

Mineralogical study on the consistency property of bentonite mixed soil

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Introduction

Bentonite is being used as a cushioning material because its primary component, Smectite, is expected to offer water cutoff, self-sealing properties, delayed sorption or migration of nuclides, and chemical buffering properties.

This study used X-ray diffraction and near-infrared spectroscopy to measure the crystal structure of high-purity homo-ionic Smectite and the vibratory motion of water molecules under controlled humidity. To compare the experimental results in detail, measurements were taken at intervals of 5% relative humidity (RH) between 0 and 100% RH on adsorption and desorption processes.

Materials and methods

Materials

Kunipia-F (Kunimine Industries Co., Ltd.), whose primary component is sodium Smectite, we refined Kunipia-F to produce high-purity homo-ionic (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) Smectite.

Water content adjustment

The humidity control unit is composed of a saturation chamber, a temperature, pressure, and flow rate controller, and an experimental chamber. The temperature of the experimental chamber was set to room temperature (25°C).

X-ray diffraction

The Ultima IV horizontal multipurpose sample X-ray diffractometer (manufactured by Rigaku) was used to take measurements. The measurement conditions were as follows. X-rays: Cu (40 kV, 40 mA), measurement method: FT measurement, step width: 0.0600° , gate time: 1 s, scanning range: $2\theta=2.000\text{--}50.000^\circ$.

Near-infrared spectroscopy

The Spectrum 400 Fourier transform infrared spectrometer (manufactured by Perkin Elmer) was used to take measurements. The measurement conditions were as follows. Measurement method: diffuse reflection, resolving power: 4 cm^{-1} , number of additions: 100 times, measurement range: $4000\text{--}7800\text{ cm}^{-1}$.

Crystal structure of Smectite

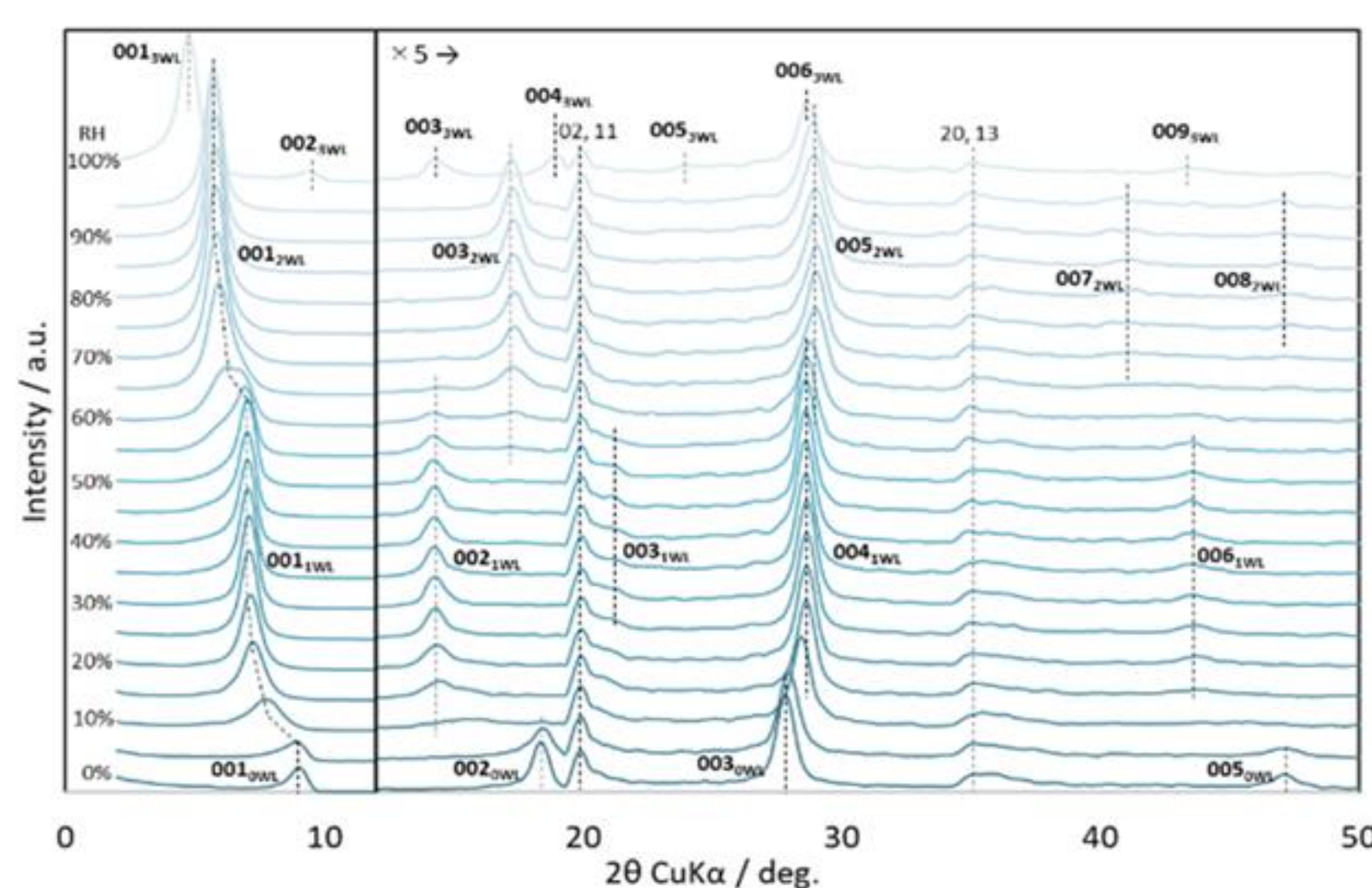


Figure 1. XRD profiles of Na-Smectite on desorption process.

Figure 1 shows an example of an X-ray diffraction profile.

The peak at the top of the profile is due to Bragg reflection, and the following relationship exists between crystal spacing d and diffraction angle 2θ .

$$n\lambda = 2d \sin \theta$$

n : positive integer, λ : wavelength of the X-ray

Figure 2 shows the humidity dependence of spacing d_{001} .

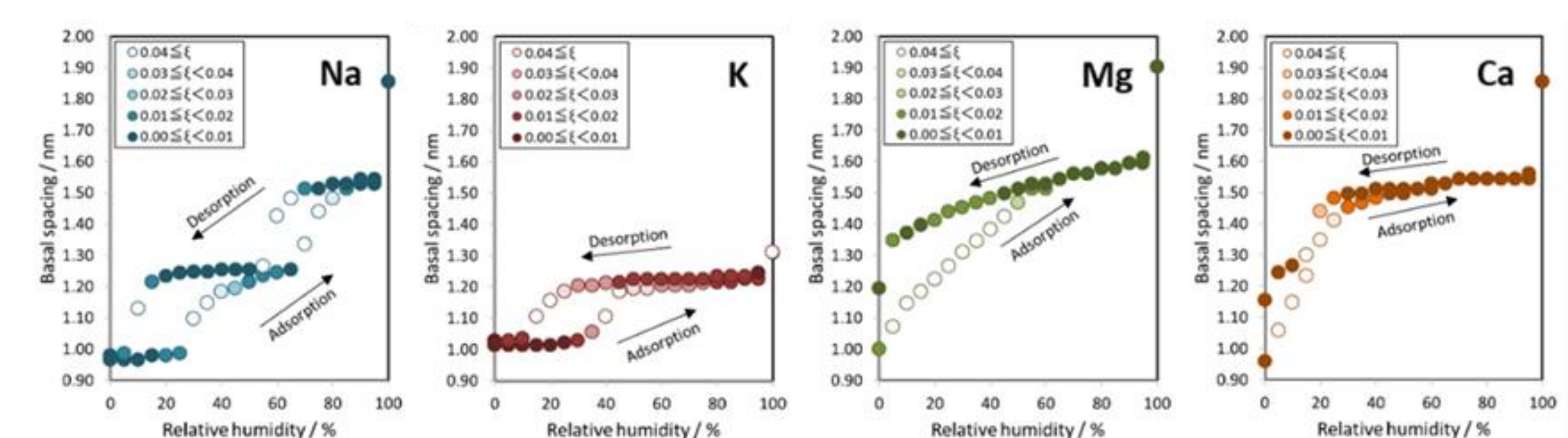


Figure 2. Changes in basal spacing d_{001} of Na-, K-, Mg- and Ca-Smectite. The color of the circles indicates degree of interstratification.

Water molecules in Smectite

Figure 3 shows an example of a near-infrared absorption spectrum. The absorption observed in this region is the combination tone ($\nu+\delta$) of the stretching vibration ν and angular vibration δ of OH groups.

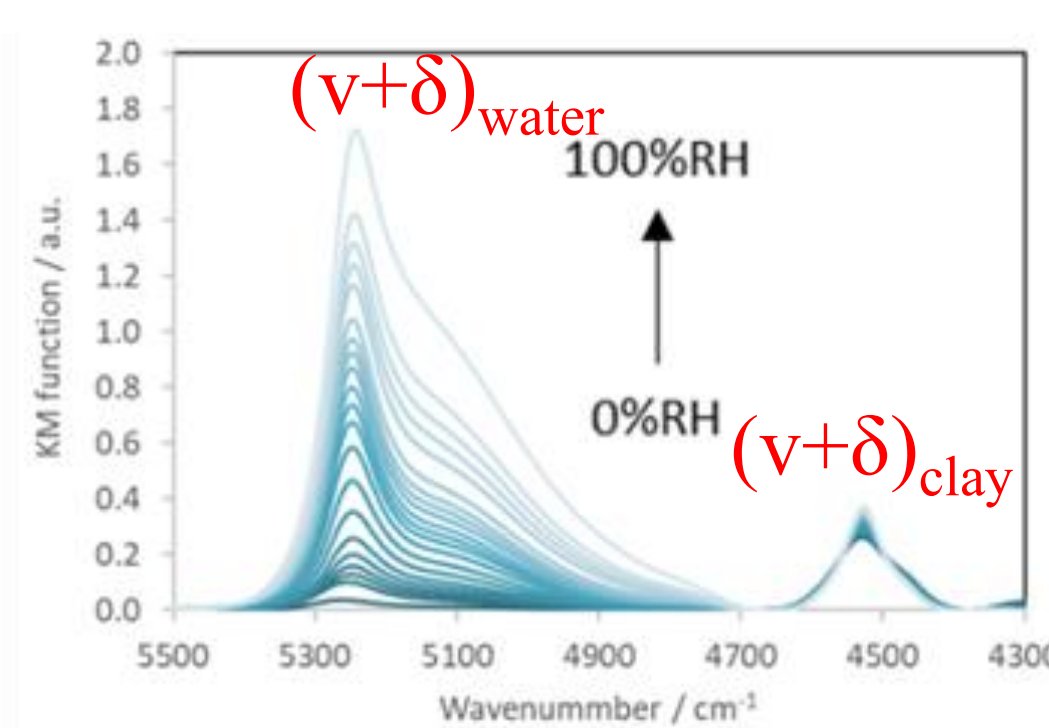


Figure 3. NIR spectra of Na-Smectite on adsorption process.

Figure 5 shows the humidity dependence of water content. Water content reflects changes in spacing. Figure 6 shows the relationship between spacing and water content. Monovalent and divalent ions exhibit very different patterns.

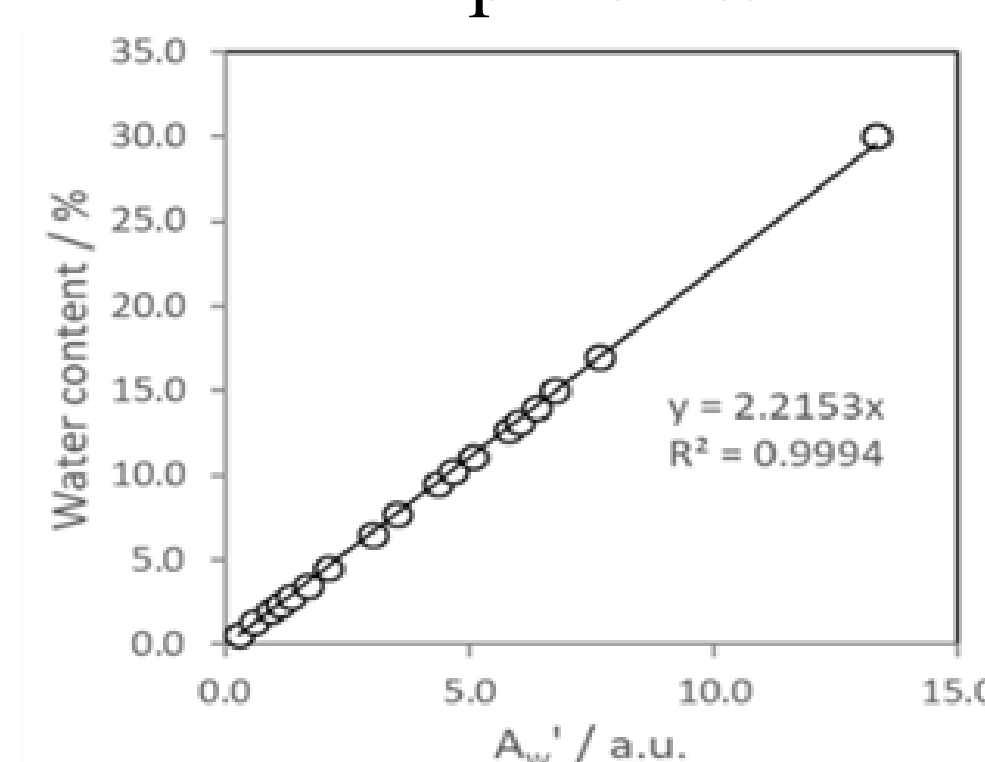


Figure 4. Relation between water content and normalized area of $(\nu+\delta)_{\text{water}} A'_w$ (Na-Smectite).

the hydrogen Smectite spectrum exhibited characteristics that were extremely similar to those of magnesium Smectite (Figure 8). This leads us to conclude that, in magnesium Smectite, hydrolysis produces H_3O^+ .

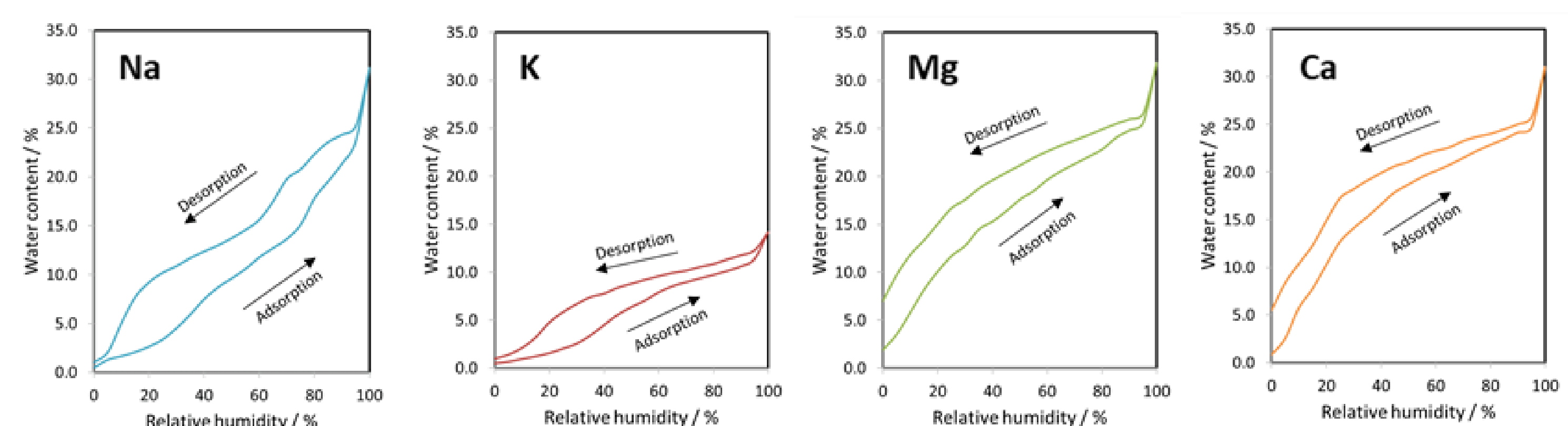


Figure 5. Changes in water content of Na-, K-, Mg- and Ca-Smectite.

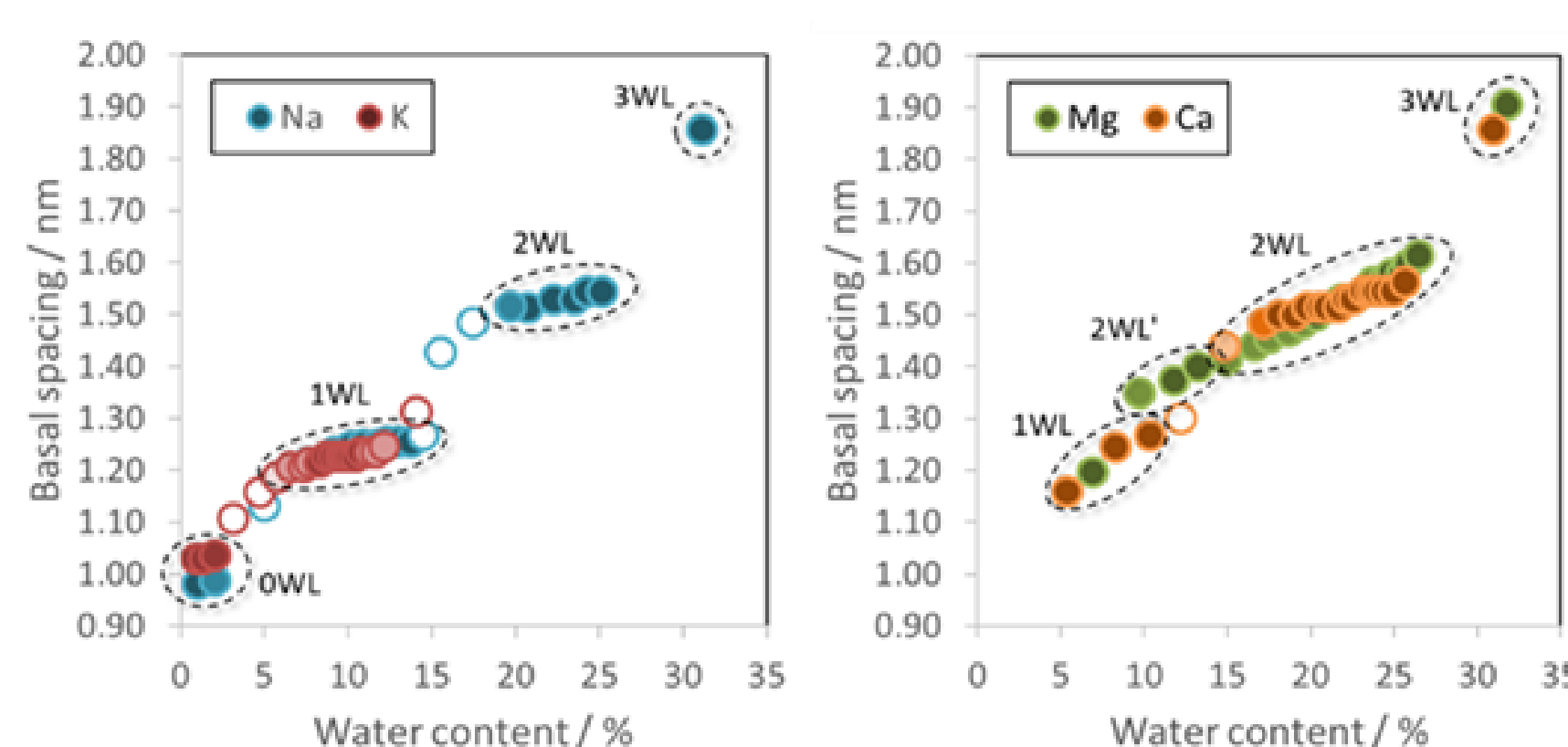


Figure 6. Relation between basal spacing and water content of Na-, K-, Mg- and Ca-Smectite on desorption process.

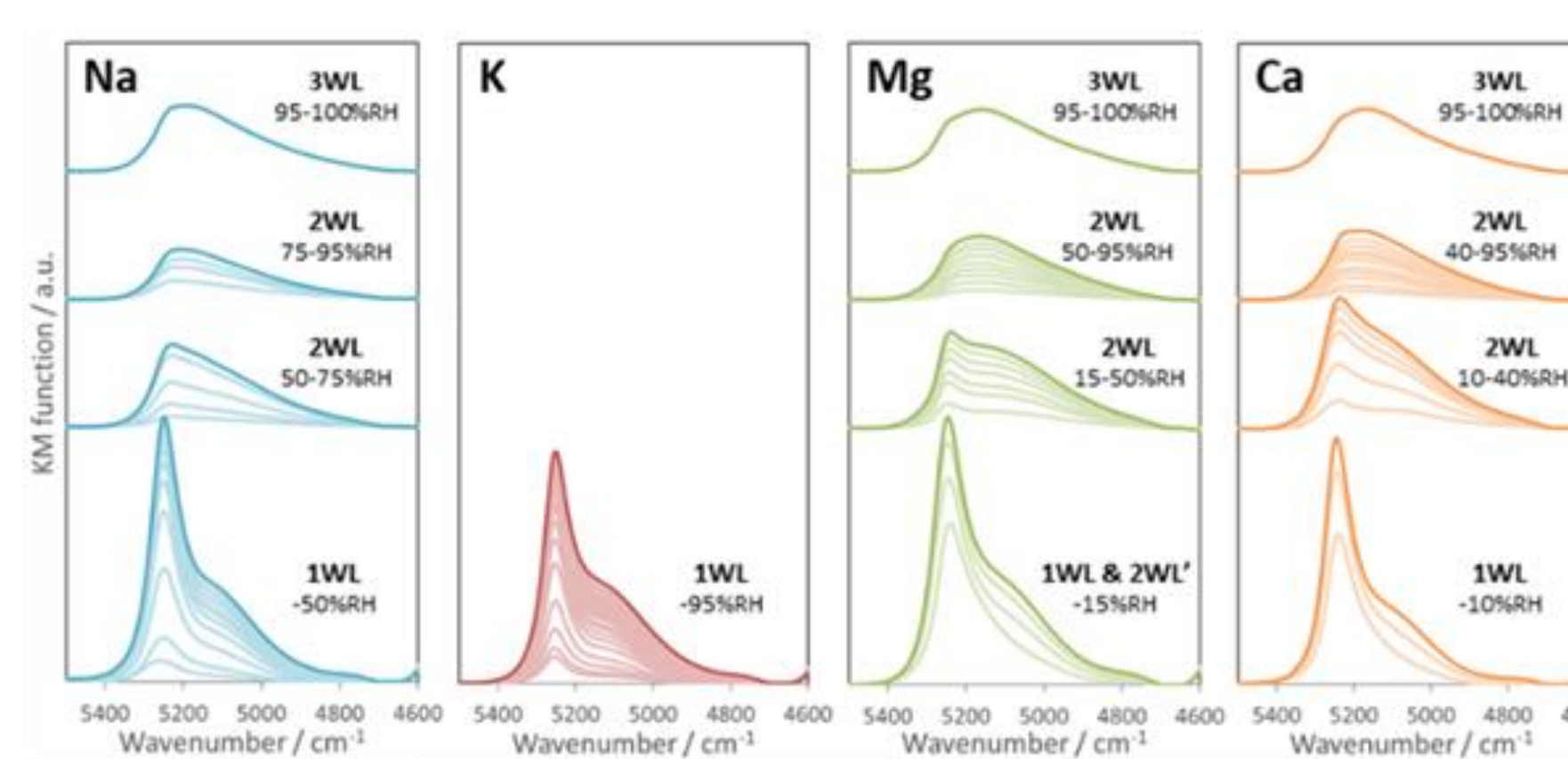


Figure 7. Different spectra of Na-, K-, Mg- and Ca-Smectite on desorption process.

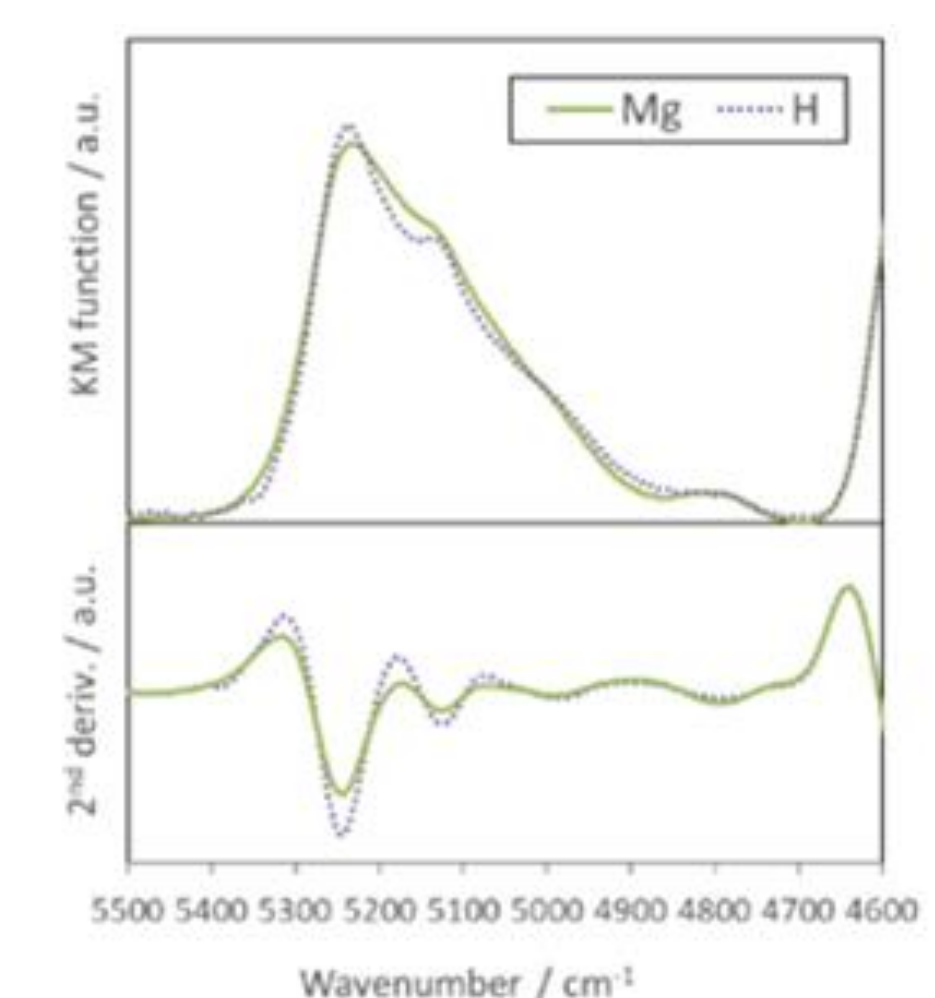


Figure 8. NIR and 2nd deviation spectra of Mg- and H-Smectite.

Conclusion

High-purity homo-ionic (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) Smectite was analyzed using X-ray diffraction and near-infrared spectroscopy, producing the below findings regarding crystal structure and the state of water molecules.

- (1) Changes in spacing relative to water content are discontinuous for monovalent ions and continuous for divalent ions. There is a possibility that divalent ions with high ion potential change the arrangement of interlayer water molecules.
- (2) For 1WL, both OH groups of interlayer water interact with the silicate layer surface facing them, and on the low-humidity side of 2WL, one OH group interacts with the silicate layer surface while the other OH group interacts with different water molecules.
- (3) From the high-humidity side of 2WL to 3WL, there is also water that is similar to pure water in terms of vibratory motion.
- (4) Water content is about $10 \pm 5\%$ for 1WL, $20 \pm 5\%$ for 2WL, and 30% for 3WL, regardless of the type of exchangeable cation.
- (5) In magnesium Smectite, hydrolysis produces H_3O^+ .