

## PREPARATION AND PROPERTIES OF REDUCED-CHARGE SMECTITES – A REVIEW

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**Abstract**—Layer charge reduction of selected homoionic swelling clay minerals upon heating is reviewed. This phenomenon is known for  $\text{Li}^+$ -montmorillonites as the Hofmann-Klemen effect. Aspects covered in the review include: mechanism of the charge reduction caused by the irreversible migration of small cations into the mineral layers; final sites of the fixed cations in the octahedral and/or tetrahedral sheets, as deduced on the basis of structural and spectroscopic data obtained in several studies; effects of octahedral and tetrahedral components of the layer charge; properties of the exchangeable cations; and the chemistry and structure of the mineral on charge reduction. Current knowledge has been summarized on the changes of various mineral properties connected with charge reduction, including the loss of swelling and the decrease in the cation exchange capacity, the most important change upon cation fixation. Also discussed are the preparation, properties, and advantages of uses of series of reduced-charge montmorillonites (RCMs) in research; interactions of RCMs with alkylammonium cations and organic cationic dyes, with some examples on the interactions with organic polymers and other organic compounds. Properties of organo-complexes and composite materials prepared from RCMs are also included in this review.

**Key Words**—Hoffman-Klemen effect, Reduced-charge Smectites, Swelling Clays.

### INTRODUCTION

Natural smectites have various chemical compositions. Non-equivalent substitutions of central atoms in the octahedra and/or tetrahedra generate a net negative charge on the layer that is balanced by hydrated exchangeable cations, e.g.  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ . The negative charge on smectite layers (layer charge, LC) is recognized as one of most important characteristics of 2:1 phyllosilicates. Layer charge is a very important criterion for the classification of 2:1 clay minerals and controls a mineral's capacity to retain cations and to adsorb water and various polar organic molecules (Mermut, 1994a). The amount of water present in smectite also depends on several other factors, such as relative humidity (RH), exchangeable cations, size and shape of the particles, and structural or crystal-chemical constraints (Bidadi *et al.*, 1988; Hrobáriková and Komadel, 2002). Since the classic work of Norrish (1954), numerous theoretical and/or experimental papers on hydration/dehydration of smectites saturated with various cations have been published (e.g. Ormerod and Newman, 1983; Bujdák *et al.*, 1992a; Park and Sposito, 2000). Greathouse and Sposito (1998) performed Monte Carlo and molecular dynamics simulations to elucidate interlayer structures in hydrated  $\text{Li}^+$ -hectorite, beidellite, or montmorillonite at low water content ( $\text{H}_2\text{O}/\text{Li}^+ = 3$ ).

The simulations showed that the nature of the interlayer  $\text{Li}^+$  solvation complexes depended critically on the location of negative charge sites within the smectite layers. Inner-sphere surface complexes with  $\text{Li}^+$  residing directly over the tetrahedral charge sites and the water molecules relegated to the midplane were observed for  $\text{Li}^+$ -beidellite which is dominated by tetrahedral charge. Outer-sphere surface complexes with  $\text{Li}^+$  located in the interlayer midplane with water molecules interposed between them and opposite siloxane surfaces were observed for  $\text{Li}^+$ -hectorite which has octahedral charge sites. Both types of surface complexes formed on  $\text{Li}^+$ -montmorillonite, the mineral with both types of charge site.

Hydration and dehydration of smectites may lead to decreased exchangeability of some cations. Wetting and drying cycles commonly occurring in nature cause fixation of  $\text{K}^+$  and  $\text{NH}_4^+$  cations, which are essential nutrients for plants (e.g. Šucha and Širáňová, 1991, Mikloš and Čičel, 1993). These cations are also important for diagenetic reactions of fine-grained sediments in the process of illitization. Fixation of  $\text{Cs}^+$  provides structural insights and is very significant for the environment (Cuadros, 2002). However, this type of fixation is different from fixation of cations upon heating, discussed below.

Many methods have been developed to determine the LC quantitatively or semiquantitatively and the quality, significance and problems associated with LC determinations are much discussed in the literature (e.g. Mermut, 1994b). Several attempts have been made to manipulate chemically the LC of smectites and thus to alter the industrially important properties of these

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minerals (Komadel, 2003; Komadel *et al.*, 2003). The LC can be increased by reduction of structural Fe(III) or decreased *via* fixation of small exchangeable cations.

Iron is the only structural element commonly present in smectite layers that has two relatively stable oxidation states. Fe(III) occurs in most dioctahedral smectites and its reduction leads to an increase in LC of these minerals. The oxidation state of structural Fe in smectites greatly influences the physical, chemical, surface and colloidal properties, such as cation exchange and fixation capacity, swelling in water, particle size, specific surface area, layer stacking order, magnetic exchange interactions, octahedral site occupancy, surface acidity, and reduction potential. Also affected is the surface chemistry of the clay particles, which influences clay-water and clay-organic interaction mechanisms (Stucki *et al.*, 2002).

Montmorillonites with decreased LC have often been prepared from their Li<sup>+</sup>-forms. Hofmann and Klemen (1950) showed that heating Li<sup>+</sup>-saturated Geisenheim bentonite caused fixation of previously exchangeable Li<sup>+</sup> ions and loss of CEC and expandability of the main clay mineral present in bentonite. Further assays proved that this behavior, known currently as the Hofmann-Klemen effect, is restricted to montmorillonites. The loss of swelling on heating Li<sup>+</sup>-smectites has been used widely to distinguish between montmorillonite and beidellite (Greene-Kelly, 1953, 1955; Schultz, 1969). In comparison with montmorillonites, much smaller decreases in CEC were observed for Fe-rich beidellite, ferruginous smectite and nontronites (Jaynes and Bigham, 1987; Madejová *et al.*, 2000a). Fixation of other small cations, such as Cd<sup>2+</sup>, Cu<sup>2+</sup>, Mg<sup>2+</sup>, Ni<sup>2+</sup>, *etc.*, have also been investigated, *e.g.* McBride and Mortland (1974), Purnell *et al.* (1991), Purnell and Lu (1993), Heller-Kallai and Mosser (1995), Mosser *et al.* (1997), Karakassides *et al.* (1999a, 1999b), Madejová *et al.* (1999), Pálková *et al.* (2003). Heating may also affect the charge of other clay minerals, as was shown in the study of the effect of heat treatments on the total charge of kaolinite saturated with Li<sup>+</sup>, Na<sup>+</sup> or Ca<sup>2+</sup> (Pennell *et al.*, 1991). This paper reviews reduction of the LC of smectites, and the properties and interactions of RCMs with organic compounds.

#### FIXATION OF Li IN HEATED Li<sup>+</sup>-SMECTITES

Heating of Li<sup>+</sup>-saturated montmorillonite at 200–300°C induces the irreversible migration of Li<sup>+</sup> cations into the layers. The final position(s) of fixed Li has been disputed and despite investigation for >50 y, no unambiguous, generally accepted answer to this question has been found. The magnitude of total charge as well as the proportion of tetrahedral and octahedral charge influence the locations where Li<sup>+</sup> ions are fixed, denoted as Li(I) later in this paper. It is supposed that higher octahedral charge enhances fixation of Li<sup>+</sup> in previously

vacant octahedral sites while tetrahedral charge induces dehydrated Li<sup>+</sup> ions to migrate from interlayer sites only to ditrigonal cavities in the tetrahedral sheets. However, there is uncertainty because structural formulae (SF) are frequently used to quantify tetrahedral and octahedral charge, and problems with SF, such as admixtures in the analyzed samples can substantially affect the calculated SF (Čížek and Komadel, 1994).

#### Li(I) in the tetrahedral sheets

Tettenhorst (1962) was one of the first to argue that Li<sup>+</sup> may be dehydrated and fixed in the ditrigonal cavities of the tetrahedral sheets. He recorded infrared (IR) spectra before and after heating (300°C) for montmorillonites from Cheto, Arizona, and San Juan, Argentina, and for a hectorite saturated with several cations. He did not observe any significant change in the OH-stretching region, except for the persistence of the sharp band at ~3600 cm<sup>-1</sup>. However, the relatively low sensitivity of dispersive IR spectrometers available at that time may not have allowed less pronounced changes in this region to be distinguished. Tettenhorst (1962) did observe a shift of the complex Si–O-stretching band to higher wavenumbers from 1035 to 1055 cm<sup>-1</sup>, for cations smaller than Zn<sup>2+</sup>. As shown later (Madejová *et al.*, 2000a), the magnitude of this shift in the Si–O band is typical for Li<sup>+</sup> fixation in Cheto montmorillonite. A similar relationship between the position of the Si–O band and the LC was reported by Kitajima *et al.* (1991) for synthetic micas; he observed a shift of the Si–O band to higher frequency with decreasing LC. The Si–O-stretching vibrations reflect structural aspects of the SiO<sub>4</sub> tetrahedra, which are influenced by the magnitude and location of LC (Madejová *et al.*, 2000a). Tettenhorst (1962) found an additional band near 810 cm<sup>-1</sup> in the spectra of heat-treated specimens containing small ions such as Li<sup>+</sup>, Mg<sup>2+</sup> or Ni<sup>2+</sup>, without providing its detailed assignment. He concluded that the size of interlayer cations determines the extent to which they migrate into montmorillonite layers and that the results are consistent with migration of cations from interlayer positions into the ditrigonal holes rather than a deeper penetration into unfilled octahedral sites.

Luca and Cardile (1988) used the <2 μm fraction of montmorillonite from Osage, Wyoming, to prepare Li<sup>+</sup>- and Na<sup>+</sup>-exchanged samples. In <sup>57</sup>Fe Mössbauer spectra obtained before and after heat treatment at 220°C, the Fe(II) doublet was about three times more intense in the Li<sup>+</sup>-montmorillonite spectrum compared with Na<sup>+</sup>-montmorillonite and the isomer shift and quadrupole splitting values were also significantly different. The authors reported that higher sensitivity of the Fe(II) resonance to the perturbations caused by the increased electric field gradient due to the Li<sup>+</sup> cation allowed the use of <sup>57</sup>Fe as a probe for the location of migrating cations within the structure. However, interlayer collapse and migration of cations into the montmorillonite structure upon heating

resulted in the oxidation of  $^{VI}\text{Fe(II)}^*$ , which was found to be present in the unheated sample. Therefore the authors reduced Fe(III) in heated montmorillonites to Fe(II) with hydrazine. Similar spectral parameters for the Fe(III) resonance of both  $\text{Na}^+$ - and  $\text{Li}^+$ -exchanged montmorillonites as well as for the Fe(II) resonance of hydrazine-treated samples were regarded as evidence that  $\text{Li}^+$  cations do not migrate into vacant octahedral sites.

The conclusions of Luca and Cardile (1988) are questionable for at least two reasons. (1) In general, the  $\text{Li}^+$  cations are supposed to migrate into the vacant octahedra located near the sites of isomorphic substitution (*i.e.* Mg(II)-containing octahedron). The SF of the Osage montmorillonite ( $\text{Na}_{0.58}\text{Ca}_{0.04}[\text{Si}_{7.90}\text{Al}_{0.10}][\text{Al}_{3.10}\text{Fe}_{0.38}\text{Mg}_{0.48}\text{Ti}_{0.02}]\text{O}_{20}(\text{OH})_4$ ) indicates, however, that the amount of adjacent Fe(III) and Mg(II) octahedra may not be sufficient to detect the presence of Li(I) in the octahedral sites. (2) Reduction of  $^{VI}\text{Fe(III)}$  to  $^{VI}\text{Fe(II)}$  is clearly connected with the modification of the montmorillonite structure (Manceau *et al.*, 2000), which can impede the identification of the structural changes related to the  $\text{Li}^+$  fixation in the octahedra.

Luca *et al.* (1989) employed solid-state  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ ,  $^{23}\text{Na}$  and  $^7\text{Li}$  magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopies to follow changes in the structure of  $\text{Li}^+$ - and  $\text{Na}^+$ -STx-1 montmorillonites caused by heating and/or exposure to different RH. They were unable to detect any features suggesting that  $\text{Li}^+$  had migrated into the previously vacant octahedral sites.

Alvero *et al.* (1994) studied two  $\text{Li}^+$ -montmorillonites (SWy-1, Wyoming and Trancos, Spain; Table 1) with different tetrahedral and octahedral charge-deficit distributions to obtain information on structural changes occurring upon heating. Re-expansion of the samples previously collapsed by heating at 300°C in air was attained by heating at 300°C under an atmosphere of water vapor at 8.5 MPa. Structural changes of the smectites after different treatments were monitored by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and  $^{29}\text{Si}$ ,  $^{27}\text{Al}$  and  $^7\text{Li}$  MAS NMR. The  $^{27}\text{Al}$  MAS NMR spectra of heated samples showed the disappearance of the  $^{IV}\text{Al}$  signal due to the lack of symmetry of the Al tetrahedra, distorted by the presence of Li(I), which strongly increases the quadrupolar coupling constant. The authors argued that their results provide direct experimental evidence that  $\text{Li}^+$  ions are located in the ditrigonal holes. Alba *et al.* (1998) used re-expanded  $\text{Li}^+$ -montmorillonite, prepared by Alvero *et al.* (1994), as a starting material for studies of the chemical behavior of  $\text{Li}^+$  ions. Two experiments were carried out: a thermal treatment was used to

evaluate the possible recollapse of the sample, and ion exchange with  $\text{Na}^+$  ions followed by thermal treatment to analyze its exchange capacity. The samples were characterized by XRD, FTIR, differential thermal analysis/thermogravimetric analysis (DTA/TG) and  $^{29}\text{Si}$ ,  $^{27}\text{Al}$  and  $^7\text{Li}$  MAS NMR. The results of the first experiment showed that  $\text{Li}^+$  ions from the re-expanded  $\text{Li}^+$ -sample were able to migrate into the silicate structure upon thermal treatment to the same extent as in a fresh  $\text{Li}^+$ -montmorillonite. The XRD pattern showed a complete recollapse of the sample after the heating at 300°C for 24 h. Regarding the second experiment, an extensive ion exchange in NaCl solution was attained, hindering layer collapse after thermal treatment. Based on the results obtained, complete reversibility of the process for  $\text{Li}^+$  ions has been concluded although irreversible damage in the silicate structure was observed.

The results reported above were obtained with hydrothermally treated montmorillonites. However, hydrothermal treatment is known to cause severe changes in the layers of montmorillonites. Beaufort *et al.* (2001) reported that the low-charge montmorillonite (Crook County, USA) was not a stable material in hydrothermal environments and the thermal effect (100–200°C) initiated important structural modifications. Transformation of montmorillonite to high-charge dioctahedral (beidellite) and trioctahedral (saponite) smectites was described. The formation of beidellite from montmorillonite is accompanied by morphological changes in clay particles, suggesting a dissolution-crystallization mechanism. This type of reaction was considered as a first step in the overall illitization process of the montmorillonite. Illite layers, detected in runs with  $\text{K}^+$ -montmorillonite, were interstratified with both high-charge and low-charge dioctahedral smectites in a three-component mixed-layer mineral. These data illustrate that both the octahedral and tetrahedral sheets in montmorillonite layers undergo substantial transformation during hydrothermal treatment and thus the loss of previously fixed Li (Alvero *et al.*, 1994; Alba *et al.*, 1998) is not surprising.

Theng *et al.* (1997) used chemical analysis, XRD,  $^7\text{Li}$  NMR and X-ray photoelectron spectroscopy (XPS) to investigate the migration of  $\text{Li}^+$  ions in “Kunipia-F” montmorillonite after heat treatment at 250°C. Unfortunately, a questionable structural formula (Table 1), cited from Iwasaki and Onodera (1995), was provided. Octahedral occupancy was 4.00, and a LC of  $-0.86 e/\text{O}_{20}(\text{OH})_4^*$  was supposed to be compensated by cations with a total charge of  $+1.01 e/\text{O}_{20}(\text{OH})_4$  (Table 1). Heating caused a large reduction in CEC and an almost complete loss of interlayer expansion with

\*VI in  $^{VI}\text{Fe(II)}$  denotes the coordination number of the iron atom in the polyhedron; (II) is the oxidation state of iron.

\*  $e$  denotes absolute value of the electric charge of one electron (electron charge) equal to  $1.6022 \times 10^{-19} \text{ C}$

Table 1. Coefficients in the structural formulae of smectites used for preparation of RCMs, their octahedral occupancy and components of the negative charge on the layers. Octahedral occupancy values <4.00 suggest Si-rich admixtures, while values >4.00 suggest Al-, Fe- and/or Mg-rich admixtures in smectites (Čížek and Komadel, 1994).

Sample*	Ex $M^+$	Coefficients per $O_{20}(OH)_4$				Octahedral occupancy	Negative charge $e/O_{20}(OH)_4$			Reference
		Tetrahedra $IV_{Si}$	$IV_{Al}$	$VI_{Al}$	Octahedra $VI_{Fe}$		$VI_{Mg}$	Te	Oc	
Sarigus	1.14	7.57	0.43	2.36	0.91	0.73	0.43	0.73	1.16	Hrobáriková <i>et al.</i> (2001)
SAz-1	1.11	8.00	—	2.67	0.15	1.20	0	1.14	1.14	Madejová <i>et al.</i> (2000a)
Jelšový Potok	1.01	7.95	0.05	2.91	0.24	0.79	0.05	0.97	1.02	Madejová <i>et al.</i> (1996)
SCa-2	1.06	7.93	0.07	2.68	0.16	1.25	0.07	0.98	1.05	Madejová <i>et al.</i> (2000a)
Olay	0.96	7.95	0.05	2.77	0.15	1.17	0.05	0.90	0.95	Hrobáriková <i>et al.</i> (2001)
Ivančice	0.94	7.79	0.21	2.84	0.42	0.74	0.21	0.74	0.95	Hrobáriková <i>et al.</i> (2001)
Stebno	0.95	7.22	0.78	1.96	1.60	0.58	0.78	0.14	0.92	Madejová <i>et al.</i> (2000a)
Jelšový Potok	0.91	7.71	0.29	3.00	0.38	0.63	0.29	0.60	0.89	Madejová <i>et al.</i> (1999)
SWa-1	0.88	7.32	0.68	0.92	2.83	0.27	0.68	0.21	0.89	Madejová <i>et al.</i> (2000a)
Trancos	0.87	7.64	0.36	3.09	0.28	0.69	0.36	0.51	0.87	Alvero <i>et al.</i> (1994)
Kriva Palanka	0.85	7.85	0.15	2.96	0.32	0.72	0.15	0.72	0.87	Hrobáriková <i>et al.</i> (2001)
Kunipia-F	1.01	7.80	0.20	3.14	0.24 <sup>a</sup>	0.62	0.20	0.66	0.86	Theng <i>et al.</i> (1997)
Jelšový Potok	0.78	7.98	0.02	3.01	0.23	0.76	0.02	0.76	0.78	Bujdák <i>et al.</i> (1991)
Camp Berteau	0.76	8.00	—	2.92	0.32	0.76	0	0.76	0.76	Calvet and Prost (1971)
Horní Dunajovice	0.73	7.89	0.11	2.70	0.52	0.85	0.11	0.64	0.75	Madejová <i>et al.</i> (2000a)
Linden	0.74	7.90	0.10	2.92	0.36	0.76	0.10	0.64	0.74	Emmerich <i>et al.</i> (1999)
Upton	0.64	7.90	0.10	3.06	0.32	0.66	0.10	0.54	0.64	Clementz and Mortland (1974)
Volclay	0.66	7.78	0.22	3.14	0.38 <sup>b</sup>	0.54	0.22	0.40	0.62	Brindley and Ertem (1971)
SWy-1	0.62	7.80	0.20	3.28	0.34 <sup>c</sup>	0.38	0.20	0.42	0.62	Sposito <i>et al.</i> (1983)
SWy-1	0.58	7.84	0.16	3.28	0.34	0.38	0.16	0.38	0.54	Alvero <i>et al.</i> (1994)

\* For more exact locations of the samples see the cited source articles.

<sup>a</sup> Fe(III) 0.20 + Fe(II) 0.04

<sup>b</sup> Fe(III) 0.34 + Fe(II) 0.04

<sup>c</sup> Fe(III) 0.30 + Fe(II) 0.04

glycerol.  $^7\text{Li}$  static and MAS NMR spectroscopies showed that the quadrupole coupling constant of Li was markedly higher for the  $\text{Li}^+$ -heated montmorillonites than for the unheated  $\text{Li}^+$ -montmorillonite and for an unheated hectorite. This indicated that Li(I) occupied structural sites of low symmetry, inconsistent with octahedral positions in the layers. The XPS showed that the binding energy (BE) for  $\text{Li}^+$  cations in unheated montmorillonite is comparable with that for other exchangeable cations. Heating broadened the Li 1s band and decreased the BE, but this was significantly higher than in minerals in which Li atoms are known to occupy octahedral sites. The data suggested that heating induced  $\text{Li}^+$  to migrate from interlayer sites to structural sites of low symmetry, probably the ditrigonal cavities in the tetrahedral sheet. However, neither the effect of relatively high tetrahedral charge nor the possibility of different sites in the layers for  $\text{Li}^+$  fixation was discussed. Tetrahedral charge is known to decrease  $\text{Li}^+$  fixation in the layers since the pioneering study of Greene-Kelly (1953). Interpretation of  $^7\text{Li}$  MAS NMR data obtained is based on direct comparison with data for hectorite but the effect of different occupancy of the octahedra of heated montmorillonite (Al, Fe(III), Fe(II), Mg, vacancies, possibly Li) from hectorite (Mg, Li) is not discussed.

#### *Li(I) in the previously vacant octahedra*

In the pioneering papers on  $\text{Li}^+$  fixation, which are focused on swelling properties,  $\text{Li}^+$  cations were considered to migrate upon heating from interlayer sites to the vacant octahedra in montmorillonite but not in beidellite (Hofmann and Klemen, 1950; Greene-Kelly, 1953, 1955). Spectroscopic techniques, such as IR and MAS NMR spectroscopies, probe local atomic environments and have the potential to provide information on chemical bonds. Most of the papers supporting  $\text{Li}^+$  fixation in previously vacant octahedra are based on analyses of IR spectra of the unheated and heated  $\text{Li}^+$ -montmorillonites and the authors frequently argue that Li(I) can also be partly trapped in the ditrigonal cavities of the tetrahedral sheets. For example, Russell and Farmer (1964) and Farmer and Russell (1967) interpreted IR data to indicate that some of the  $\text{Li}^+$  ions migrate into the octahedral positions and become entrapped, whereas the remainder react with interlayer water or structural hydroxyl groups to liberate protons. Lithium in this form remains in, or close to, the interlayer region.

Calvet and Prost (1971) in a detailed IR spectroscopic study showed that 31–92% of  $\text{Li}^+$  cations are fixed in montmorillonite from Camp Berteau on heating for 24 h at 108–220°C. This montmorillonite has no tetrahedral substitution (Table 1). The transition of  $\text{Li}^+$  to a non-exchangeable state was related to the temperature and the duration of heating. The authors inferred that  $\text{Li}^+$  ions moved into the octahedral vacancies, presumably

those that lie near sites of isomorphic substitution. This conclusion was based mainly on the changes observed in the IR spectra of oriented films in the OH-stretching region at 3300–3800  $\text{cm}^{-1}$ . After heating, the maximum of the main band shifted from 3630 to 3640  $\text{cm}^{-1}$  and a dichroic narrow band appeared near 3670  $\text{cm}^{-1}$ , which was attributed to stretching vibrations of the OH groups perpendicular to the layers and shared by three central atoms, Al, Mg and Li, in adjacent octahedra (AlMgLiOH). Dichroic behavior, *i.e.* variation in the band intensity with the angle of incidence of the IR beam, is diagnostic for trioctahedral layer silicates, while dioctahedral minerals show no change in the OH intensity. The  $\text{Li}^+$  migration apparently evoked structural modifications creating local trioctahedral configuration but only a fraction of the Li(I) was identified in octahedral positions, the remainder evidently being in the bottom of the ditrigonal cavities.

Sposito *et al.* (1983) interpreted the fundamental and near-IR (NIR) regions of spectra obtained from films of  $\text{Na}^+/\text{Li}^+$ -saturated SWy-1 Wyoming montmorillonite (Table 1) with different  $\text{Na}^+/\text{Li}^+$  ratios. The RCMs were prepared by placing the films in a muffle furnace for 24 h at 250°C. Spectra were taken after dehydrating the films in vacuum and after rehydrating the films with  $\text{D}_2\text{O}$  at 50% RH. For the Na-montmorillonite, changes in the intensities of structural OH-bending modes, particularly of the AlMgOH vibrations, were observed with dehydration. This result was interpreted as evidence that exchangeable  $\text{Na}^+$  ions lost solvation water and settled into the ditrigonal cavities of the tetrahedral sheets. The decrease in intensity of the AlMgOH-bending mode observed in the spectrum of the reduced-charge  $\text{Na}^+/\text{Li}^+$  sample was related to the fixation of  $\text{Li}^+$  in the octahedral sheet. The NIR spectra of  $\text{Na}^+$ - and  $\text{Na}^+/\text{Li}^+$ -montmorillonites did not show any pronounced shift of the principal absorption bands with charge reduction. The only significant change was a decrease in intensity of the absorption bands assigned to adsorbed water molecules.

Srasra *et al.* (1994) used IR spectroscopy to follow structural changes in  $\text{Li}^+$ -exchanged illite-smectite heated at 250°C in vacuum. Based on K content, the illitic phase represented 13 wt.% of the sample, in good agreement with 85% swelling interlayers, based on a measured surface area of 550  $\text{m}^2/\text{g}$  using the ethylene glycol (EG) adsorption method. The structural formula obtained after subtracting 13 wt.% of an illitic phase with an ideal composition was  $(M_{0.72}^+[\text{Si}_{7.56}\text{Al}_{0.44}][\text{Al}_{2.76}\text{Fe}_{0.82}\text{Mg}_{0.41}\text{Ti}_{0.02}]\text{O}_{20}(\text{OH})_4)$ . The IR spectrum of a heated  $\text{Li}^+$  sample showed new bands in the OH-bending region associated with the presence of Li(I) in previously vacant octahedral positions. The intensities of the original OH-bending bands, those also observed in the spectrum of unheated sample, suggested that fractions of octahedral sites were still vacant in the heated sample.



Madejová *et al.* (1996) prepared a series of RCMs from  $\text{Li}^+$ -montmorillonite from Jelšovský Potok (Table 1) by heating at 105–210°C for 24 h. The amount of  $\text{Li(I)}$ , 0.09–0.67 per  $\text{O}_{20}(\text{OH})_4$ , increased with increasing temperature, confirming the successful preparation of a set of samples of variable LC from the same parent  $\text{Li}^+$ -montmorillonite by varying only preparation temperature. Analysis of IR spectra for samples heated above 150°C revealed local trioctahedral domains with OH groups absorbing near  $3670\text{ cm}^{-1}$ , indicating the presence of  $\text{Li(I)}$  in previously vacant octahedral positions, presumably in those which lie near the sites of non-equivalent isomorphous substitution.

Gates *et al.* (2000) provided further evidence that the electronic and structural character of RCMs was similar to that of pyrophyllite. They analyzed the same series of RCMs as Madejová *et al.* (1996) by  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectroscopies to discern changes in electronic and structural properties that had been induced by  $\text{Li}^+$  fixation. Room-temperature  $^{29}\text{Si}$  MAS NMR spectra revealed a consistent chemical shift to more negative values and increased line-width of the main  $\text{Q}^3(\text{OAl})$  Si resonance with increasing levels of  $\text{Li}^+$  fixation in the RCM series. The main  $\text{Q}^3(\text{OAl})$  Si resonance is from Si atoms bound in the layers and having three other Si atoms and no Al atoms as the next nearest neighbors. The observed  $^{29}\text{Si}$  chemical shift of  $-95.4$  ppm for the sample prepared at 210°C agreed well with values reported for pyrophyllite (*e.g.*  $-95.4$  ppm, Sanchez-Soto *et al.*, 1993). The decreased line-width of the octahedral Al environment was attributed to formation of a more uniform electronic environment surrounding octahedral Al as charge reduction occurred. No appreciable changes in the peak assigned to the tetrahedral Al were observed for the series, except for line broadening. Correlations of  $^{29}\text{Si}$  MAS NMR chemical shifts with LC and IR-active structural vibrations indicated that distortions in the  $\text{Si-O-T}$  bond angles ( $T = \text{tetrahedral Si or Al}$ ) occurred, with the mean  $\text{Si-O-T}$  bond angle increasing, following charge reduction. Thus, the goodness of fit between the octahedral and tetrahedral sheets was diminished after charge reduction, and the RCMs developed significant pyrophyllite-like character.

Madejová *et al.* (2000a) used IR spectroscopy in the mid-IR region to follow structural changes occurring in five  $\text{Li}^+$ -saturated dioctahedral smectites upon heating. The smectites included montmorillonites SAz-1 (Cheto, Arizona), SCa-2 (Otay, California) and from Horní Dunajovice (Czech Republic), a ferruginous smectite SWa-1 (Grant County, Washington) and an Fe-beidellite from Stebno, (Czech Republic); the latter two are dominated by tetrahedral charge (Table 1). The CEC values of the montmorillonites prepared at 200°C were 13, 12 and 22%, respectively, of those of the unheated samples. A gradual decrease of the LC due to  $\text{Li}^+$  fixation led to a shift of the  $\text{Si-O}$ -stretching band to higher wavenumbers and to the appearance of new,

pyrophyllite-like bands at  $1120$  and  $419\text{ cm}^{-1}$  (Figure 1). Fixation of  $\text{Li}^+$  ions in the structure even upon heating at 120°C caused the appearance of an  $\text{AlMgLiOH}$ -stretching band near  $3670\text{ cm}^{-1}$  in the spectra of all three montmorillonites. This band confirmed the presence of  $\text{Li(I)}$  in the previously vacant octahedral positions in the montmorillonites. No similar band was observed in the spectra of heated Fe-rich smectites Stebno and SWa-1, both of which are dominated by tetrahedral charge. Both smectites also had only a small decrease in CEC with heating temperature; the samples prepared at 200°C reaching 67 and 83%, respectively, of their original values. Clearly, some fixation of  $\text{Li}^+$  cations occurred in all smectites upon heating at 200°C, though the extent of fixation decreased with decreasing proportion of octahedral charge. This is in agreement with previous studies (*e.g.* Jaynes and Bigham, 1987).

The same series of samples was investigated using diffuse reflectance spectra in the near-IR region (Madejová *et al.*, 2000b). Unheated samples showed a complex band near  $7060\text{ cm}^{-1}$  assigned to the first overtone of the OH-stretching mode of structural OH groups and bound  $\text{H}_2\text{O}$ . The OH combination bands appeared in the  $4600\text{--}4300\text{ cm}^{-1}$  region. Spectra of heated montmorillonites showed an upward shift and a splitting of the OH overtone band into two components near  $7170$  and  $7110\text{ cm}^{-1}$ . The presence of a band near  $7170\text{ cm}^{-1}$ , assigned to the overtone of the  $\text{AlMgLiOH}$ -stretching vibration ( $3670\text{ cm}^{-1}$ ), implied that local trioctahedral domains had been created upon  $\text{Li}^+$  fixation in the previously vacant octahedral positions of montmorillonites (Figure 2). The OH combination bands were shifted to higher frequencies and a new band appeared near  $4472\text{ cm}^{-1}$  in the spectra of montmor-

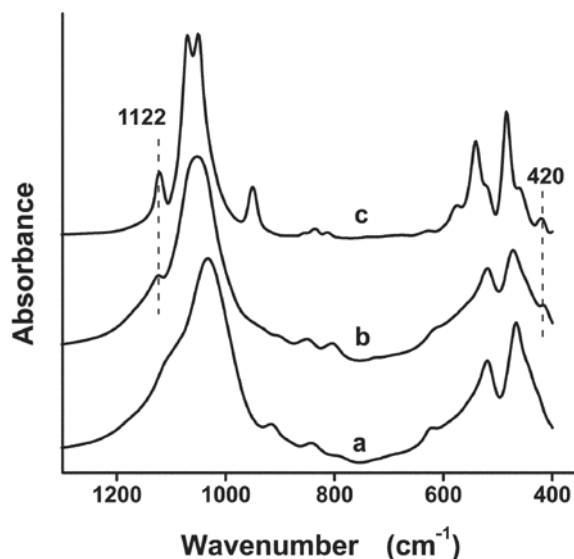


Figure 1. IR spectra of unheated  $\text{Li}^+$ -SAz-1 (a),  $\text{Li}^+$ -SAz-1 heated for 24 h at 300°C (b) and pyrophyllite (c).

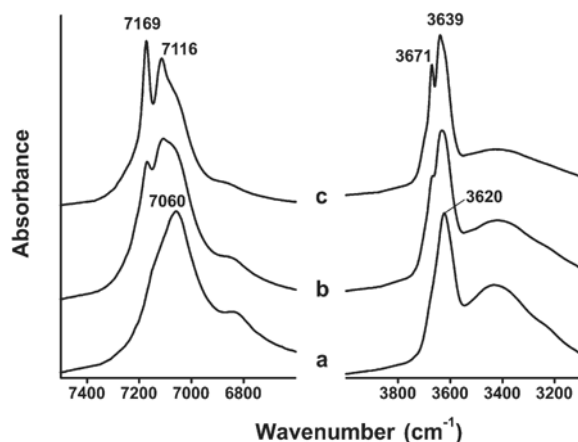


Figure 2. IR spectra of  $\text{Li}^+$ -SAZ-1 samples in the OH-overtone ( $7500\text{--}6600\text{ cm}^{-1}$ ) and OH-stretching ( $4000\text{--}3100\text{ cm}^{-1}$ ) regions: unheated sample (a) and after heating for 24 h at  $150^\circ\text{C}$  (b) and  $300^\circ\text{C}$  (c). Data from Pálková *et al.* (2003).

illonites heated above  $130^\circ\text{C}$ . No features indicating Li(I) in the structure of Fe-beidellite or ferruginous smectite were observed in the NIR spectra. The modification of all combination bands upon heating of  $\text{Li}^+$ -montmorillonites reflected perturbation of both the OH-stretching and bending modes due to the presence of Li(I) in previously vacant octahedral positions and/or in the ditrigonal cavities. The changes in the OH overtone and combination regions were very similar for three montmorillonites, indicating that  $\text{Li}^+$  fixation in the structure had occurred similarly for all montmorillonites studied.

Recently Stackhouse and Coveney (2002) employed calculations using density functional methods to examine the phenomenon of  $\text{Li}^+$  fixation in heated montmorillonite at the electronic structure level. They showed that it was energetically preferable for Li(I) to reside in the vacant octahedral sites relative to the ditrigonal cavities because the close proximity of the Li(I) to the negative charge sites in the octahedral sheet increased favorable Coulombic interactions. Occupation of octahedral sites causes structural OH groups to reorientate perpendicular to the *ab* plane. Deprotonation and dehydroxylation were not observed in molecular dynamics calculations for reported experimental temperatures. Dehydroxylation has been found to inhibit rather than facilitate cation migration. A comparison of calculated powder spectra with experimental IR spectra suggests that  $\text{Li}^+$  cations are not fixed in ditrigonal cavities when no tetrahedral Al is present.

Migration of  $\text{Li}^+$  cations towards vacant octahedral sites upon heating and consequent neutralization of the layer charge arising from nonequivalent substitutions in the octahedral sheet is frequently utilized to evaluate charge distribution between tetrahedral and octahedral sites (e.g. Srasra *et al.*, 1994). Petit *et al.* (1998) compared the deformation  $\delta(\text{NH}_4^+)$  mode in IR spectra of pairs of  $\text{NH}_4^+$ -exchanged samples prepared from

different dioctahedral and trioctahedral smectites. Each pair consisted of the  $\text{NH}_4^+$ -exchanged parent (unheated) smectite and an  $\text{NH}_4^+$ -exchanged sample that had previously been  $\text{Li}^+$ -saturated and heated to  $300^\circ\text{C}$  to evoke  $\text{Li}^+$  fixation. The intensity of the  $\delta(\text{NH}_4^+)$  band of the parent smectite reflected the total layer charge, while the decreased intensity of the band observed for the heated sample indicated a decrease of the octahedral charge due to  $\text{Li}^+$  fixation. That allowed quantitative determination of the total layer charge and tetrahedral and octahedral components in smectites.

Petit *et al.* (2002) used this method to analyze the distribution of the layer charge in the Fe-rich smectite from Ölberg, Germany. According to the method suggested by Olis *et al.* (1990) the calculated value of the mean layer charge was  $-0.72\text{ e/O}_{20}(\text{OH})_4$ . The  $\text{Li}^+$ -saturated sample was heated at different temperatures ( $105\text{--}300^\circ\text{C}$ ) for 24 h to obtain a set of samples with gradually decreasing layer charge. The vibrations of OH groups of heated  $\text{Li}^+$  samples confirmed fixation of  $\text{Li}^+$  in the formerly vacant octahedra and creation of local trioctahedral domains in which the OH group was shared by three central atoms, such as  $\text{MgFe(III)Li}$ ,  $\text{Fe(III)Fe(III)Li}$  and  $\text{AlFe(III)Li}$ .

The IR spectra of  $\text{NH}_4^+$ -exchanged samples revealed a gradual charge reduction with increasing temperature of the sample preparation up to  $250^\circ\text{C}$ . The integrated intensity of the  $\delta(\text{NH}_4^+)$  band of the sample heated at  $150^\circ\text{C}$  reflected a charge reduction  $>50\%$ . The maximum charge reduction, observed for the sample prepared at  $250^\circ\text{C}$ , was 25% of the initial value. Assuming negligible variable charge, the remaining charge ( $-0.18\text{ e/O}_{20}(\text{OH})_4$ ) was attributed to the tetrahedral charge, in good agreement with the structural formula indicating  $0.16\text{ }^{IV}\text{Al}$  per  $\text{O}_{20}(\text{OH})_4$  (Köster *et al.*, 1999).

#### *Li(I) in O-Li groups?*

In addition to layer charge reduction, surface acidification upon  $\text{Li}^+$  fixation was reported. The increased acidity was attributed to the reaction of  $\text{Li}^+$  with the structural OH groups in the octahedral sheets and consequently to the creation of O-Li(I) groups (Russell and Farmer, 1964; Jaynes and Bigham, 1987; Williams *et al.*, 1991). Jaynes and Bigham (1987) investigated in detail  $\text{Li}^+$  fixation in several dioctahedral and trioctahedral smectites, including The Clay Minerals Society's 'Source Clays and Special Clays'. They discovered that direct measurements of exchangeable  $\text{Li}^+$  after heating led to overestimates of charge reduction due to partial entrapment of  $\text{Li}^+$  in collapsed interlayers. Expansion of interlayers by washings with  $\text{MgCl}_2$  solutions and ethanol followed by determination of exchangeable  $\text{Mg}^{2+}$  provided accurate data on charge reduction. The decreases observed in CEC for dioctahedral smectites upon  $\text{Li}^+$  fixation were in reasonable agreement with the values calculated from the previously published structural formulae. The authors

claimed that excess  $\text{Li}^+$  was retained as a consequence of the deprotonation of structural OH groups coordinated to octahedral Fe and that mild acid treatment re-protonated these hydroxyls and released excess  $\text{Li}^+$  without alteration of LC. Partial acidification of Fe-rich smectites upon  $\text{Li}^+$  fixation and charge regeneration was also observed by Bujdák *et al.* (2001).

Williams *et al.* (1991) observed charge regeneration of thermally treated  $\text{Li}^+$ -montmorillonite. Treatment with a strong base involved proton extraction from the sheets, and each  $\text{Li}^+$  entering the structure was balanced by an  $\text{H}^+$  leaving it.  $\text{Li}^+$ -montmorillonite after heating above 200°C became a good catalyst for the proton-catalyzed conversion of cyclohexylamine to dicyclohexylamine. Madejová *et al.* (1996) also reported a partial deprotonation of the  $\text{Li}^+$ -montmorillonite from Jelšový Potok after treatments above 120°C, reflected in the decrease of the intensities of the OH-bending bands. Heller-Kallai (2001), reviewing literature on deprotonation of reduced-charge smectites, concluded that migration of small interlayer cations into the smectite layers decreased the overall LC due to the presence of additional cations within the layers, but this decrease might be reduced by partial deprotonation of structural OH groups. The extent of deprotonation depends on the thermal regime and is favored by the presence of structural Fe and proton acceptors in the interlayers. Deprotonation is also greater when small divalent cations are used to reduce LC rather than Li. A sample may give a strongly acidic response in the presence of a strong base, while the number of free protons in the same sample determined by an exchange reaction in neutral environment is much smaller.

#### FIXATION OF OTHER CATIONS

Protons are small, mobile cations capable of penetrating into the layers even without heating.  $\text{H}^+$ -smectites are unstable materials undergoing autotransformation to mixed ( $\text{H}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ) forms (Coleman and Craig, 1961; Janek and Komadel, 1993; Janek *et al.*, 1997). Russell and Fraser (1971) and Yariv and Heller-Kallai (1973) observed a decrease in intensity of the OH-bending bands for  $\text{H}^+$ -saturated montmorillonites as a result of the low level of hydration after evacuation or drying and attributed this to protonation of the structural OH groups and the consequent release of  $\text{H}_2\text{O}$  molecules together with the corresponding octahedral atoms. Proton affinity distributions clearly indicated up to five different proton interacting sites in the smectite-water systems. The amounts of the strongest acid sites decreased on ageing, while the amounts of all weaker acid sites increased. The strongest acid sites were due to free protons present in the dispersion, while the weaker acid sites were associated with hydrated released structural  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$  cations and/or their hydrolyzed species, and  $\text{SiOH}_2$  or  $\text{SiOH}$  groups (Janek

and Komadel, 1999). Clearly, though protons get into the smectite layers, the reaction is hydrolysis, not fixation.

In addition to  $\text{Li}^+$ , fixation of other small cations, such as  $\text{Cu}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Mg}^{2+}$  upon heating smectites has been studied. Among these,  $\text{Cu}^{2+}$  has been examined the most because electron paramagnetic resonance (EPR) spectroscopy, in addition to other methods, has proven a valuable tool to investigate the fate of these ions. McBride and Mortland (1974) studied interactions of  $\text{Cu}^{2+}$  ions with smectite layers using <2  $\mu\text{m}$  fractions of Upton montmorillonite (Table 1) heated for 24 h at different temperatures up to 270°C. Dehydration of these cations upon heating allowed the  $\text{Cu}^{2+}$  to become embedded primarily in the ditrigonal cavities. Movement of  $\text{Cu}^{2+}$  into empty octahedral positions was limited, probably by the divalent charge on the ions. The samples prepared at up to 200°C re-expanded in water, in ethanol and in a 1:1 mixture of water-ethanol, while samples heated at 270°C remained collapsed in water but did swell in the other two solvents. Resolvation caused the  $\text{Cu}^{2+}$  ions to move out of the ditrigonal holes but not from the octahedral sites. However, neither IR spectra nor EPR spectra provided unambiguous proof of Cu(II) present in the octahedral sites.

Heller-Kallai and Mosser (1995), investigating migration of  $\text{Cu}^{2+}$  ions in  $\text{Cu}^{2+}$ -montmorillonite heated with or without K halides, concluded that on heating to 350°C, most of the  $\text{Cu}^{2+}$  moved into ditrigonal holes and only a minor fraction may have penetrated into octahedral vacancies. On further heating, when dehydroxylation occurred, the  $\text{Cu}^{2+}$  ions migrated from the ditrigonal holes into the vacant octahedra. On heating in the presence of KBr or KCl, deprotonation of OH groups freed the pathway for penetration of  $\text{Cu}^{2+}$  into the octahedral sheets. Although  $\text{Li}^+$  and  $\text{Cu}^{2+}$  have similar ionic radii, the literature suggests that they behave differently in montmorillonites when heated; apparently the smaller charge of  $\text{Li}^+$  facilitates its penetration into vacant octahedra.

Mosser *et al.* (1997) heated a  $\text{Cu}^{2+}$ -montmorillonite from Wyoming and  $\text{Cu}^{2+}$ -Laponite at 100°C intervals up to 500°C and analyzed the resulting materials using various techniques. Heating at 200°C decreased the CEC to 24% and 82% of the values obtained for the unheated montmorillonite and Laponite, respectively. The interpretation of the IR, EPR and XPS data indicated that on heating,  $\text{Cu}^{2+}$  ions migrated into the vacant octahedral sites of the montmorillonite where the  $\text{Cu}^{2+}$  compensated the charge deficit of the clay layer; in Laponite,  $\text{Cu}^{2+}$  migrated into occupied octahedral sites where it replaced Li(I) and Mg(II). However, none of the spectroscopic methods used proved the location of Cu(II) to be in the octahedra. The results indicated mainly LC decrease and a change in the symmetry of Cu coordination polyhedron and other changes in the ligand sphere. Later, He *et al.* (2001) extended the investigation



of  $\text{Cu}^{2+}$ -montmorillonites and analyzed the hyperfine structure lines of the EPR spectra of a montmorillonite sample from Guangdong, China. Three signals in the EPR spectra, corresponding to  $\text{Cu}^{2+}$  ions, were recorded simultaneously. Some  $\text{Cu}^{2+}$  ions replaced the interlayer cations and some entered the ditrigonal cavities. A small fraction of  $\text{Cu}^{2+}$  ions was reported to penetrate into the octahedral vacancies. On heating, the hydrated  $\text{Cu}^{2+}$  ions in the interlayer lost the coordinating water and then entered into the ditrigonal cavities. When the heating temperature was further increased, dehydroxylation occurred, facilitating penetration of the  $\text{Cu}^{2+}$  ions from the ditrigonal cavities into the octahedral vacancies.

Madejová *et al.* (1999) examined the effect of ion size and charge of exchangeable cations on the extent of their fixation upon heating using  $\text{Cu}^{2+}$ -,  $\text{Cd}^{2+}$ - and  $\text{Li}^+$ -saturated Jelšový Potok montmorillonite. The structural formula of the parent mineral is given in Table 1. The effect of these treatments on the CEC and structure was investigated chemically and by FTIR spectroscopy. The CEC values of the mineral decreased with increasing temperature and the amount of fixed cations decreased for  $\text{Li}^+ > \text{Cu}^{2+} > \text{Cd}^{2+}$  for all temperatures studied. Based on CEC data, the  $\text{Cu}^{2+}$ -saturated sample heated at 200°C contained both unexchangeable Cu(II) and exchangeable  $\text{Cu}^{2+}$ . Partial exchange of  $\text{Cu}^{2+}$  with  $\text{Li}^+$  was performed to prepare a sample containing both  $\text{Li}^+$  and  $\text{Cu}^{2+}$  exchangeable cations. Further heating of this sample at 300°C led to preferential fixation of  $\text{Li}^+$ . The IR spectra of heated  $\text{Li}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}/\text{Li}^+$  samples revealed that most of the  $\text{Li}^+$  ions had migrated into the octahedral vacancies, thus creating local trioctahedral  $\text{AlMgLiOH}$  configurations.  $\text{Cu}^{2+}$  ions were trapped in the ditrigonal cavities of the tetrahedral sheet.  $\text{Cd}^{2+}$  ions were too large to be fixed even in the ditrigonal cavities. Selected samples from the above study were further investigated by specular reflectance IR and EPR spectroscopies (Karakassides *et al.*, 1999b). The IR spectra of heated samples showed that Li(I) occurred in two different sites: in the previously vacant octahedra and in the ditrigonal holes of the tetrahedral sheet.  $\text{Cu}^{2+}$  ions were fixed deep in the ditrigonal holes and substantially affected the vibration modes of Si–O bonds. The EPR results suggested that  $\text{Cu}^{2+}$  ions were partially coordinated with O atoms from the mineral layers and with nitrogen atoms from pyridine molecules if present in the interlayers. The larger  $\text{Cd}^{2+}$  ions did not penetrate as deeply into the ditrigonal holes and their effect on Si–O bonds was less pronounced. In conclusion, both the size and the charge affected the final position of exchangeable cations after fixation upon heating in Jelšový Potok montmorillonite.

Comparison of heat-induced migration of  $\text{Li}^+$  and other cations in montmorillonites is discussed in several papers. Calvet and Prost (1971), for example, studied fixation of different cations in Camp Berteau montmorillonite. An upward shift of the OH-bending bands on heating  $\text{Li}^+$ - and

$\text{Mg}^{2+}$ -montmorillonites was observed, but no such shift was found for  $\text{K}^+$ - and  $\text{Ca}^{2+}$ -montmorillonites. They concluded that  $\text{K}^+$  and  $\text{Ca}^{2+}$  did not migrate into the structure, while the penetration of small cations ( $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ) into the structure was a general phenomenon. Similar behavior of exchangeable cations upon heating was reported by Karakassides *et al.* (1997) for alkali-saturated Greek montmorillonite from Milos island ( $M_{0.92}[\text{Si}_{7.75}\text{Al}_{0.25}][\text{Al}_{3.21}\text{Fe}_{0.05}\text{Mg}_{0.69}\text{Ti}_{0.05}]\text{O}_{20}(\text{OH})_4$ ) and by Karakassides *et al.* (1999a) for  $\text{Li}^+$ - and  $\text{Cs}^+$ -SWy-1 montmorillonite (Table 1). Analysis of the IR reflectance spectra showed that only  $\text{Li}^+$  migrates close to or into vacant octahedral sites.  $\text{Na}^+$  and  $\text{K}^+$  enter the ditrigonal holes in the tetrahedral sheets, while  $\text{Cs}^+$  and  $\text{Rb}^+$  were unable to enter fully into these holes. Pálková *et al.* (2003) investigated the structural changes of the SAz-1 montmorillonite saturated with  $\text{Li}^+$  or  $\text{Ni}^{2+}$  upon heating at different temperatures. The IR spectra of heated  $\text{Li}^+$ -SAz showed new OH-stretching and overtone bands near  $3670\text{ cm}^{-1}$  and  $7170\text{ cm}^{-1}$ , respectively, indicating the creation of local trioctahedral domains containing Li(I) in the previously vacant octahedra. No evidence of OH groups in trioctahedral coordination was found in the spectra of heated  $\text{Ni}^{2+}$ -SAz. Although  $\text{Li}^+$  and  $\text{Ni}^{2+}$  have similar ionic radii of 0.68 and 0.69 Å, respectively, the lower charge of  $\text{Li}^+$  facilitates its penetration into the previously vacant octahedra, while Ni(II) is trapped in the ditrigonal holes of the tetrahedral sheet.

Purnell *et al.* (1991) found that controlled heating of  $\text{K}^+$ -,  $\text{Na}^+$ -,  $\text{Mg}^{2+}$ -,  $\text{Ni}^{2+}$ - and  $\text{Co}^{2+}$ -exchanged Wyoming bentonite in the presence and absence of ammonia leads to LC reductions. Migration of the exchangeable cations into the octahedral sheets did not occur, although  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  are small enough to penetrate into the octahedra. The production of non-exchangeable Mg(II), Ni(II) or Co(II) resulted from high-temperature hydrolysis leading to hydroxide or oxide formation. By contrast, Purnell and Lu (1993) found that heating ion-exchanged Texas montmorillonite led to LC reduction and that  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  migrate from the interlamellar space into the octahedral sheets. These cations either isomorphously exchanged divalent octahedral atoms (Mg(II), Fe(II)) or were trapped in the octahedral vacancies. However, all their conclusions are based on chemical analyses, which can provide results only on the amount of exchangeable and unexchangeable metals and not on their location within the structure. The authors also reported a reduction in the intensity of the OH-stretching band for  $\text{Ni}^{2+}$ -exchanged smectite and no intensity decrease for  $\text{Co}^{2+}$ - and  $\text{Zn}^{2+}$ -exchanged samples, but no dichroic band, confirming the trioctahedral environment of the OH group, was mentioned. It follows that no direct proof of the location of the fixed cations in the tetrahedral or octahedral sheets was provided.

Emmerich *et al.* (1999, 2001), investigating homoionic forms of a Linden montmorillonite (Table 1) heated at 220°C for 20 h, found that total CECs of the

$\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  forms were very similar to the values obtained for unheated samples, while CECs for the  $\text{Li}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  forms were 28, 60 and 91%, respectively. This decrease shows partial fixation of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  cations, and substantial fixation of  $\text{Li}^+$  ions. Dehydroxylation of the samples at temperatures between 510 and 630°C and rehydroxylation at steam temperatures of 300°C caused different structural effects depending on the size and the chemical character of the interlayer cation. The  $\text{Na}^+$ -,  $\text{Ca}^{2+}$ -,  $\text{Sr}^{2+}$ -saturated samples regained their full expandability. Rehydroxylation of the  $\text{Cu}^{2+}$ - and  $\text{Zn}^{2+}$ -montmorillonites did not cause re-expansion, whereas the  $\text{Li}^+$ -samples recovered a nearly complete swellability.

Reduced-charge smectites are produced mostly by the heating of montmorillonites saturated with small exchangeable cations. Jaynes and Bigham (1987) found that heating  $\text{Mg}^{2+}$ -saturated hectorite could also induce charge reduction. Loss of structural Li(I) was attributed to the migration of  $\text{Mg}^{2+}$  into the octahedral sites formerly occupied by Li(I) and acidification was related to the deprotonation of structural OH groups. Jaynes *et al.* (1992) extended the investigation of reduced-charge hectorite prepared by multiple heat treatments (250°C) of  $\text{Mg}^{2+}$ -saturated SHCa-1 hectorite. The FTIR spectra, CEC, layer charge, chemical and TG data all supported the view that Mg(II) substitution for octahedral Li(I) occurred and resulted in a more "talc-like" structure. Fluorescence measurement of adsorbed quinoline indicated that the hectorite surface was acidified during charge reduction; hydroxyl deprotonation was a possible source for the acidity. The authors concluded that charge reduction in smectites was a general phenomenon and could be induced by heat treatment with the proper exchangeable cation.

Analysis of the data presented above shows that fixation of small exchangeable cations in heat-treated smectites depends on the distribution of the layer charge between tetrahedral and octahedral sheets and on the size and charge of the exchangeable cations. Various materials and experimental techniques were utilized to confirm the final location of the trapped cations; however, a definitive solution is not available yet. Differences in declared positions of the fixed cations, mostly Li(I), are often connected with 'over-interpretation' of the data. For example, the presence of mono- or divalent non-exchangeable cations in heated smectites is often considered as evidence that the cations migrated into the previously vacant octahedral sites, and the release of  $\text{Li}^+$  and re-expansion of the layers of heated  $\text{Li}^+$ -montmorillonites after hydrothermal treatments is often interpreted as evidence that the  $\text{Li}^+$  was previously fixed in the ditrigonal cavities of the tetrahedral sheet. Another important aspect, essential when interpreting experimental data, is the structure of heated smectites. Frequently, XRD or spectroscopic data for heated  $\text{Li}^+$ -montmorillonites, in which Li(I) is assumed to be fixed

in the octahedral sites, are compared with the data obtained for trioctahedral smectites, *e.g.* hectorite. However, the structure of these minerals, though containing local trioctahedral domains, does not have long-range trioctahedral character.

Another significant problem in the literature is incomplete interpretation of the data obtained by the selected method. For example, exhaustive interpretation of  $^7\text{Li}$  MAS NMR data requires discussion of the effects of various central atoms and vacancies in the adjacent octahedra and tetrahedra on the spectral parameters obtained. Some of the changes observed may be connected with decreased LC and cannot be ascribed to  $\text{Li}^+$  fixation solely in the ditrigonal cavities or in the previously vacant octahedra. Infrared spectroscopy is frequently used to answer questions about cation fixation in smectites as it probes local atomic environments and has the potential to provide information on short-range cation ordering. A frequency shift and intensity decrease of the OH-bending bands in the spectra of heated montmorillonite are often regarded as proof of the migration of small interlayer cations into the vacant octahedral sites. In contrast, other authors interpret such changes as evidence of cation fixation in the ditrigonal holes of the tetrahedral sheets. Detailed analysis of the entire mid-IR spectral region (4000–400  $\text{cm}^{-1}$ ) is needed for correct interpretation of the observed changes. Another aspect is related to intrinsic properties of exchangeable cations. Migration of small cations into vacant octahedral sites can be achieved only when the cations are fully dehydrated. Whereas  $\text{Li}^+$  and other alkali metal cations can be reversibly dehydrated by heating, the dehydration of di- or trivalent cations, especially that of transitional metals is more difficult, often leading to the hydrolysis and the formation of hydroxocomplexes, hydroxides or oxides, the chemical species that are not mobile, at least relative to  $\text{Li}^+$  cations.

Figure 3 shows OH-stretching (A), Si–O-stretching (B) and OH-bending (C) regions in the IR spectra of SAz-1 montmorillonite saturated with  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Li}^+$  cations and heated at 300°C for 24 h. The spectra of unheated samples are very similar and thus only the spectrum for untreated  $\text{Ca}^{2+}$ -montmorillonite is presented in Figure 3 (spectrum a). Only negligible changes were observed in the OH- and Si–O-stretching regions of  $\text{Ca}^{2+}$ -SAz-1 after heating (Figure 3A and 3B, spectrum b); by contrast, a slight shift and decrease in the OH-bending bands areas is visible (Figure 3C). The spectra indicate that dehydrated  $\text{Ca}^{2+}$  cations, though unable to penetrate deeply into the ditrigonal holes of the tetrahedral sheets to become fixed, can move close enough to influence the OH-bending modes. In comparison with the  $\text{Ca}^+$  form, more pronounced changes appear in the spectra of heated  $\text{Ni}^{2+}$ - and  $\text{Li}^+$ -SAz-1 (Figure 3, spectra c and d, respectively).  $\text{Ni}^{2+}$  and  $\text{Li}^+$  cations are of similar small size, permitting their

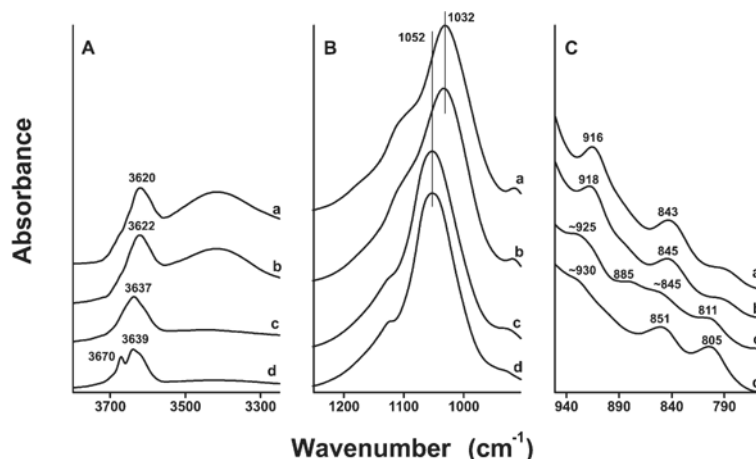


Figure 3. OH-stretching (A), Si–O-stretching (B) and OH-bending (C) regions in the IR spectra of SAZ-1 montmorillonite saturated with  $\text{Ca}^{2+}$  unheated (a) and after heating for 24 h at  $300^\circ\text{C}$  (b); saturated with  $\text{Ni}^{2+}$  and heated for 24 h at  $300^\circ\text{C}$  (c) and saturated with  $\text{Li}^+$  and heated for 24 h at  $300^\circ\text{C}$  (d). The areas of the OH-bending bands in spectrum (a):  $\text{AlAlOH}$  0.9 a.u.;  $\text{AlMgOH}$  0.8 a.u.; and in spectrum (b):  $\text{AlAlOH}$  0.7 a.u.;  $\text{AlMgOH}$  0.6 a.u.

penetration into the layers. Although the spectra of both samples show similar upwards shifts of the Si–O band, different changes in the OH-stretching and bending regions indicate different positions for these cations in the layers. The most important region for the identification of Li(I) in previously vacant octahedra is the OH-stretching region. As discussed above, a new dichroic band near  $3670\text{ cm}^{-1}$  implies creation of local tri-octahedral domains containing Li(I) in the octahedral positions. No evidence of OH groups in such coordination can be seen in the spectrum of heated  $\text{Ni}^{2+}$ -SAZ-1 (Figure 3A, spectrum c), suggesting that Ni(II) is trapped only in the ditrigonal holes of the tetrahedral sheets. It follows that detailed analysis of the OH-stretching region of reduced charge smectites is needed for any conclusion on the positions of fixed cations.

#### PARTIAL STABILIZATION OF Fe(II) IN REDUCED FERRUGINOUS SMECTITE BY $\text{Li}^+$ FIXATION

Normally Fe(II) in smectites oxidizes readily to Fe(III) on exposure to air. However, Komadel *et al.* (1999) were able to achieve partial stabilization of Fe(II) in chemically reduced ferruginous smectite by  $\text{Li}^+$  fixation upon heating. More than 80% of total Fe in the ferruginous smectite (SWa-1) was reduced to Fe(II) using the citrate-bicarbonate-dithionite method while purging the clay dispersion with  $\text{N}_2$ . The reduced smectite was  $\text{Li}^+$  saturated, washed free of excess ions, freeze dried, and heated in  $\text{N}_2$  atmosphere at  $260^\circ\text{C}$  for 24 h to evoke  $\text{Li}^+$  fixation. This treatment caused partial stabilization of Fe(II) in the mineral structure. Chemical analysis, Mössbauer spectroscopy and IR spectroscopy proved that >20% of total Fe was Fe(II) after re-oxidation with oxygen in water, the treatment which causes complete reoxidation of Fe(II) in reduced Na-

smectites. Decomposition of the OH-stretching band indicated migration of  $\text{Li}^+$  into the vacant octahedra. Some of the OH groups in the reoxidized smectite were found in local tri-octahedral domains, associated with the  $\text{AlFe(II)Li}$  or  $\text{Fe(III)Fe(II)Li}$  configurations of central atoms in the octahedral sheet.

#### PROPERTIES OF REDUCED-CHARGE MONTMORILLONITES

Layer charge significantly influences the physical, chemical, surface and colloidal properties of smectites, such as CEC, solvation and swelling, acid dissolution, adsorption and others. For example, optimal swelling properties are observed for smectites which are clay minerals of medium layer-charge densities. Pyrophyllite and talc, the minerals with no charge, do not expand due to the absence of osmotically active exchangeable cations in the interlayer spaces. Strong van der Waals forces between the layers of these minerals prevent their expansion. On the other hand, strong electrostatic forces between clay surface and interlayer cations hinder expansion of vermiculites and micas.

##### *CEC, solvation and swelling*

The reduction of LC is accompanied by collapse of the interlayer spaces and is reflected in the loss of the expandable character of smectites, which has a substantial effect on their swelling and solvation behavior. The most frequently studied liquid phase is water; however, results with other solvents, such as ethanol, ethylene glycol and glycerol, have also been reported. Usually the solvation properties are correlated with CEC, which is closely associated with the LC of the clay minerals.

Brindley and Ertem (1971) prepared RCMs with variable numbers of exchangeable cations from a Wyoming montmorillonite (Volclay, Table 1) by form-

ing mixed-cation clays with  $\text{Li}^+$  as one of the cations and  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$  as the other. Heating for 24 h at 220°C rendered most of the  $\text{Li}^+$  non-exchangeable by  $\text{NH}_4^+$  ions, but not fully in accordance with the migration of  $\text{Li}^+$  into vacant octahedral sites up to the limit of the octahedral charge deficiency. Swelling with water, acetone and 3-pentanone increased with increasing number and field strength of the interlayer cations (*i.e.* with increasing LC), which was consistent with the proposed cation-dipole interaction. In contrast, swelling was practically independent of charge with ethanol, EG and morpholine. The authors suggested that these liquids enter the interlayer spaces by another mechanism in addition to cation-dipole interactions, possibly *via* hydrogen-bonding to the silicate oxygen surfaces.

Calvet and Prost (1971) showed that the solvation properties of RCM depend on the number of exchangeable cations and on the nature of the solvent. Heated  $\text{Na}^+/\text{Li}^+$ -Camp Berteau montmorillonite containing only  $\text{Na}^+$  cations in the exchangeable positions did not swell with water when the amount of exchangeable cations was <50% of original CEC. This limit was 30% with glycerol and 20% with EG.

Clementz and Mortland (1974) investigated surface properties of RCMs prepared by heating mixtures of  $\text{Na}^+$  and  $\text{Li}^+$  forms of Upton Wyoming montmorillonite (Table 1) for 24 h at 220°C. To prevent collapse of the layers, the exchangeable  $\text{Na}^+$  and  $\text{Li}^+$  ions in low-charge samples were exchanged with tetraalkylammonium cations. Nitrogen adsorption data indicated large surface areas for the low-charge samples saturated with tetramethylammonium ( $\text{TMA}^+$ ) cations. Water adsorption isotherms reflected the hydration properties of the exchangeable cations as well as the surface area available for adsorption. Clementz *et al.* (1974) studied properties of the same series of RCMs prepared from  $\text{Li}^+/\text{Na}^+$ -Upton Wyoming montmorillonite. The RCMs were mixed with  $\text{CuCl}_2$  in an ethanol solution to achieve  $\text{Cu}^{2+}$  saturation. Regardless of the extent of charge reduction, complete exchange of cations on both internal and external sites was accomplished. For high-charge reduced  $\text{Li}^+/\text{Na}^+$ -samples a combination of ethanol  $\text{CuCl}_2$  and aqueous tetrabutylammonium chloride solutions was needed to saturate only internal sites with  $\text{Cu}^{2+}$  ions. To achieve  $\text{Cu}^{2+}$  saturation of external sites,  $\text{Li}^+/\text{Na}^+$ -RCMs were washed with aqueous  $\text{CuCl}_2$  solution. Three types of interlayers were detected by XRD analysis of the  $\text{Cu}^{2+}$ -saturated samples: (1) interlayers with hydrated  $\text{Cu}^{2+}$ , which expanded on hydration; (2) interlayers containing hydrated  $\text{Cu}^{2+}$  that only expanded with a monolayer of water molecules; and (3) completely collapsed interlayers with  $\text{Cu}^{2+}$  in the ditrigonal cavities of the tetrahedral sheets. The different swelling ability of the interlayers indicated that the LC distribution of the RCM was heterogenous.

Sposito *et al.* (1983) investigated the effect of reduced CEC on the basal plane spacing of SWy-1

montmorillonite (Table 1). The  $\text{Na}^+$ -montmorillonite hydrated at 50% RH had  $d = 12.1 \text{ \AA}$ , while the  $\text{Na}^+/\text{Li}^+$ -RCM with 58% of the original CEC showed a more asymmetric diffraction peak with  $d = 11.3 \text{ \AA}$ , indicating interstratification of collapsed ( $d = 10 \text{ \AA}$ ) and expanded ( $d = 12 \text{ \AA}$ ) layers. However, both the original and RCM gave symmetric diffraction peaks with basal spacings of  $17.2 \text{ \AA}$  after swelling in EG.

Bujdák *et al.* (1991) showed that the amount of exchangeable  $\text{Li}^+$  in heated Jelšový Potok montmorillonite (Table 1) decreased with both the temperature and the time of the treatment. The most extensive reduction in CEC (from 1.042 to 0.158  $\text{mmol g}^{-1}$ ), in swelling ability and in total hydration was achieved for the sample heated for 24 h at 210°C.

Chorom and Rengasamy (1996) investigated the effect of heating for 6 h at 100–400°C on the swelling, dispersion,  $\xi$  potential and particle aggregation of  $\text{Li}^+$ -,  $\text{Na}^+$ -,  $\text{K}^+$ -,  $\text{Mg}^{2+}$ -,  $\text{Ca}^{2+}$ - and  $\text{Al}^{3+}$ -saturated <2  $\mu\text{m}$  Wyoming bentonite. Swelling and dispersion of the bentonite was explained by the nature of the bonding between clay particles and the exchangeable cations. Before thermal treatment,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  forms dispersed spontaneously in water while the  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  forms did not. This was explained as a consequence of the more ionic nature of the bonding between  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{K}^+$  and the clay mineral surface, leading to more extensive hydration in comparison with more covalent character of the bonds for the  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  or  $\text{Al}^{3+}$  cations. Upon thermal treatment at 400°C, the bonding characteristics changed according to the size of the cations. The authors inferred that smaller  $\text{Li}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ , with ionic radii <0.7  $\text{ \AA}$ , migrated into the vacant octahedral sites, forming covalent bonds and resulting in severe charge reductions. The cations became non-exchangeable and the minerals neither swelled nor dispersed spontaneously. This process occurred even at 200°C for the  $\text{Li}^+$ -clay. Larger cations,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  did not migrate into the layers; and a large proportion of them remained exchangeable. The samples saturated with them swelled but did not disperse spontaneously.

Laird (1999) studied the influence of LC on the hydration of the different  $\text{Mg}^{2+}$ -saturated expandable 2:1 phyllosilicates. He investigated different reference smectites and vermiculites, including RCMs prepared from 10:0–6:4 mixtures of  $\text{Na}^+$ - and  $\text{Li}^+$ -SAz-1 montmorillonite *via* heating at 220°C for 24 h. Reductions of layer charge from  $-0.92$  to  $-0.68 e/\text{O}_{20}(\text{OH})_4$  and CEC of 1.25–0.91  $\text{mmol g}^{-1}$  were obtained. The  $\text{Mg}^{2+}$ -exchanged clays were equilibrated at 54% RH. All RCMs showed similar surface areas and basal plane spacings of 14.85  $\text{ \AA}$ , proving that collapsed interlayer spaces were not produced under these conditions.

Hrobáriková *et al.* (2001) and Hrobáriková and Komadel (2002) reported hydration properties of four RCMs of various chemical compositions (Table 1).  $\text{Li}^+$ -



montmorillonites prepared from  $\text{Ca}^{2+}$ -saturated samples by ion exchange were heated for 24 h at 110–300°C in order to reduce the LC in a systematic manner. Heating the samples at temperatures up to 120°C caused some  $\text{Li}^+$  fixation and decrease in CEC but only minor changes in the ethylene glycol monoethylether (EGME) surface area and water sorption. The biggest changes in the properties were observed among samples prepared at 130–200°C, while higher temperatures had rather small effects. The most extensive reduction in CEC, an 81% decrease after heating at 300°C, was obtained for the Otay montmorillonite, the mineral with the greatest octahedral and smallest tetrahedral charge and the most successful  $\text{Li}^+$ -for- $\text{Ca}^{2+}$  exchange during  $\text{Li}^+$ -sample preparation. Greater tetrahedral charge and/or a lower level of  $\text{Li}^+$  for  $\text{Ca}^{2+}$  exchange affected the CECs, the EGME surface areas and the water uptake capabilities of the prepared RCMs. The development of uncharged layers with non-swelling interlayer spaces occurred in all materials heated above 150°C. Hydration properties of the series were investigated gravimetrically at different RHs. Higher water contents were observed for desorption than for sorption and this hysteresis was present over the whole range of RHs for all samples. The samples prepared from Kriva Palanka montmorillonite by heating at 110, 130, 160 and 300°C (CECs of 89, 73, 49 and 29% of the starting mineral, respectively) were also investigated by an *in situ* XRD method using randomly oriented samples and an X-ray diffractometer equipped with a temperature humidity chamber (Komadel *et al.*, 2002). The  $d_{001}$  values of the parent montmorillonite and the samples prepared at 110 and 130°C increased with humidity, while those of materials heated at 160 and 300°C were independent of RH and remained at  $\sim 10.4$  Å.

Lim and Jackson (1986) compared solvation properties of expandable  $\text{Li}^+$ -saturated phyllosilicates in glycerol. Films prepared from different smectites (montmorillonites, nontronite, beidellites and saponites), vermiculite, mica and several soils were heated overnight at 250°C to evoke  $\text{Li}^+$  fixation. Afterwards the slides were placed over glycerol and heated at 90°C for 16 h. To differentiate montmorillonite from other smectites, solvation with glycerol was utilized because all of the  $\text{Li}^+$ -smectites studied expanded to some extent in EG after heating. The heated  $\text{Li}^+$ -montmorillonite remained collapsed ( $d = 9.4$  Å) after glycerol solvation whereas nontronite and saponite re-expanded to 18.0 Å because of their tetrahedral charge. A 70–80% decrease in CEC was observed for  $\text{Li}^+$ -montmorillonites prepared at 250°C.

The *in situ* XRD studies of a synthetic (Tamura *et al.*, 2000) and several natural montmorillonites (Sato *et al.*, 1992) exchanged with various monovalent and divalent cations showed distinct stepwise hydration with increasing RH. Differences in basal spacings were observed for samples having similar LC, showing that expansion is

due to the combined effects of the charge location and amount.

Meier and Nüesch (1999) investigated low-charge montmorillonites made from Volclay, a Wyoming montmorillonite. Mixtures of  $\text{Li}^+$ - and  $\text{Na}^+$ -saturated montmorillonites were prepared in various proportions and heated for 24 h at 220°C in order to incorporate  $\text{Li}^+$  into the layers. The exchangeable cations were exchanged with  $\text{TMA}^+$  cations to produce a fixed expanded interlayer distance not sensitive to humidity. Their XRD patterns showed a regular sequence of expanded and collapsed interlayer spaces. The calculations of the CEC for the expanded interlayer part gave a constant value of  $65 \pm 2$  mmol/100 g for fully expanded Volclay montmorillonite. This value was denoted as the lower CEC limit of montmorillonite. A model considering montmorillonite to be a stacked two-dimensional polyelectrolyte was suggested. The model proposed that interlayer spaces of the stack collapsed spontaneously by cation shifting into the neighboring interlayers, if the charge density of a montmorillonite had a value below the lower CEC value. Below the critical LC, the Van der Waals forces dominate over electrostatic repulsive forces and the interlayer spaces do not swell.

#### *Stability of RCMs in acids*

The structure of smectites may be considerably altered in the course of different chemical treatments and the layer charge is frequently an important parameter affecting the extent of their modification. Acid dissolution of smectites involves the exchange reaction between the interlayer cations and surrounding acid solution, followed by dissolution of octahedral sheets as well as tetrahedral Al. Komadel *et al.* (1996) investigated the effect of the swelling/non-swelling layer ratio on the dissolution of RCMs prepared from  $\text{Li}^+$ -saturated Jelšový Potok montmorillonite by heating at 105–210°C for 24 h. The RCMs were treated in 6 M HCl at 95°C for periods up to 30 h. Both chemical analysis and IR spectroscopy provided evidence that the extent of dissolution decreased with increasing amounts of Li(I) in the montmorillonite structure. Differences in the acid dissolution process reflected structural changes that occurred within the reduced-charge samples due presumably to different positions of Li(I). The EGME surface areas, XRD and high-resolution transmission electron microscopy (HRTEM) analyses of the samples revealed increasing amounts of non-swelling interlayer spaces in the samples prepared at higher temperatures, causing a substantially slower decomposition in HCl of the samples prepared at 160 and 210°C. The calculated XRD patterns of the samples prepared at 135 and 160°C confirmed the presence of 20% and 45% pyrophyllite-like layers, respectively, in these samples. Mixed-layer pyrophyllite-like-smectite and pyrophyllite-like crystals, containing only non-swelling interlayers, were found in a sample prepared at 210°C. The results confirmed that

the amount of swelling interlayer spaces in RCMs substantially affected their dissolution rate in HCl and that the process of dissolution did not occur from the particle edges only. This has been confirmed very recently for other smectites by Pálková *et al.* (2003) who investigated acid dissolution of  $\text{Li}^+$ - and  $\text{Ni}^{2+}$ -saturated and heated fine fractions of Cheto (SAz-1, Arizona) and Cressfield Yellow (Australia) bentonites (Figure 4). The Si–OH overtone at  $7312\text{ cm}^{-1}$  permitted the extent of acid attack of smectites to be followed by IR spectroscopy, even when no differences were observed in the  $1300\text{--}400\text{ cm}^{-1}$  region which is traditionally used to monitor this process (compare spectra c and d in Figure 4) The collapsed interlayer spaces in the samples heated at  $300^\circ\text{C}$  hindered acid attack of the layers from this direction. No significant changes were observed in the  $1300\text{--}400\text{ cm}^{-1}$  region; however, the appearance of small, though clearly resolved Si–OH overtone in the spectra of acid-treated samples indicated that the acid attack on the layers did occur. Considering collapsed interlayer spaces indicated *via* XRD, the acid attack proceeded mainly from the particle edges and/or on exposed external basal surfaces.

#### Other properties

Examples of less frequently investigated properties of RCMs are summarized in this section. Dutta *et al.* (1999) described a combined XPS and Auger electron spectroscopic investigation of  $\text{Cs}^+$  sorption in variable-charge montmorillonites, prepared *via*  $\text{Li}^+$  fixation upon heating at  $220^\circ\text{C}$ . The analysis of Cs  $3d$  photoelectron spectra showed that the binding energy of  $\text{Cs}^+$  was enhanced with the reduction of the electron population from higher- to lower-charge montmorillonites. The binding

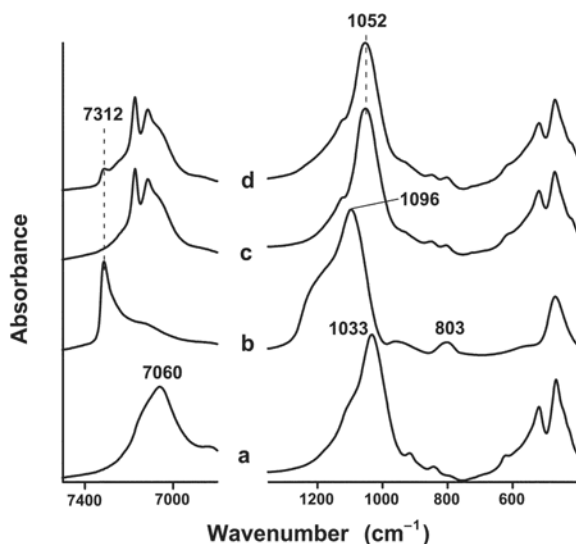


Figure 4. IR spectra of untreated samples  $\text{Li}^+$ -SAz-1 (a) and after treatment in 6 M HCl at  $80^\circ\text{C}$  for 8 h (b); untreated  $\text{Li}^+$ -SAz-1 heated for 24 h at  $300^\circ\text{C}$  (c) and after treatment in 6 M HCl at  $80^\circ\text{C}$  for 8 h (d). Data from Pálková *et al.* (2003).

energy value was nearer to CsOH than to CsCl suggesting that the bonding state of  $\text{Cs}^+$  in montmorillonite is not as ionic as in CsCl. The Cs-Auger kinetic energy was found to decrease from higher-charge RCM to lower-charge RCM, indicating a change in the bonding states of  $\text{Cs}^+$ , as the LC is reduced.

Bidadi *et al.* (1988) investigated the effect of ambient water-vapor pressure on dielectric properties of  $\sim 0.3\text{ mm}$  thick smectite films prepared from  $\text{Na}^+$ -,  $\text{Li}^+$ - and a reduced-charge montmorillonite, obtained upon heating  $\text{Li}^+$ -montmorillonite at  $250^\circ\text{C}$ . The measurements were made perpendicular to the clay films. The dielectric properties depended considerably on the amount of adsorbed water, which in turn depended strongly on the type and concentration of interlayer cations. For the swelling  $\text{Na}^+$ - and  $\text{Li}^+$ -montmorillonites, the ambient water-vapor pressure substantially affected both the dielectric constant and conductivity. These quantities were greatly diminished for RCM due to smaller exchangeable  $\text{Li}^+$  content and decreased swelling ability. They were independent of water-vapor pressure for mica.

Villemure and Bard (1990) used the  $\text{Li}^+$ -saturated  $<2\text{ }\mu\text{m}$  fraction of STx-1 montmorillonite heated at  $250^\circ\text{C}$  for 18 h as a RCM in their electrochemical studies with clay-modified electrodes. They showed that the RCM adsorbed only  $\sim 9\%$  of the amount of  $[\text{Ru}(\text{bpy})_3]^{2+}$  cation as the original STx-1. The electronic spectrum of this system was characteristic for adsorption of this cation on external surfaces of a clay mineral, and was more reminiscent of a  $[\text{Ru}(\text{bpy})_3]^{2+}$  absorption spectrum on kaolinite rather than on montmorillonite.

Thomas *et al.* (1999) investigated the effect of the layer charge on the electrophoretic mobility of smectites. Thermally treated  $\text{Cu}^{2+}$ -montmorillonite was used to cover the low-charge domain of up to  $-0.7\text{ e/O}_{20}(\text{OH})_4$ , while synthetic saponites were used for the high-charge domain up to  $-2\text{ e/O}_{20}(\text{OH})_4$ . All samples were negatively charged in a pH range from 2 to 12. Neither layer charge nor ionic strength influenced the electrophoretic mobility of smectites at neutral to alkaline pH. Under acidic conditions, high-charge and low-charge smectites, which were non-expandable, aggregated in suspension and their electrophoretic mobility then corresponded to the amphoteric sites of the edges.

Using  $\text{N}_2$  adsorption/desorption at  $-196^\circ\text{C}$ , Bahrnowski *et al.* (2002) studied the microporosity of Al-pillared RCM prepared from  $\text{Li}^+$ -montmorillonite by various thermal treatments. A correlation was observed between the decreasing sorption capacity of samples and the proportion of collapsed pyrophyllite-like areas, inactive in pillaring. The dominant micropore radius remained below  $0.35\text{ nm}$  for all pillared samples, showing that the LC reduction by Hofmann-Klemen effect did not substantially changed the lateral interpillar distances.

Feng *et al.* (2000) prepared a  $\text{LiAl}_2(\text{OH})_6^+$  intercalated montmorillonite by using a hydrothermal chemical process. As a first step,  $\text{LiAl}$  hydroxide complex ions,  $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$ , were inserted into the interlayer space by an ion-exchange reaction. In the second step, the ion-exchanged montmorillonite was hydrothermally treated to polymerize the complex ions, forming a sandwich-like layered compound. The basal spacing of the montmorillonite increased from 1.6 to 2.0 nm after the ion exchange. Two types of reactions of the ion-exchanged montmorillonite were observed under hydrothermal conditions. In the temperature range 100–150°C, the basal spacing changed from 2.0 to 1.7 nm, corresponding to polymerization of  $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$  complex ions to  $\text{LiAl}_2(\text{OH})_6^+$  layers between the silicate layers. At temperatures >200°C,  $\text{Li}^+$  ions of  $\text{LiAl}_2(\text{OH})_6^+$  layers probably migrated into the octahedral sheets of silicate layers, accompanied by a decrease in the basal spacing from 1.7 to 1.4 nm. The  $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$  complex ion was also used for pillaring montmorillonite, and a pillared montmorillonite with a basal spacing of 1.5 nm was obtained by heating of the  $\text{Li}_x\text{Al}_n(\text{OH})_m^{z+}$  ion-exchanged montmorillonite in air at 500°C.

#### INTERACTION OF SMECTITES WITH ORGANIC COMPOUNDS

Layer charge and its distribution in smectites affect the density and distribution of adsorbed cations. If there is no excess salt at the clay/water interface, the distribution of monovalent exchangeable cations roughly copies the distribution of the sites of the negative charge arising from non-equivalent isomorphous substitutions, *i.e.* the charge distribution directly rules the distances between neighboring cations. The charge density controls the space available for individual intercalated cations. This is commonly insignificant for relatively small inorganic cations but it may become important for adsorption of larger organic cations. Much research has been devoted recently to understanding the adsorption of alkylammonium cations and cationic dyes on reduced-charge smectites.

##### *Adsorption of alkylammonium cations*

The size of the cation in combination with the charge density influences the arrangement of adsorbed cations. A typical example is the charge effect on the arrangement of alkylammonium cations in the interlayer spaces of swelling clay minerals, affecting their basal spacings, a phenomenon that is frequently used for the determination of the charge-density distribution in layers (alkylammonium method, Lagaly 1994). This method is based on the relationship between the LC density and arrangement of linear alkylammonium cations in the interlayer spaces of the clay host. Besides the LC, the arrangement of the cations depends on the alkyl-chain length, *i.e.* the size of the cations. The XRD patterns of

samples saturated with organic cations of varying chain length provide detailed information on the charge distribution in layers. Although this method has been used for the determination of the LC on smectites for decades, only rarely has it been applied in studies of RCMs; a few examples are discussed below.

Jaynes and Bigham (1987) investigated several montmorillonites and found that heating  $\text{Li}^+$ -saturated samples at 250°C formed non-swelling pyrophyllite-like materials which did not expand when treated with the alkylammonium salt solutions. Expandable phases with alkylammonium monolayers or bimolecular layers existed in these materials only if the samples were saturated with mixtures of  $\text{Li}^+$  and  $\text{Na}^+$  cations prior to heating, where the basal spacing reduction was proportional to the amount of  $\text{Li}^+$  cations. By contrast, the  $\text{Li}^+$  heat treatment resulted in only a slight decrease in layer charge for ferruginous smectite SWa-1 and no decrease for nontronite NG-1, both of which are tetrahedrally charged. Similarly, no charge reduction was observed for saponite SapCa-1, hectorite SHCa-1, or vermiculite VTx-1, all of which are trioctahedral. On the other hand, the alkylammonium method can detect charge reduction upon the fixation of  $\text{Mg}^{2+}$  ions in hectorite (Jaynes *et al.*, 1992).

Based on their analysis using the alkylammonium method, Jaynes and Bigham (1987) concluded that charge reduction was a uniform process correlating well with the CEC decrease. Opposite conclusions were reported by Maes *et al.* (1979) who found that charge reduction was an inhomogeneous process and inferred heterogeneous charge distribution in the RCMs obtained from the Camp Berteau montmorillonite. The charge density values determined by the alkylammonium method were greater than those obtained from the CEC values by ~20%. Laird *et al.* (1989) observed systematic divergence of the charge, calculated from alkylammonium method data for RCMs which were prepared from SAz-1 montmorillonite containing variable portions of  $\text{Na}^+$  and  $\text{Li}^+$  cations and heated at 220°C, and deduced from the structural formula. Maes *et al.* (1987) summarized factors which could have caused the deviation of the LC determined by the alkylammonium method:  $\text{Li}^+$  back-migration; deviations due to adsorption of alkylammonium cations near clay particle edges; and interference of a collapsed, pyrophyllite-like phase. They also assumed that a local (small size) charge heterogeneity, which cannot be detected by the alkylammonium method, might contribute to the above-mentioned discrepancies. The most highly charged regions probably determine the expansion of the interlayer space upon the saturation with alkylammonium cations, regardless of the average LC.

A procedure employing both the Greene-Kelly test (Greene-Kelly, 1953) and charge determination by the alkylammonium method before and after the  $\text{Li}^+$  thermal treatment was found suitable for the determination of the

magnitudes of tetrahedral and octahedral charges and to help in the identification of beidellites and montmorillonites (Malla and Douglas, 1987; Olis *et al.*, 1990).

The alkylammonium method is based on the adsorption of organic cations in amounts equivalent to the number of negative charge sites. Washing of alkylammonium/clay complexes with ethanol is required in order to remove excess alkylammonium cations. Adsorption of long-chain alkylammonium cations from aqueous solutions occurs frequently in excess of CEC due to van der Waals forces between the alkyl chains of the cations and alkylamine molecules, which may also be in the solution. Excess cation adsorption was confirmed for dodecyl- and hexadecylammonium adsorption from aqueous solutions on RCMs made from Jelšovský Potok montmorillonite (Bujdák *et al.*, 1992b; 1993). A majority of the species adsorbed in excess of CEC are molecules, products of alkylammonium cation hydrolysis. Shorter-chain octylammonium cations were adsorbed below the CEC of fully expandable RCMs but exceeded the CECs of samples with collapsed interlayer spaces. Maximal adsorption increased nonlinearly with LC. Such trends in adsorption probably relate to structural changes and re-orientation of the alkyl chains with increasing LC as was confirmed by basal spacing data (Bujdák *et al.*, 1992b). Very similar trends were found for adsorption of toluene on the same series of RCMs and other smectites saturated by trimethylhexadecylammonium cations (Slade and Gates, 2004).

Specific sorbent materials were developed using RCMs containing tetraalkylammonium cations with small alkyl groups (methyl, ethyl, phenyl, *etc.*). Although these cations are bigger than common inorganic cations, they need not cover the entire basal surface. Cavities in the interlayer spaces between organic cations are filled with solvent molecules but can provide adsorption sites or zones, the size and polarity of which are controlled by the LC distribution and the type and size of organic cation (Clementz and Mortland, 1974). The hydrophobic character of the tetraalkylammonium cations supports application of these materials for selective adsorption of non-polar organic pollutants (Stevens and Anderson, 1996a). The basal spacing of such adsorbents is determined by the size of the organic cations and is mostly constant, regardless of the number of cations in the interlayer spaces. Charge reduction decreases the space occupied by the organic cations in favor of empty space between them, and thereby increases the interlayer volume accessible for sorbate molecules. The formation of a collapsed phase with non-swelling interlayer spaces under conditions of extensive charge reduction is the only limitation (Clementz and Mortland, 1974).

Adsorbents were prepared from RCMs using Upton Wyoming montmorillonite and saturated with TMA<sup>+</sup> and tetrapropylammonium cations. Pre-treatments leading to

charge reduction led to a significant increase in internal surface area accessible to nitrogen molecules for the TMA-treated smectites. Under optimal conditions, the surface area available for nitrogen increased by a factor of >2. Saturation with tetrapropylammonium cations was found to be less suitable because of the large size of these cations. Charge reduction was less efficient at creating “free” volume for the adsorption of nitrogen or water molecules (Clementz and Mortland, 1974). Similarly, less effect on the surface area was found for trimethylphenylammonium-exchanged RCMs with respect to TMA<sup>+</sup> materials (Stevens and Anderson, 1996a). The samples with reduced charge also adsorbed more water (Stevens and Anderson, 1996b). Water interacts with organic cations rather than with siloxane surface. The interaction is stronger in materials containing TMA<sup>+</sup> cations due to their lower hydrophobicity. Stevens *et al.* (1996) studied the adsorption of benzene and ethylbenzene on such materials. Charge reduction increased the uptake of benzene and ethylbenzene and these organics inhibited water sorption substantially, whereas water displaced benzene and ethylbenzene more easily from TMA<sup>+</sup>- and trimethylphenyl<sup>+</sup> (TMPA)-treated samples than from siloxane surfaces. The proportion of TMA<sup>+</sup> and TMPA<sup>+</sup> ions that interacted with benzene and ethylbenzene was greater for reduced-charge than normal-charge montmorillonite.

In summary, LC controls the distribution and arrangement of intercalated organic cations. Besides the LC, reaction conditions of alkylammonium adsorption should also be considered. Combination of the alkylammonium method with charge reduction can be used to determine the magnitudes of charge due to substitutions in octahedral and tetrahedral sheets. Charge reduction of smectite followed by saturation with small tetraalkylammonium cations leads to the preparation of specific sorbent materials with interesting properties, potentially applicable as sorbents of organic pollutants. Using the series of RCMs, one can find and characterize optimal charge parameters of any natural smectite.

#### *Adsorption of cationic dyes*

Distribution of adsorbed organic dye cations reflects sensitively the surface charge and can be relatively easily monitored by ultraviolet-visible (UV-Vis) spectroscopy, a technique available in many laboratories. Organic dyes adsorbed on the clay surfaces form monomers or molecular assemblies comprising two or more individual cations. These assemblies are characterized by the number of cations and by the type of intermolecular association (Bujdák and Iyi, 2002). H-dimers or larger H-aggregates are structurally based on a sandwich-type molecular association. J-dimers or aggregates with a head-to-tail association are formed less frequently. Due to electrostatic interactions between transition moments of individual cations in the aggregates, the spectral properties of adsorbed dyes are



significantly different from isolated (monomeric) dye cations (Kobayashi, 1996). For example, the formation of H-aggregates of the cationic dye, methylene blue (MB), on clay surfaces is accompanied by a shift of the main absorption band from 665 to 570 nm (Bujdák and Komadel, 1997). On the other hand, J-aggregates of this dye absorb at significantly higher wavelengths, near 760 nm (Bujdák *et al.*, 2002a). Testing the interaction of cationic dyes with RCMs played a significant role in understanding dye/clay interactions. The RCMs differ in terms of LC but are very similar in terms of most of other properties. Studies on interaction of dyes with RCMs have shown that the LC is the key parameter controlling the formation of the dye cation aggregates on the surface and hence optical properties of the reaction products.

Bujdák and Komadel (1997) investigated the visible spectra of MB in dispersions of RCMs prepared from Jelšový Potok montmorillonite (Table 1, Bujdák *et al.*, 1991). High LC density of the parent montmorillonite resulted in less distance between the neighboring adsorbed MB cations and promoted dye cation aggregation. Low LC density in samples with reduced charge caused greater distances between MB cations and inhibited MB aggregation. The aggregation was suppressed proportionally to charge reduction. With the charge reduction, the amount of H-aggregates decreased in favor of H-dimers and monomers. As each form of MB absorbs visible light at different wavelength, different LC densities induced different colors of the resulting dye/clay dispersion. An example of the spectra of MB/RCM dispersions is shown in Figure 5.

Bujdák *et al.* (2001) used a similar approach for characterization of five sets of reduced-charge smectites, prepared from three montmorillonites (SAz-1, SCA-2, and Horní Dunajovice), an Fe-rich beidellite (Stebno), and SWa-1 ferruginous smectite (Table 1). Each set included the parent sample and specimens with reduced charge, prepared by heating  $\text{Li}^+$ -exchanged forms at 110–200°C. Both the CEC values and spectra of MB-clay dispersions indicated extensive reduction of the LC density in RCMs upon  $\text{Li}^+$  thermal treatment. The extent of charge reduction depended on the temperature of thermal treatment, as well as on the octahedral charge of the montmorillonite. Reduction of LC proceeded to a much smaller extent for smectites with mainly tetrahedral charge and high Fe content (Fe-rich beidellite and ferruginous smectite). These changes were detectable with the MB spectra for RCMs prepared at only 110°C. Following heating at higher temperatures (120–160°C), slightly higher  $\text{Li}^+$  fixation was in contradiction to the absence of the further charge reduction indicated by MB spectra. The contradiction was explained by partial regeneration of LC as a consequence of  $\text{H}^+$  release after the reaction of Li(I) with structural OH groups.

The interaction of RCMs with dyes other than MB has also been investigated, including azine dyes, which

are structurally similar to MB (Bujdák and Iyi, 2002; Czímerová *et al.*, 2003), cyanine dyes (Bujdák *et al.*, 2002b; 2002c; 2003a), triphenylmethane dyes (Bujdák and Iyi, 2002) and rhodamine dyes (Bujdák *et al.*, 2003b). For these assays, sets of RCMs were prepared using montmorillonites from Jelšový Potok, Kriva Palanka, and Nanocor Inc. and SAz-1. General trends of the spectral changes for dyes with LC are independent of the structure of dye cations. It is possible that almost any cationic dye with planar groups, forming molecular aggregates with different optical properties, could be suitable for probing the LC densities of smectites. However, there are some specific aspects and dye properties which have to be considered, such as molecular size and their tendency to form aggregates

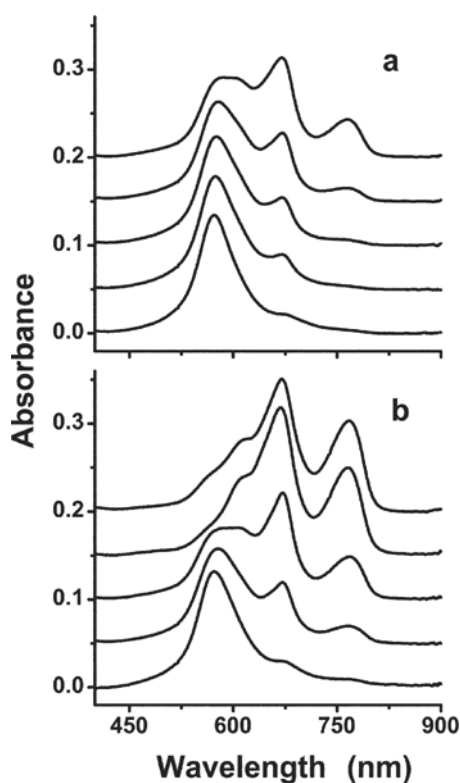


Figure 5. Vis spectra of methylene blue in dye/RCM dispersions measured 1 min after mixing the dye solution with the clay dispersion (a) and after achieving chemical equilibrium, *i.e.* after 18 h of shaking (b). RCMs were prepared by heating for 24 h at 100, 110, 120 and 130°C. The dye concentration was  $2.5 \mu\text{mol dm}^{-3}$  and the MB/clay ratio  $0.05 \text{ mmol g}^{-1}$ . Spectra are arranged in order of increasing LC of clay from top to bottom. The dye in the dispersion of highest-charge montmorillonite absorbs light mainly at low wavelengths, which is assigned to H-aggregates (570 nm). The amount of the H-aggregates decreases with charge reduction in favor of H-dimers (600 nm), isolated dye cations (660 nm) and the species absorbing at 760 nm. The last form has been assigned to J-aggregates or acidic form (protonated dye cations). The effect of the layer charge is more clearly identified in the spectra measured after achieving equilibrium (b).

of preferred type, such as J-aggregates (Bujdák *et al.*, 2002b, 2002c), and reaction conditions (Czímerová *et al.*, 2003).

Significant influence of the charge densities of RCMs on the chemical reactivity of various dyes was observed. Interestingly, if decomposition of dye occurred in clay dispersions, it was always in the presence of samples with high charge densities. On the contrary, dyes were always stabilized after the adsorption on low-charge density surfaces, *i.e.* in the presence of RCMs with medium charge. Such stabilization was even observed for some cyanine dyes which decomposed in several minutes in dilute aqueous solutions without clay. Accelerated decomposition, at high LC clay surface, is believed to be caused by molecular tension induced by the stereochemistry of the large dye molecules on high-charge-density clay surfaces. Bujdák *et al.* (2002b, 2002c) suggested using this phenomenon for characterization of clay LC.

Molecular orientation of dye cations was another essential problem that needed to be solved for understanding phenomena related to the dye-clay interactions. Hähner *et al.* (1996), based on the analysis of data from XPS and near-edge X-ray absorption fine structure spectroscopy, proved nearly perpendicular orientation of MB cations on mica surfaces. Previously, most scientists had assumed only flat orientation of planar MB cations on clay basal surfaces. However, tilted orientation of dyes on flat surfaces is common (Kobayashi, 1996). Non-flat orientation is an essential condition for the formation of one- or two-dimensional molecular aggregates, which are adsorbed on flat surfaces, to achieve contact of every molecule in an aggregate with surface. Films of RCMs with intercalated rhodamine 6G cations were prepared by adsorption of the dye on Nanocor RCMs' films (Bujdák *et al.*, 2003b). Polarized UV-Vis spectroscopy was used to characterize the molecular orientation of dye cations on the silicate surface, which was found to be inhomogeneous for rhodamine 6G cations on the surface of montmorillonite. While the isolated dye cations were only slightly tilted, an almost perpendicular orientation of cations forming H-aggregates was proven. Layer charge reduction in the silicate substrate resulted in a significant decrease in the amount and/or size of the H-aggregates, but only partially affected the orientation of chromophores. These trends were confirmed by the studies using the same series of RCMs for orientation of MB (Kaneko *et al.*, 2003) and oxazine dye cations (Kaneko *et al.*, 2004).

Studies on the interaction between cationic dyes and RCMs are significant in terms of understanding the basic aspects of the dye adsorption and aggregation on clay surfaces. The measurement of VIS spectra of dye/smectite dispersions is a simple and extremely sensitive method for the detection of LC changes in smectites. Even small differences in the charge densities can be observed visually, as differences in color of the dye/clay

dispersions. Knowledge about dye/RCM interaction can be extrapolated to similar systems, such as complexes of dyes with other inorganic layered compounds and materials, polyelectrolytes, biopolymers, and for the systems with dyes used as probes for biomaterials. Controlling the charge of clay or another substrate, one can control the optical and photochemical properties of adsorbed organic dyes. This may be important for applications in some modern industrial fields such as nanotechnology, photochemistry, supramolecular chemistry, catalysis, processing of materials for memory media, photography, signal processing, *etc.*

#### *Interaction with other organic compounds*

Delozier *et al.* (2003) used RCMs (Cloisite, Southern Clay Products) as filler components for the preparation of polyimide/clay nanocomposite materials. The RCMs were saturated with aromatic amine, which was one of the reactants in the polymerization reaction. The RCMs with a moderate charge reduction exhibited optimal properties for dispersion of organo-clay in a polymer matrix, as well as for good mechanical characteristics of final polymer/clay composite materials. Very similar trends were observed for the interaction of Li<sup>+</sup>-saturated RCMs (Jelšovský Potok, Slovakia) with the water-soluble polymer, polyethylene oxide (Bujdák *et al.*, 2000). The amount of polymer adsorbed was controlled by the LC density. When the polymer was intercalated, it replaced water molecules filling the space between the hydrated exchangeable cations. As the polymer replaced only weakly bound water molecules, its adsorption increased with the LC reduction. The formation of non-swelling interlayer spaces was the only limitation of this trend. Molecular simulations confirmed the experiments and showed that the polymer oxygen atoms did not directly associate with the exchangeable cations which were mostly coordinated to water molecules and surface oxygen atoms.

Sheng *et al.* (2002) studied the adsorption of two dinitrophenol herbicides by two montmorillonites (lower charge SWy-2 and higher charge SAz-1) and prepared RCMs. The charge density of natural minerals and RCMs also affected sorption by controlling the size of adsorption domains. Medium-charge RCMs exhibited superior properties for the adsorption of humic substances, whereas drastic charge reduction caused a significant loss of humic acid adsorption ability in non-swelling material (Varadachari *et al.*, 1991).

Annabi-Bergaya *et al.* (1979) prepared RCMs from a mixture of Li<sup>+</sup>- and Na<sup>+</sup>- forms of Camp-Berteau montmorillonite *via* heating at 240°C for 24 h. They found that about half of the total adsorbed molecules of methanol or isopropanol did not occur in the interlamellar space but rather in the micropores between the particles.

Adsorption of non-cationic organic compounds on RCMs has not been studied much. Nevertheless, it seems

that the interaction of such organic compounds is often enhanced or promoted by the charge reduction. The interpretation is, in principle, the same as for the adsorption on RCMs saturated with small tetraalkylammonium cations. The  $\text{Li}^+$  fixation leads to a decrease in the LC and a reduction in the number of hydrated exchangeable cations in the interlayer spaces, creating more free interlayer volume for the adsorption of organic molecules. Consequently, RCMs of moderate charge should exhibit better adsorption properties than the parent minerals.

## CONCLUSIONS

This review has focused on studies related to layer-charge reduction of smectites *via* thermal treatments. Heating smectites saturated with small exchangeable cations causes their dehydration, penetration into the layers and decrease in CEC and swelling ability. Various cations can find their way into the ditrigonal cavities but  $\text{Li}^+$  seems to be the only cation capable of migration in considerable amounts into the previously vacant octahedral sites without significant dehydroxylation or deprotonation of the layers. Fixation of  $\text{Li}^+$  in the octahedral sheets increases with higher octahedral and lower tetrahedral charge and with temperatures up to 300°C. Sets of RCMs prepared either from the  $\text{Li}^+$ -forms *via* heating at different temperatures or from different mixtures of the  $\text{Na}^+$ - and  $\text{Li}^+$ -forms *via* heating at the same temperature are suitable materials for investigating the effects of layer charge on various properties of smectites. Application of sets of RCMs was very useful for studying interactions of smectites with organic compounds and can be used to help design organo-clay materials with desired properties. Using RCMs helped in the interpretation of aggregation of cationic dyes in clay dispersions and adsorption of uncharged organic compounds.

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