XRD STUDY OF THE DEHYDRATION AND REHYDRATION BEHAVIOUR OF Al-PILLARED SMECTITES DIFFERING IN SOURCE OF CHARGE

S. Aceman[1]*, N. Lahav*[1] *and S. Yariv*[2]

[1]The Seagram Center for Soil and Water Sciences, Faculty of Agriculture, The Hebrew University of Jerusalem, Rehovot, 76100
[2]The Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Abstract

The swelling properties of Al-pillared clays, obtained from five different smectites, were studied using X-ray diffraction. These clays, the dioctahedral beidellite and montmorillonite and the trioctahedral saponite, hectorite and laponite differ in source of isomorphic substitution and represent a series of decreasing basicity along the siloxane plane. An Al oxyhydroxy cation was inserted between the layers to form the respective pillared clays and these clays were heated incrementally to 600°C. The XRD peaks at each stage of heating were recorded as well as the same samples subsequently wetted. Basal spacings of each clay at each stage of dehydration and rehydration indicated that the swelling of tetrahedrally substituted saponite and beidellite was indeed restricted, compared with the other three clays. This was attributed to greater basicity of the oxygen plane of beidellite and saponite due to tetrahedral substitution of Si by Al, resulting in an increase in the strength of hydrogen bonds between either water or the interlayer polyhydroxy cation and the clay.

The data from the XRD analyses helped in addition, to clarify the thermal transformations of the Keggin ion itself. According to the changes in the d-spacings of the pillared clays it was concluded that the Keggin ion lost its structural water at ~200°C and dehydroxylated in a range beginning at 350°C. Between 500 to 600°C this polymer cation, which is thought to form the Al_2O_3 oxide, did not rehydrate.

Keywords: beidellite, hectorite, Keggin ion, montmorillonite, pillared clays, saponite, XRD

Introduction

The pillaring of smectite clays by polyhydroxy cations has been known for approximately two decades [1–3]. The so-called pillared clays (or PILCS), earlier referred to as "cross-linked", are synthesized by intercalating the interlamellar space of the silicate layers with an oligomer cation. Then the intercalated

clays are heated to high temperatures (usually between 350 and 550°C) [3–8] to form what amounts to a molecular sieve. Numerous studies [1–8] have focused primarily on the various methods of preparation including substituting a wide range of pillaring agents. There is as yet, however, still much to be learned about the mechanism of linkage between the pillar and the oxygen plane of the clay mineral and, in particular, the effect of the basicity of the O-plane on the properties of the pillared clay.

According to Yariv [9–11] the basic strength of the oxygen plane of the clay is slightly higher for dioctahedral clays then for trioctahedral clays. Also, the basic strength increases with the degree of tetrahedral substitution of Si by Al. The stronger the basicity of the O-plane, the stronger the bond formed between this plane and any hydrated cation in the interlayer. In particular, hydrogen bonds between protons of the Al polyhydroxy cations and atoms of the oxygen plane which are part of the siloxane groups will result in decrease or cancellation of the swelling capacity in water and other liquids. The hydrogen bond is obtained by the interaction between the water-proton and the lone-pair electrons in a hybridized orbital of the oxygen.

We therefore undertook a study whereby an aluminum polyhydroxy cation $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}$, (the so-called Al_{13} Keggin ion) [12] was inserted or 'pillared' into five clays, namely montmorillonite, beidellite, saponite, hectorite and its synthetic analogue, laponite. These clays represent a series differing in source and extent of isomorphic substitution. The extent of swelling, as well as any changes in the size of the intercalated Al_{13} cationic species is reflected in the basal spacings of the clay as determined by X-ray diffraction.

The purpose of this study was to examine the differences in swelling behaviour of the four pillared clays, which were first of all dried at room temperature, followed by increasingly higher temperatures, and (then subsequently) wetted after each thermal treatment. It was hoped that this XRD study might shed some light on the type of bonding which occurs between the pillaring agent and the clay sheets, as well as the kind of changes which the Al_{13} cation undergoes in different stages of dehydration and rehydration.

Experimental

Materials

The four natural clays under study were purchased from the Clay Minerals Repository and included the following: a) beidellite (SBCa-1), mainly tetrahedral substitution, dioctahedral; b) montmorillonite (Swy-1), mainly octahedral substitution, dioctahedral; c) saponite (SapCa-1), mainly tetrahedral substitution, trioctahedral; d) hectorite (SHCa-1), mainly octahedral substitution, trioctahedral; e) laponite (XLG), a synthetic Na-hectorite. Laponite was kindly sup-

plied by Laporte Industries, UK. $AlCl_3$ and NaOH both of analytical grade were supplied by Merck and Reidel/deHan respectively. The dialysis tubes were supplied by Medicell International Ltd.

Methods

The aluminum pillaring solution was prepared according to the method of Lahav *et al.* [2, 3]. An aqueous 0.2 M NaOH solution was added to a solution of 0.2 M $AlCl_3$ with vigorous stirring at a rate of 1 ml min^{-1}. The final hydrolysis ratio (R value) of OH:Al was 2.3 and the final concentration of Al was 0.07 M. This solution was aged for 30 days. It has been proposed that under these conditions, the solution contains mostly isolated Al_{13} units, whereas aggregation of the Keggin ion starts at higher R values [13–15]. The clays were ion exchanged with Na (montmorillonite) or Li (beidellite, saponite, hectorite and laponite) by washing 5 times with a 1.0 N solution of NaCl or LiCl; the excess Cl was removed by dialysis. The monoionic clay suspensions were prepared with a final concentration of 1.66 g clay per liter of double-distilled water. The pillaring solution was then added dropwise under vigorous stirring to the clay suspension, so that a ratio of 5 mM Al per gm clay was obtained. After 24 h the suspensions were placed in Visking dialysis tubes dipped in double distilled water and aged for one week. The *pH* of these suspensions inside the dialysis bags was measured every day on a PHM 93 Reference pH Meter, Radiometer Copenhagen. Subsequently, several drops of each sample were placed on glass slides so as to prepare thin films for X-ray (XRD) analysis. These slides of each clay mineral were then air-dried at room temperature, followed by heating to 105, 200, 350, 400, 500 and 600°C for 8 h. After each thermal treatment the samples were immediately X-rayed. Dried and heated slides were subsequently saturated in water and enclosed in small plastic nylon bags sealed with tape. After 48 h the rehydrated samples were examined by XRD. The diffractograms were recorded by a Philips X-ray diffractometer with Fe-filtered CoK_{α_1} radiation.

Results and interpretation

pH measurements

The initial *pH* of the solution which contained the Keggin ion was 4.2. After adding this solution to the clay suspensions, the *pH* changed according to Table 1. It should be noted that the initial *pH* of the hectorite suspension was above 8 and dropped only to 7.5 when the Keggin ion was added to the suspension. At this *pH* the Keggin ion is thought to hardly exist [16–18] and it is expected that the adsorbed species have different forms. For laponite, the drop in *pH* after add-

Table 1 pH measuremets of aqueous clay suspensions during aging and dialysis

	A	B	C ⟶					
		1 hour	1 day	2nd day	3rd day	4th day	5th day	6th day
Montmorillonite	7.4	4.2	5.3	6.2	6.4	6.6	6.8	6.6
Beidellite	6.8	4.2	5.7	6.2	6.3	6.7	6.9	6.5
Saponite	7.5	4.3	5.8	6.4	6.4	6.6	7.2	6.7
Hectorite	9.3	7.5	8.3	8.3	8.6	8.9	9.0	8.7
Laponite	8.1	5.4	5.3	5.7	5.8	6.7	7.4	8.2

A – aqueous clay suspension (0.2% clay: water), 24 h after the preparation
B – 1 h after adding the Keggin solution to the clay; before dialysis
C – after adding the Keggin ion; during dialysis

ing the Al solution, was considerably greater, and was noted at 5.3. The pH for the other three Al clay suspensions was 4.2–4.3 which is the optimum pH for the formation of the Keggin ion in solution. During the dialysis process the pH of the suspension inside the dialysis bags gradually rose to higher values (~6.5). At this pH, the concentration of Al in the aqueous phase should be extremely small. According to Bradley *et al.* [19] amorphous gel formation, in which there is major rearrangement of the Al_{13} units, begins to occur between OH:Al ratios of 2.5–3.0 (i.e. pH greater than 6.0). It may therefore be concluded that the adsorption of the Keggin ion by the different clays took place during the initial mixing of the clay with the Keggin solution.

XRD measurements

Table 2 summarizes the basal spacings of the different Al_{13} treated smectites recorded after air drying, thermal and subsequent wetted treatments. Representative diffractograms of these treated clays are shown in Figs 1–6. Montmorillonite, beidellite and saponite showed similarities, whereas hectorite and laponite exhibited unique behaviour. We describe therefore, first of all the diffractograms of the former group, followed by a description of the diffractograms of hectorite and laponite.

Montmorillonite, beidellite and saponite

Slides dried at room temperature

From the X-ray diffractograms (Fig. 1; Table 2) it appears that the hydrated Keggin ion, plus the free water molecules in the interlayer space of the air dried sample can be characterized by a basal spacing of approximately 1.92 nm. The
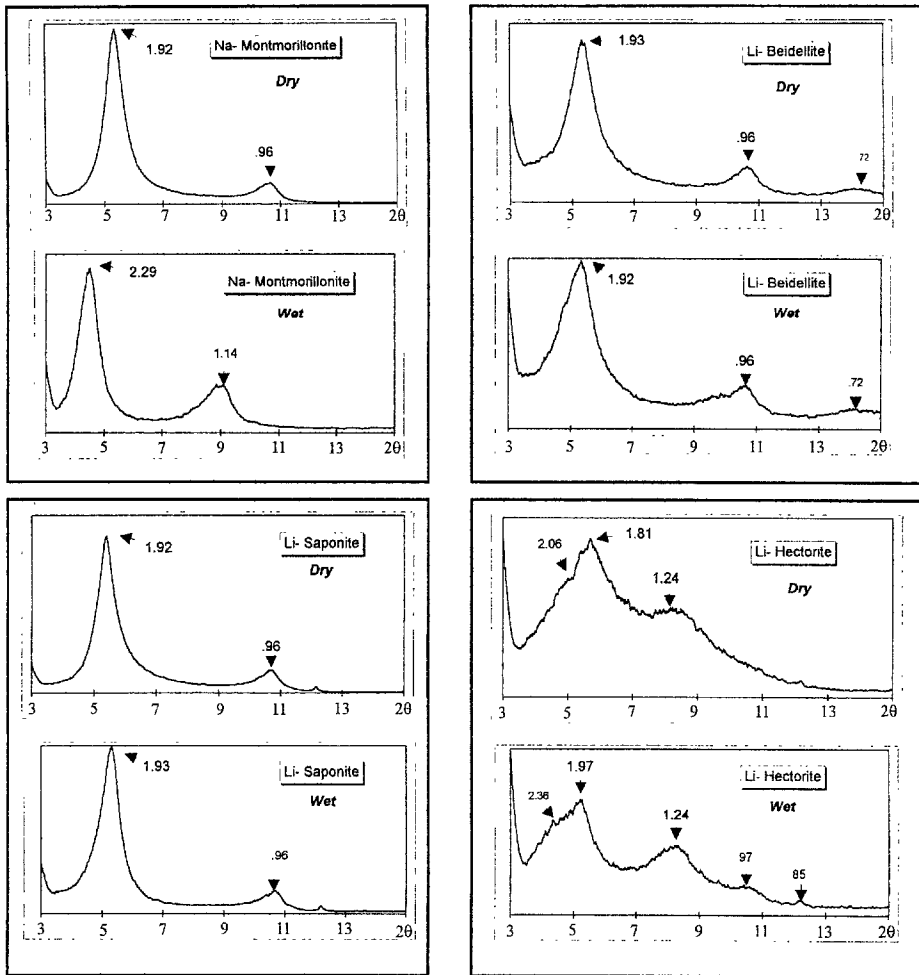
Room Temperature

Fig. 1 X-ray diffractograms of air dried and rewetted slides

swelling of montmorillonite upon wetting from 1.92 to 2.29 nm is interpreted as the addition of another layer of free water in the interlayer. Beidellite and saponite did not swell upon being wetted.

Slides heated at 105°C

Dehydration at 105°C resulted in a small collapse in the *d*-spacing from 1.92 nm to ~1.85 nm (Table 2). This is thought to be due to the escape of free water molecules from the interlayer space as well as water molecules coordinated to the Keggin ion. This dehydration seems to be reversible for montmorillonite, as, upon

Table 2 D-spacings (nm) of the five pillared clays under air dried, thermally treated and wetted conditions

	R		105°C		200°C		350°C		400°C		500°C		600°C	
	D	W	D	W	D	W	D	W	D	W	D	W	D	W
Montmorillonite	1.92	2.29	1.83	1.94	1.73	1.88	1.79	1.89	1.77	1.87	1.70	1.76	1.68	1.68
Beidellite	1.92	1.92	1.87	1.87	1.78	1.87	1.82	1.89	1.80	1.84	1.81	1.82	1.86	1.88
Saponite	1.91	1.92	1.85	1.85	1.71	1.90	1.80	1.89	1.79	1.87	1.79	1.87	1.72	1.72
Hectorite	1.81	1.97	1.87	1.93	1.87	1.88	1.81	1.89	1.80	1.83	1.79	1.79	tail	tail
Laponite	1.80	1.94	1.81	1.92	1.83	1.85	1.70	tail	1.70	1.79	1.70	1.77	tail	tail

R – room temperature; D – dry; W – rewetted; T – thermally heated

wetting, the clay swelled back to a basal spacing of ~1.94 nm. Beidellite and saponite did not swell.

Slides heated at 200°C

The basal spacing of all three clays shrank to 1.7–1.8 nm (Fig. 2; Table 2) as a result of the escape of the structural water molecules comprising the Keggin ion. This dehydration process was still partly reversible and when the samples became wet they reswelled to form the hydrated cations as well as the partially hydrated clay with free water molecules (1.88–1.90 nm).
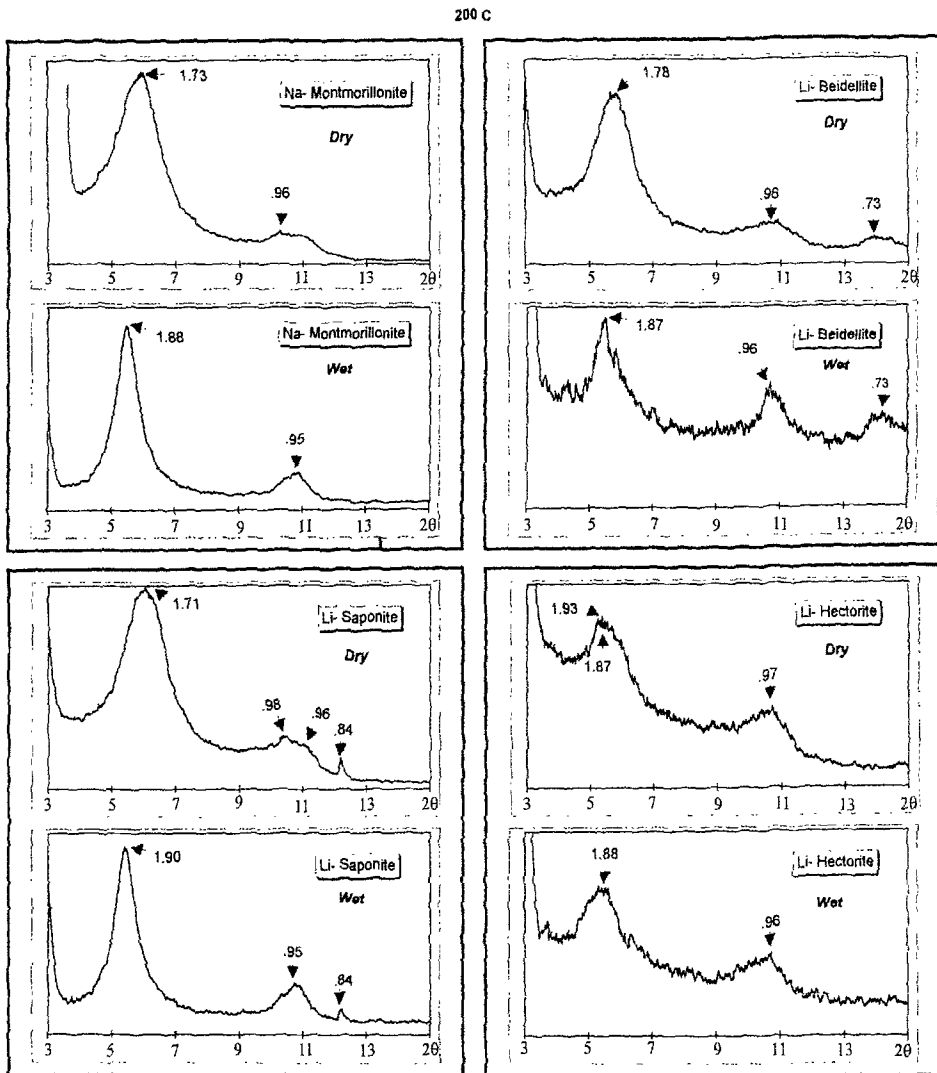

Fig. 2 X-ray diffractograms of clays heated to 200°C and rewetted

Slides heated at 350 and 400°C

At this temperature, due to the dehydroxylation of the Keggin ion [20], there was reorganization of the skeleton and a species more expanded than the Keggin ion heated, to 200°C was obtained. The Al cation likely retained 13 Al atoms in each unit. This dehydroxylation process is thought to be reversible as the *d*-spacing of the wet samples was almost the same as that of the wetted 200°C slides (Fig. 3; Table 2).
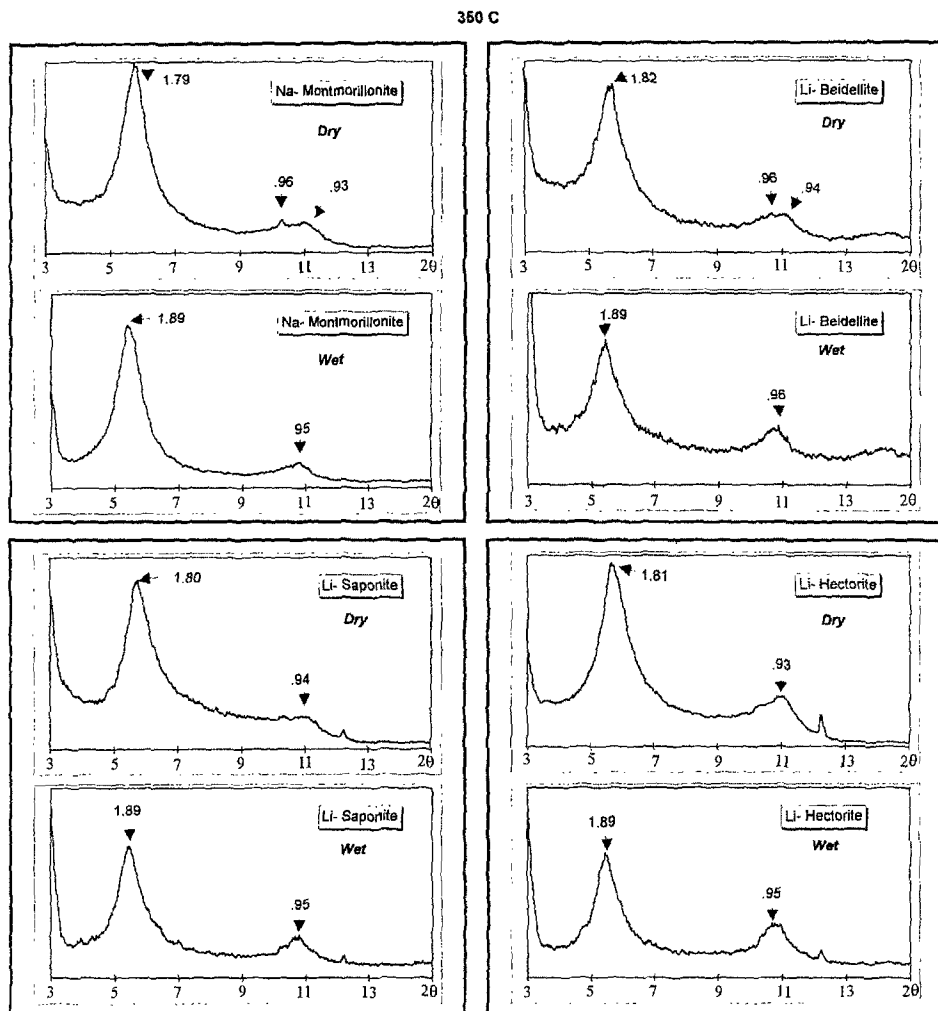

Fig. 3 X-ray diffractograms of clays heated to 350°C and rewetted

Slides heated at 500°C

The dehydroxylation of beidellite begins at this stage with some transformation to the meta form. The non-swelling property of beidellite (Fig. 4; Table 2) is probably an indication that an oxide pillar formed a bond to the silicate layer.

Dehydroxylation of beidellite occurs at lower temperatures than for the other clays. (For this particular clay the endothermic peak was determined to be 530°C) [21] and this would allow a condensation reaction to take place such that an Al–O–clay bond formed [22].
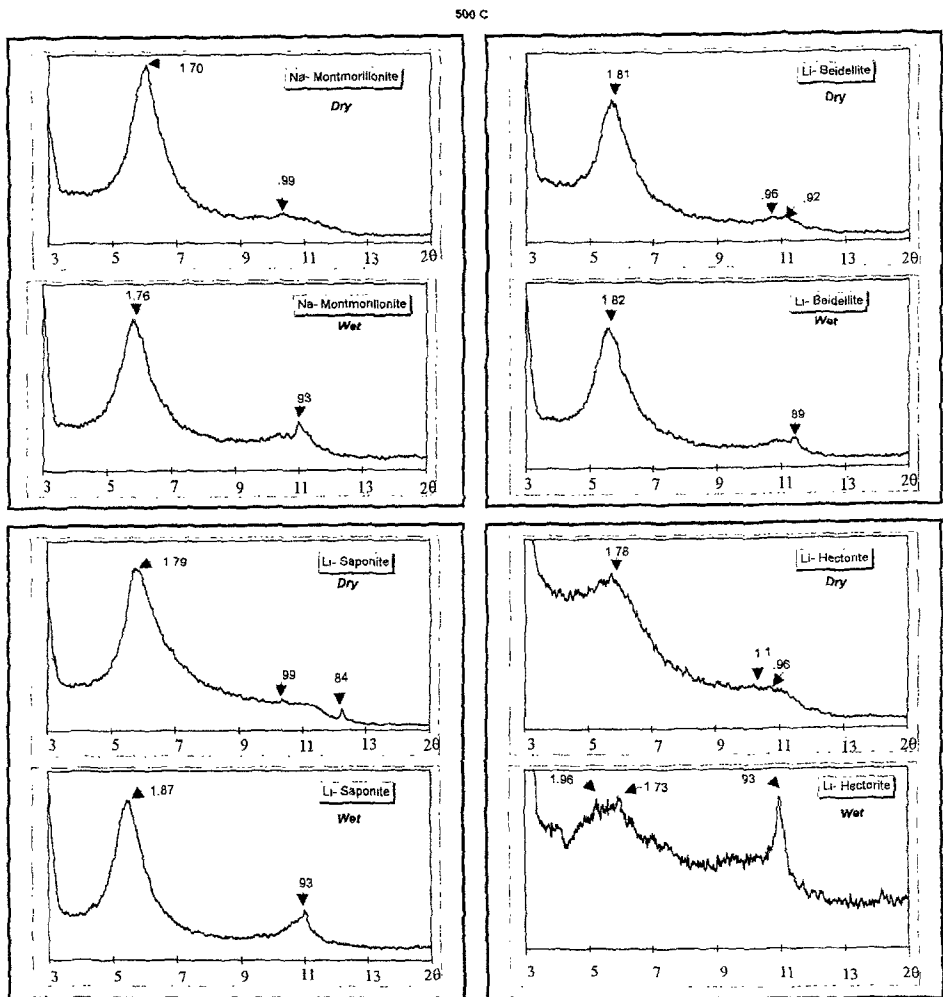

Fig. 4 X-ray diffractograms of clays heated to 500°C and rewetted

Montmorillonite and saponite, which do not undergo dehydroxylation at this temperature, showed, therefore, some rehydration, indicating that for these par-

ticular clays the condensation reaction between the pillar and the clay had not yet taken place.

Slides heated at 600°C

The dehydroxylation of montmorillonite and saponite begins at this stage. (Dehydroxylation endothermic peaks for these particular clays are 650 and 810°C, respectively [21]. Each of the clays showed variable basal spacings (Fig. 5; Table 2) but in all samples, the peaks broadened, indicating partial destruction of the clay and/or pillar. No swelling occurred in any of the clays following the wetted treatment. It is speculated that this may have been due to a condensation reaction which occurred between the pillar and the clay.
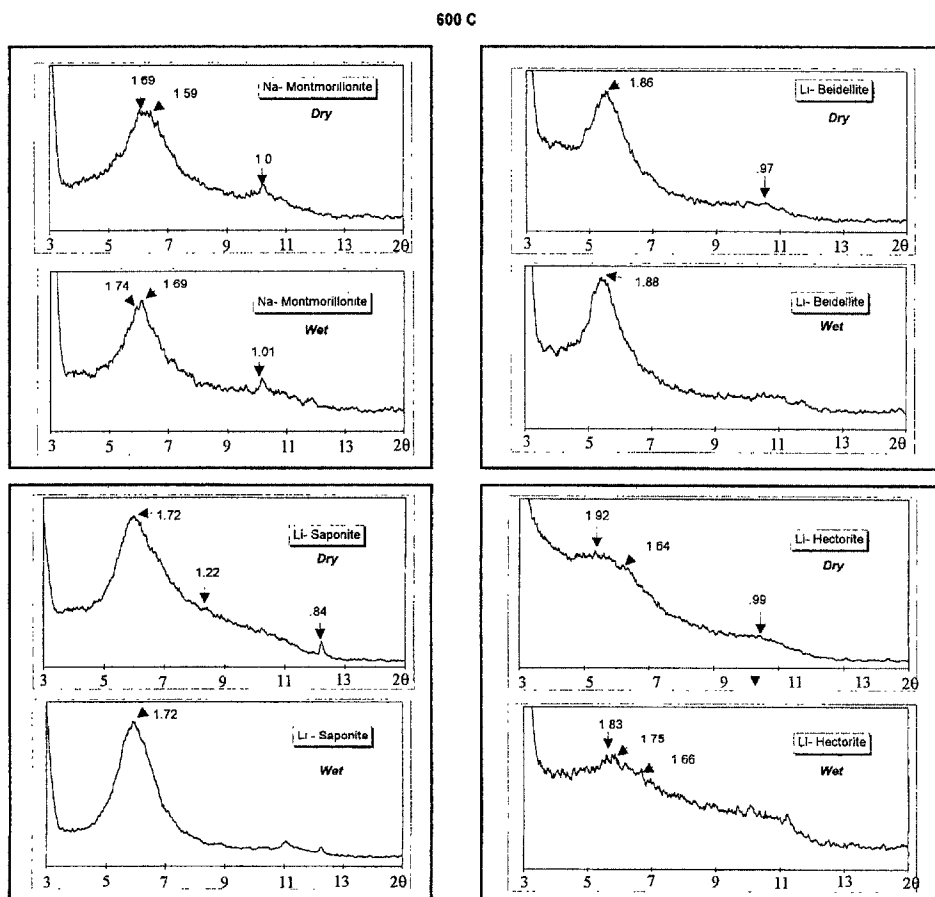
600 C

Fig. 5 X-ray diffractograms of clays heated to 600°C and rewetted

Hectorite and laponite

Slides dried at room temperature

At room temperature, the peak describing the d-spacing in the diffractograms of both of these clays (Figs 1 and 6), was very broad, with several shoulders, showing inhomogeneity of the interlayer spaces. In hectorite, besides the peak of the Keggin ion (between 1.8 and 1.9 nm), there was a distinctive broad peak starting at 1.24 nm and continuing towards higher spacings. Both clays showed
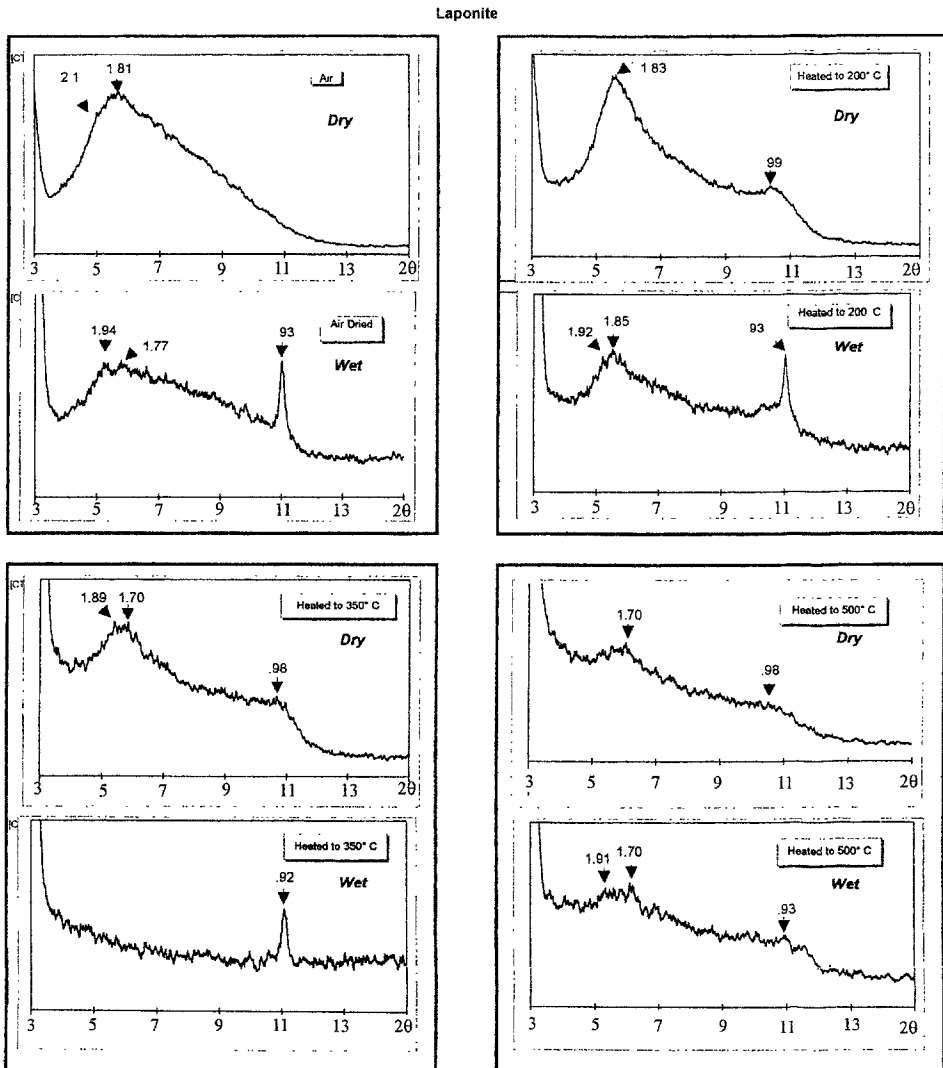

Fig. 6 X-ray diffractograms of Al-pillared laponite

swelling in the region of the Keggin ion. However the 1.24 nm peak was retained with no expansion. This is perhaps indicative of domains dominated by the presence of Al cation monomers and other small cationic polymeric species of Al between the layers of the clay.

Slides heated at 105°C

At 105°C, after some free water was evolved from the interlayer space, the peak became somewhat sharper (figure not shown). In hectorite, the maximum was located at 1.86 nm, which was similar to the spacings found in the other clays. (However in the present case the peak was much broader and relatively weak.) A peak at ~1.8 nm is characteristic of the complete Keggin ion, before the loss of structural water. The 1.24 nm peak disappeared but the 0.97 nm peak showed a long tail extending to 1.15 nm, indicating the presence of hydrated layers.

Rehydration occurred although not quite to the same extent as in the air-dried slides. The 0.97 nm peak expanded somewhat to 1.0 nm and broadened.

In laponite different behaviour was observed. A fairly sharp peak formed at 1.87 nm after the sample was heated. Upon rewetting, however, the peak lost much of its sharpness and shifted somewhat to 1.92 nm.

Slides heated at 200 and 350°C

In the diffractogram of hectorite (Figs 2 and 3), there were only slight changes in the peak position obtained after heating the clay to 200°C. This may indicate some small rearrangements in the polymeric cation. There was some expansion upon wetting although the precise location of the peak was difficult to ascertain because of its broad and irregular shape. The 0.96 nm peak held its position.

At 350°C, there were critical changes in the shape of the diffractogram, which may indicate major rearrangements in the structure of the Keggin ion. At this temperature, the dehydroxylated cation may be similar to the cation which was formed in the other smectites under similar conditions. The peak was not broad anymore and there were no shoulders, suggesting that the sample was relatively homogeneous and the amount of adsorbed water was limited. There is a distinct change in the behaviour of the wetted clay following treatment at 350°C. Its expansion was similar to the other three clays (~0.08 nm) and the peak was still sharp.

The diffractogram of laponite, (Fig. 6), which was obtained after heating the sample at 200°C was very similar to that of hectorite heated at 350°C. Consequently, the peak at 1.85 nm is relatively sharp, (although not as sharp as is the diffractogram of hectorite heated at 350°C), suggesting that in this sample the dehydroxylated cation is similar to the cation which was found in the other smectites at elevated temperatures.

At 350°C the peak broadened, (1.70–1.89 nm) indicating that considerable changes had occurred in the structure of the cationic Al polymer. The wetted

sample did not show any distinct peaks. Rewetting is thought, therefore, to bring about complete inhomogeneity in the interlayer space of laponite.

Slides heated to 500–600°C

At 500°C, there was a large change in the shape of the 001 reflection, and it appeared more like a broad tail extending from 1.78 nm to smaller values. This indicates that drastic changes occurred in the structure of the cationic Al polymer.

Following the high temperature treatment in which amorphization takes place, it was difficult to determine the precise center of the broadened and flattened peak. Like the other three clays, no expansion occurred.

Discussion

A pictoral interpretation of the different basal spacings obtained at different temperatures is shown in Fig. 7. In this interpretation we differentiate between the following types of water molecules in the interlayer space: (1) free water molecules which were located between the hydrated Keggin ions, (2) water molecules hydrating the Keggin ions which were H-bonded to surface protons of the Keggin ions, (3) the twelve structural water molecules of the Keggin ion itself, and finally (4) water molecules hydrating the O-plane of the clay in part through H-bonds. During the thermal treatment, interlayer water i.e. (1), (4), was evolved. Furthermore, the Keggin ion decomposed by losing structural water in two stages. In the first stage, water coordinated to Al and part of the $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$ polymeric species was evolved. At elevated temperatures the residue hydroxy-polymer dehydroxylated resulting in the evolution of water molecules and an oxidic cation.

At room temperature, the smectites were saturated with the Keggin ion and free water between the clay sheets as well as coordinated water hydrating the Keggin ion and the O-planes by means of H-bonds (Figs 7a, 7b). Because of the relatively high *pH* of the hectorite plus Al suspension (*pH*~8.3), we deduced that hectorite contained mainly other Al-hydroxy species apart from the Keggin ion. This was supported by the appearance of a broad secondary peak or shoulder (besides the main peak of 1.97 nm) in the X-ray diffractograms at approximately 1.23 nm. Also there was a shoulder at 2.05 nm.

Montmorillonite and hectorite which gain their charge from octahedral substitution, swelled in water, whereas beidellite and saponite, which gain their charge from tetrahedral substitution, did not swell. This was due to the strong H-bonds which were formed between the hydrated Keggin cations and the O-plane in the smectites with tetrahedral substitution. The strong H-bonds resulted in bridges between adjacent O-planes, thus preventing the swelling of beidellite and saponite, but not that of hectorite and montmorillonite. Smectites which ex-
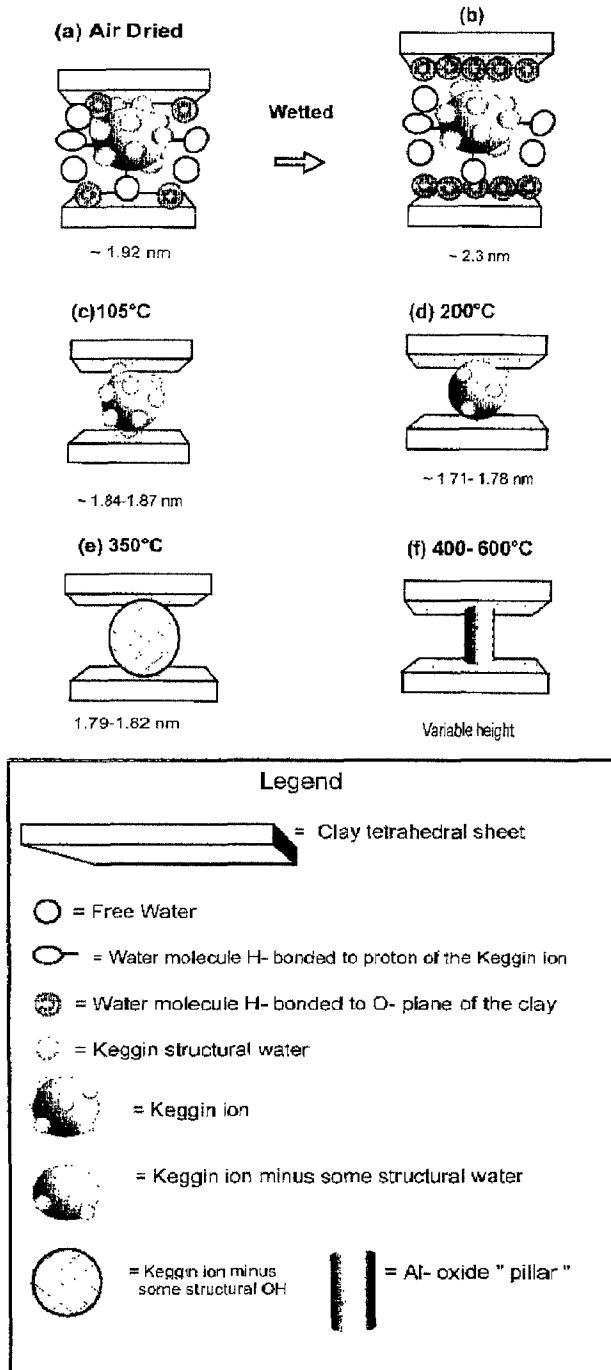
Fig. 7 Schematic representation of the Keggin ion between the clay sheets (Basal spacings in nm)

hibited octahedral substitution did not form strong H-bonds with the polymeric cation.

At 105°C the samples lost free water and water coordinated (H-bonded) to the Keggin ion and the O-plane (Fig. 7c). Since the natural montmorillonite and hectorite do have, to a small extent, some tetrahedral substitution in addition to octahedral substitution, a few H-bonds between the surface protons of the Keggin ion and the O-plane were obtained during the thermal dehydration of the clay. The swelling of these two clays was therefore also reduced after the thermal treatment, although not to the same extent as in the saponite and beidellite.

When the slides were heated to 200°C, the Keggin ion itself was partially or completely dehydrated (i.e. losing structural water which are coordinated to Al_{13}). At this higher temperature of slide preparation, all four clays showed some swelling when subsequently wetted. First of all, this was an indication that the dehydration of the Keggin ion was a reversible process as the increase in the d-spacing was attributed, in this case, largely to the rehydration of this polymer cation. Secondly, it should be recalled that at this temperature the Keggin ion, which was initially a Bronsted acid, converted to a Lewis acid which did not form H-bonds with the O-plane of the clay. Therefore some of the rehydration behaviour may also be assisted by the absence of these bonds.

At approximately 350°C, the dehydroxylation of the Keggin ion began and the d-spacing was between 1.79–1.82 nm (dry) for montmorillonite, beidellite and saponite. As a result of the dehyroxylation, a new polymeric structure was obtained which required higher d-spacing. With the continual rise in temperature, there followed a slight decrease in the d-spacing and it may be concluded that the dehydroxylation therefore was a gradual process. The dehydroxylated cation obtained at 350°C showed that upon wetting, montmorillonite, beidellite and saponite swelled, indicating that the dehydroxylation was still reversible and therefore dehydration was partially reversible. As one would expect for alumina species, with the rise in temperature, the dehydroxylation process became less and less reversible.

In the case of hectorite the dehydroxylation of the mixture of different Al-hydroxy species (which, as mentioned, were present in this clay already at lower temperatures) resulted in a sharp peak after the clay was heated to 350°C. This indicated greater homogeneity of the interlayer species similar to that obtained from the dehydroxylation of the Keggin ion alone. Hectorite did not however preserve the pillar and at higher temperatures the peak became progressively broader. At 600°C only a 'tail' was observed indicating the collapse of the pillar. Laponite behaves like hectorite.

In the other three clays the peaks broadened after being heated to 600°C indicating partial destruction of the pillar and/or the clay. The tetrahedrally substituted clays, beidellite and saponite retained the sharpest peaks with a d-spacing of 1.86 nm and 1.72 nm respectively, whereas montmorillonite showed a peak ranging from between 1.59–1.65 nm. This suggests that there was indeed a

stronger bond between the pillar and the tetrahedrally substituted clay sheet also at this elevated temperature.

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