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# A Model for the Mechanism of Fe<sup>3+</sup> to Fe<sup>2+</sup> Reduction in Dioctahedral Smectites

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**Abstract:** A model to compensate the 2:1 layer having excess negative charge owing to the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> by sodium dithionite buffered with citrate-bicarbonate in nontronite, beidellite, and montmorillonite is proposed. This model is based on reassessing published experimental data for Fe-containing smectites and on a recently published structural model for reduced Garfield nontronite. In the reduced state, Fe<sup>2+</sup> cations remain six-fold coordinated, and increases of negative charge in the 2:1 layer are compensated by the sorption of Na<sup>+</sup> and H<sup>+</sup> from solution. Some of the incorporated protons react with structural OH groups to cause dehydroxylation. Also, some protons bond with undersaturated oxygen atoms of the octahedral sheet. The amount of Na<sup>+</sup> ( $p$ ) and H<sup>+</sup> ( $n_i$ ) cations incorporated in the structure as a function of the amount of Fe reduction can be described quantitatively by two equations:  $p = m/(1 + K_0 m_{rel})$  and  $n_i = K_0 m m_{rel}/(1 + K_0 m_{rel})$ ; with  $K_0 = CEC (9.32 - 1.06m_{tot} + 0.02m_{tot}^2)$ , where  $m_{tot}$  is the total Fe content in the smectite,  $m$  is the Fe<sup>2+</sup> content,  $m_{rel}$  is the reduction level ( $m/m_{tot}$ ), CEC is the cation-exchange capacity, and  $K_0$  is a constant specific to the smectite. The model can predict, from the chemical composition of a smectite, the modifications of its properties as a function of reduction level. Based on this model, the structural mechanism of Fe<sup>3+</sup> reduction in montmorillonite differs from that determined in nontronite and beidellite owing to differences in the distribution of cations over *trans*- and *cis*-octahedral sites.

**Key Words:** CMS Source Clay SWa-1 • Dioctahedral Smectite • Iron Reduction • Structural Formula

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