

Isomorphous cation substitution in dioctahedral phyllosilicates by means of ab initio quantum mechanical calculations on clusters

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ABSTRACT

The geometrical features and electronic structure of molecular cluster models of two edge-sharing octahedrally coordinated cations, with and without a ring of six silica tetrahedra coupled to the two octahedra, were studied by means of ab initio molecular orbital calculations made with Hartree-Fock (at LANL2DZ and 6-311+G* levels) and Density Functional Theory (DFT) methods. These models represent different pairs of Al³⁺, Fe³⁺, Fe²⁺, and Mg²⁺ cations from the octahedral sheet of clays. The isomorphous substitution reactions of these cations in our molecular clusters were studied by means ofisodesmic reactions. A tendency of Mg²⁺ to mix with Al³⁺ cations along the octahedral sheet was found, agrees with experimental results. A lower tendency of Fe³⁺ to mix with Al³⁺ was found in systems with only Al and Fe octahedral cations. However, the presence of Mg²⁺ catalyses the clustering of Fe³⁺ in Al/Fe/Mg samples, giving a cation ordering tendency similar to that found experimentally. The geometry and the hydrogen-bonding interactions of the OH groups were also studied. The $\nu(\text{OH})$, $\delta(\text{OH})$, and $\gamma(\text{OH})$ vibration mode frequencies were calculated and show good agreement with experimental values for $\nu(\text{OH})$ and $\delta(\text{OH})$, which suggests that this technique is a good predictive tool for $\gamma(\text{OH})$. The octahedral cation substitution effect on the vibrations of OH groups was calculated and reproduced the experimental behavior. The hydrogen-bonding interactions with tetrahedral O atoms are important for the $\nu(\text{OH})$ frequency, but are not significant for $\delta(\text{OH})$. These results show that the effect of the tetrahedral sheet on the OH groups is constant for the different cation pairs joined to these OH groups.