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X-Ray Diffraction Study of Structural Transformations of Aluminous 2:1 Layer Silicates During Dehydroxylation

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Abstract: X-ray powder diffraction was used for the study of structural transformations of dioctahedral Al-rich smectites and illites having different distribution of octahedral cations over *trans*-vacant (tv) and *cis*-vacant (cv) sites within 2:1 layers. The main problems were to determine a model for dehydroxylated cv structures and to explain why smectites and illites consisting of cv 2:1 layers are characterized by dehydroxylated temperatures which are higher by 150-200°C than those for the same minerals consisting of tv 2:1 layers. On set of XRD experiments has been done for sample heated at different temperatures during 1 hour before measurements ("ex situ" samples) and another one has been done for samples heated during the measurements ("in situ" samples). According to the model proposed for cv dioctahedral 2:1 layer silicates the dehydroxylation takes place in two main stages. During the first one each two adjacent OH groups are replaced by the residual oxygen atom and the Al cations which originally occupied *cis*- and *trans* sites become 5- and 6- coordinated respectively. The structure corresponding to this stage of the dehydroxylation is unstable and during the second stage the Al cations migrate from the former *trans*-sites to vacant pentagonal prisms. After this stage the dehydroxylated structure of the former cv 2:1 layers is quite similar to that of the former *trans*-vacant 2:1 layers.

Résumé: La diffraction des rayons X a été utilisée pour étudier les transformations structurales dans des phyllosilicates 2:1 dioctaédriques (smectites et illites riches en Aluminium) chauffés. Les traitements thermiques ont été effectués avant les mesures (échantillons "ex situ") et pendant les mesures (échantillons "in situ"). L'objectif de cette étude est de comprendre pourquoi les smectites et les illites caractérisées par une distribution cationique dans leurs couches octaédriques du type *cis*-vacant (cv) ont des températures de déshydroxylation supérieures de 100 à 150°C à celles des mêmes minéraux du type *trans*-vacant (tv). Un modèle en deux étapes est proposé. Dans un premier temps les groupes OH adjacents sont remplacés par un atome d'oxygène résiduel, les cations Al en site *cis* passent d'une coordination 6 à une coordination 5 alors que les cations en site *trans* gardent une coordination 6. Cette structure est instable. Dans un deuxième temps les cations Al en site *trans* migrent à l'intérieur des couches octaédriques pour former une structure du type *trans*-vacant.

1. INTRODUCTION

Dioctahedral smectites and micas are characterized by a wide range of dehydroxylation temperatures [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15].

Differential thermal (DT) curves for dioctahedral smectites with different chemical compositions show that most montmorillonites have one endothermic peak near 700°C, whereas illites (fine dispersed mica), with greater structural perfection than montmorillonites dehydroxylate near 550°C. In contrast some Fe-poor montmorillonites show a peak doublet, suggesting two endothermic reactions between 500°C and 700°C and some illites have DT curves with one endothermal peak near 700°C or two peaks at about 550°C and 650°C.

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 unambiguously. For example, dehydroxylation temperatures of pyrophyllite, muscovite, and most montmorillonites are similars. In addition, these minerals have similar structures and compositions of their 2:1 layers. For these reasons, Koster van Groos and Guggenheim [10, 11] and Guggenheim and Koster van Groos [8] concluded that the dehydroxylation in montmorillonites, and in particular the CMS Source clay SWy-1 sample, is analogous to the dehydroxylation mechanism in pyrophyllite and muscovite. These authors believed that montmorillonites, like pyrophyllite and muscovite, consist of *trans*-vacant 2:1 layers [7].

Tsipursky and Drits [16] found that octahedral cations may be distributed over both the *trans*- and *cis*- sites in dioctahedral smectites. They showed that most montmorillonites consist of *cis*-vacant (cv) 2:1 layers. Most illites consist of *trans*-vacant (tv) 2:1 layers. Zvyagin et al. [17] and Drits et al. [18], however, 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. [18] and Reynolds and Thompson [19]. Recently Reynolds [20], McCarty and Reynolds [21] and Drits et al. [22] discovered I/S in which tv and cv 2:1 layers were interstratified in different proportions within "fundamental" illite particles.

Because Drits et al. [23] and Tsipursky and Drits [16] showed that tv and cv 2:1 layers are structurally unique it is reasonable to expect that these phases have different dehydroxylation process. The purpose of this paper is to relate dehydroxylation in aluminous dioctahedral 2:1 layer silicates based on these structural features.

2. STRUCTURAL TRANSFORMATIONS OF ALUMINOUS *TRANS*-VACANT 2:1 LAYER SILICATES 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 structures of tv pyrophyllite and muscovite were determined respectively, by Wardle and Brindley [24] and Udagawa et al. [25]. 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 $2(\text{OH}) \rightarrow \text{H}_2\text{O} (\uparrow) + \text{O}_\text{r}$. 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 completing 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 [26]. Dehydroxylation of these minerals increases the values of these parameters up to 5.21-5.25 Å and 9.04-9.09 Å, respectively (see below). If the structural transformation of the dehydroxylated 2:1 layer is confined to only the "residual" anion migration then the Al- O_r distance (Figure 2) will be equal to $b/6$ or $1.51 \div 1.52$ 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 $\langle \text{Al-O} \rangle$ bond length characteristic for the five-fold coordination of Al cations. For example the value of the Al- O_r bond length in dehydroxylated muscovite was equal to 1.69 Å [25]. Such rearrangement of the Al and O_r atoms is the main reason for increasing the *a* and *b* parameters compare to their original values as observed in the dehydroxylated tv muscovite and pyrophyllite samples.

According to this structural model, Drits et al. [27] demonstrated using the unit cell parameters measured by Wardle and Brindley [24], Tsipursky et al. [15] and Drits et al.

[27] that, in *tv* muscovite and *tv* illite, the relative degree of elongation of the linear size was the same along each crystallographic direction.

Figure 1 : A normal projection of the octahedral sheet of 2:1 layers with *trans*-vacant sites.
 Projection sur un plan parallèle au feuillet d'une couche octaédrique avec une distribution cationique du type *trans*-vacant.

Figure 2 : A model for the dehydroxylated octahedral sheet whose former *trans*-sites were vacant.
 Un modèle pour la couche octaédrique du type *trans*-vacant après déshydroxylation.

3. MODEL FOR STRUCTURAL TRANSFORMATIONS OF *CIS*-VACANT 2:1 LAYERS DURING DEHYDROXYLATION

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 in shared and unshared anion edges in the tv and cv octahedral sheets, respectively. 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 Al₁ (see Figure 4) cations have six-fold coordination. Figure 4 shows that the Al₁-O_r and Al₁-O_r' distances are equal to $a/2 \approx 2.50 \text{ \AA}$ 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 Al₁ 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 Al₁-O_r bond lengths (Fig. 5) increases the distance between Al₁ and Al₂ cations, decreases Al₁-Al₂ repulsion, and elongates the shared O₃ - O₄ 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, which 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 $(1 + 2 \cdot 3/5) = + 2.2 \text{ v.u.}$. In contrast, the residual anion is strongly undersaturated with respect to positive charge because it receives the positive charge only from two nearest Al cations ($+1.2 \text{ v.u.}$). The degree of undersaturation of this anion may be decreased due to the shortening of the Al₁-O_r bond length, because bond strength is inversely proportional to bond length. Figure 5 shows that the oversaturated O₅ anion and the undersaturated O_r anion form a shared edge, and there is no way to equalize the saturation of O₅ and O_r by rearranging Al₁, Al₂, O_r and O₅. Thus, the application of additional thermal energy should promote the migration of Al₁ 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.

4. SAMPLES

- montmorillonite sample consisting of the cv 2:1 layers with the composition [28];

- Illite-smectite sample containing 70-80% of cv 2:1 layers [27] with the chemical formula [21];

Differential thermal analysis were applied to these samples. The DT curves for the montmorillonite and illite-smectite sample show one endothermal peak, due to dehydroxylation, at 680 and 715°C respectively.

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

Projection sur un plan parallèle au feuillet d'une couche octaédrique avec une distribution cationique du type *cis*-vacant.

Figure 4 : A model for the dehydroxylated octahedral sheet whose former *cis*-vacant sites. Each two OH groups are replaced by the O_1 anion.

Un modèle pour la couche octaédrique du type *cis*-vacant après déshydroxylation. Les groupes OH sont remplacés par un atome d'oxygène résiduel (O_1).

5. EXPERIMENTS

XRD patterns for the samples were recorded under two different experimental conditions. In one set of experiments, the XRD pattern was recorded during sample heating ("in situ"

samples). The propose of these experiments were to measure $d(060)$ values at different temperatures.

XRD patterns for in situ samples were obtained using $\text{CuK}\alpha$ radiation with Siemens D500 diffractometer supplied with a platinum thermocouple. A sample was heated at a rate of $150^\circ\text{C}/\text{hour}$ to achieve a given temperature and then a XRD pattern was recorded during 1 hour. The temperature was increased again at a rate of $150^\circ\text{C}/\text{hour}$ to get to the next temperature, and a new XRD pattern was recorded. This procedure was continued. Intensities were measured at intervals of $0.05^\circ 2\theta$ 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 $\pm 0.001 \text{ \AA}$.

In the other experiments, samples were heated at different temperatures before the measurements ("ex situ" samples). XRD patterns for these samples were obtained using $\text{MoK}\alpha$ radiation with a INEL CPS120 diffractometer supplied with a curve position sensitive detector. This detector permits simultaneously recording of diffracted intensities in the interval of 2θ from 1° to $70^\circ 2\theta$. A sample holder was a thin tube made from Lindenman glass with the diameter equal to 1mm. A temperature rate of sample heating was equal to $150^\circ\text{C}/\text{hour}$. Each sample was heated at a given temperature for 1 hour and then cooled at air. The illite-smectite sample was heated at 300°C , 400°C , 500°C , 600°C , 650°C , 700°C and 750°C .

It is noteworthy that the XRD patterns corresponding to the "in situ" and "ex situ" illite-smectite sample heated at the same temperature were similar. For this reason we consider only some of the recorded XRD patterns corresponding to "ex situ" samples.

Figure 5 : A model for the dehydroxylated octahedral sheet of 2:1 motmorillonite layers corresponding to a intermediate stage of the structural transformation.

Une étape intermédiaire dans la transformation structurale de la couche octaédrique d'une montmorillonite du type *cis*-vacant après déshydroxylation.

6. RESULTS

6.1 XRD patterns for the illite-smectite sample at different temperatures

Figures 6 shows the X-ray powder patterns for the illite-smectite "ex situ" sample heated at 300°C , 600°C and 650°C . The low temperature pattern (Figure 6a) contains two diagnostic peaks corresponding to the 111 and 113 reflections with d values equal to $3.87 \text{ \AA}$ 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. Using d-values of the 111 and 113 reflections (Figure 6a) and d(001) and d(060) values, the average unit cell parameters for the sample were calculated (Table 1). The calculated value of $c\cos\beta/a = -0.331$ indicates that cv 2:1 layers dominates considerably over tv 2:1 layers [19]. The diffraction for the heat-treated sample at 650°C differs substantially from that of the low-temperature sample (cf, Figures 6a and 6c). Table 1 shows the unit cell parameter for Figure 6c based on the tv structure and 1M polytype. Good agreement between the experimental and calculated d-values for 112, 022, 003 and 112 reflections (Table 2) and the value of $c\cos\beta/a = -0.398$, which is the diagnostic for tv-1M mica polytype [29], show 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 6b). This suggests an intermediate heterogeneous stage of the cv layer transformation.

Table 1 : The unit cell parameters for the illite-smectite sample heated at different temperatures.
Paramètres de maille de l'échantillon illite-smectite chauffé.

Temperature (°C)	a (Å)	b (Å)	c (Å)	β (°)	$c\cos\beta/a$
300°C	5.19	9.00	10.19	99.70	-0.331
650°C	5.28	9.04	10.27	101.8	-0.398

Figure 6 : The XRD curves for the illite-smectite sample heated at 300°C (a), 600°C (b) and 650°C (c), d values are given above the corresponding peaks.

Diffractogrammes pour l'échantillon illite-smectite chauffé à 300°C (a), 600°C (b) et 650°C (c), les valeurs de d sont indiquées au-dessus des pics.

Table 2 : Experimental and calculated XRD powder data for the original (O) and dehydroxylated (D) illite-smectite sample, spacing in Å. (* correspond to two strongest reflections for a tv-1M illite variety)
 Valeurs de $d(hkl)$ en Å pour l'échantillon illite-smectite dans l'état original (O) et après déshydroxylation (D).
 (le symbole * correspond à deux pics intenses pour une illite *trans*-vacante)

	O		D	
hkl	d_{cal}	d_{exp}	d_{cal}	d_{exp}
020	4.500		4.521	4.49
110	4.455	4.46	4.496	
111	3.862	3.87		
$11\bar{2}^*$			3.690	3.70
022	3.342	3.35	3.360	3.555
003	3.330		3.350	
$11\bar{2}^*$			3.087	3.10
$11\bar{3}$	2.875	2.88		
130			2.604	2.598
200	2.560	2.559	2.585	
$13\bar{1}$	2.554			
$20\bar{2}$	2.452	2.451		
131	2.451			
201	2.385	2.383	2.345	2.396
$13\bar{2}$	2.382			
040	2.250	2.241	2.260	2.251
220	2.227		2.244	
202	2.136	2.135		
$13\bar{3}$	2.133			
060	1.500	1.500	1.507	1.507

6.2 Temperature dependance of the b parameter for the cis-vacant samples

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 7).

In situ measurements of the illite-smectite sample heated at different temperatures show that the increase of temperature increases the b parameter.

Figure 7 : The dependance between the temperature of montmorillonite sample heating and the b parameter. Variation du paramètre b en fonction de la température pour l'échantillon montmorillonite.

7. DISCUSSION

The XRD data obtained here and previously published for aluminous 2:1 layer silicates heated to high temperatures [27] are in agreement with the above models for the structural transformation of cv 2:1 layers during dehydroxylation.

The dramatical differences of the XRD patterns for the cv illite-smectite sample 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 (Figure 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, as shown in Figure 2, in accord with the earlier work of Wardle and Brindley [24] and the crystal chemical model of Guggenheim [7]. 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 the sample 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 sample are also in agreement 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_T 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, and 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 7) correspond to the temperature interval where dehydroxylation occurs for most montmorillonites (near 700°C).

The increase of temperature to 700°C provides cv montmorillonite and illite-smectite 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 montmorillonite sample whereas for the unheated samples, the b values were equal to 8.965 Å.

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

Let us consider now 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 (800-900°C) and tv illites (500-600°C) is related to the high dispersion of illite particles. This assumption can not however explain high dehydroxylation temperatures for cv montmorillonites and cv illites.

Guggenheim et al. [30], Koster van Groos and Guggenheim [10, 11] and Guggenheim [7] were the first to use detailed crystal chemical approach to explain thermal reaction from structural approach. In particular, they considered the dehydroxylation in 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 more strongly bonded 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. [30] explains both the asymmetry and broadness of the endothermic peak. Their model does not completely explain the significant differences of dehydroxylation peak temperatures for montmorillonites and illites, however, because it does not consider cv illites and cv montmorillonites. The model derived by Guggenheim for tv dioctahedral aluminous pylosilicates is completely consistent with the model described.

One possible reason for high dehydroxylation temperature of cv montmorillonite and illites may be related to the structure features of their 2:1 layers. Comparison of structural models for tv and cv octahedral sheets (cf. Figure 1 and 3) shows that the main differences consists of different distances between adjacent OH groups. According to most single crystal structural refinements of Al-rich dioctahedral micas [29], the shared OH-OH edges in tv 2:1 layers have bond length of $2.45\text{Å} \pm 0.05\text{Å}$ whereas the length of the non-shared OH-OH edges in cv 2:1 layers are expected to be considerably longer (2.85-2.88Å). 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 in cv 2:1 layers in comparison with the OH-OH edges in tv 2:1 layers may be the major factor responsible for the higher dehydroxylation temperature of cv montmorillonites and cv illites. Thus, despite of 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.

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) consisting of tv 2:1 layers [17, 31, 32], the rapid loss of hydroxyls begins at a lower temperature compared to Al-rich samples [13, 33].

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