

PROVENANCING BOG IRON: SOME METHODOLOGICAL CONSIDERATIONS.

100 μm

Title Background Image: Secondary electron image of 5 ablation spot analyses on slag (ø80μm)



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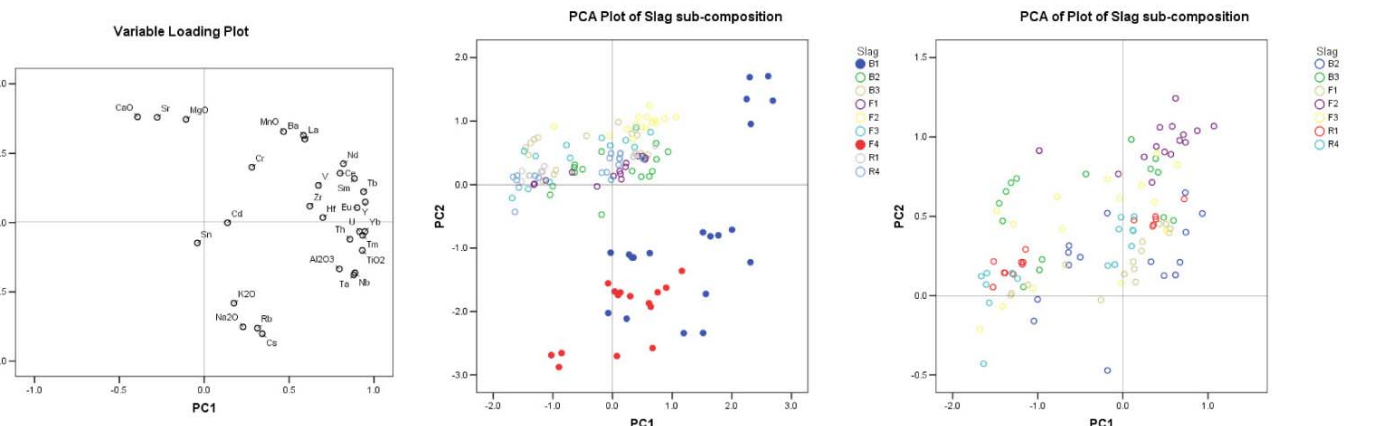
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Background and objectives

Provenance studies are a common in archaeological practice – understanding **where things come from**. Significant developments have been made in recent years in **provenancing iron**. For iron made via the traditional method of smelting (direct process), it is possible to relate an object to a production source. This relies on the study of slag (production by-product) trapped *within* the iron metal. **Entrapped slag inclusions (SI)** share the same chemical composition as smelting slags, a by-product of iron production. By comparing the composition of **production slags** to SI in iron objects, it is possible to establish/eliminate a relationship of provenance (see Figure 1 for a schematic reconstruction of the iron smelting system and behaviour of trace elements¹).

However, some **implicit assumptions** have been made in the course of developing the SI analytical method for provenancing iron. More specifically, the issue of **compositional 'variability'**. The model relies on material homogeneity. So far, it has not been demonstrated that the materials being studied (ore, slag, slag inclusions) are homogenous. Although heterogeneity has not yet been proven, such an observation would pose challenges for provenancing iron using SI analysis. To address this fundamental issue of **chemical homogeneity**, several hypotheses were formulated and tested:

1. Is there significant variability in composition within a geological **bog ore body**?
2. Is there significant variability in composition within **slag produced from a single smelt**?
3. Is there significant variability in composition **between SI** from the same iron bloom?



(Above) Figure 3: PCA loading plot of elements being studied (Variance PC1: 45.6%; PC2: 20.8%; PC3: 8.3% (75.7% cumulative)).

Data treatment

$$\text{ratio} = \frac{\text{component}}{\text{total sub set of components}}$$

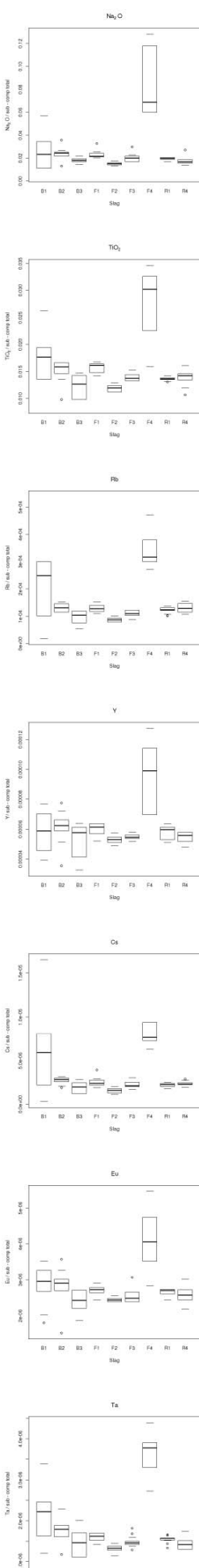
Compositional data is composed of an independent variable (i.e. sample) with multiple dependant variables (chemical composition). It is often standardised and described as being constrained or '**closed**' (i.e. adding up to 100%). Multivariate statistical methods such as principal components analysis (PCA) and hierarchical cluster analysis (CLA) should not, in theory, be performed on closed data sets. It is necessary to '**open**' the data-set in order to subject it to such multivariate methods. This is possible by transforming the data into an unstandardised form: **logged ratios**. The principle of **sub-compositional coherence** (the ratio between any two components remains constant), as expressed in logratio data, permits the full **true variability** to be expressed. A standard statistical package was used in conjunction with the 'R' package² 'compositions'³ in order to transform and manipulate the compositional data. A combination of multivariate statistics were deemed preferable than any single method.

Case study 2 described: variability in slag composition within a single smelt

A sub-composition was transformed into logratio values from a data-set consisting of 33 analysed elements, omitting the dominant major oxides exhibiting significant variance (FeO, SiO₂). A one-way multivariate analysis of variance (MANOVA) revealed a **significant multivariate main effect** for slag (Pillai's Trace = 5.328, $F = 7.2$, $p < .001$). This was confirmed by a series of one-way ANOVA's for most elements. The variance is expressed in a representative selection of boxplots presented (Figure 2).

When the sub-composition logratios are plotted against the first two principle components, B1 and F4 clearly form **discrete groups** (Figure 3). When these two samples are removed from the list of independent variables and the logratios re-plotted, with the exception of F2, **no real further grouping can be discerned**. A CLA (Ward's method) confirms this. The overlapping error bars expressed in the boxplots that persist for most of the remaining slag samples reveal little difference in variation for most elements. The trace elements, by large, show a positive correlation on the PCA as confirmed in the values obtained from the correlation matrix (≥ 0.7). Some cases show are correlated with the major and minor oxides MgO and CaO, variables whose removal from multivariate analyses is worth considering to minimise the dilution effect (like FeO and SiO₂).

Two slag samples (B1 and F4) are deemed responsible for having significant effects on the dependent variables. It is interesting to observe that **B1** represents the slag associated with the crown metal (top of the bloom) removed hot at the end of the smelt near the hot zone, and **F4** represents magnetic material consisting of partly reduced ore with slagged metal.



(Above) Figure 2: A selection of boxplots based on sub-compositional logratios highlighting the difference in variances observed in B1 and F4.

(Below) Table 1: A summary of the methods and analytical protocols adopted in this study.

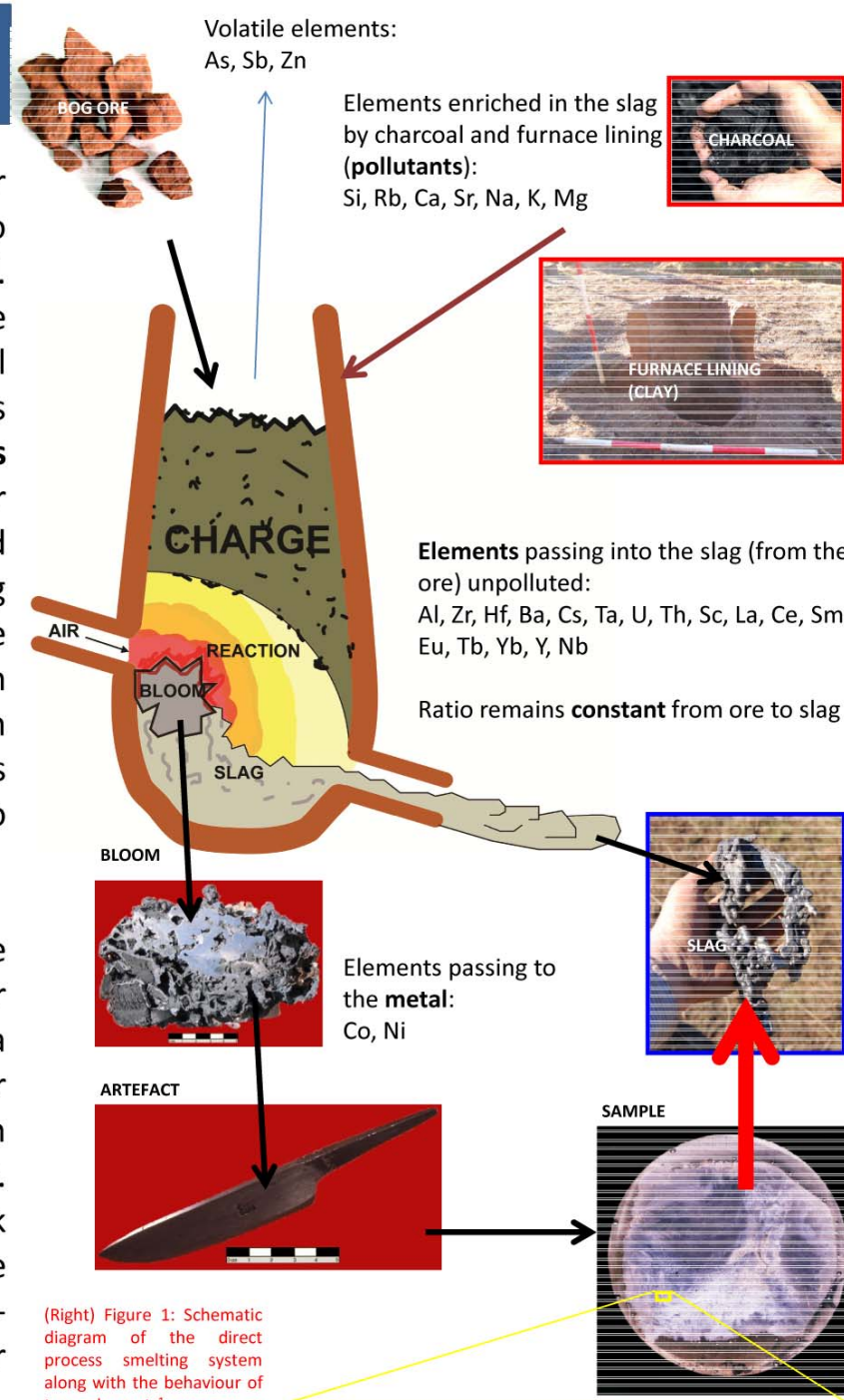
Method:	SEM-EDS	LA-ICP-MS	PGAA
Instrument:	ISIS ABT-55 SEM coupled to an Oxford Link Analytical AN10/55S EDS system	New Wave UP 213 UV Laser Ablation System coupled to an Agilent 7500c ICP-MS	PGAA facility, Budapest Research Reactor
Acquisition time	100s	RF Power 1300 W	Thermal equivalent flux at target $\approx 1 \times 10^{20} \text{cm}^{-2} \text{s}^{-1}$
Voltage	15kV	Ar carrier gas flow 1.5 L/min ⁻¹	Beam cross-section variable $\leq 2 \times 2 \text{cm}^2$
Deadtime	$\approx 40\%$	Mode laser spot	1.5m (from guide end)
Replicates	5 (≤ 5 for SI)	Readings 40 /spot	30m (from core)
Readings	40 /spot	Laser wavelength 213 nm	Detector system Compton-suppressed HPGe, with BGO shield
Laser energy output	50% 100% ($\approx 1.4 \text{mJ}$)	Pre-cleaning	Analysed Multichannel analyser
Laser spot (ϕ)	80 μm 80 μm	Analysis	Acquisition (counts) 5×10^6
Repetition rate	10 Hz 10 Hz	Laser energy output	Reactor Tank-type
Time	1s 40s	Time	Power 10 MW
Quantification	²⁹ Si internal standard	Quantification	Fuel Low-enrichment fuels
Standard Reference Materials:	Corning Museum Glasses USNM No's: 117218.001, 117218.002, 117218.003		Moderator & coolant H ₂ O
Certified Reference Materials:	National Institute of Standards and Technology (NIST) glass: 612		Flux $2 \times 10^{14} \text{cm}^{-2} \text{s}^{-1}$
	United States Geological Survey (USGS) basaltic glasses: BCR-1G, BHVO-2G, BCR-2G		

Methodology and analytical protocol

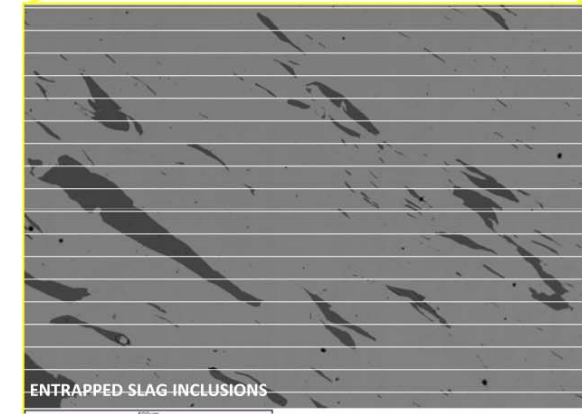
Samples representative of singular material entities were required to address the questions outlined. For ore, **six bog ore** samples were collected from the same geological deposit ($\phi \leq 100 \text{m}$). Nine samples representative of **production slags** of a single smelt were selected for analysis (pertaining to three broad categories: B1, B2, B3 = bloom slag debris; F1, F2, F3, F4 = furnace slags; R1, R4 = raked slags). In order to assess variability between SI, a **single raw iron bloom** was cross-sectioned and divided into nine sub-samples for SI analysis.

SEM-EDS and PGAA were employed to determine major oxide concentrations, and a selection of trace elements. Minor and trace element composition was determined by LA-ICP-MS. PGAA⁴ is a non-destructive bulk analytical method, based on the detection of characteristic prompt-gamma photons, emitted after radiative neutron capture.

Depending on the size of SI, between 1 and 5 ablation spots were obtained. 15 ablation spots were performed on each slag. Signals were processed into quantified amounts using the silicon internal standard method. This quantification method produced data with lower standard deviations compared to data quantified using calibration curves.



(Right) Figure 1: Schematic diagram of the direct process smelting system along with the behaviour of trace elements¹.



Acknowledgements

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References

1. Desautly, A.-M., Dillmann, P., L'Heritier, 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.
2. R Development Core Team (2011). *R: A Language and Environment for Statistical Computing*. (<https://www.R-project.org/>)
3. van den Boogaart, K. G., Tolosana, R., Bren, M. (2011). *Compositional Data Analysis*. (<https://www.stat.boogaart.de/compositions/>)
4. Révay, Z. (2009). 'Determining Elemental Composition Using Prompt γ Activation Analysis', *Anal. Chem.* 81, 6851-6859.



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