

# The influence of weathering and pedogenesis on the geochemical record of Miocene marls and Plio-Quaternary sediments, Medvednica Mt., Croatia

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## Abstract

The geochemical signature of weathering and pedogenesis in a temperate humid climate on two parent material types in the foothills of Medvednica Mt. was studied. Five soil profiles on Miocene marls and three sections of Plio-Quaternary (PIQ) proluvial sediments with overlying soil and weathered material were analyzed. The (clay) mineralogy of all profiles and sections had been determined in previous studies. The chemical composition of the samples was determined by inductively coupled plasma emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS). Poorly ordered Fe and Mn oxides were determined in the PIQ sediment and overlying soil samples by atomic absorption spectroscopy (AAS), after oxalate dissolution in the dark. The concentrations and element ratios were used to determine element enrichment/mobility and intensity of chemical weathering, material provenance, and to compare the geochemical signatures with previously obtained clay mineralogy results. Trace elements in the Miocene marls, including rare earth elements (REE), indicate the continental origin of the marl siliciclastic component, while more scattered geochemical data of the PIQ sediments reflect their proluvial/torrential nature. The mass transfer coefficient ( $\tau$ ) for major elements and element ratios of the Miocene marl profiles indicate chemical weathering and pedogenesis of lower intensity. The geochemistry of these samples shows homogeneity within the profiles. In the geochemical signature of the PIQ sections, a chaotic proluvial deposition of the material is visible, as well as the heterogeneity with the overlying soil and weathered material. Overall, the geochemistry results largely support the clay mineralogy of the samples and demonstrate how a multiproxy approach can help test hypotheses about past environments and provide valuable additional information for complex paleoenvironmental studies.

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## 1. INTRODUCTION

Weathering is a complex set of processes occurring at or near the Earth's surface, resulting in physical and chemical rock alteration. It involves processes that span many orders of magnitude in spatial and temporal scales (FRINGS & BUSS, 2019), so consequently the meaning of “weathering” may be dependent on the standpoint, which leads to the need of its precise definition (HALL et al., 2012). In this study, the term is used for parent material alteration (relating to the chemical composition) and secondary mineral formation in response to environmental factors, dominantly climate. Apart from climate, dictating the weathering rate and intensity, parent material composition sets the “starting position” and is the dominant influence on the secondary weathering products, especially in the early stages of weathering. In this case, studying the profiles in a temperate climate region formed on different parent materials, both of these factors are taken into account.

The use of (clay) minerals and geochemical signatures in studies of past weathering conditions has gained traction in the research of the critical zone, defined by BANWART et al. (2012) as the terrestrial environment extending from the top

of the vegetation canopy to the bottom of drinking water aquifers, in the past few decades (e.g., GODOY et al., 2017; ZOLLINGER et al., 2017; DINIS et al., 2020; BŁAŻEJOWSKI et al., 2023; CORENTIN et al., 2023). Clay minerals forming as secondary minerals in equilibrium with the prevalent environmental conditions serve as useful proxies for paleoenvironmental studies. The problem arises when clay minerals in recycled material undergo multiple weathering cycles, thus overwriting the past or misrepresenting more recent weathering processes. Geochemical signatures, even though also prone to the same issues, can give an additional insight and contribute to the multiproxy approach needed in this type of studies.

For this reason, geochemical analyses were included for samples where the clay mineralogy had already been analyzed. The reasoning behind adding another proxy, was the possibility of confirming or refuting conclusions drawn on the basis of mineralogical data.

This paper focuses on the effect of weathering (and pedogenesis) on the sediments of the SE slopes of Medvednica Mt., located north of the city of Zagreb in Croatia (Fig. 1), i.e. in the SW part of the Pannonian Basin System (PBS). While

the majority of the paleoenvironmental studies of the PBS so far have used sedimentological, paleontological and palynological proxies (for instance, BAKRAČ & KOCH, 1999; BAKRAČ et al., 2012), HARZHAUSER et al. (2023) have included clay mineralogy and geochemical records alongside paleontological data to study changes in the paleoenvironment of the Vienna basin during the Late Miocene. Several papers on samples and soils from Medvednica Mt. and the adjacent areas have used (clay) mineralogy and/or geochemical records (e.g., GALOVIĆ & PEH, 2014; GRIZELJ et al., 2017; KUREČIĆ et al., 2021), but mostly in terms of provenance determination, defining the sedimentary environment, or evaluating the influence of the parent material on the soil profiles. Geochemical data in the context of the weathering effect on the rocks and sediments of this area have, to the authors' knowledge, not been as thoroughly considered. The benefits of this location, aside from its lithological variety, is its position in the temperate climate zone, where transient and intermediate steps of the weathering process can be studied and the effect of small changes in weathering intensity can be seen in the mineralogy and geochemistry.

The clay mineralogy of the samples used in this study had been previously investigated (GVERIĆ et al., 2022, 2023). The profiles selected for the above-mentioned studies were developed on the Miocene marls (ranging in age from Early to Late Miocene) and Plio-Quaternary (PIQ) proluvial, molasse-type, sediments, both of which are common soil parent materials in the study area. Clay mineralogy of the studied Miocene marls bedrock and the overlying soil indicates less intense weathering, also dictated by increased pH values due to the presence of carbonates. Clay mineralogy of the marl parent material is dominated by smectite-rich illite-smectite and contains illite, kaolinite and sometimes chlorite. Changes in clay mineralogy between the parent material and soil are subtle, visible in the appearance of transient mixed-layered phases including chlorite-vermiculite and possibly hydroxyl or organic interlayering of the expandable clay minerals in the soil profile (GVERIĆ et al., 2022). In contrast, the clay mineralogy of the PIQ sediments (analyzed in GVERIĆ et al., 2023) consists of more clay mineral species typical of hot and humid areas (kaolinite, low-charge expandables), in addition to the presence of Al (oxy)hydroxides. Most of the PIQ sediments are covered with more recent proluvial material, while some are covered with older wind-blown material (loess). This loess cover is thin and usually completely degraded into a pseudogleyed loess derivate, on which Stagnosols are formed. The clay mineralogy of this overlying material and soil contains expandable clay minerals of higher layer charge and intermediary clay phases, such as hydroxyl-interlayered minerals, suggesting moderate recent and current weathering conditions.

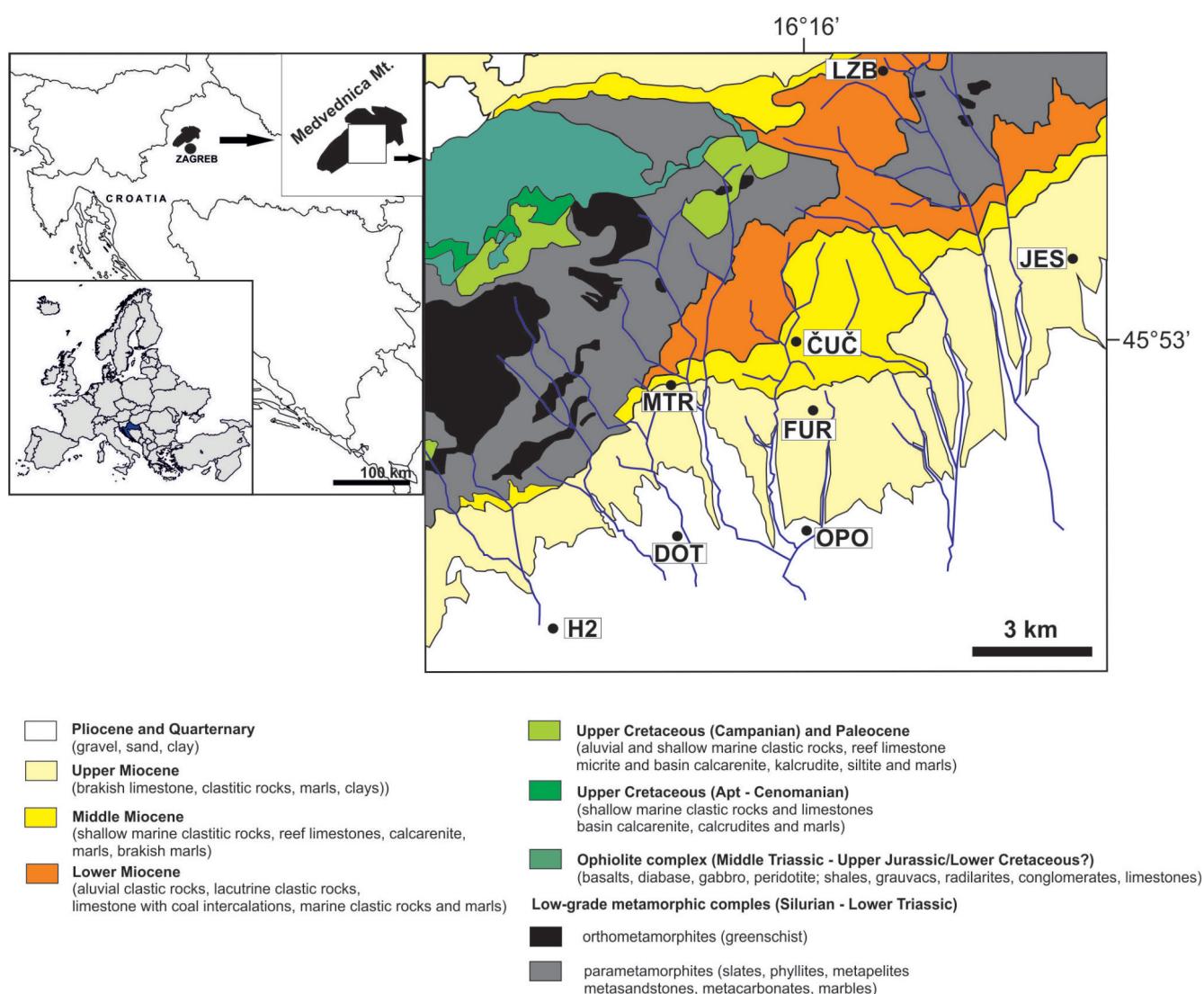
The main aim of this paper is to investigate whether the geochemical records of the investigated Miocene and PIQ sections are consistent with the composition of the clay mineralogy, i.e. with the intensity of weathering and pedogenesis inferred from the clay mineralogy. If this is the case, it would support our previous conclusions and confirm the key role of soil/sediment geochemistry together with clay minerals assemblage, in the multidisciplinary study of weathering in relation to (paleo)environmental conditions.

## 2. STUDY AREA

Medvednica Mt. is one of the inselbergs in the southwestern part of the PBS, consisting of exposed metamorphosed and non-metamorphosed sediments of Paleozoic to Mesozoic age, as well as of some Mesozoic volcanics, all surrounded by Miocene sediments (ŠIKIĆ et al., 1978; BASCH, 1981; TOMLJENOVIĆ et al., 2008; CROATIAN GEOLOGICAL SURVEY, 2009; VAN GELDER et al., 2015). The PBS was formed during Miocene extension as a back-arc basin and its sedimentary succession is characterized by the changing tectonic environment (PAVELIĆ & KOVAČIĆ, 2018). Early Miocene sedimentation was dominantly continental with fluvio-lacustrine sedimentation processes. Previous provenance research by KOVAČIĆ et al. (2011) indicates that the material originated mainly from the Inner Dinarides during the Early and Middle Miocene, while the Upper Miocene clastic detritus is mainly of Alpine-Carpathian provenance. PIQ sediments on Medvednica Mt. were deposited predominantly as unsorted, molasse type fluvial and proluvial sediments with material sourced locally from the older Medvednica Mt. lithology (ŠIKIĆ, 1995).

Based on the sedimentological and paleontological record, the Early Miocene climate was semi-dry (PAVELIĆ et al., 2016) and it became progressively warmer and more humid in the Middle Miocene (MARKOVIĆ et al., 2021). After another dry cycle in the Middle Miocene (JIMÉNEZ-MORENO et al., 2005), the Late Miocene climate became very humid and warm before cooling towards the end of the period (HARZHAUSER et al., 2007). During the Pliocene, the climate was still warmer than the present day, especially during the mid-Pliocene warm period (PRISTA et al., 2015; SZABÓ et al., 2022), but it became subsequently colder and drier. The Quaternary is marked by glaciation intervals in the Pleistocene as well as coeval loess deposition (RUBINIĆ et al., 2018). The present day climate of the area is temperate humid (Cfbwx in Köppen classification), with a mean annual air temperature of 10°C and mean annual precipitation of 1000-1100 mm, and no distinct dry period (ZANINOVIĆ et al., 2008). Vegetation cover, anthropologically substantially modified, mostly varies from deciduous forest comprising beech, hornbeam and oak (natural cover) to orchards and grassland.

Medvednica Mt. is currently 1033 m high, with the mountain's main ridge stretching in a SW-NE direction and it is divided into three distinct orographic units. Due to young tectonic movements and denudation processes, the landscape is intersected by a number of streams and valleys extending from the central massif to the foothills, perpendicular to the direction of the mountain's line of extension (Fig. 1). It is a moderately to markedly dissected hilly and mountainous relief with rather versatile sloping, which can be very steep in places with the occurrence of landslides (LOZIĆ, 2001; MIHALIĆ ARBANAS et al., 2016). Accordingly, the soils of the studied profiles are mostly thin (e.g., Leptosols and Regosols); however, some more developed soils, such as Cambisols and Stagnosols, also occur (GVERIĆ et al., 2022, 2023). In the study of parent material influence on soil properties on Medvednica Mt., spanning different lithologies, PERKOVIĆ et al. (2017) identified Dystric Cambisol, Eutric Cambisol, Calcaric Cambisol, Stagnosol, Regosol and Luvisol.



**Figure 1.** The geographical position of the sample locations and local lithology (blue lines show recent drainage directions (streams) on the SE slopes of Medvednica Mt.); modified after TOMLJENIĆ (2002). LZB – Laz Bistrički, ČUČ – Čučerje, MTR – Markuševečka Trnava, FUR – Furdini, JES – Jesenovac, DOT – Dotršćina, OPO – Oporovec, H2 – Horvatovac borehole.

### 3. MATERIALS AND METHODS

A total of 25 samples from 8 locations were studied (Table 1, Fig. 1). However, due to differences in parent material and sampling strategies, the samples are divided into two distinct groups: profiles developed on the Miocene marls and soil sections overlying PIQ sediments. As a result, the data for the two groups of samples were, in some cases, treated differently to account for the differences between them.

#### 3.1. Miocene marl and argillaceous limestone profiles: description and analytical methods

The (clay) mineralogy of these samples, along with selected physical and chemical properties, has already been presented in GVERIĆ et al. (2022). Five soil profiles are developed on Miocene marly sediments, with clay mineral content dominated by smectite-rich illite-smectite and containing illite, kaolinite and minor vermiculite. Chlorite is detected only in some parent material samples. Soil profiles overlying this parent material are poorly to moderately developed and there is no lithic discontinuity present. The texture class of

Miocene marls and the overlying soil samples is mainly silt loam and subordinately silt clay loam, the samples are calcareous throughout with  $\text{pH}_{\text{H}_2\text{O}}$  values ranging from 7.6 to 8.4 and the chemical composition is dominated by Si, Al and Ca (GVERIĆ et al., 2022).

The chemical composition of the Miocene marl profiles samples (Table 2) was determined in the Bureau Veritas (Acme Analytical Laboratories), in Vancouver, BC, Canada, using ICP-OES and ICP-MS after sample fusion with lithium metaborate as well as sample digestion in aqua regia for trace elements (e.g., Sc and Th used in provenance analysis).

#### 3.2. PIQ sections: description and analytical methods

Another three locations are located on PIQ sediments overlain by weathered material and soil (at some locations genetically unrelated, i.e. interrupted by a lithic discontinuity), with the clay mineralogy dominated by expandable clay minerals (smectite and/or vermiculite) and containing some illite and kaolinite, as well as mixed-layer and hydroxyl-interlayered

**Table 1.** Investigated samples and their clay mineralogy; Fe/Al oxides are included if present.

	LOCATION	SAMPLE LABEL and depth in cm	SAMPLE TYPE	CLAY MINERALS AND Fe/Al OXIDES PRESENT IN THE SAMPLES	
Miocene profiles	Laz Bistrički N 45.957769 E 16.090546	LZB 0-10 LZB 10-30 LZB 30-50	soil soil marl	I-S, I, V, K, Ch-V* I-S, I, V, K* I-S, I, V, K*	
	Čučerje N 45.894835 E 16.063706	ČUČ 0-20 ČUČ 200	soil marl	I-S, I, K, IM?*	
	Markuševečka Trnava N 45.880720 E 16.023345	MTR 0-20 MTR 35-40 MTR 150	soil marl marl	I-S, I, V, K, Ch-V/IM?*	
	Furdini N 45.872790 E 16.076558	FUR 0-20 FUR 20-60 FUR 70	soil soil argillaceous limestone	I-S, I, V, K, Ch-V?*	
	Jesenovec N 45.92005 E 16.14435	JES 0-20	soil	I-S, I, V, K, Ch, Ch-V?*	
		JES 20-40	soil	I-S, I, V, K, Ch, Ch-V?*	
		JES 40-90	soil	I-S, I, V, K, Ch, Ch-V?*	
		JES 220	marl	I-S, I, V, K, Ch*	
	PIQ sections	Dotrščina N 45.86028 E 16.01972	DOT 25 DOT 120 DOT 300	soil soil (proluvial) sediment	V, K, HIM** V, S, I, K, Ch-V/S?*** V, S, I, K, Gth, Gbs, Hem**
		Oporovec N 45.84974 E 16.07052	OPO 25 OPO 40 OPO 70	soil soil (proluvial) sediment	S, V, K, I, Ch-V?*** S, K, I** S, K, I, V**
Horvatovac (borehole) N 45.825910 E 15.987865		H2 25	soil	S, K, I, HIM, Gth**	
		H2 70	soil	HIM, K, I, Gth**	
		H2 150	(proluvial) sediment	S, K, I, V**	
		H2 250	(proluvial) sediment	S, K, I, Gth**	

I-S: illite-smectite, I: illite, V: vermiculite, K: kaolinite, Ch-V: interstratified chlorite-vermiculite, IM: interlayered clay mineral in which the types of interlayering were not recognized with certainty, Ch: chlorite, HIM: hydroxy-interlayered mineral, S: smectite, Ch-V/S: interstratified chlorite-expandable clay mineral, Gth: goethite, Gbs: gibbsite, Hem: hematite.

\*data from GVERIĆ et al. (2022)

\*\*data from GVERIĆ et al. (2023)

**Table 2.** Concentrations of major elements (in %) of the samples (from previous studies).

	Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	Cr <sub>2</sub> O <sub>3</sub>	LOI	Sum	Reference
Miocene profiles	LZB 0-10	28.91	8.12	3.83	2.08	25.78	0.27	1.38	0.35	0.12	0.09	0.025	28.8	99.76	GVERIĆ et al., 2022
	LZB 10-30	26.93	8.3	3.91	2.2	27.4	0.27	1.49	0.36	0.07	0.08	0.04	28.7	99.75	
	LZB 30-50	23.97	7.3	3.04	2.26	30.56	0.26	1.33	0.33	0.08	0.08	0.017	30.6	99.83	
	ČUČ 0-20	23.39	4.95	2.07	0.81	28.28	0.32	0.82	0.25	0.2	0.05	0.006	38.6	99.75	
	ČUČ 200	16.31	3.6	1.31	0.73	40.59	0.24	0.69	0.18	0.12	0.04	0.005	35.9	99.72	
	MTR 0-20	52.46	15.14	6.76	1.44	3.99	0.76	1.8	0.87	0.11	0.09	0.016	16.4	99.84	
	MTR 35-40	20.78	5.74	2.43	1.73	34.58	0.3	0.88	0.28	0.09	0.04	0.006	33	99.86	
	MTR 150	22.34	5.82	2.34	2.2	33.79	0.3	0.91	0.29	0.1	0.04	0.006	31.7	99.84	
	FUR 0-20	45.04	14.83	5.97	1.57	9.03	0.6	2.19	0.72	0.12	0.11	0.015	19.6	99.80	
	FUR 20-60	25.05	8.51	3.25	1.41	29.54	0.33	1.4	0.35	0.09	0.07	0.009	29.8	99.81	
FUR 70	26.64	8.38	3.31	1.7	27.46	0.4	1.32	0.36	0.09	0.08	0.009	30.1	99.85		
JES 0-20	38.66	12.53	4.73	3.93	13.18	0.81	2.33	0.59	0.14	0.08	0.012	22.8	99.79	GVERIĆ et al., 2023	
JES 20-40	42.48	13.85	4.84	4.04	12.56	0.91	2.48	0.64	0.11	0.07	0.014	17.8	99.79		
JES 40-90	41.01	13.82	5.39	3.69	13.9	0.92	2.51	0.6	0.11	0.08	0.013	17.7	99.74		
JES 220	47.82	15.16	5.18	4.69	7.56	1.07	2.86	0.7	0.12	0.07	0.015	14.5	99.75		
PIQ sections	DOT 25	68.58	12.75	3.82	0.81	0.47	1.20	1.54	1.26	0.10	0.13	0.01	6.2	96.90	GVERIĆ et al., 2023
	DOT 120	61.75	14.00	6.01	1.09	0.51	1.00	1.79	1.11	0.12	0.47	0.01	6.2	94.07	
	DOT 300	54.91	16.12	6.62	1.66	1.58	1.58	1.22	1.37	0.12	0.01	0.02	9.2	94.42	
	OPO 25	66.53	12.94	3.86	0.59	0.29	0.90	1.61	1.20	0.08	0.05	0.01	6.8	94.87	
	OPO 40	61.75	14.89	4.82	0.73	0.34	0.69	1.70	1.11	0.06	0.05	0.01	7.4	93.55	
	OPO 70	59.24	16.80	5.16	1.20	0.47	0.60	1.95	1.00	0.08	0.08	0.01	9.2	95.78	
	H2 25	64.71	14.43	5.57	1.01	0.67	1.09	1.78	1.19	0.11	0.14	0.01	8.2	98.94	
	H2 70	68.13	14.19	4.31	1.16	0.67	1.30	1.88	1.24	0.11	0.07	0.01	5.6	98.67	
	H2 150	62.43	16.49	4.93	0.71	0.49	0.59	1.42	1.17	0.02	0.03	0.01	8.0	96.31	
	H2 250	57.65	18.59	5.15	0.97	0.61	0.64	1.60	1.00	0.03	0.02	0.01	9.2	95.46	

**Table 3.** Weathering indices used for the samples of PIQ sections (calculated on the basis of the molar proportions of the element oxides).

Index	Formula	Reference
CIA	$[\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{CaO} + \text{Na}_2\text{O})] \times 100$	NESBITT & YOUNG, 1982
PIA	$[(\text{Al}_2\text{O}_3 - \text{K}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} - \text{K}_2\text{O})] \times 100$	FEDO et al., 1995
CIW	$[\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O})] \times 100$	HARNOIS, 1988
CPA	$[\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{Na}_2\text{O})] \times 100$	BUGGLE et al., 2011

minerals in some samples. PIQ sections are more complicated as PIQ sediments were locally covered by loess which was subsequently altered. Chaotic proluvial sedimentation during this period also resulted in substantial differences in PIQ sediment material, especially considering mineral content and granulometric properties.

The samples show variation in texture; the Dotrščina samples are silt loam throughout, while the Oporovec samples vary from silty clay to silt loam and the Horvatovac borehole PIQ sediment is silty clay with the overlying soil having silt and silt loam horizons. There is a lithic discontinuity present in the Dotrščina and Horvatovac sections. The samples do not contain carbonates; the chemical composition is dominated by Si, Al and Fe (Table 2), and the  $\text{pH}_{\text{H}_2\text{O}}$  values range from 4.2 to 6.7 (GVERIĆ et al., 2023).

The elemental composition for PIQ sections samples was determined at the Institute of Geology, Jagiellonian University, Kraków, Poland, using Spectro Arcos (ICP-OES) spectrometer (SPECTRO Analytical Instruments GmbH, Kleve, Germany) with the radially (side-on) viewed torch configuration. The samples were digested in a mixture of spectrally clean and concentrated nitric, hydrochloric, and hydrofluoric acids in the presence of boric acid in the Ethos-Up Milestone microwave oven (Milestone Srl, Sorisole (BG), Italy). Certified reference material OREAS 920 (Oreas®, Melbourne, Australia) was processed and measured in the same way as the samples in the same analytical cycle to monitor the accuracy of the analyses.

### 3.3. Provenance and selected weathering indicators

To assert provenance,  $\text{TiO}_2/\text{Al}_2\text{O}_3$  and Sm/Nd ratios were related to the Eu/Eu\* ratio in order to compare the geochemical signature of the samples to the known values for different types of rocks taken from CONDIE (1993). The values taken are for the Phanerozoic or average Paleozoic and Mesozoic protolith. The analysis of provenance based on trace and rare earth elements (REEs) was undertaken on Miocene marl samples and diagrams La-Th-Sc and Th-Sc-Zr/10 proposed by BHATIA & CROOK (1986) were used for this purpose.

REE concentrations were normalized to chondrite values (McDONOUGH & SUN, 1995) to detect any differentiation of the elements in earlier geological processes, and to Upper Continental Crust values (RUDNICK & GAO, 2014) to account for their subsequent distribution during weathering and pedogenesis.

Ratios of the major chemical elements (Na/Ti, Ca/Ti, Al/Na, Al/K, Al/Ti) as well as La/Sm ratio were used to detect element (im)mobility and to make further comparisons between the parent material and the overlying soil, with respect to the weathering intensity and its impact on the mineral and chemical record.

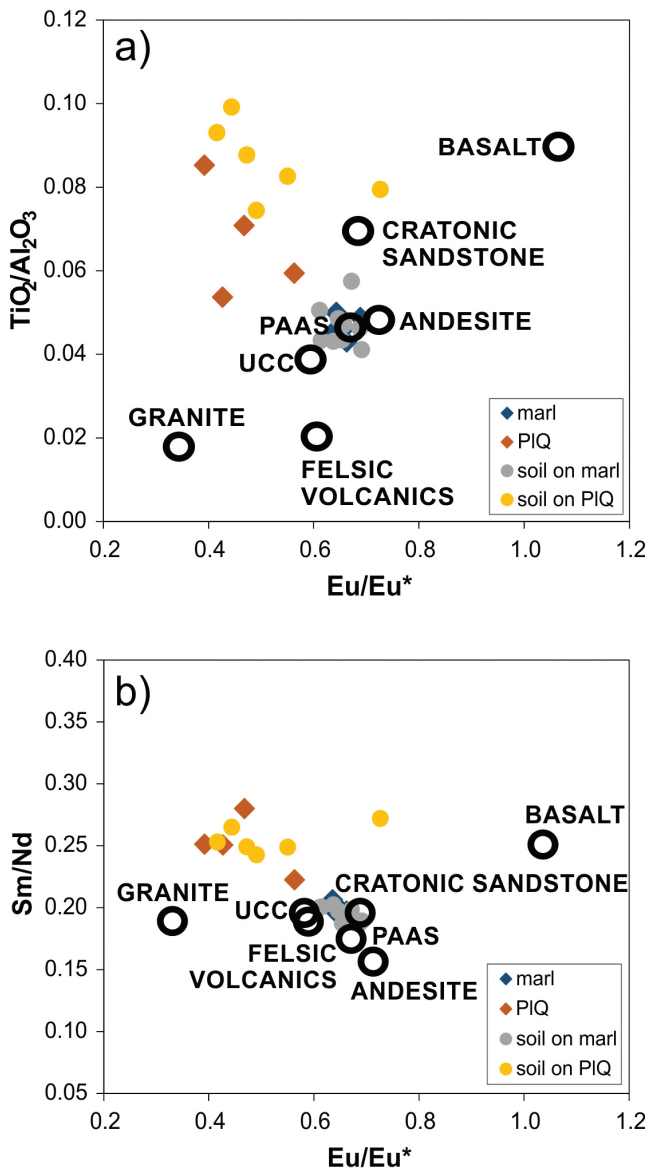
The extent of (chemical) weathering for profiles developed on Miocene carbonate sediments was inferred from calculation of a mass transfer coefficient ( $\tau$ ) for the main elements (Si, Al, Fe, Mg, Ca, Na and K) with Ti considered an immobile element (BRIMHALL & DIETRICH, 1987; CHADWICK et al., 1990; YANG et al., 2015). For PIQ sections, having a more complex development and exhibiting lithic discontinuity in two of the investigated localities, weathering indices listed in Table 3 were used. Given that the studied PIQ colluvial sediments incorporate geochemical signatures of past weathering cycles with various protoliths included, a range of different weathering indices was used and compared. The main motive was to observe the trends, not the absolute values, and also to evaluate the suitability of the indices used for proluvial material derived from multiple sources. Weathering indices used were the Chemical Index of Alteration (CIA; NESBITT & YOUNG, 1982), as the most commonly employed quantitative measure of chemical alteration, and the Plagioclase Index of Alteration (PIA; FEDO et al., 1995) which accounts for K immobilization due to clay mineral formation. We have also calculated the Chemical Index of Weathering (CIW; HARNOIS, 1988), which excludes K from the calculation due to its possible retention in some clay mineral phases, and Chemical Proxy of Alteration (CPA; BUGGLE et al., 2011), which omits both Ca and K from the calculation and is found to be the most suitable for loess and paleosol samples. The aforementioned chemical indices, although initially mostly developed to measure geochemical weathering effects in silicate rocks, have so far been used for a wide variety of soil and sediment samples (e.g., WEI et al., 2006; TABOADA et al., 2016; DINIS et al., 2020; HEIDARI et al., 2022).

The fraction of poorly ordered Fe and Mn oxides was determined for the PIQ sections after dissolution of the samples in acid ammonium oxalate (method according to SCHWERTMANN, 1964). The samples were suspended in acid ammonium oxalate and the reaction proceeded in the dark. After filtration (also in the dark), Fe and Mn concentrations (ammonium oxalate extractable iron and manganese) were measured from the filtrate using AAS (Analyst 700).

## 4. RESULTS AND DISCUSSION

### 4.1. Tectonic setting and material provenance

Relationships between Eu/Eu\* and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  as well as between Eu/Eu\* and Sm/Nd show marl samples plotting near UCC and PAAS values, while the PIQ samples' values are more scattered (Fig. 2). Provenance data for the Miocene marl samples as well as for their derivatives imply their origin from a well-differentiated continental material that can be averaged to the shale geochemical signature. When assessing the provenance and tectonic setting for PIQ samples, a proluvial



**Figure 2.** (a)  $\text{Eu}/\text{Eu}^*$  and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  binary plot, and (b)  $\text{Eu}/\text{Eu}^*$  and  $\text{Sm}/\text{Nd}$  binary plot, showing the geochemical signature of the samples in relation to the reference values of some common rock types (data from CONDIE, 1993).

nature of the sediments has to be taken into consideration; torrential streams eroded upstream rocks of various ages and origin, resulting in the accumulation of PIQ sediments in the foothills of Medvednica Mt (Fig. 1).

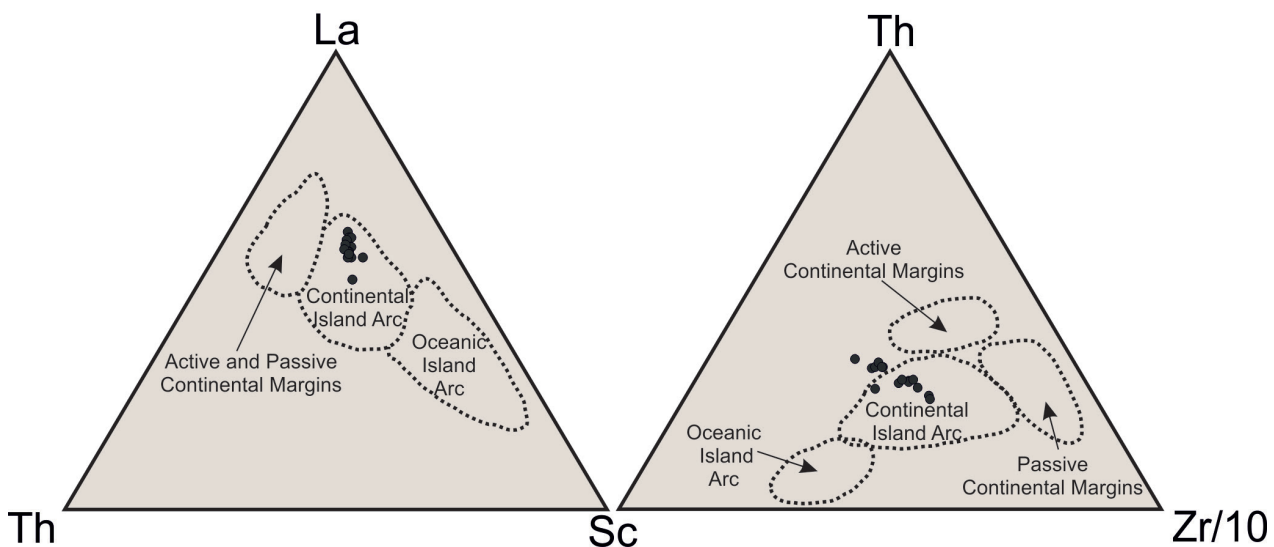
The tectonic setting for Miocene sedimentary rocks and overlying soil samples was established using trace elements discriminatory plots proposed by BHATIA & CROOK (1986). The results place the samples in the continental island arc field, thereby corresponding to the results of GRIZELJ et al. (2017), obtained for Miocene pelitic sediments of the area (Fig. 3). This also corresponds with the definition of the PBS as a back-arc basin (ROYDEN et al., 1983) and the postulated repeated extensions and inversion affecting the area since the Early Miocene (TOMLJENović & CSONTOS, 2001; TOMLJENović et al., 2008).

The use of major elements in inferring provenance and tectonic setting (such as ROSER & KORSCH, 1986) has proven to give erroneous results. The issue with the parameters used in samples containing clay minerals could be the preferential  $\text{K}^+$  retention in the interlayer space (BERGAYA et al., 2006), resulting in non-representative  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratio values.

#### 4.2. REE distribution

REE distribution (Table 4) shows the primary enrichment of REE in the source material as evidenced by chondrite normalization (Figs. 4a,b). The enrichment of LREE compared to chondrite values is particularly pronounced, with the enrichment factor from 50 to up to several hundreds. All samples, except DOT 120, show a negative Eu anomaly. The general enrichment and trend is similar for both Miocene and PIQ parent sediments as well as for their derivatives. The Eu anomaly suggests the sediments were derived from already differentiated material.

When REEs are normalized to UCC (Fig. 4c,d), all samples generally present REE abundances around those of normalization standards. A flat distribution trend indicates no preferential leaching of particular REEs during weathering or pedogenesis (see later discussion of the  $\text{La}/\text{Sm}$  ratio throughout the samples). For all normalization cases, no significant dis-



**Figure 3.** Samples from Miocene marls profiles plotted on discrimination plots for tectonic settings according to BHATIA & CROOK (1986). Data on trace element composition used are available in the supplementary materials.

**Table 4.** Concentrations of REE (in ppm) of the studied samples.

	Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Eu/Eu* (Ch)	(LREE/ HREE) <sub>UCC</sub>
Miocene profiles	LZB 0-10	19.2	20.1	37.6	4.6	16.9	3.4	0.7	3.3	0.5	3.0	0.7	1.8	0.3	1.6	0.3	0.64	0.74
	LZB 10-30	15.5	17.0	33.7	3.9	14.7	3.0	0.6	2.8	0.5	2.7	0.6	1.5	0.2	1.4	0.2	0.61	0.73
	LZB 30-50	16.3	17.0	31.3	3.8	14.2	2.9	0.6	3.0	0.5	2.7	0.6	1.5	0.2	1.4	0.2	0.64	0.74
	ČUČ 0-20	13.2	14.8	25.7	3.2	11.5	2.3	0.5	2.4	0.4	2.3	0.4	1.3	0.2	1.2	0.2	0.61	0.73
	ČUČ 200	10.6	11.2	17.6	2.5	9.2	1.8	0.4	1.9	0.3	1.8	0.4	1.1	0.1	0.9	0.1	0.64	0.71
	MTR 0-20	36.5	43.7	83.6	10.2	37.6	7.5	1.6	7.0	1.1	6.3	1.3	3.6	0.5	3.3	0.5	0.67	0.80
	MTR 35-40	12.5	14.8	27.4	3.4	12.8	2.4	0.6	2.5	0.4	2.1	0.4	1.3	0.2	1.2	0.2	0.69	0.79
	MTR 150	13.0	15.2	27.9	3.4	12.8	2.6	0.5	2.4	0.4	2.1	0.4	1.3	0.2	1.1	0.2	0.64	0.81
	FUR 0-20	29.3	39.0	72.8	8.7	32.1	6.3	1.3	5.7	0.9	5.0	1.0	2.9	0.4	2.7	0.4	0.65	0.86
	FUR 20-60	16.0	20.8	39.5	4.7	17.8	3.4	0.7	3.2	0.5	2.8	0.6	1.6	0.2	1.4	0.2	0.69	0.86
	FUR 70	16.6	21.6	39.6	4.8	17.5	3.5	0.7	3.3	0.5	2.9	0.5	1.6	0.2	1.5	0.2	0.66	0.86
	JES 0-20	23.9	30.0	57.7	6.8	25.5	4.8	1.0	4.5	0.7	4.0	0.8	2.4	0.3	2.2	0.3	0.66	0.84
	JES 20-40	24.4	31.4	61.5	7.2	27.0	5.1	1.1	4.7	0.7	4.1	0.8	2.4	0.4	2.2	0.3	0.69	0.85
	JES 40-90	23.0	30.9	59.7	7.0	26.5	5.0	1.0	4.7	0.7	4.2	0.8	2.3	0.3	2.2	0.3	0.65	0.85
	JES 220	26.2	34.0	65.4	7.9	29.4	5.7	1.2	5.2	0.8	4.7	0.9	2.7	0.4	2.5	0.4	0.66	0.84
PIQ sections	DOT 25	25.7	45.4	110.0	18.3	29.1	7.7	1.1	6.9	2.8	7.2	1.1	<5	<2	1.9	<2	0.44	1.21
	DOT 120	25.2	45.3	124.0	9.0	30.5	8.3	1.7	6.1	4.1	11.3	1.2	<5	<2	2.0	<2	0.73	0.87
	DOT 300	22.0	40.6	63.2	12.0	25.4	6.4	0.7	4.9	3.7	6.3	1.1	<5	<2	1.7	<2	0.39	0.82
	OPO 25	22.6	44.6	108.0	18.2	29.3	7.4	0.9	5.8	3.3	6.2	1.2	<5	<2	1.8	<2	0.42	1.11
	OPO 40	27.1	49.2	114.0	14.7	35.0	8.5	1.2	6.1	4.1	6.9	1.1	<5	<2	2.1	<2	0.49	1.00
	OPO 70	40.3	65.6	132.0	13.9	48.1	10.7	1.8	8.5	3.6	8.7	1.3	<5	<2	2.9	<2	0.56	1.15
	H2 25	26.0	47.7	106.0	11.7	34.3	8.5	1.3	6.1	4.0	7.4	1.2	<5	<2	2.0	<2	0.55	0.96
	H2 70	22.0	44.1	91.8	16.0	30.2	7.5	1.0	5.4	3.0	5.9	1.3	<5	<2	1.6	<2	0.47	1.11
	H2 150	20.2	38.9	94.5	9.6	23.6	6.6	0.9	4.8	2.8	5.7	0.9	<5	<2	1.5	<2	0.47	1.03
H2 250	23.8	43.3	68.4	12.2	28.4	7.1	0.9	6.0	3.3	6.6	1.2	<5	<2	1.9	<2	0.43	0.93	

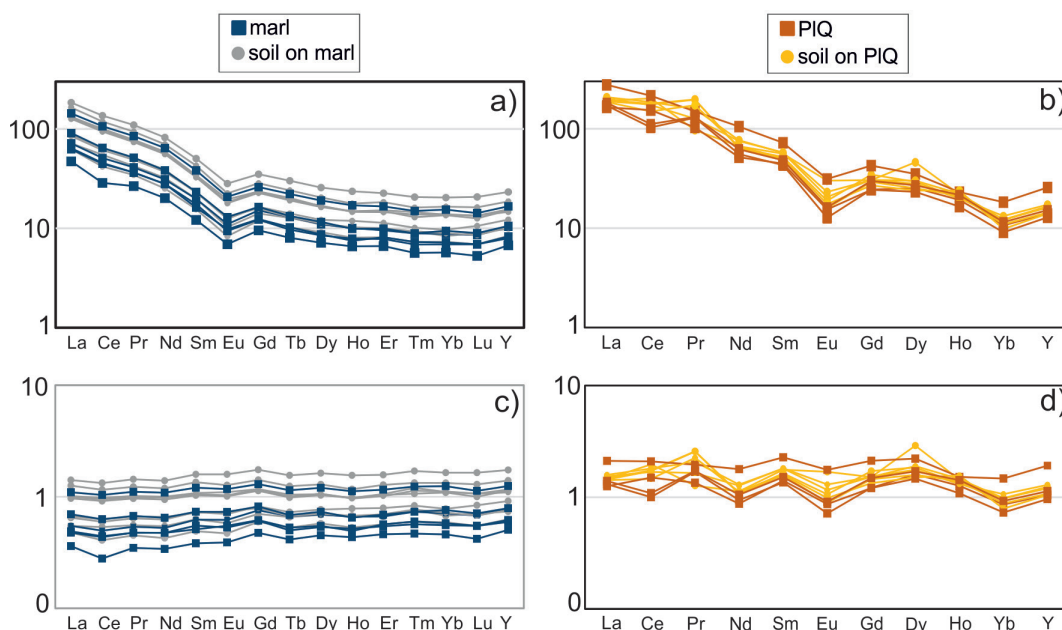
inction between the parent material and soil/weathered material is observed, supporting a presumption of overall intermediate weathering intensity.

Miocene and PIQ profiles can be readily distinguished by the magnitude and the trend of REE distribution in all normalization cases. This could be partly attributed to the granulometric variations of the samples; Miocene fine-grained

samples contrast the sand-silt-clay features of the PIQ samples. Additionally, these variations in REE distribution can also attest to different source material properties.

### 4.3. Element mobility

The mobility of chemical elements depends, among other factors, on the intensity of weathering processes. Alkali and



**Figure 4.** Normalization plots for REE: (a) samples from the Miocene marl profiles and (b) samples from the PIQ sections normalized to chondrite (McDONOUGH & SUN, 1995); (c) samples from the Miocene marl profiles and (d) samples from the PIQ sections normalized to Upper Continental Crust values (RUDNICK & GAO, 2014).

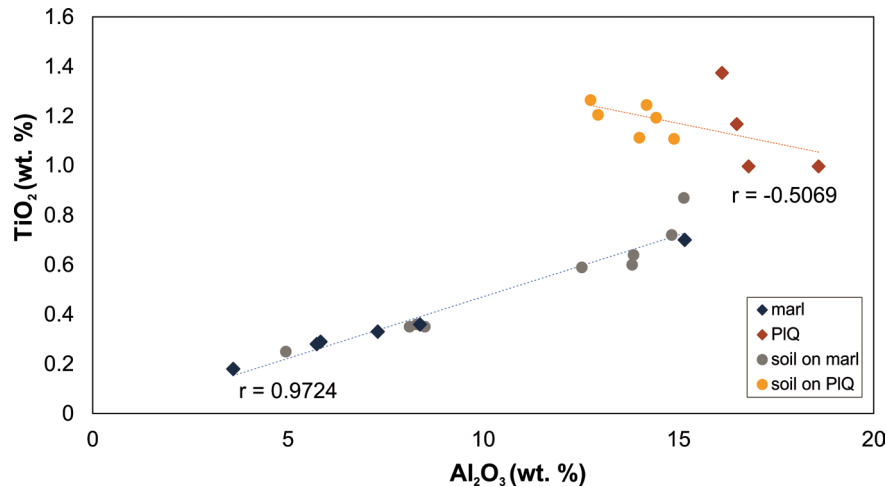


Figure 5. Correlation of  $\text{TiO}_2$  with  $\text{Al}_2\text{O}_3$  for samples of the Miocene marl profiles (blue line) and the PIQ sections (orange line).

alkaline earth elements are generally considered mobile and easily removed from the parent material during weathering (NESBITT et al., 1980; NESBITT & MARKOVICS, 1997), while elements such as Al and Ti tend to be conserved in weathered material and are considered immobile in the case of moderate chemical weathering, especially in slightly alkaline environments (NESBITT et al., 1980; PEURANIEMI & PULKKINEN, 1993; NESBITT & MARKOVICS, 1997). The strong positive correlation of the Al and Ti content in the Miocene marl profiles indicates a low mobility of the two elements

and their enrichment in the detrital component of marls, which is also reflected in the overlying soil samples (Fig. 5). The scatter of samples from the PIQ sections corresponds to their multiple source origin. The sediment samples show a clear separation from the corresponding soil samples in the PIQ sections, although the scatter, which indicates a more chaotic origin, is also preserved in the overlying soil samples.

Elemental ratios sensitive to chemical weathering were compared between parent material and topsoil samples to discern the trends within profiles (Fig. 6). Since Na and Ca are

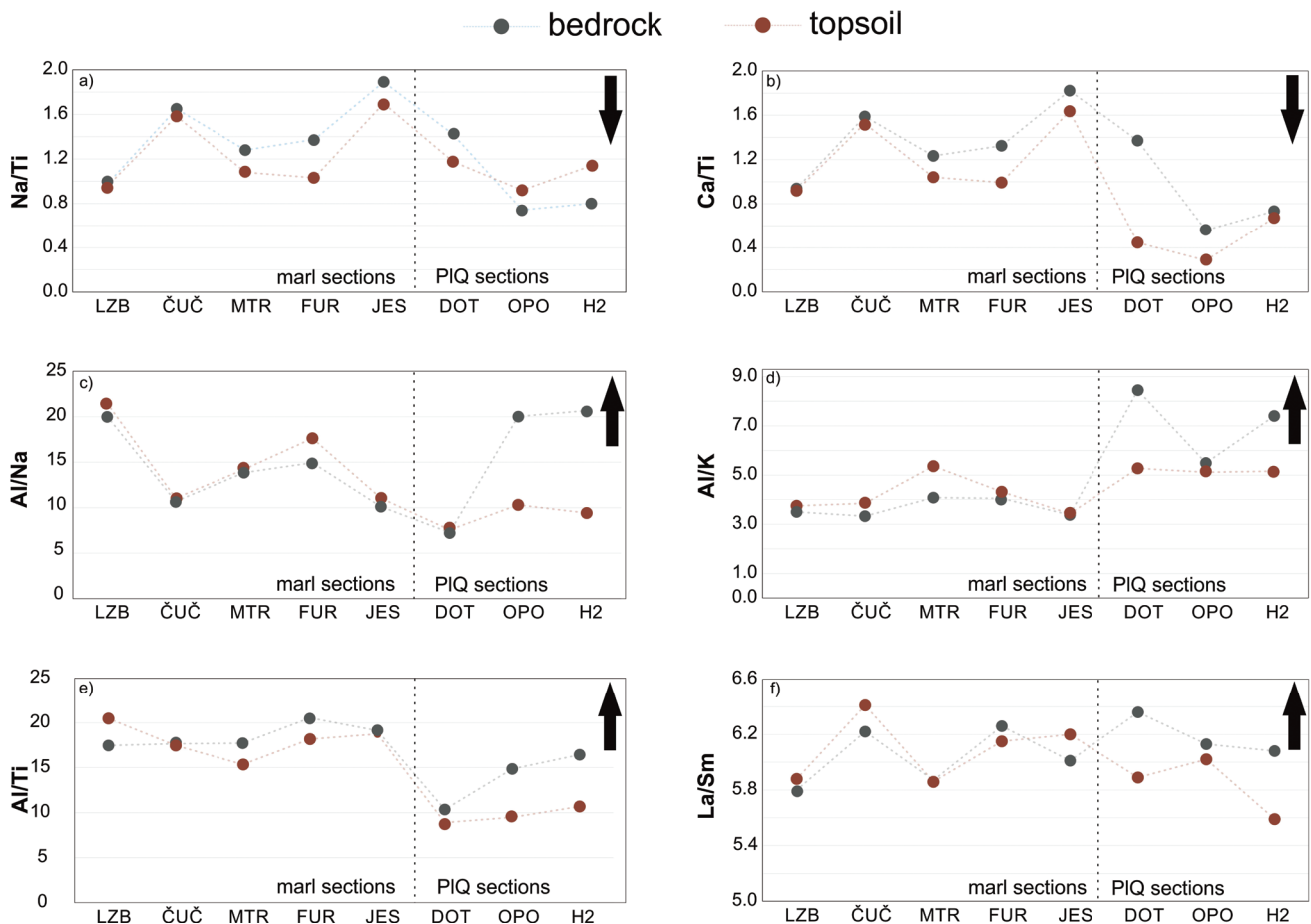


Figure 6. Elemental ratios comparison between topsoil and the parent material/bedrock. The arrows indicate trends under increased weathering intensity.



**Table 5.** Variations of major elements relative to parent material composition ( $\tau$  mass coefficient) (BRIMHALL & DIETRICH, 1987).

	$\tau_{Si}$	$\tau_{Al}$	$\tau_{Fe}$	$\tau_{Mg}$	$\tau_{Ca}$	$\tau_{Na}$	$\tau_K$
LZB 0-10	0.14	0.05	0.19	-0.13	-0.20	-0.02	-0.02
LZB 10-30	0.03	0.04	0.18	-0.11	-0.18	-0.05	0.03
ČUČ 0-20	0.03	-0.01	0.14	-0.20	-0.50	-0.04	-0.14
MTR 0-20	-0.22	-0.13	-0.04	-0.78	-0.96	-0.16	-0.34
MTR 35-40	-0.04	0.02	0.08	-0.19	0.06	0.04	0.00
FUR 0-20	-0.15	-0.12	-0.10	-0.54	-0.84	-0.25	-0.17
FUR 20-60	-0.03	0.04	0.01	-0.15	0.11	-0.15	0.09
JES 0-20	-0.04	-0.02	0.08	-0.01	1.07	-0.10	-0.03
JES 20-40	-0.03	0.00	0.02	-0.06	0.82	-0.07	-0.05
JES 40-90	0.00	0.06	0.21	-0.08	1.15	0.00	0.02

easily removed during chemical weathering (NESBITT & YOUNG, 1982), their ratio to Ti is decreased in more weathered samples. Ti is expected to stay immobile under all circumstances apart from extreme chemical weathering conditions (NESBITT & MARKOVICS, 1997; SHELDON & TABOR, 2009), which is not assumed for these samples due to the presence of feldspars and expandable clay minerals (GVERIĆ et al., 2022, 2023). There is a similarity in the distribution of both ratios in the Miocene marl samples, suggesting that topsoil is more depleted in the aforementioned elements than the parent material. However, in the PIQ samples the topsoil is depleted in Ca, while the same is not true for Na (Fig. 6a,b).

In the Miocene profiles, the Al/K ratio in the soil samples is generally higher than in the parent material, which is more pronounced in some of the studied profiles, whereas the trend is reversed in the PIQ sections (Fig. 6d). Al/K ratios tend to increase during chemical weathering of stronger intensity (WEI et al., 2006), as K will then more easily be leached out instead of incorporated into clay minerals structure (NESBITT et al., 1980). This, albeit subtly, is evident in the marl profiles and soils developed on top of the genetically related parent material, suggesting an expected weathering and pedogenesis pattern. For PIQ sections, in which soil and parent material are not necessarily genetically related, the Al/K ratio shows a geochemical signature of higher weathering intensity, (or longer weathering exposure), in the PIQ sediment material than in the overlying soil samples. La/Sm ratios, which can trace more intense chemical weathering occurrences (WEI et al., 2006), indicate a similar conclusion, showing the greatest increase in PIQ sediments of Dotrščina and Horvatovac when compared to the respective topsoil samples (Fig. 6f). Substantial differences shown in the element ratios between rock and soil samples in the PIQ sections also confirm the fact that this soil was developed on an unrelated parent material (most likely loess derivate), as previously postulated (GVERIĆ et al., 2023).

Differences in the absolute values of elemental ratios between different Miocene marl profiles can also reflect the different source material for the siliciclastic component of the marls; material of local origin (Inner Dinarides) during the Early Miocene was gradually replaced with material from more distant source areas (the Alps, Carpathians) by the Late Miocene (GRIZELJ et al., 2017). In the PIQ sections, the sediment is exclusively of local origin and was deposited in a

shorter period of time from torrents, with a composition influenced by local lithological variations, as well as the transport mechanism.

#### 4.4. Geochemical weathering signature and correspondence between geochemical and mineralogical proxies for profiles on Miocene sedimentary rocks

The clay mineralogy of marl samples indicates an intermediate weathering intensity. Clay minerals in the soil profiles developed on the Miocene marls are largely inherited from the parent material with early stages of transformation visible in the occurrence of mixed-layered species detected in the uppermost soil horizons (GVERIĆ et al., 2022). Transformations are, however, very subtle and impeded by the high pH caused by the presence of carbonates.

Changes in the major element composition in weathered material and soil samples developed on Miocene carbonate-rich sedimentary rocks (Table 5), show the greatest variations in Ca content, reflecting both carbonate dissolution in most profiles and secondary carbonate formation detected in the Jesenovac profile (GVERIĆ et al., 2022). There is no notable accumulation of Al and only a slight loss of alkali elements. Loss of K observed in some soil samples reflects the progressive loss of illite layers in mixed-layered illite smectite towards the profile surface (GVERIĆ et al., 2022).

#### 4.5. Geochemical weathering signature and correspondence between geochemical and mineralogical proxies for the PIQ sediment and overlying soil

Most indices of chemical weathering show similar trends for all the PIQ sections (Table 6). CIA values are in the range of

**Table 6.** Weathering indices calculated for PIQ sections samples.

	CIA	CIW	PIA	CPA
DOT 25	80	88	87	91
DOT 120	81	90	89	93
DOT 300	79	84	82	91
OPO 25	82	92	91	94
OPO 40	85	94	93	96
OPO 70	85	94	93	97
H2 25	80	89	88	93
H2 70	79	88	86	92
H2 150	87	94	93	97
H2 250	87	94	93	97

79 to 87, corresponding to intermediate to intense degrees of weathering (NESBITT & YOUNG, 1982; FEDO et al., 1995). CIW and PIA show similar trends and range from 84 to 94 and 82 to 93, respectively. Both indices show higher absolute values than the CIA, which is expected due to the omission of  $K_2O$  (CIW) or the correction for  $K_2O$  (PIA) in the calculations. CPA shows values of 91 to 97.

There is a general discrepancy between the PIQ sediment samples and the overlying soil samples of the Oporovec and Horvatovac localities. The sediment samples consistently have indices corresponding to more intense weathering than the overlying soil samples. This is in line with the theory of soil formation in different weathering conditions and from more recent sediments, such as subsequently deposited loess material.

Ammonium oxalate extractable Fe and Mn were measured for the PIQ samples to determine the ratio of poorly crystallized Fe and Mn to total Fe and Mn (Table 7). As a consequence of the initial stage of soil development at the sites studied, there is a higher ratio of poorly crystallized Fe ( $Fe_o$ ) to total Fe ( $Fe_t$ ) in the soil than in the parent material, as shown in Table 5. This is not evident for Mn, since Mn oxyhydroxides are very readily remobilized in soil.

Geochemistry of the PIQ sections confirms the fact postulated in the previous study (GVERIĆ et al., 2023), that the soil horizons most likely developed from subsequently deposited material. The clay minerals assemblage in the PIQ samples generally corresponds to a higher intensity and degree of weathering during the earlier PIQ sediment deposition, observed by the presence of low-charge expandable minerals (smectite) and Fe/Al (oxy)hydroxides (GVERIĆ et al., 2023). However, the presence of feldspar (and expandable clay minerals) in all of the PIQ sediment samples suggests either that those possible intense weathering periods were not long-lasting or that the material originates from multiple sources that have undergone various degrees of weathering. Subsequent weathered material and overlying soil samples in which hydroxy-interlayered minerals were detected, as well as the (locally dominant) presence of high-charge expandable minerals (vermiculite), correspond to a lower intensity and degree of weathering, also evidenced by the calculated

geochemical indices and observed  $Fe_o/Fe_t$  ratios. The only exception, Dotrščina, shows the most advanced pedogenesis and the development of a Stagnosol, i.e. a pseudogley soil (GVERIĆ et al., 2023). Even though the nature and origin of the PIQ sediments is problematic in the context of geochemically derived conclusions, all of the weathering indices used show the same trends, and correspond well with previously obtained mineralogical and pedological information.

## 5. CONCLUSIONS

The results of this study show that, in general, there is a good correlation between the geochemical and mineralogical weathering signatures in the parent materials, weathered materials and soil samples, which were analyzed in the foothill area of Medvednica Mt. The very subtle effects of weathering and pedogenesis in the Miocene profiles studied, already suggested by the mineralogical data, are now confirmed by the absence of any appreciable enrichment of Al and only a slight loss of alkali and alkaline earth elements, in agreement with the previously postulated changes in mineralogy. The geochemical weathering indices in the investigated PIQ sections also agree with the previously determined mineralogical contents and show higher values in the samples that also contain more low-charge expandable clay minerals as well as Fe and Al oxides.

While the geochemical signatures of the parent material are largely preserved in the soil profiles developed on the Miocene sediments, they show marked heterogeneity both between the PIQ sediments and the overlying soil samples. Within soils developed on Miocene sediments, we therefore observe the consequences of pedogenesis with distinct geochemical and mineralogical (shown in previous study) changes on one and the same parent material. The observed discrepancy between the soils/weathered materials and the PIQ sediments is the result of the heterogeneity of the parent materials, (as a consequence of proluvial sedimentation of these deposits) and their weathering status (pre-weathered sediments), prior to their final deposition as proluvial sediment. Likewise, the geochemical composition indicates that the Miocene marl samples are derived from a well-differentiated continental material, while the provenance signature of the PIQ sediments corresponds to their diverse multi-source origin.

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**Table 7.** Ammonium oxalate extractable Fe and Mn content (in ppm) and their fraction in total Fe and Mn of the PIQ sections. Total Fe and Mn values are recalculated from Table 2.

Sample	$Fe_o$	$Mn_o$	$Fe_o/Fe_t$	$Mn_o/Mn_t$
DOT 25	92	13	0.0034	0.0127
DOT 120	126	66	0.0030	0.0180
DOT 300*	59	8	0.0013	0.0682
OPO 25	99	3	0.0037	0.0069
OPO 40	88	3	0.0026	0.0074
OPO 70*	77	7	0.0021	0.0109
H2 25	81	14	0.0021	0.0126
H2 70	77	4	0.0025	0.0082
H2 150*	16	b.d.l.	0.0005	-
H2 250*	22	2	0.0006	0.0183

\* marks PIQ sediment samples

b.d.l. = below detection limit

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**Supplement 1.** Concentrations of trace elements (in ppm) of the samples from profiles on marls.

	LZB 0-10	LZB 10-30	LZB 30-50	ČUČ 0-20	ČUČ 200	MTR 0-20	MTR 35-40	MTR 150	FUR 0-20	FUR 20-60	FUR 70	JES 0-20	JES 20-40	JES 40-90	JES 220
Ba	222	228	223	275	210	389	188	179	408	276	279	384	412	402	605
Ni	199	270	148	45	35	65	33	31	70	44	42	51	55	62	61
Sc	8	9	8	5	4	16	6	6	14	9	8	12	12	13	14
Co	17.6	27.5	11.6	7.1	6.6	18.7	9.4	8.0	16.8	11.1	12.2	14.1	15.3	15.2	15.4
Cs	13.5	14.6	12.6	3.2	2.7	7.9	3.4	3.5	8.5	5.1	5.1	6.7	7.2	7.6	8.3
Ga	9.6	9.6	8.0	5.3	3.7	19.9	6.3	6.1	18.5	9.7	9.9	15.7	16.7	16.9	19.2
Hf	2.3	1.9	1.8	1.6	1.5	6.0	1.3	1.3	4.4	1.5	1.8	3.7	4.2	2.9	3.9
Nb	7.5	7.0	6.3	4.9	3.7	15.6	4.5	4.6	13.7	6.4	6.8	11.7	12.8	11.9	14.1
Rb	61.7	70.2	60.7	49.1	35.9	104.9	42.1	45.1	118.7	68.2	65.7	109.4	114.5	116.3	134.3
Sn	2	2	2	2	<1	3	1	1	3	2	2	3	3	3	4
Sr	459.4	507.8	608.2	1214.2	2021.1	113.9	353.0	361.2	124.8	305.4	317.3	172.2	180.1	187.9	175.8
Ta	0.5	0.5	0.4	0.4	0.3	1.1	0.4	0.3	0.9	0.5	0.4	0.8	0.8	0.8	0.8
Th	6.5	7.4	5.4	4.3	3.4	13.0	5.1	5.3	12.4	7.4	7.2	10.5	11.1	11.4	12.1
U	2.1	1.8	1.6	2.2	2.6	2.5	1.5	2.2	2.1	2.1	1.4	2.2	2.2	2.0	3.0
V	62	64	62	46	38	127	53	51	116	67	64	95	107	105	120
W	1.4	1.6	1.9	0.9	1.1	2.1	0.7	0.9	2.2	1.4	1.1	1.9	2.0	2.1	2.2
Zr	84.1	68.4	64.9	64.1	58.3	234.8	47.7	52.5	163.1	54.9	65.7	140.7	147.8	111.7	151.8