The Iron and Titanium Minerals in the Titaniferous Ferruginous Latosols of Hawaii[1]

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ABSTRACT: Titaniferous Ferruginous latosols are an important group of Hawaiian soils. They have developed by pedogenetic weathering of the volcanic materials of basic and ultrabasic lava flows and their associated pyroclastic materials, under climatic conditions having definite alternating dry and wet seasons. The annual rainfall range for these soils is 30 to 60 inches. Under the native and undisturbed vegetation, these soils have a profile of very friable silt material with very little horizon differentiation. When exposed to dehydration by removal of the protective canopy cover of the forest, as occurs after forest fires, a tremendous change occurs in the soil profile morphology. The change is greater than the morphological differences which normally occur between the profiles of the Great Soil groups. A surface indurated horizon develops in which the bulk density and particle density have an approximate two-fold increase. The mineralogical changes are substantial. The amorphous hydrated titanium and iron oxides are converted into good crystalline forms of anatase, rutile, pseudo-brookite, titanohematite and titanomaghemite. In some cases these minerals develop from the weathering of titanomagnetite-ilmenite mixed crystals. The unusual characteristic of these soils is the apparent movement of the colloidal material in a very short space of time, which results in an accumulation of titaniferous minerals in the indurated surface horizon and the accumulation of amorphous silica giving weak X-ray diffraction patterns of alpha quartz on the very surface of the soil. Rutile is also identified along with the silica at the surface. Aluminum oxides are removed to the lower horizons and in some cases accumulated as irregularly shaped gibbsite nodules in scattered pockets below the clay horizon.

TITANIFEROUS FERRUGINOUS LATOSOLS include soils which have horizons rich in titanium and iron oxides. This group of soils has formed from the basic and ultrabasic lavas and pyroclastic materials of the post-erosional volcanic activity which has occurred on the geologically old islands of the Hawaiian group. There is strong evidence that the formation of these soils may be limited to the pyroclastic materials of post-erosional origin. The pedogenetic weathering of the original primary minerals evidently has been intense, as all of the silicate minerals have been completely decomposed. Leaching has been thorough and unimpeded, as the bases have

been removed to an extremely low level. These soils have attracted much attention because of the marked changes which occur in their chemical, physical, and mineralogical composition when they have become exposed and are dehydrated by the removal of their forest canopy and tall grass cover by fire, over-grazing, or other activities of man. The profile morphology of the soil changes from a friable silt profile having little horizonal differentiation and similar to Reddish Prairie profile to one having an indurated high bulk density surface horizon and a morphology similar to that described for the laterite profile formed *in situ*. These soils have been studied and described by several workers—Fujimoto et al. (1948), Katsura et al. (1962), Sherman et al. (1948), Sherman et al. (1953), and Tamura et al. (1955).

The purpose of this paper is to identify some of the mineralogical changes which result from

exposure and dehydration, and to describe the processes leading to the marked changes in morphology and in physical and chemical properties which also occur. This report constitutes the third study of these profiles but the second in which mineral identification has been attempted. Fujimoto et al. (1948), Tamura et al. (1955), and Sherman et al. (1948) reported studies on profiles of slope bench above and below the site from which this sample was taken. Sherman et al. (1953) conducted studies on this same site.

DESCRIPTION OF THE AREA AND PROFILES

The profiles sampled were located just off the Kekaha-Kokee road near the lower boundary of the forest reserve in the Waimea district on the island of Kauai, Hawaii, and on the edge of Kokee Canyon. This area is located on a long, gentle slope not exceeding 15°. The gentle slopes break to benches of much lesser angle of slope and it is on these benches that greatest soil development occurs. In an upslope direction, rainfall gradually increases to over 150 inches per year. Downslope it decreases to less than 30 inches per year. In the sample area, the climate is definitely wet-dry and has an annual average rainfall of about 60 inches.

Vegetative cover was removed from a part of this area about 35 years ago by burning and over-grazing. There has been steady loss of vegetation due to erosion and induration of the area. Erosion has eaten its way in upslope direction leaving behind small hummocks of soil held together by the dead or dying roots of small trees and shrubs (Sherman et al., 1948). With the increasing destructive spread of the bare area, the friable surface horizons of the soil become indurated and particle density increases markedly (Table 1). This induration does not reach the degree of that occurring in the typical laterite, for the massive horizon can be crumbled with some effort into smaller particles, after which the whole, excepting concretions, is readily reduced to a very fine dust. The subsoil portions of both the indurated and the vegetatively covered areas are quite similar in all respects. They have extremely low bulk densities and are very friable, so much so that it is difficult to preserve clods for the bulk density deter-

minations. Once erosion has worked through the indurated bare soil horizons, it cuts through the friable subsoil with ease and progresses rapidly upslope by undercutting and causing the collapse of the indurated surface, much in the manner of stream erosion in areas having layers of alternating hard and soft rock.

Since 1947, this site has been under constant observation. It was first described by Sherman et al. (1948) and then later by Sherman et al. (1953). The latter described the marked difference in morphological, physical, and chemical characteristics which existed between the vegetated and bare profiles of adjacent soil profiles at this site. Tamura et al. (1955) reported the first mineral identification in a bare profile of this soil from a similar profile on slope bench above this site.

EXPERIMENTAL PROCEDURES

Field

Six profiles having as their basal lower limits a continuous clay pan were collected at the upslope boundary of the bare indurated soil area. Two of these soil profiles were sampled in detail. One of them (N-1 to N-10) was vegetatively covered and was located in the zone where trees are now dying out but where shrubs and grasses still exist. The other (N-11 to N-19) was an indurated profile, bare of vegetation, located in the indurated zone and just 6 feet from the covered profile (N-1 to N-10). This bare profile was vegetatively covered only 8 years ago, just as N-1 is today, and at that time Sherman et al. (1953) found its morphological characteristics to be identical with the vegetatively covered profile of this study (N-1 to N-10). They also compared this profile with another which had no vegetation and possessed an indurated surface similar to that of the bare profile of this study (N-11 to N-19). Erosion has now destroyed this earlier profile site, and the progressive loss of vegetation and subsequent surface induration has progressed to the site of the bare soil of this study. It is difficult to comprehend the rapid changes which occur in these soils, transforming the morphology of a soil profile from one possible Great Soil Group to another in a period of 6 to 12 months. Each

TABLE 1

SOME OF THE PHYSICAL AND CHEMICAL CHARACTERISTICS OF TWO NAIWA SOIL PROFILES, ONE WITH THE VEGETATIVE COVER AND THE OTHER EXPOSED AND INDURATED, OCCURRING ONLY SIX FEET APART ON KOKEE CANYON ROAD JUST INSIDE FOREST RESERVE

SAMPLE	DEPTH (inches)	MUNSELL COLOR		pH	C.E.C.* Meq/100g	ORGANIC MATTER %	BULK DENSITY	PARTICLE DENSITY	PORE SPACE %	H₂O %	LOI 800°C %
		WET	DRY								
				Vegetation-Covered Profile							
N-1	0–1	2.5YR2/4	2.5YR3/4	5.2	26.1	11.8	1.7	2.98	43	6.0	25.3
N-2	1–3	2.5YR2/4	2.5YR2/4	5.0	20.5	11.9	1.9	3.23	41	5.3	20.9
N-3	3–6	2.5YR3/4	2.5YR3/4	5.0	46.2	21.9	0.8	2.69	70	12.0	44.4
N-4	6–9	2.5YR3/4	5YR4/8	5.1	38.1	21.1	1.1	2.61	57	16.4	48.7
N-5	9–14	2.5YR3/4	2.5YR4/6	5.0	45.6	19.0	0.8	2.67	70	17.0	49.7
N-6	14–20	2.5YR3/4	2.5YR4/6	5.0	42.4	18.9	0.9	2.63	67	18.1	51.7
N-7	20–25	2.5YR3/6	5YR4/5	5.0	32.7	16.0	0.8	2.66	70	16.8	44.9
N-8	25–31	2.5YR3/6	5YR4/6	4.9	38.3	15.5	0.9	2.61	67	16.1	47.6
N-9	31–38	10R3/4	10R4/4	5.0	24.1	13.4	1.7	2.86	42	14.5	32.5
N-10	38+	5YR3/3	5YR4/2	5.2	16.4	3.5	1.7	2.87	42	9.7	26.2
				Bare and Indurated Profile							
N-11	0–1	10R3/1	10R3/2	5.1	4.2	1.8	2.0	4.24	54	0.9	3.6
N-12	1–3	10R2/2	10R3/2	4.4	1.8	2.1	1.7	4.15	60	1.4	5.0
N-13	3–6	5YR3/3	5YR3/3	4.3	5.6	2.2	1.8	4.09	56	2.9	9.1
N-14	6–10	10R3/2	10R3/3	4.4	7.5	2.8	1.8	4.15	58	3.0	11.1
N-15	10–12	7.5R2/2	7.5R3/2	4.7	24.0	7.0	1.4	3.28	56	7.7	23.8
N-16	12–15	10R3/3	10R3/4	4.8	43.5	17.3	0.9	2.73	67	14.3	45.3
N-17	15–19	2.5YR3/5	2.5YR4/8	4.6	48.0	17.2	0.9	2.63	66	16.9	51.4
N-18	19–25	2.5YR3/6	2.5YR4/8	5.0	27.2	11.7	1.7	2.83	41	15.0	35.9
N-19	25+	10R3/3	10R3/6	5.1	14.8	2.6	1.7	2.92	43	8.8	24.3

* C.E.C. = Cation exchange capacity.

site has been carefully observed and documented.

The remaining five profiles were sampled in two-story portions—surface and friable subsoil —so as to provide a study of progressive transformations in the soil horizons on a horizontal plane extending from the bare area to the vegetated area. All of the sampling sites were within 10 feet of N-1, the vegetatively covered profile. The samples, in order of increasing induration and exposure are as follows: 4A to 4B and 3A to 3B, both of which were under grass only; 1A to 1B, which was under patchy dying grass; and 2A to 2B and 1X to 1Z, which were completely exposed. These five profiles were not more than 2 feet apart.

It is essential to the discussion which follows to keep in mind the fact that the presently bare, indurated profiles were all originally covered with vegetation and, less than 8 years earlier, were similar in all respects to the present vegetatively covered soils (Sherman et al., 1953). The physical, chemical, and mineralogical differences between the present bare, indurated soils and the vegetatively covered profiles have all developed in this short period of time.

Sherman et al. (1948) and Sherman et al. (1953) pointed out the speed with which induration occurs after the removal of the vegetative cover. Experimental observations of denuded areas have shown definite surface induration within 6 months after exposure.

Laboratory

After collection, all of the soil samples were air dried for one month at room temperature (about 80°F) and humidity (about 70 percent). Physical measurements followed the methods given in U.S.D.A. Handbook 60 (Richards et al., 1954), except for bulk density which was determined by the waxed clod method. Organic matter determinations were after Walkley-Black (Jackson, 1958; Piper, 1944) and later confirmed by the carbon combustion method. Total wet chemical analyses were by standard methods given by Washington (1930) and Hillebrand et al. (1953), except for ferrous iron which was determined by the method of Walker and Sherman (1962). All other determinations were by methods described by Piper (1944) or by Jackson (1958). Soil color was by Munsell color

value, but it should be pointed out that the values are not exact; no chart was available which would do justice to the intense purplereds of these soils. Differential thermal analyses were made using ignited alumina as the reference standard. Kaolinite number 5 (A.P.I. Standard, Lamar Pit) was used for standardizing the instruments. X-ray diffraction powder studies were carried out on the air-dried samples using a Norelco X-ray diffractometer at the most sensitive setting. No filter was used on the iron tube, so that both K alpha and K beta peaks occur. The increased sensitivity given by this method has been shown to be essential for identification of such minerals as pseudobrookite (Katsura et al., 1962).

RESULTS AND DISCUSSION

The data presented in Table 1 provides a comparison of the physical properties of a Naiwa soil profile under its natural vegetation (N-1 to N-10), and an identical soil profile after it has been denuded by loss of its vegetative cover and its subsequent dehydration (N-11 to N-19). The denudation and dehydration have produced a tremendous change in the morphological characteristics and properties of the soil profile, as is reflected in soil color and bulk densities. The bulk density of the friable portion of the vegetation-covered profile is about 1.0 except in the surface 3 inches. The dense clay of N-9 and N-10 have a bulk density of 1.7. The bulk density (1.9) of the 1–3-inch (N-2) surface layer is higher than was obtained by Sherman et al. (1953). This would indicate that induration has been initiated under the vegetation. The bulk density of the exposed profile is higher to a greater depth (10 inches), with a 2-inch transition layer. Otherwise the bulk density is comparable to the similar horizons of the vegetative profile.

It is important to recognize the loss of volume of the soil with exposure. The depth of profiles have changed considerably—the vegetationcovered profile is 38 inches in depth to the basal clay layer, and the exposed layer is 25 inches. If one uses the bulk density of the soil above the basal clay, the equivalent cut-off point of similarity would be at 22 inches and 10 inches below the surface for the vegetation-covered and

bare profiles, respectively. In other words, the volume of the surface of the original vegetative profile has been reduced by half as a result of exposure, if loss by erosion is ignored. The loss of material by erosion is usually about the first inch or two of the surface.

The changes in particle density are very great, ranging from 2.61 in the vegetative profile to 4.24 at the surface of the indurated layer of the exposed profile. This is a tremendous change over a very short period of time. That the dehydration process is a cause of this change is shown by the loss-on-ignition measurements, which are 44 percent in N-3 of the vegetative profile and 9.1 percent in N-13 of the exposed profile.

Exposure causes a rapid decomposition of organic matter in the exposed indurated layer, as is shown in data presented in Table 1. The organic matter content of the vegetation-covered profile ranged from 11.8 to 21.9 percent in samples N-1 to N-8, the portion of soil above the dense clay layer. In the indurated layer of the exposed

profile (N-11 to N-14), the organic matter content ranged from 1.8 to 2.8 percent. In sample N-15, which is the transition horizon between the indurated and friable horizons above and below, respectively, the organic matter content was 7.0 percent. In the remainder of the profile the organic matter content was similar to that of the vegetation-covered profile.

The cation exchange capacity followed the same trend as organic matter content. It was high in the vegetatively covered profile and very low in the indurated horizons. This has been pointed out by Sherman et al. (1964) as a characteristic property of hydrated amorphous oxides when they are dehydrated and form crystalline oxide minerals such as hematite or gibbsite.

In Table 2 are given the data derived from the chemical analysis of the samples of the horizons of the vegetation-covered and bare profiles of the Naiwa soils. The vegetative profile has a relatively uniform chemical composition, except for the first 3 inches and the dense

TABLE 2

THE CHEMICAL COMPOSITION OF NAIWA SOIL OF THE TITANIFEROUS FERRUGINOUS LATOSOL
LOCATED ALONG KOKEE CANYON ROAD JUST INSIDE FOREST RESERVE

| SAMPLE | DEPTH (inches) | OXIDES IN PERCENT | | | | | | | | | | LOI % |
		SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO	MnO	CaO	MgO	K_2O	Na_2O	
		Profile Having a Vegetative Cover										
N-1	0–1	14.4	13.3	39.2	4.1	8.1	.10	.00	.69	.02	.00	19.3
N-2	1–3	11.4	11.6	47.5	3.9	9.6	.11	.00	—	.06	tr	15.6
N-3	3–6	10.8	20.1	27.9	4.0	3.8	.04	.00	.29	tr	.02	32.5
N-4	6–9	10.3	22.8	26.3	3.7	3.7	.04	.00	.27	tr	.00	32.3
N-5	9–14	12.7	23.3	23.4	4.0	3.2	.03	.00	.22	tr	.03	32.7
N-6	14–20	13.4	26.6	19.5	3.9	2.5	.03	.00	.21	tr	.02	33.6
N-7	20–25	19.7	29.0	18.1	2.2	2.2	.04	.00	.27	.00	.00	28.1
N-8	25–31	16.6	28.2	18.4	2.5	2.3	.05	.00	.21	tr	.00	31.6
N-9	31–38	27.1	30.7	18.1	1.5	3.7	.07	.00	.39	tr	tr	18.0
N-10	38+	26.7	30.5	20.2	1.8	3.5	.08	.00	.46	.00	.00	16.5
		Indurated Profile, Bare of Vegetation										
N-11	0–1	10.0	2.0	58.5	4.0	21.2	.15	.00	1.07	.20	.00	2.7
N-12	1–3	9.2	1.2	63.0	3.2	18.2	.12	.00	.91	.17	.00	3.6
N-13	3–6	5.0	4.4	70.8	1.5	11.8	.07	.00	.45	.00	.00	6.3
N-14	6–10	3.4	6.0	71.3	1.6	8.8	.05	.00	.00	.17	.00	8.0
N-15	10–12	6.3	12.5	57.0	1.9	5.7	.04	.00	.00	.00	.00	16.1
N-16	12–15	8.5	22.2	31.5	3.0	3.6	.02	.00	.14	.00	.00	31.1
N-17	15–19	12.0	25.0	22.1	3.0	3.1	.02	.00	.00	.00	.00	34.4
N-18	19–25	23.5	28.4	21.3	1.9	3.6	.05	.00	.42	.00	.00	20.9
N-19	25+	27.9	28.3	22.0	1.5	3.9	.09	.00	.72	.00	.00	15.5

clay below the friable soil horizons. The upper 3 inches is lower in Al_2O_3 and higher in Fe_2O_3 and TiO_2. In the bare soil, there are tremendous differences between the indurated horizons and the friable subsoil horizons. The SiO_2 has decreased in the entire indurated portion of the profile and in the horizons transitional to the friable horizon. In N-11 and N-12, the SiO_2 content is 10.0 and 9.2 percent, respectively, which is twice as high as that in the massive indurated horizon N-13, but all are lower than that found in corresponding horizonal areas of the vegetation-covered profile. Al_2O_3 is extremely low in the indurated horizons, N-11 to N-14, ranging from 1.2 to 6.0 percent. In the other profile, Fe_2O_3 is much higher for these same horizons, ranging from 58 to 71 percent. Likewise, TiO_2 is much higher, especially in the upper part of the indurated horizon. The content of bases is extremely low in both profiles with only magnesium being present in any appreciable amount.

It is difficult to explain the relationships in chemical composition between the vegetation-covered profile and the bare profile. Equally difficult will be the explanation of the chemical differentiation within the profile without considering the possibility of movement of mineral constituents. It cannot be entirely explained by loss of volume, which undoubtedly plays a role. Fujimoto et al. (1948) found the highest silica concentration in the colloidal fraction of the very surface horizon of this soil, indicating a movement of silica to the surface, probably by capillary action. Fujimoto et al. (1948) and Walker (1964) separated colloidal fractions having a high concentration of both hydrated colloidal iron oxide and colloidal hydrated titanium oxides. The latter amounted to 45 percent of this fraction from the transitional horizon, which corresponds to N-14 in the bare profile of this study. It is believed that the iron oxide and titanium oxides are free oxides in the colloidal fraction, but when they dehydrate they form titanoferruginous oxide minerals by crystallization. Any excess colloidal hydrated titanium oxide and soluble silicate will move toward the surface by capillary action and will be precipitated as titanium oxide (anatase), or as titaniferous ferruginous oxides at or near the surface, and as amorphous silica at the surface by dehy-

dration. Aluminum hydrated oxides move downward in the profile.

Differential thermal analysis indicated a high content of highly hydrated amorphous materials and organic matter in the vegetatively covered profile and in the samples from the friable subsoil layers of the bare profile, as evidenced by the broad endothermic peaks between 50° and 300°C. These samples have weak endothermic peaks at 325°C, indicating small amounts of sesquioxide minerals. The dense clays of the lowest horizon had a strong peak for kaolin clay between 500° to 600°C, which was similar to the halloysite standard. The amount of amorphous materials was low in this horizon of both soil profiles. The differential thermal curves for the indurated horizons of the bare soil profile showed very little thermal action, which is typical of crystalline titanium and iron oxide minerals.

X-ray diffraction studies were conducted to identify the minerals in these samples, and the diffraction patterns are shown in Figures 1a, 1b and 1c. The minerals are identified as follows in the patterns: *Ti-Fe*: hematite, Fe_2O_3; titanohematite, $(2-xFe \cdot xTi)O_3$; titanomaghemite, gamma $(2-xFe \cdot xTi)O_3$; and titanomagnetite, $(3-xFe \cdot xTi)O_4$; *Il*: ilmenite, $FiFeO_3$; *An*: anatase, TiO_2; *Ru*: rutile, TiO_2; *Pb*: pseudobrookite, $TiFe_2O_3$; *Q*: alpha quartz, SiO_2; *G*: goethite, $HFeO_2$; *GB*: gibbsite, $Al(OH)_3$; and *C*: halloysite, $Al_2Si_2O_5(OH)_4$ $4-xH_2O$. Katsura et al. (1962) studied the same soils and reported that titanomagnetite and titanomaghemite often occur as mixed crystals showing exsolution lamellae of ilmenite. They identified these minerals in samples N-1 and N-11 by X-ray diffraction methods, by the calculation of crystal parameters, by reflection microscopy, and by curie points and thermomagnetic curves. In their report they found less titanomaghemite in sample N-1 of the vegetation-covered profile than in sample N-11 from the bare profile. These workers confirmed the identification of the existence of pseudobrookite in the latter sample in studies in their laboratory at the University of Tokyo, using methods developed by Akimoto et al. (1957). In this investigation the diffraction patterns show a systematic shift of the hematite peaks to titanohematite in an ilmenite direction in all samples of these profiles.
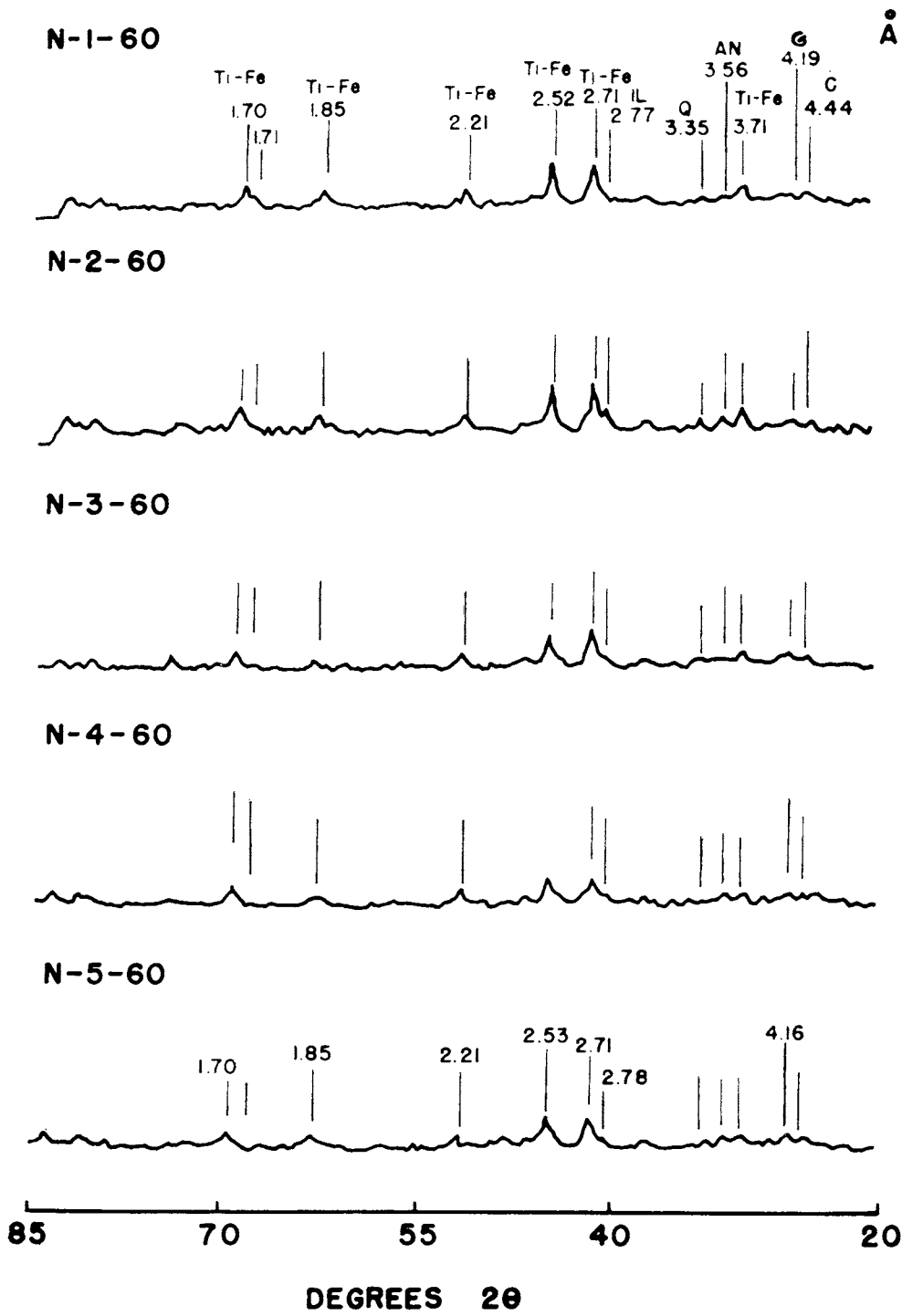
FIG. 1a. X-ray diffraction patterns from the vegetation-covered Naiwa soil profile, Kokee Road and Waimea Canyon, Kauai.
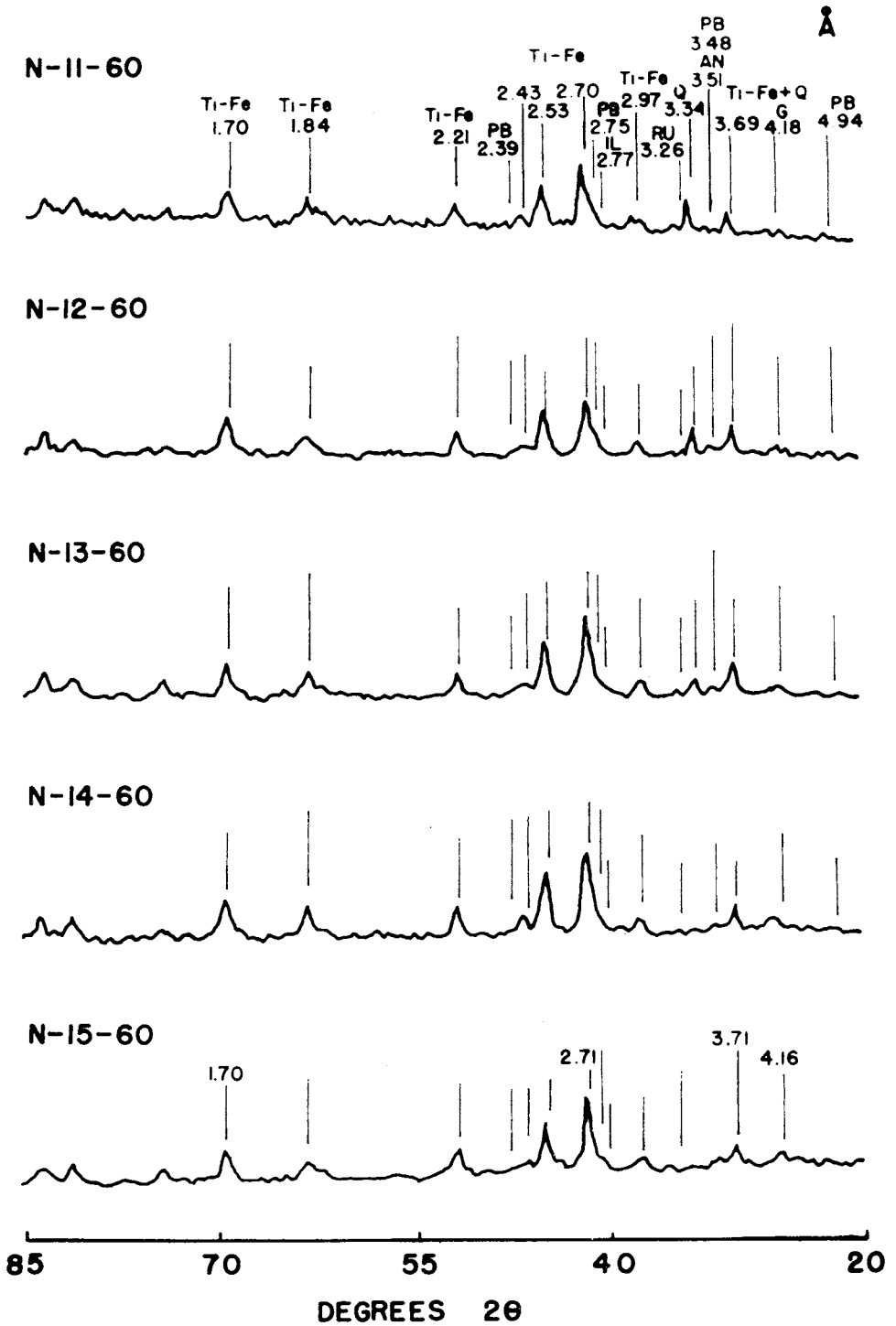
FIG. 1b.   X-ray diffraction pattern from a bare and exposed Naiwa soil profile, Kokee Road and Waimea Canyon, Kauai.

The X-ray diffraction patterns are presented in Figure 1a (N-1 to N-5 of the vegetation-covered profile), Figure 1b (N-11 to N-15 of the bare profile), and Figure 1c (N-16 to N-19 for the subsoil of the bare profile). The subsoil of the vegetative profile has an X-ray pattern identical to those of subsoil of the bare soil as shown in Figure 1c. The diffraction patterns show that the crystallinity of the oxides decreases with depth. The hydrated oxides, chiefly, and halloysite clay increase with depth, while alpha quartz, anatase, rutile, and pseudobrookite disappear. Gibbsite appears to be poorly organized in sample N-16. The chemical analysis given in
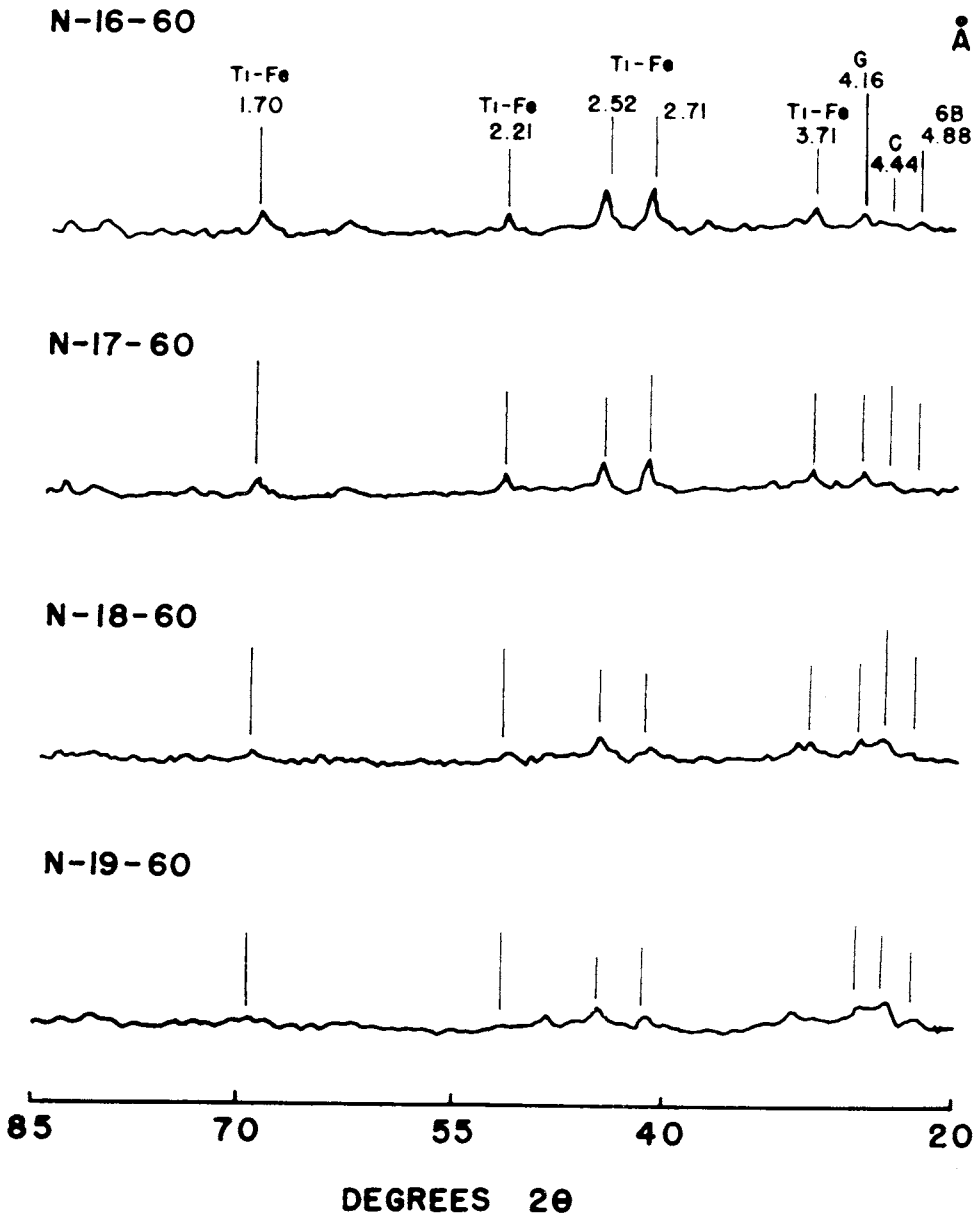

FIG. 1c. X-ray diffraction patterns from the subsoil horizons of a bare and exposed Naiwa soil profile, Kokee Road and Waimea Canyon, Kauai.

Table 2, samples N-11 to N-19, indicates that this would be the point in the profile where gibbsite might be detected. Well crystallized pure gibbsite—irregularly shaped nodules weighing as much as 25 pounds—occur in scattered pockets just below the clay pan horizon. This is evidence to support the removal of aluminum from the soil solum.

The iron and titanium minerals show a greater degree of crystallinity in the surface and indurated horizons of the bare profile. There is evidence that the Ti-Fe group of minerals, anatase, and goethite are present in the surface horizon of the vegetation-covered profile N-1. The concentration of these minerals decreases in samples N-2 to N-5. In sample N-11 from the bare profile, diffraction lines indicate not only a greater concentration of these minerals but in addition pseudobrookite and rutile. The presence of pseudobrookite has been established by optical methods in samples where the mineral has been separated and concentrated. Rutile

identification is of considerable interest as this mineral is not present in Hawaiian volcanic materials. The diffraction patterns for this mineral are weak and further studies are necessary to positively establish its presence. Rutile can form from the dehydration of anatase, which occurs as a result of desiccation of the surface of the bare profile.

The identification of alpha quartz is also of interest as the parent material does not contain quartz. One would expect to find amorphous silica at the surface, but rather large crystals of quartz would not be expected. The formation of alpha quartz occurs when amorphous silica is crystallized by desiccation. Gogolev and Anastas'eva (1964) described the formation of quartz by a similar process.

Ternary diagrams were constructed based on analysis of the data obtained in the chemical analysis of samples N-1 to N-10 and N-11 to N-19 (Table 2), and on the chemical composition data from five adjacent profiles (Table 3).

TABLE 3

A Series of Profiles Sampled to Show the Progressive Changes Occurring
As the Vegetation Dies and Induration Increases
(Samples and chemical composition are shown with loss of vegetation and increased induration in a descending order)

		OXIDES IN PERCENT										LOSS ON IGNITION
SAMPLE	DEPTH	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	%
		Covered with Grass Vegetation										
4A	Surface	9.5	11.6	47.2	3.7	8.7	.08	.00	.26	.00	Tr*	18.5
4B	Subsoil	15.0	26.1	19.9	2.1	3.5	.06	.00	.14	.00	Tr	33.1
		Under Grass Vegetation but Near Barren Area										
3A	Surface	7.7	5.5	57.6	2.8	15.1	.08	.00	.65	Tr	Tr	10.1
3AB	Transition	5.7	12.4	60.9	1.2	6.8	.04	.00	.05	.00	Tr	12.3
3B	Subsoil	5.7	18.2	28.9	3.3	3.1	.02	.00	.03	Tr	Tr	40.1
		Thin Patchy Grass Vegetation Cover										
1A	Surface	4.8	1.9	73.1	1.8	10.4	.05	.00	.31	Tr	Tr	7.0
1B	Subsoil	12.3	25.5	19.9	2.4	2.7	.01	.00	.11	.00	Tr	36.8
		Bare of Vegetation and Exposed Vertical Front										
1X	Surface	9.5	2.5	57.6	4.5	22.2	.18	.00	1.31	.00	Tr	1.9
1Z	Subsoil	9.0	20.2	32.7	2.8	5.1	.03	.00	.41	.00	Tr	29.3
		Completely Barren of Vegetation but Profile not Exposed										
2A	Surface	8.1	5.8	50.1	5.3	26.8	.12	.00	1.38	.00	Tr	1.8
2B	Subsoil	8.6	22.2	26.3	2.8	3.4	.02	.00	.30	Tr	Tr	35.9

* Tr = Trace, or less than 0.000 percent.

In Figure 2a, the $SiO_2:Fe_2O_3 + FeO + TiO_2:$ Al_2O_3 diagram shows clearly the increased amounts of Ti-Fe oxides in the indurated surface horizons, group *A*. Increased amounts of Al_2O_3 and of SiO_2 characterize the vegetatively covered surface and transitional horizons, group *B*. The ratio of total iron and titanium oxides to Al_2O_3 and SiO_2 becomes even lower in group *C*, the subsoil group. This ties in nicely with the mineralogical characteristics of these soils. In Figure 2b, the $TiO_2:FeO:Fe_2O_3$ diagram shows increasing amounts of TiO_2 relative to Fe_2O_3 with increasing induration. Sample 2A, the most indurated of all the samples, has over 45 mol percent TiO_2. Samples 1A, N-13, and

N-14 have shifted toward less TiO_2 and more Fe_2O_3 and are now found in group *B* along with the transitional horizon N-15. The ferrous iron content of groups *A* and *B* is about the same. The TiO_2 content of group *A* has increased independently of FeO. Group *C* of Figure 2b includes all of the vegetatively covered surface soils and all of the subsoils, including the clay pan. The TiO_2 content of group *C* is about the same as that of group *B* but Fe_2O_3 is slightly lower. The FeO content of these more highly hydrated, amorphous materials in the subsoil horizons is greater than that of either group *A* or *B*. The $MgO:SiO_2:Al_2O_3$ diagram in Figure 2c is very interesting for two reasons. First, it
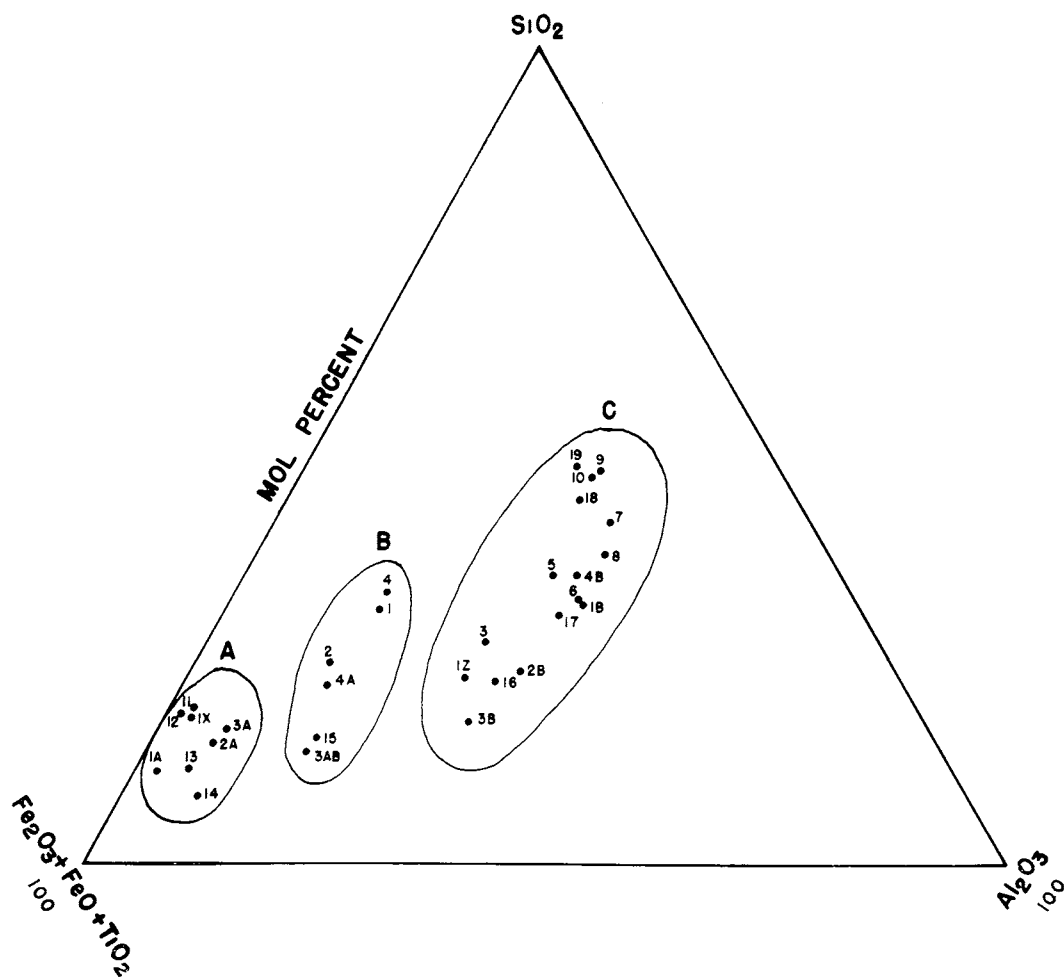

FIG. 2a. The $SiO_2:Fe_2O_3 + FeO + TiO_2:Al_2O_3$ diagram of Naiwa soils on Kokee Road and Waimea Canyon, Kauai.

points out the increased amounts of SiO_2 relative to Al_2O_3 in the indurated surface soils (group *A*), which ties in with the increasing alpha quartz content as induration progresses. Secondly, it shows a marked increase in MgO with increasing induration. This will be discussed in the concluding remarks.

DISCUSSION AND SUMMARY

The evidence presented shows the increased crystallinity of the surface horizons of the Naiwa soils with increased induration. This is accompanied by marked increases in TiO_2 and Fe_2O_3, and by definite accompanying changes in other chemical characteristics. Marked changes in the physical and mineralogical char-acter of these soils follow very shortly after the removal of vegetative cover. Two genetic processes are in operation and are important in any discussion of the mineralogy of these soils. One is the accumulation of residual resistant minerals, and the other is capillary movement of material in aqueous media and its subsequent precipitation and dehydration. In these soils, both processes operate with increased intensity as induration proceeds.

The removal of vegetation from the Naiwa soil causes induration of the surface which progresses until it attains a depth of 10 to 18 inches. In the process of induration, organic matter is decomposed. Induration also results in an approximate two-fold increase in particle density and a substantial change in soil volume.
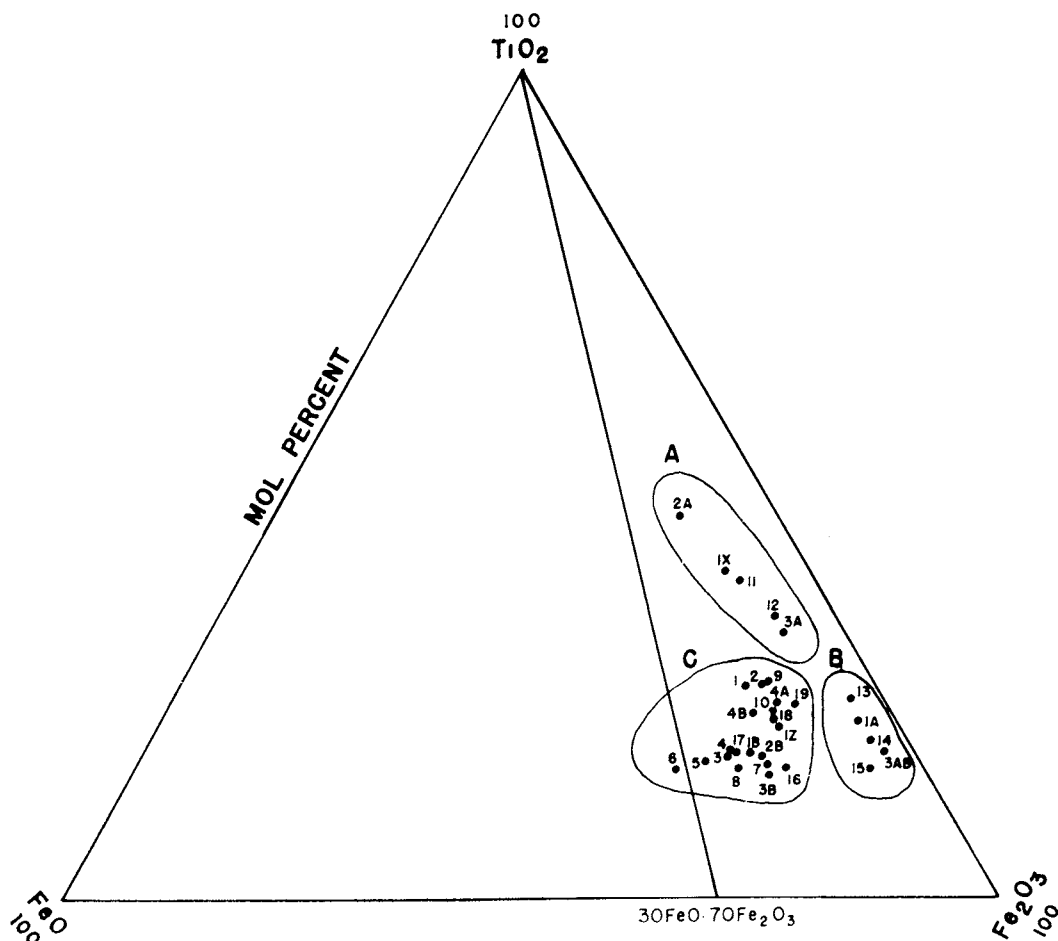

FIG. 2b.   The TiO_2:FeO:Fe_2O_3 diagram of the Naiwa soils on Kokee Road and Waimea Canyon, Kauai.

The decrease in soil volume cannot be explained by erosion. The amorphous and subcrystalline oxides become crystalline dehydrated oxide minerals, which explains the increase in particle density with induration. A substantial increase in the concentration of titanium oxide in the surface indurated horizons occurs, and there is evidence that the more indurated the horizon becomes the higher is the titanium oxide concentration. The increased titanium oxide concentration cannot be explained on the basis of accumulation of residual resistant minerals. There is good evidence that the residual resistant minerals are weathering. The high concentration of colloidal titanium oxide also indicates weathering and the formation of secondary titanium oxides such as anatase and rutile, and

titaniferous ferruginous oxides such as pseudobrookite, titanomaghemite, and titanomagnetite.

The identification of pseudobrookite clearly establishes the synthesis of the secondary minerals containing titanium, since pseudobrookite is not present in the parent material. Likewise, the formation of rutile is further evidence of secondary mineral formation. In any event, it would be a mistake to assume that all of the titanium found in these soils is in the form of residual titanium iron minerals and their weathering products. This would not account for the significant quantities of titanium that would be released by the decomposition of augite, titanoaugite, and other ferromagnesium minerals which are common in the basic and ultrabasic rocks of Hawaii.
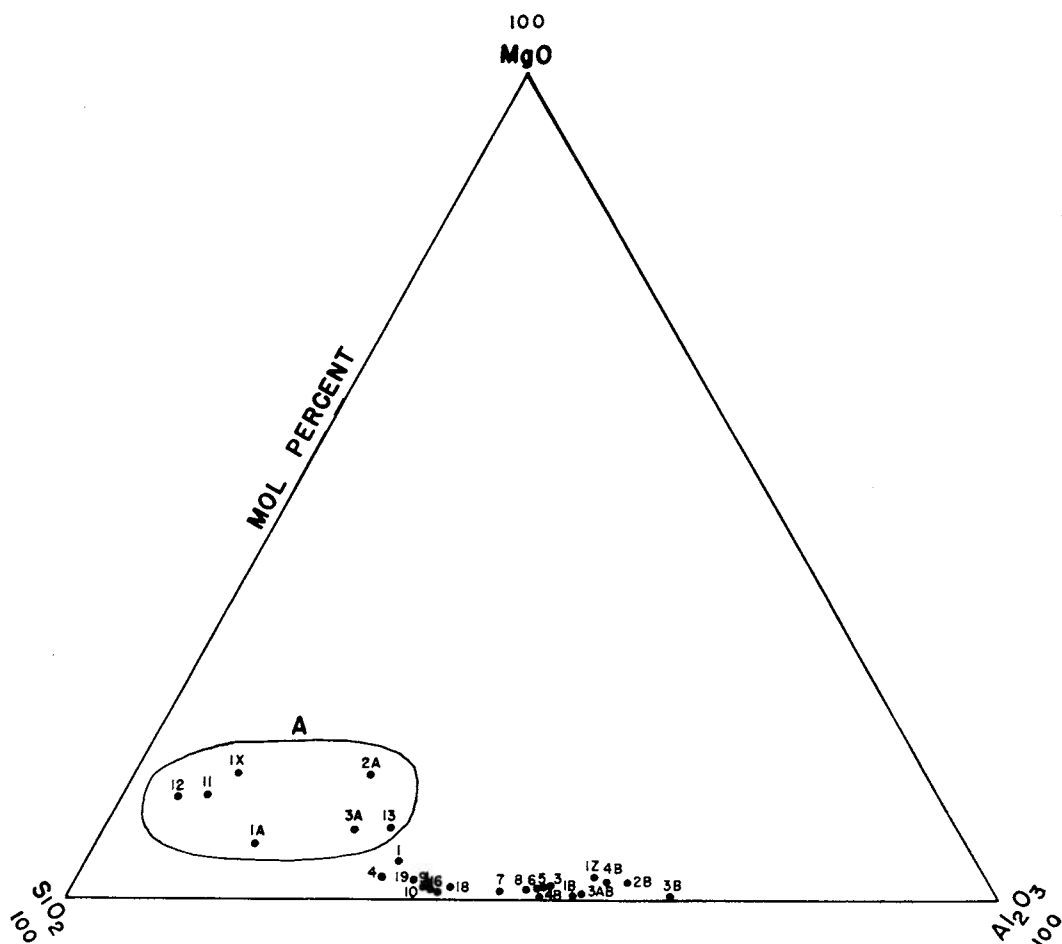

FIG. 2c. The $MgO:SiO_2:Al_2O_3$ diagram of the Naiwa soils on Kokee Road and Waimea Canyon, Kauai.

The identification of alpha quartz in these soils is of major interest and the mode of accumulation suggests its secondary origin. Because of the size of the crystals, the distribution of the mineral in the soil profiles, and its absence in any appreciable quantity in the vegetation-covered profile, it is unlikely that the presence of quartz in this soil can be explained by continental dust fall.

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