Evidence for widespread mid-Permian magmatic activity related to rifting following the Variscan orogeny (Western Carpathians)


Abstract

The Gemeric and Veporic Superunits of the Western Carpathians correlate to the Lower and Middle Austroalpine tectonic units (nappes) of the Eastern Alps. The Gemeric Superunit is characterized by small exposures of rare-metal granites, and their ages impact understanding its tectonic history and how this portion of the Carpathians relates to other Permian age granites exposed throughout Europe and the Western Mediterranean. Here we present new Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Secondary Ion Mass Spectrometry (SIMS) zircon U–Pb ages from northern (Hnilec) and southern Gemeric granite exposures (Betliar, Elisabeth Mine, Poproč) and one from the Veporic Superunit (Klenovec). Geochemical analyses of Betliar and Klenovec samples indicate they are highly differentiated and fractionated from a clay-rich source, consistent with published reports for these granites. Zircon saturation temperatures average 733 ± 27 °C (Betliar) and 756 ± 61 °C (Klenovec). Most Gemeric granitic zircons are Permian (n = 231 spots), with some inherited zircons giving Middle Ordovician to Late Silurian (n = 26), and some Triassic (n = 6) U–Pb ages. The dominant Permian U–Pb yield crystallization ages of at 264 Ma for the Gemeric granite and 265 Ma for the Veporic Superunit’s Klenovec granite (n = 26). Klenovec zircons typically show distinct yellow rims in cathodoluminescence, characteristic of lower temperature overprint (<600 °C). These granite zircon ages overlap those from the radiolarite-bearing metasediments from the Meliata Ocean exposed in the Dobšiná region (263.9 ± 2.7 Ma, LA-ICP-MS, ± 1σ). The detrital zircon U–Pb ages thus imply a possible beginning of sedimentation in the Meliata Ocean as early as the mid-Permian. The genesis of the Gemeric and the Klenovec granites is related to post-collisional extension. These data link the Western Carpathians to a regional widespread occurrence of Permian magmatism in the European Variscan and Western Mediterranean realms, consistent with regional magmatic re-equilibration of the Moho. This scenario likely occurred in response to a thermal surge that involved significant decompression and extension, lower crustal melting, upward displacement of the Moho, and delamination of the mantle-lithosphere that contributed substantially towards Variscan crustal thinning.

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events associated with Variscan assembly to Permian extension that likewise characterize the Carboniferous-Permian tectonic and magmatic evolutions of central Europe (e.g., Froitzheim et al., 2008; Lexa et al., 2003; Stampfl and Kozur, 2006; Szemerédi et al., 2020).

In this study, we present the results of a campaign to generate zircon U–Pb ages from four granite apophyses that intrude the Gemeric Superunit (Betliar, Hnilec, Poproč, Elisabeth Mine) and one from the underlying Veporic Superunit (Klenovec) (Fig. 1). We also generated whole-rock geochemical data from five distinct magmatic facies of the Betliar granite composite body to relate the results to previous work on the rare-metal granites. We supplement these data with detrital zircon U–Pb data from sedimentary rocks that overlie a fragment of obducted Meliata Ocean crust (Fig. 1). The goal is to use these zircon U–Pb ages to constrain the tectonic evolution of the Gemeric Superunit and relate its importance in broader, regional early Paleozoic and Variscan orogenic events in central and western Europe.

2. Geological background

The Western Carpathians (Fig. 1) consist of three Alpine northward-directed thick-skinned tectonic nappes termed the Tatric, Veporic, and Gemeric Superunits (Froitzheim et al., 2008). These superunits were juxtaposed during the Eo-Alpine (Late Cretaceous) orogeny, although southward-directed thrust-related deformation related to the Variscan orogeny is present in all (Jeřábek et al., 2008; Hrouda and Faryad, 2017). Permian granite intruded both Gemeric and Veporic Superunits during post-collisional extension and initial rifting of the Alpine Tethyan realm (e.g., Poller et al., 2002; Radvanec et al., 2009).

The Gemeric Superunit consists of Paleozoic (Cambrian to Late Carboniferous) meta-sedimentary assemblages, northward-verging thrust imbricates, and partial nappes, the number and terminology of which vary (see Froitzheim et al., 2008; Lexa et al., 2003; Petrasová et al., 2007; Šefara et al., 2017). The Gemeric granites intrude the Gemenic Group, which belongs to the southern segment, consisting of phyllite and metamorphosed rhyolite and basalt juxtaposed during the Variscan orogeny in the Carboniferous (e.g., Bajaník et al., 1983; Vozárová et al., 2012). In contrast, the northern segment is composed of a series of volcano-sedimentary strata reflecting Paleotethyan subduction and collision affected by polyphase metamorphic events (see

Fig. 1. Geological map of the Gemeric and southern portions of the Veporic superunits showing the locations of samples analyzed in this study. The base map was adapted from Hurai et al. (2010), Lexa et al. (2000), and Lexa et al. (2003). Inset shows the locations of the Variscan basement of the Tatric, Veporic, and Gemeric superunits in Slovakia. Red circles designate other important magnesite-talc deposits: I – Kokava, II – Sinec, III – Samo, IV – Ploské, V – Burda, VI – Jeťava, Ochtiná, VIII – Gemerská Poloma, IX – Košice (Bankov, Medveda). See Table 3 for sample GPS locations and a summary of their zircon ages.
2.1. Background of the granite assemblages

Although the Gemeric granites are only exposed as small apophyses (Fig. 1), they likely link to a continuous 5–8 km-thick post-orogenic intrusive body located at depths of 2–10 km (Šefara et al., 2017). Based on geophysical imaging, this body itself may be a distinct north-verging Alpine nappe, with its upper and lower boundaries dipping southwards (Šefara et al., 2017). The granites are thought to intrude the central portion of the Gelnica Group along deep faults or strike-slip lineaments (Fig. 1) (Finger and Broska, 1999; Hrško et al., 2002; Kohút and Stein, 2005; Petrík et al., 2011; Petrík and Kohút, 1997; Uher and Broska, 1996). The Betliar, Humel, and Zlatá Idka granites are found in a series of aligned small exposures termed the “southern hotline.” The Gušetina, gneiss unit, is also found along the southern hotline. In contrast, the Šúlava and Delava granites are associated with the Hnilec Group and are located along a “northern hotline” (Fig. 1) (Radvanc et al., 2009). The age of the granites is thought to young southwards from Hnilec to Zlatá Idka (Radvanc et al., 2009).

Table 1 lists published crystallization ages for the granites that range from 290 ± 40 Ma (Rb–Sr Kovach et al., 1986) to 246 ± 5 Ma (U–Pb, Betliar Radvanc et al., 2009). Reported younger Jurassic to Cretaceous ages appear to represent subsequent alteration and metamorphism (e.g., Cambel et al., 1989; Uher and Broska, 1996). This study also provides new insights into the character of the Permian Klenovec granite within the Veporic Superunit, which has a reported Th–Pb monazite age of ~266 Ma and tourmaline mineralization resembling that of the Gemeric granites (Hráško et al., 2002) (Table 1).

Petrographically, several types of Gemeric granites can be distinguished as composite intrusions that were subjected to hydrothermal alteration (Jalabáska and Rozložník, 1989; Uher and Broska, 1996). The granites exhibit different mineralogical textures, including coarse-grained, or porphyritic biotite at deeper structural levels, as well as medium-grained muscovite + biotite, and fine-grained greisenized (hydrothermally-altered) two mica in shallower levels (Kohút, 1997; Petrok and Kohút, 2001; Uher and Broska, 1996). In the apaxes, rare-metal granites are present (Broska and Kubíš, 2018). The two mica and porphyries show evidence for low-temperature solidi (Ts ~ 600–650 °C), low Io, and water and fluorine-rich magma interactions, and emplacement at shallow levels (e.g., 0.5–2.0 km, Uher and Broska, 1996).

In geochemical character, the Gemeric granites are high SiO2, strongly peraluminous, and fractionated with high concentrations of F, B, Rb, Li, Cs, Sn, Mo, Be and low concentrations of Sr, Ba, Zr, and V (Broska and Uher, 2001; Kohút, 1992; Petrok and Kohút, 1997; Uher and Broska, 1996). Major minerals include plagioclase, K-feldspar, quartz, muscovite, biotite, and accessory minerals include zircon, apatite, monazite, tourmaline, and garnet (Broska et al., 2002; Uher and Broska, 1996). They are considered a unique type of low temperature (Ts ~ 600–650 °C), tectono-hydrothermal ore-bearing rare metal S-type granites (Sn–F; specialized Ss-type: Breiter et al., 2015; Petrok and Kohút, 1997; Petrok et al., 2014; Uher and Broska, 1996). Their geochemistry points to melt derivation from mature, recycled, sedimentary supracrustal rocks, likely in a collisional setting. Fluids played an essential role in both the development of the granites and the generation of the rare metals found within and associated with them (e.g., Petrok et al., 2014).

The granites themselves may have been derived from crustal sources of Early Paleozoic (Cambrian to Late Carboniferous) remnants that underwent seafloor alteration and were subsequently modified by mineralizing fluids (Kohút, 2012), 87Sr/86Sr isotope values (0.711–0.734) also point to derivation from an evolved continental or sedimentary protolith (e.g., Kovach et al. 1986). They were affected by an Alpine deformational and metasomatic overprint during burial below the Meliatic and Silicic nappe system (e.g., Hrouda and Faryad, 2017). In the Gemeric granites alteration assemblages that formed during Late Cretaceous metamorphosis consist of albite, phengite, and grossular (e.g., Breiter et al., 2015; Petrok et al., 2011).

Permain A-type granites have also been reported along the northern hotline exposures of the Gemeric unit (e.g., Radvanc et al., 2009; Table 1). We included the location of one such A-type granite (Turčok granite) in the northern portion of the Gemeric unit between the Klenovec and Betliar exposures (Fig. 1).

2.2. Ophiolite exposure, meliata unit

A series of dismembered and incomplete opholite slices in the Western Carpathians comprising serpentinites, radiolarian shales and cherts, offer evidence for the presence of the former Meliata Ocean (Fig. 1) (e.g., Faryad et al., 2005; Mock et al., 1998; Plašenka et al., 2015; Putiš et al., 2012). One of these slices is the Meliata Unit, an opholite-bearing mélange that forms part of a Jurassic accretionary
flysch complex containing radiolarites, olistostromes, mélanges and ophiolitic bodies (Kozur and Mock, 1997; Mock et al., 1998; see review in Schmid et al., 2008). The Meliata Unit is overall considered a fragment of an ophiolite within an accretionary-subduction wedge that was subsequently obducted onto the Gemeric Superunit (e.g., Putiš et al., 2019). It may correlate with other reported ophiolite packages stretching from the Eastern Alps to the Hellenides (Dallmeyer et al., 2008; Kozur and Mock, 1997; Mock et al., 1998; Schmid et al., 2008), although this remains debated based on timing of obduction (Channell and Kozur, 1997). High-pressure/low-temperature and anchi-grade metamorphism affected the ophiolite and sedimentary strata associated with the Meliata Ocean as well as carbonate platform sediments of the Silica Unit that cover the tectonic nappes and comprise the overall architecture of the Western Carpathians (Faryad et al., 2020 and citations therein).

The opening of the Meliata Ocean during the Permian to early Triassic resulted either from back-arc extension during northwestern-directed subduction of the Paleoetohyian Ocean (Froitzeheim et al., 2008) (Fig. 9B) or as a result of rifting of the Neotethyan passive continental margin (e.g., Putiš et al., 2019). The Meliata Ocean records back-arc basin (BAB) and normal mid-ocean ridge basalts (N-MORB) (e.g., Faryad et al., 2005; Mock et al., 1998). Sedimentation in the Meliata Ocean continued until the Late Jurassic, after which the radiolarian chert and shale packages experienced metamorphism due to ophiolite obduction (e.g., Putiš et al., 2012). The age of the oldest pelagic sedimentary strata is Middle Triassic (Ladinian) and consists of Middle Oligocene harzburgites and lizardite serpentinites near the city of Dobšiná locality is a highly altered blueschist marble mélangé complex (e.g., Mock et al., 1998; Putiš et al., 2019). 40Ar/39Ar phengite analyses from the blueschist of the Meliata Unit, the closure of the Meliata Ocean occurred during the Late Jurassic (160–150 Ma: Dallmeyer et al., 2008; 155–152 Ma: Faryad and Hjenes-Kunst, 1997; 155–140 Ma: Maluski et al., 1993; 170–150 Ma: Putiš et al., 2019). Emplacement and loading of the nappe onto the Central Carpathians occurred in the Early Cretaceous (105.8 ± 1.5 Ma, Dallmeyer et al., 2008; 100 ± 10 Ma, Putiš et al., 2019).

3. Material and methods

3.1. Geochemistry

Overall, eight samples from the Betliar pluton (IR19A-E and IR20A-C) and seven from the Klenovec granite (VZ-3/40 m, VZ-3/93 m, VZ-4/118 m, VZ-4/142 m, LH-39/04, LH 4/04, and LH 72/04) were analyzed for major and trace elements (Fig. 1). We include a Data In Brief article that shows images of several granites and porphyroclastic thin sections, and provides details of the analytical methods (Villaseñor et al., 2021). All Gemeric granite samples consist of quartz + feldspar + albitic plagioclase + biotite ± muscovite ± chlorite ± tourmaline ± fluorite and show evidence of deformation in quartz as undulatory extinction, bulging, and grain-boundary migration. Pintitized (altered) cordierite is present in some samples. The Veporic granite samples are from a small quarry near Klenovec, described by Hraško et al. (2002) with a Permian electron microprobe monazite age (266 ± 16 Ma). The Veporic granite samples have a similar assemblage as those from the Gemeric Superunit but include Alpine garnet (almandine-grossular) that formed from Fe-rich biotite and muscovite. Chloritized biotite is present in sample TT48. Major and trace element data were collected for Klenovec granite varieties (equigranular, VZ-3/40 m, VZ-4/118 m, LH-39/04; muscovite-bearing, LH 72/04a and VZ-3/93 m; fine-grained leucocratic, VZ-4/142 m and LH-4/04). In addition, one sample was analyzed from the northern Gemeric hotline exposure (Hnišec granite, TT51), which was collected from a drill core near Medvedi potok.

Eight samples were collected from the southern hotline Betliar pluton (IR19A-E, and IR20A-C) based on textural appearance. All of the IR19 rocks are from biotite-tourmaline porphyritic portions but differ in how tourmaline appears within the assemblages. Sample IR19A contains disseminated tourmaline, whereas samples IR19B and IR19C contain tourmaline in large cross-cutting veins and nodules. Both IR19C and IR19D contain nodular tourmaline. Samples IR19E and IR20B appear the most intensely deformed and metamorphosed. Sample IR20A contains radiating black tourmaline, whereas IR20C is a dark greisen.

Granite TT07 was collected from the Elisabeth Mine and consists of K-feldspar and plagioclase, as well as biotite, muscovite, quartz, and fluorite. The Elisabeth Mine is a 20-Mt talc deposit that has been mined since 2008 by Euro Talc s.r.o. Major minerals associated with the deposit are magnesite, dolomite, talc, quartz, and pyrite, and the main talc-forming reaction has been proposed to be metasomatic alteration related to the emplacement of the Elisabeth Mine granite (Petrasová et al., 2007). In this case, the talc-forming reaction is thought to have occurred during the Permian when magnesite + quartz + H2O = t alc + CO2 formed at conditions of 1 kbar, 430 °C, and XCO2 of 0.8. Initial magnesite formation may have occurred either during Variscan-related metamorphic events (Radvanec et al., 2004), or during Eo-Alpine nappe stacking, and metamorphism was accompanied by significant hydrothermal alteration (Hurai et al., 2008). Contact zones between the Elisabeth Mine granite and surrounding phylite were affected by mylonitic Alpine deformation that occurred at lower T (430 °C) but higher P (7 kbar) (Petrasová et al., 2007).

Sample TT49 is from the Poproč pluton located in the eastern portion of the Gemeric Superunit. It was collected from a small quarry next to an abandoned antimony plant. Note that the location and lithology of sample TT49 are similar to that of sample 1 described by Jakabská and Rozložník (1989); sample TT51 similar to their sample 2, and our Betliar samples similar to their sample 3.

3.2. Geochronology

Zircons from granite samples TT51 (Hnišec), IR19A and B, and IR20A and B (Betliar), TT07 (Elisabeth Mine), TT49 (Poproč), and TT48 (Veporic, Klenovec) and sedimentary rock sample TT08 were U–Pb dated using both LA-ICP-MS (University of Texas at Austin) and SIMS (UCLA). Data acquisition parameters are presented in the Data in Brief supplement (Villaseñor et al., 2021) and are summarized in Table 3. Due to the larger uncertainty of the SIMS ages, we resorted to the LA-ICP-MS dating to generate higher-precision results from more zircons. LA-ICP-MS ages are reported at the ±2σ level. While the SIMS ages have higher uncertainties, reported at the ±1σ level, the results are consistent with the LA-ICP-MS ages.

We also report detrital zircon U–Pb LA-ICP-MS data from sample TT08, a radiolarite from the Meliata Unit that overlies blueschist and harzburgite-lizardite serpentinite near the city of Dobšiná, Slovakia (Fig. 1). The base of the Meliata Unit in the Dobšiná locality is a highly altered blueschist marble mélangé complex (e.g., Mock et al., 1998; Putiš et al., 2019). 40Ar/39Ar phengite analyses from the blueschist of the Meliata Unit yield 150–120 Ma (Árkai et al., 2003). Blueschist record metamorphic conditions of 380–460 °C and 9–12 kbar, whereas the overlying ultramafic perovskite-andradite-bearing harzburgite record temperatures of ~350–450 °C (Putiš et al., 2012). The overlying radiolaria-bearing, or pelagic sedimentary strata (including sample TT08) are thought to have been deposited in the Meliata Ocean prior to its closure in the Jurassic (e.g., Putiš et al., 2012). This package dips towards the southeast due to tectonic movements associated with obduction.

We used a FEI Nova Nano SEM Gatan Chroma CL detector to image selected grains. Color CL images are constructed by combining three images of the same area collected using a blue, green, and red filter. Although zircons are often imaged in black and white CL, the use of color allows additional information, including possible chemical changes in trace element contents during the crystallization of zircons. In general, blue-green colors correlate with higher annealing
We compared the geochemistry of the Betliar and Klenovec samples to those reported from the Gemeric granites elsewhere (Table 2, Figs. 2-4) (Breiter et al., 2015; Kubíň and Broska, 2005, 2010; Petřík et al., 2011; Uher and Broska, 1996). Loss on ignition values for the Betliar samples range from 0.71 wt% for IR19C to 2.15 wt% for IR20C. The Klenovec samples average 757 ± 62 °C (Table 2), whereas the Betliar samples average 733 ± 27 °C. The zircon saturation temperature of all samples is between 653 °C and 796 °C, with the zircons from the Klenovec pluton having the highest saturation temperature (796 °C) and the zircons from the Betliar pluton having the lowest saturation temperature (653 °C). The analyses of the Klenovec samples show lower Sm/Nd values and higher Hf/Nd values compared to the Betliar samples. The Klenovec samples also have lower REE concentrations and higher Sr/Nd values compared to the Betliar samples. Overall, the trace element abundances and ratios from the Betliar and Klenovec samples are consistent with those of the syn-collisional granites generated from a pelitic source (Fig. 3). These are strongly differentiated and fractionated granites with higher-than-average continental crustal or chondritic values for rare metals and other elements like Be, Ge, Sn, Ba, Cu, Zn, and Sr. In a SiO2 vs. Zr/Hf plot, some Betliar samples fall within the range of Sn-W-Mo-B deposits of the greisen type, Li–F granites, but others are barren (Fig. 3D). Fluorine concentrations in the Klenovec samples range from 0.05 wt% (VZ-3/93 m) to 0.15 wt% (VZ-3/40 m). Most granites are enriched in trace elements with respect to chondrite and primitive mantle (Figs. 3E and F). The analyses show significant enrichments with respect to chondrite, except for P, Ti, and Eu in the Betliar samples, whereas some analyses of Sr, Eu, and Ti are depleted with respect to the primitive mantle.

Betliar and Klenovec samples also have low REE contents. Betliar sample IR19D has the highest REE content of 224.7 ppm, whereas IR20C has the lowest with only 12.4 ppm. Of the Klenovec samples, LH-39/04 has the highest (161.7 ppm) and VZ-3/93 m (12.23 ppm) the lowest REE contents. Lower Eu contents in these highly evolved rocks are related to Eu fractionation between residual melt and high-temperature fluid interaction (e.g., Irber, 1999). All Betliar and Klenovec analyses show pronounced Eu anomalies (Fig. 4), except for IR20C, which contains <0.05 ppm Eu (below detection limits, Table 2). We explored correlations between the tetrad effect (TE1,3) and K/Rb, Y/Ho, Zr/Hf, Eu/Eu*, Sr/Eu (e.g., Irber, 1999) (Fig. 4). The majority of the previously analyzed Gemeric, Betliar, and Klenovec samples show TE1,3 values / ratios that can be related to increasing degrees of fluid-interactions (e.g., Irber, 1999; Monecke et al., 2002; Zhenhua et al., 1993). Note that this effect may have formed within the magma–fluid system before emplacement or have been inherited from an external fluid influencing the system during or after magma emplacement (Monecke et al., 2002).

## Geochemistry

### 4.1. Geochemistry

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### 4.2. Geochronology

Zircons from the southern Gemeric hotline Betliar (IR19A and B, IR20A and B), Elisabeth mine (TT07), and Poproč (TT49), and one from the northern Gemeric Hnilec body (TT51) granite bodies were U–Pb dated (Fig. 5). We also include data from the Klenovec granite (TT48) in the adjacent Veporic Superunit as a comparison to the Gemeric results. Table 3 summarizes the U–Pb results. Hnilec sample

## Table 2

Whole-rock geochemical analysis of samples from the Betliar Pluton.

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<tr>
<th>Analyte Symbol</th>
<th>IR20B</th>
<th>IR19B</th>
<th>IR19C</th>
<th>IR19E</th>
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<td>725</td>
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Veporic Granite Klenovec Pluton

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<th>LH-74/04</th>
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<sup>a</sup> See supplementary data for details of the geochemical data.
<sup>b</sup> Zircon saturation temperature T<sub>sat</sub> (°C).
<sup>c</sup> (FeOtotal)/(FeOtotal + MgO). F = ferroan, M = magnesian granites, based on classification in Frost et al. (2001).
<sup>d</sup> MALI = Modified Alkaline Lime Index, C = calcic granite, C-A = calc-alkaline granite, A-C = alkali-calcite granite.
<sup>e</sup> ASI = Aluminosaturation index.
TT51 yielded the most zircons (n = 42 grains), whereas samples IR20B and TT49 had the smallest zircon yield (only 11 in Poproč sample TT49 and 12 in Betliar sample IR20B). Villaseñor et al. (2021) show CL images of most of the zircons dated in this paper.

The oldest zircon U–Pb dates are found in Klenovec sample TT48, which yields two discordant Precambrian ages (207Pb/206Pb ages, 2552 ± 18 Ma and 2389 ± 18 Ma, LA-ICP-MS, 27.8% and 26.5% discordant in U–Pb, respectively). These ages are found in the cores of zircons with recrystallized magmatic Permian rims (Fig. 6A and B). Overall, twenty-five spots (n = 18 lased spots and 7 SIMS) were placed on ten zircons from sample TT48. Besides the inherited Precambrian ages, SIMS geochronology yields one discordant U–Pb age at 434.7 ± 43.0 Ma (Fig. 6B). All other results are Permian (Table 3). The oldest, most precise Permian age is found in the core of an oscillatory-zoned zircon (272.3 ± 4.3 Ma, LA-ICP-MS, Fig. 6C). This age overlaps within uncertainty of both the oldest and youngest ages obtained using SIMS (285.1 ± 15.0 Ma and 276.2 ± 15.8 Ma, Figs. 6D and E). The youngest, most precise Triassic age from sample TT48 are located on an inner rim (248.6 ± 3.3 Ma, LA-ICP-MS, Fig. 6E). Overall, the zircon U–Pb ages from this granite overlap with those obtained from the Gemeric Superunit (Table 3). Because magmatic assemblages likely do not crystallize over long episodes of geological time, some of the zircons may have experienced Pb loss that is not reflected in Concordia. The only distinct difference we observed between zircons from this sample compared to those from the Gemeric granites was the presence of dull to bright yellow recrystallized zones near zircon rims (identified by arrows in Fig. 6). The yellow color is observed in all zircons we extracted from the Klenovec granite.

Betliar samples that were dated (IR19A and B, and IR20A and B) are indicated for reference. See Villaseñor et al. (2021) for the numerical data.
Fig. 3. (A) Zr + Ce + Y + Nb (ppm) vs. FeO/MgO discrimination diagram (Whalen et al., 1987) showing Klenovec, Betliar, and other Gemenic granite samples (Breiter et al., 2015; Kubiš and Broska, 2005; Kubiš and Broska, 2010; Petrik et al., 2011; Uher and Broska, 1996). Fields of A-type granites fractionated and unfractionated are labeled. (B) SiO$_2$ (wt%) vs. Zr/Hf diagram after Zaraisky et al. (2008). Arrow traces the differentiation trend through the fields of rare-metal granitoids from granodiorite, biotite granite, leucogranite, Li-F granites, and Ta deposits. Sn-W-Be deposits of the greisen type and barren granite fields are also labeled. (C) Multi-element spider diagram for metal-bearing granites. Elements selected after Dehaine et al. (2019). Y and Zr are normalized to upper continental crust values of Taylor and McLennan (1985), whereas all other elements are normalized to continental crust values of Gao et al. (1998). (D) Rb-Ba-Sr ternary diagram after Horbe et al. (1991). Most Gemenic granites plot in the field of strongly differentiated granites. Also labeled are fields of normal granite (Norm. Gr.), atypical granites (Atyp. Gr.), granodiorite and quartz-diorites, and diorites. Betliar samples that were dated (IR19A and B, and IR20A and B) are indicated for reference. Trace element spider diagram with elements normalized to chondrite (E) and primitive mantle (F) using values in Sun and McDonough (1989). See Villaseñor et al. (2021) for the numerical data.
Fig. 4. (A) Chondrite-normalized REE diagram for Betliar and Klenovec (this manuscript) and Generic granite samples (see references in other figure captions). Chondrite values from Sun and McDonough (1989). (B) Plot of tetrad effect (TE1,3) vs K/Rb. The horizontal dashed line in this and other panels at TE1,3 values 1.1 and higher indicates that this effect is present in the samples. The K/Rb of chondrite is indicated (235, Sun and McDonough, 1989). K/Rb of <100 is suggested for rocks that have undergone significant degrees of fluid interaction (e.g., Irber, 1999). (C) Plot of TE1,3 vs Y/Ho. The K/Rb of chondrite is indicated (28, Sun and McDonough, 1989). Y/Ho > 28 is suggested for rocks that have undergone significant fluid interaction (e.g., Irber, 1999). (D) Plot of TE1,3 vs Zr/Hf. Average Zr/Hf values for granite (39) and pegmatite (25) are plotted (Irber, 1999). Zr/Hf > 20 is suggested for rocks that have undergone significant fluid interaction. (E) Plot of TE1,3 vs Eu/Eu*. Also indicated are samples with Eu contents that are below the detection limit. (F) Plot of TE1,3 vs Sr/Eu. The K/Rb of chondrite is indicated (125, Sun and McDonough, 1989). The bold arrow shows the direction of Rayleigh fractionation, and the thin arrow follows the trend for Fichtelgebirge granites (Germany) that fractionated to high degrees (Irber, 1999). See Villaseñor et al. (2021) for the numerical data.
Fig. 5. Concordia diagrams for zircons (filtered for <5% concordance) dated by both LA-ICP-MS and SIMS: (A–D) Betliar pluton, (E) Elisabeth Mine, (F) Poproč, (G) Hnilec, and (H) Klenovec pluton. Permian to Triassic ages are shown in red, older ages shown in gray. See Table 3 for a summary of these results.
pluton similarly show inherited (older than Permian) cores during laser depth-profiling (463 ± 11 Ma, 414.4 ± 9.1 Ma, and 353.7 ± 3.9 Ma, see Villaseñor et al., 2021 for CL images of these grains).

Inherited zircon of Silurian and Early Devonian age were also found in Betliar sample IR20B (439.2 ± 5.6 Ma and 416.7 ± 7.7 Ma), although other spots on these same grains yielded discordant results. The oldest zircon ages from Elisabeth Mine sample TT07 are imprecise Carboniferous SIMS ages (306 ± 28 Ma, 330 ± 26 Ma), and the same zircons yield more precise Permian LA-ICP-MS results (264.5 ± 2.3 Ma, 267.1 ± 2.5 Ma). While most of the zircons with inherited ages exhibit other spots on these same grains yielded discordant results. The oldest zircon ages from Elisabeth Mine sample TT07 are imprecise Carboniferous SIMS ages (306 ± 28 Ma, 330 ± 26 Ma), and the same zircons yield more precise Permian LA-ICP-MS results (264.5 ± 2.3 Ma, 267.1 ± 2.5 Ma). While most of the zircons with inherited ages exhibit

Table 3

<table>
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<tr>
<th>Sample (n)</th>
<th>Youngest age LA-ICP-MS 238U–206Pb (±2σ) Ma&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Oldest age LA-ICP-MS 238U–206Pb (±2σ) Ma&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Youngest age SIMS 238U–206Pb (±1σ) Ma&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Oldest age SIMS 238U–206Pb (±1σ) Ma&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Average s Permian LA-ICP-MS age 238U–206Pb (±2σ) Ma&lt;sup&gt;a&lt;/sup&gt;</th>
<th>WM s Permian LA-ICP-MS age 238U–206Pb (±2σ) Ma&lt;sup&gt;a&lt;/sup&gt;</th>
<th>MSWD&lt;sup&gt;h&lt;/sup&gt;</th>
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<tr>
<td>TT51 (n = 88)</td>
<td>263.7 (2.2)</td>
<td>463.0 (11.0)</td>
<td>159 (16)</td>
<td>286 (17)</td>
<td>262.9 (3.0)</td>
<td>261.5 (0.1)</td>
<td>7.0</td>
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<td>Southern Gemeric Betliar granite IR19 and IR20 (N48°44.16′, E 20°31.74′)</td>
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<tr>
<td>IR19A (n = 44)</td>
<td>252.8 (3.2)</td>
<td>458.4 (7.3)</td>
<td>–</td>
<td>–</td>
<td>268.8 (4.0)</td>
<td>268.2 (0.3)</td>
<td>3.5</td>
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<tr>
<td>IR19B (n = 41)</td>
<td>229.0 (3.6)</td>
<td>420.3 (4.9)</td>
<td>–</td>
<td>–</td>
<td>265.6 (4.3)</td>
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<td>IR20A (n = 21)</td>
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<td>297.0 (15.0)</td>
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<td>–</td>
<td>265.7 (4.7)</td>
<td>263.5 (0.5)</td>
<td>4.7</td>
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<tr>
<td>IR20B (n = 12)</td>
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<td>286.5 (4.4)</td>
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<td>TT07 (n = 46)</td>
<td>232.6 (4.3)</td>
<td>282.1 (7.1)</td>
<td>265 (15)</td>
<td>285 (16)</td>
<td>263.9 (4.0)</td>
<td>263.5 (0.3)</td>
<td>6.1</td>
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<td>Southern Gemeric Poprov TT49 (N 48°43.374′, E 20°59.004′)</td>
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<tr>
<td>TT49 (n = 11)</td>
<td>261.9 (6.5)</td>
<td>295.8 (3.4)</td>
<td>275 (16)</td>
<td>284 (14)</td>
<td>273.5 (4.0)</td>
<td>274.1 (1.7)</td>
<td>10.1</td>
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<td>Veporic unit, near Lietnica, Klencove granite TT48 (N 48°32.760′, E 19°49.4920′)</td>
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<tr>
<td>TT48 (n = 26)</td>
<td>248.6 (3.3)</td>
<td>272.3 (4.3)</td>
<td>276 (16)</td>
<td>285 (15)</td>
<td>263.1 (3.2)</td>
<td>264.0 (0.7)</td>
<td>3.2</td>
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Fig. 6. Color CL images of selected zircons from the Veporic (TT48) and Hnilec granites (TT51). Panels indicate the sample numbers (TT48 and TT51), and the scale bar is 50 μm. All ages have been determined by LA-ICP-MS (±2σ), except when indicated. SIMS ages are ±1σ in smaller font and with a smaller spot diameter. The dated spots are circled in each panel. Arrowheads indicate the locations of brighter yellow CL zones on the rims of zircons from sample TT48, which is a characteristic for this sample. Some of the red lines seen in zircons in panels B and C are an artifact of the scanning process.


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oscillatory zoning in CL, some from sample TT51 and IR20B lack zoning or show recrystallized rims. A correlation between CL color and zircon age could not be detected.

Zircon CL colors in the Hnilec granite are dull blue, purple, green, and yellow, and zircons habits range from equidimensional to prismatic (Fig. 7A–D). Most zircons show oscillatory zoning consistent with magmatic crystallization. Notable exceptions include those with weakly luminescent cores and darker rims and those luminescing in green CL with a complexly zoned core. Despite their zoning differences, these grains yielded ages indifferent from other zircons in the sample. The oldest Permian-age zircon from the Hnilec sample is 286 ± 17 Ma (SIMS). Using LA-ICP-MS, the oldest, more precise Permian age result is 278.7 ± 3.6 Ma. The youngest LA-ICP-MS zircon age from this sample is Triassic (236.7 ± 2.2 Ma) for a zircon core that luminesces a darker blue (Fig. 7D).

Southern Gemeric granite sample TT07 also yields two Triassic LA-ICP-MS zircon U–Pb ages (232.2 ± 4.3 Ma and 249.3 ± 5.1 Ma, Fig. 7E), that are remarkably similar to those of the Hnilec pluton samples. In total, forty-six spots were analyzed on eighteen zircons from sample TT07. The zircons show green and blue colors in CL, and most have distinct cores and show oscillatory zoning, consistent with magmatic crystallization. Some grains exhibit complexly zoned cores (Fig. 7E–I) but yielded ages consistent those obtained from other grains from the same sample. Two zircons yielded two highly imprecise and discordant SIMS Carboniferous ages (306 ± 28 Ma and 330 ± 26 Ma, ±1σ), but such ages are found in the central sections of zircons that yielded Permian results using LA-ICP-MS (e.g., Fig. 7I). The oldest SIMS Permian age is 285 ± 16 Ma (±1σ), which is consistent with the oldest and more precise LA-ICP-MS Permian age of 282.1 ± 7.1 Ma (±2σ) (Fig. 7I). Such ages are also found in the interior of the dated grains. The youngest SIMS age is 261 ± 15 Ma (±1σ).

Two Triassic zircons were also found in Betliar sample IR19B (229.0 ± 3.6 Ma, 241.9 ± 3.4 Ma, LA-ICP-MS). Zircons in Betliar samples IR19A (n = 44 spots) and IR19B (n = 41 spots) were dated using LA-ICP-MS depth-profiling and, therefore, were not imaged in CL. The youngest zircon age from sample IR19A is 252.8 ± 3.2 Ma, which is older than the youngest grains in sample TT51, TT07, and TT48. Two zircons extracted from IR19A and IR19B yield Ordovician, Silurian and Carboniferous ages.
(458.4 ± 7.3 Ma and 456.2 ± 7.0 Ma, and 420.3 ± 4.9 Ma and 319 ± 10 Ma, respectively). The oldest Permian grains from samples IR19A and IR19B are similar with ages of 281.2 ± 3.4 Ma and 281.5 ± 3.5 Ma, respectively. Both the average and weighted mean ages that are Permian and younger from these samples are also similar to those from the other Gemeric granite zircons dated in this study (Table 3).

Fig. 7J–N displays the CL images from Betliar samples TT20A and TT20B, which show blue or dark grey luminescence colors. Zircons from sample IR20A are euhedral and subhedral, most showing faint zoning or complexly zoned cores. The zircons were only dated using LA-ICP-MS. Twenty-one spots on 16 grains from sample IR20A yielded Permian ages only, ranging from 289.6 ± 4.5 Ma to 254.0 ± 3.4 Ma (LA-ICP-MS). Sixteen spots on 13 zircons from sample IR20B gave mostly discordant (from 0.6% to 58.2% discordance) with only three showing Permian ages (264.7 ± 7.6 Ma, 275.5 ± 4.4 Ma, and 286.5 ± 4.4 Ma). Most gave Ordovician to Devonian ages and range from 460.3 ± 5.7 Ma to 416.7 ± 7.7 Ma. Most IR20B zircons appear metamict and show no luminescence.

Eleven spots were analyzed on three zircons in Poproč sample TT49. CL zoning of those zircons that showed luminescence consistent with an igneous origin (see Villaseñor et al., 2021 for images). This sample yielded only Permian ages that range from 295.8 ± 3.4 Ma to 261.9 ± 6.5 Ma (LA-ICP-MS). The weighted mean and average ages for the granites are all inconsistent with a single population (Table 3). The oldest Permian weighted mean age (excluding sample IR20B) is from the Poproč granite, (sample TT49, 274.1 ± 1.7 Ma, MSWD = 10.1). The youngest weighted mean U–Pb age stems from the Hniléc pluton (sample TT51, 261.5 ± 0.1 Ma, MSWD = 7).

4.3. Meliata radiolarites

We dated 40 spots on 36 zircon detrital grains extracted from a radiolarite sample (TT08) that overlies altered blueschists in the Meliata Unit (Fig. 8). These detrital zircons range in age from 1522 ± 20 Ma (Mesoproterozoic) to 263.9 ± 2.7 Ma (Permian). Three other Permian zircons overlap in age with the Gemeric granites and Klenovec zircon ages (276.6 ± 5.0 Ma, 288.8 ± 3.9 Ma, and 296.6 ± 3.4 Ma). All of these analyses are concordant. CL images of the grains show green to blue colors, and the youngest zircon has a CL-dark core.

5. Discussion

The early Paleozoic zircon U–Pb ages from the Gemeric granites dated in this study are Middle Ordovician to Late Silurian (463 ± 11 Ma, 458.4 ± 7.3 Ma, 420.3 ± 4.9 Ma; Table 3, Fig. 6) and are found in the northern Hniléc and southern Betliar granite bodies. These ages are consistent with the widespread occurrence of Ordovician granite associated with arc magmatism along the northern Peri-Gondwanan convergent margin (e.g., Linnemann et al., 2007; von Raumer et al., 2002, 2013; Vozárová et al., 2012). Geochemical data from the Betliar samples indicate that the granites are strongly differentiated, of syn-collisional character and must have been generated from a very clay-rich or pelitic source (e.g., Broska and Kubiš, 2004; Kohút et al., 1997; Petrík and Kohút, 1997; Uher and Broska, 1996). The weighted mean and average ages from the Gemeric granite dated in this study (Table 3) and oldest zircons are found in the Betliar (297 ± 15 Ma) and Poproč (295.8 ± 3.4 Ma). In contrast, the youngest zircons are Triassic and are found in the Betliar pluton (229.0 ± 3.6 Ma) and the southern Elisabeth Mine granite (232.6 ± 4.3 Ma). We found no evidence of a southward-decreasing age trend for Gemeric granites, nor any zircon age differences between northern and southern hotline exposures (e.g., Radvaneck et al., 2009).

Instead, the zircon U–Pb ages demonstrate that the Gemeric granites formed during a single magmatic event and likely share a common source (e.g., Broska and Kubiš, 2019; Broska and Uher, 2001; Kohút, 2012; Petrík and Kohút, 1997; Uher and Broska, 1996). The weighted mean age of zircons dated from the Klenovec granite is likewise Permian (264 ± 0.7 Ma, Table 3), and its youngest zircon is early Triassic (248.6 ± 3.3 Ma). Hence, Permian magmatism was thus not restricted to the Gemeric Superunit and is likewise a characteristic of the Veporic Superunit. The similar intrusion ages of granites in the Gemeric and Veporic units implies that they were likely genetically-related.

Although the dated Gemeric and Veporic Superunit granite samples yielded similar Permian crystallization ages, most Veporic granitoids are Carboniferous in age with Cambrian or Lower to Middle Ordovician
inherited cores (e.g., monazite, 472 ± 4 Ma and 345 ± 3 Ma, Ondrejka et al., 2016; zircon, 514 ± 25 Ma and 348 ± 31 Ma, Putiš et al., 2001; 470–440 Ma and 440–350 Ma, Gaab et al., 2005). Rb–Sr mineral isochrons for Veporic granites are 392 ± 5 Ma and 387 ± 27 Ma (Cambel et al., 1989), whereas discordant zircon ages range from 370 ± 68 Ma and 346 ± 9 Ma (Michalko et al., 1999). Veporic porphyric metadiorites and tonalities gave early Carboniferous zircon ages (357 ± 2 Ma, Broska et al., 2013; 346 ± 1 Ma, Putiš et al., 2001). Similar inherited zircons were documented in this study from the Klenovec (Veporic) and Hnilec (Gemeric) granites. The youngest ages previously reported for the Veporic magmatic assemblages are from early Triassic plagiogranitic-aplite veins that cross-cut basement rocks (zircon U–Pb, 233 ± 4 Ma, Putiš et al., 2001) and a rifting-related biotite leucogranite (Hrončok, zircon thermal ionization mass spectrometry, U–Pb, 238.6 ± 1.4 Ma, Putiš et al., 2000; 267 ± 2 Ma, Ondrejka et al., 2021).

Late to post-Variscan Permian igneous activity has been reported throughout Western Europe (e.g., 285–280 Ma, Ziegler et al., 2004; 295–293 Ma, Timmerman, 2004; 280–240 Ma, McCann et al., 2006; 290–280 Ma). Other granites further east with the Paleo-Tethyan realm record similar ages, such as in Romania (264.2–266.7 Ma, see review in Szemerédi et al., 2020) to the Aegean (e.g., Istanbul-Zonguldak zone’s Bolu Massif 273–255 Ma, see review in Ustaömer et al., 2016) and the Cyclades (e.g., Ios Island, Flansburg et al., 2019). The Gemeric and Veporic granites likely were generated during Permian post-collisional extension (e.g., Fig. 9A). This tectono-magmatic scenario is characteristic for the Permian of the Central and Southern Alps, Western Carpathians, and Western Mediterranean (e.g., Broska and Kubiš, 2019; Putiš et al., 2000; Ustaömer et al., 2016). The widespread occurrence of Permian magmatism in the European Variscan domain has been interpreted as evidence for regional magmatic destabilization of the Moho in response to a thermal surge (e.g., Ziegler et al., 2004). The surge involved significant lower crustal melting, upward displacement of the Moho, and delamination of the mantle-lithosphere, which contributed substantially towards the thinning of the Variscan crust (e.g., Froitzheim et al., 2008).

The Veporic zircons differ from the Gemeric zircons in that they have distinct yellow rims in CL (Fig. 6), a feature not observed in the Gemeric zircons. The yellow CL color is characteristic of lower temperatures compared to blue luminescence (e.g., Tsuchiya et al., 2015). Although the narrowness and location of the rims precluded dating in spot mode on exposed cross sections, we suspect they are likely to be due to subsequent Alpine alteration or re-heating that affected the Veporic Superunit, and that this did not occur in the Gemeric samples. The zircon saturation temperatures for both Gemeric and Veporic granites are similar (Table 2), so the presence of the lower temperature overprints was likely caused by Alpine deformation events. The Veporic Superunit also experienced by Cretaceous magmatism (e.g., 75.6 ± 1.1 Ma, Poller et al., 2001; 82 ± 1 Ma, Hraško et al., 1999; 81.5 ± 0.7 Ma, Kohút et al., 2013).

Fig. 10 shows a probability density diagram for zircon U–Pb ages from the granites of the Gemeric Superunit, the Veporic Superunit’s Klenovec granite (TT48), and the Meliata Unit’s radiolarite (TT08). All plots show identical major mid-Permian age maxima for the Veporic granite (265.2 Ma), Gemeric granites (264.3 Ma), and Meliata radiolarite (264.0 Ma). The detrital zircon ages obtained for the Meliata radiolarite reveal distinct peaks in the age probability distribution that are nearly identical to the Veporic and Gemeric granites. Most of the Permian detrital zircons also show blue colors in CL and oscillatory zonning, consistent with a volcanic origin. Permian volcanic rocks have long
been recognized in different parts of the Carpathian–Pannonian region (e.g., Dostal et al., 2003; Vozárová et al., 2012; Szeremédi et al., 2020). Hence, numerous options exist for volcanic terranes in the vicinity of the Meliata Ocean that could have provided Permian igneous zircons similar to those dated in the radiolarians.

The age probability density diagram (Fig. 10) for the Meliata Unit shows that the youngest zircon dated in the sample is 263.9 ± 2.7 Ma. Based on previous published work, structural relationships, fossil contents, and proximity, we propose that the radiolite unit was deposited in the Meliata Ocean (e.g., Putiš et al., 2019) and is characterized by a 264 maximum depositional age for the Dobšiná location at that time. This age is consistent with the timing of opening of the Meliata Ocean due to the northwestern subduction of the Paleotethyan Ocean (e.g., Putiš et al., 2019). Radiolarians in carbonate strata that overlie the blueschist and harzburgite-lizardite serpentinite assemblages south of Dobšiná indicate Jurassic deposition in distal flysch (Havrilla and Ožvoldová, 1996). Fig. 9C shows a paleogeographic reconstruction of the region with the Meliata Ocean clearly developed by 230 Ma (Stampfl and Kozur, 2006). This is consistent with our zircon ages indicating that Meliata Ocean pelagic sedimentation likely initiated during the mid-Permian (~264 Ma).

The most abundant detrital zircon age peak in the probability density diagram for sample T708 is Carboniferous (~310 Ma; Fig. 10), which correlates well with the ages of ignimbrites associated with large volcanic centers that developed within the Variscan realm, such as the Teplice-Altenberg Volcanic Center (Erzgebirge, Germany) or the Brandov-Olbernhau Basin (see Hoffmann et al., 2013; Opluštil et al., 2016).

6. Conclusions

The age and composition of the granites within and surrounding the Gemeric Superunit are critical for understanding and constraining the evolution of the present Western Carpathian Mountains and deciphering its relationship to other tectonic units in central and eastern Europe exposed along the Paleotethyan Ocean (e.g., Broska and Kubíš, 2019; Froitzheim et al., 2008; Lexa et al., 2003). The Gemeric Superunit (Western Carpathians) is characterized by Permian rae metal-granites that formed from pelitic sources, likely due to post-orogenic extension of crust thickened after the collisional phase of the Variscan orogeny. Based on the inherited zircon ages and Gemeric granite geochemical compositions, the source may have accumulated detrital zircons during the Middle Ordovician to Late Silurian. The Gemeric Superunit correlates with lower structural levels of the Austroalpine nappe system. Zircon ages from northern (Hnilé) and southern Gemeric granites (Betliar, Elisabeth Mine, Poproč) yielded Permian zircon U–Pb ages that overlap with those of the Klenovec granite found in the adjacent Veporic Superunit. Color CL images of the Klenovec zircons show yellow luminescence, consistent with lower temperature and likely the result of an intensive Alpine-related imprint not found in the Gemeric zircons. The zircon ages, however, indicate similar sources and provide further evidence of widespread Permian magmatism that extends from the European Variscan internal domain to the western Mediterranean. The ages of the Gemeric and Veporic granites also overlap the youngest zircons from sediments that overlap parts of the Meliata Ocean units. Although the detrital zircons in the Meliata radiolarite may have been sourced from multiple volcanic centers active throughout the region, sedimentation in this ocean fragment may have begun during the mid-Permian (~264 Ma).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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