C - 494

THE CHARACTERISTICS AND GENESIS OF THE AKAKA AND HILO SOILS OF THE ISLAND OF HAWAII

A THESIS SUBMITTED TO THE GRADUATE DIVISION

OF THE UNIVERSITY OF HAWAII IN PARTIAL

FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

IN

SOIL SCIENCE

DECEMBER 1969

By

Roylyn Lee Voss

Thesis Committee:

G. Donald Sherman, Chairman Y. N. Kanehiro Goro Uehara We certify that we have read this thesis and that in our opinion it is satisfactory in score and quality as a thesis for the degree of aster of Science in Soil Science.

THE IS COMPITTEE

Yh airman

Yrhinin 1 Kanchies

ACKNOWLEDGMENT

The author wishes to acknowledge the financial assistance of the National Defense Education Act Fellowship under which a portion of this thesis was completed.

It is dedicated to my family without whose patience and understanding it could not have been completed.

TABLE OF CONTENTS

.

ACKNOWLEDGMENTS	i
TABLE OF CONTENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
INTRODUCTION	1
REVIEN OF LITERATURE	4
The Geologic Setting	4
The Climatic Setting	7
The Weathering of Volcanic Ash	8
Allophane Formation	8
Characteristics of Allophane	12
Bauxite Formation	14
Weathering Studies of the Hamakua Coast	
Area of Hawaii	15
The Present Classification of the Akaka	
and Hilo Soils	19
THE SOIL SITES	21
The Akaka Sites and Profile Descriptions	24
The Hilo Sites and Profile Descriptions	29
METHODS	34
Sample Selection and Description	34

14

Page

iii.

Page

_

TABLE OF CONTENTS (CONTINUED)

	Page
Sample Preparation	34
рН	34
Organic Matter	35
Total Nitrogen	35
Extractable Iron Oxide and Associated H20	35
Extractable Phosphorous	36
Total Silicate Analysis	36
Exchangeable Cations	37
Cation Exchange Capacity	37
Sample Pretreatment for Cation Exchamge Capacity	38
X-ray Diffraction Analysis	38
Differential Thermal Analysis	39
Bulk Density	39
Particle Density	39
RESULTS	40
Morphology and Soil pH	40
Water, Organic Matter, Total Nitrogen Content	
and C/N Ratios	47
Total Silicate Analysis	52
Extractable Iron Oxides	58
Extractable Cations, Extractable Phosphorous,	
Base Saturation and CEC	58

TABLE OF CONTENTS (CONTINUED)

P	a	g	e

X-ray Diffraction and DTA	60
Effect of Pretreatment on CEC	64
Mineral Allocation	69
DISCUSSION	74
Interrelationship of Some Soil Properties	74
Origin and Genesis of the Soils	74
The Classification of the Soils	76
SUMMARY AND CONCLUSIONS	78
LITERATURE CITED	80

iv.

LIST OF TABLES

.

Table		Page
1	The pH, pH, and Effect of dehydration on pH	
	of Akaka and Hilo Soils	46
2	Field Moisture, Extractable Iron Oxides, O.M.,	
	N, C/N, Si/Al Ratios, and CEC of Akaka Soils -	48-49
3	Field Moisture, Extractable Iron Oxides, O.M.,	
	N, C/N, Si/Al Ratios, and CEC of Hilo Soils	5051
4	Total Silicate Analysis of Akaka Soils	53-54
5	Total Silicate Analysis of Hilo Soils	55-56
6	Extractable Cations, Extractable P205, Base	
	Saturation, and CEC of Akaka and Hilo Soils	59
7	Effect of Pretreatment on CEC of Akaka and	
	Hilo Soils	68
8	Total Mineral and Non-mineral Content of	
	Akaka and Hilo Soils	71
9	Non-crystalline Mineral Content and Bulk	
	Density of Akaka and Hilo Soils	72

LIST OF FIGURES

Figure		Page
1	Profile of Mauna Kea Mountain from Hilo Bay 🛛	3
2a	Low Lying Cinder Cone At Pepeekeo with Mauna	
	Kea Summit in Background	5
2b	Aerial View of Cluster of Cinder Cones at	
	Pepeekeo with Mauna Loa Summit in Background	5
3	Banding of Gibbsite in Hilo Soil	17
4a	Close-up of Gibbsite Band	18
4b	Aggregated Gibbsite Separated from Gibbsite Band _	18
5	Topographic Map Showing Extent of Akaka and	
	Hilo Soil Areas in Relation to the Northeast	
	Coast of Hawaii	22
6	Geology of the Eastern Coast of Mauna Kea with	
	Sampling Sites Designated	23
7	Profile of Akaka Soil Site 2	41
8	Profile of Hilo Soil Site 1	42
9	Schematic Diagrams of O.M. Contents and Silica/	
	Alumina Ratios of Akaka Soils	43
10	Schematic Diagrams of O.M. Contents and Silica/	
	Alumina Ratios of Hilo Soils	44
11	Powder X-ray Diffraction Patterns of Akaka	
	Soil Site 2	61

LIST OF FIGURES (CONTINUED)

Figure

Page

12	Powder X-ray Diffraction Patterns of Hilo	
	Soil Site 1	62
13	Effect of Treatment on X-ray Diffraction Pattern	
	of Hilo Soil	65
14	DTA Diagram of Akaka Subsoil	66
15	Simple Correlation Coefficients of Several Soil	
	Properties of Akaka and Hilo Soils	75

INTRODUCTION

During the last ten years there has been increasing interest throughout the world on the characterization of soils containing amorphous inorganic materials. This has been particularly true in those areas of the tropics, subtropics and even a few temperate areas having large areas of soils developed from volcanic ash. Most notable among these places are Japan, New Zealand, Indonesia, the Pacific Northwest of the United States, and Hawaii.

Hawaii is exceptionally well suited for this type of study because of the wide range of climatic conditions occuring over relatively short geographical distances. As a consequence, a complete range of soil development can be examined with rather uniform parent material influence.

This type of study has been largely accomplished on the volcanic ash soils of the drier areas in Hawaii, but the work in the perhumid rainforest and former rainforest areas is piecemeal at best.

Because of rapid weathering under conditions of high rainfall, volcanic ash quickly looses nearly all of its identifying characteristics as to its origin and age. Amorphous materials develop that reflect even minor differences in particle size, mineral content and moisture holding characteristics, but at the same time the causes of these differences are completely obliterated.

With continuing development these soils ultimately form ferruginous bauxites and/or bauxites as silica is removed. Then only is the amorphous character of these soils lost as hydrated oxides of iron and aluminum crystalize out, changing the nature of the soils completely.

The Hilo and Akaka soils are representative soils of a large part of the northeast coast of the Island of Hawaii that have formed under perhumid conditions from andesitic volcanic ash.

While geologically young, these soils have been so intensively weathered that they are approaching the stage of bauxitization and are therefore somewhat different than the other large areas of volcanic ash soils that have been reported in Hawaii and elsewhere. With these factors in mind, eight profiles were described and sampled and characterized mineralogically, chemically and physically with the following objectives in view:

- To determine the proper place of the Hilo and Akaka soil families in the new comprehensive system of soil classification the Seventh Approximation.
- 11. To establish the similarities and differences in the morphology and the genesis of the Hilo and Akaka soils.
- 111. To determine the nature of the allophane amorphous hydrous oxide - gibbsite relationships in the Hilo and Akaka soils and the place of the soils on the continum of weathering to bauxite.
 - 1V. To relate the Hilo and Akaka soils to other soils of the world that have developed from volcanic ash.



Figure 1: Profile of Mauna Kea Mountain from Hilo Bay, Hawaii.

REVIEW OF LITERATURE

The Geologic Setting:

The Hilo and Akaka soils are found on the eastern slopes of Mauna Kea mountain on the island of Hawaii, the youngest and largest island of the Hawaiian Archipelago.

Mauna Kea is a volcanic dome covering 919 miles and reaching a height of 13,784 feet above sea level, Figure 1. The eastern coastal region has a drop of 500 feet per mile and is dissected by many narrow, deep erosional valleys.

The base rock of the mountain consists of two volcanic series. The older Hamakua Volcanic Series consists of olivine basalt with thin beds of vitric basaltic ash between some of the flows. Some andesite is also present in the upper members (Stearns, 1946). The second series is dominated by andesite and is designated as the Laupahoehoe Volcanic Series.

With the exception of the erosional valleys the eastern slope of Mauna Kea is nearly completely covered with weathered volcanic ash resting uncomfortably on the flow units.

There has been some question on the exact origin and character of the volcanic ash of the Hamakua coast due to this weathering and its effect on the diagnostic properties of ash.

Wentworth (1938) has stated that the production of numerous cones of fine pyroclastic material is commonly associated with the final stages of activity of a great volcanic dome.

This was true with Mauna Kea dome and the summit area has over a hundred cones ranging in size from a hundred feet high to nearly a thousand feet. These cones cover an area equivalent to 15 miles in diameter. In addition, there are a few cones on the lower slopes consisting of volcanics from the earlier Hamakua Volcanic Series. These cones include the small cones just outside of Hilo as well as the larger cones at Pepeekeo, (Figure 2a and b).



Figure 2a: Low lying cinder cone at Pepeekeo with Mauna Kea summit in background.



Figure 2b: Aerial view of cluster of cinder comes at Pepeekeo with Mauna Loa summit in background.

The ash associated with the summit cones was called the Waiau Formation by Wentworth (1938) to differentiate the Mauna Kea pyroclastic material from the more recent Pahala Ash covering a large portion of the southwestern section of the Island of Hawaii. The Waiau Formation takes its name from the small summit lake on Mauna Kea and the Pahala Ash from the town named Pahala in Kau.

The Waiau Formation includes the summit area material as well as the highly weathered and altered ash covering the Hamakua coastal area. A sub-designation was given to the weathered material, "yellow tuff phase " and the bedding of the weathered materials was attributed to rather gradual transitions in coarseness of the material as it was deposited. These differences are continuous and uniform over long distances parallel to the bedding and support the contention that the ash of the slopes of Mauna Kea originated from the summit cones.

Stearns (1946) proposed basically the same mode of formation and origin of the ash on Mauna Kea, but preferred to use the Pahala Ash designation for all the ash found on the south and east sides of the island of Hawaii.

The black ash of the upper slopes was found to be andesitic glass derived from the cones of the Laupahoehoe Volcanic Series on the summit. On the lower sections of the mountain both the ash and lapilli were found to be altered to palagonite, a yellowish-brown to orange colored, waxy, silica jel mineraloid. Late Pleistocene to early Upper Pleistocene age was given to the ash with the acknowledgement that the material in many sections has had contributions of pyroclastic material from Mauna Kea and Kilauea from its time of origin until present (Stearns, 1946).

In the Hamakua coast area the Pahala (Waiau) ash range in thickness from 10 to 15 feet at Hilo and thins to 5 to 6 feet thick at Ookala, 30 miles to the northwest. It thickens to over 20 feet at the 2,000 to 3,000 foot elevations above Hilo and is proportionately thicker above Ookala (MacDonald, 1945). In some areas there is evidence of ash of

6,

different ages present but it is impossible to distinguish any differences in the weathered material on the lower eastern slopes (Stearns, 1946).

The pattern of thickness variation towards the northwest of Hilo has led Fraser (1960) to propose that the ash of the entire area surrounding Hilo and the Hamakua coast comes from Kilauea Volcano with only small contributions from the summit cones of Mauna Kea.

The Climatic Setting:

Although Hawaii's climate is influenced by the factors of geologic location in the Pacific Ocean, latitude, and the topography and elevation of the respective islands, only the last factor is of importance when characterizing soil in a specific location or area.

The Hamakua coast of the Island of Hawaii is situated on the windward eastern side of Mauna Kea mountain and recieves from 100" of rainfall at Ookala up to 150 " of rainfall per year at Hilo. These amounts increase as elevations are increased so that the annual rainfall approaches 300 " at the 1,500 to 2,000 foot elevations above Hilo. Above this maximum the rainfall gradually tapers off to less than 20 " at the summit of Mauna Kea. Much of the summit precipitation comes in the form of snowfall between the months of November and May.

This pattern of increase and subsequent decrease of rainfall with increasing elevation is common to the higher mountains in Hawaii. It is due to the splitting effect that the mountains have on the rain-bearing tradewinds (Cline, 1955) and a temperature inversion layer occurring at approximately 2500 feet above sea level (Swindale, 1964).

Temperatures in Hilo range from a lowest monthly mean of 70.4 [•]F to a highest monthly mean of 75.4 [•]F. Annual mean temperature is 72.8 [•]F. Day to night variations in Hilo are of the magnitude of 10[°]F.

Mean temperatures generally fall between 2.5 and 3.0 °F per 1,000 foot increase in elevation. At Lake Waiau, on the summit of Mauna Kea volcano, the nightly temperature falls below 32 °F without exception.

7.

- During the Wisconsin glacial period a glacier of up to 250 feet thick covered the summit of Mauna Kea as shown by moraines and other signs of glaciation as far down as the 10,500 elevation (Stearns, 1946).

The prevailing winds on the Hamakua coast are northeasternly tradewinds but high altitude winds can be quite variable.

The rainfall pattern in the Hamakua coast is quite uniform, with no prolonged periods of dryness, although northwest of Ookala periodic late summer dry periods are known to occur.

The Weathering of Volcanic Ash:

Volcanic ash is classified geologically by its size, crystallinity, and composition (Wentworth, 1938).

a.	Grain size:	4 to $\frac{1}{2}$ mm - coarse ash
		less than $\frac{1}{2}$ mm - fine ash
b.	Crystallinity:	lacks crystallinity - vitric
		mostly crystalline - crystalline
		mostly stony - lithic
с.	Composition:	Named according to the rock name of correspond-
		ing chemical composition

These properties, along with that of porosity, contribute to the capacity factors of chemical weathering of volcanic ash.

The intensity factors such as climate, drainage, vegetation, and time affect the extent and rate of its weathering (Sherman, 1962).

Volcanic ash, possibly more rapidly than any other soil forming material, interacts through chemical weathering and biological forces to form the weathering product - volcanic ash soil.

Allophane Formation:

Mohr (1944) examined soils developed from vitric basic volcanic ash in Indonesia and found that the material is very easily attacked by weathering liquids. Under conditions of high rainfall and temperatures above 25 °C hydralysis occurs very rapidly with the pH of the system stabilizing around a pH of 7.0. Under these conditions the silica goes into solution, iron forms a hydrated gel, potassium feldspar develops into a kaolinitic gel and calcium feldspar weathers to hydrated aluminum oxide.

This appears to correspond to the formation of palagonite, a silicate mineraloid gel of variable composition (Hart, 1929).

With continued weathering some of the silica freed from the system is removed and the kaolinitic gel, allophane, develops as a logical step in the weathering sequence of andesite ash (Hendricks, 1966).

Many proposals have been put forth on the formation of allophane, but to date no good definition has been given regarding the limits of its composition and character.

From Ross and Kerr's (1934) original work, allophane has been accepted as any mutual solution of silica, aluminum, and water, with minor amounts of bases. White (1953) broadened this to include all amorphous substances associated with clay minerals, a move that did not preclude non-silicate containing materials. Grim (1953) describes allophane simply as a random arranged tetrahedral silica and octohedral aluminum with variable water in solution rather than bonded water.

More recently, while little attention has been given to the chemical nature of allophane (Marshall, 1964), there is evidence to support limiting the term allophane to those amorphous arrangements of silica and alumina to silica/alumina mole ratios between 1 and 2 (Birrel and Fieldes, 1952; Swindale, 1965; and Yoshinaga, 1966). This range includes both soil and geologic allophanes, although some high aluminum allophanes have been reported with ratios below one (Tan, 1961; and Snetsinger, 1967).

Bates (1952, 1960, and 1962) found allophane to be an intermediate amorphous product in the breakdown of halloysite and in the formation of gibbsite in the weathering sequence:

feldspar \longrightarrow halloysite \longrightarrow Al gel \longrightarrow gibbsite

The weathering conditions would determine whether an aluminum gel or allophane would form.

The sequence kaolinite to allophane to alunite was studied by Keller (1967) in Pennsylvanian shale due to silica removal by supergene sulfate weathering liquids, but the allophanes formed in non-volcanic ash materials are beyond the perview of this thesis.

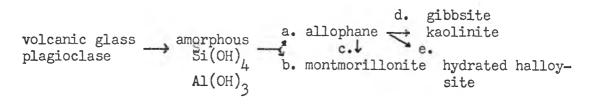
In New Zealand, Fieldes and his co-workers have been studying the problem since 1952. They have found that volcanic glass goes quickly through the weathering stages to allophane (Fieldes and Swindale, 1954). With continuing silica removal kaolinite or gibbsite may form, but under conditions of silica addition and wetting and drying montmorin clays may develop. Two different types of allophane are commonly reported in New Zealand, allophane A and allophane B. An intermediate allophane is also recognized, AB.

Allophane B is a fine grained mixture of discrete silica and aluminum. With continued wetting and drying this material increases in grain size and order. Still amorphous X-ray, this is allophane A. The sequence may then proceed through various stages of kaolinitic mineral formation such as; hydrated halloysite, halloysite, and under some conditions, kaolinite itself (Fieldes, 1954).

Hydrous feldspar, hydrous glasses, hydrogels and other amorphous materials are recognized as being in the allophanic weathering realm (Furkert and Fieldes, 1968).

Allophane is also considered to be an early weathering product in the volcanic ash soils of Japan (Sasaki, 1957). Plagioclase and vitric pumice break down to form silica, alumina, and iron oxide sols. The alumina sol can become gibbsite or by absorbing silica sol, in a weak acidic environment of pH 6 to 7, allophane. By releasing alumina or absorbing more silica sol the allophane becomes hydrated halloysite. The iron oxide sol in turn may form goethite.

Egawa (Japanese Ministry of Agri. and Forestry, 1964) has further refined this sequence from the work of his co-workers (Sudo, 1959;



- b. indicates base rich impeded drainage
- c. indicates base rich, silica rich impeded drainage
- d. indicates strong acid conditions with silica and bases absent and isolated silica reacts with gibbsite to form kaolin minerals
- e. indicates silica rich, base poor water perculating through allophane to form hydrated halloysite

More recently (Miyauchi and Aomine, 1966) a relatively high alumina amorphous gel has been found in the Imogo soil in Japan. Taking its name from the soil name, imogolite has a silica, alumina mole ratio of near one. Wada (1967 and 1968), Yoshinaga (1968), and Kanno (1968) have since characterized it as being a precursor to allophane and have indicated that aluminum in 6 coordination would change to an average of 5 coordination upon dehydration, and be further changed to four coordination by dehydroxylization.

Kanno (1968) also found that the chain structured imogolite is best separated by acid dispersion while allophane is dispersed under alkali conditions.

In Hawaii it has become quite clear that the weathering of volcanic ash follows the sequence:

ionic system --> amorphous system --> cryptocrystalline --> crystalline system clay (Sherman, 1962, 1967).

After originally placing allophane at stage 11 of their numerical weathering sequence (Jackson and Sherman, 1953), Jackson (1968) and Sherman (1967) have both concluded that allophane should be placed at stage 10 with the kaolin minerals on the weathering sequence. This recognizes the ability of allophane to weather to gibbsite (Sherman, 1958).

It has been proposed that a distinction should be made between sesquioxide allophane of relatively low silica to alumina mole ratio and halloysitic allophane with a chemical formula corresponding to the kaolin minerals (Jackson, 1965).

During the last few years the presence of allophane of various compositions has been reported throughout the world. Most of these occur in areas that have had some influence from volcanic ash.

Characteristics of allophane:

It has been well established that allophane and related amorphous hydrated oxides have a high reactivity in the soil. High cation exchange capacities, high phosphate fixing capacities, and marked changes due to dehydration have all been reported in conjunction with studies of allophane. In many cases it has been these phenomena along with the absence of crystalline clays that have led to the designation of allophane soils.

Amorphous soil clays with cation exchange capacities of over 100 milequivalents per 100 grams soil have been reported (Fieldes, 1952; Rutherford, 1962; and Tan, 1965). Much of this cation exchange capacity is pH dependent (Tan, 1965; Fieldes, 1962; Houng, 1966; and Jackson, 1965 and 1968), and has led to the proposal for a semi-quantitative method of allophane determination, the cation exchange capacity delta value (Aomine and Jackson, 1959).

This value, the difference in cation exchange capacity determined at pH 7.0 of an acid pretreated sample and an alkali pretreated sample, can be used in mineral allocation as a measure of allophane content. The alkali pretreated sample has a net negative charge created by hydronium or proton release from the surface structure. This charge is measured at pH 7.0 as cation exchange. Pretreatment with acid buffered sodium

12.

acetate completely restores the sites that had lost protons and eliminates a portion of the net charge as measured at pH 7.0 (Jackson, 1965).

The difference in measured cation exchange capacity of the sample pretreated in both ways is approximately 100 m.e. per 100 grams of soil for the sesquioxide allophane, but falls to 18 to 20 for the halloysitic allophanes (Jackson, 1965).

Charge characterization of allophane has been found difficult because of factors affecting its measured cation exchange capacity. Concentration of the leaching solutions, the nature of the saturating ion, and the strength and volume of the alcohol used have all contributed to nonreproducable results in some soils (Birrel and Gradwell, 1965).

The non-pH dependant or permanent charge of allophane is thought to be due to tetrahedrally coordinated aluminum (Fieldes, 1962; Swindale, 1965; and Houng, 1966). While 6 coordinated aluminum is neutral in charge, 4 coordinated aluminum has a negative charge. In synthetic silica and alumina systems, increasing the pH at the time of co-precipitation has been shown to increase both the cation exchange capacity and the tetrahedrally coordinated aluminum (Fripiat, 1964). Natural allophanes in Japan soils have been found to contain as high as 50 % tetrahedrally coordinated aluminum (Egawa, 1964).

This surface activity has been shown in some ways to correspond to the reactivity of amorphous aluminum silicate cracking catalysts used in the petrolium industry (Tamale, 1955 and Milliken, 1955).

The high buffering capacity shown by most allophanes can be attributed to the precipitation of $Al(OH)_3$ from the exchange sites (Kanno, 1955).

Allophanes are also noted for their high water holding capacities, relationship with high humus contents in soils, and irreversibility of dehydration (Dames, 1955; Tan, 1965; Bates, 1962; and Sherman, 1958).

Many differentially soluble methods have been used for the separation and characterization of allophanes. Boiling carbonate (Jackson, 1958), oxalic acid and potassium oxalate (Harada, 1955), and 0.5 N

13

sodium hydroxide (Hashimoto and Jackson, 1960) have all met with some success.

The method of Hashimoto and Jackson is most promising at present, though the removal of silica and aluminum by it does not necessarily indicate the presence of allophane if gibbsite or other amorphous silica and aluminum materials are present in the sample (Hashimoto and Jackson, 1960) (Jenne, 1965).

Surface area measurements, electron diffraction studies, electron microscope studies, infrared adsorption, and moisture retention characteristics have also been used to characterize various allophanic materials from throughout the world (Fieldes, 1952 and 1955; Gradwell, 1954; Aomine, 1955 and 1968; Orchiston, 1959; Alonso, 1963; and Demumbrum, 1964).

Bauxite formation:

As weathering proceeds under conditions conducive to continued silica removal from volcanic ash, bauxitization can occur.

A delicate balance exists between the reactions involving the continued breakdown of allophane. If silica is present in the weathering solution, crystallization to halloysite can occur. If silica is absent or is being continuously removed, gibbsite may form (Jackson, 1968).

With fresh water, pH 6 to 6.5, silica is many times more soluble than aluminum so that in cases where water is abundant direct bauxitization may be the general rule (Keller, 1964). It results in crystalline products under wetting and drying, or as an amorphous hydrated alumina under continuously wet conditions (Sivarajasingham, 1962). Occurence of direct bauxitization from feldspars has also been well documented (Abbott, 1958; Alexander, 1941; Edwards, 1955; Gordon, 1958; and Harrison, 1934).

Organic matter as well as sodium and potassium in solution tend to increase the solubility of silica in the process of weathering (Keller, 1965 and Ruxton, 1968). As a consequence, allophane and gibbsite or other hydrated oxides of aluminum can be found concurrently (Wada, 1966;

14

Besoain, 1964; and Glinka, 1927).

These hydrated aluminum oxides show a sequence of structural order similar to that found in allophane. Sherman has proposed the following scheme (Sherman, et al, 1967).

 $Al^{+3} \rightarrow Al(OH)_{3}^{-} \rightarrow Al(OH)_{3} \rightarrow Al(OH)_{3}$ ionic amorphous cryptocrystalline crystalline

If silica enters into this reaction sequence at any point, resilification can occur, returning the system to the allophane - halloysite sequence explained earlier. This occurs at an H_4SiO_4 concentration in the weathering solution of 2 ppm. or above. Below this value kaolinite minerals would not be able to form and gibbsite or other aluminum hydrated oxides would remein as a residual mineral (Garrels and Christ, 1965).

Weathering studies of the Hamakua coast area of Hawaii:

As early as 1898 the Hamakua coast area of the island of Hawaii gained recognition as being the site of extremely weathered volcanic ash soils. This weathering was attributed to the action of drainage waters high in sulfur dioxide originating from the surrounding sites of volcanic activity. Bauxite " of remarkable purity " (Maxwell, 1898) was found to exist in masses in the soil interlayered with material of markedly different color and composition.

Kelley (1915) and McGeorge (1917) worked with a few soil samples from the eastern coastal area of Mauna Kea, but took no special notice of the ash soils. Later, Richter (1931) and Dean (1937) took note of the high waterholding capacity, relatively high organic matter content, and irreversible drying of these soils.

In a review of the soils of Hawaii, Smith (1935) noticed the layering of the volcanic ash soils. He observed that bands of pumice or "scoria" (clinkery ash flows) were only partially weathered in the "B" horizon of the soils, but that the breakdown of these bands was complete in the "C" horizon, (Figure 3). It was postulated that the lower layers had been subjected to a more prolonged effect of percolating groundwater because of the high porosity of the soils.

Later, more comprehensive and systematic studies were accomplished by Hough (1941) and Ayres (1943), but no special notice was taken of the distinctive layering of the soils formed from volcanic ash on the Hamakua coast.

It was then proposed that the hydrol humic latosols of the island of Hawaii (Cline, 1955) could develop distinctive stratification of the parent ash due to differential weathering that occured very rapidly in the high rainfall, perhumid climate of the area (Sherman, 1949).

This concept was affirmed and the pumice layers that had been described by Smith were identified as horizons of aluminum concentration, segregation and aggregation into gibbsite (Sherman, 1957). This gibbsite may be found in tube sheetlike forms when the soil is dried, but little evidence usually exists for gibbsite when the soil is in its field moist condition, (Figure 4a and b).

Dehydration has a very marked effect on both the physical and chemical properties of the Akaka and Hilo soils. Shrinkage and water loss is irreversible as is a large portion of the cation exchange capacity. Losses of up to 75% of the CEC are reported (Kanehiro, 1956), and the soils smear under pressure due to the thixotropic nature of the colloids present.

Because of their high aluminum content numerous studies of bauxite potential in the Hawaiian Islands have included these soils in their perview.

Variable average amounts of gibbsite from a few percent to 35% have been reported in these soils (Tamura, 1955; Sherman, 1958; Tenma, 1965 and Bates, 1960). Reports of the total alumina content also vary considerably. The ore content has been reported from 17 to 22% aluminum oxide (Sherman, 1958 and Irving, 1961) to 26 to 27%

16.



Figure 3: Banding of gibbsite in Hilo soil .



Figure 4a; Closeup of gibbsite band.



Figure 4b; Aggregated gibbsite separated from gibbsite band.

(Calhoun, 1962).

Although low in grade, the 150 to 200 square miles of hydrol humic latosol has been shown to contain sufficient ore to support an aluminum industry if economic conditions were satisfactory. Benefication of the ore may be possible due to the separation of gibbsite into relatively pure aggregates upon drying (Sherman, 1958).

Low amounts of kaolin minerals may be present (Tanada, 1950; Dean, 1947; and Tamura, 1953). Larger amounts of mica, quartz, magnetite, maghemite, anatase and possibly lepidocrocite are also found (Tamura, 1953).

The present classification of the Akaka and Hilo soils:

The Akaka soil is classified under the U.S.D.A. Soil Classification System - the Seventh Approximation (1967) as a member of the thixotropic, isomesic family of typic hydrandepts and the Hilo soil as a member of the thixotropic isohyperthermic family of typic hydrandepts.

The hydrandepts belong to the inceptisol order of mineral soils having umbric or histic epipedons. The umbric epipedon is a dark colored, acid surface horizon that has less than 50% base saturation. The histic epipedon is a peaty, water saturated surface horizon found on some soils. Both the Hilo and Akaka soils have umbric epipedons, although some of the Akaka soils found in depressional areas could be expected to have histic surface horizons. They do not have horizons of iron and humus accumulations as are found in podzolic soils, and they should not contain horizons of low cation exchange capacity sesquioxide accumulations.

The order level of these soils is the andept soils. They are developed generally from volcanic ash or ash pumice and contain a high allophane content in their clay fractions or a high unweathered ash content in their sand and silt fractions, or both. Bulk density of the andepts are less than .85 grams per cubic centimeter in the surface or the elluviated subsurface and are moderately well drained to well drained. The hydrandepts great group have clays that dehydrate irreversibly into gravel sized aggregates and have moderate to warm soil temperatures.

The typic subgroup designation of these soils indicates they are deep soils that follow the norm from the concept of the soils at the family level of classification the thixotropic designation indicates that the colloids are smeary or possess thixotropic properties. Isomesic and isohyperthermic indicate uniform year round temperatures that are moderate (59 to 72 °F) to warm (72 °F and above), respectively.

These are basically the properties that have been described in the soil survey of Hawaii (Cline, 1955) for the hydrol humic latosols, but put in terms of the present classification scheme.

1.1

20

THE SOIL SITES

The Hilo soil has been entirely devoted to sugar cane production for the past 100 years. It is situated on the lower slopes of Mauna Kea at elevations of from sea level to 2400 feet and covers 58,600 acres.

The Akaka soil is situated on higher elevations from 800 to 6000 feet. Because of dense cloud cover over most of the Akaka soil area and its depressing effect on sugar cane yields, it has been left largely to forest. The Akaka extends over 196,400 acres (Cline, 1956). Figure 5 show the extent of the two soils.

The dominant species in the rainforest areas is ohia lehua (<u>Metrosideros collina</u>), with some areas of native koa (<u>Acacia koa</u>) and introduced eucalyptus (<u>Eucalyptus sp</u>.). Guava (<u>Psidium guayava</u>), fern (<u>Cyclosorus sp</u>.), staghorn fern and treefern (<u>Cibotium sp</u>.) make up the ground cover throughout most of the forested area.

Previous to cultivation of sugar cane the lower slopes were covered with rainforest similar to that of the upper slopes at present (Ayres, 1943).

The following are detailed sample site descriptions.

Colors are according to the notation of Munsell and textures are apparent field textures. Sample locations of the eight profiles and the geology of the Hamakua coast are shown in Figure 6.

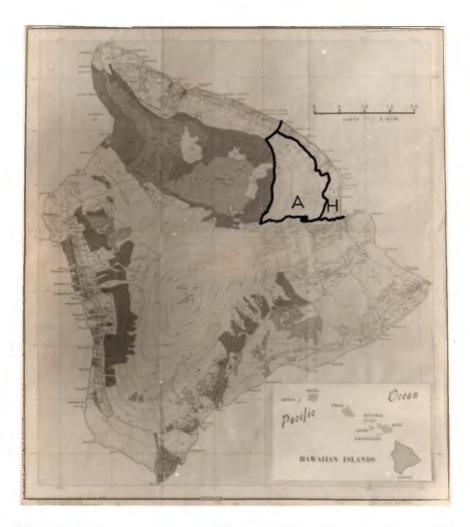


Figure 5: Topographic map showing extent of Akaka and Hilo soil areas in relation to the Northeast coast of Hawaii, (A, Akaka; H, Hilo).

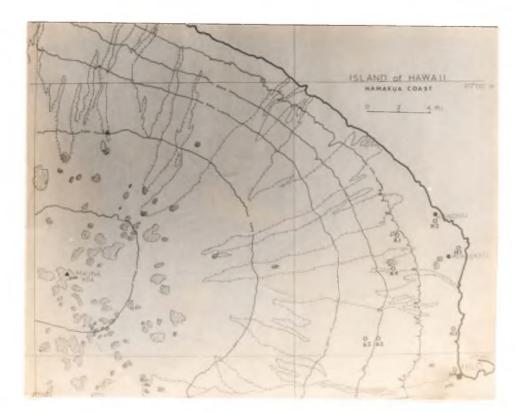
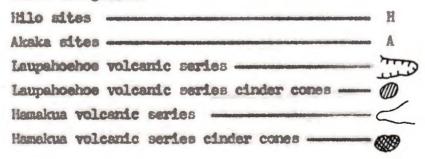


Figure 6: Geology of the eastern coast of Mauna Kea with sampling sites designated.



Akaka soil sites and profile descriptions:

Site A-1:

٠

te A-	·1		
	Ap	0–13"	Dark brown (7.5YR 3/4) loam, friable when moist, slightly plastic when wet, with medium, moderately well developed granular structure, pH 4.6.
	B2	13–20"	Yellowish red (5 YR 4/6) silty clay loam, friable when moist, plastic when wet, slightly smeary, with medium, moderate, subangular blocky structure, pH 5.1.
11	A1	2028"	Red (2.5YR 4/6) silty clay loam, friable, slightly plastic when wet, moderately smeary, medium, moderate, subangular blocky, pH 5.1.
11	B2	28–36"	STrong brown (7.5YR 5/4-4/4) silty clay loam, friable, plastic, slightly smeary, with fine, weak subangular blocky structure, pH 4.9.
111	A1	36-47"	STrong brown ($7.5YR 4/4$) silty clay loam. Firm when moist, plastic, with fine, weak subangular blocky structure, pH 5.2.
111	B21	47–52''	Reddish brown (5YR 4/4) silty clay loam, moist friable, plastic when wet, slightly smeary, with moderately developed, medium aubangular blocky structure, pH 5.2.
111	B22	52–59"	Dark brown (10YR 3/3) silty clay loam with moderate, medium subangular blocky structure. Friable when moist, plastic when wet, slightly smeary, pH 5.6.
111	B23	59-68"	Yellow red (5YR 4/6) clay loam, friable when moist, slightly plastic, moderately smeary, with weak, medium subangular blocky structure. Contain massive dark red (2.5YR 3/8) gritty clay loam inclusions with brownish yellow (10YR 6/8) gibbsite aggregates, pH 5.8.
1V	A1	68–74''	Reddish brown ($5YR 4/4$) silty clay loam, friable when moist, slightly plastic, moderately smeary, medium, moderately subangular blocky structure, pH 5.6.
1V	B21	74–83"	Reddish brown (5YR 4/5) silty clay loam, friable, slightly plastic, moderately smeary, weak, medium subangular blocky structure, pH 5.6.
1V	B22	83-89"	Yellowish red (5YR 4/6) light clay loam, friable slightly sticky, moderately smeary, medium, moderate subangular blocky structure, pH 5.6.
17	B23	89–96**	Reddish brown (5YR 4/4) silty clay loam, firm,

- P. B. C.

Plastic, slightly smeary, with medium, well developed subangular blocky structure, pH 5.6.

V A1 96-106" Red (2.5YR 4/6) silty clay loam, firm, slightly sticky, moderately smeary, with weak, medium subangular blocky structure, pH 5.6.

Site A-1 is located approximately $\frac{1}{2}$ mile below the Akaka Falls State Park_parking lot. The site is a convex slope on rolling topography at 1200 feet elevation just off the paved road to Akaka Falls.

Mean annual rainfall is 284 inches per year. The lithic contact is at 150 inches. Vegetation is sugar cane.

Site A-2:

	A1	0–10"	Dark reddish brown ($5YR 3/3$) silty loam, slightly sticky when wet, with fine, moderately developed granular structure, pH 3.9.
	B21	10–18"	Yellowish red (5YR 4/6) silty clay loam, slightly plastic when wet, ,oderately smeary, firm when moist, with fine, moderately strong subangular blocky structure, pH 5.1.
	B22	18–26"	Reddish brown (5YR 4/4) silty loam, slightly plastic when wet, firm when moist, moderately smeary, with moderate, medium subangular blocky structure, pH 5.3.
	B23	26–37"	Yellowish red ($5YR 4/6$) light silty clay loam, smeary, slightly plastic when wet, firm when moist, with medium, moderate subangular blocky structure, pH 5.7.
	B24	37-42"	Dark brown ($10YR 3/3$) silt loam, friable when moist, slightly sticky, slightly smeary when wet, with weak, fine subangular blocky structure, pH 5.7.
11	A1	42-48"	Yellowish red (5YR 4/6) loam, sticky when wet, slightly smeary, with fine, moderate subangular blocky structure, pH 5.8.
11	B2	48–52"	Yellowish red ($5YR 4/6$) loam with massive inclusions of dark reddish brown ($2.5YR 3/4$) gritty loam. Slightly sticky when wet, friable when moist with massive structure, pH 5.9.

11

111 A1	52–64"	Reddish brown (5YR 4/4) light silty clay loam, firm when moist, slightly sticky when wet, moderately smeary, with fine, moderate, subangular blocky structure, pH 5.8.
111 B21	64–69"	Yellowish red (5YR 4/6) silty loam, slightly sticky when wet, moderately smeary, with moderate, medium subangular blocky structure, pH 5.8.
111 B22	69–80"	Brown (7.5 YR $4/4$) silt loam. Slightly plastic when wet with massive structure, pH 5.4.
1V A1	80-90"	Reddish brown (5YR 4/4) silty clay loam, slightly plastic when wet, moderately smeary, with fine, moderate subangular blocky structure, pH 5.7.
1V B21	90-99"	Brown (7.5 YR $4/2$) silty clay loam, slightly plastic when wet, moderately smeary, with medium, moderate subangular blocky structure, pH 5.5.
1V B22	99–106"	Yellowish red (5YR 4/6) silty loam, slightly sticky when wet, moderately smeary, with fine, weak subangular blocky structure, pH 5.8.
V A1	106–116"	Brown (7.5YR 4/4) silty clay loam, slightly plastic when wet, moderately smeary, fine, moderate subangular blocky structure, pH 5.7.

Site A-2 is located at the upper end of Kaiwiki road 0.3 miles above site A-3 at an elevation of 2000 feet. It is located on a convex slope and rolling topography with a slope of 5 %. Roots and pores are common throughout the profile.

The lithic contact is greater than 180 inches. Rainfall is 300 inches per year. Native rainforest is the common vegetation.

Site A-3:

A 1	0–16"	Dark brown ($7.5YR 3/2$) loam, friable when moist nonplastic, slightly smeary with fine moderately developed granular structure, pH 4.9.
B21	16–30"	Yellowish red (5YR 4/6) clay loam, friable when moist, plastic, slightly smeary with fine, mode- rate subangular blocky structure, pH 5.6.
B22	3032"	Very dark grayish brown (10YR 3/2) loam, firm when moist, slightly plastic, moderately smeary,

with medium, moderate subangular blocky structure, pH 5.7.

- B23 32-48" Yellowish red (5YR 4/6) silty clay loam, very firm when moist, plastic when wet, slightly smeary, with fine moderate subangular blocky structure, pH 5.7.
- B24 48-56" Dark brown (10YR 4/3) silty clay loam, firm, plastic, slightly smeary, with fine, moderate subangular blocky structure, pH 5.6.
- 11 A1 56-61" Dark brown (7.5YR 4/2) silty clay loam, firm when moist, plastic, slightly smeary, with medium, moderate subangular blocky structure, pH 5.7.
- 11 B2 61-65" Dark reddish brown (2.5YR 3/4) gritty silt loam, with darker reddish brown (2.5YR 2/4) gritty loam inclusions. Friable when moist, sticky when wet, smeary, with fine, weak subangular blocky structure, pH 5.9.
- 111 A1 65-72" Dark brown (10YR 4/3) loam with dark grayish brown (10YR 4/2) inclusions. Slightly aticky, friable, moderately smeary, with medium, weak subangular blocky structure, pH 5.9.
- 111 B2 72-79" Dark reddish brown (2.5YR 3/4) gritty silty clay loam with darker (2.5YR 2/4) gritty inclusions as in 11 B2, pH 5.8.
 - 1V A1 79-90" Dark reddish brown (5YR 3/4) clay loam, friable, slightly plastic, moderately smeary with fine, moderate subangular blocky structure, pH 6.0.

Site A-3 is located on Kaiwiki road at an elevation of 1719 feet where the road crosses Kaiwiki stream. Topography is rolling and the soil has numerous pores and roots throughout. The rainfall is 280 inches per year and the lithic contact is 150 to 170 inches. Vegetation consists of native rainforest.

A 1	0611	Dark brown (7.5YR 3/4) loam, friable, slightly plastic, slightly smeary, with fine weak subangu- lar blocky structure, pH 4.4.
B21	6–17"	Dark grayish brown (10YR 3/3) loam, friable, slightly plastic, slightly smeary, with medium weak subangular blocky structure, pH 4.3.
B22	17-24"	Dark brown ($7.5YR 3/4$) loam, friable when moist,

nonplastic, moderately smeary, with fine, weak subangular blocky structure, pH 4.3. B23 24-29" Brown (7.5YR 4/2) silt loam, friable, nonplastic. moderately smeary, with fine, weak subangular blocky structure, pH 5.2. B24 29-33" Brown (7.5YR 4/4) clay loam, firm, slightly plastic, slightly smeary, with medium, moderate subangular blocky structure, pH 5.5. B25 33-36" Very dark grayish brown (10YR 3/2) loam, friable when moist, slightly sticky, moderately smeary, with medium, weak subangular blocky structure, pH 5.8. 11 A1 36-42" Yellowish red (5YR 4/6) silt loam, friable, nonplastic, smeary, with medium, moderate subangular blocky structure, pH 5.6. Yellowish red (5YR 4/6) silt loam, friable, non-111 A1 42-47" plastic, smeary, with medium, moderate subangular blocky structure, pH 5.6. Reddish brown (5YR 4/4) silty clay loam, friable, 47-56" 111 B21 slightly plastic, slightly smeary, with fine, moderate subangular blocky structure, pH 5.6. 111 B22 56-8-" Brown (7.5YR 5/4) silty clay loam, firm when moist, slightly plastic, slightly smeary, with medium, moderate subangular blocky structure, pH 5.6.

Site A-4 is situated just inside the forest reserve area 4 miles due west of Pepeekeo at 1750 feet elevation. Annual rainfall is 260". The site is on a gently sloping area with good drainage. Roots and pores are common throughout. The lithic contact is over 120 inches. The vegetation is introduced eucalyptus forest.

28

11.

29.

· La

Hilo soil sites and profile descriptions:

	/		F	r
1	Site H-	<u>-1</u> :		
		Ap	0–15"	Dark brown ($7.5YR 3/4$) clay loam, friable when moist, plastic, with weak fine granular structure, pH 4.5.
		B21	15-38"	Yellowish red (5YR 5/6) silty clay loam, firm, plastic, slightly smeary with medium strong sub- angular blocky structure, pH 6.0.
		B22	38-60"	Dark brown (7.5YR 3/4) silty clay loam, firm, plastic, slightly smeary, with medium, weak subangular blocky structure, pH 6.0.
		B23	60-62"	Dark red (2.5YR 3/6) silt loam, firm, slightly plastic, moderately smeary, with medium, strong subangular blocky structure, pH 6.0.
	11	A1	62-65"	Reddish brown ($5YR 4/4$) silty clay loam, friable, plastic, with medium, moderate subangular blocky structure, pH 6.0.
	11	B2	65–72"	Red (2.5YR 4/6) clay loam, friable, slightly sticky, smeary, with medium, weak granular structure, pH 6.3.
	111	A1	72–77"	Strong brown (7.5YR 4/6) silty clay loam, firm, plastic, with medium, strong subangular blocky structure, pH 6.3.
	111	B21	77-83"	Brown (7.5YR 4/4) silty clay loam, firm, slightly plastic, moderately smeary with medium, moderate subangular blocky structure, pH 6.0.
	111	B22	83-85"	Dark reddish brown (5YR 3/4) clay loam, friable, slightly sticky, smeary, with medium, weak subangular blocky structure, pH 6.1.
	1V	A1	85-90"	Brown ($7.5YR \frac{4}{4} - \frac{3}{4}$) silty clay loam, firm, slightly plastic, with medium, strong subangular blocky structure, pH 6.2.
	1V	B21	90-93"	Brown (7.5YR 4/4) silty clay loam, firm, plas- tic, with medium, moderate subangular blocky structure, pH 6.0.
	17	B22	93–102"	Brown (7.5YR 4/2) silty clay loam, firm, plastic, with medium, weak subangular blocky structure, pH 6.0.
	1V	B23	102–110''	Brown (7.5YR 4/4 - 5/4) silty clay loam, firm, slightly sticky, non-smeary, medium, moderate subangular blocky structure, pH 5.5.

The H-1 site is located 9.4 miles north of Hilo off highway 19. It is adjacent to the main northern cane hall road to Pepeekeo mill about 0.2 mile below the highway at an elevation of 170 feet. Annual rainfall is 125 inches per year. The site is on slightly rolling topography with 3 % slope. Lithic contact is 110 inches. Roots and pores are common throughout.

Site H-2:

	Ap	0–16"	Dark brown (10YR 4/3) clay loam, friable when moist, slightly plastic, medium, fine subangular blocky structure, pH 4.6.
	B21	16–31"	Strong brown (7.5YR 5/6) clay loam, friable, slightly plastic, slightly smeary, with medium, moderate subangular blocky structure, pH 5.8.
	B22	31–39"	Strong brown (7.5YR 4/6) silty clay loam, firm, slightly sticky, smeary, medium, moderate subangular blocky structure, pH 5.9.
11	A 1	39-43"	Brown (7.5YR 4/4) silty clay, firm, plastic, slightly smeary, with medium, moderate subangu- lar blocky structure, pH 6.1.
11	B21	43-46"	Brown (10YR 4/3) clay loam, firm when moist, slightly plastic, slightly smeary, medium, moderate subangular blocky structure, pH 6.2.
11	B22	46-49"	Brown (7.5YR 4/4) silty clay loam, friable, slightly plastic, slightly smeary, medium, mode- rate subangular blocky structure, pH 6.4.
111	A1	49 54"	Strong brown (7.5YR 4/6) silty clay loam, friable, plastic, with fine, moderate subangular blocky structure, pH 6.6.
111	B2	54-60"	Yellowish red (5YR 5/8) silty clay loam, friable, slightly plastic, with moderate, fine subangular blocky structure, pH 6.7.
1V	A1	6065"	Strong brown (7.5YR 4/6) silty clay loam, friable, slightly plastic, slightly smeary, with moderate, medium subangular blocky structure, pH 6.5.
1V	B21	65–68"	Yellowish red (5YR 5/6) silty clay loam, friable when moist, plastic, slightly smeary, medium, moderate subangular blocky structure, pH 6.5.

30

1k

- 1V B22 68-73" Dark reddish brown (5YR 3/4) clay loam with inclusions of brown (7.5YR 5/4) clay loam, friable when moist, slightly plastic, slightly smeary, with fine, weak subangular blocky structure, pH 6.5.
- 1V B23 73-75" Red (2.5YR 4/6) clay loam, friable, slightly smeary, slightly plastic, medium fine subangular blocky structure, pH 6.6.
 - V A1 75-95" Strong brown (7.5YR 4/4 5/4) silty clay, friable when moist, plastic, medium, moderate subangular blocky structure, pH 6.3.

The H-2 site is located on the Hilo side of the road to Akaka Falls park on Hawaii Highway 19. Elevation is 150 feet and the rainfall is 140 inches per year. The vegetation is sugar cane. Lithic contact is at 110 inches. Roots and pores are common throughout.

Site H-3:

.1

	Ap	0-18"	Dark brown (7.5YR 3/3) clay loam, friable, medium, fine subangular blocky structure, pH 5.0.
	B21	18-22"	Dark reddish brown (5YR 3/4) silty clay, fria- ble when moist, plastic, slightly smeary, medium, fine subangular blocky structure, pH 5.7.
	B22	22-30"	Dark brown ($7.5YR 3/4$) silty clay loam, friable when moist, plastic when wet, slightly smeary, moderate, fine subangular blocky structure, pH 6.1.
	B23	30-40"	Reddish brown (5YRR 4/4) silty clay loam, firm, plastic, slightly smeary, medium, moderate subangular blocky structure, pH 6.3.
11	A1	40-61"	Dark brown (7.5YR 3/4) silty clay loam, firm, plastic, moderately smeary, moderate, medium subangular blocky structure, pH 6.2.
11	B21	61–64"	Dark reddish brown (5YR 3/4) gritty silty clay loam, with dark brown (2.5YR 3/4) gritty loam inclusions. Slightly smeary, smeary, medium large subangular blocky structure, pH 6.3.
11	B22	64-68"	Dark brown ($7.5YR 3/4$) silty clay loam, plastic, medium, moderate subangular blocky structure, pH 6.2.
11	B23	68–73"	Yellowish red ($5YR 4/6$) silty loam, slightly

上面に

plastic, slightly smeary, with moderate, medium subangular blocky structure, pH 6.4.

- 11 B23 73-77" Dark reddish brown (2.5YR 3/5) silty clay loam, sticky, non-smeary, moderate, medium sized subangular blocky structure, pH 6.5.
- 111 A1 77-84" Reddish brown (5YR 4/4) silty clay loam, plastic, moderate, medium subangular blocky structure, pH 6.3.
- 111 B2 84-87" Red (2.5YR 4/6) clay loam, slightly plastic, with moderate, medium subangular blocky structure, pH 6.3.
- 1V A1 87-92" Dark reddish brown (5YR 3/4) silty clay, nonplastic, smeary, fine granular structure, pH 6.4.
- 1V B21 92-96" Dark reddish brown (2.5YR 3/4) gritty clay loam, non-plastic, slightly smeary, medium weak granular structure.
- 1V B21a Brown (7.5YR 4/2) gritty clay loam inclusion in 1V B21.
- IV B22 96-101" Brown (7.5YR 4/3) silty clay, slightly sticky, slightly smeary, moderate, medium subangular blocky structure, pH 6.0.
- 1V B23 101-110" Reddish brown (5YR 4/4) clay, plastic, nonsmeary, moderate, medium subangular blocky structure, pH 6.3.

Site H-3 is located on the upper side of Hawaii Highway 19 between Onamea and Hilo mills. Elevation is 200 feet and rainfall is 140 inches per annum. Pores and roots are common throughout and the lithic contact is 150 inches. Vegetation is sugar cane.

Site H-4:

Ap	0-8"	Dark brown ($7.5YR 3/2$) silty clay loam, friable when moist, plastic when wet, with fine, moderate granular structure, pH 5.6.
B21	8–11"	Reddish brown (5YR 4/4) silty clay, friable, plastic, with medium, moderate subangular blocky structure, pH 6.1.
B22	11-14"	Dark reddish brown (5YR 3/4) silty clay, friable, when moist, plastic, fine, weak sub-

		angular blocky structure, pH 6.2.
11 A1	14–23"	Dark brown (7.5YR 3/4) silty clay, friable, plastic, slightly smeary, medium, moderate sub- angular blocky structure, pH 6.2.
11 B21	. 23–27"	Dark reddish brown (5YR 3/4) silty clay, friable when moist, plastic when wet, slightly smeary, with moderate, medium subangular blocky structure, pH 6.1.
11 B22	2 27-34"	Brown (7.5YR 4/4) silty clay, friable, slightly plastic, medium, moderate subangular blocky structure, pH 6.3.
11 B23	3 34-36"	Dark red (2.5YR 3/6) silty clay loam, firm, fine, moderate subangular blocky structure, pH 6.2.
111 A1	36–40"	Dark reddish brown ($5YR 3/4$) silty clay, firm when moist, moderate, medium subangular blocky structure, pH 6.2.
111 B21	40-50"	Dark reddish brown (2.5YR 3/4) silty clay loam, friable when moist, with moderate, medium sub- angular blocky structure, pH 6.2.
111 B22	2 50-59"	Dark reddish brown ($5YR 3/4$) clay, friable when moist, fine, moderate subangular blocky structure, pH 6.2.
111 B23	3 59–61"	Dark reddish brown (2.5YR 3/4) silty clay, friable when moist, fine, weak subangular blocky structure, pH 6.1.
1V A1	61-70"	Dark reddish brown (5YR 3/4) clay, friable, fine, weak subangular blocky structure, pH 6.3.
1V B21	L 70–72"	Dark reddish brown (2.5YR 2/4) silty clay loam, friable, fine, medium subangular blocky structure, pH 6.1.
1V B22	2 72-74"	Very dark grayish brown (10YR 3/2) gritty clay loam, friable, non-plastic, medium, weak granu- lar structure, pH 6.1.
1V B2 <u>1</u>	3 74-76"	Dark reddish brown (2.5YR 2/4) silty clay, friable, medium, moderate subangular blocky structure, pH 6.0.
V A1	76-86"	Dark reddish brown (2.5YR 2/5) silty clay, friable, medium, weak subangular blocky structure, pH 5.9.
Site	H-4 is locate	ed south of Hilo mill on highway 19 at 100 feet elev-

Site H-4 is located south of Hilo mill on highway 19 at 100 feet elevation. Rainfall is 140 inches and the lithic contact is 150 inches.

33

METHODS

Sample selection and description:

Four profiles each of the Akaka and Hilo soil were chosen after careful study of the Hamakua Coast area and consultation with the Soil Conservation Service field staff.

At the time of collection a complete field description was taken according to the procedure of the U.S.D.A. Soil Conservation Service (Kellogg, 1951). The samples were placed in double plastic bags for shipment to the Manoa Campus of the University of Hawaii.

Sample preparation:

The freshly sampled field samples were gently pressed through a 10 mesh to the inch sieve and mixed thoroughly. They were then placed_ in quart screw cap glass jars with double plastic cover liners to prevent any drying from taking place.

Moisture determinations were taken initially and at intervals throughout the duration of the project to insure that no water loss had occured. Samples were dried at between 100 and 110°C. The first samples dried were then ground to 100 mesh and stored in glass vials for subsequent analysis.

Unless noted otherwise, all sample analysis with the exception of the total silicate analysis was done on the field moist soil samples. All analysis with the exception of total silicate analysis was done in duplicate.

No particle size separation was attempted.

pH:

Soil pH was determined by glass electrode using a Beckman pH meter. Because of the high initial water content of the soil a 1 : 1 moist soil to water was used for both the H_0O and KC1 pH determinations. All samples were allowed to equilibrate at 25°C overnight.

The pH of selected samples was determined on the hydrated samples using a 1 : 5 soil to water ratio.

Organic matter:

Organic carbon was determined by the wet digestion Walkley and Black method (Piper, 1944). Organic carbon is oxidized by dichromate in the presence of concentrated sulphuric acid, which upon dilution provides the heat necessary for the oxidization of the organic matter contained in the soil.

A recovery factor of 77 % is used and the amount of organic matter is estimated by taking the amount of organic carbon and multiplying it by the factor 1.72.

Preliminary checks on the method using moist samples showed rather incomplete digestion and a failure of the aggregates to break up during the digestion process. Because of this, the 100 mesh oven dried sample was used for organic matter analysis.

Total nitrogen:

Total nitrogen was determined by the Kjeldahl method on the moist sample (Jackson, 1958).

Extractable iron oxide and associated H2O:

Extractable iron oxide was determined by the method of Kilmer (1958). A 16 hour room temperature extraction with dithionate was modified to accomodate the larger amounts of iron oxides in tropical soils and the extraction time was lengthened to 24 hours. This was found necessary after preliminary studies showed additional iron being removed after the first 16 hours of extraction time. Longer times than 24 hours did not extract additional iron oxides.

The water associated with the extracted iron was calculated on the basis of loss of ignition of an organic matter free sample as compared to an organic matter free sample with its iron extracted. The value of 0.24 multiplied by the extracted oxide content was found on the average to give an approximation of the water content. The sum of the iron oxide and its associated water is equal to the $Fe_2O_3nH_2O$ content of the soil.

Extractable phosphorus:

Phosphorus was extracted from the moist soil using 0.02 N sulphuric acid with 3 grams of ammonium sulfate per liter added. A 1:100 soil to_ extractant ratio was maintained and the extracted phosphorus was determined by the phosphomolybdate blue colorometric method (Jackson, 1958).

Total silicate analysis:

Loss on ignition was determined by weight loss on ignition of an oven dry, 100 mesh soil in platinum ware.

The samples were then fused with sodium carbonate (Kanehiro, 1965), and silica was determined gravimetrically on the double dehydrated silica from the fusion extract with hydroflouric acid (Jackson, 1958).

Aluminum was determined gravimetrically by hydroxide precipitation after removing iron and titanium with cupferron (Jackson, 1958) and also by titration after complexing with EDTA (deLonguyen, 1958 and Swindale, 1961). Results of the two analysis agreed well.

Iron plus titanium was determined gravimetrically by cupferron separation and subsequent analysis of titanium by the colometric peroxide method (Jackson, 1958).

Calcium was determined by permanganate titration of the oxalate (Jackson, 1958).

The potassium iodate method was used to determine manganese.

Potassium was determined by flame photometer on a hydroflouric acid digested sample. A few drops of sulfuric acid were added to the digest to prevent attack on the platinum crucible (Jackson, 1958).

Total phosphorus was determined on the HF digested sample using the vanadomolybdate yellow colorimetric method (Jackson, 1958).

Exchangeable cations:

Normal symponium acetate adjusted to pH 7 was used to displace the exchangeable cations. Exchangeable calcium and magnesium were analysed for by atomic adsorption spectrophotometry following the procedures of the Beckmann Company. Lanthanum oxide was used to suppress interference in the calcium determination.

Exchangeable sodium and potassium were determined by flame photometry.

Cation exchange capacity:

Cation exchange capacities were determined using normal potassium acetate buffered at pH 7 to saturate the exchange complex. Samples were washed free of excess salts with alcohol and the potassium retained was replaced by ammonium ions added in normal ammonium acetate buffered at pH 7. The potassium released was determined by flame photometer (Swindale, 1952).

All saturation and washing was done with an International Model 11 centrifuge with Nalgene centrifuge tubes. A soil to extractant ratio of 1:20 was used. Mixing of the samples was accomplished by using a glass rod with a rubber disc attached to the end that would fit into the centrifuge tube. Gentle up and down movement mixed the hardest filter cake without fail and succeeded in thoroughly breaking down the structural aggregates in the samples so that complete exchange could be accomplished. Four washings with each of the reagents was used.

Routine care in keeping the soil extractant ratio and washing procedure constant gave reproducible results even when duplicates were run some days or weeks apart.

Sample pretreatment for cation exchange capacity experiment:

Pretreatment for the cation exchange capacity determinations included the moist samples untreated, dehydration at 100 - 110°C and ground to 100 mesh, peroxide treatment, and iron removal. The peroxide treated samples were found to contain less than 1 % organic matter. Analysis both before and after dehydration was done after washing the peroxide treated samples with water to remove extraneous salts.

Peroxide treated samples that had not been dehydrated were subjected to sodium dithionate - citrate - bicarbonate iron removal in preparation for determination of the cation exchange capacity delta value (Aomine and Jackson, 1959).

For determination of the cation exchange capacity delta value the organic matter free, iron oxide free samples were boiled for 5 minutes in 2 % sodium carbonate, washed with acetone, oven dried, weighed, and ground to 100 mesh.

Portions were then taken for boiling in normal sodium acetate buffered at pH 3.5 for 15 minutes. Similar portions were taken and boiled for 60 minutes in 2 % sodium carbonate. After these treatments the cation exchange capacity was determined by the previously outlined method using potassium as the exchanging cation. The resulting difference in cation exchange capacity between the acid (pH 3.5) and the carbonate treated sample is known as the cation exchange capacity delta value.

Cation exchange capacity was also determined on portions of the samples that had been readied for the delta value determinations but had not recieved the acid treatment or the hour long boiling in carbonate.

Finally, the exchange capacity of the moist samples with no pretreatment was determined with reagents Buffered at the average pH value of the samples analysed. In this case a pH of 5.6 was used.

X-ray diffraction analysis:

Random oriented powder samples of the samples that had been pre-

treated for the cation exchange capacity delta value determination were analysed using a Phillips - Norelco X-ray diffractometer with copper tube. Read-out was by chart at 2°20 per minute.

Differential thermal analysis:

Selected samples were analysed with the automatic D.T.A. apparatus manufactured by Stone. The CEC delta value samples were equilibrated at 52 % relative humidity and run from 30 to 1100°C at 10°C per minute using ignited alumina as reference.

Bulk density:

Bulk density as determined on paraffin coated clods. Apparent weight loss in water was corrected for the paraffin used and the weight per volume determined.

Particle density:

Particle density was determined on selected samples by picnometer after removing entrapped air from the sample by vacuum.

39.

RESULTS

上品

Morphology and soil pH:

The surfaces of both the Akaka and Hilo soils are dark brown to dark reddish brown with apparent field textures ranging from loam to silty loam in the Akaka soils to clay loam and silty clay loam in the cultivated Hilo soils.

These overlie sequences of dark brown to yellowish red subsoils and buried soils. No pattern could be found that conclusively related darker colors in the horizons with buried surface horizons. As a result, organic matter discontinuities were used to designate the buried soil sequences in both the Hilo and Akaka soils (Fig. 9 and 10).

When this critiria was used it was found that at the bottom of a sequence there is typically a reddish colored horizon that dehydrates to a yellowish red, very friable mixture of gibbsite aggregates and iron oxide. In many cases there is a darker colored horizon directly below this that can be seen to correspond to a buried "A" horizon.

The detailed descriptions have been presented earlier and show that this phenomenom is more common in the Hilo soils than the Akaka soils.

Figure 7 shows a typical Akaka profile. Horizons 11 B2 and 1V B22 are gibbsite horizons that show this distinctive dehydration. These are the "scoria" horizons of Smith (1935).

Figure 8 shows that B 23, 11 B2, and 111 B22 of the Hilo soil, site 1 also possesses these qualities. Also observable in the Hilo profile is a gray plastic clay that occurs as an upper weathered zone of the underlying basalt. This gray clay is common throughout the area of the Hilo and Akaka soils and is related to the weathered ash as a silica enriched zone promoting illite formation and serving as an impervious layer that promotes lateral drainage.

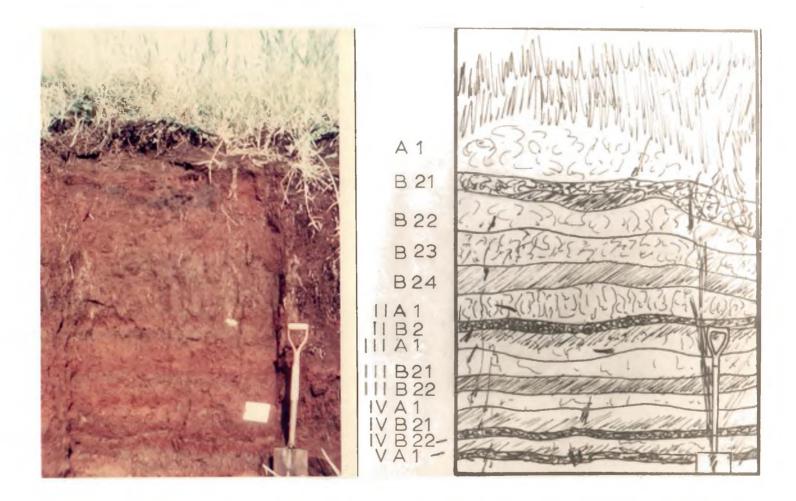


Figure 7: Profile of Akaka soil, site 2.

E

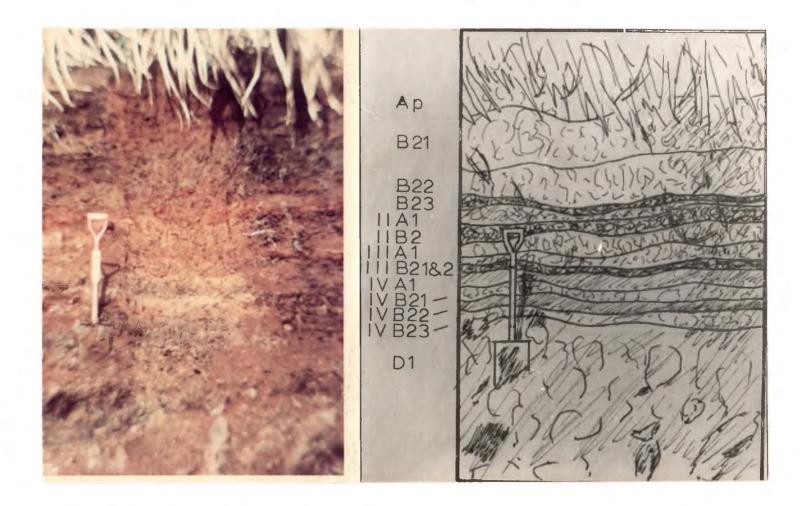


Figure 8: Profile of Hilo soil, site 1.

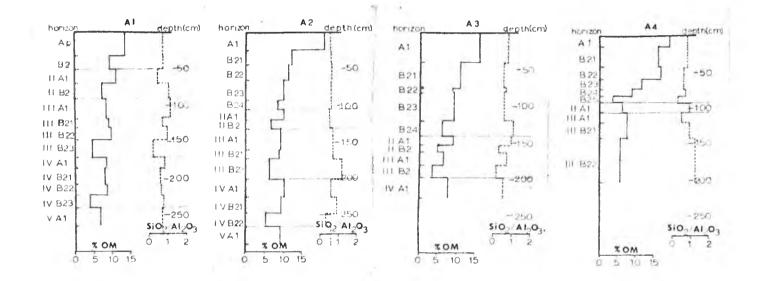
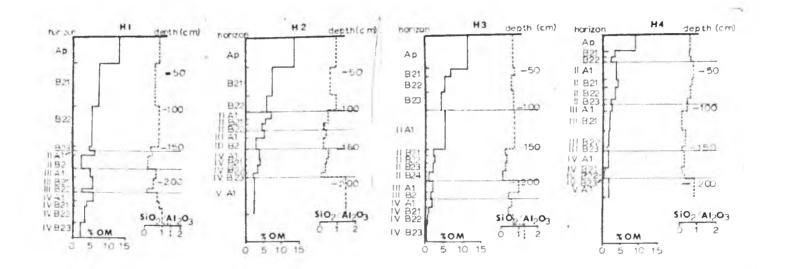


Figure 9: Schematic diagrams of organic matter contents and silica:alumina ratios of Akaka soils.



. .

Figure 10: Schematic diagrams of organic matter contents and silica:alumina ratios of Hilo soils.

÷£

44

1

The Hilo profiles were sampled to this contact, but because of the relatively deeper material of the Akaka sites no attempt was made to sample to the lithic contact.

Surface horizons are considerably more acid in both the Akaka and Hilo soils than the subsoils immediately below them. This is due to the native fern vegetation and its acid humus formation as well as the heavy use of sulfate base fertilizers in the sugar cane culture in Hawaii. The soils show high pH even with great depths with the Hilo soil uniformly higher than the Akaka soil (Table 1). The average pH of the Akaka soil is near pH 5.6 while the average pH of the Hilo soil is 6.0.

When determined in normal, neutral KCl solution the pH of the surface horizons is normally higher than when determined in water. This phenomenon sometimes continues with depth in the Akaka soil but usually does not in the Hilo soil.

In this respect, it has been shown that on the dryer, higher elevations of the northeastern slopes of Mauna Kea the soil pH in water is normally higher than that found in normal KCl. This difference, called the delta pH, was correlated with rainfall, with the delta pH decreasing in value as rainfall increases. It was suggested that this difference in pH may be due to the replacement of OH⁻ by Cl⁻ proceeding at a faster rate than the replacement of H⁺ by K⁺ in the soils of higher rainfall. Delta pH was designated as pH in water minus pH in KCl (Loganathan, 1967).

More recently it has been proposed that the delta pH be defined as the pH in KCl minus the pH in water to take into account the net surface charge of the soil system. If the delta pH is negative, ie; pH in water is greater than in KCl, the soil is said to have a net negative charge. If pH in KCl is higher than the pH in water the charge is said to be positive. If there is no difference the system would be said to have a balanced charge. High oxide soils sometimes possess net positive charge and are thought to have higher anion exchange in proportion to cation exchange, (Mekaru, 1969).

Soils and Horizon	Depth inches	рН Н2О	pH KCL (♪ pH PHKCL pH	pH (air dry) H ₂ O
<u>Akaka 2:</u> A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B21 111 B21 111 B22 1V A1 1V B21 1V B22 V A1	0-10 10-18 18-26 26-37 37-42 42-48 48-52 52-64 64-69 69-80 80-90 90-99 99-106 106-116	3.92 5.07 5.33 5.71 5.66 5.75 5.86 5.76 5.81 5.43 5.75 5.51 5.76 5.68	4.27 5.30 5.42 5.58 5.55 5.54 5.67 7.70 5.39 5.65 5.53 5.65 5.83 5.64	.35 .23 .09 13 11 21 02 09 11 04 10 .02 .07 04	3.80 4.91 4.92 5.69 5.58 5.59 5.59 5.59 5.55 5.58 5.25 5.46 5.48 5.50 5.42
Hilo 1: Ap B21 B22 B23 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 1V B23	0-15 15-38 38-60 60-62 62-65 65-72 72-77 77-83 83-85 85-90 90-93 93-102 102-110	4.46 6.01 6.03 6.02 6.00 6.33 6.03 6.03 6.08 6.22 6.00 6.02 5.46	4.86 5.98 6.00 6.01 6.00 6.20 6.04 5.95 6.03 5.96 5.75 5.68 5.31	.40 03 01 .00 13 29 08 05 26 25 34 15	5.38 5.75 5.58 5.80 5.77 5.68 5.54 5.66 5.82 5.45 5.45 5.40 5.37 5.38

Table 1 : pH, Δ pH, and effect of dehydration on pH of Akaka and Hilo Soils.

Because of the combined error of the two pH determinations needed in the delta pH determination, differences of less than 0.1 pH unit should be disregarded. Only about half of the soil delta pH values could be considered significantly different from zero (Table 1).

The pH determined on air dried soils indicates a uniform lowering of pH that may be caused by dehydration of the amorphous gels contained in the soils.

Water, Organic Matter, Total Nitrogen content and C/N ratios:

Water held in the soil under field conditions ranged from as low as 62% on the oven dry basis for a Hilo soil surface, to over 400% in some of the Akaka subsoils (Tables 2 and 3). The averages were for site 1 of the Hilo soil, 176% and for site 2 of the Akaka, 377 %.

Even with high water contents the soils remain in a moderately well drained condition. Very few mottles, even in the Akaka soil were observed.

The organic matter discontinuities were used to differentiate buried sequence within the soils (Figures 9 and 10).

The surface soils had accumulations of organic matter of up to 20 % in the Akaka soils and up to 13.6 % in the Hilo soils. The average organic matter content for site 2 of the Akaka soil is 10.4 % and for site 1 of the Hilo soil 6.2 %.

When compared, there is a high correlation between the water content and organic matter content. When sites 1 and 2 of each soil are compared with the surface horizons deleted, the regression of %field moisture on organic matter has a coefficient of .882, which is highly significant. The regression formula is % water at field condition = 4.2 + 34.7 0.M. %.

While not indicating a cause and effect, this relationship does indicate a possible common factor in the two properties of the soils. It is believed that the amorphous clay minerals can accumulate large amounts of organic matter due to clay-organic complexes (Broadbert, 1962).

Soil and Horizon	% н ₂ 0	% Ext. Fe ₂ 0 ₃	% O.M.	% N	C/N	Si0 A1203	CEC
Akaka 1: Ap B2 11 A1 11 B2 111 A1 111 B21 111 B22 111 B23 1V A1 1V B21 1V B22 1V B23 V A1	119 343 429 264 304 313 324 158 359 346 365 159 423	24.5 25.9 25.9 22.5 25.3 29.9 21.9 22.7 26.4 26.1 24.7 24.3 28.2	13.7 9.3 11.0 7.2 8.4 8.9 9.3 4.5 8.3 7.9 8.5 4.1 6.9	.462 .308 .404 .320 .309 .360 .341 .162 .274 .292 .285 .151 .371	16.9 17.5 15.8 13.1 15.9 14.4 15.8 16.0 17.5 15.8 17.2 15.9 10.8	•78 •80 •53 1.06 1.12 •73 •89 •27 •79 •55 •58 •81 •74	66.9 83.9 97.5 67.0 84.0 74.6 95.1 52.7 79.2 95.6 99.2 36.9 98.5
Akaka 2:							
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 V A1	261 385 424 424 329 432 303 424 418 295 421 369 230 492	26.4 21.6 23.4 24.5 17.5 25.6 24.5 25.3 28.9 25.8 29.6 23.3 22.8 22.8	21.5 12.6 12.2 10.6 9.0 10.3 7.0 9.5 8.7 6.5 10.2 9.2 5.3 9.1	•741 •437 •379 •328 •134 •323 •191 •338 •247 •189 •289 •211 •122 •238	16.9 16.7 18.7 18.9 24.8 18.6 21.5 16.3 20.6 20.1 20.4 25.1 25.4 22.3	•59 •62 •64 •57 •53 •72 •75 1•22 •58 •93 •33 •60	91.4 68.0 67.6 88.4 73.2 53.8 65.5 81.7 28.0 68.1 31.3 33.8 28.6 35.4

Table 2: Field moisture, extractable iron oxides, O.M., N, C/N, Silica-alumina ratios and CEC of Akaka Soils.

.

Soil and Horizon	% H ₂ 0	% Ext. Fe ₂ 03	% O.M.	% N	C/N	Si0 Al203	CEC
Akaka 3:							
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B2 1V A1	232 399 369 394 268 362 177 289 143 403	26.2 24.8 22.1 25.0 26.7 24.0 25.0 17.2 21.6 24.8	15.8 10.8 8.9 6.2 9.2 5.0 6.9 3.4 7.7	•536 •392 •315 •318 •185 •210 •138 •233 •089 •226	17.2 16.1 16.2 16.4 19.5 25.2 21.0 16.7 22.5 19.9	•73 •54 •68 •59 1.08 •92 •30 •67 •19 •53	85.0 86.5 85.2 107.7 63.5 89.6 59.2 89.1 42.9 79.7
Akaka 4: A1 B21 B22 B23 B24 B25 11 A1 111 A1 111 B21 111 B22	143 115 101 156 307 165 313 452 378 288	22.1 23.7 23.2 23.8 23.7 14.9 22.4 25.8 25.6 23.7	19.2 16.0 17.0 11.9 9.3 4.2 6.3 7.8 7.7 6.3	.636 .543 .568 .419 .246 .157 .262 .299 .246 .219	17.6 17.1 17.4 16.5 22.0 15.3 14.1 15.1 18.3 16.9	.81 .82 .64 .63 .71 .36 .96 .50 .92 1.27	80.9 63.8 66.8 65.9 73.8 52.6 64.4 78.4 74.6 61.4

Table 2: (continued) Field moisture, extractable iron oxides, O.M., N, C/N, silica-alumina ratios and CEC of Akaka soils.

LE.

Soil and Horizon	% H ₂ 0	% Ext. Fe ₂ 0 ₃	% O.M.	% N	C/N	Si0 Al ₂ 03	CEC
Hilo 1:							
Ap B21 B22 B23 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 1V B23	69 219 193 185 246 128 203 258 155 303 203 146 91	22.9 23.0 23.7 23.8 24.3 24.8 26.0 23.6 25.9 26.1 21.0 19.5 31.5	12.9 7.6 5.5 4.8 6.0 2.4 5.0 5.4 2.9 5.6 4.0 3.6 2.1	.338 .321 .164 .108 .160 .118 .169 .189 .090 .173 .138 .135 .112	22.1 13.7 19.5 25.9 21.9 11.9 17.2 16.4 18.9 19.1 16.7 15.6 10.7	.69 .54 .76 .32 .39 .15 .55 .41 .10 .65 .78 .97 1.46	42.8 44.8 37.9 47.5 58.0 23.0 49.2 40.2 16.8 41.6 31.0 22.1 16.6
Hilo 2:							
Ap B21 B22 11 A1 11 B21 11 B22 111 A1 111 B2 1V A1 1V B21 1V B22 1V B23 V A1	67 183 198 200 159 222 141 187 195 179 108 107	25.8 21.6 23.1 23.2 19.6 22.0 22.3 24.0 25.5 23.2 22.9 21.9 23.6	13.6 7.6 6.1 7.2 5.6 4.4 5.3 3.0 4.0 4.2 3.5 2.0 2.3	•533 •315 •256 •254 •195 •150 •178 •108 •179 •178 •122 •097 •154	18.2 14.0 13.7 16.5 16.9 17.3 17.4 15.7 12.8 13.5 16.4 12.4 8.4	.89 .63 .94 .48 .29 .41 .25 .48 .38 .27 .18 1.44	53.9 53.2 45.5 61.6 42.5 37.9 50.2 36.5 40.0 36.1 35.1 21.5 27.4

Table 3: Field moisture, extractable iron oxides, O.M., N, C/N, silica-alumina ratios and CEC of Hilo soils.

.

50

18.

* k.

Table 3: (continued)

Field moisture, extractable iron oxides, O.M., N, C/N, silica-alumina ratios and CEC of Hilo soils.

Soil and Horizon	% н ₂ 0	% Ext. ^{Fe} 2 ⁰ 3	% O.M.	% N	C/N	Si0 Al203	CEC
<u>Hilo 3</u> :							
Ap B21 B22 B23 11 A1 11 B21 11 B22 11 B23 11 B24 111 A1 111 B2 1V A1 1V B21 1V B21a 1V B22 1V B23	62 187 170 185 236 136 185 156 93 150 135 172 126 93 151 129	23.5 23.5 21.6 24.3 22.9 22.3 23.5 24.1 24.6 32.5 25.1 26.1 26.1 25.4 27.4 27.4 24.7	$ \begin{array}{r} 11.6 \\ 6.9 \\ 5.2 \\ 4.4 \\ 5.4 \\ 2.6 \\ 2.7 \\ 2.4 \\ 1.1 \\ 2.4 \\ 2.0 \\ 2.2 \\ 1.6 \\ 2.0 \\ 1.7 \\ 0.9 \\ \end{array} $.461 .308 .213 .159 .217 .108 .127 .070 .056 .118 .084 .101 .050 .090 .115	14.5 13.0 14.1 16.4 14.2 13.9 12.6 20.0 10.7 11.9 14.3 12.9 12.7 24.0 11.1 4.3	.62 .72 .55 .67 .70 .27 .31 .26 .15 .91 .41 .57 .35 .35 .64 1.25	45.8 61.6 56.9 55.9 86.1 32.6 48.2 34.6 22.8 35.2 30.6 25.9 20.8 13.4 37.7 33.0
Hilo 4:							
Ap B21 B22 11 A1 11 B21 11 B22 11 B23 111 A1 111 B23 1V A1 1V B21 1V B22 1V B23 V A1	107 160 151 185 222 211 148 186 110 126 199 124 93 107 143	23.7 24.0 25.4 24.3 23.6 21.8 25.2 23.9 26.7 26.7 26.7 26.7 26.7 28.0 28.6 28.6	8.9 3.9 2.5 4.0 4.5 4.0 2.6 2.8 2.4 1.3 1.7 0.9 0.8 0.7 1.8	•362 •187 •151 •212 •184 •183 •121 •156 •060 •054 •125 •051 •053 •054 •122	14.4 12.3 9.9 10.8 14.1 12.6 12.4 10.3 23.3 -14.7 8.0 9.8 9.4 7.4 8.2	•59 •57 •65 •83 •73 •63 •49 •51 •26 •27 •36 •18 •28 •36 •85	50.6 57.0 29.7 38.8 44.5 52.3 43.7 25.6 17.4 16.2 20.3 13.5 10.5 14.3 19.9

Humic versus fluvic organic clays may also affect the movement of iron on aluminum in volcanic ash soils. It has been proposed that aluminum moves in predominantly fluvic acid combinations and iron in humic acid combinations (Tan, 1966).

Nitrogen contents of the Hilo and Akaka soils are uniformly low and are correlated very highly with the organic matter contents. A simple correlation coefficient of r = .958 exists and is very highly significant.

The carbon : nitrogen ratio ranges between 10 and 25 with a few below 10. The average C/N ratio for all the soils is 16.0. The trend of increasing carbon with increasing nitrogen and increasing C/N ratio with increasing rainfall (Blomberg, 1959) is evident in the data presented here (Tables 2 and 3).

It is evident from the very significant correlation between C/N and water held at field conditions of r = .354.

Total Silicate Analysis :

The result of the total silicate analysis are given in tables 4 and 5. The failure to total 100 % is due predominantly to the irrigular loss of water at 100 - 110 $^{\circ}$ C.

This causes the base for calculation to fluctuate widely as well as giving a plus or minus 5 % error in the loss on ignition determination.

Schematic diagrams for the silica : alumina ratios of each site are presented in Figure 9 and 10. The ratios range from .10 to 1.50 in the whole soil.

In all the Akaka profiles studied the lowest horizon of the top, unburied soil sequence shows an increase of silica : alumina ratio. This occurs to a somewhat less extent on the top sequence of the Hilo soils. Field evidence indicates the presence of a tuff layer in soil sites not collected and could account for less weathering in that

52

à È

Soil and Horizon	Depth "	LOI %	SiO2	Al ₂ 03	^{Fe} 2 ⁰ 3 %	TiO. %	2 CaC %) K ₂ 0 %	MnO %	P205
<u>Akaka 1</u> :					-			· · · · · · · · · · · · · · · · · · ·		
Ap B2 11 A1 11 B2 111 A1 111 B21 111 B22 111 B23 1V A1 1V B21 1V B22 1V B23 V A1	0-13 13-20 20-28 28-36 36-47 47-52 52-59 59-68 68-74 74-83 83-89 89-96 96-106	31.4 28.8 32.2 23.5 25.5 26.7 25.2 26.3 25.7 26.8 27.6 21.2 25.8	10.5 12.0 7.7 15.5 14.4 9.5 14.0 5.7 12.0 8.7 9.3 11.7 9.5	22.6 25.4 24.5 24.9 21.8 22.0 26.8 35.4 25.8 26.7 27.2 24.3 21.7	28.3 32.9 29.4 28.7 32.2 34.3 29.4 28.6 32.9 31.3 28.2 34.8 34.4	4.0 3.8 5.7 5.2 5.9 5.5 5.4 5.9 5.5 5.4 5.9		.32 .46 .28 .78 .64 .43 .46 .08 .46 .19 .17 .63 .30		•08 •05 •04 •05 •04 •05 •04 •05 •04 •05 •05 •03 •05
<u>Akaka 2</u> :										
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 V A1	0-10 10-18 18-26 26-37 37-42 42-48 48-52 52-64 64-69 69-80 80-90 90-99 99-106 106-116	39.7 32.4 31.4 29.8 31.1 26.6 27.9 26.4 20.3 30.8 27.9 27.7 28.4	7.7 10.3 10.9 10.6 11.5 10.7 9.5 11.4 10.3 18.1 8.3 13.7 5.6	22.0 28.3 28.7 27.7 30.2 31.6 30.5 26.6 23.2 25.2 24.3 25.1 29.0 28.5	26.9 25.7 26.6 24.8 25.4 30.3 27.4 30.6 33.4 32.8 34.7 29.4 27.8 32.7	5.4 5.1 5.4 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2	•95 •94 •67 1.06 •76 1.15 •86 •90 •87 •77	•27 •69	.17 .25 .27 .23 .28 .23 .17 .25 .23 .24 .21 .14 .37 .46	• 04 • 04 • 04 • 04 • 03 • 04 • 03 • 04 • 03 • 04 • 05 • 05 • 05

Table 4 : Total silicate analysis of Akaka soils.

4.80

Soil and Horizon	Depth "	LOI %	Si0 ₂ %	Al ₂ 03 %	Fe203	Ti0 ₂ %	CaO %	К ₂ 0 %	MnO %	P205 %
Akaka 3:										
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B2 1V A1	0-16 16-30 30-32 32-48 48-56 56-61 61-65 65-72 72-79 79-90	32.9 31.4 28.8 30.1 22.9 27.0 28.2 26.3 27.6 28.6	9.8 9.6 12.1 9.9 15.5 13.8 6.3 12.0 4.5 9.2	22.7 29.7 30.1 28.1 24.3 25.4 34.8 30.5 39.1 29.5	30.5 28.9 25.6 26.2 27.0 25.9 24.9 24.0 21.9 22.5	5.2 5.2 5.2 5.5 5.3 5.3 4.5 4.5 5.4		.24 .27 .34 .31 .68 .38 .04 .18 .03 .16	•39 •26 •21 trace •19 •24 •21 •25 •15 •21	.04 .03 .03 .02 .04 .03 .05 .02 .03
<u>Akaka 4</u> :										
A1 B21 B22 B23 B24 B25 11 A1 111 A1 111 B21 111 B22	0-6 6-17 17-24 24-29 29-33 33-36 36-42 42-47 47-56 56-80	37.3 33.6 34.0 30.1 28.9 23.3 24.5 28.6 26.5 22.1	10.5 10.8 9.2 10.8 12.0 8.8 16.6 8.6 12.9 17.8	21.5 22.3 24.4 29.1 28.4 41.7 29.3 29.3 23.7 23.8	26.0 27.0 26.6 27.9 21.5 24.9 28.7 31.1 32.0	5 • 3 5 • 4 5 • 2 5 • 9 5 • 6 5 • 6 5 • 6 5 • 6 5 • 9 5 • 6	.67 1.05 .64 .60 .51 .64 .54 .41 .40 .62	.40 .40 .36 .45 .13 .60 .30 .64 .84	.19 .18 .15 .20 .23 .29 .24 .27 .25 .17	.05 .05 .04 .04 .04 .04 .04 .04

Table 4 : (continued) Total silicate analysis of Akaka soils.

人民

Soil and Horizon	Depth "	LOI %	Si0 ₂ %	Al 2 ⁰ 3 %	Fe203	TiO2	CaO %	К ₂ 0 %	MnO %	P205
Hilo 1:										
Ap B21 B22 B23 11 A1 111 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 1V B23	0-15 15-38 38-60 60-62 62-65 65-72 72-77 77-83 83-85 85-90 90-93 93-102 102-110	32.9 28.3 24.2 27.2 26.7 25.4 24.0 25.8 26.6 23.5 22.9 19.5 13.2	10.6 10.1 13.6 7.2 8.0 3.5 9.4 8.1 2.4 10.9 14.7 18.6 19.9	26.1 31.8 30.4 38.0 35.1 39.2 29.0 33.7 39.2 28.5 31.7 32.5 23.1	26.0 27.3 29.0 22.7 27.7 27.7 30.8 29.5 26.8 33.6 26.5 28.9 38.0	5.2 5.3 5.1 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2	•70 •76 •89 •31 •52 •75 •28 •89 •40 •58 •63 •53 •70	 .26 .33 .45 .13 .18 .09 .27 .14 .09 .36 .63 .66 .75 	.42 .45 .42 .26 .33 .34 .17 .14 .25 .22 .20 .20 .18	.09 .05 .09 .03 .05 .04 .03 .02 .03 .02 .03 .02 .02
Hilo 2: Ap B21 B22 11 A1 11 B21 11 B22 111 A1 111 B2 1V A1 1V B21 1V B22 1V B23 V A1	0-16 16-31 31-39 39-43 43-46 46-49 49-54 54-60 60-65 65-68 68-73 73-75 75-95	28.8 27.7 23.3 26.4 25.4 26.7 26.0 25.7 23.8 25.4 25.6 26.3 15.9	11.7 11.3 15.4 8.3 10.9 6.1 8.5 5.7 8.9 8.0 4.6 3.6 22.2	22.3 30.6 27.9 29.4 38.2 35.2 34.9 38.4 31.6 35.9 28.4 33.1 26.2	32.0 27.4 30.1 29.3 26.2 27.7 28.8 29.8 32.9 28.2 28.9 28.2 28.9 27.8 33.0	6.4 5.0 6.1 5.0 4.3 5.4 5.4 5.4 6.9	•76 •46 •64 •45 •35 •45 •39 •62 •30 •34	.32 .39 .71 .36 .26 .11 .18 .08 .23 .21 .13 .07 .92	 23 32 23 24 29 27 32 14 20 15 14 	.12 .07 .05 .06 .05 .06 .04 .04 .03 .04 .02 .03

Table 5: Total silicate analysis of Hilo soils.

Soil and Horizon	Depth "	LOI %	Si0 ₂ %	Al203	Fe203	Ti0 ₂ %	CaO %	K ₂ 0 %	MnO %	P205
			10	10	10	70	70	70	70	/0
<u>Hilo 3</u> :	0 10	00.0	0.0	0/ 7	00.0	/ -				07
Ap B21 B22 B23 11 A1 11 B21 11 B22 11 B23 11 B24 111 A1 111 B2 1V A1 1V B21 1V B21a 1V B22 1V B23	0-18 18-22 22-30 30-40 40-61 61-64 64-68 68-73 73-77 77-84 84-87 87-92 92-96 96-101 101-110	28.9 26.7 24.4 20.0 24.2 25.2 25.0 26.0 25.1 19.1 25.0 23.7 24.9 23.6 19.6 17.3	9.8 10.8 11.0 9.2 12.8 6.1 7.2 4.3 2.9 11.4 7.6 10.8 7.9 7.4 11.9 20.0	26.7 25.4 33.8 23.3 31.2 38.7 38.6 28.2 31.6 21.2 31.3 32.2 38.2 36.0 31.5 27.1	29.2 30.0 27.0 31.8 29.9 26.6 23.5 35.5 21.8 41.1 31.2 32.5 29.2 32.0 36.5 32.3	6.5967467489112263 5.4.57489112263		21 22 28 23 35 12 12 08 09 37 06 18 12 04 45 96	.14 .17 .14 .14 .13 	.07 .05 .05 .05 .04 .05 .04 .05 .04 .02 .03 .02 .03 .02 .03 .03
Hilo 4:										
Ap B21 B22 11 A1 11 B21 11 B22 11 B23 111 A1 111 B21 111 B22 111 B23 1V A1 1V B21 1V B22 1V B23 V A1	0-8 8-11 11-14 14-23 23-27 27-34 34-36 36-40 40-50 50-59 59-61 61-70 70-72 72-74 74-76 76-86	29.1 23.1 22.8 22.4 23.1 23.6 23.6 23.9 23.1 23.1 23.1 23.6 23.3 24.5 20.4 22.2 19.2	$10.2 \\ 10.5 \\ 10.7 \\ 13.4 \\ 11.3 \\ 11.7 \\ 9.7 \\ 10.1 \\ 5.6 \\ 8.6 \\ 6.0 \\ 7.4 \\ 4.2 \\ 5.9 \\ 6.1 \\ 14.1 $	29.2 30.9 27.9 27.3 26.3 31.6 33.7 33.5 36.6 33.9 37.6 35.1 38.6 35.6 29.0 28.0	28.2 25.3 26.0 28.1 27.4 24.4 25.3 25.4 30.4 25.1 28.3 28.9 30.0 34.4 30.4 31.4	5.1 5.0 5.2 5.5 5.2 5.5 5.2 5.0 5.0 5.1 90 6.2	4.06 1.07 .47 .51 .50 .55 .48 .53 .61 .14 .06 .10 .08 .06 .09 .07	28 21 15 20 08 17 07 06 14 14 09 11 15 38	.20 .29 .23 .40 .34 .44 .35 .38 .31 .36 .46 .38 .30 .46 .36	.03 .02 .01 .02 .03 .03 .04 .04 .02 .01 .02 .01 .02 .01 .02

Table 5: (continued) Total silicate analysis of Hilo soils.

horizon, or horizons, developing from the tuff.

Immediately above the lithic contact of the Hilo soils the last few ash horizonz have increased silica : alumina ratios. This is due to lack of vertical drainage caused by the gray clay from the weathered lithic contact and the horizontal drainage that it promotes. This soil zone would naturally be the last to be depleted of silica as the silica from the upper horizons and from the higher elevations move through the soil in the drainage water.

This enrichment of silica in the drainage water has been studied previously (Kunishi, 1956). While upstream areas near Pepeekeo and Hakalau had SiO_2 contents of 5.4 and 14.4 ppm respectively, downstream areas of the same streams had SiO_2 contents of 12.4 and 17.8 ppm respectively.

No significant differences exist in the average total silica content of the eight profiles studied, but there is a difference in the mean alumina contents. The Akaka soils contain a mean alumina content of 27 % and the Hilo soils contain $30.5 \% \text{Al}_20_3$. These figures, representing approximately 100 inches of development, would indicate a higher grade of bauxite than previously considered.

Total iron oxide contents of the soils vary from 20 to 40 %. No apparent patterns exist for the variations in total iron content.

The same is true for titanium. With contents ranging from 4 to 8 %, the average falls near 5.5 % TiO_2.

Manganese ranges between .10 % MnO and .80 % MnO with no apparent patterns showing up in its occurrence.

Total calcium and total phosphorus are both very low when compared to other soils of Hawaii. Levels of CaO are uniformly below 1 % and levels of P_2O_5 are less than 1000 ppm.

The total P_2O_5 is correlated with the organic matter and total nitrogen both at correlation values of r = .5. The correlation of total P_2O_5 with the carbon : nitrogen ratio is also highly significant.

Extractable Iron Oxides :

Extractable iron oxides are shown in tables 2 and 3 for the eight soils. There is no significant differences between the mean extractable iron contents of the Hilo or Akaka soils, with averages for both between 28 and 30 % Fe₂O₃.

When correlated with various other soil characters, a negative highly significant correlation was found between extractable iron oxide and total phosphorus, n = -.304 and a negative significant correlation was found between extractable iron oxide and C/N ratio, n = -.253.

No other correlations of significance were found.

If extractable iron oxide is subtracted from the total iron oxide, the "fixed" iron oxide content is found. This "fixed" iron oxide may represent the magnetic iron oxide minerals in the soil. These minerals have been shown to contain a 2 : 1 : 1 ratio of FeO : Fe_2O_3 : TiO_2 (Matsusuka, 1965).

On the average 80 - 85 % of the total iron oxide is extractable. This compares with soil developed from andesite rock with 35 to 39 % extractable iron oxide from New Zealand that had 95 % of its total iron content extractable (Claridge, 1962).

It is also believed that hydrated iron oxides may have cation exchange capacities ranging from 10 to 20 mil equivalents per 100 grams (MacKenzie, 1952).

Extractable Cations, Extractable Phosphorus, Base Saturation and CEC:

The result of cation extraction with normal, neutral ammonium acetate, extractable phosphate, % base saturation and CEC for the Akaka, site 2 and Hilo, site 1 are shown in table 6. Cation exchange capacity for the remaining soils is given in tables 2 and 3.

Exchangeable calcium, magnesium and potassium are all uniformly very low. Extractable phosphorus as P_2O_5 is extremely low, with the Akaka soil containing double the extractable phosphorus of the Hilo

<u></u>		me/	100 gram:	ppm	me/100 grams		
Soil and Horizon	Ca	Mg	K	Na	P205	B/S %	CEC
<u>Akaka 2</u> :							
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 V A1	•24 •17 •13 •20 •14 •17 •18 •29 •18 •16 •22 •18 •13 •15	1.16 .18 .16 .13 .19 .19 .47 .13 .13 .13 .19 .24 .10 .08	 22 78 04 02 03 02 03 04 04 05 05 05 06 06 06 07 08 09 09 09 09 09 00 <	•58 •39 •18 •99 •50 •78 •36 1•42 •40 •23 1•99 •26 •46 •16	2.5 1.6 3.2 2.5 3.0 3.5 1.9 3.0 2.3 1.8 2.6 3.3 1.7 3.6	2.3 2.2 .8 1.5 1.1 2.2 1.1 2.7 2.6 .8 7.8 2.1 2.5 1.2	91.4 68.0 67.6 88.4 73.2 53.8 65.5 81.7 28.0 68.1 31.3 33.8 26.6 35.4
<u>Hilo 1</u> :							
Ap B21 B22 B23 11 A1 11 B2 111 A1 111 B21 111 B21 111 B22 1V A1 1V B21 1V B22 1V B23	.87 .36 .34 .20 .14 .26 .24 .47 .30 .56 .22 .34 .31	.23 .17 .11 .05 .05 .26 .19 .04 .32 .40 .13 .25 .08	.09 .05 .04 .02 .02 .01 .02 .01 .02 .05 .04 .06 .05	.19 .73 .40 .19 .21 .90 1.27 .26 1.25 2.54 .65 .31 .22	$1.3 \\ 1.9 \\ 1.3 \\ 1.0 \\ 1.3 \\ 1.3 \\ 1.3 \\ 1.7 \\ 1.2 \\ 1.7 \\ 1.4 \\ 1.3 \\ 1.0 $	3.2 2.9 2.3 1.0 .7 6.2 3.5 1.9 11.3 8.5 3.4 4.3 4.0	42.8 44.8 37.9 47.5 58.0 23.0 49.2 40.2 16.8 41.6 31.0 22.1 16.6

Table 6: Extractable Cations, Extractable P₂O₅, Base Saturation, and Cation Exchange Capacity of Akaka and Hilo Soils.

1.4.60

soil.

An interesting pattern occurs with the extractable sodium. Those horizons with higher exchangeable sodium are either the gibbsite horizons or horizons immediately below the gibbsite horizons. This would support the concept that sodium and potassium (in this case only sodium) in the weathering solution would assist in silica removal (Keller, 1965 and Ruxton, 1968) and the promotion of accumulations of hydrated oxides of aluminum.

It would also be natural for the horizon immediately below this layer to be able to retain some of the sodium on its exchange sites as the upper horizon is leached of silica.

The large variation in % base saturation is due to large variations in cation exchange capacity rather than marked differences in the actual amounts of bases retained. In any case the % base saturation is very low when determined at pH 7.

Cation exchange capacity values range from 10 to over 100 me/100 grams of soil and can be shown to be related to organic matter content, water content, total nitrogen content, total phosphorus content, carbon: nitrogen ratio, and silica : alumina ratio by simple correlation analysis.

It is obvious that the properties of cation exchange as determined by retention of potassium from normal, neutral potassium acetate is a very complex system.

The mean value of CEC from the Akaka soil, site 2, is 60 me/100 grams. For the Hilo soil, site 1, the corresponding value is 37.3 . In each case, the mean value was adjusted for the thickness of the corresponding horizons.

X-ray Diffraction and DTA :

X-ray diffraction diagrams of the Akaka, site 2, and Hilo, site 1 are presented in figures 11 and 12. They represent the organic matter

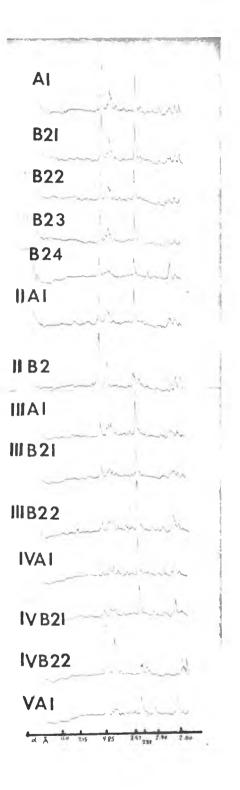


Figure 11: Power X-ray diffraction patterns of organic matter free, deferrated, oven dry, sodium saturated Akaka soil, site 2.

61

AL.

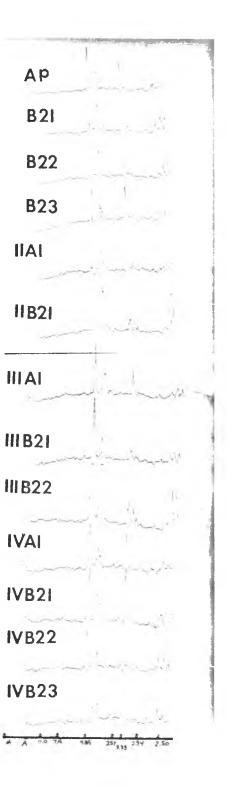


Figure 12: Power X-ray diffraction patterns of organic matter free, deferrated, oven dry, sodium saturated Hilo soil, site 1.

free, deferrated, oven-dry, sodium saturated whole soils, ground to 100 mesh.

From the Akaka soil profile it becomes apparent that the only crystalline minerals of significance are gibbsite, with X-ray diffraction maxima at 4.85 A. and quartz with a maxima at 3.34 A.

The remainder of the diffraction peaks are associated with gibbsite or quartz but are not maxima.

The first sequence of horizons, A1 to B24, shows uniform but decreasing amounts of gibbsite and quartz from the surface. At the 11 A1 horizon, the quartz and gibbsite both increase in peak size.

The 11 B2 horizon, the gibbsite or "scoria" horizon, shows a very large increase in gibbsite peak intensity, and a much smaller quartz peak.

The next sequence of horizons, 111 A1 to 111 B22 shows very little gibbsite, but higher amounts of quartz. The pattern continues through the 1V sequence of buried horizons to the 1V B22 horizon, another gibbsite accumulation.

The last horizon, V A1 shows a low gibbsite, low quartz pattern that one would have to judge was quite amorphous.

Percentages of gibbsite and quartz were estimated from the peak intensities and adjusted back to the whole sample basis for mineral allocation.

The Hilo profile does not vary so greatly as the Akaka soil from buried sequence to sequence.

The initial two horizons appear similar with less quartz in the third. The gibbsite decreases at the B23 horizon and the quartz again increases. The second sequence is a low quartz, high gibbsite sequence with the third showing much the same pattern.

The lower horizon in the third horizon of the third sequence, 111 B22, is a gibbsite horizon with low quartz.

The last sequence shows the influence of the lithic contact and shows increasing quartz with depth and decreasing gibbsite.

Just detectable in the powder diagram is the presence of clay minerals at the 10 and 7 A spacings in the lower horizons.

Additional X-ray analysis was deemed necessary by this clay mineral detection. Figure 13 shows a representative set of treatments given to the horizons suspected of containing mica or kaolin minerals.

Kaolin minerals were detected but the levels were so low as to be deemed insignificant. In the absence of any other potassium bearing minerals, the total potassium analysis was used to determine the % mica contained in each horizon of the soils.

Differential Thermal Analysis was attempted to determine amorphous mineral content and gibbsite more quantitatively.

Figure 14 is a representative diagram of the thermal reactions found. Due to the failure of the reaction to return to the zero baseline it was virtually impossible to quantify the area under the endothermic peaks for amorphous material or gibbsite.

It is thought that this phenomenon occurs due to the gradual release of combined water in the amorphous materials and the gradual crystallization to gibbsite as the water is lost. In this case, no break is obvious in the continuum from amorphous to crystalline (Sherman, 1967) and the DTA method of analysis had very little value.

Effect of Pretreatment on CEC :

Because of the complex interrelationship of factors involved in the cation exchange capacity of the Hilo and Akaka soil, a separate experiment to determine the effect of various sample pretreatments on the CEC was conducted.

The details of the pretreatments are given under the methods section of this thesis.

Briefly, the pretreatments consisted of peroxide removal of organic matter and determination of CEC on the non-dehydrated samples,

64.

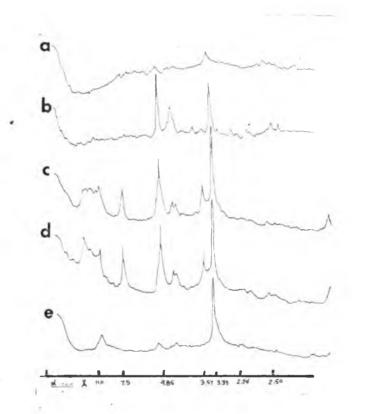
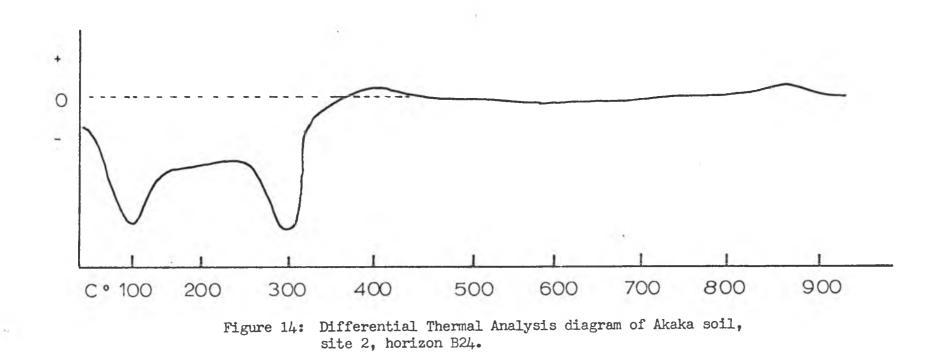


Figure 13: Effect of treatment on the X-ray diffraction pattern of Hilo soil, site 1, horizon 1V B21.

- a. wet smear.
- b. organic matter free, deferrated, sodium saturated, powder sample.
- c. oriented clay fraction from b.
- d. Mg-glycol saturated sample as c.
- e. Sample c heated to 550 C.

65

жĿ.



organic matter removal followed by dehydration, dehydration only, organic matter removal followed by deferration and dehydration, the delta cation exchange capacity pretreatments, and the determination of the cation exchange capacity when buffered at the average pH of the soil.

The results of this experiment are presented in table 7.

Upon dehydration the soils lost approximately half of their cation exchange capacity. The exceptions to this were the surface horizons, which could be expected to have had some natural dehydration, and remarkably, the buried surface horizons of the Akaka designated A1 horizons. The largest loses upon dehydration were of the magnitude of 60 %, which is in accord with previous studies (Kanehiro, 1956).

It has been previously reported that the cation exchange capacity could be attributed to the large organic matter contents found in these soils (Tenma, 1965). Although significant correlation does exist between organic matter and CEC, organic matter removal with peroxide failed to lower the CEC to any large degree on most samples. In some horizons the removal of organic matter increased the CEC by as much as 20 to 30 %. The pH of the peroxide samples all ranged near 6. It must terefore be assumed that the removal of organic matter to levels of less than 1 % with peroxide in some way unblocks an exchange system with a higher CEC than the organic matter that was removed.

The loss of CEC due to organic matter removal on the dehydrated samples is large and corresponds to the quantity of organic matter in the original soil. But, because of the lowering of the pH with dehydration, this loss can not be used as a measure of the exchange capacity of the organic matter in the non-dehydrated samples.

In this respect, acid clays in the San Joaquin Valley of California have been found to have organic matter with pH dependent charges of the magnitude of 400 me / 100 grams of soil, while amorphous clays had pH dependent charges of only 13 to 25 me / 100 grams of soil (Pratt, 1962).

Table 7: Effect of pretreatment on CEC of Akaka and Hilo soils.

.

Soils and		Pretreatment														
Horizon	None	-H20	-OM	-0M -H ₂ 0	pre. pH 3.5	pre. pH 8.3	∆ CEC	0M Fe ₂ 0	рН 3 5.6	ОСЕС (рН7- рН5.6)						
Akaka 2:				0												
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B21 111 B21 111 B22 1V A1 1V B21 1V B22 V A1	91.4 68.0 67.6 88.4 73.2 53.8 65.5 81.7 28.0 68.1 31.3 33.8 28.6 35.4	53.6 44.3 45.2 44.0 42.3 43.9 33.8 41.2 31.3 26.9 31.3 28.1 16.6 30.1	39.5 67.9 92.3 68.2 39.0 51.9 38.7 48.9 41.6 25.8 42.9 38.8 34.0 70.2	19.6 26.6 26.6 27.4 13.6 16.9 7.8 13.3 23.5 17.2 27.4 25.0 15.6 25.0	16.6 32.6 37.1 44.1 39.6 30.1 29.4 37.7 37.1 29.4 33.2 35.8 22.4 39.0	28.1 65.9 84.4 94.0 113.2 71.6 58.8 81.8 88.2 35.8 86.9 89.5 65.2 106.1	11.5 33.3 47.3 49.9 73.6 41.5 29.4 44.1 51.1 6.4 53.7 53.7 42.8 67.1	16.4 42.6 55.5 71.3 48.1 53.1 52.6 55.4 19.2 62.5 62.8 50.8 80.7	53.2 36.4 21.3 19.7 29.2 22.4 13.0 20.7 18.1 13.9 22.2 21.6 15.3 19.9	38.2 31.6 46.3 68.7 44.0 31.4 52.5 61.0 9.9 54.2 9.1 12.2 13.3 15.5						
<u>Hilo 1</u> :		÷														
Ap B21 B22 B23 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 1V B23	42.8 44.8 37.9 47.5 58.0 23.0 49.2 40.2 16.8 41.6 31.0 22.1 16.6	44.0 35.4 30.2 21.1 33.2 14.0 29.3 32.8 6.4 17.9 15.3 16.6 15.3	41.1 43.8 39.8 45.5 50.0 29.8 39.2 49.2 27.9 39.6 22.2 24.7 17.7	19.8 18.2 12.5 13.2 4.7 13.3 15.3 4.7 11.7 7.8 8.6 6.6	21.7 5.8 32.3 31.3 10.2 26.8 30.0 5.1 21.1 16.0 17.9 29.4	61.4 46.0 61.4 44.2 67.4 19.5 62.0 69.7 11.5 52.4 33.2 41.6 37.1	39.7 40.2 29.1 19.9 36.1 9.3 35.2 39.7 6.4 31.3 17.2 23.7 7.9	25.0 28.5 48.8 27.4 51.1 13.3 37.8 45.8 6.7 36.8 19.1 29.5 22.3	27.4 22.3 15.9 16.2 17.9 5.1 12.1 11.7 8.9 17.5 10.5 18.2 7.9	15.4 22.5 22.0 31.3 40.1 17.9 37.1 28.5 7.9 24.1 20.5 3.9 8.7						

Peroxide treatment has also been shown to reduce the buffering capacity of the hydrol humic latosol soils in Hawaii (Matsusuka, 1950).

The delta cation exchange capacity and the CEC of the organic matter free deferrated samples are reported without adjustment for the materials removed. These two values have a high significant correlation value with an r value of .919. They also correlate significantly with the amorphous material content of the soils.

The cation exchange capacity determined at the average pH value for the soils is uniformly low for both the Akaka and Hilo soils. It is correlated highly with organic matter but this does not mean it is a result of the organic matter. The correlation coefficient is r = .914.

It is thought that organic matter has almost no permanent charge (Coleman, 1958) and at a pH 5 has a pH dependent charge of 75 me/100 grams.

If this is true, and if the pH dependency of the inorganic colloids is great, liming will increase the soils ability to retain cations in addition to the usual benefits.

Unfortunately, previous work on the effect of liming hydrol latosols was done by determining the CEC at neutral conditions both before and after liming. It was concluded from that data (Rixon and Sherman, 1961) that the liming had no effect on the cation exchange capacity of the pH dependent charge in these soils. This pH dependency can be seen in the final column of table 7.

The variability of the values is of interest, especially when one considers that the two CEC values that they were derived from are both correlated highly with organic matter, and with each other. The correlation coefficient for CEC at pH 7.0 v.s. the CEC at pH 5.6 is r = .599 and is highly significant.

Mineral Allocation:

Organic matter and extractable iron oxide with its associated

69

water are reported in table 8. The mean values for the two profiles are 10.4 and 6.2 % organic matter in the Akaka soil and Hilo soils respectively. There is no difference in the average extractable $Fe_2_{3}^{0}nH_2^{0}$, with both soils containing a mean value of approximately 30 %. This water associated with the extracted iron oxide was calculated to facilitate allocation of minerals.

Mica allocation was on the basis of a 7.2 % $\rm K_2O$ content for Hawaiian secondary micas as determined by Juang (1965).

Gibbsite was estimated by peak intensity of the 4.85 A X-ray diffraction peak.

Quartz was estimated by X-ray diffraction peak intensities.

The fixed iron oxide is the difference between total $Fe_2^{0}_{3}$ and the extractable $Fe_2^{0}_{3}$, TiO₂ is reported as titania.

The non-crystalline mineral content, non-crystalline * , Table 9, was estimated by taking the remaining loss of ignition, silica and alumina after the other minerals were alloted according to their silica, alumina and loss on ignition as follows :

O.M. - - 100 % loss on ignition.

 $Fe_0O_3nH_0O - - 25\%$ loss on ignition.

Mica - - 45.2 % Silica, 38.4 % $\text{Al}_2^{O_3}$ and 4.5 % loss on ignition.

Gibbsite - - 65.5 % Al₂O₃ and 34.5 % loss on ignition.

Quartz - - 100 % SiO2

The silica : alumina ratio is reported for this remainder.

As a comparison, the cation exchange capacity delta values adjusted to their original organic matter and iron oxide content are reported as non-crystalline ** . Unaccountable losses on pretreatment for the delta value were of the magnitude of only a few percent as determined by weight of sample taken and final weight of organic

70

Soils and Horizon	0.M. %	Ext.Fe ₂ 0 nH ₂ 0%		Gibbsite %	Quartz %	Fixed Fe ₂ 03%	TiO ₂ %2	non- crystal%
<u>Akaka 2</u> :								
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 V A1	21.5 12.6 12.2 10.6 9.0 10.3 7.0 9.5 8.7 6.5 10.2 9.2 5.3 9.1	32.8 26.8 29.1 30.4 21.7 31.8 30.4 31.4 35.9 32.0 36.8 28.9 28.3 28.4	4.2 3.8 9.6 3.8 2.9 4.4 1.7 5.0 2.8 12.9 4.0 6.4 1.1 3.1	$ \begin{array}{r} 19.0 \\ 24.0 \\ 16.0 \\ 15.0 \\ 10.0 \\ 16.0 \\ 25.0 \\ 7.0 \\ 6.0 \\ 5.0 \\ 1.0 \\ 4.0 \\ 37.0 \\ 5.0 \\ \end{array} $	5.4 7.3 7.0 4.7 3.5 6.4 2.5 7.7 5.0 11.1 6.4 6.2 2.0 3.1	0.5 4.1 3.2 0.3 7.9 4.7 2.9 5.3 4.5 7.0 5.1 6.2 5.0 9.8	5.4 5.1 5.2 5.2 5.2 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0 5.0	13.4 18.5 22.1 28.5 41.3 30.6 24.6 31.3 30.7 23.5 31.8 32.7 9.7 39.0
mean *	10.4	30.6	5.1	12.5	6.0	4.7	5.6	26.9
<u>Hilo 1</u> :								
Ap B21 B22 B23 11 A1 11 B2 111 A1 111 B21 111 B21 111 B22 1V A1 1V B21 1V B22 1V B23	12.9 7.6 5.5 4.8 6.0 2.4 5.0 5.4 2.9 5.6 4.0 3.6 2.1	28.4 28.6 29.4 28.5 30.2 30.8 32.3 29.3 32.2 32.4 26.0 24.2 39.1	3.6 4.6 6.3 1.8 2.5 1.3 3.8 1.9 1.3 5.0 8.8 9.2 10.4	33.0 35.0 33.0 17.0 20.0 50.0 19.0 23.0 59.0 22.0 36.0 20.0 3.0	5.9 7.1 2.0 6.7 3.2 2.0 4.4 3.3 1.9 6.2 11.5 10.8 8.8	3.1 4.3 5.3 0.0 3.4 2.9 4.8 5.9 7.5 5.5 9.4 6.5	5.2 5.3 5.5 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2	9.1 10.8 16.5 36.8 30.6 6.9 24.3 28.5 0.1 17.6 5.8 22.4 25.5
mean *	6.2	29.7	5.3	29.5	5.7	4.9	5.7	16.0

Table 8: Total mineral and non-mineral content of Akaka and Hilo soils.

* Mean content adjusted for respective horizon thickness.

Soils and Horizon	non- crystal * %	non- crystal ** %	$\frac{\text{SiO}_2}{\text{Al}_2^0 2^{-3}}$	B.D. "Apparent" (dry)	B.D. "Real" (wet)
Akaka 2:				- —	
A1 B21 B22 B23 B24 11 A1 11 B2 111 A1 111 B21 111 B22 1V A1 1V B21 1V B22 V A1	13.4 18.5 22.1 28.5 41.3 30.6 24.6 31.3 30.7 23.5 31.8 32.7 9.7 39.0	5.3 20.8 27.7 29.4 51.0 24.0 18.4 26.1 28.3 3.9 29.0 33.3 28.4 42.0	.09 .20 .00 .43 .50 .20 .79 .12 .37 .12 .01 .38 1.20 .39	.27 .19 .19 .18 .24 .21 .26 .18 .19 .22 .18 .21 .33 .16	.98 .94 .97 .93 1.01 .90 1.06 .94 .96 .88 .96 1.00 1.09 .93
Hilo 1: Ap B21 B22 B23 11 A1 11 B2 111 A1 111 B21 111 B21 111 B22 1V A1 1V B21 1V B22 1V B23	9.1 10.8 16.5 36.8 30.6 6.9 24.3 28.5 .1 17.6 5.9 22.4 25.5	25.8 25.6 18.9 13.3 23.0 6.2 22.0 19.4 4.2 19.4 12.0 17.1 4.6	1.70 .21 2.43 .00 2.89 .25 .37 .37 .00 .31 .00 .38 .62	.69 .32 .38 .29 .43 .35 .27 .39 .26 .37 .40 .62	1.17 1.03 1.10 1.07 1.00 .98 1.06 .97 .99 1.03 1.11 .99 1.18

Table 9: Non-crystalline mineral content and bulk density of Akaka and Hilo soils.

* Non-crystalline as determined by difference.

** Non-crystalline as determined by delta CEC value.

matter free, defferated sample.

When considering the completely different approaches used in determining the non-crystalline component of these soils, the similarity of results is remarkable.

The mean non-crystalline content of the Akaka soil is 26.9 % and the Hilo soil, 16.0 % .

Gibbsite content is 12.5 % for the Akaka soil and 29.5 % for the Hilo soil.

The gibbsite content has a very significant negative correlation with the non-crystalline or amorphous mineral content, r = -.839.

Bulk density reflects the difference in mineralogy as well. A mean bulk density of .21 is found for the Akaka and .42 for the Hilo. Both are based on the oven dry weight of soil and are therefore called "apparent" bulk density.

Bulk density based on the field moist weights of the soils have a smaller spread and are considered "real" bulk densities.

Particle density was determined on selected horizons and found to be approximately 2.70.

DISCUSSION

Interrelationships of Some Soil Properties in the Hilo and Akaka Soils:

Throughout the presentation of the results of this thesis the results of simple correlation analysis have been presented.

A complete array of correlation coefficients that were determined for 20 different properties are given in Figure 15.

The levels of significance for the correlation of 27 and 105 pairs of observations are as follows :

	n = 27	n = 105
Significant at 0.01 level	r > .487	r > •254
Significant at 0.05 level	r between 381 and .487	r between .195 and .254
Not significant	r <.381	r < .195

One of the most striking features of this correlation data is the complexity of the cation exchange capacity experiments.

Cation exchange capacity has been shown to relate to organic matter, moisture content, bulk density, total nitrogen, total phosphorus, carbon nitrogen ratio, mica content, and silica : alumina ratio.

Even when the soils are dehydrated and the organic matter is removed, the reflection of the organic matter content is obvious in the simple correlations. This would indicate common causes rather than cause and effect are at work in these thesis.

Throughout the array of correlation coefficients this common cause relates back to the high water holding capacity of these soils. When this ability is lost by dehydration the soil completely changes its nature. In every case, this change is irreversible.

Origin and Genesis :

It is quite evident that differences between the Akaka soil profiles are slight. The same is true for the Hilo soils, but large differences between the two soils exist.

	0.M.	field H_Q	Extract Fe203	B.D.	Total N	Total P	с/ж	Mics	Quarts	Gibb- site		1 510 / A1203	C.E.C.	Base Set.	C.E.C. -H20		с.к.с. -н_э-он		C.E.C.
Pield 820	.392**		1										n.						
Extract. Fe203	148	.027 n=105	1		1				-		1		1						
8.D.	362 n-27	910* n=27	• .056 n=27		19	İ.				1			1						
Total M	.958** n=105	.3104 r=135	077 n-105	314 n=27			1					1							
Total P	+509** n=105	.063 1⊫1∪5	304++ m=105	•152 n=27	-+491** n=105														
с/м	•138 n=27	• • • • • • • • • • • • • • • • • • •	253* n=105	272 n=27	-+127 n=27	.327** n=105													
Mica	352 n=27	.188 n=105	.066 n=27	.077 n=27	.008 n=27	.031 n=105	112 n=105												
QUALTER	.027 n=27	018 n=27	009 n=27	•056 n=27	.107 n=27	210 n=.27	.037 n=27	•792*# n=27											
Gibbaite	315	584** n=27		.428* n=27	-,221 n=27	.018 n=27	210 n=27	369 n=27	363 n=27										
Amorphous	.116 п=27	•582## 5#27		436** n=27	010 n=27	.080 n=27	•387* n=27	011 n=27	•017 n=27	839** n=27						(
510,/A1203	•27}** n=135	.205* 105	.097 r=135	.126 n=27	-323** n=105	.076 n=105	083 n=105	.886** n=105	.677** m≈27	611** n=27	.236 n=27								
С.В.С.	.650** n=105	+629** n=105		474* n=27	.671** n=105	.364** n=105	.264.** n⇔105	.216= n=105	.u⊾7 n=27	303 n=27	.293 n=27	.295** n=105				1			
Base Sat.		299 n=27	-342 n=27	.247 n=27	245 n=27	323 n=27	303 n=27	140	084 n=27	•437* n=27	498** n=27	244 n=27							
C.E.CH20		•503** n=27		385* n=27	.822** n=27	.296 n=27	.096 n=27	061 n=27	027 n=27	382* n=27	•334 n=27	.039 n=27		563** n=27					
		.608** n=27		543** n=27	•453* r=27	•360 n=27	•176 p=27	164 p=27	178 n⇒27	240 n=27	•343 п=27	236 n=27	.489•€ n=27	398* n=27	.62∂•• 2⊨27				
-0.H.O	.681** 	.6.,8** n=27		550** n=27	•573** n=27	.352 n=27	.294 n=27	.027 n=27	.057 n=27	517** n=27	.369 n=27	.102 n=27			.635** n=27	+702** n=27			
.ε.c. Δ	•190 ••27	.762**		707**	.081 n= 27	.072 n=27	•395* n=27	229 n=27	249 n=27	-+492** n=27		U86	.201 n=27		-350 n=27	+533** n=27	-543** 5=27		
	======================================	+757++ 1m27		623**	.076 n=27	+143 n+27	.496** n=27	199 n=27	301 p=27	556** n=27	.721** .D=27	.015 n=27			.418* .D#27	•5∂3•• ∎=27	•585** n=27	.919** D=27	
.E.C.	-914++ -27	.30%		271	-892** n=27	.223	•142 n=27	Ula D=27	034 n=27	250 n=27	.100 n=27	.028	.59/**	-,266	•749** n=27	•337 n=27	.535** n=27	.161 n=27	-141 n=27

1

Figure 15: Simple correlation coefficients of several properties of Akaka and Hilo soils.

- ** significant at 0.01 level
- * significant at 0.05 level

75

Water contents, organic matter contents, cation exchange capacities, gibbsite content, and amorphous or non-crystalline mineral content vary greatly between the Akaka and Hilo soils.

As great as these differences are, the differences within each profile are greater.

In explaining the developmental sequence of these soils it is necessary to account for this intensive weathering of the ash forming the gibbsite horizons in the oldest portion of each major ash fall.

If we accept the hypothesis that these horizons were coarse ash or lapili layers it is not hard to assume their intensive weathering under high rainfall conditions. The rapid water intake of ash formations could very quickly account for depletion of silica from the largely glassy ash. If the coarse layers were to be situated over less pervious, formerly weathered material, they may well have become aquifers for laterally moving perched water tables, thus appreciably intensifying silica removal.

In addition, the acid forming nature of the forest debris and a small but perhaps significant CO_2 contribution from the underlying organic matter decomposition may have caused dissolution and subsequent reprecipitation of aluminum and the removal of silica from these horizons.

The Classification of the Soils:

The Akaka and Hilo soils meet the criteria designated for the typic hydrandepts in the classification of the U.S.D.A. Soil Conservation Service - The Seventh Approximation.

The gibbsite horizons, although of predominantly oxide nature, do not meet the 12-inch thickness criteria to be classified as oxic horizons. Even if they did, the fact that they occur as buried horizones exempt them from affecting the classification into the inceptisol order of soils.

The thixotropic isomesic and thixotropic isohyperthermic designa-

76

主義

tion are also appropriate for the Akaka and Hilo soils respectively.

In addition to the present classification it is suggested that the modifier "gibbsitic" be added to the Hilo soil to recognize the tendency towards greater crystallization.

The soils then would have the following designation:

Akaka - thixotropic isomesic typic hydrandept.

Hilo - gibbsitic thixotropic isohyperthermic typic hydrandept.

SUMMARY AND CONCLUSIONS

There is no evidence chemically or mineralogically that the ash forming the soils has had any recent contributions from Kilauea.

As a consequence, recent studies of ash deposits in Lake Waiau on the summit of Mauna Kea may hold significant answers about the ash that the Hilo and Akaka soils formed from. Radio-carbon dating has indicated an age of 4500 years for a coarse ash layer lying 1.5 meters deep, (Woodcock, 1966). This may correspond to the last major ash fall for the area.

It is also evident that the higher rainfall in the areas of the Akaka soils has promoted organic matter build up while not accelerating the weathering sequence. To the contrary, lateral water movement has been the contributing factor in the higher weathering of the Hilo soil.

Little or no allophane exists in these soils if we take the range of allophane to have a silica : alumina ratio of between 1 and 2. In many of the horizons studied, the only non-crystalline allophane-like material has been found to be amorphous hydrated aluminum. It appears to have the same characteristics as allophane though.

Hydrated oxides of iron have not gained a lot of attention, but they do occur in significant amounts in both soils. More study is needed on whether they follow the ionic, amorphous, crystalline sequence that has been proposed for aluminum.

These two items, the amorphous aluminum and the amorphous iron need considerable study. This is especially true for their cation exchange capacities. Electron microscopy coupled with heavy metal salvation may be able to assist in determining the nature of the exchange sites and their dependency on other factors.

Finally, the Hilo and Akaka soils are situated on a weathering sequence that includes the more common allophane containing volcanic ash soils on one hand and bauxite deposits on the other. The soils are related to both, but in reality are neither.

-

LITERATURE CITED

- Abbott, A.T., 1958. Occurrence of gibbsite on the island of Kauai, Hawaiian Islands. Economic Geology 53:842-853.
- Alexander, L.T., S.B. Hendricks and G.T. Faust, 1941. Occurrence of gibbsite in some soil forming materials. Soil Sci. Soc. of Am. Proc. 6:52-57.
- Alexander, L.T., and J.B. Cady, 1962. Genesis and hardening of laterite in soils. U.S.D.A. Tech Bul. 1282.
- Allen, V.T., 1960. Clay minerals in bauxite deposits in Europe. Economic Geology 55:1338.
- Alonso, J., 1963. Observations de Microscopie Electronique en Argiles Volcaniques de Chili et Allophanes de la Nouvelle Zelande. Int. Clay Conf. Proc. - Stockholm 1:167.
- Aomine, S., and N. Yoshinaga, 1955. Clay minerals of some well-drained volcanic ash soils of Japan. Soil Science 79:349-358.
- Aomine, S., and M.L. Jackson, 1959. Allophane determinations in ando soils by cation exchange capacity delta value. Soil Sci. Soc. of Am. Proc. 23:210-214.
- Aomine, S., and K. Wada, 1966. Grade of weathering and fertility of volcanic ash soils of Aso volcano. Soil Sci. and Plant Nutrition 12:73-79.
- Aomine, S., and H. Otsuka, 1968. Surface of soil allophanic clays. Trans. of 9th Int. Cong. of Soil Sci. - Adelaide pp. 731-739.
- Aomine, S., and K. Egashira, 1968. Flocculation of allophanic clays by electrolytes. Soil Sci. and Plant Nutrition 14:94-98.
- Atkinson, H.J., 1943. Soil colloids. Scientific Agriculture 23: 273-286.
- Ayres, A.S., 1943. Soils of the high rainfall areas of the Hawaiian Islands. Hawaii Agr. Expt. Sta. Tech. Bul. 1.
- Bates, T.F., 1952. Interrelationships of structure and genesis in the kaolinite group. Problems of Clay and Laterite Genesis (Am. Inst. of Mining and Metal Engineers - N.Y.) pp. 144-153.
- Bates, T.F., 1960. Rock weathering and clay formation in Hawaii. Mineral Industries 29:1-6.
- Bates, T.F., 1962. Halloysite and gibbsite formation in Hawaii. Proc. of 9th Nat. Conf. on Clays and Clay Minerals 9:315-328.

- Bennema, J., 1963. The red and yellow soils of the tropical and subtropical uplands. Soil Science 95:250-257.
- Besoain, E.M., 1964. Clay formation in some Chilian soils derived from volcanic materials. New Zealand J. of Sci. 7:79-86.
- Birrell, K.S., and M. Fieldes, 1952. Allophane in volcanic ash soils. J. of Soil Science 3:156-166.
- Birrell, K.S., 1952. Some physical properties of New Zealand volcanic ash soils. Proc. of First Australian - N.Z. Conf. on soil Mech. and Foundation Engineering.
- Birrell, K.S., and M. Gradwell, 1956. Ion exchange phenomena in some soils containing amorphous mineral constituents. J. of Soil Science 7:130-147.
- Birrell, K.S., 1961a. Ion fixation by allophane. New Zealand J. of Sci. 4:393-414.
- Birrell, K.S., 1961b. The absorption of cations from solution by allophane in relation to their effective size. J. of Soil Science 12:307-316.
- Birrell, K.S., 1962. Surface acidity of subsoils derived from volcanic ash deposits. New Zealand J. of Sci. 5:453-462.
- Birrell, K.S., 1966. Determination of clay contents in soils containing allophane. New Zealand J. of Agr. Res. 9:554-564.
- Blomberg, N., and W.E. Holmes, 1959. The carbon : nitrogen ratios in some Hawaiian soils. Hawaiian soils. Hawaii Agr. Expt. Sta. Tech. Prog. Rep. 122.
- Brindley, G.W., C. DeKimpe and M.C. Gastache, 1964. Low temperature synthesis of Kaolin minerals. American Mineralogist 49:1-16.
- Broadbent, F.E., 1962. Biological and chemical aspects of mineralization. Trans. of Joint Meeting of Comm. IV and V of Int. Soc. of Soil Sci. - Lower Hutt, N.Z. pp. 220-229.
- Broadbent, F.E., R.H. Jackman and J. McNicoll, 1964. Mineralization of carbon and nitrogen in some New Zealand allophanic soils. Soil Science 98:118-128.
- Buckman, H.O., and N.C. Brady, 1960. The Nature and Properties of Soils. MacMillan Co., N.Y.
- Burgess, P.S., and W.T. McGeorge, 1926. Zeolite formation in soils. Science 64:652-653.

- Burgess, P.S., 1929. The so-called "build up" and "break down" of soil zeolites as influenced by reaction. Arizona Agr. Expt. Sta. Tech. Bul. #28, pp. 101-135.
- Calhoun, W.A., and J.E. Hill Jr., 1962. Metalurgical testing of Hawaiian ferruginous bauxites. Report of Investigations 6003, U. S. Dept. of Interior, Bureau of Mines.
- Chichester, F.W., C.T. Youngberg, and M.E. Harward. 1969. Clay mineralogy of soils formed on Mazama pumice. Soil Sci. Soc. of Am. Proc. 33:115-120.
- Chukhrov, F.V., S.I. Borkhin, L.P. Ermilova, V.A. Moleva, and E.S. Rudnitskaya, 1963. Allophane from some deposits of the U.S.S.R. International Clay Conference Proc. Stockholm 1:19-28.
- Claridge, G.G.C., 1962. Extractable iron in relation to soil classification. N.Z. Journal of Science 5:269-278.
- Cline, M.G., 1955. Soil Survey of the Territory of Hawaii U.S.D.A. Soil Survey Series 1939.
- Cloos, P.A., A. Herbillon, and J. Echeverria, 1968. Allophane-like synthetic silico-alumina : phosphate adsorption and availability. Transactions of the 9th International Congress of Soil Science-Adelaide. pp. 733-743.
- Coleman, N.T., E.J. Kamprath, and S.B. Weed, 1958. Liming. Advance in Agronomy Monograph #10. pp. 475-522.
- Dames, T.W.G., 1955. The soils of East-Central Java. Institute for Soil Research - Bagor.
- Dean, L.A., 1937. Effect of rainful on the carbon and nitrogen contents and carbon-nitrogen ratio of Hawaiian soils. Soil Sci. Soc. of Am. Proc. 2:455-459.

Dean, L.A., 1947. D.T.A. of Hawaiian soils. Soil Science 63:95-105.

- DeHoniek, F., A.J. Herbillon, R. Tavernier, and J.J. Fripiat, 1968. Weathering of clay minerals and formation of amorphous material during the degradation of a Bt horizon and podzolization in Belgium. Transactions of the 9th International Congress of Soil Science -Adelaide. pp. 353-365.
- D'Hoore, J., 1957. The accumulation of free sesquioxides in tropical soils. Trans. from French by F. P. Just, C.S.I.R.O. - Adelaide.

82

1

- DeMumbrum, L.E., 1960. Crystalline and amorphous soil minerals of the Mississippi coastal terrace. Soil Sci. Soc. of Am. Proc. 24:185-189.
- DeMumbrum, L.E., and G. Chesters, 1964. Isolation and characterizations of some soil allophanes. Soil Sci. Soc. of Am. Proc. 28:355-359.
- Dudal, R. and M. Soepratohardjo, 1960. Some considerations of the genetic relationship between laterite and andosols in Java. Transactions of the 7th International Congress of Soil Science-Madison 4:229.
- Dunham, K.S., 1933. Crystal cavities in lavas from Hawaii. American Mineralogist 18:369-385.
- Edwards, A.B., 1955. The petrology of the bauxites of Tasmania. C.S.I.R.O..- Melbourne.
- Egawa, T., 1964. A study of the coordination number of aluminum in allophane. Clay Science 2:1-7.
- Eitel, W., 1964. Silicate Science Vol. I Silicate Structures. Academic Press, N.Y.
- F.A.O., 1964a, Meeting on the Classification and Correlation of Soils Formed from Volcanic Ash. World Soil Resources Report #14.
- F.A.O., 1964b, Guidebook for the F.A.O. Soil Correlation Meeting on Volcanic Ash Soils. Tokyo.
- Fieldes, M., L.D. Swindale, and J.P. Richardson, 1952. Relation of colloidal hydrous oxides to the high cation exchange capacity of some tropical soils of the Cook Islands. Soil Science 74:197-205.
- Fieldes, M., L.D. Swindale, 1954. Chemical weathering of silicates in soil formation. N.Z. Journal of Science and Technology 36B:140-154.
- Fieldes, M., L.D. Swindale, J.P. Richardson, and I.C. McDowall, 1954. Rapid method of analysis of soil clays and other silicates. N.Z. Journal of Sci. and Tech. 35:433-439.
- Fieldes, M., and K.I. Williamson, 1955. Clay mineralogy of New Zealand soils, part I, electron micrography. N.Z. Journal of Sci. and Tech. 37B:314-335.
- Fieldes, M., 1955. Clay Mineralogy of N.Z. Soils, part II, allophane and related mineral colloids. NZ. Journal of Sci. and Tech. 37B:336-350.
- Fieldes, M., I.K. Walker, and P.P. Williams, 1956. Clay mineralogy of N.Z. soils, part III, infrared absorption spectra of soil clays. N.Z. Journal of Sci. and Tech. 38B:31-43.

- Fieldes, M., 1957. Clay mineralogy of N.Z. soils, part IV, D.T.A. N.Z. Journal of Sci. and Tech. 38B:533-570.
- Fieldes, M., and N.H. Taylor, 1961. Clay mineralogy of N.Z. soils, part V, Mineral colloids and genetic classification. N.Z. Jour. of Sci. 4:679-706.
- Fieldes, M., 1962. The nature of the active fraction of soils. Transactions of the Joint Meeting of Comm. IV and V of the International Soc. of Soil Science - Lower Hutt, N.Z. pp.62-78.
- Fieldes, M., 1966. The nature of allophane in soils, part I, significance of structural randomness in pedogenesis. N.Z. Journal of Sci. 9:599-607.
- Fieldes, M., and R.J. Furkert, 1966. The nature of allophane in soils, part II, differences in composition. N.Z. Journal of Sci. 9:608-622.
- Fieldes, M., and K.W. Perrott, 1966. The nature of allophane in soils, part III, Rapid field method and laboratory test for allophane. N.Z. Journal of Sci. 9:623-629.
- Fieldes, M., 1968. Constitutional classification of soils. Transactions of the 9th International Congress of Soil Science - Adelaide pp.177-185.
- Follet, E.A.C., W.J. McHardy, B.D. Mitchell, and B.F.L. Smith, 1965. Chemical dissolution techniques in the study of soil clays. Clays Minerals 6:23-43.
- Fiskel, J.G.A., and V.W. Carlisle, 1964. DTA of some clays and Florida soil clays. Proceedings of Soil - Crop Sci. Soc. of Florida 24:114-124.
- Fraser, G.D., 1960. Pahala ash an unusual deposit from Kilauea Volcano, Hawaii. U.S. Geologic Survey Prof. Paper 400-B pp.354-355.
- Fredrickson, A.F., 1952. The genetic significance of mineralogy. Problems of Clay and Laterite Genesis (American Inst. of Mining and Metal Engineers - N.Y.) pp.1-11.
- Frink, C.R., and M. Peech, 1962. The solubility of gibbsite in aqueous solutions and soil extracts. Soil Sci. Soc. of Am. Proc. 26:236-347.
- Fripiat, J.J., 1964. Surface chemistry and soil science in Experimental Pedology, Easter School of Agricultural Science - London pp.3-13.

Furkert, R.J., and M. Fieldes, 1968. Allophane in N. Z. soils. Trans-

actions of the 9th International Congress of Soil Science - Adelaide.

- Gardiner, H.C., 1967. Genesis of a climosequence of soils in Kohala Region of Hawaii. M.S. Thesis, U. of Hawaii, Honululu.
- Garrels, R.M., and C.L. Christ, 1965. Solutions, Minerals and Equilibria. Harper and Row Co., N.Y.
- Giuseppetti, G., 1963. Weathering materials of igneous rocks and sedimentary deposits from Valsesia, Italy. International Clay Conference Proceedings - Stockholm 1:139.
- Glinka, K.D., 1927. The Great Soil Groups of the World and Their Development. Trans. from German by C.F. Marbut. Published by the translator.
- Gordon, M., J.I. Tracey Jr., M.W. Ellis, 1958. Geology of the Arkansas bauxite region. U.S. Geologic Survey Prof. Paper 299.
- Gradwell, M., and K.S. Birrell, 1954. Physical properties of certain volcanic clays. N.Z. Journal of Sci. and Tech. 36B:108-122.
- Grimm, R.E., R.A. Roland, 1942. DTA of clay other hydrous materials. American Mineralogist 27:746.
- Grimm, R.E., 1953. Clay Mineralogy. McGraw Hill Co., N.Y.
- Harada, M., 1955. Studies on the volcanic ash soils in the environs of Mount Daisen. Soil Science and Plant Food 1:81-83.
- Hardy, F., and G. Rodriques, 1939. Soil genesis from andesite in Granada, British West Indies. Soil Science 48:361-384.
- Harrison, J.B., 1934. The Katamorphism of Igneous Rocks Under Humid Tropical Conditions. Imperial Bureau of Soil Sci., Harpenden, England.
- Hashimoto, I., 1961. Differential Dissolution Analysis of Clays and its Application to Hawaiian Soils. Ph D Thesis, U. of Wisconsin, M.
- Hashimoto, I., and M.L. Jackson, 1960. Rapid dissolution of allophane and kaolinite-hallosite after dehydration. Proceedings of the 7th National Conf. on Clays and Clay Minerals. 7:102-113.
- Hart, R., 1929. Studies in geology and mineralogy of soils, II, soils of SE Scotland. Journal of Agri. Sci. 19:802-813.
- Hauser, E.A., 1952. Genesis of clay minerals. Problems of Clay and Laterite Genesis (Am. Inst. of Mining and Metal Engineers - N.Y.) pp.100-114.

- Hendricks, D.M., L.D. Whittig, and M.L. Jackson, 1977. Clay mineralogy of andesite saprolite. Proceedings of the 15th National Conf. on Clays and Clay Minerals. 15:395-407.
- Hendricks, D.M., and L.D. Whittig, 1968. Andesite weathering, part I and II. Journal of Soil Science 19:135-153.
- Hough, G.J., Z.C. Foster and P.L. Gile, 1941. Rock weathering and soil development in the Hawaiian Islands. U.S.D.A. Tech. Bul. 752.
- Houng, K.H., 1964. A Study on the Soils Containing Amorphous Materials in the Island of Hawaii. Ph D Thesis, Uni. of Hawaii, Honolulu.
- Houng, K.H., G. Uehara, and G.D. Sherman, 1966. On the exchange properties of allophanic clays. Pacific Science 20:507-514.
- Hsu,P.H., and T.F. Bates, 1962. Formation of X-ray amorphous and crystalline alumina hydroxides. Proceedings of the 11th Nat. Conf. on Clays and Clay Minerals 11:299-300.
- Humbert, R.P., 1948. The genesis of laterite. Soil Science 65:281-290.
- Iimura, K., Acidic properties and ion exchange in allophane. Clay Science 1:28-40.
- Ikawa, H., and G.D. Sherman, 1958. The gibbsite concretions of Cape York, Australia. Proceedings of the 34th Annual Meeting of the Hawaiian Academy of Science.
- Irving, D.R., 1961. Potential Sources of Aluminum. U.S. Bureau of Mines Info. Cir. 8335, pp.53-57.
- Jackson, M.L., S.A. Tyler, A.L. Willis, G.A. Bourbeau, and R.P. Pennington, 1948. Weathering sequence of clay size minerals in soils and sediment; Foundamental generalizations. Journal of Phys. and Colloidal Chem. 52:1237-1260.
- Jackson, M.L., and G.D. Sherman, 1953. Chemical weathering of minerals in soils. Advances in Agronomy Monigraph #5. pp.219-318.
- Jackson, M.L., 1956. Soil Chemical Analysis Advanced Course. Published by the Author, Madison, Wisconsin.
- Jackson, M.L., 1958. Soil Chemical Analysis. Prentice Hall, N.J.
- Jackson, M.L., 1959. Frequency distribution of clay minerals in major great soil groups as related to the factors of soil formation. Proceedings of the 6th National Conf. on Clays and Clay Minerals 6:133-143.

- Jackson, M.L., 1963. Aluminum bonding in soils; a unifying principle in soil science. Soil Sci. Soc. of Am. Proc. 27:1-10.
- Jackson, M.L., 1964. Soil clay mineralogical analysis. Soil Clay Minerals, C.I. Rich ed., U. of N.C. Press. pp. 245-325.
- Jackson, M.L., 1965. Free oxides, hydroxides and amorphous alumino silicates. Methods of Soil Analysis, C.A. Black ed. American Society of Agronomy Monograph #9 1:578-603.
- Jackson, M.L., 1968. Weathering of primary and secondary minerals in soils. Transactions of the 9th International Congress of Soil Science - Adelaide. pp.281-292.
- Japanese Ministry of Agriculture and Forestry, 1964. Volcanic Ash Soils of Japan. Tokyo, Japan.
- Jenne, E.A., 1965. NaOH Dissolution of some oxide impurities from Kaolins. Proceedings of the 12th National Conference on Clays and Clay Minerals 12:633.
- Jenny, H., 1941. Factors of Soil Formatiom. McGraw-Hill, N.Y.
- Joffe, J.S., 1936. Pedology. Rutgers University Press, N.J.
- Juang, T.C., 1965. Genesis of Secondary Micas from Basalts and Related Rocks in the Hawaiian Islands. M.S. Thesis, Univ. of Hawaii, Hon.
- Kanehiro, Y., and A.T. Chang, 1956. Cation exchange properties of the Hawaiian great soil groups. Hawaii Agr. Expt. Sta. Tech. Bul. #31.
- Kanehiro, Y., and G.D. Sherman, 1956. Effect of dehydration-rehydration on the C. E. C. of Hawaiian soils. Soil Sci. Soc. of Am. Proc. 20:341-344.
- Kanehiro, Y., 1957. A study of the fundamental factors affecting the behavior of nitrogen carriers in Hawaiian soils. Western Regional Hawaii Contributing Project \$134.
- Kanehiro, Y., and L.D. Whittig, 1961. Amorphous mineral colloids of soils of the Pacific region and adjacent areas. Pacific Science 15:477-481.
- Kanehiro, Y., and G.D. Sherman, 1965. Fusion with sodium carbonate for total elemental analysis. Methods of Soil Analysis, C.A. Black ed. American Society of Agronomy Monograph #9, 2:952-958.

Kanno, I., M. Nagai, and S. Arimura, 1955. On the nature of fresh

87 ,

volcanic ashes as parent material ejected from the Sakurajima and Aso volcances. Soil and Plant Food 1:77-80.

- Kanno, I., 1955. Glassy volcanic ash soils in Japan. Soil and Plant Food 1:1-2.
- Kanno, I., 1962. Genesis and classification of humic allophane soils in Japan. Transactions of the Joint Meeting Comm. IV and V of the International Soc. of Soil Science - Lower Hutt, N.Z. pp.422-427.
- Kanno, I., and S. Arimura, 1966. Dispersion of humic allophane soils with supersonic vibration. Soil Science and Plant Nutrition 13: 165-170.
- Kanno, I., Y. Onikura, and T. Higashi, 1968. Weathering and clay mineralogical characteristics of volcanic ashes and pumice in Japan. Transactions of the 9th International Congress of Soil Science -Adelaide 4.
- Kawasaki, H., and S. Aomine, 1966. So called 14 A clay minerals in some Ando soils. Soil Sci. and Plant Nutrition 12:144-150.
- Keller, W.D., 1964. Process of origin and alteration of clay minerals. Soil Clay Minerals, C.I. Rich ed., U. of N.C. Press. pp.1-76.
- Keller, W.D., 1965. The origin of high alumina clay minerals. Proceedings of the 12th National Conf. of Clays and Clay Minerals 12:129-151.
- Keller, W.D., R.J. Gentile and A.L. Reesman, 1967. Allophanes and Na-rich alunite from kaolinite nodules in shale. Journal of Sed. Petrology 37:215-220.
- Kelley, W.P., W.T. McGeorge and A.R. Thompson, 1915. The soils of the Hawaiian Islands. Hawaii Agr. Expt. Sta. Bul. #40.
- Kellog, C.E., 1951. Soil Survey Manual. U.S.D.A. Handbook #18.
- Kilmer, V.J., 1961. The estimation of free iron oxides in soils. Soil Sci. Soc. of Am. Proc. 24:420-421.
- Kunishi, H.M., 1956. Mineral analysis of Hawaiian Surface and Seepage waters. M.S. Thesis, U. of H., Honolulu.
- Kunze, G.W., 1965. Pretreatment for mineralogical analysis. Methods of Soil Analysis, C.A. Black ed. American Society of Agronomy Monograph #9, 1:568-577.
- Lai, S.H., 1967. Some physical and chemical properties of amorphous mineral colloids. M.S. Thesis, U. of H., Honolulu.

- Leon, L., 1962 Clay formation in some Chilean soils under natural forest vegetation and under pasture. Transactions of the Joint Meeting of Comm, IV and V of the International Soc. of Soil Science - Lower Hutt, N.Z. pp.39-44.
- Loganathan, P., 1967. The properties and genesis of four middle altitude dystrandepts from Mauna Kea, Hawaii. M.S. Thesis, U. of H., Honolulu.
- de Longuyen, Gorcey J., 1958. Rapid total analysis of Al₂03 in clays and ceramics with the help of EDTA complexes. Translated from German by R. Voss. Berlin Deutsch Keramic Geschaft 38:155-158.
- MacDonald, G.A., 1945. Ring structures of Mauna Kea, Hawaii. American Journal of Science 243:210-217.
- Nackenzie, R.C., 1952. Investigations on cold precipitation of hydrated ferric oxide and its origin in clays. Problems of Clay and Laterite Genesis (American Inst. of Mining and Metal Engineers -N.Y.) pp. 65-75.
- Marshall, C.E., 1964. The Physical Chemistry and Mineralogy of Soils, Vol. I, Soil Materials. J. Wiley and Sons, N.Y.
- Matsusaka, Y., and G.D. Sherman, 1950. Titration curves and buffering capacities of Hawaiian soils. Hawaii Agr. Expt. Sta. Bul. # 11.
- Matsusaka, Y., G.D. Sherman, and L.D. Swindale, 1965. Nature of magnetic minerals in Hawaiian soils. Soil Science 100:192-199.
- Mattson, G.Y., 1937. The laws of colloidal behavior; 19, the gel and sol complex in soil formation. Soil Science 43:453.
- Maxwell, W., 1898. Lavas and soils of the Hawaiian Islands. Hawaii Sugar Planters Assoc., Honolulu.
- McGeorge, W.T., 1917. Composition of Hawaiian soil particles. Hawaii Agr. Expt. Sta. Bul. # 42.
- McKeague, J.A., and M.G. Cline, 1963. Silica in soils. Advances in Agronomy Monograph # 15. pp. 339-396.
- Mehlich, A., 1960. Anion and cation adsorption. Transactions of the 7th International Congress of Soil Science - Madison. 2:292-302.
- Mekaru, T., 1969. Anion adsorption in Hawaiian soils. M.S. Thesis, U. of H., Honolulu.
- Milliken, T.H. Jr., G.A. Mills, and A.G. Oblad, 1950. The chemical characteristics and structure of cracking catalysts. Faraday Soc.

Discussions 8:279-289.

- Milligan, W.O., and J.L. McAtee, 1952. The structure of hydrous aluminum oxides and hydroxides. Problems of Clay and Laterite Genesis (Am. Inst. of Mining and Metal Engineers - N.Y.) pp.94-99.
- Mitchell, B.D., V.C. Farmer, and W.J. McHardy, 1965. Amorphous inorganic materials in soils. Advances in Agronomy Monograph #17. pp.327-375.
- Mitsuchi, M., 1963. Some considerations on the clay fractions of the fresh volcanic ash soil at the foot of Asuma volcano. Pedologist 7:73-83.
- Miyauchi, N., and S. Aomine, 1964. Does allophane "B" exist in Japanese volcanic ash soils ? Soil Science and Plant Nutrition 10:199-203.
- Miyauchi, N., and S. Aomine, 1966a. Effects of exchangeable cations on the high temperature exothermic peak of allophane. Soil Science and Plant Nutrition. 12:13-17.
- Miyauchi, N., and S. Aomine, 1966b. Mineralogy of the gel-like substances in the pumice bed in Kanuna and Kitakami Districts. Soil Science and Plant Nutrition 12:187-190.
- Mohr, E.C.J., 1944. Soil of the Equatorial Regions. Trans. from Dutch by R.C. Pendleton. University Press - Ann Arbor.
- Orchiston, H.D., 1959. Adsorption of water vapor; 7, Allophane and some clay minerals at 25°C. Soil Science 88:159-163.
- Patterson, S.H., 1963. Halloysitic underclay and amorphous Inorganic matter in Hawaii. Proceedings of the 12th National Conference on Clays and Clay Minerals 12:153-172.
- Pauling, L., 1960. The Nature of the Chemical Bond. Cornell Univ. Press - Ithaca.
- Piper, C.S., 1944. Soil and Plant Analysis. Interscience Publishers-N.Y.
- Pratt, P.F., and F.L. Bair, 1962. Cation exchange properties of some acid soils of California. Hilgardia 33:689-706.
- Rich, C.I., and G.W. Thomas, 1960. The clay fraction of soils. Adv. in Agronomy Monograph #12. pp.1-39.

Richter, C., 1931. Physical properties of Hawaii soils with special

reference to the colloidal fraction. Hawaii Agr. Expt. Sta. Bul. #62.

- Rixon, A.J., and G.D. Sherman, 1961. Effects of heavy lime applications to volcanic ash soils in the humid tropics. Soil Science 94:19-27.
- Robertson, R.H.S., 1963. Allophanic soil from Trail Bridge, Oregon. Clay Minerals Bulletin 5:237.
- Ross, C.S., and P.F. Kerr, 1934. Halloysite and Allophane. U.S.G.S. Prof. Paper 185G, pp.135-148.
- Rutherford, G.K., 1962. The yellow-brown soils of the highlands of New Guinea. Transactions of the Joint Meeting Comm. IV and V of the International Soc. of Soil Science - Lower Hutt, N.Z. pp.434-439.
- Ruxton, B.P., 1968. Rates of weathering of quarternary volcanic ash in N.E. Papua. Transactions of the 9th International Congress of Soil Science - Adelaide. pp.367-376.
- Sasaki, S., and Y. Ishizuka, 1957. On the volcanic ash soil in Tokach district, Hokkaido, Japan. Soil Science and Plant Food 2:177-183.
- Sherman, G.D., and Y. Kanehiro, 1948. The chemical composition of certain forest floors in the Hawaiian Islands. Hawaii Agr. Expt. Sta. Biennial Report, p.54.
- Sherman, G.D., 1949. Factors influencing the development of laterite
 and lateritic soils of the Hawaiian Islands. Pacific Science
 3:307-344.
- Sherman, G.D., 1950. Genesis and morphology of the Hawaiian ferruginous laterite crusts. Pacific Science 4:315-322.
- Sherman, G.D., 1952. The titanium content of Hawaiian soils and its significance. Soil Sci. Soc. Am. Proc. 16:15-18.
- Sherman, G.D., 1952. The genesis and morphology of the alumina-rich laterite clays. Problems of Clay and Laterite Genesis (Am. Inst. of Mining and Metal Engineers - N.Y.) pp.154-161.
- Sherman, G.D., Y. Kanehiro, and Y. Matsusaka, 1953. The role of dehydration in the development of laterite. Pacific Science 7:438-446.
- Sherman, G.D., 1957. Formation of gibbsite aggregates in latosols developed from volcanic ash. Science 125:1243.
- Sherman, G.D., 1958. Gibbsite-rich soils of the Hawaiian Islands. Hawaii Agr. Expt. Sta. Bul. #116.

- Sherman, G.D., 1962. Weathering and Soil Science. Transactions of the Joint Meeting Comm. IV and V of the International Soc. of Soil Science - Lower Hutt, N.Z. pp.24-32.
- Sherman, G.D., Y. Matsusaka, H. Ikawa, and G. Uehara, 1964. The role of the amorphous fraction in the properties of tropical soils. Agrochimica (Rome) 8:146-163.
- Sherman, G.D., and Y. Matsusaka, 1965. Occurance of gibbsite nodules in soils of the Koolau family of Kauai. Journal of Sedimentary Petrology 35:504-507.
- Sherman, G.D., J.G. Cady, H. Ikawa, and N.E. Blomberg, 1967. Genesis of the bauxitic Halii soils. Hawaii Agr. Expt. Sta. Tech. Bul.#56.
- Sherman, G.D., and H. Ikawa, 1968. Soil Sequences in the Hawaiian Islands. Pacific Science 22:458-460.
- Sivarajawingham, S., L.T. Alexander, J.G. Cady, and M.G. Cline, 1962. Laterite. Advances in Agronomy Monograph #14. pp.1-60.
- Smith, L.R., 1935. Soil survey methods of classification and study. Handbook of Hawaiian Soils, Assoc. of Hawaiian Sugar Technologists -Honolulu. pp.249-258.
- Snetsinger, K.G., 1967. High alumina allophane as a weathering product of plagioclase. American Mineralogist 52:254-262.
- Stearns, H.T., and G.A. MacDonald, 1946. Geology and ground water of the Island of Hawaii. Hawaii Division of Hydrography Bul. #9.
- Stearns, H.T., 1966. Geology of the State of Hawaii. Pacific Books, Palo Alto, California.
- Sudo, T., 1954. Clay mineralogical aspects of the alteration of volcanic glass in Japan. Clay Minerals Bul. 2:96-106.
- Sudo, T., 1959. Mineralogical Study on Clays of Japan. Maruzen Co., Tokyo.
- Swindale, L.D., and M. Fieldes, 1952. Rapid semimicro method for C.E.C. of clays and soils with the flame photometer. Soil Science 73:287-290.
- Swindale, L.D., 1961. Bauxite in the red loam soils of N.Z. Report on Bauxite Deposits of Northland. N.Z. Dept. of Sci. and Industry Resourse Information Series 32.

Swindale, L.D., 1965. The properties of soils developed from volcanic

ash. F.A.O. World Soils Report #14 - Rome.

- Swindale, L.D., and G. Uehara, 1966. Ionic relationships in pedogenesis of Hawaiian soils. Soil Sci. Soc. of Am. Proc. 30:726-730.
- Swindale, L.D., 1966. A mineralogical study of soils derived from basic and ultrabasic rocks in New Zealand. N.Z. Journal of Science 9:484-506.
- Takahashi, H., and Y. Nishimura, 1966. Formation of zeolite from halloysite and allophane. Proceedings of the 15th National Conference on Clays and Clay Minerals. 15:185-186.
- Tamele, M.W., 1950. Chemistry of the surface and the activity of alumina-silica cracking catalysts. Faraday Society Discussions 8:270-278.
- Tamura, T., M.L. Jackson, and G.D. Sherman, 1953. Mineral content of low humic, humic and hydrol humic latosols of Hawaii. Soil Science Soc. of Am. Proc. 17:343-346.
- Tamura, T., and M.L. Jackson, 1953. Structural and energy relationships in the formation of iron and aluminum oxides, hydroxides, and silicates. Science 117:381-383.
- Tan, K.H., and J. vanSchuylenborgh, 1961. On the classification and genesis of soils developed over acid volcanic material under humid tropical conditions. Netherlands Journal of Agr. Sci. 9:41-54.
- Tan, K.H., 1965. The andosols of Indonesia. Soil Science 99:375-378.
- Tan, K.H., 1966. On the pedogenetic role of organic matter in volcanic ash soils. Soil Science and Plant Nutrition 12:80-84.
- Tanada, T., 1950. Certain properties of the inorganic colloidal fraction of Hawaiian soils. Jour. of Soil Sci. 2:83-96.
- Taylor, N.H., 1933. Soil processes in volcanic ash beds. N.Z. Journal of Sci. and Tech. 14B:338-352.
- Tenma, H.H., 1965. Some Characteristics of Non-crystalline Constituents in Hawaiian Soils. M.S. Thesis, U. of Hawaii, Honolulu.
- Uehara, G., H. Ikawa, and G.D. Sherman, 1966. Desilication of halloysite and its relation to gibbsite formation. Pacific Science 20:119-124.
- U.S.D.A., 1938. Soils of the U.S. Soils and Men Yearbook of Agr. pp.1151-1161.

- U.S.D.A., 1960. Soil Classification, A Comprehensive System, the 7th Approximation. Soil Survey Staff - Washington.
- U.S.D.A., 1967. Supplement to Soil Classification System (7th Approx.), Soil Survey Staff - Washington.
- Wada, K., and S. Aomine, 1966. Occurance of gibbsite in weathering of volcanic materials at Kuroishibaru, Kumamoto. Soil Science and Plant Nutrition 12:151-157.
- Wada, K., 1967. A structural scheme of soil allophane. American Mineralogist 52:690-708.
- Wada, K., and I. Mastubara, 1968. Differential formation of allophane, "imogolite" and gibbsite in the Kitakami pumice bed. Transactions of the 9th International Congress of Soil Science - Adelaide.
- Wentworth, C.K., 1938. Ash formations of the island of Hawaii. Hawaii Volcano Observatory Spec. Report #3.
- White, W.A., 1953. Allophane from Lawrence Co, Indiana. American Mineralogist 38:634-642.
- Whittig, L.D., 1954. Crystalline and Amorphous Weathering Products of Some Soils of Tropical and Temperate Origin. Ph D Thesis, U. of Wisconsin, Madison.
- Whittig, L.D., V.J. Kilmer, R.C. Roberts, and J.G. Cady, 1957. Characteristics and genesis of Cascade and Powell soils of N.W. Oregon. Soil Sci. Soc. of Am. Proc. 21:226-232.
- Woodcock, A.H., M. Rubin, and R.A. Duce, 1966. Deep layer sediments in alpine lake in the tropical mid-Pacific. Science 154:647-648.
- Yapps, J.A., and D.W. Fuerstenen, 1964. Zero point charge of alpha alumina. Journal of Colloidal Sci. 19:61-71.
- Yoshinaga, N., 1966. Chemical composition and some thermal data of eighteen allophanes from ando soils and weathered pumices. Soil Science and Plant Nutrition 12:47-54.
- Yoshinaga, N., 1968. Identification of Imogolite in the filmy gel materials in the Imaichi and Schichinonzakura pumice beds. Soil Science and Plant Nutrition 14:238-246.
- Youngberg, C.T., and C.T. Dyrness, 1964. Some physical and chemical properties of pumice soils of Oregon. Soil Science 97:391-399.