Iron, copper and tin at Baratti, Populonia: smelting processes and metal provenances

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ABSTRACT: If the role of Populonia-Baratti as one of the most important ironworking centres of Europe in the 1st millennium BC is well documented, information about non-ferrous metal production in the area is still very scanty. We therefore started a detailed research program on four main excavation sites in the Populonia-Baratti industrial zone (Poggio della Porcareccia, Casone, Campo VI and the Baratti beach deposit) with the aim of establishing the types and extent of metallurgical activities for non-ferrous metals (mainly copper and tin), as well as on the provenance of smelted ores in the Etruscan period (c7th-3rd century BC). From analysis of stratigraphic relationships, morphological, mineralogical, textural, and chemical features of metallurgical materials we obtained the following main results:

- *although remaining archeometallurgical evidence at Baratti-Populonia can largely be ascribed to iron production, the existence of an earlier (and partly coeval) copper metallurgy is also well documented, particularly in the Baratti beach deposit*
- *two different types of copper slags, which could be related to different metallurgical steps, have been distinguished*
- *the mineralogical and compositional features of slags from the sites investigated could provide indirect evidence of local bronze production (in agreement with archaeological data), by employment of tin-rich ores*
- *analysis indicates that iron ores came was mainly from Elba and, to a lesser extent, from the Campiglia Marittima district, whereas copper and tin are mostly derived from the latter area*

Introduction

Populonia was an important metal production centre during Etruscan (7th-3rd century BC) and Roman (2nd century BC-1st century AD) times. Such a prominent role was mainly due to its strategic location, midway between the large iron deposits of eastern Elba Island and the polymetallic (Cu-Sn-Pb-Zn-Ag…) ores of the Campiglia Marittima area (*cf* Tanelli 1985; Fig 1). In particular, Populonia has long been regarded as one of the most important early iron production centres in Europe (*cf* classical writers like Livy, Strabo, etc). The huge heaps of slags (probably in excess of 40,000m^3) discharged along the foreshore of the Gulf of Baratti could therefore document a total iron production of some thousands tonnes of iron bloom (up to half a million tonnes according to Voss 1988).

Starting in 1915, and up to the 1960s, tonnes of slags were removed for re-smelting in blast furnaces, thus exposing the beautiful Etruscan necropolis in the Baratti plain, for centuries buried under this slag blanket. As exploitation of Baratti slags went on, it soon became evident that at least part of the slags were from copper, rather than iron, smelting (Dompè 1921, Fossa-Mancini 1922, D'Achiardi 1929). The latter author thus reports a copper content of 0.67-1.21 wt% for these copper slags, to be compared with the lower (but still rather high!) contents of 0.1-0.25 wt% of 'true' iron slags. More recently, Sperl (1980) found and analyzed several copper slags from the Baratti-Casone area and Voss (1988) recognized two different, stratigraphically separate, types of iron slags in the Baratti beach deposit: the lower type-1 slags (small size pieces in stratified horizons), dated to 465±100 BC (radiometric age), and the overlying type-2 slags, mostly fragments of slag-cakes with a diameter of 300-400mm. The occurrence of a 2nd-century BC furnace (170±70 BC, radiometric age) on the top of type-1 slag layers, led Voss (*ibid*) to conclude that type-1 slags (and the furnace) were of Etruscan age (5th-2nd century BC), whereas overlying type-2 slags could be Roman. Later, on the basis of direct observations and a careful review of existing data, Crew (1991) alternatively suggested that:

- a large proportion, if not the majority, of the Baratti beach slags (types I and II) could be indeed from

copper smelting,
- Voss' type-2 slags could be not only Roman, but even medieval in age,
- that some of the iron ore found associated with slags could have been used as a flux for a rather siliceous copper ore,
- the nearby Colline Metallifere could have provided the reserves for both copper and tin, employed for the production of Etruscan bronzes.

In the framework of a research project on Etruscan metallurgical activities at several sites throughout Tuscany (Progetto Finalizzato CNR 'Beni Culturali'), we started a detailed analyses on metallurgical slags found in the 'industrial zone' of Populonia, namely four sites located in the Baratti plain (Fig 1): Poggio della Porcareccia, Casone, Campo VI and the Baratti beach deposit. Archaeological excavations carried out in the late 1970s (*cf* Martelli 1981) at Poggio della Porcareccia led to the discovery of the so called 'Building A', a structure built in three major stages between the end of the 6th and the beginning of the 3rd century BC. The discovery in the lowest archaeological horizons of a pit (interpreted as remains of a tapping furnace) filled with slags and tuyères fragments, put the beginning of iron smelting activity at Populonia back to the 6th century BC (Martelli 1981), *ie* at least a century earlier than previously thought. Unfortunately today this structure is no longer visible, so the only evidence of past metallurgical activity that we could sample and analyse are some scattered fragments of slags from a clayey embankment underneath the late 4th-early 3rd century BC part of 'Building A'. Slags and relics of mineral charge were also collected from the adjoining Casone necropolis, possibly dating from the 4th century BC to the 1st-2nd century AD (*cf* Fedeli *et al* 1993). Recent excavations (1996-7) in the Campo VI area (Fig 1) revealed the existence of large defensive walls (4th-3rd century BC), paralleled by a channel (of unclear significance) some 30m long, 0.8m deep and 1.2m wide. The channel was entirely filled up with abundant metallurgical material, dating no later than the 3rd century BC and including slags, charcoal, furnace lining and mineral charge. Of particular interest were some copper slags and artefacts which are currently being investigated in detail (*cf* Mariani 2000). The remnants of furnace linings have also been analysed, in order to reconstruct the type of iron smelting furnaces employed in Etruscan times (Benvenuti *et al* 1999). Work on a detailed inventory of slags and related material forming the Baratti beach deposit is still in progress. As mentioned above, reports on both slags and remains of ancient furnaces coming from this deposit are known in the literature (Sperl 1980, Voss 1988), but no extensive research on the deposit as a whole (ie detailed stratigraphic analysis associated with mineralogical and compositional study of different materials) has yet been carried out. Therefore we have decided to start a detailed study on the deposit's stratigraphy, aimed at providing accurate data on lateral and vertical variations in type, morphology, size and distribution of the metallurgical material. The deposit is being continuously eroded by sea water. It can currently be followed along the shoreline for about 200m, and is less than 3m high. However, only a small portion of it (about 30m wide) can be safely regarded as relatively well preserved, and this was the target of our study. Selected samples have been taken from several levels within this portion of the deposit. The preliminary results of our research on this site at Baratti are reported below.

Analytical results

Methodology

All the samples were preliminarily analysed for macroscopic features (colour, streak, texture, porosity, specific gravity, etc). Mineralogy of the samples was determined by a combination of optical (binocular, transmitted and reflected light) microscopy, X-ray diffraction (XRD), and SEM/EDS observation. Major and trace metal contents were detected by means of combined X-ray fluorescence, AAS, and classical wet chemical methods. Mineral chemistry of selected phases was determined semi-quantitatively from SEM/EDS

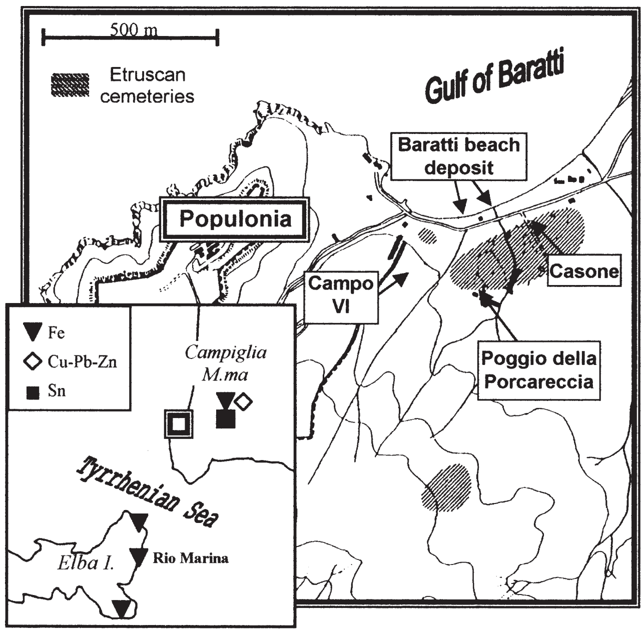

Figure 1: Map of the Populonia-Baratti area showing the sites investigated. The inset shows the main ore deposits of Elba and the Campiglia Marittima district.

Table 1: Main properties of Etruscan slags from Baratti-Populonia.

Features	Iron slags			Copper slags	
	tapped slags	furnace slags	furnace conglomerates	type A	type B
colour	dark grey	dark grey	dark grey	light grey	light grey
texture	flow	uneven	uneven	flow– uneven	flow– uneven
surficial alteration	Fe hydroxides	Fe hydroxides	Fe hydroxides	Cu carb-Fe hydrox	Cu carb-Fe hydrox
inclusions	absent	common	common	absent	absent
porosity	low to medium	high	high	low-medium	low-medium
magnetism	prominent	prominent	low	promiment	prominent
relative density (av)	>4	<4	<3	4	4

spectra, and quantitatively by electron microprobe (Jeol JSM 840, operated at 15kV and 10nA sample current). On the basis of their macroscopic, microscopic and chemical features (Tables 1-3) two main families of smelting slags have been recognized on the basis of metal extracted: iron and copper slags.

Iron slags

On the basis of their textural, mineralogical and chemical features, iron slags can be further subdivided into furnace slags, tapped slags and furnace conglomerates. Tapped slags show typical flow textures and absence (or scarcity) of blowholes while furnace slags have quite uneven, rough surfaces, and commonly contain blowholes and relics of quartz and hematite. Almost all tap and furnace slags are magnetic. As shown in Table 1, densities of furnace conglomerates are definitely lower (<3000kg/m^3) than furnace slags (3-4000kg/m^3) and tapped slags (>4000kg/m^3). The possibility that some of the 'furnace slags' actually represent smithing slags or re-smelted slags will be addressed below.

The iron slags are mainly a silicate groundmass of fayalitic olivine (with up to 1.45% CaO; Fig 2) in an iron-rich interstitial glassy matrix (up to *c*25 wt.% FeO; Fig 3), which in itself is normally a eutectic of anorthite and fayalite. Wüstite, magnetite, hercynite and partially-smelted, relic phases like quartz, hematite and scheelite, occur in variable amounts, and are especially abundant in furnace slags (Fig 4a and Table 2). In tap slags fayalite crystals occur as small laths associated with micrometric dendrites of wüstite, while in furnace slags both minerals show a significant increase in size. Unlike tapped and furnace slags, furnace conglomerates show abundant relics of hematite and quartz and a definitely more silica-rich

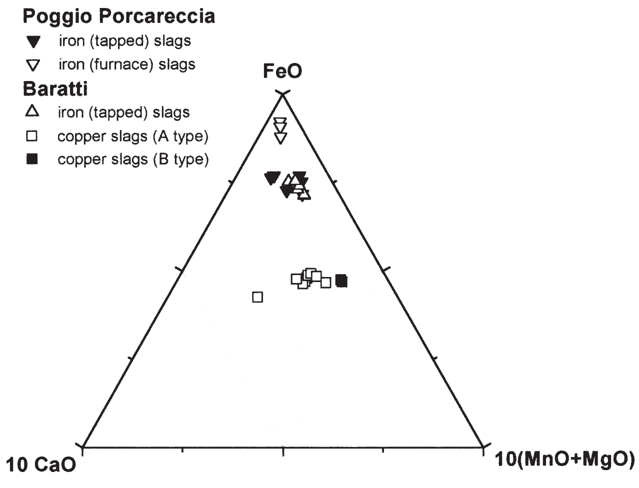

Figure 2: WDS electron microprobe analyses of olivines from iron and copper slags.

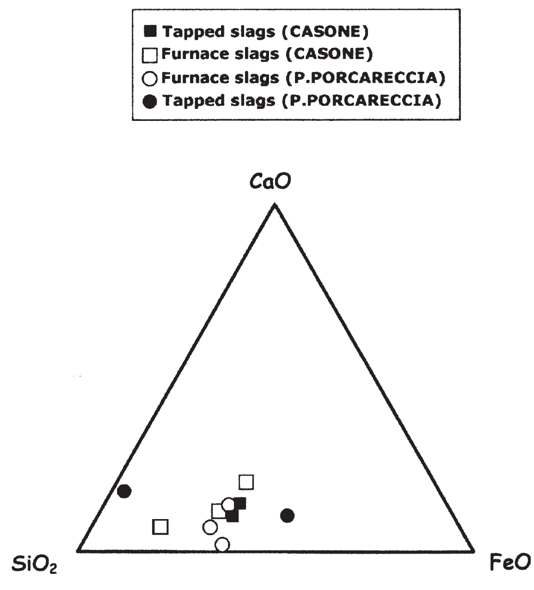

Figure 3: WDS electron microprobe analyses of the glassy matrix of iron slags.

Table 2: Mineralogical features of slags and relic mineral charge.

Description	silicates	oxides	metals	additional phases	groundmass
Iron slags					
Tapped slags	fayalite-kirsch	wüstite (magn)		Fe (Bi)	glassy
Furnace slags	fayalite-kirsch	wüstite (magn, hercinite)	Fe, Fe-Sn (Bi)	quartz, scheelite	glassy
Furnace conglomerates	fayalite	wüstite	Fe (Bi)	quartz, hematite, ilmenite	glassy
Copper slags					
Type A	fayalite, pyrox	magn	Cu, Cu-S		glassy
Type B	fayalite, pyrox	(magn)	Cu-S		glassy
Partially smelted iron ore					
	fayalite	hematite, magn		pyrite, scheelite	glassy
	fayalite	hematite, magn, wüstite		quartz, Fe-hydr	glassy
	fayalite	magn, wüstite		quartz, scheelite, Fe-hydr	glassy
Mineral charge					
		hematite		pyrite	
		hematite, magn		pyrite, Fe-hydr	
		hematite, magn		pyrite, Fe-hydr	

Note: kirsch = kirschsteinite, pyrox = pyroxine, mag = magnetite, Fe-hydr = iron hydroxides,

(and FeO-poor) glassy groundmass (see Fig 3).

In addition to silicates and oxides, all types of iron slags almost invariably contain droplets of metallic iron. A number of slags, quite similar to other iron slags, are more or less enriched in tin (see below for details) and may contain micrometric globules of iron-tin alloys (Fig 4b). Such inclusions are very small in size, around 5µm, and approximate to FeSn and $FeSn_2$ in composition (quantitative SEM/EDS analyses). The occurrence of metallic bismuth is also reported from a few iron slags.

In the ternary diagram anorthite-FeO-SiO_2 (Fig 5) iron tapped slags preferentially fall in the fayalite, low-melting field, and show no significant differences from Etrusco-Roman iron slags from Elba (data from Benvenuti *et al* 1996). Compositions for furnace slags are not unexpectedly more widely scattered, in that they do not represent an equilibrium conditions. In summary, iron slags of Etruscan age from Baratti-Populonia show the following features (*cf* Tables 1-3 and Figs 5-6):

- in general there are no major compositional differences between analyzed tap and furnace slags. The latter may either be lower than tap slags in silica and alumina (Casone) or slightly enriched in these and other oxides, like CaO, K_2O, and MnO (Poggio della Porcareccia), or, finally, almost indistinguishable, such as in the Baratti beach deposit, where only the volatiles content (loss on ignition) is higher in furnace slag than tap slag;
- metal contents of iron slags are normally low, except for a few samples (randomly distributed on all four sites) which show highly variable, but still anomalous tin contents (± other non-ferrous metals, notably copper, lead and zinc; Fig 6). Compared with our data, Sperl's (1980) 'iron slags' have definitely higher copper contents (see Table 3);
- the enrichment in tin (and other metals) is apparently not related with different types of slag, although the highest tin contents are shown by some furnace slags (see Fig 6);
- tin-rich and tin-poor tapped slags do not show appreciable differences in bulk composition;
- the highest tin contents have been detected at Campo VI (up to 3750 ppm tin; *cf* Mariani 2000) and in the Baratti beach deposit (up to 835 ppm), whereas in the CR1 zone at Poggio della Porcareccia slags with constantly anomalous (up to 222 ppm) tin contents are particularly abundant (Strillozzi 1998).

Copper slags

Copper slags have been found only in the Baratti beach deposit and within the Campo VI channel. They are easily distinguishable from iron slags based on their external properties (Table 1) and mineralogical features

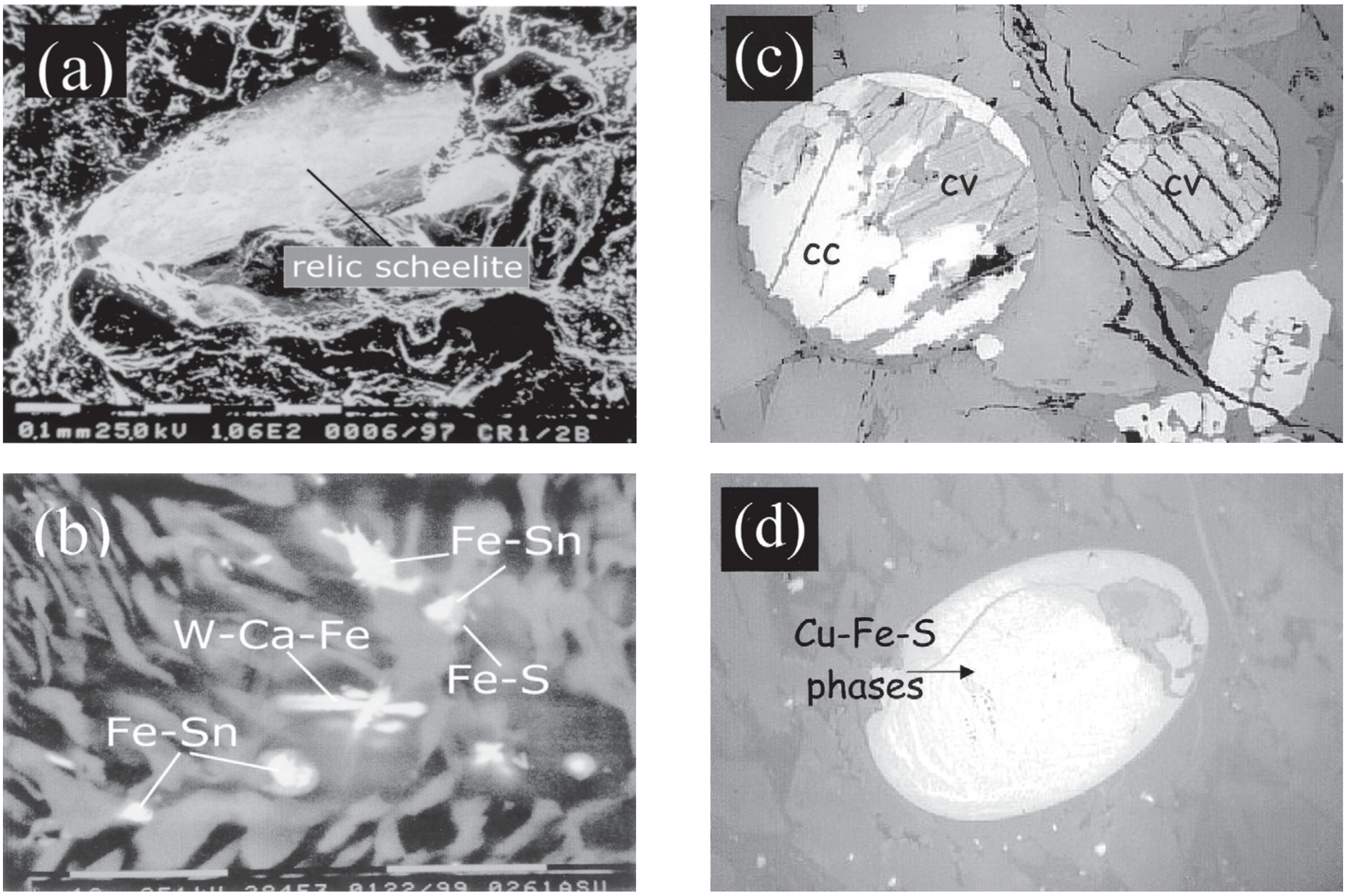

Figure 4: (a) Backscattered image of a furnace slag, showing a grain of relic scheelite. Scale=10µm. (b) Backscattered image of partially smelted mineral charge showing globules of iron-tin phases (white), sometimes surrounded by an iron-sulphur phase (~FeS_2 composition). Notice also the dendritic habit of 'scheelite-like' phases (centre). The groundmass is composed of a glassy matrix and acicular crystals of hedembergitic composition. Scale=10µm. (c) Sulphidic droplets in type-A copper slags. cc=chalcosite-djurleite, cv=covellite. Width of field c500µm. (d) Type-B copper slags showing exsolution textures among copper-iron-sulphur phases. Width of field c150µm.

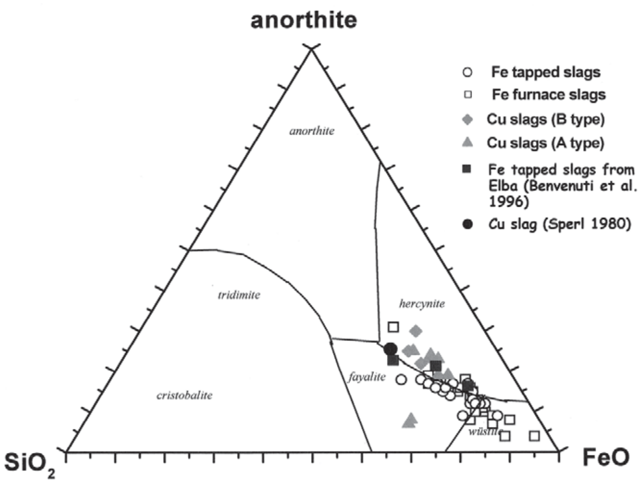

Figure 5: Composition of iron and copper slags from Populonia-Baratti in the anorthite-SiO_2-FeO ternary diagram following Bachmann's (1980) recalculation method. Chemical compositions of three tapped slags from Etrusco-Roman metallurgical sites on Elba (Benvenuti et al 1996) and one copper slag from Baratti (Sperl 1980) are also included for comparison.

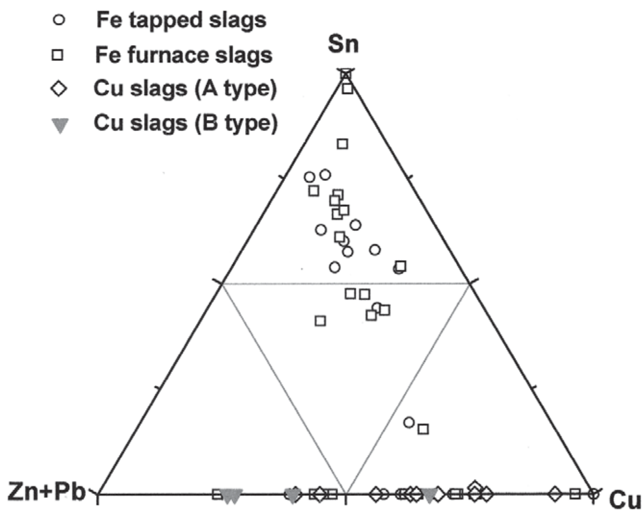

Figure 6: Non-ferrous metal contents of iron and copper slags expressed in terms of the ternary diagram Sn-(Zn+Pb)-Cu.

Table 3: Chemical composition of Populonia slags and mineral charge fragments

Provenance	Description	N		Oxides											Metals			
				SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	MnO	CaO	Na_2O	K_2O	P_2O_5	Cu	Pb	Zn	Sn
Iron slags																		
Poggio della Porcareccia	Tapped slags	11	m	18.1	0.16	4.65	60	13.37	0.55	0.17	2.01	0.21	0.68	0.1	34	9	20	72
			s	2.67	0.04	1.14	3.25	5.17	0.08	0.05	0.39	0.07	0.18	0.02	10	6	8	41
	Furnace slags	5	m	15.14	0.12	3.39	53.84	25.13	0.36	0.08	1.25	0.14	0.45	0.09	46	20	30	153
			s	4.53	0.05	1.50	8.09	12.24	0.22	0.04	0.72	0.11	0.28	0.05	12	4	6	68
Casone	Tapped slags	4	m	24.68	0.20	6.83	57.25	7.21	0.5	0.17	1.94	0.32	0.79	0.13	43	16	31	152
			s	3.56	0.04	0.67	7.65	4.93	0.1	0.08	0.53	0.06	0.08	0.03	10	5	6	18
	Furnace slags	5	m	21.43	0.16	5.50	56.74	10.81	0.55	0.15	3.42	0.31	0.76	0.18	44	<dl	25	67
			s	6.80	0.03	1.28	8.2	4.40	0.17	0.03	2.68	0.25	0.37	0.11	12	-	7	16
Baratti beach deposit	Tapped slags	3	m	13.85	0.11	3.63	65.33	13.08	0.34	0.09	2.11	0.30	0.64	0.08	51	106	24	532
			s	2.13	0.03	0.94	3.36	6.1	0.1	0.03	0.76	0.08	0.14	0.02	32	77	11	375
	Furnace slags	6	m	14.94	0.12	3.95	57.22	19.39	0.39	0.13	1.74	0.41	0.52	0.10	71	51	59	248
			s	1.84	0.02	0.65	3.78	6.45	0.08	0.03	0.97	0.07	0.24	0.03	56	66	52	305
Populonia*		3	m	13.63	-	2.63	78.47	-	0.63	0.13	1.73	-	-	0.23	253	-	-	-
			s	4.34	-	0.67	7.21	-	0.21	0.06	1.82	-	-	0.18	91	-	-	-
Copper slags																		
Baratti beach deposit	Type A	9	m	24.79	0.03	1.49	41.58	19.64	0.37	1.51	7.09	0.18	0.28	0.05	16258	192	6427	<dl
			s	2.44	0.02	0.25	3.22	4.96	0.11	0.52	2.89	0.05	0.09	0.01	13889	81	3052	-
	Type B	4	m	26.79	0.05	1.85	36.63	19.05	0.62	1.77	9.88	0.27	0.46	0.00	5573	176	8853	<dl
			s	0.59	0.02	0.20	1.33	2.21	0.26	0.1	1.89	0.12	0.25	0	1862	216	3648	-
Campo VI		1	m	27.95	0.06	2.00	27.77	26.95	1.1	1.83	9.79	0.27	0.2	0.07	9583	466	3920	<dl
Populonia*		2	m	25.05	-	2.88	58.48	-	1.13	0.98	8.75	-	-	0.43	630	-	-	-
			s	14.29	-	0.99	26.47	-	1	0.96	9.25	-	-	0.44	554	-	-	-
Other materials																		
Casone	mineral charges	3	m	1.68	<dl	0.76	7	91.65	0.18	0.06	0.19	0.19	0.05	0.05	54	52	56	525
			s	1.07	-	0.78	3.11	6.94	0.12	0.02	0.09	0.11	0.03	0.03	17	3	36	-
	partially smelted ore	3	m	4.76	0.05	1.82	44.33	47.32	0.16	0.04	0.67	0.11	0.29	0.06	69	32	48	386
			s	3.94	0.04	1.30	26.52	29.31	0.08	0.02	0.33	0.08	0.36	0.04	59	20	53	255

Note: the values are the mean (m) and standard deviation (s) of N samples. Oxides are wt% and metals ppm. * data from Sperl (1980)
<dl = below the detection limit.

(Table 2). Preliminary analyses of the Baratti beach slag deposit led to the recognition of two main types of copper slags: type-A and type-B slags (Chiarantini 2000). Type-A copper slags are characterized by a groundmass of dominant olivine, pyroxene, magnetite, and minor glass, with abundant metallic droplets, mostly fine aggregates of metallic copper, copper oxides (cuprite) and sulphides (covellite, chalcocite/dijenite) (Fig 4c). In type-B copper slags magnetite and cuprite are much less abundant, metallic copper is consistently absent, and the metallic globules (100-150mm in size) are mainly copper-iron-sulphur phases (matte) showing fine exsolution textures (Figure 4d). Both types of copper slags have high copper and zinc contents, but no or very low amounts of tin (Fig 6). Compared with iron slags from elsewhere at Baratti, both types of copper slags from the Baratti beach deposit are much more lime- and manganese-rich. In particular, olivines in type-A slags may contain up to 5.3 wt% CaO and 2.9 wt% MnO, whereas those in type-B copper slags show maximum contents of 3.1 wt% CaO and 3.2 wt% MnO (see also Fig 2).

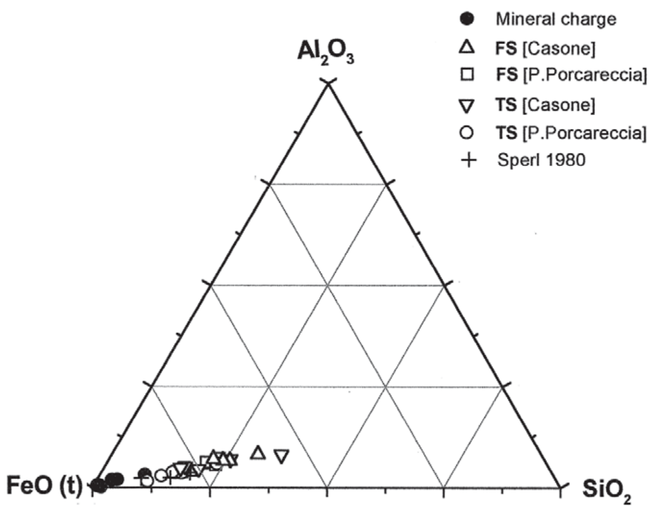

Figure 7: Composition of relic ore fragments from Casone and iron slags from Poggio della Porcareccia and Casone sites in the FeO (total)-SiO_2-Al_2O_3 ternary diagram. The linear trend points to a 'genetic' relation between ores and slags (cf Kresten 1984).

Relic ore fragments

In the Casone area a few fragments of mineral charge have been found and analysed in detail (Rescic 1998). Their most relevant mineralogical and compositional features are given in Tables 2-3. Three samples appear to be fragments of mineral charge, mostly composed of iron oxides (hematite and/or magnetite) with variable amounts of pyrite, iron hydroxides and other phases.Two of these samples contain both massive and octahedral magnetite, partly replaced by hematite, while in the third sample lamellar hematite is associated with pyrite. Three further samples probably represent partially smelted ore fragments; they contain fayalite, wüstite and a glassy matrix. In one case droplets of iron-tin phases quite similar to those previously described for iron slags occur in association with 'scheelite-like', tungsten-calcium-iron pyrometallurgical phases. Micrometric to millimetric fragments of various phases (sphalerite, chalcopyrite, etc) and bronze are frequently observed to adhere strongly to the surface of mineral charge fragments, as well as on blowholes in the slags. The presence of bronze scale may be due to fracturing and alteration of bronze artefacts, commonly found mixed with slags during the excavation works.

Following Kresten's (1984) approach, one can test on a semi-quantitative basis whether the fragments of mineral charge found at Casone and elsewhere in the Baratti plain are actually representative of the ore used in the iron smelting process. In the system Al_2O_3-FeO-SiO_2 the chemical compositions of the analysed slags and ores plot along a straight line through the FeO apex (Fig 7), thus indicating that the slags could be derived from such iron ores.

Smelting processes

Iron smelting

Most Etruscan iron slags from Populonia-Baratti sites may be ascribed to iron smelting. The relative abundance of tapped slags, often found associated with fragments of tap holes and evacuation channels, points to the use of slag-tapping furnaces, made up of sandstone linings covered with hard burnt clays (Benvenuti *et al* 1999). It is possible, however, that later on (or possibly even contemporaneously) non-slag-tapping furnaces were also used (*cf* Voss' (1988) furnace).

Mass balance calculations indicate that when considering the average composition of iron slags from the various sites at Baratti and that of the ore fragments found at Casone (see Table 3), the iron slags are significantly enriched in SiO_2, Al_2O_3, CaO, and K_2O (by factors of, respectively, 10.9, 6.2, 11.1 and 13); this could possibly indicate some incorporation of material from the furnace structure. By considering the average slag:ore enrichment factor for the above four oxides (7.27), the following relationship can be proposed for iron reduction at Baratti (*cf* Leroy 1997, Cucini Tizzoni 1999):

727g ore + Xg charcoal + Yg flux = 100g slags + 437.1g iron

In other words, to obtain 100g of iron about 166g of ore had to be smelted and about 23g of slags were produced. Although this can be only regarded as a rough estimate (for instance, the influence of lining material and/or flux is not taken into consideration), we obtain a total yield of about 60 % which would indicate a rather efficient process.

Non-ferrous metal smelting

One of the most interesting features so far detected in many of our slags (particularly those taken from Poggio della Porcareccia) is the presence of iron-tin alloys ranging in composition from FeSn to 'hardhead', $FeSn_2$. As mentioned above, tin occurs exclusively within otherwise common 'iron slags', but never in copper slags. The presence of iron-tin intermetallic compounds is also reported from slags related to tin metallurgy, like those from Cavalhelhos (Portugal), an Iron Age settlement of the 8th century BC- 2nd century AD (data by Tylecote, in Miles 1975). However, the overall low tin contents of analysed slags (constantly below 1000 ppm, except for one sample from Campo VI, containing about 0.38 wt% Sn) apparently rules out a link with tin smelting. On the other hand it should be emphasized that the data so far available in the literature are very scarce (*cf* Tylecote 1987: Table 8.9, Abraham and Morasz 1997: 224), and not completely unambiguous, if one thinks that 'most of the so called tin-slag is nothing more than weathered tin ingot material' (Tylecote 1987: 308). Therefore, further research in the Populonia-Baratti area is necessary to better define the extent and metallurgical meaning of this 'tin anomaly' in what would otherwise appear to be iron slags. At this preliminary stage of the research, we can temptatively draw three hypotheses, not necessarily mutually exclusive:

- tin smelting was carried out at Populonia, probably near the Poggio della Porcareccia area, between the end of the 6th and the beginning of the 3rd century BC (and very likely even later on). If both tin and iron were produced by independent smelting, the slags derived from such processes could have been re-utilized as charge for the production of additional iron. In this case, the slags analysed here could represent the waste material of the latter process;
- Tin-rich 'furnace slags' could actually represent smithing slags, where the metal impurities were introduced during the final stages of a smith's work (*eg* during the production of polymetallic objects, see Seernels (1994) for a discussion), although the overall mineralogical and chemical features, namely the low total metal contents, seem to conflict with this hypothesis;
- the observed anomalous tin content could be due to the utilization of iron ore containing some tin minerals (cassiterite, stannite), which would indicate a provenance for the ore in the Campiglia Marittima district (see below); during the iron smelting processes the tin present in the mineral charge would bind with some iron forming the observed iron-tin alloys.

The discovery of layers rich in copper slags at the bottom of the Baratti beach deposit is consistent with a significant production of copper at an early stage (6th-5th century BC, or even earlier), followed by a progressive increase in iron production, which probably reached its peak in the 4th-1st century BC, as indicated by both archaeological and documentary evidence (Corretti and Benvenuti, in press). A multi-stage copper smelting process may have been carried out, with type-B slags belonging to an earlier (matte production) stage than type-A slags. The abundance of zinc (3180-12300 ppm) and lead (50-500 ppm) indicates that a polymetallic sulphidic ore was utilized. The Campiglia Marittima district would be again the most suitable source region for non-ferrous metals, ie copper, lead and tin.

Metal provenance

The mineralogical and compositional features of our slags and relics of mineral charge point to two sources of metals: the island of Elba and Campiglia Marittima. It is commonly thought that iron ores from Elba have been actively exploited since the early first millennium BC, even if the evidence of this is often ambiguous. According to Corretti and Benvenuti (in press), it is reasonable to think that exploitation of Elban ores reached a climax during the 7th century BC, since this is the period in which at Populonia, as well as in many other mining districts of southern Tuscany, iron weapons and artefacts occur in great numbers. Thus the occurrence of hematitic ores (with typical lamellar habits) at Casone and Poggio della Porcareccia is not surprising, and can be safely assumed to indicate a provenance of iron ore from the Rio Marina type deposits in NE Elba. What is less common is the presence of magnetite-rich ore (two of the samples from Casone) which could still indicate an Elban provenance, but from the SE ores of the Mt Calamita type (*cf* Benvenuti 1996).

On the other hand, we have several other indicators that support a provenance of smelted ore from the Campiglia Marittima district. They include:

- the anomalous tin contents of many slags;
- the occurrence of metallic bismuth and relic scheelite in the glassy groundmass of some slags;
- the relatively common presence, for example at Casone and Campo VI, of base metal sulphides (chalcopyrite, sphalerite, bornite, stannite, etc) in the mineral charge fragments.

In fact, minerals containing tin, bismuth and tungsten are very rare on Elba, but relatively common in the Campiglia Marittima district (*eg* the M Valerio deposit of iron oxyhydroxides and cassiterite (Venerandi-Pirri and Zuffardi 1981)). It is not clear, at the present state of our knowledge, if this non-ferrous metal anomaly may be attributed to the exploitation of gossan-like deposits (dominant iron hydroxides with minor non-ferrous metal phases), lenses of iron oxides and hydroxides with scattered cassiterite grains or, alternatively, the copper-lead-zinc-iron skarn deposits. All these three kinds of ore deposits are known to occur in the Campiglia Marittima district (*cf* Tanelli *et al* 1993). One possibility is that the Etruscans employed both the iron rich ores (gossans and/or the lenticular deposits) from Campiglia Marittima for iron production, and, possibly at the same time, the non-ferrous metal resources of the same district for the production of bronze artefacts, copper and lead. It is hoped ongoing research on the lead isotope composition of slags and mineral charge will throw light on the provenance of ores smelted at Baratti-Populonia by the Etruscans.

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