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# Hydromorphic bog iron ore formation in foothill Cambisols: mineralogical and geochemical evidence from Knezovljani, central Croatia

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## Abstract

This study examines the formation and geochemical signature of Fe-rich horizons and bog iron-type accumulations in hydromorphic soils at Knezovljani, in the foothills of the Trgovska and Petrova gora massifs, central Croatia. A pedological trench with three soil profiles was described and sampled, with horizons and a hardened Fe-rich layer analysed using grain size analysis, X-ray diffraction (XRD), portable X-ray fluorescence (pXRF), with XRF and inductive couple plasma mass spectrometry (ICP-MS) for selected hardened Fe samples. The soils contain silt (50–75%) with 10–32% clay, are moderately acidic (pH 4.8–5.9), and they consist of quartz, feldspars, and illite–smectite clays with trace kaolinite, indicating intermediate weathering. One horizon shows pronounced Fe enrichment (33.8 wt% $Fe_2O_3$), with high contents of goethite and a laminated Fe-cemented facies, while other horizons contain only 5–9 wt% $Fe_2O_3$. Trace elements are elevated in Fe-rich layers, with positive correlation towards $Fe_2O_3$. Comparison with regional bog iron ores and Mn-rich occurrences represents Knezovljani as a small, hydrologically focused Fe accumulation pocket formed where Fe-bearing groundwater meets more oxidising conditions at a footslope of a hill, rather than in a microdepression. The Knezovljani Fe horizon is thin and discontinuous, indicating short-lived or spatially restricted Fe mobilisation–precipitation cycles. The findings highlight the importance of microtopography and subsurface flow in formation of secondary Fe ores, providing a framework for further studies on ore types, spatial distribution, and geochemical characterisation towards studies of bog iron ore in central Croatia.

**Keywords:**
hydromorphic soils; geochemistry; correlation matrix; pXRF; geoarchaeology

## 1. Introduction

Central continental Croatia, located between the alluvial plains of the Kupa and Sava rivers, occupies a geological and cultural crossroads between the southeastern Alps, the southern Pannonian Basin, and the northern Dinaric ophiolitic-karst zone. This position enabled mobility, exchange, and technological transfer of iron production throughout Antiquity (**Bojanovski, 1988**; **Durman, 1992**, **2002**; **Koščević, 1995**; **Karavidović and Drnić, 2022**). However, archaeological evidence for primary Iron Age iron production, associated with secondary accumulations, such as near-surface bog iron ores or mechanically transported ores in foothills and lowlands, remains scarce across the region (**Brenko et al., 2025**, and references therein). Preconditions for such production are present in the region, with near-surface ferruginous materials, abundant woodlands for charcoal, and suitable ceramic clays all widespread. Comparable Iron Age sites in the neighbouring Dolenjska region (Slovenia) exploited limonitic ores in similar lowland settings (**Črešnar et al., 2017**; **Trampuž Orel, 2012**), with cultural and chronological links to production and processing sites in Pokuplje and Posavina (e.g. Gornje Pokuplje, Sisak–Pogorelec, Topusko, Velika Vranovina; **Karavidović and Drnić, 2022**). Historical records document 19th-century exploitation of ferruginous soils in the Kupa Valley (**Marković, 2002**; **Laszowski, 1942**), alongside mining of primary ores and gossans in the adjacent mountains (**Jurković, 1993**; **Šebetić, 2000**; **Marković, 2002**).

This indicates the presence of bog iron ores, a sedimentary type of secondary Fe-deposit, formed through diagenetic and pedogenic Fe cycling in shallow groundwater environments such as floodplains, fens, and microdepressions, where redox boundaries drive iron mobilisation from protoliths and precipitation as oxyhydroxides (goethite, lepidocrocite, hematite; typically 30–50 wt.% $Fe_2O_3$) (**Ramanaidou and Wells, 2014**; **Kaczorek and Zagórski, 2007**; **Brenko et al., 2020**;

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**Karavidović and Brenko, 2022**). These discontinuous, iron-cemented horizons originate from sources such as Palaeozoic siderite–ankerite veins in local flysch and are transported to Quaternary soils (**Šikić, 1988**; **Borojević Šoštarić et al., 2009**). Although extensively documented in the Podravina floodplains of Croatia (e.g. Kalinovac–Hrastova Greda; **Brenko et al., 2020**; **Karavidović et al., 2025**), bog iron ore remains underexplored in the Dinarides–Pannonian transition zone, particularly in foothill and lowland settings without laterally continuous deposits.

This study addresses that gap by investigating shallow Fe accumulations in the foothills and lowlands of central Croatia surrounding Petrova gora and Trgovska gora, where subtle relief and groundwater promote redox-driven concentration without extensive horizons. Building on regional evidence from the Drava, Posavina, and Pokuplje lowlands (**Brenko et al., 2020**, **2025**; **Karavidović and Brenko, 2022**; **Sekelj Ivančan and Karavidović, 2021**; **Karavidović et al., 2025**), this study analyses Fe and trace elements (As, Cr, Ni, Cu, Pb, Zn) from primary ores through soil sequestration and fractionation. To achieve this, a pedological trench was excavated, exposing three soil profiles and a secondary iron ore formation, which were analysed using mineralogical, petrographic, and geochemical methods. These findings are compared with regional occurrences of secondary Fe accumulation to define formation mechanisms and archaeological potential as an iron ore during archaeological periods in the region.

## 2. Characteristics of the study area

### *2.1. Geology*

The research area is located in central Croatia, at the transition zone between the Dinarides and the Pannonian Basin transition (see **Figure 1a-b**). The region underwent significant tectonic evolution, transitioning from Adriatic carbonate platform to ophiolitic and flysch belt (**Majer and Lugović, 1985**; **Šikić et al., 1990**). The basement units generally consist of late Palaeozoic clastic successions, Carboniferous to Permian flysch including shales, siltstones, greywackes, and quartz-rich sandstones with subordinate conglomerates, followed by Triassic-Jurassic carbonates, and locally Cretaceous-Palaeogene flysch and ophiolites. Towards the study sites, the regional structures extend into the alluvial plains of the Kupa (Pokuplje) and Sava (Posavina) rivers, which occupy the south-western edge of the Pannonian Basin and are strongly influenced by Neogene-Quaternary tectonics and sedimentation.

The Pokuplje study area is comprised of the Črnomelj-Bosiljevo-Ozalj Plain, which forms part of the Upper Kupa Valley, with approximate elevations 130–300 m a.s.l. Here, loess-like silts, fluvial sands, and marshland soils overlie heterogeneous Neogene-Quaternary fills. In particular, the area is characterised by clayey strata that frequently cause waterlogging and reduced aeration, directly impacting redox geochemistry. On the other hand, the Posavina study area represents a large basin consisting of a lowland in the interior (approx. 90–110 m a.s.l.) in the Sava-Odra-Lonja depressions, rising to 140–160 m at the basin margins, and surrounded by mountains such as Medvednica, Moslavačka gora, and Vukomeričke gorice. In some areas, there are thick successions of alluvium interbedded with fine-grained, loess-like and marsh deposits.

The regional study area was also affected by hydrothermal and metasomatic processes linked to post-orogenic reactivation. These processes generated NE–SW striking vein systems and metasomatic lenses enriched in Fe- and other mineralisation, such as siderite, ankerite, quartz, and sulphide minerals (pyrite, chalcopyrite, galena, sphalerite). Such mineralisation, well documented in nearby Petrova and Trgovska gora (**Borojević Šoštarić et al., 2009**), is typically hosted by carbonate intercalations or along fracture zones within the flysch sequence. Further weathering of these mineralised veins produced iron oxide coatings, hematite and limonite alteration (**Jurković, 1990**), which can be transported in the lowland area, and then precipitated as secondary Fe phases in soil, close to the redox boundary (**Kaczorek and Sommer, 2003**).

### *2.2. Pedology*

The soils at Knezovljani and surrounding foothills reflect the interplay of low-relief topography, siliceous Palaeozoic flysch parent material, and humid temperate climate characteristic of northern Dinarides lowlands (**Filipčić, 1998; Husnjak, 2014**). On valley floors and lower slopes under Neogene-Quaternary clayey silts and alluvium, hydromorphic Gleysols and Fluvisols predominate, exhibiting periodic saturation and gleying where subsurface clays or shales impede drainage (**Šikić, 1988**). Profiles typically comprise a thin humus-rich horizon overlying gleyed horizons with clay translocation, Fe-Mn mottling, which can all be interpreted as a clear signature of redox fluctuations driven by shallow groundwater (**Brenko et al., 2020**).

The Knezovljani Depression, a tectonically subsided trough, shows amplification of these processes. Here, the fault-controlled margins channel Fe-enriched groundwater from weathered siderite-ankerite veins into fine-grained fluvio-lacustrine depression filled with clays, silts, fine sands (**Vidaček and Husnjak, 2021**). Weakly to strongly acidic (pH 3.5-5.5 in KCl), non-calcareous conditions favour $Fe^{3+}$ reduction in saturated zones, with oxidative reprecipitation as goethite nodules upon seasonal groundwater fluctuation, yielding discontinuous Fe-cemented horizons, which might have been suited for historic exploitation (**Bašić, 2013**). This lowland gleying horizon exhibits similar characteristics to

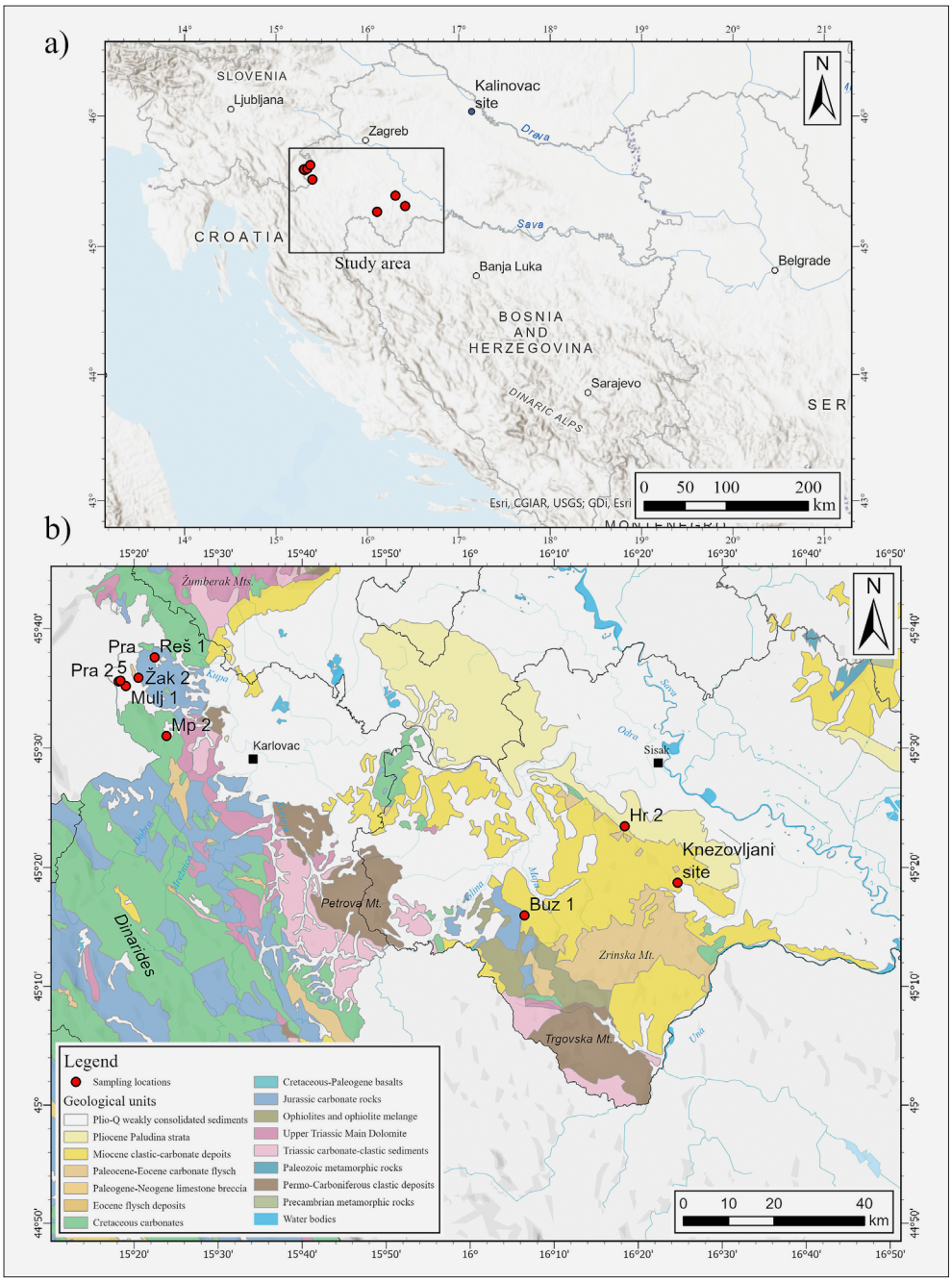



**Figure 1:** a) Map with occurrences of iron ore found within soils in the study area and the position of the comparative site in lowland Drava alluvial plain – the Kalinovac – Hrastova greda site; and b) geological map of the study area with sampling positions.

the Podravina region, linking geogenic Fe inputs to archaeometallurgical potential (**Brenko et al., 2020**).

### *2.3. Hydrology*

The Knezovljani area features a dual hydrogeological system consisting of a shallow porous aquifer within Neogene–Quaternary fluvio-lacustrine sediments and a deeper fractured aquifer in the Palaeozoic–Mesozoic basement. The unconsolidated valley-fill deposits, comprising sands, silts, and clays, form unconfined to semi-confined aquifers with moderate permeability and localised lateral flow. Recharge is primarily from precipitation and slope infiltration, while discharge occurs through small springs and seepages along the valley margins.

The underlying flysch bedrock (shales, siltstones, greywackes) has low primary porosity, with groundwater movement limited to fractures and fault zones. In mineralised areas of nearby Trgovska and Petrova gora, groundwater composition is affected by weathering of siderite–ankerite and sulphide veins, occasionally resulting in elevated Fe and Mn concentrations (**Borojević Šoštarić et al., 2009**). Overall, Knezovljani represents a heterogeneous system with limited storage capacity in fractured bedrock and shallow, seasonally fluctuating aquifers in surface sediments. Groundwater flow follows the local topographic gradient from the Trgovska gora slopes towards the low-lying valley floor (approximately 197 m a.s.l.), where perched water tables and slope seepage commonly occur after heavy precipitation.

## 3. Materials and methods

### 3.1. Sampling

The field sampling campaign was conducted in the Knezovljani area to characterise soil profiles and near-surface stratigraphy. A longitudinal pedological trench was excavated to enable *in situ* examination and sampling of soil horizons. The trench measured approximately 10 m in length, 1.2 m in width, and reached a depth of 1.9 m. It was oriented along a southwest–northeast (SW–NE) transect, extending from a topographically higher position (profile Knezovljani 1) towards a lower-lying location (profile Knezovljani 3) (see **Figure 2**). This orientation was chosen to capture lateral pedological and lithological variability along the local slope gradient and to document transitions in soil morphology, texture, and horizon development across the microtopographic sequence. The trench location was chosen based on previous knowledge of groundwater retaining in the area, and occurrences of orange and reddish mottles discovered through various depths. A total of three representative profiles were selected, further divided into intervals based on the visible macro features and field estimation of the soil texture and mineralogical changes along the profile. Within the excavation trench, hardened Fe accumulation was determined, visible between profiles 1 and 2. Around 10 kg of sample was taken from this interval, sampled from Profile 1, horizon 3.

During previous field campaigns, several hardened Fe accumulations were sampled at other sites located near the villages Pravutine, Žakanje, Reštovo, Modruš Potok in the Pokuplje and Hrastovica and Osekovo in Posavina as well as site Buzeta within the foothills of Zrinska gora. The samples were found in deeply ploughed soils (ploughing depth approx. 40 cm), and the sample from Modruš Potok was taken out of an open eroded hillside profile (see **Figure 1**).

The samples were all stored in separate plastic bags. After they were transported to the laboratory, samples were air-dried. Following this, a portion of each interval was crushed and sieved through a 2 mm sieve and further analysed for their mineralogical, geochemical and physico-chemical characteristics.

### 3.2. Laboratory analyses

A list of samples, including conducted analyses on each sample is given in **Appendix A**. The colour of the soil samples was determined using the Munsell Soil Colour Chart (**Munsell, 1994**). Soil pH was measured in accordance with the ISO 10390:2005 standard, by immersing a glass electrode in a 1:5 suspension of 5 g of air-dried soil and 25 ml of 1 M KCl solution.

Mineralogical analyses were conducted at the Laboratory for Analysis of Geological Materials, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering. Subsamples of bulk material were gently crushed and sieved to <2 mm, after which they were finely ground to obtain a powder fraction suitable for X-ray diffraction (XRD) analysis. XRD patterns were obtained using a Malvern Panalytical Empyrean diffractometer equipped with 0.5° divergent and anti-scatter slits, 0.03 and 0.04 rad soller slits, Cu–Kα radiation ($\lambda$ = 1.5406 Å), operating at 45 kV and 40 mA, and a PIXcel 3D detector. Data were collected with a step size of 0.0130° 2θ and a counting time of 78.8 s per step. Mineral phases were identified using PANalytical X'Pert HighScore software (v. 5.2.0) in conjunction with the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) database. Semi-quantitative phase analysis was attempted using the Rietveld refinement method implemented in X'Pert HighScore, with crystal structure data obtained from the Crystallography Open Database (**Gražulis et al., 2009; Vaitkus et al., 2023**).

The geochemical composition of the soil samples (major and trace elements) was determined using a Hitachi XMET 8000 Expert Geo portable X-ray fluorescence spectrometer (pXRF). Each sample was measured at least five times, with individual measurements lasting 40 s and calibrated using the MiningLE mode. The average values were calculated from replicate measurements. Analytical accuracy was monitored using the certified reference material NIST 2711 (Montana Soil). Instrumental precision, based on replicate analyses and reference standards, was estimated at ±5%. Detection limits were ~200 ppm for Al and Si, and ≤20 ppm for most other major and trace elements, consistent with previously reported values for pXRF performance in soil studies (**Rouillon and Taylor, 2016; Weindorf et al., 2014**). Detailed geochemical analyses of selected bog iron and secondary Fe-mineralisation samples (hardened Fe accumulations), including major and trace element contents, was determined by Bureau Veritas laboratory in Krakow, Poland. Major element oxide contents were determined by X-ray fluorescence analysis on fused discs. Trace element (As, Ni, Pb, Zn, Cu) contents were measured by inductively coupled plasma mass spectrometry (ICP-MS) after near-total four-acid digestion. Four internal standards and numerous blanks were used during analysis, ensuring instrumental precision of 3–5% and detection limits for all reported elements in the ppm range or lower.

Soil particle size distribution was determined using the laser diffraction method (ISO 13320:2009) with a Malvern Mastersizer 3000. The particle size classification followed the USDA system, defining sand (2000–63 μm), silt (63–4 μm), and clay (<4 μm) fractions. Approximately 0.5 g of each sample was dispersed in distilled water and soaked overnight. Samples were then treated in an ultrasonic bath for 10 min and maintained in suspension using a magnetic stirrer. Suspensions were diluted to achieve an obscuration level of 3–4% before analysis and subjected to an additional 20 s of ultrasonic

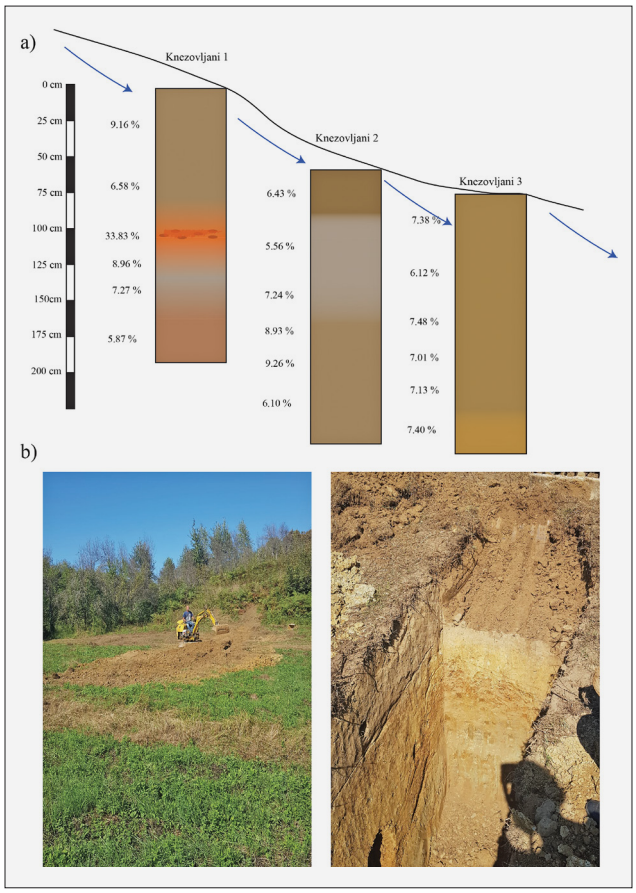



**Figure 2:** a) Schematic drawing of the three soil profiles within the trench with visible iron accumulations, contents of $Fe_2O_3$ and estimated groundwater flow direction and b) visible soil discolouration on the field and within pedological pit.

treatment immediately prior to measurement. Each sample was measured five times, and mean values were used to calculate final particle size distributions.

## 4. Results

### *4.1. Physico-chemical characteristics*

#### 4.1.1. Soil profiles

Soil texture across the three profiles is dominated by the fine fraction, with silt as the prevailing component (ranging between 50 and 75%) (see **Table 1**). Clay content varies from about 10% to 32%, with the highest values recorded in horizons Knez 3 (31%) and Knez 12 (27%), while several horizons (e.g. Knez 5–6, Knez 10) display lower clay contents (<15%). Sand is generally subordinate, typically below 20%, though higher proportions occur in deeper parts of first profile (35-38%). These results classify the soils predominantly as silt loam to silty clay loam in texture. Soil pH values range from 4.84 (Knez 1) to 5.91 (Knez 18), indicating acidic conditions throughout all profiles. A slight increase in pH with depth is observed in profiles 2 and 3, whereas profile 1 remains more variable, reflecting localised differences in parent material weathering and secondary mineral phases. Across the three studied profiles, soil colours were consistently within the 2.5Y hue range, with some variation in value and chroma. In Profile 1, most horizons exhibited yellowish-brown colours of 2.5Y 5/4, with one horizon showing 2.5Y 6/4 (Knez 4) and a distinctly redder 2.5YR 5/6 at Knez 3. Profile 2 showed generally uniform colours, ranging from 2.5Y 4/4 in the upper horizon (Knez 7), through 2.5Y 5/4 in the mid-section (Knez 10–12), to 2.5Y 6/4 in horizons Knez 8 and 9. Profile 3 was characterised by stronger chroma, with horizons predominantly coloured 2.5Y 5/6 (Knez 13–17), while the lowest horizon (Knez 18) displayed a brighter 2.5Y 6/8.

#### 4.1.2. Hardened Fe accumulations

The sample from the Knezovljani site (Knez 19), the hardened Fe accumulation is a subrounded fragment with visible lamination. Similar features are observed in smaller nodules (0.05–5 cm) and larger lamellar or subrounded fragments (3–12 cm) from nearby localities, with colours ranging from yellowish-brown to orange and black. Some correspond to hardened secondary phases typical of bog iron ore (differently sized hardened nodules), while laminated specimens show interplay between darker and lighter laminae within the samples. At Žakanje, laminated fragments occur in reddened soils near eroded fragments of gossan exposures, suggesting that hilltop gossans serve as primary sources. In contrast, on sites farther from primary ore and gossan deposits, such as Osekovo and Hrastovica, secondary Fe enrichment was identified (see **Figure 3**).

### *4.2. Geochemistry*

The geochemical composition is dominated by $SiO_2$, which ranges from 48% to 72%, followed by $Al_2O_3$ (10–15%) and $Fe_2O_3$ (6–9% in most samples; **Table 2**). One horizon of Profile 1 (Knez 3) stands out with an exceptionally high $Fe_2O_3$ content (33.8%), accompanied by lower $SiO_2$, suggesting significant enrichment in iron oxides. Other major oxides, including MgO, CaO, and $K_2O$ occur in minor to moderate amounts, typically below 2%. Trace element concentrations vary across profiles, with chromium (Cr) ranging between 304 and 430 ppm, nickel (Ni) between 58 and 171 ppm, and arsenic (As) between 12 and 38 ppm. The highest As and Ni contents are found in profiles 1 and 2 (notably Knez 3 and Knez 11), while Cr concentrations remain consistently elevated across all profiles. These results indicate that, in addition to the dominant silicate matrix, the soils are enriched in transition metals, most likely related to the presence of Fe-rich minerals and clay fractions. The hardened Fe sample, taken from profile 1, horizon Knez 3, is strongly enriched in $Fe_2O_3$ (44.02 wt%) with relatively low $SiO_2$ (40.49 wt%) and $Al_2O_3$ (8.38 wt%), indi-

**Table 1:** Physico-chemical characteristics of analysed soil profiles from the Knezovljani trench pit

| Sample ID | Depth (cm) | pH | Clay | Silt | Sand | Soil texture | Munsell soil colour | Colour name |
|---|---|---|---|---|---|---|---|---|
| Knez 1 | 0 - 40 | 4.84 | 26.71 | 72.85 | 0.45 | Silt loam | 2.5Y 5/4 | Yellowish brown |
| Knez 2 | 40 - 80 | 5.02 | 20.99 | 75.39 | 3.63 | Silt loam | 2.5Y 5/4 | Yellowish brown |
| Knez 3 | 80 - 105 | 5.61 | 31.21 | 68.05 | 0.75 | Silt loam | 2.5YR 5/6 | Red |
| Knez 4 | 105 - 130 | 5.26 | 24.81 | 74.19 | 1.00 | Silt loam | 2.5Y 6/4 | Light yellowish brown |
| Knez 5 | 130 - 160 | 5.04 | 14.87 | 50.02 | 35.11 | Silt clay loam | 2.5Y 5/4 | Yellowish brown |
| Knez 6 | 160- 190 | 5.50 | 11.65 | 50.14 | 38.21 | Silt clay loam | 2.5Y 5/4 | Yellowish brown |
| Knez 7 | 0 - 45 | 4.96 | 18.20 | 62.60 | 19.21 | Silt loam | 2.5Y 4/4 | Dark yellowish brown |
| Knez 8 | 45 - 80 | 5.17 | 18.05 | 65.24 | 16.71 | Silt loam | 2.5Y 6/4 | Light yellowish brown |
| Knez 9 | 80 - 105 | 5.23 | 14.41 | 70.48 | 15.12 | Silt loam | 2.5Y 6/4 | Light yellowish brown |
| Knez 10 | 105 - 130 | 5.46 | 9.86 | 57.42 | 32.72 | Silt loam | 2.5Y 5/4 | Yellowish brown |
| Knez 11 | 130 - 160 | 5.57 | 15.97 | 63.15 | 20.87 | Silt loam | 2.5Y 5/4 | Yellowish brown |
| Knez 12 | 160 - 190 | 5.60 | 27.16 | 52.68 | 20.17 | Silt clay loam | 2.5Y 5/4 | Yellowish brown |
| Knez 13 | 0 - 45 | 5.09 | 21.09 | 67.91 | 10.99 | Silt loam | 2.5Y 5/6 | Strong brown |
| Knez 14 | 45 - 80 | 5.46 | 28.13 | 69.13 | 2.74 | Silt clay loam | 2.5Y 5/6 | Strong brown |
| Knez 15 | 80 - 105 | 5.77 | 24.85 | 70.16 | 5.01 | Silt loam | 2.5Y 5/6 | Strong brown |
| Knez 16 | 105 - 130 | 5.81 | 19.40 | 63.57 | 17.00 | Silt loam | 2.5Y 5/6 | Strong brown |
| Knez 17 | 130 - 160 | 5.86 | 17.62 | 62.29 | 20.09 | Silt loam | 2.5Y 5/6 | Strong brown |
| Knez 18 | 160 - 170 | 5.91 | 20.25 | 54.22 | 25.52 | Silt loam | 2.5Y 6/8 | Yellow |

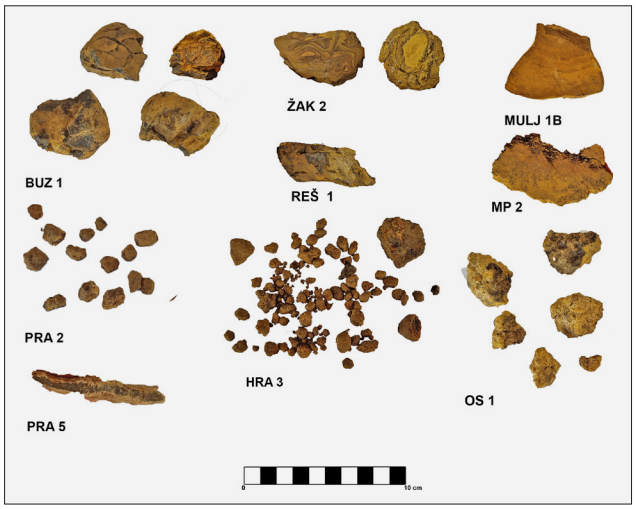



**Figure 3:** Photographs of cross-sections through various hardened Fe accumulations found in the study region

cating extensive replacement of the silicate matrix by secondary iron oxides and hydroxides, typical of mature, cemented Fe crusts. It also shows elevated trace metal contents, particularly As (58.8 ppm), Cr (313.3 ppm), Ni (195 ppm), and Zn (130.4 ppm), consistent with the scavenging of metals by Fe-oxide phases.

The major oxides in the bulk geochemistry of the studied hardened Fe accumulations show varying quantities of $SiO_2$ and $Fe_2O_3$, with $Al_2O_3$ being third in abundance but present in varying proportions (see **Table 2**). Modruš Potok (MP U-2) and Knezovljani (KNEZ 19) samples are iron-rich, with high $Fe_2O_3$ contents of 43.23 and 44.02 wt% respectively, in contrast to Pravutine (PRA U-2, OS U-1, HR U-3) and Muljevac, which have higher $SiO_2$ content, up to 67.21 wt%, and moderate $Fe_2O_3$ amounts of 7.29–23.99 wt%, indicating a silicate-rich matrix. The two most iron-rich samples, from Pravutine (PRA U-5A) and Žakanje (ŽAK 2), have very high $Fe_2O_3$ contents of 64.59 and 64.95 wt%, with correspondingly lower $SiO_2$ and $Al_2O_3$, suggesting substantial replacement of the primary silicate matrix by secondary iron oxide. The Reštovo site sample (REŠ U-1) differs from the others due to its very high MnO content (19.55 wt%) and elevated $Fe_2O_3$ (17.95 wt%). Trace elements show varying but consistently higher concentrations in all samples studied. Arsenic content ranges from 2 to 300 ppm, with most sites falling within 30–80 ppm, except for PRA U-5A, where As exceeds 300 ppm, suggesting significant As uptake at this site, facilitated by iron oxides. Nickel content is generally up to 220 ppm, but the Reštovo sample is distinct, with concentrations approaching 900 ppm, indicating a more Fe-Mn-rich matrix with abundant Ni. Copper and lead are usually present up to 100 ppm, while Zn content at all sites is predominantly 60–130 ppm, with Reštovo and Pravutine samples showing higher quantities, reflecting increased uptake associated with co-existing Fe-Mn content (see **Table 2**).

### *4.3. Mineralogical composition*

X-ray diffraction analysis (see **Table 3**) shows that quartz, with notable peaks at 20.86° and 26.65° 2Θ is the dominant mineral phase across all three soil profiles, generally occurring as a major to dominant component in all horizons. Plagioclase, with dominant peak occurring at

**Table 2:** Geochemical composition of major oxides and select trace metals in three soil profiles from Knezovljani and selected secondary Fe accumulations and bog iron from the region. Major oxides expressed as mass. %, trace elements as mg/kg.

| Sample ID | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | $P_2O_5$ | As | Ni | Cu | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Soil profiles** | | | | | | | | | | |
| KNEZ 1 | 69.04 | 0.65 | 11.28 | 9.16 | 0.24 | 0.26 | 27.80 | 81.50 | b.d.l. | 46.60 | 94.80 |
| KNEZ 2 | 70.90 | 0.76 | 12.38 | 6.58 | 0.16 | 0.16 | 29.00 | 68.33 | b.d.l. | 37.60 | 76.80 |
| KNEZ 3 | 47.93 | 0.22 | 10.62 | 33.83 | 0.88 | 0.55 | 77.40 | 171.40 | 56.20 | 56.80 | 152.20 |
| KNEZ 4 | 66.94 | 0.42 | 14.40 | 8.96 | 0.04 | 0.09 | 32.40 | 141.20 | b.d.l. | 25.00 | 109.40 |
| KNEZ 5 | 70.10 | 0.32 | 12.81 | 7.27 | 0.03 | 0.10 | 17.60 | 166.80 | b.d.l. | 27.60 | 113.80 |
| KNEZ 6 | 71.69 | 0.47 | 12.47 | 5.87 | 0.04 | 0.10 | 13.00 | 118.40 | b.d.l. | 27.40 | 78.00 |
| KNEZ 7 | 70.83 | 0.91 | 12.30 | 6.43 | 0.13 | 0.27 | 23.00 | 64.00 | b.d.l. | 31.20 | 93.20 |
| KNEZ 8 | 72.24 | 0.97 | 12.17 | 5.56 | 0.11 | 0.18 | 20.40 | 62.00 | b.d.l. | 33.00 | 72.80 |
| KNEZ 9 | 69.33 | 0.93 | 13.14 | 7.24 | 0.15 | 0.14 | 21.40 | 82.80 | b.d.l. | 37.00 | 83.80 |
| KNEZ 10 | 68.86 | 0.73 | 12.10 | 8.93 | 0.16 | 0.20 | 26.60 | 90.80 | b.d.l. | 46.00 | 93.80 |
| KNEZ 11 | 68.05 | 0.75 | 12.85 | 9.26 | 0.17 | 0.19 | 38.00 | 78.80 | 43.00 | 49.40 | 86.40 |
| KNEZ 12 | 69.38 | 1.02 | 14.05 | 6.10 | 0.08 | 0.16 | 12.80 | 58.00 | b.d.l. | 28.00 | 74.20 |
| KNEZ 13 | 68.44 | 1.04 | 13.95 | 7.38 | 0.13 | 0.14 | 20.20 | 96.80 | 40.00 | 36.40 | 100.60 |
| KNEZ 14 | 69.54 | 1.07 | 13.59 | 6.12 | 0.18 | 0.14 | 12.40 | 67.60 | b.d.l. | 26.20 | 70.60 |
| KNEZ 15 | 66.99 | 1.09 | 14.63 | 7.48 | 0.22 | 0.14 | 21.00 | 82.40 | b.d.l. | 36.00 | 84.40 |
| KNEZ 16 | 67.38 | 0.98 | 14.80 | 7.01 | 0.06 | 0.16 | 19.40 | 65.20 | b.d.l. | 29.00 | 80.20 |
| KNEZ 17 | 66.57 | 1.00 | 15.32 | 7.13 | 0.12 | 0.16 | 17.40 | 75.00 | 43.00 | 37.20 | 82.80 |
| KNEZ 18 | 67.40 | 0.95 | 14.36 | 7.40 | 0.16 | 0.19 | 21.20 | 88.80 | 44.00 | 35.60 | 84.40 |
| | **Hardened Fe accumulations** | | | | | | | | | | |
| KNEZ 19 | 40.49 | 0.10 | 8.38 | 44.02 | 0.96 | 0.83 | 58.80 | 195.00 | 49.33 | b.d.l. | 130.40 |
| MP U-2 | 35.39 | 0.59 | 8.48 | 43.23 | 1.03 | 0.54 | 82.00 | 75.00 | 48.00 | 19.00 | 123.00 |
| PRA U-2 | 67.21 | 1.33 | 14.50 | 7.29 | 0.43 | 0.10 | 26.00 | 39.00 | 28.00 | 60.00 | 60.00 |
| PRA U-5A | 10.41 | 0.41 | 8.43 | 64.59 | 0.18 | 0.34 | 303.00 | 232.00 | 61.00 | 124.00 | 340.00 |
| MULJ U-1B | 59.39 | 0.27 | 8.03 | 23.99 | 0.27 | 0.34 | 51.00 | 39.00 | 34.00 | 27.00 | 80.00 |
| ŽAK U-2 | 15.27 | 0.39 | 5.94 | 64.95 | 0.27 | 0.14 | 58.00 | 53.00 | 20.00 | 44.00 | 73.00 |
| REŠ U-1 | 32.70 | 0.93 | 12.29 | 17.95 | 19.55 | 0.17 | 201.00 | 881.00 | 226.00 | 136.00 | 470.00 |
| OS U-1 | 58.49 | 1.05 | 14.10 | 13.74 | 1.56 | 0.24 | 36.00 | 75.00 | 27.00 | 55.00 | 81.00 |
| HR U-3 | 43.83 | 0.81 | 12.40 | 9.48 | 0.26 | 0.17 | 29.00 | 71.00 | 22.00 | 38.00 | 40.00 |
| BUZ U-1 | 35.68 | 0.60 | 13.81 | 34.71 | 0.61 | 0.20 | 2.50 | 221.00 | 43.00 | 20.00 | 102.00 |

b.d.l. – below detection limit

27.97° 2Θ was consistently present as a minor to moderate component, while alkali feldspars (slightly lower 2Θ peaks at 27.53°) were detected as minor to major phases depending on the horizon (see **Table 3**). Several phyllosilicate minerals phases were also detected in minor to moderate amounts. Micaceous phases, with respective 001 peak at 8.89° 2Θ show variable contents (see **Table 3**). Additionally, based on glycerine saturation and heating at 350°C, smectite mineral phase was detected within soil profiles. Kaolinite (7 Å) was consistently identified in trace amounts throughout all samples. Goethite was detected only in profile 1, occurring in moderate amounts in horizon Knez 3 and in trace amounts in horizons Knez 1–2, while being completely absent or showing no reliable diagnostic peaks in other horizons.

Between the three profiles, some mineralogical differences were observed. Profile 1 (Knez 1–6) was characterised by greater variability in the phyllosilicate fraction, with smectite and chlorite phases reaching minor to moderate levels in horizons Knez 3 and 6, and with goethite restricted to this profile. Profiles 2 (Knez 7–12) and 3 (Knez 13–18) were more uniform, being dominated by quartz and feldspars, with only minor contributions of 10 Å phyllosilicates and consistently trace amounts of kaolinite. Profile 3 showed slightly greater variability in the 14 Å phases, with horizons Knez 16 and 17 containing moderate levels, suggesting a stronger presence of expandable clays. Overall, the mineralogical assemblage reflects a quartz- and feldspar/plagioclase-rich soil matrix, with subordinate phyllosilicates and kaolinite, and only profile 1 showing significant presence of Fe-oxide (goethite). Hardened Fe accumulations within the pedological profiles differs from soil samples, with prevalence of goethite and lepidocrocite, with moderate pres-

**Table 3:** Mineralogical composition of soil profiles and bog iron ore/hardened Fe accumulations based on the XRD analysis for grain size <2 mm (Abbreviations: Qtz – quartz, Fld – feldspar group, Pl – plagioclase group Gt – goethite, Lpc – lepidocrocite, Cal – calcite, Dol – dolomite, 7Å –7Å phyllosilicates (kaolinite), 10Å – 10Å phyllosilicates and micas, 14Å – 14Å phyllosilicates (smectite group). + = mineral present in the sample, ? = mineral is probably present in the sample but due to the low content and/or overlapping of diffraction peaks cannot be confirmed with certainty.

| Location | Sample ID | Qtz | Gt | Pl | Fld | 10A | 14A | 7A | Additional minerals |
|---|---|---|---|---|---|---|---|---|---|
| | **Soil profiles** | | | | | | | | |
| Knezovljani | **Knez 1** | ++++ | ? | ++ | ++ | ++ | + | + | |
| | **Knez 2** | ++++ | ? | ++ | +/++ | ++ | + | + | |
| | **Knez 3** | ++ | ++ | + | + | ++ | +/++ | + | |
| | **Knez 4** | +++ | - | ++ | +/++ | + | ++ | + | |
| | **Knez 5** | +++ | - | ++ | +/++ | + | ++ | + | |
| | **Knez 6** | +++ | - | ++ | +/++ | + | +/++ | + | |
| Knezovljani | **Knez 7** | ++++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 8** | ++++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 9** | ++++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 10** | ++++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 11** | ++++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 12** | ++++ | ? | ++ | +/++ | + | + | + | |
| Knezovljani | Knez 13 | ++++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 14** | +++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 15** | +++ | ? | ++ | +/++ | + | + | + | |
| | **Knez 16** | +++ | ? | ++ | +/++ | + | +/++ | + | |
| | **Knez 17** | ++++ | ? | ++ | +/++ | ++ | +/++ | + | |
| | **Knez 18** | ++++ | ? | ++ | +/++ | + | + | + | |
| | **Hardened Fe accumulations** | | | | | | | | |
| Knezovljani | **Knez 19** | ++ | +++ | ? | ? | ++ | + | + | Lpc |
| Modruš potok | **MP U-2** | ++ | +++ | ? | | + | + | ? | |
| Pravutine | **PRA U-2** | +++ | ? | + | + | ++ | ++ | | |
| | **PRA U-5A** | + | ++++ | ? | ? | ? | ? | ? | Lpc, Amorphous minerals |
| Muljevac | **MULJ U-1B** | +++ | ++ | + | + | + | + | ? | |
| Žakanja | **ŽAK U-2** | ++ | +++ | ? | ? | + | ? | ? | Amorphous minerals |
| Reštovo | **REŠ U-1** | +++ | ++ | + | ? | ? | ? | ? | Tod |
| Osekovo | **OS U-1** | ++++ | + | + | + | ++ | + | + | |
| Hrastovica | **HR U-3** | ++++ | + | + | + | ++ | + | + | Cal, Dol |
| Buzeta | **BUZ U-1** | +++ | +++ | + | + | ++ | + | + | |

+ - relative abundance of minerals within horizons based on X-ray diffraction (no quantitative value assigned to +); ++++ major component, +++ moderate component, ++ minor component; + traces.

ence of quartz and phyllosilicate mineral phases. Similar mineralogical contents, with prevalence of goethite were detected in selected hardened Fe accumulations from the region (see **Table 3**).

## 5. Discussion

### *5.1. Formation mechanisms in Knezovljani soils*

The Knezovljani soil profiles, developed on fine-grained Pannonian sediments, show features typical of moderately evolved soils formed under temperate climatic conditions with seasonal moisture fluctuations (**Klöffel et al., 2024**). Texturally, all three profiles are dominated by the fine fraction, with silt comprising between 50 and 75% of the total, accompanied by 10–32% clay and only minor sand. Such textures are characteristic of alluvial or loessic parent materials widespread across northern Croatia and the southern margins of the Pannonian Basin (**Banak et al. 2013; Rubinić et al. 2018**). Their dominance of silt, moderate clay content, and low sand fraction imply relatively low permeability but high water-retention capacity, creating conditions favourable for periodic saturation and development of redoximorphic features (**Rubinić et al., 2022**). The mineralogical assemblage, most notably quartz, feldspar, and

micas as dominant phases with subordinate smectite and trace kaolinite, supports derivation from weathered silicate sediments. Measured pH values (4.8–5.9) classify the soils as moderately to strongly acidic, reflecting leaching of basic cations and accumulation of exchangeable Al and Fe. Acidic conditions promote the solubility of $Fe^{2+}$ under reducing environments and enhance its subsequent migration upward in the profile. Knezovljani 1 profile shows greater variability in pH, likely caused by the presence of locally concentrated Fe-oxyhydroxides, which can both consume and release protons during redox transformations (**Cornell and Schwertmann, 2003**). These compositional attributes place the Knezovljani soils within a pedogenic profile similar to that of other Quaternary floodplain systems in Central Europe, where loess-derived or fine alluvial substrates undergo limited chemical alteration but marked physical rearrangement (**Birkeland, 1999; Sauer et al., 2010**).

Soil colour data provide direct visual evidence of redox processes. Across the profiles, hues cluster in the 2.5Y range, corresponding to yellowish-brown tones typical of oxidized $Fe^{3+}$ environments. The exception is horizon Knez 3, which exhibits a distinctly red hue (2.5YR 5/6) associated with the highest concentration (33.8 wt %). Such a relationship between colour and Fe content is widely recognised in hydromorphic soils (**Fiedler and Sommer, 2004; Cornell and Schwertmann, 2003**). The reddish colour indicates dominance of hematite, while yellowish hues reflect hydrated Fe-oxyhydroxides such as goethite, ferrihydrite or lepidocrocite.

Goethite detected in Knez 3 and trace amounts in adjacent horizons confirm oxidation of $Fe^{2+}$ under periodically aerated conditions. The spatial restriction of goethite to Knezovljani 1 and its immediate surrounding implies that groundwater fluctuations or lateral seepage were confined to that micro-position, generating localised Fe precipitation. Comparable colour–mineral relationships have been described in bog-iron-forming soils of northern Europe (**Crerar et al., 1979; Kaczorek and Sommer, 2003**) and in floodplain Gleysols of the Drava Basin (**Brenko et al., 2020**).

Parent-material composition exerts a primary control on mineralogy and geochemistry (**Wilson, 2019**). The dominance of $SiO_2$ (48–72 %) and $Al_2O_3$ (10–15 %) reflects a silicate-rich matrix dominated by quartz and feldspar, while the occurrence of feldspar peaks in XRD data indicates limited leaching and absence of advanced argillic alteration, while relatively low kaolinite content (< trace levels) demonstrates that prolonged leaching under warm and humid conditions has not occurred.

Weathering intensity can be further inferred from geochemical ratios such as $Fe_2O_3/SiO_2$ and $Al_2O_3/SiO_2$, which in most horizons fall within ranges typical of moderately weathered silicate sediments (**Kabata-Pendias, 2010**). The overall pattern suggests that chemical weathering is not the main agent of profile differentiation; instead, pedogenic redistribution of Fe and clay minerals has occurred under the influence of fluctuating moisture and redox potential.

**Table 4:** Characteristics and controlling factors in Knezovljani and Kalinovac bog iron sites

| Characteristic | Knezovljani | Kalinovac |
|---|---|---|
| **Clay % at Fe max** | 31% (mostly smectite) | 11% (low phyllosilicates) |
| **Fe form** | Crusts/nodules (44–65%) and diffuse horizon (31%) | Diffuse horizon (31.5%) |
| **Trace signature** | Ni/Cr/Zn/Pb/As (gossan) | As/P (aquifer) |
| **Control** | Clay + local input | Groundwater redox |
| **Outcome** | Heterogeneous precursors | Mature ore layer |

The variation in phyllosilicate composition among profiles further reflects differences in soil moisture regimes. Knezovljani 2 and 3 are dominated by illite with only trace smectite, whereas Profile 1 displays elevated smectite content in horizons Knez 3 and Knez 6. Expandable clays such as smectite typically form or persist under conditions of poor drainage and periodic reduction, while illite dominates in better-drained or more acidic environments. Therefore, the higher smectite content in Knezovljani 1 profile supports the inference of prolonged wetness or slower drainage, consistent with the occurrence of Fe-oxide enrichment in the same profile. Smectite can influence Fe dynamics by providing exchange surfaces that adsorb $Fe^{2+}$ and promote its oxidation (**Stucki, 2013**). Thus, mineralogical differences not only record hydrological variability but may actively contribute to Fe cycling. The slight increase of 14 Å minerals in deeper horizons of Knezovljani 3 (Knez 16–17) suggests that lower horizons experience longer saturation, possibly due to impeded drainage or fine texture. Such variations mirror small-scale hydrological gradients typical of colluvial or footslope positions in Pannonian landscapes (**Fiedler and Sommer, 2004**).

The generally low MgO and CaO contents (< 2 %) correspond with the absence of carbonates and indicate long-term acid leaching. Under such conditions, base-poor silicate mineralogy is preserved, and Fe becomes one of the principal active components of pedogenic transformation. The acidic environment is also favourable for the adsorption of trace elements such as As, Ni, and Cr onto Fe-oxide surfaces (**Banning, 2008; Kabata-Pendias, 2010**), explaining the observed positive correlations between these elements, especially between $Fe_2O_3$ and As, and $P_2O_5$.

Among all horizons, Knez 3 stands out for its significantly elevated $Fe_2O_3$ concentration (33.8 wt %), roughly ten times higher than the background median values for Posavina region (2.98 wt %, **Halamić and Miko, 2009**). This enrichment is coupled with a corresponding

**Table 5:** Correlation matrices of a) samples of bog iron ores from the region and b) Knezovljani soils and bog iron including bog iron ore samples from the region.

| a) | Variable | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | $P_2O_5$ | As | Ni | Cu | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | 1.00 | | | | | | | | | | |
| | $TiO_2$ | 0.57 | 1.00 | | | | | | | | | |
| | $Al_2O_3$ | 0.59 | 0.83 | 1.00 | | | | | | | | |
| | $Fe_2O_3$ | -0.86 | -0.73 | -0.78 | 1.00 | | | | | | | |
| | MnO | -0.11 | 0.27 | 0.19 | -0.24 | 1.00 | | | | | | |
| | $P_2O_5$ | -0.15 | -0.48 | -0.46 | 0.35 | -0.20 | 1.00 | | | | | |
| | As | -0.62 | -0.24 | -0.33 | 0.47 | 0.41 | 0.25 | 1.00 | | | | |
| | Ni | -0.29 | 0.15 | 0.18 | -0.09 | 0.96 | -0.17 | 0.55 | 1.00 | | | |
| | Cu | -0.22 | 0.16 | 0.12 | -0.12 | 0.98 | -0.08 | 0.56 | 0.98 | 1.00 | | |
| | Pb | -0.37 | 0.19 | 0.05 | 0.10 | 0.66 | -0.20 | 0.85 | 0.74 | 0.73 | 1.00 | |
| | Zn | -0.48 | -0.03 | -0.06 | 0.20 | 0.79 | 0.07 | 0.86 | 0.89 | 0.89 | 0.89 | 1.00 |
| **b)** | **Variable** | **$SiO_2$** | **$TiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **MnO** | **$P_2O_5$** | **As** | **Ni** | **Cu** | **Pb** | **Zn** |
| | $SiO_2$ | 1.00 | | | | | | | | | | |
| | $TiO_2$ | 0.41 | 1.00 | | | | | | | | | |
| | $Al_2O_3$ | 0.66 | 0.66 | 1.00 | | | | | | | | |
| | $Fe_2O_3$ | -0.92 | -0.56 | -0.79 | 1.00 | | | | | | | |
| | MnO | -0.32 | 0.11 | -0.02 | 0.05 | 1.00 | | | | | | |
| | $P_2O_5$ | -0.40 | -0.42 | -0.55 | 0.52 | -0.01 | 1.00 | | | | | |
| | As | -0.72 | -0.28 | -0.48 | 0.64 | 0.49 | 0.38 | 1.00 | | | | |
| | Ni | -0.40 | -0.06 | -0.03 | 0.15 | 0.95 | 0.00 | 0.60 | 1.00 | | | |
| | Cu | -0.52 | -0.01 | -0.14 | 0.29 | 0.90 | 0.21 | 0.64 | 0.89 | 1.00 | | |
| | Pb | -0.53 | 0.00 | -0.22 | 0.36 | 0.69 | 0.12 | 0.87 | 0.73 | 0.75 | 1.00 | |
| | Zn | -0.56 | -0.16 | -0.23 | 0.38 | 0.80 | 0.21 | 0.87 | 0.90 | 0.84 | 0.88 | 1.00 |

decrease in $SiO_2$, implying replacement of the silicate matrix by Fe-oxyhydroxides. XRD detection of goethite and the reddish hue together suggest that ferrihydrite, which is the typical amorphous precursor in soil, has undergone dehydration and crystallization to goethite, marking an advanced stage of Fe accumulation (**Cornell and Schwertmann, 2003**). Such mineral transformations are consistent with the progressive oxidation pathway described for bog-iron ores in temperate wetlands (**Crerar et al., 1979; Rzepa et al., 2016**).

The limited occurrence of Fe enrichment and goethite to Knezovljani 1 soil profile might lead to interpretation of low-quality and non-relevant Fe-ore deposit. However, its occurrence highlights the importance of microtopographic along mineralogical and hydrological controls on the overall formation mechanisms of bog iron ore formation. Such patterning is common in floodplain and colluvial settings where subtle relief differences control water-table fluctuations (**Fiedler and Sommer, 2004; Karavidović and Brenko, 2022; Karavidović et al., 2025**). Hydrological and mineralogical control is best represented in the coexistence of smectite clays and goethite in Knezovljani 1, since both require intermittent saturation (**Schwertmann and Cornell, 2000**). The lateral discontinuity of Fe accumulation implies that regional groundwater oscillations were insufficient to create laterally extensive bog-iron horizons, instead, Fe precipitation occurred in localized hydromorphic pockets (**Thelemann et al., 2017**). The Knezovljani profiles differ from the Kalinovac–Hrastova Greda soil profile not only in the amount of Fe accumulation, but more importantly in the way Fe is localised and stabilised within the soil system (see **Table 4**). In Kalinovac–Hrastova Greda, bog-iron formation is expressed as a laterally more continuous and cemented Fe-rich horizon, with the strongest enrichment in the 60–80 cm interval, accompanied by high As and P contents, goethite dominance, and evidence for ferrihydrite as a precursor phase. This pattern is consistent with the classic bog-iron model, in which fluctuating groundwater repeatedly intersects a stable redox boundary, causing ferrous iron transported in groundwater to oxidise and precipitate as Fe oxyhydroxides near the discharge zone. On the other hand, the Knezovljani profiles show a much more heterogeneous and spatially restricted form of Fe accumulation. This suggests that Fe precipitation in Knezovljani was governed by a more localised combination of microtopography, lateral seepage, and clay-mediated retention, rather than by a laterally extensive floodplain redox front alone. The fact that goethite is detected only in profile 1 further supports this interpretation, as it indicates that Fe oxidation and precipitation were restricted to a

limited part of the landscape where hydrological focusing created suitable redox conditions. In addition, the association of Fe enrichment with higher clay contents and the presence of smectite-bearing horizons implies that phyllosilicates may have acted as reactive surfaces that adsorbed and retained dissolved Fe, thereby promoting localised precipitation and the formation of crusts or nodules. This is important because redox cycling does not simply move Fe; it also changes the reactivity of clay minerals, and smectite in particular is known to undergo structural and surface modifications during repeated reduction–oxidation cycles, affecting its capacity to retain Fe and associated trace elements. Smectite high cation-exchange capacity and expansive interlayer surfaces enable strong sorption of $Fe^{2+}$ and $Fe^{3+}$ ions (**Favre et al., 2006**), reducing leaching and promoting retention in clay-rich B horizons, while structural Fe within smectite lattices can undergo microbial reduction under anaerobic conditions, enhancing partial mineral alteration and temporary Fe release into soil solution before reoxidation and precipitation deeper in the profile (**Stucki et al., 2002; Bishop et al., 2002**). This dual role often results in iron enrichment in smectite-dominated subsoils, particularly in vertisols or hydromorphic environments where fluctuating redox potentials drive cyclic Fe translocation and secondary accumulations, modulated by pH and organic matter (**Garg et al., 2018**).

### 5.2. *Regional variations in geochemical characteristics*

Regionally, Trgovska and Petrova gora host siderite-ankerite-quartz vein systems with associated sulphide mineralisation (pyrite, chalcopyrite, galena, sphalerite), providing a connection between Fe enrichment and Pb-Zn-Cu occurrences in the environment (**Borojević Šoštarić et al., 2009**). Weathering of such polymetallic veins supplies $Fe^{2+}$ and base metals to groundwater, which then migrates downslope through fractured flysch and colluvial cover; where this Fe-rich groundwater rises and discharges near the surface at the Knezovljani foothill, under more oxidising and slightly acidic conditions, $Fe^{2+}$ is oxidised and precipitated as Fe-oxyhydroxides, while Pb, Zn, and Cu are partly scavenged or co-precipitated with the newly formed Fe phases. In contrast, the slightly lower, wetter micro-depressions, where profiles Knezovljani 2 and 3 are situated, are likely under the influence of longer saturation and lower redox potential, favouring continued Fe mobilisation and transport rather than *in situ* accumulation. This hydrological and redox contrast, along afore mentioned clay presence, explains why pronounced Fe-oxide cementation and associated base-metal enrichment are restricted to the foothill horizon Knez 3 rather than forming a laterally continuous bog-iron layer across the entire site.

To compare soils and ore samples from the Knezovljani site with similar occurrences of iron ore in regional soils, correlation matrices were constructed to determine which trace elements correlate with major oxides (see **Table 5**). This revealed that Knezovljani samples exhibit the same geochemical behaviour as other pedogenic ore samples in the region, albeit with some smaller deviations.

In the Knezovljani soils and similar bog iron accumulations, the differing Eh–pH precipitation conditions of Fe and Mn have resulted in distinct zones of oxide formation, which regulate the fixation of heavy metals. Under the moderately to strongly reduced conditions prevailing in the profiles (pH values ranging from 4.8 to 5.9), reduction of $Fe^{3+}$ in silicates and matrix coatings to $Fe^{2+}$ occurs readily under saturation, while even low rates of $Fe^{2+}$ re-oxidation lead to rapid formation of ferrihydrite, lepidocrocite, and/or goethite in shallow redox interfaces (**Stumm and Morgan, 1996; Schwertmann and Cornell, 2000; Géhin et al., 2002**). Such conditions promote the formation of Fe oxide mottles, nodules, and crusts, well known as a secondary developmental phase of bog iron ores, observed at the Kalinovac-Hrastova Greda site in the Drava alluvial plain (**Brenko et al., 2020**). Here, further Fe-cementation led to the development of uninterrupted lenses of bog iron ore in which the fragmented structure shows clear signs of nodular particles (**Karavidović and Brenko 2022**). Similar occurrences of small nodules are evident at comparative sites in Posavina, the Osekovo and Hrastovica sites, and Pravutine in Pokuplje (see **Figure 3**). In the case of the sample from Knezovljani (Knez 19) and other sites in the wider region, where samples are represented as larger subrounded and rounded fragments or irregular angular or lamellar fragments (PRA 5a, ŽAK-2, REŠ-1, MULJ-1b, MP-2), periodic changes of the redox front led to the formation of thin, Fe-rich horizons now visible as laminae in the larger fragments (see **Figure 3** above), through successive import, oxidation, and partial dehydration of Fe-rich fluids (**Cornell and Schwertmann, 2003**). These two examples differ slightly in morphological appearance; however, the formation mechanism is consistent. At the Pravutine location, both forms appear, albeit in slightly different topographical positions, again indicating a strong correlation between microtopographical conditions and secondary ore formation The geochemical results support this conclusion. In the Knezovljani dataset, a marked inverse relationship is observed between $Fe_2O_3$ and $SiO_2$ ($r = –0.92$), reflecting replacement of the silicate fraction by secondary Fe oxyhydroxides, while direct relationships with P ($r = 0.52$) and As ($r = 0.64$) indicate effective sorption of phosphate and arsenate onto the new Fe-oxide surface. High surface area and pH-dependent sorption capacity are characteristics of Fe oxyhydroxides, whose affinity for As is well documented in various systems, along with considerable sorption capacity for Ni, Zn, Cu, and Pb in soils (both natural and contaminated) (**Smedley and Kinniburgh, 2002; Banning, 2008; Fernández-Calviño et al., 2012**). The laminae in the Knezovljani

bog iron thus represent a succession of micro-horizons strongly enriched in Fe, successively layered, in contrast to the massive bog iron ore deposits in which aggregate accumulation of Fe and trace metals is incorporated into a thicker cemented unit, ultimately resulting in layers or lenses of uninterrupted deposition. Formation of more massive Fe-cemented zones is consistent with a more stable hydrology and redox interfaces under floodplain conditions that sustained Fe oxide formation over a prolonged interval.

Mn is even more conserved in these soils. $Mn^{2+}$ is a more stable ion than $Fe^{2+}$ over a wider Eh range, and precipitation of $Mn^{3+/4+}$ oxides occurs at higher Eh and near-neutral pH; consequently, Mn oxide forms in a strongly oxidising and better-aerated microhabitat compared to Fe oxide precipitation (**Hem, 1963; Gasparatos et al., 2019**). This is indicated by strongly positive correlations between MnO and Ni (r = 0.95), Cu (r = 0.90), Pb (r = 0.69), and Zn (r = 0.80) concentrations, establishing that when Mn oxide is present, it is a highly effective scavenger of divalent trace elements in various environments (**Cornu et al., 2005**). Most Knezovljani soil samples, as well as the majority of bog iron samples, are Mn-poor but Fe-rich, while in the Reštovo sample, there is a substantial amount of Mn (~20% MnO) along with the highest concentrations of Ni and Zn, suggesting a strongly oxidising soil or bog microhabitat, which favours the formation of Mn-oxyhydroxides and metal immobilisation (**Negra et al., 2005; Peacock and Sherman, 2007; Gasparatos et al., 2019, Zhang et al., 2025**). This skews correlation factors, indicating strong positive correlation between MnO and selected trace elements.

The distribution and temporal variation of Fe and Mn control over precipitation-related zones are therefore responsible for both the laminated nature of Knezovljani bog iron and regional variations in heavy metal sequestration among laminated and unlaminated bog iron ores, and surrounding silicate-rich sediments, especially in central Croatia (**Gasparatos et al., 2005; Kabata-Pendias, 2010**).

The regional hardened Fe accumulations display substantial geochemical variability and should be considered as several different types of secondary Fe-rich materials rather than a single homogeneous bog-iron type. The most Fe-enriched samples, including Knezovljani (KNEZ 19), Modruš Potok, Pravutine PRA U-5A, and Žakanje, contain 43–65 wt.% $Fe_2O_3$ and comparatively low SiO2, indicating significant replacement of the primary silicate matrix by secondary Fe oxyhydroxides. These samples represent the most advanced stage of Fe accumulation in the regional dataset and approach mature bog-iron or ferricrete-like material. In contrast, samples from Pravutine PRA U-2, Muljevac, Osekovo, and Hrastovica retain much higher $SiO_2$ and $Al_2O_3$ contents, suggesting incomplete Fe enrichment and a stronger inheritance of the original silicate parent material. A likely local control is the influence of weathered mineralised material, where laminated fragments occur near eroded sulphide-bearing exposures. This suggests that Fe-rich parent material may have contributed to secondary Fe precipitation under near-surface hydromorphic conditions, although the precise source pathway remains to be tested.

Trace-element distributions indicate that Fe does not hold the only control on metal accumulation. Arsenic is strongly enriched in the most Fe-rich samples, especially PRA U-5A, which is consistent with adsorption of arsenic onto newly formed Fe oxyhydroxides (**Banning, 2008; Brenko et al., 2020**). By contrast, Reštovo is distinguished by exceptionally high Ni and MnO contents, implying a more Fe–Mn-rich assemblage and a different trace-metal carrier phase. This interpretation is supported by the correlation matrices (see **Table 5**), which show that in the regional dataset $Fe_2O_3$ correlates strongly with $SiO_2$ and $Al_2O_3$ depletion, but only weakly with Ni, Cu, Pb, and Zn. In contrast, MnO is strongly correlated with Ni, Cu, Pb, and Zn, indicating that Mn oxides, rather than Fe oxides alone, are the main scavengers for these elements in the regional hardened Fe accumulations. Copper, lead, and zinc are elevated in several samples but are more diffusely distributed, implying retention by a combination of Fe oxides, Mn oxides, and fine-grained silicate fractions rather than by Fe alone. The Knezovljani, and in some cases regional Fe accumulation show a somewhat stronger association between $Fe_2O_3$ and As, Pb, and Zn, suggesting that the Knezovljani material preserves a more direct pedogenic linkage between Fe precipitation and trace-element sorption than the broader regional dataset. Overall, the data indicate that regional hardened Fe accumulations reflect multiple geochemical endmembers controlled by parent material, redox cycling, hydrology, and local source-rock influence.

## 6. Conclusions

The Knezovljani soils developed on fine-grained Pannonian sediments under temperate conditions with seasonal moisture fluctuations. Their texture, mineralogy, acidity, and redoximorphic features indicate that pedogenesis was strongly influenced by periodic saturation and Fe redistribution. The dominance of silt-rich material, followed by clay, and low sand content created a low-permeability yet water-retentive substrate, while the prevalence of quartz, feldspars, micas, and minor smectite and kaolinite suggests only limited chemical weathering of the silicate parent material. Within this context, Fe accumulation was not uniform across the profiles but was concentrated in specific horizons, especially Knez 3, where elevated Fe2O3, red coloration, and goethite occurrence indicate intense secondary Fe precipitation. The restriction of goethite to profile 1, together with higher smectite content in the same profile, suggests that Fe enrichment was controlled by microtopographic po-

sition, lateral seepage, and clay-mediated retention rather than by a laterally extensive groundwater front alone.

Comparison with Kalinovac–Hrastova Greda further shows that the Knezovljani system represents a more heterogeneous and less mature Fe-accumulation pathway. Kalinovac–Hrastova Greda preserves a continuous, cemented bog-iron horizon formed under stable groundwater redox conditions, whereas Knezovljani is characterised by patchy nodules, crusts, and laminae reflecting localised hydrological focusing and repeated but spatially restricted Fe oxidation and precipitation. Smectite appears to have played an additional role in Knezovljani by providing reactive surfaces for Fe sorption and by participating in redox-sensitive clay alteration, enhancing Fe retention. This supports the view that clay mineralogy is not only a passive recorder of hydrological conditions but may actively influence the formation and preservation of secondary Fe phases.

At the regional scale, the hardened Fe accumulations reflect multiple geochemical members rather than a single bog-iron type. The most Fe-rich samples approach mature bog-iron or ferricrete-like compositions, whereas others remain silicate-rich and only weakly enriched. Trace-element patterns show that As is preferentially associated with Fe-rich samples, while Ni, Cu, Pb, and Zn are more strongly linked to Mn-rich phases, especially in the Reštovo sample. This was confirmed in correlation matrices, where Fe is mainly coupled to silicate depletion and As enrichment, whereas Mn is the primary carrier for several base and transition metals. These patterns indicate that the regional Fe accumulations were controlled by the combined effects of parent material, redox cycling, hydrological focusing, and local source-rock influence, with Fe and Mn acting as distinct but complementary geochemical filters. Overall, the study demonstrates that bog-iron formation in this part of Croatia is highly variable at the site scale and that its geochemical expression depends on both landscape position and the mineralogical framework of the host sediments.

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## SAŽETAK

### Hidromorfno formiranje močvarnoga željeza u kambisolima u podnožju uzvisina: mineraloški i geokemijski pokazatelji s lokaliteta Knezovljani, središnja Hrvatska

Ovo istraživanje ispituje formiranje i geokemijski potpis željezom obogaćenih horizonata i naslaga tipa močvarne željezne rude u hidromorfnim tlima lokaliteta Knezovljani, u podnožju masiva Trgovačke i Petrove gore u središnjoj Hrvatskoj. U okviru istraživanja opisana je i uzorkovana pedološka jama s tri profila, a horizonti tla i očvrsnuti Fe-bogati sloj analizirani su metodama određivanja granulometrijskoga sastava, mjerenja pH, rendgenske difrakcije (XRD), prijenosne rendgenske fluorescentne spektrometrije (p-XRF) te laboratorijskim analizama XRF i ICP-MS na odabranim uzorcima željezne rude. Tla su pretežno siltozna (50 – 75 %) uz 10 – 32 % gline, umjereno kisela (pH 4,8 – 5,9) i sadržavaju kvarc, feldspate te ilitno-smektitne gline uz tek tragove kaolinita, što upućuje na srednji stupanj trošenja. Jedan horizont pokazuje izraženo obogaćenje željezom (33,8 mas. % $Fe_2O_3$), crvenkastu boju, prisutnost getita, povišen udio smektita i laminirani Fe-cementirani facijes, dok ostali sadržavaju 5 – 9 mas. % $Fe_2O_3$. Koncentracije elemenata u tragovima povišene su u Fe-bogatim slojevima i pozitivno koreliraju s $Fe_2O_3$, što je u skladu s intenzivnom sorpcijom i koeksprecipitacijom na Fe-oksihidroksidima. Usporedba s regionalnim pojavama močvarnih željeznih ruda i Mn-bogatih akumulacija pokazuje da Knezovljani predstavljaju mali, hidrološki fokusiran segment akumulacije željeza nastao gdje se Fe-bogate podzemne vode susreću s oksidirajućim uvjetima na rubnome dijelu padine, na redoks-granici. Fe-horizont u Knezovljanima tanak je i diskontinuiran, što upućuje na kratkotrajne ili prostorno ograničene cikluse mobilizacije i taloženja željeza. Dobiveni rezultati naglašavaju važnost mikroreljefa i podzemnoga protoka u stvaranju sekundarnih Fe-ruda te pružaju sveobuhvatan okvir za analizu tipova ruda, njihove prostorne raspodjele i geokemijskih obilježja, pridonoseći geoarheološkim istraživanjima proizvodnje željeza tijekom arheoloških i povijesnih razdoblja u središnjoj Hrvatskoj.



**Ključne riječi:**
močvarna željezna ruda, hidromorfna tla, geokemija, korelacijska matrica, pXRF, geoarheologija


## Author's contribution

**Tomislav Brenko** (Assistant professor, PhD, geologist) conducted laboratory and data analysis, interpreted mineralogical results and presented the results. **Sibila Borojević Šoštarić** (Professor, PhD, geologist) participated in field research, interpreted geochemical data and presented results. **Tena Karavidović** (Research associate, PhD, archaeologist) provided archaeological background and research locations, field research, sampling, presentation of results. **Tajana Sekelj Ivančan** (Scientific advisor, PhD, archaeologist) participated in field research, sampling prepared results.
All authors have read and agreed to the published version of the manuscript.