

**LOCAL STRUCTURAL STATE OF ZIRCON FROM METAGRANITES –
A RAMAN SPECTROSCOPIC STUDY**

Titorenkova, R. & Mihailova, B.

Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev
Street 107, 1113 Sofia, Bulgaria
e-mail: rositorenkova@dir.bg

Zircon from amphibolite facies metagranites (Ograzhden Mountain, Serbo-Macedonian massif, Bulgaria) exhibits complex internal structures visible in cathodoluminescence (CL) and backscattered electrons (BSE) microscope images. Different processes, such as metamictization, annealing, diffusion and recrystallization, cause alteration of the protolith, magmatic zonation and form secondary internal features. The determination of the process governing the formation of a particular internal area is of a great importance for geochronological reconstructions. We have applied Raman spectroscopy, CL and electron microprobe to analyze the correlation between the local structural peculiarities and the radioactive element content of natural inhomogeneous zircon. The Raman spectroscopic data reveal different degree of structural disorder that can be estimated by the following spectral features: a) the position and the width of the peak near 1008 cm^{-1} , generated by the $\nu_3(\text{SiO}_4)$, which is sensitive to point defects and distribution in the Si-O bond lengths; b) the relative intensity of the same peak, indicating disruption of the translation symmetry in the zircon lattice; c) additional Raman signals between 150 and 650 cm^{-1} indicating a formation of ZrO_2 phases as a consequence of the zircon structure damage on nanometric scale; d) existence of a halo between 1000 - 1200 cm^{-1} , due to diffuse light scattering from dislocations and related defects resulting from the accumulations of point defects such as vacancies and broken Si-O-Zr linkages; e) additional well-pronounced peaks in the range 1100 - 1250 cm^{-1} that do not depend on the excitation light wavelength, pointing to occurrence of chain-like clusters of linked SiO_4 tetrahedra. Zircon separated from equigranular metagranites exhibits three types of spatial regions: poorly damaged zircon, for which the structural alteration consists mainly in short-range disorder of SiO_4 ; moderately damaged zircon, characterized by faults in the long range order and presence of polymerised SiO_4 tetrahedra; heavily damaged zircon, exhibiting a high degree of long- and medium-range disorder and formation of zirconia polymorphs. The studied zircon samples separated from porphyritic metagranites exhibit incipient recrystallization with presence of nuclei that enlarge upon laser-induced heating. The spectroscopic data show that the width of the peaks at 357 and 439 cm^{-1} , originating from SiO_4 rotation and bending mode, respectively, can be used for estimating the degree of metamictization of zircon.