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Density functional theory and Monte Carlo study of octahedral cation ordering of Al/Fe/Mg cations in dioctahedral 2:1 phyllosilicates

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Abstract

The ordering of octahedral Al^{3+}, Fe^{3+}, and Mg^{2+} cations in dioctahedral 2:1 phyllosilicates was studied theoretically. Quantum mechanical calculations based on density functional theory (DFT) were performed for optimizing different cation distributions along the octahedral sheet. Three systems of two species (Al^{3+}/Mg^{2+}, Al^{3+}/Fe^{3+}, and Fe^{3+}/Mg^{2+}) were studied to obtain the cation exchange potentials J_n as first, second, third, and fourth nearest neighbors. Monte Carlo (MC) simulations based on the previously calculated cation exchange potentials J_n of these binary systems showed ordering phase transition in the distribution of the octahedral cations, with different ordering patterns. Ordered phases are depending on composition and on third and fourth neighbor range interactions. The effect of hydrostatic pressure can affect the cation ordering of the octahedral sheet. The two-species model was extended to a three-species ordering MC simulation model. In our case, we do not find perfect long-range ordering in the three-species systems. Instead we find some domains with different ordering patterns.

Keywords: Smectites, cation ordering, Monte Carlo, first-principles calculations