Final research report

NKFIH/OTKA PD 121048 project

Understanding the magma evolution and eruption chronology based on combined U-Pb dating, Hf isotope and trace element characteristics of zircons in silicic volcanic rocks of the Carpathian-Pannonian Region

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Introduction

In this project, we addressed a set of key-questions what are in the frontlines of volcanological researches, such as

(1) the formation and development of large volume silicic magmas and the timescale of eruptions (Early to Mid-Miocene dacite-rhyolite volcanism);

(2) eruption chronology and the nature of magma storage beneath long dormant volcanoes (the Ciomadul volcano);

(3) occurrence of the Permian volcanics in our region (Gyűrűfű Rhyolite Fm).

In the following I will present the main results of this project divided into the three sub-projects described above. Sub-projects (1) and (2) are part also the already completed NKFIH/OTKA PD 112584 research project (2014-2018; PI: Réka Lukács) and the still ongoing NKFIH/OTKA K 116528 research project (2015-2020; PI: Szabolcs Harangi), respectively. Final report of the NKFIH/OTKA PD 112584 project was already evaluated and ranked with excellent degree (10/10 points).

In the sub-projects my principal task was to conduct zircon geochronology and geochemistry studies on various silicic volcanic systems to constrain the age of the eruptions as well as the lifetime and the nature of the subvolcanic magma storage.

Results and interpretation

(1) Miocene silicic volcanic rocks of the Carpathian-Pannonian region sub-project

The main results of this sub-project, mostly overlapping with that of my NKFIH/OTKA PD 112584 research project, are summarised below.

1. We conducted the first high-precision zircon U-Pb dating on the Miocene silicic volcanic rocks of the Pannonian basin. Interpretation of the LA-ICP-MS U-Pb dates was validated by accurate CA-ID-TIMS ages. Furthermore, we performed also (U-Th)/He zircon dating, the obtained data gave the eruption ages, suggesting that no subsequent heating or significant subsidence affected the studied silicic volcanic products.
2. All the data about zircons from the Bükkalja are published in the open access journal of Data in Brief and thus, it provides a data base for further studies such as correlation with distal areas and provenance research (e.g., Kelemen et al. 2017), among others.
3. The length of the volcanism was shorter than previously thought: it was less than 4 Ma from 18.2 Ma to 14.4 Ma based on the Bükkalja and other studied samples.
4. We could distinguish 8 main eruption phases and within that, 3 eruptions could have been large enough to cover extended area by volcanic ash. These volcanic deposits have a key significance in regional stratigraphy: (1) Harsány ignimbrite at 14.358±0.015 Ma; (2) Demjén ignimbrite at 14.880±0.014 Ma; and (3) Mangó ignimbrite at 17.055±0.024 Ma. Thus, the former rigid triple division of the pyroclastic succession has to be replaced with these new results. The former Lower rhyolite tuff (Gyulakeszi Rhyolite Tuff) could correspond to the Mangó ignimbrite unit, the Middle dacite tuff (Tar Dacite Tuff) could correspond to the Demjén ignimbrite unit,

whereas the Harsány ignimbrite unit could correspond to the Upper rhyolite tuff (Galgavölgy Rhyolite Tuff). In addition, eruption resulted in the Bogács unit at 16.816±0.059 Ma was also significant forming pyroclastic flows with welded facies overlain by a subunit with strongly heterogeneous juvenile clast population, a feature what was detected also in some boreholes south of Bükkalja.

5. Our determined eruption ages shed new light on the major block rotation events defined by palaeomagnetic rotation data (Márton and Pécskay, 1998; Márton et al., 2007). Following the former interpretation of the rotations by Márton and Pécskay (1998), i.e. they occurred between large volcanic events, we refined the age of them: the first one should have occurred between 17.055 and 16.816 Ma (50 degree CCW), whereas the second one between 16.2 and 14.88 Ma (30 degree CCW).
6. One of the largest eruptions could have yielded the Demjén ignimbrite unit of the BVF: it involves the ignimbrites found at Tar (Fehérkő quarry, NW Mátra), at Sirok (NE Mátra), at Demjén and also at Tibolddaróc. In addition to the concordant eruption ages, this correlation is supported by the similar normalized trace element distribution patterns and zircon chemistry.
7. The youngest large eruption event was the Harsány ignimbrite occurring in the eastern part of Bükkalja. It has a distinctive geochemical, including zircon trace element fingerprint compared to the Demjén ignimbrite, enabling the differentiation of their volcanic products.
8. Three eruptions (Harsány ignimbrite, Demjén ignimbrite and Mangó ignimbrite) could have expelled several hundreds of km^3 volcanic material, the volcanic ash could spread more than 1000 km distance and accumulated in the sedimentary successions of Paratethys. Thus, they can be used as important marker layers in the Paratethys chronostratigraphy. Further zircon perspective correlation studies could refine this important regional chronostratigraphic framework.
9. The cumulative volume of the volcanic material formed during this 4 Myr long silicic volcanism is estimated to be>4000 km^3, consistent with a significant ignimbrite flare-up event. These eruptions are regarded one of the most volcanic events in Europe for the last 20 Myr.
10. Mafic magmas are considered to have been formed by melting of the thinned lithospheric mantle metasomatized previously by subduction-related fluids and emplaced at the crust-mantle boundary. They evolved further by assimilation and fractional crystallization (AFC) to generate silicic magmas, which ascended into the pre-warmed upper crust and formed extended magma storage regions.
11. The silicic magma systems fed the main eruption phases could have a prolonged – several 100s thousands years - existence in the crust. Magma storage with distinct magmas could have emplaced simultaneously in the upper crust. Overall, the continental crust beneath the Pannonian basin was thermally strongly affected during the Early to Mid-Miocene.
12. The silicic volcanism in the Pannonian basin was coeval with thinning of the lithosphere and the continental crust. Zircon Hf isotope and bulk rock Sr-Nd isotopic data indicate a sharp decrease of crustal contribution and/or increase of asthenospheric mantle input after 16.2 Ma, suggesting that by this time the crust, and the lithospheric mantle was considerably thinned.
13. The silicic magmatism appears to have had a structural relationship to tectonic movements characterized by strike-slip and normal faults within the Mid-Hungarian Shear Zone (Petrik et al., 2016; Lukács et al., 2018), as well as vertical axis block rotations, when the two microplates were juxtaposed. This volcanism shows many similarities with other rift-related silicic volcanic activities such as the Taupo Volcanic Zone (New Zealand) and the Basin and Range Province (USA).

14. The Early to Mid-Miocene massive silicic volcanism resulted in volcanologically well-preserved formations, which are important geoheritage of our country and thus, they could play important role in geotourism and promotes geopark initiatives as well as could be part of the proposed Pannonian Volcano Route (Szepesi et al., 2017; 2018).
15. The volcanic deposits found in Ipolytarnóc, Nemti, Mátraszele as well as in the northern Mecsek (Máza) could be correlated to the Mangó ignimbrite unit. Volcanic deposits in the Mecsek (Hetvehely, Hidas, Mecsekjános) could belong to the Demjén ignimbrite unit. We assume correlation between the Harsány ignimbrite and the silicic volcanic deposits of the Dés tuff unit based on the same eruption ages.
16. A pre-warming stage, what is necessary for the development of large silicic magma bodies in the upper crust, could be identified before the onset of the silicic volcanism: this was characterized by formation of an extended lava dome field along the Mid-Hungarian Shear Zone. We determined the ages of the volcanic rocks drilled around Paks and obtained 18-20 Ma. The andesitic-dacitic volcanic rocks of the area show strong geochemical similarities with the Early Miocene andesites found in the Mecsek Mts. This volcanism could be related to the onset of the syn-rift phase of the Pannonian basin.
17. The silicic volcanism occurred later in the Tokaj Mts. as our preliminary zircon U-Pb ages imply and further zircon perspective research could help to refine this volcanic activity what resulted in caldera-forming eruption events as well as lava dome building stages (Szepesi et al. 2019, JVGR online published).
18. Major and trace element composition of glasses as well as mineral phases appear to be diagnostic of distinct volcanic units and therefore can be used as correlation tools in proximal areas. The zircon trace element signatures are also characteristic of the eruption units and correlate with glass trace element data. Therefore, zircons could have a primary importance in correlation with distal deposits in the lack of fresh juvenile mineral and glass phases.
19. Related to this sub-project I supervise a PhD student (Péter Gál) from September 2018, who has started to work on the distal and proximal deposits of the Demjén ignimbrite unit of the BVF, that belongs to one of the largest eruptions of the Carpathian-Pannonian region. The results of the first PhD year were presented in the ILP2019 meeting and the 10th Kőzettani és Geokémiai Vándorgyűlés.

We published our results in 5 peer-reviewed journals (ESR, Geol. Carp., Földtani Közlöny, JVGR, DIB) and presented them in several conferences. Additionally, the obtained results were involved also into further publications (Geoheritage, Földtani Közlöny, Basin Research). All together the (strictly connected) published manuscripts stand for 11.217 impact factors and already got significant amount of citation since their publication. The most significant papers were published in the Earth-Science Reviews (D1 journal with IF: 7.491) as an Invited Review paper (Lukács et al., 2018a) and a review paper in Hungarian in the Földtani Közlöny (Q4; Harangi and Lukács, 2019). All geochronology data of the Bükkalja zircons were published in the Data in Brief Open Access journal (Q1, Lukács et al., 2018b).

(2) The Late Pleistocene dacitic volcanic rocks of Ciomadul sub-project

This sub-project belongs to the on-going NKFIH/OTKA K 116528 project and within this I focused primarily on how zircons can be used to characterize the magma storage system beneath a long-dormant volcano. The main results are summarized as below:

1. We finished a very detailed eruption chronology work in the Ciomadul Volcanic Dome Field (CVDF) using zircon dating (combined (U-Th)-He, U-Pb, U-Th methods). The (U-Th)-He zircon dating was conducted by Kata Molnár as a PhD research. I helped this work as a consultant scientist and produced the U-Pb and U-Th data for it that were indispensable in order to perform U-series correction on the (U-Th)-He dating results. In this work, which was mostly implemented during this project, we dated most of the domes and almost all distinguished pyroclastic units. Our methodology was new in Hungary therefore we published its background in the Földani Közlöny, in Hungarian (Molnár et al. 2017).
2. Based on this combined zircon U-Th, U-Pb and (U-Th)/He geochronology, Ciomadul volcanism is divided into two main eruptive periods: Old Ciomadul (1 Ma – 300 ka; OCEP) and Young Ciomadul Eruptive Period (160–30 ka; YCEP). OCEP activity comprises Eruptive Epochs 1–3, whereas new ages for eight lava domes and four pyroclastic units belonging to the YCEP lead to its further subdivision into two eruptive epochs: Eruptive Epochs 4 and 5. The extrusion of most of the lava domes occurred between 160 and 90 ka (Eruptive Epoch 4) during three eruptive episodes at ca. 155 ka, 135 ka and 95 ka (Eruptive Episodes 4/1, 4/2 and 4/3, respectively) along a NE-SW lineament, which is perpendicular to the regional NW-SE trend of the Călimani-Gurghiu-Harghita volcanic chain. Eruptive Epoch 5 occurred at ca. 57–30 ka, after a ca. 40 kyr of quiescence. It is mainly characterized by explosive eruptions with minor lava dome building activities. During this eruption stage another long, i.e. several thousand of years quiescence period occurred dividing this eruptive epoch into two eruptive episodes. The age of the latest eruptions (around 30 ka) was constrained also by U-Th spot analysis on the outer 4 micron surface of zircon grains.
3. We have published the in-situ zircon U-Pb dates performed by LA-ICP-MS and SIMS in the Data in Brief journal (2018), which among others gives basis for detrital zircon geochronology studies in the area.
4. The zircon in-situ U-Th and U-Pb dates and zircon geochemistry are used to infer the nature and evolution of the magma reservoir beneath the CLDF. Our results suggest that there was nearly continuous zircon crystallization from 1.5 Ma and peak zircon crystallization always predated the eruptions by up to 100's of kys.
5. Zircons do not show significant compositional variation and crystallized mainly at 720-670°C based on Zr saturation and Ti-in-zircon thermometry. This is consistent with amphibole-plagioclase thermometry used for low-Al hornblendes and plagioclase with 30-40 mol% An content as well as Zr-in titanite thermometry results. The small systematic chemical change between the zircon crystals of the Old and Young Ciomadul Eruptive Periods refer to decreasing temperature by 50 C degree along with enhanced titanite crystallization. This trend is in accordance with a growing and therefore cooling magma reservoir which has not enough magma input to maintain the initial reservoir temperature as a result of the growing cooling surface.
6. In-situ Hf-isotope measurements in zircon crystals suggest no variation between the CVDF rocks (shoshonites were not involved in this study) and resulted in epsilon Hf values between -3.12 +/-1.24 and 1.22 +/-1.70. These results exclude the purely asthenospheric melt origin for

the petrogenesis of the Ciomadul rocks and suggest either lithospheric mantle and/or crustal melt components for the upper crustal magma that crystallized zircon.

7. We used the zircon U-Th model ages of the Young Ciomadul Eruptive Period to model the maintenance and evolution of the reservoir in a thermal field suitable for zircon crystallization from the magma of the CLDF. We modelled zircon crystallization in the crust with different magma fluxes and created synthetic zircon distributions that are compared with the Epoch 5 dates. These suggest a model with $1.5 * 10^{-4}$ km^3/y magma flux and 1.5 Ma accumulation time is appropriate to the continuous 400 ky long zircon crystallization at 7-15 km depth. In this case the total injected volume in the crust is estimated as 230 km^3 from which ~30% could be eruptible. This result is consistent with other independent model results and also with the magnetotelluric anomaly beneath the CLDF (Harangi et al. 2015; Laumonier et al., 2019).
8. In the study of Laumonier et al. (2019), we integrated petrology, thermobarometry, zircon geochronology, thermomechanical models, geophysics and in situ electrical conductivity measurements to show that the magma storage beneath Ciomadul may still hold 20 to 58 km^3 of water-rich silicic melt, constituting up to 20-58% in parts of the upper crustal crystal mush body.
9. Related to this sub-project I am co-supervising (with Szabolcs Harangi) Katalin Mészáros' MSc diploma work at the Eötvös University finishing at the end of 2019. She studies the petrographic and petrogenetic features of the Bálványos and Nagy-Hegyes dacitic lava domes. She has presented the plagioclase and amphibole crystal-chemical evolution trends of these lava dome rocks in the 9th Kőzettani és Geokémiai Vándorgyűlés as a poster presentation in 2018. She uses the zircon and titanite crystallization dates and zircon geochemistry to infer crystallization temperature, oxygen fugacity and other petrogenetic aspects of the studied two lava domes.

We published our results in 5 peer-reviewed journals (2 JVGR, Data in Brief, Földtani Közlöny, EPSL) and presented them in several conferences. Additionally, the obtained results are involved into further manuscripts from which one is submitted after revision to JQR (Harangi et al.) and one is just before submission (Lukács et al.). All together the published manuscripts stand for 9.373 impact factors and already got significant amount of citation since their publication. Most of our publications are open access.

(3) Permian volcanic rocks of Hungary (Gyűrűfű Rhyolite Formation) sub-project

Working with scientists of the Szeged University, we published new results on the Permian volcanic rocks found in Hungary, although some of them reported below are part of manuscripts under review. In addition to the zircon perspective study, I participated in the interpretation of the petrological and geochemical data.

1. We studied the petrography and stratigraphic relationships of the Permian volcanic rocks from three areas: Western Mecsek (outcrops), Villány Foreland (boreholes) and Battonya Ridge (boreholes) using all available rock samples. This work is led by Máté Szemerédi, PhD student at Szeged University, whom I co-supervise with Andrea Raucsikné Varga. Our descriptions and interpretations in these areas gave the basis for the geochemistry and

geochronology study in accordance with the research plan of this PD project. We published these results in Földtani Közlöny in Hungarian in 2016 and 2017 and we have a submitted manuscript to Central European Geology (at the moment it is under work after major revision state).

2. Two distinct Permian volcanic epochs were revealed in the Pannonian Basin (eastern Central Europe) by U-Pb zircon geochronology: an older one (~281 Ma, Cisuralian) in the ALCAPA Mega-unit (Central Transdanubia, Hungary) and a younger volcanic episode (~267–260 Ma, Guadalupian) in the Tisza Mega-unit (Southern Transdanubia and the eastern Pannonian Basin, Hungary). The former is represented by dacitic subvolcanic rocks (dykes) and lavas, while the latter is dominantly crystal-rich rhyolitic–rhyodacitic/dacitic ignimbrites and subordinate rhyodacitic/dacitic lavas. Whole-rock (major and trace element) geochemical data and zircon U-Pb ages suggest close relationship between the samples of Central Transdanubia and volcanic rocks of the Northern Veporic Unit (Western Carpathians, Slovakia), both being part of the ALCAPA Mega-unit. Such correlation was also revealed between the Permian felsic volcanic rocks of the Apuseni Mts (Romania) and the observed samples of Southern Transdanubia and the eastern Pannonian Basin that are parts of the Tisza Mega-unit. The older volcanic rocks (~281–265 Ma) could be linked to post-orogenic tectonic processes, whereas the youngest samples (~260 Ma, eastern Pannonian Basin, Tisza Mega-unit) could be formed in an extensional setting.
3. Permian rocks are well exposed in the central-western part of the Apuseni Mountains (Romania). We studied these felsic volcanic rocks using the same methodology and compared with those found in the Hungarian part of the Tisza Mega-unit for regional correlation. Petrographically, the ignimbrites are similar in both areas. All samples are enriched in Rb, Th and U and depleted in Ba, Nb, Sr and Ti and show similar REE patterns. Most of the rocks, however, are affected by post-magmatic alterations. Zircon U-Pb ages of the volcanic rocks range between 270.8 +/-2.2 Ma and 259.5 +/-2.8 Ma.
4. Apart from the Permian felsic ignimbrites and lavas in the Apuseni Mts (Romania), Permian plutonic rocks also occur in the Highis–Drocea Unit, as part of the Biharia Nappe System. We studied their relationships using petrographic, whole-rock geochemical and geochronological (zircon U-Pb dating) data. The obtained ages suggest a maximum ~ 10 Myr long lasting magmatic system in the Guadalupian with rhyolitic–dacitic composition that might have been rejuvenated several times causing dominantly explosive eruptions as well as lava flows/domes. Rejuvenation could be associated with recharge of mantle-derived mafic magmas providing heat for partial melting in the crust. Similar U-Pb ID-TIMS zircon ages (266.7 +/- 3.8 Ma and 264.2 +/- 2.3 Ma) were published by Pana et al. (2002) from the Permian anorogenic granites and diorites of the Highis massif. Their similar immobile trace element geochemistry indicates relationship between them, thus, it is possible to interpret the Highis granite as the ’frozen’ (non-rejuvenated) part of the same crystal mush system, that might produced the silicic volcanic rocks.

We published our results in two peer-reviewed papers of Földtani Közlöny (2016, 2017) in Hungarian, and have two English manuscripts under the reviewing process. One of them is after our revision and already accepted for publication in the International Journal of Earth Sciences, while the other is still under the major revision process (Central European Geology). We presented the results in several conferences and will be the major part of Máté Szemerédi’s PhD thesis (expected defence date in 2020). All the geochronological work was my duty and data were interpreted by me.

Summary

Using state-of-art methodology and high-quality geochronological and geochemical data on zircons as well as working in close collaboration with top-scientists (e.g., Prof. Bachmann, Prof Schmitt and Dr. Dunkl) we managed to have great progress in all the 3 topics of the NKFIH project within the 3 years research. We got a better knowledge on the Miocene silicic volcanism of the CPR, involving the origin of the magmas, about its role in the Miocene stratigraphy and its geodynamic relationship with the formation of an extensional basin as well as transtensional tectonics. The new geochronological data help to constrain better the major tectonic events in this period. As far as the research on the Ciomadul volcano is concerned, using zircon geochronology we provided the most complete eruption chronology of the area and improved our knowledge on the nature, longevity and evolution of the crustal magmatic system beneath it. Presently, there are a number of similar PAMS volcanos (volcanoes with Potentially Active Magma Storage) in the Earth, what poses a potential threat to society, therefore, our new results provide important aspects that have already got wide interest. Finally, we could provide new data on the ages and geodynamic relationships of the so far controversial Permian volcanic rocks of our area and proposed new constraints on their stratigraphic relationships.

We published 12 journal papers during the 3 working years, that are strictly connected to this project, among these 7 are in Q1, 1 is in Q2 and 4 are in Q4 journals. Apart from these we involved our results into 3 additional publications (in Q1, Q2 and Q4 journals), and there are 3 manuscripts strongly connected to this project under the reviewing process (two of them are already accepted for journal publication) that are the following:

Szemerédi M. and Lukács R. and Varga A., Dunkl I., Józsa S., Tatu M., Pál-Molnár E., Szepesi J., Guillong M., Szakmány Gy., Harangi Sz.: Permian felsic volcanic rocks in the Pannonian Basin (Hungary): new petrographic, geochemical and geochronological results - accepted for publishing in International Journal of Earth Sciences (revised manuscript has already been sent to editor). First three authors of the manuscript contributed equally.

Harangi, Sz., Molnár, K., Schmitt, A.K., Dunkl, I., Seghedi, I., Novothny, Á., Molnár, M., Kiss, B., Ntaflos, T., Mason, P.R.D., Lukács, R.: Fingerprinting the Late Pleistocene tephras of Ciomadul volcano, eastern-central Europe. – accepted for publishing in Journal of Quaternary Science (revised manuscript has already been sent to editor).

Szemerédi, M., Varga, A., Szepesi, J., Pál-Molnár, E., Lukács, R.: Lavas or ignimbrites? Altered and overprinted textures from Permian felsic volcanic rocks, SE Hungary (Tisza Mega-unit). – under major revision, Central European Geology.