Influence of Supercritical CO_2 on Interfacial Ion Binding and Dynamics in Smectite-NOM Composites

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Clay minerals are common constituents of rocks in potential geological CO_2 repositories, however, very few studies examine the role that natural organic matter in these rocks plays in controlling the structure and dynamics of cations, organic matter, CO_2 and water. We report the results of novel ^{13}C and ^{23}Na solid-state NMR studies performed *in situ* at 50°C and 90 bars examining the effects of $scCO_2$ and natural organic matter (NOM) on the binding and dynamics of CO_2 and Na^+ in Na-hectorite (a smectite clay) and a Na-hectorite-Suwannee River humic acid (HA) composite. We observe broadening of the ^{13}C NMR resonance for CO_2 in the composites with respect to pure $scCO_2$ indicating association of CO_2 with the solid phase that increases when HA is present. No NMR evidence of $scCO_2$ reacting to form carbonate species or new mineral phases is observed. We also observe changes in the ^{23}Na line-width, position, and intensity when $scCO_2$ is present and that the effects of $scCO_2$ on the ^{23}Na resonances are significantly more pronounced in the HA-composite. Combined with ^{23}Na relaxation data for these systems that show one of two unique dynamic domains is affected by the presence of OM and of $scCO_2$, our results suggest that NOM may promote incorporation of CO_2 into the interlayer galleries or increase its association with the exterior surface, and that $scCO_2$ stimulates more rapid Na^+ motion and the sampling of additional Na^+ structural environments. These results are consistent with published computational modeling and experimental studies of clay-polymer systems and suggest that *in situ* NMR methods hold great promise for probing the behavior of metal ions, CO_2 and water in storage reservoirs.