

# IN SITU INFRARED SPECTROSCOPIC STUDY OF THE WATER IN SMECTITE WITH VARIOUS ENVIRONMENT

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Behavior of the water in smectites can be observed by in situ infrared (IR) spectroscopy. Smectites are phyllosilicate, and the layers have negative charge by tetrahedral and octahedral cations. The layers are stacked by electrostatic interaction, and there are exchangeable cations between layers. The interlayer distance of smectites expand by containing water molecular layers (interlayer water). This property is called as swelling, and the basal spacing changes according to the structure of interlayer water. P(H<sub>2</sub>O) and exchangeable cations greatly influence the structure of interlayer water. The OH bonds in smectite can be classified into adsorbed water, interlayer water and structural OH. However, these details have not cleared.

The purpose of this study is to observe behavior of the water in smectites with various exchangeable cations at various temperature, and to compare the influence of various exchangeable cations on the water. Therefore, we newly designed and made a sample chamber which can control precisely for temperature and P(H<sub>2</sub>O) independently. Using this sample chamber with FT-IR, we can observe in situ IR spectra. Since the temperature of humidity control can be set in the accuracy of 0.01 degree, the observation can be made very precisely. Kunipia-F (smectite, from Kunimine Ltd.) was used as one of typical smectite, and we prepared Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>-exchanged Kunipia F. IR spectra in the mid- and near-IR regions were obtained.

In mid-IR region, absorption bands observed at near 1600-1750cm<sup>-1</sup> and 3000-3600cm<sup>-1</sup> due to H-O-H bending mode and O-H stretching mode of H<sub>2</sub>O molecule in interlayer, respectively. These bands suggested that interlayer water have more than two kinds of vibrational state, and probably can be assigned to molecular water coordinated and non-coordinated to exchangeable cations. When vapor pressure is increased, the integral intensity of the peak of interlayer water for Na-Kunipia F jumped at a certain P(H<sub>2</sub>O), while behavior of the peak of interlayer water for Li-, Ca- and Mg-Kunipia F changed continuously. In near-IR region, the integral intensity of the peak of the combination band of the structural OH did not changed with vapor pressure.

In this study, we discussed relation between basal spacing by XRD and quantity of the interlayer water by IR. The result revealed that they showed the same behavior. For Li-, Na-, Ca- and Mg-Kunipia F, IR spectra was compared at 2-layer hydration state, which two layer water molecules was contained in interlayer. This comparison showed that the kind of exchangeable cations influenced the position and integral intensity of the peak of interlayer water. In addition, it was revealed that they depended systematically on valence and ionic radii of exchangeable cations. They are measure of hydration power.

As the further works, we plan to improve the sample chamber to observe IR spectra at higher temperature. In addition, we will carry out the same experiment as this study by Raman spectroscopy.