
^{27}Al MAS NMR and Aluminum X-ray Absorption Near Edge Structure Study of Imogolite and Allophanes

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Abstract: This paper compares the results of ^{27}Al nuclear magnetic resonance spectroscopy (NMR) and Al-K-edge X-ray Absorption Near Edge Structure (XANES) of natural imogolite and allophanes and some crystalline reference minerals. All soil allophanes studied contain 4-coordinated Al (Al^{IV}). The highest relative proportion of Al^{IV} , 21% of the total Al, was found in Si-rich allophane. This value is close to that found in spring allophanes, which were previously considered to be different from soil allophanes. For a quantitative determination of the $\text{Al}^{\text{IV}}/\text{Al}^{\text{total}}$ ratio, NMR is more reliable than XANES, because of the sensitivity of the chemical shift to low Al^{IV} concentrations, but XANES may be used even if paramagnetic impurities (mostly Fe) are present. Al-K XANES also yields more information than NMR on the local environment of Al^{VI} and especially site multiplicity. Al^{VI} XANES of imogolite and allophanes are similar regardless of the Al/Si ratio. They yield two well-resolved resonances with maxima near 1568 and 1570 eV, which indicates the presence of a unique Al^{VI} site by comparison with crystalline references. The presence of only one Al^{VI} site indicates that imogolite and allophanes have an octahedral sheet with a structure similar to 2/1 dioctahedral phyllosilicates but different from gibbsite or kaolinite, previously considered as structural analogues. The $^{27}\text{Al}^{\text{IV}}$ MAS NMR peak maxima of allophanes are between 58.6 and 59.8 ppm, in the range observed for crystalline and amorphous framework alumino-silicates, and less positive than those of sheet silicates, which are typically in the range 65–75 ppm. $^{27}\text{Al}\text{-H}^1$ CPMAS NMR spectra suggest that both Al^{IV} and Al^{VI} have Al-O-H linkages.

Key Words: Allophane • Aluminum • Imogolite • NMR • XANES

Clays and Clay Minerals; June 1994 v. 42; no. 3; p. 276-287; DOI: [10.1346/CCMN.1994.0420306](https://doi.org/10.1346/CCMN.1994.0420306)

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