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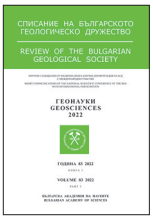

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Distribution and origin of columbite and (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals in alluvial soils and river sediments in the area of the Grantcharitsa tungsten deposit, Western Rhodopes, Bulgaria

Разпространение и произход на колумбит и (Y,REE,U,Th)-(Nb,Ta,Ti) оксидни минерали в алувиални почви и речни седименти в района на волфрамовото находище Грънчарица, Западни Родопи, България

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Abstract. Columbite-(Fe) and (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals – ishikawaite (samarskite group), euxenite-(Y) and uranopolycrase (euxenite group) and minerals of the pyrochlore group (betafite subgroup) were found in the heavy fractions of alluvial soils and river sediments in the area of the Grantcharitsa tungsten deposit. Columbite-(Fe) is the most common mineral among them and is characterized by weak compositional variations (Ta/(Ta+Nb) = 0.04–0.21, Mn/(Mn+Fe) = 0.33–0.5) and lack of fractionation trends. All (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals are metamict due to high uranium content (UO_2 17–32 wt%). Preserved relationships between minerals in some grains, some features of their chemical composition (chemical similarity: Nb >> Ta, high content of Y, Ti, U) suggest their common origin from one rock source – NYF granitic pegmatites and/or genetically associated granitoids of mantle-dominated origin. It is shown that columbite-(Fe), ishikawaite, euxenite-(Y) and uranopolycrase form zoned crystals and are of magmatic origin, while the betafite subgroup minerals are secondary phases formed under hydrothermal conditions.

Keywords: alluvial soils, NYF pegmatite, columbite, samarskite group, euxenite group, pyrochlore group.

Introduction

Columbite-tantalite and (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals are important as: (1) carriers of rare metals necessary for the modern technology, which are critical for the EU; (2) indicative minerals of the origin of granite pegmatites and parent granite magmas, geochemical fractionation and post-magmatic processes (Černý et al., 2012; Pršek et al., 2010); (3) one of the sources of geochemical anomalies of Y, REE, U, Th, Nb, Ta, Ti in soils (Vodyanskii, 2011; Fernández-Caliania et al., 2020).

Columbite-tantalite and (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals have not yet been the object of specialized mineralogical and geochemical studies at the Grantcharitsa tungsten deposit, Western Rhodopes (Bulgaria). Findings of such minerals in the granite pegmatites of Rhodopes and Rila were described in the geological literature (Ivanov, 1991, and references therein; Peytcheva et al., 2021), although they were of no economic importance. In our previous study (Tarassov et al., 2021), we reported on the distribution and modes of occurrence of W in soils in the area of the Grantcharitsa tungsten deposit. When performing this work, in some soil samples, the contents of U and Nb were found to be significantly higher than their content in the Earth’s crust. This fact encouraged us to study the reason for this enrichment. The result was establishing a large diversity of Nb-Ta-Ti-U-Th-Y-REE minerals. The purpose of this work is to elucidate their phase composition, distribution in soils and river sediments and probable origin.

Material and methods

We selected three soil sampling sites on the floodplains of the Grantcharitsa River (two sites) and its tributary Veziov Dol River (1 site). Soil samples

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were taken to a depth of 0.8–1.0 m at intervals of 0.2 m. All samples (< 0.1 mm) were quartered, and a part of them after grinding was pressed into pellets to determine chemical composition with SEM-EDS and LA-ICP-MS analysis, another part was used for extraction of a heavy fraction. In addition, 5 samples of heavy sediment fractions of the two rivers were taken. All heavy fraction samples were incorporated into epoxy resin and then polished. SEM-EDS study was carried out on a ZEISS SEM EVO 25LS with an EDAX Trident system (IMC-BAS) at acceleration voltages of 15 kV using hematite (for Fe), diopside (Ca, Mg), albite (Na, Al, Si), sanidine (K), apatite (P), anhydrite (S), calcite (C), monazite (P, LREE), metals for HREE, U, Th, Sb, Mn, Sn, Sc as standards. LA-ICP-MS analysis was performed on a PerkinElmer ELAN DRC-e ICP-MS with a New Wave UP193FX LA system (GI-BAS) under conditions described in Tarassov et al. (2021). Geochemical data of the soil samples were statistically processed, using correlation and hierarchical cluster analyses (OriginPro 2021 software).

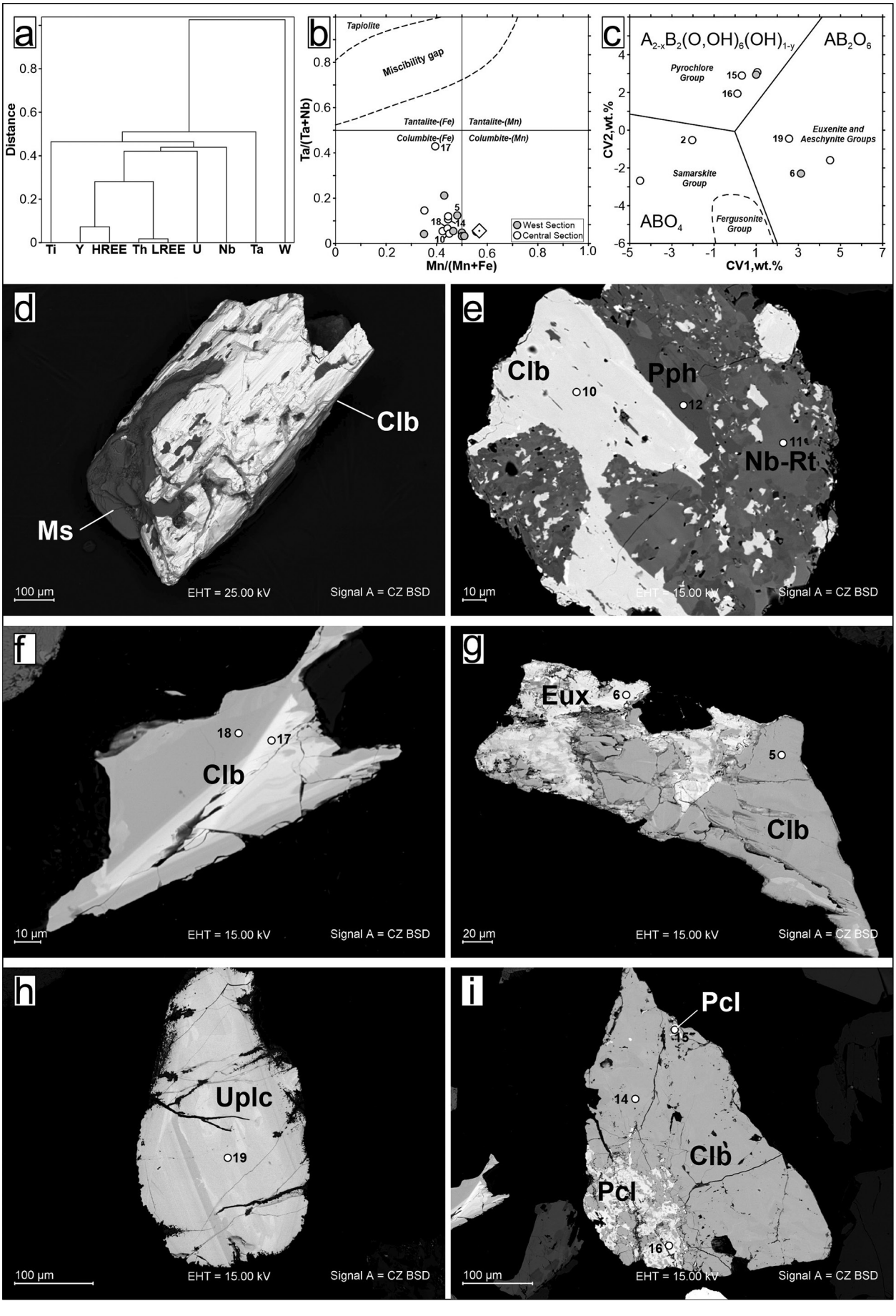
Results and discussion

Correlation and hierarchical cluster analysis of soil geochemical data. A set of 81 individual LA-ICP-MS analysis of all soil samples for Nb, Ta, Ti, U, Th, Y, LREE (La-Eu), HREE (Gd-Lu) and W was used for statistical processing. The critical value of the Pearson correlation coefficient for such a data set at a 99% confidence interval is 0.282. The obtained strong correlations were: $R_{Th\text{-}LREE}$ = 0.982, $R_{Y\text{-}HREE}$ = 0.927, $R_{U\text{-}Th}$ = 0.580, $R_{U\text{-}REE}$ = 0.570 Th, $R_{U\text{-}Nb}$ = 0.560, $R_{Nb\text{-}Ta}$ = 0.490. The results of a hierarchical cluster analysis (cluster method – nearest neighbor, distance type – Pearson correlation, clustoid – maximum distance) are shown in Fig 1a. Two clusters, Th-LREE and Y-LREE, are well distinguished, which on the next hierarchical level form a (Th-LREE)-(Y-LREE) supercluster. Superclusters of the next orders are formed with successive involvement of U, Nb, Ti and Ta. The obtained results are consistent with the mineral composition of heavy fractions of soils and sediments. Allanite-(Ce), monazite-(Ce) as carriers of LREE and Th and xenotime as a carrier of Y and HREE are the most frequently encountered accessory minerals. These minerals are the most likely explanation for the strong correlation between Th and LREE, Y and HREE, which form two clusters in Fig. 1a. All other superclusters (without W) in Fig. 1a well outline the expected Nb, Ta, Ti, U, Th, Y, REE minerals. When studying polished pellets of heavy fractions using SEM, all Nb-containing minerals were divided into 2 groups: (1) columbite, Nb-rutile (old "ilmenorutile") and ilmenite (pyrophanite), and (2) (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals.

Columbite-(Fe), niobian rutile, ilmenite. Under optical stereomicroscope these minerals are black and hardly distinguishable. They are encountered as elongated crystals (Fig. 1d) or their fragments. Sometimes they form complex intergrowths of two or three minerals (Fig. 1e). Such intergrowths of columbite and Nb-rutile are the result of subsolidus processes repeatedly described in the literature (Okrusch et al., 2003). Nb-rutile in Fig. 1e, besides Nb_2O_5 (21 wt%) contains also Ta_2O_5 (4.5 wt%), Fe_2O_3 (9.9 wt%) and SnO_2 (2 wt%). The level of incorporation of these components in the structure of pyrophanite is essentially lower (Nb_2O_5 0.6 wt%, Ta_2O_5 0.3 wt%). Besides, intergrowths with Nb-rutile, columbite is encountered in intergrowths with euxenite (Fig. 1g), or forms individual usually zoned crystals (Fig. 1f), or is replaced by pyrochlore (Fig. 1e). Chemical compositions of columbite from the Grantcharitsa deposit, plotted on the $FeTa_2O_6$-$FeNb_2O_6$-$MnNb_2O_6$-$MnTa_2O_6$ quadrilateral diagram, show a comparatively uniform scattering of points in the $FeNb_2O_6$ quartile (columbite-(Fe)) without any fractionation trends. Apart from the main components, columbite contains also TiO_2 – to 3.5 wt%, UO_2 – to 3.3 wt%, SnO_2 – 1 wt%, Sc_2O_3 – to 0.5 wt%.

(Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals. Common feature of this group of minerals is that they are metamict and significantly altered. Their UO_2 content varies between 17 and 32 wt%. Visually under a stereomicroscope, they are brownish and have an "older appearance". Their phase identification was

Fig. 1. (*a*) Hierarchical cluster analysis dendrogram for Nb, Ta, Ti, U, Th, Y, REE and W in alluvial soils of the Grantcharitsa W deposit (set of 81 analyses, cluster method – nearest neighbor, distance type – Pearson correlation, clustroid – maximum distance); (*b*) chemical composition of columbite from the Grantcharitsa deposit soils and sediments, plotted on the $FeTa_2O_6$–$FeNb_2O_6$–$MnNb_2O_6$–$MnTa_2O_6$ quadrilateral diagram; for comparison, the composition of columbite from the Vishteritsa pegmatite (Peytcheva et al., 2021) is also plotted as diamond symbol; (*c*) composition of (Y,REE,U,Th)–(Nb,Ta,Ti) oxide minerals from the Grantcharitsa deposit plotted on CV1-CV2 identification diagram (CV1 and CV2 – canonical variables of the three-group model of Ercit (2005); (*d–i*) BSE images of Nb-Ta-Ti-U-Th-Y-REE oxide minerals from the Grantcharitsa soils and river sediments: (*d*) columbite crystal with muscovite; (*e*) intergrowth of columbite-(Fe), pyrophanite and Nb-rutile; (*f*) fragment of a zoned columbite-(Fe) crystal with variable content of Ta; (*g*) columbite – euxenite intergrowth; (*h*) fragment of a zoned uranopolycrase crystal (euxenite group); (*i*) columbite partially replaced by pyrochlore. Mineral abbreviations: Clb, columbite; Eux, euxenite; Ms, muscovite; Nb-Rt, niobian rutile; Pcl, pyrochlore; Uplc, uranopolycrase (euxenite group).


a
Distance
0
0.2
0.4
0.6
0.8
Ti
Y
HREE
Th
LREE
U
Nb
Ta
W
b
Tapiolite
Miscibility gap
Tantalite-(Fe)
Tantalite-(Mn)
Columbite-(Fe)
Columbite-(Mn)
Ta/(Ta+Nb)
Mn/(Mn+Fe)
West Section
Central Section
c
A2-xB2(O,OH)6(OH)1-y
AB2O6
Pyrochlore Group
Euxenite and Aeschynite Groups
Samarskite Group
ABO4
Fergusonite Group
CV2,wt.%
CV1,wt.%
d
Clb
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EHT = 25.00 kV
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100 µm
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Signal A = CZ BSD

Table 1. Nb-Ta-Ti-U-Th-Y-REE mineral species and mineral groups found in heavy fractions of alluvial soils and river sediments in the area of the Grantcharitsa W deposit, Western Rhodopes

Mineral/Analysis in fig.1	Crystal chemical formula
	Columbite group (AB_2O_6), rutile (BO_2), ilmenite group (ABO_3)
Columbite-(Fe)/10	$(Fe_{0.490}Mn_{0.398}Sc_{0.025}Sn_{0.022}Ti_{0.053})_{0.988}(Nb_{1.773}Ta_{0.076}Ti_{0.151})_{2.000}O_6$
Columbite-(Fe)/14	$(Fe_{0.519}Mn_{0.405}Sc_{0.011}\mathbf{U_{0.008}}Ti_{0.050})_{0.993}(Nb_{1.679}Ta_{0.208}Ti_{0.113})_{2.000}O_6$
Columbite-(Fe)/17	$(Fe_{0.589}Mn_{0.380}Ti_{0.178})_{1.016}(Nb_{1.061}Ta_{0.808}Ti_{0.131})_{2.000}O_6$
Nb-rutile/11	$(Ti_{0.703}Nb_{0.142}Ta_{0.018}Sn_{0.012}Fe^{3+}_{0.092}Fe^{2+}_{0.032})_{1.000}O_2$
Pyrophanite/12	$(Mn_{0.582}Fe^{2+}_{0.384}Nb_{0.007}Ta_{0.002}Ti_{1.005})_{1.980}O_3$
	Samarskite group (ABO_4)
Ishikawaite/2	$(Y_{0.207}\mathbf{U_{0.185}}Th_{0.047}Ce_{0.003}Nd_{0.012}Mn_{0.032}Fe^{2+}_{0.285}Fe^{3+}_{0.107})_{0.878}(Nb_{0.785}Ti_{0.159}Ta_{0.178})_{1.122}O_4$
	Euxenite group (AB_2O_6)
Euxenite-(Y)/6	$(Y_{0.531}\mathbf{U_{0.219}}Ca_{0.088}Sc_{0.058}Gd_{0.033}Sm_{0.024}Fe^{3+}_{0.046})_{0.999}(Ti_{0.981}Nb_{0.758}Ta_{0.176}Fe^{3+}_{0.085})_2(O_{5.977}(OH)_{0.023})_6$
Uranopolycrase/19	$(\mathbf{U_{0.451}}Y_{0.324}Th_{0.078}Gd_{0.023}Yb_{0.020}Fe^{2+}_{0.084}Fe^{3+}_{0.021})_{1.001}(Ti_{1.252}Nb_{0.547}Ta_{0.103}\ Sb_{0.037}Fe^{3+}_{0.061})_2O_6$
	Pyrochlore group ($A_{2-x}B_2(O,OH)_6)(OH,H2O)_{1-y}$
Betafite subgroup/15	$(Ca_{1.171}\mathbf{U_{0.376}}Na_{0.157})_{1.704}(Nb_{0.768}Ti_{0.710}Ta_{0.397}Fe^{2+}_{0.073}Mn^{2+}_{0.053})_2O_6(OH)_{0.947}$ (2Ti>Ta+Nb)
Betafite subgroup/16	$(\mathbf{U_{0.313}}Ca_{0.109})_{0.422}(Ti_{1.019}Nb_{0.588}Ta_{0.371}Fe^{3+}_{0.022})_2(O_{4.407}(OH)_{1.593})_6(H_2O)_{<1}$ (2Ti>Ta+Nb)

performed on the base of their chemical composition using the CV1-CV2 identification diagram (CV1 and CV2 are canonical variables of the three-group model of Ercit, 2005) (Fig. 1c). Representative chemical compositions of these minerals recalculated in a crystal chemical formulae are shown in Table 1. Within this group, the minerals are clearly divided into two subgroups: *the first subgroup* includes minerals enriched in Y, Nb, Ti and U – ishikawaite (samarskite group) and euxenite-(Y) and uranopolycrase (euxenite group); *the second subgroup* is characterized by a high content of Ca, U, Nb, Ti and the absence of Y – betafite (pyrochlore group). Minerals of the first subgroup occur as individual usually zoned crystals (Fig. 1h) or intergrowths with columbite (Fig. 1g), while minerals of the second subgroup have a clearly secondary origin and replace columbite (Fig. 1i).

The obtained data show that columbite-(Fe), ishikawaite, euxenite-(Y) and uranopolycrase have magmatic origin, while minerals of the pyrochlore group (betafite subgroup) are formed under post-magmatic hydrothermal conditions. The preserved relationships between columbite-(Fe) and (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals, some features of their chemical composition (chemical similarity: Nb >> Ta, high content of Y, Ti, U) suggest their common origin from one rock source – NYF granitic pegmatites associated with I (or A) types granites (Černý, Ercit, 2005). It is noticeable that according to Kamenov et al. (1999) the rocks (granite-granodiorite and porphiritic granodiorite) of the Grantcharitsa body (unit I of the Rila-West Rhodopes Batholith) have a mantle dominated origin. The available geochemical data on these rocks (Kamenov et al., 1999) show Nb content up to 18 ppm.

Conclusion

The conducted studies, although based only on the heavy fractions of soils and river sediments in the area of the Grantcharitsa tungsten deposit, revealed a rich variety of minerals of Nb, Ta, Ti, U, Th, Y, REE minerals (columbite-(Fe) and (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals – ishikawaite (samarskite group), euxenite-(Y) and uranopolycrase (euxenite group) and betafite subgroup (pyrochlore group). The obtained mineralogical and geochemical data allow concluding that these minerals are derived from one and the same source – NYF type granite pegmatite. In the area of the Grantcharitsa deposit, in its northern part, several pegmatite veins are exposed, which need a subsequent detailed study.

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References

Černý, P., D. London, M. Novák. 2012. Granitic pegmatites as reflections of their sources. – *Elements*, *8*, 4, 289–294; https://doi.org/10.2113/gselements.8.4.289.

Černý, P., T. S. Ercit. 2005. The classification of granitic pegmatites revised. – *Canadian Mineral*., *43*, 2005–2026; https://doi.org/10.2113/gscanmin.43.6.2005.

Ercit, T.S. 2005. Identification and alteration trends of granitic-pegmatite-hosted (Y,REE,U,Th)-(Nb,Ta,Ti) oxide minerals: a statistical approach. – *Canadian Mineral.*, *43*, 1291–1303; https://doi.org/10.2113/gscanmin.43.4.1291.

Ivanov, I. M. 1991. *The Granite Pegmatites in Bulgaria*. Sofia, Publishing House of the Bulgarian Academy of Sciences, 206 p. (in Bulgarian with English summary).

Fernández-Caliania, J. C., A. Romero-Baenab, I. Gonzálezb, E. Galán. 2020. Geochemical anomalies of critical elements (Be, Co, Hf, Sb, Sc, Ta, V, W, Y and REE) in soils of western Andalusia (Spain). – *Applied Clay Science*, *191*, 105610; https://doi.org/10.1016/j.clay.2020.105610.

Kamenov, B., I. Peytcheva, L. Klain, K. Arsova, Y. Kostitsin, E. Salnikova. 1999. Rila-West Rhodopes Batholith: Petrological and geochemical constraints for its composite character. – *Geochem., Mineral. Petrol., 36*, 3–27.

Okrusch, M., R. Hock, U. Schüssler, A. Brummer, M. Baier, H. Theisinger. 2003. Intergrown niobian rutile phases with Sc-and W-rich ferrocolumbite: An electron-microprobe and Rietveld study. – *Am. Mineral*., *88*, 7, 986–995; https://doi.org/10.2138/am-2003-0706.

Peytcheva, I., A. von Quadt, V. Kostov-Kytin, M. Kadiyski, M. Stavrev. 2021. U–Pb dating and composition of columbite from Vishteritsa: Implication for timing of granite magmatism and rare-element granitic pegmatites in the Western Rhodopes, Bulgaria. – *Geologica Carpatica*, *72*, 3, 195–212; https://doi.org/10.31577/GeolCarp.72.3.2.

Pršek, J., J. Majka, P. Uher, P. Chudík. 2010. Niobium-tantalum minerals in the Skoddefjellet NYF granitic pegmatite, Svalbard Archipelago, Norway: Primary versus secondary assemblage. – *Neu. Jahrb. Mineral.*, *187*, 3, 235–248; https://doi.org/10.1127/0077-7757/2010/0172.

Tarassov, M., E. Tarassova, M. Stavrev, A. Benderev, E. Tacheva. 2021. Modes of occurrence of tungsten in alluvial soils and river sediments in the area of the Grantcharitsa tungsten deposit, Western Rhodopes, Bulgaria. – *Rev. Bulg. Geol. Soc.*, *82*, 3 (Geosciences 2021), 31–33; https://doi.org/10.52215/rev.bgs.2021.82.3.31.

Vodyanskii, Yu. N. 2011. Chemical aspects of uranium behavior in soils: a review. – *Eurasian Soil Sci*., *44*, 8, 862–873; https://doi.org/10.1134/S1064229311080163.