SLOVAK INDUSTRIAL MINERALS RELATED TO NEOGENE VOLCANIC ACTIVITY - GEOLOGY, MINERALOGY AND APPLICATIONS (BENTONITES, PERLITES, ZEOLITES)

UHLÍK, P.[1], LEXA, J.[2], OSACKÝ, M.[1], KODĚRA, P.[1], VARGA, P.[1], BAI, Y.[1], MILOVSKÝ, R[3], BIROŇ, A.[3], FALLICK, A.E.[4] & PALKOVÁ, H.[5]
[1]Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University, Bratislava, Slovakia
[2]Earth Science Institute, Slovak Academy of Sciences, Bratislava, Slovakia
[3]Earth Science Institute, Slovak Academy of Sciences, Banská Bystrica, Slovakia
[4]Scottish Universities Environmental Research Centre, East Kilbride, Glasgow, United Kingdom
[5]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia
E-mail: peter.uhlik@uniba.sk

Introduction

Industrial minerals generate about 43 % from total exploitation of mineral deposits in Slovakia. Total mining output has reached 30.5 Mt in 2018. Carbonates (limestone, dolomite, magnesite, marl) have a dominant position (87 %) in the industrial mineral exploitation (ŠOLTÉS *et al.*, 2020). Bentonite, perlite and zeolite also have a long-term tradition in production of industrial minerals in Slovakia. They belong to the most perspective, despite their significantly lower extraction volume compared to carbonates. Especially the production of bentonite and zeolite increases every year and Slovakia belongs to world producers.

The most exploited bentonite and two most significant perlite deposits are located in the Central Slovakia Volcanic Field (CSVF). The most important deposits are related to products of rhyolite volcanic activity of the Jastrabá Fm., which is represented by dykes, extrusive domes, cryptodomes, lava flows and related volcanoclastic rocks. The Jastrabá Fm. rhyolites yield ages ranging from 12.2±0.3 Ma to 11.4±0.4 Ma (CHERNYSHEV *et al.*, 2013). The largest zeolite accumulation with the best quality is situated in the East Slovakia Neogene Basin (ESNB). There are also some smaller bentonite deposits and perlite occurrences in the ESNB, which is a volcano-sedimentary basin located on the junction of the Western and Eastern Carpathians in the north-western part of the Trans-Carpathian depression (KOVÁČ *et al.*, 1995). The purpose of our paper is to provide an overview of recent results on geology, mineralogy, and the use of Slovak deposits of bentonite, perlite and zeolite.

Perlite

From numerous occurrences of perlite in the Slovakian part of the Western Carpathians only Lehôtka pod Brehmi (LPB) and Jastrabá (JST) represent exploitable deposits. The LPB deposit has been exploited in an open quarry since the year 1963. That led subsequently to the construction of the processing plant for the production of expanded perlite that was modernized two times. The LPB deposit is represented by a pile of extruded hyaloclastite breccia composed of grey porous and dark dense fragments. The JST deposit was discovered during a prospection campaign in the years 1974–1980. It represents the biggest deposit of perlite in the Western Carpathians (HRONCOVÁ, 1989). Currently, the deposit is ready for exploitation. Recent exploration and exploitation at both perlite deposits are operated by the company LBK PERLIT s. r. o. Production ranged from about 16 kt in 2013 to about 48 kt in 2017 (ŠOLTÉS *et al.*, 2020). Due to its quantity and quality perlite from these deposits still belongs to perspective raw materials of Slovakia.

The JST deposit is represented by glassy rhyolite breccia composed of porous grey fragments associated with an extrusive dome/coulée. Perlite at both deposits are peraluminous, calc-alkaline of high-K type, poor in phenocrysts (around 5 %) of plagioclase, biotite and minor amphibole (LPB) or sanidine/anorthoclase (JST). Glass at both deposits is silica rich (75.4–79.5 wt.% dry) with Al_2O_3, K_2O and Na_2O as other major constituents. Glass water content (3.0–6.0 wt.%) shows a weak positive correlation with its silica content and a negative correlation with its Na_2O content. Perlites show porosities 5–16 % (dark dense), 16–30 % (grey porous) and 30–44 % (pale grey pumiceous). Narrow stretched pores represent remnants after outgassing of ascending magma while open undeformed pores grew at a low pressure before quenching. The transformation of volcanic glass into perlite took place owing to the hydration by a heated mixture of liquid and vapor of meteoric origin. The hydration was supported by a significant porosity with interconnected pores and by a sustainably elevated temperature (LEXA *et al.*, 2021). Slovak crude perlites include a higher amount of loosely bound water [45–60% of total water (H_2O_t), released in the temperature range 0–250 °C] and a lower amount of strongly bound water (1–7% of H_2O_t, released at temperatures over 550 °C) compared to Hungarian and other world perlites (18–50%, respectively, 6–23% of H_2O_t). Slovak crude perlites also contain higher ratio of K_2O to Na_2O (2–2.5) when compared to other world perlites (0.7–1.4, ROULIA *et al.*, 2006). These can be important factors that cause discrepancies in the expansibility of perlites among Slovak and world perlites. On the other hand, due to the same reason, the Slovak perlites have a better mechanical stability (VARGA *et al.*, 2019).

Knowledge of the water content in perlite is crucial for a wide range of volcanological and material processing studies. For that reason a new method based on normalizing the near-IR spectra to internal standards was proposed based on the assessment of the water content using the $(\nu + \delta)H_2O$ band near 5200 cm^{-1}. The use of hexadecyltrimethylammonium bromide salt as an inner standard resulted in a better correlation with the results gained from TG or LOI than the results obtained for talc as an inner standard. After the initial experimental adjustment of the proper fractions in mixtures of perlite and inner standard the whole procedure is easy and quick to perform, needing only small amounts of samples. The method provides reasonable resolution within the narrow range of water content of perlites (PÁLKOVÁ *et al*., 2020).

Major industrial utilization of perlite is in the form of expanded perlite, which is produced by a quick heating at 800–1000 °C of grinded natural perlite. Expanded perlite has an extremely low density and a high specific surface area. Its physical-chemical properties induce high sound and thermal isolation capacity, heat resistance, chemical inertness, and high filtration ability of the expanded perlite. These properties lead to its application in various branches of economy, mainly in building industry but also in food industry, agriculture, and environmental protection.

A fine particle size (<100 μm), perlite by-product material (PBM) is not suitable for perlite expansion in Lehôtka pod Brehmi processing plant. Consequently, PBM has very limited application, recently, only as a pozzolanic, partial replacement for cement in concrete. Therefore, a conversion of PBM into zeolites was proposed to recover this by-product and to obtain value-added material with attractive sorption properties. Zeolite synthesis was performed in batch experiments in a wide range of experimental conditions and the reaction products were different zeolite species, namely phillipsite (PHI), zeolite X (FAU) and zeolite P (GIS) (OSACKÝ *et al*., 2020; HUDCOVÁ *et al*., 2021).

Bentonite

Bentonite is a raw material composed predominantly of clay minerals from the smectite group, mainly of montmorillonite. There are 30 registered bentonite deposits in Slovakia, 12 of them are exploited. Total bentonite reserves of Slovakia reach 57 Mt (ŠOLTÉS *et al*., 2020). Slovakia is the fifth largest bentonite producer in Europe and 10th in the world. The most important deposits are located in the Kremnica Mountains (e.g., Stará Kremnička – Jelšový potok, Lutila, Kopernica).

The bulk bentonites from all bentonite deposits of the Jastrabá Fm. consist of similar mineral constituents, in particular smectite, feldspars, mica, opal-CT, kaolinite, quartz, sometimes goethite. The main differences were observed in the quantity of these mineral constituents in samples from different deposits and even in samples from a single deposit. The best deposits contain 80–90 wt.% of smectite. Many authors have indicated the predominance of divalent exchangeable cations (Ca^{2+} and Mg^{2+}) in the interlayer space of smectites. Various methods confirmed that smectite from the Jastrabá Fm. is Al-Mg montmorillonite and the layer charge arises mainly from Mg for Al substitutions in the octahedral sheet. A significant positive correlation was established between cation exchange capacity (CEC) values and smectite. The best-grade bulk bentonites have a CEC about 100 meq/100 g. The insufficient fluid flow rate caused the precipitation of high amounts of opal-C or/and opal-CT (up to 45 wt.%) in some locations (e.g., UHLÍK *et al*., 2012; PENTRÁK *et al*., 2018; OSACKÝ *et al*., 2019).

The older studies have reported that bentonite deposits of the Jastrabá Fm. are primarily formed by alteration of acidic vitric volcanoclastics during diagenesis in a freshwater environment in an open or semiclosed hydrological system (e.g., KRAUS *et al*., 1994). The results of recent studies have shown a strong effect of subsurface hydrothermal fluids (mostly steam-heated meteoric water, outflowing from the Kremnica epithermal vein system located northwards) on the bentonitization of rhyolitic rocks of the Jastrabá Fm. (KODĚRA *et al*., 2014). It seems that the best grade bentonites were formed by the alteration of marginal perlitic breccias of extrusive domes and cryptodomes. The isotope geothermometry results indicated that the lateral mineral zonation in the Jastrabá Fm., namely mixed-layered illite-smectite accumulations in the northern part and smectite accumulations in the southern part of the formation, may be related to the gradual decrease in temperature of the hydrothermal fluids percolating through the rhyolitic rocks from north to south (KODĚRA *et al*., 2014). In addition to more than dozen bentonite deposits also the K-bentonite Dolná Ves deposit is located in the Jastrabá Fm. The major minerals are mixed-layered illite-smectite (I-S) and quartz. Economic accumulation of I-S is unique, only a few similar clay deposits are mined in the world. K-bentonite is used as a ceramic clay with annual production of about 6,000 tonnes (ŠOLTÉS *et al*., 2020). The clays from Dolná Ves contain pure I-S in clay fraction (ŠUCHA *et al*., 1996). In the 90-ties, prof. Šucha collected samples and sent them to the Clay Minerals Society (CMS). Since that time, I-S rich clay from Dolná Ves i.e., ISCz-1 (illite-smectite, former Czechoslovakia) is a part of the CMS Source Clays collection. The recent study confirmed that the expandability of studied I-S samples is between 20 and 42%.

Despite, that Slovakia is a significant producer of bentonite and its quality is mostly high, the home processing is falling behind of its potential and Slovak bentonite have a low added value. The most exported bentonite is in the form of raw bentonite and the second exported bentonite product is a cat litter. Consequently, in 2018 the average price of exported bentonite was 54 EUR/t but the average price of imported bentonite was 308 EUR/t (ŠOLTÉS *et al*., 2020). Slovakia as a "bentonite country" cannot be satisfied with such a price imbalance. The current challenge is to find a way how to optimize the application of Slovak bentonites to increase their added value.

Zeolite

The most important Slovak zeolite deposits occur in rhyodacite volcanoclastic rocks (Hrabovec tuff) of the Lower to Middle Badenian age. The Hrabovec tuff builds a 7 km long and up to 150 m wide belt between the villages of Pusté Čemerné, Nižný Hrabovec, Kučín, Majerovce, and Vranov in the ESNB (VARGA, 1984). Zeolite is a mostly light-green, fine-grained rock, resulting from alteration of a vitreous material. The major mineral is clinoptilolite-K and -Ca and its content is mostly between 60–80 wt.%. The second most frequent phase is opal-CT or opal-C (15–20 wt.%). Less abundant minerals are plagioclase, K-feldspar, micas, kaolinite and traces of pyroxenes, quartz, zircon and apatite (ŠAMAJOVÁ & KRAUS, 1977; TSCHEGG *et al*., 2019, our unpublished data). The Nižný Hrabovec deposit is the largest zeolite quarry in Slovakia, operated by the company Zeocem, a.s., Bystré, with an annual production of ~180 kt of zeolite. This accounts for 87% of the total mine production in Slovakia (ŠOLTÉS *et al*., 2020). Nižný Hrabovec zeolite is used in its natural and various modified forms. It has various uses in agriculture (used as feed additive, soil conditioner and fertilizer), building industry (pozzolan cement, concrete products, concrete additives), wide variety of environmental uses (excellent filtration and sorption properties are used in water and gas cleaning and treatments) and others (see zeocem.com).

The strongest zeolite alteration of the Jastrabá Fm. is hosted by the hanging wall of rhyolitic extrusive domes at the deposit Bartošová Lehôtka - Paseka, where zeolitised tuffs occur in the area of 600 x 400 m and have thickness of X m to 30–40 m (ZUBEREC *et al*., 2005). The raw material is comprised by green, light-green zeolitic tuffs and pyroclastics. Zeolites are represented by clinoptilolite and mordenite. Zeolite content ranges from a few % up to nearly 50 %. Associated micrgranitic rhyolites are affected by postmagmatic silicification and adularisation, with network of opal-chalcedony veinlets. Zeolite alteration has a zonal arrangement with mordenite (± clinoptilolite, kaolinite and opal-CT) preferably closer to the contact with rhyolite, and smectite with admixture of clinoptilolite in more distal parts (KRAUS *et al*., 1994). The deposit is mined irregularly. The raw material is applied in agriculture and environmental protection.

Acknowledgement

The authors gratefully acknowledge financial support from the Slovak Grant Agency (VEGA, projects no. 1/0196/19) and to mining companies LBK PERLIT, s.r.o., REGOS, s.r.o., SARMAT, Ing. Peter Majer, Sedlecký kaolin - Slovensko s.r.o., VSK PRO - ZEO s. r. o., ZEOCEM, a.s., for provision of samples.

References

CHERNYSHEV, I. V., KONEČNÝ, V., LEXA, J., KOVALENKER, V. A., JELEŇ, S., LEBEDEV, V. A. & GOLTSMAN, Yu. V. (2013): Geologica Carpathica, 64: 327–351.

HRONCOVÁ, Z. (1989): Mineralia Slovaca, 21: 561–564.

HUDCOVÁ, B., OSACKÝ, M., VÍTKOVÁ, M., MITZIA, A. & KOMÁREK, M. (2021): Microporous and Mesoporous Materials, 317: 111022.

KODĚRA, P., LEXA, J., FALLICK, A. E., WÄLLE, M. & BIROŇ, A. (2014): In: Garofalo, P. S. & Ridley, J. R. (Eds.): Gold-transporting hydrothermal fluids in the Earth's crust. Geological Society London, Special Publication, 402: 177–206.

KOVÁČ, M., KOVÁČ, P., MARKO, F., KAROLI, S. & JANOČKO, J. (1995): Tectonophysics, 252: 453–466.

KRAUS, I., ŠAMAJOVÁ, E., ŠUCHA, V., LEXA, J. & HRONCOVÁ, Z. (1994): Geologica Carpathica, 45: 151–158.

LEXA, J., VARGA, P., UHLÍK, P., KODĚRA, P., BIROŇ, A. & RAJNOHA, M. (2021): Geologica Carpathica, in press.

OSACKÝ, M., BINČÍK, T., PAĽO, T., UHLÍK, P., MADEJOVÁ, J. & CZÍMEROVÁ, A. (2019): Geologica Carpathica, 70: 433–445.

OSACKÝ, M., PÁLKOVÁ, H., HUDEC, P., CZÍMEROVÁ, A., GALUSKOVÁ, D. & VÍTKOVÁ, M. (2020): Microporous and Mesoporous Materials, 294/1: 109852.

PÁLKOVÁ, H., KUREKOVÁ, V., MADEJOVÁ, J., NETRIOVÁ, Z., UHLÍK, P., VARGA, P., HRONSKÝ, V. & LEXA, J. (2020): Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 240: 118517.

PENTRÁK, M., HRONSKÝ, V., PÁLKOVÁ, H., UHLÍK, P., KOMADEL, P. & MADEJOVÁ, J. (2018): Applied Clay Science, 163: 204–213.

ROULIA, M., CHASSAPIS, K., KAPOUTSIS, J. A., KAMITSOS, E. I. & SAVVIDIS, T. (2006): Journal of Materials Science, 41: 5870–5881.

ŠAMAJOVÁ, E. & KRAUS, I. (1977): The 7th Conference on Clay Mineralogy and Petrology, Karlovy Vary, 1976, 391–399.

ŠOLTÉS, S., KÚŠIK, D. & MIŽÁK, J. (2020): Slovak Minerals Yearbook 2019. The State Geological Institute of Dionýz Štúr, Bratislava.

ŠUCHA, V., ŚRODOŃ, J., ELSASS, F. & McHARDY W. J. (1996): Clays and Clay Minerals, 44 (5): 665-671.

TSCHEGG, C., RICE, A. H. N., GRASEMANN, B., MATIASEK, E., KOBULEJ, P., DZIVÁK, M. & BERGER, T. (2019): Economic Geology, 114: 1177–1194.

UHLÍK, P., JÁNOŠÍK, M., KRAUS, I., PENTRÁK, M. & ČAPLOVIČOVÁ, M. (2012): Acta Geologica Slovaca, 4: 125–137.

VARGA, I. (1984): Mineralia Slovaca, 16: 371–376.

VARGA, P., UHLÍK, P., LEXA, J., ŠURKA, J., BIZOVSKÁ, V., HUDEC, P. & PÁLKOVÁ, H. (2019): Monatshefte für Chemie – Chemical Monthly, 150: 1025–1040.

ZUBEREC, J., TRÉGER M., LEXA J. & BALÁŽ P. (2005): Mineral resources of Slovakia. Štátny geologický ústav D. Štúra, Bratislava.