OCCURENCE, CHEMICAL COMPOSITION AND ELECTRON PROBE DATING OF ACCESSORY REE-Y-TH-U MINERALS FROM IGRALISHTE GRANITE PLUTON (OGRAZHDEN BLOCK, SERBO-MACEDONIAN MASSIF)

Mihail Tarassov, Eugenia Tarassova

Central Laboratory of Mineralogy and Crystallography, BAS, G. Bonchev Str., 107, 1113 Sofia;
e-mail: mptarassov@clmc.bas.bg, etarassova@mail.bg

Key words: accessory minerals, REE, actinide elements, electron probe dating

Introduction

Accessory REE-Y-Th-U minerals from granitoid rocks have intensively been studied in the last 10 years due to their indicative properties for the source and evolution of magmas, thermobarometric parameters, age dating, etc (Förster, 1998a, 1998b; Gratz, Heinrich, 1997; Montel et al., 1996; etc). Recently, we employed the electron-probe method for age dating of monazite from Igralishte granite pluton (Ograzhden block, Serbo-Macedonian Massif - SMM) and attained very good correspondence with the zircon isotopic ages (~240 Ma) (Tarassov et al., 2004). This result encouraged us to further apply the method for other Th-U containing accessory minerals from the pluton and to associate the ages obtained with definite geological events taken place in the Igralishte magmatic system. For this purpose, occurrence, chemical composition, relationships and secondary alterations of REE-Y-Th-U minerals from Igralishte pluton were studied and correlated with the age data.

Igralishte pluton is the largest (32 km^2) intrusive body in the Ograzhden block of SMM and is embedded among high-metamorphic rocks (gneisses, gneiss-schists and amphibolites). The pluton is mainly built-up of two-mica (muscovite-biotite) granite. Another rock variety - leucocratic muscovite granite, is encountered on the western and northern periphery of the pluton. Muscovite granite also occurs throughout the plutonic body in the form of elongated vein-like thin zones. The geochemical characteristics of the intrusive (ASI 1.04-1.31) define its rocks as peraluminous S-type granites crystallized from high-potassium calc-alkaline magma. The initial strontium ratio $^{87}Sr/^{86}Sr$ (0.70804) of the rocks indicates predominant crust source of magma (Zidarov et al., 2004).

Samples for the present report were chosen from both muscovite-biotite and muscovite granites and studied by optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis.

Results and discussion

Monazite, xenotime and their alteration products (thorite/huttonite, uraninite, allanite) are found to be typical accessory REE-Y-Th-U minerals in the Igralishte granite pluton constituting about 0.3% of its volume.

Monazite occurs as inclusions in plagioclase and biotite in the form of pale-yellow anhedral to hemihedral crystals sized up to 0.5 mm and rarely as small ($\leq$0.05 mm) euhedral crystals. The anhedral (relic) outlook of the mineral is due to its replacement by alteration products (apatite and allanite). Typical microtexture of the monazite replacement is shown in Fig. 1 and includes central relic monazite core followed by zone of pseudomorphic apatite or apatite + allanite (+thorite) and then by outer mantle of epidote. The well preserved contours of pseudomorphs (Fig. 1) indicate that the primary monazite crystals were euhedral. The epidote zone in all cases overgrows the pseudomorphs capturing (replacing) the volume of the matrix (biotite or plagioclase) minerals. Detailed inspection of granite samples shows that the degree of monazite replacement varies from almost intact monazite crystals to complete pseudo-

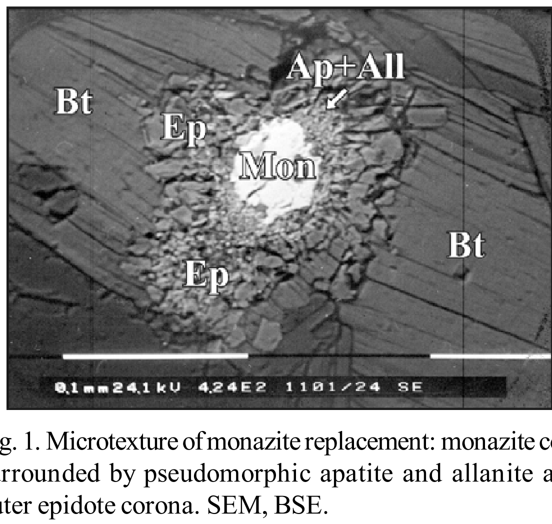

Fig. 1. Microtexture of monazite replacement: monazite core surrounded by pseudomorphic apatite and allanite and outer epidote corona. SEM, BSE.

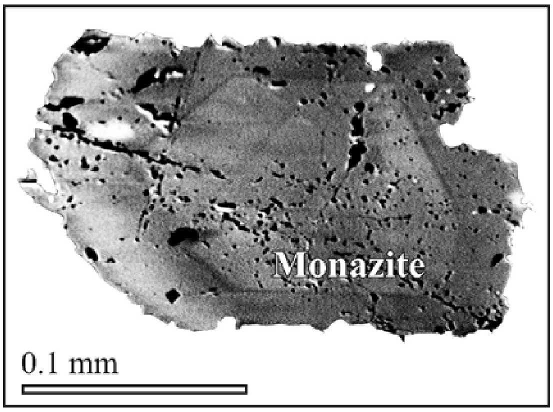

Fig. 2. Zonal microstructure of monazite. Grain from the heavy fraction. SEM, BSE image.

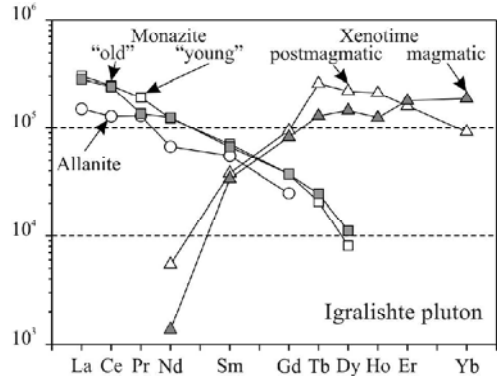

Fig. 3. Chondrite normalized REE patterns of REE-Y-Th-U minerals from Igralishte pluton. (normalizing data according to Nakamura, 1977).

morphs after monazite. As a rule, the monazite replacement in muscovite granite is less developed than that in muscovite-biotite granite. Monazite crystals are compositionally zoned (Fig. 2) or almost homogeneous. The lighter zones in back-scattered electrons (BSE) image of monazite in Fig. 2 are more enriched in Th and U (ThO_2+UO_2 is up to 10 wt.%). The mineral composition is principally the same in both varieties of granite considered here: the mineral is monazite-Ce containing up to (wt.%) 13.5 La_2O_3, 30.0 Ce_2O_3, 4.0 Pr_2O_3, 14.0 Nd_2O_3, 3.5 Sm_2O_3, 2.0 Gd_2O_3, 9.5 ThO_2. Examination of a large number of monazite crystals by electron probe dating technique reveals a very interesting fact that the monazite ages are distributed into two distinct age groups: the first one covers the range 230-250 Ma that well corresponds to the zircon isotopic age suggested to the age of crystallization of Igralishte intrusive (Zidarov et al., 2004); the second one includes a bit older ages fluctuating around 300 Ma and found in muscovite-biotite granites only. It is noticeable that both types of monazite can not be easily distinguished using just textural and compositional criteria. For example, chondrite normalized REE patterns (Fig. 3) show close similarities for both types of monazite. The secondary products as well as the replacement microtextures for the two monazites can be hardly discerned. Both monazites contain inclusions of the same minerals - apatite, zircon, quartz, allanite, thorite, and xenotime. It is noteworthy that the older monazite crystals show apparent zonal microstructure (Fig. 2) indicating their crystallization from melt. At the same time, the younger monazites are commonly more homogenous. Performing this work we have not found monazite crystals containing older cores (~300 Ma) and younger periphery (~240 Ma).

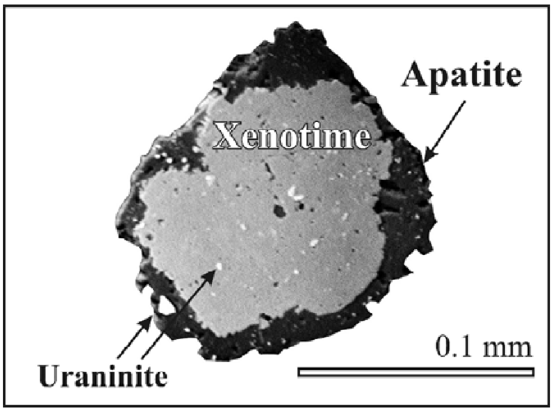

Fig. 4. Xenotime relic crystal replaced by pseudomorphic apatite + uraninite. Grain from the heavy fraction. SEM, BSE image.

Xenotime is the second after monazite widespread REE-Y-Th-U mineral in the pluton and is presented by two varieties crystallized under different conditions. The first one is found only in muscovite-biotite granite as anhedral and hemihedral crystals with saturated gray-green color in binocular microscope and size varying between 0.01 and 0.25 mm. Similarly to monazite, the xenotime considered is intensively replaced by apatite with uraninite or allanite (Fig. 4.), which form partial or complete pseudomorphs after xenotime. In optical microscope the aggregates of xenotime and its replacing minerals look like as well faced monocrystals indicating that the primary xenotime crystals were euhedral. Besides the principle components Y_2O_3 and P_2O_5, the xenotime contains up to (wt. %) 0.4 Nd_2O_3, 1.0 Sm_2O_3, 2.7 Gd_2O_3, 1.0 Tb_2O_3, 5.9 Dy_2O_3, 1.2 Ho_2O_3, 5.0 Er_2O_3, 5.0 Yb_2O_3, thus demonstrating its greater affinity to heavy REE. From the actinide elements prevails uranium giving up to 2.3 wt.% of UO_2, while the ThO_2 content rarely exceeds 1 wt.%. Chondrite normalized REE patterns of the mineral (Fig. 3) show a distribution typical for magmatic (granite) xenotime (Förster, 1998b). Electron probe dating of the mineral yields ages between 230 and 260 Ma, well corresponding to the ages of the younger monazite.

The second type of xenotime has a distinct postmagmatic origin and occurs as randomly shaped grains or veinlets inside the monazite crystals from both muscovite-biotite and muscovite granites with size not exceeding 0.01 mm. The mineral is associated with other postmagmatic phases – thorite and allanite (more rarely). The chondrite normalized REE pattern of the secondary xenotime (Fig. 3) differs significantly from the pattern of magmatic xenotime – the REE distribution curve has a maximum at Tb-Dy-Ho region.

Other (postmagmatic) REE-Y-Th-U minerals The total picture of postmagmatic alteration of the magmatic monazite and xenotime in the Igralishte pluton is rather complicated. A part of secondary phases in the apatite zones of replacement is with much smaller size (<<0.001 mm) and can be hardly identified using only SEM and electron probe microanalysis techniques. Several of the obtained point microanalyses could be related to phosphates and carbonates of REE such as britolite, bastnaesite or calcinsite. However, these data need further confirmation. More reliable data were obtained for secondary allanite, thorite and uraninite, which are encountered as comparatively large anhedral crystals (up to 0.03 mm in size). *Allanite* is a typical postmagmatic REE mineral in the Igralishte pluton formed mainly after monazite. Electron-probe analyses define the mineral as "allanite-Ce" whose chondrite normalized REE pattern follows the tendencies of the monazite pattern (Fig. 3.). As a characteristic feature of the secondary allanite can be considered the almost complete absence of Th and U in its composition (content below 0.2 wt.%). *Thorite* and *uraninite* are secondary minerals closely related to monazite and xenotime, respectively. The names "thorite" or "huttonite" (two polymorphs with ideal formulae $ThSiO_4$) are only provisionally used here because the structural investigations of these minerals were not provided for the present study. Besides the principle components ThO_2 and SiO_2, "thorite" contains also P_2O_5 (~1 wt.%), UO_2 (~8 wt%). The composition of uraninite (ideal formulae UO_2) is more variable - besides UO_2 (~85-90 wt.%) the mineral contains (wt. %) ~2.0 Y_2O_3, ~1.0 Sm_2O_3, ~1.0 Gd_2O_3. 5.0-10.0 ThO_2. The electron probe dating of both actinide minerals gave rather obscure results. For example, thorite ages obtained vary in the range 130-180 Ma thus indicating much too young ages for the postmagamtic processes in Igralishte pluton. Uraninite ages (180-220 Ma) are more acceptable, because they partially correspond to the younger monazite ages.

Concluding remarks

The technique of electron probe age dating of accessory minerals is a perspective tool for *in situ* investigation of primary and secondary processes in magmatic, metamorphic and hydrothermal systems. As is shown in the present study the primary magmatic minerals monazite ("younger monazite") and xenotime provide quite comparable ages of crystallization around 240 Ma. Almost the same textures of replacement of the two REE-Y-Th-U minerals were formed during high-temperature potassium and sodium autometasomatic processes (formation of metasomatic K-fedspar and albite) releasing Ca, Th and U from rock-forming minerals (Th and U were extracted also from monazite and xenotime). These processes lead to crystallization of postmagmatic Th, U and REE minerals. Some discrepancies in the ages obtained by us for actinide minerals may be related to further alteration of minerals or to methodological problems which require further development of the electron probe technique employed.

Monazites of the older age (~300 Ma) proved by us most probably evidence for more complicated history of the Igralishte magmatic system and the magmatic processes in the region. For example, the older monazite in the granites studied could be considered as relic form related to Paleozoic magmatic events. Its presence in well preserved zonal forms in the Igraliushte granite most likely indicates high saturation of the crust magma in REE and P and close composition of the melted substrate and the Igralishte intrusive body.

Acknowledgment: This work is supported by the Bulgarian National Science Fund, Grant ES-1304/03.

References

Gratz, R., W. Heinrich. 1997. Monazite-xenotime thermobarometry: Experimental calibration of the miscibility gap in the binary system $CePO_4$-YPO_4. – *Amer. Mineral., 82*, 772-780.

Förster, H.-J. 1998a. The chemical composition of REE-Y-Th-U-rich accessory minerals in peraluminous granites of the Erzgebirge-Fichtelgebirge region, Germany, Part I: The monazite-(Ce)-brabantite solid solution series. – *Amer. Mineral., 83*, 259-272.

Förster, H.-J. 1998b. The chemical composition of REE-Y-Th-U-rich accessory minerals in peraluminous granites of the Erzgebirge-Fichtelgebirge region, Germany, Part II: Xenotime. – *Amer. Mineral., 83*, 1302-1315.

Montel, J.-M., S. Foret, M. Veschambre, Ch. Nicollet, A. Provost. 1996. Electron probe dating of monazite. – *Chem. Geol., 131*, 37-53.

Tarassov, M., E. Tarassova, I. Peytcheva, A. von Quadt. 2004. Th-U-Pb electron microprobe age dating of monazite from Igralishte and Klissure granites: preliminary data. – *Proceedings, Annual Scientific Conference of the Bulgarian Geological Society "Geology 2004"*, 86-88.

Zidarov, N., I. Peytcheva, A. von Quadt, E. Tarassova, V. Andreichev. 2004. Timing and magma sources of the Igralishte pluton (SW Bulgaria): preliminary isotope-geochronological and geochemical data. - *Proceedings, Annual Scientific Conference of the Bulgarian Geological Society "Geology 2004"*, 116-118.

РАЗПРОСТРАНЕНИЕ, ХИМИЧЕН СЪСТАВ И ЕЛЕКТРОННОСОНДОВО ДАТИРАНЕ НА АКЦЕСОРНИ REE-Y-TH-U МИНЕРАЛИ ОТ ИГРАЛИЩЕНСКИЯ ГРАНИТЕН ПЛУТОН (ОГРАЖДЕНСКИ БЛОК, СРЪБСКО-МАКЕДОНСКИ МАСИВ)

Михаил Тарасов, Евгения Тарасова

Игралищенският плутон е най-голямото (32 km^2) интрузивно тяло в Огражденския блок на Сръбско-Македонския масив. Изграден е от двуслюден (мусковит-биотитов) гранит и от по-слабо разпространения левкократен (мусковитов) гранит. Геохимичната (ASI=1,04-1,31) и изотопната ($^{87}Sr/^{86}Sr$=0,70804) характеристики го определят като пералуминиев S-type гранит, кристализирал от висококалиево-калциевоалкална магма. Според съществуващите данни плутонът се е образувал преди около 240 Ma (Zidarov et al., 2004). От акцесорните минерали главни носители на REE, Y, Th и U в гранитите са монацитът, ксенотимът и продуктите от техните промени – аланит, торит/хътонит и уранинит, чието общо количество рядко надвишава 0,3%. Първите ни опити за прилагане на електронносондово датиране върху акцесорни монацити от Игралищенския плутон, показаха много добро съответствие с изотопната им възраст, което ни подтикна да извършим електронносондово датиране и на други Th-U-съдържащи акцесорни минерали. За тази цел бяха подбрани образци както от биотит-мусковитовите, така и от мусковитовите гранити на интрузива, в които са изследвани разпространението, химичния състав и вторичните изменения на REE-Y-Th-U акцесорни минерали. Установени са 2 типа Ce-монацит, показващи зонален строеж, близък химичен състав и асоциация от развити по тях вторични продукти, но с различна възраст – ~240 и ~300 Ma. Ксенотимът се среща като магматичен само в двуслюдения гранит, а като постмагматичен, заместващ монацита, се формира и в двата гранита. Моделите на хондрит-нормализираното разпределение на REE на двата ксенотима се различават, което е свързано с набогатяване на постмагматичния ксенотим на Tb, Dy и Ho. Електронносондовото датиране, извършено само върху магматичния ксенотим, показват вариации в границите 230-260 Ma, което добре съответства на възрастта на по-младия монацит (~240 Ma). Аланитът е представен от Ce-аланит и в асоциация с апатит замества монацита. Торитът и уранинитът са вторични минерали, развиващи се съответно по монацита и ксенотима. Получените електронносондови датирания за уранинита (180-220 Ma) могат да бъдат частично приети, но тези за торита (130-180 Ma) са твърде млади, за да бъдат свързани с хидротермално-метасоматичната дейност на Игралищенската магматична система. Получените данни за възрастовите взаимоотношения на акцесорните минерали с останалите скалообразуващи минерали, вътрешният им строеж, а също и електронносондовото им датиране позволяват да се приеме, че преди ~240 Ma в магматични условия са се формирали монацит и ксенотим. С високотемпературни алкално-автометасоматични промени е свързано образуването на вторичния Ce-аланит, ксенотим, торит/хътонит и уранинит. Възможни са две причини за по-младите електронносондови възрасти на минералите на Th-U и особено тези на торита: или тези минерали са претърпели допълнителни промени или съществуват някои методични проблеми, изискващи своето разрешаване. Установените по-стари монацити (~ 300 Ma) се схващат като реликтови, а добре запазеният им зонален строеж свидетелства, че участващият при топенето палеозойски протолит е бил с магматичен произход.