

Trace elements behaviour in direct- and indirect-iron metallurgy : the case of Pays de Bray (France)

Anne-Marie Desaulty, Clarisse Mariet, Philippe Dillmann, Jean Louis Joron, Bernard Gratuze, Cécile Le Carlier de Veslud, Philippe Fluzin

► **To cite this version:**

Anne-Marie Desaulty, Clarisse Mariet, Philippe Dillmann, Jean Louis Joron, Bernard Gratuze, et al.. Trace elements behaviour in direct- and indirect-iron metallurgy : the case of Pays de Bray (France). Archaeometallurgy in Europe 2007 : 2nd international conference (Aquileia, 17-21 June 2007) : selected papers, pp.318-334, 2007. hal-02561029

HAL Id: hal-02561029

<https://hal-univ-rennes1.archives-ouvertes.fr/hal-02561029>

Submitted on 2 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

TRACE ELEMENTS BEHAVIOUR IN DIRECT- AND INDIRECT-IRON METALLURGY: THE CASE OF PAYS DE BRAY (FRANCE)

Anne-Marie DESAULTY^{1,2}, Clarisse MARIET¹, Philippe DILLMANN^{1,2}, Jean-Louis JORON^{1,3}, Bernard GRATUZE⁴, Cecile MAHE-LE CARLIER², Philippe FLUZIN²

¹ Laboratoire Pierre Sûte CEA/CNRS UMR9956, CEA Saclay, 91191 Gif sur Yvette Cedex, France

² Laboratoire Métallurgies et Cultures IRAMAT CNRS UMR5060, UTBM, 90110 Belfort Cedex, France

³ Institut de Physique du Globe de Paris, 4 place Jussieu 75252-Paris cedex 05

⁴ Centre Ernest-Babelon, UMR 5060 IRAMAT CNRS, 3D rue de la Fêrolierie 45071 Orléans.

ABSTRACT

In order to determine the trace element chemical signature from the ore to the slag inclusion of the ferrous artefacts in the Pays de Bray (France), 143 samples were analysed by INAA, ICP-MS and LA-ICP-MS. Results show that, for geochemical reasons, some elements must be avoided to determine the chemical signature. Nevertheless, a main part of elements initially present in the ore allows to determine the chemical signature of the Pays de Bray. This signature is significantly different from the one of other regions and can be use for further studies about the commercialisation of Pays de bray ferrous artefacts in the neighbouring regions.

KEYWORDS: trace elements, bloomery process, indirect process, slag inclusions, provenance

INTRODUCTION

Major and trace element analysis of non metallic inclusions in iron archaeological objects are for about 10 years the topic of numerous studies dedicated to the distinguishing of ironmaking processes [1] but also to the determining of the artefact provenance [2-9]. These latter studies mainly focus on the link between objects and ores or archaeological sites. However, to our knowledge, despite of the fact that the behaviour of major elements initially present in the ores is relatively well known, none of published studies describes in detail the one from ore to the final artefact of the trace elements in the two ironmaking chains. Yet, the comprehension of trace element behaviour is crucial before any provenance studies. Indeed, it will be shown in the following that, for different reasons, some elements could not be chosen for determining a chemical signature.

The Pays de Bray region is very interesting for historical, archaeological and archaeometrical studies linked to ironmaking. Indeed, iron production is attested in this area on a wide temporal range (from the protohistoric to the modern age). Moreover, since the end of the 15th c., indirect ironmaking took place in this region [10]. Several ironmaking archaeological sites in the Middle Ages, covering the transition from the bloomery to the indirect process were excavated, providing many slag and products to be analysed: le Prés de Montadet (direct, from the 1st century BC to the 1st century AD), le Chemin des Flots (direct, 14th century) Glinet (indirect, 15th -16th century). Last but not least, the diffusion of the iron products from this area is documented by some historical sources: iron from the Pays de Bray was commercialised in the neighbouring city as Rouen and Beauvais. For this reason, with the final aim to precise the commercialisation of iron products from the Pays de Bray at different periods, a trace element study in order to reveal the chemical signature of the area and follow it in the slag inclusions of the metal was undertaken.

Thus, in a first part, trace element behaviours are discussed from the geochemical point of view and a first set of trace elements will be eliminated. In the second part, the specific element behaviour in the two iron-making processes will be described. These two parts will allow to choose pairs of elements that are able to characterize the chemical signature of the Pays de Bray and discriminate among those of other areas in France (Lorraine, Basse Normandie) in slag, and slag inclusions.

METHODOLOGY AND EXPERIMENTAL TECHNIQUES

The slag, laitier and ore sample for INAA (Neutron Activation) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) analyses (see table 4) have been crushed into powder in an agate shatter box, and sieved at 125 μm . After crushing the laitiers, the eventual cast iron prills were removed using a magnet.

Iron samples for LA-ICP-MS and EDS-SEM analyses (see below) have been mounted in epoxy resin and successively polished using SiC abrasive paper (grade 80 to 4000). Microscopic observation have been performed by using an OLYMPUS optical microscope under reflected light.

Bulk major element composition has been measured by Energy Dispersive Spectrometry (EDS) coupled with a Scanning Electron Microscope (SEM) at Laboratoire Pierre Sùe (CEA/CNRS, Saclay, France). The use of a Si(Li) detector with a beryllium thin window and a numerical acquisition chain allows to detect and quantify relatively light elements as Oxygen with a good accuracy (several relative percents on iron oxides and glass standards). The Idefix setup from the SAMX Company was used for acquisition and quantification. This analytical system is mounted on a Cambridge Stereoscan 120 SEM. Measurements were performed with a 15kV accelerating voltage. Minor elements can be detected and quantified for content over 0.5%_{mass}. For these content range (<1%_{mass}), it was considered that the relative quantification error is about 10%. For the other elements (>1 %_{mass}) the error is over-evaluated by considering a relative error of 2%. It has to be specified that the measurement can be considered as quantitative only when the sample does not contain elements lighter than Oxygen. This is the case for all samples in this study except some ore that are mainly constituted of iron carbonates.

Bulk trace element composition has been determined by INAA and ICP-MS in the Pierre Sùe Laboratory.

INAA analyses have been done according to the following procedure: aliquots of about 120 mg (for ore and slag) and 50 mg (for cast iron and iron object) are wrapped in high purity aluminium foils. To monitor the neutron flux an international geochemical standard is placed together with the samples in an aluminium shuttle. The irradiation is filtered by a Cd-cover to keep out thermal neutrons. All samples irradiations have been carried out at the nuclear reactor Osiris of the CEA Saclay Center (France) directly connected to Laboratoire Pierre Sue (LPS) by a closed circuit water pipe. They are irradiated under an epithermal neutron flux of $1.1 \cdot 10^{13} \text{ n.cm}^2.\text{s}^{-1}$ for 12 hours. After one week cooling, the samples are transferred into plastic tubes. The tubes are weighted before and after the transfer to avoid errors produced by possible losses during sample handling. Two counting sequences are carried out: (1) after one-week cooling: La, Sm, U are determined by 50000 s counting; (2) after one month cooling: Sc, Co, Ni, Rb, Cs, Ba, Hf, Ce, Eu, Yb, Th are determined by 20 000 to 60 000 s counting. The counting system used for the acquisition and the processing of the spectra consists of several high resolution γ -spectrometers. Each γ -spectrometer includes a Canberra Ge(Li) detector and a Nuclear Data ADC analyser coupled to a PC computer. Concentrations are calculated using a comparative method with international geochemical

standards (GSN, BEN, ACE, Centre de Recherches Pétrographiques et Géochimiques, France; GXR4, United States Geology Survey, USA) and standard made in LPS: silica doped with trace elements. Except for Zr, it was considered that the relative quantification error is inferior to 5%.

ICP-MS samples have been prepared by acid decomposition in open vessel. Measurements have been performed using a quadrupole ICP-MS spectrometer Thermo Electron X7 ICP-MS (*Thermo Fisher Scientific*) equipped with a concentric nebuliser. Signal optimization is obtained by using a 10 $\mu\text{g.g}^{-1}$ solution of Be, Mg, Co, Ni, In, Ce, Ba, Pb, Bi and U. The spectrometer is optimised to provide minimal values of the ratios CeO^+/Ce^+ and $\text{Ba}^{2+}/\text{Ba}^+$ and optimum intensity of the analytes. The methods used for calibration consists of spiking aliquots of a sample with four different quantities of a mixed standard solution (method of standard additions). For all elements, it was considered that the relative quantification error is about 7%.

The major elements composition of the slag inclusions entrapped in the metallic artefacts have been analysed by EDS coupled to SEM with the same conditions described above. Trace elements in slag inclusions were measured by using laser ablation in combination with Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) at the Centre Ernest Babelon (CNRS, Orléans). LA-ICP-MS analyses were made using a VG Plasma Quad PQXS in conjunction with Nd:YAG laser, operating at 266nm. Samples were ablated for 50 s and the diameter of the ablation crater was about 200 μm . For the calibration the international geostandard Nist 610 was used in addition to references glasses with high iron content synthesized starting from crushed slag and analyzed by INAA.

CORPUS

Different types of samples were gathered for this study: ores, slag and metallic artefacts. Hereafter will be described the different sampling contexts:

ORES FROM THE PAYS DE BRAY

Geological background

Across the end of the tertiary and beginning of the quaternary era, compressional tectonic caused the folding of the continental shield forming the Pays de Bray anticline. Consecutively, during the quaternary era, the morphological high was subjected to an intense erosion which led to the ablation of the capping limestone hard layers down to the tender layers at the core of the Pays de Bray. Such an erosional event exposed the inner geological formation (upper cretaceous, lower cretaceous and upper Jurassic). The exposed geological section on the flanks of the syncline provides several ore deposits different by enrichment and age. The geological ore source localization, together with historical documents, toponyms and traces of extractions suggest the wide exploitation of the wealdien ore (lower cretaceous) [10]. Ore samples were collected in different zones of the Pays de Bray corresponding to the wealdien period on the geological map.

The morphology of the samples corresponds rather well to the description of the wealdien ores made by previous studies [11-13]. Three types of ore can be distinguished:

- Type I: nodule surrounded by a laminated crust of a few millimeters to a few centimetres
- Type II: ferruginous sandstone characterized by centimetric vacuoles, filled with sandstone of clearer colour.
- Type III: ferruginous sandstone

X-rays diffraction allowed to identify the different iron phases which compose the ores (Table1).

Table1: Constitutive phases of the ores

| Type | Type I | | Type II | | Type III |
|--------------|----------------------------|----------------|---|---|---|
| Localization | Nodule | Crust | Phase 1 | Phase 2 | Quartz SiO ₂ Goethite FeOOH |
| Iron oxides | Siderite FeCO ₃ | Goethite FeOOH | Quartz SiO ₂ Goethite FeOOH | Quartz SiO ₂ Goethite FeOOH | |

Archaeological sites

Three archaeological sites were selected for this study : two sites where the bloomery process was performed (Prés de Montadet, dated from the Proto-historical and Gallo-roman periods, and Chemin des flots, dated by ¹⁴C between 1300 and 1445 AD excavated by Christophe Colliou [14]) and one associated to the indirect process (Glinet, excavated by Danielle Arribet [10]). At Glinet and le Prés de Montadet, ore fragments with comparable morphologies to the three geological ore types were found, sometimes in important quantities (more than 50 kg at le Prés de Montadet). The major composition of the ore have been analysed by EDS coupled to SEM (table 2).

Table 2: Average major element content of the different ores

| Average content % _{mass} | Type I Glinet | Type II Glinet | Type III Glinet | Type I Prés de Montadet | Type II Prés de Montadet | Type III Prés de Montadet |
|-----------------------------------|---------------|----------------|-----------------|-------------------------|--------------------------|---------------------------|
| O | 47 | 50 | 46 | 22 | 28 | 26 |
| Mg | 0.6 | 0.1 | 0.1 | 0.8 | 0.1 | 0.1 |
| Al | 2.2 | 1.2 | 1.1 | 1.2 | 1.8 | 3.4 |
| Si | 5.4 | 13 | 9.6 | 3.2 | 7.2 | 31 |
| P | 0.5 | 0.8 | 1.0 | 0.1 | 0.1 | 0.3 |
| S | 0.4 | 0.3 | 0.1 | 0.2 | 0.2 | 0.2 |
| K | 0.4 | 0.4 | 0.9 | 0.2 | 0.2 | 0.5 |
| Ca | 1.1 | 0.5 | 0.7 | 0.8 | 0.1 | 0.1 |
| Mn | 0.6 | 0.4 | 1.0 | 1.0 | 0.2 | 0.1 |
| Fe | 42 | 33 | 40 | 70 | 62 | 38 |

ORES FROM OTHER GEOGRAPHICAL AREAS

In order to compare the Pays de Bray chemical signature to the one of other regions, another phosphorus ore was chosen to be analysed. This ore is the minette de Lorraine provided by Cecile Mahe-Le Carlier and Marc Leroy and containing about 2%_{mass} phosphorus. These kinds of ore have been described in details in many publications [15].

SLAG FROM THE PAYS DE BRAY

Archaeological slag

As for the ore, slag have been collected in the three archaeological reference sites (i.e. Glinet, le Prés de Montadet and Chemin des flots)

Indirect process

The site of Glinet, on which a blast furnace and a refinery were excavated allow to collect typical slag of the indirect process: the laitier, a slag coming from the ore reduction stage, but also refining cakes produced during the refining of cast iron. Laitier are constituted of low iron glasses containing sometimes an important number of cast iron prills. The average major composition of these laitier is presented in table 3.

Refining slag are produced during the oxidation of cast iron to remove elements as carbon, silicone ore phosphorus; this stage takes place in an open hearth and typical plano-convex cakes are produced during the operation; several tenth of these cakes were found on the site of Glinet. They are constituted of iron oxides (wüstite, FeO), silicates (fayalite, Fe₂SiO₄) and phosphates and of glassy phases. In some cases metallic iron can be embedded in the slag. The average major element content of the Glinet refining cakes is presented in table 3.

Bloomery process

Typical slag of the bloomery process were also collected at Prés de Montadet and Chemin des Flots. On the proto-historical zone of le Prés de Montadet, slag entrapped at the bottom of the shaft furnace was found. Moreover, in the Gallo-roman zone of this site and at Chemin des flots, typical tapped slag heaps were excavated and sampled. These types of slag are mainly constituted of iron silicates and oxides with more or less glassy phases. The average major element content of the Prés de Montadet and Chemin des Flots slag is presented in table 3.

Table 3: Average major element content of the different archaeological wastes (EDS coupled to SEM)

| Average content % _{mass} | Laitiers Glinet | Refining slag Glinet | Slag Prés de Montadet | Slag Chemin des Flots |
|--------------------------------------|--------------------|----------------------------|-----------------------------|-----------------------------|
| MgO | 0.9 | 0.3 | 0.1 | 0.1 |
| Al ₂ O ₃ | 7.7 | 0.5 | 3.5 | 10 |
| SiO ₂ | 63 | 9.8 | 26 | 29 |
| P ₂ O ₅ | 0.8 | 10 | 0.6 | 2.3 |
| SO ₃ | 0.7 | 1.1 | 0.2 | 0.1 |
| K ₂ O | 1.7 | 0.7 | 0.6 | 1.8 |
| CaO | 17 | 3.6 | 0.9 | 1.0 |
| MnO | 0.8 | 0.7 | 1.0 | 0.9 |
| FeO | 7 | 72 | 66 | 54 |

Seven slag collected in various slag heaps of Pays de Bray were also analysed.

Experimental restitution of the bloomery process

In order to obtain wastes (i.e. slag) and metallic products obtained from well known ore and conditions, experimental reductions were conducted in a furnace based on the archaeological data of le Prés de Montadet. Two experiments (XP03 and 09) used a type I geological ore found near this site. Another one (XP05) used the archaeological type I ore. Tapped and entrapped slag were collected and analysed for the XP03 and XP05.

SLAGS FROM OTHER AREAS

Bloomery process

As for the ore, samples from other areas were collected to compare the chemical signatures. slag issued from experimental smelting using the minette de Lorraine. Moreover tapped and entrapped slag coming from a site situated at several 10 km from the Pays de Bray, the Merovingian site of Guichainville (Basse Normandie) were also collected and analysed. Lastly, it was also interesting to analyse some slag coming from a totally different geological context, the French Pyrénées, and coming from the site of Castel-Minier (medieval period) excavated by Florian Tereygeol [16]. This will allow us to verify that some trace element ratios are constant whatever the origin of the sample.

FERROUS ARTEFACTS FROM THE PAYS DE BRAY

In order to follow the trace element chemical signature in the slag inclusions entrapped in the metallic artefacts and formed during the ironmaking process, several objects were selected and analysed. Unfortunately, none of the archaeological excavated sites from the bloomery process gives ferrous artefacts. Thus, we chose to analyse the product of the experiments described in the precedent paragraph. Slag inclusions of the XP03 and XP09 blooms were analysed.

Indirect process

Cast iron samples from the Glinet site were collected and analysed. This ferrous alloy is a grey phosphorus cast iron with about 1-2 %_{mass} Si and P.

FERROUS ARTEFACTS FROM OTHER AREAS

Slag inclusions of the bloom issued from experimental smelting using the minette de Lorraine were analysed.

The whole of the analyzed samples are presented in table 4.

Table 4: Samples collected for the present study

| Type | Site | Number of samples | Remark |
|---------------------|---------------------------------|-------------------|--|
| Geological ores | Pays de Bray | 3 * | Wealdien type I |
| Archaeological ores | Prés de Montadet (Pays de Bray) | 12 | Pays de Bray |
| Archaeological ores | Glinet (Pays de Bray) | 23 | Pays de Bray |
| Archaeological ores | Lorraine | 5 | Minette de Lorraine |
| Laitiers | Glinet (Pays de Bray) | 25 | Indirect process |
| Refining slag | Glinet (Pays de Bray) | 6 | Indirect process |
| Entrapped slag | Prés de Montadet (Pays de Bray) | 15 | Bloomery process Proto-historical period |
| Tapped slag | Prés de Montadet (Pays de Bray) | 9 | Bloomery process Gallo-roman period |
| Tapped slag | Chemin des Flots (Pays de Bray) | 13 | Bloomery process Medieval period |
| Entrapped slag | Lorraine | 3 | From minette de Lorraine |

| | | | |
|----------------|------------------------------------|----|-----------------------------------|
| Tapped slag | Guichainville (Basse Normandie) | 4 | Merovingian period |
| Entrapped slag | Guichainville (Basse Normandie) | 4 | Merovingian period |
| Entrapped slag | Castel Minier French Pyrénées | 2 | Medieval period |
| Slag | Prés de Montadet XP03 | 4 | From geological type I ore |
| Slag | Prés de Montadet XP05 | 2 | From archaeological type I ore |
| Bloom | Prés de Montadet XP03 | 1 | From geological type I ore |
| Bloom | Prés de Montadet XP09 | 1 | From geological type I ore |
| Bloom | Lorraine | 1 | From minette de Lorraine |
| Cast irons | Glinet (Pays de Bray) | 10 | Grey cast iron |

* 2 samples from 150 kg of crushed ores
1 sample from 120 kg of crushed ores

RESULTS AND DISCUSSION

Goldschmidt stated the rules of substitution (camouflage, captures, admission) which govern the localization of the elements in traces in the mineral phases [17]. These rules of substitution show us that mainly the ionic radius and the valence define the chemical behaviour of an element [17, 18]. Thus elements which have very close ionic radius and valence behave like “quasi-isotopes”, their ratios remain constant. It will be thus useless to choose these couples to trace any regional chemical signature, since these ratios will be constant for any ores and the same than the one of the upper continental crust. This specific “quasi-isotope” behaviour is clearly observed on Figure 1. The Hf /Zr ratio (respectively valence: +IV, ionic radius: 0.78Å and valence: +IV, ionic radius: 0.79Å) and the Ce/La ratio (respectively valence: +III, ionic radius: 1.09Å and valence: +III, ionic radius: 1.13Å) are constant for samples coming from different regions (Pyrénées, Lorraine, Basse Normandie). Geochemistry gives other helpful indications: elements which are very sensitive to alteration, i.e. highly hydrophile (Na, Br...) and Cs, Rb, K, Sr, Ba, must be used with caution because their initial contents can be modified during the burying [19].

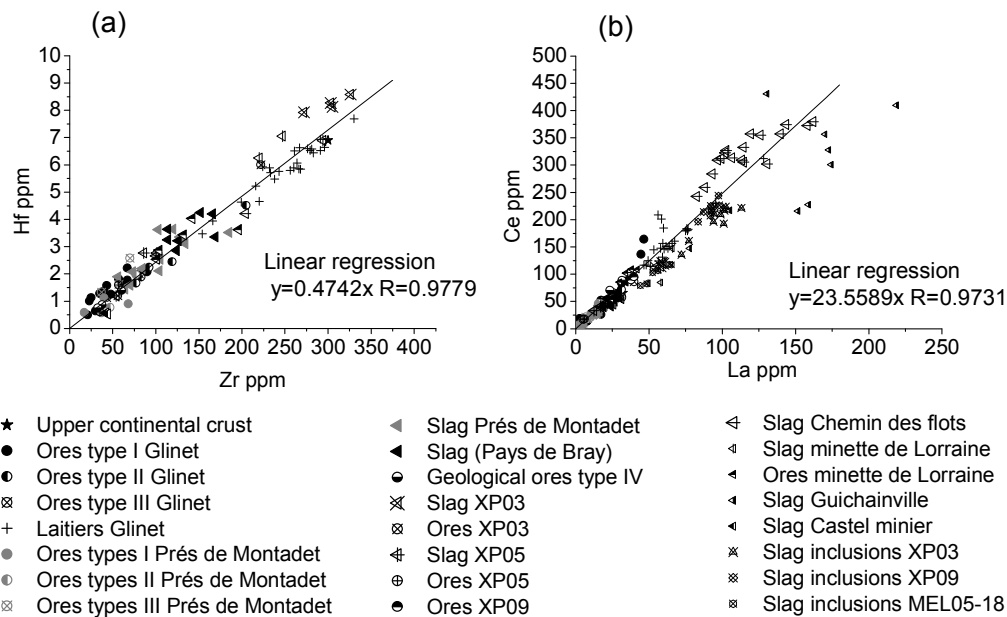


Fig. 1 Trace element variation diagrams for the pays de Bray and other regions: (a) Hf versus Zr contents; (b) Ce versus La contents

The second point that has to be taken into account for studying trace elements as far as ironmaking is concerned is the influence of the thermodynamical conditions during the different processes on the element behaviour. The analysis of ores, slag and slag inclusions of experimental bloom (see table 4 (corpus)) allow to precise this behaviour in function of the two processes (i.e. the direct and the indirect ones).

(1) The bloomery process

Hereafter elements which have a strong affinity for the silicated phases are defined as lithophile. The direct process takes place at relatively low temperature (about 1300-1400°C) and the melting point of iron is not reached. Thus, the resulting bloom will still contain part of the slag in the form of inclusion. It has been observed, that the content ratio of lithophile elements remains constant from the ore to these slag inclusion, including the slag itself, such an example for Th/U ratio is given on figure 2. This is the proof that, as summarised on figure 3, the lithophile elements present in the ore are not partitioned between slag and iron, they are completely oxidized in the bloomery furnace; such elements will be concentrated in the silicate-rich waste of the operation: the slag.

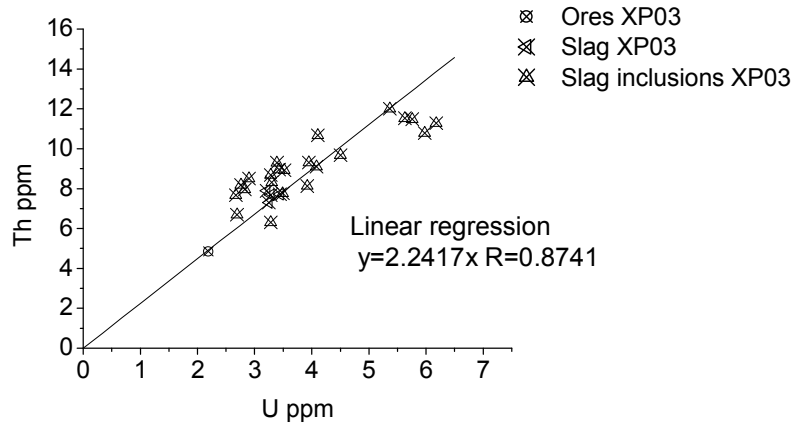


Fig. 2 Th versus U contents for XP03 ores, slag and slag inclusions

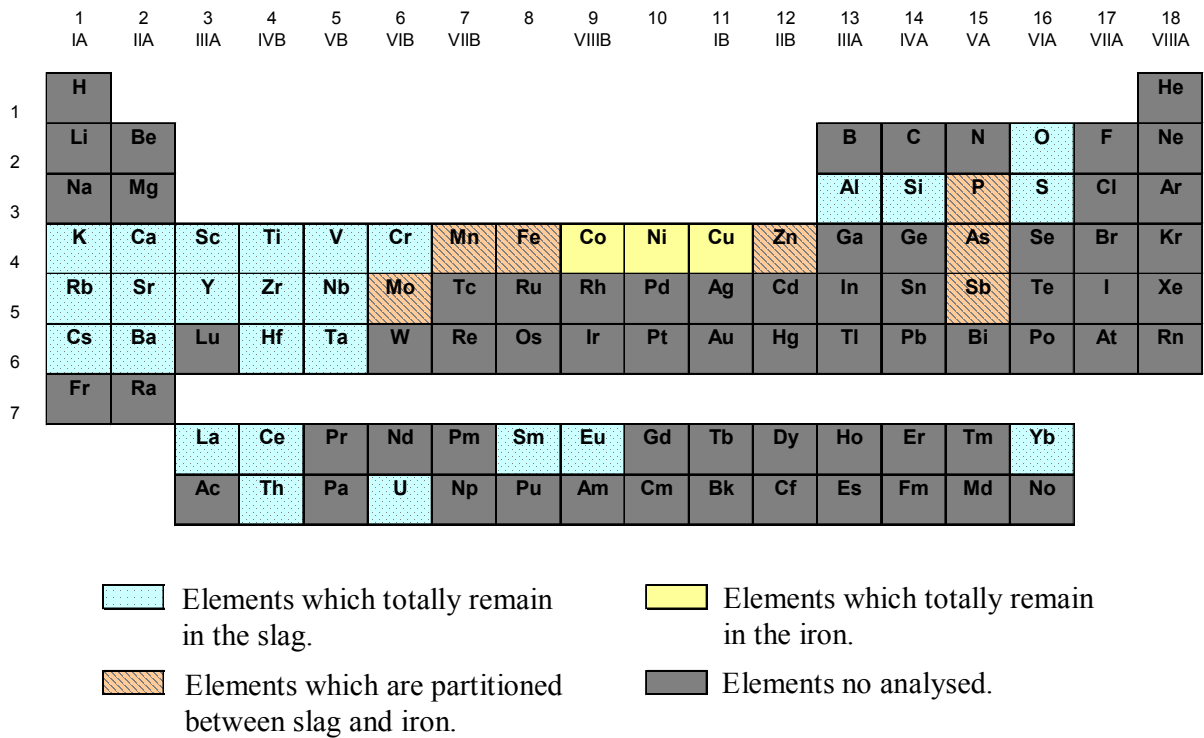


Fig. 3 The elements distribution after direct reduction

(2) The indirect method

The reduction stage of the indirect process takes place in a blast furnace in which temperatures are much higher than for the direct process and the melting point of the metal is attempted (i.e. $T > 1534^{\circ}\text{C}$). Because of that, elements which totally remained in the slag during the direct process appear to be partially reduced in the blast furnace and are partitioned between the cast iron and the slag. This can be observed on figure 4, for example for Cr, V, Zn, Rb, As, Sb, Mo and Nb that are detectable in the laitier but also in the cast iron samples. Moreover, some of them as S, Mn, Cr, Ti and V form specific mineralogical phases: carbonitride for Ti, V and Cr; carbides and sulphides for Mn [1]. Nevertheless, despite of the high temperature taking place in the blast furnace it seems that the most of the lithophile

elements are not reduced during the indirect process and are not detectable (i.e. are present in quantity lower than 0.5 ppm) in the analysed cast iron samples. Figure 5 sums up all these observations.

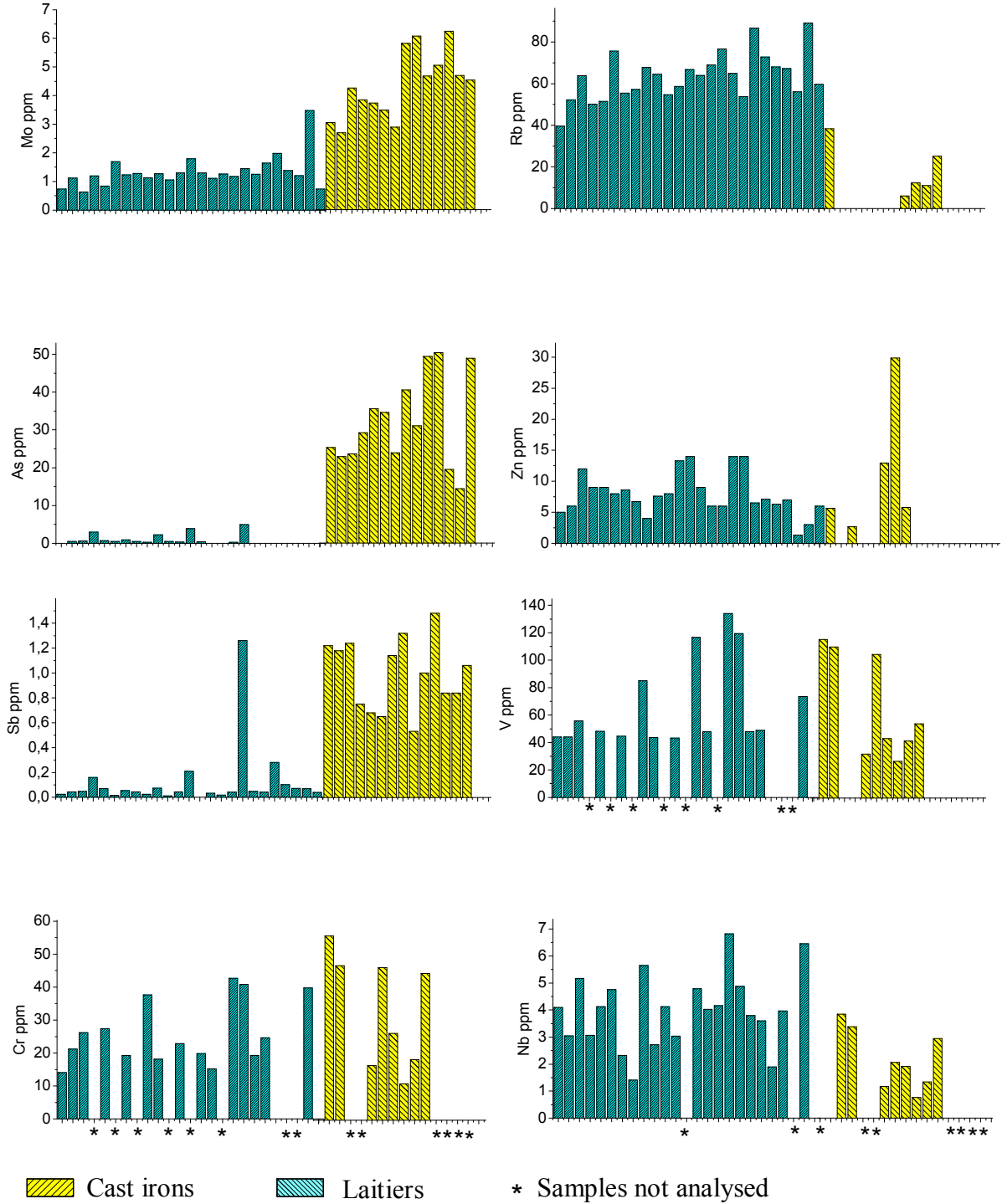


Fig. 4 Distribution of trace elements between the “laitier” and cast iron (Site of Glinet).

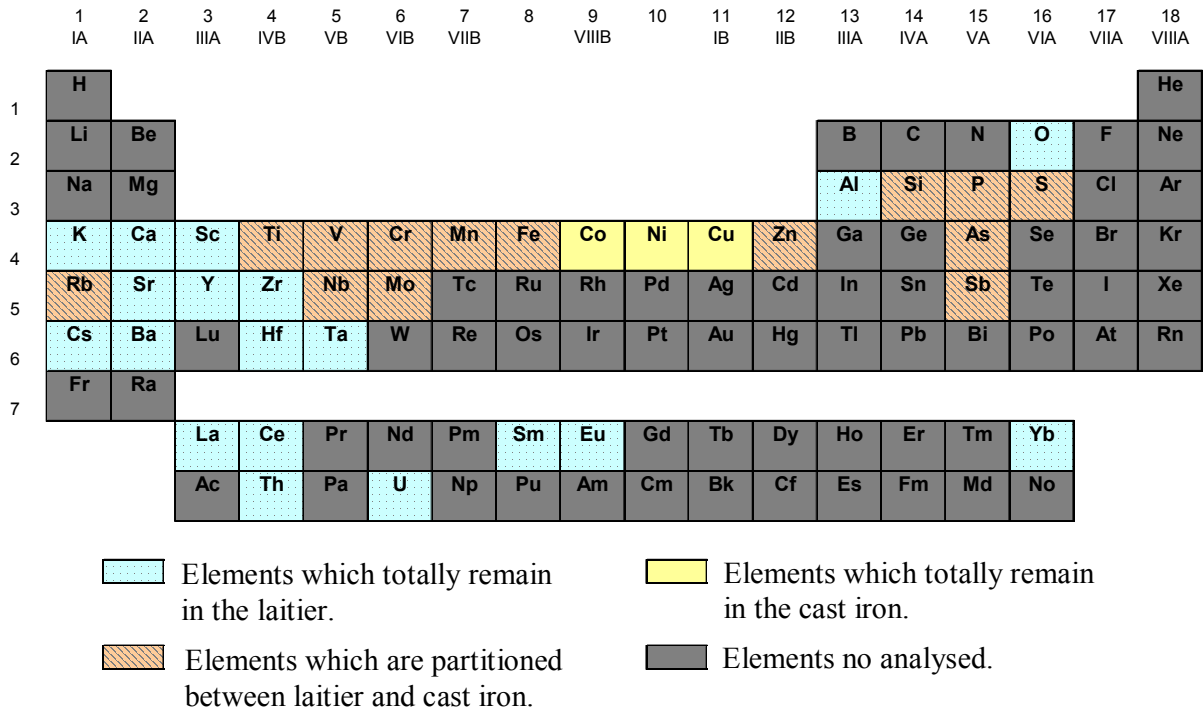


Fig. 5 The elements distribution after indirect reduction

At this stage, it appears that, for the indirect process, past all the lithophile elements coming from the ore are eliminated in the laitier during the reduction. Thus, slag and inclusions formed during refining from an oxidation of the elements constituting cast iron will contain none of these elements initially present in the ore. It implies that the reduction behaves as a filter which tends to erase the chemical signature of this ore. As a result it appears difficult to trace the indirect process from the ore to the finished object resulting from refining using trace element signature. At the opposite the filter effect of the indirect reduction looks as a powerful tool to distinguish the two processes. In fact slags obtained from direct reduction, and thus inclusions, are rich in lithophile trace elements initially present in the ore, whereas slag and inclusions resulting from the indirect refining are strongly depleted in lithophile trace elements. Therefore as it was already observed for some major elements [1, 20] lithophile elements enable to discriminate the two processes. Such behaviour clearly appears in refined slag from Glinet compared to other direct reduction slags from the Pays the Bray (i.e. obtained with the same type of ore) figure 6. The content differences for Y, La Sm, Yb, Th, and U, between the two types of slag are sufficient to discriminate between the processes. Recognizing the refining process on the base of trace elements is an important archaeometric task. These results open the way to further statistical studies. Figure 6 also shows the important among of the elements coming from pollution by charcoal, additions or refining hearth lining. Indeed whereas elements like Ba and Sr are completely absent in the cast iron, they are present in quantity higher than 50 ppm in the refining slag.

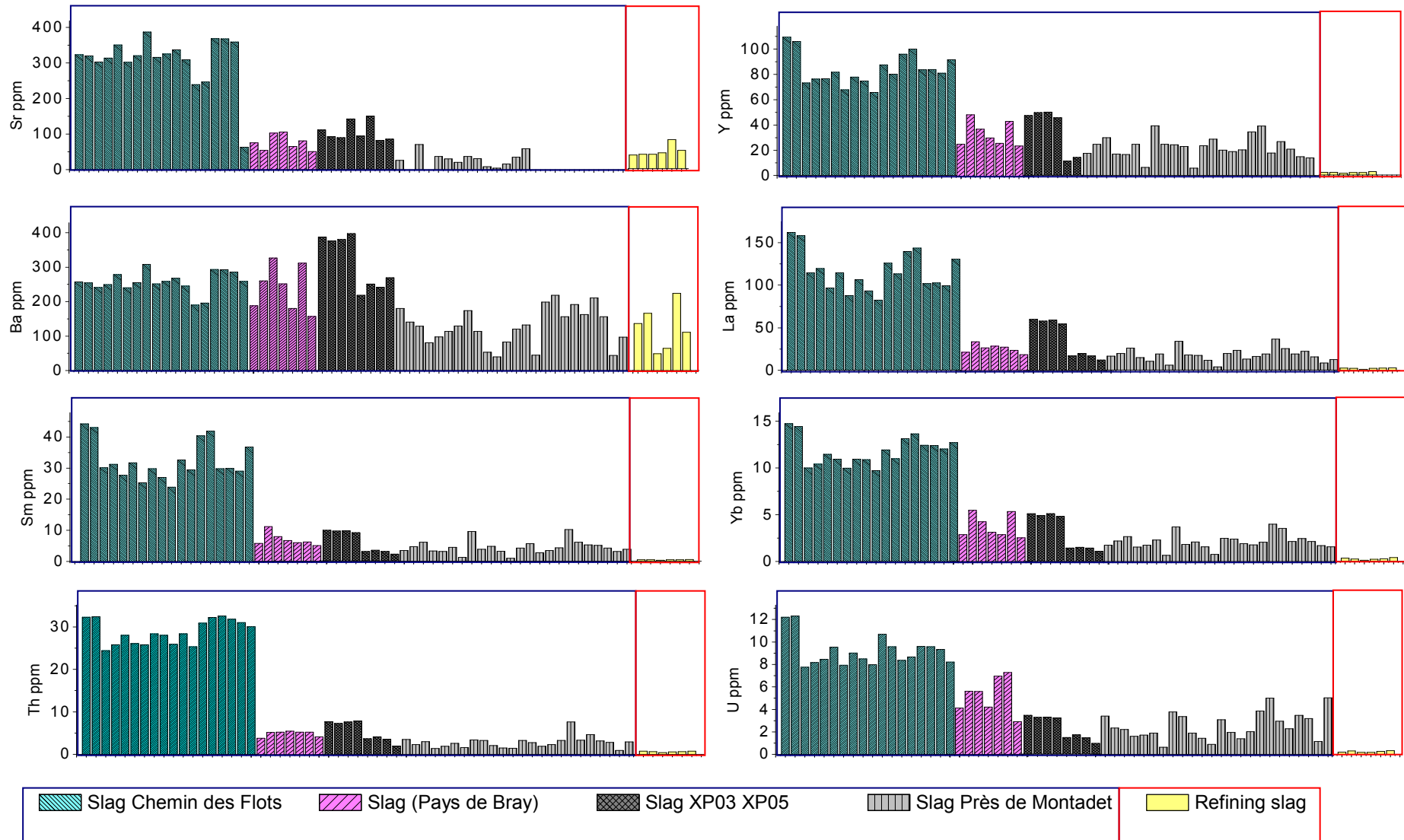


Fig. 6 Distribution of trace elements between the refining slag and reduction slag

- The chemical signature of the Pays de Bray

Based on the trace element behaviour discussed in the previous paragraphs, it is now possible to characterize the chemical signature of the Pays de Bray region. This signature is defined by using several element pairs selected according to the following characters:

- Avoiding element pairs with a “quasi-isotope” behaviour (i.e.; which ratios are always constant).
- Exclusive use of elements which pass completely into the slag during the reduction process in order to avoid misleading due to partial distribution of an element between slag and metal.
- Avoiding hydrophile elements which contents can be modified by weathering.
- Avoiding elements which could be present in calcic or sand additions during the ironmaking process (Sr, Zr.), in charcoal ashes (Sr, Rb, Ba...) or driven by pollution of the clay lining of the hearths (Ti, V...)[21, 22].

We thus selected the following ratios: Yb/Ce, Eu/Sm, Ce/Th, La/Sc, U/Th, Nb/Y. Figure 7 shows (a) Yb versus Ce contents; (b) Eu versus Sm contents; (c) Ce versus Th contents; (d) La versus Sc contents; (e) U versus Th contents; (f) Nb versus Y for various samples of the Pays de Bray. Yb/Ce, Eu/Sm, Ce/Th and La/Sc have good linear correlations ($R=0.96$, 0.99 , 0.96 and 0.94 respectively). It appears that the chemical signature of the Pays de Bray can be defined using these couples, from the ore to the slag inclusions for the direct process and to the laitier for the indirect one. This result opens the way to further provenance studies if the signature of the Pays de Bray can be distinguished from the one of ores coming from other regions. This point will be considered below.

Nevertheless, some specific couple seems to distinguish different population groups depending on the sample location. This is the case for the U/Th ratio that shows three different well separated populations within the Pays de Bray: A first population represents ores found on the archaeological sites as well as slag and slag inclusions of the experimental blooms, but also geological ores. For this population, U and Th are linearly well correlated ($y=0.42696x$; $R=0.9453$). A second population groups the Glinet laitiers, the Prés de Montadet slag, and the various other slag collected in the Pays de Bray. For this population, U, Th are also well linearly correlated ($y=1.0584x$; $R=0.9053$). A third population groups the Chemin des flots slags. These different correlations have not been elucidated yet but can be probably explained by an initial dispersion in the ore composition.

In the same way, the Nb/Y correlation also highlights different compositional groups: (i) group with the archaeological and geological ores, the slags and the slag inclusions of the experimental blooms, the Prés de Montadet slags, and the various slags collected in the Pays de Bray ($y=0.1287x$, $R=0.9307$) (ii) A group containing the Chemin des flots slags, (iii) a strongly dispersed group pertaining to the Glinet laitiers. This latter one can be explained by the fact that, as said before, Nb is an element that partly reduced during the indirect process. Despite of this fact this Nb/Y ratio was already considered because it is able to sign the Pays de Bray comparing to other regions (see below). The other groups are not elucidated yet but can be due to a slight variation of the Pays de Bray ore signature.

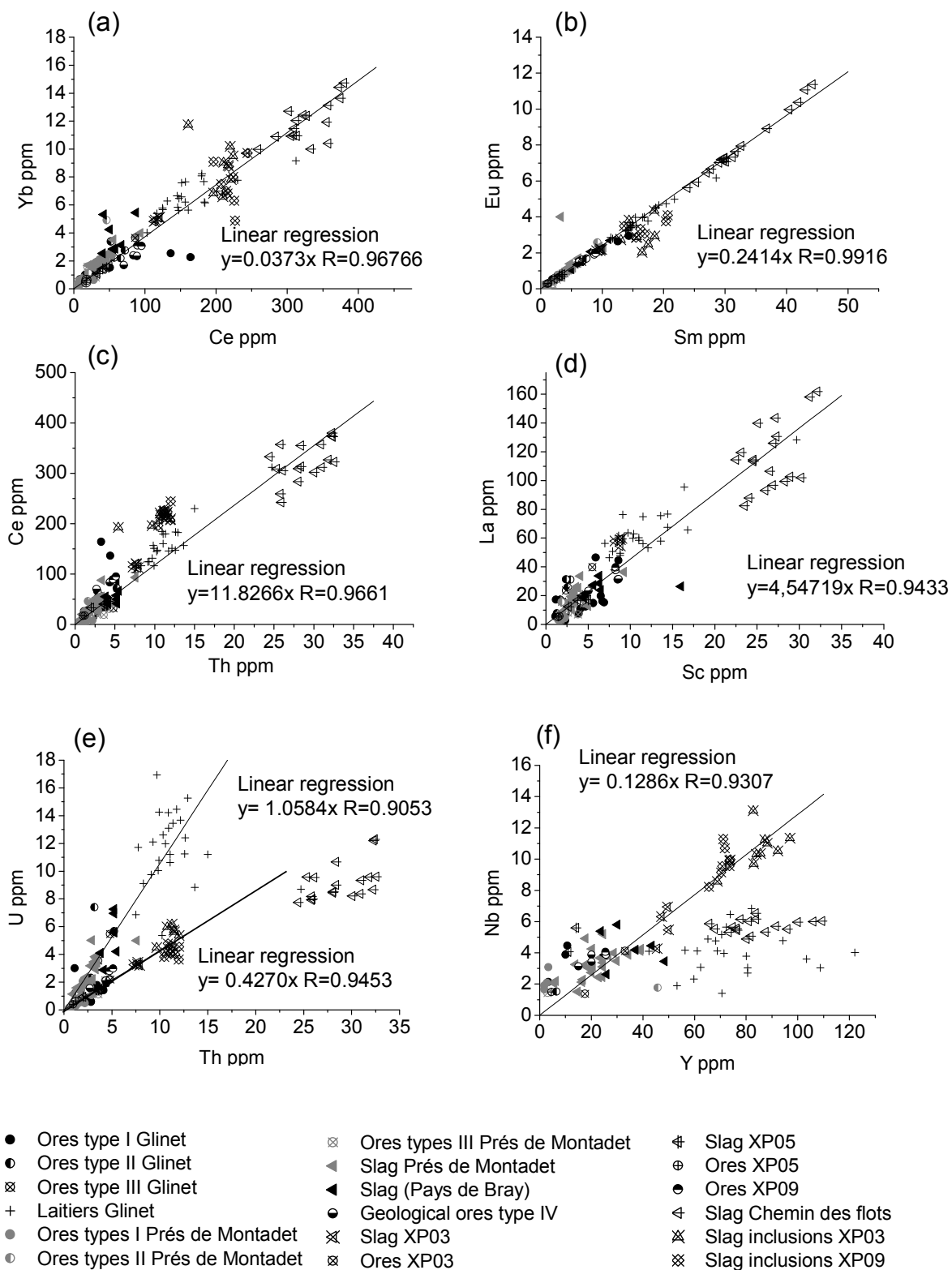


Fig. 7 Trace element content diagrams for the pays de Bray area

- Comparison with other areas

In a last step, the Pays de Bray chemical signature was compared with other regions. First another region using a phosphorus ore as for the Pays de Bray was considered: in Lorraine, the main used ore is the “minette de Lorraine”. It could be interesting to compare the trace element signature. Another interesting region is the Pays d’Evreux less than 50 km of the Pays de Bray, with the archaeological site of Guichainville.

Figure 8 shows different trace elements ratios that defined well the Pays the Bray compared to the other areas. It appears that some ratios are not able (Sm/Eu) to make any distinctions and are the same for the three regions. Some other ratios (Yb/Ce, Th/U) are efficient to distinguish ores coming from the Pays the Bray from the Minette de Lorraine. Some elements pair ratios allow to distinguish well ores coming from the three areas; this is the case for Ce/Th, La/Sc and, despite of its relative variability in the pays de Bray (see before), the Nb/Y ratio.

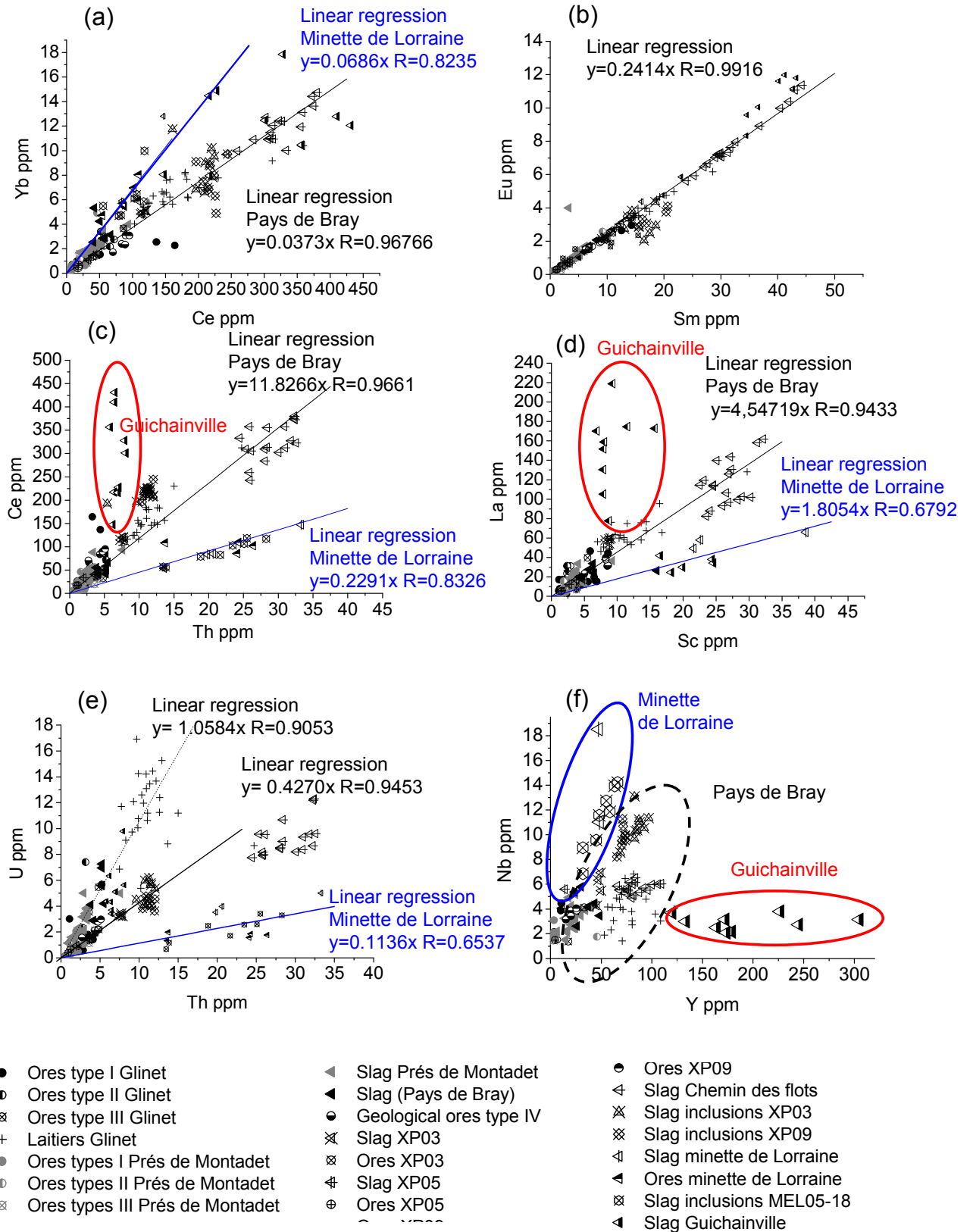


Fig. 8 Trace elements variation diagrams for the Pays de Bray

(a) Yb versus Ce contents; (b) Eu versus Sm contents; (c) Ce versus Th contents; (d) La versus Sc contents; (e) U versus Th contents; (f) Nb versus Y contents

CONCLUSION

The aim of this study was to unravel the behaviour of the trace elements in the two ironmaking processes: direct and indirect. To address this goal, 143 representative samples from the Pays de Bray as well as other areas (the Pyrenees, Lorraine, Basse Normandie) were analyzed. Trace element analyses of ores, slag, laitiers, cast irons and iron products allow stressing the following conclusions:

Several elements ratio can not be used for trace element chemical signature, on the one hand because they are “quasi-isotopes” and have the same behaviour, on the other hand because they content in the ore are influenced by alteration.

During the indirect process only Co, Ni and Cu completely pass into cast iron. All other elements partition between laitier and cast iron. As a consequence the inclusions formed after cast iron refining are strongly depleted in lithophile trace elements. This confirms same conclusions already observed for major elements by other studies [20]. An important consequence is that slag inclusions, therefore, forgot the ore chemical signature. On the contrary, in the direct process, a large spectrum of trace elements strongly passes quasi exclusively from ore to slag. They are hosted in trapped slag inclusions in the final iron. The content ratio of lithophile elements remains constant from the ore to slag inclusions. For this process it is thus possible to trace the chemical signature from the ore to the final object. Moreover, the different behaviour between the two processes allows discriminating between them.

Selected pairs of trace elements (Yb/Ce, Ce/Th, La/Sc, U/Th, Nb/Y) allowed us to characterize the chemical signature of the Pays de Bray. These couples of element allow discriminating the chemical signature of different geological and archaeological regions (Pays de Bray, Lorraine, Basse Normandie). The possibility to discriminate the provenance regions opens new perspectives in the traceability of archaeological materials as, for instance, the source of the construction irons of important historical buildings in the north of France (Amiens and Rouen).

ACKNOWLEDGEMENTS

The authors are extremely grateful to the following people for their help with this paper by providing samples: Marc Leroy, Paul Merluzzo, Christophe Colliou, Danielle Arribet-Deroin, Nolwen Zaour and Florian Tereygeol. We thank Pr Michel Treuil for its helpful discussions. Thanks also to Pr Daniele Brunelli for his help concerning the fabrication of synthesized glasses.

REFERENCES

1. DILLMANN, P., *Diffraction X, Microdiffraction X et Microfluorescence X sous Rayonnement Synchrotron et analyses comparées pour la caractérisation des inclusions. Application à l'étude de l'évolution historique des procédés d'élaboration des objets ferreux (procédés direct et indirects)*, in *Sciences Mécaniques pour l'Ingénieur*. 1998, Université de Technologie de Compiègne: Compiègne. p. 300.
2. PAYNTER, S., *Regional variations in bloomery smelting slag of the iron age and romano-british periods*. *Archaeometry*, 2006. **48**(2): p. 271–292.
3. SCHWAB, R., et al., *The provenance of iron artefacts from Manching: a multi-technique approach*. *Archaeometry*, 2006. **48**(3): p. 433-452.

4. BUCHWALD, V.F. and H. Wivel, *Slag analysis as a method for the characterization and provenancing of ancient iron objects*. *Materials Characterization*, 1998. **40**: p. 73-96.
5. HORST-MADSEN, L. and V.F. BUCHWALD, *The characterisation and provenancing of ore, slag and iron from the Iron Age settlement in Snorup*. *The Journal of the Historical Metallurgy Society*, 1999. **33**(2): p. 57-67.
6. COUSTURES, M.-P., D. BEZIAT, and F. TOLLON, *The use of trace element analysis of entrapped slag inclusions to establish ore-bar iron links: examples from two gallo-roman iron-making sites in France (Les Martys, Montagne Noire, and Les Ferrys, Loiret)*. *Archaeometry*, 2003. **45**(4): p. 599-613.
7. HEDGES, R.E.M. and C. SALTER, *Source determination of iron currency bars through the analysis of slag inclusions*. *Archaeometry*, 1979. **21**: p. 161-175.
8. DEVOS, W., et al., *Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for spatially resolved trace analysis of early-medieval archaeological iron finds*. *Fresenius J Anal Chem*, 2000. **366**: p. 873–880.
9. CHOUINARD A., *Archéologie et archéoméallurgie de la forge et des forgerons de l'habitation Loyola en Guyane*. *Cahiers d'archéologie du CELAT*. Vol. 11. 2001, Université Laval: CELAT. 112.
10. ARRIBET-DEROIN , D., *Fondre le fer en gueuses au XVIe siècle. Le haut fourneau de Glinet en Pays de Bray (Normandie)*. in *Archéologie*. 2001, Paris I Sorbonne: Paris. p. 799.
11. LAPPARENT, A.D., *Le Pays de Bray. Mémoire pour servir à l'explication de la carte géologique détaillée de la France*. 1879.
12. BARBIER, E., *Une campagne de recherches minière en Seine-Inférieure*. *Revue économique de l'Ouest*, 1921.
13. MARY, A. and A. MARY, *Etude sur l'Urgonien du Bray à Rainvilliers (Oise)*. *Compte rendu du Congrès national des sociétés savantes*, 1907.
14. COLLIOU, C., *Le Chemin du Flot, parcelle 136, commune de La Ferté St Samson*. 2005. p. 22.
15. LEROY, M., *La sidérurgie ancienne en Lorraine avant le haut-fourneau. Etude du développement historique et des conditions techniques de l'utilisation du minerai oolithique lorrain (la minette) en métallurgie de réduction directe*. 1997, CNRS: Besançon.
16. LEROY, S., et al. *First examinations of ore, slag and iron artefacts from iron-making site of castel-minier (Aulus -les-Bains,09)*. in *Archeometallurgy in Europe*. 2007.
17. VIDAL, P., *Géochimie*. DUNOD ed. 1994. 190.
18. HAGEMANN, R. and M. TREUIL, *Introduction à la géochimie et ses applications*. CEA ed. Vol. 1. 1998. 445.
19. ROLLINSON, H. 1993. *Using Geochemical Data: Evaluation, Presentation, Interpretation*. Longman Geochemistry ed. 1993
20. DILLMANN, P. and M. L'HERITIER, *Slag inclusion analyses for studying ferrous alloys employed in French medieval buildings: supply of materials and diffusion of smelting processes*. *Journal of Archaeological Science*, 2007: p. 1-14.
21. THOMAS, G.R. and T. P.YOUNG, *The determination of bloomery furnace mass balance and efficiency*. *Geoarchaeology: exploration, environments, resources*, 1999. **165**: p. 155–64.
22. SERNEELS, V., *Analyse chimique des matières premières et des produits de l'opéraion de reduction ds le four basque d'agorregi*, in *La ferreria y los molinos de Agorregi-Aia, Gipuzkoa*, Arkeolan, Editor. 2002, Diputacion Foral de Gipuzkoa - European comunity: San Sebastian. p. 93- 121.

