Vibrational study of the halloysite-(10Å) to -(7Å) transition

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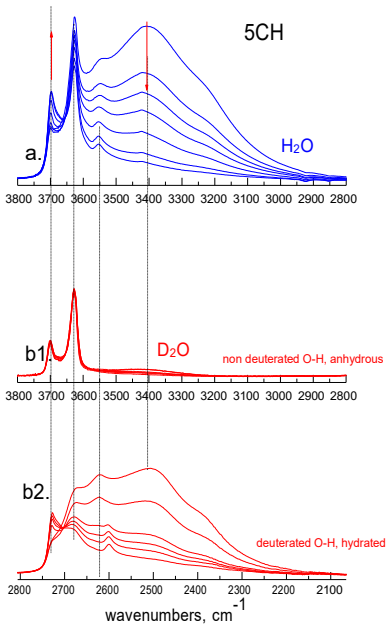
Halloysite is a polytype of kaolinite with hollow nanotubular structure and many potential industrial or environmental applications. Natural halloysite is formed with a ~10Å basal spacing owing to a monolayer of interlayer H_2O. Upon exposure to ambient humidity, most of the interlayer H_2O is irreversibly lost and the basal spacing collapses to ~7Å. Some residual H_2O in halloysite-(7Å) is observed at 3550 and 1650 cm^{-1} in the infrared spectra ("hole water").



ATR spectra of halloysite upon drying,(α) - H_2O form, (b1, b2) -D_2O form.

Due to experimental difficulties, most vibrational studies of the various types of halloysite are performed on stable halloysite-(7Å) samples. To our knowledge, this is the first detailed vibrational comparison of two cylindrical and two polygonal halloysites in their original 10Å form, saturated with either H_2O or D_2O, and as a function of *in situ* conversion to the 7Å form, by drying in the 70-2% RH (RD) range.

Attenuated Total Reflectance (ATR) spectra were acquired in the mid infrared (4000–550 cm^{-1}) using a homemade environmental cell coupled with a controlled humidity N_2 gas generator. Supporting XRD and electron microscopy data are presented.

Deuteration was expected to shift the modes of interlayer H_2O and inner surface OH groups, leaving the inner OH vibrations unaffected. Instead, the data showed that there is a significant part of the halloysite structure that is anhydrous and inaccessible to H/D exchange. Only the remaining accessible part responds in the expected manner during the 10Å to 7Å transition. The so-called "hole H_2O" is detected (albeit with broader bands) even in the hydrated state.