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Effect of heating temperature on Li-fixation, layer charge and properties of fine fractions of bentonites

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The fine fractions (<2 μm) of four bentonites, in which the dominant minerals were Al-rich montmorillonites of various chemical compositions, have been Li-saturated. The admixtures identified in the fine fractions include pyrophyllite in Otay (USA), amorphous SiO_2 in Ivančice (Czech Republic) and opal CT in Sarigus (Armenia) samples, while the Kriva Palanka sample (Macedonia) was a pure montmorillonite. The sample portions were heated at different temperatures (110 to 300 °C) for 24 h to promote Li-fixation in the layers in order to reduce the negative charge on the layers in a systematic manner. Hence a series of materials with gradually decreasing charge, cation exchange capacity (CEC) and swelling ability were prepared. The CEC of the prepared samples was affected by the admixtures present and by the extent of Li^+ for Ca^{2+} exchange in the starting material. The largest reduction in CEC (by 81%) was obtained for Otay montmorillonite, the mineral with the lowest tetrahedral and the highest octahedral charge, heated at 300 °C. The extent of Li-fixation was very sensitive to the treatment temperature in the range 110–200 °C. The development of uncharged layers with non-swelling interlayers occurred in all materials heated above 150 °C. The shift of the OH-stretching band to higher wavenumber and a new band due to an AlMgLiOH stretching vibration in the infrared spectra confirmed the penetration of Li into the previously vacant octahedral sites.

Introduction

Montmorillonite is a dioctahedral member of the smectite group of clay minerals. Its structure comprises two sheets of SiO_4 tetrahedra. These tetrahedral sheets sandwich a sheet of octahedrally coordinated cations. In dioctahedral smectites, two of the three possible octahedral sites in each unit cell contain trivalent and divalent cations, and the presence of trivalent and tetravalent cations in the tetrahedral sheet confers upon the 2:1 layer an overall negative charge. The charge balance is maintained by the exchangeable hydrated cations on the surface and within the interlayer space.

The layer charge and its distribution are among the most important characteristics of 2:1 phyllosilicates, indicating the capacity of a mineral to retain and to reline cations and to adsorb water and various polar organic molecules.[1] The combined effects of the charge location and amount influence the expansion properties.[2] The charge is used also for characterisation of clay minerals.[3] The layer charge of montmorillonites can be modified by the fixation of small exchangeable cations,[4–6] such as Li^+, or by the reduction of Fe(III) in the structure.[7,8] Lithium cations migrate from the exchange sites in the gallery into the layers upon heating. In this process, a portion of the previously exchangeable cations is fixed in the layers, and, consequently, the residual negative charge is reduced. Both duration and temperature of heating affect Li-fixation in montmorillonite.

Some authors claim that Li^+ ions migrate upon heating to the vacant octahedral sites adjacent to a centre of charge deficit, where a divalent instead of a trivalent cation is present.[9–12] Reduction of the CEC upon Li-fixation reflects the octahedral charge of smectites.[13] Alternatively, the lack of increase in the *c*-axis dimension of heat-treated smectites, along with IR evidence, supports the hypothesis that cations may reside within the pseudohexagonal cavities of the basal surface.[14–16] The changes observed in the IR spectra of Li^+ montmorillonite heated to 400 °C for four hours were not attributed to cation migration into octahedral sites.[17] Instead, the changes were ascribed to deep-recession of the Li^+ ions into the pseudohexagonal cavities of the tetrahedral sheets. Purnell and coworkers investigated the mechanism of layer charge reduction in Li-montmorillonites, using a combination of TGA and cyclohexylamine titration in the range of 200–267 °C together with Li^+ determination by flame emission spectroscopy. The results confirmed that the sequence of events is (a) thermally induced migration of Li^+ cations into the octahedral sheet, (b) interaction of Li^+ with the available OH groups present there, (c) extraction of H^+ by the cyclohexylamine into the interlamellar space.[18] The final positions of the fixed (previously exchangeable) Li(I), have not been proved unambiguously yet. It is likely to be dependent on the montmorillonite used, its total charge, and/or octahedral/tetrahedral charge ratio. The preparation of a series of reduced charge montmorillonites from the same parent minerals provides an important opportunity to investigate the effect of layer charge on the properties of these materials.

The changes in some properties of reduced charge montmorillonites have been described and numerous papers have discussed the relationship between expansion properties and crystallographic factors. It was found that the variation in basal spacing depends chiefly on the type and valency of the interlayer cations.[19,20] On the other hand, it was claimed that the total layer charge is the controlling factor influencing expansion properties.[21] X-Ray diffraction analysis provided evidence for differences in the expansion of samples with similar layer charge but different tetrahedral and octahedral charge.[22] These results showed that the basal spacings are larger when the layer charge arises predominantly from substitution in the octahedral sheets rather than the tetrahedral sheets. This suggests that expansion is due to the combined effects of interlayer cations, total layer charge and its distribution within octahedral and tetrahedral sheets.

The previous experiments were mostly performed using raw minerals from various sources, differing not only in the charge

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but also in chemical composition, the admixtures present, particle size distributions, *etc.* These variables could possibly affect the results obtained, though they were ascribed to differences in the charge. In this study, four series of montmorillonites with reduced layer charge were prepared from four parent smectites of various chemical compositions. The objective was to investigate the effect of heating temperature on the extent of Li^+ ion fixation and its influence on the cation exchange capacity and swelling ability of the prepared materials.

Experimental

Materials

Fine fractions separated from four different bentonites from Kriva Palanka (KP, Republic of Macedonia), Sarigus (Sa, Republic of Armenia), Ivančice (Iv, Czech Republic) and Otay (Ot, USA) were used as starting materials in this study. Coarse bentonites were suspended in distilled water, Ca-saturated by repeated treatment with 1.0 M $CaCl_2$, washed free of chloride, and the <2 μm fraction was collected, dried at 60 °C and ground to <0.2 mm prior to storage.

Separate dispersions of Ca-saturated fine fractions were placed in dialysis tubes and ion exchanged with 0.1–1.0 M solutions of LiCl. The Li-exchanged forms obtained were washed with distilled water until free of chloride ions, dried at 60 °C and ground to pass through a 0.2 mm sieve. Each of the materials obtained was divided into eleven parts. One specimen of each set remained unheated, while the others were heated for 24 h at 110, 120, 130, 140, 150, 160, 180, 200, 250 and 300 °C to evoke different levels of Li^+ ion fixation in the montmorillonite layers. Four series of eleven samples were thus prepared from the parent samples.

Techniques

The cation-exchange capacities (CECs) were determined by repeated saturation of the samples with 1 M ammonium acetate solution at pH = 7. The extracts obtained from the same sample were combined and analysed by atomic emission or absorption spectroscopy for Li and Ca.

Infrared spectra were obtained on a Nicolet Magna 750 FTIR spectrometer equipped with a DTGS detector in the 4000–400 cm^{-1} spectral range with a resolution of 4 cm^{-1}. The KBr pressed disk technique (0.4 and 2.0 mg sample and 200 mg KBr) was used. All spectral manipulations were performed using the OMNIC software package (Nicolet Instruments Corp.).

The X-ray powder diffraction profiles for pressed powder samples were recorded on a Philips PW 1050 diffractometer at 2° (2θ) min^{-1} using Cu-Kα radiation.

Results and discussion

Parent minerals

X-Ray diffraction and infrared spectroscopy proved that montmorillonite with an aluminium rich octahedral sheet is the dominant mineral in all four separated samples. No admixtures were detected in KP, a minor amount of pyrophyllite is present in Ot, and amorphous SiO_2 was detected in Iv. Opal-CT, the commonest form of hydrous SiO_2 consisting of disordered stacking of cristobalite-like and/or tridimite-like sequences,[23] appeared in Sa. The structural formulae (SF) of the Li-saturated montmorillonites were calculated from the chemical analyses. The sum of the octahedral coefficients in the SF (octahedral occupancy) provides information on the admixtures possibly present in the sample. It is more sensitive to the presence of free oxides than to admixtures of other layer silicates in the samples.[24] The octahedral occupancy of KP is 3.99 (compared to a theoretical value of 4.00) proving the very high purity of the separated fraction, while that of Ot is 4.08, suggesting that some Al- and/or Fe- and/or Mg-rich admixture may be present. However, no crystalline substance was identified by XRD. It follows that the admixture may be a microcrystalline oxide or oxyhydroxide, *e.g.* goethite. Al-substituted iron oxides occur frequently in soils and clays[25,26] and extraneous, readily soluble Mg phases are also common. Because the total amount of microcrystalline admixtures, present in low amounts, in the fine fractions of bentonites cannot be unambiguously quantified, no further analyses were performed. However, if such an admixture occurs in Ot, the real octahedral charge of this montmorillonite would be higher than that calculated from the bulk chemical analysis (Table 1).

The octahedral occupancies of Iv and Sa were 3.88 and 3.71, respectively, showing the presence of Si-rich admixtures in these samples, which is evident also from the coefficients of tetrahedral Si exceeding 8 (8.17 and 8.54, respectively). No diffraction from a SiO_2-rich phase appears in the X-ray diffraction pattern of Iv, however, the trace of Sa proves that opal-CT is present. This mineral, containing cristobalite-like features, has been variously described in the literature and sometimes misidentified as high-cristobalite.[23] Infrared spectra of Iv and Sa demonstrate a lower content of SiO_2 admixture in Iv than in Sa. Both the intensity and shape of the band at 797 cm^{-1} present in the spectrum of Sa (Fig. 1) are typical for cristobalite and/or opal-CT, while the low-intensity shoulder near 800 cm^{-1} in the spectrum of Iv (Fig. 2) indicates amorphous silica admixture.[27] Decreasing the SiO_2 contents in the chemical analyses of Iv and Sa by 10 and 24%, respectively, led to ideal structural formulae, *i.e.* Si coefficients <8 and octahedral occupancies equal to 4.00 (Table 1). Amounts of extraneous SiO_2 phases in Iv and Sa were thus estimated as 10 and 24%, respectively. However, these results may possibly be affected by the presence of non-montmorillonitic phases rich in Al and/or Fe and/or Mg in these samples.

The SF for Ot and KP (calculated from the chemical analyses), and those for Iv and Sa (obtained after correction for extraneous SiO_2), and octahedral, tetrahedral and total layer charges calculated from these SF are listed in Table 1. The values of the tetrahedral and octahedral components of the total charge thus obtained for all four minerals are typical for montmorillonites. Tetrahedral charge increases in the order Ot < KP < Iv < Sa. The high value for Sa is probably affected by the presence of some non-swelling illitic layers, as is suggested by the high content of K^+ in this sample. Interlayer potassium

Table 1 Tetrahedral, octahedral and total charge and structural formulae of Li-montmorillonites

	Charge ($e^-/O_{20}(OH)_4$)			
Montmorillonite	Tetrahedral	Octahedral	Total	Structural formula
Kriva Palanka	−0.15	−0.72	−0.87	$[Si_{7.85}Al_{0.15}][Al_{2.96}Fe_{0.32}Mg_{0.72}]Ca_{0.07}K_{0.03}Li_{0.68}O_{20}(OH)_4$
Sarigus	−0.43	−0.73	−1.16	$[Si_{7.57}Al_{0.43}][Al_{2.36}Fe_{0.91}Mg_{0.73}]Ca_{0.11}K_{0.21}Li_{0.71}O_{20}(OH)_4$
Ivančice	−0.21	−0.74	−0.95	$[Si_{7.79}Al_{0.21}][Al_{2.84}Fe_{0.42}Mg_{0.74}]Ca_{0.17}K_{0.02}Li_{0.58}O_{20}(OH)_4$
Otay	−0.05	−0.93	−0.98	$[Si_{7.95}Al_{0.05}][Al_{2.77}Fe_{0.15}Mg_{1.17}]Ca_{0.05}K_{0.05}Li_{0.81}O_{20}(OH)_4$

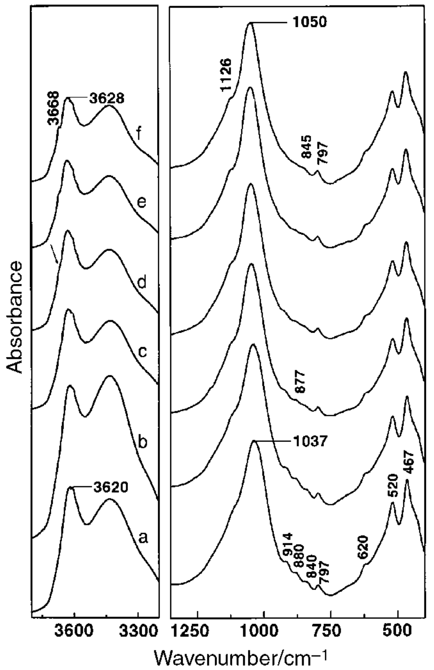

Fig. 1 IR spectra of Sarigus series: (a) unheated sample, and the samples heated for 24 h at (b) 110 °C, (c) 150 °C, (d) 160 °C, (e) 200 °C, (f) 300 °C.

present in the fine fractions of bentonites is frequently non-exchangeable, fixed in non-swelling (illitic) interlayers rather than in exchangeable positions of smectites. K^+ cations saturate about 18% of the negative layer charge in Sa, while the K^+ content in the other three samples is much lower.

Ion exchange of Ca-saturated montmorillonites in dialysis tubes with LiCl solutions was successful but incomplete, as can be seen from the Li and Ca coefficients in the structural formulae (Table 1). Incomplete removal of divalent Ca^{2+} from negatively charged montmorillonite layers upon repeated washings with solutions of monovalent Li^+ using the dialysis tube technique had been anticipated. The procedure was exactly the same for all four samples. The relative contents of Ca^{2+} and Li^+ indicate the differences in the ion exchange properties of the minerals used. The ratios $Li^+/(Li^+ + 2Ca^{2+})$ calculated from the coefficients in the structural formulae (Table 1) reveal that Li^+ occupies 89, 83, 76 and 62% of the available exchange sites (*i.e.* K^+ has not been included) in the parent Ot, KP, Sa and Iv materials, respectively. These data are in agreement with previous results from this laboratory in that ion exchange of Ca^{2+} in the fine fractions of Ivančice bentonite is rather difficult and the extent of exchange is usually lower than with other dioctahedral smectites (unpublished results). The reasons for this behaviour remain unclear.

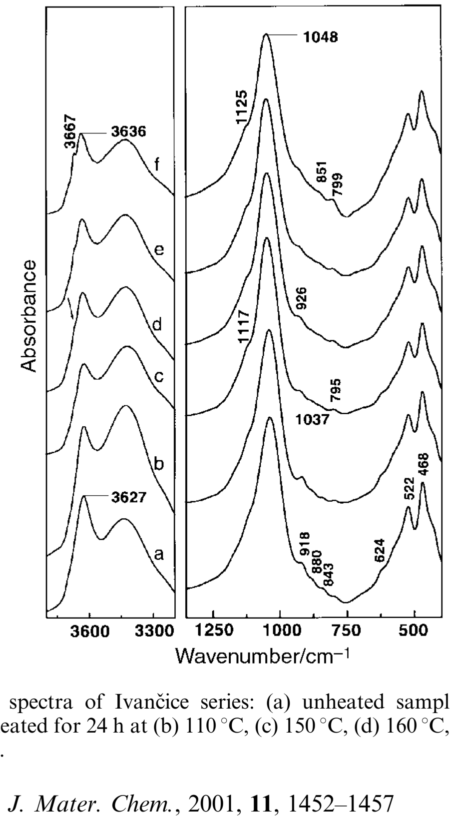

Fig. 2 IR spectra of Ivančice series: (a) unheated sample, and the samples heated for 24 h at (b) 110 °C, (c) 150 °C, (d) 160 °C, (e) 200 °C, (f) 300 °C.

Cation-exchange capacity

The CECs of unheated samples reflect their chemical and mineralogical composition as discussed above. The highest value of 1.21 mmol g^{-1} was obtained for KP, the monomineralic sample containing only montmorillonite. K^+ occupies less than 4% of the "exchangeable" positions, confirming that the content of non-swelling interlayers is insignificant. Tetrahedral charge in KP montmorillonite represents about 17% of the total charge. The extent of exchange of Ca^{2+} by Li^+ achieved is high but the residual Ca^{2+} may slightly decrease the extent of Li fixation upon heating.

The second highest CEC value is that of Iv, 1.10 mmol g^{-1}, 22% of which originates in the tetrahedral sheet. Iv has the lowest potassium content and the highest calcium content among all the samples. The relatively high tetrahedral charge and the partial Li^+ for Ca^{2+} exchange are both expected to decrease the charge reduction upon heating. The comparatively low CEC of the Ot sample (0.99 mmol g^{-1}) was unexpected but the method used for calculation of SF does not easily distinguish between variously charged layers. It is a calculation, not a determination of the probable distribution of atoms within the structure of montmorillonite.[24] The application of this method to a montmorillonite (high charge) containing a pyrophyllite admixture (no charge) leads to a SF with decreased mean charge, as is shown for Ot montmorillonite. Assuming the lowest tetrahedral component of total charge and the lowest Ca coefficient in the SF predicts that high levels of charge reduction upon heating will be possible. The lowest CEC was obtained for Sa (0.92 mmol g^{-1}), the sample with the highest charge calculated from the SF (Table 1). As discussed above, this sample contains about 24 mass% of opal-CT, a mineral of negligible CEC, and has a relatively high amount of K^+, which is probably present in non-exchangeable, illitic interlayers. Illitic layers are usually of higher tetrahedral and total charge than montmorillonite layers. Both these factors combine and contribute to the observed lower CEC value of Sa montmorillonite. High tetrahedral charge and medium Ca^{2+} content suggest that high levels of charge reduction upon heating could not be expected. The CEC is not a measure of layer charge, because CECs express total exchangeable positive charge for a sample, rather than net negative charge for a specific mineral. Positive charge associated with non-exchangeable cations (*e.g.*, K^+ in illitic layers) is excluded from CEC values, but the negative charge balanced by such cations should be included in layer charge values.[28]

The effect of heating of Li-exchanged samples at various temperatures for 24 h on their CECs is presented in Fig. 3. Increasing the treatment temperature caused a more extensive reduction of CEC values in all four series with a sharp decrease occurring after heating at 110–200 °C with the most evident changes being observed for Ot. The CECs of the samples heated at 120 and 200 °C were 0.96 and 0.26 mmol g^{-1}, respectively, which is 88 and 26% of the CEC of the unheated sample. The CECs for the samples in other series, heated at 120 and 200 °C, decreased to 83 and 38% for KP, 84 and 47% in Sa and 84 and 52% in Iv, respectively. Although heating at

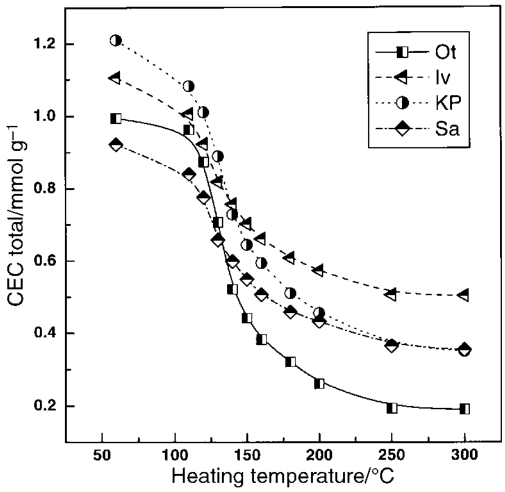

Fig. 3 The influence of heating on the CEC values in the samples: Kriva Palanka (KP), Sarigus (Sa), Ivančice (Iv), Otay (Ot).

temperatures above 200 °C caused some additional fixation of Li^+ ions most of the Li was fixed upon heating for 24 h at 110–200 °C. In accord with the previously published data,[29] the shapes of the dependences displayed in Fig. 3 show that heating at 250–300 °C causes the maximum available layer charge reduction in the samples. Upon heating at 300 °C the CECs were reduced to 19, 29, 38 and 46% of the CECs of the unheated Ot, KP, Sa and Iv, respectively.

The octahedral charge of KP, Sa and Iv montmorillonites were very similar at −0.72 to −0.74 $e^-/O_{20}(OH)_4$ (Table 1). However, the decrease in CEC upon heating of Li-saturated samples was different (Fig. 3). Two important factors combine to cause incomplete charge reduction. All three samples have a significant amount of tetrahedral charge (−0.15 to −0.43 $e^-/O_{20}(OH)_4$, Table 1), which is not decreased *via* Li-fixation.[10] The presence of exchangeable cations other than Li^+ decreases Li retention in dioctahedral smectites[13] and the Ca^{2+} content increases as KP < Sa < Iv, which suggests that the extent of Li-fixation in Iv is particularly affected by the Ca^{2+} ions present. High Ca^{2+} content and tetrahedral charge resulted in a relatively high CEC for the Iv sample heated at 300 °C (0.50 mmol g^{-1}), which is 46% of the CEC of the unheated Iv.

Ot is the sample with the lowest tetrahedral and the highest octahedral charge (−0.05 and −0.93 $e^-/O_{20}(OH)_4$, respectively). The extent of charge reduction within this series is clearly the highest and the CEC of the sample heated at 300 °C is the lowest among all the samples (0.19 mmol g^{-1}, Fig. 3) corresponding to 19% of the CEC of the unheated Ot. This value is probably affected by the residual Ca^{2+} in the sample due to incomplete exchange of Ca^{2+} by Li^+ in the dialysis tubes. The lower Li-uptake in several smectites saturated with smaller amounts of Li^+ in mixed exchangeable cations (Li^+–Na^+) demonstrates the negative effect of other cations on Li-fixation.[13]

Infrared spectroscopy

The FTIR spectra of unheated and heated samples are shown in Fig. 1, 2, 4 and 5. The absorption bands assigned to the stretching vibrations of the OH groups appear in the 3750–3200 cm^{-1} region, while absorption bands related to the OH-bending and Si–O vibrations are observed below 1200 cm^{-1}.[30]

Migration of the lithium into the layers of mineral upon heating generates changes in the structure, which are reflected in the IR spectra. The spectra of unheated samples show an absorption band near 3620 cm^{-1} due to the stretching vibrations of structural OH groups coordinated to octahedral cations and a broad band near 3400 cm^{-1} related to the stretching vibrations of water molecules. Upon heating, the structural OH band continuously shifts to higher wavenumbers. The more pronounced shift observed for Ot ($\Delta\nu = 14$ cm^{-1}) and KP ($\Delta\nu = 12$ cm^{-1}) in comparison with Iv ($\Delta\nu = 9$ cm^{-1}) and Sa ($\Delta\nu = 8$ cm^{-1}) is in agreement with the decrease in CEC (Fig. 3). A new absorption near 3670 cm^{-1} appears in the spectra of samples heated above 140 °C (Fig. 1, 2, 4, 5). This band, assigned to AlMgLiOH vibrations, proves that hydroxyl groups are in a local trioctahedral coordination, which is created when monovalent Li^+ ions penetrate into previously vacant octahedral sites. The intensity of this band gradually increases with treatment temperature due to the increasing amount of fixed Li(I). The IR spectra of samples heated to 300 °C exhibit the highest intensity trioctahedral

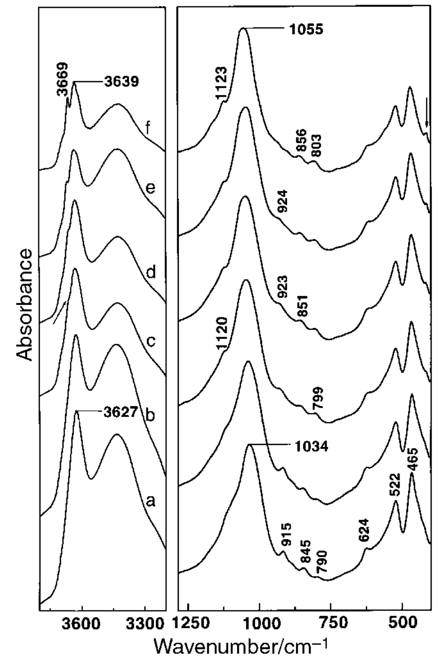

Fig. 4 IR spectra of Kriva Palanka series: (a) unheated sample, and the samples heated for 24 h at (b) 110 °C, (c) 150 °C, (d) 160 °C, (e) 200 °C, (f) 300 °C.

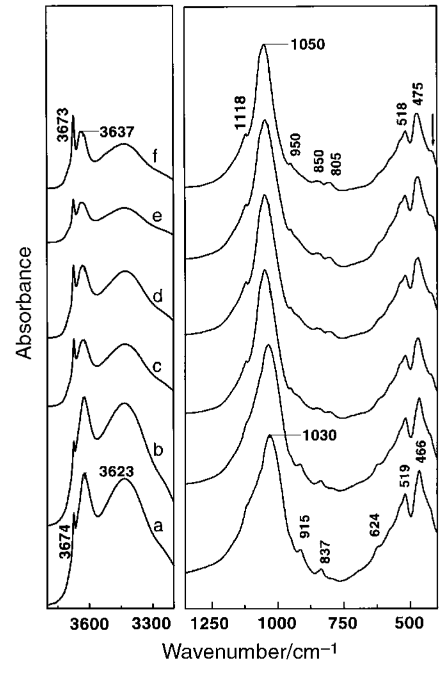

Fig. 5 IR spectra of Otay series: (a) unheated sample, and the samples heated for 24 h at (b) 110 °C, (c) 150 °C, (d) 160 °C, (e) 200 °C, (f) 300 °C.

band for KP and the lowest band intensity for Sa (Fig. 1, 2, 4, 5). The OH-stretching region of the unheated Ot sample shows, in addition to the OH band of montmorillonite at 3623 cm^{-1}, a small sharp band at 3674 cm^{-1}. This band, attributed to the OH-stretching vibration of pyrophyllite, confirms the presence of this mineral as an admixture in the Ot sample. Upon heating the AlMgLiOH groups are formed and their stretching vibration near 3670 cm^{-1} contributes to the absorption in this region. As a consequence of the increasing amount of AlMgLiOH groups with treatment temperature, the intensity of the band at 3674 cm^{-1} is enhanced.

The OH-bending vibrations of dioctahedral smectites absorb in the range 950–800 cm^{-1} The relative intensity of the bands in this region indicates the degree of octahedral substitution. The most intense band, near 915 cm^{-1}, detected in the spectra of all unheated samples is assigned to AlAlOH vibrations and confirms the high octahedral Al content. The higher Fe(III) content present in the octahedral sheet of Sa and Iv resulted in the AlFeOH band near 880 cm^{-1} and all the unheated samples exhibit an absorption band near 840 cm^{-1}, assigned to AlMgOH vibration. Upon heating, a shift to higher wavenumbers and a gradual decrease in intensity of the AlAlOH band was observed in the spectra of all samples (Fig. 1, 2, 4, 5). The intensity of the AlFeOH band in the spectra of Sa and Iv samples decreases with temperature (Fig. 1, 2), while the AlMgOH band is shifted towards higher wavenumbers and decreases in intensity upon heating to 130 °C. No further modification of this band is visible in the spectra of Sa and Iv heated above 140 °C. However, heating at higher temperature induces additional changes in the 850–800 cm^{-1} region of KP and Ot. Besides the 850 cm^{-1} band a new absorption near 805 cm^{-1} is present in the spectra of the samples heated at 150 °C. The intensities of both bands gradually increase with temperature. It is impossible to explain precisely the changes observed in the OH-bending region of montmorillonites; however, it is clear that all changes reflect strong perturbation of the OH vibrations due to the presence of Li(I) in the structure. Fixation of Li decreased the layer charge causing the structure to become more pyrophyllite-like. The broad band near 1030–1037 cm^{-1}, assigned to complex Si–O stretching vibrations in the tetrahedral sheet, moved upon heating to 1048–1055 cm^{-1} for all samples, approaching the frequency at which pyrophyllite absorbs. The more pronounced shift of the Si–O band, found for Ot ($\Delta\nu = 20$ cm^{-1}) and KP ($\Delta\nu = 21$ cm^{-1}) in comparison with Iv ($\Delta\nu = 11$ cm^{-1}) and Sa ($\Delta\nu = 13$ cm^{-1}), correlates well with the smaller charge decrease in the latter samples (Fig. 1, 2, 4, 5). The weak absorptions near 1120 cm^{-1} and 420 cm^{-1} observed in the spectra of KP and Ot heated above 150 °C resemble those of pyrophyllite, indicating decreased layer charge and the presence of pyrophyllite-like, non-swelling layers in these samples.[31]

X-Ray diffraction

The swelling of smectites depends upon their structure, chemical compositions and the type of exchangeable cations. The d_{001} spacings of unheated KP, Sa and Ot samples are all in the range 12.3–12.5 Å (Table 2), which is typical for Li-montmorillonites.[32] The slightly higher value obtained for Iv is connected with the highest Ca^{2+} content in this sample because divalent Ca^{2+} ions are more hydrated than monovalent Li^{+} ions. Hence, their presence in the interlayers is reflected in the increased spacing of the mineral layers.

The slightly higher d_{001} values obtained for the samples heated at 110–130 °C, compared with their unheated counterparts, are probably due to partial rehydration during storage between their preparation and measurement. No special care was undertaken to isolate them from ambient humidity. The spacings decreased with the treatment temperature in all four series (Table 2). Layer spacings of $\leqslant$10 Å were obtained in all the series for samples heated above 180 °C, finally reaching the value of 9.6 Å, which is the thickness of fully collapsed montmorillonite layers. A balance between the opposing forces determines the extent of clay mineral expansion. The main attractive force is due to electrostatic interactions between the interlayer cations and the negatively charged aluminosilicate surface. When these interactions dominate over hydration, which exerts a repulsive force between the silicate layers, expansion does not occur.[22] This is the case for high charged minerals, such as illites and micas, as well as for uncharged pyrophyllite and talc.

Table 2 The effect of preparation temperature on d_{001} diffraction values

	d_{001}/Å			
Heating temperature/°C	KP	Sa	Iv	Ot
unheated	12.3	12.5	13.6	12.4
110	12.4	13.2	13.3	13.2
120	12.4	12.7	13.0	13.0
130	12.1	12.7	12.3	12.8
140	10.9	11.4	11.7	11.3
150	10.5	10.9	11.3	10.6
160	10.0	10.7	11.1	10.1
180	9.7	10.2	10.0	9.7
200	9.7	9.7	10.0	9.7
250	9.7	9.6	9.7	9.6
300	9.6	9.6	9.6	9.6

Analysis of the swelling of samples prepared provides direct evidence on the effect of charge on swelling of montmorillonite. The negative layer charge and the amount of exchangeable Li^{+} available for hydration is decreased with increasing amounts of fixed lithium, achieved by heating at higher temperatures. Consequently, the attractive forces dominate in the system and the swelling ability decreases with the temperature of preparation.

Conclusions

Heating Li-saturated montmorillonites reduced the net negative layer charge due to fixation of Li within the layers in all four Li-montmorillonites of different chemical composition. A series of reduced charge materials with gradually decreasing charge were prepared by controlling the temperature of preparation within 110–300 °C. The CEC of the prepared samples was affected by the presence of admixtures and by the extent of Li^{+} for Ca^{2+} exchange in the starting material. The highest reduction in CEC (81%) was obtained when the montmorillonite with the lowest tetrahedral and the highest octahedral charge was heated at 300 °C. Li-fixation was very sensitive to the treatment temperature in the range 110–200 °C. The production of uncharged pyrophyllite-like layers with non-swelling interlayers was observed in materials heated above 150 °C. Decreases in both the CEC and the swelling ability with increasing treatment temperature were observed for all four series of samples.

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References

1 A. R. Mermut, *CMS Workshop Lectures. Vol. 6: Layer Charge Characteristics of 2 : 1 Silicate Clay Minerals*, ed. A. R. Mermut, The Clay Minerals Society, Boulder, CO, 1994, pp. 106–122.

2 S. Tsutomu, W. Takashi and O. Ryohei, *Clays Clay Miner.*, 1992, **40**, 103.

3 G. Lagaly, *CMS Workshop Lectures. Vol. 6: Layer Charge Characteristics of 2 : 1 Silicate Clay Minerals*, ed. A. R. Mermut, The Clay Minerals Society, Boulder, CO, 1994, pp. 2–46.

4 J. Madejová, J. Bujdák, W. P. Gates and P. Komadel, *Clay Miner.*, 1996, **31**, 233.

5 B. K. Theng, S. Hayashi and H. Seyama, *Clays Clay Miner.*, 1997, **45**, 718.

6 M. D. Alba, R. Alvero and J. M. Trillo, *J. Phys. Chem. B*, 1998, **102**, 2207.

7 A. Mulaba-Bafubiandi, J. Helsen, A. Maes and G. Langouche, *Hyperfine Interact.*, 1992, **70**, 1049.

8 P. Komadel and J. W. Stucki, *Clays Clay Miner.*, 1988, **36**, 379.

9 R. Calvet and R. Prost, *Clays Clay Miner.*, 1971, **19**, 175.

10 R. Green-Kelly, *Clay Miner. Bull.*, 1953, **2**, 52.

11 R. Green-Kelly, *Mineral Mag.*, 1955, **30**, 604.

12 G. Sposito, R. Prost and J. P. Gaultier, *Clays Clay Miner.*, 1983, **31**, 9.

13 W. F. Jaynes and J. M. Bigham, *Clays Clay Miner.*, 1987, **35**, 440.

14 R. Tettenhorst, *Am Mineral.*, 1962, **47**, 769.

15 V. C. Farmer and J. D. Russell, *Clays Clay Miner.*, 1967, **15**, 121.

16 M. B. McBride and T. J. Pinnavaia, *Clays Clay Miner.*, 1975, **23**, 103.

17 V. S. Komarov, A. T. Rozin and N. A. Akulich, *Zh. Prikl. Spektrosk.*, 1977, **26**, 1099.

18 J. Williams, J. H. Purnell and J. A. Ballantine, *Catal. Lett.*, 1991, **9**, 115.

19 R. W. Mooney, A. G. Keenan and L. A. Wood, *J. Am. Chem. Soc.*, 1952, **74**, 1331.

20 R. Keren and I. Shainberg, *Clays Clay Miner.*, 1975, **23**, 193.

21 I. Horváth and I. Novák, *Proc. Int. Clay Conf., Mexico City*, ed. S. W. Bailey, Applied Publishing, Wilmette, Illinois, 1975, pp. 185–189.

22 T. Sato, T. Watanabe and R. Otsuka, *Clays Clay Miner.*, 1992, **40**, 103.

23 J. B. Jones and E. R. Segnit, *J. Geol. Soc. Aust.*, 1971, **18**, 57.

24 B. Číčel and P. Komadel, in *Quantitave Methods in Soil Mineralogy*, ed. J. E. Amonette and L. W. Zelazny, Soil Science Society of America, Madison, WI, USA, 1994, p. 119.

25 E. Murad and U. Schwertmann, *Clay Miner.*, 1983, **18**, 301.

26 R. E. Vandenberghe, E. De Grave, C. Landuydt and L. H. Bowen, *Hyperfine Interact.*, 1990, **53**, 175.

27 H. H. W. Moenke, in *Infrared Spectra of Minerals*, ed. V. C. Farmer, Mineralogical Society, London, 1974, pp. 365–382.

28 D. A. Laird, in *CMS Workshop Lectures, Vol. 6*, ed. A. R. Mermut, The Clay Minerals Society, Boulder, CO, 1994, pp. 80–103.

29 U. Hofman and R. Klemen, *Z. Anorg. Allg. Chem.*, 1950, **262**, 95.

30 V. C. Farmer, in *Infrared Spectra of Minerals*, ed. V. C. Farmer, Mineralogical Society, London, 1974, pp. 331–363.

31 P. Komadel, J. Bujdák, J. Madejová, V. Šucha and F. Elsass, *Clay Miner.*, 1996, **31**, 333.

32 M. Chorom and P. Rengasamy, *Clays Clay Miner.*, 1996, **44**, 783.