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Effects of chemical composition and temperature of heating on the infrared spectra of Li-saturated dioctahedral smectites. (II) Near-infrared region

J. MADEJOVÁ^{1,*}, J. BUJDÁK¹, S. PETIT² AND P. KOMADEL¹

¹*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava, Slovakia and* ²*Université de Poitiers, CNRS UMR 6532 'HydrASA', 40, avenue du Recteur Pineau, F-86022 Poitiers Cedex, France*

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ABSTRACT: Diffuse reflectance spectra in the near-infrared region are presented for Li-saturated smectites heated up to 200°C. The smectites included three montmorillonites, an Fe-beidellite and a ferruginous smectite. Unheated samples showed a complex band near 7060 cm⁻¹ assigned to the first overtone of the OH-stretching mode of structural hydroxyl groups and bound H₂O. The OH combination bands appeared in the 4600–4300 cm⁻¹ region. Spectra of heated montmorillonites showed an upward shift and splitting of the OH-overtone band into two components near 7170 and 7110 cm⁻¹. The presence of a band near 7170 cm⁻¹, assigned to the overtone of the AlMgLiOH-stretching vibration, implied that local trioctahedral domains were created upon Li(I) fixation in the previously vacant octahedral positions of montmorillonites. The OH combination bands were shifted to higher frequencies and a new band appeared near 4472 cm⁻¹ in the spectra of montmorillonites heated to temperatures in excess of 130°C. No features indicating Li(I) in the structure of Fe-beidellite or ferruginous smectite were observed in the NIR spectra.

KEYWORDS: smectite, Li fixation, IR spectra, near-IR region, DRIFT.

In Part I of our study, the infrared (IR) spectroscopy in the mid-IR (MIR) region was used to follow structural changes occurring in five Li-saturated dioctahedral smectites upon heating (Madejová *et al.*, 2000). In addition to the MIR region, the near-IR (NIR) region (11000–4000 cm⁻¹) can also provide useful information about clay minerals since the observed bands are often affected by changes in their structure. The popularity of NIR spectroscopy has increased greatly in recent years due to significant development in FTIR spectrometers. Moreover, the application of diffuse reflectance technique (DRIFT) simplifies sample preparation in comparison with traditional solid

sampling techniques. The DRIFT is especially appropriate in the NIR region where, in contrast to the MIR region, no dilution of the sample is necessary and therefore the IR analysis can be very fast and non-destructive.

A NIR database of silicate minerals was established by Hunt & Salisbury (1970) and supplemented with additional silicates by Hunt *et al.* (1973). The assignment of NIR absorption bands of both water molecules and lattice hydroxyl groups of smectites was reported in several papers, e.g. Cariati *et al.* (1981), Bishop *et al.* (1994), etc. Bishop *et al.* (1999) showed that the NIR spectroscopy provides compositional information and thus can be used effectively for identification of montmorillonites and nontronites.

As far as we know, the only paper dealing with NIR spectra of reduced-charge montmorillonites is

* E-mail: uachjmad@savba.sk

that of Sposito *et al.* (1983). They compared the NIR spectra of the Na-montmorillonite (100% CEC) with Na/Li montmorillonite (58% of original CEC) but did not find any noticeable shift of the principal absorption bands with charge reduction. The only significant change appeared in the decrease of intensities of the absorptions assigned to adsorbed water molecules.

The aim of this study is to show the potential of DRIFT spectroscopy in the NIR region (11000–4000 cm^{-1}) to aid understanding of structural changes occurring upon heating in Li-saturated dioctahedral smectites of different chemical composition.

MATERIALS AND METHODS

The samples studied were the same as those used in Part I (Madejová *et al.*, 2000). The Li-saturated smectites, heated for 24 h at 110–200°C, are referred as SAz110 – SAz200, etc.

The NIR spectra were obtained using a Nicolet Magna 750 FTIR spectrometer with the diffuse reflectance (DRIFT) accessory ‘Collector’ from Spectra-Tech. The spectrometer was equipped with a CaF_2 beam-splitter and a PbSe detector. The powder samples were analysed without dilution in KBr. For each sample 128 scans were recorded in the 11000–4000 cm^{-1} spectral range with a resolution of 4 cm^{-1} . Spectra manipulations were

performed using the OMNIC software package (Nicolet Instruments Corp.). Band component analysis of the OH combination band was carried out using a least squares peak fitting program with the Gauss-Lorentz form of each component. The convergence criteria were six significant digits for χ^2 , and goodness of fit was evaluated at the 95% confidence interval. The wavenumbers of the NIR bands of unheated Li-smectites, their assignment and references are summarized in Table 1.

RESULTS AND DISCUSSION

The bands present in the NIR region are the result of overtones and combinations of fundamental stretching (ν) and deformation (δ) vibrations. Overtones occur when a fundamental vibrational mode is excited with two or more quanta. Combinations occur when two or more fundamentals and/or overtones of different modes add or subtract. Thus, theoretical positions of the bands observed in the NIR region of Li-smectites can be approximated from the wavenumbers of the bands found in the MIR region (Madejová *et al.*, 2000). Major NIR spectral features of smectites are located in the 7000–6000 cm^{-1} and 5000–4000 cm^{-1} regions (Fig. 1). The band near 7058 cm^{-1} is complex, containing both the overtone ($2\nu_{\text{OH}}$) of the structural OH-stretching mode ($\nu_{\text{OH}} = 3622 \text{ cm}^{-1}$) and the first overtone of water

TABLE 1. Positions of the bands and their assignments observed in the spectra of the unheated Li-smectites.

Wavenumber (cm^{-1})		Assignment	Reference
10550	all samples	$3\nu_w$	this paper
8661	all samples	$2\nu_w + \delta_w$	this paper
~7060	all samples	$2\nu_w$	Sposito <i>et al.</i> (1983)
	all samples	$2\nu_{\text{OH}}$	Bishop <i>et al.</i> (1994)
6960	SWa	$2\nu_{\text{FeFeOH}}$	this paper
~6837	all samples	$2\nu_w$	Sposito <i>et al.</i> (1983)
5239	all samples	$\nu_w + \delta_w$	Sposito <i>et al.</i> (1983)
~4520	all samples	$\nu_{\text{AlAlOH}} + \delta_{\text{AlAlOH}}$	Bishop <i>et al.</i> (1999)
~4470	ST, SWa	$\nu_{\text{AlFeOH}} + \delta_{\text{AlFeOH}}$	Bishop <i>et al.</i> (1999)
4466	SAz fit	$\nu_{\text{AlMgOH}} + \delta_{\text{AlMgOH}}$	this paper
~4370	ST, SWa	$\nu_{\text{FeFeOH}} + \delta_{\text{FeFeOH}}$	Bishop <i>et al.</i> (1999)
~4340	HD	$\nu_{\text{FeMgOH}} + \delta_{\text{FeMgOH}}$	Bishop <i>et al.</i> (1999)

Vibrations are labelled with ν (stretching) and δ (bending). The subscripts w and w' refer to water molecules strongly and weakly hydrogen bonded, respectively. Subscript OH refers to structural OH groups. SAz fit indicates position obtained from peak-fitting analysis.

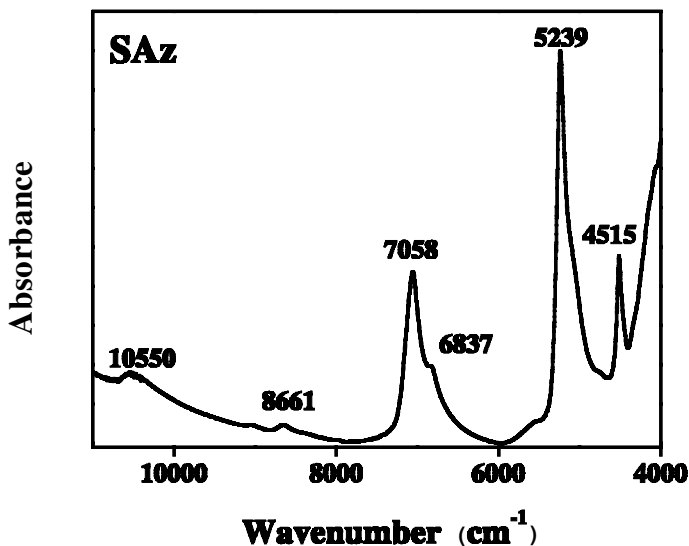


FIG. 1. NIR spectra of SAz montmorillonite.

molecules ($2\nu_w$) weakly hydrogen-bonded to surface oxygens of the tetrahedral sheets ($\nu_w = 3610\text{--}3630\text{ cm}^{-1}$; Farmer, 1974). The appearance of the overtones at lower wavenumbers than twice the fundamental is due to anharmonic character of vibrations (Szymański, 1964). The shoulder near 6837 cm^{-1} is due to the first overtone of water molecules ($2\nu_w$) involved in strong hydrogen bonds ($\nu_w = \sim 3430\text{ cm}^{-1}$). Small bands at 10550 and 8661 cm^{-1} are assumed to be due to the second overtone ($3\nu_w$) and ($2\nu_w + \delta_w$) combination of variously bound water molecules in the sample. In the region below 6000 cm^{-1} the spectrum of the SAz montmorillonite exhibits a strong band due to combination of the stretching and bending vibrations of water at 5239 cm^{-1} (Fig. 1). A band at 4515 cm^{-1} corresponds to the combination modes of the stretching and bending vibrations of structural OH groups. It has been proposed recently that combination bands originate from the addition of vibrational modes of the same OH groups (Bishop *et al.*, 1999). Thus two expected frequencies of the combination modes ($\nu_{\text{AlAlOH}} + \delta_{\text{AlAlOH}}$) at 4537 cm^{-1} ($3622+915\text{ cm}^{-1}$), and ($\nu_{\text{AlMgOH}} + \delta_{\text{AlMgOH}}$) at 4442 cm^{-1} ($3600+842\text{ cm}^{-1}$), are supposed to contribute to the complex band of SAz at 4515 cm^{-1} . Band component analysis of this band, presented in Fig. 2, reveals that its asymmetry on the low-frequency side is due to the contribution of the 4466 cm^{-1} component

($\nu_{\text{AlMgOH}} + \delta_{\text{AlMgOH}}$) to the combination mode at 4518 cm^{-1} ($\nu_{\text{AlAlOH}} + \delta_{\text{AlAlOH}}$).

All NIR spectra of unheated smectites show a similar broad band near 7060 cm^{-1} (Fig. 3). Because the first overtone of structural OH groups and the first overtone of water are overlapping in this region, small differences observed in the positions of OH-stretching frequencies in the MIR region (Madejová *et al.*, 2000) are barely distinguished in the NIR region. However, the spectrum of SWa, in addition to the band near 7060 cm^{-1} , shows a pronounced shoulder near 6960 cm^{-1} . This band, assigned to $2\nu_{\text{FeFeOH}}$, indicates that OH-stretching vibrations of ferruginous smectite absorb in the mid-IR region near 3560 cm^{-1} . Combination bands of OH-stretching and bending vibrations ($\nu_{\text{OH}} + \delta_{\text{OH}}$) appear in the $4700\text{--}4300\text{ cm}^{-1}$ region, the assignments are given in Table 1.

The Li^+ ions migrated upon heating from the interlayer space into the mineral structure. The presence of Li(I) in the previously vacant octahedral positions and/or in the hexagonal holes of tetrahedral sheets of montmorillonites significantly affected their OH-stretching and bending vibrations in the MIR region (Calvet & Prost, 1971). These structural and electronic changes are expected to influence the NIR spectra in the OH-overtone and combination regions. Figure 4 shows pronounced modification of the spectral features of heated SAz samples. The OH-overtone band decreases in

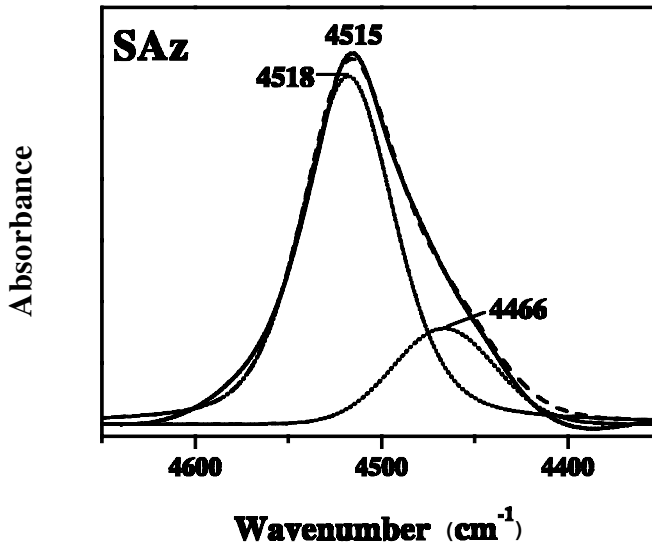


FIG. 2. Band component analysis of the OH-combination mode of SAz.

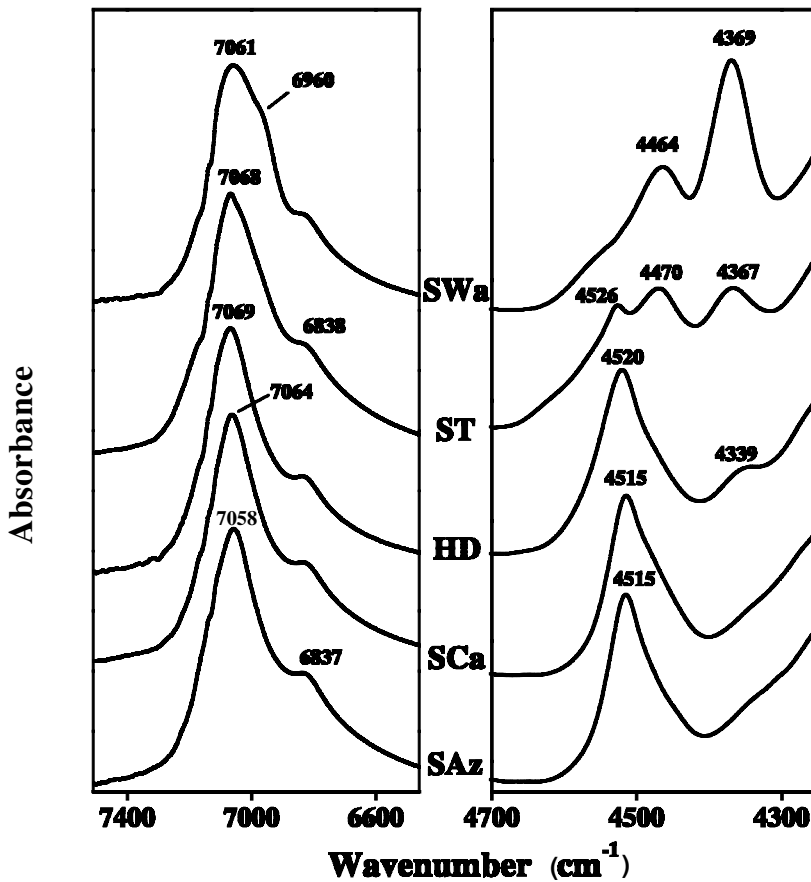


FIG. 3. NIR spectra of unheated smectites in OH-overtone and combination regions.

intensity and is gradually shifted from 7058 cm^{-1} to higher frequencies. Moreover, a new component near 7170 cm^{-1} appears in the spectra of SAz heated above 130°C . Two well resolved bands near 7170 cm^{-1} and 7110 cm^{-1} are present in the spectra of samples heated above 150°C . Since water and structural OH overtones overlap in this region, a substantial reduction in the intensity of this complex band is related mostly to the water content decrease due to dehydration of the interlayer space upon heating. The MIR spectra of the SAz series should be considered to clarify the frequency changes observed in the OH-overtone region. Madejová *et al.* (2000) reported a shift of the OH-stretching band to 3638 cm^{-1} and an

appearance of a new absorption near 3670 cm^{-1} in the spectrum of SAz200. The latter band was evidently associated with the stretching vibration of AlMgLiOH groups, after fixation of Li(I) in the previously vacant octahedral positions. To calculate the frequencies of the first OH overtones, the OH-stretching frequencies at 3638 and 3670 cm^{-1} were doubled and the values of 7276 and 7340 cm^{-1} were obtained. These values are greater by 167 and 168 cm^{-1} , respectively, than the observed frequencies (Fig. 4). Differences of similar magnitude were also observed between the calculated and measured wavenumbers for the OH overtones of kaolinites (Petit *et al.*, 1999). The actual position of the first overtone is lowered due to the anharmonicity of the

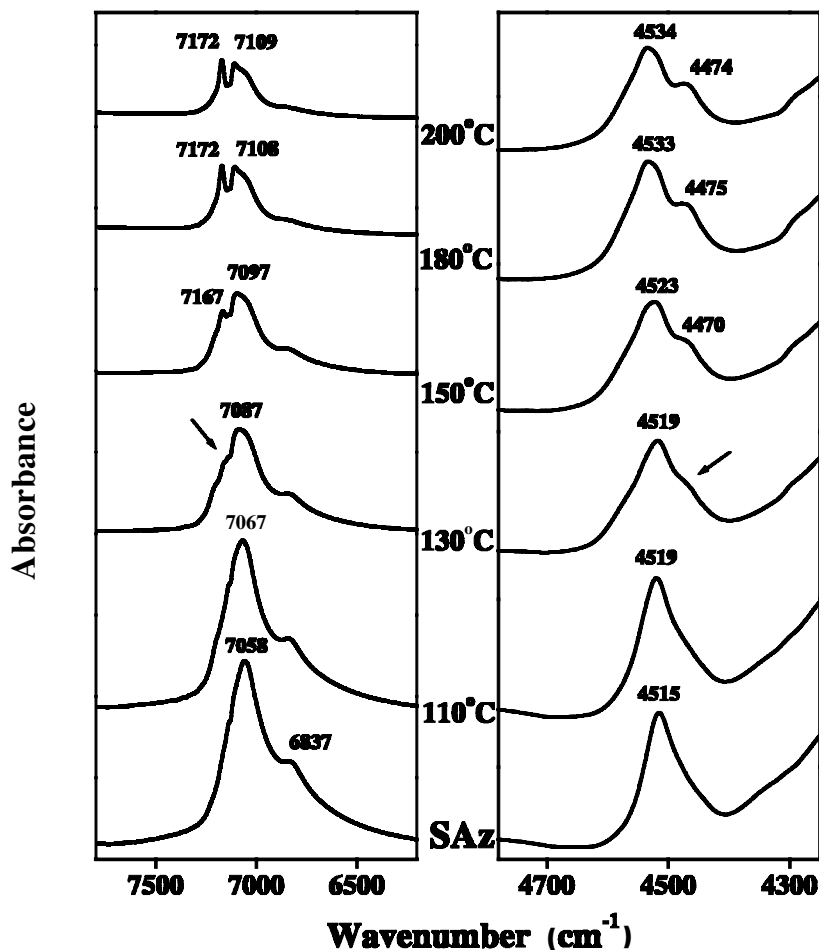


FIG. 4. NIR spectra of SAz samples in the OH-overtone and combination regions: unheated sample and after heating for 24 h at marked temperatures.

oscillator (Szymański, 1964). In contrast to the MIR spectra, the OH-overtone region does not allow for the detection of Li(I) in the octahedra in SAz samples heated below 130°C due to the overlapping of water with the structural OH-overtone bands. On the other hand, identification of the trioctahedral component near 7170 cm⁻¹ in the spectra of SAz150–SAz200 samples is unambiguous and because we used the DRIFT technique, the results were obtained very simply and quickly.

Migration of Li⁺ ions into the clay structure upon heating also influenced the spectral features near 4500 cm⁻¹. A gradual shift of the 4515 cm⁻¹ band to higher frequencies (up to 4534 cm⁻¹ for SAz200) and the appearance of a new band near 4470 cm⁻¹ is shown in Fig. 4. The expected frequencies of the combination bands of heated SAz samples can be calculated from individual OH-stretching and bending frequencies. In Part I of this study, reduced intensity and a shift of the AlAlOH-bending band from 915 to 932 cm⁻¹ was related to the presence of Li(I) in the hexagonal holes close to the structural OH groups. On the other hand, the increasing intensity of the 850 and 803 cm⁻¹ bands, observed in the spectra of SAz heated above 150°C, i.e. for the samples with substantially reduced layer charge, was associated with Li(I) fixed in the previously vacant octahedral sites. The band at 4534 cm⁻¹ observed in the NIR spectra of SAz200 may be attributed to the ($\nu_{\text{AlAlOH}} + \delta_{\text{AlAlOH}}$)

combination of the 3638 + 932 cm⁻¹ bands. However, this assignment would not reflect the observed substantial decrease in the 932 cm⁻¹ band intensity. This fact suggests a more complex character for the 4534 cm⁻¹ band, which, in addition to the ($\nu_{\text{AlAlOH}} + \delta_{\text{AlAlOH}}$) combination mode, should contain a contribution from other modes. Peak-fitting analysis was performed to obtain the individual components of this band. The number of these components was based on the number of OH-bending bands found in the MIR spectra of SAz200. Figure 5 shows the result of the fitting of the spectrum of SAz200. The components at 4558, 4527 and 4471 cm⁻¹ arise from the ($\nu_{3638} + \delta_{932}$), ($\nu_{3670} + \delta_{851}$) and ($\nu_{3670} + \delta_{803}$) combinations, respectively. Comparison of the calculated frequencies (4570, 4521 and 4473 cm⁻¹) with those acquired from band component analysis (Fig. 5) resulted in very good agreement.

Similar changes of spectral features as for the SAz series were also observed for SCa and HD montmorillonites, therefore Fig. 6 shows the OH-overtone and combination regions of selected SCa and HD samples only. Spectra of both montmorillonites show an upward shift and splitting of the $2\nu_{\text{OH}}$ band upon heating. The observed OH frequencies are almost the same for all montmorillonites (compare Figs 4 and 6). However, the slightly lower intensity of the 7170 cm⁻¹ band in the spectrum of HD200, as compared with SAz200

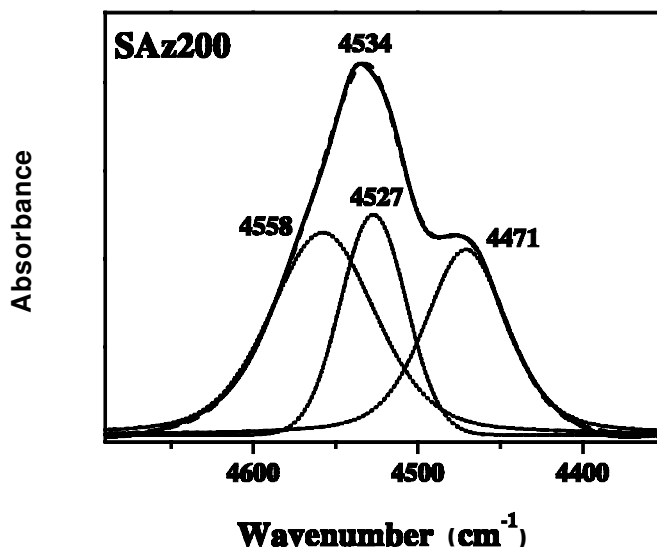


Fig. 5. Band component analysis of the OH combination mode of SAz200.

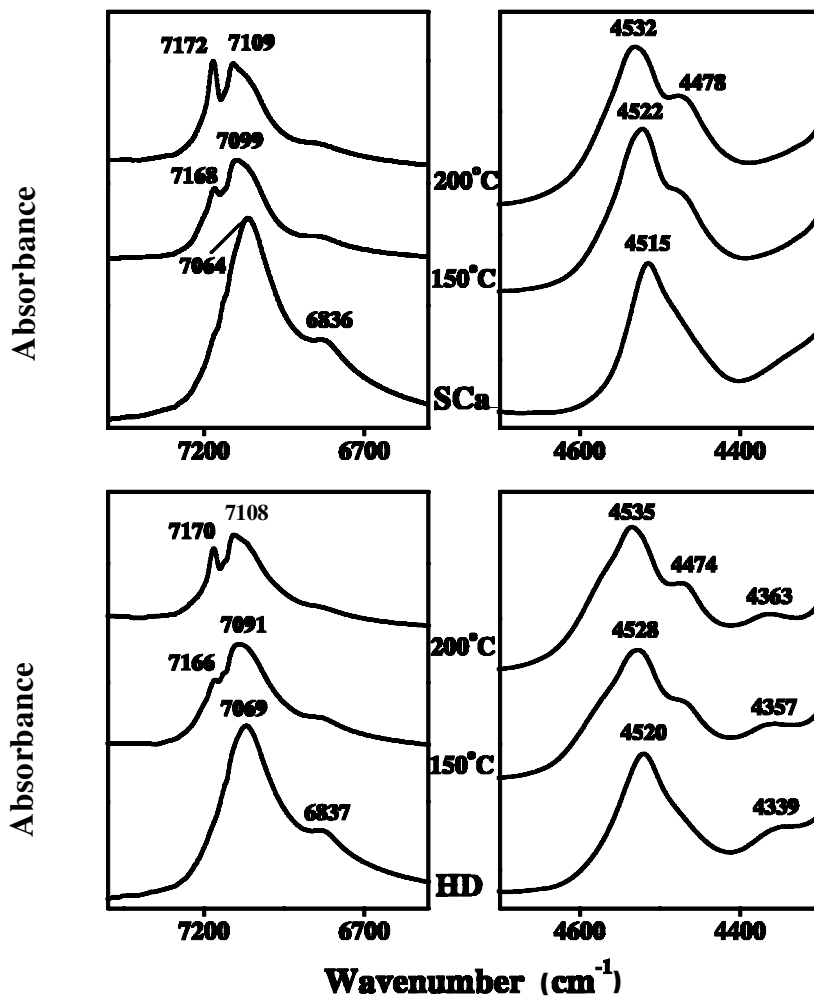


FIG. 6. NIR spectra of SCa and HD samples in the OH-overtone and combination regions: unheated sample and after heating for 24 h at 150 and 200°C.

and SCa200, infers a lower content of AlMgLi groups in the former, arising from migration of less Li(I) into the vacant octahedral positions. Chemical analyses (Madejová *et al.*, 2000) show that SCa and SAz contain much more Mg than HD (1.25, 1.20 and 0.85 Mg per O₂₀(OH)₄, respectively). The combination region of HD shows a similar pattern as for SAz and SCa montmorillonites, and a band near 4340 cm⁻¹ assigned to the ($\nu_{\text{FeMgOH}} + \delta_{\text{FeMgOH}}$) combination mode (Bishop *et al.*, 1999). Identification of the δ_{FeMgOH} bending vibration near 790 cm⁻¹ is very difficult and often impossible in the MIR spectra, because natural smectites

frequently contain various silica admixtures absorbing in the same region. Therefore no FeMgOH-bending band was identified in the MIR spectra of HD. However, the sensitivity of the 4340 cm⁻¹ band to heating suggests that this band is associated with the FeMgOH combination mode. Of all the smectites studied here, HD is the only montmorillonite with a sufficiently high content of both Mg and Fe to have enough FeMgOH groups, to make the FeMgOH combination mode apparent in the NIR spectra.

Heating decreased the layer charge of Li-montmorillonites to a similar extent, while its

effect on Fe-beidellite ST and ferruginous smectite SWa was much less pronounced (Madejová *et al.*, 2000). In both these minerals, tetrahedral charge prevails. Figure 7 shows the NIR spectra for selected ST and SWa samples. In contrast to montmorillonites, no clear, substantial changes upon heating were observed. The combination region of ST exhibits a slight upward shift of the bands at 4470 cm^{-1} and 4367 cm^{-1} , which may indicate that a limited amount of Li(I) is fixed in the hexagonal cavities upon heating to 200°C . No change in the position was observed for the

4526 cm^{-1} band related to the $(\nu_{\text{AlAlOH}} + \delta_{\text{AlAlOH}})$ combination mode of kaolinite impurity in ST (Petit *et al.*, 1999). The NIR spectra of SWa, containing the smallest amount of octahedral Mg of all the smectites studied, showed negligible changes in the positions of the combination bands. The NIR spectra, as well as the MIR spectra, indicated that the octahedral charge deficiency of ST and SWa smectites was too low to attract enough Li^+ ions into the vacant octahedra to provoke the structural changes observed in the montmorillonites by IR spectroscopy.

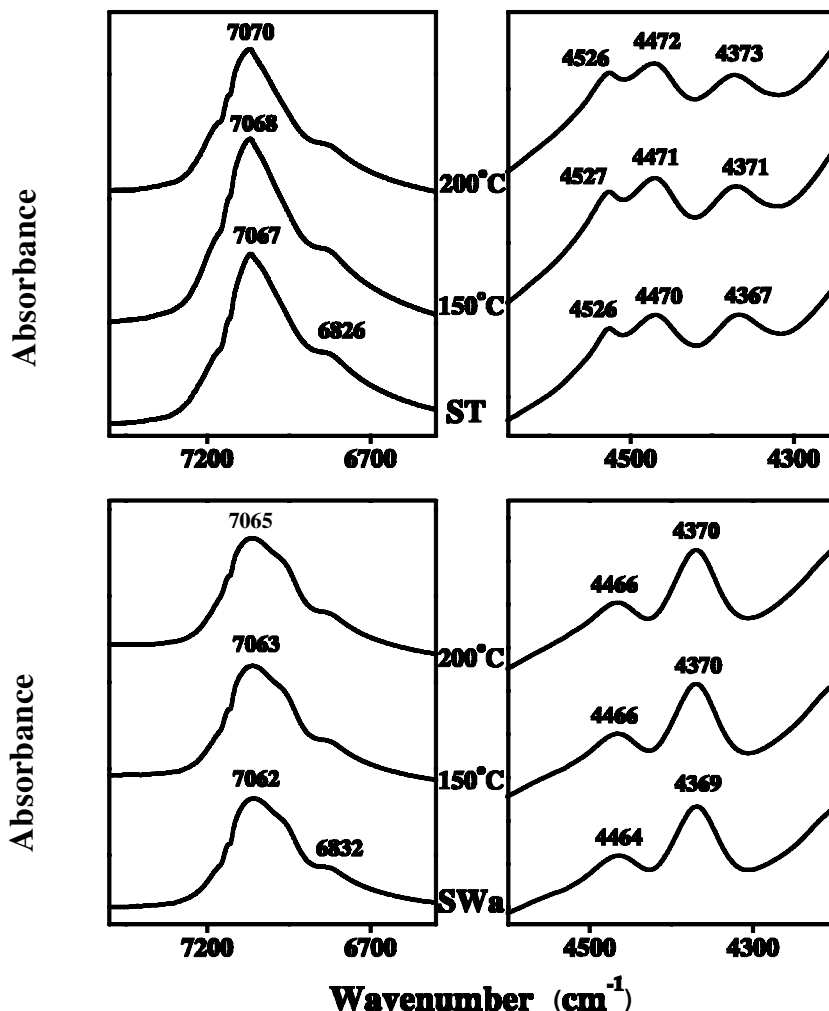


FIG. 7. NIR spectra of ST and SWa samples in the OH-overtone and combination regions: unheated sample and after heating for 24 h at 150 and 200°C .

CONCLUSIONS

The DRIFT spectroscopy in the NIR region is a simple, fast and very powerful tool to help understand Li fixation in smectites. In accordance with the MIR results, no effect of heating was found for the smectites with low octahedral and prevailing tetrahedral charge (ST and SWa). On the other hand, pronounced modifications occurred in the NIR spectra of heat-treated montmorillonites. The band near 7170 cm^{-1} was assigned to the overtone of the AlMgLiOH-stretching vibration. The modification of all combination bands upon heating of Li-montmorillonites reflected the perturbation of both the OH-stretching and bending modes due to the presence of fixed Li(I) in the previously vacant octahedral positions and/or in the hexagonal cavities. The changes in the OH-overtone and combination regions were very similar for SAz, SCa and HD montmorillonites, indicating that Li fixation in the structure occurred similarly for all montmorillonites studied.

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