

STRUCTURE OF VERMICULITE MODIFIED BY ORGANIC MOLECULES

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Intercalation of vermiculites by organic molecules is connected with an expansion of the structure in the direction vertical to the layers. Rate of expansion depends on the length of intercalated molecules, on their arrangement in an interlayer space and also on their concentration and reaction time. Natural Mg-vermiculite from Letovice location in the Czech Republic (VER-L) with the mean particle diameters equal to 194 μm and coarse grained Mg-vermiculite from Santa Olalla location in Spain (VER-S) with size of flakes up to 5 mm were used as hosts for intercalation. Three organic molecules with different length of chains were used as intercalants: octadecylamine, dodecylamine, octylamine. Intercalation was carried out by low temperature heating procedure at the temperature of 80 °C lasting 24 hours. Molar ratio of vermiculites to organic molecules was 1:6 in all samples. The XRD patterns of all intercalated samples exhibit significant changes in comparison with the patterns of non-treated vermiculites. The patterns of vermiculites intercalated by octadecylamine molecules (18 C atoms) contain the integral set of basal diffractions with d -spacings 58.4 Å, 29.3 Å, 19.5 Å for VER-L or 51.9 Å, 25.6 Å, 17.2 Å for VER-S respectively. The differences in d -spacings depend on the size of flakes. Intercalation by dodecylamine (12 C atoms) was nearly the same with both vermiculites and XRD pattern contains the set of basal diffractions 38.7 Å, 19.7 Å, 13.6 Å. The result of intercalation by octylamine (8 C atoms) is not very significant. Just one basal diffraction value namely 19.7 Å for VER-L and 24.7 Å for VER-S was recorded. The surface of VER-S flakes after intercalation was observed using atomic force microscopy technique. Nano-layers of organic molecules chains grafted during the intercalation process were found on the surface. The graft does not cover the whole surface of flakes homogenously creating the irregular net of chains with different widths. Their shape and position is influenced either by distribution of electric charge on the surface or by surface folding caused by partial dehydration of Mg-vermiculite at the temperature of 80 °C.

KEYWORDS: vermiculite, intercalation, basal diffraction, organic molecules**1. INTRODUCTION**

Many phenomena such as cation adsorption, desorption and intercalation depend highly on the physical and chemical behaviour of mineral surfaces. In consequence, to understand this behaviour, the knowledge of the structure and microtopography of mineral surfaces is particularly important. The adsorption of organic substances on phyllosilicates has been studied extensively in several areas of research (colloid science, soil science, sedimentary geology and petroleum technology, environmental science).

The intercalation of organic species into the interlayer space of smectites and vermiculites has been studied extensively because the resulting intercalates have interesting properties and are useful for many industrial applications. Organic species can be introduced into the interlayer space as neutral molecules or as cations.

Vermiculite is a 2:1 phyllosilicate, similar in appearance to mica. The interlayer space is occupied by hydrated exchangeable cations. The interlayer material takes the form of an incomplete octahedral

sheet, similar to the interlayer sheet in chlorite. Layers 2:1 are trioctahedral and Mg represents the dominant octahedral cation. Layer 2:1 with interlayer net creates characteristic structural motif with interlayer distance which equals approximately 14 Å. The structure of vermiculite calculated from the data of Shirozu and Bailey (1966) is presented in Fig. 1.

Vermiculite originates from mica or from chlorite usually by alteration and weathering. Flakes of natural vermiculite have mica-like appearance. Vermiculite undergoes expansion when heated. When the flakes are heated to the temperature of 700 up to 900 °C water from the structure evaporates. The flakes expand forming "worm-like" macrostructures and loss of interlayer water molecules during the heating leads to the collapse of the structure. The interlayer distance decreases from 14.23 Å down to 9.31 Å. After heating the re-hydration takes place and the structure of vermiculites comes back to the original value of interlayer distance, but the ability of re-hydration is influenced by the temperature to which vermiculite was heated. After exceeding a certain temperature the changes in the structure are irreversible. Because of its

Table 1 Considered host minerals, guests intercalates and reaction times for each mixture

Host	Mass [g]	Guest	Mass [g]	Heating time [hrs]
VER-L	0.33	ODA	1.09	24
VER-L	0.33	DDA	0.75	24
VER-L	0.33	OA	0.52	54
VER-S	0.33	ODA	1.09	74
VER-S	0.33	DDA	0.75	24
VER-S	0.33	OA	0.52	54

very low bulk density in its expanded form, it is used as lightweight aggregate and thermal and acoustical insulator.

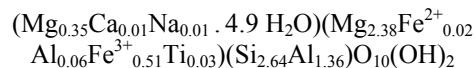
As modified forms we consider the vermiculites where the original structure in its interlayer space is modified e.g. by cation exchange or by intercalation of organic molecules.

The intercalation of vermiculites with organic substances is followed by expansion of the structure in the direction vertical to the layers. The expansion rate depends on the length of the chain of intercalated molecules, on their arrangement in the interlayer, and also on their concentration and reaction time (Weiss et al., 2003). The high rate of expansion is observed when vermiculite is intercalated by octadecylamine (ODA). Brindley (1965) calculated the interlayer distance and the angle of the inclination of intercalated molecules for amines with different carbon chain length. The molecules with six to sixteen carbon atoms in a chain provided good agreement between estimated and observed distances of interlayer space. The basic method to determine the quality of intercalation and the structure of a final intercalate is X-ray diffraction which is suitably supplemented by computer molecular modeling in works of Weiss et al. (2003), Pospíšil et al. (2003).

The aim of our work was to prepare the vermiculites intercalated by molecules of amines with different chain lengths by the method of low-temperature heating and to consider the quality of intercalations by comparison of XRD records with calculated values of basal spacings. The analysis of the vermiculite flake surface after reaction was carried out with the help of atomic force microscopy method (AFM).

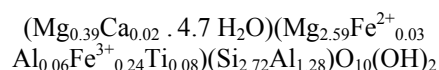
2. EXPERIMENTAL DETAILS

As a host for intercalation two samples of natural Mg-vermiculites from different localities with different size of flakes were used. Mg-vermiculite marked for the experiment as VER-L comes from the Czech Republic, locality Letovice. The structure formula was determined by Weiss et al. (1994):



The average size of the vermiculite particles was 194.4 μm . From Spain, locality Santa Olalla, a very

coarse grained Mg-vermiculite marked as VER-S was used. The structure formula was determined by de la Calle et al. (1988):



As intercalated guests three organic substances with various carbon chain lengths were used:

Octadecylamine (ODA)	$\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$
Dodecylamine (DDA)	$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$
Octylamine (OA)	$\text{CH}_3(\text{CH}_2)_7\text{NH}_2$

The molar ratio of host mineral to guest molecule was 1:6 in all samples. The intercalation was carried out by method of low temperature heating at the temperature of 80 °C. The reaction time was 24, 54, 74 hours, as stated in the Table 1.

X-ray powder diffraction patterns of intercalates were obtained using diffractometer INEL equipped with the curved position-sensitive detector. Samples were examined after cooling and exposed under the same experimental conditions. The surface of microflakes selected after intercalation of VER-L and VER-S with ODA was investigated by AFM method using AFM-Explorer from ThermoMicroscopes company at the contact mode with 8 μm Z-linearized dry scanner, silicon probe 1520-00.

3. RESULTS AND DISCUSSION

As observed in Fig. 2, the comparison of X-ray diffractograms shows changes in the values of interlayer distances d_{001} implying that the rate of the structure expansion depends on the lengths of amine molecule chain (with a higher number of carbon atoms in the chain the interlayer distance increases) and also on the size of intercalated flakes. Better results for intercalation with octadecylamine (ODA) were obtained in case of the fine grained Mg-vermiculite from Letovice. Basal spacing of intercalated Mg-vermiculite calculated by Brindley (1965) for 18 carbon atoms in the chain is 54.81 Å. Observed d-value of the first basal reflection obtained from XRD analysis of intercalated Mg-vermiculite samples with octadecylamine (ODA) was 58.4 Å for VER-L and 51.9 Å for VER-S. The intercalation by dodecylamine (12 carbon atoms) was the same in both samples and showed good agreement with calculated d_{001} values.

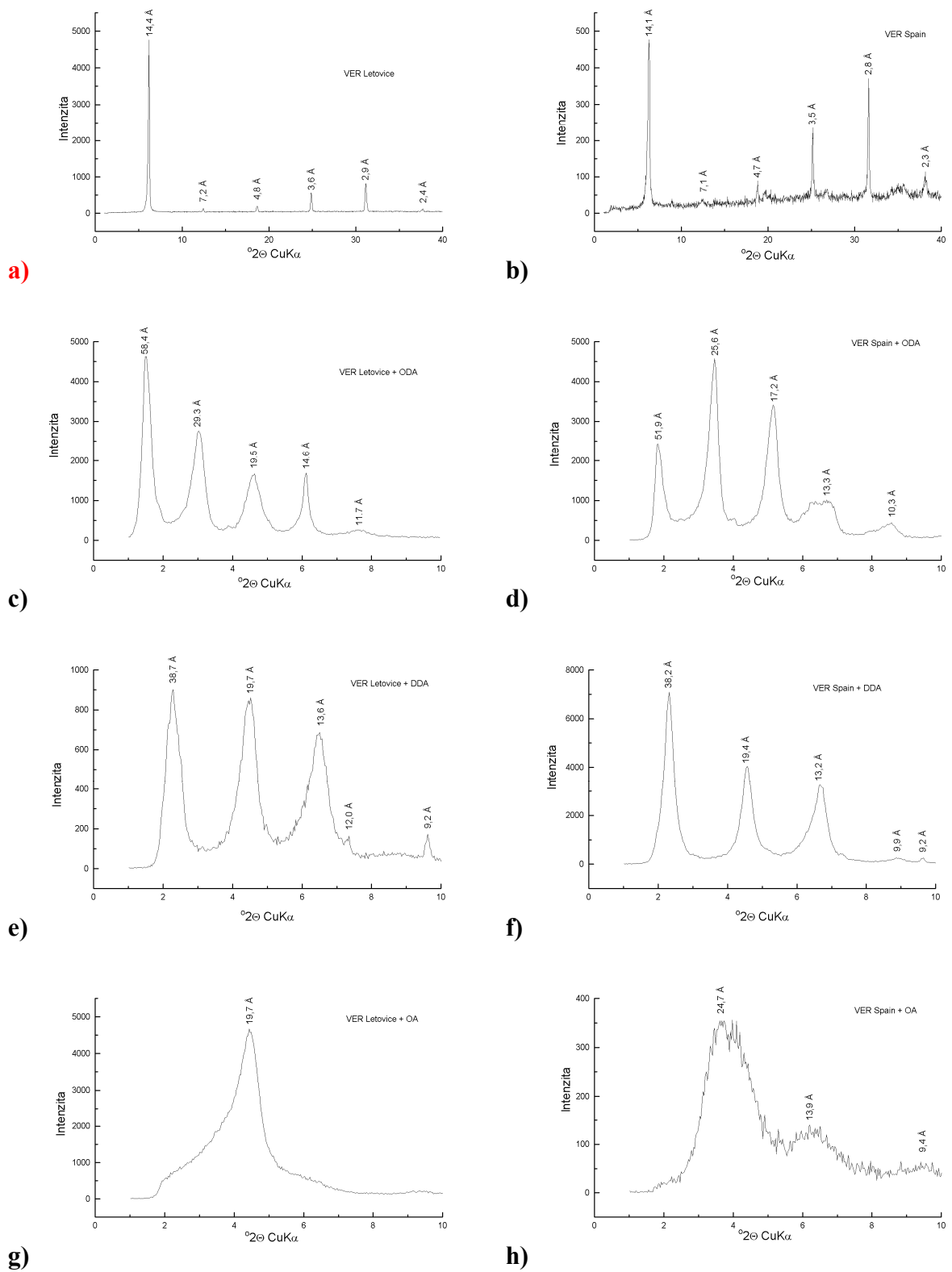


Fig. 2 X-ray diffractograms of Mg-vermiculites from Letovice and Santa Olalla localities intercalated by alcyamine molecules: octadecylamine (ODA), dodecylamine (DDA), octylamine (OA) with 1:6 molar ratio.

Basal spacing calculated for 12 carbon atoms in the chain was 41.09 Å. Observed d-value of the first basal diffraction of intercalated Mg-vermiculite samples with dodecylamine (DDA) was 38.7 Å for VER-L and 38.2 Å for VER-S. The result of the intercalation by octylamine (OA) is not very evident. Only one basal diffraction was recorded in the diagram. We suggest that the experiment should be repeated with a longer reaction time. Basal spacing calculated for 8 carbon atoms in the chain was 31.93 Å. Observed d-value of the first basal reflection of Mg-vermiculite samples intercalated with octylamine (OA) was 19.7 Å for VER-L and 24.7 Å for VER-S. In any event the reaction in this case was incomplete, consistent with the comparison of experimental and calculated values shown in Fig. 3.

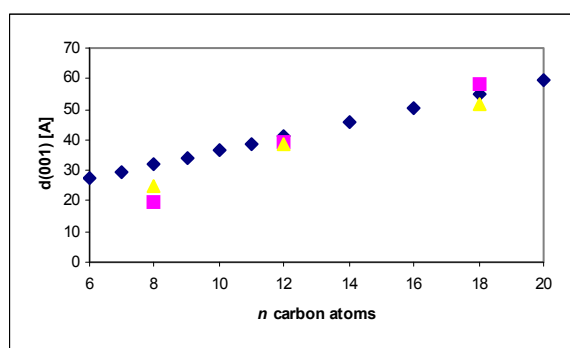


Fig. 3 The calculated interlayer distances of Mg-vermiculite intercalated by amine molecules at the increasing number of carbons from 6 to 20 (marked with lozenges) (Brindley, 1965).

Obtained values of interlayer distances of Mg-vermiculites from Letovice locality are marked with squares and those from Santa Olalla with triangles.

Flakes from the samples VER-L and VER-S intercalated by octadecylamine were selected and their surface was observed using the AFM method, in contact regime with the use of 8 µm dry scanner. The flakes were stuck on an adhesion tape and their surface layer was stripped. Layers and chains of octadecylamine on the surface of the flakes were found grafted during the intercalation reaction. The example of AFM image of ODA chain on the Mg-vermiculite surface is shown in Fig. 4. The graft of ODA does not cover the Mg-vermiculite surface homogeneously in the form of a nano-layer but it forms numerous nets of channels with different widths. These channels were used to measure the height of ODA grafts.

The height of the ODA graft varies from 8.06 nm to 12.87 nm (see Fig. 5) as found out through analysis of profiles from different parts of a flake. The width of channels among grafted chains varies from 2.1 nm to 153.4 nm. Nevertheless, there are also some homogenous surfaces covering the Mg-vermiculites as seen, e.g. a nano-layer of the size of 700 x 700 nm.

Similar grafted layers and channels were observed also on the surface of VER-S flakes intercalated by octadecylamine, but their size and shape are slightly different as seen in Fig. 6. The height of ODA graft reaches around 30 nm.

Distance	Difference of heights
1	0.200 µm 8.06 nm
2	0.289 µm 10.31 nm
3	0.334 µm 8.34 nm
4	0.523 µm 12.87 nm

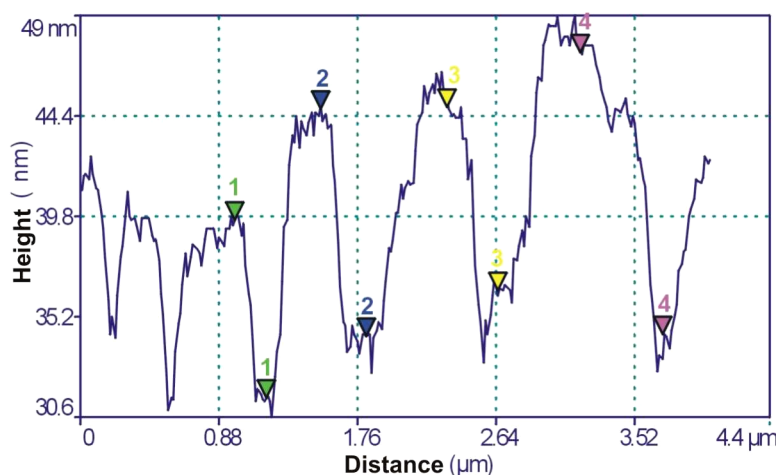


Fig. 5 The profile measurement of ODA nano-layer on the Mg-vermiculite VER-L flake surface (contact method, 8 µm dry scanner, range 10 µm x 10 µm in horizontal direction).

Shapes and positions of the ODA graft channels on the surface might be influenced by either a different distribution of the electric charge on the Mg-vermiculite surface or by a corrugation of surface in nano-scale. Partial dehydration of Mg-vermiculites takes place even at low temperature of 80 °C being accompanied not only by partial collapse of interlayer structure, when the value of interlayer distance decreases from 14.35 Å down to 13.8 Å (Weiss et al., 1994), but also by an irreversible corrugation of Mg-vermiculites surface, as observed on the surface of the flake exposed to the temperature of 80 °C (Fig. 7).

4. CONCLUSIONS

The intercalation of Mg-vermiculite VER-L by molecules of octadecylamine differs from the value stated by Brindley (1965), but shows the accordance with the values published by Weiss et al. (2003). The intercalation of Mg-vermiculite VER-S by molecules of octadecylamine was influenced by size of flakes. However, this was not evident at both samples if intercalated by dodecylamine. Both samples prove nearly the same values of basal diffractions (38.7 Å for VER-L and 38.2 Å for VER-S).

Using AFM method, apparent grafted nano-layers of ODA chains around 9.9 nm (VER-L) or 30 nm (VER-S) wide were found on the surfaces of thin micro-flakes selected from the intercalated coarse-grained sample. Grafted ODA chains create not only homogeneous nano-layers on the surface but also channels with different widths. We suggest that the existence of channels with various shapes and positions is caused by nano-scale corrugation of the surface and by irregular distribution of the electric charge on the surface. If the surface of a flake is not corrugated, it might be covered by octadecylamine homogeneously.

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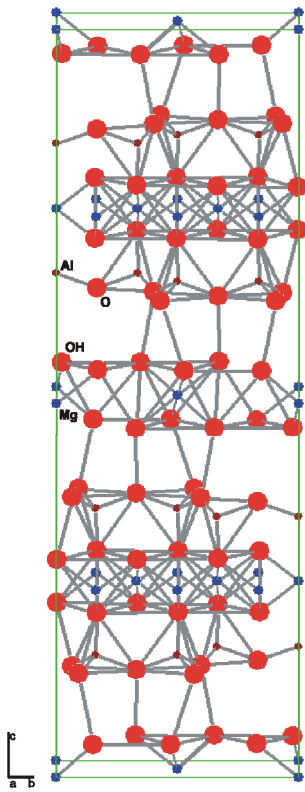


Fig. 1 [100] projection of the structure of vermiculite. The structure was calculated from the data of Shirozu and Bailey (1966) with PowderCell program.

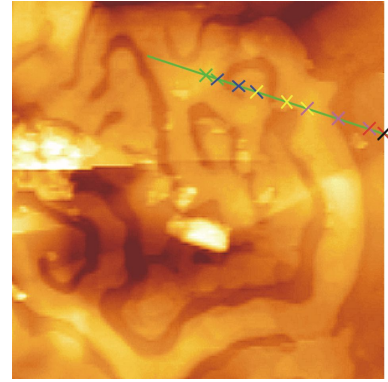


Fig. 4 AFM image of ODA nano-layer on the Mg-vermiculite VER-L flake surface (contact method, 8 μm dry scanner), range 10 μm x 10 μm in horizontal direction. The line represents the direction of profile measurement shown in Fig. 5.

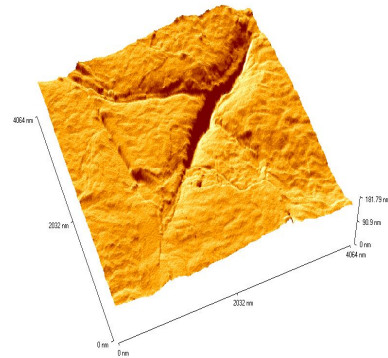


Fig. 7 3D AFM image of Mg-vermiculite surface exposed to the temperature 80°C, (contact method, 8 μm dry scanner), range 4.06 μm x 4.06 μm in horizontal direction.

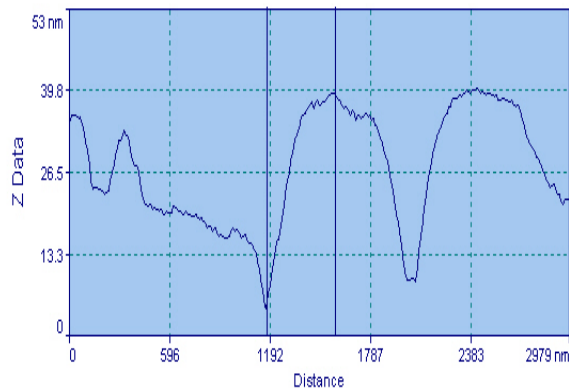
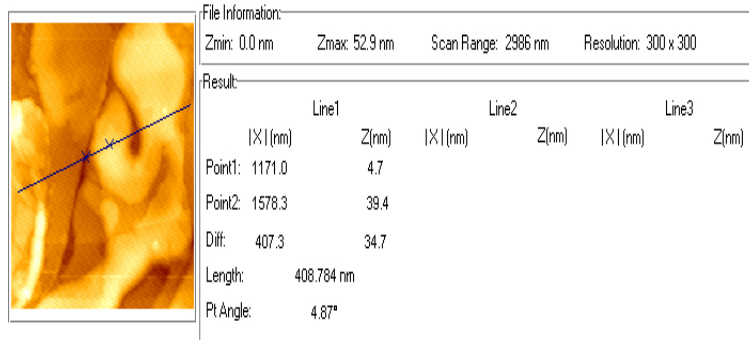


Fig. 6 The profile measurement of ODA nano-layer on the Mg-vermiculite VER-S flake surface (contact method, 8 μm dry scanner), range 2.9 μm x 2.9 μm in horizontal direction.