CRUST DEVELOPMENT IN A TITANIFEROUS FERRUGINOUS LATOSOL ON KAUAI, HAWAII

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INTRODUCTION

The Humic Ferruginous Latosols of Hawaii are characterized by a high concentration of iron and titanium minerals in the upper part of the solum. Soils of the Naiwa family may contain as much as 20-30% TiO_2 in the uppermost layers. Nowhere in the extensive literature on laterite and lateritic soils is there mention of accumulation of titanium of such magnitude outside Hawaii. Little is known, consequently, about the nature of titanium accumulation in these tropical soils.

Removal of the vegetation from soils of the Naiwa family results in the formation of an indurated surface horizon. This process may occur in a period of less than ten years. Once the indurated surface layer has formed, control of erosion, to which these soils are extraordinarily susceptible, by reforestation becomes difficult due to the hardness and the low nutrient status of the indurated layer.

This investigation was undertaken to study the effect of removal of the vegetation on the chemical, mineralogical and some morphological characteristics of a Naiwa soil on Kauai. A better insight in the genetic processes active in the formation of the indurated surface layer is a prerequisite for any attempt to control erosion and to make these soils better suited for cultivation.

REVIEW OF LITERATURE

Sesquioxide Enrichment

General

Latosols are the most widespread zonal soils of the tropical regions. They are characterized by low silica-sesquioxide ratios of clay fractions, low base-exchange capacities, low activities of the clay, low content of most primary minerals, low content of soluble constituents, a high degree of aggregate stability and (perhaps) some red color (Kellogg, 1949).

In the formation of latosols, enrichment of sesquioxides is the dominant process. Laterization has always been considered the process by which latosols are formed. Laterization can be defined as "relative accumulation of sesquioxides," or as "enrichment with iron, aluminum and some minor elements as weathering residue resulting from the loss of alkalies, earth alkalies and silica" (Schellmann, 1964). In addition to "relative accumulation of sesquioxides" (laterization), "absolute enrichment of sesquioxides" is an important process in the genesis of latosols. Many latosols have been formed as a result of a combination of both processes.

One of the final end products of lateritic weathering is a laterite crust. Aubert (1963) divided laterite crusts into ferruginous and ferrallitic crusts and defined them as follows: Indurated horizons rich in compounds of iron (oxides, hydroxides, and sometimes phosphates), or of iron and aluminum, and often manganese and titanium. The indurated horizon may be either an easily broken hardpan or a hard crust.

Relative Accumulation

Relative accumulation of sesquioxides takes place as a result of removal of other constituents, mainly bases and silica. In most cases the removal of bases and silica is achieved by leaching.

The degree to which sesquioxides will concentrate, as a result of selective leaching out of other constituents, depends upon the chemical composition of the parent rock, the permeability of the parent rock and soil profile, climate, and age or time.

The parent rock must be sufficiently rich in iron, if significant relative accumulation of iron is to take place. Ultrabasic rocks satisfy this requirement. Leaching out of bases and silica requires good permeability of the parent material and the soil and good drainage conditions.

A climate with alternating wet and dry seasons appears to be required for iron accumulation. When the wet season is too short, not enough rainfall is available for leaching. Under a continuously wet soil profile environment, on the other hand, alumina becomes the stabilized free oxide, and iron is leached out of the solum (Sherman, 1949).

According to D'Hoore (1954), relative accumulation of sesquioxides can occur at the surface or at a considerable depth in the profile. He emphasized the role of the biological factor in relative accumulation at the surface. By electron microscopy, he observed considerable physical attack of kaolin crystals, indicated by frayed edges of the kaolinite platelets, in the profile horizons where biological activity is largest. This physical attack can be considered as a first step in the chemical decomposition of the clay mineral, which in turn means loss of silica (and alumina).

Other workers, however, do not advocate an influence of biological activity on the decomposition of kaolinite. Alexander and Cady (1962) reported an example of loss of kaolin in the absence of organic matter in a hardening ornamental laterite ball in Guinea. Whittig (1954) proposed weathering of halloysite by dehydration and chemical attack in a latosol in Hawaii.

D'Hoore (1954) mentioned removal of silica from the root-zone through extraction of silica by crops and pastures, especially tropical grasses. When the plant parts are not returned to the soil, absolute silica loss takes place. In noncultivated areas, however, this factor hardly comes into play.

Absolute Accumulation

Absolute accumulation of sesquioxides is a result of importation of sesquioxides from sources outside the profile.

Absolute accumulation requires a source of potentially mobile sesquioxides located outside the zone of accumulation, a mechanism of mobilization and transport, and a mechanism of immobilization in the accumulation zone.

Enrichment by laterally moving ground water.

When topographic conditions are such that a hydraulic potential exists, enrichment of sesquioxides may occur by means of transport in laterally moving water. This phenomenon has been recognized and studied in many tropical areas, among others by Maignien in Guinea (1959), D'Hoore in the Congo (1954), and Sherman in Hawaii (1949).

A situation favorable for accumulation by laterally moving water often exists on long slopes. The upslope area, where uptake of sesquioxides takes place, must meet the following conditions. Firstly, this area has to be sufficiently rich in sesquioxides (specifically iron). Secondly, the sesquioxides have to be mobilized.

Solution of ferric hydroxide requires a pH lower than 2.2. pH values this low, however, only occur in very rare circumstances in soils. Ferrous hydroxide, on the other hand, is soluble up to pH 5.5. To reduce ferric iron to ferrous iron, anaerobic conditions and/or organic reducing agents are needed. In continuously wet areas, anaerobic conditions may be reached in the soil profile. The influence of biological factors in the reduction of ferric iron, however, appears to be much more important.

Bloomfield (1953, 1955) has reported extensive studies on the mobilization of iron and aluminum by decomposing organic matter. He found that in the presence of decomposing organic matter soluble ferrous-organic complexes were formed in neutral, aerobic conditions. Betremieux (1951) also stressed the importance of organic matter on the movement of Fe and Mn. Organic matter is provided by parts of dead plants, on the soil surface or within the soil profile, and by the soil fauna. The largest concentration occurs in the rootzone.

High rainfall in the upslope area facilitates the removal of iron, because it promotes high weathering intensity, promotes growth of vegetation and supplies the transporting agent (water).

Lateral transport on the long slopes requires an impervious layer not too deep in the profile.

Accumulation of sesquioxides in the downslope area takes place as a result of immobilization of the transported sesquioxide complexes. The most likely mechanisms of immobilization are: (1) oxidation of the ferrous to the ferric form, (2) destruction of organic complexing agents, (3) absorption of ferrous on ferric forms already present (Bloomfield, 1955), (4) adsorption on kaolin surfaces (Fripiat and Gastuche, 1952), and (5) slow accretion on microcrystals. The conditions necessary for these mechanisms are provided by alternating wet and dry seasons, savannah vegetation, and level slope benches.

Enrichment by erosional and colluvial material. Disintegration of higher lying laterite by mechanical and chemical erosion and weathering, followed by physical transport under the force of gravity, enriches the lower lying areas with sesquioxides (du Preez, 1949, and Sivarajasingham, et al., 1962).

The contact of the detrital material with the underlying rocks may be sharp. On low lying surfaces detrital material may be found as nodular forms in soil profiles or as nodules cemented in the matrix, though the site may be far from present remnants of the higher and older erosion phase.

Sesquioxide Movement within the Profile

Enrichment by downward movement in solution. In the opinion of Mohr (1932) and Pendleton (1936-1953), both cited in Maignien (1966), laterite is an illuvial horizon. Iron in the surface horizons becomes mobilized by complexing with silicic acid and/or organic decomposition products and enriches the underlying layers on immobilization (Maignien, 1966). Subsequent erosion of the surface horizon exposes the enriched layers. Maignien (1959) stated that "every surface laterite is the upper part of a truncated profile."

Schellmann (1964), in a study of the lateritic weathering of serpentine, found an absolute accumulation of Fe and Al (calculated with Cr_2O_3 as an internal standard) at a depth of 1 to 2.5 m. In his opinion, these sesquioxides may have originated from an overlying layer which since then has been eroded. Du Preez (1949) described similar laterites in Nigeria as fluvial or eluvial laterites. He considered illuvial laterites to be formed by both downward movement of sesquioxides from above and upward capillary movement from below.

Enrichment by capillary rise. Capillary rise is probably effective only a short distance above a water-saturated zone. Studies by Mohr and Van Baren (1954) indicated that water requires at least a month to rise the maximum of 2 to 2.5 m in the most favorable material. In most lateritic soils the diameter of the pores is too large to allow significant capillary rise (De Leenheer, et al., cited in D'Hoore, 1954; and Maignien, 1966). In fine textured soils, on the other hand, adsorption of the mobile sesquioxides on clay surfaces prevents these components from moving upwards appreciably.

The water regime in most tropical soils is such that the quantity of atmospheric water percolating through the soil exceeds the quantity of water brought upward by capillary rise, meaning a net downward movement of mobile components (D'Hoore, 1954; and Maignien, 1966).

D'Hoore suggested upward transport by the action of plants, i.e. assimilation of sesquioxides in the roots and restitution on the soil surface by falling plant parts and decomposition.

In barren soil, capillary rise of liquid water only takes place as long as the soil surface is moist. Experiments by Penman (1941) showed that under England-summer conditions the surface soil dries out in as little as two days. After that evaporation is extremely low, corresponding to the diffusion rate of water vapor.

Induration

Not all lateritic soils, enriched in iron, harden. The ability to harden depends more on the location, form and arrangement of sesquioxides than on their absolute quantities.

Iron plays the main role in the hardening process. Aluminous crusts exist, but larger quantities of oxide and more time seem to be required for their formation.

Hardening involves enrichment in iron, either gross or local, crystallization, and dehydration.

Enrichment

In most cases, gross enrichment of iron takes place. In some laterites, however, the difference in chemical composition between soft and hard material is only slight. The only difference between the hard crust and the lower soft material at sites in Conakry, Guinea, was in crystal size and in the content of uncombined water (Alexander, et al., 1962). Hardening in that case had been effected by local rearrangement of iron.

Studies of thin sections by Alexander, et al. (1962) showed evident reorganization and segregation of constituents, suggesting at least local movement of material. D'Hoore (1954) found that the indurated accumulation zones always exhibited hard, shiny films covering the internal surfaces of channels, pores and cracks and often even a part of the external surfaces. These films consisted almost entirely of hydrated iron oxide, usually goethite, or of iron-stained kaolinite.

As shown by Fripiat, et al. (1952), thin layers of iron oxide, probably microcrystalline goethite, are adsorbed on kaolinite crystals. This iron is thus immobilized. Hardening, is nearly always accompanied by a loss of kaolinite. Evidence of destruction of kaolin, based on thin section and electron microscope observations (frayed edges of the crystals), is abundant (D'Hoore, 1954; Alexander, et al., 1962). The immobilized iron is thus set free to move and recrystallize.

Observations by D'Hoore (1954) and Alexander, et al. (1962) indicated that hardening occurs in locations where iron precipitates in excess of the quantities adsorbed on the kaolin surfaces. This may be effected by: (1) gain in iron, (2) loss of clay, (3) removal of clay to adjacent volumes, releasing iron to move into a nodule or wall.

The more or less localized sesquioxides and clay movements are responsible for characteristic laterite features such as iron- or iron-impregnated clay films, minute spherical aggregates, concretions and aggregates.

Crystallization

On hardening, the iron oxide minerals crystallize into continuous aggregates or networks. The ferruginous skeleton of indurated laterites display a higher degree of crystallinity or greater continuity of the crystalline phase than the soft materials with which they are associated (Sivarajasingham, et al., 1964; Maignien, 1966).

Dehydration

Drying of the soil causes concentration of the soil solution, which will result in precipitation of the sesquioxides present in the soil solution. Further desiccation causes the precipitated colloidal films to age and to crystallize. When desiccation occurs in stages, as in the case of an alternating wet and dry climate, successive matrices will be packed one upon another in this way, producing a strong resistance (Maignien, 1966).

Dehydration of soils high in amorphous material (aluminum, iron, titanium, silica gels) leads to crystallization of the amorphous components, causing an increase both in bulk density and particle density and in particle size. Crystalline mineral aggregates and nodules which become stable units are formed. Soils having a high content of amorphous iron hydroxide colloids will indurate on dehydration (Sherman, et al., 1964).

The oldest, hardest crusts are high in hematite, which most likely is formed by dehydration of goethite, since younger crusts are usually higher in goethite (Alexander, et al., 1962).

Alternate wetting and drying

Alternate wetting and drying is essential for hardening. It is the main cause of the remobilization, redistribution and recrystallization of iron, necessary for cementation of the exposed horizons. The effect of alternate wetting and drying, with no external additions of iron and no effect of organic matter, was shown at a site in Guinea. In an ornamental ball, carved from a soft laterite quarry and exposed to wetting and drying for 15 years, a decrease in kaolin and an increase in gibbsite, goethite and hematite were found. Iron oxide had migrated from the matrix to the channel walls and the exterior shell, which were the hard portions (Alexander, et al., 1962). Similar soft laterite, exposed to only drying conditions, had not hardened.

Not only seasonal variation in rainfall, but also wetting and drying from rain in daily or weekly cycles is important.

Deforestation

Deforestation has two important consequences: Erosion of loose horizons overlying a zone of sesquioxide accumulation, and desiccation as a result of insolation (Lamotte, et al., 1962).

Aubert (1949) described the effects of deforestation in the Ivory Coast. Under forest cover, a concretionary lateritic soil had formed, with a non-indurated accumulation horizon at 90 cm depth. A little surface erosion occurred, evidenced by some concentration of quartz at the surface. After removal of the forest, the soil had been either covered with seasonal grasses or had become barren. In a matter of years the loose soil, overlying the accumulation zone, had been removed by erosion, and the accumulation zone, exposed at the surface, had hardened to a lateritic crust. Rainfall in this area was 1500-1800 mm and the slope was 3 percent.

Maignien (1966) stated that the presence of laterites at the surface is merely a consequence of the removal of loose surface horizons by erosion.

Removal of vegetation induces extremes of temperature at the soil surface, exposing the surface to extreme drying-wetting cycles. D'Hoore (1954) measured the following temperatures in French Guinea, at two o'clock in the afternoon:

	Barren Crust	Crust with grass vegetation	Forest	Air temperature
1 cm depth	53.5°C	50.4°C	26.9°C	36.0°C
10 cm depth	36.8°C	40.1°C	24.8°C	

It follows that dehydration of the surface zone is much stronger in the barren area and in the area with grass vegetation than in the area under forest cover.

Removal of the forest usually gives way to herbaceous vegetation. Progressive erosion and/or burning are the main reasons for a subsequent complete loss of vegetation.

Under influence of the grass vegetation, sesquioxides are mobilized in the rainy season. D'Hoore (1954) stated that the sesquioxides, present in adsorbed form, are preferentially mobilized since they offer the largest surface. In the dry season the grasses die partially, the iron oxides immobilize in non-adsorbed form and contribute to induration. According to Maignien (1959) the sesquioxides mobilized in the wet season, move down and enrich the subjacent horizon.

Time

Induration can take place in a matter of years. Alexander, et al. (1962) mentioned 15 years for a site in Guinea. Aubert (1949) reported that in the Ivory Coast the yield of a cocoa plantation had sharply decreased in a couple of years as a result of the formation of a hard crust. After clearing of a forest in Dahomey for coffee growing, a distinct hardening, even within two years, was observed (Mohr and van Baren, 1954). Experimental observations of denuded areas in Hawaii have shown definite surface induration within six months after exposure (Walker, et al., 1969).

Minerals Commonly Present in Laterites

Goethite

Goethite and hematite are the two most common forms of crystalline iron minerals in latosols and laterites. In these soils, goethite generally occurs as fine particles (Bonifas, 1959) and is often present in the form of crypto-crystalline aggregates giving excess of water in analysis (Maignien, 1959).

X-ray diffraction studies indicated that aluminum very commonly replaces iron in soil goethites (Norrish and Taylor, 1963). The aluminum content of the soil goethites studied by Norrish and Taylor ranged from 15 to 30 mol % AlO.OH. The unit cell dimensions and the particle size of the goethites decreased linearly with increasing isomorphous substitution of iron by aluminum while the water content increased (Thiel, 1963; and Norrish and Taylor, 1963).

Feitknecht and Michaelis (1962) and Schwertmann, et al. (1965 and 1966), from studies of synthetic ferric iron solutions and aging of synthetic amorphous ferric iron hydroxide, concluded that when the Fe^{3+} concentration of the solution is low, goethite crystallizes directly from solution, and that when the Fe^{3+} concentration of the solution is higher, amorphous $Fe(OH)_3$ precipitates. Depending on several environmental factors, the amorphous iron hydroxide then dehydrates to form hematite or dissolves again, followed by the crystallization of goethite from solution. Schwertmann denied formation of hematite by dehydration of goethite.

Many observations, however, point to the likely transformation of goethite into hematite. Berner (1969) substantiated this hypothesis.

He calculated the free energy of formation for the reaction:

$FeO.OH \rightarrow 1/2\ Fe_2O_3 + 1/2\ H_2O$ at 25°C to be -0.33 ± 0.08 kcal/mol.

Poorly crystallized goethite (as usually found in nature) is much more soluble, resulting in a more negative value for the energy of reaction. Berner stated that fine grained goethite is thermodynamically unstable relative to hematite water under virtually all geological conditions.

The change from goethite to hematite is pseudomorphic in character (Brown, 1961).

Hematite

In indurated laterites, the iron is usually found as hematite (Brown, 1961). Most workers share the opinion that on dehydration hematite may form from goethite. Bonifas (1959) pointed out that it is usually not the topmost horizon that contains the most hematite, which seems to exclude the possibility of selective dissolution of goethite. Hematite may also form from aging of iron hydroxide gels or from alteration of magnetite, ilmenite and chromite.

The existence of a hematite-ilmenite solid solution series is well established. At temperatures in excess of 1050°C, solid solution is complete. At normal temperature, solid solution is much more restricted. However, rapid cooling of e.g. volcanic tuffs inhibits exsolution, and members of the ilmenite-hematite series with compositions ranging from pure ilmenite to pure hematite have been reported (e.g. Akimoto, 1957; and Nicholls, 1955). Basta (1953), cited in Nicholls (1955), quoted figures showing a steady rise in the cell dimensions from hematite to ilmenite for intermediate solid solutions.

X-ray diffraction studies by Katsura, et al. (1962) established the presence of a rhombohedral phase due to the presence of ilmenite-hematite solid solutions in a Naiwa soil of Kauai, Hawaii. The _d_-spacings of this phase were found to be somewhat different from pure hematite and to be shifted systematically to those of ilmenite.

Magnetite-Maghemite

Magnetite and ilmenite are the main primary iron oxides in rocks.

Most magnetites in igneous rocks, particularly in the more basic rock types, contain appreciable amounts of titanium (Deer, et al., 1966). Extensive work has been done on the ulvospinel ($TiFe_2O_4$)-magnetite (Fe_3O_4) solid solution series, especially in relation to its striking ferromagnetic properties (Akimoto, et al., 1954-1960; Nicholls, 1955; Vincent, et al., 1954 and 1957; and Nagata, 1956). Akimoto, et al. (1957) arrived at emperical formulae for the relations between chemical composition, lattice parameter, saturation magnetization, and curie point for titanomagnetites from Japanese igneous rocks containing 0-70% ulvospinel.

Oxidation of titanomagnetite belonging to the ulvospinel-magnetite solid solution, under appropriate conditions of temperature and oxygen pressure, yields a spinel phase (Ti-maghemite) close to the $TiFeO_3$-Fe_2O_3 join in the FeO-Fe_2O_3-TiO_2 triangular field (Akimoto, 1957). Basta (1959) showed that the oxidation from magnetite to maghemite is a continuous process, involving removal of iron from the $Fe_{24}O_{32}$ unit cell of magnetite to obtain the $Fe_{21\ 1/2}O_{32}$ unit cell of maghemite. Studies by Katsura, et al. (1961) substantiated the formation of Ti-maghemite in rocks and lavas by oxidation of Ti-magnetite. The chemical composition of the Ti-maghemites in Japanese and South African rocks was close to the $TiFeO_3$-Fe_2O_3 join or even in the $TiFe_2O_5$-$TiFeO_3$-Fe_2O_3 field in the TiO_2-FeO-Fe_2O_3 ternary system. The authors presented relations between lattice parameter and degree of oxidation (expressed as 32(Fe+Ti)/O) and TiO_2 content (expressed as Fe/(Fe+Ti)).

Both Ti-magnetite and Ti-maghemite have been identified in Hawaiian soils. These minerals were found to have Fe/(Fe+Ti) ratios between 0.78 and 0.82, suggesting that they were formed by various degrees of oxidation from primary Ti-magnetites, containing 21 to 25 Mol % TiO_2 in the unoxidized state. The composition of Ti-maghemites in Humic Ferruginous Latosols was found to lie in the $TiFe_2O_5$-$TiFeO_3$-Fe_2O_3 compositional field (Matsusaka, et al., 1965).

Microscopic studies in reflected light of samples of the indurated topsoil of a Naiwa soil of Kauai, Hawaii, indicated that Ti-magnetite is gradually changing to Ti-maghemite within individual grains. Study of the chemical composition suggested that the Ti-maghemite in this horizon is formed by oxidation of Ti-magnetite having a Fe/(Fe+Ti) value of 0.748 and that further oxidation may yield a phase close or even on the TiO_2-Fe_2O_3 join in the TiO_2-FeO-Fe_2O_3 ternary system (Katsura, et al., 1962).

Other mechanisms proposed for the formation of maghemite are dehydration of lepidocrocite, ignition of amorphous ferric oxides in the presence of organic materials, action of organic matter on iron oxides (Oades, 1963; and van der Marel, 1951).

The stability of Ti-maghemite is probably a function of the Ti content, as shown by the higher pressure and temperature required for the transition to hematite by maghemite with higher Ti content (Kushiro, 1960).

Ilmenite

Ilmenite seems to be even more stable than magnetite under conditions of lateritic weathering (Bonifas, 1959). Bonifas, however, did notice zones with less metallic luster and corroded appearance on the rims of ilmenite crystals in laterites, indicating alteration. Temple (1966) concluded that the alteration of ilmenite in sand samples studied by him is due to weathering *in situ*. Under these conditions ilmenite is altered to pseudorutile ($Fe_2O_3.3TiO_2$) and hematite, and subsequently to rutile. These transformations are topotactic. At elevated temperatures oxidation of ilmenite yields hematite+rutile, while at high temperature (>900°C) pseudobrookite is formed.

As stated before, ilmenite can contain varying amounts of Fe_2O_3 in the solid solution series ilmenite-hematite.

Anatase-Rutile

Anatase is the low-temperature polymorph of titanium-dioxide. It may be formed from weathering of Ti-silicates, ilmenite or Ti-magnetite (Bonifas, 1959). As shown above, rutile may form from alteration of ilmenite (Temple, 1966).

On heating to above 730°C anatase converts to rutile. The rate of transformation depends on the fineness of the material, and on temperature, pressure and time. The reaction is slow below about 600°C (Deer, et al., 1966). Schuiling and Vink (1967) determined the free energy of the reaction anatase → rutile to be -0.25 ± 0.2 kcal, with only a slight variation with temperature below 600°C. These authors concluded that anatase has no true stability field. However, because of the near equality of the free energies of formation of rutile and anatase, anatase is commonly formed in low temperature environments instead of the stable polymorph rutile.

The anatase-rutile transformation involves a collapse of the relatively open anatase structure by distortion of the oxygen framework and by rupture of two of the six Ti-O bonds. A reducing environment facilitates this collapse (Shannon, 1964).

Pseudobrookite

Experiments by Lindsley (quoted in Wright, 1968), pointed to the fact that pseudobrookite will not form at temperatures lower than 580°C. Teufer, et al. (1966) and Temple (1966) reported the formation of pseudobrookite from ilmenite at temperatures higher than 800°C. Wright (1968), in recognition of Lindsey's findings, corrected his earlier identification of pseudobrookite in New Zealand ironsands, which was believed to be formed by low-temperature transformation of Ti-magnetite. In his opinion the phase is more likely to be rutile, the rutile-(Ti)-hematite pair being stable at low temperatures under strongly oxidizing conditions.

Quartz

There are several reports of suggested secondary formation of quartz.

Bonifas (1959) described siliceous horizons, formed by lateritic weathering of dunite, in Conakry. The appearance and composition of these horizons suggested precipitation of a silica gel contaminated with iron oxides and crystallization into quartz on ageing.

Gogolev, et al. (1964) made a special study of possible formation of secondary quartz in a Brown Mountain-forest soil, developed from quartzless andesite. The quartz content of this profile ranged from 0 % in the unweathered rock at 20 meter depth to 91 % at the surface. The quartz grains were spherulitic in form and had a micro-aggregated constitution. Particle size ranged from 20 to 40 microns. Micromorphological studies of the weathering rock showed occasional opal encrustations in the completely modified matrix at a depth of 10 meter; considerably more encrustations of opal, more frequently and better crystallized and converted to chalcedony, at a depth of 6 meter; while at 2.5 meter depth in some places the crystallization product of opal could be identified as quartz. The pH salt decreased from 5.3 at 10 meter depth to 4.1 at 2.5 meter. Increasing crystallinity of the SiO_2 phase with increasing proximity to the surface was shown by a decreasing solubility of SiO_2 in KOH extract, and the presence of quartz patterns in DTA and X-ray diffraction tracings of samples taken above 2.5 meter.

Sherman, et al. (1964) proposed the system Si → silica gel → opal silcrete → SiO_2 α quartz for Hawaiian soils. Hawaiian basalts and lavas contain no quartz. Opaline silica, however, is commonly found between layers of partially weathered lithified ash deposits and in lava tubes, while α quartz is identified in soils. The quartz content in soils increases with increasing rainfall.

Aging of amorphous siliceous acid in alkaline environment at temperatures of 100-250°C led to the subsequent formation of SiO_2-X, cristobalite and finally quartz. Extrapolation yielded a period of 25,000-30,000 years, required for the conversion of amorphous siliceous acid to quartz in alkaline environment at 20°C (Heydeman, 1964). All reported formations of secondary quartz in soils, however, took place in acid environment.

Rex, et al. (1969) proposed an eolian origin for quartz in Hawaiian soils. The oxygen isotopic composition of quartz in Hawaiian soils is almost identical to that of quartz isolated from east-central Pacific sediments. This isotopic composition is an unusual one, being at the high end of observed values for quartz in igneous and metamorphic rocks, and at the low end for quartz in low temperature chemical sediments. The authors feel that an eolian origin of quartz is substantiated by the fineness and the uniform particle size distribution of quartz in Hawaiian soils and by the fact that the morphology of the quartz particles is identical to the chips and shards in which quartz is found in deepsea pelagic sediments.

Hawaiian Humic Ferruginous Latosols, Naiwa soil series in particular

Humic Ferruginous Latosols approach the endproduct of soil formation in the Latosol suborder. Humic Ferruginous Latosols are characterized by a concentration of heavy minerals in the upper part of the solum. The profile consists of a thin A_1 horizon, a massive to crumb-structured A_2 horizon that is very high in bulk density, and a red to brown friable B horizon which grades to highly weathered parent material. Iron and titanium are concentrated in the upper part of the soil. These soils occur under rainfall ranging from 25 to 150 inches annually, under conditions of definite alternating wet and dry seasons (Cline, 1955).

Soils of the Naiwa family are the most highly developed members of the Humic Ferruginous Latosol group. They exhibit a massive crust-like layer of heavy minerals at the surface. This layer is usually unconsolidated, but the composing silt-sized particles are so tightly packed as to resemble a semi-cemented layer. The layer is purplish in color. Cultivation of soils of the Naiwa series usually causes heavy erosion. The A_1 horizon is first removed by sheet erosion. The massive A_2 horizon withstands erosion to a considerable degree, but once it is cut through, the B horizon is quickly removed, almost as a uniform sheet.

The Humic Ferruginous Latosols in Hawaii have been studied extensively.

The largest area of these soils occurs on Kauai, the oldest island geologically. They are usually situated on long slopes having a series of benches or on gently rolling slopes. Lower on the slopes soils belonging to the Low Humic Latosols have developed under less rainfall while at higher elevations, above the area of the Humic Ferruginous Latosols, Humic Latosols are found under continuously wet conditions (Sherman, et al., 1948). Humic Ferruginous Latosols have formed from basic and ultrabasic lavas and pyroclastic materials of the post-eosional volcanic activity that has occurred on the geologically old islands of the Hawaiian group (Walker, et al, 1969).

Sherman (1950) discussed the genesis of the ferruginous laterite crusts. The two factors most responsible for the development of the crusted surface horizons in his opinion are (1) lateral movement of water, containing dissolved or colloidal iron and hydrated titanium, through the friable B layer over an impervious subsurface layer and (2) an alternating wet and dry season. The dissolved iron and titanium are brought to the surface by capillary rise of the water in the dry season and stabilized by oxidation and dehydration. The iron and titanium are leaching products from soils developed in the wet areas of the higher elevations.

Sherman, et al. (1953), in his investigations of titaniferous ferruginous laterite crusts, found that the appearance of the hardened crust can be associated with dry periods (in an alternating wet and dry climate), suggesting that its formation is due to dehydration. His experimental data suggested that hardening occurs as a result of dehydration of the colloidal hydrated oxides, mainly of iron. This process causes an increase in particle density and particle size (Fujimoto, et al., 1948) and bulk density. The hardening of Hawaiian soils on exposure can occur in less than a year (Sherman, et al., 1953).

Clearing and exposure of an area of titaniferous ferruginous latosols of the Naiwa family on Molokai provided a good opportunity to study the conditions leading to the accumulation of iron and titanium oxides in and induration of the surface horizons. The indurated areas were found to contain numerous magnetic ferruginous concretions, ranging from 30 to 43 weight percent of the soil. These concretions were made up predominantly of iron oxide (as high as 72 weight percent) and titanium oxide (11-13 weight percent). The low ferrous iron content suggested the presence of maghemite as the magnetic iron oxide. The occurrence of the iron and titanium oxides in concretions was felt to be conclusive evidence of their movement in soluble form, prior to redeposition and dehydration. Some movement of soil aggregates and concretions was observed as a result of erosion (Sherman, et al., 1955).

The concretions, formed in the layer enriched in oxides on exposure of a ferruginous soil, were at first believed to develop by dehydration and precipitation of ferrous iron, carried up by ascending capillary water, around a small nucleus (Sherman, et al., 1953). More thorough investigations changed this concept. Sherman, et al. (1969) proposed the term nodule, as defined by Bryan (1952, cited in Sherman, et al., 1969) instead of concretion, since the mode of origin is not that of concretionary deposition. The work of these authors indicated that the secondary mineral aggregates commonly occurring in tropical soils, e.g. nodular iron oxides, are formed by repeated dehydrations of the amorphous hydrated oxide gels leading to an increasingly better state of crystallization with a stable inert aggregate as end-product. In a mixed aluminum-iron colloidal hydrated oxide system, aluminum oxide will separate first, making it possible for the iron oxides, with their much slower rate of transformation, to move from the interior to the outer shell of the nodule.

The titanium content of Hawaiian lavas is relatively high (2.5-3 % TiO_2, Stearns, 1966). The average titanium content of Hawaiian soils is about 5 %, while the surface horizons of the Humic Ferruginous Latosols have a titanium content of as high as 25 %. Sherman (1952) suggested that TiO_2 accumulates in tropical soils under the same conditions as iron oxide and that it is easily dehydrated near the surface to form concretions, coatings to surfaces of aggregates or particles, or a massive horizon.

Study of the magnetic minerals in Hawaiian soils revealed the presence of titanomagnetite and titanomaghemite. The value of the Fe/(Fe+Ti) ratio of most of these minerals lies between 0.78 and 0.82, suggesting their formation by various degrees of oxidation from primary titanomagnetites occurring in the basaltic and andesitic rocks. It was suggested that some titanomaghemite, having a lower titanium content and occurring in the most weathered soils, may have formed by dehydration of lepidocrocite and/or amorphous iron oxides (Matsusaka, et al., 1961 and 1965).

Katsura, et al. (1962) investigated the magnetic minerals in a Naiwa soil on Kauai. Both titanomagnetite and titanomaghemite were identified. Reflection microscope photomicrographs showed the close connection between both minerals, a relationship which is almost the same as in igneous rocks. The formation of titanomaghemite by oxidation of primary titanomagnetite was confirmed. The titanium content of the titanomaghemite was found to be quite high (33 mol %). The grain size of both titanomagnetite and titanomaghemite showed to be very small, mostly below 5 micron. In addition to the magnetic oxides, titano-hematite, Fe-ilmenite, alpha-quartz, and pseudobrookite were identified.

The Naiwa soil, developed in the area just off the Kekaha-Kokee road on Kauai, has been studied by several workers.

The chemical composition of this soil was first determined by Fujimoto, et al. (1948). Some of the properties of the soil were discussed by Sherman (1948). Mineralogical analysis was done by Tamura, et al. (1955). One of their findings was the large crystal size of hematite, the predominant mineral in the A_{22} horizon. Studies by Sherman, et al. (1950 and 1953) and Katsura, et al. (1962), mentioned earlier, included this soil. The emphasis of extensive studies by Walker (1964) was placed upon the differences in physical, chemical, and mineralogical properties between vegetated and barren, indurated profiles.

Walker, et al. (1969) pointed out the loss of volume of the Naiwa soil on exposure. The volume of the surface of the original vegetative profile was reduced by half as a result of exposure, if loss by erosion was ignored. Exposure caused a rapid decomposition of organic matter. Increased induration was coupled with increased crystallinity of the surface horizons, and with marked increases in TiO_2 and Fe_2O_3. Distinct changes in chemical, physical, and mineralogical characteristics followed very shortly after removal of the vegetative cover. Two genetic processes were proposed: (1) accumulation of residual minerals and (2) capillary movement and subsequent precipitation and dehydration of material. The identification of pseudobrookite and rutile was seen as evidence of the formation of secondary titanium minerals. Alpha-quartz was also considered a secondary mineral.

DESCRIPTION OF SAMPLE AREA AND SOIL PROFILES

Area

The sample area was situated on Kauai, just southeast of the Kekaha-Kokee road, where this road first closely approached the Waimea Canyon, just northeast of the 2319 feet bench mark (Topographic map, Kekaha, Hawaii).

The area was located on a long gentle slope, not exceeding 15°. The sample sites of profile I, II and III formed a slight rise in the general slope. The direction of the slope was NE-SW. About 1 mile NE of the sample area in the upslope direction, the slope was cut through by the Waimea Canyon.

The Waimea Canyon has formed along a fault, bounding the Makaweli depression. Formation of the Makaweli depression took place at the end of the period of major volcanism, during the Pliocene (MacDonald, et al., 1960). The Waimea Canyon isolates the west leeward slope of Kauai, on which the sample area was located, from the rainy central uplands.

The soils have developed on material of the Napali formation, consisting of thin, rapidly accumulated lava flows and associated pyroclastic rocks that accumulated on the flanks of the major Kauai shield volcano, outside the caldera. The age of this formation is probably Pliocene. The lavas of the Napali formation are predominantly olivine basalt (MacDonald, et al., 1960). Walker, et al. (1969), however, suggested that there is strong evidence that these soils have formed in pyroclastic materials of post erosional origin.

The annual rainfall in the sample area was about 60 inches, while the climate had pronounced wet and dry seasons.

The vegetation consisted of *Wilkesia argyroziphianium*, a plant native to Kauai and found nowhere else in the world. It appears to require very high titanium contents of the soil. Other types of vegetation were: Aalii (*Dodonaea viscosa*), Paspalum sp., foxtail (*Setaria* sp.), puakeawe (*Styphelia* sp.), silky oak (*Grevillea robusta*), bracken fern (*Pteridium aquilinum*), koa (*Acacia koa*), lantana (*Lantana camara*), Japanese tea (*Cassia leschenaultiana*), and purple passion flower (*Passiflora* sp.)(Walker, 1964).

A small part of the area was denuded by overgrazing and burning about 35 years ago (Walker, et al., 1969). Since then erosion and loss of vegetation had steadily progressed in upslope direction. On exposure the friable surface horizons had become indurated and bulk density had increased markedly. This induration did not become as intense as in typical laterite. The massive crust could, with some effort, be crumbled into smaller aggregates and subsequently into fine dust. Part of the denuded area was so heavily eroded as to have lost all A- and B-horizon material. Surrounding the barren area, in which profile III and IV were located, was a zone where grasses appeared in scattered patches. Profile II was situated in the latter zone. This was followed by a zone where small shrubs appeared (the sample site of profile I) and finally trees. A 2 to 3 feet wide zone of bare, indurated soil had been exposed within the last ten years (Walker, 1964).

Soil Profiles

Four soil profiles were studied. Profiles I, II and III were located within 20 feet of each other. Profile IV was located at a distance of approximately 50 feet from profile I. All four profiles were situated on the edge of a sharp escarpment exposing almost the entire solum of the soils. The escarpment formed the boundary of the severely eroded area.

Profile I was located on the highest point in the immediate surroundings. It had a vegetative cover of small shrubs. Roots were abundant in the upper 8 inches of the profile and gradually decreased in number going downwards, disappearing at around 30 inches of depth. The soil was friable from the surface down to the massive horizon at 35-inch depth, that underlaid all profiles. The layer from 16 to 35-inch depth was extremely friable. Profile I was considered to be the modal soil under vegetation, serving as a reference to the changes that took place in profile II, III and IV on progressive loss of vegetation.

Profile II was situated within six feet of profile I, on the boundary of the shrub-vegetated and the barren area. The vegetation consisted of an occasional small bush. Many roots were present throughout the profile. The soil was less moist than profile I and not friable. No induration could be observed. The massive subsurface layer occurred at 41 inch depth, while the layer from 28 to 41 inch contained fragments of the massive material, making up 50 % in volume.

Profile III, situated at a slightly lower level than profile II, was barren except for one tiny shrub. The upper 7 inches of the soil were indurated. The specific gravity of this surface layer was high;

its color was reddish purple. Nodules, ranging from highly magnetic to non-magnetic, were scattered over the surface. The soil was friable underneath the indurated surface, and was very friable just above the massive layer occurring at 31 inch depth. The friable layers contained much nodular material, which appeared to be similar to the massive subsurface material.

Profile IV was lowest in elevation. The soil was completely barren and it was obvious that erosion had taken place. No nodules were found on the surface. The upper 10 inch of the profile were strongly indurated. The specific gravity of this layer was very high. The layer was blackish-purple in color. Below the indurated topsoil, the soil was friable down to 25 inch, the depth to which the profile was sampled.

METHODS

Sample preparation

Part of the samples were air-dried at room temperature for about a week. Subsequently each sample was gently crushed while care was taken not to crush nodular material, which was separated by hand. Part of the samples were then ground to approximately 100 mesh.

Moisture content determination

Moisture content was determined in the usual way by ovendrying at 110°C.

Elemental analysis

Analysis by atomic-absorption spectrometry

The elements Fe, Al, Si and Mg were determined by Atomic Absorption Spectrometry.

The elements were brought into solution using the technique described by Suhr and Ingamells (1966). This technique involves fusion of the sample with lithium tetraborate followed by immediate addition of the melt to cold dilute nitric acid.

0.200 Gram of 100-mesh sample was mixed with 1.0 gram $LiBO_2$, transferred to a pre-ignited high-purity graphite crucible, and placed in a muffle furnace at 900°C for 20 minutes. The melt was then poured into a Teflon beaker, containing 100 ml 3 % HNO_3, and magnetically stirred for approximately 15 minutes. The samples were then diluted to the desired concentration range. Dilution factors were based upon the chemical analysis data given by Walker (1964) for similar soils. La_2O_3 was added to the solutions to be used for Mg determination, to give 1 % La_2O_3 in solution. Addition of La suppresses aluminate, silicate, phosphate, sulphate and iron interferences (Medlin, et al., 1969).

Standard stock solutions of 1000 ppm were prepared, following the procedure outlined above, using reagent grade oxides of the elements considered. The standard solutions were then diluted to yield solutions with five different concentrations within the desired concentration range for each element. Blanks were also prepared.

A Perkin-Elmer Atomic Absorption Spectrophotometer, Model 303, was used for the analysis.

The operating conditions were:

Fe

Concentration range: 0 - 20 ppm

Operating conditions:

Range: UV, wavelength 2487 A

Flame: air-acetylene oxidizing flame

Slit: 0.3 mm

Si

Concentration range: 0 - 30 ppm

Operating conditions:

Range: UV, wavelength 2516 A

Flame: nitrous oxide-acetylene reducing flame

Slit: 0.3 mm

Al

Concentration range: 0 - 30 ppm

Operating conditions:

Range: UV, wavelength 3095 A

Flame: nitrous-acetylene reducing flame

Slit: 0.3 mm

Mg

Concentration range: 0 - 2 ppm

Operating conditions:

Range: UV, wavelength 2852 A

Flame: air-acetylene reducing flame

Slit: 3 mm

X-ray spectrochemical analysis

Titanium was determined by X-ray spectrochemical analysis.

The samples, ground to 100 mesh and well-mixed, were compacted into pellets 1 1/4 inch in diameter and approximately 1/4 inch thick, at a pressure of 20,000 pounds for about 10 minutes. It was not necessary to use a binder. Care was taken to obtain and maintain a flat, shiny pellet surface for analysis.

Two types of standards were used. The first series of standards consisted of seven soils, similar to those under investigation, whose chemical composition was determined by Walker (1964). For the second series of standards synthetic oxides of Fe, Al, Si, Ti, Mn and Cr were employed plus methyl-cellulose as a binding agent. The oxides were mixed in ratios such as to most closely resemble the soil samples under investigation.

A Norelco Universal X-ray Spectrometer was used for the analysis.

Operating conditions were as follows:

Tube: Tungsten Target X-ray tube

Filter: Titanium

Detector: Gas Flow Proportional Counter; 1600 V
90 % Argon - 10 % Methane

Pulse Height Analyser: Integrated; 0.30 V baselevel

Power: 35 KV x 10 mA (for Ti)

Optical: LiF crystal; coarse collimators, Helium path

Count rate: 10^4 cps, fixed count.

In order to correct for variations in count rate due to admixture of air in the He atmosphere (on changing of the pellets) and variations in the power supply, etc., the radiation intensity of a standard count sample was measured immediately before counting each sample.

Determination of Fe, Al, Mn and Cr by X-ray spectrochemical analysis was attempted. No reliable results were obtained, however, due to apparent interrelations between the different elements and with organic matter.

The results of the elemental analysis have been expressed as oxides, in weight percent, based on ovendry soil.

X-ray diffraction analysis

Semi-quantitative mineralogical determination was performed by random powder X-ray diffraction analysis.

The samples were ground in acetone to approximately 400 mesh and placed in a Norelco bulk specimen holder. No size-fractionation or chemical treatments were employed.

The instrument used was a Norelco Wide Range X-ray Diffractometer, equipped with AMR X-ray focusing monochromator, model 3-202 with a LiF crystal.

Operating conditions were as follows:
Cu radiation: 50 kV, 40 mA.
1° divergence slit, 4° pre-slit, 1° receiving slit.
Scintillation counter: 774 V
PHA: baselevel 1V, window width 5V, amplifier gain 0
Scanspeed 1°/min; chart speed 2°/inch.

Additional runs of the magnetic nodules on the surface of profile III and of the surface horizons of profile III and IV were made with a scanspeed of 1/4°/min.

Reflection microscopy

Polished sections were studied and photographed with a Zeiss Standard Laboratory GFL polarizing Microscope, equipped with a reflected light attachment.

Several methods of sample impregnation were tried. The following method gave satisfactory results: Clods, one inch or smaller in diameter, were placed in aluminum dishes and ovendried at 110°C. The dishes were filled to a height of half an inch with a 1:2 caedex-xylene mixture, while care was taken not to wet protruding parts of clods with caedex mixture. The samples were kept on a hot plate at 40-50°C for two days, while xylene was added occasionally during the first 4 to 6 hours to make up for evaporation. The samples were then kept at 70°C on a hot plate or in an oven for two additional days and subsequently at 100°C for three days. They were then allowed to cool. The impregnated clods were mounted in laminac resin (using a few drops of accelerator) with the aid of a one inch diameter aluminum die.

Polished sections were obtained by rough grinding with carborundum powder 120 mesh, followed by grinding and polishing on the polishing machine with, in order, carbimet abrasive paper 240, 320, 400 and 600 mesh, emery abrasive powder 3200 mesh and diamond powder 1 micron.

RESULTS

Elemental analysis

The results of the chemical analysis are shown in Tables I and II and in Figures 1 through 4.

Table III gives the results of the pH and LOI determination of Naiwa soils from the same location published by Walker, et al. (1969). The pH data from Table III after Walker, et al. will be used in the following discussion when referring to pH.

The column headed "others" in Tables I and II gives the values for: $[100\%-\Sigma(SiO_2+Al_2O_3+Fe_2O_3+TiO_2+MgO)]$. A comparison of the loss on ignition (LOI) data of Walker (Table III) and "others" in Tables I and II shows great similarity between both sets of data. In the following discussion the term "others" stands for $[100\%-\Sigma(SiO_2+Al_2O_3+Fe_2O_3+TiO_2+MgO)]$ and will serve as an indication of the amount of LOI in the sample.

The massive clay layer, forming the deepest horizon in profiles I, II and III (horizons I-6, II-5A and II-6, III-6), had approximately the same chemical composition in all profiles. In profile III, the SiO_2 and Al_2O_3 contents were slightly lower and the Fe_2O_3 and TiO_2 contents were somewhat higher than in the corresponding horizons of profile I and II. In all three profiles, however, the SiO_2 content of the massive clay layer was appreciably higher than that of the overlying horizons. The SiO_2/Al_2O_3 mol ratio in the massive clay layer was 1.7, as opposed to a SiO_2/Al_2O_3 mol ratio of 0.8-1.2 in the overlying subsurface horizons. In profiles I and II, the Fe_2O_3 and

TiO_2 contents of the massive clay layer were higher than those of the immediately overlying horizon. In all three profiles the MgO content of the clay horizon was much higher and the "others" and $H_2O_{110°C}$ were appreciably lower than in the overlying subsurface horizons.

The subsurface horizons of all four profiles contained nodules ranging in size from 1/8 to 1 inch (see Table II), that were very similar to the massive clay layer, discussed above, in chemical, as well as mineralogical and morphological properties. In profile III, 25% of the volume of horizons 3, 4 and 5 was made up of these clay nodules.

Profile I was considered the modal soil under vegetation. No part of the sample area, however, was vegetated as densely as it had been decades of years ago, and some influence of loss of vegetation was evident in the upper 2.5 inches of profile I.

This surface horizon, from 1 to 2.5 inch depth, contained 60% less $H_2O_{110°C}$, 30% less "others", 30% less SiO_2, 50% less Al_2O_3 and two times as much Fe_2O_3 and MgO and three times as much TiO_2 as the subsoil.

The chemical composition of the soil from 2.5 depth to the massive clay layer at 35 inch depth was relatively uniform. There was, however, a slight increase in the SiO_2 and Al_2O_3 contents and a slight decrease in "others" with depth and the Fe_2O_3 and $H_2O_{110°C}$ contents in horizon 3 were slightly higher than those in horizons 2, 4, and 5.

Horizons 1 to 3 (0-20 inch) of profile II contained considerably less $H_2O_{110°C}$, "others", SiO_2 and Al_2O_3 and considerably more Fe_2O_3, TiO_2, and MgO than the subsoil. The surface horizon (0-3 inch) had the highest concentration of TiO_2 and MgO and a slightly higher SiO_2

content than horizon 2. The highest Fe_2O_3 concentration was encountered in horizon 2 (3-12 inch). None of the three top horizons were indurated.

Field observations suggested that the top 20 inches of profile II were erosional material. This would explain why this profile, although partly vegetated, showed Fe_2O_3 and TiO_2 accumulation and loss of $H_2O_{110°C}$, "others", SiO_2 and Al_2O_3 over a much greater depth (0-20 inch) than the barren profiles III and IV.

Horizon 4 (20-28 inch) could be considered a transition horizon between the zone of pronounced Fe_2O_3 and TiO_2 accumulation and SiO_2 and Al_2O_3 loss (0-20 inch) and the subsoil (horizon 5).

The chemical composition of horizon 5, overlying the massive clay layer, (28-41 inch), was similar to that of the subsoil of profile I, except for somewhat lower TiO_2 and MgO and higher $H_2O_{110°C}$ contents.

Profiles III (barren except of one tiny shrub) and IV (barren) demonstrated the influence of progressive loss of vegetation on the soil properties.

The SiO_2 content of the entire profile III above the subsoil massive clay layer was higher than that of the other three profiles at corresponding depths. This may have been due to the high number of nodules, consisting of material similar to that of the underlying massive clay layer, present in the profile. The nodules exhibited various degrees of hardness, giving evidence of disintegration. On disintegration and incorporation in the soil matrix material, they would increase the SiO_2 content of the soil matrix.

In the topsoil (0-7 inch) the contents of $H_2O_{110°C}$, "others",

SiO_2 and Al_2O_3 were distinctly less and the concentrations of Fe_2O_3, TiO_2 and MgO considerably higher than in the subsoil. Horizons 1 (0-4 inch) and 2 (4-7 inch) were indurated. Induration was most severe in horizon 1. This horizon displayed a 60% $H_2O_{110°C}$ and 65% Al_2O_3 loss, a twofold increase in TiO_2 and MgO content and a slight increase in Fe_2O_3 concentration, with respect to horizon 2.

Numerous very hard, strongly magnetic to non-magnetic, nodules were found on the surface. They ranged in size from 1/2 to 1 inch diameter. These nodules were made up predominantly of Fe_2O_3 (72-85%) and TiO_2 (10-22%) and contained almost no $H_2O_{110°C}$ (0.5%) and very little SiO_2 (2-4%) and Al_2O_3 (1.5-2.5%) (see Table II).

From 7 to 31 inch-depth, a gradual increase in SiO_2, Al_2O_3, and MgO and a gradual decrease in Fe_2O_3 and TiO_2 could be observed. The $H_2O_{110°C}$ and "others" in the subsoil were much lower than in the subsoil of profile I.

Profile IV was not sampled deep enough to reach the massive clay horizon. Horizon 5, however, contained nodules which were similar in composition to the clay nodules and the massive layer in the other three profiles.

The topsoil (0-10 inch) was strongly indurated. The amount of $H_2O_{110°C}$ in the upper 10 inches was very low (1.5-3%). The Al_2O_3 content in horizon 2 (3-10 inch) was one-third and in horizon 1 (0-3 inch) one-sixth of the Al_2O_3 concentration in horizon 3. The Fe_2O_3 content showed a 50% increase and the TiO_2 and MgO content a more than twofold increase, with respect to horizon 3.

Horizon 3 (10-14 inch) formed the transition layer between the strongly indurated topsoil and the friable subsoil.

The SiO_2 and $H_2O_{110°C}$ content increased gradually with depth. From 14 to 25 inches the Al_2O_3, Fe_2O_3, TiO_2, and MgO content remained fairly constant.

TABLE I. CHEMICAL COMPOSITION OF PROFILES I, II, III AND IV

	Inches	Weight percent on oven-dry basis							
Sample	Depth	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	Total	"Others"[a]	$H_2O_{110°C}$
I-1	1-2.5	10.7	14.8	45.5	8.1	0.48	79.6	20.4	8.9
2	2.5-8	14.2	27.4	21.8	2.8	0.21	66.4	33.6	20.6
3	8-16	14.8	29.3	22.6	2.7	0.20	69.6	30.4	23.2
4	16-27	16.2	30.2	22.0	2.5	0.20	71.1	28.9	21.8
5	27-35	18.2	30.1	19.9	2.6	0.23	71.0	29.0	18.5
6	35-40	30.3	31.6	22.0	3.4	0.43	87.7	12.3	8.6
II-1	0-3	8.9	6.0	62.9	15.2	0.80	93.8	6.2	3.5
2	3-12	7.1	6.9	68.3	10.9	0.44	93.6	6.4	3.9
3	12-20	6.1	11.8	66.3	7.2	0.20	91.6	8.4	7.7
4	20-28	12.4	19.9	48.1	5.2	0.22	85.8	14.2	13.9
5	28-41	14.4	30.0	20.5	2.0	0.14	67.0	33.0	31.3
5A	"	30.2	31.4	24.2	3.4	0.43	89.6	10.4	10.3
6	41+	31.1	31.8	23.9	3.3	0.45	90.5	9.5	9.9
III-1	0-4	11.9	4.3	59.3	19.3	0.98	95.8	4.2	1.7
2	4-7	15.3	12.4	55.9	9.7	0.48	93.8	6.2	4.3
3	7-13	17.8	21.5	40.8	5.8	0.29	86.2	13.8	10.1
4	13-18	21.2	24.0	35.1	4.9	0.34	85.5	14.5	10.3
5	18-31	24.2	26.2	31.8	4.6	0.38	87.2	12.8	9.5
6	31+	28.2	28.1	28.1	4.0	0.43	88.8	11.2	8.3
IV-1	0-3	6.7	3.8	65.3	15.9	1.09	92.8	7.2	1.4
2	3-10	7.8	7.1	66.5	14.3	0.83	96.5	3.5	2.8
3	10-14	9.4	21.5	44.9	6.8	0.38	83.0	17.0	7.8
4	14-16	13.2	29.8	27.3	3.5	0.31	74.1	25.9	13.7
5	16-25	17.4	28.5	27.9	3.3	0.25	77.4	22.6	16.7

[a] "Others" = 100% - $\Sigma(SiO_2+Al_2O_3+Fe_2O_3+TiO_2+MgO)$

TABLE II. CHEMICAL COMPOSITION AND VOLUME PERCENTAGE OF NODULES IN PROFILES I, II, III AND IV

Sample	Depth	Vol. %	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	Total	"Others"[a]	$H_2O_{110°C}$	comments
	Inches	Of entire horizon	Weight percent on oven-dry basis								
I-2	2.5-8	5									
3	8-16	5	29.4	31.3	20.8	3.3	0.42	85.2	14.8	10.4	
4	16-27	7.5									
5	27-35	10	29.6	31.4	20.9	3.1	0.42	85.4	14.6	9.5	
II-4	20-28	15	29.0	30.9	22.3	3.7	0.41	86.3	13.7	9.6	
5	28-41	5									
III-0	0		1.8	2.3	85.9	10.8	0.37	101.2	-	0.5	highly magnetic
ibid	ibid		4.3	1.7	71.9	13.3	0.95	92.2	7.8	0.5	moderately magnetic
ibid	ibid		3.8	2.7	79.0	22.2	0.58	108.3	-	0.5	slightly magnetic
ibid	ibid		3.9	2.3	73.7	16.2	0.95	97.1	2.9	0.5	non-magnetic
3	7-13	25									
4	13-18	25	27.1	28.2	25.9	3.7	0.41	85.3	14.7	8.8	
5	18-31	25	29.4	29.3	25.2	3.8	0.43	88.1	11.9	8.6	
IV-5	16-25	5	26.2	31.4	22.8	3.3	0.41	84.1	15.9	11.8	

[a] "Others" = 100% - $\Sigma(SiO_2+Al_2O_3+Fe_2O_3+TiO_2+MgO)$

TABLE III. THE pH AND LOSS ON IGNITION (LOI) OF
TWO NAIWA SOIL PROFILES, LOCATED ALONG KOKEE CANYON
ROAD JUST INSIDE FOREST RESERVE
After Walker, et al. (1969)

		Profile having a vegetative cover		
Sample	Depth		pH_{H_2O}	LOI
N-2	1-3		5.0	15.6
N-3	3-6	friable	5.0	32.5
N-6	14-20	friable	5.0	33.6
N-9	31-38	massive clay layer	5.0	18.0
		Indurated profile, bare of vegetation		
N-12	1-3	indurated	4.4	3.6
N-14	6-10	indurated	4.4	8.0
N-15	10-12	transition	4.7	16.1
N-17	15-19	friable	4.6	34.4
N-19	25+	massive clay layer	5.1	15.5

FIG . 1. CHEMICAL COMPOSITION OF PROFILE I

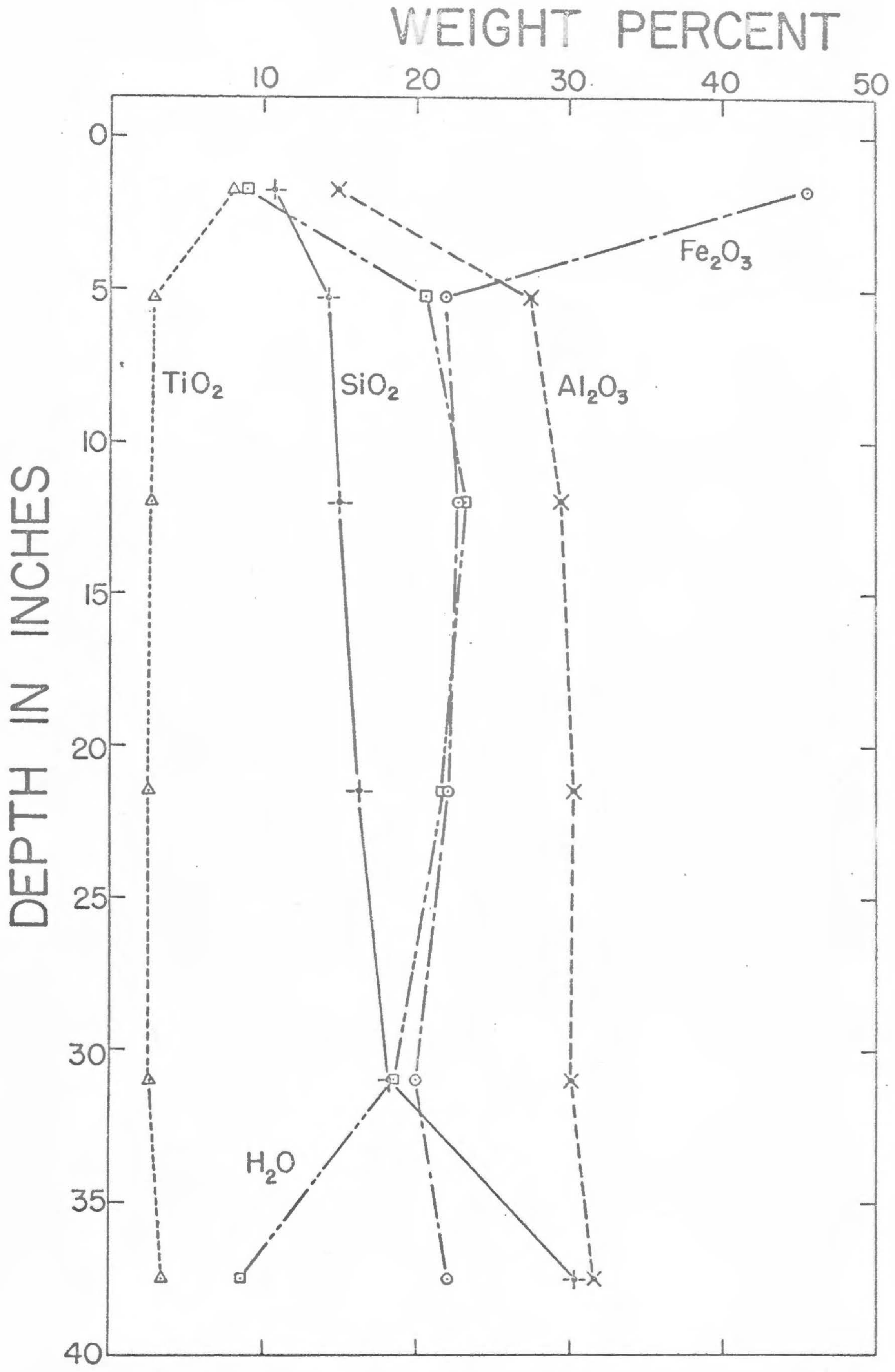

WEIGHT PERCENT
10
20
30
40
50
DEPTH IN INCHES
0
5
10
15
20
25
30
35
40
Fe$_2$O$_3$
TiO$_2$
SiO$_2$
Al$_2$O$_3$
H$_2$O

FIG. 2. CHEMICAL COMPOSITION OF PROFILE II

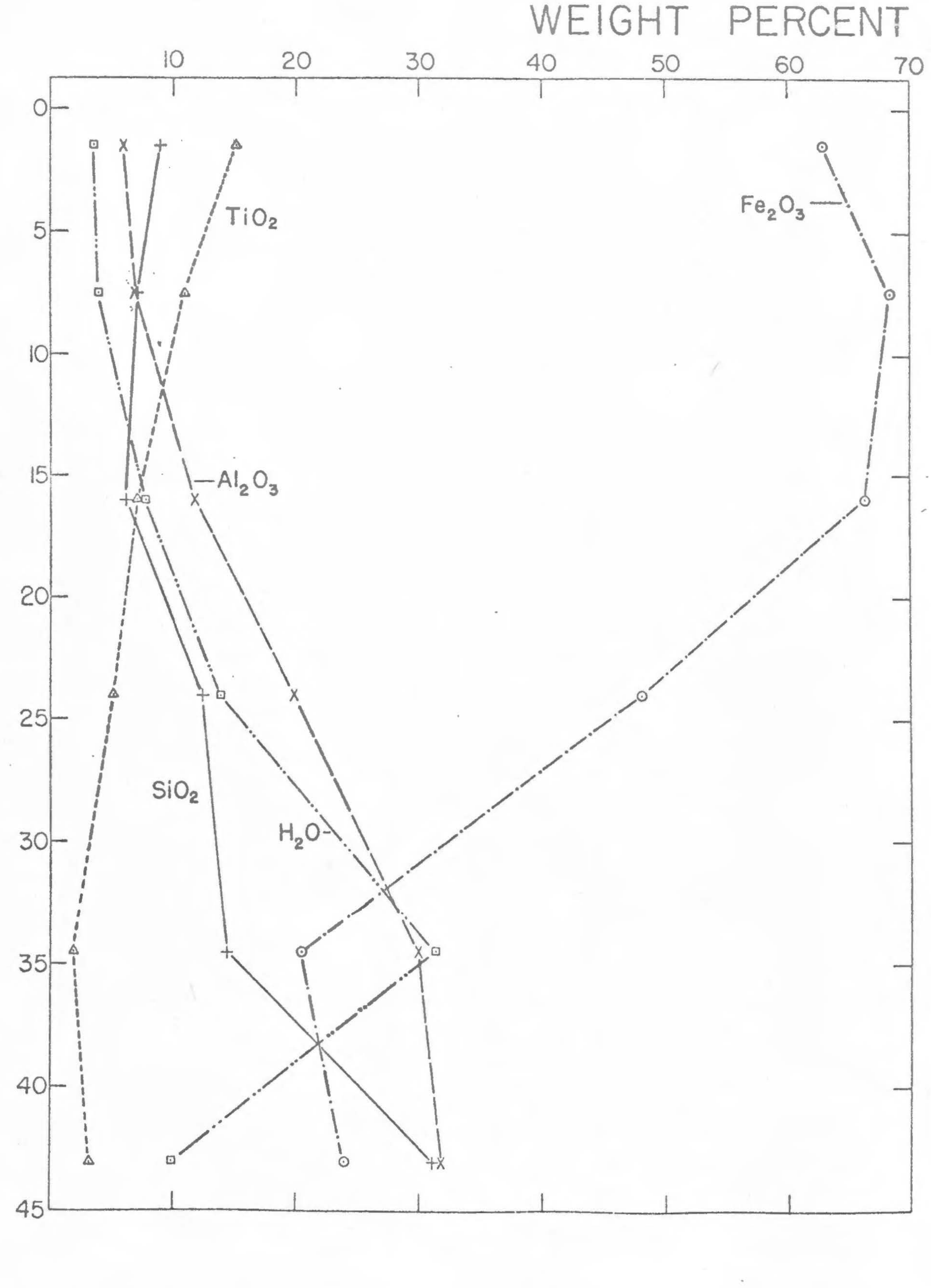
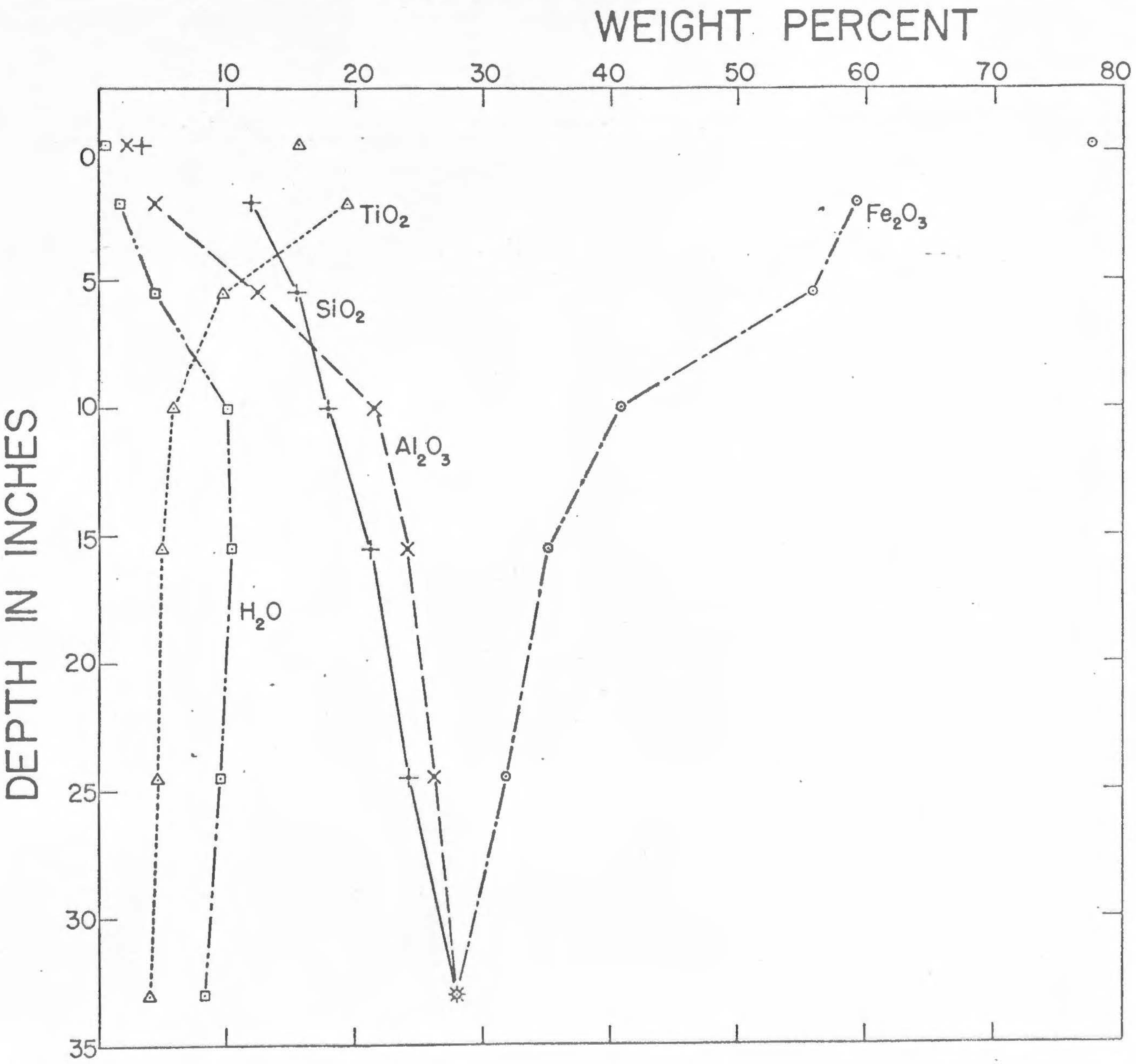

WEIGHT PERCENT
10
20
30
40
50
60
70
0
5
10
15
20
25
30
35
40
45
TiO_2
Fe_2O_3
Al_2O_3
SiO_2
H_2O

FIG. 3. CHEMICAL COMPOSITION OF PROFILE III


WEIGHT PERCENT
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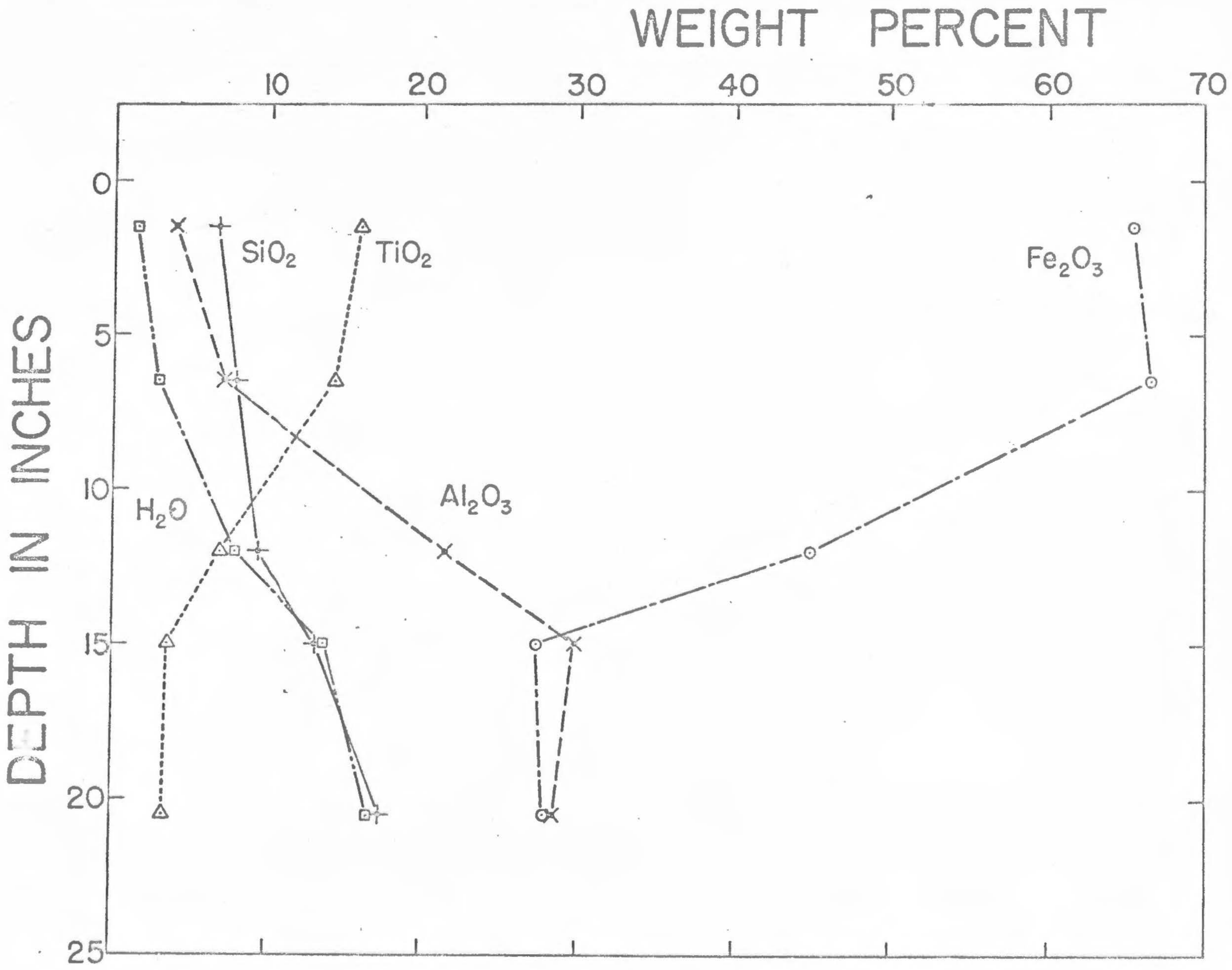
20
30
40
50
60
70
80
DEPTH IN INCHES
0
5
10
15
20
25
30
35
TiO_2
SiO_2
Al_2O_3
H_2O
Fe_2O_3

FIG. 4. CHEMICAL COMPOSITION OF PROFILE IV


WEIGHT PERCENT
10
20
30
40
50
60
70
DEPTH IN INCHES
0
5
10
15
20
25
SiO_2
TiO_2
Fe_2O_3
H_2O
Al_2O_3

X-ray diffraction analysis

The results of the X-ray diffraction analyses are presented in Table IV and Figures 5 through 9.

Hematite was the most abundant mineral in all horizons, except in the massive subsurface clay layer.

A slight shift towards higher d-spacings could be observed in the X-ray reflections of the [102] and [104] crystal planes. This shift was in the order of one tenth of an Angstrom. The existence of the shift was indicated by examination of the X-ray charts made at 1° 2θ/minute speed. It was confirmed by X-ray patterns of the top horizons and surface nodules of profiles III and IV at a speed of 1/4° 2θ/minute. A similar systematic shift of the d-spacings of hematite to those of ilmenite was observed by Katsura, et al. (1962) and Walker (1964) in soils of the same location. Walker, however, reported a larger shift. Katsura, et al. (1962) attributed the shift in d-spacings to solid solution of ilmenite with hematite. As discussed on page 15, the existence of an ilmenite-hematite solid solution series in rocks and soils is well established. The relatively high titanium content of Hawaiian lavas (see page 25) makes substitution of iron by titanium in hematite, maghemite and magnetite very likely.

In all profiles hematite was most abundant in the tophorizon. With increasing depth in the profile, the amount of hematite decreased.

Goethite was most abundant in the subsoils. The amount of goethite decreased with proximity to the surface.

The X-ray reflections of the goethite, occurring in these soils, shifted towards lower lattice-spacings, as compared to the data for standard goethite given by Rooksby (Brown, 1961). The amount of shift corresponded with an Al substitution in the order of 25-30 mol % AlO.OH (Norrish and Taylor, 1963; and van Thiel, 1963).

The broadness of the X-ray reflections indicated that the goethite had a very small particle size and/or was poorly crystallized. This agrees with the data of Norrish, et al. (1963) and van Thiel (1963), which showed that the particle size of soil goethites decreased linearly and that the water content increased with increasing isomorphous substitution of iron by aluminum.

Studies on standard magnetite and maghemite showed that, with the X-ray diffraction equipment and working conditions employed in this study, resolution was sufficiently high to allow identification of both magnetite and maghemite when both minerals were present in one sample, provided the particle size of the two minerals was equally small. The latter provision was shown to hold true for the soils in question (Katsura, et al., 1962).

Maghemite was identified as the main ferromagnetic mineral in all four profiles. The highest amount of maghemite was found in the massive subsurface clay layer. Going upward in the profile, the amount of maghemite decreased.

Judging from the broadness of the [220] and [400] plane reflections, the maghemite in the solum above the massive clay layer had a very small particle size or was poorly crystallized. In the topsoil crystallinity was improved, as indicated by sharper [220] and [400] reflections. The subsoil clay layer exhibited sharp maghemite peaks.

Appreciable amounts of magnetite were only present in the subsurface clay layer of profile I and II. Profile I appeared to contain a small amount of magnetite in the entire profile.

As discussed on page 16, most magnetites in basic igneous rocks contain appreciable amounts of titanium (Deer, et al., 1966). The magnetites and maghemites in Hawaiian rocks and soils were reported to contain 21-25 mol % TiO_2 (Matsusaka, et al., 1964; Katsura, et al., 1962). Katsura (1957) found a linear relationship between the chemical composition and the lattice parameter of members of the ulvospinel-magnetite solid solution series. The X-ray patterns of the four Naiwa profiles studied, however, did not show a shift in the d-spacings of magnetite and maghemite.

The most intense reflections of ilmenite occurred at 2.73 A. Resolution was good enough to separate the ilmenite reflection at 2.73 A from the hematite peak at 2.70 A. The presence of ilmenite was confirmed by reflections at 3.73 and 2.55 A. The most intense X-ray reflection showed a distinct shift towards lower d-spacings. This could be accounted for by assuming a composition for ilmenite intermediate between ilmenite and hematite, closer to ilmenite.

Ilmenite was present in all horizons and was concentrated in the tophorizons of all profiles. The greatest concentration occurred in the indurated tophorizons of profile III and especially profile IV. The massive clay layer deep in the profile contained more ilmenite than the overlying subsoil.

Quartz in well-crystallized form was present throughout all profiles. A distinct increase in quartz content could be observed with proximity to the surface. The degree of concentration in the surface horizon was lowest in profile I and highest in profile III.

Anatase was identified by its main reflection at 3.52 A and minor reflections at 2.38, 1.89 and 1.66 A. The minor reflections could only be observed with certainty at relatively high anatase concentrations.

Anatase was present throughout the profiles. It increased in concentration with increase in depth.

Pseudobrookite was identified by its main reflection at 3.48 A, and minor reflections at 4.90, 2.40 and 1.97 A. While the observation of the 2.40 and 1.97 A d-spacings was doubtful at low pseudobrookite concentrations, the peak at 4.90 A could usually be discerned.

Pseudobrookite was present in the topsoils of all profiles. In the subsoils of profiles I, II, and III it was found in trace amounts. The highest amounts occurred in the indurated surface horizons of profiles III and IV.

Rutile was identified by its main peak at 3.25 A and minor reflections at 1.62 and 1.36 A. When present in small amounts, the lesser peaks were difficult to observe. Occurrence of a distinct peak at 3.25 A was felt to be enough justification for the identification of rutile in the latter case.

Rutile was present in the tophorizons of all profiles. Trace amounts were found throughout profile I and III. The highest amount occurred in the surface horizons of profile III and IV.

Only profile IV contained large amounts of gibbsite. Gibbsite was concentrated in the subsoil of this profile, especially in horizon 4 (14-16 inch). No gibbsite was present in the top 10 inches of this profile. Profile I contained a small amount of gibbsite throughout the profile with the exception of the surface horizon. Trace amounts were present in profile II and the subsoil of profile III.

The X-ray patterns of the subsoil clay layer showed well defined intense peaks for kaolin. The subsoil of the four profiles above the massive clay layer contained layer silicates, as indicated by the [020] reflection at 4.46 A. Only very weak broad first order basal reflections with d-spacings from 14-20 A could be discerned. Whittig (1954), in his study of the clay minerals of a Naiwa soil profile from the same location, however, identified mica, vermiculite, montmorillonite, chlorite, halloysite, and interstratified clay minerals.

The surface horizons of profiles II, III, and IV did not exhibit X-ray reflections at 4.46 A and 14-20 A, while these reflections were only very weak in the surface horizon of profile I. No evidence of the presence of amorphous material could be found in these surface horizons. The SiO_2 content of these horizons was therefore assigned to quartz. With increasing depth in the profile the amount of quartz present decreased, attended by a reduction in the SiO_2 content assignable to quartz. The overall SiO_2 content, however, increased with increase in depth. Only small amounts of gibbsite were present in all profiles except profile IV. The amount of substitution of Al in goethite was not enough to account for all the Al_2O_3 determined in the subsoils. The fact that the increase in SiO_2 and Al_2O_3 content with depth was coupled with increase in intensity of the 4.46 and 14-20 A X-ray reflections, substantiated the suggestion that these reflections were due to layer silicates.

The X-ray patterns gave no indication of the presence of amorphous material (as indicated by an increase in background radiation at approximately 3.5 A). Other workers, however, reported a high concentration of amorphous material in similar soils (Whittig, 1954). Part of the silica and aluminum may therefore be present in amorphous form.

The SiO_2/Al_2O_3 mol ratio in the solum above the massive clay layer was much lower than that in the clay layer.

The massive clay layer underlying profiles I, II, and III and the clay nodules in the subsoils contained less hematite and more goethite, maghemite, magnetite, ilmenite, gibbsite and layer silicates than the solum above. The X-ray patterns showed well-defined peaks for kaolin..

The top 8 inches, and especially the top 2.5 inches of profile I had higher concentrations of hematite, ilmenite, quartz, pseudobrookite and rutile and lower contents of goethite, anatase, gibbsite, and layer silicates than the soil below. The subsoil, from 8-35 inches, had a uniform mineralogical composition.

Profile II had a very high hematite concentration. The concentration of ilmenite, quartz, pseudobrookite, and rutile in the top 12 inches was higher and the concentration of goethite and anatase was lower than in the subsoil. Layer silicates were only present deeper than 20 inches. Only trace amounts of gibbsite occurred.

The hematite content of profile III was high. The indurated topsoil and especially the upper 4 inches contained considerably more ilmenite, quartz, pseudobrookite, and rutile and less goethite, maghemite, anatase, gibbsite, and layer silicates than the subsoil.

The subsoil from 7-31 inches had a mineralogical composition similar to the subsoil of profile I, except for a slightly higher hematite and pseudobrookite and a lower gibbsite content.

. The nodules, scattered on the surface of profile III, were made up of mostly hematite plus maghemite. The highly magnetic nodules contained mostly maghemite, plus smaller amounts of hematite and trace amounts of quartz, rutile, pseudobrookite. The non-magnetic nodules consisted of mainly hematite, plus ilmenite, rutile, pseudobrookite, and anatase in approximately the same quantities as in horizon 1 of profile III, with smaller amounts of quartz. The moderately magnetic nodules had intermediate hematite/maghemite ratios.

The indurated top 10 inches of profile IV contained even more hematite, ilmenite, pseudobrookite, and rutile than the topsoil of profile III. The concentration of maghemite in the top 3 inches was higher than in the subsoil. The subsoil of profile IV (10-25 inches) had a high amount of gibbsite. The highest gibbsite concentration was found in horizon 4 (14-16 inches).

TABLE IV. MINERALOGICAL COMPOSITION OF PROFILES I, II, III AND IV

Sample	Depth in inches	Hematite	Goethite	Maghemite	Magnetite	Ilmenite	Quartz	Anatase	Pseudo-brookite	Rutile	Layer silicates	Gibbsite
I-1	1-2.5	4	1	1	1	1-2	2	1	1	1	1	
2	2.5-8	3	2	1	1	1-2	1-2	2	1	tr	2	tr-1
3	8-16	3	2	1	1	1	1	2	tr	tr	2	tr-1
4	16-27	3	2	2	?	1	1	2	tr	tr	2	1
5	27-35	3	2	2	?	1	1	2	tr	tr	2	1
6	35-40	2	3	3	2	1-2	1	2		tr	3	1
II-1	0-3	5	1	1		2	3	1	1	1		tr
2	3-12	5	1	1		1	2	1	1	1		tr
3	12-20	5	2	1		1	1-2	1-2				tr
4	20-28	5	2	1		1	1-2	2	tr		1	tr
5	28-41	4	2	1	1	1	1	2	tr		2	tr
5A	28-41	2	3	3	3	1		2	tr		3	1
6	41+	2	3	3	2	1	1	2	tr	1	3	1
III-1	0-4	4	1	1		3	4	1	2	1-2		
2	4-7	4	2	1	tr	1-2	2	1	1	tr	1	
3	7-13	4	2	2	1	1	1	1	1	tr	2	tr
4	13-18	4	2	2		1	1	2	tr-1		2	
5	18-31	3	3	2	tr	?	1	2	tr-1	1	2	tr
6	31+	3	3	3		2		2	?	?	3	1
IV-1	0-3	5	1	1-2		3	3	1	2	1-2		
2	3-10	4	1	1		2-3	2	1-2	1-2	1	tr	
3	10-14	3-4	2	1	tr	1	1	1-2	1			2
4	14-16	3	2	2	1	1	1	1-2	1		1-2	3
5	16-25	3	3	2	1	1	1	2	1		2	2

tr = traces 1 = little 2 = moderate 3 = much 4 = abundant 5 = very abundant

FIG. 5. X-RAY DIFFRACTION PATTERNS OF PROFILE I

	Main reflection in Angstrom	Minor reflection in Angstrom
Hematite	2.70	3.68
Goethite	4.15	2.42
Maghemite	2.51	2.95
Magnetite	2.53	
Ilmenite	2.73	3.73
Quartz	3.34	
Anatase	3.52	
Pseudobrookite	3.48	4.90
Rutile	3.25	
Layer silicates	4.45	
Gibbsite	4.85	

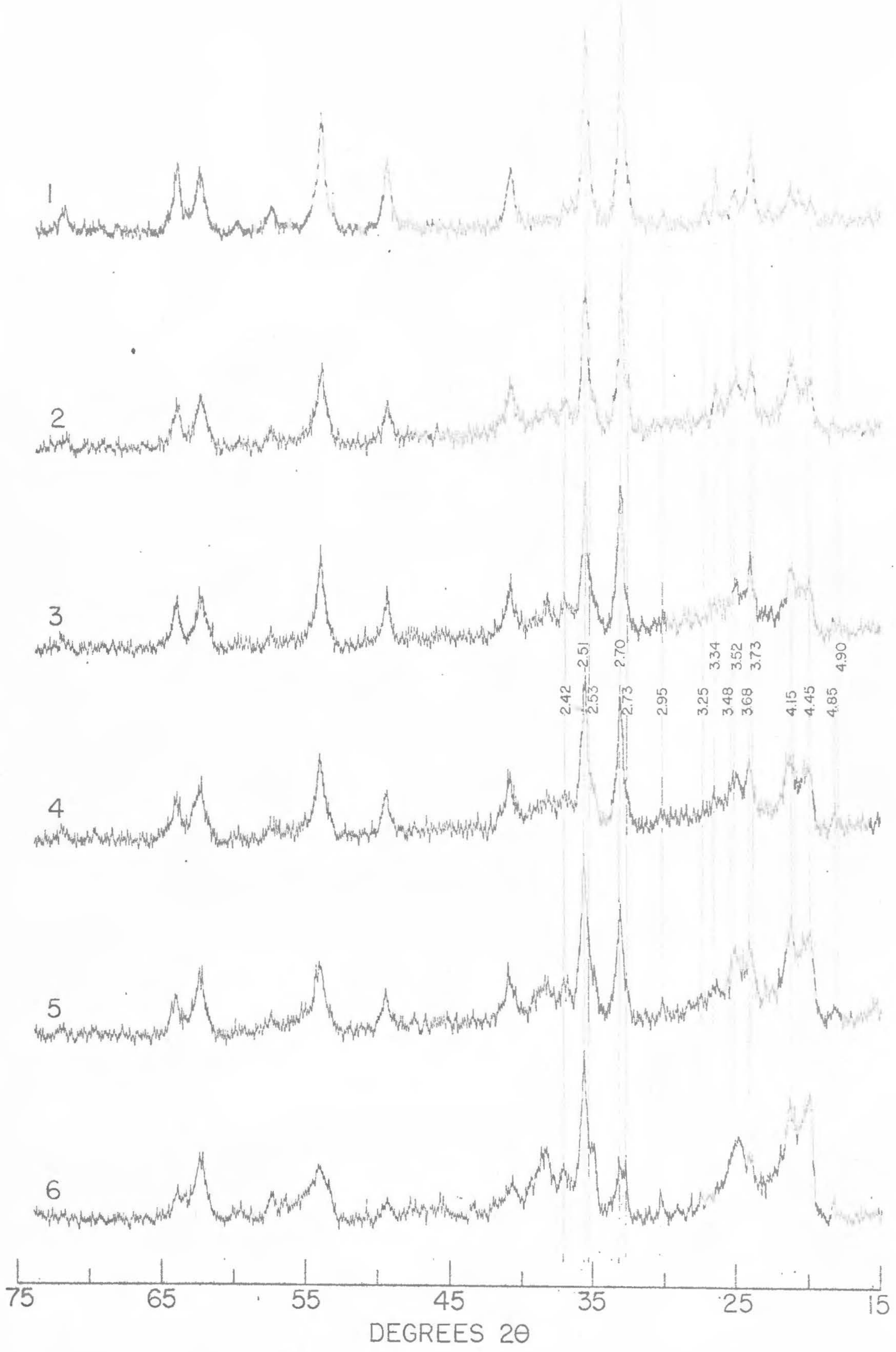

1
2
3
4
5
6
2.51
2.70
3.34
3.52
3.73
4.90
2.42
2.53
2.73
2.95
3.25
3.48
3.68
4.15
4.45
4.85
75
65
55
45
35
25
15
DEGREES 2θ

FIG. 6. X-RAY DIFFRACTION PATTERNS OF PROFILE II

	Main reflection in Angstrom	Minor reflection in Angstrom
Hematite	2.70	3.68
Goethite	4.15	2.42
Maghemite	2.51	2.95
Magnetite	2.53	
Ilmenite	2.73	
Quartz	3.34	
Anatase	3.52	
Pseudobrookite	3.48	
Rutile	3.25	
Layer silicates	4.45	
Gibbsite	4.85	

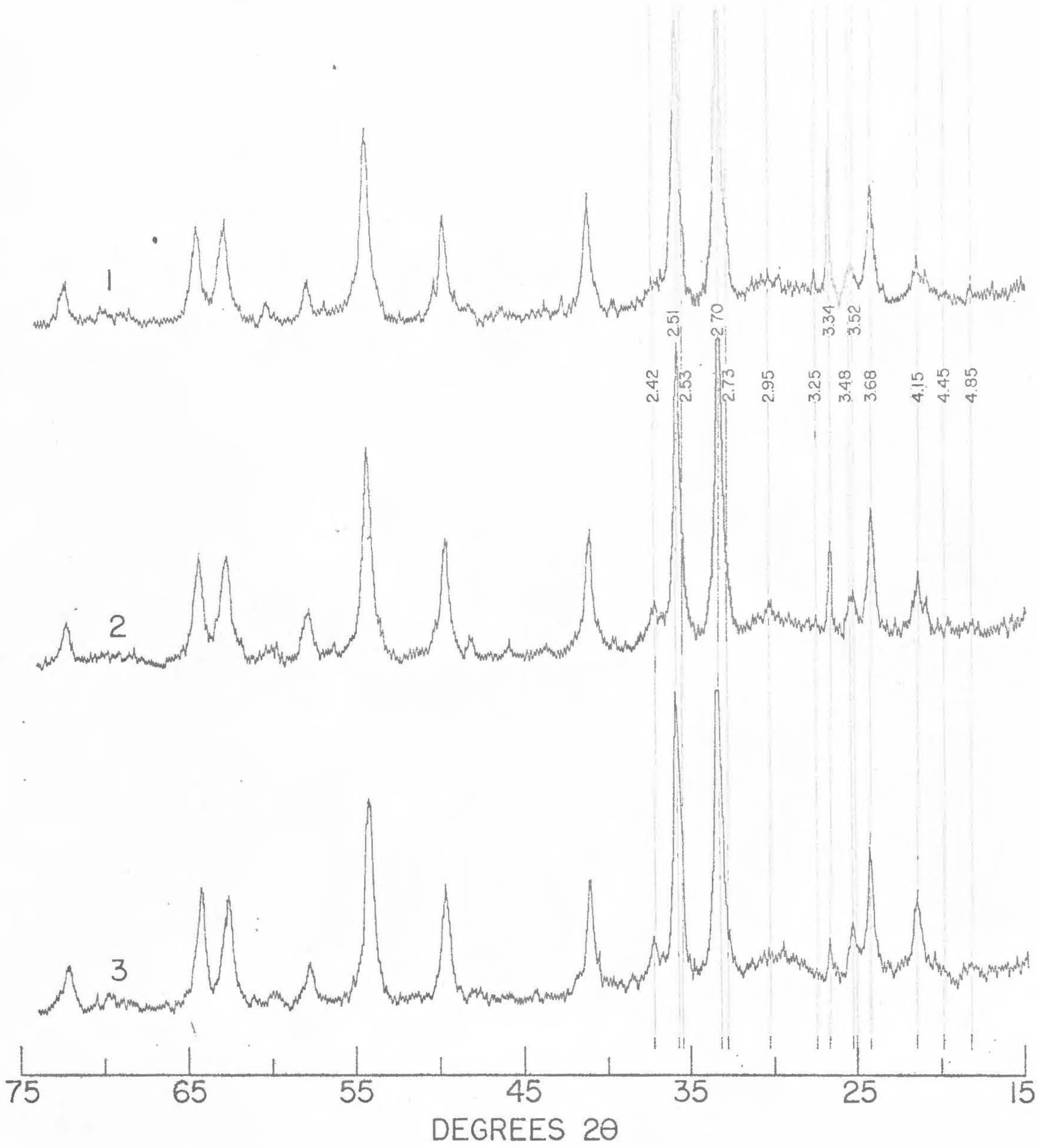

1
2
3
2.51
2.70
3.34
3.52
2.42
2.53
2.73
2.95
3.25
3.48
3.68
4.15
4.45
4.85
75
65
55
45
35
25
15
DEGREES 2θ

FIG. 6 (Continued) X-RAY DIFFRACTION PATTERNS OF PROFILE II

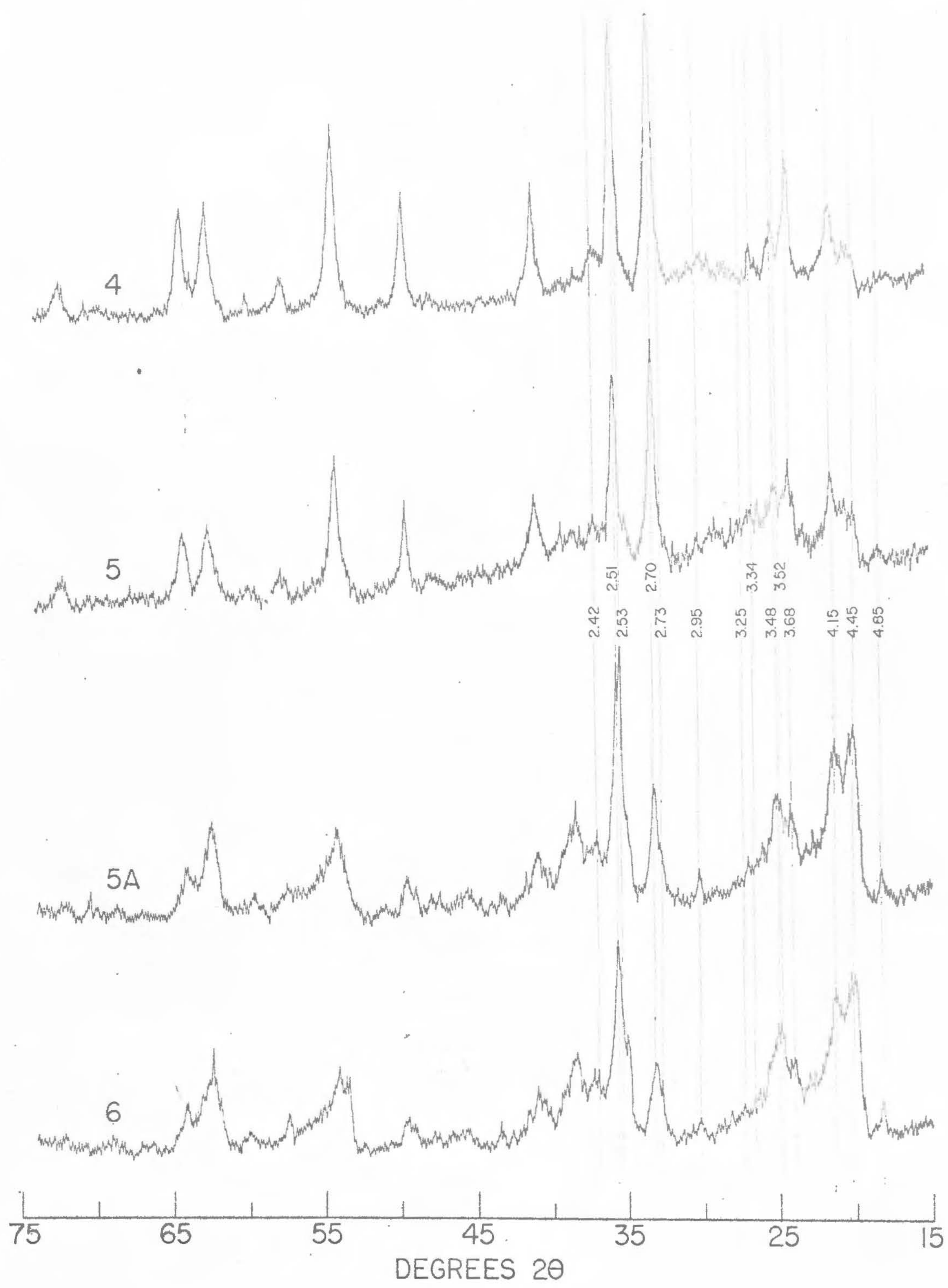

4
5
5A
6
2.51
2.70
3.34
3.52
2.42
2.53
2.73
2.95
3.25
3.48
3.68
4.15
4.45
4.85
75
65
55
45
35
25
15
DEGREES 2θ

FIG. 7. X-RAY DIFFRACTION PATTERNS OF PROFILE III

	Main reflection in Angstrom	Minor reflection in Angstrom
Hematite	2.70	3.68
Goethite	4.15	2.42
Maghemite	2.51	2.95
Magnetite	2.53	
Ilmenite	2.73	3.73
Quartz	3.34	
Anatase	3.52	
Pseudobrookite	3.48	4.90
Rutile	3.25	
Layer silicates	4.45	
Gibbsite	4.85	

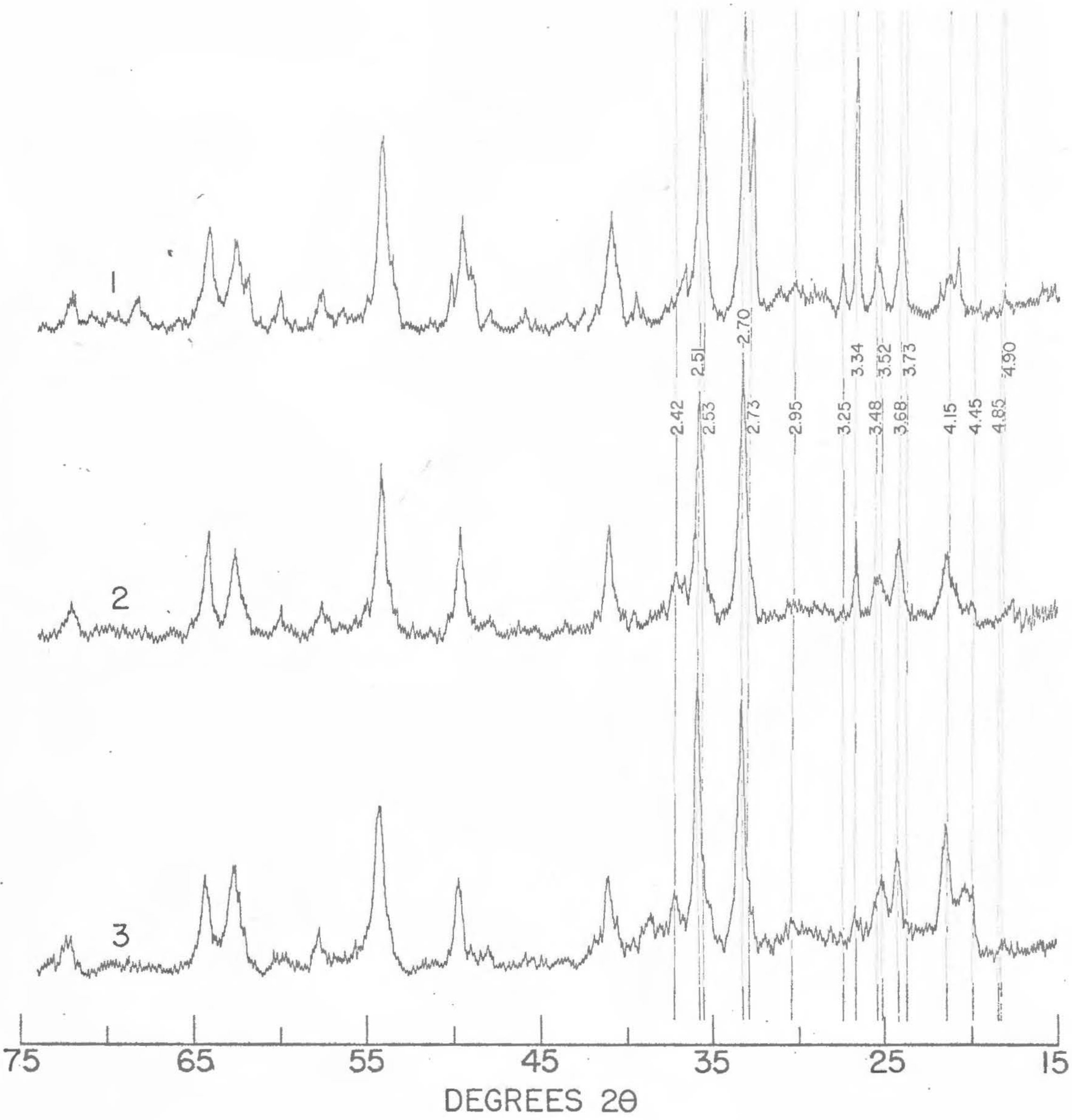

1
2
3
2.70
2.51
3.34
3.52
3.73
4.90
2.42
2.53
2.73
2.95
3.25
3.48
3.68
4.15
4.45
4.85
75
65
55
45
35
25
15
DEGREES 2θ

FIG. 7. (Continued) X-RAY DIFFRACTION PATTERNS OF PROFILE III

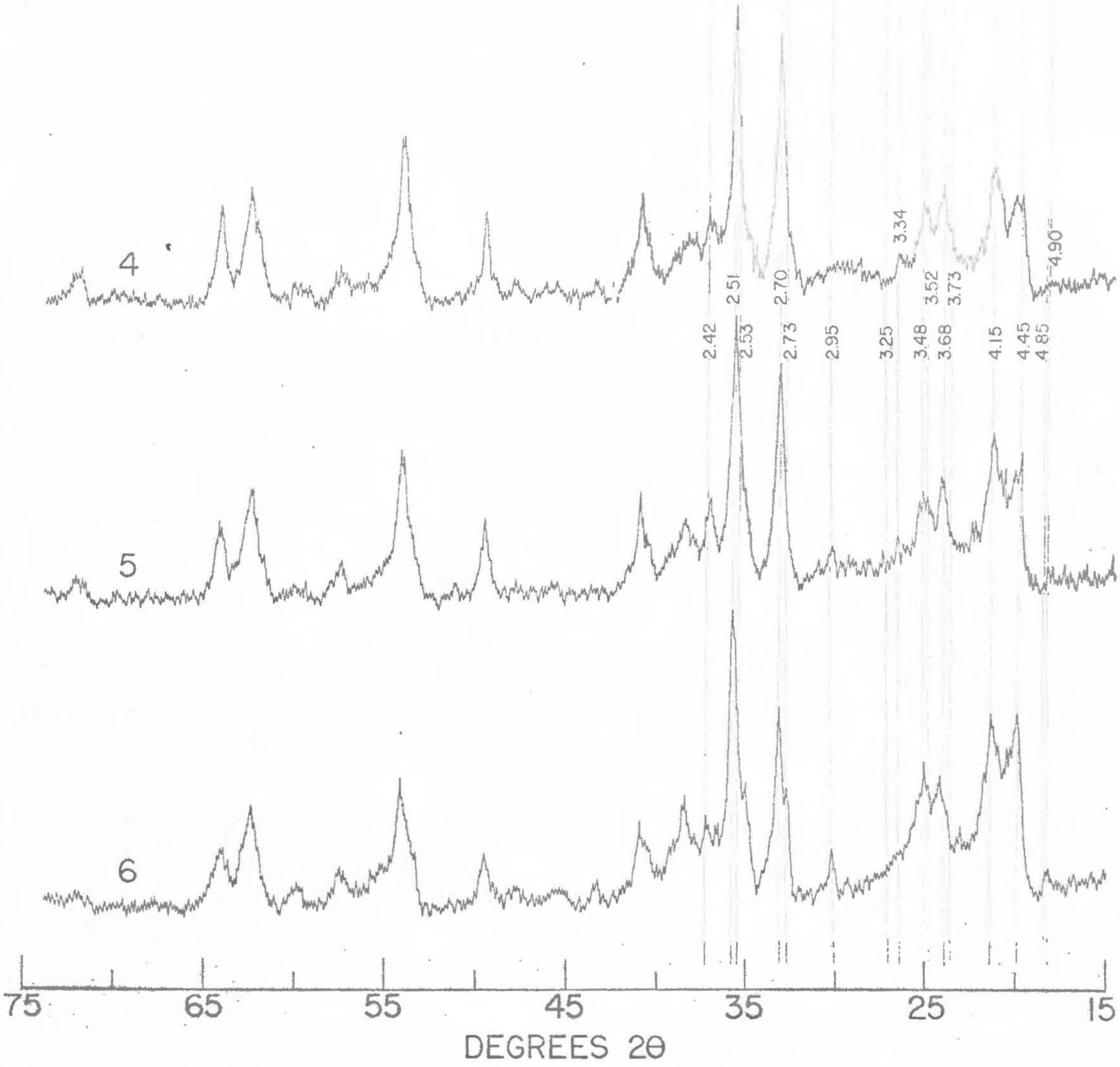

4
5
6
3.34
4.90
2.51
2.70
3.52
3.73
2.42
2.53
2.73
2.95
3.25
3.48
3.68
4.15
4.45
4.85
75
65
55
45
35
25
15
DEGREES 2θ

FIG. 8. X-RAY DIFFRACTION PATTERNS OF PROFILE IV

	Main reflection in Angstrom	Minor reflection in Angstrom
Hematite	2.70	3.68
Goethite	4.15	2.41
Maghemite	2.51	2.95
Magnetite	2.53	
Ilmenite	2.73	3.73
Quartz	3.34	
Anatase	3.52	
Pseudobrookite	3.48	4.90
Rutile	3.25	
Layer silicates	4.45	
Gibbsite	4.85	

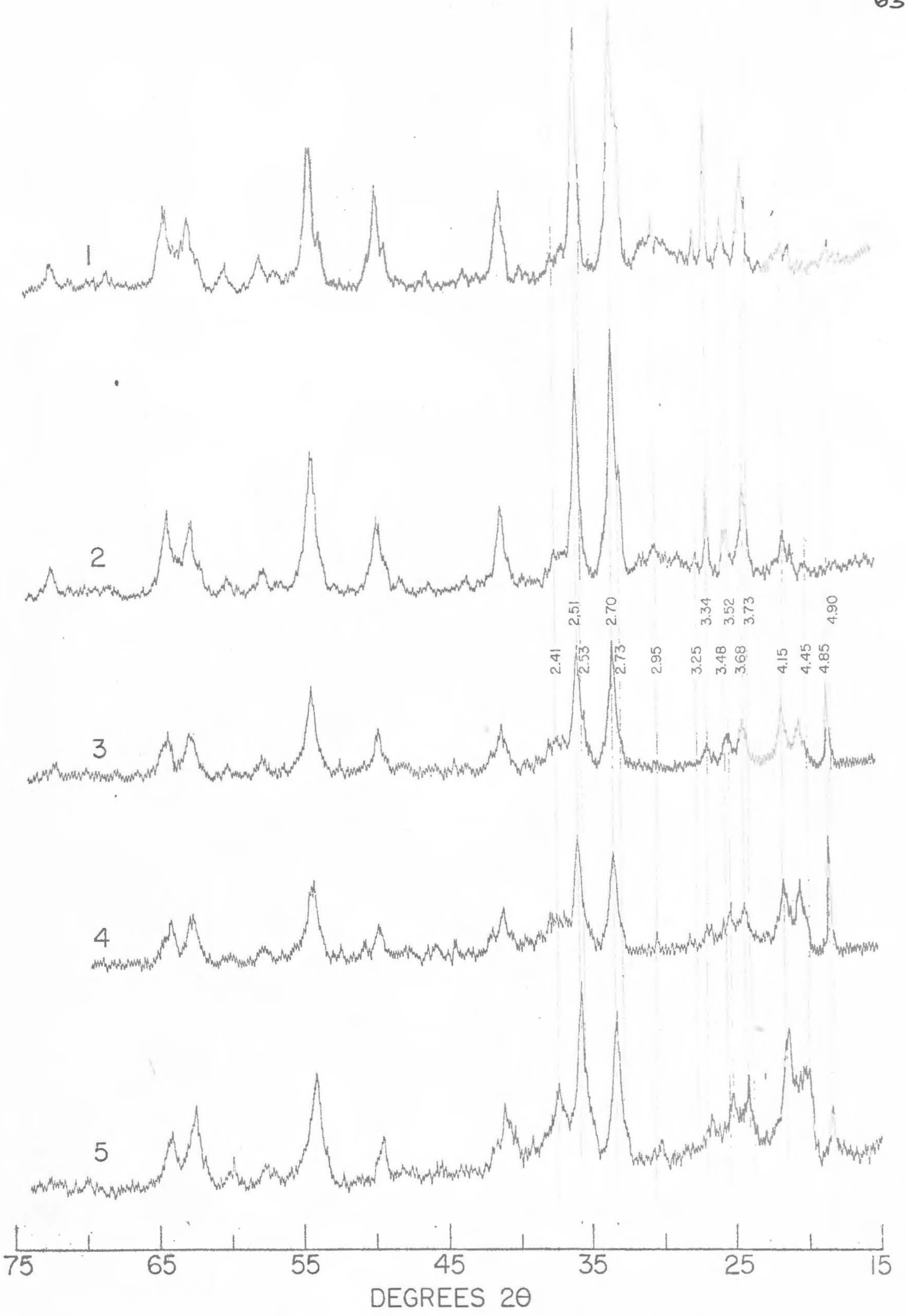
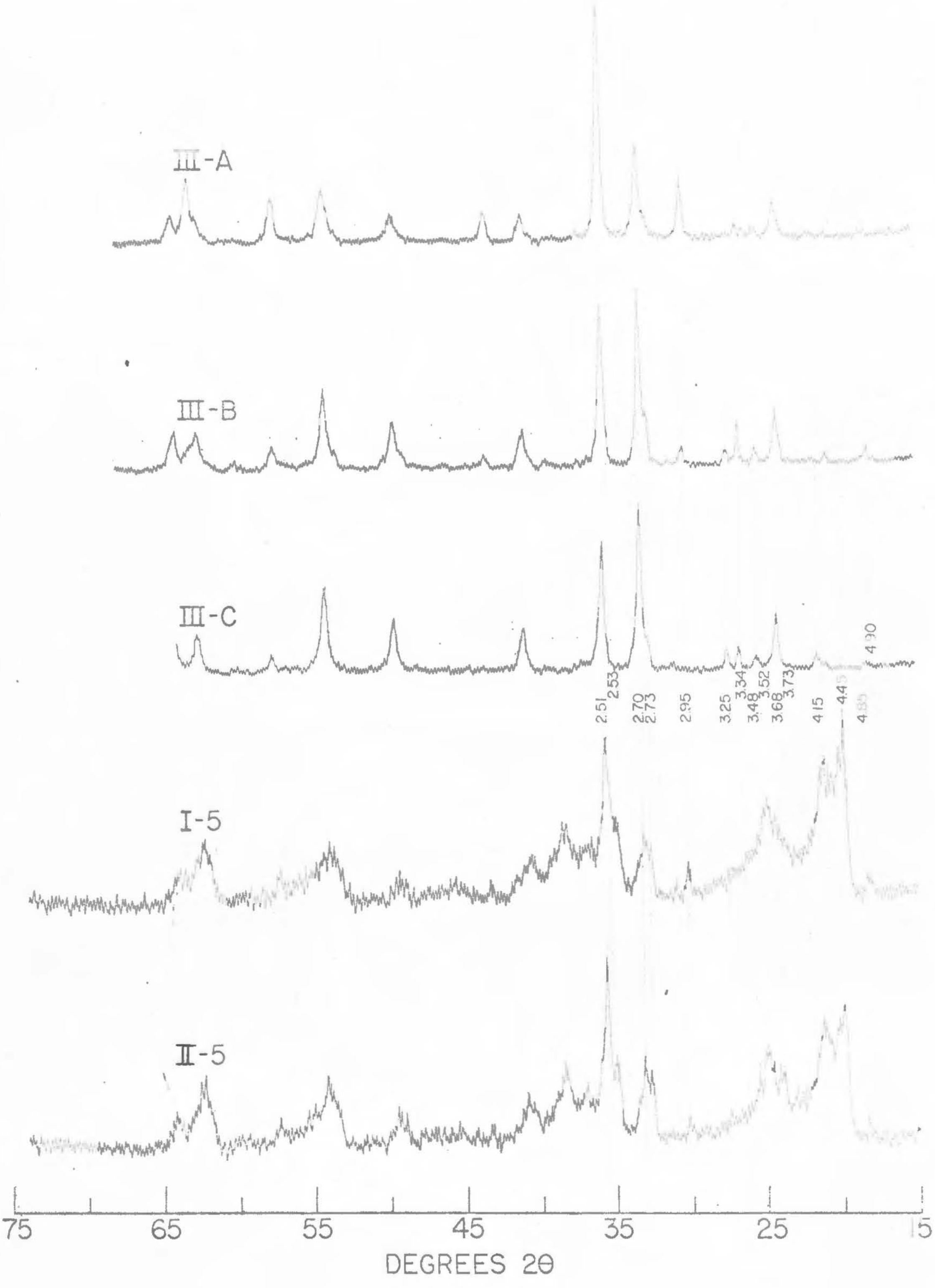

1
2
3
4
5
2.51
2.70
3.34
3.52
3.73
4.90
2.41
2.53
2.73
2.95
3.25
3.48
3.68
4.15
4.45
4.85
75
65
55
45
35
25
15
DEGREES 2θ

FIG. 9. X-RAY DIFFRACTION PATTERNS OF NODULES
IN PROFILES I, II, III AND IV

III-A	surface nodules	highly magnetic
-B	ibid.	moderately to slightly magnetic
-C	ibid.	non-magnetic
I-5	clay nodules	
II-5	ibid.	

The X-ray diffraction patterns of the clay nodules in the subsurface horizons of profiles III and IV are similar to the ones shown here.


III-A
III-B
III-C
I-5
II-5
2.51
2.53
2.70
2.73
2.95
3.25
3.34
3.48
3.52
3.68
3.73
4.15
4.45
4.85
4.90
75
65
55
45
35
25
15
DEGREES 2θ

DISCUSSION

The chemical, mineralogical, and morphological characteristics of the massive clay layer and the overlying soil horizons were quite different.

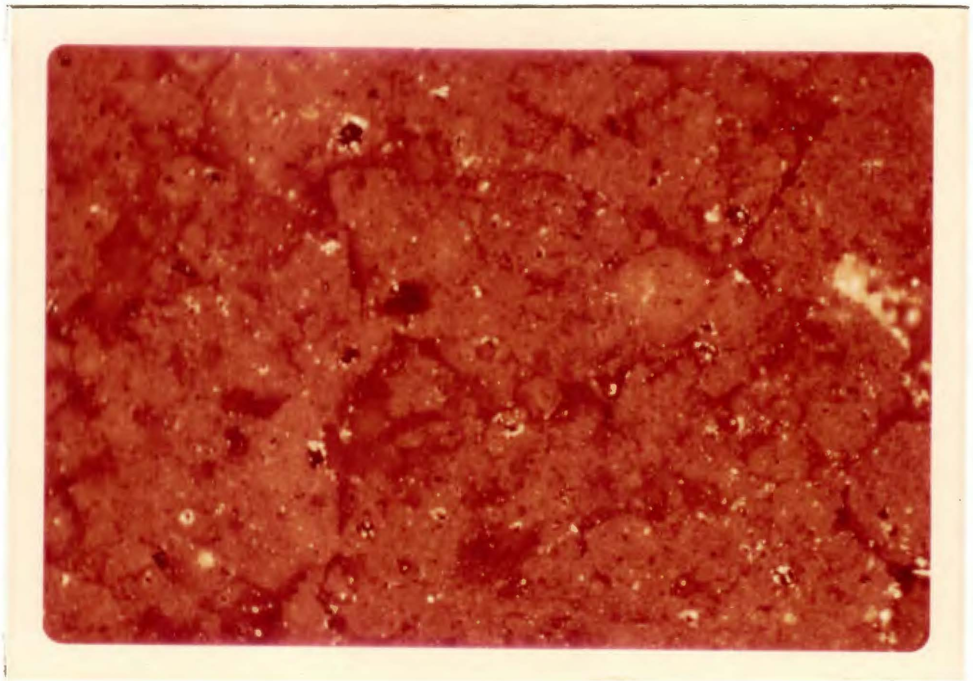
The bulk density of the soil above the massive clay layer and below the surface horizon was extremely low (approximately 0.9 g/cm^3 according to Walker, 1964). In all four profiles these subsoils contained much $H_2O_{110°C}$ and "others" and they were very friable. Photomicrographs show the porous character of the soil (Figure 10). Walker (1964) concluded from DTA and CEC data that the subsoils of the Naiwa profiles studied by him had a high content of amorphous material. Whittig (1954) reported the occurrence of a stable non-reactive form of allophane in a Naiwa soil from the same location. His electron micrographs of the clay fractions of a Haiku soil revealed a transition from well-developed halloysite rod structures to spherical, X-amorphous allophane particles. The relative proportions of amorphous silicate to halloysite increased with proximity to the surface. Whittig suggested that the allophane particles were formed by dehydration of and partial removal of silica from halloysite rods. The amount of allophane in the Naiwa soil profile, studied by him, increased from 1% in the A_1 to 37% in the C horizon. The morphological characteristics of the subsoils of the Naiwa profiles in the present study were similar to those of soils formed from volcanic ash (Soil Conservation Service and Dept. of Agronomy and Soil Science Staff, pers. comm.).

The massive clay layer contained appreciably less "others" and $H_2O_{110°C}$ and more SiO_2 than the overlying soil horizons. The bulk

FIG. 10. PHOTOMICROGRAPHS OF POLISHED SECTIONS OF PROFILE IV, HORIZON 4 (14-16 INCH). FRIABLE SUBSOIL.

plain light 96x

crossed nicols 96x



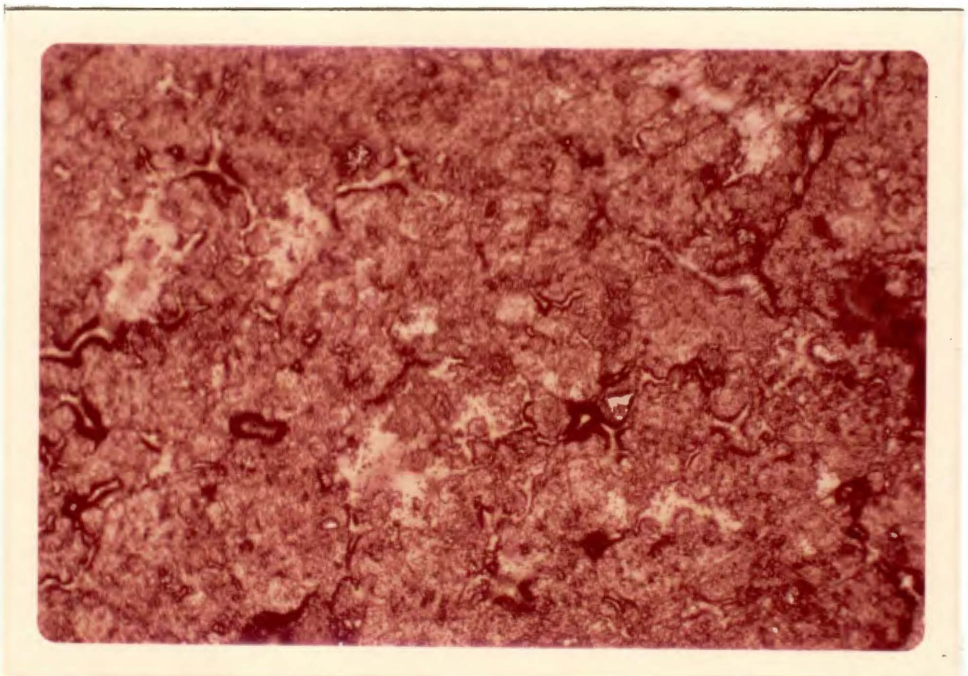
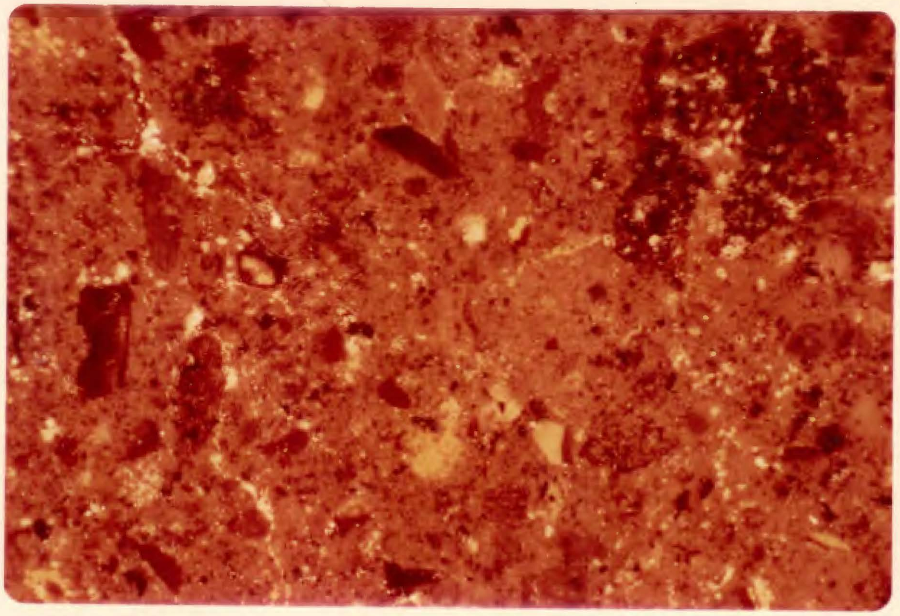
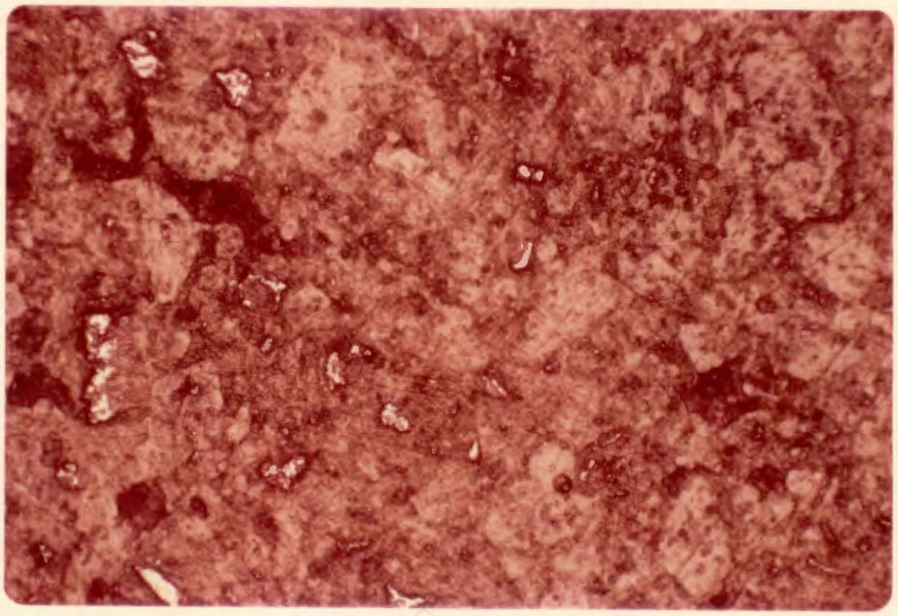


FIG. 11. PHOTOMICROGRAPHS OF POLISHED SECTIONS OF PROFILE II, HORIZON 6 (+ 41 INCH). MASSIVE CLAY LAYER.

plain light 96x

crossed nicols 96 x





density of the clay layer was 1.7 (Walker, 1964). High amounts of well crystallized kaolin were found in the clay layer while only poorly crystallized layer silicates were detected in the overlying horizons. A difference in micromorphology between the massive clay layer and the overlying soil horizons can be seen on photomicrographs (Figures 10 and 11).

The data above suggest that the massive underlying clay layer is genetically unrelated to the overlying horizons. This supports Sherman's (pers. comm.) findings. He concluded from extensive studies in the same area that the clay layer is kaolinitic saprolite after an olivine basalt unconformity. It is suggested that the massive clay layer is the remnant of an older soil profile formed in the olivine basalt of the Napali formation and that the Naiwa soil has developed in the pyroclastic material deposited on this older profile. Walker (1964) felt that other porous material, such as cinders, and porous aa and pahoehoe lava, in addition to ash, may have served as parent material for the Titaniferous Ferruginous Latosols. Walker, et al. (1969) reported strong evidence that the formation of these soils may be limited to the pyroclastic materials of post-erosional origin. This would make these soils younger than commonly thought.

The surface horizons of all four profiles contained a much higher concentration of ilmenite, pseudobrookite and rutile than the subsoils. Accumulation of these minerals was least pronounced in the surface horizon of profile I and most pronounced in the highly indurated surface horizon of profile IV. This points to a positive correlation between degree of accumulation of the Ti-minerals in the surface horizon and degree of exposure of the soil surface.

Accumulation of constituents in a soil horizon can be caused by either absolute enrichment or relative enrichment. Absolute enrichment results from importation of constituents into the soil horizon from sources outside the horizon. Absolute enrichment, thus, represents a real increase in concentration of the component. Relative enrichment of a constituent, on the other hand, takes place as a result of removal of other constituents from the soil horizon in question. Thus, in the case of relative accumulation no real increase in concentration of the component in question occurs, but after removal of other constituents, the constituent in question represents a larger portion of the soil and is thus seemingly increased in concentration. In the following discussion the terms "absolute" and "relative", in connection with gain or accumulation and loss, will have the meaning outlined above.

It is generally agreed that the iron in ilmenite is divalent and that the titanium is tetravalent. Based on oxidation potentials, considerable amounts of Ti^{3+} and Fe^{3+} are unlikely to occur together in the same mineral (Stscherbina, quoted in Basta, 1959). This means that formation of ilmenite requires a reaction between Fe^{2+} and TiO^{+}. For such a reaction to take place, the Fe and Ti must be present in soluble or gel form as ferrous hydroxide and hydrated titanium oxide, respectively. It seems highly unlikely that any appreciable amount of ferrous hydroxide would exist in the oxidizing environment of the upper part of the soil profiles studied. When importation of iron into the top horizon by lateral movement of iron in groundwater and subsequent capillary rise is considered, as proposed by Sherman (1950), it seems most reasonable to envision the mobile form of iron as an iron-organic matter complex (Bloomfield, 1953 and 1955), as discussed on page 5. On oxidation in the topsoil this soluble complex will disintegrate and the iron will precipitate as ferric hydroxide. This means that no ferrous hydroxide will become available for formation of ilmenite. Secondary formation of ilmenite in these soils, therefore, seems highly unlikely. Furthermore, there is no mention of secondary formation of ilmenite in the literature, and whether such a reaction can occur at temperatures and pressures encountered in soil is not known.

As discussed in the review of literature, pseudobrookite is considered not to form at temperatures below 580°C. Pending evidence to the contrary, this excludes a secondary formation of pseudobrookite in the surface horizons of the soils studied.

Considering the free energy of the reaction, anatase → rutile (-0.25 ± 0.2 kcal, according to Schuiling and Vink, 1967) rutile may be formed by conversion of anatase. At normal temperature and pressure, however, the reaction is so slow that anatase is considered the low-temperature polymorph of titanium-dioxide.

The above leads to the belief that the high concentration of ilmenite, pseudobrookite and rutile in the surface horizons was due mainly to loss of other constituents from this horizon. Loss of other soil constituents from the surface horizon would concentrate the ilmenite and pseudobrookite originally present in small and small to trace amounts, respectively (see mineralogical composition of the subsoils, Table IV). Rutile, concentrated in the surface horizon, was only identified in the subsoils of profile I and III in trace amounts.

Anatase, on the other hand, was more abundant in the subsoil than in the topsoil. This suggests that in the accumulation of rutile two processes may have played a role: residual accumulation and conversion of anatase to rutile. Some speculation exists as to an eolian origin of rutile, present in the soils of the Hawaiian Islands (P. F. Fan, pers. comm.).

Sherman (1952) proposed that absolute enrichment of titanium in the Humic Ferruginous Latosols takes place by lateral transport of hydrated titanium oxide in groundwater followed by capillary rise. On dehydration in the surface horizon amorphous hydrated TiO_2 converts into cryptocrystalline hydrated TiO_2 (leuxocene) and finally into crystalline TiO_2 (anatase) (Sherman, et al., 1964). In the present study, however, less anatase was detected in the surface horizons than in the subsoils. Since anatase is the TiO_2 polymorph usually found in low temperature environments (Schuiling and Vink, 1967), one would expect a higher concentration of anatase in the surface horizons than in the subsoils if absolute enrichment of titanium in the topsoils was an important process.

The arguments presented point against absolute enrichment of titanium in the surface horizons of the profiles studied. As titanium is the element most highly concentrated in the surface horizons, absolute loss of titanium from the surface horizons is unlikely. This would mean that the titanium concentration throughout the profile has remained constant, the relative accumulation of titanium in the surface horizons being due to removal of other constituents. This makes titanium suitable as an internal standard in a computation of the absolute changes in concentration of chemical components that took place as a result of exposure of the surface of these soils.

Horizon 5 of each profile will be considered the modal or reference horizon in this computation, since horizon 6, the massive clay layer, is genetically unrelated to the upper horizons, as discussed previously. This means that the concentration of each chemical component A in horizon 5 is considered 100%. Multiplication of the concentration in weight % of each chemical component A in each horizon H, as presented in Table I, page 43, with $\frac{100\%}{\text{wt\% A in horizon 5}}$ gives the concentration Y of each chemical component A in each horizon H as a percentage of the concentration of this component in horizon 5. The TiO_2 concentration is assumed to be constant throughout the profile, which means that the concentration of TiO_2 in each horizon is considered 100%. To find the concentration X of each chemical component A relative to a TiO_2 concentration of 100% in each horizon H, the concentration Y of component A is divided by: $\frac{\text{wt\% TiO}_2\text{ in hor. H}}{\text{wt\% TiO}_2\text{ in hor. 5}}$. The total formula thus becomes:

$$X = 100 \times \frac{\text{wt\% TiO}_2\text{ in hor. 5}}{\text{wt\% TiO}_2\text{ in hor. H}} \times \frac{\text{wt\% A in hor. H}}{\text{wt\% A in hor. 5}}$$

in which X is the concentration of each chemical component A in each horizon H as a percentage of the concentration of this component in horizon 5 on the assumption that TiO_2 is constant throughout the profile.

The amount of soil material f remaining in each horizon H as a percentage of the amount of soil material in horizon 5 on the assumption that TiO_2 is constant throughout the profile can be calculated as follows:

$$f = \frac{100\%}{\dfrac{\text{wt\% TiO}_2\text{ in hor. H}}{\text{wt\% TiO}_2\text{ in hor. 5}}} = 100 \times \frac{\text{wt\% TiO}_2\text{ in hor. 5}}{\text{wt\% TiO}_2\text{ in hor. H}}$$

The results of the computation are presented in Table V and Figures 12 through 15.

For further information regarding the calculations the reader is referred to Schellmann, who did a similar computation, using Cr_2O_3 as an inner standard, on laterite profiles in Borneo developed in serpentinite (1964) and in marine clay (1966). He chose Cr_2O_3 as internal standard because this element showed almost the greatest enrichment. The concentration of NiO showed the greatest enrichment but as the concentration of this element in the parent material was only 0.01%, it was not chosen. The concentration of TiO_2 in his profiles was too low (less than 1%) to consider TiO_2 as internal standard. Cline (1955) used content of titanium as a constant in calculations of losses and gains of constituents in various horizons of Humic Ferruginous Latosols in Hawaii.

When studying Table V and Fig. 12 through 15 we come to the striking conclusion that on the basis of constant TiO_2 absolute loss of iron has occurred in the surface horizons of all four profiles studied. The chemical analysis data (Table I and Fig. 1 through 4) already gave an indication of this result, as they showed that the increase in TiO_2 content in the tophorizon, compared to the TiO_2 content of the subsoil, was greater than the increase in Fe_2O_3 concentration in the topsoil relative to the subsoil. The absolute loss of SiO_2, Al_2O_3 and "others" from the surface horizons, as shown

TABLE V. CONCENTRATION OF CHEMICAL COMPONENTS IN PROFILES I, II, III AND IV AS A PERCENTAGE OF THE CONCENTRATION IN HORIZON 5 OF EACH PROFILE ON THE ASSUMPTION THAT TiO_2 IS CONSTANT

Sample	Inches Depth	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	"Others"[a]	f[b]
I-1	1-2.5	18.9	15.7	73.5	100	22.5	32.1
2	2.5-8	72.4	84.4	101.6	100	107.6	92.9
3	8-16	78.3	93.7	109.3	100	100.9	96.3
4	16-27	89.0	100.3	110.6	100	99.7	100
5	27-35	100	100	100	100	100	100
II-1	0-3	8.1	2.6	40.4	100	2.5	13.2
2	3-12	9.0	4.2	61.1	100	3.6	18.3
3	12-20	11.8	10.9	89.7	100	7.1	27.8
4	20-28	33.1	25.5	90.2	100	16.5	38.5
5	28-41	100	100	100	100	100	100
III-1	0-4	11.7	3.9	44.4	100	7.8	23.8
2	4-7	30.0	22.4	83.3	100	23.0	47.4
3	7-13	58.3	65.0	101.7	100	85.5	79.3
4	13-18	82.2	86.0	103.5	100	98.9	93.9
5	18-31	100	100	100	100	100	100
IV-1	0-3	8.0	2.8	48.6	100	6.6	20.8
2	3-10	10.3	5.7	55.0	100	3.6	23.1
3	10-14	26.2	36.6	78.1	100	36.5	48.5
4	14-16	71.5	98.5	92.2	100	108.1	94.3
5	16-25	100	100	100	100	100	100

[a] "Others" = 100% - $\Sigma(SiO_2+Al_2O_3+Fe_2O_3+TiO_2+MgO)$

[b] f = soil material remained

FIG. 12. CONCENTRATION OF CHEMICAL COMPONENTS IN PROFILE I AS A PERCENTAGE OF THE CONCENTRATION IN HORIZON 5 ON THE ASSUMPTION THAT TiO_2 IS CONSTANT

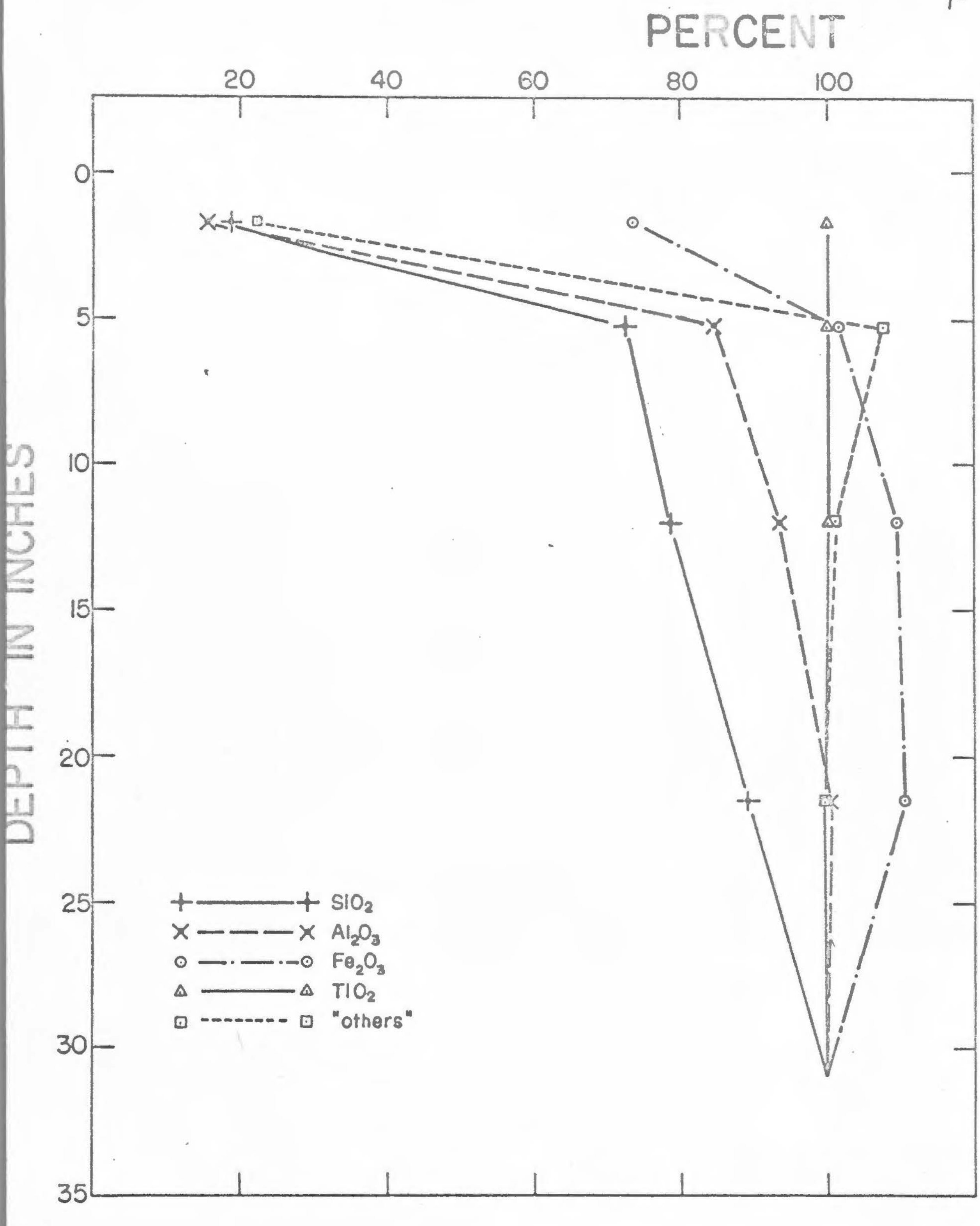

PERCENT
20
40
60
80
100
0
5
10
15
20
25
30
35
DEPTH IN INCHES
SiO₂
Al₂O₃
Fe₂O₃
TiO₂
"others"

FIG. 13. CONCENTRATION OF CHEMICAL COMPONENTS IN PROFILE II AS A PERCENTAGE OF THE CONCENTRATION IN HORIZON 5 ON THE ASSUMPTION THAT TiO_2 IS CONSTANT

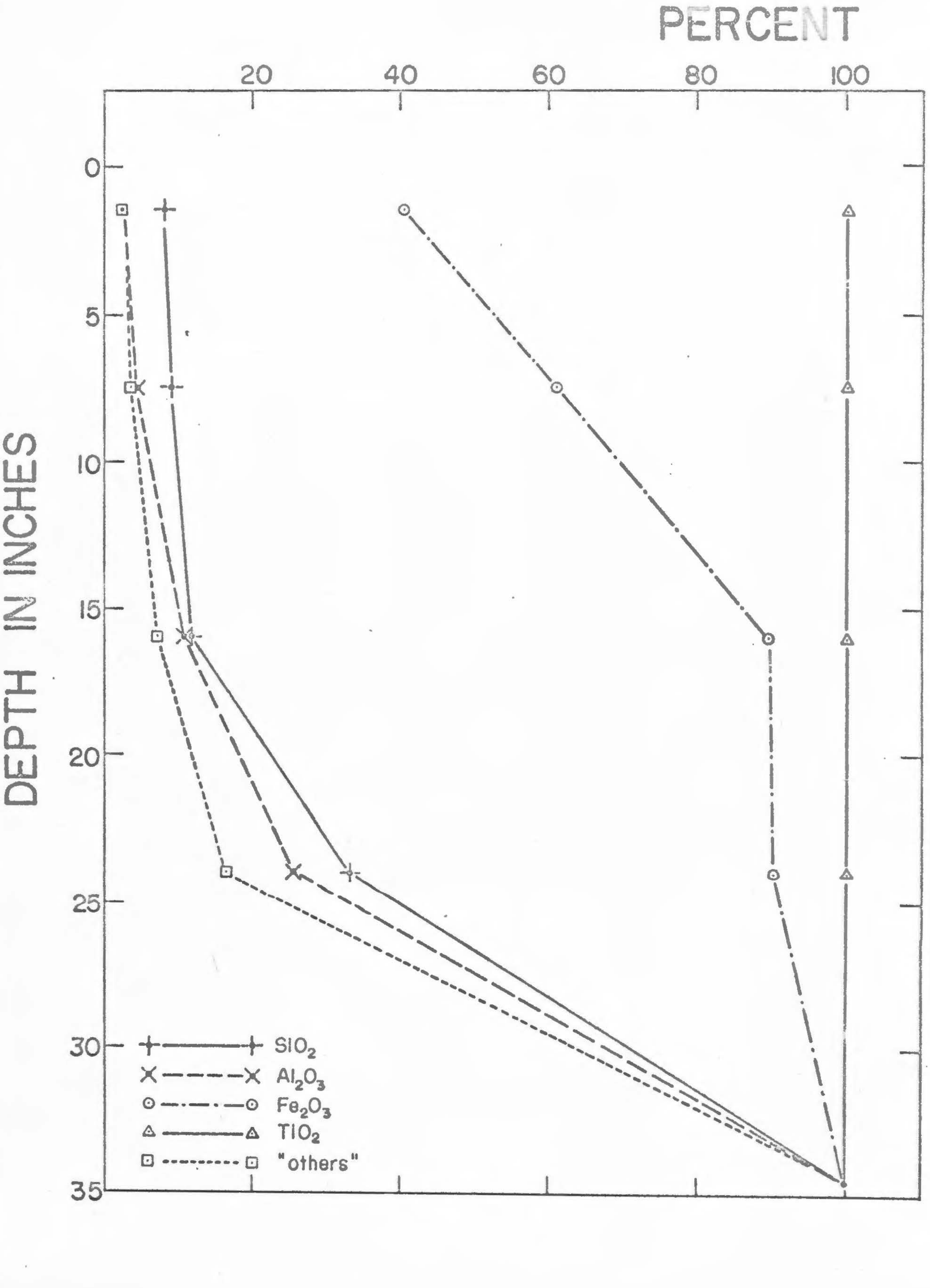

PERCENT
20
40
60
80
100
DEPTH IN INCHES
0
5
10
15
20
25
30
35
SIO₂
Al₂O₃
Fe₂O₃
TIO₂
"others"

FIG. 14. CONCENTRATION OF CHEMICAL COMPONENTS IN PROFILE III AS A PERCENTAGE OF THE CONCENTRATION IN HORIZON 5 ON THE ASSUMPTION THAT TiO_2 IS CONSTANT

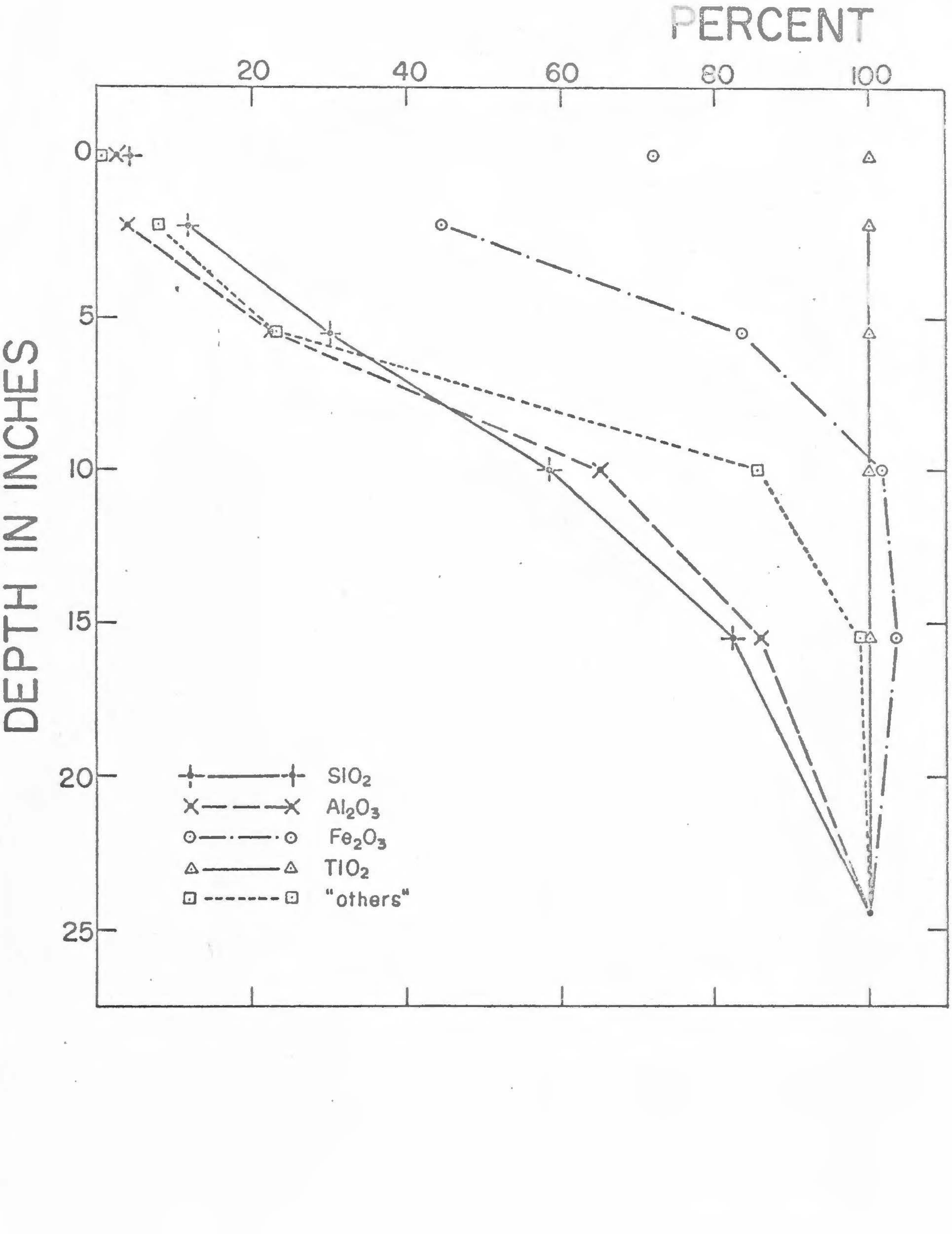
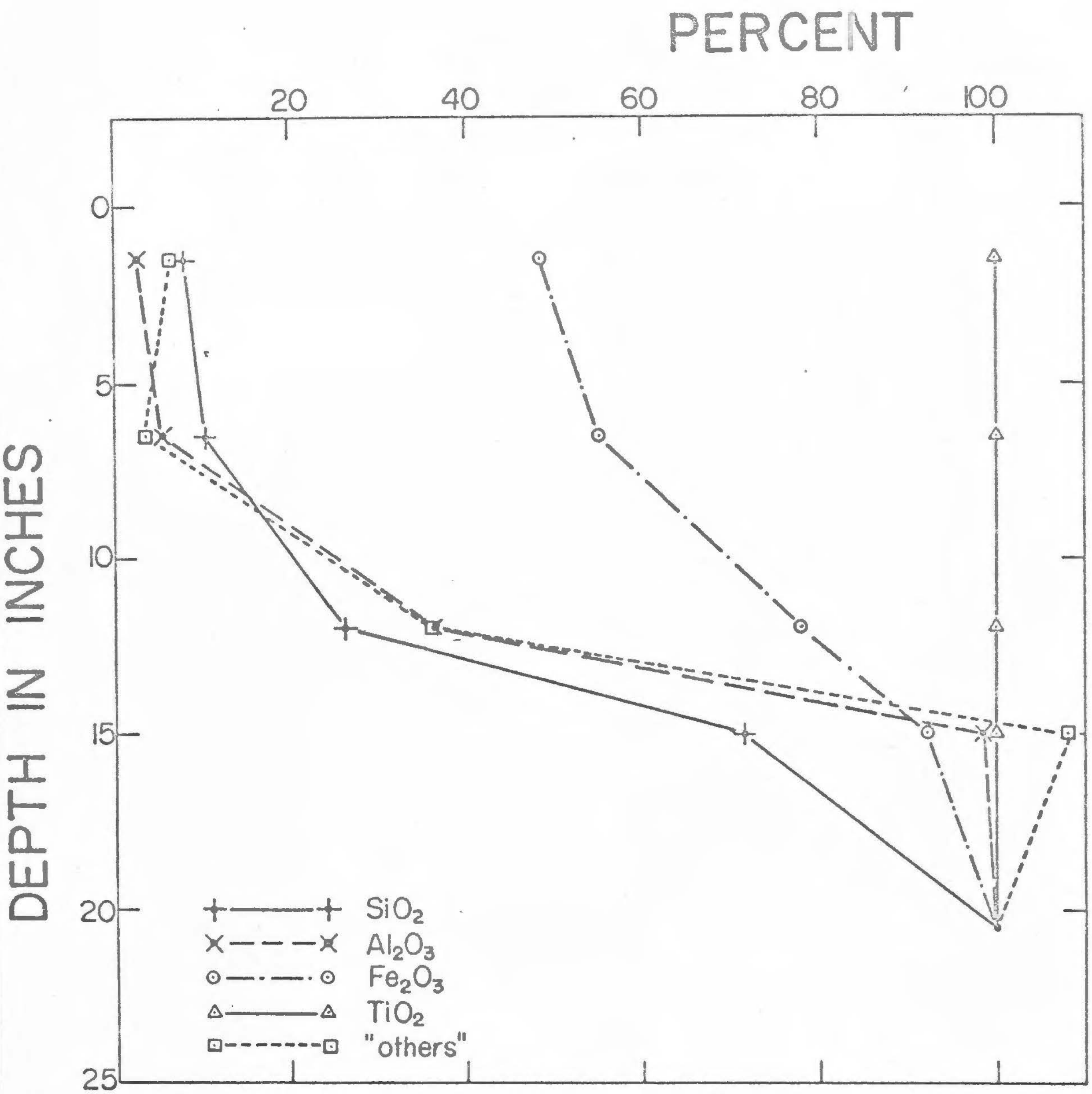

PERCENT
20
40
60
80
100
DEPTH IN INCHES
0
5
10
15
20
25
SiO_2
Al_2O_3
Fe_2O_3
TiO_2
"others"

FIG. 15. CONCENTRATION OF CHEMICAL COMPONENTS IN PROFILE IV
AS A PERCENTAGE OF THE CONCENTRATION IN HORIZON 5
ON THE ASSUMPTION THAT TiO_2 IS CONSTANT


PERCENT
20
40
60
80
100
DEPTH IN INCHES
0
5
10
15
20
25
SiO₂
Al₂O₃
Fe₂O₃
TiO₂
"others"

in Table V and Figures 12 through 15, is even more pronounced than the relative loss of these components indicated by the differences in chemical composition of top- and subsoils (Table I and Figures 1 through 4).

Absolute loss of SiO_2 and Al_2O_3 from the surface horizons ties in with the smaller amounts of layer silicates and gibbsite in the surface horizons than in the subsoils as found by X-ray diffraction analysis. The higher quartz concentration in the surface horizons is reflected in the smaller loss of SiO_2 relative to the loss of Al_2O_3.

Walker (1964) proposed secondary formation of quartz in the surface horizons of Naiwa soils. He believed that halloysite, present in the surface horizons of the vegetated profiles and disappearing with increased induration, is the source of the silica which ultimately crystallizes as alpha quartz and that additional silica is added by colloidal or solution Si carried upward by capillary action from the subsoils. Quartz was poorly crystallized and small in quantity in the vegetated soils and does not occur as a modal mineral in Hawaiian rocks. As discussed in the Review of Literature, secondary formation of quartz has also been reported by other workers. These reports, however, deal with weathering periods of thousands of years, while the changes in the surface horizons of the Naiwa profiles on exposure have been observed to occur in as little as six months (Walker, et al., 1969). The hypothesis of eolian origin of quartz in Hawaiian soils, proposed by Rex, et al. (1969), on the other hand, is well accepted to date. With this hypothesis some concentration of quartz in the soil surface horizons would be expected. In the profiles studied small amounts of quartz were found in the subsoils and higher amounts were detected in the surface horizons, the difference between the quartz concentration found in the subsoil and in the surface horizon being smallest in profile I and greatest in barren profile IV. Residual accumulation of quartz in the surface horizons, due to removal of other constituents on exposure of the soil surface, would satisfactorily explain the observed distribution of quartz in the profile.

The decrease in "others" in the surface horizons, shown in Tables I and V and Figures 1 through 4 and 12 through 15, can be explained by loss of organic matter and absorbed water occurring on exposure of the soil surface and by the loss of layer silicates and gibbsite.

Absolute loss of Fe_2O_3 from the surface horizons corresponds with the smaller amounts of goethite and possibly maghemite and the smaller increase in hematite relative to ilmenite in the surface horizons as compared to the subsoil, shown by X-ray diffraction analysis (Table IV and Figures 5 through 8). Absolute loss of Fe_2O_3 from the surface horizons also agrees with the observation that in all profiles the highest concentration of TiO_2 was found in the uppermost horizon while in profile II and IV the highest concentration of Fe_2O_3 was found in the second horizon (Table I and Figures 1 through 4).

The lower concentration of goethite in the surface horizon than in the subsoil may be caused by: _1_ conversion of goethite to hematite or _2_ removal of goethite from the surface horizon. As pointed out previously (pages 14-15), most workers are of the opinion that on prolonged lateritic weathering, accompanied by dehydration, goethite converts into hematite. Judging from the X-ray diffraction patterns, the goethite in the subsoils of the Naiwa profiles was poorly crystallized and contained 25-30 mol % AlOOH (see page 51). The slightly longer _d_-spacings of the hematite present in these soils, on the other hand, indicated substitution of titanium in the hematite crystals. Conversion of goethite to hematite, then, would mean release of aluminum from the goethite crystal structure and possible incorporation of titanium in the hematite crystal structure. This suggests that a transformation process more complicated than the topotactic transformation found to take place on conversion of goethite to hematite by dehydration (Francombe, et al., 1959; and Brown, 1961), would have to be operative. Furthermore, transformation of goethite into hematite would result in an increase in hematite content. The increase in hematite content in the surface horizons, however, relative to the content in the subsoil, appeared to be smaller than the increase in ilmenite and quartz content. Hypothesis _2_: "removal of goethite from the surface horizons" therefore seems to be more in agreement with the findings.

In the foregoing discussion relative accumulation of ilmenite, pseudobrookite, rutile, quartz and hematite was considered the most important genetic process operative in the formation of the indurated surface horizons after removal of the vegetation from the Naiwa soil studied. Other workers have expressed similar views.

Tamura (1952) suggested that Ferruginous Latosols may form as a result of residual weathering in which silica and alumina minerals are removed from the surface horizons by solution and translocation, leaving a residue of iron and titanium minerals. Whittig (1954) proposed relative accumulation of resistant iron and titanium minerals as the main genetic process in the formation of the Naiwa soils. The concentration of primary ilmenite and authigenic maghemite near the surface of the profile supported this view. He attributed the marked accumulation of hematite and anatase near the surface of the profile, on the other hand, to secondary formation of these minerals from iron and titanium brought into the surface horizon by seepage of ground water from higher elevations as proposed by Sherman (1950). Walker, et al. (1969) felt that two genetic processes: 1 accumulation of residual resistant minerals and 2 capillary movement of material in aqueous media and its subsequent precipitation and dehydration, operate with increased intensity as induration proceeds in the Naiwa soils.

In all studies of the Humic Ferruginous Latosols it was agreed that SiO_2, Al_2O_3 and organic matter were lost from the surface horizons on exposure.

The relative concentration of Fe_2O_3 and TiO_2 in these horizons, that would result from loss of only SiO_2, Al_2O_3 and "others", can be computed.

The concentrations of Fe_2O_3 and TiO_2 in the surface horizons, computed in this fashion, differ from the actual concentrations of these oxides found on chemical analysis. That is, the computed Fe_2O_3 concentration is higher than the actual concentration of Fe_2O_3 found on chemical analysis and the computed TiO_2 concentration is much lower than the actual concentration of TiO_2.

This would mean that the assumption that only SiO_2, Al_2O_3 and "others" have been lost from the surface horizons is not correct. Additional assumptions thus have to be made, namely either 1 absolute enrichment of TiO_2 and absolute loss of Fe_2O_3 or 2 absolute enrichment of both TiO_2 and Fe_2O_3, but a larger absolute enrichment of TiO_2 than of Fe_2O_3 or 3 no absolute loss or gain of TiO_2 and a large absolute loss of Fe_2O_3 or 4 absolute loss of both TiO_2 and Fe_2O_3, but a larger absolute loss of Fe_2O_3 than of TiO_2.

Assumption 3 has been discussed on pages 68-82. As pointed out on page 71, the surface horizons of all profiles contained a smaller amount of anatase than the subsoils. It has already been suggested that conversion of anatase to rutile in the surface horizons on exposure of the surface is not very likely. If absolute enrichment of rutile in the surface horizons by continental dustfall is disregarded, this would mean that anatase was lost from the surface horizons. The assumption of "no loss or gain of TiO_2" made in case 3, would thus not be valid, and we arrive at assumption 4. On assumption 4 the concentrations of the chemical components as a percentage of the concentration in horizon 5, as presented in Table V and Figures 12 through 15 for assumption 3, would be even lower.

Assumption 1 and 2 would require a supply of titanium relatively larger than of iron and/or a larger solubility and/or mobility of titanium than of iron. In Sherman's (1950) hypothesis of secondary enrichment of iron and titanium these components come from the wetter soils of the higher elevations. At the present time the Fe/Ti ratio in these Hydrol Humic Latosols is lower than the Fe/Ti ratio in the topsoil of the Humic Ferruginous Latosols. However, the titanium content of the Hydrol Humic Latosols is low compared to other Hawaiian soils (Sherman, 1950) and the relatively low iron content of these continuously moist soils is considered to be a result of leaching out of iron, this very iron being the source of enrichment for the Humic Ferruginous Latosols (Sherman, 1950). Not much literature is available on the solubility and mobility of titanium in soils. It is generally agreed, however, that iron is more soluble and mobile than titanium. Assumptions 1 and 2 are thus not likely to hold true.

Absolute enrichment of iron and titanium was considered an important genetic process in the formation of the indurated surface horizons of the Naiwa soils (Sherman, 1950; Walker, et al., 1969). These authors suggested that iron and titanium are solubilized by extensive leaching of soils of higher elevations, receiving very high rainfall, and that they are transported by laterally moving groundwater. In more level regions having an alternate wet and dry environment, they are then carried to the soil surface by capillary rise during the dry periods and they subsequently dehydrate and precipitate.

In the foregoing discussion some arguments were presented against absolute enrichment of iron and titanium in the Naiwa soil studied. Two more factors should be considered. Firstly, the area, in which the profiles studied were situated, is isolated from the upland high-rainfall areas by the faulting that produced the Makaweli depression, of which the Waimea Canyon is the present landscape remainder. This faulting took place in the Pliocene, at the end of the period of major volcanism (MacDonald, et al., 1960). This means that since Pliocene times, no transport of material from the soils of the upland high-rainfall areas to the Naiwa profiles studied could occur.

Secondly, as pointed out in the Review of Literature, pages 7-8, capillary rise of water in latosols is considered to be of very little importance. In barren soils, moreover, capillary rise of liquid water only takes place as long as the soil surface is moist. Under England-summer conditions the barren surface soil was found to dry out in as little as two days (Penman, 1941). In subtropical Hawaii one would expect this to happen even faster. Rapid decrease in capillary conductivity with decrease in moisture content in Hawaiian Low Humic Latosols was shown by Sharma, et al. (1968a and 1968b). These workers measured a drop in capillary conductivity from approximately $5x10^{-3}$ cm/sec at 0 cm water tension to approximately $3x10^{-6}$ cm/sec at 100 cm water tension.

Absolute enrichment of sesquioxides by deposition of erosional and colluvial material has been reported for latosols situated on slopes adjacent to higher areas (du Preez, 1949; and Sivarajasingham, et al., 1962).

There seems to be no doubt that the surface horizons of the profiles I, III and IV studied are genetically related to the subsoils, as the different horizons in the profiles were found to represent various transition stages between the very surface horizon 1 and horizon 5. Field observations suggested that the top 20 inches of profile II were erosional material. Within these 20 inches, however, changes in chemical, mineralogical and morphological properties had occurred similar to the changes in profile III and IV. One must keep in mind, furthermore, that induration of the surface layer after removal of the vegetation in this area, occurs in a period of less than ten years. The barren profile, studied by Walker in 1960, was vegetated when Sherman, et al. studied it in 1953. As described by Walker (1964), now, denudation of the area occurred in the following way: "About 35 years ago a small area was denuded. Since that time the barren areas have spread in an upslope direction accompanied by erosion. The death of the vegetation has been followed by rapid induration of the surface horizon of the soils." In other words, after removal of the vegetation, erosion of the soil took place, followed by induration of the surface of the soil. This means that material was removed from the denuded soil. As the area upslope of the denuded soils was still vegetated, however, transport of erosional material from these higher lying soils to the barren soils can not have been great. Absolute enrichment of sesquioxides by deposition of erosional material, thus, is not a likely explanation for the development of the indurated surface horizons in these soils.

As discussed on pages 6-7, several authors consider laterite to be an illuvial horizon. In their opinion, layers at some depth in the profile are enriched with iron moved down from the surface horizon. The surface horizon subsequently erodes, exposing the enriched layers. In this concept the iron in the surface horizons mobilizes mainly by complexing with organic decomposition products. A reducing environment promotes the mobilization of iron. Mobilization of iron, thus, would take place in the surface horizon of a vegetated soil, where organic matter would be available to complex the iron. Deeper in the profile, the iron would precipitate as a result of different physical-chemical conditions (Maignien, 1966). If erosion would subsequently remove the topsoil, the enriched layer would be exposed at the surface. In barren soils, however, no mobilization of iron in the surface horizon would occur as no organic material would be available.

Comparing the situation sketched above with the characteristics of the profiles studied, we see that the vegetated profile I showed no zone of iron enrichment deeper in the profile. Only a thin (2.5 inch) layer of iron and titanium enrichment was present at the soil surface, where the biological activity was highest and, therefore, according to the hypothesis outlined above, the iron concentration should be lowest. As no zone of enrichment was present deeper in profile I, development of the indurated surface horizons in the barren profiles III and IV cannot have occurred by erosion of the topsoil of the originally vegetated soil after denudation.

Enrichment of sesquioxides by capillary rise has been proposed. As discussed previously, however, numerous studies have shown that capillary rise of water in latosols is much less important than was thought. Furthermore, if the iron and titanium, accumulated in the indurated surface horizons of profiles III and IV, had originated from the subsoils of these profiles, the concentration of these components in the subsoils of profiles III and IV would have been much lower than in the subsoil of vegetated profile I. As Table I shows, however, almost the opposite is true.

The surface horizon of a Naiwa soil profile from the same location as the profiles studied contained 20% colloidal material and

80% material >2 micron. With depth in the profile the <2 micron fraction increased to 70% at 36 inch, and the >2 micron fraction consequently decreased to 30% (Whittig, 1954). The same trend was reported by Sherman, et al. (1953). Sherman, et al. (1948) reported the A_2 horizon of a similar Naiwa soil profile to contain 13% colloidal material and the B horizon 75%.

The surface horizon of the Naiwa soils is characterized by heavy mineral concentration (Cline, 1955). Fujimoto, et al. (1948) found that the heavy mineral fraction of a Naiwa profile similar to the ones studies increased markedly with proximity to the surface, accompanied by a decrease in the light mineral fraction.

Mineralogical analysis of the separated size fractions of the Kokee Road Naiwa soil profile by Whittig (1954) gave the following results: Layer silicates, gibbsite, and goethite were predominantly <2 micron in size, quartz and anatase were encountered in both the colloidal and the >2 micron fractions and the particle size of hematite, ilmenite, and maghemite was predominantly >2 micron. According to Rex, et al. (1969), the particle size of quartz in Hawaiian soils is mainly from 2-10 micron. On microscopic examination, Walker (1964) found the particle size of pseudobrookite in the Naiwa soil to be about 5 micron.

These findings can be summarized as follows: The upper part of the Naiwa profile had lost colloidal material. The amount of <2 micron material lost increased with proximity to the surface. The lost colloidal fraction was mainly composed of layer silicates, gibbsite, goethite and anatase. The remaining >2 micron fraction was made up mainly of heavy minerals: hematite, ilmenite, pseudobrookite, and rutile. Quartz, in these soils, was found in both the heavy and the light mineral fraction. Petrographic microscope studies showed the quartz grains to be coated with iron oxides and to have many heavy mineral inclusions (Walker, 1964). Greenland, et al. (1968) suggested that the quartz particles in the sand fractions of red earths from Australia and Indonesia examined by them, had coatings of iron hydroxides, as these particles were mostly colored red and were bleached by dithionite treatment. Jones (pers. comm.), however, found no evidence of iron coatings on quartz in Hawaiian Low Humic Latosols in high magnification electron microscope studies.

It seems justifiable to believe that we are dealing with an absolute loss of <2 micron material and not with a relative loss due to an absolute increase of the >2 micron fraction. The following factors led to this conclusion: 1 The volume of the soil decreases on exposure of the soil surface. The depth of the Naiwa profiles studied by Walker, et al. (1969) had changed considerably--the vegetation covered profile was 38 inches in depth to the basal clay layer, and the barren profile was 25 inches deep. Using the bulk density of the soil above the basal clay layer, the equivalent cut-off point of similarity would be at 22 inches and 10 inches below the surface for the vegetation covered and the bare profiles, respectively. In other words, the volume of the surface of the original vegetative profile had been reduced by half as a result of exposure, if loss of erosion was ignored. Not the entire loss of volume can be explained by loss of LOI and pore volume. 2 The subsoils of the profiles studied and the surface horizon of the vegetated profile I contained layer silicates and gibbsite. No reflections for these minerals, however, could be detected in the X-ray diffraction patterns of the exposed surface horizons of profiles II, III and IV.

Considering the evidence presented it is proposed that relative accumulation of ilmenite, pseudobrookite, rutile, quartz and hematite is the most important process operative in the formation of the indurated surface horizons of the Naiwa soil studied as a result of removal of the vegetation. It is suggested that progressive loss of vegetation results in progressive absolute loss of LOI, SiO_2, Al_2O_3, Fe_2O_3 and perhaps some TiO_2 from the surface horizons, causing a relative accumulation of TiO_2 and Fe_2O_3. It is proposed that loss of colloidal material from the surface horizons is mainly responsible for the losses in SiO_2, Al_2O_3, Fe_2O_3 and perhaps some TiO_2. Decomposition of organic matter takes place as a result of oxidation and desiccation on exposure of the soil surface.

There are several ways in which colloidal material may be lost from the surface horizons.

One hypothesis is decomposition of layer silicates and gibbsite under influence of dehydration and leaching down of their constituent elements silica and aluminum.

As discussed previously, extensive investigations on laterites in West Africa led Alexander, et al. (1962) to conclude that hardening of lateritic soil horizons is nearly always accompanied by a loss of kaolinite. Sivarajasingham, et al. (1962) stated that, although it is often impossible to be certain whether this reduction is due to an actual loss of kaolin or to enrichment of iron from outside sources, the magnitude of decrease in many cases strongly suggests that kaolin has weathered, as suggested by Jackson, et al. (1948). Evidence of destruction of kaolin in hardened lateritic horizons, based on thin section and electron microscope observations, is abundant (D'Hoore, 1954; Alexander, at al., 1962).

As mentioned on page 65, Whittig (1954) suggested formation of amorphous silicate in Hawaiian Humic Ferruginous Latosols as a result of physical and chemical disintegration of halloysite. He proposed that the increases in concentration of amorphous silicate and gibbsite with depth in the Naiwa soils were caused by movement of these components out of the upper horizon by dispersion and eluviation by downward moving solutions. He felt that alumina and alumino-silicates may have been solubilized to some extent by slightly acid solutions near the surface. Removal of silica and alumina minerals from the surface horizons of Ferruginous Latosols by solution and translocation was suggested by Tamura (1952).

Whether silica and alumina will leach down depends on their solubility under the conditions prevailing in the profile.

The pH of the exposed surface horizon was approximately 4.4 (Table III). Magistadt (1925) determined an aluminum concentration in the soil solution of temperate soils of about 30 ppm Al_2O_3 at pH 4.3 and of about 3 ppm Al_2O_3 at pH 4.5. These values were only slightly lower than the data for solubility of aluminum as $Al_2(SO_4)_3$ in water found by him. Ayres, et al. (1965), however, measured the amounts of watersoluble aluminum in Hawaiian Humic Ferruginous Latosols and found values of 0.2-1.0 ppm Al_2O_3 at pH 4.3-4.5 and of 0.3-0.6 ppm Al_2O_3 at pH 4.6-4.9.

The solubility of silica is independent of pH from pH values 2-about 9.5. At 25°C the solubility of finely powdered silica gels was found to be 135-145 ppm SiO_2 (Siever, 1962). Fox, et al. (1967 and 1969), however, measured contents of water-extractable silica in Hawaiian Humic Ferruginous and Low Humic Latosols of 2.3-5.6 ppm SiO_2.

Taking the maximum values reported by Ayres, et al. (1965) and Fox, et al. (1967 and 1969) one arrives at a solubility of Al_2O_3 of 1 ppm and of SiO_2 of 5 ppm in the surface horizons of the soils studied.

As shown in Table V, on the assumption of constant TiO_2, 80% of soil material, 92% SiO_2 and 97% Al_2O_3 were lost from horizon 1 (0-3 inch) of profile IV, as a percentage of the concentration of these components in horizon 5 of this profile. In other words, using the chemical data presented in Table I, 16 g SiO_2 and 28 g Al_2O_3 were lost from 100 g soil. The volume of horizon 1 was reduced by 80%, so the original depth of the horizon was 15 inch = 37.5 cm. Using a value of 0.9 g/cm^3 for the original bulk density of the soil [bulk density of horizon 5 = 0.9 g/cm^3, according to Walker (1964)], 100 g of soil was represented by a surface area of 2.4 cm^2. The rainfall in the sample area is 60 inches/year. Per surface area of 2.4 cm^2 this is 360 cm^3/year = 0.36 liter/year. It would thus require 3,200 liter rainwater to leach out 16 g SiO_2, assuming a solubility of 5 ppm SiO_2, and 28,000 liter water to leach out 28 g Al_2O_3, assuming a solubility of 1 ppm Al_2O_3. This would mean 8,888 years for SiO_2 and 77,777 years for Al_2O_3. The pH increased with depth in the profile, however (Table III), causing an even lower solubility of Al_2O_3 in the subsoil. Moreover, not the entire amount of yearly rainfall will be active in the leaching process. As induration of the surface horizon occurs in a matter of years, leaching out of silica and aluminum can hardly be a large contributing factor in the formation of the indurated layer.

A second hypothesis is removal of the clay sized minerals without prior decomposition. This would involve the layer silicates, gibbsite, goethite and anatase.

As mentioned previously, both Tamura (1952) and Whittig (1954) suggested translocation of silica and alumina minerals from the surface horizons of Humic Ferruginous Latosols. Whittig stated that "the accumulation of the ilmenite and quartz (in a Haiku profile) was apparently accentuated by the translocation of fine halloysite and allophane particles from the surface to greater depth in the profile."

The subsoils of both the vegetated and the barren profiles studied were extremely friable. Walker, et al. (1969) determined a pore space volume of 60-70% in subsoils of a vegetated and a barren profile from the same location. On downward movement of clay sized material, now, some of the pores in the subsoil would be expected to fill up, resulting in a decrease of friability of the soil. No difference in pore space volume and friability between the vegetated profile I and the barren profiles III and IV could be observed, however. Downward movement of colloidal material on exposure of the soil surface would also result in a higher concentration of layer silicates and gibbsite (and goethite and anatase) in the subsoil of the barren profile than in the subsoil of the vegetated profile. This would cause an absolute enrichment of SiO_2 and Al_2O_3 in the subsoils of the barren profiles. As Table V and

Figures 12 through 15 show, however, no absolute enrichment of these oxides was observed in the subsoils of profiles III and IV.

Another possibility is lateral removal of the clay fraction by superficially flowing water. Loss of protective vegetative cover and of organic matter in the exposed surface horizon makes the topsoil subject to erosion. The colloidal sized and lighter particles would be more susceptible to erosion than the silt and sand sized and heavy particles. The impact of raindrops on the barren soil surface would enhance suspension of colloidal material in the run-off water. A relative concentration of silt and sand sized, heavy particles would be effected in this way.

Studies by Ghildyal, et al. (1969) on the effect of different vegetative covers, including barren soil, on runoff and soil loss of Indian lateritic soils support this hypothesis. These authors found that soil loss by erosion was highest for the barren soil. The increase in soil loss with increase in kinetic energy of the raindrops was found to be greatest for the barren soil. At higher values of kinetic energy of the raindrops the rate of soil loss increased exponentially. Sealing of surface pores of the barren soil due to impact of raindrops was observed, resulting in a further lowering of the infiltration capacity of the soil and larger runoff. The textural composition of the soil lost from the barren plots showed a larger amount of clay fraction than that from the vegetated plots. While the plot soil was a sandy loam, the runoff soil was clay. As the runoff increased on the barren soil, the soil tended to become coarse textured.

Sherman, et al. (1953 and 1964) proposed that dehydration of the amorphous hydrated colloidal oxides of the soil is responsible for the development of the indurate laterite horizon when exposed to a drying environment. It is the opinion of several investigators (Alexander, et al., 1962; Sivarajasingham, et al., 1964; Maignien, 1966) that on hardening the iron oxide minerals crystallize into continuous aggregates or networks. Alexander, et al. (1962) felt that local movement of amorphous or microcrystalline iron oxides is an important factor in the development of the crystalline framework. As discussed in the Review of Literature, alternating wetting and drying, causing dehydration to occur in stages, was found to be essential for hardening. The different authors, mentioned above, observed that the ferruginous skeleton of indurated laterites displays a higher degree of crystallinity or a greater continuity of the crystalline phase than the soft materials with which they are associated.

The X-ray diffraction patterns of the indurated surface horizons of profiles III and IV suggested a better X-ray crystallinity of the iron and titanium minerals in these horizons than in the surface horizon of profile I and in the subsoils. Walker, et al. (1969) also reported a greater degree of crystallinity of the iron and titanium minerals in the surface and indurated horizons of the bare Naiwa profile.

It is possible that, as a result of stepwise dehydration in the alternating wet and dry climate, improvement of X-ray crystallinity and greater cohesion of the heavy minerals in the exposed surface horizons of the Naiwa soil studied takes place. Development of greater cohesion of the heavy minerals would be an additional factor in the resistance of these minerals to surface erosion, and would thus support the hypothesis of lateral removal of clay size material by runoff water.

CONCLUSIONS

The effect of removal of the vegetation on the chemical, mineralogical and some morphological characteristics of a Naiwa soil on Kauai was studied. A sequence of four profiles was included in the investigation. Profile I was vegetated, profile II was partly vegetated, profile III was barren except for one tiny shrub and profile IV was barren.

Profile I had a uniform chemical and mineralogical composition, except for the top 2.5 inches. The soil was friable throughout the profile. The subsoils of profiles II, III and IV were similar to profile I in chemical, mineralogical and morphological properties. The surface horizons of profiles III and IV were indurated. The contents of $H_2O_{110°C}$, LOI, SiO_2 and Al_2O_3 in these surface horizons were lower and the concentrations of Fe_2O_3, TiO_2 and MgO were higher than in profile I. The indurated surface horizons contained larger amounts of hematite, ilmenite, pseudobrookite, rutile and quartz and smaller amounts of goethite and anatase than the vegetated profile. No layer silicates were detected in the indurated surface horizons. Improved X-ray crystallinity of the iron and titanium minerals was observed in the indurated surface horizons of the barren profiles as compared to the vegetated profile and the subsoils.

Based on the results of this study the following conclusions can be made.

<u>1</u> The massive clay layer, underlying the four profiles, is probably the remnant of an older soil profile formed from the olivine basalt of the Napali formation, which now underlies pyroclastic

material of more recent origin from which the Naiwa soil has developed. This would make the Naiwa soil younger than commonly thought.

2 It is suggested that residual accumulation of ilmenite, pseudobrookite, rutile, quartz and hematite is the most important process operative in the formation of the indurated surface horizon of the Naiwa soil on removal of the vegetation.

3 Quartz, present in these soils, is most likely of eolian origin.

4 It is further proposed that progressive loss of fine sized material, involving layer silicates, gibbsite, goethite and anatase, from the surface horizons as a result of progressive loss of the vegetative cover is mainly responsible for the relative accumulation of ilmenite, pseudobrookite, rutile, quartz and hematite in these horizons.

5 It is suggested that removal of fine sized material from the barren surface horizons is effected by lateral movement in runoff water and perhaps to some extent by eluviation.

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