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Structural and dynamical relationships of Ca^{2+} and H_2O in smectite/^2H_2O systems

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ABSTRACT

We present an X-ray diffraction and multi-nuclear (^2H and ^{43}Ca) NMR study of Ca-exchanged hectorite (a smectite clay) that provides important new insight into molecular behavior at the smectite-H_2O interface. Variable-temperature ^{43}Ca MAS NMR and controlled humidity XRD indicate that Ca^{2+} occurs as proximity-restricted outer-sphere hydration complexes between –120 and +25 °C in a two-layer hydrate and at $T \leq -50$ °C in a 2:1 water/solid paste. Changes in the ^{43}Ca NMR peak width and position with temperature are more consistent with diffusion-related processes than with dynamics involving metal-surface interactions such as site exchange. The ^2H NMR signal between –50 and +25 °C for a two-layer hydrate of Ca-hectorite is similar to that of Na- and other alkali metal hectorites and represents ^2H_2O molecules experiencing anisotropic motion describable using the ^2H C_2/C_3 jump model we proposed previously. ^2H T_1 relaxation results for Ca- and Na-hectorite are well fit with a fast-exchange limit, rotational diffusion model for ^2H_2O dynamics, yielding GHz-scale rotational reorientation rates compatible with the C_3 component of the C_2/C_3 hopping model. The apparent activation energy for ^2H_2O rotational diffusion in the two-layer hydrate is greater for Ca-hectorite than Na-hectorite (25.1 vs. 21.1 kJ/mol), consistent with the greater affinity of Ca^{2+} for H_2O. The results support the general principle that the dynamic mechanisms of proximity-restricted H_2O are only weakly influenced by the cation in alkali metal and alkaline earth metal smectites and provide critical evidence that the NMR resonances of charge-balancing cations in smectites become increasingly influenced by diffusion-like dynamic processes at low temperatures as the charge density of the unhydrated cation increases.

Keywords: ^{43}Ca NMR, ^2H NMR, dynamics, interface, clay, water