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The Study of Trace Elements in Bloomery Iron

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The present work is devoted to the study and characterization of compositional comparison of trace elements (Cu, Ni, Co, As) and minor elements (P and S) in extracted iron, bog ore and smelting slag from various sites of Lithuania. The experimental bloomery smelting results are also discussed. Trace element data have been determined using a scanning electron microscope EVO 50 EP with X-ray spectrometer of wave dispersion and a direct current plasma emission spectrometer Beckman SpectraSpan VI. The results illustrate the potential of trace and minor elements in the research in microstructure and mechanical properties of bloomery iron and in provenance studies of bloomery iron objects.
Keywords: bloomery iron, bog ore, bloomery slag, trace elements, Lithuania.

1. INTRODUCTION

Most trace elements get into products of iron metallurgy as lumps, iron artifacts and smelting slag from ore during a smelting process. Technological processes, through which an ultimate result is obtained, also make an influence as some part of trace elements get into iron articles from ashes of fuel, flux and walls of iron smelting furnaces.

The most important trace elements in bloomery iron are nickel, copper, arsenic, cobalt and some others. Although the amount of trace elements in iron and steel is usually insignificant, nevertheless they may have an efect on microstructure of a metal matrix and mechanical characteristics. For example, enrichment with nickel increases the stability of austenite, pearlite or other carbide dispersions, whereas arsenic induces a ferrite forming process [1]. They also may help research into iron artifacts provenance as well as in technique of manufacture. Generally, iron produced from bog ore using the bloomery direct smelting process is relatively pure, with an exception of entrapped slag inclusions, as temperature of the carbothermal extraction in bloomery process does not exceed 1200 ºC – 1250 ºC and the extracted iron remains in solid state. The relatively pure sponge iron bloom formed in this way contains a large amount of smelting slag, which has to be removed by forging. Despite severe and sedulous forging a part of slag remains in the produced iron and its products in the conformation of slag inclusions. Their chemical and phase compositions are presented in works [2 – 5] and others. Authors of these studies also show the possible relations of the compositional characteristics of slag inclusions with both the smelting slag found in the iron production sites and the used ore. However, R. Gordon, with reference to the thorough researches in bloomery slag performed by S. Fells, maintains that it is difficult to trace the sources of ore or get sufficient information about the type of an iron smelting furnace and smelting technique using only the characteristics of smelting slag [6]. In the smelting process two phases – extracted iron and slag – are in a constant interaction, and all ore components – major and minor and the tracing ones distribute in these phases. Therefore, analyses of trace elements are to be carried out in metal (iron) and slag phases, furthermore, it is relevant to compare the results of the analyses with the characteristics of ore components.

One of the first studies of trace elements in bloomery iron samples is presented in a work by E. Schurmann [7]. Alongside the theoretical analysis of a direct iron extraction process, the author also presents the study results of trace elements (Cu, Ni, Cr, Al, Sn) and nonmetal inclusions in iron artifacts. Data of the further analysis of trace elements in bloomery iron and their distribution between metal matrix and slag inclusions are presented in works [2, 8 – 11]. R. F. Tylecote firstly accentuates such elements as: carbon, phosphorus, sulphur, nickel and copper as having an importance to assessing provenance of iron as well as to the technique of iron artifacts [12]. Bloomery iron may have a different degree of carburization. Carbon gets into iron from charcoal, however, avoiding the homogenizing influence of a liquid phase, it is distributed non uniformly in bloomery iron. Carburization of bloomery iron highly depends on conditions of smelting, thus, the amount of carbon is a significant indicator of the smelting process. The greater part of phosphorus comes in smelting products (iron and slag) from ore, while, some its amount also comes from fuel ashes. For example, the content of P_2O_5 in ashes of charcoal (main bloomery fuel) may vary from 4.2 wt.% to 16.7 wt.% [13]. Sulphur also gets into smelted iron and slag mainly from ore.

Recently, studies of technique and provenance of artifacts manufactured of bloomery iron attained serious attention of researchers, but the influence of trace elements is not properly revealed and data of their studies are sparse and basically connected with the samples of iron slag. In Lithuania, there are also some works related to the studies of minor and trace elements in bloomery iron, its products and slag inclusions [14 – 19]. However, relation of the characteristics of ore composition (with regard to trace elements) to smelted iron, smelting slag and their inclusions in products has not been studied as yet at all. Such studies may give an important information to

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researchers on tools, arms and other implements made of bloomery iron investigating peculiarities of microstructure and mechanical characteristics of products, their manufacturing technique and provenance.

The purpose of this paper is to present the results of a study of some trace elements (Cu, Ni, Co, As) and minor elements (P and S) of as-smelted bloomery iron samples and of bog ore and smelting slag pieces from various sites of Lithuania. A compositional comparison of trace elements in bog ore, bloomery iron and smelting slag illustrates the importance of trace element data both in metallographic examination and in provenance studies of early iron objects.

2. SAMPLES AND TECHNIQUES

In Lithuania bloomery iron was produced from local bog ore composed of iron minerals and gangue. Bog ore is rather porous and highly heterogeneous material. Bloomery slag is also non-homogenous material consisting of various phases. Therefore, both bog ore and smelting slag were carefully ground in order to prepare exploratory solutions for examination. The elemental composition of ore and slag samples was determined by optical emission spectroscopy using a direct current plasma emission spectrometer Beckman SpectraSpan VI.

Several iron clots entrapped in smelting slag and some iron artifacts were chosen for the study of elemental composition and microstructure of produced metal. Elemental composition of polished and carbon coated iron samples was examined by a scanning electron microscope EVO 50 EP (Carl Zeiss SMT AG) with a wave dispersive X-ray spectrometer (Oxford Instruments). Working conditions: acceleration voltage 20 kV and beam current 40 nA. In each sample the element concentration was measured in three (20×40) μm sites. Mean values of the measurements are presented. Polished sections were prepared for the metallographic study of iron clots and artifacts. Microstructure of the sections was examined by optical microscopes LMA-10 and Olympus BH2.

3. RESULTS

The bog ore samples were selected for examination from seven sites of Lithuania and they were related to various periods of iron metallurgy. Direct iron production carried out for centuries required large resources of bog iron ore. Only in the medieval bloomery furnaces, the amount of used bog ore in Lithuania may run into 250 – 330 thousand tons [20]. Thus, the basic and best resources of bog ore were exhausted and nowadays very few ore sources are found. For this reason currently excavated ore and ore samples from museums as well as archaeological finds of ore uncovered in iron smelting sites were used for the examinations. There were samples from Vilkaviškis Regional Museum (present-day ore), Jurė village of Kazlų Rūda district (an ore sample of the $18^{th} – 19^{th}$ c.), Telšiai "Alka" Museum (present-day ore), Rūda village of Merkinė district (an ore sample of the $17^{th} – 19^{th}$ c.), Kernavė ancient settlement in Širvintos district (ore samples of the $10^{th} – 14^{th}$ c.), Lieporiai ancient settlement in Šiauliai city (ore samples of the $4^{th} – 6^{th}$ c.) and Janoniai quarry of Anykščiai district (present-day ore). The ore samples contained various amounts of iron ranging from 33.79 wt.% in the ore from Kernavė, to 57.8 wt.% in the ore from Lieporiai. In addition to it silicon, aluminium, phosphorus, calcium and other elements were found in the ore minerals.

The analyses of chemical composition of the ore samples have revealed a negligible content of copper and nickel in the Lithuanian bog ore (Table 1). Average content of copper is scarcely 0.004 wt.% and the largest content is found in the ore of Kernavė (0.007 wt.%). Average content of nickel amounted to 0.008 wt.% and the largest content is found in the ore of Lieporiai ancient settlement (0.029 wt.%). But slightly larger contents are found of cobalt (av 0.037 wt.%) and arsenic (av 0.017 wt.%). It is important to note that in the most samples of the Lithuanian bog ore there is a relatively large amount of phosphorus. The lowest content of phosphorus (0.218 wt.%) is found in the ore of Kernavė and the largest one, reaching even 2.11 wt.% – in the ore of Merkinė. An amount of sulphur in the examined ore samples ranges from 0.004 wt.% to 0.106 wt.% and its average is 0.091 wt.%. Besides, the samples of the ore contain also some amount of chromium av 0.018 wt.% (limits 0.011 wt.% – 0.023 wt.%), molybdenum av 0.003 wt.% (from 0 wt.% to 0.009 wt.%), strontium av 0.01 wt.% (from 0 wt.% to 0.019 wt.%), zirconium av 0.003 wt.% (limits 0.001 wt.% – 0.006 wt.%), plumbum av 0.003 wt.% (from 0 wt.% to 0.008 wt.%) and of tin av 0.001 wt.% (from 0 wt.% to 0.003 wt.%). The extraction of the latter elements is considerably harder, than that of iron and during the bloomery smelting process they usually remain in the slag phase.

Bloomery iron clots present in the lumps of smelting slag were another important object of the examination. They are formed of as-extracted iron therefore their study gives valuable information on the initial elemental composition of the bloomery iron and its microstructure.

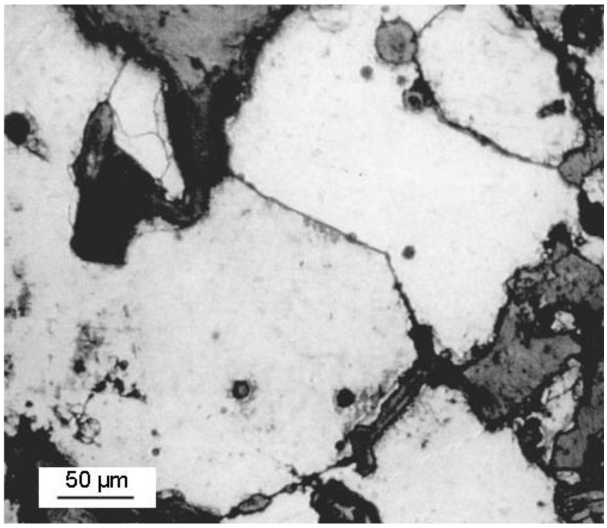

Fig. 1. A microphoto of a section of iron clot embeded in bloomery slag, sample Nr. 04.15-1 from Lieporiai. Microstructure shows coars ferrite grains (white) surrounded by fayalite slag (variable gray). The sample is etched with natal (optical microscope, reflected light)

Table 1. Analyses of trace elements in bog iron ores, iron clots, smelting slags and in some manufactured products, wt.%

Element	Bog iron ore (7 samples)		Iron clots (7 samples)		Smelting slag (3 samples)		Products		
	Average	Interval	Average	Interval	Average	Interval	Bloom from Kernave, $2^{nd} – 3^{rd}$ c.	Axe from Lazdininkai, 10^{th} c.	
								Metallic matrix	Forge weld
Cu	0.004	0 – 0.007	0.026	0.011 – 0.050	0.005	0.002 – 0.008	n.d.	tr.	0.025
Ni	0.008	0.001 – 0.029	0.009	0 – 0.029	0.002	0.001 – 0.002	0.004	0.010	0.030
Co	0.037	0.016 – 0.054	0.092	0.075 – 0.126	0.030	0.001 – 0.057	0.013	tr.	0.025
As	0.017	0.003 – 0.042	0.115	0.005 – 0.165	0.024	0.001 – 0.047	0.063	0.120	1.640
P	0.886	0.218 – 2.110	0.432	0.010 – 1.648	5.163	1.119 – 9.207	0.151	0.225	0.080
S	0.091	0.004 – 0.106	0.005	0 – 0.010	0.026	0.001 – 0.052	0.003	0.020	n.d.
Mn	0.400	0.200 – 0.574	0.019	0.006 – 0.051	0.446	0.412 – 0.481	n.d.	tr.	tr.

n.d. – not detected; tr. – traces.

Treatment of raw bloom results in drastic changes of as-smelted iron. Particularly, smiting procedures lead to the welding of iron particles, the expelling of slag, the changing of an initial microstructure of a bloom and even to some changes of elemental composition of metal. In order to avoid the influence of these processes, the iron clots present in smelting slag and not affected by any treatment have been selected for examination. However, they contained plenty of slag. A microstructure section of iron clot present in smelting slag is shown in Fig. 1. The mass of iron clots ranges from several to some tens grams. The samples have been prepared from iron clots found in the fallowing iron production sites: Jūrė of Kazlų Rūda district ($18^{th} – 19^{th}$ c.), Pučkornė ($16^{th} – 17^{th}$ c.) and Vaitakarčmis ($16^{th} – 17^{th}$ c.), both of Varėna d., Lieporiai of Šiauliai city ($4^{th} – 6^{th}$ c.), Paplienijis of Telšiai d. ($3^{rd} – 5^{th}$ c.), Lazdininkai settlement of Kretinga d., (about 2^{nd} c.) and Kereliai hill-fort of Kupiškis d. ($2^{nd} – 3^{rd}$ c.).

The analysis of the iron clots has revealed that the average contents of arsenic, cobalt and copper (0.115 wt.% As, 0.092 wt.% Co, 0.026 wt.% Cu) in the as-extracted iron are much larger than in the ores, whereas the contents of sulphur (0.005 wt.%) and phosphorus (0.432 wt.%) in the clots are considerably less than in the ores. Only nickel is found in negligible quantities, in approximate equal amounts in ores and in the clots (Table 1).

Slag formed by iron ore smelting in bloomery furnace consists mainly of compound fayalite (Fe_2SiO_4) and of a glass phase formed of non-reduced gangue minerals of ore, fuel (charcoal) ashes and other possible additions. An examination of the bloomery slags has shown that the glass phase occupies approximately 10 % – 15 % of the whole [21]. Usually bloomery slags contain also some amount of wustite (FeO) and small contents of trace elements distributed among slag phases.

The samples for the examination of trace elements had been prepared from the same lumps of slag that contained iron clots examined in this work. Thereby, it was ensured that for the analysis of slag and iron clots, the samples of the same smelting were used. As expected, the amounts of copper and nickel are very little (Table 1). A slightly larger content of cobalt (av 0.03 wt.%) is found, and an average content of phosphorus exceeds even 5 wt.% (limits 1.119 wt.% – 9.207 wt. %).

4. DISCUSSION

This study was undertaken to reveal the content of trace elements (Cu, Ni, Co, As) and minor elements (P and S) in bloomery iron produced in Lithuania. It is also important to know a compositional comparison of those elements in bog ore, in extracted iron and in smelting slag. An element way into smelted iron depends on both oxide stability and smelting process parameters. Free energy changes of formation of oxides show that Cu, Ni, Co and As could be reduced by carbon more easily than iron [22]. The reduced element goes into solution in the extracted iron. Thus, the bloomery iron would commonly involve the greater part of trace elements (Cu, Ni, Co, As) available in iron ores. Therefore, the concentration of trace elements in smelted iron is considerably higher than in the used ores. Besides, it should be noted that the amount of metal produced in the bloomery smelting process amounts only to ca 16 % – 18 % of the weight of iron available in the smelted ore [23]. The rest of trace elements stay in smelting slag. Compositional comparison of trace elements found in the Lithuanian bog ores, in extracted iron and in smelting slag is shown in Fig. 2.

It is interesting to note that similar results were received in the experimental direct iron smelting. In 2004 the authors of the study carried out an experimental iron smelting under outdoor conditions in a bloomery furnace. For the smelting, the local bog ore excavated in the fields of Žiūriai–Gudeliai village (Vilkaviškis district) was used. After the procedures of sluicing and burning the ore contained ca 75 wt.% – 76 wt.% Fe_2O_3 (ca 52.4 wt.% – 53.5 wt.% Fe) and ca 13 wt.% – 15 wt.% SiO_2. The content of other additions amounted to ca 8 wt.% – 10 wt.%. In the smelting process charcoal of deciduous trees was used, not

Table 2. Chemical analyses of ore, iron clots and slag from the experimental smelting, wt %

Element	Bog iron ore		Iron clots		Smelting slag	
	Average	Interval	Average	Interval	Average	Interval
Cu	0.006		0.014		tr.	
Ni	0.003		0.017		0.005	tr. – 0.010
Co	0.105	0.100 – 0.110	0.211	0.200 – 0.217	0.078	0.075 – 0.081
As	0.023	0.021 – 0.024	0.234	0.212 – 0.243	n.d.	
P	1.381	1.292 – 1.470	3.606	2.739 – 4.372	1.688	1.458 – 1.866
S	0.066	0.058 – 0.078	0.010	0.002 – 0.016	0.015	0.013 – 0.018
Mn	0.723	0.443 – 1.422	n.d.		2.115	1.883 – 2.407
Zn	0.010	0.008 – 0.011	n.d.		0.005	0.002 – 0.008
Cr	0.006	0.005 – 0.007	0.003		0.012	0.009 – 0.014
Mo	0.004	tr. – 0.007	0.002		tr.	
V	0.010	0.004 – 0.016	n.d.		0.012	0.007 – 0.018

n.d. – not detected; tr. – traces.

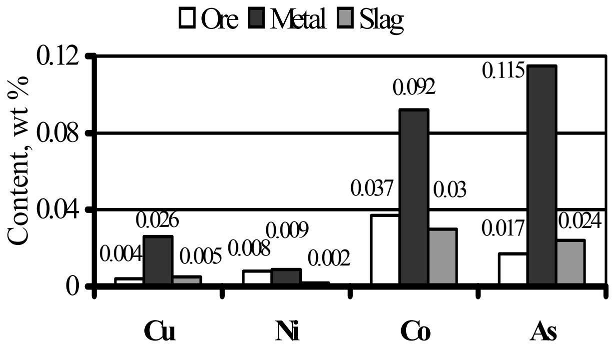

Fig. 2. Compositional comparison of Cu, Ni, Co and As in bog iron ores, extracted iron and in smelting slags

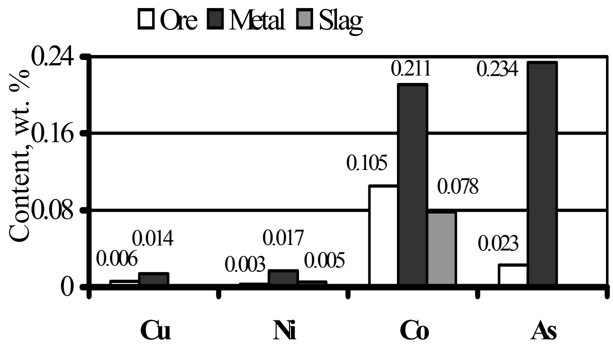

Fig. 3. Experimental smelting. Compositional comparison of Cu, Ni, Co and As in bog iron ore, extracted iron and in smelting slag

flux materials. The experimental smelting resulted in an iron-rich slag with dispersed pieces of the extracted iron imbedded in the slag. The iron clots had various content of carbon from ca 0.01 % wt.% C (low carbon ferrite) up to the cast iron level. The total weight of reduced iron amounted to ca 0.23 kg. Although the yield was rather poor, but iron was produced as a result of experimental bloomery smelting. The results of chemical analyses of ore, iron clots and slag from the experimental smelting are given in Table 2. Compositional comparison of trace elements in bog ore, extracted iron and slag from the experimental smelting is shown in Fig. 3.

The analyses of elemental composition have revealed the negligible content of copper and nickel in both the Lithuanian bog ores and extracted iron. Atomic radii of copper and nickel are relatively similar to that of iron; therefore, they easily go into substitutional solid solutions in the austenite or ferrite lattice. Inordinately little amount of these elements in iron does not have any marked influence on the metal microstructure or its mechanical characteristics. However, in the forge welds segregation of copper and nickel has been found (Table 1). The examined iron clots also demonstrate the negligible amount of sulphur, while bog ore samples contain a notable level of this element. Presumably, the greater part of sulphur has been burnt out during the smelting process and the rest of it has stayed in slag.

The overall content of cobalt in examined iron varies from 0.075 wt.% to 0.126 wt.% (av 0.092 wt.%). Cobalt has a high solubility in α- and γ-iron but a weak ferrite strengthening tendency. An alloying effect on ferrite hardness begins only from about 0.5 % – 1 % of cobalt content in iron. Thus, much larger amounts (5 % to 20 % Co) are employed in modern high-alloy steels [24]. Consequently, cobalt content found in the studied clots is too low to have an influence on the mechanical properties of iron. However, it can be an important factor in provenance studies of bloomery iron artifacts.

Arsenic and phosphorus, in particular, are present at significant levels (av 0.115 wt.% As and 0.432 wt.% P) in the examined iron clots. Arsenic is not volatile under bloomery smelting conditions, therefore, its greater part available in ore enters the extracted iron. But a good deal of phosphorus goes into the slag. R. F. Tylecote suggests that the ratio of phosphorus in the slag to that in the metal depends on both the phosphorus content in ore and the parameters of smelting process [13]. Both arsenic and phosphorus have limited solid solubility in ferrite and stabilize it. Presence of carbon reduces the solubility of arsenic in iron. J. Piaskowski asserts that there exists an inverse correlation between the amounts of arsenic and carbon in iron [25]. Arsenic distribution in ferrite and pearlite matrix in the iron clot from Kereliai is presented in Fig. 4. It has been found that phosphorus and arsenic demonstrate a high segregation in iron, thus resulting in a formation of banded structure in forged and rolled iron artefacts [1, 9, 13, 25, 26].

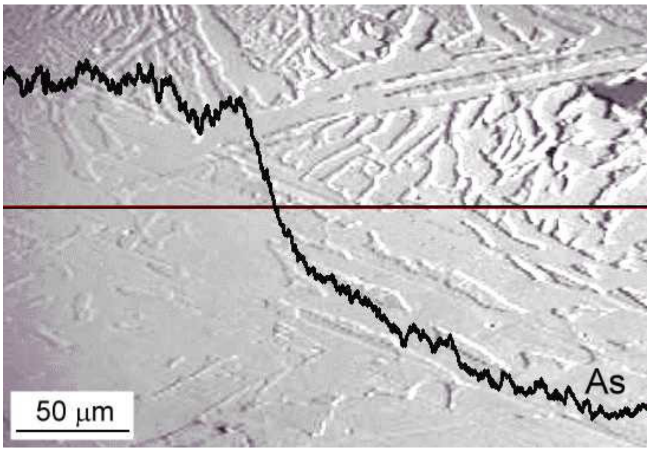

Fig. 4. Kerelian iron clot Nr. 03.15-1. SEM, back scattered electron image with As K_α line scan. Arsenic content varies from 0.19 wt.% in pearlite up to 0.37 wt.% in ferrite

The ratio of phosphorus content in examined iron clots, ores and slags demonstrates that smelters were capable of producing rather good iron from ores containing comparatively a high amount of phosphorus. During the experimental smelting the following result has not been obtained. The reason could be a lack of flux materials in the charge and comparatively high (over 1300 °C) temperature of the smelting process.

In general, phosphorus and arsenic are detrimental impurities in iron. On the other hand, some amounts of As and P (due to the solid solutions in iron) help increase the strength and hardness of the low-carbon iron. Finally, phosphorus and arsenic, in particular, may assist in an identification of provenance of iron artifacts.

5. CONCLUSIONS

1. Analyses of elemental composition of the ore samples have revealed negligible content of copper and nickel in the Lithuanian bog iron ores. Average content of Cu is scarcely 0.004 wt.% and that of Ni amounts to 0.008 wt.%. Rather larger contents of cobalt (av 0.037 wt.%) and arsenic (av 0.017 wt.%) have been found there. It is important to note that in the most samples of the Lithuanian bog iron ore there is a relatively large amount of phosphorus reaching in some ores studied even more than 2 wt.% (the ore from Merkinė). Besides, in the ore samples there were also found small quantities of S, Cr, Zn, Mo, Sr, Zr, Pb and Sn.
2. In the bloomery smelting process copper, nickel, cobalt and arsenic reduced from their oxides go into the solution in extracted iron. Thus, the results of the elemental analyses of the Lithuanian raw bloomery iron (iron clots entrapped in smelting slag) show that the average amounts of arsenic, cobalt and copper (0.115 wt.% As, 0.092 wt.% Co, 0.026 wt.% Cu) in as-extracted iron are much larger than in the ores, whereas the contents of sulphur (0.005 wt.%) and phosphorus (0.432 wt.%) in the clots are considerably lower than in the ores. Only negligible amounts of nickel have been found in iron clots. Certain segregation of trace elements in a metallic matrix and forge welds of the examined artifacts are also observed.
3. The amount of trace elements (Cu, Ni, Co and As) in bloomery slags is much lower than that in the examined iron clots. And higher concentrations of sulphur (0.026 wt.%) and phosphorus (5.163 wt.%) in slag demonstrate that the optimum smelting parameters help in reduction of sulphur and phosphorus contents in bloomery iron.

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