U-Pb geochronology related to different structural states of zircon crystals

Kis, A.[1,*], Weiszburg, T.G.[1], Váczi, T.[2], Dunkl, I.[3], Buda, Gy.[1]

[1] *Department of Mineralogy, Eötvös L. University, Budapest, Hungary*
[2] *Department of Applied and Nonlinear Optics, Institute for Solid State Physics and Optics, Wigner RCP of the H.A.S.*
[3] *Department of Sedimentology and Environmental Geology, University of Göttingen, Germany*
** E-Mail: annamari.kis@gmail.com*

Based on laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) studies of 120 selected zircon crystals we refined the genetic picture of Mórágy Subunit (Hungary) and its correlation with Rastenberg Pluton (Austria) for a better paleotectonic reconstruction of the Variscan plutonic rocks across Europe. In previous geochronology-aimed publications (Klötzli and Parrish 1996; Klötzli et al. 2004; Koroknai et al. 2010), the Variscan age of the two magmatic complexes has already been proved. Nevertheless, these investigations left open basic questions with respect to the whole history (the origin of the different rock types and the age of overprinting effect(s)) of the intrusions, mainly because of the ambiguity caused by the uncontrolled textural heterogeneity of the measured zircon crystals. In order to answer the open questions, we needed to clarify and identify the different geological processes based on their preserved traces in zircons textures from two intrusions.

In the current work, we focus on the application of comparative time-resolved U-Pb dating based on zircon ($Zr[SiO_4]$, tetragonal), the most suitable mineral for U-Pb geochronology. One of the main barriers of getting properly time-resolved zircon age data is the frequent internal inhomogeneity of the zircon crystals themselves. To overcome that limitation, some textural pre-examination steps were done before the U-Pb dating.

The detailed textural patterns (primary and secondary) of zircon crystals were identified by scanning electron microscopy (SEM), based on the comparative analysis of the cathodoluminescence (CL) and back-scattered electron (BSE) contrasts. We assigned the primary texture (growth zoning (± xenocrystic core) and sector zoning) areas to the main magmatic event, while the secondary texture (convolute zoning, fluid-mediated reactions) was regarded as the imprint of any post-magmatic event in zircon crystals.

The structural state of zircon zones was determined by Raman spectroscopy. We classified three groups of structural state of the individual zircon zones based on the full width at half maximum (FWHM) of the ν_3 (SiO_4) Raman band (Nasdala et al. 1995): 1. well crystallized (< 5 cm^{-1} FWHM), 2. intermediate (5–15 cm^{-1} FWHM), 3. metamict (>15 cm^{-1} FWHM). Our samples are generally characterized by moderate radiation damage, the bulk of the FWHM values fell mainly between 5 cm^{-1} and 15 cm^{-1}.

With the help of the detailed texture-related observations (SEM-BSE, SEM-CL, Raman spectroscopy), we marked the promising spots in the zircon crystals for geologically well interpretable age data determination. Accordingly, the strongly radiation-damaged zones (> 15 cm^{-1}) could be excluded from the LA-ICP-MS dating, because these zircon zones are not too resistant toward to the fluid-driven replacement processes (Putnis 2009). In the case of the alteration of previously radiation-damaged zircon zones we have to take into account the possibility of Pb-loss during the replacement reaction, which can modify and disturb the precise U-Pb age determination (Nasdala et al. 1998).

LA-ICP-MS analysis of 313 spots was performed on fully mapped zircons from all rock types (host granitoid rock, mafic enclave, hybrid rocks) of the Mórágy intrusion and one (main) rock type of the Rastenberg complex. Out of these, 190 were concordant (< 10 %) for the determination of crystallization age of granitoids and 123 were discordant for the dating of the overprinting event. Out of 123 discordant age data 26 analyses from Mórágy and 19 analyses from Rastenberg, showing slightly discordant age data (10 – 17 %), were plotted and evaluated. The rest, due to high discordance (> 17 %), was not interpreted.

The concordant age of the main rock type (host granitoid) of both the Mórágy and Rastenberg intrusions is the same. Additionally the two other rock types (mafic enclave, hybrid rock) from Mórágy gave the same age as well, indicating in situ unmixing for genetical relationship of the three rock types.

For the further evaluation of the concordant age data, the ISOPLOT UNMIX algorithm was used to calculate statistically distinguishable age components – assuming Gaussian distribution for each – for samples having individual dates that overlap within error. We found a bimodal age distribution for both intrusions (Mórágy: 345.9 ± 0.95 Ma and 335.6 ± 0.74 Ma; Rastenberg: 345.4 ± 3.5 Ma and 333.2 ± 4.8 Ma). These ages were invariant for zircon morphology, zircon primary texture types as well as for rock types.

These age data and our zircon texture observations suggest continuous crystallization of both granitoid plutons through a long time interval (ca. 10 Ma), giving chance for the local formation of hybrid magma during the mixing of the mafic "enclave" and the host granitoid.

The slightly discordant U-Pb age (lower intercept age) of the Rastenberg zircons shows Permian age (268 ± 19 Ma, MSWD: 7.7), while zircons from Mórágy yield Cretaceous age (115 ± 48 Ma, MSWD: 2.3). These data indicate geographically different positions for the two intrusions by the time of the first (Permian) overprinting event.

Finally, we evaluated the age data in terms of different discordance values vs. structural state of zircon zones. We found that above FWHM of 12 cm^{-1} the larger part of the age data shows high discordance (useless for age interpretation), while below that value most of the areas were suitable for age determination. Based on that observation we suggest that for age determination purposes the formerly set intermediate/metamict

crystalline state border in our case should be lifted down by 3 cm^{-1} for the FWHM value of 12 cm^{-1}. These results highlight the importance of quantitative textural assessment of radiation damage in the selection of zircon crystals for high-resolution U-Pb age determination.

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