Effects of Reduction and Reoxidation of Structural Iron on the Surface Charge and Dissolution of Dioctahedral Smectites

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Abstract: The effect of Fe oxidation state on the surface charge (CEC) and solubility of smectites were studied using the <2-μm, Na^+-saturated fraction of an Upton, Wyoming; a Czechoslovakian; and a New Zealand montmorillonite; and a Garfield, Washington, nontronite. The reduction of structural Fe^{3+} in the octahedral sheet of each clay produced a net increase in the negative surface charge of the clay. The observed cation-exchange capacities deviated from the linear relationship predicted by charge-deficit calculations, assuming changes only in the Fe^{2+}/Fe^{3+} ratio, and reversibly followed Fe reduction according to a 2nd-degree polynomial function. The deviations suggest reversible changes in mineral structure and composition during Fe reduction.

These clays were susceptible to partial dissolution in citrate bicarbonate (CB) and citrate-bicarbonate-dithionite (CBD) solutions. Small amounts of Fe and Si dissolved as a result of Fe reduction in CBD, but affected < 1% of the total clay mass except for the Czechoslovakian clay in which 2% of the clay dissolved. Although slightly more Fe dissolved than Si, no change in surface charge was noted. Almost no dissolution of these elements was detected in CB solution. In contrast, significant Al was detected in the CB solution, suggesting a heterogeneous dissolution mechanism. The CEC, however, was unchanged by the CB treatment. These results may be explained by the adsorption of hydrogen ions into the vacated Al^{3+} sites in the mineral structure. Dissolution seems to have been independent of the effects of Fe oxidation state on surface charge.

Key Words: Dissolution • Iron • Nontronite • Oxidation • Reduction • Smectite • Surface area

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