
Determination of Tetrahedral Substitutions and Interlayer Surface Heterogeneity from Vibrational Spectra of Ammonium in Smectites

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Abstract: Integrated intensities of the fundamental modes of vibrations of ammonium in heat-treated, NH_4^+ -exchanged swelling minerals permits (1) a quantitative determination of the amount of tetrahedral substitutions of Si^{4+} by M^{3+} in dioctahedral smectites, and (2) an estimate of the degree of interlayer surface heterogeneity in trioctahedral minerals to be made. This is possible because NH_4^+ cations balancing the negative charge of tetrahedral sites that are not influenced by an excess positive charge of the octahedral layer have a symmetry lower (probably C_{3v}) than the usual tetrahedral T_d symmetry of NH_4^+ . In C_{3v} symmetry the ν_1 band is infrared active whereas it is only Raman active in T_d symmetry. Protons left after deammoniating dioctahedral smectites with tetrahedral substitutions form interlayer silanol groups, the stretching vibration of which give a band that is distinct from that of octahedral OH-stretching modes.

Key Words: Ammonium • Hofmann-Klemen effect • Infrared spectroscopy • Smectite • Tetrahedral substitution

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