

# Structural and Crystal-Chemical Features of Mixed-Layer Illite-Containing Minerals from Catagenetically Altered Upper Jurassic Oil-Source Rocks

V. A. Drits<sup>a, \*</sup>, B. A. Sakharov<sup>a, \*\*</sup>, and B. B. Zviagina<sup>a, \*\*\*</sup>

<sup>a</sup> *Geological Institute, Russian Academy of Sciences, Moscow, 119017 Russia*

*\*e-mail: victor.drits@mail.ru*

*\*\*e-mail: sakharovba@gmail.com*

*\*\*\*e-mail: zbella2001@yahoo.com*

Received September 12, 2022; revised December 18, 2022; accepted January 9, 2023

**Abstract**—Illite-smectite (I-S) minerals from the Upper Jurassic oil-source shales of Denmark and the North Sea were studied by a complex of diffraction and spectroscopic methods. Detailed structures were identified to reveal the mechanism of postsedimentary transformations of these shales. Usually, oil is generated in the oil-source rocks of sedimentary basins simultaneously with the diagenetic and catagenetic I-S transformations. The results obtained demonstrate the relationship between these two reactions: NH<sub>3</sub> molecules released from kerogen during the maximum oil formation are fixed as NH<sub>4</sub> cations in smectite or vermiculite interlayers, forming mica or tobelite structural fragments. This solid-phase transformation produces the mixed-layer structures consisting of illite, tobelite, smectite, and vermiculite (I-T-S-V) layers.

**Keywords:** oil-source rocks, diagenesis of mixed-layer minerals, illite-tobelite-smectite-vermiculite, crystal-chemical features of mixed-layer minerals, solid-phase transformations

**DOI:** 10.1134/S0024490223700128

## INTRODUCTION

Mixed-layer minerals are a remarkable example of one-dimensional order–disorder in the natural and synthetic crystals (Drits, 1997). They consist of layers of different structure and composition, which are alternated in variable proportions and with different distribution. Effects of mixed layering are observed among crystals with diverse layer and pseudolayer structures: silicates, phyllosilicates, oxides, carbonates, and others. Special interest in mixed-layer structures is caused by several reasons. From the diffraction point of view, it facilitates the development of new theoretical and methodological approaches, because unusual diffraction effects of these minerals cannot be interpreted using the traditional methods of structural analysis (Drits and Sakharov, 1976; Drits and Tchoubar, 1990; Moore and Reynolds, 1997; Sakharov and Lanson, 2013). Extremely wide abundance of mixed-layer minerals in diverse continental and oceanic settings within the upper shell of the Earth, as well as the fact that the formation of some of them is related to definite geological conditions, and many other factors make it possible to consider these minerals as important geochemical indicators allowing the reconstruction of the evolution of sedimentary basins (Drits and Kossovskaya, 1990, 1991).

In this work, a complex of methods was applied to study clay minerals from the Upper Jurassic shales of the North Sea, an Upper Jurassic rift province that includes the Central Graben and Viking Graben, where these shales are the most productive oil source rocks (Drits et al., 1997a, 1997b, 2002a, 2005; Drits and Zviagina, 2009; Lindgreen, 1994; Lindgreen et al., 2000; Sakharov et al., 1999a, 1999b). Samples for study were collected from core holes drilled within this province and beyond it, in particular, in different areas of the Norwegian–Denmark basin. The Upper Jurassic shales of this basin contain immature organic matter with low vitrinite reflectance. The aim of this study was to answer two main questions:

(1) Do clay minerals formed during diagenesis–catagenesis in oil-source rocks have any specific crystal-chemical features?

(2) What is the structural mechanism of diagenetic and catagenetic transformations of these minerals?

In solving these questions, the main attention is focused on the comprehensive study of mixed-layer minerals, in particular, illite-smectites, which are most sensitive to a change of physicochemical conditions of host rocks. In addition, an interest in illite-smectites is determined by three factors:

1) Illite-smectites are an intermediate chain in the series of smectite-to-illite structural transformations known as the smectite illitization. It is generally accepted that smectite illitization, i.e., an increase of K-bearing illite layers with subsidence depth of the rocks and increasing temperature, are typical of sedimentary basins, hydrothermally altered pyroclastics, bentonites, and others.

2) Smectite is illitized simultaneously with and at the same temperatures and pressures as oil generation in oil-source rocks. The oil window is characterized by the temperature interval of 70–130°C and by the same values of vitrinite reflectance (0.5–1.0%), which correspond to the maximum smectite illitization.

3) The thermal decomposition of organic matter leading to the formation of kerogen and crude oil is accompanied by the release of NH<sub>3</sub> molecules, which under reducing conditions and moderately high pH are transformed into NH<sub>4</sub> cations. Under these conditions, these cations can be involved in the structure of mixed-layer minerals.

We developed a new approach to the interpretation of X-ray diffraction (XRD) patterns recorded from mixed-layer minerals (Drits et al., 1997a, 1997b, 2002a, 2005; Sakharov et al., 1999a; Sakharov and Lanson, 2013). Implementation of this approach made it possible to study the structural characteristics of mixed-layer illite-containing minerals from shales on a principally new level. In particular, it was found that these minerals consist of three types of layers: mica, smectite, and vermiculite layers, which are alternated depending on the postsedimentary transformations with different degree of order–disorder. The developed approach with high accuracy allowed the determination of the content of each alternating layer types. The noteworthy fact is that the height of mica layers increases from 9.98 Å typical of the K-bearing illite to 10.05 Å with increasing extent of postsedimentary transformations. It was concluded that the mica interlayers in the studied minerals, in addition to K, contain ammonium cations. Based on obtained data, two important conclusions were drawn.

1) Saturation in K and dehydration of samples from oil-source shales of the North Sea lead to the formation of mixed-layer structures, in which the K-bearing 9.98 Å layers are alternated with the NH<sub>4</sub>-bearing layers.

2) In the natural state, the illite-containing mixed-layer minerals represent the four-component structures consisting of alternating illite, tobelite, smectite, and vermiculite (I-T-S-V) layers.

Thus, the mixed-layer illite-containing minerals from oil-source rocks of the North Sea differ in their structural and crystal-chemical features from the known illite-smectite phases previously described in literature.

## METHODOLOGY

For a long time, the structural study of mixed-layer phases was limited by the two-component systems, i.e., determination of the content and distribution of alternating illite and smectite layers (Shutov et al., 1969a, 1969b; Drits and Sakharov, 1976). A general approach developed later was based on the simulation of XRD patterns of multicomponent and multiphase mixed-layer systems. In particular, a direct comparison of the calculated and experimental XRD patterns made it possible to reproduce not only the position of reflections, but also their profiles and intensity, which strongly depend on the proportions and arrangement of layers. In addition to the frequent appearance of multicomponent mixed-layer phases, a new approach proposed by Drits (Drits et al., 1997a, 1997b) and Sakharov (Sakharov et al., 1999a, 1999b) discovered the frequent coexistence of mixed-layer phases, which demonstrate an “unusual” composition and/or distribution order of alternating layers and phases (Drits et al., 1997a, 1997b, 2002a, 2002b, 2004, 2005, 2007; Sakharov et al., 1999b, 2004; Lindgreen et al., 2000, 2002; Claret et al., 2004; McCarty et al., 2004, 2008). Thus, this approach casts some doubts on the generally accepted description of smectite illitization in the diagenetic and catagenetic series, which is based on the common criteria of illite-smectite identification.

## MULTITEST METHOD FOR THE DETERMINATION OF THE PHASE COMPOSITION AND STRUCTURAL FEATURES OF ILLITE-SMECTITE MINERALS

In this section, we attempt to demonstrate how the structural model of a mixed-layer sample can be reliably determined by the procedure of maximally close simulation of experimental XRD patterns. To this aim, we analyzed XRD patterns of sample, which is saturated in diverse exchange cations (e.g., Na, Ca, Mg, K, NH<sub>4</sub>) in the air-dry and glycolated states. In this method, each treatment of sample serves as an independent verification of its statistical structural model, because it modifies the thickness and efficient scattering of expandable layers but preserves the content of expandable and nonexpandable layers and their distribution. Such approach makes it possible to determine the structural parameters, which are difficult or hardly possible to obtain by other modern methods.

### *Simulation of X-Ray Diffraction Patterns*

The high efficiency of multitest method was demonstrated by many researchers. The models of mixed-layer structures include the number (not limited by two components), nature, and proportions of different types of layers, interlayers, and their statistical alternation. The layer sequences in mixed-layer structures could obey different laws that differ in a short-range order factor (R) equal to the number of

the adjacent preceding layers, which affect the probability of the occurrence of end layer of the given type. At  $R = 0$ , the different types of layers are randomly alternated, while at  $R = 1$  the position of layer of the given type depends on the nearest layer of precursor. In the mixed-layer structures with  $R = 2$  or  $3$ , the position of definite layer depends on two or three preceding layers. The alternation of layers in two component structures, for instance, with  $R = 2$ , are described using coefficients  $P_{ijk}$  (detailed description of probability parameters, which characterize diverse variants of alternation of layers of different types with  $R = 0, 1, 2$ , or  $3$  in mixed-layer structures (Drits and Sakharov, 1976; Drits and Tchoubar, 1990; Moore and Reynolds, 1997; Sakharov and Lanson, 2013).

The diverse treatments can change the thickness and scattering ability of expandable interlayers, but do not affect the layer arrangement in crystallites. Therefore, the consistent structural model during simulating the corresponding XRD patterns can be obtained when the sequences of layers in these models are almost identical for different XRD patterns of the same sample. In addition, the relative content of different phases, which is determined by the simulation of experimental XRD patterns, should be close.

The instrumental and experimental factors (goniometer radius, length and thickness of oriented samples, mass absorption coefficients, atomic coordinates, and others) are introduced in calculations with allowance for recommendations (Drits and Tchoubar, 1990; Moore and Reynolds, 1987, 1997).

#### METHODS FOR THE DETERMINATION OF CONTENT AND DISTRIBUTION OF FIXED AMMONIUM IN ILLITE-SMECTITES

Using the isotope dilution method, Lindgreen (1994) determined the content of fixed  $\text{NH}_4$  cations in the studied I-S samples with high accuracy and concluded that the ability of ammonium cations to be involved in the mixed layer structures is higher than that of K cations. The problem is that the application of traditional methods of the interpretation of XRD patterns did not allowed one to determine unambiguously the arrangement of K and  $\text{NH}_4$  cations in interlayers of the transformed illite-smectite structures. Solution of this problem became possible with the use of samples preliminarily saturated in K cations and subsequently heated at  $150^\circ\text{C}$  (Drits et al., 1997a). It was suggested that K and  $\text{NH}_4$  cations in such dehydrated structures can be distributed by two ways. In one structure, they are evenly distributed; i.e., each interlayer contains the same number of K and  $\text{NH}_4$  cations, whereas each interlayer in other structure contains either only K or only  $\text{NH}_4$  cations; i.e., such structure is characterized by the alternation of illite and tobelite layers, the heights of which are  $9.98 \text{ \AA}$  and  $10.33 \text{ \AA}$  (Eugster and Munoz, 1966), respectively. In

each model, the XRD patterns corresponding to structures where  $\text{NH}_4 : \text{K}$  ratio increased from  $0 : 1$  to  $1 : 0$  with a step of  $0.1$  were calculated. Analysis of these patterns showed that the position of basal reflections is insensitive to the distribution of K and  $\text{NH}_4$ . Indeed, the regression equations relating the linear increase of  $d(001)$  values with the increase of  $\text{NH}_4$  contents in structures of both models seemed to be practically identical. It is noteworthy that values of  $d(001)$  and  $\text{FWHH}(00l)$  depend only on the proportions of layer types rather than on the cation occupancy of interlayers. Therefore, at fixed proportion of layer types, the  $d(001)$  and  $\text{FWHH}(00l)$  values change insignificantly at different K and  $\text{NH}_4$  contents in interlayers of  $9.98 \text{ \AA}$  and  $10.33 \text{ \AA}$  layers. When corrected for angular broadening,  $00l$  reflections in the first model had practically identical  $\text{FWHH}$  value, whereas in the second model with alternating layers of different height and scattering power, the subsequent increase of tobelite interlayers ( $W_{\text{NH}_4}$ ) and decrease of illite interlayers ( $1 - W_{\text{NH}_4}$ ) are accompanied by an increase of ratios of half-width reflections with indices  $005$  and  $002$  ( $\text{FWHH}(005)/\text{FWHH}(002)$ ) up to maximum value at  $W_{\text{NH}_4} = 0.50$ , and then decreases with further increase of half-width ratios. The obtained results were used for the interpretation of XRD patterns in the representative collection of K-saturated and heated natural samples with different  $\text{NH}_4$  content. In particular, analysis of corrected profiles of  $002$  and  $005$  reflections allowed the determination of values of  $d(002)$ ,  $d(005)$ ,  $\text{FWHH}(002)$ ,  $\text{FWHH}(005)$  and  $\text{FWHH}(005)/\text{FWHH}(002)$  ratio. These experimental values were used to determine the  $\text{NH}_4$  contents in each sample based on the interrelations between the content of tobelite and illite layers and corresponding values  $d(001) = 5d(005)$  and  $\text{FWHH}(005)/\text{FWHH}(002)$ .

Implementation of this approach made it possible to study the structural characteristics of the studied mixed-layer illite-containing minerals from shales on a principally new level. The most important result of performed studies is the fact that the  $W_{\text{NH}_4}$  content analyzed with the high accuracy for each studied sample by isotope dilution seemed to be identical or very close to the ammonium content determined by the X-ray analysis (Drits et al., 1997a).

As already mentioned, the mixed-layer minerals of oil-source shales in the North Sea consist of alternating illite, smectite, and vermiculite layers depending on the degree of postsedimentary transformations with different degree of order-disorder for each of alternating layer types. Two main conclusions were drawn.

1) Saturation in K and dehydration of samples from the oil-source shales of the North Sea leads to the formation of mixed-layer structures, in which the  $9.98 \text{ \AA}$  K-bearing layers are alternated with the  $10.33 \text{ \AA}$   $\text{NH}_4$ -bearing layers of tobelite.

2) In natural state, the illite-containing mixed-layer minerals represent the four-component structures consisting of alternating illite, tobelite, smectite, and vermiculite layers (Drits et al., 1997b).

At the same time, the study of I-S from Middle Cretaceous oil-source rocks from West Greenland (Drits et al., 2005) showed that the structural features of the  $\text{NH}_4$ -bearing I-S are more diverse than those described in structural models (Drits et al., 1997a). In particular, a combination of the high content of expandable layers and the low concentrations of fixed  $\text{NH}_4$  ions can complicate and even prevent the determination of actual distribution of K and  $\text{NH}_4$  cations over mica interlayers in I-S. In this case, the influence of average thickness of coherent scattering domain (CSD) and variations of layer thickness on the profiles of basal reflections should be taken into account. Thus, in order to develop a new more modified technique for the determination of  $\text{NH}_4$  content and distribution in illite-smectite, it is required, first, to consider the structural illite-smectite models with different K and  $\text{NH}_4$  distribution over mica interlayers and CSD variations depending on the absence or presence of fluctuations of thickness of layers of different types and, second, to develop the diffraction criteria, the application of which would allow one to solve the problem during study of natural samples.

### Structural Models

After the illite-smectite saturation in K and dehydration of smectite interlayers, the K-bearing smectite layers have thickness of 9.98 Å. The X-ray patterns of such illite-smectites demonstrate an integral series of basal reflections, which have the similar half-width at half height values (FWHH). If mica interlayers of illite-smectites together with K contain  $\text{NH}_4$ , then the latter could have one of two main distributions. In model I, cations of K and  $\text{NH}_4$  show the homogenous distribution; i.e., each mica interlayer contains similar amount of K and  $\text{NH}_4$ . In model II, mica interlayers contain either K or  $\text{NH}_4$ . The basal reflections of these models have similar index  $l$  but different FWHH( $00l$ ) values.

Model I can be divided into two varieties (Ia and Ib). In model Ia, all K-bearing smectite layers have similar thickness of 9.98 Å. Statistically weighted thickness of (K +  $\text{NH}_4$ )-bearing mica layers is defined by formula:

$$H = 10.33C_{\text{NH}_4} + 9.98C_{\text{K}},$$

where  $C_{\text{NH}_4}$  and  $C_{\text{K}}$  are the relative contents of K and  $\text{NH}_4$ .

Unlike model Ia, thickness of the K-saturated smectite layers in model Ib varies within narrow ranges relative to the average thickness. Let us suppose that thickness of the K-saturated smectite layer equals  $(9.98 \pm \epsilon)$  Å, where  $\epsilon$  is the variable. If  $\epsilon$  obeys the nor-

mal Gaussian distribution, probability of the occurrence of layers with fixed  $\epsilon$  value is determined by the Gaussian function with standard deviation  $\Delta_S = (\sum_n(\epsilon^2/n))^{1/2}$ . The higher the  $\Delta_S$ , the wider the fluctuation range of smectite layer thickness.

Model II is also subdivided into two varieties. The absence of fluctuations in layer thicknesses (model IIa) allows the consideration of K-saturated and dehydrated  $\text{NH}_4$ -bearing illite-smectites as consisting of two layer types: 9.98 Å illite and K-saturated smectite layers and 10.33 Å tobelite layers. In model IIb, the mixed-layer structures due to the fluctuations of the thickness of K-saturated smectite layers should consist of three layer types: 9.98 Å illite, 9.98 Å K-smectite, and 10.33 Å tobelite layers. The  $\Delta_S$  value for K-smectite layers is a variable parameter.

For each of the four models (Ia, Ib, IIa, and IIb), values of  $d(00l)$  and FWHH( $00l$ ) were determined using the calculated XRD patterns that have different concentrations of alternating layers. The content of 10.33 Å layers in model II changed from 0 to 50% and the CSD contained, on average, 5, 6, 8, 12, and 16 layers. Regression equations obtained for model IIa link the  $\text{NH}_4$  concentration of tobelite layers with  $d(00l)$ , FWHH( $00l$ ), and the average number of layers (N) in CSD:

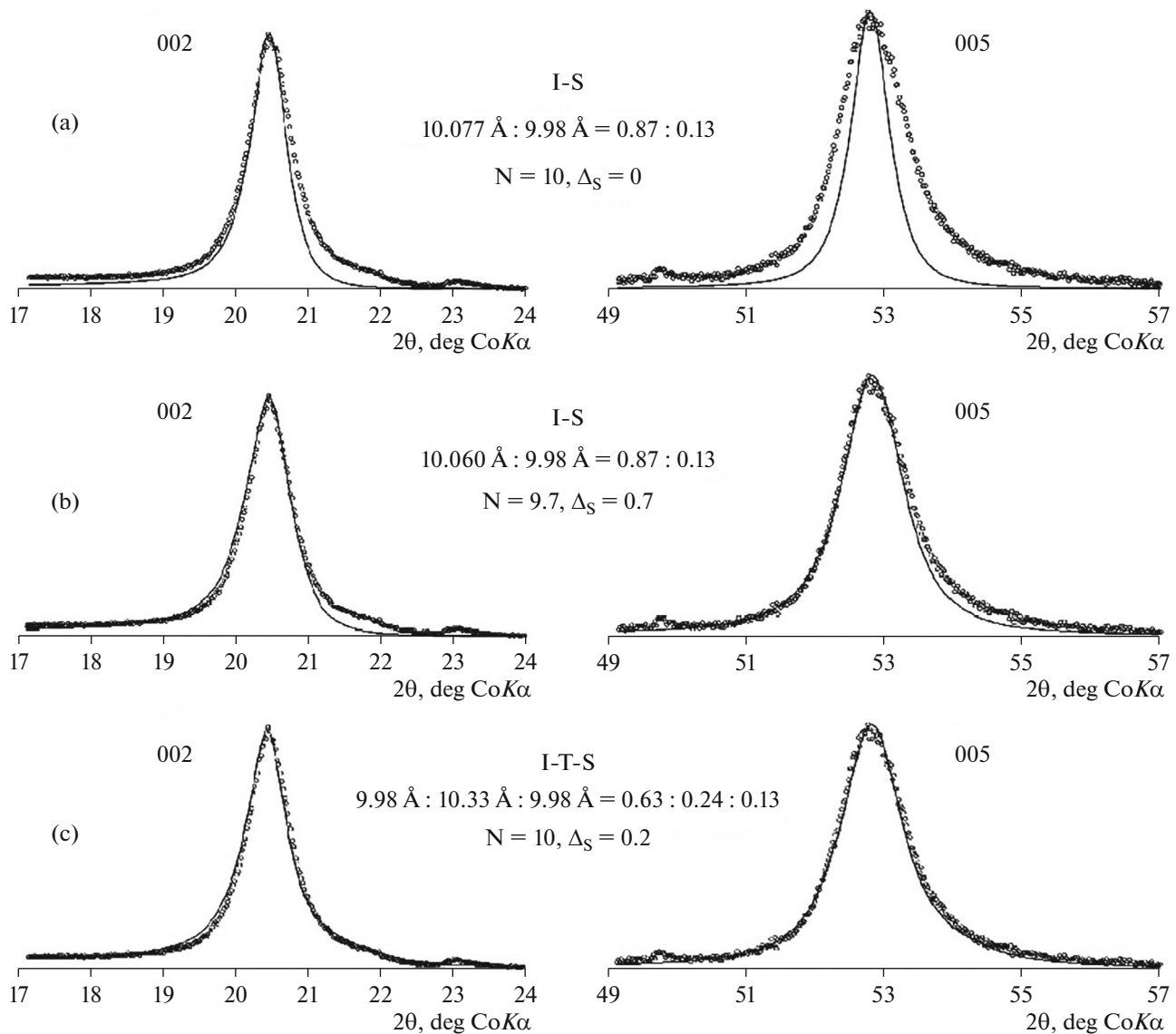
$$\begin{aligned} W_{\text{NH}_4} &= 13.910d(005) - 27.751 \\ &= 2.782d(001) - 27.751, \end{aligned} \quad (1)$$

$$W_{\text{NH}_4} = 0.5 - B_N \{ \ln [A_N / \text{FWHH}(00l)] \}^{1/2}. \quad (2)$$

In particular, for  $l = 2$ ,  $A_N = 0.001 + 6.500/N$ ,  $B_N = -0.011 + 17.273/N$ ; for  $l = 5$ ,  $A_N = 0.414 + 6.061/N$ ,  $B_N = 0.385 + 3.072/N$ . Using these equations, N and  $W_{\text{NH}_4}$  can be determined from the experimentally measured  $d(00l)$  and FWHH( $00l$ ).

In model IIb, if the additional parameter  $\Delta_S$  is taken into consideration, the problem can be solved by the modeling of XRD patterns. Results of such modeling showed that the same profiles and FWHH( $00l$ ) of basal reflections can be obtained by varying either N or  $\Delta_S$ .

Sensitivity of the X-ray diffraction to the different distribution of fixed K and  $\text{NH}_4$  cations in the  $\text{NH}_4$ -bearing I-S can be exemplified by analyzing the XRD patterns for sample UM1002. The modeling of experimental XRD pattern of this sample saturated in Mg showed that the expandable smectite layers in I-S account for 13%. According to the average content of  $\text{NH}_4$  cations,  $W_{\text{NH}_4}$ , determined using  $d(005)$  value from equation 1,  $C_{\text{K}}/(C_{\text{K}} + C_{\text{NH}_4})$  ratio in the mica-type interlayers should be equal 0.71, while the thickness of these layers is 10.077 Å. Then, the structural model consisting of randomly alternating 13% 9.98 Å K-smectite and 87% 10.077 Å mica-type layers shows, first, that the calculated FWHH(002) and FWHH(005) values practically coincide ( $0.540^\circ$  and

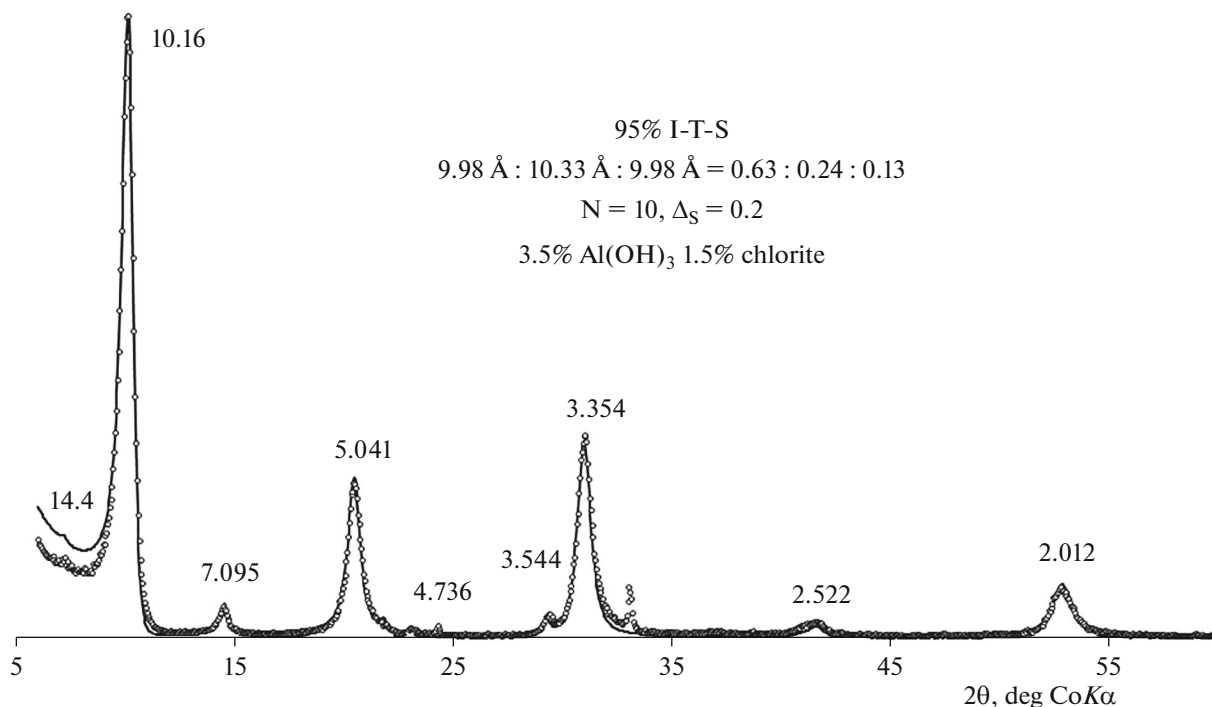


**Fig. 1.** Experimental XRD profiles (light circles) of basal reflections 002 and 005 of UM1002 sample saturated in K and heated at 150°C are compared with the calculated (solid lines) ones for two structural I-S models, in which the (K + NH<sub>4</sub>)-bearing mica-type 10.077 Å (a), 10.060 Å (b), and smectite 9.98 Å layers are alternated, and for the I-T-S model with alternating 9.98 Å illite, 10.33 Å tobelite, and 9.98 Å smectite layers (c).

0.600° 2θ) and, second, the experimental FWHH value (0.568) for reflection 002 is close to the calculated one, whereas the experimental FWHH (0.800) for reflection 005 sharply differs from the calculated one (Fig. 1a). As mentioned previously, the widening of basal reflection 005 could be reached by variations of the thickness of K-smectite layers. However, the satisfactory agreement of experimental profiles of 002 and 005 reflections observed for sample UM1002 and calculated for model, in which 13% 9.98 Å K-smectite layers are alternated with 87% of 10.06 Å mica-type layers (Fig. 1b), could be reached only if the standard

deviation of thickness fluctuations of K-smectite layers increased to unrealistically high value of  $\Delta_S = 0.70 \text{ \AA}$ . Therefore, the model of coexistence of K and NH<sub>4</sub> cations in the mica-type interlayers should be discarded. Real structure of the NH<sub>4</sub>-bearing I-S in sample UM1002 corresponds to the model implying the alternation of illite (63%), tobelite (24%), and K-smectite (13%) interlayers (Figs. 1c, 2).

Detailed analysis showed that the NH<sub>4</sub>-bearing illite-smectites correspond to model II in two cases: 1) when the structure is characterized by the low content of smectite layers ( $W_S < 20\%$ ) and 2) even at  $W_S >$



**Fig. 2.** Experimental XRD pattern (light circles) for the K-saturated UM1002 sample heated at 150°C compared to the calculated XRD pattern (solid line) for model of the disordered mixed-layer I-T-S structure with alternating 9.98 Å illite, 10.33 Å tobelite, and 9.98 Å smectite layers.

20%, when mica interlayers are characterized by  $C_{\text{NH}_4}/(C_{\text{NH}_4} + C_{\text{K}}) \geq 0.20$ .

Analysis of XRD patterns corresponding to models Ia and Ib shows that they either have similar FWHH(001) (for model Ia), or difference between FWHH(002) and FWHH(005) should be much lower than those observed for models IIa and IIb.

#### TOBELIZATION OF SMECTITE AND “TOBELITE WINDOW”

The total content of illite layers in all studied mixed-layer I-T-S-V (Drits et al., 2002a, 2002b; Sakharov et al., 1999a, 1999b) are similar and equal ( $65 \pm 3$ )% regardless of the localization, depth, and temperature of rock subsidence. This principally new and important result shows that the catagenetic transformations of oil-source rocks do not affect the content of illite layers in the mixed-layer structures, but are accompanied by an increase of tobelite layers. This means that these transformations are accompanied by tobelitization instead of illitization of smectites, i.e., smectite layers are transformed into mica layers through ammonium fixation. Analysis of dependence of the content of newly formed tobelite layers on the temperature and vitrinite reflectance showed that the concentrations of these layers are no more than 10% at  $T < 100^\circ\text{C}$  and  $R_0 < 0.60\%$ . With increase of rock depth, temperature ( $110^\circ < T < 140^\circ\text{C}$ ), and vitrinite

reflectance ( $0.6 < R_0 < 0.70\%$ ), the content of tobelite layers ( $W_{\text{NH}_4}$ ) reaches 20–22%. With increasing  $R_0$  from 0.7 to 1.0%,  $W_{\text{NH}_4}$  values show no increase. An interval of physicochemical conditions, when maximum  $\text{NH}_3$  release occurred at  $R_0 = 0.6\text{--}0.7\%$ , coincides with intense tobelitization of smectite interlayers in the illite-smectites was termed by us “tobelite window.” The “oil window” corresponds to  $80^\circ < T < 140^\circ\text{C}$  and  $0.6 < R_0 < 1.3$ . Thus, intense tobelitization characterized by “tobelite window” occurs within “oil window,” when high  $\text{NH}_4$  concentration and temperature within 110–140°C provide the fixation of these cations in smectite interlayers.

#### Cation Composition of I-T-S-V and Structural Mechanism of Their Catagenetic Transformations

Problem with the determination of structural formulas of the mixed layer I-T-S-V consisted in that the studied samples, especially at the initial catagenetic stage, contained significant amounts of kaolinite. We developed technique allowing the determination of both structural formula of I-T-S-V and kaolinite concentration. It was found that an increase of interlayer ammonium cations is not accompanied by a change of K cation number equal to  $0.38 \pm 0.02$  per formula unit. This result serves as one more evidence for the tobelitization of smectites during the postsedimentary transformation of oil-source rocks.

However, an increase of  $\text{NH}_4$  is accompanied by an increase of the tetrahedral and octahedral Al and decrease of the octahedral Fe and Mg. Thus, the tobelitization of smectites can be presented as the sequential substitution of smectite interlayers by tobelite ones through the emigration of interlayer cations and the part of tetrahedral Si cations in solution and Al and  $\text{NH}_4$  cations from solution. The substitution of Si for Al leads to an increase of the negative charge of tetrahedral sheets of 2 : 1 layers and loss of their ability to swelling. The fact that the content of K, as that of illite layers, in the mixed-layer I-T-S-V does not depend on their localization, subsidence depth of rocks, and temperatures, serves as evidence for the solid-phase transformation of these minerals.

Three main models of structural transformations of clay minerals are known: solid-phase reactions, crystallization or recrystallization, and Ostwald ripening. Each of these processes is accompanied by a change of chemical composition, but only solid-phase reactions could explain the constant contents of illite layers at the general increase of concentrations of mica layers through smectite tobelitization. The characteristic feature of solid-phase transformations is the fact that the size and shape of particles practically do not change, whereas the processes of new formation and Ostwald ripening are accompanied by the growth of particle size and acquisition of a regular shape. Independent confirmation of the solid-phase transformations of I-T-S-V was obtained using the atomic force microscopy (Drits et al., 2002a). Application of this method showed that the morphological features of individual particles of I-T-S-V and their sizes practically do not depend on the depth of rock subsidence.

#### *Selective Sorption and Fixation of Ammonium Cations*

One of the main questions is why newly formed mica layers are formed by  $\text{NH}_4$  rather than by K? The possible reason is that K concentration in solution is too low compared to  $\text{NH}_4$ . However, the analyses of pore waters revealed that K concentrations in them are several times higher than  $\text{NH}_4$  content. Moreover, there is a direct proportional dependence between amount of ammonium involved in structure and content of ammonium in the solution.

Predominant adsorption of  $\text{NH}_4$  in mica minerals could be caused by the different reaction of cations of different size to the increase of interlayer charge: the higher the cation size, the easier is the interlayer dehydration. Ion radii of  $\text{NH}_4$  and K equal 1.43 Å and 1.33 Å, respectively. At relatively low charges of smectite interlayers, all cations are hydrated. With increasing a charge, the  $\text{NH}_4$  ions are dehydrated and fixed, first, due to their larger size and, second, owing to their ability to form hydrogen bonds with basal oxygen.

#### *Sequence of the Structural Transformation of Mixed-Layer I-T-S-V Minerals during Catagenesis*

Analysis of probability parameters characterizing the content and distribution of illite, tobelite, smectite, and vermiculite layers in the I-T-S-V minerals allowed us to reveal the character of structural transformations of these minerals at different catagenetic stages. Mixed-layer minerals from shale samples collected above the “tobelite window” consist of illite, smectite, and vermiculite layers with clearly expressed tendency to their segregation. Such alternation of layers of different types is not typical of catagenetically modified mixed-layer minerals and indicates their terrigenous origin. The characteristic feature of mixed-layer I-T-S-V minerals formed within “tobelite window” is a clear tendency to ordered alternation, when pairs of smectite layers do not occur.

#### *Provenance and Initial Material of the Mixed-Layer I-S*

The fact that all studied mixed-layer minerals, regardless of their locality and depth, contain the same amount of illite layers and K cations indicates that I-S-V and I-T-S-V were derived from a single provenance. It is suggested that the initial I-S-V was transported from the Fennoscandian Shield region and was represented by weathering products of illite. The fact that the alternation of I, S, and V layers in the mixed-layer minerals, which were not subjected to catagenesis, tends to segregation indirectly confirms the terrigenous origin of these minerals, because such type of alternation of layers of different types is not typical of catagenetically altered mixed-layer structures.

### OIL-SOURCE ROCKS OF THE MIDDLE CAMBRIAN–EARLY ORDOVICIAN BLACK SHALES IN THE BALTIC REGION: SETTING OF A PROBLEM

Using Upper Jurassic oil-source rocks of the North Sea as an example (Drits et al., 1997a), it was established that the oil generation is accompanied by the tobelitization of smectites instead of their illitization as previously considered; i.e., an increase of mica layers is caused only by selective fixation of ammonium cations in the former smectite and vermiculite interlayers. The question arose whether the features established for studied mixed-layer minerals typical of only oil-source rocks of the North Sea or formation of I-T-S or I-T-S-V structures are typical of oil formation in the diagenetically transformed sedimentary rocks? Answer to this question is not only of scientific but also of practical significance. This is because formed tobelite layer is highly resistant to heating ( $>400^\circ\text{C}$ ). Under these conditions, the high content of tobelite layers in mixed-layer minerals could indicate oil generation in rocks, which for different reasons did not retain oil traces but preserve specifics of mixed-layer structures. In addition, if oil-source rocks show smec-



tite tobelitization, the K/Ar data cannot be used for dating diagenesis–catagenesis.

The study object was represented by clay minerals from the Middle Cambrian–Early Ordovician black shales of the Baltic region (Lindgreen et al., 2000). The thickness of the shale sequences varies from 130 m in Denmark to 1 m in Estonia. During formation of Caledonian fold zone, black shales in the vicinity of Denmark, along the Oslo fjords of Norway and southern Sweden were subsided up to 4.5 km and heated to 200–220°C (Jensenis, 1987; Vejebak et al., 1994). Shales from central Sweden and Estonia experienced only insignificant postsedimentary transformations. Organic matter in the latter is in immature state relative to the oil generation. Pyrolysis data indicate that this organic matter has a high potential for oil formation (high value of S2 peak), but oil generation is only at the initial stage (low value of S1 peak). However, up to present, oil-source rocks and oil reservoirs were not found in the considered area.

#### *Crystal-Chemical Features of Mixed-Layer Minerals Depending on the Degree of Postsedimentary Alteration*

Analysis of XRD patterns show that all samples could be subdivided into two main groups. The first group includes rocks subjected to initial diagenesis (Estonia and central Sweden), whereas the samples of the second group experienced deep catagenesis—initial metamorphism. Fine clay fraction (<0.5 m) of samples of the first group is represented by a mixture of two mixed-layer I-S phases. One of them, high-illite phase, contains only 5% smectite interlayers, whereas other low-illite phase consists of 75% illite and 25% smectite interlayers. In both phases, the distribution of mica and smectite layers is controlled by the maximum possible order degree at  $R = 1$ ; i.e., the structures of these phases do not contain two adjacent smectite layers. It is typical that the structural and probability characteristics of the high-illite and low-illite phases are similar for all studied samples of the first group. Different samples demonstrate a change of only relative content of high- and low-illite phases from 0.45 : 0.55 to 0.30 : 0.70.

Fine clay fractions of samples of the second group also consist of a mixture of two illite-containing phases. One of them contains 95% illite and 5% smectite layers, i.e., a complete analogue of high-illite phase found in samples of the first group. Detailed study showed that the structure of another mixed-layer phase consists of alternating K-bearing 9.98 Å illite,  $\text{NH}_4$ -bearing 10.33 Å tobelite, and expandable smectite layers. The characteristic feature of this phase is the fact that the content of illite interlayers in all studied samples equals 75% and, respectively, and the sum of tobelite and smectite layers accounted for 25%.

The revealed significant concentration of tobelite layers (up to 20%) in the studied mixed-layer I-T-S

shows that tobelite layers are stable even at anchimetamorphism and, thus, they record the oil formation prior to the metamorphic transformation of shales during the Caledonian orogeny.

The characteristic feature of all studied I-S and I-T-S is the similar content of interlayer cations K ( $0.56 \pm 0.02$ ). Within each group, samples have almost identical cation composition of octahedra and tetrahedra of 2 : 1 layers. Compared to the first group, samples of the second group have significant content of interlayer cations  $\text{NH}_4$ , the higher degree of Si substitution for Al in tetrahedra, and lower content of octahedral Mg and  $\text{Fe}^{2+}$ . The obtained data on the cation composition of the studied mixed-layer minerals, in particular, similar content of K cations, confirm the conclusion that a decrease of expandable layers in the low-illite phase was mainly caused by  $\text{NH}_4$  involvement and formation of tobelite layers.

#### *Problems with Determination of the Degree of Postsedimentary Changes of the Cambrian Black Shales in the Baltics*

Cambrian black shales in Denmark, southern Sweden, Norway, and North Germany are located closely to the front of Caledonian folding. Corresponding rocks were subsided to a depth of 4.5 km and heated up to 200–220°C, but were uplifted in the Permian. In contrast, black shales of central Sweden and Baltic countries were heated only up to 90–100°C (Thomsen et al., 1983; Brangulis et al., 1993; Buchardt et al., 1997).

The determination of vitrinite reflectance showed that samples NA, ES, and KI of the first group contains immature organic matter, whereas maturity of organics in samples KV and OP of the same group corresponds to oil generation. Samples of the second group located in the vicinity of the Caledonian folding are at the stage of anchimetamorphism. At the same time, the organochemical data obtained using Rock-Eval pyrolysis (Wrang, 1983) show that kerogen in NA, OP, and KV samples of the first group has  $T_{\text{max}} = 420\text{--}430^\circ\text{C}$  and very small S1 and S2 peaks, which determined the onset of oil generation. In contrast, samples AA, OL, and SL of the second group contain only traces of S1 and S2 peaks; i.e., they passed through stages of oil and gas generation. Samples of the second group contains over 90% mica interlayers, 10–20% of which are tobelite one. Significant amount of mica interlayers is consistent with the high degree of I-T-S transformation. However, the structural features of I-T-S disagree with concepts available in literature for mixed-layer I-S at anchimetamorphic stage. First, it is known that  $2M_1$  illites crystallize at 200–300°C, while 1M illites are also formed at lower temperatures (Eslinger and Savin, 1979). It was found that the studied samples contain admixture of 1M +  $2M_1$  illites, the total content of which is no more than 10%. The mor-



phological features of these illite particles point to their detrital origin. Second, the transition from catagenesis to anchimetamorphism usually leads to a significant increase of CSD thickness up to 200–300 Å (Arkai et al., 1996). However, the average thickness of crystallites for samples of the second group is much lower and equals 60–80 Å. It is possible that specific features of the studied mixed-layer I-T-S are related to the smectite to illite transition and the presence of organic matter.

#### CRYSTAL-CHEMICAL FACTORS CONTROLLING THE DISTRIBUTION OF OCTAHEDRAL CATIONS OVER CIS- AND TRANS- SITES IN THE DIOCTAHEDRAL 2 : 1 MICA-TYPE SILICATES

An important aspect of the general problem of structural and crystal-chemical heterogeneity of minerals is the distribution of octahedral cations over cis- and trans-sites in structures of dioctahedral 2 : 1 layer silicates and, in particular, clay minerals. The main structural element of 2 : 1 layer silicates is 2 : 1 layer consisting of octahedral sheet conjugate with tetrahedral sheets on both sides. In general, the octahedral sheet of 2 : 1 layer has three symmetrically independent positions, which differ in the mutual position of hydroxyl groups and oxygen anions. The OH groups are confined to the apexes of body diagonal in trans-octahedra and form shared edge in cis-octahedra. In the dioctahedral layer silicates, cations occupy two of three symmetrically independent octahedral sites, while the third site remains vacant. It was long considered that cations in the dioctahedral layer silicates occupy cis-sites, while trans-octahedra are vacant (*tv*-structures). However, numerous evidence were obtained for the last 40 years for the existence of dioctahedral 2 : 1 layer silicates, in octahedral sheets of which one of two symmetrically independent cis-positions (*cv*-structures) is vacant (Fig. 3). In addition, examples of the existence of *tv*- and *cv*-layers were found in structures of the mixed layer illite-smectite minerals (see review in (Drits and Zviagina, 2009) and references therein).

Thus, the identification of cis- and trans-vacant layers is required for the comprehensive study of structures of clay minerals. The structural features, methods of identification, as well as factors affecting the abundance of cis-vacant and trans-vacant layer silicates are described in detail in (Drits et al., 2006; Drits and Zviagina, 2009).

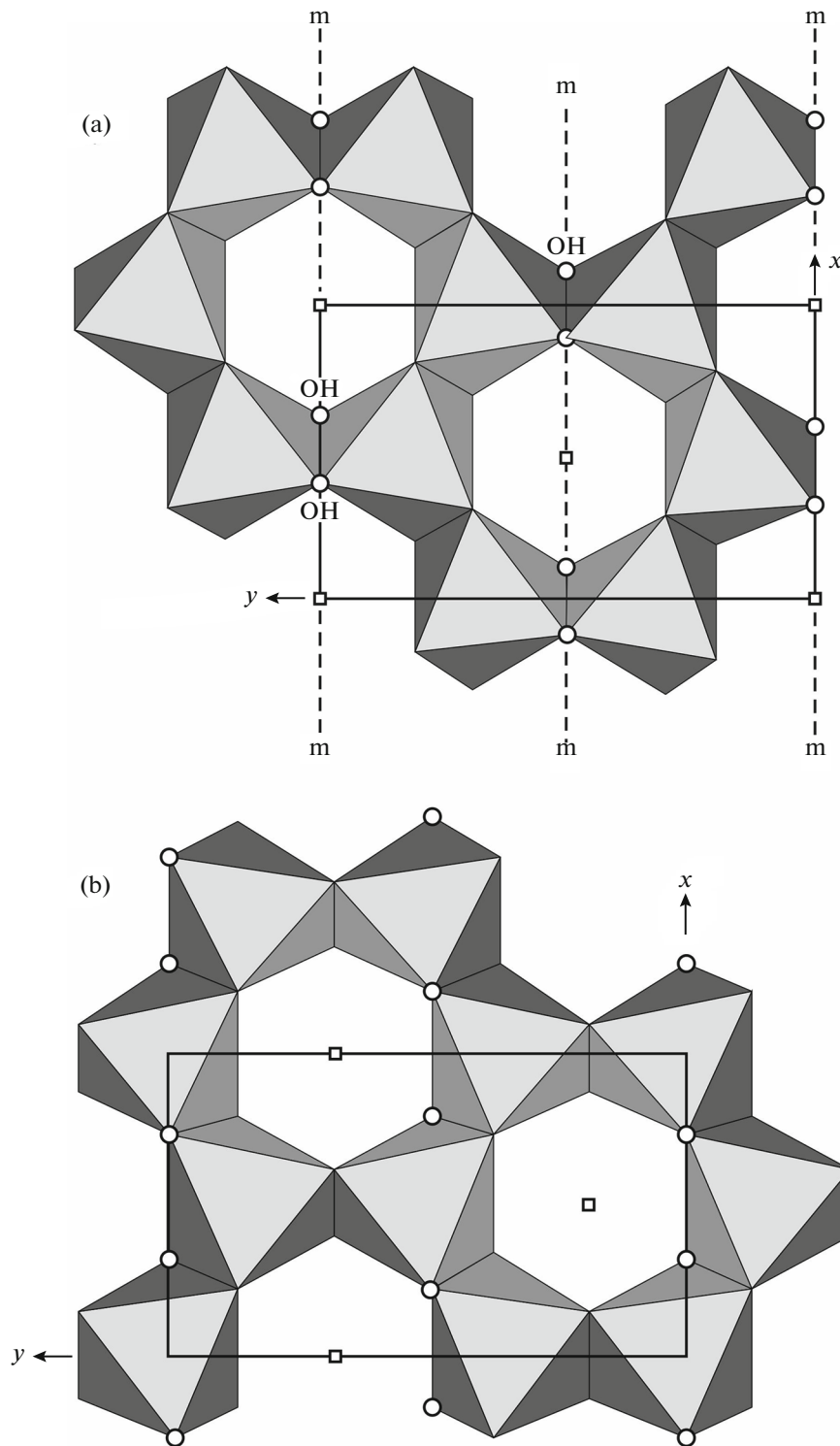
Several modern diffraction and nondiffraction methods were developed to quantify and qualify the *tv*- and *cv*-layers in the dioctahedral 2 : 1 layer silicates and clay minerals. Diffraction methods include: 1) comparison of the experimental powder XRD patterns with those calculated for different mica polytypes consisting of *tv*- or *cv*-layers; 2) the modeling of experimental XRD patterns of illites or illite fundamental

particles, in which *tv*- and *cv*-layers are alternated; and 3) semiquantitative determination of relative contents of *tv*- and *cv*-layers in the mixed-layer structures based on the generalized Mering rules (Drits and McCarty, 1996). Simple and efficient nondiffraction method for the identification of *tv*- and *cv*-layers using thermogravimetric analysis is based on the difference in dehydroxylation temperatures of *tv*- and *cv*-layers of illites and smectites (Drits et al., 1998; Drits, 2003).

In order to reveal the structural and crystal-chemical factors facilitating the formation of *cv*- or *tv*-layers, we carried out the detailed crystal-chemical analysis of several available data on the dioctahedral micaceous minerals containing *cv*- and *tv*-layers (Drits et al., 1996). It was shown that illites—finely dispersed high-Al micaceous minerals—are characterized by different forms of the existence of *cv*-layers. In particular, *cv*-1M illites can be formed as monomineral phases or in association with *tv*-1M and 2M<sub>1</sub> illites. This is consistent with data on the unit cell parameters and, in particular, monoclinic angle and value of interlayer displacement  $c \cos \beta / a$ . The last value is close to  $-0.4$  in *tv*-1M structures and to  $-0.3$  in *cv*-structures, which is an important criterion for the identification of these varieties. In addition, there are illites with alternating *cv*- and *tv*-layers, and diffraction effects in such mixed layer structures average the value of interlayer displacement according to the content of *cv*- and *tv*-layers.

It was shown that the distribution of octahedral cations over cis- and trans-sites in the dioctahedral micaceous minerals is controlled by composition. In particular, micas with high Fe and Mg contents (celadonites, glauconites, aluminoceladonites, and the majority of phengites) always have *tv*-structure. Muscovites also are trans-vacant. Illites with the Al cation content in the octahedra, tetrahedra, and total Al content, respectively, less than 1.55, 0.35, and 1.95 atoms per O<sub>10</sub>(OH)<sub>2</sub> are dominated by *tv*-layers; if the indicated parameters exceed the corresponding values, illites can be formed with practically any proportions of *cv*- and *tv*-layers. Thus, the formation of *tv*-illites in general does not depend on the cation composition of 2 : 1 layers. In contrast, the relative content of *cv*- and *tv*-layers depends on the Al content in the octahedral and tetrahedral sheets of 2 : 1 layers. Moreover, some experimental data indicate that under the lower-temperature diagenetic and hydrothermal conditions, *cv*-1M illite with high Al content can be more stable than *tv*-variety of the same composition.

The major structural factors responsible for the stability of *cv*-1M illite are as follows: 1) the high content of Al cations in tetrahedra and octahedra; 2) insignificant differences in the individual K–O distances in an interlayer; and 3) minimization of the repulsion of basal oxygen atoms. On the other hand, the asymmetric structure of octahedral sheet in *cv*-structure likely causes a decrease of the stability of *cv*-micaceous 1M



**Fig. 3.** Fragments of trans- (a) and cis-vacant (b) octahedral sheets of 2 : 1 layer in projection on ab plane. Circles and boxes designate, respectively, OH group and vacant octahedral positions; m is the mirror planes (modified from (Drits et al., 2006)).

minerals. In contrast, the symmetric structure of 2 : 1 layers facilitates the formation of *tv*-illite in spite of the less stable configuration of interlayer.

The obtained results indicate that reacting fluids with high Al content and low Fe content are required

to form *cv*-1M illites. In particular, *cv*-illites or association of *cv*- and *tv*-1M illites can be formed by hydrothermal alterations in the area of ore deposits. These deposits are formed in two stages: 1) intense leaching by acid solutions and formation of high-Al kaolinite,

dickite, pyrophyllite; and 2) formation of ore deposit and illitization of Al-rich minerals.

Thus, it can be concluded that the formation of monomineral *cv*-1M illite, its association with *tv*-1M illite and mixed-layer 1M illite with *tv*- and *cv*-layers are usually related to the hydrothermal activity of different nature. Starting material with high Al content and hydrothermal fluids with low Mg and Fe contents are required to form these minerals. Micaceous minerals containing *cv*-layers occur mainly in the areas of ore deposits, bentonites, and sandstones.

The formation of *tv*- and *cv*-layers in smectites is related to the cation composition of layers and local order–disorder in the distribution of isomorphous cations. The *tv*- and *cv*-smectites of volcanic origin differ in the composition and distribution of octahedral cations. The *cv*-smectites with high content of Mg cations show random distribution of isomorphous octahedral cations, whereas Mg cations in the Mg-bearing *tv*-smectites are distributed in such a way to reach the minimum content of Mg–OH–Mg configurations.

#### *Structural Mechanism of the Transformation of Illite-Tobelite-Smectites in Cambrian Shales*

Previously obtained data (Lindgreen et al., 2000) suggest that the I-T-S phases of the second group were formed through the transformation of low-illite phase in samples of the first group. Therefore, the new mica layers are formed only through the involvement of NH<sub>4</sub> cations in the former smectite interlayers. Thus, structural mechanism of the transformation of low-illite phase is solid-phase process, when smectite layers are transformed into tobelite ones owing to increasing Si substitution for Al in the corresponding tetrahedral sheets and NH<sub>4</sub> fixation in interlayers. In addition, cis-vacant 2 : 1 layers adjacent to the transformed smectite interlayers become trans-vacant. This structural rearrangement can be accompanied by the reorganization of tetrahedral *cv* sheets of 2 : 1 layers, which provides not only the redistribution of cations over the trans- and cis-octahedra, but also the acquisition of new azimuthal orientation of the newly formed *tv* sheets in 2 : 1 layers, or the same orientation as in adjacent layers or rotated relative to the latter at ±120°. Such mutual position of layers provides the octahedral coordination of interlayer cations, which is more stable compared to the prismatic coordination forming through mutual rotations of adjacent layers at angles divisible by (2*n* + 1)60°. The solid-phase transformation of the mixed-layer I-S into I-T-S is confirmed by the data of atomic force microscopy. Analysis of particles of samples of the first and second groups did not reveal any significant difference in their size and morphology.

Thus, the structural mechanism responsible for the formation of NH<sub>4</sub>-bearing mixed-layer minerals, both in Upper Jurassic shales of the North Sea and in Cam-

brian shales of the Baltic Basin, is the solid-phase transformation. However, there are some differences. All I-T-S-V samples from the North Sea consist of *tv* 2 : 1 layers regardless of their ability to swelling. Hence, the I-S-V transformation into I-T-S-V in the Upper Jurassic shales occurred without changes in the distribution of octahedral cations and can be described as a solid-phase transformation of smectite interlayers within crystallites. In contrast, the transition from I-S to I-T-S phase in the Cambrian shales is accompanied by the transformation of *cv* 2 : 1 layers into *tv* 2 : 1 layer in the same volume of crystallite. This difference likely reflects the different origin of these clays: IS of the North Sea were formed from the weathered illite, whereas the Cambrian I-S phase was formed from smectite of volcanic origin.

#### I-T-S AND I-T-S-V MIXED-LAYER INDICATOR MINERALS OF OIL-SOURCE ROCKS IN SEDIMENTARY BASINS

The detailed structural study of mixed-layer minerals from the Jurassic North Sea and Middle Cambrian Baltic shales shows that the oil formation in oil-source rocks is accompanied by smectite tobelitization, while the presence of I-T-S or I-T-S-V in sedimentary rocks can be considered as an independent evidence for the formation of oil even after its migration or thermal decomposition.

#### FUNDING

The studies were performed under the government-financed task of the Geological Institute, Russian Academy of Sciences.

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

#### REFERENCES

- Arkai, P., Merriman, R.J., Brinley, R., Peacor, D.R., and Toth, M., Crystallinity, crystallite size and lattice strain of illite-muscovite and chlorite; comparison of XRD and TEM data for diagenetic to epizonal pelites, *Eur J. Miner.*, 1996, vol. 8, pp. 1119–1137.
- Brangulis, A.P., Kanev, S.V., Margulis, L.S., and Pomerantseva, R.A., Geology and hydrocarbon prospects of the Paleozoic in the Baltic region, in *Petroleum Geology of North-west Europe: Proceedings of the 4th Conference*, Parker, J.R., Ed., Geol. Soc. London, 1993, pp. 651–656.
- Buchardt, B., Nielsen, A.T., and Schovsbo, N.H., The Alum shale in Scandinavia, *Geol. Tidsskr.*, 1997, vol. 3, pp. 1–30 (in Danish).
- Claret, F., Sakharov, B.A., Drits, V.A., et al., Clay minerals in the Meuse-Haute Marne Underground laboratory (France): Possible influence of organic matter on clay min-

- eral evolution, *Clays Clay Miner.*, 2004, vol. 52, pp. 515–532.
- Drits, V.A., Mixed-layer minerals, in *Modular Aspects of Minerals, European Notes in Mineralogy*, Merlino, S., Ed., Eötvös Univ. Press, Budapest, 1997, vol. 1, pp. 153–190.
- Drits, V.A., Structural and chemical heterogeneity of clay minerals, *Clay Miner.*, 2003, vol. 38, pp. 403–432.
- Drits, V.A. and Kossovskaya, A.G., *Glinistye mineraly: smektity, smeshanosloinye obrazovaniya* (Clay Minerals: Smectites and Mixed-Layer Minerals), Moscow: Nauka, 1990.
- Drits, V.A. and Kossovskaya, A.G., *Glinistye mineraly: slyudy, khlority* (Clay Minerals: Micas and Chlorites), Moscow: Nauka, 1991.
- Drits, V.A. and Sakharov, B.A., *Rentgenostrukturnyi analiz smeshanosloinykh mineralov* (X-Ray Structural Analysis of Mixed-Layer Minerals), Moscow: Nauka, 1976.
- Drits, V.A. and McCarty, D.K., A simple technique for a semi-quantitative determination of the trans-vacant and cis-vacant 2 : 1 layer contents in illites and illite-smectites, *Am. Mineral.*, 1996, vol. 81, pp. 852–863.
- Drits, V.A. and Tchoubar, C., *X-ray diffraction by disordered lamellar structures*, Heldenberg: Springer, 1990.
- Drits, V.A. and Zviagina, B.B., Trans-vacant and cis-vacant 2 : 1 layer silicates: structural features, identification, and occurrence, *Clays Clay Miner.*, 2009, vol. 57, pp. 405–415.
- Drits, V.A., Lindgreen, H., Sakharov, B.A., et al., The detailed structure and origin of clay minerals at the Cretaceous/Tertiary boundary, Stevns Klint (Denmark), *Clay Miner.*, 2004, 39, pp. 367–390.
- Drits, V.A., Lindgreen, H., and Salyn, A.L., Determination by X-ray diffraction of content and distribution of fixed ammonium in illite-smectite: Application to North Sea illite-smectite, *Am. Mineral.*, 1997a, vol. 82, pp. 79–87.
- Drits, V.A., Sakharov, B.A., Lindgreen, H., and Salyn, A., Sequential structural transformation of illite-smectite-vermiculite during diagenesis of Upper Jurassic shales from North Sea and Denmark, *Clay Miner.* 1997b, vol. 32, pp. 351–371.
- Drits, V.A., Lindgreen, H., Salyn, A.L., Ylagan R., and McCarty, D.K., Semiquantitative determination of trans-vacant and cis-vacant 2 : 1 layers in illites and illite-smectites by thermal analysis and X-ray diffraction, *Am. Mineral.*, 1998, vol. 83, pp. 1188–1198.
- Drits, V.A., Lindgreen, H., Sakharov, B.A., et al., Tobelitization of smectite during oil generation in oilsource shales: Application to North Sea illite-tobelite-smectite-vermiculite, *Clays Clay Miner.*, 2002a, vol. 50, pp. 82–98.
- Drits, V.A., Sakharov, B.A., Dainyak, L.G., et al., Structural and chemical heterogeneity of illite-smectites from Upper Jurassic mudstones of East Greenland related to volcanic and weathered parent rocks, *Am. Mineral.* 2002b, vol. 87, pp. 1590–1607.
- Drits, V.A., Sakharov, B.A., Salyn, A.L., and Lindgreen, H., Determination of the content and distribution of fixed ammonium in illite-smectite using a modified X-ray diffraction technique: Application to oil source rocks of western Greenland, *Am. Mineral.*, 2005, vol. 90, pp. 71–84.
- Drits, V.A., Lindgreen, H., Sakharov, B.A., et al., Formation and transformation of mixed-layer minerals by Tertiary intrusives in Cretaceous mudstones, West Greenland, *Clays Clay Miner.*, 2007, vol. 55, pp. 261–284.
- Eugster H.P. and Munoz, J., Ammonium micas: Possible sources of atmospheric ammonia and nitrogen, *Science*, 1966, vol. 151, pp. 683–686.
- Eslinger, E. and Savin, S., Oxygen isotope geothermometry of the burial metamorphic rocks of the Precambrian Belt Supergroup, Glacier National Park, Montana, *Geol. Soc. Am. Bull.*, 1973, vol. 84, pp. 2549–2560.
- Ferrage, E., Lanson, B., Sakharov, B.A., et al., Investigation of dioctahedral smectite hydration properties by modeling of X-ray diffraction profiles: influence of layer charge and charge location, *Am. Mineral.*, 2007, vol. 92, pp. 1731–1743.
- Jensenius, J., Regional studies of fluid inclusions in Paleozoic sediments from southern Scandinavia, *Bull. Geol. Soc. Denmark*, 1987, vol. 36, pp. 221–235.
- Lanson, B., Sakharov, B.A., Claret, F., and Drits, V.A., Diagenetic smectite-to-illite transition in clay-rich sediments: a reappraisal of X-ray diffraction results using the multispecimen method, *Am. J. Sci.*, 2009, vol. 309, pp. 476–516.
- Lindgreen, H., Ammonium fixation during illite-smectite diagenesis in Upper Jurassic shale, North Sea, *Clay Miner.*, 1994, vol. 29, pp. 527–537.
- Lindgreen, H., Drits, V.A., Jakobsen, F.C., and Sakharov, B.A., Clay mineralogy of the Central North Sea Upper Cretaceous Tertiary chalk and formation of clay rich layers, *Clays Clay Miner.*, 2008, vol. 56, pp. 693–710.
- Lindgreen, H., Drits, V.A., Sakharov, B.A., et al., The structure and diagenetic transformation of illite-smectite and chlorite-smectite from North Sea Cretaceous Tertiary chalk, *Clay Miner.*, 2002, vol. 37, pp. 429–450.
- Lindgreen, H., Drits, V.A., Sakharov, B.A., Salyn, A.L., Wrang, P., and Dainyak, L., Illite-smectite structural changes during metamorphism in black Cambrian Alum shales from the Baltic area, *Am. Mineral.*, 2000, vol. 85, pp. 1223–1238.
- McCarty, D.K. and Reynolds, R.C., Rotationally disordered illite/smectite in Paleozoic K-bentonites, *Clays Clay Miner.*, 1995, vol. 43, pp. 271–284.
- McCarty, D.K., Drits, V.A., Sakharov, B.A., et al., Heterogeneous mixed-layer clays from the Cretaceous Greensand, Isle of Wight, Southern England, *Clays Clay Miner.*, 2004, vol. 52, no. 5, pp. 552–575.
- McCarty, D.K., Sakharov, B.A., and Drits, V.A., Early clay diagenesis in Gulf Coast sediments: new insights from XRD profile modeling, *Clays Clay Miner.*, 2008, vol. 56, pp. 359–379.
- McCarty, D.K., Sakharov, B.A., and Drits, V.A., New insights into smectite illitization: a zoned K-bentonite revisited, *Am. Mineral.*, 2009, vol. 94, pp. 1653–1671.
- Moore, D.M. and Reynolds, R.C., Jr., *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*, Oxford: Oxford Univ. Press, 1989.
- Moore, D.M. and Reynolds, R.C., Jr., *X-Ray diffraction and the identification and analysis of clay minerals*, Oxford: Oxford Univ. Press, 1997.
- Sakharov, B.A. and Lanson, B., X-Ray identification of mixed-layer structures, in *Modeling of Diffraction Effects. Chapter 2.3. Handbook of Clay Science, Part B. Techniques and Applications*, Bergaya, F. and Lagaly, G., Eds., Amsterdam: Elsevier, 2013, pp. 51–135.
- Sakharov, B.A., Lindgreen, H., Salyn, A.L., and Drits, V.A., Determination of illite-smectite structures using multispec-

- imen X-Ray diffraction profile fitting, *Clays Clay Miner.*, 1999a, vol. 47, pp. 555–566.
- Sakharov, B.A., Lindgreen, H., Salyn, A.L., and Drits V.A., Mixed-layer kaolinite-illite-vermiculite in North Sea shales, *Clay Miner.*, 1999b, vol. 34, pp. 333–344.
- Sakharov, B.A., Plancon, A., Lanson, B., Drits, V.A., Influence of the outer surface layers of crystals on the X-ray diffraction intensity of basal reflections, *Clays Clay Miner.*, 2004, vol. 52, pp. 680–692.
- Shutov, V.D., Drits, V.A., and Sakharov, B.A., On the mechanism of a postsedimentary transformation of montmorillonite into hydromica, *Proc. Int. Clay Conf.*, Heller, L., Ed., Tokyo, 1969a, vol. 1, pp. 523–532.
- Shutov, V.D., Drits, V.A., and Sakharov, B.A., On the mechanism of a postsedimentary transformation of montmorillonite into hydromica: Discussion, *Proc. Int. Clay Conf.*, Heller, L., Ed., Tokyo, 1969b, vol. 2, pp. 126–129.
- Thomsen, E., Lindgreen, H., and Wrang, P., Investigation on the source rock potential of Denmark, *Geol. Mijnbouw.*, 1983, vol. 62, pp. 221–239.
- Vejbæk, O.V., Stouge, S., and Poulsen, K.D., *Palaeozoic tectonics and sedimentary evolution and hydrocarbon prospectivity in the Bornholm area*, *Geol. Surv. Denmark, Ser. A*, 1994, vol. 34, 23 p.
- Wrang, P., Source rock scanning of Lower Paleozoic deposits from Denmark and Sweden, *Geol. Surv. Denmark, Report*, 1983, 69 p.

*Translated by M. Bogina*