

## DEHYDROXYLATION BEHAVIOR OF HEAT-TREATED AND STEAM-TREATED HOMOIONIC CIS-VACANT MONTMORILLONITES

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**Abstract**—Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Cu<sup>2+</sup>, or Zn<sup>2+</sup>-saturated samples of a *cis*-vacant montmorillonite from Linden, Bavaria, were heated to temperatures between 200–700°C. Half of each heated sample was subsequently autoclaved under steam at 200°C (~1.5 MPa) to promote rehydroxylation. The smectites were characterized by cation-exchange capacity (CEC), determination of exchangeable cations, infrared (IR) spectroscopy, and thermoanalytical investigations of evolved water in a thermobalance linked with a mass spectrometer.

Changes in the montmorillonite structure and dehydroxylation behavior are related to three respective mechanisms: type of the interlayer cation, interlayer cation radius, and the movement of the interlayer cation. The migration of the smaller Li<sup>+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> ions after heating produces a strong reduction of CEC due to the Hofmann-Klemen effect before the initiation of dehydroxylation. Thereafter, the CEC of these smectites remains constant over a large temperature interval during dehydroxylation. After rehydroxylation, Cu<sup>2+</sup> and Zn<sup>2+</sup>-rich samples release 16–23 meq/100 g of Mg<sup>2+</sup> from the structure. No Mg<sup>2+</sup> release is observed for the Li<sup>+</sup>-rich montmorillonite. Also the dehydroxylation behavior after rehydroxylation differs between the Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Li<sup>+</sup>-rich samples. The mass curves of the evolved water during thermoanalysis of the rehydroxylated Cu<sup>2+</sup> and Zn<sup>2+</sup>-rich smectites show a peak doublet between 480–700°C. For the Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup>-rich montmorillonites, the second peak disappeared and a third peak at ~760°C developed after rehydroxylation. The resulting structure after rehydroxylation of all samples is celadonite-like.

**Key Words**—Celadonite, *Cis*-Vacant Octahedra, Dehydroxylation, Homoionic Montmorillonite, Mass Spectrometry, Rehydroxylation, Thermogravimetry, *Trans*-Vacant Octahedra.

### INTRODUCTION

Smectites and other dioctahedral 2:1 layer silicates lose water in three temperature ranges during heating: 1) dehydration at temperatures <220°C involves the loss of H<sub>2</sub>O from the interlayer of expandable clays, 2) OH groups bound to the surface are released between 220–350°C, and 3) dehydroxylation between 350–1000°C results from the reaction between the octahedral hydroxyls according to 2(OH) → O<sub>r</sub> + H<sub>2</sub>O↑ (Brindley and Lemaitre, 1987; Köster, 1993; Drits *et al.*, 1995), when r means residual and the oxygen atom remains in the structure.

In general, montmorillonites are characterized by dehydroxylation temperatures between 500–800°C. Three montmorillonites may be distinguished by dehydroxylation. Two types of montmorillonite show one endothermic peak in differential thermal (DT) curves at ~550 or ~700°C, whereas the third group shows a peak doublet between 500–700°C (*e.g.*, Grim and Kulbicki, 1961; Heller *et al.*, 1962; Schultz, 1969; Koster van Groos and Guggenheim, 1987, 1990; Guggenheim, 1990; Drits *et al.*, 1995). Furthermore, dehydroxylated samples regain many of the hydroxyl groups by treatment under steam between 200–300°C (*e.g.*, Grim and Bradley, 1948; Jonas, 1954; Heller *et al.*, 1962; Hamilton, 1971; Alvero *et al.*, 1994). After rehydroxylation the montmorillonites show one dehy-

droxylation peak near 600°C or two peaks near 500 and 650°C. Based on all investigations, the rehydroxylated montmorillonites apparently lose hydroxyls at lower temperatures than the original samples.

According to Tsipursky and Drits (1984), octahedral cations of montmorillonites are distributed over the *trans*- and *cis*-sites for dioctahedral smectites, *i.e.*, there exist *trans*-vacant (tv) and *cis*-vacant (cv) sites. Drits *et al.* (1995) developed a model, relating the dehydroxylation temperature to the position of the Al<sup>3+</sup> cations and their movement to other sites in the octahedral sheet. Heller-Kallai and Rozenson (1980) found, that Fe<sup>3+</sup> do not migrate. Smectites consisting of cv 2:1 layers are characterized by dehydroxylation temperatures of 150–200°C higher than those for a similar mineral consisting of tv 2:1 layers. During dehydroxylation, Al<sup>3+</sup> ions in the cv smectite move from *trans*-octahedral sites to *cis*-octahedral sites. This requires additional thermal energy and explains the higher dehydroxylation temperature of cv smectites. Drits *et al.* (1995) assumed that during heating the transformation occurs in a portion of the sample, because two dehydroxylation peaks are observed after rehydroxylation of preheated montmorillonites. For this interpretation, the heating conditions are important, because the loss of hydroxyl groups starts at lower temperatures with a slower heating rate (Hamilton, 1971).

Table 1. Variation of the CEC and exchangeable interlayer cations.

Homoionic sample	meq/100 g dry clay			$\Sigma$ exchangeable cations
	CEC <sub>theor</sub>	CEC <sub>measur</sub>	Main interlayer cation	
LI-Li	101	101	90	99
LI-Na	99	103	100	103
LI-Ca	99	101	98	102
LI-Sr	97	100	101	103
LI-Cu	98	99	96	101
LI-Zn	98	99	98	102

Drits *et al.* (1995) further noted that structural changes and  $Al^{3+}$  movement in *cv* montmorillonites during dehydroxylation are not restricted by the interlayer cations. The movement of a small  $Li^+$ ,  $Cu^{2+}$ , or  $Zn^{2+}$  cation from the interlayer to the hexagonal cavities of the tetrahedral sheet and then to the vacant octahedral positions of dioctahedral clays upon heating is a well known phenomenon. (*e.g.*, Hofmann and Klemen, 1950; Greene-Kelly, 1955; Calvet and Prost, 1971; McBride and Mortland, 1974; Heller-Kallai and Moser, 1995).

The goal of this study is to test the hypothesis that dehydroxylation behavior indicates changes in the clay structure developed after dehydroxylation and rehydroxylation depending on the type of the interlayer cations.

## MATERIAL

White to yellowish montmorillonite from Linden, Bavaria,  $Ca_{0.10}Mg_{0.08}(Na,K)_{0.01}[(Si_{3.95}Al_{0.05})(Al_{1.46}Fe_{0.18}Mg_{0.38})O_{10}(OH)_2]$  (Molecular weight: 371.3 g mol<sup>-1</sup>, cation-exchange capacity (CEC) of 100 meq/100 g) was used in this study. Free iron oxides were removed using the procedure of Mehra and Jackson (1960); 8.7 meq iron per 100 g dried (105°C) material and 17.1 meq aluminum were removed. Excess citrate was removed by dialysis. The <2- $\mu$ m fraction was obtained by sedimentation from ~2 wt. % suspension. Homoionic samples of  $Li^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  were prepared by saturating ~15 g of clay for 12 h once with 700 mL of a 0.2 M chloride solution and three times with a 0.1 M chloride solution. The clay was then dialyzed using distilled water until chloride free. The suspended samples were dried at 55°C in polyethylene bottles, gently crushed in a mortar, and stored at room temperature. CEC measurement and determination of exchangeable cations showed an exchange of 90–99% relative to the prepared starting materials (Table 1). The different interlayer cations produce a change of molecular weight and small changes in CEC. The clay shows one dehydroxylation reaction at ~670°C and was classified as a *cis*-vacant dioctahedral smectite (Drits *et al.*, 1995).

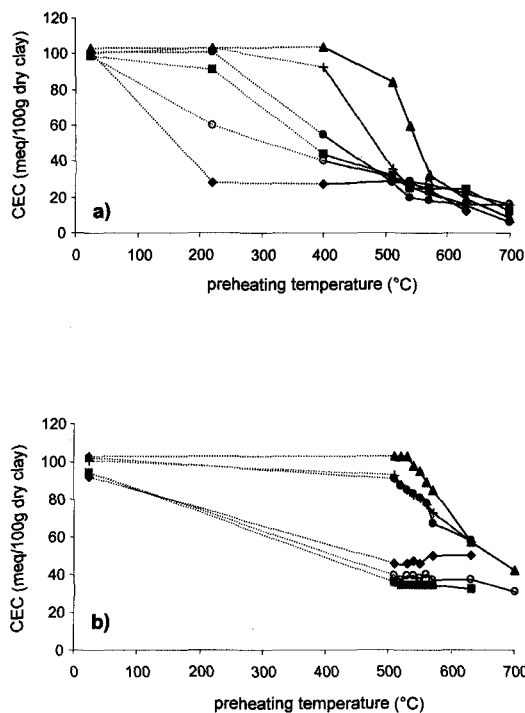


Figure 1. The evolution of the CEC (a) of the heated homoionic montmorillonites (—◆—LI-Li, —▲—LI-Na, —●—LI-Ca, —◄—LI-Sr, —○—LI-Cu, —■—LI-Zn) and (b) of the rehydroxylated homoionic montmorillonites (—◆—LI-Li rehydr., —▲—LI-Na rehydr., —●—LI-Ca rehydr., —◄—LI-Sr rehydr., —○—LI-Cu rehydr., —■—LI-Zn rehydr.).

## METHODS

Samples of 1 g of the homoionic clays were heated in a programmable furnace with a heating rate of 150°C h<sup>-1</sup> to 200, 400, and to temperatures between 510–570°C in intervals of 10°C, and also to 630 and 700°C, respectively. The final temperature was maintained for 20 h. Half of each sample was immediately rehydroxylated under steam at 200°C (~1.5 MPa) for 24 h in a stainless steel autoclave. Selected samples were also steamed at several temperatures between 120–200°C without preheating.

CEC and exchangeable cations were determined from 60 mg of each sample dried at 105°C. Cations were removed by washing with 25 mL of a 1 M ammonium acetate solution (pH = 7) for 12 h. The suspension was centrifuged and the supernatant was replaced by 25 mL of fresh 1 M ammonium acetate solution, and the sample was redispersed and centrifuged. After repeating the procedure four times, the clay was washed with ethanol six times by using the centrifuge (Mackenzie, 1951). All supernatant liquids were collected in porcelain bowls, evaporated, and prepared for atomic absorption spectroscopy (AAS) to determine exchangeable cations. For the CEC determination, the  $NH_4^+$  was exchanged by  $Na^+$  with 2 mL

50 wt. % NaOH solution. Liberated  $\text{NH}_3$  was transferred by steam distillation in a Büchi 323 distillation Unit into an Erlenmeyer flask and titrimetrically determined with 0.0067 N  $\text{H}_2\text{SO}_4$ . Potentiometric titrations were performed to determine exchangeable  $\text{H}^+$ . 20 mL of a 0.5% clay suspension were titrated with 0.01 M KOH in steps of 0.2 mL. The pH was measured every 3 min.

Thermoanalytical investigations were made in a Mettler thermobalance linked to a Balzers quadrupole mass spectrometer (MS) as described in Kahr *et al.* (1996). The combination makes it possible to register simultaneously selected masses of the evolved gases during thermal reactions in the thermobalance. Samples of 100 mg were investigated with a heating rate of  $10 \text{ K min}^{-1}$  in streaming air ( $3 \text{ L h}^{-1}$ ) in the range from 30 to  $1000^\circ\text{C}$ . MS curves of evolved water ( $m/e = \text{mass divided by charge}$  18) were used to determine the dehydroxylation temperature.

Clay samples of 100 mg were dried at  $105^\circ\text{C}$ . They were decomposed in a KOH melt, dissolved in 20 mL 1:1 HCl and adjusted to 100 mL with Aqua bidest. This solution was analyzed by AAS, excluding  $\text{K}^+$  and  $\text{Na}^+$ , which were determined in the CEC procedure. The structural formulae were computed after van Olphen (1963).

Two sample preparation methods were used for X-ray diffraction (XRD) analysis. 1) For oriented samples, 15 mg clay were ultrasonically dispersed in 1.5 mL distilled water and the suspension was pipetted onto a special glass slide and air-dried. 2) The samples were mixed with 10 wt. % LiF as internal standard for random oriented powder samples. All samples were step scanned ( $0.02^\circ/2 \text{ s}$ ) from  $1.5$  to  $65 2\theta^\circ$  in a Philips APD 1900 X-ray diffractometer with  $\text{CuK}\alpha$  radiation.

Infrared (IR) transmission spectra were obtained on a Fourier transform infrared (FTIR) spectrometer Perkin Elmer System 2000 using KBr pellets (2 mg sample diluted in 198 mg dry KBr). For every sample, 24 scans were recorded between  $4000\text{--}370 \text{ cm}^{-1}$ . The pellets were measured again after being heated for 16 h at  $150^\circ\text{C}$  (Russell and Fraser, 1994) and  $200^\circ\text{C}$ , respectively, to remove adsorbed water.

## RESULTS

### *Changes of CEC and exchangeable cations*

The effects of heating and rehydroxylation on CEC and exchangeable cations are shown in Table 2a and 2b. A good agreement exists between the CEC and the sum of exchangeable cations for the unheated homoionic montmorillonites (Table 2a). Difference of 1 or 2 meq/100 g dry material are within error.

Thermal treatment of the homoionic montmorillonites reduced the CEC with increasing temperature (Table 2a). The clays with  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Sr}^{2+}$  as interlayer

cations ( $>0.97 \text{ \AA}$  ionic radius) showed no, or just a slight, CEC reduction after heating to  $220^\circ\text{C}$ . The  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  remain fully exchangeable by  $\text{NH}_4^+$ , but 13 meq  $\text{Na}^+$  did not. Further heating caused a weak and continuous CEC decrease until  $\sim 400^\circ\text{C}$  for the  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ -rich clay and until  $510^\circ\text{C}$  for the  $\text{Na}^+$ -rich clay, followed by a sharp drop in CEC between  $510\text{--}630^\circ\text{C}$ . Heating at  $700^\circ\text{C}$  caused only a slight further reduction in CEC (Figure 1a).

For montmorillonites with smaller interlayer cations, different CEC patterns were observed. The CEC of the  $\text{Li}^+$ -rich clay reached a minimum at 28 meq/100 g after heating to  $220^\circ\text{C}$  and no significant changes of the CEC occurred for  $\text{Li}^+$ -rich samples heated at temperatures to  $570^\circ\text{C}$  (Figure 1a). Note that the exchangeable  $\text{Li}^+$  increased from 11 to 26 meq/100 g after preheating at temperatures  $>510^\circ\text{C}$ . Heating at  $630^\circ\text{C}$  entailed a further CEC reduction to 12 meq/100 g with still 25 meq/100 g exchangeable  $\text{Li}^+$ .

The CEC of the  $\text{Cu}^{2+}$ -rich clay decreased to 60 meq/100 g, after the sample was heated at  $220^\circ\text{C}$  and still 20 meq/100 g  $\text{Cu}^{2+}$  remained exchangeable. Further heating at higher temperatures caused a CEC decrease to 16 meq/100 g at  $700^\circ\text{C}$ , whereas the amount of exchangeable  $\text{Cu}^{2+}$  ions decreased to 2–4 meq/100 g above  $400^\circ\text{C}$ . Acid conditions equal to 16 meq/100 g exchangeable protons were found for the  $\text{Cu}^{2+}$ -rich montmorillonite preheated at  $540^\circ\text{C}$  from the first derivative of the potentiometric titration curves.

The behavior of  $\text{Zn}^{2+}$ -rich clay is quite similar to that of the  $\text{Cu}^{2+}$ -rich clay. The CEC underwent only a small reduction until  $220^\circ\text{C}$  and 74 meq/100 g  $\text{Zn}^{2+}$  remained exchangeable. The exchangeable  $\text{Zn}^{2+}$  reached a minimum of 6 meq/100 g at  $400^\circ\text{C}$ , whereas the CEC decreased slowly to a minimum of 12 meq/100 g during further heating to  $700^\circ\text{C}$  (Figure 1a).

The final CEC after rehydroxylation also depends on the nature of the interlayer cation (Table 2b). For the  $\text{Na}^+$ -rich clay the CEC remained at 103 meq/100 g until preheating at  $530^\circ\text{C}$  (Figure 1b), whereas the amount of exchangeable  $\text{Na}^+$  decreased to 83 meq/100 g (data not shown). After preheating at  $540^\circ\text{C}$  and higher temperatures, the CEC and the exchangeable cations decreased slowly. The reduction in the  $\text{Ca}^{2+}$ - and  $\text{Sr}^{2+}$ -rich clays was similar with a slightly greater CEC reduction from 101 to 58 meq/100 g and from 100 to 57 meq/100 g, respectively (Figure 1b).

Steaming at  $200^\circ\text{C}$  did not effect the CEC of the unheated  $\text{Na}^+$ -,  $\text{Ca}^{2+}$ -, and  $\text{Sr}^{2+}$ -rich clays, as reported also by Oscarson and Dixon (1989), but only 93–96% of these ions remained exchangeable.

The rehydroxylated  $\text{Cu}^{2+}$ -,  $\text{Zn}^{2+}$ -, and  $\text{Li}^+$ -rich clays reached a steady CEC at much lower preheating temperatures. After preheating to  $510^\circ\text{C}$  and higher, the rehydroxylated  $\text{Cu}^{2+}$ -rich clays showed an almost constant CEC of 39 meq/100 g and the  $\text{Zn}^{2+}$ -rich clays of 36 meq/100 g, which in both cases is 10 meq/100 g

Table 2a. Measured CEC and exchangeable cations [meq/100 g (105°C dried material)] of the preheated samples.

Heating T(°C)	Homoionic sample															
	Li-Li				Li-Na				Li-Ca				Li-Sr			
	Li <sup>+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Na <sup>+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Sr <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC
RT	90	7	99	101	100	2	103	103	98	3	102	101	101	1	103	100
220	11	4	16	28	87	3	92	103	99	3	103	102	99	3	104	103
400	11	3	15	27	85	3	90	104	53	2	56	55	90	3	95	93
510	26	2	29	29	73	2	76	84	20	2	23	28	24	2	28	36
540	27	1	29	28	56	1	59	60	15	1	17	20	17	2	21	26
570	25	1	27	24	31	2	34	33	11	2	14	18	13	2	17	22
630	25	1	27	12	19	2	22	19	7	2	10	15	10	1	13	16
700	3	1	5	5	8	1	10	8	3	1	5	6	4	2	8	16

<sup>1</sup> Including small amounts of exchangeable Al<sup>3+</sup>, Fe<sup>3+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>.

higher than the CEC of samples not rehydroxylated. The Li<sup>+</sup>-rich clay regained a CEC averaging 48 meq/100 g, 20 meq higher than those clays that were only preheated. For the Cu<sup>2+</sup>- and Zn<sup>2+</sup>-rich clays a remarkably high amount of exchangeable Mg<sup>2+</sup>, between 16–23 meq/100 g, was measured. Steaming at temperatures between 120–200°C of nonheated Cu<sup>2+</sup>- and Zn<sup>2+</sup>-rich montmorillonites also caused nearly the same amount of exchangeable Mg<sup>2+</sup> in interlayer positions, increasing with an increased steam temperature (Emmerich and Kahr, 1998). In contrast no exchangeable Mg<sup>2+</sup> were detected for steam treated Li<sup>+</sup>-rich samples.

#### Thermal investigations and dehydroxylation behavior

**Preheated samples.** The natural Ca<sup>2+</sup> and Mg<sup>2+</sup>-rich montmorillonite from Linden and its homoionic forms have one dehydroxylation reaction between 625–685°C (Figure 2). All homoionic samples lost 4.85 ± 0.1% of the initial weight of the dry clay as the result of dehydroxylation. This is in perfect agreement with the theoretical OH content of the dioctahedral smectite. After preheating the homoionic clays, the main dehydroxylation peak increased by ~30°C and lost intensity. A second peak near 450–480°C appeared (Figures 3 and 4).

Heating to 220°C did not apparently effect the number of OH groups, but heating to 400°C caused a small reduction of the mass of evolved water corresponding

to octahedral hydroxyl groups. Further heating produced a continuous loss of octahedral OH groups with no appreciable differences due to the saturating cation. A completely dehydroxylated state was not attained even after heating to 700°C, because the dehydroxylated montmorillonites show a spontaneous rehydroxylation in the laboratory atmosphere (K. Emmerich, unpubl. data, 1998). The clays regained nearly 10% of their initial hydroxyls, which are possibly bound to the edges of the dehydroxylated layers (Figure 5).

**Rehydroxylated samples.** After heating and rehydroxylation of Cu<sup>2+</sup>- and Zn<sup>2+</sup>-rich clays, the main MS peak increased by ~25°C and lost intensity with increasing temperature. A second peak appeared near 475–495°C and increased in intensity at higher temperature. A weak shoulder at 860°C maintained position and intensity (Figures 4 and 6).

For the Na<sup>+</sup>-, Ca<sup>2+</sup>-, and Sr<sup>2+</sup>-rich clays a different phenomenon was observed. After preheating until 520°C and rehydroxylation, the Na<sup>+</sup>-, Ca<sup>2+</sup>-, and Sr<sup>2+</sup>-rich clays and the Li<sup>+</sup>-rich clay, respectively, behaved similarly to the clays described above (curves not shown). After preheating to higher temperatures, however, the peak between 660–680°C decreased in intensity and a peak between 750–790°C became more intense than the peak at 480–495°C (Figures 3 and 6).

The water content corresponding to hydroxyl groups did not reach the initial level upon rehydroxylation

Table 2b. Measured CEC and exchangeable cations [meq/100 g (105°C dried material)] of the rehydroxylated samples (steam temperature of 200°C).

Pre-heating T(°C)	Homoionic sample															
	Li-Li				Li-Na				Li-Ca				Li-Sr			
	Li <sup>+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Na <sup>+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Sr <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC
RT	81	6	89	92	96	2	100	103	93	3	97	102	96	4	102	101
510	42	3	47	46	90	1	93	103	88	2	91	91	87	3	92	93
540	41	2	45	47	84	2	89	98	65	2	68	83	74	4	82	82
570	41	2	45	50	79	1	81	85	57	1	59	67	68	3	72	73
630	41	2	45	50	52	2	54	57	50	2	53	58	50	4	56	57
700	—	—	—	—	39	2	41	42	—	—	—	—	—	—	—	—

<sup>1</sup> Including small amounts of exchangeable Al<sup>3+</sup>, Fe<sup>3+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>.

Table 2a. Extended.

Homoionic sample							
LI-Cu				LI-Zn			
Cu <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Zn <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC
96	4	101	99	98	3	102	99
20	4	26	60	74	5	81	91
4	3	9	40	6	4	12	44
2	4	8	31	7	4	13	32
2	4	8	29	6	4	12	25
2	4	8	27	6	4	12	25
3	5	10	22	7	4	13	24
3	5	10	16	4	4	10	12

under steam at 200°C. Doubling the reaction time to 48 h did not increase the water uptake. Whereas the heated montmorillonites saturated with Na<sup>+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup> regained 75–95% of their OH groups, the Li<sup>+</sup>-, Cu<sup>2+</sup>-, and Zn<sup>2+</sup>-rich montmorillonites regained only 60–80% of their OH groups, although the number of liberated OH during preheating did not show large differences (Figure 5).

#### IR spectroscopy

**OH-stretching region.** The absorption band at 3630 cm<sup>-1</sup>, which is assigned to stretching vibrations of octahedral OH groups, was found to be independent of interlayer-cation species for the unheated homoionic montmorillonites. Also heating between 510–700°C caused similar shifts to higher wavenumbers (~3675 cm<sup>-1</sup>) for all samples. Moreover, a shoulder between 3630–3650 cm<sup>-1</sup> appears in spectra of the heated samples (spectra not shown). The absorption strongly diminished with continued dehydroxylation. Rehydroxylation resulted in increased absorption but no shifts of these bands.

**Vibrations of molecular water.** Vibrations corresponding to adsorbed water at 3440 and 1630 cm<sup>-1</sup> diminished with increasing temperature of drying of the KBr pellets. These vibrations nearly disappeared after drying at 200°C.

**OH-bending and M-O vibration regions.** Between 1200–450 cm<sup>-1</sup>, there are seven major changes, which

Table 2b. Extended.

Homoionic sample							
LI-Cu				LI-Zn			
Cu <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC	Zn <sup>2+</sup>	Mg <sup>2+</sup>	Σ <sup>1</sup>	CEC
66	18	86	94	70	17	89	94
6	16	23	39	10	16	28	36
4	23	29	39	7	19	28	34
3	19	23	37	5	19	26	34
3	22	27	37	4	16	22	32
3	20	23	31	—	—	—	—

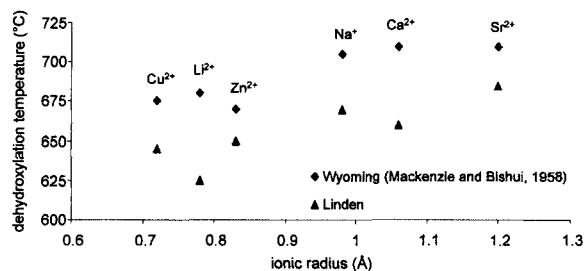


Figure 2. Dehydroxylation temperatures vs. the ionic ratio of the interlayer cations.

are described below. However, there were no significant differences in the spectra relating to saturating cations after heating the homoionic clays at temperatures between 510–700°C. Unless discussed below, rehydroxylation did not cause any other changes in the bands (Figures 7, 8, and 9). The seven major changes are: 1) The band at 798 cm<sup>-1</sup>, corresponding to OH associated with MgMg pairs (Calvet and Prost, 1971), apparently moved after heating at 510 or 540°C to wave numbers between 800–818 cm<sup>-1</sup> and returned to 799 cm<sup>-1</sup> after heating the samples at higher temperatures, as well as after rehydroxylation. Only the rehydroxylated Cu<sup>2+</sup>-rich samples show a band higher than 808 cm<sup>-1</sup>. 2) The band at 845 cm<sup>-1</sup>, assigned to OH groups surrounded by AlMg pairs (Calvet and Prost, 1971), nearly disappeared after heating for all samples and can be detected only as a small shoulder. 3) The AlFeOH band at 882 cm<sup>-1</sup> shifted to lower wave numbers (to 865 cm<sup>-1</sup>), and the AlAlOH band at 916 cm<sup>-1</sup> shifted to higher wavenumbers (to 942 cm<sup>-1</sup>). The band near 880 cm<sup>-1</sup> returned for rehydroxylated samples, which were preheated at <540°C. 4) The Si-O stretching bands at 1038 and 1115 cm<sup>-1</sup> moved to higher wave numbers at 1051 and 1135 cm<sup>-1</sup>. 5) The absorption band at 733 cm<sup>-1</sup> increased with heating of the samples at >510°C. 6) The peak at 622 cm<sup>-1</sup>, assigned to Al-O in the octahedral sheet (Madejová *et al.*, 1996), shifted to 640–647 cm<sup>-1</sup>. 7) The Si-O bending vibrations near 523 cm<sup>-1</sup>, due to Si-O-Al (Madejová *et al.*, 1996), disappeared or may have moved to 570 cm<sup>-1</sup>. After rehydroxylation, two broad absorption bands at 523 and 565 cm<sup>-1</sup> were detected. The position of the Si-O-Si vibration moved from 465 to 483 cm<sup>-1</sup>.

#### XRD

All homoionic montmorillonites show a well-defined (001) reflection with the position of this reflection dependent on the interlayer cation and its hydration state under laboratory conditions at ~24°C and relative humidity at ~45–55% (Table 3a). All samples expanded after ethylene glycol treatment to  $d(001) = 16.9\text{--}17.1 \text{ \AA}$ . The  $d(001)$  of the Na<sup>+</sup>-, Ca<sup>2+</sup>-, and Sr<sup>2+</sup>-rich montmorillonites collapsed to 9.7–9.8 Å after

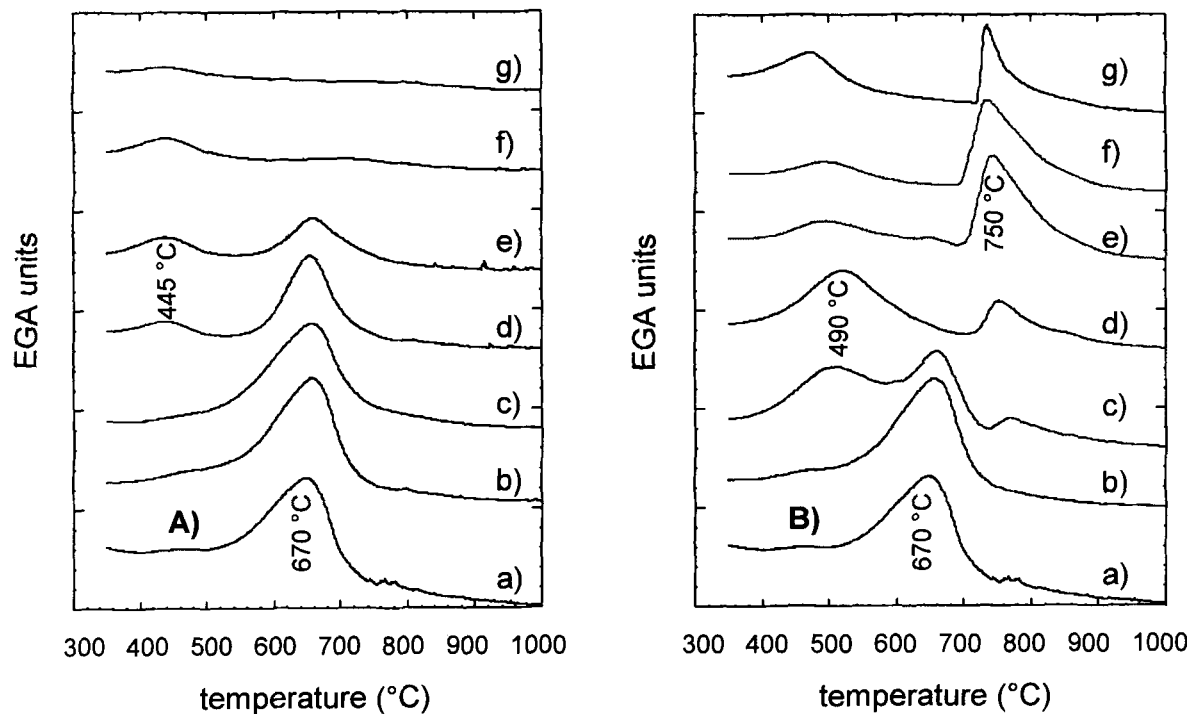


Figure 3. MS curves of the evolved water mass fragment 18 m/e (A) of Na<sup>+</sup>-montmorillonite a) untreated; and preheated b) 220°C, c) 400°C, d) 510°C, e) 540°C, f) 570°C, and g) 630°C and (B) of Na<sup>+</sup>-montmorillonite a) untreated; b) steamed at 200°C; and rehydroxylated after preheating at c) 520°C, d) 530°C, e) 550°C, f) 570°C, and g) 630°C.

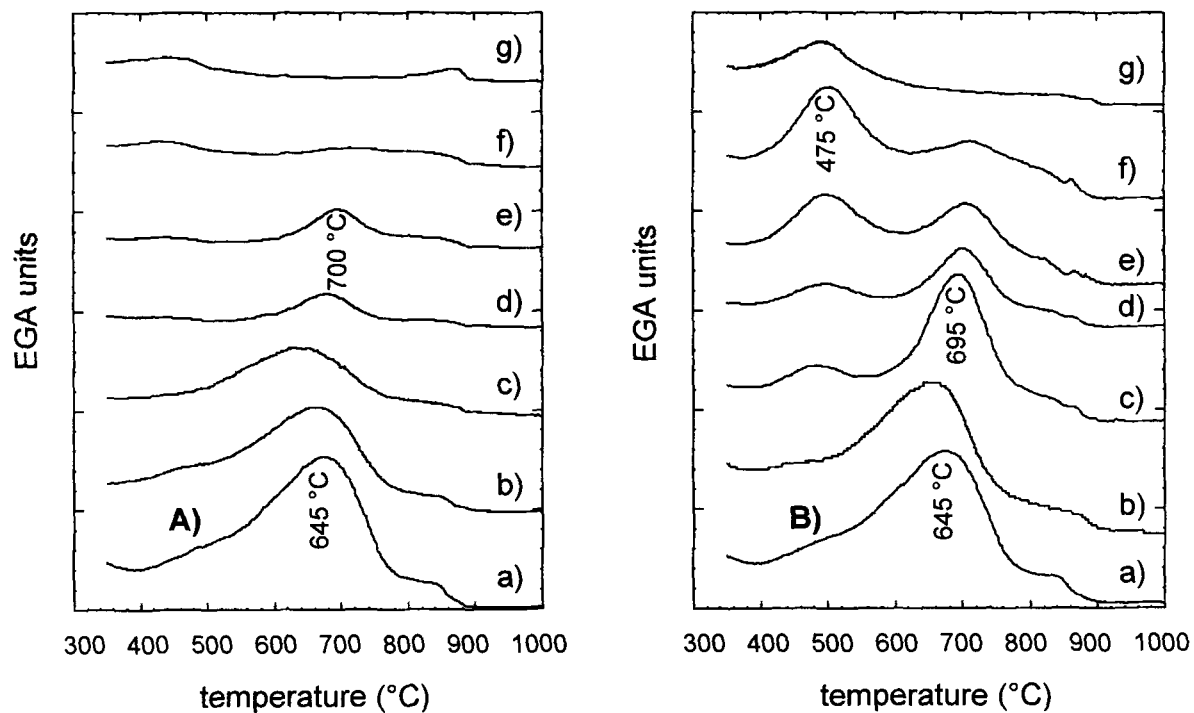


Figure 4. MS curves of the evolved water mass fragment 18 m/e (A) of Cu<sup>2+</sup>-montmorillonite a) untreated; and preheated b) 220°C, c) 400°C, d) 510°C, e) 540°C, f) 570°C, and g) 630°C and (B) of Cu<sup>2+</sup>-montmorillonite a) untreated; b) steamed at 200°C; and rehydroxylated after preheating at c) 510°C, d) 530°C, e) 550°C, f) 570°C, and g) 630°C.

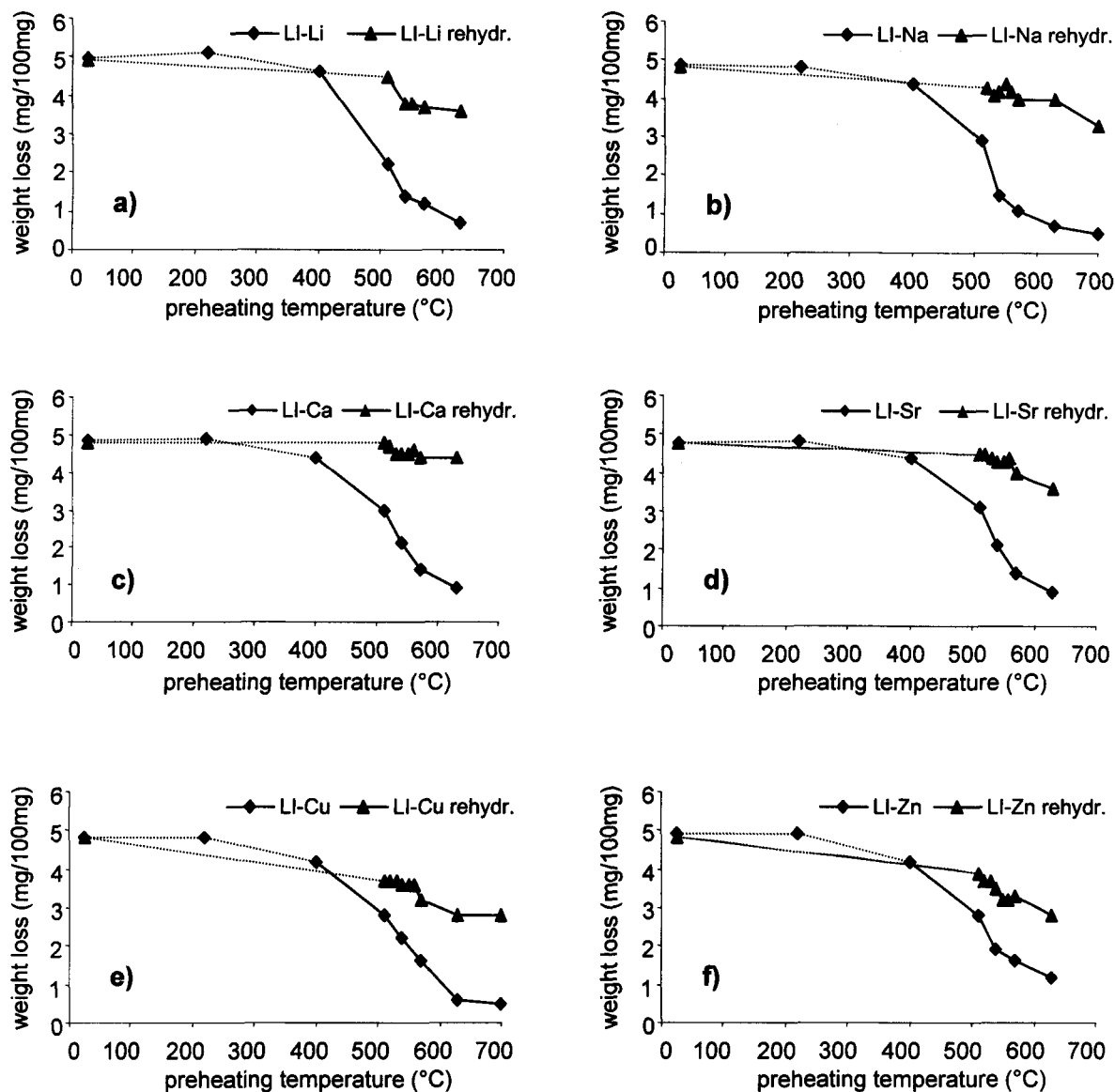


Figure 5. Weight loss caused by evolved water, which corresponds to the hydroxyl groups, during thermal analysis between 350–1000°C of the heated and rehydroxylated homoionic a) Li<sup>+</sup>-, b) Na<sup>+</sup>-, c) Ca<sup>2+</sup>-, d) Sr<sup>2+</sup>-, e) Cu<sup>2+</sup>-, and f) Zn<sup>2+</sup>-montmorillonites.

heating at temperatures of  $\geq 400^\circ\text{C}$  (Table 3a), but they expanded partially in water and ethylene glycol after rehydroxylation as shown for selected Na<sup>+</sup>-rich samples in Figure 10a. After heating at 220–700°C the Cu<sup>2+</sup>-, Zn<sup>2+</sup>-, and Li<sup>+</sup>-rich montmorillonites collapsed to 9.6–9.8 Å and did not swell with ethylene glycol. Rehydroxylation did not produce re-expansion (Table 3b). In contrast, the steamed unheated samples were still able to swell, as shown for the Cu<sup>2+</sup>-rich samples in Figure 10b.

The heated and the steam-treated samples show a peak at 3.16–3.22 Å. This peak moved toward 3.22 Å

and increased in intensity relative to the (001) reflection with increasing temperature of heating.

#### DISCUSSION

The natural Ca<sup>2+</sup> and Mg<sup>2+</sup>-rich montmorillonite from Linden dehydroxylated near 670°C. Therefore it consists of *cis*-vacant 2:1 layers (Drits *et al.*, 1995). The homoionic forms have one dehydroxylation peak between 625–685°C depending on the interlayer cations in the following order: Li<sup>+</sup> < Cu<sup>2+</sup> < Zn<sup>2+</sup> < Ca<sup>2+</sup> < Na<sup>+</sup> < Sr<sup>2+</sup>. These results are in fair agreement with the relation between the dehydroxylation temperature

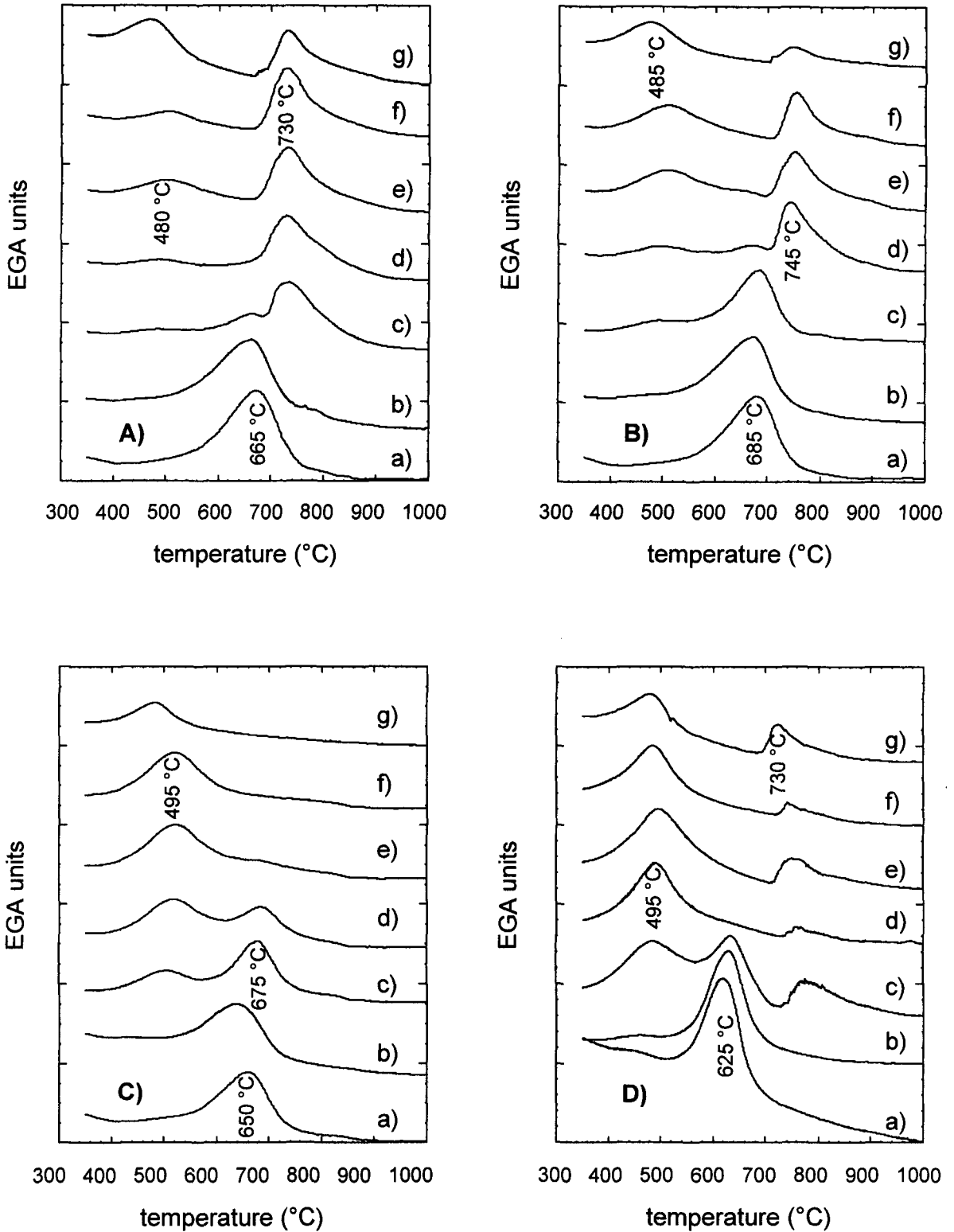


Figure 6. Mass spectrometer curves of the evolved water mass fragment 18 m/e of (A) Ca<sup>2+</sup>-montmorillonite, (B) Sr<sup>2+</sup>-montmorillonite, (C) Zn<sup>2+</sup>-montmorillonite, and (D) Li<sup>+</sup>-montmorillonite a) untreated; b) steamed at 200°C; and rehydroxylated after preheating at c) 510°C, d) 530°C, e) 550°C, f) 570°C, and g) 630°C.



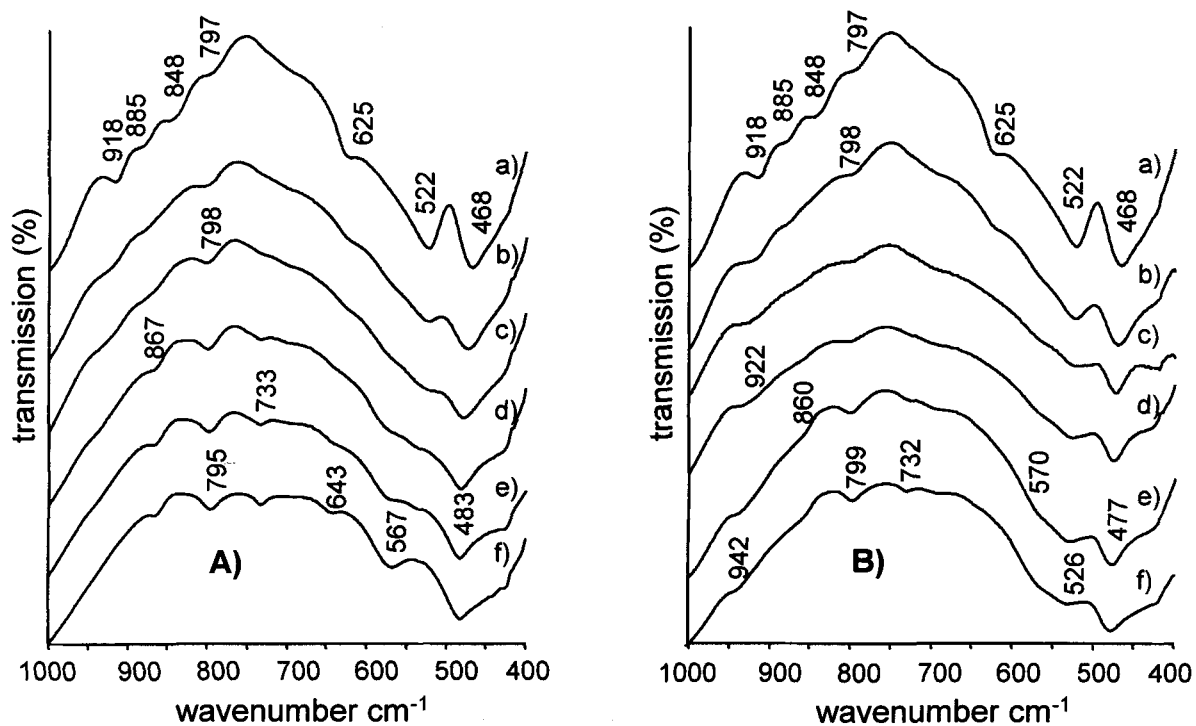


Figure 7. IR spectra (range 1000–400  $\text{cm}^{-1}$ ) of  $\text{Na}^+$ -montmorillonite; (A) preheated and (B) rehydroxylated after preheating at a) RT, b) 510°C, c) 540°C, d) 570°C, e) 630°C, and f) 700°C.

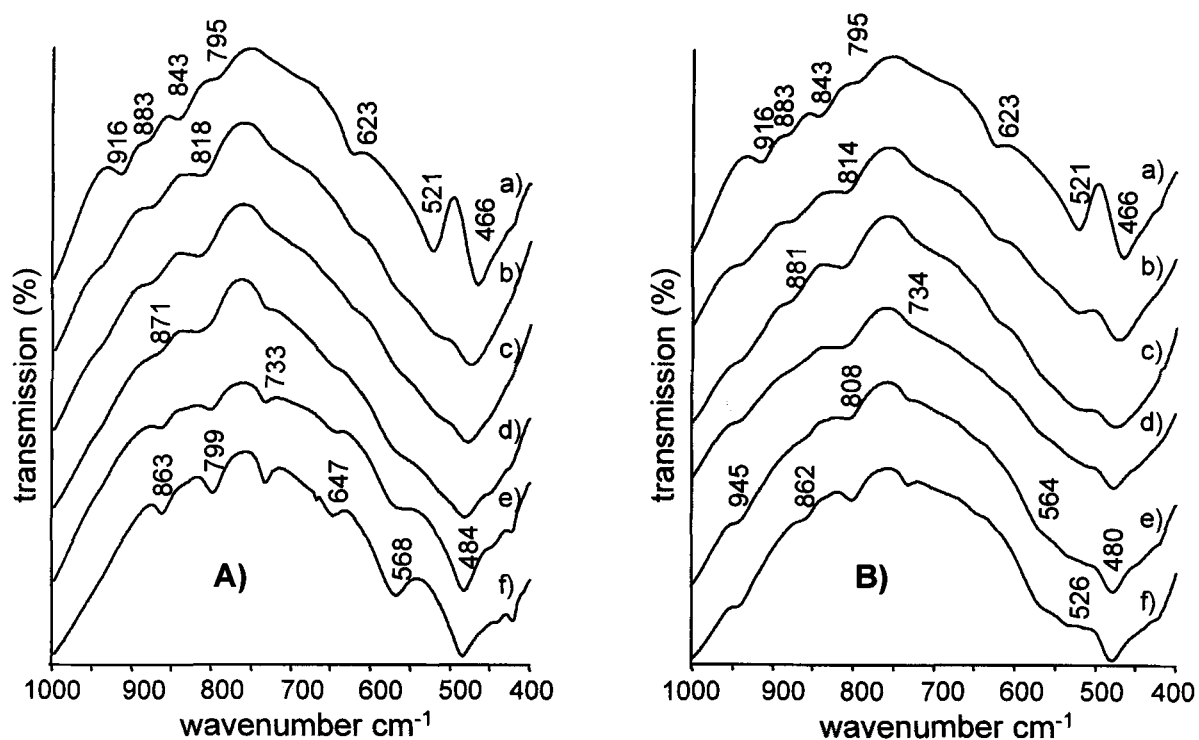


Figure 8. IR spectra (range 1000–400  $\text{cm}^{-1}$ ) of  $\text{Cu}^{2+}$ -montmorillonite; (A) preheated and (B) rehydroxylated after preheating at a) RT, b) 510°C, c) 540°C, d) 570°C, e) 630°C, and f) 700°C.

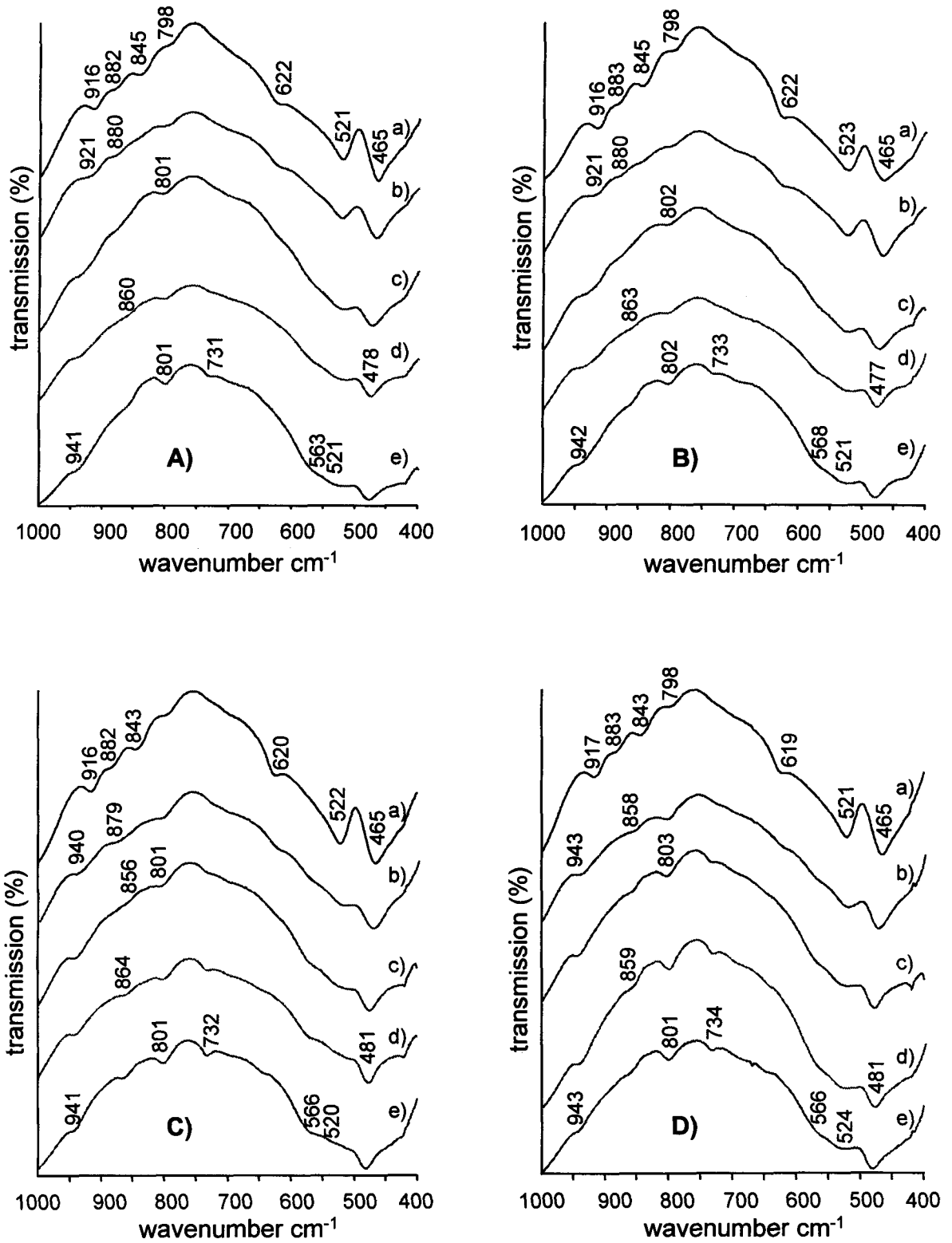


Figure 9. IR spectra (range 1000–400 cm<sup>-1</sup>) of (A) Ca<sup>2+</sup>-montmorillonite, (B) Sr<sup>2+</sup>-montmorillonite, (C) Zn<sup>2+</sup>-montmorillonite, and (D) Li<sup>+</sup>-montmorillonite a) untreated; and rehydroxylated after preheating at b) 510°C, c) 540°C, d) 570°C, and e) 630°C.

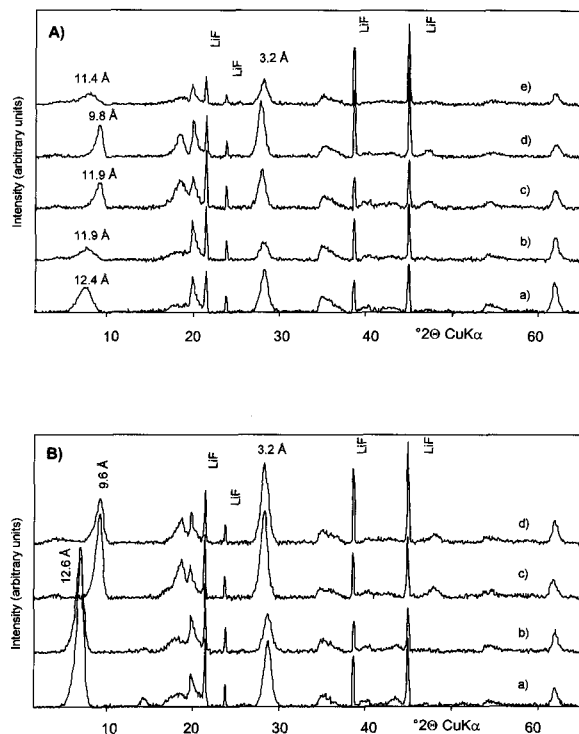


Figure 10. XRD patterns of (A) selected heat and steam treated  $\text{Na}^+$ -montmorillonites a) untreated, b) steamed at  $200^\circ\text{C}$ , c) heated at  $400^\circ\text{C}$ , d) heated at  $540^\circ\text{C}$ , and e) rehydroxylated after preheating at  $540^\circ\text{C}$ ; (B) selected heat and steam treated  $\text{Cu}^{2+}$ -montmorillonites a) untreated, b) steamed at  $180^\circ\text{C}$ , c) heated at  $400^\circ\text{C}$ , and d) rehydroxylated after preheating at  $540^\circ\text{C}$ .

and the Goldschmidt ionic radius (Mackenzie and Bis-hui, 1958) for ionic radii  $< 1.2 \text{ \AA}$  (Figure 2).

Migration kinetics of small ions into the octahedral sheet are important, because this affects the dehydroxylation temperature during thermal analysis. After heating  $\text{Li}^+$ -saturated montmorillonite at  $180^\circ\text{C}$  and maintaining this temperature for 1 h, Calvet and Prost (1971) found that 73% of the total  $\text{Li}^+$  becomes non-exchangeable and many of the  $\text{Li}^+$  migrated into octahedral sites. Thus, it appears likely that  $\text{Li}^+$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  migrate into octahedral sites during thermal analysis, and the resulting structure has a lower dehydroxylation temperature than otherwise.

#### Structural changes below $510^\circ\text{C}$

After preheating to remove ligand water, small interlayer cations ( $\text{Li}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ) migrate into the hexagonal holes of the tetrahedral sheet (McBride and Mortland, 1974) and into octahedral sites (e.g., Brindley and Ertem, 1971; Madejová *et al.*, 1996). This migration caused a CEC reduction to an apparent lower limit of 14–31 meq/100 g greater than the tetrahedral charge. This is consistent with McBride and Mortland (1974).

Table 3a. The  $d(001)$ -values of heated samples.

Heating temperature ( $^\circ\text{C}$ )	$d(001)$ -values ( $\text{\AA}$ )					
	Li-Li	Li-Na	Li-Ca	Li-Sr	Li-Cu	Li-Zn
25	12.7	12.4	15.2	15.5	12.6	14.9
220	9.8	10.3	13.8	13.6	9.7	9.8
400	9.8	9.8	9.7	9.9	9.6	9.6
510	9.8	9.8	9.7	9.7	9.6	9.6
540	9.8	9.8	9.7	9.7	9.6	9.7
570	9.8	9.8	9.7	9.8	9.6	9.7
630	9.8	9.8	9.7	9.8	9.6	9.7
700	9.8	9.8	9.8	9.8	9.7	9.7

Clays with interlayer cations of ionic radius  $> 0.97 \text{ \AA}$  show either no change in CEC after heating to  $220^\circ\text{C}$  or a small reduction upon heating to  $400^\circ\text{C}$ . Larger cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$ ) are not as mobile owing to size, and they do not move into octahedral sites after complete dehydration (e.g., Calvet and Prost, 1971).

All heated homoionic samples showed a slightly higher dehydroxylation temperature compared to the initial samples. Heating to  $400^\circ\text{C}$  caused a small reduction in evolved water, which corresponded to hydroxyl groups of the octahedra. This indicates that some of the hydroxyl groups were lost during preheating prior to the dehydroxylation event, presumably as a result of protonation of the OH groups, as reported for  $\text{Li}^+$  charge-reduced montmorillonites (Ertem, 1972; Heller-Kallai and Rozenson, 1980; Madejová *et al.*, 1996).

#### Structural changes during dehydroxylation

CEC of  $\text{Na}^+$ -,  $\text{Ca}^{2+}$ -,  $\text{Sr}^{2+}$ -rich clays decreased with increased heating temperature. These large ions do not enter octahedral sites. Apparently, the layer charge is reduced as a result of relatively small positional changes and stronger bonding to the hexagonal cavities of the tetrahedral sheets. This results in the observed decrease in basal spacing.

The dehydroxylation reaction  $\text{OH}_{cis} + \text{OH}_{cis} \rightarrow \text{H}_2\text{O}\uparrow + \text{O}_r$  produces five octahedral configurations: 1) five-fold coordinated dehydroxylated polyhedra (former *cis* positions), 2) six-fold distorted *trans* octahedra with one  $\text{O}_r$  and one OH group, 3) six-fold distorted *trans* octahedra with two  $\text{O}_r$ , 4) distorted *cis* octahedra,

Table 3b. The  $d(001)$ -values of rehydroxylated samples.

Preheating temperature ( $^\circ\text{C}$ )	$d(001)$ -values ( $\text{\AA}$ )					
	Li-Li	Li-Na	Li-Ca	Li-Sr	Li-Cu	Li-Zn
25	12.8	11.9	13.3	12.5	12.7	14.0
510	9.8	11.7	14.4	12.3	9.6	9.7
540	9.8	11.4	14.3	13.2	9.6	9.7
570	9.8	10.7	13.6	11.4	9.6	9.6
630	9.7	10.2	9.9	10.2	9.7	9.7

and 5) nearly unaffected *cis* and *trans* positions in the structure.

Guggenheim *et al.* (1987), Koster van Groos and Guggenheim (1987, 1990) and Guggenheim (1990) showed, using Pauling's rules, that Al-rich pentagonal prisms form during partial dehydroxylation. The Al-OH bond strength increases in the Al-rich octahedra having one or two shared edges with the pentagonal prisms. The OH groups that are bound more strongly with Al<sup>3+</sup> require additional thermal energy for the dehydroxylation process to proceed. Drits *et al.* (1995) described a movement of Al<sup>3+</sup> from *trans* positions into vacant *cis* positions, which requires also additional thermal energy. With respect to observed dehydroxylation, lattice distortion during partial dehydroxylation causes the movement of some Al<sup>3+</sup> from *trans* positions into *cis* positions because the thermal energy is too low (Drits *et al.*, 1995). In contrast, some Al<sup>3+</sup> are more strongly bound and cannot move until sufficient thermal energy is provided.

After heating at 540°C, the partially dehydroxylated samples show a dehydroxylation curve typical for cv 2:1 layer or a mixture of cv and tv 2:1 layer with a main peak near 700°C. The observed water release in MS curves between 420–450°C after heating the samples to <630°C is assigned to hydroxyl groups regained by spontaneous rehydroxylation under laboratory atmosphere. Rehydroxylation occurs because the clay structure is under stress by lattice distortions and by cations in the hexagonal holes. No evidence was found in IR spectra for the development of a porous network in the clay as proposed by Villieras *et al.* (1994) for dehydroxylated chlorites. This supports the single-crystal study of Zhan and Guggenheim (1995). We believe that the observed decrease of the intensity of the IR band at 1635 cm<sup>-1</sup> with preheating and the change of its intensity with relative humidity are consistent with the work of Mosser *et al.* (1997) and Trillo *et al.* (1992). Thus, this band is assigned to the hydration shell of partly dehydrated interlayer cations in hexagonal holes of the silicate ring.

It appears that the movement of Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Li<sup>+</sup> into vacant octahedral positions does not hinder the movement of Al<sup>3+</sup> parallel to the (001) plane. Thus, the mechanism of dehydroxylation is similar to that described above. Heating produces a continuous loss of octahedral OH groups without appreciable differences between the different clays.

A difference between the CEC and the total amount of exchangeable cations for the Li<sup>+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>-rich samples is related to proton liberation as suggested by Russell and Farmer (1964), Ertem (1972), and Madejová *et al.* (1996). This is confirmed by potentiometric titrations in the present study.

Note that the CEC of all heated homoionic montmorillonites converge to the value of the tetra-

edral charge (~13 meq/100 g) before lattice destruction occurs at temperatures >700°C.

#### *Structural changes during rehydroxylation*

For rehydroxylated homoionic montmorillonites, the loss of OH groups occurs at two temperatures, ~480 and ~700°C (Cu<sup>2+</sup>-, Zn<sup>2+</sup>-rich clay) and ~480 and ~760°C (Na<sup>+</sup>-, Ca<sup>2+</sup>-, Sr<sup>2+</sup>-, Li<sup>+</sup>-rich clay), respectively. The shift of the second peak to 700 or 760°C does not support the general interpretation that rehydroxylated montmorillonites lose hydroxyls at lower temperatures than the initial material. For example, montmorillonites with one endothermic peak at ~700°C showed a peak doublet at ~500 and 650°C after rehydroxylation (*e.g.*, Grim and Bradley, 1948; Drits *et al.*, 1995).

The temperature shift of the second hydroxyl loss for the rehydroxylated Na<sup>+</sup>-, Ca<sup>2+</sup>-, Sr<sup>2+</sup>-, or Li<sup>+</sup>-rich montmorillonite indicates an interaction between these cations and the regained hydroxyl groups, which causes a stabilization of the OH bond in the octahedral sheet. The observed dehydroxylation peak at 760°C may be regarded as pyrophyllite-like, because pyrophyllite is a 2:1 phyllosilicate with a vacant site in the *trans* position much like the thermally treated montmorillonite samples (Drits *et al.*, 1995) and some pyrophyllites also have one dehydroxylation peak near 760°C. However, the layer charge differs between the dehydroxylated and rehydroxylated montmorillonite and pyrophyllite. Whereas pyrophyllite layers are essentially neutral having a maximum CEC of 10 meq/100 g (Heller *et al.*, 1962), the montmorillonite regained at least four times as much CEC. Considering that Na<sup>+</sup>, Ca<sup>2+</sup>, and Sr<sup>2+</sup> did not penetrate into vacant octahedra, a tv structure similar to that of celadonite (Tsipursky and Drits, 1984) is more likely than a pyrophyllite-like structure. On the other hand, Li<sup>+</sup> migrated into vacant octahedral sites and generated a partial trioctahedral layer silicate with reduced permanent layer charge.

Also for the Cu<sup>2+</sup>, Zn<sup>2+</sup>-rich clay, a small shift of the second dehydroxylation peak in MS curves was observed. Cu<sup>2+</sup> and Zn<sup>2+</sup> occupied previously empty octahedral sites to produce sauconite-like trioctahedral areas. After steam treatment, the CEC increased and a noteworthy amount of Mg<sup>2+</sup> occupied exchangeable sites in interlayer positions, whereas the amount of exchangeable Cu<sup>2+</sup> and Zn<sup>2+</sup>, respectively, did not increase after steam treatment. The Mg<sup>2+</sup> therefore, must be displaced from octahedral positions. It is likely that H<sub>3</sub>O<sup>+</sup> ions are generated from hydrolysis caused by the acidity of Cu<sup>2+</sup> and Zn<sup>2+</sup>, which remained in the hexagonal holes after heat treatment. Then H<sub>3</sub>O<sup>+</sup> replaced Mg<sup>2+</sup> with the H<sub>3</sub>O<sup>+</sup> ions gaining access to the octahedral positions from the grain edges or through the hexagonal cavities of the tetrahedral sheet (Kaviratna and Pinnavaia, 1994). More detailed information

about this process is expected after further study. In contrast, the CEC of the rehydroxylated  $\text{Li}^+$ -rich clay also increased, but no  $\text{Mg}^{2+}$  was displaced from octahedral positions, and the amount of exchangeable  $\text{Li}^+$  increased. This is explained by the different charge and acidity of these ions.

After dispersing the rehydroxylated  $\text{Cu}^{2+}$ -,  $\text{Zn}^{2+}$ -, and  $\text{Li}^+$ -rich clays (preheating temperature of  $540^\circ\text{C}$ ) in a 5 wt. % soda solution and after washing until salt free, the CEC increased to 62 meq/100 g ( $\text{Cu}^{2+}$ -rich clay) and 50 meq/100 g ( $\text{Zn}^{2+}$ - and  $\text{Li}^+$ -rich clay). From the evolved water during thermoanalytical measurements, the following chemical formulae were calculated: (1)  $\text{Na}_{0.17}\text{Mg}_{0.017}\text{Cu}_{0.013}[(\text{Si}_{3.94}\text{Al}_{0.06})(\text{Al}_{1.42}\text{Fe}_{0.18}\text{Mg}_{0.33}\text{Cu}_{0.18})\text{O}_{10}\text{O}_{0.25}(\text{OH})_{1.5}]$ ; (2)  $\text{Na}_{0.10}\text{Mg}_{0.025}\text{Zn}_{0.02}[(\text{Si}_{3.96}\text{Al}_{0.04})(\text{Al}_{1.43}\text{Fe}_{0.18}\text{Mg}_{0.33}\text{Zn}_{0.18})\text{O}_{10}\text{O}_{0.28}(\text{OH})_{1.44}]$ ; (3)  $\text{Na}_{0.17}\text{Mg}_{0.003}\text{Li}_{0.014}[(\text{Si}_{3.92}\text{Al}_{0.08})(\text{Al}_{1.46}\text{Fe}_{0.18}\text{Mg}_{0.38}\text{Li}_{0.21})\text{O}_{10}\text{O}_{0.32}(\text{OH})_{1.46}]$ . These formulae provide the evidence of  $\text{Mg}^{2+}$  displacement by  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  and a nearly complete storage of these cations in previously vacant octahedral sites. Also, only some of the  $\text{Li}^+$  moved into octahedral positions and no  $\text{Mg}^{2+}$  was replaced. The interlayer  $\text{Li}^+$ , which migrated to the hexagonal holes of the tetrahedral sheet, became fully exchangeable after steam treatment.

In the IR spectrum, we could not clearly distinguish the influence of the interlayer cations on the OH-stretching vibrations at  $3675\text{ cm}^{-1}$  of rehydroxylated 2:1 phyllosilicates. These vibrations are more or less sharper than the vibrations of the starting material, but they are influenced in a similar way by small cations ( $\text{Li}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ) which moved into octahedral vacancies (producing trioctahedral areas) and by larger interlayer cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ) which position themselves deeper into the hexagonal holes of the tetrahedral sheet (producing nonswellable mica structures) (Mosser *et al.*, 1997; Trillo *et al.*, 1992; Russel and Fraser, 1994; Wise and Eugster, 1964).

We conclude that: 1) only one-fifth of the vacant octahedral sites are actually occupied by the small  $\text{Cu}^{2+}$  ( $\text{Zn}^{2+}$  and  $\text{Li}^+$ ) cations after rehydroxylation, 2) that a large number of nonexchangeable  $\text{Cu}^{2+}$  ( $\text{Zn}^{2+}$  and  $\text{Li}^+$ ) cations is located in the hexagonal holes of the 2:1 layers, 3) that the dehydroxylation peak at  $760^\circ\text{C}$  disappeared after dispersing the clays by soda or ultrasonic treatment, whereas the amount of hydroxyls stayed constant for the rehydroxylated  $\text{Li}^+$ -,  $\text{Na}^+$ -,  $\text{Ca}^{2+}$ -, and  $\text{Sr}^{2+}$ -rich montmorillonite, and 4) that the structural changes detected in IR spectra and XRD patterns are similar for all samples preheated at temperatures  $>510^\circ\text{C}$  and rehydroxylated. Thus, the occurrence of the proposed celadonite-like structure may be assumed for all rehydroxylated homoionic montmorillonites used in this study.

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