

Unique Properties of Volcanic Ash Soils

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Abstract

Various kinds of soils can be formed from volcanic ash depending on the individual set of soil forming factors at different sites. Among these soils, Andisols or Andosols show unique properties mostly due to abundant noncrystalline materials such as allophane, imogolite, Al-humus complexes, ferrihydrite and so on. Highly porous structures made of aggregated noncrystalline Andisol materials have a light and fluffy nature, accommodating large amounts of both plant-available and hygroscopic water. They show many other unique physical properties different from other soils. Moreover, Andisols have unique chemical properties, including aluminum-rich elemental composition, large amount of humus accumulation in A horizons, variable charge characteristics, high phosphate retention capacity, high affinity for multi-valent cations, high KCl-extractable and water-soluble Al in nonallophanic Andisols at an acidic to weakly acidic pH range, and so on. Finally, topics related to biological activity in volcanic ash soils are discussed regarding P supply from apatite and K supply from biotite for crops in fresh volcanic ash, effects of KCl-extractable and water-soluble Al on soil-borne diseases, adsorption characteristics of viruses on Andisols and P tropistic root growth of Brassica plants in P-deficient Andisols.

Key words: Andisol, Andosol, elemental composition, noncrystalline material

1. Introduction

Volcanic eruptions are mostly violent and hazardous. The land around volcanoes is intermittently attacked by pyroclastic flows, volcanic ash deposition, lahar deposition and so on. These volcanic ejecta or tephra contain various silicates and other minerals of different sizes such as volcanic glass, feldspars, quartz, hornblend, hypersthene, augite, magnetites, biotites and apatites. After tephra deposition, soil formation starts, the tephra's elemental and mineralogical composition changes and volcanic ash soils or Andisols having unique properties are formed. Many plant nutrient elements are provided to the soil environments during soil formation.

The word "Andisols" is used regarding soils that have unique and distinctive properties from other soils as mentioned by Takahashi and Shoji (this issue). The expression "volcanic ash soils" means any soil that is derived from tephra. Thus, volcanic ash soils in this sense show a wider range of properties than Andisols. Slightly or little weathered tephra are sandy or gravelly Entisols. Very old and highly weathered volcanic ash soils may no longer be Andisols but Ultisols or Oxisols (Ugolini and Dahlgren, this issue). Although a soil name is given for an individual pedon or a soil profile, the word "Andisol" is also

used here for soil samples taken from horizons that have Andic soil properties.

Some unique physical properties of Andisols are directly visible to the eye and sensible to the touch. Surface soils are rich in humus and dark in color, soil clods are light, fluffy and easy to break into small pieces. Drainage or water permeability is so high that farmers can do field work on the next day after rain. Water from volcanic areas is mostly transparent due to poorly dispersible clays in the soils at a neutral pH range. These physical properties are suitable for growing various upland crops (Shoji and Takahashi, this issue).

Volcanic ash soils or Andisols have also distinctive chemical and mineralogical properties although they are not visible directly. Chemical and mineralogical characteristics of Andisols are reflected in their physical properties and biological activities and affect the utilization of these soils. The unique chemical properties of Andisols are basically due to their aluminum-rich elemental composition, the highly reactive nature of their colloidal fractions and their high surface area. The aluminum-rich elemental composition of these soils is obtained after leaching of Si, Na, Ca and so on during Andisol formation.

The natural vegetation of Andisols is similarly abundant as in other soils under humid climatic

conditions. However, when agricultural crops are planted in newly reclaimed Andisols, they show inferior growth to that in young alluvial soils. The reasons for this are often their low content of plant-available nutrient elements, especially P, and some micronutrients, sometimes their high toxic Al content, the highly sorptive properties of the nutrient ions and stabilization of soil organic N. Ameriolation of these shortcomings is more or less conducted in agricultural Andisols in many volcanic countries.

In this paper, the unique mineralogical, physical, chemical and biological properties of volcanic ash soils, mainly Andisols, are introduced and discussed. Review articles or chapters on Andisols in textbooks have been written by Buol *et al.*, (1997), Kimble *et al.*, (2000), and Ping (2000) and by Harsh *et al.* (2002) on allophane and imogolite after a monograph of Andisols was published by Shoji *et al.* (1993).

2. Mineralogical Properties

Morphological properties of matured Andisol profiles are quite different from those of new airborne ash deposits, lahar deposits, pyroclastic flow deposits and so on. There is no horizon development as in Andisols in the new tephra deposits. However, one can easily understand that the new tephra deposits will be converted to Andisols over time by seeing the buried multi-sequence profile (see Fig. 5a of Takahashi and Shoji, this issue) underlying the new tephra deposit. It is easy to see that new tephras are different from Andisols in many aspects. Among them, mineralogical properties are the basis for understanding the differences in physical, chemical and biological properties between new tephras and matured Andisols.

2.1 Primary minerals and their roles in the soil environment

The major primary minerals in fresh tephras are volcanic glass, plagioclase, quartz, pyroxenes, opaque minerals, hornblende, biotite, olivine and so on. The relative abundance of these minerals in fresh tephras is schematically summarized in Fig. 1 as a function of rock type (Shoji, 1983; Shoji *et al.*, 1993). Mineralogical composition of tephras is also dependent on particle size: the content of crystalline minerals such as feldspar and heavy minerals tends to be more or less high in the fraction coarser than 0.1 mm in diameter and that of volcanic glass tends to be abundant in the particle size fraction finer than 0.1 mm in diameter (Yamada and Shoji, 1975).

The most abundant mineral in volcanic ash is volcanic glass. The type of volcanic glass is largely divided into noncolored and colored volcanic glass. Rhyolitic, dacitic and andesitic tephras contain non-colored volcanic glass while basaltic tephra contains colored volcanic glass. Colored volcanic glass has a lower SiO₂ content and a higher refractive index. The morphology of volcanic glass also varies depending on chemical composition, gas content of magma and type of volcanic eruption (Yamada and Shoji, 1983).

Not only major minerals but also minor minerals are important in volcanic ash because minor minerals contain some essential elements for plants. For example, apatite contains phosphorus and tourmaline, boron. Although K can be supplied from various minerals, biotite releases K very easily.

2.2 Secondary minerals and their role in soil environment

2.2.1 Allophane

A hollow spherical structure was proposed for allophane. Allophane has a diameter of 3 to 5 nm under a transmission electron microscope and its atomic Si/Al ratio ranges between 0.5 and 1 (Fig.

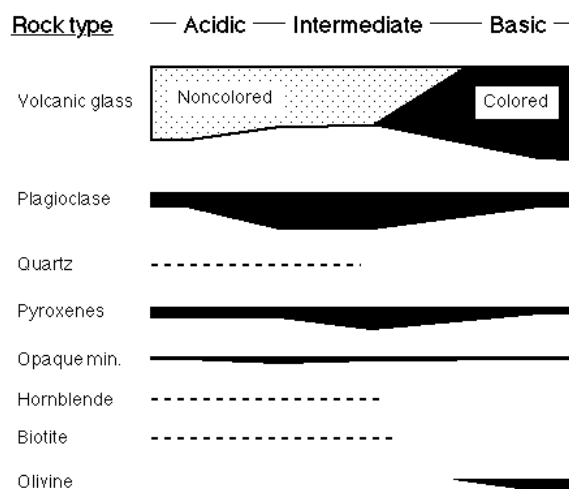


Fig. 1 Relationship between tephritic material rock types and their mineralogy (adapted from Shoji *et al.*, 1993. Copyright Elsevier, with permission).

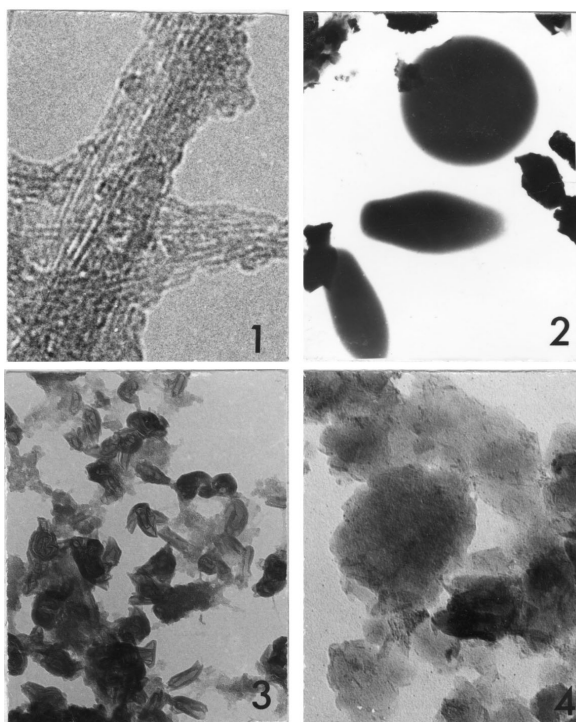


Fig. 2 Transmission electron micrographs of secondary minerals. (1) Allophane and imogolite, (2) opaline silica, (3) halloysite and (4) chloritized 2:1 minerals (courtesy of S. Shoji).

2-(1)). According to selective dissolution analysis using acid oxalate and pyrophosphate solutions, allophane with atomic Si/Al ratio of 0.5 is more common than that with about 1 (Shoji *et al.*, 1993). As in the imogolite structure, a monolayer of gibbsite sheet is thought to be located outside and silicate, inside of the hollow spherical structure. There are several deficit holes in the spherical structure. Water molecules and cations such as NH_4^+ or Ca^{2+} appear to pass through the deficit holes. Allophane shows variable charge characteristics and high selectivity for divalent cations, and is highly reactive with phosphate (Wada, 1989).

2.2.2 Imogolite

Imogolite was named after a Japanese local soil called “Imogo” in Hitoyoshi, Kumamoto Prefecture, where this mineral was first found. It has an atomic Si/Al ratio of 0.5 and a tubular structure with an inner diameter of 1 nm and outer diameter of 2 nm (Fig. 2-(1)). Imogolite tubes are more visible under a transmission electron microscope than unit particles of allophane. Imogolite has a nesosilicate structure. Imogolite occurs in volcanic ash soils mostly as a mixture with allophane. Imogolite is less reactive with phosphate than allophane (Henmi *et al.*, 1982).

2.2.3 Pedogenic opaline silica

Pedogenic opaline silica has a thin ellipsoidal shape with a diameter of up to several μm (Shoji and Masui, 1971). Pedogenic opaline silica can be morphologically distinguished from biogenic opaline silica such as plant opal or diatoms (Fig. 2-(2)). While biogenic forms have their own shapes inherited

from biological cells, pedogenic opals show a rather simple morphology. They are found in the A horizons of Andisols relatively younger than several thousands of years (Shoji *et al.*, 1993). The formation process of opaline silica is thought to be concentration and precipitation of silica released from volcanic glass by evaporation or freezing of soil water. Complexation of Al by humus appears to prevent Si from reacting with Al. Chemical functions of opaline silica are not outstanding.

2.2.4 Kaolin minerals

Halloysite (Fig. 2-(3)) is frequently found in volcanic ash soils in various amounts. Basal spacing of halloysite is 1 nm or 0.7 nm depending on the soil environment. Halloysite (1 nm) has a monolayer of water at the interlayer position of the 1:1 aluminosilicate layer. Dehydration of the interlayer water irreversibly reduces the basal spacing to 0.7 nm. It shows various morphologies such as curled plate, lath-like plate, tubular, and spheroidal. Halloysite is formed under semi-dry climatic conditions where silicate concentration in the soil solution is high. Volcanic ash soils having all of allophane, imogolite and halloysite are rather common in humid areas although their composition varies widely. Halloysite also occurs in the lower Andisol horizons where percolation of soil water is slow and water content is high. Under such conditions, SiO_2 content in the soil water appears to be greater and suitable for halloysite formation. Halloysite-rich soils often show high CEC and selectivity for K^+ and NH_4^+ (Takahashi *et al.*, 2001).

2.2.5 2:1 minerals and chloritized 2:1 minerals

Chloritized 2:1 minerals (Fig. 2-(4)) are a group of 2:1 minerals that have polymerized hydroxy Al ions and exchangeable Al ions in their interlayers. These minerals are stable under acidic soil conditions at around pH 5. Although these minerals are the major clay minerals in the A horizons of nonallophanic Andisols, properties of humus complexed with Al often appear strongly compared with those of chloritized 2:1 minerals, because, the Al-humus complex content is abundant and polymerized hydroxy Al interlayering reduces CEC occupying negatively charged sites, reduces swelling and increases water permeability. Strong treatment using hot citric acid is employed to remove hydroxy Al polymers from natural chloritized 2:1 minerals. However, an artificially prepared hydroxy Al-montmorillonite complex reacts with phosphate to release hydroxy Al polymers from their interlayers (Saha *et al.*, 1998), suggesting diversity of the polymerized hydroxy Al interlayerings.

2.2.6 Ferrihydrite

Poorly crystalline to virtually noncrystalline ferrihydrite is a major secondary iron mineral in Andisols. Ferrihydrite has a brownish color in Bw horizons of Andisols. Sorption of silicate, phosphate or organic material by ferrihydrite retards crystallization to goethite or hematite (Bigham *et al.*, 2002). The content of ferrihydrite can be estimated by multiplying 1.7 times the oxalate-extractable Fe (Fe_o). Poorly crystalline ferrihydrite has a large surface area and high phosphate retention capacity.

3. Physical Properties

Matured Andisols typically have a low bulk density of 0.9 or lower and are lowest among mineral soils. The low bulk density of Andisols can easily be recognized if one picks up an air-dried soil clod by

hand. Only organic soils or organic horizons have lower bulk densities than Andisols. The low bulk density is due to high porosity caused by well-developed aggregate structures made of noncrystalline minerals. Figure 3 shows that bulk density values decrease with an increase in the allophane content of Andisols with low humus content. The particle density of allophane is almost the same as that of other layersilicate clay minerals (Wada, 1989). Thus, allophane itself is not the reason for the low bulk density of Andisols. Accumulation of a large amount of humus, making highly porous aggregates, is also an important reason for low bulk density in nonallophanic Andisols. Figure 4 clearly shows that bulk density decreases with increasing humus content. Similarly, allophanic Andisols with low allophane content have a low bulk density if they contain a substantial amount of humus as shown in Fig. 3. Although the particle density values of humus are usually lower than 1.5 (Blake and Hartge, 1986) and the humus content of matured Andisols are mostly less than 30%, their typical bulk density is still 0.9 or lower. Using Ti content as an immobile element during Andisol formation, the soil volume increase due to humus accumulation was strongly suggested as an important factor in the low bulk density (Nieuwenhuysse and Van Breemen, 1997).

Pore size distribution in Andisols shows a wide range. With advancement in formation of noncrystalline materials, the percentage of macropores decreases and that of micropores increases. However, matured Andisols still have a macropore percentage of around 10% due to their aggregated structure. Thus, they have macropores and micropores which contribute to air permeability and retention of plant-available water, respectively. Further, high porosity contributes to quick gravitational drainage of water in the soils.

The high stability of aggregates means low dispersibility of colloids in Andisols. Not only is humus

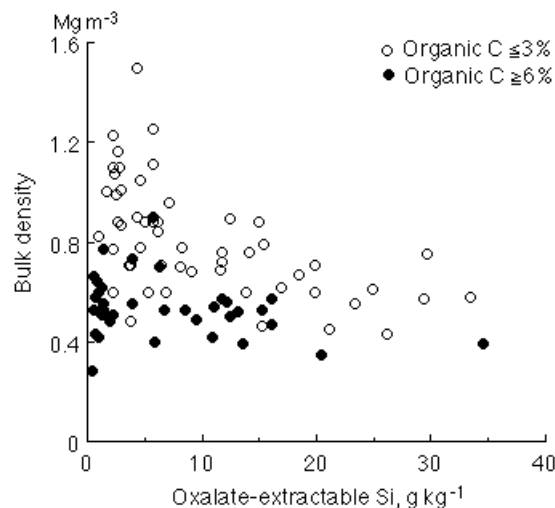


Fig. 3 Relationship between the oxalate-extractable Si and bulk density of allophanic Andisols (adapted from Shoji *et al.*, 1993. Copyright Elsevier, with permission).

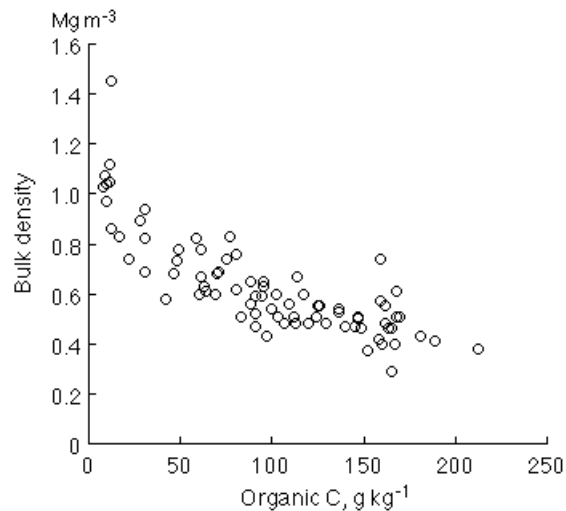


Fig. 4 Relationship between organic C content and bulk densities of nonallophanic Andisols (adapted from Shoji *et al.*, 1993. Copyright Elsevier, with permission).

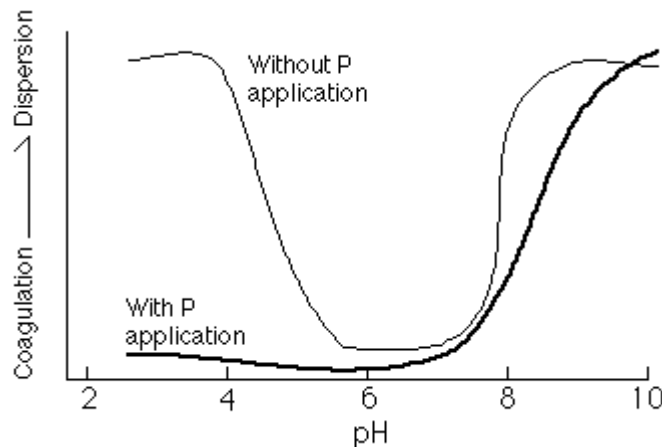


Fig. 5 Effect of pH and phosphate fertilizer application on the dispersion of allophanic clays (prepared from Nanzyo *et al.*, 1992).

digestion using hot H_2O_2 needed to disperse noncrystalline clays, but also ultrasonic treatment, pH adjustment and repeated washing with deionized water. The effect of pH on dispersion of allophanic Andisols reflects their variable charge characteristics. Allophanic clays have a point of zero charge at about neutral pH and they hardly disperse around this pH. On the other hand, allophanic clay disperses under acidic and alkaline pH conditions developing positive and negative charges, respectively (Fig. 5). Hydraulic conductivity of an allophanic Andisol with little humus decreases with addition of dilute HNO_3 due to dispersion of the allophanic clay at very low pH of 3 to 4, but not with dilute H_2SO_4 (Ishiguro and Nakajima, 2000), possibly due to the coagulative effect of the divalent anion on the positively charged colloids. The size of the domain consisting of allophanic particles in the aqueous dispersion system is hundreds of nm, dependent on pH, and is much larger than a unit particle of allophane (Karube *et al.*, 1996).

If field moist soil samples are used, their clay

content obtained by this procedure almost coincides with that calculated using the oxalate-extractable Al (Al_0) and Fe (Fe_0) content. When allophanic Andisols are air-dried, their colloidal fraction irreversibly aggregates and the sand-sized fraction increases and clay-sized fraction decreases. Surface soils may experience drying under natural conditions. Therefore, the dispersion method is often ineffective for determining the clay content of surface soils that experienced natural drying. Instead, the inorganic noncrystalline materials content can be calculated using Al_0 and Fe_0 contents. Other irreversible changes with air-drying are decreased liquid limit and plastic limit, water retention, and so on (Shoji *et al.*, 1993).

Dispersibility of allophanic clay is also affected by heavy application of phosphorus fertilizer as shown in Fig. 5 (Nanzyo *et al.*, 1992). This suggests that positive charge development is perturbed by phosphorus fertilizers due to sorption of phosphate at positive charge sites. Dispersion under alkaline pH conditions is little affected by phosphorus fertilization.

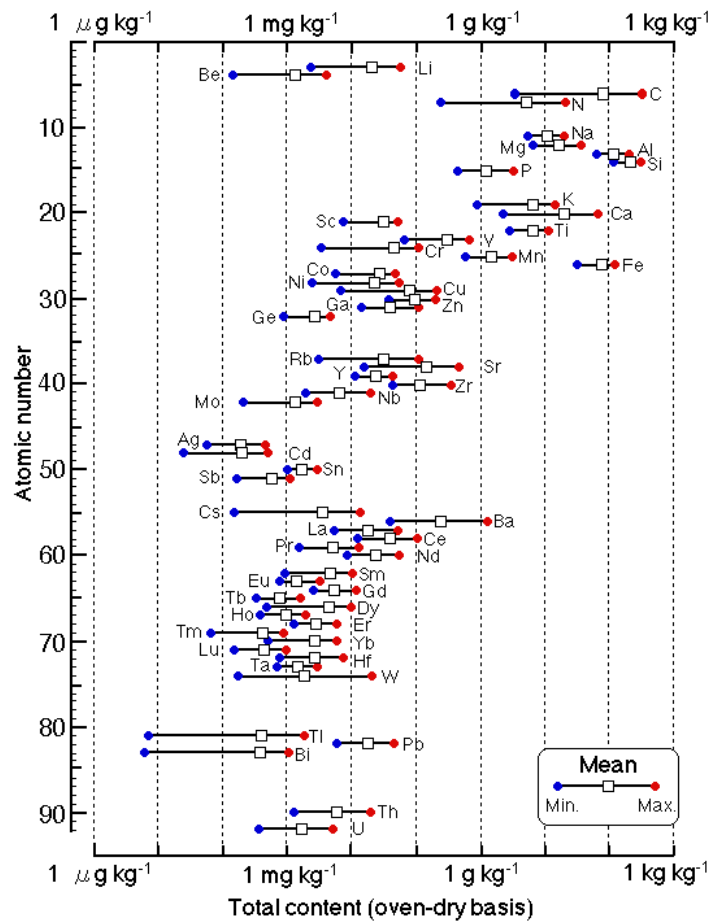


Fig. 6 Total content of elements in Andisols (adapted from Nanzyo *et al.*, 2003).

4. Chemical Properties

In accordance with changes in mineralogical properties during the formation of Andisols from fresh tephtras, changes in elemental composition of the soils also take place. The mineralogical changes are reflected in changes in soil chemical properties. The unique chemical properties of Andisols are mainly caused by their noncrystalline secondary minerals and Al-humus complex.

4.1 Elemental composition

The ranges and means of 57 total elemental analyses in allophanic Andisols are shown in Fig. 6 on a logarithmic scale. The element content was highly variable and the maximum/minimum values ranged between 2 and 300. The maximum/minimum value for Si, Al and Fe were rather narrow ranging between 2 and 4. The mean content of the 12 major elements (C, N, Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe) was more than 1 g kg^{-1} and the others were less than these. The Oddo-Harkins' law that the content of the even-numbered atomic elements is greater than those of the neighboring odd-numbered ones was clearly demonstrated for the lanthanum series elements, the atomic numbers of which proceed from 57 (La) to 71 (Lu) (Yamasaki *et al.*, 2001).

Many factors such as the rock type of the tephtras, noncrystalline material contents, and biological activity can be involved in high maximum/minimum values of the 57 element contents in volcanic ash soils. The relationship between oxalate-extractable Si (Si_0) and the total content of the 57 elements is shown in Fig. 7 (Nanzyo *et al.*, 2003). A positive and high correlation was observed both between Si_0 and the total Al content and between Al_0 and the total Al content. In contrast, the total Si content decreased with increase of both Si_0 and Al_0 . These results are compatible with the previous report that Al remains *in situ* (Ugolini, 1988), Si is leached out and allophane-imogolite and/or Al-humus are formed during the weathering of volcanic ash (Shoji *et al.*, 1993).

Alkaline and alkaline-earth elements such as Na, K, Ca and Sr significantly decreased with an increase in the Si_0 , Al_0 or Fe_0 content (Table 1). The first transition metals, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu correlated positively with the noncrystalline material contents. Thus, these elements were residually enriched in the volcanic ash soils. Fe_0 correlated more strongly with these metals than Si_0 and Al_0 (Table 1) suggesting that these elements accumulate with ferrihydrite rather than with allophane-imogolite during Andisol formation.

Regarding the total content of the lanthanum series elements, the correlation coefficients with both Si_o and Al_o gradually increased with their increasing atomic number. Among the elements shown in Fig. 7, La, Th, and U appear to show rather poor correlation with Si_o . However, the contents of these elements are

strongly dependent on the rock type of the parent tephtras. Basalttephtras have only a small content of these elements. On the other hand, dacitic tephtras have higher content and stronger correlation with Si_o . Yttrium showed a significant correlation with the non-crystalline material contents (Table 1).

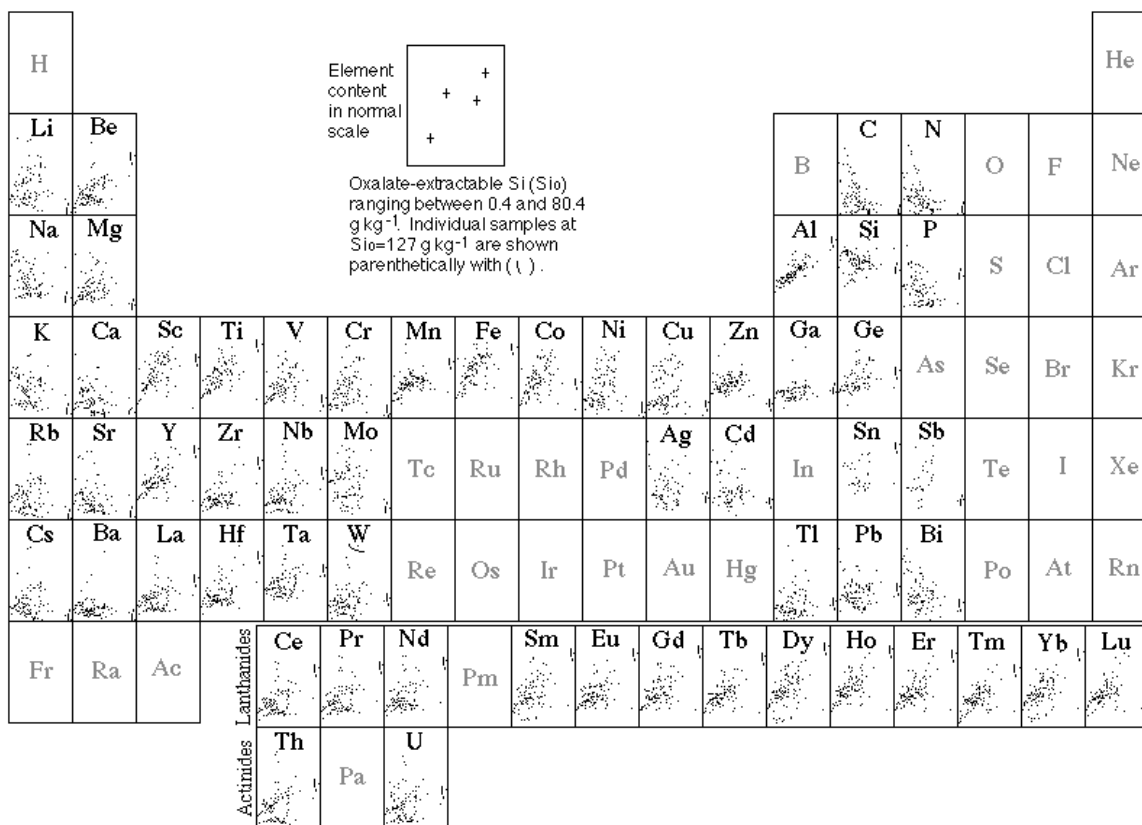


Fig. 7 Relationship between oxalate-extractable Si (Si_o) and total element content in Andisols (adapted from Nanzyo *et al.*, 2003).

Table 1 Correlation coefficients between content of oxalate-extractable Si (Si_o), Al (Al_o) or Fe (Fe_o) and those of individual elements of volcanic ash soils in Japan. A coefficient of 0.33 or more for 95 samples and 0.37 or more for 74 samples (shown in boldface) is significant at the 0.1% level.

	Si_o	Al_o	Fe_o	Li	Be	C	N	Na	Mg	Al	Si	P	K	Ca	Sc
Si_o	1.00			0.02	0.49	-0.45	-0.46	-0.39	0.00	0.80	-0.02	-0.32	-0.21	-0.32	0.39
Al_o	0.93	1.00		-0.04	0.46	-0.19	-0.24	-0.56	-0.02	0.73	-0.27	-0.22	-0.30	-0.47	0.36
Fe_o	0.37	0.46	1.00	-0.16	0.10	0.10	0.16	-0.43	0.02	0.48	-0.61	0.12	-0.47	-0.10	0.58
n*	95	95	95	95	95	95	95	95	95	95	95	95	95	95	95

*: number of samples.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	Rb	Sr	Y	Zr
Si_o	0.49	0.18	0.11	0.34	0.41	0.27	0.14	0.08	-0.10	0.17	0.36	-0.04	-0.33	0.47	0.50
Al_o	0.49	0.17	0.24	0.30	0.41	0.31	0.24	0.11	-0.14	0.14	0.38	-0.07	-0.51	0.42	0.40
Fe_o	0.79	0.58	0.48	0.42	0.72	0.71	0.48	0.74	0.04	0.42	0.63	-0.27	0.05	0.39	0.15
n	95	95	95	95	95	95	95	95	95	74	74	95	95	95	95

	Nb	Mo	Ag	Cd	Sn	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd
Si_o	0.34	-0.11	-0.10	-0.25	0.29	-0.04	-0.04	-0.10	0.29	0.41	0.39	0.41	0.44	0.49	0.51
Al_o	0.30	-0.19	-0.09	-0.30	0.14	0.01	-0.02	-0.21	0.29	0.37	0.37	0.38	0.39	0.43	0.46
Fe_o	0.03	-0.06	0.17	0.03	0.25	-0.03	-0.14	-0.05	0.04	0.09	0.19	0.27	0.26	0.52	0.44
n	95	86	74	74	33	33	95	95	95	95	95	95	95	95	95

	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Tl	Pb	Bi	Th	U
Si_o	0.52	0.48	0.54	0.53	0.53	0.51	0.56	0.52	0.33	0.16	0.14	-0.03	-0.31	0.28	0.17
Al_o	0.49	0.41	0.50	0.46	0.50	0.42	0.54	0.43	0.27	0.12	0.08	0.01	-0.30	0.26	0.12
Fe_o	0.41	0.26	0.43	0.37	0.24	0.22	0.30	0.17	-0.03	-0.08	0.24	-0.02	-0.11	-0.11	-0.12
n	95	95	95	95	95	95	95	95	95	95	92	95	92	95	95

4.2 Organic constituents

Large amounts of humus are stored in the A and buried A horizons of Andisols. Organic C content of Andisols ranges between 0 and about 200 g kg⁻¹. An important reason for the high humus accumulation is stabilization of humus by complexation with Al. In the buried A horizons, weathering of glass continues while fresh organic matter is not supplied anymore. In these buried A horizons, it appears that easily decomposable organic matter no longer remains and the humus is fully complexed with Al. Stabilization of humus by complexation with Al is strongly suggested by the linear relationship between pyrophosphate extractable Al (Al_p) and organic C content. The atomic ratio of Al_p to organic C is about one to thirteen.

The color of the humus and vertical distribution of organic C content are highly dependent on vegetation. Black humus in many cases accumulates under grassy vegetation of C4 plants and it leads to formation of a melanic epipedon. Contribution of C4 plants to formation of melanic epipedon was reconfirmed by the delta ¹³C value of the humus. It is well known that C3 plants tend to select ¹²C while C4 plants show little selection. Figure 8 shows typical delta ¹³C values of C3 and C4 plants and vertical distribution of humus-rich horizons from a Melanudand. As the present vegetation of this site is forest, the delta ¹³C value is low in the uppermost A horizon. But, the lower humus-rich horizons showed higher delta ¹³C values indicating significant contribution of C4 plants to black humus formation (Yoneyama *et al.*, 2001).

Black humus is different from others in the characteristics of the humic acid fraction. It was classified as an "A type humic acid" according to Kumada

(1981). Figure 9a shows a comparison of the elemental composition of humic acids prepared from black humus-rich horizons of Andisols and those from various soils in the world. While the C content of the black humus is almost in the same range, the O content tends to be higher and the H content tends to be lower than those of the other soils. These differences in elemental composition indicate that the humic acids from black Andisols are in a more oxidized state than those from the other soils.

Figure 9b shows the functional group content of humic acids from the black Andisols and those from other soils in Japan. Humic acids from the black Andisols tend to have larger amounts of carboxyl and carbonyl groups and lower amounts of the alcoholic hydroxyl group than those of the other soils. Thus, the functional group composition also shows that the humic acids from black Andisols are in a more oxidized state than those of other soils. The molar ratio of carboxyl groups to organic C is one to ten. This was also validated by infrared spectroscopy (Yoneyayashi and Hattori, 1988) and proton and ¹³C nuclear magnetic resonance spectroscopy (Yoneyayashi and Hattori, 1989; Yoneyayashi, 1993).

The melanic horizon enriched with the A-type humic acid is separated from the others using melanic index (Honma, 1988). Using visible range absorption spectroscopy of the alkaline extract of the melanic epipedon, almost straight lines are obtained between the logarithm of the absorbance and wavelength. The melanic index is the ratio of absorbance at 450 nm to 520 nm and the A-type humic acid has a melanic index of 1.7 or less.

P-type humic acid is found in the dark brown humus formed under forest vegetation. It has the absorption maximum at 450 nm and a minimum at 520

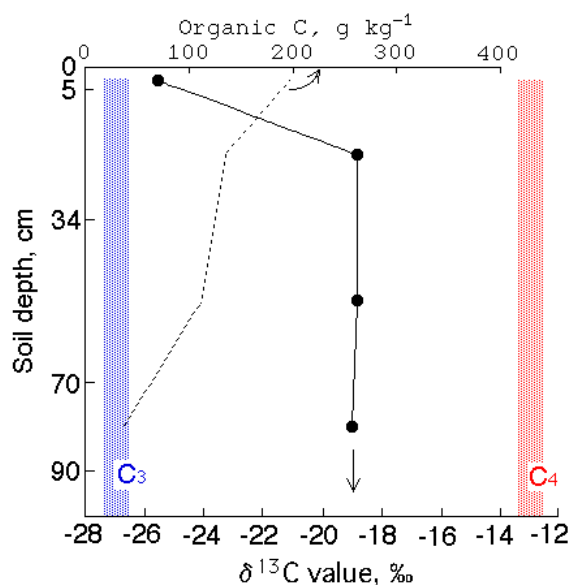


Fig. 8 Vertical distribution of $\delta^{13}\text{C}$ value of an Andosol (Imaichi), (after Yoneyama *et al.*, 2001). C3 and C4 plants show $\delta^{13}\text{C}$ values of -27 and -13, respectively. The $\delta^{13}\text{C}$ value of the uppermost A horizon of this site is -26 and is due to current C3 forest vegetation. The underlying horizons have $\delta^{13}\text{C}$ value of -19 indicating significant contribution of C4 plants.

with an increase in salt concentration and pH values. Variable positive charges are due to the protonated hydroxyl groups bound to aluminum of allophane and imogolite and those bound to iron minerals. The amount of positive charge increases with an increase in salt concentration and a decrease in pH value. However, in the allophanic A horizons, positive charges appear to be masked by carboxyl groups of humus and only the variable negative charge develops. Similarly in the humus-rich nonallophanic A horizons, only variable negative charges develop due to humus and chloritized 2:1 minerals. Both positive and negative charges develop in the allophanic Bw horizons of Andisols.

The amount of variable negative charge tends to be overestimated if it is compared with actual field conditions under humid soil moisture regimes. Because salt concentrations of soil solutions are mostly low in the field due to rainfall and soil pH is mostly weakly acidic while the amount of negative charge or cation exchange capacity is determined using an ammonium acetate solution of 1 mol L^{-1} at pH 7, values that are higher than those in the field.

The variable negative charge shows high selectivity for multi-valent cations such as Ca^{2+} , Mg^{2+} , Ba^{2+} and heavy metal cations. Selectivity for Ca^{2+} and Mg^{2+} further increase with sorbed P content in Andisols (Uhm *et al.*, 1994). KCl-exchangeable Al content, mostly in the form of Al^{3+} (Saigusa *et al.*, 1980), is abundant in the uncultivated or unlimed nonallophanic Andisols and low in allophanic Andisols except those under highly acidified conditions such as tea garden soil in Japan.

Matured Andisols show high phosphate retention capacity. The reactive components in Andisols are allophane, imogolite, Al-humus complex, ferrihydrite, KCl-extractable Al, and polymeric hydroxy Al ions in the interlayer of chloritized 2:1 minerals. The reactive Al and Fe in these components are called active Al and active Fe, respectively (Wada, 1980). The phosphate retention capacity depends on the content of these components in Andisols. Reactivity of F^- , arsenate, and so on with active Al and Fe resembles those with phosphate. These anions react not only with positively charged sites but also neutral sites, substituting some ligands such as $-\text{OH}$ and $-\text{Si}(\text{OH})_3$ and are more reactive with active Al and Fe than are Cl^- , NO_3^- , ClO_4^- , SO_4^{2-} .

Large amounts of P fertilizers are applied to Andisols in intensive agriculture. However, the P recovery rate by crops is low due to fixation by the Andisols and most of the P accumulates in the plow layer of Andisols.

The active Al in Andisols appears to retard development of low Eh (reduction potential) conditions to some extent. Andisols are mostly located on uplands but they are used in a small percentage for paddy fields in Japan. Decrease in Eh values is slower in Andisols than in lowland paddy soils. (Shoji *et al.*,

1993).

5. Properties of Volcanic Ash Soils Related to Biological Activities

Time zero of Andisol formation is the deposition of new volcanic ash. Several years after the eruption of Mt. Usu, Japan in 1977, bacterial flora started to grow (Yoshida, 1993), followed by growth of fungal flora. Regarding N fixers, anaerobic ones started to grow very early after the tephra deposition and appeared to have contributed to the initial organic matter accumulation, possibly because anaerobic N fixers can grow even with a very poor organic C source. Subsequently, the number of aerobic N fixers increased about 10 years after the eruption. Growth of yeasts was poor for about 15 years after the eruption at the Mt. Usu site.

Microbial activity is not very high in unameliorated Andisols due to P deficiency, acidic to weakly acidic pH and high stability of organic matter (Nishio, 1996). Addition of phosphates to Andisols with pH higher than 5 increases the number of aerobic bacteria, actinomycetes and fungi and enhances soil respiration. When the number of microbes was compared in uncultivated lands, Andisols had significantly more actinomycetes and anaerobic bacteria than other soils in Japan. Similar results were also obtained in cultivated lands.

Although its solubility is low (Engelstad *et al.*, 1974), the total phosphorus content of fresh tephra is generally higher than that of uncultivated alluvial soils. The major form of phosphorus in fresh rhyolitic to andesitic tephra is apatite (Kawasaki, *et al.*, 1992; Nanzyo *et al.*, 1997; Nanzyo and Yamasaki, 1998). This mineral plays an important role in crop production without phosphorus fertilization and in revegetation of areas with thick deposition of volcanic ash. Figure 11 shows SEM images of apatite from new (Fig. 11a) and old (Fig. 11b) lahar deposits (older than 500 years) in the Central Plain of Luzon. The former has a smooth surface while the latter has a rough surface and partial dissolution. Paddy soil formed from the old lahar deposit showed a lower content of total and acid-soluble P in the plowed layer than in the lower horizons. These findings suggest that apatite significantly contributed in this area to rice production. The old volcanic ash soils in the Central plain of Luzon are not Andisols but Ustepts or Ustipsamments possibly due to high Si concentration in the soil solution resulting in formation of layer silicates such as halloysite rather than allophane and imogolite. In these soils, apatite is not readily transformed into insoluble aluminum phosphate.

Biotite is also a minor component of volcanic ash, but, it can readily release K, one of the major essential plant nutrients, from an interlayer site resulting in formation of trioctahedral vermiculite (Nanzyo *et al.*, 1999; 2001). Figure 12 shows changes in K content of biotite particles during rice cultivation using

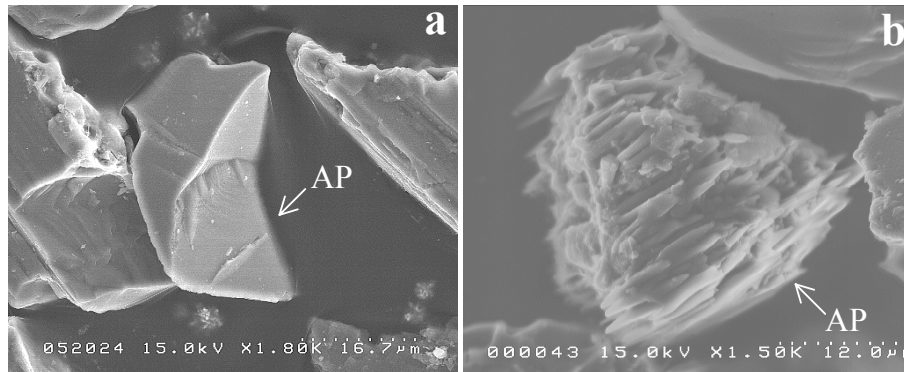


Fig. 11 SEM images of apatite (AP) particles separated from 1991 Mt. Pinatubo volcanic ash (a: adapted from Nanzyo *et al.*, 1997) and a lower horizon of a paddy field soil (b: lahar deposit older than 500 years).

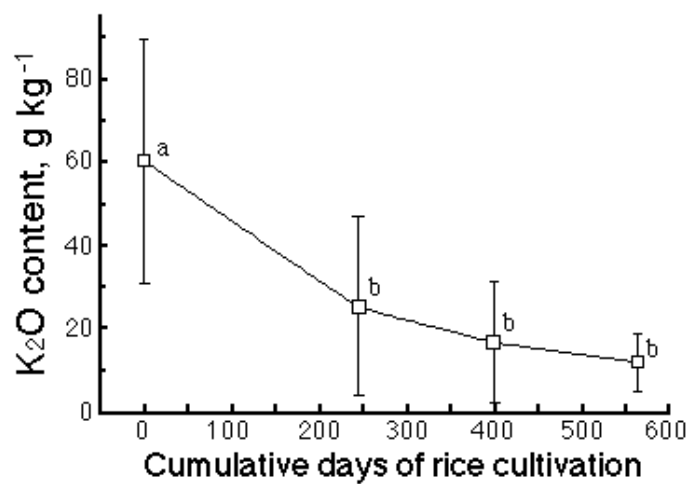


Fig. 12 Changes in K₂O content of Pinatubo biotite with lowland rice cultivation. Bars show standard deviation of measured means. Different letters by the symbols indicate significant difference at the 0.05 probability level according to the t-test (adapted from Nanzyo *et al.*, 1999).

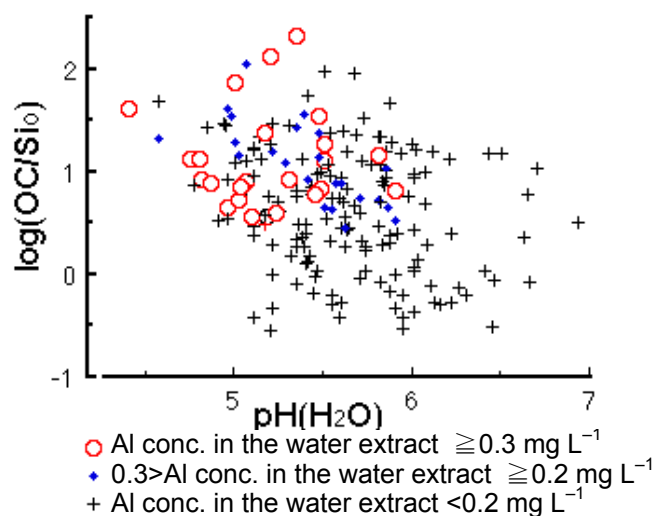


Fig. 13 Relationship between pH(H₂O) and log(OC/Si₀) of 3 groups of soils showing different Al concentrations in the water extract (adapted from Nanzyo *et al.*, 2000).

Pinatubo ash from the 1991 eruption. The K content

of the biotite particles decreased with cumulative days of rice cultivation.

Allophanic and nonallophanic Andisols show contrasting effects on the behavior of KCl-extractable and water soluble Al (Takahashi and Dahlgren, 1998). These forms of Al are toxic to many sensitive crops, but show a suppressive effect against potato scab (Mizuno *et al.*, 1998) and bean root rot (Furuya *et al.*,

1999). Content of these forms of Al is high in non-allophanic Andisols and low in allophanic Andisols. High Al concentration of 0.3 mg L^{-1} or more in the water extract is considered to provide resistance to potato scab. Although water-extractable Al is negatively correlated with soil pH values, soils with low to high levels of water-extractable Al are included between pH(H₂O) levels of 5 and 6 (Fig. 13). The im-

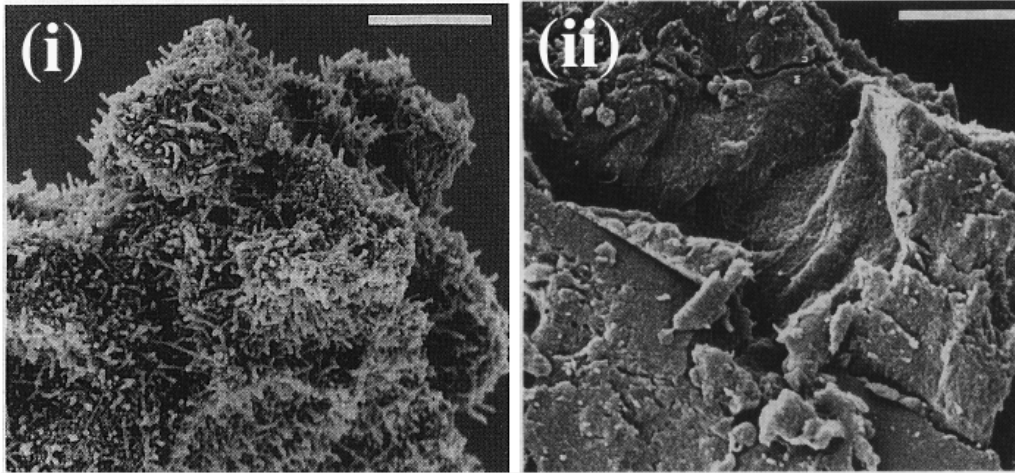


Fig. 14 SEM images of weathered Kanuma pumice with tobacco mosaic virus (TMV) adsorption (i) and acid oxalate-treated Kanuma pumice with TMV addition (ii). Scale = 1 μm (adapted from Toriyama *et al.*, 1995).



Fig. 15 (i) Development of main and lateral roots of *B. pekinensis* in a P-deficient soil. The dark spherical objects are the DCPD gel beads covered with the lateral roots. (ii) Cross section of one of the dark spherical objects in (i). Soil is located outside the root-covered DCPD gel bead. There is no soil between the roots (a) and the DCPD gel bead surface (b) (adapted from Nanzyo *et al.*, 2002).

portant factors affecting water-extractable Al levels in this pH region were organic C content and Si₀. The soils showing high water-extractable Al levels, contained a larger amount of organic C and a smaller amount of Si₀ than those with low water-extractable Al levels.

Allophanic clays adsorbed tobacco mosaic virus because adsorption of the virus was not observed after removal of allophanic clays with acid oxalate treatment (Fig. 14). Although the virus was not adsorbed by an A horizon soil of a nonallophanic Andisol, the virus ceased multiplication suggesting the soil had an anti-virus effect (Toriyama *et al.*, 1995).

Under P deficient conditions in an uncultivated Andisol, *Brassica* roots show almost P-tropic growth (Nanzyo *et al.*, 2002). The thin lateral roots of *Brassica pekinensis*, L., completely encircled DCPD gel beads (a Ca-alginate gel in which a CaHPO₄ · 2H₂O powder was suspended) and no soil area remained between the roots and the DCPD gel beads (Fig. 15). This morphological plasticity of *Brassica* roots is suitable for improving the P recovery rate because soil a few mm thick with a high P retention capacity between plant roots and P fertilizer reduces the recovery rate of P fertilizers by crops in a P-deficient soils (Nanzyo *et al.*, 1996). P-preferential root proliferation was also observed for *Fagopyrum esculentum* Moench.

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