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Modeling the dioctahedral smectites layer charge variation versus structural Iron reduction level

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Iron is one of the most common redox species in soils and sedimentary rocks. Amongst iron-bearing phases, phyllosilicates might play key roles in various bio-geochemical processes involving redox reactions, where structural Fe (Fe_{str}) can act as a renewable source/trap of electron.

A large set of data from kinetics, spectroscopic or electrochemical studies on dioctahedral smectites demonstrates that reduction of Fe_{str} impacts many clay properties such as colour, layer charge, swelling pressure, colloidal properties that are linked to layer structural changes. Experiments also suggest that this mechanism is partly reversible, depending on type and properties of the primary oxidized clay, on how the reduction is induced (chemically and/or biologically) and on extent of iron reduction level.

The complexity of the involved mechanisms makes the prediction of Fe_{str} redox properties challenging. For instance, only empirical models are currently available to quantify structural changes as a function of reduction level. However, a predictive and mechanistic model of these changes is a prerequisite to develop a thermodynamic model for Fe_{str} redox properties.

In this contribution, we propose a mechanistic statistical model to explain 2:1 layer excess negative charge changes induced by structural Fe(III) to Fe(II) chemical reduction (by dithionite). This model completes this published by Drits and Manceau (2000) and was calibrated on data from our own and from the literature.

Actually, a large number of studies on Fe_{str} redox properties (E_h and kinetics) neglects the major structural changes that occur during redox reactions of this material and that are partially reversible, and are focused in measuring a single E_h value. Actually, the complex relationship that exist between the different structural iron sites should lead to consider that not only one but several Fe(II)/Fe(III) poles (classes) must exist in the structure, thus exhibiting gradually decreasing E_h values. Hence, further developments of our model will include Crystal Field Theory (CFT) calculation to identify the variety of Fe_{str} redox potential, which arises from the varying Fe_{str} neighbouring inside the same structure and along the redox processes.

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References

Drits, V.A. and Manceau, A. (2000) *A model for the mechanism of Fe^{3+} to Fe^{2+} reduction in dioctahedral smectites.* Clays and Clay Minerals **48**:185-195.