Kulturni krajolici metalurgije željeza u slivu rijeke Save i Drave tijekom antike i ranoga srednjega vijeka: rezultati 2. godine projekta

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Introduction

- Extensive systematic study of iron metallurgy in the geomorphologically complex Drava–Danube lowlands and the Ljubija mining district, focusing on soils as carriers of the geochemical signal of ore exploitation.

- Archaeological and historical evidence indicating long-term production, processing, and circulation of iron (semi)products between lowland settlements and upland mining/smelting centres in eastern/northerneastern Croatia and northwestern Bosnia.

- Near-surface raw materials include both bog-iron–rich soils in the Drava–Danube floodplains and weathering products of primary Fe ores from the Ljubija mining district, enabling direct comparison of secondary (bog iron) versus primary ore signatures.

- Key research objective: to define the mineralogical composition and distinctive geochemical fingerprint of Pannonian bog-iron soils and Dinaric–Ljubija ore-derived materials, and to test how reliably these fingerprints can be traced in archaeological slag. metallurgical debris and surrounding soils.

Introduction

Research Objectives:

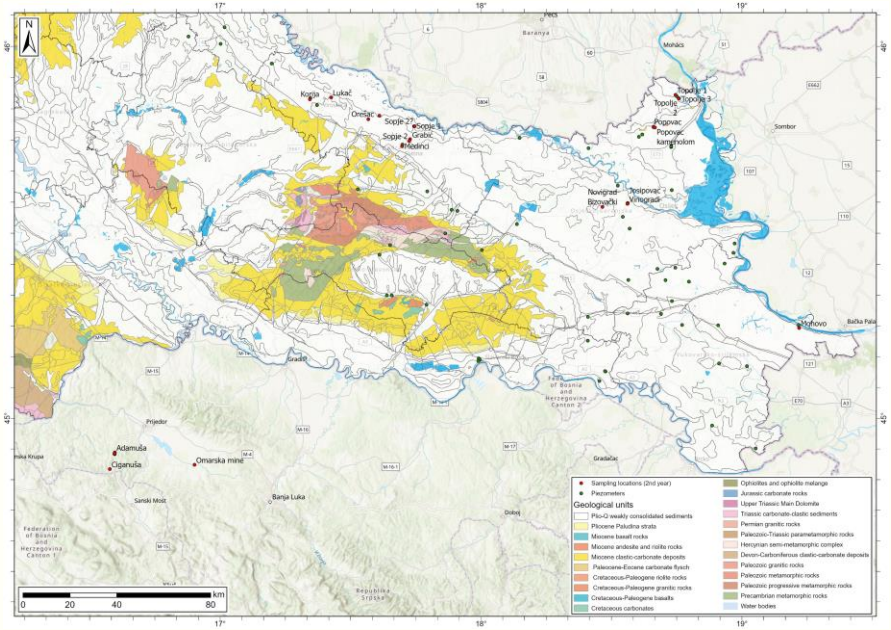
1. Suitability of alluvial plains in Eastern Croatia and Posavina for **secondary iron accumulation**.

2. **Mineralogical** and **chemical composition** of iron-enriched soils.

3. **Identifying sources** of Fe accumulation in soils.

Presentation of physicochemical parameters, granulometric, mineralogical and geochemical composition of the soils using pXRF - the possibility of formation of bog iron ore in the soils of eastern Drava/Danube region

Study area

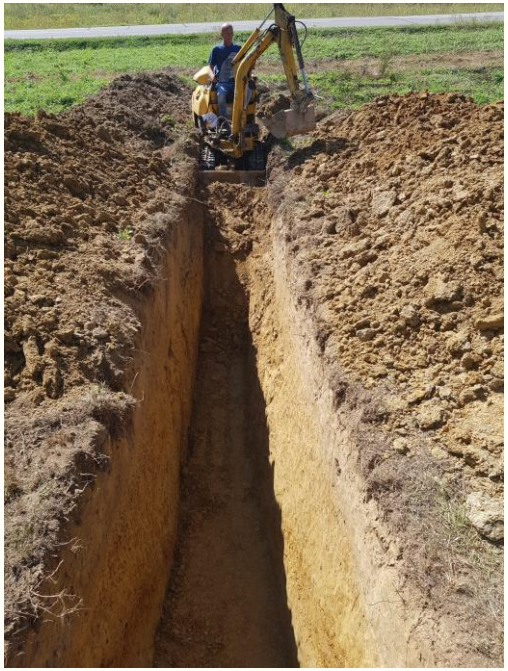


- Intersection between Alps, Dinarides and Pannonian Basin
- Iron occurrences in the region

- Alluvial plains of Drava/Danube plains
- Tertiary and Quaternary sediments surrounded by older materials
- High groundwater levels

Materials and methods

- Sampling of soil material, potential bog iron ores and surrounding lithologies
- Seven soil profiles, pedological pit with three soil profiles
- Mineral composition of samples using X-ray diffraction (XRD)
- Geochemical analysis of samples including major oxides and trace elements using portable XRF
- Physico-chemical parameters: pH and granulometry



Results

Table 1. Physico-chemical characteristics of analysed soil profiles from pedological 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 clay loam	2.5Y 5/4	Yellowish brown
Knez 2	40 - 80	5.02	20.99	75.39	3.63	Silt clay loam	2.5Y 5/4	Yellowish brown
Knez 3	80 - 105	5.61	31.21	68.05	0.75	Clay loam	2.5YR 5/6	Red
Knez 4	105 - 130	5.26	24.81	74.19	1.00	Silt clay loam	2.5Y 6/4	Light yellowish brown
Knez 5	130 - 160	5.04	14.87	50.02	35.11	Loam	2.5Y 5/4	Yellowish brown
Knez 6	160- 190	5.50	11.65	50.14	38.21	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 clay 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

Results

Table 2. Mineralogical composition of soil profiles and ferricrete based on the XRD analysis for grain size <2 mm (Abbreviations: Qtz – quartz. Fld – feldspar and plagioclase group, Gt – goethite, Lpc – lepidocrocite, 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.

Sample ID	Qtz	Gt	Fld	10A	14A	7A	Additional minerals
Knez 1	++++	?	++	++	+	+	
Knez 2	++++	?	+/++	++	+	+	
Knez 3	++	++	+	++	+/++	+	
Knez 4	+++	-	+/++	+	++	+	
Knez 5	+++	-	+/++	+	++	+	
Knez 6	+++	-	+/++	+	+/++	+	
Knez 7	++++	?	+/++	+	+	+	
Knez 8	++++	?	+/++	+	+	+	
Knez 9	++++	?	+/++	+	+	+	
Knez 10	++++	?	+/++	+	+	+	
Knez 11	++++	?	+/++	+	+	+	
Knez 12	++++	?	+/++	+	+	+	
Knez 13	++++	?	+/++	+	+	+	
Knez 14	+++	?	+/++	+	+	+	
Knez 15	+++	?	+/++	+	+	+	
Knez 16	+++	?	+/++	+	+/++	+	
Knez 17	++++	?	+/++	++	+/++	+	
Knez 18	++++	?	+/++	+	+	+	
Ferricrete	++	+++	?	++	+	+	Lpc

Results

Table 2. Geochemical characteristics of soils and ferricrete from Knezovljani area.

Sample ID	SiO2	TiO2	Al2O32	Fe2O3	MgO	CaO	MnO	K2O	P2O5	As	Cr	Ni	Cu	Pb	Zn
Knez 1	69.04	0.65	11.28	9.16	1.39	1.01	0.24	1.87	0.26	27.80	392.00	81.50		46.60	94.80
Knez 2	70.90	0.76	12.38	6.58	1.24	0.78	0.16	1.75	0.16	29.00	316.00	68.33		37.60	76.80
Knez 3	47.93	0.22	10.62	**33.83**	0.97	0.85	0.88	1.47	0.55	77.40	340.40	171.40	56.20	56.80	152.20
Knez 4	66.94	0.42	14.40	8.96	1.33	1.27	0.04	1.59	0.09	32.40	381.60	141.20		25.00	109.40
Knez 5	70.10	0.32	12.81	7.27	1.26	1.21	0.03	1.65	0.10	17.60	403.80	166.80		27.60	113.80
Knez 6	71.69	0.47	12.47	5.87	1.33	1.01	0.04	1.73	0.10	13.00	374.20	118.40		27.40	78.00
Knez 7	70.83	0.91	12.30	6.43	1.05	1.00	0.13	1.77	0.27	23.00	348.25	64.00		31.20	93.20
Knez 8	72.24	0.97	12.17	5.56	1.00	0.79	0.11	1.58	0.18	20.40	304.00	62.00		33.00	72.80
Knez 9	69.33	0.93	13.14	7.24	1.37	0.79	0.15	1.76	0.14	21.40	315.00	82.80		37.00	83.80
Knez 10	68.86	0.73	12.10	8.93	1.11	0.91	0.16	1.96	0.20	26.60	381.00	90.80		46.00	93.80
Knez 11	68.05	0.75	12.85	9.26	1.25	0.78	0.17	1.75	0.19	38.00	321.00	78.80	43.00	49.40	86.40
Knez 12	69.38	1.02	14.05	6.10	1.30	0.89	0.08	1.77	0.16	12.80	348.00	58.00		28.00	74.20
Knez 13	68.44	1.04	13.95	7.38	1.18	0.82	0.13	1.73	0.14	20.20	352.33	96.80	40.00	36.40	100.60
Knez 14	69.54	1.07	13.59	6.12	1.36	0.88	0.18	1.86	0.14	12.40	308.00	67.60		26.20	70.60
Knez 15	66.99	1.09	14.63	7.48	1.39	0.94	0.22	1.99	0.14	21.00	337.33	82.40		36.00	84.40
Knez 16	67.38	0.98	14.80	7.01	1.47	0.95	0.06	2.05	0.16	19.40	318.00	65.20		29.00	80.20
Knez 17	66.57	1.00	15.32	7.13	1.62	0.95	0.12	1.98	0.16	17.40	355.33	75.00	43.00	37.20	82.80
Knez 18	67.40	0.95	14.36	7.40	1.42	1.00	0.16	1.98	0.19	21.20	430.00	88.80	44.00	35.60	84.40
Ferricrete	40.49	0.10	8.38	**44.02**	1.71	0.62	0.96	1.11	0.83	58.80	313.33	195.00	49.33	b.d.l.	130.40

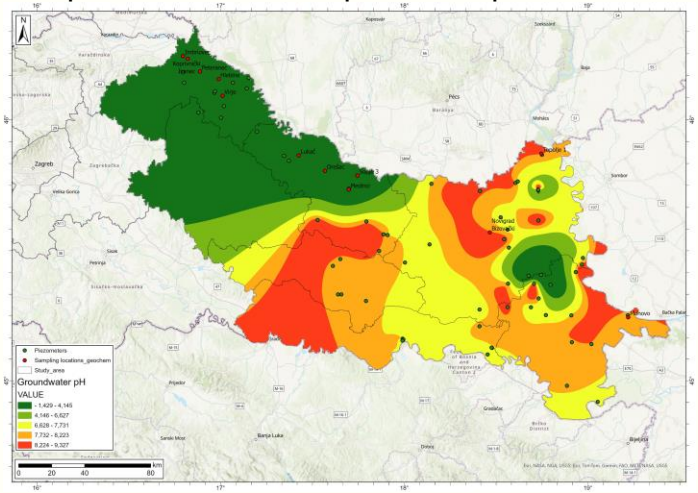
Results

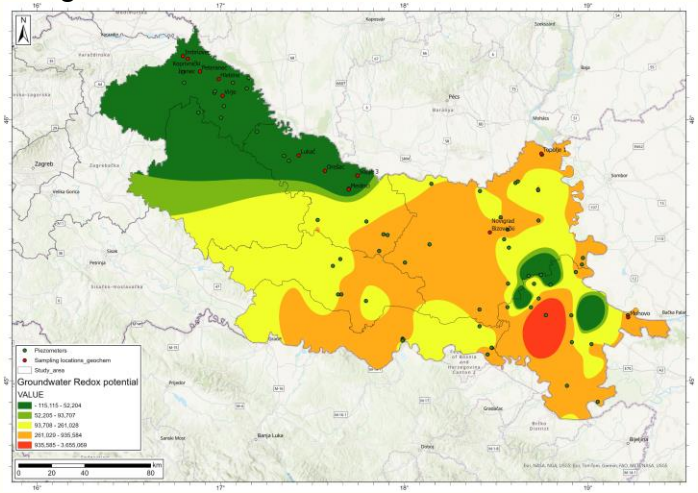
Table 2. Correlation matrix of soils and ferricrete from Knezovljani area with samples of secondary Fe accumulations in Pokuplje and Posavina regions

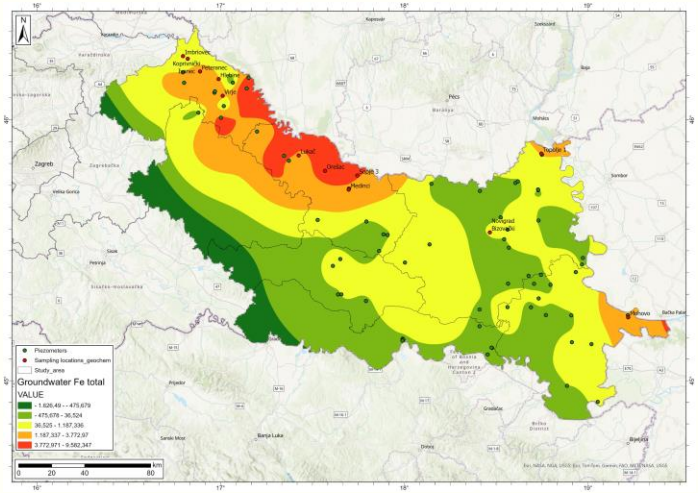
Variable	SiO2	TiO2	Al2O32	Fe2O3	MnO	P2O5	As	Ni	Cu	Pb	Zn
SiO2	1.00										
TiO2	0.41	1.00									
Al2O32	0.66	0.66	1.00								
Fe2O3	-0.92	-0.56	-0.79	1.00							
MnO	-0.32	0.11	-0.02	0.05	1.00						
P2O5	-0.40	-0.42	-0.55	0.52	-0.01	1.00					
As	-0.72	-0.28	-0.48	0.64	0.49	0.38	1.00				
Ni	-0.40	-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

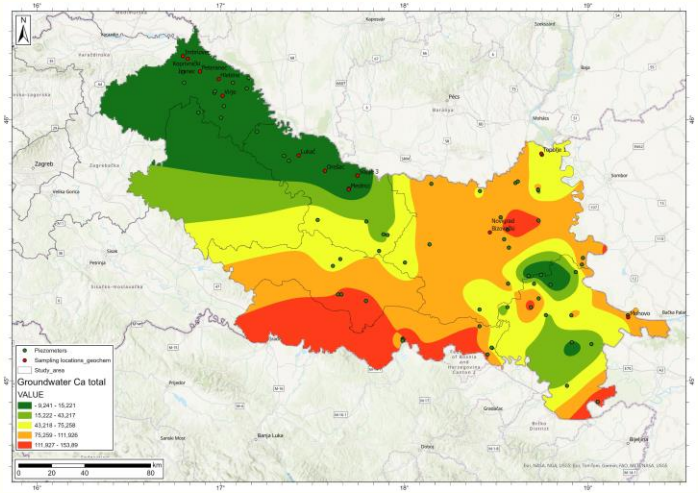
Results

Maps of distribution of pH, redox potential, Fe and Ca in groundwater in Podravina – eastern Croatia region



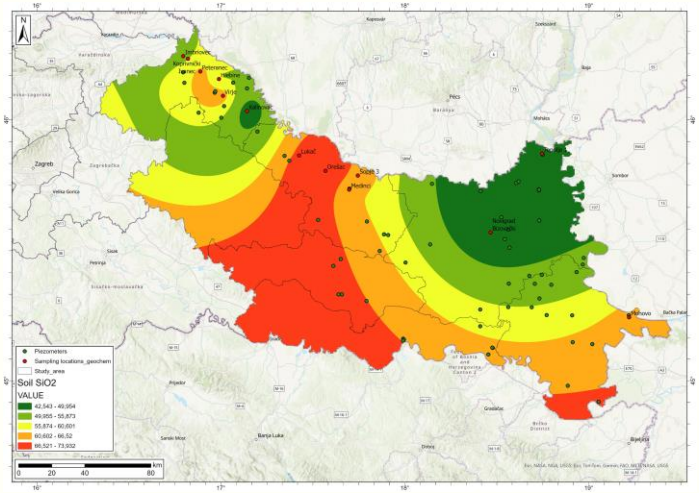


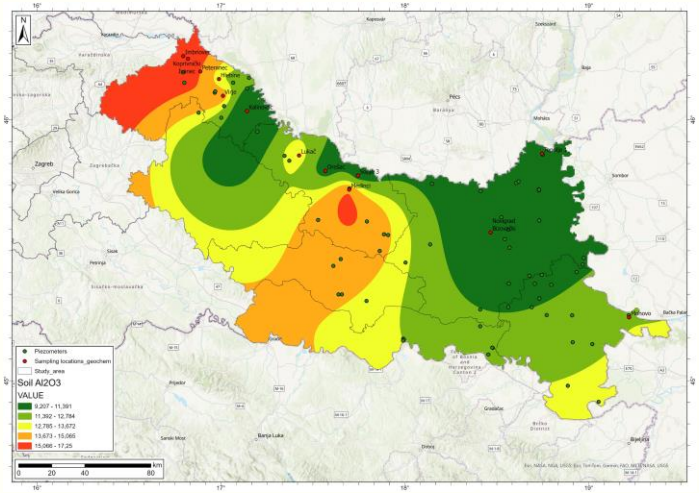


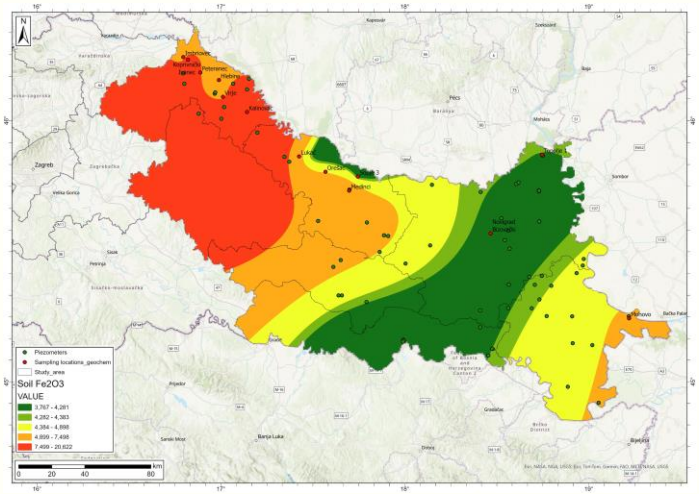


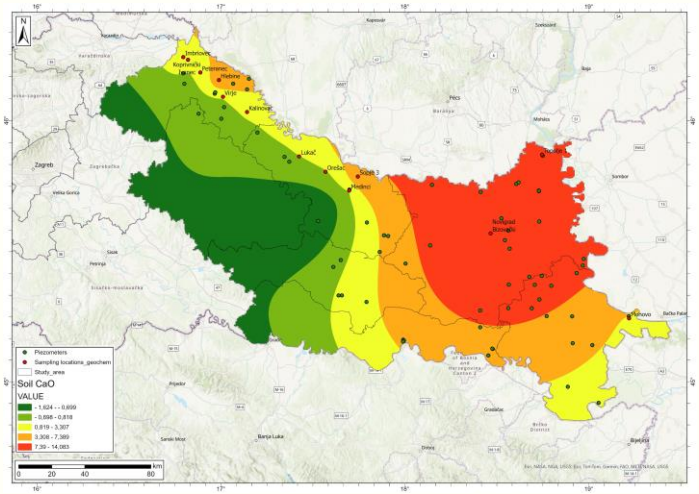
Results

Maps of distribution of SiO2, Fe2O3, Al2O3 and CaO in soils in Podravina – eastern Croatia region









Conclusions

- Knezovljani represents a small-scale, localized bog-iron–ferricrete accumulation that, despite limited lateral extent, rivals regional floodplain deposits in Fe_2O_3 content and trace-metal loading, demonstrating that hydrological focusing at slope breaks can produce ore-grade concentrations in foothill settings

- Laminated texture of the Knezovljani ferricrete records redox cycles driven by fluctuating perched water tables, contrasting with massive bog-iron ores in more stable floodplain environments and providing a temporal archive of groundwater dynamics

- The geochemical fingerprint, with high Fe_2O_3 an moderate-to-high As, Ni and Zn, low Mn, and distinctive phyllosilicate assemblage uniquely characterizes Pannonian bog-iron soils and links them unambiguously to weathering of siderite–ankerite–sulphide veins in Petrova/Trgovska Gora

Conclusions

- Integration of soil geochemistry, groundwater mapping and archaeological slag analysis can, hopefully, identify whether distinct ore-provenance fingerprints correlate with specific smelting sites, settlement clusters or production periods in the KulturFER study region

- Expanding bog-iron surveys to other foothill and colluvial settings where Pannonian fine-grained sediments overlie mineralised Dinaric basement may reveal a broader network of small, hydrologically focused iron-ore deposits that sustained pre-industrial ironworking communities

- Comparative analysis with Ljubija mining district and other Dinaric primary-ore sources will clarify how much of central Croatian iron production relied on local, secondary bog-iron resources versus upland ore imports, informing broader narratives of technological choice and regional exchange in medieval Europe

Thank You for your attention!

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