Palaeokarst with bauxite filling near Čoltovo (Slovak Karst)

Roman Aubrecht^{1,3} & Peter Bačík^{2,3}

¹Department of Geology and Paleontology, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, SK-842 15 Bratislava, Slovakia; roman.aubrecht@uniba.sk ²Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, SK-842 15 Bratislava, Slovakia; peter.bacik@uniba.sk ³Earth Science Institute, Geophysical Division, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 28 Bratislava, Slovakia

AGEOS

Abstract: In the Slovak Karst area, three quarries are situated west of the Čoltovo Village. In the southern quarry, the Anisian carbonatic Silica Nappe is uncovered. Palaeokarst clefts and cavities were revealed in the calciturbiditic Raming Limestone. They mostly contain yellowish to red sinter filling with flowstone draperies, small stalactites and stalagmites. The rest is filled with yellowish (ochre) material. The PXRD analysis (Powder X-Ray Diffraction) indicates that the material is represented predominantly by diaspore, which is an aluminium oxide hydroxide mineral, α -AlO(OH). This means that the material most likely represents a remnant bauxite deposit. By now, only several small occurrences of bauxitic ores were found in Slovakia. Diasporic bauxites were found only on Glac Plateau in the Stratenská hornatina Mts. The Čoltovo occurrence is then the second one of this type of bauxite. These occurrences share similar tectonic position, genesis and most likely also the same provenance. All these bauxitic occurrences in the Western Carpathians are invariably related to the emersion and karstification period that occurred after the main nappe thrusting phase in the West Carpathian internides, i.e., their age spans from the Late Cretaceous to Paleocene. In this period, the Western Carpathian area was in the humid tropical climate zone, which was able to promote lateritic weathering. In later periods, the climate was not suitable for such a weathering. It is not yet known, whether the bauxitic material rests in its original position or it was reworked and resedimented to younger clefts and cavities. Further research is necessary to verify the age and provenance of this new bauxite occurrence.

Keywords: Silica Nappe, palaeokarst, bauxites, Cretaceous, Paleogene

1. INTRODUCTION

Occurrences of bauxite in Slovakia are rare and economically negligible. Unlike in the adjacent, more southern Transdanubian Central Range, which is very rich in bauxite deposits (e.g., Mindszenty et al., 1986; Kelemen et al., 2023 for an overview), by contrast, there have been only a few occurrences of bauxite revealed so far in the Western Carpathians. The largest ones are situated mostly in the Strážovské vrchy Mts. (Mojtín, Domaniža, Pružina) in palaeokarst depressions developed in the Choč and Strážov nappe dolomites and limestones (*Číčel, 1958*). Much smaller occurrences were reported from the toe of the Galmus Zone (in the vicinity of Markušovce Village), which is formed by limestones of the Silicicum s.l. (Konta, 1954). In the same unit, but in the Stratenská hornatina Mts., several small bauxite occurrences were found on Glac Plateau (Novotný & Tulis, 2002). Some small occurrences were also registered in the Slovak Karst (Silica Nappe, Silicicum s.s.), e.g., in the Miglinc Valley (Matějka, 1958). This paper brings an initial report about a new bauxite occurrence with a relatively unique composition in the Slovak Karst area.

2. GEOLOGICAL SETTING, SAMPLED SITES, MATERIALS AND METHODS

In the Slovak Karst area, close to the contact with Neogene Filling of the South Slovakian Basin, three quarries are situated opposite the Čoltovo Village, at the toe of Okrúhly kopec Hill (296 m a.s.l.). The northernmost quarry is still active and two more southern ones are abandoned. In these three quarries, the Middle to Upper Triassic limestone succession of the Silica Nappe is outcropped. The southern quarry (Fig. 1) was excavated in the Anisian succession from Steinalm platform limestones, passing through Reifling and Raming limestones up to the Wetterstein Limestone (Gaál & Mello, 1983; Mello et al., 1996).

Recently, palaeokarst clefts and cavities were found, obliquely intersecting the beds of the calciturbiditic Raming Limestone in the middle of the southernmost quarry (Fig. 2A). Some are free of any sinter coatings (Fig. 2B), but most of them contain yellowish sinter filling with flowstone draperies, small stalactites and stalagmites (Figs. 2C, 3A-B). This seemingly well-preserved sinter is, in fact, strongly recrystallised, with several cm long calcitic crystals (Fig. 3C). Rest of the clefts is filled by yellowish (in some clefts also whitish to reddish) sedimentary material, which was first initially considered to be Lower Miocene schliers (Figs. 2B-C, 3A). However, the first analytical attempts revealed neither any presence of marine microfauna nor palynoflora. On the other hand, the analysis revealed that this material is predominantly non-calcareous. A cleft with the best-expressed sinter filling was sampled for the sedimentary filling. The samples were subjected to the PXRD analysis (Powder X-Ray Diffraction). Powder X-ray diffraction analyses were determined by the BRUKER D8 Advance diffractometer under the following conditions: Bragg-Brentano geometry (Theta-2Theta), Cu anticathode ($Ka_1 = 1.5406 \text{ Å}$), accelerating voltage 40 kV, beam current 40 mA, BRUKER LynxEye detector. Ni K_g filters were used for stripping of K_{β} radiation. The step size was 0.01° 2 θ , the counting time was 3 s per step, and the range of measurement was $2 - 65^{\circ} 2\theta$.



Fig. 1. Position of the examined locality. A – Position of the examined locality within the frame of the tectonic map of south-eastern Slovakia. Basal tectonic map after Bezák et al., 2004 – modified. B – Position of the studied locality in the southern Čoltovo quarry. Photo: Google Earth 2023.



Fig. 2. Field views on the palaeokarst cavities on the central basal level of the Čoltovo southern quarry. A – View on the central basal level of the quarry with marked position (yellow arrow) of the palaeokarst cavities in the bedded (calciturbiditic) Raming Limestone. B – Ochre diasporic bauxite in a cavity copying the limestone bedding. The cavity lacks a sinter filling. C – Ochre diasporic bauxite in the lower part of the outcrop covering an older cave sinter (flowstone on the left and a stalactite on the top of the photo).



Fig. 3. A – Bauxite filling a curved cleft obliquely cutting the limestone beds in the middle part of the outcrop. B – Detail of the previous photo at the hammerhead showing sinter draperies and a small stalactite covered by bauxite. C – Detail of a fallen piece of sinter showing its strong recrystallisation.

3. RESULTS

The PXRD analysis showed that one of the significant phases in the studied material is diaspore, an aluminium oxide hydroxide mineral, α -AlO(OH). It is accompanied by Fe-oxide goethite. Increased content of Fe, indicated also by the increased background due to fluorescence, is responsible for the yellow colour of the material. A significant part of the material is composed of clay minerals, including muscovite/ illite, montmorillonite, and kaolinite (Fig. 4). This suggests that the yellowish material most likely represents an allochthonous bauxitic material. Calcite in the samples is likely the contamination from the host rock.

4. INTERPRETATIONS AND DISCUSSION

4.1. Diaspore occurrences in Slovakia

Diaspore was recorded in Slovakia in non-bauxitic deposits of various genesis, e.g., in neovolcanic vein-impregnation Cu mineralisation in Banská Štiavnica (Koděra et al., 1986), Pliocene heat-proof clays near Breznička (Kraus, 1968; Kraus et al., 1971), post-volcanic mineralisation in the Vigľašská Huta – Kalinka area (Valach, 1966; Marková & Štohl, 1978), and post-volcanic secondary quartzites in Vihorlat Mts. (Derco et al., 1977).

In Slovak bauxites, the presence of diaspore was presumed at Markušovce (Zorkovský, 1952) and Mojtín (Šiške, 1949) based on VTA and chemical analyses. However, only the bauxites



Fig. 4. PXRD diffraction patterns showing the mineral composition of the bauxite. Mineral abbreviations: Mnt – montmorillonite, Ms – muscovite/illite, Kln – kaolinite, Gth – goethite, Dsp – diaspore.

found in the Stratenská hornatina Mts. (Glac Plateau) were predominantly formed by diaspore (Novotný & Tulis, 2002). The Čoltovo occurrence described herein represents only the second report of such bauxites from Slovakia.

4.2. Possible genetic relations of the Čoltovo diasporic bauxites

Diaspore bauxites are not as common as those dominated by boehmite and gibbsite. Their genesis is not fully understood yet. While gibbsite and boehmite can be synthesised under low temperatures and low pressure, the synthesis of diaspore requires higher pressure (Zhao et al., 2023 and the literature cited therein). Some even form a major portion of metabauxitic deposits, e.g., in Turkey (Gündoğan, 2022). The bauxites from Čoltovo and Glac Plateau share similar tectonic position, genesis and most likely also the same provenance. Therefore, it will be of key importance to collect as much data as possible from these bauxites and their host rocks. Detailed chemical and heavymineral analyses of the Čoltovo bauxite samples are planned to be performed soon.

4.3. Bauxite and palaeokarst timing

All the bauxitic occurrences in the Western Carpathians are invariably related to the emersion and karstification period that occurred after the main nappe thrusting phase in the Western Carpathian internides. Their age spans from the Late Cretaceous to Paleocene (in the Inner Western Carpathians it may eventually go as deep as the Early Cretaceous after the final closure of the Meliaticum in Late Jurassic – Mock et al., 1998; Aubrecht et al., 2010). At this time, the Western Carpathian area was in the humid tropical climate zone, which was able to promote lateritic weathering. Therefore, it is substantiated to presume a similar age for the bauxites revealed at Čoltovo. The Silica Nappe in the examined area is covered by Pontian Poltár Formation (variegated clays, sands and gravels), or locally by the older, Eggenburgian Bretka Formation (sandstones to conglomerates – Mello et al., 1997). Both formations are too young to indicate the timing of bauxite formation which had to occur much earlier in a tropical climate.

However, it is not yet known whether the bauxitic material rests in its original position or it was reworked and resedimented to younger clefts and cavities. Sinter forms (flowstones, stalactites, etc.) do not usually occur in palaeokarst sites older than the Paleogene. Despite an extensive literature review done by the authors, only one record of an older sinter of this type has been found. It was a sinter pebble described from the Cretaceous (Cenomanian to Coniacian) exotic conglomerates in the Klape Unit. Therefore, a Cenozoic age of the palaeokarst can be assumed. The general course of the studied palaeokarst clefts, as well as directions visible on sinter draperies or stalactites show that they are normal to the present Earth surface. It is an indication that the palaeokarst originated after the final tectonic emplacement of the unit in which it was formed. Nevertheless, the research indicates that Silicicum never forms a single simple structure but consists of several (at minimum two) partial nappes. The lower units often display a higher tectono-thermal effect. In the eastern part of the Slovak Karst area, two partial units were distinguished: the lower one, the Silica-Turňa partial unit, overlain by the Hačava-Jasov partial unit (Mello et al., 1997). Between them, marbles containing Late Cretaceous ("Senonian") microfauna are squeezed tectonically (Mello & Salaj, 1982). It indicates that the tectonic emplacement of the higher unit was post-"Senonian". Also, the bauxite occurrence reported by Matějka (1958) rests on the lower unit. A similar twofold structure of the Silicicum was reported from the Muráň Nappe (Vojtko, 2000) and from the Stratená Nappe (Mello et al., 2000), where the lower, Geravy and upper, Glac partial units were distinguished. The bauxitic occurrences described by Novotný & Tulis (2002) rest on the higher, Glac partial unit. In the Gombasek quarry, which is located in the upper partial structure of the Silica Nappe (Brezová-Plešivec partial unit sensu Bystrický, 1964), palaeokarst cavities with Late Cretaceous fillings were found (Mello & Snopková, 1973), but presence of bauxites was not detected in them (Gaál, 2008; Jacko et al., 2016). The studied locality is situated in a lower partial unit of the Silicicum (Bretka partial unit sensu Gaál & Mello, 1983), as evident by high values of the conodont alteration index (personal communication from R. Mock (+), H.-J. Gawlick and S. Missoni (+)). This unit also has a northvergent bedding inclination, which is different from the upper partial structures with a southvergent inclination (Gaál & Mello, 1983). As the bauxites may occur in both, the lower and upper units the timing of palaeokarst origin is most likely after the emplacement of all partial units. Some fossil findings of terrestrial fauna or flora, or eventually some

radiometric dating methods would provide more information about the palaeokarst age.

5. CONCLUSIONS

Palaeokarst clefts and cavities were revealed in the calciturbiditic limestones of the Raming Limestone in the southernmost of the three quarries west of the Čoltovo Village in the Slovak Karst area. They mostly contain yellowish to red sinter filling with flowstone draperies, small stalactites, and stalagmites. The rest is filled with yellowish (ochre) material. The PXRD analysis (Powder X-Ray Diffraction) indicates that the material is represented predominantly by diaspore, which is an aluminium oxide hydroxide mineral, α -AlO(OH). The material most likely represents a remnant bauxitic lateritic weathering crust.

The bauxite in Čoltovo quarry most likely shares the same tectonic position, genesis and most likely also the same provenance with diasporic bauxites were on Glac Plateau in the Stratenská hornatina Mts.

All the bauxites in Slovakia are related to the emersion and karstification period that occurred after the main nappe thrusting phase in the Western Carpathian internides, i.e. Late Cretaceous to Paleocene when the Western Carpathian area was in the humid tropical climate zone, which was able to promote lateritic weathering. Later periods were not suitable for such a weathering. The most likely age of the Čoltovo bauxite is Paleocene.

It is not yet known whether the bauxitic material rests in its original position or it was reworked and resedimented to younger clefts and cavities. Further research is necessary to verify the age and provenance of this new bauxite occurrence.

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References

- Aubrecht R., Gawlick H.-J., Missoni S., Suzuki H., Plašienka D., Kronome K. & Kronome B., 2010: Middle Jurassic matrix radiolarians from the Meliata ophiolite melange at the type Meliatic sites Meliata and Jaklovce (Western Carpathians): palaeogeographic evidence. *Geologica Balcanica*, 39, 1–2, 33–34.
- Bezák V. (Ed.), Broska I., Ivanička J., Reichwalder P., Vozár J., Polák M., Havrila M., Mello J., Biely A., Plašienka D., Potfaj M., Žec B., Vass D., Elečko M., Janočko J., Pereszlényi M., Marko F., Maglay J. & Pristaš J., 2004: Tectonic map of Slovak Republic 1: 500,000 with explanations. ŠGÚDŠ, Bratislava.
- Bystrický J., 1964: Slovenský kras. [Slovak Karst]. ÚÚG Bratislava, 1–204. [in Slovak with German summary]
- Číčel B., 1958: Príspevok k mineralógii bauxitov z okolia Mojtína. [Contribution to the mineralogy of bauxites from the surroundings of Mojtín]. *Geologické práce, Zprávy*, 14, 4–55. [in Slovak with English summary]
- Derco J., Kozáč J. & Očenáš P., 1977: Nové poznatky o mineráloch a genéze sekundárnych kvarcitov lokality Kapka v centrálnom Vihorlate. [New information about the mineralogy and genesis of secondary quartzites at Kapka

locality in the central Vihorlat Mts. area]. *Mineralia Slovaca*, 9, 3, 185–205. [in Slovak with English summary]

- Gaál Ľ., 2008: Geodynamika a vývoj jaskýň Slovenského krasu. [Geodynamics and development of caves in the Slovak Karst]. *Speleologia Slovaca*, 1, 1–166. [in Slovak with English summary]
- Gaál Ľ. & Mello J., 1983: Nové údaje o stratigrafii triasových vápencov západnej časti silického príkrovu a ich odraz v tektonickej stavbe. [New data to the stratigraphy of Triassic limestones in the western part of the Silica nappe and their consequence for tectonic subdivision]. *Mineralia Slovaca*, 15, 4, 303–330. [in Slovak with English summary]
- Gündoğan İ, 2022: Meta-bauxite deposit in the Tavşanlı Zone, NW Turkey: A new locality for gem-quality diaspore formation. *Journal of Asian Earth Sciences*, 8, 100114.
- Jacko S., Farkašovský R., Dirnerová D., Kondela J., Rzepa G. & Zakršmídová B., 2016: The Late Cretaceous conditions of the Gombasek beds sedimentation (Silica nappe, Western Carpathians). *Acta Montanistica Slovaca*, 21, 4, 259–271.
- Kelemen P., Dunkl I., Csillag G., Mindszenty A., Józsa S., Fodor L. & von Eynatten H., 2023: Origin, timing and paleogeographic implications of Paleogene karst bauxites in the northern Transdanubian range, Hungary. International Journal of Earth Sciences, 112, 243–264.
- Koděra M., Andrusovová-Vlčeková G, Belešová O., Briatková D., Dávidová Š., Fejdiová V., Hurai V., Chovan M., Nelišerová E. & Ženiš P., 1986: Topografická mineralógia Slovenska 1. [Topographic mineralogy of Slovakia 1]. SAV Bratislava, 1–577. [in Slovak]
- Konta J., 1954: Petrografické a chemické studium bauxitů of Markušovců (východní Slovensko). [Lithological and chemical investigation of the bauxites of Markušovce (Eastern Slovakia)]. *Rozpravy ČSAV*, 64, 4, 11–54. [in Czech]
- Kraus I., 1968: Mineralogical-genetical study of clay sediments of the Poltár Formation. *Geologický zborník – Geologica Carpathica*, 19, 2, 389–405.
- Kraus I, Horváth I & Dobra E., 1971: Ložiská ílových surovín na Slovensku. [Deposits of clayey raw materials in Slovakia]. *Mineralia Slovaca*, 3, 12–13, 525–550. [in Slovak with English summary]
- Marková M. & Štohl J., 1978: Niektoré poznatky o solfatárovej formácii v oblasti Kalinka – Vígľašská Huta. [New data on solfataric formation at Kalinka – Vígľašská Huta region]. Západné Karpaty, séria Mineralógia, petrografia, geochémia, metalogenéza, 5, 109–144. [in Slovak with English and Russian summaries]
- Matějka A., 1958: Výskyt bauxitických hornin od Drienovce na jižním Slovensku. [Das Vorkommen eines bauxitischen Gesteine von Drienovec in der Südslowakei]. Věstník Ústředního ústavu geologického, 33, 279–281. [in Czech with German abstract]
- Mello J. & Salaj J., 1982: Nález vápencov gosauskej kriedy v údolí Miglinc (Slovenský kras). [Trouvaille des calcaires du Crétacé développés sous facies de Gosau dans la vallée de Miglinc (Karst de Slovaquie).] Geologické práce, Správy, 77, 49–54. [in Slovak with French summary]

- Mello J. & Snopková P., 1973: Vrchnokriedový vek výplní v dutinách triasových vápencov Gombaseckého lomu. [Upper Cretaceous filling in the cavities of Triassic limestones in the Gombasek quary]. *Geologické práce, Správy*, 61, 239–253. [in Slovak with English summary]
- Mello J. (Ed.), Elečko M., Pristaš J., Reichwalder P., Snopko L., Vass D. & Vozárová A., 1996: Geological map of the Slovenský kras Mts. 1:50 000. Slovak Geological Survey, Bratislava.
- Mello J. (Ed.), Elečko M., Pristaš J., Reichwalder P., Snopko L., Vass D., Vozárová A., Gaál Ľ., Hanzel V., Hók J., Kováč P., Slavkay M. & Steiner A., 1997: Vysvetlivky ku geologickej mape Slovenského krasu 1:50 000. [Explanations to the geological map of the Slovak Karst 1:50 000]. Vydavateľstvo Dionýza Štúra, Bratislava, 1–255. [in Slovak with English summary]
- Mello J., Filo I., Havrila M., Ivan P., Ivanička J., Madarás J., Németh Z., Polák M., Pristaš J., Vozár J., Vozárová A., Liščák P., Kubeš P., Scherer S., Siráňová Z., Szalaiová V. & Žáková E., 2000: Vysvetlivky ku geologickej mape Slovenského raja, Galmusu a Hornádskej kotliny 1: 50 000. [Explanations to the geological map of the Slovenský raj – Galmus Mts. and Hornád Depression 1: 50 000]. Vydavateľstvo Dionýza Štúra, Bratislava, 1–303. [in Slovak with English summary]
- Mindszenty A., D'Argenio B. & Bognár L., 1986: Cretaceous bauxites of Austria and Hungary: Lithology and paloetectonic implications. *ICSOBA Travaux*, 16–17, 13–32.
- Mock R., Sýkora M., Aubrecht R., Ožvoldová L., Kronome B., Reichwalder P. & Jablonský J., 1998: Petrology and petrography of the Meliaticum near the Meliata and Jaklovce Villages, Slovakia. *Slovak Geological Magazine*, 4, 223–260.
- Novotný L. & Tulis J., 2002: Nálezy bauxitu v Slovenskom raji. [Discovery of bauxite in the territory of Slovak Paradise]. *Mineralia Slovaca*, 34, 2, 145–146. [in Slovak with English abstract]
- Šiške V., 1949: Příspěvek k posouzení složení bauxitu z Mojtína. [Contribution to evaluation of bauxite composition from Mojtín]. *Stavivo*, 27, 16, 280–283. [in Czech]
- Valach J., 1966: Niektoré nové poznatky o geologicko-petrografických pomeroch oblasti Vígľašská Huta Kalinka. [Einige neuen Erkenntnisse über die geologisch-petrographischen Verhältnisse des Gebietes Vígľašská Huta Kalinka (Mittelslowakei)]. *Geologické príce, Zprávy,* 38, 5–30. [in Slovak with German Summary]
- Zhao L., Liu X., Wang Q., Ma X., Liu L., Sun X. & Deng J., 2023: Genetic mechanism of super-large karst bauxite in the northern North China Craton: Constrained by diaspore in-situ compositional analysis and pyrite sulfur isotopic compositions. *Chemical Geology*, 622, 121388.
- Vojtko, R., 2000: Are there tectonic units derived from the Meliata-Hallstatt trough incorporated into the tectonic structure of the Tisovec Karst? *Slovak Geological Magazine*, 6, 4, 335–346.
- Zorkovský B., 1952: Slovenské bóksity a ich genéza. [Slowakische Bauxite und ihre Genesis]. *Geologický sborník SAV*, 3, 1–2, 89–102. [in Slovak with Russian and German summaries]