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DIAGENETIC ALTERATION OF MIOCENE ACIDIC VITRIC TUFFS OF THE JASTRABÁ FORMATION (KREMNICKÉ VRCHY MTS., WESTERN CARPATHIANS)

EVA ŠAMAJOVÁ[1], IVAN KRAUS[2] and ANNA LAJČÁKOVÁ[2]

[1] Geological Institute, Faculty of Sciences, Comenius University, Mlynská dolina, Pav. G, 842 15 Bratislava, Czechoslovakia
[2] Department of Economic Geology, Faculty of Sciences, Comenius University, Mlynská dolina, Pav. G, 842 15 Bratislava, Czechoslovakia

Abstract: Economic accumulations of bentonites as well as other exploitable types of clays and zeolites on the SW margin of the Kremnické vrchy Mts. were formed by alteration of acidic vitritic volcanoclastics of the Sarmatian - Pannonian Jastrabá Formation. The alteration took place during diagenesis of the sediments in a freshwater environment in an open or semiclosed hydrological system. The vertical zonation of alteration products represented from top to bottom by zones of perlite, smectite and high-silica zeolites, is a reflection of changes in pH and chemical composition of pore solutions percolating through the volcanoclastic complex. The original diagenetic mineral zones were locally modified by contact-thermal and hydrothermal effects of younger rhyolite bodies.

Key words: diagenesis, zonation, perlite, smectite, clinoptilolite, mordenite.

Introduction

The SW margin of the Kremnické vrchy Mts., which are a part of the Central Slovak neovolcanic mountains, is one of the most promising areas for the occurrences of nonmetallic minerals in the whole Western Carpathians. Perlites, bentonites as well as other exploitable types of clays and zeolites resulted from the alteration of Miocene acidic volcanic rocks of the Jastrabá Formation (Kraus et al. 1979; Kraus et al. 1982; Šamajová 1979; Lajčáková 1980; Šamajová & Kraus 1985).

Mineralogic studies associated with long term geological exploration have revealed mineralogically rich alteration products of rhyolite bodies. The distribution of the identified authigenic mineral assemblages: montmorillonite ± cristobalite ± kaolinite, kaolinite ± montmorillonite ± cristobalite, mixed-layer illite - smectite ± kaolinite and high-silica zeolites - clinoptilolite and mordenite + cristobalite ± smectite ± kaolinite was studied in surface outcrops and shallow exploration drillholes about 30 *m* deep. The above mineral assemblages made it possible to compile a map of nonmetallic minerals of this area (Kraus et al. 1982).

However, some genetic problems remained unresolved for a long time because of the complex geologic-tectonic structure of the territory further complicated by several mutually overlapping alteration processes and an insufficient number of outcrops and shallow drillholes.

Recent drilling exploration, whose aim was to verify the areal and vertical distribution of clays and zeolites, provided some new data which were added to earlier information on the spatial and temporal relationships of the alteration products, and which are vital for the interpretation of their genesis.

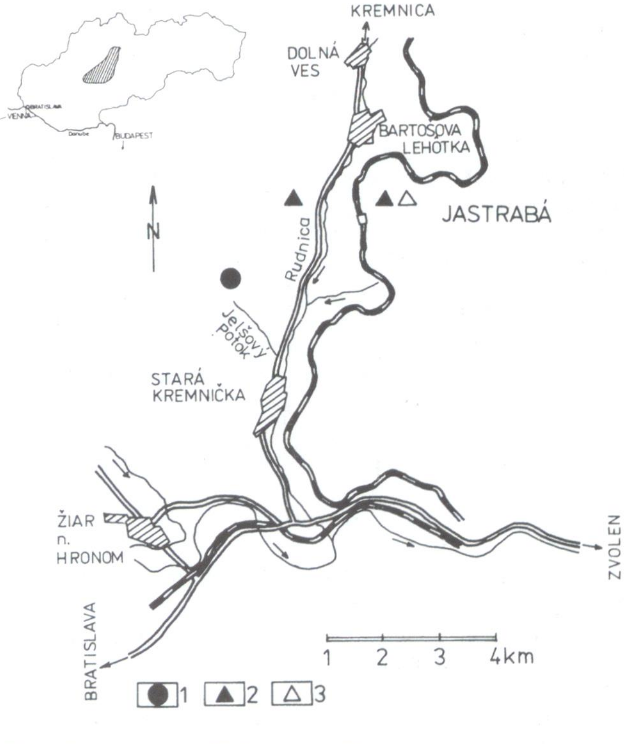

Fig. 1. Location map of SW margin of Kremnické vrchy Mts.
1 - bentonit deposit Jelšový Potok; 2 - perlite deposit Jastrabá; 3 - zeolite deposit Bartošova Lehôtka-Paseka.

Geological position

Acidic volcanics in the Central Slovakian mountains occur in three stratigraphic horizons: Eggenburgian, Badenian and Sarmatian - Pannonian. The rhyolite- and rhyodacite-type volcanism in the SW Kremnické vrchy Mts. took place in the Upper Sarmatian to Pannonian. On the basis of petrographic and petrochemical investigations, Lexa (1969) assumes that the products of this volcanism were derived from separate acidic magma. The acidic volcanics designated by Lexa as the Kremnica Rhyolites are clearly associated with N-S-trending linear systems. The products of this volcanism, denominated by Konečný et al. (1983) as the Jastrabá Formation, include extrusive as well as effusive bodies, dykes and a thick volcanoclastics complex. The initial highly explosive volcanic activity deposited thick (150 - 300 *m*) layers of volcanoclastic material in lacustrine, fluviolacustrine and terrestrial environments close to the volcanic centres. The largest volcanoclastic accumulations lie in places where the Žiar Basin passes into the Štiavnické vrchy and Kremnické vrchy Mts.. The volcanoclastics have the character of tuffs, lapilli tuffs, agglomerates, volcanic breccias, Merapi-type pyroclastics and pumice flows or phreatic eruptions (Bezák & Lexa 1983). The activity of the rhyolite volcanism in this area was concluded by the emplacement of extrusive bodies, dykes and lava flows. The rhyolite bodies are mostly zoned with zones of different degree of groundmass crystallization and glassy margins of diverse thicknesses (Lexa 1971; Lajčáková & Gerthofferová 1987).

The area studied is situated in the SW Kremnické vrchy adjacent to the Žiar Basin. The area was intensively tectonically dissected - it is cut by a system of N-S-trending parallel faults. The most conspicuous fault, along which the western tract of the area in question sunk by as much as 150 *m* (Bezák & Lexa 1983), runs along the valley of the Rudnica brook.

The location of perlite, bentonite and zeolite deposits on the SW periphery of the Kremnické vrchy Mts. is shown in Fig. 1.

Methods

About 500 samples of vitritic and altered vocanoclastic rocks were studied. The mineralogy and relative abundance of authigenic minerals in all surface and drillcore samples were determined by X-ray diffractometric anlysis using X-ray diffractometer DRON - 3 and Ni-filtered CuK_α-radiation. The mounts were run at $1^\circ 2/min.$ from 4° to 60° 2Θ. Fraction below $2\ \mu m$ was used for the identification of clay minerals. The textural and mineral-assemblage relationships of the authigenic minerals were examined in thin sections by polarizing microscopy and scanning electron microscopy (JEOL instrument) of fresh broken fragments coated with a gold alloy. The chemistry of bulk samples was determined by wet chemical analyses.

Results

Mineralogical studies of cores from exploration drillholes on the SW margin of the Kremnické vrchy Mts. have revealed a zonal pattern of the vitritic volcanoclastics alteration products. VBL-11, the first drillhole in this area to intersect the rhyolite volcanoclastic complex about 260 *m* thick, was particularly significant for the recognition of the vertical extent of the authigenic mineral assemblages. The exploration drillholes intersected the rhyolite bodies at different depths, which is an important piece of information for genetic interpretations.

From the point of view of economic geology, mineral assemblages in the altered volcanoclastics make it possible to distinguish the following zones ordered from the surface downwards:

perlite zone - perlite-type hydrated glass ± smectite ± kaolinite

bentonite zone - smectite ± cristobalite ± kaolinite

zeolite zone - clinoptilolite + mordenite + cristobalite ± adularia ± smectite ±kaolinite.

This vertical zonation corresponds to diagenetic alterations of thick vitroclastic tuffs layers in an open hydrologic system represented by a lacustrine or terrestrial environment (Hay 1986; Gottardi 1989).

The diagenetic mineral zones originally composed of smectite- and clinoptilolite-dominated mineral assemblages are now controlled by the chemical composition of the volcanic glass. The primary diagenetic zonation was locally modified by the chemical or only thermal effects of younger rhyolite bodies. The contact effect of these bodies are reflected by different mineral assemblage consisting of kaolinite, mixed-layer illite-smectite as well as mordenite formed by conversion of clinoptilolite.

The chemical compositiion of the hydrated volcanic glass (perlites) and alteration products of vitritic volcanoclastics are shown in Tab. 1.

Petrographic-mineralogic studies of drillcores suggest that the thickness of the individual zones is very variable and perlite/smectite-zone boundary is not clear. The prevailing kind of zonation throughout the investigated area is that made up of a smectite and zeolite, a good example being the Jelšový Potok - north deposit (Fig. 2). As a result of later tectonic processes, a complete zonation was only preserved as a relic at the western margin of the Jastrabá perlite deposit.

Table 1: Chemical analysis of perlite, bentonite, mordenite and clinoptilolite-rich tuffs of Jastrabá and Bartošova Lehôtka area.

Oxides	1	2	3	4
SiO_2	71.98	55.64	70.36	68.86
TiO_2	0.13	0.28	0.10	0.34
Al_2O_3	12.48	15.94	11.50	11.56
Fe_2O_3	1.69	1.80	1.40	1.78
MnO	0.09	0.03	-	-
MgO	0.33	3.32	0.37	1.01
CaO	1.12	3.18	2.18	2.16
Na_2O	1.24	0.13	0.93	0.71
K_2O	5.55	0.20	2.55	3.80
H_2O^-	0.27	11.75	-	-
H_2O^+	3.98	7.38	-	-

1 - perlite; 2 - bentonite; 3 - mordenite - rich tuff; 4 - clinoptilolite-rich tuff.

Perlite zone

The Jastrabá perlite deposit consists of two genetic types - vitric volcanoclastics and a vitric flow. The vitric tuffs to tuffoagglomerates are overlain by the younger effusive-type perlites. Clasts of the former genetic type include mainly porous varieties of glass (Fig. 2), but also characteristic perlite "sugar" glass. The water content in the vitritic volcanoclastics roughly equals that in perlites elsewhere - ranging from 3.4 to 4.6 % . The volcanoclastic perlites can be regarded as products of low-temperature hydration of volcanic glass in solid state (Lajčáková & Kraus 1987). The low resistence of volcanoclastics to alteration is shown by the dull and anomalous birefrigent glass, as well as by the presence of smectite (Fig. 3) or kaolinite. At the Jastrabá deposit, the volcanoclastic perlites are locally as much as 50 *m* thick. At the deposit 's western margin, the perlite layer is only 2 - 5 *m* thick and is underlain by a 5 *m* bentonite layer which in turn overlies zeolitized volcanoclastics.

Smectite zone

The characteristic development of the smectite zone occurs in the currently exploited Jelšový Potok bentonite deposit and its NW extension Jelšový Potok - north near Stará Kremnička. The bentonites here were formed by the alteration of rhyolite tuffs rich in porous glass in a shallow-water lacustrine environment (Kraus et al. 1982, 1989). The maximum thickness of the bentonite layer at the deposit is 50 *m*. Two technological types of bentonites have been ditinguished here. One of them, monomineralic montmorillonite (Figs. 4, 5) without cristobalite ad-

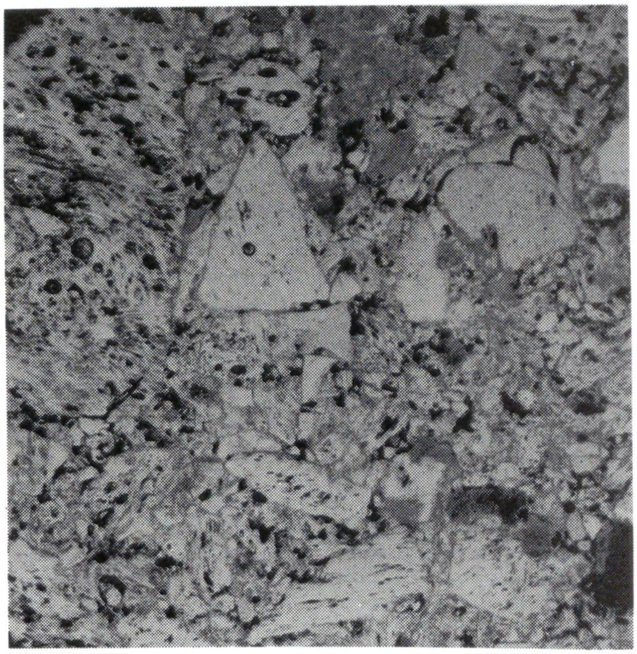

Fig. 2. Photomicrograph of unaltered vitroclastic tuff with porous glass. Magnified 40 x.

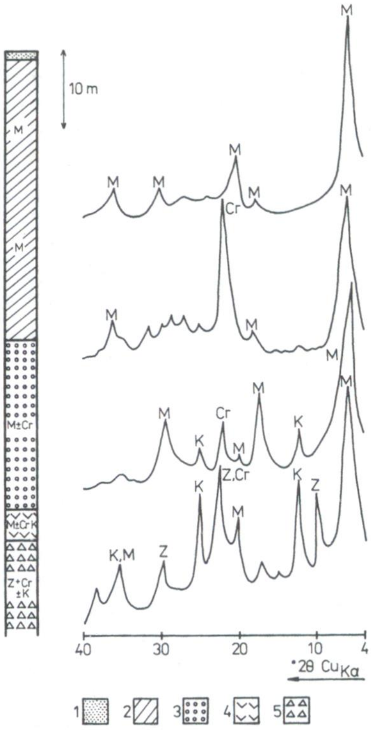

Fig. 4. The scheme of zoning from the bentonite deposit Jelšový Potok and X-ray powder diffractograms showing the mineral assemblages (M - montmorillonite, Cr - cristobalite, K - kaolinite, Z - zeolites).

Fig. 3. Scanning electron micrograph of glass with thin scales of smectite.

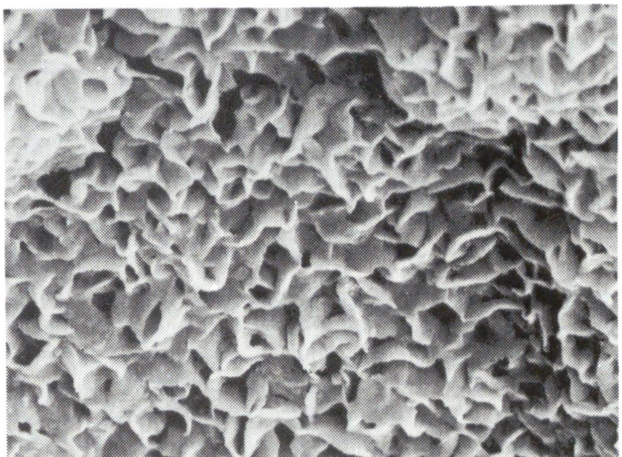

Fig. 5. Scanning electron micrograph of monomineral montmorillonite.

mixture makes up the upper part of the deposit. According to the composition of its exchangeable cations, the mineral is Ca^{2+}, Mg^{2+} montmorillonite (Čičel et al. 1974) of the following crystallochemical formula:

$$(Si_{7.81}Al_{0.19})^{IV}[Al_{3.02}Fe_{0.26}Mg_{0.70}]^{IV}Ca_{0.38}Mg_{0.10}O_{20}(OH)_3$$

The montmorillonite content in the bentonite varies from 60 to 85 %. The average chemical composition of the monomineralic bentonite is given in Tab. 1.

The second kind of bentonite, present mainly in the central part of the deposit beneath the monomineral bentonite is composed of the mineral assemologe: montmorillonite + cristobalite ± kaolinite (Fig. 4). Semiquantitative X-ray analysis has revealed that the content of kaolinite does not exceed 30 - 50 % and that of cristobalite 15 - 20 %. Increased contents of kaolinite were noted mostly in the neighbourhood of the younger rhyolite bodies.

The smectite zone throughout the investigated area is represented mainly by this type of bentonite (Kraus et al. 1982).

From the genetic point of view, it is noteworthy that the whole so far verified Jelšový Potok - north deposit is underlain by zeolitized volcanoclastics similar to those noted in surface occurrences. Drilling exploration has proved that this zonation is fairly widely distributed in the investigated area.

Zeolite zone

Regionaly distributed zeolitization of vitric volcanoclastics at the Kremnické vrchy Mts. was known on the area of some 1.5 km^2, mostly in surface outcrops (Šamajová 1979; Šamajová & Kraus 1985). Recently, the zeolitized tuffoagglomerates and pumice as well as psammitic tuffs which make up the Bartošova Lehôtka - Paseka zeolite deposit were subjected to drilling exploration to a depth of 80 - 130 *m*. Apophyses and margins of

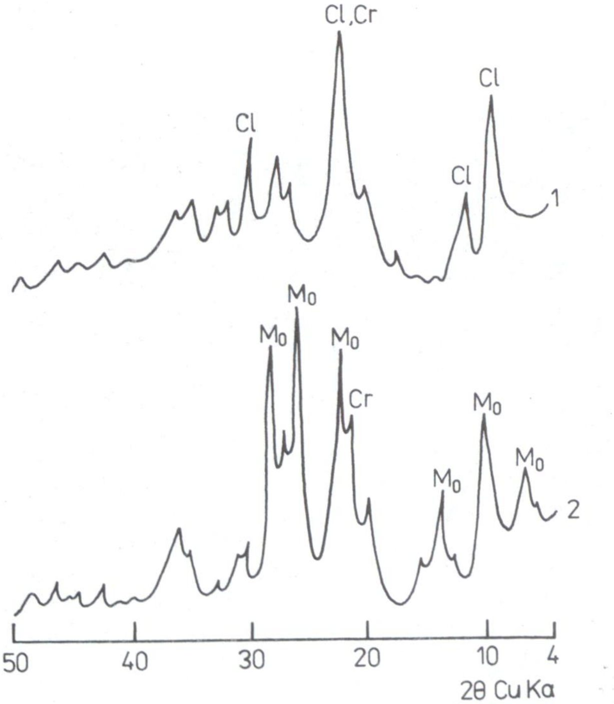

Fig. 6. X-ray diffractograms of 1 - clinoptilolite-rich tuff and 2 - mordenite-rich tuff.
Cl - clinoptilolite, Cr - cristobalite, Mo - mordenite.

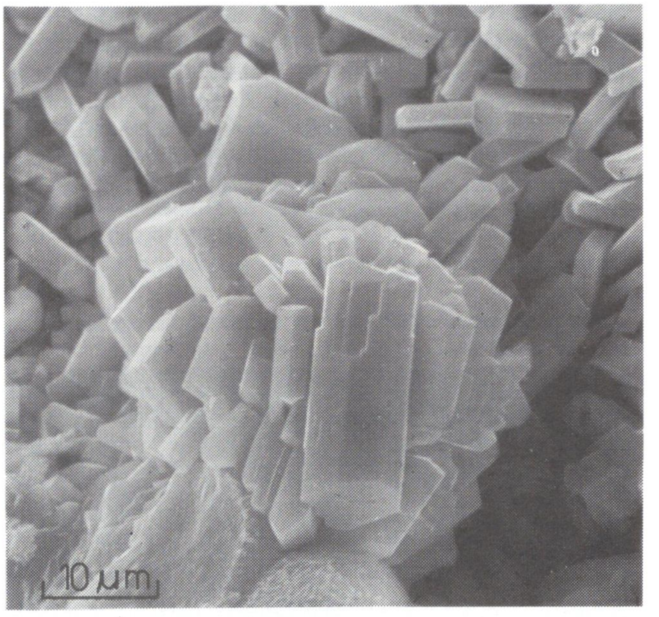

Fig. 7. Scanning electron micrograph of tabular clinoptilolite.

rhyolite bodies were found beneath the volcanoclastics (Šamajová 1989).

Zeolites of this deposit, represented by clinoptilolite and mordenite, were identified by X-ray diffraction analysis and scanning electron microscopy (Figs. 6, 7 & 8). Other authigenic minerals include cristobalite, adularia and/or smectite and kaolinite. Primary minerals comprise quartz, plagioclases and biotite. Their ion-exchange capacity and X-ray diffraction analysis suggest that the zeolite content in the tuffs does not exceed 50 % (Kozač 1984; Maďar 1984).

The degree of zeolitization as well as clinoptilolite and mordenite distribution are very variable and are controlled by petrographic composition, structure, permeability of the volcanoclastics and their spatial relationship to the younger rhyolite bodies. Increased accumulations of mordenite occur in the contact aureole of the youger rhyolite bodies, whereas clinoptilolite prevails in more external zones (Šamajová & Kraus 1985). Mineralogical studies of clinoptilolite and mordenite distribution in the Bartošova Lehôtha - Paseka deposit indicate that the former mineral is a direct alteration product of the volcanic glass during the process of diagenesis, whereas the latter was formed later at the expanse of clinoptilolite. X-ray analysis and scanning microscopy prove that the formation of mordenite was accompanied by the formation of potassic feldspar-adularia (Šamajová 1989). The conversion of clinoptilolite into mordenite and adularia in the exocontact of the rhyolite bodies is controlled by temperature and can be expressed by the following formula:

$$\underset{clinoptilolite}{2\,(Na_2K_2Ca)_3Al_6Si_{30}O_{72}\,.\,21\,H_2O} = \underset{mordenite}{(Na_2Ca)_4Al_8Si_{40}O_{96}\,.\,28\,H_2O} + \underset{adularia}{4\,KAlSi_3O} + \underset{cristobalite}{8\,SiO_2} + 14\,H_2O$$

The mutual relationships between mordenite and adularia observed by scanning microscopy suggest that clinoptilolite - adularia = mordenite + silica. In most cases, fairly large adularia crystals antedated mordenite (Fig. 9) Kirov & Šamajová (1990). Scanning microscopy also documents the conversion of clinoptilolite into mordenite characterized by the process of dissolution and subsequent crystallization (Figs. 10, 11).

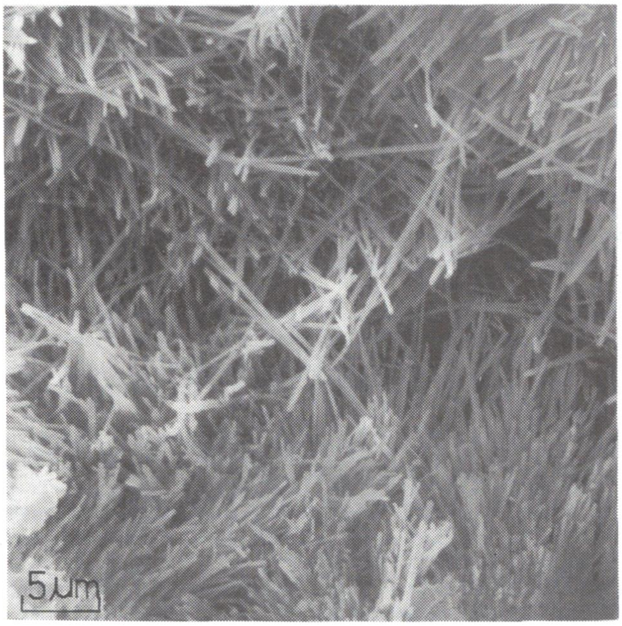

Fig. 8. Scanning electron micrograph of needle-shaped mordenite.

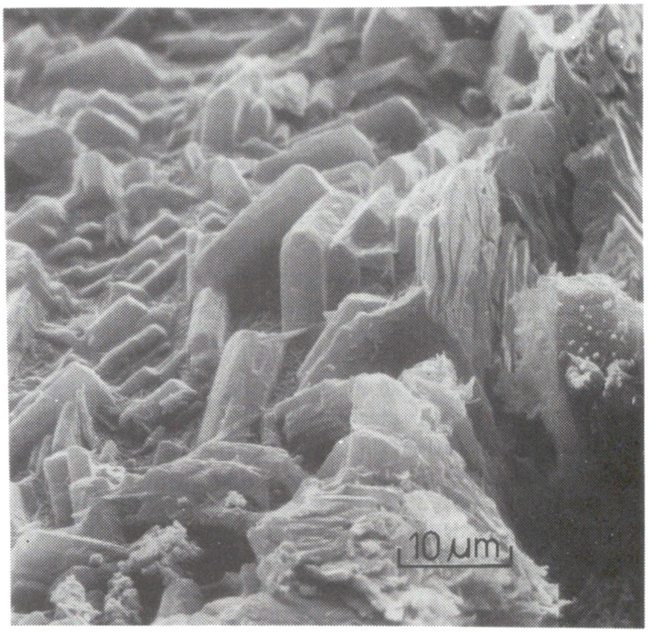

Fig. 10. Scanning electron micrograph of clinoptilolite showing obvious effects of dissolution.

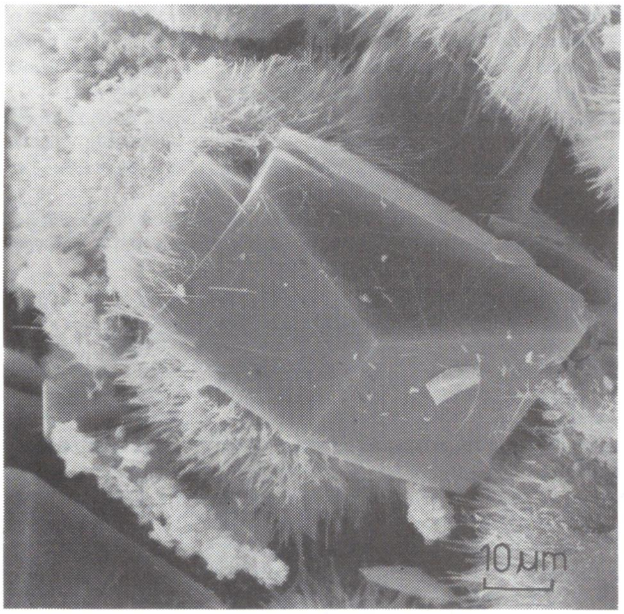

Fig. 9. Scanning electron micrograph of authigenic adularia crystal and mordenite fibers.

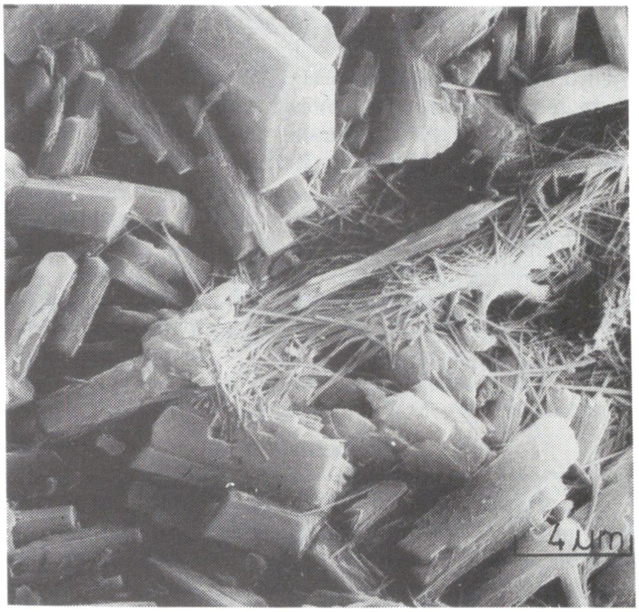

Fig. 11. Scanning electron micrograph of mordenite that grew from the dissolution surface clinoptilolite.

Discussion

New data on the distribution of alteration products of acidic vitritic volcanoclastics in space and time obtained by petrographic-mineralogic assessment of exploration drillholes located in the investigated area over the past years were applied to make genetic interpretations (Šamajová et al. 1991). It has turned out that the vertical zoning pattern of alteration products in the Jastrabá Formation volcanoclastic complex composed of a smectite zone passing into a zeolite zone at depth has regional distribution.

Earlier reconnaissance for nonmetallic minerals based on surface outcrops and shallow drillholes to a depth of about 30 *m* was only able to identify lateral transitions between individual authigenic mineral zones and often came across a single zone (Kraus et al. 1982; Šamajová & Kraus 1985; Šamajová 1989). These mineral zones were dominated by montmorillonite, kaolinite, mixed-layer illite-smectite and zeolites. The insufficient vertical range of the applied exploration methods gave rise to different opinions on the polygenetic origin of the studied mineral assemblages which are frequently of economic importance.

The vertical zonation of the vitritic tuffs alteration products on the SW margin of the Kremnické vrchy Mts. originated in a fresh-water environment in an open or semiclosed system during diagenesis. The diagenetic mineral zones were formed as a result of gradual changes in chemical composition and pH of pore solutions percolating through vitric tuffs layers. In the course of gradual hydration and hydrolisis of the vitritic component and simultaneous formation of smectite in the upper tuff layers, pore solutions became enriched in alkalies and silicium eventually attaining mineralization and pH sufficient for clinoptilolite crystallization.

The upper monomineralic montmorillonite zone originated from alterations in an open system. Increasing amounts of low cristobalite in deeper parts of the smectite zone and its constant presence in the underlying zeolite zone suggest a relatively more closed hydrologic system. Hay (1986) points out that numerous montmorillonitic-clay deposits were formed from vitritic acidic tuffs by leaching in an open hydrologic system.

Field investigations and scanning microscopy of the zeolite tuffs indicate that, in the process of diagenesis, clinoptilolite is an original alteration product of acidic volcanic glass (Šamajová 1989; Kirov & Šamajová 1990). Velde (1977) has noted that the alteration of potassic volcanic glass in acidic volcanoclastics at low temperatures characteristic of diagenetic alterations gives rise mostly to clinoptilolite which makes up the original zeolite assemblage.

The emplacement of extrusive rhyolite bodies as well as their apophyses, or hydrothermal solutions caused changes in the physico-chemical properties of the environment, which in turn may have been responsible for considerable changes in the chemistry, concentration and pH of pore solutions. This was also reflected by the changing mineral assemblages of the original diagenetic zones. Kaolinite and montmorillonite, and similarly also zeolite and kaolinite were not formed simultaneously.

Their common occurrences resulted from changing physicochemical conditions during the alterations of rhyolite tuffs as far as hydrothermal alterations of rhyolite tuffs are concerned, the most important mineral assemblage is that of mixed-layer illite-smectite. Clays of this kind, devoid of montmorillonite, concentrate in the Dolná Ves deposit (Kraus et al. 1982).

Metastability, particularly that of alkaline zeolites, significantly controls the formation and preservation of zeolite mineral assemblages and their zonal distribution reflecting changes in thermal and chemical gradient. Contact, especially thermal effects of younger rhyolite bodies caused conversion of clinoptilolite into more stable, higher temperature mordenite in the exocontact of these bodies.

Conclusions

The acidic vitritic volcanoclastics in the SW Kremnické vrchy Mts. provided basic alumosilicate material for clay and zeolite accumulations. The alteration of the vitric tuffs took place in a fresh-water environment in an open or semiclosed hydrologic system during the diagenetic process. Vertical zonation represented by a perlite, smectite and clinoptilolite zone reflects changing pH and chemistry of pore solutions percolating through the volcanoclastic complex. Mineral assemblages of zones formed by the diagenetic process were locally modified by contact-thermal and hydrothermal effects of younger rhyolite bodies.

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