

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at SciVerse ScienceDirect

Journal of Archaeological Science

journal homepage: <http://www.elsevier.com/locate/jas>

The medieval iron market in Ariège (France). Multidisciplinary analytical approach and multivariate analyses

S. Leroy^{a,b,*}, S.X. Cohen^b, C. Verna^c, B. Gratuze^d, F. Téreygeol^a, P. Fluzin^a, L. Bertrand^b, P. Dillmann^a

^aIRAMAT LMC, UMR5060 CNRS and SIS2M/LAPA, UMR3299 CEA/CNRS, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France

^bIPANEMA, UPS3352 CNRS, Synchrotron SOLEIL, BP 48 Saint-Aubin, Gif-sur-Yvette, France

^cUniversité de Paris 8, Saint-Denis, France

^dIRAMAT CEB, UMR5060 CNRS, Orléans, France

ARTICLE INFO

Article history:

Received 22 July 2011

Received in revised form

24 November 2011

Accepted 27 November 2011

Keywords:

Iron provenance

Ariège

Slag inclusions

Trace elemental signature

Multivariate analyses

ABSTRACT

The medieval iron market in Ariège (French Pyrenees) is characterised by its complexity leading to many questions regarding the ore used in relation to the artefacts encountered in archaeological settings. Despite the conclusive study of the treaty that regulated iron vs. coal exchanges from the 14th to the 19th c. by Verna et al., many questions remain unanswered concerning provenance and circulation of ores and products. Based on a combination of trace elemental analysis and multivariate statistical methods (discriminant analysis, hierarchical clustering analysis), we propose to follow an elemental-based signature from ore to artefacts, suited to the direct iron process, to clarify provenance hypotheses. We define the chemical signature of the Ariège area and compare it to that of slag inclusions in artefacts uncovered in several main archaeological sites from the Ariège area but also outside of this region. The results from this study are consistent with prior knowledge from historical sources. In the Ariège region, results highlight the multiple origins of products encountered at Montréal-de-Sos, a site close to known trade routes, whereas the isolated Castel-Minier site primarily contained objects from local ores and most objects retrieved from the Mirabat castle (Couserans) are coming from outside Ariège, possibly an indirect consequence from the exchange treaty. The presence of pins made of Ariègean ores is also demonstrated in the far more distant Capestang collegiate (near Narbonne, outside Ariège). This opens the way to finer studies in the politico-economical control of the iron supply for the building of medieval monuments in Southern France.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

In the Middle Ages the exploitation of manganese-rich ores is attested in several European bloomery iron-production areas (for example: the Pyrenees, Catalonia, Lombardy, the French Alps, Champagne, Burgundy, Southern Germany and Carinthia) (Sclafert, 1926; Verna and Benoit, 1991; Belhoste, 2001; Verna, 2001). The specific properties of these ores are thought to have been recognised by metalworkers since they could lead more easily to carburised alloys during the bloomery smelting stage (Truffaut, 1994). For the French Pyrenees, a historical study by Verna (2001), based on documentary sources, shed light on the iron-making activities from the 13th to the 16th centuries in the Ariège area. This area

witnessed the uncommon persistence of the bloomery process during the late Middle Age until the 19th century. This is particularly due to the development of the *mouline*, a particular type of bloomery process forges using the hydraulic force for bellows and hammers since the late 13th century (Verna, 2001, 2008). In this area, the geological (Tollon, 1964; Dubois, 1996, 2000) and historical studies (Verna, 2000, 2001) suggest the widespread exploitation of the Mont Rancié iron mines in the Vicdessos valley, which during the Middle Ages were the main suppliers of ore for the County of Foix (Fig. 1).

A dynamic iron-making activity centred on the Vicdessos valley developed. The production of the *moulines* supplied local and regional iron markets via the major trade road that connected the County of Foix to Toulouse. This city was therefore a focal point of the iron market (Verna, 2001). Historical sources mention that Ariègean iron made of Mont Rancié ores was distributed from Toulouse to Narbonne (more than a hundred kilometres NE from the Ariège area) and the Provence area (in Southeastern France) where iron from different sources were attested (Verna, 2001).

* Corresponding author. IRAMAT LMC, UMR5060 CNRS and SIS2M/LAPA, UMR3299 CEA/CNRS, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France. Fax: +33 169086923.

E-mail address: stephanie.leroy@cea.fr (S. Leroy).

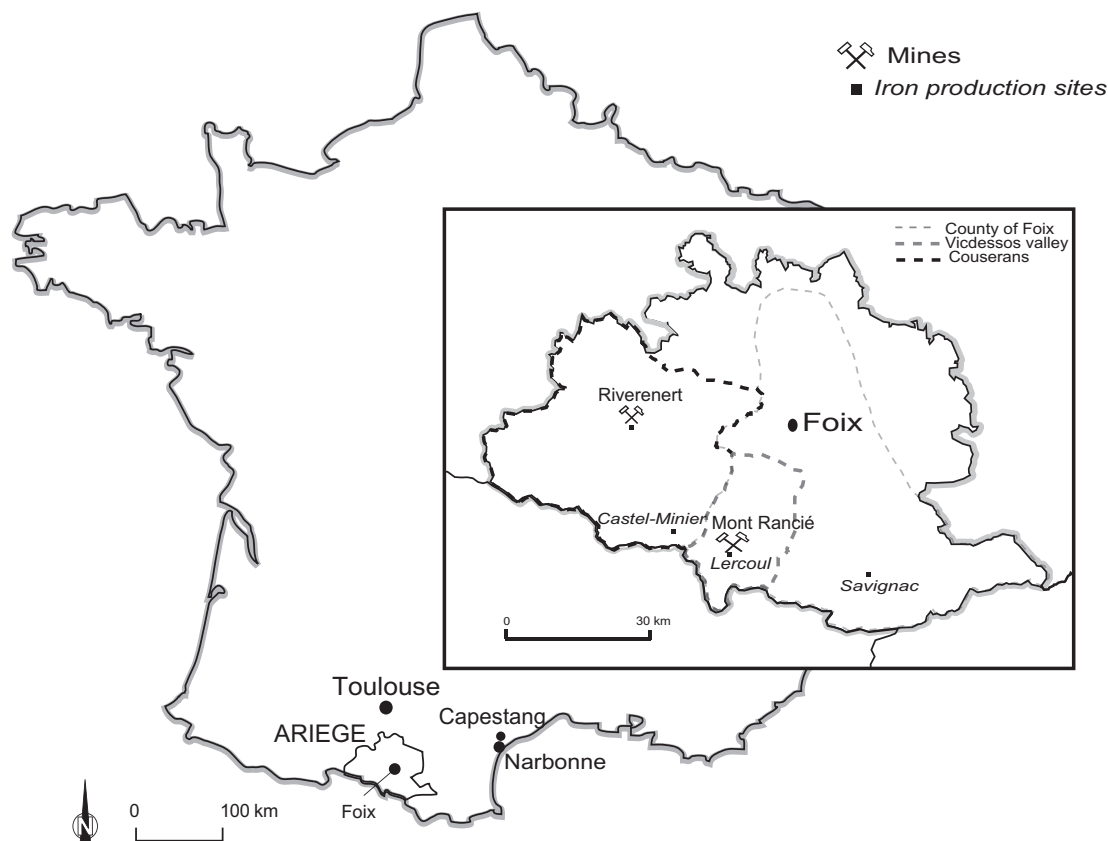


Fig. 1. Location of the Ariège area and Capestang. The main iron mines and the archaeological sites of Castel-Minier, Lercoul, Riverenert, Savignac are represented within the Ariège area. For better localisation, the current borders of France and Ariège are given.

Verna (2001) mentions in particular the use of Ariègean iron in the Lion tower at Arles (in Provence). Textual evidence shows that the County of Foix was also supplied by iron produced in neighbouring areas (Verna, 2001). Lastly, in the specific case of the Ariège area, ore from the Videssos valley was exported to the Couserans (Fig. 1) following an ore-charcoal exchange treaty concluded in 1347–1348 that remained in force until the 19th century (Chevalier, 1956; Verna, 2001). Under this treaty, the Videssos supplied ore to some hydraulic forges in the eastern part of the Couserans (Ercé and Massat valleys) and received in exchange the wood and charcoal needed by the forges of the Videssos valley (Verna, 2001). Given that some or many exchanges are not documented by the textual sources, the precise distribution conditions of ore and iron products in the Ariège area, and the socioeconomic relationships they represent, remain difficult to elucidate.

This study proposes to consider the archaeological findings and particularly the iron-based artefacts, to complement textual evidences on the complex Ariègean iron market. Several castles were built and occupied during the late medieval period and their excavation has provided various iron artefacts (nails, knives, etc...). Determining the origin of these artefacts and verifying whether they were made from local or distant ore would provide crucial complementary data to historical sources. Further away from the Ariège area, probing the possible presence of Ariègean iron is also a challenging goal.

Many researchers have tried to analyse iron objects, bloom, slag material and potential ores in order to establish the origin of iron artefacts made by the bloomery process. They have used several approaches such as the examination of isotopic ratios (Gale et al., 1990; Schwab et al., 2006; Degryse et al., 2007); the analysis of trace elements in the metal of the iron artefacts (Devos et al., 2000);

the analysis of the major elements in slag inclusions (hereafter, SI) (Hedges and Salter, 1979; Buchwald and Wivel, 1998; Blakelock et al., 2009); and more recently, the analysis of the trace elements in SI (Coustures et al., 2003, 2006; Schwab et al., 2006; Desaulty, 2008; Desaulty et al., 2009). Recently published work by Desaulty et al. (2009) demonstrated the effectiveness of combined analyses of major and trace elements on ores, slag samples and SI to follow the elemental signatures from a given iron ore to the SI in the artefacts in order to test provenance hypotheses when the metallurgical characteristics of the objects have previously been thoroughly examined. It is important to stress here that trace elemental study must be performed only on those SI selected using a major elements filtering process, as proposed by Dillmann and L'Héritier (2007) to select inclusions coming from the smelting stage and not from the smithing stage (see experimental part § 2.2.2). The trace elemental analytical methodology developed by Desaulty et al. (2009) consists of the following three steps: (1) "elements that pass completely in the slag (*lithophilic elements*) without being contaminated by lining or charcoal during the smelting are selected", (2) "elements with similar valences and ionic radii, but that are not *quasi-isotopes*, are selected to form couples in order to define the elemental signature", (3) "the trace element ratios measured in samples were compared one by one to test the compatibilities between the elemental signature of a given area and any artefact of unidentified origin". This approach has proven to be effective in excluding a potential source but should be handled with care when validating a provenance hypothesis. Not considering simultaneously the full range of elemental pairs may indeed lead to a loss of crucial elemental information and the overlooking of some significant chemical patterning in particular considering that some ratios of concentrations can be similar between geographically distinct iron-making areas. However, enlarging the list

of characteristic elements from a given area leads to difficulties as it requires the joint testing of a large number of elemental ratios. For example, if 15 elements are considered, 105 ratios need to be studied and compared two by two. We therefore developed a synthetic multivariate methodology to consider simultaneously all the concentration data to test a potential origin.

The multivariate methodology developed is applied here to study the organisation of the Ariègean iron market. To this end, iron artefacts of unidentified origin, from archaeological sites within the production region but also from outside this area were selected and studied to examine their origin by comparison to ores, slags, forged bars and objects of known source.

2. Sample sets and methods

2.1. Sample sets

This study considered three sample sets. The first one, the reference corpus, consists of samples (ores, slags and metal samples) produced with Ariègean ores that were used to characterise the Ariègean elemental signature. The second, a calibration one, consists of artefacts of known provenance – either from Ariège or not – in the multivariate approach, it sets the boundaries around the compatibility and incompatibility domains (see § 2.3.3). These two sets taken together form the “*learning set*” of our supervised classification procedure. A third set consists of artefacts of unidentified origin for which we tested a possible Ariègean provenance.

2.1.1. Reference set: ores, slags and metal pieces of Ariègean origin

We collected a reference set (Table 1) made of:

- Ore samples from three sectors:
 - From different levels in the NW side of the Mont Rancié near nine entrances of the Sem mines.
 - From the Lercoul archaeological site on the Southern side of the Mont Rancié including a medieval exploitation nearby (Fig. 1).
 - From the archaeological excavations on the Castel-Minier bloomery site. The Vicdessos was supplying with ore the

forges in the Eastern part of the Couserans where Castel-Minier is located (Verna, 2001). Leroy (2010) showed that the ore reduced on the bloomery site came from the Mont Rancié mines.

- Slag samples originating from four iron-production sites (Fig. 1):
 - Lercoul that used the ore mined nearby.
 - Riverenert, the adjacent mine being the only medieval iron mine known in the Couserans (Verna, 2001).
 - Savignac-les-Ormeaux.
 - Castel-Minier. The slag samples we selected were recovered from slag heap 1 (Florsch et al., 2011) and clearly linked to the smelting activities of the site.
- Slag samples obtained during a smelting experiment (Leroy and Colliou, in press).
- Metal samples (gromps, semi-finished products) uncovered on the Castel-Minier site from the area linked to smelting activities using Ariègean ore.

2.1.2. Calibrating set: metal samples of known origin

At first, we used those Ariègean metal samples coming from Castel-Minier (Table 1) that were also used to define the Ariègean elemental signatures. Secondly, we considered non Ariègean metal pieces, coming from various iron-production areas that reduced various kinds of ores: some with major elemental composition very close to the Ariègean ones as manganese-rich ores from Lombardy (Northern Italy) and from the Provence area (Southeastern France), as well as clearly distinct ones such as phosphorus-rich ore from the Lorraine area (Northeastern France) (Table 2).

2.1.3. Set of unidentified origin: iron artefacts of unidentified origin

We selected (Table 3):

- Well-dated ferrous artefacts of diverse typologies (nails, weapons, projectiles, blades, etc...) from four main archaeological sites within the Ariège area (Fig. 1):
 - The Montréal-de-Sos castle (Guillot, 2008).
 - The Castel-Minier site (Téreygeol, 2009). We chose finished objects related to the castle and its silver mine that are clearly

Table 1

Reference set: samples selected for the characterisation of the Ariègean elemental signature.

| Nature | Type | Origin | Number of samples | Remark |
|-----------------------------|--|---|-------------------|--|
| Ore samples | Geological | Sem mines, Northwestern side of the Mont Rancié | 19 | Prospections carried out by S. Leroy et al. |
| | Geological | Mine near Lercoul, Southern side of the Mont Rancié | 1 | |
| | Archaeological | Castel-Minier | 10 | |
| Archaeological slag samples | Entrapped, tapped | Lercoul | 14 | Ores known to originate from Sem mines (Verna, 2001). Excavations carried out by F. Téreygeol over several summers since 2005 (Téreygeol, 2009) |
| | Tapped | Riverenert | 6 | |
| | Tapped | Savignac-les-Ormeaux | 3 | |
| | Entrapped, tapped | Castel-Minier | 17 | |
| Experimental slag samples | Tapped | Experimental smelting (XP07) | 2 | Ores known to originate from Sem mines (Verna, 2001). The iron production was shown to be effective from the end of the 12th century to the first half of the 16th century as terminus post quem (Téreygeol, 2009) |
| Metal pieces | Rod, ingot, gromps, curved sheet iron, plate, piece of a bloom | Castel-Minier | 8 | Ore from a Sem mine. Performed in 2007 on the Melle platform (France) directed by F. Téreygeol Ores known to originate from Sem mines (Verna, 2001; Leroy, 2010) |

Table 2

Calibrating set: metal samples of known origin analysed for the development of the methodology based on the multivariate approach.

| Nature | Type | Origin | Number of metal pieces | Remark |
|---------------------------|--|---|------------------------|--|
| Ariegean metal pieces | Rod, ingot, gromps, curved sheet iron, plate, piece of a bloom | Castel-Minier in Ariège area, Southwestern France | 8 | Ores known to originate from Sem mines (Verna, 2001) |
| Non Ariegean metal pieces | Architectural anchor | Bugnate in Lombardy, Northern Italy | 1 | Provided by M. Tizzoni |
| | Tool blank | Schilpario in Lombardy, Northern Italy | 1 | Provided by M. Tizzoni |
| | Bloom n°1 | Mimet in Provence area, Southeastern France | 1 | Provided by M. Berranger |
| | Bloom n°2 | Experimental smelting using ore from the Lorraine area, Northeastern France | 1 | Provided by M. Leroy |

not archaeologically connected to the neighbouring iron smelting site.

- The Mirabat castle (Lasnier, 2007).
- The Sainte-Catherine castle (Rouch, 2006).

- Artefacts further away from the Ariegean production area. We incorporated samples of iron reinforcing bars used in the St-Etienne collegiate church of Capestang, a hundred kilometres away, near Narbonne (courtesy of P. Bernardi and M. Bourin).

2.2. Determination of the elemental compositions

Our analytical methodology builds on the recent work by Desaulty et al. (2009). We followed two protocols respectively for ore and slag analysis, and for the SI analysis.

2.2.1. Protocol for ore and slag analysis

Ore and slag samples were analysed using bulk methods of analysis that provide an average elemental composition of the sample. The samples were first crushed into powder in an agate shatter box before being sieved at 125 µm. Pellets were then prepared by agglomerating and compressing the fine powders.

The major element composition was determined using an Energy Dispersive Spectrometry system (IDEX setup, SAMx company) coupled with a Cambridge Stereoscan 120 Scanning Electron Microscope (SEM-EDS, using a 15 kV accelerating voltage).

In iron containing slags, the relative accuracy errors were estimated to be 2% for measurements of major elements, and 10% for minor elements with concentrations lower than 1 wt%, down to 0.5 wt% (detection limit) (Dillmann and L'Héritier, 2007; Pagès et al., 2011). The detection system allows the quantification of relatively light elements down to oxygen with good precision. A reliable quantification is therefore performed on samples that do not contain carbon or hydrogen when all the major elements constituting the sample are detected. Conversely, the analysis of some iron carbonates present in ores is precluded. We expressed the results as oxides concentration. In order to obtain a representative measurement of the average composition, the entire surface of the pellets (several mm²) was analysed and an average content was calculated for bulk composition.

The bulk trace elemental composition was determined following a procedure adapted from Desaulty et al. (2008). Two techniques were used: Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Aliquots of 120 mg of the samples for INAA and 50 mg for ICP-MS analyses were prepared. For ICP-MS analysis, samples were prepared by acid dissolution of silicate matrix in open vessels using a new acid digestion procedure. In the context of this work, we developed and implemented a simpler, less expensive and safer procedure by substituting the conventional HF/HClO₄ mixture by NH₄F (Mariet et al., 2008). ICP-MS measurements were carried out using the Thermo Electron X7 quadrupole spectrometer at the

Table 3

Artefacts of unidentified origin collected at the Montréal-de-Sos, Castel-Minier, Mirabat and Ste-Catherine castles, and at the Collegiate church of Capestang.

| Type | Sample name | Archaeological site | Dating |
|-------------|--|---|----------------------|
| Knife | MdS8844 | Montréal-de-Sos | 13th–15th |
| Knife | MdS 8858 | (from areas of the dungeon) | |
| Knife | MdS 8889 | | |
| Knife | MdS 9227 | | |
| Frame nail | MdS 29336 | | |
| Iron plate | MdS 29342 | | |
| Equine iron | MdS 29409 | | Post mid 14th |
| Frame nail | MdS 29421 | | 13th–15th |
| Nail | MdS 29431 | | |
| Projectile | MdS 29522 | | 14th–15th |
| Unknown | MdS 29566 | | 13th–14th |
| Unknown | MdS 29591 | | 13th–15th |
| Unknown | CM05-2-31 | Castel-Minier (from the castle area) | 13th–15th |
| Unknown | CM05-2-34 | | |
| Unknown | CM05-2-36 | | |
| Little rod | CM05-2-54 | | |
| Ring | CM05-2-59 | | |
| Nail? | CM06-2002-1 | | 15th–16th |
| Unknown | CM07-2044 | | |
| Chisel | i10013 | Castel-Minier (from the silver mine) | Late 13th–15th |
| Nails | MIR 1 to MIR 3 ; MIR 5 to MIR 12 | Mirabat (from the cistern) | Late 13th–14th |
| Unknown | Ste Cath n°2, Ste Cath n°4, Ste Cath n°5 | Sainte-Catherine (from the <i>caput castris</i>) | Late 13th–early 14th |
| Pins | CAP 1, CAP 3 | St-Etienne collegiate church of Capestang (from a pinnacle) | Probably 15th |

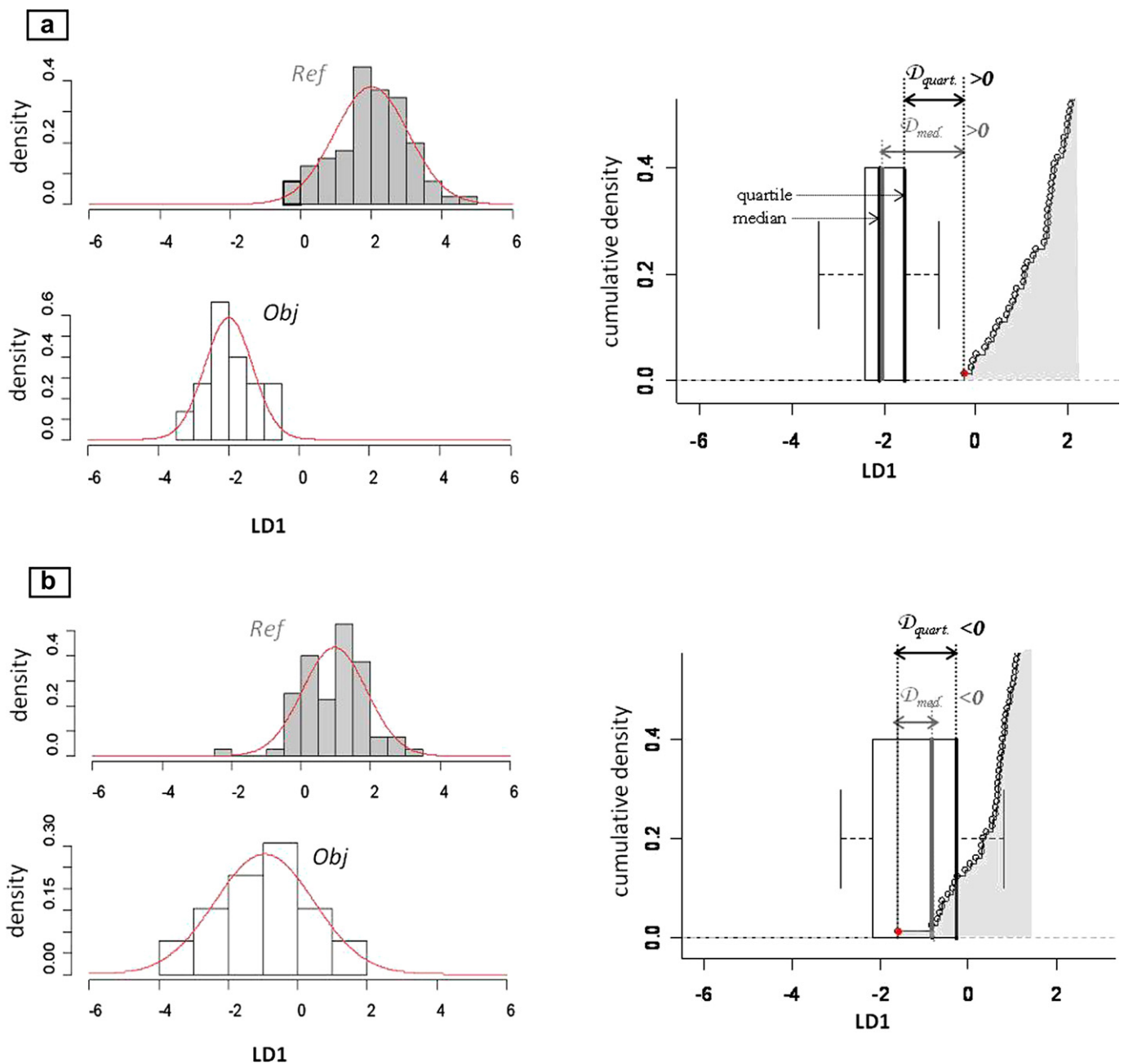


Fig. 2. (left) Projections on LD-1 of *Ref* and *Obj*: (a) when the *Obj* and the *Ref* domains are not overlapping, D_{med} and D_{quart} are both positive; (b) when the *Obj* domain has a significant overlap with the *Ref* domain, D_{med} and D_{quart} are both negative. (right) The projections of *Ref* are displayed as an empirical cumulative distribution and the projections of *Obj* are represented as boxplot displaying five values: the lowest value, the first quartile, the median, the third quartile, and the highest value for all SI analysed in the artefact.

Service Interdisciplinaire sur les Systèmes Moléculaires et les Matériaux (SIS2M, Saclay CEA Centre, France) equipped with a concentric nebuliser (Thermo Fisher Scientific). The relative uncertainty on results was estimated at 7% (Desaulty et al., 2008). Concentrations were determined by comparison to international geochemical standards (GSN, BEN, ACE, Centre de Recherches Pétrographiques et Géochimiques, France; GXR4, United States Geology Survey, USA), and trace element-doped silica standards prepared at SIS2M. For the INAA analyses, all sample irradiations were carried out at the nuclear reactor Osiris (Saclay CEA Centre, France). The relative uncertainties on results were estimated to be below 5%, except for Zr (Joron et al., 1997).

2.2.2. Protocol for SI analysis

Metal samples were cross-sectioned to expose both the metallic matrix and the slag inclusions entrapped in the matrix. Cross sections were embedded in epoxy resin, cut in smaller transverse sections and polished using SiC abrasive paper (grades 80–4000). Samples were subsequently examined with an OLYMPUS light microscope (BX51 model) under reflected light to select regions of interest, to qualify the nature and the distribution of the SI and to visualise possible welding lines.

The major element composition of SI was determined using SEM-EDS with operating parameters identical to those adopted for ore and slag analysis. Data processing was performed following

Dillmann and L'Héritier (2007: pp. 1812–1817) on SI in medieval iron construction. (1) Between 30 and 50 SI per artefact were analysed. (2) SI composition of compounds that are not reduced (noted NRC for Non Reduced Compounds: mainly Al_2O_3 , SiO_2 , K_2O , CaO , and MgO) are plotted two by two and fitted by a linear model passing through zero. If the determination coefficient (R^2) is over 0.7 the ratio is considered as constant and is assumed to be the slope of the modelled line. In this case, SI were demonstrated to be representative of the smelting stage. (3) If R^2 is below 0.7 but a linear behaviour can be shown for a majority of the inclusions, the “outlying data” are deleted from the NRC data bivariate plots in iterative steps. This procedure is necessary because erratic SI are primarily caused by local concentration effects or by SI corresponding to additives during forging. These SI are eliminated here since they cannot be used to define the elemental signature of the artefact. Note that the analysis of SI is a very effective means of detecting recycling. In case of recycling, Dillmann and L'Héritier (2009) showed that different constant ratios are identified. Finally, in some cases, constant NRC ratios cannot be identified in the SI composition of an artefact and thus its origin cannot be studied. (4) By eliminating all these possible pitfalls, an average weighted major element content is expressed per artefact, taking into account the surface of each analysed SI. It is combined to a pseudo bulk average content and thus compared to macroscopic slag composition. This average weighted content will be noted with a * symbol following the oxide name (e.g. MnO^*).

For the trace element analyses, between 10 and 15 SI per artefact were selected, when possible, among the SI representative of the smelting stage. Their trace element composition was determined using the Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) at the Ernest Babelon Centre (UMR-5060 IRAMAT CNRS, Orléans, France). After probing a large range of possible operating parameters, the laser repetition rate was set to 6 Hz, the ablation time to 50 s and the ablation crater to 80 μm in diameter. We used the quantification procedure developed by Gratuze (1999) and Gratuze et al. (2001) using both internal standardization and external calibration. Silicon values determined by SEM-EDS were used to calculate trace element concentrations instead of normalising all contents to 100% as it is done in the classical procedure. As the amount of removed material is not the same for each ablation, the signal obtained for each trace element for the different ablations was compared to that of the internal standard: the isotope ^{29}Si . Accuracy error calculated by Gratuze et al. (2001) is usually better than 12% for trace elements, but

could reach 20% for trace elements below ppm level. With this method, a significant number of trace elements (up to 39) are quantified in the SI.

2.3. Methodology for identifying a provenance

Previous studies (Desaulty, 2008; Desaulty et al., 2009) showed that some trace element concentrations are not significantly affected during smelting and partition equally between metal and slag, consequently conserving their respective concentration ratio. These specific elements can be used to define an elemental signature of a given ore extraction area. To define the elemental signature of the Ariège area and identify the origin of an iron artefact, the following steps were applied:

- (1) Examination of the MnO and P_2O_5 contents as a first filter.
- (2) Application of multivariate analyses to compare elemental signatures based on trace elements selected to define the signature of the Ariège area.

2.3.1. First filter of the MnO and P_2O_5 contents

Since the content of the major elements is influenced by other components of the reduction system (furnace lining, charcoal ash...) than the ore, the ratios of NRC (mainly $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{K}_2\text{O}/\text{CaO}$, $\text{MgO}/\text{Al}_2\text{O}_3$) are generally highly scattered even for objects of a same provenance (Dillmann and L'Héritier, 2007; Blakelock et al., 2009). Nevertheless, the absolute content of particular major elements, e.g. MnO and/or P_2O_5 , that come from the ore and are not or only slightly modified during the smelt can be used as a first raw filter (Desaulty et al., 2009). Because a part of the iron from the ore is reduced into metal during the smelting, some concentration effects can occur from the initial ore to the slag (and SI), hence a correction has to be made. We decided to normalise the elemental contents to 100% excluding FeO (Fig. 5). These normalised composition values will be denoted by the ** symbol, and calculated as follows: $\% \text{Oxide}^{**} = (\text{Oxide} \times 100) / (100 - \text{FeO})$ for ore and slag samples and $\% \text{Oxide}^{**} = (\text{Oxide}^* \times 100) / (100 - \text{FeO}^*)$ for SI. The purpose of this normalisation is to enable the direct comparison of concentrations in ores, slags and SI, as visible in Fig. 5. The Ariègean ores are well known for their high MnO and low P_2O_5 contents (Ploquin, 2000; Verna, 2001). We therefore defined the limits of MnO^{**} and $\text{P}_2\text{O}_5^{**}$ composition domains to be used as a first filter, from the examination of the ores, slags and SI from the Ariège area.

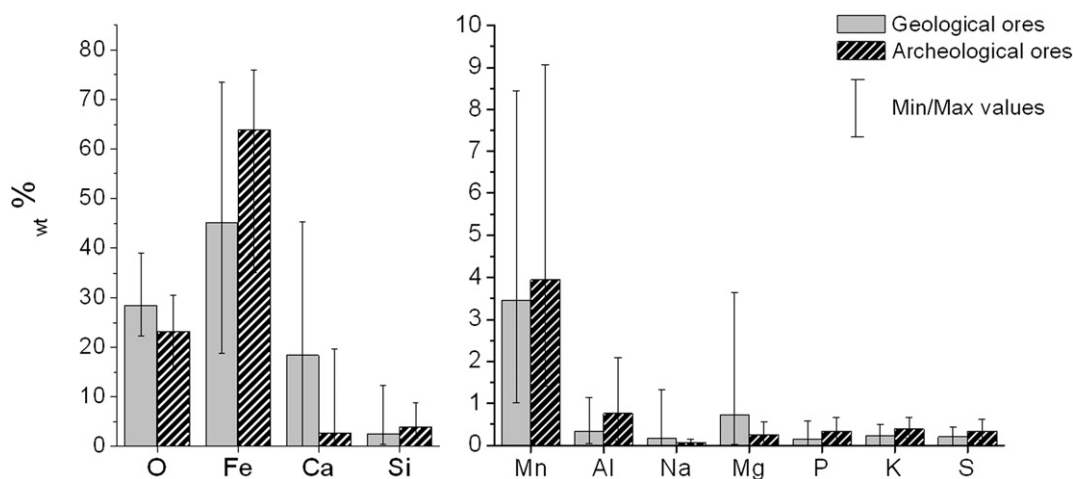


Fig. 3. Average composition in major elements from geological and archaeological ores from the Ariège area. Thin bars represent the minimum and maximum values. All data from SEM-EDS.

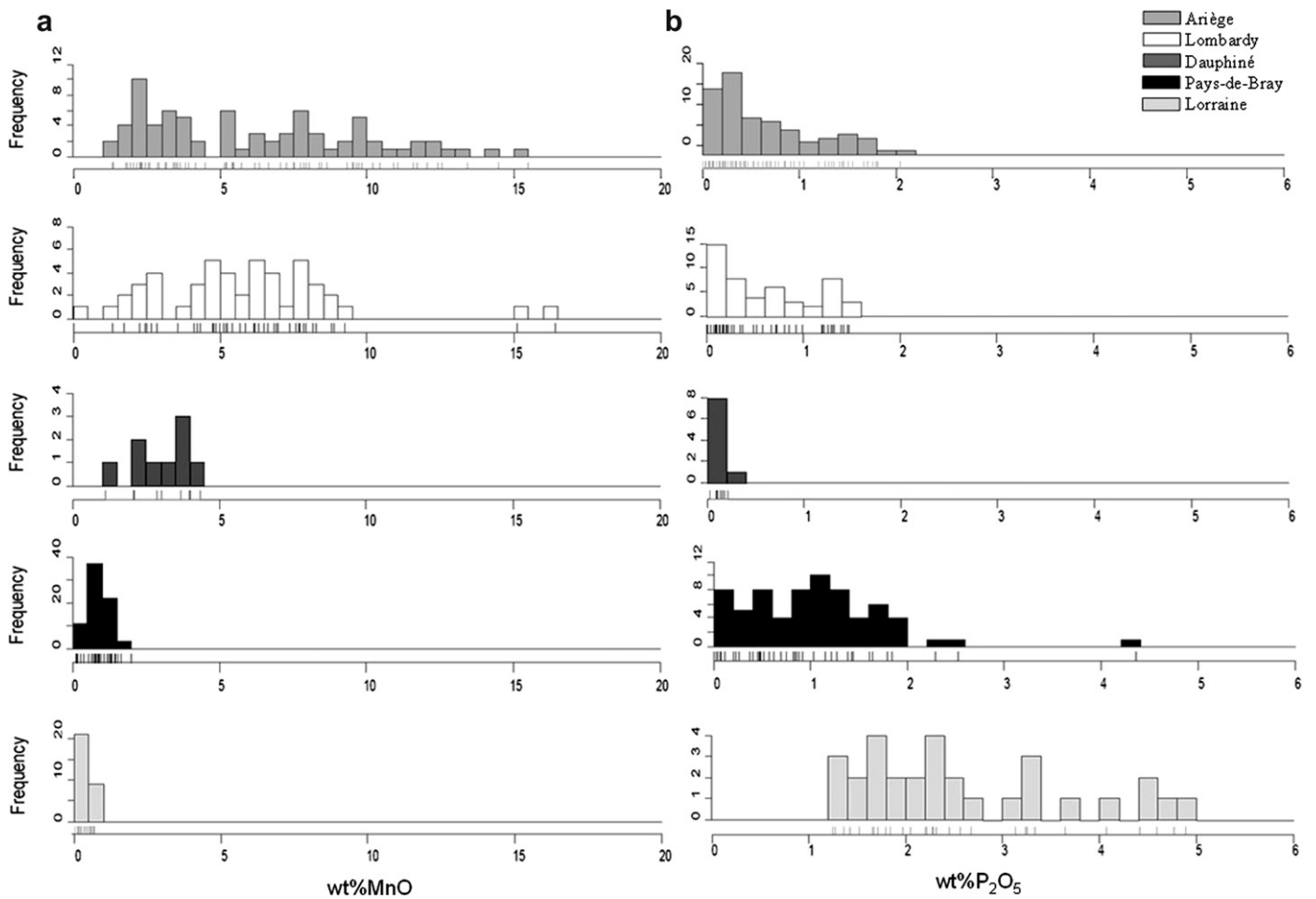


Fig. 4. Frequency distribution in (a) MnO content for ores and slags from Ariège, Lombardy, Dauphiné, Lorraine and Pays-de-Bray; (b) P₂O₅ content for ores and slags from the same regions. All data from SEM-EDS.

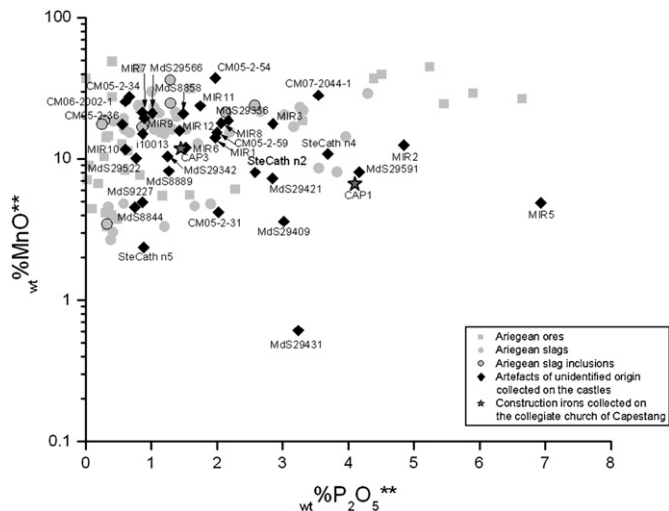


Fig. 5. Comparison of the MnO^{**} and P₂O₅^{**} values measured in ores, slags and SI from the Ariègean reference corpus. Note that this set contains 8 objects. Comparison of these values with those measured in the SI of artefacts of unidentified origin. All data from SEM-EDS.

2.3.2. Multivariate analyses

Among the elements that were shown to be lithophilic and not significantly contaminated by other parts of the furnace charge, only a restricted set could be quantified with an acceptable accuracy of measurement at the concentrations observed in Ariègean samples: Y, Nb, Cs, La, Ce, Nd, Sm, Eu, Yb, Hf, Th, U. This full set of elements was used to define the Ariègean signature.

Our multivariate analysis of the elemental signature is based on a scale invariant representation of the trace elements concentration: in this representation, the signature stays constant when all concentrations are multiplied by a constant scaling factor; hence it stays constant along the reduction process. Such a scale invariant representation can be obtained by dividing the concentration of all elements by the concentration in a given element, chosen as internal standard. Here we propose to use not a single element but the geometrical mean of the set of best measured elements as the internal standard; the main advantage being to reduce the uncertainties on the internal standard. For each element, *E*, we represent its concentration [*E*] by Eq. (1):

$$X_E = \log([E]) - \frac{1}{N} \sum_{k=1}^N \log([E_k]) \tag{1}$$

where the elements (*E_k*) *k* ∈ [1, *N*] are the *N* best measured elements, jointly for all considered samples. In the current study these elements are Y, La, Ce, Sm and Eu (*N* = 5); each of those

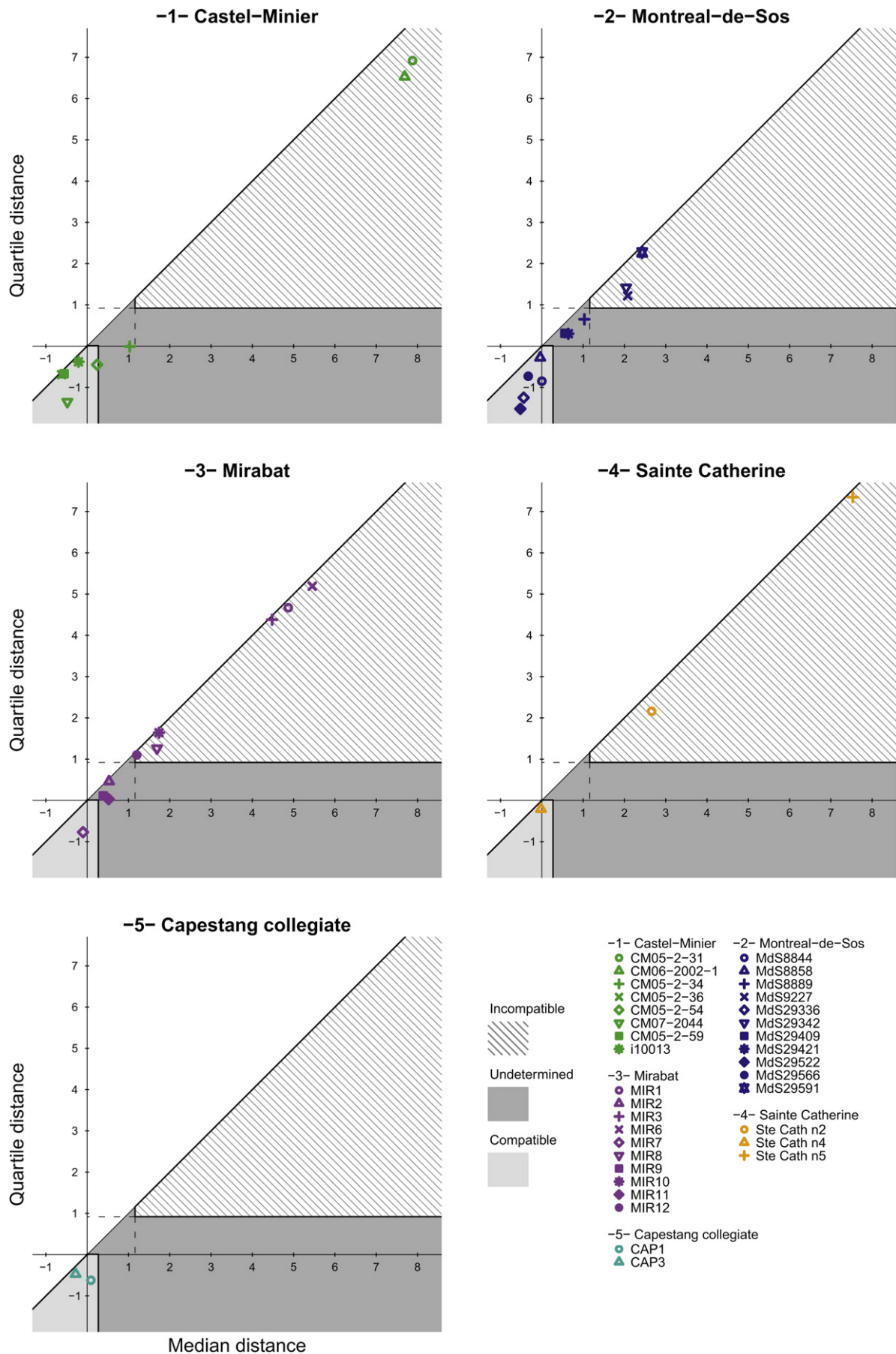


Fig. 6. Diagram of compatibility applied to the artefacts collected on the castles and at the Collegiate church of Capestang. The dotted lines show the D_{med} and D_{quart} thresholds.

elements are below the detection limit in less than 2% of the performed analyses. We also have to ignore one of those elements in this scale invariant representation since, by construction, we have the following linear dependence (Eq. (2)):

$$\sum_{k=1}^N X_{E_k} = 0 \quad (2)$$

We selected arbitrarily the element Eu that has the highest atomic number.

The use of a logarithmic scale is advantageous here to convert the relatively uniform relative uncertainties into uniform absolute uncertainties which are more appropriate for the linear analysis we are about to perform.

Using this representation, the problem we face is a supervised classification problem: we compare the elemental composition of a small set of all analysed SI from the studied object to the data obtained from ore, slag and objects of known origin. For objects of known origin, we considered an average value for the SI to not amplify the influence of the objects compared to ore and slag for the definition of the Ariègean signature. The dimension of the problem, here 12, is large relative to the number of data in the reference corpus, in the range of a hundred. To reduce the variance, we project the data on the most discriminating direction (LD-1) between the two classes of data: datapoints from the studied object's SI on one hand (*Obj*), datapoints from ores, slags and artefacts known to originate from the region of interest on the other (*Ref*).

The experimental design is such that a standard analysis such as principal components analysis (PCA) would provide little if any information, the dataset being largely dominated by the reference corpus, such an analysis would maximise the spread of the artefacts from the reference corpus rather than performing any discrimination between the studied object and the reference corpus. Hence we decided to take an alternative approach: Linear Discriminant Analysis (LDA). Under the hypothesis (H_0) that the studied object is not originating from the same region as the reference corpus, the large dimension of the problem generally enables the LDA to perform a clear separation between the two classes: the separation under this hypothesis dominates stochastically the separation under the alternative hypothesis (H_1), that the elemental signature of the studied object is compatible with the region of the reference corpus. The two extreme values of the projections of *Ref* on LD-1 are selected to delimit the extension of the definition domain of the reference region. Practically, the separation between the two classes is measured through two distances: from the median point of *Obj* to the closest extreme point of *Ref*, and from the third quartile of *Obj* to the closest extreme point of *Ref*, respectively noted D_{med} and D_{quart} . These distances are depicted in Fig. 2.

Since we lack an estimation of the probability distribution of these distances, we have to calibrate the threshold for the test using the calibrating set of objects of known origin divided in a first subset of objects originating from the same region as the reference corpus, and a second subset of objects known to be originate outside the region of the reference corpus. The first subset of objects was initially integrated in the reference corpus to define the Ariègean chemical signatures. That is why each of these objects was temporarily left out of the reference corpus *Ref*, when comparing *Ref* to *Obj*.

Clearly the obtained thresholds depend on the objects used in the calibrating process and as such they will evolve as the number of artefacts studied with this methodology increases. Threshold values also depend on the exact implementation of the LDA method used.

The conjunction of the two distances partitions the plan (D_{med} , D_{quart}) in 3 regions as depicted in Fig. 7: *compatible*, *incompatible* and *undetermined*, therefore leading to a compatibility diagram. Objects in the *compatible* domain were fabricated from ores likely

coming from the region of interest. Objects in the *incompatible* domain were fabricated from ores likely coming from outside the region of interest. Finally this process does not lead to origin information when the object is in the *undetermined* domain of the (D_{med} , D_{quart}) plan.

For *compatible* objects from archaeological sites within the Ariège area, the proximity of the object trace elemental signature to those of each sample of the reference corpus can be assessed using the Euclidean distance in the X_E space. In particular this distance can be used to perform hierarchical clustering analysis (HCA) of the set made of the union of the samples of the reference corpus and the mean X_E of the SI of the studied object. Note that ore and slag samples with several elemental contents below the limit of detection cause scattering in the chemical signature of the reference corpus since their position in the X_E space is estimated with large inaccuracy.

3. Results

3.1. Major elements

Analysis of the major elemental composition of the geological and archaeologically excavated ores in the Ariège area confirms that they are characterised by their high manganese content (average: 3.8 wt%, lowest: 1 wt%) and their low phosphorus content (average: 0.2 wt%, highest: 0.7 wt%) (Fig. 3). The MnO and P₂O₅ compositions of ores and slags from the Ariège area were compared to those from various iron-making areas in France, analysed in Leroy (2010) or provided by the PalSid (PaléoSidérurgie) database (Ploquin, 1994): Pays-de-Bray, Lombardy, Lorraine and Dauphiné (French Alps) (Fig. 4). The MnO content in samples of some areas (Ariège, Lombardy, Dauphiné) is shown to be higher than the ore and slag compositions in other areas (Lorraine, Pays-de-Bray). P₂O₅ contents are lower (<2 wt%) compared to samples from the Lorraine region well known for its P₂O₅-rich ore (Leroy, 1997). This comparison confirms that the Ariègean elemental signature is characterised by high MnO and low P₂O₅ contents.

The MnO** and P₂O₅** values measured in ores and slags from the Ariège reference corpus were shown to be consistent with MnO** and P₂O₅** values from SI of the same set (Fig. 5). We can therefore define the first filter of the Ariège area for P₂O₅ and MnO based on the observed cluster. The lowest observed MnO** value is 2.7 wt%. Thus, to maintain a sufficient safety margin, we will consider in the following that artefacts with average SI MnO content leading to MnO** value below 2wt% are not compatible with the Ariège signature. The highest observed P₂O₅** value is 6.6wt%. As a limited contamination in P₂O₅ could come from the charcoal (Crew, 2000; Serneels, 2002), we will arbitrarily consider that P₂O₅** values greater than 9 wt% preclude an Ariègean provenance.

The MnO** and P₂O₅** values measured in artefacts of unidentified origin were compared to the Ariègean signature. All objects were shown to be located in the Ariègean domain except artefact Mds29431 which MnO** value is below 1 wt% (Fig. 5).

3.2. Trace elements: diagram of compatibility

3.2.1. Construction of the Ariègean diagram

The D_{med} and D_{quart} values obtained for all objects of known origin (calibrating set) and Ariègean samples as reference set are compared and reported in Table 4:

- For the artefacts coming from the Ariège area, the highest measured D_{med} and D_{quart} values are respectively 0.27 and 0.01.
- For the artefacts not coming from the Ariège area, D_{med} and D_{quart} values are significantly higher than those above and the

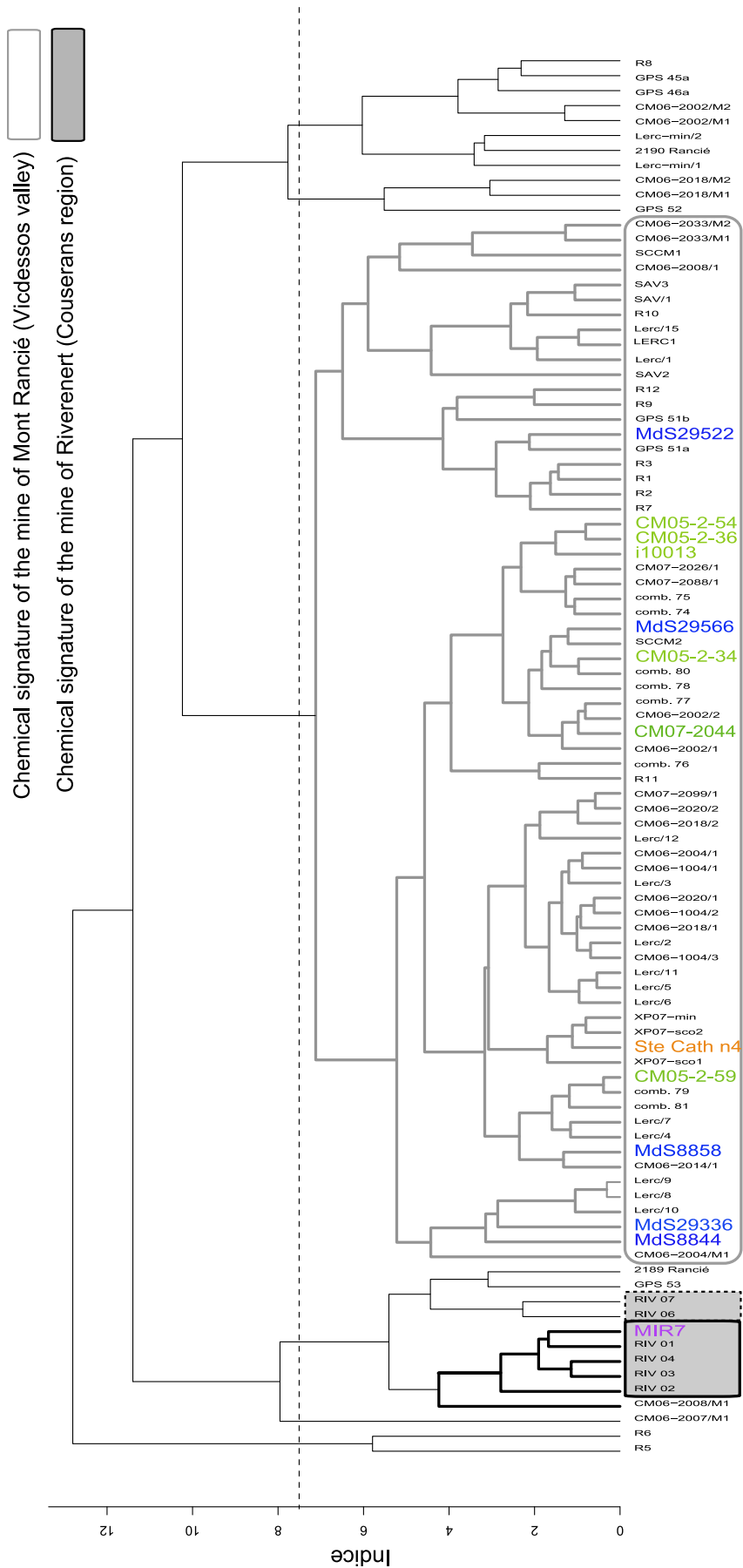


Fig. 7. Hierarchical clustering analysis carried out jointly on the reference set and the group of artefacts of unknown origin compatible with the Ariègean elemental signature. Dotted line: threshold of groups discrimination. Samples in bold: artefacts of unknown origin. Samples not bordered: samples with several elemental contents below the limit of detection, these samples are exclusively ore samples. Samples bordered in grey, branches linked in grey: samples from the iron-production sites of Castel-Minier, Lercoul and Savignac. Samples with a grey background: samples from the Riverenert site. Samples bordered in black, branches linked in black: samples associated with MIR7.

lowest measured D_{med} and D_{quart} values are 1.16 and 0.92 respectively.

These extreme values can now be used to discriminate artefacts originating from the Ariège area from those with another provenance. In the following, this study will therefore consider that:

- The tested artefacts are likely made from ores of the Ariège area when the D_{med} and D_{quart} values are respectively lower than 0.27 and 0.01.
- The tested artefacts are likely based on ores originating from outside the Ariège area when the D_{med} and D_{quart} values are respectively higher than 1.16 and 0.92.

3.2.2. Application of the Ariègean compatibility diagram

The diagram of compatibility with an Ariègean origin, built with the values of Table 4, is used to test the hypothesis of provenance from Ariège for objects of unidentified origin (Fig. 6, Table 5).

Among the 34 archaeological artefacts retained after the first filter, fourteen are located in the *compatible* domain. Note that both samples from the Capestang Collegiate church (CAP1 and CAP3) also belong to the *compatible* domain and consequently could have been produced from an iron ore extracted in the Ariège area. Seven specimens belong to the *undetermined* domain for which no clear conclusion on the ore origin can be drawn: an origin from the Ariège area is neither excluded nor confirmed for these artefacts. Thirteen objects belong to the *incompatible* domain so that these objects appear to be of a different ore origin, most probably imported to the Ariège area.

3.3. Distinction between iron mines within the Ariège area

Considering the artefacts defined as *compatible* with the Ariège area, we tested the possibility to distinguish their initial ore deposits by hierarchical clustering analysis (Fig. 7). The primary aim is to discriminate artefacts fabricated from the two main ore Ariègean sources, Riverenert and Mont Rancié. The discriminating threshold of the HCA was set from visualisation of the dendrogram by selecting a value giving discrimination consistent with our prior knowledge (Fig. 7).

The main homogeneous group contains samples from the iron-production sites of Castel-Minier, Lercoul and Savignac supplied with ores extracted from the Mont Rancié mine (Téreygeol, 2009; Dubois, 2000; Grimbert, 2006). Slag samples collected from the Riverenert site form a distinct group. The dendrogram shows that the majority of the artefacts of unknown origin and compatible with the Ariègean elemental signature are located in the group of the Mont Rancié rather than in that of Riverenert. Sample MIR7 is the only one located in the group of the Riverenert mine and was probably produced with ore coming from this mine.

Table 4

D_{med} and D_{quart} values calculated for all objects of known origin (calibrating set, see Table 2). In bold: extreme values for each subset of samples.

| Samples | Metal piece n°1 | Metal piece n°2 | Metal piece n°3 | Metal piece n°4 | Metal piece n°5 | Metal piece n°6 | Metal piece n°7 | Metal piece n°8 |
|--|-----------------|-----------------|-----------------|-----------------|----------------------|-----------------|-----------------|-----------------|
| <i>Artefacts coming from the Ariège area</i> | | | | | | | | |
| D_{med} | -1.70 | -1.48 | -0.83 | -0.77 | -0.71 | -0.39 | 0.10 | 0.27 |
| D_{quart} | -2.23 | -1.85 | -0.92 | -1.27 | -1.15 | -0.96 | -0.50 | 0.01 |
| Samples | Bloom n°2 | | Tool blank | | Architectural anchor | | Bloom n°1 | |
| <i>Artefacts not coming from the Ariège area</i> | | | | | | | | |
| D_{med} | 1.16 | | 1.20 | | 1.83 | | 2.14 | |
| D_{quart} | 1.12 | | 0.92 | | 1.32 | | 1.74 | |

Table 5

Compatibility with an Ariègean origin for artefacts of unidentified origin.

| Compatibility domains: | Compatible | Undetermined | Incompatible |
|-----------------------------|--|---|--|
| Castel-Minier | <ul style="list-style-type: none"> • CM07-2044 • CM05-2-59 • CM05-2-54 • CM05-2-36 • i10013 | <ul style="list-style-type: none"> • CM05-2-34 | <ul style="list-style-type: none"> • CM06-2002 • CM05-2-31 |
| Montréal-de-Sos | <ul style="list-style-type: none"> • MdS8844 • MdS8858 • MdS29336 • MdS29522 • MdS29566 | <ul style="list-style-type: none"> • MdS8889 • MdS29409 • MdS29421 | <ul style="list-style-type: none"> • MdS9227 • MdS29342 • MdS29591 • MdS29431^a |
| Mirabat | <ul style="list-style-type: none"> • MIR7 | <ul style="list-style-type: none"> • MIR2 • MIR9 • MIR11 | <ul style="list-style-type: none"> • MIR1 • MIR3 • MIR6 • MIR8 • MIR10 • MIR12 |
| Sainte-Catherine | <ul style="list-style-type: none"> • SteCath n°4 | | <ul style="list-style-type: none"> • SteCath n°2 • SteCath n°5 |
| Capestang Collegiate church | <ul style="list-style-type: none"> • CAP1 • CAP3 | | |

^a The incompatibility of artefact MdS29431 was obtained from the first filter of the MnO** and P₂O₅** values.

4. Discussion

The following discussion is focused on archaeological and historical questions raised by the results of the present study. We will chiefly discuss here the supply of iron ores. We will separately consider the sites located in valleys supplied with ore from Rancié (Montréal-de-Sos, Castel-Minier) and the sites located in the Couserans (Mirabat, Sainte-Catherine).

At Montréal-de-Sos, three of twelve objects are of undetermined origin after the analysis: an architectural nail, a mule iron and a knife. Five out of the twelve studied objects are compatible with iron ores from Mont Rancié. Nevertheless, despite iron-production workshops using local ore being located very near the castle, four out of the twelve iron artefacts transpired to have a non-local origin. Excavation studies showed that Montréal-de-Sos became a central place in the supervision of activities related to metallurgy in the 14th century (Guillot, 2008) exactly as Castel-Minier in another valley. The Montréal-de-Sos castle is rather isolated but located not far from the major trade route to Andorra (Verna, 2001, 2005; Fig. 8). Textual sources mention the circulation along this route of objects of various origins. In particular, exchanges of precious knives from Parma are attested in the 15th century in the Vicdessos (Verna, 2001: p. 153). Therefore, we may assume that some of these products may end on the site. Our results, showing a variety of distinct origins for the ferrous artefacts found at the site, perfectly support this historical vision.

For the Castel-Minier castle, the results give a different overview. The objects found on the site were fabricated almost

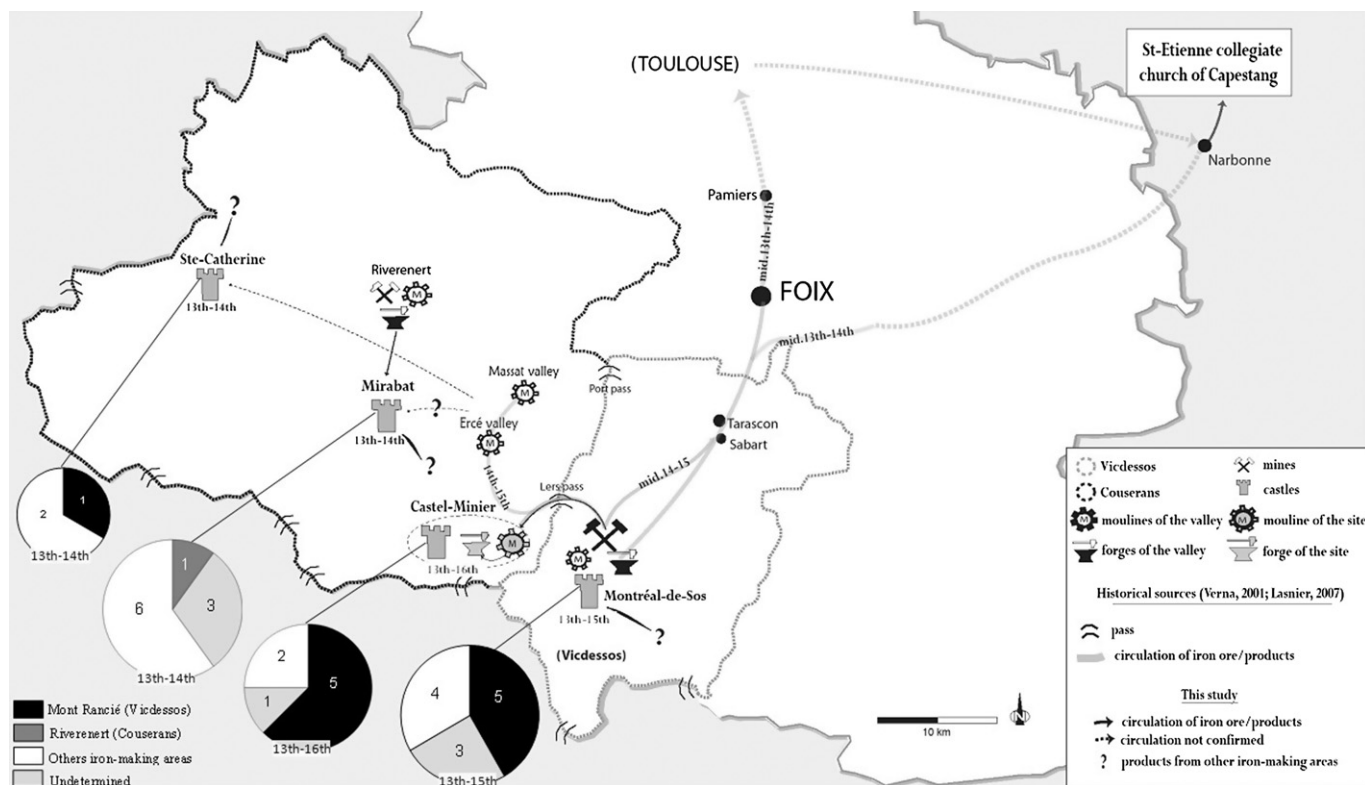


Fig. 8. Synthesis of the origin of objects uncovered on castles within Ariège and at the collegiate church of Capestang. Dates are specified for each trade route since different periods are considered. Circular diagrams: origin of the artefacts. The figures within the diagrams indicate the number of artefacts associated to each category of origin. Major circulation routes of the iron ore are derived from Verna (2001).

exclusively with the ore from the Mont Rancié mine, independently of the type of artefact (nail, ring, but also a chisel found in the silver mine of the site). Two out of eight objects are not made out of iron ore from the Mont Rancié, among which one could be a fragment of horseshoes and thus mobile artefact by definition. Historical studies revealed that, from the 14th century onward and in agreement with the exchange treaty concluded in 1347–1348, ore from the Mont Rancié supplied, through the Lers pass, the *moulins* of the Ercé and Massat valleys in the Couserans. Besides, the ore from the Videssos valley does not come freely in these valleys but is the result of a controlled distribution (Verna, 2001). Due to its location near the Lers pass (Fig. 8), the production of the *mouline* of Castel-Minier would be entirely dependent on this ore supply. In addition, the site occupied a particular position at the bottom of a valley in the Couserans region and is not close to a major circulation path where objects of different origin could be found. Our results clearly reflect this situation. Due to the extreme isolation of the site, the presence of external supplies seems to be much rarer at Castel-Minier than at Montréal-de-Sos.

Focusing on more distant sites from the Videssos, in the Couserans, the Mirabat castle in particular, leads to a different picture. Admittedly, the set of samples consists only of nails and consequently might be relatively biased as these objects can be fabricated in abundance everywhere. An important issue to stress is that only one nail presumably comes from the Ariège area (MIR7). In addition, our hierarchical clustering analysis shows that this artefact would have been made from ore extracted from the local deposits at Riverenert, and not from ore from Mont Rancié. This is consistent with the distance between the two sites of Riverenert and Mirabat being only 15 km. There is a clear lack of historical data about the circulation of iron in the region. Extrapolating our results, most iron found in this part of the Couserans would originate from other

regions than Mont Rancié which would bring interesting new insight by supporting the hypothesis that the strength of the exchange treaty that obliged *moulins* in the Mont Rancié area of influence to use its ore – seems to have the side effect to exclude the use of this ore in the Couserans.

A last aim of our work was to study the circulation of iron from the Videssos beyond the production area, in the context of regional exchanges. The presence of iron made with ores from the Videssos in the construction of a prestigious building, such as the collegiate church of Capestang was highlighted. This result would confirm that Narbonne received iron produced in the Videssos as demonstrated for other products, such as textiles and pastel (Verna, 2001). Our analysis shows that a part of iron from the Videssos was used in the area dominated by Narbonne which opens the way to finer historical and material studies on the socio-political and socioeconomic issues controlling iron supply for the building of medieval monuments.

5. Conclusion

The present study reveals the potential of a methodology based on the combination of trace elemental and multivariate analyses to examine the provenance of iron artefacts. In addition to previous works on the study of ore geographical origin, the presented methodology renders possible the validation of a given provenance. A limitation is that this methodology requires the collection and the treatment of a large quantity of data.

Here, as a first stage, to compare the elemental signatures of a given ore extraction area with the ones of objects of unidentified origin, a filter of absolute contents of Mn and P oxides was used. It allows the exclusion of artefacts smelted from an ore that does not have a signature characterised by these major elements. In a second

stage, the determination of an object origin is based on a provenance compatibility diagram established using linear discriminant analysis projections coupled with an empirical calibration. The threshold values used in the area inclusion/exclusion process are experimentally determined from our data. These values change as a function of the set of artefacts of known origin used in the calibration process, be it from the area of interest or out of it. Due to the relatively small set of artefacts in the calibration, a large confidence interval had to be used leading to a large undetermined sector in the compatibility abacus described. Increasing the base on which these thresholds are determined should lead to better discrimination. For that purpose, new analytical data must be gathered on objects of known ore origin, coming from the area studied and from elsewhere.

This method was used on samples uncovered in different archaeological sites within the Ariège area but also outside this region, in the vicinity of Narbonne. Some characteristics of the Ariègean iron market sensed by the historical sources were thus detailed. First, the complexity of the iron market in the Vicdessos valley, from an economical point of view, was pointed out thanks to the analysis of objects excavated from a castle located near the Mont Rancié mine (Montréal-de-Sos castle). The observed diversity of origins is related to the site location that is close to the trade routes. In the Couserans area, the political control over the supply of the ore from the Mont Rancié in the Ercé and Massat valleys during the 14th–15th centuries has been highlighted through our approaches (Castel-Minier castle). Our results have demonstrated that the majority of iron from West of the Couserans was smelted from ore of other iron-making areas. Their origin remains unidentified for the time being. By revealing a consistency with the available historical and archaeological data, the results consolidate the validity of the methodology. Finally, by applying this new approach our results enriched the description of the Ariègean iron market. This work underlines that iron from the Vicdessos is present among the building materials of the St-Etienne collegiate church of Capestang, in the neighbourhood of Narbonne. The exportation of iron from Foix towards the East is therefore confirmed.

This new methodology will permit to better understand the iron market in the Couserans for which textual sources have not survived. To this aim, one must also consider other production areas identified by history and archaeology as potential iron suppliers in the Ariège area (Catalonia, Minervois, Comminges, Roussillon). To understand the diffusion of the iron from the Vicdessos, the study of iron from constructions built outside of the production area of Ariège and in different regions, is also crucial.

The authors would finally like to emphasise that all provenance studies must be supported by well-developed historical and archaeological contexts, and an in-depth preliminary metallurgical study of the objects and samples.

Acknowledgements

The authors are extremely grateful to the following people for providing ores, slag samples and iron artefacts: Philippe Bernardi, Monique Bourin, Olivier Codina, Marie-Pierre Coustures, Claude Dubois, Florence Guillot, Thibaut Lasnier, Cécile Mahé Le-Carlier, Alain Ploquin, and Philippe Rouch. Moreover, we thank Clarisse Mariet and Jean-Louis Joron for their contribution to the trace element analyses. This research was funded by grants from the Centre National de la Recherche Scientifique and the Synchrotron SOLEIL. We thank the French Agence Nationale de la Recherche project (ACEUR project) for financial support. The IPANEMA platform is jointly developed by CNRS, MNHN, the French Ministry of

Culture and Communication and SOLEIL, and benefits from a CPER grant (MESR, Région Île-de-France).

Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jas.2011.11.025.

References

- Belhoste, J.-F., 2001. Mutations techniques et filières marchandes dans la sidérurgie alpine entre XIIIe et XVe siècle. In: Braunstein, Ph (Ed.), *La sidérurgie alpine en Italie (XIIe–XVIIe siècles)*. Ecole Française de Rome, Rome, pp. 515–592.
- Blakelock, E., Martinon-Torres, M., Veldhuijzen, H., Young, T., 2009. Slag inclusions in iron objects and the quest for provenance: an experiment and a case study. *Journal of Archaeological Science* 36, 1745–1757.
- Buchwald, V.F., Wivel, H., 1998. Slag analysis as a method for the characterization and provenancing of ancient iron objects. *Materials Characterization* 40, 73–96.
- Chevalier, M., 1956. *La vie humaine dans les Pyrénées ariégeoises*. Genin, Paris.
- Coustures, M.-P., Béziat, D., Tollon, F., 2003. 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* 45 (4), 599–613.
- Coustures, M.-P., Rico, C., Béziat, D., Djaoui, D., Long, L., Domergue, C., Tollon, F., 2006. La provenance des barres de fer romaines des Saintes-Maries-de-la-Mer (Bouches-du-Rhône). *Etude archéologique et archéométrique*. Gallia 63, 243–261.
- Crew, P., 2000. The influence of clay and charcoal ash on bloomery slags. In: Tizzoni, C.C., Tizzoni, M. (Eds.), *Il Ferro Nelle Alpi*. Actes du colloque Iron in the Alps, Bienna, pp. 38–48.
- Degryse, P., Schneider, J., Kellens, N., Waelkens, M., Muchez, P., 2007. Tracing the resources of iron working at ancient Sagalassos (south-west Turkey): a combined lead and strontium isotope study on iron artifacts and ores. *Archaeometry* 49 (1), 75–86.
- Desauty, A.-M., Mariet, C., Dillmann, P., Joron, J.L., Fluzin, P., 2008. The study of provenance of iron objects by ICP-MS multi-elemental analysis. *Spectrochimica Acta Part B* 63, 1253–1262.
- Desauty, A.M., Dillmann, P., L'Héritier, M., Mariet, C., Gratuze, B., Joron, J.L., Fluzin, P., 2009. Does it come from the Pays de Bray? Examination of an origin hypothesis for the ferrous reinforcements used in French medieval churches using major and trace element analyses. *Journal of Archaeological Science* 36 (10), 2445–2462.
- Desauty, A.-M., 2008. Apport des analyses chimiques multi technique à la compréhension du comportement des éléments traces dans les filières sidérurgiques anciennes. Application des études de provenance et à la distinction des procédés. Le cas du Pays de Bray normand. Unpublished Ph.D. Thesis, University Technologique de Belfort-Montbéliard.
- Devois, W., Senn-Luder, M., Moor, C., Salter, C., 2000. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for spatially resolved trace analysis of early-medieval archaeological iron finds. *Journal of Analytical Chemistry* 366, 873–880.
- Dillmann, P., L'Héritier, M., 2007. Slag inclusion analyses for studying ferrous alloys employed in French medieval buildings: supply of materials and diffusion of smelting processes. *Journal of Archaeological Science* 34 (11), 810–823.
- Dillmann, P., L'Héritier, M., 2009. Récupération et emploi du fer pour la construction des monuments de la période gothique. In: *Collection de l'Ecole Française de Rome. Il reimpiego in architettura: recupero, trasformazione, uso*. Ecole Française de Rome, Rome, pp. 157–175.
- Dubois, Cl, 1996. Métallurgie du fer en Ariège de l'Antiquité au XVIII^e siècle: le point sur les données archéologiques. In: Vulcain (Ed.), *Actes du Symposium Paléomé-tallurgie du fer et cultures*. Belfort, pp. 387–396.
- Dubois, Cl, 2000. Elements sur l'origine de la production du fer en Ariège: le site de Lercoul. In: d'Andorra, Governà (Ed.), *6è curs d'arqueologia d'Andorra 2000, L'obtenció del ferro pel procediment directe entre els segles IV i XIX*. Andorra, pp. 176–188.
- Florsch, N., Llubes, M., Téreygeol, F., Ghorbani, A., Roblet, P., . Quantification of slag heap volumes and masses through the use of induced polarization: application to the Castel-Minier site. *Journal of Archaeological Science* 38 (2), 438–451.
- Gale, N.H., Bachmann, G., Rothenberg, B., Stos-Gale, Z.A., Tylecote, R.F., 1990. The adventitious production of iron in the smelting of copper. In: Rothenberg, B. (Ed.), *The Ancient Metallurgy of Copper: Archaeology, Experiment, Theory*, pp. 182–191.
- Gratuze, B., Blet-Lemarquand, M., Barrandon, J.-N., 2001. Mass spectrometry with laser sampling: a new tool to characterize archaeological materials. *Journal of Radioanalytical and Nuclear Chemistry* 247 (3), 645–656.
- Gratuze, B., 1999. Obsidian characterization by Laser Ablation ICP-MS and its application to prehistoric trade in the Mediterranean and the Near East: sources and distribution of obsidian within the Aegean and Anatolia. *Journal of Archaeological Science* 26, 869–881.
- Grimbert, L., 2006. Savignac-les-Ormeaux, un atelier sidérurgique moderne (XVIe–XVIIIe s.). *Documents Finaux de Synthèse*. Institut National de Recherches Archéologiques Préventives.

- Guillot, F., 2008. Rapport final de fouilles programmées triennales, Montréal-de-Sos-Ariège. Mairie d'Auzat, Ariège.
- Hedges, R.E.M., Salter, C.J., 1979. Source determination of iron currency bars through the analysis of slag inclusions. *Archaeometry* 21, 161–175.
- Jarrier, C., 1993. Minéralogie, pétrologie, et géochimie des résidus sidérurgiques galloromains (Ariège et Montagne Noire); comparaison avec les résultats des essais in situ de réduction directe du fer. Unpublished Thesis, University Paul-Sabatier, Toulouse III.
- Joron, J.L., Treuil, M., Raimbault, L., 1997. Activation analysis as a geochemical tool: statement of its capabilities for geochemical trace element studies. *Journal of Radioanalytical and Nuclear Chemistry* 216 (2), 229–235.
- Lasnier, T., 2007. Les fortifications médiévales en Haut Couserans. Prospection thématique. Rapport 2007.
- Leroy, S., Colliou, C., in press. Approche archéométrique de l'expérimentation: étude du comportement des éléments chimiques du minerai à l'objet ferreux pour les problématiques de provenance. Actes de la table-ronde Archéologie expérimentale à Melle, Saclay, 10–11 Dec. 2009.
- Leroy, M., 1997. La sidérurgie ancienne en Lorraine et les conditions de l'utilisation du minerai oolithique lorrain en réduction directe. L'exemple de l'atelier de Frouard (Ve – VIe s.). In: Belles Lettres, Les (Ed.), La sidérurgie ancienne de l'Est de la France dans son contexte européen: archéologie et archéométrie. Actes du colloque international de paléométaballurgie de Besançon, pp. 41–56. Besançon.
- Leroy, S., 2010. Circulation au Moyen Âge des matériaux ferreux issus des Pyrénées ariégeoises et de la Lombardie. Apport du couplage des analyses en éléments traces et multivariées. Unpublished Ph.D. Thesis, University Technologique de Belfort-Montbéliard.
- Mariet, C., Belhadj, O., Leroy, S., Carrot, F., Métrich, N., 2008. Relevance of NH₄F in acid digestion before ICP-MS analysis. *Talanta* 77, 445–450.
- Pagès, G., Dillmann, P., Fluzin, P., Long, L., 2011. A study of the Roman half-products of Saintes-Maries-de-la-Mer (Bouches-du-Rhône, France). A proposal for a comprehensive metallographic approach. *Journal of Archaeological Science* 38 (6), 1234–1252.
- Ploquin, A., 1994. Palsid: un prototype de base de données paléosidérurgiques. In: Les Belles Lettres (Ed.), La sidérurgie ancienne de l'Est de la France dans son contexte européen: archéologie et archéométrie. Actes du colloque international de paléométaballurgie de Besançon, pp. 83–84. Besançon.
- Ploquin, A., 2000. Une introduction à la pétrographie des scories paléosidérurgiques. In: d'Andorra, Governa (Ed.), 6è curs d'arqueologia d'Andorra 2000, L'obtenció del ferro pel procediment directe entre els segles IV i XIX, pp. 289–334. Andorra.
- Rouch, P., 2006. Rapport de sondage et de dégagement de bâti, Sainte-Catherine 2006.
- Schwab, R., Heger, D., Hoppner, B., Pernicka, E., 2006. The provenance of iron artefacts from Manching: a multi-technique approach. *Archaeometry* 48 (3), 433–452.
- Sclafert, Th., 1926. L'industrie du fer dans la région d'Allevard au Moyen Âge. In: Bourdeau, P., Duillard, S., Fourny, M.-C. (Eds.), *Revue de Géographie Alpine* n° 14, pp. 239–355. Grenoble.
- Serneels, V., 2002. Analyse chimique des matières premières et des produits de l'opération de réduction dans le four basque d'agorregi. In: Urteaga, M. (Ed.), La ferreria y los molinos de Agorregi-Aia, Gipuzkoa. II – Arqueologia experimental. Diputacion Foral de Gipuzkoa – European community, San Sebastian, pp. 93–121.
- Téreygeol, F., 2009. Le Castel-Minier (Aulus-les-Bains). Rapport intermédiaire. Service Régional de l'Archéologie, Midi-Pyrénées.
- Tollon, Fr., 1964. Etude minéralogique de la région de Vicdessos (Ariège). Unpublished Ph.D. Thesis, University Sciences de Toulouse.
- Truffaut, E., 1994. Contribution du manganèse au développement historique de la sidérurgie. In: La Revue de Métallurgie-CIT, Aspects Techniques (Ed.), La Revue de Métallurgie, pp. 1703–1719.
- Verna, C., Benoit, P., 1991. La sidérurgie de Clairvaux au Moyen Âge (XIIe-XVe siècles). In: Némont (Ed.), Les Actes du Colloque Histoire de Clairvaux. Bar-sur-Aube, pp. 90–92.
- Verna, C., 2000. De la forge au marché des fers: les espaces emboîtés de la réduction directe. In: d'Andorra, Governa (Ed.), 6è curs d'arqueologia d'Andorra 2000, L'obtenció del ferro pel procediment directe entre els segles IV i XIX, pp. 63–78. Andorra.
- Verna, C., 2001. Le temps des Moulines. Fer, technique et société dans les Pyrénées centrales (XIIIe - XVIe siècles). Publications de la Sorbonne, Paris.
- Verna, C., 2005. Pyrénées morcelées, traversées, contournées: la forge et la circulation des pondéreux, dans Circulation des marchandises et réseaux commerciaux dans les Pyrénées (XIII^e-XIX^e siècle). In: Minovez, J.M., Poujade, P. (Eds.), Colloque international d'Andorre, octobre 2003, pp. 608–623. Toulouse.
- Verna, C., 2008. Moulin à fer, L'Héritage de Bertrand Gille. In: Durand, A. (Ed.), Jeux d'eau. Moulins, meuniers et machines hydrauliques, XIe-XXe siècle, Etudes offertes à Georges Comet, pp. 273–286. Aix-en-Provence.