The Structure and Thermal Transformations of Allophanes Studied by ^{29}Si and ^{27}Al High Resolution Solid-State NMR

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Abstract: Examination of two volcanic and two precipitated allophanes by solid-state NMR, thermal analysis and X-ray powder diffraction shows three of the samples to contain structural features similar to both tubular imogolite and defect layer-lattice aluminosilicates such as kaolinite. The fourth allophane, a precipitated sample from New Zealand, had no imogolite-like features and contained tetrahedral as well as octahedral aluminum. The imogolite-like units in allophane are less stable thermally than tubular imogolite. The NMR spectra and their changes on heating can be accounted for by a structural model in which a two-sheet, kaolinite-like structure containing defects (holes in the tetrahedral sheet) is curved into a sphere in which imogolite-like orthosilicate units are anchored into the octahedral sheet and fit into the tetrahedral defects. Computer simulation shows that the model is crystallographically sound, and accounts for all the known facts, including the spherical morphology, the solid-state NMR spectra and the thermal dehydroxylation behavior of all except the New Zealand allophane, which is of a different structural type.

Key Words: Allophane • Imogolite • Dehydroxylation • Crystal structure • Nuclear magnetic resonance • Thermal treatment • X-ray powder diffraction

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