

Direct determination of allophane and imogolite in Andosols using nuclear magnetic resonance spectroscopy

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Abstract

Allophane and imogolite are the major weathering products of volcanic materials at early stage of the soil formation processes of Andosols. In general, the amounts of allophane plus imogolite in soils are determined by a selective dissolution methods using acid-oxalate, although the accuracy of the indirect method is not well understood. In the present study, the amounts of allophane plus imogolite in Andosol profiles were determined directly by using solid-state ²⁹Si nuclear magnetic resonance (NMR) spectroscopy and compared the results with those by the selective dissolution method. The result suggested that the amounts of allophane plus imogolite determined by the both methods were roughly correlated for many Andosol samples. For soil samples containing large amount of pumice and organic materials, however, it was suggested that the acid-oxalate would underestimate and overestimate the amounts of allophane plus imogolite, respectively. Acid-oxalate is a convenient and well studied reagent to dissolve allophane and imogolite from soils, but it might not always be reliable depending on the properties of samples. Non-destructive determination by ²⁹Si NMR could validate the acid-oxalate analysis.

Key Words

Acid-oxalate, NMR, allophanic constituents, selective dissolution methods, volcanic ash soils, weathering

Introduction

Many soil properties have been characterized by responses to the addition of chemicals. For example, the amounts of allophane plus imogolite, which are poorly crystalline aluminosilicates, have been estimated from acid-oxalate extractable Si (Si_{OX}: Parfitt *et al.*, 1983; Parfitt and Wilson, 1985; Wada, 1989; Parfitt, 1990; Dahlgren, 1994). However, if the acid-oxalate dissolves Si not only from allophane and imogolite but also from other soil components, then the amount of allophane plus imogolite could be overestimated. On the other hand, it is possible that not all allophane and imogolite are completely dissolved and the amount of allophane plus imogolite could be underestimated. Therefore, a non-destructive and direct analysis that can characterize soil samples without any chemical treatment would be helpful in characterizing soil properties and in confirming analyses determined by such chemical dissolution techniques.

Nuclear magnetic resonance (NMR) is one of the most powerful non-destructive and direct analytical tools used in the characterization and speciation of atoms. To characterize soils without any chemical treatment, NMR instruments should be optimized for the solid-state measurement, although their resolutions are much worse than those of liquid-state NMR (Hiradate, 2004). In the present study, the authors determined the amounts of allophane plus imogolite in soil samples from three representative allophanic Andosols in Japan by using solid-state ²⁹Si NMR, and the results were compared with those by the acid-oxalate extraction method.

Methods

Soil samples

Soil samples from the horizons of three allophanic Andosol profiles were collected in Tochigi Prefecture, Japan: Funyu (FF) soil at a broad-leaved and red pine mixed forest in Funyu Experimental Forests of Utsunomiya University in Shioya town; Kiwadashima (KF) soil at a broad-leaved forest in Imaichi city; and Kawaraya-cho (KO) soil at a reclaimed orchard land in an experimental field of Tochigi Prefectural Agricultural Experimental Station in Utsunomiya city. All of the three soils were classified into Silandic Andosols (FAO *et al.*, 1998).

Chemical analyses

Soil samples were air-dried and sieved (< 2 mm). The amounts of acid-oxalate extractable Si (Si_{OX}) were determined following the method described by Blakemore *et al.* (1981).

Solid-state ^{27}Al and ^{29}Si NMR analyses

Solid-state NMR spectra of soil samples were recorded with an FT NMR system (Alpha 300, JEOL, Tokyo). Soils were finely ground with a mortar, and ~200 mg was tightly packed into a high-speed spinning NMR tube. Signals of ^{27}Al were recorded at 78.2 MHz in a single-pulse experiment without decoupling, and with a flip angle of $\pi/2$ for ^{27}Al (0.9 μs as a pulse width), an observation band of 80 kHz, a number of observation points of 4096 (resolution; 19.5 Hz), an acquisition time of 0.013 s, a pulse interval of 2 s, a number of scans of 600–22,000 (0.5–13 h), and 8 kHz of magic angle spinning (MAS). The standard chemical shift (0 ppm) was adjusted externally using 1 mol/L AlCl_3 solution. Signals of ^{29}Si were recorded at 59.6 MHz in a single-pulse experiment without decoupling, and with a flip angle of $\pi/2$ for ^{29}Si (5.0 μs as a pulse width), an observation band of 50 kHz, a number of observation points of 4096 (resolution; 12.2 Hz), an acquisition time of 0.082 s, a pulse interval of 10 s, a number of scans of 6,000–35,000 (16–99 h), and 6 kHz of MAS. Chemical shifts were quoted with respect to tetramethylsilane but were determined by referring to an external sample of silicon rubber (-22 ppm). A broadening factor of 100 Hz was employed in the Fourier transform procedure for all NMR experiments.

Results

Solid-state ^{27}Al NMR is able to differentiate tetrahedral $^{\text{IV}}\text{Al}$ (resonated at around 50 ppm) from octahedral $^{\text{VI}}\text{Al}$ (ca. 0 ppm). In Andosols, $^{\text{IV}}\text{Al}$ is incorporated in volcanic glasses, feldspars, and 2:1 aluminosilicates with isomorphic substitution in Si tetrahedral sheets containing Al, such as micaceous minerals, vermiculite, and beidellites, whereas $^{\text{VI}}\text{Al}$ is contained in Al-humus complexes, allophane, imogolite, gibbsite, and aluminosilicates having Al octahedral sheets such as micaceous minerals, montmorillonite, vermiculite, and kaolins (Hiradate, 2004). In solid-state ^{29}Si NMR spectra of Andosols, three major signals are detectable: allophane plus imogolite at -78 ppm, layer silicates at around -90 ppm, and SiO_2 including volcanic glass, quartz, cristobalite, opal phytoliths, and silica gel-like constituents at around -105 ppm (Hiradate, 2004). Fresh volcanic ash is composed mainly of volcanic glass (Shoji *et al.*, 1993), which gives resonance peaks at around 50 ppm in ^{27}Al NMR (corresponds to $^{\text{IV}}\text{Al}$) and at around -105 ppm in ^{29}Si NMR (Hiradate and Wada, 2005). Although all the three soils analysed in the present study are younger than 25,000 ^{14}C y old, the major portion of these soil materials had been weathered and secondary components had been formed, as indicated by intensive resonance peak for $^{\text{VI}}\text{Al}$ than $^{\text{IV}}\text{Al}$ (Figure 1). Solid-state ^{29}Si NMR also suggested the rapid weathering of volcanic glass (ca. -105 ppm) into other components in the soils (Figure 1).

Barron *et al.* (1982) showed that imogolite in soils could be determined quantitatively by solid-state ^{29}Si NMR. It has also been shown that Si in allophane has identical chemical surroundings as those in imogolite, i.e., comprising isolated Si tetrahedron coordinated with three $^{\text{VI}}\text{Al}$ on gibbsite sheet and one H through O bonds, resulting in the same chemical shift (-78 ppm) in ^{29}Si NMR spectrum (Hiradate and Wada, 2005). Therefore, solid-state ^{29}Si NMR can detect both allophane and imogolite at -78 ppm. In the present study, it was clarified that allophane and imogolite were abundant in B horizons for all the tested soil profiles (Figure 1), probably because allophane and imogolite had been mainly formed in the B horizons. In the humus-rich A horizons, the amounts of allophane plus imogolite were much lower than those in the B horizons. It has been believed that Si in allophane and imogolite is selectively dissolved by acid-oxalate. Therefore, the amount of allophane plus imogolite in soils has been estimated by multiplying the amount of Si dissolved by acid-oxalate (Si_{OX}) by a factor which had been determined from the chemical composition of allophane in soils, which is typically 7 for Al-rich allophane (Parfitt and Henmi, 1980; Parfitt and Wilson, 1985; Parfitt, 1990; Dahlgren, 1994; Dahlgren *et al.*, 2004). In the present study, the Si_{OX} values were compared with the amounts of Si determined by ^{29}Si NMR at -78 ppm ($\text{Si}_{-78\text{ppm}}$) which can be also assigned for allophane plus imogolite (Figure 2). It was shown that many of the Si_{OX} values were roughly correlated with $\text{Si}_{-78\text{ppm}}$ values, but some samples deviated from 1:1 relationship. Soil samples from three horizons of KF soil, 4Bw, 4Bw2, and 4Bw3 horizons (Figure 2, ▲), which were composed mainly of Imaichi pumice, tend to show lower Si_{OX} values (44.1, 27.9, and 36.1 g/kg, respectively) than $\text{Si}_{-78\text{ppm}}$ values (50.2, 68.0, and 56.0 g/kg, respectively), indicating that at least a part of Si in allophane and imogolite in these samples was not dissolved by acid-oxalate. For the uppermost horizons of FF, KF, and KO soils (Figure 2, ●), Si_{OX} values (11.7, 9.8, and 22.2 g/kg, respectively) were significantly higher than $\text{Si}_{-78\text{ppm}}$ values (4.2, 5.4, and 7.1 g/kg, respectively). It might be possible that acid-oxalate dissolves Si not only from allophane and imogolite but also from other soil components.

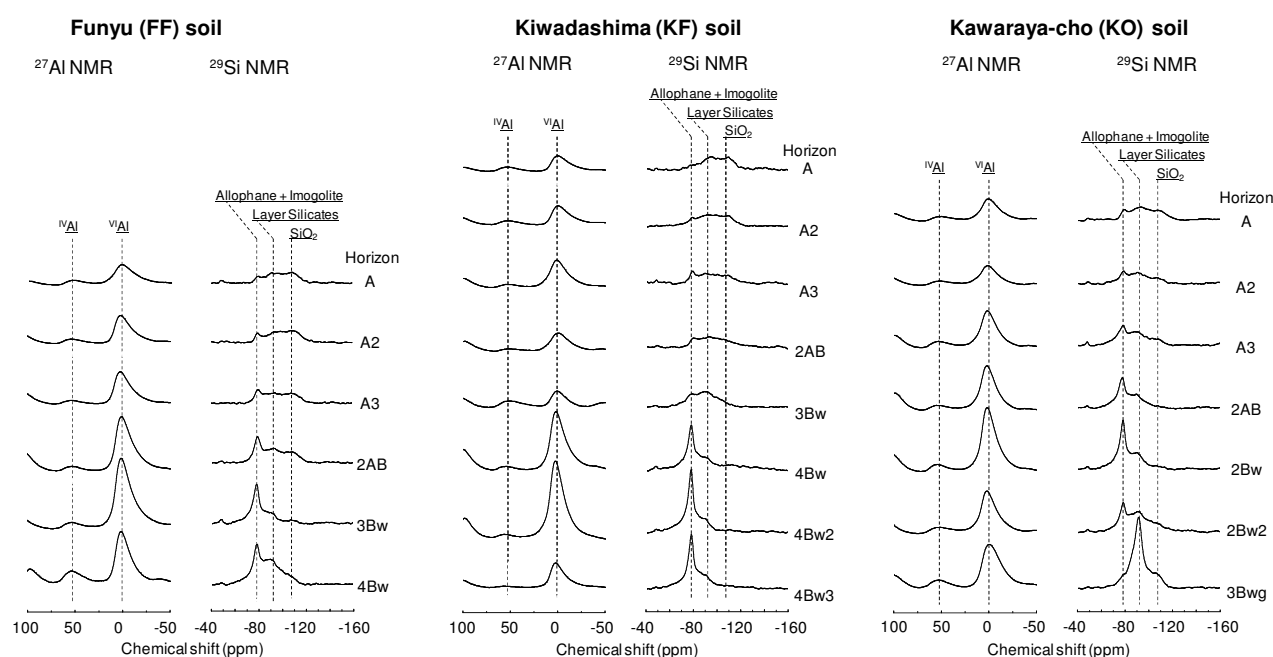


Figure 1. Solid-state MAS ^{27}Al and ^{29}Si NMR spectra of soil samples from three allophanic Andosols, named Funyu (FF), Kiwadashima (KF), and Kwaraya-cho (KO) soils. The y-axes of NMR spectra for each nuclide are adjusted to the same scales.

The acid-oxalate is a convenient and well-studied reagent to dissolve allophane and imogolite from soils, but it might not always be reliable depending on the properties of samples. Non-destructive determination by ^{29}Si NMR could validate the acid-oxalate analysis.

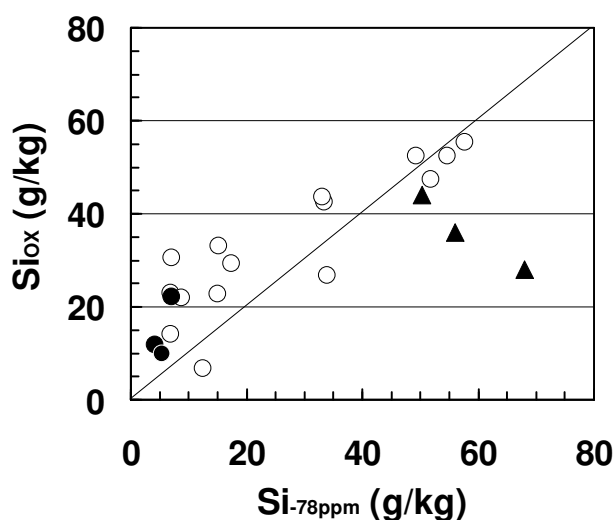


Figure 2. Comparison of the amount of Si dissolved by acid-oxalate (Si_{ox} , y-axis) and the amount of Si determined at -78 ppm by solid-state MAS ^{29}Si NMR ($\text{Si}_{-78\text{ppm}}$, x-axis) for soil samples from Funyu (FF), Kiwadashima (KF), and Kwaraya-cho (KO) soils. ●; uppermost horizons, ▲; 4Bw, 4Bw2, and 4Bw3 horizons of Kiwadashima (KF) soil (composed mainly of Imaichi pumice), ○; other horizons.

Conclusion

Atomic status of Al and Si in three allophanic Andosol profiles from Japan were non-destructively analysed with solid-state ^{27}Al and ^{29}Si NMR. It was observed that $^{\text{IV}}\text{Al}$ in volcanic glass was weathered into $^{\text{VI}}\text{Al}$ and Si was converted into allophane and imogolite especially in B horizons. For some samples, the amounts of allophane and imogolite determined by the acid-oxalate dissolution method were significantly different from those by ^{29}Si NMR. It might be possible that the acid-oxalate method might not always be reliable depending on the properties of samples. Non-destructive determination by ^{29}Si NMR could validate the acid-oxalate analysis.

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