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STRUCTURAL TRANSFORMATIONS OF INTERSTRATIFIED ILLITE-SMECTITES FROM DOLNÁ VES HYDROTHERMAL DEPOSITS: DYNAMICS AND MECHANISMS

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Abstract—Structural transformations of illite-smectite samples of hydrothermal genesis with increasing contents of illite layers were studied by X-ray powder diffraction. The samples were K-saturated and subjected to wetting and drying cycles to increase three-dimensional structural ordering. Diffraction profiles were analyzed with the help of a specially devised computer program based on the approximation of individual diffraction reflections by "bell-shaped" functions, with minimization of the differences between experimental and simulated profiles. The data indicate that the transformations of these illite-smectite samples were accompanied not only by variations in the proportion of illite and smectite layers and in the pattern of their alternation, but also by a change in structure within 2:1 layers.

Key Words—Cis-octahedron, Illite-smectite, Illitization, Phase Transformations, Trans-octahedron.

INTRODUCTION

Interstratified illite-smectites (I/S) are abundant in diverse geological environments. Special attention is paid to I/S for a number of reasons. First, their structural features may reflect changes in physico-chemical conditions in the enclosing rocks. Postsedimentary alterations in sedimentary basins are known to be accompanied by illitization via a series of I/S minerals having an increasing content of illite interlayers and an increase in ordering of the layer distribution. Similar reactions are found in regions of intensive hydrothermal activity. Second, mixed-layer minerals, and I/S in particular, represent an example of natural phase transformations in which a new mineral is formed from the matrix of an initial mineral.

There is extensive literature on the methods of identification of I/S and on the mechanisms of I/S formation at different stages of postsedimentary and hydrothermal alteration of rocks (Drits and Sakharov 1976; Środoń and Eberl 1984; Drits and Kossovskaya 1991; Reynolds 1980; Nadeau et al. 1984, 1985). Recently, Eberl (1993) presented a general theory concerning the problem of phase transformations of I/S in sedimentary basins.

The basic deficiencies in the previous works include: 1) that the main attention has been paid only to the study of I/S expandability; 2) the determination of order/disorder in the distribution of illite and smectite interlayers; 3) the analysis of texture alterations; and 4) variations in the chemical composition of layers of different types. Therefore, I/S structure studies normally were confined to the analysis of the I/S structure projected on an axis normal to the layers. Only basal reflections were analyzed using X-ray diffraction (XRD) while electron microscopy was used to determine shape and thicknesses of particles, including fundamental illite particles (Nadeau 1985), and high-resolution transmission electron microscopy was used to image the distribution of interlayer types (Peacor 1992).

In the rare cases where XRD patterns from disoriented I/S samples were described, their analysis was confined to the statement that their non-basal reflections corresponded to the 1M polytype. Šucha et al. (1992) mentioned an I/S sample with abnormal relationships among the unit cell parameters that are unusual for 1M illites. However, the authors did not analyze the nature of these effects in detail.

It is possible that variations in the proportion of illite and smectite interlayers in I/S minerals are accompanied by a restructuring of the 2:1 layers. This inference is based on the fact that in dioctahedral 2:1 layers, only two of the three symmetrically independent octahedral sites are occupied by cations. Tsipursky and Drits (1984) showed that in montmorillonite 2:1 layers, as a rule, one of the two symmetrically independent cis-octahedra is vacant, whereas illites normally consist of 2:1 layers with vacant trans-octahedra. These authors showed that different patterns in the distribution of cations over the available trans- and cis-octahedra are accompanied by differences in the structural distortions of the corresponding 2:1 layers. Drits (1987) reported that illitization of montmorillonites during postsedimentary alterations of acidic pyroclastic rocks in a deep (greater than 4 km) section of a coal-bearing formation of the Karaganda basin (Kazakhstan) is accompanied not only by increasing proportions of illite layers and ordering in their distribution in I/S structures, but also by a variable proportion of 2:1 layers having vacant cis- and trans-octahedra.

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Reynolds (1993) has shown that fundamental illite particles in I/S consist of randomly interstratified trans- and cis-vacant 2:1 layers, based on the agreement between experimental and calculated XRD powder patterns containing hkl reflections.

The present work analyzes XRD patterns from disoriented I/S samples saturated by K and subjected to wetting-and-drying (WD) cycles in order to increase their three-dimensional structural ordering. The problem involved revealing the nature of structural transformations of I/S samples of hydrothermal genesis with increasing contents of illite layers.

SAMPLES AND METHODS

Geologic and Mineralogical Data

I/S samples came from shallow wells (up to 50 m) covering the entire areal extent of a hydrothermal deposit which is located in the SW part of Kremnica Mts (Šucha et al. 1992). The rocks of this region are composed of rhyolitic volcanoclastics of explosive origin. A typical feature of the final volcanic activity was sedimentation of volcanic sediments in lacustrine and fluviolacustrine environments, where they were converted to clay minerals, and in particular to I/S minerals.

The proportion of illite interlayers, W_I, in the I/S studied varied from 55 to 94%, with the short-range ordering factor R = 1 (for $W_I < 85\%$) and R = 3 (for $W_I > 85\%$), and there is a clear correlation between W_I and the number of fixed interlayer cations. It was assumed that the I/S minerals were formed as a result of the reaction between smectites and K-containing hydrothermal solutions. A zonation in expandability was observed in the studied area. It decreases from the south to the north and is related to a decrease in the temperature of hydrothermal solutions coming from the north. The solutions probably had temperatures that ranged between 120° and 200°C (Šucha et al. 1992).

Sample Preparation

Collected samples were mixed with distilled water and disaggregated using an ultrasonic probe. Then the less than 1 μm fraction was separated by centrifugation. The separated fractions were exchanged with 1 N KCl solution and subjected to WD cycles to increase the degree of three-dimensional ordering. 250 mg of sample in K-form was wetted with 25 ml of distilled water and then dried at 60°C. The procedure was repeated 60 times. This treatment favored the mica-like stacking of the adjacent 2:1 layers separated by smectite interlayers (Tsipursky and Drits 1984).

The following procedure was applied to obtain the greatest possible degree of particle disorientation for XRD analysis. The sample was mixed with rosin (1:1 by volume) and ground to a powder. After a thorough stirring, the sample was placed into a porcelain crucible and heated on a gas burner until the rosin melted (t° = 60–70°C). After cooling and solidification, the mixture was ground into powder. Note that the presence of rosin did not noticeably increase the XRD background.

Experimental

The XRD patterns were obtained using a DRON-4 powder diffractometer, with CuKα radiation, 30 kV and 30 mA. Three vertical slits were used, 0.5, 1.0 and 0.5 mm wide, respectively, and two Soller slits, 2° each; a planar graphite monochromator was placed in front of the detector. Step scanning was applied, with steps of 0.05° 2θ and a count time of 20–30 sec. The data obtained was recorded on a diskette and then processed by an IBM PC.

The XRD profiles were analyzed using a computer program that we developed. It is based on an approximation of individual XRD peaks by "bell-shaped" functions, with minimization of the difference between the experimental and calculated profiles. Our experience in working with the DRON-4 diffractometer showed that the smallest discrepancy between the observed and simulated profiles is obtained if the approximating function is a combination of two Gaussian profiles. One describes the profile of the top of the XRD peak with steep slopes (the upper Gaussian), and the other (the lower Gaussian), which was twice as wide, describes the lower less steep part (Salyn 1988).

It was shown through the experiment that the asymmetry in the upper part of the XRD reflection differs substantially from that in the lower part, especially for reflections located in the low-angle region. In order to take this asymetry into account, a "bell-shaped" function was used, with varied relative contributions and asymmetries for the "upper" and the "lower" Gaussians. Since Kα radiation was used in the XRD experiment, the function involved was a combination of the two functions for $K\alpha_1$ and $K\alpha_2$.

The quality of the approximation using these functions was tested by analyzing the profiles of individual reflections for reference samples, for example, the R factor did not exceed 1%. The latter factor was determined as the difference between the experimental profile and the curve synthesized after summation of individual $K\alpha_1 - K\alpha_2$ reflections.

RESULTS

Although the XRD patterns of the samples under study showed intensity modulations corresponding to hkl reflections, the profiles of the basal reflections with d close to 5 Å and 3.3 Å remained relatively broad. This effect indicated that either the coherent scattering domains (CSD) are very thin or the WD cycles did not completely eliminate interstratification effects, so that strict 10 Å thickness was not achieved for K-containing smectite layers. The analysis of XRD curves

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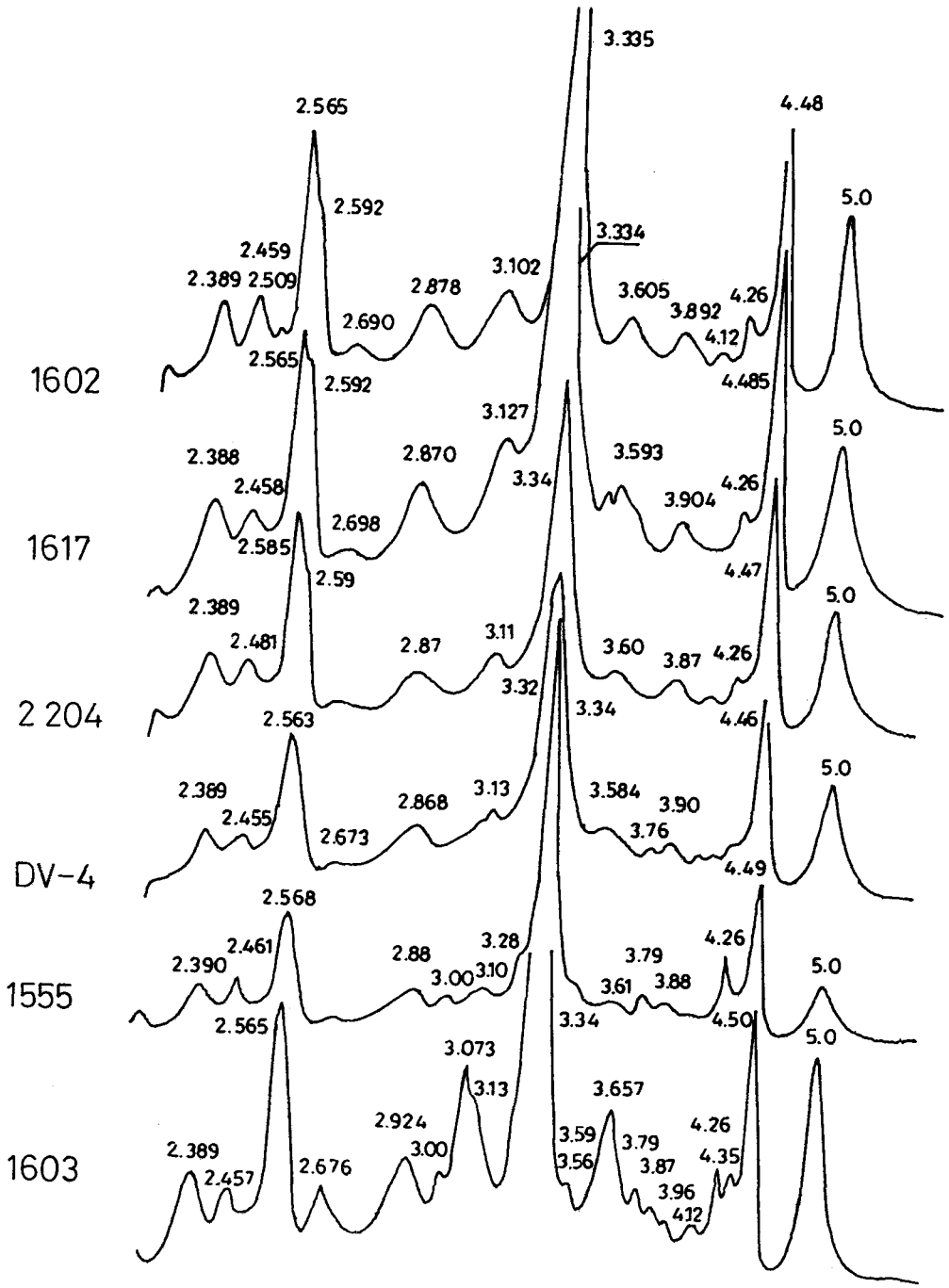


Figure 1. XRD patterns of random K-saturated I/S, subjected to WD-cycles and heated at 350° for 2 hours. Numbers above reflections are d values in Å.

obtained for the same samples heated up to 300°C for one h supports the latter hypothesis. Removal of the water molecules from I/S smectite interlayers with heating was accompanied by "equalizing" the thicknesses of illite and K-containing smectite interlayers leading to a considerable decrease in the width at half-height for basal reflections (Figure 1). In the XRD curves of the heated samples, hkl reflections became better defined, and additional reflections appeared because of the narrower 003 reflections (d = 3.33 Å).

Qualitatively, the XRD curves of the samples under study can be classified into three groups according to the positions and intensities of hkl reflections. The first group contains samples DV-3, DV-4, 2198 and 1617;

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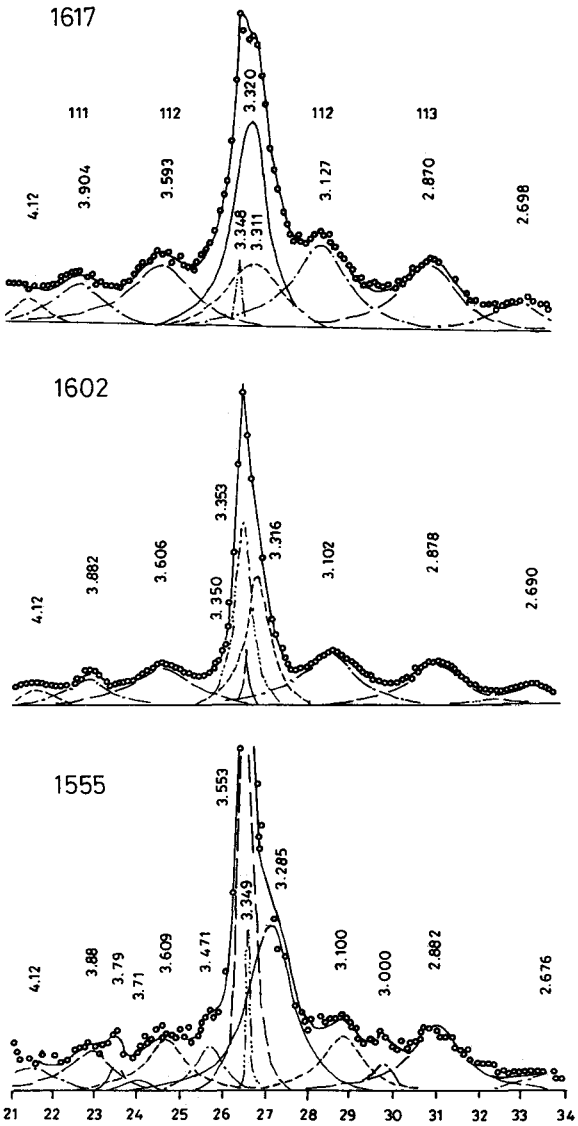


Figure 2. Portions of experimental (circles) and simulated (solid lines) XRD patterns for I/S samples 1617, 1602, and 1555. Individual reflections with the corresponding d values (Å) are shown under the XRD curves.

the second, samples 1602, 2223 and 1555; the third, sample 1603.

As an example, Figure 2 shows portions of the XRD curves for samples 1617, 1602 and 1555, and the results of the decomposition of these curves into individual reflections using the technique described in the previous section. The corresponding d values are given near each reflection; above the reflections, hkl indices are shown that are common for reflections having closed d values. The indexing of the reflections corresponds to the 1M polytype. According to the results obtained, a consecutive variation is observed for the d values for each reflection with the given hkl indices

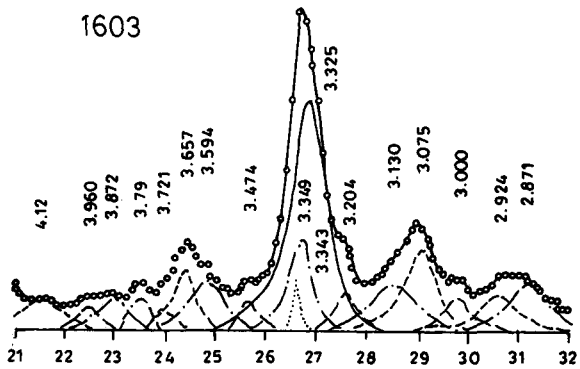


Figure 3. Portions of experimental (circles) and simulated (solid lines) XRD patterns for I/S sample 1603. Individual reflections with the corresponding d values (Å) are shown under the XRD curve.

when proceeding from the XRD curve for sample 1617 to that for sample 1555. Indeed, the d value for the 112 reflection decreases from 3.127 Å for sample 1617 to 3.100 Å for sample 1555, whereas the d value for the $11\bar{2}$ reflection increases from 3.593A for sample 1617 to 3.606 Å and 3.609 Å for sample 1555. Figure 3 shows the result of the decomposition of the XRD curve for sample 1603 into individual reflections, with the d values shown for each reflection.

The data obtained can be interpreted in terms of the structural and diffraction criteria formulated by Drits et al. (1984, 1993) for the identification of structural varieties of one-layer illites. These authors considered the following structural models:

tv-1M illites, with vacant trans-octahedra;
cv-1M illites, with vacant cis-octahedra;
m-1M illites where, within each 2:1 layer octahedral cations occupy cis-octahedra as well as trans-octahedra;
tv/cv-illites, in whose microcrystal layers having either cis- or trans-vacant octahedra alternate in various proportions.

Each of the above varieties is characterized by specific relationships between unit cell parameters a, c, and β (Drits et al. 1984, 1993). In particular, $|c \cos \beta / a|$ is 0.400 for trans-vacant 1M illites and 0.300 for cis-vacant 1M illites. Depending on the occupancies of trans-octahedra (for m-1M illites) or on the proportions of the 2:1 layers with either cis- or trans-vacant octahedra (for tv/cv illites), $|c \cos \beta/a|$ should be intermediate between the above values for tv-1M and cv-1M varieties.

Diffraction characteristics of the structural varieties also differ substantially. XRD patterns of tv-1M illites contain strong reflections $11\bar{1}$, $11\bar{2}$ and 112, whereas the 111 reflection has zero intensity. Conversely, XRD patterns of cv-1M illites have the reflections 111, $11\bar{2}$, 112 and $11\bar{3}$ with similar intensities (Figure 4).

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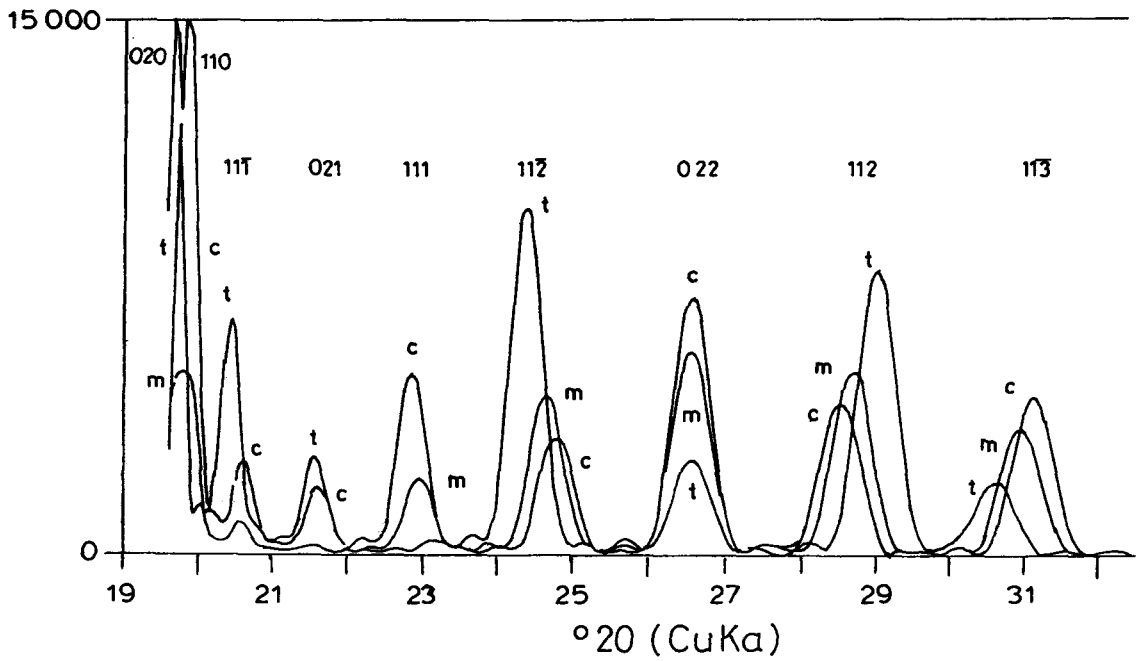


Figure 4. XRD patterns calculated for tv-1M, cv-1M and m-1M illite varieties. Letters tv, m and cv refer to the peaks corresponding to tv-1M, m-1M, cv-1M structures. The hkl indices are given above the corresponding reflections.

Because of different relationships between unit cell parameters, reflections having the same hkl indices for different illite varieties can differ substantially in d(hkl) values. The principal difference between m-1M and tv/cv-1M illites consists of dramatically different relations between intensities of the peaks at 4.50 Å and 2.565 Å. In XRD patterns for disoriented tv/cv illite samples these peaks are approximately equal in intensity, whereas in the case of m-1M illites, the reflection at 4.5 Å is less than one-half of that at 2.565 Å (Drits et al. 1984, 1993).

In the light of the above structural and diffraction features of the illite varieties, the experimental data obtained for the samples under study can be treated as resulting from irregular alternation of 2:1 layers having either trans- or cis-vacant octahedra within the CSD. Such an interpretation is supported, first by the fact that the observed d(hkl) values with $k \neq 3n$ differ from those corresponding to tv-1M or cv-1M illites (Drits et al. 1993). Second, the model that involves statistical distribution of cations over cis- and trans-position within the same layer should be discarded because in all experimental XRD patterns the peaks at 4.47–4.50 Å and 2.565 Å are of similar intensity (Figure 1), whereas in the simulated SRD curve they differ dramatically in intensity.

Table 1. Values $p = |c \cos \beta/a|$ and $W_{cv}(\%)$ calculated from (1) and (2), proportions of expandable interlayers (W_s), and K contents per formula unit (n_{fix}) in I/S under study.

Sample	P		P_{cp}	W_{cv}	W_s	n_{fix}
	Based on d(112) and d(112)	Based on d(112) and d(113)				
DV4	0.303	0.300	0.30	100	45	0.43
2198	0.306	0.305	0.30_5	95	37	0.45
1617	0.310	0.308	0.31	90	40	0.46
2204	0.319	0.313	0.31_5	85	19	0.49
2223	0.314	0.317	0.31_5	85	25	0.46
DV3	0.322	0.320	0.32	80	37	0.45
1602	0.337	0.332	0.33_5	65	14	0.56
1555	0.341	0.337	0.34	60	21	0.52
1603†	0.389	0.388	0.39	10	8	0.61
	0.308	0.308	0.31	90		

† The sample is a mixture of 1M illites in each of which either tv or cv 2:1 layers prevails.

To evaluate the proportions of 2:1 layers differing in the octahedral cation distribution the following equations were used:

$$W_{cv} = [1 - (p - 0.3)10]100\%,$$
$$\text{where } p = |c \cos \beta/\alpha|$$
$$W_{tv} = 1 - W_{cv}. \quad [1]$$

The value for p is readily obtained from the relationships:

$$p = d^2(002)[1/d^2(112) - 1/d^2(11\bar{2})]/2$$
$$= 2d^2(002)[1/d^2(11\bar{2}) - 1/d^2(111)]/3 - 0.5$$
$$= 2d^2(002)[1/d^2(11\bar{3}) - 1/d^2(112)]/5 - 0.5. \quad [2]$$

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Table 1 gives the p values calculated from d(11$\bar{2}$), d(112) and d(11$\bar{3}$) determined from the analysis of the XRD patterns of the samples (Figures 1–3). In the same Table, the proportion of 2:1 layers having vacant cis-octahedra, contents of expandable interlayers (W_S) and K contents per formulae unit (n_{fix}) are given for each sample. Table 1 shows that the $|c \cos \beta/a|$ values vary from 0.30–0.31 for samples 2198, DV-4, 1617, which is typical for illites having vacant cis-octahedra, to 0.33–0.34 for samples 1555 and 1602, which corresponds to illites in which the proportion of 2:1 layers having vacant trans-octahedra is close to 33%. The non-zero occupancy of trans-octahedra in the samples under study is confirmed not only by the $|c \cos \beta/a|$ values, but also by the intensity distribution for the 111, 11$\bar{2}$, 112, and 11$\bar{3}$ reflections. Figure 1 shows that for all the samples except 1603, the intensities of the 11$\bar{2}$ and 112 reflections are close to those of the 111 and 11$\bar{3}$ reflections, which is typical for 1M illites having relatively high occupancies of trans-octahedra (Drits et al. 1984, 1993).

The set of reflections and the corresponding d values obtained from the decomposition of the XRD pattern of sample 1603 show that the sample is a physical mixture of tv-1M illite with the occupancy of trans-octahedra less than 10%, and cv-1M illite with similar low occupancy of cis-octahedra (< 10%) (Table 1). The presence of tv-1M illite is indicated by two strong reflections, 11$\bar{2}$ at 3.657 Å and 112 at 3.075 Å. Figure 1 shows that the XRD pattern of this sample contains a fairly strong 11$\bar{1}$ reflection at 4.35 Å, which is also typical for the variety in question. The low occupancy of trans-octahedral sites is shown by the $|c \cos \beta/a| = 0.389$ value. Reflections were of approximately equal intensity for 111 at 3.872 Å, 11$\bar{2}$ at 3.594 Å, 112 at 3.130 Å and 11$\bar{3}$ at 2.871 Å, corresponding to cv-1M illite having $|c \cos \beta/a| = 0.308$. The reflections at 3.79 Å, 3.474 Å, 3.204 Å, and 3.000 Å most probably correspond to a feldspar.

Note that a small amount of feldspar is present in sample 1555, which is indicated by reflections at 3.79 Å, 3.47 Å and 3.00 Å. The characteristic strong reflection at 3.20–3.18 Å for these mineral varieties in the XRD pattern of the heated sample is apparently overlapped by a broad and relatively strong 003 reflection from mixed-layer illite-smectite at 3.285 Å (Figures 1 and 2).

Another serious argument in favor of the presence of cations in trans-octahedra for the samples 1602 1617, 1555 and others is provided by the positions of peaks near the 020 and 110 reflections. Drits et al. (1993) showed that in the case of 1M illites having vacant trans-octahedra, the XRD curves contain a strong 020 reflection at about 4.50 Å, whereas for those having vacant cis-octahedra, the 110 reflection at 4.46 Å is stronger. Figure 1 shows that the XRD curve for sample 1603 contains a strong peak at 4.50 Å, which confirms that 1M illite having vacant trans-octahedra prevails in the sample. In the XRD curves of the other samples, the corresponding peaks are shifted toward high θ angles and have $d \cong 4.46 - 4.48$ Å.

Errors in the determination of the proportions of 2:1 layers having vacant cis- or trans-octahedra largely depend on the errors in the positions of 11l reflections. For the samples with absolute prevalence of either vacant cis-octahedra (1617, DV-4, 2198) or vacant trans-octahedra (1603) the proportions of layer types are determined with errors ± 5%. Difficulties in accurate determination of d(11l) values arose when the reflections analyzed had clearly asymmetric profiles, e.g., reflections 11$\bar{2}$ and 112 in the XRD curves of 2204 and 2211. For such samples, errors in the absolute values for proportions of layers having vacant cis- or trans-octahedra may be as large as ±10%.

DISCUSSION

The data obtained indicates that transformations of I/S are accompanied not only by change in the proportions of illite and smectite layers and in the ordering of their alternation, but also by the restructuring of 2:1 layers.

As mentioned above, a model with all 2:1 layers having the same cation distribution over the available cis- and trans-positions can be considered an alternative to mixed-layer tv/cv illite. Drits et al. (1984) showed that such model will lead to XRD patterns in which the positions of reflections coincide with those in XRD patterns simulated for tv/cv illite if the occupancy of trans-octahedra in the first model equal to the proportion of 2:1 layers with vacant cis-octahedra for the mixed-layer structure.

Two considerations lead us to discard the model with disordered cation distributions over the available octahedral sites in each 2:1 layer of 1M illite. First, XRD patterns from disoriented tv/cv illite samples contain peaks at 4.46–4.49 Å and 2.565 Å of approximately equal intensity (Figure 1). This effect is not observed in XRD patterns calculated for structures where cis- and trans-octahedra have equal occupancies in each 2:1 layer. Second, disordered distribution of cations over the available cis- and trans-octahedra within individual 2:1 layers is unfavorable for local change balance because it leads to cation combinations consisting of three, two and one octahedral cations that coordinate with the nearest anion. With trivalent Al cations prevailing in octahedra, the first of the above cation combinations would lead to considerable "oversaturation" of the anion by positive valences, whereas the third combination would lead to serious valency "undersaturation" of the anion.

Another possible model for the samples under study is of a physical mixture of illite fundamental particles having either cis- or trans-octahedra vacant. It is

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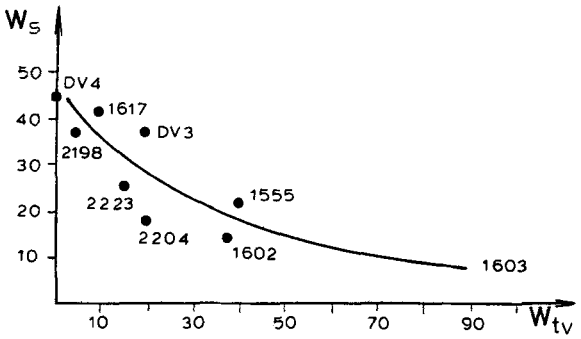


Figure 5. Proportion of 2:1 layers with vacant trans-octahedra (W_{tv}) vs contents of smectite interlayers (W_S) in I/S under study.

known that in interstratified I/S, fundamental illite particles are particles separated from each other by the nearest smectite interlayers. Such particles contain only a few illite interlayers, for example they are very thin. One can suppose that some of the fundamental illite particles in the samples under study consist of 2:1 layers with vacant trans-octahedra, whereas others consist of those having vacant cis-octahedra. Small thicknesses of fundamental particles consisting of 2–5 illite interlayers (with expandability of I/S less than 15–20%) should lead to a very broad XRD maxima. Therefore, XRD effects for a model consisting of fundamental particles with alternating 2:1 layers having either cis- or trans-octahedra vacant are similar to XRD effects for a model of fundamental particles differing in ordered distribution of cations over cis- and trans-octahedra. Similar XRD effects should be observed for both models if the occupancy of trans-octahedra are averaged for all of the 2:1 layers. The main reason for the similarity of XRD powder patterns for the models discussed is the very thin thickness of fundamental illite particles. This leads to an overlap of reflections having the same 111 indices and similar d values, such that the position of the resulting intensity maximum generally reflects the proportions of 2:1 layers with vacant cis-octahedra and those with vacant trans-octahedra.

Figure 5 shows that the I/S samples studied tend to have increasing contents of 2:1 layers having vacant trans-octahedra with decreasing proportions of smectite interlayers. The contents of 2:1 layers with vacant trans-octahedra in the samples DV-4, 1617 and 2198 with the highest expandability (W_S = 37 – 45%), is zero to less than 10%.

Samples with lower expandability (1602, W_S = 14%; 2211, W_S = 20% and 1555, W_S = 21%) have higher contents of 2:1 layers with vacant trans-octahedra. In individual fundamental illite particles, these layers either are segregated, or alternate with 2:1 layers having vacant cis-octahedra. In 1603, the sample with the minimum expandability (6%), relatively narrow and strong 111 reflections of the tv-1M illite variety correspond to fundamental illite particles having dominant trans-vacant 2:1 layers.

Therefore, the structural mechanism for illitization of smectites can be imagined as follows: Since the 2:1 layers in the initial montmorillonite have vacant cis-octahedra, I/S formation at relatively low temperatures and/or low K contents in the solution proceeded generally as a solid-phase reaction, without appreciable restructuring of 2:1 layers. Illite interlayers appeared only between 2:1 layers having K cations adsorbed in the centers of ditrigonal rings of the adjacent tetrahedral sheets. The fundamental illite particles formed should be very thin and contain 1–2 illite interlayers, which would lead, with the number of layers in CSD being small, to relatively high contents of smectite interlayers and to considerable half-width at half-height for basal reflections.

The thickness of fundamental illite particles can be estimated from the formula of Środoń et al. (1992):

$$T = \frac{0.89}{0.89 - n_{fix}} (nm) \quad [3]$$

where n_{fix} is the number of irreversibly fixed interlayer cations per structural formula determined from the chemical analysis of the sample.

If we suppose that n_{fix} is equal to the number of K atoms per formula unit (Table 1), then, for the samples of the first group (2198, DV4, 1617), the mean thickness of fundamental particles is about 2 nm. Such thin particles can be formed through a solid-phase reaction either as a result, such as a heterogeneous charge redistribution in individual 2:1 layers or under the influence of other factors.

It was found that the samples closest to the source of hydrothermal solutions have the smallest proportion of smectite interlayers in I/S. This process was evidently accompanied by dissolution-reprecipitation. The thinnest illite fundamental particles having vacant cis-octahedra became unstable under new physicochemical conditions and were therefore dissolved, and the newly-formed 2:1 layers had vacant trans-octahedra. We can imagine (Figure 6) that the newly-formed 2:1 layers were attached to the existing fundamental illite particles having vacant cis-octahedra, thus forming interstratified tv/cv fundamental particles. The higher the temperature and K concentration in the solution, the higher the proportion of the newly-formed 2:1 layers having vacant trans-octahedra. Simultaneously, as the thickness of illite fundamental particles increase the proportion of expandable layers in CSD decreased and the short-range ordering factor, R, became 3. In the limiting case (sample 1603) the basic illite component contained no more than 10% 2:1 layers with vacant cis-octahedra.

In some aspects, the mechanism described is similar to that proposed by Nadeau et al. (1985). According

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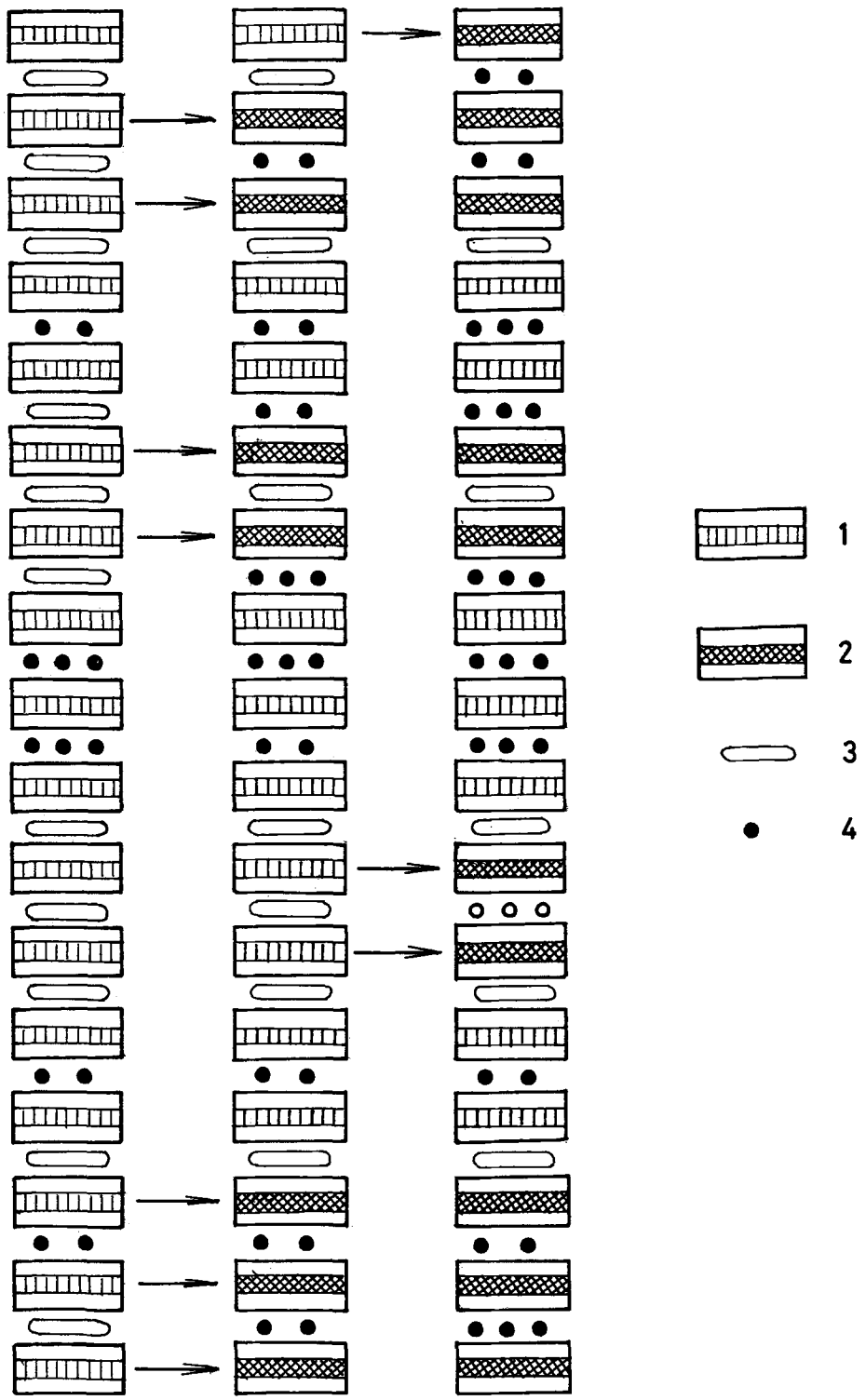


Figure 6. Schematic representation of consequent stages in the formation of fundamental illite particles consisting of 2:1 layers with either cis- or trans-octahedra vacant. Increase in the thickness of fundamental particles results from dissolution of 2:1 layers with vacant cis-sites and layer-by-layer growth of thicker particles containing layers with two types of octahedral cation distribution. 1, cv-layers; 2, tv-layers; 3, smectite interlayers; 4, K cations.

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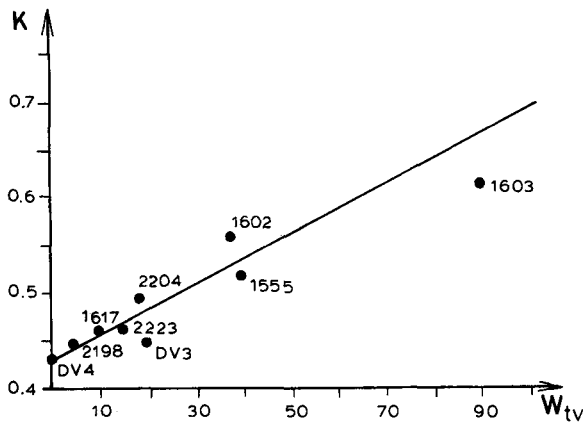


Figure 7. Interrelationship between the proportion of 2:1 layers with vacant trans-octahedra (W_{tv}) vs content of interlayer K.

to their model, smectite is converted to illite due to dissolution of smectite layers and the precipitation/growth of "illite" particles.

Figure 7 illustrates the interdependence between the contents of non-exchangeable K cations per formula unit and the proportion of 2:1 layers with vacant trans-octahedra in the I/S samples under study. It is clearly seen that increasing K contents leads to increasing proportions of 2:1 layers having vacant trans-octahedra. The data of Figure 7 can be treated as indirect evidence that changes of physicochemical conditions connected with increasing temperature and/or K concentration in the solution, lead to a recrystallization of illite fundamental particles that is accompanied not only by an increase in their thickness and a decrease in the proportion of smectite interlayers, but also by a consecutive increase of the contents of 2:1 layers with vacant trans-octahedra in these particles. The model also allows an increase in the proportion of fundamental illite particles consisting only of 2:1 layers with vacant trans-octahedra.

According to the model the solid-state transformation of the I/S phases having cis-vacant 2:1 layers replaced by the reaction of the cis-vacant 2:1 layer dissolution and trans-vacant 2:1 layer reprecipitation. In some respects this process of the I/S transformation is in agreement with the two-stages illitization mechanism described by Drits (1987) and Eberl (1993).

CONCLUSION

Mixed-layer I/S minerals coming from Dolná Ves hydrothermal deposit were studied by XRD. Expandability of the I/S samples decrease with temperature increase of the hydrothermal solutions. The three-dimensional periodicity of the K-saturated samples was increased by 60 wetting and drying cycles. XRD powder patterns of the treated I/S samples contained hkl reflections. Analysis of the reflection spacings has shown that all samples studied can be classified into three groups.

The first group contained samples consisting of cis-vacant 2:1 layers and is characterized by the highest expandability. The samples of the second group consisted of randomly alternating cis- and trans-vacant 2:1 layers. The sample of the third group is a physical mixture of the tv-1M illite with the occupancy of trans-octahedra less than 10% and cv-1M illite with similar low occupancy of cis-octahedra. Thus, the transformation of the I/S samples was accompanied not only by variations in the proportion of illite and smectite layers and the patterns in their distribution, but also by a change in structure within 2:1 layers. According to the model proposed, the transformation of the I/S minerals was accompanied by dissolution of cis-vacant 2:1 layers and reprecipitation of trans-vacant 2:1 layers. Simultaneously an increase of the interlayer K cations took place during the neoformation of trans-vacant illite layers.

It is interesting to compare the data obtained for these hydrothermal I/S samples with results of McCarty and Reynolds (1995) who studied Ordovician K-bentonites of the Appalachian Basin (USA). These authors also concluded that the I/S samples consisted of alternating 2:1 layers with vacant trans- and cis-octahedra. According to their data, the higher the Al content, the higher the contents of 2:1 layers with vacant cis-octahedra. No such correlation was observed in the set of the I/S samples that we studied. McCarty and Reynolds (1995) found no relationship between expandability of I/S with vacant trans-octahedra and the proportions of 2:1 layers with cis-octahedra. This comparison indicates that processes for the formation of I/S minerals having different origins are not universal. For this reason, additional investigations are required in order to clearly determine the crystal-chemical nature of mixed-layer illite-smectites of different origins, the mechanism and dynamics of their structural transformations and the factors controlling the existence of 2:1 layers differing in cation distribution.

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REFERENCES

Drits VA. 1987. Mixed-layer minerals: Diffraction methods and structural features. Proc. Intern. Clay Conf. Denver, 1985. Schultz LG, van Olphen H, Mumpton FA, editors. Bloomington (Ind.):Clay Miner. Soc. 33–45.

Drits VA, Kossovskaya AG. 1991. Clay minerals: smectites and mixed-layer formations. Moscow:Nauka. 212p. (in Russian).

https://doi.org/10.1346/CCMN.1996.0440203 Published online by Cambridge University Press

Drits VA, Plançon A, Sakharov BA, Besson G, Tsipursky SI, Tchoubar C. 1984. Diffraction effects calculated for structural models of K-saturated montmorillonite containing different types of defects. Clay Miner 19:541–562.

Drits VA, Sakharov BA. 1976. X-ray diffraction structure analysis of mixed-layer minerals. Moscow:Nauka. 252p. (in Russian).

Drits VA, Weber F, Salyn AL, Tsipursky S. 1993. X-ray identification of one-layer illite varieties: application to the study of illites around uranium deposits. Clays & Clay Miner 41:389–398.

Eberl DD. 1993. Three zones for illite formation during burial diagenesis and metamorphism. Clays & Clay Miner 41: 26–37.

McCarty DK, Reynolds RC. 1995. Rotationally disordered illite/smectite. Clays & Clay Miner 43:271–284.

Nadeau PH. 1985. The physical dimensions of fundamental clay particles. Clay Miner 20:499–514.

Nadeau PH, Wilson MJ, McHardy WJ, Tait JM. 1984. Interstratified clay as fundamental particles. Science 225: 923–925.

Nadeau PH, Wilson MJ, McHardy WJ, Tait JM. 1985. The conversion of smectite to illite during diagenesis: evidence from some illitic clays from bentonites and sandstones. Mineralogical Magazine 49:393–400.

Peacor DR. 1992. Diagenesis and low-grade metamorphism of shales and slates. In:Buseck PR, editor. Minerals and reactions at the atomic scale: transmission Electron Microscopy. Reviews in Mineralogy. Washington:Mineralogical Society of America 27:335–380.

Reynolds RC. 1980. Interstratified clay minerals. In:Brindley GW, Brown G, editors. Crystal structures of clay minerals and their X-ray identification. London:Mineralogical Society. 249–303.

Reynolds RC. 1993. Three-dimensional X-ray powder diffraction from disordered illite: simulation and interpretation of the diffraction patterns. In:Reynolds RC, Walker JR, editors. Computer applications to X-ray powder diffraction analysis of clay minerals. CMS workshop lectures, 5. Boulder: Clay Miner Soc of Am. 43–78.

Salyn AL. 1988. X-ray diffraction quantitative phase analysis of mixture of polytype or polymorph modifications. PhD Thesis, Moscow, Moscow University (in Russian).

Šucha V, Kraus I, Mosser Ch, Hroncova Z, Siranova V. 1992. Mixed-layer illite/smectite from the Dovna Ves hydrothermal deposit, the Western Carpathians Kremnica MTS. Bratislava: Geologia Carpathica, Clays. series 1. 1:13–21.

Środoń J, Eberl DD. 1984. Illites. In:Baily SW, editor. Micas. Reviews in Mineralogy. Mineral Soc Am 13:495–544.

Środoń J, Elsass F, McHardy WJ, Morgan DJ. 1992. Chemistry of illite-smectite inferred from TEM measurements of fundamental particles. Clay Miner 27:137–158.

Tsipursky SI, Drits VA. 1984. The distribution of octahedral cations in the 2:1 layers of dioctahedral smectites studied by oblique texture electron diffraction. Clay Miner 19:177–192.

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