



Iron isotopes as a potential tool for ancient iron metals tracing



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ABSTRACT

Provenance studies of iron artefacts have become an important topic in archaeology to better understand the socio-economic organization of ancient societies. Elemental and isotopic tracing methods used so far for iron metal provenance studies showed some limitations, and the development of new additional tracers are needed. Since the last decade, the rise of cutting edge analytical techniques allows for the development of new isotopic tools for this purpose. The present study explores for the first time the use of iron isotopes analyses as a potential method for ancient iron metal tracing. Ore, slag and metal samples from two experimental reconstitutions of iron ore reduction by bloomery process were collected. Their Fe isotope compositions were measured by Multi Collector – Inductively Coupled Plasma – Mass Spectrometry (MC-ICP-MS) to assess the possible impact of smelting on the Fe isotope composition of the metal produced. Our results show that the iron isotope compositions of the slag and metal are for 8 out of 9 samples analyzed undistinguishable from that of the starting ores. This suggests that overall, no significant Fe isotope fractionation occurs along the *chaîne opératoire* of iron bars production, even if slight isotopic differences might be found in blooms before refinement. This fact, combined with the natural isotopic variability of iron ores, as reported in the literature, may allow the use of Fe isotopes as a relevant tracer for archaeological iron metals. This new tracing approach offers many perspectives for provenance studies. The combination of elemental and Fe isotope analyses should thus be useful to validate origin hypotheses of ancient iron artefacts.

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1. Introduction

Tracing metal provenances has become a major issue in archaeometallurgy. Indeed, determining the provenance of iron artefacts could help to understand the socio-economic organization of ancient societies and to restore trade networks. Until medieval times, iron was produced by ore reduction in bloomery furnace (direct process). Combined with archaeological evidences, the analysis of material from archaeological iron smelting sites could help identifying the ancient processes of metal production. Some experimental approaches (e.g. Tylecote, 1986; Crew, 2000; Leroy et al., 2015; Benvenuti et al., 2016) have allowed defining a

theoretical *chaîne opératoire* of bloomery process. However, ancient smelting techniques can be highly different, depending on the period and region of iron production, the cultural sphere, or the nature of exploited ores.

1.1. Ancient smelting process in the Montagne Noire massif (SW of France)

In this study, we focused on the smelting process used in the Montagne Noire massif during the Roman period. Successive archaeological studies have allowed to determine well the Roman process of iron production in the Montagne Noire massif (e.g. Domergue et al., 1993; Fabre et al., 2016). The theoretical *chaîne opératoire* of iron production is presented in Fig. 1a.

Gossans represent the major ores in the Montagne Noire. They are mainly composed of iron oxyhydroxides and can contain some remains of iron carbonates or iron sulfides. Once sorted, the roasting step of the ore in an oxidizing environment, such as an open fire, allowed removing water from oxyhydroxides, CO₂ from

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carbonates and sulfur from sulphides. It also induced the destruction of ore and made crushing easier. This preliminary treatment induced changes of mineralogical and chemical compositions of the ore before it was introduced in the furnace. A schematic model of the reactions involved in the reduction process is presented in Fig. 1b. More detailed models of iron reduction are given in Bachmann (1982), or in Jarrier (1993), Mahé-Le Carlier (1997), Mangin (2004) and Leroy et al. (2015).

Reduced iron and siderophile elements accumulated and formed an iron bloom which stays in a “pasty” state because of the temperature that did not exceed the iron fusion point of 1538 °C. Impurities, consisting mainly lithophile elements, formed the liquid slag at 1300 °C (Jarrier, 1993) and flowed out of the bloomery furnace (Fig. 1a). When reduction was achieved, the iron bloom was extracted from the furnace and refined during a purification step by hammering while hot to remove a maximum of slag and charcoal incorporated in the bloom. It was then shaped by smithing until getting a “semi-product” which was transformed into objects (Pleiner, 2000). Ancient metal tracing aims to recover the *chaîne opératoire* from ores to metal and to determine the origin of archaeological artefacts.

1.2. Tracing methods of ferrous metals

For several decades, the development of increasingly precise and accurate analytical methods allowed the use of geochemical tools to trace ferrous materials. The more frequently used method consists in major, minor and trace element analyses on slag inclusions remaining in archaeological artefacts (e.g. Hedges and Salter, 1979; Tylecote, 1986; Rostoker and Bronson, 1990; Buchwald and Wivel, 1998; Coustures et al., 2003; Dillmann and L'Héritier, 2007; Blakelock et al., 2009; Desaulty et al., 2009; Leroy et al., 2012; Dillmann et al., 2015; Benvenuti et al., 2013, 2016; Mameli et al., 2014). The underlying assumption of the earlier studies is that the elemental chemical composition of slags inclusions reflects that of the ores (Hedges and Salter, 1979). Other studies have demonstrated that the composition of slag inclusions

can be influenced by charcoal and furnace lining contribution (e.g. Tylecote, 1986; Rostoker and Bronson, 1990; Paynter, 2006; Dillmann and L'Héritier, 2007; Charlton et al., 2010; Benvenuti et al., 2013, 2016; Disser et al., 2014). Nevertheless, some major elements, such as MgO, Al₂O₃, SiO₂, K₂O and CaO are totally re-oxidized at the end of the process. Ratios between these compounds thus remain relatively homogeneous in slag inclusions (Dillmann and L'Héritier, 2007). In the same way, Coustures et al. (2003) identified some trace element pairs, having comparable ionic radius and number of valence electron, whose ratio remains unchanged during the smelting process. The comparison of these ratios between slag inclusions in iron objects and archaeological materials allows establishing provenance hypothesis. However, it turns out that for some elements, the composition of slag inclusions is related to a specific production system (ores-charcoal-pollutants) rather than a specific ore (e.g. Coustures et al., 2003; Dillmann and L'Héritier, 2007; Blakelock et al., 2009; Charlton, 2015). The analysis of slag inclusions resulting from ore reduction rather than that formed during smithing operations (e.g. Disser et al., 2014; Dillmann et al., 2015), and the choice of pertinent elemental tracers inherited from ore (e.g. Desaulty et al., 2009; Benvenuti et al., 2013, 2016; Mameli et al., 2014) can permit to relate metal provenance to a specific mine. Moreover, despite possible overlapping compositions of ores, slags or metals from distinct regions, statistical multivariate treatments allow distinguishing ore sources with their elemental signature (e.g. Charlton et al., 2010, 2012; Charlton, 2015; Leroy et al., 2012; Mameli et al., 2014). Elemental analyses are a powerful tool for iron provenance studies, but detection of relevant slag inclusions in metal objects may induce an important deterioration of artefacts which can be problematic for some museum pieces.

Schwab et al. (2006) used Pb isotopes for iron artefact tracing, in addition to trace elements analyses. However, the generally low Pb and high U concentrations lead to an important Pb isotopic heterogeneity of many iron ores, which limits provenance determinations. Strontium and Os isotopes have also been tested (Degryse et al., 2007; Brauns et al., 2013), but Sr could derive from

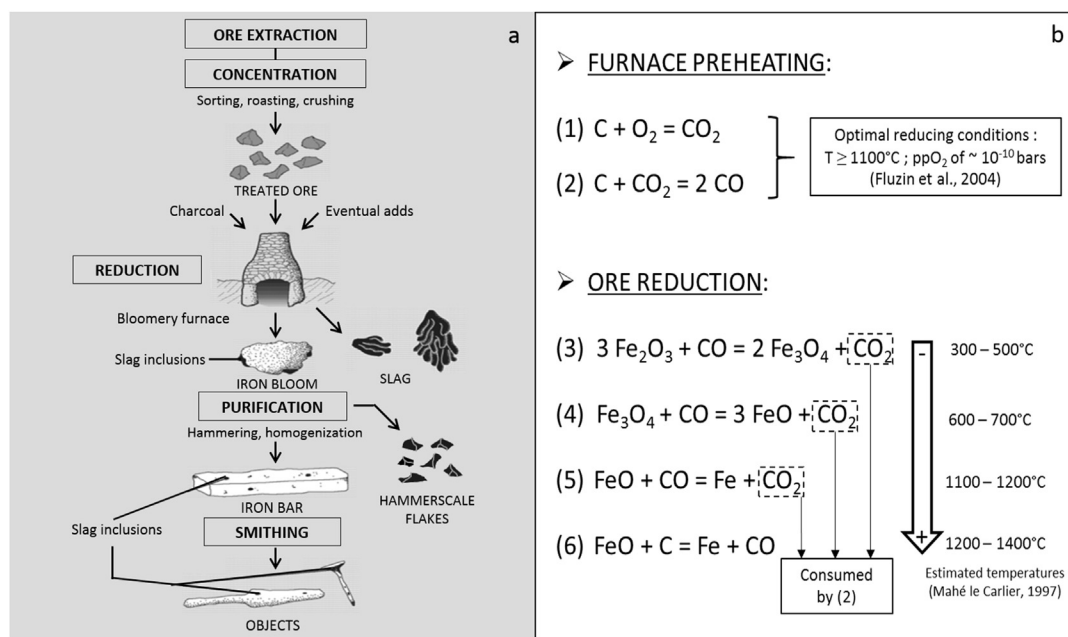


Fig. 1. (a) Theoretical *chaîne opératoire* of iron production by bloomery process (modified after Baron et al., 2011), and (b) schematic model of reactions involved in the reduction step (this figure reports estimated temperatures and oxygen partial pressure, cf Mahé-Le Carlier, 1997 and Fluzin et al., 2004). During the descent of ore from the top to the bottom of the furnace, reaction (3), (4), (5) and (6) became successively dominant when the temperature increased towards the bottom of the furnace.

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