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## Organic Carbon Accumulation in Andosols: (3) Occurrence of Apatite and Biotite in Young and Matured Volcanic Ash Soils, and Discussions on Nutrient Supply for Ecosystems

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### *Abstract*

Carbon sequestration in soil is one of the current topics in the soil ecosystem. Andosols show a high C content, especially in the A-horizons, among mineral soils. The major C source of the soils is plant biomass and sufficient nutrient elements are indispensable for rich plant biomass production. Phosphorus and K are the major essential elements for plants that must be supplied from the soils under natural conditions. Thus, the contribution of the P and K content to C sequestration in Andosols was evaluated using soil chemical data. The P content showed a significant positive correlation ( $r=0.60^{***}$ ,  $n=53$ ) with the C content of the A-horizons in Andosols, suggesting the contribution of P to C sequestration under natural conditions. Ap horizons were not included in this correlation analysis because abundant P fertilizer is applied to maximize agricultural production. In contrast, the K content of Andosols tended to correlate weakly and negatively with the C content possibly due to leaching loss from the A-horizons with Andosol formation under a humid climate.

### *Introduction*

Volcanic ash soils are located near volcanic areas in the world. The soils are derived from nearly pure ash in the areas with abundant recent ash deposits. In other volcanic or peri-volcanic areas, the volcanic ash soil is more or less a mixture with other soil materials. Although apatite and biotite are minor components in volcanic ash, these minerals contain important nutrients, P and Ca in the former (Nanzyo et al., 1997; Nanzyo and Yamasaki, 1998), and K, Mg, Fe, etc., in the latter (Nanzyo et al., 1999). Weathering

of these minerals is relatively rapid under humid and warm climatic conditions. These nutrients are considered to play an important role in the development of natural ecosystems at least at the initial stage of volcanic ash soil formation (Nanzyo et al., 2000; 2003) and also in forming a thick, humus-rich A-horizon of the volcanic ash soils.

### *Apatite and biotite in tephra and Andosols*

Fresh tephra contains 1 – 3 g kg<sup>-1</sup> or more of P<sub>2</sub>O<sub>5</sub> in some cases. These P<sub>2</sub>O<sub>5</sub> contents are greater than those for sedimentary rocks. The major P-bearing mineral in the tephra is apatite (Nanzyo et al., 1997). Although the particle size of apatite in volcanic ash is mostly small, the particles are crystalline and much less soluble than those of sedimentary origin.

In spite of being hardly soluble, apatite in the tephra must be an important P source for plants and other living organisms in the tephra-affected areas where P-containing fertilizers are not applied (Nanzyo et al., 2003). Apatite particles can be found in the heavy fine sand fraction of the fresh tephra using an element mapping technique under a scanning electron microscope and energy dispersive X-ray analysis. Fresh apatite particles show a smooth surface (Fig. 1) while those in the volcanic ash soils show a partially dissolved rough surface (Fig. 2).

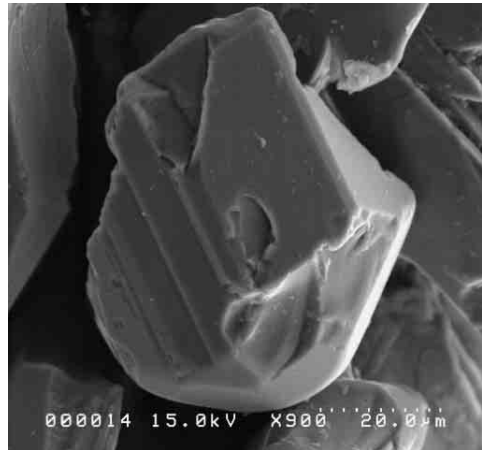
A small amount of macroscopic biotite is often found in the new tephra as dark-colored platy particles (Fig. 3). Biotite in the new lahar deposit from Mt. Pinatubo, Philippines, was easily converted to vermiculite during lowland rice-cultivation in pots. The K<sub>2</sub>O content gradually decreased, and the peak intensity of the X-ray diffraction at 1.4 nm increased

during seven cultivations of the paddy rice (Nanzyo *et al.*, 1999). The weathered biotite particle shows a frayed edge (Fig. 4). The vermiculite found in the clay fractions of the soils derived from the old lahar deposits in this area was the tri-octahedral type and it appears to be of biotite origin (Nanzyo, *et al.*, 2001).

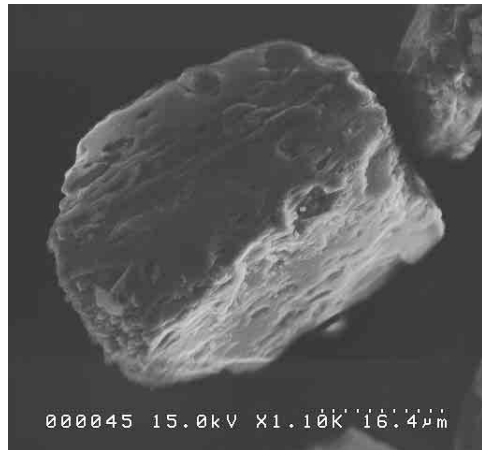
#### ***Factors affecting the element concentration in Andosols***

The process of Andosol formation is primarily characterized by accumulation of active Al and Fe (Shoji *et al.*, 1993). The active Al materials are allophane, imogolite and Al-humus complex. The major active Fe material is ferrihydrite. To evaluate the contribution of nutrient elements to C accumulation in Andosols, changes in element concentrations during Andosol formation were examined focusing on the C content. Soil chemical data were chosen from those of allophanic Andosol areas all over Japan (Saigusa and Matsuyama, 1998) and were cited from Wada (1986).

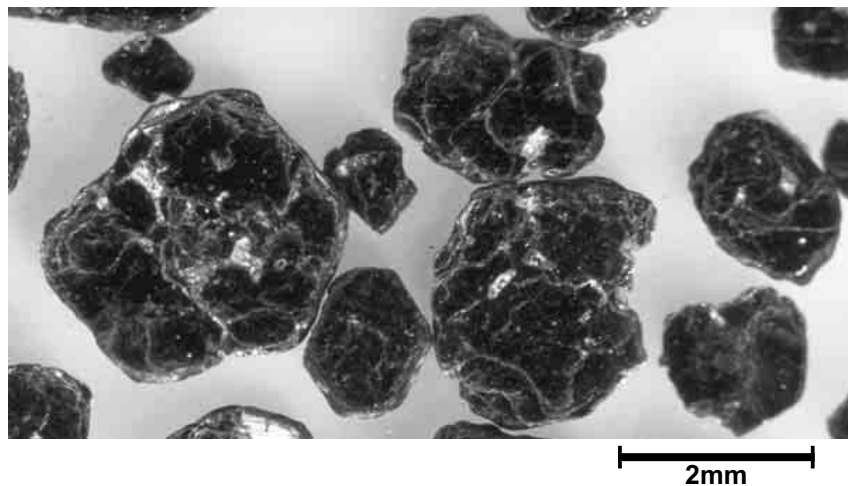
With an advance in Andosol formation, Al, Fe and other immobile elements are concentrated as exemplified in Fig. 5, while mobile elements such as Si, Ca, Na, etc., are depleted (Nanzyo *et al.*, 2007; 2009). However, the C and N contents in Andosols show no correlation with indices related to Andosol formation (Fig. 6 and 7) because these elements are mostly incorporated in soil by biological activities. In contrast, the N content shows a strong correlation with the C content (Fig. 8) as in other soils, although the C/N ratio is higher than that of other soils. Thus, there are at least three different factors affecting the element concentration in Andosols, weathering, biological ac-



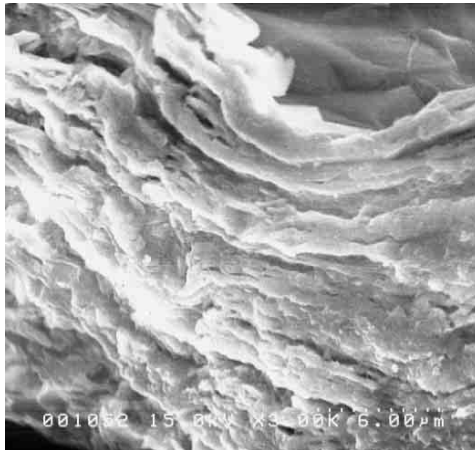
**Fig. 1.** An apatite particle in a new pyroclastic flow deposit at Mt. Unzen, Japan.



**Fig. 2.** A partially weathered apatite particle in a soil derived from an old lahar deposit in Central Luzon, Philippines.



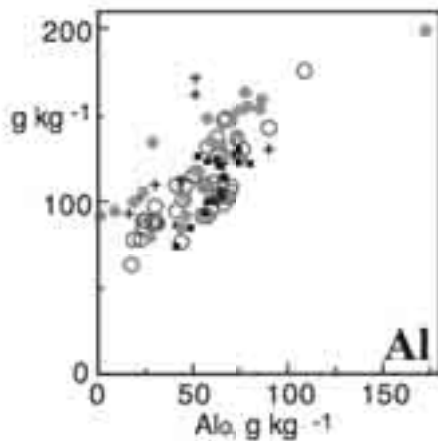
**Fig. 3.** Biotite particles in a new pyroclastic flow deposit from Mt. Unzen, Japan.



**Fig. 4.** An edge face of a weathered biotite particle in a soil derived from an old lahar deposit in Central Luzon, Philippines.

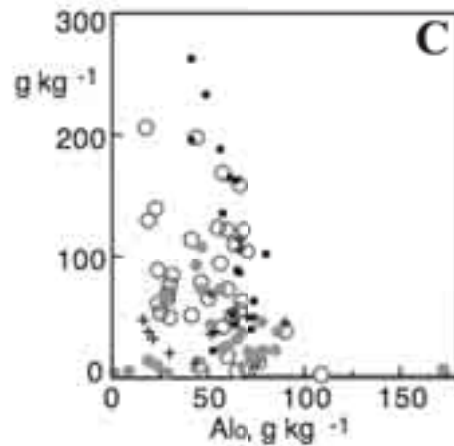
tivities, rock type of parent tephra, etc.

Although  $Al_0$  and the C content show no significant correlation in Andosols, a pyrophosphate-extractable fraction ( $Al_p$ ), which is a part of  $Al_0$ , significantly correlates with the C content of the A-horizons, except for those existing at the uppermost layers. Because pyrophosphate extracts Al from an Al-humus complex, little from allophane and imogolite, the weathering product of volcanic glass partly contributed to the accumulation of C in the volcanic ash soil under natural conditions. According to the relationship between the contents of  $Al_p$  and C, one mole of  $Al_p$  is complexed with a unit of humus having 13 moles of C. A rational formula for the Al-humus complex can be estimated as shown in Fig. 9, assuming that every



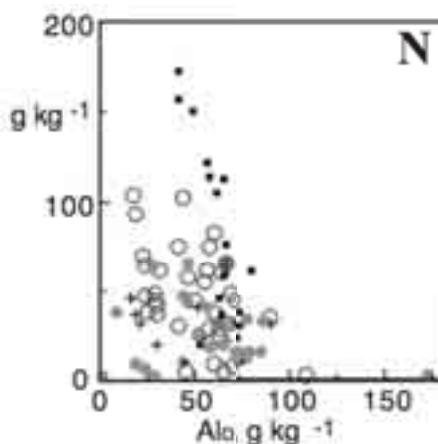
○:Dacitic, □:Andesitic, △:Basaltic-andesitic, ■:Basaltic

**Fig. 5.** Relationship between  $Al_0$  and the Al content in allophanic Andosols.



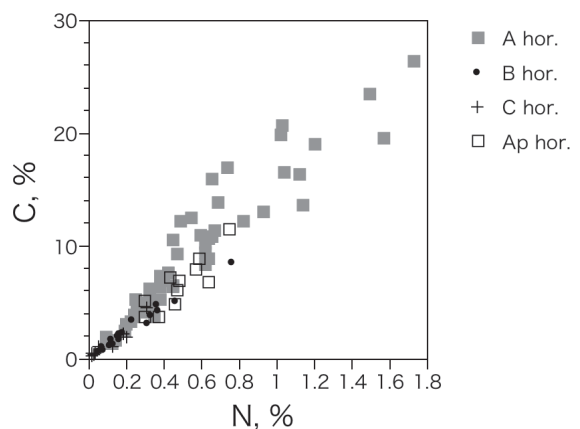
○:Dacitic, □:Andesitic, △:Basaltic-andesitic, ■:Basaltic

**Fig. 6.** Relationship between  $Al_0$  and the C content in allophanic Andosols.



○:Dacitic, □:Andesitic, △:Basaltic-andesitic, ■:Basaltic

**Fig. 7.** Relationship between  $Al_0$  and the N content in allophanic Andosols.



**Fig. 8.** Relationship between the N and C contents in allophanic Andosols.

40 carbons have 4 carboxyl groups (Yonebayashi and Hattori, 1982), 3 Al<sub>p</sub>s and one negative charge at pH 7 (Nanzyo and Shoji, 1993).

Charred materials are also included in the C content of Andosols (Fig. 10). The C from the charred materials was reported to range between 3.8 and 32.7% of the C content in Andosols (Honma *et al.*, 2002; Nishimura *et al.*, 2006). The charred materials can be supplied by burning vegetation through human activities and natural fire during the soil formation process, and also by fire during volcanic eruption. The role of charred materials in the accumulation of highly humified humic acid in Andosols is under discussion. The charred material was not considered in constructing the formula shown in Fig. 9.

**Relationship between the P and C contents in Andosols**

Although P originates in the parent tephra and is

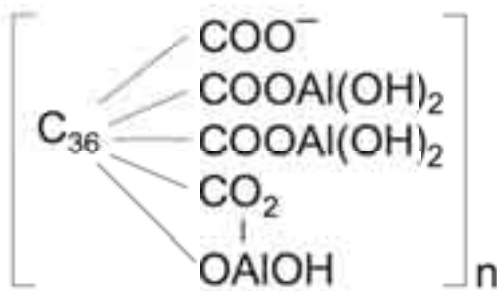


Fig. 9. An estimated rational formula for Al-humus in Andosols.

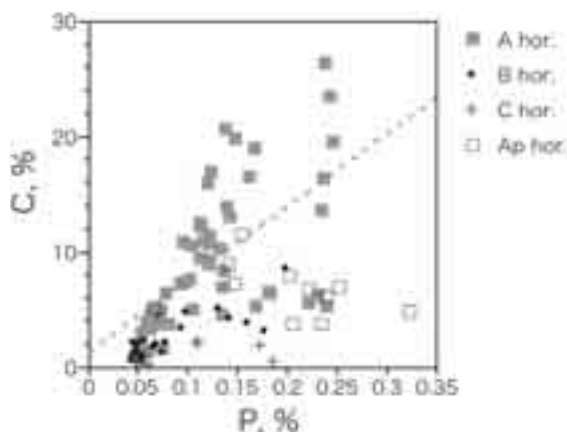


Fig. 11. Relationship between the P and C contents in Andosols (Regarding the A-horizon,  $r=0.60^{***}$ ,  $n=53$ ).

strongly sorbed by active Al and Fe materials, the correlation between the P content and Al<sub>p</sub>, even after grouping the volcanic ash soils with rock types of the original tephra, is not significant. However, significant correlation can be found between the P and C contents in the A-horizon soils (Fig. 11) excluding the Ap horizons that have P from fertilizers. Thus, it is considered that P weakly contributes to C accumulation in the A-horizon soils of natural Andosols probably through P supply from volcanic ash for vegetation. Thus, the biological activities may be affected by the content of P in Andosols.

**Relationship between the K and C contents in Andosols**

Biotite is easily weatherable, it releases K, and K

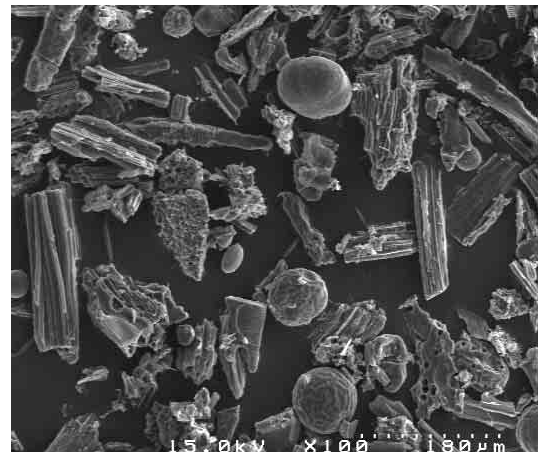


Fig. 10. SEM image of light fraction ( $d < 2$ ) including charred materials (mainly rectangular particles, prepared from the A2 horizon of Yunodai, Towada, Japan).

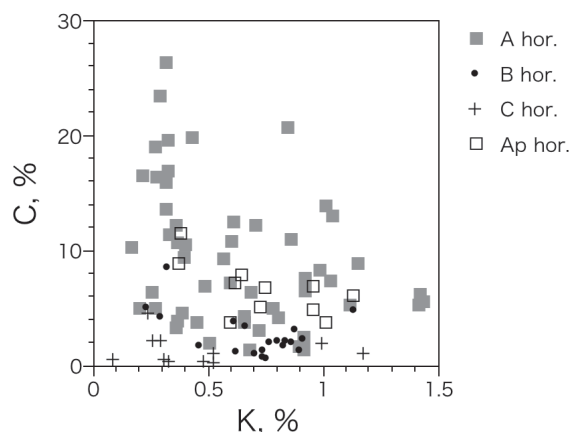


Fig. 12. Relationship between the K and C contents in Andosols.

can be used by organisms. Potassium is commonly one of the major essential nutrients for plants. However, the C content in the A-horizon soils of Andosols tends to decrease with the total K content ( $r = -0.36^{**}$ ,  $n=53$ , Fig. 12) with very high scattering. It is difficult to obtain evidence that K contributes to C accumulation from Fig. 12. Possible reasons may be (i)  $K^+$  in the plant residue is easily lost under a humid climate, (ii)  $K^+$  does not show preference for humus compared with divalent exchangeable cations, (iii) the K content of tephra depends on the rock type, etc.

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