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Organic contaminant transformation by Fe(II)-reduced clay minerals

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Clay minerals are ubiquitous in the environment and most clay minerals contain Fe in their structure, which can be reduced both microbially and chemically. We have recently demonstrated that aqueous Fe(II), an abundant reductant in anoxic environments, is also capable of transferring electrons to structural Fe in clay minerals, resulting in the formation of clay mineral Fe(II) and an Fe(III) oxidation product. It is unclear (i) how reduction with Fe(II) and the presence of an *in situ*-formed solid Fe(III) oxidation product affect the reactivity of clay minerals towards organic contaminants, and (ii) whether the clay mineral reactivity differs for Fe(II)-reacted clay minerals with high and low Fe content.

To assess the reactivity of Fe(II)-reduced clay minerals, we used nitroaromatic compounds as reactive probes. We compared the probe compound transformation kinetics in suspensions of Fe(II)-reduced and chemically (dithionite) reduced Fe-rich clay mineral NAu-1. Our results demonstrate that dithionite and Fe(II)-reduced NAu-1 with the same Fe(II)/Fe(III) ratios exhibit the same redox reactivity, suggesting a negligible effect of the Fe(III) oxidation product on the bulk reactivity. Interestingly, we observed significant differences between dithionite and Fe(II)-reduced NAu-1 at at Fe(II)/Fe(tot) ratios at and below 5% and are currently investigating the mechanism(s) involved.

To explore the impact of clay mineral Fe content on both Fe(II)-Fe(III) electron transfer and resulting clay mineral Fe reactivity, we used Fe-poor clay mineral SWy-2 in similar experiments. In contrast to NAu-1, where clay mineral Fe reduction was limited to 10%, extensive amounts of structural Fe(III) of up to 78% were reduced in SWy-2. Further results from sequential extractions and Mössbauer spectroscopy suggest that Fe(II)-Fe(III) electron transfer occurs through the basal planes of SWy-2. We are currently examining the impact of the extensive electron transfer on the redox reactivity of SWy-2, using reactive probes.