

WEATHERING PROCESS OF VOLCANIC GLASS TO ALLOPHANE DETERMINED BY ^{27}Al AND ^{29}Si SOLID-STATE NMR

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Abstract—To clarify the weathering process of volcanic glass to allophane, solid-state ^{29}Si and ^{27}Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) signals of four Japanese volcanic glasses and two (Al- and Si-rich) allophanes were assigned. The volcanic glasses showed a broad ^{29}Si NMR signal between -80 and -120 ppm with the peak centered at ~ -104 ppm, indicating that they were rich in Si–O–Si bridging structure (silica gel-like polymer Si). Aluminum was present in tetrahedral form in the four volcanic glass samples. In both Al- and Si-rich allophanes, octahedral Al (3 ppm by ^{27}Al NMR) and imogolite-like Si ($Q^3\text{VIAl}$, -78 ppm by ^{29}Si NMR) were the major components. In a Si-rich allophane, NMR signals centered at around -85 ppm for ^{29}Si and 55 ppm for ^{27}Al were also observed, although it is possible that those signals were derived from impurities. Impurities could have originated from the soils and/or been unexpectedly synthesized during the purification procedures, e.g. during hot 2% Na_2CO_3 treatments. Based on the NMR spectra of size-fractionated soil samples, the weathering process of volcanic glass to allophane was proposed as follows: (1) dissolution of Al from volcanic glass accompanied by the transformation of IVAl to VIAl ; (2) formation of a gibbsite-like sheet resulting from the hydrolysis of the dissolved Al; (3) dissolution of silica gel-like polymer Si in volcanic glass resulting in the formation of monosilicic acid; and (4) formation of $\text{Si}(\text{OH})(\text{OVIAl})_3$ structure ($Q^3\text{VIAl}$) as a result of the reaction between the gibbsite-like sheet and the monosilicic acid. These formation reactions of allophane could occur in solution as well as on the surface of volcanic glass.

Key Words—Allophane, Imogolite, Solid-state MAS NMR, Speciation of ^{27}Al and ^{29}Si , Volcanic Glass.

INTRODUCTION

Volcanic ash contains volcanic glass as a major component, accompanied by some minor components such as plagioclase, feldspar, quartz and pyroxene (Dahlgren *et al.*, 1993). Volcanic glass is spread over a wide area through volcanic activity and then weathered to secondary minerals. In soil conditions where there is a low organic ligand concentration, volcanic glass is transformed into poorly crystalline aluminosilicates, such as allophane and imogolite, in the early stage of weathering. Allophane is composed of spherical hollow particles with a diameter of 3.5–5.0 nm whereas imogolite is composed of hollow thread tubes with inner and outer diameters of 1.0 and 2.0 nm, respectively. In the next stage of the weathering process, allophane and imogolite are transformed into halloysite, metahalloysite, and/or gibbsite. Halloysite could be formed after 2000 to 30,000 y of volcanic ash or pumice deposition depending on the weathering conditions (Wada, 1989). From the point of view of geological history, allophane and imogolite are regarded as transi-

tion products in the transformation of primary minerals to secondary minerals. Allophane and imogolite strongly affect soil chemical properties, because they have large amounts of active surface hydroxyls, which cause pH-dependent charge and strong ligand exchange reactions. Although allophane and imogolite are associated with soils derived from volcanic ash, they could also occur in any environment where sufficient Si and Al exist in solution to precipitate these rapidly forming minerals (Harsh *et al.*, 2002).

Volcanic glass is the most ‘weatherable’ component in volcanic ash. With weathering, clear glass becomes discolored to a shade of yellow-brown and then it turns semi-opaque (Dahlgren *et al.*, 1993). The initial rapid weathering of volcanic glass is accompanied by a release of cations. The kinetics of the release of Na and K is reported as parabolic, whereas that of Al and Si is linear (Dahlgren *et al.*, 1993). This process enriches the Al and Si in the framework. Silica-aluminum complexes would be formed in solution through co-precipitation or adsorption of Si on Al hydroxides, and then allophane, imogolite and halloysite would be formed depending on their Si/Al ratio (Yoshinaga *et al.*, 1973). In a pumice bed, allophane is found within the pumice grains, whereas imogolite occurs as macroscopic “gel films” filling the grain interstices (Yoshinaga *et al.*, 1973). Detailed formation processes of allophane and imogolite

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from volcanic glass, however, are not yet well understood.

The chemical structure of imogolite is well defined, because imogolite gives broad but important signals in X-ray diffraction (XRD) analysis. It has an ideal chemical formula of $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, very close to an experimental formula of $1.1\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2.5\text{H}_2\text{O}$. In imogolite, all Al is octahedral and makes up the gibbsite sheet. Each Si tetrahedron displaces the H from the three OH groups surrounding the Al octahedron in the gibbsite sheet. The fourth Si–O bond points away from the sheet and is neutralized by a proton to form Si–OH (Wada, 1989). The chemical structure of allophanes, however, continues to be debated, because allophanes give an X-ray amorphous XRD pattern (Wada, 1989). The chemical compositions of allophanes are extremely variable and have the empirical formula $x\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot y\text{H}_2\text{O}$, where x ranges from 0.8 to 2 and y is >2.5 (Harsh *et al.* 2002). To date, at least three kinds of allophanes have been reported: Al-rich allophane, Si-rich allophane and Silica Springs allophane. Aluminum-rich allophane has a Si/Al molar ratio of ~ 0.5 and is considered to have a gibbsite sheet and an imogolite-like Si tetrahedron. Silicon-rich allophane has a Si/Al molar ratio of ~ 1.0 and is proposed to have an incomplete tetrahedral silicate layer inside the gibbsite sheet with the imogolite-like Si tetrahedron (MacKenzie *et al.*, 1991). Other structural models for Si-rich allophane, which has an additional Si tetrahedral unit bound to the imogolite-like Si on Al-rich allophane forming a Si tetrahedron dimer and/or trimer, is also proposed (Henmi, 1988; Henmi *et al.*, 1997; Padilla *et al.*, 2002). Silica Springs allophanes are composed of more or less complete spherules with diameters of 2–3 nm and other partial spherules, with varying Si/Al molar ratios (0.6–1.0) depending on the precipitation environment. It has been proposed that the chemical structure of Silica Springs allophane is based on fragments of a single curved 1:1 aluminosilicate layer, in which the Si tetrahedral sheet (outer-shell) is more or less complete with a Si:^{IV}Al ratio of 3:1, and in which the ^{VI}Al octahedral sheet (inner component) is incomplete (Childs *et al.*, 1990). Silica Springs allophane lacks an imogolite-like Si tetrahedron. Ildefonse *et al.* (1994) reported that natural allophanes contained ^{IV}Al together with ^{VI}Al and that the (^{IV}Al)/(total Al) ratio increased as the Si/Al molar ratio increased. Childs *et al.* (1999) also reported that Silica Springs allophane contained Al^V together with ^{IV}Al and ^{VI}Al.

To clarify the chemical status of nuclei in solid form without destruction, nuclear magnetic resonance (NMR) spectroscopy has been used by applying a high-speed magic angle spinning (MAS) system and a high magnetic field. In the present study, to clarify the weathering process of volcanic glass to allophane, ²⁹Si and ²⁷Al MAS NMR signals of four Japanese volcanic glasses and two (Al- and Si-rich) allophanes were assigned, and size-fractionated soil

samples were subjected to NMR analyses. A selective dissolution technique was also applied to identify ²⁷Al and ²⁹Si NMR signals of allophane.

MATERIALS AND METHODS

Preparation of volcanic glass and allophane samples

Two volcanic glass samples, Hakusan and AT, were supplied by Dr Shigemitsu Arai. The Hakusan volcanic glass was collected from a volcanic glass layer embedded in a humus-rich horizon of alpine soil in Mt. Hakusan of Japan's North Alps, from which the 100 to 200 mesh-fraction was subjected to NMR analyses. The Hakusan volcanic glass is considered to have been deposited 6400 y B.P. and to be derived from Mt. Hakusan (Ohsumi, 1970; Ohsumi and Kumada, 1971; Ohsumi *et al.*, 1971). The AT volcanic glass (22,000–23,000 y B.P.) was collected from a volcanic glass layer (268–273 cm) of a peat soil in Ohnohara, Tsukude, Aichi, Japan (Arai *et al.*, 1988) and a coarse fraction ($>75 \mu\text{m}$) was subjected to NMR analysis. A volcanic glass, To-H (Towada-Hachinohe), was the pyroclastic flow deposit erupted from Towada caldera (12,000–13,000 y B.P.), and collected from Gonohe, Aomori, Japan (Machida and Arai, 1992). A coarse-sand fraction (0.2–2 mm) separated from a weathered volcanic ash collected at Uemura, Kumamoto, Japan, was used as another volcanic glass sample (Uemura). It was separated by repeated sonification and wet sieving followed by flotation in a heavy liquid.

Pure imogolite gelled films were collected from a buried pumice layer in Kitakami, Iwate, Japan, and subjected to NMR analysis after air drying (KiG film). Two allophanes (KiP and PA) were separated from weathered pumices collected in Murasakino, Iwate, Japan (KiP), and Choyo, Kumamoto, Japan (PA). A portion of each pumice sample was ground gently in a mortar, and the resultant slurry was passed through a 0.2 mm screen and fractionated into fine-clay, coarse-clay, silt and fine-sand fractions following the procedure described by Wada (2001). The Si/Al molar ratio of the separated allophane (fine clay fraction) was 0.51 for KiP (Al-rich allophane) and 0.71 for PA (Si-rich allophane).

Acid-oxalate treatment (Schwertmann, 1964)

A 100 mg sample of PA allophane ($<0.2 \mu\text{m}$) was shaken with 200 mL of 0.2 M NH_4 oxalate-oxalic acid solution (pH 3.0) at 120 rpm in the dark for 2 h at 30°C. The residue was collected by centrifugation at 10,000 rpm ($8600 \times g$) for 30 min. It was then freeze dried and subjected to solid-state MAS NMR analysis. By this treatment, 92% of the original PA allophane ($<0.2 \mu\text{m}$) was removed and 8% recovered.

2% Na_2CO_3 treatment

150 mg of KiP allophane ($<0.2 \mu\text{m}$) were suspended in 10 mL of a 2% Na_2CO_3 solution and refluxed for 6 h

by boiling. The residue was washed with deionized water, freeze dried, and subjected to solid-state MAS NMR analysis.

Solid-state MAS NMR analysis

A powder sample (~200 mg) was transferred into a high-speed spinning NMR tube (rotor, zirconia; cap, Vespel; 6 mm diam.; JEOL, Tokyo), and NMR signal was recorded with a JNM- α 300 FT-NMR system (JEOL, Tokyo). Signals of ^{27}Al were recorded at 78.2 MHz in a single-pulse experiment without decoupling, with a flip angle of $\pi/2$ for ^{27}Al (0.9 μs as a pulse width), an observation band of 80 kHz, an observation point of 4096 (resolution; 19.53 Hz), acquisition time of 0.013 s, pulse delay of 2 s, and 8 kHz of MAS. The standard chemical shift (0 ppm) was adjusted externally using 1 mol L $^{-1}$ of AlCl_3 solution. Signals of ^{29}Si were recorded at 59.6 MHz in a single-pulse experiment without decoupling, with a flip angle of $\pi/2$ for ^{29}Si (5.0 μs as a pulse width), an observation band of 50 kHz, an observation point of 4096 (resolution; 12.21 Hz), acquisition time of 0.082 s, pulse delay of 10 s, and 6 kHz of MAS. The standard chemical shift (–22 ppm) was adjusted externally using silicon rubber. A broadening factor of 100 Hz was employed in the Fourier transformation procedure for both ^{27}Al and ^{29}Si NMR experiments.

RESULTS AND DISCUSSION

To represent structures of silicate anions, Q^n notation is used in this study, where Q represents a Si atom bonded to 4 O atoms forming a tetrahedron. The superscript n indicates the connectivity, *i.e.* the number of other tetrahedra or octahedra attached to the SiO_4 tetrahedron. For aluminosilicates, the number of Al atoms bound to the central Si of a Q^n unit is given after Q^n , *e.g.* $Q^m\text{Al}$ means a SiO_4 tetrahedron connected via oxygen bridges to m Al and $n-m$ other Si tetrahedra, where $0 \leq m \leq 4$, and $m \leq n$.

^{29}Si NMR is sensitive to the chemical and structural surroundings of the Si atoms. Empirical relations have been established between the ^{29}Si chemical shift and the kind, number and structural arrangement of the nearest and second nearest neighbor atoms of the Si atoms. The ranges of the ^{29}Si chemical shifts of $Q^n\text{Al}$ coordination in silicates are: $Q^4\text{Al}$; –105 to –120 ppm, $Q^3\text{Al}$; –91 to –102 ppm, $Q^2\text{Al}$; –73 to –94 ppm, $Q^1\text{Al}$; –66 to –83 ppm, $Q^0\text{Al}$; –60 to –82 ppm (Engelhardt, 1996). In aluminosilicates, the ^{29}Si chemical shift ranges are: $Q^4\text{Al}$; –97 to –105 ppm, $Q^3\text{Al}$; –92 to –100 ppm, $Q^2\text{Al}$; –86 to –95 ppm, $Q^1\text{Al}$; –82 to –92 ppm (Wilson, 1987). In layered aluminosilicates, the chemical shift ranges of Si in tetrahedral sheets are: $Q^3\text{Al}$; –89 to –99 ppm, $Q^2\text{Al}$; –84 to –91 ppm, $Q^1\text{Al}$; –81 to –86 ppm, $Q^0\text{Al}$; –75 to –79 ppm (Engelhardt, 1996). In the present study, all four volcanic glasses

showed broad ^{29}Si MAS NMR signals between –80 and –120 ppm with the peak centered at \sim –104 ppm (Figure 1). Farnan *et al.* (1987) reported that silica glass which was composed of $Q^4\text{Al}$ and $Q^3\text{Al}$ gave sharper resonance peaks centered at –111 and –101 ppm, respectively (\sim 10 ppm of full width at half height). Therefore, the broad ^{29}Si NMR signals of the four Japanese volcanic glasses observed in the present study could not be explained by the presence of amorphous silica glass alone. They seemed to be close to those of hydrothermal products of Na aluminosilicate glass (SiO_2 ; 71%, Al_2O_3 ; 17%, Na_2O ; 12%, Yang and Kirkpatrick, 1989). It was likely that at least some of the Si in the four Japanese volcanic glasses were bonded to Al through an O bridge, resulting in the shift of the ^{29}Si NMR peak to a lower magnetic field (higher chemical shift value).

Judging from the information described above, the majority of Si in these volcanic glasses would be present as $Q^4\text{Al}$, $Q^3\text{Al}$, $Q^2\text{Al}$ and $Q^1\text{Al}$. Similar conclusions have been reached for some Italian volcanic glasses by two-dimensional phase-adjusted spinning sidebands (2D-PASS) ^{29}Si NMR (Slejko *et al.*, 2003). Therefore, the four Japanese volcanic glasses are rich in the Si–O–Si bridging structure. Several natural volcanic glasses in Italy have been reported to show broader ^{29}Si NMR signals centered between –93.5 and –97.8 ppm (Petrini *et al.*, 1999, 2001). Silicates in the four Japanese volcanic glasses seemed to be more polymerized, and the presence of a Si–O–Si bridging structure in them would be more abundant than in those of Italian volcanic glasses.

A chemical shift of solid-state ^{27}Al MAS NMR is not sensitive to the nuclear environment and structural features, because of the extreme line broadening of the quadrupole. However, it is possible to differentiate tetrahedral Al (resonates at \sim 50–90 ppm) from octahedral Al (–10 to 20 ppm). The four Japanese volcanic glasses gave an intense resonance peak centered at 49 ppm in ^{27}Al NMR, which corresponds to tetrahedral Al (Figure 1). In the AT, Hakusan and Uemura volcanic glasses, a minor peak was also observed at \sim 0–10 ppm, which corresponded to octahedral Al. Slejko *et al.* (2003) reported that ^{27}Al NMR of two Italian volcanic glasses showed a single resonance peak centered at 51.2 and 52.7 ppm. Petrini *et al.* (1999) also studied ^{27}Al NMR spectra of two other Italian volcanic glasses and showed that one was composed of tetrahedral Al alone (resonated at 53.9 ppm) and the other was composed of tetrahedral Al (52.0 ppm) as a major component and octahedral Al (12.7 ppm) as a minor component, the same as the three Japanese volcanic glasses (AT, Hakusan and Uemura). It might be possible that the octahedral Al in these three Japanese volcanic glasses is derived from a component of weathered products of volcanic glasses. Yang and Kirkpatrick (1989) studied hydrothermal products of albite and aluminosilicate

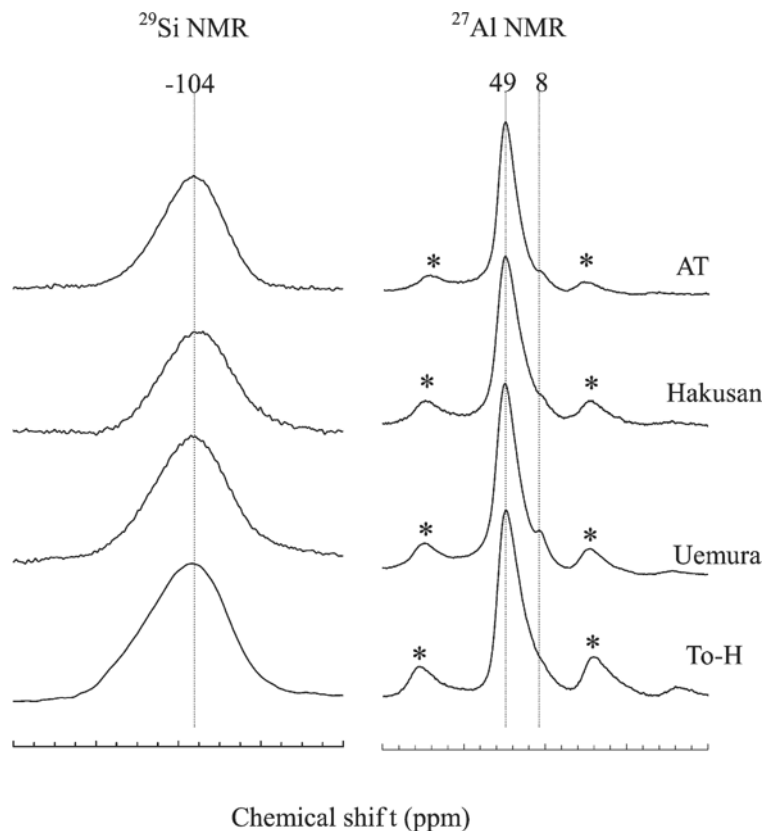


Figure 1. ^{29}Si and ^{27}Al MAS NMR spectra of four Japanese volcanic glasses. *: spinning side band (SSB).

glass using a ^{27}Al - ^1H cross polarization (CP) MAS NMR technique and concluded that tetrahedral Al in these minerals was converted to octahedral Al as a constituent of kaolinite.

Aluminum-rich KiP allophane ($<0.2\ \mu\text{m}$) showed a sharp resonance peak at $-78\ \text{ppm}$ in ^{29}Si NMR (Figure 2A, left), which corresponds to the imogolite-like Si tetrahedron attached to three aluminol groups (Al-OH) of the gibbsite sheet and one silanol group (Si-OH) ($Q^3\text{VIAl}$). The ^{27}Al NMR spectrum of KiP allophane indicated that almost all Al in this allophane is present as octahedral Al (Figure 2A, right). Both ^{29}Si and ^{27}Al NMR spectra of Al-rich KiP allophane are similar to those of imogolite (Figure 2B), indicating that the chemical structure of Al-rich KiP allophane is very close to that of imogolite, in agreement with previous studies (MacKenzie *et al.*, 1991; Padilla *et al.*, 2002).

In the case of Si-rich PA allophane ($<0.2\ \mu\text{m}$), the ^{29}Si NMR spectrum also showed the sharp imogolite-like Si peak at $-78\ \text{ppm}$ together with some accessory minor peaks which resonated at -85 and $-92\ \text{ppm}$ (Figure 2C, left). These minor peaks were also observed in Al-rich KiP allophane, but they were more intense in Si-rich PA allophane. Tetrahedral Al which resonated at $55\ \text{ppm}$ in ^{27}Al NMR was also more obvious in Si-rich PA allophane (Figure 2C, right) than in Al-rich KiP allophane (Figure 2A, right).

To assign ^{27}Al and ^{29}Si NMR signals of Si-rich PA allophane, a selective dissolution technique was applied. It is well known that acid-oxalate is a good reagent for dissolving allophanes and imogolites selectively (Wada, 1989). After treating the PA allophane ($<0.2\ \mu\text{m}$) with acid-oxalate, the resonance peaks at -78 and $-85\ \text{ppm}$ in ^{29}Si NMR spectrum were weakened, and other broad peaks centered at -92 , -102 and $-107\ \text{ppm}$ were strengthened (Figure 2D, left), indicating that ^{29}Si NMR signals observed at -92 , -102 and $-107\ \text{ppm}$ could have been derived from impurities other than allophane. These impurities might include 1:1 aluminosilicates, volcanic glasses and silica gels (Hiradate, 2004). Both ^{29}Si NMR signals which resonated at -78 and $-85\ \text{ppm}$ were removed by the acid-oxalate treatment. Therefore, they might be regarded as constituents of Si-rich PA allophane. MacKenzie *et al.* (1991) assigned both ^{29}Si NMR signals which resonated at -78 and $-85\ \text{ppm}$ to allophane itself. However, it might still be possible that the latter signal ($-85\ \text{ppm}$) could have been derived from impurities.

Some impurities could have originated from soils, but it could also be possible that the artifacts are unexpectedly synthesized during the purification procedures. For example, 2% Na_2CO_3 treatments have commonly been used to purify allophanes and imogolites, because it has been believed that this treatment can remove "allo-

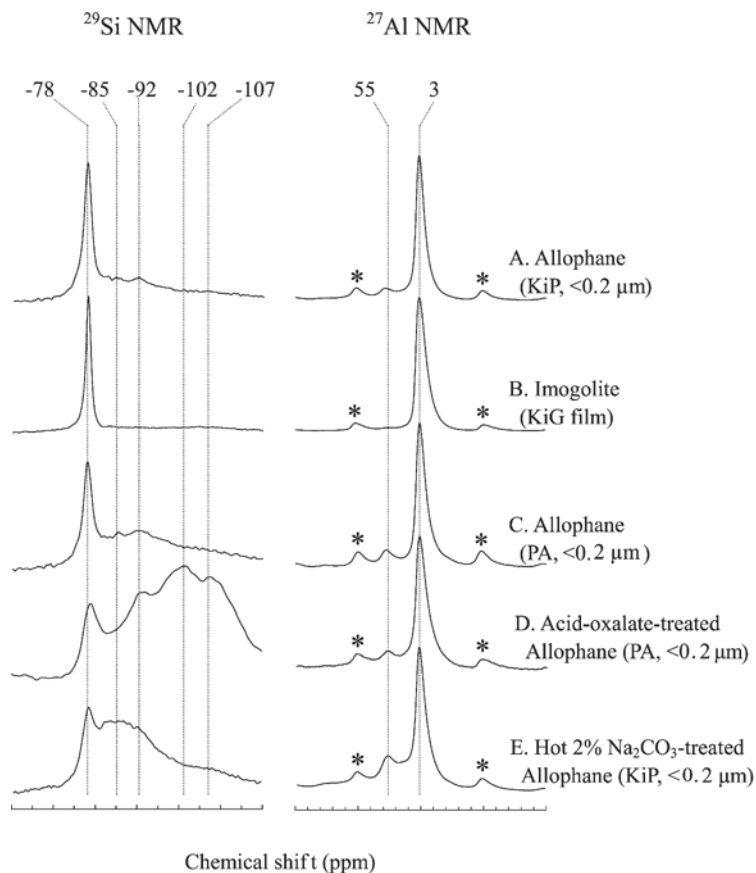


Figure 2. ^{29}Si and ^{27}Al MAS NMR spectra of (A) Al-rich KiP allophane ($<0.2\ \mu\text{m}$), (B) imogolite (KiG film), (C) Si-rich PA allophane ($<0.2\ \mu\text{m}$), (D) acid-oxalate-treated Si-rich PA allophane, and (E) hot 2% Na_2CO_3 -treated Al-rich KiP allophane. *: spinning side band (SSB).

phane-like” constituents and/or “proto-imogolites” without dissolving allophane and imogolite (Wada, 1989). Farmer *et al.* (1977), however, pointed out that hot 2% Na_2CO_3 treatment converted allophane and imogolite into new amorphous phases, in which the infrared spectra of the new phases showed some analogy with those of zeolites. Therefore, Farmer *et al.* (1977) recommend cold 5% Na_2CO_3 treatment for 16 h to avoid this problem. In the present study, the effects of the hot 2% Na_2CO_3 treatment for 6 h on ^{29}Si and ^{27}Al NMR spectra of Al-rich KiP allophane were demonstrated. It was clearly shown that the hot 2% Na_2CO_3 treatment decreased the peak intensity at $-78\ \text{ppm}$ for ^{29}Si NMR and increased the peak intensities centered at $-85\ \text{ppm}$ for ^{29}Si NMR and $55\ \text{ppm}$ for ^{27}Al NMR (Figure 2E). Therefore, the increased NMR signals centered at $-85\ \text{ppm}$ for ^{29}Si and $55\ \text{ppm}$ for ^{27}Al in Figure 2E could be attributed to the impurities which were unexpectedly synthesized by the hot 2% Na_2CO_3 treatment. These NMR signals would correspond to the zeolite-like new X-ray amorphous phases transformed from allophane and imogolite described in the experiment of Farmer *et al.* (1977). Ildefonse *et al.* (1994) concluded that both Si- and Al-rich allophanes contained

tetrahedral Al. MacKenzie *et al.* (1991) detected NMR signals centered at $-85\ \text{ppm}$ for ^{29}Si and $50\ \text{ppm}$ for ^{27}Al and assigned them to allophanes, although hot 2% Na_2CO_3 treatment was applied to some of the allophane samples. For the structural study of allophanes, the purity of the samples should be considered. In any case, imogolite-like Si ($-78\ \text{ppm}$ by ^{29}Si NMR) and octahedral Al ($3\ \text{ppm}$ by ^{27}Al NMR) could be the major components in both Al- and Si-rich allophanes.

In general, the influence of weathering is more prominent in fine-soil fractions than in coarse fractions. Therefore, if weathering has occurred *in situ*, the weathering process would be recorded on a series of size fractions. From this point of view, soil samples (weathered pumice layers), from which KiP and PA allophanes were collected, were then size-fractionated into three classes (fine sand, silt and fine clay), and their ^{29}Si and ^{27}Al NMR spectra were measured to clarify the weathering processes of volcanic glass into allophane (Figure 3). As mentioned previously, volcanic glass is mainly composed of silica gel-like Si polymer which is rich in Si—O—Si bridging structure (which resonated at $\sim -104\ \text{ppm}$ for ^{29}Si NMR) and tetrahedral Al ($\sim 49\ \text{ppm}$ for ^{27}Al NMR), and major components of both Al- and

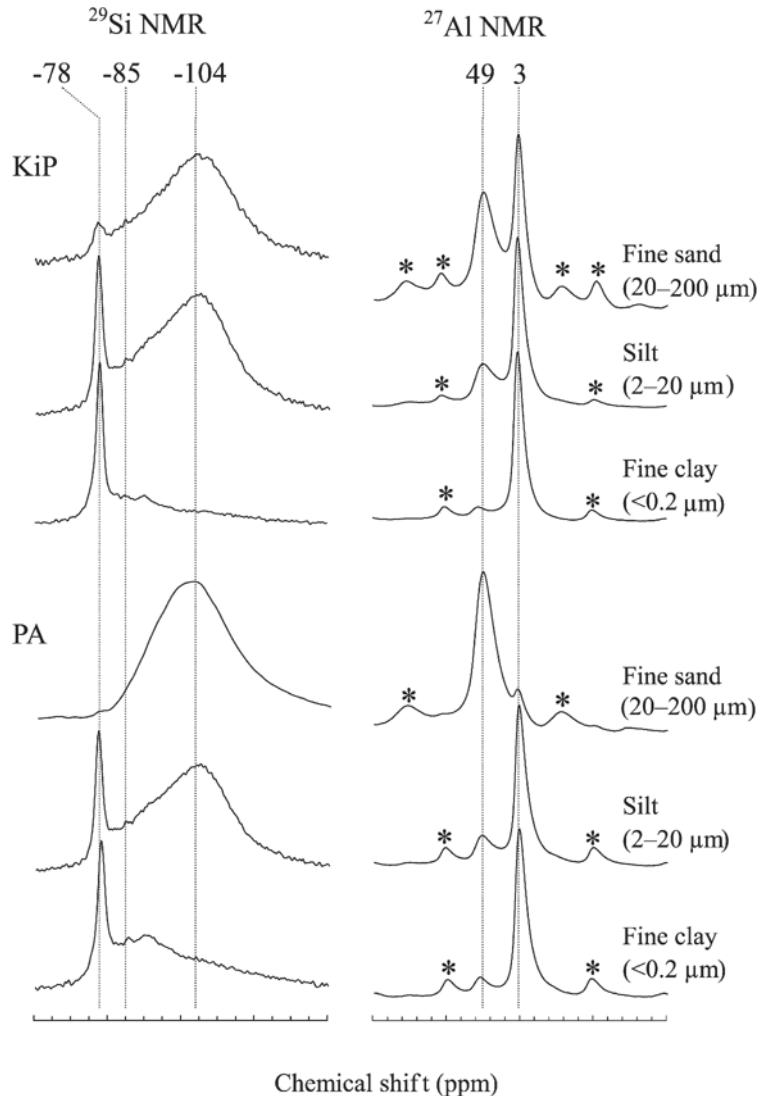


Figure 3. ^{29}Si and ^{27}Al MAS NMR spectra of size-fractionated KiP and PA soils. *: spinning side band (SSB).

Si-rich allophanes would be imogolite-like Si (-78 ppm for ^{29}Si NMR) and octahedral Al (3 ppm for ^{27}Al NMR). In both KiP and PA size-fractionated soil series, ^{29}Si and ^{27}Al NMR signals which correspond to volcanic glass were observed in fine sand and silt fractions, and NMR signals which correspond to allophane were found to be more concentrated with decreasing particle size. Obviously, the transformation of $Q^4\text{Al}$ -, $Q^3\text{Al}$ -, $Q^4\text{Al}$ - and $Q^3\text{Al}$ -type Si to imogolite-like Si needs dissolution of monosilicic acid from volcanic glass matrix. Therefore, the weathering process of volcanic glass into allophane in KiP and PA soils would include hydrolytic leaching of monosilicic acid and the transformation of tetrahedral Al into octahedral Al, together with the formation of $\text{Si}(\text{OH})(\text{O}^{\text{VI}}\text{Al})_3$ structure ($Q^3\text{Al}$), as in the case of imogolite. It is interesting to note that there were only two major phases (volcanic

glass and allophane) found in ^{29}Si NMR spectra in these size fractions (Figure 3), and that they coexisted in the silt fractions of both soil series. This implies that Si in volcanic glass is transformed into allophane without passing through a major intermediate phase. It is likely that the first step of the formation reaction of allophane is the dissolution of Si and Al from volcanic glass and then allophane is synthesized (precipitated) in the solution. Figure 3 showed that the transformation of $^{\text{IV}}\text{Al}$ into $^{\text{VI}}\text{Al}$ was faster than the disappearance of the silica gel-like polymer Si in volcanic glasses, indicating that the dissolution of Al from volcanic glass precedes the dissolution of the silica gel-like polymer Si. The dissolved Al would be hydrolyzed very quickly and form gibbsite-like sheets, and once the dissolved monosilicic acid reacts with the gibbsite-like sheet, $Q^3\text{Al}$ would be formed (Figure 4). These reactions could occur in

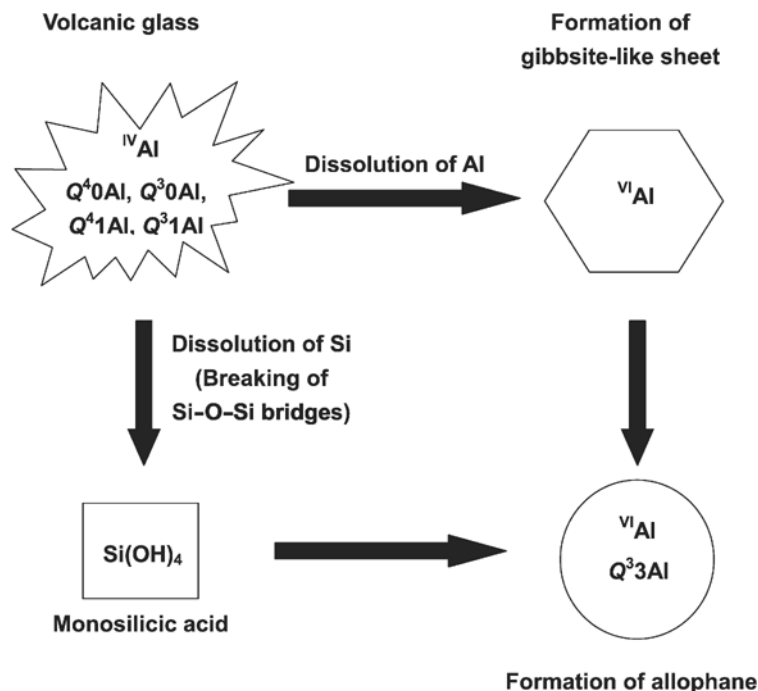


Figure 4. Schematic representation of the weathering process of volcanic glass into allophane as proposed in this study.

solution as well as on the surface of volcanic glass, because the imogolite-like Si tetrahedron was detected in the silt and even in the fine-sand fractions.

CONCLUSIONS

In four Japanese volcanic glasses, Si was present mostly as $Q^{40}Al$, $Q^{30}Al$, $Q^{41}Al$ and $Q^{31}Al$ (resonations centered at ~ -104 ppm by ^{29}Si NMR, rich in Si–O–Si bridging structure), and Al was present in tetrahedral form (~ 49 ppm by ^{27}Al NMR). In both Al- and Si-rich allophanes, octahedral Al (3 ppm by ^{27}Al NMR) and imogolite-like Si ($Q^{33}^{VI}Al$, -78 ppm by ^{29}Si NMR) were the major components. The weathering process of volcanic glass into allophane would be initiated by the dissolution of Al from volcanic glass accompanied by the transformation of ^{IV}Al into ^{VI}Al , followed by the formation of a gibbsite-like sheet. Simultaneously, a silica gel-like polymer Si of volcanic glass would be dissolved forming monosilicic acid in the solution. Allophane would then be formed by reacting the gibbsite-like sheet with the dissolved monosilicic acid, resulting in $Si(OH)(O^{VI}Al)_3$ structure ($Q^{33}^{VI}Al$) formation. These formation reactions of allophane could occur in solution as well as on the surface of volcanic glass.

In some research, NMR signals from Si-rich allophane samples centered at -85 ppm for ^{29}Si and 55 ppm for ^{27}Al (tetrahedral Al) are assigned to allophane itself. In the present study, however, some of these signals could be attributed to impurities, *i.e.* contaminants from the original soils which were unexpectedly synthesized

during the purification procedures, *e.g.* hot Na_2CO_3 treatments.

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