Zircon grains in A-type granite and their inclusions as recorder of upper mantle conditions in the Croatian segment of the Late Cretaceous collisional zone between Europe and Adria

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Zircon, one of the ubiquitous accessory minerals in granites is a valuable indicator of various geological processes. In addition, it includes and preserves various types of inclusions and serves as a natural preservation capsule allowing inside views into earlier stage(s) of the (geodynamic) evolution. The so-called Sava(-Vardar) Zone is one of the still geologically intriguing areas in the SE Europe with a suture zone after closing the western Neotethys branch following collision of the southern margin of the European plate with the Adria plate (Pamić 1993; Schmid et al. 2008; Ustaszewski et al. 2010). This zone shows rare outcrops of various types of granitic rocks. Among them is the peculiar red-coloured Cretaceous granite from Mt. Požeška Gora (N Croatia). This granite, associated with rhyolites, crops out as several small intrusive bodies covering a total area of approx. 6-7 km² (Pamić 1987) and caught our attention due to its geotectonic position, appearance, colour, accessory mineral content and still disputable age (Pamić et al 1988; Jamičić 2007).



Fig. 1. BSE images of a Mt. Požeška gora granite texture; Fsp=alkali feldspar, Hem=hematite, Qtz=quartz. b hematite with crystallographically oriented ilmenite exsolutions

The Mt. Požeška Gora granite is massive with a fine- to coarse-grained granitic texture. It is mainly composed of alkali feldspar and quartz (Fig. 1a), with small amounts of plagioclase, white mica and hematite with crystallographically oriented ilmenite exsolutions (Fig. 1b). Alkali feldspar is dominantly perthite whereas plagioclase is almost pure albite. Quartz-alkali feldspar intergrowths and micrographic textures are common.

Accessory minerals found by polarizing microscope include zircon, apatite and Fe-(Ti)-oxides.

The analyzed zircon population consists of 184 grains ranging from 60-75 μ m in the long and 25-35 μ m in the short axis. Aspect ratios range from 1.7:1 to 2.9:1, with the median value of 2.2:1. The external morphology is governed by predominantly developed {100} prisms and {101} >> {211} bipyramids (Fig. 2a), among them prevail D (50 % of the total population), J5 (30 %) and J4 (11 %) types after Pupin's (1980) zircon typology (Fig. 2b). Zircon crystals are colourless to slightly yellowish with high transparency and birefringence. Cathodoluminescence (CL) and back-scattered electron (BSE) images reveal clear signs of growth oscillatory zoning typical of magmatic growth conditions without any signs of dissolution of the surface, which indicates saturation of Zr in the melt. The morphology of the zircon grains separated out of the Mt. Požeška Gora granite combined with whole rock granite geochemistry points to a high-temperature, dry A-type granite (Balen et al. 2017).



Fig. 2. a Typical morphology of Mt. Požeška Gora zircon. b Modified zircon typology diagram

Zircon grains are found included in the lately crystallized minerals, alkali feldspar and quartz, and some of them comprise inclusions of hematite, apatite and early zircon. The Raman spectra of inclusions (Fig. 3) in zircon (preliminary findings) also revealed tiny (<10 μ m) minerals of kokchetavite and kumdykolite(?) (polymorphs of K-feldspar and albite, respectively) representing metastable phases in melt inclusions that require rapid cooling (Ferrero et al. 2016). The findings set magma genesis to the depth (most likely) corresponding to the upper mantle source, as predicted by zircon typology and reveal the early path of A-type granite magma evolution.



Fig. 3. Raman spectra of kokchetavite and kumdykolite(?) from inclusions in zircon

All analyzed zircons from the Mt. Požeška Gora granite have variable uranium (398-1988 ppm) and thorium (263-1371 ppm) contents, with Th/U ratios ranging from 0.61 to

0.97, consistent with a magmatic origin (Hoskin and Schaltegger 2003). According to their external typology, internal structure, and chemical composition (high U_{mean}=903 ppm and Th_{mean}=666 ppm, Th/U=0.74, Zr/Hf=54.96) it is suggested that they crystallized in deep magma chambers at relatively high and constant temperature. The calculated Zr saturation temperatures of the magma and the onset of the zircon crystallization (Watson and Harrison 1983) show values of up to 878 °C, indicating its formation in a high-temperature environment. Existence of hematite (norm 2.7 wt. %), that paints the granite reddish, indicates an oxidised magma type. The positive Ce anomaly in zircon REE patterns (Fig. 4a) also provides evidence of a positive oxidation potential of the magma. Exsolution lamellae of ilmenite in hematite with crystallographically oriented texture resulted from relatively rapid cooling and/or pressure drop.



Fig. 4. a REE patterns normalized to chondrite (Boynton 1984) for zircons and host granite. **b** P-T diagram showing the granitic solidus and isopleths for the Si content in white mica and melt volume. The intersection of the solidus and a specific Si isopleth for white mica indicates the intrusion level of the host granite

Emplacement P-T conditions were estimated with PERPLE_X calculations of the intersection of the specific Si isopleth (3.10 Si p.f.u.), according to late-crystallized white mica, with the solidus for the host granite in a P-T diagram (Fig. 4b). The obtained values are 5.2 kbar and 615°C, which correspond to a crustal intrusion level of ca. 20 km, and fit the P-T ranges resulting from the application of the Or-Ab-Qtz (300-1000 MPa) and An-Ab-Or (600-650°C) ternary systems.

The finding of red granite pebbles at the base of the Santonian-Campanian-Maastrichtian geological column (e.g. Jamičić 2007) was in contradiction with the previously reported Maastrichtian age (71.5±2.8 Ma, Rb/Sr isochron) for three granite and two cogenitic rhyolite samples (Pamić et al. 1988). Ages obtained in our study on zircon using a LA-ICP-MS are ${}^{207}Pb/{}^{235}U=85.8\pm1.1$ Ma, ${}^{206}Pb/{}^{238}U=86.1\pm1.5$ Ma and ${}^{208}Pb/{}^{232}Th=87.7\pm1.9$ Ma (RMSD), which are in agreement with stratigraphic constraints.

The Late Cretaceous subduction of the western Neotethyan branch in the study area was terminated and changed to a post-subduction rift-like tectonic process. The subsequent extension caused rhyolite volcanism along deep faults and younger extension-related basaltic volcanism (Belak et al. 1998). The A-type granite with its specific zircon typology originated at great depths and high-temperatures (upper mantle conditions) and intruded rapidly mid- to shallow-crustal levels. The presented evidence fits this scenario that invokes a geodynamic change from a compressional to an extensional regime during the Late Cretaceous.

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References:

- Balen D, Schneider P, Massonne H-J, Opitz J, Petrinec Z (2017) A Cretaceous A-type granite from the Europe-Adria collisional zone: a marker of geodynamic changes. Goldschmidt 2017 Abstract
- Belak M, Halamić J, Marchig V, Tibljaš D (1998) Upper Cretaceous-Palaeogene Tholeiitic Basalts of the Southern Margin of the Pannonian Basin: Požeška gora Mt. (Croatia). Geol Croat 51:163–174
- Boynton WV (1984) Geochemistry of the rare earth elements: meteorite studies. In: Henderson P (ed) Rare earth element geochemistry. Elsevier, Amsterdam, pp 63–114
- Ferrero S, Ziemann MA, Angel RJ, O'Brien PJ, Wunder B (2016) Kumdykolite, kokchetavite, and cristobalite crystallized in nanogranites from felsic granulites, Orlica–Snieznik Dome (Bohemian Massif): not evidence for ultrahigh–pressure conditions. Contrib Mineral Petrol 171:3 doi: 10.1007/s00410-015-1220-x
- Hoskin PWO, Schaltegger U (2003) The composition of zircon and igneous and metamorphic petrogenesis. Rev Mineral Geochem, vol 53, Mineral Soc Am, pp 27-62
- Jamičić D (2007) Upper Cretaceous deposits of the Požeška gora Mt. (Croatia). Natura Croatica 16:105–120
- Pamić J (1987) Mladoalpinski alkalijsko-feldspatski graniti (aljaskiti) Požeške gore u Slavoniji (Young-Alpine alkali feldspar granites (alaskites) from Mt. Požeška Gora in Slavonia, northern Yugoslavia). Geologija 30:183–205
- Pamić J (1993) Eoalpine to Neoalpine magmatic and metamorphic processes in the northwestern Vardar Zone, the easternmost Periadriatic Zone and the southwestern Pannonian Basin. Tectonophysics 226:503–518
- Pamić J, Lanphere M, McKee E (1988) Radiometric ages of metamorphic and associated igneous rocks of the Slavonian Mountains in the southern part of the Pannonian Basin, Yugoslavia. Acta Geol 18:13–39
- Pupin JP (1980) Zircon and granite petrology. Contrib Mineral Petrol 73:207–220
- Schmid SM, Bernoulli D, Fügenschuh B, Matenco L, Schefer S, Schuster R, Tischler M, Ustaszewski K (2008) The Alps–Carpathians–Dinarides connection: a compilation of tectonic units. Swiss J Geosci 101:139– 183
- Ustaszewski K, Kounov A, Schmid SM, Schaltegger U, Krenn E, Frank W, Fügenschuh B (2010) Evolution of the Adria-Europe plate boundary in the northern Dinarides: From continent-continent collision to backarc extension. Tectonics 29:TC6017 doi: 10.1029/2010TC002668
- Watson EB, Harrison TM (1983) Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. Earth Planet Lett 64:295–304