Mineralogical and geochemical characteristics of ore for possible iron production in Podravina region, NE Croatia

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7.12.2018.
Zagreb, Croatia

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Introduction

- 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

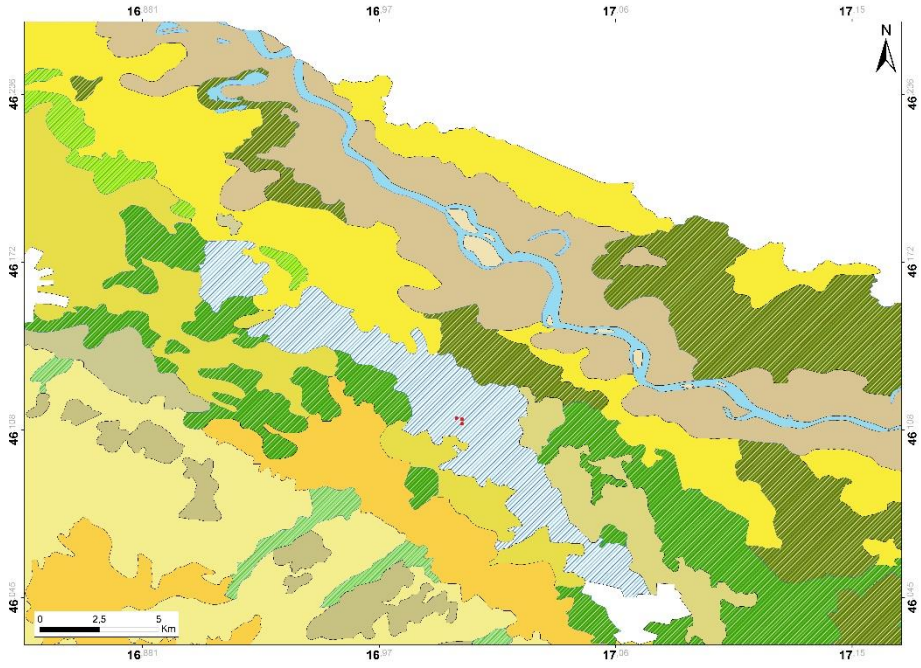
- Podravina region recognized for iron smelting and iron production – over 120 possible remains of smelting furnaces

- Archeological sites Virje–Volarski Breg, Virje–Sušine and Hlebine–Velike Hlebine

- <u>Bog iron ore as main source of iron ore?</u>

Study area

- Large alluvial plain dominated by meandering Drava River and its tributaries
- Several abandoned riverbeds, some of them still containing water, forming still waters and pond areas
- Two main pedological units: Fluvisols and Gleysols
- Agricultural area located between Molve and Virje



Samples and methods

- Mineral composition of samples was investigated using X-ray diffraction (XRD)
- Geochemical analysis of samples was obtained using inductively coupled plasma mass spectroscopy (ICP-MS) and atomic absorption spectroscopy (AAS)
- Additional geochemical, mineralogical and morphological data were obtained using scanning electron microscopy with adjoining energy dispersive X-ray spectroscopy (SEM-EDS)
- 3 samples representing potential bog iron ore

NP-MB 16

- found during pipeline construction at depth of 2 meters
- weighing over 2 kilograms
- visible different phases

NP-MB 17

- found at the surface during geological studies
- 10 centimeters in diameter
- visible two main phases; black and orange

NP-MB 18

- found at the surface of agricultural field
- different sizes and shapes
- again different phases
- total weight of samples over 500 grams

Results

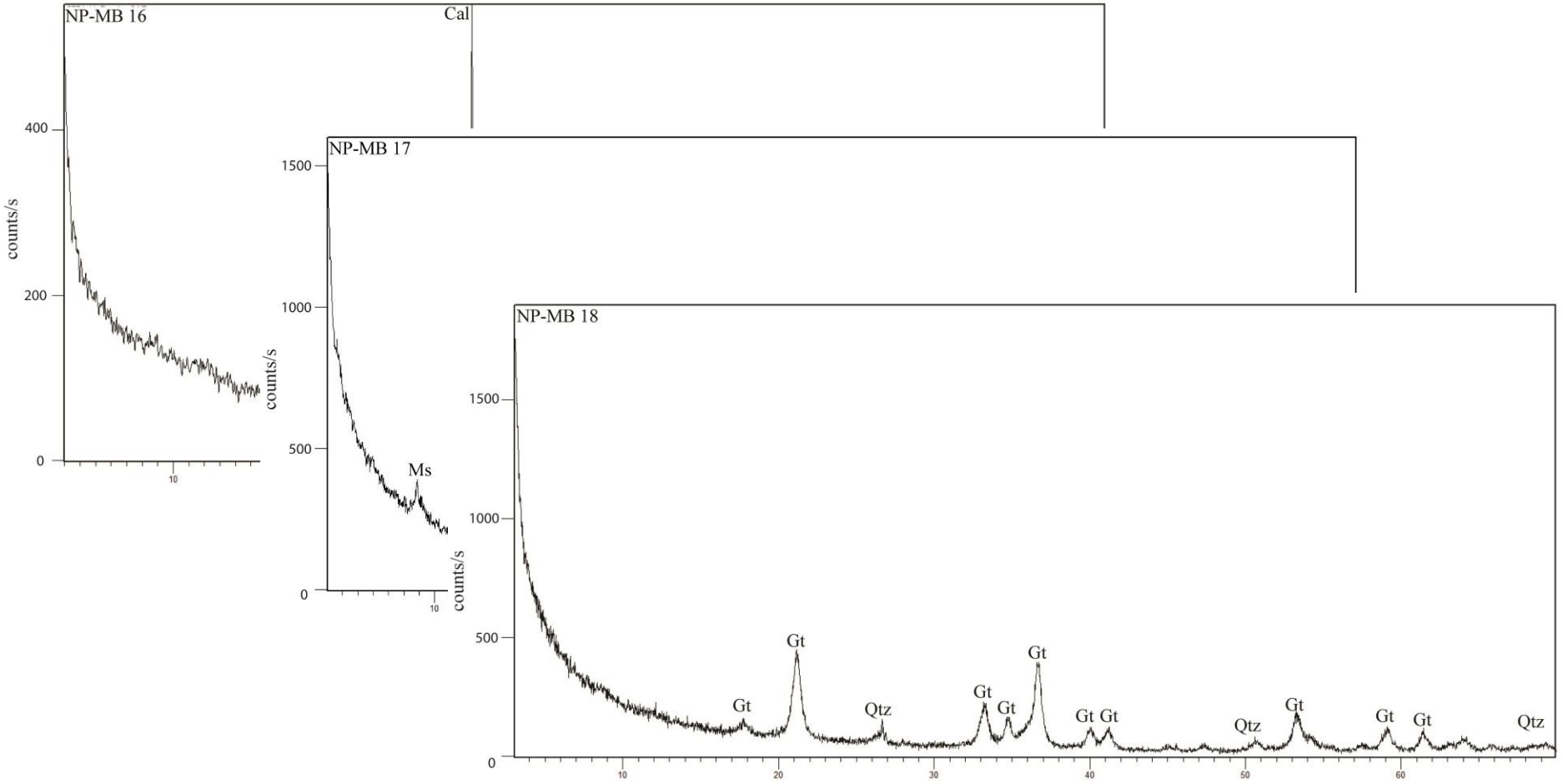
X-ray diffraction

Table 1. Mineral composition of potential bog iron samples. (Abbreviations: Gt – goethite, Qtz – quartz, Ms – muscovite, Pl – plagioclase, Pyr – pyrolusite, Cal – calcite, AM – amorphic matter)

Sample	Gt	Qtz	Ms	Pl	Pyr	Cal	AM
NP-MB 16	+++	+++	-	+	-	++	+
NP-MB 17	+++	+++	+	+	+	-	?
NP-MB 18	++++	+	-	-	-	-	?

Results

X-ray diffraction



Results

Geochemistry

Table 1. Major elements concentration, wt. %

Location	Sample	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
Novigrad Podravski - Milakov Berak	NP-MB 16	9.05	0.1	2.25	39.06	0.63	19.17	7.21	0.36	0.2	<0,01	0.14	0.84	0.67
	NP-MB 17	9.4	0.08	2.6	37.86	0.61	27.42	1.63	0.38	0.22	<0,01	0.2	1.23	0.5

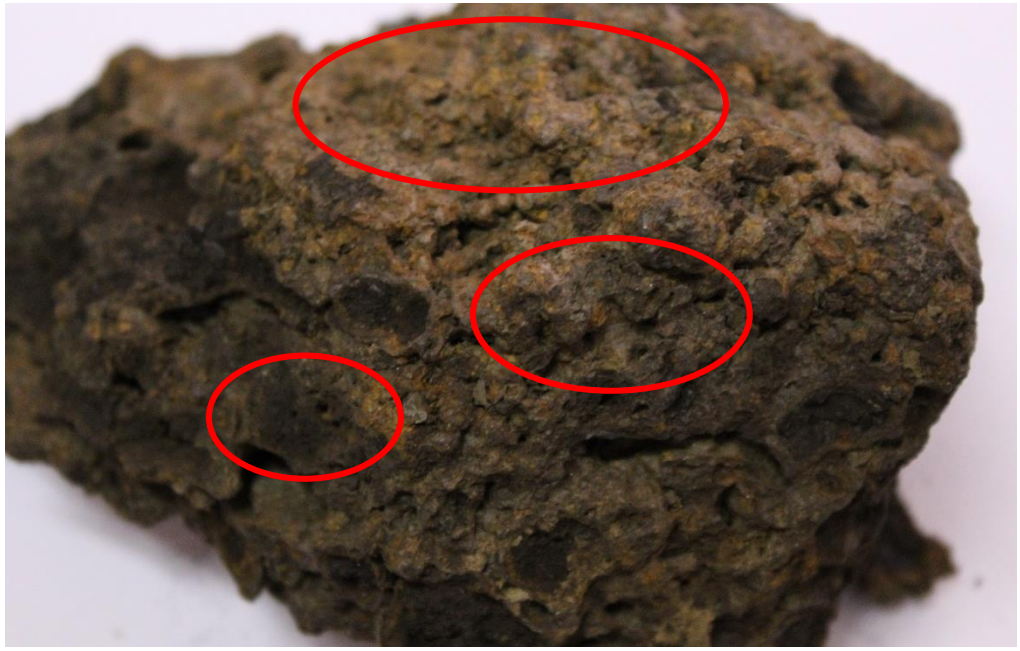
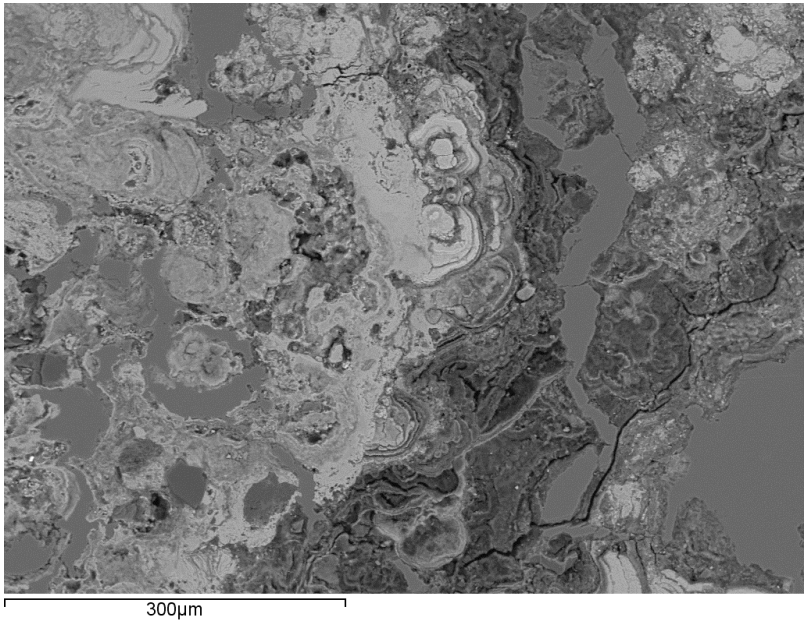
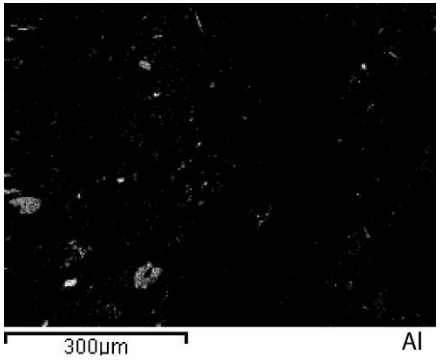


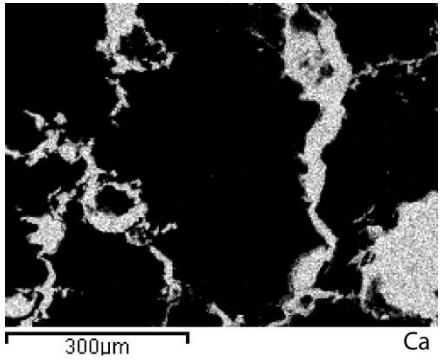
Table 2. Iron concentration in different parts of sample NP-MB 16

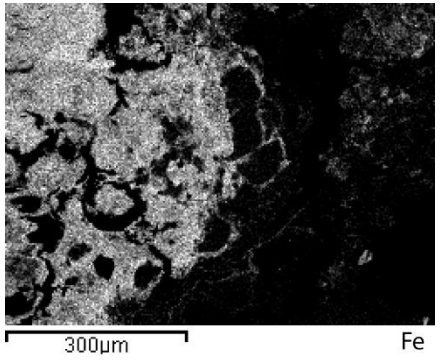
Sample	Sample part	Fe, wt. %
NP-MB 16	whole sample	40.09
	dark black section	32.02
	brown section	45.71
	grayish section	28.55

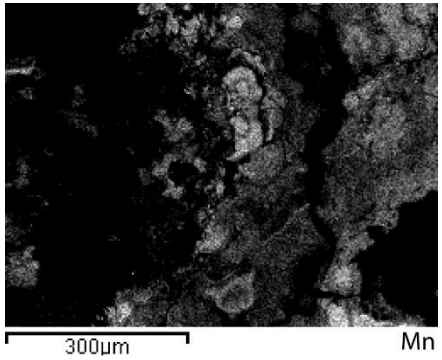
Scanning electron microscopy

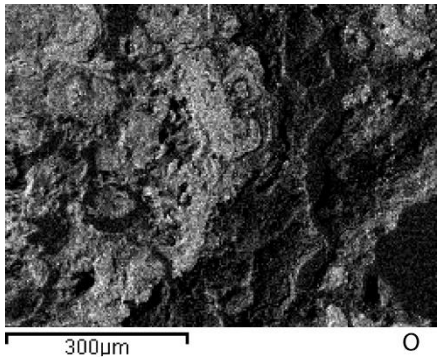


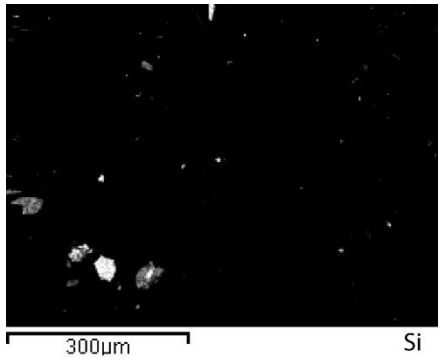








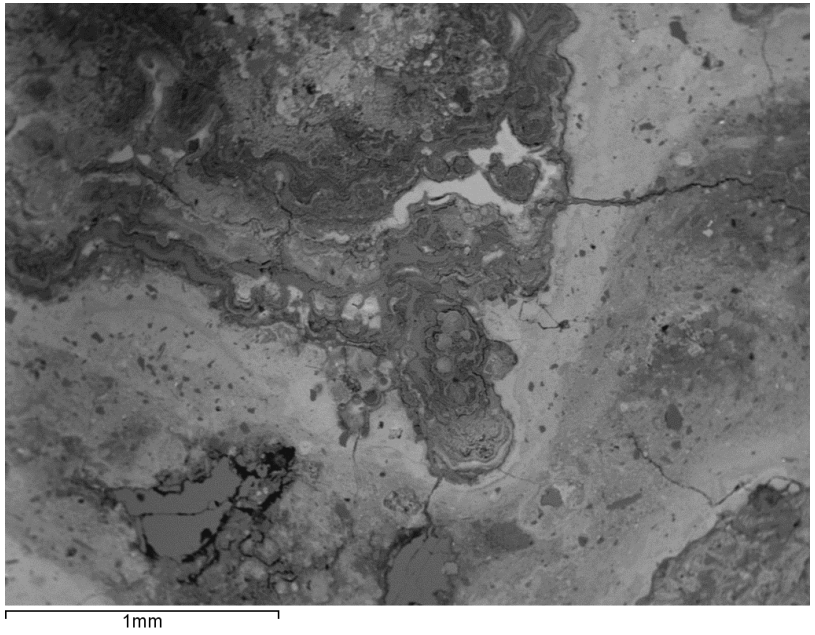


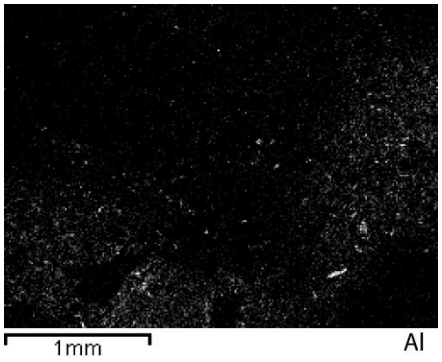


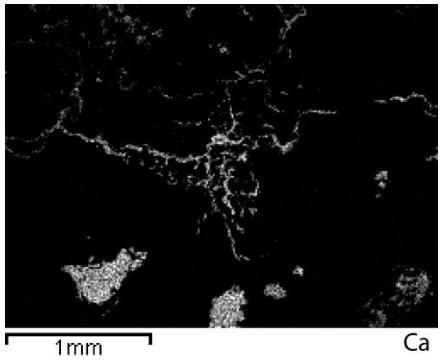
NP-MB 16

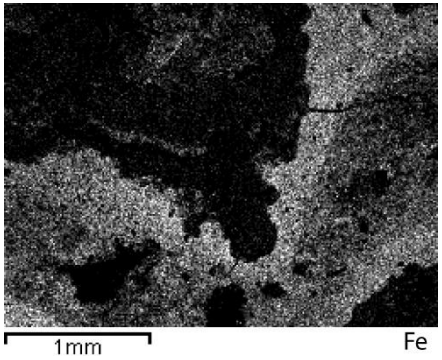
Site of interest 2

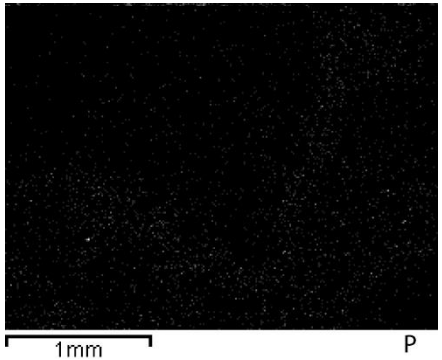
	Al	Ca	Fe	Mn	O	Si	Total
wt. %	0.78	10.25	21.62	16.47	47.20	1.85	98.17

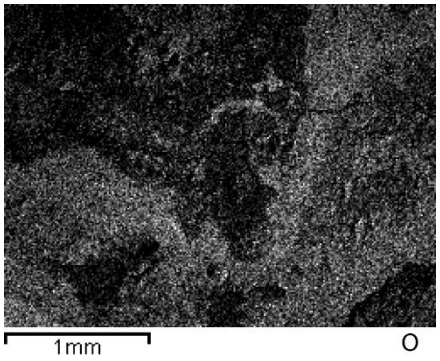


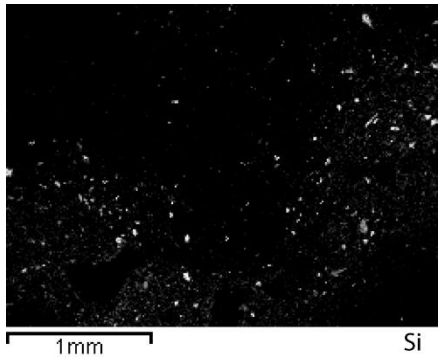








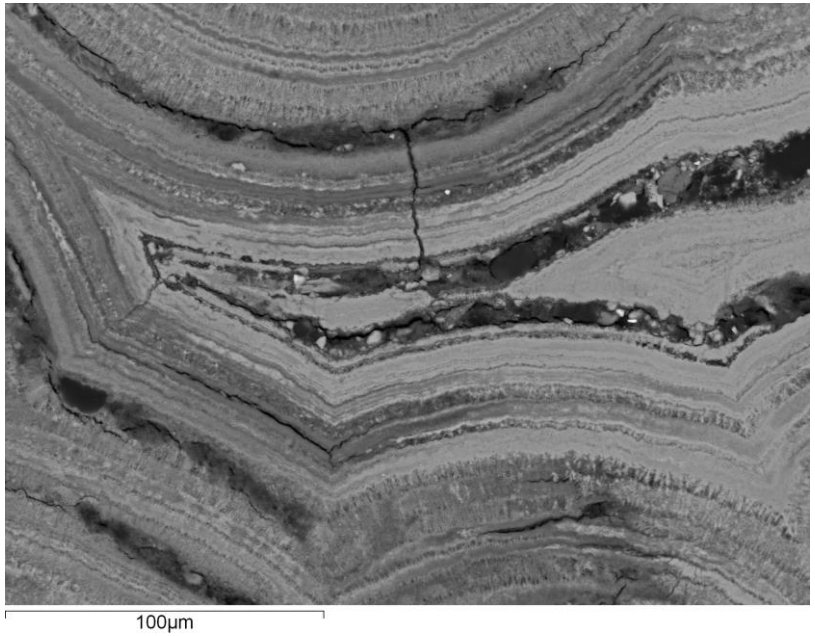


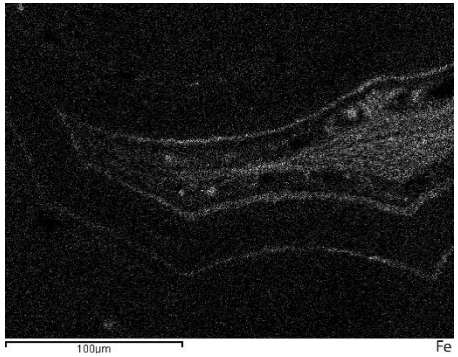


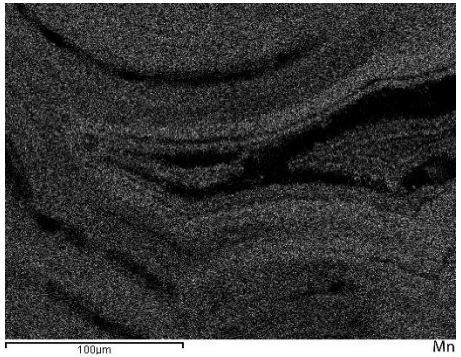
NP-MB 16

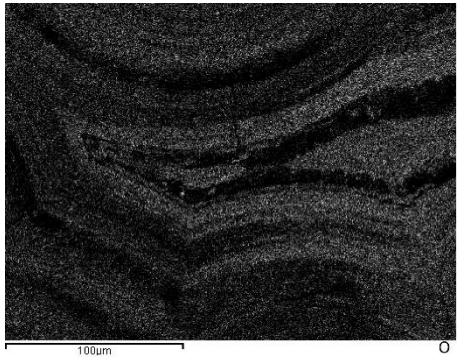
Site of interest 4

	Al	Ca	Fe	Mn	O	Si	Total
wt. %	2.27	4.70	26.74	13.53	44.48	4.88	96.6







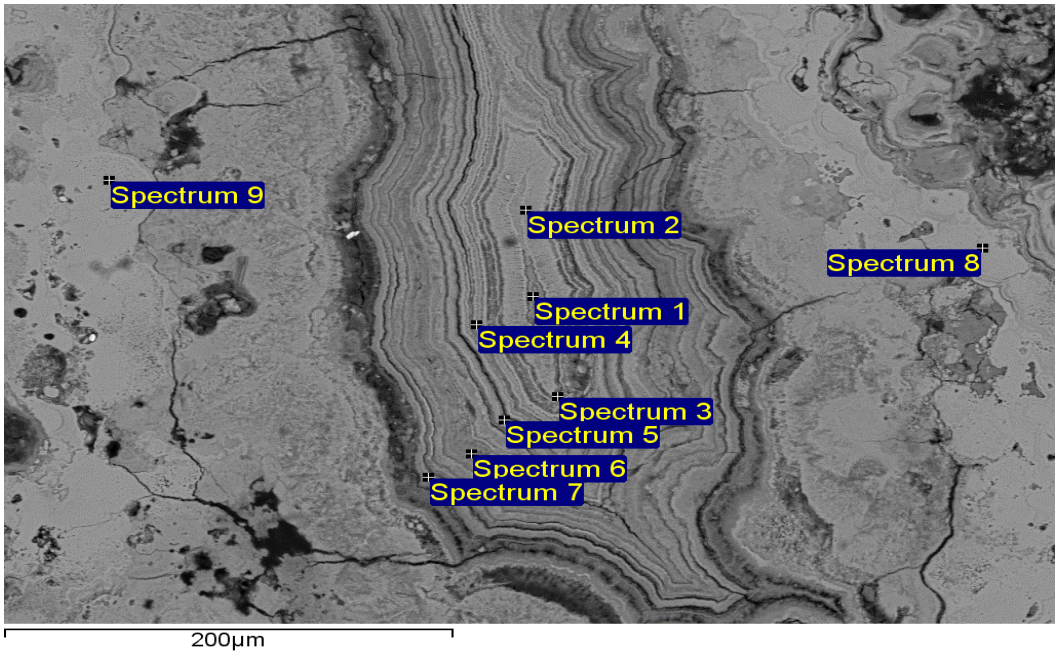


NP-MB 18

Site of interest 1

	Ca	Fe	Mg	Mn	Na	O	Total
wt. %	1.69	2.56	1.32	25.14	1.14	66.67	98.52

NP-MB 18
Site of interest 3

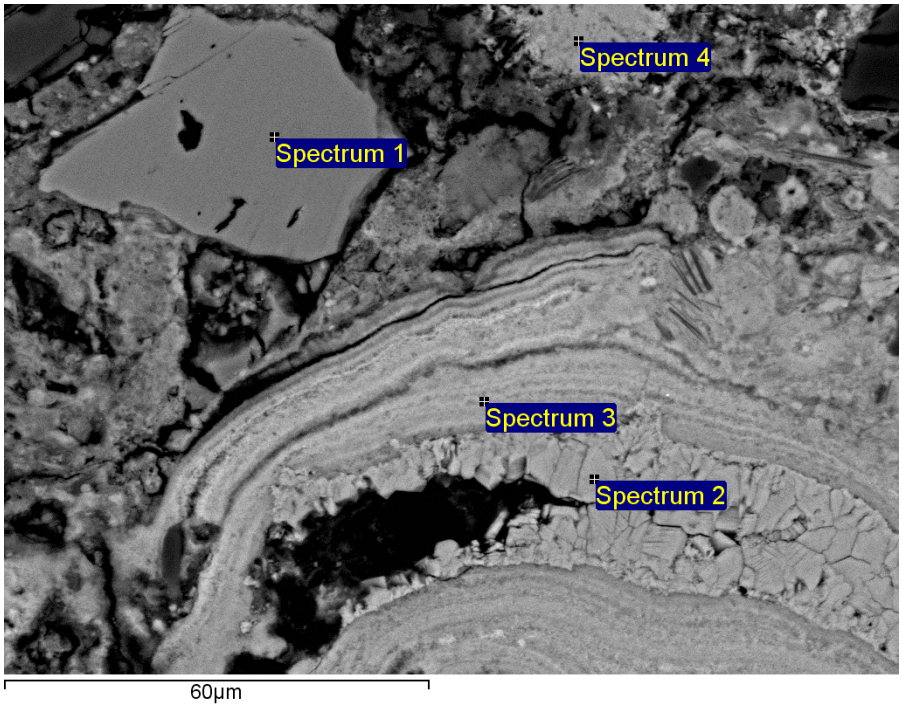


						Weight %					
Spectrum	Ca	Cl	Fe	K	Mg	Mn	Na	O	P	Si	Total
Spectrum 1	0.72		48.61			10.28		37.61	0.58	2.2	100
Spectrum 2	0.86		41.65			15.52		39.94	0.33	1.69	100
Spectrum 3	0.36		51.77			2.09		43.11	0.53	2.14	100
Spectrum 4	1.16		36.63			22.1		37.7	0.59	1.82	100
Spectrum 5	2.28		7.39	0.62	1.07	55.09	1.35	32.2			100
Spectrum 6	2.39	0.36	5.6	0.83	1.03	53.68	1.37	34.33		0.41	100
Spectrum 7	1.56		25.75	0.32	0.52	34.84		36.04		0.99	100
Spectrum 8			55.59			1.18		41.25	0.33	1.66	100
Spectrum 9	0.19		54.85			1.52		41.36		2.08	100

- Small scale oscilations of iron and manganese – variable redox conditions in soil

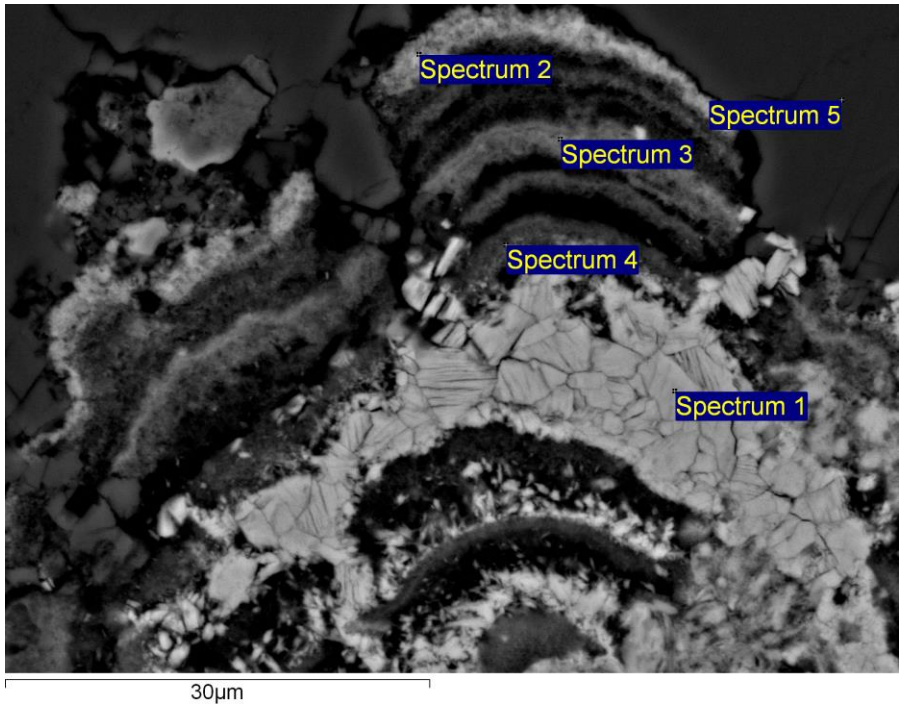
NP-MB 16

Site of interest 2



Spectrum	O	Ca	Ti	Mn	Fe	Ba	Total
Spectrum 1	43.83	0.16	55.08	0.17	0.76	0	100
Spectrum 2	39.21	0.53	0	59.31	0.68	0	100
Spectrum 3	36.6	1.7	0	52.72	1.49	6.4	100
Spectrum 4	39.62	0.74	0	42.1	15.87	0.49	100

Site of interest 9



Spectrum	O	Na	Mg	Ca	Mn	Fe	Ba
Spectrum 1	68.76	0	0	0.51	30.29	0.24	0
Spectrum 2	68.2	0.69	0.8	2.28	25.36	0.86	1.14
Spectrum 3	63.24	0.98	0.59	1.89	30.34	0.8	1.25
Spectrum 4	60.73	0.81	0.51	2.35	32.76	0.79	0.92
Spectrum 5	75.99	0	0.39	23.42	0.19	0	0

Conclusions

- XRD analysis show that all three samples contain **goethite** and quartz, usually with feldspars (plagioclase), pyrolusite, some phyllosilicates and various amount of amorphic matter
- Geochemical analysis shows **elevated concentrations of iron (37.86–39.04 wt.%**) and manganese (19.17–27.42 wt.%)
- SEM-EDS showed existance of **crystallic and amorphic, colloidal phases**, different types of manganese minerals and existance of secondary calcitization
- Small scale oscilation of Fe and Mn – variable redox conditions
- Formation mechanism is **colloidal precipitation from (ground)water**
- Different concentration of Ba in different phases – elevated concentration in amorphic phase – two different Mn-solutions?
- **Bog iron ore**
- **Use as iron ore** – high amount of iron, accesible, easy to process

Thank You for your attention!

This work has been fully supported by Croatian Science Foundation under the project TransFER (5074).