Rem: Revista Escola de Minas
ISSN: 0370-4467
editor@rem.com.br
Universidade Federal de Ouro Preto
Brasil

Rocha Maia, Rafael; Susaki Dias, Marcelli; de Farias Azevedo, Cesar Roberto; Gomes Landgraf, Fernando José

Archaeometry of ferrous artefacts from Luso-Brazilian archaeological sites near Ipanema River, Brazil

Rem: Revista Escola de Minas, vol. 68, núm. 2, abril-junio, 2015, pp. 187-193
Universidade Federal de Ouro Preto
Ouro Preto, Brasil

Archaeometry of ferrous artefacts from Luso-Brazilian archaeological sites near Ipanema River, Brazil

Arqueometria de peças de ferro de sítios arqueológicos luso-brasileiros localizados próximos do Rio Ipanema, Brasil

http://dx.doi.org/10.1590/0370-44672015680151

Rafael Rocha Maia
Doutorando e técnico do Laboratório de Caracterização Microestrutural Hubertus Colpaert
Escola Politécnica da Universidade de São Paulo
Dep. de Engenharia Metalúrgica e de Materiais
São Paulo - São Paulo – Brazil
rafael.maia@usp.br

Marcelli Susaki Dias
Estudante de Graduação
Escola Politécnica da Universidade de São Paulo
Dep. de Engenharia Metalúrgica e de Materiais
São Paulo - São Paulo – Brazil
marcelli.susaki@gmail.com

Cesar Roberto de Farias Azevedo
Professor Doutor
Escola Politécnica da Universidade de São Paulo
Dep. de Engenharia Metalúrgica e de Materiais
São Paulo - São Paulo – Brazil
c.azevedo@usp.br

Fernando José Gomes Landgraf
Professor Associado
Escola Politécnica da Universidade de São Paulo
Dep. de Engenharia Metalúrgica e de Materiais e Presidente do Instituto de Pesquisas Tecnológicas do Estado de São Paulo S.A.
São Paulo - São Paulo – Brazil
f.landgraf@usp.br

Abstract

The present investigation analysed iron artefacts collected in two sites around Araçoaiaba Hill. A known methodology was adapted to investigate several samples collected at the Royal Iron Factory of São João do Ipanema and Sardinha sites. EDX microanalysis results of non-metallic inclusions were plotted in bivariate graphs. Linear regression (with and without the zero-intercept constraint) and line intercept significance tests were applied to interpret these results. The analysis did not allow the identification of the provenance of the production systems of Sardinha and Ipanema sites. The presence of Ti-rich inclusions was an unambiguous attribute of the samples collected at the Sardinha site.

Keywords: archaeometry, inclusion, linear regression, intercept significance test.

Resumo

A presente investigação analisou artefatos de ferro coletados em dois sítios arqueológicos na Montanha de Araçoaiaba. Uma metodologia conhecida foi adaptada para investigar várias amostras coletadas na Real Fábrica de Ferro de São João do Ipanema e no sítio de Sardinha. Resultados de microanálise EDX de inclusões não metálicas foram inseridos em gráficos bivariantes. Regressão linear (com e sem a restrição de intersecção pela origem) e testes de significância do intercepto da reta foram usados para interpretar esses resultados. Essa análise não permitiu identificar a assinatura dos sistemas produtivos de Sardinha e Ipanema. A presença de inclusões ricas em Ti foi uma característica típica dos artefatos coletados no sítio de Sardinha.

Palavras-chave: *arqueometria, inclusões, regressão linear, teste significância do intercepto.*

1. Introduction

In the late 16th century, Afonso Sardinha discovered magnetitic iron ore in Araçoiaba Hill, located one hundred kilometres from São Paulo city. The existence of water and iron ore in this site enabled him to establish a bloomery there (Lemes 1954; Rodrigues 1966). The ruins of this enterprise were discovered in 1977 by Salazar and the layout of the stone buildings suggested that the area contained a metal smith shop and a bloomery- a furnace for direct reduction of iron (Salazar 1982; Zequini 2006). In the 1980s, Prof. Margarida Andreatta excavated this site and the results of the thermoluminescence dating of a few European style pottery fragments found there indicated they were 520 ± 75 years old (Zequini 2006). In 1807, when Napoleon´s army invaded Portugal, the Portuguese court was forced to flee to Brazil and Rio de Janeiro became the capital of the Portuguese empire. In 1809, the Portuguese king, João VI, launched three large projects to construct ironmaking facilities, two in the State of Minas Gerais and one in the State of São Paulo. The latter, located near the same iron ore occurrence of Araçoiaba Hill, gave rise to a public-private enterprise named as "Royal Iron Factory of São João do Ipanema", which built twin blast furnaces in Brazil similar to the ones being operated at that time in Portugal (Rogers 1962; Campos and Solórzano 2004; Zequini 2006; Medeiros 2009; Landgraf *et al*. 1995). The technical difficulties during the operation of the blast furnace and finery of the Royal Iron Factory of Ipanema created a situation where both direct and indirect iron reduction processes coexisted in the same factory for the production of iron artefacts (Araújo *et al.* 2010). The slag inclusions from the ferrous artefacts produced by the direct process featured higher P_2O_5 and FeO contents when compared to the slag inclusions from artefacts produced by the direct process. Additionally, the slag inclusions from the ferrous artefacts manufactured by the direct process featured higher contents of Al_2O_3, MgO and K_2O (Dillmann and L'Heritier 2007). The analysis of microstructure and chemical composition of slag inclusions of iron artefacts has been used in an attempt to identify their manufacturing process, such as direct or indirect reduction, and the "signature" of their production system (Rostoker and Dvorak 1990; Gordon 1997; Buchwald and Wivel 1998; Starley 1999; Dillmann and L'Héritier 2007; Desaulty *et al*. 2008; Blakelock *et al*. 2009; Maia 2014). For instance, Dillmann and L'Héritier (Dillmann and L'Héritier 2007) studied the microanalysis of numerous non metallic inclusions of ferrous artefacts. They plotted bivariate graphs (SiO_2 content versus Al_2O_3 content; CaO content versus K_2O content; MgO content versus Al_2O_3 content) and applied a constrained linear regression model (line going through zero), deleting ''abnormal data'' from these bivariate graphs in iterative steps until the coefficient of determination (R^2) became higher than 0.7. The provenance of various iron artefacts was identified by comparing the resulting constant ratios of these bivariate graphs. According to authors (Dillmann and L'Heritier 2007; Disser *et al*. 2014), data refining procedure was aimed to remove the abnormal slag compositions from the bulk analysis, which may occur due to use of additives during forging, and the chemical compositions of small inclusions, which might be biased by a local concentration effect. Blakelock *et al*. (Blakelock *et al*. 2009) reproduced experiments of direct reduction and refinement of iron to explore the relationship between the chemical composition of the slag inclusions and the chemical compositions of iron ore, furnace lining, fluxes and reducing agents. They tested the proposed constrained linear regression model (Dillmann and L'Héritier 2007) to analyse non metallic inclusions in iron objects produced under experimental conditions. Even under controlled experimental conditions, they explained they would have to apply the data cleaning process to up to 50% of the non metallic inclusions to obtain an acceptable value for the coefficient of determination ($R^2 > 0.7$). They pointed out that this practice could distort their results and observed patterns. Sophisticated multivariate statistical methods have been applied since 2009 to analyse the microanalysis results and investigate the production provenance of iron artefacts (Blakelock *et al*. 2009, Charlton *et al*. 2012, Disser *et al*. 2014). The present investigation will explore a methodology based on previous investigation (Dillmann and L'Héritier 2007) to compare the constraint linear regression model (CLRM) and unconstraint linear regression model (ULRM) during the investigation of the provenance of several samples collected at the Royal Iron Factory of São João do Ipanema and Sardinha sites.

2. Materials and methods

Six ferrous artefacts (one bar, three nails, one hinge and one plate) from Andreatta's collection (Zequini 2006) were selected for characterization. Three of the iron artefacts (identified as I82, I84 and I99) were collected at the Ipanema site and the remaining three (identified as S106, S107 and S111) at the Sardinha site. Metallographic samples were prepared and characterized by conventional microscopy, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy microanalysis (Saphire Si(Li) – SUTW EDAX EDX detector) on at least 30 inclusions for each ferrous artefact, using 15 kV, area mode and acquisition time of at least 60 s. Microanalyses on the non-metallic inclusions with length and width larger than 5 μm were performed in area mode, covering areas larger than 25 um^2, imposing as a constraint that all the elements in the non metallic inclusions were in the form of stoichiometric oxide (see average results in Table 1). All the artefacts presented a predominant ferritic microstructure with inclusions occupying area fraction from 4 to 13%. The results of non metallic inclusion microanalysis were used to plot bivariate graphs, such as FeO versus SiO_2 content, SiO_2 content versus Al_2O_3 content; CaO content versus K_2O content; MgO content versus Al_2O_3 content; and P_2O_5 content versus the [(Al_2O3 + MgO + K_2O)/ FeO]) ratio, as proposed by Dillmann and L'Heritier (Dillmann and L'Heritier, 2007) for the partial discrimination of direct and indirect reduction products. Two linear regression models (CLRM and ULRM) were applied without any data-cleansing (due to the larger size of inclusions used in the present investigation) to investigate the strength of the correlation for various bivariate graphs. Additionally, the calculation of the surface weighing the average composition for each object (giving more weight to large inclusions and less to smaller ones) was not performed in the present investigation, as suggested elsewhere (Dillmann and L'Heritier 2007). In the first scenario, the linear regressions (CLRM) were forced to pass through the origin (b=0), while in the second scenario they were performed without any constraint. Student t-test and Student's t-cumulative distribution function were used to evaluate the significance of the intercept of the line equation in the cases when $b \neq 0$. The |t| value of the Student t-test and the Student's t-cumulative distribution function were calculated via Origin Lab 8.5 software and analysed in accordance with Manson et al. (Manson *et al*. 2003). If $|t| > 2$ and $p < 0.05$ (95% confidence interval) the intercept of the linear regression was significant. Finally, the values for the coefficient of determination (R^2) for the linear regression for both linear regression models (CLRM and ULRM) were compared to explore the origin of the iron artefacts.

3. Results

The microstructure of the Sardinha site inclusions differ significantly as they all presented a phase non present in the Ipanema artefacts inclusions, a Ti-rich phase. The average microanalyses results of the non metallic inclusions of each iron artefact are given in Table 1 and they indicated that the main difference between the non metallic inclusions of both sites is the TiO_2 content, which is much higher in the samples collected at the Sardinha site. Additionally, samples I99 and S107 showed comparatively lower average values for the FeO content and a more detailed analysis of these results will be shown in Figures 2 and 3.

Table1
Average EDX microanalysis of slag inclusions (% weight) of the samples collected at the Royal Iron Factory of São João do Ipanema (I) and Sardinha sites (S).

Samples	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	MnO	FeO
I82	0.9 ± 0.6	2.1 ± 0.5	14.6 ± 4.7	2.1 ± 2.3	0.5 ± 0.1	1.5 ± 0.5	0.4 ± 0.1	0.3 ± 0.2	1.6 ± 0.8	75.7 ± 5.6
I84	1.3 ± 0.6	1.6 ± 0.5	10.1 ± 4.0	4.9 ± 3.7	0.3 ± 0.2	1.5 ± 1.1	0.4 ± 0.3	0.5 ± 0.4	2.3 ± 1.6	76.6 ± 9.5
I99	1.8 ± 0.4	2.6 ± 0.8	28.7 ± 9.5	3.2 ± 1.5	2.5 ± 1.3	9.5 ± 4.1	0.4 ± 0.2	0.5 ± 0.2	0.7 ± 0.2	49.7 ± 7.2
S106	1.1 ± 0.2	1.9 ± 0.5	13.8 ± 4.6	1.0 ± 0.4	1.1 ± 1.1	2.5 ± 0.9	5.7 ± 1.6	-	0.8 ± 0.2	72.1 ± 7.2
S107	3.6 ± 1.6	2.2 ± 0.8	33.1 ± 14.5	3.7 ± 0.4	2.3 ± 1.2	12.9 ± 6.9	1.6 ± 0.8	1.6 ± 1.1	1.9 ± 0.7	36.6 ± 23.1
S111	1.1 ± 0.3	1.8 ± 0.6	11.8 ± 6.7	1.0 ± 0.7	0.9 ± 0.9	2.3 ± 1.9	6.9 ± 3.5	1.5 ± 0.7	0.8 ± 0.2	71.6 ± 10.7

The microstructural characterization of non metallic inclusions is shown in **Figures 1-a** and **1-b**. **Figure 1-a** shows a typical multiphase non metallic inclusion found in the artefacts found in the Royal Iron Factory of São João do Ipanema, showing dendrites of wustite (FeO) in a SiO_2-rich matrix. Figure 1-b shows two types of inclusions, both richer in Ti: dendrites of wustite (FeO) and polygonal ilmenite ($FeTiO_3$) in a SiO_2-rich matrix (centre); and dendrites of wustite (FeO), polygonal ilmenite ($FeTiO_3$) and fayalite ($2FeO.SiO_2$) in a SiO_2-rich matrix. Bivariate graphs showing the various relationships between the main constituents of the non metallic inclusions found in each one of the ferrous artefacts are shown in **Figures 2-a** to **2-d** (FeO versus %SiO_2; %SiO_2 versus %Al_2O_3; %Al_2O_3 versus %MgO; and %CaO versus %K_2O). **Figure 2-a** illustrates the inverse relationship between FeO and SiO_2 in the slag inclusions, while **Figures 2-b** to **2-d** show an apparent direct relationship between the contents of SiO_2 and Al_2O_3, CaO and K_2O, Al_2O_3 and MgO, respectively. A subsequent qualitative analysis by visual assessment of **Figures 2-b to 2-d** could not separate distinct clusters representing the Ipanema and Sardinha sites, but this same evaluation suggested that I99 sample was different from the other artefacts from Ipanema site and that S107 sample was also similarly different from the other artefacts from Sardinha site.

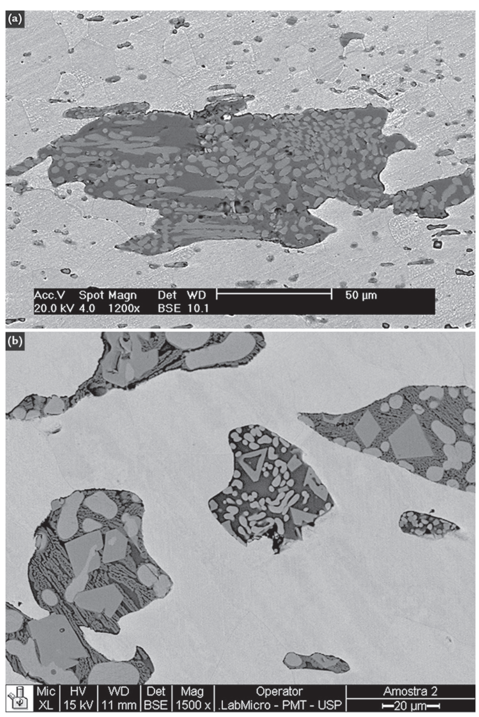

Figure 1
a) Detail of a slag inclusion of an artefact collected at Ipanema site (sample I84), showing dendrites of wustite (FeO) in a SiO_2- rich matrix.
b) Detail slag inclusions of an artefact collected at Sardinha site (sample S106) showing two types of inclusions. SEM-BEI.

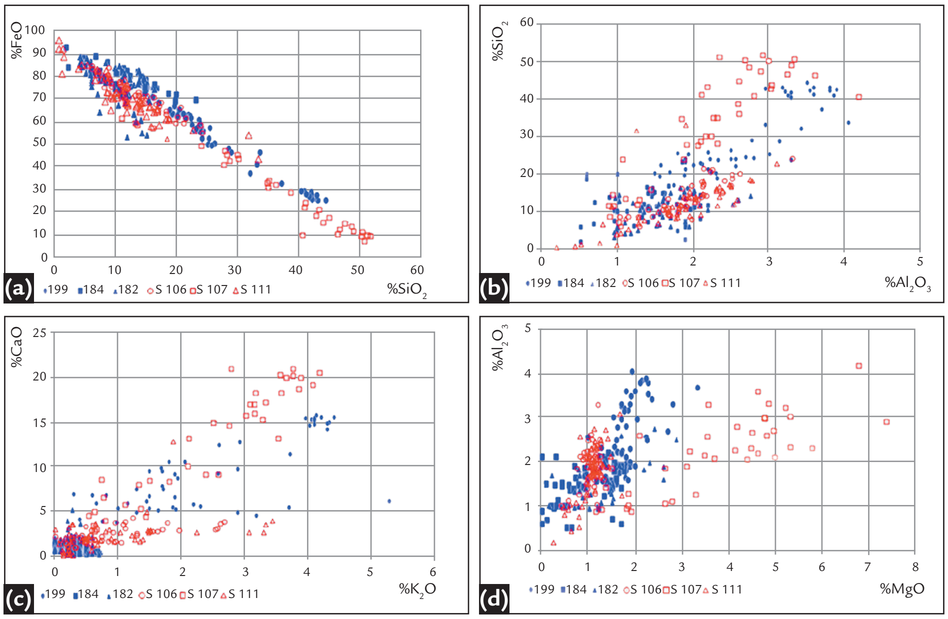

Figure 2
Bivariate graphs of the chemical composition of the non metallic inclusions for both sites of Araçoiaba Hill (S: Sardinha in red and I: Ipanema in blue):
a) Graph showing the content of FeO versus SiO_2;
b) Graph showing the content of SiO_2 and Al_2O_3;
c) Graph showing the content of CaO and K_2O;
d) Graph showing the content of MgO versus Al_2O_3.

The results of the statistical tests for the significance of the intercept are shown in **Tables 2** and **3**. The statistical test results for the artifacts collected at the Royal Iron Factory of São João do Ipanema (see **Table 2**) indicated that the CLRM without data-cleansing was not valid for 7 out of the 9 samples. The results for the artifacts collected at the Sardinha site (see **Table 3**) indicated that the CLRM was valid for 5 out of the 9 samples. These results indicated that CLRM without data-cleansing was not suitable for the present investigation. Additionally, **Table 4** compares the values of the coefficients of determination (R^2) for both regression models. The CLRM presented $R^2 \geq 0.7$ (indicative of an acceptable value for the strength of the linear relationship) for 77.7% of the individual results, while the ULRM showed suitable values of R^2 for only 22% of the individual results. This simple comparison showed that the use of the zero intercept model (CLRM) increased the values of the coefficients of determination in 95% of the samples by an average value of 260%.

Finally, **Figure 3** shows a graph of the P_2O_5 content in the non metallic inclusions versus the $[(Al_2O_3+ MgO+ K_2O) / FeO])$ ratio for each one of the ferrous artefacts. This graph was proposed by Dillmann and L'Heritier (Dillmann and L'Heritier, 2007) for partial discrimination of direct and indirect reduction products. This figure shows that most of the iron artefacts found in the Sardinha site are located in the direct reduction field (except sample S107), but this same figure could not identify the reduction process for the iron artefacts found in the Royal Iron Factory de São João de Ipanema, which were mostly located within the "undefined reduction process" field, with the exception of sample I99, for which most points are located in the direct reduction field.

Relation	Sample	|t|	p	Can the linear regression go through the origin?	Slope (a)	Intercept (b)
$\%SiO_2$ versus $\%Al_2O_3$	I99	0	0.97	Yes	10.8	-0.1
	I82	1.9	0.07	Yes	7.2	11
	I84	4.8	0	No	4.2	3.6
$\%Al_2O_3$ versus %MgO	I99	2.3	0.03	No	0.9	1
	I82	7.4	0	No	0.3	1.2
	I84	9.4	0	No	0.5	1
%CaO versus $\%K_2O$	I99	4.5	0	No	0.4	1.6
	I82	5.9	0	No	-0.9	1.1
	I84	6.6	0	No	-1	1.8

Table 2
Samples of the Royal Iron Factory of São João do Ipanema: test of significance of the intercept for the linear regression (y= ax + b).

Table3
Samples of the Sardinha site: test of significance of the intercept for the linear regression (y= ax + b).

Relation	Sample	|t|	p	Can the linear regression go through the origin?	Slope (a)	Intercept (b)
$\%SiO_2$ versus $\%Al_2O_3$	S106	1.7	0.1	Yes	8.5	-2.7
	S107	0.3	0.8	Yes	15.1	-0.8
	S111	0.1	0.92	Yes	6.7	-0.2
$\%Al_2O_3$ versus %MgO	S106	2.9	0.01	No	0.8	1.1
	S107	4.1	0	No	0.5	0.4
	S111	0.4	0.67	Yes	1.6	0.1
%CaO versus $\%K_2O$	S106	12.2	0	No	0.3	2.2
	S107	1.8	0.08	Yes	4.4	2.7
	S111	4.5	0	No	0.9	1.5

Table 4
Comparison of the linear correlation coefficients (R^2) for the linear regression models.

Sample	Constraint linear regression model (R^2)			Unconstraint linear regression model (R^2)		
	$\%Al_2O_3$ x %MgO	%CaO x $\%K_2O$	$\%SiO_2$ x $\%Al_2O_3$	$\%Al_2O_3$ x %MgO	%CaO x $\%K_2O$	$\%SiO_2$ x $\%Al_2O_3$
I99	0.94	0.92	0.74	0.32	0.62	0.74
I82	0.74	0.48	0.77	0.13	0.03	0.24
I84	0.88	0.33	0.88	0.41	0.06	0.32
S106	0.94	0.61	0.94	0.13	0.24	0.72
S107	0.98	0.93	0.96	0.92	0.62	0.83
S111	0.94	0.54	0.86	0.21	0.23	0.42
Average R^2 increase	3.9 times	4.9 times	1.9 times	-	-	-

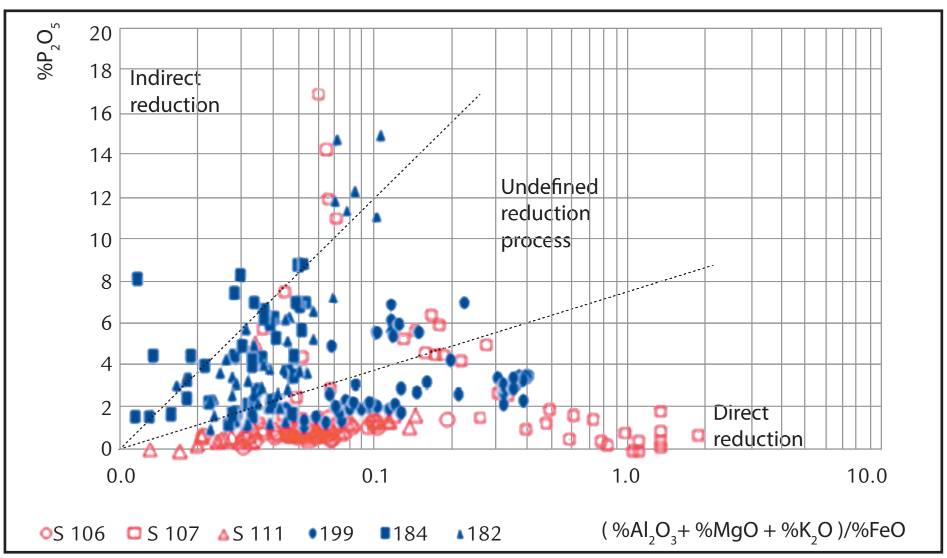

Figure 3
Graph showing the content of $\%P_2O_5$ versus the [($\%Al_2O_3$+ %MgO+ $\%K_2O$)/ %FeO]) ratio found in the slag inclusions of each iron artefact of both production sites of Araçoiaba Hill (S: Sardinha and I: Ipanema).

4. Discussion

The present results (see **Tables 2** and **3**) indicated that the constrained linear regression model was valid for only seven out of eighteen bivariate relationships. The present investigation, however, did not use any data cleansing to improve this result, as proposed elsewhere (Dillmann and L'Heritier, 2007) due to the large size of the investigated inclusions. Additionally, the low values for the coefficient of determination ($R^2 < 0.7$) for the unconstrained regression model (see **Table 4**) when compared with the constrained linear regression model indicated that the hypothesis of forcing the linear regression passing through the origin, as proposed by other authors (Coustures et al. 2003; Dillmann and L'Heritier, 2007), should be used with care, as this assumption drastically changes the values of the linear correlation parameters. The results in **Tables 2 and 3** indicated that the CLRM without data-cleansing was not valid for 78% of the bivariate relationships on the artefacts collected at the Ipanema site and for 45% of the bivariate relationships on the artefacts collected at the Sardinha site. As a matter of fact, the use of the zero intercept model (CLRM) increased the values of the coefficients of determination in 95% of the samples by an average value of 260%, which may lead to the "unrealistic" identification of the provenance of iron artefacts. As a result, the present investigation could not identify the signature of the productive systems of Sardinha and Ipanema sites using any of the linear regression models.

However, a qualitative analysis of **Figures 2-a** to **2-d** suggested that I99 sample was different from the other objects collected at the Ipanema site, and that S107 sample may also be different from the other objects collected at the Sardinha site. This simple observation indicated that the number of investigated artefacts from Ipanema and Sardinha sites must be increased to produce more meaningful conclusions about the provenance of these iron artefacts. For instance, **Figure 3** showed that most of the iron artefacts found in the Sardinha site are located in the direct reduction field (except sample S107), but this figure did not show any information for the iron artefacts found in the Royal Iron Factory de São João de Ipanema (direct and indirect reduction), which were mostly located within the "undefined reduction process" field, with the exception of sample I99, for which most points are located in the direct reduction field. As a matter of fact, a large number of points of Ipanema samples fall into the very large overlap region occupied by objects with different technological origins (direct or indirect reduction) in the graph proposed by Dillmann and L'Heritier (Dillmann and L'Heritier, 2007).

Finally, another important attribute of the inclusions of the samples collected at the Sardinha site when compared to the samples collected at the Ipanema site was its higher TiO_2 content associated with the presence of polygonal ilmenite ($FeTiO_3$) in the microstructure. In this case, the microstructural characterization was able to differentiate the artefacts collected at Sardinha and Ipanema sites.

5. Conclusions

- The present investigation could not identify by linear regression models the signature of the productive systems of Sardinha and Ipanema sites. The number of investigated artefacts from Ipanema and Sardinha sites should be increased in order to produce stronger conclusions about the provenance of the iron artefacts collected at these sites.
- The constrained linear regression model (CLRM) without data-cleansing must be used with extreme care, as the assumption of having a line passing through the origin of the bivariate graphs increased the coefficients of determination (R^2) in 95% of the samples by an average value of 260% when compared to the unconstrained linear regression model (ULRM).
- The graph of the P_2O_5 content versus the $[(Al_2O_3 + MgO + K_2O) / FeO]$ ratio in the non metallic inclusions indicates that that most of the iron artefacts found in the Sardinha site are located in the direct reduction field (except sample S107). This same graph could not identify the reduction process for the iron artefacts found in the Royal Iron Factory de São João de Ipanema.
- Another particular attribute of the inclusions of the ferrous artefacts from Sardinha site, when compared to the samples of Ipanema site, was their higher TiO_2 content associated with the presence of polygonal ilmenite ($FeTiO_3$) in their microstructure. In this case, the microstructural characterization was useful to differentiate the ferrous artifacts collected at Sardinha and Ipanema sites.

6. Acknowledgments

The authors would like to thank: Ministério do Meio Ambiente do Brasil; Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis; and Instituto Chico Mendes de Conservação da Biodiversidade for allowing the use of the iron artifacts from Andreatta collection; Santander Undergraduate University Grant; Dr. L. B. Regalado; Prof. A. C. Neiva and Dr. M. Andreatta for their valuable support.

7. References

ARAÚJO, P.E.M., SPORBACK, S.-G., LANDGRAF, F. J. G. Start up da siderurgia brasileira. ***Metalurgia & Materiais***, v. 66, n. 2, p. 197-202, 2010.

BLAKELOCK, E., MARTINÓN-TORRES, M., VELDHUIJZEN H. A., YOUNG T. Slag inclusions in iron objects and the quest for provenance: an experiment and a case study. ***Journal of Archaeological Science***, v. 36, n. 8, p. 1745-1757, 2009.

BUCHWALD, V. F. WIVEL, H. Slag analysis as a method for the characterization and provenancing of ancient iron objects. ***Materials Characterization***, v. 40, n. 2,

p. 73-96, 1998.
CAMPOS, G. N., SOLÓRZANO, I.G. Microanalytical study of a ferrous agricultural tool recovered from a historical site in Rio de Janeiro. ***Applied Physics A: Materials Science & Processing***, v. 79, n. 2, p. 315-318, 2004.
CHARLTON, M. F., BLAKELOCK, E,. MARTINÓN-TORRES, M., YOUNG T. Investigating the production provenance of iron artifacts with multivariate methods. ***Journal of Archaeological Science***, v. 39, n. 7, p. 2280-2293, 2012.
COUSTURES, M. P., BÉZIAT, D., TOLLON, F., DOMERGUE, C., LONG, L., REBISCOUL, A. The use of trace element analysis of entrapped slag inclusions to establish ore-bar links: examples from two Gallo-Roman iron-making sites in France (Les Martys, Montagne Noire, and Les Ferrys, Loiret). ***Archaeometry***, v. 45, n. 4, p. 599–613, 2003.
DESAULTY A.-M., MARIET C., DILLMANN P., JORON J. L., FLUZIN, P. A provenance study of iron archaeological artefacts by Inductively Coupled Plasma-Mass Spectrometry multi-elemental analysis. ***Spectrochimica Acta Part B: Atomic Spectroscopy***, v. 63, n. 11, p. 1253-1262, 2008.
DILLMANN, P., L'HÉRITIER, M. Slag inclusion analyses for studying ferrous alloys employed in French medieval buildings: supply of materials and diffusion of smelting processes. ***Journal of Archaeological Science***, v. 34, n. 11, p. 1810-1823, 2007.
GORDON, R. B. Process deduced from ironmaking wastes and artefacts. ***Journal of Archaeological Science***, v. 24, n. 1, p. 9-18, 1997.
LANDGRAF, F. J. G., TSCHIPTSCHIN, A. P., GOLDENSTEIN, H. G. Notas sobre a história da metalurgia no Brasil (1500-1850). In: VARGAS, M. ***História da Técnica e da Tecnologia no Brasil.*** São Paulo: Editora da Universidade Estadual Paulista, cap.5, p.107-130.414 p.
LEMES, P. T. A. P. ***Notícias das minas de São Paulo e dos sertões da mesma Capitania.*** São Paulo: Itatiaia, 1954. 240 p.
MAIA, R.R. ***Análise de inclusões de escória em amostras metálicas da Fábrica de Ferro de Ipanema.*** São Paulo: Escola Politécnica da Universidade de São Paulo, 2014. 209 p. 2014. (Masters of Engineering Dissertation)
MANSON, R. L., GUNST, R. F., HESS, J. L. Statistical design and analysis of experiments, with applications to engineering and science. Second Edition. New Jersey: John Wiley & Sons, 2003. cap. 14, p. 461-485. 728 p. (Linear regression with One Predictor Variable).
MEDEIROS, L. A Ferraria da Foz do Alge: elemento patrimonial submerso. ***Apontamentos de Arqueologia e Patrimônio***, v. 4, p. 71-76, 2009.
RODRIGUES, L. M. P. As minas de ferro em Araçoiaba (São Paulo, séculos XVI--XVII-XVIII). In: SIMPÓSIO DOS PROFESSORES UNIVERSITÁRIOS DE HISTÓRIA, 3 ***Anais...***, Franca: 1966. p. 171-25
ROGERS, E. J. The iron and steel industry in Colonial and Imperial Brazil. ***The Americas***, v. 19, n. 2, p. 172-184, 1962. (http://www.jstor.org/stable/978891)
ROSTOKER, W., DVORAK J. R. Wrought irons: distinguishing between processes. ***Archaeomaterials,*** v. 4, p. 153-166, 1990.
SALAZAR, J. M. O. ***Esconderijo do Sol: a história da Fazenda Ipanema, desde a primeira forja do Brasil até a Real Fábrica de Ferro.*** Brasília: Ministério da Agricultura, Brasília, 1982. 132 p.
STARLEY, D. Determining the technological origins of iron and steel. ***Journal of Archaeological Science***, v. 26, n. 8, p. 1127-1133, 1999.
ZEQUINI, A. Arqueologia de uma fábrica de ferro: Morro de Araçoiaba, Séculos XVI-XVIII. São Paulo: Universidade de São Paulo, 2006, Museu de Arqueologia e Etnologia, 2006. 223 p. (Phd Thesis).

Received: 14 August 2014 - Accepted: 21 January 2015.