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Geochemical and mineralogical evidences for possible bog iron formation in Podravina region, NE Croatia

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TransFER

Table of content

Introduction

- TransFER project – geoarchaeological project

  ↳ Type of mineral resources, iron smelting methods

- Iron smelting in the Podravina region – over 150 locations with signs of iron smelting, slags and furnaces

- Type of used iron ore? → No iron ores on geological maps in Podravina?!

- Bog iron ore
  - sedimentary type of iron deposits
  - occurring in low-lying areas with groundwater table close to the surface
  - iron content 30–50 wt.% Fe (up to 90 wt. %)
  - fast formation and „regeneration" of deposits
  - currently no economical value; most used type of iron ore in the past
  - easy to locate and exploit

Archaeological field surveys

- main goal: locating smelting and smithing workshops → first extensive field survey started 20 years ago

- fragments of smelting furnaces, tuyers, smelting slag, iron objects, roasted iron ore

Figure 1. Furnace tuyers, smelting slag (photo: Tajana Sekelj Ivančan, IARH)

Main questions

- Several main questions:

1. What are the soil types, and what are their geochemical characteristics throughout the Podravina region?

2. What were the formation mechanisms for the formation of bog iron ore in the Podravina region?

3. Is (or was) the Podravina region suitable for the formation of the bog iron ore deposits?

Regional and local settings

Geology

- study area covers around 500 km^2
- large alluvial plain dominated by meandering Drava river
- presence of ponds, swamps, bogs and still waters

Pedology

- most common soil types include Gleysols and Fluvisols

Hydrology

- hydrological regime sometimes leading to flooding of the surrounding river terraces
- aquifer system enriched with Fe, As and Mn

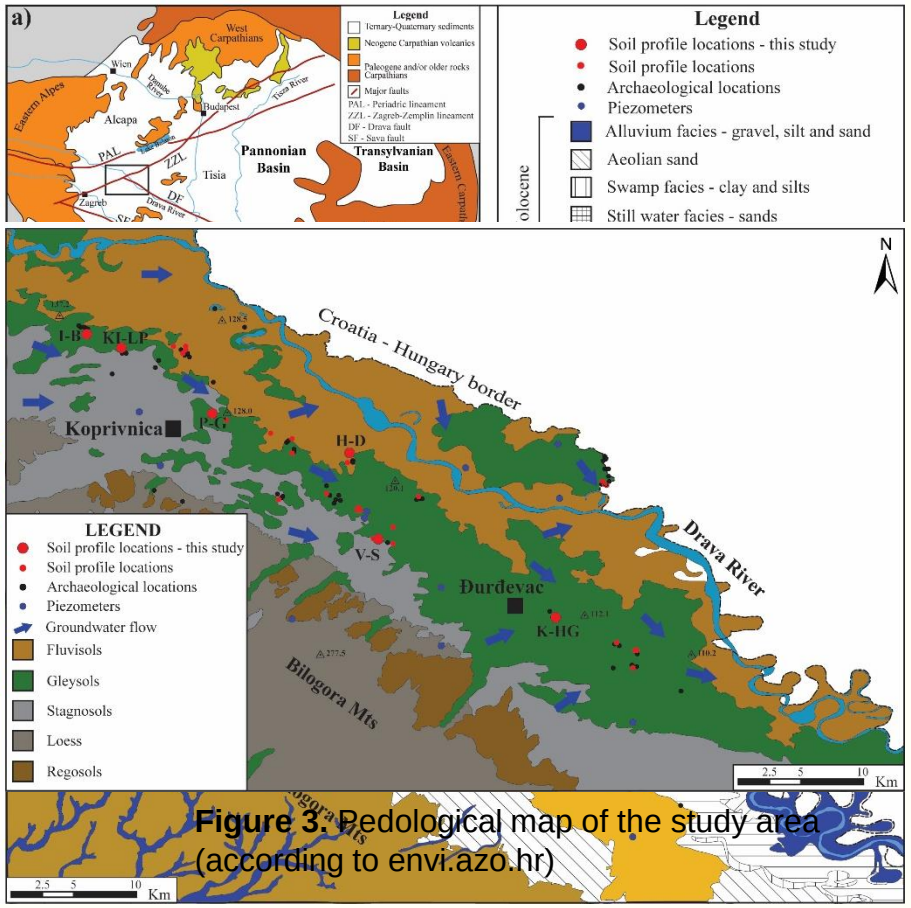


Figure 3. Pedological map of the study area (according to envi.azo.hr)

Figure 2. Geological map of the study area (according to Galović and Marković, 1979; Korolija and Crnko, 1985; Hećimović, 1986; Hećimović, 1995.)

Materials and methods

- soil sampling – Eijekelkamp auger set for soil
  - over 44 soil profiles
  - field determination and classification of soils
  - soil profiles divided into intervals and stored separately
  - six profiles chosen based on visible iron features – red and orange discolorations, iron linings and pore masses

Figure 4. Kalinovac – Hrastova greda 60-80 cm soil interval

Figure 5. Peteranec soil profile with visible iron discoloration

Materials and methods

Geochemical and mineralogical evidences...

- mineralogical composition
  - X-ray powder diffraction (XRD)
- geochemical composition
  - inductively coupled plasma mass spectrometry (ICP-MS)
  - major oxides, major, minor and trace elements
- textural analysis
  - soil texture using laser diffractometer (LS-13230)
- additional analyses
  - pH, electrical conductivity, carbonate content

Results

- 6 chosen soil profiles

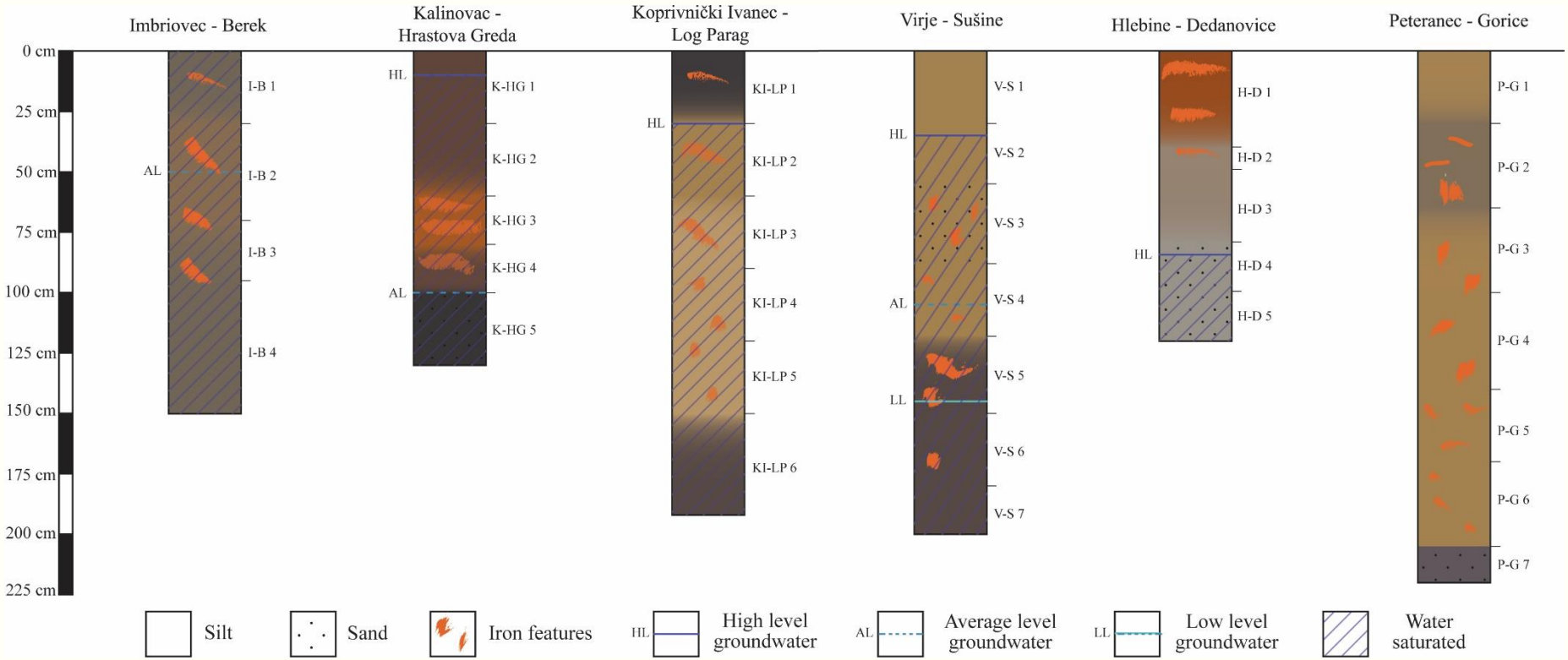


Figure 6. Schematic drawing of the six selected soil profiles with visible iron redoximorphic features and groundwater depths

Results

- mineral composition

Location	Sample ID	Depth (cm)	Qtz	Gt	Ms	CM	Pl	Or	Dol
Imbriovec - Berek	I-B 1	0 - 30	+++	-	+	+	+	+	-
	I-B 2	30 - 70	+++	?	+	+	+	?	-
	I-B 3	70 - 95	+++	+	+	+	+	?	-
	I-B 4	95 - 150	+++	-	+	+	+	?	+
Kalinovac - Hrastova Greda	K-HG 1	0 - 30	+++	+	+	+	+	-	-
	K-HG 2	30 - 60	++	+	++	+	++	-	-
	K-HG 3	60 - 80	++	+++	?	+	+	-	-
	K-HG 4	80 - 100	++	+++	?	+	+	-	-
	K-HG 5	100 - 130	+++	?	?	+	+	-	-
Koprivnički Ivanec - Log Parag	KI-LP 1	0 - 30	+++	+	+	+	+	-	-
	KI-LP 2	30 - 60	+++	+	+	+	+	+	-
	KI-LP 3	60 - 90	+++	-	+	+	+	+	-
	KI-LP 4	90 -120	+++	?	+	+	+	-	-
	KI-LP 5	120 - 150	+++	?	+	+	+	+	-
	KI-LP 6	150 - 192	+++	-	+		+	+	-

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

Location	Sample ID	Depth (cm)	Qtz	Gt	Ms	CM	Pl	Or	Dol
Virje - Sušine	V-S 1	0 - 30	+++	-	+	+	+	-	-
	V-S 2	30 - 55	+++	+	+	+	+	+	-
	V-S 3	55 - 88	+++	+	+	+	+	+	-
	V-S 4	88 - 118	+++	?	+	+	+	+	-
	V-S 5	118 - 150	+++	+	+	+	+	?	-
	V-S 6	150 - 180	+++	+	+	+	?	-	-
	V-S 7	180 - 200	+++	-	+	+	+	?	-
Hlebine - Dedanovice	H-D 1	0 - 40	+++	+	++	+	+	+	?
	H-D 2	40 - 50	+++	?	++	+	+	?	+
	H-D 3	50 - 80	+++	-	++	+	+	-	+
	H-D 4	80 - 100	+++	+	++	+	+	+	+
	H-D 5	100 - 120	+++	?	++	+	+	-	+
Peteranec - Gorice	P-G 1	0 - 30	+++	?	+	+	+	-	-
	P-G 2	30 - 65	+++	+	+	+	++	+	-
	P-G 3	65 - 100	+++	+	+	+	+	-	-
	P-G 4	100 -140	+++	+	+	+	+	+	-
	P-G 5	140 - 170	+++	?	+	+	+	+	-
	P-G 6	170 -205	++	-	+	+	+	+	+
	P-G 7	205 -220	+++	-	+	+	+	-	-

Table 1. Mineral composition based on XRD analysis for grain size <2 mm (Abbreviations: Qtz – quartz, Gt – goethite, Ms – muscovite, Pl – plagioclase, Or – orthoclase, Dol – dolomite, CM – clay minerals).

Results

- major oxides
- high Fe_2O_3 for all soils
- K-HG standing out
- high enrichment factors

Location	Depth (cm)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	K_2O	Na_2O	Cr_2O_3	SrO	BaO	P_2O_5	LOI	Total
I-B 1	0 - 30	46,88	0,82	18,63	**6,46**	2,06	0,05	1,43	2,3	0,79	0,02	0,02	0,07	0,22	20,13	99,88
I-B 2	30 - 70	56,44	0,94	17,15	**7,59**	2,31	0,07	1,67	2,65	1,39	0,02	0,02	0,07	0,26	9,33	99,91
I-B 3	70 - 95	56,03	0,93	16,5	**7,18**	3,03	0,07	3,33	2,7	1,52	0,02	0,02	0,06	0,21	9,2	100,8
I-B 4	95 - 150	60,69	0,98	14,82	**6,38**	2,61	0,07	2,65	2,38	1,59	0,01	0,02	0,06	0,18	7,66	100,1
K-HG 1	0 - 30	48,42	0,46	9,15	**17,77**	0,93	0,21	1,24	1,02	0,7	0,01	0,01	0,04	0,59	18,18	98,73
K-HG 2	30 - 60	44,59	0,47	10,18	**22,71**	1,1	0,27	1,39	1,09	0,64	0,01	0,01	0,05	0,72	17,96	101,19
K-HG 3	60 - 80	38,9	0,37	7,98	**31,52**	0,93	0,16	1,26	0,87	0,52	<0,01	0,01	0,04	1,02	17,48	101,05
K-HG 4	80 - 100	49,31	0,48	9,54	**20,53**	1,1	0,1	1,38	1,12	0,78	0,01	0,01	0,04	0,59	16,43	101,42
K-HG 5	100 - 130	57,68	0,54	9,57	**8,86**	1,07	0,07	1,46	1,22	1,06	0,03	0,01	0,04	0,22	18,97	100,8
KI-LP 1	0 - 30	47,45	0,85	17,42	**9,11**	1,91	0,37	1,43	2,18	0,8	0,02	0,02	0,08	0,3	19,47	101,41
KI-LP 2	30 - 60	54,49	0,96	15,35	**9,81**	1,61	0,7	1,2	2,26	1,19	0,01	0,02	0,1	0,38	11,42	99,5
KI-LP 3	60 - 90	61,31	1,05	15,3	**8,06**	1,54	0,24	1,18	2,32	1,47	0,01	0,02	0,07	0,31	8,51	101,39
KI-LP 4	90 -120	61,4	1,06	15,41	**7,82**	1,59	0,11	1,16	2,41	1,47	0,01	0,02	0,06	0,29	7,95	100,76
KI-LP 5	120 - 150	57,21	1	16,49	**7,03**	1,85	0,07	1,22	2,57	1,3	0,01	0,02	0,07	0,22	11,01	100,07
KI-LP 6	150 - 192	50,81	0,83	16,86	**6,89**	2,11	0,07	1,42	2,5	1,03	0,02	0,01	0,07	0,22	18,36	101,2
V-S 1	0 - 30	63,79	1,08	12,97	**5,68**	1,31	0,11	1,08	1,74	1,34	0,01	0,02	0,05	0,19	9,66	99,03
V-S 2	30 - 55	71,26	1,54	11,08	**5,99**	1,12	0,17	1,23	1,44	1,44	<0,01	0,02	0,04	0,17	4,12	99,62
V-S 3	55 - 88	72,78	1,86	9,48	**6,59**	1,01	0,19	1,3	1,11	1,25	<0,01	0,01	0,03	0,18	2,93	98,72
V-S 4	88 - 118	69,53	1,19	11,78	**5,82**	1,24	0,14	1,08	1,67	1,25	0,01	0,01	0,04	0,2	5,91	99,87
V-S 5	118 - 150	52,8	0,94	16,21	**10,53**	1,71	0,22	1,17	1,99	0,72	0,01	0,01	0,06	0,48	12,99	99,84
V-S 6	150 - 180	49,04	0,82	20,5	**8,38**	2,12	0,06	1,26	2,43	0,52	0,02	0,01	0,07	0,18	15,07	100,48
V-S 7	180 - 200	57,68	0,77	17,35	**6,23**	1,7	0,06	1,2	2,06	0,86	0,02	0,01	0,06	0,09	12,01	100,1
H-D 1	0 - 40	51,17	0,84	15,52	**10,9**	2,47	0,17	3,03	2,47	1,48	0,01	0,02	0,07	0,32	13,33	101,8
H-D 2	40 - 50	49,29	0,84	15,47	**7,00**	4,11	0,1	6,73	2,57	1,56	0,01	0,02	0,06	0,17	13,24	101,17
H-D 3	50 - 80	63,5	0,83	11,48	4,41	3,25	0,08	5,24	1,72	1,96	<0,01	0,02	0,04	0,16	8,22	100,91
H-D 4	80 - 100	64,61	0,84	10,5	3,97	3,1	0,09	6,07	1,57	1,86	<0,01	0,02	0,04	0,16	9	101,83
H-D 5	100 - 120	53,32	0,79	12,21	4,57	3,85	0,11	5,85	2	1,66	<0,01	0,02	0,05	0,14	17,08	101,65
P-G 1	0 - 30	50,11	0,94	17,62	**8,88**	1,51	0,14	0,95	2,28	0,71	0,02	0,01	0,06	0,29	16,35	99,87
P-G 2	30 - 65	53,16	0,92	18,33	**9,53**	1,69	0,13	1,18	2,27	0,93	0,02	0,02	0,06	0,22	13,05	101,51
P-G 3	65 - 100	58,02	0,95	16,42	**8,82**	1,53	0,1	1,17	2,16	1,15	0,02	0,02	0,05	0,21	9,82	100,44
P-G 4	100 -140	66,21	1,08	14,33	**7,43**	1,53	0,09	1,37	2,18	1,61	0,01	0,02	0,05	0,26	5,71	101,88
P-G 5	140 - 170	64,69	1,09	15,54	**6,54**	1,7	0,07	1,34	2,43	1,8	0,02	0,02	0,06	0,25	5,38	100,93
P-G 6	170 -205	63,75	1,04	14,16	**7,21**	2,25	0,08	2,12	2,27	1,79	0,02	0,02	0,05	0,26	6,12	101,14
P-G 7	205 -220	73,85	0,99	9,22	4,93	2,03	0,11	2,7	1,23	1,33	0,04	0,02	0,03	0,16	4,15	100,79

Table 2. Geochemical characteristics of selected soil profiles in the Podravina region

Results

- minor and trace element concentrations
- all selected soil profiles have similair parent material

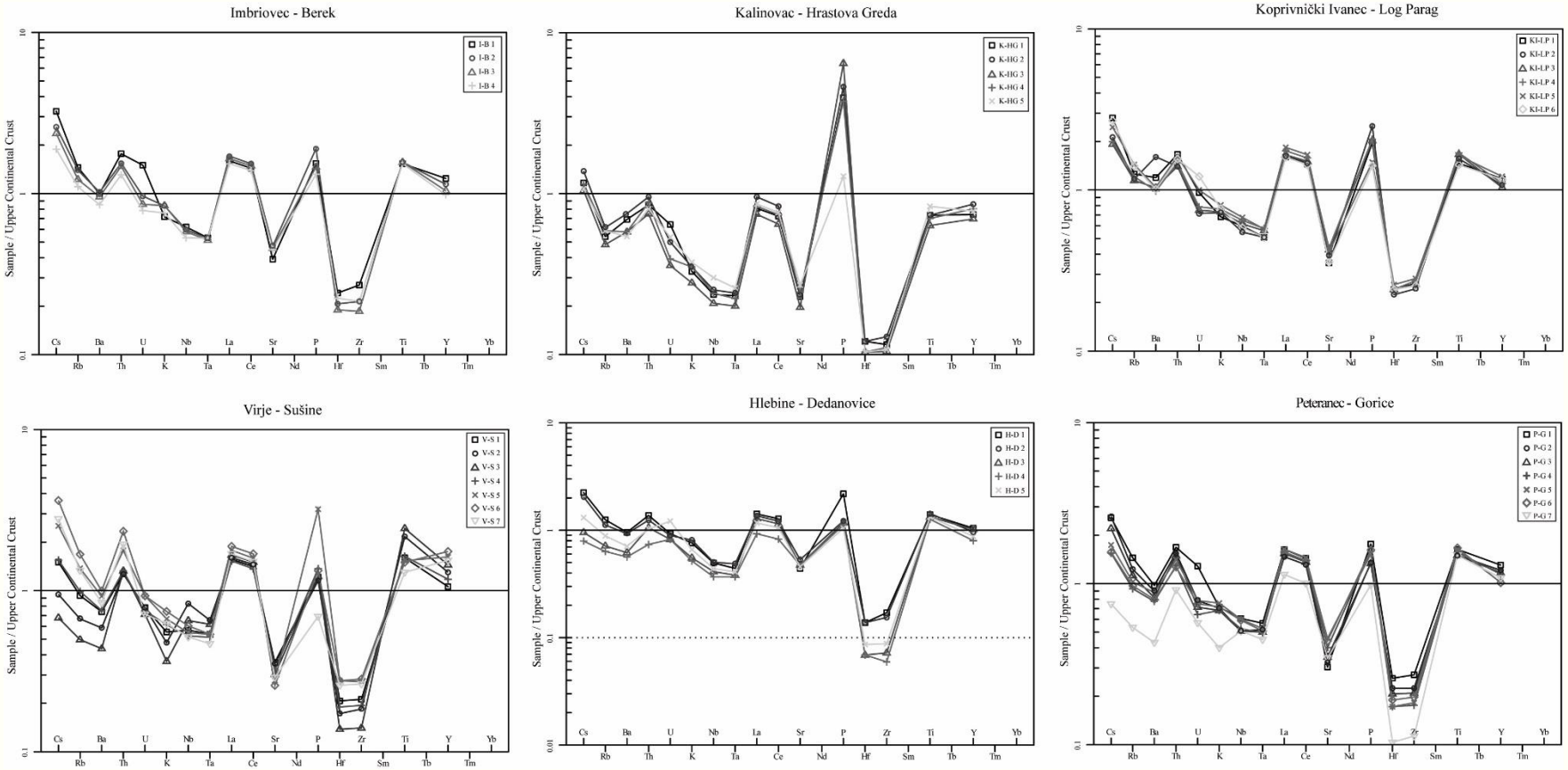
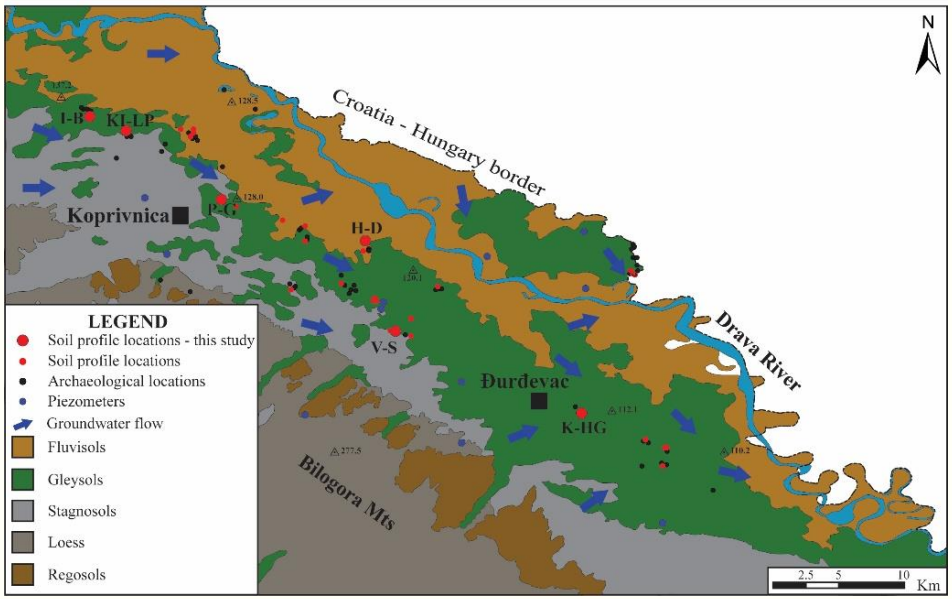


Figure 7. Spider diagrams for the six selected soil profiles (according to Taylor and McLennan, 1985).

Discussion

- archaeological surveys found significant number of primary iron processing and manufacturing locations
- only a few occurences of potentional bog iron ore
- main reasons:
  - land use throughout the history
  - previous mining actitivites
  - agricultural activities (melioration)
  - climate change



Discussion

- similair parent material, but different Fe enrichments
- different influences of groundwater in different locations

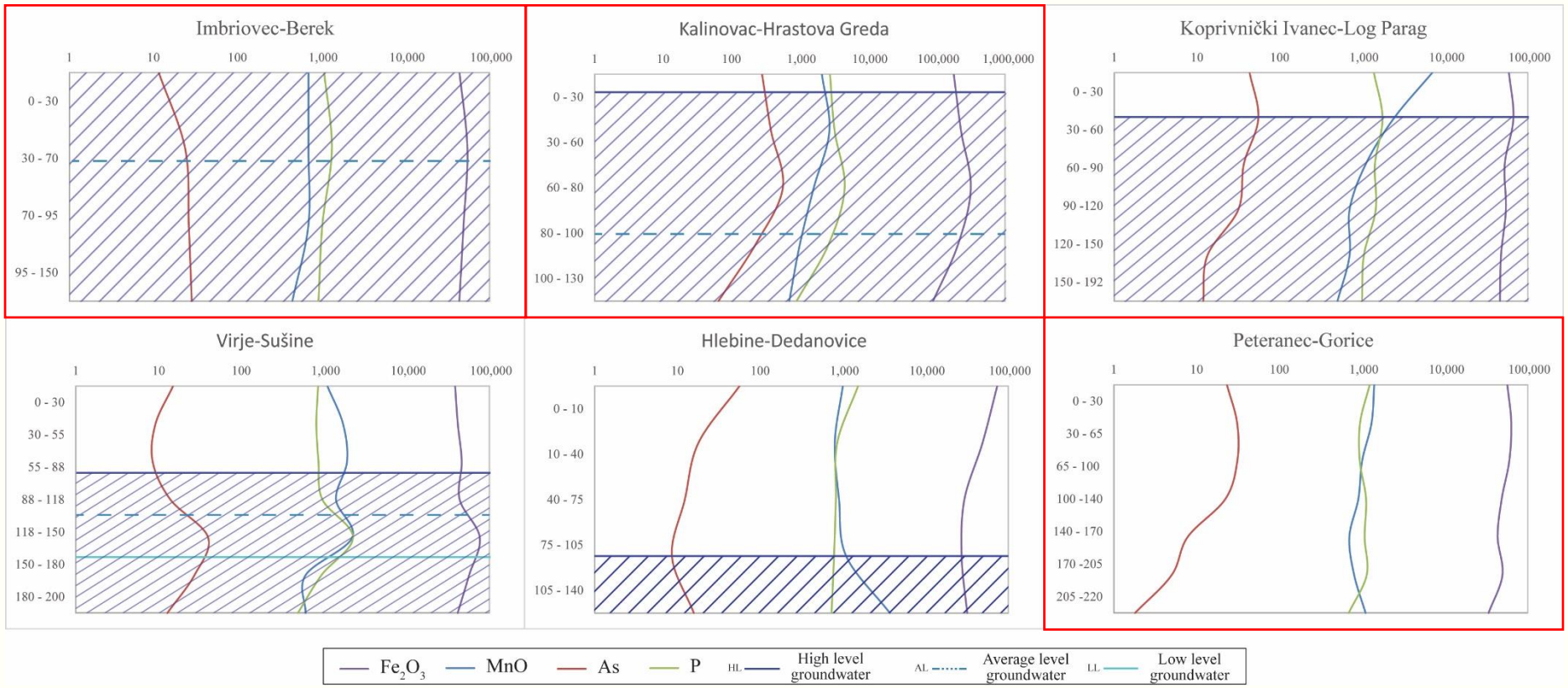


Figure 8. Correlation of groundwater depth to Fe_2O_3, MnO, As and P concentrations in the soil profiles.

Discussion

- Podravina region suitable for bog iron formation?

  - ✓ meandering Drava river
  - ✓ presence of oxbow lakes, swamps, bogs
  - ✓ close to the surface groundwater table
  - ✓ fluctuation of groundwater – interchanges of redox conditions
  - ✓ soils enriched with iron

Conlusions

- Podravina region suitable for bog iron formation
- large number of archaeological findings indicate extensive iron processing in the area
- 6 selected soil profiles; 5 Gleysols and 1 Fluvisol
- visible signs of Fe accumulation
- groundwater fluctuations as main formation mechanism
- high probability of current bog iron formation in Kalinovac-Hrastova greda

Thank You for your attention!
Questions, comments?

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