

Structural Studies of Imogolite and Allophanes by Aluminum-27 and Silicon-29 Nuclear Magnetic Resonance Spectroscopy

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Abstract. High-resolution aluminum-27 and silicon-29 nuclear magnetic resonance spectra of natural and synthetic imogolites and allophanes obtained using high-field "magic-angle" sample-spinning (MASS) techniques indicate that the imogolite and protoimogolite components of allophanes are characterized by sharp (≈ 3 ppm) silicon-29 resonances at -78 ± 1 ppm from tetramethylsilane (in accord with Barron et al. 1982), and quite narrow (≈ 10 ppm at 11.7 Tesla) aluminum-27 resonances, at 5.2 ± 1 ppm from $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (in accord with Wilson et al. 1984). However, the spectra of natural allophanes usually contain significant intensity arising from a less well defined material, characterized by a broad (≈ 20 ppm) silicon-29 resonance centered at -90 ± 2 ppm from tetramethylsilane, and a second relatively narrow (≈ 15 ppm at 11.7 Tesla) aluminum-27 resonance at 58.5 ± 2 ppm from $\text{Al}(\text{H}_2\text{O})_6^{3+}$. Similar characteristic spectral features are exhibited by a synthetic amorphous Si:Al (1:1) gel, and presumably indicate the presence of framework aluminosilicate materials in the gel, and in most allophanes.

Introduction

Since the proposal by Farmer and co-workers (1980, 1981, 1982) that imogolite and imogolite-like allophane (designated proto-imogolite allophane) are produced during podzolization, and the demonstration by the same group of workers (1979a, 1979b) that they can be synthesized under controlled conditions in the laboratory, much interest has centered on these materials. Early investigations by infrared (IR) spectroscopy (Russell et al. 1969) indicated the presence of a non-polymerized silicate anion in the imogolite structure, and subsequent work by Cradwick et al. (1972) confirmed the presence of orthosilicate. These workers established that imogolite has a tubular structure, the orthosilicate anion lying over vacant sites in a gibbsite sheet, which is then constrained into the observed tubular morphology. A cross-sectional structure of an imogolite tube is shown in Figure 1. Farmer et al. (1977) showed that imogolite, and compounds containing imogolite-like structures, can be recognized by a characteristic IR absorption band occurring at 348 cm^{-1} , and subsequently they used this feature to identify the formation of imogolite-like organization during imogolite synthesis. These workers also showed that an aluminosilicate, having structural analogies with imogo-

lite, as judged by IR and electron diffraction, is produced as a precursor to imogolite (Farmer et al. 1979b), and that isolation of this sol, either by increasing pH or by salt flocculation, gives an amorphous product referred to as proto-imogolite allophane. Proto-imogolite is envisaged as a non-tubular aluminosilicate with an incompletely formed imogolite structure. Allophane is used in this paper to refer to x-ray amorphous clay minerals that consist of a solid solution of silica, alumina and water. Proto-imogolite allophane with Al:Si=2 is one of several allophanes defined as amorphous aluminosilicates of variable composition, by Ross and Kerr (1934).

Nuclear magnetic resonance (NMR) spectroscopy has already been shown to be capable of providing considerable information about the structures of aluminosilicates (e.g. Klinowski et al. 1981; Lippmaa et al. 1981; de Jong et al. 1983; Smith et al. 1983) including clay minerals (e.g. Barron et al. 1982; Kinsey et al. 1985; Alma et al. 1984). The position of the silicon resonance is affected primarily by its degree of polymerization, and by the nature of the nearest neighbor cations, whereas the aluminum resonance is sensitive primarily to the number of atoms in its immediate coordination environment, i.e. to whether the aluminum is four- or six-fold coordinated by oxygen.

In this study we use both aluminum-27 and silicon-29 solid-state NMR to investigate the structures present in syn-

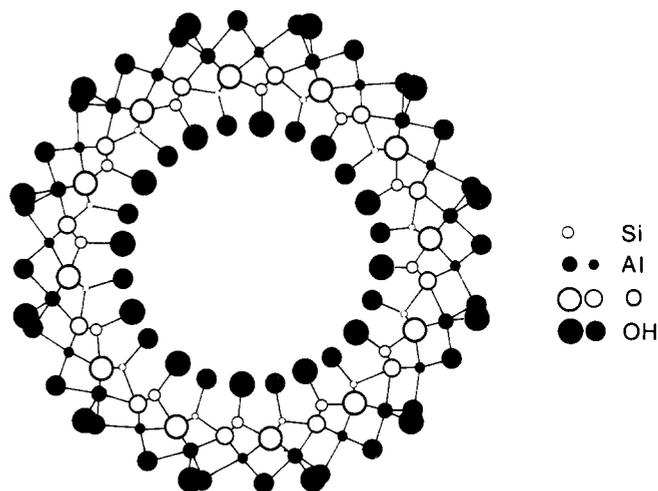


Fig. 1. A cross-section of the structure of an imogolite tube

thetic and natural imogolite, proto-imogolite, and a variety of naturally occurring allophanes. Synthetic imogolite and proto-imogolite appear indistinguishable by NMR, whereas the presence of imogolite-like and more polymerized (framework) components in the natural allophane samples are readily distinguished.

Experimental

Materials. Five natural allophanes and one natural imogolite were investigated, and, for comparison, a synthetic imogolite, a synthetic allophane and a co-precipitated aluminosilicate gel were also studied. Details of the samples are given in Table 1, where the analytical data were taken from the original authors. The natural imogolite from Kurayoshi and the allophanes from Derbyshire, Kakino and Okamoto were separated clay fractions (either $<0.4 \mu\text{m}$ or $<0.2 \mu\text{m}$), whereas the other specimens were unfractionated. Apart from drying, the samples received no other treatment.

Methods. NMR spectra were recorded using a "home-built" Fourier transform spectrometer at 11.7 Tesla. Samples were packed into Delrin rotors (rotor volume $\approx 0.3 \text{ ml}$, sample weights $\approx 100 \text{ mg}$) and spectra recorded under "magic-angle" sample-spinning (MASS) conditions (Andrew 1971) at a spinning frequency of 3–4 kHz. The 90° (solid) pulse widths were $\approx 4 \mu\text{seconds}$ for all samples. Chemical shifts are expressed relative to an external sample of tetramethylsilane for silicon-29 NMR (Smith et al. 1983), and with respect to 1 M $\text{Al}(\text{H}_2\text{O})_6\text{Cl}_3$ in H_2O for the aluminum-27 spectra. The accuracies of the reported chemical shifts vary from about 0.3–1.0 ppm, depending on the line-width observed. Chemical shifts for ^{27}Al have not been corrected for possible second-order quadrupole shifts, which, because of the narrow lines observed, and the high field strengths employed, are expected to be $<1 \text{ ppm}$.

Table 1. Natural and synthetic aluminosilicates and their Al:Si ratios

Sample	Source	(Al:Si) Ratio	Reference
Imogolite	synthetic	2	Farmer and Fraser (1979a)
Proto-imogolite			
Allophane	synthetic	2	Farmer et al. (1979b)
Si-Al gel	synthetic	1	Mitchell et al. (1964)
Imogolite	Kurayoshi, Japan	1.7	Yoshinaga and Yamaguchi (1970)
Proto-imogolite			
Allophane	Bealey Spur, N.Z.	2.3	Young et al. (1980)
Allophane	Derbyshire, U.K.	2.7	MacKenzie (1970)
Allophane	Kakino, Japan	1.1	Parfitt et al. (1980)
Allophane	Okamoto, Japan	1.2	Yoshinaga and Aomine (1962)
Allophane	Silica Springs, N.Z.	1.4	Wells et al. (1977)

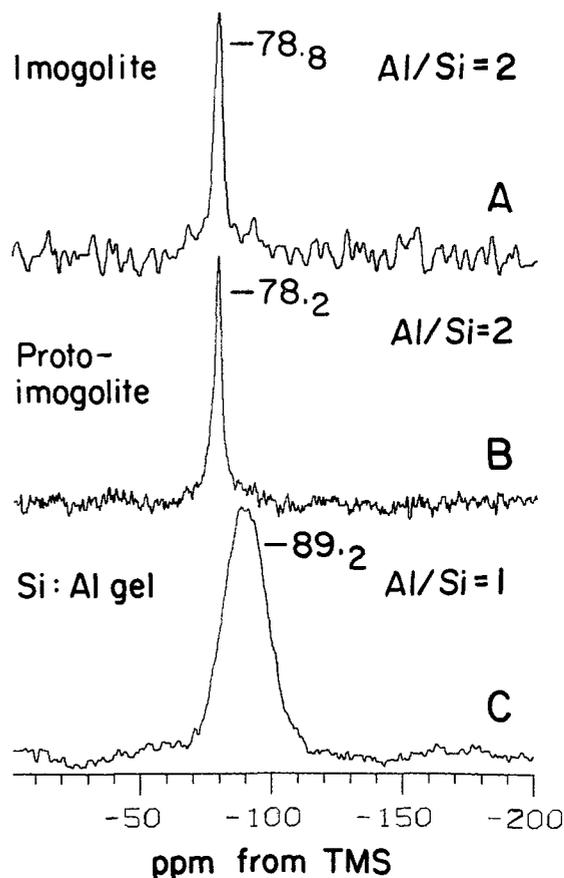


Fig. 2. 99.3 MHz (11.7 Tesla) silicon-29 "magic-angle" sample-spinning NMR spectra of (A) synthetic imogolite, (B) synthetic proto-imogolite and (C) a Si:Al (1:1) gel

Results and Discussion

We show in Figure 2 the 99.3 MHz silicon-29 MASS NMR spectra (corresponding to a magnetic field of 11.7 Tesla) of synthetic imogolite, synthetic proto-imogolite, and of a synthetic Si:Al(1:1) gel. As expected on the basis of previous work by Barron et al. (1982), a single sharp resonance at -78.8 ppm is observed for imogolite. At first sight this highly shielded chemical shift for ^{29}Si in a Q^0 site appears surprising. However, the ^{29}Si shifts for the Al_2SiO_5 polymorphs andalusite and kyanite, which have Q^0 sites in coordination with Al, are at -79.9 and -83.2 ppm , respectively, so that a substantial shielding due to Al over that observed with, e.g., the Ca^{2+} , H^+ or Na^+ nesosilicates, is actually unsurprising. We note also that the predicted chemical shift for an SiO_4^{4-} unit coordinated exclusively with Al^{3+} is -84.2 ppm (Janes and Oldfield 1985), close to the $\sim -79 \text{ ppm}$ found in imogolite. An essentially identical result is obtained for proto-imogolite (Fig. 2A, B). By contrast, the silicon spectrum of the synthetic Si:Al(1:1) gel is broadened by roughly 20 ppm, and has a larger negative shift, indicating either the presence of a rather wide Si-O-Si angle distribution, an increase in silica polymerization, or the occurrence of a range of Si-O-Si and Si-O-Al structures. The centre of this resonance at -89.2 ppm , is significantly deshielded from that of silica gel, for which Maciel and Sindorf (1980) reported values of -109.3 , -99.8 and -90.6 ppm , respectively, for 0, 1 and 2 hydroxyl groups attached to the silicon. These systems serve as models for

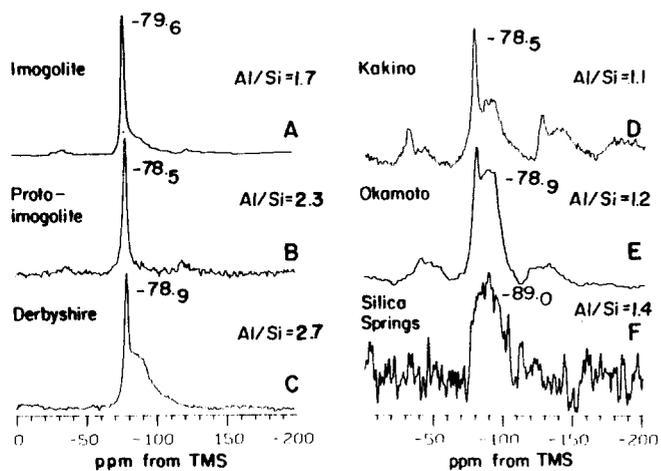


Fig. 3. 99.3 MHz (11.7 Tesla) silicon-29 "magic-angle" sample-spinning NMR spectra of (A) natural imogolite, (B) natural proto-imogolite (Bealey Spur allophane), (C) Derbyshire allophane, (D) Kakino allophane, (E) Okamoto allophane and (F) Silica Springs allophane. The spinning-sidebands in (D) probably arise from the presence of magnetic impurities

our interpretation of the spectra of the natural imogolite/allophane samples discussed below.

We show in Figure 3 the 99.3 MHz silicon-29 MASS NMR spectra of natural imogolite and proto-imogolite samples, together with spectra of allophanes from four different locations. It is immediately seen that, to a first approximation, all spectra are composed of two components: a sharp (≈ 3 ppm) peak at -78 to -79 ppm (imogolite/proto-imogolite), and a broad (≈ 20 ppm) centered at about -90 ppm, this latter feature being due to the presence of more polymerized silicon species. We show below that the amounts of the latter species correlate with the fraction of four-coordinate aluminum, suggesting the presence of more polymerized, aluminous, structural units. These more polymerized units have been interpreted as feldspathoid-like aluminosilicates, on the basis of results from IR spectroscopy (Farmer et al. 1979b). The silicon-29 chemical shifts in the broad peak cover the range from about -80 to -115 ppm, which covers virtually the entire range of chemical shifts (-75 to -120 ppm) observed for silicon in framework aluminosilicates with from 4 to 0 next-nearest neighbor Al atoms (Smith et al. 1983), and encompasses the range -92.5 to -104.2 reported for feldspars (Lippmaa et al. 1980).

The aluminum-27 NMR spectra of the synthetic specimens are shown in Figure 4. Essentially identical results are obtained for synthetic imogolite and proto-imogolite. Both spectra consist of a main peak at 5.5 ± 1 ppm, flanked by a set of spinning-sidebands. The chemical shifts of 5.5 ppm indicates that the aluminum is six-coordinated with oxygen (Müller et al. 1981; Kinsey et al. 1985), and is close to that found for gibbsite (7.8 ppm, Kinsey 1984). These spectra also exhibit a very small peak of $\approx 5 \pm 2$ percent of the intensity of the main peak, at 63 ± 1 ppm, due in part to Al in four-fold coordination, together with a small contribution from the second spinning-sideband from the main, six-coordinate peak. Synthetic imogolite is known to contain a small amount of more-disordered gel-like material, removal of which (by dissolution in cold carbonate solution) results in a product which displays sharper IR bands and electron diffraction rings. This component could be the source of the weak Al(4) peak.

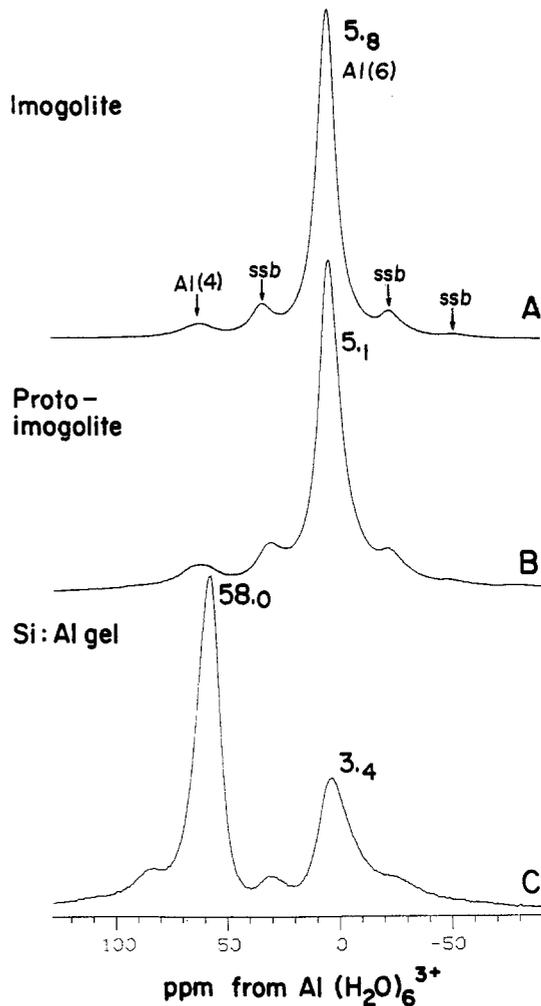


Fig. 4. 130.3 MHz (11.7 Tesla) aluminum-27 "magic-angle" sample-spinning NMR spectra of (A) synthetic imogolite, (B) synthetic proto-imogolite, and (C) a Si:Al (1:1) gel

In contrast to the aluminum NMR spectra of imogolite and proto-imogolite, the aluminum-27 MASS NMR spectrum of the Si/Al(1:1) gel consists of two intense peaks, having shifts of 3.5 ± 1 and 58 ± 1 ppm (Fig. 4C). These shifts are indicative of the presence of both six- and four-coordinate oxygen environments around aluminum, respectively, a conclusion in accordance with the suggested interpretation of the shift to lower frequency of the Si-O stretching band of silica gel as arising from Al substitution into the silicate framework (Mitchell et al. 1964).

For naturally-occurring imogolite and proto-imogolite, ^{27}Al results and IR data (not shown) are very similar to those of synthetic imogolite (Fig. 4A, B and 5A, B), which together with the considerable similarity between the silicon-29 NMR results (Fig. 2A, B and 3A, B) suggest structural similarities. However, there are considerable differences between the aluminum-27 NMR spectra of the different allophanes (Fig. 5C-F). For Derbyshire allophane (Fig. 5C), the aluminum-27 NMR results indicate that most aluminum is in six-fold oxygen coordination, although the IR spectra (unpublished results and Farmer et al. 1977), indicate that it has only weak imogolite character, and the silicon NMR results (Fig. 3C) show significant quantities of the more-polymerized component. The spectrum of the Kakino sample (Fig. 5D) shows a complex pattern of side-

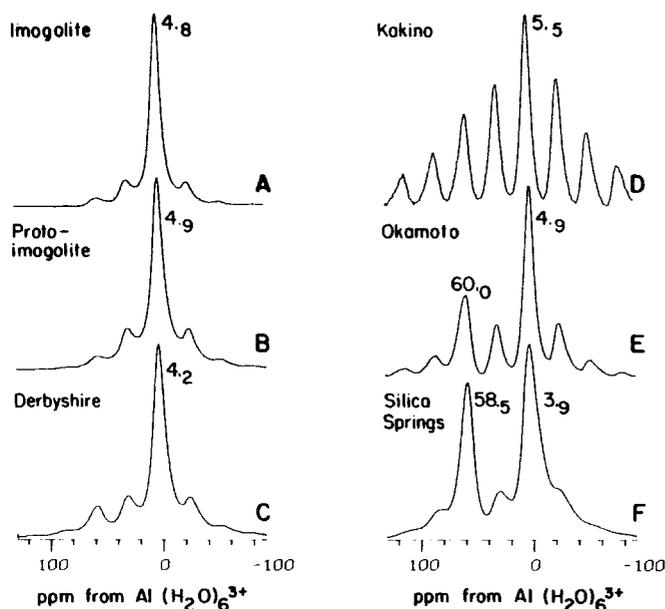


Fig. 5. 130.3 MHz (11.7 Tesla) aluminum-27 "magic-angle" sample-spinning NMR spectra of (A) natural imogolite, (B) natural proto-imogolite (Bealy Spur allophane), (C) Derbyshire allophane, (D) Kakino allophane, (E) Okamoto allophane and (F) Silica Springs allophane. The spinning-sidebands in (D) probably arise from the presence of magnetic impurities

bands, presumably due to the presence of magnetic impurities (Oldfield et al. 1983; Grimmer et al. 1983). This complicates the spectral analysis, but the asymmetry of the sideband distribution is consistent with the presence of a small amount of four-coordinate aluminum, in accord with our interpretation of the broad component in the silicon-29 spectrum (Fig. 3D) as arising from a more polymerized aluminosilicate species. The remaining two allophanes, from Okamoto and Silica Springs, give rather simpler aluminum-27 NMR spectra, showing the presence of both four- and six-coordinated aluminum (Fig. 5E, F), which in all respects seem to resemble the result obtained with the Si/Al(1:1) gel (Fig. 4C). Thus, the Okamoto and Silica Springs samples exhibit peaks at 4.9, 60.0 and 3.9, 58.5 ppm, respectively, corresponding to six- and four-coordinated aluminum, whereas the Si:Al (1:1) gel shows peaks at 3.4 and 58.0 ppm (Fig. 4C). The increased amount of four-coordinated aluminum in these materials compared with the other allophanes is paralleled by increased intensity of the broad -90 ppm component in the silicon-29 NMR spectra (Fig. 3E, F). The IR spectrum of the Silica Springs allophane strongly resembles that of a feldspathoid (Farmer et al. 1979b), in which the SiO_4 tetrahedra are located in framework structures.

Overall, the aluminum-27 and silicon-29 MASS NMR results presented above indicate that the structures of the natural allophanes appear to be described as a mixture of two main species: one is imogolite-like, whereas the second contains more polymerized silicon species, most likely framework aluminosilicates, with perhaps small contributions from sheet structures.

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