RGNZ/MGPB

Bog iron ores in central Croatia – mineralogical and geological case study on soil profiles

Rudarsko-geološko-naftni zbornik
(The Mining-Geology-Petroleum Engineering Bulletin)
UDC: 550.4
DOI: 10.17794/rgn.2025.2.11

Original scientific paper

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Abstract

The Pokuplje and Posavina regions (central Croatia) offer unique insight into the environmental conditions that favour the formation of iron (Fe) ores in low-lying areas. Three soil profiles from Žakanje, Osekovo and Pravutine, located in the Kupa and Sava river plains, were analysed to understand their mineralogical and geochemical composition, with a focus on Fe enrichment and trace metal content. The presence of impermeable clay horizons in these profiles contributes to the formation of a redox boundary that favours the precipitation of Fe in the form of oxyhydroxides. The reddish mottling observed in the middle horizons suggests that the studied soils may represent an early stage of bog iron ore formation. Geochemical analysis shows that these soils are moderately to slightly acidic, with silt as the dominant granulometric fraction and variable Fe oxide content in the profiles. The high Fe concentrations are consistent with the depth of groundwater fluctuations, which must have driven the redox cycle and promoted mobility and deposition of Fe. The contents of several trace metals (Cr, Ni, Zn, Pb and As) showed correlation with Fe. This implies regional occurrences of siderite and Fe-containing hydrothermal zones as a possible source of Fe, transported and precipitated into soil via hydrological processes. Overall, the results suggest that the combination of clay-rich, flood-prone landscapes and seasonal groundwater fluctuations provide ideal conditions for the formation of bog iron ore in central Croatia. These types of ores could have been an economically viable source for iron production during archaeological periods.

Keywords:
bog iron ore; Kupa River; Sava River; trace metals; geoarchaeology

1. Introduction

The central continental region of Croatia and the microgeographical areas in the alluvial plain of the Kupa and Sava rivers (Pokuplje and Posavina) are located at the intersection of geographical and cultural regions - the south-eastern Alps, the southern Pannonian basin, the western Balkans and the northern Dinaric Ophiolite zone. Due to its location, it can be assumed that the area played an important role in communication networks during the archaeological periods, from the Iron Age, Antiquity to the Middle Ages. Archaeological data on primary Fe production and processing in the region are scarce, but the existing finds and the presence of natural resources indicate the possibility of using regional ore sources for Fe production during the Iron Age, Antiquity and the Middle Ages (**Bojanovski, 1988; Durman, 1992; 2002; Koščević, 1995; Karavidović and Drnić, 2022; Nemet et al., 2018; Bugar, 2022**). In the mountainous part of the wider region (Trgovska, Zrinska, Petrova gora Mountains.), there are numerous high-quality Fe ore deposits that were extensively exploited in historical times, during the 18th – 20th centuries (**Marković, 2002; Jurković, 1993; Šebetić, 2000**), and are presumed to have been exploited earlier, most notably during Roman times (**Durman, 1992; 2002; Koščević, 1995**). The town of Sisak, Roman Siscia and Iron Age Segestica are historically connected to iron production through all periods, even today (**Durman, 2002**). However historical records rarely document exploitation of Fe ores found within the Pliocene - Pleistocene clays, sands and sandy gravels, such as those at positions near the villages along the Kupa River and nearby tributaries, exploited during in the 19th century (**Marković, 2002; Laszowski, 1942**). The latter presumably refers to the weathered and eroded limonitic ores in secondary layers and/or ores formed by precipitation at increased concentration of Fe ions in the soil solution. Use of limonitic ores is known from iron production sites dated to Iron Age sites in Dolenjska region (Slovenia) (**Črešnar et al., 2017**) that are culturally, temporally and geographically connected to Iron Age sites with traces of iron production and/or processing of

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semi-products located within the Pokuplje and Posavina regions (Gornje Pokuplje, Sisak-Pogorelec, Topusko-Velika Vranovina) (**Karavidović and Drnić, 2022**). These ores are found in lowland and slightly hilly areas of the Dolenjska region, as layers and/or concretions in clayey and sandy soil (**Trampuž Orel, 2012: 19–20; Črešnar et al., 2017**).

The possibility of the formation and exploitation of bog iron ore in the alluvial plain of the Sava River is suggested by an ore sample found in the archaeological record of iron production at the Okuje I site, dated to Antiquity and the Early Middle Ages, together with smelting and primary smithing waste (**Nemet et al., 2018; Nemet Karavidović, 2022; Bugar, 2022**). The iron production at the site is most probably dated to the Early Middle Ages, 7/8th centuries, as radiocarbon analysis of a charcoal sample found incorporated into the postreduction slag suggests (**Bugar, 2022**). Earlier archaeological and geoarchaeological investigations of the Drava lowland basin (**Sekelj Ivančan, 2007; 2009; 2014**) only recently pointed to the possibility of the formation of bog iron ore on the territory of the Republic of Croatia (**Brenko et al., 2020; Karavidović and Brenko, 2022**) and its use in Late Antiquity and the Early Middle Ages (**Brenko et al., 2021; Sekelj Ivančan and Karavidović, 2021; Karavidović and Brenko, 2022**). Use of bog iron ore is extensively documented on archaeological sites throughout Europe, dating from the Iron Age to the Middle Ages, and beyond, into the Modern period. The archaeological finds on sites in the Sava and Kupa river valleys and in the wider region prove that ore deposits in lowland and slightly hilly areas, such as redeposited, clastic sediments or bog iron ores, could have been an important resource in archaeological periods, along with the large known deposits of hydrothermal ores and their weathering zones in the mountainous parts of the wider region (Zrinska, Trgovska, Petrova gora Mountains). As these were not considered economically viable in recent, historical and modern periods, they are often overlooked, rarely mapped or analysed in detail, which in turn limits the potential of archaeological research into strategies and areas of iron ore exploitation.

Bog iron ores are a special type of sedimentary Fe ore deposits that usually form in a low-lying area (**Ramanaidou and Wells, 2014**), such as meandering river valleys or smaller local depressions (**Kaczorek and Zagórski, 2007**), where groundwater is shallow and usually less than one metre from the surface (**Brenko et al., 2020**). The typical mineral composition of the ores and the surrounding soils in which the ores occur consists of Fe oxides and oxyhydroxides (e.g. goethite, lepidocrocite, ferrihydrite, etc.), with occurrences of typical soil minerals such as clay minerals, feldspar, mica and the like. The Fe content in bog iron ores usually varies between 30 and 50 wt.% Fe_2O_3, but can also reach over 80 wt%, while Fe_2O_3 contents in soils tend to be lower and rarely exceed 30 wt.% (**Brenko et al., 2020**). The fundamental process in the formation of Fe ore in peatlands is the precipitation of the solid phase in the presence of dissolved atmospheric oxygen. Groundwater percolating through regional rock tends to get enriched with ferrous Fe^{2+} through the dissolution of minerals such as sulphides, silicates and carbonates. These minerals are dissolved by (bio)chemical weathering, especially under acidic conditions (**Postawa and Hayes, 2013**). Iron is dissolved in the groundwater in the form of ions or hydroxides and transported through the groundwater flow (**Kaczorek et al., 2004**). When it reaches zones with higher concentrations of dissolved atmospheric oxygen, the oxidation of ferrous to ferric form begins, leading to precipitation of iron in the pore spaces of soil. Previously empty pore space, located between primary soil minerals such as quartz, feldspars and clay minerals, is gradually getting occupied by the Fe^{3+} oxide/hydroxide matrix.

The potential for the formation of sedimentary iron ore in the soils and the potential for unmapped existing deposits in the lowland areas of the alluvial plains of Kupa and Sava rivers today and in the past can be surmised to a certain extent from the data of geochemical analysis of saturation with Fe in the topsoil and the geological environment of the lowland areas of the region (**Karavidović and Drnić 2022**). This paper deals with research questions on the soils and the potential for the formation of bog iron ore in the alluvial plains of the Kupa and Sava rivers, a natural setting where primary processing of Fe ore and production of iron is present during Antiquity/Early Middle Ages (Okuje I site) and secondary, post reduction waste and semi-products (Sisak-Pogorelec and Gornje Pokuplje) in the Iron Age. Based on the geological, hydrogeological and pedological characteristics, it was investigated whether 1) the alluvial plains of the Kupa and Sava rivers are suitable for the secondary accumulation of Fe and thus for the formation of bog iron ore, 2) what is the typical the mineralogical and chemical composition of the Fe-enriched soils in this region, and 3) is it possible to determine possible sources for Fe accumulation in the soil?

2. Study area

2.1. Geotectonic and geomorphological characteristics

The alluvial plains of the Kupa and Sava rivers, within the Pannonian basin and are influenced by the adjacent mountain ranges, have complex geological and tectonic features characterised by tectonic movements and various sedimentary deposits. The north-western part of the Kupa River Plain, the Pokuplje region, lies in a tectonically active zone created by the interaction of the African and European plates. This area has undergone various geological processes, including rifting, inversion and neotectonic movements, which have uplifted older rock layers and created a heterogeneous stratigra-

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phy. In this context, north-west Croatia lies on a tectonic boundary between the Alps, the Dinarides and the Pannonian basin, which is cut by the Periadriatic-Balaton-Sava-Drava fault systems (see **Figure 1a**). These fault systems have a considerable influence on the Neogene-Quaternary tectonics of the region (**Biondic et al., 2003**).

The geomorphology of the Kupa Plain includes the Upper Kupa River as part of the Črnomelj-Bosiljevo-Ozalj Plain with elevations between 130 and 300 m. above sea level (a.s.l.). Loess-like sediments and swampy, poorly drained soils are also found in areas such as Karlovac and Jastrebarsko, where eolian processes and fluvial deposits have played a key role in sediment distribution. In these regions, impermeable clayey horizons often cause seasonal waterlogging, creating anoxic soil conditions which influence both local soil chemistry and vegetation patterns.

The geomorphology of the Croatian part of the Sava River basin includes the central lowland areas in the valleys of the Sava, Odra and Lonja rivers, where the elevation in the central floodplain is between 90 and 110 m.a.s.l. and gradually rises to 140 to 160 m along the basin margins. This lowland region is bordered by mountain ranges such as the Medvednica, Moslavačka gora and Vukomeričke gorice, which form a natural boundary around the floodplain. The basin is also characterised by alluvial deposits and fine-grained, loess-like sediments in regions such as Jasenovac and Lonjsko Polje, indicating a mixture of marshy conditions and periodic flooding that contributed to sediment distribution through both fluvial and aeolian processes (**Cvetković, 2013**). In addition, the marshy, loess-like sediments in Stružec-Osekovo indicate a shallow water environment with intermittent landfalls where wind and water deposited terrigenous material (**Brkić, 2017**).

2.2. Geological composition and hydrology

The Kupa River catchment area is geologically very diverse and originates in the Risnjak National Park, where Jurassic limestone come in contact with hornfels and similar Tertiary and Permian rock types. In its middle course near Ozalj, the Kupa passes through Lower Pliocene clastites and limestones, while in the Črnomelj-Bosiljevo-Ozalj Plain reddish bauxite clays from the Tertiary period can be observed. The alluvial plain of the Sava River is dominated by Quaternary and, in some places, Pliocene deposits, with significant floodplain and terrace sediments from the Holocene. The peat loess in Stružec-Osekovo consists of silts and clays that were probably deposited under alternating shallow water and alluvial conditions, suggesting a dynamic sedimentary environment (see **Figure 1b**).

Hydrologically, both regions have sedimentary layers with different levels of permeability. In the area of Ozalj, Karlovac, Duga Resa and Slunj, the geological base of Tertiary and Quaternary sediments (including marl and clay) is generally of low permeability, but there are also areas of high permeability, especially in Miocene limestones and conglomerates. This different permeability results in isolated areas where groundwater accumulates at higher elevations and occasionally surfaces in the Kupa River Plain. In the Sava Plain, Gleysols form on Holocene and Pleistocene sediments in areas with shallow groundwater, exhibiting redoximorphic features due to fluctuating waterlogging conditions (**Husnjak, 2014**).

2.3. Fe occurrences and mineralization in the region

The Kupa and Sava River plains are known for their iron ore deposits, which exhibit different mineralization patterns influenced by geological and environmental factors. According to **Marković** (**2002**), five different types of Fe mineralization can be observed in the Kupa River region:

1. Quartz-siderite veins with limonite from siderite oxidation.
2. Ankeritized limestone deposits with limonite.
3. Iron mineralization in Middle Triassic deposits associated with submarine volcanic exhalations, resulting in hematite, limonite and specularite formations.
4. Hunsrück-type sedimentary deposits with limonite in clays and sands precipitated from iron hydroxide during sedimentation.
5. Limonite concretions, nuggets and crusts found in sands and clays formed by chemical precipitation and mechanical transport.

Iron is also occurring as a part of hydrothermal mineralization in the wider region. Numerous studies (**Jurković, 1959; 1962, 1988; Jurković and Durn, 1988; Borojević Šoštarić et al., 2009**) confirm the presence of Fe-containing sulphides, such as pyrite, chalcopyrite, arsenopyrite, etc. Present alongside them are polysulphide mineralization such as galena, arsenopyrite, millerite, sphalerite, chalcopyrite, tetrahedrite, tennantite, cassiterite, enargite, bournonite, boulangerite, chalcocite, covellite, or carbonate mineralization such as siderite and ankerite, with elements such as Cu, Pb, Zn, Ag, Co, Ni, Sn, Sb and As having the same hydrothermal origin as Fe. Therefore, these elements might give insight into the origin of Fe-enrichment in soils.

Previous studies discovered Fe accumulations in the Sava Plain, mainly in the form of limonitic concretions in two locations: southwest of Sunja and near Osekovo (**Crnko and Vragović, 1990**). At Sunja, up to 1-2 m thick limonitic concretions were found embedded between Pleistocene clays and Pliocene silts or sands, while at the Osekovo location, decametre-long deposits of limonite interlayers and Mn concretions in Pleistocene silts were recorded. Based on previous analyses, chemical composition of a sample from Sunja contains significant concentrations of Fe_2O_3 (19.8 %), indicating the unique Fe mineralogical and geochemical characteristics of the region.

3. Materials and methods

3.1. Fieldwork and sampling

In order to answer research questions, during the spring in 2024, several field campaigns were carried out in the Pokuplje and Posavina regions with the common goal of identifying possible bog iron ore deposits or indications of bog iron ore formations (see **Figure 1**). Numerous soil profiles and potential bog iron ore samples were collected. Potential sampling locations were selected based on possible association with previously discovered archaeological sites or proximity to historically known Fe sources or toponyms that would indicate either marshy environment or the presence of Fe. Three soil profiles (two from the Kupa alluvial plain and one from the Sava alluvial plain) were selected based on visual field observations of soil discolouration, with signs of Fe enrichment due to presence of reddish mottles. One analysed soil profile from the Pokuplje region is located near the village of Pravutine, while the other is located near the neighbouring village of Žakanje. Both toponyms are mentioned in association with iron ore exploitation in 19th century (**Laszowski, 1942; Marković, 2002**). The soil profile consists of a 90 cm thick humus interval located in a slightly elevated, non-agricultural area and a 60 cm thick soil interval located topographically below the first interval in an agricultural area. The soil profile from the Posavina region is located north of the village of Osekovo. Although the location is not in the immediate vicinity to known archaeological site Okuje I where iron production took place, or the town of Sisak (site of ancient Siscia and Iron age site Sisak-Pogorelec) where some form of iron production or processing is presumed, it lies in the same geological setting, the alluvial plain of the Sava River (see **Figure 1**). In each case, drilling was carried out until a greenish-grey interval occurred. All analysed soil profiles were determined on site and divided into intervals based on visible macrofield observations and estimates and stored in separate plastic bags. After being transported to the laboratory, the samples were air-dried. Then, a portion of each interval was carefully crushed and sieved through a 2 mm sieve.

3.2. Laboratory analyses

The colour of the soil was determined using the Munsell soil colour chart (**Munsell, 1994**). The pH of the soil was measured according to the ISO 10390:2005 standard by immersing a glass electrode in a 1:5 suspension of 5 ml soil and 25 ml 1M KCl suspension.

Mineralogical analysis was conducted in the Laboratory for analysis of geological materials at the University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering. A portion of each bulk sample was gently crushed and sieved through a 2 mm sieve, after which samples were ground to a powder fraction. The powder fraction of each sample was analysed using X-ray powder diffraction on the Malvern Panalytical Empyrean diffractometer using 0.5° divergent and anti-scatter slits, 0.03 and 0.04 rad soller slits, Cu–Kα radiation, 45 kV, 40 mA and a PIXcel 3D detector. The measurement time per step was 78.8 s with a step size of 0.0130°2θ. The mineral composition of each sample was identified using PANalytical X'Pert HighScore 5.2.0. software with standardised Powder Diffraction Files (PDF) of the International Centre for Diffraction Data (ICDD). Semi-quantitative composition of the samples was established using built-in Rietvald fitting feature within X'Pert Highscore based on the crystal structure obtained from the Crystallography Open Database (**Vaitkus et al., 2023, Gražulis et al., 2009**).

The geochemical contents of major and trace elements were measured using a Hitachi XMET 8000 Expert Geo portable X-ray fluorescence (pXRF) instrument. Each sample was measured five times, with each measurement lasting 40 s and using a MiningLE calibration. From this, the average value for each sample was calculated. The accuracy of the analysis was controlled by analysing the standard material for soil samples (NIST 2711) in the sample batches tested. Based on five measurements, usage of replicas and standards, estimated instrumental precision was ±5%. Detection limits for Al and Si were 200 ppm, while for other major and trace elements, the detection limits were 20 ppm or lower.

Soil texture was characterised by the laser diffraction method using the Malvern Mastersizer 3000. In this study, the 2000-63-4 μm system was used to determine the sand, silt and clay size fractions. About half a gram of each sample was placed in a laboratory glass with distilled water and soaked overnight. They were subsequently placed in an ultrasonic bath for 10 min to further disperse the sample and then placed on a magnetic stirrer to keep them in suspension. A small amount of the suspension was added to the measurement module to an obscuration level of 3-4 % and treated with ultrasound for 20 s before measurement. Each sample was measured five times, and the average values were calculated.

3.3. Statistical analysis and enrichment factors

Basic descriptive statistics, including minimum, maximum, mean and standard deviation, were generated for all analysed samples. The major oxides, together with selected trace elements, were compared with their respective median values for each region. From this, enrichment factors (EF) were calculated according to the formula of **Simex and Helz (1981)**:

$$EF = \frac{\text{Element(soil)}}{\text{RE(soil)}} \Big/ \frac{\text{Element(background)}}{\text{RE(background)}} \quad (1)$$

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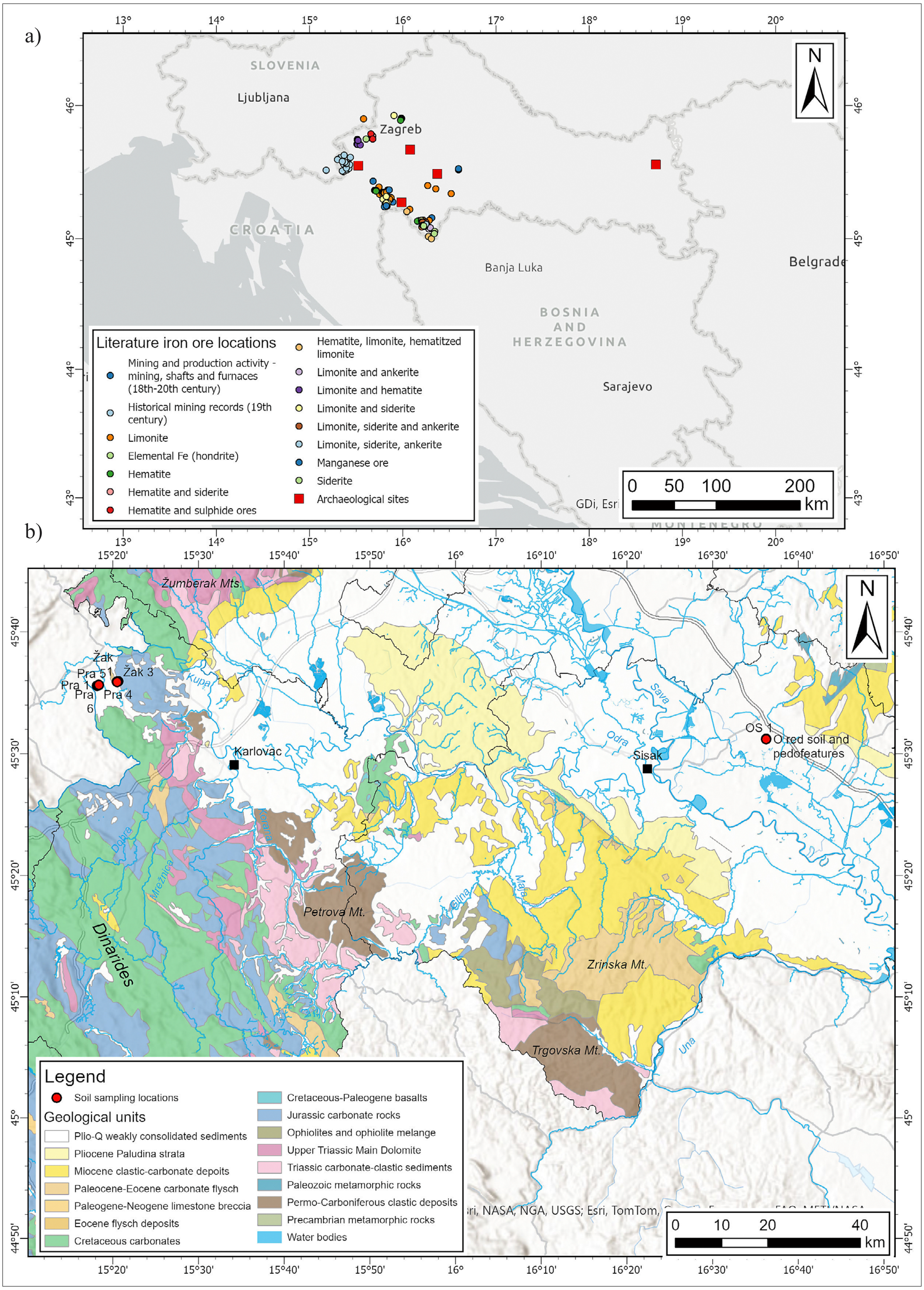

Figure 1: a) Regional map with occurrences and findings of iron ore in literature (according to **Laszowski, 1942; Bojanovski 1988; Jurković, 1993; Marković, 2002**) and b) geological map with soil sampling positions.

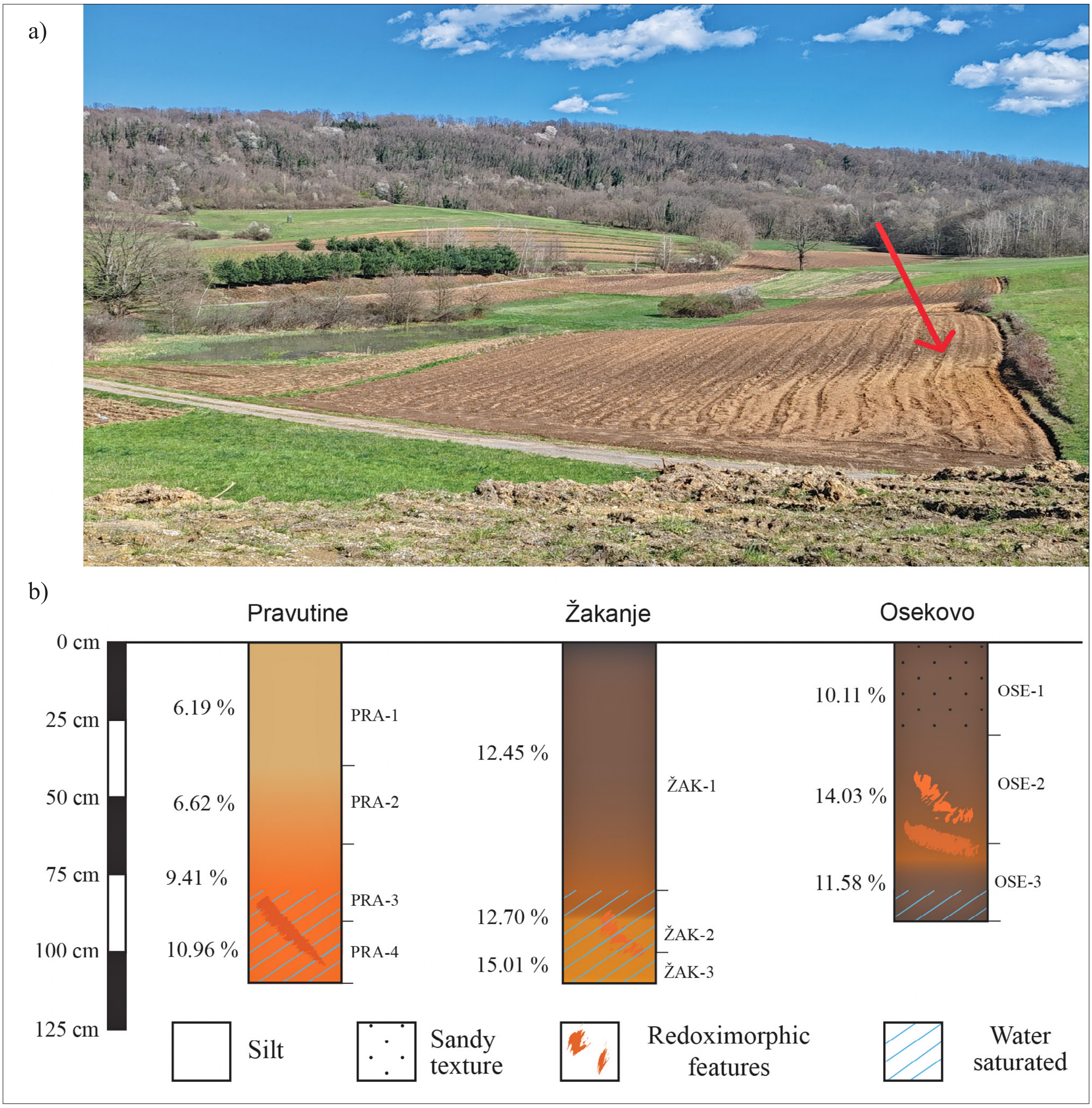

Figure 2: a) Visible soil discoloration with profile position (red arrow) at Žakanje site and b) Schematic drawing of the three soil profiles with visible iron redoximorphic features, Fe contents and estimated groundwater depths.

where Element(soil) and Element(background) refers to the contents of the observed elements both in the analysed soil profile and as regional median values, and RE(soil) and RE(background) refers to the determined contents of references element in the soil and median values in the region. Median values for each analysed element in Central Croatia were taken from Geochemical Atlas of the Republic of Croatia (**Halamić and Miko, 2009**). Elements used as a reference represent an element that is stable in the soil and is not mobilised from the soil, especially under variable redox conditions. Titanium was chosen as the reference element for this study (**Isakson et al., 1997**). Titanium was also used for the calculation of EF in the soils of the Podravina region and allows a comparison of the enrichment factors in different regions. EF is often categorised into classes that define the enrichment or contamination with a particular element. Values of $0.5 \leq EF \leq 1.5$ indicate that the metal content originates from completely natural weathering processes. The EF index can be used as an indicator of soil quality based on values that fall into different classes ranging from EF < 2 (Deficiency to minimal enrichment) up to EF > 40 (Extremely high enrichment) (**Loska and Wiechuła, 2003**).

Table 1: Physico-chemical characteristics of analysed soil profiles

Location	Sample ID	Depth (cm)	Munsell soil colour	Colour name	pH	Clay	Silt	Sand	Soil texture
Žakanje	Žak-1	0-90	2.5Y 6/4	light yellowish brown	5.34	19.57	80.31	0.11	Silt loam
	Žak-2	90-110	10YR 6/6	brownish yellow	5.76	22.37	74.94	2.69	Silt loam
	Žak-3	110-130	7.5YR 5/6	strong brown	6.51	25.17	74.82	0.00	Silt loam
Pravutine	Pra-1	0-40	2.5Y 6/4	light yellowish brown	4.72	10.37	86.33	3.28	Silt
	Pra-2	40-65	2.5Y 7/4	pale yellow	4.91	20.47	79.53	0.00	Silt loam
	Pra-3	65-90	10YR 6/6	brownish yellow	5.13	16.32	71.01	12.67	Silt loam
	Pra-4	90-110	10YR 6/6	brownish yellow	4.32	19.17	78.70	2.13	Silt loam
Osekovo	Ose-1	0-30	2.5Y 6/4	light yellowish brown	4.59	4.70	67.43	27.87	Siltloam
	Ose-2	30-65	2.5Y 6/6	olive yellow	5.07	16.74	83.25	0.00	Silt loam
	Ose-3	65-90	2.5Y 6/4	light yellowish brown	4.82	13.81	85.21	0.99	Silt loam
Minimum					4.32	4.70	67.43	0.00	
Maximum					6.51	25.17	86.33	27.87	
Mean					5.12	16.87	78.15	4.97	
St. deviation					0.60	5.70	5.81	8.45	

Table 2: Results of mineral composition based on the XRD analysis for grain size<2 mm (Abbreviations: Qtz – quartz, Pl – plagioclase, Fld – feldspar, Gt – goethite, Kln - kaolinite, Sme – smectite group, Chl – chlorite 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	Depth (cm)	Qtz	Pl	Fld	Gt	Kln	Mica / Illite	Sme	Chl	Additional minerals
Žakanje	Žak-1	0-90	+++	+	+	+	+	++	+	+	Hematite, rutile?
	Žak-2	90-110	+++	+	+	+	+	++	+	+	Hematite, rutile?
	Žak-3	110-130	+++	+	?	+	+	+	+	+	Hematite, rutile?
Pravutine	Pra-1	0-40	+++	?			+	++	+	+	Rutile?
	Pra-2	40-65	+++	?		?	+	++	+	+	Rutile?
	Pra-3	65-90	+++	+	?	+	+	++	+	+	
	Pra-4	90-110	+++	+	?	+	+	++	+	+	
Osekovo	Ose-1	0-30	+++	+	?		+	++	+	+	Rutile?
	Ose-2	30-65	+++	+	?	+	+	++	+	+	
	Ose-3	65-90	+++	+	?		+	++	+	+	

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

4. Results

The analysed soil profiles and their physico-chemical properties are listed in **Table 1**. Schematic representations of the three selected soil profiles can be found in **Figure 2**. The colour of the soil varies with increasing depth and ranges from a light yellow-brown to a strong brown. Orange-reddish masses or pore linings can be observed in all profiles, indicating presence of Fe mineralization. In some cases, the entire sample interval is orange-reddish in colour, indicating a stronger Fe presence. In the case of the Osekovo profile, smaller dark brown to black nodules are visible in the upper and centre part of the profile. The pH value of the soil indicates a moderate to slightly acidic soil in all cases. There is no regularity in the variation of pH with depth, with pH decreasing with depth in some cases and increasing with depth in others.

The granulometric analysis revealed that silt is the dominant phase in all soils at all three sites (see **Table 1**). The silt contents vary from 67.43 vol.% in the uppermost part of the Osekovo profile to 86.33 vol.% in the upper part of the Pravutine profile. This is followed by the clay content, which ranges from 4.70 vol.% in the uppermost part of the Osekovo profile to 22.37 vol.% in the central part of the Žakanje profile. Contents of sand are generally below several vol.%, with increased contents in the middle part of Pravutine profile (12.67 vol.%) and upper-most part of Osekovo profile (27.87 vol.%). Based on the soil texture classification of the

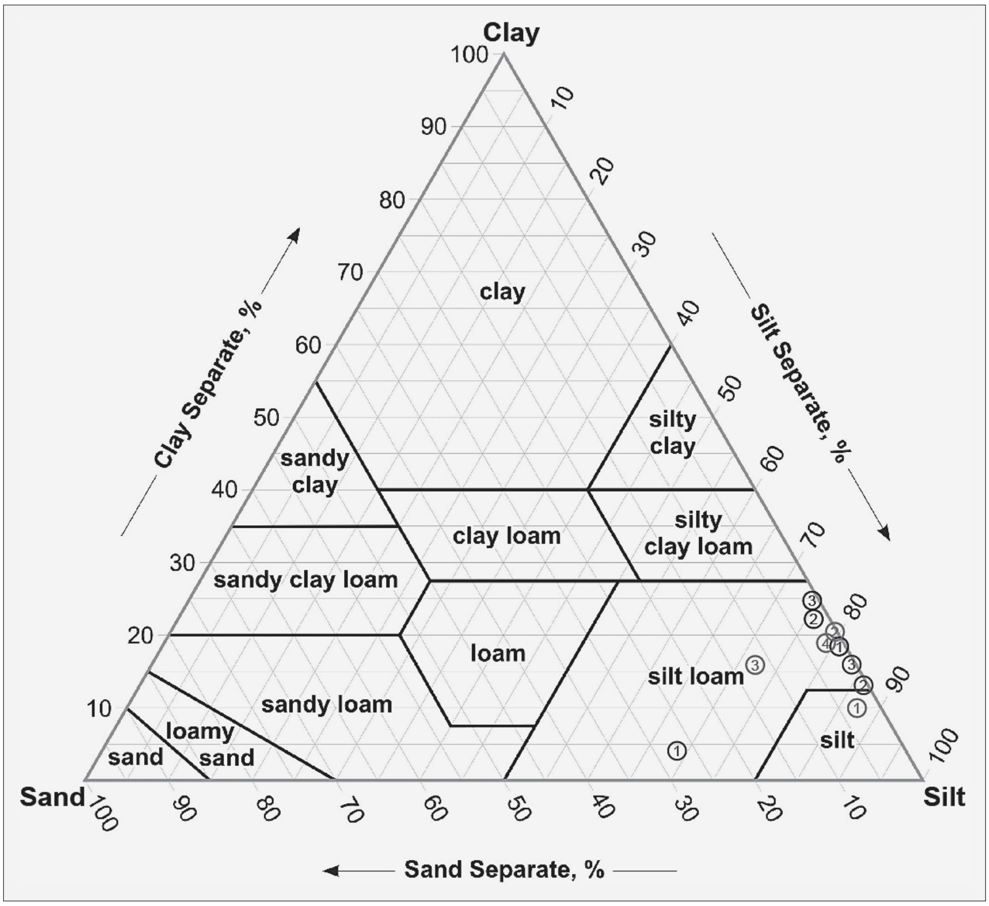

Figure 3: Ternary soil diagram for the three analysed soil profiles.
Legend: black - Žakanje profile; red - Pravutine profile, blue - Osekovo profile

IUSS working group WRB (**2015**), all soil samples fall into the silt loam and silt categories (see **Figure 3**).

The XRD analysis revealed that all three soil profiles have a similar mineral composition (see **Table 2**). Quartz is the dominant mineral phase in all three profiles, followed by several phyllosilicate mineral phases, especially mica and clay minerals. Mica phases are characteristic by their 10Å 001 peak, along the 002 and 003 peaks. Widening of the 10Å peak suggests presence of illite mineral phase. Based on the XRD patterns, there are clear indications that both 7 and 14Å clay minerals (kaolinite and smectite groups) are present. Widening of the peak at 7Å suggests the presence of kaolinite, with distinctive 001 peak at 7.1Å, and a secondary peak at 7.25Å indicates a 002 peak of smectite. In addition, occurrences of feldspars and plagioclase were determined, although they represent trace mineral phases, often present below 5%. Fe phases are mostly represented by goethite, with notable peak in the 21.20 – 21.40 2θ range. The occurrence of goethite is generally lower in the uppermost part of the profiles and gradually increases with depth. Additionally, there are indications for the presence of hematite mineral phase at the Žakanje site, based on several peaks in the 33 – 36 2θ range, while other Fe-oxyhydroxides were not detected.

The soil profiles were analysed for the content of major oxides and selected trace elements, in particular arsenic (As), lead (Pb) and zinc (Zn), as there are known Pb-Zn mineralization occurrences in the region, as well as known positive correlation between Fe in bog irons and As (see **Table 3**) (**Brenko et al., 2020**). The most abundant elements found in the analysed soils were silicon (SiO_2) with quantities ranging between 49.12 and 68.01%. (average 60.34 %) and aluminium (Al_2O_3) with contents between 14.77 and 25.45% (average 18.22 %). Iron, with varying contents between different sampling sites is the third most abundant element in the observed soils. The highest average values were found at the Žakanje site, where the contents vary between 12.45 and 15.01% (avg. 13.39%). The Osekovo site has the second highest average Fe content, ranging from 10.11 to 15.01% (average 11.91%), while Pravutine has the lowest Fe_2O_3 content (6.19 – 10.96%, avg. 8.29%). Comparison to the Clarks values for the upper continental crust (**Rudnick and Gao, 2003**) shows that Fe, Mn, As, Cr and Ni have increased contents; consistent with enrichment factors. The Žakanje profile shows a moderate enrichment (see **Table 4**) of Cr (2.58 – 3.08) and As (2.03 – 2.54), with a low enrichment of Fe. The Pravutine profile shows a moderate enrichment of Fe in the deepest part of the pro-

Table 3: Geochemical composition of major oxides and select trace metals in soil of Pokuplje and Posavina regions. Major oxides expressed as mass. %, trace elements as mg/kg.

Sample name	Depth (cm)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	P_2O_5	As	Ba	Cr	Ni	Pb	Sr	Zn
Žak-1	0-90	57.86	1.36	18.45	12.45	0.83	1.16	0.20	2.56	0.29	36.80	263.75	477.00	101.20	61.80	53.00	152.60
Žak-2	90-110 (0-20)	56.26	1.52	20.41	12.70	0.66	1.51	0.20	1.80	0.25	39.80	204.00	452.20	98.40	57.00	49.80	146.80
Žak-3	110-130 (20-40)	49.12	1.48	25.45	15.01	0.84	1.53	0.10	1.75	0.18	48.40	210.00	433.40	202.00	49.20	59.80	240.80
Pra-1	0-40	68.01	1.13	15.82	6.19	0.38	0.93	0.09	2.01	0.17	15.20	205.00	b.d.l.	b.d.l.	33.20	55.00	74.40
Pra-2	40-65	67.50	1.18	15.89	6.62	0.36	0.99	0.08	2.04	0.14	18.40	b.d.l.	b.d.l.	b.d.l.	33.00	55.60	64.40
Pra-3	65-90	61.80	0.99	19.29	9.41	0.44	0.90	0.04	2.12	0.13	21.00	b.d.l.	310.00	57.00	25.60	42.80	69.40
Pra-4	90-110	60.58	0.52	19.70	10.96	0.44	0.78	0.03	2.02	0.15	23.20	226.00	405.00	62.20	27.80	35.80	85.00
Ose-1	0-30	62.33	0.78	14.91	10.11	0.99	2.43	0.30	2.82	0.26	25.60	360.20	333.33	73.60	45.00	154.40	138.40
Ose-2	30-65	59.99	0.80	14.77	14.03	0.79	1.52	0.26	2.91	0.27	35.40	426.20	363.00	88.80	77.80	140.60	149.60
Ose-3	65-90	59.94	0.94	17.50	11.58	0.71	1.77	0.06	2.56	0.17	30.80	378.60	303.67	78.20	49.40	147.40	128.80
Min.		49.12	0.52	14.77	6.19	0.36	0.78	0.03	1.75	0.13	15.20	204.00	303.67	57.00	25.60	35.80	64.40
Max.		68.01	1.52	25.45	15.01	0.99	2.43	0.30	2.91	0.29	48.40	426.20	477.00	202.00	77.80	154.40	240.80
Avg.		60.34	1.07	18.22	10.91	0.64	1.35	0.14	2.26	0.20	29.46	284.22	384.70	95.18	45.98	79.42	125.02

file (3.23). This Fe enrichment in the lower part of the profile is followed by an enrichment of Cr (6.83), Ni (2.35) and As (3.45). The Osekovo profile shows enrichment of Fe (2.02 – 2.75), Mn (2.74 – 3.27), Cr (2.76 – 3.64), As (2.43 – 3.29) in the entire upper and middle part of the profile and enrichment of Ni (2.12) and Pb (2.60) in the middle section of the profile.

The correlation matrix of the observed soil parameters is shown in **Table 5**. Based on the t-test performed, about half of the observed data show statistically significant values. Iron shows a positive correlation towards CaO (0.70), Cr (0.88), Ni (0.91), Zn (0.85), As (0.93) and Pb (0.70). On the other hand, SiO_2 shows a significant negative correlation with the same elements. Soil pH shows a strong positive correlation with clay (0.67), TiO_2 (0.82), Al_2O_3 (0.75), Ni (0.79), Zn (0.78) and As (0.81).

5. Discussion

5.1. Formation settings of the potential bog iron ore occurrences

Bog iron ore, which is classified as a chemical or biochemical iron deposit, was used for iron production from the Iron Age to the Middle Ages (**Pleiner, 2000**). The deposits are largely concentrated in the northern hemisphere (**Staton, 1972**), where low-lying marshes with slow groundwater circulation allowed interaction between iron-rich groundwater and organic material, which favoured iron precipitation. This interaction often occurs where clay layers restrict drainage, creating the anoxic conditions necessary for iron accumulation. This is consistent with the study area, where all three analysed soil profiles are located in lowland areas with near-surface groundwater levels that fluctuate at a depth of about 1 m, as determined during on-site sampling. Profiles are located in wetter margins of extensive river plains, which is consistent with the typical environmental conditions for the formation of bog iron ores; as numerous studies have similarly documented bog iron ores along the lowland margins of large river basins of Europe (**Kaczorek et al., 2009; Thelemann et al., 2017, Nauta et al., 2024**).

The occurrence of bog iron ore in the Croatian part of the Pannonian basin is closely linked to the extensive alluvial plain of the Drava River (Podravina region). Over 150 archaeological sites with traces of iron production have been documented in this area, providing evidence of its exploitation and use during archaeological periods (**Sekelj Ivančan and Karavidović 2022; Brenko et al., 2020**). The Podravina region is characterised by extensive floodplains crossed by Drava River, similar to Kupa and Sava rivers in Pokuplje and Posavina. These rivers contribute to regular flooding, especially in early spring and autumn when water levels approach the surface, as observed in Podravina (**Brkić and Briški, 2018**), which favours the anoxic conditions that are essential for the accumulation of Fe ore in the lowlands. It

Table 4: Enrichment factors for selected major and trace elements with Ti as reference element. Bolded values represent moderate enrichment.

Sample ID	Al	Fe	Ca	Mg	Mn	K	P	Cr	Ni	As	Ba	Pb	Zn	Sr
Žak-1	0.71	1.40	0.57	0.50	1.33	0.63	1.08	**3.08**	1.46	**2.09**	0.32	1.09	1.00	0.04
Žak-2	0.70	1.29	0.41	0.58	1.21	0.40	0.84	**2.62**	1.28	**2.03**	0.22	0.90	0.86	0.03
Žak-3	0.90	1.56	0.53	0.61	0.64	0.40	0.64	**2.58**	**2.70**	**2.54**	0.23	0.80	1.45	0.04
Pra-1	0.73	0.84	0.31	0.48	0.75	0.60	0.79	n/a	n/a	1.04	0.30	0.71	0.59	0.05
Pra-2	0.71	0.86	0.29	0.49	0.60	0.59	0.61	n/a	n/a	1.21	n/a	0.68	0.49	0.05
Pra-3	1.02	1.46	0.41	0.53	0.36	0.72	0.70	**2.75**	1.13	1.64	n/a	0.62	0.62	0.05
Pra-4	1.97	**3.23**	0.78	0.87	0.53	1.31	1.47	**6.83**	**2.35**	**3.45**	0.71	1.28	1.45	0.07
Ose-1	1.10	**2.02**	0.76	1.60	**3.27**	1.23	1.30	**3.64**	1.79	**2.43**	0.77	1.53	1.59	1.23
Ose-2	1.07	**2.75**	0.60	0.98	**2.74**	1.24	1.32	**3.89**	2.12	**3.29**	0.89	**2.60**	1.69	1.10
Ose-3	1.08	1.93	0.46	0.97	0.55	0.93	0.73	**2.76**	1.59	**2.43**	0.67	1.40	1.24	0.98
Minimum	0.70	0.84	0.29	0.48	0.36	0.40	0.61	2.58	1.13	1.04	0.22	0.62	0.49	0.03
Maximum	1.97	3.23	0.78	1.60	3.27	1.31	1.47	6.83	2.70	3.45	0.89	2.60	1.69	1.23
Mean	1.00	1.74	0.51	0.76	1.20	0.80	0.95	3.52	1.80	2.21	0.51	1.16	1.10	0.36
St. deviation	0.36	0.73	0.16	0.34	0.95	0.33	0.30	1.33	0.51	0.75	0.25	0.57	0.42	0.49

is noteworthy that both the Kupa and Sava rivers have recorded significant flood events in recent decades, emphasising the importance of floodplains for Fe deposition in these regions (**Frančišković-Bilinski et al., 2012; Sokol Jurković, 2016**).

Fluctuating groundwater levels have a significant impact on oxygen availability and create periodic anoxic conditions that promote the mobilisation of Fe and other elements (**Mansfeldt et al., 2012**). The observed Fe enrichment at 30 to 90 cm depth corresponds to groundwater dynamics in the Podravina region, where groundwater typically fluctuates between 40 and 80 cm below the surface and can rise during flood events (**Brkić and Briški, 2018**). It is presumed that in the Podravina region, bog iron ores form in micro-depressions where the water table almost reaches the surface, creating ideal conditions for iron accumulation. Seasonal flooding and fluctuating groundwater levels in the Pokuplje and Posavina regions in central Croatia also create alternating oxic and anoxic conditions. During anoxic periods, Fe is reduced, dissolved and mobilised, only to oxidise and precipitate as iron oxyhydroxides when water levels fall, forming goethite and lepidocrocite, the most common Fe mineral phases in these bog iron ores.

The Fe-enriched soils in central Croatia, especially the middle horizons with iron-rich mottling, resemble the first developmental phase of bog iron ores, commonly known as "soft bog iron" (**Brenko et al., 2020**). Soft bog iron represents an early accumulation stage in which the Fe_2O_3 content exceeds 10% and begins to visibly accumulate as patches and pore space fillings. Over time, these Fe-enriched horizons could further transform into more mature bog iron ores, e.g. "hard bog iron", where the iron mineralisation forms more compact layers. Bog iron deposits typically form and evolve from "soft bog iron" to "hard bog iron" due to continuous redox cycling between oxic and anoxic conditions (**Kaczorek et al., 2004; Thelemann et al., 2017**), suggesting that the soils from this study may also undergo a similar transition if redox dynamics persist over geological time scales. All three analysed profiles show orange to reddish-orange staining and shading in the upper to middle parts of the profiles, confirming potential Fe accumulation. The profiles are moderately to slightly acidic and have a low carbonate quantity based on the CaO content and XRD analysis. Prevalence of quartz, with low quantities of feldspars, plagioclase and phyllosilicates is in line with previous studies of Kupa and Sava river drainage basins (**Frančisković-Bilinski, 2008**). Distinct characteristics in oxide composition and trace element content is noticeable, when compared to similar soils from Podravina and other European regions, especially areas known for bog iron ore or similar Fe-rich soil formations, such as Fe-nodules (**Šegvić et al., 2018; Gasparatos et al., 2019**). The amounts of Fe_2O_3 in the analysed soils of the Pokuplje and Podravina region range from 6.19 to 15.01%. Normally, Fe_2O_3 contents in bog iron ores vary from 30 and 50 mass. % (**Joosten et al., 1998; Sitschick et al., 2005; Charlton et al., 2010**). The amounts of Fe_2O_3 in the analysed soils of the Pokuplje and Posavina region range from 6.19 to 15.01%. The Fe_2O_3 content in bog iron ores is overall variable, dependant on the development stage and presence of gangue minerals. Examples of fully developed and exploited ores can vary from 30 and 50 mass. % (**Joosten et al., 1998; Sitschick et al., 2005; Charlton et al., 2010**), and reach up to 95% Fe_2O_3 (**Thelemann et al., 2017**). The Fe_2O_3 content in the soil of the Podravina region varies between 3.97 and 31.52%, with an average value of 9.15%, which is lower than the average Fe_2O_3 content of soils in Pokuplje and Posavina (average

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10.91%). Such low Fe contents in soil samples do not initially indicate viable iron ore deposits. Compared to mature bog iron ores, the observed soils contain lower Fe_2O_3 concentrations alongside higher amounts of SiO_2 and Al_2O_3, indicating a less advanced process of iron concentration. However, the existence of bog iron ore deposits i.e. matured ores in Podravina region is testified through samples found in geological (site Kalinovac-Hrastova Greda, Novigrad Podravski) and archaeological context (Virje-Volarski breg, Virje-Sušine), where Fe_2O_3 content is between 32 and 71 mass. % (**Brenko et al. 2021**) indicating that there are microregional positions where bog iron ores can fully develop. This is in line with enrichment factors indicate significant Fe-accumulation in the soils, with enrichment factor values similar to that of Fe-Mn nodules (**Gasparatos, 2012; Tan et al., 2006**). Although current Fe concentrations in these soils are modest compared to conventional bog iron ores, the high Fe contents in certain horizons combined with environmental conditions suggest that these soils could progress to denser Fe accumulations with long-term redox cycling. This potential for continued Fe enrichment could lead to higher Fe_2O_3 concentrations over longer time periods, as observed in the more developed European bog iron ores, provided that these soils experience consistent groundwater fluctuations, microbial activity and clay-rich sediment inputs (**Kaczorek et al., 2004; Brenko et al., 2020**). **Halamić and Miko** (**2009**) report that iron concentrations in the soils of Central Croatia range from 0.60% to 6.94%, with a median of 2.96%, which is slightly lower than the national average. Elevated iron concentrations are mainly found in areas such as the Sava Valley downstream of Zagreb, the Lonja Valley and the Medvednica Mountains, due to the influence of ferromagnesian minerals from the surrounding igneous and metamorphic rocks (**Lugović et al., 2006; Mišur et al., 2023; Slovenec et al., 2024; Smirčić et al., 2024**). Fe is transported to lowland areas via groundwater and surface runoff, where it accumulates under fluctuating pH and redox conditions. These changing conditions, as previously explained, are common in waterlogged valleys, promoting the mobilisation and precipitation of Fe-oxyhydroxides such as goethite and lepidocrocite in bog iron deposits.

The presence of high Fe contents in combination with low pH and variable redox conditions suggests that the Pokuplje and Posavina regions could serve as analogues to other bog environments as early stages of iron accumulation. Due to low carbonate content, these soils are likely susceptible to seasonal flooding and episodic waterlogging, mirroring similar bog regions in Europe and world, where prolonged waterlogging is essential for iron precipitation. Consequently, this environment creates favourable conditions for the transition of Fe from dissolved forms in groundwater to stable precipitates in the soil matrix, forming horizons of reddish Fe mottling, similar to iron accumulations in soft bogs. Several parameters play key role in these processes. Microbial pro-

Table 5: Correlation matrix of selected major oxides, trace elements and other soil parameters in the study area

	pH	Clay	Silt	Sand	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	P_2O_5	As	Ba	Cr	Ni	Pb	Sr	Zn
pH	1.00																			
Clay	0.67	1.00																		
Silt	-0.20	0.08	1.00																	
Sand	-0.32	-0.73	-0.74	1.00																
SiO_2	-0.79	-0.58	0.27	0.20	1.00															
TiO_2	0.82	0.53	-0.03	-0.34	-0.41	1.00														
Al_2O_3	0.75	0.72	-0.27	-0.30	-0.81	0.49	1.00													
Fe_2O_3	0.60	0.45	-0.13	-0.22	-0.91	0.19	0.53	1.00												
CaO	0.34	-0.16	-0.32	0.33	-0.59	0.12	0.08	0.70	1.00											
MgO	0.10	-0.45	-0.37	0.56	-0.28	-0.02	-0.16	0.37	0.84	1.00										
MnO	0.10	-0.32	-0.27	0.40	-0.14	0.07	-0.36	0.35	0.75	0.70	1.00									
K_2O	-0.43	-0.59	0.07	0.35	0.19	-0.49	-0.68	0.15	0.55	0.53	0.60	1.00								
P_2O_5	0.20	-0.13	-0.08	0.14	-0.31	0.20	-0.20	0.52	0.77	0.55	0.91	0.56	1.00							
As	0.81	0.56	-0.13	-0.29	-0.94	0.51	0.63	0.93	0.69	0.38	0.36	-0.04	0.53	1.00						
Ba	-0.14	-0.38	0.25	0.08	-0.24	-0.32	-0.28	0.52	0.71	0.65	0.59	0.70	0.65	0.38	1.00					
Cr	0.41	0.33	-0.36	0.02	-0.82	0.08	0.51	0.88	0.64	0.30	0.32	0.14	0.52	0.76	0.39	1.00				
Ni	0.79	0.48	-0.29	-0.13	-0.98	0.39	0.75	0.90	0.68	0.37	0.22	-0.10	0.35	0.93	0.30	0.77	1.00			
Pb	0.37	0.15	0.22	-0.25	-0.44	0.24	-0.09	0.70	0.69	0.46	0.72	0.52	0.84	0.70	0.69	0.49	0.47	1.00		
Sr	-0.24	-0.60	0.04	0.38	0.04	-0.38	-0.51	0.22	0.63	0.82	0.55	0.81	0.41	0.11	0.78	0.06	0.07	0.49	1.00	
Zn	0.76	0.35	-0.17	-0.12	-0.89	0.45	0.57	0.85	0.79	0.53	0.42	0.03	0.52	0.94	0.46	0.65	0.94	0.63	0.24	1.00

- values in green indicate positive correlation over 0.70; values in red indicate negative correlation lower than -0.70

cesses play a crucial role in the formation of bog iron ore, as they facilitate the reduction and oxidation of iron compounds in fluctuating groundwater levels (**Smith et al., 2024**). In many European bog iron deposits, iron-oxidising bacteria such as *Gallionella* and *Leptothrix* are known to precipitate Fe^{3+} as iron oxyhydroxides, a process that probably contributes to iron enrichment in the soils of central Croatia. These microbial processes produce the characteristic porous structure and Fe-rich nodules found in the soft bog iron, suggesting that a similar microbial influence may be present in Pokuplje and Posavina, especially where redox boundaries are sharp (**Ramanaidou and Wells, 2014**).

The predominance of clay and silt fractions in the central Croatian soils (see **Table 1**), in contrast to the more sand-dominated textures in the Podravina soils indicates a different depositional environment. European bog iron ores also show different textures depending on the depositional environment; some have a higher sand content, which contributes to better drainage and cyclic oxidation (**Kaczorek and Sommer, 2003**). Soils in central Croatia are more finely textured and have slower drainage, improving reducing conditions that allow Fe accumulation and selective adsorption of elements to clays. This unique texture favours long-term Fe accumulation in the form of coatings or soft precipitates rather than in coarser, more compact forms as in sandier environments (**Sokolova et al., 2013; Długosz et al., 2018**). Clay minerals play key roles in formation and accumulation of Fe-oxyhydroxides in soil (**Stucki, 2013; Van Groeningen et al., 2020**). In most cases, the highest Fe concentrations can be found near the horizon with the highest clay content, confirming that the formation mechanism involves impermeable clay horizons with the formation of an oxidative-reductive boundary leading to Fe precipitation in the form of goethite and other Fe oxyhydroxides (**Ramanadaiou and Wells, 2014; Thelemann et al., 2017**). These dense clay layers form a redox boundary that facilitates the redistribution of iron and associated elements (**Thomas and Strobel, 2022; Borch et al., 2010**). Directly above these impermeable clay layers, iron-rich horizons usually develop in which iron oxides and hydroxides accumulate and bind trace elements to their reactive surfaces. Dissolved, aqueous Fe^{2+} can be adsorbed to clay mineral surfaces during cation exchange processes on permanently charged face or edge surfaces, or by forming surface complexes or clusters and precipitates. Although clay minerals can be influenced by some forms of reductive dissolution (**Pentráková et al., 2013; Jung et al., 2022**), they are generally considered stable under variable redox conditions. Therefore, a considerable amount of available Fe in waterlogged soils is believed to be adsorbed or incorporated into clay minerals (**Stucki et al., 1988**).

The formation of bog iron ore in central Croatia is thus influenced by a combination of geogenic mineral sources, hydrological dynamics and seasonal redox shifts, all of which promote the mobilisation and accumulation of iron and the formation of metal-enriched iron phases.

5.2. Possible sources of iron

Determining the exact source of iron for bog iron ore formation in central Croatia is a challenge, as iron can occur in both mobile Fe^{2+} and immobile Fe^{3+} forms, depending on the oxygen content in the soil. The geochemical signature of a specific region can be traced for hundreds of kilometres downstream, depending on factors such as the intensity of weathering, climate, geomorphology, and the types of rocks or ores present (**Salminen et al., 2005**).

The geology of central Croatia is dominated by various lithological units, including different types of igneous, metamorphic and sedimentary rocks. Chromium and Ni, for example, are typically associated with ultramafic and mafic rocks containing minerals such as olivine, pyroxene and serpentine (**Kierczak et al., 2021; Ettler et al., 2024**). These types of rocks are present in several areas, such as Medvednica Mountain or Zrinska gora (**Putak Juriček and Garašić, 2024**). Several inselbergs with occurrences of Fe-rich minerals are located in a several hundred kms wide region surrounding the Pokuplje and Posavina regions, such as Petrova gora Mountain, Trgovska gora Mountain, Samoborsko gorje, Papuk, Psunj, Ivanščica, Medvednica Mountain, Prosara, Kozara or Motajica (**Balen et al., 2015; Belak et al., 2022; Borojević Šoštarić and Brenko, 2022**). The presence of minerals, such as biotite, hornblende, pyroxene, or secondary minerals, such as siderite-barite mineralization present at Petrova gora, Trgovska gora, release iron during weathering. These minerals weather over time and release Fe, along with various trace metals into soil and groundwater (**Halamić and Miko, 2009**). Pb and Zn mineralisation in the region is especially pronounced in the vicinity of Petrova and Trgovska gora, where Pb-Zn ores were mined on a small scale in the past (**Palinkaš et al., 2016**). Galena and sphalerite are the common minerals in these ore deposits, and weathering of these sulphides releases Pb and Zn, which are then transported to the neighbouring alluvial soils by alluvial processes.

Although numerous inselbergs are present in the region, source of Fe most likely lies in a zone situated between Medvednica Mountain, Samoborsko gorje Mountains, Petrova gora Mountain and Zrinska gora Mountain. This can be presumed based on the direction of the groundwater flow, as the Fe transport via groundwater is a key formation aspect (**Scott et al., 2011**). Hydrological and hydrogeological studies in the region determined that groundwater, especially during high groundwater levels, flows from Medvednica Mountain towards the south, and directly towards the Osekovo site, indicating possible transportation route for the Fe^{2+} (**Brkić et al., 2010; Parlov et al., 2019**). Furthermore, Trgovska and Petrova gora represent hilly areas, with elevation over 400 m, and a well-developed network of rivers and streams, eroding the primary hydrothermal Fe mineralization, and then transporting and depositing Fe in sec-

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ondary forms in low-land areas such as the Sava and Lonja river alluvial plains. In the Pokuplje region, groundwater flows towards east, indicating possible sources of Fe are originating in Slovenia. This is in line with significant occurrences of both primary and secondary forms of Fe-mineralization found in central and southeastern Slovenia, such as the Dolenjska region (**Trampuž Orel, 2012; Črešnar et al., 2017**).

Trace elements As, Pb and Zn are significant in the observed soils and are under the influence of depositional environment through complexation with Fe minerals. Bog iron ores are rich in low-crystalline and amorphous iron oxyhydroxides, as well as site-dependent phases such as haematite (Fe_2O_3) and magnetite (Fe_3O_4). These amorphous iron phases have a large specific surface area and high reactivity, which enables the adsorption of heavy metals and trace metals on their surfaces (**Huang et al., 2017; Shen et al., 2020**). Bog iron ores act as sink or sorbents of trace elements, especially heavy metals and often retain trace elements in fluctuating redox zones, which makes these soils potential deposits of trace metals due to the adsorption onto Fe-oxyhydroxides (**Banning, 2008; Rzepa et al., 2009; Mansfeldt et al., 2012; Gaj and Cybulska-Szulc, 2014; Tuchowska et al., 2019**). This adsorption can provide clues to the origin of the iron in these soils, as trace elements co-occurring with iron can reflect the mineralogy and geochemical properties of the parent material. Arsenic is often associated with Fe-rich phases in bog environments, as it adsorbs to iron oxyhydroxides under certain pH and redox conditions (**Mansfeldt et al., 2012**). Arsenic often occurs as a trace contaminant in iron-rich minerals, including pyrite (FeS_2), which releases As along with Fe upon oxidation, contributing to its enrichment in Fe-enriched soils. These metals are present in the surrounding lithologies of Pokuplje and Posavina, with known Pb-Zn mineralisation in Petrova and Trgovska gora, southwest of Posavina (**Palinkaš et al., 2016**).

In addition, the role of siderite in the overall formation of bog iron ores in central Croatia may be one of the key factors influencing the overall formation mechanism. Siderite deposits in central Croatia, especially in the Samobor and Banovina areas of Central Croatia, represent a potential source of heavy metals in Fe-enriched soils and bog iron ores (**Bilić and Garašić, 2021**). Siderite can be associated with trace metals such as Mn, Co, Ni and occasionally Pb and Zn, especially in siderite-rich sedimentary environments or hydrothermal deposits (**Erdem and Özverdi, 2005; Sengupta et al., 2020: Kądziołka-Gaweł et al., 2023**). When siderite is weathered or dissolved, it releases Fe together with accompanying trace metals into the soil and groundwater. In floodplain areas where groundwater fluctuates seasonally, the dissolution and precipitation cycles of siderite can mobilise Fe and associated heavy metals, contributing to the metal-rich properties of bog iron ores and Fe-enriched soils. Nickel is commonly associated with siderite in low-temperature sedimentary and hydrothermal environments and can be released by the dissolution of siderite during groundwater fluctuations. Lead and zinc can also occur as trace elements in siderite-bearing rock layers, especially in areas where sedimentary siderite overlaps with sulphide mineralisation, resulting in mixed mineralogical sources of Fe and metals (**Palinkaš et al., 2016**). Hydrothermal mineralisation zones, especially around Petrova and Trgovska gora, have a long history of Pb-Zn mineralisation and mining activities. These hydrothermal systems often contain veins and precipitates of sulphide minerals such as galena, sphalerite and chalcopyrite, which contain not only Pb and Zn, but also traces of As, Cd and other metals. When these minerals weather, they release heavy metals into nearby soils and waters, especially when exposed to oxidising conditions in the near-surface environment. In Germany and Poland, bog iron ores near hydrothermal or siderite-bearing formations show enrichment of elements such as Ni, Pb, Zn and As due to weathering and leaching of local mineral deposits (**Kaczorek et al., 2009; Mansfeldt et al., 2012**). Similarly, elevated levels of Fe, Pb, Zn, Cr, Ni and As have been found in soils in central Croatia, which can be associated with both hydrothermal mineralisation and sedimentary siderite deposits (**Halamić and Miko, 2009**).

5.3. Bog iron ores as possible sources of iron production in archaeological periods

The established potential for the formation of bog iron ore in the Sava and Kupa river valleys presents an opportunity to identify and address historically unknown deposit types, areas and exploitation strategies of the past societies. This, in turn, broadens the scope of current knowledge concerning iron production potential within central continental Croatia across multiple archaeological periods. Current archaeological data on iron production and processing in the region is rather limited (**Bojanovski, 1988; Durman, 1992; 2002; Koščević, 1995; Karavidović and Drnić, 2022; Nemet et al., 2018; Bugar, 2022**), primarily due to the lack of systematic archaeological fieldwork as well as extensive mining activities in the recent past (**Marković, 2002; Jurković, 1993; Šebetić, 2000**), which may have degraded or erased traces of mining and iron production from archaeological periods. The region is abundant in iron ore resources, which differ in mineral composition, quality, and paragenesis (**Marković, 2002**). These resources are located in different natural environments, ranging from lowland to mountainous areas. Such diverse conditions likely influenced the mining practices and exploitation strategies employed by past communities. Bog iron ores, as well as weathered and redeposited limonitic ores, found on or just below the soil surface, are easily extractable and could have been economically feasible for past communities. Natural indicators such as soil discolouration, oily patches on stagnant water, a humid environment with hygrophilous vegetation indicate bog iron ore deposits (**Ramandiou and Wells, 2014; Stanton et al., 2007; Thelleman et al., 2017**) and may have been recognised as potential mining areas by past communities (**Karavidović and Brenko, 2022**). In addition to the ores, these regions have all the natural resources that were necessary for Fe production in the past - clay and water resources for the production of furnaces and wood (charcoal) as an essential fuel component in the process of Fe ore smelting and iron processing (**Pleiner, 2000**). Oxy(hydroxide) ores such as goethite, limonite and hematite are easily processed by direct reduction, a method used in all the mentioned archaeological periods (**Pleiner, 2000**). Other types, such as carbonate ores (siderite), theoretically necessitate a preparation process to convert the metal components into oxides that can be directly reduced. Additionally, the level of porosity and the quantity and nature of gangue constituents may also play a crucial role in effective reduction, again pointing towards more economical use of oxide ores, whether bog iron ores or limonitic weathered, secondary mineralisation (redeposited or in primary positions).

In the case of early Middle Ages iron production in the Podravina region, the workshops for primary production were most likely intentionally located close to natural resources, especially the bog iron ore and wood for charcoal production (**Karavidović and Brenko, 2022**). A similar strategy can be proposed for the concurrent Okuje I site located in the Sava alluvial plain with clear implication of iron production via direct process (**Bugar, 2022**) and sample of bog iron ore (**Nemet et al., 2018**) in the archaeological record.

Regarding Iron Age sites in the Pokuplje and Posavina region (Gornje Pokupje, Sisak-Pogorelec) (**Karavidović and Drnić, 2022**), another implication for the potential use of bog iron ores or limonite ores presumably present in the vicinity of sites (see **Figure 1**) is the geographical, cultural and temporal analogy with archaeological sites with traces of primary iron production and limonite (unprocessed) and hematite (roasted limonite) ores in the archaeological record, located in the Dolenjska region in Slovenia (**Trampuž Orel, 2012; Črešnar et al., 2017**). The results of soil profile analysis further implicate potential similarity in ore sources that could have been used on these sites, the mechanism of bog iron ore formation and origin of Fe^{2+} in the groundwater, that flows from the east (Dolenjska region) into the Pokuplje region. Although, we can state that these types of ores are economically more viable sources, the discussion on the provenance of ores used for iron production or processing in archaeological periods is a matter of future research based on comparative analysis of ore-slag geochemical signatures, on individual sites.

6. Conclusions

The formation of bog iron ore in the Pokuplje and Posavina regions in central Croatia is a complex interplay of geological, hydrological and geochemical processes that together create favourable conditions for iron accumulation in lowland soils. These alluvial areas, dominated by alluvial and Plio-Quaternary sediments, have unique environmental characteristics that favour the development of iron ore in peatlands, namely periodic water saturation and fluctuating groundwater levels. Field analyses of soil profiles in the region show a shallow water table, typically less than one metre below the surface, which promotes the redox cycle that is crucial for the precipitation of iron oxyhydroxides. This study confirms that these profiles, located in extensive floodplains, share numerous features with documented bog iron ore deposits throughout the northern hemisphere, where slow groundwater flow, clay-rich horizons and seasonal waterlogging promote the reducing conditions necessary for iron mobilisation and eventual precipitation.

The soil profiles from Žakanje, Osekovo and Pravutine, for example, show key indicators of bog iron ore formation, including Fe-enriched horizons characterised by reddish mottling and iron oxide colouration. These features correspond with fluctuating groundwater levels that create alternating oxidative and reductive conditions that drive the cyclic dissolution, mobilisation and precipitation of iron. In particular, the depth of iron accumulation varies from profile to profile - it is shallow in the Žakanje profile and deeper in Pravutine and Osekovo - suggesting that local hydrological differences such as groundwater fluctuations and flooding cycles directly influence the spatial distribution of iron accumulation. The acidic to moderately acidic pH and clayey soil structure in these profiles also contribute to iron retention, as clay layers restrict drainage and increase anoxia, concentrating iron in stable forms. The similarities in soil texture and structure between these Croatian profiles and other European bog iron formations emphasise the importance of alluvial morphology and seasonal water dynamics in the process of bog iron formation.

In addition to hydrological and redox factors, the mineral composition and lithological environment in central Croatia also play an important role in iron accumulation in the region. This study suggests that both sedimentary and hydrothermal sources contribute iron to the alluvial soils. Local igneous and metamorphic rock types rich in ferromagnesian minerals release iron during weathering, while siderite deposits in regions such as Samobor and Banovina act as significant geogenic sources. Siderite, an iron carbonate mineral that is often associated with trace elements such as Ni, Mn, Co, Pb and Zn, releases both iron and heavy metals into the groundwater during weathering. These elements subsequently precipitate and accumulate under the anoxic conditions of the alluvial soils. In the process, they form Fe-oxyhydroxide complexes that combine with the trace metals and thus form a repository for elements such as Cr, Ni, Zn, Pb and As. The trace metal associations observed in these profiles, particularly with arsenic and lead, are typical of bog iron ores and reflect the geo-

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chemical character of the surrounding lithologies, especially the ultramafic and siderite-bearing formations. In particular, the presence of these trace metals together with iron phases, even in the absence of high Fe_2O_3 concentrations as found in mature bog iron ores, indicates a gradual accumulation process with the potential for future enrichment if environmental conditions persist.

While iron accumulation in Croatian soils is currently below thresholds for economic mining, the persistent redox cycling, periodic anoxia and heavy metal associations suggest that these soils could develop into economically significant deposits in the long term if environmental conditions remain stable. The cyclical flooding of rivers such as the Sava and Kupa in combination with the observed flood events contribute to periodic iron mobilisation and may enhance metal adsorption, as observed in Podravina. The floodplain topography and soil hydrology in regions such as Pokuplje and Posavina thus represent a promising analogue to the bog iron environments documented throughout Europe, which have similar potential for the development of iron-rich horizons. Although current archaeological knowledge on the presence of iron exploitation and production sites in the region underscores the historical significance of these deposits, Central Croatia was an important area for iron exploitation during several archaeological periods. Continued research into these deposits will enhance understanding of their formation mechanisms, potential economic value, and historical exploitation, contributing valuable insight into both geoscientific and archaeological studies.

Acknowledgement

This work has been fully supported by the Croatian Science Foundation under the project KulturFER (Grant No. IP-2022-10-1846) and created within the project Synergy of Diversity: Archeology of Landscape and Technological Traditions in Continental and Adriatic Croatia (SirAkt), funded by the European Union-NextGenerationEU.

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SAŽETAK

Močvarna željezna ruda u središnjoj Hrvatskoj: mineraloška i geokemijska studija na profilima tla

Pokuplje i Posavina u središnjoj Hrvatskoj nude jedinstvene uvide u topografske i geokemijske uvjete koji pogoduju formiranju močvarne željezne rude u nizinskim područjima. U ovoj studiji analizirana su tri profila tla iz Žakanja, Osekova i Pravutine, koji se nalaze u ravnicama Kupe i Save, kako bi se utvrdio njihov mineraloški i geokemijski sastav s fokusom na obogaćenost Fe i sadržaj metala u tragovima. Prisutnost nepropusnih glinenih horizonata u ovim profilima pridonosi stvaranju redoks-granice koja pogoduje taloženju Fe u obliku oksihidroksida. Crvenkaste mrlje uočene u srednjim horizontima svakoga profila sugeriraju da ta tla mogu predstavljati ranu fazu stvaranja močvarne željezne rude. Geokemijska analiza pokazuje da su ta tla umjereno do blago kisela, s prahom kao dominantnom granulometrijskom frakcijom i promjenjivim sadržajem Fe oksida u profilima. Visoke koncentracije Fe u skladu su s dubinom fluktuacija podzemnih voda koje vjerojatno pokreću redoks-ciklus i potiču mobilizaciju i taloženje željeza. Osim toga, metali u tragovima kao što su Cr, Ni, Zn, Pb i As koreliraju s Fe, što upućuje na vezu s prirodnim izvorima, uključujući regionalne zone siderita i hidrotermalne mineralizacije, i hidrološkim procesima koji prenose te elemente iz okolnih litologija. Sve u svemu, rezultati sugeriraju da kombinacija krajolika bogatih glinom, sklonih poplavama i sezonskim kolebanjima podzemnih voda osigurava idealne uvjete za potencijalno stvaranje močvarne željezne rude u središnjoj Hrvatskoj. Te vrste ruda mogle su biti ekonomski zanimljiv izvor za proizvodnju željeza tijekom arheoloških razdoblja.

Ključne riječi:
močvarna željezna ruda, rijeka Kupa, rijeka Sava, metali u tragovima, geoarheologija

Author's contribution

Tomislav Brenko (1) (Assistant professor, PhD, geologist) participated in field research, conducted laboratory and data analysis, interpreted mineralogical results and presented the results. **Sibila Borojević Šoštarić (2)** (Professor, PhD, geologist) participated in field research, interpreted geochemical data and presented the results. **Tena Karavidović (3)** (Senior assistant, PhD, archaeologist) participated in field research, provided information on archaeological background and research locations, participated in the presentation of the results. **Tajana Sekelj Ivančan (4)** (Scientific advisor, PhD, archaeologist) provided archaeological background and input to key locations for sampling, prepared the results.