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Tightly bound water in smectites

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Abstract

Smectites are able to retain molecular tightly bound water (TBW) at temperatures above 100 °C, even after prolonged drying. The presence of TBW affects the stable isotope ratios, the dehydroxylation behavior of smectites and smectite-rich samples and also has implications in measuring various properties of clay-rich rocks. Five reference smectites, in Mg-, Ca-, Na-, and Cs-exchanged forms were subjected to different drying protocols followed by the determination of TBW contents using precise thermogravimetric (TG) analysis. Activation energies (E_a) of the removal of different water fractions at temperatures up to 1000 °C were determined in non-isothermal TG experiments using model-independent methods. Additionally, 4A and 13X zeolites were examined in both cases as apparent OH-free references.

After drying at 110 °C, all smectites still contained up to 3 water molecules per interlayer cation. The TBW contents in smectites were found to be primarily dependent on the isothermal drying temperature. For a given temperature, TBW contents decreased with respect to the type of interlayer cation in the following order: Mg > Ca > Na > Cs. The influence of the time of drying and the smectite layer charge were found to be negligible. The E_a of dehydration below 100 °C, as determined by the Friedman method, was quite constant within the 45–60 kJ/mol range. The E_a of TBW removal increased along with the degree of reaction from 90 to 180 kJ/mol, while the E_a of dehydroxylation was found in the 159–249 kJ/mol range, highly depending on the sample's octahedral sheet structure and the interlayer cation. The Mg^{2+} cation can hold H_2O molecules even beyond 550 °C, making it available during dehydroxylation or—for geologic-scale reactions—pass H_2O to metamorphic conditions.

High similarities between the TBW contents and the E_a of dehydration for smectites and cationic (low Si/Al-) zeolites lead to the conclusion that TBW in smectites is remarkably similar to zeolitic water in terms of cation bonding and diffusion characteristics. The optimal drying protocol for smectites is to substitute interlayer cations with cations of a low-hydration enthalpy, such as Cs, and to dry a sample at 300 °C, provided that the sample is Fe-poor. Fe-rich smectites should be dried at 200 °C to avoid dehydroxylation that occurs below 300 °C.

Keywords: Smectite, thermogravimetry, clay-bound water, dehydration, activation energy