

Cation arrangement in the octahedral and tetrahedral sheets of *cis*-vacant polymorph of dioctahedral 2:1 phyllosilicates by quantum mechanical calculations

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ABSTRACT

Density functional theory (DFT) calculations were performed to study the crystallographic properties of the *cis*-vacant form of dioctahedral 2:1 phyllosilicates. Samples with different layer charges are studied; only tetrahedrally charged, only octahedrally charged, or mixed octahedrally/tetrahedrally charged. The isomorphous cation substitutions were explored in different relative positions with substitutions of octahedral Al³⁺ by Mg²⁺ or Fe³⁺, tetrahedral substitution of Si⁴⁺ by Al³⁺, and different interlayer cations (IC) (Na⁺, K⁺, and Ca²⁺). X-ray diffraction patterns of *cis*-vacant and *trans*-vacant forms of phyllosilicates were simulated and compared. The experimental observation of clustering tendency of Fe³⁺ and dispersion tendency of Mg²⁺ in the octahedral sheet is reproduced and explained with reference to the relative energies of the octahedral cation arrangements observing the same tendency that in the *trans*-vacant forms. These energies are higher than those due to the IC/tetrahedral and IC/octahedral cations relative arrangements. The tetrahedral and octahedral substitutions that generate charged layers tend also to be dispersed. The energy difference between the *cis*-vacant and *trans*-vacant polymorphs is smaller than that of cation arrangements.

Keywords: DFT, clays, cation-ordering, phyllosilicate, polymorph, *cis*-vacant