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


1Environmental Geochemistry Group, LGIT-IRIGM, University Joseph Fourier and CNRS, 38041 Grenoble Cedex 9, France
2LPEC, Université du Maine-Le Mans, av. Olivier Messiaen, BP535 72085 Le Mans cedex, France
3Department of Natural Resources and Environmental Sciences, University of Illinois, W-317 Turner Hall, 1102 South Goodwin Avenue, Urbana, Illinois 61801, U.S.A.

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 Fe$^{3+}$. The partitioning of 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-1. 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 [310], and [310] 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).

INTRODUCTION

Nontronite is a hydrous Fe$^{3+}$-bearing dioctahedral phyllosilicate that occurs widely in soils, weathering formations, and sediments. Its structure and chemical reactivity are reviewed by Güven (1991) and Stucki (1988). The general structural formula for nontronite is $(Si_{8-x-y}Al_xFe_y^{3+})_{Tet}(Fe^{3+}_{4-z}Al_z)_{Oct}Ex^{+}_xO_{20}(OH)_4\cdot nH_2O$, where Tet, Oct, and Ex represent tetrahedral, octahedral, and interlayer cations. Nontronite is a 2:1 clay mineral, and thus contains two tetrahedral sheets per octahedral sheet (Fig. 1a). Tetrahedral sites are predominantly filled by Si ions but substitutions of Al, and occasionally of Fe$^{3+}$, can occur. Octahedral sites contain predominantly Fe$^{3+}$, with Al and a minor amount of Mg. The octahedral sheet has two different sites denoted M1 and M2. M1 is the trans octahedron with OH groups located at opposing corners whereas M2 is the cis octahedron with the two OH groups located on the same edge (Fig. 1a). Only two of the three octahedral positions per half unit cell (2 M2 + M1) are occupied, which can be either the two M2 sites (denoted herein as trans-vacant, tv), or the M1 and one of the two symmetrically independent M2 sites (denoted herein as cis-vacant, cv).