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A provenance study of iron archaeological artefacts by Inductively Coupled Plasma-Mass Spectrometry multi-elemental analysis

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ABSTRACT

Raw materials and wastes (i.e. ore, slag and *laitier*) from ironmaking archaeological sites have been analyzed in order to understand the behavior of the trace elements in the ancient ironmaking processes and to find the significant-most elements to characterize an iron making region. The ICP-MS (Inductively Coupled Plasma Mass Spectrometry) appears to be an excellent technique for this type of studies. The comparison between the ICP-MS results obtained with the Standard Addition method and the INAA (Instrumental Neutron Activation Analyses) results proved that Sc, Co, (Ni), Rb, Cs, Ba, La, Ce, Sm, Eu, Yb, Hf, Th, U contents in the ores, slag and *laitiers*, and Co and Ni contents in the cast iron can be successfully determined by ICP-MS after wet acid digestion (low detection limits, good sensitivity and precision). By using significant trace element pairs (Yb/Ce, Ce/Th, La/Sc, U/Th, Nb/Y) present in the ores, *laitiers* and slag, it is possible to discriminate different French ironmaking regions as the Pays de Bray, Lorraine and Pays d'Ouche. These results open the way to further studies on the provenance of iron objects. The comparison between the ICP-MS results obtained with the Standard Calibration Curves method and the INAA results shows that matrices rich in iron, affect the ICP-MS analyses by suppressing the analytes signal. Further studies are necessary to improve understanding matrix effects.

1. Introduction

Provenance studies of iron archaeological objects, based on major and minor elements systematic analyses, have been carried out in the last few years [1–4]. They show that these elements potentially give a rough indication of the used ore (for example presence or absence of P and Mn) or the eventual homogeneity of a given corpus [5]. However, they are not able to precisely characterize ironmaking regions. In fact, major and minor element contents are strongly affected by addings during the ore reduction process or the metal transformation (Si, Ca…) or by pollution by the clay lining of the hearths or furnaces (Al, Ti, V…) or charcoal ashes (Ca, K, Sr…) [6]. Several authors pointed out the high potential of studies based on trace elements [7–9]. Those studies try to link an archaeological object to the ore produced by the bloomery process by analyzing the trace element composition of non metallic slag inclusion embedded in the object. Nevertheless, to our knowledge, no systematic study of the trace element behavior from ore to the final object, discussing the influence of the thermodynamic conditions in the different stages of the ancient processes is available in literature. Thus, our goal is to enhance the use of trace elements by studying their behavior in all steps of the two ironmaking processes that succeeded in the history: the bloomery and the indirect processes.

The bloomery process used a shaft furnace in which temperature is under the iron melting point, the waste produced during the operation and constituted by non reduced compounds of the ore and any other constituent of the system (i.e. furnace lining, charcoal ashes,…) is called slag. The product of the reduction is a heterogeneous bloom already containing an important part of slag inclusions embedded in the metal.

The indirect process consists in a two stage process: first cast iron is produced during reduction of the ore in a blast furnace at higher temperatures than for the bloomery process (over the melting point of iron). The typical waste of this operation is called *laitier* and do not contain high level of iron oxide, contrary to the bloomery process slag. In the second stage, to obtain iron or steel, the cast iron is refined in an open hearth in which temperature is mainly under metal smelting temperature. The waste of this operation is also a slag containing high levels of iron oxide. The product is a bloom containing an important part of refining slag inclusion entrapped in the metal.

This description of the ancient ironmaking processes shows that at the end of the process, important quantities of non metallic slag inclusions remain in the iron or steel artefact. They come from the reduction stage in the bloomery process and from the refining stage in the indirect one. The slag inclusions have the same composition than

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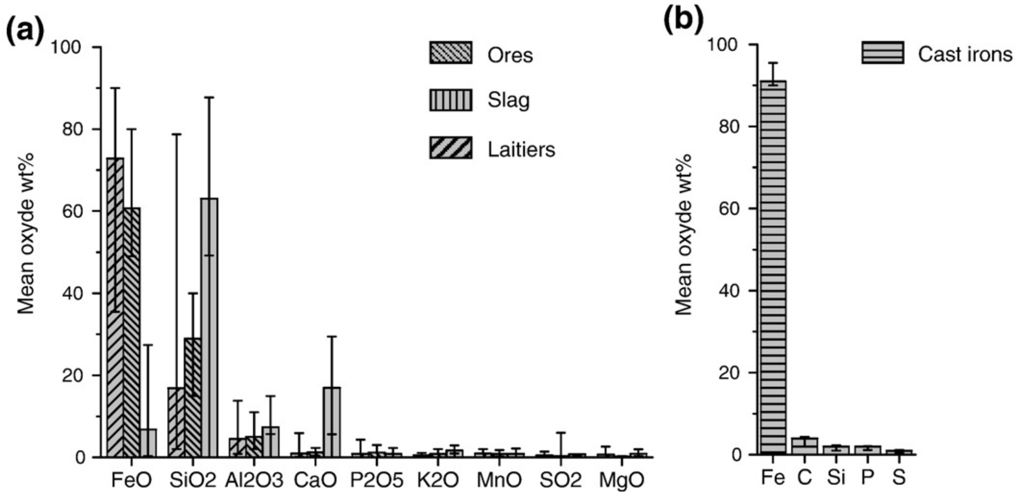

Fig. 1. Average major compositions of slag, *laitiers*, ores (a) and cast irons (b).

the macroscopic slag produced during these operations. It is thus interesting to follow the trace element chemical signature from the ore to the slag and slag inclusions for the two processes, in order to verify if this signature is conserved during the process. Nevertheless, an obligatory first step before any slag inclusion analysis for this kind of studies is, for each region of interest, to determine its chemical signature and the trace element behavior in macroscopic raw materials and archaeological wastes (i.e. ore, slag and *laitier*).

Consequently, this study aims understanding the behavior of trace elements in the two processes. It is focused on materials excavated on the archaeological sites of the Pays de Bray region (France). In order to find the significant-most elements for this region, raw materials, wastes and products (ores, slag, *laitier*, cast iron) samples will be analyzed. Moreover, in order to evaluate the potential to distinguish different provenances by trace element analyses, ores and slag from two other regions (i.e. Lorraine and Pays d'Ouche) were also analyzed and compared to the first one.

To analyze this kind of samples coming from ironmaking sites, a technique which allows bulk analyses to overcome the heterogeneous nature of the specimens is needed. Moreover establishing the provenance of an object asks for the maximum number of elements to be analyzed [10]. Until now Instrumental Neutron Activation Analyses (INAA) has been the most popular technique in provenance studies because of its ability to determine simultaneously a large number of elements [11,12]. It consists in a purely instrumental method which does not require any chemical treatment. However INAA has some major disadvantages: it is time consuming, expensive and requires a suitable reactor and long times prior to measurements due to sample cooling. Another well known technique in archaeometry is X-Ray Fluorescence (XRF) essentially used for major and minor element estimation. It is however known to achieve poor detection limits for trace elements particularly REE which are basic to this study [13]. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) appears to be the method with the highest potential with respect to detection limits, sensitivity, precision and multi elemental determinations and short analytical times. In the past few years, this technique has been used to characterize archaeological materials either coupled with a laser ablation unit (LA-ICP-MS) [14–16] or classical sample dissolution mode [10,17]. LA-ICP-MS allows in-situ measurements, obviates the need for time-consuming sample dissolution procedures and minimizes contamination. However the compositional heterogeneity of the samples studied (slag, ore, laitier) requires a bulk analysis, thus we performed ICP-MS in liquid mode.

Critical of ICP-MS is finding the correct procedure for the complete dissolution of the samples by chemical digestion. The most commonly used methods are the acid decomposition in open vessel, the microwave digestion and the alkali fusion. Alkali fusion requires a high flux to sample ratio (4:1) necessary to completely decompose the sample. This entails a strong matrix effect and the introduction of a great amount of polluting elements also leading to a possible contamination of the torch and other parts of the analytical apparatus (e.g. boron rich flux) [10,18,19]. By a consequence the solution must be strongly diluted (f_d, dilution factor, $f_d=5000$) dramatically lowering the detection limits. Moreover Si-rich samples (as the laitier samples in this study: $\%SiO_2 \approx 63$) generally result in solutions enriched in total dissolved solids (TDS) which can cause analytical drift by reducing the diameter of the cone orifice [10]. Furthermore high Si content may involve important isobaric interferences which prevent to analyze certain elements like the ^{45}Sc (interference: $^{17}OH + ^{28}Si$). The microwave digestion may leave un-dissolved residues [10,20] making necessary the addition of flux, thus generating the same problematic of the alkali fusion. Moreover when working on samples rich in C like cast iron ($>4\%_{mass}$), their decompositions may lead to dangerous overpressures as we experienced during microwave-assisted sample digestion ETHOS (Thermo Optek) [21].

Open vessel acid decomposition was chosen because it allows achieving the wanted detection limits and the complete sample

Table 1
Measurement conditions

Instrument	
Thermo Electron X7	
Normal continuous nebulization (concentric)	
Plasma	
Plasma gas	Argon
Forward/reflected power	1350 W/<7 W
Aerosol carrier gas flow rate	0.74 L min^{-1}
Auxiliary gas flow rate	0.90 L min^{-1}
Plasma gas flow rate	13 L min^{-1}
Spray chamber water-cooled at 3 °C	
Mass spectrometer	
Interface vacuum	1.9×10^{1} hPa
Analyser vacuum	3.6×10^{-7} hPa
Ni made Xi sample (1 mm ϕ) and skimmer (0.7 mm ϕ)	
Acquisition parameters	
Full quantitative scan mode	
Dwell time	10 ms/element
Replicates	4
Ion collection mode	Pulse counting
Measuring time	90 s