DEHYDRATION CURVES AND DIFFERENTIAL THERMAL CURVES OF CLAYS FROM HAWAIIAN SOILS

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INTRODUCTION

The fine particle clay fraction is the active part of soils, and it determines to a great extent the physical and chemical properties of soils. This fine particle fraction is made up primarily of relatively stable, weathered secondary minerals, and some amorphous materials (27). In agriculture, the nature and the amount of clay play a major role in determining the moisture content of the soil, base and water supplying capacity, acidity, tilth and the general physical and chemical properties. It is also important in soil classification and in the study of soil genesis. (28).

For the past twenty years, intensive investigations have been made to identify and study the nature and properties of these fine particle minerals. Among the methods that have been used are chemical analysis, cation exchange capacity, adsorption of water vapor and dyes, swelling, titration curves, optical method, X-ray analysis, electron microscope, dehydration curves and differential thermal analysis. It is difficult to identify the minerals with one or two methods, but if the results from several methods are studied together, more definite conclusions may be drawn.

Information on the mineral constituents of tropical soils is rather limited. In this research, the dehydration method and the differential thermal method are used to investigate the mineral constituents in representative soils from the major Great Soil Groups of the Hawaiian Islands. There are three parts in this study:

(1) separation of soils into sand, silt and clay fractions.

(2) dehydration curves

(3) differential thermal curves

The first objective is to determine if the thermal methods could be used to identify the mineral constituents in Hawaiian soils. If this is successful, the second objective is to estimate the content of soil minerals.

HISTORICAL REVIEW

Thermal studies of clays started with the classical work of Le Chatelier in 1887. (36). His purpose was to characterize and identify a few clay specimens by studying the temperature of dehydration. He found that when a small quantity of clay was heated rapidly at a uniform rate, the rate of the rise in temperature was perceptibly slowed down at the moment of dehydration, and that this point of slowing down could be utilized to establish a distinction among the various hydrated aluminum silicates. For a thermocouple, Le Chatelier used pure platinum and platinum +10 percent rhodium and the observations were recorded by a photographic method. The platinum cone containing the clay sample was placed in a furnace which was heated to 1000°C, at a rate of 120°C per minute. Le Chatelier observed not only the slowing-up of the dehydration but also sharp accelerations indicating the phenomenon of an evolution of heat. Five distinct types of clays were characterized: halloysite, allophane, kaolin, pyrophyllite and montmorillonite.

Barnes (3) in 1895 was probably the first investigator to show the actual losses in weight when clays were heated to different temperatures. In 1902, Kennedy (3), reported a definite, distinctive dehydration curve of kaolinite. Ashley, (3), in 1910, heated several kaolinite samples in an electric furnace and brought the temperature up to 1000°C in 100 minutes, or 10°C per minute, which was a much slower rate than that of Le Chatelier. He reported that retardation occured at a much lower temperature than that of Le Chatelier's.

Brown and Montgomery (9) in 1913 reported that kaolin clays lost most of their water between 400° and 500°C.

Posnjak and Merwin (45), in 1919, made a thorough study of several hydrated ferric oxides, such as turgite, goethite, limonite and xanthosiderite. They found that crystalline goethite decomposed at a slightly higher temperature than the amorphous hydrated ferric oxide. All the hydrated ferric oxides lost their combined water between 150° and 250°C.

Ross (47) in 1927, Hendricks et al. (18) in 1930, and Kelley et al. (24) in 1930, showed that montmorillonite, kaolinite, and illite were crystalline and that these minerals in their crystalline forms made up the essential parts of soil colloids. Previously, soil minerals were assumed to be amorphous. This discovery was a great forward step, and the study of soil minerals was intensfied in 1930's, resulting in better apparatus and better techniques.

Ross and Kerr (48) (49), with the aid of dehydration curves, showed that kaolin was not a single mineral, but it was comprised of four distinct minerals, which were named kaolinite, dickite, nacrite and halloysite. This work explained why former investigators in kaolinite obtained different results.

Insley and Ewell (20), in 1935, studied the crystal structure of kaolinite at the endothermic and exothermic peaks, using the thermal methods and the X-ray.

In 1939, Norton wrote a comprehensive paper, "Critical study of the differential thermal method for the identification of the clay minerals" (43). His improved apparutus was shown in a drawing, and it was described in detail. It served as a model for later investigators. Differential thermal curves of standard minerals, such as montmorillonite, kaolinite, illite and several hydrated oxides, were shown to serve as standards of identification. A method for estimating the amount of minerals in a mixture was discussed, and probably this paper was the first to do so.

This publication was followed by other excellent papers which discussed improved apparatus, refined techniques, and greater scope of differential thermal curves. Among the modern investigators who contributed much to the study of thermal methods are Grim (12) (13) (14) (15) (16) (17), Hendricks (18) (19), Kelley (25) (26) (27) (29), Kerr (30) (32), Kulp (33) (34) (35), and Ross (48) (49) (50) (51).

Alexander et al. (2) in 1939, estimated the kaolinite content of soil colloids by the X-ray method and differential thermal curves. The results from the two methods, shown in Table I, were fairly close.

In 1940, Nagelschmidt et al. (41), estimated the mineral content of two Indian soils, using the X-ray, chemical analysis, optical data and dehydration curves. These soils are of particular interest because the black cotton soil and the red earth of India seem to be similar to the Dark Magnesium Clay soil and the Low Humic Latosols of Hawaii. Table II shows the mineral constituents of the two

Table I. Estimates of mineral components of soil colloids (< 0.3u), from Alexander et al. (2)

Soil Series	Great Soils Group	Differential Thermal Analysis, Kaolin	X-ray				Clay (2u) by mechanical analysis
			Kaolin	Hydrous Mica	Montmorillonite	Crystalline Iron Oxides	
Cecil	Red Podzolic	80	80	Abs.	Abs.	G.H.*	44%
Greenville	Red Podzolic	90	80	Abs.	Abs.	G.H.	42
Decatur	Red Podzolic	50	80	10	Abs.	G.H.	49
Dewey	Red Podzolic	60	80	10	Abs.	G.H.	36
Fullerton	Yellow Podzolic	70	70	30	Abs.	G.	49
Frederick	Gray Brown Podzolic	70	70	20	Abs.	G.	70
Hagerstown, Pa.	Gray Brown Podzolic	70	70	20	Abs.	G.H.	55
Hagerstown, Md.	Gray Brown Podzolic	50	50	50	Abs.	G.H.	70
Hagerstown, Mo.	Gray Brown Podzolic	40	50	50	Abs.	G.	39
Chester	Gray Brown Podzolic	40	60	30	Abs.	G.H.	20
Chester	Gray Brown Podzolic	40	60	30	Abs.	G.H.	25
Chester	Gray Brown Podzolic	40	60	30	Abs.	G.H.	17
Manor	Gray Brown Podzolic	50	60	30	Abs.	G.H.	24

Table I. (continued)

Soil Series	Great Soils Group	Differential Thermal Analysis, Kaolin	X-ray				Clay (2u) by mechanical analysis
			Kaolin	Hydrous Mica	Montmorillonite	Crystalline Iron Oxides	
Miami	Gray Brown Podzolic	10	10	80	-	-	51
Carrington	Prairie	30	50	30	10	-	24
Barnes	Chernozem	20	30	40	20	-	36
Desert Soil	Desert	20	20	80#		-	36
Desert Soil	Desert	20	20	80#		-	35
Desert Soil	Desert	20	20	80#		-	30
Desert Soil	Desert	20	20	80#		-	14

*G. and H. indicate presence of goethite and hematite

The principle mineral present in these soil colloids is of the mixed layer type.

Table II. Minerals present in clay fractions of Indian soils, from Nagelschmidt (41)

	Black cotton soil, 12-18 in.			Red earth, 18-24 in.		
	Coarse	Fine	Superfine	Coarse	Fine	Superfine
	1.4-0.1u	0.1-0.06u	< 0.06u	1.4-0.1u	0.1-0.06u	< 0.06u
Beidellite	30%	70%	90%	-%	(?) 15%	(?) 30%
Kaolinite	15	10	-	40	50	60
Mica	15	15	-	30	15	-
Quartz	30	5	-	10	3	-
Hematite and goethite	5	-	-	8	10	10

Indian soils.

Kellogg and Davol (60) found 20 to 60 per cent kaolinite in the clay fraction of Latosols from Belgian Congo in Africa.

In 1945, Ross and Hendricks published a comprehensive paper, "Minerals of the montmorillonite group, their origin and relation to soils and clays" (51), in which the following were recognized as belonging to the montmorillonite group: Montmorillonite, beidellite, nontronite, hectorite and saponite. Chemical and physical properties of these member minerals were discussed in detail.

A study of the mineral content of Hawaiian soils has been made by Dean (11), and Tanada(54). Dean applied the differential thermal method on several Hawaiian soils, and estimated the kaolinite content, using the cosecant method. The kaolinite content varied from zero to 60 per cent. Table III shows the result of Dean's findings.

Tanada (54) segregated the colloids of Hawaiian soils into five groups and used the dehydration method to estimate the kaolinite content of each group.

Group I-Very young soils- less than 25% kaolinite.

Group II- Low rainfall, less than 40 inches- 45 to 60% kaolinite, or more.

Group III- Moderate rainfall, 40 to 75 inches, 25 to 40% kaolinite.

Group IV- High rainfall, greater than 75 inches- less than 15% kaolinite, large amount of limonite and bauxite.

Table III. Kaolinite content of surface soils from the Hawaiian Islands and Tahiti, from Dean (11)

Location	Parent material	Rainfall inches	Kaolin per cent
Aiea, Oahu	Weathered basalt	50	63
Ewa, Oahu	Weathered basalt	20	57
Poamoho, Oahu	Weathered basalt	45	45
Waimanalo, Oahu	Weathered basalt	90	31
Nuuanu, Oahu	Weathered basalt	90	21
Halemanu, Oahu	Weathered basalt	80	20
Makiki, Oahu	Alluvium	30	17
Pensacola, Oahu	Volcanic ash	30	17
Paauhau, Hawaii	Weathered basalt	65	14
Aiea, Oahu	Volcanic ash	75	12
Kona, Hawaii	Aa lava	70	10
Papara, Tahiti	Alluvium	100	10
Hilo, Hawaii	Volcanic ash	165	7
Naalehu, Hawaii	Volcanic ash	45	< 5
South Point, Hawaii	Aeolin material	15	< 5
Honomu, Hawaii	Volcanic ash	250	< 5
Haapape, Tahiti		65	< 5
Kaiwiki, Hawaii	Volcanic ash	115	< 5
Kilauea, Kauai	Weathered basalt	65	< 5
Tantalus, Oahu	Volcanic ash	100	< 5
Hamakua, Hawaii	Volcanic ash	120	< 5
Olaa, Hawaii	Aa lava	170	< 5

Group V -Anaerobic condition and low temperature, extracted from ceramic clay- moderate amount of kaolinite, and presence of illite is suspected.

Table IV. Information on soil samples used in this study. Data from Cline et al. (10)

Soil Number	Soil Group	Soil Family	Symbol	Horizon	pH	Annual Rainfall (inches)	pH* Soil samples
48-454	Low Humic Latosols	Molokai	N1	A	6.0-7.5	15-30	6.6
48-455	Low Humic Latosols	Molokai	N1	B	6.0-7.5	15-30	4.7
48-456	Low Humic Latosols	Wahiawa	N3	A	5.5-6.5	30-60	6.0
48-457	Low Humic Latosols	Wahiawa	N3	B	5.0-6.5	30-60	6.5
48-460	Low Humic Latosols	Kohala	N5	A	5.5-6.5	40-70	5.6
48-461	Low Humic Latosols	Kohala	N5	B	5.0-6.5	40-70	5.6
48-583	Humic Latosols	Honolua	A2	A	4.0-5.0	75-150	4.1
48-584	Humic Latosols	Honolua	A2	B	4.0-5.0	75-150	4.2
46-519	Hydrol Humic Latosols	Koolau	K3	A	4.0-5.0	100-200	4.5
46-520	Hydrol Humic Latosols	Koolau	K3	B	4.0-5.0	100-200	4.7
49-951	Hydrol Humic Latosols	Akaka	K8	A	4.0-5.0	120-240	5.2
49-952	Hydrol Humic Latosols	Akaka	K8	Dark Layer		120-240	
49-953	Hydrol Humic Latosols	Akaka	K8	B	4.0-5.5	120-240	
49-954	Hydrol Humic Latosols	Hilo	K6	A	5.0-5.7	120-200	5.4

Table IV. (Continued)

Soil Number	Soil Group	Soil Family	Symbol	Horizon	pH	Annual Rainfall (inches)	pH* Soil Samples
49-955	Hydrol Humic Latosols	Hilo	K6	Dark Layer		120-200	5.7
49-956	Hydrol Humic Latosols	Hilo	K6	B	5.2-5.8	120-200	
47-443	Humic Ferruginous Latosols	Mahana	T1	A	4.5-6.5	25-40	4.5
47-445	Humic Ferruginous Latosols	Mahana	T1	B	4.5-6.5	25-40	4.6
47-248	Humic Ferruginous Latosols	Naiwa	T2	A	4.0-6.0	60-100	6.3
47-249	Humic Ferruginous Latosols	Naiwa	T2	Titanium Layer		60-100	6.5
47-250	Humic Ferruginous Latosols	Naiwa	T2	AB		60-100	6.3
47-251	Humic Ferruginous Latosols	Naiwa	T2	B	4.0-6.0	60-100	6.2
47-252	Humic Ferruginous Latosols	Naiwa	T2	C	4.0-6.0	60-100	5.5
47-256	Humic Ferruginous Latosols	Haiku	T3	A	4.5-6.5	60-150	4.6
47-259	Humic Ferruginous Latosols	Haiku	T3	B	4.0-6.0	60-150	4.4
49-998	Reddish Brown	Waikaloa	RB	A	6.0-7.5	20-50	6.7
49-999	Reddish Brown	Waikaloa	RB	B	6.0-7.5	20-50	7.4
49-56	Reddish Prairie	Waimea	C2	A	6.0-7.5	25-50	6.9
49-57	Reddish Prairie	Waimea	C2	B	6.0-7.5	25-50	7.3

Table IV. (Continued)

Soil Number	Soil Group	Soil Family	Symbol	Horizon	pH	Annual Rainfall (inches)	pH* Soil Samples
49-59	Brown Forest	Hanipoe	F1	A	5.5-6.5	20-40	5.7
49-61	Brown Rorest	Hanipoe	F1	AB		20-40	6.7
49-62	Brown Forest	Hanipoe	F1	B	5.5-6.5	20-40	6.4
49-64	Brown Forest	Olinda	F4	A	5.5-7.0	40-60	5.5
49-65	Brown Forest	Olinda	F4	B	5.5-7.0	40-60	5.2
48-575	Gray Hydromorphic	Honouliuli	H1	A	7.0+	10-30	7.6
48-576	Gray Hydromorphic	Honouliuli	H1	B	7.0+	10-30	7.3
48-577	Gray Hydromorphic	Kalihi	H2	A	5.0-6.5	10-30	6.7
48-578	Gray Hydromorphic	Kalihi	H2	B	5.0-6.5	10-30	7.8
48-581	Gray Hydromorphic	Kaloko	H3	A		10-30	7.7
48-582	Gray Hydromorphic	Kaloko	H3	B		10-30	7.7
48-571	Dark Magnesium Clays	Lualualei	M	A		15-40	7.8
48-572	Dark Magnesium Clays	Lualualei	M	B		15-40	8.0

*pH of soil samples was determined in laboratory.

EXPERIMENTAL PROCEDURE

SOILS USED IN THIS EXPERIMENT

The soils studied in this work are representative of the major Great Soil Groups of the Hawaiian Islands. Data on these soils are given in Table IV.

SEPARATION OF SOIL SAMPLES INTO SAND, SILT AND CLAY FRACTIONS.

Modified Jackson's method (in mimiograph instruction form) was used for preparing soil samples for dipersion. About 100 ml. water were added to 20 gram samples. The suspensions were brought to pH 4.0 with N H NO_3, and souble salts were removed by decanting off the clear supernatant liquid until a test with $(NH_4)_2 C_2O_4$ and $AgNO_3$ showed no calcium and chlorine in the decantate. Organic matter was oxidized with 30% H_2O_2, at 60°C. Small portions of H_2O_2 were added from time to time until there was no bubbling reaction; upon further addition. Soil samples were kept at pH 4.0 Some soils, such as the Low Humic Latosols and Hydrol Humic Latosols, were treated with H_2O_2 for over a month. This treatment destroys most of the organic matter, about 85 to 90 per cent. (39).

Slightly modified Puri's ammonium carbonate method (46) was used for dispersing the soils. He showed that this method gave the best dispersion, especially in lateritic soils.

To the above soil samples, from which soluble salts and organic matter have been removed, 250 ml. of N $(NH_4)_2CO_3$ were added, and the mixtures were boiled down to 125 ml.

Then 20 ml. of N NaOH were added, the volume was brought up to 250 ml. with hot water, and the suspensions were boiled down again to 125 ml. After cooling, the pH of the samples was adjusted to 10.5, and they were stirred for five minutes in a Waring Blender. In this work, all changes in pH were brought about with N HNO_3 and N NaOH.

The dispersed soils were separated into various fractions, following the procedure of Jackson (22). Data for centrifuging and sedimentation were obtained from tables by Tanner and Jackson (55).

Separation at 2 microns was done by sedimentation method. The beakers were marked at a height of 8 cm., the dispersed suspensions were brought up to this mark with water, stirred vigorously, and were allowed to stand for eight hours. At the end of this period, the turbid supernatant portion was decanted off and kept for separation at 0.2 micron. When the supernatant portion became less turbid, pH of the samples was adjusted to 10.5, and they were stirred in a Waring Blender for two minutes. This procedure was continued until the supernatant portion became relatively clear.

Separation at 0.2 micron fraction was done by centrifuging the turbid supernatant portion from the above sedimentation procedure. International Centrifuges No.1 and No.2 were used. After centrifuging, the turbid supernatant portion was flocculated with N HNO_3, the solid was air-dried, and then ground in an agate mortar to pass a 100 mesh screen.

This fraction contains particles that are smaller than 0.2 micron in diameter.

The sediment at the bottom of the centrifuge tubes was also air-dried and ground to the pass a 100 mesh screen. The particles in this fraction are between 2.0 and 0.2 micron in diameter.

Sediment from the 2 micron separation was wet-sieved through a 300-mesh screen with a small stream of water and a rubber policeman. The coarse material left on the screen is larger than 50 microns, and it is the sand fraction. The material that passed the 300-mesh screen was separated at 2 microns and 5 microns, by sedimentation method.

Table V shows the percentages of sand, silt and clay fractions of Hawaiian soils studied.

This thermal study is made on the fine particle fractions of the Hawaiian soils, namely, 2.0-0.2 micron and < 0.2 micron fractions because these fine particles are the active portion that largely determines the soil properties. In humid, tropical climates, the mineral constituents in fractions below 2 microns are essentially relatively stable, weathered secondary minerals. Primary minerals, such as feldspars, are rare. Truog et al. (56) showed that the cation exchange capacity increased in the 2 micron fraction, and still more markedly in the $<$ 0.2 micron fraction.

Table V. Percentages of sand, silt, and clay fractions of some Hawaiian soils.

Soil Number	Symbol	Sand > 50u	Silt 50-2u	Clay Fraction 2.0-0.2µ	< 0.2u	Total
48-454	N1-A	0.09	13.26	20.75	58.00	78.75
48-455	N1-B	0.01	13.00	16.04	66.08	82.12
48-456	N3-A	0.05	7.45	21.28	58.16	79.44
48-457	N3-B	0.01	7.67	16.42	67.36	83.78
48-460	N5-A	0.02	8.67	13.57	64.05	77.63
48-461	N5-B	0.01	5.55	20.50	63.05	83.55
48-583	A2-A	0.38	20.03	17.18	50.18	67.36
48-584	A2-B	0.97	6.64	10.69	71.23	81.92
46-519	K3-A	0.47	27.80	10.78	39.84	50.62
46-520	K3-B	0.48	33.84	14.44	37.07	51.50
49-951	K8-A_1	3.98	10.27	10.56	41.17	51.73
49-952	K8 Dark Layer		6.60	24.44	63.77	88.21
49-953	K8-B		2.03	21.47	58.47	79.94
49-954	K6-A		9.27	22.33	43.43	65.76
49-955	K6 Dark Layer		7.16	29.54	57.94	87.48

Table V. Percentages of sand, silt, and clay fractions of some Hawaiian soils.

Soil Number	Symbol	Sand >50u	Silt 50-2u	Clay Fraction 2.0-0.2u	<0.2u	Total
49-956	K6-B		2.68	17.82	61.09	78.91
47-443	T1-A	1.25	28.60	14.55	36.02	50.55
47-445	T1-B	0.81	52.41	16.08	18.02	34.11
47-248	T2-A	2.69	55.16	23.27	9.73	33.00
47-249	T2 Ti Layer	2.85	59.34	27.44	7.90	35.34
47-250	T2-AB	1.59	28.07	34.72	23.20	57.92
47-251	T2-B	1.27	29.35	30.00	23.34	53.34
47-252	T2-C	2.10	49.26	19.12	14.38	33.50
47-256	T3-A	0.84	44.13	21.04	19.42	40.46
47-259	T3-B	0.10	15.65	10.92	63.54	74.46
49-998	RB-A	2.23	31.38	21.58	18.30	39.88
49-999	RB-B	1.02	37.22	18.29	24.16	42.44
49-56	C2-A	2.28	30.87	21.06	16.82	37.87
49-57	C2-B	0.60	16.18	19.81	38.73	58.53

Table V. Percentages of sand, silt, and clay fractions of some Hawaiian soils.

Soil Number	Symbol	Sand > 50u	Silt 50-2u	Clay Fraction 2.0-0.2u	< 0.2u	Total
49-59	F1-A	1.70	21.53	14.26	20.51	34.77
49-61	F1-AB	0.34	23.37	13.84	43.18	57.02
49-62	F1-B	0.14	15.42	17.60	31.76	49.36
49-64	F4-A	0.49	29.27	22.35	32.55	54.90
49-65	F4-B	0.60	22.04	22.67	27.79	50.46
48-575	H1-A	5.91	35.65	26.25	20.93	47.19
48-576	H1-B	3.29	36.53	13.82	32.30	46.12
48-577	H2-A	4.03	49.55	9.87	20.24	30.11
48-578	H2-B	1.89	39.76	8.50	37.32	45.81
48-581	H3-A	1.95	29.64	13.25	37.99	51.24
48-582	H3-B	3.47	34.07	20.90	25.75	46.65
48-571	M-A	3.03	44.66	9.67	32.05	41.73
48-572	M-B	5.41	43.20	12.65	27.93	40.58

STANDARD MINERALS

Dehydration curves and differential thermal curves were ade on several standard minerals to serve as standards for omparison. Minerals that are suspected to be found in Hawaiian oils were selected. The following list gives the source of these tandards.

Kaolin- Mc Namee Mine, South Carolina.

Kaolin- Mc Namee Clay, R.T. Vanderbilt Company.

Halloysite- Bedford, Indiana.

Bentonite- Rock River, Wyoming.

Bentonite- American Colloid Co., Chicago, Illinois.

Illite- Fithian, Illinois.

Hematite- Dr. H.S. Palmer, Geology Department,
University of Hawaii.

Goethite- Ishpeming, Michigan.

Limonite- Tuscaloosa County, Alabama.

Ilmenite- Kragero, Norway.

Bauxite- Little Rock, Arkansas

Bentonite was taken as representative of the montmorillonite roup. It is defined in the "Glossary of clay mineral mames" (31) s a rock composed essentially of a crystalline clay-like mineral, sually the mineral montmorillonite, but less often beidellite.

It was desirable to have samples of beidellite, montronite, d vermiculite, but these were not available.

These minerals were also ground to pass the 100-mesh screen. Particles of this size were fine enough to give good contact with the thermocouples in the specimen holes of the differential thermal apparatus, and yet the crystal structure of the minerals was not affected. Kulp et al. (35) has shown that the differential thermal curves are not affected appreciably until the particles are ground finer than the 200 mesh size. The 100 mesh size was used most often. (53) (23) (25).

RELATIVE HUMIDITY

The standard minerals and the soil clays were brought under a standard moisture condition. The relative humidity of room atmosphere is not constant, so the samples were put in desicators in which a relative humidity of 50 per cent was maintained with 1.329 specific gravity H_2SO_4. (59). An experiment showed that a period of 25 to 30 days is required for the samples to come to equilibrium with this atmosphere. The 50 per cent relative humidity was adopted for this study because it was used by many investigators, thus making the results more comparable. (40) (1). Grim and Rowland (14) used 46 per cent relative humidity. It has been found in this study that the relative humidity greatly affects the thermal curves in the lower temperature zones.

THERMAL METHODS OF STUDYING SOIL CLAYS

Thermal methods of studying soil clays are based on Le Chatelier's findings (36) that each mineral has its characteristic dehydration reactions. Heating may be done statically by bringing the samples to equilibrium at a given temperature before it is raised to a new temperature, or dynamically by raising the temperature at a constant rate.

DEHYDRATION METHOD

The dehydration method used by Nutting of the United States Geological Survey (44) was adopted for this study. Samples, about one gram in weight, were put in platinum or porcelain crucibles, and heated from 50° to 900° C. At each 50° interval, the crucibles were cooled in desicators and weighed, until the weights were constant after heating for six hours. The weight of the samples at 100°C was taken as the basis for calculating the percent loss in weight. The samples were heated at 50° and 100°C in an electric oven, and from then on up to 900°C, in an electric muffle furnace. The temperature was controlled automatically and even at high temperatures, the fluctuation was less than 5°C. The pyrometer of the muffle furnace was calibrated with an accurate Hoskins Pyrometer at all the 50° increments.

It is interesting to note that a much longer period, four or five days, was required for the samples to reach constant weight at the critical temperature zones in which the combined water was driven off. For instance, in the ase of kaolinite, the 400° to 450°C zone required six days, ndicating that this type of water is removed with great ifficulty. Posnjok and Mervin (45) reported that the etermination of dehydration curves of hydrated ferric oxides equired over four months.

Since the dehydration method is slow and is therefore sed rarely, its accuracy and reproducibility are not known. o determine the reliability of this method, several soil amples and a standard kaolinite were heated again some ight months after the first run. The two sets of curves ere practically identical, and the kaolinite percentages erived from the curves of the two runs differed only by one r two per cent. Table VI shows the comparison of the two runs.

In the dehydration curve graphs, temperature is on the bscissa, and the per cent loss in weight is on the ordinate. ince the weight at 100°C was taken as the basis, loss at 00°C is zero.

DIFFERENTIAL THERMAL ANALYSIS

In the differential thermal analyses, the soil samples nd an inert calcined Al_2O_3 powder are heated at a constant ate to about 900°C. The thermocouples, with one end in the ample and the other end in the inert Al_2O_3, show the ifference in temperatures between the two materials. The hermocouples are connected to a sensitive galvanometer that eflects a beam of light to a numbered scale, and the readings

Table VI Comparison of per cent weight losses between two runs of dehydration curves, on 48-454, 2.0- 0.2u fraction.

Temperature	Per cent weight losses First run	Second run	Difference
25°C	3.55%	3.45%	0.10%
50	1.07	1.17	0.10
150	0.28	0.14	0.14
200	1.02	1.05	0.03
250	2.42	2.47	0.05
300	3.07	2.99	0.08
350	3.51	3.32	0.19
400	3.84	3.99	0.15
450	9.12	9.19	0.07
500	9.74	9.74	0
550	10.02	10.19	0.17
600	10.38	10.36	0.02
650	10.66	10.63	0.03
700	10.75	10.66	0.09
750	10.75	10.75	0
800	10.95	10.79	0.16
850	10.95	10.85	0.10
900	11.09	10.89	0.20

on this scale indicate directly the amount of difference in temperature. If water is liberated in a sample during the heating, the rate of rise in temperature is decreased, while the temperature of the inert Al_2O_3 rises at a constant rate. The apparatus is so constructed that this difference in temperatures is registered on the scale as minus (-) values. On the other hand, if heat is liberated in the sample, as due to a crystallization or oxidation of organic matter, the scale readings register plus (+) values. These values were plotted graphically, with temperature on the abscissa, and the scale readings on the ordinate. Thus, when water is liberated, the peak is downward from the base line, forming an endothermic peak. On the contrary, when the scale readings are plus, the peak is upward, forming an exothermic peak.

Through the kind cooperation of the Pineapple Research Institute, their differential thermal apparatus was used in this study.

Several investigators (14) (53) (43) (34) have pointed out that many factors affect the differential thermal curves. Some of these factors are:

1. Relative humidity in which the samples are kept.
2. Particle size of samples.
3. Amount of sample for each determination
4. Packing of sample in the furnace hole.

5. Position of thermocouples.
6. Size of furnace holes.
7. Rate of temperature rise.

In this study, all the factors were standardized and made as nearly the same as possible for all the samples. The relative humidity was maintained at 50 per cent, samples were screened through 100 mesh screen, 0.400 gram samples were taken, samples were packed lightly into the furnace holes with a glass rod, the thermocouples were kept at a same height and in the middle of the holes, the size of the holes were the same, and the temperature was raised to about 900°C at a constant rate of 15°C, ± 1°C, per minute. After a little practice, this temperature rate was controlled very accurately with a powerstat. It was desirable to investigate the thermal reactions between 900° and 1000°C, but unfortunately the thermocouple wires and heating wires of the furnace usually burned out above 900°C.

The accuracy of the differential thermal apparatus was tested in several ways, and the results were very good. The pyrometer of the apparatus agreed closely with the accurate Hoskins Pyrometer. A sharp endothermic peak of quartz at 573° to 575°C is a delicate test of the apparatus. (4) (52) (7). When the apparatus was tested with quartz, there was a sharp peak at 574°C, indicating that the apparatus is very accurate. Standard kaolin was run from time to time test the magnitude of the endothermic peak, and the temperature at which it occurred. Differential thermal curves were also made on several clay fractions to test the reproducibility. The two runs on the fine fraction, <0.2 micron, of soil sample 48-583, were made a few days apart. The endothermic peaks occurred at 580°C on the first run, and 585°C on the second run. The areas of the peaks were 0.55 and 0.62 square inch, which were equivalent to 32 per cent and 34 per cent kaolinite, respectively.

Fig. 1 to 11 show the dehydration curves and differential thermal curves of the standard minerals and of the clay fractions from the Hawaiian soils.

The results of the dehydration curves and the differential thermal curves of standard minerals are summarized in Tables VII and VIII, respectively.

Vermiculite may be present in Hawaiian soils, but unfortunately, standard samples were not available. Nutting (44) showed a dehydration curve of vermiculite, but the loss in weight is gradual, and there are no definite, critical losses. Another curve, presented by Walker (58), showed a smooth curve to 600°C, then a 5 per cent loss between 600° and 900°C. This loss at high temperatures may be significant.

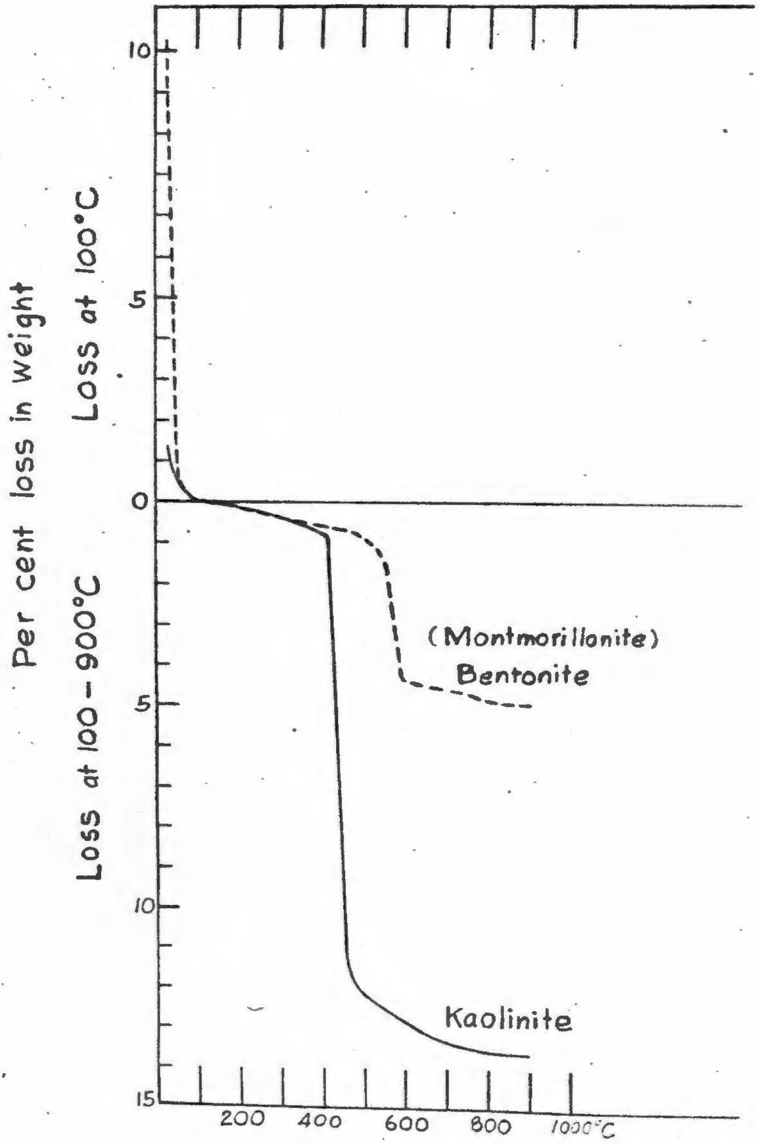

Fig. 1. Dehydration curves of standard minerals, bentonite and kaolinite.

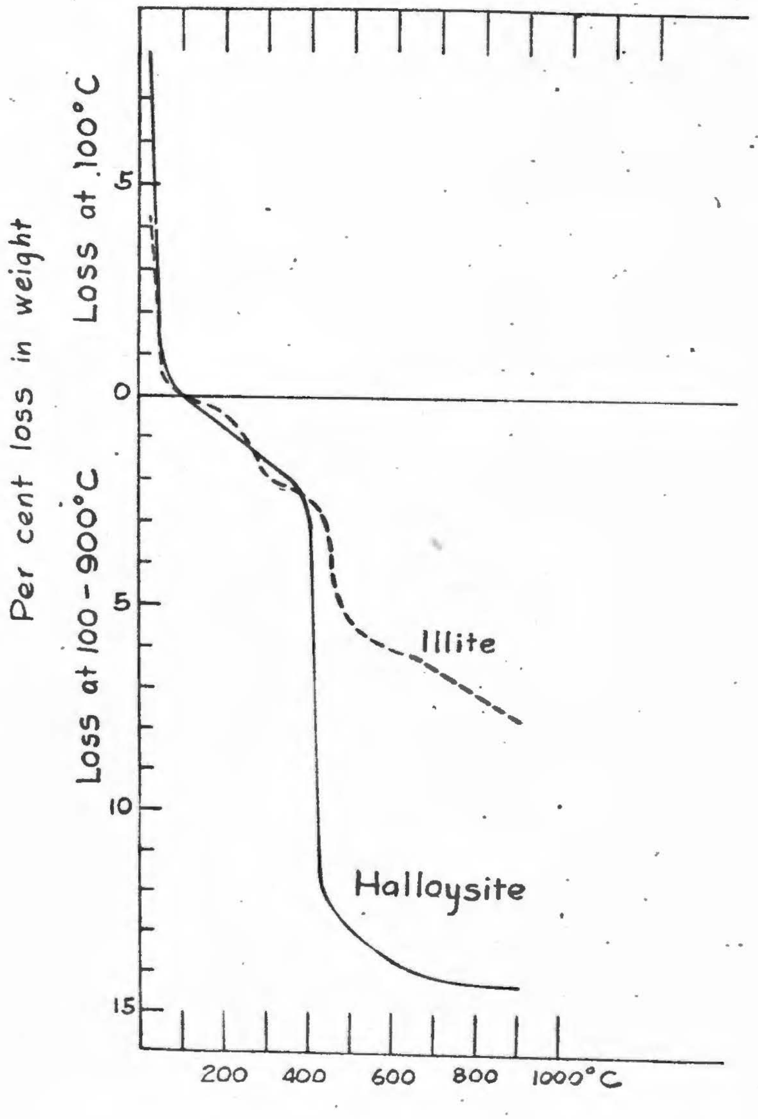

Fig. 2. Dehydration curves of standard minerals, illite and halloysite.

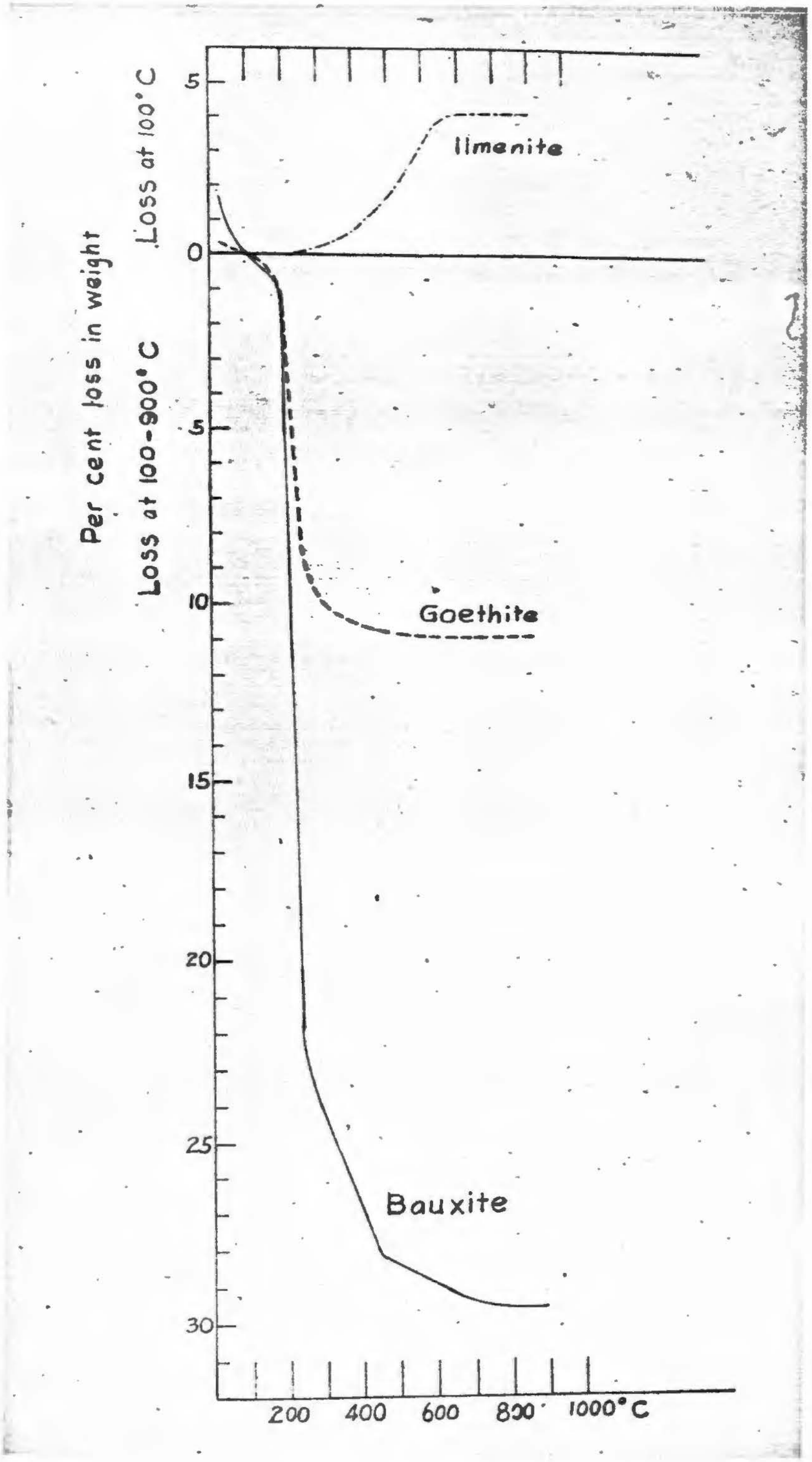

Fig. 3. Dehydration curves of standard minerals, ilmenite, goethite and bauxite.

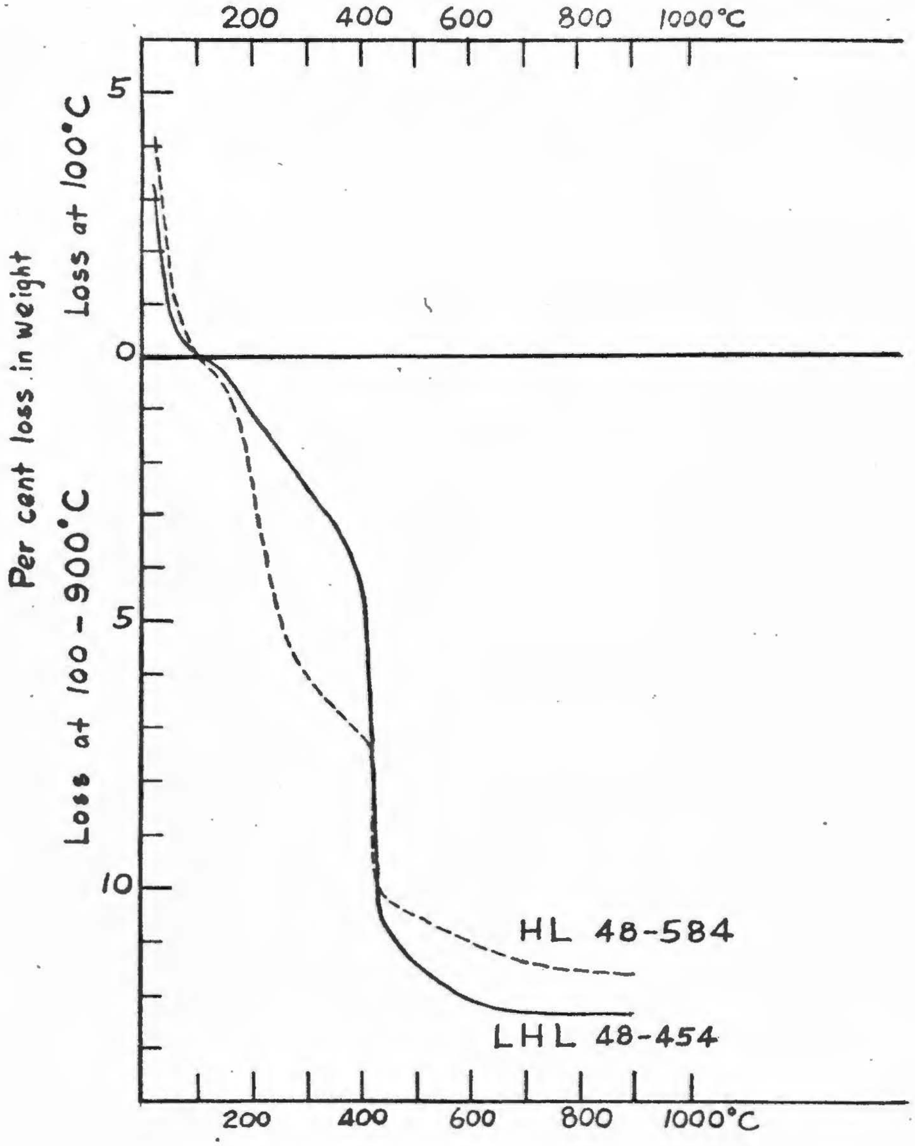

Fig. 4. Typical dehydration curves of clay fractions from Hawaiian soils. HL= Humic Latosol; LHL= Low Humic Latosol.

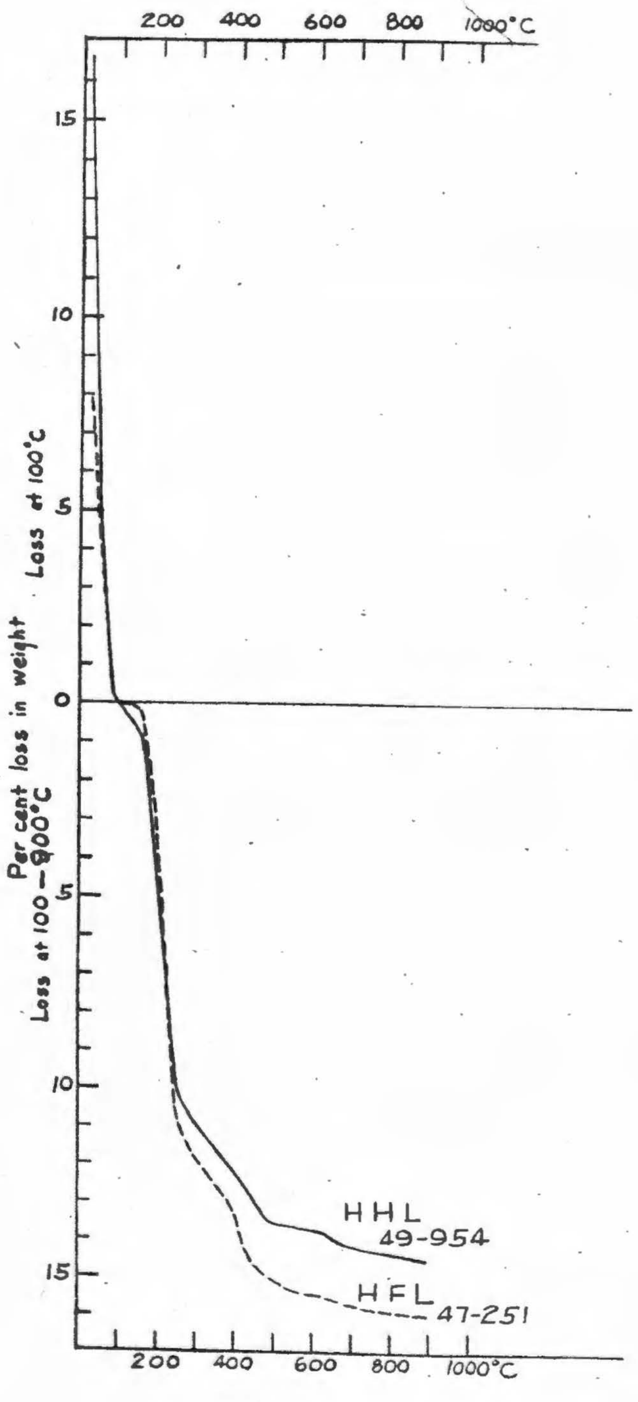

Fig. 5. Typical dehydration curves of clay fractions from Hawaiian soils. HHL= Hydrol Humic Latosol; HFL= Humic Ferruginous Latosol.

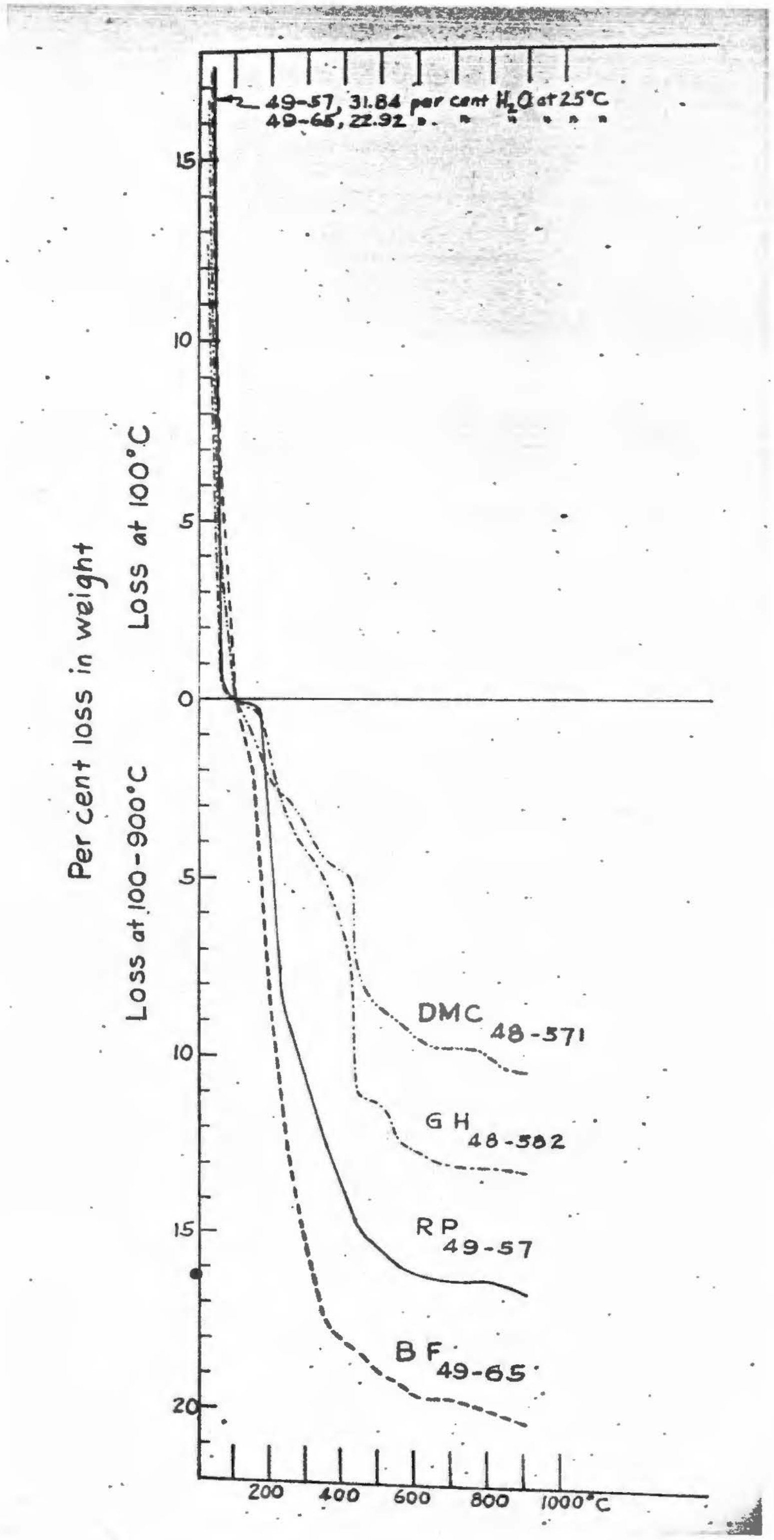

Fig. 6. Typical dehydration curves of clay fractions from Hawaiian soils. DMC= Dark Magnesium Clay; GH= Gray Hydromorphic; RP= Reddish Prairie; BF= Brown Forest.

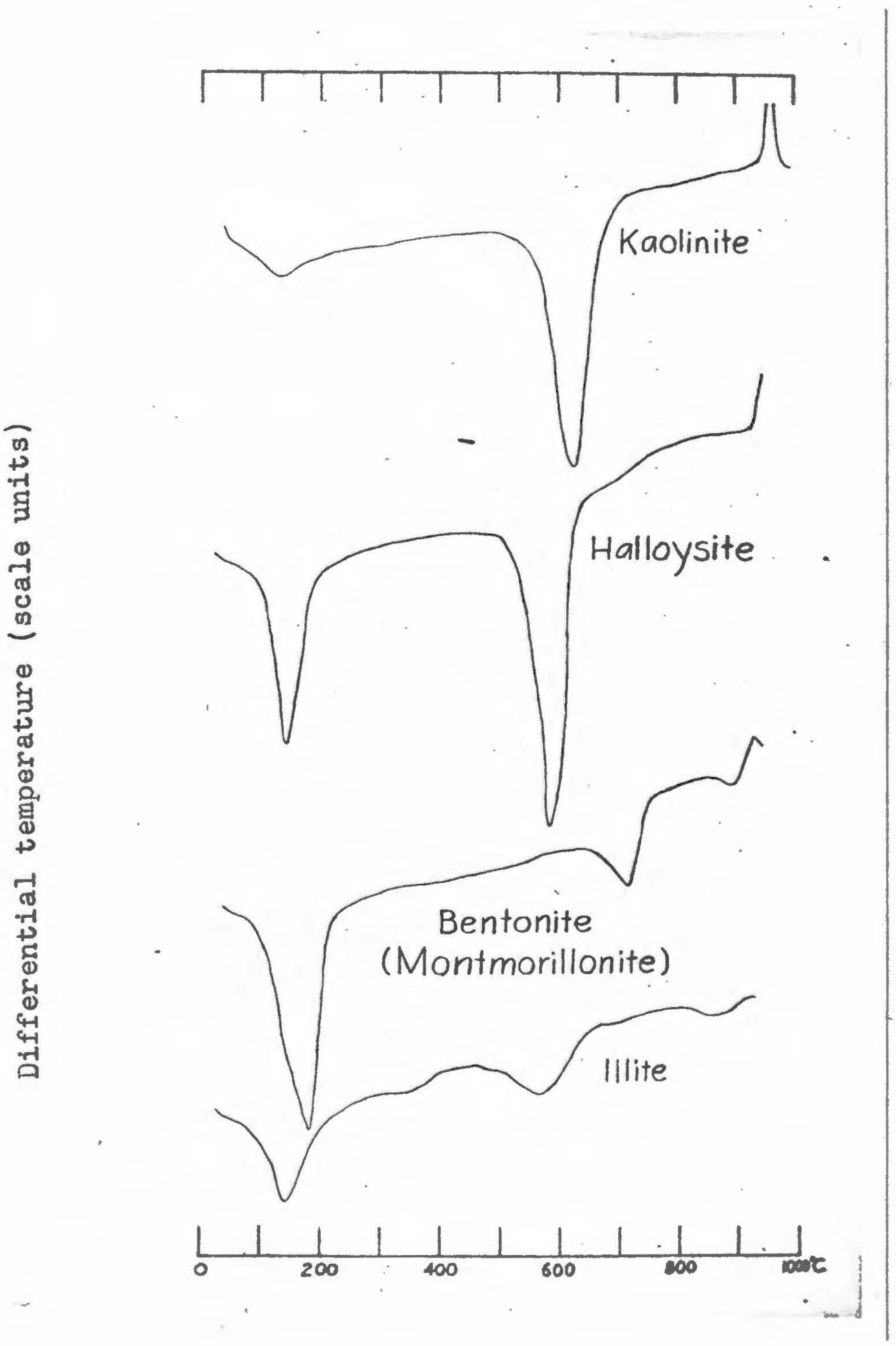

Fig. 7. Differential thermal curves of standard minerals, kaolinite, halloysite, bentonite and illite.

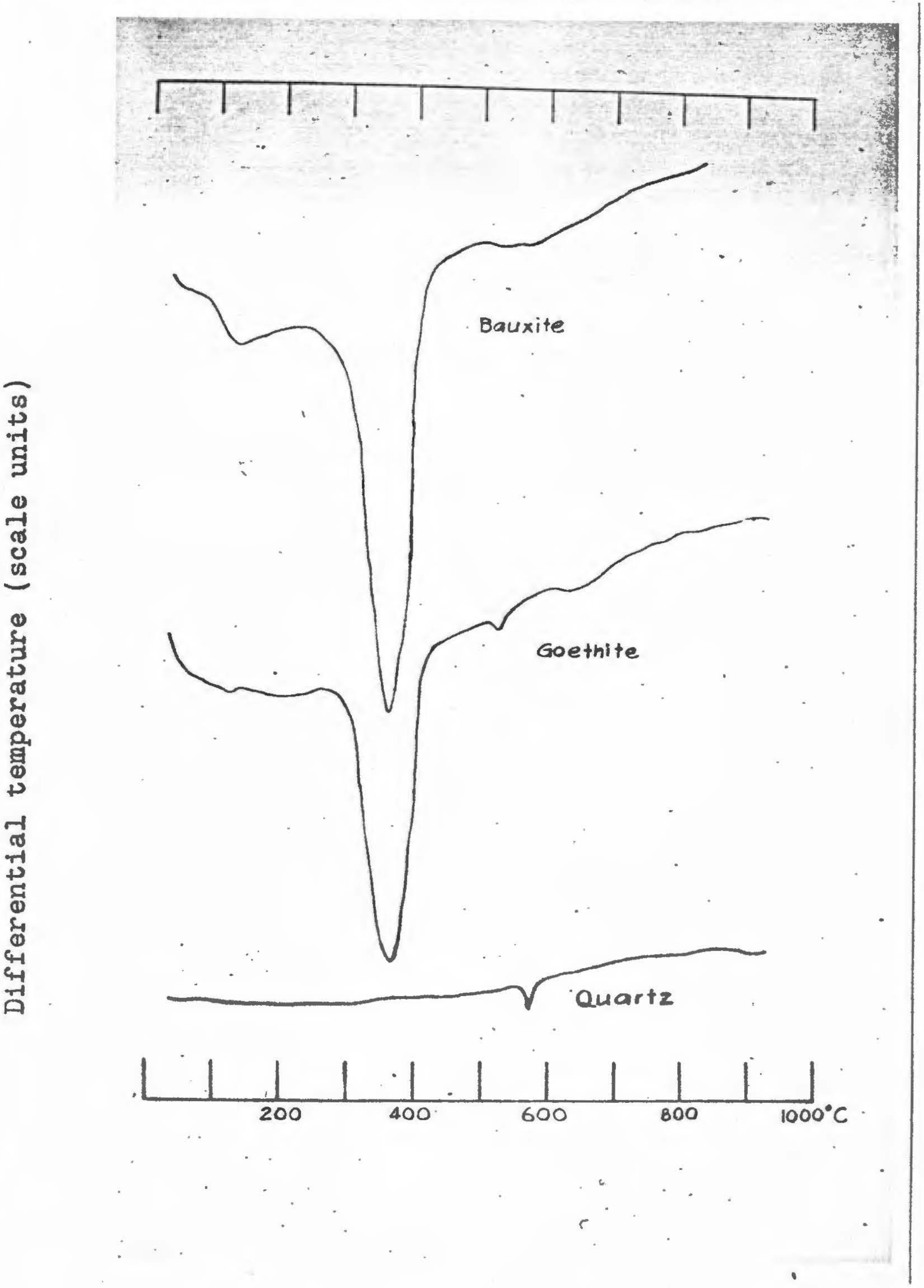

Fig. 8. Differential thermal curves of standard minerals, bauxite, goethite and quartz.

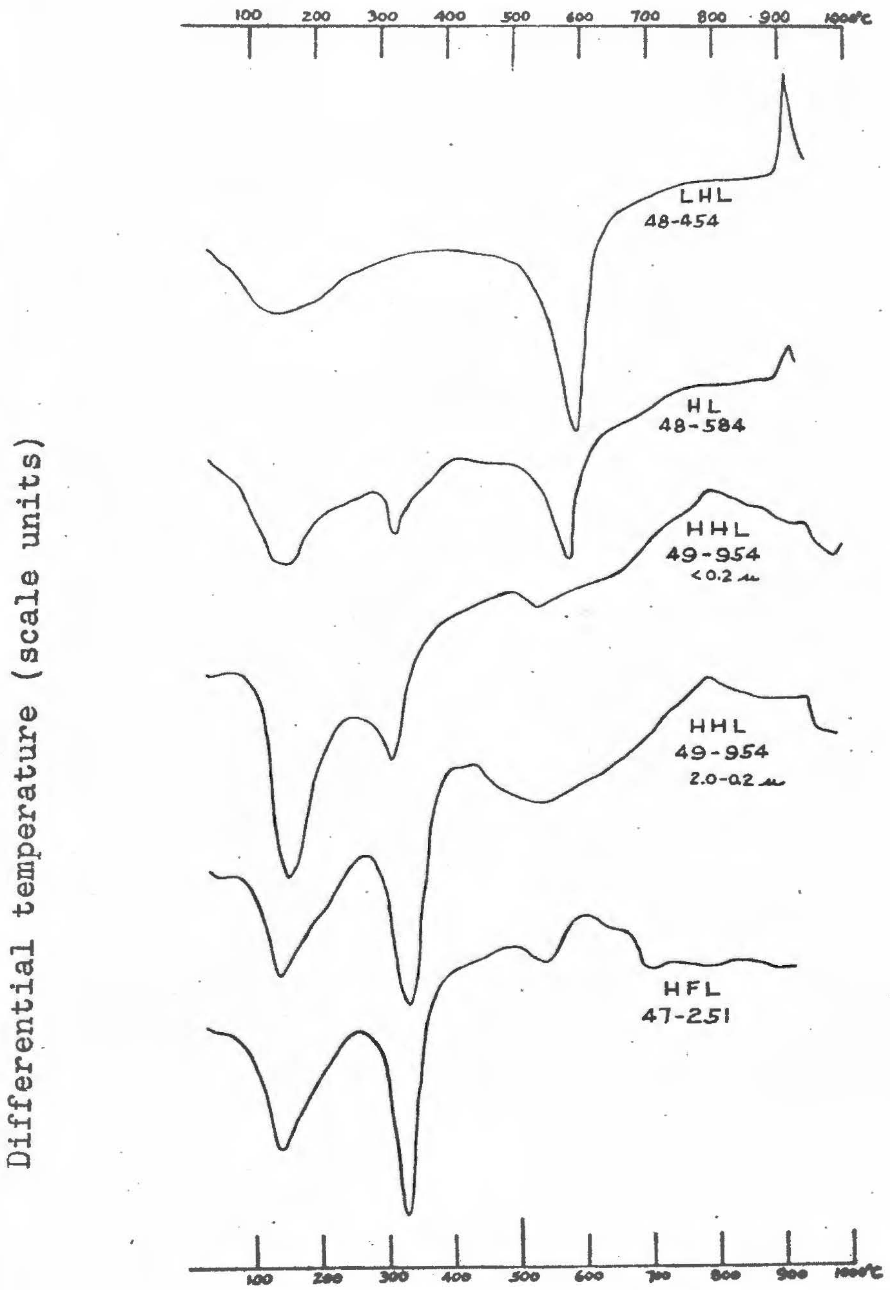

Fig. 9. Typical differential thermal curves of clay fractions from Hawaiian soils. LHL= Low Humic Latosol; HL= Humic Latosol; HHL= Hydrol Humic Latosol; HFL= Humic Ferruginous Latosol.

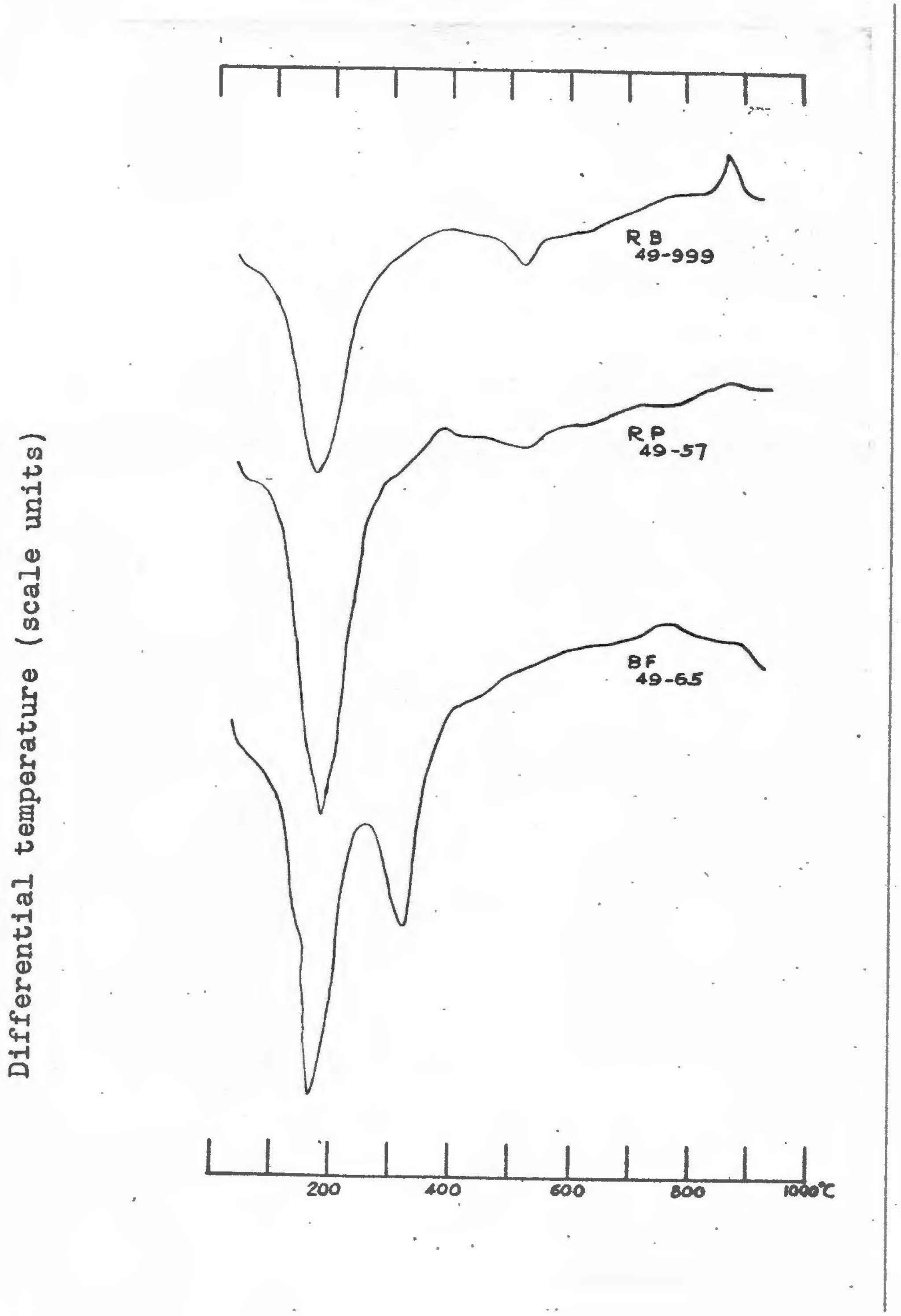

Fig. 10. Typical differential thermal curves of clay fractions from Hawaiian soils. RB= Reddish Brown; RP= Reddish Prairie; BF= Brown Forest.

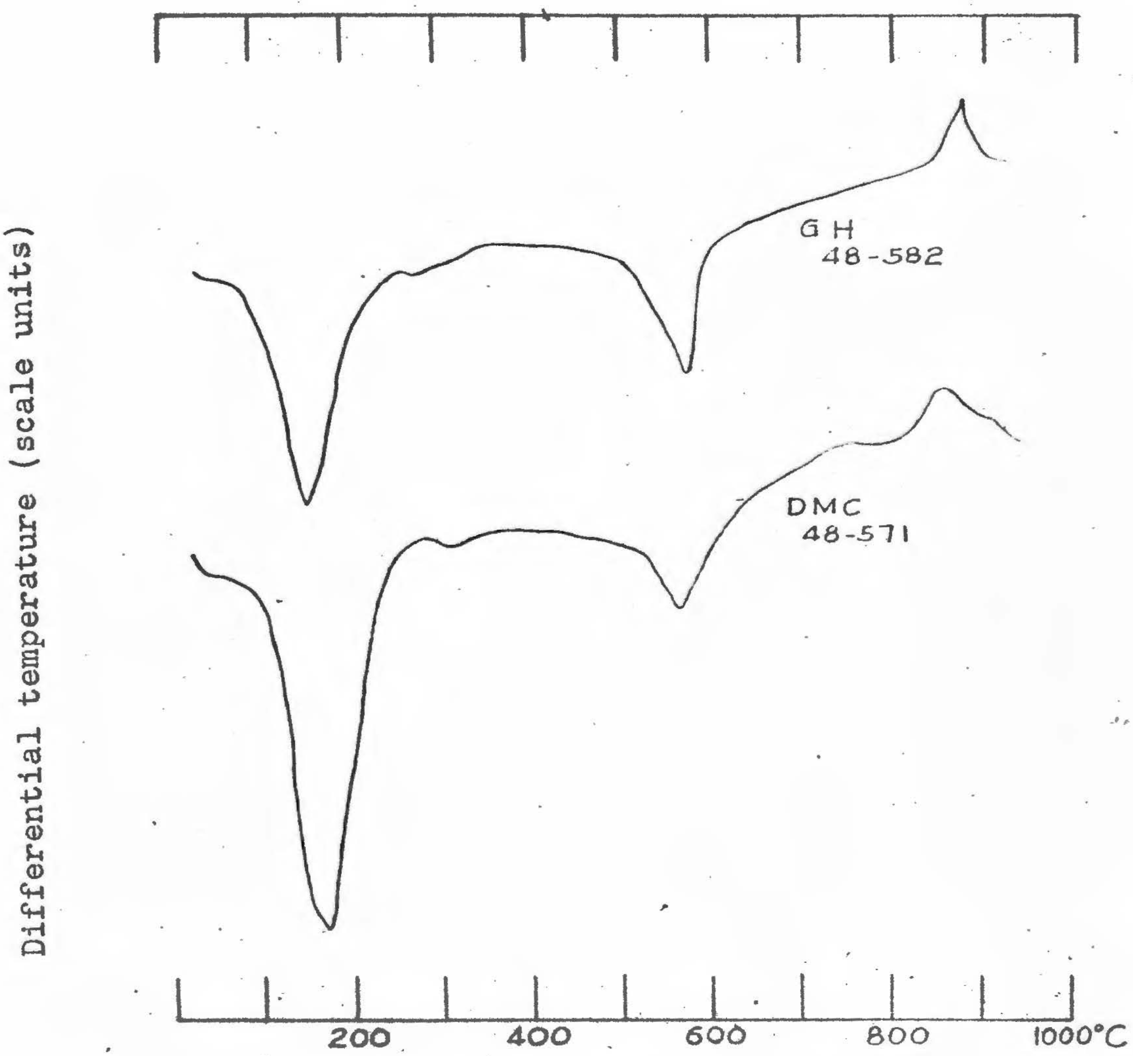

Fig. 11. Typical differential thermal curves of clay fractions from Hawaiian soils. GH= Gray Hydromorphic; DMC= Dark Magnesium Clay.

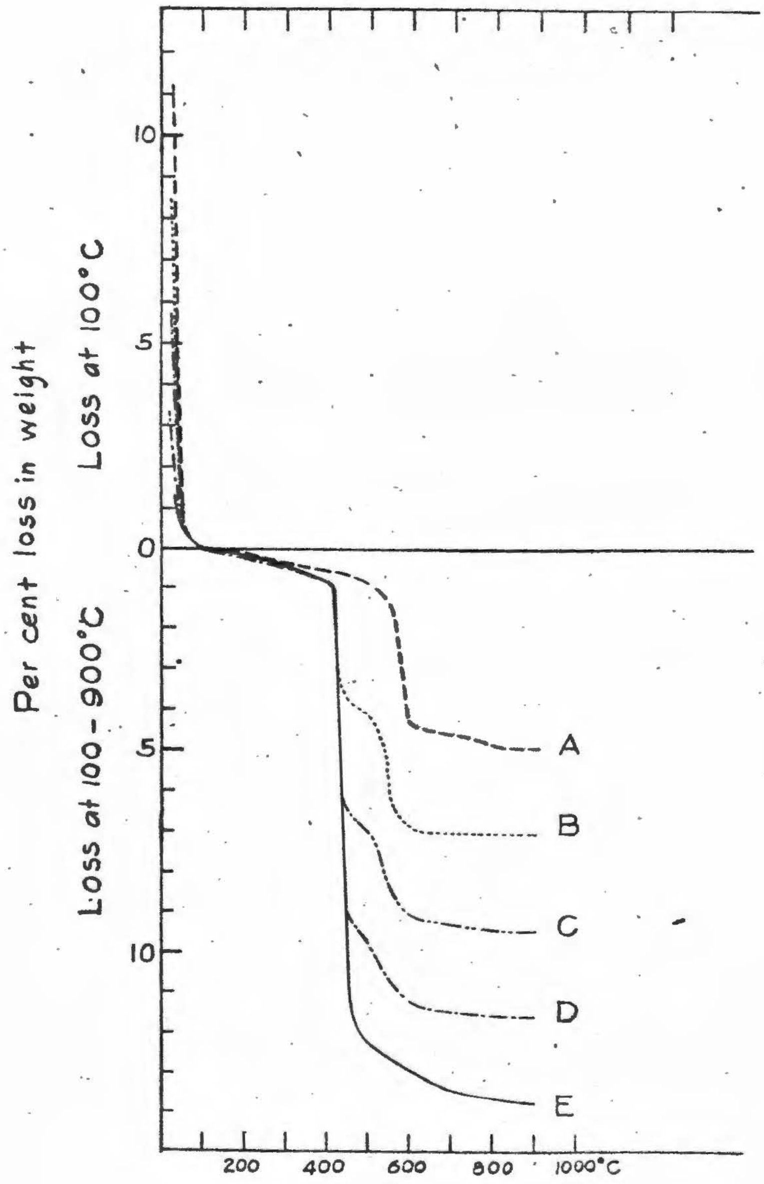

Fig. 12. Dehydration curves of kaolinite-bentonite mixtures: A= 100 per cent bentonite; B= 25 per cent kaolinite, 75 per cent bentonite; C= 50 per cent kaolinite, 50 per cent bentonite; D= 75 per cent kaolinite, 25 per cent bentonite; E= 100 per cent kaolinite.

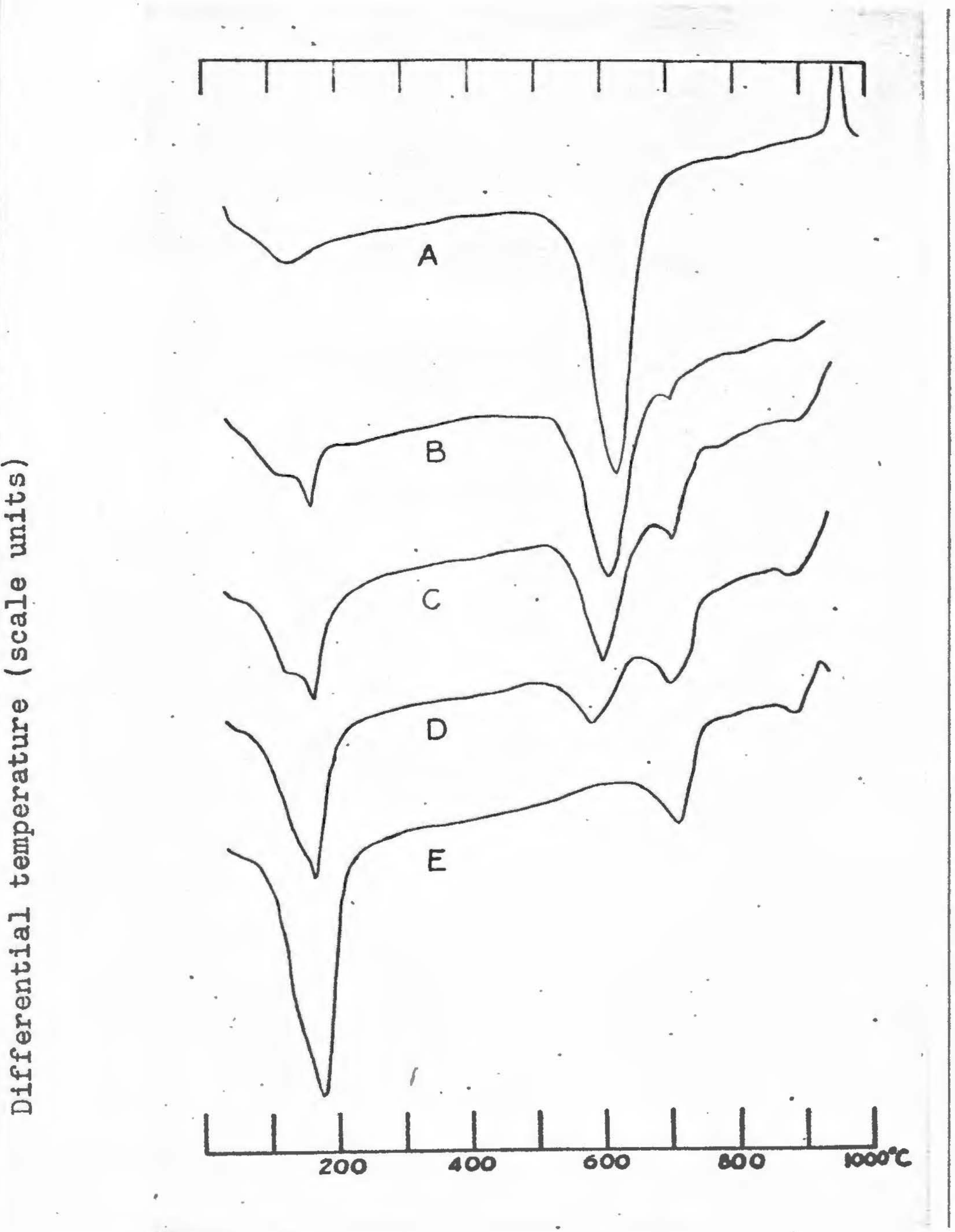

Fig. 13. Differential thermal curves of kaolinite-bentonite mixtures: A= 100 per cent kaolinite; B= 75 per cent kaolinite, 25 per cent bentonite; C= 50 per cent kaolinite, 50 per cent bentonite; D= 25 per cent kaolinite, 75 per cent bentonite; E= 100 per cent bentonite.

Table VII. Dehydration losses of standard minerals at critical temperatures.

Standard minerals	Per cent loss at 100°C	Per cent loss at critical dehydration temperatures
Kaolinite	1.31	10.64, at 400°-500°C
Halloysite	8.03	10.89, at 350°-500°C
Montmorillonite	11.16	3.47, at 500°-600°C
Illite	4.24	1.53, at 200°-300°C
		2.99, at 400°-500°C
Bauxite	1.67	23.85, at 150°-300°C
Goethite	0.32	9.67, at 150°-300°C
Limonite	1.62	9.09, at 150°-300°C
Hematite	0.21	None
Ilmenite	0.03	+3.87, at 250°-650°C
Quartz	0.01	None

Table VIII. Critical peaks and their temperatures on differential thermal curves of standard minerals.

Standard	Critical peaks and their temperatures
Kaolinite	Big endothermic at 620°C
	Sharp exothermic at 950°C
Halloysite	Medium endothermic at 150°C
	Big endothermic at 580°C
	Sharp exothermic at 940°C
Montmerillonite	Big endothermic at 170°C
	Small endothermic at 710°C
	Small endothermic at 880°C
	Weak exothermic at 940°C
Illite	Medium endothermic at 150°C
	Small endothermic at 350°C
	Medium endothermic at 570°C
	Small endothermic at 870°C
	Weak exothermic at 925°C
Bauxite	Very Big endothermic at 360°C
Goethite	Very Big endothermic at 360°C
Limonite	Very Big endothermic at 340°C
Hematite	None
Ilmenite	None
Quartz	Sharp endothermic at 574°C

DISCUSSION OF RESULTS

PARTICLE-SIZE DISTRIBUTION OF HAWAIIAN SOILS

As shown in Table V, the Low Humic Latosols have the highest clay content, averaging about 80 per cent, and the younger soils, such as the Reddish Brown Soil, have a rather low content, 40 per cent. The clay percentages of other soils fall between these values, being higher in more weathered soils. However, the Humic Ferruginous Latosols are rather low in clay, about 50 per cent. This may be due to crystal growth of mineral oxides or to the high specific gravity of these oxides. The silt content is high, about 40 per cent, while the sand fraction is very low, 2 per cent. The highest sand content is found in the Gray Hydromorphic and Dark Magnesium soils, and the lowest in Low Humic Latosols.

A comparison of Table I and Table V shows that the clay content of Hawaiian soils is much higher than that of the mainland United States soils. According to the textural class diagram of the Bureau of Plant Industry, Soils and Agricultural Engineering, United States Department of Agriculture (57), the Low Humic Latosols with 80 per cent clay are definitely "clays", but these soils feel and have the physical characteristics of a light silty clay loam. On the other hand, the Dark Magnesium Clay and the Gray Hydromorphic soils, with only 40 per cent clay, have all the physical properties of "clays". Thus it seems that the mineral constituents, whether they be predominantly kaolinite, montmorillonite, or oxides, are just as much, or more important, than the percentages of clay fraction.

DEHYDRATION of MINERALS by THERMAL METHODS

In this report, the term kaolinite is used to mean the mineral group which includes nacrite, dickite, kaolinite, and halloysite (48) (49) (8). Kaolinite is a hydrous aluminosilicate, with an approximate chemical formula of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The crystal structure is composed of one silica tetrahedral sheet and one alumina octahedral or gibbsite sheet, so kaolinite is said to be of the 1:1 type. Kaolinite is believed to have a fixed lattice and thus it does not shrink or swell with moisture changes (37). Richardson (8) reported that X-ray data showed no evidence of water molecules penetrating into the crystal layers. The dehydration curves and differential thermal curves seem to substantiate Richardson's finding. The small initial dehydration at the low temperatures is therefore believed to be due to adsorbed water. The great initial loss in halloysite may be due to adsorbed water on the very fine crystals which are hollow tubes (5). Until recently, halloysite was believed to be amorphous (49).

Insley and Ewell (20) made a thorough study of the decomposition of kaolinite at high temperatures. The great loss of weight between 400° and 500°C on the dehydration curves, and the big endothermic peak at 610°C on the differential thermal curves, were due to the destruction of kaolinite crystal structure with the formation of water vapor and amorphous alumina and amorphous silica. The X-ray patterns of the decomposition product consist of a broad, diffuse band, characteristic of amorphous materials. The exothermic peak at 950°C was found to be due to a rapid evolution of heat when amorphous alumina was recrystallized. The X-ray showed definite crystalline alumina. The network of the amorphous silica, in intimate mixture with amorphous alumina, is believed to hold back the recrystallization of alumina, and as the result of this delay, the exothermic effect is sudden and sharp. In other words, amorphous silica acts as a "trigger." The intensity of the exothermic effect depended upon the intimacy of contact and the ratio between alumina and silica. In the $Al_2O_3 \cdot 2SiO_2$, $Al_2O_3 \cdot SiO_2$, and $2Al_2O_3 \cdot SiO_2$ coprecipitated gels, the exothermic effect was of about the same magnitude as in kaolinite. The $4Al_2O_3 \cdot SiO_2$ and $Al_2O_3 \cdot 4SiO_2$ gels showed small heat effects. In the $4Al_2O_3 \cdot SiO_2$ gel, the small amount of silica present was sufficient to keep only a part of the Al_2O_3 from crystallizing until 925°C, most of the Al_2O_3 crystallizing over a broad temperature range below 925°C without observable heat effect. In the $Al_2O_3 \cdot 4SiO_2$ gel, there was sufficient silica present, but the amount of Al_2O_3 was small, and therefore the heat effect was small. The optimum ratio of the $Al_2O_3 \cdot SiO_2$ for a large heat effect appears to lie between 1:1 and 1:2, which is about the ratio in kaolinite.

The term montmorillonite is given to the group of minerals which includes the mineral members montmorillonite, beidellite, nontronite, hectorite and saponite (51).

The molecules of montmorillonite have two silica tetrahedral sheets and one alumina octahedral or gibbsite sheet, with the gibbsite sheet lying between the two silica sheets. This type of structure is called the 2:1 crystal lattice. The characteristic of this type is the loosely-held sheets between which a large amount of water can be held. The exchange of cations in crystal lattice is also possible, giving rise to several similar minerals.

The evaporation of adsorbed water and the interlamellar water is shown by the great loss of weight at 100°C. on the dehydration curves, and the large endothermic peak at 170°C on the differential thermal curves. This low- temperature water is usually reversible upon re-wetting. The loss in weight between 500° to 600°C. on the dehydration curves and the corresponding endothermic peak at 710°C on the differential thermal curves are due to the loss of combined water which is an essential part of the crystal lattice (51). Mac Ewan (8) found that when montmorillonite was heated above 600°C, the X-ray patterns were destroyed, but at 500°C, the patterns were clear and sharp. The small endothermic peak at 880°C is believed to be due to the final destruction of the crystal structure, but this is not shown in dehydration curves.

Probably dehydration was brought to completion by the static heating at 600°C. The weak exothermic peak at 940°C is due to recrystallization of both alumina and silica (8).

Grim and Bradley (13) also investigated the effect of heat on montmorillonite, using the X-ray and optical methods. Their findings agree with Mac Ewan's (8).

Illite represents a group of minerals that are not well characterized (12). The crystal structure is similar to that of montmorillonite, but the sheets are so tightly held by the potassium ions that there is little shrinkage or expansion (37).

Grim and Bradley (13) studied the effect of heat on illite by X-ray and optical methods. They found that combined water of the crystal lattice was lost between 350° and 600°C. This corresponds to the losses in weight at 300°C, and between 400° and 500°C on the dehydration curves, and the two endothermic peaks at 350° and 570°C on the differential thermal curves. The final destruction of the illite lattice at 850°C corresponds to the small endothermic peak at 870°C. This is followed by a slight exothermic peak at 925°C, which is due to the formation of a spinel.

IDENTIFICATION OF MINERALS IN SOILS

The thermal properties of kaolinite have been studied extensively because of its importance in the ceramic industry. The large loss of weight in the narrow temperature zone between 400° and 500°C seems to be the criterion by which kaolinite may be identified. Ross and Kerr (48) (49) working with standard minerals, Aleixandre (1) with Spanish clays, Nagelschmidt et al. (41) with Indian soil colloids, and Tanada (54) with Hawaiian soil colloids, all found the critical loss of water in kaolinite to be between 400° and 500°C. Some investigators found that the loss occured between 500° and 550°C (44). The discrepancies may be due to several factors:

(1) Investigators may study different minerals of the kaolinite group.

Ross and Kerr (48) (49) have shown that the kaolinite group is composed of kaolinite, dickite, nacrite and halloysite. These minerals have similar dehydration curves, but each mineral loses its water at sightly different temperatures: kaolinite, between 400° and 500°C; dickite, between 500° and 600°C; nacrite, between 500° and 700°C; and halloysite, between 350° and 500°C. However, Ross and Kerr also reported that dickite and nacrite are formed by hydrothermal processes, so therefore, would not be usually found in surface soils, whereas halloysite and kaolinite are produced by surface weathering, so therefore would be found in surface soils. In this dehydration curve study of Hawaiian soils, it was found that most of the water is lost between 400° and 450°C, and in some cases the loss begins from 350°C, indicating that halloysite and kaolinite are the minerals present in Hawaiian soils, and not dickite or nacrite. Also, the great loss of water at 100°C may be due to halloysite.

(2) Degree of crystallization.

The better crystallized samples have a slightly higher temperature of dehydration (48) (45).

(3) Constant weight of samples at critical temperature.

Many investigators heat the samples for only four or five hours. In this experiment, it was sometimes necessary to keep the samples at 450°C for six or seven days to attain constant weight. Brown and Montgomery (9) found that most of the water was lost at 450°C if the samples were heated long enough. They reported that when the run at 450°C was carried out for 57½ hours, almost all of the combined water was lost. Posnjak and Merwin (45) reported that their dehydration curve study of hydrated iron oxides required over four months. Their curves were very sharp, the samples losing almost all their water between 150° and 250°C.

On the differential thermal curves, the mineral kaolinite has two critical peaks that distinguish it from other minerals: the sharp endothermic peak at about 600°C, and a sharp exothermic peak at 950°C. Halloysite has a sharp endothermic peak at 150°C, and the main peak at 580°C, slightly below that of kaolinite. There may be other minerals, such as diaspore and carbonate minerals that have endothermic peaks at about 500° or 600°C, but only the minerals of the kaolinite group have the sharp exothermic peak at around 950°C (16) (6) (23).

An examination of the dehydration curves and differential thermal curves of Hawaiian soils show that kaolinite may be identified. The Low Humic Latosols clearly show the characteristic thermal reactions of kaolinite.

It is difficult to identify montmorillonite in Hawaiian soils. The initial large endothermic peak at 170°C and the loss of water at 100°C are characteristic of montmorillonite, and these symptoms are shown by many Hawaiian soils, but the other characteristic thermal reactions at higher temperatures, such as the critical endothermic peaks at 700° and 880°C, and the loss of water between 500° and 600°C, are not clearly shown. The thermal reactions at the lower temperatures may not be definite symptoms as they may be due to adsorbed moisture of the amorphous materials or to organic matter that was not destroyed with hydrogen peroxide. Kelley and Page (27) used differential thermal analysis and X-ray method to study the colloids of several Hawaiian soils. They found amorphous material in all of these soils, but it was particularly abundant in the two samples from Naalehu and South Point, Hawaii, their respective cation exchange capacities being 120 and 88 m.e./100 gm. Kelley and Page reported that these two colloids gave no definite evidence of montmorillonite. Kaolinite was definitely identified in a soil from Aiea, Oahu. The differential thermal curves of these two colloids from Naalehu and South Point, as shown by Kelly and Page, are very similar to those of Dark Magnesium Clay, Reddish Prairie, and Reddish Brown soil clay fractions of this experiment.

Dean, in "Differential thermal analysis of Hawaiian soils"(11), reported that only kaolinite could be identified. Tanada, (54) also working with Hawaiian soils, reported that montmorillinite could not be identified by dehydration curves. Even the young soils with high cation exchange capacity, such as those from Naalehu, did not show appreciable loss of water between 500°and 600°C.

Nagelschmidt's dehydration curves of the black cotton soil of India (41), which was shown to contain a large amount of montmorillonite by the X-ray method, also did not show appreciable loss of water between 500°C and 600°C.

Illite is also difficult to identify. Its thermal characteristics are all weak, and they all occur at the temperatures where they may be masked by the stronger reactions of other minerals, particularly the kaolinite.

Since bauxite, goethite and limonite all show large endothermic peaks at about 350°C on the differential thermal curves and a great loss of weight between 150° and 300°C on the dehydration curves, it is difficult to identify each mineral. In this study, it is only possible to identify the substance as hydrated oxides of either iron or aluminum, or both.

Hematite in soils could not be identified by the thermal methods since it does not show any peak or loss of weight.

It is difficult to identify ilmenite on the differential thermal curve as the rise is gradual, and there are no characteristic peaks. On the dehydration curve, ilmenite gains weight. This gain in weight probably is due to oxidation of $FeO \cdot TiO_2$ to $Fe_2O_3 \cdot TiO_2$, but it may be masked by the loss in weight of other minerals. However, in this experiment, there was no case of any gain in weight.

Quartz could not be identified on the dehydration curves because it does not lose or gain weight. On the differential thermal curve it has a small, sharp endothermic peak at 574°C, but it may be masked by kaolinite.

ESTIMATION OF KAOLINITE

In the dehydration method, it seems there is essentially only one criterion for estimating the kaolinite content of soils. The ratio of the loss of weight between 400° and 500°C by soil amples to a similar loss of weight by a standard kaolinite gives the kaolinite content of soils.

In this study, this method was used. The following mixtures were made:

0 per cent kaolinite, 100 per cent Al_2O_3
25 per cent kaolinite, 75 per cent Al_2O_3
50 per cent kaolinite, 50 per cent Al_2O_3
75 per cent kaolinite, 25 per cent Al_2O_3
100 per cent kaolinite, 0 per cent Al_2O_3
0 per cent kaolinite, 100 per cent montmorillonite
25 per cent kaolinite, 75 per cent montmorillonite
50 per cent kaolinite, 50 per cent montmorillonite
75 per cent kaolinite, 25 per cent montmorillonite

These mixtures were heated and treated the same as the soil samples. The dehydration losses of kaolinite were practically the same in the kaolinite- Al_2O_3 and kaolinite-montmorillonite mixtures, indicating that there is little interfering action between kaolinite and montmorillonite. The dehydration curves of the kaolinite-montmorillonite mixtures are shown in Fig. 12.

When the kaolinite percentage and the per cent loss in weight were plotted on a graph, the points formed a straight line. Kaolinite content of soils was obtained by referring to this graph the per cent loss in weight between 400° and 500°C. Per cent kaolinite was estimated to the nearest five per cent.

In the differential thermal analysis, three methods are used for estimating the kaolinite content. Norton (43) was probably the first to develop a method for estimating the percentage of individual minerals in a mixture. He measured the characteristic peak areas of the various standard minerals, and by comparing these with the corresponding peak areas of the mixtures, he was able to estimate the percentages of the constituent minerals. Dean (11) and Mackenzie (38) used the cosecant method to estimate the kaolinite content. In this method, the cosecant values of the kaolinite peaks in soil samples are compared to those of a standard kaolinite. But the back slope of the peak becomes considerably steeper with finer particles (32). In this study, the clays were separated into coarse and fine clay fractions, and when this cosecant method was applied, the kaolinite content was much higher than that estimated from the dehydration curves, particularly in the fine fraction.

Kerr et al. (32) suggested that the amplitude of the endothermic peak be used to estimate kaolinite content. However, Kulp et al. (35) found that the amplitude was also appreciably affected by particle size, but that the peak area remained relatively constant.

The area method was therefore used in this study. Differential thermal curves were made on the kaolinite- Al_2O_3, and kaolinite-montmorillonite mixtures, the same mixtures that were used previously for calibrating the dehydration curves. The areas of the kaolinite endothermic peaks were measured with a planimeter, and these values and their corresponding kaolinite percentages were plotted on a graph. The points formed a practically straight line. Thus, by referring to this graph the areas of the kaolinite endothermic peaks of soils, the kaolinite content was readily estimated. The estimation was done to the nearest five per cent.

The differential thermal curves of the kaolinite-montmorillinite mixtures are shown in Fig. 13. The peak temperature of kaolinite occurs at lower temperature as the kaolinite percentage decreases: peak temperature of standard kaolinite is 620°, while that of 25 per cent kaolinite is 580°C. The kaolinite-Al_2O_3 mixtures gave similar results, indicating there is no interfering action between kaolinite and montmorillonite. Speil et al. (53) studied the effect of dilution with kaolinite-quartz mixtures, and obtained similar results.

Table IX shows the estimated kaolinite content of all the soil samples in this study. Estimation by the two thermal methods agrees fairly well, the widest difference being 15 per cent, and the average difference, 6 per cent. The kaolinite content varies widely, ranging from zero to 85 per cent. In almost every case, the fraction that is less than 0.2 micron in diameter, contains more kaolinite, indicating that kaolinite is concentrated in the finer fraction. An exception is the Hydrol Humic Latosol in which there is slightly more kaolinite in the 2.0-0.2 micron fraction. However, the percentages are so low that accuracy in estimating is questionable.

Alexander et al. (2) estimated the kaolin content of the mainland United States soils by the differential thermal analysis and X-ray method. The estimated values, shown in Table I of this report, are fairly close. Aleixandre (1)

Table IX. Kaolinite content in Hawaiian soil clay fractions, estimated by the two thermal methods.

		Per cent kaolinite			
Soil Number	Soil Symbol	Differential Thermal Analysis		Dehydration Curves	
		2.0-02u	<0.2u	2.0-0.2u	<0.2u
48-454	N1-A	55	65	50	60
48-455	N1-B	45	65	45	65
48-456	N3-A	65	65	50	65
48-457	N3-B	80	85	65	75
48-460	N5-A	35	45	35	55
48-461	N5-B	50	55	50	60
48-583	A2-A	25	30	30	30
48-584	A2-B	25	35	35	30
46-519	K3-A	30	10		
46-520	K3-B	25	25		
49-951	K8-A	15	0		
49-952	Dark Layer	0	0		
49-953	K8-B	15	0		
49-954	K6-A	10	0	10	10
49-955	Dark Layer	5	0	5	10
49-956	K6-B	15	10	10	10
47-443	T1-A	5	30		
47-445	T1-B	0	20		
47-248	T2-A	50	45	35	45
47-249	Titanium Layer	15	25		
47-250	T2-AB	10	30		

Table IX. (cont.)

Soil Number	Soil Symbol	Per cent Kaolinite Differential Thermal Analysis 2.0-0.2u	<0.2u	Dehydration Curves 2.0-0.2u	<0.2u
47-251	T2-B	20	5	15	15
47-252	T2-C	35	15		
47-256	T3-A	0	5		
47-259	T3-B	5	0		
49-998	RB-A	0	5		
49-999	RB-B	5	15		
49-56	C2-A	0	10	10	10
49-57	C2-B	0	5	10	15
49-59	F1-A	0	10		
49-61	F1-AB	0	0		
49-62	F1-B	5	5		
49-64	F4-A	0	0	5	5
49-65	F4-B	0	0	5	5
48-575	H1-A	45	45		
48-576	H1-B	40	45		
48-577	H2-A	5	5		
48-578	H2-B	0	5		
48-581	H3-A	40	40	40	45
48-582	H3-B	35	35	40	40
48-571	M-A	15	25	20	30
48-572	M-B	15	20	25	30

estimated the kaolinite content of Spanish clays and kaolins by the differential thermal analysis and the dehydration method, and found that the results agreed very well.

In this report, kaolinite content is estimated primarily by the information furnished by the dehydration curves and the differential thermal curves. It is assumed that the characteristic thermal reactions, namely, loss of water between 400° and 500°C, and endothermic peak between 500° and 600°C, are due to kaolinite only. Some minerals, such as beidellite and illite may be present in Hawaiian Soils, and their thermal reactions may coincide with those of kaolinite, but as it was discussed previously, their other characteristics, such as endothermic peaks at about 700°C and 850°C, are absent. However, the prominent exothermic peaks near 900°C seem to indicate that kaolinite is predominant. Nagelschmidt (42) reported that illite is almost never found in the wet tropics, except in very young soils. The dehydration loss and endothermic peak of standard illite are equivalent to about 20 per cent kaolinite, so probably the interfering effect of illite is negligible.

There has always been a question that the soil clay fractions might be affected by the rather severe treatment during the dispersion procedure, and that the crystal structures might have been alterred. To answer this question, dehydration curves and differential thermal curves were run on several natural soils. The curves of these natural soils are very similar to those of the clay fractions extracted from these soils, thus indicating that crystal structures were not appreciably affected.

DISCUSSION OF THERMAL CURVES OF HAWAIIAN SOILS

Typical dehydration curves and differential thermal curves of the clay fractions from the major Hawaiian Great Soil Groups are shown in Fig. 4,5,6,9,10 and 11. These curves are from the <0.2 micron fractions because mineral constituents seem to be concentrated in this smaller fraction, except the hydrated oxides of iron and aluminum which are found more concentrated in the 2.0-0.2 micron fraction.

The dehydration curves and the differential thermal curves show definitely that kaolinite is the predominant mineral in the Low Humic Latosols. In fact, the clay fraction is almost pure kaolinite. In the Humic Latosols, kaolinite content has decreased somewhat, and a small amount of hydrated oxides is present. In the Hydrol Humic Latosols, kaolinite has almost disappeared, and hydrated oxides have increased greatly, as shown best in the 2.0-0.2 micron fraction. The Humic Ferruginous Latosols also show that kaolinite content is low, and hydrated oxides are high. This whole pattern seems to agree with Jackson's theory of weathering sequence (21).

The mineral constituents of the younger soils, namely Reddish Brown, Reddish Prairie, Brown Forest, Gray Hydromorphic, and Dark Magnesium Clay soils are more difficult to identify. In all of these soils, as well as in the Hydrol Humic Latosols, the outstanding feature is the great initial loss of water at lower temperatures. As it was explained earlier in this report, this large loss of water is one of the characteristics of montmorillonite, a 2:1 type, but other endothermic peaks at 700° and 870°C, and significant losses of water between 500° and 600°C, are not shown by the soils that were studied in this work. Under these circumstances, the initial loss in these soils can not be attributed to montmorillonite.

In the case of the Reddish Prairie soil, there is only one major endothermic peak at 180°C, which is about three times as great as the peak of standard bentonite. The loss in weight at 100°C is 31 per cent, while that of standard bentonite is 11 per cent. There is also a great loss of weight between 150° and 300°C, but this dehydration is not reflected in the differential thermal curve. These great thermal reactions at low temperatures are likely due to some 2:1 type mineral, or to some very fine amorphous material, or to both. It was pointed out earlier that Kelley and Page (27) found amorphous material in Hawaiian soils, and that it was particularly high in the younger soils.

Nagelschmidt (40) defined amorphous material as a substance with a fair percentage of water, a smooth dehydration curve of the adsorption type, and X-ray diagram with no sharp definite lines.

These younger soils have little or no kaolinite. The small endothermic peaks at about 550°C may be due to beidellite, but the sharp exothermic peaks just below 900°C, as shown by the Reddish Brown and Gray Hydromorphic soils, seem to indicate that these high temperature reactions are due primarily to kaolinite. This stand is substantiated by the dehydration curves which show that in every case, most of water is lost between 400° and 450°C, and little between 500° and 600°C. However, the loss of water between 500° and 600°C is sightly more in these younger soils than in the older soils, and in the Gray Hydromorphic and Dark Magnesium clay soils, the loss is about one per cent, which may be significant.

SUMMARY

Representative soils of the major Great Soil Groups of the Hawaiian Islands were separated into sand, silt, and clay fractions. The clay fractions were further separated into 2.0-0.2 microns and $<$0.2 micron fractions. These clay fractions were studied for their mineral constituents, using the dehydration method and the differential thermal method. The findings of this study may be summarized as follows:

(1) Clay content of Hawaiian soils is very high, varying from 40 per cent in the young Reddish Brown soil, to 80 per cent in the older Low Humic Latosols. It then decreases to 50 per cent in the most highly weathered oxide soils, the Humic Ferruginous Latosols.

(2) Some Hawaiian soils that are high in clay content, such as the Low Humic Latosols, do not have the physical and chemical properties that are characteristic of clay soils. Also some soils, with about the same clay content, such as the Humic Ferruginous Latosols and the Dark Magnesium Clays, have very different chemical and physical properties.

(3) Only kaolinite could be identified and estimated by the thermal methods. The sharp endothermic peak at about 580°C and the exothermic peak at about 900° C on the differential thermal curves, and a great loss of water between 400° and 500°C

on the dehydration curves, which are characteristic features of kaolinite, are clearly evident in Hawaiian soils.

(4) The kaolinite contents, estimated by the dehydration curves and the differential thermal curves, agree fairly well, the widest difference being 15 per cent, and the average being 6 per cent.

(5) Kaolinite content in clay fractions varies from zero to 80 per cent. It is low in the young soils, like the Reddish Brown, highest in the Low Humic Latosols, and then declines again in the older soils, the Humic Ferruginous Latosols and the Hydrol Humic Latosols.

(6) Montmorillonite and illite could not be identified by the thermal methods in this experiment. The characteristic peaks and losses in weight are not clearly evident in Hawaiian soils. Furthermore, some of these features are masked by the more dominant kaolinite.

(7) Hydrated oxides of iron and aluminum, bauxite and goethite, both have similar endothermic peaks and losses in weight which occur at about the same temperatures. These thermal reactions are all observed in Hawaiian soils, so one mineral could not be distinguished from the other.

(8) Hematite has no thermal reactions.

(9) Ilmenite gains in weight gradually between 250° and 650°C, but no gain in weight was observed in Hawaiian

soils. On the differential thermal curve, ilmenite shows only a gradual exothermic reaction with no definite peaks, so it could not be identified.

(10) Amorphous materials and unclassified 2:1 type minerals are suspected to be present in Hawaiian soils.

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