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A thermo-FTIR-spectroscopy analysis of Al-pillared smectites differing in source of charge, in KBr disks

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Abstract

The reactions occurring by the clay framework during the thermal treatment of montmorillonite, beidellite, saponite, hectorite and Laponite saturated with the Keggin ion $[\mathrm{Al^{IV}O_4Al^{VI}_{12}(OH)_{24}(H_2O)_{12}}]^{7+}$) were investigated by gradual heating KBr disks of the clay samples up to 600°C and recording their FTIR spectra at each 50° increment. During the thermal treatment the Keggin ion undergoes dehydration, dehydroxylation and rearrangements, the latter is seen from changes in the $\mathrm{Al^{IV}}$–O and $\mathrm{Al^{VI}}$–O vibrations. From 500°C clays dehydroxylate and are transformed into new phases with some silanol groups on the surfaces of the tetrahedral sheets. This reaction occurs at lower temperatures in the Keggin-treated smectites compared with Li- or Na-exchanged smectites. At 550°C, there is a condensation reaction of the dehydroxylated Keggin cation with Si–O-groups on the surface of the tetrahedral sheet, giving rise to new bands at 614 and 402 $\mathrm{cm^{-1}}$. This condensation reaction increases considerably at 600°C. The framework of the heated pillared clay preserves the layer structure of the precursor smectite. The adsorption of water by the pillared clays becomes very intense after heating the disks to 600°C.

Keywords: Al-pillared smectites; $\mathrm{A1_{13}}$-treated smectite; Beidellite; Hectorite; Keggin ion-treated smectites; Laponite; Montmorillonite; Saponite; Thermo-IR-spectroscopy analysis

1. Introduction

Pillared clays, sometimes referred to as "cross-linked" clays, are smectites saturated with metal-polyhydroxy cations in the interlayer space. Because of the large distance between the TOT layers, they have the potential of serving as molecular sieves as well as specific adsorbing agents for large molecules, substrates for slow release and cracking catalysts. Al-pillared clay is synthesized in our laboratory by treating Li- or Na-smectite with an aqueous solution of the polyhydroxy cation $[\mathrm{Al^{IV}O_4Al^{VI}_{12}(OH)_{24}\cdot(H_2O)_{12}}]^{7+}$ the so-called "Keggin ion" or $\mathrm{Al_{13}}$. The Keggin-treated clay is then purified by one-week dialysis with double distilled water and the solid phase is gradually heated to 600°C. At 105°C interlayer water is evolved and at higher temperatures the Keggin ion loses its structural water and hydroxyl groups, resulting in an Al-polyoxo cation. At elevated temperatures condensation of the pillaring cation and the surface oxygen plane of the silicate layer may occur. Some investigators define the unheated clay as "pillared" while others call the heated products "pillared clays".

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This work follows a previous XRD study on the thermal behavior and swelling ability of water by the Keggin-treated montmorillonite, beidellite, saponite, hectorite and Laponite (a synthetic hectorite) [1]. All samples were heated stepwise from room temperature up to 600°C, and at each stage, the basal spacings were measured by X-ray diffraction (XRD). They dropped from 1.92 nm at room temperature to 1.68–1.86 nm at 600°C. The same samples were then rehydrated in liquid water, and their swelling by hydration was also determined by changes in the basal spacings. Differences in the swelling behavior of the smectites were related to the differences in the strength of the surface basicity of the O-plane of the TOT layer [2,3].

At room temperature, montmorillonite, hectorite and Laponite which gain their charge mainly from octahedral substitution, swelled in water up to 2.3 nm. Tetrahedrally substituted beidellite and saponite, did not swell, due to the greater basicity of the O-plane of the clay, thereby allowing the formation of stronger H-bonds between either water or the interlayer polyhydroxy cation, and these clays. Swelling of clays heated at 105–500°C in water, was attributed to the dehydrated or dehydroxylated Keggin cation, indicating that dehydroxylation of the cation was still reversible. At 600°C, no swelling occurred in any of the clays, suggesting that some form of condensation had taken place between the pillar and the clay.

The phenomenon of swelling, dehydration, and dehydroxylation in clays, under similar water vapor, pressure and temperature, are determined by the kind and valency of the interlayer cation, the net layer charge, and its location [3–12]. In general basal spacings of tetrahedrally charged smectites are smaller than those of octahedrally charged smectites under the same hydration conditions. Recently, Garfinkel-Shweky and Yariv [13] concluded from the electronic spectrum of adsorbed acridine orange that the basicity of the O-atoms plane was greater for tetrahedrally than for octahedrally substituted smectites. As well, dioctahedral clays exhibited greater surface basicity in the O-atoms plane than did the trioctahedral clays.

In regard to Al-pillared clays, there has been discrepancy as to contribution of the net layer charge and the charge location on the type of bond formed between the oxygen plane and the pillaring ion as the sample is heated. Plee et al. [14] and Pinnavaia et al. [15] reported that no covalent bond was formed between the clay and the Al-pillar at the mild calcination temperature of 350°C. Kloprogge et al. [16] studied the effect of thermal treatment on some of the properties of hydroxy-Al-pillared montmorillonite and beidellite. They concluded that upon calcination at 300°C in pillared beidellite a structural transformation links the pillar to inverted tetrahedra of the tetrahedral sheet, whereas no reaction was observed between the pillars and montmorillonite. This was based on the appearance of a strong OH-band at 300°C which was located in the IR spectrum of pillared beidellite at 3457 cm^{-1}. This band also appeared in pillared montmoriilonite but was considerably weaker. They attributed this band to an Al-silanol (Si–OH–Al)$_{\text{sheet}}$ group which gained its proton from the pillar upon heating. They postulated that during the condensation with the Al-polyhydroxy cation, this Al-silanol group would likely yield an $\mathrm{Al}^{\mathrm{IV}}_{\mathrm{sheet}}{-}\mathrm{O}{-}\mathrm{Al}^{\mathrm{VI}}_{\mathrm{pillar}}$ linkage, rather than a $\mathrm{Si}{-}\mathrm{O}{-}\mathrm{Al}^{\mathrm{VI}}_{\mathrm{pillar}}$ linkage. Sterte and Shabtai [17], however, noted that upon calcination at temperatures between 400°C and 600°C, a gradual condensation between the internal surface and the intercalated Al_{13}oligocation, in montmorillonite did result in the formation of stable covalent Si–O–Al bonds. This assessment was based on changes in basal spacings and surface area that occurred with thermal treatment. Tennakoon et al. [18] concluded from XRD study of Al-pillared montmorillonite that the anchoring of the pillar occurs at temperatures in excess of 400°C and nearer to 500°C. NMR and FTIR results suggested that at ~500°C, there is a condensation of residual hydroxyl groups on the polymeric species with those of the octahedral lattice hydroxyls, to anchor the pillar to the octahedral sheet. That is to say, there occurs a condensation of a pair of adjacent bridging hydroxyl groups, from both above and below the sheet, with a pair of hydroxyl groups on the polymeric species. Such a mechanism, requires a very high activation energy, since it involves the penetration of the Keggin-OH group through the tetrahedral sheet to react with the inner OH-group of the clay.

Bukka et al. [19] noted that the clay–pillar bond may occur through two possible pathways. Firstly, there may be an interaction of the Al_{13} polymer with preexisting tetrahedral OH-groups (as with beidellite), or secondly, with other OH reactive groups formed as intermediates by high temperature (e.g., above 450°C) cleavage reactions of the internal surface layer of the smectite, which may or may not have tetrahedral substitution. Finally, Li et al. [20] studied the NMR peaks and IR-bands of Al-pillared tetrahedrally substituted synthetic saponite, heated in stages to 650°C. Shifts in the NMR peaks, and a decrease in the intensity of the Si–O–Al bending IR-band at $646\,\mathrm{cm}^{-1}$ suggested that, at higher temperatures, reactions between the Si–OH–Al-bridges and the Al_{13} pillars took place on the Si site rather than the Al site.

Clearly, there is the need for further research, to determine the factors in Al-pillared clays, which contribute to the linkage, especially at higher temperatures, between the clay and the pillar. In the present work, we have investigated by using thermo-FTIR-spectroscopy analysis [21], the thermal behavior of the same source clays used in our previous X-ray diffraction study, treated in the same way with the Keggin ion and dialyzed for seven days.

2. Experimental

2.1. Materials and methods

The five clay samples (montmorillonite, beidellite, saponite, hectorite and Laponite), methods of preparation of Li- and Na-smectites, their treatment with the Keggin ion solution and the dialysis of the Keggin-treated clays have been previous described [1].

Infrared spectra were recorded in KBr disks by means of a Nicolet FTIR spectrophotometer. Each disk was prepared by careful abrasion of the KBr (150 mg) with either ground alkali clay or with Keggin-treated clay (2 mg). The disks were then pressed at 10 tonne, reground and repressed, and then entered into an oven, where they were heated for 12 h at 105°C. After this thermal treatment, each disk was repressed for 5 s and was entered immediately into the FTIR instrument in order to minimize the readsorption of water. The same disks were then heated to 150°C, repressed and the spectra were recorded again. This procedure was repeated, each time increasing the temperature in increments of 50°, up to a maximum of 600°C. During heating, water is evolved from the KBr disk forming microholes which cause the disk to be opaque. The disks were carefully repressed without regrinding after each thermal treatment so as not to cause damage. After repressing, the disks became transparent, and the rehydration of the clay was minimized.

Fourier self-deconvolution (FSD), which mathematically separates overlapping spectral features, was carried out by the computer program, *Omnic*, which is a trademark of Nicolet Instruments Corporation.

3. Results and discussion

3.1. The OH stretching vibrations of the smectites and heated smectites

Representative spectra of the hydroxyl stretching region of dioctahedral beidellite, and the trioctahedral hectorite, heated from 105°C to 550°C are shown in Fig. 1. The locations of the framework OH stretching bands as determined at 150°C (not shown in the figure) of the alkali (Na- or Li-) smectites, and of the same smectites treated with the Keggin ion, and their assignments, are summarized in Table 1.

The Keggin OH stretching and water bands in the normal FTIR spectra of Keggin-treated montmorillonite, beidellite and saponite disappear at 250°C. In the spectra of Keggin-treated hectorite and Laponite the OH-bands are first broadened at 200°C, whereas the water bands disappear (Fig. 1). However, the OH-bands are detected by FSD analysis of the spectra of all five Keggin-treated smectites, up to 350°C. These observations prove our previous assumption that during the thermal treatment, the Keggin ion dehydrates and dehydroxylates [1].

During the thermal treatment, the smectites dehydrate and dehydoxylate forming amorphous layered structural phases referred to as metasmectites. In the KBr disks the thermal reactions are more complicated. KBr reacts with the clay, OH-groups are deprotonated, HBr is evolved and K^+ enters into the framework of the phyllosilicate. Heller-Kallai [22,23] heated several montmorillonites saturated with different cations in KBr up to 520°C and showed that most of the exchangeable cations and some of the protons of the hydroxyl groups were replaced by K^+. The ability of the clay to expand decreased and air-dried specimens collapsed to 10 nm. Heller-Kallai and Rozenson [24] compared the dehydroxylation of montmorillo-

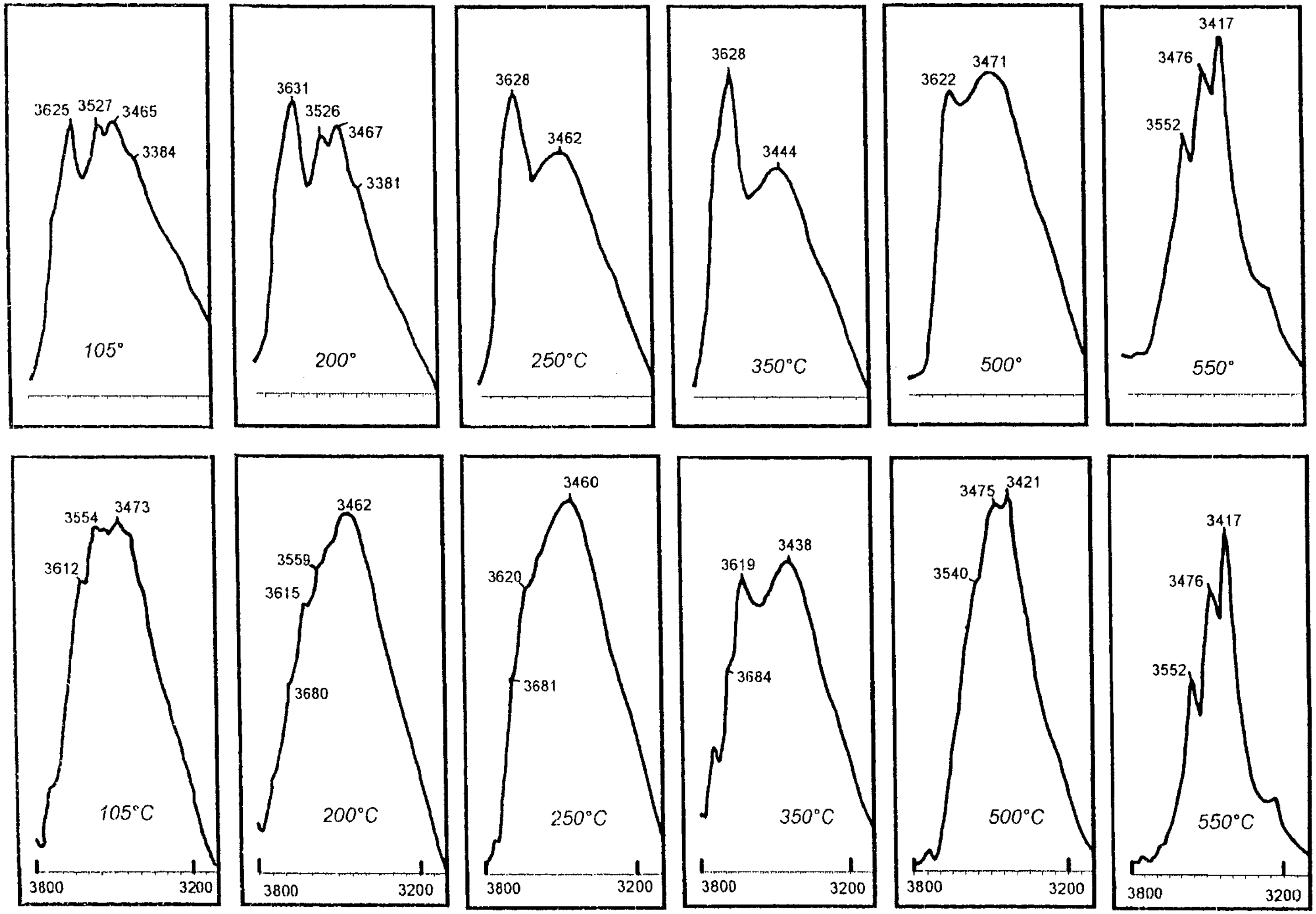

Fig. 1. FTIR spectra of Keggin-treated beidellite (upper curve) and Keggin-treated hectorite (lower curve) after thermal treatments at 105°C, 200°C, 250°C, 350°C, 500°C and 550°C.

Table 1
FTIR frequencies of major bands in monovalent (Li- or Na-) and Keggin-treated smectites heated in KBr disks to 150°C[a]

Assignment	Montmorillonite		Beidelite		Saponite		Hectorite		Laponite	
	A	B	A	B	A	B	A	B	A	B
Framework OH stretch	–	–	–	–	3676	3678	3675	3675	3687	3687
	3631	3627	3633	3627	3617	3627	3628	3628	3630	3630
Keggin OH stretch	–	3526	–	3526	–	3526	–	3526	–	3551
	–	3470	–	3470	–	3464	–	3470	–	3467
Interlayer and Keggin	3428	–	3424	–	3426	–	3427	–	3434	–
H_2O stretch	–	3382[b]	–	3371[b]	–	3375[b]	–	3376	–	3376
	–	–	–	–	–	–	–	3334	–	3334
HOH def.	1643	1640	1641	1641	1643	1645	1640[b]	1647	1641	1638
Si–O stretch	1042	1042	1033	1018	1017	1027	1009	1015	1007	1016
Al–OH–Al bending	911	917	927	918	918	919	–	918[b]	–	–
Keggin–$Al^{(IV)}$OOH	–	749	–	757	–	750	–	750	–	755

[a] A: alkali smectite; B: Keggin-treated smectite. Dashes indicate that bands were not visible.

[b] A shoulder, location determined by FSD analysis.

nite with that of montmorillonite–KBr disk and showed that in the presence of KBr the dehydroxylation is completed at 600°C, whereas in its absence it is completed only at 700°C. The XRD parameter *d*(060) was equal in both cases. It showed a slight decrease between 500°C and 600°C. A minor increment between 600°C and 700°C is slightly higher (by 0.2 pm) in the absence of KBr. From these observations we conclude that up to 600°C, the use of KBr disks in the thermo-IR-spectroscopy analysis of smectites and Keggin-treated smectites should give reliable information on thermal changes in the silicate.

The dehydroxylation is manifested by the weakening and disappearance of the mineral framework OH-bands. However, the formation of the thermal product, is accompanied by the appearance of three new very sharp OH stretching bands at 3417, 3476 and 3553 cm^{-1}. The temperatures at which the mineral framework OH-bands disappear, and at which the three new OH stretching bands appear are summarized in Table 2. Each smectite is characterized by a temperature range, in which the silicate framework is transformed into the new form. It should be remembered that since the measurements were carried out in

Table 2
Temperatures (°C) of the appearance of silanol OH-groups and the disappearance of the framework OH-groups during heating KBr disks of alkali- and Keggin-treated smectites

Smectite	Alkali-exchanged			Keggin-treated		
	A (°C)[a]	*B* (°C)[b]	*C* (°C)[c]	*A* (°C)[a]	*B* (°C)[b]	*C* (°C)[c]
Montmorillonite	550	550	600	400	400	500
Beidellite	550	550	600	500	500[d]	550
Saponite	550	550	>600[e]	400	<500[f]	>550[g]
Hectorite	550	550	>600[e]	450	500	500
Laponite	550	550	>600[e]	450	<550[f]	>550

[a] Lowest temperature in which at least one of the ~3420, 3474 or 3555 cm^{-1} peaks first appear in the FSD spectrum.

[b] Lowest temperature in which at least one of the ~3417, 3475 or 3552 cm^{-1} peaks first appear in the normal spectrum, but may not be fully developed.

[c] Lowest temperature in which the framework OH band is not detected.

[d] Only the band at 3471 cm^{-1} is clearly seen.

[e] A weak framework OH band is detected at this temperature.

[f] The three bands are very intense indicating that a fast reaction started at a lower temperature.

[g] A trace of framework OH band is still detected at this temperature.

intervals of 50°, determination of the exact temperature in which the transformation begins or ends was somewhat limited. Also, the fact that the thermal treatments were carried out in KBr disks, should affect the beginning temperature and the rate of the transformation. Halide ions compete for the protons released from interlayer water and framework hydroxyls [22–24]. This will lead to a fast decrease in the intensity of the OH-band. On the other hand, the evolved gas is, in part, trapped in the disk and thus slows down the reaction [21].

The lowest temperature in which at least one of the 3417, 3476 and 3553 cm^{-1} bands appears for the first time indicates the beginning of a thermal transformation. These temperatures, which are shown in Table 2, Column A, were determined from FSD analyses of the spectra. This technique is useful for detecting bands of species present in small amounts and not observed in normal spectra because their bands overlap absorptions of the principal species. For the natural alkali-exchanged smectite, the thermal product appears for the first time at 550°C. For the synthetic Li-Laponite, the appearance of this product begins already at 500°C, probably because of its very small particles. For the Keggin-treated smectites, the thermal products appear for the first time at lower temperatures.

The reaction rate becomes high enough for the products to be detected in the normal spectrum at the temperatures which are recorded in column B. Table 2 shows that the transformation of the framework occurs at lower temperatures in the Keggin-treated smectites than in the alkali-exchanged smectites. This is due to the release of protons from the acidic Keggin ion, resulting in a self-destructive attack on the clay sheets. These protons migrate into the ditrigonal holes and reach the hydroxyl groups at the O-, OH-planes where they act as catalysts and promote the dehydroxylation process.

Column C represents the lowest temperatures in which the original framework OH stretching and deformation bands of the clay are no longer seen in the spectra. At this temperature, the smectite has been completely dehydroxylated. In the alkali-exchanged, dioctahedral smectites, this is below 600°C. However, the spectra of the alkali-exchanged trioctahedral smectites which are thermally more stable than the dioctahedral smectites, still show at 600°C the presence of the framework OH group at ~3672 cm^{-1}. It was impossible to heat the disks at higher temperatures, because of sublimation of the KBr. In the Keggin-treated smectites the reaction is already completed at 500–550°C. It is to be noted that apart from beidellite, the temperatures of dehydroxylation for the clays in the KBr disks are lower than those recorded for the same smectites in the DTA, TG, and ETA work of Malek et al. [25]. Beidellite, montmorillonite, Laponite and saponite showed dehydroxylation peaks at 530°C, 650°C, 730°C and 810°C, respectively. Besides the effect of KBr, which was discussed, this phenomenon is due to the fact that the rise in temperature, in the latter systems is dynamic, whereas a static heating process is carried out in our FTIR study.

During the thermal transformation of the smectite, water, which is released from the dehydroxylation of the clay, is partly trapped in the disk, and associates with the Si–O–Si, Si–O–Al^{IV}, Si–O–Al^{VI}, and Si–O–Mg bonds, forming through hydrolysis, Si–OH, Al–OH and/or Mg–OH–groups. The fact that the bands at 3417, 3476 and 3553 cm^{-1} appear in the spectra of the heated phases of both di- and trioctahedral clays, i.e., with octahedral Al and Mg, respectively, and in clays with and without tetrahedral substitution, suggests that these bands are predominantly OH-stretching bands of silanol groups. This requires further study.

Silanol is a surface group, and can be obtained on the surface O-plane of the tetrahedral sheet. For this group to be present, it is required that the silicate layer will have high surface area as well as vacancies, cracks and other defects. The thermal products are rich with lattice defects. Fig. 2 shows the spectra of Na-montmorillonite and of Keggin-treated montmorillonite, after they have been heated to 600°C. The figure reveals that the absorbance of the OH-bands in the latter is much higher than in the former. The figure also shows that the intensities of the OH stretching bands relative to the Si–O-band at 1009–1018 cm^{-1} are much higher in the Keggin-treated montmorillonite, compared to the monovalent clay. This is also true for the other four smectites, as shown in Table 3, in which the absorbance of the OH-bands relative to those of the Si–O–bands are given for 550°C and 600°C. This observation indicates that the amount per unit mass of the surface OH-groups in the calcined Keggin-treated smectites, is much higher than in the calcined alkali-exchanged smectites, suggesting that the framework components of the former have larger surface areas than those of the latter. This supports our XRD observations

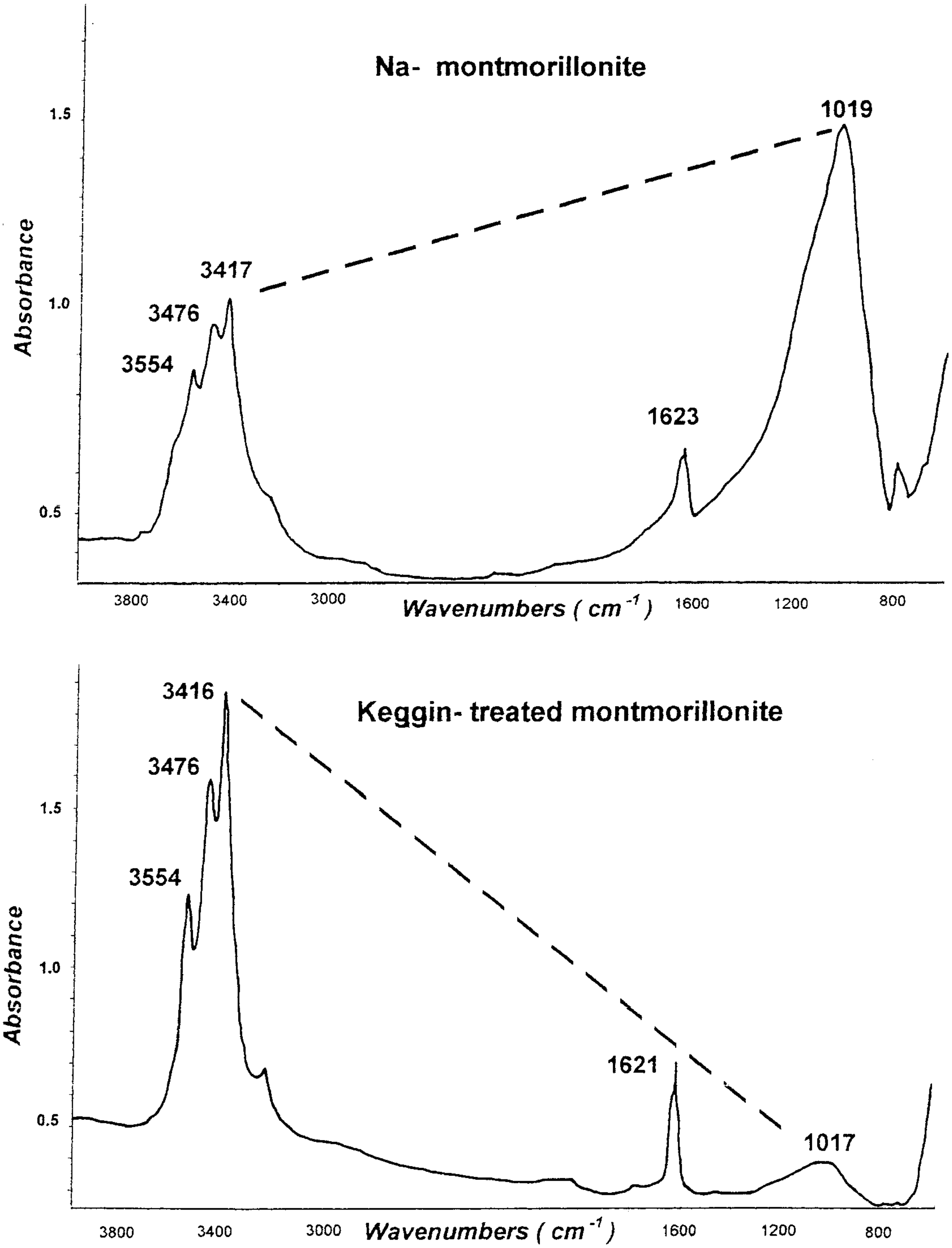

Fig. 2. Comparison of OH Stretching bands to Si–O stretching band in Na and Keggin-treated montmorillonite gradually heated to 600°C.

Table 3
Absorbance rations of the O–H stretching bands relative to the main Si–O stretching band in alkali-exchanged and Keggin-treated smectities, heated in KBr disks at 550°C and 600°C[a]

	Alkali-exchanged clays			Keggin-treated clays		
	Ratio 3/4	Ratio 2/4	Ratio 1/4	Ratio 3/4	Ratio 2/4	Ratio 1/4
Montmorillonite						
550°C	0.01	0.02	–	0.46	0.30	0.13
600°C	0.15	0.07	0.10	4.69	2.33	1.95
Beidellite						
550°C	0.04	0.03	0.01	0.36	0.22	0.19
600°C	0.22	0.13	0.18	1.80	0.81	0.87
Saponite						
550°C	0.02	0.04	0.01	0.40	0.24	0.22
600°C	0.80	0.40	0.47	1.07	0.65	0.81
Hectorite						
550°C	0.03	0.04	0.02	0.84	0.39	0.36
600°C	0.77	0.34	0.46	2.76	1.21	1.31
Laponite						
550°C	0.06	0.04	0.03	0.18	0.08	0.07
600°C	0.50	0.25	0.28	1.08	0.48	0.54

[a] Bands 1,2, and 3 are OH stretching bands at 3535, 3478 and 3417 cm^{-1}, respectively. Band 4 is the Si–O stretching band. Location of band 4 at 550°C and 600°C is given in Fig. 4. Absorbance ratios were determined by the computer program *Omnic,* a trademark of Nicolet Instruments Corporation.

that in pillared clays, the TOT layers are separated one from another by the pillar also at 600°C [1].

Table 3 also shows that the intensity ratios of the OH : Si–O-bands are higher at 600°C compared with 550°C. This indicates that the hydrolysis of the different oxo groups is much higher at 600°C as compared to 550°C. Finally, the table shows that the amount of hydroxyls per unit mass (and the surface area), in the phase obtained from the alkali-exchanged trioctahedral saponite is higher than in those obtained from the dioctahedral smectites. The relation is reversed in the Keggin-treated smectites. In this case, the amount of OH-groups per unit mass (and surface area) in the heated silicate component are higher in the dioctahedral smectites. The Keggin-treated trioctahedral hectorite is an exception, but this mineral and Laponite behave in a different manner which requires further clarification.

3.2. *The water deformation band*

The behavior of water under the influence of temperature in the alkali-exchanged and pillared clays can be derived from the intensity of the deformation water band (1638–1647 cm^{-1}). For this purpose, changes in the absorbance of the water band were determined as a function of temperature. Absorbance curves (absorbance vs. temperature) derived from the spectra of alkali and Keggin-treated smectites, are given in Fig. 3. From these absorbance curves, only trends in dehydration and rehydration behavior can be obtained, and not quantitative data. The highest water content for all clays is found before any thermal treatment of the disks. Under these conditions, the HOH-band intensity is extremely high and not reproducible, and therefore is not included in this figure. All spectra, obtained after heating the disks at 105°C, were recorded after the loss of considerable amounts of free and interlayer water.

The behavior of water in the alkali-exchanged smectites, as determined from the absorbance curves of the H_2O deformation band, is as follows. With montmorillonite, beidellite and saponite, there is a very slight interlayer water loss, due to evaporation, as the disk is heated above 100°C. From 150–250°C, the three alkali smectites show a gradual but slight increase up to 550°C. At 600°C, as a result of dehydroxylation of the clay, and the formation of water

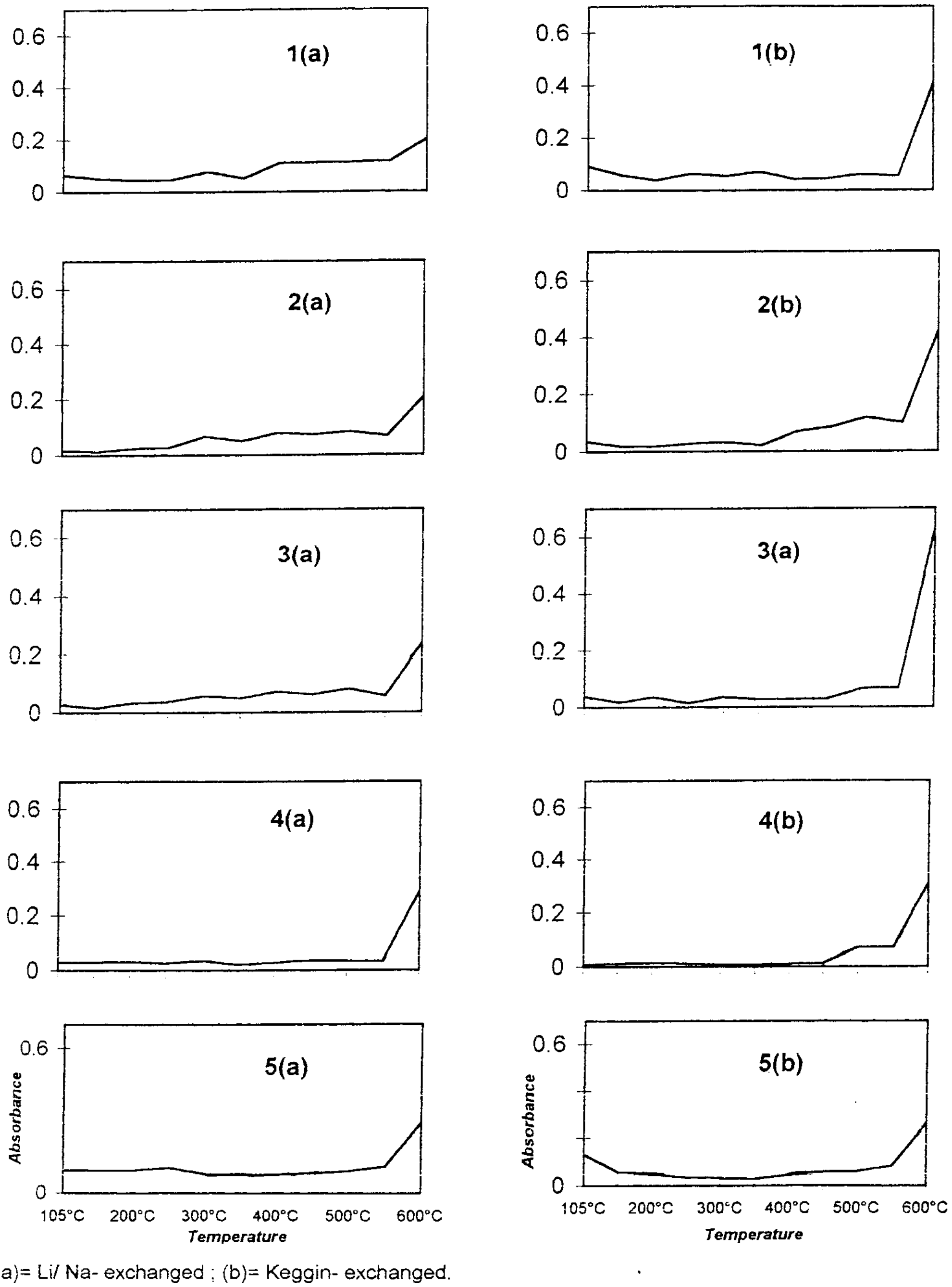

Fig. 3. The effect of temperature on absorbance (a.u.) of the H_2O deformation band in five clays. 1, montmorillonite; 2, beidellite; 3, saponite; 4, hectorite; 5, Laponite. Left, alkali smectites; right, Keggin-treated smectites.

from this process, there is a sudden rise in water content. This evolved water is trapped in the disk and is adsorbed by the silicate framework.

No significant changes were observed in the water band absorbance curves of Li-hectorite and Li-Laponite from 105°C up to 550°C. Between 550°C and 600°C, there is a sudden rise in the water content, as was shown for the other three smectites. Water adsorption by the trioctahedral clays, at this stage, is higher than the adsorption by the dioctahedral clays.

The behavior of water in the Keggin-treated smectites is as follows. The Keggin montmorillonite, beidellite and saponite show a slight water loss up to 150–200°C. At this stage, when the Keggin ion begins to dehydrate and reorganize, there is first of all a plateau, followed by a slight increase in water content up to 550°C. At 600°C, there is also a large jump in the intensity of the water band, as was seen in the alkali-exchanged clays. But with the Keggin-smectites, this jump is about 2.5 times the intensity of the absorbance seen in the curves of the alkali-smectites. As mentioned previously, the hygroscopic thermal treated smectites readsorb water evolved from dehydroxylation and perhaps also from the atmosphere.

The Keggin-treated hectorite shows a plateau between 105°C and 450°C. Water content then increases at 500°C. As with the other Keggin-treated clays, there is a jump in the water content at 600°C, but the value of the absorbance is about the same as that of the alkali-exchanged hectorite, and is much smaller compared to Keggin-treated montmorillonite, beidellite and saponite. The Keggin-treated Laponite loses water up to 150°C, followed by a slight loss up to 350°C. Above 350°C, there is a slight rise in the absorbance up to 550°C. Again at 600°C, there is a jump in the absorbance, but is similar in intensity to that shown in Keggin-treated hectorite and the alkali clays. As with hectorite, this absorbance is much smaller compared with the Keggin-treated montmorillonite, beidellite and saponite.

These experiments suggest that the products obtained at 600°C from the Keggin-treated montmorillonite, beidellite and saponite have very high adsorption capacities, much higher than those of the heated alkali-smectites. The adsorption capacity of the pillared smectites decreases in the order: saponite, beidellite and montmorillonite. The products obtained from Keggin-treated hectorite and Laponite at 600°C differ from those obtained from the other three smectites and their capacity to adsorb water is much smaller.

3.3. The Si–O stretching band

The location of the Si–O stretching band at 150°C lies at 1009–1042 cm^{-1} (Table 1). Apart from Laponite, at temperatures above 450°C, this band in the spectra of the alkali-exchanged smectites is gradually shifted to lower frequencies (Figs. 4 and 5). This is due to the penetration of cations (including K^+ from KBr) into the silicate sheet [22,23]. This shift is significant in the spectra of the dioctahedral smectites, but is smaller in the trioctahedral clays in agreement with the greater number of vacancies found in the framework of the former. Shifts to lower frequencies at elevated temperatures are also observed in the spectra of the Keggin-treated montmorillonite and beidellite, and to a smaller extent in the spectra of saponite and hectorite. No systematic changes were obtained with the Keggin-treated Laponite.

Since the same disk was gradually heated from room temperature to 600°C, without adding or removing material, it is expected that changes in the absorbance of the Si–O-band, versus temperature (absorbance curves), should be reliable in giving information on trends in possible changes in the structure of the clay skeleton, in which the Si–O bond is involved. The absorbance curves of the five Keggin-treated smectites are almost linear.

The absorbance curves of the five alkali-exchanged smectites show two steps, at 105–250°C, and at 300–600°C, with a rise in the absorbance. In the case of montmorillonite, the rise continues up to 400°C. In general, the absorbance of the second step is about 1.5–3.0 times higher than that of the first step. In the case of beidellite, absorbance of the second step is 7.5 times higher than that of the first step. The first step absorbance of the Si–O group is higher in the octahedral substituted clays and lower in the tetrahedral substituted clays. Furthermore, the second step absorbance is higher in the dioctahedral and lower in the trioctahedral clays. This suggests that the changes between the original phase and the thermal product are more significant in the dioctahedral, compared with the trioctahedral smectites.

Any change in absorbance should be associated with a change in the direction of the dipoles which

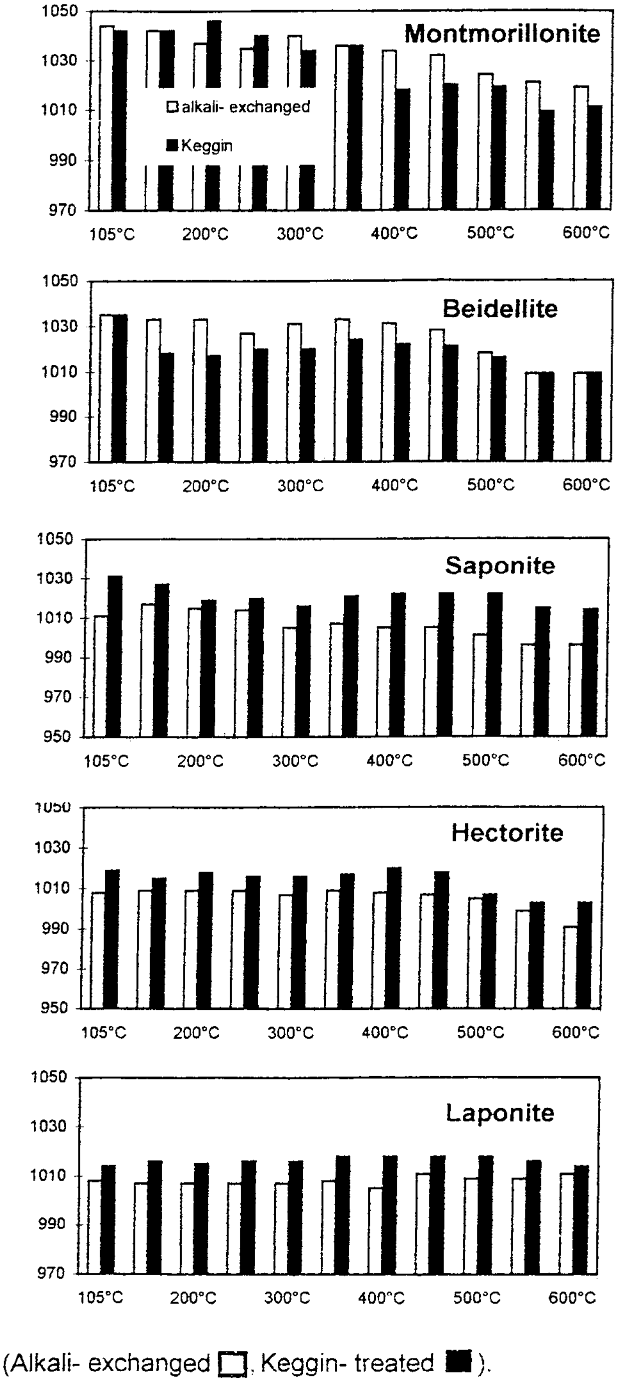

Fig. 4. The effect of temperature on the frequencies of the principle Si–O stretching band in five alkali and Keggin-treated smectites.

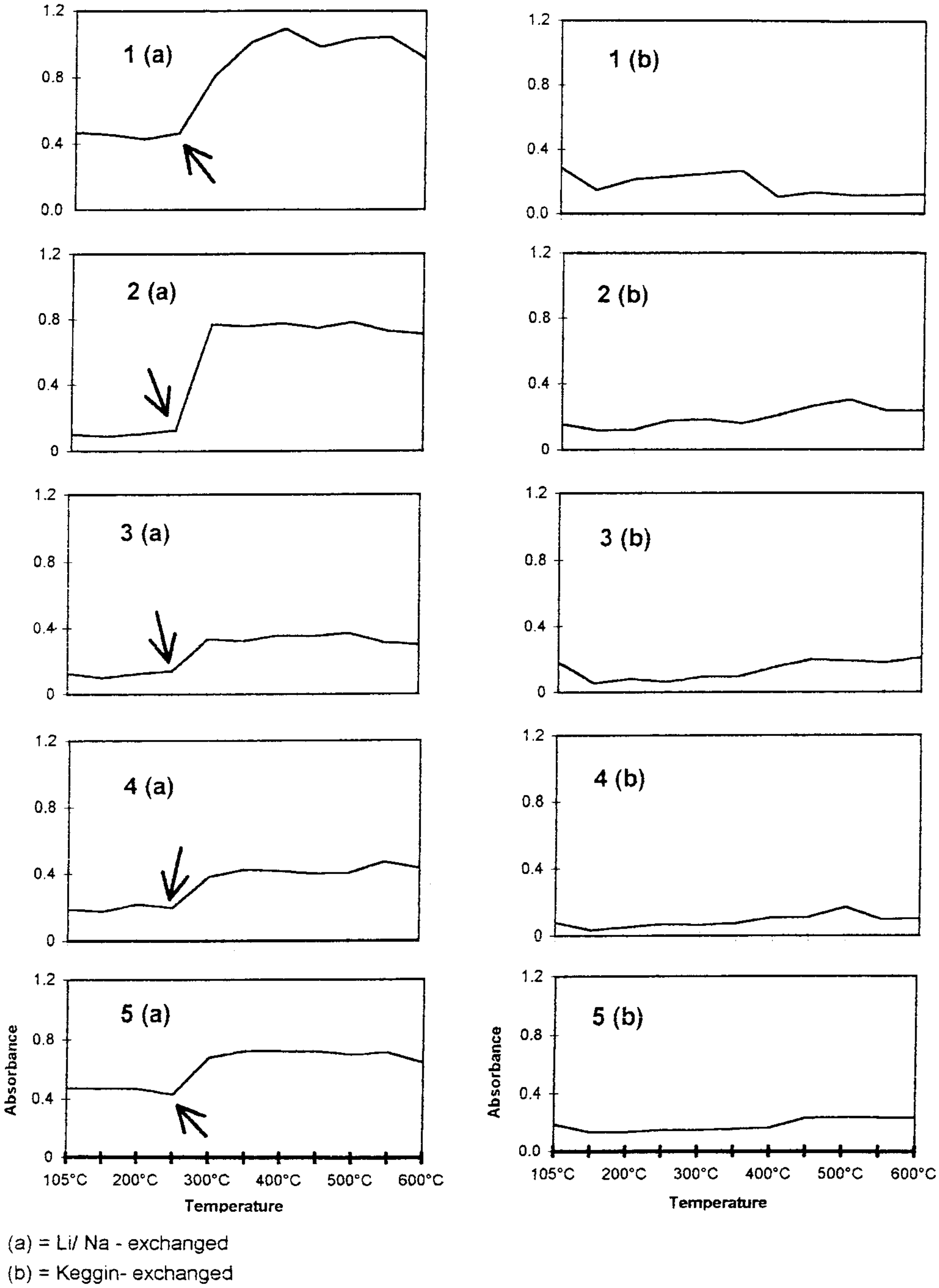

Fig. 5. Absorbance (a.u.) of the Si–O stretching band of five clays heated from 105°C to 600°C. 1, montmorillonite; 2, beidellite; 3, saponite; 4, hectorite; 5, Laponite. Left, alkali smectites; right, Keggin-treated smectites.

exist in the silicate framework. In the present study, the rise in absorbance, which was observed in the spectra of the alkali-exchanged smectites with the rise in temperature, may indicate a new order in the Si–O framework such that the dipoles are more strongly coupled. This was not observed in the spectra of the Keggin-treated smectites with thermal treatment, indicating that in these complexes the original skeleton of the TOT layer persisted even at 600°C. This, in turn, suggests that the silicate framework which is formed in the presence of the Al-polyoxo cation differs from the framework which was formed in its absence. The former preserves the layer structure of the precursor clay, and consequently shows a well defined peak in X-ray diffraction, even after thermal treatment at 600°C [1].

3.4. The Al^{IV}–O stretching band of the Al-oligoineric cation

In the spectra of pillared montmorillonite, beidellite and saponite, a very weak band is observed at room temperature between 748 and 756 cm^{-1}. A band at 729 cm^{-1}in the spectrum of the salt Keggin-sulfate was attributed by Bradley et al. [26] to Al^{IV}–O. The band in our pillared samples may therefore reveal the presence of tetrahedral aluminum in the Al-oligomeric cation. This band shifts to slightly higher frequencies and becomes even weaker with a rise in temperature (150–350°C), indicating that structural changes occur during the dehydration and dehydroxylation of the Keggin ion. However, at 400°C, it intensifies, forming a prominent band at 750 cm^{-1}. The strong band persists up to 550°C, but becomes weak or disappears again at 600°C. Fig. 6 shows the FTIR spectra of Keggin-treated montmorillonite, beidellite, saponite, hectorite and Laponite in the 650–830 cm^{-1} range and the changes in these spectra with temperature. These observations may indicate that the adsorbed Al polycation undergoes rearrangements at different temperatures. The rearrangement which was observed to give a strong FTIR-band starting from 400°C, is in agreement with our X-ray diffraction study, which also showed rearrangements occurring at ≥350°C [1].

A small band is observed at 795 cm^{-1} which overlaps a quartz band. This band appears in the spectrum of the Keggin-treated Laponite which does not contain quartz, indicating that its origin is not from the clay sample, but rather from the added Keggin ion. In the other clays, the band is always stronger in the spectra of the Keggin-treated samples compared with the monovalent samples. This band is weak at the lower temperatures. During thermal treatment, it becomes more intense relative to the 755 cm^{-1} band. It reaches a maximum at 500°C in montmorillonite, beidellite, saponite and Laponite. In hectorite, however, this band is at a maximum at 300°C. At higher temperatures, the relative intensity of this band decreases. At 600°C, it has almost disappeared. These changes in relative intensity indicate that this band is not of quartz, but rather of adsorbed species, which have undergone rearrangements with the change in temperature as were previously observed from X-ray diffractions (Fig. 7 in [1]). This band probably has a contribution from Al^{VI}–O.

3.5. The bands at 614 cm^{-1} and 402 cm^{-1}

At 550°C, the spectra of the Keggin-treated clays show two new medium-sized bands at ~614 and ~402 cm^{-1} which are considerably intensified at 600°C (Fig. 7). The spectra of the monovalent dioctahedral smectites at 550°C, show only very weak shoulders in these two regions, which slightly intensify at 600°C. We suggest that these bands have a contribution from Si–O–A1-groups which are formed during the dehydroxylation of the smectite, by the condensation of the Al-polyoxo ion with siloxane groups of the tetrahedral sheet. Similar groups should be present as well in the heated alkali montmorillonite and beidellite, due to tetrahedral substitution of Al for Si in these clays. When the trioctahedral alkali smectites (Li-saponite, hectorite and Laponite) are heated at 550–600°C, the spectra show a weak band at 612, 606 and 608 cm^{-1}, respectively, which may be related to Si–O–Mg absorption. However, when the trioctahedral Keggin-treated clays are heated to 550–600°C, a very prominent band appears at 614 cm^{-1}, together with a weak band at 402 cm^{-1}.

The intensities (in absorbance units) of the main band at 614 cm^{-1} in the spectra of the alkali- and Keggin-treated clays at 550°C and 600°C, are depicted in Table 4, together with those of the Si–O vibrations. The values given in the table show drastic effects of the Al-oligomer on the intensity of this band in the spectra of montmorillonite, beidellite

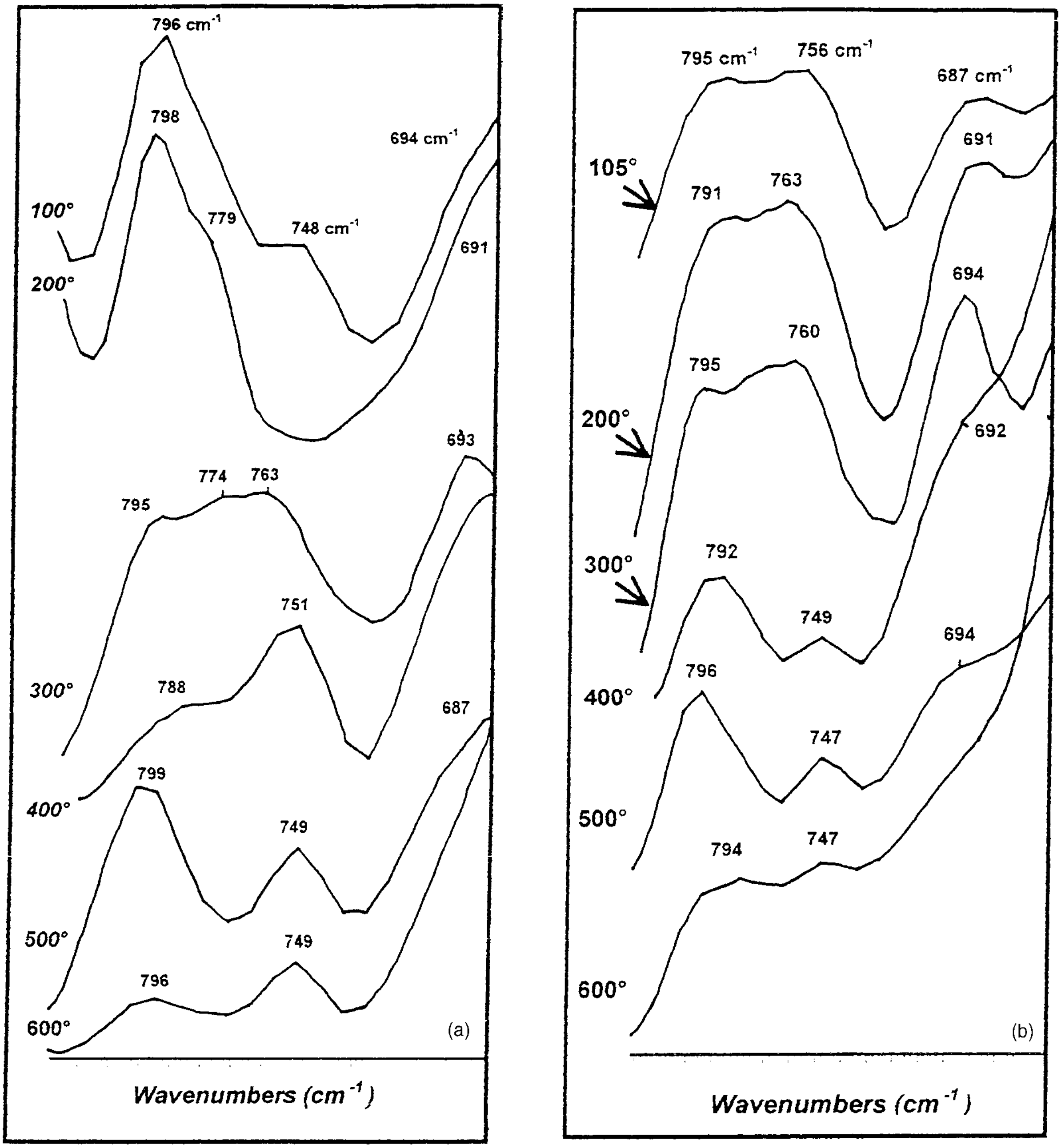

Fig. 6. FTIR spectra of Keggin-treated smectites showing changes in the Al^{IV}–O and Al^{VI}–O absorption band with temperature: (a) montmorillonite; (b) beidellite; (c) saponite; (d) hectorite; (e) Laponite.

and saponite, and smaller effects in the spectra of hectorite and Laponite, in agreement with the fact that the pillaring in the latter takes place to a small extent only.

4. Conclusions

IR absorption spectra were used to study the thermal reactions of the smectite framework during the

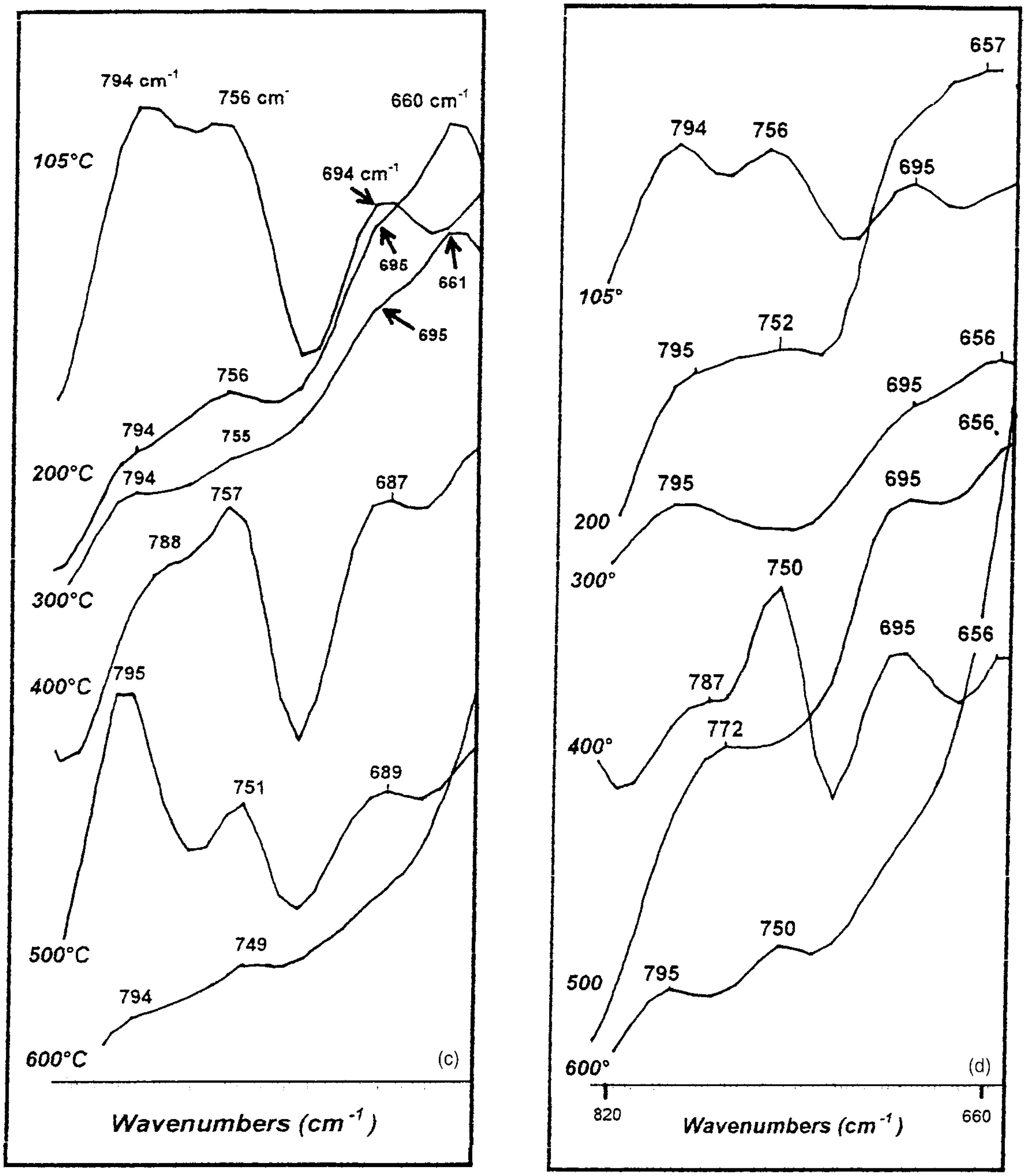

Fig. 6. (*Continued*).

heating of the Keggin-treated smectites to accomplish our previous XRD study of the dehydration and dehydroxylation of these clays [1]. Upon heating the smectite phase is dehydroxylated and converted to a new layered phase with some silanol surface groups. The presence of the Al-oligomeric cations in the interlayer, catalyses the dehydroxylation of the smectite framework which takes place at lower

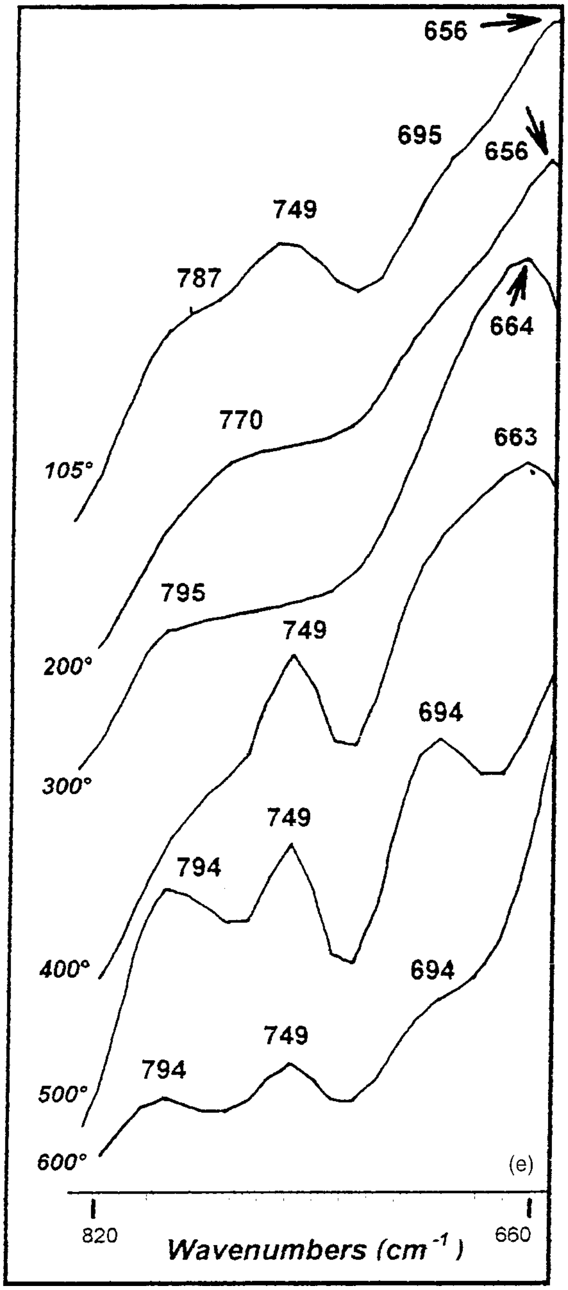

Fig. 6. (*Continued*).

temperatures compared with similar thermal reactions in alkali smectites. The thermal products of the Keggin-treated smectites differ from those obtained from alkali smectites. The former preserve the layer structure of the precursor clay, whereas the latter develop a

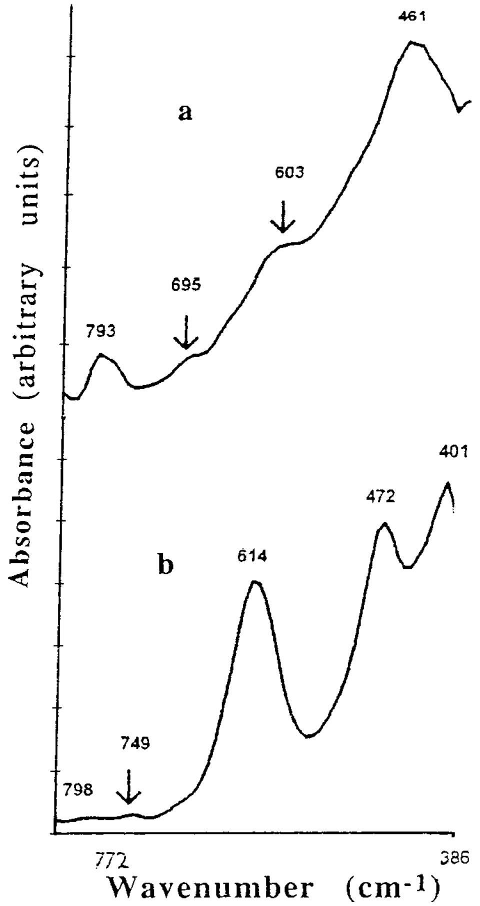

Fig. 7. FTIR spectra in the 380–800 cm^{-1} range of Na-montmorillonite (a) and Keggin-treated montmorillonite (b), heated gradually to 600°C.

new order in the Si–O framework, such that the dipoles are more strongly coupled.

Our previous XRD data was compatible with the assumption that during the thermal treatment of these smectites, the adsorbed Keggin ion is dehydrated and dehydroxylated [1]. Below 600°C, these thermal processes are reversible, and the XRD study showed that the heated samples readsorb water and expand. Heating the dehydroxylated Keggin-smectite is accompanied by changes in the Al–O skeleton of the cation. In the present work these changes are manifested by changes in the locations and intensities of the Al^{IV}–O and Al^{VI}–O absorption bands with temperature, parallel to the changes in the basal spacings which were described in our previous paper [1].

Table 4
Intensities (absorbance units per 2 mg clay/150 mg KBr) of the Si–O stretching and deformation bands (Columns A and C, respectively) and of the M–O–Si vibration (Column B) in alkali and Keggin-treated smectites

Smectite	Temp. (°C)	Alkali-exchanged smectites			Keggin-treated smectites		
		A (l000–1025 cm^{-1})	B (602–615 cm^{-1})	C (460–475 cm^{-1})	A (l000–1025 cm^{-1})	B (602–615 cm^{-1})	C (460–475 cm^{-1})
Montmorillonite	550°	1.039	0.019	0.410	0.108	0.026	0.040
	600°	0.961	0.040	0.319	0.123	0.297	0.133
Beidellite	550°	0.745	0.003	0.335	0.244	0.028	0.089
	600°	0.689	0.019	0.260	0.236	0.245	0.127
Saponite	550°	0.300	0.050	0.08S	0.190	0.027	0.058
	600°	0.330	0.097	0.144	0.220	0.286	0.165
Hectorite	550°	0.424	0.005	0.216	0.098	0.040	0.046
	600°	0.374	0.119	0.157	0.103	0.168	0.096
Laponite	550°	0.715	0.001	0.286	0.247	0.016	0.111
	600°	0.630	0.124	0.250	0.231	0.144	0.107

At 550°C, two new bands appear in the FTIR spectra. These two bands become very intense at 600°C, and are thought to be characteristic of the products of condensation of the Al-polyoxo cations with siloxanes at the surfaces of the tetrahedral sheets. As a result of this condensation reaction, the smectites lose their expansion ability, nevertheless, the greatest amounts of water were adsorbed by the pillared montmorillonite, beidellite and saponite after thermal treatment at 600°C. Keggin-treated hectorite and Laponite show most of these thermal phenomena, but to a smaller degree. The FTIR results support our previous suggestion, that in the interlayer space of these two smectites, different types of AI-polyhydroxy cations exist. This will be further investigated at a later stage of our work.

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