Provenance of Iron Age iron in southern Germany: a new approach

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Ores, slag, and blooms from an Early Iron Age smelting site in the Black Forest, southern Germany, were analysed in view of their possible provenance in combination with products from a modern smelting experiment. Rather than employing lead isotope ratios, like in a previous study, osmium and strontium isotope ratios are used for the discussion of provenance. The results of the smelting experiment with iron ores from the archaeological site and their comparison with original finds show the high potential of osmium as a tracer to determine provenance. Strontium may be an additional indicator but possible contaminations need to be assessed. A Celtic iron ingot has also been analysed to check the potential of osmium for further provenance studies.

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1. Introduction

The provenance of prehistoric iron is one of the key questions of the archaeology of the Iron Age. Accordingly, the application of scientific methods suggested itself since the beginnings of analytical chemistry to the present day. In a previous paper a review of the different approaches for source determination of iron artefacts was given and basic problems discussed (Schwab et al., 2006). A summary of more recent work is given by Leroy et al. (2012). Most attempts relied on the chemical compositions of slag inclusions and of the metal to link iron to ore, albeit with quite different techniques. Similar studies are still in progress and further efforts are made to improve this approach with sophisticated data evaluation and smelting experiments (e.g. Desaulty et al., 2007, 2008, 2009; Senn et al., 2010; Leroy et al., 2012).

In a pilot study a series of iron finds dated to the Late Iron Age from the Celtic oppidum of Manching in southern Bavaria (Germany) were analysed in view of the provenance of the iron by a combination of the minor element concentrations of slag inclusions performed by electron microprobe (WDX-EMPA) and of the iron metal determined by atomic spectrometry (ICP–AES and AAS). Lead isotopic ratios, well established in non-ferrous archaeometallurgy but hardly employed for iron, were introduced as a new approach (Schwab et al., 2006).

As a result it was possible to distinguish various occurrences of iron ore near the settlement some of which could be excluded as sources. Generally, it was found that bog ores are the most likely sources for the iron found at Manching. However, it turned out that the isotopic inhomogeneity is relatively large in many iron ore deposits due to generally low lead and high uranium concentrations.

This makes the discrimination of iron ores from different locations uncertain. Only with the combination of their minor element patterns it was possible to identify one local bog ore deposit which matches the characteristics of the iron artefacts examined in all aspects (Schwab et al., 2006). Accordingly, for a large-scale transregional study it is desirable to have more discriminating parameters available for the characterisation of the iron ores and these should not be too much altered by the production processes.

In this context, the prehistoric bi-pointed or bi-pyramidal iron bars and some currency bars that are mainly distributed in southern Germany, Switzerland and eastern France are of particular interest. Several distribution maps of such bi-pyramidal and/or currency bars are published by e.g. Jacobi (1974), Pleiner (1980), Doswald (1994), Kurz (1995) and by Wischenbarth et al. (2001).
Since these ingots most likely represent raw metal that has hardly been altered, they provide an ideal link between primary iron production and finished iron artefacts. If the provenance of these objects could be determined, a much better understanding of the economic and social organisation in the Iron Age of central Europe could be achieved.

At present the most developed and established method to link iron ores with archaeological or historical iron objects is the analysis of major and trace element concentrations in slag inclusions using a combination of X-ray microanalysis and laser ablation coupled mass spectrometry (Coustures et al., 2003, 2006; Desaulty et al., 2007, 2008, 2009; Leroy et al., 2012). This method is limited by the size of the inclusions depending on the diameter of the laser beam and the loss of information when the iron became liquid (see Desaulty et al., 2009). A minimum spot size of 30–50 μm is commonly used to obtain a sufficient count rate and thus data with the required analytical quality.

In a more recent paper Degryse et al. (2007) proposed to use the combination of lead isotope ratios with those of strontium for provenancing iron objects as it has been already introduced for ancient glass.

Strontium as a lithophile element will be preferentially taken up by the slag, whereas lead as an element with siderophile–chalcophile affinities would be predicted to enter the iron metal. Actually, lead seems to partition between slag and metal so that the lead concentrations in iron artefacts are often too low and therefore it is often difficult or even impossible to determine the isotope ratios. This and the variable lead isotope ratios of the deposits are severe limitations to the application of lead isotopes as tracers for archaeological iron. Strontium is one of the most abundant elements, so that the strontium signature of an ore may be easily influenced by a small admixture of strontium bearing components, like charcoal, lime or clay.

Therefore, we explored the possibility to use osmium isotope ratios for provenance investigations of iron, since osmium, like lead, is one of the few heavy elements that have a variable isotope composition due to the radioactive decays of \(^{187}\)Re (β decay, half-life 41.6 \times 10^4 years, Smoliar et al., 1996) and \(^{190}\)Pt (α decay, half-life 3.7 \times 10^{11} years, Tavares et al., 2006). Osmium belongs together with Ru, Pd, Pt, Ir to the platinum group elements (PGE) with common chemical and geochemical characteristics. For our purpose it is most useful that they are highly siderophile, i.e. they are strongly partitioned into the metal phase in metal-silicate systems. The partition coefficients \(D_{\text{metal/sil}}\) are \(5 \times 10^{10}\) for rhenium (Ertel et al., 2001) and about \(10^9\) for osmium (Brenan and McDonough, 2009). Consequently, they are concentrated in the Earth's core and their concentration levels are in the order of \(\mu\) g kg\(^{-1}\) in the mantle and crust (Taylor and McLennan, 1985). Thus they are also termed “highly-siderophile elements” (HSE) together with rhenium and gold. Since iron smelting also involves metal-silicate fractionation it can be assumed that practically all of the osmium in the silicate melt will be taken up by the iron formed due to the extreme siderophile character of osmium. One complication, however, has to be taken into account: On strong oxidation like the roasting of the ore volatile OsO\(_4\) is formed so that part of the osmium may be lost on the way between the iron ore and the raw metal. On the other hand, under mildly oxidising conditions like in open air or buried in the ground, when iron corrodes osmium is quite immobile and thus less prone to alteration (Jaffe et al., 2002).

The range of osmium isotopic variations is much larger than in other radiogenic systems due the different chalcophile behaviour of rhenium and osmium. Whereas rhenium is readily taken up by sulphides with distribution coefficients between sulfide and silicate melt between \(10^1\) and \(10^3\), osmium still behaves a compatible element with distribution coefficients between \(3.0 \times 10^4\) and \(4.8 \times 10^4\) for Os (Roy-Barman et al., 1998). An extreme case is the

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**Fig. 1.** Location of the iron production centre at Neuenburg with different smelting sites dated from the late Hallstatt to the early La Tène periods.
mineral molybdenite (MoS₂) that can contain up to a few percent rhenium (McCandless et al., 1993), which results in the virtual absence of common Os (not derived from 187Re decay) in the mineral's structure and consequently in huge 187Os/188Os ratios.

Unlike our previous study which was focused on a possible relation between ores and final products, we started at the beginning of the chaîne opératoire of iron production. This study deals with blooms, slag, charcoals and furnace material from a well dated archaeological site as well as with similar materials from a modern smelting experiment. The major goal was the investigation of the behaviour of osmium and its isotope ratios during iron smelting and to check the potential of strontium isotopes. We then extended the study to ingots in order to assess the method for future applications.

2. Production and circulation of iron in the Iron Age of southern Germany

It has already been mentioned that there is a discrepancy between the large number of iron implements and the number of excavated furnaces dated to the La Tène period, in particular to the late phase (Schwab et al., 2006). Indeed, during the last years several new smelting sites could be located in southwest Germany dating from the early to the middle La Tène period (Wischenbarth et al., 2001; Gassmann et al., 2005, 2006; Rösch et al., 2009).

The most comprehensive research was performed at the iron ore deposit near Neuenbürg in the Black Forest (Enzkreis, Baden-Württemberg, Fig. 1) since 2004. About 70 small slag piles and other smelting relics have so far been discovered. The excavated slag piles and furnaces were dated from late Hallstatt to early La Tène by associated pottery. Already in the 1920s, an Early La Tène hilltop settlement was discovered on the castle hill of Neuenbürg, which may have controlled the production and distribution of iron in this period (Gassmann et al., 2006; Rösch et al., 2009). Recent excavations in the nearby Grösseltal (Neuenbürg-Waldrennach), at a linear distance of about 1.5 km away from the castle hill (Fig. 1) revealed another well preserved ensemble of remains from early Celtic iron production. Slag piles that usually comprise about 20 t of slag, bloom and furnace material are associated with smelting furnaces, forges and anvil stones for reheating, stone pebble tools for crushing and depots for ores and charcoal...
(Gassmann and Wieland, 2008, 2009). The furnaces are typical cunpo or domed furnaces with front pits and upper fitted shafts, known from all over Europe in regions showing Celtic influences (Pleiner, 2000; Gassmann et al., 2005). They are usually embedded in hillsides and with the exception of a small channel in the front wall without any additional air supply. The furnaces near Neuenburg are different from this standardised construction insofar as they are smaller and have an additional air supply above the channel in the front wall. According to the very different diameters of these additional vents the furnaces were operated with natural draught or with bellows (Gassmann et al., 2006). The blooms, or what is left from the blooms produced within these furnaces typically contain heterogeneous, but highly carburised blooms, or what is left from the blooms produced within these natural draught or with bellows (Gassmann et al., 2006). The number of furnaces and the configuration of the smelting sites suggest an overproduction of iron for regional purposes so that the surplus may have been available for trade.

The geological basis for this large production was provided by manganese-rich limonite ores which crop out in the form of veins along tectonic faults, together with barite and fluorite. The small widths of these ore veins did not make them suitable for modern mining and provides ideal conditions to identify ores which were already used in Celtic times and to relate iron ore with iron metal. In addition, a smelting experiment was carried out in 2009 with local ore from Neuenburg, which belongs to the same lode as the ores in the Grösseltal and with local clay for the furnace construction. A description of the samples from the archaeological excavations in the Grösseltal and from the smelting experiment used for this study is given in Table 1.

The fortunate circumstances for this study are somewhat impained by the fact that we do not know where and how the iron produced in Neuenburg was circulated. Ingots are usually not found at early La Tène smelting sites like Neuenburg. A few ingots are found in Celtic oppida and other settlements, but the majority derives from hoards as well as from rivers and lakes (Jacobi, 1974; Pleiner, 1980; Doswald, 1994; Kurz, 1995). Several bi-pyramidal ingots have already been investigated metallographically and/or chemically (Rupe and Müller, 1916; Hanemann, 1930; Fry, 1952; Rädeker and Naumann, 1961; France-Lanord, 1963; Zwicker, 1967; Kimmig and Gersbach, 1971; Schulz et al., 1983; Wischenbarth et al., 2001; Mangin, 2004; Bauvais and Fluzin, 2007; Berrang and Fluzin, 2007), but their origin and even their exact dating are still unclear. There are a few examples associated with the late Hallstatt period; the Roman date of a few others is in dispute so that they are generally considered to be mainly of La Tène, most probably of late La Tène origin (Pleiner, 1980; Doswald, 1994; Kurz, 1995).

The metallographic investigations of bi-pyramidal ingots so far published yielded variable results. Some are interpreted to have been forged from several blooms and others from one bloom (Rädeker and Naumann, 1961; France-Lanord, 1963; Mangin, 2004). For any provenance study of ingots it is necessary to know how homogeneous they are concerning the element concentrations or isotope ratios measured.

Most of the ingots were found at the beginning of the 20th century and it was usual at that time to apply electrolytic or electrochemical reduction of the corrosion layers. Today most ingots do not have their exact original shape or weight any more. Due to the complete removal of the oxides of the corrosion crust they often show a clearly visible central welding seam between two halves. One of 17 bi-pyramidal ingots from a hoard near Renningen in Baden-Württemberg was investigated metallographically and chemically by Zwicker and co-workers (Zwicker, 1967; Schulz et al., 1983). A small piece (orig. Nr. BW 86) from that investigation, embedded in resin for metallographic examination, came to the Curt-Engelhorn-Zentrum Archäometrie as part of the “Zwicker collection”. A quarter of this ingot survived in the Landesmuseum Württemberg in Stuttgart (Fig. 2) and was provided as reference material for reinvestigation.

3. Sampling strategy and analytical methods

The chamber of the scanning electron microscope (ZEISS EVO 60 MA 25) is large enough to accommodate the whole ingot and allow the analysis of the non-metallic inclusions without any additional sampling with an energy-dispersive X-ray analyser. After re-grinding and re-polishing of the embedded sample (original number BW 86) the microstructure was investigated by optical microscopy. After it was established that the ingot consists of two different parts (see below), drill samples were taken from both sides.

Ore and bloom samples, which were mostly heavily corroded were crushed (&lt;1 mm, ore samples were then milled to powder with a grain size &lt;63 μm), iron samples were mechanically separated from adhering slag and gangue as well as possible. The bloom samples which are described as slaggly blooms (Table 1) consist of spongy iron embedded in slag. Their compositions approximately represent the slag fraction (Tables 1 and 2). The microstructure of the bloom (MA-093254) in Fig. 3 shows a partially solidified liquid within a decomposed hypereutectoid steel matrix, which is nearly slag-free and which could be mechanically separated from the adhering slag.

Re–Os isotope analyses were carried out following methods described in Brauns et al. (2000) and Brauns (2001). Samples weighing 50 mg–100 mg (metals) or about 1 g (powder samples) were weighed into pre-spiked [185Re–186Os] tracer with \( \frac{185\text{Re}}{186\text{Os}} \) = 51.03) Carius tubes, followed by dissolution and equilibration with inverse aqua regia at 240 °C. Osmium was extracted by distillation of the volatile tetroxide, condensed on a very small volume (2 μl) of chilled H₂SO₄ and then collected in 1.5 ml of 6.8 N HBr. Final purification of Os was achieved by micro-distillation (e.g. Birck et al., 1997).

Os isotope ratios were measured by ion-counting on a modified Finnigan-MAT 261 mass spectrometer (Volkerring et al., 1991) operated in NTIMS mode (Walczyk et al., 1991) and corrected for mass bias and oxides (Reisberg and Meisel, 2002). Internal (2 SD) precision for unknowns was &lt;±0.2%. Final \( \frac{187\text{Os}}{188\text{Os}} \) ratios are corrected for blank (0.1 ± 0.05 pg Os, \( \frac{187\text{Os}}{188\text{Os}} \)blank ∼ 0.108).

Fig. 3. Typical microstructure of a chilled bloom from the Grösseltal after etching with Klemm I reagent shows the interface between the relics of hypereutectic white cast iron and a hypereutectoid steel with pearlite and Widmannstätten cementite plates.
assuming an Os yield of 85% (Brauns, 2001). Blank contribution for samples with low Os concentrations are less than 0.5%. During the course of this study, DTM-Os yielded an average $^{187}\text{Os}/^{188}\text{Os}$ ratio of $0.17393 \pm 0.00038$ ($n = 5$), consistent with published results from other laboratories (e.g. two sets of long term averages from DTM: $0.17429 \pm 0.00055$, $0.17396 \pm 0.00038$, Shirey, 1997; two sets of averages from Monash University, Australia: $0.17367 \pm 0.00058$, $0.17400 \pm 0.00021$, Lambert et al., 1998; McBride et al., 2001).

Strontium isotope ratios were determined using a VG Axiom magnetic sector field MC-ICP-MS (Multi-Collector Inductively Coupled-Plasma Mass Spectrometer) and corrected according to the exponential mass fractionation law to $^{87}\text{Sr}/^{86}\text{Sr} = 8.375209$. Blank values were less than 10 pg strontium during the whole clean lab procedure, including digestion, strontium separation and measurement. The Eimer & Amend standard that was run along with the samples yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70803 $\pm$ 0.000009 and 0.70799 $\pm$ 0.000006. The long term mean is 0.70802 $\pm$ 0.000007. The interlaboratory mean is 0.708027 $\pm$ 0.000035 (Muller-Sohnius, 2007).

The results are summarised in Table 1.

4. Results and discussion

In Fig. 4 the strontium isotope ratios are plotted against elemental concentrations in materials from the archaeological excavations in the Grösseltal and remains from the smelting experiment using exposed iron ore from Neuenbürg. There is good agreement within the standard deviation between of the ores from the Grösseltal and the exposed iron ore from the same load used for the smelting experiment. This suggests that the Neuenbürg iron ore deposit is characterised by small variations of the strontium isotope ratios (Table 1). However, all blooms and slag from the archaeological excavation as well as from the smelting experiment have slightly higher radiogenic strontium isotope ratios than the ores (Fig. 4). In one archaeological bloom (MA-093201) the strontium was significantly more radiogenic than the iron ore and the charcoal. It is obvious that there was a contribution of radiogenic strontium from other materials used in the production of iron. It is well known that especially charcoal and furnace lining are potential pollutants for strontium (Desaulty et al., 2009). Fig. 5 shows all components which are involved in the smelting of iron and which could have influenced its products. Since the archaeological charcoal sample has similar strontium isotope ratios as the iron ores and most of the blooms, only the furnace lining could contribute radiogenic strontium, but the question remains, if the mass balance is reasonable given its low strontium concentration.

An isotopically relevant mass balance for the slag after simple ore-charcoal mixing can be calculated as:

$$
{\frac{^{86}\text{Sr}}{^{87}\text{Sr}}}_{\text{slag}} = \left( \frac{w_{\text{ore}} \cdot c_{\text{ore}}^{^87}\text{Sr} + w_{\text{charcoal}} \cdot c_{\text{charcoal}}^{^87}\text{Sr}}{w_{\text{ore}} \cdot c_{\text{ore}}^{^86}\text{Sr} + w_{\text{charcoal}} \cdot c_{\text{charcoal}}^{^86}\text{Sr}} \right)
$$

With the proportions of ore and charcoal by weight ($w$), which were 1:1 in the experiment, and the strontium concentrations ($c$) measured for ore and charcoal used for the experiment (Table 1), a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71352 can be obtained, which is not in agreement with the ratios measured for the slag from the smelting experiment (Table 1). A similar calculation for the furnace lining yields
$^{87}\text{Sr} / ^{86}\text{Sr}$ ratios from 0.71379 to 0.71454, which has been measured for the slag. The ratio of the ore-charcoal mixture to the furnace lining should have been between 5:1 and 2:1, which is only reasonable for the first ratio when the slag is in direct contact with the furnace lining. If we apply the same equations on the archaeological materials (Table 1), only a few of the isotope ratios calculated are in agreement with the ratios measured for all the slag from the excavations.

Comparing the strontium concentrations of the experimental and of the excavated furnace linings, there is a difference by an order of magnitude, which is however still too low to explain the contamination. At the ratio of 5:1 of ore-charcoal mixture to furnace lining 180 mg kg$^{-1}$ strontium would be required to obtain the highest $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio of 0.71862. Both assumptions are quite unrealistic. The most likely source for more radiogenic strontium may be the iron ore itself. $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios of barite overgrown by...
osmium (e.g. Kellwasser limestone, unpublished data) and thus could have influenced the Os isotopic composition. Indeed, the experimentally produced bloom and all archaeological slaggies blooms comfortably fit into the variation defined by the iron ores (Fig. 6). Only the archaeological metallic bloom (MA-093254) has a more radiogenic $^{187}$Os/$^{188}$Os ratio of 1.026. It is unlikely that this difference is caused by the loss of volatile OsO$_4$ assuming that radiogenic $^{187}$Os is more easily volatilised. The smelting experiment shows that the isotope ratios survive the complete smelting process (Fig. 6) and the experimental bloom shows that osmium is enriched in the iron by a factor of nineteen over the iron ore used despite possible losses due to volatilisation on roasting (Table 1). A contribution of osmium from another component like the furnace lining is unlikely, because of the very low abundance of rhenium and osmium in silicates. The relatively high osmium concentrations in the iron ores are to be expected, as osmium is effectively absorbed by iron (hydro)-oxides. Therefore, the possibility of contamination with osmium from other materials during iron smelting is much smaller than with strontium, because the ore is the main osmium bearing component in the smelting process. Hence, the most likely source for radiogenic osmium is again the ore itself. The ore from Engelsbrand has an $^{187}$Os/$^{188}$Os ratio of 0.9882, indicating that substantial isotopic heterogeneity of osmium exists in the same deposit.

Concerning the ingots which are doubtful in date, but can safely be regarded as trade iron, the results are encouraging. As it has been already been pointed out by Schulz et al. (1983) and is confirmed now, that the ingot from Renningen is welded from two heterogeneously carburised halves (blooms), which are incompletely joined (Fig. 7). The microstructure already published in detail by Schulz et al. (1983) consists of a banded structure of heterogeneously carburised hypoeutectoid steel with segregations of phosphorus. The element concentrations on one side are nearly two times higher than on the reverse side (Table 2). Compared with the data of Senn et al. (2010) measured in blooms from smelting experiments, this elemental range is to be expected in different smelting runs with a similar ore. The osmium isotope ratios in both parts of the ingot are indistinguishable within the standard deviation and, accordingly, it can be assumed that both parts have the same origin (Table 1, Fig. 6).

### Table 2

<table>
<thead>
<tr>
<th>Sample no</th>
<th>Samples (Inv. Nr.)</th>
<th>Site</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>As</th>
<th>Pb</th>
<th>% Mn</th>
<th>% Fe</th>
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<td>MA-093194</td>
<td>Pure iron ore</td>
<td>Größetal</td>
<td>&lt;5</td>
<td>27.1</td>
<td>28.4</td>
<td>4.74</td>
<td>477</td>
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<td>Iron ore mixed with sandstone</td>
<td>Größetal</td>
<td>&lt;5</td>
<td>27.3</td>
<td>32.3</td>
<td>13.6</td>
<td>204</td>
<td>2.0</td>
<td>1.9</td>
<td>53</td>
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<td>Archaeological slaggie bloom 23 (TPI 2/E 95)</td>
<td>Größetal</td>
<td>10.3</td>
<td>27.3</td>
<td>49.1</td>
<td>49.9</td>
<td>30.6</td>
<td>&lt;1</td>
<td>1.3</td>
<td>54</td>
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<td>Größetal</td>
<td>26.0</td>
<td>9.91</td>
<td>5.80</td>
<td>45.6</td>
<td>4.21</td>
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<td>8.6</td>
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<tr>
<td>MA-093251</td>
<td>Archaeological slaggie bloom 35 (TPI 2-3/E90)</td>
<td>Größetal</td>
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<td>8.60</td>
<td>14.8</td>
<td>10.5</td>
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<td>8.57</td>
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<td>50.9</td>
<td>63.6</td>
<td>224</td>
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<td>&lt;1</td>
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<td>&lt;5</td>
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<td>5.71</td>
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<td>157</td>
<td>300</td>
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<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;1</td>
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<td>&lt;1</td>
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<td>Größetal</td>
<td>8.42</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
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<td>&lt;5</td>
<td>2.8</td>
<td>0.1</td>
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<td>Natural clay (s. oben)</td>
<td>Neuenburg</td>
<td>41</td>
<td>10</td>
<td>39</td>
<td>27</td>
<td>19</td>
<td>16</td>
<td>0.05</td>
<td>3.5</td>
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<tr>
<td>MA-092813</td>
<td>Natural clay (s. oben)</td>
<td>Neuenburg</td>
<td>19</td>
<td>4</td>
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<td>7</td>
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<td>14</td>
<td>6</td>
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<td>Renningen</td>
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This would suggest that one sample of an ingot may be sufficient to determine its origin.

5. Conclusion

With regard to the small data base of analysed ores so far, the conclusions are somewhat limited. However, the smelting experiment clearly shows that the osmium isotopic composition of the iron ore is not altered during the process, although the osmium isotope composition of one archaeological bloom remains as yet unexplained. Osmium is a highly siderophile and immobile element indicating the local geological environment of the ore deposit of Neuenbürg can be characterised by the (relatively) large \(^{187}\text{Os}/^{188}\text{Os}\) variation of 0.85–1.03, then all iron coming from smelting sites around Neuenbürg should contain this signature. This may be regarded as significant for the deposit, because the natural variation of osmium isotope ratios is much larger.

If there are other ore deposits having overlapping osmium isotope compositions, a second discriminating parameter will be necessary. One could be the concentrations of osmium in the analysed materials while the use of strontium, a highly lithophile element, seems to be of little value. Mass balance calculations show that radiogenic strontium could derive from the furnace lining, but most of the strontium isotope compositions are probably dominated by strontium-rich barite.

Another limitation is the amount of strontium that can be obtained in samples of archaeological iron. This depends very much on the volume fractions of slag inclusions, so that sample weights of several hundred milligrams to some grams of iron may be needed to obtain enough strontium for measurement. An alternative would be the isotope analysis with a combination of laser ablation and MC-ICP-MS, but the adaptation of an established method like the slag inclusion methodology (Desauty et al., 2009; Leroy et al., 2012) seems more promising and is certainly much wider applicable. Therefore, in summary, the combination of a siderophile isotope system which is not prone to any alteration with a geochemical fingerprint of lithophile elements conserved within the slag inclusions at present appears to be the best choice for a large-scale transregional provenance study of prehistoric iron.

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References

Coustures, M.P., Brodard, E., Béziat, D., Djouadi, D., Long, L., Domergue, C., Telouk, P., 2008. An alternative would be the isotope analysis with a combination of laser ablation and MC-ICP-MS, but the adaptation of an established method like the slag inclusion methodology (Desauty et al., 2009; Leroy et al., 2012) seems more promising and is certainly much wider applicable. Therefore, in summary, the combination of a siderophile isotope system which is not prone to any alteration with a geochemical fingerprint of lithophile elements conserved within the slag inclusions at present appears to be the best choice for a large-scale transregional provenance study of prehistoric iron.


