Mineralia Slovaca, Web ISSN 1338-3523, ISSN 0369-2086, https://doi.org/10.56623/ms.2023.55.1.4
55, 1 (2023), 53 – 70, © Authors 2022. CC BY 4.0

Stratiform U-Cu mineralization in the Lopejské Čelno valley near Podbrezová (Veporic Unit, Western Carpathians)

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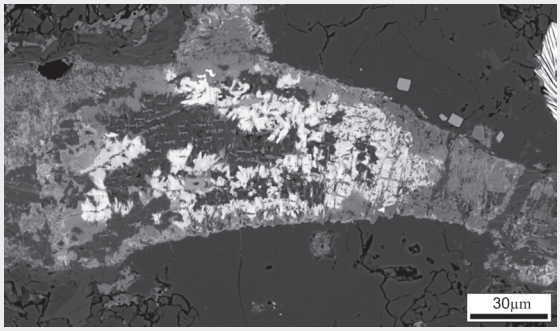
Abstract: The studied mineralization is located on the eastern slopes of Lopejské Čelno valley, south of the Lopej village (cadastral area of Podbrezová village, Central Slovakia). The U occurrence was described and classified as U-Cu stratiform mineralization. The mineralization is located in the Ľubietová Zone of Veporic Unit, and is bound to the arkosic sandstones containing Permian volcanoclastic material. The host rock of mineralization underwent low-grade metamorphism and limonitization. Lens shaped ore bodies are characterized by disseminated pyrite, rutile, chalcopyrite, leucoxene and metatorbernite. Small cavities and cracks in rock are also filled and/or coated by goethite, Mn oxides and malachite. Uranium is irregularly distributed within the host rock and is bound to the U-Ti oxides, brannerite and torbernite/metatorbernite. Brannerite and leucoxenized U-Ti oxides are the only one primary uranium U^{4+} minerals, for the first time identified in studied occurrence. Brannerite forms clusters of needle-like crystals (up to 100 μm in size). It occurs in close spatial and genetic association with U-Ti oxides, rutile, leucoxene and clay minerals. Chemical composition of brannerite and U-Ti oxides differs in ratio of U/(U + Ti): from 0.22 to 0.29 apfu for brannerite and from 0.09 to 0.22 apfu for U-Ti oxides. Metatorbernite forms light green crystals, typically occurs in small cavities and fractures in rock. It shows an unusual light green luminescence under UV radiation. The average chemical composition of metatorbernite can be expressed by empiric formula $(Cu_{0.75}Ba_{0.06}Ca_{0.03}K_{0.04}Al_{0.02}Mg_{0.01}Fe_{0.01})_{\Sigma 0.94}$ $(UO_2)_{\Sigma 2.00}$ $(PO_4)_{\Sigma 2.01}$ $(H_2O)_8$. Occasionally torbernite/metatorbernite directly replaces single crystals of apatite.

Key words: U-Cu mineralization, U-Ti oxides, brannerite, metatorbernite, Veporic Unit, Western Carpathians

Graphical abstract



Highlights

- Mineralized grains of U-Cu mineralization near Podbrezová in Lopejské Čelno valley are composed of brannerite, U-Ti oxides, rutile, leucoxene and clay minerals
- Mineralization was created during alteration (chloritization) of biotite connected with hydrothermal processes and the subsequent *"Pronto-reaction"* – adsorption of uranium onto the formed Ti oxides
- Mineralization forming correlates with the temperature generated during the Alpine orogeny, or by its fading

Introduction

Primary ores processed in the nuclear industry mostly include uraninite and coffinite. Unconventional target ores include brannerite (UTi_2O_6) and U-Ti oxides (uranoferous leucoxene), because of its high U content of up to 55 wt % U (Patchett & Nuffield, 1960). Brannerite (UTi_2O_6) is found among the major uranium-bearing minerals in many ore deposits and variety of geological environments including hydrothermal and pegmatitic, which represent the most frequent occurrences. In the Western Carpathians, brannerite and U-Ti oxides were studied in Košice-Kurišková and Novoveská Huta U-Mo deposits, also at several mineralogical, resp. deposit occurrences such as Gemerská Poloma-Peklisko, Prakovce-Zimná voda, Kálnica, Krompachy, etc. (Rojkovič, 1997).

Brannerite and U-Ti oxides were also uniquely identified during the revision research of U-Cu mineralization in the Lopejské Čelno site near Podbrezová. The main goal of this study is to clarify the genesis of the primary U^{4+} mineralization, represented by brannerite and U-Ti oxides.

Geological setting

In the 1960s, in the vicinity of the villages of Podbrezová, Ľubietová and Osrblie, the geological survey focused on U ores was carried out, for the purpose of searching for industrial uranium concentrations. The studied occurrence of U-Cu mineralization is located about 1.5 km south of the Lopej village center (cadastre of the Podbrezová village) in the Lopejské Čelno valley, on the west-facing slopes of the Belohrad elevation (764 m a.s.l.). The geographic coordinates of the central part of the occurrence are N 48.8042° and E 19.5085°. Geological survey took place here in 1964–1965. Mineralization was verified by three boreholes (in 1964) and by a narrow-profile adit. After the excavation of the tunnel was completed, two exploratory wells were drilled from its face. Additional exploratory wells with a depth of 300 m were drilled in the valley in 1965. However, the survey work did not confirm economic concentrations of uranium and the geological survey was terminated in the same year (Daniel, 2006).

Mineralization is developed in the Ľubietová Zone of the Veporic tectonic unit (Fig. 1a). The crystalline complexes of the Ľubietová Zone (Fig. 1b) are characterized with three basic zones. The northernmost part consists of orthogneisses to migmatites (also bodies of paragneisses, leucocratic granites, amphibolites). Zones of mylonitization are abundant. The more southerly zone is built by paragneisses, micaschists and amphibolites (frequently diaphtorized). Phyllites and diaphtorites (phyllonites) mainly form the southernmost zone. Bodies of granitic and granodioritic porphyres are less frequent (Slavkay et al., 2004). Orthogneisses are considered to be either a product of paragneiss anatexis (Maheľ et al., 1967), or represent a product of regional metamorphism of granitoids (Kamenický, 1977), rhyolites, dacites and their pyroclastics, respectively (Kamenický, 1982). Granitic porphyres represent younger element of crystalline complexes. According to older opinions (e.g., Zoubek, 1958), the bodies of granite porphyry are inlet channels of Permian volcanism, emerging in the Permian sediments of the Ľubietová Group (Harnobis horizon, Brusno Formation). The Lower Permian age of granite porphyries is evidenced by finds of their fragments in the Upper Permian Predajná Formation (Vozárová, 1979). Chemical U-Th-Pb dating of the monazite from the granite porphyries at Osrblie gave an age of 265 ± 9 Ma (Bezák et al., 2008), SHRIMP dating of zircons from them (Predajnianske Čelno valley) indicates an age of 273 ± 4 Ma (Vozárová et al., 2016). The younger age of 184 ± 9 million years determined by the Rb/Sr method (Spišiak & Siman, 2014) can probably be justified by the reactivation of the primary age of the granite porphyries, which was caused by a tectonothermal event related to the development of the Meliata Ocean. In the wider vicinity of the studied locality, the crystalline shell is represented by the Permian Ľubietová Group (Vozárová, 1979), formed by Brusno (lower) and Predajná (upper) formations. Both consist of clastic sedimentary rocks (arkosic shales, sandstones), accompanied by quartz porphyry bodies. Sedimentary rocks of Brusno Formations are divided by the volcanogenic Harnobis horizon (dacite, tuffs, ignimbrites). The Permian age of the sediments was evidenced by the palynomorph community (Planderová & Vozárová, 1982), SHRIMP dating of magmatic zircons of Harnobis volcanics yielded ages of 273–279 Ma ± 4 Ma (Upper Cisuralian – Lower Guadalupian; Vozárová et al., 2016). The boundary between the complex of the Early Paleozoic metamorphics and the Permian rocks form a 200 m thick thrust line, along which the Early Paleozoic rocks of the Ľubietová Zone were thrust onto the Late Paleozoic rocks. Its general direction is NE–SW and dip 40–45° to the SW. Lower-order tectonic faults course in the NW-SE direction (Daniel, 2006).

U-Cu mineralization in the Lopejské Čelno occurrence is bound to Permian, limonitized, altered arkosic sandstones containing bodies of acid volcanics.

Mineralogy of the Lopejské Čelno site was previously studied by Rojkovič and Novotný (1993), who described it as a stratiform accumulation of poor U-Cu ores. Rojkovič (1997) revealed the contents of some elements at this occurrence as follows: U 40–460 ppm, Cu 30–300 ppm, Ti 1 600–3 000 ppm, Mo < 3 ppm, Pb 20–210 ppm, V 40–140 ppm, Ni 10–20 ppm, Zr 120–260 ppm, Co 4–7 ppm, Y 10–40 ppm and C_{org} 400–4500 ppm. Mineralization was traced in the zone with length of 200 m (NW-SW direction), dipping 40–60° to the SE. Pyrite, rutile, leucoxene, chalcopyrite, goethite and torbernite were identified in ore lenses (up to 1 m in size; Rojkovič & Novotný, 1993).

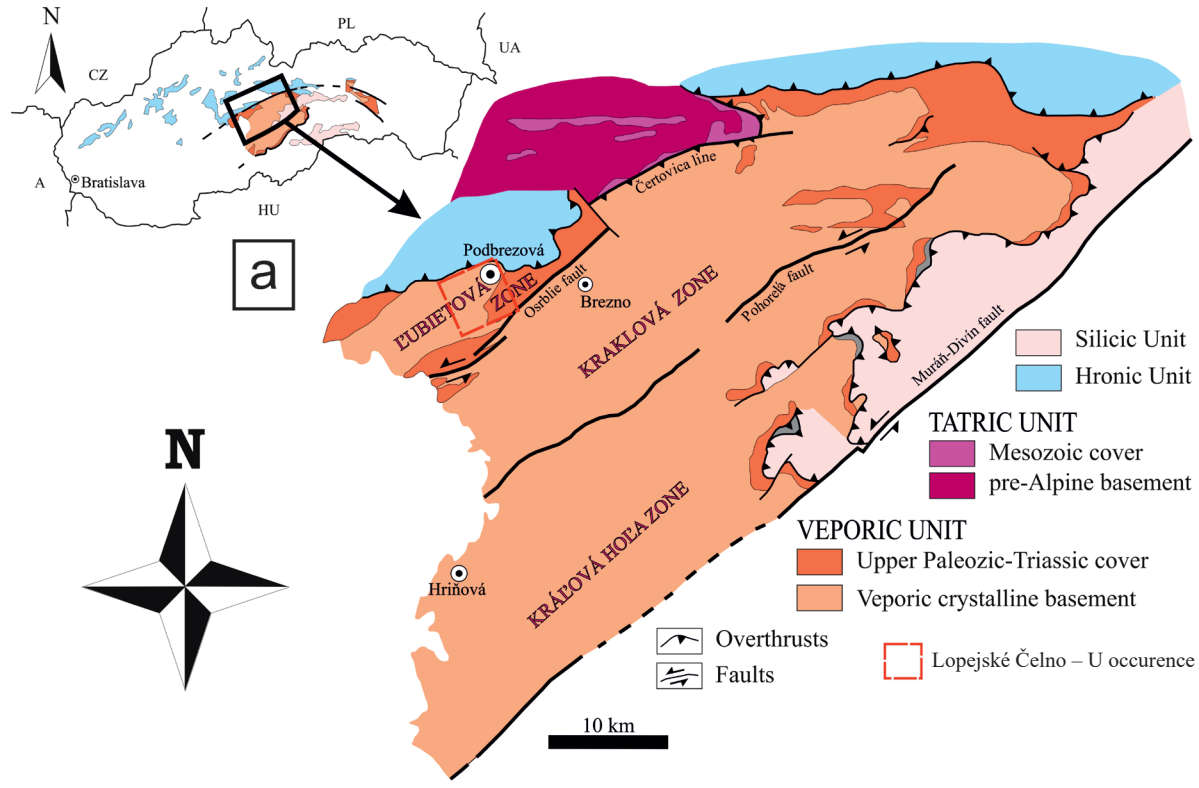
Methods used

Samples with increased radioactivity were searched in the outcrops along the forest road (Fig. 2), using a SGR – Scintillation Gamma Radiometer detector (sample activity measured in cps), with a measuring range of 400–3 000 keV and a measurement step of 0.2 s.

Polished thin sections were observed in both, reflected and transmitted light applying a Nikon ECLIPSE LV 100 POL polarising microscope (Faculty of Natural Sciences UMB, Banská Bystrica).

Photo documentation of the minerals was done using binocular magnifier Nikon SMZ1500 with camera SD-Fi2. Luminescence of minerals under UV radiation was observed using Raytech R5-FLS-2V lamp at wavelength of 400–315 nm (Faculty of Natural Sciences UMB, Banská Bystrica).

X-ray diffraction analysis (PXRD) was performed on a Bruker D8 Advance equipment (Earth Science Institute of Slovak Academy of Sciences – SAS, Banská Bystrica;



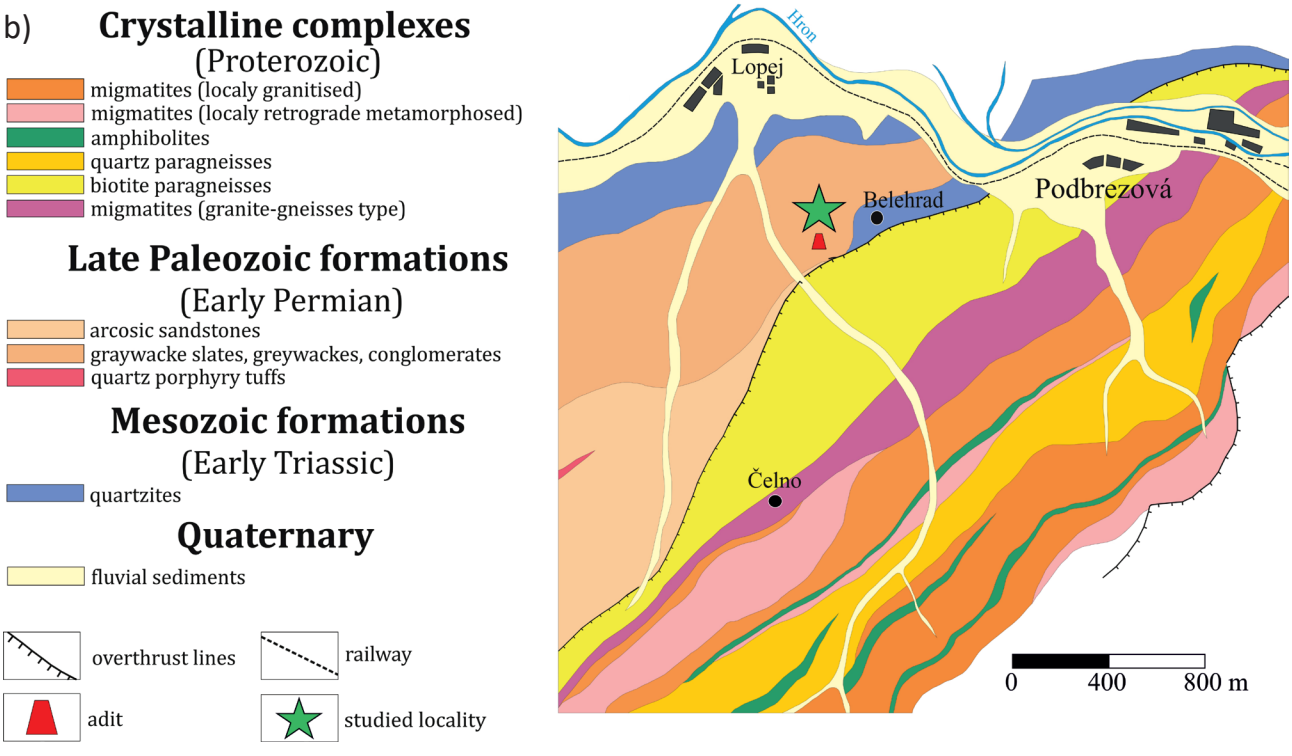


Fig. 1. a – Geological map of the wider surroundings of the studied locality (according to Zoubek, 1936, 1958). b – Detailed geological map of the U-Cu mineralization occurrence in Lopejské Čelno (according to Drnzík, 1963).

analysed by RNDr. Adrián Biroň, PhD.) using CuK_{α} (1.5418 Å) radiation generated at a voltage of 40 kV and a current of 30 mA. The powder mount was placed in an ethanol suspension onto a Si single crystal. Subsequently, diffraction data were obtained under the following conditions: apertures 0.3° – 6 mm – 0.3° – 0.2 mm, primary and secondary Soller aperture 2.5°, step 0.02° 2Θ/1.25 s, measuring range 2.0–65.0° 2Θ, EDS detector Sol-XE. Diffraction patterns were evaluated using the ZDS software (Ondruš, 1993). Individual reflections were indexed according to structure data available in Downs and Hall-Wallace (2003).

The chemical composition of minerals was determined using an electron microanalyser Jeol-JXA-8530F (Institute of Earth Sciences SAS, Banská Bystrica). The microanalyser was used to determine chemical composition of minerals using energy-dispersive spectrum (EDS) and wave-dispersion microanalysis (WDS).

WDS microanalyses of metatorbernites were performed under the following conditions: accelerating voltage 15 kV, measuring current 15 nA. The diameter of the electron beam ranged from 5 to 10 μm. The ZAF matrix correction was used. The following elements (standard, X-ray line) were measured: orthoclase (KKα), diopside (CaKα), UO_2 (UMß), crocoite (PbMß), baryte (SKα), apatite (PKα), fluorite (FKα), albite (Na Kα), celestite (SrLα), albite (Si Kα), corundum (AlKα), $GaAs_2$ (AsLα), olivine (MgKα), willemite (ZnKα), cuprite (CuKα), Co (CoKα), Bi_2S_3 (BiLα), olivine (FeKα), baryte (BaLα). Silicates were analysed under the following conditions: accelerating voltage 15 kV and measuring current 20 nA. The diameter of the electron beam ranged 5–10 μm The following elements (standard, X-ray line) were measured: quartz (SiKα), orthoclase (KKα), rutile (TiKα), albite (AlKα, NaKα), hematite (FeKα), rhodonite (MnKα), diopside (MgKα, CaKα), $ScVO_4$ (VKα), Cr_2O_3 (CrKα), fluorite (FKα) and NaCl (ClKα). Chemical analysis of brannerites and U-Ti oxides were acquired at 15 kV of accelerating voltage, 20 nA current and 2 μm beam diameter. The following lines and standards were used: diopside (CaKα), orthoclase (KKα), uranium oxide (UMß), thorianite

Fig. 2. Sampling site with U mineralization in the Lopejské Čelno – ore lenses in the forest road cut and directly in the road (photo Š. Ferenc, 2017).

(ThMα), crocoite (PbMß), $LiNbO_3$ (NbLα), cubic zirconia (ZrLα), apatite (PKα), YPO_4 (YLα), fluorite (FKα), albite (NaKα), celestite (SrLα), orthoclase (SiKα), albite (AlKα), diopside (MgKα), $HoPO_4$ (HoLß), $YbPO_4$ (YbLα), $GdPO_4$ (GdLß), $DyPO_4$ (DyLα), $TbPO_4$ (TbLα), $EuPO_4$ (EuLα), $NdPO_4$ (NdLα), $CePO_4$ (CeLα), $LaPO_4$ (LaLα), willemite (ZnKα), hematite (FeKα), rhodonite (MnKα),vanadinite (VKα), rutile (TiKα) and $ScVO_4$ (ScKα).

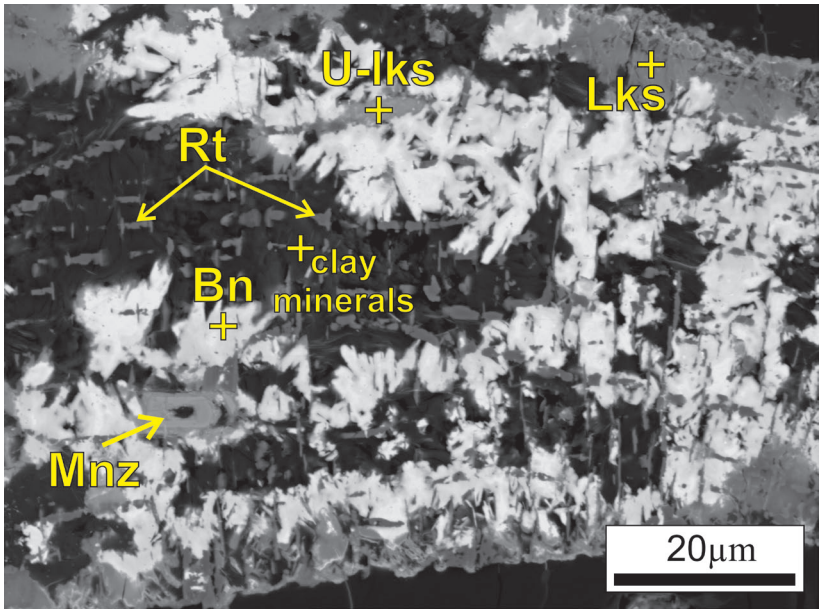


Fig. 3. Grain formed by brannerite (*Bn*), rutile (*Rt*), U-Ti oxides (*U-lks*) and leucoxene (*Lks*). BSE image (photo T. Mikuš).

The detection limit for individual elements ranged from 0.01 to 0.03 wt. %. Elements whose content values are below the detection limit are not included in the tables below. X-ray element distribution maps were obtained (the same device) with an accelerating voltage of 15 kV and probe current of 15 nA.

Raman spectral analysis (Institute of Earth Sciences SAS, Banská Bystrica; analysed by RNDr. Stanislava Milovská, PhD.) was performed on a LabRAM-HR 800 (Horiba Jobin Yvon). The instrument consists of an Olympus BX 41 microscope, a Czerny-Turner type spectrometer. Calibration of the instrument was performed using a laser line (0 cm^{-1}) and Si standard (520,6 cm^{-1}). Raman spectra were taken in two acquisitions, for a period of 20 to 60 seconds per spectral window, in the range of 60 to 4 000 cm^{-1}, using lasers with λ 532 and 633 nm and a source power of 60 respectively 17 mW, with a diffraction grating of 600 streaks/mm and a confocal slit of 100 µm. Laser beam diameter on sample is 2 µm. Spectra were corrected for background subtraction using the math function by LabSpec 5 software. The results were compared with the LabSpec databases and RRUFF (Lafuente et al., 2015).

Infrared spectroscopic analyses (IR) in the spectral range from 4 000 to 400 cm^{-1} were performed on a Nicolet iS50 instrument (Matej Bel University, Banská Bystrica), using a conventional attenuated total refraction (ATR) technique with synthetic diamond as a measuring crystal. For each measurement, 32 scans were performed in steps of 4 cm^{-1}. The detected infrared spectra were compared with several internet databases (RRUFF; lisa.chem.ut.ee) and published works.

Chemical composition of chlorite group mineral phases was calculated applying software WinCac (Yavuz et al., 2015).

Results

Petrography of the host rocks

The host Permian arcosic sandstones are mainly formed by clasts of mono- and polycrystalline, subangular, undulose quenching quartz (up to 1 cm in size), muscovite aggregates (up to 0.2 mm) and

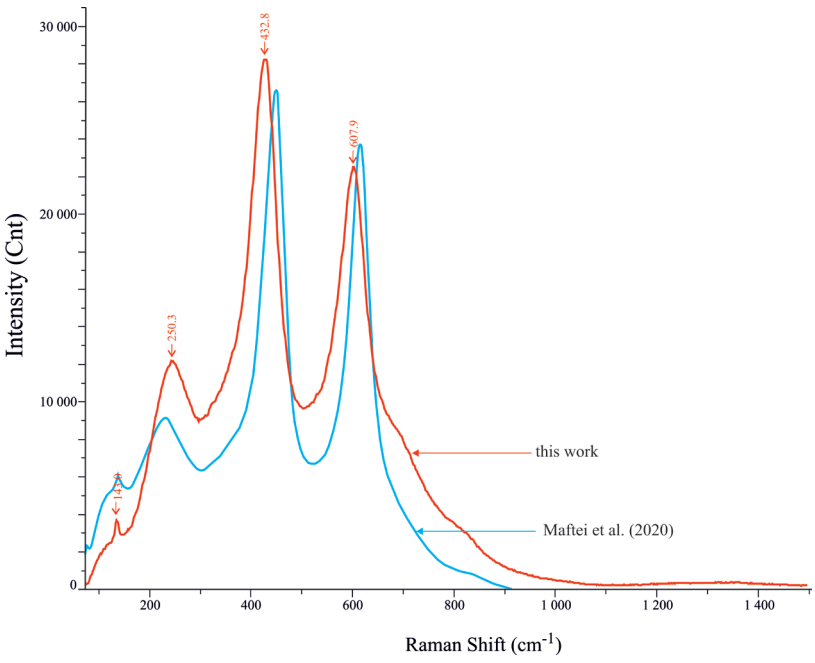


Fig. 4. Raman spectrum of rutile from the Lopejské Čelno (red colour) compared with previously published spectrum (Maftei et al., 2020; blue colour).

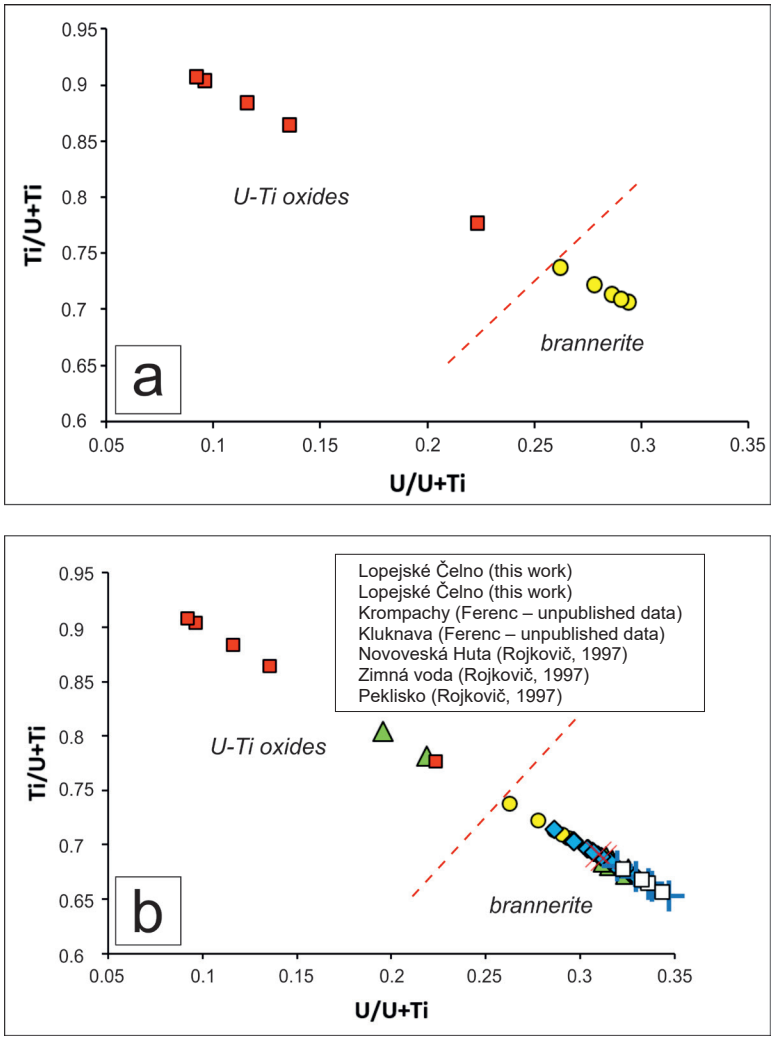


Fig. 5. Differences in the chemical compositon of brannerite and U-Ti oxides from the Lopejské Čelno (a) compared with composition in other occurrences in the Western Carpathians (b). Border line between brannerite and U-Ti oxides constructed according to Lumpkin et al. (2012).

chlorite. Rarely were found biotite and K-feldspars, which, however, are often chloritized and sericitized. Rock matrix is microcrystalline, quartz-sericitic to sericitic. Mineralized (U-Cu) rock is, in addition, in a great extent limonitized. It shows obscure tectonic directing and foliation, indicating weak Alpine metamorphic reworking. Small cavities and fissures in the rock have goethite and unspecified black Mn oxides fill. Uranium is distributed irregularly in the rock and is bound to the U-Ti oxides, brannerite and uranyl phosphate metatorbernite.

Mineralogical characteristic

Primary mineralization

Primary mineralization was detected only rarely in mineralized grains with a size of up to 120 µm (Fig. 3).

Rutile was identified in close association with brannerite, leucoxene, U-Ti oxides a clay minerals. Cationic position in dominantly occupied by Ti (81.29–86.10 wt. %; up to 0.86 apfu Ti), increased contents of Si (6.92–8.20 wt. %; up to 0.11 apfu Si) and Al (3.01–3.94 wt. %; max. 0.06 apfu Al) were also detected. Rutile (like polymorph TiO_2) was confirmed also by Raman spectroscopy (Fig. 4).

Brannerite is the only identified primary (U^{4+}) uranium mineral at the occurrence, observed only very rarely. It forms clusters of needle-like crystals (length up to 100 µm). It occurs in close spatial association with U-Ti oxides (*uranoferous leucoxene*), rutile and clay minerals. Uranium is dominant in the cationic position (47.43–43.79 wt. % UO_2; up to 0.68 apfu U), Ti (37.76–31.60 wt. % TiO_2; max. 1.76 apfu Ti). Trace elements are represented by Si (max. 5.82 wt. % SiO_2; 0.37 apfu Si), Ca (max. 2.68 wt. % CaO; 0.18 apfu Ca), Fe (up to 2.64 wt. % FeO; 0.14 apfu Fe), also by weakly increased content of Y, Al, K, Mg, Mn, Pb, Zr, As and REE.

U-Ti oxides, also known as *uranoferous leucoxene*, were identified in association with brannerite and rutile. Unlike brannerite, their chemical composition is characteristic mainly by decreased U content (16.80–41.95 wt. % UO_2; max. 0.55 apfu U) and, vice versa – increased contents of P (up to 5.92 wt. % P_2O_5; 0.26 apfu P) and Si (max. 7.80 wt. % SiO_2; 0.40 apfu Si).

The differences in the chemical composition of brannerite and U-Ti oxides (ab. 1), can be expressed by their content ratio (in apfu, or in atomic %) U/(U + Ti): 0.22-0.29 in brannerite and 0.09–0.14 for U-Ti oxides (Fig. 5a). Both studied mineral phases were compared with their occurrences in other sites in the Western Carpathians (Fig. 5b).

Supergene minerals

Metatorbernite (spontaneously dehydrated torbernite to a more stable phase) forms light green, tabular crystals up to 2 mm in size (Fig. 6a). Their aggregates fill fissures in the rock, or small cavities after leached rock-forming minerals (Fig. 6b, c). Occasionaly replaces fluorapatite crystals (Fig. 12). As for metatorbernite chemical composition (Tab. 3), cationic position is dominantly occupied by Cu (3.37–7.77 wt. % CuO; up to 0.93 apfu Cu; Fig. 7) and U (57.22–66.66 wt. % UO_3; max. 2.10 apfu U). K (max. 0.36 wt. % K_2O; 0.72 apfu K), Ca (up to 0.64 wt. % CaO; 0.10 apfu Ca) and Mg (up to 0.11 wt. % MgO; 0.03 apfu Mg) are less abundant. For anionic position there is characteristic dominant P (13.27–16.72 wt. % P_2O_5; up to 2.08 apfu P), only weakly increased contents of As and Si

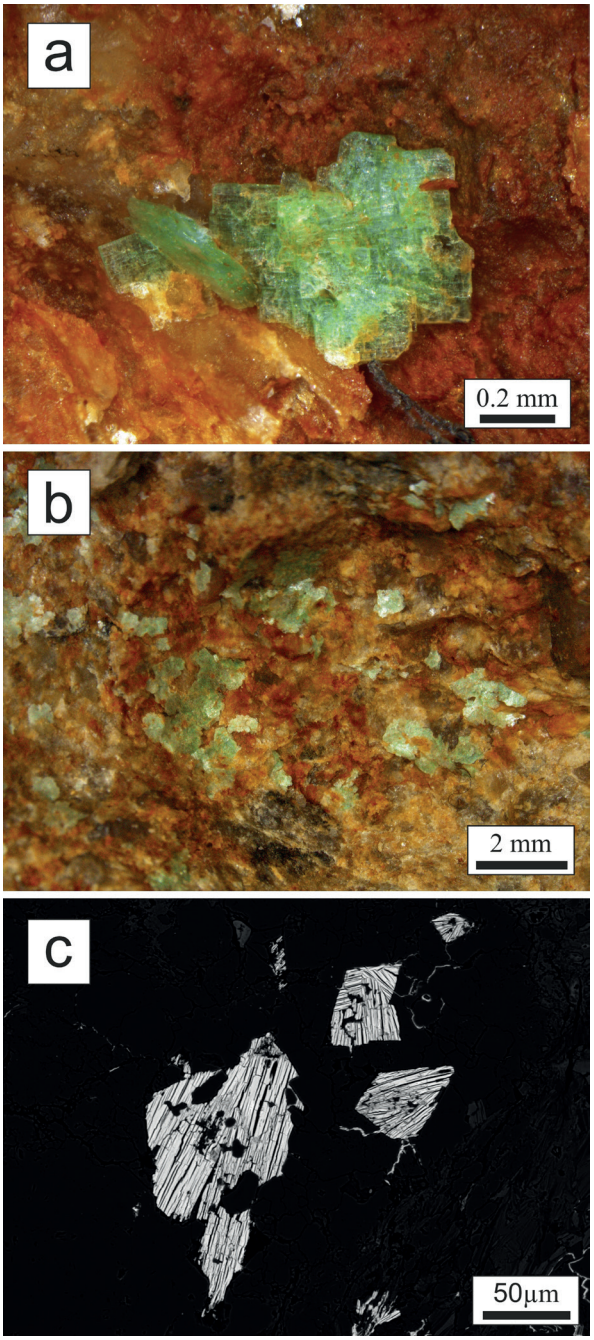


Fig. 6. Aggregates of light green, tabular metatorbernite crystals (**a**, **b**; photo R. Kopáčik) often form filling of cavities and cracks in the rock (**c**; BSE image; photo T. Mikuš).

were found. Average empirical formula (6 WDS analyses) of metatorbernite from Lopejské Čelno occurrence is $(Cu_{0.75}Ba_{0.06}Ca_{0.03}K_{0.04}Al_{0.02}Mg_{0.01}Fe_{0.01})_{\Sigma 0.94}(UO_2)_{\Sigma 2.00}(PO_4)_{\Sigma 2.01}(H_2O)_8$.

Several bands were detected in the IR spectrum of the studied metatorbernite (Fig. 8). The band at 902 cm^{-1} can be assigned to the antisymmetric valence vibration ν_3 UO_2^{2+} and the bands at 843, 810 and 789 cm^{-1} to

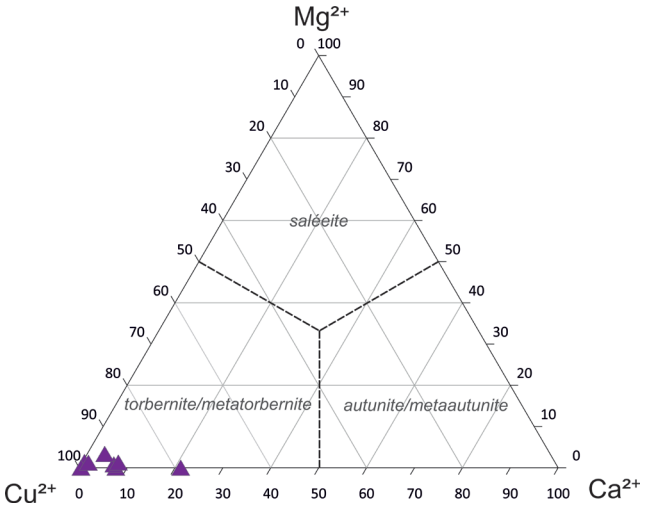


Fig. 7. Chemical composition of metatorbernite from Lopejské Čelno in the ternary diagram of the system Cu-Ca-Mg (according to Plášil et al., 2009).

the symmetric valence vibration ν_1 UO_2^{2+}. Bands 673, 607 cm^{-1} apparently correspond to the liberation modes of molecular water. Triple degenerate antisymmetric valence vibration ν_4 PO_4^{3-} is represented by bands at 461 and 539 cm^{-1}. Band at 987 cm^{-1} represents triple degenerated ν_3 PO_4^{3-} valence vibration. Band at 1 636 cm^{-1} is manifest of deformation vibration of H_2O. Valence vibration ν OH of water molecules corresponds with bands at 2 924, 3 341 and 3 403 cm^{-1}. The obtained spectrum corresponds very well with previously published data for torbernite / metatorbernite (Čejka et al., 1984; Čejka & Urbanec, 1990; Frost, 2004; Frost et al., 2005; Plášil et al., 2009).

Malachite is relatively rare. It forms thin crusts covering up to 3 cm on the rock debris or fillings of fissures and cavities in the rock. It was identified by PXRD analysis, while the measured diffractometric data agree well with the previously published data for this mineral phase (Süsse, 1967; Downs et al., 1993).

Discussion and conclusion

In the Western Carpathians, a similar type of mineralization occurs in the Malé Karpaty Mts. at Lošonec and Smolenice (Rojkovič, 1997), in the Nízke Tatry Mts. at Benkovský potok, Ipoltica and Nižný Chmelienec occurrences (Hronic Unit; Drzník, 1969; Rojkovič, 1998; Rojkovič & Vozár, 1972; Václav & Vozárová, 1978; Hoppanová et al., 2021). In the Northern Gemeric Unit U ± Cu mineralization in so-called copper sandstones, occurs near Novoveská Huta and Stratená villages (Ondrejkovič et al., 1964; Grecula et al., 1995; Števko, 2014; Ferenc et al., 2022).

Increased contents of uranium and accompanying elements is present in the Permian acid volcanics and these

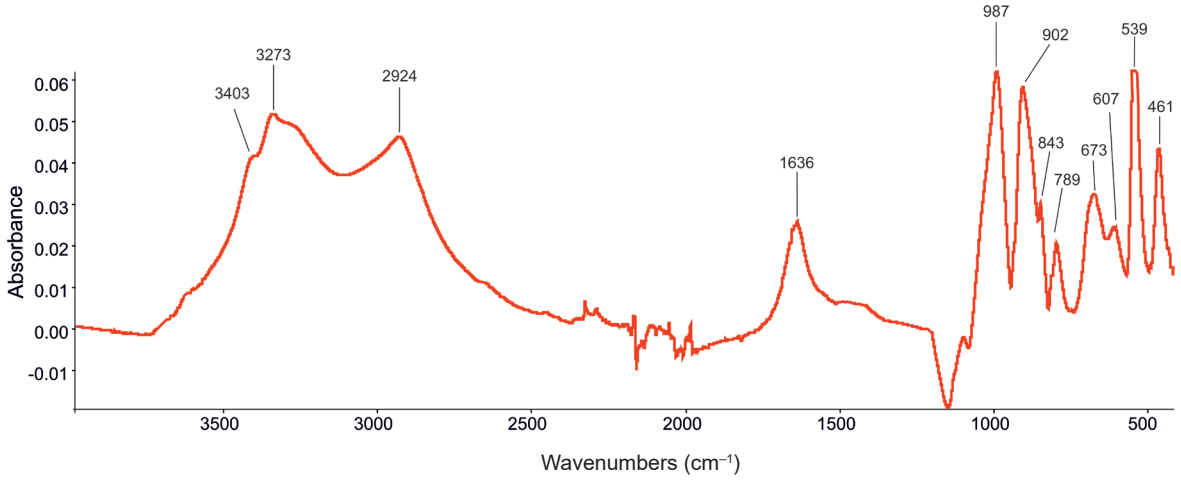


Fig. 8. Infrared spectrum of metatorbernite from Lopejské Čelno occurrence.

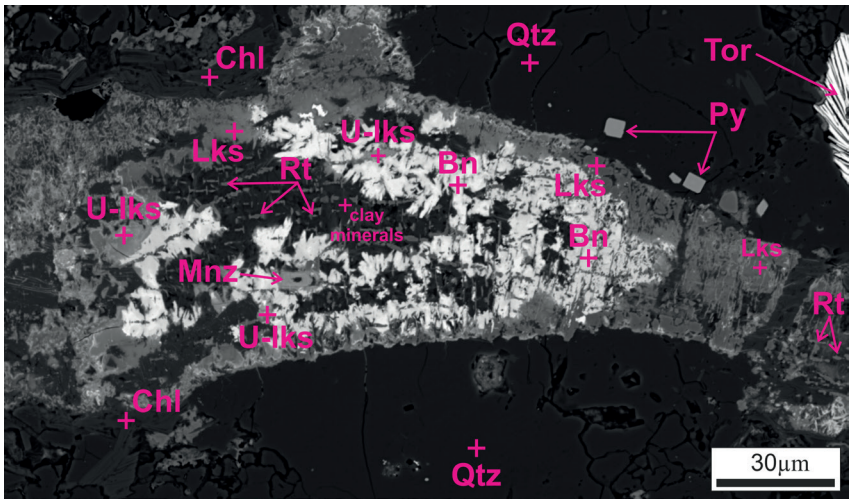
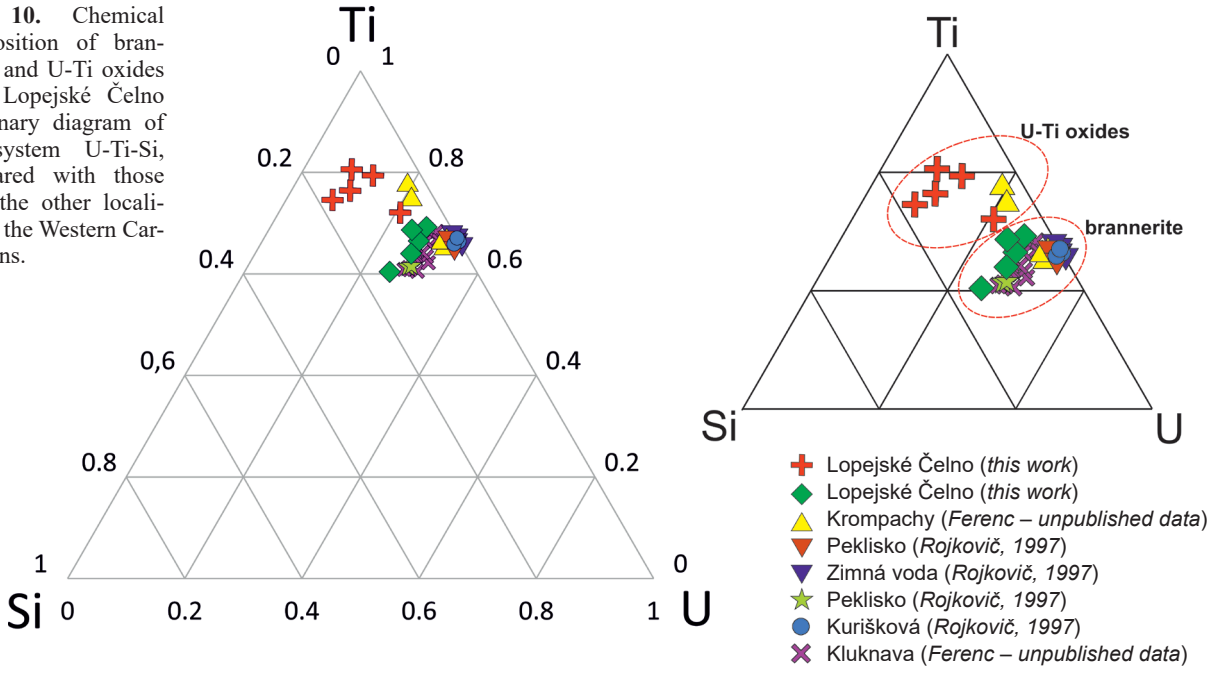


Fig. 9. Grain of altered biotite with U^{4+} minerals brannerite (*Bn*) and U-Ti oxides (*U-Lks*) and magmatic monazite-(Ce) (*Mnz*), in close space association with decay products of biotite hydrothermal alteration: rutile (*Rt*), leucoxene (*Lks*), *clay minerals* and chlorite (*Chl*). Surrounding of grain form quartz (*Qtz*) with pyrite (*Py*) and metatorbernite (*Tor*). BSE image (photo T. Mikuš).

Fig. 10. Chemical composition of brannerite and U-Ti oxides from Lopejské Čelno in ternary diagram of the system U-Ti-Si, compared with those from the other localities in the Western Carpathians.



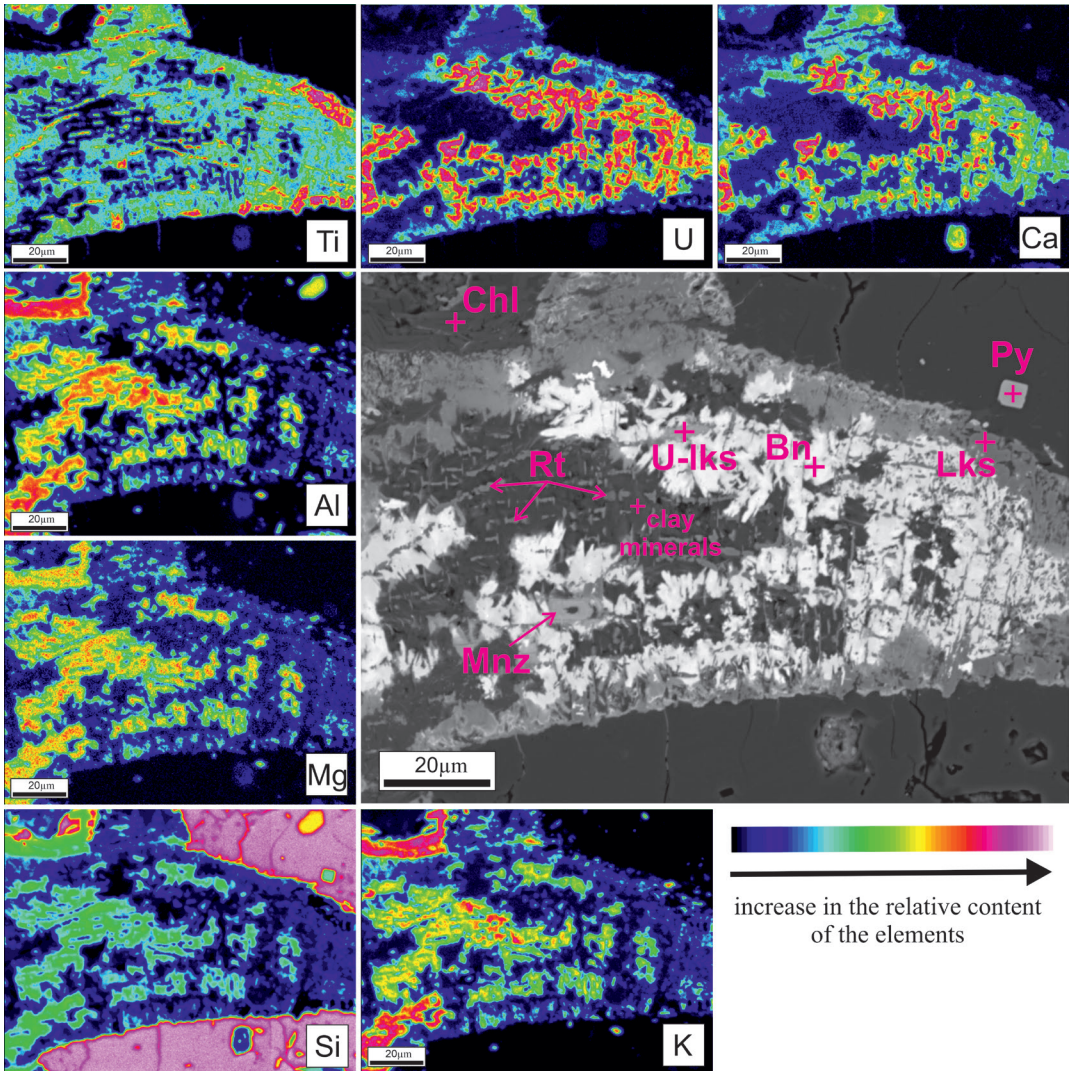


Fig. 11. Back-scattered electron (BSE) images and X-ray element distribution maps in uranium-bearing grain from Lopejské Čelno (photo and maps T. Mikuš).

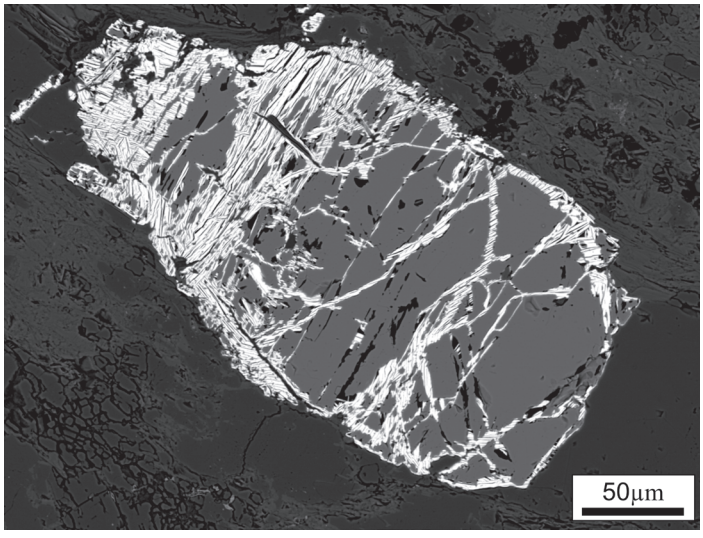


Fig. 12. Hypidiomorphic grain of fluorapatite (grey) replaced by metatorbernite (white). BSE image (photo T. Mikuš).

are therefore a potential source of uranium (Rojkovič et al., 1989). Uranium was released from devitrified acid volcanic glass. Subsequently, together with other ore elements, it precipitated in a reducing environment under the influence of the adsorption of some minerals (Ti oxides, Fe oxides, clay minerals). This process resulted in the formation of stratiform U ore accumulations in the continental Permian (poor grade ores) of the Western Carpathians (Rojkovič & Mihál', 1991). Remobilization and concentration of stratiform Hercynian ore mineralization during Alpine orogenesis caused formation of richer U mineralization (Rojkovič & Novotný, 1981).

Primary mineralization and its genesis

The revision study of mineralization in Lopejské Čelno brought new knowledge. Primary U^{4+} mineralization represented by brannerite and U-Ti oxides was identified here; accompanying

minerals are rutile, Ti oxides (leucoxene) and clay minerals (probably illite). Because primary mineralization occurs only rarely, even only in grains with a size of up to 120 μm (Fig. 9), its mineral phases are in close spatial association and often overgrow; it is complicated to clarify its genesis with certainty. The most probably explanation for its formation is the alteration (chloritization) of biotite connected with hydrothermal processes and the subsequent adsorption of uranium onto the formed Ti oxides, while the source of Ti was biotite. This sequence of geochemical processes could have been caused by the Alpine metamorphic processes with following p-T conditions: 300–700 MPa at 300–500 °C in the Permian sediments of the Ľubietová Zone (Kamenický, 1978; Slavkay et al., 2004); 500–1 100 MPa at of 430–620 °C in the crystalline basement of the Veporic Unit (Plašienka et al., 1999; Janák et al., 2001; Jeřábek et al.; 2008). Vozárová (1979) also describes completely altered biotite at the site.

Biotite easily decomposes during hydrothermal processes. The most common secondary products of its alteration are chlorite, muscovite, sericite, clay minerals, leucoxene, epidote-zoisite, rutile, recrystallized biotite accompanied with a number of minerals with small or no relation to the chemical composition of biotite (Schwartz, 1958). The release of titanium and the formation of Ti oxides represent one of the most characteristic features of biotite alteration (Lovering, 1949; Schwartz, 1958; Bisdom, 1967; Deer, 1992).

Adsorption of uranium onto newly formed Ti oxides closely relates to the so-called "*Pronto-reaction*". This process described Ramdohr (1957), who reported the formation of brannerite and U-Ti oxides in situ either by adsorption of uranium to Ti/Fe-Ti mineral phases, or by binding of titanium to uraninite to form uranotitanates, according to the chemical equation:

$$UO_2 + 2 - 3TiO_2 \rightarrow UTi_{2-3}O_{6-8}.$$

The "Pronto-reaction" takes place in hydrothermal systems that reach temperatures of around 225 °C (Schidlowski, 1996), which in the case of Lopejské Čelno, correlates with the temperature generated during the Alpine orogeny, or by its fading.

Most of natural brannerites are metamict (Smith, 1984). Metamictization is caused by damage of the brannerite crystal structure due bombardment with α-particles from the uranium decay (Lian et al., 2002). For this reason, the crystal structure parameters of naturally occurring brannerite are not certainly known. In addition, the uranium in brannerite is usually partially oxidized (presence U^{4+}, U^{5+} also U^{6+} valences), either, brannerite itself is often hydrated (Finch & Murakami, 1999). In hydrothermal brannerites, Ca, Th, Y, and REE replace uranium, while Si, Al and Fe replace titanium due to oxidation and partial hydration (Smith, 1984). Brannerite from Lopejské Čelno has an increased content of Si (max. 0.37 apfu), Ca (up to 0.18 apfu), Fe (max. 0.14 apfu) and Al (max. 0.14 apfu). U-Ti oxides also have higher values of Si (up to 0.30 apfu), Ca (up to 0.11 apfu), Fe (up to 0.16 apfu) and Al (up to 0.21 apfu), which confirms the hydrothermal nature of the mineralization. Compared to the data of Finch (1996), brannerites in the Veporic Unit could have formed already during the main phase of Alpine metamorphism at medium to high temperatures (temperatures close to 400–600 °C), by direct precipitation from solutions containing the uranyl ion UO_2^{2+}, while the source of uranium was devitrified volcanic glass. An important role play releasing of titanium from biotite during its alteration and the formation of Ti/Fe-Ti oxides. The subsequent fading of the Alpine orogeny (reduction of p-T conditions, mainly temperature) created conditions for the adsorption of the remaining uranium on U-Ti oxides, which can be evidenced by the lower concentration of uranium in U-Ti oxides. A similar mechanism of formation of U mineralization was observed at the deposits Zadní Chodov and Rožná (Czech Republic), where the Ti released during the biotite chloritization played an important role in the brannerite formation (René & Dolníček, 2017).

In samples from Lopejské Čelno, clay minerals fill the space between brannerite, rutile, leucoxene and U-Ti oxides (U-leucoxene). According to Bisdom (1967), titanium minerals in close spatial association with clay minerals in the places of fully or partially altered biotite often form a pattern that roughly coincides with the interlamellar positions in the altered biotite. Equivalent orientation of rutile was also found in mineralized grains from Lopejské Čelno, while rutile admixtures in mafic minerals here were observed by Vozárová (1979; Fig. 9). On the edge of the mineralized grains and in the host rock, chlorite and muscovite are abundantly represented (Tab. 3).

The distribution of individual elements is shown in Fig. 10 and correlates well with the described mineral phases. According to Schwartz (1958), the presence of several mineral phases with different chemical composition within one grain (phenocryst) indicates, that hydrothermal solutions are the decisive factors in biotite transformation. Another important factor is the variability of rock permeability, when in one part of the rock; biotites can be completely altered, while in another part they remain intact.

Oxidation zone

In the Lopejské Čelno occurrence, malachite, goethite and torbernite/metatorbernite represent the supergene alteration of mineralized rocks.

Precipitation of uranyl phosphates takes place in a low pH environment (Langmuir, 1978). The formation of

metatorbernite (and uranyl phosphates in general) in the oxidation zone is conditioned by the oxidation of U^{4+} to U^{6+}, forming the uranyl cation UO_2^{2+} (Civetta & Gasparini, 1972). If there is an active exchange of oxygen-rich waters, the destruction of primary uranium minerals and the formation of uranyl ions occurs:

$$UO_2 + H_2O + 1/2O_2 = UO_2^{2+} + 2OH^-.$$

The occurrence of sulphides (mainly pyrite) with the formation of sulphuric acid has a great influence on the destruction of uranium ore:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4.$$

The resulting acidic solutions intensify the decay of primary uranium minerals. Uranium is usually found in natural solutions in the form of complexes. The formation of stable soluble uranyl complexes enables the migration of U and the formation of secondary uranium minerals (Tripathi, 1983; Liu & Neretnieks, 1990). For the formation of metatorbernite, as well as other uranyl phosphates, the addition of phosphorus in the form of PO_4^{3-} anions is important. The dominant uranyl-phosphate complexes are $[UO_2H_2PO_4]^+$, $[UO_2HPO_4]^0$ and $[UO_2PO_4]^-$ (Langmuir, 1978). These are provided to the system as a product of the interaction of meteoric waters with the surrounding rocks, while there is an interaction with accessory apatite (and other rock-forming minerals containing P), which is unstable in acidic conditions and decomposes according to a chemical reaction (Vinogradov, 1963):

$$Ca_5(PO_4)_3F + 5H_2SO_4 \rightarrow 3H_3PO_4 + 5CaSO_4 + HF.$$

The subsequent fall in pH, together with changes of other chemical and physical factors (Eh, chemical composition of solutions, p-T conditions) in solutions causes destruction of uranyl-phosphate complexes and precipitation of metatorbernite (Chernikov, 1981; Baes & Mesmer, 1976; Langmuir, 1997). The source of Cu for metatorbernite at the Lopejské Čelno occurrence was mostly chalcopyrite. Rarely, hypidiomorphic fluorapatite crystals directly replaced by metatorbernite can be observed in sandstones from here (Fig. 12).

An unusual phenomenon in metatorbernite from Lopejské Čelno is a weak yellow-green luminescence. Luminescent torbernites were also identified at other localities in the Western Carpathians: Novoveská Huta, Peklisko, Zimná voda (Ferenc et al., 2003), Brezno-Skalka (our unpublished data) or in Bohemia (Medvědín; Plášil et al., 2009). Based on a comparison of the chemical composition with metatorbernite without luminescence ("normal" metatorbernite), it can be concluded, that luminescence is not caused by a change in chemical composition, i.e. the presence of a luminophores. Therefore, luminescence can be caused either by defects in the crystal lattice of luminescent metatorbernites, or by an admixture of nanoparticles of another mineral (Plášil et al., 2009).

Acknowledgements

This work was supported by the Ministry of Education, Slovak Republic VEGA-1/0563/22 project, as well as the Slovak Research and Development Agency under the contract APVV-19-0065. Authors express their thanks to J. Sejkora (National Museum Prague) and M. Števko (Slovak Academy of Science) for detailed reviews and improvement of the manuscript.

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Tab. 1

Chemical composition of brannerite and U-Ti oxides from Lopejské Čelno

	Bn	Bn	Bn	Bn	Bn	U-Ti	U-Ti	U-Ti	U-Ti	U-Ti
UO_2	48.64	47.43	46.14	45.41	43.79	41.95	20.48	15.89	16.80	22.45
ThO_2	0.12	0.19	0.22	0.17	0.22	0.17	0.47	0.30	0.48	0.31
Na_2O	0.03	0.04	0.02	0.01	0.05	0.03	0.00	0.02	0.12	0.01
K_2O	0.08	0.45	0.35	0.34	0.62	0.13	0.42	0.59	0.49	0.34
MgO	0.00	0.02	0.07	0.12	0.20	0.00	0.16	0.25	0.18	0.04
CaO	2.68	2.37	2.23	2.44	1.84	1.71	1.19	0.53	0.74	0.52
SrO	0.14	0.00	0.05	0.03	0.08	0.09	0.00	0.03	0.00	0.00
MnO	0.20	0.06	0.08	0.06	0.16	0.10	0.04	0.12	0.03	0.00
FeO	2.64	2.41	2.25	2.55	1.56	1.56	3.87	2.42	2.09	1.68
PbO	0.37	0.35	0.26	0.65	0.25	0.88	4.61	4.24	4.55	4.13
Al_2O_3	0.22	0.61	0.79	1.35	1.80	0.30	3.52	3.41	3.11	2.34
V_2O_3	0.17	0.00	0.00	0.19	0.00	0.26	0.26	0.00	0.00	0.00
Y_2O_3	0.67	0.41	0.41	0.41	0.34	0.51	0.09	0.15	0.12	0.06
Ce_2O_3	0.13	0.09	0.06	0.07	0.00	0.15	0.18	0.24	0.21	0.15
Nd_2O_3	0.22	0.14	0.15	0.10	0.20	0.14	0.14	0.11	0.10	0.15
Sm_2O_3	0.39	0.00	0.00	0.15	0.00	0.20	0.01	0.00	0.00	0.00
Eu_2O_3	0.14	0.00	0.00	0.05	0.00	0.13	0.04	0.00	0.00	0.00
Gd_2O_3	0.29	0.31	0.13	0.24	0.33	0.25	0.17	0.08	0.10	0.08
Tb_2O_3	0.15	0.00	0.00	0.19	0.00	0.25	0.12	0.00	0.00	0.00
Dy_2O_3	0.23	0.00	0.00	0.08	0.00	0.16	0.09	0.02	0.03	0.00
Ho_2O_3	0.00	0.00	0.00	0.05	0.00	0.13	0.14	0.00	0.00	0.00
Yb_2O_3	0.25	0.00	0.00	0.14	0.00	0.06	0.02	0.00	0.00	0.00
SiO_2	1.67	2.69	3.62	2.85	5.82	3.23	6.17	7.80	5.12	3.29
TiO_2	37.37	34.95	32.80	37.76	31.60	43.14	46.19	44.18	48.92	42.42
ZrO_2	0.34	0.32	0.34	0.43	0.43	0.42	0.93	0.60	0.62	0.48
P_2O_5	0.04	0.15	0.05	0.26	0.01	0.06	4.61	4.85	5.92	5.24
As_2O_5	0.00	0.78	0.70	0.00	0.57	0.00	0.00	0.00	0.00	0.19
Nb_2O_5	0.12	0.00	0.00	0.13	0.00	0.34	0.16	0.00	0.00	0.00
Total	97.28	93.77	90.70	96.21	89.87	96.34	94.04	85.83	89.69	83.86
Brannerite and U-Ti oxides [apfu] – based on 3 cations										
U	0.68	0.68	0.68	0.61	0.62	0.55	0.22	0.18	0.19	0.29
Th	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00
Na	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
K	0.01	0.04	0.03	0.03	0.05	0.01	0.03	0.04	0.03	0.03
Mg	0.00	0.00	0.01	0.01	0.02	0.00	0.01	0.02	0.01	0.00

Tab. 1 – continuation

	Bn	Bn	Bn	Bn	Bn	U-Ti	U-Ti	U-Ti	U-Ti	U-Ti
Ca	0.18	0.16	0.16	0.16	0.13	0.11	0.06	0.03	0.04	0.03
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00
Fe	0.14	0.13	0.12	0.13	0.08	0.08	0.16	0.10	0.09	0.08
Pb	0.01	0.01	0.00	0.01	0.00	0.01	0.06	0.06	0.06	0.06
Al	0.02	0.05	0.06	0.10	0.14	0.02	0.20	0.21	0.18	0.16
V	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00
Y	0.02	0.01	0.01	0.01	0.01	0.02	0.00	0.00	0.00	0.00
Ce	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sm	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Eu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gd	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Tb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dy	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ho	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Si	0.10	0.17	0.24	0.17	0.37	0.19	0.30	0.40	0.26	0.19
Ti	1.76	1.69	1.63	1.71	1.51	1.93	1.70	1.71	1.84	1.86
Zr	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.01
P	0.00	0.01	0.00	0.01	0.00	0.00	0.19	0.21	0.25	0.26
As	0.00	0.03	0.02	0.00	0.02	0.00	0.00	0.00	0.00	0.01
Nb	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
	0.89	0.89	0.88	0.81	0.84	0.69	0.33	0.28	0.29	0.36
	0.06	0.03	0.02	0.03	0.02	0.05	0.02	0.01	0.01	0.01
	0.01	0.01	0.00	0.01	0.00	0.01	0.06	0.06	0.06	0.06
Σ A site	0.95	0.92	0.91	0.85	0.86	0.75	0.41	0.35	0.36	0.43
	1.88	1.90	1.90	1.91	1.92	2.14	2.22	2.34	2.37	2.33
	0.16	0.18	0.19	0.23	0.22	0.11	0.37	0.31	0.27	0.24
Σ B site	2.05	2.08	2.09	2.15	2.14	2.25	2.59	2.65	2.64	2.57
Σ CAT	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
O	5.60	5.61	5.62	5.59	5.60	5.74	5.65	5.72	5.76	5.83
OH^-	0.40	0.39	0.38	0.41	0.40	0.26	0.35	0.28	0.24	0.17
Σ AN	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00

Tab. 2

Representative WDS microanalyses of metatorbernite from Lopejské Čelno. H_2O* – H_2O content calculated assuming 8 H_2O molecules in ideal metatorbernite formula.

	1	2	3	4	5	6
K_2O	0.19	0.21	0.13	0.18	0.27	0.21
MgO	0.05	0.00	0.05	0.00	0.03	0.11
CaO	0.02	0.02	0.07	0.35	0.31	0.17
BaO	0.00	0.00	0.08	2.42	2.23	1.72
FeO	0.00	0.00	0.10	0.00	0.07	0.05
CuO	7.12	5.82	7.77	5.96	5.89	6.21
Al_2O_3	0.02	0.05	0.04	0.06	0.08	0.50
SiO_2	0.01	0.04	0.03	0.08	0.04	0.69
P_2O_5	13.27	16.72	15.58	15.67	15.93	15.69
As_2O_5	0.00	0.02	0.09	0.12	0.10	0.00
UO_3	57.22	66.01	62.84	62.59	61.70	62.06
H_2O	17.92	18.39	18.22	18.07	18.21	18.41
Total	77.91	88.87	86.76	87.42	86.65	87.42
Total*	95.83	107.26	104.98	105.49	104.86	105.83
Based on 12 O						
K	0.04	0.04	0.02	0.04	0.05	0.04
Mg	0.01	0.00	0.01	0.00	0.01	0.03
Ca	0.00	0.00	0.01	0.06	0.05	0.03
Ba	0.00	0.00	0.00	0.14	0.13	0.10
Fe	0.00	0.00	0.01	0.00	0.01	0.01
Cu	0.92	0.65	0.89	0.68	0.68	0.70
Al	0.00	0.01	0.01	0.01	0.01	0.09
ΣA site	0.99	0.70	0.96	0.93	0.94	0.99
Si	0.00	0.01	0.00	0.01	0.01	0.10
P	1.93	2.08	2.00	2.02	2.05	1.98
As	0.00	0.00	0.01	0.01	0.01	0.00
ΣT site	1.93	2.09	2.01	2.04	2.07	2.08
U	2.06	2.03	2.00	2.00	1.97	1.94
H_2O	8.00	8.00	8.00	8.00	8.00	8.00

Tab. 3

Representative WDS microanalyses of chlorite and muscovite

	Chlorites						**Muscovites**						
SiO_2	27.08	24.71	23.95	23.77	24.31	23.67	50.07	46.06	46.92	46.86	45.12	49.29	46.85
TiO_2	0.05	0.12	0.11	0.03	0.07	0.10	0.10	0.23	0.29	0.37	0.26	0.06	0.30
Al_2O_3	23.93	22.99	22.53	22.12	22.54	22.02	26.11	34.94	32.50	31.56	32.98	26.13	29.95
Cr_2O_3	0.01	0.03	0.05	0.00	0.01	0.02	0.04	0.00	0.00	0.00	0.00	0.00	0.03
FeO	25.63	28.15	29.03	28.09	27.31	27.85	3.14	1.17	2.41	1.97	1.53	3.26	2.62
MnO	0.44	0.67	0.54	0.49	0.43	0.46	0.05	0.06	0.00	0.00	0.05	0.03	0.02
MgO	8.42	9.04	9.61	9.43	9.71	9.59	3.48	0.70	1.34	1.89	1.20	3.47	1.82
CaO	0.02	0.03	0.03	0.03	0.04	0.04	0.00	0.00	0.00	0.02	0.01	0.02	0.05
BaO	0.17	0.13	0.13	0.18	0.05	0.12	0.25	0.29	0.21	0.23	0.36	0.09	0.19
Na_2O	0.03	0.02	0.02	0.03	0.03	0.05	0.06	0.81	0.43	0.35	0.54	0.14	0.34
K_2O	1.12	0.26	0.11	0.06	0.15	0.08	11.43	10.35	10.46	10.86	10.88	11.11	10.34
F	0.00	0.00	0.37	0.00	0.37	0.00							
Cl	0.01	0.00	0.01	0.01	0.01	0.00							
O = F	0.00	0.00	0.16	0.00	0.16	0.00							
O = Cl	0.00	0.00	0.00	0.00	0.00	0.00							
Total	86.90	86.14	86.33	84.23	84.87	84.00	94.74	94.61	94.56	94.12	92.93	93.59	92.51
H_2O	11.28	10.97	10.72	10.69	10.65	10.67							
Total*	98.18	97.11	97.04	94.92	95.52	94.67							
Based on 10 O and 8 OH							Based on 11 O						
Si	2.88	2.70	2.64	2.67	2.69	2.66	3.40	3.09	3.17	3.18	3.11	3.39	3.24
Ti	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.00	0.02
Al^{4+}							0.60	0.91	0.83	0.82	0.89	0.61	0.76
Al^{6+}	3.00	2.96	2.92	2.92	2.94	2.92	1.50	1.86	1.75	1.71	1.79	1.50	1.68
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	2.28	2.57	2.67	2.63	2.53	2.62	0.18	0.07	0.14	0.11	0.09	0.19	0.15
Mn	0.04	0.06	0.05	0.05	0.04	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	1.33	1.47	1.58	1.58	1.60	1.61	0.35	0.07	0.13	0.19	0.12	0.36	0.19
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.10	0.06	0.05	0.07	0.02	0.05
K	0.15	0.04	0.02	0.01	0.02	0.01	0.99	0.89	0.90	0.94	0.96	0.97	0.91
F	0.00	0.00	0.13	0.00	0.13	0.00							
Cl	0.00	0.00	0.00	0.00	0.00	0.00							

Stratiformná U-Cu mineralizácia v Lopejskom Čelne pri Podbrezovej (veporikum, Západné Karpaty)

Lokalita sa nachádza približne 1,5 km južne od centra bývalej obce Lopej (dnes kataster obce Podbrezová) v doline Lopejské Čelno. Je vyvinutá v ľubietovskom pásme tektonickej superjednotky veporika (obr. 1, 2), pričom je viazaná na limonitizované alterované arkózové pieskovce s polohami acidných vulkanitov permského veku. Mineralogické pomery na lokalite v minulosti študovali Rojkovič a Novotný (1993). Mineralizáciu opisujú ako U-Cu stratiformnú, kde v zrudnených šošovkách bol opísaný pyrit, rutil, leukoxén, chalkopyrit, goethit a torbernit (Rojkovič a Novotný, 1993). Revíznym štúdiom mineralizácie v Lopejskom Čelne bola identifikovaná primárna mineralizácia.

Primárna U mineralizácia sa v doline Lopejské Čelno vyskytuje len veľmi ojedinele v zrnách s veľkosťou do 120 μm (obr. 3). Z U^{4+} minerálov bol identifikovaný brannerit a U-Ti oxidy (obr. 5, 10; tab. 1) v úzkej priestorovej a genetickej asociácii s rutilom (obr. 4), Ti oxidmi (leukoxénom) a ílovými minerálmi (obr. 9, 11). Mineralizácia s najväčšou pravdepodobnosťou vznikala počas procesu alterácie biotitu spätého s hydrotermálnymi procesmi a adsorpciou uránu na Ti oxidy, pričom za zdroj Ti sa považuje práve biotit. Adsorpcia uránu na Ti oxidy, tzv. *Pronto-reakcia*, prebieha v hydrotermálnych systémoch pri teplote, ktorá koreluje s teplotou generovanou počas alpínskej orogenézy, resp. s jej doznievaním. Všetky spomínané minerálne fázy obsiahnuté v mineralizovaných zrnách sú typickými produktmi alterácie biotitu (Lovering et al., 1949; Schwartz, 1958; Bisdom, 1967; Deer et al., 1992; Finch, 1996; René a Dolníček, 2017). Na okraji mineralizovaných zŕn a v samotnej hornine sú hojne zastúpené chlority a muskovit (tab. 3).

Oxidačnú zónu zastupuje malachit, goethit a U^{6+} minerál metatorbernit (obr. 6, 7, 8). Vznik metatorbernitu (tab. 2) je spätý s deštrukciou primárnych U^{4+} minerálov v kyslých podmienkach a oxidáciou U^{4+} na U^{6+} za vzniku uranylového iónu UO_2^{2+}. Ostatné konštrukčné prvky (Cu, P) boli do metatorbernitov dodávané z minerálov obsiahnutých v hornine a z horninotvorných minerálov (chalkopyrit, apatit; obr. 12). Nezvyčajným javom pri metatorbernite z Lopejského Čelna je jeho luminiscencia, ktorá je pravdepodobne zapríčinená defektmi v kryštálovej štruktúre minerálu alebo vplyvom prímesí nanočastíc iného minerálu (Civetta a Gasparini, 1972; Langmuir, 1978; Plášil et al., 2009).

Doručené / Received: 17. 4. 2023
Prijaté na publikovanie / Accepted: 30. 6. 2023