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## **Chemical Analysis of Iron Slags and Metallic Artefacts from Early Iron Age**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors contributed in practical work and managed the analysis of the study. All authors read and approved the final manuscript.*

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### **ABSTRACT**

Eight samples of iron slag and two metallic artefacts from two Early Iron Age sites in central Bosnia and Herzegovina, Čolaci and Pod, were analysed using chemical instrumental methods. Atomic absorption spectrometry was applied to determine major (Fe, Al, Ca, Na, Mg, K and Mn) and trace elements (Cr, Cu, Co, Ni and Zn), while gravimetric method and molecular visible spectrometry were applied to determine Si and Ti, respectively. Infrared spectrum of selected samples was recorded during different phases of analysis and the results show that the primary ore was hematite. Results also indicate that residents from both sites, which are adjacent, used the same ore source. Low values of Ca, whose compounds are used as flux in later stages of the processing of iron ore, show that the processing of iron at the study sites was in the beginning stage of its development. Based on the obtained results, metallic artefacts found at the site Čolaci probably came from site Pod. Graphical presentation of the content relationship between the selected metal oxides in the slag was performed to present differences between samples from two sites. Analysis of trace elements in the analysed slags confirmed that they originate from Early Iron Age.

**Keywords:** Iron slag; metallic artefact; Early Iron Age; spectrometry; Bosnia and Herzegovina.

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## **1. INTRODUCTION**

In the early stages of archaeological science, slag was not commonly observed as an important factor, but rather considered as waste which occurred in the processes of making a final metal product. As archaeometallurgy, from Bronze Age to the recent past [1] was developing, so the slag became a very important part of the scientific study. By analysing the slag we can gather information about processes that were undertaken from the ore to the final product and about the quality of the process itself. Also, we can gain knowledge about how much one society has been developed and about relationship between different communities, because metallurgy was an important social and economic part of their lives. Hauptmann [2] discusses a Levy and Shalev model from 1989, which describes the relationship of processes in the system: ore → smelting → final product/waste product. This model is applicable and it is composed of four parts: smelting is always undertaken in the vicinity of the ore source; smelting is usually connected with production of great amounts of slag; smelting is connected with the issues of fuel procurement and metallurgy which takes place outside of settlement and is restricted on the processing of finished metal product (e.g. casting of iron). The chemical composition of the slag is in the direct relationship with the furnace temperature, redox conditions, and rate of the reaction processes and chemical composition of the finished product [3]. Chemical analysis involves contribution determination of chemical elements or element oxides in the slag, whereby they can be present as major or trace elements. Most of the authors divide trace elements in two groups: siderophile and lithophile [4-6]. According to Kronz [6] the behaviour of siderophile elements such as C, P, Co, Ni, Cu and As plays an important role due to their partitioning into slag and metal and although highly siderophile elements ( Co, Ni, Cu and As ) enter quantitatively to the metal, the partition coefficient between P in the silicic melt and the metal is variable. In that case Cu, Ni, Co can be used in metal artefacts for provenance studies, while P and C are good indicators of the thermodynamic conditions under which these metals were formed or modified [6]. Heimann et al. [4] associate V with the siderophiles, and include in the lithophile group: P, S, As, Ba and Mn, elements that are concentrated inside the slag. Coustures et al. [5] add to above mentioned lithophile elements Rb, Sr, Zr and Th, elements incompatible compared with the main mineral phases so that they will keep the same ratio in the slag as in the ore, making them very important for the provenance studying.

The aim of this study was to determine the content of selected elements and their oxides in eight slag samples and two finished metal artefacts from the Early Iron Age from two sites in Bosnia and Herzegovina in order to confirm that they originate from Early Iron Age. Determination of major elements (Fe, Si, Al, Na, K, Mg, Ca, Mn and Ti) and trace elements (Cr, Ni, Zn, Co and Cu) was carried out by applying instrumental methods of analysis. Fourier transform infrared spectrometry (FTIR) was also performed, providing information about the structure and bonds in samples and changes that occur when different archaeological samples are subject of temperature changes. Published data describing a similar treatment of archaeological samples like the treatment of samples given in this study are scarce. Manoharan et al. [7] use the same method of analysis for ceramics from 300 BC and Sheikh et al. [8] for the analysis of slag from 400 AD.

## **2. MATERIALS AND METHODS**

### **2.1 Study Area**

Slag, the subject of the analysis, originates from two sites in central Bosnia and Herzegovina. The distance between these sites is about 10 km. Both of them, Čolaci near

Donji Vakuf and Pod near Bugojno were part of the Centralbosnian culture group of Early Iron Age, whose characteristics and development was described by Borivoj Čović [9].

Pod near Bugojno (Latitude 44°03' N and Longitude 17°26' E), a hill fort settlement was first documented by Austrian archaeologist Karlo Patsch in 1895 [10]. Currently this site has a status of national monument of Bosnia and Herzegovina. Findings from Pod helped to make a complete periodization of the Centralbosnian culture group. In the layer from the 7 century BC were findings of the secondary iron processing, but the most interesting finding is the limonite sample found in a vessel from an older time period (most lately 900 BC). It is assumed that the limonite sample has been brought from one of the iron ore deposits in the near vicinity of Pod [9].

Čolaci near Donji Vakuf (Latitude 44°09' N and Longitude 17°23' E), as it is the case with Pod, represents a hill fort settlement that can be attributed to the Centralbosnian culture group. This site is abundant with residues of hematite ore and slag that remains after refining, melting and ore smelting [11]. Trial excavations from 2010 show that the site is abundant with ceramics, metal and stone material, which points toward intensely and continuous settling. This metallurgical findings point that metal processing was used for the production of metallic objects and an active metallurgical iron industry was established in the settlement. The settlement was a possible metallurgical centre, prove of this are findings of significant amounts of slag and hematite (172 kg) [11].

## 2.2 Samples

Samples for the chemical analysis were obtained from the National Museum in Sarajevo, Bosnia and Herzegovina: four samples from Pod (marked with P), four samples from Čolaci (marked with C) and two finished metallic products (Mp) from Čolaci. Inventory numbers, labels used in this work, dimensions and site from which the sample was excavated are given in Table 1. Images of samples with labels are presented in Fig. 1. By visual examination it was evident that samples SC1, SC2, SC3 and SC4 were probably samples of a primary slag. Sample SP4 can be crumbled by fingers, what along with remarkably yellow colour indicate that this slag is most probably under influence of atmospheric conditions and physical and chemical processes limonitized. Sample MpC1 is a metallic object and it looks like a small knife. Sample MpC2 is also a metallic object of an unknown purpose.

**Table 1. Inventory numbers of samples, labels used in this work, dimensions and the site from where the samples were excavated**

<b>Inventory numbers</b>	<b>Label</b>	<b>Dimensions (cm)</b>	<b>Site</b>
Hematite (assumed)	SP1	16 x 6.4	Pod
Pod 76, WXXXI	SP2	15.5 x 5.5	Pod
Pod 65, O – XVI	SP3	15.3 x 4.5	Pod
50437 Pod	SP4	17.5 x 4	Pod
SJ 4 /45 (larger piece)	SC1	16.1 x 6.2	Čolaci
Čol. SJ 54	SC2	14 x 3.7	Čolaci
PN 71 (SJ 44/45 relationship with SJ 50/51 burial/pit)	SC3	17.9 x 5.3	Čolaci
SJ 44/45 (small piece)	SC4	9 x 2.8	Čolaci
knife	MpC1	9.3 x 1.3	Čolaci
metallic object (unknown purpose)	MpC2	6.2 x 1.2	Čolaci

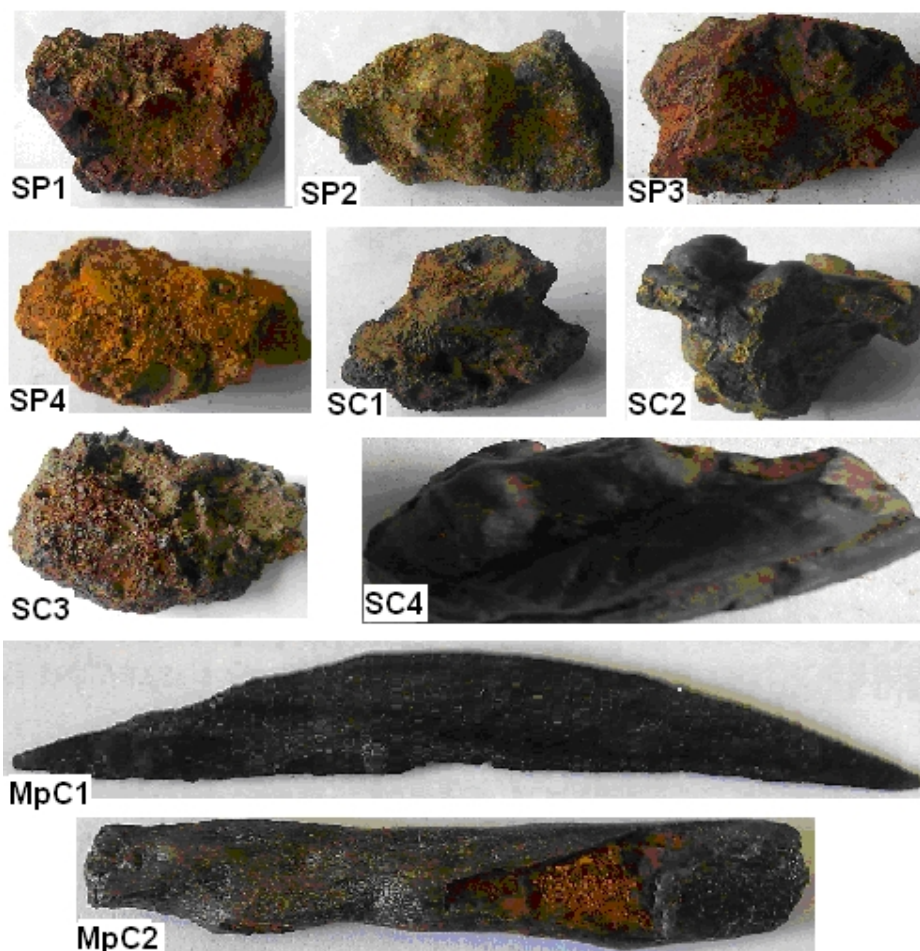


Fig. 1. Images of analysed samples

### 2.3 Samples Preparation and Treatment

Samples were obtained by drilling with a hand drill, which has a carbide auger, they were drilled in three different places on the slag, and about 2g of each slag sample, and about 0.2g of metal objects samples were taken. Samples were homogenized and for the final analysis 0.5g of each slag sample was weighed, using the analytical balance with accuracy of 0.1mg. Three probes of the same slag sample are prepared for the analysis. For the analysis of metal object samples, less weight was taken and about 0.05g of the sample was weighed, since these artefacts are valuable and taking a lot of their weight could change their authenticity. Samples are dissolved in aqua regia (conc. HCl+HNO<sub>3</sub>, in the ratio of 3 :1) with addition of 30% solution of hydrogen peroxide and heated. Cold solutions were filtrated and quantitatively transferred into the volumetric flask of 100mL. The undissolved part of the sample and the part that left on the filter paper were burned in a porcelain pot and then annealed on the temperature at 800°C in an oven. Mass of the undissolved part is calculated as a mass of SiO<sub>2</sub>.

All reagents used were of analytical grade purity: HCl (37%), HNO<sub>3</sub> (65%), H<sub>2</sub>SO<sub>4</sub> (98%), H<sub>3</sub>PO<sub>4</sub> (85%), SrCl<sub>2</sub> x 6H<sub>2</sub>O, KNO<sub>3</sub> and CsCl (Merck, Darmstadt). Standard solutions of Pb, Fe, Cd, Zn, Co, Cr, Cu, Mn, Ni, Zn, Mg, Ca, K, Na, Al and Ti (1000 mg/L, CertiPUR, Merck Darmstadt). Metals Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn are determined by flame atomic absorption spectrometry (FAAS), K and Na are determined by flame emission spectrometry (FES), and for the determination of Ti, molecular visible spectrometry was used. SiO<sub>2</sub> was determined by gravimetric analysis in the form of precipitate after dissolving samples in aqua regia. Spectrum of chosen samples in different stages of chemical analysis (original samples and samples after dissolving and annealing) are recorded by using Fourier transform infrared spectrometry.

Flasks with the filtrate were made up to the mark with redistilled water, and that solution was used to determine the concentration of other elements. Concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn were determined by FAAS directly from given solutions, and concentrations of Ca, Fe and Mg were determined after dilution. K and Na were determined, after dilution of primary solutions, by FES. Titanium is determined by using molecular visible spectrometry at 410 nm, after developing of the colour with hydrogen peroxide. Calibration curve method was used for the determination of elements with FAAS, FES and molecular visible spectrometry. Instrumentation used in this study is listed below:

Analytical balance: Mettler-Toledo, New Classic MF, ML204; Laboratory oven: Carbolite, Aston Lane, Hope Sheffield, S302RR, England; UV/VIS spectrophotometer: Varian 50 Probe; AAS spectrophotometer: Varian 240 FS; FTIR: Perkin Elmer BX.

### **3. RESULTS AND DISCUSSION**

#### **3.1 Quantitative Analysis**

After the chemical analysis we obtained the content of the most contributed metal oxides in slags, and for metals which can be present as trace elements. Lead and cadmium are below the determination limit for the applied method in all samples. Graphical comparison of the concentration (% wt) of particular element oxides was done to determine the differences in metallic artefacts from two sites. Results of the analysis are given as average value of 3 replicates of each sample. Results of 8 slag samples from two sites in Bosnia and Herzegovina and two samples of metallic objects were expressed as concentration (% wt) of element oxides (major and minor elements), trace element compositions are expressed as parts per million (ppm) (Table 2). The results of analysed slag samples, given in Table 2 show a very high content of iron oxide. The content of FeO ranged from 39.52% to 62.20%, with the exception of sample SP2 (23.55%). Sample SP2 contains the highest silicon content of all analysed samples, which may indicate that SiO<sub>2</sub> derived from parts of a potential furnace during ore melting, resulting in a lower amount of iron in this sample. It is a known fact that the process of ore smelting to the final product is not effective enough because it was not possible to develop enough high temperature and apply the appropriate reduction conditions. In this period of time, the used ore smelting was so-called a direct method in a bloomery, where iron ore was reduced in a single step. The granulated ore reacted with the added fuel (wood or charcoal), with the formation of porous iron mass that did not exceed the liquid state [12,13]. Achieved temperatures, in the bloomery of that time, were below the melting point of iron and the waste products (slag) incurred during the operation contained components that have not been reduced and also other components (e.g. parts of bloomery, ash, etc.). The iron ores (especially hematite) are known to contain significant number of

impurities including silica, calcium carbonate, phosphorus and manganese, sulphur, aluminium, titanium and water [14]. As the value of the calcium content of the samples do not exceed 2%, it is clear that there was no added flux of this kind. From Tables 2 and 3 it can be seen that slag samples from Pod have lower content of manganese in the relation to the Čolaci site. According to Veldhuijzen and Rehren [15] the slag with lower manganese content belongs to the secondary slag. The slag from site Čolaci is likely a primary slag which can be confirmed by the higher content of FeO in samples from this site (Tables 2 and 3) and by visual examination of the slag before the analysis. Important in this process is that a large number of trace elements almost completely transfer from the ore to the slag and their content remains constant [16]. For this reason it is possible to follow the chemical composition of the slag and the final product, which will contain inclusions that originate from the elements present in the process of iron production [16]. The presence of certain trace elements such as chromium, cobalt and nickel in the slag samples analysed in this study (Tables 2 and 3) suggest that the ore is likely to contain a certain amount of these elements. Specifically, in the soil, these elements are in the average concentrations of 7-150ppm (chromium), 4-50ppm (nickel) and 0.1-10ppm (cobalt) [17], while in the present study concentrations of analysed slag samples are from 0.06-1.12ppm; 0.08-0.28ppm and 0.03-0.19ppm, for chromium, nickel and cobalt, respectively, which is far below the value that can be found in the soil. So the possibility of slag contamination with mentioned elements from the soil can be excluded, and on the other side all of three elements are present as impurities in the iron ore from the territory of Bosnia and Herzegovina. Higher content of  $Al_2O_3$  in the samples from the site Čolaci indicate that aluminium in the slag from this site probably originated from the bloomery in which ore smelting was performed. The bloomery was made of clay that is known to contain significant amounts of  $Al_2O_3$ . The reason for the presentation of iron as FeO rather than Fe lies in the fact that the process of refining iron was still underdeveloped and the reached temperature was not sufficient for high-quality ore reduction process starting from the  $Fe_2O_3$  to the metallic iron. This caused less reductive conditions (less reduction power of CO/ $CO_2$  gas system). In such conditions, the process of transition of FeO to Fe was not enough efficient, resulting in a slag containing higher amounts of FeO than is the case with the slags that are now obtained as by-products in iron production. High temperatures were not used at the time for smelting of the ore because bloomeries that were made of clay were incapable to withstand high temperatures [14]. The content of all nine oxides were higher in slag samples from the site Čolaci. The content of Ni has the same value at both sites, but the content of the remaining four analysed metals (Co, Cr, Cu and Zn) is higher at the site Pod. Comparing the results of the trace elements contents found in slag samples from the two sites, Pod and Čolaci, it can be unequivocally stated that the analysed slags do not significantly differ in the content of these metals and the values are very close for both sites (Table 3).

**Table 2. Compositional data: concentration (% wt) of metal oxide and metal concentration (ppm) in 8 slag samples and 2 metallic objects**

Sample	Concentration (% wt)								Concentration (ppm)					
	MnO	FeO	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Cr	Cu	Co	Ni	Zn
SP1	0.05	53.86	0.18	0.14	0.48	0.22	3.01	0.27	12.46	0.18	0.17	0.05	0.15	0.86
SP2	0.03	23.55	0.37	0.13	0.04	0.30	0.69	0.11	32.21	0.21	0.76	0.15	0.19	0.34
SP3	0.09	43.74	0.45	1.50	0.26	0.18	2.18	0.28	16.70	0.08	1.48	0.19	0.09	1.37
SP4	0.05	39.52	0.45	0.70	0.23	0.36	2.33	0.45	14.23	1.12	0.30	0.09	0.12	1.53
SC1	0.33	62.20	0.37	0.78	0.54	0.23	4.55	0.35	28.38	0.73	0.27	0.07	0.28	0.68
SC2	1.18	45.81	0.46	0.70	0.57	0.39	6.62	0.28	24.25	0.09	0.56	0.09	0.11	0.45
SC3	0.51	46.27	0.54	1.41	0.64	0.29	11.2	0.33	14.34	0.16	0.18	0.08	0.08	0.56
SC4	2.00	50.02	0.43	1.81	0.95	1.43	5.81	0.68	14.64	0.06	0.06	0.03	0.09	0.21
MpC1	0.06	61.79	0.28	0.69	0.08	0.26	ND	1.37	ND	0.19	0.06	0.04	0.07	3.88
MpC2	0.04	73.47	0.30	0.24	0.03	0.16	ND	0.33	ND	0.04	0.20	0.33	0.19	0.56

\*ND – not detected, lead and cadmium are below the determination limit for the applied method

**Table 3. Average values of metal oxides and trace elements in slag from the sites of Pod and Čolaci**

Site	Concentration (% wt)								Concentration (ppm)					
	MnO	FeO	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	SiO <sub>2</sub>	Cr	Cu	Co	Ni	Zn
Pod	0.054	40.17	0.37	0.62	0.26	0.27	2.06	0.28	18.9	0.40	0.68	0.12	0.14	1.03
Čolaci	1.01	51.08	0.45	1.18	0.68	0.59	7.05	0.41	20.40	0.26	0.27	0.07	0.14	0.48

This leads to the conclusion that the population at both sites probably used the same ore source, which is not surprising since we know that the Radovan mountain is in the vicinity of both sites. On the other hand, the differences that exist in oxides of major elements between the two sites probably come from the different ways of ore smelting, the amount of fuel and the type of fuel used (it is possible that they used different types of wood containing different concentrations of alkali and alkaline earth metals) which contributed that on the basis of "nuances" we conclude that metal objects, primarily knife originated from the Pod site. Samples MpC1 and MpC2 have a higher content of iron in relation to the slag; it is expected since these samples in their appearance suggest that they are finished products. Also, a higher content of trace elements in these samples compared to slag samples shows that these elements are concentrated in each of the next stage of smelting, which agrees with the conclusions of Navasaitis et al. [18] and other authors which state that the highest content of these elements is in the final product.

Graphical presentation of the relationship between oxides of elements in slag samples can provide more information about the origin of samples within two or more sites [19-22]. Most authors graphically present the obtained results for inclusions in the ferrous materials, while in the present study, a different approach was applied. Hence, the analysis attempted to show that based on the oxide and elements values for a bulk sample we can distinguish the slag from two sites. It was assumed that the values of elements in the samples are a chemical image which is the same in each part of the sample. Graphical presentation of the content relationship between the selected metal oxides in the slag is given in Fig. 2.: MnO-SiO<sub>2</sub>, MnO-CaO, MnO-MgO, MnO-Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-FeO, Al<sub>2</sub>O<sub>3</sub>-CaO, Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O, K<sub>2</sub>O-CaO and K<sub>2</sub>O-MgO. Although analysis of four samples of slag from both sites cannot provide an exact picture of the origin of the samples, from the chart in Fig. 2. it is clear that there is a distinction between samples from two study sites.

Manganese is an element that completely exceeds from the initial ore into the slag and can play an important role in determining the geographical location from which the slag and ore used in the production of iron originates [19]. For this reason, the results for MnO in the slag were compared with results of four other oxides (SiO<sub>2</sub>, CaO, MgO and Na<sub>2</sub>O), as it can be seen from Fig. 2. (a, b, c and d). From this charts a clear distinction between the slags from two different sites can be seen. Aluminium in slag plays a significant role and the results were compared with the results of four other oxides (SiO<sub>2</sub>, FeO, CaO, and K<sub>2</sub>O), which is presented in Fig. 2. (e, f, g and e). These charts also show a clear distinction between the samples from Pod site and the ones from Čolaci. Fig. 2 (i and j) presents relationship of oxides of alkali and alkaline earth metals in the analysed slag and content of potassium oxide according to the ratio of calcium and magnesium. It can be clearly seen from the chart that slag originates from two separate sites. In samples MpC1 MpC2 found on the site Čolaci, Si and Al were not analysed (low concentration). To determine the origin of the samples; we presented relationships of MnO and K<sub>2</sub>O content in relation to the other oxides Fig. 2. (b, c, d, i and j). From the chart, it can be concluded that metallic objects MpC1 and MpC2 that were found on the site Čolaci probably originate from the site Pod. Since the objects are final products, there is a possibility that the objects are produced in Pod and were transferred to the site Čolaci. This possibility is quite realistic considering that the mentioned sites are relatively close to each other.



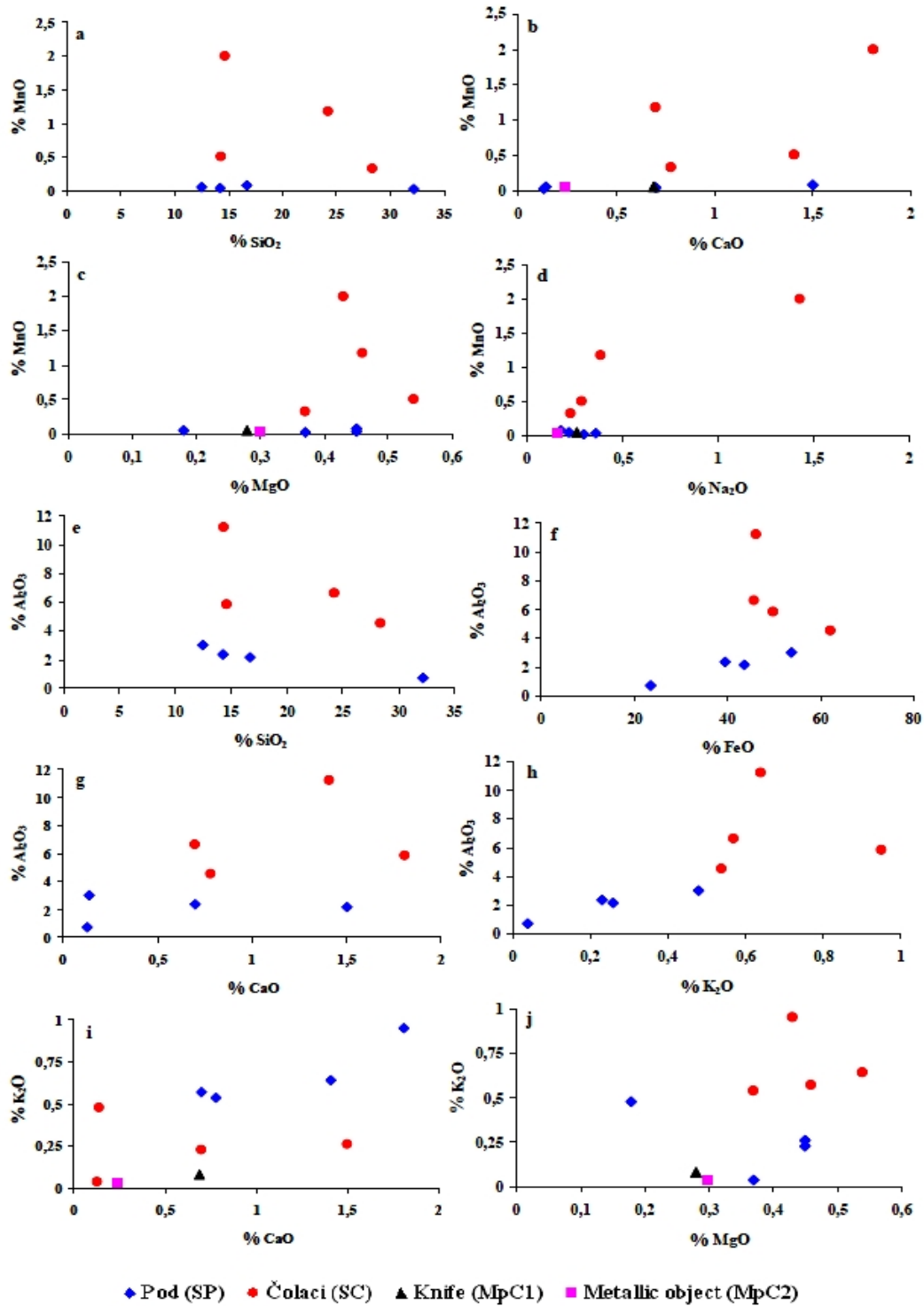
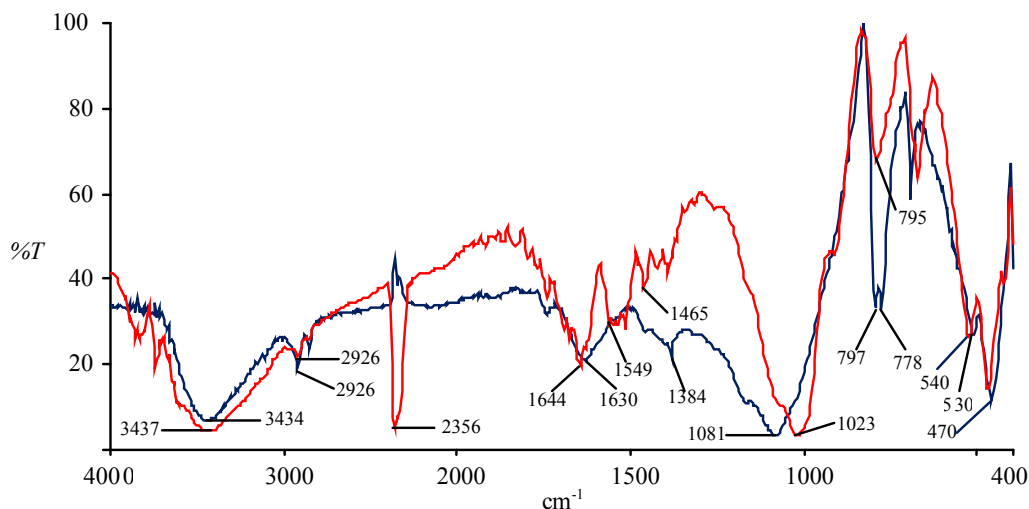


Fig. 2. Relationships between the individual oxides in slags and final products from two sites

### 3.2 IR analysis

According to the IR analysis, all spectra showed characteristic absorptions of hydrated silicate material. Fig. 3 shows IR spectra of sample SP2, before and after dissolution in aqua regia and thermic treatment. Absorptions centred around 3465, 1630 and 1030  $\text{cm}^{-1}$  are attributed to asymmetric and symmetric stretching of silicate materials; absorptions at 470  $\text{cm}^{-1}$  are attributed to the bending of Si-O-Si bond; absorptions centred around 540  $\text{cm}^{-1}$  are attributed to Fe-O vibration from hematite. The Fe-O vibration about 540  $\text{cm}^{-1}$ , together with the absorption at 530  $\text{cm}^{-1}$  and a sharp band at 470  $\text{cm}^{-1}$  in the publications treating problems of samples containing iron (initial ore, slag, pottery, ochre colour) are always attributed to the hematite [7,23,24]. Absorptions in the region 1644-1630  $\text{cm}^{-1}$  belong to bound water bending frequencies. The most intense bands in all spectra belong to Si-O asymmetric stretching and appear in the region 1023-1121  $\text{cm}^{-1}$  which can be explained by the different environment of  $\text{SiO}_4$  tetrahedral and different content of metal ions, primarily Fe and Al and their different affinity for metal oxygen bond. From the comparative spectra of sample SP2 Fig. 3, before and after dissolution in a mixture of acids and annealing at 800°C, we can see a reduction in the intensity of absorption of Fe-O. Based on these results, we have concluded that the residue after dissolving the samples and annealing at 800°C is mainly  $\text{SiO}_2$ . After heating, the spectra differ mainly in the absorptions related to bound water and changes in symmetry of  $\text{SiO}_4$  structural units. The bands around 2360  $\text{cm}^{-1}$ , which is combination of symmetric stretching vibrations of bonded water, disappeared after heating at 800°C. Band at 795  $\text{cm}^{-1}$ , assigned to Si-O-Si symmetric stretching vibration, is split in to two absorptions at 797 and 778  $\text{cm}^{-1}$  as a result of the partial loss of bound water. The bands in the region 1300-1550  $\text{cm}^{-1}$  represent the typical pattern of absorption of phosphate. Weak absorptions around 2930  $\text{cm}^{-1}$  indicate the contamination of samples with organic material.



**Fig. 3. Comparative spectra of SP2 sample before and after dissolution and annealing (red line before, blue line after dissolution and annealing)**

### 4. CONCLUSIONS

Based on these results, it can be concluded that the analysed slag contains a significant content of FeO and  $\text{SiO}_2$ , which is typical for the period of Early Iron Age and the beginning

of smelting the iron ore. Furthermore, the slag from Pod contains a lower content of iron oxide compared to samples from site Čolaci, which is an indication that the residents of site Pod had more technical knowledge about the process of smelting the iron ore. The result is a slag with less amount of residual iron. Additionally, significant amount of FeO in the slag from site Čolaci shows that this slag is a primary slag. A lower content of CaO in the analysed samples shows that during the smelting of the ore, there was no intentional addition of flux while the high value of Al<sub>2</sub>O<sub>3</sub> in the slag probably originates from the furnace in which the ore was processed. Based on the results of trace elements, we can say that residents from both sites probably used the same source of iron ore. Metallic objects most likely originate from site Pod and arrived to the site Čolaci by exchange. Moreover, infrared spectra are consistent with the analytical data (absorption intensity correlates with the iron content in the samples), while the absorption centred around 540cm<sup>-1</sup> is characteristic of the mineral hematite, which together with a high iron content in slag suggests that this mineral was used as initial ore in the process of obtaining iron. Analysis of trace elements in the analysed slags confirmed that they originate from the Early Iron Age.

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## **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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