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PORTUGUESE IRONS OF THE LATE BRONZE. A GEOCHEMICAL VIEW

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ABSTRACT

The discovery of iron objects in Portugal, dated from the end of the Bronze Age (12th-11th century BC) in the context of habitats, forces us to reconsider the question of their significance. We present the results of a geochemical approach by the comparative analysis of archaeological irons and Portuguese ores. The p-XRF analysis of 15 artifacts from 4 different sites in Beira Interior (Monte do Trigo, Moreirinha and Monte do Frade) and Central (Baiões), indicates that the smelted iron probably derived from two distinct ores. The local typology and the association of the finds with bronze workshops requires a reexamination as to the question of their origin. The chemical characterization of the irons of Beira Interior, indicates that they are of primitive elaboration given their low quality, while that of Baiões already shows a metallurgical evolution which would be understandable if it were more recent. A comparison with other Bronze Age irons underscores their chemical specificity. Local iron rich ores cropping out near Salvador (Penamacor, Beira Interior), were sampled and analyzed by ICP-AES and ICP-MS and compared with various types of iron ores. The composition of Salvador ores compared to that of the Beira Interior artifacts implies a definite consanguinity. The importation of finished objects, such as ingots with local forging must be excluded. The processing of the local ore and its forging by experienced metallurgists but novices in iron metallurgy, is a new and robust explanatory hypothesis in accordance with all the constraints already mentioned. This is the first time that Bronze Age irons can be related to a very likely ore source. The Mediterranean influences, marking the importation of a new and extremely recent know-how, therefore correspond, at least in part, to exchanges from the east and perhaps even to the movement of people. This exotic contribution would be linked to the profound movements in the Mediterranean context of the 12th century, probably from the Mediterranean East with possibly relays in the central Mediterranean.

KEYWORDS: Late Bronze Age, Portugal, 12th-11th century BC, Beira interior, Baiões, metallurgy, Mediterranean, iron ore, chemical, forging

1. INTRODUCTION

The economic and cultural relations between Iberia and the Mediterranean at the end of the Bronze Age and in the early Iron Age have been the subject of recent studies which update our vision of these exchanges of goods and people, as well as technical and cultural concepts (Krueger at al., 2021; Rodriguez-Corral, 2017; Bottaini et al., 2017). In this context, iron can be considered as an element of choice, as we will see below, and this is one of the main reasons that led us to deepen the nature and possible origin of recent discoveries of iron in Portugal.

Iberian irons have been the subject of relatively recent discoveries (Renzi et al. 2013; Álvarez Sanchís et al. 2016). This modifies our vision of the Mediterranean world and requires updating, or even reconstructing, an old and now outdated pattern of iron diffusion (see for example Yalcin, 1999).

The oldest irons of the Iberian Peninsula date from the Late Bronze Age, at the end of the 2nd millennium and the beginning of the 1st millennium B.C. The discoveries in the context of Bronze Age settlements in Portugal in the 1990s and later (Silva et al. 1984; Almagro Gorbea 1993; Vilaça 1995, 2006), particularly in the region called "Beira Interior", constitute a surprising result with regard to contacts with the Mediterranean world during the Late Bronze Age and the presence of well dated iron artifacts. Independently, one of us recently argued that all Bronze Age irons before 1200 B.C. are derived from meteoritic iron (Jambon, 2017), the Final Bronze Age being not a transition period but a period during which here and there appear sporadically a few iron objects. The exact date of the discovery of iron smelting, if still to be clarified, would probably be around 1150 BC, according to archaeological finds from the eastern Mediterranean (Waldbaum, 1999; Sanidas et al. 2016; Jambon and Doumet-Serhal, 2018). The place of this invention cannot be precisely located: this is to be linked on the one hand to the troubles in the Middle East from the end of the 13th century which led to the disappearance of the powers in place and consequently to a certain discontinuity of the archaeological record (writings and furniture) and on the other hand to the finds of iron artifacts in greater number than in previous periods and almost simultaneously in geographically and culturally distinct sites, suggesting a rapid diffusion in the Eastern Mediterranean World.

Vilaça (2006, 2013a) showed that a number of irons from Portugal could certainly be dated to the eleventh century, and perhaps even to the end of the twelfth for the oldest. This early date in the history of iron metallurgy in a place far from the Mediterranean East, the presumed region of invention, is unexpected

and undoubtedly indicative of rapid and longdistance movements. Note here the contrast with Europe north of the Alps where the oldest irons seem to date from the ninth century (Hallstatt culture). It follows that early Portuguese irons bear witness to a recent invention and take an exceptional place in our understanding of iron dissemination. Their interpretation must therefore be reassessed in this new perspective: do they result from the trade of finished objects or were they crafted locally from imported raw material (ingots, bars...) or to the local mastering of iron smelting?

The first Portuguese irons come from settlements concentrated in the central and especially interior region of Portugual, although they are not limited to it (Fig. 1). We know of five well-dated sites between the 12th and 9th centuries B.C. (Vilaça 2013a, Fig. 3). Other sites in the Iberian Peninsula from the same age range or more recent will be the subject of future investigations. Indeed, the first results obtained on the late Bronze irons of Beira Interior provide a reference for iron analyses of the first Iron Age (from Cachouça, Idanha-a-Nova) and investigating to what extent they differ from older local production. In the region defined by the Douro and Tagus rivers, we find a remarkable number of iron artefacts from five settlements with an occupation also dated to the Late Bronze Age. The first three are located in the "Beira Interior" and the other two in the "Beira Central".

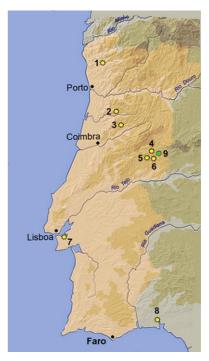


Figure 1. Location map of iron artifact find sites and ore samples analyzed (according to Vilaça 2013a adapted and completed). 1 São Julião, 2 Baiões, 3 Outeiro dos Castelos, 4 Monte do Frade, 5 Monte do Trigo, 6 Moreirinha, 7 Quinta do Marcelo, 8 Huelva, 9 Salvador.

The objective of this work consists in discussing the possible origin of these irons which could be imported objects, objects of local elaboration from imported iron ingots or even irons elaborated from a local ore. In either case the significance will be completely different from trading with the Levant to the introduction of craftmanship in Portugal long before the presence of Phoenicians. To this end we compare the compositions of Beira Interior irons (their inclusions) with other Bronze age irons already published and various types of ores including Salvador iron ore located a few kilometers from the Bronze Age settlements. This strategy to determine the origin of the irons is applied here for the first time.

2. SAMPLES AND METHODS

We focused on four of the five oldest sites for artifact accessibility reasons: Monte do Frade (Penamacor), Monte do Trigo, Moreirinha (Idanha-a-Nova) and Baiões (Viseu). We analyzed 21 fragments from these 4 sites probably coming from 15 distinct artifacts, (Almagro Gorbea 1993 , Vilaça 2006 and Fig. 2).

Portable X-ray fluorescence (p-XRF) chemical analysis makes it possible to obtain the chemical composition of the surface of any mineral material. In the case of sufficiently well-preserved metal objects, it makes it possible to obtain reliable values for the transition elements: manganese, iron, cobalt, nickel and copper, as well as phosphorus, elements of importance for determining the origin of the iron, but also for the inclusions of slag contained in the metal essentially from the values of silicon, aluminum and calcium. The analytical method (p-XRF) was presented previously by Jambon (2017). The analytical errors are as follows (wt. %): Al: 0.52, Si:0.15, P: 0.043, S: 0.025, Ca: 0.02, Ti: 0.012, V: 0.008, Cr: 0.013, Mn: 0.015, Fe:0.50, Co: 0.035, Ni: 0.035, Cu: 0.013 and Zn:0.004. Conventionally the detection level is three times the error.

Iron ores were analyzed in the same way initially, in the field, then by ICP-AES and ICP-MS after sampling of a few g according to the procedures described by Barrat et al. (2012).

Table 1. Type and age of the specimens investigated.

				Calibrated Age BC	Mean Age	
Site	Age BP	±	Sample	2 sigma	ВС	Reference
Monte do Frade	Small blade					
	2805	15	Charcoal	1003-913	958	Vilaça, 1995; 2006
	2850	45	Charcoal	1192-1132	1162	
	2920	50	Charcoal	1292-946	1119	
	2780	100	Charcoal	1257-790	1023.5	
Moreirinha	8 pieces (knife and	saw blac	des)			
	2910	45	Charcoal	1262-949	1105.5	Vilaça, 1995; 2006
	2780	70	Charcoal	1117-808	962.5	
	2940	45	Charcoal	1296-1010	1153	
	2785	15	Charcoal	973-906	939.5	
Monte do Trigo	11 pieces (knife and	d saw bla	ades)			
	3020	60	Charcoal	1419-1057	1238	Vilaça, 2006; 2008
	2990	50	Charcoal	1387-1056	1221.5	
	2960	45	Charcoal	1368-1022	1195	
	2960	45	Charcoal	1368-1022	1195	
	2913	41	Charcoal	1262-997	1129.5	
	2880	45	Charcoal	1211-925	1068	
	2880	33	Charcoal	1193-937	1065	
Baiões	Bimetallic chisel					
	2650	130	Charcoal			Vilaça, 2008
	2745	40	Peas	993-979	986	
	2680	40	Peas	906-796	851	
	2650	35	Peas	895-787	841	

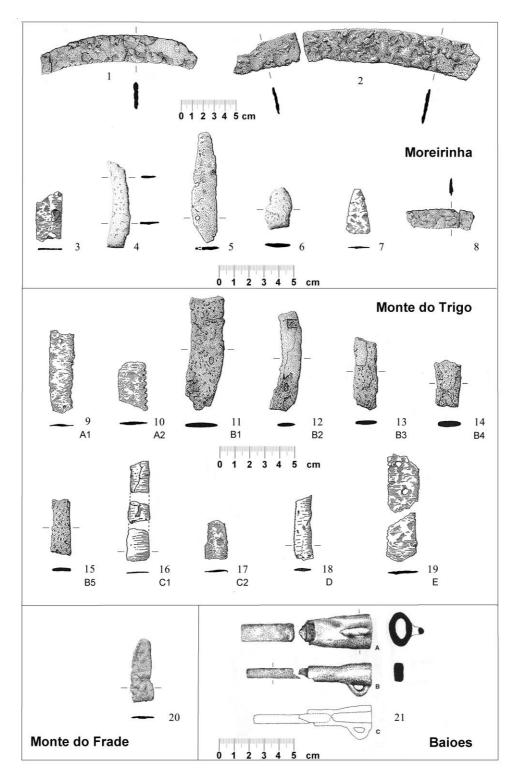


Figure 2. The analyzed specimens. n° 1-8: Moreirinha, n° 9-19: Monte do Trigo, n° 20: Monte do Frade, n° 21: Baiões. Letters correspond to Vilaça (2006: 90).

3. RESULTS

The analytical results are reported in Tables 2-3. It should be noted that the Ni is always below the detection limit. From the detailed discussion presented in Jambon (2017), we conclude that we are dealing

with irons of terrestrial origin without possible discussion even taking into account the advanced state of corrosion of the material, which is in accordance with previous interpretations.

Table 2. Analytical results. Ni and Mg are below the detection limit. Na and K are not analyzed. The empty boxes correspond to values below the detection limit. Note the absence of Ni. The values obtained for Al, Si, S and Ti correspond to inclusions (slag).

Ref.	Al	Si	P	s	Ca	Ti	V	Cr	Mn	Fe	Со	Cu	Zn
Moreirinha 1	5.42	5.29	2.79	0.52	0.63	0.07	0.01	0.07	0.09	85.46	0.16	0.11	0.02
Moreirinha 1	10.30	30.50	3.46	1.50	0.51	0.24	0.04	0.09	0.06	53.66		0.02	0.01
Moreirinha 1	3.31	2.63	1.40	0.20	0.48			0.06	0.33	91.77	0.26	0.01	0.02
Moreirinha 1	4.61	4.15	1.66	0.40	0.40		0.01	0.07	0.04	88.85	0.16	0.05	0.02
Moreirinha 2	7.33	6.64	4.25	0.15	0.38	0.05	0.02	0.07	0.03	81.04	0.37	0.03	0.02
Moreirinha 2	7.64	8.14	2.80	0.16	0.59	0.07	0.02	0.10		80.69	0.32	0.03	0.03
Moreirinha 2	6.13	5.50	2.62	0.10	0.30		0.01	0.06		85.28	0.22		0.03
Moreirinha 2	3.20	2.30	3.33	0.09	0.30		0.01	0.07	0.13	90.58	0.25		0.02
Moreirinha 2	3.44	2.75	3.31	0.10	0.32			0.07	0.08	90.00	0.22	0.02	0.02
Moreirinha 3	9.15	7.21	2.07	0.14	0.53	0.03	0.01	0.07	0.05	81.02	0.21	0.02	0.02
Moreirinha 3	2.06	1.59	0.51	0.21	0.27			0.06		95.33	0.20		
Moreirinha 3	8.73	8.10	1.93	1.57	0.57	0.11	0.02	0.10	0.03	78.95	0.42	0.02	0.02
Moreirinha 4	3.45	2.67	4.07	0.11	0.56	0.03	0.02	0.09	0.02	89.15	0.28	0.08	0.03
Moreirinha 4		0.49	0.32	0.65	0.18			0.08		97.69	0.20	0.03	
Moreirinha 4	0.89	0.55	0.50	0.08	0.20			0.07		97.66	0.20	0.03	
Moreirinha 5	3.73	3.87	2.15	0.12	0.42		0.01	0.07		89.65	0.28	0.08	0.03
Moreirinha 5	4.21	4.45	2.94	0.13	0.50	0.03	0.02	0.07	0.02	87.63	0.35	0.11	0.02
Moreirinha 5	3.55	3.29	2.09	0.11	0.39			0.06		90.49	0.26	0.12	0.02
Moreirinha 6	6.31	5.88	3.09	0.07	0.54	0.02	0.01	0.07	0.03	84.18	0.28	0.06	0.02
Moreirinha 6	8.25	9.12	3.17	0.09	0.58	0.05	0.02	0.08	0.04	78.76	0.33	0.06	0.02
Moreirinha 6	7.13	6.65	3.41	0.08	0.60	0.05	0.02	0.07	0.04	82.18	0.29	0.05	0.02
Moreirinha 7	3.19	1.88	2.95	0.10	0.39		0.01	0.07		91.55	0.23	0.01	0.01
Moreirinha 7	3.97	3.67	2.18	0.05	0.34		0.01	0.08		89.74	0.27	0.02	0.01
Moreirinha 7	4.08	3.08	2.57	0.09	0.42		0.01	0.08	0.02	89.76	0.26	0.02	0.02
Moreirinha 8	5.22	2.93	1.87	0.09	0.32		0.01	0.06	0.04	89.45	0.23	0.07	0.02
Moreirinha 8	5.16	2.87	2.09	0.10	0.35		0.01	0.06	0.03	89.39	0.20	0.07	0.02
Moreirinha 8	6.60	4.65	1.00	0.09	0.29			0.06		87.22	0.17	0.14	0.02
MonteDoFrade 20	3.87	3.62	1.34	0.09	1.41	0.02	0.01	0.02	0.07	37.95		0.02	0.01
MonteDoFrade 20	7.86	10.50	3.13	0.23	0.34	0.04	0.02	0.07	0.09	77.71	0.19	0.06	0.02
MonteDoFrade 20	4.97	3.57	1.44	0.25	0.53		0.01	0.07		89.38	0.18	0.04	0.01
Baiões 21	0.50	0.91	<0.1	0.15	4.10			0.05		94.22		0.50	
Baiões 21	0.10	1.33	< 0.1	0.25	0.65			0.08		93.30	0.24	3.63	

3.1 The Irons of Beira Interior (Penamacor, Idanha-a-Nova)

We mentioned that Ni is always below the detection limit (< 1050 ppm). An addition of all the spectra makes it possible to obtain an order of magnitude of the Ni content of 850 ppm. This approach is justified since, according to the other chemical criteria, the population is very homogeneous. For cobalt (Co) only two analyzes give a value below the detection limit. Consequently, and taking into account the detection

limit for Ni, the Co/Ni ratio is >1 which is a characteristic of metallurgical irons.

Iron metal contains neither silicon (Si) nor aluminum (Al). The analyzes yield Si contents varying between 0.4 and 10.5% - average 4.5% - and Al between 0.9 and 9.1% - average 5% - which are high and corresponds to inclusion rich irons.

The objects analyzed have all an oxidized surface and the reported values are calculated without oxygen, which makes it possible to avoid variable degrees of oxidation. The Fe content then averages

90.2% (79-99.5%). The copper content is considered insignificant because of possible contamination by copper or bronze objects found in the vicinity during excavations.

The Al and Si contents therefore characterize the nature and quantity of the incorporated inclusions which appear quite abundant. We represent the results in an Al/Fe vs Si/Fe diagram. This procedure permits to compare iron artefacts and potential ores

in the same diagram. It also makes it possible to highlight a relationship between Si and Al independently of the iron content as we shall see next. The excellent correlation between Al/Fe and Si/Fe (Fig. 3) can be interpreted as a mixing line between two constituents, one of which is obviously the iron matrix (placed at the origin of the coordinates) and the other the composition of the inclusions. If the points fall on a single line, this means that the inclusions have a unique composition.

Table 3. Monte do Trigo analytical results. The average value for Ni is 0.083% obtained by summing all the spectra.

Ref.	Al	Si	P	S	Ca	Ti	V	Cr	Mn	Fe	Co	Cu	Zn
MonteDoTrigoA1	6.81	5.92	2.63	0.16	0.30	0.13	0.03	0.08	0.16	82.82	0.40	0.78	0.05
MonteDoTrigoA1	5.35	5.21	1.62	0.13	0.30	0.09	0.02	0.07	0.16	85.57	0.36	1.34	0.04
MonteDoTrigoA1	5.01	5.24	1.93	0.09	0.36	0.11	0.02	0.07	0.21	84.64	0.34	2.26	0.06
MonteDoTrigoA2	4.40	3.99	1.26	0.12	0.31	0.07	0.02	0.07	0.12	89.43	0.26	0.18	0.07
MonteDoTrigoA2	5.88	4.99	1.17	0.15	0.33	0.04	0.01	0.06	0.12	87.14	0.23	0.13	0.07
MonteDoTrigoB1	4.21	2.88	0.37	0.08	0.24			0.06		92.27	0.10	0.02	0.01
MonteDoTrigoB1	3.68	2.47	0.45	0.08	0.23		0.01	0.07		93.09	0.13	0.02	0.01
MonteDoTrigoB1	4.10	2.71	0.63	0.10	0.26		0.01	0.07		92.19	0.14	0.02	0.01
MonteDoTrigoB2	3.65	4.93	0.73	0.14	0.43	0.10		0.06	0.03	90.18	0.14	0.01	0.02
MonteDoTrigoB2	4.98	4.59	1.26	0.15	0.55	0.07		0.06	0.04	88.62	0.19		0.02
MonteDoTrigoB3	3.71	3.15	0.58	0.19	0.34			0.06	0.02	92.13	0.13	0.01	0.01
MonteDoTrigoB3	5.04	5.29	0.63	0.14	0.30	0.08		0.07	0.06	88.45	0.18	0.02	0.02
MonteDoTrigoB4	3.28	3.61	0.70	0.3	0.26	0.03	0.02	0.07	0.04	91.57	0.23	0.11	0.05
MonteDoTrigoB4	3.47	3.64	0.68	0.28	0.26	0.03	0.02	0.07	0.03	91.45	0.19	0.09	0.05
MonteDoTrigoB5	3.07	2.69	0.36	0.15	0.22		0.01	0.07		93.47	0.15		0.01
MonteDoTrigoB5	2.75	2.54	0.37	0.16	0.22			0.07		93.93	0.14		0.02
MonteDoTrigoB5	3.23	2.63	0.58	0.24	0.23		0.01	0.06	0.03	93.00	0.16		0.03
MonteDoTrigoC1	4.85	3.18	0.67	0.24	0.51	0.01		0.06	0.07	90.63	0.07	0.22	0.02
MonteDoTrigoC1	4.07	3.35	0.55	0.42	0.25			0.06	0.06	91.04	0.16	0.23	0.01
MonteDoTrigoC2	3.30	2.48	0.99	0.37	0.40			0.06		91.76	0.16	0.81	0.01
MonteDoTrigoC2	6.71	4.89	0.86	0.28	0.41	0.03		0.06	0.03	86.34	0.17	0.57	0.01
MonteDoTrigoD	5.09	3.83	0.9	0.20	0.35	0.03	0.01	0.06	0.04	89.25	0.22	0.34	0.02
MonteDoTrigoD	6.09	4.27	0.70	0.19	0.35	0.01	0.01	0.06	0.03	88.22	0.14	0.27	0.01
MonteDoTrigoD	5.43	3.75	1.32	0.18	0.48	0.03		0.06	0.04	88.51	0.25	0.40	0.02
MonteDoTrigoE	4.83	3.92	1.15	0.18	0.31	0.02	0.01	0.06	0.02	89.49	0.15	0.15	0.01
MonteDoTrigoE	4.57	3.82	0.98	0.17	0.31	0.02		0.07	0.03	89.87	0.15	0.29	0.02
MEAN	4.52	3.84	0.93	0.19	0.33	0.06	0.01	0.07	0.06	92.04	0.21	0.33	0.03
SD	1.11	1.03	0.53	0.09	0.09	0.04	0.01	0.01	0.05	4.77	0.09	0.47	0.02

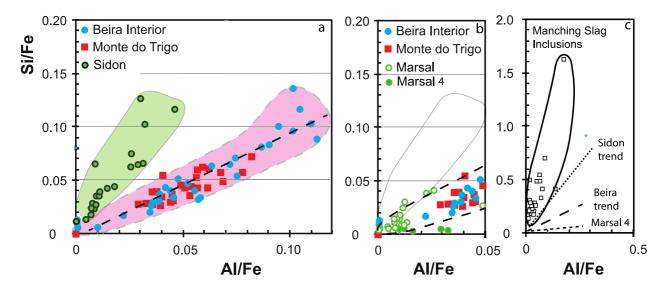


Figure 3. Al/Fe vs. Si/Fe correlation for Portuguese artifacts. Comparison of Beira Interior irons with a: Sidon irons; b: Marsal ingots; c: slag inclusions in Manching irons (notice the different scales). Sidon irons are of the same age but derived from a different ore, both contain abundant inclusions. Marsal ingots are more recent (La Tène) with a significantly lower level of inclusions. Manching data are EMPA analyzes from Schwab (2006). Notice that Beira Interior, Sidon, Marsal 4 and Manching exhibit different Al/Si ratios.

One single correlation is observed for the different Beira Interior sites (Fig. 3), indicating that the slag included in the metal is chemically identical, suggesting a common ore source with an Al/Si ratio slightly greater than unity, or a typically residual ore (lateritic) possibly rich in kaolinite-type clays whose Al/Si ratio is theoretically equal to 0.96 and devoid of quartz (Al/Si = 0). The constant Al/Si ratio suggests the presence of one single phase carrying both Al and Si rather than a mixture of quartz and an Al rich phase which would result in more variable Al/Si ratios.

The P content is quite high and not very variable with a very low Ca/P ratio. The abundance of this element varies according to the nature of the ores, a rather interesting result for their characterization.

The abundance of all these elements in the metal could be interpreted in two ways: the objects are polluted on the surface by sediments (clays for example) or they contain a large quantity of inclusions due to poor slag removal during the purification step. The samples analyzed are all relatively clean and the comparison with the analyses of other iron objects suggests that these are rather inclusions contained in the metal. It should be noted that the soil, a potential source of pollution, is granitic (Al/Si = 0.1-0.2).

Electron microprobe analysis (see for example Erb-Satullo et al. 2014, Schwab et al. 2006) therefore at the micrometric scale has shown that inclusions are rich in FeO. In the majority of cases, the Fe content of the inclusions results partly from the composition of the slag in the furnace, but also from a secondary evolution resulting from the incorporation of FeO into the inclusions during forging (purification and /or shaping) by oxidative dissolution of the surrounding

metal. If we therefore want to characterize the composition of the slag included, it is necessary to overcome the iron content by considering, for example, the Al/Fe and Si/Fe ratios: for a given slag, Al/Si will not vary whatever the secondary dissolution of iron in the slag. Among the archaeological objects that we have been able to analyze as well as among the objects analyzed by other authors, the Si/Fe ratios always remain low and are rarely greater than 0.04 and it is the same for the Al/Fe ratio. In the case of Portuguese irons, these ratios can be as high as 0.14 (Si/Fe) and 0.11 (Al/Fe), some of the values being normally low (<0.04). We see there the mark of a moderate forging, of an incomplete elimination of inclusions, characteristic of a primitive metallurgy.

3.2 The Iron of Baiões (Beira Central)

There is only one iron artifact in Baiões. It is a composite object with a bronze socket and the particular geometry did not allow us to carry out more than two analyses. The composition of the metal appears to differ from that of the Beira Interior in several respects (Table 2). First of all, the quantity of impurities is much lower as indicated by the Al and Si contents, there is indeed only one Moreirinha artifact (one out of 8 specimens; two out of three analyses) which is roughly comparable. The two analyzes are however quite different from each other, but in both cases the Si/Al ratio is much higher than for all samples from Beira Interior. The low Al content therefore suggests that the ore is of the quartzite type (presence of quartz), unlike the previous set.

The Ca content is higher than for the previous set, especially considering the low content of inclusions.

Phosphorus is below the detection limit, excluding a contribution of calcium phosphate and indicating an indisputable excess of Ca, because silicates are almost absent and no other mineral in the ore can provide calcium. It indicates that in this case the ore was smelted in the presence of lime (CaO), which fluidifies the slag and significantly improves the separation of the metal from the slag. The abnormal Ca value in one of the analyzes (4.1%) likely corresponds to a micro inclusion of residual lime. All this can explain the much lower level of silicate impurities in the metal. So, if we consider these analyzes at face value, we must conclude that the metal is of much better quality than in Beira Interior and the high calcium content implies the addition of lime, the witness of a more elaborate iron metallurgy. Importantly, it is likely that the quality of the metal is precisely the result of the use of lime as a flux.

3.3 Discussion

The population analyzed in Beira Interior (Penamacor, Idanha-a-Nova) appears to be homogeneous both with regard to the siderophile elements dissolved in the metal and the inclusions of slag, suggesting that all these irons have the same origin. The high content of included slag included reveals a poor control of the purification step as can be expected for a primitive metallurgy. Moreover, a high Al/Si ratio associated with a low Ca content leading to an excessive viscosity of the slag, can be considered as a primitive character of this metallurgy. Metallurgists of the time mastered the bronze processing very well and one can think that the composition of the slag should be more or less understood, if not the role of the iron oxide itself. In fact, in the extractive metallurgy of copper, iron oxide can act as a flux, as it is a fairly common constituent of the ore. In an iron ore, iron oxide is the element to be recovered, letting it go into the slag is a failure because it corresponds to a loss of yield but it is a common character in the Iron Age slag for lack of mastery of a complex process. Its abundance in the slag partly depends on the reducing conditions in the furnace: under slightly oxidizing conditions, part of the iron will remain in the form of wüstite (FeO) in addition to fayalite (Fe₂SiO₄) and possibly hercynite (FeAl₂O₄). Under very reducing conditions the slag will be low in FeO, with the unfortunate consequence of the high viscosity of the slag but a higher metal yield. Under such reducing conditions, the melting of the slag and its fluidity would be greatly favored by the addition of a flux. The question of the fluidity of the slag could be resolved by adding calcium in the form of lime (CaO), which possibly poses the problem of its supply in a granitic region. In Beira Interior, the Ca content is low since there is an average Ca/(Al+Si) ratio of 0.07, whereas this ratio can be as high as 0.4 for lime-enriched slags.

Adding lime corresponds to the partial replacement of Fe by Ca in the slag and Fe can then be reduced to yield more metal. Note however that for an ore low in impurities, increasing the amount of slag is a disadvantage for reasons of coal consumption. Solving this problem required the acquisition of knowhow and an economic evaluation depending on the cost of the ore, the lime and charcoal and the quality of the metal obtained. The option that was chosen in Beira Interior is the simplest possible: rich ore and charcoal, without any additions. Despite being a primitive metallurgy it should also be noted that this is possible in the case of an iron rich ore, giving little slag.

The iron from Baiões is unique in its kind and the conclusions that we are going to draw about it are therefore less firmly established. This iron is of much better quality than those of Beira Interior suggesting a better mastered metallurgy. The ore is most likely different based on the Si/Al ratio of the inclusions. Moreover, the composition of the inclusions indicates that the process used is different, with probably the addition of lime as a flux. The dating obtained at Baiões are among the most recent for the sites studied here, but it is by no means certain that any of the Beira Interior irons are not contemporaneous, the ¹⁴C dating not allowing such fine dating. In all cases, the cultural contexts based on the typologies of archaeological materials, notably ceramics and metals, are similar. One can just suggest but absolutely not prove that the irons of Baiões corresponds to a more elaborated metallurgy. It is perhaps this very difference that has led to an evolution in metallurgical practices but this evolution may have occurred over a very short laps of time.

Another possibility according to the specificity of the Baiões specimen, including its typology and composition, would be an extra-peninsular origin.

3.4 Comparison to other early irons.

The comparison of Portuguese iron objects with other contemporary objects, can be made from a chemical and typological point of view.

3.4.1 Typological comparison.

Knives or saw blades are utilitarian objects, corresponding to finds in habitats and not in burials. The disadvantage of everyday objects such as knives is that their typology is totally commonplace and intercultural variability is low.

While the knives or saw blades may correspond to replicas of native objects in bronze, it is important to note that, from a typological point of view, the Baiões piece has no direct parallel in the contexts of the Late Bronze Age of Portugal. Indeed it is a bimetallic object by necessity, because at the very beginning of iron metallurgy the art of making a fitting by forging was not available. An intermediate socket is then made between the iron blade and the handle, in copper or bronze, using the lost wax technique, as was practiced in the Bronze Age on meteoritic iron (e.g. Ugarit axe) or at the very beginning of the Iron Age (axes from Luristan) (Schaeffer, 1939). There is an obvious convergence here, but the presence of a single object of this type in Portugal does not allow us to affirm that it is an oriental influence.

It follows that it will not be only the type of ore or the more elaborate quality of production that distinguishes the iron objects of Baiões.

3.4.2 Chemical comparison.

Surface analysis of corroded artefacts requires being cautious. The chemical composition recorded is that of the metal to which must be added the inclusions of slag as well as any surface pollution either by the ground or by surrounding objects. An example of the latter case is the occasional presence of copper which comes from bronze objects found in the vicinity at the time of the excavations. Precisely, some of

the iron objects from Monte do Trigo were part of small bimetallic deposits (iron and bronze) in habitat context (Vilaça 2006, 2013c, Fig. 4 to 6). To overcome this difficulty, the replication of the analyzes makes it possible to evaluate to what extent the result obtained is robust or random, knowing that the scale of the analysis is a surface of approximately 5 mm in diameter and that the residual slag inclusions are significantly smaller. The most significant elements are those which characterize the metal (P, Mn, Cr, Co) on the one hand and those which characterize the slag on the other (Si, Al, Ca).

As for the metal, the Portuguese irons analyzed here have a rather interesting feature. They have a high average P content. To be sure, a comparison with other smelted irons is necessary. We gathered comparable results (p-XRF analyses) on irons from Byblos and Sidon (Lebanon, eleventh century BC), Dijon and Bourget lake (France, eleventh-tenth century and La Tène), Neuchâtel lake (Switzerland, eleventh century BC), from Hallstatt and Stutzendorf (Austria, eighth century BC)(Jambon, 2017; Jambon and Doumet-Serhal, 2018; Jambon and Kerouaton, 2019). The results are shown in Fig. 4.

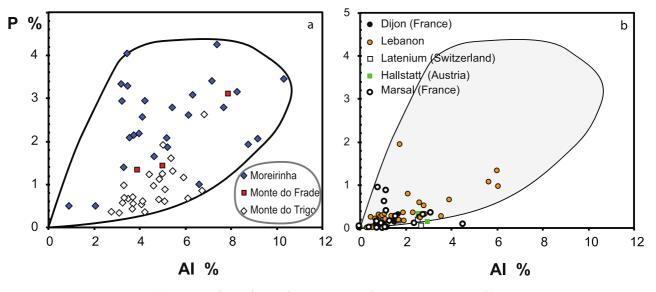


Figure 4. Portuguese irons (a) compared to other early European and Near Eastern irons (b). Portuguese irons are on average significantly richer in phosphorus.

The diagram representing P as a function of Al (Fig. 4) sums up the essentials. Portuguese irons are rich in Al and P, much more than all other irons except four Lebanese specimens (out of 31). With regard to the silicates presumably slags, the same comparison is essential.

The two Lebanese sites (Byblos and Sidon) also show a good correlation between Si and Al (Fig. 3), which suggests a homogeneity of the ore with an average Si/Al ratio of 3, much higher than that of the

Portuguese irons (Si/Al = 1.0) with a restricted variability in each case precluding a common value (Fig. 3). If we rely on these results, we must conclude that Portuguese irons have a well-defined signature characterized by poor iron quality both in terms of its chemical composition (rich in P) and the quantity of slag inclusions. This can be interpreted as the signature of a sedimentary ore rich in phosphorus and a poorly controlled metallurgy, which is not surprising at such a remote date. The Al/Si ratio of the Lebanese irons is quite banal unlike the case of the Beira Interior

irons and their origin is therefore different. A second example is that of the more recent Marsal ingots (Meurthe et Moselle, France; La Tène) which exhibit two types: one with an Si/Al ratio comparable to the Beira Interior but with a much lower level of inclusions and the other Marsal 4, with a low Si/Al ratio and again a very low level of inclusions. The last example is taken from the literature (Schwab et al. 2016). Microprobe analyzes of slag inclusions in irons from Manching (La Tène) show a high Si/Al ratio. We therefore have four examples with a quite well defined Si/Al ratio, variable and characteristic of the ores used.

3.4.3 Some thoughts on Portuguese Bronze Age irons.

The ¹⁴C dates, the stratigraphy, the number of objects and sites concerned do not allow us to minimize the importance of the discoveries of iron objects dated to the end of the Bronze Age (12th-9th century) in Portugal, that is to say before the arrival of the Phoenicians (Álvarez Sanchís et al. 2016).

The archaeological contexts of these irons include other objects and materials of Mediterranean origin or extent, such as glass, amber, weights, a typically Syrian-Palestinian decorative style on bronzes, etc. (Vilaca 2008, 2013b). It has been underscored by several scholars that irons were part of this corpus shared between different communities in the Center of Portugal, also revealing the existence of regional networks (e.g. Almagro Gorbea 1993, Ruiz-Gálvez Priego 1993, 2008, Vilaça 2006, 2008, 2013a). Consequently, these networks had to be articulated with others involving different actors and regions, so that we cannot see this presence of the Mediterranean in Beira Interior as an epiphenomenon (Vilaça 2013b).

3.4.4 Hypotheses Regarding the Origin of Iron.

3.4.4.1 Import of objects.

This is in agreement with a contextualization with Mediterranean influence, but the typology of the objects does not make it possible to affirm without ambiguity an imported character. In any case, it can be observed that among the iron objects there are essentially knife blades, a type extremely rare in the indigenous contexts of the Bronze Age, but frequent in the western Mediterranean (Vilaça 2006: 95, with reference therein; Waldbaum, 1999). The absence of any iron processing workshop is in agreement with this hypothesis but can in no way be considered as proof since in the Near East, the first metallurgical workshops discovered are much more recent than the first metallurgical iron objects (Veldhuizen and Rehren, 2006). In the Iberian Peninsula it will only be at the end of the 8th century B.C. and in the Phoenician sites that are found the oldest testimonies of iron production (Álvarez Sanchís et al., 2016, with references therein). On the contrary, Portuguese iron objects are associated with bronze objects and it is usually considered that the first iron craftsmen were bronze craftsmen.

3.4.4 2. Iron importation in the form of semi-finished products (bars, plates, etc.) and local shaping.

This would explain the local typology of some objects and the lack of identification of smelting workshops on the one hand and the association with bronze objects. The bronze metallurgy in the background suggests that local craftsmen were able to acquire mastery of iron shaping, as they mastered bronze metallurgy (furnaces and forges) although iron forging is a very specific technique. This hypothesis was initially proposed by Almagro Gorbea (1993: 88) for the Iberian Peninsula and was considered quite suggestive for the available and specific archaeological data of Beira Interior (Vilaça 2006: 95).

3.4.4.3 Local production.

This hypothesis is not favored by any author so far, perhaps because it is totally revolutionary in relation to the idea of a rather slow propagation wave of know-how from the Near East. This idea in fact was based implicitly on the assumption of iron smelting in the beginning of the Bronze Age which, we learned recently, is a wrong idea. The absence of meteoritic irons in Western Europe may suggest that metallurgy was clearly behind compared to what it was in the East, while it was perhaps more simply a cultural characteristics in particular in the Early and Middle Bronze Age. As for the Final Bronze, the treasure of Villena (Alicante) (Soler, 1965) is the only exception.

The absence of iron slag could be explained in this hypothesis:

- by the low level of production at that time
- by the reduction on the site of the mines, therefore outside the habitats
- either in the habitats themselves, but in their most peripheral zone (and not excavated); this hypothesis could have some ethnographic and historical inspiration because the production of iron is traditionally seen as a mysterious and therefore dangerous process that must take place out of sight of the community (e.g. Haaland et al., 2002).
- by the association with the production of other metals (copper and bronze) for which the slag is more abundant and difficult to distinguish.

Most iron objects of the eleventh century were found in a restricted area, close to potential iron ores; the exceptions are São Julião, which is about fifty km away, and Quinta do Marcelo, on the edge of the ocean, which seems to have been occupied more recently (Fig. 1).

A simple explanation would be that iron is originally found near deposits only and that this metal is considered more of a curiosity than a utility. Production is limited. The diversity of tools is not yet developed, weapons will only appear in the Iron Age. Simply because it does not appear to be a necessity, the potential of the new metal is not yet understood, especially since at that time it is of poor quality compared to bronze. Interestingly, Renzi et al., (2013) provide a metallographic analysis and hardness measurement for Moreirinha 1 (their Fig. 1b) and a picture of Monte do Trigo 9 (their Fig. 1a) incorrectly labeled as being from Moreirinha (I. Montero pers. com. 2023). Beside the presence of numerous slag inclusions, the hardness measurement on Moreirinha 1 shows the heterogeneous character of the carburization and limited hardness (from 100 to 250 HV) contrasting with that of a modern steel of comparable composition free of inclusions and very homogeneous (Araque et al., 2023).

The very frequent presence of bronze workshops associated with iron objects suggests that this cannot be a coincidence.

The diversity of objects is very limited and these are objects of everyday use. The knife is, as in the eastern Mediterranean, the most common object. Part of the explanation would be that it is technically the easiest item to make; one can start from a small piece taken from the furnace bottom and make a blade without it being necessary to weld a second piece to it. Oxidation of iron being quite easy, welding two pieces of iron requires a new know-how.

Throughout the Mediterranean world, the oldest smelted irons became frequent (but not yet very widespread) in the eleventh century even if one can think that this metallurgy began in the twelfth century (objects more or less well dated and not analyzed). The discovery of iron smelting was probably made in the eastern Mediterranean world but to date there is no sufficient evidence to be able to establish it precisely. The Portuguese finds must therefore be considered extremely early and geographically exceptional.

For a certain number of reasons, the appearance of (smelted) iron in the eastern Mediterranean was contemporaneous, during the second half of the twelfth century approximately, with migrations of populations among which the "Peoples of the Sea" towards the south, the Phrygians and Armenians to the east, the Sicels and Serdanes to the west, and several peoples from mainland Greece (Achaeans, Dorians, etc.). These migrations would accompany the dispersion of smelted iron in the Near East and throughout the Mediterranean world on a short time scale. Notice

that N. of the Alps iron smelting will appear in the ninth century only.

We can therefore consider that the introduction of iron into Portugal, simultaneously with other Mediterranean influences, is an indirect manifestation of intensive exchanges with peoples from the Mediterranean East mainly via Sardinia, as previously mentioned, that need to be better documented. The existence of contacts, mobility, circulation of products, etc., across the Mediterranean Sea since the 3rd millennium and even before is no longer questionable today. The know-how necessary for the shaping of iron and/or its smelting from ores requires the permanent installation of craftsmen who can pass on a complex know-how that can quickly be assimilated by populations who master bronze metallurgy. This transmission of know-how for iron metallurgy is comparable to the transmission of know-how for turned pottery that we see appearing at the same time in the western Mediterranean, but in Portuguese territory this only occurs from the 8th century, with the Phoenician presence, therefore in the next phase to the one that concerns us here.

The possible integration of these craftsmen would have led to the manufacture of objects partly of local typology. The presence of pre-Phoenician Mediterranean artisans integrated into indigenous communities is a hypothesis previously proposed by Ruiz Gálvez-Priego (e.g. 2008: 39) and which finds additional arguments here.

In the case of iron, the importation of ingots would allow this local shaping very well before smelting be controlled. What arguments can we put forward to support our hypotheses?

It is observed that iron objects are objects of common use and not very diversified, which is characteristic for a new material whose applications are yet to be discovered and tamed at the cost of changing habits. Diversification will come when the metal has been technically and culturally tamed, when its potential has been discovered, starting with its low cost when ore is available, a much more frequent case than for copper, without even mentioning tin.

It has been written that the knives are inspired by what is known in Cyprus and that they were used for animal sacrifices. Without being so precise, the arrival of Mediterranean objects would be associated with a cultural influence, at the level of tastes and ideas. Religious tradition is always very conservative and therefore the use of a new material for animal sacrifices of strong symbolic and cultural value would require further discussion. One could of course argue that meteoritic iron was used for sacrificial knives and then one could have switched from meteoritic iron to smelted iron. However, there are difficulties. In the Iberian Peninsula meteoritic irons are almost absent,

the only notable exception being possibly the Villena hoard. In the Near East, objects of meteoritic iron are better known both from archaeological finds and from texts. It will be noted that these are jewels, prestige objects (royal) but not really cult objects except possibly meteorites which are the subject of a cult as extra-terrestrials (but in this case they are not metallic apparently). No text mentions iron (meteoritic) as an important element participating in sacrifices. The iron knife typically appears as the archetype of the iron object as early as the twelfth century (Waldbaum, 1999). The bronze knives already existed, those of iron imitate them from the typological point of view. The preponderance of knives at that time is probably linked to technical difficulties not yet mastered to manufacture other objects. It will be remembered that all other metals are usually cast and that iron requires specific shaping technique that will have to be acquired. The Portuguese knife is probably not a remarkable import from the eastern Mediterranean, it is first of all a technical evidence and this can be seen as a simple convergence.

If iron were an import material, it would be more profitable to trade in jewelry rather than knives or ingots. We are in fact at a time when iron is not yet essential, so it is a product on which one could make a substantial profit provided that it is desirable, we are not yet in the weapon traffic where technicality is essential and the motivation very different.

If ingots of a rare material were imported, would the priority be to make knives? Wouldn't one make more prestigious objects?

Finally, forging imported iron requires a specific know-how as much as smelting. In the case where the tradition of forging meteoritic iron already existed as in the Near East, only smelting in a furnace is an innovation, but in the case of the Iberian Peninsula no tradition of the use of meteoritic iron is documented. Imagining that the iron was of local origin, however, assumes that ore is available with chemical characteristics compatible with the iron objects of that time, which we will investigate now.

4. THE IRONS ORES OF PORTUGAL

The main resource in Portugal consists of ordovician quartzites, rich in magnetite and located mainly to the north, in the region of Moncorvo (Trás-os-Montes) in particular. These are important deposits both

in terms of their thickness (up to 150 m) and their lateral extension. The iron oxide content is on average low for an ore (37% iron) at the current standard, but the variability is significant and certain levels are sufficiently rich to have given rise to recent exploration permits. The ores pass laterally to iron-poor quartzites. The extension of the Ordovician in the form of folded layers during the Variscan orogen is clearly visible on the geological map (Fig. 5) and a syncline outcrops near Monsanto just one km east of Moreirinha near the village of Salvador (Penamacor). On the satellite pictures a red soil is observed. We sampled the ferruginous layers at the village of Salvador. An initial p-XRF analysis of the sampled blocks confirmed that these rocks had a sufficient Fe content to be considered as an ore. We then carried out laboratory analyzes by ICP-AES (major elements) and ICP-MS (trace elements). The results are presented in Tables 5 and 6.

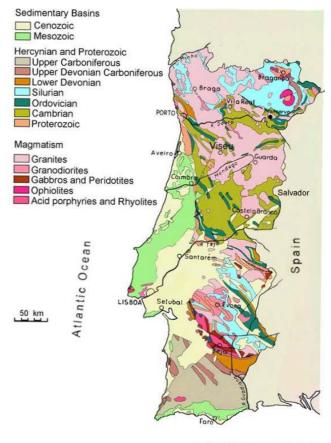


Figure 5. Geological map of northern Portugal highlighting the extension of Ordovician quartzites bearing iron mineralization.

Table 5. Major element analyzes (ICP-AES) for samples from Salvador (A-D), compared to the richest Fe2O3 samples from the Moncorvo region (Urbano, 2018)

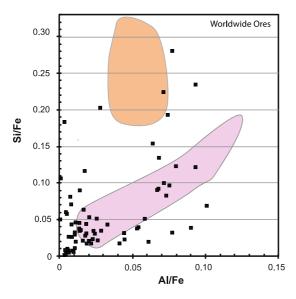
	Salvador				Felgueiras	Reboredo	Mua
	SA	SB	SC	SD	FEL1	SM-039	SM-096
Fe ₂ O ₃ t	73.33	80.81	81.11	73.74	66.96	63.52	68.56
SiO_2	11.72	6.91	5.47	11.93	20.99	27.02	20.41
TiO ₂	0.46	0.14	0.23	0.42	0.13	0.12	0.25
Al_2O_3	6.01	1.41	3.13	6.01	3.38	3.96	5.71
K_2O	1.32	0.11	0.69	1.35	0.45	0.81	1.33
CaO	0.03	<dl< td=""><td><dl< td=""><td><dl< td=""><td>2.67</td><td>0.09</td><td>0.09</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>2.67</td><td>0.09</td><td>0.09</td></dl<></td></dl<>	<dl< td=""><td>2.67</td><td>0.09</td><td>0.09</td></dl<>	2.67	0.09	0.09
P_2O_5	0.95	1.45	1.02	0.73	2.32	1.86	0.88
Na ₂ O	0.05	0.00	0.01	0.02	< 0.01	0.15	0.21
MgO	0.11	0.02	0.05	0.09	0.54	0.05	0.09
MnO	0.03	0.09	0.05	0.03	0.07	0.04	0.04
LOI	6.63	8.12	7.67	4.13	2.28	1.73	1.59
Total	100.66	99.04	99.42	98.46	99.79	99.35	99.16

Table 6. Trace element concentrations (ppm) in Salvador samples and in the Moncorvo ores listed in table 4.

	SA	SB	SC	SD	FEL1	SM-039	SM-096
Sc	7.78	8.83	3.01	7.64			
\mathbf{V}	47.1	24.9	28.5	46.4	230.0	459.0	369.0
Cr	85.0	78.6	62.8	117.4	41.0	50.0	30.0
Mn	269.9	660.1	365.8	206.6			
Co	26.4	47.8	29.4	12.0	10.0		
Ni	114.7	234.8	145.4	81.3	20.0		
Cu	50.3	98.8	38.8	24.7	20.0		
Zn	377.3	605.7	425.0	206.7	130.0		
Ga	12.0	7.8	11.8	9.8	25.6	16.3	8.2
Rb	38.8	4.5	18.4	37.1		50.0	44.7
Sr	33.2	73.9	13.5	57.2	370	423	423
Y	32.5	10.5	7.5	18.7	82.7	78.3	67.6
Zr	169.2	90.2	54.4	133.5	460.0	67.0	49.0
Nb	8.8	2.8	3.8	7.7	14.0	4.0	3.0
Cs	1.7	0.2	0.8	1.6		2.6	3.0
Ba	358.1	598.2	174.5	326.7	179.0	1604.0	642.0
La	30.3	35.3	11.3	31.1	48.6	21.3	18.4
Ce	65.1	54.2	23.5	65.4	108.0	53.2	47.0
Pr	7.34	7.59	2.73	7.54	112.80	6.40	5.40
Nd	26.8	27.2	10.2	28.7	50.7	29.0	24.7
Sm	5.02	6.42	1.87	5.44			
Eu	0.91	1.41	0.30	0.92			
Gd	4.21	7.64	1.42	4.10			
Tb	0.65	0.91	0.21	0.53			
Dy	4.27	3.88	1.23	2.69			
Ho	0.85	0.52	0.25	0.50			
Er	2.20	1.07	0.72	1.40			
Yb	2.43	0.76	0.73	1.43			
Lu	0.29	0.11	0.11	0.21			
Hf	4.74	2.73	1.60	3.99		1.80	1.30
Ta	0.69	0.22	0.31	0.61	1.10	0.20	0.10
Pb	10.21	9.54	5.42	7.83	10.00	0.00	
Th	18.14	9.87	5.93	12.61		4.80	4.40
U	8.81	6.93	10.02	11.34		6.10	5.20

According to their chemical composition it appears that the samples from Salvador are first quality ores, significantly better than the samples from Moncorvo analyzed by Urbano (2018). Reduction of this ore would lead to a slag whose viscosity would be essentially controlled by the incorporation of FeO since the other cations (Ca, K, Na) are virtually absent. It is important to compare the composition of this ore with the Beira Interior artifacts found a few km away. By

plotting the compositions in a Si/Fe vs. Al/Fe it can be seen that there is a similarity between these compositions and those of the artefacts (Fig. 6). On the contrary, the Moncorvo ores located further north show a significantly different composition in terms of the Si/Al ratio (Table 5). We also note that Portuguese ores are rich in P a characteristic of slag inclusions in the iron artefacts analyzed.



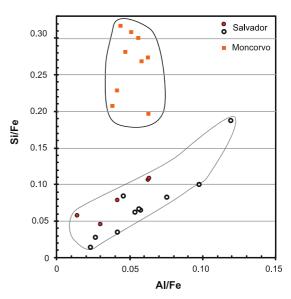


Figure 6. Comparison between iron artifacts (Fig. 3 above) and ores from Salvador (right). In this diagram there is a similarity for Si and Al normalized to Fe for artefacts and Salvador ores. Other ores including Moncorvo (Urbano, 2018) do not match. Iron ores: average values for Australia, Brazil, Canada, China, France, India, Nigeria, Russia, Sudan, Uganda, USA, South Africa, showing that the relationship of Si to Al can vary widely, in particular Moncorvo (Portugal) is quite different from Salvador. Adeleke et al. (2010), Asuke et al. (2019), Bubenicek (1964), Dankwah et al. (2019), Guo et al. (2015), Jiang (2016), Mohanty et al. (2010), Mousa and Ghali (2015), Muwanguzi et al. (2012), Rehren (2001) and Zhiyun (2019).

To strengthen the argument, it is necessary to show that different iron ores have specific signatures as was shown for artefacts from different provenances. We therefore plotted in Fig. 6 the compositions of iron ores from different geographical origins and different geological types. The Salvador ores exhibit the same Al/Fe vs Si/Fe trend as the ions of Beira interior (Fig. 6), this trend being different from that observed for Bronze Age irons of other locations (Fig. 3). According to the geographical proximity Salvador ores are the most likely iron source for the Beira Interior specimens. It is the first time that an iron ore can be connected with Bronze age artefacts.

The multiplication of analyzes to document the variability of ores is important. The geographic and chronological dispersion of the sources collected is such that there is no systematic *a priori* bias, the similarity between two deposits being fortuitous. Several authors have attempted to characterize archaeological irons by the trace elements contained in the metal and in the inclusions of slag with mitigated results.

We carried out the analysis of trace elements in the ores of Salvador which can be compared to those obtained on the ores of Moncorvo (Urbano, 2018). The variability of the trace elements being much greater, it can be seen that the difference is much less clearcut. Only Sr and V appear significantly different. For the other elements either the variability is too great to conclude or the data are missing. The comparison with the traces in the inclusions of the archaeological irons would obviously be interesting but in the state of our current know-how this would require the removal of a fragment from the core of the metal. It is to be hoped that in the near future less invasive analyzes will become possible; we can then compare the ores of Salvador with the iron artefacts in terms of trace elements.

5. CONCLUSIONS

According to our recent work, smelted iron was not discovered before the mid 12th century BC. most likely in the near eastern Mediterranean (Jambon,

2017). Older irons were extremely rare and meteoritic. Beira Interior's irons are dated from the very beginning of iron metallurgy in a place far remote from eastern Mediterranean possibly as soon as the end of the 12th century. Finding such objects in Portugal is therefore a priori surprising because it implies exchanges with the Near East well before the arrival of the Phoenicians, in the phase that Almagro-Gorbea (1993) described as "pre-colonial". In any case, it is important to note that the relations between the western peninsular and the eastern Mediterranean in the post-Mycenaean but pre-Phoenician phase were not necessarily direct but perhaps rather developed through Sardinia (where iron is known precisely since the 12th century B.C.) and with multi-ethnic intermediaries, Cypriots, Sardinians, etc. (Ruiz Galvez-Priego, 1993; 2008).

Moreover, the analysis of these objects rich in slag inclusions and their comparison with iron artefacts from abroad on one hand and local ores on the other unambiguously shows the consanguinity of the two types of materials excluding a foreign origin. The local processing of the ore and the manufacture of these objects therefore becomes a robust hypothesis with strong implications on population exchanges between Portugal and the Middle East, perhaps via the central Mediterranean, at the end of the 12th century, beginning of the 11th, long before the arrival of Phoenician traders, far from the ports that could have served as their trading posts in a region where mining activity was undoubtedly the main attraction and therefore in a socio-economic register unrelated to the activity of those who will be called Phoenicians about two centuries later. This is the first time that Bronze Age irons can be related to a specific iron ore, showing that they are not a by product of copper metallurgy, even though the craftsmen were certainly experienced copper metallurgists.

In summary: the communities had raw material for the manufacture of iron objects; these potential resources are compatible with the chemical signature of the analyzed objects. Other potential iron ores from Portugal or elsewhere, present sufficiently different characteristics to be ruled out and although it can never be said that all possibilities have been considered, the hypothesis of an ore from the region of Salvador which is unique in its compositional characteristics is the strongest hypothesis. The iron artefacts were not traded but elaborated locally, which implies the introduction of the new metallurgy by eastern outsiders. Local communities could have learned iron metallurgy thanks to the presence of locally settled Mediterranean craftsmen; alternatively, local elements might have learned outside. The presence of outsider craftsmen could be explained by the regional mineral wealth in relation to trade towards the Mediterranean.

But in addition to the availability of resources and know-how, it is equally important to ask whether the local communities were socially prepared to develop ironworking. In this case the answer is no, and external cultural influences become necessary. The 12th century Mediterranean was the scene of in-depth disorders in relation to the activity of the Sea Peoples, armed bands moving across the sea and if we are to believe the ancient texts, of various origins. Their establishment in the Eastern and Central Mediterranean could even be traced by Mediterranean influences for which iron is one specific tracer. The question of the route taken for these exchanges in the Iberian Peninsula is usually considered to be a land route from Andalusia, which is in agreement with the absence of signs of violent incursions into the Beira Interior region and of incursions by Sea Peoples in the Iberian Peninsula. The motivation for these exchanges being partly linked to the presence of metallic ores, it would not be surprising if the know-how related to iron metallurgy had been transmitted by this same route. It is important to notice that the smelting of iron in Europe north of the Alps, as far as we know of, did not emerge until two centuries later.

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REFERENCES

Adeleke R. A., Cloete T.E., Bertrand A., Khasa D.P. (2010), Mobilisation of potassium and phosphorus from iron ore by ectomycorrhizal fungi. *World J. Microbiol. Biotechnol.* DOI 10.1007/s11274-010-0372-0

Almagro Gorbea M. (1993) La Introduccion Del Hierro En La Peninsula Iberica. Complutum, 4, pp. 81-94.

- Álvarez Sanchís, J., Lorrio Alvarado, A., Ruiz Zapatero, G. (2016) Los primeros elementos de hierro en Iberia. *Anejos a CuPAUAM*, 2, pp. 149-165.
- Araque Gonzalez R., Bastian Asmus B, Baptista P., Mataloto R., Pablo Paniego Díaz P., Rammelkammer V., Richter A., Vintrici G., Ferreiro Mählmann R. (2023) Stone-working and the earliest steel in Iberia: Scientific analyses and experimental replications of final bronze age stelae and tools. Journal of Archaeological Science 152, 105742.
- Armbruster, B. (2002-2003) A metalurgia da Idade do Bronze Final Atlântico do Castro de Nossa Senhora da Guia, de Baiões (S. Pedro do Sul, Viseu), *Estudos Pré-históricos*, 10-11, pp. 145-155.
- Asuke F., K. A. Bello, M. A. Muzzammil, D. G. Thomas, K. Auwal and S. A. Yaro (2019), Chemical and Mineralogical Characterization of Gidan Jaja Iron Ore, Zamfara State, Nigeria. *Nigerian Journal of Technology* 38, (1), pp. 93 98.
- Barrat J.A., Zanda B., Moynier F., Bollinger C., Liorzou C., and Bayon G. (2012) Geochemistry of CI chondrites: Major and trace elements, and Cu and Zn isotopes. *Geochim. Cosmochim. Acta* **83**, pp. 79-92.
- Bottaini C., Vilaça R., Montero-Ruiz I., Mirão J., Candeias A. (2017) Archaeometric Contribution to the Interpretation of the late Bronze Age "Hoard" Porto do Concelho (Maçao, Central Portugal). *Mediterranean Archaeology and Archaeometry*, 17, 217-231. DOI: 10.5281/zenodo.400779
- Bubenicek L. (1961), Recherches sur la constitution et la répartition des minerais de fer dans l'Aalénien de Lorraine Thèse d'Ingénieur-Docteur- Faculté des Sciences de Nancy.
- Dankwah, J. R., Baah, E. O., Dankwah, J. B., Dankwah, J., Agbenuvor, B. S., Amankwaa-Kyeremeh, B. and Koshy, P. (2019), Production of Iron Nuggets from the Akpafu-Todzi Iron Ore and Artisanal Ferrous Slag using Post Consumer Thermosets (Waste Electrical Sockets) as Reductants. *Ghana Mining Journal*, Vol. 19, No. 2, pp. 41-49.
- Erb-Satullo Nathaniel L., B.J.J. Gilmour, N. Khakhutaishvili. (2014) Late Bronze and Early Iron Age copper smelting technologies in the South Caucasus: the view from ancient Colchis c. 1500-600 BC. *Journal of Archaeological Science* 49, pp. 147-159.
- Guo Dabin Guo, Mian Hu, Chengxi Pu, Bo Xiao, Zhiquan Hu, Shiming Liu, Xun Wang, Xiaolei Zhu (2015), Kinetics and mechanisms of direct reduction of iron ore-biomass composite pellets with hydrogen gas. *International journal of hydrogen energy* 40, pp. 4733-4740.
- Haaland, G., Haaland, R., Rijal, S. (2002) The Social Life of Iron. Anthropos, 97, pp. 35-54.
- Jambon A. (2017) Bronze Age Iron: Meteoritic or not? A Chemical Strategy. *Journal of Archaeological Science*. 88C, 47-53. Doi.org/10.1016/j.jas.2017.09.008
- Jambon A. & Doumet-Serhal C. (2018) La Transition du fer Météoritique au fer Terrestre à Sidon (College Site). *Archaeology and History in the Lebanon,* pp. 82-95.
- Jambon, A. & Kerouanton, I. (2020) Objets en fer de l'Âge du Bronze final. Le cas du lac du Bourget, approche chimique. Journées nationales de l'archéologie, 2017, Aiguebelette. Les Dossiers du Musée Savoisien (on line).
- T. Jiang, L. Yang, G. Li, J. Luo, J. Zeng, Z. Peng & M. Liu (2016) Separation of aluminium and preparation of powdered DRI from lateritic iron ore based on direct reduction process, *Canadian Metallurgical Quarterly*, 55:3, pp. 345-355, DOI:10.1080/00084433.2016.1185837
- Krueger M., Brandherm D., Krueger M. and Niedzielski P. (2021), Archaeometric Analysis of Late Bronze Age and Early Iron Age Pottery from Setefilla (SW Spain), *Mediterranean Archaeology and Archaeometry* 21, 21-36. DOI:10.5281/zenodo.4284405
- Mohanty M, N Kumar Dhal, P Patra, B Das, and P Sita Rama Reddy (2010), Phytoremediation: A Novel Approach for Utilization of Iron-ore Wastes. D.M. Whitacre (ed.), *Reviews of Environmental Contamination and Toxicology*, 29, 206.DOI 10.1007/978-1-4419-6260-7_2, C
- Mousa E. A., S. Ghali (2015), Mathematical Analysis of the Parameters Affecting the Direct Reduction of Iron Ore Pellets. *Journal of Metallurgical Engineering* 4, pp. 78-87. doi: 10.14355/me.2015.04.010
- Muwanguzi A. J. B., A. V. Karasev, J. K. Byaruhanga and P.G. Jönsson (2012), Characterization of Chemical Composition and Microstructure of Natural Iron Ore from Muko Deposits, *International Scholarly Research Network ISRN Materials Science*, 2012, Article ID 174803, 9 p. doi:10.5402/2012/174803
- Rehren T. (2001) Meroe, Iron and Africa. *Mitteilungen der Sudanarchäologischen Gesellschaft zu Berlin* e.V. 12, pp. 102-109.
- Renzi M., Rovira S., Rovira M.C., and Montero-Ruiz I. (2013) Questioning Research on Early Iron in the Mediterranean. In: J. Humphris and Th. Rehren eds: The World of Iron, Archetype Publications, London, pp.178-187

- Rodriguez-Corral J. (2017) Entangled Worlds: Materiality, Archaeometry and Mediterranean-Atlantic Identities in Western Iberia. *Mediterranean Archaeology and Archaeometry*, 17, pp. 159-178. DOI: 10.5281/zenodo.290668
- Ruiz-Gálvez Priego, M. (1993) El ocidente de la Península Ibérica, punto de encuentro entre el Mediterráneo y el Atlántico a fines de la Edad del Bronce. *Complutum* 4, pp. 41-68.
- Ruiz-Gálvez Priego, M. (2008) Writing, counting, self-awareness, experencing distant worlds. Identity process and free-lance trade in the Bronze Age/Iron Age transition. In Celestino, S., Rafel, N., Armada, X.-L. (eds.), Contacto cultural entre el Mediterráneo y el Atlántico (siglos XII-VII ane). La precolonización a debate, Madrid, CSIC, pp. 27-40.
- Sanidas G. M., Y. Bassiakos, M. Georgakopoulou, E. Filippaki, B. Jagou, N. Nerantzis (2016) Polymektos Sideros: à propos du fer en Grèce Antique. *Rev. Arch.* 2, pp. 279-301.
- Schwab R., D. Heger, B. Höppner and E. Pernicka (2006) The Provenance of Iron Artefacts From Manching: A Multi-Technique Approach. *Archaeometry* 48, 3, pp. 433–452.
- Silva, A. C. F., Silva, C. T., Lopes, A. B. (1984) Depósito de fundidor do final da Idade do Bronze do castro da Senhora da Guia (Baiões, S. Pedro do Sul, Viseu). *Lucerna Homenagem a D. Domingos de Pinho Brandão*, pp. 73-109.
- Soler, J.M. (1965) El tesoro de Villena. Excavaciones Arqueológicas en España, 36. Madrid, Ministerio de Educación Nacional.
- Urbano E.E. (2018) Génese do Jazigo de Ferro de Moncorvo e Avaliação do Uso de Equipamentos Portateis de FRX e DRX para a Exploração Mineral deste Tipo de Jazigos. Thèse Université de Tras-os-Montes e Alto Douro.
- Velhuijzen X. and Rehren T., (2006) Iron Smelting Slag Formation at Tell Hammeh (Az-Zarqa), Jordan. 34th International Symposium on Archaeometry 3-7 May 2004 Zaragoza, Spain
- Vilaça, R. (1995) Aspectos do povoamento da Beira Interior (Centro e Sul) nos finais da Idade do Bronze, Trabalhos de Arqueologia 9, 2 vols, Lisbonne.
- Vilaça, R. (2006) Artefactos de ferro em contextos do Bronze Final do território português: novos contributos e reavaliação dos dados, *Complutum*, 17, 81-101.
- Vilaça R. (2013a) L'arrivée des premiers fers dans l'Occident atlantique. Mélanges de la Casa de Velázquez 43 Les transferts de technologie au premier millénaire av. J.-C. dans le sud-ouest de l'Europe. 39-64.
- Vilaça R. (2013b) Late Bronze Age: Mediterranean impacts in the Western End of the Iberian Peninsula (actions and reactions). In Aubet, E., Pau, S. (coord.), *Interacción Social y Comercio en la Antesala del Colonialismo: Los Metales como Protagonistas*, Actas del Seminario Internacional, *Cuadernos de Arqueología Mediterránea*, 2011-2012, Universidad Pompeu Fabra de Barcelona, 21, 13-30.
- Waldbaum, J.C., 1999. The coming of Iron in the Eastern mediterranean: Thirty years of Archaelogical and Technological research in The archaeometallurgy of the Asian World, V.C. Pigott ed. *MASCA Research papers in Science and archaeology* 16, pp. 27-57.
- Yalçın, Ü., 1999. Early Iron Metallurgy in Anatolia. Anatolian Studies 49, pp. 177-187.
- Zhiyun Ji, Yuanjie Zhao, Min Gan, Xiaohui Fan, Xuling Chen and Lin Hu (2019). Microstructure and Minerals Evolution of Iron Ore Sinter: Influence of SiO2 and Al2O3. *Minerals* **9**, 449; doi:10.3390/min9070449.