

FIVE-COORDINATE ALUMINUM IN ALLOPHANE

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Abstract—Samples of Silica Springs allophane from Tongariro National Park, New Zealand, having Al/Si atomic ratios in the range 1.1–1.9, were studied by ²⁷Al nuclear magnetic resonance (NMR) spectroscopy with high field strength (9.4 and 11.7 T) and fast magic-angle spinning (MAS) (9–13 kHz). Spectra for all samples show peaks for 6- and 4-coordinate Al and also for 5-coordinate Al. For 1 sample, the peak for 5-coordinate Al is dominant. Use of 2 instruments and 2 field strengths allowed the integrity of the spectra and the assignment of 5-coordinate Al to be verified. The “true” chemical shift (after a small correction for quadrupolar shift) observed for 5-coordinate Al in Silica Springs allophane is 36 ± 1 ppm, which is consistent with shifts reported for 5-coordination in well-characterized crystalline structures. We suggest that 5-coordination in Silica Springs allophane is associated with the edges of fragments of incomplete octahedral sheets that are bonded to disordered, though more complete, curved tetrahedral sheets in the primary particles of this allophane. Other allophanes with Al/Si < 2, and which are poor in octahedra relative to tetrahedra, may also have significant Al in 5-coordinate sites.

Key Words—Allophane, Five-coordinate Aluminum, NMR Spectroscopy, Silica Springs.

INTRODUCTION

Five-coordinate Al has been identified in at least 7 different well-characterized crystalline substances (Table 1). In all of these, the relevant site is a distorted bipyramid and the ²⁷Al NMR chemical shifts lie in the range 31 to 41 ppm. This range is clearly distinct from the ranges of –10 to 20 ppm for octahedral sites and 50 to 80 ppm for tetrahedral sites (Müller et al. 1986).

The presence of ²⁷Al NMR signals within, or close to, the chemical-shift range 31 to 41 ppm has been used as evidence for 5-coordinate Al in a number of less-well-characterized solids, such as zeolites (Gilson et al. 1987; Kellberg et al. 1991; Rocha and Klinowski 1991; Coster et al. 1994), aluminosilicate glasses (Risbud et al. 1987; Kohn et al. 1991; Sato et al. 1991), pyrophyllite dehydroxylate (Fitzgerald et al. 1989), Al hydroxyphosphates (Duffy and vanLoon 1995), amorphous and crystalline Al borates (Simon et al. 1995), amorphous aluminosilicates (De Witte et al. 1995) and partly dehydrated gibbsite (Kunath-Fandrei et al. 1995). Five-coordinate Al has not been reported in allophanes previously, but most of the relevant literature has been confined to descriptions of NMR spectra obtained with a medium magnetic field strength (Childs et al. 1990; MacKenzie et al. 1991), for which the signals from tetrahedral and octahedral sites are so broad that they overlap, or with MAS at 3 to 4 kHz (Goodman et al. 1985), which is too slow for a clear distinction between centerband and spinning-sideband signals. A recent study combined a high magnetic field strength with fast MAS (He et al. 1995), but the study was confined to a single sample of allophane that did not show 5-coordinate Al.

The term “allophane” has been used in various ways (Wada 1989) but is now commonly used as a group name for essentially noncrystalline hydrous aluminosilicates (Parfitt 1990; Wada 1995). The Al/Si ratios of known allophanes typically range from ~1 to ~2.5, but ratios up to 4 have also been reported (Parfitt 1990). Soil allophanes with Al/Si ~2 are common; their structure seems to relate closely to that of imogolite and they are sometimes known as “imogolite-like” or “proto-imogolite” allophanes (Wada 1989; Parfitt 1990). Their structure is thought to be based on a “backbone” of a disordered single octahedral sheet formed into a spherule of ~5 nm diameter. Each silicate tetrahedron is bound to the octahedral sheet through the sharing of 3 oxygens surrounding octahedral sites but no, or relatively few, Si-O-Si bonds are present. Allophane structures with Al/Si ~1 appear to contain tetrahedra polymerized into a disordered sheet (Childs et al. 1990; Parfitt 1990) and are sometimes likened to “defect kaolin structures” (Wada 1980).

“Silica Springs allophane” is the name given to the creamy white deposit in the streambed below the vents of Silica Springs on Mount Ruapehu, Tongariro National Park, New Zealand. The site and general characteristics of the allophane are described by Wells et al. (1977). The Al/Si ratio of Silica Springs allophane changes from ~2 to ~1 with increasing distance and pH downstream from the site of initial precipitation. Its structure is believed to differ from that of “imogolite-like” allophanes because IR spectra indicate a significant degree of silicate polymerization (Childs et al. 1990) and because it adsorbs significantly less phosphate at low solution concentrations (Theng et al.

Table 1. Literature data for well-characterized examples of pentacoordinated Al.

Substance	Reference to crystal structure	^{27}Al chemical shift (ppm)	Quadrupolar coupling constant (MHz)	Reference to NMR data
Grandierite	Stephenson and Moore 1968	41	8.7	Smith and Steurnagel 1992
$\text{Al}_2\text{Ge}_2\text{O}_7$	Agafonov et al. 1986	36	8.8	Massiot et al. 1990
$\text{LaAlGe}_2\text{O}_7$	Jarchow et al. 1985	36	7.2	Massiot et al. 1990
Andalusite	Burnham and Buerger 1961	35	5.7	Aleman et al. 1991
Augelite	Araki et al. 1968	31	5.7	Bleam et al. 1989
Senegalite	Keegan et al. 1979	36	<3	Bleam et al. 1989
Barium aluminate glycolate	Cruikshank and Dent Glasser 1985	35	—†	Cruikshank et al. 1986

† Not reported

1982). Silica Springs allophane has been termed a “stream deposit allophane” (Parfitt 1990) and a “hydrous feldspathoid” (Farmer et al. 1979). Whether its structure deviates significantly from those of soil allophanes with $\text{Al}/\text{Si} \sim 1$ remains unclear.

A study based on several methods including medium-field “quantitative” ^{27}Al and ^{29}Si NMR spectroscopy concluded that Silica Springs allophane contained Al in both octahedral (Al^{VI}) and tetrahedral (Al^{IV}) coordination (Childs et al. 1990). The areas of the asymmetric and overlapping peaks were estimated by 2 manual methods and an approximately constant $\text{Al}^{\text{VI}}/\text{Si}$ ratio of $\sim 1/3$ was found for 3 samples representing a range of Al/Si ratios. This and other evidence led to the suggestion of a structure based on a disordered and incomplete single curved 1:1 aluminosilicate layer. The tetrahedral sheet was considered to form the “backbone”, being largely complete, whereas only incomplete fragments of the octahedral sheet were present and probably lay on the inner surface of the curved tetrahedral sheet. Electron micrography showed that some of the primary particles formed

more or less complete spherules of 2–3 nm in diameter and that the primary particles were associated into aggregates up to several hundred nm in size.

Since our earlier medium-field study (Childs et al. 1990), we have gained access to ^{27}Al NMR instruments with high magnetic field strength (~ 10 T) and fast MAS both in New Zealand at Industrial Research Ltd and in Japan at the National Institute of Materials and Chemical Research. We report here new spectra for samples of Silica Springs allophane.

MATERIALS AND METHODS

Samples

Six samples of Silica Springs allophane were selected for study. Details of 3, PC828 (site A), PC829 (site B) and PC830 (site C), have been described previously (Wells et al. 1977; Childs et al. 1990). Three further samples were collected in February 1994 approximately 30 m downstream from site A (R1 and R2) and at approximately 30 m upstream from site C (R3). Samples were lightly crushed with an agate mortar and pestle, dried in air and, apart from R2 and R3, used without further treatment. Samples R2 and R3 were treated with boiling 30% H_2O_2 to reduce contamination by organic matter before analysis; the treated samples were designated R2(HP) and R3(HP).

Powder X-ray diffraction (XRD) patterns were obtained with a Philips 1710 diffractometer fitted with a Co tube and operated at 40 kV and 60 mA. X-ray fluorescence (XRF) analyses were carried out using a Siemens 303AS spectrometer and ignited (1000 °C for 1 h) subsamples incorporated into lithium tetraborate flux.

NMR at 9.4 T

Samples were spun at MAS frequencies between 10 and 12 kHz for ^{27}Al NMR at 104.3 MHz in a Bruker MSL-400 spectrometer. Protons were decoupled during data acquisition, but no change was observed without decoupling. Chemical shifts (Figure 1) were measured relative to the signal from 1 M $\text{Al}(\text{NO}_3)_3$. The usual single-pulse sequence was used: pulse width 1 μs ; recovery time for probe ringing 8 μs ; and recycle

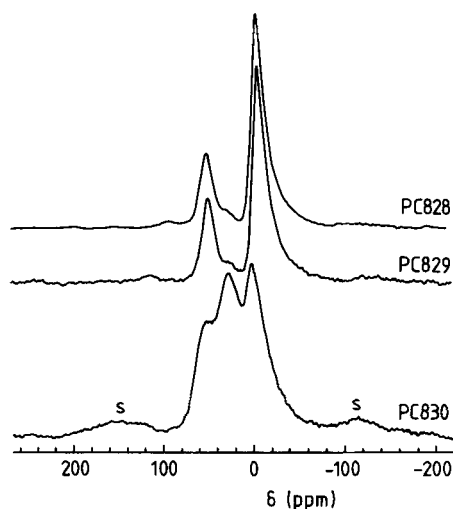


Figure 1. ^{27}Al MAS NMR spectra of 3 samples of Silica Springs allophane run at a magnetic field strength of 9.4 T. Signals assigned to MAS sidebands are labeled “s”.

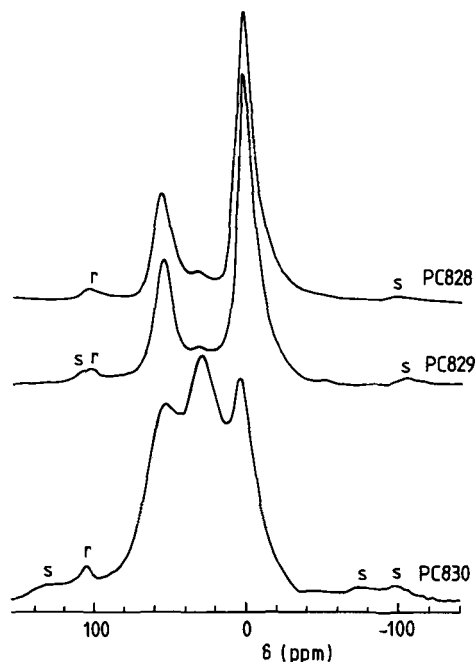


Figure 2. ^{27}Al MAS NMR spectra of 3 samples of Silica Springs allophane run at a magnetic field strength of 11.7 T. Signals assigned to MAS sidebands are labeled "s", and a signal assigned to AlN in the rotor is labeled "r".

time 1 s. The flip angle of the pulse was smaller than $\pi/12$.

NMR at 11.7 T

Between 0.05 and 0.13 g of sample was packed in a 5-mm-diameter cylindrical silicon nitride rotor and sealed with Vespel end caps. The rotor was spun at frequencies between 12 and 13 kHz (Figure 2) or 9 kHz (Figure 3) in a MAS probe (Doty Scientific, Inc.) for ^{27}Al NMR at 130.2 MHz in a Varian Unity-500 spectrometer. Each 1.0- μs radiofrequency pulse was followed by a delay of 2 μs to ensure the discharge of all transmitter power, then 4 ms of data acquisition and a recovery delay of 0.1 or 0.2 s. Transients from at least 800 pulses were averaged and transformed so that 65,536 data points spanned a spectral width of 1 MHz. A weak signal (labelled "r") in Figure 2, is assigned to a trace of aluminum nitride in the rotor (Coster et al. 1994).

The NMR spectrum of 1 sample (PC828) was run again, with the recovery delay increased from 0.1 to 1.0 s. No changes were observed, so the delay of 0.1 s was considered adequate for all other samples. Chemical shifts (Figure 1) were measured relative to the signal from 1 M $\text{Al}(\text{NO}_3)_3$.

RESULTS AND DISCUSSION

Sample Purity

Comparison of element analyses for the 3 most recently collected samples (Table 1) with those reported

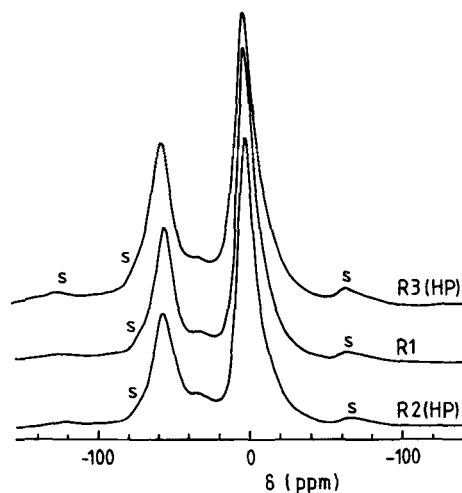


Figure 3. ^{27}Al MAS NMR spectra of 3 samples of Silica Springs allophane run at a magnetic field strength of 11.7 T. Signals assigned to MAS sidebands are labeled "s".

earlier for PC828–PC830 (Wells et al. 1977) indicate the relatively high degree of "purity" of R1, R2(HP) and R3(HP), that is, relatively low concentrations of elements analyzed other than Al and Si.

XRD patterns (not shown) are very similar to that shown previously for PC828 (Childs et al. 1990) with broad and nearly symmetrical bands at 0.34, 0.22 and 0.14 nm. In particular, the absence of any extraneous peaks or shoulders, attributable for example to feldspars, augite or phyllosilicates, indicates minimal, if any, contamination from rock material in the streambed or from other aluminosilicates.

NMR at 9.4 T

The spectra of 3 samples run at a magnetic field strength of 9.4 T (Figure 1) all show peaks at 56 ppm (4-coordinate ^{27}Al) and 4 ppm (6-coordinate ^{27}Al). The spectrum of sample PC828 (Figure 1) shows the 2 principal peaks clearly resolved, unlike the ^{27}Al NMR spectrum of the same sample run at a magnetic field strength of 4.7 T, in which the peaks overlap (Childs et al. 1990). The spectra in Figure 1 also show a peak at 32 ppm (PC828, PC829) or 28 ppm (PC830), assigned to 5-coordinate Al.

NMR at 11.7 T

The spectra of 3 samples run at a magnetic field strength of 11.7 T (Figure 2) all show the same peaks as those in Figure 1, with similar relative signal strengths. Significantly, the apparent chemical shifts are similar for both 9.4 T and 11.7 T spectra. Peaks assigned to 4-coordinate and 6-coordinate Al appear at 57 and 5 ppm, and to 5-coordinate Al at 33 ppm (PC828, PC829) or 31 ppm (PC830). The similarity between Figures 1 and 2 is important because the signals represent the central transition, that is, the (1/2,

$-1/2$) transition, of a quadrupolar nucleus, and are therefore subject to a second-order quadrupolar interaction which displaces each signal from its true chemical shift (Samoson 1985). The true chemical shift, δ_{true} , can be estimated by applying a correction:

$$\delta_{\text{true}} = \delta_{\text{CG}} - \delta_{\text{QS}} \quad [1]$$

where δ_{CG} is the apparent shift, estimated from the center of gravity of the peak, and δ_{QS} is the "quadrupolar shift", that is, the displacement caused by the quadrupolar interaction. Samoson (1985) has provided a general expression for δ_{QS} which reduces, in the present context, to:

$$\delta_{\text{QS}} = -2000(C_Q/\omega_L)^2(3 + \eta^2) \quad [2]$$

where the nuclear quadrupolar coupling constant, C_Q , and the NMR frequency, ω_L , are both expressed in the same units (such as MHz), η is the asymmetry parameter and the result is expressed in ppm.

Raising the magnetic field strength from 9.4 T (Figure 1) to 11.7 T (Figure 2) displaces the peak assigned to 5-coordinate Al by 2 ppm. We do not know the value of η to be inserted in Equation [2], but a 2 ppm displacement corresponds to $C_Q = 3 \pm 1$ MHz regardless of whether η takes the extreme permissible values of 0 or 1, or any value in between. The "true" chemical shift is then 36 ± 2 ppm. This chemical shift is consistent with published values (Table 1) for sites identified by crystal-structure determinations as 5-coordinate.

Table 1 shows that values of C_Q for 5-coordinate sites can vary over a wide range between different structures, from <3 MHz to 8.8 MHz. Similar variations have been reported for 4-coordinate and 6-coordinate sites, for example, $C_Q = 4.5$ and 15.5 MHz for 6-coordinate sites in *augelite* (Bleam et al. 1989) and *andalusite* (Alemany et al. 1991). It seems that the chemical shift, rather than C_Q , provides the more reliable test of coordination number.

Severe distortion of a 4-coordinate site could displace a signal into the chemical-shift range assigned to 5-coordinate sites, but this would require a value of C_Q so large that raising the magnetic field strength from 9.4 T to 11.7 T would cause a signal displacement several times larger than that observed. Severe distortion of a 6-coordinate site would displace the signal to a chemical shift $\ll 0$. In other words, severely distorted sites cannot account for the signal near 32 ppm.

Schmücker and Schneider (1996) have suggested that signals in the vicinity of 30 ppm might arise from 4-coordinate sites with elongated Al–O bonds, rather than 5-coordinate sites. It is not possible to test this alternative assignment in the absence of crystal-structure determinations for substances with elongated Al–O bonds, but our field-dependency experiments indicate that all 4 Al–O bonds would have to be elongated

by the same amount. Uneven elongations would result in an electric field gradient and a consequential elevation of C_Q .

Quantitative NMR

Problems encountered in using a medium-field (4.7 T) NMR spectrometer to compare the relative amounts of 4-coordinate and 6-coordinate ^{27}Al in allophanes have been discussed previously (Childs et al. 1990). In particular, severe signal decay occurred in a gap of 40 μs between switching off the transmitter and acquiring the first data point of the free induction decay. This problem did not occur in the present work, because 1) wide-band detection allowed us to shorten the gap from 40 μs to 2 μs ; and 2) the stronger magnetic fields resulted in narrower linewidths for the central transition, and therefore slower decay of signal strength.

Time constants for the decay of signal strength were measured at 11.7 T, for PC830, as follows: 150 ± 9 μs (4-coordinate Al), 71 ± 3 μs (5-coordinate Al), 72 ± 5 μs (6-coordinate Al). These time constants are all much longer than the 2- μs gap used in the present work.

The overlap between peaks prevents reliable measurements of the percentage of Al in 5-coordination, but a sketch of boundaries between the relevant peak areas by eye suggests a level of a few percent in PC828, rising to about 10% in PC829 and considerably higher in PC830, where it appears to be the dominant signal (Figures 1 and 2).

Reproducibility

The reproducibility of results was tested by collection of further samples (R1, R2 and R3) in February 1994 more than 21 y after the initial sampling. Unfortunately, the site where PC830, which gives the largest signal for 5-coordinate Al (Figures 1 and 2), was collected in 1972, was subsequently buried under a large landslide and resampling exactly at that site was not possible in 1994. Nevertheless, the spectra of the samples collected in 1994 (Figure 3) show 5-coordinate ^{27}Al at levels similar to the other original samples. The spectra for samples R2(HP) and R3(HP), which were pretreated with H_2O_2 to remove contaminant organic material prior to analysis, are consistent with the spectra for samples that were not treated.

Origins of 5-coordinate Al

Álvarez et al. (1995) performed a molecular-dynamics simulation of a $\gamma\text{-Al}_2\text{O}_3$ microcrystal and found 5-coordinate Al relatively concentrated in a superficial poorly ordered phase. This association with poor ordering is consistent with observation of 5-coordinate Al in *Silica Springs* allophane, which is regarded as having only short-range order (Childs et al. 1990).

Table 2. XRF analyses of samples of Silica Springs allophane.

Element	R1 (%)	R2(HP) (%)	R3(HP) (%)
Fe	0.07 ± 0.01	0.12 ± 0.00	1.01 ± 0.01
Mn	<0.02	0.08 ± 0.00	0.30 ± 0.00
Ti	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
Ca	0.14 ± 0.00	0.14 ± 0.00	0.25 ± 0.00
K	<0.02	<0.02	0.02 ± 0.00
P	<0.02	<0.02	0.03 ± 0.00
Si	13.7 ± 0.3	13.6 ± 0.1	16.0 ± 0.1
Al	24.0 ± 0.5	24.2 ± 0.1	20.3 ± 0.1
Mg	0.06 ± 0.00	0.08 ± 0.01	0.11 ± 0.00
Na	<0.03	<0.03	<0.03
LOI	25.5 ± 0.8	25.4 ± 0.2	26.8 ± 0.2
Al/Si	1.82	1.85	1.35

Values are based on 105 °C-dry weights and are means of 4 replicates; LOI, loss of weight on heating from 105 to 1000 °C for 1 h; Al/Si, atomic ratio.

A number of occurrences of 5-coordinate Al have been linked to the presence of significant amounts of elements other than Al and Si, notably P (Duffy and vanLoon 1995), B (Simon et al. 1995) and F (Kohn et al. 1991). This does not seem to apply to our samples. All 3 elements, P, B and F, were below detection in the waters from which Silica Springs allophane precipitated (Wells et al. 1977); see also Table 2.

An apparent inverse correlation between the contents of 5-coordinate and 6-coordinate Al (see figures) may be significant. The correlation can be extended by considering also the New Mexico allophane studied by He et al. (1995). The MAS NMR spectrum for their sample is dominated by a peak assigned to 6-coordinate Al, with only a relatively weak signal from 4-coordinate Al and no detectable 5-coordinate Al. This apparent inverse correlation leads us to suggest a model, based on Figure 6 of Childs et al. (1990), with the addition of 5-coordinate Al associated with defects which must be common in allophanes in which the octahedral sheet is incomplete and fragmented.

This model is consistent with a recent study of Silica Springs allophane by X-ray photoelectron spectroscopy (Childs et al. 1997) which shows that the binding energies for Al, Si and O electrons are similar to those in kaolinite. Analysis of the surface/near surface by XPS also showed that the surfaces of aggregates of Silica Springs allophane samples are enriched in Al relative to the bulk.

Five-coordinate Al occurs in andalusite in association with 6-coordinate Al (Burnham and Buerger 1961), each trigonal bipyramid sharing an edge with an octahedron. Bleam et al. (1989) have reviewed evidence that indicates 6-coordinate Al sites are more easily distorted than 4-coordinate sites. We therefore suggest that 5-coordination in Silica Springs allophane is associated with the edges of fragments of incomplete octahedral sheet that are bonded to disordered,

though more complete, curved tetrahedral sheets in the primary particles of this allophane. It follows that 5-coordination may also occur in other allophanes, especially those with atomic Al/Si < 2 and whose structure is poor in octahedra relative to tetrahedra.

Finally, our results in this paper based on ²⁷Al NMR spectroscopy with higher field strengths and faster MAS supersede those in the earlier paper (Childs et al. 1990) where overlap between the peaks for 4- and 6-coordinate Al obscured any signal for 5-coordinate Al. In our earlier interpretation, contributions from 5-coordinate Al to the spectral envelope would have been quantitatively included, mostly with 6-coordinate Al. We believe, therefore, that the substance of our discussion regarding the ratio of tetrahedral Al to Si and the implications for the structure of Silica Springs allophane (Childs et al. 1990) is not affected.

Note added in proof: A further high-field ²⁷Al NMR spectrum of sample PC829 has recently been published (Allard T, Calas G, Ildefonse P, Morin G, Muller J-P. 1997. Impurities and defects in low temperature mineral components: Tracers of their history. CR Acad Sci Paris, Earth & Planetary Sci 325:1–10). Obtained at 11.7 T and spinning frequency 10.9–11.1 kHz, this spectrum shows similar features to those for PC829 in Figures 2 and 3, including a small peak around 34 ppm which is attributed to 5-coordinate Al.

ACKNOWLEDGMENTS

The authors thank Dr R. H. Meinhold for assistance in obtaining the 11.7 T NMR spectra. CWC thanks the Japan Society for the Promotion of Science for the award of a Senior Fellowship and the late Prof. K. Inoue, Iwate University, Morioka, for hospitality and helpful discussions during completion of this work.

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(Received 4 August 1997; accepted 4 August 1998; Ms. 97-068)