
A ^{19}F Nuclear Magnetic Resonance Study of Natural Clays

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Abstract: A series of natural clays, including 1:1 layer silicates (serpentines, kaolin minerals), smectites, vermiculite, micas, talc, pyrophyllite, sepiolite, and palygorskite, were studied by ^{19}F magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. The ^{19}F chemical shift in these layer silicates is characteristic of the structure, in particular, to the local octahedral cation occupancy. Fluoride ions bonded to three Mg octahedral cations have a chemical shift of about -177 ppm and those bonded to two Al cations and a vacancy have a chemical shift of about -134 parts per million (ppm). The shift at -182.8 ppm in hectorite is apparently associated with fluoride bonded to two Al cations and a Li cation. Surprisingly, the difference in chemical shift of the interlayer and inner fluoride in 1:1 layer silicates is insufficient to distinguish these sites. Based on trends in chemical shift, it appears that fluoride substitution for inner hydroxyls in clays with octahedral substitution is not random. Fluoride is apparently preferentially associated with Mg rather than Al in the octahedral sheet as no resonance due to a fluoride bonded to two Al cations and a vacancy is observed in clays such as SAz-1.

Key Words: ^{27}Al • Aluminum • Clay minerals • ^{19}F • Fluorine • MAS • NMR • Solid

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