Molecular-Scale Ion Binding and Dynamics at Hydrated Smectite-NOM Interfaces: Insights from NMR

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Natural organic matter (NOM) is known to play important roles in metal ion sorption and transport, and NOM is often found associated with minerals in the soils, oil shales, and suspended colloids in natural waters. However, the impact of NOM on the interfacial dynamics of ions and H_2O in hydrated mineral systems (particularly smectites and other phyllosilicates) has yet to be explored in great detail and is essential to understand a variety of issues in geochemistry and energy science. In this work, we present variable temperature ^{43}Ca and ^{23}Na solid-state nuclear magnetic resonance (NMR) results that provide unique insight into the types of cation binding environments and molecular-scale dynamics in Suwannee River NOM-hectorite (a smectite clay) composites. Our data from composites equilibrated at two different H_2O activities show that the ^{43}Ca NMR signal is more like that of the base Ca-hectorite than Ca^{2+} bound in aggregated NOM despite evidence of significant Ca^{2+} association with the OM. The data also show that the presence of OM broadens the ^{43}Ca resonances at all temperatures compared to the base Ca-hectorite, shifts the resonance frequency to more negative values, and leads to line narrowing between 198 K and 173 K not observed when OM is absent, yet the Ca^{2+} dynamics appear to be dominated by fast motion effects. The specific NOM fraction (humic acid, fulvic acid, etc.) has little influence on the Ca^{2+} behavior. Na^+ in Na-hectorite-OM systems generally yields interlayer peaks with kHz-scale dynamics and sharp peaks for H_2O-accessible Na^+ with MHz-scale dynamic averaging. Sites appear similar to the base Na-hectorite, but the dynamic rates are changed when OM is present. Residual Na^+ in the Ca-hectorite-OM composites shows either unique dynamics or selective retention of a specific Na^+ population during Ca^{2+} ion exchange/NOM intercalation. We conclude that Ca^{2+} and Na^+ binding structures and dynamics at hydrated smectite interfaces are affected by the inclusion of NOM, which may have significant consequences for predicting the fate and transport of metal contaminants in soils.