

## Hydrothermal mineralogy of Keolu Hills, Oahu, Hawaii<sup>1</sup>

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### Abstract

The mineralogy of the hydrothermally altered basalts of the Kailua Volcanic Series from Keolu Hills, Oahu, Hawaii, was examined by X-ray diffraction analysis. Vertical and horizontal clay-mineral alteration zones were found. In the vertical zones, mixed-layer chlorite-vermiculite occurs more commonly than chlorite, whereas in the horizontal zones, mixed-layer chlorite-montmorillonite and chlorite are both more common. The occurrence of the two clay minerals kaolinite and mixed-layer chlorite-montmorillonite in the soil is not related to the parent rock but to differences in drainage. The zeolites are calcium zeolites which commonly coexist with quartz; laumontite is the dominant zeolite in the study area. The widespread distribution of laumontite 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.

### Introduction

Keolu Hills is located about 1250 m inland from the coast of Kailua Bay, with elevations ranging from 10 to 130 meters. Rainfall averages about 40 inches per year. 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 from the study area (Macdonald, 1973). Residential development and road construction within the study area has facilitated sampling, by exposing fresh rock on ridges that once were inaccessible. The purpose of this study was to analyze the mineralogical composition of the hydrothermally altered Keolu Hills basalts by X-ray diffraction, to determine if clay-mineral alteration produced zoning in those rocks, and to correlate the mineralogy with previous studies of hydrothermal alteration.

Eakle (1931) identified many of the amygdule minerals in the Kailua Volcanic Series, of which the Keolu Hills basalts 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 some Waimanalo samples. From soil surveys of the Hawaiian Islands, Foote *et al.* (1972) produced a detailed soil map of Keolu Hills and a brief mineralogical description of each soil type.

The Koolau volcano erupted about 2 to 2.6 million years ago (McDougall, 1964). The lavas of the Waimanalo-Kailua Kaneohe series are notably more massive and less permeable than the rocks of the Koolau Volcanic Series. For that reason and because of their relatively low topographic position, Stearns and Vaksvik (1935) believed they represented 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 (Fig. 1). They realized that, instead of being older than the adjacent Koolau Volcanic Series, the rocks of the Kailua Volcanic Series actually are 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 rose through the lavas from the magma chamber below (Macdonald and Abbott, 1970), weakening the dense basalts to easily erodable material. When eruption of the

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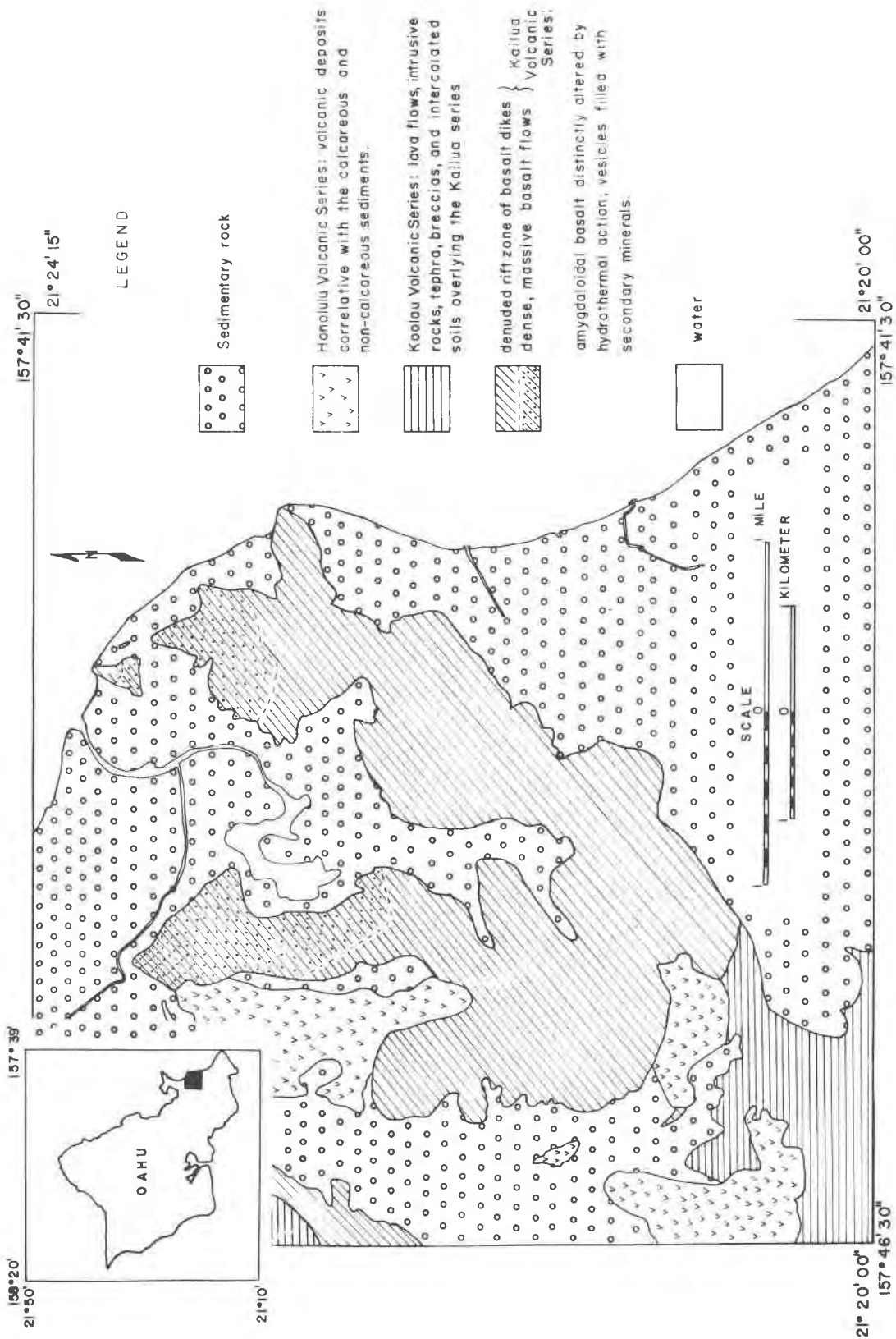


Fig. 1. Geologic map of Keolu Hills and surrounding areas (after Stearns and Vaksvik, 1935).

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 westward until unaltered rocks were encountered on the western side of the caldera, and erosion slowed considerably. The amphitheater-headed valleys forming the present cliff of the Pali along the northeast coast of Oahu mark the approximate boundaries of the Koolau caldera.

Outcrops of the Kailua Volcanic Series consist of flows of aa and pahoehoe basalt up to 60 feet thick. The basalts are amygdaloidal and altered by hydrothermal action. As a result, the joints and vesicles are virtually filled with quartz, zeolites, and other secondary minerals, leaving the rock almost impermeable (Stearns and Vaksvik, 1935). The lava flows have been deformed into a gentle elliptical basin with its center positioned west of Kailua (Fig. 1). The Keolu Hills lie on the southern flank of the basin and the lava flows in them dip north to northwestward at angles generally less than 20°, except near Alala Point (locations A-11 and W-14, Figure 2) where the beds dip gently southwestward. The lavas are cut by numerous dikes, most of them nearly vertical and trending 230°–250°; they range in width from a few inches to 8 feet.

#### Sample locations

Samples were collected from amygdaloidal rocks in the Keolu Hills. Sample sites are shown in Figure 2. 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 fill the entire cavity, and as a result the crystals are generally small.

#### Laboratory procedures

All samples were ground to a fine-clay grain size by one hour of wet grinding. 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. 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 in a desiccator to prevent hydration and curling of samples.

The oriented slides were X-rayed using a Norelco diffractometer with copper  $K\alpha$  radiation at 35 kilo-

volts and 20 milliamperes. Although the quantitative accuracy of X-ray diffraction data is highly variable, relative mineral abundances appear to be reliable. A semiquantitative percentage of each mineral was calculated, 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 1 and 2. The rock and soil samples contained quartz, cristobalite, and plagioclase feldspar, and occasionally augite, hematite, and calcite, but the clay minerals constituted the bulk of the material studied. Brown's (1972)  $d$ -spacing tables were used for the identification for most of the minerals. Bradley and Weaver's (1956) criteria were used for identification of chlorite-vermiculite. Earley and Milne's (1956) and Earley *et al.*'s (1956) criteria were used for identification of mixed-layer chlorite-montmorillonite.

#### Results

All the clay minerals found in the study (chlorite, mixed-layer chlorite-vermiculite, and mixed-layer chlorite-montmorillonite) have been previously reported in hydrothermal bodies (Kerr, 1955; Grim, 1968; Steiner, 1953; Eslinger and Savin, 1973). The mineral assemblage of the chlorite zone in the Matsukawa Geothermal Area, Japan (Sumi, 1969), corresponds closely to that found in Keolu Hills area. 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) indicates formation at low temperatures (Brown, 1972).

The types of clay minerals in the study area and their present elevation (Table 1) were compared to find any indication of vertical zonation. Chlorite is the clay mineral most often found at the lower elevations of the Kailua Volcanic Series. Mixed-layer chlorite-vermiculite generally occurs at a higher level than the chlorite or mixed-layer chlorite-montmorillonite. The differences in the compositions of the clay minerals may be accounted for by variations in the parent rock, in the hydrothermal solutions, in the degree of alteration, and in pressures and temperatures during alteration. In addition, the chemistry of the hydrothermal solutions rising through the rock changes through interaction with the host rock, and clay mineral fronts are formed. Material that is closer to the hot source is often altered to a mineral which is different from that produced farther away. Eslinger and Savin (1973) report that the occurrence of expandable layers decreases with increasing temperature and pressure. This gener-

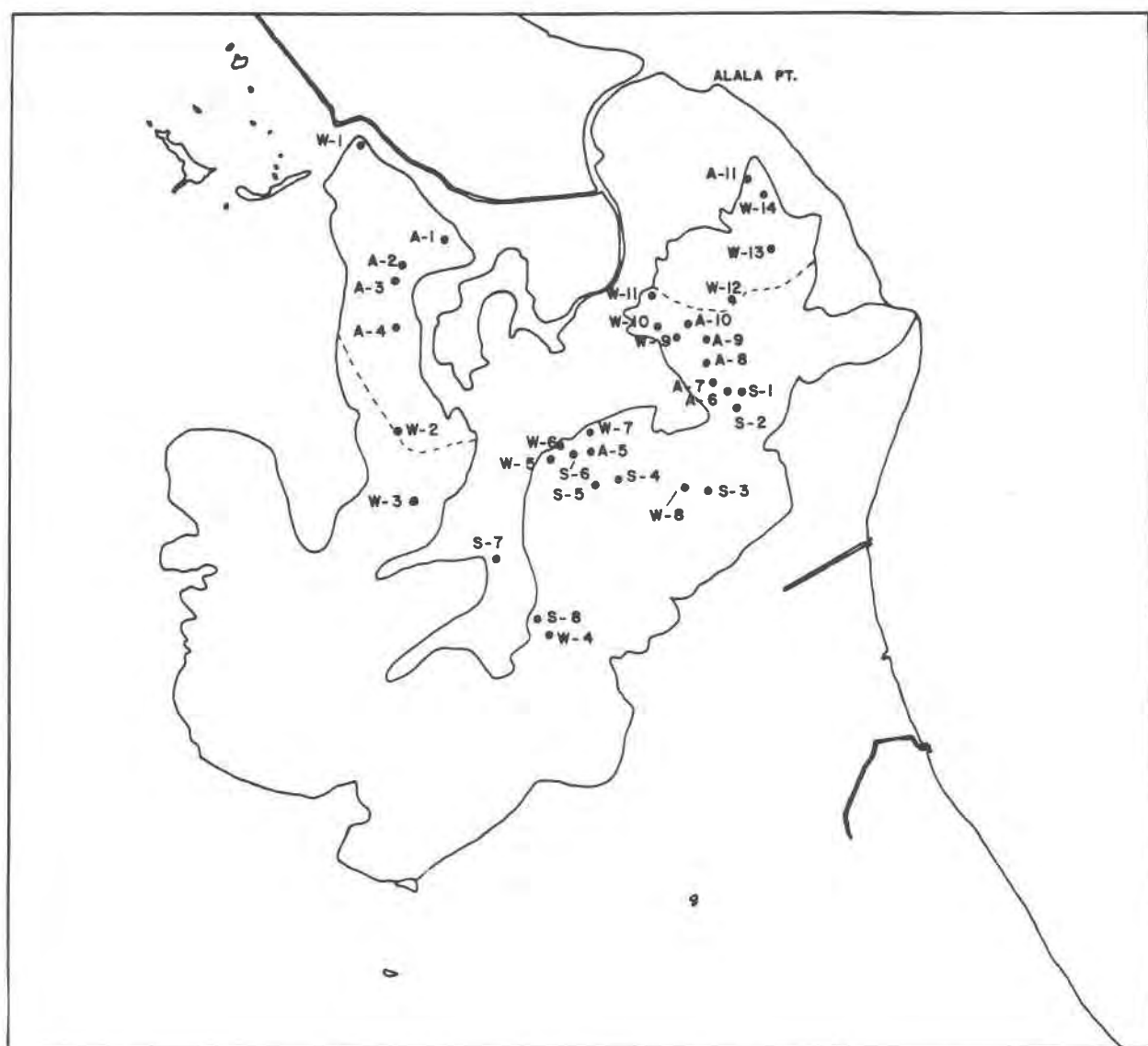


Fig. 2. Location map of rock and soil samples.

alization appears to hold for the vertical zonation of clays in the Keolu Hills: mixed-layer 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 mixed-layer chlorite-vermiculite. However, mixed-layer chlorite-montmorillonite occurs only at four closely grouped sites (A-2, A-3, A-4, and W-3, Fig. 2). (Because W-3 is a weathered sample, the mont-

morillonite at this site may be a product of weathering.) The study area appears to represent two horizontal zones of hydrothermal alteration: an inner mixed-layer chlorite-montmorillonite zone and an outer chlorite/mixed-layer chlorite-vermiculite zone. The inner zone of the former suggests a transition from a dominantly montmorillonite zone to a chlorite zone. The abundance of chlorite in both zones indicates that the Keolu Hills area is situated at the outer limits of hydrothermal activity. The positions of the inner zone sites suggests that if more intense alteration zones exist, the zones are situated generally north of the study area.

The clay mineralogy of the study area delineates

Table 1. Mineral composition of rock samples from Keolu Hills, Oahu, Hawaii

Sample No.	Minerals													Elevation (feet)
	Chlo.	Ch-Ve.	Ch-Mo.	Kaol.	Mica	Mont.	Calc.	Iim.	Quar.	Plag.	Augi.	Hema.	Side.	
W-1	--	A	A	--	T	--	--	--	--	T	--	--	--	40
A-1	C	--	--	--	T	--	--	--	T	P	T	--	--	80
A-2	--	--	A	--	T	--	--	--	--	T	--	--	--	120
A-3	--	--	A	--	--	--	--	--	T	T	--	T	--	120
A-4	--	--	A	--	T	--	--	--	T	--	--	--	--	160
W-2	--	C	--	--	T	--	--	--	T	P	T	T	--	200
W-3	--	--	A	--	--	--	--	--	T	T	T	T	--	200
W-4	A	--	--	--	T	--	--	--	T	T	T	T	--	120
W-5	--	A	--	--	T	--	--	--	T	T	--	T	--	120
W-6	--	P	--	--	T	--	--	--	T	C	T	P	--	120
A-5	C	--	--	--	T	--	--	--	T	P	T	T	--	200
W-7	C	--	--	--	T	--	--	--	T	P	T	--	--	150
W-8	P	P	P	--	--	--	--	--	P	C	T	--	--	200
A-6	C	--	T	--	--	--	--	--	T	P	T	--	--	200
A-7	--	C	P	--	T	--	T	--	T	P	T	T	T	160
A-8	--	C	--	P	T	--	--	--	P	P	T	--	--	120
A-9	--	P	--	T	--	--	--	--	P	C	T	T	--	160
A-10	A	A	A	--	--	--	--	--	T	T	--	--	--	280
W-9	--	A	--	--	T	--	--	--	T	T	T	T	T	260
W-10	--	P	--	--	T	--	--	--	P	P	T	P	--	140
W-11	--	A	--	--	--	--	--	--	--	T	--	T	--	80
W-12	P	P	P	--	--	T	--	T	T	C	T	T	--	600
W-13	T	T	--	T	--	--	--	--	P	C	T	--	--	560
W-14	A	--	--	--	--	--	--	--	T	T	T	T	--	160
A-11	A	--	--	--	T	--	--	--	T	T	--	--	--	120

Note: A -- Abundant                      P -- Present  
 C -- Common                              T -- Trace

the vertical and horizontal alteration zones resulting from hydrothermal activity within the former caldera. The zones were formed by the reaction between the preexisting rock and chemically changing hydrothermal solutions. In addition, the vertical zones are apparently affected by increasing temperatures and pressures with depth; this covariance decreases the amount of expandable layers in the mixed-layer clay minerals. This covariance suggests that the variables controlling the mineral zoning are temperature and pressure.

### Soil samples

The clay minerals in the Keolu Hills soil consist of mixed-layer chlorite-montmorillonite and kaolinite (Table 2), the weathering products of the Kailua Volcanic Series. Chlorite or mixed-layer chlorite-vermiculite occur as hydrothermally altered clay minerals.

According to Grim (1968), the factors controlling the weathering processes are parent rock, climate, topography, vegetation, and time. Since all soil sam-

Table 2. Mineral composition of soil samples from Keolu Hills, Oahu, Hawaii

Sample No.	Minerals										
	Chlo.	Chl-Mont.	Chl-Ver.	Kaol.	Mica	Verm.	Cris.	Hema.	Iim.	Plag.	Quar.
S-1	--	--	C	T	T	--	--	--	--	P	T
S-2	--	--	C	P	--	--	--	--	--	T	T
S-3	C	--	--	P	--	--	--	--	--	P	P
S-4	P	P	P	T	--	--	--	--	--	P	C
S-5	--	--	--	C	--	--	--	P	--	T	P
S-6	--	--	--	C	--	--	T	T	--	--	P
S-7	--	--	--	C	--	--	T	--	T	--	P
S-8	--	--	--	--	--	A	--	T	--	P	T

Note: A -- Abundant                      P -- Present  
 C -- Common                              T -- Trace

ples in the Kailua Volcanic Series are weathered products and the area from which they were collected is small, most of these factors may be eliminated. It would appear that the character of the drainage accounts for the different weathering products found here as well as 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) concluded that good drainage would result in the formation of kaolinite, and poor drainage that of montmorillonite. Soil developing on the slopes in the Kailua area are kaolinitic, indicative of good drainage and resultant intense leaching and oxidation, whereas montmorillonite occurs where the topography flattens and the poor drainage favors retention of bases and silica (Uehara and Sherman, 1956).

Results of the soil analyses were compared with a soil map (Fig. 3) compiled by Foote *et al.* (1972). All samples with mixed-layer chlorite-montmorillonite as the dominant clay were located in the areas designated as montmorillonitic on the map. The soil map shows that the eastern half of the Kailua Volcanic Series is dominantly montmorillonitic and that the western half, rich in iron oxide minerals, is probably kaolinitic.

#### Amygdule samples

In the Kailua amygdaloidal basalts, Eakle (1931) identified calcite, quartz, opal, aragonite, and the zeolites chabazite, 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 progression of zeolite formation, from K zeolites to Ca-Na zeolites to Na zeolites, because of the gradual change in the composition of the groundwater percolating through the tuff during palagonitization.

Many earlier zeolite studies involved amygdules. 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. These groups are: (a) highly siliceous zeolites which

are stable with reference to quartz in solutions supersaturated in silica; (b) zeolites which coexist with quartz; and (c) silica-poor zeolites favored by an environment lacking in quartz. Two of the three zeolites (laumontite and heulandite) found in Keolu Hills fall into the second category—phases coexisting with quartz. Walker (1960) studied the well-marked zonal distribution of the amygdule minerals in the Tertiary basalts of eastern Iceland. He divided the regional distribution of zeolites in the tholeiite lavas 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 a common association. The higher, zeolite-poor zone extends to an elevation 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 calcium zeolites are complex because of the great number of possible phases and the considerable range of composition of a single phase. Coombs *et al.* (1959) experimented with zeolite syntheses. Their data suggest that laumontite may be stable near 300°C. 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 the position of laumontite within the pile is found to be low. 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 the Keolu Hills outcrops suggests a former overburden of lava as much as 3,500 feet thick.

Because of their present-day association with secondary minerals, the zeolites of Keolu Hills were probably formed considerably after the eruption and initial cooling of the lavas of the Kailua Volcanic Series. Studies by Stoiber and Davidson (1959) and Walker (1960) have demonstrated that amygdule zone boundaries cross lava stratigraphic boundaries. The heat to support zeolitization is 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). Calcium zeolites having a silica content which allows them to coexist with quartz are created by hydrothermal activity. The widespread occurrence of laumontite suggests that the following conditions existed during its formation: (1) the temperature within the caldera was not greater than 300°C during zeolitization; and (2) the thickness

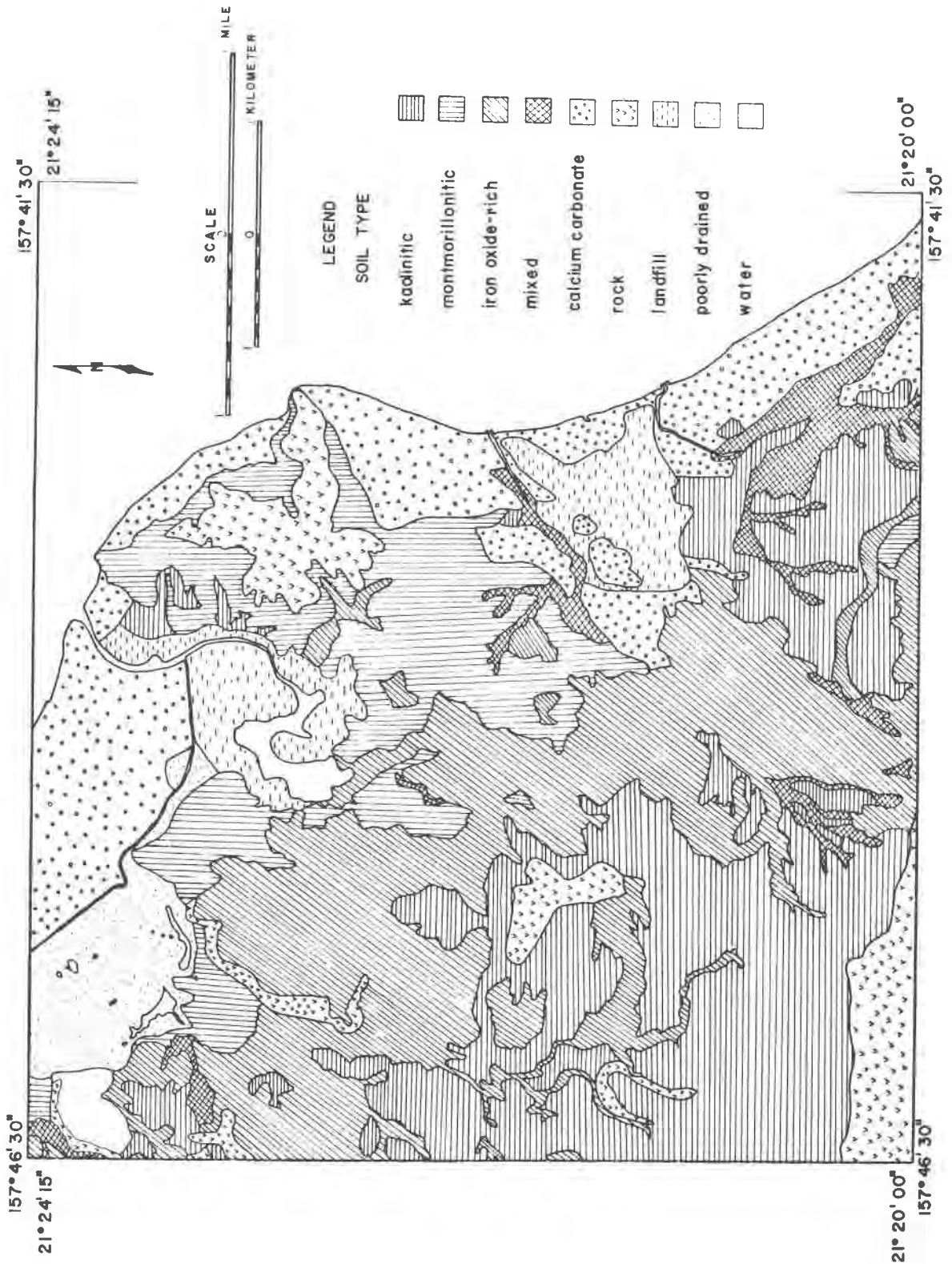


Fig. 3. Soil map of Keolu Hills and surrounding areas (after Foote *et al.*, 1972).

of the caldera basalts ranged up to 3,500 feet above sea level.

### Conclusion

The Kailua Volcanic Series occurs in a deeply eroded caldera on northeastern Oahu. The basalts are 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 zonal boundary between chlorite (lower) and mixed-layer chlorite-vermiculite (higher) at elevations greater than 150 feet; and (2) a horizontal zonation between mixed-layer chlorite-montmorillonite and chlorite (or mixed-layer chlorite-vermiculite) aureole. The zonations were caused by changes that took place in the chemistry of the hydrothermal solutions as the solutions progressed through the flows. Increasing temperatures and pressures with increasing depth resulted in a lower incidence of expandable layers (e.g., chlorite). The horizontal zoning corresponds to a model where higher temperatures occur at the center of the caldera and a change in the hydrothermal solutions occurs as the solutions migrate upward and outward from the central area.

The clay mineralogy of the soil bears no correlation to the clay mineralogy of the parent material. The soil clays, mixed-layer 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 mixed-layer chlorite-montmorillonite.

The amygdule minerals consist of quartz, calcite, and three calcium zeolites—laumontite, heulandite, and chabazite. Laumontite and heulandite typically coexist with quartz. Laumontite is by far the dominant zeolite in Keolu Hills. 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 top of the caldera. This suggests that within a time span of about 2 million years, the work of waves, rain, and streams has eroded nearly 3,500 feet of the weakened caldera basalts.

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