

## TRANS-VACANT AND CIS-VACANT 2:1 LAYER SILICATES: STRUCTURAL FEATURES, IDENTIFICATION, AND OCCURRENCE

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**Abstract**—A comprehensive study of clay minerals should include determination of the vacancy pattern of the dioctahedral sheet. The purpose of this report is to consider the advantages and limitations in various diffraction and non-diffraction methods for the determination of the layer types in clay minerals. Identification of *trans*-vacant (*tv*) and *cis*-vacant (*cv*) clay minerals reported here is based on powder X-ray diffraction (XRD) patterns calculated for different polytypes consisting of either *tv* or *cv* layers, on the simulation of experimental XRD patterns corresponding to illite or illite fundamental particles in which *tv* and *cv* layers are interstratified, and on the semi-quantitative assessment of the relative content of the layer types in the interstratified structures by generalized Méring's rules. A simple and effective method for identification of *tv* and *cv* layers in dioctahedral 2:1 layer silicates employs thermal analysis and is based on different dehydroxylation temperatures for *tv* and *cv* illite and smectite layers.

Crystal chemical analysis of various dioctahedral 2:1 layer silicates consisting of *tv* and *cv* layers indicates that compositional control is present in the distribution of octahedral cations over *trans*- and *cis*-sites. In dioctahedral smectites the formation of *tv* and *cv* layers is related to the layer composition and local order-disorder in the distribution of isomorphous cations. Dioctahedral 1M micas with abundant Fe<sup>3+</sup> and Mg occur only as *tv* varieties. In contrast, 1M-*cv* illite, as well as *cv* layers in illite fundamental particles of I-S, can form only as Fe- and Mg-poor varieties. In illites and illite fundamental particles of I-S consisting of *tv* and *cv* layers, *cv* layers prevail when the amounts of Al in octahedra and tetrahedra are >1.55 and >0.35 atoms per O<sub>10</sub>(OH)<sub>2</sub>, respectively.

The main factors responsible for the stability of *cv* and *tv* illites have been established. Monomineral *cv* 1M illite, its association with *tv* 1M illite, and interstratified *cv/tv* illite occur around ore deposits, in bentonites, and in sandstones mostly as a result of different types of hydrothermal activity. The initial material for their formation should be Al-rich, and hydrothermal fluids should be Mg- and Fe-poor.

*Tv* and *cv* smectites of volcanic origin differ in terms of octahedral cation composition and distribution of isomorphous octahedral cations. Mg-rich *cv* smectites have random distribution of isomorphous octahedral cations, whereas in Mg-bearing *tv* smectites octahedral Mg cations are dispersed so as to minimize the amount of Mg-OH-Mg arrangements.

**Key Words**—*Cis*-vacant Layers, Illite, Illite-smectite, Smectite, Thermal Analysis, *Trans*-vacant Layers, XRD.

### INTRODUCTION

An important aspect in the general problem of structural and crystal-chemical heterogeneity of minerals is the distribution of octahedral cations over the *trans*- and *cis*-sites in dioctahedral 2:1 phyllosilicates and, in particular, clay minerals. A 2:1 layer consists of two tetrahedral sheets linked through an octahedral sheet. In the general case the octahedral sheet contains three symmetrically independent sites (one *trans*- and two *cis*-octahedra) which differ in terms of the arrangement of OH groups and oxygen anions coordinating octahedral cations: in the *trans*-octahedra the OH groups lie across the space diagonal whereas in the *cis*-octahedra the OH groups form a shared edge. The widely held view for some time has been that in

dioctahedral 2:1 phyllosilicates, and clay minerals in particular, the *trans*-sites are vacant.

The existence of 2:1 dioctahedral phyllosilicates with one of the two symmetrically independent *cis*-octahedra vacant was first reported by Méring and Oberlin (1971) for a sample of Wyoming montmorillonite. Drits *et al.* (1984) deduced unit-cell parameters and atomic coordinates for a one-layer monoclinic *cis*-vacant (*cv*) illite model (1M-*cv*), calculating powder XRD patterns for periodic 1M-*cv* and *trans*-vacant (*tv*) 1M structures (1M-*tv*), as well as for models in which *tv* and *cv* layers were interstratified, and formulating diffraction criteria for the identification of these illite varieties. Tsipursky and Drits (1984) studied numerous dioctahedral smectites and discovered a wide variety of occupancies of the available *cis*- and *trans*- octahedral sites including *cv* (most montmorillonites) and *tv* samples (nontronites, beidellites, and some montmorillonites) samples, as well as samples consisting of interstratified *cv* and *tv* layers. The major factor affecting the cation distribution over *trans*- and *cis*-sites was the amount of Al-for-Si substitu-

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tion (Tsipursky and Drits, 1984). Zvyagin *et al.* (1985) described a monomineral Al-rich *1M-cv* mica sample, and Reynolds (1993) demonstrated, for the first time, that illite fundamental particles in mixed-layer illite-smectite (I-S) consist either of *tv* or *cv* layers, or both layer types are interstratified in these particles. Since then, various forms of occurrence of *cv* and *tv* layers in dioctahedral smectites, illites, and I-S in various geological environments have been reported (e.g. Drits *et al.*, 1993; McCarty and Reynolds, 1995, 2001; Reynolds and Thomson, 1993; Lee, 1996; Lanson *et al.*, 1996; Zhukhlistov *et al.*, 1996; Drits *et al.*, 1996; Altaner and Ylagan, 1997; Cuadros and Altaner, 1998a, 1998b; Ylagan *et al.*, 2000; Lindgreen *et al.*, 2000, 2002; Sainz-Diaz *et al.*, 2001; Drits, 2003 and references therein; Drits *et al.*, 2002, 2004, 2006, 2007; McCarty *et al.*, 2008).

A comprehensive study of clay minerals should therefore include determination of the layer types in their structures. However, in spite of the ever-increasing interest in the study of layer types in clay minerals and considerable progress in the field, problems remain with the interpretation of the structural features and with identification of *tv* and *cv* layers in phyllosilicates. Furthermore, the correlations between the layer types in clay minerals, on the one hand, and the physicochemical conditions and geological environments of mineral formation, on the other, still need to be elucidated.

The aim of the present work was to: (1) review the methodologies used for identification of *tv* and *cv* layers in 2:1 phyllosilicates, and (2) analyze the interdependencies between the structural features of clay minerals containing *tv* and/or *cv* layers, their conditions of formation and their occurrence in specific geological environments.

## METHODS FOR DETERMINING LAYER TYPES

### *Identification of periodic cv and tv dioctahedral mica varieties*

Analysis of the XRD patterns simulated for structural models of *1M*, *2M<sub>1</sub>*, *2M<sub>2</sub>*, *3T*, and *2O* dioctahedral micas consisting of either *tv* or *cv* layers provided a number of diffraction criteria that form a basis for the identification of these structural varieties (Zviagina *et al.*, 2007). The differences in the unit-cell parameters and, specifically, the absolute value of the overall layer displacement, which result from the specific structural distortions of *tv* and *cv* layers, lead to the differences in the positions of reflections having the same indices in the XRD patterns for Al-rich *tv* and *cv* *1M*, *2M<sub>1</sub>*, and *2M<sub>2</sub>* mica varieties, which can therefore be distinguished using powder XRD. Note, however, that the differences between the absolute values of the overall layer displacements in *tv* and *cv* micas decrease with increasing Mg and/or Fe contents. For example, the layer displacement  $|c \cos\beta|$  decreases almost linearly with the total number of divalent octahedral cations in *1M-tv* micas (Drits *et al.*,

1997a). Accordingly, the differences in reflection positions for these *tv* and *cv* varieties should decrease with increasing Mg and/or Fe contents, thus complicating their identification.

Furthermore, the apparent as well as true similarities revealed in the XRD patterns for various dioctahedral mica varieties lead to serious complications. For example, Drits *et al.* (1993) noted that in the powder XRD patterns of *trans*-vacant *3T* (*3T-tv*) and *1M-cv* mica polymorphs, *hkl* reflections have similar intensities and positions. For this reason, all illite varieties previously described as *3T-tv* (Warshaw, 1959; Ey, 1984; Halter, 1988) turned out to be either *1M-cv* illite or illite structures in which *tv* and *cv* layers are interstratified (Drits *et al.*, 1993). Zviagina *et al.* (2007) found that the XRD pattern simulated for *1M-cv* structure is similar to that for not only *3T-tv*, but also the *3T* structure with the vacancies in the right-hand *cis*-sites, *i.e.* located to the right of the edge formed by the adjacent OH groups (*3T-cv1*). On the other hand, both the peak positions and intensity distribution in the diffraction pattern of *1M-tv* illite are very similar to those for the *3T* structure consisting of layers with the vacancies in the left-hand *cis*-sites (to the left of the edge formed by the adjacent OH groups (*3T-cv2*)).

The identification of dioctahedral mica structure varieties will become even more difficult if *tv* and *cv* layers are interstratified within the same structure (this will be dealt with in greater detail below). Additional complications should also be expected in the case of structures containing stacking faults, which may affect both peak positions and intensities (Drits and Tchoubar, 1990).

In general, the interpretation of powder XRD patterns of dioctahedral mica structural varieties should be treated with caution, bearing in mind the inherent limitations in the method. In some cases, therefore, the only possible identification method would be simulation of diffraction effects for structural models and comparison of simulated and experimental XRD patterns.

### *Diffraction methods for determining layer types in interstratified cv/tv structures in illites and illite fundamental particles*

Interstratification of *tv* and *cv* layers often occurs in illites and illite fundamental particles in I-S (Reynolds, 1993; Drits, 2003, and references therein). Different distributions of octahedral cations over *trans*- and *cis*-sites in 2:1 layers are accompanied by specific distortions of *cis*- and *trans*-octahedra (Drits *et al.*, 1984, 2006). The projection of the *c* axis on the *ab* plane,  $T = c \times \cos\beta$ , in the *1M-tv* illite, therefore, differs significantly from that in the *1M-cv* illite. In a *tv* layer, the center of the ditrigonal ring of the upper tetrahedral sheet is shifted from the center of the lower tetrahedral sheet in a projection on the *ab* plane by more than the ideal  $-a/3$  value (Bailey, 1984). As a result, in *1M-tv*

illites,  $T_{tv} = -(0.38 \sim 0.40)a$  depending on the octahedral cation composition of the 2:1 layers. In the  $cv$  layer, the absolute value of this shift is  $<a/3$ , and in  $1M-cv$  illites  $T_{cv} = -(0.30 \sim 0.31)a$  (Drits *et al.*, 1984, 1993; Tshipursky and Drits, 1984; Zvyagin *et al.*, 1985; Reynolds and Thomson, 1993). Thus, interstratification of  $tv$  and  $cv$  layers is associated with interstratification of two different translations and is accompanied by significant variations of positions, intensities, and profiles of  $hkl$  reflections with  $h \neq 0$  in the powder XRD patterns.

Several different diffraction methods are used for the determination of coexistent  $tv$  and  $cv$  layer contents in illite structures.

*Semi-quantitative calculation of the amount of interstratified tv and cv layers from  $d_{11l}$  values.* This technique is based on the ability of XRD to average the parameters of a defective structure (Drits and McCarty, 1996). For illites consisting of  $tv$  and  $cv$  layers, diffraction should average interstratified inter-layer translations. This means that a given interstratified structure should be characterized by a statistically weighted layer displacement equal to  $T_{ef} = W_{cv}T_{cv} + W_{tv}T_{tv}$ , where  $W_{cv}$  and  $W_{tv}$  are the occurrence probabilities for  $cv$  and  $tv$  layers, respectively. Taking into account that  $W_{cv} + W_{tv} = 1$ , we have  $W_{cv} = (T_{tv} - T_{ef}) / (T_{tv} - T_{cv})$ . For a  $tv/cv$   $1M$  structure,  $T_{ef}$  is given by

$$T_{ef} = \frac{c \cos \beta}{a} = 0.125 (c \sin \beta)^2 \left[ \frac{1}{d_{112}^2} - \frac{1}{d_{112}^2} \right] = 0.125 (c \sin \beta)^2 \left[ \frac{1}{d_{113}^2} - \frac{1}{d_{111}^2} \right] - 1,$$

where the  $d_{11l}$  values are calculated from the observed  $11l$  reflections (Drits and McCarty, 1996).

A similar approach to the calculation of  $W_{cv}$  is based on the generalization of Méring's (1949) rules by Drits and McCarty (1996), according to which the non-basal reflections of an interstratified structure are located between the neighboring  $hkl$  reflections of the periodic phases, the elementary layer units of which are interstratified. The positions of these reflections depend on the relative proportions of the interstratified interlayer translations. Therefore, in a  $1M$  structure in which  $tv$  and  $cv$  layers are interstratified,  $11l$  reflections are located between the  $11l$  reflections corresponding to pure  $tv$  and pure  $cv$  micas (Drits and McCarty, 1996; Drits, 2003). The proportions of  $tv$  and  $cv$  layers can be determined either using a graphical technique suggested by Drits and McCarty (1996) or from the equations

$$W_{cv} = \frac{1/d_{112_{obs}} - 1/d_{112_{tv}}}{1/d_{112_{cv}} - 1/d_{112_{tv}}} = \frac{1/d_{112_{rv}} - 1/d_{112_{obs}}}{1/d_{112_{rv}} - 1/d_{112_{cv}}} = \frac{1/d_{113_{obs}} - 1/d_{113_{tv}}}{1/d_{113_{cv}} - 1/d_{113_{tv}}}$$

Here  $d_{11l_{obs}}$  is the spacing of the  $11l$  reflection corresponding to  $tv/cv$  illite, which is situated between

the nodes of  $tv$  and  $cv$   $1M$  illites that have the same  $11l$  indices and  $d_{11l_{tv}}$  and  $d_{11l_{cv}}$  spacings, respectively.

The above techniques are simple and reliable, but in general, they only provide semi-quantitative estimation of the layer types because peak positions are sensitive to rotational stacking faults.

*Quantitative determination of the layer types from modeling of the experimental diffraction patterns.* This more reliable method is based on calculation of XRD patterns from different structural models containing interstratified  $tv$  and  $cv$  layers, as well as rotational and translational stacking faults (Drits *et al.*, 1984; Reynolds, 1993; Drits, 2003). Examples of effective application of this approach are given by Reynolds (1993), McCarty and Reynolds (1995, 2001), Cuadros and Altaner (1998a, 1998b), and Ylagan *et al.* (2000). However, even qualitative identification, let alone quantitative determination, may prove problematic in some cases. For example, Drits and Sakharov (2004) found that both the positions and shapes of  $hkl$  reflections in simulated XRD patterns of the  $2M_1-tv$  and  $3T-tv$  mica varieties are very similar to those for the interstratified  $2M_1-tv/cv$  and  $3T-tv/cv$  structures, respectively. Therefore, reliable and unambiguous identification of such complicated structures may require application of alternative methods.

*Application of the Rietveld method.* A modified Rietveld technique, based on the recursive method, was suggested by Ufer *et al.* (2008) for phase quantification of mixed-layer structures. The recursive method can be implemented in a Rietveld model using a supercell approach in combination with a complex manipulation of the structure-factor calculation, to determine the contents of different layer types. This approach, however, is restricted to mixed-layer structures with low expandabilities.

*Determination of tv and cv layers in turbostratic I-S and smectite structures.* Neither of the techniques described above can be applied if powder XRD patterns do not contain three-dimensional diffraction maxima in the diagnostic region containing the  $11l$  and  $02l$  reflections, as in the case of smectites and high-expandability I-S with turbostratic structures having random displacements and rotations of adjacent layers.

However, even for these minerals, essential information on the distribution of octahedral cations over *trans*- and *cis*-sites can be obtained by simulation of diffraction effects. Drits *et al.* (1984) showed that the intensity of the two-dimensional  $02,11$  band for dioctahedral micas and dehydrated smectites is constant if their layers are either  $tv$  or  $cv$ , and decreases significantly if octahedral cations are randomly distributed over *trans*- and *cis*-sites within the same layer. At the same time, the intensity of the  $20,13$  band does not depend on the cation distribu-

tion. Therefore, the intensity ratio of the 02,11 and 20,13 bands is sensitive to the distribution of octahedral cations between *cis*- and *trans*-sites within the same octahedral sheet. Taking into account this result, Manceau *et al.* (2000) compared the experimental and calculated intensity of the 02,11 and 20,13 bands for different occupancies of *trans* and *cis* sites in four nontronite samples and found that 100% of *cis*-sites in their structures are occupied by cations.

Another way to determine the distribution of octahedral cations over *trans*- and *cis*-sites in a smectite structure involves artificial increase of its three-dimensional structural order by saturation with large, anhydrous K or Cs cations and introduction of wetting-and-drying cycles, with subsequent dehydration, according to the technique of Mamy and Gaultier (1976). Powder XRD patterns of the treated smectites contain significant intensity modulation in the diagnostic region of 021 and 111 reflections. Using this technique, the actual distribution of octahedral cations over *cis*- and *trans*-sites was revealed for dioctahedral smectites (Besson *et al.*, 1983; Tsipursky and Drits, 1984; Cuadros, 2002).

*Dehydroxylation and rehydroxylation behavior of dioctahedral 2:1 phyllosilicates: implications for determination of the vacancy pattern of the octahedral sheet*

*Structural transformations of Al-rich and Fe,Mg-rich tv and cv phyllosilicates.* The structural mechanisms in the dehydroxylation and rehydroxylation of micas, smectites, and I-S depend on their chemical composition, as well as on the distribution of octahedral cations over *cis*- and *trans*-sites (Drits *et al.*, 1995; Muller *et al.*, 2000a, 2000b, 2000c; Dainyak *et al.*, 2006).

The dehydroxylation of Al-rich *tv* clay minerals proceeds in one stage, when each two adjacent OH groups, which form a shared octahedral edge, are replaced by a single residual oxygen atom, O<sub>r</sub>, so that the octahedral cations become five-coordinated. The O<sub>r</sub> atoms are located at the same *z* coordinate as the octahedral cations and midway between them (Guggenheim *et al.*, 1987). In this case, dehydroxylation occurs at temperatures <600°C for illite and smectite layers alike. During the rehydroxylation process, the structural rearrangement takes place in reverse order and the original structural arrangement of the 2:1 layers is recovered (Heller-Kallai *et al.*, 1962; Muller *et al.*, 2000c).

In *cv* structures, dehydroxylation occurs in two stages (Drits *et al.*, 1995). At the first stage, each two adjacent hydroxyls are replaced by a residual oxygen atom, and the cations that originally occupied *cis*- and *trans*-sites become 5- and 6-coordinated, respectively. The resulting structure, however, is unstable, and no shift of octahedral cations or anions can compensate for the charge imbalance. Therefore, when additional thermal energy is

applied, each cation initially occupying a *trans*-site migrates to the nearest five-fold coordination polyhedron corresponding to the initially vacant *cis*-site, and the resulting structure is the same as that in the case of dehydroxylated *tv* layers. This complex structural rearrangement of *cv* layers increases the dehydroxylation temperature of *cv* structures to 650–750°C. During rehydroxylation these heat-treated layers preserve their *tv* structure (Muller *et al.*, 2000c).

During dehydroxylation of Fe,Mg-rich *tv* 2:1 phyllosilicates, adjacent OH groups are replaced by a residual O<sub>r</sub> oxygen atom located in one of the two adjacent former OH positions, which provides five-fold coordination for each cation in the dehydroxylated octahedral sheet, and the octahedral cations migrate from *cis*- into the former *trans*-sites (Tsipursky *et al.*, 1984; Muller *et al.*, 2000a, 2000b, 2000c; Dainyak *et al.*, 2006). Such an arrangement ensures appropriate Fe–O<sub>r</sub> bond lengths and stabilizes the dehydroxylated structure. According to Muller *et al.* (2000c), the rehydroxylation of celadonite preserves the octahedral-cation distribution formed after dehydroxylation, so that most 2:1 layers of celadonite that rehydroxylate have *cv* structure. In contrast, for a glauconite sample with a large amount of octahedral and tetrahedral Al, the rehydroxylation is accompanied by the reverse cation migration and most of the 2:1 layers are transformed into *tv* layers.

*Determination of tv and cv layers in micas, smectites, and I-S using thermal analysis.* The different dehydroxylation behaviors of *tv* and *cv* phyllosilicates allow the proportions of *tv* and *cv* layers to be determined with the help of a non-diffraction method based on analysis of loss of structural water during dehydroxylation. Comparison of the results obtained by XRD and thermal analysis showed that losses of structural water above and below 600°C occurred during dehydroxylation and are proportional to the amounts of *cv* and *tv* layers, regardless of whether smectite or illite is involved (Drits *et al.*, 1998; Drits, 2003).

Application of the thermal analysis, however, may encounter complications. Firstly, sophisticated equipment is involved: quantitative determination of structural H<sub>2</sub>O released requires a DTA device combined with either a mass spectrometer or a gas outlet to non-dispersive infrared H<sub>2</sub>O and CO<sub>2</sub> detectors (evolved water analysis (EWA), Morgan, 1977). The advantage of both techniques is that the loss of hydroxyls is recorded separately and the amount of structural water released during dehydroxylation can be determined quantitatively and with great sensitivity. Secondly, the method is an indirect one, and the experimental data should be treated with caution; for example, the results may be misinterpreted in the presence of significant amounts of Fe, which decreases considerably the dehydroxylation temperature. Another complication may be associated with the presence of kaolinite and/or chlorite layers and other

impurities that dehydrate at  $\sim 400\text{--}750^\circ\text{C}$ , as the amounts of  $\text{H}_2\text{O}$  per unit cell in kaolinite and chlorite are greater than in mica, smectite, and I-S.

*Determination of the octahedral vacancy pattern in 2:1 phyllosilicates by solid-state NMR.* Takahashi *et al.* (2008) applied  $^{27}\text{Al}$  multiple quantum (MQ) magic angle spinning nuclear magnetic resonance (MAS NMR) to the local structural analysis of octahedral Al positions in a Na-montmorillonite. Three octahedral Al positions differing in isotropic chemical shift and quadrupole product can be distinguished by  $^{27}\text{Al}$  5QMAS NMR. These three sites originate from different configurations of OH groups around Al in the *cis*- and *trans*-positions. Two of the Al sites, having smaller isotropic chemical shifts, were assigned to Al in the *cis*-sites, and the third, to Al in the *trans*-site. The Na-montmorillonite sample under study was shown to have *cv* structure.

#### CRYSTAL-CHEMICAL FACTORS AND PHYSICO-CHEMICAL CONDITIONS RESPONSIBLE FOR THE FORMATION OF *CV* LAYERS IN CLAY MINERALS

*Structural and chemical factors favoring the formation of *tv* and *cv* layers in illite and illite fundamental particles in I-S*

Crystal-chemical analysis of a representative collection of illites and illite fundamental particles in I-S differing in chemical composition and contents of *tv* and *cv* layers revealed compositional control over the distribution of octahedral cations between *trans*- and *cis*-sites (Drits *et al.* 2006). In illites and illite fundamental particles of I-S consisting of *tv* and *cv* layers, *cv* layers prevail when  $\text{Al}_{\text{oct}} > 1.55$  and  $\text{Al}_{\text{tet}} > 0.35$  atoms per  $\text{O}_{10}(\text{OH})_2$ . Accordingly, when  $\text{Al}_{\text{total}}$ ,  $\text{Al}_{\text{oct}}$ , and  $\text{Al}_{\text{tet}}$  are less than those values, the occurrence probability for *cv* layers in illites and illite fundamental particles of I-S decreases significantly.  $\text{Fe}^{3+}$ - and Mg-rich dioctahedral micas (celadonite, glauconite, Al-celadonite, and most phengite) occur as *tv* varieties only. The occurrence of *tv*

illites and *tv* illite fundamental particles in I-S does not depend significantly on the cation composition of the 2:1 layers. In contrast, *cv* 1M illite and illite fundamental particles in I-S can only form as Fe- and Mg-poor varieties. Importantly, under low-temperature diagenesis and hydrothermal conditions, Al-rich 1M-*cv* illite may have the same or even greater stability than the 1M-*tv* polymorph (Drits *et al.*, 1993; Lanson *et al.*, 1996).

To explain these regularities and reveal the main structural factors that favor the formation of *cv* layers in illite and illite fundamental particles in I-S, simulations of atomic coordinates and interatomic distances for periodic 1M-*tv* and 1M-*cv* illite structures were used (Drits *et al.*, 2006). Analysis of the structural models showed that the structures of the interlayer cavities in the 1M-*tv* and 1M-*cv* varieties differ owing to the different arrangements of six depressed and non-depressed oxygen atoms nearest to the interlayer K. In the 1M-*tv* structure, the distances between K and the depressed O atoms are significantly longer than those between K and four non-depressed ones (Figures 1 and 2). In contrast, due to mutual rotation of the adjacent tetrahedral sheets by  $120^\circ$ , in the interlayer of the 1M-*cv* structure the depressed O atoms across the interlayer are arranged in such a way that a minor shift of K toward the nearest depressed oxygens significantly equalizes individual K–O interatomic distances.

Furthermore, in 1M-*tv* illite, the depressed O atoms of the adjacent tetrahedral sheets are almost directly superimposed onto each other in projection down  $c^*$  and, therefore, the distances between them are significantly greater than those between the nearest non-depressed O atoms. In contrast, in the interlayer of the 1M-*cv* illite (Figure 1b) each depressed O atom has a non-depressed O for a nearest neighbor. As a result, the edge lengths in the polyhedron around K are equalized. Interlayer structures of this kind should decrease the mutual repulsion of the nearest basal oxygen atoms of the adjacent tetrahedral sheets.

The interlayer K in the 1M-*cv* has an environment which is similar to that in  $2M_1$  muscovite because the

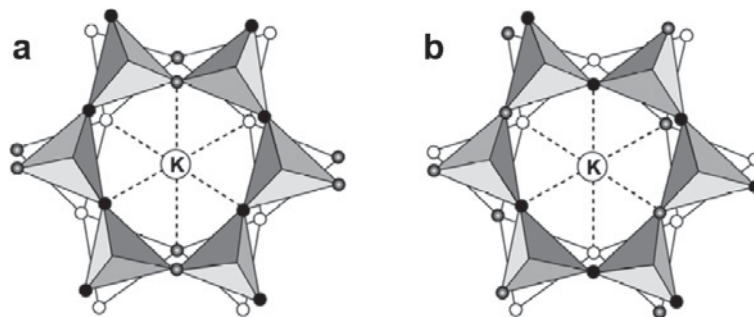


Figure 1. Projection on the *ab* plane of adjacent tetrahedral sheets bonded to interlayer K in (a) the 1M-*tv* and (b) 1M-*cv* illite structure. Shaded circles represent depressed basal oxygens, and filled and open circles represent non-depressed basal oxygens in the upper and lower tetrahedral sheets, respectively.

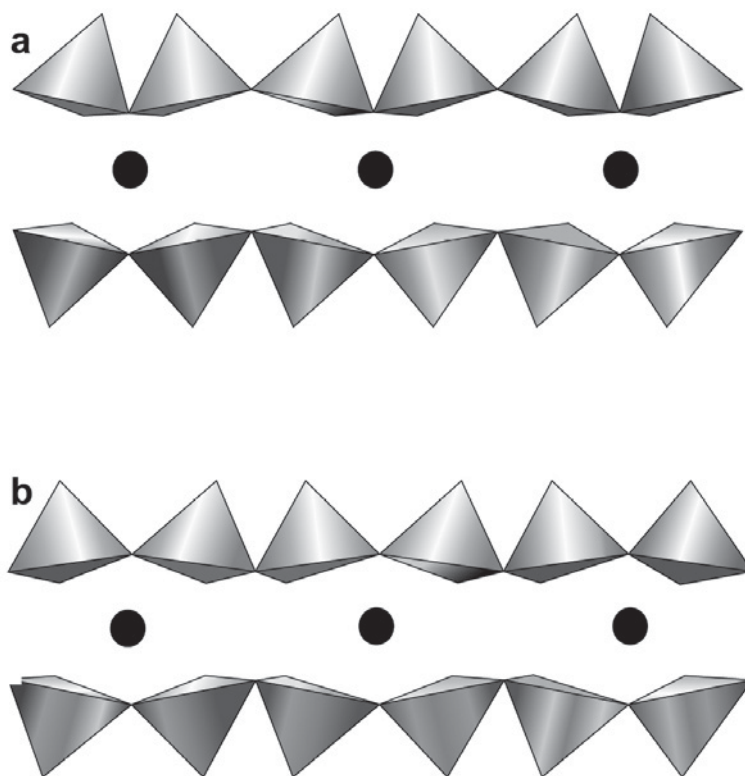


Figure 2. Side view of adjacent tetrahedral sheets bonded to interlayer K in (a) the  $1M$ - $cv$ , and (b)  $1M$ - $tv$  illite structure.

upper and lower tetrahedral sheets across the interlayer are rotated by  $120^\circ$  in both  $1M$ - $cv$  and  $2M_1$ - $tv$  structures. Because  $2M_1$  muscovite is a stable mica polytype, the similarity in the interlayer arrangements in both  $1M$ - $cv$  and  $2M_1$ - $tv$  can be assumed to be one of the main factors responsible for the stability of  $1M$ - $cv$  illites in natural environments.

The role of the above factors, however, should decrease with increasing contents of large Mg,  $Fe^{2+}$ , and  $Fe^{3+}$  cations and decreasing tetrahedral Al content, as this reduces the differences in the dimensions and shape of the vacant and occupied octahedra and, consequently, in the amounts of tetrahedral rotation and tilt (Bailey, 1984; Brigatti and Guggenheim, 2002; Drits *et al.*, 2006), thus leading to a less significant difference in interlayer arrangement.

To summarize, the large octahedral and tetrahedral Al contents, the small difference between individual K–O basal bond lengths, and the minimization of the repulsion of the basal oxygen atoms are the main factors responsible for the stability of  $1M$ - $cv$  illite where the interlayer environment is similar to  $2M_1$  muscovite. The asymmetry of the  $cv$  octahedral structure, where the occupied *trans*-octahedra are elongated along the  $a$  axis while the occupied *cis*-octahedra are stretched along the  $b$  axis, should decrease the stability of  $1M$ - $cv$  minerals.

On the contrary, the symmetrical structure of the  $tv$  2:1 layers, where the occupied octahedra have the same shape and size, favors  $1M$ - $tv$  illite despite the less stable arrangement of the interlayer configuration.

#### *Potential role of crystal-chemical features in the formation of $tv$ and $cv$ smectites*

An explanation of the origin of  $cv$  and  $tv$  smectites was proposed by Cuadros (2002). Based on the octahedral size effect and a correlation between idealized tetrahedral and octahedral  $b$  dimensions, he suggested that a  $cv$  octahedral sheet should have very little or no tetrahedral Al, whereas a  $tv$  sheet should have more Al-for-Si substitution. Along with some inherent logical contradictions, this hypothesis does not explain the existence of  $tv$  montmorillonites. Furthermore, in contrast to nontronite, beidellite was excluded from this consideration as it falls out of the correlation between idealized tetrahedral and octahedral  $b$  parameters.

A different approach based on the analysis of the local charge compensation was developed by Drits *et al.* (2006). In the nontronite–beidellite series, where the main negative charge is located in the tetrahedral sheets and octahedral cations are mainly trivalent, both  $tv$  and  $cv$  arrangements of these cations provide local charge compensation for the anions in the octahedral sheets

equally well. The *tv* structure typically observed in the nontronite–beidellite series may be associated with the symmetrical arrangement of a *tv* octahedral sheet, where the occupied octahedra have the same size and shape. In contrast, distortions in the occupied octahedra in a *cv* sheet may decrease the stability of the structure. Low-charge members in the nontronite–beidellite series may, however, have *cv* structure. For example, low-charge beidellite samples were described by Tsipursky and Drits (1984). Recently Lantenois *et al.* (2008) described a low-charge *cv* beidellite synthesized under hydrothermal conditions.

In Mg,Fe<sup>2+</sup>-rich montmorillonites with random distribution of octahedral cations, a *cv* octahedral sheet seems more favorable than a *tv* sheet from the local charge compensation point of view. Indeed, whenever a Mg-OH-Mg arrangement occurs in a *tv* sheet, two adjacent OH groups will be bonded with two Mg-cations and the OH oxygens will be strongly under saturated. In contrast, in a *cv* octahedral sheet, two adjacent OH groups are bonded with three octahedral cations, thus ensuring more favorable conditions for local charge compensation. Probably for this reason the majority of the Mg-rich montmorillonites studied with random distribution of octahedral cations are *cis*-vacant. On the other hand, Mg-bearing montmorillonite may be *trans*-vacant if the distribution of isomorphous octahedral cations is not random and octahedral Mg cations are dispersed so as to minimize the amount of Mg-OH-Mg arrangements. As an example, Mg-bearing *tv* montmorillonite with ordered distribution of Mg cations was described by Drits *et al.* (2004).

In general, however, the role of the octahedral cation composition and distribution of isomorphous cations in the formation of *tv* and *cv* layers in smectites is still insufficiently understood. For example, it is still unknown why Al-rich smectites, in which the layer charge is located in both octahedral and tetrahedral sheets, can be either *tv* or *cv*, as shown by Tsipursky and Drits (1984). Similarly, the influence of the content of octahedral Fe on the distribution of cations between *trans*- and *cis*-sites is not clear.

Diocahedral smectites have useful technological properties, which are used widely in industrial applications. Further research is needed, however, to gain sufficient insight into the relationships between the physicochemical properties of smectites and the structure of smectite layers in order to ensure purposeful application of physicochemical properties of smectites.

*Physicochemical conditions and geological environments favorable to the formation of cv illite and cv layers in illite fundamental particles of I-S*

Analysis of the structural features of *1M-cv* illites explains why structural and compositional control pre-determines the occurrence of these mica varieties in specific geological environments: the initial reaction

fluids for formation of *1M-cv* illite must be Al-rich and Mg- and Fe-poor. Monomineral *1M-cv* illite, its association with *1M-tv* illite, and interstratified *cv/tv* illite structures are most often formed as a result of hydrothermal activity of different origin (Drits *et al.*, 2006, and references therein). In particular, *1M-cv* or an association of *1M-cv* and *1M-tv* illites may be formed as products of hydrothermal alteration such as around ore deposits. Drits and Kossovskaya (1991) noted that the formation of such deposits may occur in two stages: (1) intense leaching of rocks by acid solutions and the formation of associations of Al-rich minerals such as kaolinite, dickite, pyrophyllite, *etc.*, and (2) ore-deposit formation and illitization of the Al-rich minerals. For example, *1M-cv* illite with and without *1M-tv* association was found in illite from hydrothermal alteration of kaolinite around uranium deposits in the Athabasca basement (Canada) (Drits *et al.*, 1993). *Cis*-vacant *1M* illite and its association with *1M-tv* may form by hydrothermal alteration of kaolin minerals in sedimentary rocks (Zvyagin *et al.*, 1985; Lanson *et al.*, 1996; Lee, 1996; Gavrilov and Tsipursky, 1988; Reynolds and Thompson, 1993). Monomineral *1M-cv* or interstratified *tv/cv* *1M* illites or illite fundamental particles in I-S may be formed by hydrothermal transformation of volcanic ash or tuff of rhyolitic composition (Horton, 1983; Drits *et al.*, 1996; Cuadros and Altaner, 1998a, 1998b; McCarty and Reynolds, 1995, 2001; Ylagan, 2000).

Insight into the crystal-chemical factors responsible for the formation of *tv* and *cv* layers provided interpretation for the data of McCarty and Reynolds (1995, 2001), which explains how bentonites originally having the same bulk composition can be transformed to either *tv*- or *cv*-dominated illite or I-S structures depending on their geological settings (Drits *et al.*, 2006). The *tv*-dominated samples of McCarty and Reynolds (1995, 2001) are from imbricated over-thrust sheets and strongly folded strata located in the southern part of the Appalachian Basin, where the abundance of dolomitic rocks may be considered as evidence for the existence of Mg-rich brines. Therefore, not only K but also Mg cations may have been involved in the formation of the I-S. The 2:1 layers of these I-S are indeed enriched by Mg, and the formation of the *tv*-dominated illite fundamental particles in the southern I-S is probably related to their structural and chemical features, namely, relatively low tetrahedral rotation and small basal surface corrugation. In contrast, I-S samples from the northern Appalachian Basin were obtained from flat-lying undeformed strata, and the Al-rich cation composition of the I-S may have been inherited from that of the original Al-rich bentonitic material. As a consequence, illite fundamental particles of the I-S are characterized by greater tetrahedral rotation and basal surface corrugation values, which favors formation of *cv* layers. Thus, the difference in fluid composition probably controlled the production of *cv* and *tv* illite layers in the I-S samples of this particular region.

*Structural mechanisms in the formation of I-S containing  $tv$  and  $cv$  layers.* Illitization of smectite through a series of mixed-layer illite-smectites (I-S) is a typical reaction for burial diagenesis and hydrothermal activity (Środoń, 1999). Until recently, the structural study of I-S by XRD was confined to the determination of the contents and distribution of the interstratified illite and smectite interlayers along the  $c^*$  axis. In order to reveal the actual mechanism in smectite illitization, however, the octahedral vacancy pattern in the interstratified layers should be determined.

Two basic structural mechanisms are possible in the formation of I-S containing interstratified  $tv$  and  $cv$  layers: (1) the so-called solid-state transformation (SST) mechanism, which consists of gradual, layer-by-layer replacement of smectite by illite layers within the mineral matrix (Cuadros and Altaner, 1998a, 1998b); and (2) the dissolution-precipitation (DR) mechanism which involves multiple stages of nucleation and crystal growth, so that the synthesis of the I-S includes simultaneous growth of  $tv$  and  $cv$  layers in each individual I-S crystal (Ylagan *et al.*, 2000). In addition, smectite illitization may proceed through SST to a certain stage, after which a further increase in the fraction of illite layers is accompanied by a DR process (Drits *et al.*, 1996).

The interpretation of the transformation of smectite into illite layers should take into account the crystal-chemical features favorable for formation of  $tv$  and  $cv$  layers. An increase in the amount of illite layers in Mg-rich I-S may be expected to lead to a  $tv$ -dominant structure formation when  $cv$ -smectite layers are replaced by  $tv$ -illite layers. In contrast, when the formation of illite layers in I-S is accompanied by a significant increase in Al in both tetrahedral and octahedral sheets of the 2:1 layers, the occurrence probability for  $tv$ - or  $cv$ -dominated structures depends mostly on particular thermal conditions because the crystal-chemical features of Al-rich illite particles are equally favorable for both  $tv$  and  $cv$  layers. For example, the Al contents remained high throughout the illitization reaction during hydrothermal transformation of rhyolitic volcanoclastites from Dolna Ves, Slovakia (Drits *et al.*, 1996). At the first stage of the process, which was a SST of smectite to illite layers, of up to 50% illite layers, all the 2:1 layers in I-S had *cis*-sites vacant, whereas further increases in the amount of illite layers, up to 90%, proceeded through a DR process, during which  $cv$  layers were replaced by  $tv$  2:1 layers.

*Geological conditions favoring formation of  $tv$  and  $cv$  smectites. Implications for indicator characteristics of I-S*

To date, no systematic analysis has been performed regarding the correlations between the layer types in clay minerals, on the one hand, and the physicochemical conditions and geological environments of mineral

formation, on the other. As a result, the physicochemical conditions leading to either ordered or random distribution of octahedral cations in  $tv$  and  $cv$  smectites of the same composition are not altogether clear, nor are the conditions favoring the formation of interstratified  $tv/cv$  smectites.

Interpretation of the origin and evolution of I-S in different geological environments may depend on the crystal-chemical features of the initial smectite, including  $cv$  and/or  $tv$  layer structure. Insufficient information about the occurrence of different structural forms of smectites in specific geological environments can, therefore, lead to incorrect assumptions about indicator characteristics of I-S structures.

Based on the generally accepted notion that the  $cv$  smectites are primary products of weathered or hydrothermally altered volcanoclastic rocks of rhyolitic composition, I-S consisting of  $tv$  and  $cv$  layers have, for a long time, been typically associated with volcanic materials (McCarty and Reynolds, 1995, 2001; Drits *et al.*, 1996, 1998, 2002; Altaner and Ylagan, 1997; Cuadros and Altaner, 1998a, 1998b; Ylagan *et al.*, 2000). In contrast, I-S primarily formed from weathered illitic material typically consists of  $tv$  2:1 layers independent of the content of I and S layers, *e.g.* as found for I-S from the Upper Jurassic oil-source rocks (Drits *et al.*, 1997b). Drits *et al.* (1998) suggested that I-S formed from volcanic material contains a significant amount of  $cv$  layers, whereas I-S formed from weathered illitic material consists of  $tv$  2:1 layers, and this was supported by investigations of smectite illitization of K-bentonites (Cuadros and Altaner, 1998a, 1998b), hydrothermally altered rhyolitic volcanoclastics (Drits *et al.*, 1996), and shales (Lindgreen *et al.*, 2000). Strong evidence for this assumption was provided by the investigation of I-S in one Upper Jurassic Kimmeridgian mudstone core from East Greenland (Drits *et al.*, 2002). The I-S samples located at different levels in the core were found to differ dramatically in terms of the amounts of  $cv$  layers. Drits *et al.* (2002) concluded that the interstratification of I-S with different amounts of  $tv$  and  $cv$  layers must be due to different sources of parent material. I-S with a large proportion of  $cv$  layers probably formed from volcanic material, whereas the other samples with a large proportion of  $tv$  layers probably formed by weathering of micaceous material. Such findings reflect episodes of volcanic activity during Kimmeridgian time, as suggested by Lindgreen and Surlyk (2000).

Based on these data, Lindgreen *et al.* (2002) assumed that the North Sea Maastrichtian chalk clays were formed from weathered illitic material because the illite-smectites consist predominantly of  $tv$  layers. However, after the discovery of Mg-bearing  $tv$  smectites in clays from the K/T boundary layer at Stevns Klint, Denmark, formed from volcanic ash (Drits *et al.*, 2004), this assumption had to be revised. First, the clay samples

in the North Sea chalk clays and clays in the K/T boundary consist of physical mixtures of low-smectitic and high-smectitic I-S, and the proportions of illite and smectite layers in the respective high- and low-smectitic phases in these mixtures are almost the same. Second, the structural and chemical features of the mixed-layer phases which make up the North Sea chalk clays and clays in the K/T boundary (little substitution of Si for Al, large amount of octahedral Mg, small amount of octahedral Fe, vacancy of *trans*-sites, short-range ordering in distribution of octahedral Al and Mg cations in the *tv* layers) were found to be nearly identical. This similarity should be considered as strong evidence of the common origin of both clays, so that the North Sea Maastrichtian clays should also be regarded as having volcanic origin (Drits *et al.*, 2004).

Interestingly, the formation of *tv*-smectites from alteration of volcanic material is not unique. Tsipursky and Drits (1984) described *tv*-smectite from the Gumbrin and Ascan bentonites from Georgia. However, further investigations have shown that most of the bentonitic smectites are *cis*-vacant and the existence of bentonitic *tv*-smectites was forgotten. McCarty *et al.* (2008) described samples from different depths in the Oligocene Frio formation (offshore Gulf of Mexico) containing smectite that was found to be of volcanic origin and have *tv* structure.

Furthermore, according to Sokolova *et al.* (1976, 1978) *tv* aluminoceladonite and mixed-layer *tv* aluminoceladonite-smectites are formed from alteration of volcanic material in evaporitic basins. The distribution of isomorphous octahedral cations in these *tv* samples was not analyzed.

The results of Drits *et al.* (2004) illustrate that *tv* and *cv* smectites having volcanic origin, in fact, differ substantially as regards both octahedral cation composition and distribution of isomorphous octahedral cations. For example, the I-S sample HSI from the K/T boundary layer at Stevns Klint, Denmark, consists of two phases: 70% of a high-smectitic (HS) phase with 95% low-charge montmorillonite and 5% illite layers; and 30% of a low-smectitic (LS) phase with 50% smectite and 50% illite layers. The low-charge montmorillonite in the HSI sample consists of *tv* layers. In contrast, SAz-1 montmorillonite (Arizona, USA) has *cv* structure. The montmorillonite in HSI, however, has less Mg than SAz-1, and the octahedral Al and Mg cations in its 2:1 layers are distributed to form the most homogeneous local cation environments around Al, *i.e.* on average each Al has one Mg neighbor. In contrast, the cationic pairs of SAz-1 are randomly distributed to create larger variations of the local electronic structure for the Al environment. As mentioned above, such patterns in the distribution of isomorphous octahedral cations in a smectite 2:1 layer favor the formation of *tv* and *cv* structure, respectively, which, in turn, may be due to different physicochemical conditions of formation; HSI may have been formed

under more stable physicochemical conditions than those for the SAz-1.

Whereas certain insight has been gained into the structural and crystal chemical features of smectites having volcanic origin, little is known about the layer types in smectite which act as the predecessor of diagenetically transformed I-S. In young sedimentary basins the pure smectite phase may be masked by variability of smectite contents in random I-S from surface samples. Jennings and Thompson (1986) and Velde and Vasseur (1992) showed that surface I-S may recrystallize to form pure smectite at burial depths ranging from several hundreds of meters in older rocks to 1–2 km depth in younger ones; this smectite is the starting point for the smectite-to-illite transformation in diagenesis (Velde and Iljima, 1988). No data exist, however, on the octahedral vacancy pattern in the minerals involved in this process.

## CONCLUSIONS

A variety of sophisticated diffraction and non-diffraction methods have been developed for both qualitative and quantitative determination of *tv* and *cv* layers in dioctahedral 2:1 phyllosilicates and clay minerals. Each method has inherent problems and limitations.

The latest achievements in the methodologies for the study of layer types in clay minerals has made possible the revelation of crystal-chemical factors, physicochemical conditions, and geological environments favoring the formation of *tv* and *cv* layers in illite and illite fundamental particles in very illitic I-S. On the other hand, correlation between the physicochemical conditions of smectite formation and the specific vacancy patterns in octahedral sheets requires further study in order to elucidate the physicochemical conditions leading to either ordered or random distribution of isomorphous octahedral cations in *tv* and *cv* smectites and the factors favoring the formation of interstratified *tv/cv* smectites. Additional studies are also needed to reveal the interdependencies between the structural and crystal-chemical characteristics of smectites and I-S and specific geological environments of their formation. In particular, the layer types in surface I-S and pure smectite in young sedimentary rocks should be investigated.

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## REFERENCES

- Altaner, S.P. and Ylagan, R.F. (1997) Comparison of structural models of mixed-layer illite-smectite and reaction mechanisms of smectite illitization. *Clays and Clay Minerals*, **45**, 517–533.

- Bailey, S.W. (1984) Crystal chemistry of the true micas. Pp. 13–66 in: *Micas* (S.W. Bailey, editor). Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C.
- Besson, G., Glaeser, R., and Tchoubar, C. (1983) Le césium révélateur de structure des smectites. *Clay Minerals*, **18**, 11–19.
- Brigatti, M.F. and Guggenheim S. (2002) Mica crystal chemistry and the influence of pressure, temperature and solid solution on atomistic models. Pp. 1–97 in: *Micas: Crystal Chemistry and Metamorphic Petrology* (A. Mottana, F.E. Sassi, J.B. Thompson Jr., and S. Guggenheim, editors). Review in Mineralogy and Geochemistry, **46**, Mineralogical Society of America with the Accademia Nazionale dei Lincei, Roma, Italy.
- Cuadros, J. (2002) Structural insights from the study of Cs-exchanged smectites submitted to wetting-and-drying cycles. *Clay Minerals*, **37**, 473–486.
- Cuadros, J. and Altaner, S.P. (1998a) Characterization of mixed-layer illite-smectite from bentonites using microscopic, chemical and X-ray methods: constraints on the smectite-to-illite transformation mechanism. *American Mineralogist*, **83**, 762–774.
- Cuadros, J. and Altaner, S.P. (1998b) Compositional and structural features of the octahedral sheet in mixed-layer illite-smectite from bentonites. *European Journal of Mineralogy*, **10**, 111–124.
- Dainyak, L.G., Zviagina, B.B., Rusakov, V.S., and Drits, V.A. (2006) Interpretation of the nontronite dehydroxylate Mössbauer spectrum using EFG calculations. *European Journal of Mineralogy*, **18**, 753–764.
- Drits, V.A. (2003) Structural and chemical heterogeneity of layer silicates and clay minerals. *Clay Minerals*, **38**, 403–432.
- Drits, V.A. and Kossovskaya, A.G. (1991) *Clay Minerals: Micas and Chlorites*. Nauka, Moscow, 175 pp. (in Russian).
- Drits, V.A. and McCarty, D.K. (1996) A simple technique for a semi-quantitative determination of the *trans*-vacant and *cis*-vacant 2:1 layer contents in illites and illite-smectites. *American Mineralogist*, **81**, 852–863.
- Drits, V.A. and Sakharov, B.A. (2004) Potential problems in the interpretation of powder X-ray diffraction patterns from fine-dispersed  $2M_1$  and  $3T$  dioctahedral micas. *European Journal of Mineralogy*, **16**, 99–110.
- Drits, V.A. and Tchoubar, C. (1990) *X-ray Diffraction of Disordered Lamellar Structures. Theory and Application to Microdivided Silicates and Carbons*. Springer Verlag, Berlin, 242 pp.
- Drits, V.A., Plançon A., Sakharov, B.A., Besson, G., Tshipursky, S.I., and Tchoubar, C. (1984) Diffraction effects calculated for structural models of K-saturated montmorillonite containing different types of defects. *Clay Minerals*, **19**, 541–562.
- Drits, V.A., Weber F., Salyn, A., and Tshipursky, S. (1993) X-ray identification of  $1M$  illite varieties: Application to the study of illites around uranium deposits of Canada. *Clays and Clay Minerals*, **41**, 389–398.
- Drits, V.A., Besson, G., and Muller, F. (1995) Structural mechanism of dehydroxylation of *cis*-vacant 2:1 layer silicates. *Clays and Clay Minerals*, **43**, 718–731.
- Drits, V.A., Salyn, A.L., and Šucha, V. (1996) Structural transformations of interstratified illite-smectites from Dolna Ves hydrothermal deposits: dynamics and mechanisms. *Clays and Clay Minerals*, **44**, 181–190.
- Drits, V.A., Dainyak, L.G., Müller, F., Besson, G., and Manceau, A. (1997a) Isomorphous cation distribution in celadonites, glauconites and Fe-illites determined by infrared, Mössbauer and EXAFS spectroscopy. *Clay Minerals*, **32**, 153–180.
- Drits, V.A., Sakharov, B.A., Lindgreen, H., and Salyn, A. (1997b) Sequential structural transformation of illite-smectite-vermiculite during diagenesis of Upper Jurassic shales from the North Sea and Denmark. *Clay Minerals*, **32**, 351–372.
- Drits, V.A., Lindgreen, H., Salyn, A.L., Ylagan, R., and McCarty, D.K. (1998) Semiquantitative determination of *trans*-vacant and *cis*-vacant 2:1 layers in illites and illite-smectites by thermal analysis and X-ray diffraction. *American Mineralogist*, **83**, 31–73.
- Drits, V.A., Sakharov, B.A., Dainyak, L.G., Salyn, A.L., and Lindgreen, H. (2002) Structural and chemical heterogeneity of illite-smectites from Upper Jurassic mudstones of East Greenland related to volcanic and weathered parent rocks. *American Mineralogist*, **87**, 1590–1607.
- Drits, V.A., Lindgreen, H., Sakharov, B.A., Jakobsen, H.J., and Zviagina, B.B. (2004) The detailed structure and origin of clay minerals at the Cretaceous/Tertiary boundary, Stevns Klint (Denmark). *Clay Minerals*, **39**, 367–390.
- Drits, V.A., McCarty, D.K., and Zviagina, B.B. (2006) Crystal-chemical factors responsible for the distribution of octahedral cations over *trans*- and *cis*-sites in dioctahedral 2:1 layer silicates. *Clays and Clay Minerals*, **54**, 131–152.
- Drits, V.A., Lindgreen, H., Sakharov, B.A., Jakobsen, H.J., Fallick, A.E., Salyn, A.L., Dainyak, L.G., Zviagina, B.B., and Barfod, D.N. (2007) Formation and transformation of mixed-layer minerals by Tertiary intrusives in Cretaceous mudstones, West Greenland. *Clays and Clay Minerals*, **55**, 261–284.
- Ey, F. (1984) Un exemple de gisement d'uranium sous discordance: les minéralisations protérozoïques de Cluff Lake, Saskatchewan, Canada. Thèse de doctorat, Université Louis Pasteur, Strasbourg I, France.
- Gavrilov, Y.O. and Tshipursky, S.I. (1988) Clay minerals from low- and middle-Jurassic deposits of different structural and facial zones of the central Caucasus. *Litologia and poleznye iskopaemye*, **6**, 57–72 (in Russian).
- Guggenheim, S., Chang, H.Y., and Koster van Groos, A.E. (1987) Muscovite dehydroxylation: high-temperature studies. *American Mineralogist*, **72**, 537–550.
- Halter, G. (1988) Zonalité des altérations dans l'environnement des gisements d'uranium associés à la discordance du Protérozoïque moyen (Saskatchewan, Canada). Thèse de doctorat, Université Louis Pasteur, Strasbourg I, France.
- Heller-Kallai, L., Farmer, V.C., Mackenzie, R.C., Mitchell, B.D., and Taylor, H.E.W. (1962) The dehydroxylation and rehydroxylation of triphormic dioctahedral clay minerals. *Clay Minerals Bulletin*, **5**, 56–72.
- Horton, D. (1983) Argillitic alteration associated with the amethyst vein system, Creede Mining District, Colorado. Ph.D. dissertation, University of Illinois, Urbana-Champaign, Illinois, USA.
- Jennings, S. and Thompson, G.R. (1986) Diagenesis of Pliocene sediments of the Colorado River delta, Southern California. *Journal of Sedimentary Petrology*, **56**, 89–98.
- Lanson, B., Beaufort, D., Berger, G., Baradat, J., and Lacharpeque, J.C. (1996) Illitization of diagenetic kaolinite-to-dickite conversion series: Late-stage diagenesis of the Lower Permian Rotliegend sandstone reservoir, offshore of the Netherlands. *Journal of Sedimentary Research*, **66**, 501–518.
- Lantenois, S., Muller, F., Beny, J.-M., Mahiaoui, J., and Champallier, R. (2008) Hydrothermal synthesis of beidelites: characterization and study of the *cis*- and *trans*-vacant character. *Clays and Clay Minerals*, **56**, 39–48.
- Lee, M. (1996)  $1M(cis)$  illite as an indicator of hydrothermal activities and its geological implication. 33<sup>rd</sup> Annual meeting of the Clay Minerals Society, program and abstracts. 15–20 June, 1996, Gatlinburg, Tennessee, USA, p. 106.

- Lindgreen, H. and Surlyk F. (2000) Upper Permian-Lower Cretaceous clay mineralogy of East Greenland: provenance, palaeoclimate and volcanicity. *Clay Minerals*, **35**, 791–806.
- Lindgreen, H., Drits, V.A., Sakharov, B.A., Salyn, A.L., Wrang, P., and Dainyak, L.G. (2000) Illite-smectite structural changes during metamorphism in black Cambrian Alum shales from the Baltic area. *American Mineralogist*, **85**, 1223–1238.
- Lindgreen, H., Drits, V.A., Sakharov, B.A., Jakobsen, H., Salyn, A.L., Dainyak, L.G., and Kroyer, H. (2002) The structure and diagenetic transformation of illite-smectite and chlorite-smectite from North Sea Cretaceous-Tertiary chalk. *American Mineralogist*, **87**, 429–450.
- Mamy, J. and Gaultier, J.P. (1976) Les phenomenes de diffraction de rayonnements X et electronique per les reseaux atomiques: application a l'etude de l'ordre dans les mireraux argileux. *Annual Agronomiques*, **27**, 1–16.
- Manceau, A., Lanson, B., Drits, V.A., Chateigner, D., Gates, W.P., Wu, J., Huo, D., and Stucki, J.W. (2000) Oxidation-reduction mechanism of iron in dioctahedral smectites. I. Crystal chemistry of oxidized reference nontronites. *American Mineralogist*, **85**, 133–152.
- McCarty, D.K. and Reynolds R.C., Jr. (1995) Rotationally disordered illite-smectite in Paleozoic K-bentonites. *Clays and Clay Minerals*, **43**, 271–284.
- McCarty, D.K. and Reynolds R.C., Jr. (2001) Three-dimensional crystal structures of illite-smectite minerals in Paleozoic K-bentonites from the Appalachian basin. *Clays and Clay Minerals*, **49**, 24–35.
- McCarty, D.K., Sakharov, B.A., and Drits, V.A. (2008) Early clay diagenesis in Gulf Coast sediments: new insights from XRD profile modeling. *Clays and Clay Minerals*, **56**, 359–379.
- Méring, J. (1949) L'interférence des rayons X dans les systèmes à stratification désordonnée. *Acta Crystallographica*, **2**, 371–377.
- Méring, J. and Oberlin, A. (1971) Smectites. Pp. 193–229 in: *The Electron-Optical Investigation of Clays* (J.A. Gard, editor). Monograph 3, Mineralogical Society, London.
- Morgan, D.J. (1977) Simultaneous DTA-EGA of mineral and natural mineral mixtures. *Journal of Thermal Analysis*, **12**, 245–263.
- Muller, F., Drits, V.A., Plançon, A., and Besson, G. (2000a) Dehydroxylation of Fe<sup>3+</sup>, Mg-rich dioctahedral micas: (I) structural transformation. *Clay Minerals*, **35**, 491–504.
- Muller, F., Drits, V.A., Tsipursky, S.I., and Plançon, A. (2000b) Dehydroxylation of Fe<sup>3+</sup>, Mg-rich dioctahedral micas: (II) cation migration. *Clay Minerals*, **35**, 505–514.
- Muller, F., Drits, V.A., Plançon, A., and Robert, J-P. (2000c) Structural transformation of 2:1 dioctahedral layer silicates during dehydroxylation-rehydroxylation reactions. *Clays and Clay Minerals*, **48**, 572–585.
- Reynolds, R.C., Jr. (1993) Three-dimensional X-ray diffraction from disordered illite: simulation and interpretation of the diffraction patterns. Pp. 44–78 in: *Computer Applications to X-ray Diffraction Methods* (R.C. Reynolds and J. Walker, editors). Workshop Lectures Series, 5, The Clay Minerals Society, Bloomington, Indiana, USA.
- Reynolds, R.C., Jr. and Thomson, C.H. (1993) Illites from the Postam sandstone of New York, a probable noncentrosymmetric mica structure. *Clays and Clay Minerals*, **41**, 66–72.
- Sainz-Diaz, C.I., Hernandez-Laguna, A., and Dove, M.T. (2001) Theoretical modeling of cis-vacant and trans-vacant configurations in the octahedral sheet of illites and smectites. *Physics and Chemistry of Minerals*, **28**, 322–331.
- Sokolova, T.N., Drits, V.A., Sokolova, A.L., and Stepanov, S.S. (1976) Structural and mineralogical characteristics and conditions of formation of leucophyllite from salt-bearing deposits of Inder. *Litologia and poleznye iskopaemye*, **6**, 80–95 (in Russian).
- Sokolova, T.N., Sakharov, B.A., and Drits, V.A. (1978) Mixed-layer leucophyllite-montmorillonite minerals. *Litologiya i Poleznye Ikopayemye*, **6**, 87–101 (in Russian).
- Środoń, J. (1999) Nature of mixed-layer clays and mechanisms of their formation and alteration. *Annual Reviews in Earth and Planetary Science*, **27**, 19–53.
- Takahashi, T., Kanehashi, K., and Saito, K. (2008) First evidence of multiple octahedral Al sites in Na-montmorillonite by <sup>27</sup>Al multiple quantum MAS NMR. *Clays and Clay Minerals*, **56**, 520–525.
- Tsipursky, S.I. and Drits, V.A. (1984) The distribution of octahedral cations in the 2:1 layers of dioctahedral smectites studied by oblique-texture electron diffraction. *Clay Minerals*, **19**, 177–193.
- Ufer, K., Kleeberg, R., Bergmann, J., and Dohrmann, R. (2008) Rietveld phase quantification of mixed-layer structures. *4<sup>th</sup> Mid-European Clay Conference 2008 MECC'08, 22-27 September, 2008, Zakopane, Poland* (K. Gorniak, T. Szydlak, M. Kasina, M. Michalik, and B. Zych-Habel, editors). Mineralogia, Special Papers, **33**, 169.
- Velde, B. and Iijima, A. (1988) Comparison of clay and zeolite mineral occurrences in Neogene age sediments from several deep wells. *Clays and Clay Minerals*, **36**, 337–342.
- Velde, B. and Vasseur, G. (1992) Estimation of the diagenetic smectite to illite transformation in time-temperature space. *American Mineralogist*, **77**, 967–976.
- Warshaw, C.M. (1959) Experimental studies of illites. *Clays and Clay Minerals*, **7**, 303–316.
- Ylagan, R.F., Altaner, S.P., and Pozzuoli, A. (2000) Reaction mechanisms of smectite illitization associated with hydrothermal alteration from Ponza island, Italy. *Clays and Clay Minerals*, **48**, 610–631.
- Zhukhlistov, A.P., Dragulesku, E.M., Rusinov, V.L., Kovalenker, V.A., Zvyagin, B.B., and Kuz'mina, O.V. (1996) Sericite with non centrosymmetric structure from gold-silver-polymetallic ores of Banska Stiavnica deposit (Slovakia). *Zapiski Vserossiyskogo Mineralogicheskogo Obshchestva*, **125**, 47–54 (in Russian).
- Zvyagin, B.B., Rabotnov, V.T., Sidorenko, O.V. and Kotelnikov D.D. (1985) Unique mica consisting of non-centrosymmetric layers. *Izvestiya Akademii Nauk S.S.S.R, Seriya Geologicheskaya*, **35**, 121–124 (in Russian).
- Zviagina, B.B., Sakharov, B.A., and Drits, V.A. (2007) X-ray diffraction criteria for the identification of trans- and cis-vacant varieties of dioctahedral micas. *Clays and Clay Minerals*, **55**, 467–480.

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