

Article

Observations Suggesting the Use of Manganese-Rich Oxidized Clay Iron Stone Concretions for Iron Production During the Early Roman Imperial Period in the Inner Barbaricum—A Multi-Method Approach

Christian Helmreich ^{1,2,*} , Florian Kobbe ², Horst Kierdorf ³, Uwe Kierdorf ³  and Martin Sauerwein ¹

¹ Institute of Geography, University of Hildesheim, 31141 Hildesheim, Germany; martin.sauerwein@uni-hildesheim.de

² Archaeological Open Air and Research Museum NAKUBI, 31275 Lehrte, Germany; nakubi@grafhorn.de

³ Department of Biology, University of Hildesheim, 31141 Hildesheim, Germany; kierdorf@uni-hildesheim.de (H.K.); uwe.kierdorf@uni-hildesheim.de (U.K.)

* Correspondence: helmreich@uni-hildesheim.de; Tel.: +49-5121-883-40908

Abstract

This article reports results of the geoarchaeological investigation of an early historical bloomery iron smelting site in northern Central Europe. Based on earlier field archaeological and experimental archaeological findings, which date back to an excavation in Sehnde (Hanover Region, Lower Saxony, Germany) in 2017, further experimental archaeological iron smelting experiments (furnace runs) have now provided information about the raw materials used in Sehnde during the Early Roman Imperial Period in Germania Magna (Inner Barbaricum) and the smelting process itself. The results of the present study suggest that no bog iron ore (BIOre) was smelted. Rather, manganese-rich carbonatic clay ironstone concretions (OCISCs) that had been oxidized by weathering and that were very rich in iron were apparently used as ores. Our study provides insights into metallurgical operations in the southern North German Plain during the Early Roman Imperial Period using a sampling and experimental archaeological test design created specifically for the local conditions.

Keywords: bloomery iron workshop; ore; clay iron stone concretions; bog iron ore; Roman Period; Northern Germany; experimental archaeology; XRF; EDS; LIBS; trace elements



Academic Editors: Nuno Leal, Amélia Dionísio and Joaquim Simão

Received: 2 October 2025

Revised: 25 November 2025

Accepted: 28 November 2025

Published: 1 December 2025

Citation: Helmreich, C.; Kobbe, F.; Kierdorf, H.; Kierdorf, U.; Sauerwein, M. Observations Suggesting the Use of Manganese-Rich Oxidized Clay Iron Stone Concretions for Iron Production During the Early Roman Imperial Period in the Inner Barbaricum—A Multi-Method Approach. *Minerals* **2025**, *15*, 1274. <https://doi.org/10.3390/min15121274>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction and Research Questions

1.1. Study Area and the Findings at the “Sehnde 9” Site

In 2017, groundwork to construct a new development area took place in the area of the city of Sehnde (federal state of Lower Saxony, Germany), located approximately 10 km southeast of Hanover (Figure 1). During this work, traces of early historic smelting sites were uncovered that due to the lack of decoration on the ceramic finds could not be dated further [1]. In the archaeological rescue excavation carried out at the site referred to as “Sehnde 9”, more than 430 findings were made, including more than 30 bloomery furnace sites and 10 finding complexes that were interpreted as the remains of pit houses [1] (Figure 2).



Figure 1. Location of the site “Sehnde 9” in northern Central Europe.

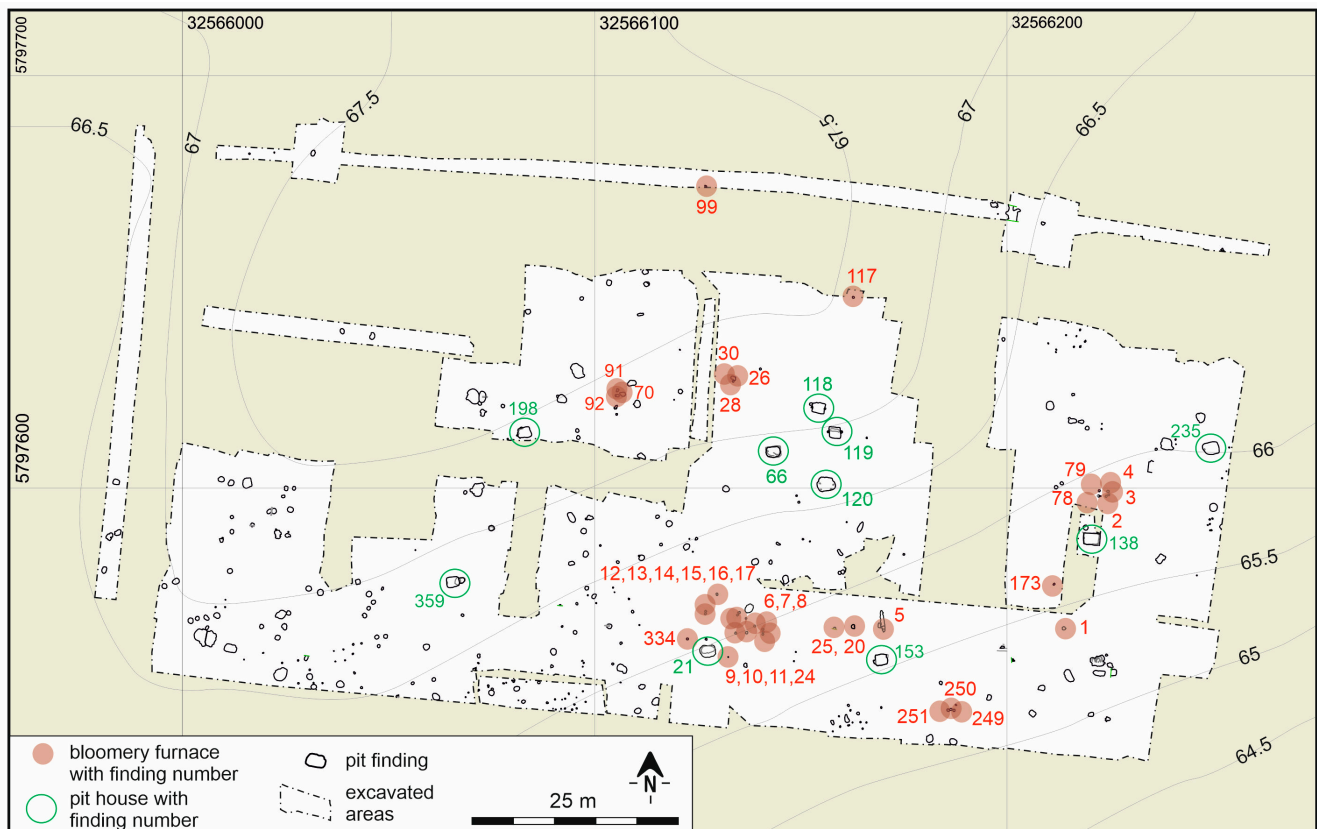


Figure 2. Excavation plan (with contour lines) of the Sehnde 9 site.

Throughout the Roman Imperial Period, the study area formed part of a region referred to as “Inner Barbaricum” or “Germania magna”, which was situated northeast of the Roman provinces of that time [2].

The excavation site covers an area of 17,500 square meters (Figure 2). The area under consideration (study area), which includes the excavation site and the neighboring recent ore deposits, covers 24 square kilometers.

1.2. The Supposedly New Type of Iron Ore Used at the Sehnde 9 Site

Until now, only bog iron ore (BIOre) has been considered a possible raw material source for iron production in the formerly glaciated area of northern Central Europe [3–8].

However, findings from the excavation site in Sehnde indicate that a different ore was used, namely oxidized clay ironstone concretions (OCISCs) (Figure 3). About 10 kg of OCISC was found at the Sehnde 9 site.

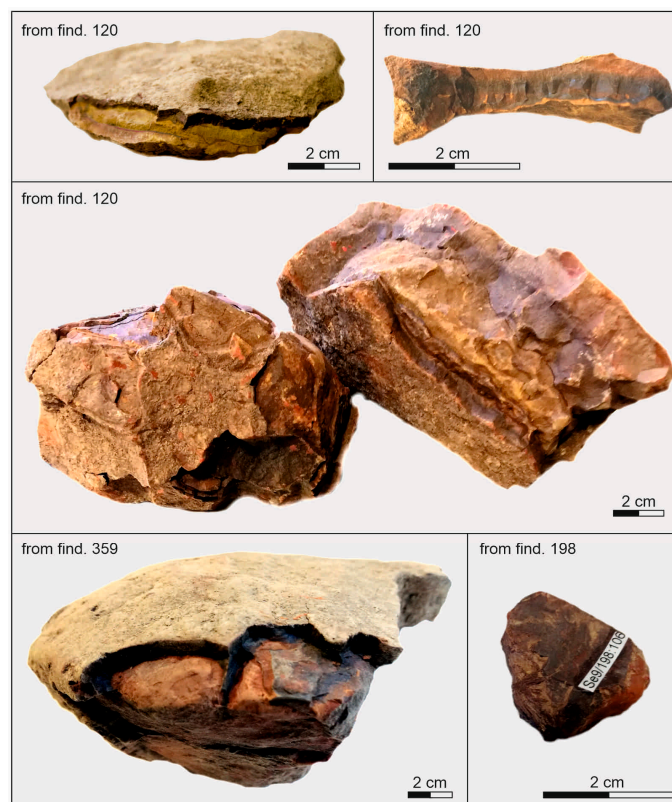


Figure 3. Roasted fragments of oxidized clay ironstone concretions (OCISCs) from pit house findings of the Sehnde 9 site. Note reddish color indicative of hematite.

The fragments of OCISC from the pit house findings at the Sehnde 9 site exhibit ferromagnetic properties. A ferromagnetic material can be magnetized by placing it in a strong magnetic field. Determining this property with a permanent magnet is a diagnostic field method for quickly checking whether a suspected ore had been roasted over a fire and thus prepared for a smelting process [5]. The magnetic property is only present if the goethite (FeOOH) was first roasted over a fire and the crystal water expelled, causing formation of first hematite (Fe_2O_3) and then ferromagnetic magnetite (Fe_3O_4) [9]. This transformation is not caused by weathering processes in mid-latitudes [10]. The red hematite is partially visible in the ore finds shown in Figure 3. This led to the hypothesis that clay iron stone geodes were used as source ore for iron smelting at the Sehnde 9 site.

1.3. Geological Situation and Iron Ore Occurrence

The geological situation of the study area is mainly characterized by two factors. Firstly, this is the salt tectonics of the Sarstedt-Lehrte salt dome, which has caused the uplift and subsequent erosion of Mesozoic layers, which would otherwise be located at a depth of several hundred meters [11]. Secondly, the landscape in the study area, like that of large parts of Northern Germany, has been shaped by the glaciation phases of the Pleistocene (Figure 4) with formation of often relatively shallow deposits.

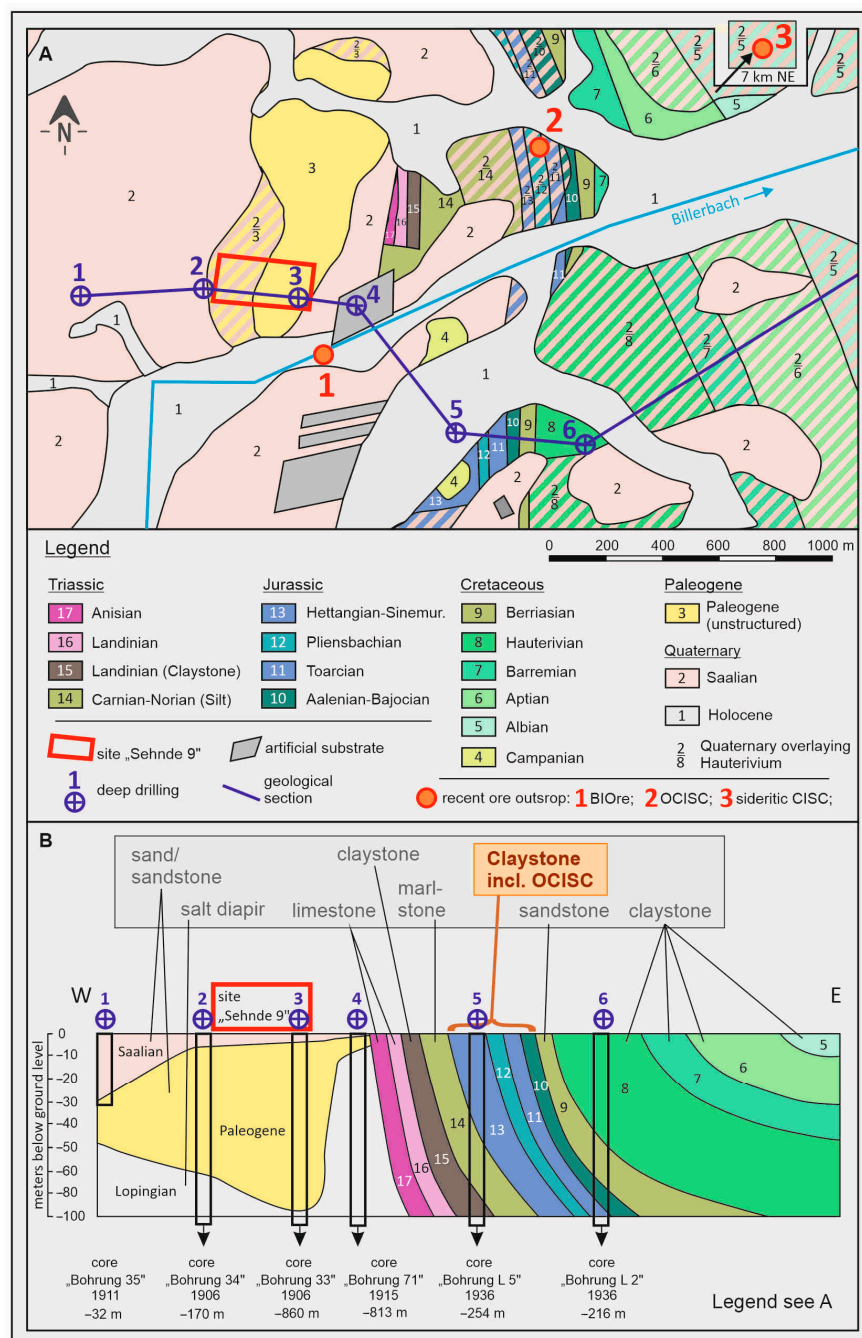


Figure 4. Study area including the archaeological site “Sehnde 9”. (A): Geology of the study area. Own representation based on the geological map of Lower Saxony 1:25,000 (sheet 3625 Lehrte) [12]; (B): geological section through the study area. Own representation based on data of the drilling profiles (“Bohrung”) from [13]. BI ore: Bog iron ore; OCISC: oxidized clay iron stone concretion; CISC: clay iron stone concretion.

Where the Pleistocene deposits are less than two meters thick or completely missing, the Mesozoic bedrock layers are shown in Figure 4 as either slightly overlain by the former (diagonally hatched) or upcoming (monochrome). This indicates that various suitable raw material deposits in the Mesozoic bedrock were accessible in Roman and more recent times.

It is therefore assumed that the clay ironstone concretions (CISCs) embedded in the Mesozoic claystones were rather easily exploitable during the Early Roman Imperial Period. Clay-containing sideritic concretions that have an ellipsoidal shape and are therefore also called “geodes” are usually referred to as “clay iron stone geodes” [14]. Clay ironstone is a

solid rock that mainly consists of the mineral siderite (FeCO_3) [15–17]. However, under certain conditions it can weather to form limonite ores [16], called OCISCs in this study.

The second iron ore, which occurs a few meters from the excavation area, is BIOre. Its origin and occurrences have been described repeatedly [3,5,7]. These ores are mostly Holocene near-surface precipitates from the groundwater fluctuation zone [7,18].

A third kind of possible parent ore is represented by the pure sideritic (FeCO_3) clay ironstone geodes (SCISCs) found at the locality of Arpke, which are embedded in Aptian claystones and crop out about 7 km northeast of the Sehnde 9 site (Figure 4). There are also iron concretions that formed in sandstone layers (SandISCs). However, these are not smeltable and were therefore not considered in this study.

1.4. Genesis of OCISCs and SCISCs and Their Early Use in Central Europe

Animal or plant fossils are often found in the core of sideritic clay-ironstone geodes [19]. This suggests that, for example, bacterial decomposition of the organic material causes a dramatic rise in pH (due to formation of ammonia and amine), and that the alkaline environment favors siderite precipitation, as the solubility of carbonates decreases with increasing pH [20]. However, this requires that sufficient Fe^{2+} ions are present in the environment and that other conditions necessary for geode formation exist. In such cases, the concretions can continue to grow along a concentration gradient until conditions change to such an extent that further siderite precipitation is no longer possible.

The SCISCs and OCISCs occurring at the study area are often spatially associated with bituminous material [12,21,22]. Since the majority of all clay-ironstone geodes found worldwide are embedded in layers within the surrounding mudstones, these horizons are considered evidence of periods of increased organic input [20,23,24].

In the case of the SCISCs and OCISCs from the study area, these layers within mudstones are marine formations that originated during both the Lower Jurassic and Lower Cretaceous periods in a sedimentary area of the Lower Saxon Basin far from the coast, where clay particles were deposited. They occur in all mudstones of the Lower Jurassic outcrops, as well as in the mudstones of the Lower Cretaceous, with the exception of the Barrenian (Wealden) [12,20,22,25,26]. The Aptian clay ironstone geodes are compact concretions of 10 to 20 cm thickness and often irregular shape that are usually weathered to a depth of only a few millimeters.

The Jurassic geodes can be recovered from the exposed claystone at the edge of a former clay pit near the Sehnde 9 site [22]. In contrast to the previously described Cretaceous geodes, the Jurassic geodes exhibit a multi-layered structure (Figure 5). Upon opening, the color reveals that often only the core is still sideritic, while most of the shells surrounding the core have already weathered into ochre-colored goethite (or lepidocrocite). Fragments of these geodes can be found on the surface of the terrain.

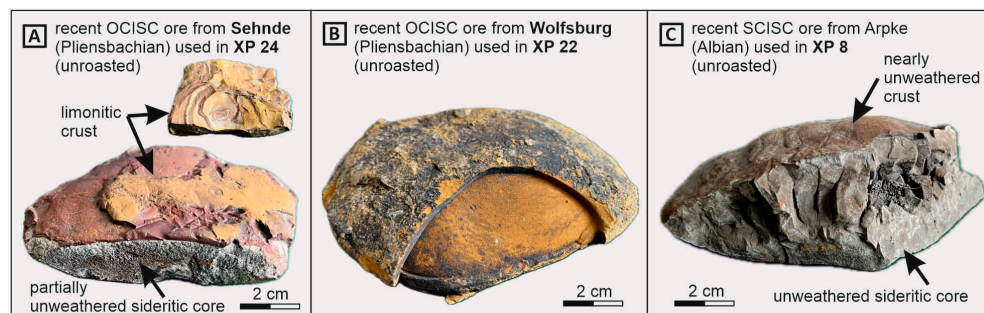


Figure 5. Different OCISC and SCISC ores used in experimental bloomery furnace runs (XP 8, XP 22, and XP 24).

SCISC and OCISC ores occur in multiple layers in the study area (Figure 6) [12]. Globally, the occurrence of clay iron stone concretions (CISCs) is much more widespread than was previously assumed [27]. Thus, in the mudstones of Yorkshire (Westphalian, Carboniferous), CISCs make up 4 to 18% of the total material, which is why they were still considered economically important at the end of the 20th century and are referred to as “iron ore” [27,28]. Clay ironstone concretions were used as raw materials for iron extraction from the Middle Ages until the 1980s [24]. OCISC and SCISC deposits in our study area are now largely owned by private steelworks [29].

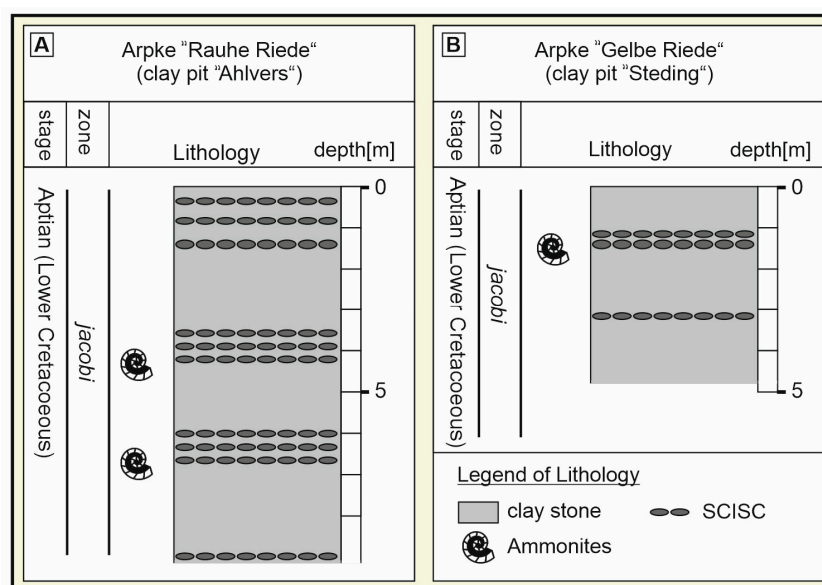


Figure 6. Recent occurrence of sideritic clay iron stone concretions (SCISCs) in banks of concordant Mesozoic sediments in the study area (ore outcrop 3, see Figure 4) after [24]. (A) Abandoned clay mining pit “Ahlvers”; (B) abandoned clay mining pit “Steding” (Arpke, Region of Hanover, Lower Saxony, Germany; both outcrop 3, see Figure 4).

Prehistoric and protohistoric use of such ores for iron production in Europe has so far only been documented in southeast England (Sussex) from the “Wealden” region [30] and in Poland (Holy Cross Mountains) [31,32].

1.5. The Bloomery Smelting Process

The pre- and protohistoric bloomery smelting process is well known and has been described several times [33–36]. Knowledge about the process is based either on geochemical and mineralogical investigations of archaeological smelting products or on the results of experimental smelting furnace runs [30,37–39]. Therefore, only a brief overview of the most important process steps will be given here: Alternating layers of ore and charcoal were presumably added to the opening of a bloomery furnace shaft, which in the Inner Barbaricum was usually located above a pit for collecting slag (Figure 7). According to current research, air was supplied through tuyeres installed in the furnace wall just above the ground surface. Bellows were probably used for insufflation. This allowed reaching temperatures of up to 1200 °C in the furnace [39,40], resulting in liquid slag phases [36,37]. Solid iron crystallized from the melt and formed at the bottom of the furnace as an iron bloom, which could be recovered after the process was completed [33,37]. Carbon monoxide and elemental carbon reduced the iron oxide to elemental iron [35,39–41]. If roasting of the ores prior to the bloomery furnace process was omitted, the conversion of iron hydroxide to iron oxide would only occur in the bloomery furnace shaft. Expulsion of the crystal water, including evaporation through the shaft opening, would cool the bloomery furnace process to such

an extent that the required temperature of ≥ 1200 °C could hardly be reached [5,6,33,40]. During the smelting process, various types of slag are formed, as shown in Figure 7. Part of the slag, which remains in the area of the tuyere, exhibits no flow structures. This type of slag is referred to as furnace slag.

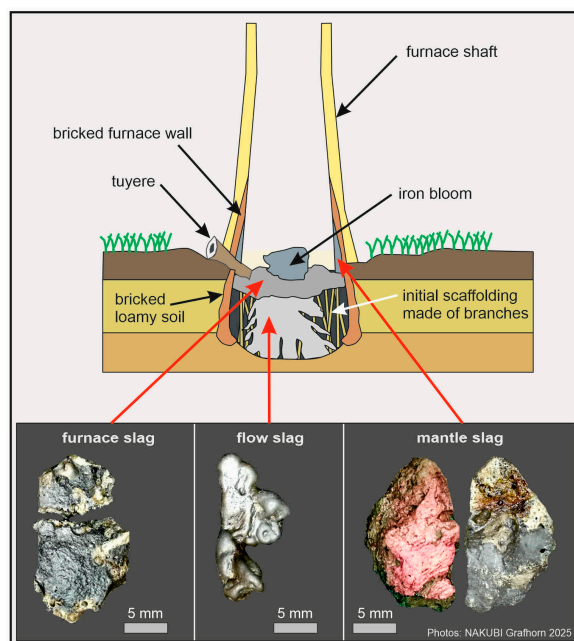


Figure 7. Different types of slag from different locations in an experimental bloomery furnace (experiment XP 10).

However, the majority of the slag flows downward into the slag pit as flow slag. To prevent the entire mixture of charcoal and ore from prematurely sinking to the bottom of the slag pit, a supporting structure made of branch wood covered with a layer of straw was erected during the construction of the furnace. Several archaeological findings indicate the use of this method [4,6]. The slag from the transition area between the furnace slag and the flow slag at the Sehnde 9 site also bears imprints of branch wood from the slag pit (Figure 8).

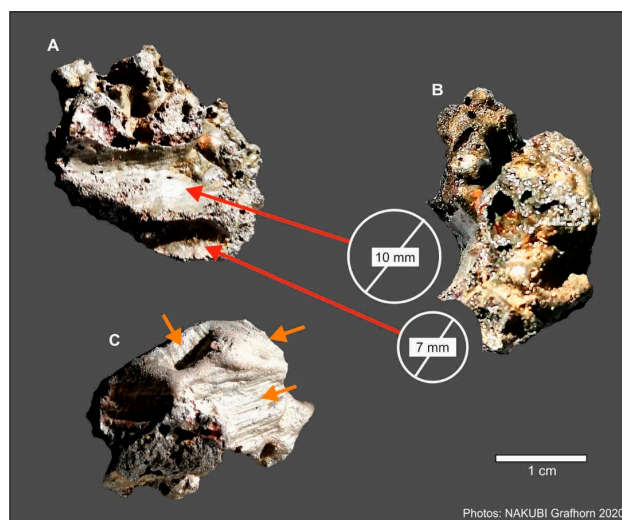


Figure 8. Slag fragment from the transition area between furnace slag and flow slag with branch wood imprints—side view (A) and top view (B) from Find 99, slag pit of a bloomery furnace. Further wood or charcoal imprints (arrows) can be seen on the reverse side (C).

The third type of slag is called mantle slag [42] or furnace lining slag [30,33,36,43]. Mantle slag consists of melted and re-solidified material from the furnace wall and is frequently found in archaeological and experimental findings on unmelted but bricked (calcined) fragments of the former furnace wall or on the outside of recovered slag blocks.

1.6. Research Questions and Study Design

Based on the findings obtained so far, the following research questions arose:

- I. How old are the bloomery smelting remains from the Sehnde 9 site?
- II. Do the slag remains originate from an iron smelting facility?
- III. Is the spatial distribution of the slag within the site homogeneous?
- IV. Are fragments of OCISCs a useful ore source?
- V. What kind of ore was used in ancient times in Sehnde and where was it mined?
- VI. What iron yield can be expected at the Sehnde 9 site?

The approach used to answer these research questions is shown in Figure 9.

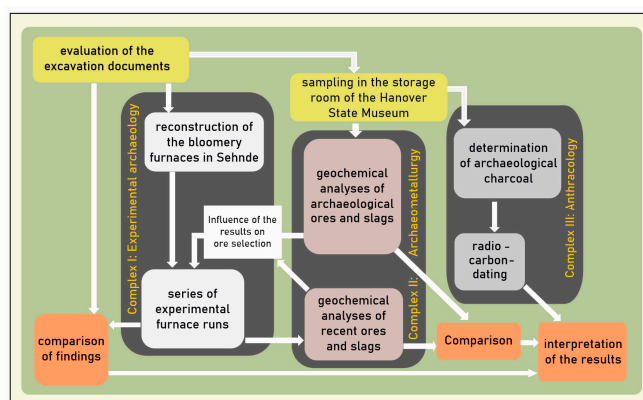


Figure 9. Design of the study.

Complex I (Figure 9) encompasses the experimental archaeology approach. Complex II includes the archaeometallurgical investigations of both selected archaeological finds and experimental archaeological materials, i.e., slags from the bloomery furnace experiments. Complex III comprises anthracological investigations. The latter served as preparation for the selection of suitable charcoal for radiocarbon dating. Complexes I and II, in particular, are closely intertwined. For example, the findings from the smelting experiments can be compared with the corresponding archaeological findings, while the experimental slags, like the archaeological slags, were archaeometallurgically investigated and compared. Following initial findings from the study of the archaeological smelting slags, further experiments could be developed that match the deduced ancient techniques more closely.

2. Materials and Methods

2.1. Anthracology and Radiocarbon Dating

Ninety-three particles of archaeological charcoals from the bloomery furnace findings of Site Sehnde 9 were available for analysis. The charcoal particles were determined after Schweingruber [44]. To establish the age of the charcoal, four samples from four different findings were sent to an analytical laboratory (Beta Analytic Inc., Miami, FL, USA) where radiocarbon dating was performed using the Accelerator Mass Spectrometry (AMS) method. In order to answer the question of whether the smelting site was used within a relatively short period of time or over a more extended one, the dated charcoal samples were taken from slag samples distributed as widely as possible within the site (Figure A1, Appendix A). Since in only one case a suitable charcoal particle from a relatively short-lived tree species

with a maximum lifespan of 80 years, namely *Prunus avium* (wild cherry), could be selected, charcoal from knotty wood had to be used to exclude an old wood effect for the other samples. In accordance with today's standard procedure, the main calibrated data were determined for all four samples, in addition to the conventional age. Other dating methods (thermoluminescence, archaeomagnetic dating), performed directly on the objects of interest rather than on associated organic remains, were not considered by the excavation team and can no longer be performed now.

2.2. Energy Dispersive X-Ray Spectroscopy (EDS)

The EDS analyses were performed to achieve an overview of the mineralogical composition of the slags. For the analyses, a Bruker Quantax 200 (Billerica, MA, USA) probe was used in a ZEISS EVO MA15 (Oberkochen, Germany) scanning electron microscope (SEM). The slag samples were first embedded in epoxy resin (Biodur) and sawn open, and the cut surfaces ground and polished using an established method [45]. This ensured a flat specimen surface, which for analysis was positioned perpendicular to the detector. The measurements were performed at a 20 kV excitation voltage and a working distance of 10 mm, with the measurement points previously defined in a backscattered electron (BSE) image captured with the SEM.

2.3. X-Ray Fluorescence Spectroscopy (XRF)

All 41 ore and 38 flow slag samples (partially shown in Figure 10) studied in this work were submitted to X-ray fluorescence analysis (XRF) in a certified laboratory (CRB Analyse Service GmbH, Hardeggen, Germany). The sample material was comminuted to a particle size of <40 µm using a vibratory disk mill. Loss on ignition (LOI) was determined by first drying the powder in a muffle furnace at 105 °C and weighing it, then annealing it at 1025 °C and weighing it again. The difference in mass is given as LOI in mass percent of the total sample. It describes the proportion of volatile components expelled during annealing. The sample material then either poured to a homogeneous melting pellet at 1200 °C or was pressed into a powder pellet. The pellets were examined for 20 elements using a wavelength-dispersive X-ray fluorescence device (AXIOS PW 2400, Malvern Panalytical, Almelo, The Netherlands).



Figure 10. Selected analyzed samples of archaeological slags (upper two rows) and ores (lower row) from the Sehnde 9 site.

The major elements are given as oxides in weight percent, while the trace elements (V, Ce, Ba) are given in parts per million (ppm = mg/kg).

The examined specimens were ore remains (OCISCs) from the archaeological findings, recent OCISCs and sideritic clay iron stone concretions (SCISCs, Figure 5C) from various outcrops near the excavation site, BIOre from the direct vicinity of the site “Sehnde 9”, as well as archaeological and recent (experiments XP 10, XP 22, and XP 24) slags. In order to ensure comparability, both experimental and archaeological material was used. In the case of experiment XP 10, the iron bloom was not removed directly at the end of the furnace run, but after all components had cooled down. For this purpose, the furnace shaft was removed and a profile line was defined, along which the remaining furnace base and slag pit were opened. This was followed by “in situ-sampling” along a transect in the flow slag of XP 10, and sampling of the other slag types. This procedure was used to check the homogeneity of the slag in the furnace [46].

2.4. Laser-Induced Breakdown Spectroscopy (LIBS)

A Keyence VHX 7000 microscope coupled with an elemental analyzer (Keyence EA-300, Osaka, Japan) was used to map the elements at the surfaces of the samples. Oxygen detection was deactivated to demonstrate only the distribution of metal ion presence.

2.5. Experimental Bloomery Furnace Runs

A total of 25 bloomery furnace test runs were carried out at the NAKUBI Grafhorn open-air museum (district of Hanover, Lower Saxony), four of which (experiments XP 8, XP 10, XP 22, and XP 24) are part of this work. For this purpose, bloomery furnaces were built that matched those reconstructed on the basis of the archaeological findings as closely as possible.

Preserved furnace shafts from archaeological findings in Central Europe are extremely rare. In northern Central Europe, furnace wall fragments have been recovered at two sites: Salzgitter-Lobmachtersen and Scharmbeck (Harburg district) [47,48]. Fragments of two furnace shafts were discovered in Scharmbeck. An almost complete furnace shaft could be reassembled that offers an excellent demonstration object for a bloomery furnace shaft from the Early Roman Imperial Period of Germania Magna (Figure 11E) [33,47]. This shaft is about one meter high with a deep slag pit and a slag tapping furnace. The shaft probably had four insufflation holes near its base. The inside diameter at the shaft base is 31.5 cm, while the opening at the shaft top measures 22.5 cm in diameter. The wall thickness is around 5 cm at the bottom and around 2 cm at the top [47]. The shape and dimensions of this early historical bloomery furnace shaft have served as a template for the construction of numerous experimental archaeological bloomery furnace shafts [49,50].

Assuming that the archaeological bloomery furnaces in Sehnde also had a slag pit below the furnace shaft and therefore represent “slag pit furnaces” according to [33], for finding 334 a slag pit with a diameter of 44 cm about 8 cm above its base was reconstructed (Figure 11D). As detailed archaeological findings for Sehnde are not available, the well-documented findings from Scharmbeck were used as a “proxy” for the construction of the furnaces [47].

The depth of the pit can only be estimated, but was probably between 30 and 60 cm. For the experiments, pits of similar size were each lined with clay. Based on the findings from Scharmbeck, a furnace shaft made of locally collected clay and straw was built above the pit with a height of 1 m for each experiment. The number of tuyeres per furnace at the Sehnde 9 site is unknown, as no corresponding finds have been made. For the experiments, we constructed furnaces with a single tuyere.



Figure 11. Reconstruction of a bloomery furnace at the site Sehnde 9 according to [33]; (A): finding 334 from the Sehnde 9 site; (B): documentation drawing by the archaeological company [46]; (C): reconstruction plan with assumed shaft and slag pit dimensions; (D): reconstructed bloomery furnace at Sehnde; (E): almost completely preserved archaeological furnace shaft from Scharmbeck with a total height of about one meter (modified image after [47]).

For the experimental bloomery furnace runs, OCISC ores collected near the Sehnde 9 site (Pliensbachian stage, XP 24) and near Wolfsburg (about 50 km from the Sehnde 9 site; XP 22), as well as nearly unoxidized SCISC ore (XP 8) from Arpke were available (Figure 5). For XP 10, Pliensbachian OCISC ore and BIOre, both originating from Sehnde, were used at a ratio of 2:1. Insufflation was ensured during all experimental smelting processes using hand-operated bellows. Temperature was measured with an infrared thermometer (BT-Meter 1500) through the tuyere in what was assumed to be the hottest area of the furnace. Prior to smelting, the ores were roasted over a fire to expel the water of crystallization [6,33].

3. Results

3.1. Anthracology and Radiocarbon Dating

The combined mass of all 93 analyzed charcoal flakes amounted to just over 90 g, with a few heavy and many light samples. Accordingly, the arithmetic mean of the samples was 0.97 g, while the median was only 0.071 g. The preponderance of light samples is caused by the fragility of the charcoal samples, especially those from the genus *Quercus* (oak). During the separation of the charcoal samples from the slag material, most of the charcoals broke into many small pieces. The genus *Quercus*, which cannot be identified to the species level by anthracological means [44], accounts for 65% of the determined charcoal mass. A share of 33% belongs to the genus *Alnus* (alder), 2% to the genus *Acer* (maple), and only one charcoal fragment weighing 0.028 g could be unequivocally identified as charred wood of *Prunus avium* (wild cherry).

In terms of taxon distribution of the charcoal particles, 59% of the samples belong to the genus *Quercus*, 22% to the genus *Alnus*, 18% to the genus *Acer*, and 1% to *Prunus avium*.

The results of the radiocarbon dating of the charcoal samples are summarized in Table 1. Four radiocarbon dates were obtained on selected and previously anthracologically determined charcoal fragments, each of which comes from flow slag from the “Sehnde 9” site. They all date close together to the 1st century AD and thus into the Early Roman Imperial Period. The whole dataset is presented in Figure A1 (Appendix A).

Table 1. Results of radiocarbon dating of four samples from the Sehnde 9 site.

Sample	A	B	C	D
source of the charcoal sample	finding 15	finding 334	finding 78	finding 251

Table 1. Cont.

Sample	A	B	C	D
wood taxon	<i>Acer spec.</i>	<i>Prunus avium</i>	<i>Acer spec.</i>	<i>Quercus spec.</i>
sample mass [g]	0.019	0.028	0.083	0.046
laboratory number	Beta-558501	Beta-558502	Beta-558504	Beta-558503
conventional age	1940 ± 30 BP	1930 ± 30 BP	1940 ± 30 BP	1920 ± 30 BP
cal. BP (probability %)	1950–1820 (94.2%)	1946–1820 (95.4%)	1950–1820 (94.2%)	1947–1812 (95%)
cal. BP (probability %)	1926–1864 (65%)	1900–1861 (43.5%)	1926–1864 (65%)	1894–1825 (68.2%)

3.2. Location of the Archaeological Slag and Ores at the Sehnde 9 Site

A large part of the recovered finds from the Sehnde 9 site is stored at the Hanover State Museum and accessible for study. This includes a total of 92 kg of slag (Table A1). A review of the excavation documentation [1] and of all finds yielded the following results: Approximately half of the 92 kg of recovered slag is flow slag, the other half is furnace slag. Only one sample of mantle slag was recovered, which had been located at the outer edge of a large furnace slag block. While 39% of the total slag mass was located in the house pits of the pit house finds, 55% of the slag was found in the remains of the slag pits of the bloomery furnaces. Only 6% was found in other pits. However, 96% of the mass of the flow slag came from the bloomery furnace finds and only 4% from the pit houses. Furnace slag, on the other hand, accounted for 80% of its total mass in the pit house finds and 20% in the bloomery furnace finds.

3.3. Occurrence of Recent Ore Deposits

The amount of recent ore deposits can be quantified as fragments per square meter of land surface, with the fragments used for analyses and experimental bloomery furnace tests having an average mass of approximately 15 g with a range of 5 to 80 g. The OCISC ores at site 2 (Figure 4) occur at the present-day surface (arable land) in varying frequencies. The Hettangian ores occur at a frequency of 17 fragments per m², those from the Sinemurian at about 1 fragment per m². The Pliensbachian ores, on the other hand, show a frequency of 24 fragments per m².

3.4. Experimental Bloomery Smelting

The experimental bloomery furnace smelting at XP 22 yielded 10.5 kg of slag and 2.03 kg of iron (18.75 kg ore input). XP 24 yielded 2.8 kg of slag and 0.475 kg of iron (4.16 kg ore input). XP 8 yielded only little slag (2.9 kg) and almost no iron (0.03 kg) although 24 kg of ore were added. Here, the slag pit contained mostly unaltered CISC ore.

3.5. Analytical Results

The results of the EDS analyses are given in Table A2. Figure 12 shows BSE images of polished surfaces of bloomery flow slags. In Figure 12A–C, EDS measurement locations are indicated by green numbers. The results of the XRF analyses for the ore and slag are shown in Tables 2 and 3, respectively.

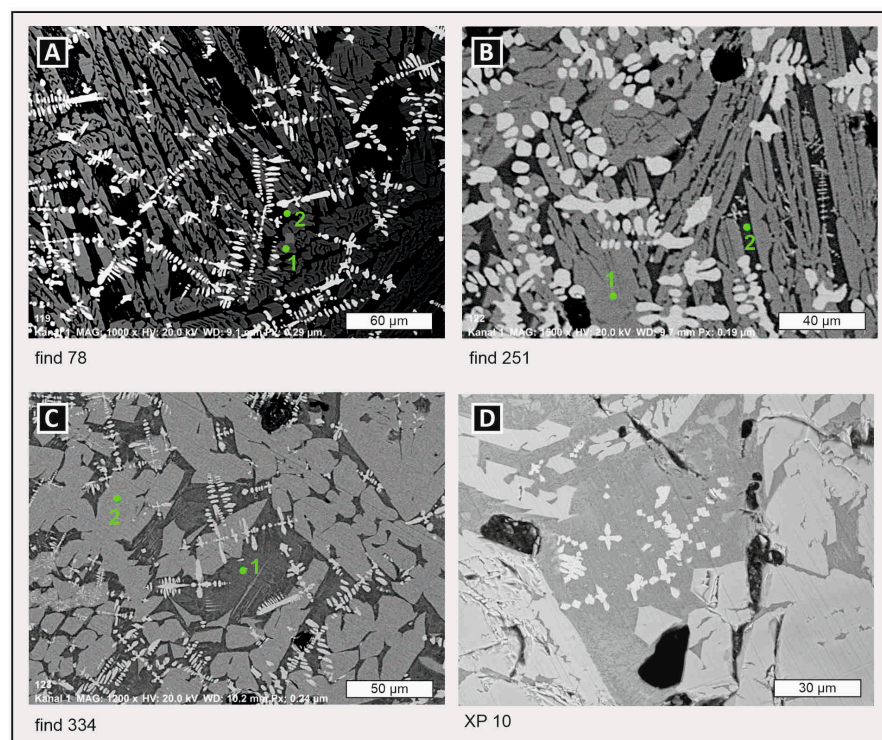


Figure 12. Backscattered electron images of polished surfaces of bloomery flow slags. (A–C): Archaeological slags with wustite (light gray), fayalite (medium gray) and glassy matrices (dark gray–black). (D): experimental slag with a crystal structure similar to (A–C). Green numbers indicate EDS measurement locations. Results of EDS analyses are given in Table A2.

Table 2. Results of XRF analyses of the studied ores. Concentrations given in wt. % for oxides of major elements and in ppm (mg/kg) for trace elements (V, Ce and Ba), (* data from [46], nm: not measured, bdl: below detection limit, np: not possible).

#	Sample Name	Remark	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	Total	RIOI	V	Ce	Ba
1	P 42 OCISC fragm. roasted “Sehnde 9”-arch. find. 198		65.74	11.28	6.67	1.86	0.703	0.326	4.132	4.54	0.5	bdl	bdl	4.05	99.87	0.5	41	bdl	500
2	P 44 OCISC fragm. roasted “Sehnde 9”-arch. find. 120		59.25	16.06	5.22	2.32	0.656	0.246	3.823	1.15	0.62	bdl	0.09	10.41	99.92	0.7	46	bdl	280
3	P 45 OCISC fragm. roasted “Sehnde 9”-arch. find. 120		66.27	9.57	5.87	3.95	0.691	0.303	3.809	6.33	0.43	bdl	bdl	2.63	99.93	0.4	34	45	340
4	Probe 2 OCISC fragm. roasted “Sehnde 9”-arch. find. 120	*	55.71	15.38	4.88	5.31	0.832	0.233	6.14	1.57	0.61	0.12	bdl	8.79	99.84	0.7	nm	nm	880
5	P 1 OCISC fragm. roasted “Sehnde 9”-arch. find. 120	*	59.55	13.46	4.54	5.14	1.21	0.241	6.3	1.07	0.62	0.13	bdl	7.47	99.84	0.6	nm	nm	1070
6	P 2 OCISC fragm. roasted “Sehnde 9”-arch. find. 359	*	74.59	8.1	2.44	0.76	1.23	0.128	2.27	1.23	0.34	0.06	bdl	8.66	99.89	0.3	nm	nm	380
7	Mean OCISC fragm. roasted arch. find site “Sehnde 9”		63.5	12.3	4.9	3.2	0.9	0.2	4.5	2.6	0.5	0.1	np	7.0	99.88	0.5	40	nm	575
8	P 87 OCISC fragm. recent Sehnde jurass. Sinemur.		72.25	8.04	2.06	0.52	2.2	0.16	0.19	0.64	0.29	0.15	0.14	13.26	99.91	0.3	35	115	nm
9	P 88 OCISC fragm. recent Sehnde jurass. Sinemur.		71.07	8.16	2.96	0.55	3.01	0.14	0.32	0.45	0.37	0.13	0.08	12.68	99.91	0.3	32	41	nm
10	P 89 OCISC fragm. recent Sehnde jurass. Sinemur.		62.59	9.27	2.11	1.37	3.97	0.084	0.31	1.22	0.35	0.15	0.07	18.41	99.92	0.4	25	47	nm
11	P 147 OCISC fragm. recent Sehnde jurass. Sinemur.		57.55	13.05	2.82	3.26	7.24	0.113	2.16	0.54	0.59	0.34	bdl	12.09	99.75	0.5	43	186	708
12	P 148 OCISC fragm. recent Sehnde jurass. Sinemur.		58.55	9.48	3.16	4.26	6.94	0.147	2.88	0.58	0.57	0.47	bdl	12.66	99.69	0.4	71	262	703
13	P 150 OCISC fragm. recent Sehnde jurass. Sinemur.		68.53	5.48	2.04	0.78	8.29	0.079	0.419	0.43	0.28	0.37	bdl	13.15	99.84	0.2	31	90	629
14	P 151 OCISC fragm. recent Sehnde jurass. Sinemur.		67.52	6.59	2.77	0.86	7.35	0.09	1.46	0.49	0.33	0.35	bdl	12.03	99.84	0.2	34	308	455
15	P 152 OCISC fragm. recent Sehnde jurass. Sinemur.		69.85	7.43	3.55	0.71	1.95	0.143	1.61	0.64	0.37	0.38	bdl	13.29	99.92	0.3	92	105	87
16	P 153 OCISC fragm. recent Sehnde jurass. Sinemur.		78.77	6.58	3.02	0.38	0.614	0.149	0.125	0.42	0.28	0.38	bdl	9.22	99.94	0.2	18	103	205

Table 2. Cont.

#	Sample Name	Remark	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	Total	RIOI	V	Ce	Ba
17	Mean OCISC fragm. recent Sehnde jurass. Sinemurian		67.4	8.2	2.7	1.4	4.6	0.1	1.1	0.6	0.4	0.3	0.1	13.0	99.9	0.3	42	140	465
18	P 84 OCISC fragm. recent Sehnde jurass. Pliensb.		43.98	8.94	4.08	16.71	0.32	0.2	11.06	0.64	0.52	0.41	0.41	12.28	99.52	0.5	135	722	nm
19	P 85 OCISC fragm. recent Sehnde jurass. Pliensb.		64.17	7.21	2.95	2.88	0.77	0.14	1.55	1.92	0.35	0.19	0.2	17.6	99.94	0.3	111	80	nm
20	P 86 OCISC fragm. recent Sehnde jurass. Pliensb.		48.41	21.19	8.53	2.66	1.37	0.4	1.58	1.15	1.33	0.22	0.92	12.12	99.86	1.1	162	195	nm
21	P 103 OCISC fragm. recent Sehnde jurass. Pliensb.		50.74	19.35	7.76	2.85	1.3	0.356	1.68	1.13	1.22	0.23	0.83	12.38	99.84	1.0	159	198	211
22	P 104 OCISC fragm. recent Sehnde jurass. Pliensb.		51.82	18.35	7.53	2.7	1.67	0.341	1.54	1.1	1.2	0.19	0.64	12.78	99.85	0.9	166	190	241
23	P 108 OCISC fragm. recent Sehnde jurass. Pliensb.		72.64	6.29	2.54	1.79	0.75	0.135	1.32	0.66	0.3	0.18	0.11	13.06	99.79	0.2	85	74	57
24	P 109 OCISC fragm. recent Sehnde jurass. Pliensb.		46.98	8.61	3.82	15.01	0.342	0.19	9.92	0.59	0.48	0.39	0.55	12.56	99.43	0.5	135	654	167
25	P 110 OCISC fragm. recent Sehnde jurass. Pliensb.		58.37	8	2.92	9.68	0.655	0.159	2.74	0.7	0.39	0.21	0.08	15.99	99.9	0.4	133	137	99
26	P 149 OCISC fragm. recent Sehnde jurass. Pliensb.		51.89	9.95	3.9	11.06	0.875	0.194	6.58	1.13	0.55	0.51	bdl	13.21	99.85	0.5	156	196	215
27	P 128 OCISC fragm. recent Sehnde jurass. Pliensb.		41.86	14.06	6.18	18.31	0.972	0.213	0.33	0.99	0.72	0.26	0.05	15.89	99.83	0.9	348	90	289
28	P 129 OCISC fragm. recent Sehnde jurass. Pliensb.		64.42	14.84	6.47	4.02	2.59	0.276	1.05	1.31	0.9	0.2	0.04	3.72	99.84	0.6	186	180	512
29	P 130 OCISC fragm. recent Sehnde jurass. Pliensb.		74.95	10.46	3.93	2.63	1.97	0.194	1.84	0.94	0.58	0.24	0.1	2.09	99.92	0.4	157	150	204
30	Mean OCISC fragm. recent jurass. Pliensbachian		55.9	12.3	5.1	7.5	1.1	0.2	3.4	1.0	0.7	0.3	0.4	12.0	99.80	0.6	161	239	222
31	P131 OCISC fragm. recent roasted WOB jurass. Pliensb.		68.69	13.83	5.69	3.59	0.712	0.248	0.937	1.78	0.68	0.26	0.07	3.34	99.82	0.5	151	89	140
32	P132 OCISC fragm. recent roasted WOB jurass. Pliensb.		45.21	32.68	15.43	0.38	0.381	0.523	0.282	1.52	1.54	0.32	bdl	1.42	99.86	1.9	401	165	266
33	P133 OCISC fragm. recent roasted WOB jurass. Pliensb.		73.68	11.4	4.55	2.68	0.873	0.198	2.04	1.46	0.53	0.33	0.15	1.97	99.9	0.4	213	134	90

Table 2. Cont.

#	Sample Name	Remark	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	Total	RIOI	V	Ce	Ba
34	Mean OCISC fragm. recent roasted WOB jurass. Pliensbachian		62.5	19.3	8.6	2.2	0.7	0.3	1.1	1.6	0.9	0.3	0.1	2.2	99.86	0.8	255	129	165
35	P 105 SISC fragm. recent Sehnde triass. Rhaetium		4.73	88.97	2.72	0.15	0.153	0.358	0.033	0.14	0.75	0.23	bdl	1.61	99.84	48.2	27	40	174
36	P 106 SISC fragm. recent Sehnde triass. Rhaetium		8.84	83.04	2.98	0.16	0.029	0.361	0.035	0.14	0.96	0.43	0.3	2.64	99.91	24.9	bdl	bdl	183
37	P 107 SISC fragm. recent Sehnde triass. Rhaetium		4.96	88.58	2.88	0.14	0.108	0.332	0.036	0.16	0.78	0.22	bdl	1.69	99.88	46.3	29	38	156
38	Mean SISC fragm. recent Sehnde Norian-Hettangian		6.2	86.9	2.9	0.2	0.1	0.4	0.0	0.1	0.8	0.3	0.3	2.0	99.88	36.7	28	39	171
39	P 82 Bog iron ore Sehnde Billerbach recent		48.51	24.69	3.73	1.98	5.28	0.25	1.53	0.45	0.83	0.47	0.12	11.68	99.53	1.2	40	41	nm
40	P 83 Bog iron ore Sehnde Billerbach recent		52.85	22.84	3.09	1.77	3.55	0.21	1.65	0.42	0.7	0.38	0.12	12.01	99.58	1.1	42	39	nm
41	P 46 Bog iron ore Sehnde Billerbach recent		54.95	18.12	2.61	1.97	5.783	0.172	1.986	0.43	0.57	0.16	0.14	12.6	99.95	0.8	34	20	3830
42	P 8 Bog iron ore Sehnde Billerbach recent	*	39.17	39.42	4.28	2.22	5.04	0.338	1.15	0.55	1.16	0.41	0.09	0.74	99.98	2.3	56	nm	3610
43	P 4 Bog iron ore Sehnde Billerbach recent	*	44.96	30.92	3.43	1.52	5.21	0.273	1.06	0.5	0.94	0.41	0.09	10.28	99.89	1.6	101	nm	2940
44	P 9 Bog iron ore Sehnde Billerbach recent	*	49.81	30.61	2.56	1.35	2.94	0.176	1.59	0.42	0.71	0.33	0.06	4.4	99.9	1.5	73	nm	1640
45	Mean Bog iron ore Sehnde Billerbach recent		48.4	27.8	3.3	1.8	4.6	0.2	1.5	0.5	0.8	0.4	0.1	8.6	99.81	1.4	58	33	3005
46	Probe 3 SCISC fragm. Arpke cretac. Aptian	*	68.9	4.37	2.06	5.87	1.91	0.08	0.69	3.73	0.28	0.12	0.05	11.9	99.94	0.2	nm	nm	nm
47	P 7 SCISC fragm. Arpke cretac. Aptian	*	58.9	3.90	1.75	4.66	1.50	0.07	0.54	3.11	0.24	0.08	0.04	25.2	99.98	0.2	nm	nm	nm
48	Mean SCISC fragm. Arpke cretac. Aptian		63.88	4.14	1.91	5.27	1.71	0.07	0.61	3.42	0.26	0.10	0.05	18.55	99.96	0.2	nm	nm	nm

Table 3. Results of XRF analyses of the studied slags. Concentrations given in wt. % for oxides of major elements and in ppm (mg/kg) for trace elements (V, Ce and Ba), (* data from [43], nm: not measured, bdl: below detection limit).

#	Sample Name	Source	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	Total	RII	V	Ce	Ba
49	P 3 Sehnde 9-arch. find. 117, flow slag	*	62.7	24.7	4.26	3.7	6.21	0.242	1.32	1.54	0.98	0.27	bdl	−6.03	99.94	0.9	77	nm	260
50	P 4 Sehnde 9-arch. find. 173, flow slag	*	70.28	25.92	5.35	0.64	1.39	0.422	0.64	0.77	0.91	0.12	bdl	−6.53	99.96	1.0	62	nm	120
51	P 47 Sehnde 9-arch. find. 6, flow slag		61.62	24.6	5.32	2.98	6.326	0.387	2.734	0.82	0.99	bdl	bdl	−5.95	99.91	1.0	84	bdl	580
52	P 48 Sehnde 9-arch. find. 9, flow slag		57.5	26.72	5.78	3.6	6.173	0.386	2.954	0.82	1.3	0.11	bdl	−5.52	99.93	1.1	87	bdl	890
53	P 49 Sehnde 9-arch. find. 9, flow slag		59.67	29.28	5.51	2.26	4.049	0.388	1.952	0.75	1.25	bdl	bdl	−3.30	99.86	1.2	67	55	360
54	P 50 Sehnde 9-arch. find. 10, flow slag		70.68	23.11	3.8	2.58	2.178	0.242	1.23	1.43	1.09	0.06	bdl	−6.50	99.93	0.8	29	34	200

Table 3. Cont.

#	Sample Name	Source	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	Total	RII	V	Ce	Ba
55	P 51 Sehnde 9-arch. find. 21, flow slag		58.31	22.74	5.21	4.97	8.902	0.283	1.692	1.97	1.17	0.15	0.1	−5.60	99.96	0.9	46	60	100
56	P 52 Sehnde 9-arch. find. 26, flow slag		63.28	22.93	5.37	6.47	2.638	0.304	1.616	1.91	0.98	0.07	0.1	−5.76	99.95	0.9	67	42	100
57	Probe 1 Sehnde 9-arch. find. 26, flow slag	*	62.64	25.94	4.88	5.31	2.25	0.292	1.41	1.66	1.05	0.2	0.07	−5.79	99.93	1.1	67	nm	280
58	P 53 Sehnde 9-arch. find. 24, flow slag		56.86	30.61	6.05	3.02	3.76	0.361	1.87	1.17	1.3	0.13	bdl	−5.24	99.93	1.3	102	61	120
59	P 54 Sehnde 9-arch. find. 30, flow slag		64.9	23.77	4.75	6.436	6.436	0.271	0.98	1.12	1.03	0.07	bdl	−6.25	99.94	0.9	39	53	120
60	P 55 Sehnde 9, arch. find. 120, flow slag		56.32	23.21	4.9	6.49	7.83	0.262	2.472	2.66	0.86	0.15	0.13	−5.37	99.95	0.9	54	bdl	bdl
61	P 56 Sehnde 9-arch. find. 274, flow slag		73.21	21.27	6.06	0.91	2.289	0.289	0.517	1.19	0.82	bdl	bdl	−6.60	99.95	0.7	50	bdl	bdl
62	Mean Sehnde 9-arch. find. flow slag		62.9	25.0	5.2	3.8	4.6	0.3	1.6	1.4	1.1	0.1	0.1	−5.7	99.9	1.0	66	51	285
63	P 43 mantle slag “Sehnde 9”, find. 120		3.47	77.68	9.23	1.52	0.098	0.795	0.593	0.84	3.72	0.51	bdl	1.4	99.9	57.7	60	177	150
64	P 90 XP 10-1, flow slag		62.6	27.44	6.69	2.7	1.54	0.31	2.7	1.54	2.07	0.19	bdl	−5.82	99.89	1.1	55	57	nm
65	P 91 XP 10-2, flow slag		75.78	22.63	5.31	2.08	1.25	0.23	2.08	1.38	1.74	0.17	bdl	−11.11	99.92	0.8	49	67	nm
66	P 92 XP 10-3, flow slag		70.85	27.28	6.76	3.68	1.19	0.34	3.68	1.49	2.61	0.18	bdl	−14.97	99.9	1.0	76	82	nm
67	P 93 XP 10-4, flow slag		41.28	42	10.12	4.4	2.46	0.47	4.4	2.53	3.96	0.26	bdl	−7.91	99.85	2.5	103	100	nm
68	P 94 XP 10-5, flow slag		62.79	26.88	8.28	2.42	1.33	0.36	0.45	1.39	1.83	0.17	bdl	−5.98	99.91	1.1	62	79	nm
69	P 20 XP 10, flow slag, sample 9	*	52.2	29.57	6.34	8	1.87	0.323	3.21	1.37	1.53	0.26	0.13	−5	99.8	1.4	nm	nm	nm
70	P 17 XP 10, flow slag, sample 3	*	48.58	32.06	6.6	8.54	2.01	0.323	3.39	1.27	1.39	0.26	0.17	−4.82	99.78	1.7	nm	nm	nm
71	P 18 XP 10, flow slag, sample 11	*	54.73	30.23	5.66	7.05	1.93	0.289	3.31	1.15	1.16	0.25	0.07	−6.04	99.78	1.4	nm	nm	nm
72	P 23 XP 10, flow slag, sample 4	*	51.35	32.35	5.81	8	1.85	0.284	3.175	1.2	1.2	0.23	bdl	−5.63	99.81	1.6	nm	nm	nm
73	P 21 XP 10, flow slag, sample 6	*	54.09	28.62	6.09	7.94	1.85	0.3	3.26	1.27	1.4	0.25	0.05	−5.34	99.77	1.4	nm	nm	nm
74	P 22 XP 10, furnace slag, sample 10	*	53.25	31.08	5.69	7.48	1.99	0.297	3.201	1.28	1.12	0.25	bdl	−5.85	99.79	1.5	nm	nm	nm
75	Mean XP 10 slag from OCISC ore jurass. Sinemur. with BIO flux		57.0	30.0	6.7	5.7	1.8	0.3	3.0	1.4	1.8	0.2	0.1	−7.1	99.84	1.4	69	77	
76	P 120 XP 24-1 flow slag from Pliensb. OCISC Sehnde		55.39	15.97	5.49	20.77	1.34	0.255	2.15	1.63	0.93	0.48	bdl	−4.64	99.76	0.7	219	180	514
77	P 121 XP 24-2 flow slag from Pliensb. OCISC Sehnde		55.84	15.6	5.43	20.86	1.36	0.235	2.12	1.6	0.93	0.47	bdl	−4.63	99.81	0.7	218	202	492
78	P 122 XP 24-3 flow slag from Pliensb. OCISC Sehnde		56.31	16.33	5.67	19.21	1.37	0.243	2.23	1.63	0.91	0.54	bdl	−4.62	99.83	0.8	214	168	488
79	P 123 XP 24-4 flow slag from Pliensb. OCISC Sehnde		55.98	15.69	5.46	20.42	1.36	0.241	2.1	1.66	0.92	0.56	0.04	−4.6	99.83	0.7	221	184	509

Table 3. Cont.

#	Sample Name	Source	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	MgO	K ₂ O	Na ₂ O	SO ₃	LOI	Total	RII	V	Ce	Ba
79	P 123 XP 24-4 flow slag from Pliensb. OCISC Sehnde		55.98	15.69	5.46	20.42	1.36	0.241	2.1	1.66	0.92	0.56	0.04	−4.6	99.83	0.7	221	184	509
80	P 124 XP 24-5 flow slag from Pliensb. OCISC Sehnde		54.43	16.92	5.89	20.01	1.28	0.257	2.22	1.63	0.83	0.77	0.05	−4.48	99.81	0.8	224	161	476
81	P 125 XP 24-6 flow slag from Pliensb. OCISC Sehnde		75.11	13.08	4.7	20.42	1.15	0.247	2.51	2	0.92	0.37	bdl	−20.74	99.76	0.5	364	233	685
82	P 126 XP 24-7 furnace slag from Pliensb. OCISC Sehnde		52.68	18.5	6.22	19.9	1.22	0.266	2.28	1.57	0.91	0.82	0.05	−4.57	99.84	0.9	215	170	501
83	P 127 XP 24-8 furnace slag from Pliensb. OCISC Sehnde		54.28	11.77	4.75	22.78	1.14	0.232	7.19	1.16	0.074	0.52	0.07	−4.83	99.8	0.6	207	385	529
84	Mean XP 24 slag from OCISC ore jurass. Pliensb. Sehnde		57.5	15.5	5.5	20.5	1.3	0.2	2.9	1.6	0.8	0.6	0.1	−6.6	99.81	0.7	235	210	524
85	P 135 XP 22-1 from OCISC ore jurass. Pliensbach. WOB		63.91	18.16	6.07	9.98	0.839	0.283	2.24	2.57	1.25	0.37	0.08	−5.89	99.86	0.7	174	159	691
86	P 136 XP 22-2 from OCISC ore jurass. Pliensbach. WOB		49.3	26.29	6.95	14.04	0.776	0.326	2.53	2.14	1.6	0.37	0.13	−4.57	99.88	1.4	236	282	385
87	P 137 XP 22-3 from OCISC ore jurass. Pliensbach. WOB		63.79	18.22	6.09	9.99	0.832	0.286	2.24	2.58	1.22	0.33	0.12	−5.84	99.85	0.7	175	176	668
88	P 138 XP 22-4 from OCISC ore jurass. Pliensbach. WOB		62.94	18.93	6.07	9.98	0.825	0.282	2.23	2.53	1.24	0.35	0.19	−5.7	99.85	0.8	172	157	663
89	P 139 XP 22-5 from OCISC ore jurass. Pliensbach. WOB		63.92	18.08	6.04	10	0.833	0.277	2.24	2.53	1.23	0.35	0.24	−5.89	99.85	0.7	175	158	674
90	Mean XP 22 slag from OCISC ore jurass. Pliensb. WOB		60.8	19.9	6.2	10.8	0.8	0.3	2.3	2.5	1.3	0.4	0.2	−5.6	99.86	0.9	186	186	616

4. Discussion

4.1. How Old Are the Bloomery Smelting Remains from the Sehnde 9 Site?

Based on the radiocarbon findings, the smelting remains from the Sehnde 9 site are dated to the Early Roman Imperial Period (first century AD). A comprehensive archaeological evaluation of the finds is still pending, so that so far only few of them can with certainty be assigned to this time period. Therefore, the “Sehnde 9” site cannot be described as dating entirely to the Early Roman Imperial Period. The ceramic finds from the Sehnde 9 site cannot support an Early Roman Imperial Period classification as they were not dated [1].

4.2. Are the Slags Those of an Iron Smelting Workshop?

The mass fractions of oxide iron and silicon dioxide in both the archaeological and experimental slags are within the typical range of fayalitic slags, such as those produced in low-melting furnaces [36,38,40]. This clearly indicates that the examined slags from the “Sehnde 9” site originated in bloomery furnaces. The mineralogical structure of the archaeological slags, consisting of wustite and fayalite crystals embedded in a glass matrix (Figure 12A–C), is also typical of smelting slags, as is shown by the comparison with an experimental iron smelting slag (Figure 12D).

In principle, non-ferrous metal smelting is also conceivable, which can also produce fayalitic slags [51]. However, the relative distribution of other elements such as Al, Ca, Mn, Mg, K, Ti, and P, shown as oxides in Table 3, as well as the absence of copper, lead, and zinc, identify the slags as waste products from iron production.

4.3. Is the Spatial Distribution of the Slags Within the Site Geochemically Homogeneous?

Initially, it was assumed that the slag chemistry would be rather homogeneous across the entire excavation area if the cluster of bloomery furnaces represented an industrial area used for a relatively short time as suggested by the results of radiocarbon dating, that is, an area not used over an extended timespan (multiple periods) (see Section 4.1). It was assumed that in this case only one ore type and the same smelting recipe were used in each case, whereas multi-period use with longer time intervals would have resulted in more divergent slag compositions. However, the results, of the ratios of selected major elements (Figure 13) show markedly wider ranges for manganese, calcium, and titanium for the Sehnde 9 site than the comparable values for the sites Kammburg (Schleswig-Holstein, Northern Germany, [5]) and Glienicke (Brandenburg, Northeastern Germany, [4]) for which multi-period use has been documented. In addition to some settlement findings, around 500 slag pits from the Late Roman Imperial Period have been excavated at the “Kammburg” site near Joldelund in recent decades [5]. At the site “Glienicke 14,” eight La Tène Period (4th/3rd century BC) smelting furnaces have been excavated, which, however, were obviously used multiple times [4]. At the latter smelting sites, BIOre has demonstrably been used, which evidently has a very similar geochemical composition over a large area, whereas the marine sedimentary OCISC ores vary significantly more in their composition. This can be explained by the fundamentally different deposition and formation conditions of OCISC ores compared to BIOre. Many millions of years may have passed between the formation of the individual bank-like layers of clay ironstone geodes on the floor of the Jurassic Sea, during which time the environmental and geochemical conditions may have changed numerous times. BIOre, on the other hand, forms as a soil horizon in a relatively short time as an accumulation of precipitates from groundwater [7]. A rather homogeneous geochemistry can therefore be assumed for BIOre. The heterogeneity of the slag chemistry suggests that no BIOre was smelted in Sehnde, but it does not allow conclusions to be drawn about possible time periods or multiple uses of the Sehnde 9 site as a smelting site.

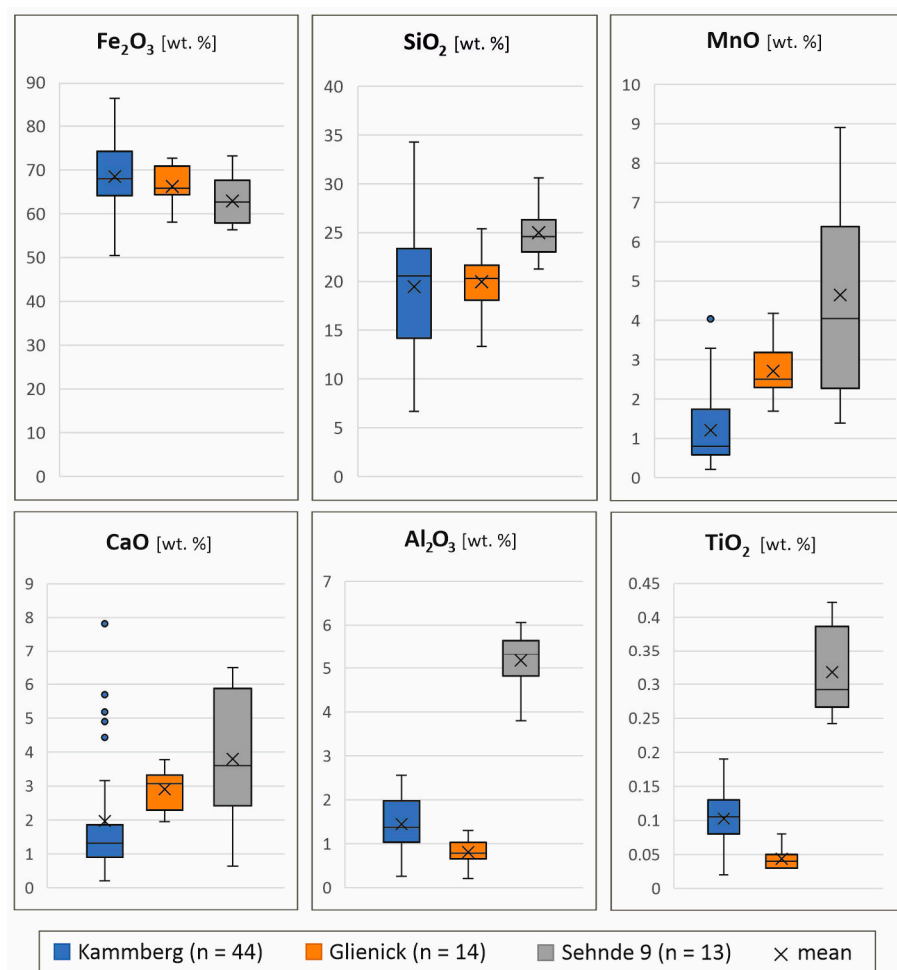


Figure 13. Boxplots of selected main element concentrations for slags from Kammberg [5], Glienick [4], and Sehnde 9 [this study]. Results of XRF analyses. Box: interquartile range, whiskers: non-outlier range, line in box: median, dots: outliers.

4.4. Are Fragments of OCISCs a Useful Ore Source?

The mineral fayalite has the molecular formula Fe₂SiO₄ [16]. In the binary system FeO-SiO₂, bloomery smelting slags usually exhibit a ratio of 2 (FeO):1 (SiO₂), which is very close to that of the mineral fayalite (Fe₂SiO₄ corresponds in quantity ratio to 2 FeO + 1 SiO₂). This is because the lowest melting point in this binary system, the eutectic point, lies within this ratio. The goal of the metallurgist is to lower the melting point of the gangue (approx. 1150 °C) below that of iron (1538 °C). The gangue, usually SiO₂ along with lithophile elements in mostly small amounts, is intended to flow away as a liquid phase, i.e., as slag, in order to separate it from the solid iron [40]. Even if the ancient metallurgists may not have been familiar with chemistry, they certainly empirically approximated the “recipe for success”. The binary system FeO-SiO₂ even has two optima, whose eutectics are quite close to each other at similarly low temperatures. Charlton et al. [36] investigated FeO + MnO/SiO₂ ratios of slags and derived the so-called Reducible Iron Index (RII): The molar ratio r in the case under consideration is the value of the quotient of the molar amount of FeO and the molar amount of SiO₂ and corresponds to the quantitative ratio ζ multiplied by 2 (according to the quantity ratio) Equation (1). This results in a value of 2.39. If this value is multiplied by the measured wt. % value of SiO₂ and the product divided by the sum of the wt. % values of FeO and MnO, this results in the so-called “Reducible Iron Index” (RII) according to [36] Equation (2). MnO is not reducible in the bloomery furnace process, but Mn replaces the iron in the slag and releases it for the solid

iron (bloom). Therefore, it is part of this analysis. If the RII value is less than 1, there is an excess of FeO in the slag that has not been reduced; if the value is greater than 1, there is an excess of SiO₂ that was not fluxed. Charlton et al. [36] deduced from this that, assuming the use of geochemically uniform ore, the process control in the furnace must have changed. The RII therefore only refers to slag and is intended as a tool for determining the efficiency of furnace control or the addition of flux.

$$r_{FeO/SiO_2} = \zeta_{FeO/SiO_2} \cdot \frac{M_{FeO}}{M_{SiO_2}} = 2 \cdot \frac{71.85 \text{ g} \cdot \text{mol}^{-1}}{60.08 \text{ g} \cdot \text{mol}^{-1}} = 2.39 \quad (1)$$

$$RII = \frac{2.39 * SiO_2^2}{(FeO + MnO)} \quad (2)$$

In order to enable statements about the “successful smelting of ores determined by general chemical analysis,” the present study calculated the RII for the ores. However, this requires first converting the iron oxide values from Fe₂O₃ to FeO fractions, followed by normalizing all oxides to a total of 100 percent.

The LOI in the case of the OCISC “Sehnde Pliensbachian” averages 12%. This is unlikely to play a role in the reaction process of the melt of a bloomery furnace, as all volatile substances should have already been outgassed. Therefore, if the values without LOI are used and then normalized to 100%, this shows that in this case the ore contains an average of 62 wt. % FeO. Since a typical fayalitic slag ideally contains about 65 wt. % FeO for the reasons mentioned above, the OCISC “Sehnde Pliensbachian” might at first glance appear “unsmeltable.” When the SiO₂ content of the ore is considered, it averages approximately 15 wt. % (without LOI and normalized to 100% if iron is represented as FeO), while fayalitic slag contains approximately 25 wt. % SiO₂. Thus, the mean RII in the case of the OCISC “Sehnde Pliensbachian” according to Equation (2) is 0.6 and thus significantly less than 1. Thus, the OCISC Sehnde Pliensbachian can be considered to be well smeltable, meaning that a significant iron yield can be expected from them. Thus, Equation (2) can be used to determine a reducible iron ore index (RIOI), whose calculation is given in Equation (3). The RII values of the slags and the RIOI values of the ores are thus directly comparable.

$$RIOI = \frac{2.39 * wt. \% SiO_2 \text{ ore [normalized to 100\%]}}{(wt \% FeO \text{ ore [converted and normalized]} + wt \% MnO \text{ ore [normalized to 100\%]})} \quad (3)$$

The Fe₂O₃ (or FeO) content of ores analyzed using a general chemical method gives only a relative content with respect to all analyzed components. It must therefore be related, in addition to the related manganese values, to the other main component in the eutectic FeO-SiO₂, namely silicon dioxide. Only then valid statements about the theoretical smeltability of an ore can be made. Using this approach, average RIOI values for the OCISC ore “Sehnde Sinemurian” of 0.3 and of 0.8 for the OCISC “Wolfsburg Pliensbachian” can be calculated. Thus, these ores can be described as at least theoretically well smeltable, leading to the recovery of iron.

4.5. Experimental Checks

Although the authors of this study have some experience regarding bloomery furnace smelting, with 25 experiments run so far, we cannot claim to be as experienced as the metallurgists of the Roman Period. Our lack of expertise in temperature and process control in particular suggests that the quality and quantity of the iron yield in the experimental replication of bloomery furnace operations is lower than those of comparable operations during Roman times. Nevertheless, general statements can be made about the suitability of the tested ores. The results of the XP 22 and XP 24 experiments with Pliensbachian

ores show that OCISC ores are suitable for bloomery iron extraction. With an ore input of 18.75 kg (XP 22) and 4.16 kg (XP 24), the iron yields of, respectively, 2.03 kg (10.8%) and 0.475 kg (11.4%) can be considered acceptable.

Sufficient quantities of OCISC fragments were not available for a furnace run with Sinemurian OCISC ore. However, it was shown that OCISC ores are very well suited for bloomery iron smelting, as can be expected from the RIOI.

4.6. Why Not Use Sideritic Clay Iron Stone Concretions (SCISCs) as Ore?

The SCISC ore from Arpke has an RIOI of 0.2 and might therefore be considered a useful ore. However, this ore is not an oxide, but a carbonate (FeCO_3). Therefore, for the direct reduction process that takes place in the bloomery furnace, the iron must first be converted into iron oxides such as hematite (Fe_2O_3) or magnetite (Fe_3O_4) using a roasting fire. However, the oxidation only penetrates the SCISC fragments to maximally 5 mm during the roasting process (Figure 14).

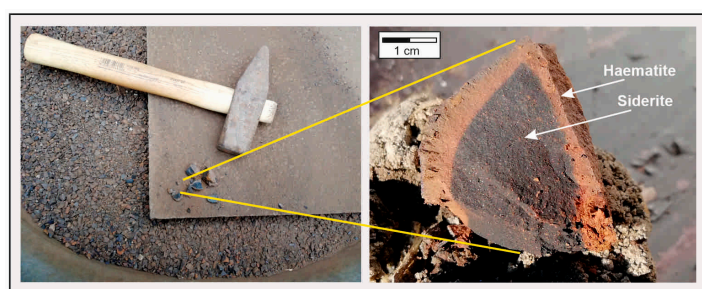


Figure 14. Result of an attempt to roast sideritic ore (experiment XP 8).

The SCISC fragments therefore remain sideritic inside and are merely darkened by the thermal effects on the numerous organic components that already cause the dark grey color of the siderite. Pre-crushing to a grain size of 4–5 mm appears impractical due to the extreme hardness of the material. Evidently, the conditions in the roasting process are too reducing to convert carbonate SCISC fragments predominantly into iron oxides. This explains the need for special procedures in today's roasting processes with sideritic ore for smelting in bloomery furnaces [52].

It also explains the low slag formation at XP 8 with almost no iron yield. As expected, the siderite is also not oxidized into hematite and magnetite in the predominantly reducing bloomery furnace process. This shows that sideritic clay ironstone geodes must first weather naturally in order to be considered a suitable ore source for ancient iron production.

4.7. Which Kind of OCISC Ore Was Used in Ancient Times in Sehnde and Where Was It Mined?

It seems plausible that the OCISC fragments discovered in the archaeological record (Figure 3) belong to the type of ore that was used in the bloomery furnaces at Sehnde. However, ore residues at excavation sites with smelting activities may also be found because they were deliberately discarded as they did not meet the quality criteria set by the ancient smelters [42]. Also, the chemical composition of the ores may have changed over the past 2000 years due to weathering processes [42]. Moreover, deposits of marine concretions (OCISCs) can be geochemically inhomogeneous (see Section 4.3). The nearest OCISC deposits are located approximately 650 m from the Sehnde 9 site. The concretions are embedded in banks of marine sediments of the Norian (Upper Triassic), Hettangian, Sinemurian, and Pliensbachian (Lower Jurassic) chronostratigraphic stages, which were deposited over a period of approximately 35 million years. Therefore, a certain geochemical heterogeneity of the OCISC deposits has to be expected, even though the outcrops of the concretion formations are located relatively close to each other (Figure 15A). Samples of

OCISC fragments were collected from the various depositional stages (Figure 15A) and analyzed (Table 2). This allows both geochemical heterogeneities within a chronostratigraphic phase and geochemical differences between the phases to be identified (Figure 15). For example, fragments containing more than 2 mass percent MnO occur only in the Sinemurian ores (Figure 15B). Concretions that appear completely unsuitable for smelting, and those that are noticeably sandy and thus too rich in silicon dioxide, also occur in a bank-like arrangement (Figure 15B). These concretions have an RIOI of >1 (Table 2, Figure 15B) and were therefore presumably already sorted out by the ancient metallurgists during ore collection.

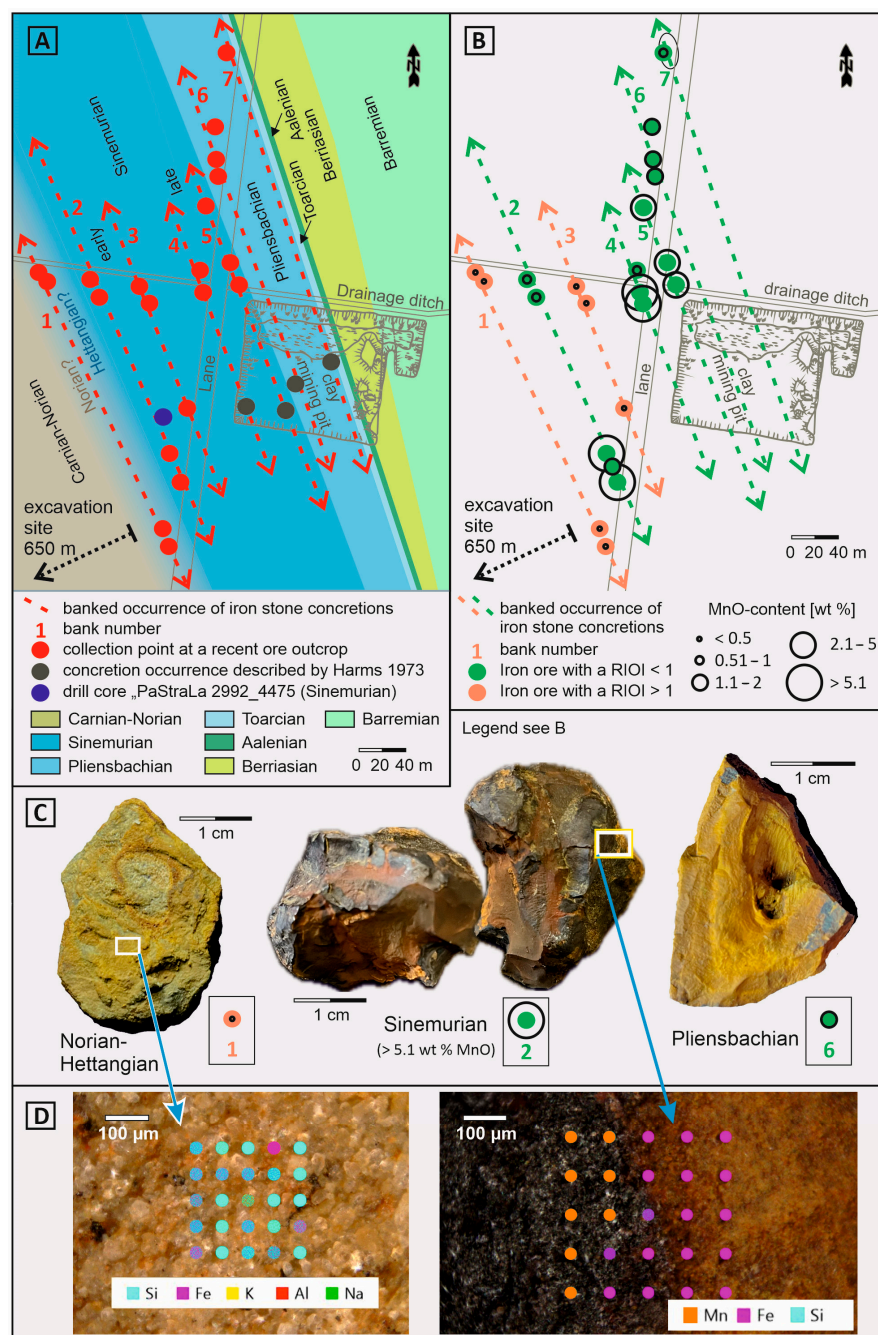


Figure 15. OCISC occurrence in the study area. (A,B): Collection points of ore fragments along a banked occurrence of OCISC. (C): Overview photos of ore samples. (D): Results of the LIBS measurements of selected ore samples.

While an excessive sand content could already have been detected during ore collection, similar to today's field method for determining soil type, the ore had to be washed to further assess whether it was of the desired quality. This allowed adhering silty and clayey material to be removed and the color of the OCISC fragments to be assessed, with the darkest ones selected for use. As shown by the XRD and LIBS analyses, the dark-appearing OCISC fragments are rich in manganese (Figure 15C,D). The ancient smelters were most likely unaware of the presence of manganese, but they had empirical knowledge about a special quality of iron that could be achieved by smelting these dark ores: The manganese activates the FeO in the smelt, and the iron can be better carburized into hardenable steel [40].

A key question is whether the archaeological slags from the Sehnde 9 site can be assigned to the OCISCs and perhaps even to a chronostratigraphic stage, or whether the BIOre, which is located directly next to the site, was smelted?

Figure 16 shows the distribution of some major elements in the archaeological slag from the Sehnde 9 site and that of the potential source ores, which either also originate from the archaeological record or are from recent outcrops located near the site. For this illustration, the LOI was subtracted and the values then normalized to 100 percent, because it can be assumed that both the input ore and the resulting slag lose all their volatile components in the bloomery furnace. Furthermore, this allows for comparability, as the LOI of the recent ores reaches values of up to 18 mass percent. The archaeological and experimental slags exhibit a negative LOI because they were oxidized by the preparing process for XRD. It is worth mentioning that the freshly produced experimental slags (LOI of -5.6 to -7.1 wt. %) and the archaeological slags (LOI of -5.7 wt. %) each have similar values on average. That means that the archaeological slags apparently are not chemically altered secondarily by the influence of moisture and oxygen.

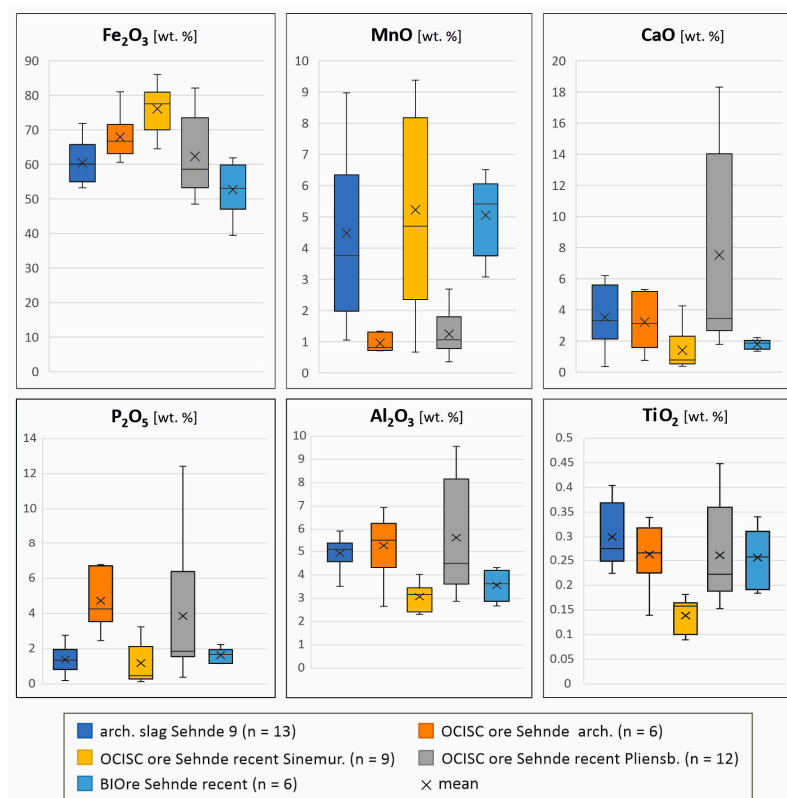


Figure 16. Main element values of the archaeological slag (Sehnde 9) and possible parent ores from the study area. Results of XRF analyses. Box: interquartile range, whiskers: range, line in box: median.

The iron oxide content in BIOre considered as FeO, with an average of 53 weight percent (range 39 to 61 wt. %), is far too low to produce the archaeological slags, which have an average of 60 mass percent (range 53 to 67 wt. %) FeO. This ore has an RIOI of 1.4. The average RII of the archaeological slag is lower, at exactly 1. This alone rules out BIOre as the source ore. The high barium content in BIOre, ranging from 1640 ppm to 3830 ppm (average 3005 ppm for $n = 4$), also shows that it cannot be the source ore, as the Ba content of the archaeological slags is either below the detection limit or reaches a maximum of 890 ppm (average 285 ppm for $n = 11$) (Table 3). Experiments XP 22 and XP 24 show that the barium enriches in the slag compared to the source ore, since high barium contents can be found in charcoal ash. The magnitude can also remain roughly constant if the charcoal contains little barium. The barium content is species-specific, but can also vary within a plant [53]. Barium is a lithophile element and does not alloy with iron [54]. Therefore, Ba depletion by a factor of 10 in the process is not possible.

The iron oxide values of the OCISC ore present in the archaeological record are high enough to have generated the archaeological slag and simultaneously yielded iron (Figure 16). This also applies to the OCISC fragments from the Pliensbachian sedimentary layers.

However, if the other elements are taken into consideration, only the OCISC fragments from the Sinemurian layers appear suitable as the source ore, as they contain sufficient manganese, not too much calcium and phosphorus, and aluminum. The apparent discrepancy between the titanium and aluminum values of the slag and the Sinemurian ore is explained in the following chapter. All other ores exceed or fall markedly below the values for at least one of the element oxides compared and can therefore be excluded as source ores used in the smelting process (Figure 16).

4.8. Bloomery Furnace Mass Balance

The fact that, on first sight, the aluminum and titanium values in the favored OCISC ore from the Sinemurian appear too low when compared to those in the archaeological slag can be explained by the influence of the furnace wall. The slag contains significantly more silicon dioxide than the supposed parent ore (Sinemurian OCISC), and this increase cannot be explained solely by the loss of iron, that is, the desired and ultimately extracted product from the smelting system. In this case, all other lithophile elements remaining in the slag would also have experienced the same percentage increase. As this is, however, not the case, the silicon, as well as the aluminum and titanium, must derive primarily from the molten inner wall of the furnace shaft. The furnace wall, measured as shell slag, exhibits significantly higher aluminum and titanium values than the ore. To substantiate a corresponding assumption, Charlton et al. [36] and Morel and Serneels [54] used a multiple linear regression analysis of the measured or published values of charcoal ash. The percentages of ore, furnace wall, and charcoal ash, with a simultaneous yield of elemental iron, are calculated approximately according to the mass balance in the bloomery furnace process to explain the slag composition (Equation (4) according to [37,43,55]).

$$\text{ore} + \text{furnace wall} + \text{charcoal ash} = \text{slag} + \text{iron (bloom)} \quad (4)$$

Table 4 shows that given this mass balance Equation (4), in the case of the archaeological slags, with an iron yield of 23 percent, the share of the OCISC ore of the Sinemurian must have been about 81 percent, that of the furnace wall about 16.5 percent, and that of the charcoal ash about 2.5 percent.

Table 4. Mass balance of material flows. Calculation of a slag from Sinemurian Sehnde ore. Total iron distribution: 85% slag = 15% Iron yield (oxidic iron) -> 77.% of the yield as elemental iron (* data from [56]).

	FeO	SiO ₂	Al ₂ O ₃	CaO	MnO	TiO ₂	P ₂ O ₅	MgO	K ₂ O	
mean of measured flow slag “Sehnde 9”-arch. findings	56.62	24.98	5.17	3.80	4.65	0.32	1.65	1.37	1.06	
mean of measured ore OCISC Sehnde jurass. Sinemurian	76.07	10.35	3.02	1.55	5.81	0.15	1.32	0.76	0.48	Percentage shares
measured mantle slag “Sehnde 9”, arch. find. 120	3.12	77.68	9.23	1.52	0.10	0.80	0.59	0.84	3.72	
measured ash (*)	1.39	6.82	2.76	54.27	2.03	0.11	8.73	6.47	13.9	
calculated influence ore		8.38	2.44	1.26	4.70	0.12	1.07	0.62	0.39	
calculated influence mantle slag “Sehnde 9”, arch. find. 120		12.82	1.52	0.25	0.02	0.13	0.10	0.14	0.61	81.0
calculated influence ash		0.17	0.07	1.36	0.05	0.00	0.22	0.16	0.35	16.5
sum		21.37	4.03	2.87	4.77	0.26	1.38	0.92	1.35	2.5
calculated slag composition		25.00	4.72	3.35	5.58	0.30	1.62	1.07	1.58	factor 1.17

The calculated values for the main elements are very close to the measured ones and also explain the origin of the calcium, potassium, and magnesium, namely from the ash. It should be noted that archaeological charcoal ash was, of course, no longer available for analysis. Therefore, published values [56] were used here, which will certainly differ from the actual values [37]. This also explains the relatively larger deviations between the calculated values and the measured values for the elements potassium, magnesium, and calcium in the archaeological slags. As with barium, these elements can also vary greatly in their proportions in plant biomass [53]. Nevertheless, the results of the anthracological analysis show that a large proportion of oak charcoal was used. Therefore, published ash values for oak charcoal were used for these calculations.

In conclusion, the results clearly show that the OCISC ores from the Sinemurian must have been the parent ore for the archaeological slags, as demonstrated, for example, by the wide range of manganese in both cases (Figure 16). As indicated by their respective RIOIs, the other OCISC ores are also, in principle, smeltable (Table 2). Nevertheless, there must have been a reason why they were deliberately excluded, as the example of the archaeological ore remains from the site shows, which demonstrates high similarities to recent Pliensbachian ores (Figure 14).

Further evidence that only the Sinemurian OCISC ores are suitable as raw material for the slags from the Sehnde 9 site is provided by the representation of the mass percentage values in the ternary phase diagram of the FeO + MnO, Al₂O₃, and SiO₂ system (Figure 17). Here, it is clearly visible that the values of the ores, the archaeological slags, and the mantle slag lie on a straight line, while the values of the other ores lie outside this narrow range. It also shows that the values of the archaeological slags are closer to Optimum II, one of the two optima in the double eutectic of the FeO and SiO₂ system. This is to be expected given the high iron content in relation to the relatively low silicon dioxide content of the Sinemurian ore. It is evident that the melting system has drawn in the silicon dioxide to form the fayalitic slag from the furnace wall along with other lithophile elements, such as aluminum.

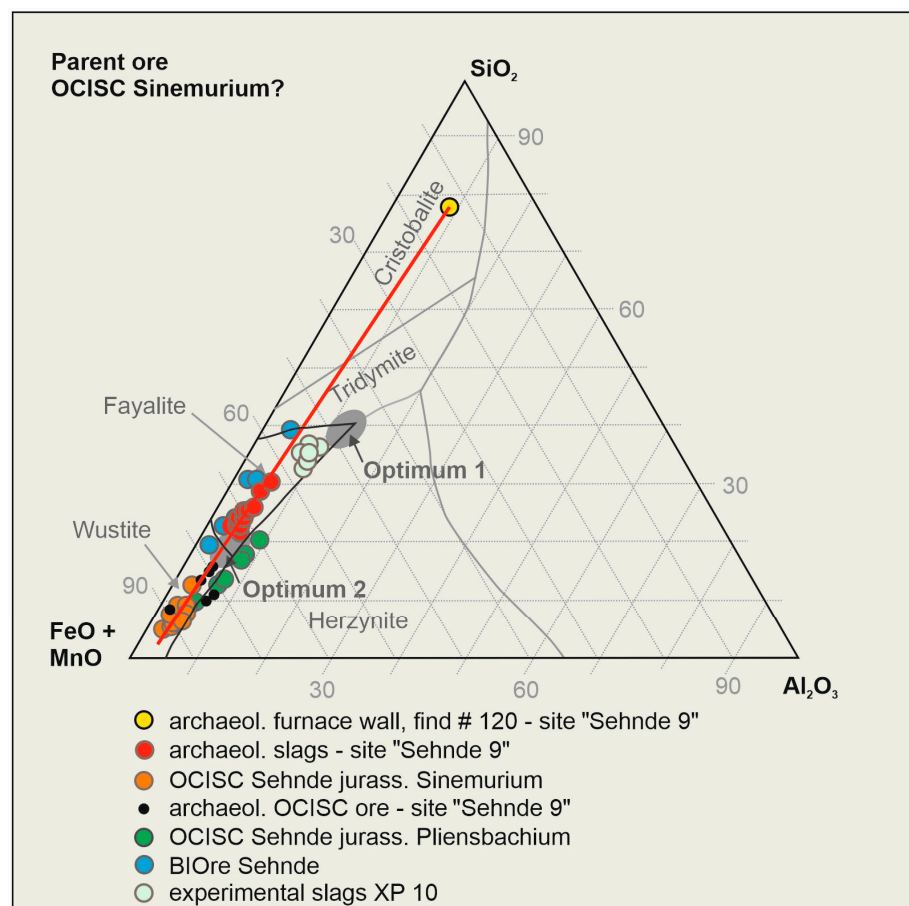


Figure 17. Measured values of ores and slags in the ternary phase diagram in the system FeO-SiO₂-Al₂O₃.

The experimental slags from test XP 10, in which Pliensbachian OCISC ore was mixed with the recently outcropped BIOre from Sehnde at a ratio of 2:1, are, as expected, closer to Optimum I in the double eutectic (Figure 17). The BIOre is relatively rich in SiO₂, and the Pliensbachian OCISC ore is relatively richer in aluminum than the Sinemurian OCISC ore. If this ore mixture had been used at that time, the values of the archaeological slags, assuming a similar furnace wall composition, would have been closer to a straight line in the region of more highly enriched aluminum in the ternary phase diagram. This mixture of ores was initially assumed because, as already discussed, the OCISC ores from the archaeological record do not contain sufficient manganese to explain the values of the archaeological slags [46]. The BIOre from Sehnde, on the other hand, has higher manganese values, but is excluded, even as an aggregate in a concentration of about 33%, solely due to the high barium content, as the current study now shows.

4.9. Current Ore Abundance

Ancient ore mining pits are not detectable in the present landscape in the vicinity of the current OCISC ore deposits, but they may no longer be recognizable due to current and past land use. An indication of the current relative rarity of the favored dark-appearing (manganese-rich) Sinemurian OCISC ores from Ore Location 2 (Figure 4) could be their early historical exploitation [42]. However, it is also possible that these OCISC ores formed less frequently than others. The limited access to this ore is the reason why there was insufficient ore available for another experimental furnace run to produce reference slag. The ore fragments are not evenly distributed across the entire accessible land surface, but occur in narrow bands of 2–3 m, the bank-like outcrop deposits in the Jurassic sediments, which

are now steeply sloped due to salt tectonics (Figure 4). For the collection of approximately 60 kg of unroasted ore, which would be necessary for experimental furnace traversing, an average 2.5 m wide band would have to be accessible over a length of approximately 1600 m, which is not currently the case in the study area.

4.10. What Iron Yield Can Be Expected at the Sehnde 9 Site?

A calculated iron yield of 15 percent (Table 4) does not mean that the iron bloom, assuming an ore input of perhaps 50 kg (represented as FeO, equivalent to 55.6 kg Fe₂O₃) of ore per bloomery furnace, would have yielded 7.5 kg of elemental iron according to the mass balance. The calculation was performed using iron in oxidation state 2 (FeO), as can be assumed in the case of the smelting process. However, the iron is reduced to the pure element. The oxygen bound in the ore escapes as carbon dioxide in the furnace top gas. In mass percent, this means that, optimally, a maximum of 77.8 percent by weight of the iron oxide was present in elemental form as iron bloom. In the assumed case of 50 kg of smelted ore (FeO and a yield of 15 percent (FeO), this would be 5.84 kg of elemental iron (11.9% yields, respectively, 10.5% of 55.6 kg Fe₂O₃). The experimental furnace runs XP 22 and XP 24, which also used low RIOI-OCISC ores, always resulted in values close to 10% (of total ore mass represented as Fe₂O₃), both measured and calculated. This approach is particularly interesting for questions regarding the quantification of raw materials (wood) used and the resulting environmental impacts [57,58]. Although more than 30 furnace findings have been excavated in Sehnde, no finding has revealed a nearly complete slag block. Therefore, the total ore mass used per furnace can neither be calculated nor estimated. The calculated yields are not suitable as relative values for quantifying the ore mass, but they do provide an indication of the average efficiency of the furnaces at the Sehnde 9 site.

5. Conclusions and Outlook

The Sehnde 9 site dates into the Early Roman Imperial Period and includes slags as remains of an iron smelting facility. Even if the slag within the site appears geochemically inhomogeneous, it does in our view not originate from multi-phase use of the site employing different parent ores and smelting recipes. The geochemical variability of the archaeological slags is rather due to the geochemical heterogeneity of the ores used. For the area under investigation, the former Inner Barbaricum, the detection of OCISC ores as the source ore for smelting activities is a new discovery. Our smelting experiments have shown that OCISC fragments are a useful ore source. Previously, it was assumed that only BIOre was smelted in this region. Furthermore, it has been proven that Mn-rich and thus dark-appearing ores from Sinemurian deposits in the study area were a preferred ore source. Multiple linear regression analysis, combined with trace element values, indicates that only the manganese-rich OCISC ores qualify as the source ore. The other ores can be ruled out, as they would not have produced the chemical fingerprint of the archaeological slag. According to different authors [37,40,59], manganese-rich ore produces hardenable steel, which represents a qualitative advantage over soft iron from other ores. To identify the actual OCISC ore processed, large-scale screening of OCISC occurrence near the site was necessary.

Thus, for the first time, the use of manganese-rich OCISC ores for iron production during the Early Roman Imperial Period in the northern Central Europe (Inner Barbaricum) could be demonstrated by the present study.

The following questions require further investigation. (1) Where did the recipe and knowledge of the ores originate? (2) Did the ancient smelters apply field diagnostic methods developed by them for identification of suitable ores or did they rely on external specialists for that? (3) Are there other smelting sites in northern Central Europe with

similar conditions? For ore identification on other sites, also large-scale screening of ore occurrences is required.

Author Contributions: Conceptualization, C.H. and M.S.; methodology; validation, U.K., H.K., M.S. and F.K.; formal analysis, C.H. and F.K.; investigation, all authors; resources, U.K., H.K. and M.S.; data curation, C.H., M.S.; writing—original draft preparation, C.H.; writing—review and editing, all authors; visualization, C.H.; supervision, M.S.; project administration, C.H.; funding acquisition, C.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the VGH Foundation, Hanover, Germany grant number 3845 And The APC was funded by the University of Hildesheim, Germany.

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors would like to express their explicit gratitude to the following individuals and institutions who supported this work: Ute Bartelt (Municipal Archaeology Region of Hanover), Ulrike Weller (Collection Management State Museum Hanover), and Arne Butt (VGH Foundation). Thanks are also due to the VGH Foundation for their financial support for the 14C analyses and to the “CRB” laboratory in Hardegsen, Lower Saxony, Germany, for the prompt processing of the samples and the helpful advice. We gratefully acknowledge the helpful comments and suggestions by the three anonymous reviewers.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

BSE	backscattered electron
CISC	clay iron stone concretion
EDS	energy dispersive X-ray spectroscopy
LIBS	laser-induced breakdown spectroscopy
LOI	loss on ignition
OCISC	oxidized clay iron stone concretion
RII	reducible iron index
RIOI	reducible iron ore index
SandISC	sand iron stone concretion
SEM	scanning electron microscope
SCISC	sideritic clay iron stone concretions
XRF	X-ray fluorescence spectroscopy

Appendix A

Table A1. List of all slag finds from the “Sehnde 9” site stored in the archives of the state museum Hanover.

Finding	Number of Fragments	Description	Mass [g]	From Finding Complex
99	92	Slag fragments with vertical flow structures, medium grey, slightly porous	2047	bloomery furnace
76	40	Slag fragments with vertical flow structures, medium grey, slightly porous	308	pit
78	80	Slag fragments with vertical flow structures, medium grey, slightly porous, some with charcoal inclusions	816	bloomery furnace
79	20	Slag fragments with vertical flow structures, medium grey, slightly porous	125	bloomery furnace
92	32	Slag fragments with vertical flow structures, medium grey, slightly porous	1948	pit

Table A1. Cont.

Finding	Number of Fragments	Description	Mass [g]	From Finding Complex
334	84	Slag fragments with vertical flow structures, medium grey, slightly porous, some with charcoal inclusions	1240	bloomery furnace
249	81	Slag fragments with vertical flow structures, medium grey, slightly porous, some with charcoal inclusions	561	bloomery furnace
250	32	Slag fragments with vertical flow structures, medium grey, slightly porous	261	bloomery furnace
251	89	Slag fragments with vertical flow structures, medium grey, slightly porous, some with charcoal inclusions	1549	bloomery furnace
6	51	Slag fragments with vertical flow structures, medium grey, slightly porous	3970	bloomery furnace
7	93	Slag fragments with vertical flow structures, medium grey, slightly porous	3206	bloomery furnace
8	5	Slag fragments with vertical flow structures, medium grey, slightly porous	56	bloomery furnace
9	24	Slag fragments with vertical flow structures, medium grey, slightly porous	1780	bloomery furnace
26	200	Slag fragments with vertical flow structures, medium grey, slightly porous	5352	bloomery furnace
10	78	Slag fragments with vertical flow structures, medium grey, slightly porous	2824	bloomery furnace
11	9	Slag fragments with vertical flow structures, medium grey, slightly porous	199	bloomery furnace
17	116	Slag fragments with vertical flow structures, medium grey, slightly porous	1039	bloomery furnace
17	2	Furnace slag fragments, compact, dark grey to black, no flow structures visible	783	bloomery furnace
15	57	Slag fragments with vertical flow structures, medium grey, slightly porous, some with charcoal inclusions	2041	bloomery furnace
24	201	Slag fragments with vertical flow structures, medium grey, slightly porous	1010	bloomery furnace
24	2	Furnace slag fragments, compact, dark grey to black, no flow structures visible	5430	bloomery furnace
26	65	Slag fragments with vertical flow structures, medium grey, slightly porous	4770	bloomery furnace
28	28	Slag fragments with vertical flow structures, medium grey, slightly porous	858	bloomery furnace
30	1	Slag fragments with vertical flow structures, medium grey, slightly porous	2685	bloomery furnace
42	1	Furnace slag fragments, compact, dark grey to black, no flow structures visible	1909	pit
21	42	Furnace slag fragments, compact, dark grey to black, no flow structures visible	3059	pit house
117	214	Slag fragments with vertical flow structures, medium grey, slightly porous	6243	bloomery furnace
117	1	Furnace slag fragments, compact, dark grey to black, no flow structures visible	1705	bloomery furnace
173	10	Slag fragments with vertical flow structures, medium grey, slightly porous	207	bloomery furnace
66	8	Slag fragments with vertical flow structures, medium grey, slightly porous	207	pit house
63	2	Slag fragments with vertical flow structures, medium grey, slightly porous	261	pit
257	6	Slag fragments with vertical flow structures, medium grey, slightly porous	590	pit
274	16	Slag fragments with vertical flow structures, medium grey, slightly porous	524	pit
306	1	Furnace slag fragments, compact, dark grey to black, no flow structures visible	73	pit
359	29	Furnace slag fragments, compact, dark grey to black, no flow structures visible	21,814	pit house

Table A1. *Cont.*

Finding	Number of Fragments	Description	Mass [g]	From Finding Complex
118	10	Furnace slag fragments, compact, dark grey to black, no flow structures visible	2076	pit house
153	4	Furnace slag fragments, compact, dark grey to black, no flow structures visible	305	pit house
173	12	Furnace slag fragments, compact, dark grey to black, no flow structures visible	193	pit
198	10	Furnace slag fragments, compact, dark grey to black, no flow structures visible	2892	pit house
198	2	Slag fragments with vertical flow structures, medium grey, slightly porous	75	pit house
235	10	Furnace slag fragments, compact, dark grey to black, no flow structures visible	4234	pit house
235	2	Slag fragments with vertical flow structures, medium grey, slightly porous	149	pit house
120	3	Slag fragments with vertical flow structures, medium grey, slightly porous	202	pit house
120	22	Furnace slag fragments, compact, dark grey to black, no flow structures visible	304	pit house
Total mass of all slag fragments (g)			91,880	
Total number of slag fragments			1887	

Table A2. Results of EDS analyses of archaeological slags from the “Sehnde 9” site. Concentrations are given for elements (weight percent, atomic percent) and compounds (oxides, weight percent).

Finding	Measuring Point, Characterization	Element	Concentration (wt. %, Normalized)	Concentration (at.%)	Compound (Oxid)	Concentration (wt. %, Normalized)
15	1, fayalite	C	0.00	0.00		
		O	31.70	56.80		
		Mg	0.84	1.00	MgO	1.40
		Al	1.49	1.58	Al ₂ O ₃	2.81
		Si	12.64	12.91	SiO ₂	27.05
		K	0.23	0.17	K ₂ O	0.28
		Ca	1.38	0.99	CaO	1.94
		Mn	1.13	0.59	MnO	1.46
		Fe	50.57	25.96	FeO	65.06
15	2, glass matrix	C	0.00	0.00		
		O	35.81	57.96		
		Na	0.30	0.33	Na ₂ O	0.40
		Mg	0.15	0.16	MgO	0.25
		Al	8.20	7.87	Al ₂ O ₃	15.49
		Si	11.91	10.98	SiO ₂	25.48
		P	1.60	1.33	P ₂ O ₅	3.66
		K	2.50	1.66	K ₂ O	3.01
		Ca	7.45	4.81	CaO	10.43
		Fe	32.09	14.88	FeO	41.28
15	3, wustite	C	0.00	0.00		
		O	25.63	52.69		
		Al	1.67	2.03	Al ₂ O ₃	3.15
		Si	3.80	4.45	SiO ₂	8.13
		K	0.21	0.18	K ₂ O	0.26
		Ca	0.79	0.65	CaO	1.10
		Fe	67.90	40.00	FeO	87.35

Table A2. Cont.

Finding	Measuring Point, Characterization	Element	Concentration (wt. %, Normalized)	Concentration (at.%)	Compound (Oxid)	Concentration (wt. %, Normalized)
15	1, fayalite	C	0.00	0.00		
		O	31.70	56.80		
		Mg	0.84	1.00	MgO	1.40
		Al	1.49	1.58	Al ₂ O ₃	2.81
		Si	12.64	12.91	SiO ₂	27.05
		K	0.23	0.17	K ₂ O	0.28
		Ca	1.38	0.99	CaO	1.94
		Mn	1.13	0.59	MnO	1.46
		Fe	50.57	25.96	FeO	65.06
15	2, glass matrix	C	0.00	0.00		
		O	35.81	57.96		
		Na	0.30	0.33	Na ₂ O	0.40
		Mg	0.15	0.16	MgO	0.25
		Al	8.20	7.87	Al ₂ O ₃	15.49
		Si	11.91	10.98	SiO ₂	25.48
		P	1.60	1.33	P ₂ O ₅	3.66
		K	2.50	1.66	K ₂ O	3.01
		Ca	7.45	4.81	CaO	10.43
15	3, wustite	Fe	32.09	14.88	FeO	41.28
		C	0.00	0.00		
		O	25.63	52.69		
		Al	1.67	2.03	Al ₂ O ₃	3.15
		Si	3.80	4.45	SiO ₂	8.13
		K	0.21	0.18	K ₂ O	0.26
		Ca	0.79	0.65	CaO	1.10
15	4, wustite	Fe	67.90	40.00	FeO	87.35
		C	0.00	0.00		
		O	25.54	52.66		
		Al	1.52	1.86	Al ₂ O ₃	2.87
		Si	3.69	4.34	SiO ₂	7.90
		K	0.20	0.17	K ₂ O	0.24
		Ca	0.71	0.59	CaO	1.00
		Ti	0.21	0.15	TiO ₂	0.36
78	1, fayalite	Fe	68.12	40.24	FeO	87.64
		C	0.00	0.00		
		O	31.44	56.42		
		Mg	0.60	0.71	MgO	0.99
		Al	2.32	2.46	Al ₂ O ₃	4.38
		Si	10.20	10.43	SiO ₂	21.82
		P	1.20	1.11	P ₂ O ₅	2.75
		K	1.32	0.97	K ₂ O	1.60
		Ca	3.16	2.26	CaO	4.42
		Mn	5.70	2.98	MnO	7.36
		Fe	44.07	22.66	FeO	56.69

Table A2. Cont.

Finding	Measuring Point, Characterization	Element	Concentration (wt. %, Normalized)	Concentration (at.%)	Compound (Oxid)	Concentration (wt. %, Normalized)
78	2, glass matrix	C	0.00	0.00		
		O	32.81	56.99		
		Mg	0.54	0.61	MgO	0.89
		Al	3.37	3.47	Al ₂ O ₃	6.38
		Si	10.60	10.49	SiO ₂	22.68
		P	1.89	1.69	P ₂ O ₅	4.32
		K	2.20	1.56	K ₂ O	2.64
		Ca	4.90	3.40	CaO	6.85
		Mn	5.33	2.70	MnO	6.89
		Fe	38.36	19.09	FeO	49.35
251	1, fayalite	C	0.00	0.00		
		O	29.92	55.43		
		Mg	0.79	0.97	MgO	1.31
		Al	2.72	2.98	Al ₂ O ₃	5.13
		Si	8.82	9.31	SiO ₂	18.87
		P	0.25	0.24	P ₂ O ₅	0.57
		K	0.79	0.60	K ₂ O	0.95
		Ca	1.54	1.14	CaO	2.16
		Mn	4.52	2.44	MnO	5.83
		Fe	50.66	26.89	FeO	65.17
251	2, glass matrix	C	0.00	0.00		
		O	30.85	55.83		
		Mg	0.83	0.99	MgO	1.38
		Al	3.81	4.09	Al ₂ O ₃	7.21
		Si	9.02	9.30	SiO ₂	19.30
		P	0.56	0.52	P ₂ O ₅	1.29
		K	1.30	0.96	K ₂ O	1.56
		Ca	2.26	1.63	CaO	3.16
		Mn	4.42	2.33	MnO	5.71
		Fe	46.94	24.34	FeO	60.39
334	1, glass matrix	C	0.00	0.00		
		O	32.31	57.20		
		Mg	0.55	0.64	MgO	0.92
		Al	2.72	2.86	Al ₂ O ₃	5.14
		Si	10.94	11.03	SiO ₂	23.41
		P	1.41	1.29	P ₂ O ₅	3.23
		Ca	2.65	1.87	CaO	3.71
		Mn	6.21	3.20	MnO	8.02
		Fe	43.20	21.91	FeO	55.57
334	2, fayalite	C	0.00	0.00		
		O	31.47	56.73		
		Mg	0.62	0.74	MgO	1.03
		Al	1.44	1.54	Al ₂ O ₃	2.72
		Si	11.25	11.55	SiO ₂	24.06
		P	0.93	0.87	P ₂ O ₅	2.14
		K	0.45	0.33	CaO	0.54
		Ca	1.93	1.39	MnO	2.70
		Mn	6.85	3.59	FeO	8.84
		Fe	45.06	23.27	MgO	57.97

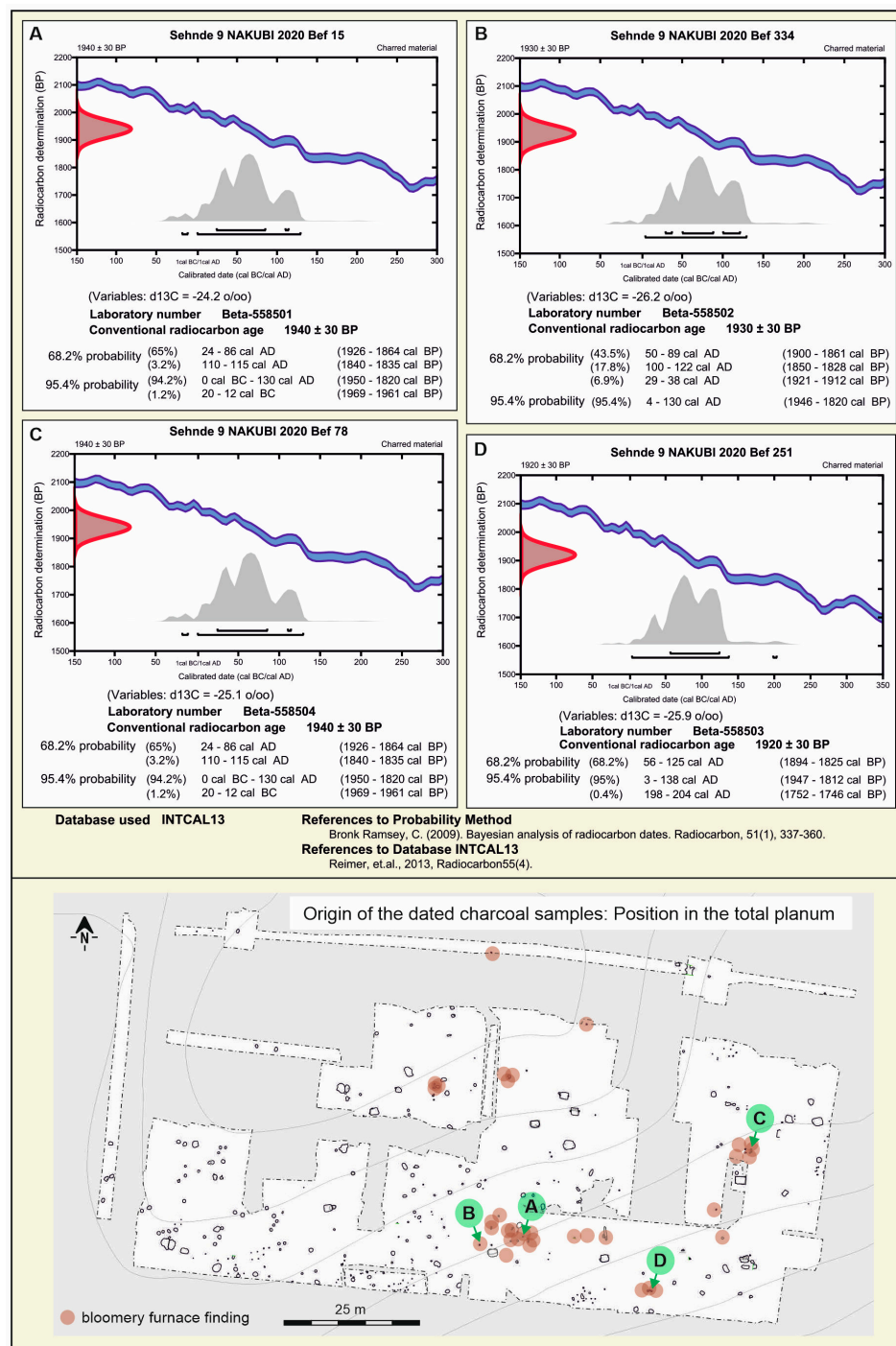


Figure A1. Results of Radiocarbon dating and Location of the associated findings. (A–D): Sampling points of the examined charcoal. Reference to Probability Method [60]. Reference to Database INTCAL13 [61].

References

1. Arcontor Projekt GmbH. Bericht Zur Archäologischen Untersuchung vom 03.-11.05.2017 und 10.07.-17.11.2017: Unveröffentlichte Grabungsdokumentation; unpublished excavation documentation; State Office for Monument Preservation: Braunschweig, Germany, 2017.
2. von Olberg, G. Gemeinde. Germanische Altertumskunde Online GAO Database 2010; De Gruyter Brill: Berlin, Germany, 2010.
3. Graupner, A. Raseneisenstein in Niedersachsen: Entstehung, Vorkommen, Zusammensetzung und Verwendung; Forschungen zur niedersächsischen Landeskunde; Verlag Göttinger Tageblatt: Göttingen, Germany, 1982.

4. Brumlich, M.; Meyer, M.; Lychatz, B. Archäologische und archäometallurgische Untersuchungen zur latènezeitlichen Eisenverhüttung im nördlichen Mitteleuropa. *Præhist. Z.* **2013**, *87*, 433–473. [[CrossRef](#)]
5. Ganzelewski, M. Archäometallurgische Untersuchungen zur frühen Verhüttung von Raseneisenerzen am Kammberg bei Joldelund, Kreis Nordfriesland. In *Frühe Eisengewinnung in Joldelund, Kr. Nordfriesland: Ein Beitrag zur Siedlungs- und Technikgeschichte Schleswig-Holstein. 2: Naturwissenschaftliche Untersuchungen zur Metallurgie- und Vegetationsgeschichte*; Haffner, A., Jöns, H., Reichstein, J., Eds.; Universitätsforschungen zur prähistorischen Archäologie; Habelt: Bonn, Germany, 2000; Volume 59, pp. 3–100.
6. Jöns, H. Eisengewinnung im norddeutschen Flachland. *Archäologie Dtschl. Sonderh.* **1993**, *1*, 63–69.
7. Thelemann, M.; Bebermeier, W.; Hoelzmann, P.; Lehnhardt, E. Bog iron ore as a resource for prehistoric iron production in Central Europe—A case study of the Widawa catchment area in Eastern Silesia, Poland. *CATENA* **2017**, *149*, 474–490. [[CrossRef](#)]
8. Sitschick, H.; Ludwig, F.; Wetzel, E.; Luckert, J.; Höding, T. Raseneisenerz—Auch in Brandenburg ein mineralischer Rohstoff mit bedeutender wirtschaftlicher Vergangenheit. *Brand. Geowiss. Beiträge* **2005**, *12*, 119–128.
9. Wu, Y.; Fang, M.; Lan, L.; Zhang, P.; Rao, K.V.; Bao, Z. Rapid and direct magnetization of goethite ore roasted by biomass fuel. *Sep. Purif. Technol.* **2012**, *94*, 34–38. [[CrossRef](#)]
10. Khan, M.A.; Kerr, A.C.; Abdullah, K.; Kakar, H.U.; Tariq, M.; Naeem, A. Major and trace elements geochemistry of Ziarat laterite deposits, Ziarat district, Western Pakistan. Implications for source rock materials and ore genesis. *Carbonates Evaporites* **2025**, *40*, 24. [[CrossRef](#)]
11. Harms, F.-J. Der Sarstedt-Lehrter Salzstock: Zeitschrift für Paläontologen. *Arbeitskreis Paläontologie Hann.* **1973**, *6*, 1–8.
12. Dietz, C. *Lehrte: Erläuterungen zu Blatt Nr. 3625 Lehrte*; Geologische Karte von Niedersachsen; hrsg. vom Niedersächsischen Landesamt für Bodenforschung: Hannover, Germany, 1973; Bl. 3625.
13. Dietz, C. *Lehrte: Erläuterungen zu Blatt Nr. 3625 Lehrte, Ergänzungsheft*; Geologische Karte von Niedersachsen Lehrte; hrsg. vom Nds. Landesamt für Bodenforschung: Hannover, Germany, 1974; Bl. 3625.
14. Stapf, K.R.G. Biogene fluvio-lakustrine Sedimentation im Rotliegend des permokarbonen Saar-Nahe-Beckens (SW-Deutschland). *Facies* **1989**, *20*, 169–197. [[CrossRef](#)]
15. Kholodov, V.N.; Butuzova, G.Y. Problems of siderite formation and iron ore epochs: Communication 1. Types of siderite-bearing iron ore deposits. *Lithol. Miner. Resour.* **2004**, *39*, 389–411. [[CrossRef](#)]
16. Okrusch, M.; Matthes, S. *Mineralogie: Eine Einführung in die spezielle Mineralogie, Petrologie und Lagerstättenkunde, 7., Vollständig Überarbeitete, Erweiterte und Aktualisierte Auflage*; Springer: Berlin/Heidelberg, Germany, 2005. [[CrossRef](#)]
17. Kholodov, V.N.; Butuzova, G.Y. Siderite formation and evolution of sedimentary iron ore deposition in the earth's history. *Geol. Ore Depos.* **2008**, *50*, 299–319. [[CrossRef](#)]
18. Kaczorek, D.; Sommer, M. Micromorphology, chemistry, and mineralogy of bog iron ores from Poland. *CATENA* **2003**, *54*, 393–402. [[CrossRef](#)]
19. Marshall, J.D.; Pirrie, D. Carbonate concretions—Explained. *Geol. Today* **2013**, *29*, 53–62. [[CrossRef](#)]
20. Lippmann, F. Ton, Geoden und Minerale des Barrême von Hoheneggelsen. *Geol. Rundsch.* **1955**, *43*, 475–503. [[CrossRef](#)]
21. Gedenk, R.; Zimmerle, W. Bitumenimprägnation in Siderit-Konkretionen des Ober-Apt (Clansayes) von Lohne bei Hannover. *Geol. Jahrb.* **1982**, *19*, 147–157.
22. Harms, F.-J. Die Grube Sehnde der Ziegelei Stoevesandt: Zeitschrift für Paläontologen. *Arbeitskreis Paläontologie Hann.* **1973**, *6*, 9–13.
23. Leonowicz, P. Origin of siderites from the Lower Jurassic Ciechocinek formation from SW Poland. *Geol. Q.* **2007**, *51*, 67–78.
24. Witkowska, M. Palaeoenvironmental significance of iron carbonate concretions from the Bathonian (Middle Jurassic) Ore-Bearing Clays at Gnaszyn, Kraków-Silesia Homocline, Poland. *Acta Geol. Pol.* **2012**, *62*, 307–324. [[CrossRef](#)]
25. Mutterlose, J. Die Unterkreide-Aufschlüsse (Valangin-Alb) im Raum Hannover-Braunschweig. In *Mitteilungen aus dem Institut für Geologie und Paläontologie der Universität Hannover*; Geologisches Institut der Universität Hannover: Hannover, Germany, 1984; Volume H. 24.
26. Lehmann, J.; Friedrich, O.; Barga, D.; Hemker, T. Early Aptian bay deposits at the southern margin of the Lower Saxony basin: Integrated stratigraphy, palaeoenvironment and Oae 1a. *Acta Geol. Pol.* **2012**, *62*, 35–62. [[CrossRef](#)]
27. Curtis, C.D.; Pearson, M.J.; Somogyi, V.A. Mineralogy, chemistry, and origin of a concretionary siderite sheet (clay-ironstone band) in the Westphalian of Yorkshire. *Mineral. Mag.* **1975**, *40*, 385–393. [[CrossRef](#)]
28. Oertel, G.; Curis, C.D. Clay-ironstone concretion preserving fabrics due to progressive compaction. *Geol. Soc. Am. Bull.* **1972**, *83*, 2597. [[CrossRef](#)]
29. Bergwerkseigentum (Mine Property). Available online: <https://nibis.lbeg.de/cardomap3/> (accessed on 25 August 2025).
30. Paynter, S. Regional variations in bloomery smelting slag of the Iron Age and Romano-British periods. *Archaeometry* **2006**, *48*, 271–292. [[CrossRef](#)]

31. Heliasz, Z.; Ostaficzuk, S. Historical residues of iron ore mining in environs of the Holy Cross Mountains (the Góry Świętokrzyskie) are recognizable on the Digital Terrain Elevation Model (DEM) derived from the LIDAR data. *Gospod. Surowcami Miner.—Miner. Resour. Manag.* **2023**, *36*, 161–186. [\[CrossRef\]](#)
32. Wrona, P.; Róžański, Z.; Pach, G.; Niewiadomski, A.P.; Veiga, J.P. Historical outline of iron mining and production in the area of present-day Poland. *Minerals* **2021**, *11*, 1136. [\[CrossRef\]](#)
33. Pleiner, R. *Iron in Archaeology: The European Bloomery Smelters*; Archeologický ústav AVČR: Praha, Czech Republic, 2000.
34. Joosten, I.; Jansen, J.B.H.; Kars, H. Geochemistry and the Past: Estimation of the Output of a Germanic Iron Production Site in the Netherlands. *J. Geochem. Explor.* **1998**, *62*, 129–137. [\[CrossRef\]](#)
35. Yalcin, Ü. Zur Technologie der Eisenverhüttung. *Arb.-Forschungsberichte Sächs. Bodendenkmalpfl.* **2000**, *42*, 307–316.
36. Charlton, M.F.; Crew, P.; Rehren, T.; Shennan, S.J. Explaining the evolution of ironmaking recipes—An example from Northwest Wales. *J. Anthropol. Archaeol.* **2010**, *29*, 352–367. [\[CrossRef\]](#)
37. Kronz, A.; Eggers, T. Archäometallurgische Untersuchungen eisenzeitlicher Funde aus dem Hügelgräberfeld Hillesheim, Kreis Daun. *Trier. Zeitschr. Gesch. Kunst Trier. Landes Seiner Nachbargeb.* **2001**, *64*, 69–109.
38. Paynter, S.; Crew, P.; Blakelock, E.; Hatton, G. Spinel-rich slag and slag inclusions from a bloomery smelting and smithing experiment with a sideritic ore. *Hist. Metall.* **2017**, *49*, 126–143.
39. Cavallini, M. Thermodynamics applied to iron smelting techniques. *Appl. Phys. A* **2013**, *113*, 1049–1053. [\[CrossRef\]](#)
40. Straube, H. *Ferrum Noricum und die Stadt auf dem Magdalensberg*; Springer: Vienna, Austria, 1996. [\[CrossRef\]](#)
41. Zavyalov, V.I.; Terekhova, N.N. Bloomery process as the basis of ancient metallurgy. *Teor. Prakt. Arkheologicheskikh Issled.* **2023**, *35*, 23–41. [\[CrossRef\]](#)
42. Kriete, C. Geochemische Untersuchungen der Rennfeuerschlacken aus dem Siedlungsgebiet der vorrömischen Eisenzeit und älteren Römischen Kaiserzeit von Salzgitter-Fredenbergl im Hinblick auf die Herkunft der verwendeten Erze. *Nachrichten Niedersachs. Urgesch. NNU* **2009**, *78*, 37–56.
43. Thomas, G.R.; Young, T.P. The Determination of bloomery furnace mass balance and efficiency. *Geol. Soc. Lond. Spec. Publ.* **1999**, *165*, 155–164. [\[CrossRef\]](#)
44. Schweingruber, F.H. *Microscopic Wood Anatomy*, 3rd ed.; Verlag Kessel: Remagen, Germany, 2016.
45. Kierdorf, U.; Stock, S.R.; Gomez, S.; Antipova, O.; Kierdorf, H. Distribution, structure, and mineralization of calcified cartilage remnants in hard antlers. *Bone Rep.* **2022**, *16*, 101571. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Helmreich, C.; Kobbe, F.; Sauerwein, M. Den Erzen auf der Spur—Experimentalarchäologische und archäometallurgische Untersuchungen zur Identifizierung der Ausgangserze von Eisenverhüttungsschlacken einer archäologischen Fundstelle in Niedersachsen. *Bilanz* **2021**, *20*, 196–209.
47. Wegewitz, W. Ein Rennfeurofen aus einer Siedlung der älteren Römerzeit in Scharmbeck (Kreis Harburg). *Nachrichten Niedersachs. Urgesch. NNU* **1957**, *26*, 3–25.
48. Osann, B. Rennstahlgewinnung in einer germanischen Siedlung beim heutigen Salzgitter-Lobmachersen. *Nachrichten Niedersachs. Urgesch. NNU* **1960**, *29*, 28–34.
49. Reepen, B.; Drexler, H.-J. Rennofenversuche am Sachsenhof in Greven—Ein Erfahrungsbericht. In *Experimentelle Archäologie in Europa. Bilanz 2004*; Isensee F. Oldenburg, Germany, 2005; pp. 159–166.
50. Paysan, A. Nachhaltige Energiewirtschaft? Ph.D. Thesis, Kiel University, Kiel, Germany, 2011.
51. Hauptmann, A. Study of archaeometallurgical slag and metal. In *The Archaeometallurgy of Copper*; Hauptmann, A., Herrmann, B., Wagner, G.A., Eds.; Natural Science in Archaeology; Springer: Berlin/Heidelberg, Germany, 2007; pp. 157–215. [\[CrossRef\]](#)
52. Oeters, F.; Ottow, M.; Senk, D.; Beyzavi, A.; Güntner, J.; Lungen, H.B.; Koltermann, M.; Buhr, A. Iron, 1. Fundamentals and principles of reduction processes. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2019; pp. 1–82. [\[CrossRef\]](#)
53. Abreu, C.A.; Cantoni, M.; Coscione, A.R.; Paz-Ferreiro, J. Organic matter and barium absorption by plant species grown in an area Polluted with scrap metal residue. *Appl. Environ. Soil Sci.* **2012**, *2012*, 476821. [\[CrossRef\]](#)
54. Goldschmidt, V.M. *Geochemistry*; Clarendon Press: Oxford, UK, 1954.
55. Morel, M.; Serneels, V. Interpreting the chemical variability of iron smelting slag: A case Study from northeastern Madagascar. *Minerals* **2021**, *11*, 900. [\[CrossRef\]](#)
56. Matthes, W.E.; Matthes, W. *Grundlagen, Eigenschaften, Rezepte, Anwendung, Orig.-Ausg., 2. [Dr.]*; Keramische Glasuren/Wolf Matthes; Müller: Köln, Germany, 1986.
57. Speier, M. *Vegetationskundliche und paläoökologische Untersuchungen zur Rekonstruktion prähistorischer und historischer Landnutzungen im südlichen Rothaargebirge*; Abhandlungen aus dem Westfälischen Museum für Naturkunde; Westfälisches Museum für Naturkunde: Münster, Germany, 1994.

58. Dörfler, W. Palynologische Untersuchungen zur Vegetations- und Landschaftsentwicklung von Joldelund, Kr. Nordfriesland. In *Frühe Eisengewinnung in Joldelund, Kr. Nordfriesland: Ein Beitrag zur Siedlungs- und Technikgeschichte Schleswig-Holstein. 2: Naturwissenschaftliche Untersuchungen zur Metallurgie- und Vegetationsgeschichte*; Haffner, A., Jöns, H., Reichstein, J., Eds.; Universitätsforschungen zur prähistorischen Archäologie; Habelt: Bonn, Germany, 2000; Volume 59, pp. 147–208.
59. Iles, L. The exploitation of manganese-rich 'ore' to smelt iron in Mwenge, western Uganda, from the mid second millennium AD. *J. Archaeol. Sci.* **2014**, *49*, 423–441. [[CrossRef](#)]
60. Bronk, R.C. Bayesian analysis of radiocarbon dates. *Radiocarbon* **2009**, *51*, 337–360. [[CrossRef](#)]
61. Reimer, P.J.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Ramsey, C.B.; Buck, C.E.; Cheng, H.; Edwards, R.L.; Friedrich, M.; et al. IntCal13 and Marine13 radiocarbon age calibration curves 0–50,000 years cal BP. *Radiocarbon* **2013**, *55*, 1869–1887. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.