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The zircon proxy in tephrostratigraphy and magma evolution studies. Fingerprinting Miocene silicic pyroclastic rocks in the Pannonian Basin and its surroundings.

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We used combined trace element and U-Pb isotopic data of zircon from dacitic to rhyolitic pyroclastic rocks and Si-rich ash-bearing deposits to assess their tephrostratigraphic potential. Data were collected using LA-ICP-MS analyses, a rapid and cost-effective method, to obtain simultaneously trace element contents and U-Pb ages of a large number of zircon grains. The rationale in using zircon crystals for characterizing tephra deposits is that zircon is a resistant mineral phase and is usually a late crystallizing mineral in highly evolved magmas. Therefore, they are assumed to be in equilibrium with the erupted melt phase represented by the volcanic glass. Knowing the zircon/melt partition coefficients, equilibrium melt composition can be calculated even in cases when the volcanic glass in the pyroclastic material has undergone severe post-depositional alteration.

We studied Miocene silicic pyroclastic deposits in a broad area including the Pannonian Basin (eastern-central Europe) and its surroundings to characterize and correlate the explosive volcanic products. In regional scale, these deposits are usually assigned as important stratigraphic key horizons within sedimentary successions and thus, they help to understand better the chronostratigraphic framework and palaeoenvironmental changes having affected the highly-dynamic Mediterranean-Paratethys system.

The early to middle Miocene silicic pyroclastic deposits within the Pannonian basin are estimated to be more than 4000 km³ in volume within 4 Myr, suggesting an important ignimbrite flare-up event. At least 4 main eruption units were distinguished and characterized, each could have regional (>>100 km) effects. We demonstrate here the power of multivariate discriminant analyses as well as machine learning techniques in distinguishing the main eruptive units and their correlation with unclassified distal deposits based on zircon trace element data. The machine learning algorithms were trained using our zircon database with trace elements as input

parameters. Both the discriminant analysis and the machine learning methods gave reliable results, i.e. distinguished the main 4 pyroclastic units and found the link of the distal deposits to them. As a result, we provide a robust zircon-based fingerprint that can be used as a proxy in tephrostratigraphy.

Zircon trace element compositions indicate distinct silicic magmas resided partly coeval in the upper crust. Using trace element content of zircon and glasses from the same samples of crystal-poor ignimbrites, we determined zircon/melt partition coefficients. The obtained values of the 4 main units are very similar and comparable with published data for silicic volcanic systems. This suggests that zircon/melt partition coefficients in calc-alkaline silicic systems are not significantly influenced by melt composition at >70 wt% SiO₂. These findings let us use these zircon/melt partition coefficients to calculate the equilibrium melt compositions for the pyroclastic occurrences even in case when no glass data were available. The zircon proxy approach can be limited by the non-existence of zircon in the rocks and also by the fact that no systematic compositional difference is found between eruption products, although the latter problem similarly stands for glass chemistry-based tephrostratigraphic studies.

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