“Switching on” Fe(III) in the octahedral sheet of Fe-phyllosilicate

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Iron residing in clay mineral structures can be a catalyst or directly participate in electron transfer reactions. The apparent redox potential of this iron species depends on the total iron content, layer charge, and redox history. The redox potential for the Fe(II)/Fe(III) couple in nontornite, estimated using crystal field theory, is 0.710 V. The standard redox potential of the As(III)/As(V) couple is 0.56 V, therefore, NAu-1 is expected to oxidize As(III) to As(V); however, this reaction does not occur under ambient conditions.

We were able to activate the surface of NAu-1, as well as the surface of its synthetic analog produced in our lab (SIP), and promote the oxidation of As(III) to As(V) in batch reactors. This activation requires that a fraction of Fe (< 20% of total) is reduced to Fe(II), leaving the majority of the octahedral iron as Fe(III). We used citrate-bicarbonite-dithionite procedure to achieve this partial reduction. The oxidation of As(III) to As(V) proceeds within several hours, under both oxic and anoxic conditions. The extent of As(III) oxidation is higher in the presence of dissolved O_2; however, it is also significant under anoxic conditions. We conclude that activation causes the clay mineral surface to act both as a catalyst and as an e^- acceptor. Similarly, but less pronounced, activation is achieved following an addition of aqueous Fe(II) to the batch reactors with NAu-1 or SIP in place of the partial reduction treatment. Proposed reaction pathways will be discussed.

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