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 ^{27}Al 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

Clays and Clay Minerals; February 1999 v. 47; no. 1; p. 64-69; DOI: 10.1346/CCMN.1999.0470107

Clay Minerals Society (www.clays.org)