

RESEARCH ARTICLE



Nb–Ta mineralization in Ti-oxide minerals from the Bagolyhegy Metarhyolite Formation (Bükk Mountains, NE Hungary)

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Received: October 13, 2020 • Accepted: August 30, 2021

Published online: December 15, 2021

ABSTRACT

The foliated low-grade metamorphic rocks of the Triassic Bagolyhegy Metarhyolite Formation, mainly of pyroclastic origin, host post-metamorphic quartz-albite veins containing abundant tourmaline and occasionally rutile/ilmenite. The study of the Ti-oxide-mineralized veins with SEM-EDX revealed an unusual mineral assemblage comprising fine-grained Nb–Ta-bearing oxides (columbite-tantalite series, fluorcalciomicrocline and other Nb–Ti–Y–Fe–REE-oxide minerals) intergrown with Nb-rich polymorphs of TiO₂ (anatase, rutile), ilmenite and zircon enriched with hafnium. This high field strength elements (HFSE)-bearing paragenesis is unexpected in this lithology, and was not described from any formation in the Paleozoic-Mesozoic rock suite of the Bükk Mountains (NE Hungary) before. The host metavolcanics are significantly depleted in all HFSE compared to the typical concentrations in felsic volcanics and the mineralized quartz-albite veins have even lower Ti–Nb–Ta concentration than the host rock, so the mineralization does not mean any enrichment. From proximal outcrops of the Triassic Szentistvánhegy Metavolcanics, potassic metasomatized lenses with albite-quartz vein fillings containing rutile/ilmenite are known. We studied them for comparison, but they only contain REE mineralization (allanite-monazite-xenotime); the Nb–Ta-content of Ti-oxide minerals is undetectably low. LA-ICP-MS measurements for U–Pb dating of Hf-rich zircon of the Nb–Ta-rich mineral assemblage gave 71.5 ± 5.9 Ma as lower intercept age while dating of allanite of the REE mineralized quartz-albite veins gave 113 ± 11 Ma as lower intercept age. The REE-bearing vein fillings formed during a separate mineralization phase in the Early Cretaceous, while the Nb–Ta mineralization was formed by post-metamorphic alkaline fluids in the Late Cretaceous, controlled by fault zones and fractures.

KEYWORDS

Bükk Mountains, ilmenite, metavolcanics, Nb–Ta-oxide, pegmatite, rutile, vein

INTRODUCTION

Niobium and tantalum are registered as critical elements in the EU (Blengini et al., 2020), because despite their economic importance, no significant mineral resources are known in the region. Mineralization containing Nb and Ta minerals usually occurs related to carbonatite, alkaline intrusive rocks, or pegmatite, enriched in high field strength elements in magmatic processes (e.g., de Kun, 1962; Shaw and Goodenough, 2011). In other rock types Nb and Ta are of low concentration and hosted mainly by Ti-oxide minerals.

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The Triassic Bagolyhegy Metarhyolite (BMR) of the Bükk Mts, NE Hungary, cropping out between Bükkszentkereszt and Bükkszentlászló (Fig. 1), was sampled and studied by the Institute of Mineralogy and Geology, University of Miskolc in the framework of the CriticEl project (assessment of critical raw materials potential of Hungary; Földessy, 2014). The main target was a U–Be–HREE anomaly related to manganiferous, phosphoritic rocks found by previous ore exploration (Kubovics et al.,

1989; Szabó and Vincze, 2013; Zajzon et al., 2014), but country rocks including vein rocks were also tested for critical element-bearing minerals. Columbite-(Fe), a Nb-oxide mineral was identified by the study of rutile grains, collected from the debris of quartz-albite veins penetrating and overprinting the low-grade metamorphic fabric of the felsic metavolcanics in the Hidegvíz Valley (Fig. 2). The host BMR is significantly depleted in all HFSE including Nb and Ta, so the late or post-metamorphic mineralization revealed

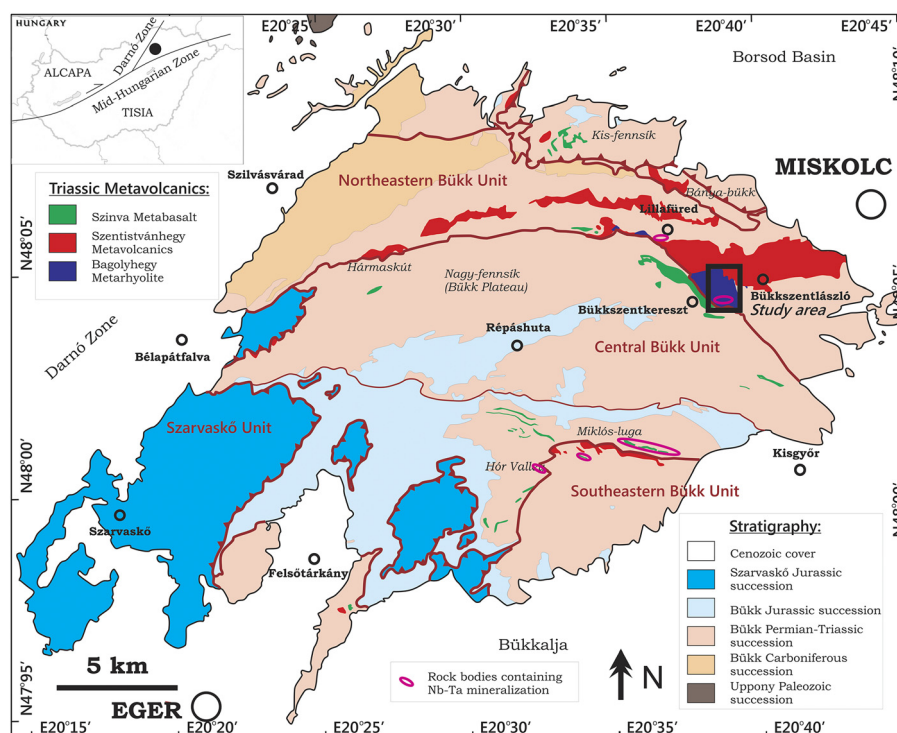


Fig. 1. Simplified geologic map of the Bükk Mountains (based on Less et al., 2005), indicating major stratigraphic divisions, the outcrops of the Triassic metavolcanics formations, Nb–Ta enriched rock bodies (magenta ellipses) and the study area (black frame). Dark red lines indicate major structural boundaries. Lines with triangles mark inferred nappe boundaries

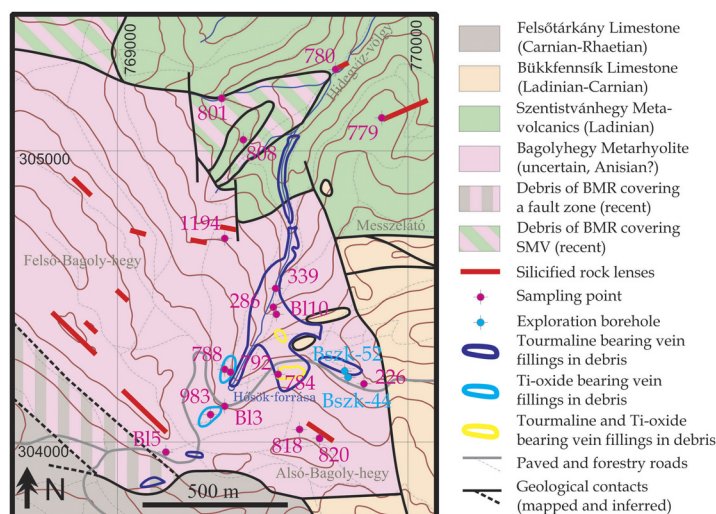


Fig. 2. Geologic map of the study area indicating sampling points and exploration boreholes referred to in the text. Grid: EOv (Hungarian National Grid)

by our subsequent studies is unexpected and atypical for this environment.

This paper documents this newly recognized mineralization containing Nb–Ta oxides, niobian rutile, ilmenite, zircon and some further Nb-bearing mineral phases using results of field observations, electron probe microanalysis, whole-rock chemical analysis and laser ablation ICP-MS tests of selected grains. In search of the source of the hydrothermal fluids, and for comparison, we studied a nearby metavolcanics-hosted occurrence of an ilmenite- and REE mineral-bearing paragenesis. We also wanted to find suitable phases for dating the mineralization by U–Pb LA-ICP-MS geochronology. Nb-containing Ti-oxide and aeschynite-type minerals were also identified elsewhere in the Bükk Mts. in HFSE-enriched, metasomatized bodies (Németh et al., 2016, 2018). The mineralization was compared to these assemblages and to other Nb–Ta mineral occurrences of the Carpathian-Pannonian region.

GEOLOGIC SETTING

The Bükk Mts. is a low mountain range not exceeding 1,000 m elevation, located in NE Hungary, containing Carboniferous to Jurassic sedimentary and volcanic rocks rising from the surrounding Neogene basins (Fig. 1). There are sediments and magmatic rocks of oceanic origin in the SW (Szarvaskő Unit), but the major part of its area is the outcrop of the shelf-derived Bükk Parautochthonous Unit. These successions were interpreted as analogies of the Jadar Block and Sana-Una in the Dinarides (Balogh, 1964; Filipović et al., 2003; Less et al., 2005; Kovács and Haas, 2010), displaced a few hundred kms to the NE along the SSW–NNE-trending Mid-Hungarian Fault Zone (Schmid et al., 2008; Kovács and Haas, 2010; Haas and Budai, 2014).

The Triassic sequences of the Bükk Mts. contain volcanics in three horizons (Balogh, 1964; Less et al., 2005), well distinguished by their geochemical character. The few hundred meters-thick, calc-alkaline, felsic-neutral, strato-volcanic complex of the Szentistvánhegy Metavolcanics (SMV; Szoldán, 1990; Less et al., 2005) yields an Early Ladinian (240.3 ± 1.3 Ma) zircon U–Pb age (Gál et al., 2018) and lies conformably within Anisian–Ladinian carbonate-dominated successions. In our study area, unlike other outcrops of this SMV, felsic metavolcanics of the Bagolyhegy Metarhyolite (BMR) lie over it with a southward dipping contact. BMR occurs only here. Zircon U–Pb data suggest older but uncertain ages due to a metasomatic overprint (Gál et al., 2018), so the stratigraphic position of the BMR is ambiguous. The Carnian carbonate sediments fragmented into basins and platforms contain several small basaltic volcanic bodies, named as Szinva Metabasalt. In general, these volcanic bodies have an alkaline character (Szoldán, 1990; Less et al., 2005; Németh et al., 2016). The Ladinian and Carnian volcanism is related to the Middle Triassic rifting known from the Dinarides and the Southern Alps (Cros and Szabó, 1984; Harangi et al., 1996).

The study area (Fig. 2) is situated at the border of two structural units of different tectofacies divided by a regional fault zone of NW–SE strike (Csontos, 1999). The NE unit (Northeastern Bükk Unit on Fig. 1) contains extensive outcrops of the BMR (ca. 2 km² area between the Bükkszentkereszt and Bükkszentlászló settlements) and of the SMV (a ca. 10 km² area north of the BMR). Massive, platform-facies Bükkfennsík Limestone occurs southeast of the study area, contacted by subvertical faults and several trimmed fault blocks with both metavolcanics formations. The southwestern unit (Central Bükk Unit on Fig. 1) contains Upper Carnian cherty limestone (Felsőtárkány Limestone Formation) at the contact with intercalated small bodies of the Szinva Metabasalt. The metamorphic history varies by tectonic units, from anchi- to epizonal regional metamorphism at max. 250–300 °C temperature during the Cretaceous (Árkai, 1973, 1983). White mica K/Ar ages range from ~120 to ~80 Ma; in the BMR the measured age is 78 Ma (Árkai et al., 1995). Before the regional metamorphism, postmagmatic hydrothermal activity also caused metasomatic alterations in all volcanic horizons, with local differences. The distribution of rocks affected by potassium metasomatism in the study area was mapped by radiometric survey (Németh et al., 2015).

Nb–Ta-mineralized rocks in the Bagolyhegy Metarhyolite

Detailed studies providing the original description of the BMR are not recent and their terminology is partly out of date (Szentpétery, 1931; Selmecziné, 1974; Kubovics et al., 1989); here we give a short characterization based on these and on own observations (Gál et al., 2018). The most abundant rock type has a strongly oriented porphyritic texture with grey or pale green, microcrystalline matrix composed of quartz, sericite, and feldspars. The fabric is dominated by anastomosing cleavage domains consisting of phyllosilicates enveloping the phenocrysts, often deformed and resorbed, comprising quartz, K-feldspar and albite (together in several cases in altered grains). Cm to dm-sized, elongate and altered pyroclasts were recognized in several samples; thus, their protolith was rhyolite tuff or ignimbrite.

The rock is penetrated by veins which were grouped into quartz-orthoclase-albite, quartz-albite, quartz-orthoclase-albite-chlorite, and quartz-orthoclase-albite-tourmaline types by Selmecziné (1974). The vein rocks usually are some cm or dm thick, but a 3 m-long section of tourmaline-bearing veins was recorded in the Bszk-44 and Bszk-52 converging drillholes (Szabó and Vincze, 2013). Some veins crosscut the cleavage; thus, they were formed after the synmetamorphic ductile deformation (Selmecziné, 1974). Subsequent brittle deformation of the vein rocks produced a cataclastic and micro-brecciated texture, containing fragments of the country rock. The tourmaline is the schorl species, which was formed from boron-enriched hydrothermal fluids both as microcrystalline cement of the breccia and as large euhedral crystals (Fehér, 1998–99, 2015).



Several lens-shaped, K-metasomatized and silicified rock bodies were outlined, forming cliffs and supporting blocky debris in the study area (Fig. 2) (Németh et al., 2015). Intergrown K-feldspar and quartz are dominant in the microcrystalline matrix, but minor sericite and pyrite were also identified. The phenocrysts are rare and commonly strongly resorbed. The rock is penetrated by goethite-jarosite-quartz veins, in which Nb-containing minerals were also detected.

Quartz-albite-Ti-oxide veins in the Szentistvánhegy Metavolcanics

Similarly to the BMR, the SMV also contains some 10 or 100 m-long, elongated cliffs of K-metasomatized and silicified rock bodies. Their geochemistry indicates andesitic-dacitic origin, but volcanic textures are strongly overprinted. Metasomatized rock bodies are lens-shaped, oriented parallel to the cleavage, but the texture of the silicified, competent rock shows weak or no orientation except for the chlorite-rich domains. Their fine-grained, altered matrix contains quartz, sericite, K-feldspars and subordinate chlorite. Phenocrysts are usually albite grains. These rocks are intensively penetrated by quartz-albite veins of a few cm, occasionally of dm thickness. The veins contain pyrite, goethite, opal (hyalite), jarosite, ilmenite, rutile, chlorite and anatase as accessories. Nb–Ta content of the rutile from the NE occurrences was reported as not detectable (Szakáll et al., 2011).

Other rocks in the Bükk Mts. containing Nb–Ta-mineralization

Nb–Ta enriched rocks were found recently along the continuation of the major fault zone forming the southwestern border of the BMR, in Triassic siliciclastic rocks at Lillafüred (Hegyestető Formation) and at another tectofacies-bordering fault zone in Triassic metabasalts and metasediments (Szinva Metabasalt) in the southeastern part of the Bükk Mts. (Fig. 1). Peperitic metavolcanics and phengitic metasediments embedded in limestone are enriched in potassium and high field strength elements (HFSE). The bulk Nb content ranges from 100 to 200 ppm, the Ta ca. 10 ppm. The host phase of the Nb and Ta is a fine-grained Ti-oxide mineral, commonly associated with K-feldspars, μm -sized zircon, and monazite-(Ce) (Németh et al., 2016).

Beyond the Ti-oxide minerals described above, ca. 10 μm -sized, elongate, REE-containing Nb–Ti-oxide mineral grains were also identified from the Lillafüred site (Németh et al., 2018).

ANALYTICAL METHODS

Dozens of samples (ca. 50) were collected from the rock types of the BMR and SMV during the mapping within the framework of the CriticEl project in 2013–14. Relatively fresh, silicified metavolcanics, and vein-filling samples were

included in this study. Usually samples larger than 2 kg were collected to achieve representative geochemical data.

For mineralogical and textural observations, we used a Zeiss Stemi DV4 stereomicroscope of the Institute of Mineralogy and Geology, University of Miskolc, Hungary.

The samples for chemical analyses were split in half; one half was ground below 2 mm-grain size at the Institute of Raw Material Preparation and Environmental Processing, University of Miskolc, Hungary. Aliquots of 250-g were further ground below 75 μm . The accredited bulk rock chemistry measurements of 13 samples were performed at the analytical laboratory of the Mining and Geological Survey of Hungary, Budapest. Following Li-metaborate digestion the major and minor elements (Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Sr) and some trace elements (Cd, Co, Cr, Cu, Mo, Ni, Ti, V, Zn) were identified by ICP-OES, and other trace elements (Ag, Be, Bi, Cs, Ga, Ge, Hf, In, Nb, Pb, Rb, Sb, Sc, Se, Sn, Ta, Te, Th, Tl, U, W, Y, Zr) by ICP-MS.

Seven polished slabs were prepared from the samples for SEM-EDX studies (Samples 226, 779, 780, 784, 788, 801, 983). The standardless EDS analyses were made with a JEOL JXA 8600 Superprobe instrument, fully upgraded with SAMX control (15–20 kV, 20 nA, SDD-detector) at the Institute of Mineralogy and Geology, University of Miskolc, Hungary. On BSE images names of the identified minerals are abbreviated according to (Whitney and Evans, 2010): Qz – quartz, Ab – albite, Kfs – K-feldspar, Ms – muscovite, Py – pyrite, Ilm – ilmenite, Ilm* – ilmenite with high Nb–Ta-content (niobian ilmenite), Rt – rutile, Ttn – titanite, Col – columbite, Zrn – zircon, Cst – cassiterite, Aln – allanite, Mnz – monazite.

Laser ablation ICP-MS (LA-ICP-MS) U–Pb dating measurement was performed on Samples 780 and 784 at the Georg-August University of Göttingen on a Thermo Element 2 SF-ICP-MS equipped with an ASI Resolution 155 ablation system (measurements were performed with 23 and 33 μm spot-sizes). More reference materials were measured as secondary standards to calibrate the results more accurately. Concentration profiles of ilmenite were recorded to clarify the zonal distribution of Nb, Ta and other trace elements.

MINERALOGICAL AND TEXTURAL CHARACTERISTICS

Ti–Nb–Ta minerals of quartz-albite-Ti-oxide-(schorl) veins of the BMR

Abundant quartz-albite veins penetrate the rocks of the BMR, but they only contain tourmaline and Ti-oxide minerals in the debris covering the few hundred meters vicinity of the Hösök Spring (Fig. 2). The studied vein rocks consist of quartz, subordinate albite and schorl in a coarse-grained, “pegmatitic” texture. In some cases, they form oriented, columnar crystal aggregates with equal abundance of all three minerals. Accessory minerals are K-feldspars, muscovite (sericite) and other phyllosilicates, pyrite (altered mostly



to goethite pseudomorphs), rutile, ilmenite, anatase, brookite, zircon, apatite, jarosite and chlorite.

Three samples with macroscopic Ti-oxide minerals were examined by means of polished sections. In samples 983 and 788, rutile forms 5–20 mm-sized, compact or loose aggregates of 0.1–1 mm-sized columnar, acicular crystals, or 1–2 mm-sized anhedral grains. In Sample 784 ilmenite was identified as a cm-sized aggregate of thin platy crystals (Fig. 3). Sample 983 is composed mainly of quartz with small amounts of albite. Samples 788 and 784 are built up by quartz and albite in equal quantity. Sample 784 also contains schorl. The SEM-EDX and LA-ICP-MS identified mineral phases are summarized in Supp. Table 3.

Several different compositional phases of ilmenite can be observed on the BSE images of Sample 784. The grey phases have low Nb–Ta content; their brightness depends on their Mn-content (Figs. 3 and 4/b, e–g, Supp. Table 1). The bright elongated phases along cleavage planes and the encrusting rims on the lower parts of the large ilmenite aggregate usually have variable but high Nb–Ta content (Figs. 3, 4/f–g, and 8, Supp. Table 2a). The Nb–Ta-rich ilmenite also has significant Al, P, U, Pb, Zr, Th, Y and REE content, but it is strongly Zn-depleted compared to normal ilmenite (Supp. Table 1). Rare, small aggregates of tabular crystals with similar high Nb–Ta-content also occur in this sample (Fig. 4/d).

Rutile crystals of Sample 983 show a compositional growth-zoning (dark and bright zones). The dark area is composed mainly of TiO_2 with minor Fe and Nb substitution, while bright areas are enriched in Fe and Nb with higher Nb/Ta and Fe/Ta ratios (Fig. 4/h, Supp. Table 2b). Hypidiomorphic–idiomorphic rutile crystals of 50–200 μm size can be found in Sample 788 as multiple twins (Fig. 5/a) and knee-shaped twins (Fig. 5/b), and they show Nb–Fe–W chemical zonation. The types of zonation can be totally irregular (Fig. 5/d), banded (Fig. 5/b), or enriched in trace elements at the rims (Fig. 5/a). Rutile appears as 100 μm -sized, idiomorphic, columnar inclusions in the large ilmenite

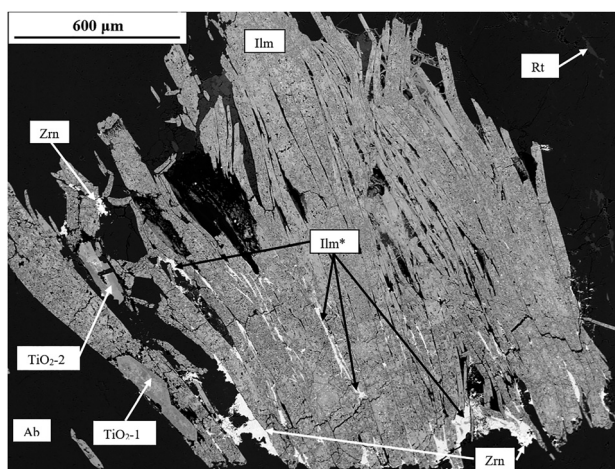


Fig. 3. BSE image of a large ilmenite aggregate of Sample 784. Abbreviated mineral names are shown in Chapter Analytical methods, TiO_2 -1-2: identifiers in Supp. Table 1

crystal of Sample 784 (Fig. 4/a), crosscutting the ilmenite table. Disseminated, hypidiomorphic–xenomorphic, columnar or acicular, few tens of μm -long, sometimes Fe–Nb–Ta–W-enriched (Fig. 4c) rutile crystals can be found enclosed in quartz. Inhomogeneously distributed, 10 μm sized, xenomorphic rutile grains with high Ta–Nb–Fe-content were formed inside the large ilmenite crystal aggregate as alteration product of the ilmenite (Fig. 4/e).

In sample 784 two idiomorphic, tabular crystals of an undefined, brookite-like TiO_2 mineral were measured with LA-ICP-MS. Phase TiO_2 -1 is Ta-rich with a slightly smaller amount of Fe and Nb, and significantly less W, while Phase TiO_2 -2 is Fe-rich with a slightly smaller amount of Nb, W and Ta and slightly enriched in Sn. Irregular chemical zoning of the crystals is observable; one edge of Phase TiO_2 -2 is W-depleted and Y-REE-rich (Supp. Table 1).

In Sample 788, thin parallel lamellae in rutile were identified as columbite-(Fe) (Fig. 5/d). Another occurrence of columbite-(Fe) is xenomorphic crystals up to 200 μm together with a not precisely identified Ti–Nb–Y-REE-oxide phase (Fig. 5/c). Xenomorphic columbite-(Fe), 5–20 μm sized, was also identified in Sample 784, showing weak chemical zonation caused by the varying Ta substitution (Fig. 4/b). Some columbite crystals contain a high amount of manganese close to the iron content; even the occurrence of columbite-(Mn) can be assumed (Supp. Table 2c).

Tantalite-(Fe) occurs as xenomorphic crystals (1–10 μm) within ilmenite (Fig. 4e, Supp. Table 2c). Figure 6 show the element map and EDX test results of the tantalite-(Fe) inclusion within ilmenite in sample 784.

A Ca–Na–F-rich mineral, identified as fluorcalciomicrolite, was found as a single grain with the same appearance as the tantalite-(Fe) in Sample 784 in the large ilmenite aggregate (Fig. 4/e, Table 2d).

Unidentified Ti–Nb–Y-(Fe)-REE-oxide mineral phases appear in rutile and columbite-(Fe) as 10 μm -sized or rarely larger xenomorphic grains in Sample 788 (Fig. 5/c). A similarly composed, but significantly Fe-richer phase was also recognized as 20–100 μm -sized, later stage, xenomorphic grains in the Nb–Ta-rich ilmenite association in Sample 784 (Fig. 4/f). According to the chemical analyses (Supp. Table 2e), the minerals may be pyrochlore, polycrase, euxenite or aeschynite.

At the rim of the large ilmenite crystal of Sample 784, xenomorphic zircons, exceeding 100 μm in size, can be found, which have an outstandingly high Hf-content (Fig. 4/g, Supp. Tables 1 and 2d). In Sample 788, irregular cassiterite aggregates with the maximum size of 10 μm were found associated with rutile and columbite-(Fe) (Fig. 5/b, Supp. Table 2d).

Ti–Nb–Ta minerals of sericitic metarhyolite of the BMR

Two different compositional types of rutile were identified in Sample 226: the first one is enriched in Nb and Ta, while the second one is Mn, Zn-enriched with low Nb and Ta content (Fig. 5e, Supp. Table 2b).

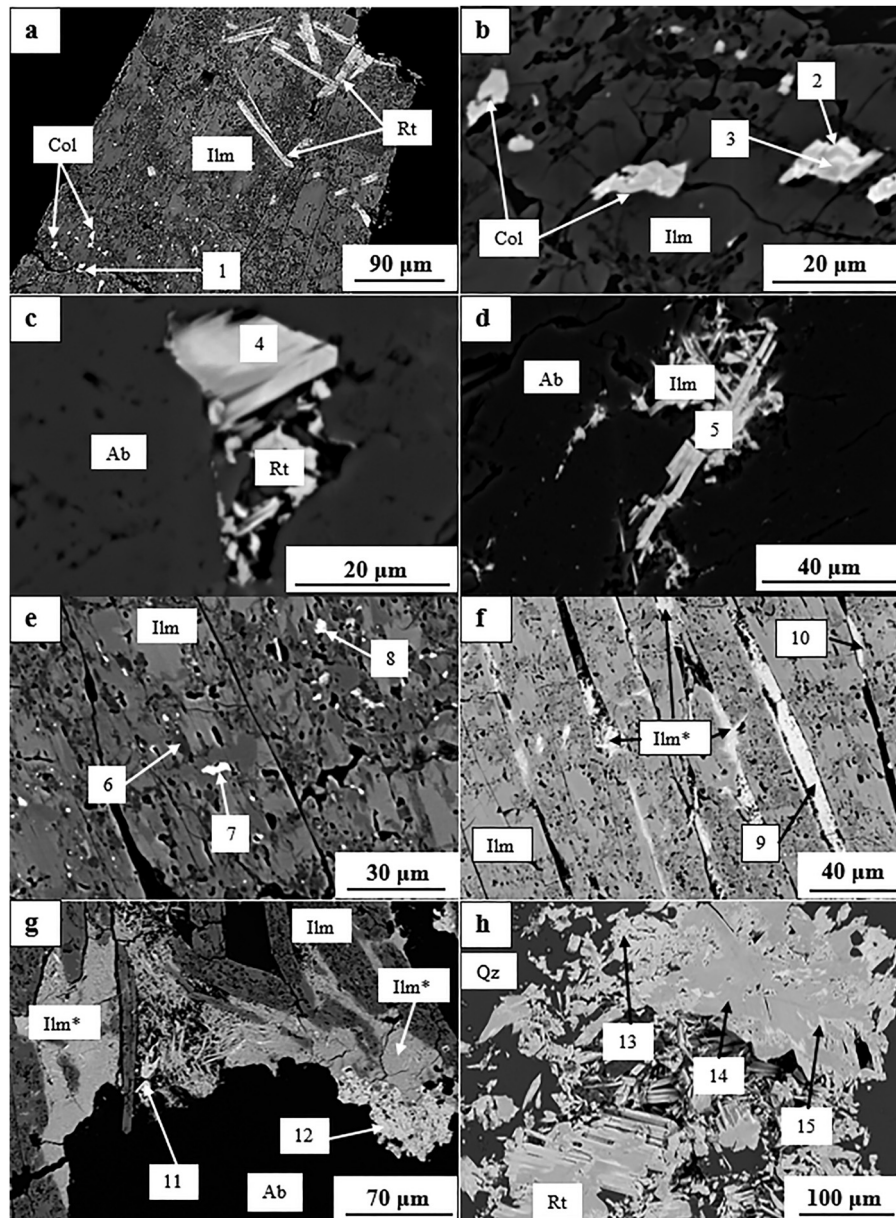


Fig. 4. BSE images of the studied minerals from Sample 784 (a–g) and 983 (h). (a) Ilmenite crystal containing columbite-(Fe) (1) and needle-shaped inclusions of rutile. (b) Zoned columbite-(Fe) crystals (2–3). (c) Rutile with high Nb-Ta-W content (4). (d) Nb-Ta-rich, slightly zoned ilmenite (5). (e) Irregular zones with more (darker grey) or less (lighter grey) Mn content in ilmenite, rutile (dark grey) as alteration product (6) and Ta-oxide minerals: locally abundant tantalite-(Fe) (7) and rare fluorcalciomicrocline (8). (f) Nb-Ta enriched ilmenite (9) and a Ti-Nb-Y-REE-oxide mineral (10) as fracture-filling. (g) Late exsolution phases at the edge of the ilmenite aggregate: Ti-Nb-Y-REE-oxide (11) and Hf-rich zircon (12) in Nb-Ta-rich ilmenite. (h) Zoned rutile: the rim (13) is more enriched in Fe and Nb than the core (14), which contains W-rich spots (15). The number (1–15) show SEM_EDS analysis locations

Ti-Nb-Ta minerals in the K-metasomatic, silicified metarhyolite of the BMR

In Sample 801, μm -sized niobian rutile (Supp. Table 2) and REE minerals were observed, mostly associated with albite next to a goethite-jarosite vein (Fig. 7, Supp. Table 2b). A 100 μm -sized, hypidiomorphic Ti-Nb-Y-REE mineral of aeschynite-like composition (similar to the ones found in Sample 784) was also observed intergrown with niobian rutile in albitized environment (Fig. 5f, Table 2e).

Ti-oxide vein fillings of K-metasomatic, silicified metaandesite-metadacite of the SMV

The metasomatic host rock in Samples 779 and 780 is built up from irregular intergrowth of quartz and K-feldspar with abundant disseminated idiomorphic crystals of 50–100 μm -sized pyrite and 1–20 μm -sized zircon. Sample 779 contains 100–1,000 μm long, idiomorphic, tabular ilmenite and 10–50 μm -sized hypidiomorphic-xenomorphic rutile in a quartz vein (Fig. 8). Sample 780 is rich in 10–500 μm -sized

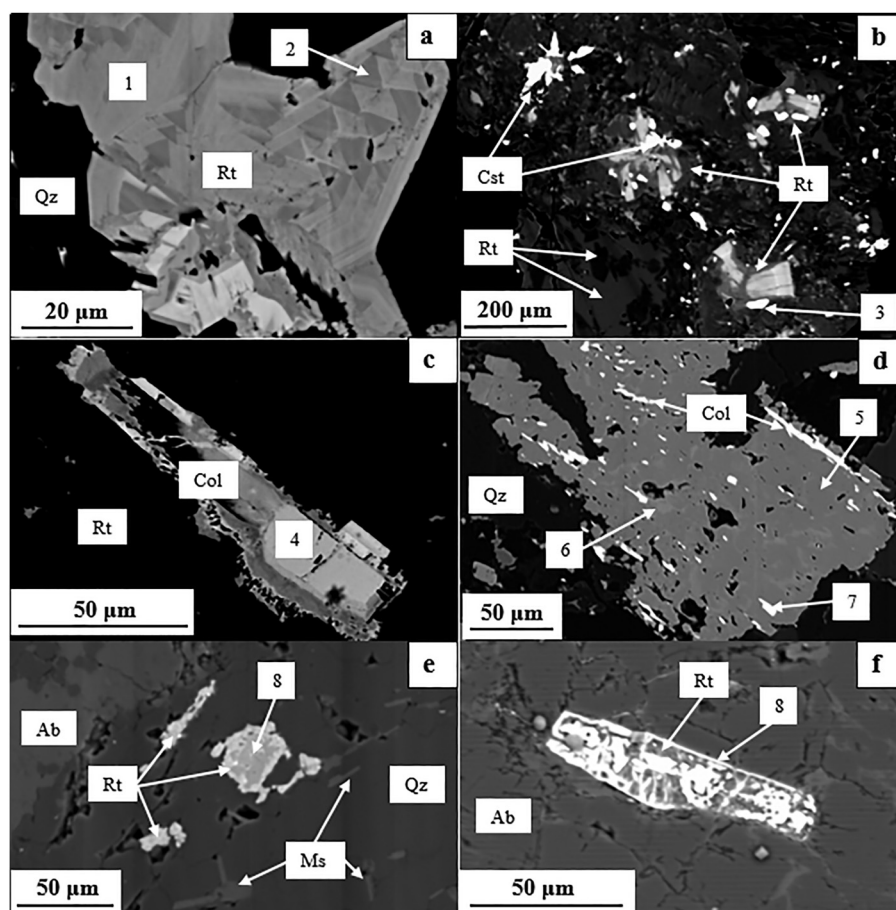


Fig. 5. BSE images of the studied minerals from Sample 788 (a–d), 226 (e) and 801 (f). (a) Twinned and zoned rutile with slight differences (1–2) in Fe–Nb–W content. (b) Twinned Nb-zoned rutile crystals with cassiterite (3) in Nb–Ta-poor rutile. (c) Unidentified Ti–Nb–Y–Fe–REE-oxide mineral (4) with columbite-(Fe) in rutile. (d) Nb–Ta-zoned rutile (5–6) with columbite bands (7). (e) Zoned Nb–Ta-bearing rutile with high Fe–Mn–Zn content (8). (f) Grain of the unidentified Ti–Nb–Y–Fe–REE-oxide mineral (9) with niobian rutile. The numbers (1–9) show SEM_EDS analysis locations

hypidiomorphic-xenomorphic crystals of allanite-(Ce) (Fig. 9/a, Supp. Table 2d), and 10–100 µm-sized xenomorphic crystals of rutile and fluorapatite. Monazite-(Ce) and xenotime-(Y) occurs as xenomorphic, <10 µm sized individual crystals or inclusions in allanite (Fig. 9/b). Some titanite grains were also observed associated with rutile. The rutile of the studied samples contains a detectable but very low amount of Nb; Ta was below the detection limit. No Nb and Ta were detected in ilmenite, but it contains small amount of Mn (Supp. Table 2a).

GEOCHEMISTRY

The bulk rock geochemical assays of the studied samples are summarized in Supp. Table 4. The major element composition and the trace element pattern changed significantly in all rock types compared to the original magmatic composition, due to postmagmatic and metamorphic alterations. Probably the unsilicified metarhyolite of pyroclastic origin is the chemically least altered rock type; therefore, its

composition can be regarded as geochemically relevant to the protolith (Németh et al., 2015). Beyond these, strongly K-metasomatized rocks and the bulk veins were also assayed.

The least altered sericitic metarhyolite of the BMR is rich in Si and K (72.8–78.4 wt% SiO₂ and 3.75–4.12 wt% K₂O) but has a low Ti concentration (0.05 wt% TiO₂). High K enrichment (8.5–10.8 wt% K₂O) compensated by depletion of Na (0.46–1.57 wt%) and moderate Si content (68.4–74.4 wt% SiO₂) are characteristic for the K-metasomatized metarhyolites, while other major element concentrations are the same as in the unaltered rocks. The quartz-albite vein fillings have high Si and Na concentrations (76.4–88.2 wt% SiO₂, 3.3–12.9 wt% Na₂O), but the K content is extremely low (0.6–0.8 wt% K₂O) (Fig. 10). The major element composition of the metasomatized SMV samples are influenced by the quartz vein penetration, causing excess SiO₂. Ti concentrations are significantly higher than in the BMR.

The K-metasomatic metarhyolite is slightly enriched in U compared to these, while Y content tends to be lower. As for vein rock samples, Sample 784 yielded relatively high Nb,

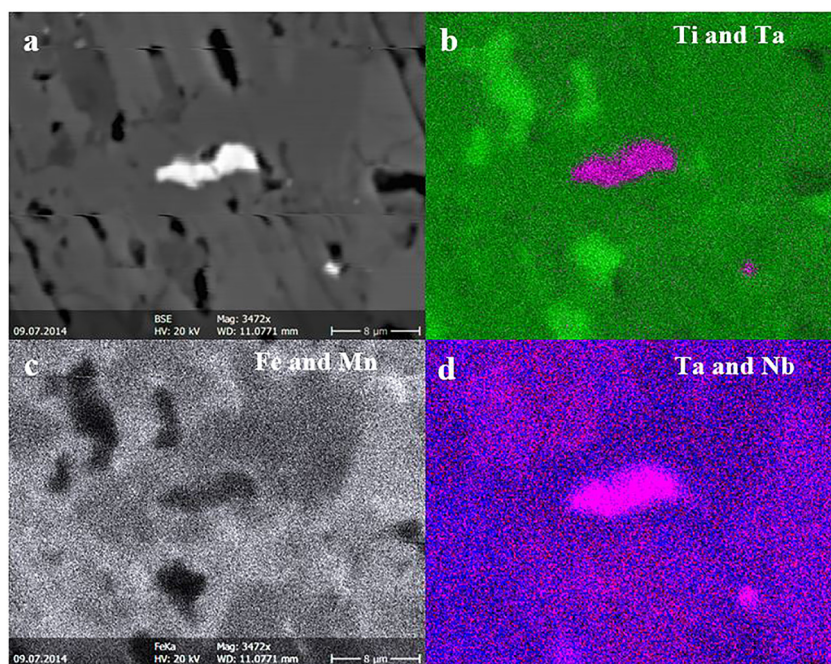


Fig. 6. BSE image and element maps of tantalite inclusions in an ilmenite-rutile association in Sample 784 (Fig. 4/e). (a) BSE image showing an 8 μm-long tantalite in the middle and a much smaller one at the bottom right. (b) Distribution of Ti (green) and Ta (pink). Ti is most abundant in the bright green spots indicating rutile, Ta is most abundant in the pink spots indicating tantalite. (c) Distribution of Fe (white): the bright areas represent ilmenite, but Mn is distributed unevenly within it; the brightest zones are the poorest in Mn. Tantalite displays weak zoning; its rim is Fe enriched. (d) Distribution of Ta (pink) and Nb (purple): Ta is most abundant in two tantalite spots; in ilmenite and rutile these elements show irregular distribution

Ta and Ce; Sample 792 relatively high REE concentrations compared to the country rocks (Fig. 10).

The Nb and Ta concentration of the BMR is very low, and lower still in the K-metasomatized metarhyolite. The quartz-albite vein fillings are significantly depleted in Ti, Nb and Ta (except for Sample 784). In most of the samples the Ti, Nb and Ta concentrations are correlated both in the metarhyolites and vein fillings. Though the SMV meta-volcanics have a significantly higher Ti content than meta-volcanics of the BMR, Nb–Ta contents are similarly low.

GEOCHRONOLOGY

Geochronological constraints on the different facies of the Bagolyhegy Metarhyolite Formation were obtained from several grains of zircon from Sample 784 representing the quartz-albite-Ti-oxide veins, and allanite-(Ce) from Sample 780 representing veins of the SMV (Table 6). In Sample 784 seven laser spots hit zircon crystals containing a $^{238}\text{U}/^{206}\text{Pb}$ ratio higher than 3, and these data indicate on the Tera-Wasserburg diagram (Ludwig, 1999) a lower intercept age of 71.5 ± 5.9 Ma (Fig. 11a). The allanite crystals detected in the quartz vein of Sample 780 contain ca. 32 ppm U and the Th/U ratio is 29. The projection points of 37 laser ablation data are arranged along a well-developed mixing line between non-radiogenic and radiogenic compositions and the matrix-corrected lower intercept is 113 ± 11 Ma (Fig. 11b). The measured data are shown in Table 5.

GENETIC RELATIONS OF THE STUDIED MINERALIZATION PHASES

HFSE mineralization is generally related to highly differentiated and alkaline magmatic rocks, which are enriched in these trace elements incorporated in primary magmatic mineral phases (Kogarko, 1990). As mobility of HFSE during rock alterations is rather restricted in most cases (Jiang et al., 2005), hydrothermally mineralized veins are also hosted by such rocks, most frequently by pegmatite, in which HFSE are concentrated by a combination of magmatic and subsequent hydrothermal processes (Salvi and Williams-Jones, 2005; Sheard et al., 2012; Williams-Jones et al., 2012).

Mineralization of magmatic or pegmatitic origin, often associated with albite-dominated dykes or veins, were described from several granite bodies of the Western Carpathians (e.g., Uher and Broska, 1995; Uher et al., 1998a, 2009; Broska et al., 2002; Chudík et al., 2011). Non-pegmatitic hydrothermal assemblages (Uher et al., 1998b) or alluvial occurrences (Uher et al., 2007) were also interpreted as secondary products of such mineralization. The Middle Triassic alkaline intrusive rocks of the Ditrău Complex in the Eastern Carpathians are also known to host niobian rutile and columbite in carbonate veins (Săbău, 2009; Honour et al., 2018). Regarding other alkaline volcanics or dykes of the Pannonian region, Nb-enriched Ti-REE-minerals were found in the Early

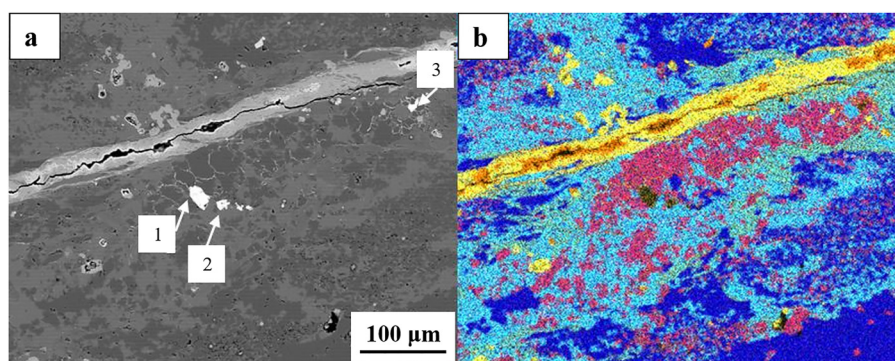


Fig. 7. BSE image (a) and the element map (b) of Sample 801. K-metasomatized, silicified metarhyolite rich in K-feldspar (light blue) and quartz (dark blue) with some albite (pink) near to a jarosite (yellow) and goethite (orange) vein. Nb-rich rutile (green) occurs associated with albite. Some grains (1–3) were analyzed by EDX

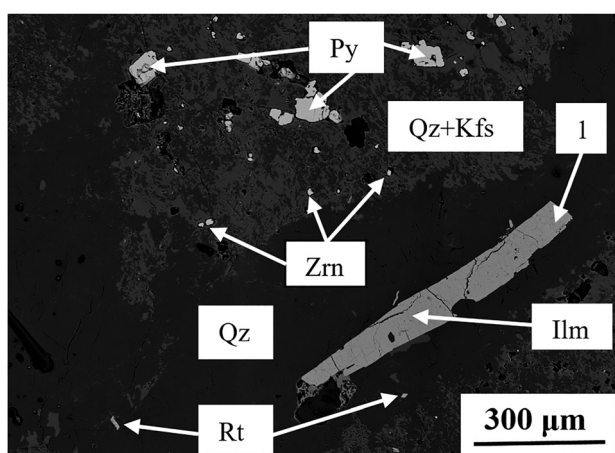


Fig. 8. BSE image of a large ilmenite crystal (1) in a quartz vein of the potassium metasomatized metaandesit-metadacite in Sample 779. The number (1) shows SEM_EDS analysis location

Cretaceous phonolite of the Mecsek Mts. (Szakáll et al., 2014a) and niobian rutile was described from the Late Cretaceous beforite dykes of the Velence Mts. (Szakáll et al., 2014b).

Rhyolite bodies may also contain postmagmatic hydrothermal HFSE mineralization, when the magma was enriched in HFSE (e.g., Jowitt et al., 2017). In the BMR, on

the other hand, the mineralized veins are hosted by a rock strongly depleted in all HFSE. The texture and mineral composition correspond to pegmatite, but as these veins crosscut the cleavage, showing brittle deformational features only; the mineralization seems to be later and independent of the magmatism, formed after the synmetamorphic ductile deformation. Nb-bearing minerals, however, are scarce and there is no enrichment in any HFSE compared to the host rock. This does not indicate HFSE input to the system, so the source of the elements may be the breakdown of some existing phases (potentially phyllosilicates).

In Sample 784 the most peculiar phases: “niobian ilmenite”, the unknown Y–Nb–Fe–Ti-oxide mineral, and Hf-rich zircon occur as crack filling or overgrown on the ilmenite aggregate, so they are late exsolution phases. The measured $Zr/Hf = 5$ ratio in zircon is characteristic for hydrothermal origin from pegmatite, in magmatic zircons this ratio is much higher (Uher and Černý, 1998). The discernible deficiency in the A cation site of the “niobian ilmenite” is caused by the significant amount of large Nb^{5+} and Ta^{5+} cations replacing Ti^{4+} (Chakhmouradian and Mitchell, 1999). However, enrichment of several of the listed elements (especially Nb and Ta) in ilmenite is very atypical. Possibly this measured phase is a mixture of ilmenite and submicroscopic-sized Nb–Ta–REE–U-oxide and REE-phosphate inclusions (Supp. Tables 1 and 2a).

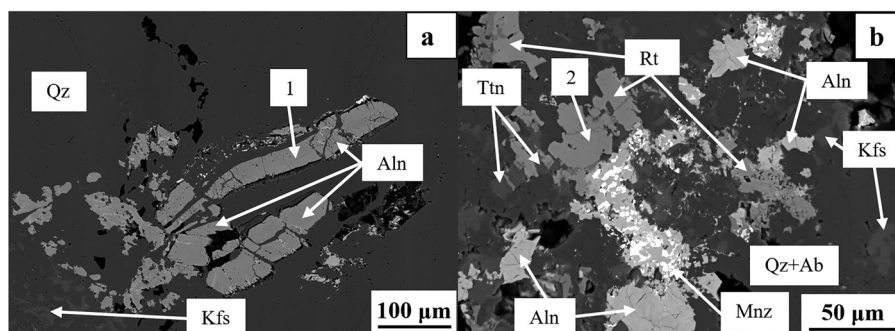


Fig. 9. BSE images of the studied minerals of Sample 780. (a) Allanite-(Ce) crystals (1) in a quartz vein. (b) Intergrowth of rutile (2) and allanite-(Ce) crystals, the allanite-(Ce) has monazite-(Ce) inclusions. The numbers (1–3) show SEM_EDS analysis locations

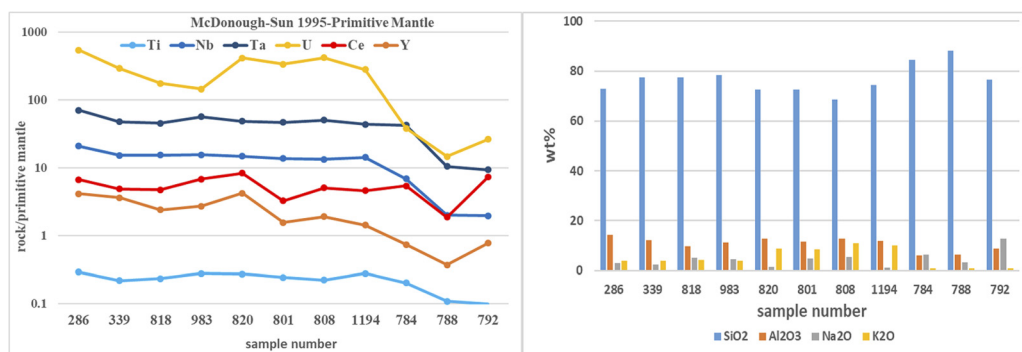


Fig. 10. Variation in some major element (right) and trace element (left) concentrations in rock types of the BMR

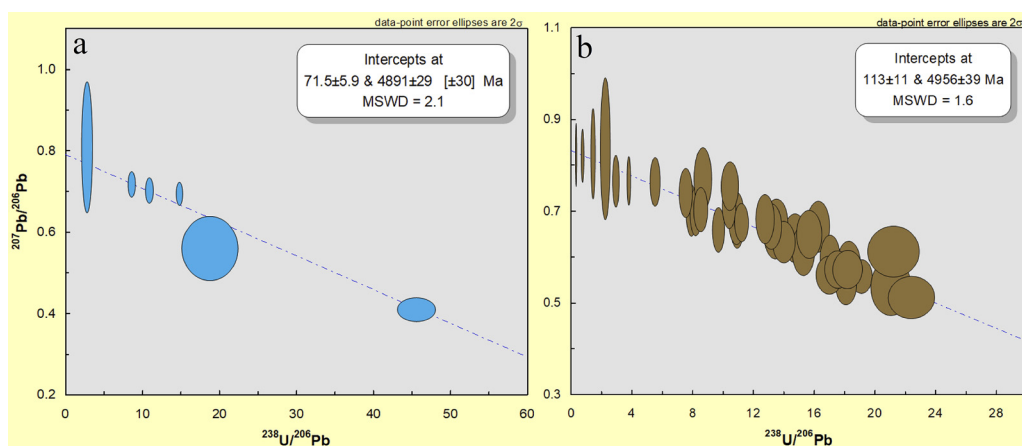


Fig. 11. (a) Tera-Wasserburg diagram of U–Pb results obtained on the zircon crystals grown on the rim of the ilmenite aggregate of Sample 784 (see Fig. 3). (b): Matrix-corrected Tera-Wasserburg plot of 37 laser ablation data of the allanite crystals in Sample 780

The Nb–Ta–Zr–REE enrichment of the peperitic metabasalts of the southeastern Bükk Mts. and the siliciclastic sediments at Lillafüred shows an obvious connection between the fault zones and the mineralization (Németh et al., 2016). The Nb and Ta are always incorporated into Ti-oxide minerals in this alteration, and the mineralization overprints the synmetamorphic ductile deformation as well as in the BMR. On the other hand, here the alteration minerals are connected to metasomatism of siliciclastic layers in limestone and are associated with K-enrichment, potassic feldspars and micas instead of Na-enrichment and albitization of Nb–Ta mineralized vein rocks of the BMR.

The Ti-oxide bearing quartz-albite veins of the SMV are not related to the same mineralization as the veins of the BMR. Lack of detectable Nb–Ta content in Ti-oxide mineral phases indicate no mobilization of these metals, but a low-grade REE enrichment in Sample 780 in connection with allanite-(Ce) mineralization shows REE mobilizing potential of the hydrothermal fluids. U–Pb age measured from this allanite shows the SMV-hosted mineralization being significantly older than the BMR-hosted one.

The two hydrothermal events indicated by U–Pb ages of the two minerals match well with the mica K–Ar ages published by Árkai et al. (1995). In metavolcanics samples

from the vicinity of our study area, 77–82 Ma was obtained, slightly older than the zircon U–Pb age (71.5 ± 5.9 Ma) of the BMR-hosted vein. This is because the sheet silicates were formed and closed for Ar during the regional metamorphism, while the U–Pb content of the zircon register the mineralization event controlled by brittle structures post-dating the peak metamorphism. The U–Pb age of the allanite of the SMV-hosted vein is close to the mica K–Ar ages of 115–119 Ma obtained from metasediments of the southwestern parts (and similarly from the northwestern parts) of the Bükk Mts., which may indicate a relationship with an earlier period of the metamorphic history.

The Nb–Ta-bearing mineralization has different characteristics in the BMR vein rocks and the southeastern Bükk peperitic metabasalts, but it cannot be ruled out that their origin was related with the same source, e.g., upwelling alkaline fluids migrating along faults. Intrusives of a Late Cretaceous alkaline magmatism are known from the Transdanubian region (Szakáll et al., 2014b), but not in the Bükk Mts. Metamorphism-related fluids could also cause short distance mobilization of HFSE elements, originated from a recently undefined late metamorphic event. Lack of any HFSE enrichment support the remobilization of HFSE from the host metavolcanics.

CONCLUSIONS

Nb–Ta-bearing minerals of the studied paragenesis are hosted mostly by the quartz–albite veins, although sporadically they were also found in other rock types of the Bagolyhegy Metarhyolite. Nb and Ta are mostly incorporated in rutile and ilmenite, with a Nb content generally greatly exceeding that of Ta. Rare Nb–Ta-oxide minerals, mostly columbite-(Fe) were also detected as small, mostly <10 µm-sized grains associated with them. The high Nb–Ta concentration is correlated with the enrichment of W, Sn, Sc, Y, U and REE, and in some cases an Y–Nb(Fe)–Ti-oxide mineral was also observed as a member of the paragenesis. We compared this mineralization with other Nb–Ta-mineralized rocks of the Bükk Mts. and many Nb–Ta-enriched rocks of the Carpathian-Pannonian region, but none of these can be accepted as analogous.

The bulk quartz–albite–rutile–ilmenite vein samples of the BMR are strongly depleted in almost all trace elements; thus, the formation fluids did not precipitate excess trace element content compared to the host rock. Despite this situation, a Ti–Nb–Ta–Zr mineralization was formed, which resembles the mineralization characteristic of pegmatite, but exotic in this environment.

In-situ U–Pb dating of vein-hosted hydrothermal allanite and zircon crystals yield 113 ± 11 Ma and 71.5 ± 5.9 Ma ages, indicating the presence of (at least) two distinct hydrothermal phases in the Early and Late Cretaceous respectively. These are related to metamorphic processes resulting in HFSE mobilization with different characteristics. Our study reveals, through complex mineralogical, petrographic, geochemical and geochronological results, that Nb–Ta-mineralization and a pegmatite-like mineral assemblage can be formed in a late metamorphic phase without the enrichment of any HFSE element.

ACKNOWLEDGEMENT

The research was carried out at the University of Miskolc both as part of the project implemented in the framework of the Thematic Excellence Program funded by the Ministry of Innovation and Technology of Hungary (Grant Contract reg. nr.: NKFIH-846-8/2019) and the project supported by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund in line with the Grant Contract issued by the National Research, Development and Innovation Office (Grant Contract reg. nr.: TKP-17-1/PALY-2020).

SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at <https://doi.org/10.1556/24.2021.00101>.

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