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RESEARCH ARTICLE

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Key Points:

- A geochemical/petrographic database was assembled for the main Mesozoic and younger magmatic arcs of the Carpathian-Pannonian region
- Database is freely available and up to date as of summer of 2021
- Paleocrustal thickness estimates are calculated for the three of the better studied segments of these arcs as an example of the utility of the database

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

M. Vlasceanu,
mihaivlasceanu10@gmail.com

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Carpathian-Pannonian Magmatism Database

Mihai Vlasceanu[1], Mihai N. Ducea[1,2], Peter Luffi[3,4], Anca Barla[2], and Ioan Seghedi[3]

[1]Faculty of Geology and Geophysics, University of Bucharest, Bucharest, Romania, [2]University of Arizona, Tucson, AZ, USA, [3]Sabba Stefanescu Institute of Geodynamics, Bucharest, Romania, [4]Geological Institute of Romania, Bucharest, Romania

Abstract A database containing previously published geochronologic, geochemical, and isotopic data on Mesozoic to Quaternary igneous rocks from the Carpathian-Pannonian region is presented. Georeferenced data making up this database belong mostly to rocks sampled from five magmatic arcs: (a) the South Apuseni Jurassic island arc/backarc province, (b) a small volume mid-Cretaceous arc of the northernmost South Carpathians, (c) a late Cretaceous arc, locally known as "banatitic," marking the closure of the Neotethys, (d) a regionally extensive Miocene ignimbrite flare-up, and (e) the Miocene-Quaternary collisional arc and associated extension-related basalts of the Pannonian and Transylvanian basins. The database is anchored by location and ages of various igneous rocks, as well as geochemical and isotopic data, where available. The database is publicly available online (https://osf.io/23kdg/), as well as a Supporting Information S1 attached to this manuscript. We exemplify the utility of the database by calculating paleo crustal thicknesses in the Carpathians as a function of time using well-calibrated geochemical paleo-mohometers.

1. Introduction

Magmatic arcs and intracontinental extensional domains active in the geological past of the Carpathian-Pannonian region host a wealth of plutonic and volcanic suites, which have been studied in various details over the past decades. Today, the primary geochemical information delivered by different studies—a valuable resource for new regional petrogenetic and tectonic interpretations—is still scattered in well over one hundred papers that are more or less accessible to the interested researchers. In order to facilitate the access of the geoscience community to this information, here we present an up-to-date compilation of geochronologic, geochemical and isotopic data characterizing the region.

The area covered in this compilation is shown in Figure 1. The aggregate Carpathian Mountains start in the west from near Vienna (Austria) and form a broad east-west arc (the West and East Carpathians), followed by a sharp bend in the Vrancea region; the east-west oriented South Carpathians complete geographically this segment of the long scar marking the closure of various Alpine and Neotethyan basins, which extends from the Alps in the west, to the Himalayas in its far east. The Carpathians have a complex geologic history, but the present-day mountain ranges and basins formed as a result of Cenozoic compression and crust consumption by subduction and collision (Schmid et al., 2020) of a series of back arc basins, whereas the main Tethyan Ocean was located further to the south. A prominent fold and thrust belt of Miocene and younger ages marks the suture between the Eastern European craton to the east and mobile Europe, represented by several peri-Gondwanan terranes (Balintoni et al., 2014). To the interior of this arc lies the Pannonian-Transylvanian basin, a continental extensional domain most recently related to the rollback of the slab since the early Miocene (Royden & Burchfiel, 1989). A smaller mountain range, the Apuseni Mountains, occupies a less extended area within the eastern part of the Pannonian basin.

Magmatic products of this region span an 800 Ma range, from a Neoproterozoic arc preserved in the basement of the South Carpathians (Balintoni et al., 2014) to the youngest volcanoes found in the Carpathian bend region; here, at least one volcanic center, Ciomadul, is documented to be active (e.g., Harangi et al., 2015; Popa et al., 2012). We did not compile data on igneous rocks making up various basement terrains, which are Neoproterozoic to late Paleozoic in age; many of those have been metamorphosed during the Paleozoic (Medaris et al., 2003). We did, however, include the following igneous provinces composed of unmetamorphosed volcanic and/or intrusive rocks of the region; (a) a Jurassic island arc province found in the South Apuseni Mts. and buried under younger rocks of the Transylvanian basin (Gallhofer et al., 2017),

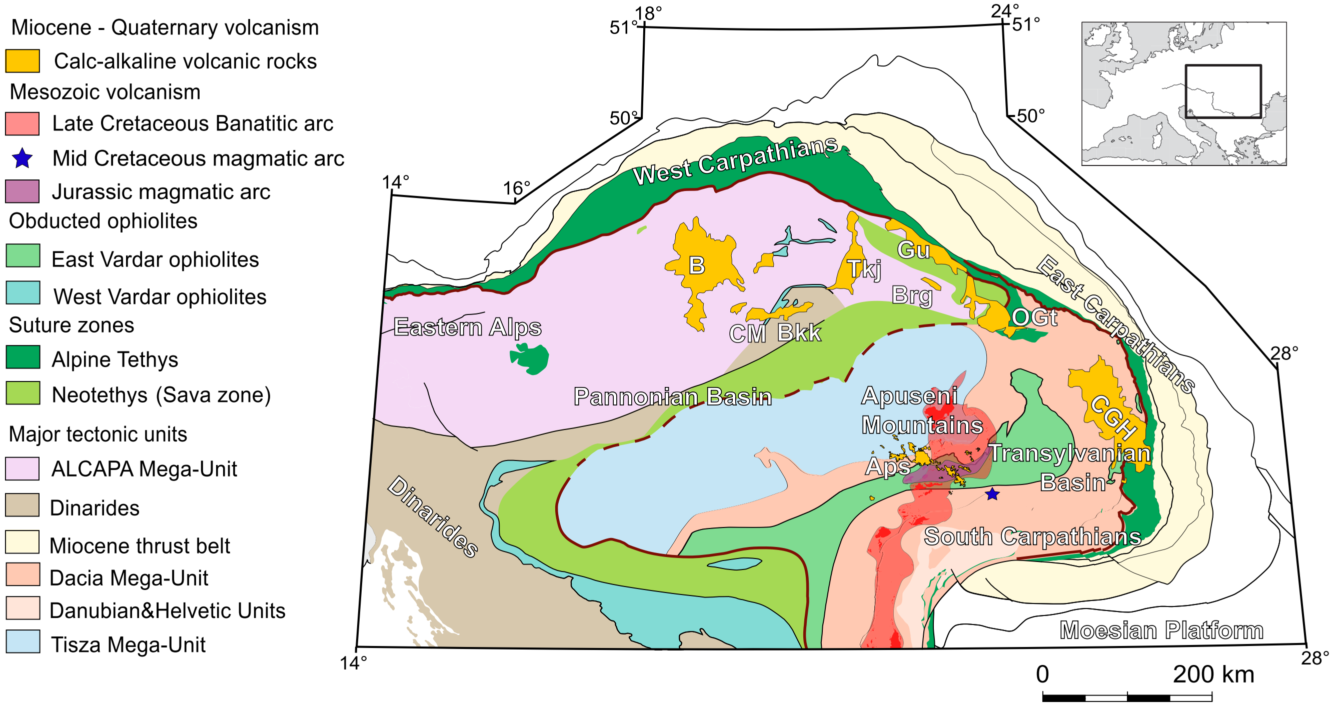

Figure 1. Tectonic map of the Carpathian-Pannonian region, simplified after Schmid et al. (2008) and Gallhofer et al. (2017). Distribution of the Miocene-Quaternary calc-alkaline magmatism after Seghedi et al. (2004). Distinct magmatic fields are (Aps, Apuseni; B, Börzsöny, CM, Cserhát-Mátra, Bkk, Bükk foreland; Tkj, Tokaj; Gu, Gutinski; Brg, Beregovo; OGt, Oaș-Gutâi; CGH, Călimani-Gurghiu-Harghita).

(b) a poorly known mid-Cretaceous low-volume arc found along the northern margin of the modern South Carpathians (Dobrescu et al., 2010), (c) a latest Cretaceous, Neotethys related arc known locally as "banatitic" in SW Romania (Berza et al., 1998; Gallhofer et al., 2015), (d) a regionally extensive early to mid-Miocene province of calc-alkaline tuffs and ignimbrites making up an enigmatic gigantic eruptive flare-up in central-eastern Europe (Lukács et al., 2015), and (e) the principal, collision-related Miocene to modern calc-alkaline arc bordering the interior of the Carpathians and also exposed in the Apuseni Mts. (Pécskay, Lexa, & Kovacs, 1995; Seghedi et al., 2004). Extension-related alkali basalts (Downes et al., 1995), formed synchronous with the latter stages of this arc-like magmatism, are also included in the database.

The spatiotemporal volcanic puzzle of the Miocene and younger rocks near the Carpathian bend has been a subject of several review papers (e.g., Seghedi et al., 2004; Szakács et al., 2018) and is important for understanding collisional magmatism and its relationship to the formation of Cu-Au, Te and other mineral deposits (among other aspects, e.g., Roșu et al., 2004), but arguably remains unresolved because of the complexity of igneous products here. This was the principal motivating factor in creating this database. Additionally, well known and widely used global geochemical databases either do not cover much of the area or have major gaps and incomplete data sets in which locations are missing or are inaccurate. Many data originate from earlier literature prior to the practice of georeferencing or are from obscure literature and require local toponymy knowledge even for assigning a semi-quantitative location. Assigning an age to a datapoint usually requires some knowledge of local geology/geography, if not explicitly presented in the original data source. Regional review papers (Pécskay, Lexa, & Kovacs, 1995; Seghedi et al., 2004) are not accompanied by such databases. The recent paper by Bracco Gartner and McKenzie (2020) does contain a thorough database for the Carpathian-Pannonian region, being the first such effort that resembles a modern geochemical database anchored by rock age and location; however, that paper only discusses (and compiles) Quaternary basalts.

In the later parts of the paper, we apply this new compilation to determine paleo crustal thickness of the Jurassic, late Cretaceous and Pliocene arcs using a set of novel geochemical parameters and compare our findings to regional geologic constraints for crustal thickness evolution in the region.

2. Database

The data organized in Microsoft Excel™ have been contributed to Open Science platform OSF (https://osf.io/23kdg/) to be best viewed in GeoMapApp™ (http://www.geomapapp.org/) and are also available as an Excel file accompanying this manuscript (Data Set S1). The database is built on the skeleton of a compilation available in GEOROC (http://georoc.mpch-mainz.gwdg.de/georoc/). The original GEOROC effort was aimed primarily at the younger (Miocene-Quaternary) volcanic rocks, is incomplete and lacks critical information such as detailed location for many samples. Our database too is incomplete provided that significant amounts of data (primarily major elemental chemistry) available in the regional geologic literature are hampered by incomplete reporting (lack of locations, lack of information regarding age, analytical techniques and errors), which makes a large body of work not suitable for the database, at least for the moment. Even the product we report on here, the compiled database as described below, which to us contains sufficient quality information to be used by others, cannot be contributed to EarthChem (earthchem.org) because much of the literature reporting data from this region does not have the rigorous quality control required by the metadata input scheme designed for EarthChem.

3. Data

All samples are igneous (whole) rocks and their petrographic, chemical, isotopic and chronologic data come from sources that have been either peer-reviewed or come from unpublished/in review data. A list of references to the original data source is included as a separate sheet in our Data Set S1. Locations are reported in decimal degree format (N latitude and E longitude) using the WGS 84 reference coordinate system. Sample ages are crystallization ages (in Ma) and are based on the mean or "interpreted" age reported in the data source. Age uncertainties are reported as provided in the data source and are not always provided at the 2σ level. Age data come from a variety of geochronologic methods, the best of which are zircon U-Pb data for intermediate and silicic rocks, and Ar-Ar data for mafic rocks. However, the great majority of Carpathian (Cenozoic) ages regionally are K-Ar values obtained in the laboratory of Zoltán Pécskay at the MTA Institute of Nuclear Research in Budapest (e.g., Pécskay et al., 2000). This laboratory has produced accurate but often imprecise age data for decades (e.g., Lukács et al., 2015; Márton & Pécskay, 1998); until better sets of zircon U-Pb ages with smaller errors become available, these data remain the golden standard for Carpathian Neogene-Quaternary volcanic chronology. Some samples are geochemically analyzed from a single location or igneous body, not yet dated. In these cases, an approximate age is assigned to each sample; however, no age uncertainty is assigned in the database. Several tuffs and other igneous rocks are known to be of a certain age based on geologic (e.g., stratigraphic) relationships. In those cases, where the age was known as an interval, we estimated as best as possible the known error. Because the data set is meant to be used as much as possible quantitatively, in the case of ages reported as intervals we assumed the middle of those intervals to represent the ages and half of their width to be the age errors.

Samples commonly but not always have petrographic descriptions in the data source; that information is imported in the database as a comment. To automate the process of populating the database, a MATLAB script has been developed for automatic rock name recognition (see Supporting Information S1). Using the TAS (Le Bas et al., 1986) and QAPF diagrams (Middlemost, 1994; Streckeisen, 1974), the script names the rock name for each sample according to their chemical composition.

Major elements are reported in weight percent oxide (wt%) and trace elements are reported in parts per million (ppm = μg/g). Isotopic data are presented as measured (modern day, not age corrected) isotopic ratios in the case of Sr, Nd, and Pb isotopes. We also report modern day epsilon Nd values normalized to 0.512638, calculated from the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios using DePaolo (1988). $\delta^{18}\text{O}$ values are reported in per-mille (‰) normalized to Standard Mean Ocean Water for minerals and whole-rock values. Data coverage is uneven, for example, the Neogene volcanism present in Gutâi, Călimani, Gurghiu, and Harghita Mountains represent ~70% of the data set, while the Mesozoic igneous data represents ~20%. The remainder is from the smaller arcs.

Figure 2a shows the distribution of Miocene to Quaternary volcanic rocks from the East Carpathians and Apuseni Mountains distinguished by silica content, whereas Figure 2b shows the distribution of Miocene and younger magmatism by age in the same area. Figure 2a illustrates the complex compositional spatial

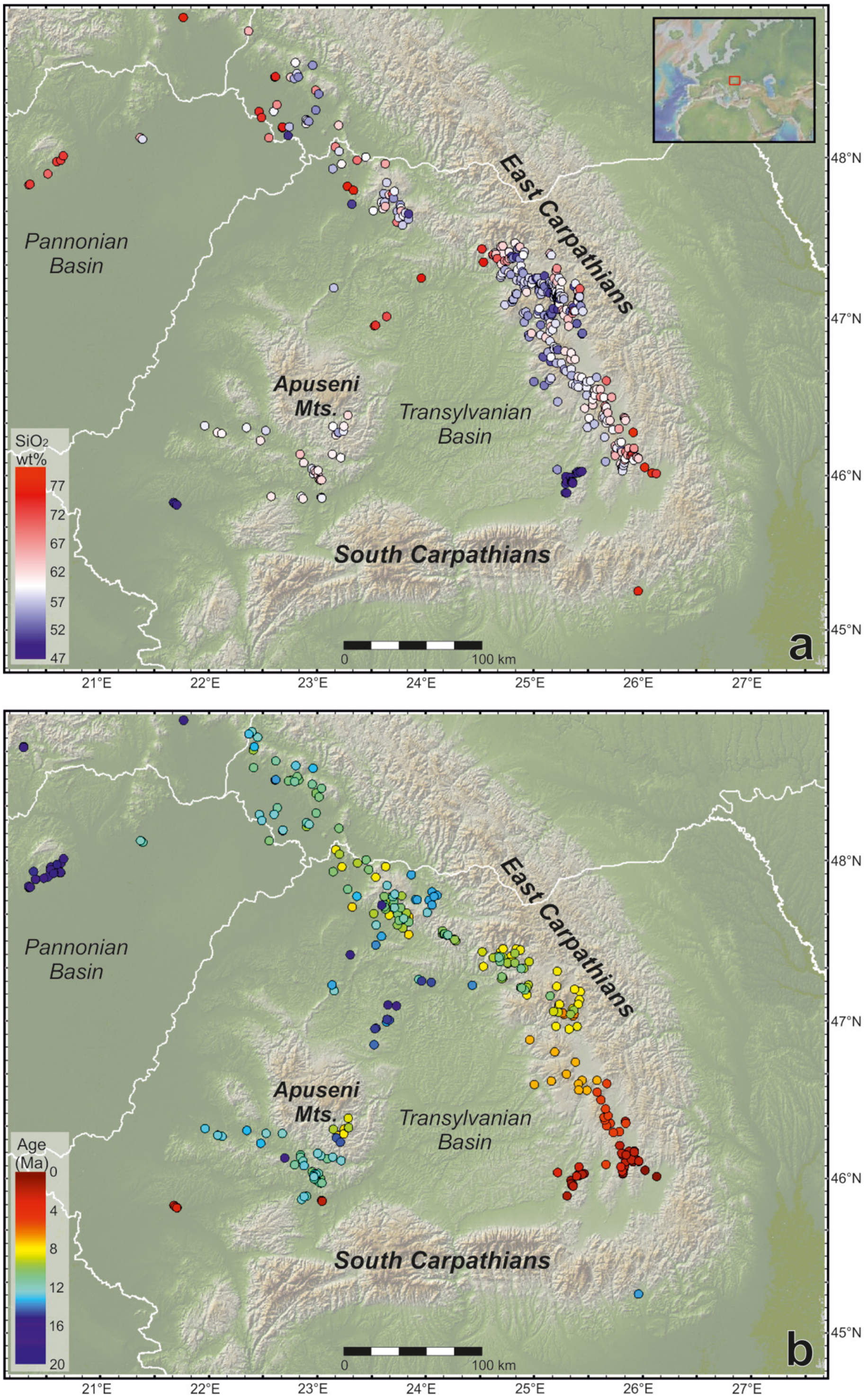

Figure 2. Spatial distribution of Miocene to Quaternary volcanic rocks from the East Carpathians and Apuseni Mts. represented in GeoMapApp™, color coded by (a) silica content and (b) age.

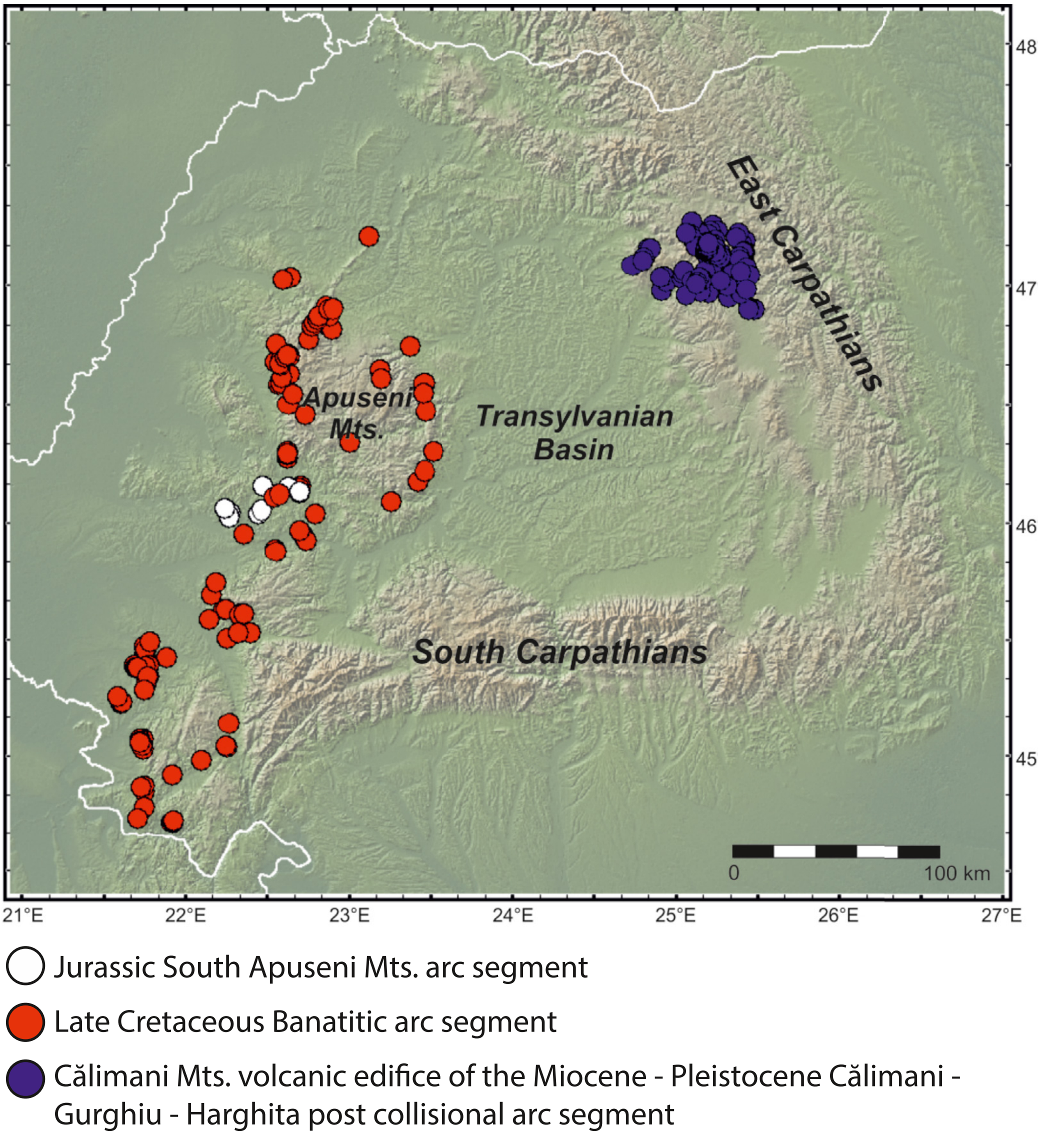

Figure 3. Paleo-mohometry focus areas. Filled circles represent individual samples with well-constrained locations.

distribution of young volcanic rocks near the double bend of the Carpathians, whereas Figure 2b shows that age patterns in surface magmatic products common in typical arcs, determined by inboard or outboard migrations relative to trench over time, are not distinguishable in the Carpathian collisional magmatism. Instead, here geochronological data indicate that much of the igneous activity was characterized by a peculiar trench-parallel migration (Pécskay, Edelstein, et al., 1995, Pécskay, Lexa, & Kovacs, 1995).

4. Application to Paleo-Mohometry

The link between crust thickness and the composition of magmas from modern arcs has long been recognized worldwide (e.g., Coulon & Thorpe, 1981; Leeman, 1983; Miyashiro, 1974; Plank & Langmuir, 1988), but only recently has started to be quantified with the purpose of approximating the thickness of ancient arcs. Trace element ratios Ce/Y, Sr/Y, La/Yb, and Eu/Eu* analyzed at whole-rock and mineral scales have been proposed as proxies for Moho depths beneath arcs (Chapman et al., 2015; Hu et al., 2017; Mantle & Collins, 2008; Profeta et al., 2015; Tang et al., 2020), and are now broadly employed to approximate the thickness of various paleoarcs that contributed to the formation and modification of continental crust from the Precambrian to the Late Cenozoic (Figure 3).

Taking advantage of the fact that, alike Ce/Y, Sr/Y, La/Yb, numerous other chemical parameters (i.e., major and trace elements and their ratios, such as Ca, Mn, Ba, Sc, Zr/Y, La/Sm) in arc magmas are sensitive to Moho depth variations, and fine-tuning and expanding on previous approaches (Chapman et al., 2015; Profeta et al., 2015), Luffi (2019) calibrated a set of 41 "mohometers," that is, whole-rock geochemical sensors of arc-crust thickness, which rely on a large volcanic data set representative of modern oceanic and continental arcs with known crustal thicknesses. These mohometer models account for the effects of differentiation on magma composition by including MgO as an independent variable, and are thus suitable to evaluate crust thickness using a broad range of magma compositions common in arcs, from primitive basalts to rhyolites. Due to their statistical, global-scale foundation, mohometers in general require sample populations that are large enough to be statistically meaningful, and cover spatial lengthscales (commonly tens to hundreds of kilometers) at which the cumulated chemical effects of local magmatic processes are attenuated.

Here we apply the mohometers of Luffi (2019) to three convergent tectonic settings relevant to the Mesozoic and Cenozoic evolution of the Carpathian realm: the Jurassic South Apuseni Mts. arc segment, the Late Cretaceous Banatitic arc segment, and the Miocene-Pleistocene Călimani-Gurghiu-Harghita post-collisional arc segment (Figure 2b), as follows. First, in each case study, the targeted chemical data set is filtered for samples that fall outside the calibration range (MgO >10 wt%, SiO_2 <45 wt%, SiO_2 >80 wt%), show evidence of significant alteration (sum of major oxides <97 wt% or >101 wt%), or display anomalous element concentrations. Next, the remaining samples are sorted into 1 wt% wide MgO bins, in which median values are then calculated for all chemical parameters available to serve as mohometers. With help of the mohometer models, an individual Moho depth is computed at the scale of each MgO bin from each median chemical parameter, and then a representative primary median Moho depth is calculated for each applicable mohometer from the corresponding MgO-binned results. The obtained primary results are filtered according to quality criteria aimed to eliminate estimates that rely on compositions associated with too large model uncertainties (typically >3–4 km), or show striking differences among different MgO bins, indicating inconsistency with the model. In the absence of sufficient samples or spatial coverage, results produced by mohometers more susceptible to local influences (e.g., crustal assimilation, magma mixing) may significantly decouple from the others and are excluded from further considerations. Finally, all MgO-binned results passing the quality filtering procedure are used to obtain an overall median Moho depth and associated median absolute deviation (MAD) for the source region sampled by the entire chemical data set.

4.1. The Jurassic South Apuseni Mountains Arc Segment

Supra-subduction submarine mafic-intermediate rocks previously referred to as "ophiolites" (Savu et al., 1981) and associated calc-alkaline granitoids and intermediate and silicic volcanic rocks of latest Jurassic age from the South and East Apuseni Mountains represent a relatively well-preserved section of the East Vardar suture zone (Schmid et al., 2020). They were most recently interpreted as remnants of a 153–159 Ma old island arc accreted onto the continental Dacia Mega-Unit (Gallhofer et al., 2017). We estimated the thickness of the South Apuseni Jurassic arc using 40 calc-alkaline whole-rock compositions (Bortolotti et al., 2004; Gallhofer et al., 2017; Nicolae & Saccani, 2003) that passed the above-outlined sample filtering protocol. Our calculations relying on 27 mohometers applicable to this sample set, retained after quality filtering the primary results, suggest Moho depths of 35 ± 6 km (Figure 4a). Moho depths indicated by the vast majority of individual sensors exceed 30 km, a value that is consistently greater than crustal thicknesses of typical modern island arcs built on oceanic crust but could represent an arc developed on a thin continental margin.

4.2. The Late Cretaceous Banatitic Arc Segment

Isolated segments of the Late Cretaceous magmatic arc developed along the Carpathian–Balkan orogen during the closure of the Neotethys Ocean, coined as "Banatitic arc," are preserved in the Apuseni Mountains, Banat, Timok, Panagyurishte, and Eastern Srednogorie (Berza et al., 1998; Gallhofer et al., 2015). Here we focus on the Apuseni and Banat segments active in the 84 to 71 Ma time period (Gallhofer et al., 2015), for which 127 whole-rock samples selected from recent publications (Dupont et al., 2002; Gallhofer et al., 2015; Vander Auwera et al., 2016) can be used after data filtering. 35 mohometers applicable to these samples

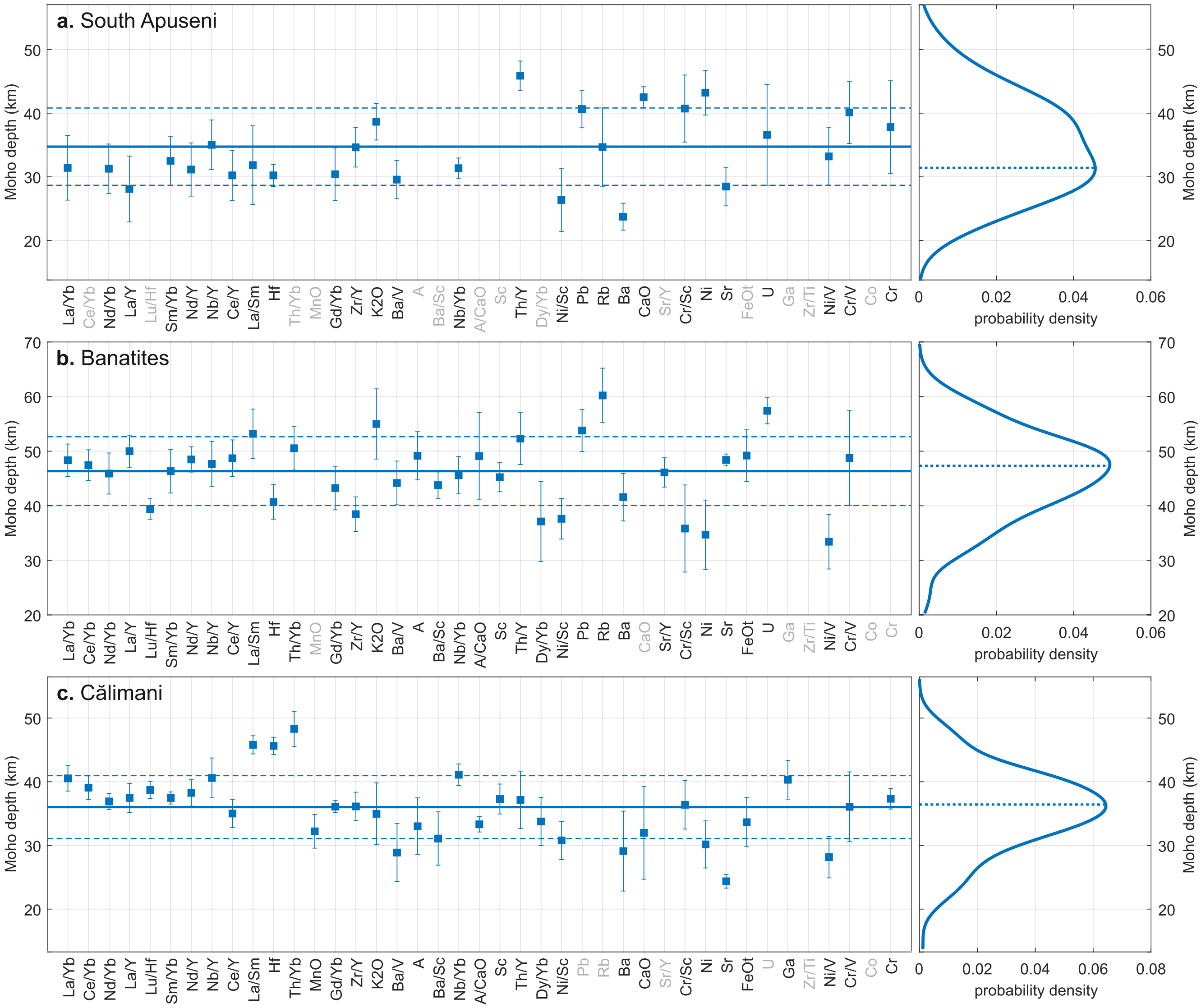

Figure 4. Carpathian paleo-mohometry case studies: (a) South Apuseni Mts.; (b) Banatitic arc; (c) Călimani Mts. Median estimates and associated median absolute deviations (MAD) shown as error bars for individual mohometers are calculated from MgO-binned median compositions. Overall median ± MAD values integrating all results are shown as continuous and dashed horizontal lines, respectively. Grayed-out mohometers are not used either because they are missing relevant data, or because they do not meet the imposed quality criteria in the case of the examined data set. A = $Na_2O + K_2O$.

yield a crust-mantle transition at 46 ± 6 km (Figure 4b). In contrast, present-day Moho depths beneath the Apuseni and Banat are significantly shallower, averaging about ∼30–35 km (Bala et al., 2017; Molinari & Morelli, 2011), implying that significant crustal thinning followed the demise of the Late Cretaceous magmatism. Two major extensional events could be responsible for crustal thinning since late Cretaceous, an Eocene episode responsible for the unroofing of the Danubian units in the South Carpathians (Fügenschuh & Schmid, 2005) and the Miocene and younger extension that led to the formation of the Pannonian basin (Schmid et al., 2020).

4.3. The Miocene-Pleistocene Călimani-Gurghiu-Harghita Post-Collisional Arc Segment

The Călimani-Gurghiu-Harghita segment represents the youngest member of the East Carpathian Miocene-Pleistocene volcanic range. It is dominated by calc-alkaline, mostly andesitic, extrusive products (Mason et al., 1996; Seghedi et al., 1995); emplaced in the 10.2–0.03 Ma interval (Pécskay, Edelstein, et al., 1995, Pécskay, Lexa, & Kovacs, 1995; Szakács et al., 2015), following the collision of the Tisza–Dacia microplate system with the East-European and Moesian continental margins, marked by the development of the East-Carpathian nappe stack (Matenco and Bertotti, 2000; Seghedi et al., 2004). Because no significant variations in thickness of the local crust are expected over the past 10 Ma, here we test the applicability of geochemical mohometry to post-collisional magmatism. Călimani Mts. is the oldest (10.2–6.8 Ma) and most prominent edifice of the segment, featuring compositionally diverse volcanic and sub-volcanic outputs that range from basalts to rhyolites, well suited for testing. To estimate Moho depths beneath Călimani Mts., we combined literature data (Mason, 1995; Mason et al., 1996) with our unpublished new data. When applied to 99 samples passing the data filters, 35 mohometers retained after quality filtering the primary results indicate a Moho depth in the 36 ± 5 km range (Figure 4c), in excellent agreement with geophysical constraints in the area, which are suggesting a somewhat diffuse crust-mantle transition in the 35–40 km depth interval (Borleanu et al., 2021; Ivan, 2011; Molinari & Morelli, 2011; Răileanu et al., 2012). Similar results (not shown) are obtained for the compositionally less documented Gurghiu and North Harghita Mts. In contrast, in the case of the youngest, southernmost Harghita volcanism characterized by a distinctly adakite-like signature (Seghedi et al., 2004), geochemically estimated Moho depths (49 ± 9 km) significantly exceed the results derived by geophysical methods (30–35 km). Such a difference can be ascribed to the fact that mohometer calibrations relying on modern arc data, which do not include adakitic compositions, may not capture the particularities of composition-Moho depth relationships in the case of such unusual rock suites.

5. Concluding Remarks and Outlook

The database represents a comprehensive effort that allows for an in-depth analysis of geochemical parameters of igneous rocks from the Carpathian-Pannonian realm, offering support for better understanding the magmatism associated with subduction and collision processes shaping the region during the Mesozoic and Cenozoic, and facilitates the evaluation of the included data in a continental and global context. Furthermore, it lays the foundation for a larger scale magmatic database also integrating data from the neighboring Balkans, Dinarides and beyond, furthering thereby new research opportunities for those interested in the geochemical, petrologic, and tectonic evolution of the broader region.

Data Availability Statement

Data set for this study is included in the Supporting Information S1 of this paper. It is also available online at OSF.io via https://doi.org/10.17605/OSF.IO/23KDG (https://osf.io/23kdg/) with no registration required and no license.

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