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Influence of layer charge on the hydroxyl stretching of trioctahedral clay minerals: A vibrational study of synthetic Na- and K-saponites

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ABSTRACT

To understand the behavior of octahedral hydroxyl-stretching modes (ν_{OH}) as a function of increasing tetrahedral layer charge, infrared and Raman spectroscopic studies were carried out on a series of synthetic saponites. The nature of the monovalent interlayer cation (Na or K) and the hydration of the samples were shown to strongly influence spectral features. In the case of hydrated Na-samples, the ν_{OH} position shifts from 3678 to 3686 cm^{-1} with increasing layer charge. For hydrated K-saponites, two components are observed around 3720 and 3680 cm^{-1}, assigned to OH perturbed by compensating cation and free OH groups, respectively. In the case of dehydrated samples both K and Na-saponites exhibit two components at 3677 and 3720 cm^{-1}. A linear relationship between the relative area of these two ν_{OH} components and the layer charge was then evidenced. To assign the features obtained for hydrated Na-samples in the OH-stretching modes domain, the Raman spectra were decomposed using four ν_{OH} components around 3675, 3680, 3685, and 3690 cm^{-1}. The evolution with layer charge of the relative proportions of these four components can be described by taking into account the location of hydrated cations, related to the distribution of tetrahedral substitutions. Such an assumption was confirmed using a simple statistical model that yields four populations of OH groups in the octahedral layer of hydrated Na-saponites.