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NOTES

AMMONIUM AND POTASSIUM FIXATION IN SMECTITE BY WETTING AND DRYING

Key Words—Smectite, Potassium, Ammonium fixation, IR determination

Papers dealing with the problems of potassium fixation in smectites, and the subsequent change of expandable layers into nonexpandable (illite) layers are plentiful. This reaction is one of the most frequently observed diagenetic reactions in fine-grained sediments. In the laboratory, potassium fixation can be achieved by two methods: (1) heating of smectites hydrothermally in the presence of K^+ (Eberl and Hower, 1976) and, (2) cyclic wetting and drying of K-smectites (Eberl *et al.*, 1986). Of course, potassium also enters into interlayer space when smectite is treated with potassium solutions. However, this reaction usually does not lead to irreversible fixation, because the K remains exchangeable (Weaver, 1958; Horváth and Novák, 1975; Číčel and Machajdík, 1981).

Considerably less attention has been devoted to the fixation of NH_4^+, a cation that is similar in its behavior to K^+ (Page *et al.*, 1967; Číčel and Machajdík, 1981). The lesser interest in NH_4^+ probably results from the apparent rarity of ammonium illites. However, occurrences of ammonium illite continue to be reported (Kozáč *et al.*, 1977; Środoń and Eberl, 1984; Juster *et al.*, 1987; Šucha 1991). In addition, NH_4^+ and K^+ fixation is an important process in soils, where both cations are essential biological nutrients. In the present work, seven smectites were studied for their ability to fix NH_4^+ during wetting and drying cycles.

MATERIALS AND METHODS

Seven smectites from various localities (Table 1) were fractionated into the <2 micrometer size fraction, and were converted to K^+ or NH_4^+ forms using 1 N chloride solutions (the samples were treated 3 times for 12 hours). Chloride anions were removed by dialysis. Subsequently, the samples were subjected to wetting and drying cycles (~250 mg samples were wetted by 20 ml of distilled water and dried at 60°C). After a determined number of cycles, exchangeable cations (K^+ or NH_4^+) were replaced by treating the samples with 0.1 N $SrCl_2$ solution overnight (Eberl *et al.*, 1986). After dialysis and drying, oriented specimens were prepared by settling on glass slides. The specimens were treated with ethylene glycol vapor (8 hours at 60°C), and were analyzed by X-ray diffraction (Philips 1050/25).

All samples were analyzed by IR spectroscopy as KBr pellets. Five pellets were prepared for each sample (1.5 mg of the sample in 300 mg KBr). The analysis was carried out with a Perkin-Elmer 597 IR spectrometer.

RESULTS

Expandability measurements by XRD

The illite content (nonexpandable) layers was determined using the peak position method (Środoń, 1980, 1981). Results of XRD analyses are listed in Table 1.

Table 1. Percentage of illite layers formed after 100 W/D cycles for K-smectites and NH_4-smectites (exchanged with 0.1 N $SrCl_2$).

Sample	Percent of illite layers				Layer charge
	K-form (1)	K-form (2)	NH_4-form (3)	NH_4-form	
Wyoming	N	8	5	8	0.36 (2)
Texas	24	22	16	23	0.41 (2)
Fe-smectite	45	43	35	45	0.46 (2)
Jelšový p.	20	N	12	18	0.47 (5)
Kinney	N	33	25	35	0.49 (2)
Cheto	N	41	30	43	0.56 (2)
Otay	55	51	40	55	0.61 (2)

N = not analyzed; (1) = this study; (2) = after Eberl *et al.* (1986); (3) = this study, measured after Środoń (1980, 1981); (4) = this study, measured using Figures 1–3; (5) = after Číčel and Machajdík (1981).

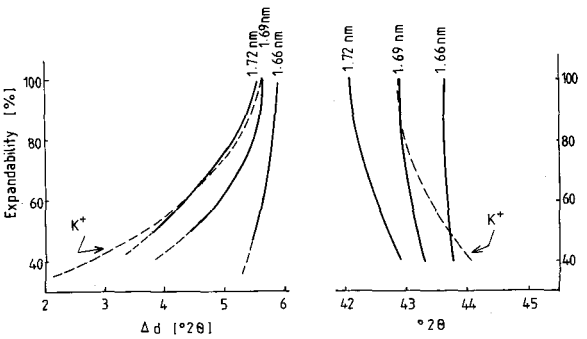


Figure 1. The plot for measuring the expandability of the mixed-layer illite/smectite minerals with ammonium in the illite interlayer, based on the angular distance Δd between the reflection in the 42–48°2-theta region. The reflection between 42–45°2-theta is used to select the thickness of the ethylene glycol complex. Dashed lines represent the same for K-illite.

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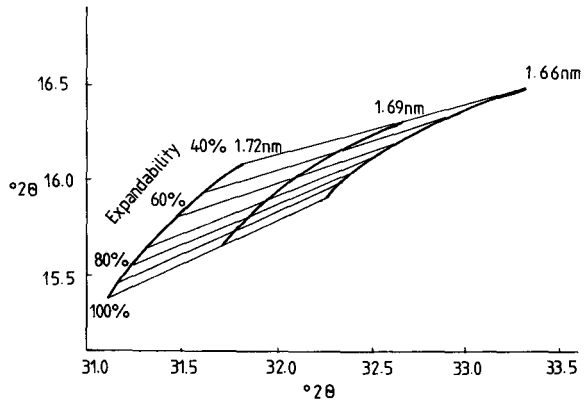


Figure 2. The plot for measuring the expandability of illite/smectites with ammonium in the illite interlayer using two reflections between 30–33°2-theta and 15–17°2-theta.

The results of K^+ fixation by the method of wetting and drying published by Eberl *et al.* (1986) are consistent with our results. On the other hand, results obtained from the same samples under the same conditions, but using the NH_4^+ cation rather than K^+, indicate that considerably fewer illite layers were produced.

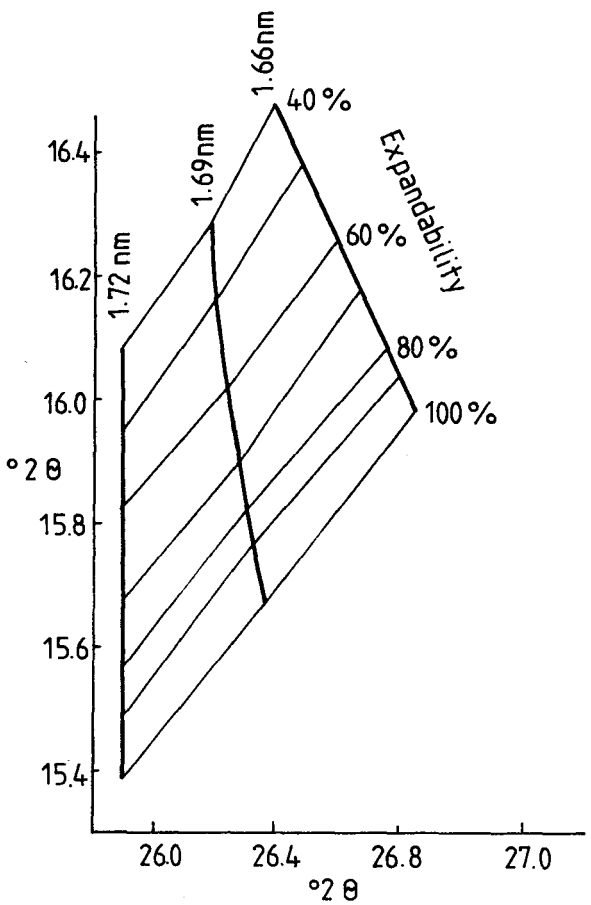


Figure 3. The plot for measuring the expandability of I/S minerals with ammonium in the illite interlayer.

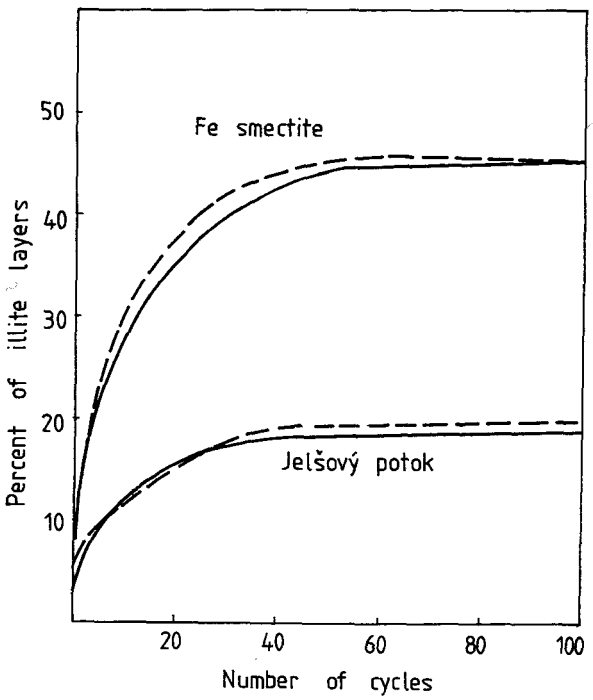


Figure 4. Percentage of illite layers versus number of W/D cycles for Fe-smectite and Jelšový potok smectite in potassium (dashed line) and ammonium forms (exchanged with 0.1 N $SrCl_2$).

Because of the partially different properties of the ammonium cation, we tested Środoń's method using the NEWMOD computer program (Reynolds, 1985). Our results are systematically underestimated. With the same number of cycles less illite layers were formed following ammonium fixation. This made it necessary to calculate new plots for measurements of expandability (Figures 1–3).

The results were approximately the same for both K^+ and NH_4^+ smectites after reevaluation of the percentage of illite layers formed by wetting and drying of the NH_4^+ form.

For two samples (smectite from Jelšový Potok and Fe-smectite) we compared the rate of K^+ and NH_4^+ fixation (Figure 4). It appears that the rate of fixation for both potassium and ammonium are the same. The principal factor that controls the amount of fixation for both ammonium and potassium ions is the magnitude of the layer charge. The correlation between illite layer content and layer charge is linear (Figure 5).

IR data

Samples subjected to wetting and drying cycles, and subsequently treated by 0.1 N $SrCl_2$ also were analyzed

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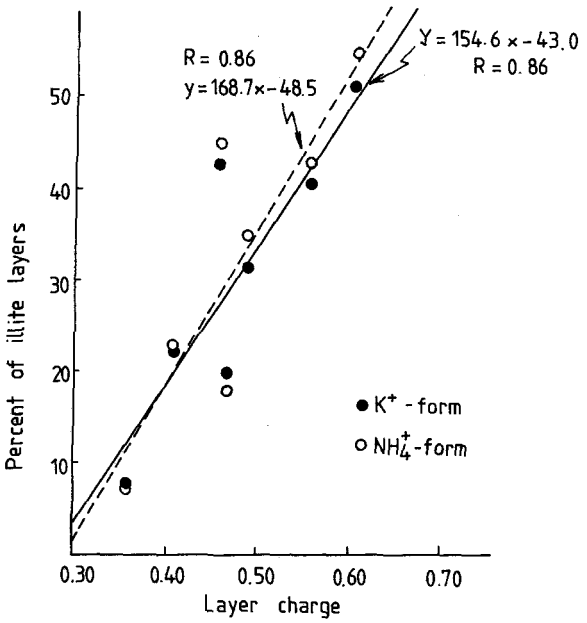


Figure 5. Percentage of illite layers versus layer charge for K-smectites and NH_4-smectites after 100 W/D cycles.

by IR spectroscopy. Attention was given to the N-H vibration at 1400 cm^{-1}. For samples prepared under the same conditions (especially sample weight), the magnitude of the N-H vibration was greater in samples with more illite layers (Figure 6).

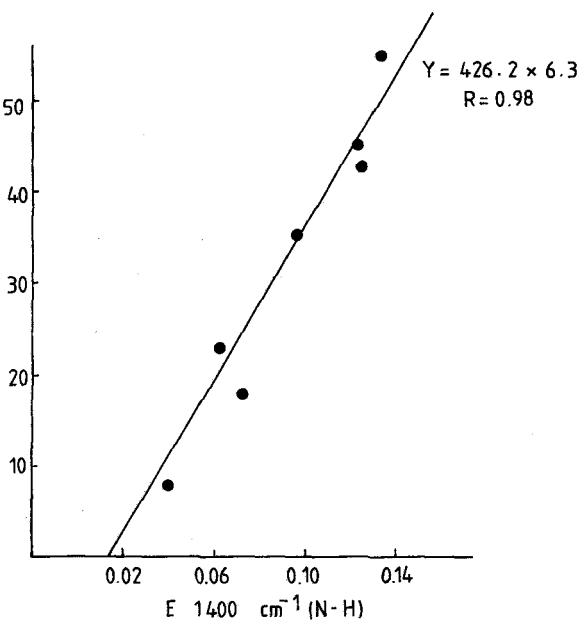


Figure 6. Relation between the intensity of the N-H vibration at 1400 cm^{-1} and the percentage of illite layers in NH_4-smectites after 100 W/D cycles.

CONCLUSIONS

Seven smectites were subjected to wetting and drying cycles in the presence of potassium or ammonium cations. Both cations were fixed in smectites. However, in order to determine the correct percentage of illite layers formed during fixation it is necessary to use plots calculated separately for both K-illite and NH_4-illite.

For the same number of cycles, approximately the same number of illite layers were formed in the presence of both K^+ and NH_4^+.

The fixation of the NH_4^+ cation and the related formation of illite layers is reflected in the IR spectrum by the N-H vibration at 1400 cm^{-1}. The magnitude of this vibration is directly proportional to the number of illite layers containing NH_4^+. This vibration could be used for estimating the content of ammonium-containing illite layers in natural illites, where it is more difficult to determine the ratio of K/NH_4 by chemical methods.

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