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AN IMPROVED MODEL FOR STRUCTURAL TRANSFORMATIONS OF HEAT-TREATED ALUMINOUS DIOCTAHEDRAL 2:1 LAYER SILICATES

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Abstract—An improved model for the interpretation of thermal effects during dehydroxylation in aluminous dioctahedral 2:1 layer phyllosilicates considers *trans*-vacant (tv) and *cis*-vacant (cv) 2:1 layers and leads to very different temperatures of dehydroxylation for these tv and cv vacant modifications. In particular, smectites and illites consisting of cv 2:1 layers are characterized by dehydroxylated temperatures which are higher by 150°C to 200°C than those for the same minerals consisting of the tv 2:1 layers. A considerable lengthening of the OH-OH edges in cv 2:1 layers in comparison with the OH-OH edges in the tv 2:1 layers is postulated as the reason for the higher dehydroxylation.

Dehydroxylation in aluminous cv 2:1 layer silicates should occur in two stages. Initially, each two adjacent OH groups are replaced by a residual oxygen atom and the Al cations, which originally occupied *cis* -and *trans*-sites, become 5- and 6-coordinated, respectively. The structure of 2:1 layers corresponding to this stage of the dehydroxylation is unstable. Thus the Al cations migrate from the former *trans*-sites to vacant pentagonal prisms. The resulting dehydroxylated structure of the original cv 2:1 layers is similar to that of the former tv 2:1 layers.

Diffraction and structural features of the cv dehydroxylates predicted by the model are in agreement with X-ray diffraction effects observed for cv illite, illite-smectite and montmorillonite samples heated to different temperatures. In particular, the diffusion of Al cations to empty five-fold prisms during dehydroxylation of the tv 2:1 layers explains why dehydroxylation of reheated cv montmorillonites occurs at temperatures lower by 150°C to 200°C than samples that were not recycled.

Key Words—Beidelites, *Cis*-vacant octahedra, Dehydroxylation, Illites, Montmorillonites, *Trans*-vacant octahedra.

INTRODUCTION

Dioctahedral smectites (montmorillonites, beidellites, nontronites) and finely dispersed micas (illites, glauconites, celadonites, leucophyllites) are characterized by a wide range of dehydroxylation temperatures (Brindley 1976; Grim *et al* 1937, 1951; Grim 1968; Green-Kelly 1955, 1957; Guggenheim 1990; Guggenheim and Koster van Groos, 1992; Heller-Kallai *et al* 1962; Koster van Groos and Guggenheim 1987, 1990; Mackenzie 1957, 1982; Mackenzie *et al* 1949; Tsipursky *et al* 1985).

Differential thermal (DT) curves for dioctahedral smectites with different chemical compositions show that most montmorillonites have one endothermic peak near 700°C, whereas beidellites and nontronites dehydroxylate near 550°C. In contrast some Fe-poor montmorillonites show a peak doublet, suggesting two endothermic reactions between 500°C and 700°C.

It is noteworthy that montmorillonites with one endothermic peak near 700°C will regain their initial hydroxyls upon cooling in the presence of water vapor. However, the DT curves of these rehydroxylated montmorillonites have either one peak at near 600°C or two peaks at about 500°C and 650°C, respectively. The ratio of the sizes of these two peaks and the reaction temperatures depend on the rehydroxylation conditions. In general, however, the rehydroxylated montmorillonites lose hydroxyls at a lower temperature than the original.

It is remarkable that beidellites and illites, with greater structural perfection than montmorillonites, have a dehydroxylation peak at near 550°C. These minerals and muscovite, can also regain structural OH water after heat-treatment and dehydroxylation. However the loss of hydroxyls from rehydroxylated samples occurs, at temperatures near the dehydroxylation temperature of the original samples. Some illites have DT curves with one endothermal peak near 700°C or two peaks at about 550°C and 650°C.

The above results, described by Mackenzie (1957) and Grim (1968) and others, have not been adequately explained for the various clay mineral species. Green-Kelly (1957) noted that the high temperature of dehydroxylation for montmorillonite may be related to Si content, because fine-grained micas and all dioctahedral smectites, except montmorillonites, dehydroxylate near 500°C. Except for montmorillonite, the negative layer charge for these species is located in tetrahedral sites due to AL substitution for Si. This explanation does not explain the occurrence of "abnormal" endothermic temperatures for some montmorillonites

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and illites when dehydroxylation of montmorillonite samples occurs at temperatures typical for illites and beidellites and, on the contrary, illite samples dehydroxylate at the temperatures typical for montmorillonites.

The decrease of dehydroxylation temperature for rehydroxylated samples also needs to be explained. Moreover, there is no correlation between the dehydroxylation temperature and the tetrahedral cation content of dioctahedral smectites and dispersed micas (Guggenheim 1990). For example, leucophyllite, with a tetrahedral sheet mainly of Si, similar to that of montmorillonite, dehydroxylated at near 550°C (Sokolova *et al* 1976).

Two dehydroxylation reactions may be related to interstratification of illite (I) and smectite (S) layers. Cole and Hasking (1957) divided their I/S samples on the basis of expandability. One set dehydroxylated between 525°C and 625°C and another between 650°C and 725°C. However, they failed to correlate the size of the two endothermic peaks and the proportion of I and S for each series. This suggests that interstratification is not a factor to understand the observed effects.

Factors inhibiting correct interpretation of thermal effects include high dispersion and low crystallinity, which make these complex objects for the study of structural changes during dehydroxylation. Therefore, structural changes involving thermal decomposition are often described based on similarities of thermal effects of macrocrystalline phyllosilicates whose dehydroxylated structure have been determined unambigously. For example, dehydroxylation temperatures of pyrophyllite, muscovite, and most montmorillonites are similar. In addition, these minerals have similar structures and compositions of their 2:1 layers. For these reasons, Koster van Groos and Guggenheim (1987, 1990) and Guggenheim and Koster van Groos (1992) concluded that the dehydroxylation of montmorillonites, and in particular the CMS Source clay SWy-1 sample, is analogous to the dehydroxylation mechanism for pyrophyllite and muscovite. These authors believed that montmorillonites, like pyrophyllite and muscovite, consist of *trans*-vacant 2:1 layers (Guggenheim, 1990).

Tsipursky and Drits (1984) found that octahedral cations may be distributed over both the *trans*- and *cis*-sites for dioctahedral smectites. They showed that most montmorillonites, including Wyoming standards, consist of *cis*-vacant (cv) 2:1 layers while 2:1 layers of beidellites, including the Black Jack Mine standard, have vacant *trans*-sites. Most illites consist of *trans*-vacant (tv) 2:1 layers. However, Zvyagin *et al* (1985) and Drits *et al* (1993a) described Al-rich 1M illites with vacant *cis*-octahedra. Mixtures of 1M illites containing vacant *cis*- and *trans*-octahedra were described by Drits *et al* (1993a) and Reynolds and Thompson (1993). Recently Reynolds (1993), and McCarty and Reynolds (1995) discovered I/S in which tv and cv 2:1 layers were interstratified in different proportions within "fundamental" illite particles.

Because Drits *et al* (1984) and Tsipursky and Drits (1984) showed that tv and cv 2:1 layers are structurally unique, it is reasonable to expect that these phases have different dehydroxylation processes. The purpose of this paper is to relate dehydroxylation of aluminous dioctahedral 2:1 layer silicates to these structural features.

COMPARISON OF STRUCTURAL TRANSFORMATIONS OF *TRANS*- AND *CIS*-VACANT 2:1 LAYERS DURING DEHYDROXYLATION

Figure 1 shows a projection of an octahedral sheet of the tv 2:1 layers. According to Pauling rules, shared edges of octahedra occupied by Al cations are shortened to screen Al-Al repulsions. In particular, the two adjacent OH groups form short edges. The dehydroxylated structure of pyrophyllite was determined by Wardle and Brindley (1972), muscovite by Udagawa *et al* (1974). Both minerals consist of tv 2:1 layers. Comparison of these dehydroxylates shows that the octahedral tv sheet is similar to its original form, but contains five-coordinated Al cations instead of Al octahedra (Figure 2). The decrease of the Al cation coordination number results from the reaction between the two hydroxyls according to $2(OH) \rightarrow H_2O\,(\uparrow) + O_r$. The water molecule migrates out of the mineral structure, whereas the residual oxygen anion O_r, moves to the same Z coordinate position as that of the octahedral cations and locates itself midway between two closest Al cations to complete their five-fold coordination.

Prior to dehydroxylation, the values of the *a* and *b* unit cell parameters of aluminous illites and smectites are 5.15–5.20 Å and 8.95–9.02 Å (Moore and Reynolds 1989). Dehydroxylation of these minerals increases the values of these parameters to 5.21–5.25 Å and 9.04–9.09 Å, respectively. If the structural transformation of the dehydroxylated 2:1 layer is confined to only the "residual" anion migration, the Al-O_r distance (Figure 2) will be equal to $b/6$ or 1.51 ÷ 1.52 Å. This value is too small for the pentagonal coordination of Al cations. Therefore, Al cations must migrate away from each other to increase the Al-O_r bond length and shorten the distances with the other four anions to give a mean value of the ⟨Al-O⟩ bond length characteristic for the five-fold coordination of Al cations. For example, the value of the Al-O_r bond length for dehydroxylated muscovite was equal to 1.69 Å (Udagawa *et al* 1974). Such rearrangement of the Al and O_r atoms is the main reason for increasing the *a* and *b* parameters compared to their original values as observed for the dehydroxylated tv muscovite and pyrophyllite samples.

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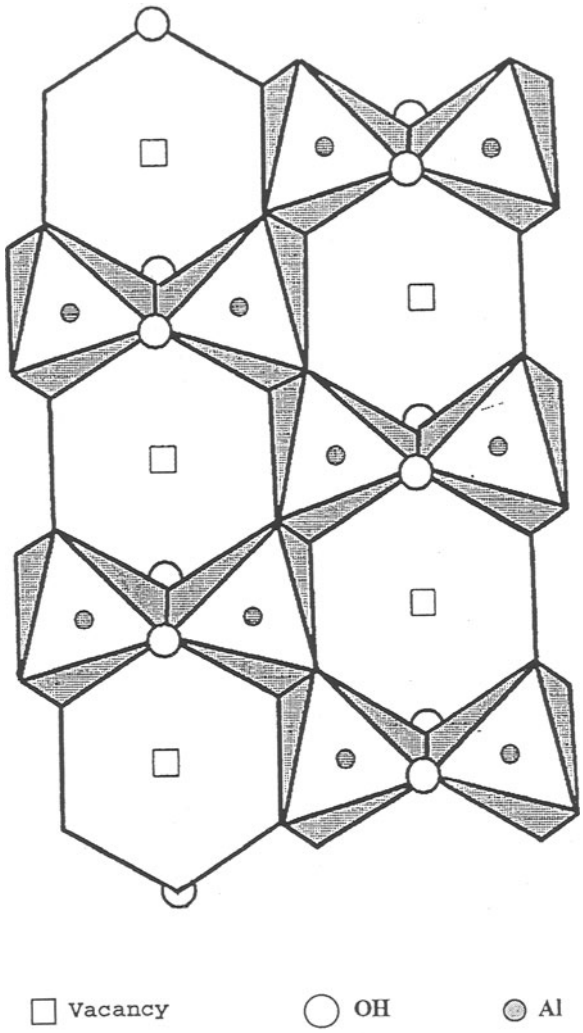


Figure 1. A normal projection of the octahedral sheet of 2:1 layers with *trans*-vacant sites.

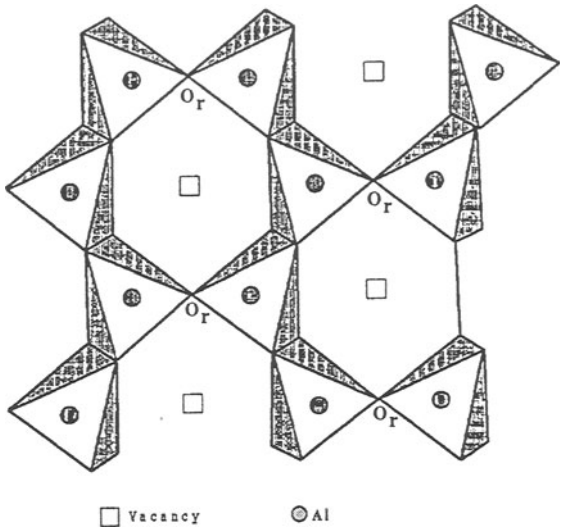


Figure 2. A model for the dehydroxylated octahedral sheet whose former *trans*-sites were vacant.

Figure 3 shows the major features of the cv octahedral sheet. The large *cis*-vacant octahedral site is surrounded by six Al octahedra each of which is linked by sharing anion edges with adjacent Al octahedra. Due to cation repulsion, the shared edges are shorter than the unshared ones. Comparison of Figures 1 and 3 shows that two adjacent OH groups occur as shared anion edges for tv and unshared anion edges for cv octahedral sheets. This difference accounts for different structural transformations during thermal decomposition. Figure 4 shows a model of the dehydroxylated cv octahedral sheet in which each two adjacent OH groups are replaced by a residual oxygen. Like the tv octahedra, the residual oxygen has the same Z coordinate as that of the Al cations and positions midway between the two reacted OH groups. This sheet now contains both *cis*- and *trans*-occupied sites. The Al cations originally occupying *cis*- and *trans* sites become 5 and 6-coordinated, respectively. The former *trans*-octahedra become very deformed and only Al_1 (Figure 4) cations have six-fold coordination. Figure 4 shows that the Al_1-O_r and Al_1-O_r' distances are equal to $a/2 \approx 2.50$ Å, which are unrealistically long. Under these conditions O_r and O_r' anions are strongly undersaturated with respect to positive charge. Thus, the movement of the Al_1 cations and O_r anions toward each other should occur to stabilize the dehydroxylated structure and decrease the degree of undersaturation of the residual anions. Shortening of the Al_1-O_r bond length (Figure 5) increases the distance between Al_1 and Al_2 cations, decreases Al_1–Al_2 repulsion, and elongates the shared 03–04 edges. The described rearrangement of atomic positions will decrease the *a* and *b* cell parameters in comparison to the original 2:1 layers. This adjustment also requires tetrahedral rotation so that the tetrahedral sheets conform to the smaller dimensions of the octahedral sheet.

To estimate the relative stability of dehydroxylated cv sheets the Pauling electrostatic valency principle can be used; the principle states that the sum of the bond strengths received by the anion from the nearest coordinating cations should be nearly equal to valency of this anion. The bond strength is defined as the cation charge divided by the cation coordination number and is expressed in valency units (v.u.).

Each anion of the dehydroxylated cv sheet belonging to one Si-tetrahedron and two Al-pentagonal prisms is oversaturated with respect to positive charge because it receives from the nearest cations (1 + 2*3/5) = + 2.2 v.u. In contrast, the residual anion is strongly undersaturated with respect to positive charge because it

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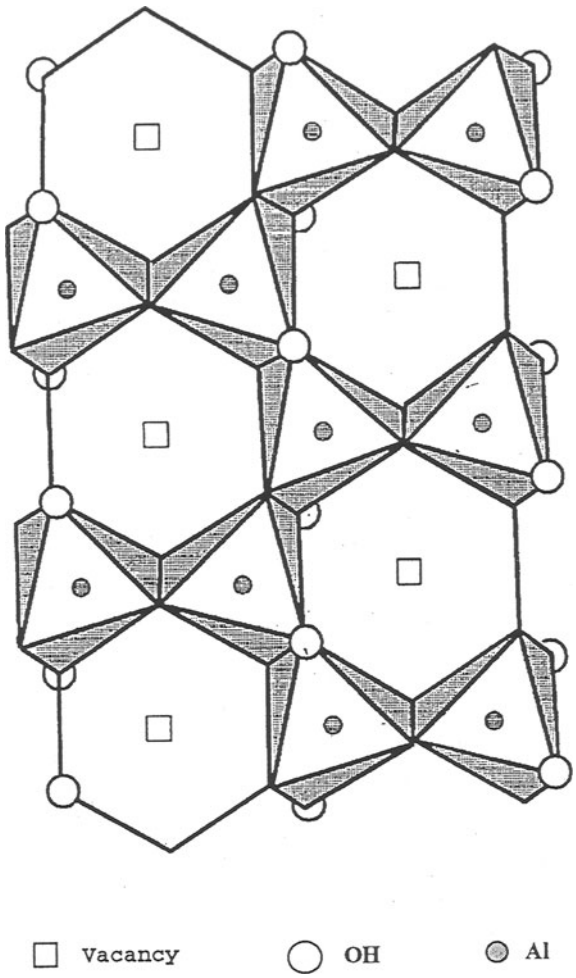


Figure 3. A model for the octahedral sheet of 2:1 layers with *cis*-vacant sites.

receives the positive charge only from two nearest Al cations (+1.2 v.u.). The degree of undersaturation of this anion may be decreased due to the shortening of the Al_1-O_r bond length, because bond strength is inversely proportional to bond length. Figure 5 shows that the oversaturated O_5 anion and the undersaturated O_r anion form a shared edge, and there is no way to equalize the saturation of O_5 and O_r by rearranging Al_1, Al_2, O_r and O_5. Thus, the application of additional thermal energy should promote the migration of Al_1 cations to the empty pentagonal prisms.

The structure corresponding to this stage of thermal transformation is identical to that of the tv dehydroxylates, in which Al cations provide homogeneous local charge compensation without appreciable deformation of the 2:1 layers, interlayers, or layer stacking. However, the dehydroxylated structure of the first and the second stages of the cv 2:1 layer transformation will have different diffraction patterns.

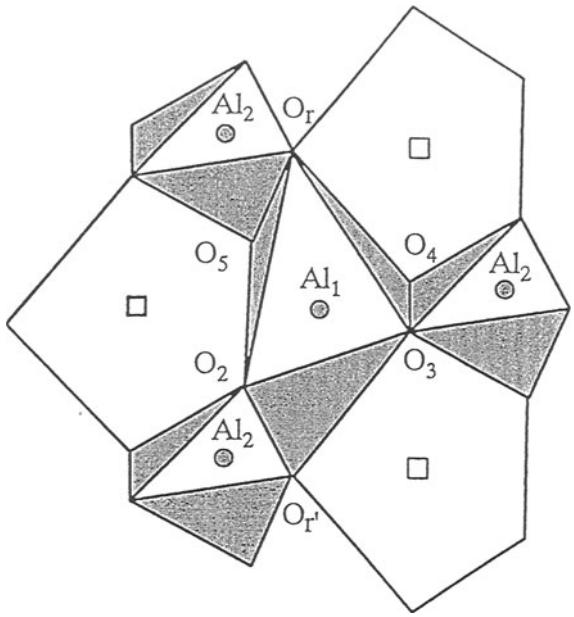


Figure 4. A model for the dehydroxylated octahedral sheet whose former *cis*-sites were vacant. Each of the two OH groups, which formed unshared edges, are replaced by the O_r anion.

SAMPLES AND EXPERIMENTS

X-ray powder diffraction and differential thermal analysis were applied to:

1) a montmorillonite sample consisting of the cv 2:1 layers with the composition (Bartoli 1993);

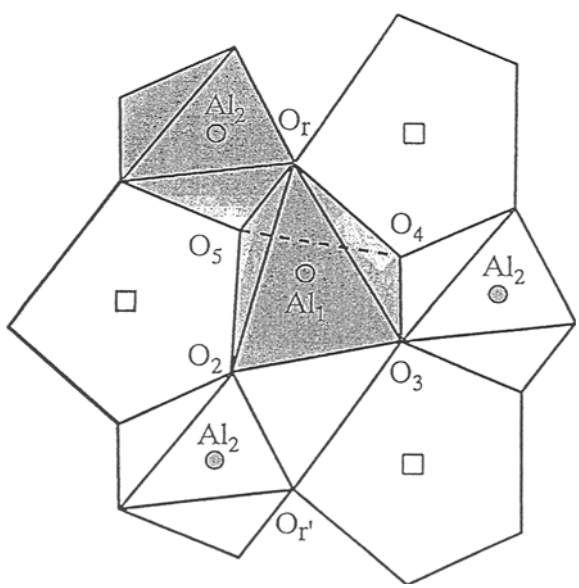


Figure 5. A model for the dehydroxylated octahedral sheet of 2:1 montmorillonite layers corresponding to an intermediate stage of the structural transformation of the *cis*-vacant 2:1, dehydroxylate into the *trans*-vacant 2:1 dehydroxylate.

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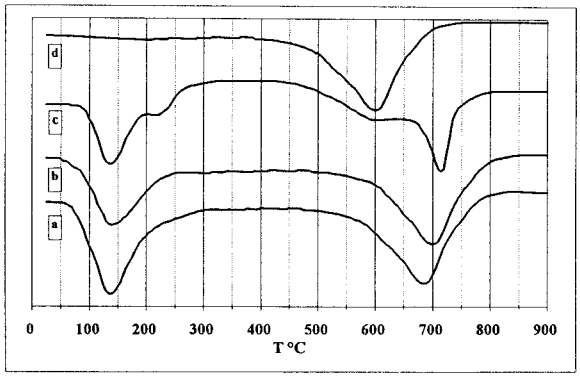


Figure 6. Differential thermal curves for the montmorillonite (a), WT5-B (b), Ballaker illite (c) and synthetic muscovite (d) samples.

$$Na_{0.27}K_{0.03}(Si_{3.97}Al_{0.03})(Al_{1.29}Fe^{3+}{}_{0.33}Mg_{0.39}Mn_{0.01})\cdot O_{10}(OH)_2$$

2) an illite-smectite (sample WT5-B, R = 3, Ws = 15%) from K-bentonites with the chemical formula (McCarty and Reynolds 1995);

$$K_{0.69}Ca_{0.25}(Si_{3.33}Al_{0.67})(Al_{1.47}Fe_{0.1}{}^{3+}Mg_{0.39})O_{10}(OH)_2$$

3) an illite from Ballaker described by Mackenzie *et al* (1949) having "abnormal" dehydroxylated temperature and the composition;

$$K_{0.66}Na_{0.02}(Si_{3.4}Al_{0.6})(Al_{1.75}Fe^{3+}{}_{0.03}Fe^{2+}{}_{0.01}Mg_{0.15}\cdot Mn_{0.01})O_{10}(OH)_2$$

4) an illite-smectite (sample 1603, R = 3, W_s = 6 %) from the Doina'Ves hydrothermal deposit with a chemical formula (Sucha *et al* 1992) of:

$$K_{0.61}(Si_{3.57}Al_{0.43})(Al_{1.69}Fe^{3+}{}_{0.14}Mg_{0.16})O_{10}(OH)_2$$

5) a synthetic fine-dispersed muscovite having the chemical formula;

$$K_{0.82}(Si_{3.18}Al_{0.82})Al_{2.0}O_{10}(OH)_2.$$

Figure 6 shows DT curves for the samples under study. The curves for the montmorillonite and sample WT5-B show one endothermal peak, due to dehydroxylation, at 680 and 715°C, respectively. The Ballaker illite DT curve contains a very broad shallow endothermic effect with a peak at about 570°C and a sharp medium-sized endothermic effect at 713°C (Mackenzie *et al* 1949). The synthetic muscovite gives a DT curve with one endothermal peak near 600°C.

XRD patterns for the samples were recorded under two different experimental conditions. For one set of experiments, the XRD pattern was recorded during sample heating ("in situ" samples). The purpose of these experiments was to measure d(060) values at different temperatures.

XRD patterns for in situ samples were obtained using CuK_α radiation with Siemens D500 diffractometer supplied with a platinum thermocouple. A sample was heated at a rate of 150°C/hour to achieve a given temperature and then an XRD pattern was recorded during 1 hour. The temperature was increased again at a rate of 150°C/hour to get to the next temperature, and a new XRD pattern was recorded. This procedure was continued. Intensities were measured at intervals of 0.05° 2θ and a count time of 30s per step. XRD patterns were recorded from 300°C to 800°C. The error in the determination of the d(060) values do not exceed ±0.001 Å.

For the other experiments, samples were heated at different temperatures before the measurements ("ex situ" samples). XRD patterns for these samples were obtained using MoK_α radiation with a INEL CPS120 diffractometer supplied with a curve position sensitive detector. This detector permits simultaneous recording of diffracted intensities for the interval of 2θ from 1° to 70° 2θ. A sample holder was a thin tube made from Lindenman glass with the diameter equal to 1 mm. A temperature rate of sample heating was equal to 150°C/hour. Each sample was heated at a given temperature for 1 hour and then cooled by air. The I/S sample was heated at 300°C, 400°C, 500°C, 600°C, 650°C, 700°C and 750°C whereas, the Ballaker sample illite was heated only at 750°C. It is noteworthy that the XRD patterns corresponding to the "in situ" and "ex situ" WT5-B and Ballaker samples heated at the same temperature were similar. For this reason we consider only some of the recorded XRD patterns corresponding to "ex situ" samples.

RESULTS

Comparison of the XRD patterns for the WT5-B, Ballaker and 1603 samples at different temperatures

Figures 7, 8 and 9 show the X-ray powder patterns for the WT5-B, Ballaker and 1603 "ex situ" samples respectively. Figure 7 contains the patterns for the WT5-B sample heated at 300°C, 600°C and 650°C. The low temperature pattern (Figure 7a) contains two diagnostic peaks corresponding to the 111 and $11\bar{3}$ reflections with d values equal to 3.87 Å and 2.88 Å, respectively. These diffraction features are characteristic for illites consisting of cv 2:1 layers and containing large numbers of rotational stacking faults. According to McCarty and Reynolds (1995), this sample consists of nearly 90% cv 2:1 layers. The WT5-B sample contains 70 to 80% cv 2:1 layers. Using d-values of the 111 and $11\bar{3}$ reflections (Figure 7a) and d(001) and d(060) values, the average unit cell parameters for the WT-5 sample were calculated (Table 1). According to Drits *et al* (1993a), the calculated value of $|c\cos\beta/a| = 0.331$ indicates that cv 2:1 layers dominates considerably over tv 2:1 layers. The diffraction for the heat-

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Table 1. The unit cell parameters for the cis-vacant WT5-B and Ballaker samples, as well as for trans-vacant Fe-illite and pyrophillite samples heated at different temperatures.

Temperature (°C)	a (Å)	b (Å)	c (°)	β (Å)	ccosβ/a
			WT5-B		
300°C	5.19	9.00	10.19	99.70	−0.331
650°C	5.28	9.04	10.27	101.8	−0.398
			Ballaker illite		
20°C	5.19	9.00	10.10	98.90	−0.300
750°C	5.31	9.10	10.30	102.3	−0.413
			Fe-illite[1]		
20°C	5.22	9.04	10.20	101.5	−0.389
750°C	5.24	9.09	10.32	101.5	−0.392
			pyrophillite[2]		
20°C	5.161	8.957	9.351	100.37	−0.326
900°C	5.192	9.122	9.499	100.21	−0.324
			sample 1603		
600°C	5.30	9.07	10.28	101.8	−0.398

[1] After Tsipursky *et al* (1987).
[2] After Wardle and Brindley (1972).

treated sample at 650°C differs substantially from that of the low-temperature sample (Figures 7a and 7b). Table 1 shows the unit cell parameter for Figure 7c based on the tv structure and 1M polytype. There is good agreement between the experimental and calculated d-values for $11\bar{2}$, 022, 003 and 112 reflections (Table 2). The value of $I c\cos\beta/aI = 0.398$, which is the diagnostic for tv-1M mica polytype (Bailey 1984), shows that the sample heated at 650°C corresponds to tv-1M illites. Thus, during dehydroxylation, cv 2:1 layers were transformed into tv 2:1 layers. The diffractogram for the heat-treated sample at 600°C does not contain any intensity modulation within d-values from 4.0 Å to 2.6 Å (Figure 7b). This suggests an intermediate heterogeneous stage of the cv layer transformation.

Changes in the patterns of the Ballaker illite at room temperature and 750°C are similar to those observed for the WT5-B sample. The pattern for the starting material (Figure 8a) shows the 021 refections at 4.083 Å, 111 at 3.874 Å, $11\bar{2}$ at 3.62 Å, 022 at 3.33 Å, 112 at 3.09 Å and $11\bar{3}$ at 2.866 Å which corresponds to a pure cv-1M illite. However, reflections with different hkl indices have different widths. In particular, the 111 and $11\bar{3}$ reflections are more narrow than the $11\bar{2}$ and 112. One explanation is that the sample is a mixture of cv-1M and tv-1M illites. Using the d-values for the 111, 003 and $11\bar{3}$ reflections value of $I c\cos\beta/aI = 0.301$ was determinated. According to Drits *et al* (1984, 1993a), this value is characteristic for pure cv-1M illites. The main diffraction feature of tv-1M illites is that the two strongest reflections are at d-values of 3.65-3.66 Å ($11\bar{2}$) and 3.06-3.07 Å (112). The cv-1M variety has the same indices with d-values of 3.58-

Table 2. Experimental and calculated XRD powder data for the original (O) and dehydroxylated (D) WT5-B and Ballaker samples, spacing in Å.

	WT5-B sample				Ballaker sample			
	O		D		O		D	
hkl	d_{cal}	d_{exp}	d_{cal}	d_{exp}	d_{cal}	d_{exp}	d_{cal}	d_{exp}
020	4.500		4.521	4.49	4.495	4.46	4.552	4.50
110	4.455	4.46	4.496		4.456		4.508	
021					4.099	4.083	4.147	4.12
111	3.862	3.87			3.879	3.874		
$11\bar{2}$[1]t			3.690	3.70	3.655	3.63	3.719	3.73
$11\bar{2}$					3.574			
022	3.342	3.35	3.360	3.555	3.343	3.335	3.376	3.372
003	3.330		3.350		3.328		3.370	
112					3.124	3.09		
$11\bar{2}$[1]t			3.087	3.10	3.073		3.087	3.09
$11\bar{3}$	2.875	2.88			2.860	2.866		
130			2.604	2.598				
200	2.560	2.559	2.585		2.565	2.565	2.595	2.588
$13\bar{1}$	2.554				2.554			
$20\bar{2}$	2.452	2.451			2.440			
131	2.451				2.458	2.455		
201	2.385	2.383	2.345	2.396	2.397	2.382	2.395	2.409
$13\bar{2}$	2.382				2.375		2.433	
040	2.250	2.241	2.260	2.251	2.247	2.240		
220	2.227		2.244		2.228		2.254	2.257
132					2.226			
202	2.136	2.135			2.151	2.136		
$13\bar{3}$	2.133				2.126			
060	1.500	1.500	1.507	1.507	1.500	1.500	1.517	1.517

[1] Corresponds to the two strongest reflections for a t-1M illite variety.

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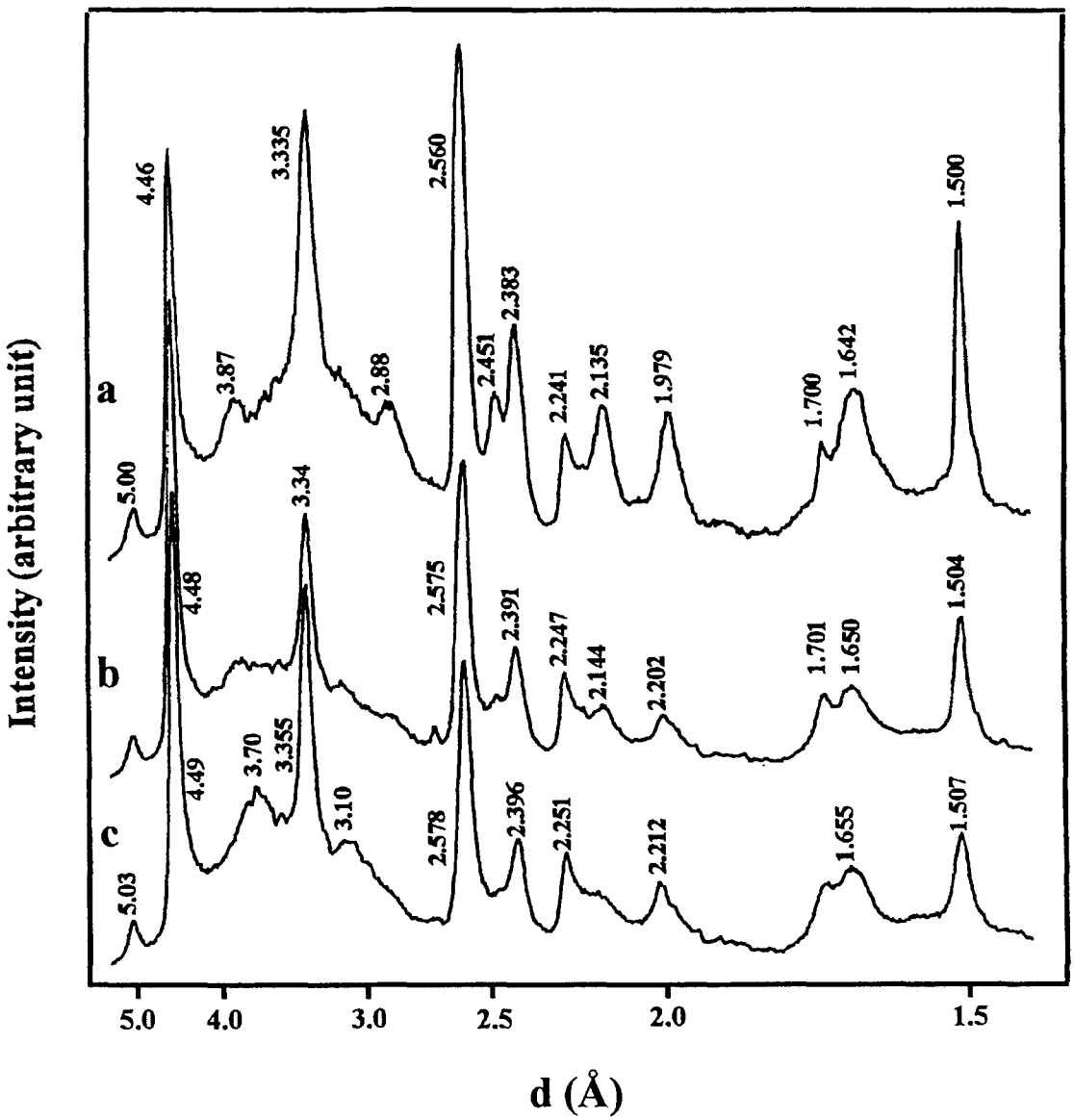


Figure 7. The XRD curves for the WT5-B sample heated at (a) 300°C, (b) 600°C, and (c) 650°C; d-values are given above the corresponding peaks.

3.59 Å ($11\bar{2}$) and 3.12–3.13 Å (112) (Drits *et al* 1993a). The near superposition of reflections with the same indices, but corresponding to different illite polymorphs explains peak broadening (Figure 8a). Thus, the Ballaker illite consists of two coexisting illite varieties with the proportion of the cv-1M modification prevailing over the tv form. The XRD curve for the sample heated at 750°C (Figure 8b) is characteristic of the tv illites. Using the d-values for $11\bar{2}$, 112, d(00l), and d(060) values, the unit cell parameters for the dehydroxylated sample were calculated (Table 1). Table 2 compares the d_{exp} and d_{cal} values. The value of $Ic\cos\beta/aI = 0.413$ indicates the transformation of the original cv 2:1 layers into tv dehydroxylated 2:1 layers in the heated sample.

The powder pattern for sample 1603 is typical for tv illites (Figure 9a). Note reflections $11\bar{2}$ at 3.65 Å and 112 at 3.075 Å. The value of $Ic\cos\beta/aI = 0.39$ indicates tv-sites. The sample contains minor microcline reflections at 3.80 Å, 3.47 Å, 3.26 Å, 3.02 Å and 2.92 Å. The pattern for the dehydroxylated sample resembles the major diffraction features characteristic of the original sample (Figure 9). Using d-values for 003, 060, $11\bar{2}$ and 112 reflections, the unit cell param-

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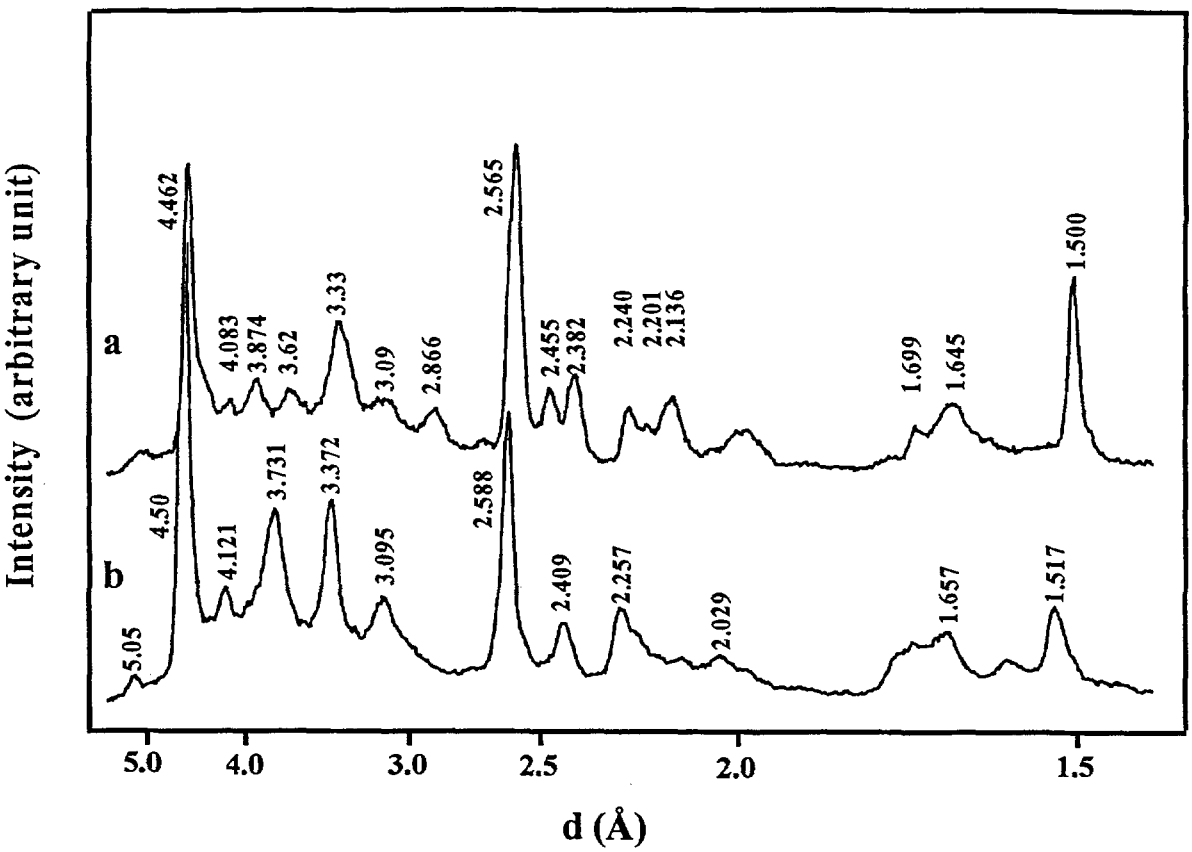


Figure 8. The XRD curves for the Ballaker illite sample recorded at (a) room temperature and (b) after heating at 750°C, d-values are given above the corresponding peaks.

eters for the dehydroxylated structure were determinated (Table 1).

Temperature dependence of the unit cell parameters

The change in unit cell parameters with respect to temperature may be determinated by previously published data and data presented here for samples whose structure and chemistry were determined unambigiously. Tables 1 and 3 compare the unit cell parameters for the original and heated samples. These tables contain the data for *cis*-vacant WT5-B and Ballaker samples, and for the tv muscovite, illite and pyrophyllite described, respectively, by Guggenheim *et al* (1987), Tsipursky *et al* (1985), Wardle and Brindley (1972). Relationships between the sample temperature and the *b* parameter observed during "in situ" measurements are shown in Figure 10 for synthetic muscovite and Ballaker illite and in Figure 11 for montmorillonite. Figure 10 also shows the temperature dependance for two muscovite samples described by Guggenheim *et al* (1987). Figure 11 contains the *b* parameter values obtained by Heller-Kallai and Rozenson (1980) for the Wyoming montmorillonite sample heated in open crucibles at different temperatures and cooled by air.

The tv muscovite and tv illite sample. As expected the cell parameters of the dehydroxylated aluminous dioctahedral tv 2:1 layer silicates have higher values, than those of the original samples (Tables 1 and 3, Figure 10). Moreover, Tables 1 and 3 reveal a set of relationships between the unit cell parameters of the muscovite and illite samples in their original (a_o, b_o, c_o, β_o) and partially or completely dehydroxylated (a_d, b_d, c_d, β_d) states: $\beta_o \approx \beta_d$, $a_o/a_d \approx b_o/b_d \approx c_o/c_d$ depending upon temperature of sample heating. For this reason, the values of $Ic\cos\beta/aI$ do not change during dehydroxylation.

These relationships are satisfied especially well for the muscovite samples whose unit cell parameters were measured by Guggenheim *et al* (1987) with high precision. These results are rather unexpected because heating of samples to different temperatures leads to restructuring tv octahedral sheets of 2:1 layers, which determine the value of $Ic\cos\beta/aI$. We should suggest that for partially and completely dehydroxylated tv muscovite and illite, the structural transformation of

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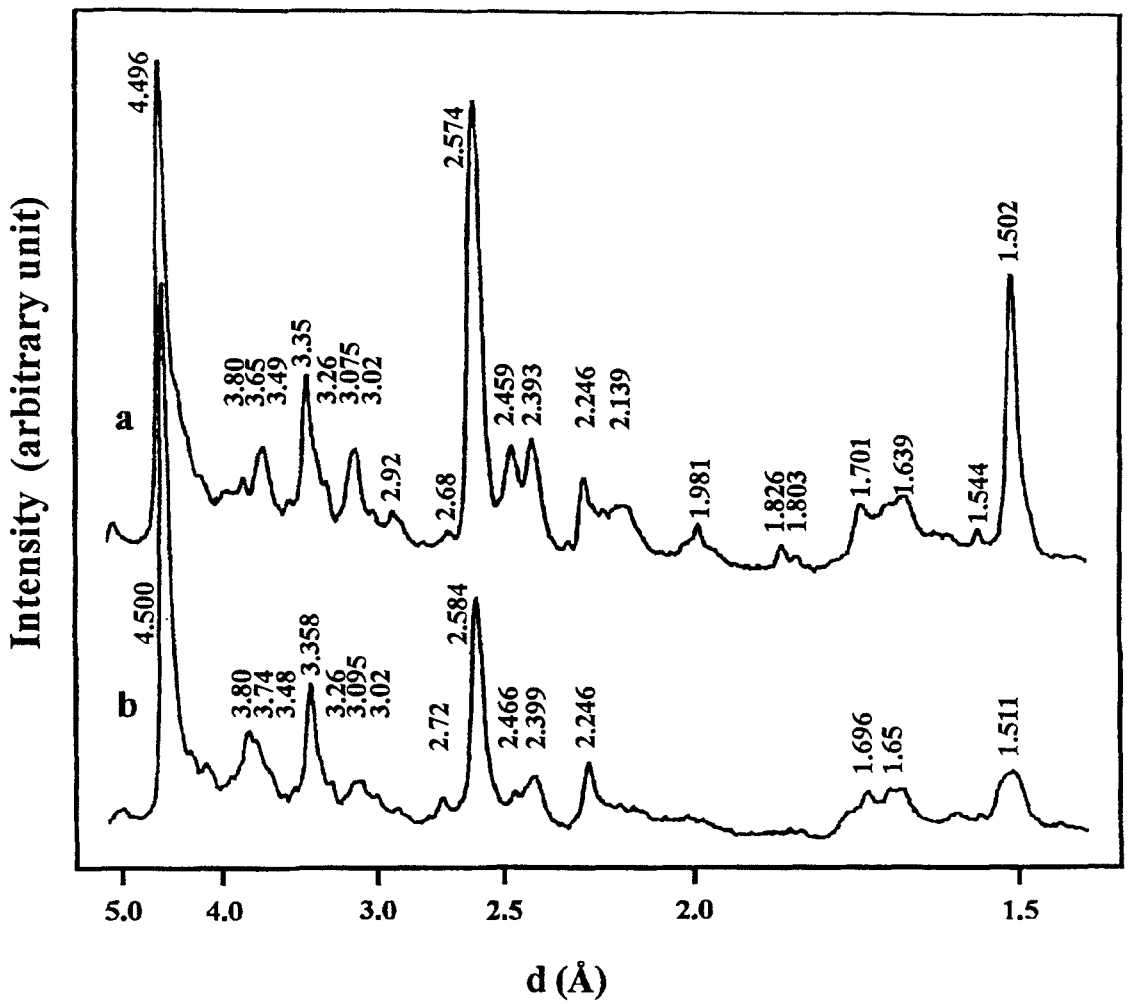


Figure 9. The XRD curves for the sample 1603 recorded at (a) room temperature and (b) after heating at 600°C, d-values are given above the corresponding peaks.

their 2:1 layers does not change relative values of interlayer displacements ($c\cos\beta/a$ = const) as well as ratios of the unit lengths ($c_o/a_o = c_d/a_d$).

The cis-vacant samples. The dependence of the *b* parameter on the temperature of sample heating for cv montmorillonites differs significantly from that for the tv 2:1 layer silicates (Figure 2). In situ measurements show that the *b* parameter for montmorillonite does not change (8.965 Å) within the temperature interval of 20°C to 400°C, and then decreases slowly between 400°C and 600°C. It rapidly changes to 8.942 Å at 650°C. The further increase in temperature increases the *b* parameter, the value of which is 8.985 Å at 800°C (Figure 11).

Figure 11 shows that the *b* parameter of the Wyoming montmorillonite sample is equal to 8.97 Å until 500°C, then it decreases to 8.93 Å at 600°C, and subsequently increases to 9.01 Å at 800°C. It is noteworthy that Wyoming montmorillonites (Tsipursky and Drits 1984) consist of cv 2:1 layers. In situ measurements of the WT5-B sample heated at different temperatures shows that the increase of temperature increases the *b* parameter.

DISCUSSION

The XRD data obtained here and previously published for aluminous 2:1 layer silicates heated to high temperatures are in agreement with the above models for the structural transformation of tv and cv 2:1 layers during dehydroxylation.

Unheated and dehydroxylated tv muscovites, illites, and pyrophyllites have similar diffraction patterns. For example, the oblique texture electron diffraction (OTED) pattern of tv 1M illite sample after heating to 750°C contains two strong reflections ($11\bar{2}$, 112) in the first ellipse (Tsipursky *et al* 1985). The same features

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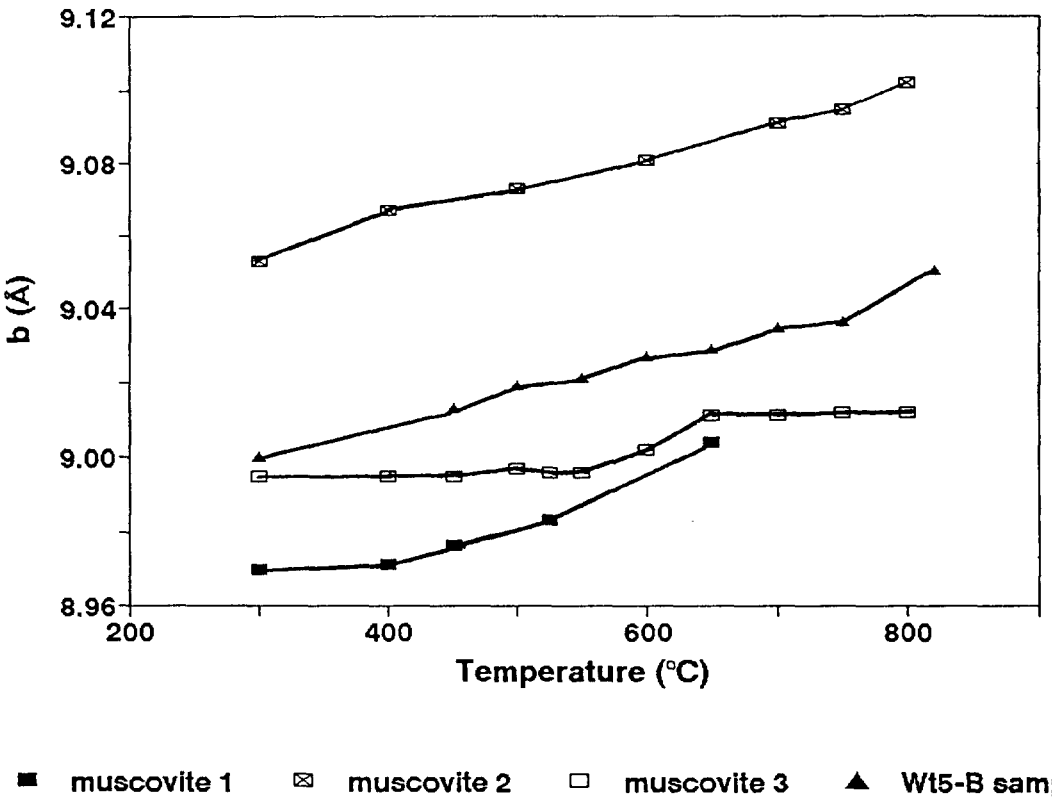


Figure 10. The dependence between the temperature of sample heating and the b parameter. Muscovite 1 and 2 corresponds to the samples from Panasqueira and Diamond mine described by Guggenheim *et al* (1987) and muscovite 3 to the synthetic muscovite.

are observed in the XRD patterns for the unheated and dehydroxylated sample 1603 in which *trans*-vacant 2:1 layers dominate (Figure 9). This feature and the characteristic value $c\cos\beta/a$ are diagnostic for the identification of the dehydroxylated tv 1M illite. The structural mechanism of dehydroxylation in beidelite consisting of tv 2:1 layers is the same as for tv illites (Drits *et al* 1994).

The dramatic differences of the XRD patterns for the WT5-B and Ballaker samples suggest that a structural transformation occurs from unheated cv 2:1 layers to dehydroxylated tv 2:1 layers due to the migration of Al cations from the original trans-octahedral sites (Figures 4, 5) to formerly unoccupied five-fold prisms. The values of the $|c\cos\beta/a|$ parameter obtained for the unheated and heated samples also correlate with the structural model of the dehydroxylated aluminous 2:1 layer silicates containing the Al cations in the five-fold polyhedra. This is shown in Figure 2, in accordance with the earlier work of Wardle and Brindley (1972) and the crystal chemical model of Guggenheim (1990). Unfortunately we have no pure cv-1M illite having three-dimensional periodicity. It is likely that stacking faults and the presence of different layer types in some samples under study explain the observed discrepancies between the experimental and calculated d(hkl) values for the dehydroxylated samples (Table 2).

The temperature dependance of the *b* parameter found for the cv montmorillonite samples agree with the model of the dehydroxylation of these minerals. The structural transformation of cv montmorillonite layers, which is accompanied by the decrease of the *b* parameter, corresponds to the model shown in Figure 5. In this case, the displacement of the Al_1 cations and O_r anions toward each other decreases the *a* and *b* parameters of the octahedral sheets. Interlayer cations in montmorillonite structures do not restrict the tetrahedral sheets. These sheets will adjust their lateral dimensions to those of the octahedral sheets by tetrahedral rotation. The minimum values of the *b* parameter of montmorillonite samples (Figure 11) correspond to the temperature interval where dehydroxylation occurs for most montmorillonites (near 700°C, Figure 11). The Wyoming montmorillonite has a *b* parameter minimum corresponding to 600°C rather than near 700°C probably because the measurement was not performed at 700°C (Figure 11). Different conditions of sample heating may also have an influence on the dependance between the *b* and temperature values.

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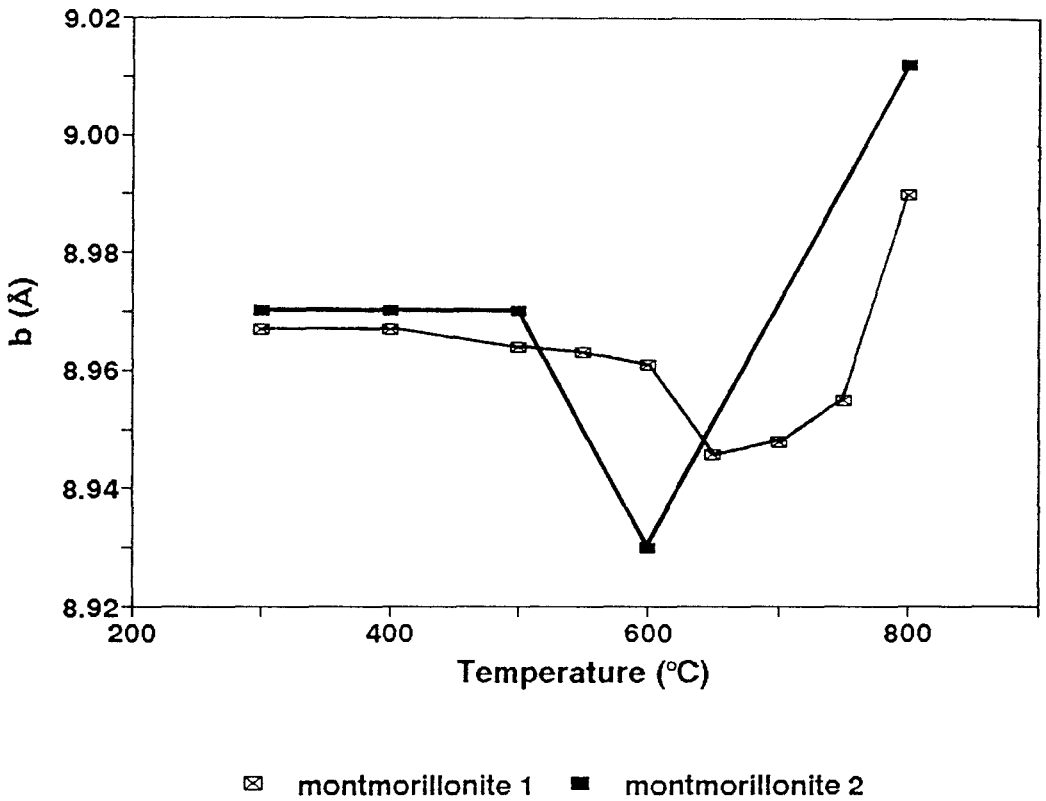


Figure 11. The dependence between the temperature of sample heating and the *b* parameter. Montmorillonite 1 and 2 correspond to the samples studied in the paper and by Heller-Kallai and Rozenson (1980) respectively.

The increase of temperature to 700°C provides cv montmorillonite and illite samples with sufficient thermal energy for the migration of the Al cations from the *trans*-sites to vacant pentagonal prisms. Note that the structural transformation produces a greater *b* value than those for unheated samples. For example, the *b* parameter values at 800°C were equal to 8.985 Å for the "in situ" sample and 9.01 Å for the Wy sample. Whereas for the unheated samples, the *b* values were equal to 8.964 Å and 8.97 Å, respectively.

The temperature effect on the *b* cell parameter for cv montmorillonite, illite-smectite and illite may be

Table 3. Temperature dependance on the unit cell parameters for muscovite samples (Guggenheim *et al* 1987).

Temperature (°C)	a (Å)	b (Å)	c (Å)	β (°)	ccosβ/a
		muscovite, Panasqueira, Portugal			
20°C	5.158	8.950	20.071	95.74	−0.390
300°C	5.170	8.970	20.171	95.71	−0.388
400°C	5.175	8.971	20.177	95.72	−0.389
450°C	5.178	8.9763	20.193	95.70	−0.387
525°C	5.182	8.9835	20.232	95.75	−0.391
650°C	5.189	9.004	20.256	95.74	−0.390
		muscovite, Diamond mine			
20°C	5.200	9.021	20.072	95.71	−0.384
300°C	5.215	9.053	20.15	95.72	−0.385
400°C	5.221	9.067	20.18	95.73	−0.387
500°C	5.225	9.073	20.20	95.74	−0.386
600°C	5.229	9.081	20.24	95.72	−0.386
700°C	5.235	9.091	20.26	95.73	−0.386
750°C	5.237	9.095	20.26	95.73	−0.386
800°C	5.240	9.102	20.28	95.73	−0.386

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explained structurally. In montmorillonite, tetrahedral rotation is not restricted by the interlayer cation, and it is a function primarily of the octahedral cation content of the 2:1 layers. In contrast, the tetrahedral rotation in illite is restricted by the interlayer K cation. Thus, during dehydroxylation, Al cations and anions can adjust their positions readily in cv montmorillonite but not in cv illites.

Indirect evidence for the models developed here is found in the thermal effects observed for the rehydroxylated montmorillonites and illites described by Grim (1968) and Mackenzie (1957). Each mineral heated at the dehydroxylation temperature will regain OH groups if subsequent cooling occurs in water vapor. The rehydroxylation reaction $O_r + H_2O \rightarrow 2(OH)$ reconstructs the six-fold coordination of Al cations. Because of the absence of the cation migration in the dehydroxylated tv illites (Figure 2) their rehydroxylates have the same structure as that of the original (Figure 1). For this reason, the loss of hydroxyls in rehydroxylated illites occurs at nearly the same temperature (500°C) as that of the initial dehydroxylation (550°C) (Grim 1968).

For rehydroxylated montmorillonites, the loss of hydroxyls usually occurs at two different temperatures, near 500°C and 650°C, despite the fact that DT curves of the original samples contain one endothermal peak near 700°C. To explain these thermal effects, we assume that during heating of the initial sample the structural transformation involving the loss of hydroxyls and the migration of the Al cations into vacant pentagonal sites occurs only for a portion of the sample. The structural transformation of the other portion corresponds to the first stage of dehydroxylation of cv 2:1 layers without cation migration (Figure 4).

Thus, a cv montmorillonite sample transforms after rehydroxylation to a mixture of two montmorillonites, one having tv and the other cv 2:1 layers. It is likely that the sizes of the two peaks (500°C, 650°C) in DT curves of the rehydroxylated montmorillonite reflect the proportions of tv and cv layers. The occurrence of endothermal peaks at 570°C and 713°C in the DT curve of the Ballaker illite (Mackenzie *et al* 1949) probably reflects the fact that the sample is a mixture of the tv and cv 2:1 layers. Moreover, the weak peak at the lower temperature correlates with a smaller proportion of the tv-1M illite variety in the sample.

Let us consider possible reasons for different dehydroxylation temperatures for tv and cv aluminous dioctahedral 2:1 layer silicates. The particle size and crystalline perfection are important. For example, strong differences in dehydroxylation temperatures for tv muscovites (800 to 900°C) and tv illites (500 to 600°C) is related to the high dispersion of illite particles. This assumption can not explain high dehydroxylation temperatures for cv montmorillonites and cv illites.

Guggenheim *et al* (1987), Koster van Groos and Guggenheim (1987, 1989) and Guggenheim (1990) were the first to use detailed crystal chemical approach to explain thermal reaction from structural approach. In particular, they considered the dehydroxylation of aluminous dioctahedral tv 2:1 layer silicates by considering the dynamics of the process. Based on Pauling's rules, they suggested that during partial dehydroxylation at relatively low temperatures the formation of pentagonal prisms occupied by Al cations increases the Al-OH bond strength in the Al octahedra having one or two shared edges with the pentagonal prisms. The OH groups that bonded more strongly with Al cations require additional thermal energy for the dehydroxylation process to proceed. Each step of dehydroxylation creates structural fragments with a new proportion and mutual disposition of five-fold and six-fold coordinated polyhedra, increasing the Al-OH bond strength, with the result that more thermal energy is required for the next step of the reaction. The process of dehydroxylation as proposed by Guggenheim *et al* (1987) explains both the asymmetry and broadness of the endothermic peak. However, their model does not completely explain the significant differences of dehydroxylation peak temperatures for montmorillonites and illites because it does not consider cv illites and cv montmorillonites. The model derived by Guggenheim for tv dioctahedral aluminous phyllosilicates is completely consistent with the model described.

One possible reason for high dehydroxylation temperature of cv montmorillonite and illites may be related to the structural features of their 2:1 layers. Comparison of structural models for tv and cv octahedral sheets (Figures 1 and 2) shows that the main differences consist of different distances between adjacent OH groups. According to most single crystal structural refinements of Al-rich dioctahedral micas (Bailey 1984) the shared OH-OH edges in tv 2:1 layers have bond length of 2.45 Å ± 0.05 Å. Whereas, the length of the non-shared OH-OH edges in cv 2:1 layers are expected to be considerably longer (2.85–2.88) Å. Perhaps the probability for hydrogen to jump to the nearest OH group to form a water molecule strongly depends on the distance between the adjacent OH groups. The shorter the distance, the lower the thermal energy required for the dehydroxylation of OH pairs. Therefore, a considerable lengthening of the OH-OH edges for cv 2:1 layers in comparison with the OH-OH edges for tv 2:1 layers may be the major factor responsible for the higher dehydroxylation temperature of cv montmorillonites and cv illites. Thus, despite extremely high dispersion and very low crystallinity of montmorillonites, the structure of their cv 2:1 layers provides a resistance to thermal decomposition. In general, the dehydroxylation of aluminous cv layer silicates is a heterogenous process related to the redistribution of Al-O and Al-OH bond strengths as Al cations migrate to empty five-coordinated sites.

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The absence of any correlation between the proportions of illite and smectite interlayers in I/S samples and the sizes of the two endothermic peaks in the corresponding DT curves (Cole and Hasking 1957) may be explained also. According to Reynolds (1993) and McCarty and Reynolds (1995) "fundamental" illite particles in I/S samples consist of tv and cv layers alternating in different proportions. Thus, the size of each endothermic peak in the DT curves of I/S, probably reflect the proportions of tv and cv layers in the samples under study.

The chemical composition of dioctahedral 2:1 clay minerals also is important in dehydroxylation. For example, for Fe-rich smectites (nontronites), and micas (glauconites and celadonites), the rapid loss of hydroxyls begins at a lower temperature compared to Al-rich samples. Tsipursky and Drits (1984), Drits (1987) and Sakharov *et al* (1990) showed that nontronites, glauconites, and celadonites consist of tv 2:1 layers. It seems likely that dioctahedral 2:1 clay minerals, in which octahedral Fe dominates over other cations, always consist of tv 2:1 layers. The structural mechanism of the dehydroxylation of nontronites, glauconites, and celadonites have been studied by Tsipursky *et al* (1985) and Drits *et al* (1993b). They showed that in dehydroxylated Fe^{3+}-rich dioctahedral tv 2:1 phyllosilicates, octahedral cations migrate from *cis-* to *trans*-vacant sites. The main reason for the different behavior of the Al-Fe^{3+}-rich tv 2:1 layer silicates probably relates to the steric limitations caused by the different ionic sizes of Al and Fe^{3+}.

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