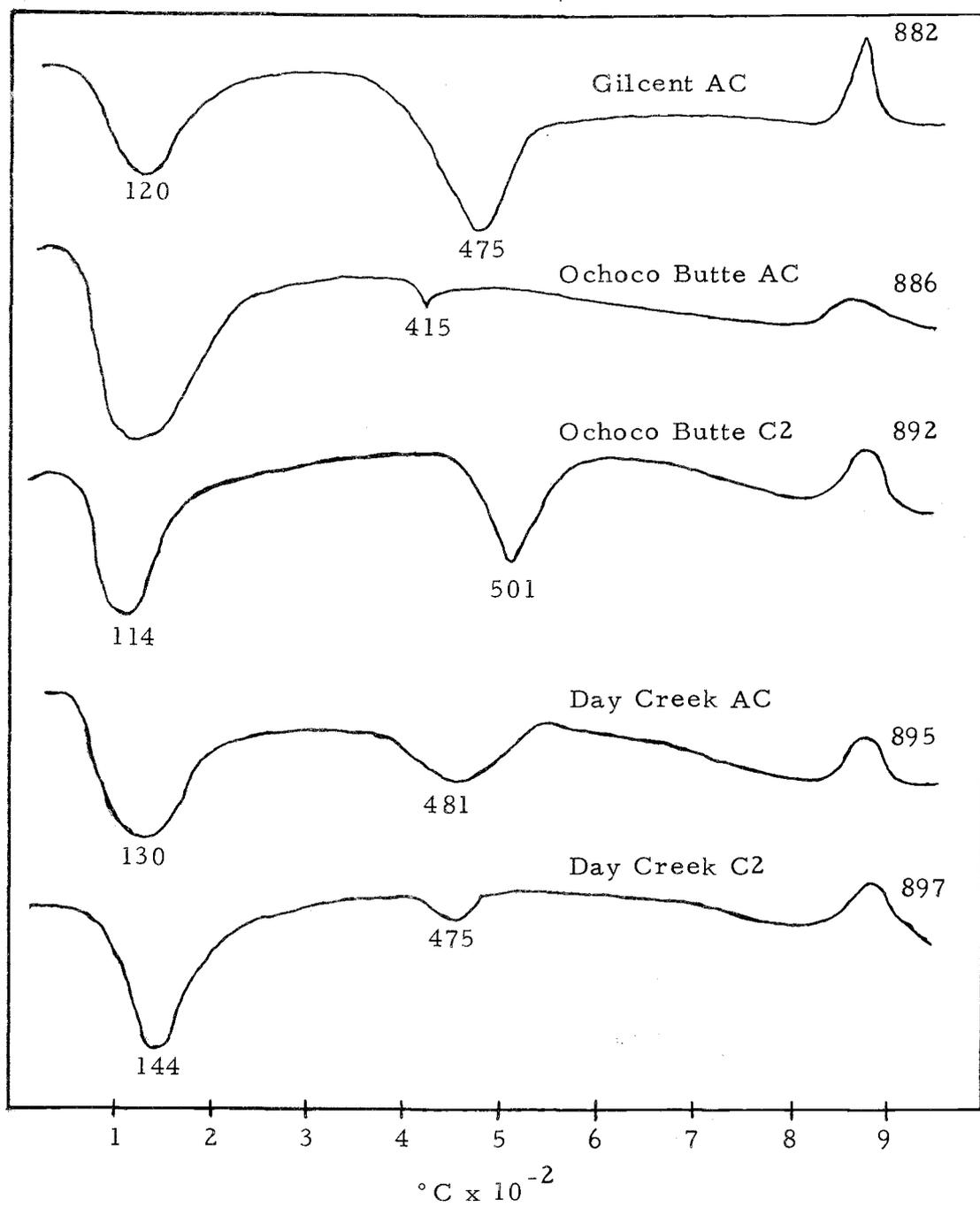


Figure 4. DTA patterns of the $<2\mu$ fraction of soils from Mazama transect sites. Samples were Na saturated and equilibrated at 58% R. H.

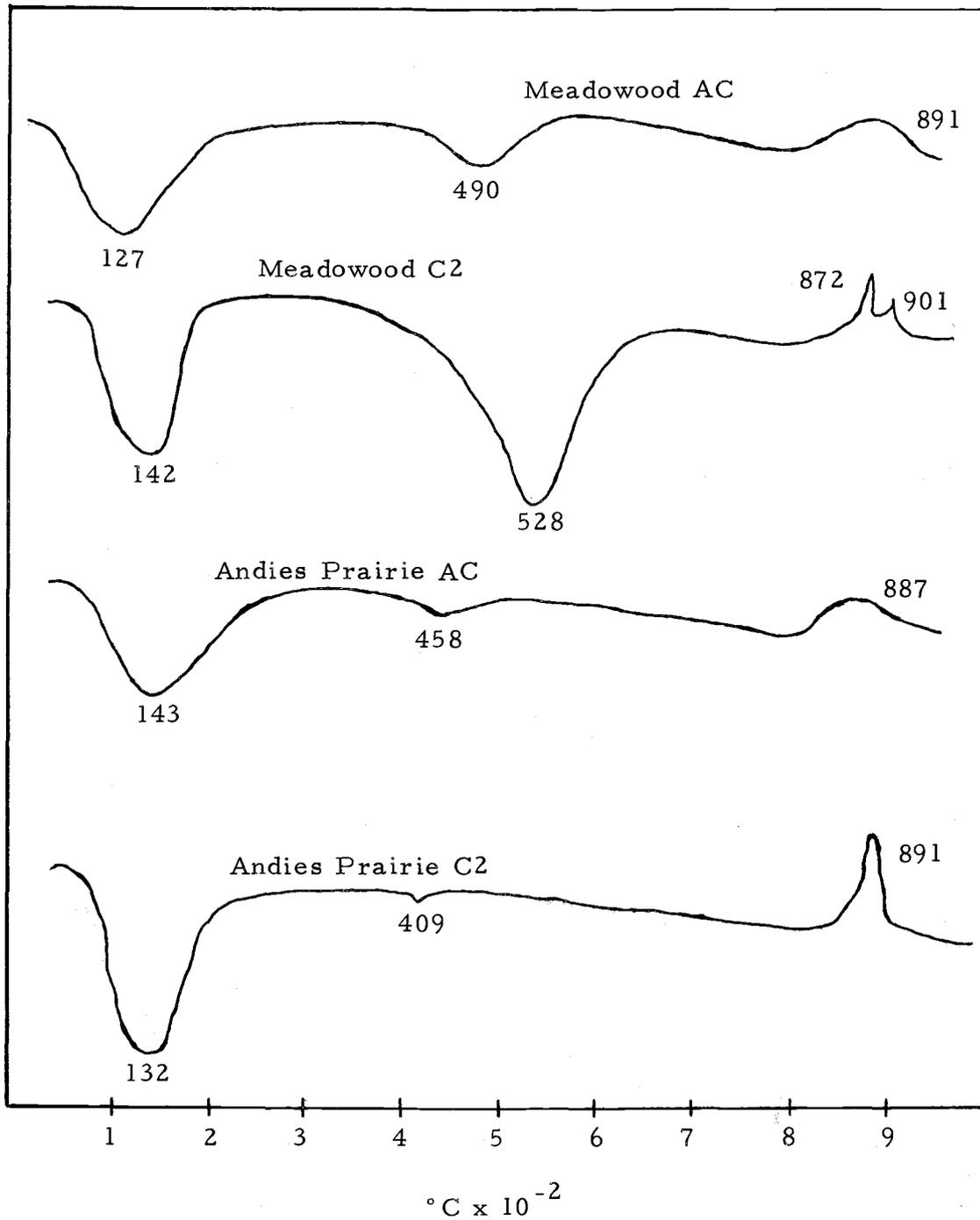


Figure 5. DTA patterns of the $<2\mu$ fraction of soils from Mazama transect sites. Samples were Na saturated and equilibrated at 54% R.H.

Electron Microscopy Analysis

Morphological data was also obtained on the clays from each site with the electron microscope. Results from the Gilcent site show that the clay fraction contains abundant crystals of halloysite ranging in size from 1000-2000 Å long and about 500 Å wide (Plate 4). The crystals are curled along the edge, with some having a flat coiled morphology. These coiled particles are about 1000 Å in diameter and seem to have a disk shape as inferred from the penetration of electrons across the specimen (Plate 5). These particles did not provide sufficient electron diffraction data for identification probably because of their orientation. Sieffermann and Millot (1969) have shown material of similar morphology from soils in Cameroon. They concluded that the material was globular halloysite. It is not known whether this is another polymorph of halloysite or if this morphology results from drying in the microscope vacuum. In addition to halloysite, strands of material having a morphology similar to imogolite can be seen bridging several particles. These strands range in size from 20-150 Å in diameter. Glass shards in the sample appear to be highly devitrified.

The Ochoco Butte site has a much drier microenvironment but shows much alteration of particles (Plate 6). The predominate material appears to be glass shards covered with gel. The gel

Plate 4. Electron micrographs of the $<53\mu$ fraction from the Gilcent site.

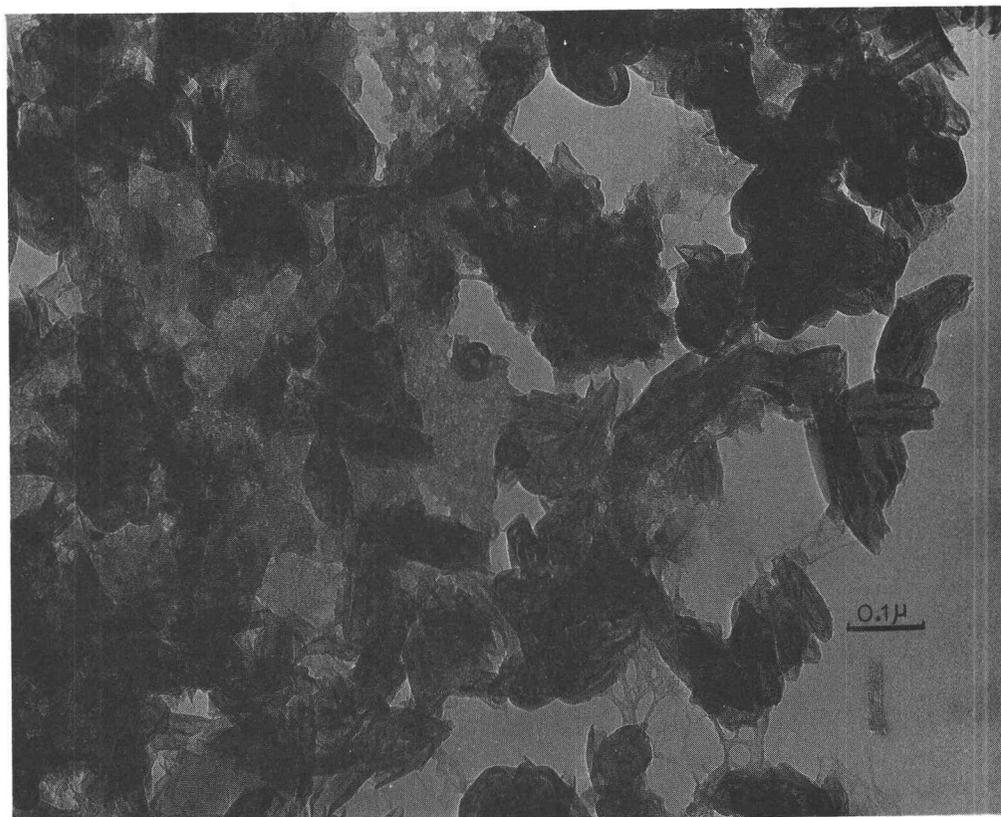
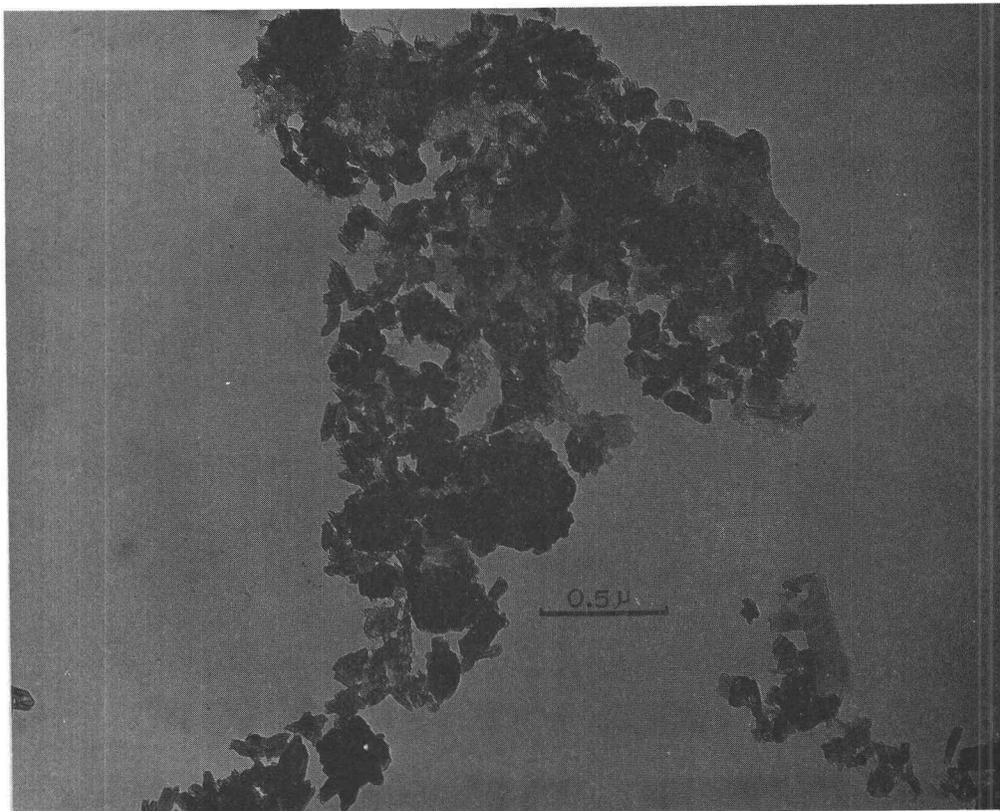


Plate 5. Electron micrograph of coiled halloysite.

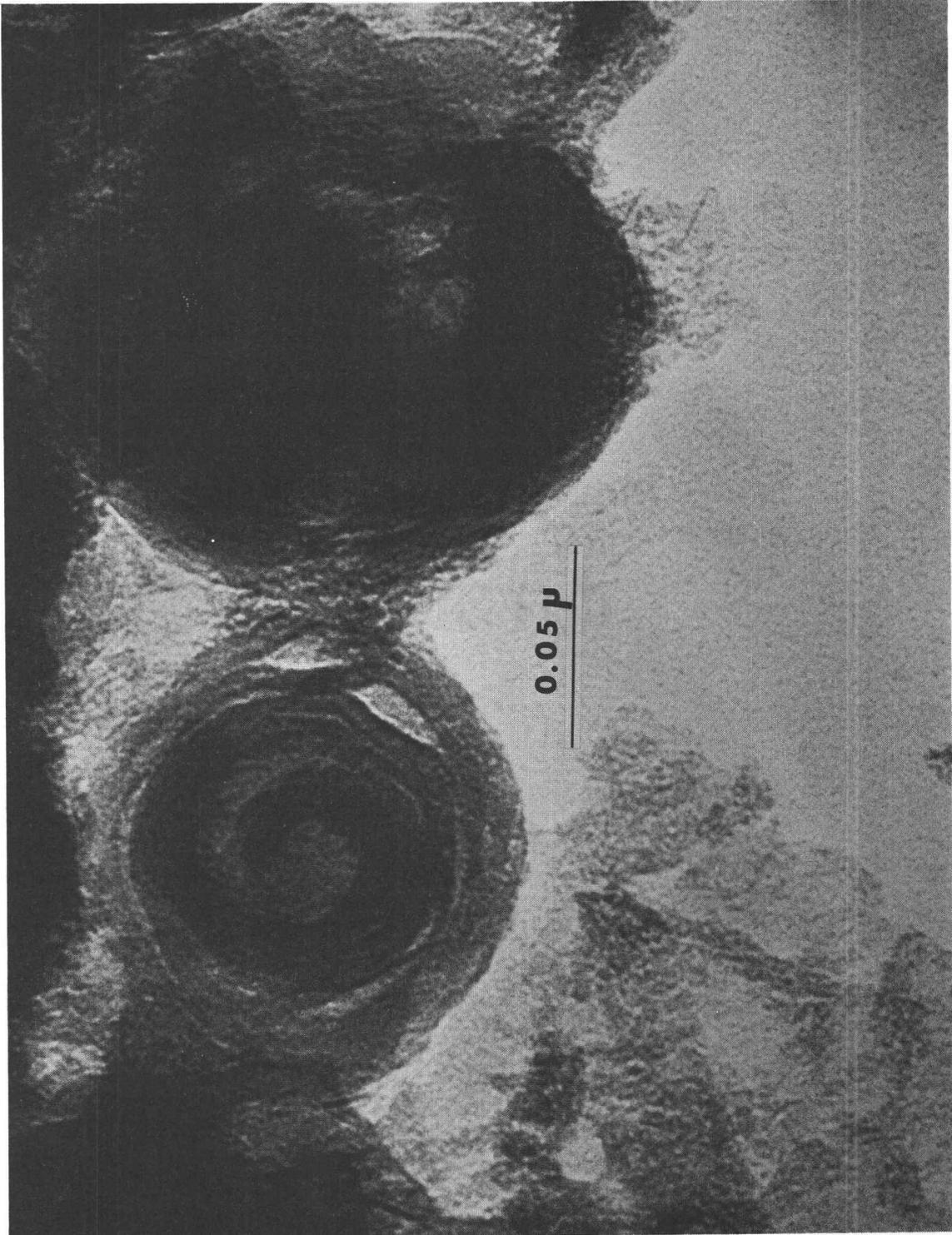
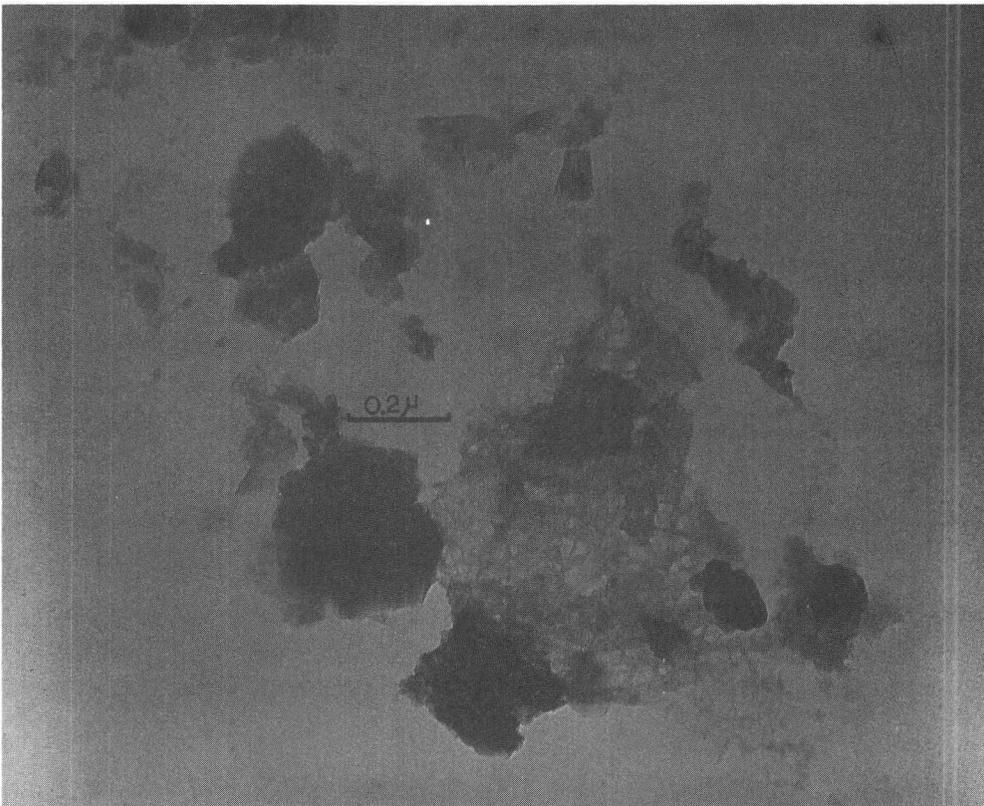
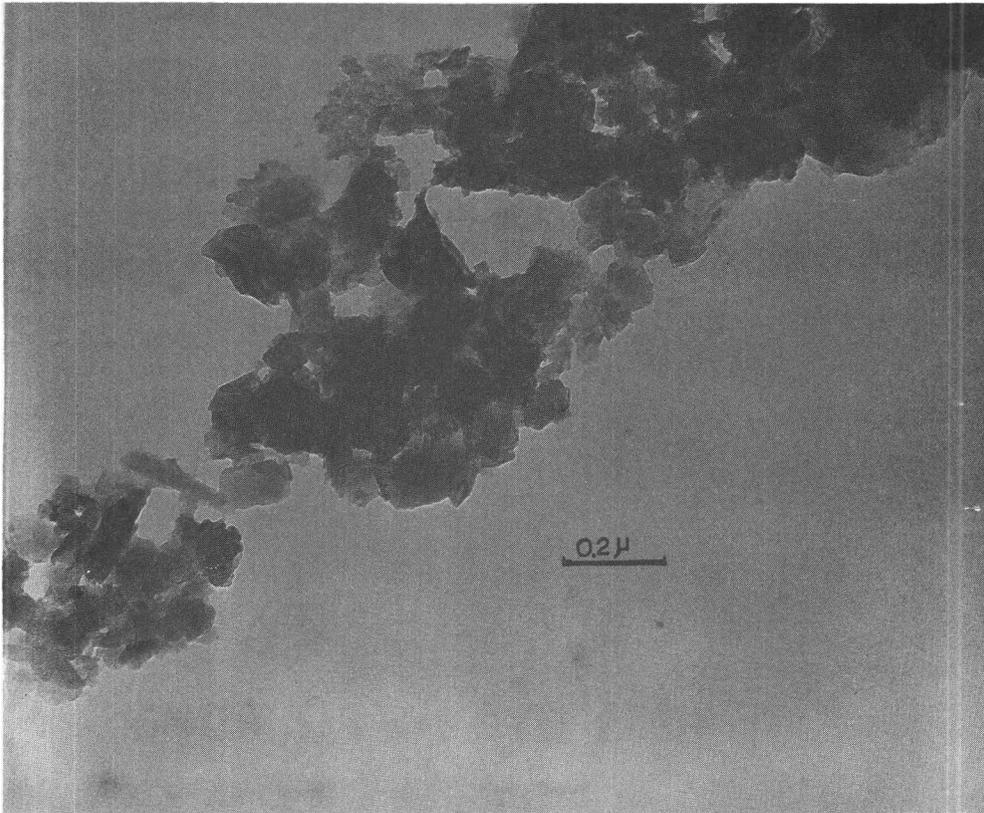


Plate 6. Electron micrograph of the $<53\mu$ fraction from Ochoco Butte C2 horizon.



appears to be non ordered but grainy in appearance. Bridging between adjacent particles with gel can be seen. Few crystals of halloysite are apparent. Some of the gel material appears to have fibrous morphology similar to imogolite. This may be a view of the very earliest stage of imogolite formation from tephra.

The Day Creek site is located in an environment similar to that of Ochoco Butte. The variety of clays found in the unmixed air fall ash were more numerous. Glass shards have devitrified to form gel coatings. Some show strands of imogolite beginning to form (Plate 7). Some very small crystals of halloysite can be seen along with the iron oxides and a tabular component of irregular shape (Plate 8). Silica bodies are also present and have a morphology similar to those reported for colloidal silica by Beutelspacher and Van Der Marel (1968) and Iler (1955). The beads of silica are about 200 \AA in diameter and always appear in clusters. The electron micrographs of the colloidal fraction of this sample show it to be far more complex than x-ray or DTA patterns indicate. This is probably due to the amount of most phases being much less than the gel and thus not detectable by x-ray or DTA methods.

The AC horizon of the Meadowood site has abundant gel material surrounding most particles (Plate 9). The gel forms bridges between some particles and has a fibrous morphology when viewed in thin areas. Some fragments of diatoms were also found at this site

Plate 7. Electron micrographs of the <53 micron fraction of the Day Creek C2 horizon.

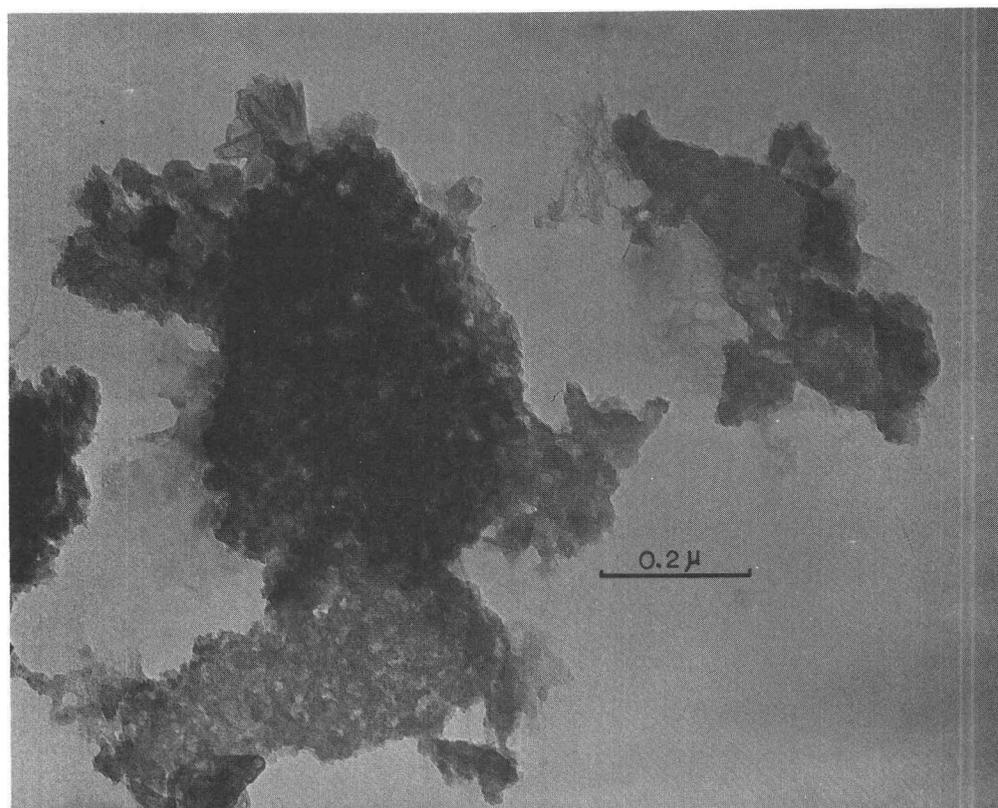
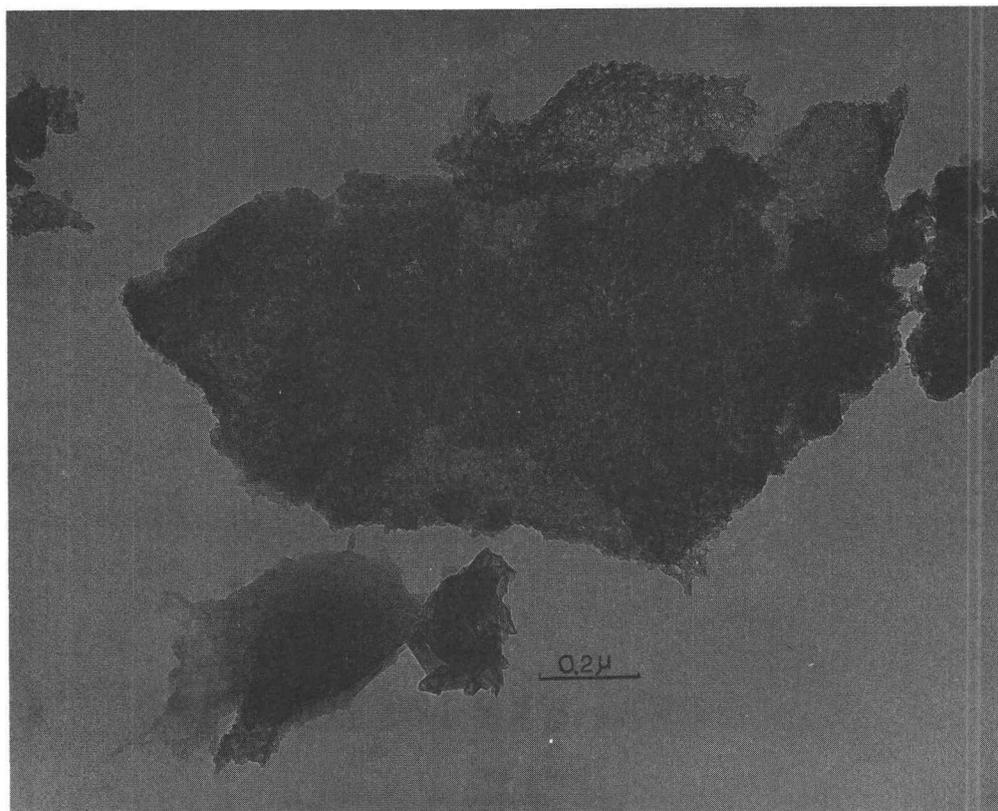


Plate 8. Electron micrographs of the Day Creek C2 sample showing silica bodies and a tabular mineral.

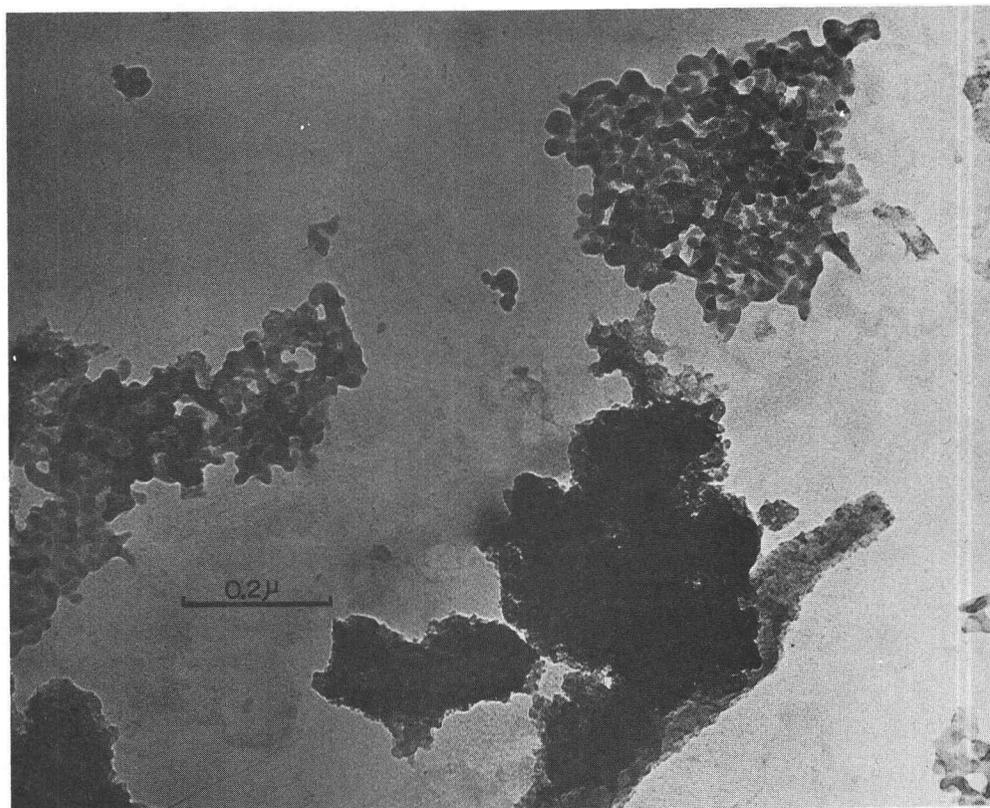
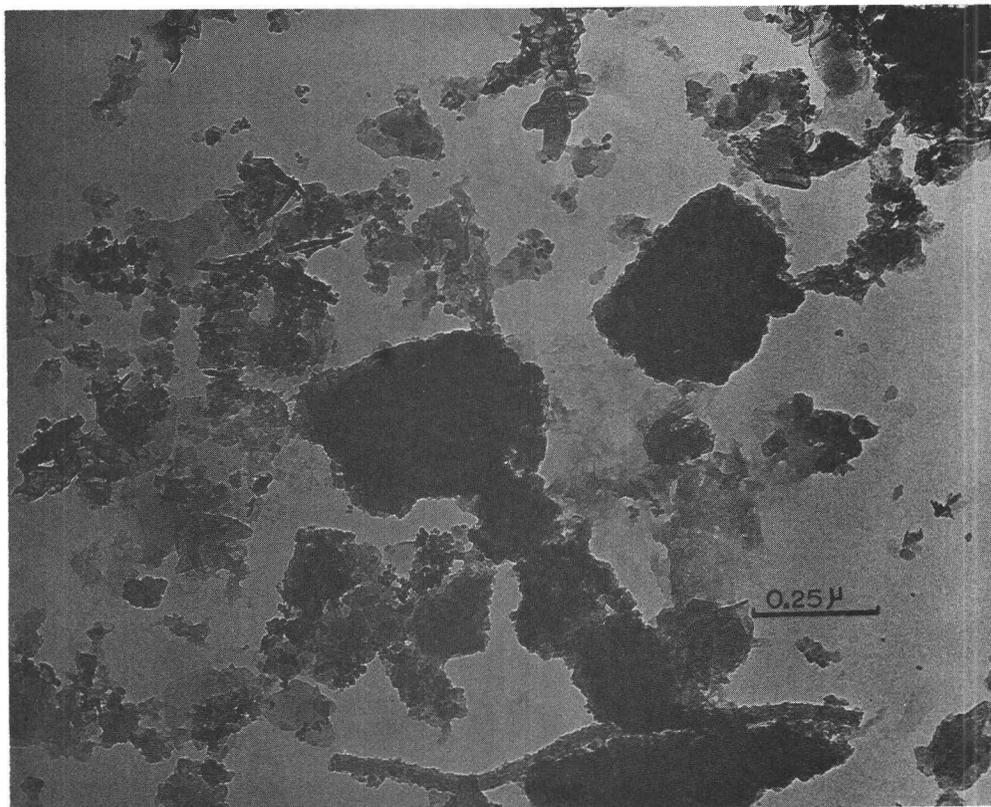
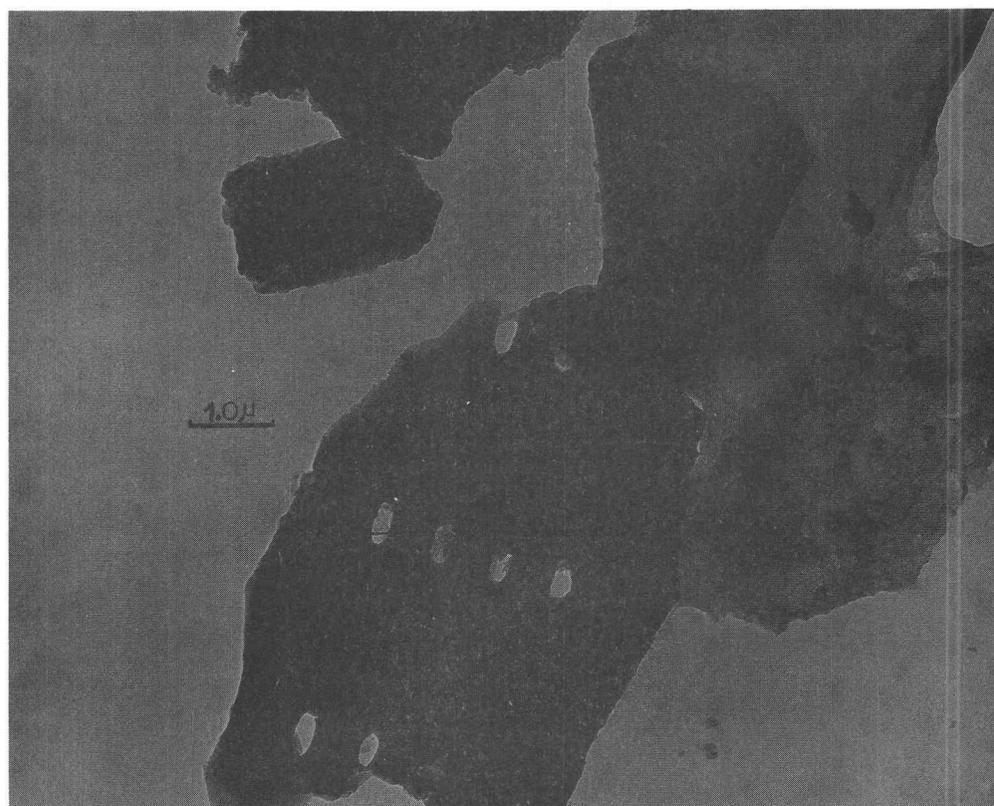
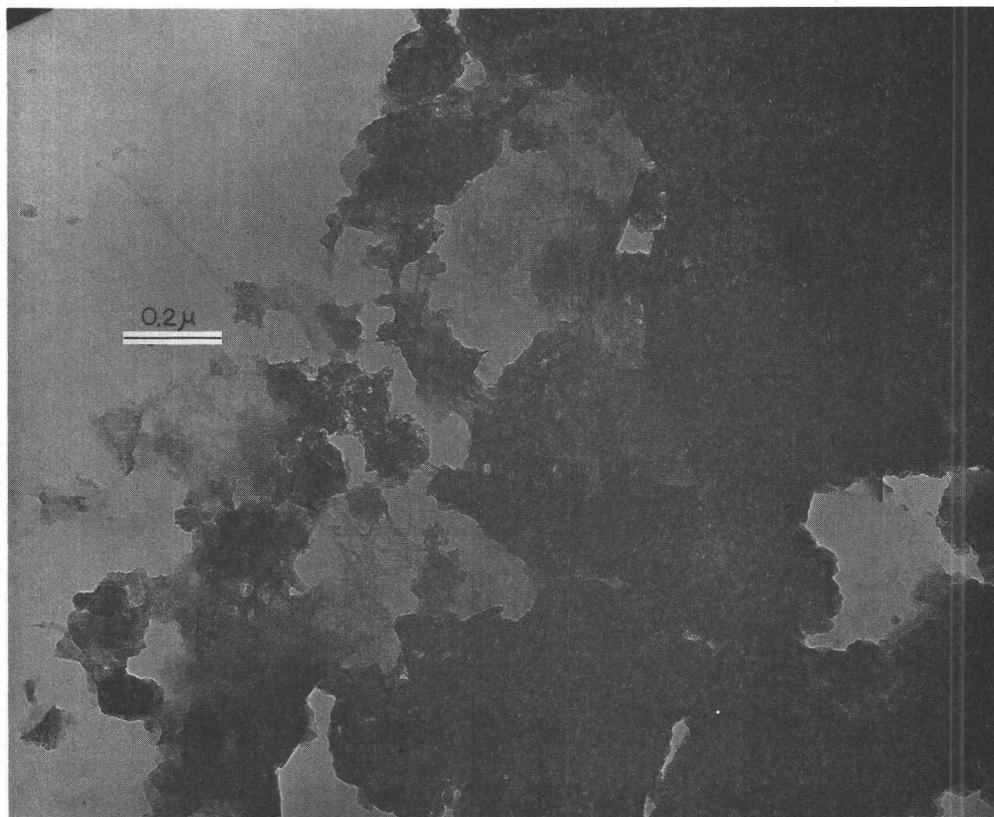


Plate 9. Electron micrographs of the <53 micron fraction
from the Meadowood AC horizon.



which may be indicative of a wind blown component added to the ash. The C2 horizon has much gel material with some very small particles of halloysite about 500 Å in length (Plate 10). The glass is highly devitrified and has an irregular porous structure (Plate 10). None of the gel material appears to have a fiber structure as noted in other samples from the horizon above. Even though this site has had the greatest amount of non-ash materials added to it, there seems to be fewer different types of amorphous clays than other less contaminated sites. The micrographs support previous DTA data which indicate that allophane and fine grain halloysite dominate the colloidal fraction.

The Andies Prairie site is located near the Meadowood location but is found in a much wetter environment. It was anticipated that the clay fraction would be similar to that of the GC site which was poorly drained and contained halloysite. Electron micrographs of the AC horizon support x-ray and DTA data, and show the clay to be mostly an amorphous gel. The clay fraction contained 10% carbon but is not identifiable in the electron micrograph (Plate 11). A few faint strands of imogolite can be seen mixed in with the gel phase. Some diatom fragments were found in other fields of view. In contrast to the upper horizon the C2 contained abundant fibers of imogolite with less gel (Plate 11). The fibers link other particles of devitrified glass together into a complex web like pattern. Individual shards appear to have selectively dissolved leaving the thread like fragments. The

Plate 10. Electron micrographs of the <53 micron fraction
from the Meadowood C2 horizon.

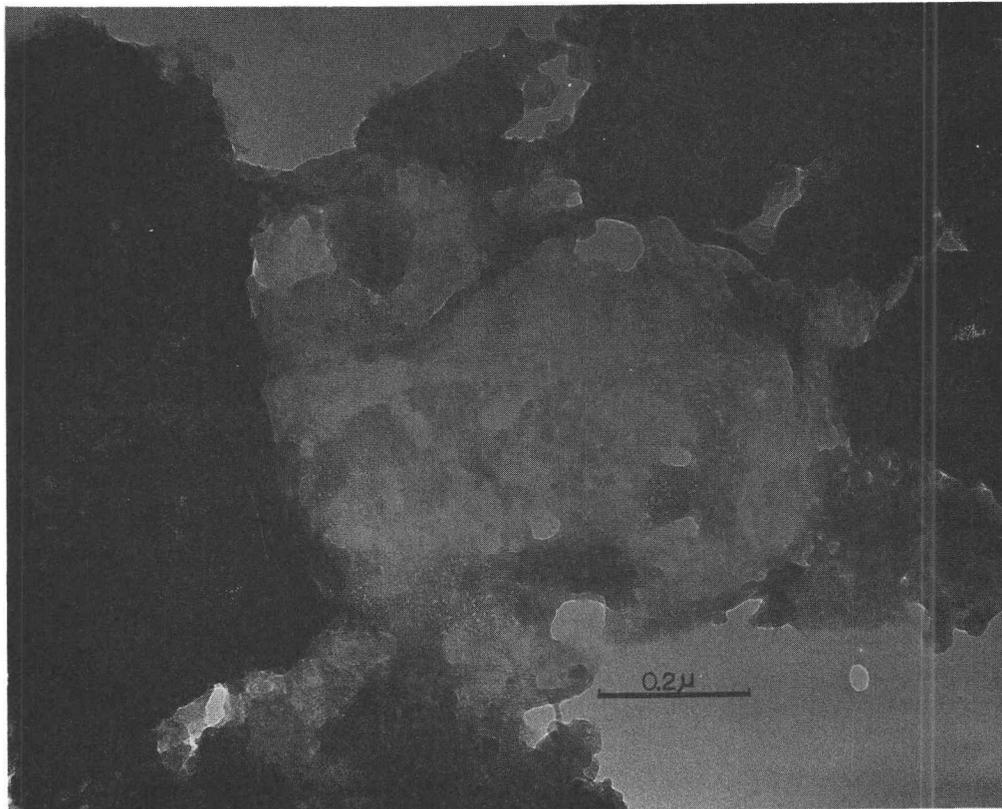
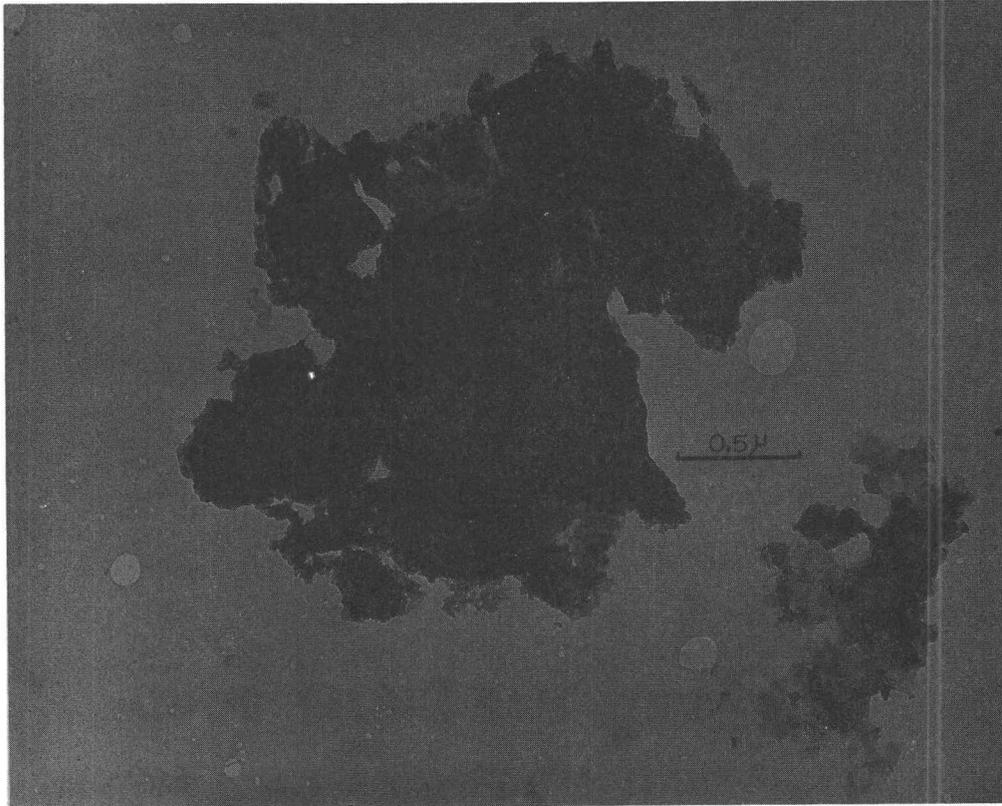
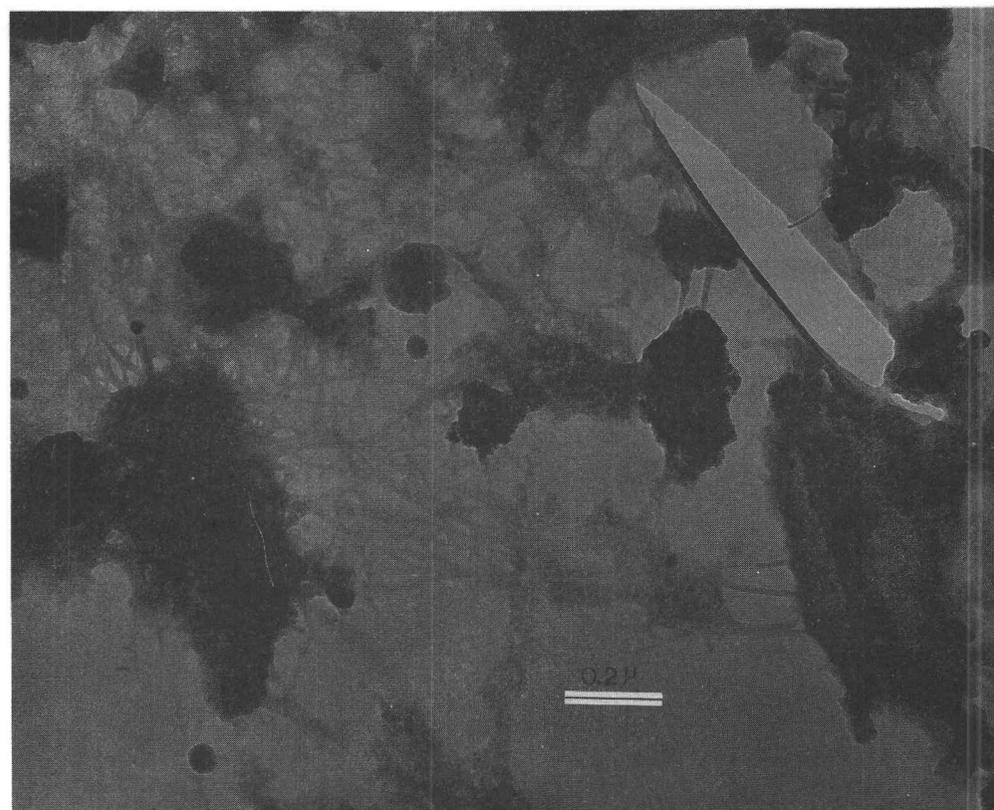
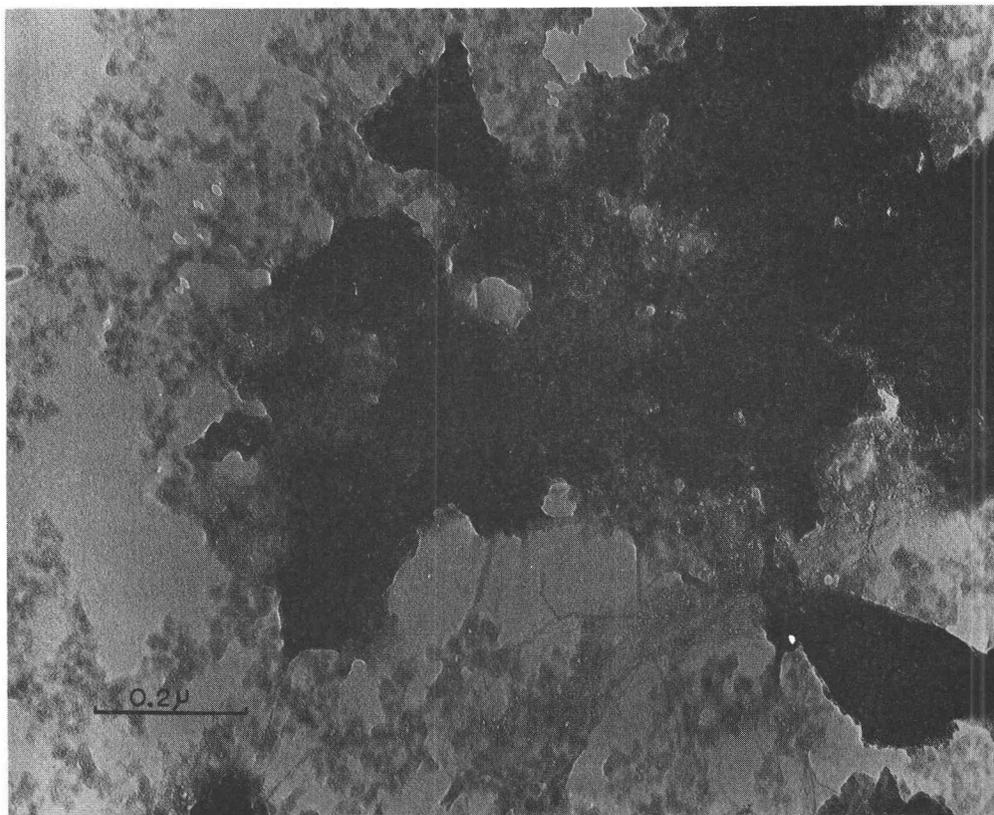


Plate 11. Electron micrographs of the <53 micron fraction from the Andies Prairie AC and C2 horizons respectively.



strands appear as bundles about 100 \AA in diameter. Single strands are about one-tenth this size. Several crystals of a tabular hexagonal mineral about 0.05 micron in diameter are also present. They resemble the morphology of kaolinite but are much smaller in size than more classical specimens. DTA and x-ray patterns indicated that the clay fraction was mostly amorphous. Since the DTA pattern did not show a strong endotherm at 415°C the thread like material may be another polymorph of Imogolite. Other crystalline clay components were found in the C2 sample as shown by the electron micrograph and selected area diffraction pattern (Plate 12). Calculation of d spacings for the mineral gave the following reflections: 4.39, 2.56, 2.19, and 1.42 \AA based on a method by Heindenreich (1964). These lines agree well with chlorite data (Brown, 1961) although positive identification could not be made.

Summary and Implications to Weathering

The types of colloids found in the Mazama tephra are similar to those reported in soils developed from pumice deposits of Japan and New Zealand. Allophane was found in all the sites studied (Table 5). Imogolite was found at all sites along the transect but appeared to be a minor constituent in all samples with the exception of Andies Prairie C2. Silica bodies were found in the DCC2 sample only. All

Plate 12. Electron micrographs of a crystalline clay and its diffraction pattern from the Andies Prairie C2 horizon.



Table 5. Summary of the types of clays found in soils developed on Mazama tephra.

Location	Horizon	Depth	x-ray	DTA	TEM
Gilcent	AC	5-20	Halloysite Quartz	Halloysite	Halloysite, Imogolite, Allophane, Glass shards
Ochoco Butte	AC	5-10	Quartz	Allophane	
Ochoco Butte	C2	90-104		Halloysite	Halloysite, Allophane, Glass shards, Imogolite
Day Creek	AC	5-15	Halloysite Quartz	Halloysite	
Day Creek	C2	65-70		Allophane	Halloysite, Glass shards, Silica bodies, Iron oxide nodules, Smectite?, Allophane, an unidenti- fied tabular mineral, Imogolite
Meadowood	AC	0-15	15 Å mineral Feldspar Quartz	Halloysite	Diatoms, Imogolite, Allophane, Glass shards
Meadowood	C2	60-70		Halloysite	Halloysite, Allophane, Glass shards
Andies Prairie	AC	1-10	15 Å mineral Quartz Feldspar	Allophane	Allophane, Glass shards
Andies Prairie	C2	40-50	Quartz	Allophane	Imogolite, Glass shards, Allophane, Kaolinite?, Chlorite?

the sites except Andies Prairie contained halloysite. The sample from the Gilcent location contains abundant halloysite while those from Andies Prairie have allophane and imogolite. This presents an enigma in that both locations are poorly drained but have similar microenvironments. Changes in parent material components were measured by thin section analysis. These studies show that the amount of feldspars decrease with distance from the source. At Andies Prairie the ash is composed of 96 percent glass (Table 6). The wet environment and large glass content probably favors the formation of imogolite while the presence of feldspars favor the formation of halloysite. The tendency for imogolite to form in glass materials has been reported for Japanese soils (Wada, 1967). The formation of Halloysite from feldspar has been well documented by Alexander et al. (1943), Sand (1956) and Kunze (1964). Mechanisms for the formation of hydrated halloysite from allophane have been suggested by others (Tamura and Jackson, 1953; Fields, 1955; Aomine and Wada, 1962). All these differ in details, but they assume an intermediate gibbsite like sheet structure in the silica-alumina gel initially followed by the addition of silica tetrahedra. No one at this point however, has shown that a gibbsite-like sheet structure occurs in soil allophane. The conditions for the formation of allophane and imogolite is less apparent. In some cases it appears that imogolite is forming from the glass shards directly (Plate 11). At other

Table 6. Thin section analysis of undisturbed tephra along the Mazama transect.

Sample	Horizon	Distance (km)	% Composition
Gilcent	AC	60	22% Feldspar 5% Lithic 3% Ferromags 1% Magnetite 69% Glass
Ochoco Butte	C2	215	19% Feldspar 2% Lithic 1% Ferromags 1% Magnetite 77% Glass
Day Creek	C2	300	15% Feldspar 1% Lithic 1% Ferromags 2% Magnetite 80% Glass
Meadowood	C2	445	15% Feldspar 1% Lithic 1% Ferromags 2% Magnetite 81% Glass
Andies Prairie	C2	450	2% Feldspar 1% Lithic 1% Magnetite 96% Glass

locations the allophane and imogolite seem to occur together in a gelatinous matrix. Linear polymers can be formed by the polymerization of both silicic acid (Iler, 1955) and aluminohydronium ion (Jackson, 1960) given suitable environmental conditions. Allophane may then form in soils that have a readily available source of silica and aluminum in a condition suitable for co-precipitation. As these gels age further crystallization into linear strands of imogolite probably occurs.

Observation of the Mazama Clays seem to indicate the following pathway of clay formation:

Amorphous Glass —> Allophane —> Imogolite

Feldspars —> Halloysite

IV. CHEMICAL PROPERTIES OF CLAYS FROM MAZAMA TRANSECT SOILS

Introduction

Several studies on the distribution and importance of volcanic ash in soils of the Pacific Northwest have been completed (Dyrness, 1964; Norgren, 1962; Youngberg and Dyrness, 1964; Cochran, 1966; Doak, 1971, Western Regional Soil Survey Work Group, 1964). These studies have been directed primarily toward understanding the physical and chemical properties of pumice soils for agricultural production. Only a few clay mineralogy studies have been done on these soils, however (Kanehiro and Whittig, 1961; Tidball, 1965; Chickester, 1967). For the most part, these studies have recognized that the clay fraction is dominated by amorphous colloids. The chemical properties of these clays have not been studied in much detail. In order to understand the colloidal system developing from Mazama tephra additional information about chemical properties of the clay fraction was needed. Furthermore, information gained about the chemical nature of the amorphous clays in the Mazama pumice should be useful in making management decisions about other soils influenced by volcanic ash which contain similar amorphous clays.

The objective of this phase of the study was to: characterize the chemical nature of the Mazama clays with respect to ion exchange

capacity, pH dependent charge, phosphate retention, chemical composition, and buffering capacity.

Materials

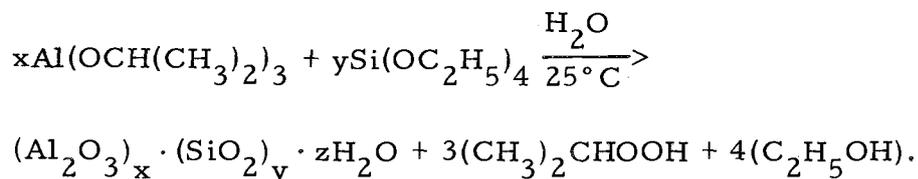
The <2 micron fraction from each of the Mazama transect sites was obtained by dispersion in distilled water adjusted to pH 5.0. The clays were flocculated with NaCl; washed free of excess salt, dried at 60° C and finally stored at 54% relative humidity until used.

The clay fraction of a sample high in imogolite separated as above was also used as an amorphous standard for comparisons. The sample was collected by M. E. Harward on a field trip to Kyushu, Japan from a Choyo soil studied the by Japanese. The tephra from which the Choyo soil was formed came from the Aso volcano. Pyroclastics from this vent covers about two-thirds of Kyushu and is mostly andesitic and rhyolitic in composition.⁴ Age of the pumice deposit other than late pliestocene period is unknown.

Synthetic alumino-silicate gels were also used for comparisons to natural clays and as a means of standardizing methods. These gels were prepared by a slow hydrolysis reaction of aluminum isopropoxide and tetraethylorthosilicate by a method similar to that used by Cloos et al. (1969). The synthesis was carried out in plastic beakers by

⁴Guide to Field Trips B, C and D. 1969 International Clay Conference. Tokyo, Japan.

first adding tetraethylorthosilicate to 500 milliliters of water and then slowly introducing the aluminum isopropoxide over a period of one hour. The following reaction takes place slowly yielding the aluminosilicate gel and alcohols:



Reagents were combined in amounts to yield gels with silica and aluminum contents bracketing the range reported for amorphous clays in soils. The reagents were stirred continuously for 24 hours. The synthetic allophane was recovered by flocculation with NaCl, washed free of excess salt, dried at 60°C and finally stored at 54% relative humidity until used.

Methods

The aluminum, silicon and iron content of the Mazama clays and synthetic gels were determined with atomic adsorption spectroscopy by a modification of a method used by Suhr and Ingamells (1966). About 0.1 gram of oven dry sample was placed in a platinum crucible with 0.5 g of lithium tetraborate and heated to 1000°C in a muffle furnace. The flux was then dissolved in 20 ml of 0.5 N HNO₃, diluted to 500 ml, and immediately analyzed. The accuracy of the method

was checked by analyzing U.S.G.S. standard GSP-1.

The CEC values for all samples were determined by a method proposed by Frink (1964), and consisted of the following steps:

- a. Saturation of the sample with a 1.0 N solution of index ion.
- b. Equilibration of the sample with a dilute solution of the same index ion.
- c. Determination of the amount of entrained excess salt solution by weighing.
- d. Displacement of the total content of index ion.

The CEC can then be determined from c and d. All determinations were made using about 150 mg of clay in 50 ml glass centrifuge bottles. For this study $MgCl_2$ was used as the index solution and $NaNO_3$ as the extractant so that both cation and anion exchange values could be determined from the same extract. The ideal concentration of the equilibrium solution was determined by measuring the effect of solution concentration on the CEC value of a synthetic allophane. Magnesium was determined by atomic adsorption and chlorine by specific ion electrode.

The pH dependent charge on the Mazama clays was obtained by determining the CEC and AEC at pH 4.0 and 7.0 using non-buffered $MgCl_2$. The samples were washed several times with the pH adjusted index solution until the supernatant did not change pH upon exposure to the clay. A few drops of dilute HCl or NaOH were added

initially to the sample suspension to reduce the number of washings used to obtain equilibrium at the desired pH. Duplicate CEC and AEC values were determined as indicated before.

The phosphate sorption potential of the Mazama clays was determined by equilibrating duplicate 0.1 gram samples with 20 ml of molar NaH_2PO_4 for 170 hours at pH 4.0. The colloid was then washed free of soluble phosphate with ethanol and water. The samples were then fluxed with lithium tetraborate, dissolved, and analyzed for PO_4 by the molybdovanadophosphoric acid method.

The buffering characteristics of the Mazama clays were determined by titration. Approximately 1.0 g of clay was placed in 100 ml of 0.2 N NaCl and amounts of HCl or NaOH were added to give from 0.2 meq of acid to 1.0 meq of base per gram of sample in steps of 0.2 meq per gram. The pH of the equilibrium supernatant was measured with a Beckman pH meter.

Results and Discussion

Chemical Composition

The SiO_2 content of the clay fraction from all the Mazama sites was always higher in the samples from the C2 horizons (Table 7). The amount of silica in the clays is always less than the concentration in unweathered pumice while the aluminum percent is 20-30% higher.

Table 7. Chemical composition of the Mazama clays.

Sample	%SiO ₂	%Al ₂ O ₃	%Fe ₂ O ₃	$\frac{*SiO_2}{Al_2O_3}$
Gilcent AC	44.0	37.1	1.44	2.04
Ochoco Butte AC	34.5	38.8	1.40	1.51
Ochoco Butte C2	38.1	43.2	1.65	1.50
Day Creek AC	39.4	41.4	1.42	1.63
Day Creek C2	48.1	44.1	1.33	1.85
Meadowood AC	42.8	32.9	1.17	2.23
Meadowood C2	43.2	42.6	1.66	1.73
Andies Prairie AC	31.5	36.0	1.40	1.47
Andies Prairie C2	51.1	32.8	1.33	2.62
Unweathered pumice	69.1	14.3	1.52	8.21

* Molar ratio. Oven dry basis.

These data indicate that as the glass phase is weathered and converted to a colloidal phase, silica is lost from the system while aluminum is selectively retained. The molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ for the clay samples is generally between 1 and 2 as compared to 8.2 for the unweathered pumice. Wada and Yoshinaga (1969) report a similar trend in molar ratio for amorphous clays in Japanese soils. From their data they postulated that two clay end members exist for the system studied with allophane having a molar ratio of 1.0 and imogolite a ratio of 2.0. Their observations do not seem to be the same as for the Mazama clays except in the case of the Andies Prairie site. At this location the AC horizon had only amorphous clay with a molar $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 1.47 while the C2 horizon had mostly imogolite and a ratio of 2.62. The Gilcent site had a ratio of 2.04 but the clay fraction contained predominately halloysite. Other sites had ratios that were generally between 1 and 2 with clay fractions having several components present but being dominately amorphous.

Charge Characteristics

The CEC of the synthetic allophane sample was found to vary considerably with the concentration of the equilibrium solution used in step b for exchange capacity measurements (Figure 6). For solutions between 0.05 and 0.15 N, the CEC increased only slightly when compared with the extremes of the curve. Similar results have been

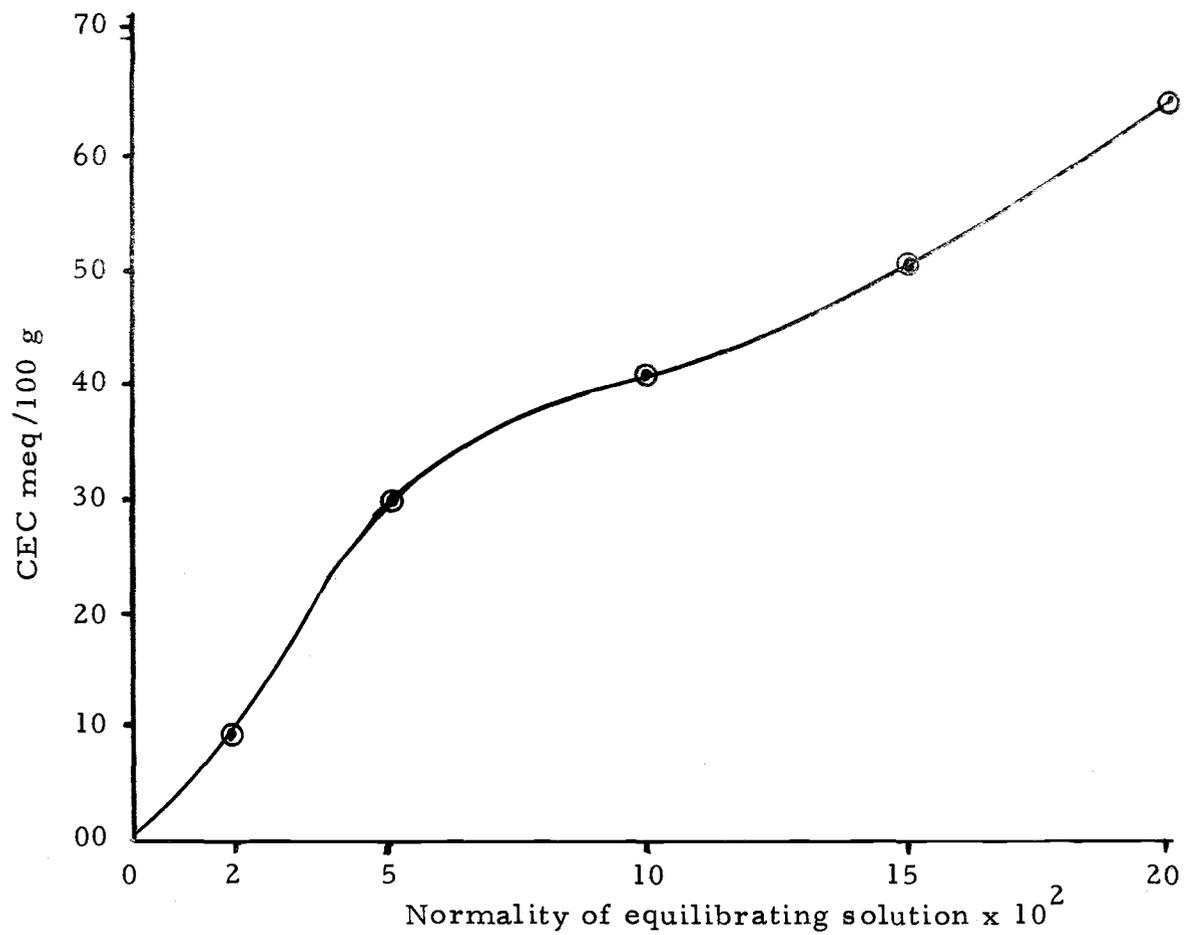


Figure 6. Variation in CEC of a synthetic gel with equilibrium solution concentration.

reported by Wada and Harada (1969, 1971) for soil amorphous clays. From the curve 0.05 N was chosen as the concentration of the equilibrium solution that would serve as a reasonable estimate of the true exchange capacity of the amorphous clays. Three washings with the 0.05 N solution in step b were required to establish equilibrium before displacement.

The CEC values of the clays recovered from the Mazama soils were found to be quite varied (Table 8). The Gilcent site had the largest amount of clay (Table 4) but next to the lowest CEC (Table 8). The Andies Prairie site had the highest amount of organic matter present and the most imogolite but the lowest CEC. The values for sites between these locations have the highest CEC values yet are less weathered and contain less organic matter. This is probably due to the kinds and amounts of amorphous clay present at these locations. The amount of 2:1 crystalline clay contaminants reported at these sites by Dudas (1972) would not be sufficient to account for the high values. Comparison of CEC values from the AC horizon samples with those of the C2 generally show that the surface horizons had higher values than the C2 material just above the paleosol. This is probably due to the increased organic matter content of the samples from near the surface. It is interesting to note that the AP AC site had 10 percent carbon but a CEC of 24 meq/100. This value is very low for either soil organic matter or amorphous clays and may be indicative

of a complex clay-organic colloid in which exchange sites for magnesium were blocked. Most of the values reported here are comparable to those reported by Chichester (1967) for other Mazama sites.

Table 8. Cation exchange capacity of Mazama clays.

Sample	Horizon	CEC meq/100g
Gilcent	AC	37.4
Ochoco Butte	AC	71.0
	C2	51.9
Day Creek	AC	52.1
	C2	58.2
Meadowood	AC	57.2
	C2	50.7
Andies Prairie	AC	24.3
	C2	21.4
Montmorillonite 21	Lit. value ⁵	This method
	88.0	88.2

The values of CEC were approximately 2-3 times higher at pH 7.0 than at 4.0 for all samples except the Kyushu imogolite which had received the defferation treatment (Table 9). A drastic reduction in pH dependent charge was induced in this sample by the DCB extraction. The synthetic gel had a similar pH dependent charge characteristic as the Mazama samples but gave results slightly lower at pH 4.0 and somewhat higher at pH 7.0 than samples of the latter.

⁵Dudas and Harward, 1971.

Table 9. pH dependent exchange capacities (meq/100 g) of natural and synthetic clays.

Sample	pH 4.0		pH 7.0	
	CEC	AEC	CEC	AEC
Synthetic				
Gel 3	28.5	15.9	76.3	0
Mazama				
Gilcent AC	37.6	7.5	51.6	0
Ochoco Butte AC	33.2	7.8	61.2	0
Ochoco Butte C2	36.0	7.9	49.4	0
Day Creek AC	29.0	10.2	52.9	0
Day Creek C2	33.5	9.3	52.8	0
Meadowood AC	35.8	6.1	64.8	0
Meadowood C2	44.9	12.3	48.8	0
Andies Prairie AC	42.1	8.5	74.5	0
Andies Prairie C2	23.2	1.4	47.5	0
Kyushu				
untreated	19.2	11.8	59.0	0
After DCB	55.6	<1.0	63.8	0

The composition of the gels as well as DCB treatment significantly affected their CEC values (Table 10). The defferation treatment resulted in a rather large increase in CEC with values being similar to those found for natural clays regardless of original gel composition. The treatment did not destroy the gels as noted by DTA data in Chapter 2, but did remove significant amounts of aluminum. Furthermore, it is interesting to note that the CEC of the gels is maximum when the $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio was about 4.0. This contrasts with that reported by de Villiers (1971) who observed a maximum CEC when the ratio was 6.0. His method of preparation was by co-precipitation of

AlCl_3 and sodium silicate at pH 7.0. The synthetics he made also had CEC values near 300 meq/100 g, but he does not indicate how the parameter was determined.

Table 10. Composition and CEC characteristics of synthetic alumino-silicates at pH 6.0.

Gel	% Al_2O_3	% SiO_2	CEC*	CEC ⁺	SiO_2^{++}
					Al_2O_3
1	61.2	28.4	27.2	80.1	0.75
2	44.7	45.3	44.0	74.5	1.70
3	27.1	62.2	63.0	98.2	4.01
4	10.6	80.1	35.5	77.4	13.3

* Non-buffered.

⁺ After defferation with DCB.

⁺⁺ Molar ratio.

The anion exchange capacity of the Mazama samples was highest at pH 4.0 with none being detectable at pH 7.0. The AEC values did not appear to be related to CEC or the amount of pH dependent charge of the clays (Table 9). The DCB treatment on the Kyushu sample resulted in a loss of AEC at pH 4.0 and significantly reduced the amount of pH dependent charge on the clay. These results are not easy to explain but could have been due to the gel material left on the imogolite by the DCB treatment blocking exchange sites as observed by TEM analysis in Chapter 3.

Phosphate Sorption

The clays from all the Mazama sites were found to adsorb large quantities of phosphate (Table 11). These data along with observations previously described in Chapter 2 indicate that samples highest in halloysite had the lowest amount of phosphorus sorbed while those highest in amorphous clays retained the most. The values obtained for the Mazama clays are slightly higher than those reported for amorphous clay from Japanese soils (Wada, 1958).

Table 11. Phosphorus sorbed by soil clays after 7 days equilibration in 1.0N NaH_2PO_4 at pH 4.0.

Sample	Horizon	PO_4 Sorbed mg/g
Gilcent	AC	707
Ochoco Butte	AC	1312
Day Creek	AC	1091
Meadowood	AC	826
Andies Prairie	AC	1296

The sorption mechanism was not studied here. Others have reported that the phosphate forms an insoluble mineral phase by reaction with clays (Haseman et al., 1950; Kittrick and Jackson, 1956; Wada, 1958). The data suggest that possible soil fertility problems could be encountered with Oregon soils having large amounts of amorphous clays present.

Buffering Capacity

The buffering curves of the amorphous clays from the Mazama sites show that the AC horizons always have a higher buffering capacity than subsurface C2 material at a given site (Figure 7). These results could be due to either differences in organic matter content or differences in the nature of amorphous clays for the two horizons. The strongest buffering capacity for most of the samples appears to be below their equilibrium pH which ranged from pH 7.2 for the GC AC to pH 5.4 for the AP AC in 0.2 N NaCl. An additional buffering range occurred in all samples except MW AC and the Day Creek clays. The Andies Prairie samples were buffered much more than any of the others and may have been due to the substantial amount of organic matter present. Comparisons of buffering curves for C2 horizons, show that the sample high in imogolite (AP C2) was buffered at lower pH values than other samples that contained mostly allophane. The buffering curve for the Gilcent sample, which contained abundant halloysite, had weak acid properties similar to other samples but always at higher pH values.

Summary

The chemical composition of the Mazama amorphous clays is similar in molar $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio to those reported by Japanese

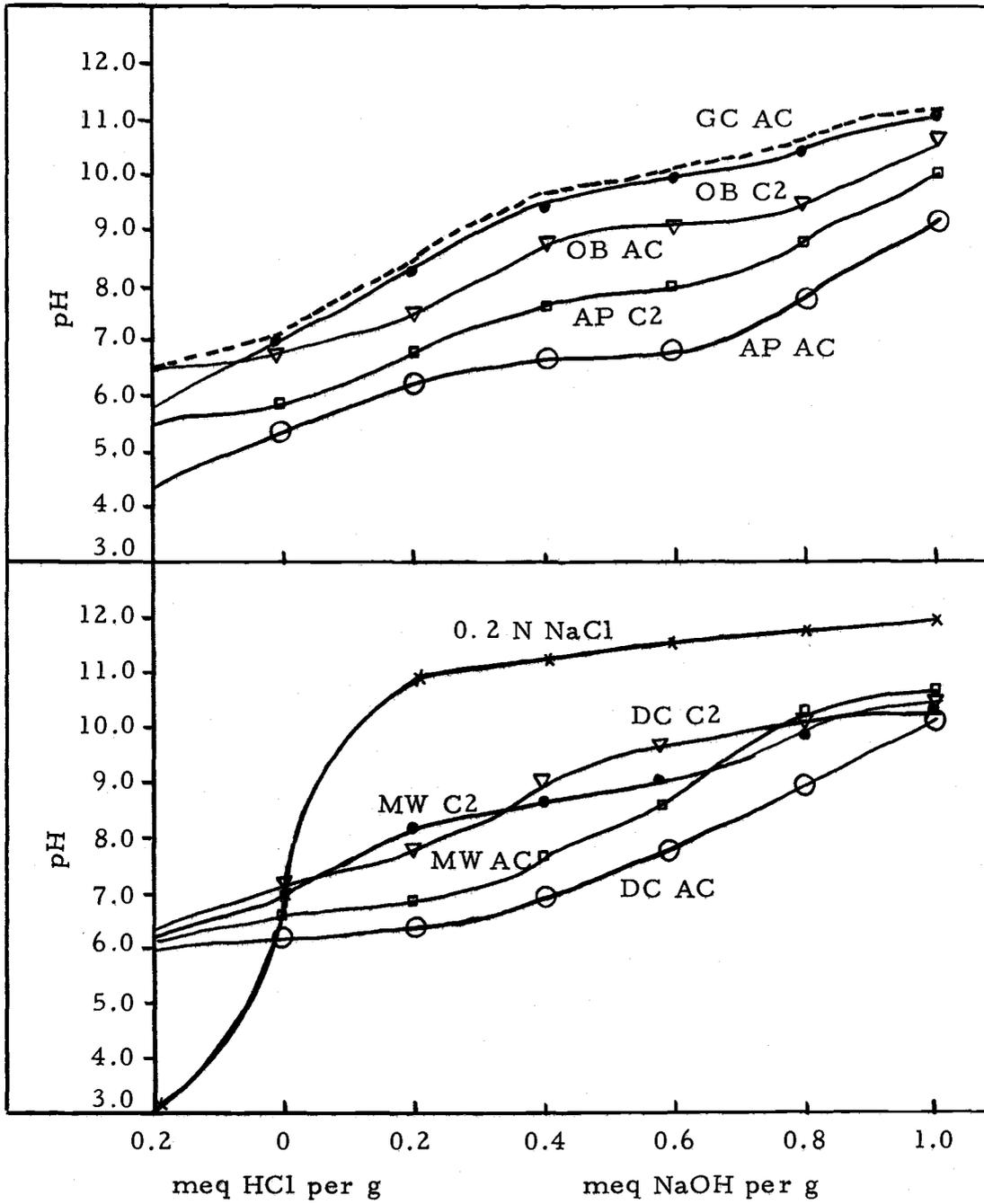


Figure 7. Titration curves of clays from Mazama tephra in 0.2 N NaCl.

researchers. When compared to the synthetic gel that had the largest CEC, the natural clays always contain more aluminum but very similar charge characteristics. The changes in CEC values following defferation with DCB supports the data presented in Chapter 3 that significant alterations occur in the amorphous clays by this chemical treatment. All samples had significant amounts of pH dependent anion and cation exchange properties even though mineralogy varied among samples. Copious quantities of phosphate were adsorbed by the Mazama clays and suggest that soil fertility problems could occur on soils with similar amorphous colloids. The buffering curves indicate that the weak acid properties of the clays is strongest below the equilibrium pH in 0.2 N NaCl. A sample high in halloysite had a buffering curve distinctly different from a sample containing much imogolite and gel.

V. SUGGESTIONS FOR FURTHER STUDY

The significance of amorphous clays in Oregon soils has not been fully established. However, several studies that have been completed indicate that they can be a contributor to land use problems in the state. A study by Dryness (1967) on landslides in the H. J. Andrews Experimental Forest revealed that the greatest percent of mass movements occurred on soils formed from tuff. Similar relationships have been reported for some areas of the Oregon coast range by Schlicker (1972). A study by Paeth (1970) on the mineralogy of some soils and tuff layers involved in landslides revealed that amorphous clays composed from 35 to 68 percent of the clay fraction. Other studies that have been completed suggest that amorphous clays can be significant contributors to reservoir turbidity (Youngberg and Klingeman et al., 1971). Preliminary investigations in the present study indicate that some cutbank failures along Oregon highway 34 occurred in soil materials that contained abundant fine crystalline halloysite and amorphous gels as revealed by TEM analysis. Problems with phosphate availability on several ando like soils in the state have been observed (Personal communication, T. L. Jackson, O. S. U.).

Other geologic formations and soils need to be studied further to determine more about the distribution of amorphous clays in Oregon. Further work needs to be done to determine what influence these

amorphous clays have on soil mass movement, permeability to water and solutions, site suitability for road locations, reservoir turbidity and soil fertility.

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APPENDICES

APPENDIX I

Ochoco Butte: OB

Wheeler County, Oregon, Ochoco area, south half SE 1/4, NE 1/4, Sec. 11, T. 13S., R. 20E.; about 50 feet W of F.S. road 127 on the southern tip of ash body, on aerial photograph EJL-7-140. About 5760 feet elevation, 2% SE slope, well drained soil from ash over buried soil (after Rai, 1971).

Horizon	Depth (cm)	
O1	2-0	Partially decomposed litter.
A1	0-22	Dark yellowish brown (10YR 3/4) loamy sand, pale brown (10YR 6/3) dry; massive; soft, friable, nonplastic, nonsticky; many very fine interstitial pores; boundary clear, smooth.
AC	22-32	Dark yellowish brown (10YR 4/4) loamy sand, light yellowish brown (10YR 6/4) dry; massive, soft, friable, nonplastic, nonsticky; many very fine interstitial pores; about 25% very pale brown (10YR 8/4) and yellow (10YR 7/6) sand grains; boundary clear, smooth.
C1	32-70	Light yellowish brown (10YR 6/4) loamy sand, very pale brown (10YR 7/3) dry; massive; soft, friable, nonplastic, nonsticky; many very fine interstitial pores; sand size pumice grains as in above horizon; boundary clear, smooth.
"C1 or C2"	70-90	Very pale brown (10YR 7/4) loamy sand, very pale brown (10YR 8/4) dry; massive; soft, friable, nonplastic, nonsticky; many very fine interstitial pores; pumice grains as in above horizon; boundary abrupt, smooth.
C2	90-110	Very pale brown (10YR 7/3) coarse loam, white (10YR 8/2) dry; massive; soft, friable, nonplastic, nonsticky; many very fine interstitial pores; pumice grains of same color as matrix; boundary abrupt, smooth. This horizon is banded, the boundary between the bands is abrupt, smooth. The sample of this horizon comprised of all bands.

Horizon	Depth (cm)	
IIBb	110-120 ⁺	Dark brown (7.5YR 3/2) silt loam, brown (10YR 5/3) dry; moderate very fine subangular blocky; friable, slightly plastic, slightly sticky; about 10% pebbles.

Day Creek

Grant County, Oregon, Beech Creek area, SE 1/4, NE 1/4, Sec. 24, T. 11S., R. 30E.; about 200 feet E. of F.S. road 1130 from point on road about 200 feet S of edge of scabland, on aerial photograph EPK 8-12.

About 5840 feet elevation, 2% S slope, well drained soil from ash over buried soil, on a broad, level to gently sloping summit, cut off by side drainages from the main area of the summit (after Rai, 1971).

Horizon	Depth (cm)	
01	2-0	Partially decomposed litter; variable in thickness; boundary abrupt, smooth.
A1	0-25	Could be designated B2. Dark brown (7.5YR 4/4) loam, light yellowish brown (10YR 6/4) dry; weak very fine granular or massive; very friable, nonplastic, nonsticky; abundant very fine interstitial pores; few black crystals; 5 to 10% soft, mostly 10YR 7/3 when moist, medium and fine sand grains (pumice); boundary clear, smooth. At upper boundary, nearly black, intermittent horizon less than 1 cm thick.
AC	25-45	Yellowish brown (10YR 5/4) loam, very pale brown (10YR 7/3) dry; massive; very friable, nonplastic, nonsticky; abundant very fine interstitial pores; few black crystals, 10% sand grains as above; boundary clear, wavy.

Horizon	Depth (cm)	
C1	45-60	Yellowish brown (10YR 5/4) loam, very pale brown (10YR 8/3) dry; massive; very friable, nonplastic, nonsticky; abundant very fine interstitial pores; few black crystals, 10% sand grains as above; intermittent and variable in thickness with fragments similar to horizon below in places; boundary abrupt, irregular. This boundary apparently due to mechanical disturbance. Charcoal was sampled from lower part of this horizon.
C2	60-72	Very pale brown (10YR 7/3) very fine sandy loam, white (10YR 8/2) dry; massive; slightly hard, friable, brittle nonplastic, nonsticky; abundant very fine interstitial pores; few black crystals; 10% sand grains as above but without color contrast with groundmass.
IIBb	72-80 ⁺	Dark brown (7.5YR 3/3) moist loam; moderate very fine subangular blocky structure; friable, slightly plastic, slightly sticky; abundant very fine tubular pores.

Meadowood

Umatilla County, Oregon, Tollgate area, SW 1/4, SW 1/4, SW 1/4, Sec. 29, T.4N., R.37E.; about 200 feet east of Meadowood dirt road junction with highway 204 and 50 feet north of highway 204, at top of rise.

About 3900 feet elevation, 2% N slope, well drained soil from ash over loess (after Rai, 1971).

Horizon	Depth (cm)	
01 and 02	4-0	Partially decomposed litter.
A1	0-10	Very dark grayish brown (10YR 3/2) silt loam, dark grayish brown (10YR 4/2) dry; weak very fine granular; soft friable, slightly plastic, slightly sticky; abundant roots; boundary clear, wavy.

Horizon	Depth (cm)	
A12	10-30	Dark brown (10YR 3/3) silt loam, brown (10YR 4/3) dry; weak very fine granular; soft, friable, slightly plastic, nonsticky; abundant roots; boundary clear, wavy.
AC	30-38	Yellowish brown (10YR 4/3) silt loam, yellowish brown (10YR 5/4) dry; massive; soft, friable, nonplastic, nonsticky; abundant roots; boundary clear, wavy.
C1	38-50	Yellowish brown (10YR 5/4) silt loam, very pale brown (10YR 7/4) dry; massive; soft, friable, nonplastic, nonsticky; common roots; boundary abrupt, wavy.
C2	50-65	Light yellowish brown (10YR 6/4) very fine sandy loam, very pale brown (10YR 8/3) dry; massive; soft, friable, nonplastic, nonsticky; few roots; boundary abrupt, wavy.
IIBb	65-170 ⁺	Brown (10YR 5/3) silt loam, pale brown (10YR 6/3) dry; moderate fine subangular blocky; slightly hard, firm, slightly plastic, slightly sticky; few fine brownish clay films, clay content inc. with depth; few roots.

APPENDIX II

Plate 13. Electron micrographs of synthetic allophane and amorphous gel from an ando soil sample respectively.

