Pakistan J. Sci. Ind. Res., 12, 222-226 (1969)

A STUDY OF MINERALS IN SOME HAWAIIAN SOIL COLLOIDS*

erise and and the case of the cases of the cost of a second second

M. S. HUSSAIN

Department of Soil Science, University of Dacca, Dacca

(Received November 21, 1968)

This work deals with the mineral content in the clay fraction of a number of soils in the Tropics. Kaolinite is found to be the dominant mineral. The presence of pedogenic mica in high rainfall area is reported.

Introduction

A knowledge of minerals present in the colloidal fraction of a soil is very important in any study of pedogenesis. The secondary minerals in soils usually form at the expense of the primary minerals. During pedochemical weathering the primary minerals in the parent material is weathered to form new mineral species with possible losses of some constituents from soil profiles. The conditions under which the primary minerals weather and the kind and conditions of formation of weathering products are all of considerable importance in understanding the genesis of secondary minerals. Mineral analysis in the colloidal fraction of soils, therefore, can give valuable information regarding the environment in which they were formed, provided the original minerals present in the parent materials of the soils are known.

There are two categories of minerals that may be present in the colloidal fraction of any soil. In the first group come the minerals that are synthesised in the soil environment from the constituents released by the chemical decomposition of the primary minerals. In this group of minerals come the secondary silicate clays. When the coarse grained primary minerals are physically weathered, fine, resistant colloid-sized minerals develop. Their chemical composition is the same as those from which they have been formed but with respect to size of the mineral particle they fall within the colloidal fraction. The minerals in the latter category, however, have no genetic relationship with the environment in which they are found.

The Hawaiian islands which are situated in the middle of the Pacific Ocean lie under the influence of tropical climate. This place is, therefore, very suitable for the study of weathering phenomenon in the tropics. Since the rocks are of volcanic origin, there is hardly any contamination in the parent material of the soils. One can find out with considerable degree of certainty the nature of parent material at the start of weathering.

The objective of the present study was: (1) to find out the dominant clay minerals in some soils of Hawaii and throw some light on their synthesis, (2) to find out the distribution of pedogenic mica (illite) in the soils under study, and (3) to find out how the genesis of clay minerals in the soils are related to the amount and distribution of rainfall when the parent rock is the same.

Literature Review

Not all minerals respond to the action of weathering with equal speed. Depending on the resistance of the minerals towards the effect of weathering, several authors have suggested mineral stability series. The stability to weathering action of a mineral species is the function of a large number of factors such as hardness, cleavage, original cracks in the crystal, coefficient of expansion and solubility under a specific environment.^I Some other factors such as grain size and specific surface may also be important in some cases.

Depending on the frequency of occurrence of a number of mineral species in rocks of increasing age Pettijohn² proposed a stability sequence of minerals. This sequence was actually a stability table in which the more stable minerals appeared first in the sequence and the degree of stability decreased from anatase to olivine. Later on some other authors also have proposed mineral stability series basing on different qualities of the minerals.³⁻⁵

Jackson and Sherman⁴ and Hseung and Jackson⁶ proposed a weathering sequence for claysized minerals consisting of thirteen stages. This includes mineral species that are normally recognised as secondary minerals formed during pedochemical weathering. According to this arrangement of minerals, the simpler the structure

^{*}This work was performed by the author at the United States Salinity Laboratory at Riverside, California, when he was on a special training there during the summer of 1966. The author is indebted to Dr. Saleem Ahmed, Agronomy Officer, ESSO Fertiliser Company in West Pakistan, for collecting the soil samples and sending them to the author.

the more stable is the mineral. Interstratified minerals are regarded as less stable than montmorillonite, which is less stable than kaolinite, which again, is less stable than the oxides and hydroxides of iron and aluminium.

Fieldes and Swindale⁵ proposed that the first stage of weathering of primary minerals is the destruction of the crystal lattice and the consequent release of amorphous hydrous oxides which may subsequently age to form crystalline oxides or be resilicified to form secondary layer silicates. This may be shown as follows:

Primary Chemical	Secondary
silicates — → Amorphous –	 \rightarrow silicates
weathering	

Correns and Engelhardt⁷ investigated the mechanism of weathering of potash felspars and concluded that potash, alumina and silica are all at first removed in ionic form with the relative proportions of these constituents depending on the acidity of the extracting medium. In course of time a number of silicate clays depending on the pH of the medium may form.

Fredrickson⁸ on the other hand proposed that the mechanism of weathering is essentially a base exchange process. He visualised the mechanism as a process in which the H⁺ of crystalline water are base-exchanged for the metallic ions of minerals. The small size of the H⁺ and its introduction into a crystal system is an exothermic reaction which makes the process possible. The mechanical effect of this base exchange reaction is a net expansion in the reacting layer of the crystal which causes the rock to exfoliate and become more chemically reactive. The minerals will break down into colloids depending on the Si:Al ratio in the crystal lattice.

Brewer⁹ pointed out that the formation of secondary mineral species in soils is controlled by the constituents that are released, the opportunity for their interaction and the suitability of the micro-environment. He mentions that free drainage tends to remove the products of weathering, while impeded drainage holds them within the soil material thus increasing the opportunity of their interaction. This is probably the reason that under free drainage condition kaolinite is the dominant mineral and under poor drainage montmorillonite is the dominant mineral.^{10–12} Crompton¹³ suggested that the ratio of rate of weathering/rate of leaching is extremely important in creating the microenvironment suitable for any particular mineral species and also in allowing the different constituents to interact with one another.

In the tropics, the dominant clay mineral in the soils is kaolinite. Kerr¹⁴ reported that weathering of granite under tropical environment produced kaolinitic masses and the texture of granite was preserved in the weathered material. Sand and Bates¹⁵ noted that kaolinite was formed only from the weathering of felspars and under conditions of intense leaching is formed from both pyroxenes and amphiboles. Primary micas, on the other hand, always change to vermicular kaolinite. Potash felspars, where leaching is not intense, pass through an intermediate stage of secondary mica, changing finally to vermicular kaolinite. This may be shown as follows:

P.otash	felspars	Less intense	Secondary	Less intense	Vermicular
	_	>	mica	\longrightarrow	Kaolinite
	-	weathering		weathering	1
		Intense	weatherin	g	

But halloysite forms from plagioclase, apparently without passing through any intermediate stage.

Under tropical conditions acid water may be responsible for the formation of extensive kaolinite deposits. Mohr *et al.*¹⁶ noted that kaolinite would form in tropical soils as a result of weathering of felspars under the influence of pure water or water containing sulphuric or carbonic acid. Under the influence of alkali or OH^- ions, montmorillonite is more likely to form.

Kerr¹⁷ noted that an alkaline environment which gives a sufficient supply of magnesium or ferric or ferrous iron in addition to silica and alumina, is apt to lead to the development of montmorillonite. Whereas in wet and warm climates, where the weathering and oxidising conditions are comparatively rapid, kaolinite and latosolic soils are likely to form. In their study of Hawaiian soils similar results, as above, have been reported by Sherman *et al.*¹⁰ Uehara *et al.*¹⁸ and Hussain.¹²

Materials and Method

The soil samples used in this study were collected from the Island of Oahu in the Hawaiian islands. The soils were collected from a transect that lies on the northern slope of the Kawailoa ridge under the Waialua Sugar Plantation. This transect lies from north to south; and both elevation and rainfall increases from north to south. Rainfall is low near the base of the slope (annual rainfall 10 in) and increases with elevation up to a maximum of 100 in annually. Parent rock of all the soils under this study was basalt.¹⁹ The soil samples include members of Gray Hydromorphic, Low Humic Latosol and Humic Latosol Great Soil groups.²⁰ Soil Survey maps of the island were used in locating the various soil sampling sites.

Soils were collected from eleven sites along the transect, more or less 1 mile apart. From each location two soil samples were collected-one surface soil and the other subsurface soil. Each of the samples was air-dried, crushed with a wooden roller, screened through a 10-mesh sieve and then thoroughly mixed. Since soils contain lots of impurities which may disturb during the x-ray diffraction analysis, the present soil samples were purified according to the method described by Jackson,²¹ in which the soils were treated first with I N NaOAc solution buffered at pH 5.0 to remove free carbonates and soluble salts, if any. After washing by centrifugation the soils were treated with H_2O_2 to destroy organic matter as much as possible. The samples were then washed by centrifugation. After removing organic matter the colour of the samples became bright red. The soils were then deferrated 4 times to remove free iron oxides according to the method of Jackson.²¹ After washing, the samples were treated with 2% Na₂CO₃ and boiled for 5 min to remove free silica and free aluminium oxides. After washing thrice by centrifugation the soils were dispersed in dilute Na₂CO₃ solution.

The seperation of clay fraction $(\langle 2\mu \rangle)$ was made from the above suspension by centrifugation. The colour of the seperated clay suspension was white and x-ray diffraction analysis was done on this purified clay sample. All the samples were treated under similar conditions so that the x-ray data could be used for quantitative measurement.

X-ray diffraction analysis was made on the K⁻ as well as Mg-sturated, oriented clay fractions by the use of N-filtered Cu-radiation $(K\alpha)$ generated by a Norelco x-ray diffraction unit at 35 KV and 20 ma. A Geiger Muller counter and a chart recorder were used. K-saturated samples were heated at different temperatures and x-rayed at each interval to examine the changes in structure of the clay minerals. Mgsaturated samples were glycerol-solvated before x-ray diffraction analysis to find out the maximum expansion of clay lattice along oor axis.

Sub-surface Soils-



Fig. 1.-X-ray diffraction charts of oriented, Mg-saturated and glycerol-solvated clay fractions.

26

28

Fig. 2.-X-ray diffraction charts of oriented, k-saturated clay fractions heated at 55°C.

Results and Discussion

X-ray diffraction diagrams of the soils under study have been presented in Figs. 1 and 2. From the figures it appears that kaolinite is the dominant mineral in all the soils except soil No. 1 and 2. This is seen from the presence of the first and second order diffraction peaks at 7.23 A and 3.65 Å respectively. In soil No. 11 which occurs at the lowest elevation and rainfall, there is a small peak at 17.9 Å when the sample is Mg-saturated and glycerol-solvated. This is an indication of the presence of a 2:1 expanding lattice secondary silicate i.e. montmorillonite. This kind of montmorillonite distribution in the Gray Hydromorphic soils of Hawaii has been reported by Gill and Sherman.²² and Hussain.¹² As the rainfall increases, the amount of montmorillonite clay in the soils decreases. Soil No. 10 has a trace amount of this mineral but as the rainfall increases further, the montmorillonite in the soils ultimately vanishes. With the increase of rainfall the weathering intensity increases and as a result the montmorillonite mineral breaks down to form kaolinite. Kaolinite is dominant in those soils where the rainfall is medium and decreases where the rainfall is very high as in Soil No. T₁, T₂, T_3 and S_1 , S_2 , and S_3 . This shows that under very high rainfall kaolinite is not a stable mineral and breaks down to form minerals like gibbsite and other free oxides of aluminium and iron.

Another interesting finding of this study is the distribution of illite or secondary mica in these soils. From Figs. 1 and 2 it is evident that the illite content is high in those soils which have higher rainfall and decreases with decrease of rainfall (Soil Nos. 1, 2, 3, 4 and 5). This kind of distribution of illite with rainfall has been reported by Juang and Uehara.²³ They noted that this illite is formed in soil during pedogensis. They suggested that recycling of K⁺ by plants is the main source of potassium for the formation of illite. The above authors further reported that the illite content decreases with depth in the soil profiles. From the hkl spacing of the illite mineral these authors concluded that the illite in the Hawaiian soils are dioctahedral in nature. They calculated a chemical formula from the chemical analysis of a purified illite sample which is as follows:

$$\begin{array}{c} (\mathrm{Na}_{0\cdot\mathbf{11}}\mathrm{NH}_{4} & \mathrm{K}_{1\cdot\mathbf{24}}) & (\mathrm{Si}_{6\cdot\mathbf{35}}\mathrm{Al}_{1\cdot\mathbf{65}}) \\ (\mathrm{Al}_{3\cdot\mathbf{54}}\mathrm{Fe}_{0\cdot\mathbf{16}} & \mathrm{Mg}_{0\cdot\mathbf{55}})\mathrm{O}_{20}(\mathrm{OH})_{4}. \end{array}$$

Swindale and Uehara²⁴ studied the equilibrium of illite in the Hawaiian soils from the point of view of ionic activity of different ions such as K^+, H_4SiO_4 and H^+ in the soil solution.

In soil No. 1, which occurs in the area of the highest rainfall, gibbsite is present but in the soils of lower rainfall there is no trace of any gibbsite. This is an indication that probably gibbsite forms in the area of high weathering intensity.

A number of authors have examined the formation of secondary minerals from basalt by chemical weathering.^{25–27} According to Abbott²⁵ basalt during chemical weathering goes directly to gibbsite which by resilication under suitable environment may form halloysite. Bates²⁶ on the other hand believes that basalt on weathering first changes to halloysite and on further weathering halloysite breaks down to form gibbsite. If the environment is suitable halloysite may be a stable mineral for a long time.

Uehara et al.¹⁸ studied the sequence of weathering of basalts in Hawaii. According to these authors basalt under medium rainfall changes to halloysite which ultimately may change to gibbsite under continuous disilication process. Sherman et al.¹⁰ noted that basalt in the same weathering region changes to halloysite where the drainage is good and in poor drainage area the major mineral is montmorillonite. Jackson et al.²⁸ noted that both resilication and disilication of minerals is possible if the soil environment is suitable.

In the soils under the present study the major clay minerals are montmorillonite, illite, kaolinite and gibbsite the quantity of which varies with the amount of rainfall. All the above minerals have been formed during soil formation and it seems that as the rainfall increases montmorillonite is replaced by kaolinite; and kaolinite in turn is replaced by gibbsite. Desilication seems to be the likely process of weathering in the present soils. This may be shown as follows:

	desilication		desilication	2.8 1
Montmorillonite		Kaolinite	\rightarrow	Gibbsite ***
	low pH		low pH	A. S.
				Se and

Rainfall and weathering intensity increases

From the assymmetrical first order x-ray diffraction peaks for kaolinite in the present soils it appears that the 1:1 mineral is really not kaolinite but dehydrated halloysite.²⁹ This kind of features have been reported by Sherman and Uehara²⁷ and Bates.²⁶ The dehydrated halloysite and kaolinite both have similar lattice spacing in the oo1 axis but they differ in shape of crystal. Halloysite alters to kaolinite on aging and that is why halloysite is regarded as a transitional mineral which ultimately transforms to kaolinite.²⁹ The weak type of x-ray diffraction peaks in soil No. I is probably an indication of the presence of a considerable amount of amorphous mineral namely allophane there.5 Gardinar³⁰ reported the presence of allophane in some soils of high rainfall areas in Hawaii.

Summary

Minerals in the clay fraction $(\langle 2\mu \rangle)$ of a number of soils belonging to a transect on the northern slope of the Kawailoa Ridge under the Waialua Sugar Plantation in the Hawaiian islands were studied with the help of X-ray diffraction analysis. All the soils of this transect developed on basalt. Rainfall is low at the lower elevations and increases with increasing elevation. The most interesting finding of this study is the distribution of illite and kaolinite in the soils. Illite content in the soils increases with increasing rainfall in the uphill direction and in the soil of maximum rainfall there is considerable amount of amorphous materials probably allophane. Soils of the higher rainfall zone also contain a considerable amount of gibbsite. There is a general trend of enrichment of kaolinite mineral with decrease of rainfall. In other words, the soils of the lower elevations have higher concentration of kaolinite in them, There is a slight increase of 2:1 type expanding lattice minerals in the soils of lower elevations. It has been suggested that the illite has formed during soil formation and the K⁺ has been supplied by K⁺ recycling by the native vegetation.

References

- I. J.F. Haseman and C. E. Marshall, Mo. Agr. Exp. Sta. Res. Bull., 387, 75 (1945).
- F. J. Pettijohn, J. Geol., 49, 610 (1941). 2.
- R. Weyl, Z. Pflanzenernachr. Dung., 3. Bodenk., 57, 135 (1952).
- M.L. Jackson and G.D. Sherman, Advan. 4. Agron., 5, 219 (1953).
- M. Fieldes and L.D. Swindale, New Zealand 5. J. Sci. Technol., 36B, 140(1954).
- Y. Hseung and M.L. Jackson, Soil Sci. Soc. 6. Am. Proc., 16, 294(1952).
- 7. C.W. Correns and W. Englhardt, Nene Untersuchungen uber die Verwitter ung des Kalifeldspates. (abstract): Min Abstract., 7, 405 (1938). 8. A.F. Frederickson, Bull. Geol. Soc. Am.,
- **62,** 221 (1951).
- R. Brewer, Fabric and Mineral Analysis of 9. Soils (John Wiley, New York, 1964).
- 10. G.D. Sherman, H. Ikawa, G. Uehara and E. Okazaki, Pacific Sci., 16,57(1962).

- L.D. Swindale and M.L. Jackson, Trans. II. 6th, Intern. Congr. Soil Sci. Paris (1956), Com. V, pp. 233-34.
- M.S. Hussain, A Genetic Study of the Gray 12. Hydromorphic Soils of the Hawaiian Islands, Ph.D. Thesis, University of Hawaii, Honolulu, Hawaii, 1967.
- 13. E. Crompton, The significance of the weathering/leaching ratio in the differentiation of major soil groups with particular reference to some very strongly leached brown earths of the Hills of Britain. Trans. Intern. Congr. Soil Sci. 7th, Madison (1960) Com. V. pp. 406-12.
- P.F. Kerr, Am. Mineralogist, 27, 487 (1942). 14.
- L.B. Sand and T.F. Bates, Mineralogy and 15. Petrology of the Residual Kaolins of the Southern Appalachian Region, Penn. State College Tech. Rep., 7, 1952.
- E.C. J. Mohr and Van Busen, Tropical Soils 16. (N. V. Uitgeverij W. Van Hoeve, The Hague, 1959), pp. 179-211.
- P.F. Kerr, Proc. Nat. Conf. on Clays and Clay 17. Technol., 5th Washington, D.C. (1955), pp. 1932.
- G. Uehara, H. Ikawa and G.D. Sherman, 18. Pacific Sci., 20, 119 (1966).
- C.K. Wentworth and H. Winchell, 1947. 19. Koolau Basalt Series, Oahu, Hawaii Bull. Geol. Soc.. Am., 58,49 (1947).
- M.G. Cline et al., Soil Survey, Territory of 20. Hawaii, USDA, Soil Survey Series, U.S. Govt. Printing Press 1939, issued 1955.
- M. L. Jackson, Soil Chemical Analysis, 21. Advanced Course (University of Wisconsin, Madison, Wisconsin, 1956).
- W.R. Gill and G.D. Sherman, Pacific Sci., 22. 6, 137 (1952).
- T.C. Juang and G. Uehara, Soil Sci. Soc. 23. Am. Proc., **32,** 31 (1948).
- L.D. Swindale and G. Uehara, Soil Sci. 24. Soc. Am. Proc., 30, 726 (1966).
- A.T. Abbott, Occurrence of Gibbsite on the 25. Island of Kauai, Hawaiian Islands, Eco. Geol., 5, 842 (1958).
- 26. T.F. Bates, Proc. Nat. Conf. on Clays and Clay Minerals, 9, 315 Washington, D.C. (1962).
- G.D. Sherman and G. Uehara, Soil Sci. 27. Soc. Am. Proc., 20, 337 (1956).
- M.L. Jackson, S.A. Taylor, A.L. Wills, G.A. 28. Bourbean and R. P. Pennington, J. Phys. Chem., **48**, 1237 (1948).
- 29. H. Kimura, Differentiation of Low Humic Latosols formed from Basalt and Andesite by Discriminatory Analysis (Masters Thesis, University of Hawaii, Honolulu, Hawaii, 1966).
- 30. H.C. Gardinar, personal communication, 1969.