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### Sulfuric acid speleogenesis and surface landform evolution along the Vienna Basin Transfer Fault: Plavecký Karst, Slovakia

Pavel Bella <sup>1,2\*</sup>, Helena Hercman <sup>3</sup>, Šimon Kdýr <sup>4</sup>, Petr Mikysek <sup>4</sup>, Petr Pruner <sup>4</sup>, Juraj Littva <sup>2</sup>, Jozef Minár <sup>5</sup>, Michał Gradziński <sup>6</sup>, Wojciech Wróblewski <sup>6</sup>, Marek Velšmid<sup>7</sup>, and Pavel Bosák <sup>4</sup>

<sup>1</sup>Department of Geography, Faculty of Education, Catholic University in Ružomberok, Hrabovská cesta 1, 031 04 Ružomberok, Slovakia <sup>2</sup>State Nature Conservancy of the Slovak Republic, Slovak Caves Administration, Hodžova 11, 031 01 Liptovský Mikuláš, Slovakia <sup>3</sup>Institute of Geological Sciences, Polish Academy of Sciences, ul. Twarda 51/55, 00 818 Warszawa, Poland

<sup>4</sup>Institute of Geology of the Czech Academy of Sciences, Rozvojová 269, 165 00 Praha 6-Lysolaje, Czechia

<sup>5</sup>Department of Physical Geography and Geoinformatics, Komenský University, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava 4, Slovakia <sup>6</sup>Institute of Geological Sciences, Faculty of Geography and Geology, Jagellonian University, Gronostajova 3A, 30-387 Kraków, Poland <sup>7</sup>Cavers Plavecké Podhradie, o.z. 906 36 Plavecké Podhradie 284, Slovakia

- Abstract: Hypogene caves in the Plavecký hradný vrch Hill (Western Slovakia, Central Europe) were formed by waters ascending along faults in fractured Triassic carbonates related to the horst-graben structure at the contact of the Malé Karpaty Mountains and the NE part of the Vienna Basin. The Plavecká jaskyňa and Pec caves mostly contain horizontal passages and chambers with flat corrosion bedrock floors, fissure discharge feeders, wall water-table notches, replacement pockets, as well as a few other speleogens associated with sulfuric acid speleogenesis. The low-temperature sulfuric acid development phases of the Plavecká Jaskyňa are also indicated by the presence of sulfate minerals (i.e., gypsum and jarosite). Subaerial calcite popcorn rims were precipitated from water condensation at the edges of feeding fissures that were still active as thermal vents when the water table dropped. Hydrogen sulfide involved in the sulfuric acid speleogenesis was likely derived from anhydrites and/or hydrocarbon reservoirs with sulfate-saline connate waters in the fill of the adjacent Vienna Basin. It ascended to the surface along deep-rooted sub-vertical fault zones at the contact of the Vienna Basin with neighboring mountains. Three cave levels at 295 to 283 m asl in the Pec Cave, and five levels at 225 to 214 m asl in the Plavecká jaskyňa corresponded to phases of stable local erosional base levels in the bordering part of the Vienna Basin, most likely during periods of strongly decelerated and/or interrupted subsidence. Cave levels separated by vertical differences of only a few meters may also be related to the Pleistocene climatic cycles. The subhorizontal parts of the Pec Cave are probably of late Early Pleistocene age (>0.99-1.07 Ma?). The two highest levels of the Plavecká jaskyňa developed during the early Middle Pleistocene (>600 ka). Fine-grained sediments in the passage at 225 m asl with normal magnetic polarity contain jarosite. The middle level of the Plavecká jaskyňa at 220 m asl was formed in the mid-Middle Pleistocene, while the lower and lowermost levels formed in the late Middle Pleistocene (>270 ka). The water table in the lowermost cave level probably dropped after the tectonic reactivation of the Podmalokarpatská zníženina Depression just in the front of a marginal horst structure of the Malé Karpaty Mountains.
- **Keywords:** multi-level hypogene cave, sulfuric acid speleogenesis, magnetostratigraphy, U-series dating, tectonics, Western Carpathians

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### INTRODUCTION

Sulfuric acid caves, which were produced by the oxidation of sulfides beneath the surface, are a specific

type of hypogenic speleogenesis (e.g., Egemeier, 1981; Hill, 1987, 1990; Palmer & Hill, 2005; Audra, 2008; Audra et al., 2009; Plan et al., 2012; Palmer, 2013; De Waele et al., 2016; D'Angeli et al., 2019a, b). They have been the subject of ongoing research in many parts of the world and because of their close connection to the water table (base) level, they can precisely record past geomorphological settings (De Waele et al., 2016; Columbu et al., 2021; Polyak et al., 2022). Bella et al. (2019a, b) described the hypogene caves (Plavecká jaskyňa Cave, Pec Cave) in the Plavecký hradný vrch Hill (Plavecký Karst, Malé Karpaty Mountains, Western Carpathians) with some morphological indicators of sulfuric acid speleogenesis (SAS) for the first time in Slovakia.

This article provides a morphological description of parts of the Plavecká jaskyňa, which were newly discovered in October 2018 (the Herzov dóm Chamber and adjacent passages and vertical segments) and the higher-lying Pec Cave, as well as mineralogical evidence of the SAS. The results of paleomagnetic analysis of fine-grained sediments and carbonate speleothems and U-series dating of carbonate speleothems enabled the reconstruction of development phases in the karst area related to surface landforms and the tectonic evolution of the Malé Karpaty Mountains (MKM) and the adjacent part of the Vienna Basin.

### **CAVE LOCATION AND GENERAL DATA**

The Plavecká jaskyňa and Pec caves are located on the north-western margin of the MKM known as the Plavecké predhorie Foothills. They occur in the northern part of the Plavecký hradný vrch Hill (431 m asl), near the village of Plavecké Podhradie (Fig. 1).



Fig. 1. A) Location of the study area in Slovakia (VBTF – Vienna Basin Transfer Fault); B) Location of the caves in the Plavecký hradný vrch (Plavecký Castle Hill, Photo by P. Bella); C) Geological setting of the surroundings (from Mahel' and Cambel, 1972; Baňacký and Sabol, 1973; Polák et al., 2011; Fordinál et al., 2012a), simplified and adjusted on the LIDAR background obtained from the Geodesy, Cartography and Cadastre Authority of the Slovak Republic: 1. Fatricum Unit, Mesozoic, predominantly carbonates; 2. Hronicum Unit, Paleozoic, predominantly non-carbonate rocks; 3. Hronicum Unit, Mesozoic, predominantly carbonate rocks; 4. Paleogene sediments (organogenic limestones, siliciclastic rocks); 5. Neogene sediments (predominantly marine to continental clastics); 6. Quaternary sediments of alluvial terraces and proluvial fans; 7. Quaternary floodplain sediments; 8. Late Pleistocene–Holocene eolian sands; 9. Late Pleistocene–Holocene colluvial and deluvial sediments; 10. fault; 11. expected Quaternary fault; 12. sole thrust; 13. other thrust; 14. spring.

The Plavecká jaskyňa is 1,253 m long (Tencer, 2021) with a vertical extent of 37 m. Its upper narrow discovery entrance is situated at 236 m asl. An artificial tunnel at 221 m asl (Tencer, 1991; Hubek & Magdolen, 2008) connects the foot of the Plavecký hradný vrch and the cave (Fig. 2). Together with the nearby 70 m-deep Plavecká priepasť Shaft (see Butaš, 2003), the Plavecká jaskyňa is among the warmest caves in Slovakia with air temperature of 11.0 to 12.8°C, which is increased by slightly warmer water (13.0–13.1°C) in its lowermost part (Košel, 2005; see also Briestenský & Stemberk, 2008; Velšmid, 2011).

The Pec Cave, 208 m long and 15 m deep, is among the higher-lying caves of the Plavecký hradný vrch with its entrance at ~295 m asl (Velšmid, 2013). Its upper level is regarded as an important archeological site (Bárta, 1982). The Stenlyho Jaskyňa Cave (entrance at 295 m asl, 22 m long and 5 m deep) is situated south of the Pec Cave (Šmída, 2010; Fig. 1).

### **GEOLOGICAL SETTING**

The origin and evolution of the territory was influenced by its position at the tectonic contact of the MKM with the Vienna Basin (Fig. 1). The MKM represent the westernmost core mountains of the Carpathian Mountain Range and form a NE–SW-trending horst separating the Neogene Vienna and Danube basins. The MKM crystalline basement is overlain by autochthonous Upper Paleozoic-Mesozoic sediments, allochthonous nappe stack of the Mesozoic Fatricum Unit, and Upper Paleozoic to Mesozoic Hronicum Unit. In some places, the nappe pile is covered by the posttectonic Upper Cretaceous to Neogene sediments (e.g., Maheľ & Cambel, 1972; Maheľ, 1986, 1987; Plašienka et al., 1991; Polák et al., 2011, 2012).

The neighboring Vienna Basin represents a NNE-SSW-oriented Miocene pull-apart basin (e.g., Royden, 1985; Fodor, 1995; Decker, 1996; Arzmüller et al., 2006) filled mainly with Miocene to Quaternary marine, lacustrine, and terrestrial sediments (a.o. Fordinál et al., 2012a, b). The basin was internally divided into a system of smaller depressions and elevations after the termination of thermal subsidence at the Miocene/Pliocene boundary (e.g., Lankreijer et al., 1995; Arzmüller et al., 2006; Fordinál et al., 2012b; Lee & Wagreich, 2017).

The Plavecká jaskyňa and Pec caves are formed in the isolated horst structure of Plavecké Predhorie. Triassic carbonates (Hronicum Unit) crop out predominantly as a distinct NE-SW-trending topographic ridge flanked by two (neo)tectonic depressions (Maglay et al., 1999). The graben of the Bukovská brázda Furrow, which is filled with Paleogene shallow to deep-sea siliciclastic rocks, separates the foothills from the main mountain body (Polák et al., 2011, 2012; Fordinál et al., 2012a, b). The Plavecké predhorie is divided by several transverse incised valleys (Liška, 1976). To the NW, the foothills are flanked by the Podmalokarpatská zníženina Depression (PMZ), which is one of the youngest internal depressions of the Vienna Basin that is filled with thick Quaternary sequence (>50 m) composed predominantly by proluvial sediments (Vaškovská, 1971; Kullman, 1980).



Fig. 2. Ground plans (A) and simplified cross-sections of the Plavecká jaskyňa and Pec caves with marked sampling sites and cave levels (B, right – minimum ages of cave levels). Topography: Plavecká jaskyňa Cave – after the surveys of Magdolen et al. (2002–2007; printed in Hudek & Magdolen, 2008) and Velšmid (2019–2021; complemented); Pec Cave – after Velšmid (2013).

The boundary of the MKM and the Vienna Basin is located at NE–SW-oriented marginal faults – the system of Leitha faults – a significant transfer fault system in the Vienna Basin (VBTF) that continues along this area from the eastern edge of the Austroalpine zone (see a.o. Buday & Špička, 1959; Marko & Jureňa, 1999; Fordinál et al., 2012b, Fig 1A). It separates the Plavecké predhorie from the PMZ. Quaternary reactivation of the fault system resulted in an array of depressions along the fault zone (e.g., Decker et al., 2005; Beidinger & Decker, 2011; Weissl et al., 2017).

The geological structure, namely the marginal Leitha faults, offers suitable conditions for the deep circulation of meteoric waters. Springs of karst groundwater at 205–208 m asl occur ~120–150 m west from the Plavecká jaskyňa. Their water temperatures range from 11.6 to 13.6°C (Košel, 2005) and are up to 3°C warmer than the regional mean annual air temperature. The nearest  $H_2$ S-rich water springs are located near the villages of Plavecký Mikuláš and Plavecký Peter (Fig. 1), about 3.7 and 6.1 km northeast from the studied caves.

### **METHODS**

# Structural geological and geomorphological research

Published structural plans of the Pec and Plavecká jaskyňa caves (Bella et al., 2019b, c) were complemented by measurements in newly discovered spaces (Herzov dóm in Fig. 2). Particular attention was paid to the structures predisposing the fissure floor feeders of the Herzov dóm.

Bedrock morphologies were (1) investigated, documented, and classified in detail to clarify the genesis of the studied caves and (2) compared with knowledge and data on sulfuric acid caves (e.g., Egemeier, 1981; Hill, 1987, 1990; Palmer & Hill, 2005; Audra, 2008; Audra et al., 2009; Plan et al., 2012; Palmer, 2013, 2016; Vattano et al., 2013; De Waele et al., 2016; D'Angeli et al., 2019a, b), as well as hypogene caves of successive carbonic and sulfuric acid speleogenesis (e.g., Temovski et al., 2013).

The principal development phases of the caves were distinguished on the basis of their morphology and morphostratigraphic relationships. Obtaneid data were interpreted in terms of the morphotectonic development of the MKM and PMZ. Regional geological and geomorphological publications, including the detailed geological map (Fordinal et al., 2012a, b), borehole documentation from the State Geological Institute of Dionýz Štúr, LIDAR digital elevation model DMR 5.0 produced by the Geodesy, Cartography and Cadastre Authority of the Slovak Republic, and data from the field geomorphological mapping were used for the reconstruction of integral subsurface–surface landform evolution.

### Mineralogical analysis

Following previous analyses (Bella et al., 2019c), we sampled deposits in the newly discovered part of the

Plavecká jaskyňa to find mineralogical evidence of the former SAS. A total of 10 X-ray diffraction (XRD) analyses were performed (for their location see Figures 2 and 3): Pla-12 to Pla-15 from the artificial trench in the access low passage to the Herzov dóm, Pla-16 and Pla-17 from the wall of the Herzov dóm, and morphologically and morphogenetically different segments of Pla-15 to Pla-17 (Pla-15b, Pla-16\_white crystals, Pla-16c\_brownish crystals, Pla-17\_coating). Samples were analysed in the Department of Analytical Methods at the Institute of Geology of the Czech Academy of Sciences in Praha.



Fig. 3. Sampled sedimentary profile in the access low passage to the Herzov dóm Chamber (Photo by P. Bella).

The preparation of powdered samples for XRD included dry crushing on a steel plate and pulverizing to a very fine powder using a corundum mill. Afterwards, approximately 5–10 mg of the fine powder was mixed with ethanol into a suspension and applied on a silicon plate. XRD investigation was carried out with a Bruker D8 Discover diffractometer equipped with a silicon-strip linear LynxEye detector and a focusing germanium primary monochromator of Johansson type providing CuKa1 radiation ( $\lambda = 1.54056$  Å). Data for mineral identification were collected in the  $2\Theta$  range of  $4-75^{\circ}$  with a step size of  $0.017^{\circ}$  and counting times of 1 second at each step with a detector angular opening of 1.996°. Phase identification was performed with DIFFRAC.EVA software v5.2 and ICDD PDF-4/Axiom database (Bruker AXS GmbH, Karlsruhe, Germany; 2020). Semi-quantitative estimation of the mineral composition was calculated by the reference intensity ratio method implemented in DIFFRAC.EVA software.

### U-series dating and stable isotope analyses

To reconstruct the main development phases of both studied caves, flowstone samples from flat corrosion bedrock floors (or the flat bedrock floor surface of lateral notches) in different altitudes (PE 1–4, PEC 1–5, PJ 1; Figs. 2 and 4) were taken for the U-series dating. Moreover, two samples from calcite popcorn (Pla-11, Fig. 2; see also Fig. 11 in Bella et al., 2019c) and former floating cave rafts (PJ 5; Figs. 2 and 5) – thin, sheet-like crystalline deposits precipitated on the water table of cave pools (Hill & Forti, 1997), also known as calcite rafts (Jones, 1989) or calcite crystal rafts (Taylor & Chafetz, 2004), were analyzed and dated to determine the time when the lowermost evolution level of the Plavecká jaskyňa was flooded.

U and Th chemical separation was conducted at the U-series Laboratory of the Institute of Geological Sciences, Polish Academy of Sciences (Warszawa, Poland) using the chromatographic method with TRU-Resin (following the method described by Hellstrom, 2003). Internal standard and blank samples were prepared and processed in parallel to the studied samples. The isotopic composition of U and Th was measured at the Institute of Geology, the Czech Academy of Sciences (Praha) using a double-focusing sector-field ICP mass analyser (Element 2, Thermo Finnigan MAT). U-series ages were iteratively calculated from the <sup>230</sup>Th/<sup>234</sup>U and <sup>234</sup>U/<sup>238</sup>U activity ratios. All uncertainties, except for uncertainties associated with decay constants, were considered when assessing age uncertainties using error propagation rules.



Fig. 4. Location of samples for U-series dating of flowstones: PJ 1 – the upper level of the Plavecká jaskyňa; PEC 1, PEC 2, and PE 3 – the lower level of the Pec Cave (Jacuzzi); PEC 3, PEC 4, and PEC 5 – the middle level of the Pec Cave (Photo by P. Bella).



Fig. 5. A lateral view of accumulated and cemented cave rafts, sample PJ 5 – the lowermost level of the Plavecká jaskyňa Cave (Photo by W. Wróblewski).

The presence of <sup>232</sup>Th isotope indicates contamination from detrital sources. The obtained ages of samples with <sup>230</sup>Th/<sup>232</sup>Th activity ratios below 300 (Hellstrom, 2006) were adjusted for detrital contamination using typical silicate activity ratios ratios <sup>230</sup>Th/<sup>232</sup>Th of 0.83  $\pm$  0.42, derived from a <sup>232</sup>Th/<sup>238</sup>U activity ratio of 1.21  $\pm$  0.6, a <sup>230</sup>Th/<sup>238</sup>U activity ratio of 1.0  $\pm$  0.1, and a <sup>234</sup>U/<sup>238</sup>U activity ratio of 1.0  $\pm$  0.1 (e.g., Cruz Jr. et al., 2005; Lundberg et al., 2010). The initial value of the <sup>234</sup>U/<sup>238</sup>U activity ratio was calculated based on the corrected activity ratios and corrected ages.

The oldest samples dated by the  ${}^{230}$ Th/ ${}^{234}$ U technique are out of method range, which is 500–600 ka as indicated by radioactive equilibrium between  ${}^{230}$ Th and  ${}^{234}$ U. Based on the lack of radioactive equilibrium between  ${}^{234}$ U and  ${}^{238}$ U (activity ratios different than 1), we can assume an age of those samples as less than 1.2 Ma.

Analysis of  $\delta^{13}$ C and  $\delta^{18}$ O in the samples of cave calcite rafts from the lowermost evolution level of the Plavecká jaskyňa were performed in the Stable Isotope Laboratory of the Institute of Geological Sciences, the Polish Academy of Sciences (Warszawa, Poland) in the dual inlet system using a KIEL IV Carbonate Device (Thermo Scientific) coupled to a Delta Plus IRMS (Finnigan MAT). The results were calculated using three international standards, NBS 19, NBS 18, and IAEA CO 8, and were reported relative to the V-PDB international standard. The reproducibility of the analysis was controlled by long-term measurements of the NBS 19 standard and was better than ±0.03‰ for  $\delta^{13}$ C and ±0.08‰ for  $\delta^{18}$ O.

### **Paleomagnetic analysis**

Paleomagnetic analyses were conducted in the Department of Paleomagnetism, Institute of Geology, the Czech Academy of Sciences in Průhonice. Unconsolidated clastic sediments were sampled in small non-magnetic plastic cubes (outer side 2.24 cm long, with a volume of about 6.7 cm<sup>3</sup>; Natsuhara Giken Co., Ltd., Japan). Samples were oriented in situ: the direction of dip was measured by the geological compass. Oriented hand samples from speleothem (PEC 1 to PEC 5 and PJ 4; Figs. 2 and 4) were drilled by a diamond core drill bit (1 inch in diameter) and formatted by a non-magnetic saw into 2.1 cm long specimens.

Measurement of the natural remanent magnetization (NRM) of the samples was performed with a cryogenic magnetometer 2G model 755R-4K, which includes an online AF degausser capable of producing a peak field of 130 mT. All unconsolidated and some speleothem samples were subjected to detailed alternating field (AF) demagnetization in 14 progressive steps from 0 to 100 mT. In addition, a few speleothem samples were thermally-demagnetized (TD) in 14 steps (from 80 to 600°C with 40°C steps) using the MAVACS (Magnetic Vacuum Control system; Příhoda et al., 1989) equipment. The volume magnetic susceptibility (MS) was measured using an AGICO MFK1-FA kappa bridge or KLF-4 magnetic susceptibility meter. The isothermal remanent magnetization (IRM) and the saturation isothermal remanent magnetization (SIRM)

were determined using the PAM1 unit (AGICO) in a range of 2–20 mT and impulsed magnetizer MMPM10 in a range of 25–2,000 mT.

Multi-component analysis was applied to separate the Characteristic Remanent Magnetization (ChRM) components for each sample. Results derived from the paleomagnetic measurements were analysed with Remasoft software (Chadima & Hrouda 2006). A-components of remanence are mostly of viscous or chemoremanent (weathering) origin; they can be removed by AF demagnetization with an intensity of 5–10 mT and/or in a temperature range of 80–120°C. The ChRM component is stable and can be isolated in the AF (ca 10-80 mT) and/or in a temperature range 160-600°C. For each measured sample, a graph of normalized values of remanent magnetization as a function of the alternating field M/Mo = f(t), the corresponding Zijderveld diagram, and the stereographic projection of the directions of remanent magnetization during AF or TD demagnetization from the natural state were compiled. The aim of paleomagnetic and magnetostratigraphic study is to determine the principal magnetic polarity directions in deposits, compare them with the standard Geomagnetic Polarity Timescales (GPTS; Cande & Kent 1995), and calibrate them with the ages based on Cohen & Gibbard (2019). The magnitude of natural remanent magnetization and the interpretation of the magnetic polarity record depends on the concentration and type of magnetic minerals present in the sediment (Butler, 2004).

### RESULTS

### Geological control and cave morphology

The Herzov dóm is the largest cavity in the newlydiscovered part of the Plavecká jaskyňa (Herz & Velšmid, 2018). It occurs in the NE part of the cave and represents the uppermost evolution level at 225 m asl. The lower-lying evolution levels at 223, 220, 216, and 214 m asl were distinguished and described by Bella et al. (2019b). Their altitudes are specified from the cross-sections of M. Velšmid from 2021 (Fig. 2).

The Herzov dóm is a chamber 10-15 m high (a fissure part up to 20 m) and 8-12 m wide. Its origin was controlled by the NE-SW-striking and NW (ca 309°) gently dipping tectonic fracture (~37°). It is distinctly observable on the ceiling as well as on the floor, where it predisposes one of the fissure feeders (Fig. 6A, B). Several other tectonic fractures, but with much steeper dips  $(65-90^\circ)$ , were observed in the chamber walls. Feeders on the chamber floor are also pre-disposed by them with the addition of one E–W-trending tectonic fracture. Feeders located on the fracture either offset or join two overstepping feeders and thus could have formed in the later stages of progressing deformation. Small fractures of the corrosion speleogens are associated with two feeders, therefore suggesting that the fractures might have been gravitationally or tectonically reactivated.



Fig. 6. Plavecká jaskyňa Cave, Herzov dóm Chamber: A and B) fissure discharge feeder and flat bedrock floor; C) fissure discharge feeder (a caver descending to a depth of 20 m) and vents, downward view (Photos by P. Staník).

Fissure discharge feeders (also called feeder slots or discharge slots - see Egemeier, 1981; Audra, 2008; Audra et al., 2009; De Waele et al., 2016) divide a flat corrosion bedrock floor up to 10–12 m wide, which is the widest in the caves of the Plavecký hradný vrch (Fig. 6A, B). In several places, the fissure discharge feeders are enlarged to oval tubes; some are only a few centimeters in diameter, while the largest can be entered by cavers. Generally, the nearly flat bedrock floor is dissected by fissure discharge feeders and vents, also by shallow depressions (up to about 0.2 m deep) created from former pools (with dimensions of up to  $0.5 \text{ m} \times 1.5 \text{ m}$ ). A large part of the flat bedrock floor is covered by fine-grained sediments, debris, flowstones, and dripstones, mostly along its eastern edge. The flat bedrock floor terminates at the sides with a water-table notch, laterally reaching up to 1-2m below overhanging walls (its height is about 0.2-0.3 m). The fissure discharge feeders reach a depth of about 20 m (narrow, but in places up to caver-sized; Fig. 6C). Numerous small half-spherical depressions with a diameter of a few centimeters (replacement pockets) and boxwork-like structures occur on the lower part of the overhanging chamber walls (Fig. 6A and B). Geological control and morphologies in the other parts of the Plavecká jaskyňa were described by Bella et al. (2019b).

The Pec Cave was predisposed mainly by the NE– SW- to ENE–WSW-trending faults. N–S-trending joints were observed too, but with negligible contribution to the cave formation. The cave consists of three subhorizontal passages and halls with cupolas, ceiling spherical holes, water-table notches, flat corrosion bedrock floor surfaces (corrosion tables), wall niches, and upward wall channels. Subhorizontal segments are interconnected by steep to vertical oval feeders formed along the above-mentioned structures.

The highest-lying segment - Stará Pec (Old Pec) was remodeled by frost weathering, while the lowerlying parts preserve original solution morphologies. Stará Pec represents the oldest known passage at an altitude of ~295 m asl. The middle segment, at an altitude of 286 to 288 m asl, was discovered in 2013 from the Stará Pec through a feeder and consists of the Nová Pec (New Pec) and the Prvý dóm (First Chamber) connected by a passage. The fissure discharge feeder is partly exposed in the eastern part of the Nová Pec. The lowermost segment at ~283 m asl consists of a hall with the Jacuzzi (below the Nová Pec), the passage west of Jacuzzi, and the Druhý dóm (Second Chamber). The lowermost-lying oval feeder enters the floor of the Jacuzzi (Fig. 7A, C). Since there is no chimney or other oval depression on the ceiling above the feeder, the water from the feeder ascended to an underground lake. The floor of the pool-shaped depression rises slightly from the feeder towards its opposite edge and extends to the southwest. The fissure discharge feeders occur along the NE-SWtrending fracture at the end of the passage leading southwest of the Jacuzzi.



Fig. 7. Pec Cave, Jacuzzi: cupola-shaped chamber (A) with feeder (C), water table notch and corrosion plates (B, C, and D) (Photo by P. Bella).

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In the middle and lower segments, lateral notches that had deepened into the bedrock walls indicate the presence of the stabilised groundwater table or underground lakes. The most significant water-table notch, 0.5 to 2 m wide, is carved along a widespread depression in the feeder mouth named the Jacuzzi (Fig. 7). The flat bedrock floor surface (corrosion table) of the notch indicates that it was formed by intense lateral corrosion in shallow water or along the water table of the underground lake. Its smooth surface is mostly covered by infiltrated fine-grained sediments and flowstones. The sloping ceiling surface rises and gradually passes into the ceiling cupola-like part of the chamber (Fig. 7A). The flat bedrock floor of the Nová Pec is also covered by fine-grained sediments, later transported mainly through a feeder leading to the Stará Pec. The original flat corrosion bedrock floor in the Nová Pec is partly uncovered along the feeder rising from the lower passage.

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Other water-table notches are observed in the passages connecting the halls, especially in the lower subhorizontal segment west of the Jacuzzi. Overhanging parts of walls above the water-table notches are mostly divided by wall niches, from which shallow rising channels lead upwards. More deepened upward channels have formed above the edges of the discharge fissure feeders. Numerous small half-spherical depressions with a diameter of a few centimeters (replacement pockets) occur on the cupola-like ceilings of the Prvý dóm and Druhý dóm, as well as above the Jacuzzi.

#### **Mineralogy of clastic sediments**

Mineral composition of samples from the profile in the artificial trench in the access low passage to the Herzov dóm (Pla-12 to Pla-15; Fig. 3) shows considerable similarity (Table 1). Quartz, micas, clay micas, and feldspars (K-feldspars > plagioclases) dominate. Other minerals, such as kaolinite  $[Al_2Si_2O_5(OH)_4]$  and chlorites, were determined as minor constituents. In addition, some accessory minerals (calcite, gypsum and jarosite [KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>]) were identified. Jarosite was confirmed in all samples and the highest content is shown in sample Pla-13.

Samples from the wall of Herzov dóm (Pla-16 and Pla-17) show a different phase composition compared to the sedimentary profile. The dominance of gypsum (Pla-16) and calcite (Pla-17), respectively, was revealed from the XRD analyses (Table 1). In addition, aragonite was detected in both samples. The presence of a trace amount of quartz and kaolinite was probably caused by contamination from the surrounding rock or they possibly represent corrosion residues.

Table 1. Semi-quantitative mineral composition of bulk samples determined by XRD (composition in wt%). <sup>a</sup> illite, muscovite; <sup>b</sup> clinochlore, chamosite; <sup>c</sup> microcline, orthoclase; <sup>d</sup> series between albite and anorthite.

	Pla-12	Pla-13	Pla-14	Pla-15	Pla-16	Pla-17
Quartz	30–35	30–35	25–30	30–35	<1	<1
Kaolinite	5–10	3–5	3–5	3–5	<1	-
Mica group <sup>a</sup>	35–40	40–45	40–45	40–45	-	-
Chlorite group <sup>b</sup>	5–10	<3	<3	<3	-	-
K-feldspars°	5–10	5–10	5–10	5–10	-	-
<b>Plagioclases</b> <sup>d</sup>	3–5	3–5	3–5	3–5	-	-
Calcite	-	-	-	<3	<1	95–100
Aragonite	-	-	-	-	<1	3–5
Gypsum	-	<1	-	-	98–100	-
Jarosite	<1	<3	<1	<1	-	-

### Radiometric age and stable isotopes of speleothems

The results of U-series analyses of samples are presented in <u>Supplementary Table S1</u>. Dated calcite speleothems belong to several generations: >600 ka, 439 ka (Marine isotope stage/MIS 12), 395–331 (MIS 10), 315–299 (MIS 9b), 273–253 (MIS 8), 237 ka (MIS 7e), 228 ka (slight warming within the MIS 7d), 207 ka (MIS 7a), 174–133 kyr (MIS 6), 84 ka (MIS 5b) and 13.9 ka (Allerød oscillation, nearly at the end of the last glacial period – MIS 2).

The bottom part of flowstones, which precipitated on the flat corrosion bedrock floors at 223 m asl (sample PJ 1/1, Plavecká jaskyňa), at 283 m asl (samples PE 2/1 and PEC 1/1, Pec Cave – lower segment), as well as at 288 m asl (sample PEC 4/1, Pec Cave – middle segment), are older than 600 ka and younger than 1.2 Ma (Supplementary Table S1, Fig. 4). The flowstone on the inclined bedrock wall of pool-depression (sample PE 3/2, Fig. 4) in the lower segment of the Pec Cave, deepened below the corrosion plate of the large lateral notch (Fig. 7), is also older than 600 ka and younger than 1.2 Ma. The lower part of popcorn from the wall of the lowermost evolution level of the Plavecká jaskyňa is 270 ka old (sample Pla-11) and the cave rafts (sample PJ 5, Fig. 5) from the same evolution level are 228 ka old (Supplementary Table S1).

The stable isotopic composition of the cave rafts, which accumulated and cemented into the cluster ( $\delta^{13}$ C values of -9.23 to -9.40‰ and  $\delta^{18}$ O values of -8.82 to -8.92‰ VPDB; Table 2), suggests that they formed in a pool of meteoric water (cf. Hill, 1987). Their  $\delta^{13}$ C values imply that the water was charged with soil CO<sub>2</sub>.

Table 2. Stable isotopes of cave rafts from the lowermost evolution level of the Plavecká jaskyňa Cave (sample PL 10.1 - 10.4 selected from the sample PJ 5-rafts).

Sample	δ <sup>13</sup> C VPDB [‰]	<b>SD</b> [‰]	δ <sup>18</sup> Ο VPDB [‰]	SD [‰]
PL 10.1	-9.40	0.03	-8.86	0.09
PL 10.2	-9.23	0.03	-8.82	0.05
PL 10.3	-9.24	0.03	-8.92	0.06
PL 10.4	-9.30	0.03	-8.92	0.04

# Paleomagnetic and petromagnetic results of clastic sediments

A total of 12 oriented laboratory samples were studied in the profile in the access low passage to the Herzov dóm. They were taken densely with the distance between samples being only a few centimetres (high-resolution; Fig. 3). Sediments of allochthonous origin were characterised by a small scatter of both NRM intensities (0.40-0.68 mA/m) and the MS values (65–150  $\times$  10-6 SI units). Fisher (1953) statistics were employed for the calculation of mean directions of the NRM components derived by the multi-component analysis. The AF demagnetization of samples from the Herzov dóm detected only normal (N) polarity (Table 3; Fig 8A). The mean paleomagnetic directions of ChRM components with normal polarity were  $D = 8^{\circ}$ ,  $I = 68^{\circ}$  indicate substantially low dispersion (Fig. 8B).

Table 3. Mean paleomagnetic directions of samples of clastic sediments, from the access low passage to the Herzov dóm Chamber. Explanations: N – normal polarity; D, I – declination, the inclination of the remanent magnetization;  $\alpha_{95}$  – the semi-vertical angle of the cone of confidence calculated according to Fischer (1953) at the 95% probability level; K – precision parameter; n – number of analysed samples.

Sample	Polarity	Mean paleomagnetic directions		α <sub>95</sub> [°]	к	n
		<b>D</b> [°]	I [°]			
PL 22 – PL 48	Ν	8.2	67.6	6.1	63.8	10

Except for one sample, the maximum angular deviation (MAD) values are generally lower than 10°; therefore, the paleomagnetic directions are well-determined. The sample with the MAD value greater than 10° is interpreted also with N polarity belonging to the Brunhes Chron. The example AF demagnetization procedures is displayed in Figure 9C.

# Paleomagnetic and petromagnetic results of speleothems

A total of 17 oriented and formatted laboratory samples (PEC 1 to PEC 5 and PJ 4) were studied. They are characterised by very low intensity and the large scatter of the NRM values (0.001-0.652 mA/m) and MS values reveal mostly diamagnetic behaviour (from -11.4 to 2.1 × 10-6 SI units). Almost each studied sample subjected to TD or AF demagnetization yields reliable paleomagnetic directions. A-components of

remanence are mostly of viscous or chemoremanent (weathering) origin; they can be removed by AF demagnetization with an intensity of 5 mT and/or by TD of 80°C temperature. The ChRM (high-field) component is stable and can be isolated in the AF (ca 10–70 mT) and/or in the temperature of 160–600°C, excluding sample PJ 4\_2.

Except for 13 samples with very low intensity, the maximum angular deviation (MAD) values are generally lower than  $10^{\circ}$ ; therefore, the paleomagnetic directions are well-determined (Supplementary Table S2). Samples with values (MAD) greater than  $10^{\circ}$  are interpreted with transient polarity. The ChRM directions were clearly dominated by N polarity (positive inclinations) and/or reverse (R) polarity (negative inclinations). To test the possible influence of phase changes of magnetic minerals during laboratory TD processing, diagrams of kt/kn values vs. laboratory thermal demagnetizing field t (°C) were also constructed.

Examples of TD and AF demagnetization procedures are displayed in Figure 9. They refer to two samples with N paleomagnetic directions (samples PEC 1–1 and PEC 1–2) and one sample with R paleomagnetic direction (sample PEC 2A).

With respect to the U-series ages of speleothems (Supplementary Table S1) and paleomagnetic parametres, all N- and R-polarized samples are interpreted as belonging to the Brunhes Chron, except for sample PEC1, which at most can belong to Jaramillo Subchron (Cande & Kent, 1995). Nevertheless, the Brunhes Chron includes several reversal excursions (Guyodo & Valet, 1999; Singer, 2014). Detected R signals in speleothems may correspond to one or more of these excursions. Their identification needs future detailed and specialized research.

### INTERPRETATION AND DISCUSSION

## Mineralogical and morphological evidence, and tectonic control of inactive sulfuric acid caves

The presence of jarosite in sediments of the access low passage to the Herzov dóm and gypsum on the wall of the Herzov dóm proves the SAS of the Plavecká jaskyňa, at least of its upper level. Both minerals are among diagnostic mineralogical evidence of the SAS (e.g., Hill, 1990; Polyak & Provencio, 2001; Galdenzi & Maruoka, 2003; D'Angeli et al., 2018). Reaction of sulfides (e.g., hydrogen sulfide-bearing fluids) with oxidizing meteoric waters can ensure the production of sulfate ions in the late stage of epigenesis. In addition, the presence of aragonite on the wall of Herzov dóm suggests the effect of magnesium and sulfate ions as calcite-inhibitors (Rowling, 2004). Magnesium ions can be released from chlorites identified from samples in the access passage to the Herzov dóm. Also, flat corrosion bedrock floor (wide up to 10-12 m) and fissure discharge feeders in the Herzov dóm represent significant morphological evidence of the SAS. Despite the general influence of the main, gentlydipping fracture on the morphology of the Herzov dóm, the fissure discharge feeders on the floor tend to

be predisposed on the steeper-dipping fractures with their dip presumably making them a more suitable pathway for the ascending groundwater. Their strikes (NNE–SSW to NE–SW) probably indicate a genetic link to the main fault, and they formed in the same stress regime as well (probably synthetic/antithetic fractures).



Fig. 8. Paleomagnetic properties of clastic sediments in the Plavecká jaskyňa. A – principal magnetic and magnetostratigraphy parameters (M – natural remanent magnetization, Susc – magnetic susceptibility, D – declination, I – inclination; magnetic polarity interpretation); B – direction of ChRM components of remanence of samples with normal polarity (stereographic projection, full small circles represent projection onto the upper hemisphere), the mean direction calculated according to Fisher (1953) is marked by a crossed circle, the confidence circle at the 95% probability level is circumscribed around the mean direction; C – examples of AF demagnetization and IRM acquisition/demagnetization of sample PL48 (located at 48 cm from top of the section) (left – a stereographic projection of the natural remanent magnetizing; middle left – Zijderveld diagram; middle right – a graph of normalized values of the remanent magnetic moments versus demagnetizing fields, M – modulus of the remanent magnetization (mT); right – a graph of remanent versus acquisition/ demagnetization magnetic field).

Several morphological features – mostly fissure discharge feeders, flat corrosion bedrock floors, and associated wall water-table notches and replacement pockets – also point to the SAS of lower-lying levels of the Plavecká jaskyňa and the Pec Cave located above it. In the lowermost level of the Plavecká jaskyňa, the SAS was partly evidenced also by pale yellow sand with gypsum and alunite [KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>], and calcite popcorn rims (Bella et al., 2019c). Calcite popcorn rims, as one of the typical features of sulfuric acid-water table caves (see De Waele et al., 2016), occur also in the other levels of Plavecká jaskyňa and Pec caves.

Hydrogen sulfide  $[H_2S]$  involved in the SAS ascended along a deep-rooted sub-vertical fault zone separating the Vienna Basin from the adjacent MKM.  $H_2S$  was probably derived from anhydrites or hydrocarbon reservoirs, as well as sulfate-saline connate waters in the Vienna Basin. Its origin is related to biochemical reduction of sulfates (e.g., Květ, 1971; Šmejkal et al., 1971; Remšík et al., 1989; Rupprecht et al., 2019). Sulfate waters migrated from the center of the Vienna Basin towards fault-controlled edges along the subhorizontal boundaries of formations/lithosomes with different permeability (Květ, 1971).

About 45 km southwest of the Plavecký hradný vrch, the Bad Deutsch Altenburg sulfuric acid caves are known at the south-eastern edge of the Vienna Basin in Austria (Plan et al., 2009; De Waele et al., 2016; Spötl et al., 2017).

### Origin and development of cave levels

Five evolution levels in the Plavecká jaskyňa, as well as three in the Pec Cave represent the basis for the reconstruction of the speleogenesis in the Plavecký hradný vrch. They formed along the former standing water table. Caves consist of horizontal passages and chambers with flat corrosion bedrock floors divided by fissure discharge feeders. Since flat corrosion floor surfaces in the studies caves are laterally associated with wall water-table notches, their origin can be linked with the water table and its repeated slight oscillations, especially when the passage was partly flooded by sulfidic water (see Galdenzi, 2012). In some places, silt was deposited on the cave floor and protected limestone from dissolution (see Hill, 1990). Silts represent insoluble limestone residues deposited on the rock floor and infiltrates. Allochthonous fluvial sediments are completely missing in the studied caves.



Fig. 9. Examples of thermal (A – normal polarity) and AF (B – normal polarity; and C – reverse polarity) demagnetization of flowstone samples. Explanations: upper left – a stereographic projection of the natural remanent magnetization; upper right – Zijderveld diagram; bottom left – a graph of normalized values of the remanent magnetic moments versus demagnetizing temperature (Fig. 9A) or fields (Fig. 9B and C), M – modulus of the remanent magnetic moment of a sample subjected to T (°C) or AF (mT) demagnetization (mT); bottom right – a graph of volume normalized magnetic susceptibility versus demagnetizing temperature (Fig. 9A) or a graph of isothermal remanent magnetic moment versus acquisition/demagnetization magnetic field (Fig. 9B and C).

The cave levels originated under the epiphreatic conditions during the stabilization of the local basis of erosion, i.e., at strong deceleration and/or interruption of vertical movements along the interface of the horst structure of the MKM and the half-graben structure of the PMZ. However, only a few meters of vertical differences among evolution levels in both caves could also reflect variations of the local erosion base or small changes in the local spring outlet during Pleistocene climatic cycles. Basal flowstones were deposited subsequently or after a longer hiatus on the flat corrosion bedrock floor under vadose conditions when the water table dropped below the cave level. U-series dating and paleomagnetic analysis of these flowstones point to the older epiphreatic development of cave levels.

The cave levels in the Pec Cave developed during the late Early Pleistocene. Their flat bedrock floors at 283 m asl are directly covered by flowstones dated to >600 ka and <1.2 Ma (Table 4) with N magnetic polarity and belong either to the Brunhes Chron or Jaramillo Subchron. The Stenlyho jaskyňa and the destroyed upper parts of the Plavecká priepasť (indicated by collapsed depressions) are situated at almost the same altitude. They likely correspond to the position of former springs of ascending waters and are among one of the oldest expected phases of hypogenic speleogenesis in the Plavecký hradný vrch. The caves currently represent relics of originally more extensive caves both in horizontal and vertical directions due to significant denudation of the upper part of the fault slope.

The lower-lying cave levels more than 50 m in the Plavecká Jaskyňa, which had developed during the Middle Pleistocene (Table 4), are better preserved. Sulfuric acid phases in the two uppermost levels of the Plavecká Jaskyňa (225 and 223 m asl) are dated to the early Middle Pleistocene (>600 ka). Finegrained sediments with jarosite, in the passage at 225 m asl, have a N magnetic polarity, and flowstones precipitated on the flat bedrock floors in the passage at 223 m asl are older than 600 ka and younger than 1.2 Ma; however, they could by deposited still during the Brunhes Chron, but also earlier. The sulfuric acid phase in the lowermost level of the Plavecká jaskyňa (214 m asl) acted before 270 ka according to the age of the basal part of popcorn (sample Pla-11; Supplementary Table S1). Popcorn precipitated under subaerial (vadose) conditions at the edge of flat corrosion bedrock floor, which had been divided by the discharge fissure feeder (see the stable isotopic composition of this popcorn in Bella et al., 2019c).

The final phase of the development of the lowermost level in the Plavecká jaskyňa most likely corresponds to the formation of cave rafts on the water table of the cave lake (sample PJ 5; <u>Supplementary Table S1</u>) dated to 228 ka. They point to the existence of at least a periodic level of groundwater table (see Ford et al., 1993; Gradziński et al., 2012). A short-lived shallow lake is evidenced also by the thin, white-layered part of studied popcorn (sample Pla-11) corresponding to stable isotopic composition of subaqueous coralloids ( $\delta^{13}$ C values of -7.2 to -7.5‰ and  $\delta^{18}$ O values of -4.0 to -5.2‰ VPDB – Bella et al., 2019c). The groundwater table likely dropped after the formation of the PMZ in front of the marginal horst structure of the MKM which, according to Salcher et al. (2012), started 250–300 kyr ago (Fig. 10). The sulfuric acid phase in the lowermost level (214 m asl) was most likely active during the late Middle Pleistocene (>270 ka). U-series and paleomagnetic ages represent minimum ages for speleogenesis, since the time between the solution origin of cave passages/chambers and the deposition of their fills is still unknown.

A part of deeply circulating waters ascending along the marginal fault probably penetrated from carbonates into the aggrading more permeable Late Pleistocene sedimentary fill of the PMZ (>50 m thick, mostly proluvial and deluvial deposits - e.g., Vaškovská, 1971; Kullman, 1980). Therefore, the amount of water entering the lower parts of the Plavecká jaskyňa might be reduced. In the eastern part of the PMZ near the villages of Plavecké Podhradie and Plavecký Mikuláš, the water from the left tributaries of the Rudava River is sinking into the sediments of the proluvial cones in a volume up to 50 L/s, reaching dropped groundwater table, similar to the neighboring part of the PMZ near the village of Sološnica (Sološnica Depression) with the groundwater table at ~10-12.5 m below the surface (Kullman, 1980). The map of present groundwater levels indicates the flow towards the Rudava River (Šubová et al., 1973).

### Implications for the surface landform evolution

Three evolution levels have been interpreted in the Pec Cave at 295, 287, and 283 m asl with a vertical

span of 12 m, and five levels in the Plavecká jaskyňa at 225, 223, 220, 216, and 214 m asl with a vertical span of 11 m. Minimum ages of the evolution levels were dated by U-series and paleomagnetic methods. Early Pleistocene (Pec Cave) and Middle Pleistocene (Plavecká jaskyňa) main stages of the stabilization of local erosion base are reflected in the evolution phases of caves as a consequence of strong deceleration and/ or interruption of vertical movements at the fault contact of the MKM and the Vienna Basin. Levels can also reflect the response to more detailed variations of tectonic activity and/or of the Pleistocene climatic cycles. This can be supported by the vertical distances of climatically-driven Early Pleistocene river terraces (~15-20 m - Škvarček, 1971; Fordinál et al., 2012a, b) corresponding to altitude spans of levels in the Pec Cave (12 m), and Middle Pleistocene terraced alluvial fans (~10 m – Fordinál et al., 2012a) corresponding to those in the Plavecká Jaskyňa (11 m).

Nevertheless, no signs exist of the stabilization of local erosion base between the formation of the lowermost level in the Pec Cave and the uppermost level in the Plavecká jaskyňa. No cave levels between 283 and 225 m asl (a vertical span of 58 m) have been discovered in the Plavecký hradný vrch as of yet. This indicates a likely significant continuous, early to mid-Middle Pleistocene tectonic subsidence of the adjacent part of the Vienna Basin. Coincidence with the start of the second (late Quaternary) neotectonic stage of the Western Carpathians development (Vitovič et al., 2021) can point to the wider regional driver.

Table 4. Basic phreatic and epiphreatic carbonic and sulfuric development phases of the Plavecká jaskyňa and Pec caves (following Bella et al., 2019c).

Development phases	Cave morphology and sediments	Period/Altitude	
Phreatic development of the primary conduits of the Pec Cave	Formation of fault-controlled feeders and primary larger cavities by rising carbonic waters	Early Pleistocene	
Epiphreatic development of the upper, middle, and lower levels of the Pec Cave	Formation of flat corrosion bedrock floors and associated water- table notches by sulfuric dissolution, ceiling and wall speleogens originated by condensation corrosion above the water table	late Early Pleistocene (>0.99–1.07 Ma?) 283–295 m asl	
Phreatic development of the primary conduits of the Plavecká jaskyňa	Formation of fault-controlled high and more or less narrow chimneys by rising carbonic low-thermal waters – the upper discovery opening and the high chimney above the north-eastern edge of Kvapľová sieň most probably representing the oldest groundwater outlets to the surface (Bella et al., 2019c)	early Middle Pleistocene ~225–236 m asl	
Epiphreatic development of two highest levels of the Plavecká jaskyňa	Formation of flat corrosion bedrock floor and associated water- table notch by sulfuric dissolution, ceiling and wall speleogens originated by condensation corrosion above the water table, accumulation of fine-grained sediments, and their partly alteration to jarosite	early Middle Pleistocene (>600 ka) 223–225 m asl	
Epiphreatic development of the middle level of the Plavecká jaskyňa	Formation of flat corrosion bedrock floor and associated water- table notch by sulfuric dissolution, ceiling, and wall speleogens originated by condensation corrosion above the water table	mid-Middle Pleistocene 220 m asl	
Epiphreatic development of the lower and lowermost levels of the Plavecká jaskyňa	Formation of flat corrosion bedrock floors and associated water-table notches by sulfuric dissolution, ceiling, and wall speleogens originated by condensation corrosion above the water table, less intense accumulation of fine-grained sediments in which a low content of alunite was found (Bella et al., 2019c)	late Middle Pleistocene (>270 ka) 214–216 m asl	
	Precipitation of cave rafts (sample PJ 5) in the shallow lake (calcite speleothems), probably also the thin white layered part of popcorn (sample Pla-11) during short-lived shallow lake	~228 ka 214 m asl	
Recent groundwater table	main spring near the Plavecká jaskyňa lake at the bottom of the Plavecká priepasť	208 m asl 205 m asl	



Fig. 10. Development stages of landform evolution, simplified geological sketch through the Plavecký hradný vrch Hill, Malé Karpaty Mountains (including the studied caves) and the adjacent Záhorská nížina Lowland, a part of Vienna Basin (after Fordinál et al., 2012a; modified and completed): 1. limestones (Triassic); 2. marine clays and sandy clays with sand and gravel interbeds (Miocene); 3. fluvial gravels (Early Pleistocene); 4. fluvial sandy gravels (early Middle Pleistocene); 5. fluvial sands, minor fine-grained gravels (late Middle Pleistocene); 6. fluvial sands, sandy gravels (Late Pleistocene); 7. eolian sands (Late Pleistocene); 8. colluvial and deluvial sediments (Late Pleistocene–Holocene); 9. fluvial loams, sands and gravels (Holocene); 10. eolian sands (Holocene); 11. fault; 12. spring; 13. cave (with marks of the evolution level).

The Pec Cave, Stenlyho jaskyňa and the collapsed depressions of the former upper parts of the Plavecká priepasť are situated only a few tens of meters below the planation surface (pediment) known as "riverside level" and spread over the whole territory of Western Carpathians. It was dated to Late Pliocene (e.g., Lukniš, 1962; Mazúr, 1965, Škvarček, 1975), however, after extending the Quaternary down to 2.58 Ma, it can be considered Early Pleistocene (e.g., Minár et al., 2004; Zuchiewicz, 2011; supported also by dating of allochthonous gravels from the main evolution level of the Domica-Baradla cave system by Bella et al. (2019a). Its remnants are preserved at ~300–350 m asl along the western edge of the MKM (115–135 m above the MKM foothills – Škvarček, 1966) and at 260–300 m asl along the southern part of the MKM (~130–140 m above the Danube Gate between Devínska Kobyla and the Braunsberg hills, as well as above the adjacent parts of the surrounding lowlands – Mazúrová, 1973; Urbánek, 1992). All caves in the Plavecký hradný vrch lie deeply below remnants of the older "mid-mountain" planation surface (Late Miocene) preserved in the Plavecký Karst at ~450– 540 m asl; including the flat top of the Pohanská Hill (495 m asl) ~800 m southeast of the studied caves (Stankoviansky, 1974; Liška, 1976; Fig. 10).

Flat elevations at 280-290 m asl in the northern part of the Lakšárska pahorkatina Hilly Land (northern part of the Záhorská nížina Lowland) are considered remnants of pre-Quaternary planation surface that had developed on Neogene marine finegrained clastics (Škvarček, 1971). Lower-lying large flat erosional surfaces at 230-250 m asl most likely represent the remnant of tectonically subsided Early Pleistocene pediment ("river-side level"). In places, both planation surfaces are covered by a thin veneer of Late Pleistocene eolian sands. The altitude of Early Pleistocene proluvial and fluvial sediments corresponds roughly to the position just below the denuded sediments of the "river-side level" in the central part of the Záhorská nížina. Early Pleistocene fluvial sediments of the high-lying terrace of the Morava River are preserved at ~215-230 m asl (Fordinál et al., 2012a, b) on the lower southern part of the Lakšárska pahorkatina (Lakšáry Elevation) west of the studied caves (Fig. 10).

The half-graben of the PMZ developed mostly from the late Middle to Late Pleistocene due to reactivated tectonic activity of the Vienna Basin (see also Salcher et al., 2012) involving repeated seismic events (Šujan et al., 2022), i.e., probably after the formation of the lowermost level of the Plavecká jaskyňa. The average relative subsidence in this part of the PMZ (west of the Plavecký hradný vrch), since the precipitation of the dated cave rafts has been ~240-260 m/Ma as calculated from the vertical span between the above-mentioned cave level and the bottom of the Quaternary sedimentary fill ~40-45 m thick (Kullman, 1966, 1980; Fordinál et al., 2012a). The subsidence rate in the centre of the Sološnica Sub-Basin, which is southwest of the Plavecký hradný vrch, was significantly more intensive, probably more than two times as estimated from the >100 m thickness of the late Middle to Late Pleistocene sediments (Kullman, 1966, 1980; Vaškovská, 1971; Fordinál et al., 2012b). It is roughly comparable to the uplift rate of 150–160 m/ Ma during the last 300 kyr in the Hainburg Hills - the southermost part of the MKM (Neuhuber et al., 2020).

The formation of the uppermost to lowermost cave levels of the Plavecká Jaskyňa took part from >600 ka to >270 ka, including decelerations and/or interruptions during formation of levels placed between them. Therefore, the relative subsidence of the adjacent area of the Vienna Basin was only ~20–30 m/Ma. Data from Salcher et al. (2012) and Neuhuber et al. (2020), as well as our own results show that tectonic movements at the Alpine-Carpathian transition have intensified, at least since the late Middle Pleistocene.

The middle and upper cave levels of the Plavecká Jaskyňa are situated approximately at the same altitudes as the surface of Miocene sediments, mostly covered by Early Pleistocene fluvial gravels of the high-lying terrace of the Morava River at the top parts of the horst structure of the Lakšáry Elevation (later, mostly covered by Late Pleistocene eolian sands) in the central part of the Záhorská Nížina (see Buday & Špička, 1959; Vaškovská, 1971; Kullman, 1980; Fordinál et al., 2012a; Fig. 10). Despite this, the cave levels likely developed later in the early and mid-Middle Pleistocene. Subsequently, they were tectonically uplifted to their current altitudes. Similarly, the lower cave levels, which probably formed in the late Middle Pleistocene, presently lie at the altitude of earlier Middle Pleistocene river terraces of the Lakšáry Elevation. It can be considered that the cave levels of the Plavecká jaskyňa were formed before the intensified subsidence of the PMZ. Directional change of the main watercourses in the central part of the Záhorská nížina in Middle Pleistocene (Fordinál et al., 2012a) caused the Rudava River to begin to flow through the descending PMZ. Two river terraces at the relative heights of 10-12 m (Saalian/Riss) and 3-5 m (Weichselian/Würm) were formed (Škvarček, 1975).

As the Vienna Basin repeatedly subsided, H2S moved from its center towards the direction of the fault-controlled edges (Květ, 1971). While evolution levels in the Pec and Plavecká jaskyňa caves were formed during phases of the decelerated and/or interrupted subsidence (both having vertical spans of 11/12 m), and probably also due to Pleistocene climate cycles, the vertical span of 58 m between the nearest evolution levels of both caves can be linked with the more intensive continuous subsidence, probably with a rate of ~150 m/Ma when the Early Pleistocene "river-side level" was tectonically differentiated.

### CONCLUSIONS

The Plavecká jaskyňa and Pec hypogene caves in the Plavecký hradný vrch, with interpreted carbonic and sulfuric development phases (largely proven by Bella et al., 2019c), represent the first caves of this type in Slovakia. They complete a wide range of genetic types of Slovak caves (cf. Bella, 2016).

Morphologically, these caves consist mainly of flat corrosion bedrock floors with fissure discharge feeders arranged in several evolution levels. They record Early and Middle Pleistocene multi-phased development of the landforms at the tectonic interface of the MKM and the Vienna Basin. The cave levels formed during periods of strongly decelerated and/or interrupted subsidence in the adjacent part of the Vienna Basin; levels separated by vertical differences of only a few meters can be related to Pleistocene climatic cycles too. Three evolution levels of the Pec Cave likely developed in the late Early Pleistocene and represent a denudation remnant of a larger, original cave. The two highest levels of the Plavecká Jaskyňa formed during the early Middle Pleistocene. Tectonically uplifted, they are situated at approximately the same altitude as the remants of the "river-side level" of the Lakšáry Elevation (the opposite edge of the PMZ), covered by Early Pleistocene fluvial sediments and subsequently by Late Pleistocene eolian deposits. Different altitudes of the "river-side level" in the MKM and Lakšárska

pahorkatina (Záhorská nížina) most likely resulted from the vertical tectonic movements (so far, no cave levels are known between the Pec Cave and Plavecká jaskyňa; they probably did not form). This tectonic event looks to be synchronous with the beginning of the late Quaternary neotectonic stage of the Western Carpathians development (Vitovič et al., 2021). The PMZ itself began to form by subsidence after the formation of the lowermost cave level in the Plavecká jaskyňa, i.e., the late Middle Pleistocene.

Detailed future research of the Plavecká priepasť is needed to complete the full history of speleogenesis in the Plavecký hradný vrch.

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**Authorship statement:** PBE and PBO designed and directed the study and took samples in the field; JL studied the cave geology and PBE the cave morphology; PM was responsible for mineralogical analyses and interpretations; ŠK and PP carried out paleomagnetic analyses of cave sediments, data processing and interpretation and PBO participated in data interpretation; HH performed the Th-U dating of speleothems; MG and WW participated in field research and analysed cave rafts; MV surveyed newlydiscovered parts of the Plavecká jaskyňa; PBE, PBO, JM, and JL reconstructed cave origin and development and associated surface landforms; PBE and PBO compiled the paper with input from all authors.

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