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University of Zagreb
FACULTY OF MINING, GEOLOGY AND PETROLEUM ENGINEERING

The mineralogical and geochemical composition of different bog iron ore types from the Podravina region, NE Croatia

Secrets of iron – from raw material to an iron object

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Introduction

- TransFER project – geoarchaeological project
- Defining type of iron ore, smelting and smithing processes and influence on identity and dinamics of socio-cultural relations from Late Antiquity to Middle Ages

  ↳ Type of mineral resources, iron smelting methods

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

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

Introduction

- Archaeological surveys for the past 30 years
- Numerous archaeological localities of Antique and Middle Ages
- Iron slags, iron furnaces, iron workshops
- geophysical magnetometric explorations – *in-situ* furnace

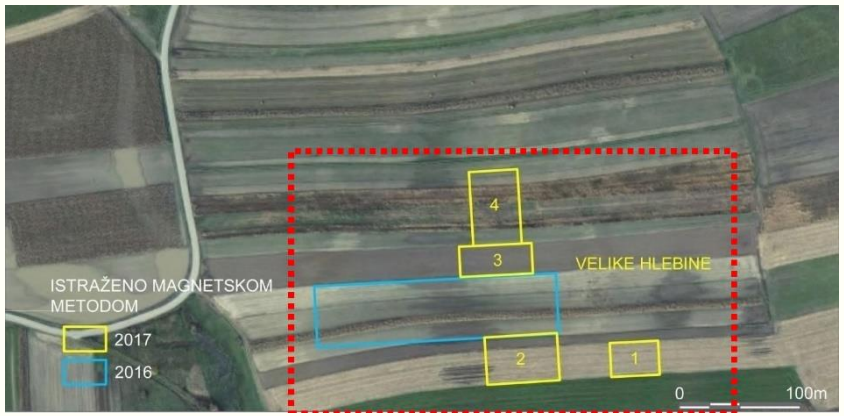

Figure 2. Hlebine – Velike Hlebine aerial photography

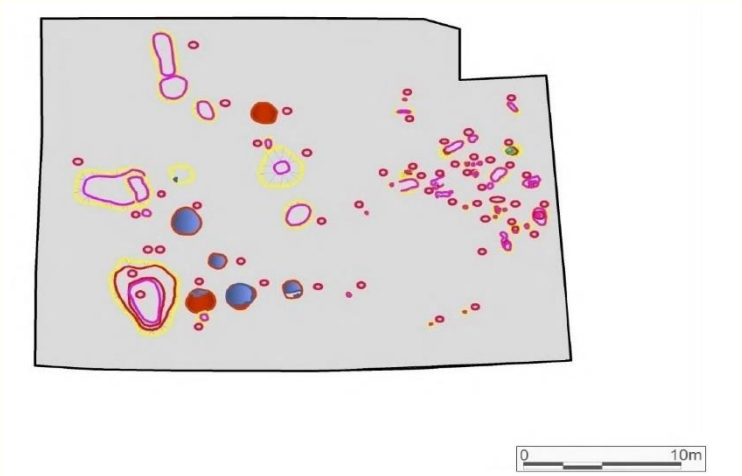

Figure 3. Hlebine – Velike Hlebine geophysical surveys

Introduction

- 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_2O_3 (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

Figure 4. Bog iron ore found close to soil surface (image taken from: https://www.haraldthesmith.com/wp-content/uploads/2018/02/OreHeader.jpg

Figure 5. Bog iron ore collecting (image taken from: https://scienceforums.net/topic-80008)

Overview of previous studies

- 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

Brenko et al. (2020): Evidence for the formation of bog iron ores in the soils of the Podravina region, NE Croatia: Geochemical and mineralogical study. Quat. Int. 536, 13–29. https://doi.org/10.1016/j.quaint.2019.11.033

Regional and local settings

Geology

- study area covers around 500 km^2
- large alluvial plain dominated by the 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

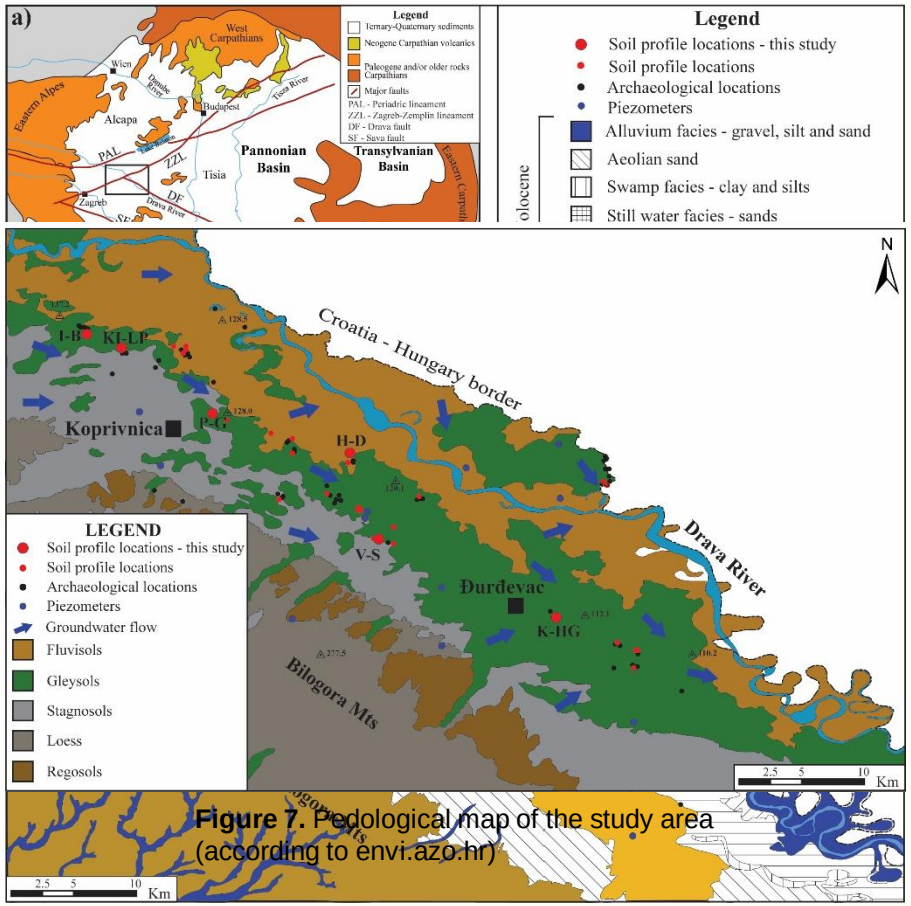

Figure 7. Pedological map of the study area (according to envi.azo.hr)

Figure 6. Geological map of the study area (according to Galović and Marković, 1979; Korolija and Crnko, 1985; Hećimović, 1986; Hećimović, 1995.)

Materials and methods

Geological and archaeological sampling:

- Soil samples
  - vertical soil profiles using auger
  - depth of profiles 1–3.5 m
  - signs of Fe enrichment
- Nodule samples
  - surface and subsurface nodule samples
  - found in soils
  - three locations
- Fragment samples
  - surface finds in soils (geological surveys)
  - subsurface finds (archaeological surveys)
  - found in several locations

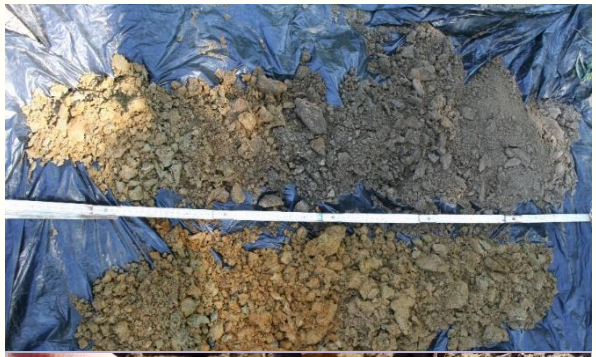

Figure 8. Bog iron soils.

Figure 9. Bog iron nodules

Figure 10. Bog iron fragments

Materials and methods

The mineralogical and geochemical composition...

- mineralogical composition
  - three different bog iron types
  - X-ray powder diffraction (XRD)
  - scanning electron microscopy with EDS detector (SEM-EDS)

- geochemical composition
  - inductively coupled plasma mass spectrometry (ICP-MS)
  - major oxides; major, minor and trace elements; rare earth elements
  - scanning electron microscopy with EDS detector (SEM-EDS)

- additional analyses
  - soil texture, soil parameters (pH and EC)

Results

Mineral composition - XRD

- dominant phases are quartz and goethite
- lowest goethite and highest quartz amounts in soils
- vice-versa in fragments

- variable clay contents

- pyrolusite (Mn-mineral) notted in fragments from Novigrad Podravski location

Table 1. Mineral composition of different bog iron ore types from geological and archaeological surveys. Mineral abbreviations: AM – amorphous matter; Cal – calcite; CM – clay minerals; Gt – goethite; Or – orthoclase; Pl – plagioclase; Pyr – pyrolusite; Qtz – quartz.

Sample	Location	Bog iron ore type	Qtz	Gt	Pl	Or	Pyr	Cal	CM	AM
K-HG 1	Kalinovac–Hrastova greda	Nodules	+++	+	+	+			+	
K-HG 2		Soil	+++	+	+				+	
K-HG 3		Soil	++	++	+				?	
NP-MB 16	Novigrad Podravski–Milakov Berek	Fragments	+	+++	+		+	++		++
NP-MB 17		Fragments	++	++	+		+		+	+
NP-MB 18		Fragments	+	+++			?			++
D-BG	Draganci–Bokčev grob	Nodules	+++	+	+	+			+	
P-C	Peteranec–Ciglene	Nodules	+++	+	+				++	
M-T	Molve–Topolovo	Soil	+++	+	+	+			++	
V-VB 1	Virje–Volarski Breg	Fragments	++	++	+					?
V-VB 2		Fragments	++	++	+					?
V-VB 3		Fragments	++	++						?
V-S 1	Virje–Sušine	Fragments	+	+++	+					
KI-LP 1	Koprivnički Ivanec–Log Parag	Fragments	++	++	+				+	+
KR-R	Koprivnička Reka–Rudina	Fragments	++	++						

Results

SEM-EDS

- soil minerals interlaminated with Fe- and Mn-rich layers (cementation)
- clear visible distinction between the phases
- goethite in the form of micro-crystalline aggregates
- recognizable Mn-phases in bog iron fragments
- appearance of pyrolusite

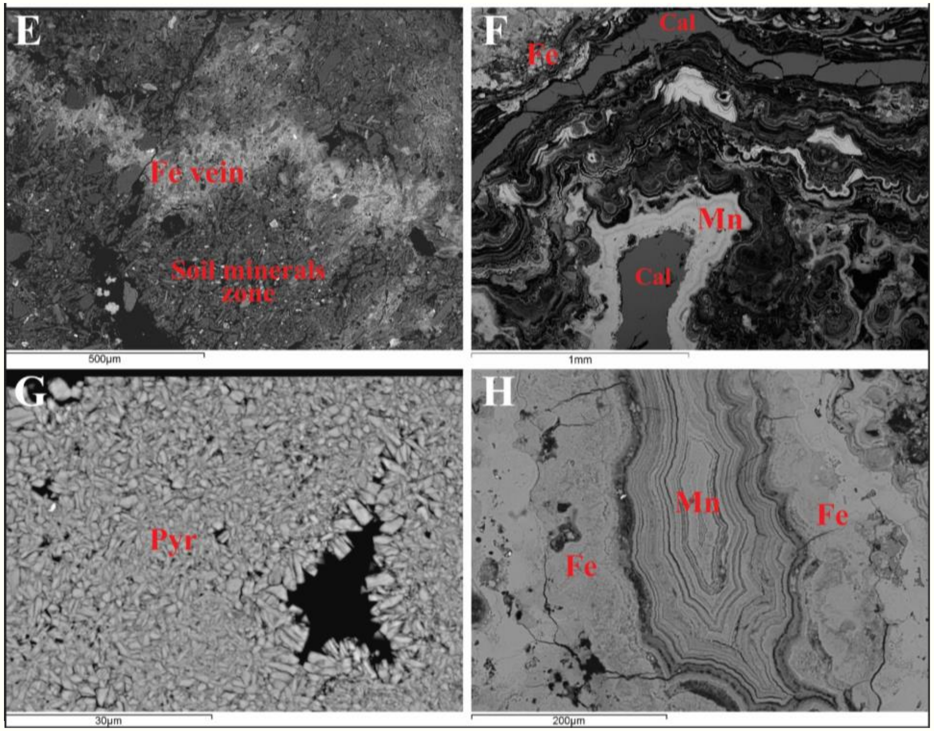

Figure 12. Mineralogy and internal microtextures of the bog iron nodules and fragments (backscattered electron images). (E) Soil minerals zone with Fe oxides in the form of vein (light gray) in the matrix part of one KUL-P 1 fragments. (F) Highly Mn laminated zone with post-depositional carbonate veins (Cal) in Novigrad-Podravski NP-MB 16 fragment sample. (G) Mineralization of Mn oxides in the form of pyrolusite in the bog iron fragments from Novigrad-Podravski location. (H) Different Fe and highly laminated Mn zone, surrounded by microcrystalline goethite (Gt) in NP-MB 18 fragment

Results

Geochemical composition – ICP-MS

Table 2. Geochemical composition of bog iron ore samples in the Podravina region. Concentration in mass. %

Sample	Location	Bog iron ore type	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	MnO	CaO	K_2O	Na_2O	P_2O_5	BaO	SrO	LOI	TIC	TOC	Total
K-HG 1	Kalinovac–Hrastova greda	Nodules	38.46	0.32	5.67	36.02	0.47	2.89	0.72	0.72	0.69	0.54	0.30	0.01	11.49	0.03	0.61	98.30
K-HG 2		Soil	63.38	0.44	7.34	14.43	0.67	0.10	0.83	0.92	0.97	0.38	0.03	<0.01	9.03	0.04	0.64	98.52
K-HG 3		Soil	50.75	0.38	6.82	27.93	0.68	0.31	0.83	0.85	0.90	0.31	0.04	<0.01	9.27	0.04	0.66	99.07
NP-MB 16	Novigrad Podravski–Milakov Berek	Fragment	8.69	0.06	2.50	32.03	0.70	21.04	5.67	0.42	0.44	0.62	0.76	0.15	21.39	0.81	0.51	94.47
NP-MB 17		Fragment	10.98	0.07	3.25	45.35	0.48	14.85	1.18	0.45	0.36	0.70	0.74	0.09	15.95	0.03	0.43	94.45
NP-MB 18		Fragment	3.59	0.01	0.57	68.41	0.16	5.68	0.62	0.12	0.08	1.00	0.12	0.02	15.14	0.03	0.41	95.52
D-BG	Draganci–Bokčev grob	Nodules	27.06	0.39	7.29	39.54	0.76	4.32	1.04	0.94	0.74	1.86	0.24	0.01	15.31	0.03	1.62	99.50
P-C	Peteranec–Ciglene	Nodules	44.10	0.76	12.24	22.99	0.95	0.57	0.78	1.76	0.96	1.87	0.08	0.01	11.29	0.05	1.02	98.36
M-T	Molve–Topolovo	Soil	57.92	0.68	12.35	13.20	1.18	0.10	1.14	1.33	1.04	0.28	0.04	0.01	9.52	0.05	1.24	98.79
V-VB 1	Virje–Volarski Breg	Fragment	24.16	0.30	8.72	37.28	0.59	5.25	0.97	0.86	0.34	0.24	0.15	<0.01	15.45	0.04	0.46	94.31
V-VB 2		Fragment	30.67	0.37	8.58	38.94	0.59	1.59	0.72	0.90	0.46	0.66	0.07	<0.01	13.29	0.04	0.43	96.84
V-VB 3		Fragment	25.92	0.29	7.52	46.86	0.48	1.69	0.60	0.80	0.34	0.45	0.06	<0.01	13.43	0.03	0.42	98.44
V-S 1	Virje–Sušine	Fragment	10.12	0.03	1.90	70.89	0.14	0.98	0.34	0.30	0.13	0.49	0.09	<0.01	11.91	0.04	0.6	97.32
KI-LP 1	Koprivnički Ivanec–Log Parag	Fragment	16.67	0.12	4.53	49.45	0.65	3.13	1.27	0.79	0.42	1.90	0.19	0.01	16.02	0.02	0.48	95.15
KR-R	Koprivnička Reka–Rudina	Fragment	29.09	0.45	5.99	45.82	0.83	0.04	1.28	1.07	0.27	0.28	0.02	<0.01	10.57	*	*	95.71

Results

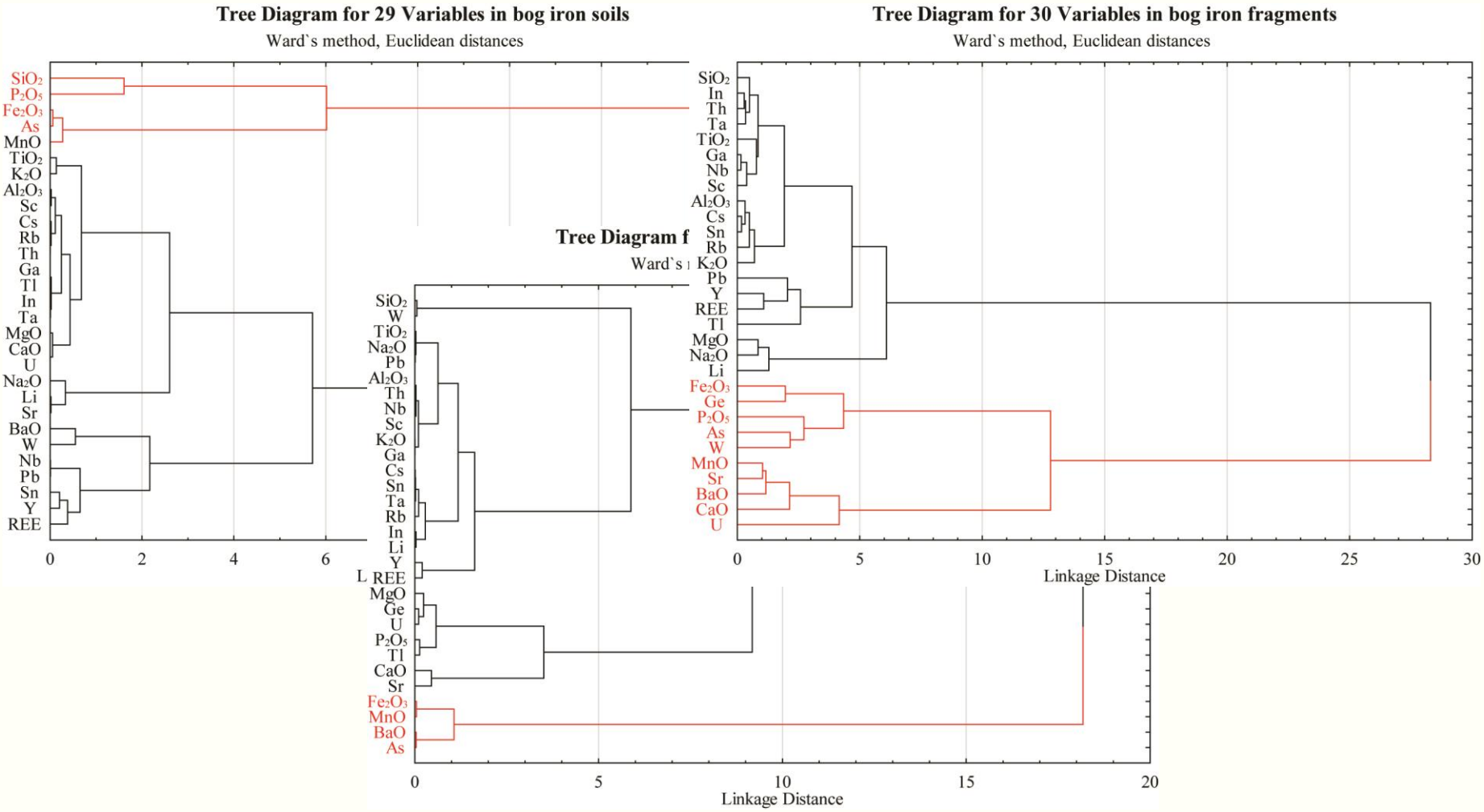

Figure 13. Hierarchical cluster analysis of a) bog iron soils, b) bog iron nodules and c) bog iron fragments

Discussion

Occurences of bog iron ore in the Podravina region

- archaeological surveys found significant number of iron workshops
- bog iron occurrences are located on the Drava River alluvial terrace
- only a few occurences of the potentional bog iron ore

- probable reasons:
  - land use throughout the history
  - previous mining actitivites
  - agricultural activities (melioration)
  - climate change

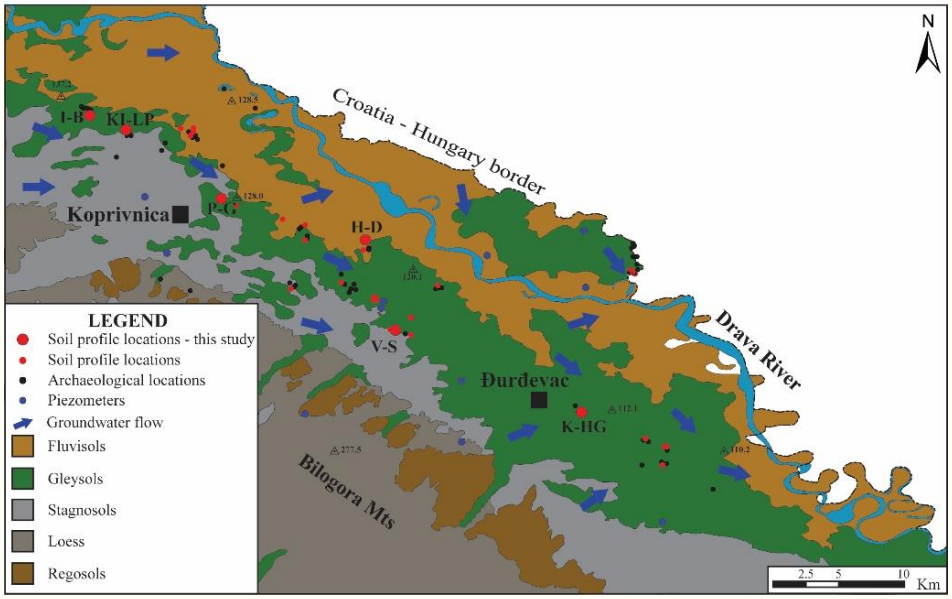

Figure 7. Pedological map of the study area (according to envi.azo.hr)

Discussion

Formation mechanisms and phases

- three stages of bog iron formation based on SiO_2 and Fe_2O_3 contents

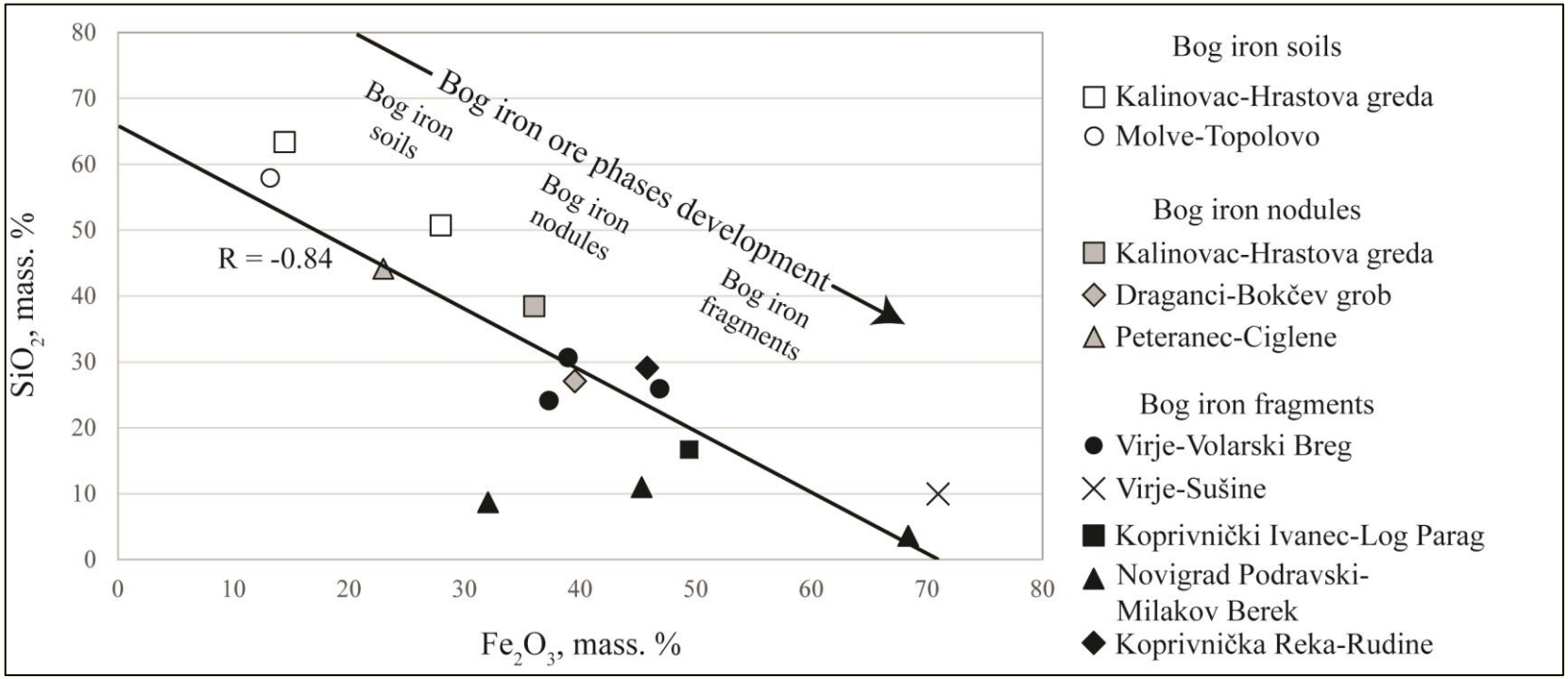

Figure 14. Total least square regression model of iron and silicon oxide contents in the bog iron ores with visible grouping of different bog iron ore types

- different bog iron ore evolution?

Discussion

Usage as iron ore?

- empirical boundary 79–86 wt. % Fe_2O_3 (Pleiner, 2000)
- experimental direct iron smelting in the last decades (Crew, 1991, 2011; Thiele, 2010)
- lower iron contents of up to 49 wt. % Fe_2O_3 are usable for smelting
- fragments were used for iron smelting
- soils and nodules usage?

Conclusions

- sparse, yet occurring bog iron ore in the study area
- three different bog iron types were recognized
- formation from fluctuating groundwater
- differentiation based on mineral and geochemical characteristics
- locally different Eh/pH conditions
- bog iron fragments in the Podravina region usable for iron smelting

Literature

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Thank You for your attention!

Questions, comments, suggestions

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