Clays and Clay Minerals, Vol. 53, No. 6, 653–658, 2005.

STRUCTURAL CHANGES OF ALLOPHANE DURING PURIFICATION PROCEDURES AS DETERMINED BY SOLID-STATE ^{27}Al AND ^{29}Si NMR

SYUNTARO HIRADATE*

Department of Biological Safety Science, National Institute for Agro-Environmental Sciences (NIAES), 3-1-3 Kan-nondai, Tsukuba, Ibaraki 305-8604, Japan

Abstract—Allophanes are poorly crystalline and quasi-stable aluminosilicate minerals, the structures of which are sensitive to chemical treatment. In the present study, solid-state ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) spectra of allophane samples were monitored as they went through several purification procedures. It was confirmed that no significant structural changes were caused by boiling with 6% H_2O_2 to remove organic matter, by size fractionation (sonification), by sedimentation, by precipitation at pH 4.0, or by dithionite-citrate-bicarbonate treatment for the removal of Fe (hydr)oxides. Hot 5% Na_2CO_3 treatment for the removal of reactive silica-alumina gels and adsorbed citrate from allophane samples, however, decreased signal intensity corresponding to imogolite-like Si ($Q^3 3^{VI}Al$, −78 ppm in ^{29}Si NMR) and increased signal intensities corresponding to ^{IV}Al (55 ppm in ^{27}Al NMR) and possibly X-ray amorphous aluminosilicates (centered at −85 ppm in ^{29}Si NMR). Cold (room temperature) 5% Na_2CO_3 treatment for 16 h proved to be effective in avoiding these structural changes.

Key Words—^{27}Al NMR, Imogolite, KiP Pumice, Kitakami Pumice, ^{29}Si NMR, Solid-state MAS NMR, Volcanic Glass.

INTRODUCTION

Allophanes are aluminosilicates with primarily short-range structural order; they occur as very small particles, especially in soils formed from volcanic ash and pumice, as do imogolites. They could also occur in any environment where sufficient Si and Al exist in solution from which these rapidly forming minerals precipitate (Harsh *et al*., 2002). Allophanes affect soil chemical properties through their large amount of active surface hydroxyls, which cause pH-dependent charge and strong ligand-exchange reactions (Wada, 1989).

The chemical structures of allophanes have not been made entirely clear, however, because allophanes are amorphous to X-rays (Wada, 1989). The chemical compositions of allophanes are extremely variable, having the empirical formula $xSiO_2 \cdot Al_2O_3 \cdot yH_2O$, 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 is composed of hollow spherical particles with diameters of 3.5−5.0 nm and a Si/Al molar ratio of ~0.5. It consists of a gibbsite sheet outer sphere and an imogolite-like Si tetrahedron inner sphere (MacKenzie *et al*., 1991). Silicon-rich allophane has similar morphology to Al-rich allophane, but a different Si/Al molar ratio of ~1.0. MacKenzie *et al*. (1991) proposed a structural model for the Si-rich allophane which was composed of a gibbsite sheet outer sphere and an incomplete tetrahedral silicate layer and imogolite-like Si tetrahedron ($Q^3 3^{VI}Al$) inner sphere. A different structural model for the Si-rich allophane, which had an additional Si tetrahedral unit bound to the imogolite-like Si of Al-rich allophane forming Si tetrahedron dimer and/or trimer, was also proposed (Henmi, 1988; Ghoneim *et* al., 2001; Padilla *et al*., 2002). Silica Springs allophanes are composed of more or less complete spherules with diameters of 2 to 3 nm and other partial spherules, with varying Si/Al molar ratios (0.6−1.0) depending on the precipitation environment. Childs *et al*. (1990) proposed a structural model of Silica Springs allophane based on fragments of single-curved 1:1 aluminosilicate layers, in which the Si tetrahedral sheet (outer sphere) was more or less complete (Si: ^{IV}Al ratio of 3:1) and the ^{VI}Al octahedral sheet (inner sphere) incomplete. The Silica Springs allophane lacks the 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 ^{V}Al together with ^{IV}Al and ^{VI}Al.

For structural studies of allophanes, isolated and purified allophane samples have been subjected to analyses. The purities of the allophane samples, however, have not been well established. Farmer *et al*. (1977) pointed out that the treatment of allophanes or imogolites with 5% Na_2CO_3 solution at 95ºC for 2 to 100 h for their purification led to the formation of solid products different in structure and composition from the

* E-mail address of corresponding author:
hiradate@affrc.go.jp
DOI: 10.1346/CCMN.2005.0530611

Copyright © 2005, The Clay Minerals Society

https://doi.org/10.1346/CCMN.2005.0530611 Published online by Cambridge University Press

starting materials. Hiradate and Wada (2005) also observed an increase of ^{IV}Al and a decrease of imogolite-like Si after boiling the fine clay fraction (<0.2 μm) of an allophane sample for 6 h in the presence of 2% Na_2CO_3. It is likely that poorly crystalline allophanes and imogolites are unstable to chemical treatments. In the isolation and purification procedures of allophanes and imogolites, structural changes should therefore be monitored sequentially as they go through the procedures, *i.e.* removal of organic matter by boiling in the presence of H_2O_2, size fractionation by sonification, sedimentation, and precipitation at pH 4.0, removal of Fe (hydr)oxides by dithionite-citrate-bicarbonate (DCB) treatment, and removal of reactive silica-alumina gels and adsorbed citrate by Na_2CO_3 treatment. In the present study, structural changes of allophanes were monitored as they went through the purification procedures by solid-state ^{27}Al and ^{29}Si NMR spectra.

MATERIALS AND METHODS

Purification of natural allophane

Weathered pumice was collected from a 4C horizon (pumice bed, >85 cm depth) of a volcanic ash soil (Alic Fulvudand, Soil Survey Staff, 1999; Hyperdystric Andosol, FAO, 1998), Kitakami, Japan (Wada, 1986). This horizon has an orange to bright yellowish brown color (8.25YR6/8) and is derived from Murasakino pumice (40,000−70,000 y BP, Wada, 1986). The pumice grain is mainly composed of volcanic glass and Al-rich allophane (Yoshinaga *et al*., 1973).

The process of purification of allophane from the pumice is summarized in Figure 1. Large grains were selected and their surfaces scraped off to remove imogolites. After washing with water, these grains were ground with a mortar (KiP-G). To remove organic matter from the ground pumice (KiP-G), 6% H_2O_2 was added and refluxed on a hot plate (KiP-GH). To disperse allophanes, the KiP-GH sample was suspended in a solution at pH 4.0 and sonificated. The clear supernatant liquid was replaced with distilled water, and the suspension was adjusted to pH 4.0 and sonificated. This procedure was repeated until allophanes were dispersed. Subsequently, the sample was fractionated into coarse sand (KiP-GHF$_{CS}$; 500−63 μm), fine sand (KiP-GHF$_{FS}$; 63−20 μm), silt (KiP-GHF$_{ST}$; 20−2 μm), coarse clay (KiP-GHF$_{CC}$; 2−0.2 μm), and fine clay (KiP-GHF$_{FC}$; <0.2 μm) fractions with sieving and sedimentation (siphon). Dispersed clay fractions were precipitated by the addition of NaCl. To remove Fe (hydr)oxides, the KiP-GHF$_{FC}$ sample was subjected to dithionite-citrate-bicarbonate (DCB) treatment following the procedures of Mehra and Jackson (1960) as follows: sample (KiP-GHF$_{FC}$) was suspended in a mixed solution of 100 mL of 0.3 mol L^{-1} sodium citrate and 12.5 mL of 1 mol L^{-1} sodium bicarbonate at 80ºC, and 1 g of sodium dithionite was added. The mixture was incubated for 15 min with occasional shaking, and then the supernatant liquid was removed by centrifugation (~300 × g; KiP-GHF$_{FC}$D). To remove reactive silica-alumina gels and adsorbed citrate, the KiP-GHF$_{FC}$D sample was treated with 5% Na_2CO_3 at room temperature for 16 h (KiP-GHF$_{FC}$DS$_{C16}$), or treated with 5% Na_2CO_3 by boiling on a hot plate for 0.5 h (KiP-GHF$_{FC}$DS$_{H005}$), 1 h (KiP-GHF$_{FC}$DS$_{H01}$), 2 h (KiP-GHF$_{FC}$DS$_{H02}$), 4 h (KiP-GHF$_{FC}$DS$_{H04}$), and 8 h (KiP-GHF$_{FC}$DS$_{H08}$). The ratio of KiP-GHF$_{FC}$D to 5% Na_2CO_3 added was 1 to 250. At each stage of the purification procedure, a small portion was freeze dried and subjected to NMR analyses.

Solid-state NMR analysis

The powder sample (~200 mg) was transferred into a high-speed spinning NMR tube (rotor; zirconia, cap; vespel, 6 mm i.d., JEOL, Tokyo), and the NMR signal was recorded with JNM α300 FT-NMR system (JEOL). Signals of ^{27}Al were recorded at 78.2 MHz in a single-pulse experiment without decoupling, with a flip angle of π/2 for ^{27}Al (0.9 μs as a pulse width), an observation band of 80 kHz, an acquisition time of 0.013 s, a pulse delay of 2 s, and 8 kHz of magic-angle spinning. In the ^{27}Al NMR experiment, 4096 points were collected (resolution; 19.53 Hz). The standard chemical shift (0 ppm) was adjusted externally using 1 mol L^{-1} $AlCl_3$ solution. Signals of ^{29}Si were recorded at 59.6 MHz in a single-pulse experiment without decou-

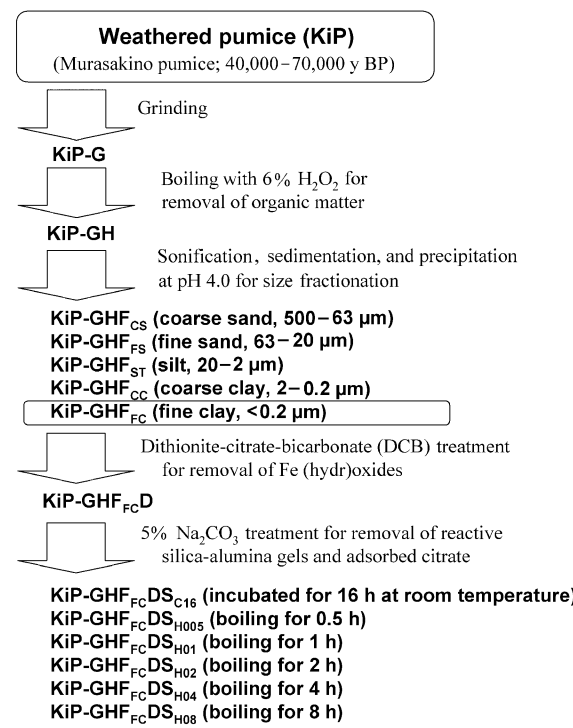


Figure 1. Purification procedure of allophane from weathered pumice (Murasakino pumice; 40,000−70,000 y BP).

https://doi.org/10.1346/CCMN.2005.0530611 Published online by Cambridge University Press

pling, with a flip angle of $\pi/2$ for ^{29}Si (5.0 μs as a pulse width), an observation band of 50 kHz, an acquisition time of 0.082 s, pulse delay of 10 s, and 6 kHz of magic-angle spinning. In the ^{29}Si NMR experiment, 4096 points were collected (resolution; 12.21 Hz). Chemical shifts were quoted with respect to tetramethylsilane but were determined by reference to an external sample of silicon rubber (−22 ppm). 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

Allophanes show a sharp and characteristic resonance peak at −78 ppm in ^{29}Si NMR spectra, which corresponds to the imogolite-like Si tetrahedron attached to three aluminol groups (Al-OH) of gibbsite sheet and one silanol group (Si-OH) ($Q^3 3^{VI}Al$; Wilson, 1987). Other minor peaks in ^{29}Si NMR spectra are also reported (MacKenzie *et al*., 1991), although some of them could be assigned to impurities (Hiradate and Wada, 2005). Aluminum-27 NMR is effective in differentiating ^{IV}Al (detectable at ~50 to 90 ppm) from ^{VI}Al (-10 to 20 ppm) (Hiradate, 2004). In allophanes, ^{VI}Al and ^{IV}Al have been reported to exist as major and minor components, respectively (MacKenzie *et al*., 1991; Ildefonse *et al*., 1994), although some ^{IV}Al is attributable to impurities (Hiradate and Wada, 2005).

Ground pumice showed resonance peaks at 3 and −78 ppm in ^{27}Al and ^{29}Si NMR spectra, respectively (Figure 2, KiP-G), indicating the dominant presence of allophane containing ^{VI}Al and imogolite-like Si tetrahedron. Removal of organic matter by boiling the ground pumice suspension in 6% H_2O_2, had no effect on the ^{27}Al and ^{29}Si NMR spectra (Figure 2, KiP-GH).

In the size-fractionation procedure, the H_2O_2-treated ground pumice (KiP-GH) was subjected to sonification at pH 4.0 for dispersion and sedimentation by adding NaCl. Figure 3 showed that this procedure successfully fractionated allophane into coarse (KiP-GHF_{CC}) and fine clay (KiP-GHF_{FC}) fractions without causing structural alteration. Silicon-29 NMR revealed that the silt fraction (KiP-GHF_{ST}) also contained appreciable amounts of allophane (−78 ppm), although mixed with volcanic glass-like constituents (around −110 ppm). In fine (KiP-GHF_{FS}) and coarse sand (KiP-GHF_{CS}) fractions, allophane was not detected. Volcanic glass and feldspar might be concentrated in these fractions.

The color of the coarse (KiP-GHF_{CC}) and fine clay (KiP-GHF_{FC}) fractions was reddish yellow. This color was probably due to the presence of Fe (hydr)oxides. To remove the Fe (hydr)oxides, the fine clay fraction of the H_2O_2-treated ground pumice (KiP-GHF_{FC}) was subjected to DCB treatment, which resulted in a white gel. The ^{27}Al and ^{29}Si NMR spectra clearly show that the DCB treatment does not have significant effect on the chemical structure of allophane (Figure 4), although the treatment tends to increase signal intensities of impurities containing ^{IV}Al (~55 ppm in ^{27}Al NMR) and possibly X-ray amorphous aluminosilicates (−80 to −90 ppm in ^{29}Si NMR).

To remove reactive silica-alumina gels and adsorbed citrate, DCB-treated allophane samples are frequently treated with Na_2CO_3 solution. However, Farmer *et al*. (1977) pointed out that hot 2% Na_2CO_3 treatment converted allophane and imogolite into new X-ray amorphous phases: their infrared spectra showed some analogy with those of zeolites. On this basis, to avoid structural alteration, the authors recommended the use of cold 5% Na_2CO_3 treatment for 16 h. Hiradate and Wada (2005) also reported that hot 2% Na_2CO_3 treatment for 6 h of the allophane sample decreased signal intensity at −78 ppm in ^{29}Si NMR (imogolite-like Si) and increased signal intensities centered at −85 ppm in ^{29}Si NMR

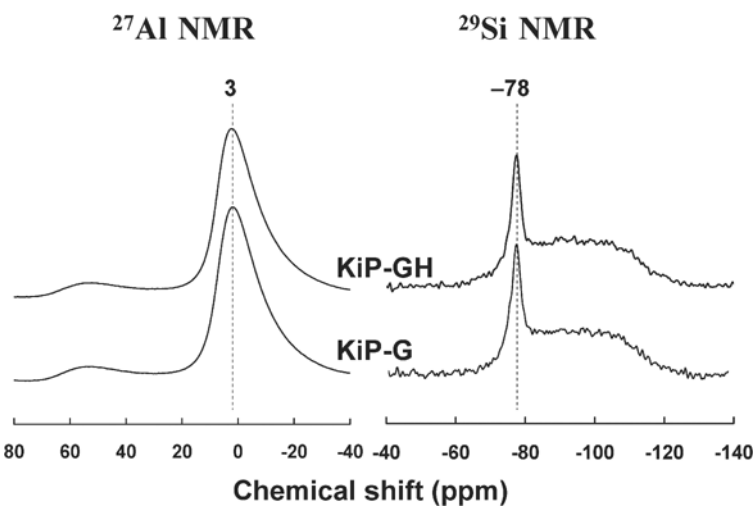


Figure 2. Solid-state ^{27}Al and ^{29}Si NMR spectra of untreated (KiP-G) and 6% H_2O_2-treated (KiP-GH) ground pumice.

https://doi.org/10.1346/CCMN.2005.0530611 Published online by Cambridge University Press

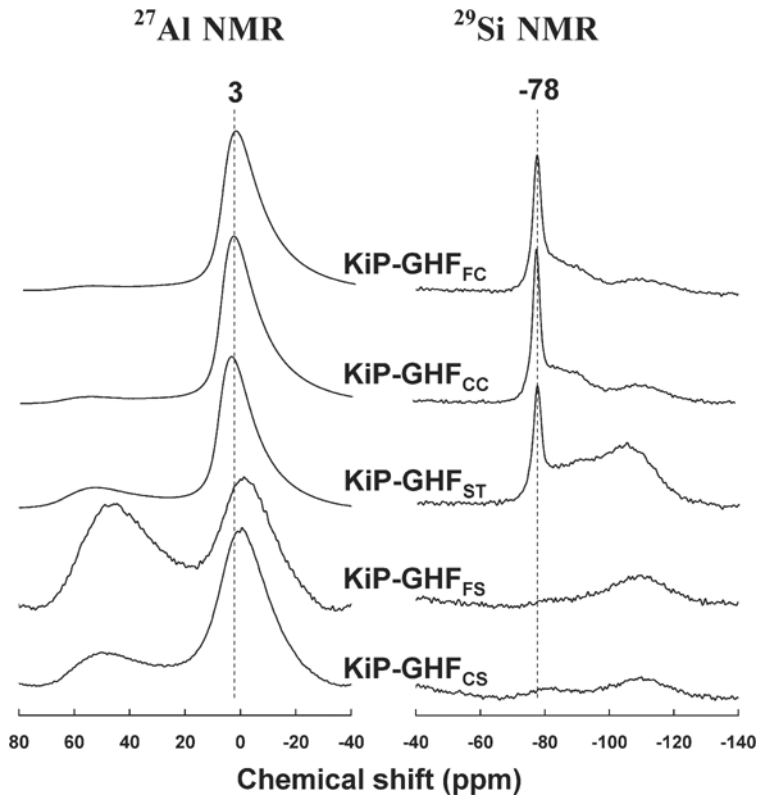


Figure 3. Solid-state ^{27}Al and ^{29}Si NMR spectra of coarse sand (KiP-GHF$_{CS}$; 500−63 μm), fine sand (KiP-GHF$_{FS}$; 63−20 μm), silt (KiP-GHF$_{ST}$; 20−2 μm), coarse clay (KiP-GHF$_{CC}$; 2−0.2 μm), and fine clay (KiP-GHF$_{FC}$; <0.2 μm) fractions of the H_2O_2-treated ground pumice (KiP-GH).

(possibly X-ray amorphous aluminosilicates) and at 55 ppm in ^{27}Al NMR (^{IV}Al). In the present study, similar spectral changes were observed when allophane was subjected to boiling for 0.5 h in 5% Na_2CO_3 (Figure 5; KiP-GHF$_{FC}$DS$_{H005}$). After 8 h of boiling (Figure 5; KiP-GHF$_{FC}$DS$_{H08}$), the imogolite-like Si signal of allophane (−78 ppm in ^{29}Si NMR) almost disappeared, and a signal intensity of ^{IV}Al at ~55 ppm increased to a comparable level to that of ^{VI}Al at ~3 ppm. It is clear that impurities which contain Al

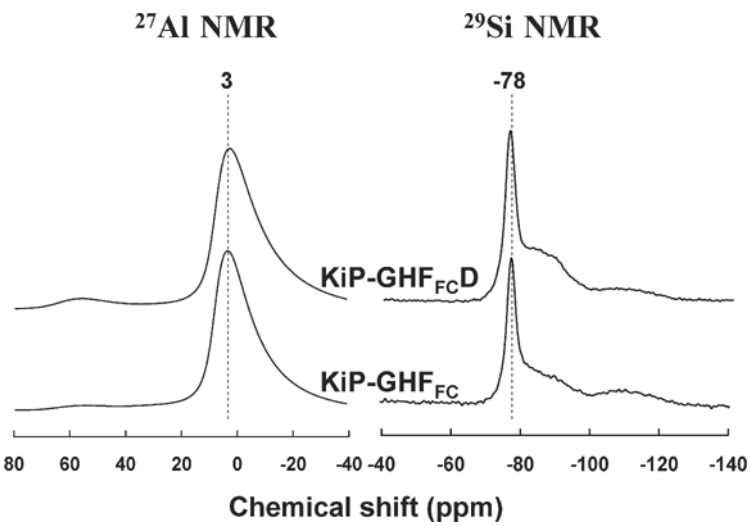


Figure 4. Comparison of solid-state ^{27}Al and ^{29}Si NMR spectra between before-(KiP-GHF$_{FC}$) and after-(KiP-GHF$_{FC}$D) dithionite-citrate-bicarbonate treatment of the fine clay fraction of the H_2O_2-treated ground pumice.

https://doi.org/10.1346/CCMN.2005.0530611 Published online by Cambridge University Press

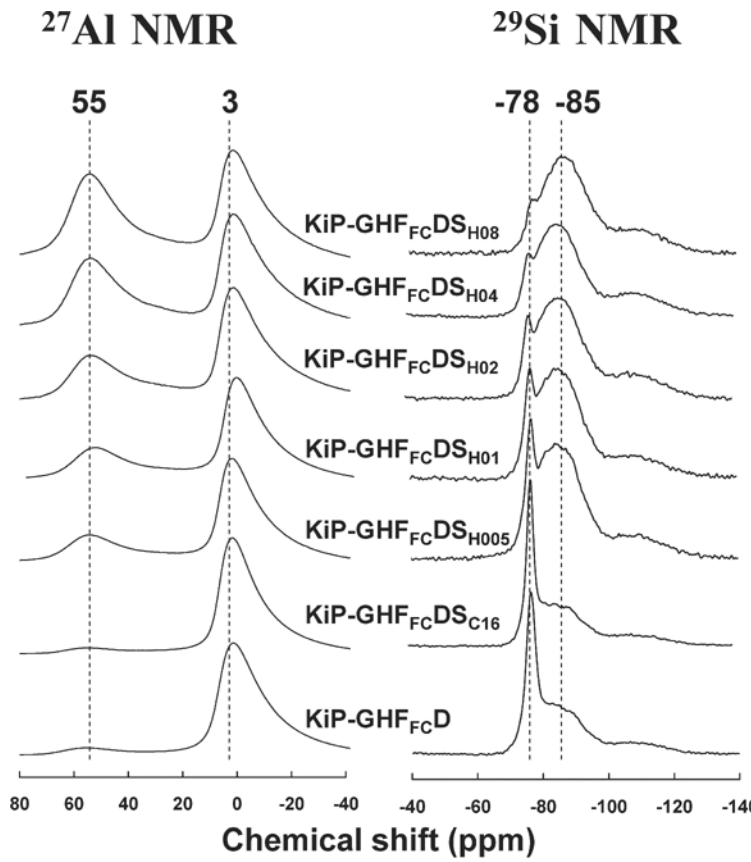


Figure 5. Influence of 5% Na_2CO_3 treatment on solid-state ^{27}Al and ^{29}Si NMR spectra of allophane. KiP-$GHF_{FC}D$; untreated control, KiP-$GHF_{FC}DS_{C16}$; incubated for 16 h at room temperature, KiP-$GHF_{FC}DS_{H005}$; boiling for 0.5 h, KiP-$GHF_{FC}DS_{H01}$; boiling for 1 h, KiP-$GHF_{FC}DS_{H02}$; boiling for 2 h, KiP-$GHF_{FC}DS_{H04}$; boiling for 4 h, KiP-$GHF_{FC}DS_{H08}$; boiling for 8 h.

detectable at 55 ppm in ^{27}Al NMR and Si detectable at −85 ppm in ^{29}Si NMR are formed by the hot 5% Na_2CO_3 treatments. Similar impurities have also been reported to form when a silica-alumina mixed solution was incubated in the imogolite synthesis procedures (Hu *et al*., 2004). As pointed out by Farmer *et al*. (1977), cold (room temperature) 5% Na_2CO_3 treatment for 16 h did not alter either the ^{27}Al or the ^{29}Si NMR spectra of allophane (KiP-$GHF_{FC}D$). It was also observed that signal intensity at −85 ppm in ^{29}Si NMR for KiP-$GHF_{FC}D$ was decreased by the cold 5% Na_2CO_3 treatment for 16 h (KiP-$GHF_{FC}DS_{C16}$). This indicates that the cold 5% Na_2CO_3 treatment is effective at removing some impurities, which possibly include X-ray amorphous aluminosilicates.

CONCLUSIONS

Boiling with 6% H_2O_2 to remove organic matter, size fractionation by sonification, sedimentation, and precipitation at pH 4.0, and DCB treatment for the removal of Fe (hydr)oxides did not significantly alter the chemical structure of allophane. Cold 5% Na_2CO_3 treatment for 16 h should be applied to remove reactive silica-alumina gels and adsorbed citrate from allophane samples, instead of hot 5% Na_2CO_3 treatment which alters the chemical structure of allophanes significantly. In some structural studies, hot Na_2CO_3 treatment had been applied to purify allophanes. In these cases, contamination caused by impurities should be taken into account in the interpretation of the experimental results. These findings would also be applicable in the purification of imogolites.

REFERENCES

Childs, C.W., Parfitt, R.L. and Newman, R.H. (1990) Structural studies of Silica Springs allophane. *Clay Minerals*, **25**, 329–341.

Childs, C.W., Hayashi, S. and Newman, R.H. (1999) Five-coordinate aluminum in allophane. *Clays and Clay Minerals*, **47**, 64–69.

FAO (1998) *World Reference Base for Soil Resources*. World Soil Resources Reports **84**, FAO, Rome.

Farmer, V.C., Smith, B.F.L. and Tait, J.M. (1977) Alteration of allophane and imogolite by alkaline digestion. *Clay Minerals*, **12**, 195–198.

Ghoneim, A.M., Matsue, N. and Henmi, T. (2001) Zinc adsorption on nano-ball allophanes with different Si/Al ratios. *Clay Science*, **11**, 337–348.

Harsh, J., Chorover, J. and Nizeyimana, E. (2002) Allophane

https://doi.org/10.1346/CCMN.2005.0530611 Published online by Cambridge University Press

and imogolite. Pp. 291–322 in: *Soil Mineralogy with Environmental Applications* (J.B. Dixon and D.G. Schulze, editors). Soil Science Society of America Book Series **7**, Soil Science Society of America, Madison, Wisconsin.

Henmi, T. (1988) Mode of the presence for the SiO_4 tetrahedra in the structure of allophanes. *Japanese Journal of Soil Science and Plant Nutrition*, **59**, 237–241 (in Japanese).

Hiradate, S. (2004) Speciation of aluminum in soil environments: application of NMR technique. *Soil Science and Plant Nutrition*, **50**, 303–314.

Hiradate, S. and Wada, S.-I. (2005) Weathering process of volcanic glass to allophane determined by ^{27}Al and ^{29}Si solid-state NMR. *Clays and Clay Minerals*, **53**, 401–408.

Hu, J., Kannangara, G.S.K., Wilson, M.A. and Reddy, N. (2004) The fused silicate route to protoimogolite and imogolite. *Journal of Non-crystalline Solids*, **347**, 224–230.

Ildefonse, P., Kirkpatrick, R.J., Montez, B., Calas, G., Flank, A.M. and Lagarde, P. (1994) ^{27}Al MAS NMR and aluminum X-ray absorption near edge structure study of imogolite and allophanes. *Clays and Clay Minerals*, **42**, 276–287.

MacKenzie, K.J.D., Bowden, M.E. and Meinhold, R.H. (1991) The structure and thermal transformations of allophanes studied by ^{29}Si and ^{27}Al high resolution solid-state NMR. *Clays Clay Minerals*, **39**, 337–346.

Mehra, O.P. and Jackson, M.L. (1960) Iron oxide removal from soils and clays by dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals*, **7**, 317–327.

Padilla, G.N., Matsue, N. and Henmi, T. (2002) Change in surface properties of nano-ball allophane as influenced by sulfate adsorption. *Clay Science*, **12**, 33–39.

Soil Survey Staff (1999) *Key to Soil Taxonomy*, 8th edition. Soil Conservation Service/USDA/Pocahontas Press, Blacksburg, Virginia.

Wada, K. (1986) *Ando Soils in Japan*. Kyushu University Press, Fukuoka, Japan.

Wada, K. (1989) Allophane and imogolite. Pp. 1051–1087 in: *Minerals in Soil Environments* (J.B. Dixon and S.B. Weed, editors). 2nd edition. SSSA Book Series **1**, Soil Science Society of America, Madison, Wisconsin.

Wilson, M.A. (1987) *N.M.R. Techniques and Applications in Geochemistry and Soil Chemistry*. Pergamon Press, Oxford, UK.

Yoshinaga, N., Nakai, M. and Yamaguchi, M. (1973) Unusual accumulation of gibbsite and halloysite in the Kitakami pumice bed, with a note on their genesis. *Clay Science*, **4**, 155–165.

(*Received 24 March 2005; revised 11 June 2005; Ms. 1031; A.E. Randall T. Cygan*)

https://doi.org/10.1346/CCMN.2005.0530611 Published online by Cambridge University Press