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## ORIGIN AND DISTRIBUTION OF CLAYS RESULTING FROM ALTERATION OF RHYOLITE VOLCANIC ROCKS IN CENTRAL SLOVAKIA (CZECHOSLOVAKIA)

(Figs. 3)



**Abstract:** In the area under study, rhyolites and Upper Sarmatian-Pannonian rhyolite tuffs altered into clay minerals and zeolites. Four mineral assemblages have been distinguished by the mineralogical study: 1. MONTMORILLONITE  $\pm$  kaolinite and cristobalite; 2. KAOLINITE  $\pm$  montmorillonite, halloysite and cristobalite; 3. MIXED-LAYER MINERAL ILLITE-MONTMORILLONITE  $\pm$  kaolinite; 4. ZEOLITE comprising clinoptilolite and morденite  $\pm$  kaolinite, montmorillonite and cristobalite. The mineral assemblages resulted from combined endogenous and exogenous processes.

Distribution of the above mentioned mineral assemblages shows a tendency to zonal ordering. In the inner zone are clays containing mixed-layer mineral illite-montmorillonite with a variable admixture of kaolinite. The outer zone is formed by montmorillonite (bentonite) with admixture of kaolinite and cristobalite.

**Резюме:** В рассматриваемой области риолиты и риолитовые туфы верхнего сарматско-панонского возраста изменились в глинистые минералы и цеолиты. Минералогическим исследованием были выделены четыре минеральные ассоциации: 1) Монтмориллонит  $\pm$  каолинит и кристобалит; 2) Каолинит  $\pm$  монтмориллонит, галлуазит и кристобалит; 3) смешаннопластовый минеральный иллит-монтмориллонит  $\pm$  каолинит; 4) цеолит содержащий клиноптилолит и морденит  $\pm$  каолинит, монтмориллонит и кристобалит. Минеральные ассоциации следуют из комбинированных эндогенных и экзогенных процессов.

Распределение вышеупомянутых минеральных ассоциаций доказывает тенденцию к зональной последовательности. В внутренней зоне глины содержат смешаннопластовый минеральный иллит-монтмориллонит с изменчивой примесью каолинита. Внешняя зона формирована монтмориллонитом (бентонит) с примесью каолинита и кристобалита.

### Introduction

In the West Carpathians the Upper Sarmatian-Pannonian acid rhyolite volcanism is forming in the Central-Slovakian neovolcanic region the SW margin of the Kremnické vrchy Mts. Among many petrographical varieties a comparatively most intense alteration affects rhyolites with hyaline matrix. Rhyolite volcanism is highly explosive and results in extensive volcanoclastic complexes

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of tuffs, tuffobreccias and tuffites. In contrast to rhyolites, alteration of volcanoclastic rocks is far more extensive.

Altered products of rhyolite volcanism were studied in a N–S belt over a length of 7.5 km and approximately 20 sqkms area. (Fig. 1). The altered products are on the southern periphery of the hydrothermal vein deposit of Au-Ag-Sb ores Kremnica. The deposit had been exploited intensively more than 700 years.

### *Mineral composition*

Semiquantitative X-ray analysis was the main method applied in mineralogical studies. Our classification of alterations is based upon mineral assemblages. A mineral assemblage means a common occurrence of minerals

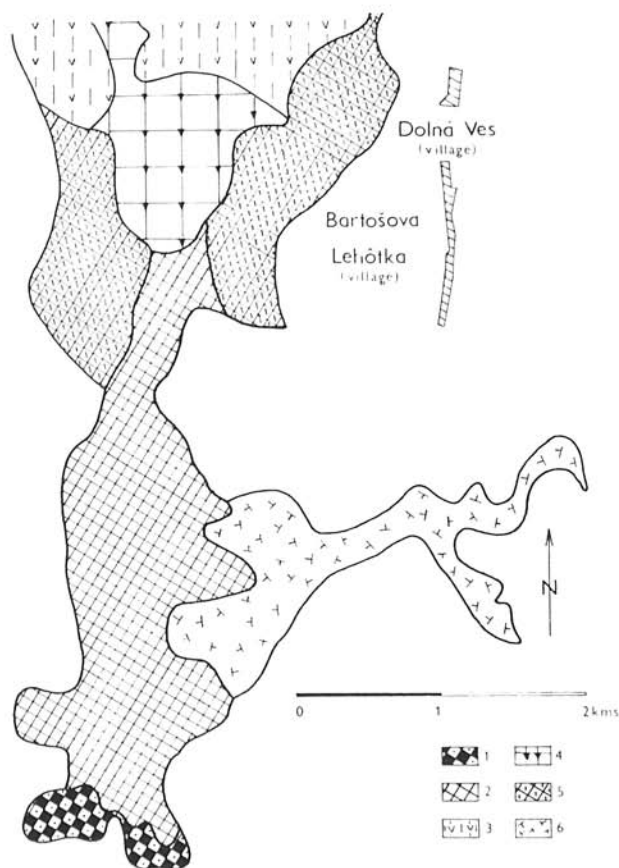


Fig. 1. Scheme of distribution of mineral assemblages on SW periphery of Kremnické vrchy Mts. 1 – monomineral bentonite; 2 – bentonite with admixture of kaolinite and cristobalite; 3 – kaolinized rhyolite; 4 – mixed-layer mineral illite-montmorillonite; 5 – kaolinite-montmorillonite clays; 6 – zeolite tuffs.

in altered rocks in situ. In the most frequent montmorillonite mineral assemblage, three types can be distinguished:

Monomineral bentonite contains among clay minerals only montmorillonite without cristobalite admixture. It resulted from alteration of rhyolite tuffs with vitroclastic texture and form the southern part of the area studied. (Fig. 1). (The exploited deposit Jelšovský potok). Montmorillonite of Jelšovský potok may be characterized by the following average crystallochemical formulae:

$(\text{Si}_{7.6} \text{Al}_{0.4}) (\text{Al}_3 \text{Fe}_{0.35} \text{Mg}_{0.65}) (\text{Ca}_{0.5} \text{O}_{20}(\text{OH})_4$ . The montmorillonite content in bentonite is variable and depends upon the degree of alteration of the parent rock. As a rule, it is not lower than 70 %.

Bentonite with admixture of kaolinite and cristobalite results from alteration of rhyolite tuffs with vitroclastic texture. It is most frequent in the area studied. (Fig. 1). The kaolinite admixture is not greater than 30–35 % and cristobalite does not exceed 15–20 %. Kaolinite content in this type of bentonite increases from south to north.

Montmorillonitized rhyolite form the southern part of the area under study. It is characterized by a comparatively low degree of alteration and shows no character of bentonite.

Kaolinite mineral assemblage results mostly from alteration of rhyolites. Kaolinized rhyolites form a continuous belt in the northern part of the area studied (Fig. 1). The matrix underwent silicification and alteration to clay minerals. In parts affected by intense alteration are adularia, sporadical antimonite and cinnabar. Kaolinite is a dominant clay mineral. Montmorillonite appears regularly as admixture and its content decreases with depth. Admixture of dehydrated halloysite is occasionally present. Kraus and Horváth (1978) confirmed that kaolinite is characterized by well ordered structure.

Kaolinite-montmorillonite clays have kaolinite and montmorillonite mineral assemblages in approximately equal proportion. They are formed from rhyolite tuffs, rarely of rhyolites. This type of clays has been found on the western and eastern margins of mixed-layer mineral illite-montmorillonite. (Fig. 1).

Mixed-layer mineral illite-montmorillonite assemblage is associated with alteration of pumiceous rhyolite tuffs affected at the same time by intense silicification. Among other clay minerals, kaolinite is sometimes present. Lower parts are locally impregnated by pyrite and marcasite.

In mixed-layer mineral illite-montmorillonite only nonswelling (illite) layers (10 Å) and swelling (montmorillonite) layers (16.8 Å) were determined in samples saturated with ethylenglycol. The amount of 10 Å layers vary in analyzed samples between 50 and 80 %. Materials with similar mineralogical composition are known from Füzérradvány area (Hungary). Their crystallochemical characteristic according to Némecz and Varjú (1970) is given in Fig. 2.

In accordance with changes of mineralogical composition vary the chemical composition of samples especially the K/Ca ratio. The total charge per unit structure as calculated from formal crystallochemical formulae increases from 0.96 to 1.30 elementary charges per unit cell. Charge density on the illite (10 Å) layers vary between 1.45 and 1.64 elementary charges per unit cell. Hower and Mowatt (1966) have demonstrated that layer charge of illite layers

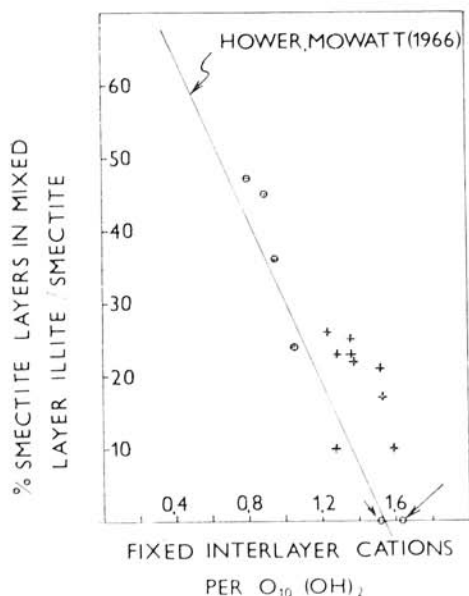


Fig. 2. Percent montmorillonite layers in mixed-layer illite-montmorillonite vs. number of fixed cations in illite layers (from Hower and Mowatt, 1966). ○ present paper, + hydromuscovite from Kremnica (Böhmer et al., 1969), illite, Petrovka (Novák and Vtělen-ský, 1960), + samples from Füzérrad-vány, Hungary (Nemecz and Varju, 1970).

(10 Å) is 1.5 elementary charges per unit cell. Eberl (1980) has found the layer charge necessary for potassium dehydration equal to 1.54 elementary charges per unit cell. The presented samples show the charge densities on illite layers (10 Å) narrowly clustered around this value. Fixed interlayer cations calculated from crystallochemical formulae for presented samples fit reasonably in the plot published by Hower and Mowatt (1966). (Fig. 2).

Zeolites are associated with the alteration of rhyolite tuffs with a typical greenish colour, and only scarcely with alteration of rhyolites. Zeolites are in continuous belt of approximately W – E direction, running across a zone along which the products of rhyolite volcanism alter into clay minerals. (Fig. 1). X-ray analysis and scanning electron microscope showed mordenite and clinoptilolite in an assemblage with clay minerals (montmorillonite, kaolinite) and cristobalite. The content of zeolites ranges from several percent to almost 90 %, in dependence upon the structure of tuffs.

#### *Origin of altered products of rhyolite volcanism*

Monomineral bentonites resulted from alteration of rhyolite tuffs in aqueous environment of a lacustrine basin. Rhyolite tuffs alternate repeatedly with silicite beds resulting from low-thermal activity during rhyolite volcanism. In this area silicites are denoted as limnoquartzites. They formed when alkalic solutions with high  $[SiO_2]_n$  content entered a lacustrine basin with a low pH value, where peat formed. In this process the alkalic solutions with high  $[SiO_2]_n$  content caused increased alkalinity of waters in the lacustrine basin. In the following period volcanic in the tuffs altered by hydration into montmorillonite.

Bentonites with admixture of kaolinite and cristobalite have been formed in consequence of the alteration of rhyolite tuffs on dry land by weathering. The origin of kaolinite was decisively affected by the pH-value of infiltrating atmospheric water during weathering.

Montmorillonitized rhyolites have been formed by activity of low thermal alkalic solutions during rhyolite volcanism. Relationship between montmorillonite and kaolinite is determined by the pH value of the penetrating hydrothermal solutions.

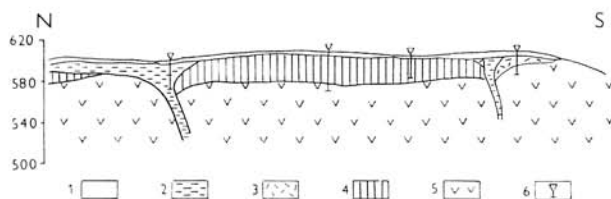


Fig. 3. Geological profile of the deposit of clays mixed-layer mineral illite-montmorillonite Dolná Ves. 1 — scree; 2 — hydroquartzite; 3 — silicified rhyolite tuff; 4 — mixed-layer illite-montmorillonite; 5 — rhyolite tuff; 6 — bore hole.

Kaolinization of rhyolites proceeds in the studied area as both endogenous and exogenous processes. In the course of rhyolite volcanism, when kaolinized rhyolites with a comparatively low degree of alteration formed, hydrothermal kaolinization was primary. The kaolinized rhyolites show increased  $K_2O$  content and are indicative of K-metasomatism during hydrothermal processes on the southern periphery of the metallic deposit Kremnica. Under favourable conditions of intense infiltration of atmospheric waters the secondary, local surficial weathering of hydrothermally kaolinized rhyolites takes place. Irregular kaoline "pocket" has been formed. They are up to 25 m thick with a small areal extension and the content of fraction under 0.02 mm ranges above 70 %.

Mixed-layer mineral illite-montmorillonite is product of the influence of hydrothermal activity upon rhyolite tuffs. Ascent of hydrothermal solutions is indicated by hydroquartzite bodies around which the alteration of parent rock is most intensive. (Fig. 3).

The process of K-metasomatism is characteristic of the Kremnica metallic deposit, where adularia and hydromuscovite together with kaolinite are a part of vein filling and wallrock alterations. (Böhmer et al., 1969).

Čičel and Machajdík (1981) saturated exogenous montmorillonite from the Jelšovský potok with  $K^+$  and got thus mixed-layer mineral illite-montmorillonite with illite layers (10 Å) ranging up to 54 %. Such portion of 10 Å layers is also in some mixed-layer mineral illite-montmorillonite in the area studied. We presume that mostly due to exogenous factors, the rhyolite tuffs were affected by bentonitization and kaolinization. The following transport of  $K^+$  by hydrothermal solutions caused transformation of montmorillonite into mixed-layer mineral illite-montmorillonite, with the portion of illite layers (10 Å) ranging from 50 to 80 %.

*Distribution of mineral assemblages*

Most intense alterations in the area studied are associated with the N – S zone which is a direct continuation of the Kremnica ore veins. In the northern part of the zone the rhyolites and rhyolite tuffs altered on land under the influence of weathering and hydrothermal processes. In the southern part of the zone, the rhyolite tuffs decomposed in a lacustrine basin without direct influence of hydrothermal solutions. Generally, montmorillonite content increases from north to south in the zone studied.

Lateral zonation is good expressed in the proximity of outcrop of mixed-layer mineral illite-montmorillonite. (Fig. 1). The central zone is formed by mixed-layer mineral illite-montmorillonite with variable admixture of kaolinite. In this zone montmorillonite is completely absent. We suppose that conditions favourable for formation of mixed-layer mineral illite-montmorillonite were in the place of ascent of hydrothermal solutions rich in  $K^+$ . In the external zone are kaolinite-montmorillonite clays and bentonites with admixture of kaolinite and cristobalite. In the external zone the mixed-layer mineral illite-montmorillonite is absent. Weathering was most active there.

Complicated spatial relations between the mineral assemblages affected their chronology. In the first stage, during rhyolite volcanism (Upper Sarmatian Pannonian boundary), bentonitization and kaolinization of rhyolite tuffs, controlled by physico-chemical conditions proceeded on land and in limnic environment. Under the influence of low-thermal solutions connected with rhyolite volcanism, altered rhyolites and rhyolite tuffs formed either kaolinite (kaolinized rhyolites), montmorillonite (montmorillonitized rhyolites) or zeolites (zeolitized tuffs).

In the second stage, the rhyolite volcanism (Pannonian) is followed by the endogenous hydrothermal Au-Ag-Sb formation, known on the Kremnica deposit. K-metasomatism is a significant manifestation of hydrothermal processes. (Böhmér, 1966). On the southern periphery of the Kremnica deposit the transport of  $K^+$  in hydrothermal solutions causes in a part of altered rhyolite tuffs the transformation of montmorillonite into mixed-layer mineral illite-montmorillonite.

The third stage (Pliocene and Quaternary) is characterized by surficial weathering of rhyolite tuffs altered in the preceding stages. Local kaolinization or bentonitization take place.

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