GEOLOGICA CARPATHICA, 45, 3, BRATISLAVA, JUNE 1994
151 - 158

DIAGENETIC AND HYDROTHERMAL ALTERATIONS OF VOLCANIC ROCKS INTO CLAY MINERALS AND ZEOLITES (KREMNICKÉ VRCHY MTS., THE WESTERN CARPATHIANS)

IVAN KRAUS[1], EVA ŠAMAJOVÁ[1], VLADIMÍR ŠUCHA[1]
JAROSLAV LEXA[2] and ZUZANA HRONCOVÁ[3]

[1]Faculty of Sciences, Comenius University, Mlynská dolina G, 842 15 Bratislava, Slovak Republic
[2]Dionýz Štúr Institute of Geology, Mlynská dolina 1, 817 04 Bratislava, Slovak Republic
[3]Geological Survey, Kyncelovská cesta, 974 01 Banská Bystrica, Slovak Republic

(Manuscript received March 31, 1993; accepted in June 30, 1993)

Abstract: The suggested model for the alteration of the rocks from the Kremnica ore district and from the SW margin of the Kremnické Vrchy Mts., is based on the existence of three mutually associated processes of different origins: the diagenetic alteration rhyolite tuffs, hydrothermal alteration of rhyolites and finally, hydrothermal alteration of andesites and rhyolite tuffs in the neighbourhood of the veins from the Kremnica ore district. Spatial coincidence in the mineral composition of rhyolites and rhyolite tuffs was confirmed in all the distinguished alteration processes. Polygenetic zoning mixed-layer illite/smectite + kaolinite, zeolites and smectite developed at the southern periphery of the Kremnica ore district in the direction from north to south. Hydrothermal alteration of the Kremnica ore zone belongs to the adularia-sericite type in the sense of Heald et al. (1987).

Key words: diagenesis, hydrothermal activity, zoning, smectite, mixed-layer illite/smectite, clinoptilolite.

Introduction

Economic accumulations of bentonites, as well as other exploitable types of clays and zeolites of the Kremnické Vrchy Mts., were formed by the alteration of acidic vitric tuffs (Kraus et al. 1979; Šamajová 1979; Lajčáková & Kraus 1987). Kraus et al. (1982) have identified four authigenic mineral assemblages which were formed by the alteration of acidic vitric tuffs and rhyolites: 1 - smectite ± kaolinite, clinoptilolite, mordenite and cristobalite; 2 - kaolinite ± smectite and cristobalite; 3 - mixed-layer illite/smectite ± kaolinite; 4 - clinoptilolite and mordenite ± smectite, kaolinite, cristobalite and adularia.

Recent studies have confirmed that the given mineral assemblages formed in a certain time sequence and their own very special complicated polygenetic character (Kraus 1989; Šamajová et al. 1991, 1992; Šucha et al. 1992). The results and observations have equipped us to present a general concept of the processes which function in the studied area mainly in the alteration of the products of rhyolite and partly also andesite volcanisms. They include:

- diagenetic alteration of rhyolite tuffs subsequent to their deposition;
- hydrothermal alteration of rhyolites in the course of their cooling;
- hydrothermal alteration of andesite and rhyolite tuffs in the vicinity of ore veins.

Geological setting

The studied area at the SW margin of the Kremnické Vrchy Mts. belongs to the Jastrabá Formation, distinguished by Konečný et al. (1983). The Jastrabá Formation contains extrusions, intrusions, flows and dykes of rhyodacite and rhyolite compositions, which are accompanied by different types of volcanoclastics, limnoquartzites and clays with a total thickness ranging from 100 to 300 m. Biostratigraphic data from limnoquartzites, rhyolite tuffs and clays indicate an Upper Sarmatian to Lower Pannonian age (Konečný et al. 1983). Radiometric dating of rhyolites has yielded data within the range of 12.9 to 10.7 m.y. (Konečný et al. 1969; Repčok 1982).

N-S trending faults display a significant influence in the Jastrabá Formation at the SW margin of the Kremnické Vrchy Mts. The best evidenced fault proceeds through the valley of the stream Rudnica from the Dolná Ves to Stará Kremnička. The western part of this area subsided along the mentioned fault (Lexa et al. 1984). This fact has played a significant role and affected the intensity of the alteration of rhyolite volcanism products. Therefore, from this point of view, the fault zone is also significant, containing the veins of the Kremnica ore district (Fig. 1).

Lexa et al. (1984) distinguish three evolutionary stages with the characteristic type of products within the Jastrabá Formation. The oldest ones are the bodies of rhyodacites near Bartošova Lehôtka and secondly, the horizon of rhyodacite volcanoclastics in direct overlier of older rocks and Sarmatian sediments of the Žiarska Kotlina Depression, developed at Jastrabá, which had been radiometrically dated to 12.0 + 0.3 m.y. This horizon gradually wedges out in the direction to the west in the underlier of younger products.

The younger evolutionary stage comprises mainly the main mass of the Jastrabá Formation - extrusions of rhyolites and volcanoclastics. Within volcanoclastics there are tuffs, lapilli tuffs, aglomerates, volcanic breccias, depositions of pumiceous flows, depositions of pyroclastic flows of the Merapi

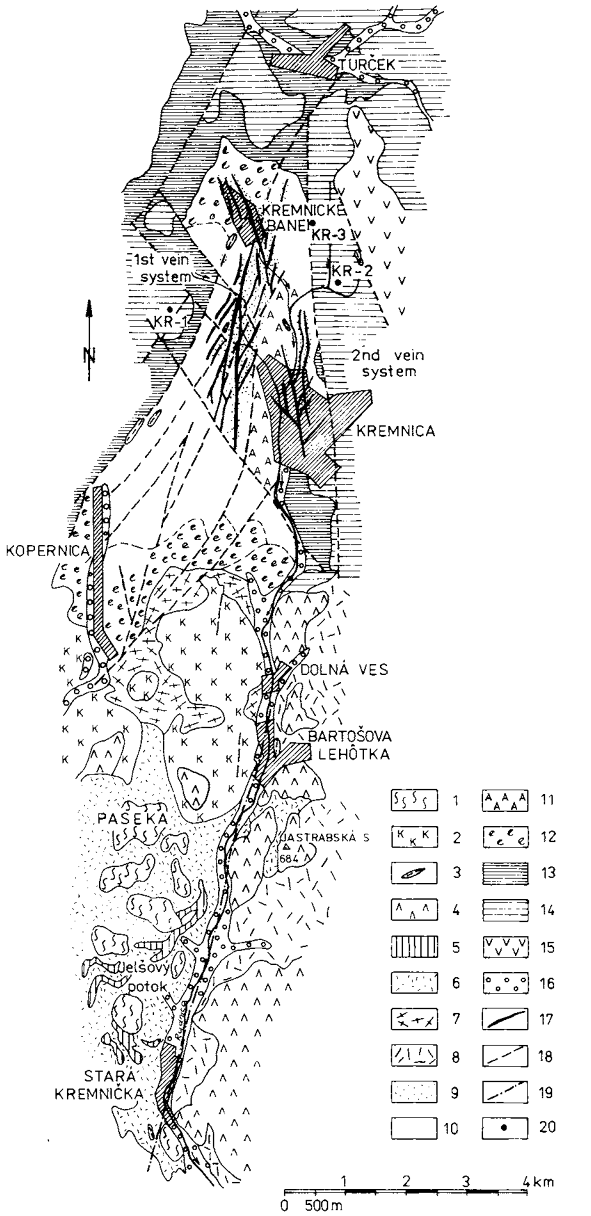

Fig. 1. Scheme of diagenetic and hydrothermal alteration compiled for the basis of geological-tectonic sketch of Lexa (in Lexa et al. 1981). Explanations: the Jastrabá Formation (Upper Sarmatian - Lower Pannonian) **1** - hydrothermally altered rhyolite extrusions with prevalence of smectite; **2** - hydrothermally altered rhyolite intrusions with prevalence of kaolinite; **3** - rhyolite dykes in the neighbourhood of the veins from the Kremnica ore district, hydrothermally kaolinized; **4** - rhyolite extrusions, intrusions and lava flows not affected by hydrothermal alteration leading to the origin of clay minerals and zeolites ; **5** - limnoquartzites; **6** - diagenetically altered rhyolite volcanoclastics with prevalence of smectite and clinoptilolite; **7** - hydrothermally altered rhyolite volcanoclastics with prevalence of mixed-layer illite/smectite and kaolinite; **8** - volcanoclastics not affected by hydrothermal alteration leading to the origin of clay minerals and zeolites. The Zlatá Studňa Formation (Lower and Upper Badenian); **9** - hydrothermal wall rock alteration of andesites and andesite porphyres with kaolinite, illite, mixed-layer illite/smectite and adularia; **10** - prophyllitized andesites and andesite porphyres with prevalence of smectite; **11** - intrusive body of amphibolite-pyroxenic andesite porphyry; **12** - effusive complex of pyroxenic andesite; **13** - unclassified. Turček Formation (Upper Badenian - Lower Sarmatian) - lava flows, pyroclastics and epiclastics of basaltoid and pyroxenic and leucocrate andesite: **14** - unclassified formation of the Kremnický Peak (Upper Badenian) - effusive amphibolite-pyroxenic andesite; **15** - the Krahulská Formation (Lower Sarmatian) - extrusions of biotitic-amphibolite andesite; **16** - aluvium; **17** - veins of the Kremnica ore district; **18** - dislocations with assumed continuation of the veins of the Kremnica ore district; **19** - fault; **20** - boreholes.

type, depositions of freatic eruptions and prevailing redeposited pyroclastics and epiclastics (Bezák & Lexa 1983). The mainly build the formation E of the stream Rudnica. Fragments of extrusive rhyolites in volcanoclastics of this horizon were subjected to radiometric dating, yielding the age of 11.3 ± 0.4 m.y. (Repčok 1982).

In the course of the youngest period, volcanoclastics of this horizon were intruded by dykes and depositional bodies of rhyolites (laccoliths), mainly in the northern part of the formation. Lava flows of rhyolites with sanidine are also attributed into this evolutionary stage in the uppermost part of the formation. Their younger age is also indicated by the results obtained from radiometric dating, 10.9 ± 0.4 m.y. (Repčok 1982), or 10.7 ± 0.3 m.y. respectively (Konečný et al. 1969). Dykes of rhyolites occurring in the Kremnica ore district are the youngest and have narrow time span and spatial relation to the veins of the Kremnica ore district (Böhmer 1966).

The most significant horizon of these two evolutionary stages of the Jastrabá Formation from the view of the alteration processes is represented by redeposited, partly also autochthonous rhyolite tuffs in the upper part with the position of limnoquartzites in subsided block W of the stream Rudnica. They contain economically significant deposits of bentonites, zeolites and in the future also mixed-layer illite/smectite minerals. Their origin was affected by the process of diagenetic and hydrothermal alterations (Fig. 1).

Diagenetic alteration of rhyolite tuffs

Diagenetic alteration affects the complex of mostly redeposited, partly also autochthonous rhyolite tuffs which are emplaced in tectonically subsided block W of the valley of the stream Rudnica between the villages Bartošova Lehôtka and Stará Kremnička (Fig. 1). They represent volcanogeneous-sedimentary sequence of the Jastrabá Formation and had sedimented together with limnoquartzites in shallow lakes and swamps.

The study of the distribution of selected mineral assemblages on the basis of boreholes situated into the depth approximately 300 m from the surface, enabled to distinguish two zones in the vertical direction: bentonite zone - with the mineral assemblages smectite ± kaolinite, clinoptilolite and cristobalite and zeolite zone - with the mineral assemblage clinoptilolite ± smectite, kaolinite and cristobalite.

Bentonite zone is best developed in the southern part of the studied area at the deposit Jelšový Potok and Jelšový Potok - north. Bentonites were formed here by the alteration of vitric tuffs rich in porous glass in a shallow - water lacustrine environment (Kraus et al. 1982, 1989). Close spatial association between bentonites and limnoquartzites was confirmed (Kraus 1967).

Maximum thickness of bentonite layer at the deposit equals 50 m. Two mineralogical types of bentonites have been distinquished here. One of them, monomineral bentonite without cristobalite admixture makes up the upper part of the zone. The second type, which forms the lower part of the zone, is located below monomineral bentonite. It is formed by smectite with admixture of cristobalite and clinoptilolite (Fig. 2).

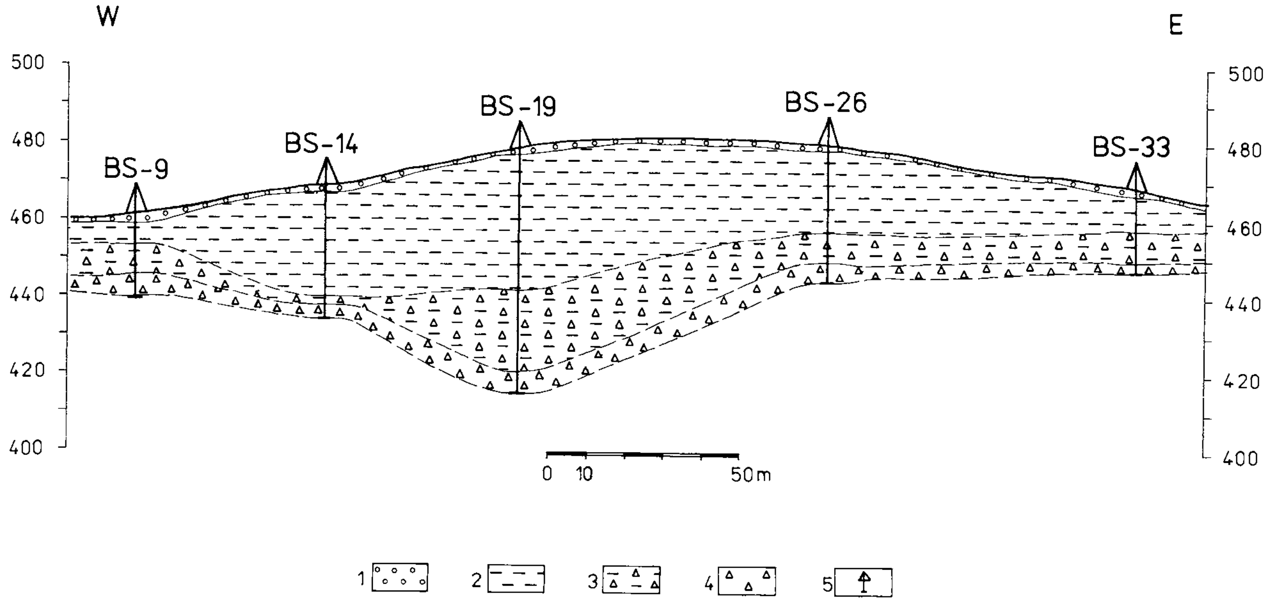

Fig. 2. Geological profile of the deposit Jelšový Potok - north. Explanations: **1** - debris; **2** - monomineral bentonite without cristobalite admixture; **3** - bentonite with admixture of clinoptilolite and cristobalite; **4** - zeolite (clinoptilolite + mordenite) with admixture of smectite and cristobalite.

Zeolite zone was ascertained on the area of some 1.5 km, mostly in surface outcrops (Šamajová 1979; Šamajová & Kraus 1985). Recently the zeolitized tuffs which make up the Bartošova Lehôtka - Paseka zeolite deposit, were subjected to drilling exploration to a depth of 80 - 130 m. Zeolitized tuffs of a similar character to those occurring both in surficial occurences and at the deposit Bartošova Lehôtka - Paseka, have also been identified at the bentonite deposite Jelšový Potok - north. The zone of zeolites is here usually emplaced below the bentonite zone of the mineral assemblage smectite ± kaolinite, cristobalite and clinoptilolite. Zeolites represented by clinoptilolite ± mordenite with admixture of smectite, kaolinite and cristobalite (Fig. 2).

Hydrothermal alteration of rhyolites

Hydrothermal alteration of rhyolites affect with similar intensity mainly the extrusions and intrusions of rhyolites of the Jastrabá Formation emplaced in the subsided block W of the fault which proceeds through the valley of the stream Rudnica (Fig. 1). Extrusions of rhyolites occur in the southern part of the studied area. Most of the bodies display dome-shaped form and in the inner part they are formed by massive felsitic rhyolite with irregular block cleavage, often with fluidal structure. They are formed by quartz-plagioclase and quartz-sanidine-plagioclase rhyolite. The transition into extrusive breccias, often glassy ones, can sometimes be observed at the margins.

Extrusive bodies near Stará Kremnička own preserved glassy margins attaining the thickness up to 5 m. At the contact between rhyolite and glassy margin there occurs transitional zone of glassy spherulitic rhyolite. Glassy spherulitic rhyolite and glassy margin of rhyolite consisting of perlite are entirely fresh. The alteration into clay minerals is concentrated in marginal parts of the extrusions where it affects plagioclases, forming main mass and glassy main mass. The prevailing clay mineral of rhyolite extrusions in SW part of the studied are in the neighbourhood of Stará Kremnička is in certain cases almost exclusively smectite and in others kaolinite and cristobalite in the form of admixture.

Intrusions of rhyolites have the character of laccoliths and occur mainly in the northern part of the studied area (Fig. 1). Their dome-shaped parts display breccia character, while at the margins of these bodies we can not observe the transitions into glassy varieties. They are quartz-plagioclase-sanidine rhyolites with microgranitic, more rarely felsitic main mass. In the upper part they are often affected by the silicification of different intensity for which chalcedony, CT-opal (lussatite), veiny and in cracks crystalline quartz are responsible. Plagioclases (albite-oligoclase) are usually decomposed to certain measure, but K-feldspars remain fresh. A part of them belong to authigenic adularia which indicates K-metasomatosis and forms well shaped tiny crystals of rhombic section present in veinlets together with hydrothermal quartz, or pseudomorphoses after decomposed plagioclase (Kraus 1989). The dominant clay mineral in intrusive rhyolites is kaolinite. It has regularly present admixture of montmorillonite (Fig. 3). Zeolites have hitherto only partly explained position in the alteration of intrusive rhyolites.They have hitherto ascertained in several boreholes W of Bartošova Lehôtka, where mordenite together with kaolinite are present mainly in silicified rhyolite breccias which show developed zeolitized rhyolite tuffs with prevalence of mordenite at the contact.

Hydrothermal alteration of rocks in the neighbourhood of ore veins

It was studied in the Kremnica ore district, defined and delimited by Böhmer (1966). It is a system of veins and veiny zones trending NNE - SSW, in which the following may be distinguished: **a** -the northern marginal zone where on the 1st veiny system in the neighbourhood of the Kremnica mines there is Au-Ag-Pb-Zn-Cu-Te mineralization developed and S of Horný Turček there is hydrothermal alteration of rocks in the neighbourhood of

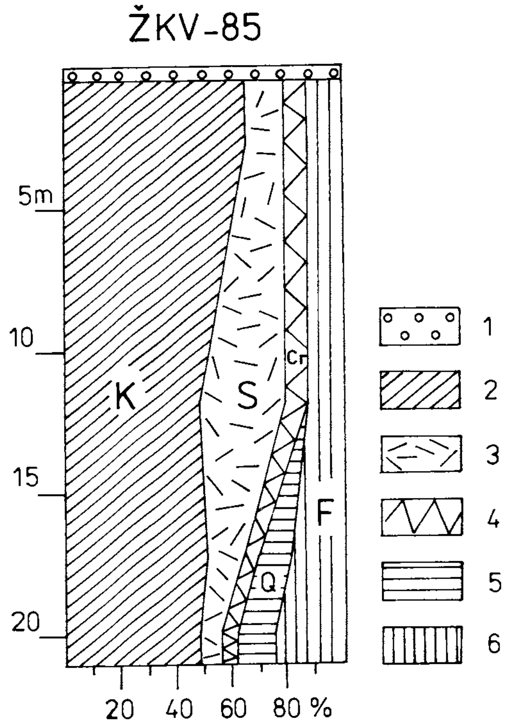

Fig. 3. Presence of minerals in the fraction below 0.005 mm on the basis of semiquantitative X-ray diffraction analysis in altered intrusive rhyolite in borehole ŽKV-85 W of Bartošova Lehôtka. Explanations: 1 - debris; 2 - kaolinite; 3 - smectite; 4 - cristobalite; 5 - quartz; 6 - feldspar.

old randing works, **b** - central zone with Au-Ag-Sb mineralization developed on the 1st and 2nd veiny systems, **c** - the southern marginal zone with assumed occurrence of Au, Sb veins and Hg mineralization W of Dolná Ves and Bartošova Lehôtka. According to Konečný et al. (1983), the northern marginal and central zones belong to the Zlatá Studňa Formation, Turček Formation and the formation of the Kremnický Peak. The southern marginal belt falls into the Jastrabá Formation (Fig. 1).

In the northern marginal zone a hydrothermal alteration was studied in boreholes KR-1, KR-2 and KR-3 (Fig. 1). It is the level with the maximal widespread smectitization. Increased accumulations of kaolinite can only be found in few intervals always in the neighbourhood of the uppermost parts of vein structures formed by opal and low-temperature chalcedony-carbonate gangue with pyrite. Recently a mineral assemblage identical with the central zone: mixed-layer illite/smectite + kaolinite ± chlorite and smectite, was ascertained also on the 1st veiny system of the northern marginal zone.

Alunite is a significant authigenic mineral of altered rocks from the northern marginal zone. It was identified in andesites near Horný Turček together with opal and pyrite by Polák (1957). The next occurrence of alunite in the northern marginal zone was introduced by Böhmer (1996).

The following symmetrical zoning was determined in the central zone on the 2nd veiny system by Böhmer et al. (1969) on the basis of the study of clay minerals from the vein filling and from hydrothermally altered andesites approximately up to the distance of the 10 m from ore veins:

- the inner zone confined to the veins of gold-bearing quartz, in which of the clay minerals, illite is exclusively present;
- the central zone, evolved symmetrically in the overlier and underlier of the inner zone with the mineral assemblage illite and kaolinite;
- the outer zone, evolved symmetrically in the overlier and underlier of the central zone with the mineral assemblage kaolinite + mixed-layer illite/smectite ± chlorite and smectite.

In the central zone on the 1st veiny system, Šamajová et al. (1993) determined a mineral assemblage formed by mixed-layer illite/smectite + kaolinite ± chlorite and smectite in hydrothermally altered breccia andesites approximately 100 m from ore veins.

Illite present here belongs to a polytype modification 1M and mixed-layer illite/smectite having expandability 10 per cent (Šucha et al. 1992). At the same time, adularia is a significant authigenic mineral of hydrothermally altered rocks of the central zone. Böhmer (1966) determined adularia which metasomatically replaces plagioclase in andesites and adularia present in vuggy quartz. The content of K_2O in hydrothermally altered rocks of the central zone varies within the range from 7 to 10 per cent. Dykes of rhyolites, which are in the central zone in direct neighbourhood of ore veins, are intesively altered, while in the clay fraction there is present only kaolinite.

The southern marginal zone testifies to hydrothermal alteration of rhyolite tuffs of the Jastrabá Formation W of Dolná Ves at the deposit mixed layer illite/smectite (Kraus & Zuberec 1976; Kraus et al. 1982, Fig. 1). The expandability of mixed-layer illite/smectite ranges between 50 and 6 per cent. The samples with the largest amount of expandable layer are K-rectorites with regularly interstratified 1.0 and 1.7 nm layers (Šucha et al. 1992). Mixed-layer illite/smectite is in hydrothermally altered tuffs accompanied by variable admixture of kaolinite, but smectite is always absent.

Model of diagenetic and hydrothermal alterations

Diagenetic alteration

The concept about diagenetic alteration of rhyolite tuffs in SW part of the studied area is based on the ascertained zoning in the nieghbourhood of bentonite deposite Jelšový Potok, which had been determined at the deposit Jelšový Potok-north (Fig. 2).

Diagenetic zones were formed as a result of gradual changes in chemical composition and pH of porous solutions percolating through vitric tuff layers. In the course of gradual hydration and hydrolysis of the vitric component and simultaneous formation of smectite in the upper tuff layers, porous solutions became enriched in alkalies and silicon eventually attaining the mineralization and pH sufficient for clinoptilolite crystallization (Šamajová et.al. 1992). The upper monomineralic bentonite zone originated from alterations in an open system (Hay 1986; Gottardi 1989). Increasing amounts of low cristobalite in deeper parts of the bentonite zone and its constant presence in the underlying zeolite zone suggest a relatively more closed hydrologic system. The position of boundaries between diagenetic mineral assemblage zones is determined by groundwater hydrology and chemistry.

Hydrothermal alteration of rhyolite extrusions and intrusions

In the course of cooling process of rhyolite extrusions and intrusions of the Jastrabá Formation, the hydrothermal alteration has, from the view of fluids, an autohydrothermal character.

During the alteration of rhyolite extrusions the mineral assemblage originated, dominated by smectite. Smectitization of rhyolite extrusions, as a result of the influence of the near-neutral pH character of fluids, probably proceeded under different conditions than in rhyolite intrusions and probably was to certain degree affected by the circulation of meteoric waters. It took place only after the termination of cooling of glassy perlite margin, which has been preserved in several places, always in fresh state. Rhyolite extrusions affected by smectitization can be found in the section between the elevation point Paseka and the village Stará Kremnička and they form the most external zone in the studied area (Fig. 1).

In the course of the alteration of rhyolite intrusions a mineral assemblage originated in which kaolinite displays a dominant position. We assume that mainly the intrusive character of the bodies is the cause of relatively extensive kaolinization and accompanying silicification of not only marginal, but also inner parts, due to the affects of fluids with increased content of SO_2 which had been released during the crystallization of magma in the conditions of a more closed system. The alteration did not affect the rocks in an equal way. Sometimes there are light parts of rhyolite with elevated content of kaolinite alternating with violet parts because of low kaolinite content. According to the mineral and chemical compositions, kaolinized rhyolite intrusions are identical with hydrothermally altered acid volcanites used in treatment for the manufacturing of porcelain (Magidovič & Finko 1975; Kraus et al. 1979).

There is only sporadical evidence supporting hydrothermal zeolitization of rhyolite intrusions. The presence of mordenite, often accompanied by variably present kaolinite in silicified marginal breccias were recorded in several samples from boreholes localized W of Bartošova Lehôtka. The value of chemical potential SiO_2 is a significant factor which controls the formation of zeolites. Acid volcanic glass stimulates the origin high-silica zeolites as mordenite and clinoptiliolite which crystallize from the solutions oversaturated by SiO_2 with regard to quartz (Senderov 1963). Partly preserved features of vitrophyric-felsitic texture, observed on thin sections, indicate glassy character of the original rock.

Similar authigenic mineral assemblage in the whole hitherto studied area can be found in the contact zones of rhyolite bodies with altered glassy volcanoclastics, whereas in volcanoclastics from the contact of more distant ones, clinoptilolite is dominant (Fig. 4). Elevated accumulations of mordenite in exocontact of rhyolite bodies are a result of the transformation of the original clinoptilolite originated during the diagenesis via direct alteration of volcanic glass. The change of clinoptilolite into mordenite represents a reaction which is mainly depended on the change of geothermic gradient in the aureole of rhyolite bodies (Šamajová 1988; Šamajová et al. 1992). Chemical composition of mordenite from volcanoclastics corresponds to K-Ca-Na variety (Kozáč 1984). Seki (1992) experimentally confirmed the results of field observations that Ca content in mordenite grows with the temperature of its origin. Literature data on the occurrences of mordenite in many countries (Bulgaria, Japan, Cuba, Georgia, USA), as well as experimental works point to analogical relation between the temperature and distribution of clinoptilolite and mordenite (Gogišvili 1979; Sheppard et al. 1988). Besides elevated temperature in contact aureole, the process of mordenitization favourably affects higher content of Na in the original rock or its transport from the neighbourhood, which is unambiguously evidenced by the results obtained from hydrothermal synthesis of zeolites (Kirov et al. 1979; Phillips 1983), as well as from the modelling of hydrothermal transformation of clinoptilolite into mordenite (Kusakaba 1982). The given experimental works enlighten the relation in the area of the stability of clinoptilolite and mordenite as the function of the temperature, pH and Na^+ concentration. They show that the change of clinoptilolite for mordenite shifts towards relatively higher temperature at lower pH solution and lower Na^+ concentration.

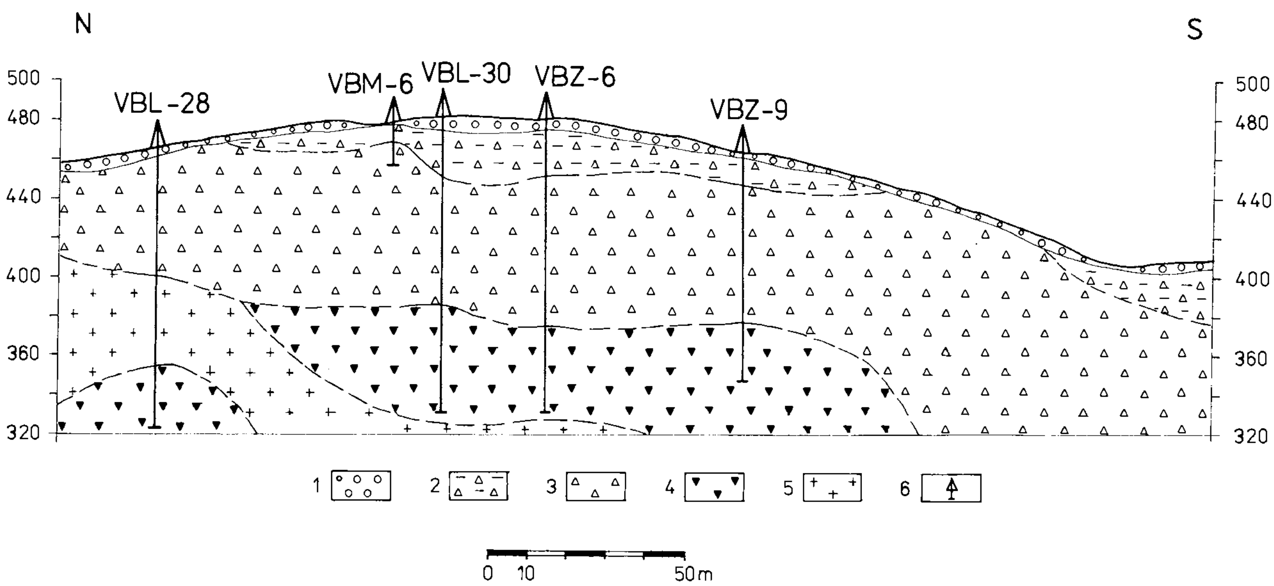

Fig. 4. Geological profile of zeolite deposite Bartošova Lehôtka - Paseka. Explanations: **1** - debris; **2** - bentonite with admixture of clinoptilolite and cristobalite; **3** - zeolite (clinoptilolite) with admixture of smectite and cristobalite; **4** - zeolite (mordenite) with admixture of smectite, kaolinite and cristobalite; **5** - silicified rhyolite; **6** - borehole.

Hydrothermal alteration in the neighbourhood of ore veins

The model of hydrothermal alteration in the course of the formation of veins in the Kremnica ore district on the basis of the distribution of distinguished assemblages of clay minerals was presented by Kraus (1989). In his view, clay minerals in relation to ore veins were formed in two stages.

In the first - pre ore stage, the influence of hydrothermal solutions with relatively low value of pH caused the formation of kaolinite and gradual increase in the pH value during the penetration of the rocks caused that smectite was generated, or chlorite respectively. The stage is situated shortly before or at the beginning of the 1st quartzy introductory period, distinguished by Böhmer (1966). Kaolinization in this stage is most markedly expressed in direct neighbourhood of ore veins and in the alteration of rhyolite dykes which, according to generally accepted view, represent the introductory phase of the mineralization on the 1st and 2nd veiny systems of the central zone.

In the second, ore stage, hydrothermal solutions gained alkaline character as a result of high K^+ content. It is a process of K-metasomatosis, in the Kremnica ore district for the first time studied in detail by Böhmer (1966), who proved its direct association with precious-metal (Au-Ag) mineralization. During this stage, favourable conditions were created for the origin of illite, or mixed-layer illite/smectite respectively.

Both stages are best developed in the central zone of the Kremnica ore district on the 1st and 2nd veiny systems. Identified deviations in other zones are associated with different petrographic composition and permeability of the surrounding rocks, different character of fluids and different distance from their source.

From the northern marginal zone of the Kremnica ore district we have only now the first data on the mineral composition of the products of hydrothermal alteration in association with a complex precious-metal-polymetallic mineralization in the sence of Knésl & Knéslová (1991) as well as the contact-metasomatic mineralization established by Böhmer & Šímová (1976). Preliminary results did not confirm the presence of the association of kaolinite with alunite, pyrophyllite or diaspor.

In the southern marginal zone of the Kremnica ore district the 1st and 2nd stages were actives in hydrothermal alteration or rhyolite tuffs at the deposite of mixed-layer illite/smectite minerals Dolná Ves, W of the village (Fig. 1). Original diagenetic smectite is converted here into mixed-layer illite/smectite. At the present time we verify also the second alternative according to which mixed-layer illite/smectite was formed by illitization of the original hydrothermal K-rectorite. Kaolinite remained unchanged in the course of K-metasomatosis and it represents a relict mineral of the 1st stage. The expandability of mixed-layer illite/smectite in the Dolná Ves deposit increases from north to south. This increase also probably marks the direction of K-hydrothermal solution transport. It also corresponds with geologic data concerning the direction of fluid transport in the Kremnica ore district (Böhmer 1966).

The problem remains to solve the cause of the systematic change in expandability. There are two possibilities: **1** - decrease of temperature from north to south during the penetration of hydrothermal solutions; **2** - decrease in potassium content of hydrothermal solutions from north to south. The test of K-fixation in samples with highest expandability may support the first possibility.

The expandability of mixed-layer illite/smectite often correlates with the temperature of active geothermal environments and is used as a paleothermometer. Using the data from the Eastern Slovak Basin we estimated lower temperature limit (100 - 130 °C) in the Dolná Ves region (Šucha et al. 1992).The upper limit (about 200 °C) was estimated by analogy to other papers dealing with the same type of clays (Horton 1985; Eberl et al. 1987).

Discussion and conclusions

Presented model of rock alteration at the SW margin of the Kremnické Vrchy Mts. and in the Kremnica ore district is based on the existence of three more or less mutually associated processes of different origin: diagenetic alteration of rhyolite tuffs after their deposition, hydrothermal alteration of rhyolite extrusions and intrusions during their cooling and hydrothermal alteration of volcanic rocks of different composition and age in the neighbourhood of the veins of the Kremnica ore district. Their mutual coexistence, not observed in other neovolcanic mountains of the Western Carpathians is associated with the whole volcano-tectonic development, but namely with the course of the significant structural phenomenon - north-sourthern graben in the sense of Štohl (1976), Konečný & Lexa (1979), which includes all tectonic zones and faults to which the mentioned

Table 1. Scheme of succesion and genesis of altered products of the Kremnické Vrchy Mts. Abreviations: **S** - smectite, **K** - kaolinite, **I/S** - illite/smectite, **Cr** - cristobalite, **Cl** - clinoptilolite, **Ch** - chlorite.

	Stage-age	**Formation process**	**Mineral assemblage**	**Host rock**
I.	Upper Sarmatian -	diagenesis	SMECTITE ± Cl, Cr	rhyolite tuff
	Lower Pannonian		CLINOPTILOLITE ± S, Cr	rhyolite tuff
II.	Upper Sarmatian -	autohydrothermal	SMECTITE ± K, Cr	extrusive rhyolite
	Lower Pannonian		KAOLINITE ± S, Cr	intrusive rhyolite
			MORDENITE ± S, K, Cr	intrusive rhyolite rhyolite tuff
III.	Upper Pannonian	wall rock hydrothermal	KAOLINITE + ILLITE + I/S ± S, Ch	andesite rhyolite tuff
IV.	Pontian	weathering	KAOLINITE ± S, Cr	andesite rhyolite rhyolite tuff

alteration processes are spatially related. Indirect evidence for the continuation of fault zones belonging to the Kremnica ore district and its present southern boundary is considered to be hydrothermally altered rhyolite tuffs W of Dolná Ves with the leading position of mixed-layer illite/smectite and kaolinite.

An open question remains mutual relationship between diagenetic alteration of rhyolite tuffs and hydrothermal alteration of rhyolite extrusions and intrusions. For diagenetic alteration the best conditions were formed in mostly redeposited rhyolite tuffs which has sedimented together with limnoquartzites in the environment of shallow lakes and swamps in subsided block of Jastrabá Formation W of the fault proceeding throug the valley of the stream Rudnica. Only in this zone an intensive hydrothermal alteration of rhyolite extrusions and intrusions of the autohydrothermal type was confirmed. Both processes proceeded in one time phase (Tab. 1), but it is not possible to delimite the consequence of autohydrothermal alteration from rhyolites into rhyolite tuffs without using isotope analyses of oxygen in clay minerals, the only exception of conversion being clinoptilolite into mordenite. On the other hand, generally spatial coincidence in the mineral composition of rhyolites and rhyolite tuffs in the Jastrabá Formation in all distinguished alteration processes was confirmed (Fig. 1). W of Bartošova Lehôtka hydrothermally kaolinized rhyolite intrusions are corresponded by hydrothermally altered rhyolite tuffs with the assemblage mixed-layer illite/smectite + kaolinite at the deposite Dolná Ves. In the area of the elevation point Paseka zeolitized rhyolites (confirmed hitherto only by boreholes) are corresponded by zeolite tuffs at the zeolite deposit Bartošova Lehôtka - Paseka (Fig. 4) and by bentonites with zeolites at the deposit Jelšový Potok - north (Fig. 2). Finally, smectitized rhyolite extrusions of NW of Stará Kremnička are corresponded by bentonites at the deposit Jelšový Potok (Fig. 1). At the southern periphery of the Kremnica ore district in the direction from north to south polygenetic zoning formed: mixed – layer illite/smectite + kaolinite, zeolites and smectite. Hydrothermal alteration in the surroundings of ore veins (including hydrothermally altered rhyolite tuffs at the deposit Dolná Ves) is younger, on diagenetic and autohydrothermal alterations. The youngest process appears to be surficial weathering. We can situate it mainly into Pontian and it may be significant for kaolinite (Tab. 1).

The study of alteration processes on epithermal precious-metal and polymetallic deposits in recent period has significantly grown in importance. The main reason is that obtained knowledge from numerous world deposits may be utilized to distinguish mineralization produced by two contrasting deep fluids having respectively near-neutral pH, and acid pH (Hayba et al. 1983; Heald et al. 1987; Hedenquist 1987). Hydrothermal alteration related to the near-neutral pH and acid pH deep fluids has been variously described. Heald et al. (1987) used the terms "adularia-sericite" and "acid sulphate", respectively, Bonham (1986) used the terms "low sulphur" and "high sulphur", instead of which today the terms "low sulphidation" and "high sulphidation" are used (White & Hedenquist 1990). Berger & Henley (1989) have suggested to replace the fluid term "acid sulphate" by the mineralogic term "kaolinite-alunite" to achieve a consistent basis with the "adularia-sericite" grouping. It seems that it is not possible to work out mechanical classificaton of hydrothermal deposits into these two groups on the basis of ascertained association of the alteration processes. At the same time, it is necessary to study thermobarometric conditions of gas-liquid inclusions, to establish theirsalinityand the changes in the content of isotope ^{34}S coexisting sulphides and sulphates.

From this point of view, it is evident that the distinguished hydrothermal alteration of the Kremnica ore district represents an adularia-sericite type in the sense of Heald et al. (1987). In the central zone, at the same time, it indicates typical Au-Ag mineralization of the Kremnica ore district on the 1st and 2nd veiny systems and in the southern zone of the origin of the deposit of mixed-layer illite/smectite W of Dolná Ves. In the northern marginal zone of the Kremnica ore district with the change of precious–metal mineralization (Au-Ag) into a complex precious-metal-polymetallic (Au-Ag-Pb-Zn-Cu-Te), the assemblages of clay minerals in both stages did not substantially change. Similarly, we do not have enough evidence yet to distinguish a separate kaolinite-alunite type in the sense of Heald et al. (1987) in connection with contact metasomatic mineralization established by Böhmer & Šímová (1976) in the neighbourhood of Miocene intrusive basic body and at the same time, to attribute kaolinite of pre-ore stage in the Kremnica ore district to this type.

Acknowledgement: The study was completed within the Grant O2/11 of Grant Agency for Science of Slovak Republic.

Refferences

Berger B.R. & Henley R.W., 1989: Advances in the understanding of epithermal gold-silver deposits - with special reference to deposits of the Western United States. In: Keays R., Ramsay & Groves D. (Eds.): The geology of Gold Deposits: The Prospective in 1988. *Econ. Geol. Monogr.*, 6.

Bezák V. & Lexa J., 1983: Genetic types of rhyolite volcanoclastics from the Žiar nad Hronom region. *Geol. Práce, Spr.*, 79, 83 - 112 (in Slovak).

Bonham H.F. Jr., 1986: Models for volcanic-hosted epithermal precious metal deposits: A review. International Volcanological Congress, New Zealand, Proc. Symp. 5, 13 - 17.

Böhmer M., 1966: Gold veins and paragenetic minerals from the central part of the Kremnica ore deposit. *Acta geol. geogr. Univ. Comen., Geol.*, 11, 1 - 123 (in Slovak).

Böhmer M., Gerthofferová H. & Kraus I., 1969: To the problems of alterations of Central Slovakian neovolcanites. *Geol. Zbor. Geol. Carpath.*, 20, 47 - 68.

Böhmer M. & Šímová M., 1976: Contact metasomatic aureole of Miocene intrusives in the Kremnické hory Mts. *Acta geol. geogr. Univ. Comen., Geol.*, 30, 119 - 137 (in Slovak).

Eberl D.D., Srodoň J., Lee M., Nadeau P.H. & Northrop H.R., 1987: Sericite from the Silverton caldera, Colorado: Correlation among structure, composition, origin and particle thickness. *Amer. Miner.*, 72, 914 - 934.

Gogišvili G.V., 1979: Epigenetic origin of stratified deposits of high-silica zeolits (on example of Zakavkaz). In: Nonmetallic raw materials. *Nedra*, Moskva, 65 - 75 (in Russian).

Gottardi G., 1989: The genesis of zeolites. *Europ. J. Mineral.*, 1, 479 - 487.

Hay R.L, 1986: Geologic occurrence of zeolites and some associated minerals. In: Murakami Y., Iijima A. & Ward J.W. (Eds.): Proc. 7th Internat. Zeolite Conf., Tokyo, 35 - 40.

Hayba D.O., Bethke P.M., Heald P. & Foley N.K., 1985: The geological, mineralogical and geochemical characteristics of volcanic-hosted epithermal deposits. In: Berger B.R. & Bethke P.M. (Eds.): Geology and Geochemistry of Epithermal Systems. Soc. Econ. Geol., *Rev. Econ. Geol.*, 2, 129 - 168.

Heald P., Hayba D.O. & Foley N.K., 1987: Comparative anatomy of volcanic-hosted epithermal deposits: acid-sulfate and adularia sericite types. *Econ. Geol.*, 82, 1 - 26.

Hedenquist J.W., 1987: Mineralization associated with volcanic-related hydrothermal systems in the circum-Pacific Basin. In: Horn M.K.

(Ed.): Transaction of the Fourth Circum-Pacific Energy and Mineral Resources Conference, Singapore. *Am. Assoc. Petrol. Geol.*, 513 - 524.

Horton D.G., 1985: Mixed-layer illite/smectite as a paleotemperature indicator in the Ametyst vein system. Creed district, Colorado, USA. *Contrib. Mineral. Petrol.*, 91, 171 - 179.

Kirov G.N., Pechigargov V. & Landzheva E., 1979: Experimental crystallization of volcanic glasses in a thermal gradient field. *Chem. Geol.*, 26, 17 - 28.

Knésl J. & Knéslová A., 1991: Contemporary view on the geology, metalogenesis and ore forecasts of the Kremnica Mts. ore district. *Miner. slovaca*, 23, 4, 283 - 294 (in Slovak).

Konečný V., Bagdasarjan G.P. & Vass D., 1969: Evolution of Neogene volcanism in Central Slovakia and its confrontation with absolute ages. *Acta Geol. Acad. Sci. Hung.*, 13, 245 - 258.

Konečný V. & Lexa J., 1979: Structural-geological scheme of Central Slovak neovolcanites in the scale 1:100 000. *Manuscript, archive of Geol. Inst. D.Štúr*, (in Slovak).

Konečný V., Lexa J. & Planderová E., 1983: Stratigraphical distribution of the Middle Slovakian neovolcanites. *Západ. Karpaty, Sér. Geol.*, 9, 1 - 203 (in Slovak).

Kozáč J., 1984: Zeolite tuffs of Jastrabá - Bartošova Lehôtka, applied research. *Manuscript, Geofond Bratislava*, 1 - 220 (in Slovak).

Kraus I., 1967: Petrographic-mineralogic conditions and genesis of clay sediments of the Žiarska kotlina depression. *Geol. Práce, Zprávy*, 43, 25 - 52 (in Slovak).

Kraus I., 1989: Kaolins and Kaolinite Clays of the West Carpathians. *Západ. Karpaty, Sér. Mineral. Petrogr. Geochém. Metalogen.*, 13, 1 - 287 (in Slovak).

Kraus I. & Zuberec J., 1976: Bentonites and kaolins at the SW margin of the Kremnické pohorie Mts., in the neovolcanic region of Central Slovakia. 7th Conf. Clay Miner.Petrol., Karlovy Vary, Geol., Univ. Carol. Pragensis, 439 - 449.

Kraus I., Šamajová & Zuberec J., 1979: Mineral composition altered products of rhyolite volcanism at the SW margin of the Kremnické pohorie Mts. 8th Conf. Clay Miner. Petrol., Teplice, Geol., Univ. Carol. Pragensis, 137 - 144.

Kraus I., Číčel B., Šamajová E. & Machajdík D., 1982: Origin and distribution of clays resulting from alteration of rhyolite volcanic rocks in Central Slovakia (Czechoslovakia). *Geol. Zbor. Geol. Carpath.*, 33, 3, 269 - 275.

Kraus I., Hroncová Z., Horský S. & Mihalič A., 1989: Deposits and occurrences of bentonites in territory of Slovakia. *Miner. slovaca*, 21, 521 - 531 (in Slovak).

Kusakabe H., 1982: An interpretation of zeolitic zoning around Kuroko ore deposits on the basis of hydrothermal experiments. *Mining geol.*, 32, 6, 435 - 442.

Lajčáková A. & Kraus I., 1987: Acid volcanic glasses in the Western Carpathians. 2nd Internat. Conf. on natural Glasses, Prague, 121 - 127.

Lexa J., Hojstričová V., Halouzka R., Dovina P., Šucha V., Onačila D. & Planderová E., 1984: Explanations to sheet 36 - 312 Stará Kremnička. *Manuscript, archive Geol. Inst D. Štúr*, Bratislava (in Slovak).

Lexa J., Knésl J., Hroncová Z. & Stolár M., 1989: Explanations to the regional map of deposits and prognosis of mineral raw deposits - the Kremnické vrchy Mts. *Manuscript, archive Geol. Inst. D.Štúr*, Bratislava, (in Slovak).

Magidovič V.I. & Finko V.I., 1975: Porcelaine rocks. New kinds of nonmetallic useful fossils. *Izd. Nauka*, Moskva, 46 - 62 (in Russian).

Phillips L.V., 1983: Mordenite occurrences in the Marysvale are a Piute County Utah: A field and experimental study. *Birgham Young University Geology Studies*, 30, 1, 95 - 111.

Polák S., 1957: On the alunite and alunization in the vicinity of Horný Turček in the Kremnické hory Mts. *Věst. Ústř. Úst. geol.*, 32, 5, 362 - 365 (in Slovak).

Repčok J., 1982: Dating of neovolcanites from the West Carpathians. *Manuscript, archive Geol.Inst. D.Štúr*, Bratislava, (in Slovak).

Seki Y., 1973: Ionic substitution and stability of mordenite. *J. Geol. Soc. Jpn.*, 79, 10, 669 - 676.

Senderov E.E., 1963: Crystallization of mordenite under hydrothermal conditions. *Geochemistry*, 9, 848 - 859.

Sheppard R.A., Gude A.J. & Fitzpatrick J.J., 1988: Distribution, characterization and genesis of mordenite in Miocene silicic tuffs at Yucca Mont., Nye County, Nevada. *US Geol. serv. bull.*, 1777, 1 - 22.

Šamajová E., 1979: Zeolites in acid volcanoclastics of the Kremnické pohorie Mts. 8th Conf. Clay Miner. Petrol. Teplice, Geol., Univ. Carol. Pragensis, 267 - 275.

Šamajová E., 1988: Zeolites in tuffaceous rocks of the West Carpathians (Slovakia). In: Kalló D. & Sherry (Eds.): Occurrence properties and utilization of natural zeolites. Budapest , 49 - 57.

Šamajová E. & Kraus I., 1985: Distribution of smectites and zeolites in the West Carpathians. 5th Meeting Europ. Clay Groups, Univ. Carol., Prague, 321 - 328.

Šamajová E., Kraus I. & Lajčáková A., 1991: Volcanic glass and its relation to the zeolite and clay minerals in the West Carpathians. In: Störr M., Henning K.H. & Adolphi (Eds.): Proc. 7th Euro-clay Conf., Dresden 1991, 909 - 913.

Šamajová E. , Kraus I. & Lajčáková A., 1992: Diagenetic alteration of miocene acidic vitric tuffs of the Jastrabá Formation (Kremnické vrchy Mts., Western Carpathians). *Geol. Carpath., Sér. Clays*, 1, 27 - 30.

Šamajová E., Kraus I. & Maťo L., 1993: Origin of the clay minerals in hydrothermally altered volcanic rocks in the Kremnica ore district. 11th Conf. Clay Miner. Petrol., České Budějovice., Geol., Univ. Carol., Pragensis, 37 - 46.

Štohl J., 1976: Ore mineralization of Central Slovak neovolcanites connected with central Carpathian lineament. *Západ. Karpaty, Sér. Mineral. Petrogr. Geochém. Lož.*, 2, 7 - 40 (in Slovak).

Šucha V., Kraus I., Mosser Ch., Hroncová Z., Soboleva K.A. & Širáňová V., 1992: Mixed-layer illite/smectite from the Dolná Ves hydrothermal deposit, the Western Carpathians, Kremnica Mts., *Geol. Carpath., Sér. Clays*, 1, 13 - 19.

White N.C. & Hedenquist J.W., 1990: Epithermal environments and styles of mineralization: variations and their causes, and guidelines for exploration. *J. Geoch. Explor.*, 36, 445 - 474.