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Oxidation-reduction mechanism of iron in dioctahedral smectites: I. Crystal chemistry of oxidized reference nontronites

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ABSTRACT

The crystal chemistry of Fe in four nontronites (Garfield, Panamint Valley, SWa-1, and NG-1) was investigated by chemical analysis, X-ray goniometry, X-ray absorption pre-edge spectroscopy, powder and polarized extended X-ray absorption fine structure (EXAFS, P-EXAFS) spectroscopy, and X-ray diffraction. The four reference nontronites have Fe/(Fe + Al + Mg) ratios ranging from 0.58 to 0.78, and are therefore representative of the different chemical compositions of dioctahedral ferruginous smectites. Pre-edge and powder EXAFS spectroscopy indicate that NG-1 contains 14 to 20% of tetrahedrally coordinated Fe^{3+}, whereas the other three samples have no detectable $^{IV}Fe^{3+}$. The partitioning of $^{VI}Fe^{3+}$ between cis (M2) and trans (M1) sites within the octahedral sheet was determined from the simulation of X-ray diffraction patterns for turbostratic nontronite crystallites by varying the site occupancy of Fe. Based on this analysis, the four nontronite samples are shown to be trans-vacant within the detection limit of 5% of total iron. The in-plane and out-of-plane local structure around Fe atoms was probed by angular P-EXAFS measurements performed on highly oriented, self-supporting films of each nontronite. The degree of parallel orientation of the clay layers in these films was determined by texture goniometry, in which the half width at half maximum of the deviation of the c^* axis of individual crystallites from the film plane normal, was found to be 9.9° for Garfield and 19° for SWa-1. These narrow distributions of orientation allowed us to treat the self-supporting films as single crystals during the quantitative analysis of polarized EXAFS spectra. The results from P-EXAFS, and from infrared spectroscopy (Madejova et al. 1994), were used to build a two-dimensional model for the distribution of Fe, and (Al,Mg) in sample SWa-l. In this nontronite, Fe, Al, and Mg atoms are statistically distributed within the octahedral sheet, but they exhibit some tendency toward local ordering. Fe-Fe and (Al, Mg)-(Al,Mg) pairs are preferentially aligned along the [010] direction and Fe-(Al,Mg) pairs along the [3$\bar{1}$0], and [3$\bar{1}$0] directions. This distribution is compatible with the existence of small Fe domains separated by (Al,Mg), and empty octahedra, which segregation may account for the lack of magnetic ordering observed for this sample at low temperature (5 K) (Lear and Stucki 1990).