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Characterization of Bloom Iron Smelting Site Remains in Pržanj, Slovenia

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Abstract: This paper gives an overview of findings, connected with metallurgical activity, at the Pržanj archeological site near Ljubljana, Slovenia. More than 230 kg of slag and other remains connected with early medieval (from the 5th to the 12th century AD) metallurgical activities was found at the excavation site. The remains were grouped into four categories, i.e., furnace remains, ore, slag and a ferrous product, and analyzed in detail to obtain their chemical composition, microstructural characteristics, and mineral phase composition. The furnace wall remains, identified by their morphology and chemical composition, revealed an intensive iron processing activity at the site. The iron ore at the site was identified as goethite (FeO(OH)), a surprising find in Slovenia where limonite is typically used, and its presence suggests the potential exploitation of local bog iron ore, given the site's geological context. Abundant slag remains at the site, identified by their shape, molten microstructure, and mineral components like wuestite, fayalite, and hercynite, indicated sophisticated smelting practices, including the use of CaO-rich materials to lower the melting temperature, a technique likely preserved from antiquity. Findings of ferrous products at ancient metallurgical sites are rare due to their value, but the discovery of a corroded iron bloom conglomerate at this site, initially mistaken for furnace remains, highlights the challenges in identifying small, corroded ferrous fragments that are often misidentified as ore. The results indicate extensive metallurgical activity at the excavation site, marking it as the first documented early medieval iron smelting production site in Slovenia.

Keywords: bloom iron; bloomery slag; archaeometallurgy; microstructure

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1. Introduction

The bloom iron smelting site in Pržanj, Ljubljana, Slovenia, is an important archaeological site that sheds light on the early medieval iron production in Europe. The site was excavated in 2004 and is located near Ljubljana, Slovenia. It dates to the early medieval times between the 5th and the 12th century AD [1]. A portion of the site features a hollow area that was filled with a layer of grey clay, which suggests that the area was submerged for an extended period of time. As the groundwater level gradually receded, the hollow became covered with vegetation. Maps showing the location of the site are shown in Figure 1.

Archaeological research in 2004 undoubtedly established that there was a settlement from Late Antiquity and the Early Middle Ages on the meadow at the southern foot of the Gradišče hill. The discovered small finds, architectural remains, and ^{14}C dating indicate that there was a fundamental change in the activities that took place within this settlement between the late antique and the early medieval periods. Probably in Late Antiquity, in the 5th or 6th century, a simple settlement with square or rectangular above-ground buildings was built in Pržanj. These buildings had six or more supporting columns for the roof. The choice of this place for settlement during the 5th and 6th centuries was unusual, since it was a lowland and a non-protected settlement in very dangerous and turbulent times. The late antique settlement was probably agrarian, as evidenced by preserved charred seeds or fruits of cultivated plants, which prove the cultivation of millet, barley, two-grain wheat, and vines.

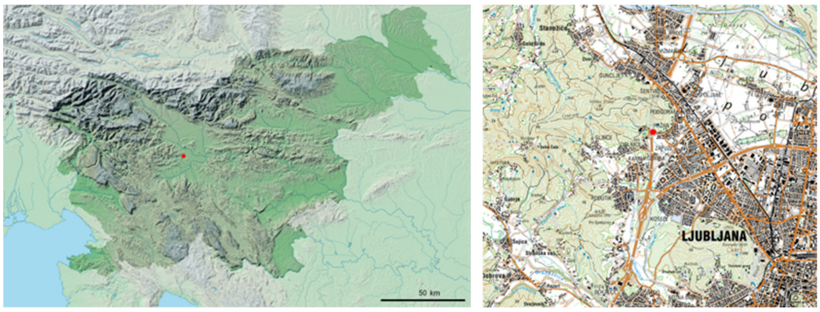


Figure 1. Location of the Pržanj archeological site (red dot) in Slovenia.

In the Early Middle Ages, probably from the 7th century onwards, major changes took place in the settlement. According to the amount of early medieval pottery discovered in most of the buildings and ^{14}C dating from large oval pit dwellings, this was also the period of most intensive use of the excavated area. The architecture of the buildings changed; the new buildings included underground (dug-in) parts that were preserved in the form of a large oval pit. A strong indication of metallurgical activity, namely, ancient bloom iron production, was discovered at the archeological site. The archeological findings consist of slag, ore, and furnace clay-lining remains; a piece of bloom iron was also excavated [2].

Ancient bloom iron production refers to the process of smelting iron from iron ore using bloomery furnaces [3]. Bloomery furnaces were used to process iron ore by heating it with charcoal under an increased airflow, obtained by bellows. At high temperatures (around 1300 °C), carbon from charcoal, combined with carbon monoxide generated by the oxidation of charcoal under the airflow, yields metallic iron and slag. The end goal was to obtain an iron bloom, a sponge-like structure produced at the bottom of the furnace, which is metallic iron that contains slag impurities. The iron bloom was then hammered while it was still hot to force out the slag impurities and close the porous structure [4,5]. The refined iron bloom was used to make wrought iron products. This process was widely used throughout Europe, Asia, and Africa from the Iron Age until the medieval period [6–10], when it was gradually replaced by more efficient methods such as blast furnaces. Iron blooms are rarely found, as they were very valuable, but the byproducts and raw materials for bloomery furnaces are the most common archeologically remains of metallurgical activity. These include metallurgical slag, charcoal, ore, and burnt furnace linings. Slag is the most common and is produced during the high-temperature reduction of iron ore. It consists of oxides, most commonly iron and silicon oxides, as well as other stable oxides like aluminum, calcium, and magnesium oxides. These oxides represent the gangue in the ore and typically reduce the iron yield. However, the slag itself is useful during ore reduction, as it can provide a liquid medium that helps in the transportation of the reduced metallic iron parts. Due to the low melting temperature of some oxide phases, especially fayalite ($2FeO \cdot SiO_2$) [8,11], the slag is usually liquid during the process or, in some cases, becomes partially melted and sintered. The composition, crystallography, and microstructure of the slag are, however, enough to not only confirm operations at high temperatures, and therefore metallurgical activity, but also to give some other insights into the production process. The lag remains are the most numerous, not only because slag is the most common byproduct of the iron smelting process, but also because it was of low value to the ancient metallurgists.

Pržanj is the first site in Slovenia where the smelting of iron ore has been documented and is now confirmed, which makes it an exceptional site for understanding early medieval metallurgy in Slovenia in general. Around 230 kg of slag remains were discovered at the Pržanj excavation site, which is why this site is unique and stands out from the other contemporary researched settlements in Slovenia. Together with the settlement site of Dragomelj [12], it represents a specific type of lowland settlement in the northern part of the Ljubljana Basin. Furthermore, the Pržanj site is the first—and so far, the only one—that offers an insight into the iron smelting processes of the Early Middle Ages in today's Slovenian territory. Also, given the radiocarbon dates and ceramic material, it was concluded that this metallurgic site may have been in use as early as in Late Antiquity.

2. Materials and Methods

The metallurgical remains found at the Pržanj archeological excavation site were sorted into 4 categories, based on visual inspection: furnace remains, ore, slags, and ferrous product. All together, 15 samples were analyzed in detail.

2.1. Chemical Composition Analysis

The slag samples were grinded in a ball mill in order to obtain a fine powder suitable for chemical analysis using an optical emission spectrometer with inductively coupled plasma ICP-OES (Agilent 720). The results of the analyses are expressed as element weight % content and were not recalculated to oxides.

2.2. X-ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD, Panalytical XPert Pro PW3040/60, Malvern, UK) was used for crystalline phase analysis. The ground powders were mounted onto suitable powder diffraction holders. The spectra were recorded using a Cu X-ray anode set at 45 kV and 40 A, with Kα1 radiation at 1.5406 Å and Kα2 radiation at 1.54443 Å; the Kα1/Kα2 ratio was 0.5. The diffractograms were acquired in the 2Θ range from 15° to 90°, with step size 2Θ 0.002° and time per step of 30 s. The diffractograms were analyzed in HighScore Plus software 3.0. Rietveld refinement of the XRD spectra was also performed with HighScorePlus analysis software, using the COD (Crystal Open Database) [13] for phase matching. The search–match algorithm was used to find the best matching phases of the experimental XRD spectra.

2.3. Metallographic Analyses

Metallographic specimens were also produced. The samples were mounted into cold metallographic mounts using epoxy resin (EpoFix, Struers, Leduc, AL, Canada) with a curing time of 12 h. The specimens were ground with graded grinding paper and polished with 3 µm diamond polish (Abramin, Struers, West Perth, Australia). The specimen containing ferrous material was also etched with 5 vol. % of Nital to reveal the microstructure. The polished specimens were imaged with the light optical microscope Microphot FXA, Nikon (Nikon, Minato City, Japan), with the 3CCD video camera Hitachi HV-C20A (Hitachi, Ltd., Tokyo, Japan).

2.4. Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (EDS) and Electron Backscatter Diffraction (EBSD)

For the scanning electron microscopy analyses, the samples were first sputter-coated with approximately 3 nm Au/Pd conductive coating (Precision Etching and Coating System, PECS, Gatan, Walnut Creek, CA, USA) using 10 kV Ar^+ ions and 350 µA sputtering gun currents. Images were acquired with a JEOL JSM 6500-F scanning electron microscope (JEOL, Tokyo, Japan) equipped with energy-dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD) detectors (EDS: Inca Energy 450, EBSD: Nordlys II detector). The images were recorded using a secondary electron detector and a backscattered electron detector at 15 kV beam energy and approximately 500 pA current. The EDS data were acquired in spot mode, at 15 kV and approximately 1 nA electron beam current, averaging 10 frames. The data were analyzed with INCA (EDS) and Channel 5.0 (EBSD) software.

3. Results and Discussion

3.1. Furnace Remains

Figure 2 shows a piece of furnace wall remains, and Table 1 gives the chemical composition of the furnace wall piece.

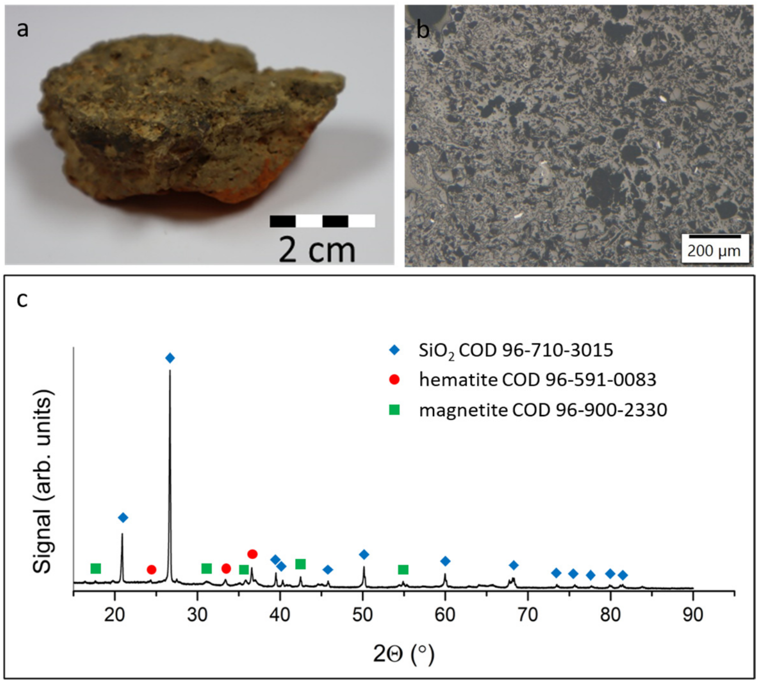


Figure 2. Furnace remains. (**a**) Piece of furnace remains, (**b**) microstructure of the furnace lining, (**c**) XRD analysis of the furnace remains.

Table 1. Chemical analysis (weight %) of the furnace wall remains.

	Ba	Mn	Ti	Ca	K	Al	P	Si	Fe	Bal.
furnace	0.03	0.06	0.62	0.12	1.9	7.6	0.10	22.1	7.2	59.9

The furnace wall remains were identified by their morphology, as they contained a layered surface of partially melted oxides on what looked like clay (Figure 2a). The furnace remains were composed of burnt clay, charcoal, and a reaction zone between the furnace lining and the slag or ore. Carbon black was present as an amorphous phase in the clay and was most likely the product of the thermal decomposition of straw, which was most probably used to reinforce the clay furnace walls.

The chemical analysis of the furnace walls showed that the most abundant elements in the wall remains were Si and Al, which is typical for clay, and some Fe was also present. The XRD analysis of the ground furnace wall piece confirmed the presence of quartz (SiO_2) and smaller amounts of hematite and magnetite iron oxides. Rietveld refinement of the XRD spectrum showed that the composition of the ground sample was about 85 wt.% quartz (SiO_2), 10 wt. % magnetite, and around 5 wt. % hematite.

Bloomery furnaces were typical in that period and were constructed from clay and sand found in the vicinity [14,15]. The remains of smelting furnaces undoubtedly testify to a settlement with a very intensive iron processing activity. Due to the lack of other indicators of a habitation purpose of the large oval pits during the early medieval phase of the settlement's existence, we concluded that these, and probably also the associated smaller pits, as well as accumulations of stones and canopies in the investigated area, were exclusively crafted facilities for processing iron. However, since only fragments of the furnaces were found, it is not possible to entirely reconstruct the furnace type used [16].

3.2. Ore

The iron ore was present in the goethite (FeO(OH)) form. Figure 3a shows a piece of ore that was found at the archeological site. The microstructure of the metallographically prepared sample can be seen in Figure 3b, and the XRD spectrum (Figure 3c) confirmed that the mineral phase of the ore was goethite. No other significant phases could be seen from the XRD spectrum, and also the microstructure did not show any other phases. An additional EBSD analysis confirmed again the presence of a goethite phase. A chemical analysis (Table 2) showed a very small impurity content, thus confirming that the piece was, in fact, goethite ore that was most probably used in the smelting process.

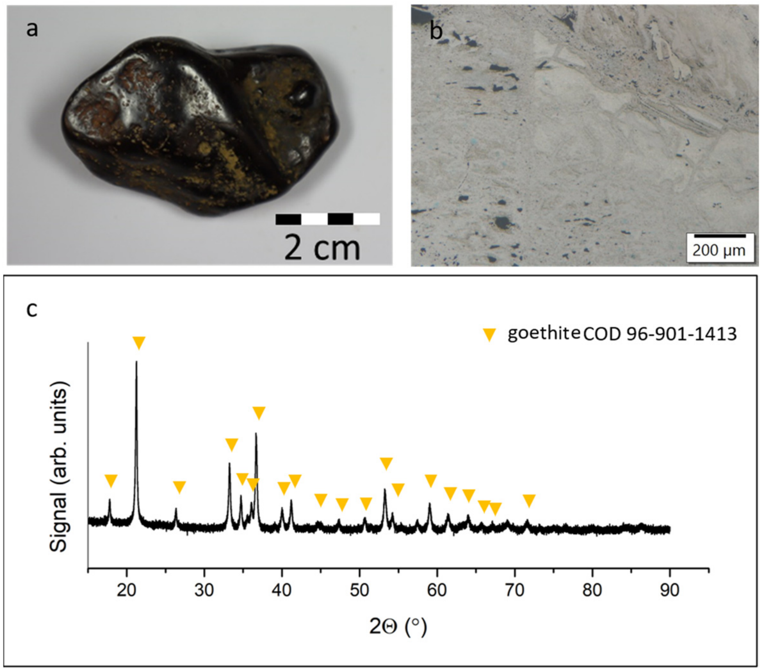


Figure 3. Goethite ore. (**a**) The found piece of ore, (**b**) light optical micrograph, and (**c**) XRD spectrum of the ore piece.

Table 2. Chemical analysis of the ore piece in weight %.

	As	Mn	Cr	Ca	K	%Al	Si	Fe	Bal
ore	0.33	0.06	0.10	0.17	0.14	0.38	0.64	35.42	33.6

The discovery that goethite iron ore was used is surprising in the Slovenian context, as early iron mining is usually associated with the processing of limonite, an ore that is readily available in several regions of Slovenia. The presence of goethite does not mean that people did not use the local ore—called "bobovec"—as goethite and limonite are related minerals and can be present in the same ore [17]. However, the finding certainly raises the question of whether they may have exploited the so-called "bog" iron ore. Mineralogically, bog iron consists of goethite, quartz, and variable amounts of aluminosilicates. The mineralogical and chemical composition of the samples from the Pržanj site may support this possibility, which is reinforced by the fact that the site lies at a location where a hilly area flows into the lowland part at the edge of the Ljubljana Marshes. Also, the thick clay layers discovered at the site indicate that the micro location was swampy for a long time [18].

3.3. Slag Remains

The most abundant archeometallurgical finds at the site were slag remains. The shape of the slag samples (Figure 4a) indicated that they were molten at the processing temperatures. The lumpy smooth surface suggests that the slag flowed freely from the furnace opening. Such findings are common, as slag is frequently released from the furnace to stop it from clogging the airflow.

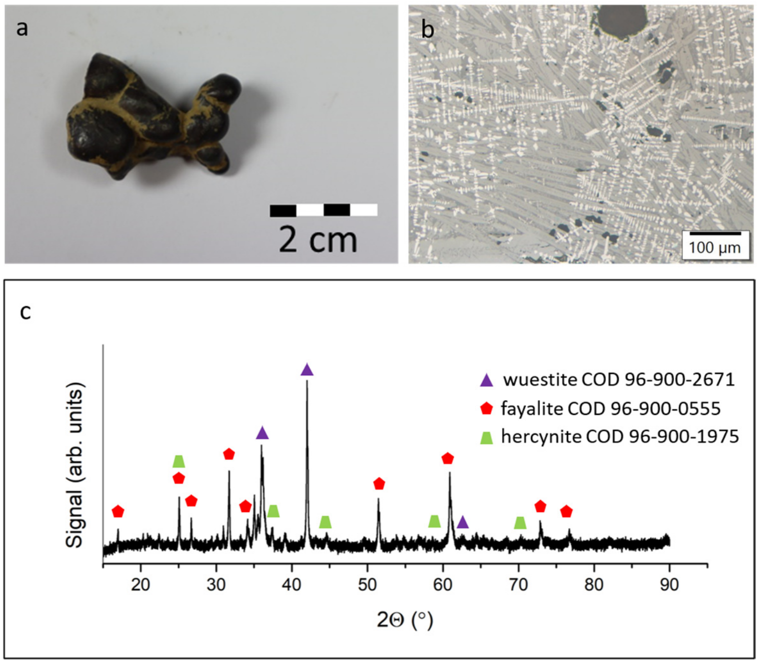


Figure 4. Remains of slag. (**a**) A piece of slag, (**b**) microstructure of the slag with wuestite dendrites and fayalite needles, and (**c**) XRD analysis of the slag.

The microstructural analysis of the slag (Figure 4b) further confirmed that it was molten and solidified; the dendritic structure of wuestite and the needle-like dendrites of fayalite are considered as evidence of the solidification process [19–21]. A representative XRD analysis (Figure 4c) of a slag specimen showed a large number of peaks, and the main components were fayalite, hercynite, and wuestite.

We analyzed seven different samples of the slag, and the XRD spectra of all samples are shown in Figure 5. For clarity, only the largest peaks are labeled. The slags exhibited similar XRD peaks, but there was some variation in the peak intensities. We performed Rietveld simulation for all the analyzed slag samples, and the phase composition results are presented in Table 3.

Table 3. Results of the XRD analysis of the 7 slag specimens.

	Wuestite	Fayalite	Hercynite	Quartz	Lime
Slag 1	21	66	11	2	
Slag 2	25	57	12	6	
Slag 3	25	57	12	6	
Slag 4	39	34	25	1	
Slag 5	34	33	29	1	3
Slag 6	32	63	12	3	
Slag 7	32	49	7	8	4

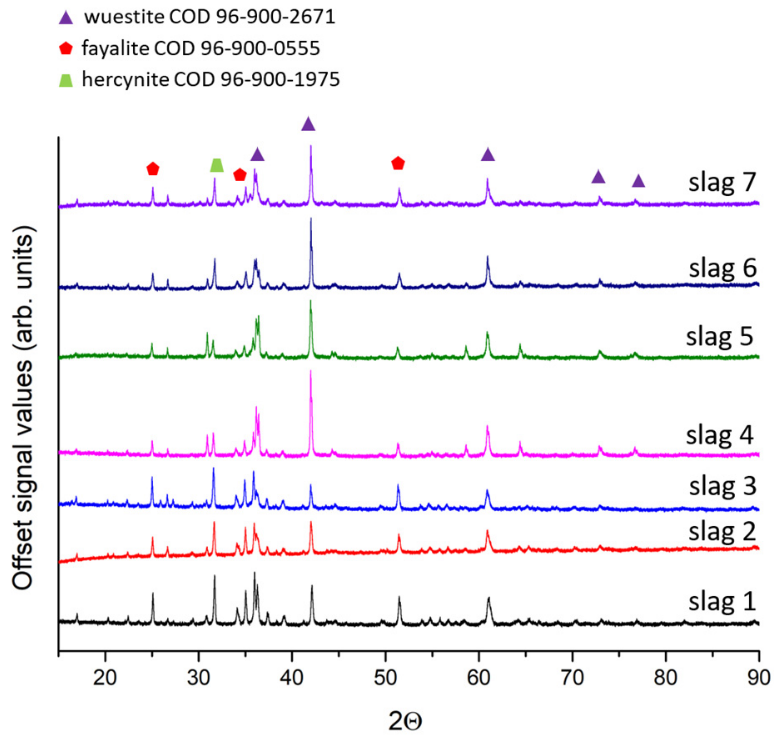


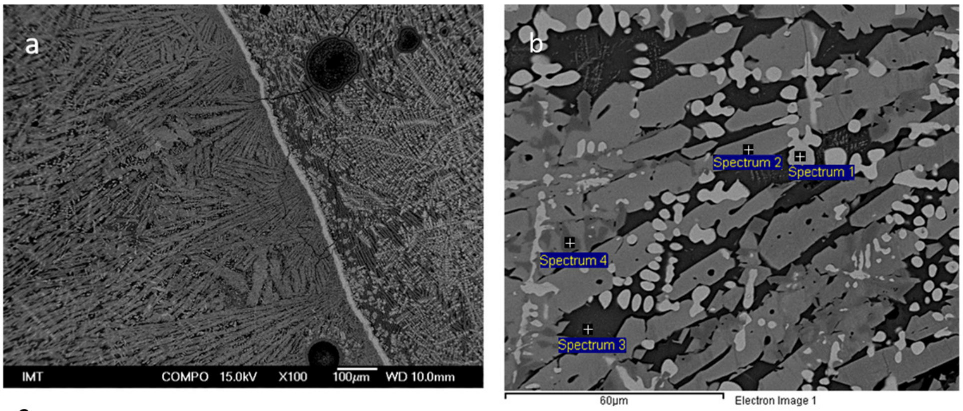
Figure 5. XRD diffractograms of the 7 slag specimens.

The slags usually contained wuestite (a high-temperature iron oxide common for bloomery slags [22]), small amounts of quartz (ore gangue and possible flux agent), fayalite (a low melting eutectic of iron oxide and silicon oxide), and hercynite (a mineral that contains iron oxides and aluminum oxides, a product of reaction between the lining and the ore) [23]. This suggests that the ore was combined with quartz as a flux to ensure a fluid slag [19,22]. There were noticeable differences in the components of the slag samples, as some samples also contained lime. While lime was most probably gangue and ash [8,19,24], it is possible that it was intentionally used to increase the slag basicity and possibly as a flux or to protect the iron oxides from excessive fayalite formation. Large additions of quartz can be detrimental to the iron reduction process, as they cause excessive formation of fayalite and stop the reduction of iron oxides, due to the thermodynamic stability of fayalite [25]. This composition is typical for slag remains of bloomery furnaces and has been documented in other archeological sites [8,24,26–29].

A more detailed SEM analysis was used to help better determine the phase composition of the molten and solidified slag. The slag remains did not form all at once, as the microstructure (see Figure 6a, where a clear solidification line can be observed) indicated two different solidification fronts, meaning that one part of the slag had already solidified when a top layer formed again, maybe in two slag tapings.

The results of the EBSD analysis are reported in Figure 7. The individual Kikuchi patterns of the fayalite, wuestite, and hercynite additionally confirmed the slag phase composition measured by XRD [30]. The distribution and composition of each phase are shown in Figure 6b,c.

Archeometallurgical analyses of the slag showed that the people of Pržanj were familiar with different smelting methods. One of them consisted of adding CaO-rich materials such as limestone or bones to the furnace as a flux to lower the melting temperature; at Pržanj, these were most probably quartz and quartz sandstone, which were detected in large quantities in early medieval pits. The knowledge that calcium oxide can lower the melting temperature and thus either shorten the process or facilitate the smelting of harder ores was already present in antiquity. The Greek lexicographer Pollux mentions adding limestone during the smelting process to help the liquefaction of slag and the formation of smelting droplets, but also the flow of the iron extracted from an ore. For Aristotle, these very properties, i.e., less slag in the bloom and the viscosity of the extracted iron, are indicative of the quality of the iron extracted. Plutarch, a 1st-century AD philosopher, reports that marble was added in smelting furnaces [31].



Spectrum	O	Na	Mg	Al	Si	P	K	Ca	Ti	Fe	Phase
Spectrum 1	28.7			0.8	0.8				0.5	69.2	wuestite
Spectrum 2	36.3		1.3	0.4	13.7			0.2		48.1	fayalite
Spectrum 3	43.0	0.9		9.9	19.4	0.5	8.1	3.6		14.5	amorphous
Spectrum 4	39.8			22.5	0.8				0.7	36.3	hercynite

Figure 6. SEM and EDS analysis of the slag. (**a**) SE image showing the solidification front, (**b**) BE image and locations of the EDS analyses, and (**c**) results of the EDS analysis.

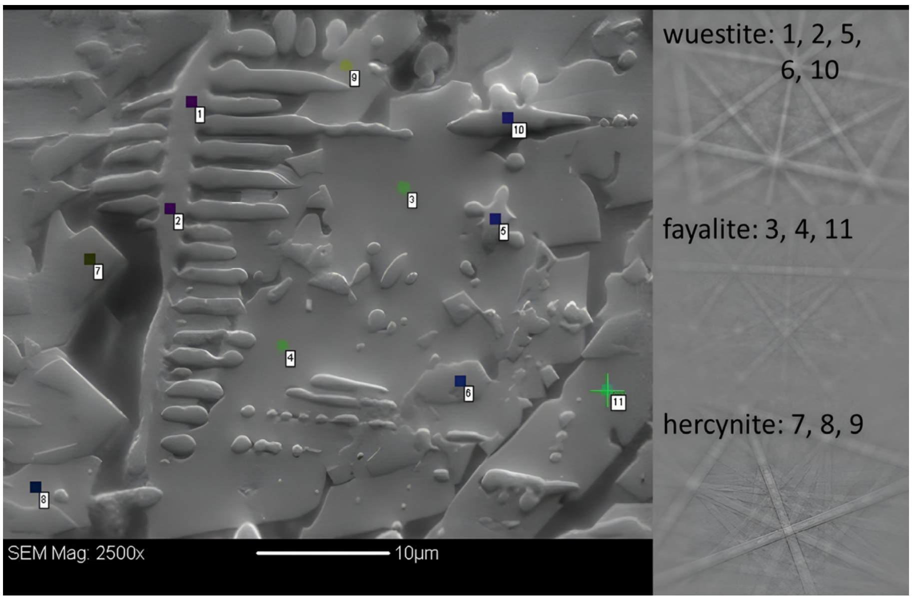


Figure 7. EBSD analysis of the phases present in the slag. Three distinctive Kikuchi patterns were present, corresponding to wuestite, fayalite, and hercynite.

If this was the practice in antiquity, in Slovenia also documented in the Late Antique fortified settlement of Castra [21], we may conclude that the recipe for smelting iron ore with the addition of CaO-rich materials, observed in both Late Antique and early medieval pits at Pržanj, survived from antiquity. This also suggests there were people who maintained this knowledge and transferred it into the Early Middle Ages.

3.4. Ferrous Products

Findings of ferrous products in ancient metallurgical sites are not common, as they were very valuable. Large iron blooms were easily identified by ancient smelters and almost impossible to forget at the production sites. Smaller ferrous fragments were, on the other hand, easier to misidentify as waste material and were left behind by the ancient metalworkers on production sites. The problem with identifying them now is that they are small, corrode quickly, and can be misidentified as ore, due to the high amounts of iron oxides they contain. In our case, a conglomerate (shown in Figure 8) was found and first characterized as furnace remains, due to its macroscopic shape.

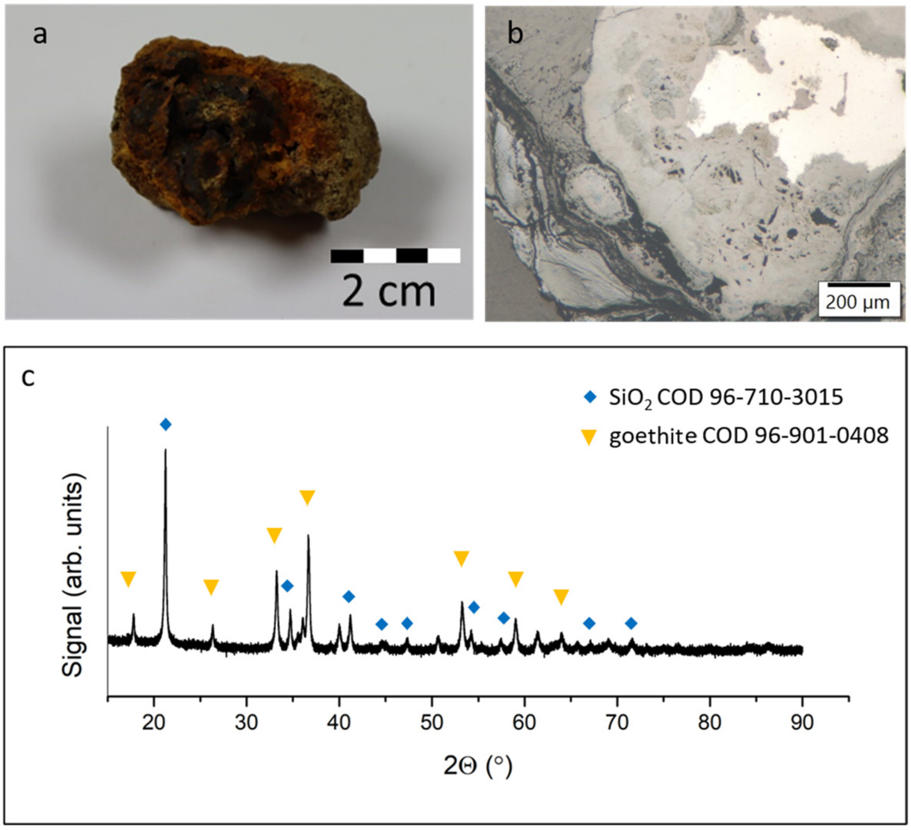


Figure 8. Remains of a ferrous product. (**a**) Piece of ferrous product, (**b**) microstructure of the polished sample, and (**c**) XRD analysis of the ferrous product.

The XRD analysis (Figure 8c) showed that it contained quartz, goethite, and a very small amount of hercynite. A chemical analysis (Table 4), on the other hand, showed large amounts of Si and Al.

Table 4. Chemical analysis of the found piece of iron bloom in weight %.

	Ba	Mn	Cr	Ti	Ca	K	Al	P	Si	Fe	Bal
bloom	0.04	0.10	0.11	0.23	0.58	0.85	4.5	0.17	7.8	48.98	34.6

The corroded ferrous piece was at first mistaken for ore, as the iron oxides had combined with water and formed the mineral goethite—a newly formed weathering phase in this case. However, the presence of hercynite ($FeO{\cdot}Al_2O_3$), along with a high Al content shown in the chemical analysis, was highly unusual, as this compound only forms at high temperatures, which can be reached during a reduction process. The accompanying high SiO_2 content was also unusual, as SiO_2 was not found in the ore, and the piece seemed to be a conglomerate. The conglomerate structure also indicated partial melting and sintering. The piece was identified as a small piece of ferrous material with attached slag. The etched microstructure (Figure 9) showed cementite needles and a fine pearlite microstructure, which indicated a relatively fast cooling, most probably in air.

A high concentration of carbon makes iron hard to work; therefore, it was probably deemed unworkable by the ancient metalworkers, who valued low-carbon, easy-to-work iron [32–36]. The occurrence of small reduced pieces of iron is not uncommon in a bloom furnace [19]. Most of them eventually end up as part of the main bloom, but some may become stuck to the furnace wall or end up in a cooler part of the furnace and are therefore unable to fuse with the main ferrous bloom. Another explanation may be that the piece simply chipped off the bloom during the initial mechanical slag refining process. Not all of the bloom had tightly fused, and might have broken off during hammering. The piece could also have chipped off due to poor workability caused by the high carbon content. Other archeological metallurgical sites do not usually have ferrous metallic products. Metallic products or semi-products like bipyramidal bars are usually found outside their functional context without associated material. Ferrous products typically contain a low amount of carbon, and only a few sections are eutectoid (0.7–0.9 wt.% C) [37]. Such metallurgical activity was typical in Late Antiquity and the Early Middle Ages. Bloomery furnace iron production was carried out till the industrial revolution in the 19th century. Blast furnaces slowly replaced the bloomery furnaces around the Late Middle Ages [38].

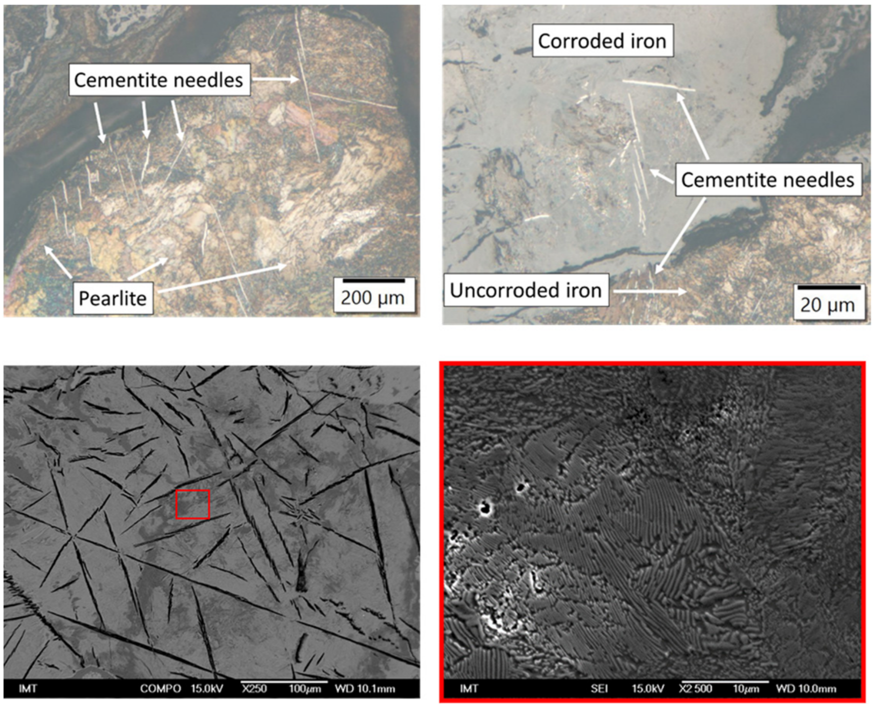


Figure 9. Microstructure of the corroded bloom piece. Upper panel: etched specimen, light optical microscopy. Lower panel: SEM images at two different magnifications, showing cementite needles and pearlite microstructure.

4. Conclusions

The archeological artifacts found in Pržanj prove ferrous metallurgical activity. The amount of slag found at the site is unusual for late antique and early medieval sites in Slovenia, indicating a large-scale production. Pržanj is the first early medieval site in Slovenia where intensive smelting of iron ore into iron has been documented. The fact that there was a real smelting plant here is confirmed by the presented metallographic research, which shows that very high temperatures were reached in the smelting furnaces. This changes the perception of the early medieval economics of the area, as until now it was believed that iron was most likely imported or recycled.

The analyzed metallurgical remains were categorized into four groups:

Furnace remains: These were identified by their layered structure and contained clay, charcoal, and partially melted oxides. The chemical analysis confirmed the presence of silicon, aluminum, and iron. Since there were no indications of habitation, we can conclude that the pits were exclusively crafted for iron processing.

Ore: The ore was identified as goethite (iron oxide) through visual inspection, microscopy, and X-ray diffraction (XRD). The chemical analysis showed minimal impurities. This finding is also surprising in the Slovenian context, because early iron mining is usually associated with limonite ore. It is possible that "bog iron" ore was used.

Slag remains: These were the most abundant finds and exhibited evidence of melting and solidification. The XRD analysis revealed the presence of wuestite, fayalite, and hercynite. The composition varied slightly between the samples, suggesting differences in flux usage. This is an indication that the people of Pržanj were familiar with different smelting techniques. Since the technique of using CaO to lower the melting temperature was already known and exploited in antiquity, we may conclude that the recipe for smelting iron ore with the addition of CaO-rich materials was maintained deep into the Early Middle Ages.

Ferrous product: A single small iron bloom fragment was found and initially mistaken for ore due to corrosion. However, the presence of hercynite and a high silicon content indicated a ferrous material with attached slag. The microstructure revealed cementite needles and pearlite. The high carbon content likely made it difficult to work this piece.

This analysis provides valuable insights into the iron smelting practices at the Pržanj site. The use of goethite ore, flux materials, and bloomery furnaces is consistent with early iron production techniques.

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