

SWELLING OF SMECTITE WITH VARIOUS CATIONS USING IN SITU XRD IN VARIOUS ENVIRONMENT

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Swelling behavior of clay minerals can be observed by in situ powder X-ray diffraction method. Clay minerals 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. Some of clay minerals have a property that the interlayer distance increase with adsorbed water molecules from air. This property is called as swelling. This phenomena is believed that water molecules of interlayer hydrate to exchangeable cations. But the details are not clear.

The object of this study is to observe swelling behavior of smectite with various cations at various temperature to 150C, and to compare the swelling behavior of smectite with various cations. Therefore we newly designed and made a sample chamber which can control precisely for temperature and humidity independently. Since the temperature of humidity control can be set in the accuracy of 0.01, the observation can be made very precisely. The measurements were carried out at temperatures of 50C,70C,90C,120C and 150C, and vapor generator temperature is raised by 1-5 from low temperature as 3C to just below the sample temperature. Kunipia-F (smectite, from Kunimine Ltd.) was used as one of typical smectite by exchanged with various cations Mg²⁺,Ca²⁺,Sr²⁺,Ba²⁺,Li⁺,Na⁺,K⁺, and Cs⁺ .

At high temperature and low humidity conditions for Cs-, K-, Ba-Kunipia-F, the interlayer distances was larger than that of Na-Kunipia-F (9.9A) at 0-layer hydration state (Cs was ca. 11.2A, K ca. 10.2A, Ba ca. 10.2A). Mg-Kunipia-F at 150C was still hydrated as d001 = 11.2A. For Mg-, Ca-, and Li-Kunipia-F, the interlayer distance changed with humidity continuously. For Ba-, and Na-Kunipia-F, the interlayer distance jumped from 1-layer hydration state to 2-layer hydration state. K-Kunipia-F swelled only up to 1-layer hydration state. Cs-Kunipia-F swelled little even for high humidity.

It seems that these difference of swelling behavior to exchangeable cations caused by valence and radius of exchangeable cations. In this study for large cations, the interlayer distance is expanded at 0-layer hydration state. The summary of differences of swelling behavior to various cations are 1, For Mg-, Ca-, Sr-, Li-Kunipia-F having large hydration power the (001) distance changed continuously and the fullwidth at half-maximum (FWHM) of the (001) peak is narrow, 2, For Ba-, and Na-kunipia-F having rather weak hydration power the 001 distance jumped between 0 and 1(Na), and 1 and 2 layer hydration (Na, Ba), though the peak that was seemed at intermediate state is presence, FWHM is wide, and 3, For K-, and Cs-kunipia-F having very weak hydration power swelling was only up to 1-layer hydration state.

As the further works, we plan to measure of La³⁺-Kunipia-F and produce a device working above 100C and relative humidity to 100percent.