Energy dispersive X-ray analysis (SEM-EDS) on slag samples from medieval bloomery workshops – the role of phosphorus in the archaeometallurgy of iron in Somogy County, Hungary

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ABSTRACT

Several archaeometrical investigations were carried out on archaeological iron artefacts and iron blooms in recent years and it can be stated that although P is an avoided element in modern industry, iron with enhanced phosphorus content (P-iron) was used in different parts of the world in medieval times. We have conducted several smelting experiments using copies of excavated, embedded type of furnace smelting P-rich bog iron ores from Somogy County. P-iron was regularly extracted in these experiments. Nevertheless, there is very little archaeometrical evidence of producing and using P-iron in the Carpathian basin.

Based on our earlier experimental observations, the main goal of our recent study was to answer the question of whether phosphorus has a role in the archaeometallurgy of iron in the Carpathian basin, especially in Somogy County.

In order to answer this question we have carried out SEM-EDS analyses on iron slag samples originating from five excavated bloomery workshops from the 8th-10th centuries. P appeared in 2-5wt% in these samples, and the typical microstructure of the slag samples was needled tricalcium-phosphate. The slag samples also contained a high amount of Ca (5-21wt%), which was situated mostly in the olivine phase.

Concerning the results of SEM-EDS analysis of the slag samples we can state that P-rich local bog iron ores were smelted during the bloomery process in Somogy County and adding limestone to control the P content of the resulted iron bloom can also be inferred.

KEYWORDS

bog iron ore, controlling P content, P-iron, SEM-EDS.

Introduction

The P-iron

In recent years it has been indicated by archaeometric investigations that phosphoric iron was widely used in different parts of the world in medieval times (Tylecote 1986, Buchwald 2005, Kumar & Balasubramaniam 2002, Preßlinger & Eibner 2009). The term, phosphoric iron (P-iron), is used in archaeometallurgy for iron containing more than 0.1wt% (e.g. Vega et al 2003). Based on numerous studies of P-iron, it can be seen that P was the second most important element in the archaeometallurgy of iron after carbon.

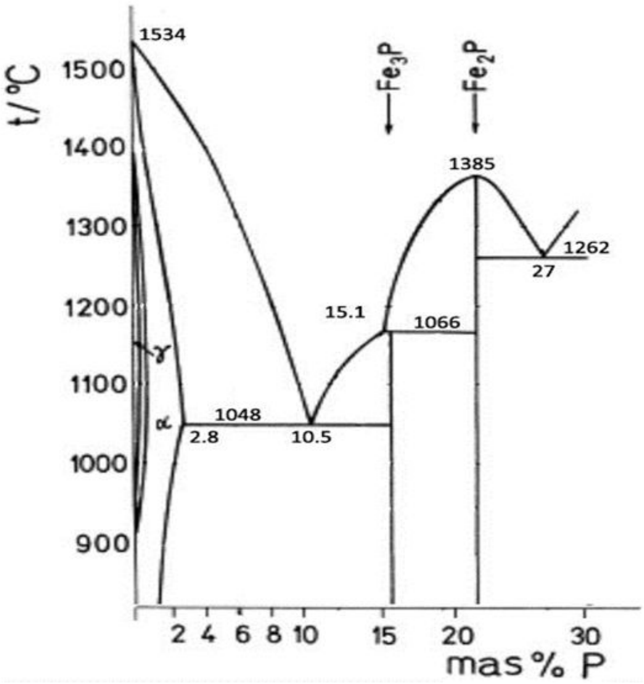


Fig. 1. Fe-P dual phase diagram.

P is an avoided element in the modern steel industry. Its detrimental effects include various forms of embrittlement, which reduce the toughness and ductility of steel. P is a ferrite stabilizing element, which can be dissolved up to the maximum of 2.8wt% in ferrite, as the Fe-P dual phase diagram shows in Fig. 1. (Okamoto 1990).

The melting point of the eutectic of Fe and P (Fe-Fe_3P, steadite) is 1048°C. Above a certain temperature and the P content (1048°C and P=2.8 wt%) molten phase appears on the grain boundaries. P-iron of high P content is not

forgeable as the Fe-Fe_3P eutectic melts on the grain boundaries above the eutectic temperature. On the other hand, P-iron of low P content cracks during cold-working due to its reduced ductility (cold shortness). In our P-iron bloom forging experiments we observed that if the amount of the Fe-Fe_3P eutectic is low, it is possible to forge weld the ferrite grains after the molten eutectic effuses just as the molten slag does.
Nevertheless, P has positive effects as well. P-iron was used for decorative purposes in the case of pattern-welded sword or knife blades in medieval times because P increases the corrosion resistance (Tylecote & Gilmour 1986, Thomsen 1989). The strengthener effect of P is another positive feature which has been properly examined (Goodway & Fisher 1988). This effect was also utilized in the cutting edge of knife blades (Blakelock & McDonell 2007).

One of the three most important iron smelting sites of medieval Hungary is Somogy County, where several bloomery workshops have been excavated from the Avar and Árpád age (6^{th}-13^{th} century) (Gömöri 2000). High P content is a common feature of recent bog iron ore deposits in Somogy County, thus it can be inferred that mainly P-iron was produced in this area.

Archaeological background

Archaeological research of the medieval iron culture of Somogy County started when a large iron smelting centre was found in Zamárdi from the Avar age. The systematic excavations of the bloomery workshops of the Árpád age started with the excavation of Somogyvámos-Gyümölcsény, where furnaces from the 10^{th} century were found. During archaeological field surveys it was possible to identify and explore the most important archaeometallurgical sites in Somogy County.

The most important bloomery workshops were excavated in Somogyfajsz, dated to the second half of the 10^{th} century and in Bodrog-Alsóbű dated also to the 10^{th} century. The Bloomery Museum was erected over the excavated workshop in Somogyfajsz supported by Dunaferr Ltd (Gömöri 2006). This museum is still open for visitors. In the garden of the museum, smelting experiments and iron smelting camps take place each year. Important archaeological excavations were also conducted in Lábod-Petesmalom and in the Gyékényes-Lankóci forest, where bloomery workshops from the Avar age were found.

During archaeological field surveys, traces of iron smelting were found near former brooks, which are mostly marshes nowadays. Iron slags and bog iron ores were also found in several parts of Somogy County. As a result of the field surveys and the excavations, we now know more than 50 archaeological deposits (mostly slag deposits) connected to the period iron smelting activity in Somogy County (Költő 1999).

Experimental background

We have found bog iron ore deposits in Somogy County. Samples of bog ores were analysed using XRF and XRD methods. We established that these bog ores contain a high amount of P (P_2O_5=2-7wt%) and high CaO (CaO=3-22wt%), which seems a common property of bog ores from this region (paper under publication about this topic).

Several smelting experiments were conducted using P-rich bog iron ores collected in Somogy County. In these experiments copies of the so-called "Fajszi-type" furnace were used. The Fajszi-type furnace was an embedded furnace of the 10^{th} century, excavated in Somogyfajsz. We carried out metallographical and SEM-EDS investigations on samples of the extracted slag and iron bloom (Thiele 2010, Thiele 2012). Experiments were also carried out under laboratory conditions using laboratory models (Thiele & Dévényi 2012). Smelting P-rich bog iron ores containing a low amount of CaO collected in Somogy County yielded P-iron blooms (P=0.5-3.5wt%) both in smelting experiments and laboratory model experiments. In these iron blooms we could observe the typical microstructures of the P-iron (coarse-grained ferrite and a varying amount of Fe-Fe_3P eutectic on the grain boundaries).

At this point we would like to refer to Crew's and Salter's experimental work whereby they also smelted P-rich bog iron ores (P_2O_5=3wt%) originating from iron ore deposits of different parts of Shopshire, Britain. P-iron was extracted with a P content of 0.02-16wt% (Crew 2000, Salter & Crew 1998). They also found that the P content of the bloom depends on the air rate (Crew & Salter 1993) supplied during the smelting process.

The effect of lime

The P_2O_5 content of the slag and the C content of the solid iron bloom take part in an exchange reaction, which results in the formation of P dissolved in the iron bloom, and CO bubbles appearing in the molten slag. In the solid bloom the C diffuses outwards quickly, whereas the P diffuses inwards more slowly. When the P content of the surface has reached a certain volume, the liquid Fe-Fe_3P eutectic phase appears between the molten slag and the solid iron. The speed of P diffusion can be accelerated through that liquid phase.

The higher the basicity (CaO/SiO_2) of the slag (which is affected by the chemical composition of the iron ore, adding limestone, and the charcoal:ore ratio), the lower the activity factor of P_2O_5 in the slag due to the formation of a complex compound of $3CaO \cdot P_2O_5$ (tricalcium-phosphate), hence the lower P content dissolved in the iron. In the case of slag with relatively high basicity, the P content is low in the bloom without the formation of Fe-Fe_3P eutectic phases.

Another positive effect of charging limestone into the furnace is the increased iron yield because Fe can be substituted by Ca in the olivine phase of the slag.

There is another question: the influence of increased basicity on the viscosity of the slag under metallurgical thermal conditions in bloomery furnaces. It is possible that the temperature was high enough in some areas of the hearth of the medieval furnaces to influence the viscosity and formation of slag advantageously.

In our smelting experiments we stated that smelting bog iron ores containing a relatively high volume of CaO or charging limestone decreases the P content of the iron bloom (Török & Thiele 2013). The CaO content of the ash from the charcoal can also increase the basicity of the slag (Crew 2007).

Questions and goals

There is only very little archaeometrical evidence of producing P-iron in the Carpathian basin. Although several iron slag samples from different archaeological excavations of Hungary have been examined (Gömöri & Török 2002, Török 2010, Török & Kovács 2011), the presence of P was negligible. However, slag samples from Somogy County, where recent P-rich bog iron ore deposits were widespread, were not examined thoroughly enough. One of the excavations of Somogy County, from which some iron ore and iron bloom samples have been examined, was conducted in Somogyfajsz. Based on the results of these analyses (Ágh & Gömöri 1999) it can be seen that both the iron ores smelted and the iron blooms produced in this workshop had a high P content. The examined four iron blooms had a P content of a range of 0.4-1.22wt%.

Based on our experimental observations, the main goal of our recent study was to answer the question: does phosphorus have a role in the archaeometallurgy of iron in Somogy County?

Methods and results

Archaeological field surveys and collecting slag samples

During archaeological field surveys in Somogy County we visited the most important excavated bloomery workshops and slag deposits, collecting slag samples for further examination. Samples were collected from the following five Avar and Árpád-age archaeometallurgical sites: Bordog-Alsóbű (S1), Somogyvámos (S2), Somogygeszti (S3), Alsóbogát (S4) and the Bloomery Museum of Somogyfajsz (S5), locations can be seen in Fig. 2.

On a morphological basis, archaeometallurgical studies differentiate tap slag and cinder. Tap slag often froze outside the furnace after slag tapping, or at the bottom of the furnace after trickling down between the charcoal pieces. As for the morphology of the tap slag, bunch-like flowing can usually be seen on the surface with small blow holes inside.

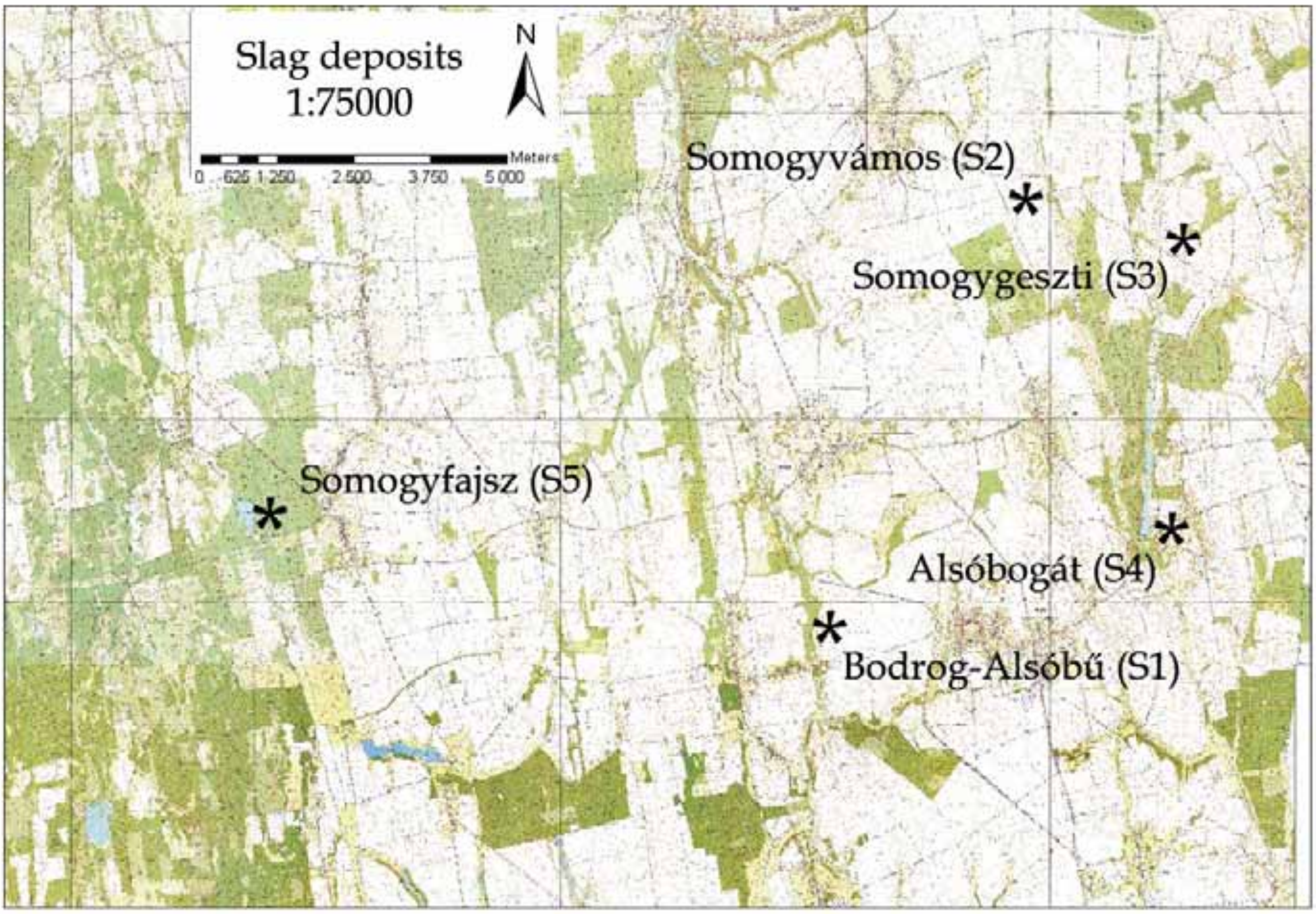


Fig. 2. Location of the excavated bloomery workshops and slag deposits.

The other group of bloomery slags is cinder, which usually remains inside the furnace up to the end of the smelting process. They are sponge-like, full of gas lunkers and are of lower density than tap-slag.

In our research examining tap slag samples is more important as this kind of slag was in direct connection with the iron bloom, so chemical reactions could take place between the molten slag phase and the solid iron bloom (e.g. P-distribution). We collected only tap slag samples.

SEM-EDS analysis of slag samples

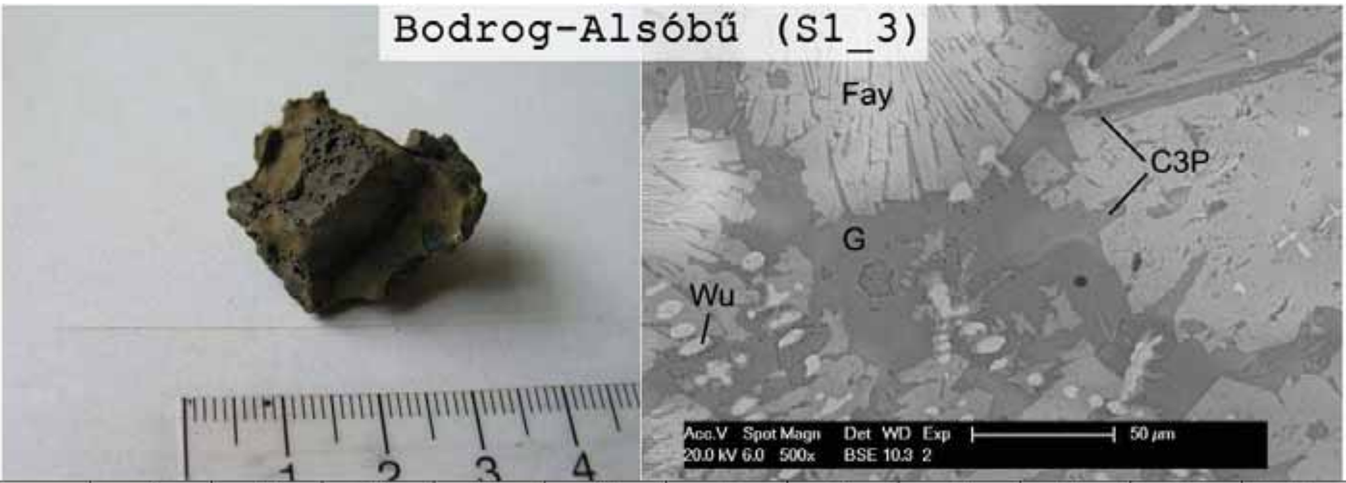
We chose some typical slag samples from each slag deposit for further examination. We examined the microstructure and the chemical composition of the samples using a Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray Spectrometer (EDS). To identify the different phases, we also measured their chemical composition. The chemical compositions of the iron inclusions in the slag samples were also measured. Nevertheless, the results do not give any representation of the exact chemical composition of the iron bloom related to the slag sample. The results of the SEM-EDS analyses can be seen in the following pictures (Pic. 3-11.)

	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Fay	28.83	0.00	1.77	0.08	21.69	0.55	0.16	11.29	0.11	2.92	32.60
C3P	22.06	0.45	0.27	0.17	8.40	18.33	0.19	43.18	0.74	1.05	5.16
G	24.60	1.00	0.00	8.21	27.83	3.87	4.60	17.26	0.89	0.36	11.38
Av	20.00	0.27	0.44	4.05	21.18	2.26	1.94	13.59	0.61	2.39	33.26

Fig. 3. Slag sample S1_1 from Bodrog-Alsóbű bloomery workshop. Left: The sample. Right: SEM picture of the sample and the observed microstructures. Bottom: Table of the EDS results. In the table elements in wt%, Wü – wustite, Fay – fayalite, C3P – tricalcium-phosphate, G – glass, Av – average, Fe(inc) – iron inclusion.

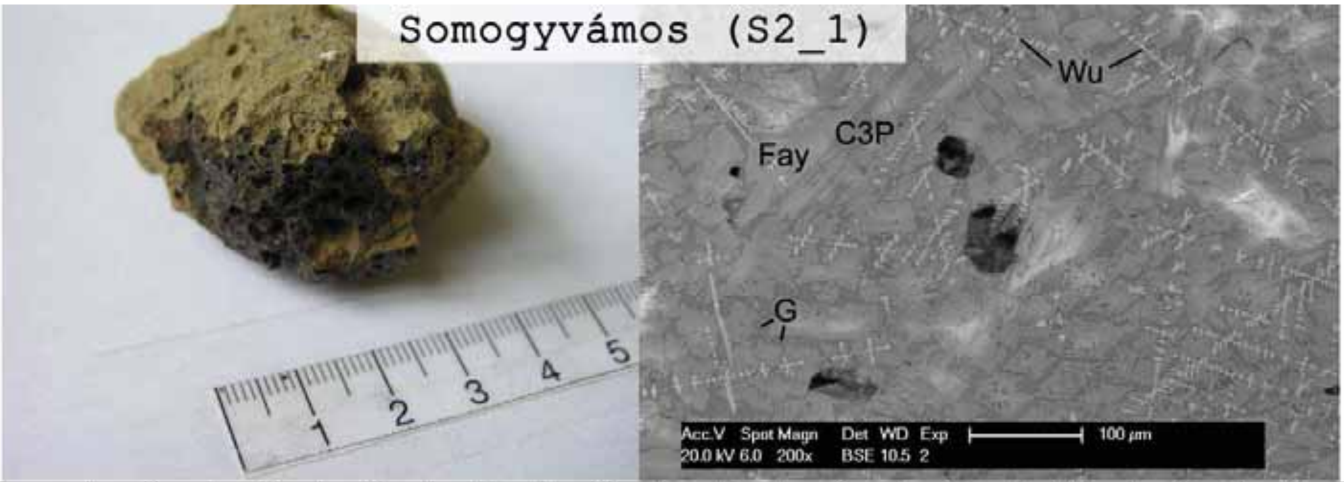
	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
G	26.91	0.81	0.97	2.22	19.39	2.91	1.11	20.84	0.30	2.50	22.03

Fig. 4. Slag sample S1_2 from Bodrog-Alsóbű bloomery workshop.



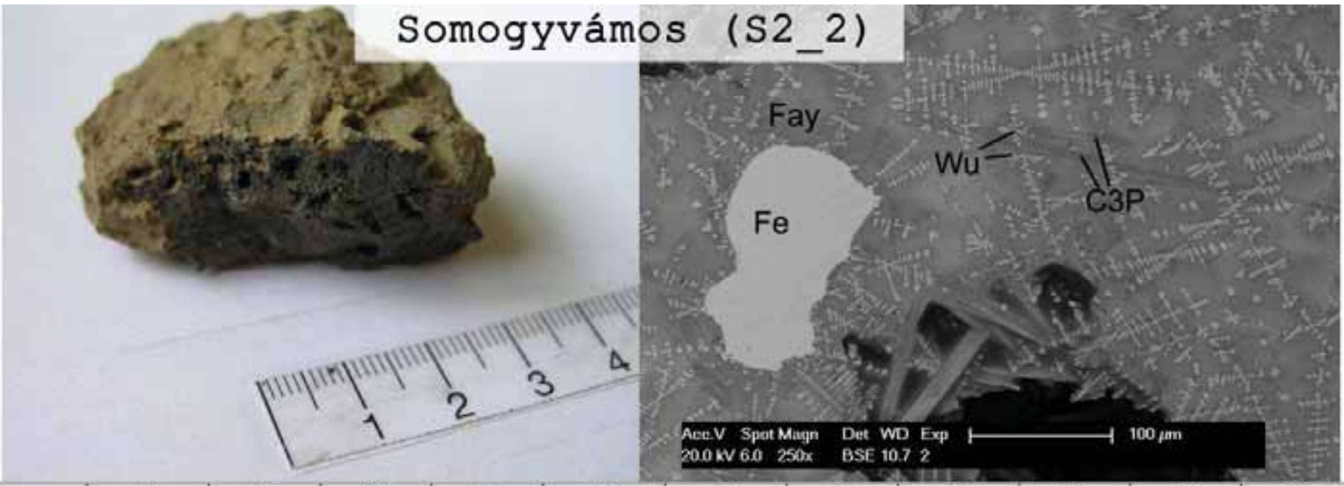
	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	12.44	1.45	1.16	2.51	1.60	0.70	0.21	0.55	2.33	0.83	76.19
Fay	26.70	0.00	2.43	0.00	21.60	0.49	0.00	3.71	0.08	4.16	40.82
C3P	31.31	0.78	0.57	0.37	2.20	23.72	1.13	34.58	0.47	0.74	4.14

Fig. 5. Slag sample S1_3 from Bodrog-Alsóbű bloomery workshop.



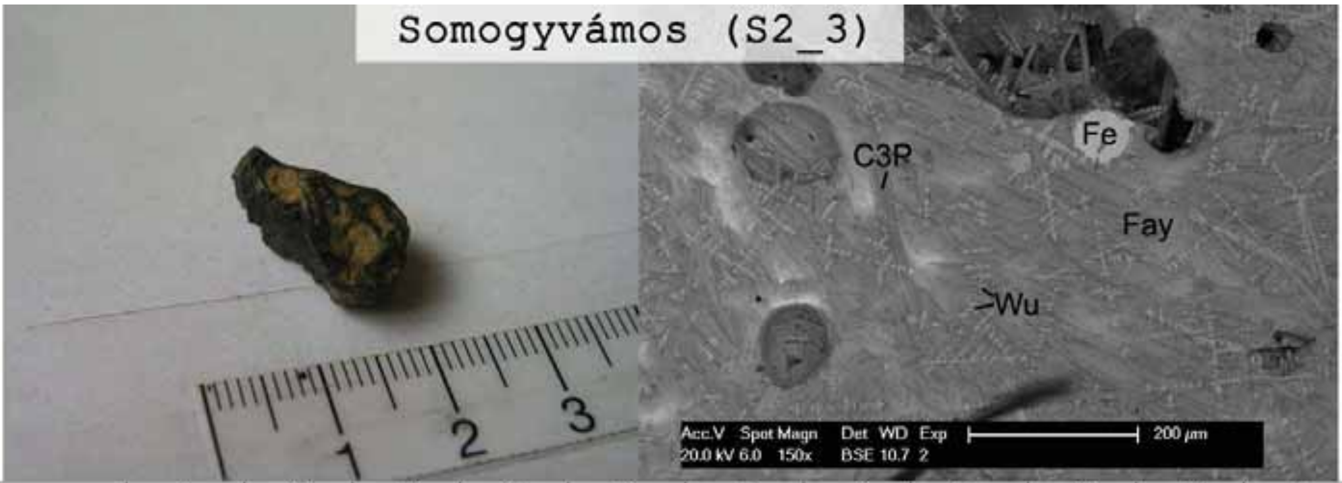
	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	12.62	1.69	1.44	2.02	2.75	0.79	0.19	1.27	0.73	0.61	75.90
Fay	19.84	0.26	0.92	4.10	16.69	1.25	0.11	20.86	0.20	3.14	32.63
C3P	30.76	0.00	0.08	0.26	8.12	18.05	0.32	38.30	0.59	0.71	2.81
G	23.74	0.47	0.08	10.59	18.95	2.90	1.82	15.08	0.74	1.34	24.27
Av	20.84	0.33	0.79	2.50	16.02	4.51	0.59	20.00	0.34	2.28	31.80

Fig. 6. Slag sample S2_1 from Somogyvámos bloomery workshop.



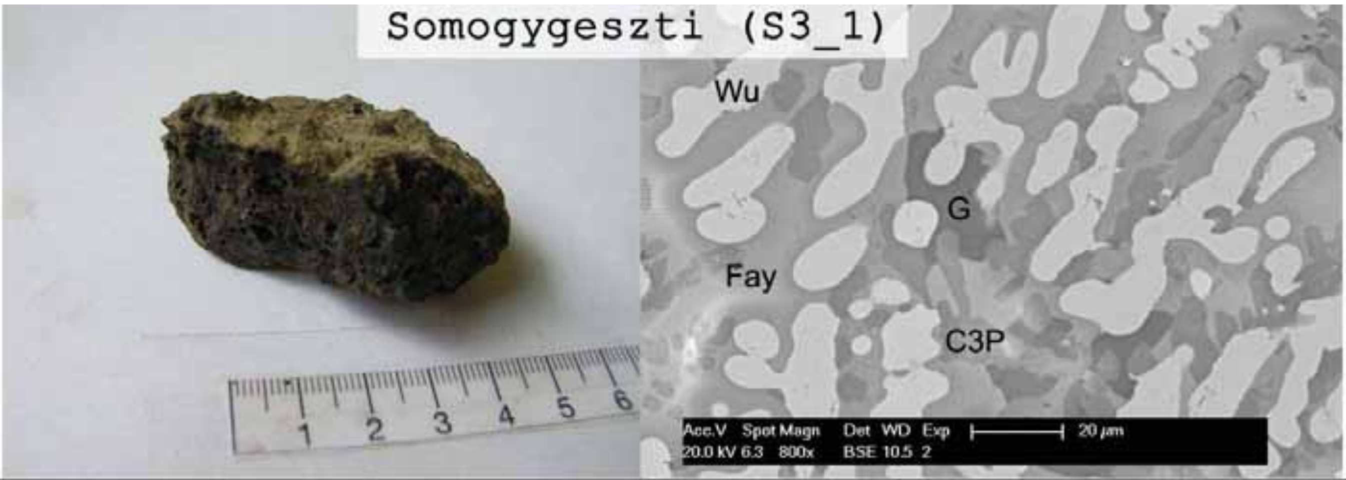
	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	13.94	2.14	1.84	1.70	2.20	0.91	0.33	1.30	0.23	2.01	73.40
Fay	22.99	0.45	0.98	3.15	20.94	3.33	1.25	17.15	0.41	2.96	26.39
C3P	23.17	0.00	0.12	0.39	8.29	17.82	0.44	44.30	0.35	0.64	4.48
Fe	-	-	-	-	-	-	-	-	-	-	100
Av	20.13	0.17	0.61	2.67	16.29	4.56	1.13	17.56	0.43	2.78	33.68

Fig. 7. Slag sample S2_2 from Somogyvámos bloomery workshop.



	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Fe (inc)	-	-	-	-	-	-	-	-	-	-	100
Av	20.98	0.51	0.47	2.49	15.93	2.30	0.70	17.99	0.38	2.99	35.25

Fig. 8. Slag sample S2_3 from Somogyvámos bloomery workshop.

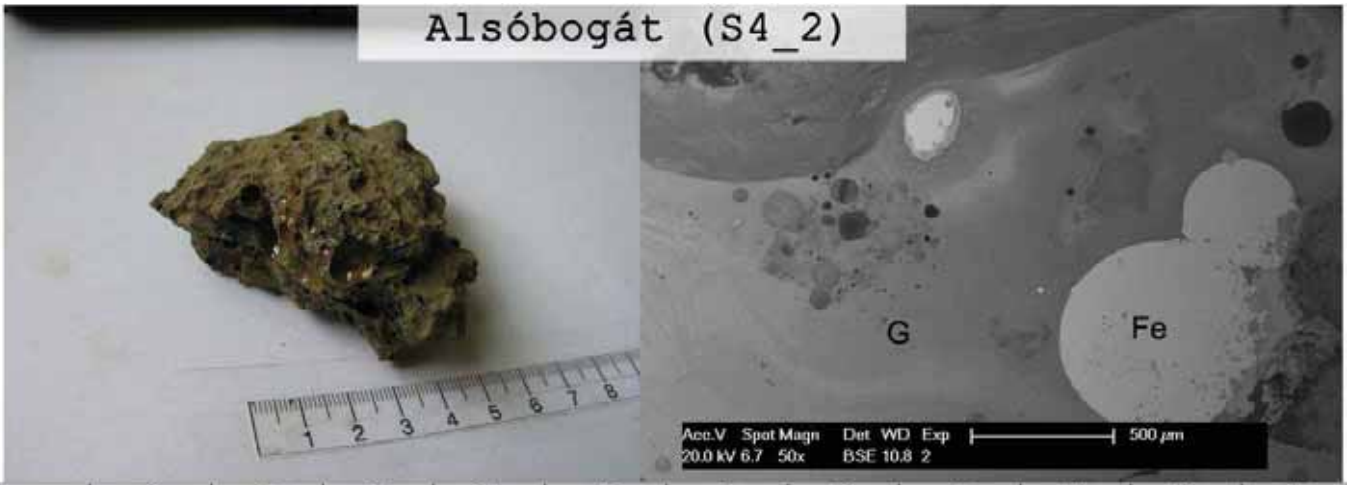


	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	16.09	2.21	1.49	1.27	1.22	0.50	0.07	0.56	0.29	2.50	73.82
Fay	24.26	0.49	1.11	0.57	19.68	0.89	0.25	21.89	0.16	3.98	26.72
C3P	30.84	0.53	0.35	1.15	8.30	15.47	0.33	36.42	0.07	1.70	4.84
G	21.93	0.71	0.19	18.52	22.93	0.45	25.07	0.97	0.28	0.51	8.44
Av	18.61	0.00	0.34	2.98	10.21	3.33	1.41	12.31	0.34	3.37	47.11

Fig. 9. Slag sample S3_1 from Somogygeszti bloomery workshop.

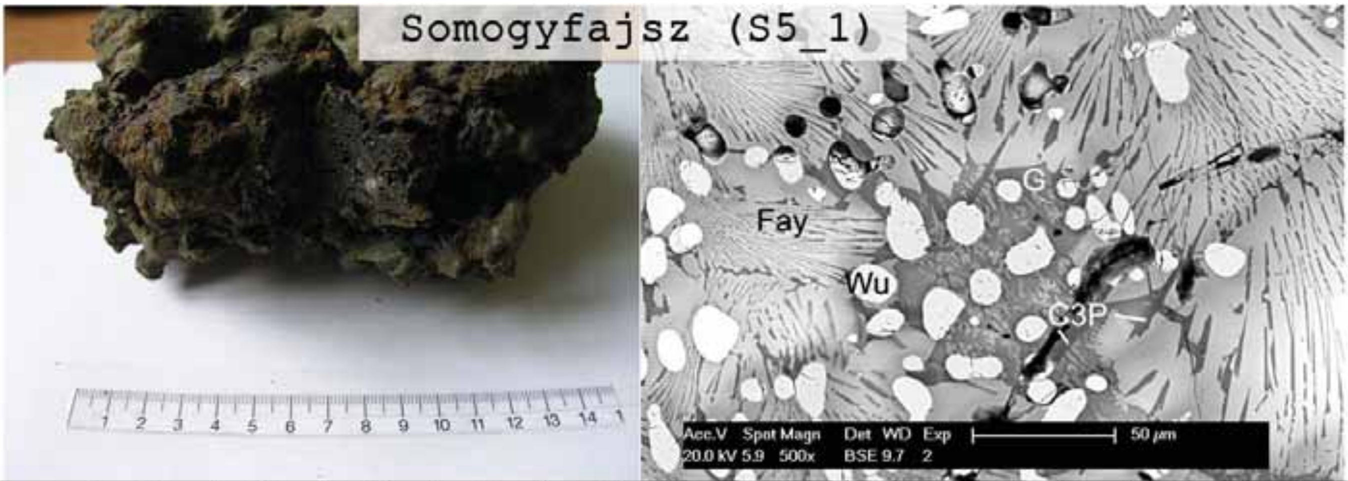
	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	14.97	0.00	0.00	0.51	0.67	0.27	0.36	0.42	0.61	0.47	81.72
Fay	30.71	0.25	2.01	2.98	22.83	0.20	0.63	5.32	0.23	0.43	34.40
G	34.25	0.86	1.51	4.77	28.09	0.88	1.88	8.81	0.32	0.15	18.47

Fig. 10. Slag sample S4_1 from Alsóbogát bloomery workshop.



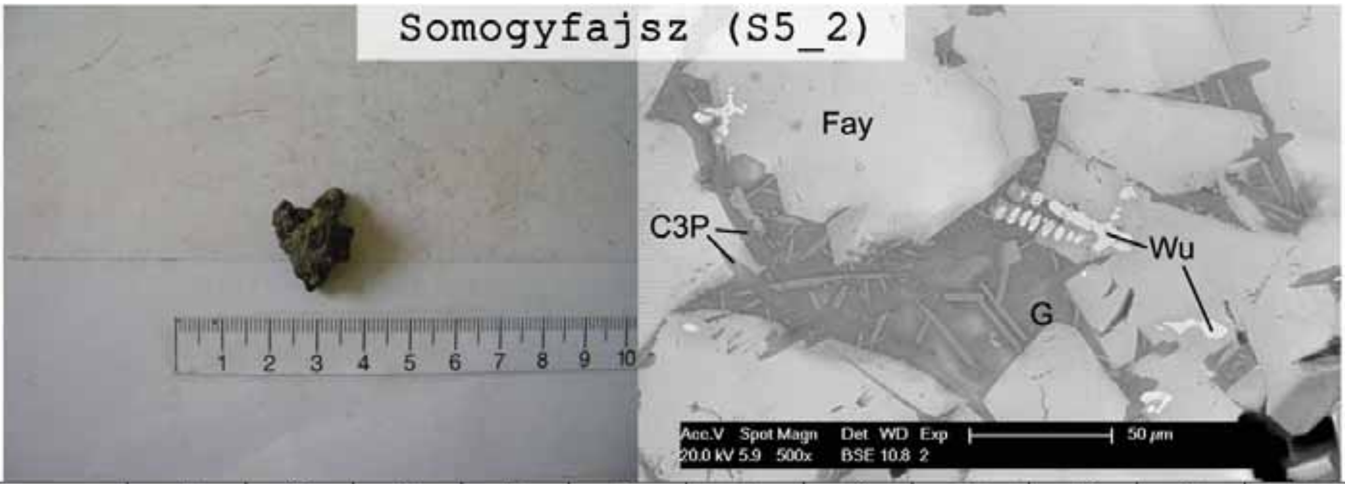
	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Fe	–	–	–	–	–	2.27	–	–	–	–	97.73
G	29.62	0.89	1.23	5.97	34.58	0.00	3.82	4.95	0.59	0.66	17.70

Fig. 11. Slag sample S4_2 from Alsóbogát bloomery workshop.



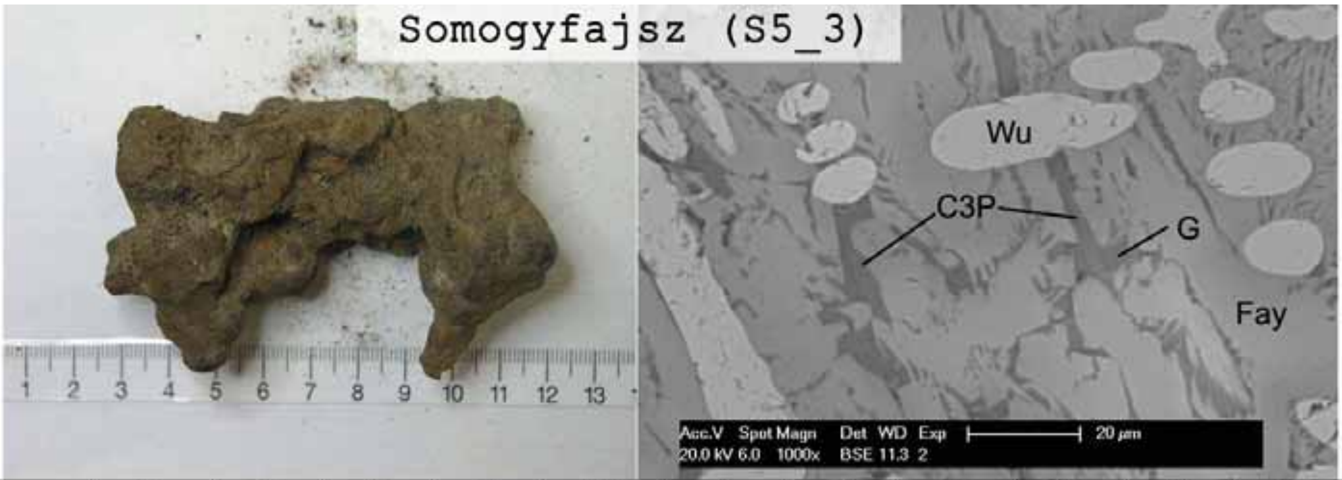
	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	12.57	1.39	0.90	1.21	1.05	0.48	0.16	0.18	0.24	1.47	80.34
Fay	21.23	0.26	0.47	0.00	20.08	0.45	0.19	5.10	0.13	4.11	47.98
C3P	25.23	0.71	0.31	0.00	2.16	23.16	1.23	38.62	0.29	0.82	7.49
G	23.14	0.54	0.00	7.96	21.48	3.03	2.56	14.11	1.00	1.59	24.60
Fe	–	–	–	–	–	–	–	–	–	–	100
Av	16.68	0.30	0.50	1.32	13.38	3.14	0.47	7.03	0.26	3.83	53.10

Fig. 12. Slag sample S5_1 from Somogyfajsz bloomery workshop.



	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	12.89	0.18	0.00	0.78	1.72	0.38	0.21	0.61	0.72	0.99	81.53
Fay	19.84	0.18	0.79	0.09	18.82	0.25	0.13	2.58	0.08	3.75	53.49
C3P	24.70	1.03	0.11	0.97	2.11	23.19	1.39	38.56	0.76	0.61	6.57
G	26.03	1.96	0.30	13.82	25.39	1.69	7.36	11.05	1.19	0.16	11.05
Fe (inc)	-	-	-	-	-	0.84	-	-	-	-	99.16
Av	19.10	0.36	0.48	3.12	17.36	2.30	1.04	6.06	0.52	3.17	46.4

Fig. 13. Slag sample S5_2 from Somogyfajsz bloomery workshop.



	O	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
Wu	11.84	1.58	0.99	1.03	0.88	0.30	0.10	0.40	0.27	0.88	81.74
Fay	25.22	0.00	0.69	0.18	19.74	0.86	0.11	3.21	0.10	3.02	46.86
C3P	23.31	1.30	0.52	0.83	4.16	20.96	1.47	36.53	0.68	0.51	9.71
G	28.41	1.43	0.00	11.37	21.69	4.37	5.35	13.29	1.07	0.58	12.44
Av	16.63	0.31	0.21	1.79	12.99	3.15	0.64	7.64	0.31	2.20	54.14

Fig. 14. Slag sample S5_3 from Somogyfajsz bloomery workshop.

In the SEM pictures it can be observed that with the exception of the two slag samples from Alsóbogát (S4_1, S4_2) and one of the slag samples from Bodrog-Alsóbű (S1_2), which are of a glassy microstructure, all of the slag samples crystallized typically. The usual phases can be identified: Wustite (Wu) dendrites, Fayalite (Fay) plates and the Glass phase (G). Besides these phases Tricalcium-phosphate (C3P) nails appeared intruding into the Fayalite plates. Iron inclusions have been observed only in two samples from Somogyfajsz (S5_1, S5_2) and in two samples from Somogyvámos (S2_2, S2_3).

The P content of the glass phase was between 2-5wt%, with the exception of only the two samples from Alsóbogát (S4_1, S4_2), in which the P content was under 1wt%. The Ca content of the glass phase was high, over 10wt%, except for one sample from Somogygeszti (S3_1), in which the Ca content was only 1wt%. The Ca content of the Fayalite phase was also unusually high, between 15-20wt% in the samples from Somogyvámos (S2_1, S2_2, S2_3) and Somogygeszti (S3_1), while in the samples from Somogyfajsz (S5_1, S5_2, S5_3) and from Bodrog-Alsóbű (S1_1, S1_2, S1_3) it was between 5-10wt%. The iron inclusion had a P content of 2.23wt% in one of the slag samples from Alsóbogát (S4_1). The P content of the iron inclusions observed in two samples from Somogyfajsz (S5_1, S5_2) and in two samples from Somogyvámos (S2_2, S2_3) was much lower, between 0-0.8wt%.

The average chemical composition of the slag samples was also measured (EDS measurement on a 1 x 1mm area). The average P content was high, between 2-5wt%, and the average Ca content was also high, between 5-21wt% in all the slag samples except the two slag samples from Alsóbogát (S4_1, S4_2).

Discussion

Based on the SEM-EDS results it can be stated that phosphorus had an important role in the archaeometallurgy of iron in Somogy County. P-rich bog ores were smelted on the examined achaeometallurgical sites because the slag samples and/or the iron inclusions in the slag samples had a high P content.

Furthermore, it can be seen that most of the slag samples also had a high Ca content. Some samples had specifically basic characteristics, therefore, the deliberate charging of limestone or chalky iron ores into the furnace during the bloomery process can be inferred. Medieval iron smelters could see that charging limestone decreases the P content and so it decreases the brittleness of the iron bloom. Moreover, P free iron bloom can also be extracted. It can also be supposed that they could control the P content of the iron bloom by charging limestone to the iron ore in the proper ratio. Discovering this method could be very important for producing P-iron in large quantities.

Another, yet unpublished, observation confirms the supposition of the deliberate charging of limestone. The appearance of limestone layers above the bog iron ore layers is typical, so limestone could be available for the medieval iron smelters in Somogy County.

Conclusions

Phosphorus had an important role in the archaeometallurgy of iron in Somogy County and the following summarised conclusions can be drawn:

1. High P and Ca content of the slag samples originating from archaeometallurgical sites of Somogy County can be established on the basis of the SEM-EDS analysis results.
2. Typical phases in the microstructure of the slag samples were the tricalcium-phosphate nails, which appeared in all of the crystallized samples.
3. It can be stated that P-rich bog ores were smelted in the examined achaeometallurgical sites because the slag samples and/or the iron inclusions in the slag samples had a high P content.
4. It can be supposed that P-iron was produced in the examined archaeometallurgical sites.
5. It can be supposed that medieval iron smelters in Somogy County could discover how to control the P content of the iron bloom by deliberately charging limestone into the furnace during the bloomery process.

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