Thesis - Geology

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HYDROTHERMAL MINERALOGY OF KEOLU HILLS, OAHU, HAWAII

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
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ABSTRACT

The mineralogy of the hydrothermally altered basalts of the Kailua Volcanic Series present in Keolu Hills, Oahu, Hawaii was examined by X-ray diffraction analysis, and clay mineral alteration zones found. In the vertical zones, chlorite-vermiculite occurs higher than chlorite; and horizontal zones of chlorite-montmorillonite (inner) and chlorite (outer) occur. The two clay minerals kaolinite and chlorite-montmorillonite found in the soil are not related to the parent rock, but to differences in drainage which result in different alteration products. The zeolites in Keolu Hills are calcium zeolites which commonly coexist with quartz. Laumontite is the dominant zeolite in the study area. Its widespread distribution in the Kailua Volcanic Series suggests that low temperatures (approximately 300° C) prevailed during the formation of secondary minerals and indicates that as much as 3,500 feet of weathering has occurred since caldera formation.

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INTRODUCTION

Purpose of the Study

The purpose of this study is to analyze the mineralogical composition of the hydrothermally altered basalt in Keolu Hills by X-ray diffraction, to determine if clay mineral alteration produced zoning in these rocks, and to correlate the mineralogy with previous studies of hydrothermal alteration. Argillaceous alteration products resulting from hydrothermal action are often associated with hot springs, vesicles of igneous rocks, fractures, and metalliferous deposits. The Keolu Hills basalts lie within the ancient caldera of the Koolau volcano, in which hydrothermal alteration and an abundance of clay minerals in the rocks can be expected. Although the area is no longer volcanically active, subsurface alteration may still be occurring as suggested by the presence of warm water in a drill hole at Waimanalo, approximately two miles away from the study area (Macdonald, 1973). Residential development and road construction within the study area facilitated sampling because it exposed fresh rock on ridges that were once inaccessible.

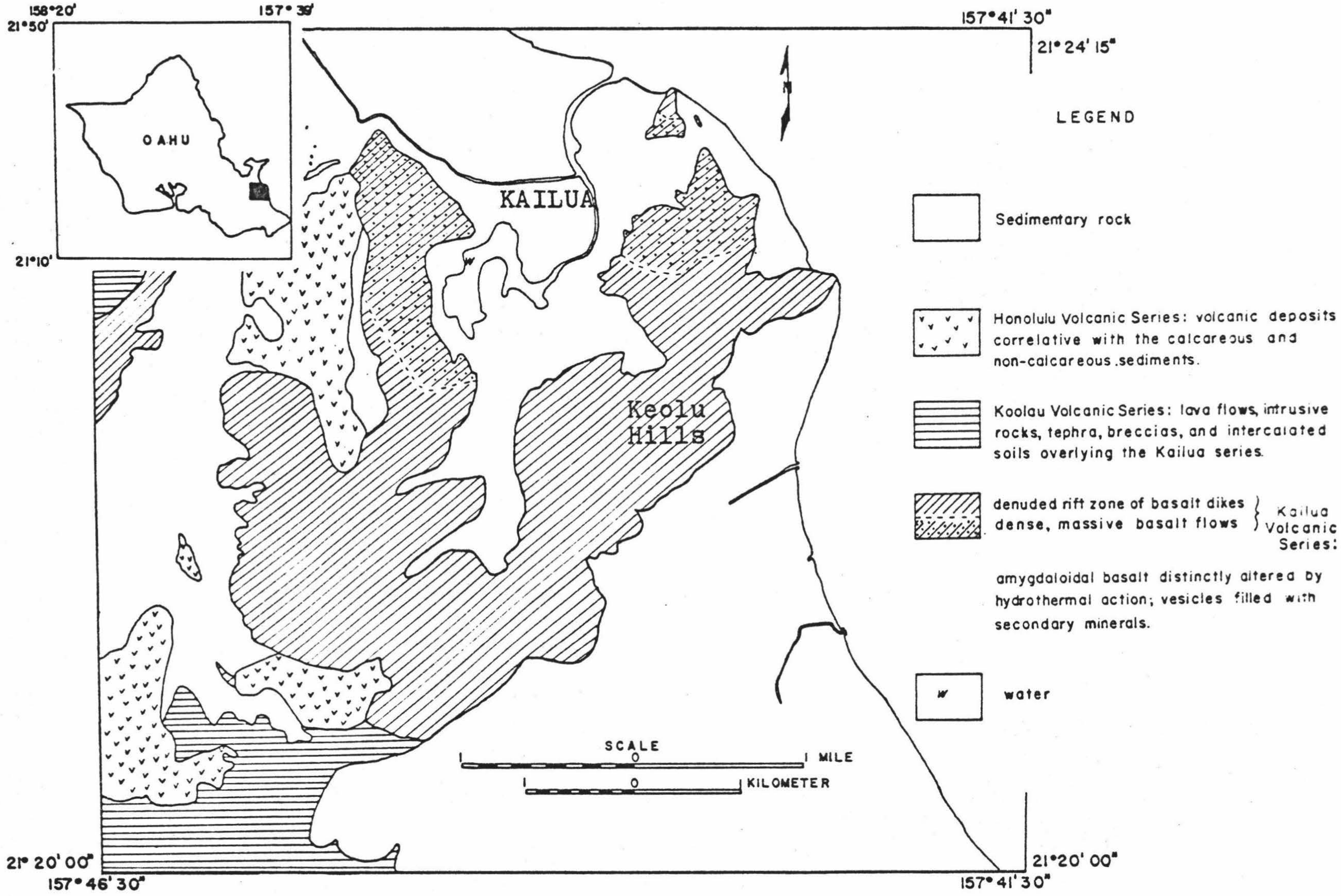
Previous Work

In 1931 Eakle identified many of the amygdule minerals in the Kailua Volcanic Series, of which the Keolu Hills are a part. Stearns and Vaksvik (1935) mapped the lava flows and provided a brief description of the hydrothermally altered Kailua Volcanic Series. While examining the oxygen-isotopic composition of quartz from Hawaiian soils, Rex, *et al*. (1969) studied hydrothermal quartz from Waimanalo samples. From soil surveys of the Hawaiian Islands, Foote, *et al*. (1972) of the U. S. Department of Agriculture have produced a detailed soil map of Keolu Hills and brief mineralogical descriptions of each soil type.

Geologic History

The Koolau volcano erupted from about 2 to 2.6 million years ago. The lava rocks of the Waimanalo-Kailua-Kaneohe area are notably more massive and less permeable than the rocks of the Koolau Volcanic Series, and for that reason, and their relatively low topographic position, Stearns and Vaksvik (1935) believed them to represent the top of an older volcano buried by the Koolau Volcano, and named them the Kailua Volcanic Series, after the town of Kailua where they are well exposed (Figure 1). Later, Stearns (1939) realized that the rocks of the Kailua Volcanic Series,

Figure 1. Geologic Map of Keolu Hills and Surrounding Areas (after Stearns and Vaksvik, 1935).

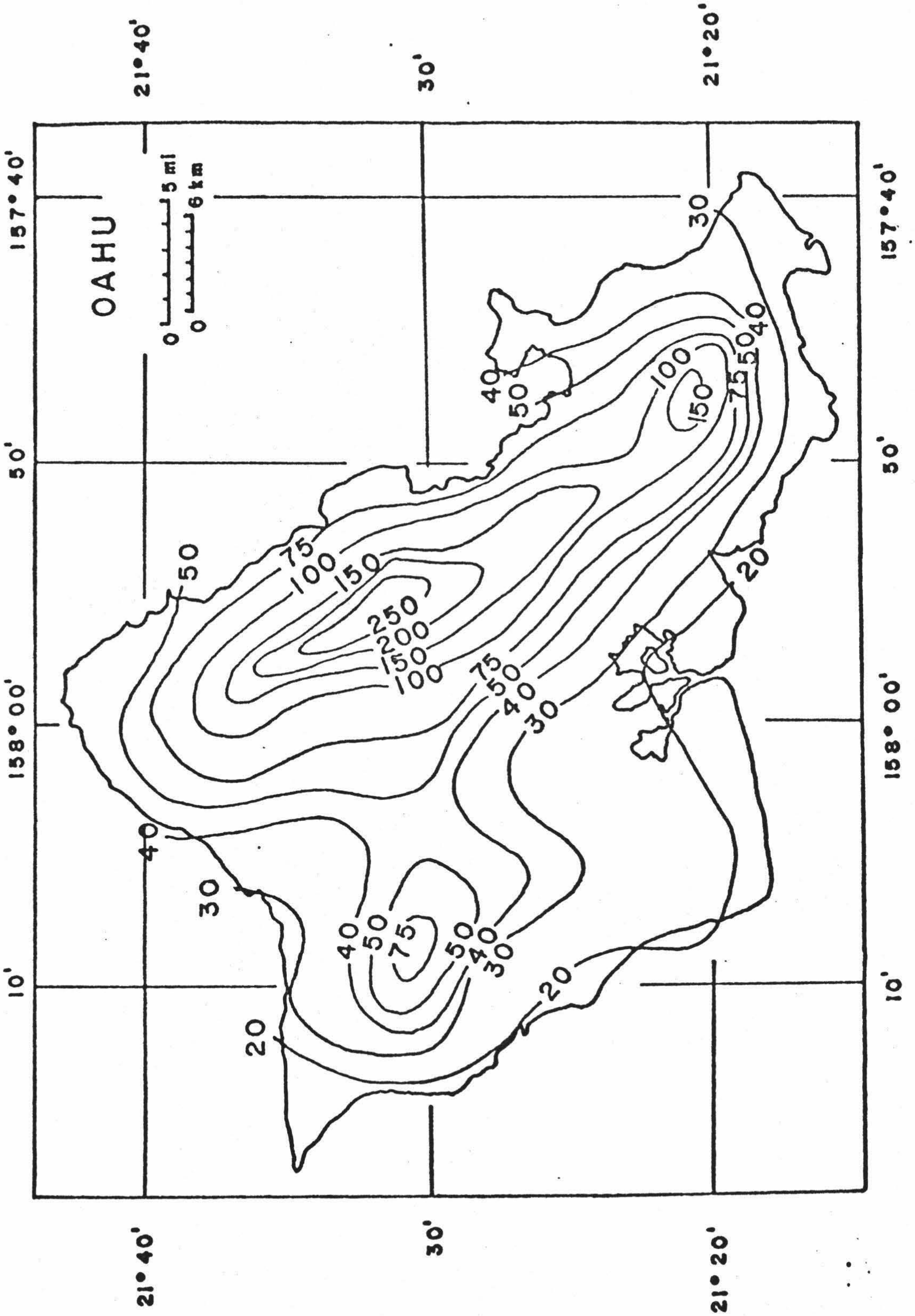

158°20'
157° 39'
21°50'
21°10'
OAHU
157°41' 30"
21° 24' 15"
KAILUA
Keolu Hills
N
LEGEND
Sedimentary rock
Honolulu Volcanic Series: volcanic deposits correlative with the calcareous and non-calcareous sediments.
Koolau Volcanic Series: lava flows, intrusive rocks, tephra, breccias, and intercalated soils overlying the Kailua series.
denuded rift zone of basalt dikes
dense, massive basalt flows
Kailua Volcanic Series:
amygdaloidal basalt distinctly altered by hydrothermal action; vesicles filled with secondary minerals.
W
water
SCALE
1 0 1 MILE
1 0 1 KILOMETER
21° 20' 00"
157° 46' 30"
21°20' 00"
157°41' 30"

instead of being older than the adjacent Koolau Volcanic Series, are actually younger, and represent lavas that accumulated in the caldera of the Koolau volcano. The thick, massive flows filling the caldera were altered by gases which for centuries rose through the lavas from the magma chamber below (Macdonald and Abbott, 1970), weakening the dense basalts to easily eroded material. When eruption of the Koolau volcano ceased, weathering and erosion by rainfall and trade-wind waves destroyed the northeast side of the shield volcano. The altered caldera rocks rapidly eroded as amphitheater valley heads retreated westward, until erosion slowed down on the western side of the caldera where unaltered rocks were encountered (Macdonald and Abbott, 1970). The amphitheater-headed valleys along the southeast coast forming the present cliff of the Pali mark the approximate boundaries of the Koolau caldera.

Geologic Setting

Keolu Hills is located about 1250 meters inland from the coast of Kailua Bay and has an elevation ranging from 10 to 130 meters. It borders Kaelepulu Pond, which is a remnant of a swamp now filled for residential development. Rainfall averages about 40 inches per year (Figure 2). Kaelepulu Stream is usually isolated from the ocean by a sand bar. It flows into Kailua Bay, usually by seepage

Figure 2. Mean Annual Rainfall Map of Oahu
(isohyets in inches)
(after <u>Climatologic Stations in Hawaii</u>, 1973).


OAHU
0 5 mi
0 6 km
157°40'
50'
158°00'
10'
21°40'
30'
21°20'
20
30
40
50
75
100
150
200
250

through the sand bar, but occasionally through an open channel. The vegetation on Keolu Hills is typical of a semi-arid belt in Hawaii, and is largely composed of haole koa, kiawe, finger-grasses, cactus, and holly (Stearns and Vaksvik, 1935).

Outcrops of the Kailua Volcanic Series consist of flows of aa and pahoehoe basalt up to 60 feet thick. The Kailua basalts are amygdaloidal and altered by hydrothermal action. As a result, the joints and vesicles are virtually all filled with quartz, zeolites, and other secondary minerals, leaving the rock almost impermeable (Stearns and Vaksvik, 1935).

The Kailua lava flows have been deformed into a gentle elliptical basin, with its center west of Kailua. The Keolu Hills lie on the southern flank of the basin, and the lava flows in them dip northward to northwestward at angles generally less than 20°, except near Alala Point (locations A-11 and W-14, Figure 3), where the beds dip gently southwestward. The lavas are cut by numerous dikes. Most of the dikes are nearly vertical and most trend N.50°-70°W., ranging in width from a few inches to eight feet.

MATERIALS AND METHODS

Sample Collection

Samples were collected from amygdaloidal rocks in the Keolu Hills, within the Kailua Volcanic Series as mapped by Stearns and Vaksvik (1935). Sample sites are shown in figures 3 and 4. The rock samples were collected at sites where natural outcroppings or roadcuts exposed fresh rock. Samples which appeared altered but not weathered were selected at most sites. This distinction was made by selecting green-colored rocks (chlorite-rich), instead of reddish-brown rocks characteristic of oxidation due to weathering. At a few sites the rock was slightly weathered in addition to being altered. Soil samples were collected from eight sites where the regolith appeared to be undisturbed for comparison with the parent material. Amygdule samples were collected at most rock sites. The amygdule minerals often filled the entire cavity, and as a result the crystals were generally small.

Sample Preparation

All samples were ground to a fine clay grain size by one hour of wet grinding in a model 155 Fisher mortar

Figure 3. Location Map of Rock and Soil Samples.

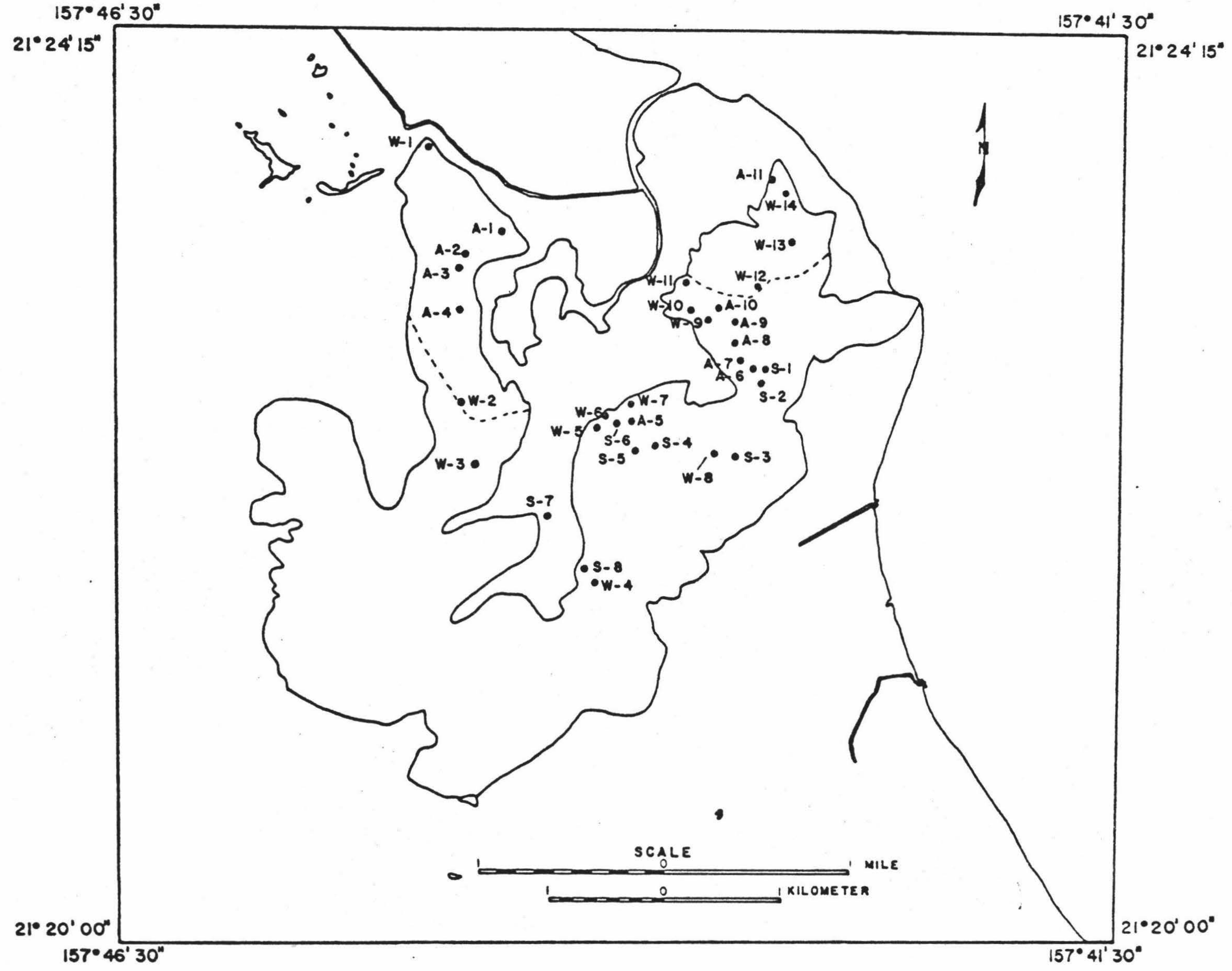
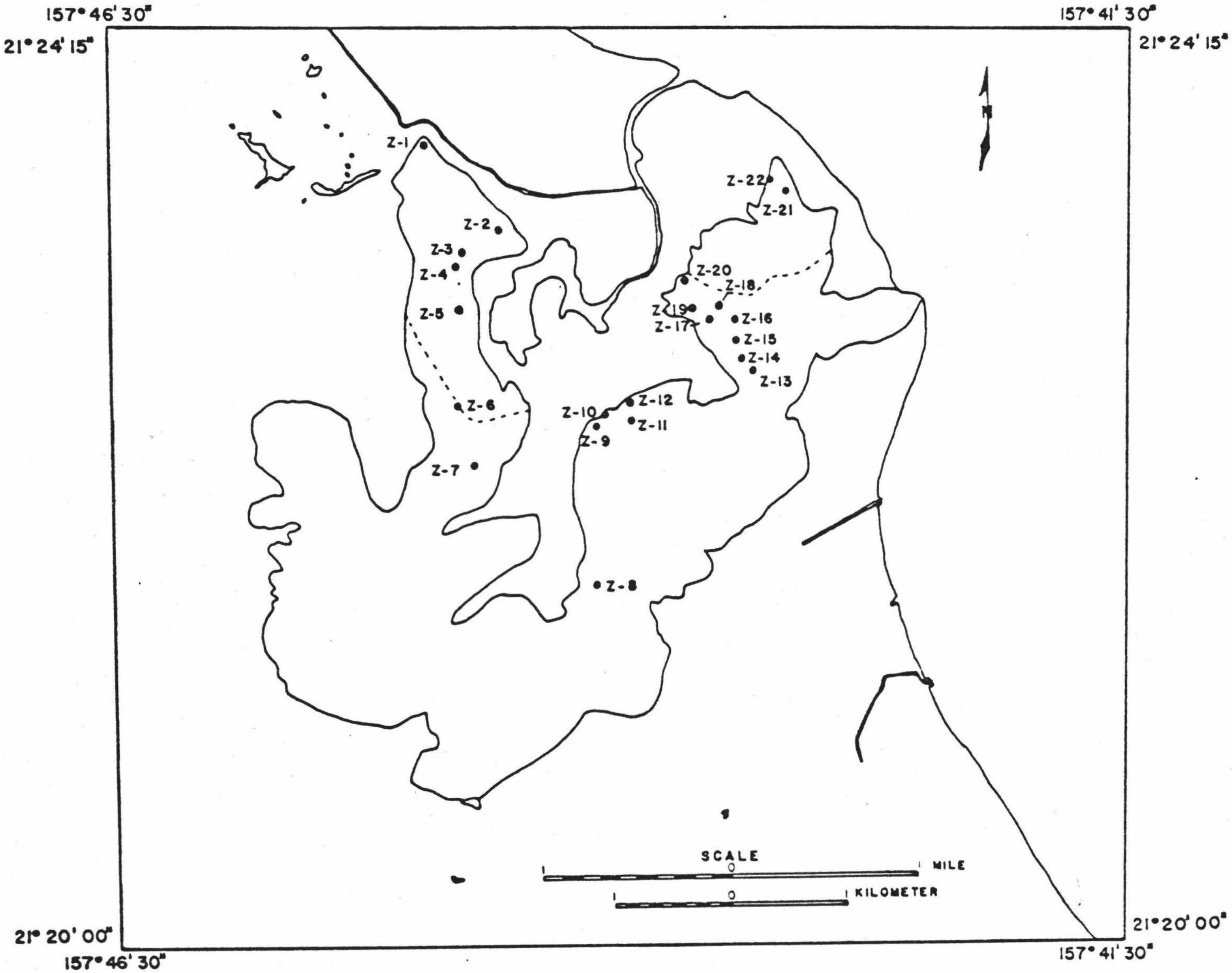

157° 46' 30"
21° 24' 15"
157° 41' 30"
21° 24' 15"
N
W-1
A-1
A-2
A-3
A-4
W-2
W-3
A-11
W-14
W-13
W-12
W-11
W-10
A-10
W-9
A-9
A-8
A-7
A-6
S-1
S-2
W-6
W-7
W-5
A-5
S-6
S-4
S-5
S-3
W-8
S-7
S-8
W-4
SCALE
1
0
1 MILE
1
0
1 KILOMETER
21° 20' 00"
157° 46' 30"
21° 20' 00"
157° 41' 30"

Figure 4. Location Map of Amygdule Samples.


157° 46' 30"
21° 24' 15"
157° 41' 30"
21° 24' 15"
21° 20' 00"
157° 46' 30"
21° 20' 00"
157° 41' 30"
Z-1
Z-2
Z-3
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Z-5
Z-6
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Z-9
Z-10
Z-11
Z-12
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Z-15
Z-16
Z-17
Z-18
Z-19
Z-20
Z-21
Z-22
SCALE
1
0
1 MILE
1
0
1 KILOMETER

grinder. Slides with preferred grain orientation parallel to the basal plane are desirable for X-ray diffraction analyses of clay and zeolite minerals due to the structure of these minerals. To obtain this orientation, a thick aqueous suspension of the well-dispersed clay was allowed to dry on a glass slide (Warshaw and Roy, 1961). Samples with peaks between 13-15 Å were sprayed with a fine mist of ethylene glycol to swell any expandable clay mineral layers. All slides were kept within a dessicator to prevent hydration and curling of samples.

Mineral Identification

The oriented slides were X-rayed using a Norelco diffractometer (Philips Electronic Instruments) type number 12215/2 with copper K_{α} radiation at 35 kilovolts and 20 milliamperes. The following diffractometer settings were used:

(1) for untreated rock samples and amygdule samples--rate meter multiplier at 5, time constant at 2.0 seconds, rate meter full scale at 10^2 counts/second; and

(2) for glycolated rock samples and soil samples--rate meter multiplier at 2, time constant at 4.0 seconds, rate meter full scale at 10^3 counts/ second.

Although the accuracy of X-ray diffraction data is highly variable, relative mineral abundances appear to be excellent. A semi-quantitative percentage of each mineral was calculated (Table 1) using the peak height method and mineral factors given by Fan and Rex (1972). Mineral compositions of each sample are presented as percentages in Tables 2 and 3. D-spacing tables for mineral identification in Carver (1971) and Brown (1972) were used for the identification of most of the minerals. The rock and soil samples often contained quartz, cristobalite, plagioclase feldspar, and sometimes augite, hematite, and calcite, but the clay minerals constitute the bulk of the material studied.

Some clay minerals can be differentiated on the basis of whether they absorb ethylene glycol with resultant changes in their basal spacings, appearing as a peak shift in the diffractogram of the glycolated material. Diffractogram peaks at low angles are characteristic of the most important d-spacings from clay minerals as a result of their crystalline structure (Carroll, 1970). All samples which produced low angle reflections ranging from 15-13 Å were saturated with a fine mist of ethylene glycol and allowed to dry. These samples resulted in reflections between 17 and 13 Å.

Table 1

Mineral Factors Used for Semi-quantitative
Mineral Composition Analysis
(after Fan and Rex, 1972)

mineral	factor
chlorite	4.95
chlorite-vermiculite	2.65
chlorite-montmorillonite	2.65
kaolinite	2.25
cristobalite	9.00
quartz	1.00
plagioclase	2.80
calcite	1.65
augite	5.00
hematite	3.33
siderite	1.15

Table 2

Mineral Composition of Rock Samples
(Figures represent percentages)

Sample Number	chlorite	chlorite-vermiculite	chlorite-montmorillonite	cristobalite	quartz	plagioclase feldspar	calcite	augite	hematite	siderite	Elevation (feet)
W-1		92.9				25.2					40
A-1	74.0			7.3	2.4	12.2		4.1			80
A-2			97.1			2.9					120
A-3			78.8		5.1	14.7			1.4		120
A-4			95.2		4.8						160
W-2		54.1		11.1	5.2	20.6			8.2	0.8?	200
W-3			80.0	6.7	1.1	3.9		4.8	3.5		200
W-4	82.3			3.5	0.5	9.3		2.4?	2.0		120
W-5		66.0		11.8	3.9	14.7			3.6		120

Table 2 (continued) Mineral Composition of Rock Samples

Sample Number	chlorite	chlorite-vermiculite	chlorite-montmorillonite	cristobalite	quartz	plagioclase feldspar	calcite	augite	hematite	siderite	Elevation (feet)
W-6		94.1			0.6	2.4			2.9		120
A-5	99.2				0.2	0.6					200
W-7	62.9			9.2	1.5	21.3		5.1?			150
W-8		96.7				3.3					200
A-6	63.3			11.4	2.0	14.6		8.7			200
A-7		42.4		13.5	2.8	28.0	5.1	3.1	4.2	0.9?	160
A-8		35.2		25.0	10.7	22.2		6.9			120
A-9		27.7		21.8	9.2	24.2		12.1	5.0		160
A-10		87.3			2.7	10.0					280

Table 2 (continued) Mineral Composition of Rock Samples

Sample Number	chlorite	chlorite-vermiculite	chlorite-montmorillonite	cristobalite	quartz	plagioclase feldspar	calcite	augite	hematite	siderite	Elevation (feet)
W-9		63.9		8.1	7.3	10.0		3.0?	6.6	1.1?	260
W-10		78.3		7.9	1.0	3.1		3.8	5.9		140
W-11	93.8				0.8	3.6			1.7?		80
W-12		72.3			4.3	23.4					600
W-13		56.6			1.6	28.2		13.5			560
W-14	70.0			6.1	2.4	10.2		6.8	4.5		160
A-11	91.5				2.4	6.1					120

Table 3

Mineral Composition of Soil Samples
(Figures represent percentages)

Sample Number	chlorite-montmorillonite	kaolinite	cristobalite	quartz	plagioclase feldspar	hematite
S-1	66.9	12.8		1.5	18.8	
S-2	64.8	4.7		2.8	27.6	
S-3	37.4	4.9	26.1	7.2	24.3	
S-4	26.9		28.1	8.4	36.6	
S-5		28.0		41.0		31.0
S-6		39.7		60.3		
S-7		15.8	59.8	9.6		14.8
S-8	82.9			1.7	15.4	

RESULTS

Chlorite

In igneous rocks chlorites are commonly found as secondary minerals resulting from the hydrothermal alteration of biotite, hornblende, and other minerals. The occurrence of chlorite in the study area is indicated by the light olive-green color of the unweathered rocks. Its presence was confirmed by X-ray diffraction. Warshaw and Roy (1961) identify chlorite by little or no change in the 14 Å reflection after glycolation. In addition, Biscaye (1964) identified chlorite reflections at 3.56-3.55 Å. These d-spacings occurred in eight samples with percentages ranging from 99.2% to 62.9% (Table 2).

Chlorite-montmorillonite

Many clay materials are composed of more than one clay mineral, interlayered as mixed-layer clays. The difficulty of identifying mixed-layer minerals lies in their variability in layer arrangement. The mixed-layer structures produce composite X-ray reflections whose position and intensity vary with the relative abundance of the different individual layers (Grim, 1968).

Earley and Milne (1956) studied amygdaloidal basalt from Mozambique and found that montmorillonite-chlorite occurred as the dominant clay mineral in the form of fibrous rosettes. They concluded that mixed-layer silicates are often found as intermediate stages in the alteration of micas and other silicates to clay minerals. In the argillaceous siltstone of the Yates Formation, Texas, montmorillonite-chlorite is the dominant clay occurring as cementing material (Earley, et al., 1956). The data from Earley and Milne (1956) and Earley, et al. (1956) on the basal spacings of montmorillonite-chlorite are presented in Table 4.

In four rock samples and most soil samples from the Keolu Hills the clay peak expanded from approximately 15 Å to about 16.6 Å, a characteristic swelling of the montmorillonite group (Biscaye, 1965; Carroll, 1970). However, other clay peaks in these samples corresponded with d-spacings of chlorite. The basal reflections of this clay were compared with the basal reflections of the chlorite-montmorillonite studied by Earley and Milne (1956) and Earley, et al. (1956). The results are presented in Table 4 and appear to match well. The variations are attributed to slight differences in structures and/or differences in relative humidity.

Table 4

Basal Reflections from Untreated and Expanded Chlorite-montmorillonite
(Figures represent d-spacings in Å)

Earley and Milne (1956)		Earley, *et al*. (1956)		This Study	
untreated	glycerol	untreated	glycerol	untreated	ethylene glycol
14.5 7.2	15.8 7.83	14.5 7.25 4.85	16.1 8.01 5.34	15.0 7.55 4.92	16.6 8.34 5.55

Chlorite-vermiculite

Vermiculite is a mineral frequently listed as a hydrothermal alteration product of biotite and has an expanding lattice, but it differs from montmorillonite in that expansion can take place only to a limited degree (Grim, 1968). Mixed-layer chlorite-vermiculite clay has been described from the clay residue of the Upper Mississippian Brazer limestone, Colorado (Bradley and Weaver, 1956), and from a weathered diabase in the Pretoria Series, South Africa (Heystek, 1956). D-spacings of the chlorite-vermiculite from Colorado are presented in Table 5.

Most of the clay minerals in the study area expanded from approximately 14.6 Å to 15.5 Å. The individual reflections for chlorite and vermiculite (Carroll, 1970) matched well with reflections from these samples. The reflections suggested the presence of a mixed-layer chlorite-vermiculite. The values of basal reflections from the chlorite-vermiculite found in Keolu Hills are very close to those determined by Bradley and Weaver (1956) from the Brazer limestone (Table 5).

Kaolinite

Kaolinite occurs only in the soil samples, indicating that it is a product of weathering. This clay mineral,

Table 5

Spacings from Untreated and Expanded Chlorite-vermiculite
(Figures represent d-spacings in Å)

Bradley and Weaver (1956)		This Study	
untreated	ethylene glycol	untreated	ethylene glycol
14.6	15.5	14.6	15.5
9.7	10.2*	9.64	N.R.+
7.30	7.7	7.29	7.63
4.90	5.12	4.84	5.14
4.17*	4.40	N.R.	4.42
3.63	3.84*	3.63	N.R.
3.27*	3.44	N.R.	3.44

*Intensities are small.

+N.R. = no reflection detected.

whose presence is generally suggested by the reddish color of associated ferric oxide, is found in most of the samples, but it is the dominant clay in only a few places.

Pyrite

In hand specimens of samples A-8 and A-9, a mineral not identified in the X-ray diffractograms was found, namely pyrite. The pyrite occurs as small, pale yellow cubes often altered at the outer edges to a brownish mass which may be limonite or a fine-grained goethite (Heinrich, 1965). Pyrite is a common iron oxide occurring in hydrothermally active areas and is often a subject of vein studies because of its association with gold and many other metallic ores (Bonorino, 1959; Tooker, 1963).

Amygdules

The amygdules are composed of calcite, quartz, and zeolite minerals. Calcite and quartz were readily identified by X-ray analysis. The zeolites chabazite, heulandite, and laumontite, were recognized in diffractograms by their three major peaks (Smith, *et al.*, 1965; Borg and Smith, 1969). The values are given in Table 6.

Table 6

Major Peaks of Zeolites Found in the Kailua Volcanic Series

zeolite	d-spacings		
chabazite*	9.41	5.54	5.04
heulandite+	8.93	3.93	2.95
laumontite+	9.46	6.84	3.51

*Smith, et al. (1965)

+Borg and Smith (1969)

By far, the dominant zeolite is laumontite. The peak intensities of this dominant zeolite do not correspond with any calculated zeolite intensities, but the X-ray diffraction pattern of the laumontite standard match the pattern of this dominant zeolite (Figure 5). There are many prominent peaks in the diffractogram and their intensities often vary. The most prominent peaks occur at d-spacings of 9.41, 6.86, 4.73, 4.15, 3.51, 3.28, 3.15, and 3.03 Å. The small peak at 6.19 Å and the twin-like peaks between 3.51, 3.28, and 3.03 Å are highly characteristic of laumontite.

In samples z-5, z-6, z-7, z-13, z-15, and z-22, quartz and/or calcite were found, and no zeolites were detected. Laumontite occurred in the remaining samples,

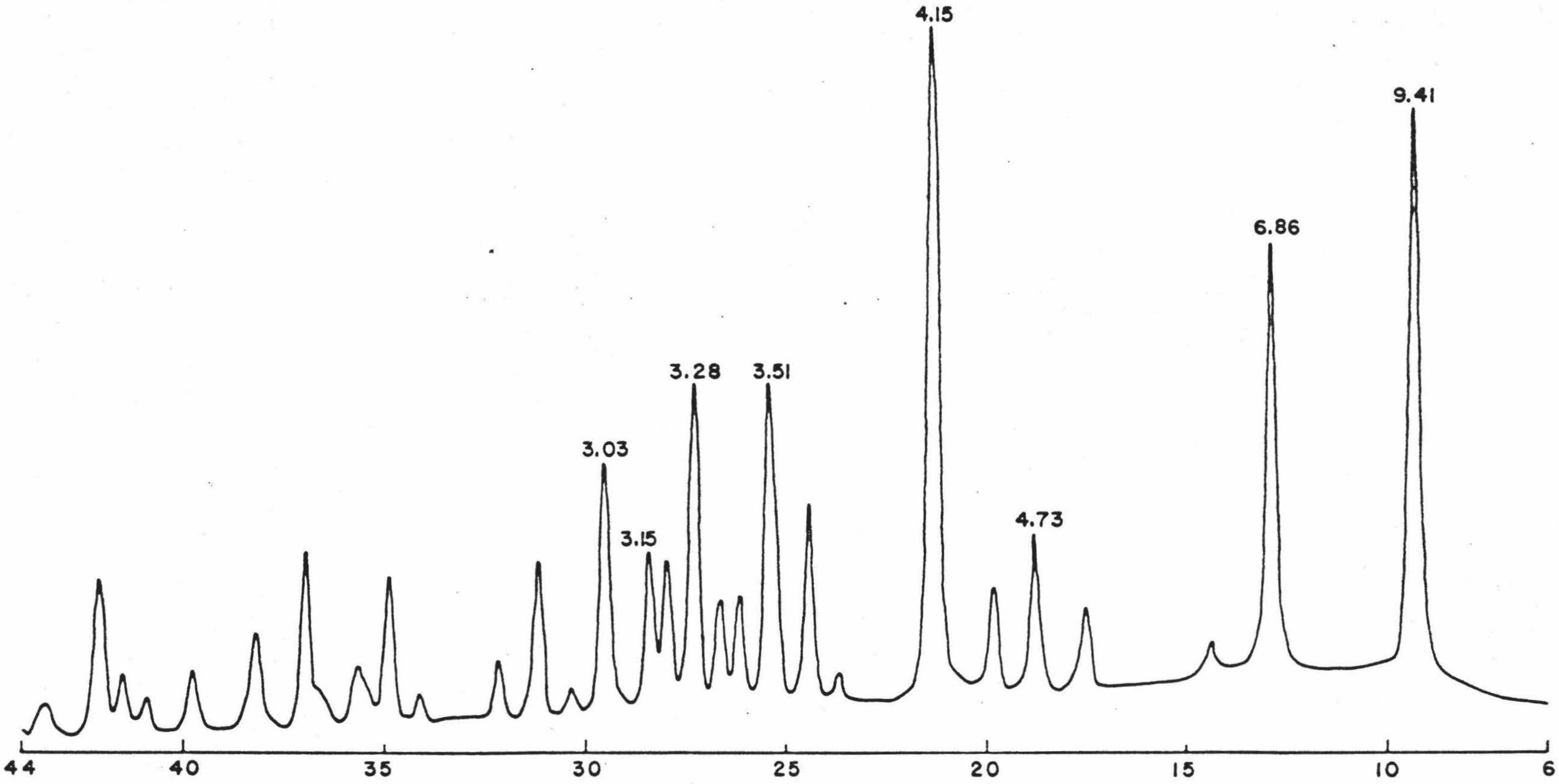


Figure 5. Laumontite X-ray diffraction pattern.

accompanied by small amounts of calcite and, in some, quartz. In addition, z-14 contained a small amount of chabazite, and samples z-10 and z-21 contained small amounts of heulandite.

DISCUSSION

Rock Groundmass Samples

Kerr (1955) states that chloritization in intrusive rocks is a common feature in the early stages of hydrothermal alteration. He points out that permeability, porosity, and conduits permitting fluid penetration are important in determining the alteration products, depending on whether the constituents are derived from the invaded rocks or from below. In Grim (1968), Sudo and Hayashi described chlorite and montmorillonite in hydrothermal wall-rock alteration associated with sulfide ore deposits of Japan. A study by Bassett and by Varley (in Grim, 1968) found vermiculite forming by hydrothermal action at the contact of acid intrusives and basic rocks.

Vertical zoning in hydrothermally altered rock has been studied by Steiner (1953) at Wairakei, New Zealand. Cores from exploratory drilling provided an opportunity for the study of clay mineral development by hydrothermal activity. Steiner found a superficial zone (zone of sulfuric acid leaching) containing kaolinite and alunite extending to 100 feet below the surface. This zone is followed at depths down to 250 feet by a zone of argillization in which smectite is dominant and where temperatures increase to about 150°C. Below 250 feet temperatures reach 600 to 700°C, and zeolite and adularia have been formed as alteration products in a zone of zeolitization. At greater depths sericite is formed (zone of feldspathization). Steiner concluded that the hydrothermal agents are initially acidic, becoming neutralized and then alkaline as they ascend to the surface. Eslinger and Savin (1973), in studying hydrothermally altered rocks of the Ohaki-Broadlands area of New Zealand, concluded that chemical equilibrium was indicated by a decrease of expandable layers in mixed-layer clays with increasing depth and temperature. At temperatures above about 230°C expandable layers disappeared completely.

Studies of horizontal zonation around ore deposits have found that chlorite is the dominant clay mineral on the outer fringe (Grim, 1968). In the outermost alteration fringe hornblende and biotite often changed to chlorite, and smectite (montmorillonite) became the dominant alteration product toward the vein (Sales and Meyer, 1948, in Grim, 1968). Iwao (1953, in Grim, 1968), after studying many hydrothermal clay deposits in Japan, found a general horizontal zoning of pyrophyllite (innermost), sericite, montmorillonite, and chlorite (outermost). Bonorino (1956, 1959) found that hydrothermal alteration patterns in Boulder County and the Front Range mineral belt, Colorado, are characterized by five zones: phlogopite (outermost), montmorillonite, kaolinite, orthoclase, and hydromica (innermost). The complex hydrothermal alteration patterns are explained as chemical fronts which developed when altering fluids migrated away from the conduit. Reacting with the wall rock, the fluids changed in composition, successively reaching stability fields of the various secondary minerals. Sumi (1969) found a horizontal zoning of chlorite (outer) and montmorillonite (inner) in the Matsukawa Geothermal Area, Japan. At Matsukawa the mineral assemblage of the chlorite zone is predominantly chlorite, laumontite, hydromica, mixed-layer sericite-montmorillonite, quartz, and pyrite.

All the clay minerals found in the study of Keolu Hills (chlorite, chlorite-vermiculite, and chlorite-montmorillonite) have been reported in hydrothermal bodies. The mineral assemblage of the chlorite zone in the Matsukawa Geothermal Area, Japan, corresponds closely to that found in Keolu Hills. The non-clay minerals found in the rocks of the Kailua Volcanic Series are characteristic of hydrothermal products, and the presence of cristobalite and sometimes siderite (Table 2) indicate formation at low temperatures (Brown, 1970).

The types of clay minerals in the study area and their present level of elevation (Table 2) were compared to find any occurrence of vertical zonation. Chlorite is the clay mineral often found at the lower elevations of the Kailua Volcanic Series. Chlorite-vermiculite generally occurs at a higher level than the other two clays, chlorite and chlorite-montmorillonite. Chlorite-montmorillonite occurred in only four samples--A-2, A-3, A-4, and W-3--which were taken within close proximity of one another (Figure 3). The differences between the clay minerals may be accounted for by differences in the parent rock, in the hydrothermal solutions, in the degree of alteration, and in pressure and temperature during alteration. In addition, the hydrothermal solutions, rising through the rock, will change in chemistry through interaction with the host rock, and clay mineral fronts will form. Material which is closer to the hot source is often altered to a different mineral from what is produced farther away. Eslinger and Savin (1973) report that the occurrence of expandable layers decreases with increasing temperature and pressure. This generalization appears to hold for the vertical zonation of clays in the Keolu Hills: chlorite-vermiculite, which is expandable to a limited degree, occurs at higher elevations (generally greater than 150 feet); whereas chlorite with no expandable layers is found at lower elevations, deeper within the caldera flows.

The clay minerals and their areal distribution were studied for the possible occurrence of horizontal zoning. Chlorite occurrences are interspersed with those of chlorite-vermiculite. However, chlorite-montmorillonite occurs only at four closely grouped sites (A-2, A-3, A-4, and W-3, figure 3). (Because W-3 is a weathered sample, the montmorillonite at this site may be a product of weathering.) The study area appears to represent two horizontal zones of hydrothermal alteration: an inner chlorite-montmorillonite zone and an outer chlorite/chlorite-vermiculite zone. The inner zone of chlorite-montmorillonite suggests a transition from a dominantly montmorillonite zone to a chlorite zone. The abundance of chlorite indicates that Keolu Hills is situated at the outer limits of hydrothermal activity. The position of the chlorite-montmorillonite sites suggests that if more intense alteration zones exist they are situated generally north of the study area.

The clay mineralogy of the study area forms alteration zones due to hydrothermal activity within the former caldera. A vertical zoning occurs with chlorite-vermiculite at higher levels and chlorite at greater depths, and a horizontal zoning occurs with chlorite-montmorillonite closer to the center of the caldera and chlorite and chlorite-vermiculite at the outer fringe. These zones were formed by the reaction between the pre-existing rock and chemically-changing hydrothermal solutions. The vertical zones were affected by increasing temperature and pressure with depth, which decreased the amount of expandable layers in the mixed-layer clay minerals.

Soil Samples

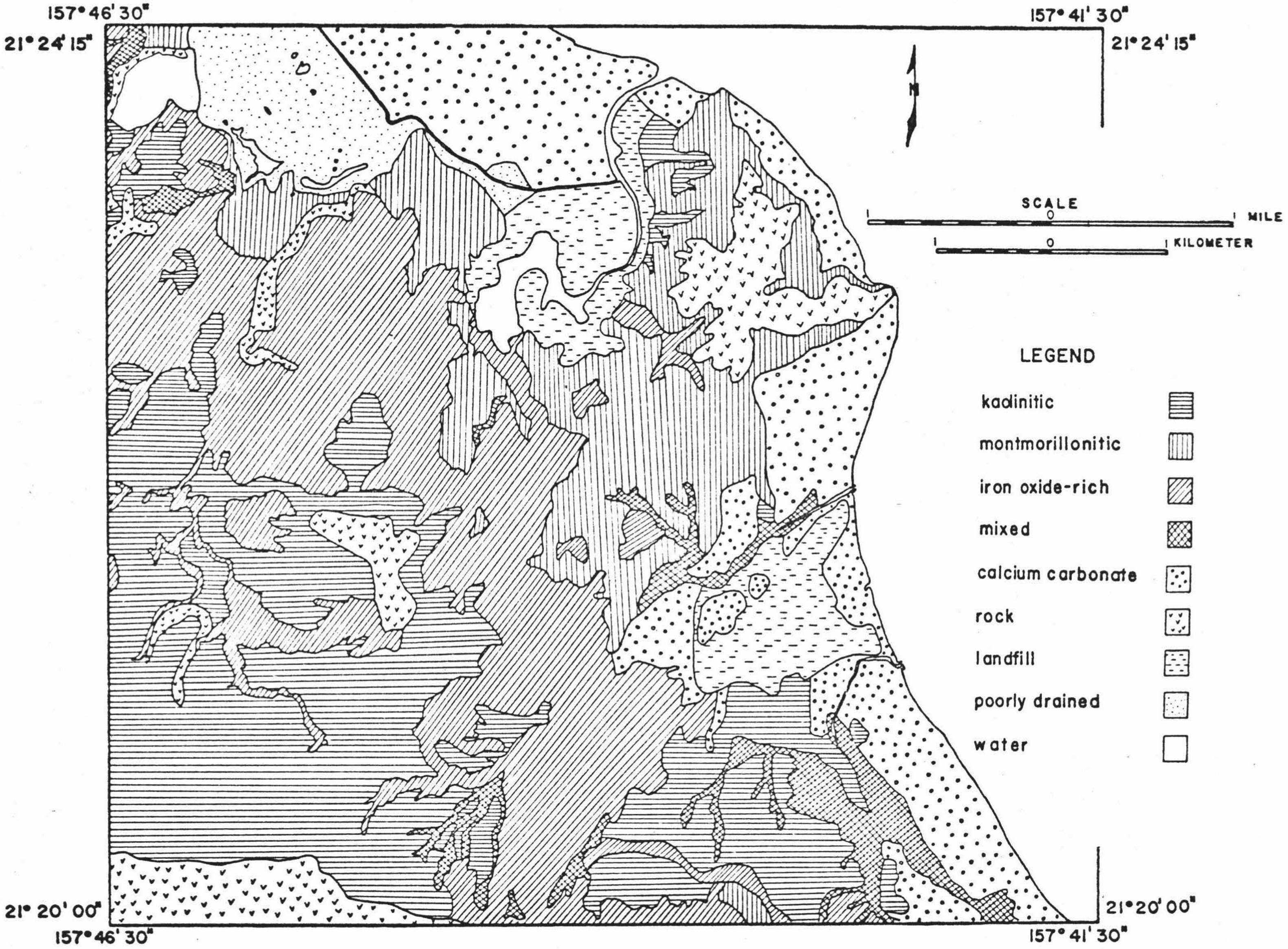
The clay minerals in the Keolu Hills soil are chlorite-montmorillonite and kaolinite (Table 3). From mineralogical studies of the rock near these soil sites, chlorite or chlorite-vermiculite occur as the hydrothermally altered products. Weathering has altered these clay minerals to new clays in the soil, but the new minerals do not follow any discriminatory pattern that compares with the zoning patterns of the hydrothermal clay minerals in the rocks.

According to Grim (1968), the factors controlling the weathering processes are parent rock, climate, topography, vegetation, and time. Since all soil samples are weathered products from the Kailua Volcanic Series and the area from which they were collected is small, many factors controlling soil type formation may be eliminated: climate, vegetation, time, pH, and composition of the parent rock (especially the presence of alkalies and alkaline earths). The character of the drainage accounts for the different weathering products found in most areas of the Hawaiian Islands. In a study of the red (kaolinite) and black (montmorillonite) soils of the Hawaiian Islands, Uehara and Sherman (1956) conclude that good drainage will result in kaolinite and poor drainage in montmorillonite.

Drainage in Keolu Hills is affected by permeability of parent material and topography. Permeability of the parent rock was not studied by the writer, but Stearns and Vaksvik (1935) found the Kailua Volcanic Series almost impermeable because of filling of most cavities by secondary minerals. The importance of permeability in weathering was pointed out by Dorfman (1960, in Grim, 1968) who found that chemical weathering has progressed to a depth of 500 meters along fractures within the nepheline syenites of the Khibiny mass, U.S.S.R. Soil developing on the slopes in the Kailua area are kaolinitic, and montmorillonite occurs where the topography flattens. Good drainage causes intense leaching and oxidation which favors kaolin formation, and poor drainage favors retention of bases and silica forming montmorillonite (Uehara and Sherman, 1956).

Results of the soil analyses were compared with a soil map (Figure 6) compiled by Foote, et al. (1972) of the U.S. Department of Agriculture. All samples with chlorite-montmorillonite as the dominant clay correspond to a montmorillonitic area on the map; all except one kaolinitic sample correspond to iron oxide-rich areas. The one exception (S-5) is probably a local variation in the soil. The soil map illustrates that the eastern half of the Kailua Volcanic Series is dominantly montmorillonitic and the

Figure 6. Soil Map of Keolu Hills and Surrounding Areas (after Foote, _et_ _al_., 1972).


157° 46' 30"
21° 24' 15"
157° 41' 30"
21° 24' 15"
N
SCALE
1 0 1 MILE
1 0 1 KILOMETER
LEGEND
kaolinitic ▤
montmorillonitic ▥
iron oxide-rich ▨
mixed ▩
calcium carbonate
rock
landfill
poorly drained
water ☐
21° 20' 00"
157° 46' 30"
21° 20' 00"
157° 41' 30"

western half rich in iron oxide minerals (and probably kaolinite). This difference of weathering from the same parent rock may be explained by variations occurring in the local topography. The eastern part of the area is generally lower and less well drained than the western part. The locally dominant clay results from the amount of leaching and oxidation and from the amount of bases and silica retained in the soil.

Amygdule Samples

In the Kailua amygdaloidal basalts, Eakle (1931) identified calcite, quartz, opal, aragonite, and the zeolites heulandite, epistilbite, laumontite, and ptilolite (mordenite). Macdonald and Abbott (1970) include nontronite as occurring in this area. Other studies of zeolites on Oahu (Hay and Iijima, 1968; Iijima and Harada, 1969) show that the principal zeolites occurring as cements in palagonite tuffs are phillipsite, gismondine, chabazite, gonnardite, natrolite, analcime, faujasite, and thomsonite. Iijima and Harada (1969) found a regular succession of zeolite formation from K zeolites to Ca-Na zeolites to Na zeolites because of a gradual change in composition of percolating groundwater through the tuffs during palagonitization.

Many earlier zeolite studies have been associated with amygdules. Stoiber and Davidson (1959) studied the amygdule minerals of the Portage Lake lava series in Michigan. In examining the three overlapping mineral zones, they found that zone boundaries cross stratigraphic horizons, indicating that the amygdule minerals were deposited after many of the flows extruded from the vent. The most widespread Portage Lake zeolite is laumontite; analcite, thomsonite, natrolite, chabazite, and heulandite have a more restricted distribution. Coombs, et al. (1959) found the zeolite facies of the New Zealand Geosyncline to be of regional extent. From zeolite occurrences they reached two broad generalizations: (1) the water content increases for lower temperatures of formation in accordance with theoretical expectations; and (2) the zeolites can be divided into three groups based on silica content (Figure 7). These groups are: (A) highly siliceous zeolites which are stable in solutions supersaturated in silica with reference to quartz; (B) zeolites which coexist with quartz; and (C) silica-poor zeolites favored by an environment lacking in free silica. Two of the three zeolites found in Keolu Hills fall into the second category--phases coexisting with quartz. Chabazite has a general tendency to be undersaturated with respect to quartz, but Coombs, et al. (1959) point out that many exceptions do exist. T. C. Walker and Parsons (1922, in Coombs, et al., 1959) have reported the association of quartz with chabazite from the Nova Scotia traps. G. P. L. Walker (1960) studied the well-marked

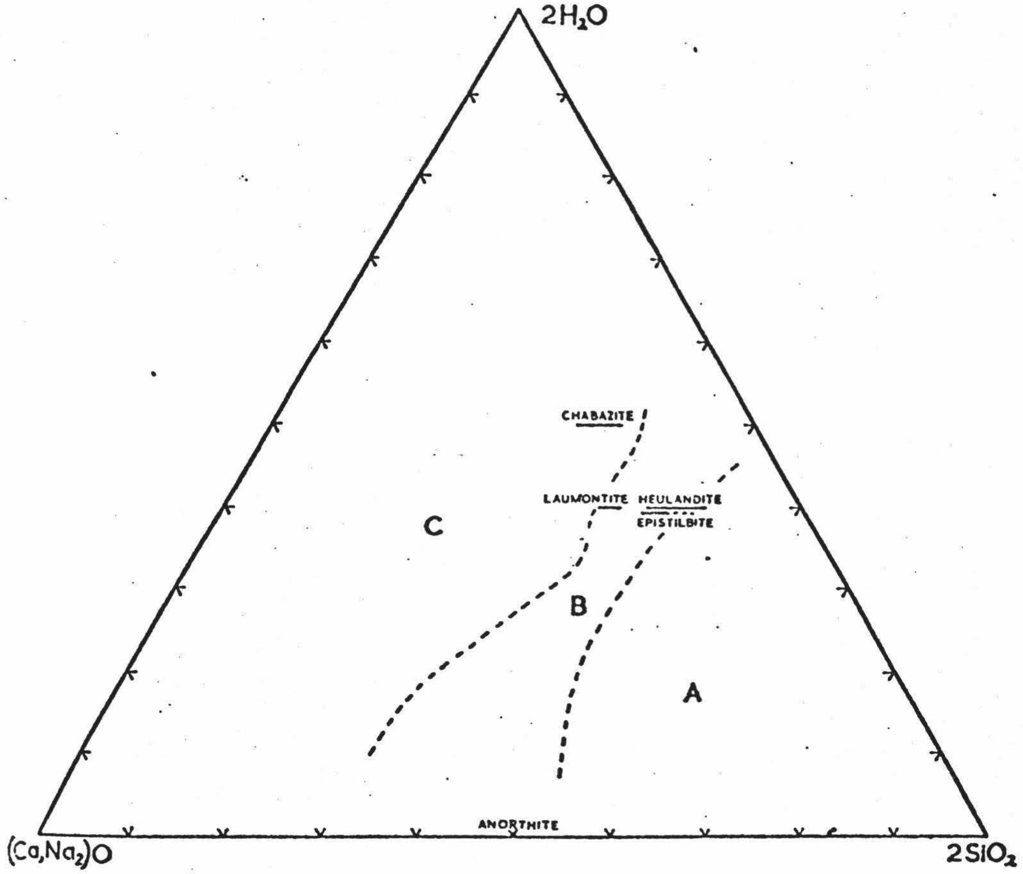


Figure 7. Composition in molar proportions of lime-rich zeolites. A. Field of phases favored by supersaturation in silica. B. Field of phases which can commonly coexist with quartz. C. Field of phases favored by a silica-deficient environment. (after Coombs, et al., 1959.)

zonal distribution of the amygdule minerals in the Tertiary basalts of eastern Iceland. Like the amygdule minerals of Michigan, these minerals occupy flat-lying zones which bear no relationship to the stratigraphy of the lava pile. The regional distribution of zeolites in the olivine-basalts forms three zones: (1) a lowest zone rich in mesolite and scolecite, with an abundance of laumontite at the lower depths, extending from below sea level to an altitude of about 2,500 feet; (2) a middle zone characterized by analcime having a thickness of about 500 feet; and (3) a highest zone comprising mostly chabazite and thomsonite extending up to the top of the mountains. The regional distribution of zeolites in tholeiite lavas is divided into two zones. The lower zone, extending to 1,000 feet above sea level, is characterized by an abundance of stilbite, heulandite, scolecite, and epistilbite. In this zeolite-rich zone quartz and chalcedony are common associations. The higher, zeolite-poor zone extends to an altitude of 2,500 feet and contains chalcedony, quartz, and mordenite, with widespread chlorophaeite and celadonite.

The amygdules of the present study are composed of calcite, quartz, chabazite, heulandite, and the dominant zeolite laumontite. The zeolites found in the Kailua Volcanic Series are calcium zeolites (Coombs, et al., 1959). The calcium zeolites are complex because of their great number of possible phases and the considerable range of composition of a single phase. Some of the possible compositions of the calcium zeolites which occur in Keolu Hills are listed in Table 7. Coombs, et al. (1959) experimented with zeolite syntheses. Their data suggest that laumontite, the dominant Kailua zeolite, may be stable near 300°C. G. P. L. Walker (1960) found that the position of the top of a lava pile can be deduced remarkably well from the zeolite zones. In his studies, laumontite, the dominant Kailua zeolite, is found low within the pile of olivine-basalts. The lowest zone extends to about 2,500 feet above sea level, and the higher zones reach thicknesses of at least 1,000 feet. From these observations, the predominance of laumontite in Keolu Hills suggests a former overburden of lava as much as 3,500 feet thick.

The zeolites of Keolu Hills were probably formed considerably after the eruption and initial cooling of the lavas of the Kailua Volcanic Series because of their association with secondary minerals. In addition, studies by Stoiber and Davidson (1959) and G. P. L. Walker (1960) have demonstrated that amygdule zone boundaries cross lava stratigraphy. The heat to support zeolitization was supplied by dikes, by the slow accession of heat from the magma below, and by exothermic hydration of the lavas themselves (Macdonald and Abbott, 1970). The lavas supplied the cavities and chemical raw materials for formation of the zeolites. The zeolites created by the hydrothermal activity

Table 7

Possible Compositions of Three Calcium Zeolites
(after Coombs, *et al.*, 1959)

zeolite	composition
heulandite	An*+ 8 SiO_2 + 8 H_2O; An + 5 SiO_2 + 6 H_2O;
	An + 4 SiO_2 + 5.3 H_2O; An + 3.2 SiO_2 + 4.8 H_2O.
chabazite	An + 3.2 SiO_2 + 7.2 H_2O; An + 1.3 SiO_2 + 5.3 H_2O.
laumontite	An + 2 SiO_2 + 4 H_2O.

*An = anorthite = $CaAl_2Si_2O_8$.

are calcium zeolites having a silica content which allows them to coexist with quartz. The widespread occurrence of laumontite suggests the following conditions existed during formation of this zeolite: (1) the temperature at the present level of the flows within the caldera was not more than 300°C during zeolitization; and (2) the thickness of these caldera basalts ranged up to 3,500 feet above sea level.

GENERAL SUMMARY AND CONCLUSIONS

The Kailua Volcanic Series occurs in a deeply eroded caldera on southeastern Oahu. The basalt is characterized by amygdules and a chloritized appearance due to hydrothermal alteration. The three clay types found in the altered rock form two types of zones: (1) a vertical zonation between chlorite (lower) and chlorite-vermiculite (higher) at elevations greater than 150 feet; and (2) a horizontal zonation between an inner chlorite-montmorillonite and outer chlorite (or chlorite-vermiculite) aureole. The cause of the vertical zonation is a change in the chemistry of the hydrothermal solutions as they ascend through the flows. Increasing temperatures and pressures with increasing depth result in a lower incidence of expandable layers (e.g., chlorite). The horizontal zoning is the result of higher temperatures at the center of the caldera and a change in the hydrothermal solutions as they migrated from the central area.

The clay mineralogy of the soil bears no correlation to the clays of the parent material. The soil clays, chlorite-montmorillonite and kaolinite, are the result of differences in drainage during the weathering process. The better drained areas, found on the western half of the Kailua Volcanic Series, intensify leaching and oxidation, producing kaolinite. Areas of poorer drainage on the eastern half of the series retain bases and silica, forming a montmorillonitic soil of chlorite-montmorillonite.

The amygdule minerals consist of quartz, calcite, and three calcium zeolites--laumontite, heulandite, and chabazite. Laumontite and heulandite typically coexist with quartz, and the association of chabazite with quartz has been reported (Walker and Parsons, 1922, in Coombs, *et al.*, 1959). Laumontite is by far the dominant zeolite in Keolu Hills. From mineral synthesis experiments of Coombs, *et al.* (1959) it is probably stable at temperatures of 300°C. In Iceland (Walker, 1960) laumontite occurs deep in olivine-basalt lavas 3,500 feet below the top of the series of flows. The widespread distribution of laumontite in the Kailua Volcanic Series may have been vertically zoned, occurring at temperatures of not more than 300°C and at depths of about 3,500 feet below the floor of the caldera. This suggests that within a timespan of about 2 million years, the work of waves, rains, and streams has eroded nearly 3,500 feet of the weakened caldera basalts.

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