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Copper metallurgy in ancient Etruria (southern Tuscany, Italy) at the Bronze-Iron Age transition: a lead isotope provenance study

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ABSTRACT

The Etruscan site of Populonia-Baratti (Southern Tuscany, Italy) became in the first millennium BCE one of the most important iron metalworking sites in the Mediterranean region thanks to the exploitation of nearby Elba Island iron ores. Recent studies, however, have demonstrated that, before iron, copper was smelted therein (9th–8th century BCE). The ancient Hellenistic text *De mirabilibus auscultationibus* by Pseudo-Aristotle states that the ancient inhabitants of Elba Island firstly exploited copper and that, later in, iron was won from the same mines by the inhabitants of Populonia. However, copper occurrences are extremely scanty on the island, while mainland southern Tuscany hosts a number of copper-rich deposits which could have been profitably exploited since Eneolithic. In order to investigate if, and to what extent, copper mining and smelting/working was practiced in this area in Final Bronze Age (FBA) to Early Iron Age (EIA), we have thus compared the lead isotope composition of copper slags found in the Populonia-Baratti area and dated to the 9th–8th century BCE with those of copper-rich ore deposits of southern Tuscany and Elba Island. In addition, few copper-based items from to FBA-EIA hoards of Elba Island have been investigated as well. All copper slag from Baratti-Populonia have lead isotope composition fully comprised within the nearby Campiglia Marittima district, but the ophiolitic copper (either form Tuscan mainland or the neighboring island of Elba) was never worked in this site. Differently, all items from the island of Elba do not show clear genetic relationship neither with Elban nor with the Tuscan mainland copper ores but display a “foreign” Pb signature, suggesting that, even before iron exploitation started, the island of Elba - one of the main crossroads of the Mediterranean Sea - was probably involved in metal trading (rather than metal working) with other regions.

1. Introduction

After the abandonment of small coastal settlements during the FBA (12th–10th century BCE), in the Early Iron Age (9th–first half of 8th century BCE) a village was probably established by ancient Villanovan clans at Poggio del Telegrafo, just on the top of Populonia promontory (southern Tuscany, Italy) (Acconcia et al., 2006). This hilltop settlement, dominating the large coastal lagoon connected with the Gulf of Baratti, was easy to defend and permitted to control the trade exchanges with the nearby Elba Island, separated from the Channel of Piombino (Fig. 1), the whole Tuscan Archipelago up to the islands of Corsica and Sardinia. Although it is likely that these ancestors of the Etruscans chose this site mostly for its strategic position, they were also surely attracted by the large availability of iron, copper, lead, (tin?) and silver from the nearby ore districts of Elba Island and Colline Metallifere - Campiglia Marittima (Fig. 1).

The new village on the top of Populonia promontory (Poggio del Telegrafo) –as it happened in many other areas of ancient Etruria (Bartoloni, 2004) - probably resulted from unification of previously independent political entities in a city with a state organization and centralization of all the political and economic activities. No clear traces of metallurgical activities (slags, ore relics ore semi-finished

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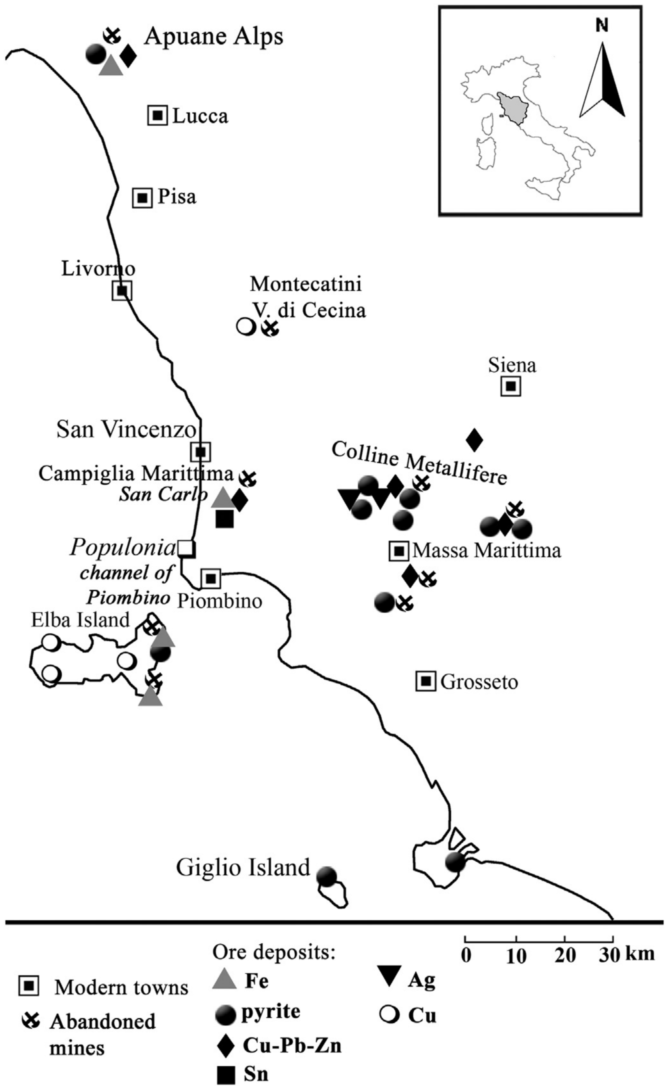

Fig. 1. Sketch map of the distribution of the main copper deposits of Tuscany. (After Tanelli, 1983, simplified.)

objects) belonging to this period have been ever found on the Populonia promontory, with the exception of two clay molds for pins (beginning of the 8th century BCE) that may suggest some bronze-working activities (Fedeli et al., 1993).

At Populonia the first clear evidence of copper production is provided in the slag beach deposit of San Cerbone along the Gulf of Baratti (Fig. 2), where layers of copper slags have been discovered at the bottom of a well-preserved stratigraphic sequence (Chiarantini, 2005). Radiocarbon dating of charcoal fragments associated with copper slag points to an early phase (9th–8th century BCE: Cartocci et al., 2007) of a highly efficient, copper metallurgy (Chiarantini et al., 2009). On the other hand, the close proximity of several FBA-EIA settlements to copper ores both in the island of Elba and the Colline Metallifere - Campiglia Marittima districts has been repeatedly claimed to indicate that these ores were exploited for copper/bronze production (for instance, Zifferero, 2002; Acconcia and Milletti, 2015).

As indicated by radiocarbon dating of the earliest iron slag horizon in the Baratti slag beach deposit (Chiarantini et al., 2009), the shift from copper to iron production took place between the 8th and early 6th century BCE (late Orientalizing period), presumably when Populonia took complete and direct control of iron ore deposits of Elba Island (Maggiani, 2006). It must be said, however, that the exact beginning of iron mining on the island of Elba is still largely undetermined (Corretti et al., 2014). Accordingly, the earliest phase of iron production identified in the "industrial quarters" of Populonia has been dated to the 6th century BCE (Fedeli et al., 1993). It is not yet clear why iron smelting was no deeply practiced within Elba Island in this period, but metallurgical activity probably moved to the Gulf of Baratti toward Populonia even before the 6th century BCE (cf. Corretti and Benvenuti, 2001; Corretti, 2004a). In addition to classical hypotheses (the reduction, or even exhaustion, of forestal resources on the island), one can suggest that the Etruscan inhabitants from Populonia had already achieved a high metallurgical skill inherited by a long-lasting copper smelting tradition (Chiarantini et al., 2009).

Between the 6th century BCE and 1st century AD, under the Etruscan and subsequent Roman rule, Populonia became one of the most important metalworking sites in the Mediterranean region, particularly for iron production (Corretti and Benvenuti, 2001). In this period the Etruscan merchants from Populonia traded goods with Sardinia and Corsica, southern Etruria and the Aegean region, as testified by the tumulus tombs of the San Cerbone and Casone necropolises, extremely rich in jewels and objects from eastern Mediterranean (Fedeli et al., 1993). As a result of this long-lasting metallurgical activity, heaps of slag and other metallurgical debris have been discharged over a surface of about 220.000 m^2 in the Gulf of Baratti (D'Achiardi, 1929) (Fig. 2). The greatest part of these slag heaps was dismantled in the past century (1922–1959) for re-smelting in modern blast furnaces. The modern excavators, besides bringing to light the monumental tombs of an Etruscan necropolis, also profoundly upset the original stratigraphy of archaeological layers thus destroying most of the evidence (e.g. furnaces) of metalworking activity in this area.

The link between iron smelted at Populonia and Elban iron ores, clearly predictable on the basis of documentary, geographic and archaeologic evidence, has been recently confirmed by the Sn-W geochemical anomaly of Elban hematite ores which is still detectable in smelting slags and (rare) iron blooms found at Populonia (Benvenuti et al., 2013, 2016).

But what can we say about the provenance of copper smelted at Populonia? Despite copper deposits on Elba Island are few and of very small size (see next chapter), in a famous, somehow puzzling Hellenistic text ("*De mirabilibus auscultationibus*", 93) written by Pseudo-Aristotle, it is said that copper (and, later on, iron) was exploited from mines in the island of Elba (see Section 2.2). In principle, one cannot rule out with absolute certainty that the Villanovan inhabitants of Populonia smelted copper mined from the island of Elba.

In order to assess the provenance of copper smelted at Populonia, we have compared the mineralogical, textural and compositional features (including lead isotope composition) of metallurgical wastes from copper production found in the Baratti Gulf with those of copper-rich ore deposits in the targeted areas (i.e., southern Tuscany and Elba Island districts). In addition, we have also analyzed a few copper-based items from FBA-EIA archaeological sites of Elba Island in order to make a comparison with copper ore deposits and establish possible connections (if any).

2. The copper deposits of southern Tuscany and Elba island

2.1. Ore geology and mineralogy

Almost three millennia of exploitation in Tuscany yielded significant productions of iron, pyrite, base metals, silver, antimony, mercury, gold, as well as industrial minerals and rocks (cf. Cipriani and Tanelli, 1983). The genesis of many of these deposits is associated with volcano-sedimentary, magmatic, metamorphic and geothermal environments of pre-Tethyan and Alpine ages (Lattanzi et al., 1994).

Copper deposits of southern Tuscany are mainly hosted along a belt which extends from the Tyrrhenian coast (at Piombino) towards Siena to the east and only minor copper ore showings are present in Elba Island (Fig. 1).

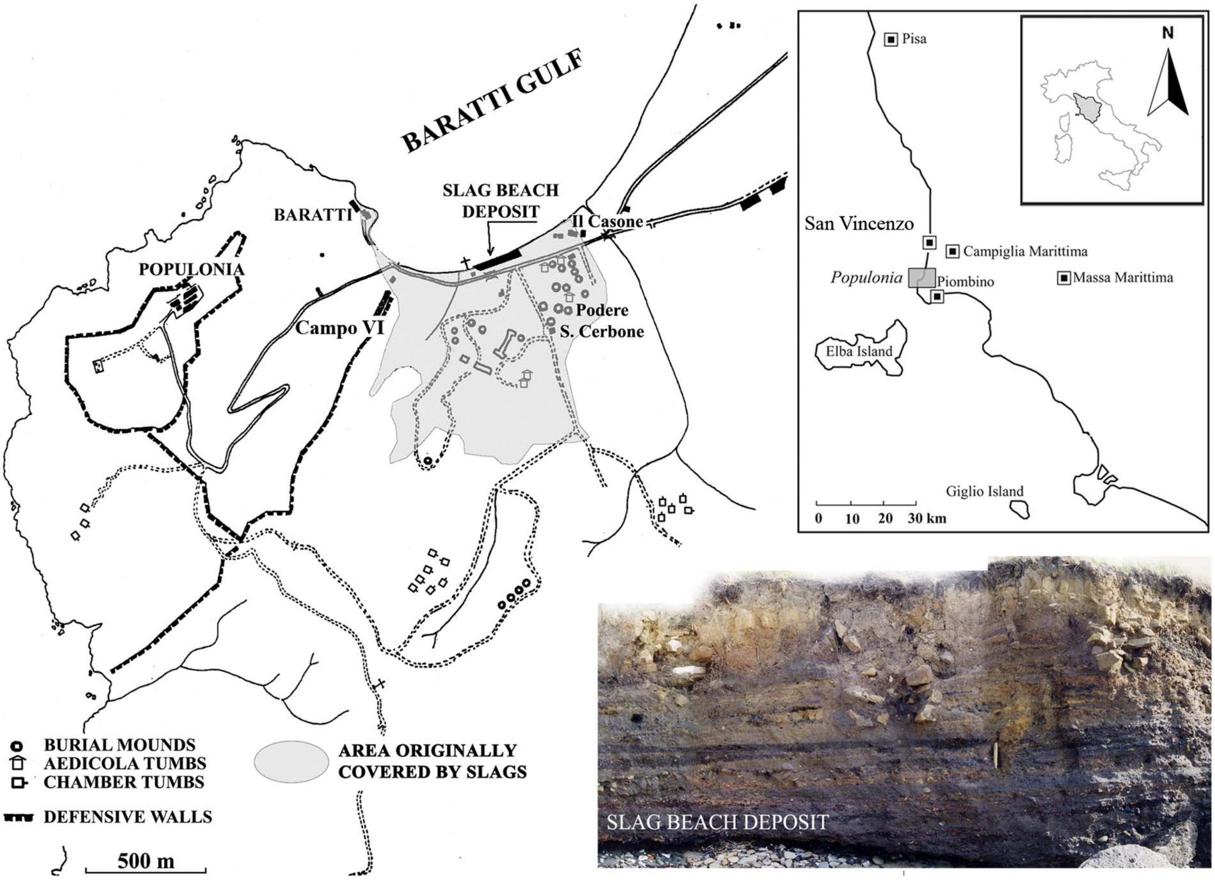

Fig. 2. The Populonia-Baratti archaeological area. Inset: photograph of the Baratti slag beach deposit: samples of copper slag were taken for this study from the lowermost layers.

Two main types of copper deposit occurring in the study areas are so far considered (*cf.* Tanelli, 1989): a) volcano-sedimentary deposits of copper sulphides, carbonates and native copper spatially and genetically associated with ophiolitic suites; b) polymetallic sulphidic (Cu-Pb-Zn-Ag ± Au) ores, preferentially associated with tectonic lineaments and presumably emplaced by late-Apenninic magmatic-meteoric hydrothermal fluids (Lattanzi et al., 1991).

The former type is constituted by dominant chalcopyrite and pyrite with variable, commonly minor amounts of bornite, sphalerite, galena, chalcocite, covellite, hematite and enargite associated with gangue minerals like quartz and calcite (Klemm and Wagner, 1982). As shown in Fig. 1, Montecatini V. di Cecina was the most relevant deposit belonging to this type (D'Achiardi, 1921; Dini and Boschi, 2017). Notably, minor copper ore deposits occurring on Elba Island are associated with basalts and serpentinites from ophiolitic suites (Fig. 3a) and consist of native copper ± copper oxides and sulphides (Pomonte, Santa Lucia, Colle Reciso-M.Orello, Norsi, Sant'Andrea, M.Perone, Punta Le Tombe, Acquacalda: Mascaro et al., 1991; Tanelli et al., 2001).

Polymetallic sulphidic (Cu-Pb-Zn-Ag) ores are much more abundant, particularly in the southern Tuscany district. The strata-bound pyrite deposits of the Colline Metallifere (Maremma) belt have variable spatial relationships to, and may be associated with, Cu-Pb-Zn sulfide showings, mostly uneconomic (Tanelli and Lattanzi, 1983). Of particular relevance for this study are the copper deposits of the Campiglia Marittima, Temperino Valley mining district, that has long been known for Cu-Pb-Zn(± Fe, Ag, Sn) skarn deposits (Corsini et al., 1980; Vezzoni et al., 2016; see Fig. 3b) exploited since pre-Etruscan times up to the the 80s of past century (Cipriani and Tanelli, 1983). These deposits lie 1–2 km E-NE of the 5.7 Ma Botro ai Marmi "granitic" stock (ranging from granodiorite to sienogranite in composition; Lattanzi et al., 2001). Skarn complexes are completely enclosed in white marbles, derived from contact metamorphism of the Liassic carbonatic formation of "Calcare Massiccio" (Tuscan Units) by the Botro ai Marmi and/or related intrusions (Corsini et al., 1980; Benvenuti et al., 2004). Ore mineralogy at Campiglia Marittima-Temperino Valley mainly includes chalcopyrite, magnetite, sphalerite, pyrrhotite and Ag-bearing galena with minor, pyrite, hematite and traces of bismuthinite, galenobismutite and many other phases (Corsini et al., 1980; Vezzoni et al., 2016). Gangue minerals include hedenbergite, manganoan ilvaite, johannsenite, diopside with wollastonite, garnets, epidote, quartz, and calcite (Dini et al., 2013). A wealth of secondary copper minerals were produced by supergene processes, including native copper, cuprite, covellite, chalcocite, digenite, atacamite, paratacamite, malachite, azurite, aurichalcite, brochantite, antlerite, chalcanthite, chrysocolla and many others (Tanelli and Benvenuti, 1998).

At Elba Island occurrences of copper mineralization of the second type, i.e., not associated with ophiolitic suites, are very limited and restricted to minor ore shoots associated with Fe skarn deposits of eastern Elba (Benvenuti et al., 2004: Fig. 3a). Sulphides, which are very rare or absent in the north-eastern iron deposits (Rio Marina – Rio Albano) are significantly more abundant at Ortano, south of Rio Marina, and in the magnetite-type skarn deposits of the Calamita promontory, where they mostly formed at a late paragenetic stage. Masses of Cu-Fe sulfides (chalcopyrite, pyrrhotite, pyrite ± malachite, azurite, chalcanthite, etc.) were exploited from the Grotta Rame stope (meaning "copper cave") in the Capo Calamita mine, at the contact between the garnet skarn and the magnetite lenses (Torrini, 1990).

2.2. Ancient mining

There is no definite archaeological evidence for exploitation in pre-Industrial times of the otherwise limited copper showings from Elba

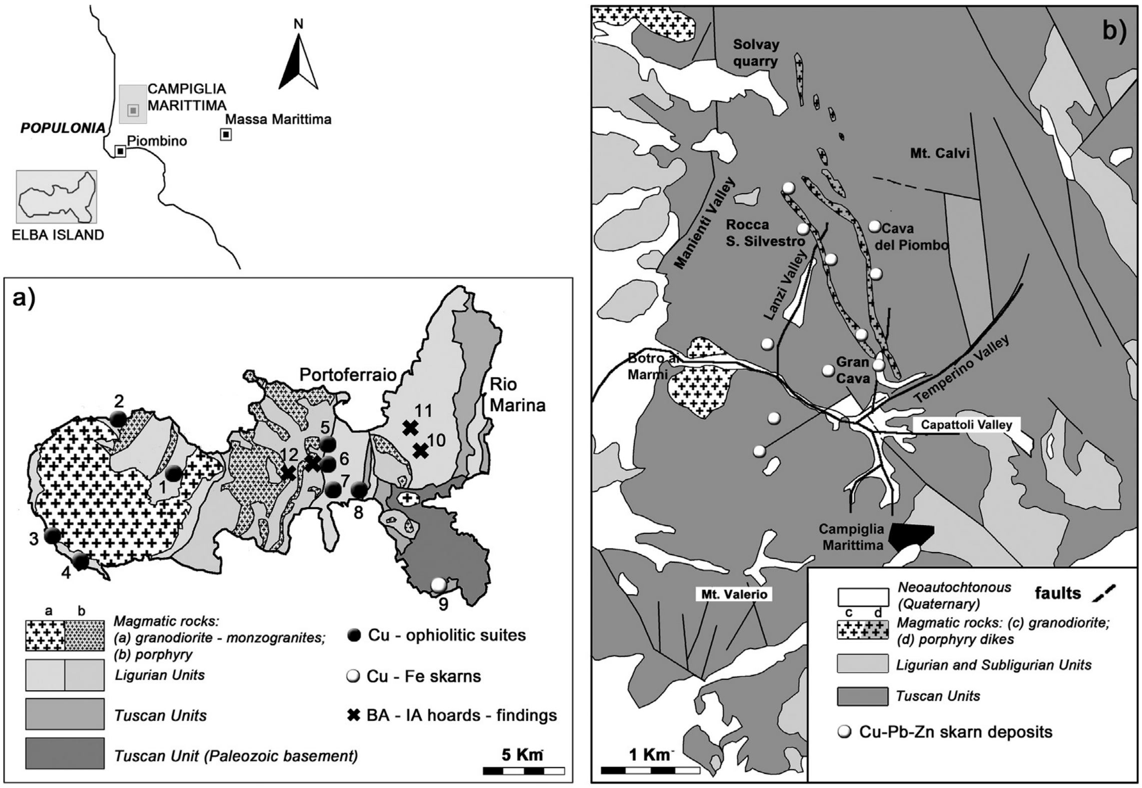

Fig. 3. a) Geological sketch map of Elba Island (modified after Tanelli et al., 2001 and Dini et al., 2008) with location of copper deposits and Late Bronze Age - Early Iron Age hoards: (1) = M.Perone; (2) = Sant' Andrea; (3) = Pomonte - Ogliera; (4) = Punta Le Tombe; (5) = Santa Lucia; (6) = Colle Reciso-M. Orello; (7) = Acquacalda; (8) = Norsi; (9) = Capo Calamita; (10) Cima del Monte; (11) = Volterraio; (12) = San Martino. b) Geological sketch map of Campiglia Marittima ore district (modified after Tanelli et al., 1993) with the location of Cu-Pb-Zn skarn deposits.

Island above described (mostly associated with ophiolites). The already mentioned, early Hellenistic text *De mirabilibus auscultationibus* by Pseudo-Aristotle, says that: "In Etruria there is said to be a certain island named Aethaleia, in which out of a certain mine in former days copper was dug, from which they say that all the copper vessels amongst them have been wrought; that afterwards it could no longer be found: but, when a long interval of time had elapsed, from the same mine iron was produced, which the Etrurians, who inhabit the town called Populonium, use to the present day*"* (Ps. Arist., Mir, 93, translation by Smith and Ross, 1909). Although the meaning and interpretation of this text have been the matter of much debate (see Corretti and Benvenuti, 2001) and this statement need to be critically evaluated, we can admit that the anonymous writer, or his source, reminded of the existence on the island of "ancient" copper mines, possibly predating the "urban" development of Populonia, i.e., before the late 8th–middle 7th century BCE (Corretti, 2004a, 2004b). Although one of the earliest copper-rich hoards in the island of Elba, the sepulchral site of Grotta San Giuseppe at Rio Marina, dates back to late Eneolithic (end of the 3rd millennium BCE - beginning of the 2nd millennium BCE: Grifoni Cremonesi, 2001) many others (e.g. San Martino, Pomonte, Santa Lucia, Colle Reciso, Cima del Monte, etc.) have a younger chronology (FBA-EIA). The close proximity to some copper showings (Fig. 3a) some of these sites may suggest that some exploitation of Elban copper ores could have taken place in that period (i.e., FBA-EIA). On the other hand, at Santa Lucia copper slags have been described by Simonin (1858); unfortunately, they have not preserved until today and are not available for study. In addition, a mold (for copper/bronze casting?) has been recently reported from Colle Reciso (Acconcia and Milletti, 2015).

Moving to the mainland, the San Carlo site at the Solvay Quarry of San Vincenzo (not far from the village of Campiglia Marittima; Fig. 3b) copper slags and copper prills were discovered in 1991 in association with Eneolithic potsherds (Fedeli et al., 1993). This material has been recently investigated in detail and radiocarbon dated to the 3400–3100 BCE (Artioli et al., 2016b). San Carlo thus represents one the earliest copper-working sites of Tuscany and Italy as well. For instance, it appears to be almost coeval with the copper-rich burials Grotta della Spinosa (Massa Marittima) and Ponte San Pietro (Viterbo). This is in agreement with Dolfini's (2010) suggestion that technologically advanced copper-working developed in this area during the early/mid-fourth millennium BCE. Copper ingots found at Cavalleggeri (San Vincenzo) and San Michele (Campiglia Marittima), dated to FBA (Fedeli et al., 1993) but never studied in detail, may constitute further evidence of relevant mining and copper-working in the Colline Metallifere-Campiglia Marittima districts before EIA.

Even if traces of pre-modern, "ancient" mining (e.g. old shafts, pits, and adits) are abundant in the Campiglia Marittima district, it is difficult to date them accurately because modern-time mining often canceled (partially or totally) archaeological traces of older workings (Casini and Francovich, 1992). However, many pre-Medieval settlements, attributed to either the Etruscan or the Roman period, are positioned in close proximity to ore occurrences (Fig. 3b), preferably on top of the hills, thus suggesting they are part of a complex network established for the direct control of mining activities (Zifferero, 2002). After the discovery of furnaces, metallurgical debris (copper slags) and a few lamps and potsherds dating from the Villanovan to the Orientalizing period in Fucinaia and Capattoli valleys (Campiglia Marittima ore district: Fig. 3b) Minto (1954) established a link between Etruscan settlements and mining/metallurgical activity (for copper production). However, Minto's furnaces have been more recently reinterpreted as brick/tile kilns (cf. Sperl, 1981), perhaps even much younger in age (Middle Age). Later on, in the Middle Ages, a system of mine workings developed in Lanzi and Manienti valleys around the fortified village of Rocca S. Silvestro (10th–14th century AD; Fig. 3b) to

Table 1
List of analyzed samples, with a short mineralogical description. FBA = Final Bronze Age; EIA = Early Iron Age.

Samples	Locality	Description	Main (mineralogical) phases	Other phases	Age
Ores					
AD1	Elba Island, Capo Calamita mine	Cu ore	native copper		–
AD2	Elba Island, Capo Calamita mine	Cu ore	chalcopyrite		–
AD3	Elba Island, Capo Calamita mine	Cu ore	malachite		–
AD4	Elba Island, Capo Calamita mine	Cu ore	chrysocolla		–
AD5	Elba Island, Santa Lucia	Cu ore	native copper		–
AD6	Elba Island, Santa Lucia	Cu ore	chalcopyrite		–
AD7	Elba Island, Pomonte-Ogliera	Cu ore	chalcopyrite		–
AD8	Elba Island, Sant'Andrea	Cu ore	chalcopyrite (+pyrite)		–
T1	Campiglia Marittima/Temperino Valley	Cu ore	chalcopyrite (+sphalerite, pyrite, galena)	hedenbergite, quartz	–
T2	Campiglia Marittima/Temperino Valley	Cu ore	chalcopyrite (+sphalerite, pyrite, pyrrhotite)	ilvaite	–
T3	Campiglia Marittima/Temperino Valley	Cu ore	chalcopyrite (+sphalerite, pyrrhotite)	hedenbergite, quartz	–
T4	Campiglia Marittima/Temperino Valley	Cu ore	chalcopyrite (+sphalerite, pyrite, pyrrhotite)	ilvaite	–
E 5–1	Campiglia Marittima/Temperino Valley	Cu ore	chalcopyrite (+pyrite, magnetite)	quartz	–
E 5–7	Campiglia Marittima/Temperino Valley	Cu ore	chalcopyrite (+pyrite, magnetite)	quartz	–
MT1b	Campiglia Marittima/Temperino Valley	Cu ore	malachite		–
CT1	Campiglia Marittima/Temperino Valley	Cu ore	chrysocolla		–
CT2	Campiglia Marittima/Temperino Valley	Cu ore	chrysocolla (+azurite)		–
M	Montecatini V. di Cecina	Cu ore	bornite		–
M1	Montecatini V. di Cecina	Cu ore	bornite (+digenite)		–
MP	Montecatini V. di Cecina	Cu ore	bornite (+chalcocite)		–
Copper slags and archaeological samples					
C6–52/3b	Populonia - Campo VI	partially roasted copper ore	chalcopyrite (+ Cu sulphides, wüstite, cuprite)	malachite, Fe-hydroxides	max 3rd cent. BCE
Z2b	Populonia - Baratti	copper slag	fayalite, hedenbergite, magnetite	Cu, matte	9th–8th cent. BCE
Y B11–1u	Populonia - Baratti	copper slag	fayalite, hedenbergite, magnetite	Cu, matte	9th–8th cent. BCE
W B11-4a	Populonia - Baratti	copper slag	fayalite, hedenbergite, magnetite	Cu, matte	9th–8th cent. BCE
W B11–1	Populonia - Baratti	copper slag	fayalite, hedenbergite, magnetite	Cu, matte	9th–8th cent. BCE
W2	Populonia - Baratti	copper slag	fayalite, hedenbergite (+ magnetite)	matte	9th–8th cent. BCE
W B11–2	Populonia - Baratti	copper slag	fayalite, hedenbergite (+ magnetite)	Cu, matte	9th–8th cent. BCE
W B11-3d	Populonia - Baratti	copper slag	fayalite, hedenbergite (+ magnetite)	matte	9th–8th cent. BCE
VT1	Elba Island, Volterraio	copper lump	copper	As-Sb-Pb oxides	uncertain
SM 2236	Elba Island, San Martino	copper lump	copper	Cu sulfides	FBA
CR5/2	Elba Island, Colle Reciso	copper lump	copper	As-Sb-Pb oxides	EIA
CM1	Elba Island, Cima del Monte	bronze fragment	Cu-Sn α-phase	Cu sulphides, Pb inclusions	FBA–EIA
CM2	Elba Island, Cima del Monte	irregular bronze lump	Cu-Sn α-phase	Cu sulphides, Pb inclusions	FBA–EIA
2411	Rocca S. Silvestro	(Cu-rich) lead slag	hedenbergite, fayalite (+wüstite, magnetite)	Pb(Ag), Cu, matte	medieval

exploit the surrounding Cu-Pb-Ag (Fe) ore deposits (Guideri, 1995; Cuteri and Mascaro, 1995).

Archaeological data are not available to assess with certainty that ophiolitic copper ores in the Tuscan mainland (e.g., Montecatini V. di Cecina) have been exploited in the early 1st Millennium BCE or even earlier. However, according to Tanelli (1989), the presence of surface outcrops of these oreshoots presumably have favored their discovery and exploitation since antiquity, as documented in many parts of the world (e.g., Cyprus: Constantinou, 1992; Oman: Hauptmann, 1985; Ergani mines, Turkey: Bamba, 1976).

3. Sampling and analytical methods

A total of 31 samples have been selected for this work, including copper ores (from Campiglia Marittima and Elba Island), copper slags and a relic of copper ore from the copper-working site of Populonia and five "archaeological" copper-based items from Elba Island (Table 1). Locations of sampling sites are also reported in Fig. 1, 2 and 3.

3.1. Copper ore samples

After an inventory of already published lead isotope data of copper ores from adjoining mining districts (southern Tuscany and Elba Island), we chose to obtain additional data from the Campiglia Marittima and Elba Island ore districts.

Eight samples of copper ores from Elba Island were taken for analysis (Fig 3a): four from Grotta Rame stope at Capo Calamita (samples AD1–AD2–AD3–AD4) and the others from ophiolitic outcrops (AD5-AD6: Santa Lucia; AD7: Pomonte-Ogliera; AD8: Sant' Andrea).

A total of nine samples from the Cu (Pb-Zn) orebodies of the Temperino Valley mine (Campiglia Marittima) were analyzed for their mineralogical, chemical and lead isotope signature. More in detail:

- four chalcopyrite-rich samples from pre-modern (Etruscan?) mine waste fillings (T1-T2-T4) and mine dumps (T3);
- two chalcopyrite-rich samples from 19th-century Temperino mine (E3–3 from Gowet shaft; E4-101 from Gran Cava shaft; E5-1 and E5-7 from Earle shaft);
- three samples of secondary copper ores from Temperino mine (MT1b-CT1-CT2).

Three additional samples of Tuscan ophiolitic copper (bornite-rich ores from Montecatini V. di Cecina mine: M, M1, MP) have been analyzed to augment the existing dataset.

3.2. Copper slags and archaeological samples

We have analyzed for lead isotope composition seven samples of copper slag from the Populonia-Baratti beach deposit, previously analyzed for their mineralogical, textural and geochemical features (Chiarantini et al., 2009). In addition, a (rare) fragment of partly roasted copper ore from the Baratti-Populonia mineral charge recovered during the 1996–7 excavations at Campo VI (Fig. 2). The sample was found in a stratigraphic layer of uncertain age (but surely not later than the 3rd century BCE) associated with copper slags, charcoal, remnants of furnace linings and potsherds.

For comparison, we have also analyzed one lead smelting slag from the medieval settlement of Rocca S. Silvestro (Fig. 3b), in the Campiglia Marittima ore district (*cf.* Mascaro et al., 1995).

We also selected five copper or copper alloy (bronze) items ("archaeological samples"), discovered on Elba Island within sites dating from FBA to EIA (Table 1; Fig. 3a) and now on exhibition in Museum collections (Archaeological Museum of the mining District at Rio nell'Elba; Archaeological Museum at Portoferraio). We were particularly interested in raw copper-based materials (lumps of copper, ingots, metal scraps, etc.) which – at least hypothetically - could have been produced in situ (i.e., on Elba Island). Five samples which, after preliminary tests, displayed sufficient lead contents for lead isotope analysis were thus selected. It is likely that the Pb isotope analyses of these copper artifacts from Elba Island are – to our knowledge - among the first ever published in the literature.

Samples CM1 and CM2 from Cima del Monte belong to a small metal hoard of copper bars from a settlement dated to FBA-EIA, recently excavated by Soprintendenza Archeologia della Toscana (Alderighi et al., 2012). Sample CM1 is a sort of small bar with an elliptic cross-section, while the other (CM2) is a lump of metal with uneven shape (Fig. 4).

The Colle Reciso metal hoard, dated to the EIA (Delpino, 1981; Zecchini, 2001; Acconcia and Milletti, 2015), is composed of several kinds of metallic items (axes, spearheads, nails, rods and uneven lumps). First described by Cocchi (1865), this site occurs at a short distance from an outcrop of ophiolitic copper (see Fig. 3a). We have analyzed a small copper ingot (CR 5/2) of irregular shape (Fig. 4).

The FBA-EIA San Martino copper hoard was discovered in the 19th century and consists of axes, fibulae, and chains (Delpino, 1981; Acconcia and Milletti, 2015). The sample SM 2236 (belonging to the Foresi Collection) is a copper lump with an elliptical shape and plano-convex cross-section (Fig. 4).

Sample VT1 is a stray find of uncertain age from the Volterraio area; it is a copper lump with uneven shape (Fig. 4).

During the sampling campaign we also took some fragments of copper items (nails and blades) from Grotta S. Giuseppe, a sepulchral site dating to the Eneolithic (cf. Grifoni Cremonesi, 2001). However, due to the very low Pb contents that hindered isotope measurements, these samples have not been included in the discussion of results.

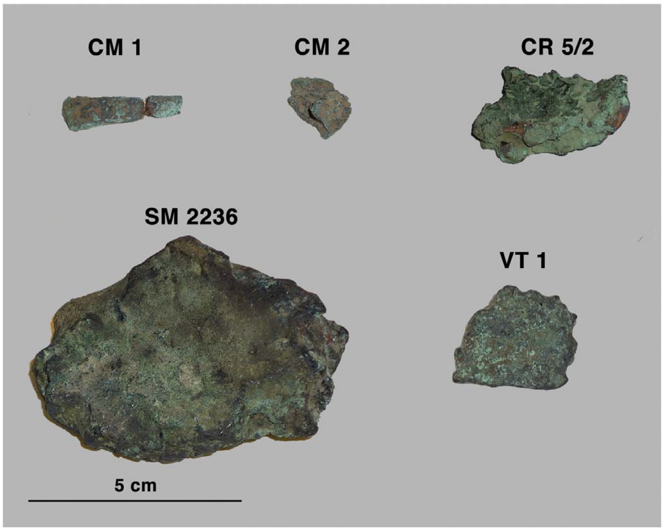

Fig. 4. Copper and bronze items from Elba Island metal hoards, dating from FBA to EIA, investigated in this paper: CM1 and CM2 from Cima del Monte (FBA-EIA); CR 5/2 from Colle Reciso (EIA); SM 2236 from San Martino (FBA) and VT1 from Volterraio (uncertain age).

3.3. Analytical methods

Mineralogy of investigated ore samples was determined by reflected light microscopy and X-Ray powder diffraction (Philips PW 1710, Co-Fe rad., 40 kV, 20 mA).

The five "archaeological samples" have also been analyzed for their bulk and metallic phase chemistry by SEM/EDS. Semiquantitative results were obtained by using a Philips 515 instrument, equipped with EDS Edax 9800, and a Zeiss EVO MA15 equipped with an EDS detector and Oxford INCA250 microanalysis program at the MEMA laboratories in Florence.

Thirty-eight lead isotope analyses (including four duplicates) of copper ores, slag, mineral charge and metal artifacts have been performed for this work. Sixteen lead isotope analyses were carried out at the Laboratory of Isotope Geology at the University of Bern (Switzerland) using a Nu Instruments™ multicollector inductively coupled plasma mass spectrometer. The samples were dissolved in concentrated nitric acid or aqua regia. The Pb was purified with cation exchange resins, as detailed in Villa (2009). Thallium was added to samples prior to mass spectrometer analysis to correct for instrumental mass fractionation.

Twenty-two lead isotope analyses (including all the samples from the island of Elba) were carried out at the Institute of Geoscience and Georesources of CNR (Pisa, Italy) by means of a Finnigan Mat 262 multi-collector Thermal Ionization Mass Spectrometer (TIMS). Samples were dissolved with HNO_3 and HF, dried and re-dissolved first in HNO_3, then in HCl and finally in HBr, before loading onto ion-exchange cationic resins. After elution, the lead was dissolved in H3PO4 and loaded onto Re using silica gel.

Several measurements of the standard NIST SRM 981, performed to estimate the precision of the spectrometry, yielded values that compare favorably with those reported in the literature (Galer and Abouchami, 1998). Four samples were analyzed in duplicate in both isotope laboratories in order to estimate inter-laboratory reproducibility (Table 3). Differences were smaller than 0.1% and can be accounted for by a small fractionation correction (between −0.02 and +0.03%/amu) that probably affected the TIMS measurements, for which no independent fractionation monitor (such as the thallium doping used in ICP analyses) exists.

4. Results and discussion

4.1. Mineralogy and textures

Primary copper mineralization from Temperino Valley mine (Campiglia Marittima) is made of dominant chalcopyrite and pyrite ± variable amounts of pyrrhotite, sphalerite, galena, magnetite and hematite associated with typical skarn silicates like hedenbergite, ilvaite, and quartz. Malachite and chrysocolla are the most common secondary copper phases in the Temperino Valley mine (Table 1). Ophiolite-associated copper mineralizations from Elba Island are constituted by predominant chalcopyrite (± native copper, pyrite), whereas the four samples from the Fe(Cu) skarn ore deposit of Capo Calamita mine are a selection of various types of ore minerals including chalcopyrite and secondary phases like malachite, chrysocolla and native copper (Table 1).

Copper slags from Populonia-Baratti are characterized by a groundmass of fayalitic olivine, hedenbergite, magnetite and scarce glass with variable (but always minor) amounts of matte (Cu–Fe ± Zn) sulfides and metallic copper (Table 1: cf. Chiarantini et al., 2009). Depending on relative proportions of the different metal-bearing phases, these authors distinguished "(metallic) Cu-rich slag", "matte-rich slags" and "matte-Cu slags".

The lead (Cu-rich) medieval slag from Rocca S. Silvestro is characterized by fibrous to dendritic hedenbergite and fayalite associated with dendritic wüstite, droplets of metallic copper, lead and large Cu-Fe-Zn-S matte inclusion (*cf.* Mascaro et al., 1995)

The ore fragment from Baratti-Campo VI (sample C6-52/3b) contains relics of chalcopyrite associated with copper sulfides (close to covellite in composition) and small dendrites of wüstite; veinlets and masses of secondary phases (including iron hydroxides and copper oxides/carbonates) are abundant.

Archaeological bronze and copper items from the island of Elba display variable textural and compositional features. The two fragments from Cima del Monte (CM1, CM2) are made of a Cu–Sn α-phase with about 6.5 wt% Sn (6.1 and 7.1 wt%, respectively) occurring as equiaxed twinned grains with tiny inclusions of copper sulfides (with less than 0.01 wt% Pb) along grain boundaries. Minor contents of Ni have been detected in CM2 Cu–Sn α-phase (Table 2). Textural features suggest hot working of the alloys for both samples from Cima del Monte.

Sample CR5/2 from San Martino is made of almost pure copper. Textural analysis revealed the presence of deformed copper grains enclosing flattened inclusions of copper sulfides and globules of the eutectic assemblage copper/cuprite. Rare inclusions (about 10 μm in size) of metallic lead have also been observed.

The other two samples of raw copper from Volterraio and Colle Reciso display similar textural and compositional features. Both are made of small, pure copper grains associated with abundant globules of eutectic assemblage copper/cuprite and prills (up to 50 μm large) of a cuprite-like (± As, Sb, Pb) phase. These two samples display higher lead (0.9 and 0.2 wt%, respectively) and arsenic (2.1 and 1.2 wt%) bulk contents with respect to the other ones (Table 2).

4.2. Lead isotope composition

Lead isotopes have been extensively used in provenance studies of metal artifacts and associated metallurgical products, including slags (Cattin et al., 2009; Stos-Gale and Gale, 2009). The available lead isotope database of copper-rich ores from southern Tuscany includes about forty analyses already published, mostly referred to polymetallic ore deposits from the Campiglia Marittima and Colline Metallifere districts (Lattanzi et al., 1997; Stos-Gale et al., 1995), with a few additional analyses of ophiolitic copper ores (Lattanzi et al., 1992).

For the present work, we have analyzed a total of twenty additional samples of Tuscan copper ores (nine from Campiglia Marittima/Temperino Valley, eight from the island of Elba and three from Montecatini V. di Cecina: cf. Table 3). The analyzed samples have been plotted together data points of relevant copper districts from a selected area in the diagrams of Fig. 5(a/b). It is evident that the samples of ophiolitic copper from the island of Elba and Montecatini V. di Cecina mine fall close to the compositional field of Tuscan ophiolites (Lattanzi et al., 1992) but far from any other copper ore deposit of Southern Tuscany. As shown in detail in Fig. 6, the new lead isotope analyses of copper ores from Campiglia Marittima (Temperino Valley mine) fall close to other data points from the same district obtained in previous works (Lattanzi et al., 1997; Stos-Gale et al., 1995).

The Campiglia M.ma (Marittima) copper ores are isotopically similar (but distinguishable from) other copper ores of the Colline Metallifere belt. As expected, no significant lead isotope fractionation between primary (sulphidic/oxidic ores) and secondary minerals (malachite and chrysocolla) is observed at Temperino Valley mine (Table 3).

It is noteworthy that the four samples from Capo Calamita mine (Grotta Rame stope) are isotopically very similar to copper ores from the Campiglia M.ma district, although they show slightly lower Pb^{206}/Pb^{204} ratio (Fig. 6).

Bronze and copper "archaeological" artifacts of the island of Elba show very scattered and heterogeneous lead isotope compositions, which clearly fall outside the fields of both southern Tuscany polymetallic and ophiolitic copper ores (Fig. 5a–b). On the other hand, plots of the tin bronze scraps from Cima del Monte (CM1, CM2) and of the raw copper lump from Volterraio (VT1) into the diagrams of Fig. 5 fall in proximity to the compositional fields of Sardinia, Triassic Iberia or (VT1 only) the Apuane Alps district. The copper lumps from central Elba (Colle Reciso, CR5/2, and San Martino, SM 2236) cannot be surely derived from nearby ophiolitic copper outcrops. Theoretically, mixing of proper amounts of copper from Elban ophiolites and Southern Tuscany polymetallic district could provide a final product with the lead isotope signature. But a totally 'foreign' provenance, similar to that proposed for the CM1, CM2 and VT1 samples, seems equally possible.

At odds with the "archaeological" samples from the island of Elba, copper slags and the partially roasted ore fragment from Populonia-Baratti fall within the Campiglia M.ma compositional field, very close to the Temperino Valley copper ores (Fig. 6). In addition, as expected, the medieval lead (Cu-rich) slag from Rocca S. Silvestro fall within the compositional field of the Campiglia M.ma district.

4.3. The copper archaeological artifacts from the island of Elba

As already mentioned we do not have any clear archaeological evidence of an early (i.e., pre-Industrial) exploitation of copper from the island of Elba and the lead isotope data presented in this paper may

Table 2

Bulk composition of the analyzed metallic items expressed as mean values of semi-quantitative SEM/EDS raster analyses (two to four rasters of about 4–6 mm^2 have been performed on each sample). The mean composition of the main metallic phases identified in "archaeological" artifacts of the island of Elba is also reported as mean values of five semi-quantitative (SEM/EDS) point analyses.

	Bulk mean composition (wt%)								Mean composition of main metallic phase (wt%)			
	N/σ	Cu	Sn	As	Sb	Pb	Cl	S	N/σ	Cu	Sn	Ni
CM1	4	93,22	6,12				0,67		5	94,84	5,16	
	σ	1,21	0,76				0,48		σ	0,08	0,08	
CM2	3	92,03	7,14				0,82		5	92,18	7,58	0,24
	σ	0,01	0,32				0,31		σ	0,15	0,48	0,41
CR5/2	2	98,56		1,22		0,22			5	100		
	σ	1,35		1,35		0,38			σ			
SM2236	2	98,75						1,25	5	100		
	σ	0,38						0,38	σ			
VT1	2	96,55		2,15	0,44	0,86			5	100		
	σ	0,99		0,37	0,63	0,01			σ			

Table 3
Lead isotope composition of investigated samples.

Samples	Pb (wt%)	^{206}Pb/^{204}Pb	2σ	^{207}Pb/^{204}Pb	2σ	^{208}Pb/^{204}Pb	2σ	Laboratory
Ores								
AD1	< 0.01%	18.730	0.003	15.684	0.004	38.964	0.007	IGG
AD2	< 0.01%	18.722	0.003	15.677	0.005	38.952	0.006	IGG
AD3	0.10%	18.732	0.003	15.679	0.004	38.938	0.007	IGG
AD4	0.20%	18.738	0.003	15.681	0.004	38.955	0.005	IGG
AD5	< 0.01%	18.054	0.004	15.512	0.004	37.662	0.006	IGG
AD6	< 0.01%	18.086	0.003	15.510	0.004	37.642	0.006	IGG
AD7	< 0.01%	18.120	0.003	15.526	0.005	37.689	0.006	IGG
AD8	< 0.01%	18.093	0.003	15.524	0.004	37.725	0.005	IGG
T1	0.04%	18.756	0.002	15.686	0.001	38.977	0.003	IGB
T2	< 0.01%	18.757	0.003	15.672	0.004	38.930	0.006	IGG
T3	< 0.01%	18.758	0.003	15.687	0.003	38.972	0.007	IGB
T3 rep	< 0.01%	18.758	0.003	15.687	0.004	38.971	0.005	IGG
T4	< 0.01%	18.772	0.002	15.690	0.002	38.988	0.005	IGB
E 5-1	< 0.01%	18.718	0.001	15.679	0.002	38.914	0.006	IGB
E 5-7	< 0.01%	18.76	0.002	15.69	0.001	38.974	0.004	IGB
MT1b	0.10%	18.764	0.003	15.688	0.004	38.979	0.005	IGG
CT1	0.20%	18.753	0.002	15.688	0.004	38.978	0.006	IGG
CT2	0.30%	18.761	0.004	15.692	0.004	38.992	0.007	IGG
M	< 0.01%	18.080	0.003	15.476	0.004	37.654	0.005	IGG
M1	< 0.01%	18.078	0.004	15.444	0.004	37.683	0.006	IGG
MP	< 0.01%	18.108	0.003	15.486	0.004	37.684	0.006	IGG
Copper slags and archaeological samples								
C6-52/3b	< 0.01%	18.731	0.004	15.666	0.005	38.893	0.016	IGB
Z2b	0.02%	18.738	0.003	15.669	0.003	38.915	0.011	IGB
Y B11-1u	0.03%	18.752	0.001	15.684	0.001	38.961	0.004	IGB
Y B11-1u rep	0.03%	18.742	0.003	15.674	0.004	38.944	0.006	IGG
W B11-4a	0.02%	18.743	0.003	15.671	0.005	38.920	0.017	IGB
W B11-4a rep	0.02%	18.757	0.002	15.686	0.002	38.965	0.004	IGG
W B11-1	0.04%	18.761	0.002	15.691	0.002	38.982	0.005	IGB
W2	0.05%	18.725	0.004	15.673	0.004	38.916	0.009	IGB
W2 rep	0.05%	18.736	0.002	15.679	0.002	38.938	0.004	IGG
W B11-2	0.10%	18.748	0.002	15.688	0.002	38.970	0.005	IGB
W B11-3d	0.09%	18.748	0.001	15.687	0.002	38.970	0.005	IGB
VT1	0.85%	18.343	0.004	15.643	0.002	38.477	0.004	IGG
SM 2236	< 0.01%	18.495	0.001	15.647	0.001	38.624	0.001	IGG
CR5/2	0.50%	18.532	0.001	15.623	0.001	38.596	0.001	IGG
CM1	< 0.01%	18.154	0.003	15.681	0.001	38.360	0.003	IGG
CM2	< 0.01%	18.238	0.003	15.732	0.001	38.612	0.003	IGG
2411	15%	18.746	0.003	15.687	0.003	38.950	0.007	IGB

suggest that these otherwise small, scattered copper occurrences of the island were probably not exploited during FBA-EIA. In other terms, it is confirmed that neither the location of FBA-EIA hoards close to copper ophiolitic occurrences nor the discovery of a tomb dated to the Early Iron Age within a cave in the Capo Calamita mine area (Delpino, 1981) is reliable indicators of coeval copper exploitation. Unfortunately, it is not possible to gain further information from the copper slags of Santa Lucia described by Simonin (1858), since they have gone lost. Finally, the mold from Colle Reciso reported by Acconcia and Milletti (2015) does not *per se* indicate the use of local copper occurrences, since, for instance, it could have been used for remelting/recycling of used copper objects.

So, where does the metal used for these artifacts come from? It is impossible to establish the provenance of Elba copper-based artifacts merely on the base of their lead isotope composition. The main purpose of our investigation was to verify if these items could be associated, on the basis of their lead isotope signature, with copper ores cropping out in the island, often in close proximity to the metal hoards in which they were found.

Hopefully, the investigation of a larger set of archaeological copper samples from Elba Island, eventually including the analysis of both chemical (trace elements) and isotopic tracers could help to find the source(s) of copper items collected on Elba Island, as made, for instance, by Begemann et al. (2001) on almost coeval Sardinian hoards of copper/bronze artifacts. Nevertheless, a few considerations on the possible provenance of investigated samples can be drawn.

The two tin bronze fragments from Cima del Monte (CM1 and CM2) are characterized by different shape and quite high tin contents. Their lead isotope composition is close (but not equal) to some Sardinian copper deposits (especially from the Iglesiente area). Textural analysis showed that these pieces were surely hot-worked. Moreover, although the low lead contents (< 0.1 wt%) could indicate that they have not been deliberately leaded, it is not straightforward to compare their lead isotope signature with copper sources only, excluding tin ores (cf. Molofsky et al., 2014). In addition to mixing/recycling of bronzes, an intriguing alternative is that these two items are evidence of trade exchanges between Elba and Sardinia in the Final Bronze Age, in accordance with the findings of spearheads, axes, and daggers of "Sardinian shape" in many hoards of the island (Alderighi et al., 2012; Acconcia and Milletti, 2015).

The other three archaeological samples (VT1, CR5/2 and SM 2236) are made of almost pure copper and do not display textural evidence of metalworking, with the exception of sample SM 2236 from San Martino, which displays partly deformed sulfide inclusions. Samples VT1 and CR5/2 have relatively high contents of antimony (VT1) and/or arsenic (both). In principle, this compositional feature could rule out remelting, since this process should cause significant depletion of both elements in the final product with respect to the original metal source, unless the latter is particularly enriched in As and Sb. However, as already suggested, the lead isotope composition of two of these samples (CR5/2 and SM 2236) is compatible with the mixing (in proper amounts) of raw metal from Elba Island (ophiolitic copper) and

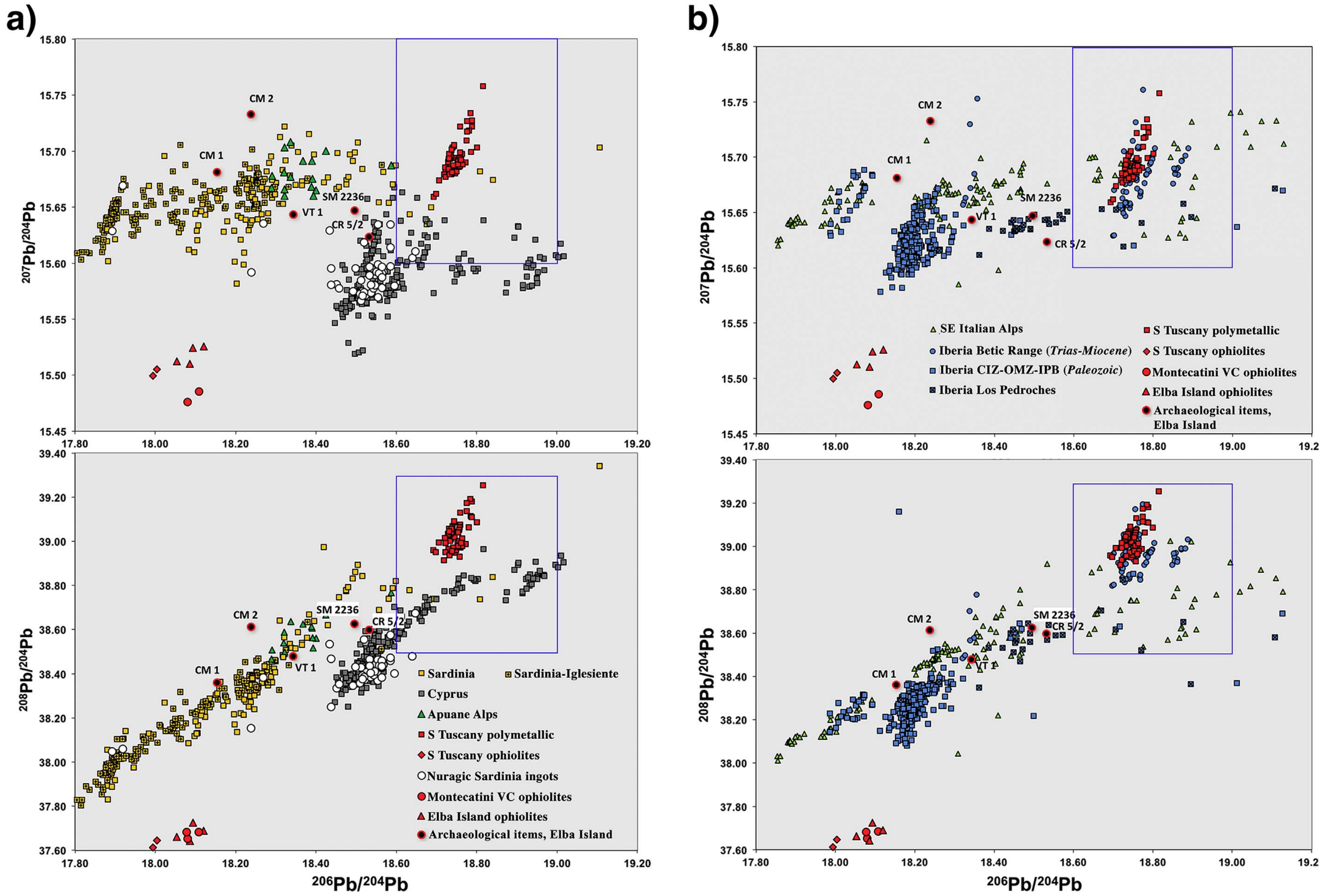

Fig. 5. a) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{2046}Pb$ (top) and $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ (bottom) diagrams for archeometallurgical samples from the island of Elba compared with polymetallic and ophiolitic copper ores from Tuscany (this paper, Lattanzi et al., 1997; Stos-Gale et al., 1995), Sardinia (Boni and Koeppel, 1985; Begemann et al., 2001; Swainbank et al., 1982; Ludwig et al., 1989; Stos-Gale et al., 1995), Apuane Alps (Lattanzi et al., 1992) and Cyprus (Stos-Gale et al., 1997). b) $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{2046}Pb$ (top) and $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ (bottom) diagrams for archeometallurgical samples from the island of Elba compared with polymetallic and ophiolitic copper ores from Tuscany (sources: see Fig. 4A) Iberia Betic Ranges, Central Iberian Zone (CIZ), Ossa Morena Zone (OMZ), Iberian Pyrite Belt (IPB) (Graeser and Friedrich, 1970; Arribas Jr. and Tosdal, 1994; Stos-Gale et al., 1995; Marcoux, 1998; Pomiès et al., 1998; Marcoux et al., 2002; Santos Zalduegui et al., 2004; Klein et al., 2009) and South Eastern Italian Alps (Artioli et al., 2016a). The portions of the diagrams enclosed by rectangular boxes have been enlarged in Fig. 6.

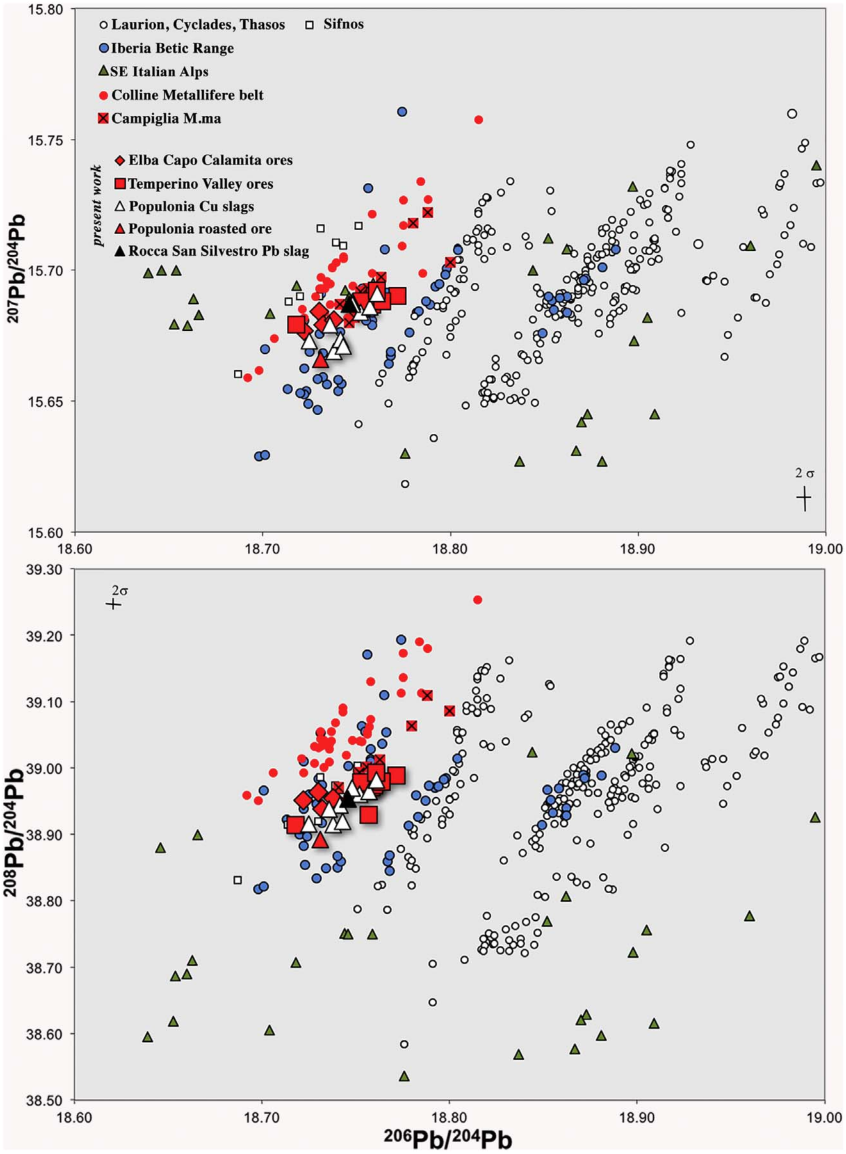

Fig. 6. ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{2046}Pb (top) and ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb (bottom) diagrams for samples of copper ores, slags and "archaeological" items analyzed in this paper. Data points from the whole southern Tuscany district (Lattanzi et al., 1997; Stos-Gale et al., 1995) and selected Mediterranean copper district (Laurion, Cyclades and Thasos: Gale, 1978; Gale and Stos- Gale, 1981; Stos-Gale et al., 1996; Spain and South Eastern Italian Alps: see Fig. 5) are reported for comparison. For samples investigated in this paper, the analytical error (2s) is generally less than the size of the symbols.

southern Tuscany (copper-rich, polymetallic ores). To be noticed that the latter ore district is notoriously As- and Sb-rich (cf. Morteani et al., 2011).

On the other hand, if mixing and recycling is not taken into consideration, VT1 sample is compatible with isotopic signature of Sardinian, Iberian or Alpine ore-fields, while SM 2236 falls in proximity to both Iberia (Los Pedroches PBT: Klein et al., 2009) and Cyprus fields (Fig. 5a–b). The copper lump CR5/2 from Colle Reciso (probably dated to the EIA) falls within the field of many Nuragic Sardinian oxide ingots (Begemann et al., 2001), which, unlike other Sardinian artifacts found in the same LBA hoards, plot entirely within Cyprus' field. The possibility that sample CR5/2 is somehow related to Cypriot oxhide ingots is fascinating, although to be confirmed with additional data.

The results obtained for our archaeological copper-based items may thus suggest that the island of Elba was not exploited for copper during FBA –EIA but that it was part of important trade exchanges through the Mediterranean Sea, possibly extending from the Far East (Cyprus?) to the West (Sardinia? Iberia?). Of course, additional data are required to verify these suggestions. Of particular interest could be the analysis of earlier copper-tich hoards, like the Eneolithic settlement of Grotta S. Giuseppe, to better evaluate the evolution with time of metalworking and commercial exchanges centered around the island of Elba.

4.4. *Provenance of the copper smelted at Baratti-Populonia*

The lead isotope data of copper slags (9th–8th cent. BCE) and the partially roasted ore fragment from Populonia-Baratti perfectly fit with compositions of the Campiglia M.ma district, which is located at a short distance (Fig. 1). It is noteworthy that all copper slags contain appreciable amounts of Zn (0.37–2.13 wt%) and Pb (50–1060 ppm) (Chiarantini et al., 2009), metals which have been won for centuries from the sphalerite-galena-chalcopyrite ores in the Campiglia M.ma ore deposits (Corsini and Tanelli, 1974; Corsini et al., 1980).

Although the Capo Calamita copper deposit (Grotta Rame, Elba) is isotopically indistinguishable from the Campiglia M.ma a copper ores, its small size makes it unlikely that it represented a major source for Populonia's coppersmiths. In fact, the Capo Calamita copper ores seem to have been exploited only in modern times.

The lead isotope signature of the Populonia-Baratti copper slags is completely different from that of Laurion and Cyprus districts, major sources for copper trade in the Mediterranean region during the whole Bronze age and the Early Iron Age (Stos-Gale et al., 1997). Fig. 6 shows some overlap with copper mines from Sifnos, but they apparently did not yield significant copper production in the Late Bronze Age/Early Iron Age (Stos-Gale et al., 1996; Stos-Gale, 2000).

Fig. 5b shows a similar lead isotope signature, with partial overlap, of the Baratti copper slags with polymetallic ores from the Cartagena and Almeria ore districts (Betic Cordillera) in south-eastern Iberia, but in Roman times lead and silver (and not copper) were apparently the main metal products from these districts (Orejas and Sánchez-Palencia, 2002; Stos-Gale et al., 1995; Hunt Ortiz, 2003). On the other hand, the lead isotope signature of Rio Tinto mines (Iberian Pyrite Belt, SW Iberia), which were exploited for copper by the Phoenicians, is completely different and can be excluded with certainty.

Coming back to the Hellenistic text *De mirabilibus auscultationibus* by Pseudo-Aristotle, although it is certainly a paradoxographical work not to be literally interpreted, it is interesting that the anonymous writer reported – in agreement with recent studies (e.g. Chiarantini, 2005; Chiarantini et al., 2009) - a chronological evolution from copper to iron mining and smelting in the Elba-Populonia area. On the other hand, now we know that ancient inhabitants of this territory had a long and sound metallurgical expertise in copper production which dates back to the Eneolithic, as demonstrated by the recent discovery of the metallurgical settlement of San Carlo (San Vincenzo) (Fedeli and Galiberti, 2016). The metallurgical slags of San Carlo show a low viscosity and witness an advanced slagging control, unlike many other examples of Chalcolithic copper-working centres (Bougarit, 2007; Addis et al., 2015; Artioli et al., 2015), but similar to the much later EIA copper slags found in the slag beach deposit at Baratti-Populonia. To be noticed that, in both cases, copper was mined from the same orebodies (Campiglia M.ma district). It is noteworthy that two Eneolithic copper axes, the first belonging to the famous Iceman mummy Ötzi found in Alto Adige (3300–3100 BCE: Artioli et al., 2016c) and the second one recently excavated at Zug-Riedmatt, Switzerland (3250–3100 BCE: Gross et al., 2017), both display a lead isotope signature typical of the Southern Tuscany ore districts.

A study of FBA copper ingots found at Cavalleggeri (San Vincenzo) and San Michele (Campiglia Marittima) (Fedeli et al., 1993), including lead isotope analysis, could help to unravel more in detail the evolution with time of copper mining and working in the Colline Metallifere-Campiglia M.ma districts. The state-of-art of our present knowledge allows us, however, to highlight the major role played by this territory in the production and trade of copper items for a long lapse of time, i.e. from Eneolithic up to EIA.

5. Conclusions

Two main types of copper deposit occur in southern Tuscany: the polymetallic (Cu-Pb-Zn(± Fe,Ag,Sn) sulphidic deposits of the Campiglia M.ma and Colline Metallifere ore districts in the Tuscan mainland (with the addition of Grotta Rame at the Capo Calamita mine in the island of Elba) and the copper ores associated with ophiolitic suites, common throughout the island of Elba and the Tuscan Apennines (e.g., Montecatini V. di Cecina).

As expected, but never directly tested before, in the present paper we have shown that the copper, skarn-type orebody mined at Grotta Rame (Capo Calamita mine, Elba) show lead isotope composition similar to copper ore deposits from the Campiglia M.ma district, which define a well distinct group within the larger compositional field of the southern Tuscany district. In addition, the lead isotope composition of ophiolitic copper is very close to that of enclosing rock suites and completely different from any other copper deposit of the polymetallic southern Tuscany district.

In general, the new lead isotope analyses performed in this study permitted to increase our knowledge of the long-lasting mining and metallurgical treatment of southern Tuscany copper ores, particularly for the territory extending from Elba Island to the Populonia-Campiglia Marittima territory in the FBA-EIA period.

The ancient Villanovan clans that established their settlement on the top of Populonia promontory at the beginning of the first millennium BCE, surely exploited copper ores from the nearby Campiglia M.ma Cu (Pb-Zn) district. The shift from copper to iron production probably took place between the 8th and early 6th century BCE (late Orientalizing period), when Populonia took complete and direct control of the iron ore deposits of Elba becoming one of the most important metalworking sites in the Mediterranean region.

On the other hand, the island of Elba apparently did not play a significant role in copper mining and working, particularly during FBA-EIA. In fact, none of the copper-based items from the island of Elba examined in this paper and collected from FBA-EIA metal hoards, showed clear genetic relationships with copper ores of any type from the island herself or the Tuscan mainland. Although additional data are necessary for a more reliable interpretation, we can guess that these copper or bronze items display a “foreign” lead isotope signature, possibly from Sardinia, Iberia or even Cyprus. This is in perfect agreement with the well-established role played by the island of Elba since the Bronze Age as a natural bridge between the Tuscan mainland on one side, and Corsica and Sardinia on the other one, thus permitting the diffusion of materials and metal working knowledge (Zifferero, 2002; Lo Schiavo et al., 2013; Acconcia and Milletti, 2015). Our study help to reinforce the idea that the island of Elba was, even before the beginning of iron production, at the crossroads of ancient trade routes through the Mediterranean Sea.

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References

Acconcia, V., Milletti, M., 2015. Il ripostiglio di San Martino e la metallurgia elbana tra Bronzo Finale e prima età del Ferro, Rivista di Scienze Preistoriche. LXV. pp. 217–251.

Acconcia, V., Milletti, M., Carraro, C.C., De Castro, F.R., Gabrielli, L., Galluzzi, G., Mottolese, C., Nomi, F., Palone, V., Picucci, S., Re, V., Taloni, M., 2006. Scavi sulla sommità del Poggio del Telegrafo: campagne 2003–2004. In: Aprosio, M., Mascione, C. (Eds.), Materiali per Populonia 5, edizioni ETS, Pisa, pp. 13–78.

Addis, A., Angelini, I., Nimis, P., Artioli, G., 2015. Late Bronze Age copper smelting slags from Luserna (Trentino, Italy): interpretation of the metallurgical process. Archaeometry 58 (1), 96–114.

Alderighi, L., Benvenuti, M., Buracchi, A., Chiarantini, L., Dini, A., Firmati, M., Milanesi, A., Pagliantini, L., Quaglia, L., 2012. Elba centrorientale: gli insediamenti antichi di Monte Moncione e Cima del Monte. In: Notiziario della Soprintendenza per i Beni Archeologici della Toscana. 8/2012. pp. 67–83.

Arribas Jr., A., Tosdal, R.M., 1994. Isotopic composition of Pb in ore deposits of the Betic Cordillera, Spain: origin and relationship to the other European deposits. Econ. Geol. 89, 1074–1093.

Artioli, G., Angelini, I., Tecchiati, U., Pedrotti, A., 2015. Eneolithic copper smelting slags in the Eastern Alps: local patterns of metallurgical exploitation in the Copper Age. J. Archaeol. Sci. 63, 78–83.

Artioli, G., Angelini, I., Nimis, P., Villa, I.M., 2016a. A lead-isotope database of copper ores from the Southeastern Alps: a tool for the investigation of prehistoric copper metallurgy. J. Archaeol. Sci. 75, 27–39.

Artioli, G., Angelini, I., Addis, A., Canovaro, C., Chiarantini, L., Benvenuti, M., 2016b. Ceramiche tecniche, scorie, minerali e metalli: interpretazione del processo metallurgico. In: Fedeli, L., Galiberti, A. (Eds.), Metalli e metallurghi della preistoria: l'insediamento eneolitico di San Carlo-Cava Solvay, Tagete Edizioni, Pontedera, pp. 68–81.

Artioli, G., Angelini, I., Canovaro, C., 2016c. Lead isotope investigation of Iceman copper axe: provenance of the metal. In: Abstract of the 3rd Bolzano Mummy Congress - Ötzi: 25 Anni di Ricerca, 19–21September 2016 - Bolzano, Italy.

Bamba, T., 1976. Ophiolite and related copper deposits of the Ergani mining district, Southeastern Turkey: Ankara, Turkey. Mineral Res. Explor. Inst. Turk. Bull. 86, 36–50.

Bartoloni, G., 2004. Populonia: l'insediamento delle prima età del ferro. In: Gualandi, M.L., Mascione, C. (Eds.), Materiali per Populonia 3, Firenze, pp. 327–349.

Begemann, F., Schmitt-Strecker, S., Pernicka, E., Lo Schiavo, F., 2001. Chemical composition and lead isotopy of copper and bronze from Nuragic Sardinia. Eur. J. Archaeol. 4 (1), 43–85.

Benvenuti, M., Boni, M., Meinert, L., 2004. Skarn deposits in Southern Tuscany and Elba Island (Central Italy). In: 32th IGC Firenze 2004, Field Trip Guide B18, Mem. Descr. Carta Geol. Italia, Roma, 63 (2). B18. pp. 1–24.

Benvenuti, M., Dini, A., D'Orazio, M., Chiarantini, L., Corretti, A., Costagliola, P., 2013. The tungsten and tin signature of iron ores from Elba island (Italy): a tool for provenance studies of iron production in the Mediterranean region. Archaeometry 55, 479–506.

Benvenuti, M., Orlando, A., Borrini, D., Chiarantini, L., Costagliola, P., Lazzeri, L., Mazzotta, C., 2016. Experimental smelting of iron ores from Elba Island (Tuscany, 1″ Italy): results and implications for the reconstruction of ancient metallurgical processes and iron provenance. J. Archaeol. Sci. 70, 1–14.

Boni, M., Koeppel, V., 1985. Ore-lead isotope pattern from the Inglesiente-Sulcis area (SW Sardinia) and the problem of remobilisation of metals. Mineral. Deposita 20, 185–193.

Bougarit, D., 2007. Chalcolithic copper smelting. In: La Niece, S., Hook, D., Craddock, P. (Eds.), Metals and Mines. Studies in Archaeometallurgy. The British Museum-Archetype Publications, London, pp. 3–14.

Cartocci, A., Fedi, M.E., Taccetti, F., Benvenuti, M., Chiarantini, L., Guideri, S., 2007. Study of a metallurgical site in Tuscany (Italy) by radiocarbon dating. Nucl. Instrum. Methods Phys. Res., Sect. B 259, 18–22.

Casini, A., Francovich, R., 1992. Problemi di archeologia mineraria nella toscana medievale: il caso di Rocca San Silvestro. In: Les techniques Minieres de l'antiquitè au XVIII siecle, Actes du colloque international reuni dans le 113e Congres National des Societes Savantes (Strasbourg, 5–9 avril 1988), Editions du C.T.H.S., Paris, pp. 249–265.

Cattin, F., Guénette-Beck, B., Besse, M., Serneels, V., 2009. Lead isotopes and archaeometallurgy. Archaeol. Anthropol. Sci. 1, 137–148.

Chiarantini, L., 2005. Approccio integrato con traccianti multipli allo studio archeometallurgico di antichi siti di estrazione e trattamento di minerali metalliferi della Toscana meridionale. Unpublished PhD Thesis. University of Florence.

Chiarantini, L., Benvenuti, M., Costagliola, P., Fedi, M.E., Guideri, S., Romualdi, A., 2009. Copper production at Baratti (Populonia, southern Tuscany) in the early-Etruscan period (IX-VIII cent. BC). J. Archaeol. Sci. 36, 1626–1636.

Cipriani, C., Tanelli, G., 1983. Le risorse minerarie della Toscana: note storiche ed economiche. In: Atti e Memorie Dell'accademia Toscana di Scienze e Lettere, “La Colombaria”. 48. pp. 241–283.

Cocchi, I., 1865. Di alcuni resti umani e degli oggetti di umana industria dei tempi preistorici raccolti in Toscana. In: Mem. Soc. It. Sc. Nat., I, tav. II, 1-1a.

Constantinou, G., 1992. Ancient copper mining in Cyprus. In: Marangou, A., Psillides, K. (Eds.), Cyprus, Copper and the Sea. Nicosia, pp. 43–74.

Corretti, A., 2004a. Fuliggine all'Elba? Storie di metallurghi e navigatori. In: Bruni, S., Caruso, T., Massa, M. (Eds.), Archaeologica Pisana. Scritti per Orlanda Pancrazzi, Giardini Editori, Pisa, pp. 122–129.

Corretti, A., 2004b. Per un riesame delle fonti greche e latine sull'isola d'Elba nell'Antichità. In: Gualandi, M.L., Mascione, C. (Eds.), Materiali per Populonia 3. Edizioni all'Insegna del Giglio, Firenze, pp. 269–289.

Corretti, A., Benvenuti, M., 2001. The beginning of iron metallurgy in Tuscany; with special reference to Etruria Mineraria. Mediterr. Archaeol. 14, 127–145.

Corretti, A., Chiarantini, L., Benvenuti, M., Cambi, F., 2014. The Aithale project: men, earth and sea in the Tuscan Archipelago (Italy) in antiquity. Perspectives, aims and first results. In: Cech, B., Rehren, Th. (Eds.), Early Iron in Europe. Proceedings of the Conference on “Early Iron” Sept 8–12th 2008, Hüttenberg (A), Instrumentum Monographies. 50. pp. 181–196.

Corsini, F., Tanelli, G., 1974. Analisi alla microsonda elettronica delle blende del giacimento della Valle del Temperino (Campiglia M.ma, Toscana). Rend. Soc. It. Min. Petr. 30 (1), 205–221.

Corsini, F., Cortecci, G., Leone, G., Tanelli, G., 1980. Sulfur isotope study of the skarn-(Cu-Pb-Zn) sulfide deposit of Valle del Temperino, Campiglia Marittima, Tuscany, Italy. Econ. Geol. 75, 83–96.

Cuteri, F., Mascaro, I., 1995. Colline metallifere, inventario del patrimonio minerario e mineralogico. Aspetti naturalistici e storico-archeologici. Edizioni Regione Toscana, Florence.

D'Achiardi, A., 1921. L'industria mineraria in Toscana dal tempo degli Etruschi ai giorni nostri. In: La Miniera Italiana anno V. 9. pp. 265–269.

D'Achiardi, G., 1929. L'industria metallurgica a Populonia. Studi Etruschi 3, 397–404.

Delpino, F., 1981. Aspetti e problemi della prima età del ferro nell'Etruria settentrionale marittima. In: L'Etruriamineraria. Proceedings of XII Convegno di Studi Etruschi e Italici (Firenze-Populonia-Piombino 1979), pp. 265–288.

Dini, A., Boschi, C., 2017. I giacimenti cupriferi delle ofioliti toscane. Geologia e ipotesi genetiche. Rivista Mineralogica Italiana 2 (2017), 84–101.

Dini, A., Mazzarini, F., Musumeci, G., Rocchi, S., 2008. Multiple hydro-fracturing by boron-rich fluids in the Late Miocene contact aureole of eastern Elba Island (Tuscany, Italy). Terra Nova 20, 318–326.

Dini, A., Orlandi, P., Vezzoni, S., 2013. Temperino e Lanzi. Le paragenesi primarie dello skarn. Rivista Mineralogica Italiana 1 (2013), 28–39.

Dolfini, A., 2010. The origins of metallurgy in central Italy: new radiometric evidence, To the memory of Lawrence Barfield, Renato Peroni. Antiquity 84 (325), 707–723.

Fedeli, F., Galiberti, A. (Eds.), 2016. Metalli e metallurghi della preistoria: l'insediamento eneolitico di San Carlo-Cava Solvay. Tagete Edizioni, Pontedera.

Fedeli, F., Galiberti, A., Romualdi, A., 1993. Populonia e il suo territorio profilo storico-archeologico. Edizioni All'insegna del Giglio, Firenze.

Gale, N.H., 1978. Lead isotopes and Aegean metallurgy, Thera and the Aegean World I. In: Thera and the Aegean World, London.

Gale, N.H., Stos- Gale, Z.A., 1981. Cycladic lead and silver metallurgy. In: The Annual of the British School at Athens. 76. pp. 169–224.

Galer, S., Abouchami, W., 1998. Practical application of lead triple spiking for correction of instrumental mass discrimination. Mineral. Mag. 62A, 491–492.

Graeser, S., Friedrich, G., 1970. Zur Frage der Alters-stellung und Genese der Blei-Zink-Vor- kommen der Sierra de Cartagena in Spanien. Mineral. Deposita 5, 365–374.

Grifoni Cremonesi, R., 2001. La Grotta San Giuseppe all'Isola d'Elba e l'eneolitico in Toscana Edizione ETS, Pisa.

Gross, E., Schaeren, G., Villa, I.M., 2017. The copper axe blade of Zug-Riedmatt (Canton of Zug, Switzerland) – a key to chronology and metallurgy in the second half of the fourth millennium BC. Archäologische Informationen 40, 213–227.

Guideri, S., 1995. Il contributo dell'archemetallurgia per lo studio di un territorio a vocazione mineraria: le Colline Metallifere nella Toscana Medievale. PhD Unpublished Thesis. University of Siena.

Hauptmann, A., 1985. 5000 Jahre Kupfer in Oman. Bd. 1: Die Entwicklung der Kupfermetallurgie vom 3. Jahrtausend bis zur Neuzeit. Der Anschnitt 4, 1–137.

Hunt Ortiz, M., 2003. Prehistoric mining and metallurgy in South West Iberian Peninsula. In: BAR International Series. S1188 Archaeopress, Oxford.

Klein, S., Domergue, C., Lahaye, Y., Brey, G.P., von Kaenel, H.M., 2009. The lead and copper isotopic composition of copper ores from the Sierra Morena (Spain). J. Iber. Geol. 35, 59–68.

Klemm, D.D., Wagner, J., 1982. Copper deposit in ophiolites of southern Tuscany. Ofioliti 7, 331–336.

Lattanzi, P., Hansmann, W., Koeppel, V., 1991. Preliminary data on the Pb-isotope composition of mineral deposits in Southern Tuscany. In: Pagel, M., Leroy, J.L. (Eds.), Source, Transport and Deposition of Metals, Proceedings of the 25 Years SGA Anniversary Meeting. Balkema, Rotterdam, pp. 317–320.

Lattanzi, P., Hansmann, W., Koeppel, V., Costagliola, P., 1992. Source of metals in metamorphic ore-forming processes in the Apuane Alps (NW Tuscany, Italy): constraints by Pb-isotope data. J. Mineral. Petrol. 45, 217–229.

Lattanzi, P., Benvenuti, M., Costagliola, P., Tanelli, G., 1994. An overview on recent research on the metallogeny of Tuscany, with special reference to the Apuane Alps. Mem. Soc. Geol. Ital. 48, 613–625.

Lattanzi, P., Benvenuti, M., Gale, N.H., Hansmann, W., Koeppel, V., Stos Gale, Z., 1997. Pb-isotope data on ore deposits of Southern Tuscany. Plinius 18, 123–124.

Lattanzi, P., Benvenuti, M., Costagliola, P., Maineri, C., Mascaro, I., Tanelli, G., Dini, A., Ruggieri, G., 2001. Magmatic versus hydrothermal processes in the formation of raw ceramic material deposits in southern Tuscany. In: Proceedings 10th Int. Symposium on Water-rock Interaction, Villasimius, 10–15 June 2001, pp. 725–728.

Lo Schiavo, F., Falchi, P., Milletti, M., 2013. Sardegna ed Etruria tirrenica: identità in formazione. Ripostigli e scambi della fase di transizione fra la fine del Bronzo Finale e la prima età del Ferro. In: Bruni, S., Cianferoni, G.C. (Eds.), Δόσις δ'ολίγη τε φίλη τε. Studi per Antonella Romualdi, Firenze, pp. 371–416.

Ludwig, K.R., Vollmer, R., Turi, B., Simmons, K.R., Perna, G., 1989. Isotopic constraints on the genesis of base-metal ores in southern and central Sardinia. Eur. J. Mineral. 1, 657–666.

Maggiani, A., 2006. Rotte e tappe nel Tirreno settentrionale. In: Gli Etruschi da Genova ad Ampurias, Atti del XXIV Convegno di Studi Etruschi e Italici, Pisa-Roma, pp. 435–449.

Marcoux, É., 1998. Lead isotopes systematics of the giant massive sulphide deposits in the Iberian Pyrite Belt. Mineral. Deposita 33, 45–58.

Marcoux, É., Pascual, E., Onézime, J., 2002. Hydrothermalisme anté-Hercynien en Sud-Ibérie: apport de la géochimie isotopique du plomb. In: Comptes Rendus Géoscience. 2002, 334. Elsevier Masson, pp. 259–265.

Mascaro, I., Benvenuti, M., Guideri, S., 1991. Inventario del patrimonio minerario e mineralogico in Toscana. Aspetti naturalistici e storico-archeologici. Volume 1 (Schede e bibliografia) Edizioni Regione Toscana, Florence.

Mascaro, I., Benvenuti, M., Tanelli, G., 1995. Mineralogy applied to Archeometallurgy: an investigation of medieval slags from Rocca San Silvestro (Campiglia M.ma, Tuscany). Sci. Technol. Cult. Herit. 4 (1), 87–98.

Minto, A., 1954. L'antica industria mineraria in Etruria ed il porto di Populonia. Studi Etruschi 23, 291–293.

Molofsky, L.J., Killick, D., Ducea, M.N., Macovei, M., Chesley, J.T., Ruiz, J., Thibodeau, A., Popescu, G.C., 2014. A novel approach to lead isotope provenance studies of tin and bronze: applications to South African, Botswanan and Romanian artifacts. J. Archaeol. Sci. 50, 440–450.

Morteani, G., Ruggieri, G., Möller, P., Preinfalk, C., 2011. Geothermal mineralized scales in the pipe system of the geothermal Piancastagnaio power plant (Mt. Amiata geothermal area): a key to understand the stibnite, cinnabarite and gold mineralization of Tuscany (central Italy). Mineral. Deposita 46 (2), 197–210.

Orejas, A., Sánchez-Palencia, F.J., 2002. Mines, territorial organisation and social structure in Roman Iberia: Carthago Nova and the Peninsular Northwest. Am. J. Archaeol.

106, 581–599.

Pomiès, C., Cacherei, A., Guerrot, C., Marcoux, E., Lancerot, J., 1998. Assessment of the precision and accuracy of lead-isotope ratios measured by TIMS for geochemical applications: example of massive sulphide deposits (Rio Tinto, Spain). Chem. Geol. 144, 137–149.

Santos Zalduegui, J.F., García De Madinabeitia, S., Gil Ibarguchi, J.I., 2004. A lead isotope database: the Los Pedroches – Alcudia area (Spain); implications for archaeometallurgical connections across southwestern and southeastern Iberia. Archaeometry 46 (4), 625–634.

Simonin, M.L., 1858. De l'explotation des mines et de la metallurgie en Toscane pedant l'antiquite et le moyen age. In: Ann. Des Mines 5. vol. XIV Paris.

Smith, M.A., Ross, W.D., 1909. The works of Aristotle translated into English. *De mirabilibus Auscultationibus*. Henry Frowde, M.A. Publisher to the University of Oxford, Oxford.

Sperl, G., 1981. Untersuchungen zur Metallurgie der Etrusker. In: L'Etruria Mineraria, Proceedings 12th Convegno Studi Etruschi e Italici, Florence, pp. 29–50.

Stos-Gale, Z.A., 2000. Trade in metals in the Bronze Age Mediterranean: an overview of lead isotope data for provenance studies. In: Pare, C.F.E. (Ed.), Metals Make the World Go Around. Oxbow Books, Oxford, pp. 56–69.

Stos-Gale, Z.A., Gale, N.H., 2009. Metal provenancing using isotopes and the Oxford archaeological lead isotope database (OXALID). Archaeol. Anthropol. Sci. 1, 195–213.

Stos-Gale, Z.A., Gale, N.H., Houghton, J., Speakman, R., 1995. Lead isotopes from Isotrace Laboratory, Oxford: archaeometry database 1, ores from western Mediterranean. Archaeometry 37 (2), 407–415.

Stos-Gale, Z.A., Gale, N.H., Annetts, N., 1996. Lead isotope data from the Isotrace Laboratory, Oxford: archaeometry data base 3, ores from the Aegean, part 1. Archaeometry 38, 381–390.

Stos-Gale, Z.A., Maliotis, G., Gale, N.H., Annetts, N., 1997. Lead isotope characteristics of the Cyprus copper ore deposits applied to provenance studies of copper oxhide ingots. Archaeometry 39 (1), 83–124.

Swainbank, I.G., Shepherd, T.J., Caboi, R., Massoli-Novelli, R., 1982. Lead isotopic composition of some galena ores from Sardinia. Period. Mineral. 51, 275–286.

Tanelli, G., 1983. Mineralizzazioni metallifere e minerogenesi in Toscana. Mem. Soc. Geol. Ital. 25, 91–109.

Tanelli, G., 1989. I depositi metalliferi dell'Etruria e le attività estrattive degli Etruschi. In: Proceedings 2nd Congresso Internazionale Etrusco, Firenze, 26 maggio – 2 giugno 1985. Supplemento da "Studi Etruschi", Edizioni G. Bretschneider, Roma, pp. 1409–1417.

Tanelli, G., Benvenuti, M., 1998. Guida ai minerali dell'isola d'Elba e del Campigliese. Edizioni Il Libraio, Portoferraio.

Tanelli, G., Lattanzi, P., 1983. Pyritic ores of Southern Tuscany, Italy. Spec. Publ. Geol. S. Afr. 7, 315–323.

Tanelli, G., Morelli, F., Benvenuti, M., 1993. I minerali del Campigliese: beni ambientali, culturali e industriali. Boll. Soc. Geol. Ital. 112, 715–728.

Tanelli, G., Benvenuti, M., Costagliola, P., Dini, A., Lattanzi, P., Manieri, C., Mascaro, I., Ruggieri, G., 2001. The iron mineral deposits of Elba Island: state of the art. Ofioliti 26 (2a), 239–248.

Torrini, G., 1990. Studio del giacimento a skarn e magnetite di Capo Calamita, Isola d'Elba (cantieri settentrionali). Unpublished Thesis. University of Florence.

Vezzoni, S., Dini, A., Rocchi, S., 2016. Reverse telescoping in a distal skarn system (Campiglia Marittima, Italy). Ore Geol. Rev. 77, 176–193.

Villa, I.M., 2009. Lead isotopic measurements in archaeological objects. Archaeol. Anthropol. Sci. 1, 149–153.

Zecchini, M., 2001. Isola d'Elba: le origini. In: Studi e testi, Accademia lucchese di scienze, lettere e arti, 65, S. Marco Litotipo, Lucca.

Zifferero, A., 2002. Attività estrattive e metallurgiche nell'area tirrenica. Alcune osservazioni sui rapporti tra Etruria e Sardegna. Etruria e Sardegna centro-settentrionale tra l'età del bronzo finale e l'arcaismo. In: Proceedings 21st Convegno studi etruschi ed italici, Sassari-Alghero-Torralba 13-17 ottobre 1998. Istituti Editoriali e Poligrafici Internazionali, Pisa/Roma, pp. 179–212.