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Th-U-Pb ELECTRON MICROPROBE AGE DATING OF MONAZITE FROM IGRALISHTE AND KLISSURA GRANITES: PRELIMINARY DATA

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The technique of monazite dating with electron microprobe developed at the beginning of the 90-s of the past century by research groups in Japan (Suzuki et al., University of Nagoya) and France (Montel et al., University of Clermont-Ferrand), marks an important advance in the geological science. At present, a great number of geologists has access to *in-situ* dating with highly local (2-3 μm), comparatively fast and inexpensive method in the numerous conventional electron microprobe laboratories of the world. The basic idea of the method is that the radioactive decay of actinide elements (Th, U) with time may produce the radiogenic lead in quantities sufficient for electron microprobe measurement, thus giving possibility to perform Th-U-(total Pb) chemical dating. The theoretical basis of the method consists in resolving the equation connecting the concentrations of radiogenic Pb with those of Th and U, the coefficients of radioactive decay of the actinide isotopes, and the time (Montel et al., 1996). A number of reasons makes monazite, $(Ce,La,Y,Th)[PO_4]$, the most appropriate object for this aim. These reasons are: (i) wide spreading of monazite as accessory mineral; (ii) increased contents in the mineral of actinide elements (especially of Th being up to 15 wt.%); (iii) negligible (or nearly zero) content of common Pb; (iv) almost complete absence of diffuse processes at $t<700^oC$); (v) relative steadiness of the mineral to postmagmatic alteration.

The present communication reports preliminary data concerning the adaptation of the electron-microscopic technique available in the Central Laboratory of Mineralogy and Crystallography, BAS, to the purpose of electron microprobe dating, as well as the first results of electron microprobe dating of monazite from the Igralishte and Klissura granites. The control and assessment of the accuracy of electron microprobe dating were performed through the comparison of the obtained data with those of isotopic study carried out in the Institute of Isotopic Geology and Mineral Resources (ETH-Zurich, Switzerland). Two isotopic methods were used: (1) Isotope Dilution – Thermal Ionisation Mass Spectrometry (ID-TIMS), and (2) in-situ Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). For LA-ICPMS and electron microprobe analysis the samples were prepared by mounting the monazite grains into epoxy resin and then polishing the obtained tablets with abrasives not containing lead. The samples for electron microprobe investigations were additionally covered by a conductive layer of carbon.

Brief data on geology and petrography of Igralishte and Klissure plutons

The *Igralishte pluton* is embedded among the high-metamorphic rocks (migmatized gneisses and amphibolites) in the vicinity of Igralishte village, Blagoevgrad region. The igneous body is built up of coarse- to medium-grained two-feldspar muscovite-biotite granite that in its periphery parts gradually turns to muscovite granite. The main rock-forming minerals in the succession of their formation are: plagioclase, biotite (muscovite), quartz, K-feldspar. The accessories are presented by titanite, apatite, zircon, ilmenite, magnetite, garnet, monazite, xenotime. Epidote, sericite, chlorite, pyrite and zeolites are encountered as postmagmatic minerals. According to the TAS classification the pluton chemical composition corresponds to those of normal to sub-alkaline granites and leucogranites, and the ASI coefficient (equal to 1.05) assigns the pluton rocks as low-peraluminous S-type granites. According to the commonly accepted geological concept based on the relationships of the igneous body with the enclosing rock, the pluton intrusion is thought to be of Paleozoic age. (unpublished data of Boyadzhiev (1956) and Zidarov (1967)). The new U-Pb isotopic dating based on the zircon ages proves Pre-Alpine age of the pluton (~240 Ma) (see Zidarov et al., this volume). For the present study we used sample A-7 of the Igralishte granite.

The Klissura leucocratic pegmatoid granite is cropped out in the core of the Berkovitza anticline near the village Barzia, Montana region. Main rock-forming minerals in the granite are plagioclase, quartz, K-feldspar, biotite, muscovite, and amphibole. Accessory minerals are magnetite, apatite, zircon, allanite, garnet, monazite (Dimitrova & Arnaudova, 1977). Until now there is no commonly accepted opinion about the genetic position of the intrusion among the plutonic rocks of Stara Planina calcium-alkaline magmatic formation (according to Str. Dimitrov, 1958). Some investigators (Haydoutov et al., 1979; Carrigan et al., 2003) regard Klissura granites as a diatectite of the Barzia migmatic complex with U-Pb zircon ages of 527±18 Ma. Other investigators (Malinov et al., this volume) consider the Klissura granites as a Variscan intrusion overprinted by a late Apline event. The material for the present investigation was kindly provided by the „Ceramics Aspida" Ltd performing at the present prospecting works in the area of Barzia village. Monazite grains studied were separated from the drill core (drilling C-1, 16 m, sample AvQ135-C1).

Results

Methodological background. The Central Laboratory of Mineralogy and Crystallography (BAS) is in possession of scanning electron microscope Philips 515 SEM, equipped with an analytical system WEDAX-3A including EDAX-9100 (energy-dispersive) and WDX-2A (wave-dispersive) spectrometers. The spectrometer WDX-2A used for the present study contains 4 diffracting crystals **LiF**, **PET**, TAP and LOD disposed in the crystal turret. The principle feature of the wave-dispersive system is that it permits the measurement of only one X-ray emission line during one and the same time. With regards to this, two analytical protocols were considered and applied in this work. The first one ("complete analysis) presents a conventional approach of electron probe analysis requiring the measurement of all elements whose content is above a definite detection limit of the method. In the studied monazites these elements were P, Si, Ca, Y, **Th**, **U**, **Pb**, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb. The second protocol ("partial analysis") involves measuring of only Th, U and Pb. The matrix corrections in the latter protocol are introduced using the data for the "average composition of monazite" (Montel et al., 1996). The following X-ray lines free of interference were chosen by us: P Kα, SiKα, CaKα, Y Lα_1, **ThMα**, **U Mβ**, **PbMα**, LaLα_1, CeLα_1, PrLβ_1, NdLβ_1, SmLβ_1, GdLβ_1, TbLα_1, DyLα_1, HoLβ_1, ErLβ_1, YbLα_1. This set of X-ray-lines is close to that recommended by Scherrer et al. (2000) differing in the following lines preferred by us: Mα for Pb, Lα_1 for Tb and Dy, and Lβ_1 for Er. According to the value of λ (Å) of the X-ray lines and the type of the diffracting crystal used, all the elements were subdivided into three groups, each one measured separately: (1) P, Si, Ca, Y; (2) Th, U, Pb; (3) REE. The most critical point of the considered methodology was the stability of the PET crystal employed for the measurement of ThMα, U Mβ, PbMα. To overcome the "crystal drift" we used the procedure including consecutive measurement of a reference sample, unknown sample and a standard, the reference sample and standard being one and the same material. As reference samples and standards were used galena, PbS, (for PbMα), metal Th (for ThMα) and metal U (for U Mβ). The increased values of the analysis parameters, namely, acceleration voltage of 25 kV and electron beam current of 150 nA, were chosen specially to improve the X-ray statistics and detection limit for Pb and U. The time duration of each measurement for the principle X-ray lines (including two background points) for the unknown and the standard, respectively, was 900 and 300 sec (for PbMα), 600 and 300 sec (U Mβ), and 450 and 300 sec (for ThMα).

Age dating of monazite from Igralishte pluton. The ID-TIMS investigation shows that the monazites under study are discordant with apparent Pb/U ages varying between 170 and 223 Ma, which is an indication that a part of the lead was lost during overprinting processes. The highest monazite age (223 Ma) is close to the zircon age ($\cong$ 240 Ma) as is presented in Zidarov et al. (this volume) and proposed to be the time of the granite intrusion. It is noteworthy that, opposite to the isotopic Pb/U ages of monazite, the electron microprobe dating performed by us (Table 1) shows smaller age variation 210-247 Ma and better correspondence to the zircon age. The reason for this can be sought in the fact that the content of Th in monazite is significantly higher than that of U (see for example Table 1), and the radiogenic Pb in monazite is mainly derived from the Th radioactive decay.

Table 1. Electron microprobe dating of monazites from Igralishte granites.

Sample/grain	Th, wt.%	U, wt.%	Pb, wt.%	Age, Ma
A7"A"Rim1	5.086	0.160	0.056	225
A7"A"C	5.668	0.166	0.059	219
A7"A"Rim2	5.607	0.149	0.057	210
A7"C"Rim1	3.383	0.128	0.037	219
A7"C"C	6.209	0.441	0.076	224
A7"C"Rim2	3.941	0.393	0.057	247
				Mean value = 224$\pm$13

Age dating of monazite from Klissura pluton. Both the ID-TIMS and LA-ICPMS methods are used for the study of monazite from Klissura pluton. The ID-TIMS data give evidence for lead loss in the monazites which together with the studied zircons define a discordia line with an upper intercept age of 329±8 Ma (assigned as the age of magmatic crystallization), while the lower intercept with the concordia marks an Alpine event (62±17 Ma). The data of electron microprobe dating (Table 2) show the two groups of ages as well, being 290-317 Ma (only two measurements) and 63-101 Ma (8 measurements), which is in a good agreement with the isotopic data. It should be noted that the increased contents of Th (up to ~14 wt.%) and U (up to ~ 1 wt.%) in the studied monazites (Table 2) allowed us to do the electron microprobe dating of the comparatively "young" monazites (bellow 100 Ma) without any particular efforts and approaches.

Table 2. Electron microprobe dating of monazite from Klissura granite.

Sample/grain	Th, wt.%	U, wt.%	Pb, wt.%	Age, Ma
A135-1"C"	8.204	0.654	0.046	101
A135-1"Rim"	10.311	0.312	0.044	87
A135-2	5.399	0.557	0.020	63
A135-3	10.046	0.510	0.040	77
A135-4	8.165	0.393	0.026	63
A135-5	13.754	0.403	0.046	69
A135-7"C"	7.077	0.867	0.042	96
A135-7"Rim"	9.839	1.011	0.040	69
135-8	3.195	0.064	0.044	290
135-9	2.344	0.719	0.066	317

The obtained two groups of monazite ages associate with the two definite types of monazite clearly discernable in the BSE images: the older mineral grains are almost entirely homogeneous, while the younger monazite crystals demonstrate a distinct zonal structure. The case of the young monazite is shown in Fig. 1 where additionally are depicted the places dated with ^{232}Th/^{208}Pb LA-ICPMS (large circles) and with electron microprobe (small circles). As seen, the LA-ICPMS ages vary in a narrow range 60-66 Ma and well correlate with the ID-TIMS data (the lower interception age). Although the electron microprobe dating shows more significant variations in the ages (Table 2), the method reveals some additional details. For example, all our measurements show that the central parts of the monazite crystals are always older (96-101 Ma) than their peripheral parts (69-87 Ma) (see Fig. 1) thus being in a good accordance with the normal growth zonality of the crystal.

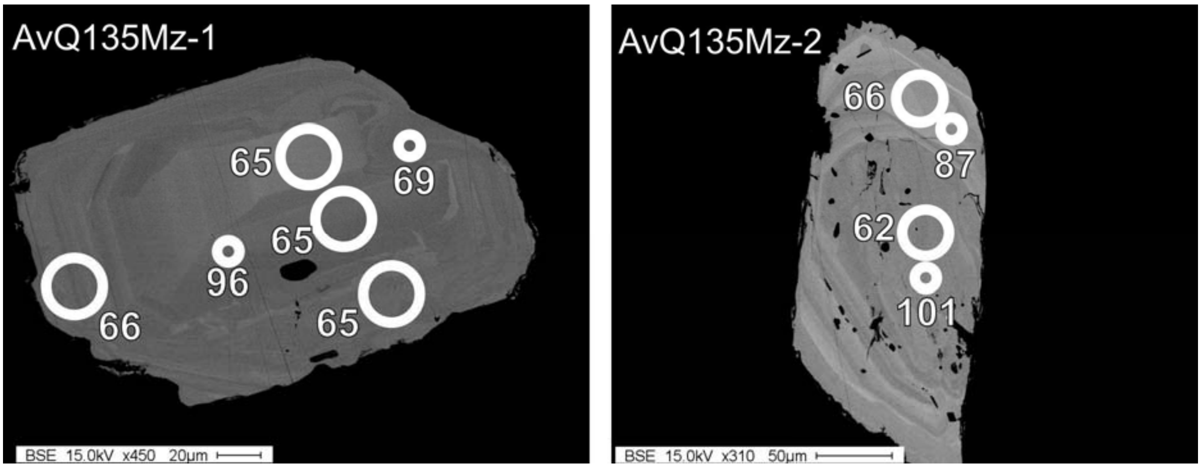

Fig. 1. Backscattered electrons images of the in-situ analyzed monazite grains from Klissura granite. The marked circles indicate the positions of electron microprobe (smaller circles) and LA-ICPMS (larger circles) spots.

Concluding remarks. The present study shows good perspectives for the employment and development of electron microprobe dating in Bulgaria. Some of the results obtained here need further detailed investigation and comparison with the conventional isotopic methods.

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