

ORIGIN OF CLAY-SIZE VERMICULITE IN SANDY VOLCANIC ASH SOILS DERIVED FROM MODERN PINATUBO LAHAR DEPOSITS IN CENTRAL LUZON, PHILIPPINES

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ABSTRACT

Vermiculite (Vt) was found in the clay fraction of sandy volcanic ash soils around Mt. Pinatubo, Philippines. Origin of the clay-size Vt was examined selecting two horizons from two pedons with different land use, from a paddy rice and a sugarcane field. In order to concentrate Vt, 2–0.4 μm fraction was taken because halloysite and a small amount of smectite and quartz were also included in these clay fractions. Regarding (060) diffraction spacing, two major peaks were found at 0.153 and 0.149 nm in both samples. With heating at 600°C, intensity of the diffraction peak at 0.149 nm was greatly reduced and that at 0.153 nm remained almost unaffected, indicating that the diffraction peak at 0.149 nm was mostly due to halloysite. Overlap between diffraction peaks at 0.154 nm of quartz and that at 0.153 nm was only partial in these samples. Thus, it was concluded that the diffraction peak at 0.153 nm was assigned to trioctahedral Vt.

Weathered particles of biotite were found with the naked eye and under an optical microscope in the sand fractions of these soils. In the silt fractions, Vt and biotite were suggested by X-ray diffraction (XRD) analysis. XRD peak intensity indicated that vermiculitization of biotite in the sand fractions was more advanced in the paddy field than in the sugarcane field. However, Vt was dominant in the silt and clay fractions of both soils. From these results, it was strongly suggested that clay-size Vt was inherited from biotite in these soils.

Key words: Volcanic ash soils, Weathering, Biotite, Vermiculite

INTRODUCTION

Most of the volcanic ash soils or Andisols in Japan have a large amount of highly-reactive colloidal materials such as allophane, imogolite, Al-humus complex, ferrihydrite, and so on. These Andisols can be divided into two groups based on colloidal composition. One is allophanic Andisols and the other is nonallophanic Andisols. The colloidal fraction of allophanic Andisols is mainly allophane and imogolite and that of nonallophanic Andisols is Al-humus and 2:1–2:1:1 intergrade minerals (Dahlgren et al., 1993). These Andisols have little vermiculite (Vt) with no hydroxy Al interlayering as a major component of their clay fractions.

In contrast, volcanic ash soils which are distributed near Mt. Pinatubo, Philippines,

have only a very small amount of reactive colloidal materials, although the gravel-size pumice is partially weathered and fragile. The clay fractions of these volcanic ash soils are dominated by halloysite, Vt, smectite and so on. The objective of this study was to examine the origin of the clay-size Vt in these Mt. Pinatubo volcanic ash soils. It is generally assumed that Vt can be formed only by alteration of a micaceous mineral except for a few examples (Douglas, 1989; Nishiyama, 1985). Vt in volcanic ash soils have been described so far by Aomine and Kawasaki (1963), Egawa and Oshikamo (1963), Cortes and Franzmeir (1972), Calhoun *et al.* (1972), Yamada *et al.* (1978) and in the cited literatures. However, differentiation between trioctahedral and dioctahedral structure was not made in many cases. Sand-size Vt reported by Cortes and Franzmeir (1972) was trioctahedral, and hydroxy Al interlayering in the Vt was suggested by X-ray diffraction (XRD) analysis. Weathered sand-size biotite was also observed in the present soil samples. In this study, differentiation of trioctahedral and dioctahedral structures of the clay-size Vt was attempted and changes in the XRD peak intensity at 1.0 and 1.4 nm with decreasing particle-size were examined in relation to Vt in the clay fraction.

MATERIALS AND METHODS

According to Newhall *et al.* (1996), the modern Mt. Pinatubo eruptions during the Holocene and late Pleistocene were clustered in at least 6 periods, >35 ka, 17 ka, 6–5 ka, 3.9–2.4 ka and 0.5 ka of radiocarbon ages. These modern tephra from the Mt. Pinatubo area are widely distributed in Pampanga, Tarlac and Zambales provinces as pyroclastic flow deposits, ash deposits or lahar deposits (Yoshida and Takahashi, 1992; Newhall *et al.*, 1996). Examination of soils from 13 sites (Fig. 1) revealed that the major parent material of these soils was andesitic to dacitic tephra and a small amount of weathered biotite particles was contained in all the soils. Clay fractions of these soils were in many cases dominated by halloysite. Pedons I and VIII of which the clay fraction showed a stronger peak intensity of Vt than others were selected for the present study. Pedon I was located at the concaved place and was used as a paddy rice field (15° 08'50" N., 120° 36'29" E., 70 m a.s.l.). Pedon VIII was located at the convexed place and the land use was a sugarcane field (15° 25'12" N., 120° 33'59" E., 65 m a.s.l.). Both pedons I and VIII were classified as Vitrandic Haplustept according to Keys to Soil Taxonomy (Soil Survey Staff, 1998).

Particle-size distribution was determined with wet sieving and a pipet method after digesting 10 g of air-dried soils with H₂O₂. After dithionite-citrate-bicarbonate (DCB) treatment of the clay fractions, XRD patterns of the Mg-saturated specimen (air-dry and glycerol-solvated) and of the K-saturated specimen (air-dry and heated at 300 and 550°C) were obtained using Rigaku X-ray diffractometer (Cu K α , 30 mA, 45 kV) to examine mineralogical composition. Organic carbon content (dichromate oxidation method, Marumoto *et al.*, 1978), pH(H₂O), pH(KCl) at soil: solution ratio of 1:2.5, phosphate retention percentage, cation exchange capacity (NH₄ acetate method) and oxalate-extractable Al (Al₀) and Fe (Fe₀) content (Blakemore *et al.*, 1981) of the air-dried soils were determined to elucidate some chemical characteristics of the soils.

Differentiation between trioctahedral and dioctahedral Vt was made based on the (060)

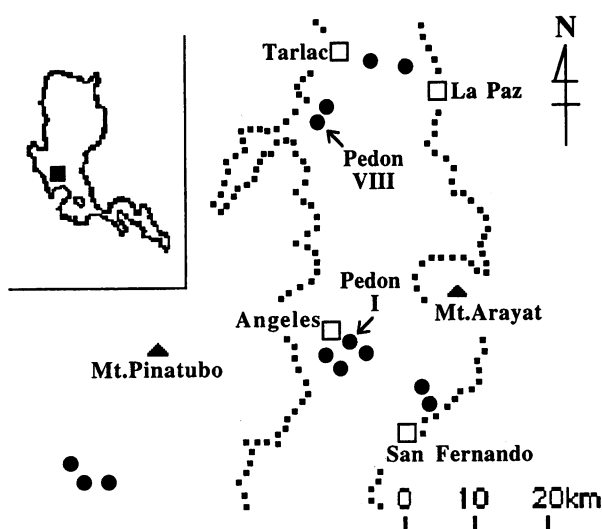


FIG. 1. Locations of the sampling sites (●). Sandy soils are distributed between dotted lines (10 sites) in the Central Plain of Luzon. Three sites were to the southeast of the Mt. Pinatubo area in the Zambales mountain range.

diffraction spacing selecting Bw horizon soil of pedon I (I-Bw) and 2A horizon soil of pedon VIII (VIII-2A). In order to concentrate Vt, 2–0.4 μm fraction was taken with centrifugation. After air-drying and grinding into powder in an agate mortar, an XRD pattern between 59 and 64 degrees (2θ) was obtained packing into a glass holder (random powder mount) at a scan speed of 0.5 degrees per min ($\text{CuK } \alpha$, 30 mA, 45 kV).

Biotite tends to be converted to Vt with 1 mol L^{-1} of NaCl or DCB treatments (Douglas, 1967; Nanzyo et al., 1999). In order to minimize this artificial vermiculitization, 20–30 g of soil samples were shaken with 400 mL of distilled water for 2 hr and then particle-size fractions of 2–0.2, 0.2–0.05, 0.05–0.02, 0.02–0.002 mm and less than 0.002 mm fractions were separated with wet sieving and siphoning. Weathered biotite particles were collected from 2–0.2, 0.2–0.05 mm fractions by hand picking under an optical microscope and oriented on a slide glass with wetting and air-drying (oriented mount) to obtain XRD patterns. XRD patterns were also obtained from 0.05–0.02 mm fractions after grinding in an agate mortar, and from 0.02–0.002 mm and less than 0.002 mm fractions (oriented mount).

RESULTS AND DISCUSSION

Properties of soils

Selected chemical properties and particle-size distribution of the soils are summarized in

TABLE 1. Selected chemical properties and particle-size distribution of the soils

Depth cm	Horizon	pH(H ₂ O)	pH(KCl)	P ret. ^a %	O.C. ^b ----- g	Al ₀ ^c kg ⁻¹	Fe ₀ ^c -----	Gravel %	Sand ^d	Silt ^e ----- % ^g	Clay ^f -----
<i>Pedon I</i>											
0-12	Ap1	4.6	3.9	8.4	6.5	0.4	3	28	85	10	5
12-27	Ap2	5.6	4.5	7.5	4.6	0.4	1.7	6	80	11	9
27-49	AB	6.6	5.4	9.4	3.8	0.8	2.9	0	74	19	6
49-80	Bw	6.8	5.4	14.2	2.6	0.8	4.2	9	80	13	7
80-120	BC	6.8	5.3	11.2	1.8	0.6	2.3	10	82	9	8
<i>Pedon VIII</i>											
0-40	Ap	5.5	4.2	7.8	5.4	0.5	1.1	2	88	7	4
40-71	C	6.5	4.8	3.7	1.3	0.6	0.9	0	93	5	2
71-115	2A	6.5	4.9	13.5	4.1	0.9	2.8	0	65	21	14
115-137	2BC	6.6	4.8	16.9	3.7	0.8	3.3	6	72	13	15
137-160	2Cg1	6.6	4.9	18.9	2.7	1.4	3.5	4	73	12	15
160-210	2Cg2	6.7	5.0	11.5	0.9	0.5	2.4	52	91	5	4

^a phosphate retention percentage, ^b organic carbon content, ^c oxalate extraction, ^d 2-0.02 mm, ^e 0.02-0.002 mm, ^f 0.002 mm >, ^g percentage of H₂O₂-digested fine earth fraction.

Table 1. Sand content of the soils from these two pedons were 72-93%, although the gravel content was low. Clay content of these soils was 2-15%. Ap horizons showed acidic pH(H₂O) of 4.6-5.6 and pH(H₂O) values of the lower horizons were almost neutral (6.5-6.8). Organic carbon content of all the soils was 6.5 g kg⁻¹ or less. VIII-2A was a buried soil and the organic C content and clay content of VIII-2A was higher than the overlying C horizon. As the phosphate retention percentage were less than 19% and Al₀ + Fe₀/2 was 3 g kg⁻¹ or less in all the horizons, there was no horizon to meet Andic soil properties (Soil Survey Staff, 1998) in these two pedons.

Clay mineralogical composition

Most of the Mg-saturated clay fractions of pedons I and VIII showed a strong XRD peak at 1.4 nm (Fig. 2). As a major part of the 1.4 nm peak of the Mg-saturated specimen shifted to 1.0 nm after K-saturation at room temperature and did not shift to a lower angle with glycerol solvation, these clay fractions contained Vt (Fig. 3). A broad XRD peak at 0.7 nm with tailing to a lower angle indicated that halloysite was also a major clay mineral in these soils. These specimens also contained a small amount of mixed layer mineral such as hydrobiotite because small XRD peaks were observed at 2.4, 1.2 and 1.0 nm (Fig. 3b, g). VIII-2A contained smectite also because a part of 1.4 nm of Mg-saturated specimen shifted to 1.8 nm with glycerol solvation (Fig. 3f). Weathered volcanic glass was also observed in the clay fractions of I-Bw and VIII-2A by transmission electron microscope.

Hydroxy Al interlayers are common in Vt in Japanese soils (Aomine and Kawasaki, 1963; Egawa and Oshikamo, 1963; Yamada, *et al.*, 1978). However, hydroxy Al interlayers were not suggested in the clay-size Vt of I-Bw and VIII-2A by XRD analysis (Fig. 3). The reasons for the absence of hydroxy Al interlayers in the Vt of Central Luzon may be near

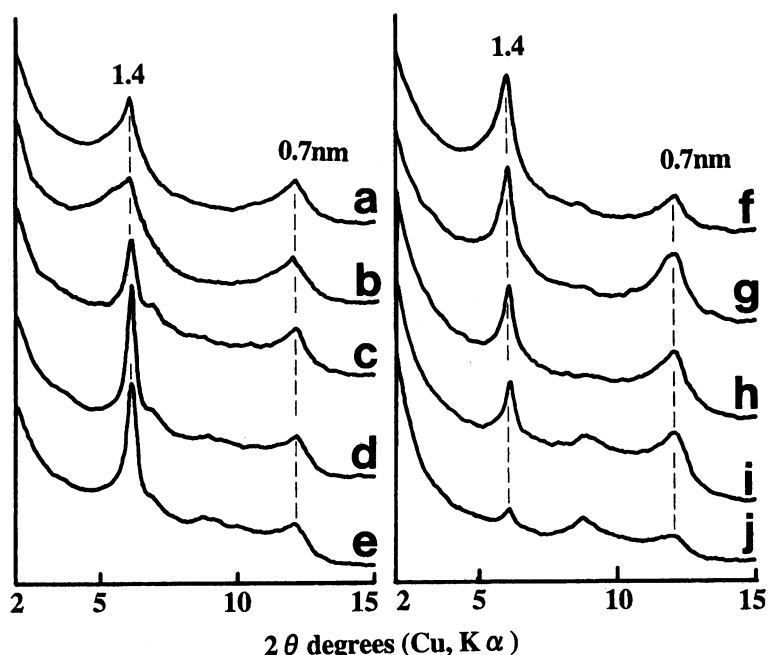


FIG. 2. X-ray diffraction patterns of the Mg-saturated clay fractions in the soil horizons of pedons I (a: Ap1; b: Ap2; c: AB; d: Bw; e: BC) and VIII (f: Ap; g: 2A; h: 2BC; i: 2Cg1; j: 2Cg2).

neutral pH(H₂O) and virtual lack of noncrystalline clays. Very low content of noncrystalline clays can be due to an ustic soil moisture regime of the study site (Hamasaki and Paningbatan, 1992). In an udic (near ustic) soil moisture regime in New Zealand, halloysite-dominant soil in its clay fraction was formed from Si-rich tephra probably due to high Si concentration in the soil solution (Parfitt, 1990).

Differentiation between trioctahedral and dioctahedral structure of V_t

The new volcanic ash erupted from Mt. Pinatubo in 1991 contained a small amount of biotite (Nanzyo et al., 1999) and its (060) diffraction peak appeared at 0.153 nm which indicated a trioctahedral structure (Fig. 4g). If the clay-size Vt in I-Bw and VIII-2A had a trioctahedral structure, it is highly probable that the Vt was inherited from biotite in these soils as mentioned above (Douglas, 1989).

These 2–0.4 μ m fractions showed XRD peaks at 0.153 and 0.149 nm (Fig. 4, a and c). Furthermore, these specimens contained halloysite and a small amount of quartz which may affect differentiation between trioctahedral and dioctahedral Vt. However, after heating at 600°C, the intensity of the XRD peak at 0.149 nm was greatly reduced and that at 0.153 nm remained almost unaffected (Fig. 4, b and d). Thus, the clay-size Vt in I-Bw

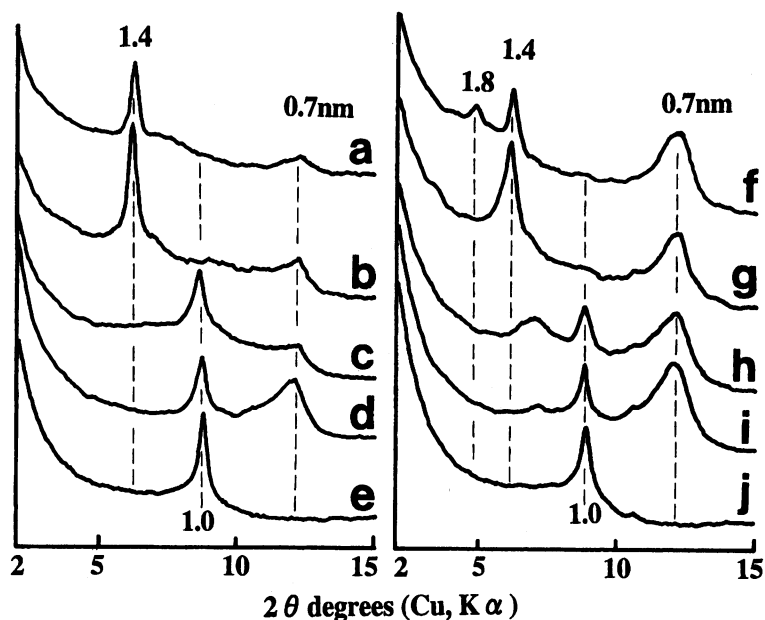


FIG. 3. X-ray diffraction patterns of clay fractions in the Bw horizon soil of pedon I (a–e) and the 2A horizon soil of pedon VIII (f–j) after Mg saturation and glycerol solvation (a and f), Mg-saturation (b and g), K-saturation (c and h), K-saturation and heating at 300°C (d and i) and K-saturation and heating at 550°C (e and j).

and VIII-2A was close to trioctahedral from the position of (060) diffraction spacing and it is most probable that they were inherited from biotite. However, chemical composition of the clay-size Vt was not determined because separation of the Vt from halloysite was incomplete in this study. A small peak at 0.149 nm remained in the XRD pattern of VIII-2A (Fig. 4d) after heating at 600°C was assigned to a small amount of smectite in this specimen (Fig. 3b).

In the XRD pattern of the 2–0.4 μm fraction of VIII-2A, a small diffraction peak was observed at 0.154 nm (Fig. 4, c and d). This diffraction peak was due to quartz because the intensity of this peak was almost doubled (Fig. 4e) when it was mixed with 3 wt% of powdered quartz (Fig. 4f) separated from the sand fraction of VIII-2A. Although the diffraction peak of quartz at 0.154 nm was partly overlapping with that for the (060) diffraction peak of Vt, the latter (broad peak) was differentiated from the former (sharp peak) due to the difference in the peak width as well as their peak position (Fig. 4, c and d). The 0.154 nm XRD peak of quartz was very small in the 2–0.4 μm fraction of I-Bw (Fig. 4, a and b).

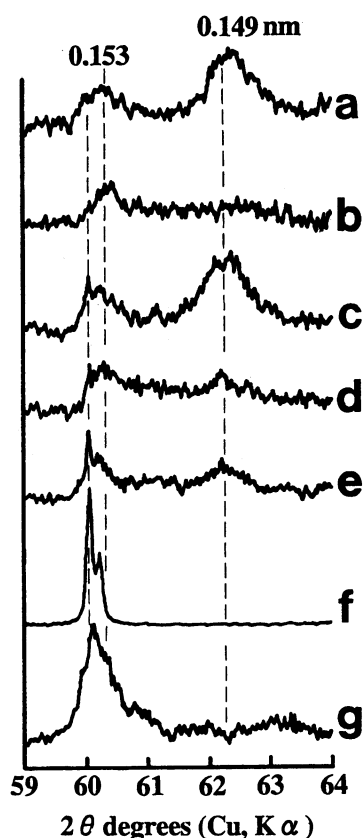


FIG. 4. X-ray diffraction patterns to examine the position of 060 reflection of coarse clay fractions ($2\text{--}0.4\ \mu\text{m}$). a and c: air-dried random samples; b and d: heated random samples at 600°C ; a and b: Bw horizon soil of pedon I; c and d: 2A horizon soil of pedon VIII; e: mixed sample of d and 3 wt% of powdered quartz (f); g: powdered biotite separated from the Mt. Pinatubo volcanic ash which erupted in 1991.

Weathering of biotite in different particle-size fractions

XRD patterns of the weathered biotite particles in the sand and silt fractions are shown in Fig. 5. Differences in the weathering of the biotite particles were indicated in the 3 sand fractions of I-Bw and VIII-2A. The peak intensity at 1.4 nm of the $2\text{--}0.2\ \text{mm}$ fraction of I-Bw was much stronger than that at 1.0 nm and most of the biotite was already converted to Vt. The peak intensity at 1.4 nm from $0.2\text{--}0.05$, $0.05\text{--}0.02$, $0.02\text{--}0.002\ \text{mm}$ was also much stronger than that for 1.0 nm (Fig. 5, b, c and d). In contrast, the peak intensity at 1.4 nm of the weathered biotite particles in the $2\text{--}0.2\ \text{mm}$ and $0.2\text{--}0.05\ \text{mm}$ fraction of

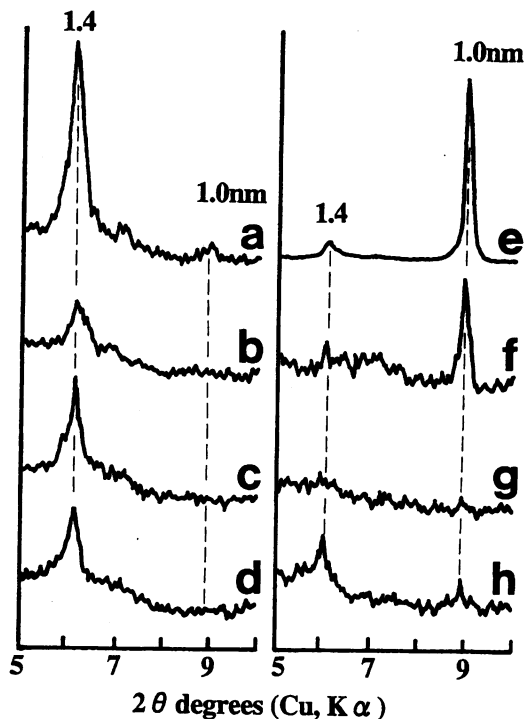


FIG. 5. X-ray diffraction patterns of the weathered biotite contained in different particle-size fractions in the Bw horizon soil of pedon I (a–d) and in the 2A horizon soil of pedon VIII (e–h). a and e: 2–0.2 mm fraction; b and f: 0.2–0.05 mm fraction; c and g: 0.05–0.02 mm fraction; d and h: 0.02–0.002 mm fraction.

VIII-2A was much weaker than that for 1.0 nm (Fig. 5e). Although the peak intensity at both 1.4 and 1.0 nm was weak in the 0.05–0.02 mm fraction of VIII-2A (Fig. 5g) possibly due to dominance of volcanic glass or other minerals, the 1.4 nm peak was stronger than the 1.0 nm peak in the 0.02–0.002 mm fraction (Fig. 5h). The clay fractions prepared with water only from I-Bw and VIII-2A showed XRD patterns similar to that with Fig. 3b and g, respectively. Thus, biotite content decreased with decreasing particle-size in both I-Bw and VIII-2A. These observations coincide with the assumption that trioctahedral Vt was inherited from trioctahedral mica (Douglas, 1989) also in the Mt. Pinatubo volcanic ash soils.

The difference in the degree of biotite weathering observed between I-Bw and VIII-2A in the 2–0.2 mm and 0.2–0.05 mm fractions may be due to the difference in land use of these sampling sites. About half of the iron in the biotite particles of Mt. Pinatubo volcanic ash in 1991 was ferric iron. This Pinatubo biotite was more readily converted to Vt with dithionite treatment than ordinary biotite samples with low ferric to ferrous iron

ratio (Nanzyo et al., 1999). Although the I-Bw was one of the lower horizons of the paddy rice field after harvest, it was close to the water table depth of 80 cm at the time of sampling. I-Bw could be under reducing conditions during rice growing or the rainy season. On the other hand, land use of pedon VIII was a sugarcane field and it was located at the convexed place and no water table was observed to the depth of 210 cm. Although iron mottling was observed in the 2C horizons of pedon VIII (Table 1), 2A horizon showed no evidence of reducing conditions.

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