CHEMICAL WEATHERING OF LAYER SILICATE CLAYS IN LOESS-DERIVED TAMA SILT LOAM OF SOUTHWESTERN WISCONSIN

by

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ABSTRACT

Chemical weathering of layer silicate clay minerals in the major horizons of the Tama silt loam Prairie soil profile was followed down to 10 ft, where the calcareous parent loess was encountered, and on down to a depth of 13 ft. The predominant constituents of the clay fraction ($-2\ \mu$) at all depths in the soil profile were montmorillonite (42 percent) and illite (20 percent), although vermiculite (12 percent), kaolinite (5 percent) and amorphous material (15 percent) were also in fair abundance. Deposition of secondary interlayer alumina was appreciable in the uppermost soil horizons but became less in amount in the deeper soil horizons. Quartz was not found in the clay fractions of less than $0.2\,\mu$ in diameter at any depth in the soil profile, although both quartz and feldspars occurred in the coarse clay.

Vermiculite decreased from about 18 percent in the coarse clay and 5 percent in the fine clay of the deeper calcareous horizons to small amounts toward the soil surface, disappearing altogether in the fine clay ($-0.08\,\mu$). Little variation was found in the montmorillonite percentage of the clay in the subsoil and lower horizons (64 to 75 percent of the fine clay), but a decrease in the 18 Å diffraction intensity of montmorillonite concurrent with an increase in amorphous silica and alumina (15 to 27 percent of the fine clay) was observed in the upper, acid, soil horizons, suggesting that montmorillonite is not a stable weathering product in the latter. Elemental analyses of the fine clays showed about 1.1 out of 4 octahedral positions to be Fe, 2.5 to be Al, and 0.4 to be Mg. A slight decrease in Fe and increase in Al in the montmorillonite octahedral structure occurred progressively in approaching the more intensely weathered zones near the soil surface.

The results suggest that dioctahedral montmorillonite has formed to considerable extent in both the calcareous and noncalcareous horizons by chemical weathering of trioctahedral ferromagnesian mica, through a vermiculite intermediate stage. The decrease in amount of the silt fractions of density greater than 2.66 g/cm^3 (found to be composed mainly of biotite, chlorite, and amphiboles) in going from the calcareous horizons toward the soil surface approximately equalled the increase in montmorillonite percentage of the soil, suggesting that montmorillonite of the loess originated by chemical weathering of the ferromagnesian minerals of the silt. The genesis of the loessial montmorillonite begins long before the free $CaCO_3$ has been leached out (6 percent montmorillonite in the loess at 13 ft) and continues to a maximum (14 percent) in the B horizon. Some eluviation of montmorillonite from the A horizon into the B horizon was evident.

INTRODUCTION

Tama silt loam is a well drained medial Prairie soil (Brunizem) derived from deep loess in the upper Mississippi valley (Smith, Allaway and Riecken, 1950).

In Wisconsin it occurs in the unglaciated southwestern section of the state, and is one of the most productive agricultural soils of that area (Hole, 1956). The Tama profile used in this study was sampled about three miles east of the Mississippi River in Grant County where the parent loess is around 20 ft deep and of nearly uniform texture throughout. Leaching of carbonates has occurred to a depth of 110 in. and the calcium carbonate equivalent of the loess at a depth of 150 in. is 16.3 percent.

The mineral transformations that have occurred during soil formation from the original calcareous loess (high pH and abundant bases) through horizons leached of carbonates and weakly acid, to horizons where moderate to strong acidity has developed, thus could be studied.

REVIEW OF LITERATURE

Hydrous mica interleaved with montmorillonite was found to dominate the clay of desert soils, whereas clays of Red-Podzolic soils were dominated by kaolinite, and clays of certain Gray-Brown Podzolic soils (on shale-derived till) contained large amounts of illite (Alexander, Hendricks and Nelson, 1939). Montmorillonite was found to increase in abundance with increasing soil depth in Arizona soils (Buehrer, Robinson and Deming, 1949). Studies on the relation of biotite to vermiculite revealed that cations differ in their ability to expand micas (Barshad, 1948). Potassium replacement by Mg and oxidation of structural iron was described in early stages of weathering of biotite in Scotland soils, while advanced weathering stages were characterized by release of iron from the mineral structure with replacement by magnesium to give a trioctahedral vermiculite product (Walker, 1949). Soils in New Zealand that are developed with less than 20 in. of rainfall contain illite and vermiculite but no montmorillonite, while soils developed from similar parent material with 30 or more in. of rainfall contain montmorillonite (Fieldes and Swindale, 1954). Olivine basalt in Hawaii was found to weather to montmorillonite where leaching of bases is restricted, while the same material weathers to kaolinite where leaching occurs freely (Sherman and Uehara, 1956). Muscovite was found to weather to a dioctahedral vermiculite by cleavage and loss of potassium in a soil derived from muscovite schist in Virginia (Rich, 1958). Brown and Jackson (1958) described transformations of illite through vermiculite–chlorite to montmorillonite in a Podzol in northern Wisconsin. Other soils in northern Wisconsin were found to contain minerals of mixed-layer components in the C horizons, with increasing proportions of first vermiculite and then montmorillonite with increasing proximity to the soil surface (Whittig and Jackson, 1955). The montmorillonite component of montmorillonite-rich clays of loess-derived soils in Illinois was postulated to have originated from the montmorillonite and bentonitic soils and sediments of the Great Plains region, and not from glacial alluvium on the floodplains of local rivers (Beavers and others, 1955; Beavers, 1957). It has been noted that much of the montmorillonite of clays from loess may likely have formed through secondary chemical weathering of mica particles (mostly less than 50 μ in size) abundant in loess (Jackson, 1959).

MATERIALS AND METHODS

The Tama soil used for this investigation is a medial Prairie soil and was sampled in the NE 1/4, SE 1/4, Sec. 13, T. 3 N., R. 3 W., town of Glen Haven, Grant County, Wisconsin. Six horizons, the A_{12}, B_1, C_3, C_4, C_5 and C_6 were selected to represent the entire chemical weathering profile, to a depth of 157 in. Samples of 50-g size were freed of carbonates, organic matter, and iron oxides, and dispersed and size-segregated by the methods outlined by Jackson (1956). Soil acidity values were measured on saturated pastes using a Cameron pH meter. Cation exchange capacities of clays were determined by flame emission photometry, employing calcium as the determined cation in a 1 N sodium acetate system. The instrument used for detection was a Beckman, model DU, flame photometer with photomultiplier, and calcium was read on the 424 mμ line. Elemental analyses were made by the rapid semi-microchemical method of Corey, Jackson, Whittig and Swindale (in Jackson, 1958). The percentage of expanding layer silicates was measured by mono-interlayer and duo-interlayer specific surface (Mehra and Jackson, 1959a, 1959b). Illite was determined by elemental K_2O on the basis of an illite K_2O content of 10 percent (Mehra and Jackson, 1959a). Amorphous oxides and kaolinite were measured by rapid alkali dissolution after preheating the clays to 110° and 500°C for 4 hr, respectively (Hashimoto and Jackson, 1960). Heat-weight loss values were run in a muffle furnace on hydrogen-saturated specimens dried from benzene. All analyses are based on 110°C oven-dry weight.

Specimens of clays for x-ray analysis were given parallel orientation on glass microscope slides (25×45 mm). The instrument used was a General Electric XRD-3 diffraction unit with copper target. A scanning speed of 2 degrees per minute was used. Two specimens of each clay fraction were prepared, one exchange-saturated with magnesium and glycerated, the other exchange-saturated with potassium and glycerated (Jackson, 1956, p. 184). The magnesium-saturated specimens were x-rayed after drying at room temperature, whereas the potassium-saturated specimens were x-rayed after drying at room temperature, and again after heating for 4-hr periods at 300° and 500°C, respectively. When chlorite was evident, specimens were given an additional heating at 600° for 4 hr. Clay specimens that had been subjected to rapid alkali dissolution treatments to dissolve amorphous oxides and kaolinite were also saturated with magnesium and potassium and x-rayed.

RESULTS AND DISCUSSION

x-*Ray Diffraction Analysis*

x-Ray diffraction patterns of the clays (Figs. 1, 2 and 3) include patterns of specimens receiving the conventional x-ray preparations (control), specimens

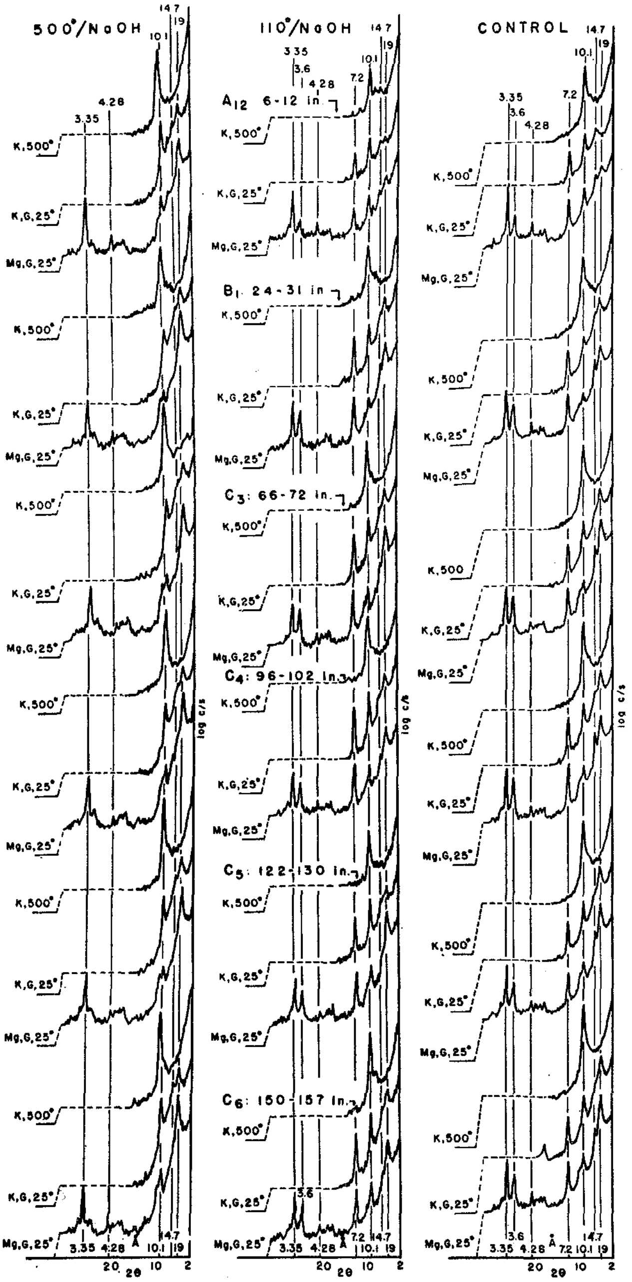

FIGURE 1.—X-Ray diffraction patterns of parallel orientation specimens of the 2–0.2 μ clay fraction of various Tama silt loam horizons from 6 to 157 in. in the soil, showing the effects of magnesium saturation–glycerol solvation and potassium saturation–glycerol solvation-heat treatments on (right) specimens receiving no pretreatments other than conventional preparations (control), (center) specimens preheated at 110°C and boiled in 0.5 N NaOH for 2.5 min (110°/NaOH), and (left) specimens preheated at 500°C and boiled in 0.5 N NaOH for 2.5 min (500°/NaOH).

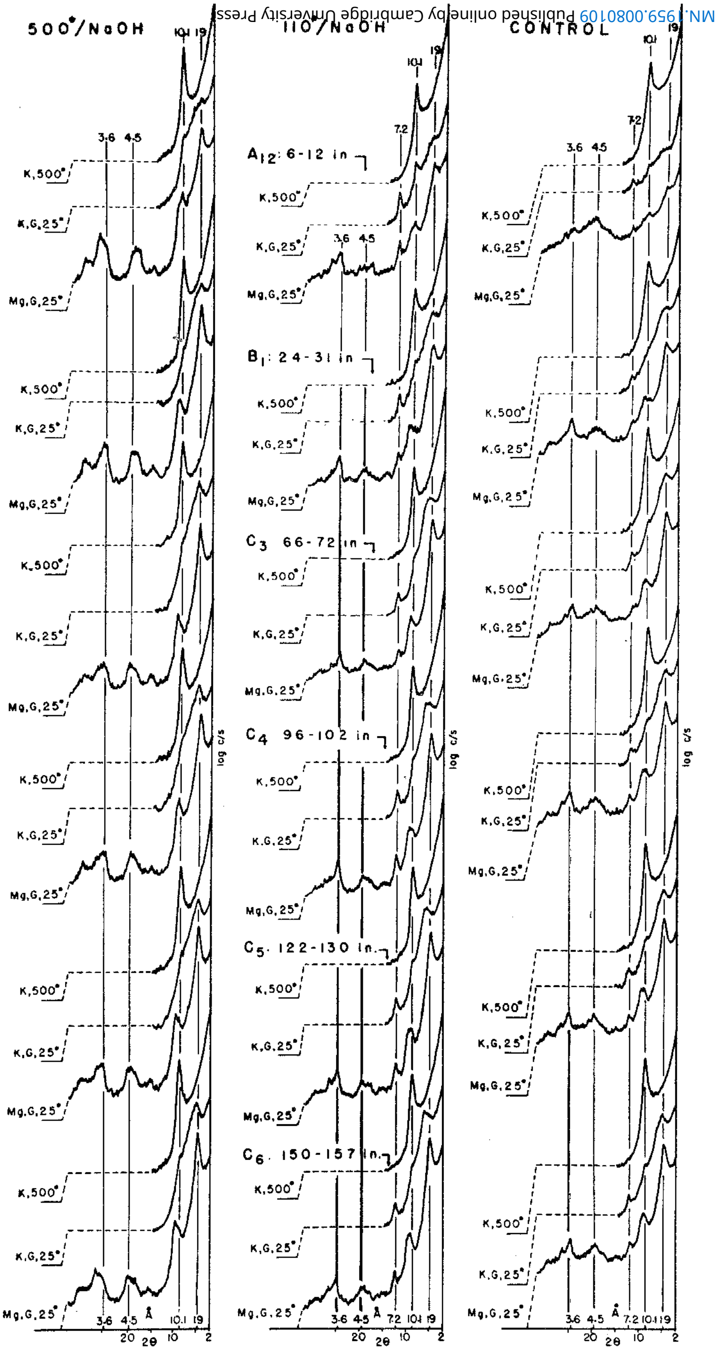

FIGURE 2.—x-Ray diffraction patterns of parallel orientation specimens of the 0.2–0.08 μ clay fraction of various Tama silt loam horizons from 6 to 157 in. in the soil, showing the effects of magnesium saturation–glycerol solvation and potassium saturation–glycerol solvation-heat treatments on (right) specimens receiving no pretreatments other than conventional preparations (control), (center) specimens preheated at 110°C and boiled in 0.5 N NaOH for 2.5 min (110°/NaOH), and (left) specimens preheated at 500°C and boiled in 0.5 N NaOH for 2.5 min. (500°/NaOH).

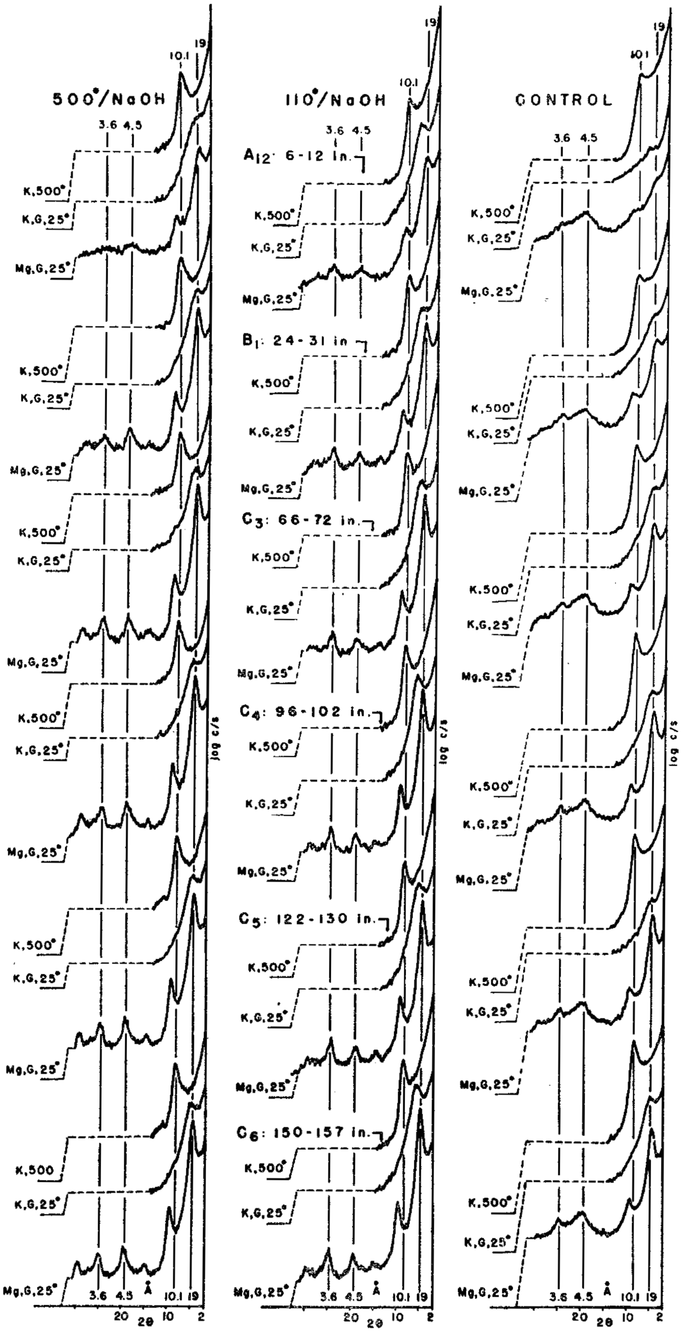

FIGURE 3.—x-Ray diffraction patterns of parallel orientation specimens of the less than 0.08 μ clay fraction of various Tama silt loam horizons from 6 to 157 in. in the soil, showing the effects of magnesium saturation–glycerol solvation and potassium saturation–glycerol solvation-heat treatments on (right) specimens receiving no pretreatments other than conventional preparations (control), (center) specimens preheated at 110°C and boiled in 0.5 N NaOH for 2.5 min. (110°/NaOH), and (left) specimens preheated at 500°C and boiled in 0.5 N NaOH for 2.5 min. (500°/NaOH).

preheated at 110°C and boiled in NaOH for 2.5 min to dissolve amorphous material (110°/NaOH), and specimens preheated at 500°C and boiled in NaOH for 2.5 min. to dissolve kaolinite and halloysite (500°/NaOH). The minerals that could be identified from the x-ray patterns of the coarse clay (2–0.2 μ) are illite (10Å), vermiculite (14.7Å), montmorillonite (19Å), kaolinite (7.2Å), quartz (4.28Å) and feldspar (3.2Å and 3.25Å). The coarse clay (2–0.2 μ, Fig. 1) also contains small amounts of heat-stable chlorite along with small amounts of an intergradient, aluminous, chlorite–vermiculite–montmorillonite material (not heat stable) (Rich and Obenshain, 1955; Klages and White, 1957; Tamura, 1958; Dixon and Jackson, 1959) which decreases in abundance from the A horizon downward in the profile. Major minerals in the medium clay (0.2–0.08 μ, Fig. 2) are illite, montmorillonite, and kaolinite, while montmorillonite was the only mineral giving good peaks in the fine clay (−0.08 μ, Fig. 3). The behavior of the medium and fine clay on K-saturation and heating to 500°C indicates that some intergradient chlorite–montmorillonite is also present in these fractions in the A and B_1 horizons. This is shown by incomplete collapse of higher spacings to 10Å by heating in the control treatment.

Removal of amorphous colloids by the 110°/NaOH treatment of the clays from the upper soil horizons resulted in better parallel orientation of the clay particles, as evidenced by greatly enhanced intensity of the major peaks in the Mg saturated, glycerated specimens, especially those in the medium and fine clay. Heating of specimens at 500°C, followed by boiling in NaOH afterward gave further increases in the intensity of the montmorillonite peaks. There was also complete collapse of higher spacings to 10Å on K-saturation and heating to 500°C after this latter dissolution treatment. The further increase in the montmorillonite peak intensity over that obtained by removal of amorphous material is probably due to free expansion of the montmorillonite plates as a result of removing aluminum interlayer bonds. The 500°C heat treatment apparently was effective in dehydroxylating the aluminous interlayers which in turn were dissolved by the boiling alkali treatment afterward. Dixon and Jackson (1959) found this series of treatments to be effective in dissolving the aluminous interlayers from intergradient chlorite–vermiculite–montmorillonite in soil clays.

Rapid Alkali Dissolution of Amorphous Materials and Kaolinite–Halloysite

Silica and alumina that were dissolved (Table 1) by the 2.5-min NaOH-boiling treatment after the clays were preheated at 110°C, along with iron extracted by free iron oxide removal treatments afterwards, were allocated to amorphous materials. Silica, alumina, and iron similarly extracted from the clays after preheating to 500°C (Table 2), less the quantities dissolved after the 110°C-NaOH boiling, were allocated to kaolinite–halloysite and nontronitic montmorillonite (Hashimoto and Jackson, 1960). The net silica and alumina thus dissolved (Table 2, columns 6, 7 and 8) from the coarse clay well fitted the 2 : 1 SiO_2/Al_2O_3 molar ratio of kaolinite, giving a simple allocation to kaolinite in this fraction. In the medium clay, all the alumina that dissolved after the 500° heat treatment was allocated to kaolinite along with enough silica to give the theoretical 2 : 1 silica : alumina molar ratio of kaolinite. Allocations were not made to kaolinite in the fine clay because the x-ray patterns suggest that kaolinite is absent in this fraction. It is evident from the SiO_2/Al_2O_3 ratios that some 2 : 1 layer silicates (nontronitic) were dissolved from the medium clay after the 500° heat treatment; however, since the kaolinite content of this fraction is small only a small error results when all the alumina is allocated to this mineral.

Table 1.—Amorphous Materials Dissolved from Clays by Rapid NaOH Boiling and Free Iron Removal Treatments after Clays were Preheated at 110°C

Horizon and Depth, inches	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	Total %	Molar Ratio	
					$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{R_2O_3}$
		$-0.08\ \mu$				
A_{12}: 6–12	15.30	8.90	2.31	26.51	2.93	2.50
B_1: 24–31	12.83	6.81	2.50	22.14	3.20	2.60
C_3: 66–72	10.49	4.56	2.75	17.80	3.89	2.81
C_4: 96–102	9.75	3.43	2.28	15.46	4.85	3.40
C_5: 122–131	8.90	2.48	2.70	14.08	6.09	3.59
C_6: 150–157	9.11	3.02	2.48	14.61	5.14	3.37
		$0.2–0.08\ \mu$				
A_{12}: 6–12	7.48	4.05	1.43	12.96	3.15	2.57
B_1: 24–31	7.58	4.40	1.59	13.57	2.93	2.38
C_3: 66–72	8.50	3.12	1.54	13.16	4.64	3.53
C_4: 96–102	7.50	2.33	1.57	12.90	5.48	3.83
C_5: 122–131	6.54	1.74	1.37	9.59	6.37	4.24
C_6: 150–157	7.15	2.20	1.53	10.88	5.51	3.81
		$2–0.2\ \mu$				
A_{12}: 6–12	5.56	1.11	0.31	6.98	8.50	7.24
B_1: 24–31	3.79	1.62	0.54	5.95	3.97	3.26
C_3: 66–72	3.67	1.22	0.36	5.25	5.10	4.27
C_4: 96–102	4.08	0.96	0.24	5.28	7.23	6.24
C_5: 122–131	3.63	0.81	0.14	4.58	7.62	6.93
C_6: 150–157	3.76	0.81	0.19	4.76	7.90	6.92

The content of amorphous materials in the fine clay, as determined by this method, ranged from 27 percent in the A_{12} horizon to 14 percent in the lower C horizons. In the medium clay, the content of amorphous materials ranged from 13.6 percent in the B horizon to 9.6 percent in the C_5 horizon, while that of the coarse clay ranged from 7 percent in the A_{12} horizon to 4.6 percent in the C_5 horizon.

The SiO_2/Al_2O_3 molar ratios for the amorphous components (Table 1) show an increase in silica relative to alumina both with increasing particle-size and soil depth. The lowest ratios occurred in the A_{12} horizon of the fine clay and in the B_1 horizon of the medium and coarse clay. In the coarse clay the largest ratio (8.5) occurred in the A_{12} horizon. This is more than twice the silica : alumina of 2 : 1 layer silicates, and presumably is due to the presence of siliceous relics (Jackson, 1956, p. 531) of weathered layer silicates, derived by mobilization of the aluminum into the intergradient chlorite–vermiculite–montmorillonite found in clays of these horizons.

TABLE 2.—MATERIALS DISSOLVED FROM CLAYS BY RAPID NaOH BOILING AND FREE IRON REMOVAL TREATMENTS AFTER CLAYS WERE PREHEATED AT 500°C

Horizon and Depth, inches	Dissolved after Heating to 500°C			Net Oxides[1]		
					Molar Ratio	
	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	%	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{R_2O_3}$
		−0.08 μ				
A_{12} 6–12	26.45	13.88	2.62	16.4	3.81	3.65
B_1: 24–31	22.23	11.41	5.27	16.8	3.47	2.53
C_3: 66–72	18.74	6.83	5.99	13.8	5.07	3.29
C_4: 96–102	16.50	5.18	6.58	11.6	6.54	3.08
C_5: 122–131	16.44	4.93	6.28	13.6	5.20	2.74
C_6: 150–157	16.50	5.14	6.30	13.3	5.86	1.89
		0.2–0.08 μ				
A_{12}: 6–12	16.76	9.98	1.55	15.3	3.66	2.63
B_1: 24–31	16.72	9.42	2.92	15.5	3.09	2.66
C_3: 66–72	13.29	6.65	2.55	9.3	2.31	1.95
C_4: 96–102	13.78	6.26	2.66	11.3	2.73	2.28
C_5: 122–131	12.80	5.69	1.87	10.7	2.70	2.47
C_6: 150–157	11.85	5.12	2.55	9.6	3.32	2.23
		2–0.2 μ				
A_{12}: 6–12	10.38	5.20	0.48	8.9	2.00	1.96
B_1: 24–31	10.02	6.45	0.85	11.2	2.26	2.12
C_3: 66–72	9.81	6.16	0.87	11.1	2.11	2.00
C_4: 96–102	10.92	6.53	0.67	12.4	2.09	1.97
C_5: 122–131	9.38	5.05	0.77	10.0	2.30	2.09
C_6: 150–157	9.25	5.81	0.78	10.5	1.88	1.74

[1] After subtraction of respective percentages dissolved after 110°C heating (Table 1).

It is of interest to note that the silica : alumina ratio of the material dissolved from the coarse clay by the 500°/NaOH treatment (after subtraction of the amorphous components determined on the 110° sample) does not fall below the theoretical 2 : 1 kaolinite ratio as might be expected from the fact that this treatment also extracted some aluminum from the interlayers of the intergradient chlorite–vermiculite–montmorillonite material. Apparently only a small amount of aluminum is required to bond a relative large number of interlayers, a fact also noted by Dixon and Jackson (1959).

Elemental Analysis and Montmorillonite Formulas

The elemental analyses (Table 3) show that the clays of the Tama soil are low in magnesium and high in structural iron. The magnesium content of the clays does not change significantly with changes in particle size and profile depth. Iron, on the other hand, is much more abundant in the fine clay than in the coarse and is considerably less abundant in the A horizon than in lower horizons. Total K_2O does not differ significantly in the A and deep C horizons but is substantially lower in the B_1 and C_3 horizons than in the A horizon. The K_2O content increases three to four fold from the fine to the coarse clay. The small amounts of sodium found in the fine and medium clay presumably could occur in the micas or indicate traces of feldspar. In the coarse clay, enough sodium is present to suggest the occurrence of a little feldspar in this fraction. Calcium also occurs in small amounts in the coarse clay. Total weight loss at 900°C was highest in the fine and medium clay in the A horizon and is probably related to the higher content of amorphous materials in this horizon.

Formulas of the montmorillonite component of the fine clay were calculated (Table 4) by assuming a net negative charge of 44 units on the unit cell, arising from 20 oxygens and 4 hydroxyls (Jackson, 1956, p. 546). Total negative layer charge was calculated from the cation exchange capacities (Table 5). All K_2O, along with accompanying amounts of silica and alumina for the theoretical composition of muscovite, were subtracted from the analysis and allocated to illite. Sodium was assumed to be negligible and was not included in the calculations. Titanium was attributed to small amounts of anatase. Amorphous material, as determined by rapid dissolution (Table 1), was also subtracted prior to the final formula calculations (Table 4).

Removal of amorphous constituents did not appreciably change the formula of the montmorillonite in the fine clay of the C horizons. In the C_6 horizon removal of amorphous material changed the formula from

$$(Si_{7.7}Al_{0.3})(Al_{2.44}Fe_{1.18}Mg_{0.31})$$

to

$$(Si_{7.65}Al_{0.35})(Al_{2.43}Fe_{1.14}Mg_{0.38}),$$

slightly but not significantly increasing the amount of tetrahedral charge. In the A_{12} horizon the change incurred by removal of amorphous material was from

$$(Si_{7.39}Al_{0.61})(Al_{2.91}Fe_{0.91}Mg_{0.38})$$

to

$$(Si_{7.65}Al_{0.35})(Al_{2.55}Fe_{0.98}Mg_{0.37}),$$

Table 3.—Elemental and Heating-Weight Loss Analysis of Clay Fractions

Oxide	Percentage of Oxides by Horizon and Depth					
	A_{12} 6–12 in.	B_1 24–31 in.	C_3 66–72 in.	C_4 96–102 in.	C_5 122–131 in.	C_6 150–157 in.
			−0.08 μ			
SiO_2	52.10	53.30	55.92	55.62	55.96	55.62
Al_2O_3	23.16	23.09	20.54	20.04	19.46	19.79
Fe_2O_3	7.82	8.85	10.00	10.62	10.50	10.80
MgO	1.05	1.24	1.35	1.49	1.40	1.39
CaO	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.07	0.09	0.07	0.07	0.09	0.07
K_2O	1.19	0.81	0.80	1.15	1.21	1.17
TiO_2	0.44	0.43	0.37	0.40	0.40	0.41
H_2O, 110–200°C	2.81	1.52	1.70	1.93	1.33	1.23
200–350°C	2.35	3.22	2.84	3.47	2.72	3.29
350–540°C	7.03	5.67	4.04	3.75	4.89	4.96
540–900°C	1.11	1.29	2.70	1.71	1.45	1.38
H_2O (Total)	13.10	11.70	11.28	10.86	10.39	10.86
Total Oxides	98.93	99.51	100.33	100.25	99.41	99.11
			0.2–0.08 μ			
SiO_2	54.74	53.95	55.50	56.48	57.84	55.46
Al_2O_3	22.38	24.63	20.87	20.75	19.18	19.96
Fe_2O_3	6.61	7.46	7.96	7.71	8.26	8.47
MgO	1.38	1.36	1.45	1.58	1.50	1.72
CaO	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.15	0.12	0.11	0.11	0.20	0.17
K_2O	2.79	1.70	2.06	2.48	2.72	2.62
TiO_2	0.89	0.68	0.75	0.71	0.66	0.67
H_2O, 110–200°C	1.50	1.37	1.97	1.90	2.28	1.90
200–350°C	7.21	2.14	2.97	2.82	2.58	3.30
350–540°C	6.57	5.22	3.55	3.55	3.46	3.14
540–900°C	1.32	1.93	1.84	1.80	1.66	1.92
H_2O (Total)	11.60	10.66	10.33	10.07	9.98	10.26
Total Oxides	100.54	100.56	99.03	99.89	100.34	99.33
			2–0.2 μ			
SiO_2	67.52	60.12	61.42	62.87	63.05	64.61
Al_2O_3	16.60	22.18	18.97	18.96	19.82	18.43
Fe_2O_3	2.54	3.43	4.04	3.10	3.14	3.28
MgO	0.95	1.21	1.15	1.27	1.26	1.25
CaO	0.14	0.14	0.14	0.15	0.20	0.20
Na_2O	0.58	0.37	0.52	0.69	0.72	0.68
K_2O	4.16	3.02	3.24	3.47	3.68	3.66
TiO_2	1.29	1.21	1.45	1.07	1.20	1.22
H_2O, 110–200°C	1.23	1.15	1.51	1.55	1.33	0.62
200–350°C	1.23	1.32	1.09	1.35	1.23	1.14
350–540°C	3.94	4.12	3.85	3.55	3.28	3.58
540–900°C	0.53	1.77	1.73	1.47	1.85	1.20
H_2O (Total)	6.93	8.36	8.18	7.92	7.69	6.54
Total Oxides	100.71	100.04	99.11	99.50	100.76	99.87

TABLE 4.—FORMULAS FOR THE MONTMORILLONITE COMPONENTS OF THE FINE CLAY ($-0.08\,\mu$), BASED ON ISOMORPHOUS SUBSTITUTION IN THE UNIT CELL, $Si_8Al_4O_{20}(OH)_4$

Horizon and Depth, inches	Tetrahedral		Octahedral Coordination				Layer charge per formula weight, X
	Si^{4+}	Al^{3+}	Al^{3+}	Fe^{3+}	Mg^{2+}	Σ	
A_{12}: 6–12	7.65	0.35	2.55	0.98	0.37	3.90	1.00
B_1: 24–31	7.52	0.48	2.72	0.95	0.37	4.04	1.00
C_3: 66–72	7.71	0.29	2.56	0.99	0.37	3.92	0.92
C_4: 96–102	7.62	0.38	2.40	1.15	0.41	3.96	0.91
C_5: 122–131	7.70	0.30	2.48	1.06	0.38	3.92	0.94
C_6: 150–157	7.65	0.35	2.43	1.14	0.38	3.95	0.90

TABLE 5.—PERCENT CLAY, CATION EXCHANGE CAPACITY, AND SPECIFIC SURFACE OF CLAY FRACTIONS

Horizon and Depth, inches	Percent of Soil[1]	Cation Exchange Capacity, meq/100 g	Specific planar surface	
			Total	Montmorillonite
			m^2/g	m^2/g
		$-0.08\,\mu$		
A_{12}: 6–12	7.4	71.7	441	495
B_1: 24–31	9.2	83.9	553	556
C_3: 66–72	6.1	84.3	579	575
C_4: 96–102	5.4	82.6	579	565
C_5: 122–131	6.0	86.0	587	548
C_6: 150–157	5.3	82.3	604	565
		$0.2–0.08\,\mu$		
A_{12}: 6–12	8.4	49.9	348	309
B_1: 24–31	10.0	65.3	440	394
C_3: 66–72	6.8	70.2	432	348
C_4: 96–102	5.2	68.1	440	348
C_5: 122–131	5.8	71.9	471	363
C_6: 150–157	5.0	73.9	448	371
		$2–0.2\,\mu$		
A_{12}: 6–12	8.3	25.8	111	82
B_1: 24–31	10.1	43.7	286	139
C_3: 66–72	8.6	43.3	251	156
C_4: 96–102	6.8	38.2	252	133
C_5: 122–131	7.8	39.0	266	129
C_6: 150–157	7.5	38.1	286	147

[1] Carbonate-free mineral portion of soil basis.

appreciably lowering the tetrahedral charge. It is interesting that the formula of the montmorillonite in the A_{12} horizon does not vary greatly from that of the C_6 horizon after removal of amorphous constituents, especially in regard to the tetrahedral constituents. The main variation in the octahedral position is a slight increase in aluminum and a slight decrease in iron. The fine clay in the upper soil horizons contains trace amounts of intergradient chlorite–montmorillonite (as pointed out above), which raises the aluminum analysis (Table 3). The latter is not sufficiently extensive to give a sum of octahedral ions (Table 4) in excess of 4 (Sawhney and Jackson, 1958) but it lowers the cation-exchange capacity (Table 5). It is possible that the ferruginous portion of the ferruginous-aluminous montmorillonite has weathered faster, enriching the clay with a more aluminous octahedral composition, the tetrahedral composition remaining unchanged between the C and A horizons. Also, it is possible that the increment of montmorillonite attributable to formation in the acid portion of the column (as developed in a later paragraph) has a higher aluminum content.

Trends in Mineral Content of Clay Fractions

The relative amounts of individual minerals and the number of mineral species present in the clay fraction varies greatly with particle size in Tama silt loam (Table 6). Montmorillonite and illite are the major minerals in each of the clay fractions, while vermiculite is important in the medium and coarse clay. Trace amounts of intergradient chlorite–montmorillonite occur in the fine and medium clay of the A and B horizons, whereas appreciable amounts of intergradient chlorite–montmorillonite or chlorite–vermiculite occur in the coarse clay of the same horizons. The amount of kaolinite (including any halloysite, if present) is appreciable in the coarse and medium clay while amorphous material increases in the fine clay. Quartz and feldspar occur in the coarse clay but not in the fractions of less than $0.2\,\mu$ diameter.

Illite, as determined from K_2O analysis, is an important component (up to 42 percent) of each clay fraction at all depths in the loess column and soil profile. The importance of illite as a component in the clay of this loess deposit (which is normally considered to carry mainly montmorillonite) should not be overlooked. The illite content of the clay increases about three-fold with increasing particle size from the fine to the coarse clay. The percentage of illite in each clay fraction is approximately equal in the A and deep C horizons but is considerably lower in the B_1 and C_3 horizons, apparently because of dilution by montmorillonite eluviated from the A horizon.

Vermiculite was detected by specific surface methods in amounts up to 5 percent of the fine clay of the C_5 and C_6 horizons but was absent in the fine clay of the A_{12} and B_1 horizons. In contrast, montmorillonite is the major mineral of the fine clay in all horizons and comprises from 64 percent of the fine clay of the A_{12} horizon to 71–75 percent in the lower horizons. Little variation occurs with soil depth in the montmorillonite content of the medium clay except for a slight bulge in the B horizon (Table 6).

The mineral content on a whole clay basis (calculated from the data of Tables 5 and 6; plotted in Fig. 4, left) shows a slight relative enrichment in montmorillonite and decrease in illite in the B horizon, attributable to illuviation of montmorillonite from the A horizon. Vermiculite increases and amorphous material decreases slightly in going from top to bottom of the loess column. The striking feature is the uniformity of mineral species *percentage of the whole clay fraction.*

TABLE 6.—MINERAL CONTENT OF CLAY FRACTIONS

	Minerals Identified as Percent of Clay Fraction							
Horizon and Depth, inches	Feld-spar	Quartz[1]	Illite	Vermi-culite	Montmo-rillonite	Chlo-rite[2]	Amor. material	Kao-linite
				$-0.08\ \mu$				
A_{12}: 6–12	—	—	12	—	64	tr	27	—
B_1: 24–31	—	—	8	—	72	tr	22	—
C_3: 66–72	—	—	8	tr	75	—	18	—
C_4: 96–102	—	—	12	2	73	—	15	—
C_5: 122–131	—	—	12	5	71	—	14	—
C_6: 150–157	—	—	12	5	72	—	15	—
				$0.2–0.08\ \mu$				
A_{12}: 6–12	—	—	28	5	45	tr	13	13
B_1: 24–31	—	—	17	6	51	tr	14	11
C_3: 66–72	—	—	21	11	45	tr	13	8
C_4: 96–102	—	—	25	12	45	—	13	8
C_5: 122–131	—	—	27	14	47	—	10	9
C_6: 150–157	—	—	26	10	48	—	11	5
				$2–0.2\ \mu$				
A_{12}: 6–12	5	12	42	4	11	7	7	9
B_1: 24–31	5	8	30	19	18	5	5	11
C_3: 66–72	8	5	32	12	20	4	5	10
C_4: 96–102	10	4	35	16	17	2	5	12
C_5: 122–131	10	5	37	18	17	2	4	9
C_6: 150–157	7	7	37	18	19	1	5	11

[1] Estimated from x-ray diffraction.

[2] Estimated from x-ray diffraction; mostly chlorite–montmorillonite intergrade.

In contrast, the clay mineral species *percentage of the whole soil* (Fig. 4, right) shows an increasing content of montmorillonite from the calcareous loess to the soil surface. A correction for the C_5 and C_6 horizons, which contain 11.4 and 16.3 percent by weight of free carbonates, respectively, to a carbonate-free basis brings the montmorillonite percentage of the soil to 7.5 percent, uniform from 100 in. downward. A gradual increase to 14 percent occurs in going upward to the B horizon. The increase noted in clay illite in the A horizon corresponds to a greatly decreased intensity of the 10Å peaks in the silt fractions of this horizon.

Origin of the Montmorillonite in the Loess Column

The distribution of heavy minerals in the coarse (50–20 μ) and medium (20–5 μ) silt fractions (Table 7) indicates that much of the montmorillonite (Fig. 4, right) in the loess has developed by chemical weathering of micas as proposed by Jackson (1959):

$$\begin{tikzcd}
\text{Biotite} \arrow[r] \arrow[dr] & \text{Chlorite} \arrow[r] & \text{Montmorillonite} \\
 & \text{Vermiculite} \arrow[u] \arrow[ur] &
\end{tikzcd}$$

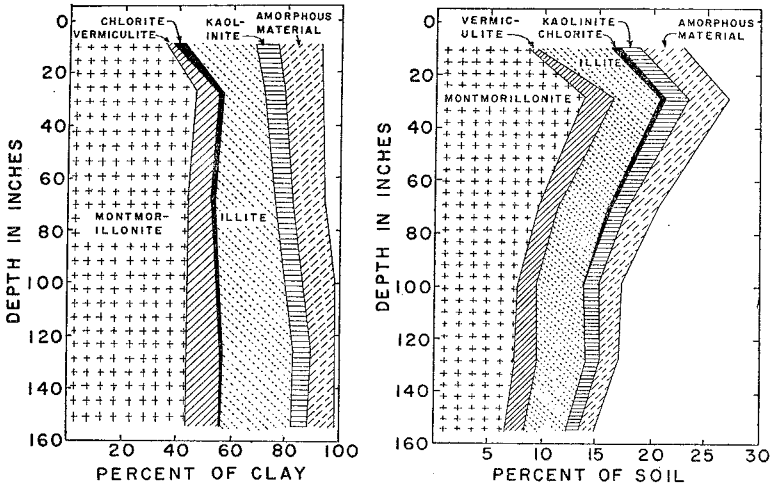

Figure 4.—Mineral species present in Tama silt loam clay fractions (weighted average at each depth of all fractions less than two microns) expressed as percentage of the $-2\,\mu$ clay fraction (left) and as percentage of the mineral portion of each soil horizon (right).

The mica component found in the 2.66 to 2.95 density fractions of the silts appears to be a mixture of muscovite and biotite, but mostly biotite (Fig. 5), as indicated by a low intensity of the 5Å peak relative to a high intensity of the 10Å and 3.3Å peaks. Generally, the 10Å, 5Å, and 3.3Å peaks of muscovite are approximately equal in intensity, while reinforcement of the 3.3Å peak occurs in muscovite–biotite mixtures (Brindley and Robinson, 1951).

A vermiculite component of interstratified vermiculite–mica–chlorite in the heavy minerals of the C horizons was confirmed by collapse of a large part of the 12.6Å as well as 14.7Å material to 10Å on K saturation at room temperature. The occurrence of this vermiculite component even in the calcareous zones suggests that chemical weathering of the biotite (Barshad, 1948) has been actively going on in these calcareous zones. It is proposed that

TABLE 7.—PERCENTAGE OF SILT FRACTIONS OF TAMA SILT LOAM, AND THE RESPECTIVE PERCENTAGES OF HEAVY MINERALS, CARBONATE-FREE MINERAL SOIL BASIS

Horizon and Depth, in.	Percent of Soil or Fraction ( )						
	50–20 μ Fraction			20–5 μ Fraction			Total Silt[2]
	Total	G[1] = 2.95	G = 2.95–2.664	Total	G = 2.95	G = 2.95–2.664	
A_{12}: 6–12	44.5	0.74 (1.65)	1.30 (2.42)	20.5	Trace	0.43 (2.04)	71.2
B_1: 24–31	46.6	1.02 (2.18)	2.53 (5.42)	14.7	—	1.34 (9.27)	65.4
C_3: 66–72	53.1	1.65 (3.10)	2.81 (5.27)	14.3	—	1.98 (14.30)	71.2
C_4: 96–102	57.8	1.93 (3.34)	4.02 (6.96)	14.1	—	2.07 (14.70)	75.8
C_5: 122–131	53.8	1.40 (2.61)	3.15 (5.87)	17.8	—	2.66 (15.00)	75.3
C_6: 150–157	55.5	1.32 (2.39)	3.72 (6.70)	18.5	—	2.81 (15.20)	78.6

[1] G = Specific gravity.

[2] The fine silt (5–2 μ) ranged from 4 to 6 percent of the soil. The sands (>50 μ) ranged from 4 to 7 percent of the soil.

chemical weathering of biotite under the influence of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in the percolating waters, over the period of 10,000 to 25,000 years since deposition of the loess, has produced not only the vermiculite noted in the silt and clay, but also has produced a substantial part of the montmorillonite which occurs in the calcareous loess zones, amounting to 7.5 percent of the total calcareous loess material (carbonate-free basis) as shown above. Since the montmorillonite content is uniform below 100 in., one may conclude that the weathering to montmorillonite is progressing at a uniform rate in the calcareous zones, and that weathering to montmorillonite is accelerated by the leaching of free carbonates from the upper acid part of the column.

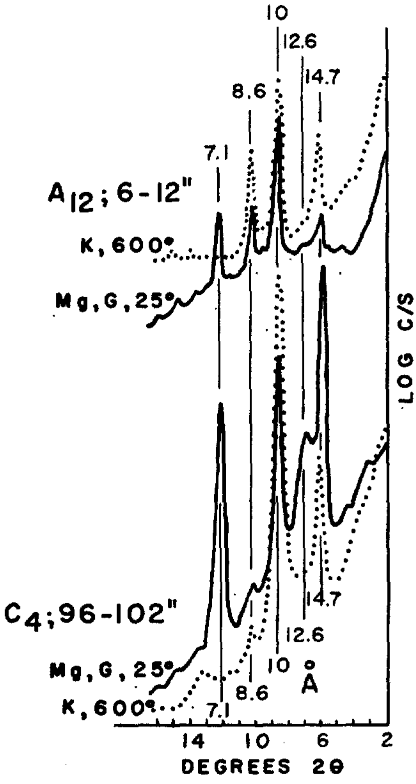

Figure 5.—x-Ray diffraction patterns of medium silt particles (20–5 μ) of Tama silt loam, separated in heavy liquids to obtain the density range of 2.66 to 2.95 g/cm³, and oriented in parallel on glass slides.

Observations made on these high density mineral fractions, employing x-ray and microscopic techniques, show that 50 percent or more of the

>2.95 density fraction of the coarse silt of the C_4 horizon consists of amphiboles. Amphiboles are also present in the 2.66 to 2.95 density fraction of both the coarse and medium silt but in lesser amounts than found in the >2.95 density fraction. Weathering of amphibole (amphibole→montmorillonite) may be responsible for part of the increase in montmorillonite content in the acid section of the loess column. It is recalled that the montmorillonite formulas are similar in all parts of the column.

Minerals of density >2.95 in the coarse silt decrease from 1.93 to 0.74 per cent of the mineral portion of the soil in going from the C_4 to the A_{12} horizons (Table 7). Negligible amounts of minerals of this density occur in the medium silt. Minerals in the density class between 2.66 and 2.95 in the coarse silt decrease from 4 to 1.3 percent of the mineral portion of the soil in going from the C_4 to A_{12} horizons. The great decrease of the high-density mineral fractions is indicative of their ease of weathering. The decrease in amount (7.9 percent decreasing to 2.5 percent, giving a 5.4 percent of the soil net decrease) of heavy minerals in the two size fractions of silt studied in detail parallels the increase in montmorillonite (7.5 percent of the carbonate-free mineral soil increasing to 14 percent, a 6.5 percent net increase) in going from the calcareous loess to the A horizon of the soil (Fig. 4, right).

The relative intensities of the various chlorite peaks (low intensity of the 001 and 003 and high intensity of the 002 and 004 orders) accompanied by loss of the 7.2 Å peak intensity and intensification of the 14.7 Å peak on heating to 600°C resemble the properties of the iron chlorite (Brindley and Robinson, 1951). Some feldspars and quartz, probably of increased density due to inclusions, were also found in the 2.66 to 2.95 density class. Weathering of the dense, ferruginous minerals to montmorillonite both before and after the leaching out of free carbonates is consistent with the large content of structural iron found in the montmorillonite of the fine clay in all horizons of the loess column. Expulsion of part of the Fe from the ferromagnesium minerals on weathering accounts for the abundant goethite seams observed in the lower part of the soil column, even in the calcareous zone.

The distribution of mica, vermiculite, and chlorite in the fine silt ($5-2\,\mu$) is similar to that found in the medium and coarse silt fractions. The fine silt of each horizon also contains considerable amounts of kaolinite and about 7 percent montmorillonite. The ratio of montmorillonite to vermiculite in the fine silt ranges from 7 : 1 in the A horizon to 7 : 6 in the C_6 horizon. Weathering of the less dense minerals of the various silt fractions could of course contribute part of the increase in montmorillonite. Also, part of the 14 percent of montmorillonite in the B horizon is attributable to eluviation from the A horizon.

Weathering of the Montmorillonite

Weathering of montmorillonite in the Tama soils is evident although not extensive. Loss of montmorillonite from the fine clay in the A horizon, concurrent with an increase in amorphous silica and aluminum, indicates that montmorillonite is unstable in the acid horizons of intense weathering in this soil. Also, there is some accumulation of kaolinite in the A and B horizons. This mineral makes up approximately equal percentages of the coarse clay in all horizons and increases slightly in amount toward the soil surface in the medium clay.

Intergradient chlorite–montmorillonite or chlorite–vermiculite, which occurs most abundantly at the soil surface, may represent an intermediate weathering stage of the transition:

montmorillonite → intergradient chlorite–montmorillonite → kaolinite.

Kaolinite formation in this way would require (1) completion of gibbsite interlayering with expulsion of interlayer Fe and Mg (aluminum interlayering presently is known to increase in loess-derived soils progressively from the Wisconsin locality south to the Gulf of Mexico), (2) complete resubstitution of silica in all tetrahedral positions of the dioctahedral montmorillonite (in keeping with the substantial resilication that has occurred in the weathering of micas to montmorillonite in this profile), and (3) inversion of one sheet of silica tetrahedra (a shift already proposed to occur in chlorite and other clay structures in several recent papers by various workers).

SUMMARY

Ferruginous montmorillonite is the dominant clay mineral in Tama silt loam soil of southwestern Wisconsin and in the underlying loess column. Illite (mica) is second most abundant, being more abundant in the coarse clay (40 percent) while giving way to great predominance (70 percent) of montmorillonite in the fine clay. Vermiculite constitutes 18 percent of the coarse clay at 13-ft depth, decreasing to 5 percent in the finer fractions, and not occurring in the finer fractions near the soil surface. Amorphous material and chlorite increase in amount with proximity to the soil surface; increase in secondary (aluminous) montmorillonite–chlorite intergrade also occurs with proximity to the soil surface. The overall increase of montmorillonite from 7.5 to 14 percent of the loess (carbonate-free basis) and mineral portion of the soil is mainly accounted for by the decrease in the heavy minerals (predominantly biotite–vermiculite, with chlorite and amphibole) of the silt fractions. The total silt made up 79 percent of the parent material (carbonate-free basis) and some silt fractions at great depth were as much as 15 percent heavy minerals, decreasing to 1 percent in the upper soil horizons.

ACKNOWLEDGMENTS

This contribution from the Department of Soils, University of Wisconsin, was supported in part by the University Research Committee through a grant of funds from the Wisconsin Alumni Research Foundation. The Soil Survey Division, Wisconsin Geological and Natural History Survey, University of Wisconsin, cooperated in locating and sampling the soil profile.

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