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# Aluminum ordering and clustering in Al-rich synthetic phlogopite: The influence of fluorine investigated by {$^{19}$F/$^{1}$H} $^{29}$Si CPMAS NMR spectroscopy

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## Abstract

The influence of fluorine on cationic and anionic ordering in the mica mineral phlogopite has been investigated using $^{29}$Si, $^{1}$H, and $^{19}$F MAS as well as {$^{1}$H}/{$^{19}$F} → $^{29}$Si CPMAS and CP-depolarization NMR spectroscopies. It can be shown that the mere presence of fluorine achieves a tremendous loss of capability to incorporate aluminum into the phlogopite structure. Fluorine is usually located in Mg-rich octahedral and Si-rich tetrahedral clusters of the phlogopite structure while hydroxyl groups are located in Al-rich octahedral and tetrahedral clusters as derived from {$^{1}$H}/{$^{19}$F} → $^{29}$Si CPMAS NMR spectroscopies. The ordering effect in these two basic structural clusters can also be proven by a smaller $^{29}$Si linewidth in the {$^{19}$F} → $^{29}$Si CPMAS NMR experiments compared to the usual $^{29}$Si MAS NMR experiment showing a stronger ordering of Si environments near the two different anion types fluorine and hydroxyl. Intensities of the {$^{1}$H}/{$^{19}$F} → $^{29}$Si CPMAS NMR signals as function of the contact-time show a deviation from the classical I-S model and can be attributed to the *I-I*-S* model. Time constants like the proton/fluorine spin diffusion time ($T_{df}$), the spin-spin relaxation time ($T_2$), the λ parameter (λ), and the proton/fluorine spin-lattice time in the rotating frame ($T_{1\rho}$) were extracted to give information about the local structure.

**Keywords:** $^{1}$H, $^{19}$F, $^{29}$Si, solid state, NMR, MAS, CPMAS, depolarization, phlogopite, fluorine