

## Heavy minerals as indicators of source material in soils on carbonates

Barbara Čeplak<sup>a,\*</sup>, Miloš Miler<sup>a</sup>, Nina Zupančič<sup>b,c</sup>, Simona Jarc<sup>b</sup>

<sup>a</sup> Geological Survey of Slovenia, Dimičeva ulica 14, 1000 Ljubljana, Slovenia

<sup>b</sup> University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Aškerčeva cesta 12, 1000 Ljubljana, Slovenia

<sup>c</sup> ZRC SAZU Ivan Rakovec Institute of Paleontology, Novi trg 2, 1000 Ljubljana, Slovenia

### ARTICLE INFO

#### Keywords:

Phaeozem  
Upper Triassic dolomite  
Flysch layers  
Trace elements  
SEM/EDS

### ABSTRACT

The origin of the soils formed on carbonate rocks remains uncertain, as they are probably of polygenetic origin. Of particular interest are the elevated contents of some trace elements detected in these soils, as they can hardly be attributed to insoluble residues of carbonate rock. The aim of this study was to uncover the relationship between heavy minerals in bedrock and soil and to identify other sources that influence the mineral and chemical composition of soil. We investigated representative samples of soils and dolomite bedrock as well as sandstones and marlstones from the nearby flysch basin as an expected source of the aeolian contribution. XRD and SEM/EDS showed that mineral diversity is higher in soils compared to the dolomites. Heavy minerals found in dolomite insoluble residue include sphalerite, Ti-oxide (probably rutile), zircon, fluorite, pyrite, minerals of REE phosphates and apatite group, interpreted as terrigenous detrital material. The mineral composition of soil heavy fraction is only partly following insoluble residues of bedrock and indicates possible aeolian contribution. Comparison with nearby flysch sandstones and marlstones showed similarities in mineralogical diversity by the presence of chromite and Fe-Cr(Mn) oxides (probably carmichaelite). Other minerals present in soils and flysch layers, such as Ti-oxide (probably rutile), zircon, REE phosphates, and pyrite grains, however, show similarities in mode of occurrence and transport indications. Signs of aeolian transport on the grains detected in soils were further confirmed by SEM/EDS.

### 1. Introduction

There are approximately 15% of the world's land surface composed of carbonate rocks (Goldscheider et al., 2020) while in Slovenia this type of rock covers as much as 40% of the area (Komac, 2005). Consequently, carbonate rocks represent an important soil parent material that affects soil formation and subsequently regulates soil properties and their usability (Kabata-Pendias, 2011; Tangari et al., 2021). Focusing on soils formed on carbonate rocks, it was found that they not necessarily reflected the parent material's characteristics (Pinheiro Junior et al., 2021a). Namely, carbonate parent material sedimented in distinct environments can have various inputs of compositionally different terrigenous material, resulting in various geochemical fingerprints in the soils (Zupančič et al., 2018), including the presence of specific trace elements.

The process of soil formation on carbonate bedrock in addition to bedrock depends on topography, landscape (Sharma et al., 2005), non-mineral organic matter, climate (Pinheiro Junior et al., 2021a; Zupančič, 2017), vegetation (Zupančič, 2012) and duration of pedogenesis

(Tangari et al., 2021; Čeru and Šegina, 2021). It was found, that the mineral composition of soil formed on carbonate bedrock at the Adriatic Dinaric carbonate platform is not uniform. Babić et al. (2013) focused on the Late Pleistocene aeolian sands deposited on older carbonate rocks of the southeastern Adriatic islands and concluded that their preservation and accumulation are influenced by a specific karstic terrain formed by deformation, karstification, and by local fluvial processes. Also Skaberne et al. (2009) claim that the allochthonous material of the carbonate rocks in the West Karawanks Mountains and the plateaus of the Julian Alps is related to the deglaciation of the Drava glacier and the subsequent aeolian and fluvial transport of the material. The importance of aeolian transport for soil formation on carbonate rocks in this area was also shown in the studies of Durn et al. (1999, 2007); Durn (2003); Küfmann (2003) and Zupančič et al. (2018). In addition, the diversity of mineral composition of soils could also be a consequence of other factors, including topography, climatic characteristics, vegetation, aqueous solutes from leaching water, etc. (Feng et al., 2009; Sharma et al., 2005; Zupančič, 2012).

\* Corresponding author.

E-mail addresses: [barbara.ceplak@geo-zs.si](mailto:barbara.ceplak@geo-zs.si) (B. Čeplak), [milos.miler@geo-zs.si](mailto:milos.miler@geo-zs.si) (M. Miler), [nina.zupancic@ntf.uni-lj.si](mailto:nina.zupancic@ntf.uni-lj.si) (N. Zupančič), [simona.jarc@ntf.uni-lj.si](mailto:simona.jarc@ntf.uni-lj.si) (S. Jarc).

<https://doi.org/10.1016/j.geodrs.2023.e00735>

Received 25 July 2023; Received in revised form 19 October 2023; Accepted 29 October 2023

Available online 31 October 2023

2352-0094/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

The main minerals in carbonate rocks are calcite, dolomite, magnesite, aragonite, and organic skeletons formed of calcite and aragonite (Alderton, 2021). The most common minor minerals are quartz, feldspars, ilmenite, etc. (Gregorič, 1969). However, trace metals and minerals content in carbonate rocks is generally low compared to silicate rocks (Salomons and Förstner, 1984) as carbonate rocks have a low content of detrital material. On carbonate rocks almost all carbonate minerals are removed in the first stage of pedogenesis so in this case the nature of the soil formation is determined by the insoluble residue (Gregorič, 1969). The quantity of terrigenous material of carbonate rocks depends on the environment in which these rocks were sedimented (Zupančič et al., 2018). In some cases, karst soils may have been formed exclusively from the insoluble residues of carbonate rocks, but more often this type of soil consists of material derived from more than one source, for example loess, desert dust and volcanic ash (Durn et al., 1999). Usually, trace elements are linked with clay minerals, Fe, Mn and Al oxides and hydroxides (Pinheiro Junior et al., 2021b; Zupančič, 2017) or are associated with heavy minerals (Lovrenčić Mikelić et al., 2013).

The relationship between the mineral composition of the crystalline bedrock and the corresponding soils in the aspect of the presence of heavy minerals has been the subject of several earlier studies (Durn et al., 2007; Gregorič, 1969; Tangari et al., 2021; Valera Fernández et al., 2022). Some of them, however, focused on the origin of specific minerals e.g. Cr-spinel's (Bónová et al., 2018), garnets (Krippner et al.,

2014) and rutile (Zack et al., 2004), which have been detected in both media, bedrock and soil.

The soils formed on carbonates might have high contents of some trace elements, which is hardly attributed only to insoluble residue. According to the earlier studies, the highest contents of Zn, Pb and Cr in Croatia's karst region were found to be 974 mg/kg, 382 mg/kg and 524 mg/kg, respectively, while in Southwestern China these values in soils in the karst region were 732 mg/kg, 528 mg/kg and 1442 mg/kg for Zn, Pb and Cd respectively (Wen et al., 2020). Also, soils in the research area are enriched in Co, Cr, Ni, Cu, Pb, and Zn (Gosar et al., 2019; Zupančič, 2012, 2017). The maximum reported contents were 65 mg/kg, 250 mg/kg, 117 mg/kg, 133 mg/kg, 255 mg/kg and 710 mg/kg for Co, Cr, Cu, Ni, Pb and Zn (Zupančič, 2012, 2017). The source of these high concentrations may be related to organic material, clay minerals, human activities, weathering of the parent material (Zupančič, 2012, 2017) as well as to the transport of aeolian material.

Objective of the study is to determine the possible correlation between the heavy minerals in bedrock insoluble residue and soil's heavy mineral fraction as well as to identify the influence of other sources affecting soil's mineral and chemical composition, i.e., aeolian deposition of Eocene flysch particles, which has already been found as a possible factor that affects heavy metal content in soil in the Mediterranean area (Zupančič, 2017). The study aims to stress the importance of understanding soil formation on carbonate rock and upgrade the

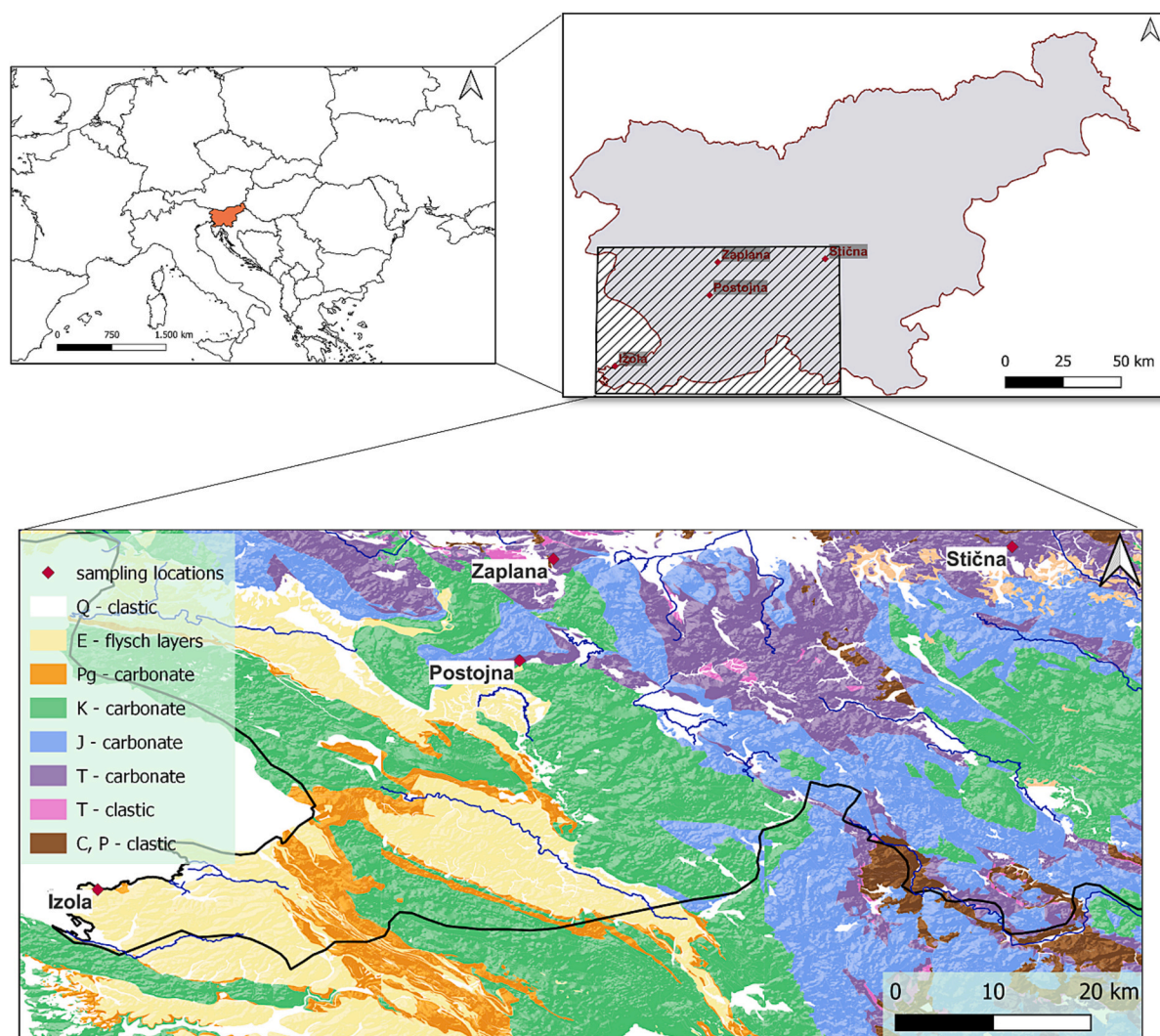


Fig. 1. Simplified geological map of the investigated area with the main lithological units (Buser et al., 1967, 1968a, 1968b; Babić et al., 1969; Šikić et al., 1972; Savić and Dozet, 1984).

knowledge of these complex systems.

## 2. Materials and methods

### 2.1. Geological setting

The investigated area encompasses three locations on Slovenian territory, namely Postojna (PO), Zaplana (ZA) and Stična (ST) (Fig. 1). The area consists mainly of dolomites and limestones covered with Phaeozem, brown soils and leached soils (Vidic et al., 2015). The typical vegetation of the studied area is forests and grassland. Hill ridges have a northwest-southwest direction. At all three locations bedrock is the same – Upper Triassic Main Dolomite (Fig. 1); they are all at the approximately same elevation: around 600 m a.s.l., SW slope insolation, and at various distances from the sea and Istria and Brkini flysch basins (Babić et al., 1969; Buser et al., 1968a).

Geologically, the studied area belongs to the External Dinarides of the Dinaric carbonate platform, which is part of a huge Adriatic Dinaric Carbonate platform (AdCP) evolved from the Middle Permian to the Eocene (Vlahović et al., 2005). The Dinaric carbonate platform represents the relics of the Southern Tethyan Mega platform and is characterized by very thick carbonate deposits formed mostly in shallow marine environments (Vlahović et al., 2005). During the Late Permian to Middle Triassic intense tectonic activity took place, leading to Middle Triassic volcanism throughout Adria. The volcanic rocks are especially common on Internal Dinarides, while External Dinarides are built mostly of dolomite, limestone (Pamic, 1984), and occasionally also of marlstone, sandstone and claystone (Pleničar et al., 2009). In Jurassic, the disintegration of AdCP began establishing several carbonate platforms (Adriatic, Apenninic and Apulian). Sinesedimentary tectonics, which was especially widespread in the Late Cretaceous, resulted in the final disintegration of the AdCP (Vlahović et al., 2005). In the Paleocene flysch sedimentation started and continued up to the Middle Eocene (Buser and Pavšič, 1978). Istrian flysch extends from Trieste through southwestern Slovenia, Istria, Croatian Coastland and Dalmatia to Boka Kotorska and is composed of hemipelagic marls and various gravity flow deposits (Petrijak et al., 2021).

### 2.2. Sampling and sample preparation

Three locations selected for sampling were Postojna (marked as PO), Zaplana (ZA) and Stična (ST). Four topsoil (0–15 cm) samples were collected at each site, comprising two samples of forest (F)-covered soils and two samples of grassland (G)-covered soils without organic horizons weighing about 2 kg each (labels of collected samples: PO-1G, PO-2G, PO-3F, PO-4F, ZA-1G, ZA-2G, ZA-3F, ZA-4F, ST-1G, ST-2G, ST-3F, ST-4F). The sampling sites were selected at approximately the same elevation, on the same SW insolation and on the same parent rock avoiding possible anthropogenic influences. One 2 kg sample of non-weathered dolomite bedrock was also collected at each site (labels of collected samples: PO-K, ZA-K, ST-K). The soil type at all three sites was Phaeozem (Vidic et al., 2015). Besides dolomite samples and soil samples, the four samples of Istrian flysch (sandstone and marlstone) near Izola, were also collected (F1, F2, F3, F4).

All soil samples were dried in an oven at 40 °C. After drying, soil samples were sieved through a 2 mm sieve. To estimate heavy minerals in soils, between 10 g and 25 g of each soil sample were sieved below 2 mm were subjected to a heavy-liquid separation using bromoform (density of 2.89 g/cm<sup>3</sup>).

To identify heavy minerals, polished thin sections were prepared from unweathered dolomite samples from each site (PO-K, ZA-K, ST-K) as well as from sandstone and marlstone samples (F1, F2, F3, F4). In addition, about 10 g of each dolomite sample was finely hand crushed in porcelain mortar and dissolved in 60 ml of 6 N HCl. Afterwards, the insoluble residue was obtained by filtration through polycarbonate (PC) membrane filter with pore diameter of 0.45 μm.

Some representative samples of soil (PO-2G and PO-3F), bedrock (PO-K), and flysch rock (F1, F2, F3, F4) were homogenized, grinded, quartered to reduce sample size to 10 g, and subsequently sieved below 0.063 mm.

### 2.3. Analytical methods

The general mineral composition of rocks and soils was performed by X-Ray powder diffraction (XRD) using a Philips PW3710 diffractometer (PANalytical B.V.) equipped with CuK $\alpha$  radiation and a graphite monochromator. X-rays were generated with a voltage of 10 kV and a current of 10 mA. The data were recorded in the range  $2^\circ \leq 2\theta \leq 70^\circ$  with the wavelengths of K $\alpha$  1.5406 Å. The mineral compositions of the samples were determined using the X'pert Highscore Plus database. XRD analyses were performed on three samples, namely PO-2T, PO-3G, and PO-K, providing a rough estimate of mineral composition that can also be considered for the other two sites. Heavy mineral fraction of soils, polished thin sections and insoluble residue of bedrock were examined by applying scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS). Similarly, sandstone and marls samples were further inspected by SEM/EDS and transmitted polarizing light microscopy on the polished thin section. Prior to SEM/EDS analyses, all samples were carbon-coated and then observed in high vacuum in backscattered electron (BSE) mode using JEOL JSM 6490LV SEM coupled with an Oxford INCA Energy 350 EDS at an accelerating voltage of 20 kV, a working distance of 10 mm, and an acquisition time of 60 s. Minerals were assessed from the atomic proportions of the constituent elements and comparison with atomic proportions of constituent elements in known stoichiometric minerals obtained from known mineral databases (Anthony et al., 2009; Barthelmy, 2010). The EDS software was calibrated for quantification using premeasured universal standards included in the EDS software, according to fitted standards procedure (Goldstein et al., 2003) referenced to a Co optimization standard. The correction of EDS data was performed on the basis of the standard ZAF-correction procedure included in the INCA Energy software (Oxford Instruments, 2006).

Relative abundance of heavy minerals in samples was estimated from the distribution of constituent elements, obtained by EDS elemental mapping at 80 $\times$  magnification (soil heavy fraction) and 1200 $\times$  magnification (bedrock insoluble residue) of a randomly selected field of view in each sample according to the established procedure (Miler et al., 2022 and references therein) and by comparison with mineral grain percentage composition charts for sediments (Compton, 1962).

The geochemical composition of the flysch samples (sandstones labeled F1, F2, F3 and F5, and marlstone labeled F4) was analysed using the Niton XL3t GOLDD 900 handheld X-ray fluorescence (XRF) instrument. Analytical accuracy for Cr, verified using standard materials NIST -2709a, W-2, SCo1, and NIST-1633a, and precision based on replicate samples were acceptable.

## 3. Results

### 3.1. General mineral composition of bedrock and soils

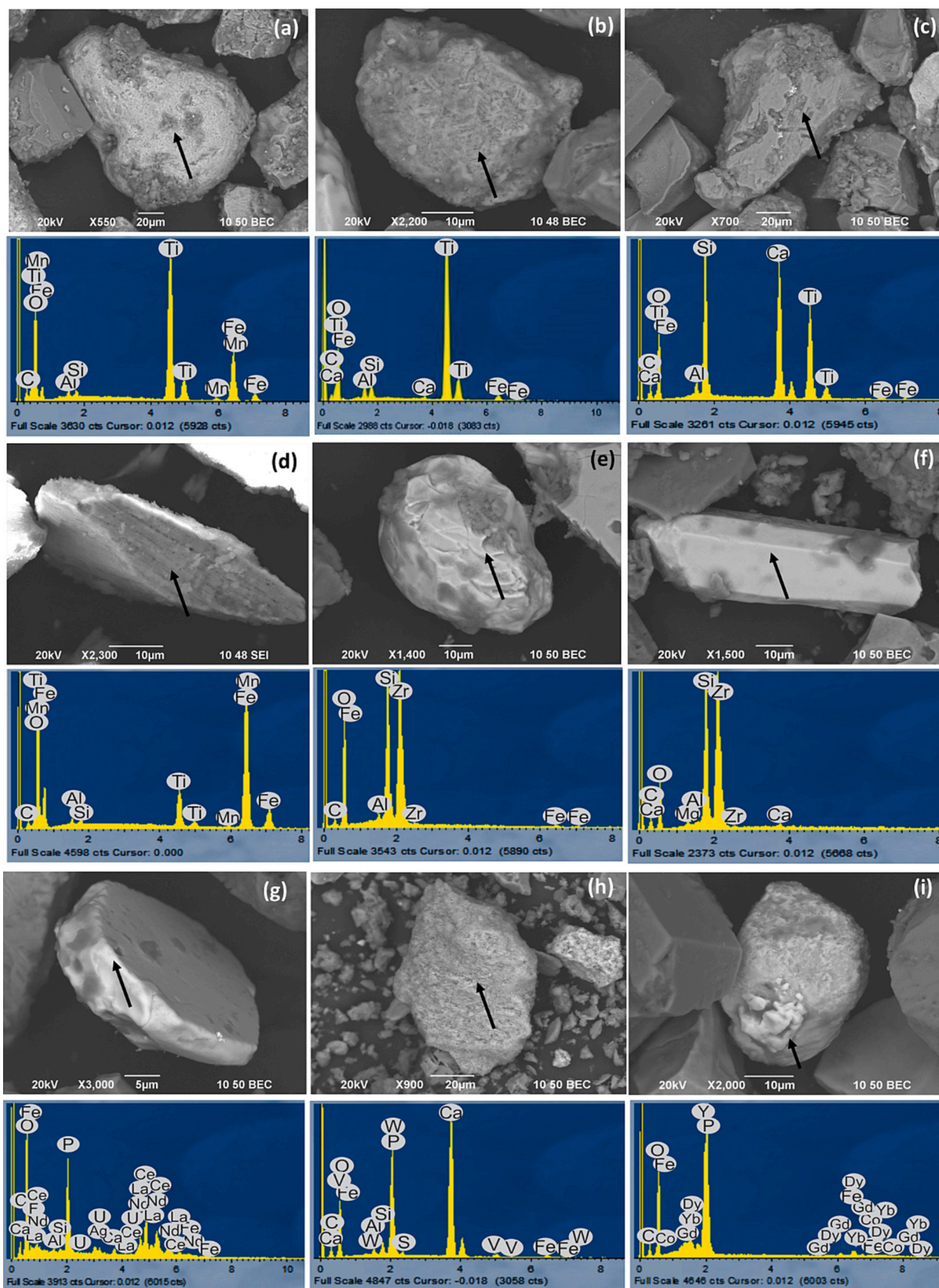
XRD analysis of bedrock (dolomite) confirms pure dolomite, with no other minerals detected (Fig. 2). The result is confirmed by the very small amount of insoluble residue in dolomite ranging from 0.03 wt% in dolomite from Postojna to 0.70 wt% in dolomite from Zaplana. Observation is in line with the previous studies on a Slovenian territory (Gosar, 2007; Ogorelec and Rothe, 1992), where low quantities of insoluble residues of carbonate rocks were detected.

Soil samples have approximately homogenous mineral compositions. XRD analysis of selected samples i.e. PO-2 T and PO-3G, showed prevalence of dolomite and quartz, over muscovite and clay minerals such as illite and chlorite group of minerals. The dolomite content in soils is influenced by fine unweathered bedrock fragments. The portion of

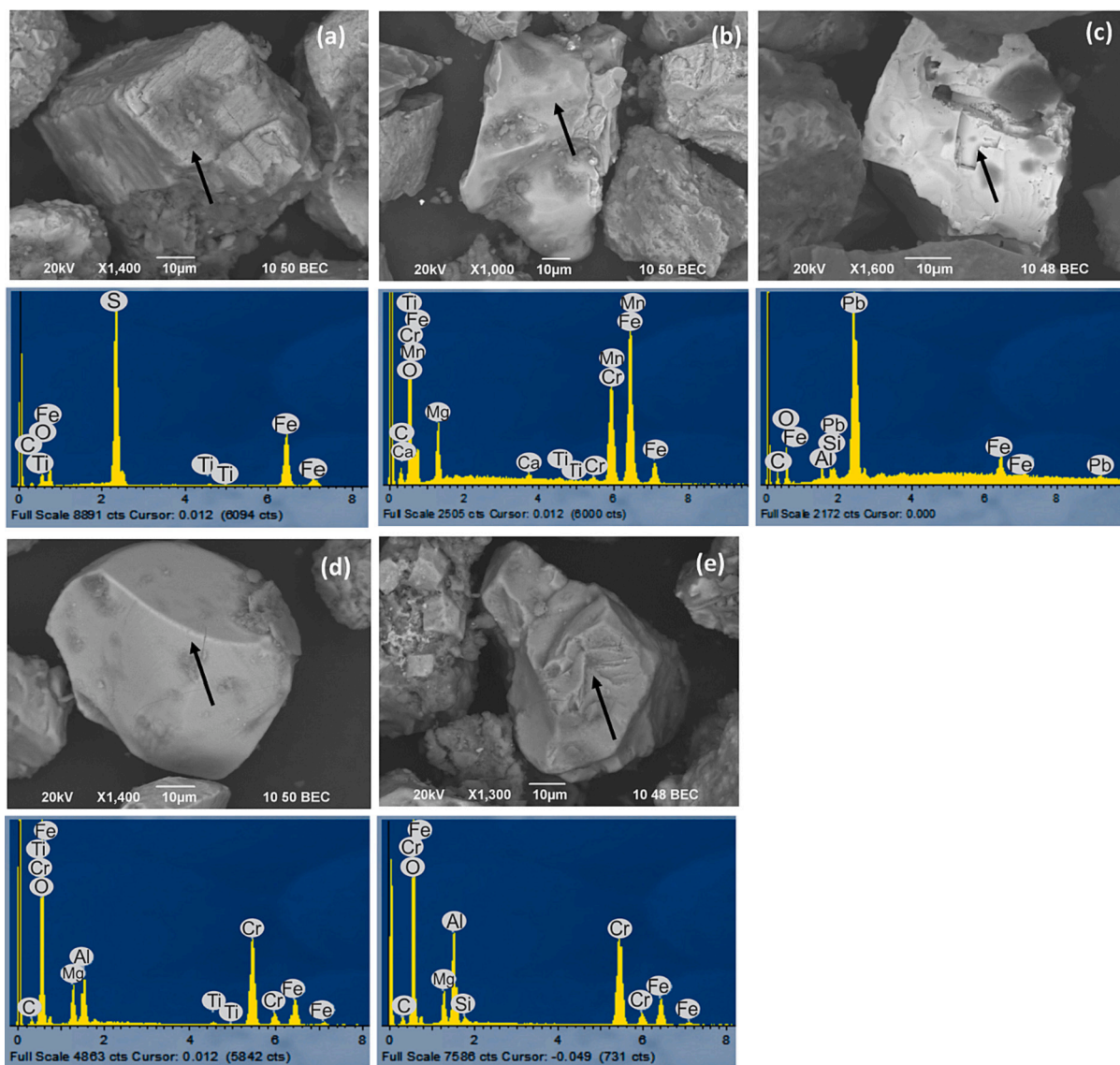








**Fig. 3.** SEM images and EDS spectra of minerals in soil samples: a) rounded ilmenite (ZA, grassland), b) sub-rounded Ti-oxide (probably rutile) (PO, forest), c) anhedral titanite (ST, forest), d) subhedral titanomagnetite (PO, grassland), e) rounded zircon (ST, grassland), f) prismatic zircon (PO, grassland), g) monazite group mineral (ZA, forest), h) apatite group mineral (ZA, grassland), i) xenotime in zircon grain (ZA, forest).



**Fig. 4.** SEM images and EDS spectra of minerals in soil samples: a) pyrite (ZA, grassland), b) anhydrous Fe-Cr(Mn) oxide/hydroxide (PO, forest), c) Pb oxide/carbonate (PO, grassland), d) subhedral chromite (ST, grassland) and e) anhydrous magnesiocromite (PO, grassland).

in soils is 40  $\mu\text{m}$ . Occasionally, anhydrous xenotime grains (10  $\mu\text{m}$ ) are found as inclusions in other minerals (e.g., zircon) (Fig. 3i). In dolomite, the grains of phosphate minerals are mostly anhydrous up to 3  $\mu\text{m}$  for monazite (Fig. 5 d) and 5  $\mu\text{m}$  for the apatite group (Fig. 5e).

Pyrite is rarely present, but is found in both media. Grains up to 60  $\mu\text{m}$  and with slightly rounded edges were found in the Zaplana soil (Fig. 4a), whereas the pyrite grains in the dolomite are smaller (up to 2  $\mu\text{m}$ ) and have an anhydrous to subangular shape (Fig. 5f). In contrast to the soil samples, the dolomite samples occasionally consist of sphalerite (Fig. 5g) and fluorite (Fig. 5h) grains. They have a rounded to subangular shape and are between 2 and 4  $\mu\text{m}$  in size.

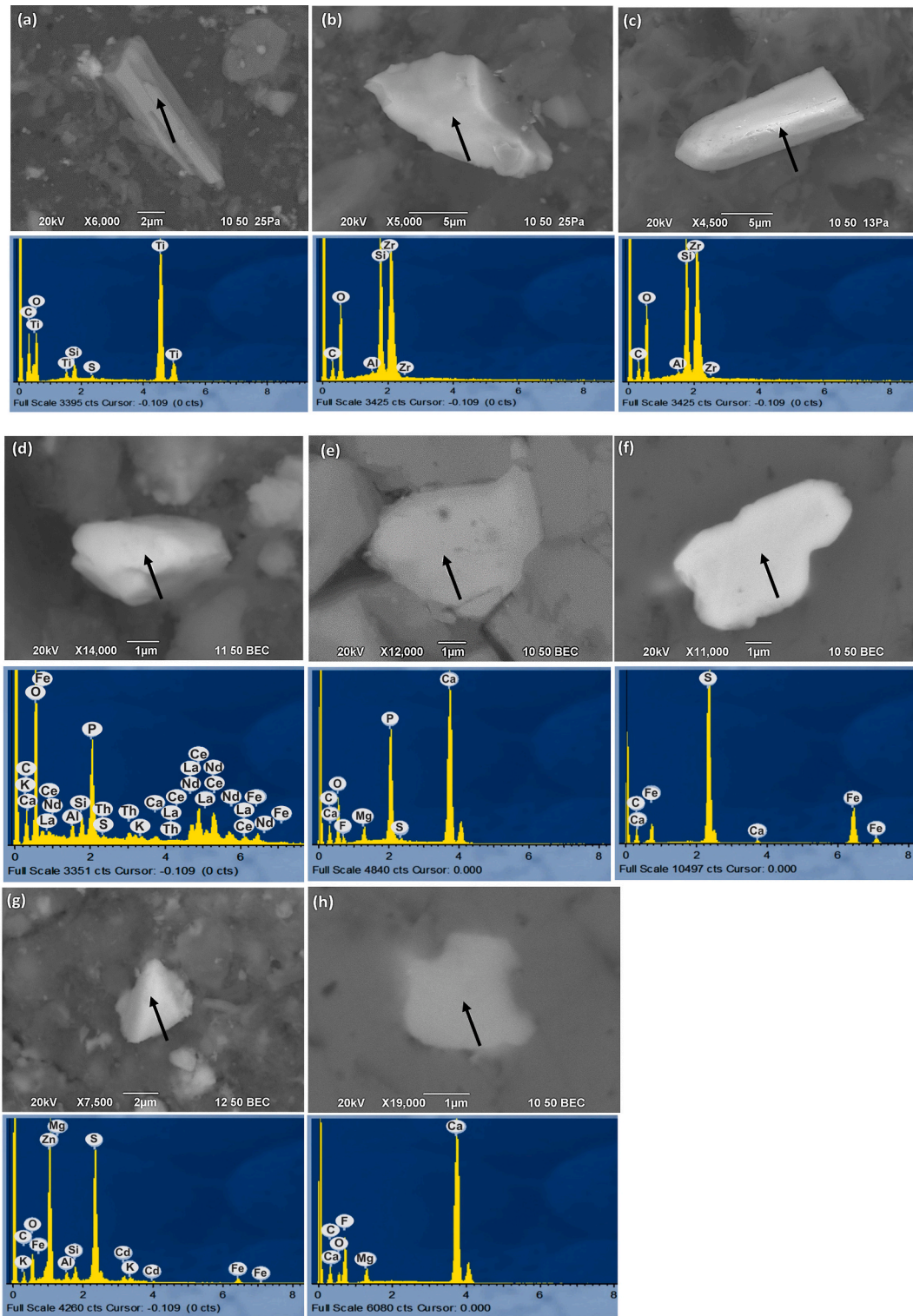
Rarely detected minerals in soils are also lead oxide/carbonate, while grains of iron oxides/hydroxides are observed quite frequently. Iron oxides/hydroxides are about 90  $\mu\text{m}$  in size. The grains are generally anhydrous with subangular edges (Fig. 4b); however, well-rounded grains are occasionally observed. The angular lead oxide/carbonate grain measures 50  $\mu\text{m}$  (Fig. 4c). Chromite, although rare, is detected in all samples (Fig. 4d). The subhedral grains are mostly round and measure between 45  $\mu\text{m}$  and 120  $\mu\text{m}$ . Another Cr mineral found in samples from Postojna is magnesiocromite (Fig. 4e), which was detected in both grassland and forest soils as subhedral grains measuring about 100  $\mu\text{m}$ .

### 3.3. Heavy minerals in sandstones and marlstones

XRF analysis of flysch rocks shows their high carbonate content, i.e. 17% of  $\text{CaO}$ .  $\text{Fe}_2\text{O}_3$  content in sandstones and marlstones is approximately 3% and about 2%, respectively.  $\text{TiO}_2$  content is in both rock types around 0.4%, and MnO around 1%. Analysis confirmed high Cr and Ni contents. Cr content in sandstones are around 115 mg/kg and 260 mg/kg in marlstones. Sandstones contain around 150 mg/kg of Ni, and marlstones 140 mg/kg.

The SEM/EDS analysis detects the presence of the following accessory minerals: Zircon, Ti-oxide (probably rutile), pyrite, monazite and xenotime group minerals, sphalerite, chromite, Cr-spinel, Fe-Cr(Mn) oxide/hydroxide, barite and grains of almandine/spessartine. Zircon grains are generally subangular in size between 25 and 100  $\mu\text{m}$  with average of 35  $\mu\text{m}$  (Figs. 6 a, b). Occasionally, grains of xenotime are found as outgrowths on zircon (Fig. 6b). Grains of Ti-oxide (probably rutile) are subhedral shaped and have a size between 10 and 100  $\mu\text{m}$  (Fig. 6a). Grains of pyrite are also observed in sandstone, occasionally having a round shape of 15  $\mu\text{m}$  (Fig. 6a), however larger grains up to 100  $\mu\text{m}$  were also observed. The grains of chromite and Cr-spinel are generally subangular or subrounded and range in size from 20 to 45  $\mu\text{m}$ ,



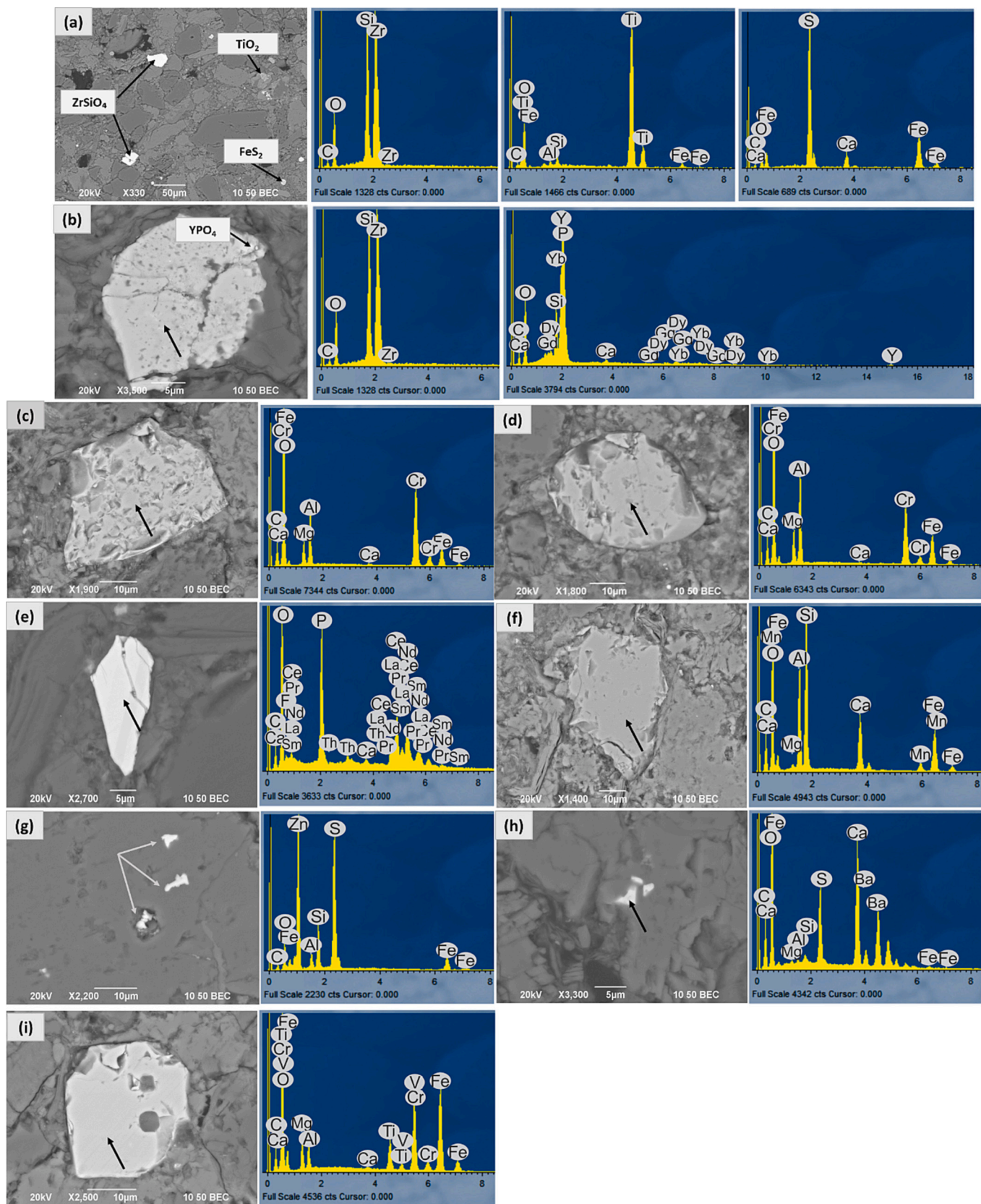


**Fig. 5.** SEM images and EDS spectra of heavy minerals in the dolomite: a) acicular grain of Ti-oxide (probably rutile) (ST), b) angular grain of zircon (ST), c) prismatic zircon (ST), d) anhedral grain of monazite group mineral (PO), e) subhedral grain of apatite group mineral (ST), f) angular grain of pyrite (ST), g) sub-rounded grain of sphalerite (PO) and h) sub-rounded grain of fluorite (ST).

averaging about 30  $\mu\text{m}$  (Figs. 6c, d). Minerals of the monazite group are euhedral shape with a size of about 25  $\mu\text{m}$  (Fig. 6e). Grains of garnet minerals (e.g., almandine/spessartine) are about 50  $\mu\text{m}$  in size and have a subangular shape, while grains of sphalerite and barite have an anhedral shape with a size of up to 10  $\mu\text{m}$ . Very often samples of flysch rocks also consists of Fe-Cr(Mn) oxide/hydroxide. The grains are

subangular with average size of 30  $\mu\text{m}$  (Fig. 6i).





**Fig. 6.** SEM/EDS images and spectra of minerals in flysch: a) Ti-oxide (probably rutile), zircon and pyrite, b) subangular zircon with minerals of xenotime group, c) subangular chromite, d) subrounded Cr-spinel, e) angular grain of monazite group of minerals, f) subangular grain of almandine/spessartine, g) anhedral grains of sphalerite, h) anhedral barite and (i) subangular grain of Fe-Cr(Mn) oxide/hydroxide.

## 4. Discussion

### 4.1. Comparison between soils and corresponding bedrock

The mineral composition of the dolomite and soil samples at all three locations is similar, with small differences between locations (Table 1). As expected, soil samples are mineralogically more diverse than dolomite due to the long-lasting processes of soil formation on the carbonate rock. In general, grains of minerals detected in soil are frequently corroded, which means they were more likely to experience more chemical weathering than grains with smooth unaltered surfaces (Föllmi et al., 2009). The most common minerals predominating in soil, and which are also detected in dolomite were grains of zircon and Ti-oxide minerals (Table 1). In both mostly angular grains of zircon and Ti-oxide (probably rutile) (Figs. 3,5) are identified which reflect high resistance to chemical weathering and mechanical abrasion of these two minerals (Velbel, 2007). The occurrence of slightly rounded grains of zircon and Ti-oxide (probably rutile) in dolomite (Fig. 5) could also represent older particles that were once transported (Dozet and Silvester, 1979). Focusing on the size of these two minerals, much larger grains are detected in soils compared to dolomite. In soils, an average size for Ti-oxide (probably rutile) and zircon are 70 and 60  $\mu\text{m}$ , while in dolomite these values are 8 and 5  $\mu\text{m}$ , respectively.

In addition to zircon and Ti-oxides' grains, soils and dolomite frequently also consist of minerals of the monazite group. In dolomite, grains are mostly sub-angular up to 3  $\mu\text{m}$ , while in soil samples they are sub-rounded with an average size of 35  $\mu\text{m}$ . Rounded grains as well as grains with no intact crystal faces have likely endured more chemical and physical weathering than euhedral grains (Föllmi et al., 2009). Unlike dolomite samples, soil samples rarely contain minerals of the apatite group as this type of mineral weathers easily (Nezat et al., 2008). The average sizes of minerals of apatite group are 130  $\mu\text{m}$  and 5  $\mu\text{m}$  for soils and dolomite, respectively.

These observations show that the mineral composition of soils is influenced not so much by the weathering of the parent material, but by other factors. The latter is consistent with the previous studies which emphasize the importance of other factors that control the process of soil formation on carbonate rocks, including strong erosion processes (Skaiberne et al., 2009), exposure to aeolian deposits (Durn et al., 1999; Gosar, 2007; Wen et al., 2020), other natural (e.g., climate, vegetation, precipitation, topography, etc.) (Gregorič, 1969; Sharma et al., 2005; Zupančič, 2012; Čeru and Šegina, 2021) and anthropogenic factors (Zhao et al., 2021).

### 4.2. Influence of aeolian material

It has been established that aeolian transport plays an important role in the process of soil formation (Durn et al., 1999; Gosar, 2007; Küfmann, 2003; Zupančič et al., 2018). In the studied area wind blowing from SW to NE over flysch basins into the interior of the Slovenian territory has been found as a possible source of aeolian transport. Based on the mineralogical identification of sandstone and marlstone from the flysch layers in Izola, the presence of the following heavy minerals, which are potential carriers of heavy metals, is established: Ti-oxide (probably rutile), Cr minerals (mainly chromite and Cr-spinel), zircon, REE phosphates (e.g., minerals of monazite and xenotime group), sphalerite, Fe-Cr(Mn) oxide/hydroxide, pyrite, barite and minerals of garnet group. The presence of these and other minerals, such as tourmaline, has been already mentioned in previous studies (Lenaz et al., 2003; Wiesender, 1960). Considering the size and morphology of these heavy minerals, some similarities are noted between heavy mineral grains in insoluble residues of soils and flysch rocks, suggesting the possibility of the same origin (Table 1).

The morphological similarities were found in grains of Ti-oxide (probably rutile), chromite, zircon, monazite, Fe-Cr(Mn) oxide/hydroxide and pyrite. Grains of heavy minerals have either the same shape

and size or have similar sights of weathering. For instance, some grains of Ti-oxide (probably rutile) found in soils and flysch rocks are subhedral in size around 25  $\mu\text{m}$  (Figs. 3b, 6a), while chromite grains are subhedral and between 45  $\mu\text{m}$  and 120  $\mu\text{m}$  in size in soils (Fig. 4d). In flysch layer these grains are generally smaller in size up to 50  $\mu\text{m}$  (Figs. 6a, c). The chromium-rich minerals in the flysch are associated with the Cretaceous convergence and the simultaneous contraction of the oceanic crust and the ascent of peridotites from the chromium-rich mantle (Lenaz et al., 2003). Cr-minerals from peridotites are characterized by low Ti content and high level of  $\text{Fe}^{2+}/\text{Fe}^{3+}$ , while Cr-minerals originated from volcanic source has high Ti level (Lenaz and Princivalle, 2005). Based on XRF and SEM/EDS analyses, Ti content exceeds 0.2 wt%, implying that these Cr minerals could be associated with volcanic sources, but Ti has been found only occasionally as a trace element in this type of mineral. In addition, the Fe content in these minerals is high, which means that the Cr minerals could be associated with peridotites.

Zircon grains in flysch layers are subhedral with size up to 100  $\mu\text{m}$ , while in soils, subhedral grains with an average size of 60  $\mu\text{m}$  are occasionally detected. Furthermore, both in the flysch and in soils the presence of zircon grains with REE is also detected (Figs. 3i,6b). Grains of pyrite are between 15 and 100  $\mu\text{m}$  in flysch and up to 60  $\mu\text{m}$  in soils respectively. Furthermore, in both also monazite grains are detected in size around 25  $\mu\text{m}$ . In both media occur the Fe-Cr(Mn) oxide/hydroxide with the presence of other trace elements e.g. Ti. The grains are generally subangular in flysch rock and become anhedral in soils, occasionally even rounded. Well-rounded grains of Fe-Ti minerals are very common in the aeolian environments of deposition (Dill, 2007).

Another similarity can be also linked with the presence of specific heavy minerals only in soils from Postojna (e.g., Ti-magnetite and Pb oxide/carbonate). Compared to the other two places, Postojna is closest to the flysch basins which means that it is the most susceptible to the wind transport of particles brought from flysch. Furthermore, with the effect of aeolian transportation we can also explain more diverse mineralogical composition of soils from grassland compared to those from forest; highlighted already in the study by Zupančič (2012), who concluded more wind-deposited material in more open space.

## 5. Conclusions

Soils formed on carbonate rocks are very likely of polygenetic origin, and their frequency in Slovenia and worldwide has led to the fact that geochemical knowledge of these soils should not be disregarded. A study conducted in the karst region of the Mediterranean has yielded several conclusions that can be applied to similar karst areas with comparable pre-basis.

The correlation between the heavy minerals found in the insoluble residues of the bedrock and the heavy mineral fraction in the soils is low. The morphological characteristics of the heavy minerals detected in the soils and corresponded dolomite varies. In the soils, the grains of heavy minerals are generally larger with signs of transportation compared with those in the dolomite. This suggests that there is an additional source, besides weathering of the parent material, that influences the presence of heavy minerals in karst soils. The heavy minerals detected in the dolomite can be, however, considered as terrigenous detrital material.

The mineral composition of soils in the karst region is influenced by the aeolian (wind-driven) transport of particles. The latter is mainly confirmed by the presence of chromite and Fe-Cr(Mn) oxides/hydroxides, which were present both in the soil and in the sandstones and marlstones. Furthermore, grains of certain heavy minerals such as Ti-oxide (probably rutile), zircon, chromite, REE phosphate, pyrite, and Fe-Cr(Mn) oxide/hydroxide show similar morphological characteristics (i.e., size and shape) in both, soils and flysch. Consequently, we can confirm the influence of prevailing winds blowing from southwest to northeast over the Eocene flysch basin, carrying and subsequently depositing small particles of heavy minerals inland.

This study emphasizes the importance of natural factors, especially



the influence of aeolian transports, in soil formation on carbonate rocks and highlight the importance of applicability of SEM/EDS technique for proving such important contribution. Further research could investigate other factors, such as pedoclimatic factors, topography, and erosion to improve our understanding of soil formation in fragile systems such as the karst region.

### Declaration of Competing Interest

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

### Data availability

Data will be made available on request.

### Acknowledgements

The presented study was supported by the Slovenian Research and Innovation Agency (ARIS) in the frame of the young researcher program and the following research programs No. P1-0025, P1-0195 and P1-0008. We thank Neli Ivanović for helping with data on the mineralogical characterization of flysch sandstones and marlstones. We thank the reviewers for comments and suggestions, which helped to improve the article.

### References

- Alderton, David, 2021. Carbonates (Ca, Mg, Fe, Mn). In: Elias, S.A. (Ed.), Alderton, D. Elsevier Ltd., Encyclopedia of Geology, pp. 382–394. <https://doi.org/10.1016/b978-0-08-102908-4.00088-6>.
- Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C., 2009. The handbook of mineralogy. Mineralogical Society of America, Chantilly, VA (accessed 10 June 2023). <http://www.handbookofmineralogy.org/>.
- Babić, L., Blašković, I., Ferjančič, L., Grad, K., Grimani, I., Juriša, M., Mamuzić, P., Milan, A., Mioč, A., Nosan, A., Orehek, A., Petriček, V., Pleničar, M., Polšak, A., Rijavec, J., Šikić, D., Šparica, M., Šriбар, L., Šušnjar, M., Vujić, D., Zlebnik, L., 1969. Basic Geological Map of SFR Jugoslavija, 1:100,000 Sheet Trst. Belgrade, Serbia.
- Babić, L., Zupanić, J., Vidović, J., Razum, I., Lužar-Oberiter, B., Crnjaković, M., 2013. Preservation of hanging aeolian deposits in insular karst depressions: sediment sources and implications for the Pleistocene palaeogeography of the SE Adriatic archipelago. *Aeolian Res.* 11, 171–189. <https://doi.org/10.1016/j.aeolia.2013.06.003>.
- Barthelmy, D., 2010. The Mineralogy Database. <http://webmineral.com/>.
- Bónová, K., Mikuš, T., Bóna, J., 2018. Is Cr-spinel geochemistry enough for solving the provenance dilemma? Case study from the palaeogene sandstones of the western Carpathians (eastern Slovakia). *Minerals* 8 (12), 543. <https://doi.org/10.3390/min8120543>.
- Buser, S., Pavšič, J., 1978. Pomikanje zgornjekrednega in paleogenskega bazena v zahodni Sloveniji. In: 9. Jugoslovanski Geološki Kongres. Sarajevo, pp. 74–81.
- Buser, S., Ferjančič, L., Grad, K., Turnšek, D., Mencej, Z., Orehek, A., Pavlovec, R., Pleničar, M., Prestor, M., Rijavec, J., Šriбар, L., 1967. Basic Geological Map of SFR Jugoslavija, 1:100,000 Sheet Postojna. Belgrade, Serbia.
- Buser, S., Cajhen, J., Gadžić, S., Gospodarić, R., Hinterlechner-Ravnik, A., Mioč, P., Orehek, S., Pavlovec, R., Pavlović, B., Pleničar, M., Pohar, V., Pohar, J., Prestor, M., Šriбар, L., 1968a. Basic Geological Map of SFR Jugoslavija, 1:100,000 Sheet Gorica. Belgrade, Serbia.
- Buser, S., Dozet, S., Cajhen, J., Ferjančič, L., Grad, K., Kerčmar, A., Turnšek, D., Mioč, P., Nosan, A., Orehek, A., Pleničar, M., Ramovš, A., Rijavec, J., Šriбар, L., Vujić, D., 1968b. Basic Geological Map of SFR Jugoslavija, 1:100,000 Sheet Ribnica. Belgrade, Serbia.
- Compton, R., 1962. Manual of field geology. Wiley & Son, New York.
- Čeru, T., Šegina, E., 2021. Some Aspects on the Role of Sediments in the Development of Karst Surface Morphology (Island of Krk, Croatia). SSRN Electronic Journal 1-51. <https://doi.org/10.2139/ssrn.3935584>.
- Dill, H.G., 2007. Grain morphology of heavy minerals from marine and continental placer deposits, with special reference to Fe-Ti oxides. *Sediment. Geol.* 198, 1–27. <https://doi.org/10.1016/j.sedgeo.2006.11.002>.
- Dozet, S., Silvester, M., 1979. Scythian and upper Carnian rocks from the Kočevje region. *Geologija* 22, 327–336.
- Durn, G., 2003. Terra Rossa in the Mediterranean region: parent materials, composition and origin. *Geol. Croat.* 56, 83–100. <https://doi.org/10.4154/GC.2003.06>.
- Durn, G., Ottner, F., Slovenec, D., 1999. Mineralogical and geochemical indicators of the polygenetic nature of terra rossa in Istria, Croatia. *Geoder.* 91, 125–150. [https://doi.org/10.1016/S0016-7061\(98\)00130-X](https://doi.org/10.1016/S0016-7061(98)00130-X).
- Durn, G., Aljinović, D., Crnjaković, M., Lugović, B., 2007. Chapter 28 heavy and light mineral Fractions Indicate Polygenesis of Extensive Terra Rossa Soils in Istria, Croatia. *Dev. Sedimentol.* 58, 701–737. [https://doi.org/10.1016/S0070-4571\(07\)58028-3](https://doi.org/10.1016/S0070-4571(07)58028-3).
- Feng, J.L., Zhu, L.P., Cui, Z.J., 2009. Quartz features constrain the origin of terra rossa over dolomite on the Yunnan-Guizhou plateau, China. *J. Asian Earth Sci.* 36, 156–167. <https://doi.org/10.1016/j.jseas.2009.05.003>.
- Föllmi, K.B., Hosein, R., Arn, K., Steinmann, P., 2009. Weathering and the mobility of phosphorus in the catchments and forefields of the Rhône and Oberaar glaciers, Central Switzerland: implications for the global phosphorus cycle on glacial-interglacial timescales. *Geochim. Cosmochim. Acta* 73, 2252–2282. <https://doi.org/10.1016/j.gca.2009.01.017>.
- Goldscheider, N., Chen, Z., Auler, A.S., Bakalowicz, M., Broda, S., Drew, D., Hartmann, J., Jiang, G., Moosdorf, N., Stevanovic, Z., Veni, G., 2020. Global distribution of carbonate rocks and karst water resources. *Hydrogeol. J.* 28, 1661–1677. <https://doi.org/10.1007/s10040-020-02139-5>.
- Goldstein, J., Newbury, D., Joy, D., Lyman, C., Echlin, P., Lifshin, E., Al, E., 2003. Scanning electron Microscopy and x-Ray Microanalysis, 3rd ed. Kluwer Academic/Plenum Publishers, New York.
- Gosar, M., 2007. Trace element distribution in three karst soil profiles from Slovenia. *Geologija* 50, 147–156. <https://doi.org/10.5474/geologija.2007.012>.
- Gosar, M., Šajn, R., Bavec, Š., Gabersček, M., Pezdriž, V., Miler, M., 2019. Geochemical background and threshold for 47 chemical elements in Slovenian topsoil. *Geologija* 62, 7–59. <https://doi.org/10.5474/geologija.2019.001>.
- Grogorić, V., 1969. Nastanek tal na triadnih dolomitih (soil formation on the triassic dolomite). *Geologija* 12, 201–230.
- Kabata-Pendias, A., 2011. Trace elements in soils and plants, fourth edition. CRC Press, Boca, Raton, London, New York.
- Komac, M., 2005. Statistics of the Geological Map of Slovenia at scale 1: 250.000. *Geologija* 48, 117–126. <https://doi.org/10.5474/geologija.2005.011>.
- Krippner, A., Meinhold, G., Morton, A.C., Von Eynatten, H., 2014. Evaluation of garnet discrimination diagrams using geochemical data of garnets derived from various host rocks. *Sediment. Geol.* 306, 36–52. <https://doi.org/10.1016/j.sedgeo.2014.03.004>.
- Küfmann, C., 2003. Soil types and eolian dust in high-mountainous karst of the northern calcareous Alps (Zugspitzplatt, Wetterstein Mountains, Germany). *Catena* 53, 211–227. [https://doi.org/10.1016/S0341-8162\(03\)00075-4](https://doi.org/10.1016/S0341-8162(03)00075-4).
- Lenaz, D., Princivalle, F., 2005. The crystal chemistry of dentritic chromian spinel from the southeastern Alps and outer Dinarides: the discrimination of supplies from 41 areas of similar tectonic setting? *Can. Mineral.* 43, 1305–1314. <https://doi.org/10.2113/gscanmin.43.4.1305>.
- Lenaz, D., Kamenetsky, V.S., Princivalle, F., 2003. Cr-spinel supply in the Birkinj, Istria and Krk Island flysch basins (Slovenia, Italy and Croatia). *Geol. Mag.* 140, 335–342. <https://doi.org/10.1017/S0016756803007581>.
- Lovrenčić Mikelić, I., Oreščanin, V., Barišić, D., 2013. Distribution and origin of major, minor, and trace elements in sediments and sedimentary rocks of the Kaštela Bay (Croatia) coastal area. *J. Geochem. Explor.* 128, 1–13. <https://doi.org/10.1016/j.jexplo.2013.01.003>.
- Miler, M., Bavec, Š., Gosar, M., 2022. The environmental impact of historical Pb-Zn mining waste deposits in Slovenia. *J. Environ. Manag.* 308 <https://doi.org/10.1016/j.jenvman.2022.114580>.
- Nezat, C.A., Blum, J.D., Yanai, R.D., Park, B.B., 2008. Mineral sources of calcium and phosphorus in soils of the northeastern United States. *Soil Sci. Soc. Am. J.* 72 <https://doi.org/10.2136/sssaj2007.0344>.
- Ogorelec, B., Rothe, P., 1992. Mikrofazies, Diagenese und Geochemie des Dachsteinkalkes und Hauptdolomits in Süd-West-Slovenien. *Geologija* 35, 81–181. <https://doi.org/10.5474/geologija.1992.005>.
- Oxford Instruments, 2006. INCA Energy Operator Instruments Analytical Ltd. (High Wycombe) 84p.
- Pamić, J.J., 1984. Triassic magmatism of the Dinarides in Yugoslavia. *Tectonophysics* 109. [https://doi.org/10.1016/0040-1951\(84\)90145-8](https://doi.org/10.1016/0040-1951(84)90145-8), 273–277, 281–307.
- Petrinjak, K., Budić, M., Bergant, S., Korbar, T., 2021. Megabeds in istrian flysch as markers of synsedimentary tectonics within the dinaric foredeep (Croatia). *Geol. Croat.* 74, 99–120. <https://doi.org/10.4154/gc.2021.07>.
- Pinheiro Junior, C.R., Cipriano da Silva, R., da Silva Neto, E.C., de Azevedo, A.C., do Nascimento, C.W.R., Fontana, A., de Souza Júnior, V.S., dos Anjos, L.H.C., Pereira, M.G., 2021a. Influence of carbonate rocks on soil properties in the humid tropical climate of atlantic forest, Rio de Janeiro –Brazil. *J. S. Am. Earth Sci.* 112 <https://doi.org/10.1016/j.james.2021.103582>.
- Pinheiro Junior, C.R., Pereira, M.G., de Azevedo, A.C., Van Huyssteen, C., dos Anjos, L.H.C., Fontana, A., da Silva Neto, E.C., Vieira, J.N., Santos, T.G., 2021b. Genesis and classification of carbonate soils in the state of Rio de Janeiro. *Brazil. J. South Am. Earth Sci.* 108 <https://doi.org/10.1016/j.james.2021.103183>.
- Pleničar, M., Ogorelec, B., Novak, M., 2009. The Geology of Slovenia. Geološki zavod Slovenije, Ljubljana.
- Salomons, W., Förstner, U., 1984. Metals in the Hydrocycle. Springer-Verlag Berlin Heidelberg.
- Savić, D., Dozet, S., 1984. Basic Geological Map of SFR Jugoslavija, 1:100,000 Sheet Delnice. Belgrade, Serbia.
- Sharma, B.D., Mukhopadhyay, S.S., Arora, H., 2005. Total and DTPA-extractable micronutrients in relation to pedogenesis in some alfisols of Punjab, India. *Soil. Sci.* 170, 559–572. <https://doi.org/10.1097/01.ss.0000175343.07293.e1>.
- Šikić, D., Pleničar, M., Šparica, M., 1972. Basic Geological Map of SFR Jugoslavija, 1: 100,000 Sheet Ilirska Bistrica. Belgrade, Serbia.



- Skaberne, D., Kralj, P., Budkovič, T., 2009. Soils on the late Triassic carbonate rocks in the west Karavanke Mountains and the high plateaus of the Julian Alps (Slovenia). *Geologija* 52, 49–68.
- Tangari, A.C., Le Pera, E., Andò, S., Garzanti, E., Piluso, E., Marinangeli, L., Scarciglia, F., 2021. Soil-formation in the Central Mediterranean: insight from heavy minerals. *Catena* 197, 104998. <https://doi.org/10.1016/j.catena.2020.104998>.
- Valera Fernández, D., Solleiro Rebolledo, E., Sedov, S., Pustovoitov, K., 2022. Provenance, and environment context of pedogenic carbonates formation from MIS 3 to MIS 1 in the Teotihuacan Valley, Mexico. *Quat. Int.* 618, 52–69. <https://doi.org/10.1016/j.quaint.2021.03.019>.
- Velbel, M.A., 2007. Chapter 4 surface textures and dissolution processes of heavy minerals in the sedimentary cycle: examples from pyroxenes and amphiboles. *Dev. Sedimentol.* 58, 113–150. [https://doi.org/10.1016/S0070-4571\(07\)58004-0](https://doi.org/10.1016/S0070-4571(07)58004-0).
- Vidic, N.J., Prus, T., Grčman, H., Zupan, M., Liseč, A., Al, E., 2015. Soils of Slovenia with Soil Map 1:250 000. European Commission Joint Research Centre (JRC): Publications Office of the European Union, Luxembourg.
- Vlahović, I., Tišljar, J., Velič, I., Matičec, D., 2005. Evolution of the Adriatic carbonate platform: Palaeogeography, main events and depositional dynamics. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 220, 333–360. <https://doi.org/10.1016/j.palaeo.2005.01.011>.
- Wen, Y., Li, W., Yang, Z., Zhang, Q., Ji, J., 2020. Enrichment and source identification of Cd and other heavy metals in soils with high geochemical background in the karst region, Southwestern China. *Chemosphere* 245. <https://doi.org/10.1016/j.chemosphere.2019.125620>.
- Wiesender, H., 1960. *Petrographie und Petrologie der eozanen Flyschsandsteine. Verhandlung. Geol. Bundesanst.* 166–171.
- Zack, T., von Eynatten, H., Kronz, A., 2004. Rutile geochemistry and its potential use in quantitative provenance studies. *Sediment. Geol.* 171, 37–58. <https://doi.org/10.1016/j.sedgeo.2004.05.009>.
- Zhao, Yuyan, Zhang, Z., Li, B., Zhao, Yu, Lu, J., Tang, X., 2021. Accurate determination and comprehensive evaluation of heavy metals in different Soils from Jilin Province in Northeast China. *Anal. Lett.* 54, 1901–1928. <https://doi.org/10.1080/00032719.2020.1828908>.
- Zupančič, N., 2012. The influence of vegetation type on metal content in soils. *Mater. Geoenviron.* 59, 229–244.
- Zupančič, N., 2017. Influence of climate factors on soil heavy metal content in Slovenia. *J. Soils Sediments* 17, 1073–1083. <https://doi.org/10.1007/s11368-016-1614-z>.
- Zupančič, N., Turniški, R., Miler, M., Grčman, H., 2018. Geochemical fingerprint of insoluble material in soil on different limestone formations. *Catena* 170, 10–24. <https://doi.org/10.1016/j.catena.2018.05.040>.