

# CHEMISTRY AND MORPHOLOGY OF ZIRCON IN METAGRANITES FROM MALESHEVSKA AND OGRAZH DEN MOUNTAINS, SMM, SW BULGARIA

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**Abstract:** External morphology, inner structure and chemical composition of zircon crystals from high-grade quartz-feldspar gneisses from the Bulgarian part of SMM are studied. These data confirm the magmatic origin of the protolithes and trace back their evolutionary trend during consecutive stages of crystallization and alteration.

**Keywords:** Back-scattered electron (BSE), Cathodoluminescence (CL), Metamorphism, Serbo-Macedonian Massif, Zircon, Zonality.

## Introduction

The stability of zircon in most geological processes, its low solubility and low elemental diffusion enables it to survive almost any crustal processes and make it a suitable mineral in studying metamorphic terrains with complex polyphase evolution. It is proposed that a complex investigations on zircon - external morphology, inner structure and chemical composition of the major and trace elements to could give valuable information on the main stages of metamorphism and deformation. In this reason we try to apply zircon peculiarities to clarify some unresolved questions, coupled with the nature of the protolithes of the metamorphic rocks from the Maleshevaska and Ograzhden Mnts., SW Bulgaria and their geological evolution.

## Geological setting

The metamorphic rocks from the most southeastern part of Serbo-Macedonian Massif (SMM), SW Bulgaria, were studied. They belong to the Maleshevaska and Belasishka groups of the Ograzhdenian complex (Zagorchev, 1988) and are present mainly by high-grade gneisses, migmatites, amphibolites and metapelites. The current field and petrological investigations of quartz-feldspatic gneisses proved the magmatic origin of the main part of these rocks, participating in different nape structures. Two types of metagranites have been distinguished: one with equigranular structure, and another

porphyritic after K- feldspar. Up to now these rocks have been considered as different morphological types of migmatites and anatectites with metasedimentary origin.

### **Analytical techniques**

Zircon concentrates were obtained from crushed rock samples (two from equigranular metagranites, two from porphyritic metagranites and two from microgranular enclaves in equigranular metagranites) using heavy liquids and electromagnetic separation technique. Randomly chosen 100 zircon crystals from each sample (fraction 103-155  $\mu$ ) were studied using a microscope and SEM. The idiomorphic and subidiomorphic populations were plotted in the typological diagram and the mean point and T.E.T. (typologic evolutionary trend) of each population were calculated according to the typology method of Pupin (1980).

The zircon inner structure was studied by back-scattered electrons (BSE) and cathodoluminescence (CL) microscopy. Various morphological types of zircon, structures of growth and alteration were established, related to different stages of formation, namely magmatic and metamorphic or such connected with the presence of fluids.

Selected zircon crystals were analysed for major (Zr, Si) and trace (Hf, Y, U, P, Fe, Yb, Dy, Er, Th, Al) elements on automated SEMQ microprobe at the University of Bristol. Operating conditions during all analyses were: 15 kV accelerating voltage, 50nA sample current and 1- $\mu$ m beam diameter. Detection limits for trace elements were in range 0.01-0.03 oxide wt%.

## **RESULTS**

### **External morphology**

The typology distributions of the studied populations (Fig.1) and their T.E.T. show that zircons from *equigranular metagranites* lie in the field of aluminous anatectic granites of crustal or mainly crustal (collisional) origin. The zircon populations include mainly S<sub>1</sub>, S<sub>6</sub> and L<sub>1</sub> subtypes with predominantly developed prism {110} and steep bipyramid {211}. The typology distribution tends to a Q -L type from the one side and from the other side to G type. Asymmetric crystals are often also present in this type of rocks.

The *K-feldspar porphyritic metagranites* are more strongly affected by processes of migmatization than the equigranular ones. The zircons are transparent, colourless, or reddish in colour. The most abundant subtypes are S<sub>1</sub>, S<sub>3</sub> and S<sub>6</sub>. In general their typology trend coincides with that of the equigranular metagranites, but curved and resorbed

surfaces and constitute aggregate forms dominate. All these features indicate that a part of these crystals could be recrystallized.

The variety of zircon crystal morphotypes is the most splendid for the *microgranular enclaves* in metagranites. The prevailing subtypes are S<sub>4</sub>, S<sub>5</sub> and S<sub>3</sub>, but the types S<sub>20-24</sub> and L<sub>4-5</sub>, G are also present. The indices I.A and I.T of the population vary from 200 to 700 and suggest that some crystals are derived from basic magma protoliths, while the low temperature zircon morphotypes indicate the action of a more acid melt. They plot in the field of Ca-alkaline rock series with hybrid origin.

### **Inner structure and chemical composition**

#### *Zircon crystals from equigranular metagranites.*

Almost all of the zircon crystals have an inherited core. Most frequently the core is small in size, rounded or irregularly shaped, resorbed. The following fine, oscillatory zonality, with generally pyramidal development, we interpret as magmatic growth in a large melt volume, during high zircon supersaturation. The core and magmatic overgrowth are different in size. Consequently, the morphological distribution of the magmatic population depends on the shape of the inherited population and on the degree of the core resorption. According Pupin (1994), large cores with (100) prism leads to new zircon growth with well developed (100) prisms, whereas small cores lead to S<sub>1-8</sub> morphotypes, which is typical for peraluminous anatectic melt.

Another zircon variety, characterized by the presence of idiomorphic or resorbed magmatic cores, quenches the CL emission and shows a thin, bright recrystallized zone rim of later metamorphic origin. Typical of this kind of zircon is a faint and irregular distributed cathodoluminescent light emission, which is due to radioactive decay damages (Fig. 3a) and structural defects.

Magmatic zircons from this rock type have high contents of Y, U, and Th and of the trace elements. The highest contents of Y<sub>2</sub>O<sub>3</sub> (up to 2 wt%), HfO<sub>2</sub> (up to 2,5-wt%) and of P<sub>2</sub>O<sub>5</sub> (up to 1,9%) and all the other analyzed trace elements, including UO<sub>2</sub> and ThO<sub>2</sub> were registered in dark CL areas. The content of trace elements typical increases in the lower temperature morphotypes - P, G and L. This is in agreement with the results of Wark & Miller (1993); Pupin (1992) and Vavra (1994), that the content of trace elements increases from early to late growth stages. The inherited cores reveals significantly low content of all analysed elements (Fig. 3b).

#### *Zircon crystals from porphyritic metagranites*

Zircon crystals from migmatized porphyritic metagranites reveal a continuous, oscillatory magmatic zonation, smoothed and partially erased, also sometimes preferably sector imposed during the migmatitic stage of metamorphism (Fig. 2d). They are formed on partially dissolved and recrystallized cores of the same morphological characteristics. In this case, it is difficult to distinguish clearly the inherited core from the magmatic overgrowth.

Asymmetric zircon crystals originating from two cores with a mutual zonal overgrowth are also present. The cores and overgrowths are of the same chemical characteristics. The content of  $P_2O_5$  is in the range from 0.1 to 0.49 wt%, that of  $Y_2O_3$  is from 0.05 to 0.6-wt%. The main difference with respect to equigranular metagranites is the distribution of  $UO_2$  (up to 0.37%) and of  $ThO_2$ , which content is below the detection limit.

#### *Zircons from microgranular enclaves in equigranular metagranites*

In most cases zircon crystals from melanocratic enclaves exhibit rounded in different degree edges. They contain roundly shaped or idiomorphic cores, which always reveal clear zonation (Fig. 2a,c). Partially homogenized, magmatic overgrowth with primary zonation is developed on the cores.

The zircons from microgranular enclaves are of nearly constant content of  $HfO_2$  (1.13-1.8 wt%). The content of  $Y_2O_3$  (0.04 and 0.2%) and that of  $P_2O_5$  (up to 0.15 wt%) is lower than in zircon from metagranites. The concentrations of Al, Fe, Yb, Er and Dy are below the detection limit, which is also sometimes the case with that of  $UO_2$  and  $ThO_2$ .

## **Conclusions**

The high frequency of the abundance of the well-preserved subtypes of a low I.T index, suggests that the evolution of the population is related to a relatively high content of water in magma. The solubility of zircon increases with increasing the water content, thus leading to crystallization of zircon at lower temperatures (Watson and Harrison, 1983). This evolutionary trend towards low T indexes is supported by the CL images and EMPA analyses.

The external morphology, the inner structure and chemical features of zircons allow us to propose the following geological evolution of the studied rocks.

- 1) The crystallization of evolved igneous protoliths gives rise to the formation of idiomorphic oscillatory zoned magmatic zircon crystals. During this stage the magmatic dissolution (when the zircon supersaturation in the melt is low) lead to a partial resorption of the magmatic crystals. The alteration processes by annealing cause reorganization of

the crystal lattice, induced by large differences in the concentration of U and Th in the adjacent growth zones. It is a solid-state reaction, caused by the radioactive decay, not affecting the external form of the crystals.

2) Prograde metamorphic stage leading to the formation of metamorphic zircon overgrowths and to smoothing of the fine oscillatory zones in the most strongly affected by migmatitic event areas. The metamorphic process causes different degrees of homogenisation and erasing of the primary grown structures, as also migration of Th, and U in the crystals, which leads to chemical homogenisation;

3) Retrograde metamorphic stage leading to partially recrystallization (surface- or cracks-controlled), related also to fluids (Fig. 2b). This process is evident in some zircons from equigranular metagranites, probably due to their higher degree of deformation. This is a heterochemical process of substitution leading to purifying and rejuvenation.

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**Fig. 1.**

**Fig. 2.**

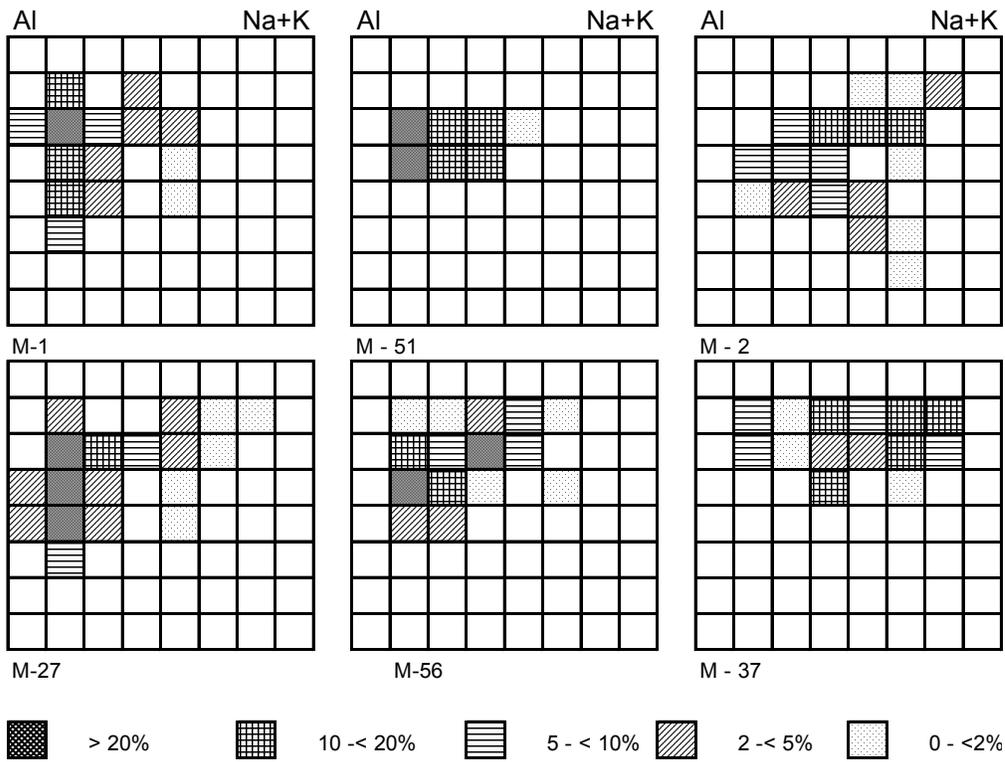


Fig. 1. Typologic distribution of the zircon populations: equigranular metagranites (M-1, M-27); porphyritic metagranites (M-51, M-56); microgranular enclaves (M-2, M-37).

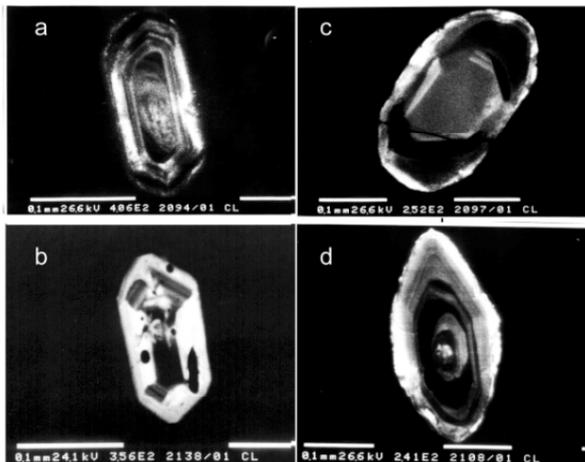


Fig. 2. CL- images of zircon from: a, c) microgranular enclaves; b) equigranular metagranites- recrystallized magmatic crystal; d) porphyritic metagranites

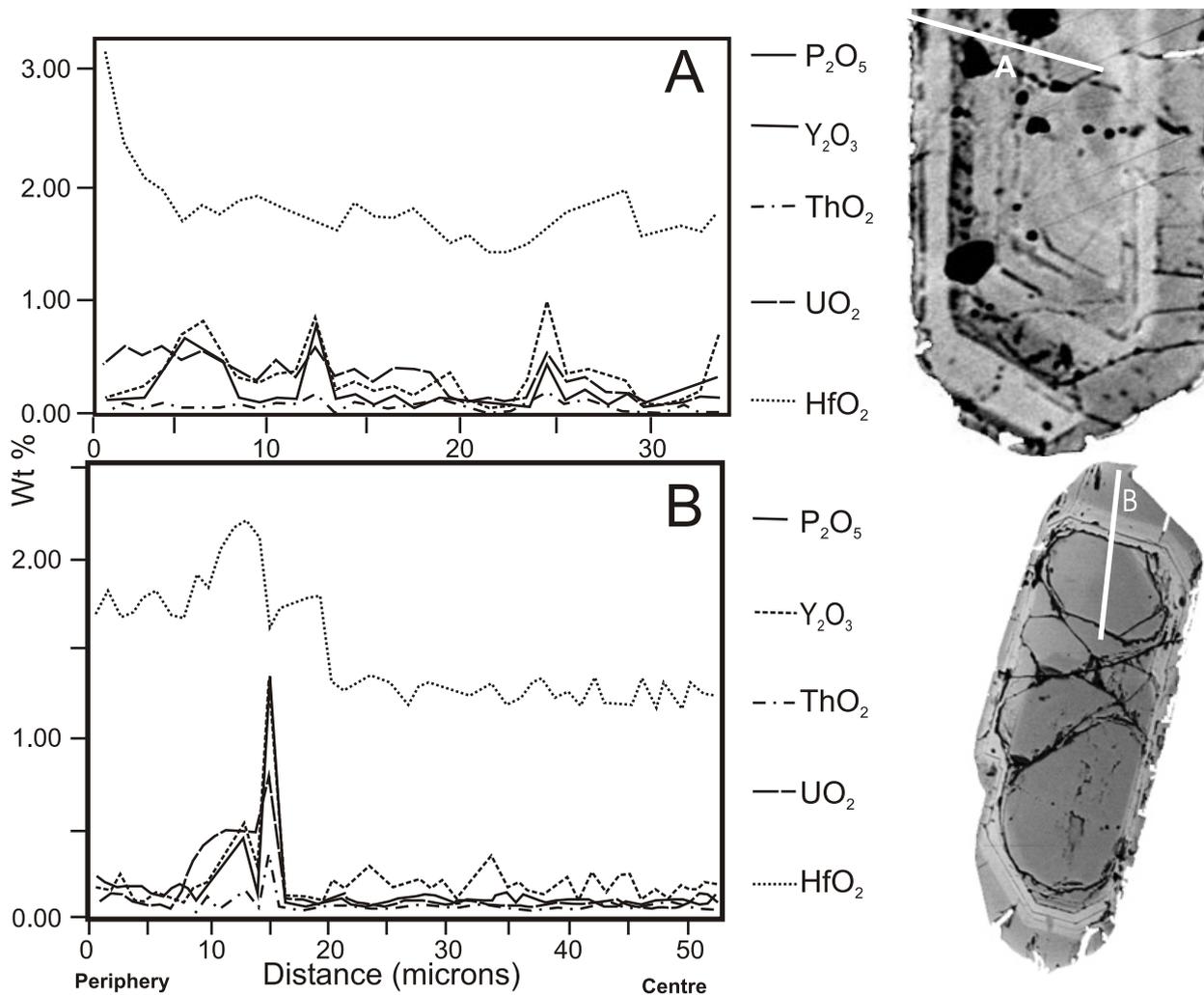


Fig.3. Electron microprobe traverses across zircons from equigranular metagranites:  
 A --zircon crystal with magmatic zonation ; B -zircon crystal with core and overgrowth zones (BS images)