GEOLOGICA CARPATHICA, 50, 5, BRATISLAVA, OCTOBER 1999
353–364

USE OF ILLITE FOR K/Ar DATING OF HYDROTHERMAL PRECIOUS AND BASE METAL MINERALIZATION IN CENTRAL SLOVAK NEOGENE VOLCANIC ROCKS

IVAN KRAUS[1], IGOR V. CHERNYSHEV[2], VLADIMÍR ŠUCHA[1], VLADIMÍR A. KOVALENKER[2], VLADIMÍR A. LEBEDEV[2] and EVA ŠAMAJOVÁ[1]

[1]Faculty of Science, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovak Republic
[2]Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, Staromonetny Pereulok 35, 109017 Moscow, Russia

(Manuscript received December 9, 1998; accepted in revised form June 22, 1999)

Abstract: In all important stages of hydrothermal precious and base metal mineralization in the Central Slovak Neogene volcanic rocks the characteristic assemblages of clay minerals can be distinguished, in which illite and mixed-layer illite/smectite of various polytypes play an important role. Our study has confirmed that the illite polytypes can provide information on the thermodynamic conditions that prevailed during the formation of precious and base metal mineralization in the Central Slovak Neogene volcanic area. The results of K/Ar dating of illites from hydrothermally altered zones, such as those observed in most hydrothermal precious and base metal mineralizations in the Central Slovak Neogene volcanic area are reported for the first time. They bring new information on the time interval of the hydrothermal mineralization. The main stages took place 12.4±0.1–11.03±0.1 Ma in all the important ore districts within the Central Slovak Neogene volcanics.

Key words: stratovolcanoes, advanced argillitic alteration, mineral assemblage, illite polytypes, mixed-layer illite/smectite.

Introduction

The age determinations performed by radiometric/isotopic geochronological methods are an important part of the metallogenetic model of the hydrothermal, precious and base metal mineralization in the Banská Štiavnica and Kremnica stratovolcanoes. Onačila et al. (1995) proposed a metallogenetic model for the Central Zone of the Banská Štiavnica stratovolcano which visualizes several stages of mineralization spanning the time of some 6 Ma. The age determination made on the intrusive rocks from the Central Zone of the Banská Štiavnica stratovolcano and on sericite[1] from epithermal, vein precious and base metal mineralization using K/Ar dating, reported in the paper of Chernyshev et al. (1995), reduced the time span of the Banská Štiavnica stratovolcano rocks and the base metal mineralization to approximately 1–2 Ma. Geochronological datings of analogous epithermal, precious and base metal mineralizations, made worldwide during the past 25 years confirmed a similar time range (Silberman et al. 1972; Ashley & Silberman 1976; Silberman 1985; Noble et al. 1991; Setterfield et al. 1992; Conrad et al. 1993; Alderton et al. 1998). One of the reasons why the timing used in the metallogenetic model of the Central Zone of the Banská Štiavnica stratovolcano is incompatible with the world-wide data is the absence of geochronological study of clay minerals which occur in the altered salband zones, or directly within the vein fillings. The illite appears to be most suitable for the K/Ar dating, especially when its origin is concurrent with the hydrothermal mineralization and when its development was monomineral.

This is the reason why a complex mineralogical-geochemical study of altered zones, especially in the epithermal precious and base metal deposits in the areas underlain by Neogene volcanic rocks, is so important. In the area of outcrop of Neogene volcanic rocks in Central Slovakia we used this method to date illite and mixed-layer illite/smectite, which formed during the most significant stages of hydrothermal mineralization in the Banská Štiavnica and Kremnica stratovolcanoes. Our work was inspired by the results of Chernyshev et al. (1995) who presented the first K/Ar datings made on illite from epithermal, precious and base metal veiny mineralization of the Banská Štiavnica-Hodruša ore district (Terézia vein).

In present paper we do not intend to address the problems related to the geology and mineralizing conditions of the Banská Štiavnica and Kremnica stratovolcano, because these were already addressed in detail and reported by several authors (Štohl 1976; Burian et al. 1985; Štohl & Kaličiak 1989; Knésl & Knéslová 1991; Kovalenker et al. 1991; Onačila & Rojkovičová 1992; Onačila et al. 1995; Lexa et al. 1997). We do, however, focus on the synoptic characterization and timing of different stages of hydrothermal mineralization and of the altered zones in the Banská Štiavnica and Kremnica stratovolcanoes.

Characteristic features of the hydrothermal mineralization of the Banská Štiavnica and Kremnica stratovolcanoes

Our classification of the hydrothermal mineralization of the Central Zone of the Banská Štiavnica stratovolcano is based on the concepts of Štohl & Lexa (1990), Štohl et al. (1994) and Onačila et al. (1995), and we summarize it as follows:

[1] In the paper of Chernyshev et al. (1995) the term sericite has only a petrological meaning. We use this term for the mineral in separated fraction composed of particles measuring less then 4 μm across and having on the XRD difractogram the d(001) reflex within the range 1.0 nm, as in illite.

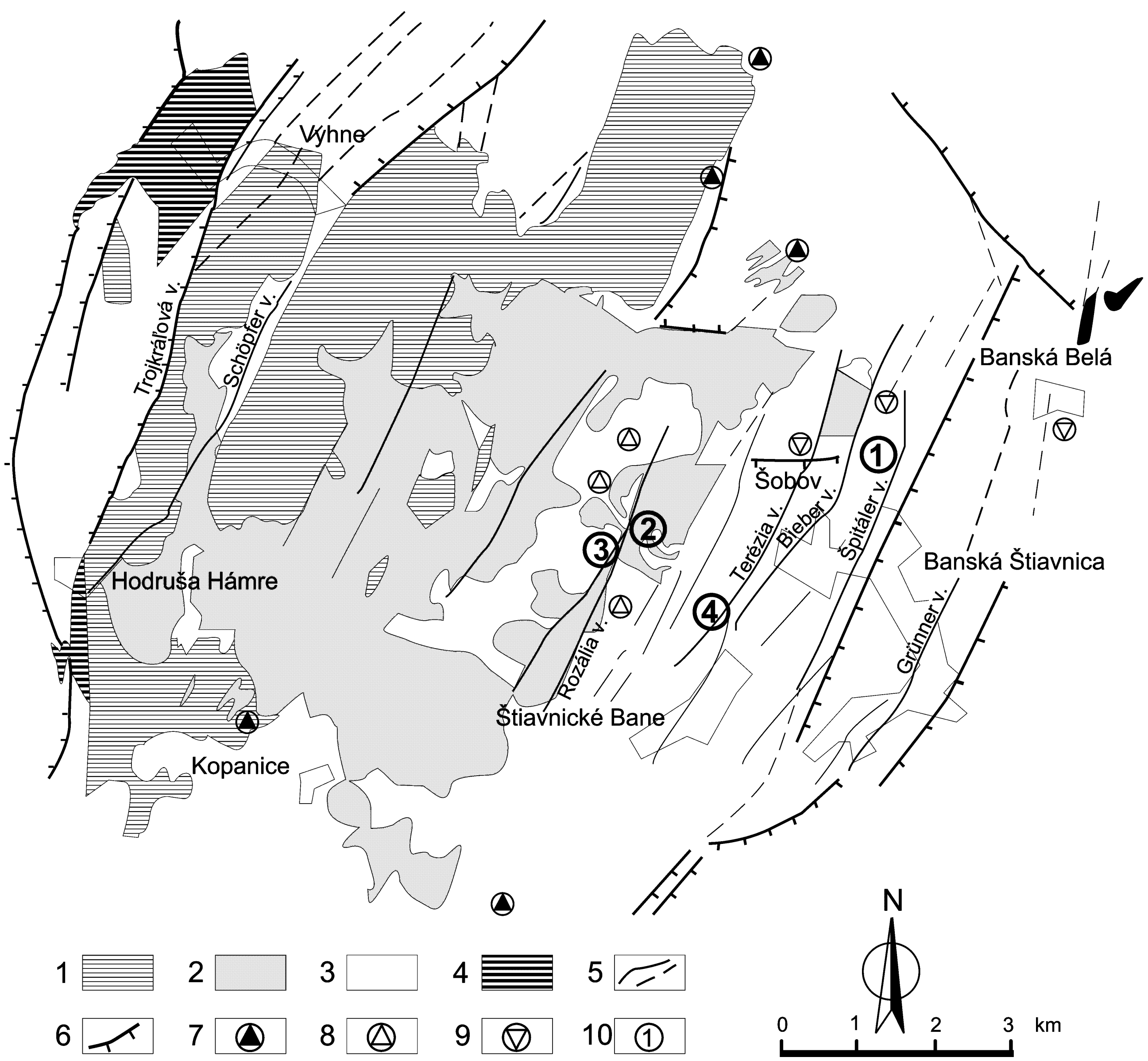

Fig. 1. Structural and metallogenetic scheme of the Banská Štiavnica-Hodruša ore district of the Central Zone of the Štiavnica stratovolcano. Settled according to Lexa et al. (1999). *Explanations:* 1 — basement; 2 — granodiorite, diorite, granodiorite porphyry, and quartz-diorite porphyry (Upper Badenian); 3 — propylitized andesite and andesite porphyry complex (Upper Badenian); 4 — rhyolites (Upper Sarmatian-Lower Pannonian); 5 — ore veins (a) and unmineralized faults (b); 6 — marginal faults of the resurgent horst; 7 — porphyry/skarn copper deposits and occurrences; 8 — stockwork/disseminated base metal deposits and occurrences; 9 — advanced argillic (high sulphidation) alterations; 10 — location of the samples collected for K/Ar dating from the Banská Štiavnica stratovolcano.

The older types of hydrothermal mineralizations, which include the stockwork-disseminated base metal mineralization of the Šobov hydrothermal system near Banská Štiavnica (Štohl & Lexa 1990), the stockwork-disseminated base metal mineralization in the surroundings of the Rozália vein near Banská Hodruša (Gavora 1983) and the porphyry-copper mineralization of skarn type, among which the Zlatno deposit is the most important (Rozložník & Zábranský 1971), developed under compressional, disjunctive, tectonic conditions during the pre-caldera stage. The presumed sources of energy and fluids are related to quartz-diorite, granodiorite and quartz-diorite porphyry intrusions of the Central Zone of the Banská Štiavnica stratovolcano. Hydrothermal wallrock alteration associated with the above mentioned types of ore mineralization is predominantly of zonal character. Using Nakovnik's (1964) concept, it can be assigned to the formation of secondary quartzites, whereas in the Sillitoe's (1973) concept, it belongs to the advanced argillitic alteration, or to a phyllic zone.

The ganister quartzites which occur near Šobov and next to the Rozália vein near Banská Hodruša (Fig. 1) and are the products of these hydrothermal alteration processes in the Central Zone of the Banská Štiavnica stratovolcano, became the subjects of our study.

The younger type of hydrothermal, precious and base vein metal mineralization developed under extensional tectonic conditions, during the post-caldera stage and with intensive participation of meteoric waters. The rhyolites of the Jastrabá Formation, defined by Konečný et al. (1983) are presumed sources of energy and fluids. Hydrothermal wallrock alteration associated with the vein mineralization has a linear character. For a detailed study of the hydrothermal alteration products found within the Central Zone of the Banská Štiavnica stratovolcano, we selected those from the Svetozár and Rozália vein systems near Banská Hodruša, from the Terézia vein near Banská Štiavnica (Fig. 1) and from the Central and Southern parts of the Kremnica stratovolcano (Fig. 2).

Analytical methods

Samples from hydrothermally altered zones of the precious and base metals vein mineralization of the Banská Štiavnica and Kremnica stratovolcanoes were studied using optical polarization microscope. The fraction below 2 μm was isolated using the sedimentation method and both, oriented and non-oriented slides were prepared for the XRD analysis. The latter were prepared by mixing the clay fraction with the melted colophony. The oriented preparates were studied in natural form and after saturation with ethylene glycol (8 hours in ethylene glycol vapour at 60 °C). The lattice parameters in the assemblages of clay minerals selected from samples containing illite and/or mixed layer illite/smectite and their polytypes were measured using the PW 1710 Philips XRD instruments, operating with Ni filtered Cu/Kα radiation.

The K-Ar dating of illite samples was performed with use of a highly-sensitive mass-spectrometer low-blank complex which includes a M1-1330 mass-spectrometer as well as a gas extraction system. Static regime of argon isotope analysis was realized. A total blank of all the system units was less than 8×10^{-3} ng of ^{40}Ar. The isotope dilution method with the ^{38}Ar monoisotope was used. The $^{40}Ar_{rad}$ and potassium determinations errors exhibited in the Table are individual for $^{40}Ar_{rad}$ and K, whereas K-Ar age values attended by 1σ-errors. The age calculations were made using the following constants: $\lambda_\beta = 4.962\times10^{-10}$ years, $\lambda_e = 0.581\times10^{-1}$ years^{-1}, $^{40}K/K = 0.01167$ at. %.

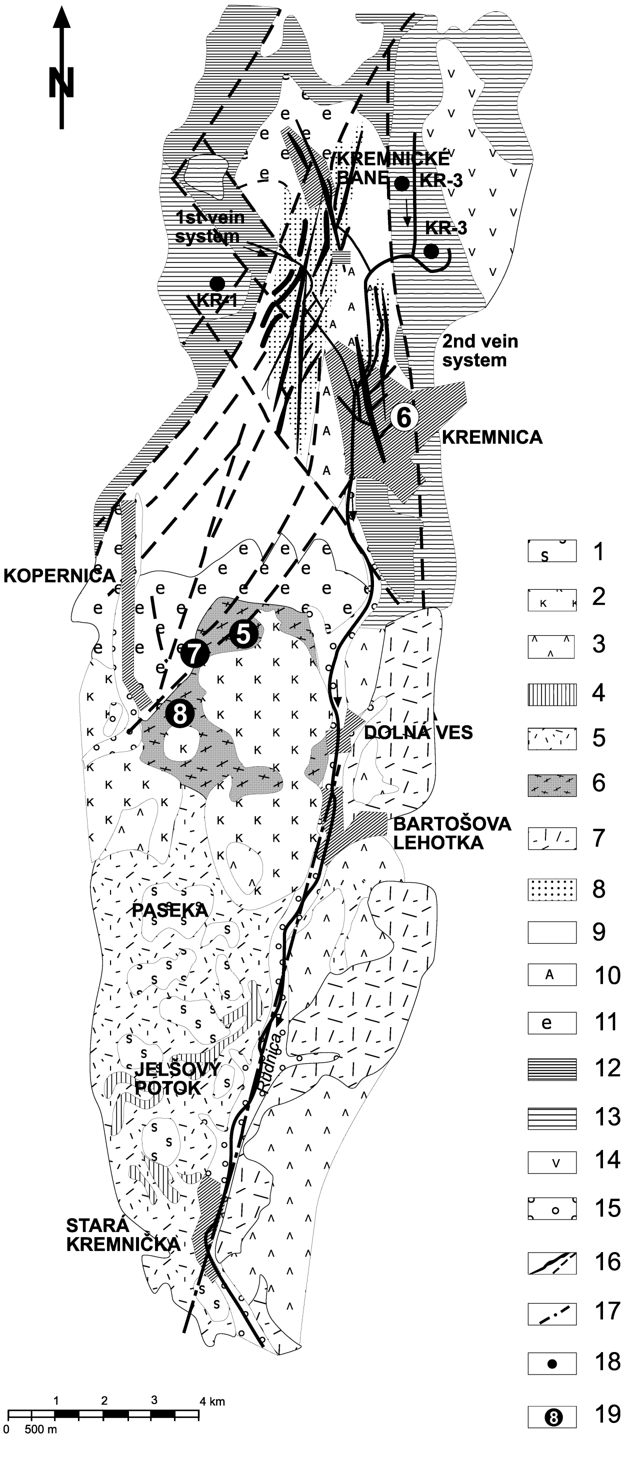

Fig. 2. Scheme of diagenetic and hydrothermal alteration of the Kremnica ore district in the Central and Southern parts of the Kremnica stratovolcano (according to Kraus et al. 1994). Explanations: the Jastrabá Formation (Upper Sarmatian-Lower Pannonian) 1 — hydrothermally altered rhyolite extrusions with prevalence of smectite; 2 — hydrothermally altered rhyolite intrusions with prevalence of kaolinite; 3 — rhyolite extrusions, intrusions and lava flows not affected by hydrothermal alterations; 4 — limnoquartzites; 5 — diagenetically altered rhyolite volcanoclastics with prevalence of smectite and clinoptilolite; 6 — hydrothermally altered rhyolite volcanoclastics with prevalence of mixed-layer illite/smectite and kaolinite; 7 — volcanoclastics not affected by hydrothermal alterations. The Zlatá Studňa Formation (Lower and Upper Badenian); 8 — hydrothermal wall rock alteration of andesites and andesite porphyries with kaolinite, illite, mixed-layer illite/smectite and adularia; 9 — propylitized andesites and andesite porphyres with prevalence of smectite; 10 — intrusive body of amphibolite-pyroxenic andesite porphyry; 11 — effusive complex of pyroxenic and leucocrate andesite; 12 — The Turček Formation (Upper Badenian-Lower Sarmatian): lava flows, pyroclastics and epiclastics of basaltoids and pyroxenic and leucocrate andesite; 13 — The Kremnický Peak Formation (Upper Badenian): effusive amphibolite-pyroxenic andesite; 14 — The Krahule Formation (Lower Sarmatian): extrusions of biotitic-amphibolite andesite; 15 — aluvium; 16 — ore veins (a) and weakly mineralized faults (b); 17 — faults; 18 — boreholes; 19 — location of the samples collected for K/Ar dating from the Kremnica stratovolcano.

Assemblages of clay minerals from the Banská Štiavnica and Kremnica stratovolcanoes

All important stages of hydrothermal, precious and base metal mineralization in the Banská Štiavnica and Kremnica stratovolcanoes have the characteristic assemblages of clay minerals. Illite and/or mixed layer illite/smectite of various polytypes are common constituents.

The Sillitoe's (1973) stage of advanced argillitic alteration is in the Central Zone of the Banská Štiavnica stratovolcano genetically and spatially bound to an older, stockwork/disseminated base metal mineralization. For several years it was a subject of studies in the broader surroundings of the quartzite deposit at Šobov, a source of ganister production, in the Rozália vein and at other occurrences studied in detail by Žáková in Štohl et al. (1988). Advanced argillitic alteration of the Šobov hydrothermal system has the spatial and chronological links to the quartz-diorite intrusive activity. On the other hand, the advanced argillitic alteration associated with the stockwork/disseminated base metal mineralization in the Rozália vein is spatially and temporally linked to the granodiorite (Štohl et al. 1988).

Our investigations, as well as the results of other authors (Polák 1963; Radzo 1969; Oružinský 1989; Žáková & Štohl 1992; Žáková et al. 1995; Onačila et al. 1995; Uhlík & Šucha 1997) have shown that four mineral associations, all important in terms of the alterations and formation of clay minerals (Table 1), can be distinguished in the Šobov hydrothermal system.

The first is the mineral assemblage dominated by pyrophyllite. Another most common mineral is kaolinite which occurs mainly in marginal parts of the quartzite bodies. Alunite and diaspore occur only sporadically.

The second is the mineral assemblage in which the illite of the polytype $2M_1$ is the most common clay mineral of the Šobov hydrotermal system. It associates with pyrophyllite, but the two minerals may also occur separately (Fig. 3). There are indications that illite preferably concentrates in the marginal parts of the quartzite bodies (Uhlík & Šucha 1997). Chlorite sporadically associates with illite.

The third is the mineral assemblage dominated by mixed-layer illite/smectite, which occurs in the area of Červená Studňa, at the western end of Šobov. The XRD difractogram and the crystallochemical formulas indicate the presence of regular mixed-layer illite/smectite-like rectorite, but its K_2O content is low (Table 2, Fig. 4).

The fourth assemblage consists of adularia and illite, identified by Štohl et al. (1987) in the 12^{th} horizon of the Šobov hydrothermal system, 500 m below the Šobov quarry. However, we did not study the illite from this assemblage.

Advanced argillitic alteration in the surroundings of the Rozália vein has several features in common with the Šobov hydrothermal system (Table 1). However, a different situation is found in the surroundings of the Rozália vein where the illite predominates over pyrophyllite. Diaspore and alunite are totally absent, as is adularia. The presence of a mixed-layer mineral is very probable, but was not yet identified precisely.

Hydrothermal alteration adjacent to precious and base metal veins always has a linear course. Maťo et al. (1996) distinguish "mesothermal" and "epithermal" stages here. Because

Table 1: The assemblages of clay minerals on advanced argillic alteration. *The sample with K/Ar dating.

Deposit	Banská Štiavnica-Šobov	Banská Hodruša-Rozalia vein
mineral assemblage		
I.	pyrophyllite±kaolinite, diaspor, alunite	±pyrophyllite, kaolinite
II.	*illite $2M_1$±pyrophyllite, chlorite	*illite $2M_1$>>1M
III.	regular mixed-layer I/S like rectorite	?
IV.	illite + adularia	–

Table 2: Crystallochemical formulas of regular mixed-layer rectorite like minerals. Explantions: 4488 and 4490 — the Červená Studňa Formation, near the Šobov hydrothermal system; B-2/590 m — bore hole Banská Belá, the North eastern part of the Banská Štiavnica-Hodruša ore district; DV-4 — bore hole Dolná Ves, the Southern part of the Kremnica ore district. *Analyzed in Sr form, ** analyzed in Na form.

Sample	type of illite/smectite	Si	$Al^{(IV)}$	$Al^{(VI)}$	Fe	Mg	Na	K	Sr
4488	rectorite	6.77	1.23	3.67	0.16	0.28	0.37	0.43	0.22*
4490	rectorite	6.71	1.29	3.72	0.11	0.33	0.30	0.40	0.22*
B-2/590	K-rectorite	7.07	0.93	3.71	0.08	0.33	0.07	0.85	
DV-4	K-rectorite	7.00	1.00	3.62	0.16	0.26	0.18**	0.85	

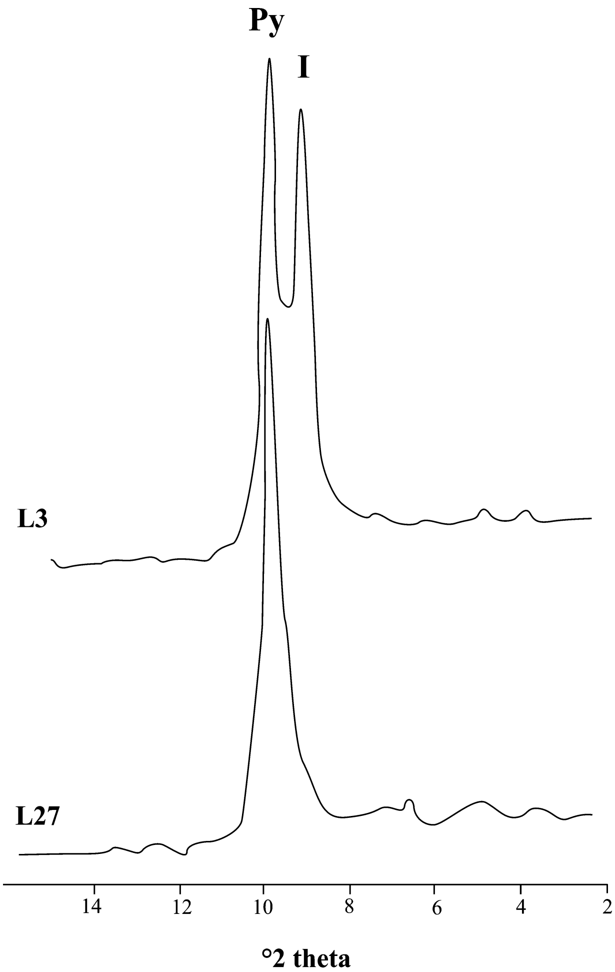

Fig. 3. XRD-pattern of pyrophyllite /P/ and pyrophyllite with admixture of illite /I/. Mineralization of advanced argillic alteration, Banská Štiavnica-Šobov.

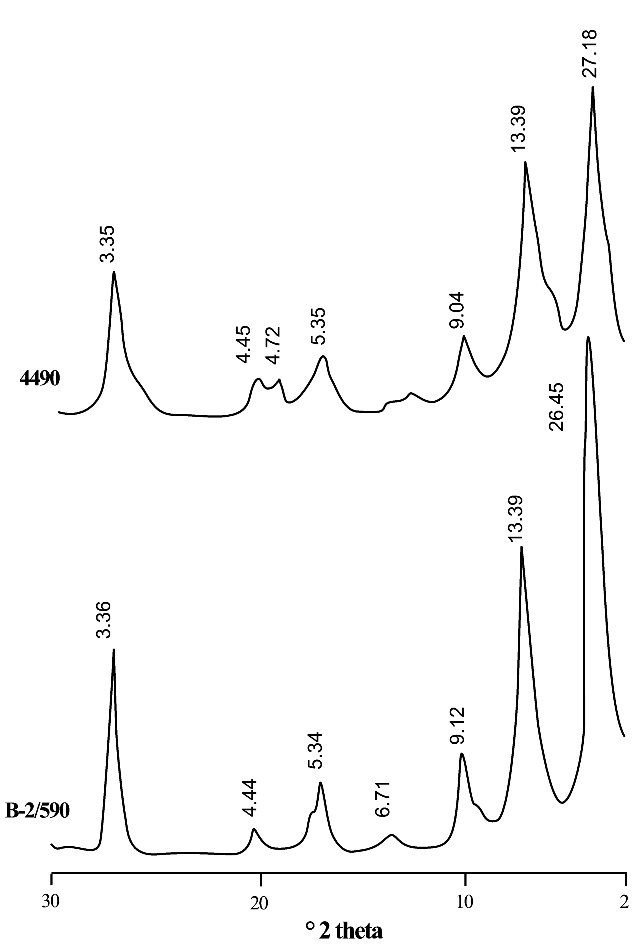

Fig. 4. XRD-pattern of regular mixed-layer minerals illite/smectite-like rectorite, Banská Štiavnica stratovolcano. *Explanations:* 4490 — mineralization of advanced argillic alteration, Banská Štiavnica-Červená Studňa, B-2/590 m — mineralization of epithermal vein precious and base metal, bore hole B-2, Banská Belá.

we think that the term "higher temperature epithermal stage" is more suitable instead "mesothermal", we adhere to it in the following text.

We assign the assemblage of clay minerals with adularia from the Svetozár vein, a part of the precious and base metal deposit of Banská Hodruša, to the higher temperature epithermal stage. It consists of several generations of quartz and carbonates, with gold of high fineness (Maťo et al. 1996). The wallrock alteration appears in a narrow zone along the vein. The illite in it occurs as the $2M_1$ and 1M polytypes. In some sections in the external part, chlorite predominates. In the higher temperature stage, kaolinite and mixed-layer ilite/smectite are absent (Table 3).

Compared with the higher temperature epithermal stage, the mineral assemblage of the epithermal stage is more complicated. The materials from the Rozália and Terézia veins and from the Central and Southern Zones of the Kremnica ore district were studied. In the wallrock alteration zone of the Rozália and Terézia veins, the polytypes of illite 1M and $2M_1$ were found, which is analogous to the findings of Rusinov et al. (1993).

Gold of low fineness and electrum, both hosted by quartz and sulphides, predominate in the epithermal veins of the Kremnica ore district (Böhmer 1966). In the Kremnica ore district, the altered salbands of the epithermal stage are more intensely disintegrated than those in the Rozália deposit, near Banská Hodruša and attain a thickness of some 10 m. In the epithermal, precious and base metal vein mineralization we distinguished three mineral assemblages, as did Böhmer et al. (1969), Kraus (1989), Šucha et al. (1992) and Kraus et al. (1994) before. During the first, the conditions were favourable for the development of kaolinite with local smectite and chlorite admixtures. During the second, the 1M polytype illite and adularia formed and as at deposits with the advanced argillitic alteration, the mineralization was concluded when the conditions became suitable for the formation of regular mixed layer illite/smectite-like rectorite. The XRD difractogram and crystallochemical formulas indicate a presence of regular mixed layer illite/smectite, with increased content of K_2O, similar to K-rectorite (Table 2, Fig. 4). It is of interest that regular mixed layer illite/smectite-like K-rectorite was not only found in the southern part of the Kremnica ore district, near Dolná Ves, but also in the northeastern part of the Banská Štiavnica-Hodruša ore district near Banská Belá (Table 2).

Determination of illite polytypes

The illite polytypes are suitable for use in modeling of the geological and metallogenetic processes (Velde 1965; Eberl et al. 1987). Our study has confirmed that the illite polytypes can provide information on the thermodynamic conditions that pre-

Table 3: The assemblages of clay minerals on higher temperature epithermal and epithermal vein precious and base metal deposits. *The sample with K/Ar dating.

stage	higher temperature epithermal	epithermal		
deposit	Banská Hodruša Svetozár vein	Banská Hodruša Rozália vein	Banská Štiavnica Terézia vein	Kremnica and Dolná Ves Central and Southern part of Kremnica ore district
mineral assemblage				
I.	*$2M_1$>>1M illite + chlorite, adularia	kaolinite ± smectite, chlorite		
II.	–	*1M>>$2M_1$ illite + adularia		*1M illite + adularia
III.	–	*regular mixed-layer I/S-like K-rectorite		

vailed during the formation of precious and base metal mineralization in the Central Slovak Neogene volcanic rocks (Fig. 5).

The presence of $2M_1$ polytype in the stockwork/disseminated base metal mineralization, accompanied at Šobov by advanced argillitic alteration, has been confirmed. In the surroundings of Rozália vein, where the advanced argillitic alteration is accompanied by the stockwork/disseminated mineralization, as well as in the Svetozár vein, in which the higher temperature epithermal precious and base metal mineralization occurs, the $2M_1$ illite polytype contains an admixture of $1M(2M_1>>1M)$. In the epithermal precious and base metal vein mineralization found in the Terézia vein in Banská Štiavnica, the predominance of 1M illite polytype was confirmed, but small amounts of $2M_1$ illite polytype and $(1M>>2M_1)$ also occur. A specific feature of the epithermal precious and base metal vein mineralization in the Central and Southern Zones of the Kremnica ore district is the exclusive presence of 1M illite polytype. A similar pattern of illite polytypes was also confirmed in the altered zones of the epithermal precious metal Neoid mineralization in Nevada (Hauff et al. 1991).

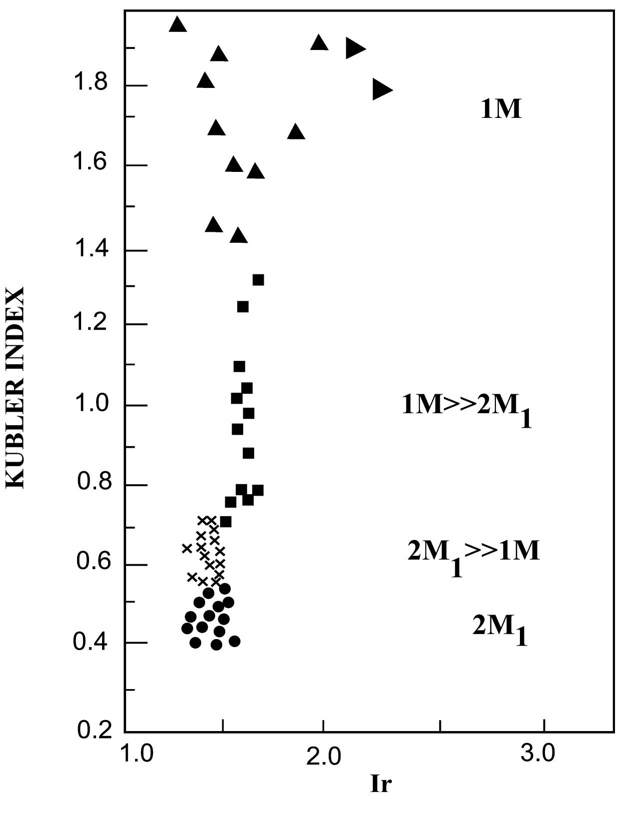

Fig. 5. Plot of illite crystallinity index (Kubler 1968) versus Ir index (Środoń 1984). Ir index should represent trace contents of expandable interlayers in illite structure. Explanations: ● advanced argillic alteration of the Šobov hydrothermal system, Banská Štiavnica-Šobov; × advanced argillic alteration of the stockwork/disseminated base metal mineralization, Banská Hodruša-Rozalia vein, outcrop; ✕ higher temperature epithermal vein precious and base metal mineralization Banská Hodruša-Svetozár vein; ■ epithermal vein precious and base metal mineralization, Banská Štiavnica-Terézia vein; ▲ epithermal vein precious and base metal mineralization, Kremnica ore district — Central part; ▶ epithermal vein precious and base metal mineralization, Kremnica ore district—Southern part.

At the same time at all occurrences relationships exist between the Kubler's crystallinity indexes obtained from illites and illite polytypes. The highest degree of crystallinity was found in the illite of the $2M_1$ polytype, which forms exclusively under advanced argillitic alteration conditions in the stockwork disseminated base metal mineralization of the Šobov hydrothermal system. The crystallinity of illite gradually decreases through the higher temperature epithermal to epithermal precious and base metal vein mineralization of the Banská Štiavnica and Kremnica statovolcanoes. In the Kremnica stratovolcano, a more advanced differentiation took place within the Central and Southern Zones of the Kremnica ore district. With increasing content of expanded layers in mixed-layer illite/smectite, the crystallinity of illite layers decreases from north to south indicating that the temperatures of hydrothermal solutions dropped.

High sulphidation and low sulphidation types of hydrothermal alterations in the Banská Štiavnica and Kremnica stratovolcanoes

Since the second half of eighties, the importance of study of the alteration processes at epithermal, precious and base metal vein deposits dramatically increased. This is mainly because the knowledge of hydrothermal alteration processes in many world deposits, located mostly in Neogene volcanic rocks, became standard criteria to determine which of the two contrasting fluid types was involved in the mineralization. One of them has the pH value indicative of an acid environment and the other has values close to a neutral environment. To classify them, Bonham (1986) coined the term "high sulphur" and "low sulphur". Meanwhile, Heald et al. (1987) introduced the terms "acid sulphate" and "adularia-sericite". Hedenquist (1987) recommended use of the terms "high sulphidation" and "low sulphidation" and it is these terms that are now mostly used in the Western Carpathians.

It was shown that it is not right to classify the hydrothermal deposits as two types on the basis of minerals present in the altered zones alone, but it is also necessary to determine the temperature, pressure and salinity of the hydrothermal solutions, as well as the changes in the ^{34}S isotope ratio in coexisting sulphides and sulphates, in the CO_2/H_2S ratios etc. Most data from the region made up of the Central Slovak Neogene volcanic rocks were obtained very recently (Kovalenker et al. 1991; Rusinov et al. 1993; Háber et al. 1998; Štohl et al. 1994; Onačila et al. 1995) and the age determinations are reliable, thus they can be fully used in modeling of metallogenetic processes.

All illites and mixed-layer illite/smectite in the altered salbands located in the Banská Štiavnica and Kremnica stratovolcanoes, which were used for K/Ar dating or age determination of precious and base metal mineralization, can be assigned to two contrasting mineralization types, characterized above.

Most high sulphidation types of hydrothermal alteration in the Central Slovak Neogene volcanic rocks associate with the advanced argillitic alteration which was brought about by the stockwork/disseminated base metal mineralization. Pyrophyllite was shown to be a typomorphic mineral for the high sulphidation systems, probably for the whole region of the Central Slovak Neogene volcanic rocks and, unambiguously, also for the Central Zone of the Štiavnica stratovolcano. High amounts of illite belonging exclusively to the $2M_1$ polytype and a low share of alunite and diaspore are characteristic features of the high sulphidation in the Šobov hydrothermal system. Onačila et al. (1995) explain the sporadic presence of alunite as a consequence of erosion of the upper part of the Šobov quartzites.

A characteristic feature of the high sulphidation type of the hydrothermal alteration in the area of Rozália vein is that $2M_1{>>}1M$ illite prevails over pyrophyllite.

On the basis of the stability diagram of the mineral phases in the altered rocks and the dependence on the activity of individual components and sulphur (Titley & Bean 1981; Hayba et al. 1986) in the Šobov hydrothermal system we presume the following time succession for the high sulphidation alteration process: alunite (?) $\rightarrow$ diaspore $\rightarrow$ pyrophyllite + kaolinite $\rightarrow$ illite $2M_1$ $\rightarrow$ regular illite/smectite-like rectorite (?).

The stability of pyrophyllite begins at temperatures around 270 °C and diaspore is usually present in the deeper parts of the high sulphidation systems. Using our present knowledge of the distribution of alunite, its position is problematic. To assign its position in the succession scheme we set out from the assumption that in the Šobov hydrothermal system, the content of sulphur was either gradually reduced, or its oxidation state has changed. This is indicated by the younger, low sulphidation type of mineralization consisting of sericite–adularia mineral assemblage, found by Štohl et al. (1987) some 500 m below the level of the Šobov quarry. This implies that illite, uncontaminated by illite polytypes and belonging to other, younger mineralization stages (Fig. 5) formed within the longest interval, during the existence of the Šobov hydrothermal system. The regular mixed-layer mineral illite/smectite-like rectorite with a low content of K_2O (Table 2) may belong to the high sulphidation type, but this is not yet unambiguously confirmed. This is due to the fact that the hydrothermal alteration of the Červená Studňa Formation, in which this mineral was found, was not definitely identified as part of the Šobov hydrothermal system (Lexa et al. 1997).

The statement of Žáková (in Onačila et al. 1995) is of essential importance for the characterization of the high sulphidation hydrothermal alteration in the area of Rozália mine near Banská Hodruša. She discovered that the presence of an illite generation belonging to the younger, epithermal, precious and base metal mineralization at Rozália vein cannot be excluded. This is a contrary to the Šobov hydrothermal system. It is superimposed on the generation of illite which belongs to the high sulphidation type of hydrothermal alteration which formed in connection with the stockwork/disseminated base metal mineralization. This circumstance may be indicated by the presence of two illite polytypes, the $2M_1$, present exclusively in the Šobov hydrothermal system and the 1M, represented mostly in the epithermal vein precious and base metal mineralization.

In the Central Slovak Neogene volcanic rocks, low sulphidation types of hydrothermal alterations form in association with the epithermal vein precious and base metal mineralization. Of the clay minerals, the illite and regular mixed-layer illite/smectite-like K-rectorite are shown to be typomorphic minerals of the low sulphidation systems, probably for the whole region of the Central Slovak Neogene volcanic rocks outcrop, which is definitely also valid for the epithermal vein precious and base metal mineralization in the Banská Štiavnica-Hodruša and Kremnica ore districts. With decreasing temperature, the share of $2M_1$ polytype in the low sulphidation type of the Banská Štiavnica-Hodruša ore district also decreases at the expense of 1M polytype (Fig. 5). In the low sulphidation type of the Kremnica ore district, the 1M polytype is exclusively present in illite, and the regular mixed-layer illite/smectite-like K-rectorite.

In the low sulphidation type of the higher temperature epithermal vein precious and base metal mineralization, the conditions in the altered salband zone are relatively simple. Of the clay minerals, the $2M_1{>>}1M$ illite polytype forms in the inner part of the zone, while chlorite prevails in the outer part of the zone.

The succession of clay mineral formation in the low sulphidation type of epithermal vein precious and base metal mineralization in the Kremnica ore district was studied by Kraus (1989) and Kraus et al. (1994). These results, as well as the temperature determinations, pH values and fluid salinities from the epithermal, vein precious and base metal mineralization in the Banská Štiavnica-Hodruša and Kremnica ore districts (reported by Onačila et al. (1995), Háber et al. (1998) and Bebej & Dubaj (1993)) confirm the concept that clay minerals of the low sulphidation type developed in two stages.

During the first stage, the conditions were suitable for transformation of kaolinite and with the increasing pH value of fluids, smectite and chlorite developed. At the beginning of the second stage, potassium metasomatism caused the formation of 1M illite (Kremnica ore district) or illite $1M{>>}2M_1$ (Banská Štiavnica-Hodruša ore district). At the end of this stage the conditions were favourable for the formation of regular mixed-layer illite/smectite-like K-rectorite. This is shown by the conditions that prevailed in the northeastern part of the Banská Štiavnica-Hodruša ore district near Banská Belá, or in the southern part of the Kremnica ore district near Dolná Ves (Table 2, Fig. 4).

Šucha et al. (1992) and Fuchs (1994) confirmed that the degree of K-rectorite illitization during the K-metasomatism decreases from north to south, that is towards the sinking temperature of hydrothermal solutions. This is in good agreement with the results of study of gaseous-fluid inclusions (Bebej & Dubaj 1993).

There is no doubt that adularia is a typomorphic, non-clay mineral of the low sulphidation type of hydrothermal alterations throughout the Central Slovak Neogene volcanic rocks. According to information from various authors (Böhmer 1966; Hojstričová in Štohl et al. 1987; Kraus 1989), adularia forms due to metasomatic replacement of plagioclases and of the matrix of andesites, rhyolites and their volcanoclastic derivatives. Adularia is a part of quartz veins in these rocks, or forms separate crystals in rhyolite tuffs. The contents of K_2O in hydrothermally altered rocks of this type varies within the range between 7 and 10 %.

Age of hydrothermal alterations

To determine the age of hydrothermal alterations that took place during separate ore-forming processes in the Banská Štiavnica and Kremnica stratovolcanoes using K/Ar dating, we strictly selected the monomineral and precisely defined illite polytypes. Detailed investigation of altered salband zones with determination of the mineral assemblage with which illite is associated in different deposits confirmed its synchronous position within the individual mineralizing stages. The characterization of individual samples and the results of K/Ar datings are shown in Tables 4 and 5.

The oldest hydrothermal alteration process in the area under study is the advanced argillitic alteration found in the deposit of ganister quartzite at Šobov, which gave the age 12.4 ± 0.1 Ma. Štohl & Lexa (1990) associate the stockwork/disseminated base metal mineralization of the Šobov hydrothermal system with quartz diorite. Onačila et al. (1995) do not report any datings of quartz diorites from the Šobov hydrothermal system, because they are intensely altered.

Our age determination of advanced argillitic alteration associated with the stockwork/disseminated base metal mineralization in the surroundings of Rozália vein gave the age 11.5 ± 0.3 Ma. On the basis of geological criteria, Štohl & Lexa (1990) genetically and spatially associate this mineralization with the granodiorite body which intruded the Central Zone of the Banská Štiavnica stratovolcano after the intrusion of quartz diorite. On the basis of K/Ar dating of amphibole from the granodiorite located near the stockwork/disseminated base metal mineralization, Štohl et al. (1994) report its age as 15.9 ± 0.7 Ma. Chernyshev et al. (1995) published the age of 12.6 ± 0.8 and 12.5 ± 0.6 Ma for granodiorite porphyry and for quartz porphyry of the second and third volcanic stage of the Central Zone of the Banská Štiavnica stratovolcano as defined by Onačila et al. (1995). On the basis of structural-superpositional relations, biostratigraphical data and the results of K/Ar dating of pyroxenic and amphibole-pyroxene andesites of the first volcano-tectonic stage of the Central Zone of the Banská Štiavnica stratovolcano (Kantor & Durkovičová 1985; Kantor et al. 1988), the pre-caldera stage of the Central Zone of the Banská Štiavnica stratovolcano and of the mineralization associated with it, is placed within the time interval 16.4–14.8 Ma (Onačila et al. 1995).

Considering the K/Ar dating of $2M_1$>>1M illite polytype which gave the age of 11.9 ± 0.3 Ma, the setting of the higher temperature epithermal vein precious and base metal mineralization distinguished by Maťo et al. (1996) in the Svetozár vein system in the 14th horizon of the Rozália mine seems to be justified.

Most K/Ar datings made so far on the 1M>>$2M_1$ polytype of illites were obtained from epithermal vein precious and base metal mineralization from the Terézia vein. The isochrone from four samples constructed by Chernyshev et al. (1995) gives the age 12.1 ± 0.2 Ma. The sample of a monomineral illite, taken from the Terézia vein to support the results of this paper gave an age of 11.4 ± 0.2 Ma.

In the metallogenetic model of Onačila et al. (1995), the epithermal vein precious and base metal mineralization of the Central Zone of the Banská Štiavnica stratovolcano is assigned to the post-caldera stage on the basis of dating of rhyolite of the Jastrabá Formation (12.4–10.7 Ma) and on structural-superpositional and biostratigraphical grounds. An age of 13.5–12.0 Ma is assigned to the initial stage of epithermal, mostly base metal mineralization. The subsequent stage of epithermal, mostly precious metal mineralization, was assigned an age of 12.0–10.5 Ma.

We have paid much attention to the dating of 1M polytype illite and to regular mixed-layer illite/smectite such as K-rectorite from the Central and Southern parts of the Kremnica ore district. The illite developed during the main phase of epithermal vein precious and base metal mineralization. K/Ar dating of two samples gave practically identical ages of 11.1 ± 0.1 and 11.03 ± 0.1 Ma. The closing stage of the epithermal vein formation was already free of significant precious metal mineralization. The conditions became suitable for the development of regular mixed-layer illite/smectite-like K-rectorite. K/Ar dating of two samples taken from the southern part of the Kremnica ore district (Fig. 2) gave the youngest ages corresponding to 10.4 ± 0.1 and 10.1 ± 0.1 Ma. Both represent the mixed-layer illite/smectite with a high amount of expanded

Table 4: Location and brief description of the samples collected for K/Ar dating from the Banská Štiavnica (BS) and Kremnica (KRA) stratovolcanoes.

No	Sample	Location	Stratovolcano	Mineralization	Polytype of illite
1	ŠI	Banská Štiavnica-Šobov, surface outcrop	BS	advanced argillic alteration of Šobov hydrothermal system	$2M_1$
2	P-22/94	Banská Hodruša-Rozalia vein, surface outcrop	BS	advanced argillic alteration of stockwork/disseminated base metal	$2M_1$ » 1M
3	4673	Banská Hodruša-Rozália mine, 14-th horizon, Svetozár vein	BS	higher temperature epithermal vein precious and base metal	$2M_1$ » 1M
4	4830	Banská Štiavnica-Weiden, Terézia vein	BS	epithermal vein precious and base metal	1M » $2M_1$
5	DV-8	Dolná ves, southern part of Kremnica ore district bore hole	KRA	epithermal vein precious and base metal	1M
6	31	Kremnica, central part of 2-nd vein system, Václav vein	KRA	epithermal vein precious and base metal	1M
7	DV-7	Dolná Ves, southern part of Kremnica vein system, bore hole	KRA	epithermal vein precious and base metal	1M
8	2931	Dolná Ves, southern part of Kremnica vein system, bore hole	KRA	epithermal vein precious and base metal	1M

Table 5: K/Ar isotope data of the illite from the Banská Štiavnica and Kremnica stratovolcanoes.

No	Sample	K (%)	$^{40}Ar_{rad.}$ [1] (ng/g)	$^{40}Ar_{rad.}$ [1] (%)	Age ± 2δ (Ma)
1	ŠI	6.96 ± 0.05	5.99 ± 0.06	81.4	12.4 ± 0.1
2	P-22/94	5.64 ± 0.05	4.52 ± 0.13	16.9	11.5 ± 0.3
3	4673	7.18 ± 0.04	5.95 ± 0.15	19.1	11.9 ± 0.3
4	4830	7.77 ± 0.08	6.16 ± 0.06	77.1	11.4 ± 0.2
5	DV-8	7.29 ± 0.04	5.65 ± 0.05	82.6	11.1 ± 0.3
6	31	6.90 ± 0.04	5.30 ± 0.05	79.1	11.03 ± 0.1
7	DV-7	4.05 ± 0.04	2.93 ± 0.04	50.0	10.4 ± 0.2
8	2931	6.30 ± 0.10	4.43 ± 0.05	65.0	10.1 ± 0.2

1 — radiogen ^{40}Ar

layers and come from the most external part of the Kremnica ore district.

The age data obtained from illite and mixed-layer illite/smectite from the altered salband zones of the Kremnica ore district are in good agreement with the data obtained from rhyolites and perlite of the Jastrabá Formation of Chernyshev et al. (1995), which vary within the range between 11.6 ± 0.3 and 11.4 ± 0.4 Ma.

Discussion

Comparison of hydrothermal mineralizations, but mainly of high sulphidation and low sulphidation alteration systems associated with them indicates some asymmetry between the Banská Štiavnica and Kremnica stratovolcanoes. In the Banská Štiavnica stratovolcano, especially in its Central Zone, the older, stockwork/disseminated base metal mineralizations and the younger, hydrothermal vein and base metal mineralizations can be reliably distinguished (Štohl & Lexa 1990; Štohl et al. 1994; Onačila et al. 1995). Besides other features, the older base metal mineralizations are characterized by alterations at regional scale, in which the associated clay minerals are reliable indicators of the high-sulphidation type of deposits. Although, there are some indications justifying the assignment to an older base metal mineralization in the Kremnica stratovolcano, we still do not have reasonable proofs to specify their character. The first indication was found in the borehole KR-3, in the northern part of the Kremnica ore district (Fig. 2). Böhmer & Šímová (1976) observed a diorite body at a depth of some 700 m below the surface, with an indistinct stockwork/disseminated base metal mineralization at the contact zone where the andesites also occur, accompanied by an association of sillimanite, andalusite, cordierite, topaz and garnet which suggests that secondary quartzites occur there. This finding led several authors studying the metallogeny of the Kremnica stratovolcano (Böhmer 1981; Burian et al. 1985; Knésl & Knéslová 1991), to presume that an older metallogenetic stage exists in the Kremnica ore district. On the basis of this data Štohl et al. (1994), examining the northern part of the Kremnica ore district, distinguished a stockwork/disseminated base metal mineralization of a high-sulphidation type, equivalent to the mineralization in the central zone of the Banská Štiavnica stratovolcano.

Mineralogical study of samples taken from the boreholes KV and KVŠ drilled in the northern part of the Kremnica ore district to intersect the mineralization at the contact with the diorite body, did not confirm the presence of pyrophyllite and alunite in any of them. In the altered zones, the association of kaolinite, illite and mixed-layer illite/smectite, which corresponds to associations encountered in the epithermal, precious and base metal vein mineralizations in the southern part of Kremnica ore district, is always present.

Polák (1957) reported an occurrence of alunite accompanied by opal and pyrite in an altered pyroxenic andesite host in the old tunnels driven in the past to follow the precious metallic veins in the mentioned, northern part of the Kremnica ore district near Horný Turček village. At that time we confirmed this finding using the XRD analysis. Alunite has a kaolinite admixture in opalline matrix. The isotopic research can give clues as to the origin of the high-sulphidation alterations (Rye et al. 1992). To obtain this information it is necessary to determine δDOH, $\delta^{18}O/SO_4$, $\delta^{18}O/OH$ and $\delta^{34}S/SO_4/$ in alunite. Up to now only the $\delta^{34}S/SO_4/$ + 10.04 ‰ value was determined in the alunite from the surroundings of Horný Turček (Repčok et al. in Žáková et al. 1995), which can neither confirm, nor discard its supergene origin.

The problems discussed above, related to the existence of an older metallogenetic stage in the Kremnica ore district indicate that exact data on mineral associations in the hydrothermally altered systems are needed, but are not available for the northern part of Kremnica stratovolcano, the only exception being those reported in the paper of Bebej & Dubaj (1993). On the other hand, a good example is available from the epithermal precious metal veins of the "Kremnica type" which occur in the surroundings of Banská Belá, at the NE margin of the Banská Štiavnica-Hodruša ore district, showing how helpful an exact identification of clay minerals from the altered perivenous zones can be (Fig. 1). Lexa et al. (1997) studied the structures and concluded that the Banská Belá veins cannot represent the NE continuation of the Banská Štiavnica veins. Thus, they are usually assigned to an independent, "Kremnica type" of mineralization which was the main source of precious metals in the past. This setting is also supported by the presence in the borehole B-2/520 m, of regular mixed-layer illite/smectite, similar to K-rectorite with parameters almost identical with those found in this mineral in the southern part of the Kremnica ore district, near Dolná Ves (Table 2, Fig. 4). It would be very useful to date this mineral from the Banská Belá vein system using the K/Ar method, and thus to date this hydrothermal mineralization. This type of regular mixed-layer illite/smectite-like K-rectorite from Banská Štiavnica, from predominantly base metal vein mineralization, was not yet determined.

The results of K/Ar dating of the illites from the hydrothermally altered zones, such as those affecting most hydrothermal precious and base metal mineralizations in the Banská Štiavnica and Kremnica stratovolcanoes, are reported for the first time. They bring a new aspect into the time interval of the hydrothermal mineralization. The main stages took place within the range 12.4 ± 0.1–11.03 ± 0.1 Ma in all the important ore districts located within the Central Slovak Neogene volcanics.

At present, the valid model of the metallogenetic development of the Banská Štiavnica stratovolcano is based on the combination of structural-superpositional relationships, biostratigraphic and geochronological data. It places the main stages of hydrothermal precious and base metal mineralization within the approximate time interval between 16.0 and 10.5 Ma (Štohl & Lexa 1990; Onačila et al. 1995). The results of K/Ar dating of illites from hydrothermal altered zones clearly confirmed the existence of the succession of individual metallogenetic stages in the valid metallogenetic model of the Central Zone of the Banská Štiavnica stratovolcano (Tables 4, 5). At the same time, both schemes could bring similar dating of the metallogenetic stage associated with the epithermal hydrothermal vein precious and base metal mineralization, which shows that fluids were energetically and substantially linked to the rhyolite volcanism of the Jastrabá Formation defined by Konečný et al. (1983). This is because previous K/Ar determinations gave the age range of the Jastrabá Formation between 12.4 and 10.7 Ma (Bagdasarian et al. 1968; Konečný et al. 1969; Burian et al. 1985), which are in good agreement with the ages of 11.6 ± 0.3–11.4 ± 0.3 Ma obtained for the rhyolites and perlites of the Jastrabá Formation by Chernyshev et al. (1995). Besides, our K/Ar data obtained from illites and mixed-layer illites/smectites of the Kremnica ore district show that the main stage of precious metal mineralization probably took place during a narrow time period, from 11.1 ± 0.1 to 11.03 ± 0.1 Ma. More K/Ar datings must be available to determine the age more precisely. The hydrothermal process, especially the one that took place in the area of Bartošova Lehôtka, in the southern part of the Kremnica ore district (Fig. 2), faded out without detectable precious metal mineralization between 11.0 ± 0.2 and 10.1 ± 0.2 Ma ago. This means that the whole process of epithermal vein precious and base metal mineralization in the Banská Štiavnica and Kremnica stratovolcanoes took place approximately during the time span 12.0 ± 0.2–11.0 ± 0.1 Ma. This is why we do not consider that the assignment of epithermal, vein precious and base metal mineralization to two stages, 1) Ag-Pb-Zn veins and base metal metasomatic mineralization ± Ag, Au with the age 13.5–12.0 Ma, and 2) Au-Ag veins with the age 12.5–10.5 as proposed by Onačila et al. (1995) is reasonably supported. This also applies to structural-superpositional relationships.

The main point why the metallogenetic model of Onačila et al. (1995) disagrees with our results is the dating of the older stockwork/disseminated base metal mineralizations associated with the advanced argillitic alteration of the pre-caldera stage, defined by Štohl & Lexa (1990). This model is supported by fairly small number of K/Ar dates, mainly from quartz diorites and granodiorites of the Central Zone of the Banská Štiavnica stratovolcano, which they tried to outweigh with arguments based on structural-superpositionl relationships. Other problems are of methodological types, which were already addressed by Chernyshev et al. (1995). As was shown, the selection of suitable minerals for the K/Ar dating of rocks is important. Minerals with relatively low K_2O contents, be it amphiboles, or plagioclases, give substantially older ages than biotites. This difference may reach 3 Ma for the biotite-amphibole andesites and may serve as a key argument in solving the disputed problem. It could also affect the age of the granodiorite which is spatially close to the stockwork/disseminated base metal mineralizations in the surroundings of Rozália Mine near Banská Štiavnica, and its age of 15.9 ± 0.7 Ma was determined from amphibole (Štohl et al. 1994).

In our dispute, Lexa proposed that the ages obtained from the illites of the older stockwork/disseminated base metal mineralizations in the surroundings of Rozália vein near Banská Štiavnica were either partly, or completely rejuvenated as a result of long-term overheating during the formation of the younger epithermal precious and base metal mineralization (Central zone of the Banská Štiavnica and Kremnica stratovolcano).

On the other hand, our K/Ar dating of illites, based on an analysis of mineral associations and on assessment of polytypes confirms their synchronous relationship to individual mineralization stages. It contains a younger, superimposed illite generation which developed during a younger epithermal, vein precious and base metal mineralization may be present at the Rozália vein. This is indicated by the age of 11.5 ± 0.3 Ma, practically identical with the age of 11.4 ± 0.2 Ma for an illite collected from the epithermal vein precious and base metal mineralization of the Terézia vein.

Conclusions

1) In all important stages of hydrothermal precious and base metal mineralizations of the Banská Štiavnica and Kremnica stratovolcanoes, associations of clay minerals can be distinguished, in which illite and mixed-layer illite/smectite play an important role.

2) All the illites and mixed-layer illite/smectites which we used for K/Ar age determination of hydrothermal precious and base metal mineralizations in the Banská Štiavnica and Kremnica stratovolcanoes, belong to the high-sulphidation and low-sulphidation types of Hedenquist (1987).

3) The high-sulphidation types of hydrothermal alterations in the Central Slovak Neogene volcanics developed in association with the advanced argillitic alteration, which was brought about by stockwork/disseminated base metal mineralization. Pyrophyllite is the typomorphic mineral for the high-sulphidation type of deposits. The low-sulphidation types of hydrothermal alterations in the Central Slovak Neogene volcanics developed in association with the epithermal, vein precious and base metal mineralization. Apart from adularia, the illite and the regular mixed-layer illite/smectite such as K-rectorite are the typomorphic minerals for the low-sulphidation types of deposit.

4) K/Ar dating of illite and of mixed-layer illite/smectite confirmed that the entire process of hydrothermal precious and base metal mineralization in the Banská Štiavnica and Kremnica stratovolcanoes took place approximately within the period 12.5 ± 0.1–11.0 ± 0.1 Ma.

Acknowledgements: This research was carried out as part of scientific technical cooperation between the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences, the Faculty of Sciences Comenius University and the Geological Institute of the Slovak Academy of Siences, with the financial support of project Grant No. 1/4090/97 and project Grant No. 98-05-64052 of Russian Basic Research Foundation.

References

Alderton D.H.M., Thirlwall M.F. & Baker J.A., 1998: Hydrothermal alteration associated with gold mineralization in the southern Apuseni Moutains, Romania: preliminary Sr isotopic data. *Miner. Dep*., 33, 520–523.

Ashley R.P. & Silberman M.L., 1976: Direct dating of mineralization at Goldfield, Nevada, by potasium-argon and fission track methods. *Econ. Geol.,* 71, 904–924.

Bagdasarian G.P., Vass D. & Konečný V., 1968: Results of absolute age determination of Rocks in Central and East Slovakia. *Geol. Zbor. Geol. Carpath*., 19, 419–425.

Bebej J. & Dubaj D., 1993: Volutile components in hydrothermal systems Part 2: Practical interpretation in the case of Kremnica deposit, Central Slovakia. *Miner. slovaca*, 25, 301–312 (in Slovak).

Bonham H.F. Jr., 1986: Models for volcanic-hosted epithermal precious metal deposits: *A review. Inter. Volcan. Congress*, Hamilton, New Zealand, *Proc. Symposium,* 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 problem of alterations of Central Slovakian neovolcanites. *Geol. Zbor. Geol. Carpath.,* 20, 47–68.

Böhmer M. & Šímová M., 1976: The contact-replacement halo of Miocene intrusives in the Kremnické vrchy Mts. *Acta Geol. Geogr. Univ. Comen., Geol.,* 30, 119–137 (in Slovak).

Böhmer M., 1981: Contribution to the problem of deposit of Au, Ag in Central Slovak Neogene volcanic rocks. In: Geológia a surovinové zdroje neovulkanitov. *Symposium Proc*., Bratislava, 4, 192–196 (in Slovak).

Burian J., Slavkay M., Štohl J. & Tözsér J., 1985: Metallogenesis of neovolcanites in Slovakia. *Alfa*, Bratislava, 1–269 (in Slovak).

Conrad J.E., McKee E.H., Rytuba J.J., Nash J.T. & Utterback W.C., 1993: Geochronology of the Sleeper Deposit, Humboldt Countury, Nevada: of a Silicic Flow-Dome complex. *Econ. Geol*., 88, 317–327.

Eberl D.D., Środoň 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. Mineralogist*, 72, 914–934.

Fuchs P., 1994: The alteration of rhyolite of Kremnické vrchy Mts., to the relation ore deposits. *Manuscript-Diploma work,* archive Faculty of Sciences Univ. Comenius, Bratislava, 1–62 (in Slovak).

Gavora S., 1983: Final report and calculation of reserv of precious and base metal stockwork deposit Hodruša. *Manuscript, archive Geofond*, Bratislava, 1–136 (in Slovak).

Háber M., Jeleň S., Maťo Ľ. & Kovalenker V., 1998: Modelling of mineral-forming processes at the Banská Štiavnica epithermal deposit Western Carpathians, Slovak Republic. *Proc. of Ninth Quadrenial IAGOD Symposium. E. Schweizerbart'sche Verlagsbuchhandlung,* Stuttgart, 183–203.

Hauff P.L., Kruse F.A. & Madrid R.J., 1991: Defining gold ore zone using illite polytypes. In: Raines G.L., Lisle R.E., Schafe R.W. & Wilkinson W.H. (Eds.): Geology and ore deposits of the Great Basin. *Symposium Proc*., *Geol. Soc. Nevada*, Reno, 239–247.

Hayba D.O., Bethke P.M., Heald P. & Foley N.K., 1986: Geologic, mineralogic and geochemical characteristics of volcanic-hosted epithermal precious-metal deposits. *Rev. Econ. Geol*., 81, 129–167.

Heald P., Foley N.K. & Hayba D.O., 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.): Transactions of the Fourth Circum-Pacific Energy and Mineral Resources Conference, Singapore. *Amer. Assoc. Petrol. Geol.,* 513–524.

Chernyshev I.V., Háber M., Kovalenker V.A., Ivanenko V.V., Jeleň S. & Karpenko M.I., 1995: The age of the magmatic events and epithermal Au-Ag-base metals mineralization in the Central zone of the Banská Štiavnica stratovolcano: K/Ar data. *Geol. Carpathica*, 46, 327–334.

Kantor J. & Ďurkovičová J., 1985: The genetic characterization of selected mineralization in Western Carpathians. *Manuscript*, *archive of Geofond,* Bratislava (in Slovak).

Kantor J., Ďurkovičová J., Eliáš K. & Repčok I., 1988: Isotopic research of metallogenetic, petrogenetic and hydrogenetic processes of the Western Carpathians. *Manuscript*, *archive of Geofond,* Bratislava (in Slovak).

Knésl J. & Knéslová A., 1991: The contemporary view on the geology, metalogenesis and ore forecast of the Kremnica Mts., ore district. *Miner. slovaca,* 23, 283–294 (in Slovak).

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

Konečný V., Lexa J. & Planderová E., 1983: Stratigraphy of the Central Slovakia volcanic field. *Západ. Karpaty, Ser. Geol.,* 9, 1–203 (in Slovak).

Konečný V. & Lexa J., 1990: Geological building of the central zone of the Banská Štiavnica stratovolcano. *Manuscript*, *archive of Geofond,* Bratislava (in Slovak).

Kovalenker V.A., Jeleň S., Levin K.A., Naumov V.B., Prokofyev V. Yu. & Rusinov V.L., 1991: Mineral assemblages and physical-chemical model of the formation of gold-silver-polymetallic mineralisation on the deposit Banská Štiavnica (Central Slovakia). *Geol. Zbor. Geol. Carpath*., 42, 291–302.

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

Kraus I., Šamajová E., Šucha V., Lexa J. & Hroncová Z., 1994: Diagenetic and hydrothermal alterations of volcanic rocks into clay minerals and zeolites (Kremnické vrchy Mts., the Western Carpathians). *Geol. Carpathica*, 45, 151–158.

Kubler B., 1968: Evalution quantitative du métamorphisme par la cristallinité de l' illite. *Bull. Centre rech. Pau,* 2, 385–397.

Lexa J., Koděra P., Onačila D., Rojkovičová Ľ., Žáková Ľ. & Tréger M. 1997: The completion evalution of prognostic resources of mineral raws in the region of Central zone of the Banská Štiavnica stratovolcano. *Manuscript, archive Geological Survey of Slovak Republic*, Bratislava, 1–225 (in Slovak).

Lexa J., Štohl J. & Konečný V. 1999: The Banská Štiavnica ore district: relationship between metalogenetic processes and the geological evolution of a stratovolcano. *Mineralium Deposita*, 34 (in press).

Maťo Ľ., Sasvári T., Bebej J., Kraus I., Schmidt R. & Kalinaj M., 1996: Structurally-controlled vein-hosted mesothermal gold-quartz and epithermal precious and base metal mineralization in the Banská Hodruša ore field, Central Slovakia neovolcanites. *Miner. slovaca*, 28, 455–490 (in Slovak).

Nakovnik N.I., 1964: Secondary quartzites of USSR. *Nedra,* Moscow, 1–265 (in Russian).

Noble D.C., Weiss S.I. & McKee E.H., 1991: Magmatic and hydrothermal activity, Caldera geology, and regional extension in the western part of the southwestern Nevada volcanic field. In: Raines G.L., Lisle R.E., Schafer R.W. & Wilkinson W.H. (Eds.): Geology and ore deposits of the Great Basin. *Symposium Proc*., *Geol. Soc. Nevada*, Reno, 913–934.

Onačila D. & Rojkovičová Ľ., 1992: Precious metal mineralization on the Hodruša ore field veins. *Miner. slovaca,* 24, 245-256 (in Slovak).

Onačila D., Lexa J., Marsina K., Rojkovičová Ľ., Káčer Š., Hojstričová V., Žáková E., Štohl J., Konečný V., Nemčok M., Koděra P., Repčok I., Hurai V., Háber M., Jeleň S., Maťo Ľ., Sasváry T., Schmidt R., Zvara T. & Grant T., 1995: The metallogenetic model and prognosis of Central zone of the Banská Štiavnica stratovolcano. *Manuscript*, *archive of Geofond*, Bratislava, 1-231 (in Slovak).

Oružinský V., 1989: High silica rocks of the Central Slovak neovolcanic area. *Miner. slovaca*, 21, 533-537 (in Slovak).

Polák S., 1957: On the alunite and alunitisation in the vicinity of Horný Turček in the Kremnické hory Mts. *Věst. ÚÚG*, 32, 362-364 (in Slovak).

Polák S., 1963: To the genesis of deposit of ganister quartzites in Šobov near Banská Štiavnica. *Geol. Práce, Spr.,* 29, 147-155 (in Slovak).

Radzo V., 1969: Hydromuscovite of Banská Štiavnica and its relation to hydrothermal alterations of volcanic rocks. *Miner. slovaca*, 1, 251-269 (in Slovak).

Rozložník L. & Zábranský F., 1971: On the copper mineralization occurrence of stockwork-impregnation type between the villages of Banská Hodruša, Vysoká and Uhliská. *Miner. slovaca*, 3, 85-94 (in Slovak).

Rusinov V.A., Kovalenker V.A., Matiusheva I. & Naumov V.B., 1993: Zoning and metasomatism of ore deposits in the Banská Štiavnica ore field (Central Slovakia). *Geol. Rud. Mestor*., 35, 246-261 (in Russian).

Rye R.O., Bethke P.M. & Wasserman M.L., 1992: The stable isotope geochemistry of acid sulfate alteration. *Econ. Geol.,* 87, 225-262.

Setterfield T.N., Musset A.E. & Oglethorpe R.D.J., 1992: Magmatism and associated hydrothermal activity during the evolution of the Tavna Caldera: $^{40}Ar/^{39}Ar$ dating, of the volcanic, intrusive and hydrothermal events. *Econ. Geol*., 87, 1130-1140.

Silberman M.L., Chesterman C.W., Kleinhampl F.J. & Gray C.H. Jr., 1972: K/Ar ages of volcanic rocks and gold bearing guartz-adularia veins in the Bodie mining district, Mono County, California. *Econ. Geol.,* 67, 597-604.

Silberman M.L., 1985: Geochronology of hydrothermal alteration and mineralization: Tertiary epithermal precious-metal deposits in the Great Basin. *U.S. Geol. Surv. Bull.*, 1646, 55-70.

Sillitoe R.H., 1973: The tops and bottoms of porphyry cooper deposits. *Econ. Geol*., 68, 799-815.

Środoń J., 1984: X-ray identification of illitic materials. *Clays and Clay Miner*., 32, 337-349.

Štohl J., 1976: Space and age of the Pb-Zn-Cu-Au-Ag ore forming processes in the Middle Slovakia neovolcanites associated with the Central Carpathian Lineament. *Západ. Karpaty, Ser. Mineral. Petrogr. Geochém. Metalogen*., 2, 7-40 (in Slovak).

Štohl J., Lexa., Konečný V., Onačila D., Hojstričová V., Žáková E., Hók J., Marsina K., Rojkovičová Ľ., Mihaliková A., Danillová J. & Brlay A., 1987: Metallogenetic research of the Central Zone of the Banská Štiavnica stratovolcano. *Manuscript, archive of Geofond,* Bratislava, 1-224 (in Slovak).

Štohl J., Lexa., Konečný V., Onačila D., Hojstričová V., Žáková E., Hók J., Marsina K., Rojkovičová Ľ., Mihaliková A., Danillová J. & Brlay A., 1988: Metallogenetic research of the Central Zone of the Banská Štiavnica stratovolcano. *Manuscript*, *archive of Geofond,* Bratislava, 1-338 (in Slovak).

Štohl J. & Kaličiak M., 1989: Common features and differences in metallogenesis of Middle and East Slovak neovolcanites. *Miner. slovaca*, 21, 397-402 (in Slovak).

Štohl J. & Lexa J., 1990: Metallogeny related to intrusive complex in the Central Zone of the Banská Štiavnica stratovolcano. In: Prínos 50 ročnej činnosti Geologického ústavu D. Štúra k rozvoju slovenskej geológie. *Symposium Proc., GÚDŠ*, Bratislava, 81-92 (in Slovak).

Štohl J., Lexa J., Kaličiak M. & Bacsó Z., 1994: Genesis of stockwork base metal mineralizations in the Neogene volcanics of Western Carpathians. *Miner. slovaca*, 26, 75-117 (in Slovak).

Šucha I., 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. Carpathica, Ser. Clays*, 1, 13-19.

Titley S.R. & Beane R.E., 1981: Porphyry cooper deposits. In: Skinner B.J. (Ed.): Seventy-Fifth Anniversary Volume. *Econ. Geol.,* 214-269.

Uhlík P. & Šucha V., 1997: Distribution of pyrophyllite in the Šobov deposit and comparison with pyrophyllite from Vígľašská Huta deposit (Central Slovakia). *Miner. slovaca*, 29, 73-79 (in Slovak).

Veld B., 1965: Experimental determination of muscovite polymorph stabilities. *Amer. Mineralogist*, 50, 436-449.

Žáková E. & Štohl J., 1992: Multistage metallogeny and alteration development within the Banská Štiavnica ore district — Slovakia. *Book of Abstracts*, *12-th Conference Clay Mineralogy and Petrology*, Bratislava, 107.

Žáková E., Hojstričová V. & Lexa J., 1995: Evolution of hydrothermal alteration processes in the Banská Štiavnica-Hodruša ore district: spatial, temporal and genetic aspects. *Geol. Carpathica, Ser. Clays*, 4, 122.

Žáková E., Hojstričová V., Konečný V., Lexa J., Marsina K., Onačila L., Repčok I., Rojkovičová Ľ., Stolár M., Štohl J., Horváth I. & Filo M., 1995: The raw potention of metasomatites in the region of Dekýš. *Manuscript*, *archive of Geofond,* Bratislava (in Slovak).