

Characterization of metallic artefacts from the Iron Age culture in Campania (Italy): a multi-analytical study

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Abstract. — Sixteen archaeological findings of Iron age from three sites in the Campania region have been examined for their mineral components, chemical and Pb-isotope composition by a multi-technique approach (XRD, SEM-EDS, ICP-MS, AAS and LIRMS). Mineralogical analyses have emphasized the occurrence of three types of objects, Pb- and Cu-based artefacts and finds made of Fe-bearing phases. Qualitative and quantitative chemical analyses have allowed the characterisation of different elements from the metal and slag objects. Pb-isotope signatures suggest a wide range of possible provenances of the source ores throughout the Mediterranean realm. The results are discussed in relation to mineral characterization, to some aspects of local metallurgical techniques and metal source areas.

Riassunto. — Sono state esaminate le caratteristiche mineralogiche, chimiche e isotopiche di sedici reperti risalenti all'Età del Ferro provenienti da tre siti archeologici della Campania, tramite un approccio multianalitico (XRD, SEM-EDS, ICP-MS, AAS e LIRMS). Le analisi mineralogiche hanno evidenziato la presenza di tre tipologie di manufatti, reperti a piombo e rame prevalente e reperti con

fasi ricche in ferro. Le analisi chimiche qualitative e quantitative hanno premesso la caratterizzazione dei diversi elementi presenti negli oggetti metallici e nelle scorie. I dati isotopici del piombo suggeriscono un ampio spettro di possibili provenienze concernenti i giacimenti originari nell'ambito del Mediterraneo. I risultati sono discussi in relazione alla caratterizzazione mineralogica, ad alcuni aspetti delle antiche tecniche metallurgiche e alle possibili aree di provenienza dei metalli.

Key words: *Southern Italy; Campania; Iron Age culture; archaeological metal artefacts; mineral assemblages; chemical composition; lead isotope ratios.*

Introduction

It is well known that a great abundance of metallic artefacts and fragments of scrap-metals occur in several archaeological sites in the Campania region (Southern Italy), bearing witness of local metal working activities throughout several cultures. Nevertheless, detailed mineralogical and geochemical studies aimed to clarify the composition of the objects and raw materials of prehistoric and historical times found in this region

are still quite scarce. Since the 18th century several analytical methods have been used to identify the chemical composition of the archaeological artefacts and the technology involved in their production. In the last decades the analyses have been carried out with many techniques, like X-ray fluorescence and diffraction and/or microdiffraction, scanning electron microscopy, SEM and microprobe, mass spectrometry and other spectroscopy techniques (i.e. Freestone and Middleton, 1987; Corsi *et al.*, 2005; Kuleff, *et al.*, 2006; Maggetti and Messiga, 2006; Rapp and Hill, 2006; Schwab *et al.*, 2006; Zasztovszky, *et al.*, 2008).

The characterization of the archaeological artefacts is also aimed to the study of the production of metals in antiquity, as well as the processing and smithing technologies (Pernicka, 2004 and references therein), and to detect the source of the raw materials used in their manufacture for investigating on trade exchanges and other form of cultural interactions (Craddock, 1995; Pinarelli, *et al.* 1995; Stos-Gale *et al.*, 1997; Tykot, 2004). The geological source areas of most metals objects can be mainly established by their elemental and isotopic composition and ratios. In particular, the lead isotopes have been extensively used in archaeometry and archaeometallurgy to trace the provenance of metal ores, because they are not fractionated during ore processing (Gale and Stos-Gale, 2000). However, it can be also considered that lead isotope signature of the ore districts may overlap considerably (Degryse *et al.*, 2007 and reference therein). Many works have been devoted to this topic in the last years (e.g. Stos-Gale *et al.*, 1995, 1996; Chalkias *et al.*, 1988; Rohl, 1996; Sayre *et al.*, 2001; Ceyhan, 2003; Niederschlag *et al.*, 2003; Santos Zalduegui *et al.*, 2004; Höppner *et al.*, 2005; Wilkinson *et al.*, 2005). More recently, isotope ratios of other metals have been exploited for archaeological provenance aims, such as tin, copper, osmium, zinc, iron and gold (Begeman *et al.*, 1999; Junk and Pernicka, 2003; Klein *et al.*, 2004; Rehren and Pernicka, 2008; Eugster *et al.*, 2008).

As regards southern Italy, it is known that Campania and surrounding areas do not have metallic ore deposits, so most of the metals used in antiquity have been necessarily imported from other countries, likely throughout in the Mediterranean realm. For this area, Pb-isotopic studies are widely

dedicated both to the genesis of ore deposits in the Mediterranean basin (e.g. Lattanzi *et al.* 1992, 1994, 1997; Arribas and Tosdal, 1994; Boni and Köppel, 1995; Velasco *et al.*, 1996; Jebrak *et al.*, 1998) and to archaeological provenance studies (e.g. Boni *et al.*, 1998, 2000a, b; Begemann *et al.*, 2001; Balassone *et al.*, 2002).

In the present research we have applied several bulk analytical techniques, such as X-ray powder diffraction (XRD), scanning electron microscopy and energy dispersive spectrometry (SEM-EDS), inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS), as well as lead isotope ratio mass spectrometry (LIRMS), to the characterization and provenance study of a set of metallic artefacts from Iron age cultures in the Campania region.

The Archaeological context and the MATERIALS studied

In the Campania region various sites of the Iron Age culture occur (Fig. 1). Their ages range generally span between the IX and the VIII century B.C. The archaeological artefacts investigated in this study come from three Iron Age sites: 1) Longola-Poggiomarino (near Pompeii), 2) the Sarno river valley and 3) the Castel Vetrano necropolis (near Salerno).

The Longola-Poggiomarino protohistorical village was discovered in the year 2000 along the Sarno river not far away (almost 10 km) from the ancient estuarine area, which is located nearby the harbour of the roman town of Pompeii. The site has been thoroughly investigated by drilling and digging of trenches (Albore-Livadie and Cicirelli, 2003). It has been inhabited from BM3 and the late Bronze Age. Current investigations are concerned with the stratified sections belonging to the early Iron Age and to the *Orientalizing* period, until the early twenty years of the VI century B.C., when the site was definitely abandoned (Cicirelli *et al.*, 2006). This is the first protohistoric village discovered in this area; other two similar nearby sites are currently under investigation. The Longola-Poggiomarino settlement occurs in a wet environment strongly controlled by human activity. A great abundance of metallic objects has been found; few objects have been also encountered

in the dwellings and the surrounding areas. The objects display a variety of types and diversified materials (lead, bronze, iron and gold), pointing to several distinct working/smelting sites throughout the village. In these working sites, fair evidences of heating have been detected on several materials. The numerous metallic objects found at Longola-Poggiomarino include several metal scraps, half-worked parts, small rods, filaments and working tools, while many smelting slags have been also found mostly in the sandy sediments corresponding to the infill of the main channel cutting through the village. The slags are mainly derived from bronze casting. Some small lead ingots have been also recorded.

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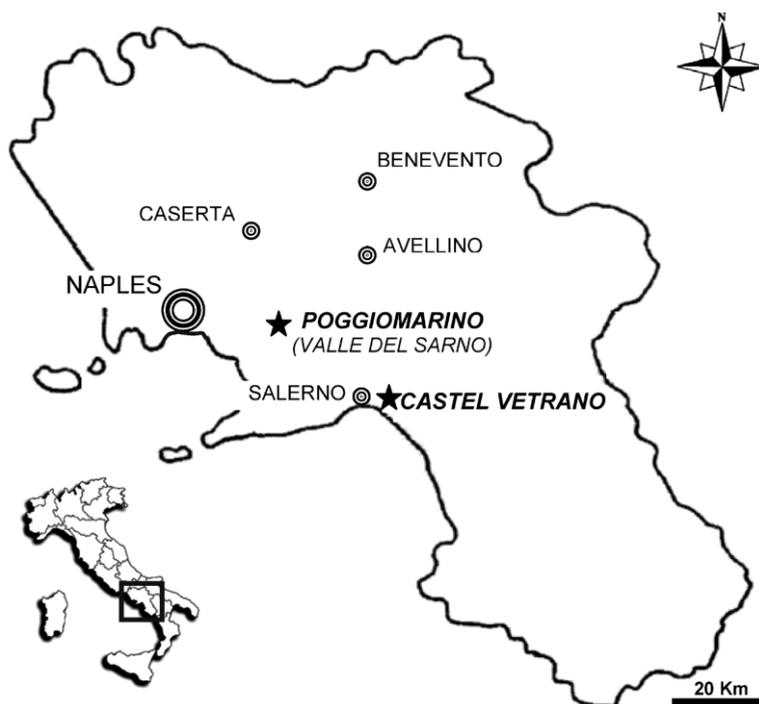


Fig. 1 – The sampling localities of this study, Campania region (Italy).

several distinct working/smelting sites throughout the village. In these working sites, fair evidences of heating have been detected on several materials. The numerous metallic objects found at Longola-Poggiomarino include several metal scraps, half-worked parts, small rods, filaments and working tools, while many smelting slags have been also found mostly in the sandy sediments corresponding to the infill of the main channel cutting through the village. The slags are mainly derived from bronze casting. Some small lead ingots have been also recorded.

Many other necropolises and graves of comparable ages are known in the Sarno valley. In this area more than hundreds graves have been discovered, spanning in time between the second half of IX century B.C. and VI century A.D. (de' Spagnolis, 2001, 2006).

Close to the towns of Salerno, Benevento and Caserta many areas are also known to host Iron Age cultures (D'Agostino and Gastaldi, 1989; Gastaldi, 1998; Johannowsky, 1994). In the municipality of Salerno two large Iron Age necropolises have been discovered during the preliminary geoarchaeological prospections, requested by the Superintendence of Salerno before starting a new

phase of road workings for the Salerno-Reggio Calabria motorway. The necropolises date back to the second half of the 8th century B.C. and consist of pit graves delimited and covered by cobbles, where the body was laid in a supine position. The funerary set is made of *impasto* pottery and of bronze and iron ornaments, mainly *fibulae*. In one of the graves, set in the Castel Vetrano necropolis, several well-preserved leaden objects were found (Fig. 2).

A total of 16 samples with different typologies have been considered for the present work. The detailed description and localization of each sample is reported in Table 1, and the most representative artefacts are shown in Fig. 3. Taking into account their macroscopic features, they consist of lead- and copper-rich objects and slag fragments. Most of the investigated specimens were collected in *Trench A* (samples A1a, A1b, A1c, A2, A3, A5a, A5b, P05-10) and *Trench B* (samples B1, B2, B3 and B4) of the Longola-Poggiomarino settlement.

The specimen named P05-4 has been sampled from a necropolis of the Sarno valley. It consists of a lead fragment with a withish patina.

Two lead artefacts in form of small animals were collected in the tomb T88 of Castel Vetrano,

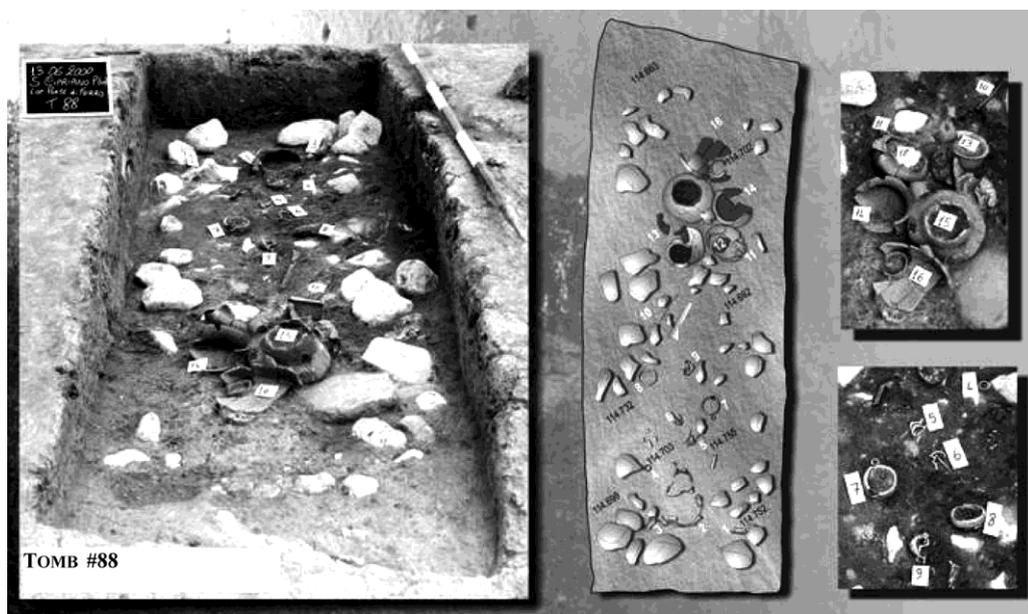


Fig. 2 – The Castel Vetrano necropolis, Tomb #88. On the right the funerary set.

Table 1
Label, composition and localization of the analysed samples at the archaeological site

<i>Sample</i>	<i>Localization</i>	<i>Materials</i>	<i>Methods*</i>
A1a	Longola-Poggiomarino - Trench A - US 30 US 28	Lead plate	XRD, ICP-MS, LIRMS, SEM-EDS
A1b	Longola-Poggiomarino - Trench A - US 30 US 28	Small leaden scrap	XRD, ICP-MS, LIRMS, SEM-EDS
A1c	Longola-Poggiomarino - Trench A - US 30 US 28	Small leaden scrap	XRD, ICP-MS, SEM-EDS
A2	Longola-Poggiomarino - Trench A - US 21 QD6	Small leaden scrap	XRD, ICP-MS, LIRMS, SEM-EDS
A3	Longola-Poggiomarino - Trench A - US 19 QC2	Flat lead fragment	XRD, ICP-MS, LIRMS, SEM-EDS
A4	Longola-Poggiomarino - Trench A - US 99 QD2	Copper scrap	XRD, ICP-MS, LIRMS, SEM-EDS
A5a	Longola-Poggiomarino - Trench A - US 21 B QA7	Lead scrap	XRD, ICP-MS, LIRMS, SEM-EDS
A5b	Longola-Poggiomarino - Trench A - US 21 B QA7	Lead scrap	XRD, LIRMS, SEM-EDS
P05-10	Longola-Poggiomarino - Trench A - US 771 MAF 14	Lead scrap	XRD, ICP-MS, LIRMS, SEM-EDS
B1	Longola-Poggiomarino - Trench B - US 2010 QM7	Spongy, dark brown slag	XRD, ICP-MS, AAS, LIRMS, SEM-EDS
B2	Longola-Poggiomarino - Trench B - US 2009 QP8	Leaden object	XRD, ICP-MS, LIRMS, SEM-EDS
B3	Longola-Poggiomarino - Trench B - US 2010 QM4	Leaden object	XRD, ICP-MS, SEM-EDS
B4	Longola-Poggiomarino - Trench B - US 2010 QM4	Spongy, dark brown slag	XRD, ICP-MS, AAS, LIRMS, SEM-EDS P05-
4	Sarno Valley - Necropolis # 20946-121096	Lead scrap	XRD, ICP-MS, LIRMS, SEM-EDS
A-T88	Castel Vetrano - Tomb #T88	Lead object, small bird	XRD, LIRMS, SEM-EDS
B-T88	Castel Vetrano - Tomb #T88	Lead object, small monkey	XRD, LIRMS, SEM-EDS

* XRD, powder X-ray diffraction. ICP-MS, inductively coupled plasma mass spectrometry. AAS, atomic absorption spectrometry. LIRMS, lead isotope ratio mass spectrometry. SEM-EDS, scanning electron microscopy, energy-dispersive spectrometry.

which is a woman's tomb located in the "southern quarter" of the necropolis. Sample A-T88 is a small bird, and sample B-T88 can be identified as a small monkey (Fig. 3g and 3f, respectively).

Small chips from the archaeological specimens were separated under a stereomicroscope for the

Analytical Methods

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instrumental analyses. No samples from the two finds A-T88 and B-T88 could be available for chemical determinations, due to the invasive nature of this kind of analyses. Powder X-ray diffraction data were collected with a Seifert–GE MZVI diffractometer, under the following conditions: CuK α radiation at 40 kV and 15 mA and 1 and 2 mm divergence slits, 1 mm receiving slit 0.1 mm, antiscatter slit 1 mm, step scan 0.05°, counting time 5 sec/step. The software package RayfleX (GE Inspection Technologies, 2004) was used for

data processing, phase identification was made by means of the ICDD-PDF2 database.

SEM micrographs and EDS spectra of selected specimens have been obtained by a JEOL-JSM instrument 5310, equipped with a Link EDS operating at 15 kV. Data were processed by the software INCA version 4.08 (Oxford Instrument, 2006).

Chemical analyses for selected major, minor and trace elements have been performed using ICP-MS by ACME (Environment Research and Service

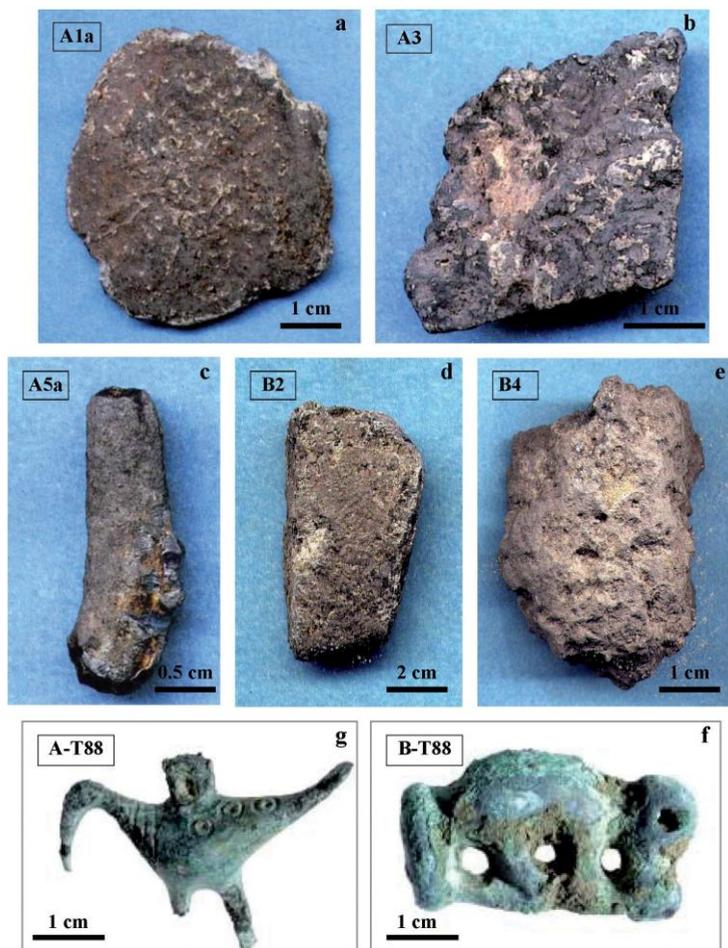


Fig. 3 – Selected measured objects. a) Round leaden plate, Poggiomarino; b) flat fragment of metallic lead, Poggiomarino; c) fragment of metallic lead elongated with a shape of a small paw, Poggiomarino; d) lead fragment with a patina, Poggiomarino; e) metallic slag, Poggiomarino; f) leaden object in form of a small bird, Castel Vetrano; g) leaden object in form of a small monkey, Castel Vetrano.

Laboratories, Vancouver), on 1 g of bulk samples. Atomic absorption spectroscopy was employed to measure Si content, by a Perkin Elmer 2100 instrument.

Pb-isotopic analyses have been carried out at the Institut für Geologie, Universität Bern, by one of us (I.M. Villa). For the analysis of the lead objects, the external crust was scraped away from a small segment with a steel blade. From the interior part of the cleaned portion, a ca. 1 mg chip was pried out with a steel needle. The samples were then dissolved in doubly distilled HCl. The resulting solution was diluted down to ca. 100 ng Pb and analysed on a Nu Instruments™ multicollector inductively coupled plasma mass spectrometer. Instrumental fractionation was corrected adding natural Tl. The external reproducibility on the NIST SRM 981 reference material amounted to $\pm 0.005\%$ (1σ standard deviations) very similar to the individual in-run precision on unknown samples. For the other metallic samples, we have performed a chemical separation as follows. The samples were first dissolved in hot *aqua regia* and evaporated. The chlorides were converted to nitrates, evaporated, re-dissolved in 1M nitric acid and loaded onto a miniature columns, entirely made of Teflon™ and contained Sr•Spec™ resin (Horwitz *et al.*, 1992). The resin volume was 0.05 mL whereby the column diameter was reduced to 3 mm; the aspect ratio increased accordingly, thereby optimising retention and release. Matrix elements were washed out with 1 mL (=20 resin volumes) 1M nitric acid. Pb was eluted with 3 mL 0.01 M nitric acid. Analyses were performed on ca. 100 ng Pb (or less, for small and/or Pb-poor samples).

Results

The SEM micrographs of selected Pb-based archaeological artefacts from Longola-Poggiomarino are presented in Fig. 4 (a,b), whereas the results of bulk XRD analyses (both alteration patinae and inner parts) are showed in Fig. 5 and Table 2. SEM images show the alteration surfaces, mainly consisting of an association of lead carbonates and oxides (and variable amounts of lead sulphate-carbonates and phosphates), which encrust the metallic Pb matrix. In the samples labelled “A” (except sample A4,

Tables 1 and 2) metallic lead is always present (main diffraction peaks at 2.85, 2.47, 1.74 and 1.48 Å), associated to various amounts of cerussite (PbCO_3), hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] and lead oxides (litharge and massicot, PbO). In sample A3 additional peaks, like those at 2.98 and 2.96 Å *d*-spacings, were assigned to pyromorphite [$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$]. Sample P05-10 is mainly composed by litharge, with minor hydrocerussite, leadhillite [$\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_3$], lead and traces of lanarkite [$\text{Pb}_2\text{O}(\text{SO}_4)$] (Fig. 5a, b, c, e).

Sample A4 (Fig. 5d) is a Cu-based slag, whose XRD analysis shows the typical pattern of metallic Cu with the three main peaks at 2.09, 1.18 and 1.28 Å. Minor contents of cuprite (Cu_2O) and trace amounts of delafossite (CuFeO_2) have been revealed as well.

The SEM images and the XRD patterns of B1 and B4 slags are shown in Fig.4 (c,d) and Fig.5 (f,i), respectively. These samples are similar to smithy materials; in sample B1 (Fig. 4c), which on visual observation appears mainly formed by a dark-brown to black, amorphous to glassy matrix, numerous micro-gaps can be observed, probably derived from trapped gas bubbles. Sample B4 (Fig. 4d) is fairly differentiated throughout its surface, with parts showing evidences of vitrification coexisting with more crystalline parts. X-ray diffraction spectra of samples B1 and B4 have revealed that they are composed by iron-rich and amorphous materials; only a limited amount of crystalline phases can be pointed out. In the sample B1 two major peaks are assigned to magnetite (Fe_3O_4), whereas two minor weak peaks may be possibly associated to wüstite (FeO , *d*-spacings at 2.48 and 2.15 Å). Vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] also occurs with two *d*-spacings at 2.97 and 6.77 Å. Sample B4 is composed by an association of the clinopyroxene hedenbergite ($\text{CaFeSi}_2\text{O}_6$) and the pyroxenoid ferrobustamite [$(\text{Ca,Fe})\text{SiO}_3$]. The mineral ferrihydrite $\text{FeO}(\text{OH})$ was also detected in traces. Samples B2 and B3 are again Pb-based slags (Fig. 5g and h). In sample B2, Pb metals is prevailing, followed in order of decreasing abundance by cerussite, hydrocerussite and lead oxide (litharge-massicot). Sample B3 is quite similar to B2 but cerussite is prevailing over Pb metal; hydrocerussite and litharge are always detected and additional peaks are assigned to lanarkite and to traces of galena (PbS), anglesite (PbSO_4) and massicot.

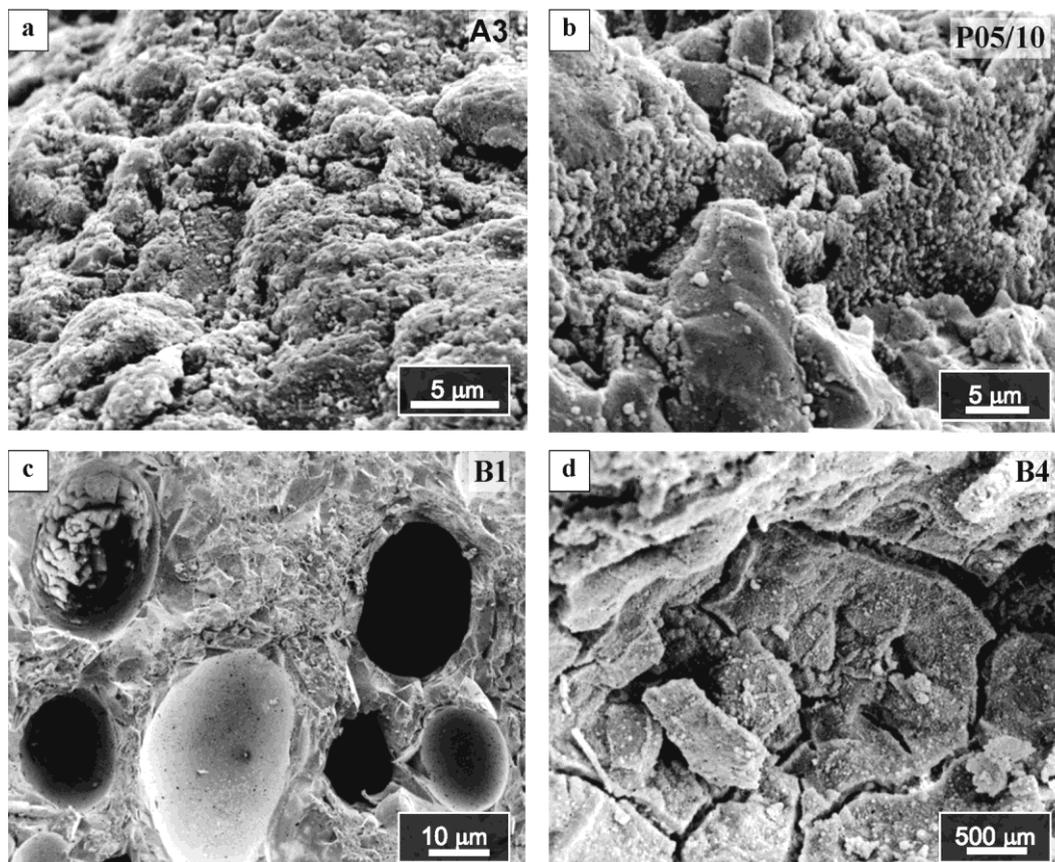


Fig. 4 – SEM images of Pb-based artefacts (a, b) and Fe-rich slags (c, d).

X-ray diffraction analysis of the Sarno valley sample P05-4 (Table 2) reveals that it is mostly made by litharge, accompanied by minor lanarkite, leadhillite and lead metal in traces. The samples A-T88 and B-T88 from the Castel Vetrano necropolis are mostly composed of lead metal.

The bulk chemistry of major, minor and trace elements of the samples studied is shown in Table 3, whereas a representative micro-chemical composition (EDS) of the studied artefacts is presented in Fig. 6. Samples A1a, A1b, A1c, A2, A3, A5a, A5b and P05-10 are chemically rather similar. As demonstrated by the minerals detected by XRD, lead is the predominant element, with percentages varying in accord to the quantitative differences in metallic lead, cerussite, hydrocerussite and Pb-oxides forming the mineral

assemblages. Among minor and trace elements, only copper can reach quite significant amounts (up to 6.10 wt% in sample A1b), whereas silver occurs up to 595 ppm (Table 3 and Fig. 6a, b and d). Minor contents of As and Sb may occur, and Bi, Co, Cr, Ni, Zn and Au are randomly detected and always in quite low amounts. Iron, phosphorous and lithophile elements (Al, Ca, K, Mg, Na, Ti) can be related to surface impurities an/or alteration encrustations due to post-depositional interaction with the pyroclastic/alluvial host materials and burial conditions. In sample A3, the occurrence of pyromorphite detected by XRD is confirmed by the presence of both Cl and P detected in the EDS spectrum (Fig. 6b) as well as by elemental analyses (0.64 wt% P, Table 3). In the sample P05-10, the occurrence of leadhillite and possibly of lanarkite,

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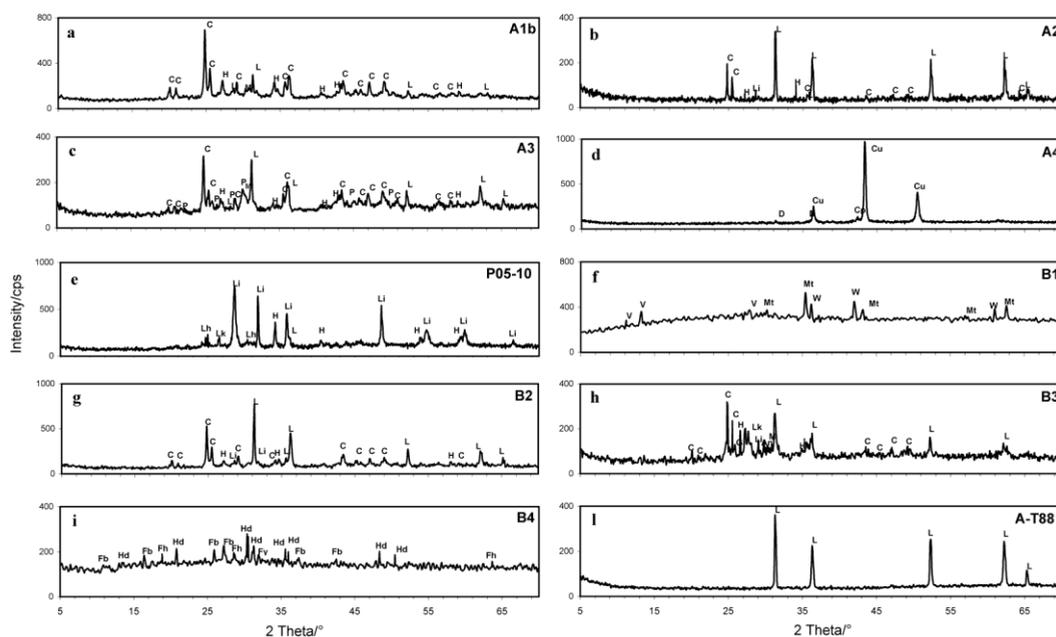


Fig. 5 – XRD diffraction patterns of selected finds (L, lead. C, cerussite. H, hydrocerussite. Li, litharge. M, massicot. P, pyromorphite. Lh, leadhillite. Lk, lanarkite. Cu, copper. Cp, cuprite. D, delafossite. Mt, magnetite. W, wüstite. V, vivianite. An, anglesite. G, galena. Hd, hedenbergite. Fb, ferrobustamite. Fh, ferrihydrite).

can be confirmed by the sulphur peak emphasized in the EDS spectrum (Fig. 6d).

The copper-rich sample A4 presents a fair high content of lead as an alloy (10.27 wt%, Table 3), as also monitored by the EDS spectrum, which even displays minor content of Fe (Fig. 6c). Traces amounts of Ag, As, Au, Co, Ni, Sb and Zn have been detected.

The iron slag B1 is characterized by a Fe content of 59.90 wt%, in agreement with its iron oxides-bearing assemblage, and by fairly high amounts of lithophile elements, like Si, Al, Ca, K, and Na (Table 3 and Fig. 6e), partly contained in the amorphous matrix. Sample B4 shows a similar elemental distribution in EDS spectrum (Fig. 6f), but with higher content in Si and Ca, due to the ferrobustamite-hedenbergite association. Other lithophile elements (Na, K, Ti) can enter in the silicate lattices and/or form the glass material, together with iron, silicon, aluminium and calcium.

Specimens B3 and B4 are chemically lead-prevailing (74.34 and 56.78 wt%, respectively)

but very rich in copper impurities (9.95 and 10.06 wt%, respectively). Only traces of Ag, As, Ni and Sb have been randomly detected.

The leaden find P05-4, mainly composed by a mineral assemblage of lead oxides, carbonates and sulphates, has a content of 55.61 wt% Pb, with 0.17 wt% Cu, 278 ppm Ag and 101 ppm Sb.

The two lead objects from the Castel Vetrano necropolis, A-T88 and B-T88 were analysed in EDS only for their semiquantitative elemental composition (Fig. 6g); they appear mainly composed by metallic lead, as also confirmed by the XRD patterns.

The results of the LIRMS of Longola-Poggiomarino samples and of the few other specimens from Castel Vetrano and the Sarno valley necropolis are reported in Table 4 and graphically shown in Fig. 7. The Pb-isotopic ratios define for almost all specimens a quite restricted field (“Hercynian”), where most values of both $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{217}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ can be allocated (with only two exceptions). The isotopic data in the abscissa $^{206}\text{Pb}/$

Table 2
Mineral assemblages deduced by XRD, listed in order of decreasing abundance

Sample	Minerals*
A1a	cerussite, lead, hydrocerussite, litharge
A1b	cerussite, hydrocerussite, lead, litharge, massicot
A1c	cerussite, lead, hydrocerussite, litharge
A2	lead, cerussite, hydrocerussite, litharge
A3	cerussite, lead, pyromorphite, hydrocerussite, massicot, litharge
A4	copper, cuprite, delafossite
A5a	lead, cerussite, hydrocerussite, litharge
A5b	lead, cerussite, hydrocerussite, litharge
P05-10	litharge, hydrocerussite, leadhillite, lead, lanarkite
B1	magnetite, wüstite, vivianite
B2	lead, cerussite, hydrocerussite, litharge
B3	cerussite, lead, hydrocerussite, litharge, lanarkite, galena, anglesite, massicot
B4	hedenbergite, ferrobustamite, ferrihydrite
P05-4	litharge, lanarkite, leadhillite, lead
A-T88	lead
B-T88	lead

*: lead (Pb), cerussite (PbCO₃), hydrocerussite [Pb₃(CO₃)₂(OH)₂], litharge (PbO), pyromorphite [Pb₃(PO₄)₃Cl], leadhillite [Pb₂(SO₄)(CO₃)₂(OH)₂], lanarkite [Pb₂O(SO₄)], copper metal (Cu), cuprite (Cu₂O), delafossite (CuFeO₂), magnetite (Fe₃O₄), wüstite (FeO), vivianite [Fe₃(PO₄)₂·8H₂O], anglesite (PbSO₄), lanarkite, galena (PbS), ferrobustamite [(Ca,Fe)SiO₃], hedenbergite (CaFeSi₂O₆), ferrihydrite FeO(OH)

²⁰⁴Pb range between 17.90 and 18.37, with most values concentrated between 18.33 and 18.34. Most ²⁰⁸Pb/²⁰⁴Pb results occur between 38.43 and 38.52, whereas the ²⁰⁷Pb/²⁰⁴Pb ratios vary between 15.66 and 15.67. Also the values measured in the copper sample A4 occur in the same field. The iron slags (B1 and B4) have isotopic ratios similar to those of the metallic specimens. Exactly the same “Hercynian” values have been measured in the leaden object from the tomb of the Sarno valley. Also the two small objects A-T88 and B-T88 from Castel Vetrano necropolis have very similar isotopic signatures: ²⁰⁸Pb/²⁰⁴Pb = 38.29-38.56, ²⁰⁷Pb/²⁰⁴Pb = 15.64-15.66 and ²⁰⁶Pb/²⁰⁴Pb = 1817-18.39. Specimen A3 is slightly different: it has a ²⁰⁸Pb/²⁰⁴Pb ratio of 37.98, while the ²⁰⁷Pb/²⁰⁴Pb

ratio corresponds to 15.64 and ²⁰⁶Pb/²⁰⁴Pb to 17.90. A completely different isotopic signature has been detected in the leaden fragment P05-10 from Longola-Poggiomarino, whose ²⁰⁸Pb/²⁰⁴Pb isotopic ratio is 38.88, ²⁰⁶Pb/²⁰⁴Pb 18.85 and ²⁰⁷Pb/²⁰⁴Pb 15.69.

discussion and conclusions

In the Pb-bearing artefacts, cerussite and litharge are the commonest alteration product of lead, followed by hydrocerussite, leadhillite, lanarkite and massicot. These minerals occur in a large number of worldwide findings as corrosion phases (Kutzke *et al.*, 1996). The type of Pb mineral phases

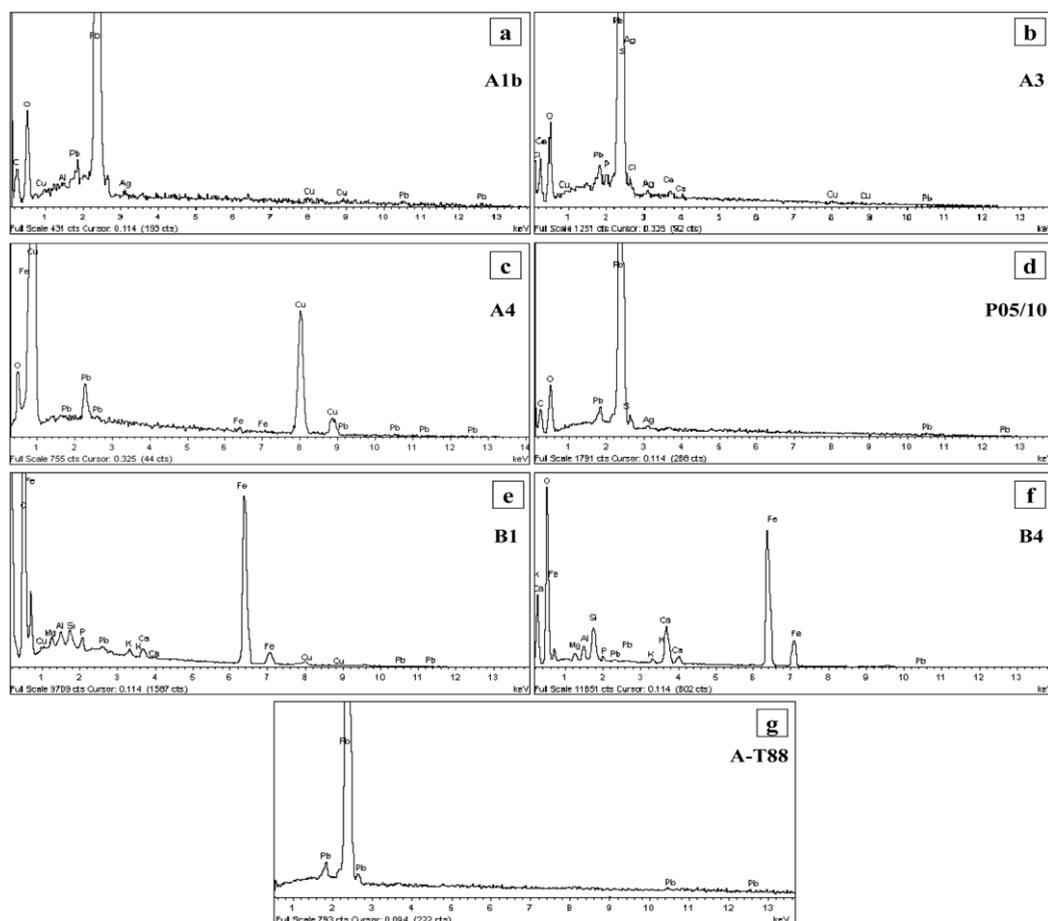


Fig. 6 – EDS X-ray energy spectra of representative samples.

that result from oxidation of metallic Pb artifacts buried in soils appear to depend from a number of factors, like geochemical environment (Eh and pH), temperature, soil type, burial load and water circulation. In general, surfaces of some corroded lead finds preferentially encased by cerussite (and hydrocerussite) can be related to the insolubility of the lead carbonate, which provides a barrier for the accumulation of litharge in the corrosion layers (Reich *et al.*, 2003). Then, the long-term resistance of lead artefacts to complete disintegration in soils is due to the stable Pb crusts composed of lead carbonates, which can form in both acidic and alkaline environments (Essington *et al.*, 2004).

The predominance of litharge over massicot on most of the samples hints that the first mineral phase is thermodynamically stable relative to the second one in the burial environments. Litharge and massicot can form concurrently during the oxidation of Pb at terrestrial temperatures and pressure, but massicot is a metastable fast-former that in time reverts to litharge. The presence of massicot together with anglesite in one of the finds may be the result of acidic conditions of the soil environment, that supports low CO_3^{2-} relative to SO_4^{2-} activities, thus favoring the formation of the lead sulfate mineral (Essington *et al.*, 2004).

Pyromorphite, detected in only one sample, is a quite unusual secondary mineral. It was observed,

Table 3
The bulk chemical composition by ICP-MS and AAS of selected metallic objects and slags

Sample	Al	Ag	As	Au	Bi	Ca	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	Sb	Si	Ti
	wt%	ppm	ppm	ppb	ppm	wt%	ppm	ppm	wt%	wt%	wt%	wt%	wt%	ppm	ppm	wt%	wt%	ppm	wt%	ppm
A1a		27		62	4	0.02			0.02	0.01							91.28		n.a.	0.02
A1b	0.05	106	316	1666	12	0.64	2	2	6.10	0.11	0.03	0.02	53	220	33	0.53	86.05	164	n.a.	0.01
A1c	0.02	41	222	864	5	0.13	2	2	4.75	0.03	0.01	0.01		90	27	0.10	94.58	95	n.a.	0.01
A2		57		96	14	0.01			0.04				9				90.06		n.a.	0.01
A3		55		6					0.01	0.01						0.64	90.18		n.a.	0.04
A4		69	51	115	22		2		85.45	0.42			84		30		10.27	31	n.a.	0.06
A5a	0.01	129		48		0.05			0.04	0.01					3	0.01	85.76	59	n.a.	0.01
P05-10		595	15		25			32	0.07						8		54.95	563	n.a.	
B1	3.27	2	32			3.47	183	29	0.07	59.90	1.89	0.62	0.30	2760	92	4.63	0.01	2	8.54	0.16
B2		70	107						9.95	0.02					53	0.01	74.34	127	n.a.	
B3						0.01			3.25	0.05					54	0.01	56.78	34	n.a.	
B4	6.04		42			11.24	64	15	0.03	10.06	4.01	1.69	0.20	9550	72	1.38	0.07	2	9.62	0.14
P05-4		278	8		28			42	0.17						11		55.61	101	n.a.	

blank= below detection limit
n.a. = not analysed

Table 4
Pb-isotopic ratios of the analysed samples.

Sample	²⁰⁸ Pb/ ²⁰⁴ Pb	±1σ	²⁰⁷ Pb/ ²⁰⁴ Pb	±1σ	²⁰⁶ Pb/ ²⁰⁴ Pb	±1σ
A1a	38.50	0.05	15.67	0.02	18.33	0.02
A1b	38.51	0.05	15.67	0.02	18.34	0.02
A2	38.43	0.06	15.67	0.02	18.27	0.02
A3	37.99	0.04	15.64	0.02	17.90	0.01
A4	38.52	0.05	15.67	0.02	18.35	0.01
A5a	38.52	0.05	15.67	0.01	18.34	0.01
A5b	38.51	0.07	15.66	0.03	18.34	0.03
P05-10	38.88	0.06	15.69	0.02	18.86	0.02
B1	38.54	0.08	15.67	0.03	18.37	0.03
B2	38.55	0.04	15.68	0.01	18.34	0.01
B4	38.52	0.04	15.67	0.02	18.34	0.01
P05-4	38.52	0.04	15.67	0.02	18.33	0.01
A-T88	38.30	0.01	15.64	0.02	18.17	0.04
B-T88	38.56	0.01	15.67	0.03	18.40	0.03

for example, in some archaeological bronze alloys from areas where pyrometallurgy had been carried out (Tharros, Sardinia), as result of interaction between the metallic components and soil constituents rich in decomposing fragments of burned bones (Ingo *et al.*, 2006).

In archaeological finds, vivianite, detected in small amounts in one of the iron-rich samples, can be generally related to environment conditions with low pH and Eh, presence of organic matter and iron-rich materials (Maritan and Mazzoli, 2004).

The elemental analysis reveals that all the Pb artefacts always contain silver, but generally the amount of other minor and trace elements is low, as in many deposits of the MVT type. A rich assemblage of trace elements would indicate an origin from hydrothermal veins related to magmatic activity or volcanogenic massive sulphides (VMS).

The two metallic objects from Castel Vetrano consist of lead with high purity. According to

Cincotti *et al.* (2003), who analysed lead objects from late Bronze to early Iron age in Sardinia, impurity-free lead manufacts can be yielded employing almost pure galena crystals and working at low temperature, with a technique rather similar to the low furnace method (Healy, 1993).

In the Cu-based finding from Longola-Poggiomarino, copper is alloyed to Pb in appreciable concentrations. This is in line with the data of Pernicka (2004), who reported that in archaeological copper findings Pb, Sn and, starting from the late Hellenistic period, also Zn were the main metals occurring in the alloy. The coexistence of metallic copper (Cu⁰) with the oxides (cuprite and delafossite) of the metal (Cu¹⁺) may indicate that the oxidation state of the melt was heterogeneous and that there was a continuous supply of oxygen by means of forced aeration. In these cases the equilibrium redox conditions were compatible with the coexistence of both oxidation states (Saez *et al.*, 2003).

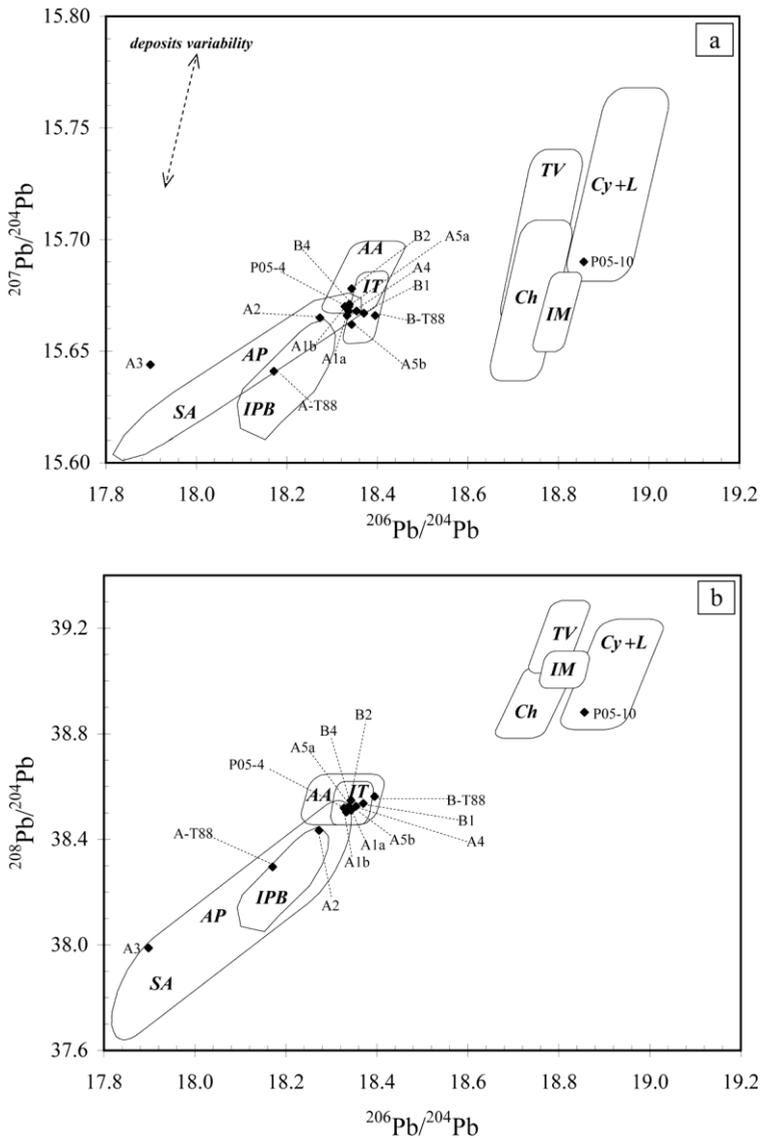


Fig. 7 – a) $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, with sample labels as in Table 1. The fields represent the isotopic compositions of some Pb-Zn-Fe mines: Cy, Cyclades-Laurion-Thasos (Stos-Gale *et al.*, 1995); Ch, Chalkidiki (Frei, 1992); TV, Southern Tuscany veins (Lattanzi *et al.*, 1997); IM/IT, Iberia, Miocene/Triassic (Arribas and Tosdal, 1994); BM/BC Britain, Mendips/Cornwall (Rohl 1996); SA, Sardinia (Boni and Köppel 1985; Boni *et al.* 1992); AA, Apuane Alps (Lattanzi *et al.* 1992); IPB, Iberian Pyrite Belt (Marcoux, 1998); AP, Alcadia-Los Pedroches (Santos Zaldegui *et al.*, 2004). b) $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. Symbols and abbreviations as in a).

The iron slags analysed for the present study are of two types, oxide-dominated (magnetite and minor wüstite) and silicate-dominated (ferrobusstamite-hedenbergite). The first mineral

assemblage is a typical oxidation product formed during smelting processes, commonly found in archaeometallurgical by-products of metalworking sites (Bjorkenstam, 1985; Gimeno Adelantado *et*

al., 2003; Alamri, 2007). Typically, the ferrous ore charge passes through various reactions, yielding firstly magnetite (at about 550-700°C). With a temperature increase, magnetite is reduced to form wüstite and finally metallic iron, under extremely reducing conditions; the lack of this latter phase in the studied assemblage demonstrates an incomplete reaction in those conditions. The second slag type shows a pyrometallurgical phase assemblage recognized in some Ca-rich iron slags of different ages (Manasse and Mellini, 2002). The occurrence of a pyroxene+pyroxenoid association might be due to the use employment of a mixture of silicates-carbonates as flux material inside the furnace, whereas the presence of vivianite might be partly related to the addition of bones as fluxes as well.

The Pb-isotopic data of the studied objects are generally restricted to a small field, with the exception of findings A3 and P05-10 from Longola-Poggiomarino, which show fairly scattered isotopic ratios. The analyzed objects seem to derive mostly from pre-Tertiary metallogenic districts of the Mediterranean realm. Likely sources both from the isotopic and historical point of view may be the island of Sardinia and southern Spain. In Sardinia both the Sarrabus and Arburese mining districts, where the hydrothermal influence of the Hercynian granites was overwhelming, can be taken into account as likely sources (Boni and Köppel, 1995; Stos-Gale *et al.*, 1995). In southern Spain the Alpujarride (Arribas and Tosdal, 1994) and/or the Alcudia-Los Pedroches-Linares La Carolina mining districts (Santos Zalduegui *et al.*, 2004) fulfill the same isotopic and historical requirements. The latter district has a very old history of exploitation, not only for silver and lead but also for copper, which dates at least to the Bronze age).

Anyway, it is worth to mention that the isotopic signatures of the studied metallic findings are not unambiguous, and might also fit to other mining districts, like the eastern alpine ores (e.g. Carinthia, Köppel, 1983), the Ivrea-Verbano complex (Cumming *et al.*, 1987) and the Anatolia region (Sayre *et al.*, 2001; Ceyhan, 2003), even though there is no clear archaeological evidence of commercial exchanges between those mining areas and the Iron Age cultures in southern Italy. The Apuane Alps (Bottino) area might be ruled out

among the likely metal sources, due to the higher $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratios of its ores compared with the values observed in this study (Lattanzi *et al.*, 1994). Moreover, it has not been ascertained yet if the small metal-bearing horizons in the Apuane Alps were exploited before the Etrurian mining activity. Our Pb-isotopic data are incompatible with most ores derived from Greece (Boni *et al.*, 2000a; Chalkias *et al.*, 1988), southern Tuscany (Lattanzi *et al.*, 1997) and the southeastern “Alpine” mining district of Cartagena in Spain (Arribas and Tosdal, 1994).

Regarding samples A3 and P05-10, which do not fit into the general pattern, some other possibilities might be suggested. Sample A3 shows an isotopic composition quite similar to the galenas found in the vein- and paleokarst Pb-Ag ore type of southwestern Sardinia (Iglesiente-Sulcis, Boni and Köppel, 1985; Ludwig *et al.*, 1989), on account both of its Pb-isotopic ratios and of the low concentration of minor and trace elements. However, a possible provenance from some of the Alcudia-Los Pedroches ores may be also envisaged (Santos Zalduegui *et al.*, 2004).

The measured ratios of the object P05-10 are the only ones that may fit to the “Alpine” (Tertiary) Pb-isotopic ratios, typical of some Greek deposits (i.e. Laurion), even if an evidence of such an ancient exploitation seems doubtful in the case of the Laurion mines (Braudel, 1998).

The Pb-isotopic analyses of the two objects A-T88 and B-T88 found in the Iron Age necropolis of Castel Vetrano show values very similar to those of the main field of the objects found at Poggiomarino. The isotopic ratios of B-T88 are perfectly in line with most Longola-Poggiomarino samples, while those of A-T88 are lower for $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$. The latter isotopic values might be assigned both to the hydrothermal vein ores of Sardinia and to the VMS (polymetallic) deposits from the Iberian Pyrite Belt in Spain (Rio Tinto-Huelva, Marcoux 1998).

Likely commercial trades concerning both rough ores and refined metals, between southern Spain and southern Italy (via Sardinia?) at the beginning of Iron Age (Cicirelli *et al.*, 2006) might be therefore hypothesized.

In conclusion, with a series of analytical methods (mineralogy, geochemistry and Pb-isotopic geochemistry), it was possible to characterize and

typify the nature of a set of archaeological findings of Iron Age cultures from Campania. However, in order to obtain more reliable information regarding the smelting processes they have undergone and their source of raw materials, further studies on larger number of samples are still required.

AcKnowledGements

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