

Oxidation-reduction mechanism of iron in dioctahedral smectites: II. Crystal chemistry of reduced Garfield nontronite

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ABSTRACT

The crystallochemical structure of reduced Garfield nontronite was studied by X-ray absorption pre-edge and infrared (IR) spectroscopy, powder X-ray diffraction, polarized extended X-ray absorption fine structure (P-EXAFS) spectroscopy, and texture goniometry. Untreated and highly reduced (>99% of total Fe as Fe²⁺) nontronite samples were analyzed to determine the coordination number and the crystallographic site occupation of Fe²⁺, changes in in-plane and out-of-plane layer structure and mid-range order between Fe centers, and to monitor the changes in structural and adsorbed OH/H₂O groups in the structure of reduced nontronite. Contrary to earlier models predicting the formation of fivefold coordinated Fe in the structure of nontronites upon reduction, these new results revealed that Fe maintains sixfold coordination after complete reduction. In-plane P-EXAFS evidence indicates that some of the Fe atoms occupy trans-sites in the reduced state, forming small trioctahedral domains within the structure of reduced nontronite. Migration of Fe from cis- to trans sites during the reduction process was corroborated by simulations of X-ray diffraction patterns which revealed that about 28% of Fe²⁺ cations exist in trans sites of the reduced nontronite, rather than fully cis occupied, as in oxidized nontronite. Out-of-plane P-EXAFS results indicated that the reduction of Fe suppressed basal oxygen corrugation typical of dioctahedral smectites, and resulted in a flat basal surface which is characteristic of trioctahedral layer silicates. IR spectra of reduced nontronite revealed that the dioctahedral nature of the nontronite was lost and a band near 3623 cm⁻¹ formed, which is thought to be associated with trioctahedral [Fe²⁺]₃OH stretching vibrations. On the basis of these results, a structural model for the reduction mechanism of Fe³⁺ to Fe²⁺ in Garfield nontronite is proposed that satisfies all structural data currently available. The migration of reduced Fe ions from cis-octahedra to adjacent trans-octahedra is accompanied by a dehydroxylation reaction due to the protonation of OH groups initially coordinated to Fe. This structural modification results in the formation of trioctahedral Fe²⁺ clusters separated by clusters of vacancies in which the oxygen ligands residing at the boundary between trioctahedral and vacancy domains are greatly coordination undersaturated. The charge of these O atoms is compensated by the incorporation of protons, and by the displacement of Fe²⁺ atoms from their ideal octahedral position toward the edges of trioctahedral clusters, thus accounting for the incoherency of the Fe-Fe1 and Fe-Fe2 distances. From these results, the ideal structural formula of reduced Garfield nontronite is Na_{1.30}[Si_{7.22}Al_{0.78}][Fe_{3.65}²⁺Al_{0.32}Mg_{0.04}]_{17.93}(OH)₅ in which the increased layer charge due to reduction of Fe³⁺ to Fe²⁺ is satisfied by the incorporation of protons and interlayer Na.