

HALLOYSITIC UNDERCLAY AND AMORPHOUS INORGANIC MATTER IN HAWAII*

by

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ABSTRACT

Plastic clay deposits underlie peat beds in several swamps on the island of Kauai, Hawaii. These underclays are appreciably different in mineralogical and chemical composition from the associated well-drained weathered rocks (saprolite). The underclay is much higher in silica and lower in iron oxide than the saprolite. The underclay is composed chiefly of halloysite minerals, with minor amounts of gibbsite, anatase, quartz, goethite, and illite. The saprolite is predominately gibbsite, goethite, and hematite, with minor amounts of titaniferous magnetite, anatase, and halloysite minerals. Apparently both the clay and saprolite have formed by weathering from the same type of parent rock and have undergone similar geologic histories; therefore, differences in drainage and the presence or absence of an overlying peat layer appear to be the principal genetic variables.

The underclay and saprolite are believed to contain amorphous gels and allophane because X-ray intensities for many samples are low, and estimated amounts of identifiable minerals are not adequate to account for the whole samples. Attempts to isolate the amorphous materials in samples from Kauai have not been successful, but both an alumina-silica gel and allophane were found in saprolite at one locality on Maui, Hawaii. These materials were collected from the face of a freshly bull-dozed roadcut at a depth of 2 to 6 ft. They occur as veins and as fillings and coatings on vesicles, vugs, and cracks in a dark-brown saprolite closely associated with hard basalt. The allophane is white, and most of it is covered by a clear or light-colored gel. Some of the gel occurs in clear irregular masses ranging in size from microscopic specks to about one-fourth inch in diameter and is similar to a mass of frog eggs or thick gelatin. Some occurs as light-grayish brown, paper-thin laminae that extend along cracks for several inches.

Both the allophane and dried gel are similar in composition, containing approximately 50 per cent alumina and 22 to 26 per cent silica. The close association and similar composition indicate that allophane forms from the alumina-silica gel. Gibbsite and halloysite minerals occur in a manner very similar to that of the allophane and gel, suggesting that these amorphous materials are intermediate phases in the formation of gibbsite and halloysite. This is supported by the small amount of gibbsite present in the dried gel.

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INTRODUCTION

PLASTIC underclays occur below peat beds in several bogs on weathered basalt on the island of Kauai, Hawaii. The bogs lie in belts where annual rainfall ranges from 100 to 200 in. according to the U.S. Weather Bureau maps, the heaviest rainfall being at the highest altitude. The bogs are formed where the water table is locally permanently perched at the surface. Clay deposits in five bogs ranging in altitude from 400 to 4000 ft (Fig. 1) were investigated as part of the study of low-grade ferruginous bauxite deposits on the islands of Kauai and Maui, Hawaii, made in 1959 to 1962 by the U.S. Geological Survey in cooperation with the Hawaii Division of Land and Water Development. Two of the bogs are on gently sloping ridge tops that are less than 200 yd wide at most places and are surrounded by deep, steep-walled valleys. The other three are in gently sloping flat areas adjacent to highlands. Rainfall is the only water reaching the bogs on the ridges, but groundwater probably contributes to the others. Preservation of the bogs is partly due to the slow rate of evaporation caused by heavy fogs much of the year. Some of the bogs cover more than 20 acres. The bogs support low-growing vegetation consisting in part of dwarfed forms of species that grow as large trees in the surrounding, dense rain forests. The underclays of the bogs grade downward into saprolite and weathered basalt.

A brief description of the underclay in the bog at 4000 ft altitude was

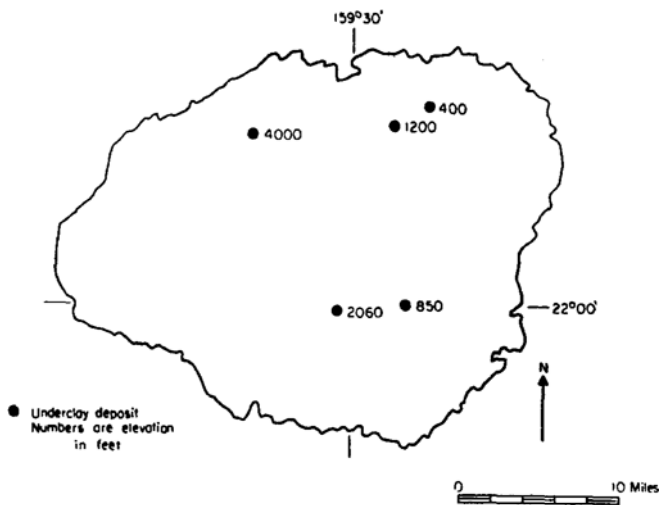


FIGURE 1.—Location of underclay deposits investigated on Kauai.

given by Wentworth, Wells, and Allen (1940, pp.11-13) who investigated primarily the Koolau clay on Oahu. The Koolau clay and the clays on Kauai are similar, but the Kauai deposits are much larger and the mineralogy of the deposits on the two islands is somewhat different. Gibbsite is common in the clays on Kauai and was not reported in the Koolau deposits. Probably the Kauai deposits are older and more mature than the one on Oahu.

The underclay and most thoroughly weathered saprolite near the surface have distinctly different mineral and chemical compositions, though they are essentially the end products of weathering of the same type of basalt country rock. Their geologic histories are similar except for drainage conditions and peat development. The differences in mineral composition between the two types of rock (Table 1) are based on investigations of more than 40 samples of underclay and approximately 100 samples of saprolite.

TABLE 1.—APPROXIMATE AMOUNTS OF MINERALS PRESENT IN UNDERCLAY AND IN SAPROLITE AT SHALLOW DEPTHS, KAUAU. (NUMBERS REPRESENT PARTS OF TEN; TR=TRACE).

Mineral	Amount in underclay	Amount in saprolite
Halloysite	5 to 8	tr to 1
Illite	0 to 3	0
Quartz	0 to 2	0
Gibbsite	1 to 3	2 to 4
Goethite	tr	2 to 4
Hematite	0	1 to 2
Magnetite	tr	1 to 2
Ilmenite	tr to 1	tr
Anatase	tr to 2	tr to 1
Mineraloids	0 to 4(?)	0 to 2(?)

Whole samples were examined by X-ray diffraction and differential thermal analysis methods; selected samples were investigated by the electron microscope technique by John C. Hathaway; and clay, non-clay, magnetic, and heavy mineral fractions of selected samples were investigated by optical, X-ray diffraction, and differential thermal analysis methods. Without exception the thoroughly weathered saprolite in well-drained areas is high in iron and low in silica, and the underclay high in silica and low in iron. The mineral compositions of the clay in all five bogs are similar; however, potassium and titanium contents are somewhat higher in the clay at 4000 ft (Table 2, samples Al-6 and Al-10) than in clays at lower elevations. The sample from the bog at 850 ft altitude (Table 2, sample GF-2) is representative of the clay at lower elevations. Although no amorphous materials could be separated from either the clay or saprolite on Kauai, both a gel and allophane were collected from an exposure on

TABLE 2.—CHEMICAL ANALYSIS OF UNDERCLAYS AND SHALLOW SAPROLITE

Sample number	Underclay			Saprolite	
	Al-6	Al-10	GF-2	Ki-50	PR-29
Sample interval * (depth in feet)	½ to 15	8 to 15	½ to 10	2 to 4	1 to 4
SiO ₂	34.0	33.1	29.5	2.4	1.0
Al ₂ O ₃	34.8	26.7	34.6	21.7	24.9
Fe ₂ O ₃	2.2	2.2	1.8	44.1	43.5
FeO	0.67	1.5	0.68	0.93	1.1
CaO	0.00	0.00	0.00	<0.10	—
Na ₂ O	0.08	0.22	0.08	0.06	0.10
K ₂ O	0.21	1.7	0.28	0.15	0.09
H ₂ O-	6.8	6.1	10.8	} 18.3	18.7
H ₂ O+	13.5	9.3	12.6		
TiO ₂	7.5	17.5	8.9	6.5	7.3
P ₂ O ₃	0.4	0.31	0.31	0.29	0.67
MnO	0.08	0.16	0.08	0.08	0.08
MgO	0.06	0.54	0.10	0.36	0.55
CO ₂	<0.05	<0.05	<0.05	<0.05	<0.05
Sum	100	99	100	95†	98
Loss on ignition				23.6	21.0

* Interval above underclay occupied by peat and that above saprolite is A horizon soil.

† Sample contained an appreciable amount of organic matter.

Maui. Probably amorphous matter similar to that of the Maui exposure is present in both the clay and saprolite on Kauai.

VOLCANIC ROCKS OF KAUAI AND MAUI

The rocks on the island of Kauai consist of the Waimea Canyon Volcanic Series of probable Pliocene age and the Koloa Volcanic Series of Pleistocene and Recent age (Macdonald, Davis, and Cox, 1960, p.20). The Waimea Canyon Series forms the mass of rocks in the central dissected shield volcano. Flows of the Koloa Series lie chiefly on the eastern and southern flanks of the principal volcano. A long period of volcanic quiescence and erosion followed the accumulation of the older series, resulting in the major unconformity between the two series.

Most of the rocks in the Waimea Canyon and the Koloa Volcanic Series are similar petrographically, but there are significant structural and textural differences. The Waimea Canyon Series is almost entirely olivine basalt, but it contains minor amounts of basalt poor in olivine, picrite

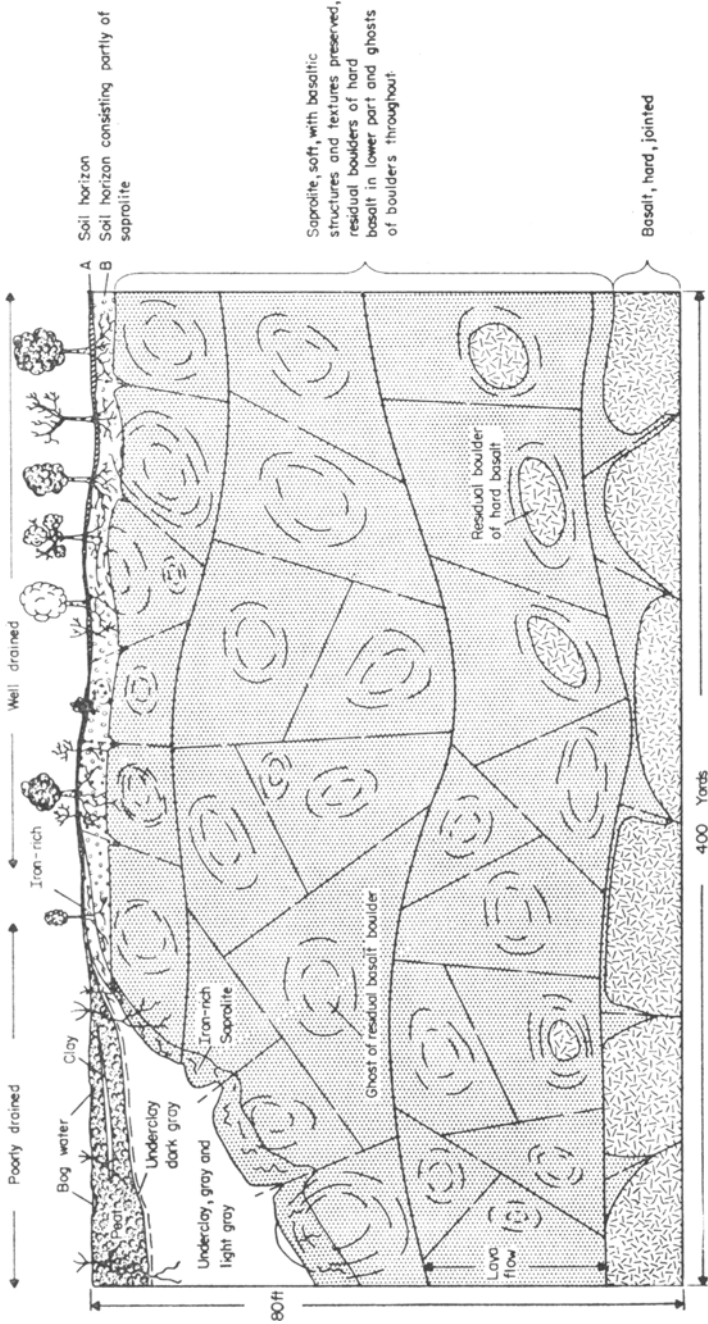


FIGURE 2.—Diagrammatic section of weathered basalts in poorly drained and well-drained areas

basalt rich in olivine, and basaltic andesite. These rocks consist chiefly of plagioclase, pyroxene, olivine, and magnetite. Most of the Koloa Series is olivine basalt and picrite basalt of the mimosite type, and the mineral compositions of these rocks are similar to those in the Waimea Canyon Series. Koloa rocks in several areas, however, are undersaturated with silica, and melilite and nepheline occur in place of plagioclase. Olivine phenocrysts are generally much smaller and darker in the Koloa than in the Waimea Canyon rocks. The Waimea Canyon Series consists chiefly of thin, highly vesicular flows, and Koloa rocks are mostly thick massive flows. Koloa rocks commonly are much finer grained and less vesicular than those in the older series.

The only rocks on the island of Maui referred to in this article are part of the Kula Volcanic Series of probable Late Tertiary age, though several series having complex geologic histories and rock types are present. The Kula Series extends over the entire northern and western slopes of Haleakala volcano (Stearns and Macdonald, 1942, pl.1), and it also occurs at other localities in the southern and eastern parts of East Maui. The flows in this series consist of dense and vesicular jointed basaltic andesite, andesite basalt, and picrite basalt. Most of the rocks are aphanitic and tend to be much more massive than rocks in other series in East Maui.

SAPROLITE

Most of the areas having heavy rainfall on the island of Kauai and many of those on Maui are blanketed by a mantle of red, brown, and gray, deeply weathered rock that is locally more than 125 ft thick. This weathered rock is a saprolite, as most of the textures and structures of the parent volcanic rocks have been preserved (Fig. 2), but nearly all original minerals have been replaced during weathering. The saprolite is sufficiently soft to be easily removed with a pick, and it erodes rapidly where the protective vegetation has been destroyed. It is sufficiently cohesive to stand in steep hillsides and roadcuts without sliding, but is plastic when ground and wet. The change from parent rock to saprolite is accompanied by only very slight loss in volume, as is indicated by the preserved textures and structures and absence of evidence of collapse. Major loss of density takes place during the change, however; the average dry weight of 60 samples of saprolite derived from the Koloa Volcanic Series is less than 70 pounds per cubic foot and that of 120 samples of fresh rock is 174 pounds per cubic foot. The soil and upper portions of the saprolite are so porous that ordinary rainfall is absorbed and surface runoff takes place only during very heavy storms or when gentle rain falls for long periods. Below depths of 20 ft to 50 ft the presence of abundant halloysite in the saprolite reduces permeability, impedes groundwater movement, and causes ephemeral perched water tables. In most places the saprolite is more permeable than the

underlying hard rock, and a second zone of perched water is commonly present at the base of the saprolite.

The pH of the ground water in saprolite measured at 36 localities in the field ranged from 4.0 to 5.9; the average was pH 4.5.

On Kauai the saprolite in well-drained areas having heavy rainfall varies appreciably in chemical and mineralogical composition with depth (Fig. 3). Very little silica occurs near the surface, but it increases sharply at depths below 10 to 20 ft (Fig. 3). Alumina is a major constituent of both shallow

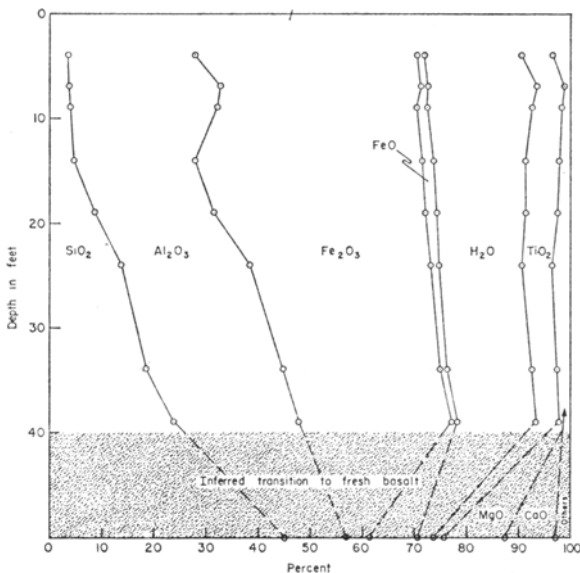


FIGURE 3.—Variation in chemical composition of saprolite in depth.

and deep saprolite. Near the surface nearly all of it is contained in gibbsite (Table I); at depth it occurs chiefly as endellite. Iron oxide in the form of goethite, hematite, and titaniferous magnetite is a major constituent of the saprolite. With few exceptions iron oxide minerals, particularly hematite, increase toward the surface. Goethite occurs in veins, irregularly rounded nodules, clay-size particles disseminated throughout the saprolite, and in pseudomorphic replacements of the outer portions of olivine crystals. Hematite is in veinlets, irregular nodules, finely disseminated materials, and crusts on magnetite grains. Titaniferous magnetite is in euhedral and subhedral crystals, most of which are of fine silt size or smaller. Magnetite crystals appeared to be finely intergrown with ilmenite in one polished section examined microscopically with reflected light. The titania content of the saprolite is approximately twice as great as in the fresh rock; however, it is only a minor constituent of the saprolite. Titania generally increases

from depth toward the surface. Much of the titania in saprolite is in titaniferous magnetite and probably ilmenite, but trace amounts of anatase are commonly present. Only very small fractions of the calcium and magnesium of the fresh rock remain in the saprolite. Only small amounts of potassium are present in the fresh rock, and only traces can be found in most of the saprolite.

UNDERCLAY DEPOSITS

The underclays are light-colored, nonbedded, irregular lenticular deposits covered by a layer of loose spongy peat as much as 8 ft thick (Fig. 2). The clays and the overlying peat are thickest in the central parts of the bogs and thin sharply toward the edges of the bogs. Several holes augered by both hand and with a power auger failed to penetrate the base of the clay at depths of 20 ft. Deeper holes were not successful because of poor recovery, but a few cuttings from greater depths indicate that maximum thickness exceeds 30 ft. The peat and underclay generally wedge out in the zone where the dwarfed bog vegetation is replaced by the enclosing normal forest growths. The thickest peat is in the bog at 4000 ft altitude (Fig. 1); it is as much as 4 ft thick in the bog at 2060 ft and less than 1 ft thick in bogs at lower altitudes.

Most of the clay is very light gray, but some of it is darker shades of gray, and parts of the deposits in contact with the overlying peat are ordinarily so rich in decaying organic material that they are almost black. Lower margins of deposits are commonly tan or brown and are richer in iron than middle and upper parts. Relict masses of brown and gray saprolite are common near the base of deposits, and large residual boulders of nepheline basalt are scattered through the clay in the bog at 1200 ft (Fig. 1). The cores of these boulders are dark-colored hard rock, but their outer rims, an inch or two thick, are light colored and are softer than the cores. Most of the iron has been leached from the rims, and nepheline has been altered to clay. Though the altered rims are in sharp contact with the enclosing structureless clay, a change from the basalt to clay is indicated by the light color, abundant halloysite, and decreased hardness of the rims. The mass of clay in this bog, as well as in other deposits investigated, grades downward into iron-rich saprolite, which is the parent of most of the clay.

The saprolite below underclay is similar to saprolite at depth in well-drained areas. The saprolite below underclay, however, contains much more goethite in the form of veins and veinlets, vesicle and vug fillings, and other ferruginous accumulations.

The underclay is generally structureless, but one uniform 6- to 8-in. light-gray clay interbedded in peat, which overlies a thick underclay, extends over much of one bog. This is the only evidence of clay bedding and of peat and clay interbedding found in the surficial bog deposits.

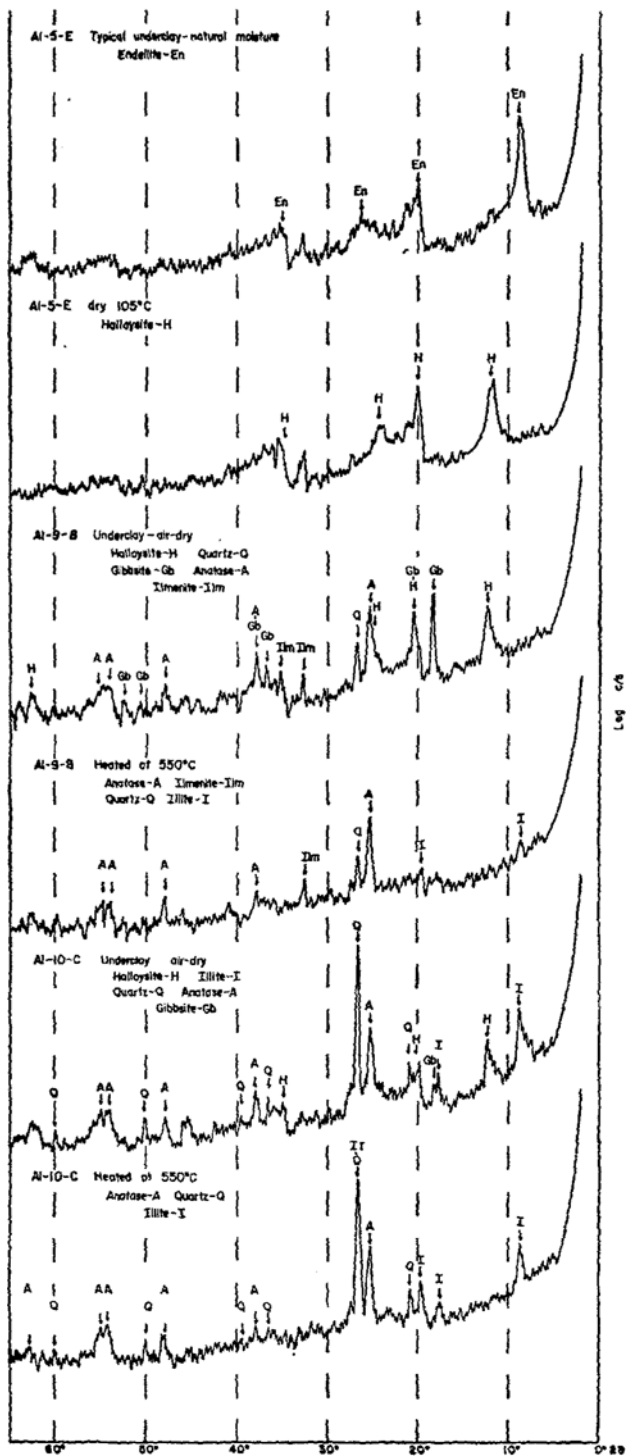


FIGURE 4.—X-ray diffraction traces of underclays, Kauai, Hawaii, $CuK\alpha_1$ filtered radiation.

All the clay is very plastic, and some water-logged deposits are almost fluid, as shown by the fact that a 2-in. diameter hand auger weighing about 30 pounds sank under its own weight at several localities. The pH of water in the clay at four localities that had been partly drained artificially ranged from 4.5 to 5.5. The pH of water in peat measured at five localities ranged from 3.5 to 4.5, and pH of a sample of open bog water was 3.5.

The underclay consists chiefly of halloysite minerals, most of which is endellite, with variable amounts of illite, gibbsite, quartz, anatase, ilmenite, probably appreciable amounts of amorphous materials, and traces of goethite and magnetite (Table 1). Halloysite was identified by both X-ray diffraction and electron-microscope techniques. X-ray diffraction traces of the underclay with its natural moisture (Fig. 4, Al-5-E) showed broad basal reflections at 10\AA that collapsed to 7\AA with drying, indicating the presence of endellite. X-ray traces of most samples, however, showed minor reflections at about 7\AA , corresponding to the less hydrous form of halloysite. Electron micrographs of underclay samples, not illustrated, show the presence of some poorly developed tubular structures characteristic of halloysite and much fine-grained material that John C. Hathaway, who made the micrographs, interpreted as endellite (written communication, June 23, 1961).

Illite is generally not an abundant mineral in the underclay, but in places it makes up as much as 30 per cent of the deposits. It was found to be uncommonly abundant in one bog below 8 ft of peat, the thickest peat penetrated in augering, and in the one thin clay interbedded with peat in another bog. Illite was identified by its 10\AA spacings in samples that had been dried to collapse the 10\AA halloysite (Fig. 4, Al-9-B-550°C, Al-10-C-550°C). Illite probably contains nearly all the K_2O in the underclay, inasmuch as the sample richest in potassium oxide (Table 2, Al-10) also contained considerable illite, and no other K_2O -bearing minerals have been identified in the clay. Gibbsite occurs as irregular nodules, ranging from silt size (less than $1/16$ mm diameter) to more than 6 in. in longest dimension, scattered throughout most of the clay. However, in some zones gibbsite is absent, and in other zones small nodules are so abundant that the clay has a granular texture and is difficult to auger by hand. Examination of a thin section of one gibbsite nodule revealed a complexly involuted interlamination of paper-thin gibbsite layers with laminae containing minor amounts of halloysite, part of which is iron stained. Most of the quartz in the underclay is too fine grained to be studied by optical methods, a form similar to that in the Koolau clay on Oahu (Wentworth, Wells and Allen, 1940, p.25). However, minor amounts of fine silt sized quartz was present at a few localities. Some of these grains were angular, but a few were irregular shaped and had optical properties similar to that of chert. Anatase is the principal titanium mineral in the clay, and it is most abundant in the less-than-two-micron fraction, but some is also present

in the largest gibbsite nodules. Anatase is identified by its strongest X-ray spacing at 3.51Å (Fig. 4, Al-9B-550°C); heat treatment to destroy the halloysite structure is required for this identification, because 002 of halloysite at 3.6Å masks the strongest anatase peak. Ilmenite is rare in most of the clay, but a few zones contain as much as 10 per cent of this mineral. Most of the ilmenite is in the fine silt fraction, but a few grains are as large as grains of fine sand. The presence of much amorphous material in the clay is suspected, because the intensities of X-ray reflections from minerals in many samples are low, and estimated amounts of identifiable minerals are inadequate to account for the composition of whole samples. Also, electron micrographs of the clay showed finely dispersed materials that were interpreted by Hathaway as being amorphous materials. The amorphous materials in the clay that could not be isolated probably are composed chiefly of alumina, silica, and water and are similar to the amorphous materials on Maui discussed on the following pages. Traces of goethite and magnetite were identified in silt and sand fractions separated from the clay, but neither of these minerals were sufficiently abundant in whole samples to be identified by X-ray methods.

ALUMINA-SILICA GEL AND ALLOPHANE

The alumina-silica gel and allophane on Maui were the only amorphous inorganic materials found during several months' field work that were sufficiently pure for analysis and study, though these materials probably occur extensively in weathered rocks in Hawaii. The amorphous materials on Maui occur in rocks that are less weathered but otherwise similar to sapolite associated with the underclay on Kauai; amorphous materials on both islands are probably very much alike. Nearly pure accumulations of gel can be observed only occasionally, inasmuch as they are rarely in masses sufficiently large to be seen, change with drying, and are washed away or become intermixed with microscopic plants or very fine grained minerals when wet conditions continue. The inorganic matter disseminated throughout much of the weathered rocks is intimately intermixed with very fine grained minerals, and cannot be isolated in the laboratory. The presence of gels is known in Hawaiian soil (G. D. Sherman, oral communication, July 1959), as is the presence on Maui of "Al-Fe-Si gel material" described as "electron-diffraction-amorphous" (Bates, 1962, pp.325-327). Gel-like materials intimately intermixed with microscopic plant life, clay, and very fine grained minerals of other types are a common occurrence at the surface in sluggish drainage and seepages of ground water.

The alumina-silica gel and allophane were collected July 4, 1960, from a freshly bulldozed cut at an altitude of 4240 ft on the northwest slope of Haleakala volcano, East Maui. The cut is at a point a quarter of a mile west of where Waikomoi stream is crossed by a trail extending eastward

from Olinda Prison. The average yearly rainfall in this vicinity is 250 in., according to U.S. Weather Bureau maps. The vegetation is classified as typical of the wettest rain forest environment (Selling, 1948, p.42). The gel and allophane occurred 2 to 6 ft below the surface that existed prior to the excavation. The cut is below a small drainage a few feet deep, and both seepage and surface water were flowing over the face of the cut at the time samples were collected. The soil (A horizon) at the top of the cut is approximately 6 in. thick and is extremely rich in decaying organic matter.

The host rock of the gel and allophane is saprolite formed by weathering of jointed, vesicular basalt of the Kula Volcanic Series. Conversion of the joint blocks to saprolite has progressed from the outer surfaces toward the centers, and most blocks still contain irregularly rounded residual boulders of hard basalt. The gel and allophane occur within the saprolite as fillings in structures inherited from the parent basalt such as vesicles and small depressions in the walls of vugs and as coatings on the walls of vugs and cracks.

The allophane is white, soft, and open textured, and some of it has a sugary appearance. In the exposure from which it was collected, most of the allophane was coated by gel, which gave it an appearance similar to flowstone or a sheet of ice. The gel occurs partly in masses resembling frog spawn or thick gelatin and is made up of clear irregular bodies ranging in diameter from microscopic specks to about a quarter of an inch, and partly in cloudy, laminated, paper-thin layers a square inch or more in area. Most of the masses of clear gel extend laterally into laminae of the cloudy gel. Parts of the gel contain small nuclei of light-colored semisolid matter, and the laminated gel includes many specks of semisolid(?) brown and dark-colored matter.

The water lost from the gel in air drying at room temperature cannot be measured accurately because some dehydration takes place before excess water has been removed from all parts. Water lost by three air-dried gel samples amounted to 94.6, 94.4, and 86.4 per cent, respectively, and the average air-drying loss is approximately 90 per cent. Loss on ignition of one sample of air-dried gel at 1000°C is approximately 4 per cent of the gel before drying. This loss is chiefly water, but a small part of it is CO₂. Total loss between air-drying temperatures and 1000°C varies appreciably with humidity during the drying.

The air-dried gel and the allophane are similar in composition (Table 3). The Al₂O₃ content of the air-dried gel and the allophane ranges from 49.5 to 50.5 per cent; the SiO₂ content from 20.0 to 26.0. This composition corresponds approximately to that of halloysite mixed with gibbsite and minor impurities. The approximate composition of halloysite and gibbsite mixed in equal quantities would be about 52 per cent Al₂O₃, 23 per cent SiO₂, and 25 per cent H₂O.

Both the gel and allophane are essentially amorphous, but the air-dried gel contains a small amount of gibbsite as revealed by X-ray diffraction

TABLE 3.—PARTIAL CHEMICAL ANALYSES OF ALLOPHANE AND ALUMINA-SILICA GEL*

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Approximate percentage weight loss in air drying	Approximate percentage loss on ignition 1000°C	Organic carbon	Loss on ignition 120° to 1000°C
Allophane	26.0	50.5	1.0	0.1	—	25.0	—	—
Clear gel	2.2	4.9	0.3	—	90	—	—	—
Laminated gel	2.2	4.6	0.4	—	90	4.0	—	—
Air-dried gel clear	22.0	49.5	3.0	0.6	—	—	1.77†	18.5‡
Air-dried laminated gel	20.0	51.7	4.0	0.9	—	—	—	—

* Percentage of oxide determined by X-ray emission methods.

† Percentage determined by induction-furnace method by I. C. Frost.

‡ Percentage determined gravimetrically by I. C. Frost.

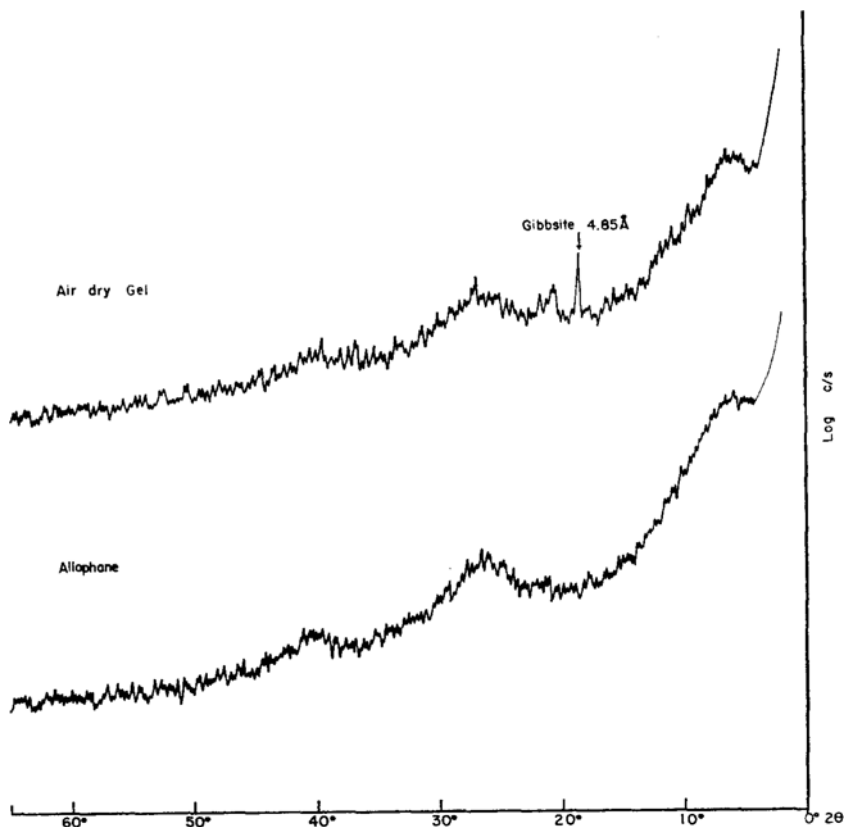


FIGURE 5.—X-ray diffraction traces of alumina-silica gel and allophone, Maui, Hawaii, $\text{CuK}\alpha_1$ filtered radiation.

trace reflections at 4.85Å and 4.37Å (Fig. 5). The X-ray diffraction trace of the undried gel showed no identifiable minerals as would be expected for any material composed 90 per cent of water. Traces of the allophone show that it contains very little crystalline material (Fig. 5).

The differential thermal analysis curves of the allophone and the air-dried gel (Fig. 6) are similar to the curves illustrated for allophone by Mackenzie (1957, p.124) in that they show low-temperature endothermic and high-temperature exothermic reactions; at intermediate temperatures no thermal reactions characteristic of the clay minerals are indicated. The maximum endothermic reaction resulting from the removal of water takes place at about 180°C , but a temperature of about 300°C is reached before this reaction is completed, suggesting that some water-bonding forces are present. The DTA curve for the gel (Fig. 6) shows a distinct endothermic

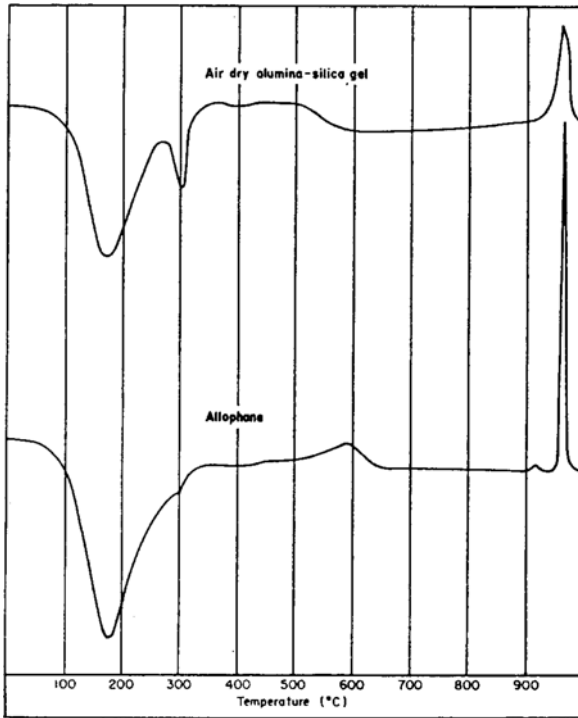


FIGURE 6.—Differential thermal curves for air-dried alumina-silica gel and allophane, Maui, Hawaii.

reaction at slightly above 300°C, probably caused by very fine grained gibbsite reacting at a temperature 30° to 40° lower than for the typical mineral. The intensity and size of this reaction, as compared to reactions for several prepared mixtures containing various proportions of gibbsite, indicates that the amount of gibbsite present is between 15 and 20 per cent. A very small downward inflection at 300°C on the curve for the allophane (Fig. 6) probably indicates a trace of gibbsite in that material. The exothermic reaction at 975°C is much more pronounced in the allophane than in the gel. The pronounced high-temperature reaction is similar to the reaction in kaolin minerals attributed by Mackenzie (1957, p.103) to the formation of mullite, but only slightly more mullite was present in the material formed from the allophane than from the gel with heating to 1000°C, suggesting that this reaction may be caused by something other than mullite formation.

ORIGIN OF UNDERCLAY AND AMORPHOUS MATERIALS

The underclay is found only in bogs and is directly related to the overlying peat and poor drainage conditions. Some of the underclay forms directly from hard volcanic rocks, but iron-rich saprolite is the immediate parent material of the clay at most places. Endellite, illite, quartz, ilmenite, and anatase are much more abundant in the underclay than in the saprolite and gibbsite, goethite, hematite, and magnetite are much more abundant in the saprolite than in the underclay. Significant differences in chemical composition between the two types of rocks lie in the high silica and low iron content of the underclay and very low silica and high iron content of the saprolite. Titanium and potassium also tend to be much more abundant in the underclay than in the saprolite.

The weathering of volcanic rock to form saprolite probably began soon after the lavas cooled, as plant life has been found on modern flows in Hawaii 4 months after volcanic activity ceased. As indicated by clays associated with rocks of the Koloa Series that are older than mid-Pleistocene, the formation of clays by weathering has probably proceeded in places for more than one-half million years and for much longer in the bog at 4000 ft where underclays rest on the older volcanic series. The thickness of the peat indicates that the bogs have existed for some time, and the absence of evidence for any significant change in the bog environment leads to the conclusion that both underclay and peat are still forming today. The earliest date that now can be established for the beginning of underclay formation is the close of the last glacial period. This date is based on analysis of pollen (Selling, 1948, p.118) that occurs near the base of the thickest peat which overlies thick underclay deposits in the bog at 4000 ft (Fig. 1).

Part of the endellite in the underclay probably formed in the bogs and part has been preserved from a saprolite already rich in this mineral. That some of the clay formed in place and is probably still forming is indicated by the several stages of replacement of nepheline by endellite in the altered rims of residual boulders in one bog. Formation of much of the clay by preservation of the endellite already present in the parent saprolite is indicated by the isolated saprolite masses in the lower parts of clay bodies and by the gradation of clay downward into saprolite. The endellite in the saprolite had previously formed by alteration of the alumina-silicate minerals in volcanic rock, and it is concentrated in underclay chiefly by the removal of iron minerals from the saprolite. The preservation of endellite in the bog environment is partly due to water movement so sluggish that it cannot leach silica, whereas in well-drained saprolite, desilication and removal of calcium and alkalis are the most important changes during weathering (Sherman, 1958, pp.5-6; Bates, 1962, pp.315-

316). Silica, calcium, and alkali contents are lower in ground water in saprolite than in water which has passed first through the saprolite, then through a zone in which hard rock was altering to saprolite, and then into fresh rock (Patterson and Roberson, 1961, p.C197). The existence of potassium-bearing illite in parts of the underclay also is further evidence that leaching in bogs is much less effective than it is in well-drained areas.

The major role of peat is apparently in the removal of iron from the underclay. The presence of much more hematite, goethite, and magnetite in the saprolite than in the underclay indicates that mobilization and leaching of iron is related to the appreciable amounts of organic acids that result from decaying organic matter in the peat. The presence of such acids is indicated by the low pH of water in the bogs and in the peat. Possibly the acid and the accompanying reducing conditions change the iron from trivalent to bivalent form, rendering it sufficiently soluble to be flushed out by even the weak downward movement of water in the bogs. Iron may also be removed as complexes of chelates of organic substances. For some unknown reason much of this iron has been concentrated around and below the clay deposits as goethite veins and other ferruginous accumulations. Evapotranspiration may have concentrated the iron in solution near the surface in areas surrounding the bog, but there is no reason to believe that any drying could have taken place below the bogs. Probably oxidizing conditions are present in the saprolite, and iron was precipitated as the solutions pass from the reducing conditions in the bog into the surrounding oxidizing environment.

The abundant gibbsite in well-drained saprolite forms primarily by the desilication of halloysite and the dehydration of alumina gels, according to evidence presented by Bates (1962, p.327) and confirmed by the results of the investigations reported in this article. Gibbsite is therefore a normal residual accumulation of aluminum hydroxide after silica has been leached from saprolite, but the present of gibbsite nodules in underclay is problematical. Many authorities on the origin of gibbsite agree that some drying, such as may take place above the water table, is required, and that its formation is particularly favored by alternating wet and dry seasons. The gibbsite in shallow saprolite fulfills these conditions to a considerable extent, and, in addition, desilication processes are very effective. The gibbsite in underclays, however, exists in a permanently wet environment where wet and dry cycles have little effect. The underclay probably never dried sufficiently to influence the formation of gibbsite, and the presence of abundant endellite and some quartz indicates that desilication is very ineffective in the deposits. Some desilication must nevertheless have taken place in the underclays to free aluminum hydroxide and allow gibbsite to form. The conclusion that gibbsite does form under permanently wet conditions after the removal of silica from alumina-silicate minerals conforms to views expressed by Van Kersen (1956, pp. 289, 367-368) who found that bauxitization has taken place in Recent swamp deposits in Surinam,

where drying was not possible. In the Surinam swamps, gibbsite develops from a parent material of illitic clay, and halloysite is formed at an intermediate stage in the process.

Much of the underclay contains more titania than the saprolite, and the titanium minerals in the two rocks are different. Nearly all the titanium in the underclay is in very fine grained anatase, whereas most of the titanium in the saprolite appears to be in titaniferous magnetite, and only small amounts of anatase are present. The anatase in saprolite probably develops mainly after the destruction of pyroxene; the anatase in the underclay probably forms from titania inherited from both pyroxenes and titaniferous magnetite. The uncommonly high concentrations of anatase in certain zones and the few ilmenite-rich zones in the clay may have formed from parent rocks that were exceptionally rich in titanium minerals or from the residual concentration of a parent material several times the volume of the present clay deposits. The presence of ilmenite-rich zones and the virtual absence of magnetite in the clay suggest that ilmenite is more resistant to alteration than magnetite under conditions existing in bog environments and that the reverse relationship exists in well-drained areas. Much of the very fine grained ilmenite in underclay probably consist of residual intergrowths remaining after the magnetite has been leached.

The varying amounts of quartz in the underclay and its virtual absence in the saprolite reflect the difference in the effectiveness of leaching under the two conditions. Clearly quartz cannot withstand the leaching of ground water in well-drained areas, but is preserved in bog deposits. The very fine-grained angular quartz observed in a few samples, probably was a constituent of the volcanic rock, although quartz was not identified in unweathered rocks on Kauai, either in this investigation or in petrographic studies by Macdonald (1960). Very fine-grained, extremely angular quartz was present in the uniform bed of thin clay interstratified with peat in one bog. This quartz probably was introduced with other pyroclastic material from a nearby vent.

The origin of potassium-bearing illite in the underclay is difficult to explain because the traces of biotite in the volcanic rock on Kauai are inadequate to supply a micaceous parent material, and the saprolite on which the clay formed must have already been leached of potassium. The problem is further complicated because two of the samples analyzed (Table 2, Al-6, GF-2) contained approximately the same proportions of K_2O as the fresh volcanic rock, whereas one sample from a clay developed on the Waimea Volcanic Series (Table 2, Al-10) is more than three times as rich in K_2O as the most potassium-rich fresh Waimea Canyon rock that has been analyzed (Macdonald, 1960, p.112). Clearly potassium tends to remain and may be concentrated in the reducing and poor drainage conditions of peat bogs on Kauai. Even a tendency for an alkali to remain in a bog contrasts sharply with conditions in well-drained areas. A genetic relationship between the peat and illite is suggested by the concentration of illite

under the thickest peat and in a thin clay bed interbedded with peat. Probably potassium was concentrated by plants whose roots penetrated through the clay or into saprolite surrounding the bogs. These plants, while undergoing decay and after conversion to peat, released potassium which was carried downward into the clay where it became fixed in the form of illite.

Information leading to an explanation of the amorphous materials in underclays could not be obtained, inasmuch as these materials cannot be isolated for study. However, the high alumina-silica content of the clay suggests that the amorphous materials are probably similar to the alumina-silica gel and allophane on Maui. The amorphous materials in underclays may be an intermediate stage between the destruction of the silicate minerals in the parent rocks and the formation of clay minerals, or they may form during the gradual desilication of the clay minerals and formation of gibbsite.

The gel at the locality on Maui probably forms in acid ground water by concentration of soluble materials that were leached from aluminum silicate minerals in rocks of the Kula Volcanic Series or from clay minerals in the saprolite. The high humic acid content of the water is indicated by the 1.77 per cent organic carbon present in the air-dried gel (Table 3). Paper-thin laminae in part of the gel indicate its accumulation in cycles corresponding to wet and dry periods. Presumably these layers reflect individual rainfalls and intervening dry periods, inasmuch as monthly rainfall averages for this locality do not vary appreciably throughout the year, and there are no pronounced wet and dry seasons. Layering of the gel may be caused by variations in pH of percolating ground water, resulting from dilution of humic acids by heavy rainfalls and concentration of acids by evapotranspiration during dry periods. The close association of the gel and allophane, their similar compositions and flowstone appearance, all point to precipitation of allophane by dehydration of gel.

A genetic relation between the gel, allophane, gibbsite, and halloysite is indicated by their similar compositions, and by the sharp contrast of their nearly white colors with the dark red, brown and gray of the other minerals forming the saprolite hosts. The composition of the dried gel and the allophane corresponds to that of an intimate mixture of halloysite and gibbsite which occurs widely in saprolite within veins, vesicle fillings, and as coatings on the walls of larger vugs. The manner in which all these materials occur indicate their introduction by ground water. The presence of minor amounts of gibbsite in the dried gel suggests that gibbsite forms as gel dehydrates; however, gibbsite does not always form as aluminous gels dehydrate because no more than a trace of this mineral is present in the allophane. Possibly some gels are completely amorphous and others contain scattered unit cells of gibbsite or nuclei of semi-orderly arranged aluminum atoms and hydroxyls that develop into gibbsite as chemically precipitated or dehydrated. More than simple dehydration is involved in

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the formation of halloysite, because no evidence for this mineral was found in the dried gel or allophane. Endellite probably forms much more commonly than the less hydrous form of halloysite, because it is the most common aluminous mineral in saprolite at depth and little drying can take place in this environment. The fine involuted interlaminations of gibbsite with minor amounts of halloysite found in gibbsite nodules in underclay indicate a cyclic origin from a material similar to the laminated gel.

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