

Reactivation of Variscan subduction-modified mantle during Middle Triassic rifting: Insights from andesitic pyroclastics of northern Adriatic passive margin (Mt. Žumberak, NW Croatia)

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ABSTRACT

This study presents mineralogical, petrological, and geochemical data on Middle Triassic (Late Anisian; Illyrian) pyroclastic rocks interstratified with siliciclastic and carbonate sediments within the volcano-sedimentary succession of Mt. Žumberak. The succession represents part of the Northwestern Croatian Triassic Rift Basin (NCTRB) located at the junction of the Southern Alps, the Pannonian domain, and the Dinarides. The pyroclastic material is dominated by crystal–vitric tuffs. Whole-rock geochemical signatures indicate an andesitic composition of calc-alkaline to shoshonitic affinity. Geochemical systematics reveal that magma generation was strongly controlled by inheritance from earlier subduction processes. The subcontinental lithospheric mantle source was metasomatically modified during Variscan subduction through the addition of sediment-derived components, producing a chemically heterogeneous lithospheric mantle domain enriched in fluid- and melt-mobile elements. During subsequent Middle Triassic lithospheric extension, rift-related adiabatic melting selectively reactivated the preconditioned mantle domains, resulting in hybrid magmas that retain a clear subduction-related geochemical imprint despite formation in an extensional tectonic regime. Explosive volcanism was focused along deep-seated crustal discontinuities that acted as inherited structural pathways, linking mantle melting zones with the evolving rift architecture. Pyroclastic material was transported by density currents and/or atmospheric dispersal and deposited together with deep-marine siliciclastic and carbonate sediments within a short-lived, aborted intracontinental extensional or half-graben syn-rift basin. The NCTRB developed along the northern margin of the Adriatic Plate (Greater Adria) during the Middle to Late Anisian and Late Ladinian. Pyroclastic rocks from Mt. Žumberak show a strong positive correlation with genetically related andesitic tuffs of equivalent age exposed elsewhere within the NCTRB, particularly in the Mt. Ivanščica area, supporting a basin-wide magmatic imprint sourced from subduction-modified lithosphere.

KEYWORDS Middle Triassic. Intermediate pyroclastic rocks. Petrology and geochemistry. Mt. Žumberak. NW Croatia.

INTRODUCTION

Middle Triassic magmatism in the western Tethyan realm is expressed by multiphase lava-flow extrusions, diverse types of volcanoclastic deposits, and locally developed intrusive bodies. In a broad geodynamic sense, this magmatic activity is commonly linked to the progressive disintegration of Gondwana and consequently of the Adriatic Plate and/or to the subduction of the Paleotethys Ocean (Castellarin *et al.*, 1988; Philip *et al.*, 1995; McCann, 2008; Storck *et al.*, 2018). Despite this general framework, the petrogenetic and tectonomagmatic models proposed for the origin of Middle Triassic magmatic and volcanoclastic series today present in the Southern Alps, the Dinarides, and the Alpine–Carpathian domain remain highly debated. Significant uncertainties persist regarding magma sources, the relative roles of subduction-related inheritance versus syn-rift processes, and the temporal and spatial evolution of magmatism across these orogenic systems (Aljinović *et al.*, 2010; Casetta *et al.*, 2018; Castellarin *et al.*, 1988; Castorina *et al.*, 2020; Crisci *et al.*, 1984; De Min *et al.*, 2020; Grimes *et al.*, 2015; Harangi *et al.*, 1996; Lustrino *et al.*, 2019; Nardini *et al.*, 2025; Obenholzner, 1991; Ogonye *et al.*, 2024; Pamić, 1984; Pamić and Balen, 2005; Saccani *et al.*, 2015; Slovenec *et al.*, 2023, 2025; Smirčić, 2017; Storck *et al.*, 2018; Trubelja *et al.*, 2004; Velicogna *et al.*, 2023; Velledits, 2006; Vukovski *et al.*, 2026).

Volcanic activity that developed along the northern margin of the Adriatic Plate during the Middle Triassic is today exposed at the surface as hectometre- to kilometre-scale volcano-sedimentary slivers, documented at several localities within the intra-Pannonian Mountains of northwestern Croatia, including Ivanščica, Strahinjščica, Desinić Gora, Kuna Gora, Ravna Gora, and Žumberak (Fig. 1). While basic volcanic rocks, predominantly basalts, dominate the volcanic record of these mountain blocks (Slovenec and Šegvić, 2021; Slovenec *et al.*, 2025), intermediate pyroclastic deposits represented by andesitic tuffs are rare and occur exclusively at Mt. Ivanščica (Slovenec *et al.*, 2020) and Mt. Žumberak. Volcanism was expressed mainly through submarine effusion of basaltic lava flows, accompanied by subordinate but recurrent explosive eruptions producing volcanoclastic material of andesitic to rhyolitic composition (Slovenec and Šegvić, 2021; Slovenec *et al.*, 2023, 2025; Vukovski *et al.*, 2026). Volcanic, pyroclastic and volcanoclastic rocks are commonly interstratified with sedimentary successions, together forming well-developed volcano-sedimentary sequences that record the syn-rift evolution of the basin system (Kukoč *et al.*, 2023).

Although the Middle Triassic volcano-sedimentary successions of the Northwestern Croatian Triassic Rift Basin exposed on Mt. Ivanščica, Mt. Strahinjščica, and Mt. Kuna Gora have been the subject of several studies over the past

decade (Goričan *et al.*, 2005; Kukoč *et al.*, 2023; Slovenec and Šegvić, 2021; Slovenec *et al.*, 2023, 2025; Smirčić *et al.*, 2024; Vukovski *et al.*, 2026), the pyroclastic rocks of Mt. Žumberak have remained essentially unstudied. Previous investigations of the broader Žumberak area were limited to regional mapping projects conducted during the preparation of the Basic Geological Map of the SFR Yugoslavia at a scale of 1:100,000 (Pleničar *et al.*, 1975; Šikić *et al.*, 1977; Fig. 1C). The main objective of this study is, therefore, to provide a detailed mineralogical, petrological, and geochemical characterization of the Middle Triassic pyroclastic rocks of Mt. Žumberak that are interstratified with siliciclastic and carbonate sediments. Furthermore, this work aims to constrain the tectonomagmatic setting of their formation and to establish correlations with compositionally and stratigraphically equivalent Middle Triassic units from the wider region of northwestern Croatia. These results provide new constraints on the geological processes and the geodynamic evolution of the northern margin of the Adriatic Plate (Greater Adria) during the Middle Triassic.

GEOLOGICAL SETTING

In a geotectonic sense, the Mt. Žumberak area belongs to two major tectonic units, namely the Pre-Karst–Bosnian Flysch domain of the Adriatic Plate and the High Karst, as defined by Schmid *et al.* (2008) (Fig. 1A). Recent structural, tectonic, and stratigraphic investigations of Middle Triassic volcano-sedimentary successions within the intra-Pannonian Mountains of northwestern Croatia indicate that these successions belong to the Northwestern Croatian Triassic Rift Basin (NCTRB; Kukoč *et al.*, 2023) today preserved in the northernmost segment of the Dinarides, more precisely to the Pre-Karst unit of the Internal Dinarides (Vukovski *et al.*, 2024), not to the Southern Alps as previously suggested (Schmid *et al.*, 2008, 2020; van Gelder *et al.*, 2015). In this context, the Mt. Žumberak area can be interpreted both as part of the Dinaridic domain and as the southwestern segment of the NCTRB.

Mt. Žumberak is mostly composed of Triassic dolomite, and to a lesser extent of clastic and carbonate deposits ranging in age from the Permian to the Quaternary (Pleničar and Premru, 1977; Šikić *et al.*, 1979). Simplified geological map of the neighbouring area (SW Croatia and E Slovenia) is shown in Figure 2B, and more detailed geological map in Figure 2C.

The immediate area around the recorded sections is composed of Lower Triassic clastites, Middle and Upper Triassic dolomite, Upper Cretaceous calcareous flysch-like sediments and deep-water limestone in the southwestern part of the terrain, and clastites of Neogene age in the south-eastern part (Fig. 1C).

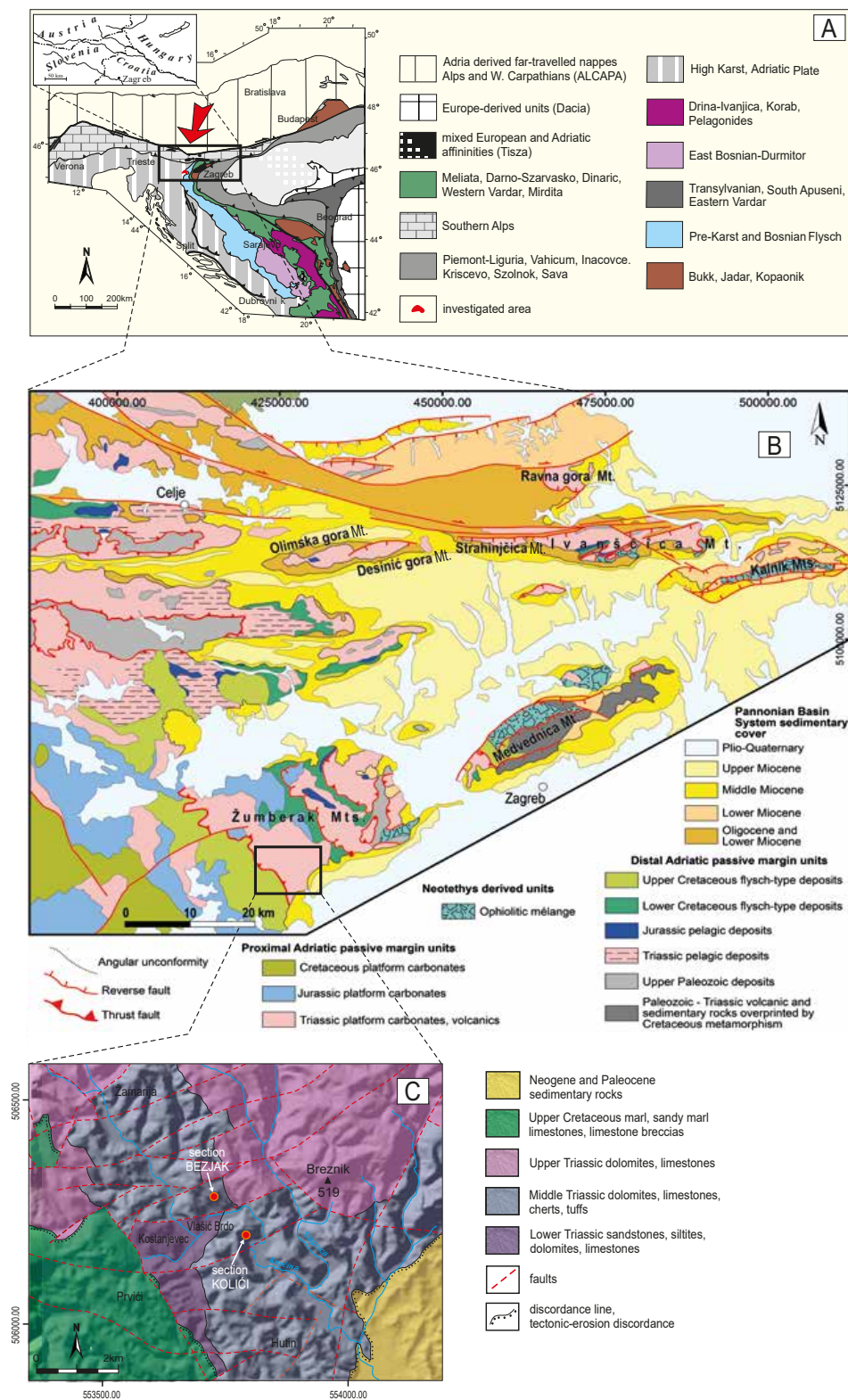


FIGURE 1. A) Geotectonic sketch map of the major tectonic units of the Alps, Carpathians and Dinarides (simplified after Schmid *et al.*, 2008). The inserted map (upper left corner): regional geographic overview. B) Geological map of the SW Croatia and E Slovenia (simplified and modified after Basic Geological Maps of former Yugoslavia on the 1:100,000 scale, sheets Celje (Buser, 1977), Rogatec (Aničić and Juriša, 1984), Varaždin (Šimunić *et al.*, 1982), Novo Mesto (Plenić *et al.*, 1975), Zagreb (Šikić *et al.*, 1977) and Ivanić Grad (Basch, 1981)). C) Detailed geological map of the investigated area (after Basic Geological Maps of former Yugoslavia on the 1:100,000 scale, sheets Novo Mesto (Plenić *et al.*, 1975) and Zagreb (Šikić *et al.*, 1977)).

Lower Triassic strata are mostly clastics. The lower part is siliciclastic, made of violet and reddish micaceous sandstone and siltstone, with lesser amounts of reddish-brownish ooid limestone (Fig. 1C). The upper part is made of carbonate clastites, represented by an alternation of ooid limestone and marl, with some dark grey micritic limestone and dolomite near the boundary with the Anisian (Avanić *et al.*, 2000).

The Anisian is represented mostly by dolomite (Fig. 1C; Bukovac *et al.*, 1995; Grgasović, 2007). The dolomite is crystalline, especially in the upper part of the Anisian, or there is an alteration of dolostromatolite, dolopelmicrite and fenestral dolopelmicrite. Very rare foraminifera *Meandrospira dinarica* and *Pilamina densa* are found, besides fragments of the dasyclad alga *Physoporella pauciforata* (Grgasović, 2022), that corroborated the Anisian age of deposits. Within the Anisian dolomite, a thin interval composed of reddish sandy marl occurs, representing a short episode of clastic input onto the platform.

The Upper Anisian succession is characterized by very complex lithology (Grgasović, 2007; Vidaković *et al.*, 2023). Basal part is usually made of crystalline dolomite, occasionally of shallow-marine limestone with “nests” of sparite cement similar to those described on Mt. Ivanščica (Goričan *et al.*, 2005). These are followed by a lithologically varied succession of greenish pyroclastic, reddish and grey ‘filamentous’ thin-bedded and nodular limestone, tuffaceous and silicified limestone, chert, radiolarite and siltstone. The uppermost part occasionally consists of very dark grey and black siltstone with intercalations of tuff (Fig. 1C). A rich fossil content, including microfossils (Goričan *et al.*, 2005; Grgasović, 2007) and ammonites (Vidaković *et al.*, 2023) have been found in this interval. This succession stems from rifting that gave rise to the interruption of carbonate sedimentation accompanied by volcanic activity. The shallow-water depositional environment was reestablished in Ladinian, characterised by formation of crystalline dolomite, which is deposited on top of the Anisian deep-water sediments that filled the newly formed tectonic grabens/basins.

The Upper Triassic consists of very thick dolomite succession (Fig. 1C; Grgasović, 1997, 2007; Pavičić *et al.*, 2021). The Carnian is represented by well-bedded dolomite with rhythmical (shallowing-upward) alternations of dolomicrite, fenestral dolomicrite and dolostromatolite, with thin intercalations of yellow siltstone. In the upper level of the Carnian, very dark dolomudstone with intercalations of black kerogenous shale and coal are locally present. Carnian age has been documented by fossil foraminifera and algae (Grgasović, 1997) and palynomorphs (Bukovac *et al.*, 1997; Grgasović, 2007). Continuously overlying

the Carnian dolomite is a thick Norian–Rhaetian “Main Dolomite” (“Hauptdolomite”) formation. It is characterised by the frequent alternation of dolomicrite, fenestral dolomicrite and dolostromatolite. Bedding planes are not pronounced, and dolomite occurrences have a massive appearance, typically with stylolites. The crystalline “sucrose” dolomite is also common. Fossil content is low, but point out to Norian–Rhaetian age of dolomite (Bukovac *et al.*, 1997; Grgasović, 1997, 2007).

MATERIALS AND ANALYTICAL METHODS

This study is based on data obtained from two lithostratigraphic sections, Kolići and Bezjak (Fig. 2), logged in the Mt. Žumberak area of northwestern Croatia (Fig. 1C). Although the primary focus of the investigation was pyroclastic rocks, sedimentary units interstratified with them were also briefly analysed and interpreted from both lithostratigraphic and biostratigraphic perspectives. Following preliminary optical microscopic characterization, eight representative pyroclastic rock samples were selected for further analytical procedures. Classification of pyroclastic rocks was conducted according to the scheme proposed by Schmid (1981).

X-Ray powder Diffraction (XRD) was used to infer on the modal mineral composition of all representative samples (Appendix Table I; for details see Table 2 in Šegvić *et al.*, 2023). The measurements were carried out at Texas Tech University’s Geosciences Clay Laboratory using a Bruker D8 Advance diffractometer. The XRD procedure included a step scan in the Bragg-Brentano geometry with CuK α radiation (40 kV and 40 mA). Analysed material was scanned for 1.8 s per 0.02°, from 3° to 70 °2 θ . The interpretation of XRD traces was conducted using the Bruker EVA software coupled with the PDF4 database released by the International Centre for Diffraction Data.

Whole-rock chemical compositions of eight representative pyroclastic rock samples (Appendix Table II) were determined by X-Ray Fluorescence (XRF) for major elements and Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) for trace elements at Texas Tech University’s GeoAnalytical Laboratory. Analytical accuracy and precision for trace element determinations were assessed using the USGS BHVO-2 analytical glass standard (Jochum, 2005; for analytical details see Šegvić *et al.*, 2022). Major and trace element concentrations were measured with accuracies better than $\pm 1\%$ and $\pm 5\%$, respectively, corresponding to 3σ at ten times the detection limit. Detection limits were as follows: TiO $_2$ and MnO = 0.001 wt.%; SiO $_2$, Al $_2$ O $_3$, Fe $_2$ O $_3$, MgO, CaO, Na $_2$ O, K $_2$ O, and P $_2$ O $_5$ = 0.01 wt.%; Lu = 0.002 ppm; Eu = 0.005 ppm; Ta, Pr, Sm, Gd, Ho, Er, Yb, and U = 0.01 ppm; Th, La,

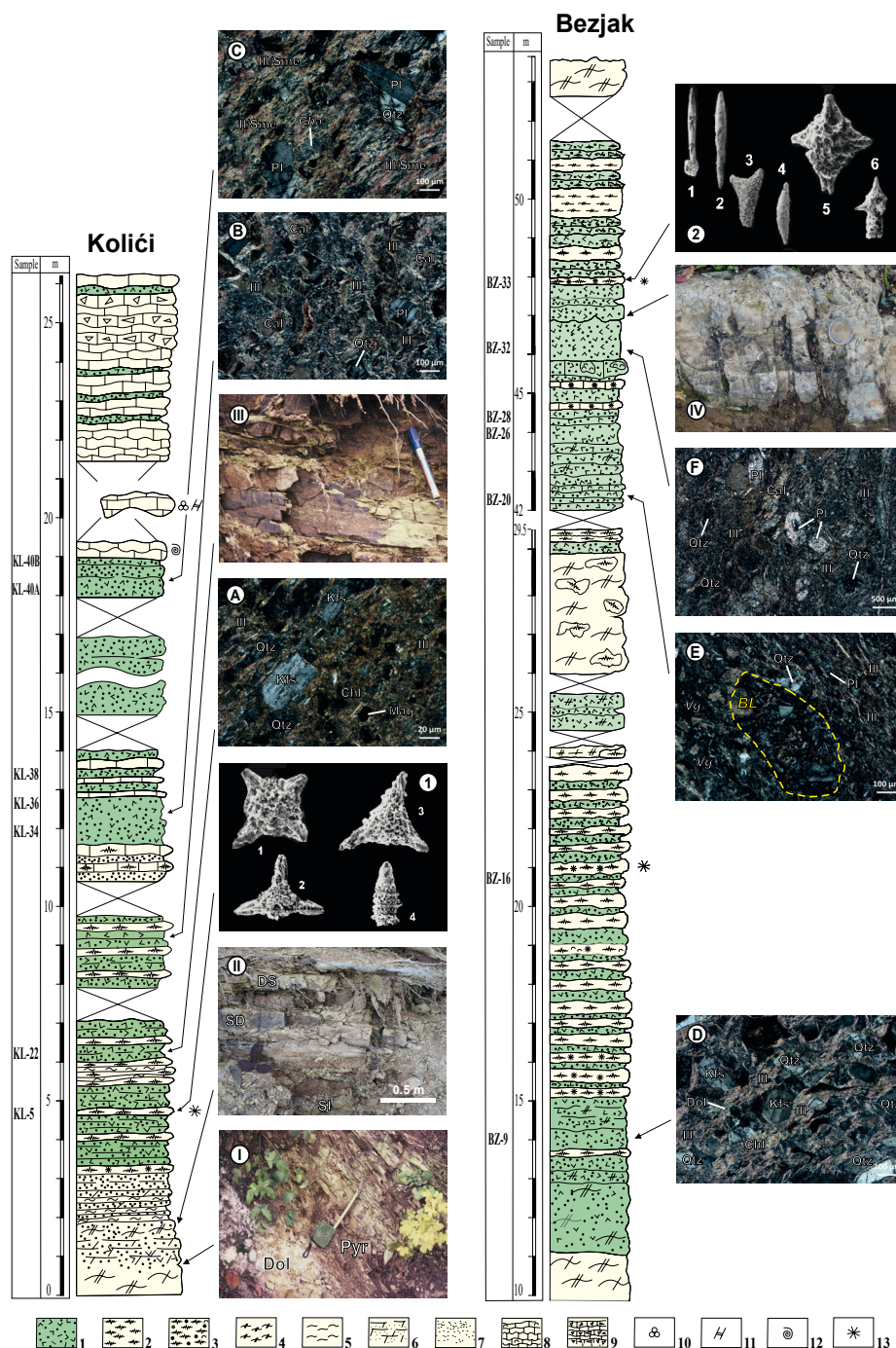


FIGURE 2. Lithological sections of the investigated area in the southern part of the Mt. Žumberak. Legend: 1 = tuff; 2 = chert; 3 = radiolarian chert; 4 = massive dolomite; 5 = shale; 6 = silty dolomite; 7 = siltstone; 8 = pelecypode limestone; 9 = breccated dolomite; 10 = foraminifera; 11 = calcareous algae; 12 = cephalopoda; 13 = radiolarians. Representative photographs of a I) gradual transition from crystalline dolomite (Dol) in left lower corner over tuffitic dolomite to tuffite (Pyr) on the right side of the picture (scale = 25 cm); II) intercalation of gray silty dolomites (SD) and greenish dolomitic siltstones (DS) with green-gray siltstones (SI); III) thick layered fine-grained vitric/crystal-vitric tuffs; IV) fine-grained crystal-vitric tuff. Microphotographs of thin section of a A) fine-grained crystal-vitric andesite tuff (sample KL-22) N+; B) fine-grained crystal-vitric andesite tuff (sample KL-36) N+; C) crystal-vitric andesite tuff (sample KL-40A) N+; D) vitric-crystal andesite tuff (sample BZ-9) N+; E) fine-grained lithic-vitric andesite tuff (sample BZ-20) N+; F) crystal-vitric andesite tuff (sample BZ-32) N+. Abbreviations (after Whitney and Evans, 2010): Cal = calcite, Chl = chlorite, Ill/Sme = illite/smectite, Kfs = K-feldspar, Mag = magnetite, Pl = plagioclase, Qtz = quartz. Cha = chalcedony; Vg = volcanic glass; BL = basalt lithoclast. Radiolarian taxa from chert (Goričan et al., 2005; not to scale). The scanning electron micrograph number is indicated for each illustration. 1) 1 = *Tiborella anisica* Kozur and Mostler – Late Anisian; 2 = *Eptingium manfredi* Dumitrica – Late Anisian; 3 = *Eptingium ramovsi* Kozur, Krainer and Mostler – Late Anisian; 4 = *Triassocampe deweveri* Nakaseko and Nishimura – Late Anisian; 5) 1 = *Paroertispongia multispinosus* Kozur and Mostler – Late Anisian; 2 = *Paroertispongia multispinosus* Kozur and Mostler – Late Anisian; 3 = *Archaeospongoprunum bispinosum* Kozur and Mostler – Late Anisian; 4 = *Archaeospongoprunum mesotriassicum* Kozur and Mostler – Late Anisian; 5 = *Tiborella* cf. Florida (Nakaseko and Nishimura) – 200X – Late Anisian; 6 = *Tetraspinocyrtis* sp. – Late Anisian.

Ce, Nd, and Tm = 0.05 ppm; Cs and Hf = 0.1 ppm; Nb = 0.2 ppm; Y = 0.5 ppm; Sc, Rb, and Zr = 1 ppm; Sr = 2 ppm; Ba = 3 ppm; V and Pb = 5 ppm; and Cr and Ni = 20 ppm. Analytical quality was further monitored by replicate analyses performed on approximately 12 % of the samples.

Neodymium and Sr isotopic compositions of three bulk rock samples (Table 1) were measured at the Noble Gas Laboratory Pacific Centre for Isotopic and Geochemical Research, University of British Columbia using a Triton Plus mass spectrometer. Normalizing ratios of $^{146}\text{Nd}/^{144}\text{Nd}$ = 0.7219 and $^{86}\text{Sr}/^{88}\text{Sr}$ = 0.1194 were assumed. The average JNd-i standard run at $^{143}\text{Nd}/^{144}\text{Nd}$ = 0.512079 $\pm$ 0.000008 (n = 22, 2σ). The data is reported relative the recommended value of $^{143}\text{Nd}/^{144}\text{Nd}$ = 0.512115 (Tanaka et al., 2000). The BCR-2 USGS standard run at $^{143}\text{Nd}/^{144}\text{Nd}$ = 0.512642 $\pm$ 0.000008, within error identical to the reference value of $^{143}\text{Nd}/^{144}\text{Nd}$ = 0.512637 $\pm$ 0.000012 (Weis et al., 2006). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the NBS 987 Sr standard for the period of measurement was 0.710242 $\pm$ 0.000030 (n = 92, 2σ). Total procedural blanks were ~500 pg and ~150 pg for Sr and Nd, respectively.

RESULTS

Short description of lithologies and biostratigraphy

The studied geological sections are located on the south-eastern slopes of Mt. Žumberak in the valley of the Kupčina River on its right bank (Fig. 1C).

Section Kolići

The base part of section (0-0.7 m) consists of grey, crystalline dolomite that in the lower part (0.7-3.2 m) transition from grey, silty dolomite and greenish tuffitic dolomitic siltstone to an alternation of green siltstone (Figs. 2, I-II) with cm- to dm-thick interlayers of grey metasomatic chert. At the middle part of the section (3.2-12.8 m), green and dark red pyroclastic rocks (crystallovolcanic (Figs. 2, III) and lithocrystallovolcanic tuff) with interlayers of dark grey, orange, and red glassy chert with radiolarian skeletons are registered. The middle part of the section

ends with an alternation of dark red calcite siltstone and nodular, grey-red, silicified limestone with pelecypods (12.8-14 m). Partly covered interval (14-19 m) consists of an alternation of green weathered pyroclastites and green-violet siltstone follows, at the top of which grey-red weakly silicified limestone with ammonites occur (19-19.4 m). In the covered interval of the upper part of the section (19.4-21.4 m), grey nodular silicified limestone was recorded. The upper part of the section (21.4-26.2 m) is composed of silicified plate to layered brecciated limestone interbedded with cm-thick weakly tuffitic siltstones.

In the lower part of the section (~ 5 m; Fig. 2 - sample KL-5) a rich radiolarian fauna was determined (Goričan et al., 2005). It defines the Upper Anisian (Illyrian) age of these deposits: *Paroertlispongia rarispinus* Kozur and Mostler, *Eptingium ramovsi* Kozur, Krainer and Mostler, *Tiborella anisica* Kozur and Mostler, *Triassocampe deweveri* (Nakaseko and Nishimura). *Eptingium ramovsi* Kozur, Krainer and Mostler and *Tiborella anisica* Kozur and Mostler are known only from the Illyrians.

Additionally, the foraminifera *Meandrosira dinarica* Kochansky-Devidé and Pantić and *Endotriadella wirzi* (Koehn-Zaninetti), and the algae *Macroporella alpina* Pia and *Thaumatoporella parvovesiculifera* (Raineri) were determined within the limestone boulder of uncertain primary origin (Fig. 2 - upper part of the section). The age was determined as Pelsonian-Lower Illyrian.

Two poorly preserved ammonites have been found in nodular limestone of this section and described by Sakač (1994) as *Flexoptychites* sp. and *Arcestes* (*Proarcestes*) *subtridentinus*. Later Vidaković et al. (2023) corrected this determination as *Flexoptychites acutus* (Mojsisovics) and *Proarcestes* sp. At the nearby locality of Vlašić Brdo (Fig. 1C) Sakač (1994) found in secondary samples relatively rich ammonite assemblage, that is determined by Vidaković et al. (2023) as *Japonites raphaeliszoja* (Tommasi), *Falsanolcites recubariensis* (Mojsisovics), *Protrachyceras ladinum* (Mojsisovics), *Flexoptychites acutus* (Mojsisovics), *Gymnites* cf. *incultus*, *Monophylites* sp., *Sturia* sp. *Proarcestes* sp. and *Discoptychites* sp.

TABLE 1. Nd and Sr isotope data of the andesite tuffs from the Žumberak Mt. (NW Croatia)

Sample	Location	Rock type	Sm/Nd	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	Rb/Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}_{(t)}$	$\varepsilon_{\text{Nd}(t)}$ ^a	$^{87}\text{Sr}/^{86}\text{Sr}_{(t)}$ ^b	Time(t) [*]
KL-40B	1	At	0.19868	0.120112	0.512341(4*10 ⁻⁶)	0.89286	2.585409	0.712426(15*10 ⁻⁶)	0.512150	-3.42	0.703526	243 Ma
BZ-32	2	At	0.18808	0.113704	0.512370(6*10 ⁻⁶)	0.88732	2.569290	0.712039(11*10 ⁻⁶)	0.512189	-2.65	0.703195	243 Ma

Errors in brackets for Nd and Sr isotopic ratios are given at the 2 σ -level. The method of calculating the errors is presented in the analytical techniques chapter.

¹⁴⁷Sm/¹⁴⁴Nd calculated from the ICP-MS concentrations of Sm and Nd following equation: $^{147}\text{Sm}/^{144}\text{Nd} = (\text{Sm}/\text{Nd}) \cdot [0.53151 + 0.14252 \cdot (^{143}\text{Nd}/^{144}\text{Nd})]$.

The $^{87}\text{Rb}/^{86}\text{Sr}$ ratios calculated from Rb and Sr ICP-MS concentrations (displayed in ppm) following the equation: $^{87}\text{Rb}/^{86}\text{Sr} = (\text{Rb}/\text{Sr}) \cdot [2.6939 + 0.2832 \cdot ^{87}\text{Sr}/^{86}\text{Sr}]$.

^aInitial $\varepsilon_{\text{Nd}(t)}$ calculated assuming $^{147}\text{Sm}/^{144}\text{Nd}_{\text{CHUR}} = 0.1966$, and $\lambda_{\text{Sm}} = 6.54 \cdot 10^{-12} \text{ a}^{-1}$. ^bInitial $^{87}\text{Sr}/^{86}\text{Sr}_{(t)}$ calculated assuming $\lambda_{\text{Rb}} = 1.42 \cdot 10^{-11} \text{ a}^{-1}$.

^{*}Corresponding time for the initial ε_{Nd} and initial isotopic ratios for Nd and Sr. B = basalt. At = andesite tuff. The locations of the samples are shown in Figure 1C.

This association, after Vidaković et al. (2023), indicates that the upper portion of the succession spans at least the Avisianum subzone (upper Illyrian)–Longobardicum subzone (“middle” Longobardian), but additional data is needed for drawing more robust conclusions.

At the nearby Vlačić Brdo locality, in the probably lower stratigraphic level than that of the investigated sections, within the gray micrite limestone with filaments, the Middle Triassic foraminifera *Arenovidalina chialingchiangensis* and *Ophthalidium* spp., as well as the alga *Anisocellula fecunda*, described from the upper Pelsonian of the dolomite by Senowbari-Daryan et al. (1993) have been documented.

Section Bezjak

The Bezjak section is located about 1 km northwest of Kolići section, on the left bank of Kupčina River (Fig. 1C). The lower part of the section (0–11 m), consists of massive light grey to yellowish microcrystalline dolomite. In the upper part of this package, the colour of the dolomite changes to olive greenish, and reddish spots of the ferruginous component appear in the rock. The greenish colour comes from the admixture of tuffaceous component. Towards the top of the section (11–15 m), the amount of tuff increases and the rock turns into tuffite with admixtures of dolomitic component. The transition to a package of rocks about 10 m thick (15–23.8 m) with an alternation of medium- to coarse-grained vitrocrytalloclastic greenish andesite tuffs and gray-reddish glassy and radiolarian cherts is gradual with an increase in the yield of tuff material. After a few meters of the partially covered part (23.8–26 m), light gray massive intensely silicified fine-crystalline dolomite is documented (26–28.9 m). Silicification is expressed in the form of nodules of gray vitreous chert likely of metasomatic origin. The upper part of the package (28.9–29.5 m) is covered by layered grey chert alternating with tuffitic dolomite with barely visible lamination. After the covered interval (29.5–42 m), there is an alternation of fine-grained lithovitroclastic and crystallo-vitroclastic andesite tuff (Figs. 2, IV) with radiolarian greyish-reddish chert with rare cm-thick interlayers of grey tuffitic limestone with filaments (42–51.5 m). The following radiolarian fauna was determined in that part (Fig. 2 - sample BZ-33) *Paroertlispongos multispinosus* Kozur and Mostler, *Archaeospongoprimum bispinosum* Kozur and Mostler, *Archaeospongoprimum mesotriassicum* Kozur and Mostler, *A. mesotriassicum* Kozur and Ostrer, *Tiborella* cf. *florida* (Nakaseko and Nishimura), *Eptingium manfredi* Dumitrica s.l., *Tetraspinoctyrtis* cf. *anisica* Kozur and Mostler, *Tetraspinoctyrtis* sp., *Bulbocyrtium* sp., and *Triassocampe* cf. *coronata* (Bragin) which indicates an Illyrian age (Goričan et al.,

2005). After the covered interval (51.5–52.7 m) the top part of the section (52.7–53.8 m) is composed of massive, light grey medium-grained crystalline dolomite.

Petrography of pyroclastic rocks

The dominant type of pyroclastic rocks comprises crystal–vitric tuffs (Figs. 2, III), whereas vitric and lithic–vitric varieties of greyish-green colour occur subordinately. Although volcanic material predominates in most of the analysed tuff samples (exceeding 90 vol.%) relative to sedimentary components, samples from the lower part of the Kolići section contain a significant terrigenous component and, therefore, represent transitional varieties toward tuffite (Figs. 2, I). Rock structures are crystallo–vitrophyric, litho–crystallo–vitrophyric, and vitrophyric, whereas textures are predominantly massive with locally pronounced parallel orientation of phyllosilicate flakes (Fig. 2A–F).

The tuff matrix, which commonly constitutes more than 70 vol.% of the total rock volume, is predominantly devitrified in all analysed samples and is composed mainly of dioctahedral micaceous phases (Fig. 2A–F). In X-ray diffraction patterns, their 001 reflections are markedly broad and asymmetric toward lower θ angles, whereas the 111 and 021 reflections are poorly defined. The measured $d(060)$ values range between 1.503 and 1.504 Å. These features indicate presence of either i) illitic component enriched in Fe and/or Mg, ii) celadonic component (*sensu lato*, not celadonite), or iii) mixtures of both phases. Smectite was detected only in subordinate amounts and exclusively in sample KL-40A (Table I; Fig. 2C). The tuff matrix is also commonly composed to a significant extent of cryptocrystalline quartz (chalcedony; Fig. 2C). In XRD traces, quartz reflections appear relatively broader pointing out to quartz crystallites smaller than ~ 100 μm . Chalcedony aggregates in these pyroclastic rocks represent products of partial to complete devitrification of volcanic glass. Relicts of volcanic glass are only locally preserved (Fig. 2E), and amorphous component detected by XRD in several samples from the Kolići section (Table I) is most likely related to these glass remnants. Further products of glass devitrification include zeolite (heulandite or clinoptilolite) identified in samples from the Bezjak section while subordinate chlorite is likely of detrital origin (Fig. 2A, D). Variable amounts of calcite are present in several analysed samples (Fig. 2B, F), whereas dolomite occurs in significant proportions only in sample BZ-9 (Fig. 2D). Accessory phases include opaque magnetite (?) and ilmenite, together with their alteration products limonite (?) and leucoxene, and very rare pyrite.

Depending on the tuff variety, crystalloclasts and rare lithoclasts are embedded within an altered crypto- to microcrystalline matrix, predominantly of psammitic

grain size (up to 0.8 mm). Magmatic crystalloclasts in the tuff are represented by idiomorphic to allotriomorphic K-feldspar, plagioclase, and secondary albite (Fig. 2A–F). Although generally well preserved, plagioclase and K-feldspar in the upper part of the Bezjak section are strongly heterogeneous and altered to sericite, chlorite, and calcite, resulting in the preservation of only relic crystal morphologies (Fig. 2F; sample BZ-32). Subordinate amounts of angular terrigenous quartz crystalloclasts are present in samples from both sections (Fig. 2A, C–F), together with larger volcanic glass fragments (up to 0.1 mm; Fig. 2E) and particles of volcanic ash. Lithoclasts (up to 1.2 mm) consist of angular, altered ophitic andesite with turbid textures, observed exclusively in the upper part of the Bezjak section (Fig. 2E; sample BZ-20).

Whole rock chemistry of pyroclastic rocks

Table II presents the results of eight whole-rock chemical analyses of representative Middle Triassic pyroclastic rocks from Mt. Žumberak. Nd and Sr isotopic compositions of two selected pyroclastic samples are reported in Table 1. The analysed tuffs are characterized by relatively high SiO_2 , K_2O , and Loss On Ignition (LOI) contents, combined with low MgO , CaO , Na_2O , and P_2O_5 concentrations. Elevated SiO_2 values (up to 68.65 wt.%) are most likely related to a high modal abundance of quartz and/or to passive silica enrichment during sedimentation and/or subsequent diagenesis of the tuffs (Di Leo *et al.*, 2002). Increased K_2O contents in most samples (up to 6.21 wt.%) reflect the significant

proportion of dioctahedral micaceous minerals as well as a substantial modal contribution of K-feldspar. The rocks are characterized by generally high LOI values (up to 10.14 wt.%), and by selective enrichment of moderately mobile Large-Ion Lithophile Elements (LILE), particularly Cs and Ba (Table II). Concentrations of compatible elements Cr and Ni, although moderately variable, are generally low (Cr = 5–128 ppm; Ni = 3–31 ppm), and similar behaviour is observed for V (12–125 ppm). Collectively, these features indicate that whole-rock geochemical data must be interpreted with considerable caution. To evaluate element mobility, elemental concentrations were plotted against Zr (Fig. 1), which was used as a standard differentiation index (Pearce, 1975; Shervais, 1982; Staudigel *et al.*, 1996). The lack of correlation between most major element oxides (except TiO_2 and P_2O_5), as well as LILE and transitional metals, with Zr on variation diagrams clearly indicates their moderate mobilization and demonstrates that they have not retained their primary magmatic abundances. In contrast, positive correlations of High-Field-Strength Elements (HFSE; e.g., Th, Nb, Ta, Hf, Y) and Rare-Earth Elements (REE) with Zr suggest their largely immobile behaviour during post-magmatic processes, implying preservation of their primary magmatic concentrations. This allows petrogenetic interpretations to be primarily based on HFSE and REE systematics, whereas LILE and transitional metals are considered only with caution. Accordingly, instead of the conventional Total Alkali Silica (TAS) classification scheme (Cox *et al.*, 1979), the more robust Nb/Y versus $\text{Zr}/\text{TiO}_2 \times 0.0001$ discrimination

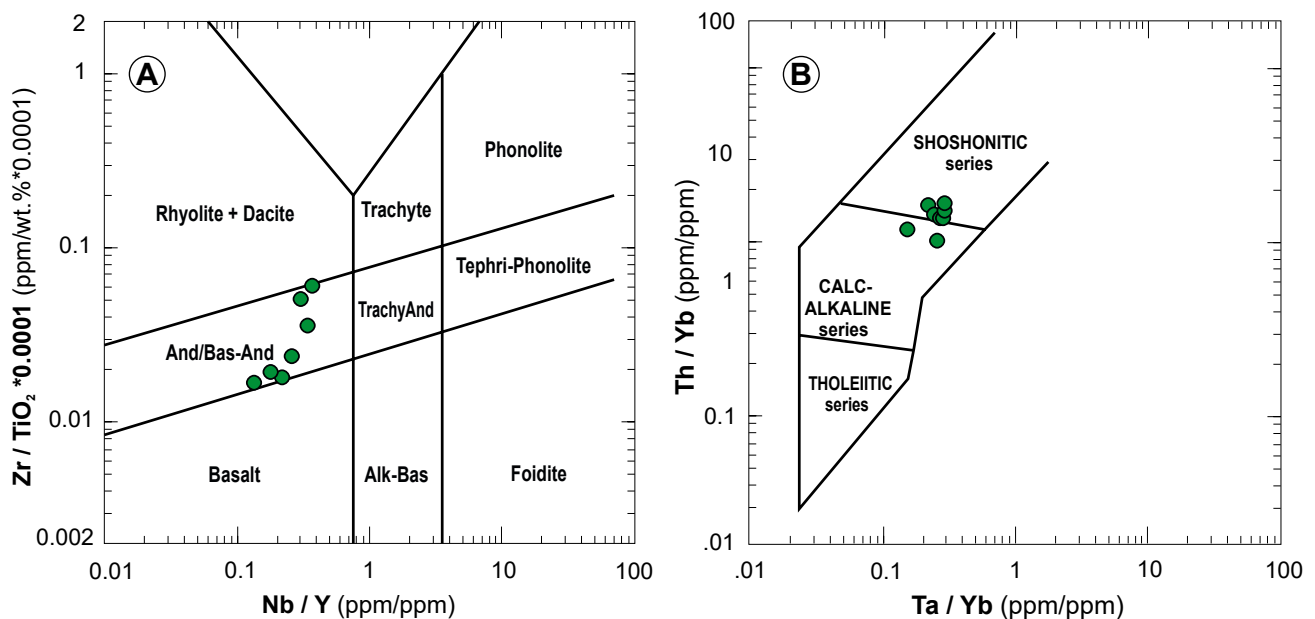


FIGURE 3. A) Classification diagram Nb/Y – $\text{Zr}/\text{TiO}_2 \times 0.0001$ after Pearce (1996) and B) Ta/Yb – Th/Yb discrimination diagram after Müller *et al.* (1992) for the Mt. Žumberak andesite tuffs.

diagram proposed by Pearce (1996) was applied. On this diagram, the analysed rocks plot exclusively within the subalkaline basaltic andesite to andesite fields (Fig. 3A). Elevated Th/Yb ratios (>1) further indicate affinity with the calc-alkaline to shoshonitic series (Fig. 3B). However, examination of HFSE and REE concentrations along both logged lithostratigraphic sections, from base to top, reveals no systematic vertical enrichment or depletion trends (Fig. 2; Table II).

Primitive Mantle (PM)-normalized multi-element variation diagrams display highly uniform geochemical characteristics for all analysed samples (Fig. 4A). All patterns show pronounced enrichment in LILE (Cs, Rb, K) and Th relative to HFSE and REE, with enrichment factors ranging from 63 to 1329 times PM values. Except for distinct negative Nb-Ta, Sr, P and Ti anomalies, HFSE and REE display a continuous decrease from La to Lu, forming moderately inclined patterns. Heavy Rare Earth Elements (HREE) vary within a narrow range of approximately 4-10 times PM. All rocks show negative Nb-Ta anomalies $[(\text{Nb}/\text{La})_{\text{PM}} = 0.25\text{--}0.44]$, together with pronounced Ti depletion $[(\text{Ti}/\text{Gd})_{\text{PM}} = 0.18\text{--}0.59]$, and positive Pb spikes $[(\text{Pb}/\text{Pr})_{\text{PM}} = 6.41\text{--}15.60]$. Chondrite-normalized REE patterns exhibit consistent Light Rare Earth Elements (LREE) to HREE fractionation, with $(\text{La}/\text{Lu})_{\text{CN}}$ ratios ranging from 3.17 to 8.25 (Fig. 4B). In the HREE segment, patterns are nearly flat $(\text{Tb}/\text{Lu})_{\text{CN}} = 1.04\text{--}1.54$ at concentration levels approximately 8-25 times higher than chondritic values, suggesting the absence of residual garnet in the mantle source. All samples display variable negative Eu anomalies $(\text{Eu}/\text{Eu}^* = 0.28\text{--}0.75)$, which, together with sharp negative Sr anomalies, indicate significant feldspar fractionation during magma evolution (Sun and Nesbitt, 1978).

The two representative tuff samples show very similar Nd and Sr isotope compositions (Fig. 5A, B; Table 1). The values of the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary between 0.512341 and 0.512370, and 0.712039 and 0.712426, respectively. Given that a well-constrained Late Anisian (Illyrian) age of the volcano-sedimentary succession has been established based on radiolarian assemblages, initial ϵNd values and initial Sr isotopic ratios were calculated for 243 Ma, interpreted as the most probable age of analysed pyroclastic rocks. Initial ϵNd values range from -2.65 to -3.42 , whereas initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary between 0.703195 and 0.703526. The moderately negative $\epsilon\text{Nd}(t)$ values, lower than those of the bulk silicate Earth and approaching values typical of Subducted Continental Material (SCM) (Fig. 5A, B).

DISCUSSION

The deposition of the investigated volcano-sedimentary succession of Mt. Žumberak, characterized by alternating sedimentary carbonate-siliciclastic deposits (crystalline dolomite, silty dolomite, dolomitic/tuffitic siltstone, siltstone; Figs. 2, I), chert, and nodular silicified limestone, together with pyroclastic rocks (tuff; Figs. 2, II-III), took place during the Late Anisian (Illyrian) and most likely continued into the Ladinian. This is corroborated by the findings of radiolarian fauna (Goričan *et al.*, 2005) which suggest the Illyrian (Upper Anisian) age of Kolići and Bezjak sections. This is further supported by ammonite findings in Kolići section (Sakač, 1994; Vidaković *et al.*, 2023). Based on the data from the neighbouring area, the deep water sedimentary-volcanic interval is likely to extent to the Fassanian (Lower Ladinian), but Longobardian

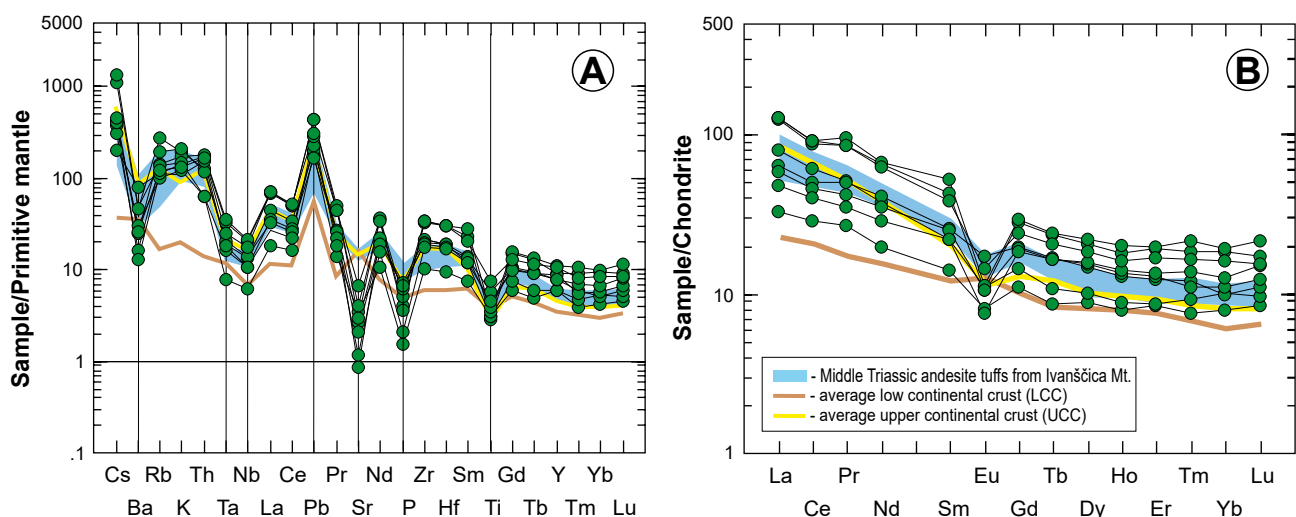


FIGURE 4. A) Primitive mantle-normalised multi-element (Sun and McDonough, 1989) and B) REE patterns (Taylor and McLennan, 1985) for the Mt. Žumberak andesite tuffs. Pattern for the Middle Triassic andesite tuffs from Ivanščica Mt. (Slovenec *et al.*, 2020) and lower/upper continental crust (LCC/UCC; Rudnick and Gao, 2014), are plotted for correlation constraints.

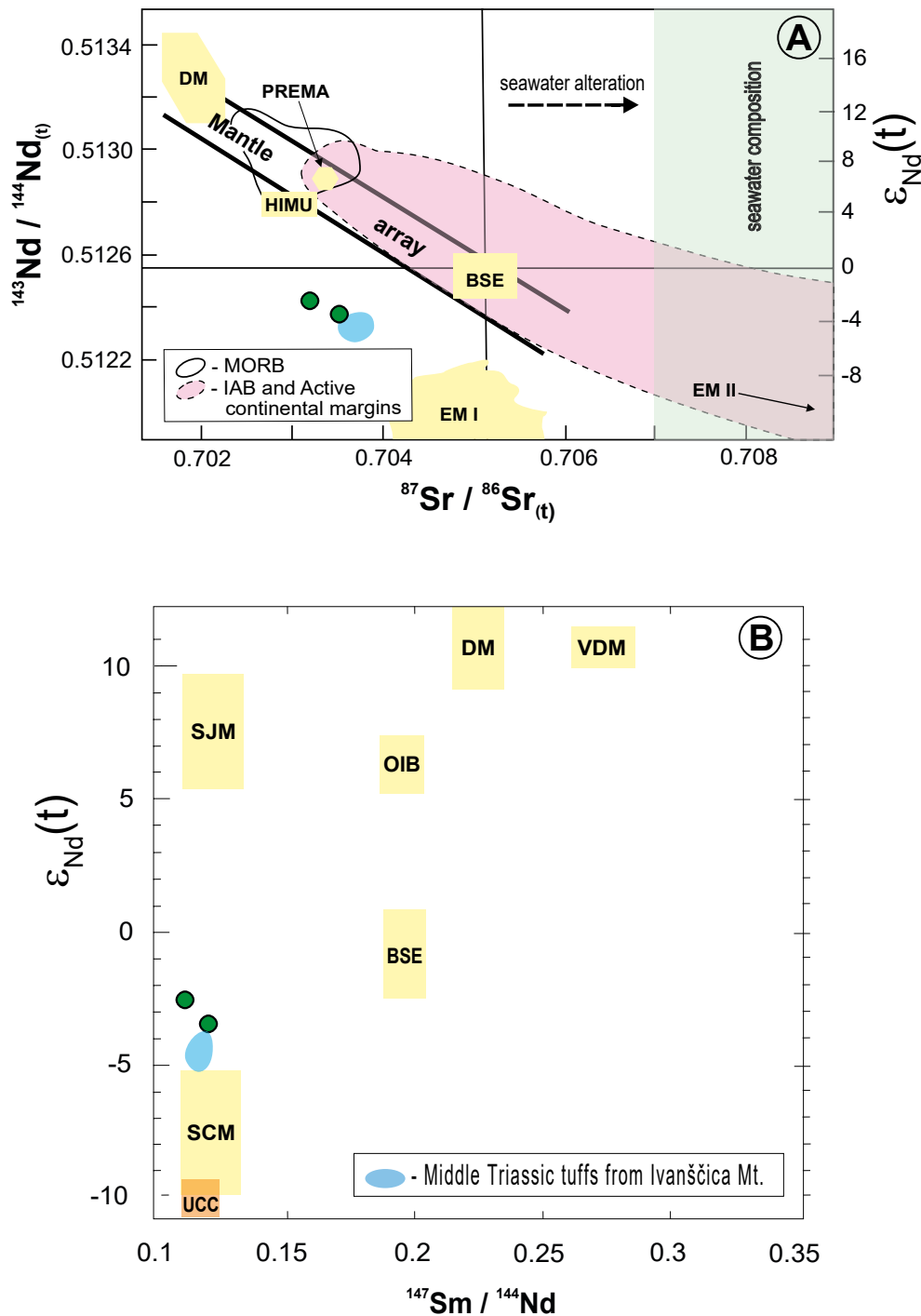


FIGURE 5. A) Initial $^{143}\text{Nd}/^{144}\text{Nd}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios diagram for the Mt. Žumberak andesite tuffs showing the main oceanic mantle reservoirs of Zindler and Hart (1986). DM= Depleted Mantle, BSE= Bulk Silicate Earth, EM I and EM II= Enriched Mantle, HIMU= Mantle with High U/Pb ratio, PREMA= PREvalent MANTle composition. The mantle array is defined by many oceanic basalts and a bulk Earth value for $^{87}\text{Sr}/^{86}\text{Sr}$ can be obtained from this trend. Data for mid-ocean ridge basalts - MORB compiled from Wilson (1989) and references therein and Cousens *et al.* (1994), references therein and Peate *et al.* (1997). Data for oceanic island arcs and active continental margins - IAB compiled from Wilson (1989) and references therein, Cousens *et al.* (1994) and references therein, Pearce *et al.* (1995) and Peate *et al.* (1997). The field for $^{87}\text{Sr}/^{86}\text{Sr}$ values affected by syn- or post-magmatic alteration in contact with seawater (light-green shading) is from Ustaszewski *et al.* (2009). B) $^{147}\text{Sm}/^{144}\text{Nd}$ – $\epsilon_{\text{Nd}}(t)$ isotope ratios diagram for the Mt. Žumberak andesite tuffs. Hypothetical mantle sources: DM = depleted mantle (not refractory), VDM= Very Depleted Mantle (refractory), SJM= Subducted Juvenile Material (subducted oceanic crust; slab with little pelagic sediment), SCM= Subducted Continental Material and BE= Bulk Earth. The observed compositions and hypothetical end members sources calculated for the Middle Triassic following Swinden *et al.* (1990). Fields for Middle Triassic andesite tuffs from Ivanščica Mt. (Slovenec *et al.*, 2020) are plotted for correlation constraints.

(Upper Ladinian) age is yet to be confirmed. Dolomite in the base of investigated sections may be of Pelsonian age, subject to further investigation. No fossil record was reported from the overlying dolomite. The discovery of the first index Carnic fossils about 200 m higher in the section suggests that part of the dolomite from the studied section is also of Ladinian age (Grgasović, 2007). Deposition of investigate deposits occurred in a deep-water environment located along the marginal part of the basin (Goričan *et al.*, 2005).

Although a stratigraphic succession locally comparable to that of the Alpine domain, characterized by platy limestone, chert, and pyroclastic rocks in the lower part (“Buchenstein beds”), overlain by dark shale with *Daonella* (“Wengen beds”), can only occasionally be recognized (e.g. Gregurić Brijeg locality, Goričan *et al.*, 2005) this interval is generally marked by pronounced lateral variability. This is evident from comparisons with Middle Triassic lithostratigraphic successions from northwestern Croatia (Goričan *et al.*, 2005; Grgasović, 2007; Kukoč *et al.*, 2023; Smirčić *et al.*, 2024; Vidaković *et al.*, 2023). At certain localities, the volcano-sedimentary succession directly overlies platform dolomite, as observed in the Kolići section (this study) and in the Brezovica 1 section (Strahinjščica Mt.; Kukoč *et al.*, 2023). In other cases, slope breccias occur at the base of the succession, such as at the Belski Dol locality and partly at the Očura section (Ivanščica Mt.; Goričan *et al.*, 2005). The proportion of black siltstone also varies significantly between sections, from 10 to 60 m (Kukoč *et al.*, 2023) and 25 m (Goričan *et al.*, 2005). Particularly pronounced are variations in the thicknesses of pyroclastic units and basaltic lava flows (Goričan *et al.*, 2005; Kukoč *et al.*, 2023; Slovenec *et al.*, 2025). These pronounced lateral and vertical heterogeneities reflect intense synsedimentary tectonic activity and already developed basin-floor paleorelief.

Petrogenetic, tectonomagmatic and geodynamic significance

The analysed pyroclastic rocks indicate intense, most likely multiphase explosive volcanic activity that persisted throughout the entire period of sediment accumulation (Fig. 2). Volcanism is characterized by a relatively uniform mineralogical composition of andesitic, predominantly crystal-vitric tuffs containing only rare lithoclasts of andesitic lava (Fig. 2A-F). However, due to seafloor hydrothermal alteration processes active during and after accumulation of pyroclastic material, primary mineral phases, clinopyroxene and feldspar, as well as the volcanic glass of the matrix, were extensively replaced by secondary minerals, including clay minerals (illite-smectite), celadonitic mica, chlorite, calcite, quartz (chalcedony), and zeolites (Table I; Fig. 2A-F).

The geochemical and isotopic signatures of analysed high calc-alkaline to shoshonitic andesitic tuffs from Mt. Žumberak indicate that the primary chemical composition of these rocks was modified by secondary hydrothermal alteration and weathering processes (Polat and Hofmann, 2003; Polat *et al.*, 2002), and their petrogenesis involved both the contribution of subducted slab-derived melts and contamination by continental crust. A subduction-related affinity and melt-related subduction metasomatism as well as involvement of subducted crustal material are supported by enrichment in LILE and Th, depletion in HFSE, and the presence of pronounced negative Nb-Ta and Ti anomalies (Fig. 4A; Arculus and Powel, 1986; Elburg *et al.*, 2002; Hofmann, 1997; Pearce, 1983; Pearce *et al.*, 1984; Wallin and Metcalf, 1998), as well as elevated (Hf/Sm)_{PM} ratios (>1; Fig. 6A; La Flèche *et al.*, 1998). In contrast, moderately negative initial εNd(t) values (down to -3.42) and low ¹⁴⁷Sm/¹⁴⁴Nd ratios (≤ 0.120112; Table 1; Fig. 5), together with strongly positive Pb spikes (up to 15.60; Fig. 4A) and the systematic trends of discriminant element ratios shown in Figure 6B-D, represent robust geochemical indicators of continental crustal involvement (Plank, 2005; Swinden *et al.*, 1990; Taylor and McLennan, 1985), which indicates a significant contribution of continental crustal components during genesis of Mt. Žumberak andesitic tuffs. The subcontinental lithospheric mantle source from which the Middle Triassic pyroclastic rocks of Mt. Žumberak were derived through partial melting and subsequent fractional crystallization was therefore most likely strongly preconditioned by incorporation of earlier subducted continental material, probably during Late Palaeozoic Variscan subduction events (Figs. 5B, 6D). This inherited component was subsequently overprinted to a lesser extent by melt-related subduction metasomatism (Fig. 6A). Such processes may have resulted in selective enrichment of LILE within the mantle wedge (Keppler, 1996), the original concentrations of which were later variably modified by secondary hydrothermal alteration. In addition to subduction-related contamination, further assimilation of continental crust may have occurred during magma ascent, most likely during slow and prolonged transport through tectonically weakened zones of the continental lithosphere (Bialas *et al.*, 2010; Huppert *et al.*, 1985).

The tectonomagmatic setting of the investigated Middle Triassic pyroclastic series, as inferred from geochemical and isotopic data, is not straightforward. Key discrimination criteria based on incompatible trace element and REE systematics indicate a subduction-related magmatic affinity for these high calc-alkaline to shoshonitic rocks (Figs. 4A, 7A-C). Such geochemical signatures are characteristic of an ensialic mature volcanic arc environment developed along an active Andean-type

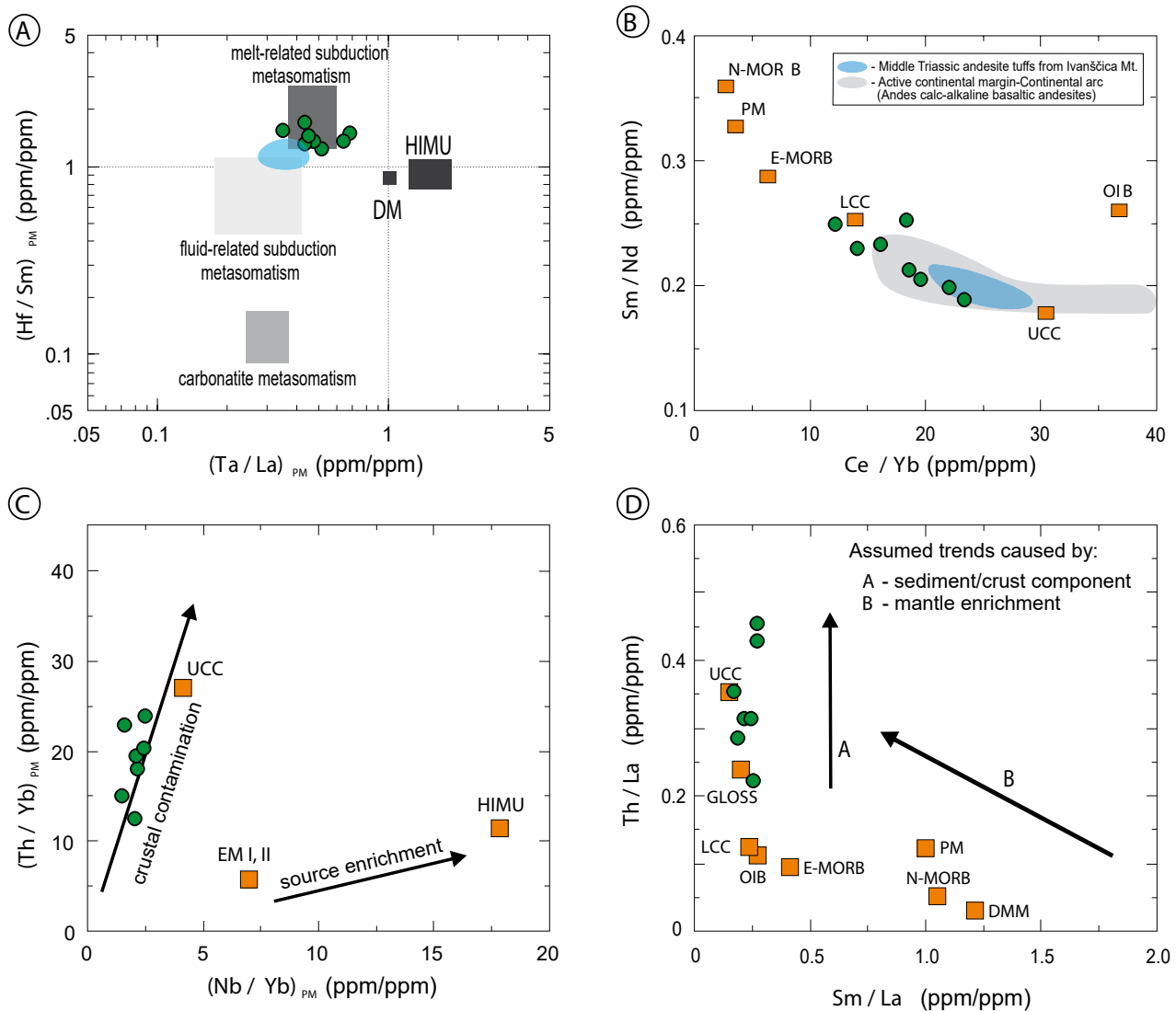


FIGURE 6. Discrimination diagrams for the Mt. Žumberak andesite tuffs. A) $(\text{Hf}/\text{Sm})_{\text{PM}} - (\text{Ta}/\text{La})_{\text{PM}}$ diagram (after La Flèche *et al.*, 1998). B) $\text{Sm}/\text{Nd} - \text{Ce}/\text{Yb}$ diagram. C) $(\text{Th}/\text{Yb})_{\text{PM}} - (\text{Nb}/\text{Yb})_{\text{PM}}$ diagram. D) $\text{Th}/\text{La} - \text{Sm}/\text{La}$ diagram (after Plank, 2005). Abbreviations: [N-MORB= Normal Mid-Ocean Ridge Basalts; E-MORB= Enriched MORB; OIB= Ocean Island Basalts; PM= Primitive Mantle (Sun and McDonough, 1989)]; [UCC= Upper Continental Crust; LCC= Lower Continental Crust (Taylor and McLennan, 1985)]; [GLOSS= Global Subduction Sediment (Plank and Langmuir, 1998); DM/DMM= Depleted MORB Mantle (Workman and Hart, 2005); EM I, II= Enriched Mantle (Condie, 2001); HIMU= Mantle with High U/Pb ratio (Condie, 2001). Field for active continental margin-Continental arc is from Wilson (1989). Fields for Middle Triassic andesite tuffs from Ivanščica Mt. (Slovenec *et al.*, 2020) are plotted for correlation constraints.

continental margin (Fig. 7A-C). However, despite their apparent arc-like geochemical affinity and the clear imprint on the lithospheric mantle, these signatures are more plausibly interpreted as inherited characteristics derived from earlier subduction-modified lithosphere formed during Late Palaeozoic Variscan subduction of the Paleotethys Ocean. A similar interpretation was proposed by Slovenec *et al.* (2020) for compositionally comparable Late Anisian andesitic tuff exposed on the nearby Mt. Ivanščica (Fig. 1B), and likewise by Pe-Piper (1998) and *et al.* (1990) for Triassic volcanic rocks of the Hellenides formed along the northeastern margin of Gondwana.

In this context, the origin of the Late Anisian andesitic pyroclastic series of Mt. Žumberak can be interpreted within two alternative paleogeographic frameworks. The first model, proposed by Stampfli and Borel (2002, 2004) and Stampfli and Hochard (2009), invokes active Middle Triassic northward subduction of the Paleotethyan lithosphere beneath the Eurasian (Adria) Plate, accompanied by hydrous melting within the mantle wedge (Fig. 8A1, A2). The second model, advanced by van Hinsbergen *et al.* (2020) and van Hinsbergen and Schouten (2021), favours passive continental rifting along the northeastern margin of Greater Adria following the rollback of the Paleotethys

slab (Fig. 8B1, B2). In this second scenario, the rift domain was located at a considerable distance from the trench, thereby precluding a direct trench-controlled influence on magma chemistry. The investigated pyroclastic material was, therefore, most likely generated by explosive volcanic activity sourced from the subduction-modified lithospheric mantle and erupted along tectonically weakened crustal zones. Pyroclasts were subsequently transported by density

currents and/or as air-borne material prior to deposition. The Mt. Žumberak pyroclastic deposits were ultimately accumulated together with deep-marine siliciclastic and carbonate sediments (Fig. 2) within an intracontinental simple or half-graben syn-rift basin — the Northwestern Croatian Triassic Rift Basin (*sensu* Kukoč *et al.*, 2023; Fig. 8A2, B2). This basin developed in response to syndimentary extensional tectonics, lithospheric

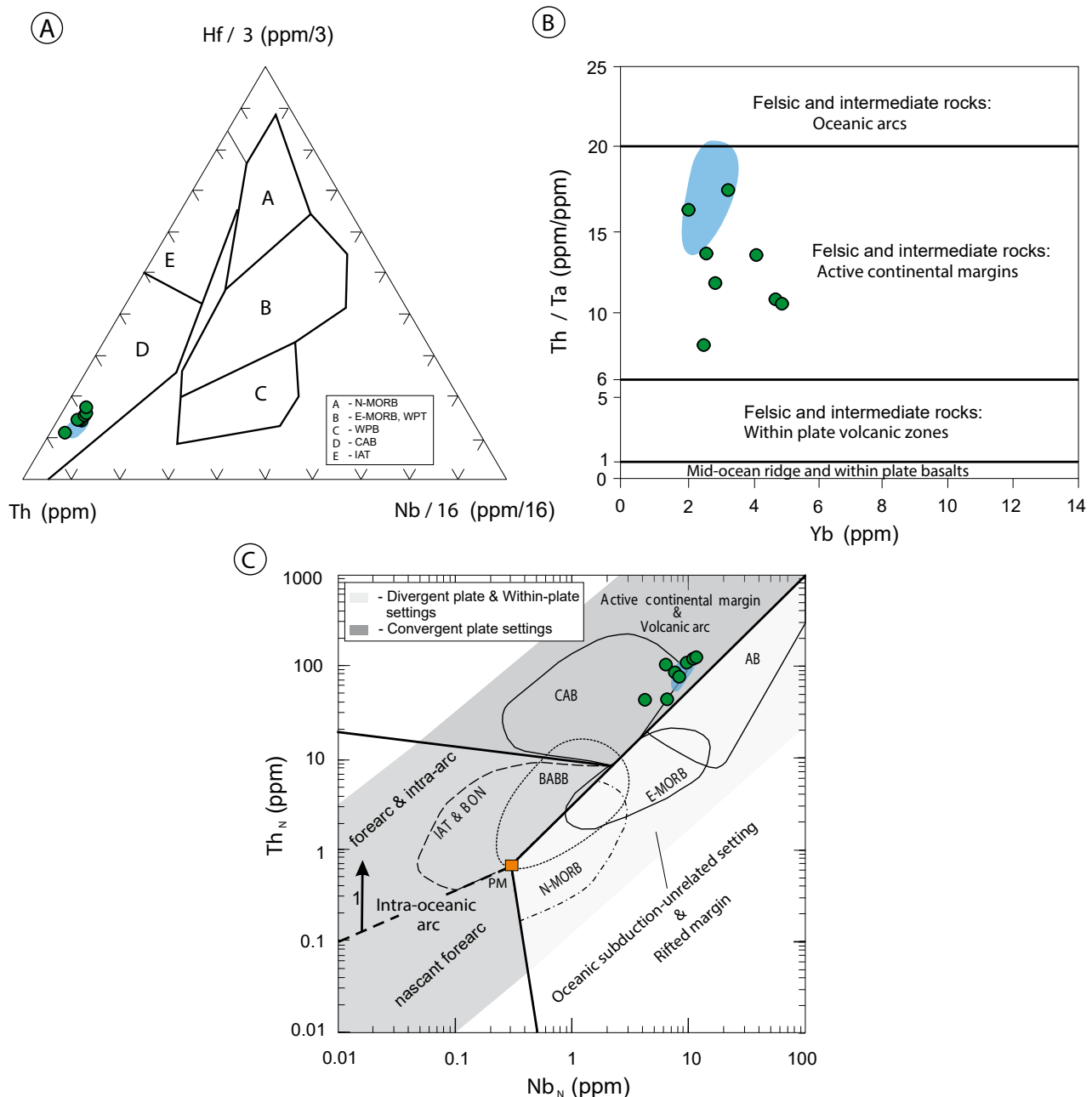


FIGURE 7. Discrimination diagrams for the Mt. Žumberak andesite tuffs. A) Th–Nb/16–Hf/3 diagram (after Wood, 1980). B) Th/Ta–Yb diagram (after Gorton and Schandl, 2000). C) Th_N–Nb_N diagram (after Saccani, 2015). Th and Nb normalized to N-MORB composition (Sun and McDonough, 1989). Abbreviations: PM= Primitive Mantle, AB= Alkali Basalts, BABB= Back-Arc Basin Basalts, BON= BONinites, CAB= Calc-Alkali Basalts, IAT= Island-Arc Tholeiites, N-MORB= Normal Mid-Ocean Ridge Basalts, E-MORB= Enriched MORB, WPT/T= Within Plate Basalts/Tholeiites. Fields for Middle Triassic andesite tuffs from Ivanščica Mt. (Slovenec *et al.*, 2020) are plotted for correlation constraints.

disintegration, and progressive subsidence along the incipient margin of the Adriatic Plate (Greater Adria) during the Middle to Late Anisian. Owing to its short-lived evolution (~3 Ma), the basin persisted only until the Late Ladinian (Kukoč *et al.*, 2023; Smirčić *et al.*, 2024) and did not evolve into a fully developed oceanic domain. Instead, it represents a locally developed, short-lived aborted rift system related to the newly formed Adriatic passive margin facing the immature Neotethys Ocean (Slovenec and Šegvić, 2024; Fig. 8A2, B2). It is important to emphasize that intermediate volcanism generated within the NCTRB, which produced Mt. Žumberak pyroclastic series, although temporally coeval with the regionally widespread alkaline basaltic volcanism of the Maliak/Balkan Neotethys back-arc rift, was not directly petrogenetically related to that system (Slovenec and Šegvić, 2024; Slovenec *et al.*, 2020; Fig. 8A2, B2).

Correlation with similar pyroclastic rocks of the Northwestern Croatian Triassic Rift Basin

Late Anisian pyroclastic rock series represented by calc-alkaline to shoshonitic andesitic tuffs are very rare within the Northwestern Croatian Triassic Rift Basin. In addition to the Mt. Žumberak area, such rocks are exposed only on the eastern slopes of Mt. Ivanščica (Cerina locality; Fig. 1B). To evaluate the potential genetic relationship between these two occurrences, a detailed correlation analysis was performed. Based on their petrographic, geochemical, and isotopic characteristics, as well as their concordant stratigraphic age, the investigated Middle Triassic pyroclastic series of Mt. Žumberak can be positively correlated with the equivalent rock suite exposed approximately 80 km to the northeast at Mt. Ivanščica (Cerina locality; Slovenec *et al.*, 2020; Fig. 1B). Comparison of geochemical datasets (Figs. 47) demonstrates that both andesitic tuff series are genetically very similar, indicating a shared petrogenetic history. Nevertheless, slightly higher MgO/FeO_{tot} ratios and Mg# values of the Mt. Žumberak tuffs relative to those from the Cerina locality on Mt. Ivanščica (0.74–1.63 vs. 0.42–0.57 and 56.9–74.4 vs. 42.7–57.6, respectively) suggest a less evolved geochemical character of the former. Although magmas feeding both pyroclastic series were most likely derived from a common subcontinental lithospheric mantle source, the geochemical record of the Mt. Žumberak tuffs indicates predominantly melt-related subduction metasomatism, in contrast to the Ivanščica tuffs, which record a combined melt- and fluid-related subduction metasomatic signature (Fig. 6A). This distinction implies that, although both pyroclastic series formed contemporaneously, the Mt. Žumberak volcanism likely developed at a greater distance from the old (Variscan) accretionary mantle wedge, in a domain less directly influenced by subduction-zone fluids. Consequently, considering the subsequent Mesozoic–

Cenozoic compressional tectonic events that affected the wider region (Vukovski *et al.*, 2024), it can be inferred that although calc-alkaline to shoshonitic andesitic pyroclastic products are today only sparsely preserved at the surface within the NCTRB, such explosive volcanic activity was probably far more widespread across the incipient Adriatic passive margin, in the Paleotethyan subduction realm during the Late Triassic (Fig. 8).

CONCLUSIONS

Pyroclastic rocks interstratified with siliciclastic and carbonate deposits forming the volcano-sedimentary succession of Mt. Žumberak, located in the contact zone between the Internal (Pre-Karst Unit) and External (High Karst Unit) Dinarides, are of Middle Triassic (Late Anisian; Illyrian) age.

Multiphase explosive volcanic activity persisted throughout the entire period of sediment accumulation.

The pyroclastic succession is dominated by crystal–vitric tuffs with a devitrified matrix composed of illitic and/or celadonic mica, chalcedony, zeolite, chlorite, and calcite, containing crystalloclasts of K-feldspar and plagioclase. Fragments of volcanic glass and andesitic lithoclasts are very rare. Due to presence of terrigenous material, part of the succession represents transitional varieties toward tuffites.

Secondary seafloor hydrothermal alteration processes, accompanied with subsequent weathering, affected the entire pyroclastic series.

The tuffs are of andesitic composition and belong to calc-alkaline to shoshonitic series. They were generated by partial melting and fractional crystallization within the subcontinental lithospheric mantle. The mantle source was most likely strongly contaminated by previously subducted continental material (sediments) during Late Palaeozoic Variscan subduction events and was subsequently modified to a lesser extent by melt-related subduction metasomatism. Additional contamination by continental crust may be attributed to slow and prolonged magma ascent through tectonically weakened zones of the continental crust.

Formation of the Mt. Žumberak volcano-sedimentary series reflects short-lived but highly intense rifting processes and multiphase explosive volcanism along extensional faults developed along the northern margin of the Adriatic Plate (Greater Adria). Pyroclastic material, transported by density currents and/or air-borne dispersal, was deposited during the Late Anisian (Illyrian) together

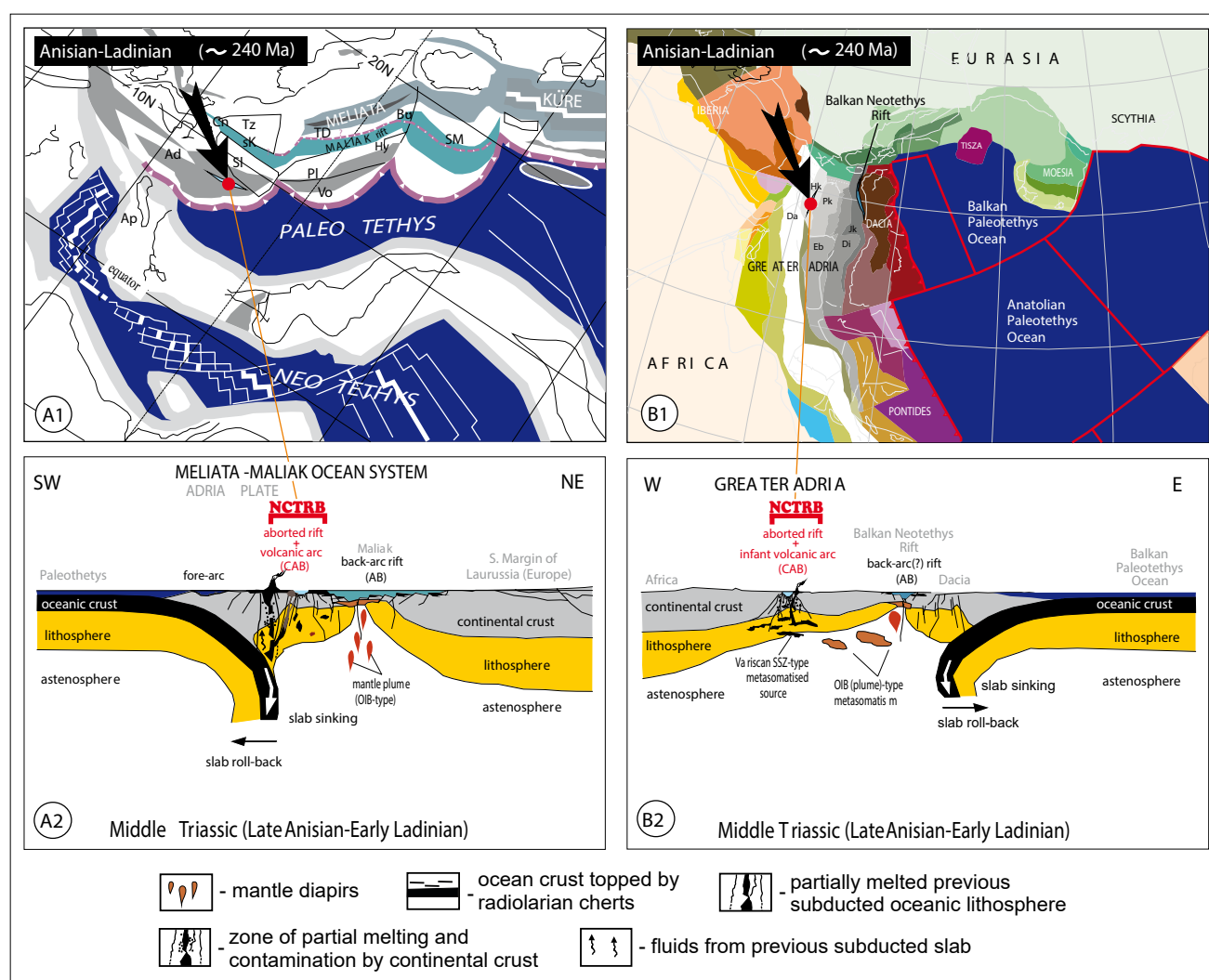


FIGURE 8. Middle Triassic palaeogeographic reconstruction of the Mediterranean region: A1) Anisian–Ladinian (~240 Ma) simplified after Stampfli and Borel (2004) [Ad= Adria Plate s. str., Ap= Apulia s. str., Bū= Bükk, Cn= Carnic-Julian, Hk= High karst, Hy= Hydra, Pl= Pelagonian, sK= south-Karawanken fore arc, Sl= Slavonia, SM= Serbo-Macedonian, TD= Trans-Danubian, Tz= Tisza, Vo= Vourinos (Pindos)] and the second north Balkan subduction zone introduced by Neubauer *et al.* (2019) and Spahić (2024); B1) Anisian–Ladinian (~240 Ma) simplified and slightly modified after van Hinsbergen *et al.* (2020) [Da= Dalmatian Nappe, Di= Drina-Ivanjica Nappe, Eb= East Bosnian-Durmitor Nappe, Jk= Jadar-Kopaonik Nappe, Pk= Pre-Karst Nappe] with location of investigation area (marked with black arrow and red dot symbol). Schematic geodynamic model (scale is approximate) [slightly modified after Slovenec and Šegvić 2024] for: A2) interaction of active continental margin magmatic activity (subduction-related ensialic volcanic arc magmatism) and roughly contemporaneous proto back-arc rifting according to Stampfli and Borel (2004) palaeogeographic reconstruction shown in A1. B2) Ensialic infant arc-back-arc rifting in the central part of the Mediterranean region according to van Hinsbergen *et al.* (2020) palaeogeographic reconstruction shown in B1. Abbreviations: NCTRB= Northwestern Croatian Triassic Rift Basin; CAB= Calc-Alkaline and shoshonitic Basalts/volcaniclastites, AB= Alkaline Basalts, OIB= Ocean Island Basalts.

with deep-marine siliciclastic and carbonate sediments within a short-lived (aborted) intracontinental simple or half-graben syn-rift basin — the Northwestern Croatian Triassic Rift Basin.

Mineralogical–petrological and lithostratigraphic correlation between Mt. Žumberak pyroclastic series and equivalent successions exposed elsewhere within the Northwestern Croatian Triassic Rift Basin (Mt. Ivanščica; Cerina locality) indicates a clear genetic relationship between these volcanic events.

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DISCLOSURE STATEMENT

The authors declare that they have no conflict of interest.

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APPENDIX I

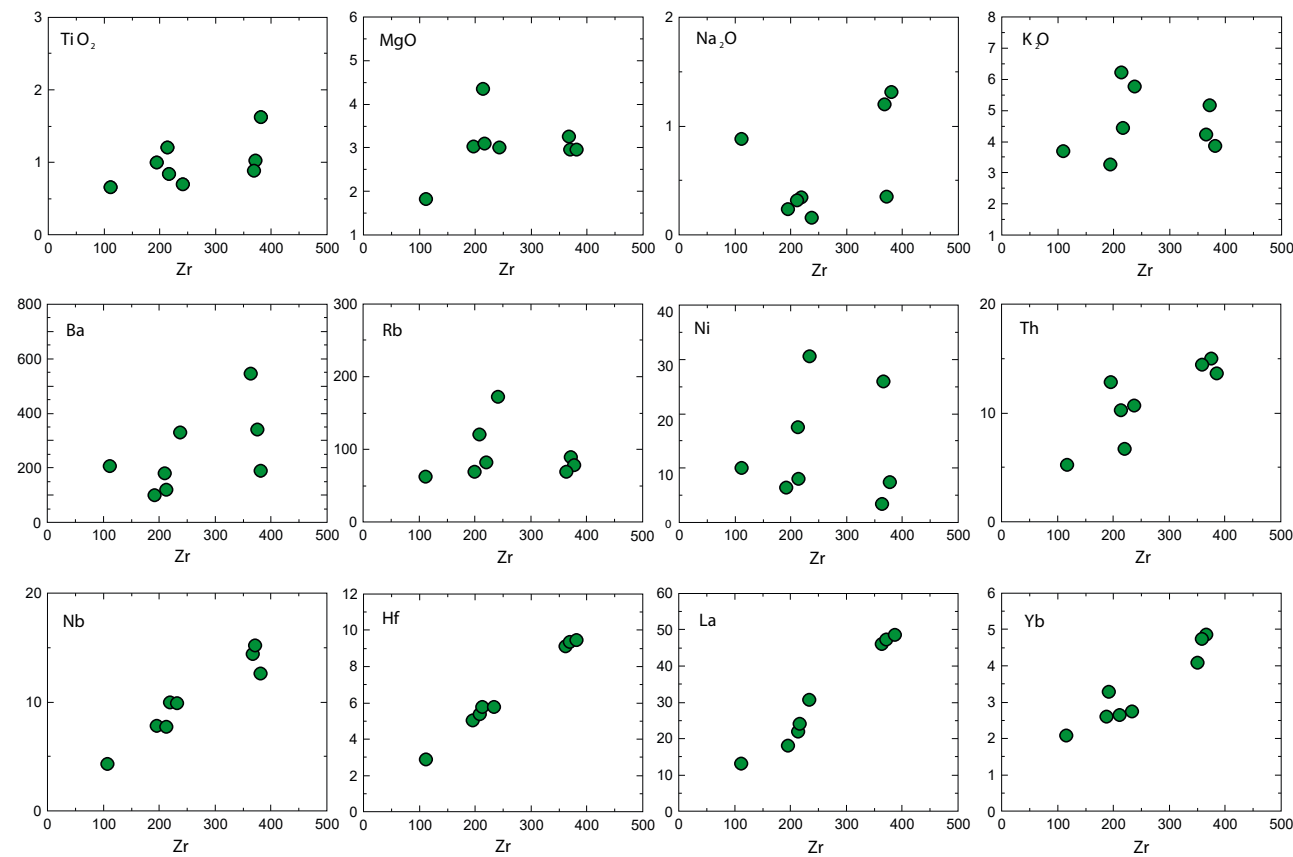


FIGURE I. Variation diagrams for selected elements with Zr as index of differentiation for the Mt. Žumberak andesite tuffs.

TABLE I. Distribution and XRD relative abundances of primary and alteration phases in andesite tuffs from the Žumberak Mt. (NW Croatia)

Sample	Qtz	Kfs	Pl	Ill	Sme	Chl	Cal	Dol	Zeol	AC
KL-22	++	++		+++		+				
KL-34	++		+	+++						+
KL-36	+		+	+++			+			+
KL-38	+		+	+++			+			+
KL-40A	++		+	++	+					+
KL-40B	+		++	+++						+
BZ-9	++	+		+++		+		++		
BZ-20	++		++	+++					+	
BZ-26	++		++	+++					+	
BZ-28	+		++	+++					+	
BZ-32	++		++	++			+		+	

Abbreviations: AC = Amorphous Component; Cal = Calcite; Chl = Chlorite; Dol = Dolomite; Ill = Illite; Kfs = K-feldspar; Qtz = Quartz; Pl = Plagioclase; Sme = Smectite; Zeo = Zeolite; +++ = indicated dominant phase, ++ = indicated significant phase, + = indicated low/very low present phase. Mineral abbreviations after Whitney and Evans (2010).

TABLE II. Chemical compositions of andesite tuffs from the Žumberak Mt. (NW Croatia)

Sample Location	KL-22 1	KL-34 1	KL-36 1	KL-40A 1	KL-40B 1	BZ-9 2	BZ-20 2	BZ-32 2
SiO ₂	67.98	60.94	54.73	66.87	61.05	61.34	63.12	68.65
TiO ₂	0.66	0.84	1.21	0.29	0.62	0.67	0.50	0.66
Al ₂ O ₃	13.52	16.34	16.37	11.92	15.09	15.65	14.58	13.55
Fe ₂ O _{3total}	3.66	3.70	5.10	4.62	5.18	5.45	3.10	2.92
MnO	0.07	0.01	0.01	0.01	0.01	0.02	0.01	0.01
MgO	1.98	3.09	4.36	3.04	2.97	3.00	3.26	1.83
CaO	0.28	0.41	0.94	0.53	1.31	0.55	1.46	1.16
Na ₂ O	0.25	0.33	0.32	0.24	1.31	0.16	1.20	0.88
K ₂ O	6.16	4.45	6.21	3.24	3.87	5.69	4.21	3.67
P ₂ O ₅	0.10	0.12	0.23	0.04	0.07	0.14	0.08	0.21
LOI	5.02	9.49	10.14	8.98	8.13	6.95	8.07	6.16
Total	99.67	99.72	99.62	99.78	99.61	99.62	99.59	99.72
Cs	11	2	3	3	4	9	2	3
Rb	109	85	121	72	95	175	72	63
Ba	257	142	151	149	176	325	637	216
Th	7.16	5.3	10.0	14.8	13.8	10.7	14.6	5.3
Ta	0.55	0.55	0.84	0.73	1.01	0.78	1.33	0.32
Nb	6.2	4.2	10.0	6.5	12.6	9.3	14.7	4.4
Sr	33	18	44	24	84	56	141	71
Zr	59	67	122	155	225	69	199	62
Hf	2.8	2.9	5.4	6.8	9.3	3.4	9.1	2.6
Y	106	34	35	34	46	23	42	24
Sc	13	16	18	14	20	14	9	14
V	54	78	61	17	23	125	12	106
Cr	46	128	17	5	10	125	7	91
Ni	36	18	8	6	7	31	3	10
Pb	25.3	11.6	16.0	19.9	21.7	14.0	30.4	13.3
La	120.00	24.20	18.00	18.00	48.50	30.20	46.70	12.30
Ce	122.00	27.90	45.60	29.20	90.20	60.50	86.70	28.50
Pr	31.10	7.03	5.97	4.96	12.00	7.29	12.00	3.80
Nd	125.00	29.90	25.70	20.90	45.70	27.70	47.90	14.50
Sm	28.40	6.14	6.01	5.21	9.08	5.21	10.20	3.33
Eu	6.33	1.53	0.94	0.67	1.29	0.98	0.95	0.73
Gd	27.10	6.16	6.11	5.77	7.54	4.50	8.94	3.51
Tb	4.23	1.01	0.98	0.98	1.24	0.64	1.39	0.52
Dy	22.90	5.73	6.07	6.18	7.74	3.96	7.99	3.45
Ho	3.96	1.14	1.18	1.24	1.61	0.78	1.59	0.69
Er	9.91	3.16	3.27	3.49	5.18	2.21	4.89	2.16
Tm	1.29	0.44	0.40	0.50	0.80	0.34	0.68	0.28
Yb	8.56	2.50	2.44	5.49	4.09	1.99	4.68	2.02
Lu	1.28	0.43	0.38	0.59	0.91	0.38	0.77	0.33

Major elements in wt.%, trace elements in ppm. LOI = Loss On Ignition at 1100 °C. The location number corresponds to the location number in Figure 1C.