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Allophane and imogolite: role in soil biogeochemical processes

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ABSTRACT: The literature on the formation, structure and properties of allophane and imogolite is reviewed, with particular emphasis on the seminal contributions by Colin Farmer. Allophane and imogolite occur not only in volcanic-ash soils but also in other environments. The conditions required for the precipitation of allophane and imogolite are discussed. These include pH, availability of Al and Si, rainfall, leaching regime, and reactions with organic matter. Because of their excellent water storage and physical properties, allophanic soils can accumulate large amounts of biomass. In areas of high rainfall, these soils often occur under rain forest, and the soil organic matter derived from the forest biomass is stabilized by allophane and aluminium ions. Thus the turnover of soil organic matter in allophanic soils is slower than that in non-allophanic soils. The organic matter appears to be derived from the microbial by-products of the plant material rather than from the plant material itself. The growth of young forests may be limited by nitrogen supply but growth of older forests tends to be P limited. Phosphorus is recycled through both inorganic and organic pathways, but it is also strongly sorbed by Al compounds including allophane. When crops are grown in allophanic soils, large amounts of labile P are required and, accordingly, these soils have to be managed to counteract the large P sorption capacity of allophane and other Al compounds, and to ensure an adequate supply of labile P. Because of their physical and chemical properties, allophanic soils are excellent filters of heavy metals and pathogens.

Allophane and imogolite are clay-size minerals commonly associated with volcanic ash soils where there is sufficient moisture for leaching of silica to take place. They also occur in some non-tephric soils and sediments, as well as in stream beds and drains. Ming *et al*. (2006) reported that allophane also occurs on Mars. There are three main types of allophane, namely, Al-rich soil allophanes, Si-rich soil allophanes, and stream-deposit allophanes.

Ross and Kerr (1934) showed that allophane was an X-ray amorphous material commonly associated with the clay mineral halloysite. They suggested that "the name allophane should be restricted to mutual solid solutions of silica, alumina, water and minor amounts of bases but should include all such

materials, even though the proportions of these constituents may vary". Other definitions were given by van Olphen (1971), Wada (1977), and Farmer & Russell (1990). In light of work in the 1970s, Ross and Kerr's definition needs to be modified to exclude imogolite (Farmer & Russell, 1990) and allow for broad peaks in the X-ray diffraction (XRD) patterns of allophane (Parfitt, 1990a) as well as synthetic allophanes that may not contain bases at low pH. The definition given by Parfitt (1990a) is "Allophane is the name of a group of clay-size minerals with short-range order which contain silica, alumina and water in chemical combination". Imogolite, a tubular clay mineral found in association with allophane, is excluded from this definition because it has long-range order in one dimension (Farmer & Russell, 1990).

STRUCTURES

The unit particle of imogolite is a hollow tubule with an outer diameter of ~2.1 nm and a wall thickness of ~0.7 nm (Fig. 1). The wall consists of an outer gibbsite-like curved sheet, while the inner surface consists of O_3SiOH, with oxygens replacing the inner hydroxyls of the gibbsite sheet (Cradwick *et al.*, 1972; Farmer & Fraser, 1979). The structural formula of imogolite is $(OH)_3Al_2O_3SiOH$, giving an Al:Si atomic ratio of 2.0. Levard *et al.* (2008) reported on the synthesis of a single-walled aluminogermanate nanotube with the imogolite
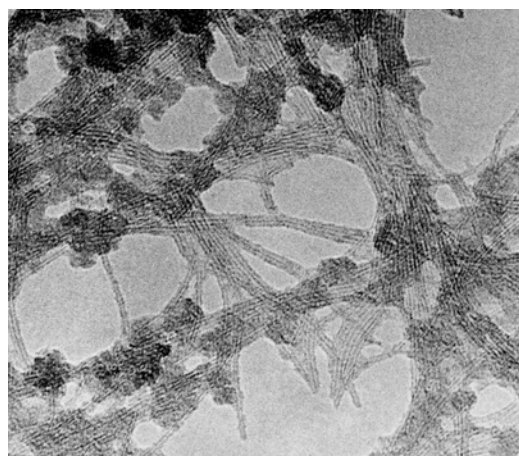
structure. Guimarães *et al.* (2007) recently studied the stability and the electronic and mechanical properties of 'zigzag' and 'armchair' imogolite nanotubes using the density-functional tight-binding method. The (12,0) imogolite tube had the greatest stability of all tubes studied. Uniquely for nanotubes, imogolite had a minimum in the strain energy for the optimum structure. This was in agreement with experimental data, as shown by comparison with the simulated XRD spectrum.

Allophane is made up of hollow spherules with an outer diameter of 4−5 nm (Henmi & Wada, 1976) (Fig. 2). Al-rich allophane has an imogolite-like structure with an Al:Si ratio of ~2, while Si-rich allophane contains polymerized silicate and has an Al:Si ratio of ~1. Stream-deposit allophanes have Al:Si ratios of 0.9−1.8, with Al substituting for some Si in the polymeric tetrahedra.

Al-rich soil allophanes

Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic studies have shown that Al-rich soil allophanes have the imogolite structure over a short range (Farmer *et al*., 1977a; Tait *et al*., 1978; Parfitt & Henmi, 1980; Barron *et al*., 1982; Wilson *et al*., 1984). The ^{27}Al NMR spectrum of allophane from Andisols showed that the Al was largely in octahedral coordination (Wilson *et al*., 1984). The ^{29}Si NMR spectra of Al-rich allophanes from Spodosols and Andisols (Barron *et al*., 1982;

FIG. 1. Electron micrograph of imogolite (external diameter of the tubes is ~2.1 nm and internal diameter is ~0.7 nm).
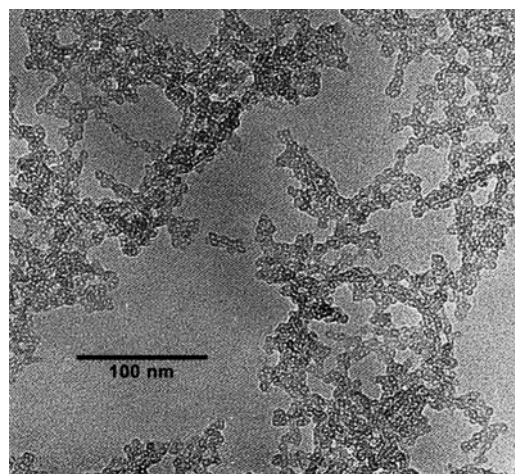

FIG. 2. Electron micrograph of an Al-rich allophane (external diameter of the spherules is 4−5 nm).

Goodman *et al.*, 1985) show a signal with a chemical shift of −78 ppm. Being identical to that of imogolite, this signal is indicative of the presence of tri-substituted O_3SiOH tetrahedra. The resonance line width for allophane, however, is larger than that for imogolite, suggesting the structure of allophane is relatively disordered.

Soil allophanes with Al:Si ratios close to 2:1 would therefore appear to be made up of fragments having the imogolite atomic structure over a short range (Parfitt & Henmi, 1980). The fragments link to form a porous, hollow spherule with water molecules occupying the spherule interior space as well as being adsorbed to the outer AlOH surface (Henmi & Wada, 1976). Accordingly, Al-rich allophanes have been referred to as proto-imogolite allophanes (Farmer & Russell, 1990), or imogolite-like allophanes (Parfitt & Wilson, 1985).

Proto-imogolite allophane has been used as a reference point in the allophane group of minerals. Relatively pure samples can be obtained from within lapilli, whereas imogolite is found outside pumice granules (Yoshinaga & Aomine, 1962; Parfitt & Henmi, 1980).

Some Al-rich soil allophanes have Al:Si ratios as high as 4:1 (Farmer & Fraser, 1982; Farmer & Russell, 1990; Parfitt & Kimble, 1989) where up to half the O_3SiOH tetrahedra on the inner surface of the spherules are, presumably, replaced by hydroxyls. Alternatively, fragments of spherules may be present with no Si attached to edge sites (Farmer, 1986). These allophanes are found in the B and C horizons of some podzolized soils.

The XRD patterns of Al-rich allophane have broad lines at 1.2, 0.43, 0.34, 0.22, 0.19, 0.17 and 0.14 nm. The XRD patterns of air-dry allophane films deposited on glass slides have an additional line at ~2.7 nm arising from X-ray scattering by spherical particles. Using these data, van der Gaast *et al.* (1985) calculated that the diameter of allophane spherules is ~4.0 nm.

Electron micrographs of Al-rich allophane show globular aggregates of varying size and shape. Each aggregate is composed of many hollow spherules with external diameters of 4.0−5.5 nm (Wada & Wada, 1977). Small-angle neutron-scattering measurements by Hall *et al.* (1985) gave an average spherule diameter of 5.6 nm for Al-rich allophane, and a specific surface area of 638 m^2 g^{-1} estimated from ethylene glycol retention. A similar value (581 m^2 g^{-1}) was obtained by adsorption of nitrogen at 77 K (Vandickelen *et al.*,

1980). The data, however, are subject to various uncertainties because of the porous nature of allophane (Paterson, 1977), the presence of impurities, and assumptions about monolayer coverage.

One model for allophane suggests that the unit particle of allophane is a hollow spherule with defects in the wall structure, giving rise to micropores of 0.3−2.0 nm diameter (Paterson, 1977; Wada & Wada, 1977). The external surface area of allophane calculated for this model is 800 m^2 g^{-1}. The defects in the structure may arise when the proto-imogolite fragments make edge-to-edge contacts to form spherules. These conclusions are supported by recent data from Creton *et al.* (2008) who used molecular dynamics calculations to propose a structure for allophane. Their model structure was characterized by a Si/Al ratio of 0.49, had external and internal diameters of 5.0 and 4.0 nm, respectively, and contains six holes of ~0.7 nm size. The calculated XRD pattern and Raman spectrum of the structure were in a good agreement with the corresponding experimental data. Their calculations for hydrated allophane showed that the model reproduced the main experimental findings on the adsorption of water molecules in the void of allophane and the exchange between the "internal" and "external" water. The adsorption of water molecules occurred mostly in the regions with negative electrostatic potential, where the molecules find an environment close to that in bulk liquid water that explains the significant water retention by allophane.

Electron paramagnetic resonance (EPR) spectroscopy indicates that Fe^{3+} in natural, Al-rich allophanes occupies two distinct sites: a regular and a distorted octahedral site (Parfitt & Henmi, 1980). Some Fe may substitute for Al in the proto-imogolite structure. In natural samples with an Fe:Al atomic ratio >1:10, the Fe may be present as a separate phase such as ferrihydrite (McBride *et al.*, 1984).

Si-rich soil allophanes

The IR spectrum of Si-rich soil allophane with Al:Si ratio close to 1:1 differs from that of proto-imogolite allophane in that the intense Si−O stretching band occurs at a greater frequency (1020 cm^{-1}) and the band at 348 cm^{-1} is much weaker, indicating that some of the silicate is polymerized (Parfitt *et al.*, 1980). The presence of polymerized silicate (together with some ortho-

silicate) is also indicated by the ^{29}Si NMR spectrum (Goodman *et al.*, 1985). Although some Al may occupy tetrahedral sites, the bulk of the Al is apparently present in octahedral sites (Kirkman, 1975; Goodman *et al.*, 1985). Thus, the (gibbsitic) Al octahedral sheet also provides the structural framework for Si-rich soil allophanes but this is now linked to silicate polymers (Parfitt *et al.*, 1980). The Al in tetrahedral sites is probably associated with the silicate polymers. The band at −78 ppm in the ^{29}Si NMR spectrum indicates the presence of some proto-imogolite structures.

Thermal analysis of Si-rich allophanes (Na saturated) shows exotherms at a lower temperature (950ºC) than that of Al-rich allophanes (975ºC). The temperature at which mullite begins to form when Si-rich allophanes are heated is >1000ºC whereas, for Al-rich allophanes, this transformation occurs at 900ºC, suggesting that the two types of allophane have different structures (Henmi, 1980).

Alternative names for Si-rich allophanes are defect kaolin allophane or halloysite-like allophane (Yoshinaga, 1986).

Stream-deposit allophanes

Stream-deposit allophanes have Al:Si ratios of 0.9−1.8. The unit particles are hollow spherules with a diameter of <3 nm, forming globular aggregates (Wells *et al.*, 1977). Their structure, however, differs from that of soil allophanes in that the polymerized SiO_4 tetrahedra form the framework. The IR spectrum shows some substitution of Al for Si in tetrahedral sites. The NMR spectroscopy and elemental analysis indicate that the Al:Si ratio of the outer tetrahedral sheet is close to 1:3 (Childs *et al.*, 1990). The remaining Al forms an incomplete (fragmented) octahedral sheet, the positive charge of which balances the negative charge of the outer tetrahedral sheet (Goodman *et al.*, 1985).

Stream-deposit allophanes have been called hydrous feldspathoids (Farmer & Russell, 1990; Childs *et al.*, 1990). As Al^{IV} is the dominant Al species in solution at pH > 6, allophanes that form in soils at relatively high pH values may have similar structures to hydrous feldspathoids (Childs *et al.*, 1990).

One sample of a stream-deposit allophane developed less charge than soil allophane, and adsorbed less phosphate at a low solution concentration (Theng *et al.*, 1982; Parfitt & Henmi, 1980).

This is consistent with the stream-deposit allophane having less active AlOH groups than soil allophanes.

IDENTIFICATION AND ESTIMATION

Allophane deposits in the field may be identified by their characteristic greasy feel. At large water contents, the consistence ratings for allophane are strongly smeary, slightly plastic, slightly sticky, and slightly fluid (Wells & Childs, 1988). As little as 2% allophane in soil can be detected in this way.

Allophane in the field may also be chemically identified by the NaF (Fieldes & Perrott, 1966) or toluidine blue test (Wada & Kakuto, 1985). The fluoride test, however, is not specific for allophane because fluoride also reacts with Al in Al-humus complexes.

In the laboratory, allophane in soil samples may be identified by dissolution in boiling NaOH (Hashimoto & Jackson, 1960), hot Na_2CO_3 (Mitchell & Farmer, 1962), HCl/NaOH (Segalen, 1968), acid oxalate (Higashi & Ikeda, 1974), and from selective dissolution (Wada & Greenland, 1970). Differential XRD shows that acid oxalate is effective at dissolving allophane (Campbell & Schwertmann, 1985). Dissolution in acid oxalate reagent, and measuring the concentrations of Al and Si in solution, are routinely used for the quantitative analysis of allophane (Farmer *et al.*, 1983; Parfitt & Wilson, 1985: Parfitt, 1990a; Parfitt & Childs, 1988). However, if the sample contains >~0.5% carbon (C), the contribution of Al from dissolution of Al-humus complexes must be estimated separately (Parfitt, 1990a). Imogolite, gibbsite, and hydroxy-Al interlayers also dissolve in acid oxalate, but their concentrations are small, at least in New Zealand soils (unpublished data).

The values of Si and Al extracted by acid oxalate are used in conjunction with the value of Al extracted from Al-humus complexes by pyrophosphate (Al_p) (Parfitt & Wilson, 1985). The Al:Si ratio of the allophane, calculated from $(Al_o−Al_p)/Si_o$, ranges from 0.4 to 4.0 with a median value of 1.9, close to that for proto-imogolite allophane (Parfitt & Kimble 1989). The amount of allophane in the sample is estimated by multiplying Si by the relevant factor that depends on the Al:Si ratio (Parfitt & Wilson, 1985; Parfitt, 1990a). Allophane contents of up to 60% (w/w) have been measured for B horizons of soil profiles, and deeper layers of

tephra (Stevens & Vucetich, 1985). The limit of detection is 0.5% for allophane with an Al:Si ratio of 2.

Allophane in the clay fraction of soils can also be identified by IR spectroscopy, provided the bands from layer silicates do not obscure those of allophane (Farmer *et al.*, 1977a; Parfitt & Henmi, 1982), while imogolite may be estimated quantitatively by electron microscopy and differential thermal analysis (Parfitt, 1990b).

PROCESSES OF FORMATION

Laboratory synthesis

Our understanding of the processes underlying the formation of allophane and imogolite has been greatly improved by the work of Colin Farmer and colleagues at the Macaulay Institute (Farmer *et al.*, 1979; Farmer & Fraser, 1982; Farmer, 1986). They showed that proto-imogolite could be synthesized using acid solutions of Al and silicic acid (Farmer *et al.*, 1977b; Farmer & Fraser, 1979). If the concentration of free silicic acid in solution is between 3 and 15 mg Si l^{-1}, the Al:Si ratios of the product range from 1.8 to 2.2; but if this concentration is between 1 and 3 mg Si l^{-1}, the Al:Si ratios range from 2.2 to 4. The formation of imogolite and proto-imogolite in soil requires that the soil solution is supersaturated with respect to imogolite. For typical Si concentrations of ~3 mg Si l^{-1}, the concentration of Al^{3+}, $AlOH^{2+}$ and $Al(OH)_2^+$ in equilibrium with proto-imogolite must be close to that in equilibrium with gibbsite (Farmer & Fraser, 1982). The magnitude of this concentration is predicted to fall rapidly from 10^{-4} M at pH 4 to $<10^{-6}$ M at pH 5. If the concentration of Al in the soil solution is $<3 \times 10^{-5}$ M, proto-imogolite does not form at pH <4 and may not form at pH <4.5 (Farmer, 1986). The formation of allophane and imogolite is also inhibited by the presence of organic ligands and humic substances (Inoue & Huang, 1986, 1990).

The laboratory synthesis of allophane containing some tetrahedral Al requires neutral or alkaline conditions (Farmer *et al.*, 1979; Wada & Wada, 1981; Wada *et al.*, 1988). At pH >5.5, $Al(OH)_4^-$ begins to form, becoming dominant at pH >6. Precipitates formed at pH >7 with Al:Si <1 have almost all of the Al in a tetrahedral network. These precipitates have been called hydrous feldspathoids and are similar to stream-deposit allophanes.

Lindner *et al.* (1998) synthesized allophane using organic reactants (aluminium trialkylates and tetraalkyl orthosilicates) and alkanes as solvents. Slow addition of water via the gaseous phase, followed by hydrolysis and condensation, produced allophane with a structure similar to that of stream-deposit allophanes. The synthetic allophane consisted of hollow spherules with an outer diameter of 3–4 nm and wall perforations of ~0.35 nm in diameter. The wall was made up of a tetrahedral silicon oxide/hydroxide sheet with partial replacement of Si by Al. Octahedrally coordinated Al species acted as counter-ions on the inner surface of the spheres.

Aluminosilicate particles of short-range order have also been synthesized from solutions containing decimolar concentrations of $AlCl_3$ salts and tetraethyl-orthosilicate with varying Al:Si and OH:Al molar ratios (Montarges-Pelletier *et al.*, 2005). Transmission electron microscopy (TEM) showed condensed aggregates with a homogeneous elemental composition, and an Al:Si molar ratio ranging from 0.2 to 1.7. As the Al:Si ratio gradually increased up to 1.3, allophane-like materials with macropores, mesopores and micropores developed successively. When the Al:Si ratio exceeded 1.3, materials with a small surface area were formed. The results indicated a gradual increase in particle condensation as the Al:Si molar ratios increased from 0.8 upwards.

Abidin *et al.* (2007) combined experiments with molecular orbital calculations to show that certain metal ions in solution facilitate allophane formation but inhibit the formation of imogolite in the order: Na, K < Ca, Mg. This is because metals affect the dissociation of the Si-OH group of orthosilicic acid. Structure optimization of the proto-imogolite model showed that when the Si-OH was undissociated, the proto-imogolite adopted an asymmetrical configuration, which then curled to form an imogolite tubule. On the other hand, when the Si-OH was dissociated, the proto-imogolite model had a symmetrical configuration which curved to make a hollow allophane spherule with the orthosilicic acid inside.

Lumsdon & Farmer (1995) have shown that the activity of Al species in the soil solution is greatly modified as SiO_4^{2-} concentrations increase. Bi *et al.* (2001) have used theoretical modelling and computer simulation of Al in soil solution, in equilibrium with the mineral phase imogolite, to explain the distribution of Al species in the presence of silicic acid. Increasing concentrations

of silicic acid may effectively inhibit the formation of polymeric alumino-hydroxo species, and remove Al toxicity.

White *et al*. (2008) found that allophane precipitated inside the digestive gland of freshwater snails. In view of the environmental abundance of both Si and Al, the authors suggested that precipitation of Al and Si in living cells provides a defence against Al toxicity.

Precipitation and solubility in soils formed in tephra

Allophane formation and weathering in tephra and Andisols have been reviewed by Lowe (1986) and Dahlgren *et al.* (2004). The rate of formation is controlled chiefly by macro- and micro-environmental factors together with the mineralogical and physicochemical composition of the parent deposits. The effect of time is subordinate to these factors. The important environmental factors are the activity of silicic acid in the soil solution, the availability of Al species, the opportunity for co-precipitation, leaching regime, soil organic matter, and pH. In turn, these factors are influenced by climate, drainage, vegetation, tephra thickness, depth of burial, and additions of fresh tephra. Generally, allophane forms from tephra at $pH(H_2O)$ values between 5 and 7, and a pH of at least 4.8 is required for allophane to precipitate (Parfitt & Kimble, 1989). Allophane is generally formed *in situ* in Andisols with very little translocation (Dahlgren *et al.*, 2004).

The presence of Al in both octahedral and tetrahedral coordination was observed in the coarse particle-size fractions, which contained both allophane and rhyolitic glass (Campbell *et al.*, 1977). Tetrahedrally coordinated Al is presumably present in the glass. Hiradate & Wada (2005) and Hiradate *et al.* (2006) studied the weathering of volcanic glass to allophane using solid-state ^{29}Si and ^{27}Al magic-angle-spinning NMR. The volcanic glass showed a broad ^{29}Si NMR signal between −80 and −120 ppm, with the centre at −104 ppm. This signal was indicative of Si-O-Si bridging structures. The Al in volcanic glass was present in tetrahedral coordination. On the other hand, octahedral Al (3 ppm by ^{27}Al NMR) and imogolite-like Si (−78 ppm by ^{29}Si NMR) were the major components in both Al- and Si-rich allophanes. Based on the NMR spectra of size-fractionated soil samples, they proposed the

following weathering sequence: (1) dissolution of Al from volcanic glass accompanied by the transformation of Al^{IV} to Al^{VI}; (2) formation of a gibbsite-like sheet resulting from the hydrolysis of the dissolved Al; (3) dissolution of silica gel-like polymer in volcanic glass resulting in the formation of monosilicic acid; and (4) formation of an imogolite-like structure as a result of the reaction between the gibbsite-like sheet and monosilicic acid. These precipitation reactions could occur in solution as well as on the surface of volcanic glass.

In old soils (170,000 y) of Hawaii, Chadwick *et al.* (2003) found that weathering and soil properties changed in a non-linear fashion with increasing rainfall. In areas where rainfall was >1400 mm, most of the base cations and Si, but only 60% of Al, were lost from the old basaltic tephra and lava by leaching. At all sites, the secondary clay mineral assemblage was dominated by metastable non-crystalline weathering products.

Allophane can form rapidly from fine-grained glass particles (Kirkman, 1980). On the face of open soil pits containing rhyolitic tephra, allophane has been observed to precipitate in a matter of months (Parfitt, unpublished data). Allophane is relatively stable in soils. Indeed, under favourable conditions, it can persist in tephra beds for at least 250,000 y (Stevens & Vucetich, 1985).

Precipitation and solubility in soils in the presence of soil organic matter

Soil organic matter can affect the formation of allophane in soils. Working in Iceland, Sigfusson *et al.* (2008) showed that soil solutions from field soils, soil cores and repacked soils with an allophane content of 2−22% and a C content of 11−42% were all highly undersaturated with respect to basaltic glass. Field samples were supersaturated with respect to allophane and imogolite, while samples from the repacked soils were often undersaturated with respect to allophane and imogolite. The dissolution rate was dictated by the $(H^+)^3/(Al^{3+})$ activity ratio in the soil solution; the rate was slower by up to 20% in field soils compared with repacked soils, because of decreasing undersaturation. Dissolution rates, predicted by the $(H^+)^3/(Al^{3+})$ activity ratio, increased up to seven-fold in the field, and by 37-fold in the repacked soils by speciating Al^{3+} with oxalate. Speciation of Al^{3+} with oxalate, which

represents the maximum effect of the dissolved organic C (DOC) on dissolution rates, generally had more effect near the surface than at deep levels in the soil profile. This study showed that for a given temperature, reactive surface area, and volcanic glass composition, the chemical weathering rates of Andisols were dictated by: (1) aeolian deposition rates and drainage both of which affect the saturation state and $(H^+)^3/(Al^{3+})$ activity ratio; (2) the production of organic anions in the soil; and (3) the external supply of anions capable of complexing Al^{3+}.

Mineral dissolution kinetics were used by Yagasaki *et al*. (2006) to investigate the mechanisms controlling the activity of free Al in soil solutions, and their implications for pedogenesis in two Japanese volcanic-ash soils. The A and AB horizons of the soils were rich in organic matter, organically-bound Al, and imogolite and proto-imogolite. Nevertheless, the A horizons were undersaturated with respect to imogolite and proto-imogolite. This suggested that the dissolution rate of these minerals was low, possibly due to their interactions with organic matter. Organic acids, however, can also dissolve allophane; thus the accumulation of organic matter combined with the depletion of imogolite and proto-imogolite are important long-term processes in the formation and development of soils from volcanic-ash.

Al-humus complexes are the dominant constituents in some old volcanic-ash soils of Japan which account for 30% of these Andisols (Dahlgren *et al.*, 2004). The availability of Al^{3+} appears to be a major factor in the formation of Andisols with a pH < 5 and large amounts of C. Under these conditions, organic acids are the main proton donors, lowering pH and Al activity through the formation of Al-humus complexes. In allophanic Andisols, where the capacity of soil organic matter for complexing Al becomes saturated, the excess Al can react with Si to form allophane (Dahlgren *et al.*, 2004).

Precipitation of imogolite and halloysite

Imogolite is often found together with allophane, but classical pure imogolite in Japan occurs as gel films over the surface of lapilli (Yoshinaga & Aomine, 1962). Stability diagrams show that imogolite is more stable than halloysite over a wide range of Si activity (Percival, 1985). Above a certain level of Si activity, halloysite is more stable than imogolite. Both halloysite and imogolite,

however, are less stable than kaolinite. The stability lines of these minerals are not dependent on either pH or basic cations. The stability line for proto-imogolite allophane is parallel to that of imogolite but may lie either above or below the line for imogolite (Percival, 1985). If the allophane line lies above that of imogolite, imogolite will be more stable than allophane, and kaolinite will be more stable than imogolite.

Since halloysite often occurs in older tephras, allophane may weather to halloysite when the Si activity in the soil solution is high. Thus, this transformation is more likely to occur in rhyolitic tephra than in basaltic and andesitic tephra (Kirkman & McHardy, 1980; Dahlgren *et al.*, 2004). For proto-imogolite allophane to weather to halloysite would require a rearrangement of crystal structures which can only take place by dissolution and reprecipitation.

Halloysite can also form directly from volcanic glass when the Si activity in the soil solution is high (Parfitt *et al.*, 1984; Parfitt & Wilson, 1985). Singleton *et al.* (1989) showed that halloysite forms in preference to allophane when the Si activity exceeds 10 mg l^{-1} while allophane forms in preference to halloysite when this activity is <10 mg l^{-1}. Halloysite formation may occur in microsites within an allophane matrix (Aomine & Wada, 1962). In New Zealand aeolian soils, halloysite (and no allophane) is found where the rainfall is 1000 mm, while only allophane is found where the rainfall is 1600 mm. Kaolinite may be present in A horizons of Andisols that also contain halloysite and where seasonal desiccation occurs, but it is absent in B horizons (Dahlgren *et al.*, 2004).

Since Si activity in the soil solution is controlled by drainage, climate, vegetation and tephra composition, volcanic-ash soils may contain various proportions of allophane and halloysite. Where allophane predominates, the soils are usually Andisols, but where halloysite predominates, the soils range from Inceptisols to Alfisols, Ultisols and Oxisols. Where tephra, drainage, parent material and/or climate are the dominant controlling factors, the soil pattern in the landscape can be predicted (Lowe, 1986; Singleton *et al.*, 1989; Lowe & Palmer, 2005). Where Si in the soil solution is close to 10 mg l^{-1}, either halloysite or allophane may predominate, and the pattern of soils in the landscape is difficult to predict (Parfitt *et al.*, 1984; Parfitt & Wilson, 1985).

Precipitation and solubility in other soils

Allophane forms not only from volcanic glass but also from feldspar and/or biotite (Parfitt & Kimble, 1989). Rapid weathering of feldspar occurs at pH = 5, while allophane precipitates at pH = 4.8. There is, therefore, a narrow pH range where feldspar weathers to allophane (Parfitt & Kimble, 1989).

Allophane and imogolite formation in Spodosols and related soils has been described by Tait *et al.* (1978), Young *et al.* (1980), Farmer *et al.* (1980, 1983), Childs *et al.* (1983), Parfitt & Saigusa (1985), Parfitt & Kimble (1989), Dahlgren & Ugolini (1989), Gustafsson *et al.* (1995), Göttlein & Stanjek, (1996), van Hees *et al.* (2000), and Karltun *et al.* (2000). Up to 20% Al-rich allophane has been found in the Bs horizons having pH(H$_2$O) values between 5.1 and 5.4.

Zysset *et al.* (1999) investigated Al extractability and solubility in six horizons of a Typic Haplohumod from Switzerland. Pyrophosphate and oxalate extractions as well as successive acid leaching indicated that in the upper horizons, reactive Al was mainly bound to soil organic matter, whereas in the lower horizons, where imogolite was present, Al was of inorganic nature. Batch equilibrium experiments showed that in the upper horizons, Al solubility was controlled by complexation reactions to soil organic matter. Kinetic studies with samples of the lower horizons showed that ion activity products with respect to both Al(OH)$_3$ and imogolite reached a constant value after reaction times of 16 days. For pH >4.1, the data were consistent with either Al solubility control by imogolite-type material, which dissolves incongruently, or a simultaneous equilibrium with imogolite and hydroxy-Al interlayers of clay minerals. For pH <4.1, data indicated solubility control by poorly crystalline kaolinite.

Simonsson & Berggren (1998) examined the Al solubility and dissolution kinetics of Al and Si in the upper B horizon of podzols and its relation to the solid phase of the soil. Oxalate and pyrophosphate extractions suggested that secondary Al was mainly organically bound in most soils, and imogolite-type materials seemed to constitute much of inorganic secondary Al. No single gibbsite or imogolite equilibrium could explain Al^{3+} activities. In all samples, Al solubility was closely related to the molar ratio of Al to C in the pyrophosphate extracts (Al$_p$/C$_p$). Solubility increased with the Al$_p$/C$_p$ ratio until the latter reached ~0.1. This indicated that solubility was controlled by organic complexation, at least when Al$_p$/C$_p$ was small. The Si dissolved slowly in most soils used in the kinetic experiments. Therefore, imogolite-type materials in the upper B horizon dissolved slowly because of coating with humic substances or ageing or both.

Giesler *et al.* (2000) showed that Si, Al, and Fe within the humus layer (O horizon) play an important part in the biogeochemical cycling of these elements in podzolic soils. The process of podzolization was reviewed by Lundström *et al.* (2000).

Allophane has been found in soils from quartzo-feldspathic loess overlying stony alluvium (Parfitt & Webb, 1984). These soils are not podzolized but are Ochrepts having an ustic soil moisture regime. Since there is leaching throughout the B horizon of these soils, particularly in winter, the Si levels in the soil solution may be low enough for allophane to form.

Allophane can also form in drains (Farmer, pers. comm.), tuffs (Silber *et al.*, 1994), lava (Jongmans *et al.*, 1995), lacustrine sediments (Warren & Rudolph, 1997), Silurian sediments (Moro *et al.*, 2000), and limestone (Farmer *et al.*, 1977a). Allophane is also involved in the formation of indurated layers or pans in soils and sediments (Thompson *et al.*, 1996; Wilson *et al.*, 1996; Jongmans *et al.*, 2000). Allophane, however, is most commonly found in tephra layers under humid climates, where volcanic glass dissolves to produce allophane.

PROPERTIES

Allophane and imogolite have large specific surface areas (700–1500 m^2 g^{-1}), have positive and negative charges (Parfitt, 1990a), and interact strongly with anions, such as phosphate and arsenate. Organic matter is also strongly bound to allophane and imogolite, decomposing only slowly in allophane-rich soils. Such soils are usually very porous and have high water content.

Laboratory experiments showed that sorption of organic matter (humic substances) carrying negatively charged functional groups, increases the negative surface charge of allophane (Perrott, 1978; Yuan *et al.*, 2000). Humic substances are apparently adsorbed to allophane surfaces by ligand exchange (Parfitt *et al.*, 1977; Yuan *et al.*, 2000) and up to 25% C is associated with allophanic soil clay fractions (Parfitt & Henmi, 1982; Churchman

& Tate, 1986). Similarly, the high affinity of 5′-adenosine monophosphate (AMP) for allophane may be ascribed to ligand exchange involving the phosphate group of the nucleotide (Hashizume & Theng, 2007). On the other hand, positively charged alkylammonium ions are physically adsorbed by allophane (Theng, 1972), while neutral amino acids (at pH 6) adsorb as zwitterions through electrostatic interactions (Hashizume & Theng, 1999). Interestingly, some allophanes can apparently discriminate between optical isomers of alanyl-alanine (Hashizume *et al.*, 2002).

Interaction with organic matter and organic matter stabilization

Allophanic soils occupy 0.8% of the global land area, and contain 5% of the global soil C (Dahlgren *et al.*, 2004). The residence time of C in allophanic soils measured by C-14 is much greater than that of other soil orders (Nierop *et al.*, 2007). The large C content of allophanic soils partly account for their excellent physical and water-storage properties, and high productivity (Dahlgren *et al.* 2004). Under natural conditions with high rainfall, allophanic soils are usually formed under forests. Forest growth on young volcanic soils tends to be limited by nitrogen availability, while on old volcanic soils primary production tends to be limited through lack of P (Herbert & Fownes, 1995). The C in soil, derived from the forest biomass, is stabilized both by interaction with allophane and Al ions (Torn *et al.*, 1997). In New Zealand soils that are now under pasture, but had

been converted from native forest, the amount of C was related to Al (extracted in pyrophosphate) rather than to the percentage of clay (Fig. 3) (Percival *et al.*, 2000). In Costa Rica, soil C concentrations were positively correlated with allophane, imogolite, and ferrihydrite at high elevation sites, and to Al in organo-metal complexes at low elevation sites (Powers & Schlesinger, 2002).

In measuring changes in soil C over 20 y in soils under long-term pasture in New Zealand, Schipper *et al.* (2007) found only small losses of dissolved organic C and bicarbonate. They also reported that 0.9 ± 0.2 T C/ha/y could be lost from soils under dairy farming, possibly as a result of land-use intensification (MacLeod & Moller, 2006) where inputs of C were lower than losses by mineralization (to CO_2) and leaching. In the case of allophanic soils, however, the loss was 0.4 ± 0.3 T C/ha/y (Parfitt *et al.*, 2007). This would suggest that a fraction of the soil C was stabilized by allophane and Al, and C mineralization was less than in non-allophanic soils (Saggar *et al.*, 1994).

Parfitt *et al.* (1997) reported that, under long-term pasture, an allophanic soil $(0-20$ cm) contained 144 T C/ha, while a Recent soil formed in alluvium contained 73 T C/ha (Table 1). After cropping for 20 y, the C content decreased by 23 T C/ha in the Recent soil, but by only 10 T C/ha in the allophanic soil where the C was more stable. Modelling with *Century* (Metherall *et al.*, 1993) suggested that the passive pool of the allophanic soil contained more C in the decadal pool. The alkyl groups, present in the clay fraction of the
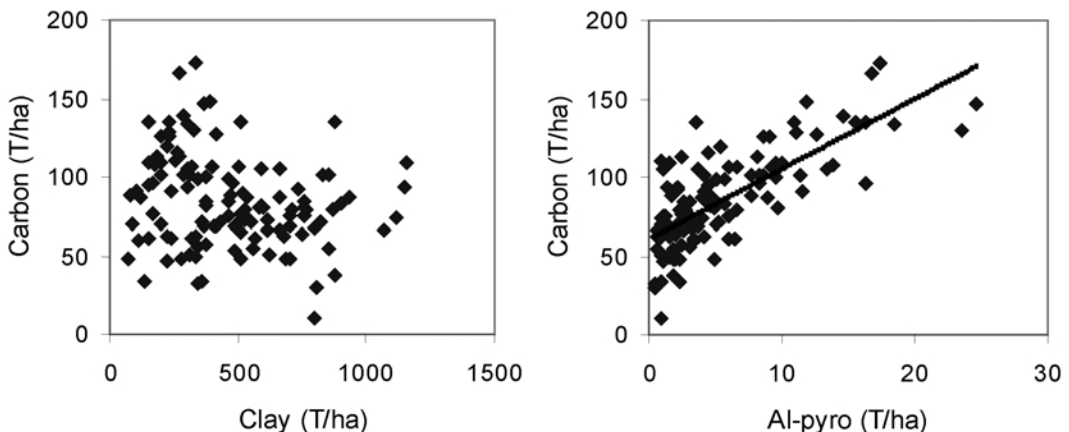

Fig. 3. Relationship between soil carbon, clay and pyrophosphate-extractable Al in New Zealand soils $(0-20$ cm) under pasture (after Percival *et al.*, 2000).

TABLE 1. Carbon in allophanic and non-allophanic soils
(after Parfitt *et al.*, 1997)

	Pasture 100 y	Crop 20 y
Allophanic soil	144	134
Alluvial Inceptisol	73	50

allophanic soil, may be resistant to decomposition; complexation by Al also causes the organic matter to be less susceptible to biological attack and mineralization to CO_2 (Baldock & Nelson, 2000). In Andisols from the Canary Islands, Rodríguez Rodríguez *et al.* (2004, 2006) found that allophane and Fe oxides not only sequestered C but also gave some resistance to soil erosion by rain. Dahlgren *et al.* (2004) suggested that organic matter in Andisols might also be stabilized by sorption to micropore surfaces, since such pores are inaccessible to microbes and their extracellular enzymes.

Parfitt *et al.* (2002) investigated the stability of C in an allophanic soil and a gley soil by measuring stable C isotopes (delta C-13) and bomb C-14 under both permanent pasture (C3 plants) and continuous (25 y) maize (a C4 plant) on the same farm. The C contents under pasture and maize were similar but the allophanic soil contained more C than the gley soil. Within the plough layer the input of maize C (and the loss of pasture C) over 25 y was 27 T/ha

for the allophanic soil and 31T/ha for the gley soil, indicating that the mineralization of fresh C was not very different. They suggested that it was the old pasture C and old forest C that was stabilized by allophane and Al in the allophanic soil. Similarly, Buurman *et al.* (2007) and Paul *et al.* (2008) found that recently incorporated soil organic matter in Andisols under tropical pastures was not well stabilized.

In highly allophanic soils, the organic matter appears to interact rather slowly with allophane. Nevertheless, allophane-organic matter complex formation accounts for the slower rates of C and N mineralization in these soils compared with non-allophanic soils (Broadbent *et al.*, 1964; Zunino *et al.*, 1982; Legay & Schaefer, 1984). This slow mineralization was first shown by bomb C-14 measurements on an allophanic and a non-allophanic soil between 1960 and 1970 (Rafter & Stout, 1970). These data were recently modelled by Troy Baisden, Rafter Lab, GNS Science, New Zealand (Fig. 4), and show that the incorporation and turnover of C is slower in allophanic soils. The process also accounts for the observation that, per unit of organic C, biochemical activities, including most enzyme activities, are lower in allophanic than non-allophanic soils (Ross *et al.*, 1982).

Osher *et al.* (2003) measured stable C isotopes in Hawaiian soils where pasture and sugar cane (C4 plants) had been grown for 100 y on land that had previously been under forest (a C3 plant). Within
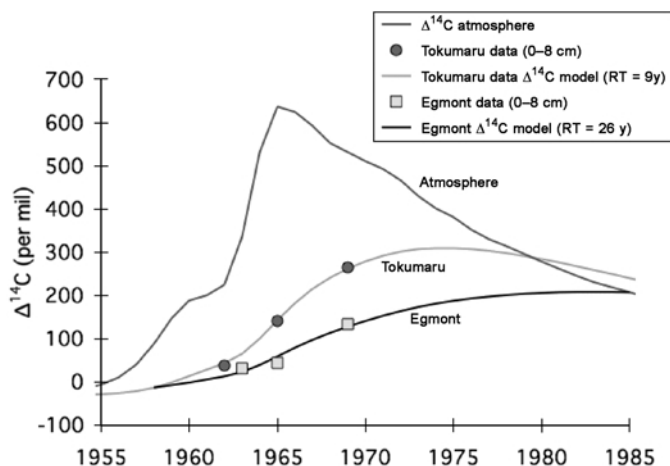

FIG. 4. Bomb C-14 incorporation in allophanic (Egmont) and non-allophanic (Tokomaru) soils under similar climate and land-use (after Rafter & Stout (1970); data and residence times, courtesy of Troy Baisden, Rafter Lab, GNS Science, New Zealand).

the pasture root zone (0−40 cm), additions of pasture (C4) organic matter were offset by losses of C3 carbon. The concentration of Fe/Al oxides appeared to control the quantity of C stored in the soils, as well as changes in the depth and magnitude of stored C that occurred with each type of land-use change. Growing sugar cane appeared to induce both dissociation of Fe/Al oxide-humus complexes, and losses of oxide-associated organic matter from the profile. Under pasture, these complexes were translocated to deeper soil horizons, leading to an increase in C storage and apparent C turnover time below 50 cm depth. In this high-rainfall region, soil C was apparently lost by downward movement, either as colloids or in solution, or by emission to the atmosphere as CO_2.

Working in Ecuador, Lopez-Ulloa et al. (2005) and Paul et al. (2008) measured delta C-13 in paired plots where C4 pasture was converted to C3 secondary forest in Andisols and sedimentary Inceptisols. Soil C contents were greater in Andisols than in Inceptisols. The mean residence time of forest-derived C in pastures increased from 37 to 57 y with increasing silt + clay content in the Inceptisols, but was independent of such soil properties in Andisols. These results further indicate that long-term organic C stabilization is effected through complexation with metals and allophane in Andisols, and through sorption to clay minerals in Inceptisols. There is good evidence to show that recently incorporated C is not stabilized in Andisols while, in Inceptisols, part of this C is stabilized by interaction with poorly crystalline oxides (Lopez-Ulloa et al., 2005; Paul et al., 2008).

Basile-Doelsch et al. (2005, 2007) used ΔC and $\Delta^{13}C$ data, and density fractionation to study C sequestration by minerals in a volcanic soil of La Réunion. The buried horizons of the soil contained much proto-imogolite and proto-imogolite allophane. These minerals stored large amounts of organic matter that turned over very slowly; the residence time of organic C in the most stabilized buried horizon was 163,000 y. Although there may have been a contribution from black C (charcoal), this value is comparable to that for organic C stabilized in Hawaiian volcanic soils. A large part (83%) of the soil organic matter in the 3Bw horizon (below 52 cm) was present as organo-mineral complexes. More organic matter was immobilized by imogolite-type materials than by Fe oxides. The amounts of imogolite-type materials were found to be midway between that of allophane and Al in Al-

humus complexes, and Basile-Doelsch et al. (2005, 2007) suggested polymerization could be limited by the presence of organic matter.

Hiradate et al. (2006) investigated three representative allophanic Andisols from Japan using solid-state C-13, Al-27 and Si-29 NMR spectroscopy and δC-13 measurements. Aliphatic, O-alkyl, and carbonyl C were relatively abundant in the uppermost horizons, whereas aromatic C was concentrated in the subsurface horizons, where it persisted and showed resistance to degradation. The contribution ratio of C4-plant-derived C (mainly from *Miscanthus sinensis*) to the total C, evaluated from δC-13 values, was 35−42%, 59−62%, and 50−53% in the subsurface horizons, and 12, 23, and 48% in the uppermost horizons. The lower C4/total C ratio in the uppermost horizons reflected the influence of recent vegetation. The NMR results indicated that most of the Al^{IV} in volcanic glass had already converted into Al^{VI}, while large amounts of allophane, imogolite, allophane-like constituents, and proto-imogolite were formed in the B horizon within the past 25,000 y. The concentrations of these non-crystalline minerals, determined by Si-29 NMR spectroscopy, were generally similar to those determined by acid-oxalate dissolution.

Rasmussen et al. (2006, 2007) studied soils formed from three different parent rocks under conifers in California. The andesitic soils were dominated by non-crystalline materials (allophane, Al-humus complexes), the granitic soils by crystalline minerals (kaolinite, vermiculite), and the basaltic soils by a mix of crystalline and non-crystalline materials. Soil C mineralization rates for the soils followed the order andesitic < basaltic < granitic, and correlated negatively with the content of Fe-oxyhydroxides, Al-oxyhydroxides, and Al-humus complexes, suggesting mineral control of C mineralization. Data for respired CO_2 suggested that soil mineralogy also controlled the increased rate of C mineralization after adding C-13 labelled forest litter. This observation, however, may reflect differences in the nature of the microbial communities among the three groups of soils.

Organic matter composition

Buurman et al. (2007) investigated a catena of allophanic and non-allophanic soils in perhumid Costa Rica using gas chromatography-mass spectroscopy (GC-MS) and analytical pyrolysis techniques. The molecular chemistry of the organic fractions

indicated intensive decomposition of plant-derived organic matter and a major contribution of microbial sugars and N-compounds to the soil organic matter. Both the decomposition of plant-derived organic matter, including the relatively recalcitrant constituents, and the relative contribution of microbial organic matter, were greater in allophanic than in non-allophanic samples. Buurman *et al.* (2007) suggested that chemical protection did not act on primary organic matter, although it could influence the accumulation of secondary organic matter in these soils. The effect of allophane on organic matter might be due to the incorporation of decomposition products and microbial organic matter in very fine aggregates that had large water contents for much of the year. Although large concentrations of aliphatics were found with allophane, there was no evidence for any specific mineral-organic interaction. These results, together with those of Parfitt *et al.* (2002), suggest that plant materials are not bound to allophane, Al or Fe, as much as the microbial by-products of decomposition.

Volcanic-ash soils from Atlantic volcanic islands were studied by Naafs & van Bergen (2002) and Nierop *et al.* (2005), also using GC-MS and analytical pyrolysis techniques. In contrast to many non-volcanic-ash soils, the soil organic matter was dominated by polysaccharides and protein derivatives, while lipids and lignin were depleted. The polysaccharides may partly (>13%) be stabilized by interaction with allophane as suggested by Parfitt *et al.* (1999) in the case of podzols.

Gonzalez-Perez *et al.* (2007) found large amounts of both alkyl and carbohydrate-derived compounds in the pyrolysates of Andisols. This might be because the components from which they originated were stabilized by interaction with short-range-order minerals. Non-andic soils contained relatively little stabilized C. The humic and fulvic acids in the allophane-rich soils gave rise to complex pyrograms and compound assemblages. The alkylic compounds in the humic acids from the allophane-rich soils were highly condensed, whereas those from Cambisols were more loosely joined fatty acids and other alkylic structures. The authors suggested that microbial and plant metabolites were rapidly incorporated and stabilized within the allophane-rich soils.

In investigating volcanic-ash soils under varied vegetative covers along an altitudinal transect near the upper forest line in Ecuador, Nierop *et al.* (2007) found that all the mineral horizons "were characterised by a high degree of aliphatic compounds". Small differences were found within the lipid constituents, while polysaccharides and lignin were virtually absent from the A and Bw (mineral) horizons containing <6% allophane. The small abundance of polysaccharides in soils that have undergone severe organic matter decomposition is not unusual, but is uncommon in Andisols. The presence of lipids was ascribed to the low pH of these soils, while the absence of polyphenols suggested rapid decomposition (Nierop *et al.*, 2005, 2007; Lorenz *et al.*, 2007).

These results and conclusions about the fractions of soil organic matter and their stabilization in soils containing allophane are summarized in Tables 2 and 3.

TABLE 2. Fractions of soil organic matter (SOM) that are influenced by the presence of allophane

SOM stabilized by allophane in Podzols and Andosols	References
Dominated by carbohydrate and protein	Gonzalez-Perez *et al.* (2007) Nierop *et al.* (2005) Naafs & van Bergen (2002) Parfitt *et al.* (1999)
Aliphatic compounds present	Nierop *et al.* (2007) Gonzalez-Perez *et al.* (2007) Parfitt *et al.* (1997)
Depleted in lignin, polyphenols, lipids	Nierop *et al.*, (2005, 2007) Naafs & van Bergen (2002)
Plant-derived material strongly decomposed	Buurman *et al.* (2007)
Microbial sugars and N compounds	Buurman *et al.* (2007)

TABLE 3. Recent conclusions about soil organic matter stabilization in soils containing allophane.

Conclusion	References
Fresh organic matter is not stabilized	Paul *et al.* (2008) Buurman *et al.* (2007) Lopez-Ulloa *et al.* (2005) Parfitt *et al.* (2002)
Plant-derived material may not bind to Al or allophane	Buurman *et al.* (2007) Parfitt *et al.* (2002)
Microbial products stabilized slowly	Buurman *et al.* (2007) Parfitt *et al.* (2002)
Carbon persists for thousands of years	Basile-Doelsch *et al.* (2007) Basile-Doelsch *et al.* (2005) Chadwick *et al.* (2003)

Leaching of organic matter

In investigating leaching of material from a non-allophanic Andisol under forest in the Vosges Mountains (France), Aran *et al.* (2001) found very small concentrations of dissolved organic C, Al and Fe in soil solutions collected with zero-tension plate lysimeters over a period of 7 months. The concentrations of water-dispersible clays were also small, suggesting that no significant translocation of clays occurred in the soil profile. The low mobility of DOC, together with its strong resistance against mineralization, probably accounted for the large accumulation of C in this soil.

Nevertheless, some dissolved organic carbon (DOC) does move through allophanic soils. Neff *et al.* (2000) measured fluxes of DOC, dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) in the laboratory using samples from the O horizons of Hawaiian volcanic soils varying in age, nutrient availability and mineralogy. They found that physical desorption, dissolution, and chemical sorption were the principal factors controlling the release of dissolved organic matter from these surface horizons. The sole exception to this pattern was at the oldest of three sites where there was a significant relationship between DOC and CO_2 flux. The oldest site also contained the smallest mineral and allophane contents, while the correlation between respiration and DOC indicated that microbial activity influenced DOC flux at this site.

Perakis & Hedin (2007) analysed water samples from small streams running through old growth forests in Chile and Argentina. The concentration of DOC in these waters ranged from 0.2 to 9.7 mg C/l,

while that of DON ranged from 0.008 to 0.135 mg N/l. The concentrations of DOC and DON were positively related to mean annual precipitation (accounting for 64% of the variation). When the soil parent material was included in the multiple regression analysis, 79% of the variation in watershed DOC could be accounted for. The ratio of DOC:DON averaged 29 for waters with volcanic ash and basalt geology, and 73 for waters with a non-volcanic geology, suggesting strong adsorption of hydrophobic molecules with a low C:N ratio by andic materials.

Lilienfein *et al.* (2004a,b) studied leaching of dissolved organic matter and the associated nutrient elements in andesitic soils from California. The ability of the soils to adsorb and retain dissolved organic matter increased with soil age and soil development, reflecting an increase in allophane concentrations. Analysis of the soil solutions collected with suction cups during the main snow melt period suggested the older soils adsorbed more DOP and phosphate (PO_4). Stepwise multiple regression analyses showed that allophane concentrations controlled the adsorption of DOP and PO_4 in these soils. Tests of preferential adsorption of DOP *vs.* PO_4 and DOC *vs.* DOP showed that the adsorption strength increased in the order: DOC < DOP < PO_4. Consequently, the tendency of DOP and PO_4 to leach from these andesitic soils decreased as soils and ecosystems developed.

Phosphate and arsenate adsorption

Most Andisols originally occurred under rain forest. In Hawaii, precipitation is the major factor

determining forest productivity in forests that contain N-fixing organisms. In high rainfall sites, P supply and availability play important roles in controlling productivity and soil-organic matter dynamics (Idol *et al.*, 2007). Although P is strongly sorbed by Al and allophane (Parfitt *et al.*, 1989), it is also recycled through both inorganic and organic pathways (Dahlgren *et al.*, 2004). In New Zealand and Hawaiian soils, microbial demand for P may control its availability (Parfitt *et al.*, 1989; Olander & Vitousek 2005). Liu *et al.* (2006) found that tree roots were less able to mobilize soil P from an allophanic soil than from a pumice soil. This is because the allophanic soil has a greater P-retention capacity, and a smaller concentration of plant-available P. For the same reasons, allophanic soils that are used for agriculture generally require larger amounts of fertilizer-P applications than non-allophanic soils (Edmeades *et al.*, 2006).

When phosphate solutions are added to allophane at pH 5–6 in the presence of $CaCl_2$, the first increments of P are rapidly and strongly adsorbed. As surface coverage increases, subsequent increments of P are more weakly adsorbed (Parfitt, 1989; Parfitt *et al.*, 1989). The amount of P which is strongly adsorbed ranges from 50 to 200 μmol g^{-1}, equivalent to 2–8 P ions per allophane spherule. The extent of adsorption increases with the Al:Si ratio of the allophane samples, and differs for natural and synthetic allophanes (Parfitt & Henmi, 1980; Clark & McBride, 1984). Phosphate is adsorbed by ligand exchange involving $Al(OH)$ and $Al(H_2O)$ groups at defect sites on the allophane surface. This exchange is followed by a slow reaction by which the allophane structure is disrupted and aluminium phosphate may precipitate (Rajan, 1975; Parfitt, 1989). Allophanic Andisols sorb less P than their non-allophanic counterparts that contain large amounts of Al-humus complexes and reactive AlOH groups (Dahlgren *et al.*, 2004).

Arai *et al.* (2005) investigated arsenate reactivity and surface speciation on a synthetic allophane. The adsorption experiments indicated that arsenate adsorption was initially rapid followed by a slow continuous uptake, and the adsorption processes reached steady state after 720 h. X-ray absorption spectroscopic analyses suggested that arsenate predominantly formed bidentate binuclear surface species on Al octahedral structures, and these species were stable for up to 11 months. There was no evidence of crystalline precipitates. They concluded that the adsorption mechanisms at the allophane–water interface involved ligand exchange reactions between arsenate and surface-coordinated water molecules and hydroxyl and silicate ions. This implied that dissolved tetrahedral oxyanions (e.g. $H_2PO_4^{2-}$ and $H_2AsO_4^{2-}$) are readily retained on amorphous aluminosilicate minerals in waters and soils at near neutral pH. This inner-sphere adsorption mechanism is probably important in controlling dissolved arsenate and phosphate in amorphous aluminosilicate-rich low-temperature geochemical environments.

Besides being adsorbed by allophanic soils, P can also be lost by leaching (McDowell & Condron, 2004). The amount leached increases with the P status (soil test value) of the soil, and decreases with its P-retention capacity. Soils with a high P-retention capacity can remove most of the P from leachates. Nevertheless, the P concentration in the leachate from allophanic soils may be large enough to support algal growth in streams and rivers (McDowell & Condron, 2004), and this is an area requiring further research.

PHYSICAL PROPERTIES

Allophanic soils generally have a high porosity and a low bulk density. The allophane spherules, produced by weathering and dissolution of tephra, interact strongly, particularly when dried, to form both silt-size and sand-size aggregates (Wells & Theng, 1985; Churchman & Tate, 1987). The interaction between undried aggregates, however, is weak. Viscometry suggests interactions between individual allophane spherules involve both electrostatic and van der Waals attraction. The strongest interactions occur at pH ~6 when about equal amounts of positive and negative charges are present on the allophane surface (Wells & Theng, 1985).

Highly weathered and porous Andisols show pronounced shrinkage. Being more weathered and more porous, Bw horizons shrank more than Ah horizons (Bartoli *et al.*, 2007). The more pronounced the shrinkage, the more irreversible is the mechanical change. Samples of allophanic soils, taken with a corer that is quickly pushed into the soil, appear to expand and have a smaller bulk density compared with samples taken by carving the soil (Schipper *et al.*, 2007).

Since allophanic soils do not usually have continuous macropores, they are excellent filters, capable of removing faecal coliforms and bacteriophages from effluents (McLeod *et al.*, 2008).

Allophanic soils can also sorb and remove heavy metals (Adamo *et al.*, 2003). When Na-contaminated waste waters were applied to allophanic soils, the saturated hydraulic conductivity decreased, but only at high Na adsorption ratios (Menneer *et al.*, 2001). At this point, the concentration of DOC increased in the leachate, but no dispersed clay was observed. Irrigation with such waste waters could cause structural deterioration in the soil matrix. At high-moisture contents, however, the flow of leachate in the field was sufficient to overcome any adverse effects.

CONCLUDING REMARKS

This review was presented at a meeting of the Clay Minerals Group of the Mineralogical Society of Great Britain & Ireland (September 2008, at the Macaulay Institute) in memory of Colin Farmer, in acknowledgement of his contributions. I first met Colin in 1964 at Michigan State University where he helped me to enrol as a Masters student in the Soil Science Department. I also had the privilege of working with Colin at the Macaulay Institute in the 1970s. Colin was active in research well into his retirement, publishing his most recent paper in 2005 (Farmer *et al.*, 2005). Dealing with phytoliths as a source and sink of Si in solution of some European forest soils, this publication has so far been cited 16 times. His papers on allophane and imogolite have been cited more than 100 times, and have been used by many scientists. To quote the 12th century theologian and author John of Salisbury in *Metalogicon*, his treatise on logic, written in Latin in 1159: "We are like dwarfs sitting on the shoulders of giants. We see more, and things that are more distant, than they did, not because our sight is superior or because we are taller than they, but because they raise us up, and by their great stature add to ours." Indeed, we stand on the shoulders of giants.

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