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First LA-ICP-MS U-Pb dating and trace element composition of columbite from Vishteritsa rare-metal pegmatites, Western Rhodopes, Bulgaria

Първи LA-ICP-MS U-Pb датировки и елементи-следи в колумбит от редкометални пегматити Вищерица, Западни Родопи, България

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Introduction

Pegmatites keep the interest of mineralogists, petrologists and economic geologists for hundreds of years due to the diversity of minerals and complexity of the producing processes. A variety of geological processes on the Bulgarian territory produced abundant granite pegmatites of various morphology, structure and mineralogical-geochemical features (Ivanov, 1991). They were studied intensively in the 60-ies of last century and exploited for industrial minerals, mainly feldspars and micas, rarely quartz. Here, we focus on the Vishteritsa pegmatites in the Western Rhodopes, Bulgaria and one of its strategic minerals – the columbite.

Columbite, Columbite-Tantalite (CT), and Tantalocolumbite are multiple oxides of the general formula AB_2O_6, in which two crystallographically nonequivalent positions can be occupied by the elements Nb, Ta, Fe, Mn, Mg, Ca, U, Th. Since 2007, the International Mineralogical Association (IMA) has used the name columbite as a group name and separated a Columbite series of formula from $FeNb_2O_6$ to $(Mn,Fe)(Nb,Ta)_2O_6$, from the Tantalite series with formula from $FeTa_2O_6$ to $MnTa_2O_6$. Previous studies have shown that columbite-tantalite minerals can accommodate minor to trace amounts of Ti, Sn, W, Zr, Hf, Sc, REE, and U (e.g., Melcher et al., 2015). The U concentration is sufficiently high in CT group minerals and they contain almost no common Pb, which make them suitable for dating granitic rocks and pegmatites. In this study, LA-ICP-MS U-Pb technique with a new X36 columbite standard reference material (von Quadt et al., 2019) is applied for age dating of the columbite. The LA-ICP-MS technique is also applied to study the minor and trace element composition and zonation of a fragment from the biggest columbite crystal found in Vishteritsa and preserved currently in the National Museum of Natural History of the Bulgarian Academy of Sciences, Sofia.

Geological setting and previous studies on Vishteritsa pegmatites

The Rhodopes are a main tectonic unit on the Balkan Peninsula and is referred as Rhodope Zone, Rhodope Massif or Rhodope Metamorphic Complex (RMC). Tectonic interpretations agree on its complex Alpine (Late Jurassic to late Oligocene) tectono-metamorphic history comprising earlier compressional and later extensional periods. The Alpine evolution in the western parts of this tectonic unit is related with intensive granitoid magmatism. The main pluton in the western parts of RMC is the Rila-West Rhodopes batholith (RWRB). Isotope-geochronological mineral and whole rock studies distinguished two major magmatic events: Late Cretaceous (71–68 Ma) represented by hornblende-biotite and biotite granodiorites, and Paleogene (~40 Ma) with biotite- and two-mica, leucocratic and aplitic granites. Extensive pegmatite veins and fields are related to the granitoids of RWRB. They

are hosted in the pluton or intrude the metamorphic basement. In the western and southern parts of the batholith the latter corresponds to the Middle and Upper Allochthones of RMC and include a variety of metamorphic lithotectonic units: the Sarnitsa, Mesta, Slashten, Malyovitsa (Middle Allochthon) and Obidim, Ograzhden (Upper Allochthon, Sarov et al., 2008).

Vishteritsa is a pegmatite field located ~40 km south of Velingrad town in the upper reaches of Vishteritsa River. The pegmatite veins are hosted by coarse-grained and porphyritic biotite granites of presumably Paleogene age. Close to the summit Malak Beslet they were exploited for K-feldspar and muscovite till 1961. The biggest outcropped vein of Vishteritsa deposit is a 13–15 m thick pegmatite vein, differentiated and with clear zonation (Arnaudov, Petrusenko, 1967). The main constituent minerals are K-feldspar (microcline), quartz, albite and muscovite, rarely biotite. Accessories minerals include magnetite, ilmenite, amphibole, apatite, zircon, monazite, xenotime, columbite, garnet, beryl, gahnite. A well-expressed trend of increase of the Mn, Hf, U, REE and Ta content towards the internal zones of the pegmatite is described, along with increase of the size and amount of rare-metal minerals (Arnaudov, Petrusenko, 1967). Vishteritsa pegmatites are dated by Arnaudov et al. (1969) on cyrtolite (hydrous Hf, U, Th, REE-rich zircon) using U-Pb isotope method and older techniques. The obtained $^{206}Pb/^{238}U$ age is 50±5 Ma.

Recently, Kostov-Kytin et al. (2020) provided new Scanning electron microscopy (SEM), Energy-Dispersive X-ray Spectroscopy/Analysis (EDS/EDXA), and single crystal X-ray diffraction analysis (SXDA) studies on columbite from Vishteritsa. Based on the single-crystal studies, the chemical analyses performed by previous researchers on Vishteritsa columbite samples, the mineral was defined as ferrocolumbite – Columbite-(Fe) which crystal chemical formula derived by the SXDA can be expressed as follows: $(Nb_{0.54}Mn_{0.30}Pb_{0.016})(Nb_{0.69}Fe_{0.16}Ti_{0.055}Ta_{0.035})_2O_6$. Fragments of the same columbite sample were used for the present studies.

Results

Sixteen in-situ LA-ICP-MS U-Pb analyses are performed in two different days at same analytical conditions (repetition rate 2 Hz and LA-crater 20 μm). The individual analyses are mostly concordant and the $^{206}Pb/^{238}U$ ages spread from 51.6±2.5 Ma to 45.8±1.6 Ma. Excluding those single analysis with an apparent age older than 50 Ma a Concordia age

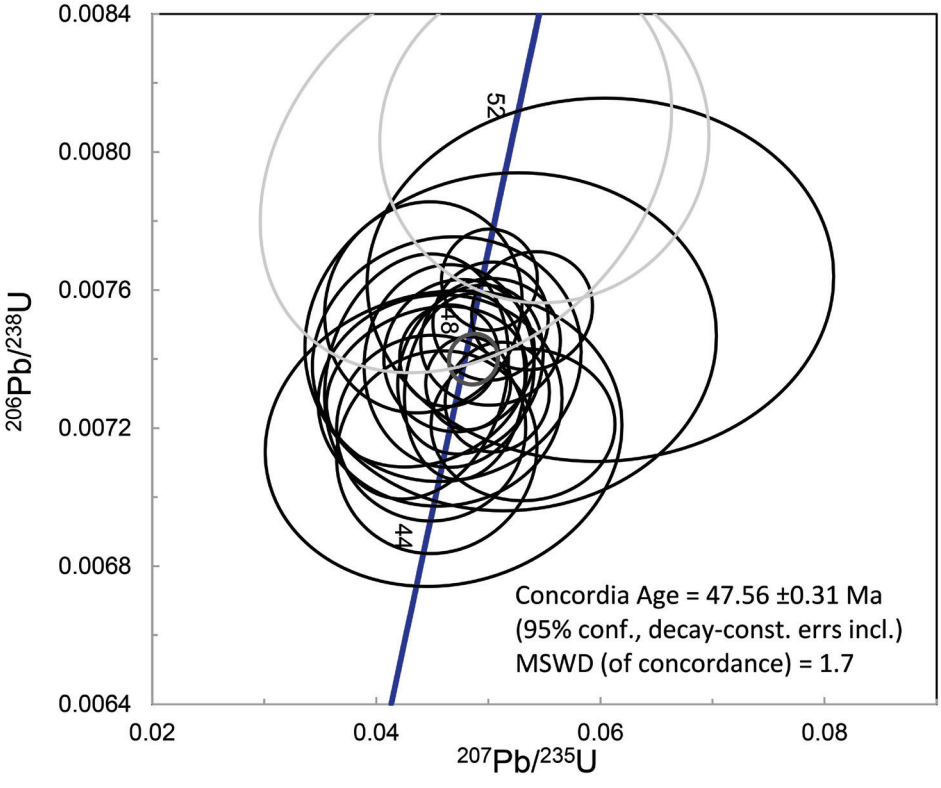

Fig. 1. Concordia diagram with LA-ICP-MS U-Pb columbite isotope data of the Vishteritsa pegmatites. The Concordia age is calculated excluding the single analyses older than 50 Ma (shown in grey).

of 47.56±0.31 Ma (95% confidence, decay-const. errs included, MSWD of concordance = 1.7) can be calculated (Fig. 1).

The in-situ LA-ICP-MS analyses performed in a general profile through the crystal fragment argue for an average formula $(Fe_{0.40}Mn_{0.71})_{1.11}(Nb_{1.73}Ta_{0.10}Ti_{0.16}U_{0.02})_{2.01}O_6$. The Nb_2O_5 content is the highest and varies between 65.14 wt% in a central zone of the crystal fragment to 68.14 wt% in an outer porous zone. The rest of major oxides vary in wider range, whereas the increase in Fe and Ti is combined with a decrease of Ta and Mn. The U (1300–15 260 ppm) behavior is not showing a clear trend but rather depends on the proximity to cracks, porous and outer zones, where it reveals the lower concentrations. Other elements in higher concentration are zirconium (Zr, 4136–6500 ppm), yttrium (Y, 441–1113 ppm), tungsten (W, 1210–2100 ppm), hafnium (Hf, 379–508 ppm) and zinc (Zn, 386–577 ppm). The sum of rare earth elements in the columbite of Vishteritsa is in the range 408–940 ppm. The mineral is enriched in heavy REE (HREE) and depleted in light REE (LREE). Deep Eu anomaly is observed in the chondrite-normalized patterns of the REE.

Discussion and concluding remarks

The new LA-ICP-MS data for the major and trace elements in the Vishteritsa Ta-Nb oxides are in agreement with former data for its general composition and affiliation to the columbite series. The refined formula $(Fe_{0.40}Mn_{0.71})_{1.11}(Nb_{1.73}Ta_{0.10}Ti_{0.16}U_{0.02})_{2.01}O_6$ defines the mineral as ferro-mangano columbite. The application of the new technique establishes a series of typical trace elements – U, Zr, Y, W, Hf and Zn, that are usually found in a content >500 ppm. The columbite is enriched in rear earth elements (REE) and especially in heavy REE (HREE sum 400–850 ppm) and depleted in light REE and europium. These geochemical characteristics are collectively interpreted as evidence for crystallization from highly fractionated fluid-rich magma. High U content reaching 2.0–2.1 wt% is characteristic for Vishteritsa columbite. The decrease of U proximal to cracks and in outer crystal zones document U-mobility during overprinting (hydrothermal?) processes.

The obtained columbite Concordia age 47.59 ±0.38 Ma (with spread of individual $^{206}Pb/^{238}U$ ages between 45.7 and 51.3 Ma) is in agreement with earlier isotope dating of Vishteritsa pegmatites although the latter was defined by using old chemical isotope separation and analytical techniques (Arnaudov et al., 1969). This age argues for possible incremental growth of the RWRB in the Late Cretaceous and Paleogene time.

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