

## **Effect of Fe oxidation state on the IR spectra of Garfield nontronite**

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### **ABSTRACT**

The effects of Fe oxidation state on the infrared (IR) spectra of dioctahedral smectite were studied using a purified and Na<sup>+</sup>-saturated fraction of the Garfield nontronite reference clay. The nontronite was first reduced with sodium dithionite for a period of 10 to 240 min to obtain various Fe reduction levels. The reduced samples were then reoxidized by bubbling O<sub>2</sub> through the suspensions for 8 to 12 h. IR spectra were collected on the initially unaltered, the reduced, and the reduced-reoxidized samples. After reduction, changes were observed in the spectral regions of O-H stretching, O-H deformation, and Si-O stretching, indicating that the clay structure was significantly modified beyond merely a change in Fe oxidation state. Furthermore, a new component band in the O-H stretching region of the reduced samples exhibited a pleochroic effect, indicating the possible existence of trioctahedral domains. A large (up to 43 cm<sup>-1</sup>) downward shift of the main Si-O stretching band of the reduced samples was also observed. Such a large shift indicates that the change in Fe oxidation state in the octahedral sheet strongly affects the structural properties of the tetrahedral sheet, which might further affect physical and chemical properties of the mineral surface. The spectral differences across all three studied regions between unaltered and reoxidized samples after up to 240 min of reduction indicated that the redox process involving sodium dithionite is in some respects irreversible, even though virtually all structural Fe<sup>2+</sup> can be reoxidized.