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Lead Isotopes Analysis: possible risks and probable errors

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Abstract

Lead Isotopes Analysis (LIA) is a well-established technique, that is used to determine the origin of copper in an artefact under investigation (i.e. "provenancing"), through lead isotopes ratios.

By comparing the ratios of the lead isotopes 204, 206, 207 and 208, the isotopic signature of an archaeological relic, whether it appears as an artefact, semi-finished or remnant, can be characterized in a three-dimensional space.

This characterization can be compared with that obtained from samples, taken in mines or in ore fields, that were supposedly used in ancient times.

However, this technique introduces many risks that cannot be unspoken which, if not properly evaluated, can lead to conclusions even far from reality.

These risks were examined and investigated by many authors.

In this paper, I'll focus only on two major risks: the lack of geographic coverage of the possible ancient ores and the possibility that, starting at least from 12th century BC, the pick-ingots have been produced from many plano-convex ingots and therefore from different copper sources.

1 http://www.openstreetmap.org
2 http://opendatacommons.org e http://creativecommons.org
3 http://www.openstreetmap.org/copyright

Introduction

The Lead Isotopes Analysis (LIA) technique is well-known and described by many authors[4], as it also appears from the bibliography cited in Oxford Archaeological Lead Isotope Database (OXALID)[5].

These authors point out not only the benefits but also the risks arising from the use of this technique.

In particular, Pernicka emphasizes[6] that: *"it is not possible to regard the provenance of an artefact as proven, even it shares the same isotopic signature as an ore deposit. The reason for this is that although the variation of lead isotopes ratios in ore deposits is much smaller than that of trace element concentrations, there exist the possibility that another deposit has the same lead isotope ratios."*

Consequently, prior to each survey, it would be good to check the completeness of the geographic coverage of isotopic signatures for at least all potential candidate areas such as mining fields. In fact, even on an incomplete isotopic signature database, since the classification is usually carried out with the "Minimum Distance" technique, it is possible that an isotopic signature of an ore field exists[7] to be considered as "minimal" from that of the artefact under examination.

The "completeness" of the geographic coverage of ancient mineral ores is a necessary condition[8], though not sufficient to allow an attribution.

The final assignment, if possible[9], must be corroborated and validated by additional identifying elements such as:

- Copper isotopic ratios such as $^{63}Cu/^{65}Cu$[10];
- Traces of other elements (Sb, As, Ni, Co, Ag, Se, Bi)[11];
- Concentrations of the REE (Rare Earth Elements[12]) group.

Obviously, the reference databases of the old mines will also have to contain the latter types of information. So before you can proceed to any "assignment" procedure for antique artefacts under examination, it will be good to document not only the completeness of the geographic coverage of the ancient mining fields, but even if it contains all the information that is needed for a correct and safe assignment.

Lastly, I would like to recall a fact, remembered by many scholars, that is, the feasibility of extracting a given mineral with the technology of the time.

By way of example I will mention the fact that there are deposits in Anatolia and Sardinia containing tin. But in such a percentage that can only be exploited with modern industrial technologies[13].

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4 From the classic A.B. Knapp - European Journal of Archaeology Vol. 3 - 2000, at the most recent E. Pernicka - Archaeometallurgy in Global Perspective - Springer Science + Business Media – New York - 2014

5 http://oxalid.arch.ox.ac.uk/bibliography/bibliography.htm

6 Cf. Pernicka (2014)

7 Although the "minimum Euclidean distance" is equal to the instrumental error or half, as Stos-Gale & Gale (2009) assures, the resulting assignment can not always be considered as absolutely certain and true.

8 Cf. Pernicka (2004)

9 You can not overlook the possibilities of metal mixing, reuse, and the absence of references even in the presence of a "complete" Data Base.

10 Cf. F. Colpani, G. Artioli et alii (2006); Marelli, Artioli et alii (2010); I. Giunti (2011)

11 According to Pernicka (1999), the elements to be analyzed to make a significant contribution to the "origin" are: Au, Ag, Bi, Ir, Ni, Os, Pd, Pt, Rh, Ru.

12 La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (lanthanides)

13 Cf. Z. Stos-Gale, N. Gale (2004): *"Zn, Pb, cassiterite bearing deposit at Canale Serci, Villacidro (from which cassiterite could not be extracted, or even recognized, in the Bronze Age)"*

The incomplete list of the ores

The birth of metallurgy in the *Etruria Mineraria*

In the narrow sense, the medieval definition of "*Etruria Mineraria*" applies to the Metalliferous Hills (Colline Metallifere) that extend to the Tuscan provinces of Pisa, Livorno, Siena and Grosseto.

In a broad sense, it applies to the areas that used to supply metals for the Etruscan civilization and for those who preceded it in the same area[14]. In this sense the term does not refer to Tuscany alone, but also to upper Lazio.

Tuscany is the most important Italian region from a mining and mineralogical point of view.

In the 1861-1913 period[15], it produced nearly 13 million tonnes of iron (equivalent to 90% of the national total) and 2.4 million tonnes of copper (equivalent to 85% of the national total). It also contributed to the entire national tin production.

In the same period, Sardinia contributed marginally to copper production (0.13%) and iron (2.28%) but contributed 96% to domestic lead production, 87% to zinc and for 100% to that of silver.

It is good to remember that for most of the 19th century, the Caporciano (Montecatini Val di Cecina) mine was considered to be the most important copper mine in the whole of Europe with a production of more than 50,000 tons (1827-1900) of copper[16].

Moreover, it is estimated that iron production from Elba from the beginning of the 13th century to the present day was just about 50 million tonnes[17].

Having said that, we must observe that all this has little or nothing to do with metallurgy of the Bronze Age.

What is said in fact refers mostly to an industrial exploitation and the few links that can be derived from the documents that report the observations that geologists or mineralogical experts have carried out over the centuries during their inspections.

Among other things, this information is very useful both because they speak of now completely disappeared mineral deposits[18] and because they provide useful information about antique mines[19] and, in industrial times, also chemical analyses.

The great industrial production of recent centuries has completely destroyed the landscape and every trace of possible prehistoric mines.

Despite everything, we have a series of information that comes from many surveys with the result of:

1. Some instruments (stone and deer horn mandrils[20]) found in the cinnabar mines of Amiata:

[14] Most scholars now begin Etruscan civilization from the Protovillanovian. Personally, I join those few protohistory experts (Cocchi Genick -2002) who, instead, retrograde the dawn to the *Grotta Nuova* facies.

[15] C. Ciccarelli, S. Fenoaltea (2010)

[16] P. Orlandi - 27 Luglio 2006 - Provincia di Pisa

[17] G. Vanagolli (2012)

[18] Such as the iron mines of Casentino and Rapolano frequently remembered in medieval documents.

[19] Medieval documentation is very rich. Remember the "Mining Code", which is included in the statute of the commune of Massa Marittima (1311-1325), which is one of the oldest texts of this kind in Europe. It guaranteed the freedom of extractive research and required that every stage of the production activity be followed by appropriate municipal magistrates.

[20] C. Giardino, D. Steiniger (2011)

Cornacchino[21] (in the municipality of Castell'Azzara), Cortevecchia[22] (in the municipality of Semproniano), Bagnore-M. Labbro[23] (in the municipality of S. Fiora) and Solforate-M. Civitella[24] (in the municipality of Piancastagnaio) all having radiocarbon datings between 4,780 and 4,460 BC;

2. the remains of ovens for copper processing such as those of Orti Bottagone[25] (Campigliese) dated to the late Neolithic[26] (late V millennium BC) and Solvay quarry of S. Carlo[27] dated[28] to the first Eneolithic[29] [30];
3. metallurgical ateliers of the beginning of the Eneolithic (3,500 BC), which used the nearby native copper outcrops (Sesto Fiorentino: Neto-via Verga[31] and Podere Pietrino[32]);
4. copper plano-convex ingots found in mining wells such as Cugnano[33] (Monterotondo Marittimo) or near mines such as La Speziala[34] (dated to EBA) and Serrabottini[35] (between Eneolithic and EBA);
5. Ötzi copper axe analysis (dated approximately 3,350 to 3,000 BC), which clearly indicates a

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21 Quartzite pound with median groove (Zifferero - 1991)

22 It appears as Corte Vecchia in the work of C. Giardino

23 It appears indicated as S. Fiora in C. Giardino's work

24 Appeared as Sele-Solforate in C. Giardino's work. It is possible that the author also refers to the nearby Siele-Carpine mine in the municipality of Piancastagnaio and in any case a cinnabar mine.

25 Artioli (2007) tells us that "*the samples from Tuscany (CS1 from San Carlo and OB1 from Orti Bottagone) contain iron phase that may be the product of metallurgical processes.*" I'm personally inclined to believe or a case due to the composition of minerals, or that the dating is lower.

26 Even Artioli (2007): "*If the neolithic date of the preliminary archaeological reports for Orti Bottagone occurrence are confirmed (doubtful given the" presentation "of the surface of the finds), the presence of copper smelting lags in Tuscany at the end of the Neolithic, much before (after recent dating by Dolfini in 2011, the time distance was reduced to less than 300 years) the metallurgical developments related to the Rinaldone culture ... is an important piece in the reconstruction of the metallurgical puzzle* ".

27 They show the use of poly-metallic sulphides similar to the alpine Falherz of which Tuscany is rich and also of a technique as Dolfini tells us: "*revealing that copper extraction was efficient enough to allow for the almost complete separation of the slag from the molten Matte* "(2014).

28 G. Artioli: *"Radiocarbon dating of charcoal fragments present within the metallurgical slags of San Carlo indicates a calibrated age around 3400–3100 BC (95% confidence level at 2σ)".*

29 Cf. F. Fedeli (1995)

30 Cf. G. Artioli (2016)

31 The numerous radiocarbon dating on relevant remains on the Neto-Via Verga (Sesto Fiorentino) 5 horizon unfortunately stumble over a thousand years (sample LTL1481A: 3,100 BC; sample LTL1482A: 4,400 BC. For details, see Manfredini - 2009). Consequently, in the text I have indicated the traditional dating (half of the IV millennium BC). Contra C. Giardino (2008) which states: "*In Etruria are located some of the oldest claims of copper processing of the entire Italian Peninsula. In Sesto Fiorentino (Neto - Via Verga and Podere Pietrino) fragments of scorched crucibles and copper artifacts have been found in late-Neolithic contexts, chronologically attributed to the mid-fifth millennium BC. (Martini, Sarti 1999, 37, Giachi, Pallecchi, Sarti 2001, p. 638). Although no specific investigations have been carried out to identify the origin of the raw material, such as the analysis of the isotopic lead ratio, it is striking to associate these presences with the large Tuscan deposits, especially at such an initial stage of metallurgy. It should be remembered that from the fields of Impruneta, located just twenty kilometers from the site, have been found in the outcropping ofiolytic rocks - such as Poggio alla Carraie and Sassi Neri - also native copper samples of many kilograms.* " I remember that the chronology of the older site for copper extraction and metallurgy in the whole central and western Europe is that of Brixlegg in the Inn Valley (4,200 BC). Cf. Hoppner (2005). Certainly, if you add the various elements, namely: dating to 4,400 BC of the LTL1482A sample, the dating at 4,200 – 4100 BC of Orti Bottagone's site, and the use of metallurgical processes extensively evolved both in Orti Bottagone and in San Carlo, it is supposed that Dolfini's intuition about the metallurgical primacy of Tyrrhenian central Italy should not only be followed, but also strengthened.

32 F. Martini, L. Sarti (2006)

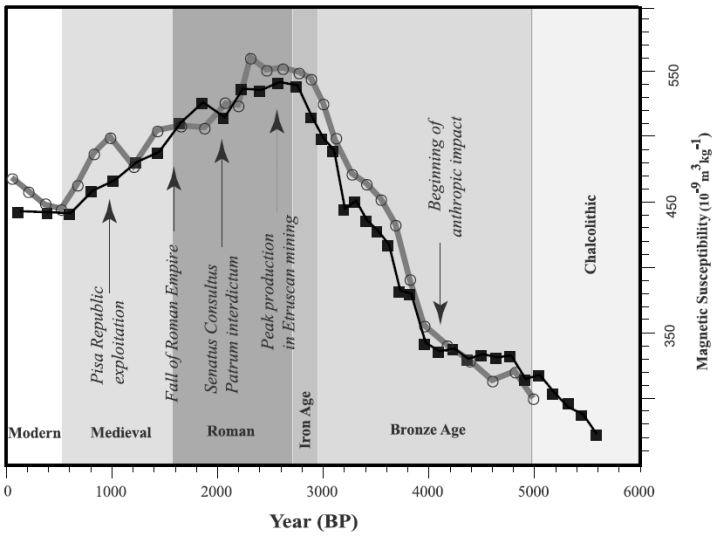
33 Cf. B. M. Aranguren, L. Dallai (2007)

34 Cf. B. M. Aranguren (2006)

35 Cfr. Aranguren (2006)

source of copper from the Campigliese[36]. Even the shape of the axe is much more similar to those found in areas that will then give birth to Etruscan civilization rather than those of the Alpine area. The consequence is obvious: Ötzi was spending in Tuscany and not only for copper but the well-finished stuff.

6. Analytical results on metal finds from Maremma[37]: antimony and silver (about 3,780 BC); silver (about 3,500 BC[38]); copper (arsenic copper: ca. 2,750 BC to: copper with As and Sb: approx. 2,950 BC[39]) and the first European pyrotechnic finding of glass[40] in eneolithic horizon;
7. Analytical results[41] on vases of a necklace in the hole of Spaccasasso (near Alberese, Maremma Natural Park): pure silver (about 2,700 BC). Of particular interest is the contemporary presence in the site of aspects related to the culture of Laterza (Apulia) as well as Transalpina[42];
8. Analytical results on a bronze ring[43] by Poggio Olivastro near Vulci[44] dated to the late Eneolithic;
9. LIA surveys on EBA finds found in Switzerland[45] indicating the raw material coinciding with the isotopic signatures of the mines around Accesa lake (Primary mining field Serrabottini, mines of Serrabottini - Castelborello - Scabbiano - Fenice Capanne - Accesa which also includes La Pesta indicated by Oxalid);
10. LIA surveys on the EBA[46] findings at Monte S. Savino which propose a proximity[47] of the spectral signature found on the artefacts (a dagger and a halberd) with that of the Tuscan mining fields;
11. LIA investigations on Ligurian finds[48] which indicate for many artefacts and for a large period of time (Eneolithic, Bronze Age) a source from the mines in the Tuscan coastal area;
12. *Other recent surveys, including those on marine sediments[49], which analyses the magnetic susceptibility of the sea beds at Elba (see figure to the side) concludes: "archaeometallurgic activity started on Elba Island in the II Millennium BC, much earlier than before assumed. "*



36 G. Artioli (2017)
37 P. Petitti et alii (2011)
38 Cf. Anzidei (2007)
39 So they align the scenario with the conclusions of A. Dolfini (various work since 2010) and update the previous proposals of De Marinis (2006)
40 This is an intermediate product in glass production. Cf. Bellintani (2003)
41 Cf. P. Pallecchi et alii (2007)
42 See the couple of T-shaped metal spools, with spiral wrap loop head. These are Straubing type transalpine specimens, which are paired in the burials referring to the lattice ceramic horizon (Schnurkeramik) and chronologically framed in an advanced phase of the recent Chalcolithic of Central Europe.
43 Analysis: 92.5% Cu; 6.2% Sn; 1.4% Ni; 1.3% As; 1.2% Sb; 1.2% Ag.
44 Cf. Bulgarelli (2008)
45 Cf. F. Cattin (2007, 2011)
46 In fact, they are between the late Eneolithic and the beginning of the EBA. Cf. E. Buresta (2006)
47 No convincing attribution can be made. But the database of the Tuscan mines is extremely limited.
48 Cf. Campana (1996)
49 Cf. Vigliotti (2003)

All this information leads us to a series of certain conclusions that Andrea Dolfini[50] sums up:

"Therefore, it could be suggested that metallurgical knowledge, coming from eastern Europe, was simultaneously introduced into both the northern and the southern Alpine region, whence it would have rapidly spread to the central Italian peninsula, Sardinia, and later to the remainder of the central Mediterranean. Notably, this scenario ties in with the proposal that metal technology would have spread throughout Europe in a north-westerly direction, following either a single invention event in Anatolia or independent rediscovery in the central Balkans. On the contrary, claims for Aegean origins seem far less probable given the lack of early evidence from southern Italy and Sicily, while the Iberian transmission hypothesis aired by Pearce does not stand in the light of the later developments of metalworking west of the central Mediterranean. Similar claims for the independent invention of metallurgy in Sardinia can also be dismissed, since early smelting and metalworking on this island are not appreciably older than in Italy, and might be later."

Regarding instead the next Bronze Age C. Giardino[51] specifies:

"In the early Bronze Age metallurgy, Etruria observes basically the transition from arsenic to stannic alloys. The relatively high iron content that characterizes the finds of this period found in the region is a serious indication that copper was obtained from its minerals by resorting to extraction techniques leading to the formation of slags, probably from sulphides such as chalcopyrite. It should be remembered that degrading processes are far more efficient than non-scorching and that the latter characterize somewhat primitive stages of metallurgy. "

The Tuscan mines

The Tuscan mines have been exploited since the Eneolithic because they are also rich in native copper. Native copper is found in Impruneta, in the Monti Rognosi[52], in the area of Rapolano (Asciano and Sinalunga), at Castiglioncello, at Miemo in the Val di Cecina, at Chianni in Valdera, near Castellina Marittima in the Metalliferous Hills near Pisa, at Casal di Pari and Murlo just to quote the most significant of a total of 17.

Oxford University's Data Base, named OXALID[53], holds a file[54] that contains the isotopic ratios of Italian mining fields. As far as Tuscany is concerned, there are listed 48 values referring to 8 mines and 2 mining fields (Giglio, Elba). If you compare this data with those found in the Regional Inventory made between 1991[55] and 1995[56], you can see how partial and incomplete are the isotopic signatures listed in the file.

From the aforementioned "Inventory" there are 168 mines[57] or mining fields of metallogenic minerals (Cu: 46; Fe: 31; Ag: 22; Pb: 14; Sn: 3), for which the contributors to the investigation state that, at a different level of probability, 21 could have been exploited in prehistoric ages.

What is still to be done about the reference Data Base is demonstrated, for example, by the fact that of the 168 sites (mines or mining fields) described in the Regional Inventory, only 16 are in the province

[50] Cf. A. Dolfini (2014), which also bases his thesis on a vast radiometric campaign (2011)

[51] Cfr. C. Giardino (2008)

[52] Along with Cuprite and Malachite

[53] OXford Archaeological Lead Isotope Database

[54] Italian ores Isotrace 8May2011

[55] "Inventory of Mining and Mineral Resources in Tuscany - Naturalistic and Historical Archaeological Heritage" - Department of Environment - Tuscany Region - 1991

[56] "Metalliferous Hills: Mining and Mineral Heritage Inventory - Naturalistic and Historical Archaeological Aspects" - Department of Environment - Tuscany Region - 1995

[57] They are 200 in the List of Mining Sites in Tuscany published by LAMMA (CNR) and made in 2011 from RIMIN (ENI) data which actually lists 467 "mining sites".

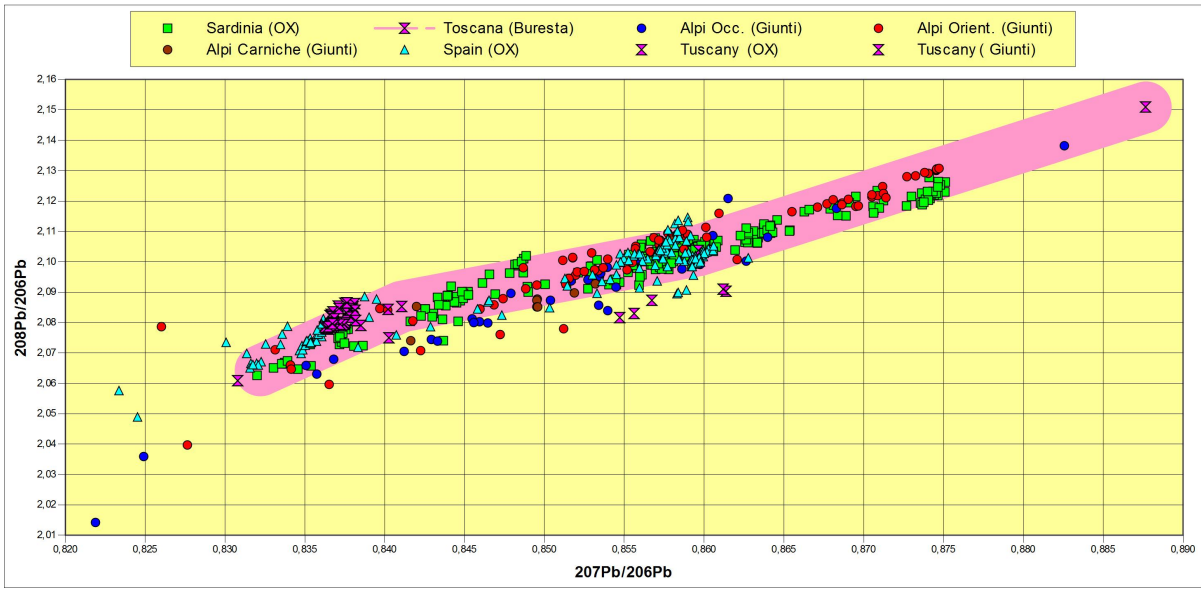
of Pisa. A more recent census, carried out on behalf of the Province of Pisa, cited[58] 110 sites in place of 16 citations. The number of isotopic signatures we have is not sufficient enough : the only sensible choice is to significantly increase the few measurements currently available.

It is recalled, for example, that neither the argentiferous galenas[59] of Apuan Alps nor the native copper deposits (both mentioned above), both potentially attractive to metallurgists of the copper age, are present on Oxalid. Moreover, the few additional isotopic measurements carried out as those of Buresta[60] show data[61] that, in one case, show much lower radiogenicity than those of all Italian mines[62], while another indicates exactly the opposite[63].

The other two measurements made by the Buresta team suggest isotopic ratios that if in Rapolano[64] they are not so far from those of the coastal mines on Oxalid, however, those in the Sinalunga area[65] seem to be near some of Sardinia's deposits. Buresta's data indicate extreme variability of isotopic signatures, probably due to the geologic history of the extremely complex and varied region[66].

The following graph shows in magenta the extent of lead isotopic ratios in the Tuscan mines, compared with Oxalid ratios in Spain, Sardinia and Alpine measurements of Giunti.

Isotopic ranges in Italian mines



Therefore, statements like *"The ores from the Sardinian exhibit a much greater isotopic variation than the ores from Tuscany"*[67] are valid when referring to Oxalid, but in absolute terms no.

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58 Cf. P. Orlandi (2006).

59 As far as the municipality of Stazzema (10 sites on the Inventory) is available, a very detailed survey carried out by M. Ciampa, which lists (2006) 25 active and 91 abandoned quarries, then merged into 12 mines.

60 Cf. E. Buresta et alii (2006)

61 The Buresta survey looked at four copper deposits near the finds.

62 See the sample from Il Convento in the Monti Rognosi (Anghiari): with $^{208}Pb/^{206}Pb$ of 2,150866 and $^{207}Pb/^{206}Pb$ of 0,887676 which may indicate a very high formation age or, as G. Ferrara (1985) says: *"It is impossible to use the Rb/Sr or U/Pb methods because of the extremely low content of the radioactive isotopes of these rocks "*

63 See the ore field of S. Alberto (Asciano): con $^{208}Pb/^{206}Pb$ di 2,060802 e $^{207}Pb/^{206}Pb$ di 0,830792 which has three carbonates: two of copper (azurite and malachite) and one of iron (goethite).

64 Sheet n° 90 with chalcopyrite, bornite, native copper, malachite, azurite

65 Malachite

66 The measurements of Ferrara (1985) indicate ophiolitic complexes dating between 160 and 185 Million years; for the Apuan Alps between 11 and 17 My; for islands between 5 and 15 My; for the volcanic rocks of the SW area between 2 and 5 My; for Amiata less than 1 My.

67 R. Jung, M. Mehofer, E, Pernicka (2011)

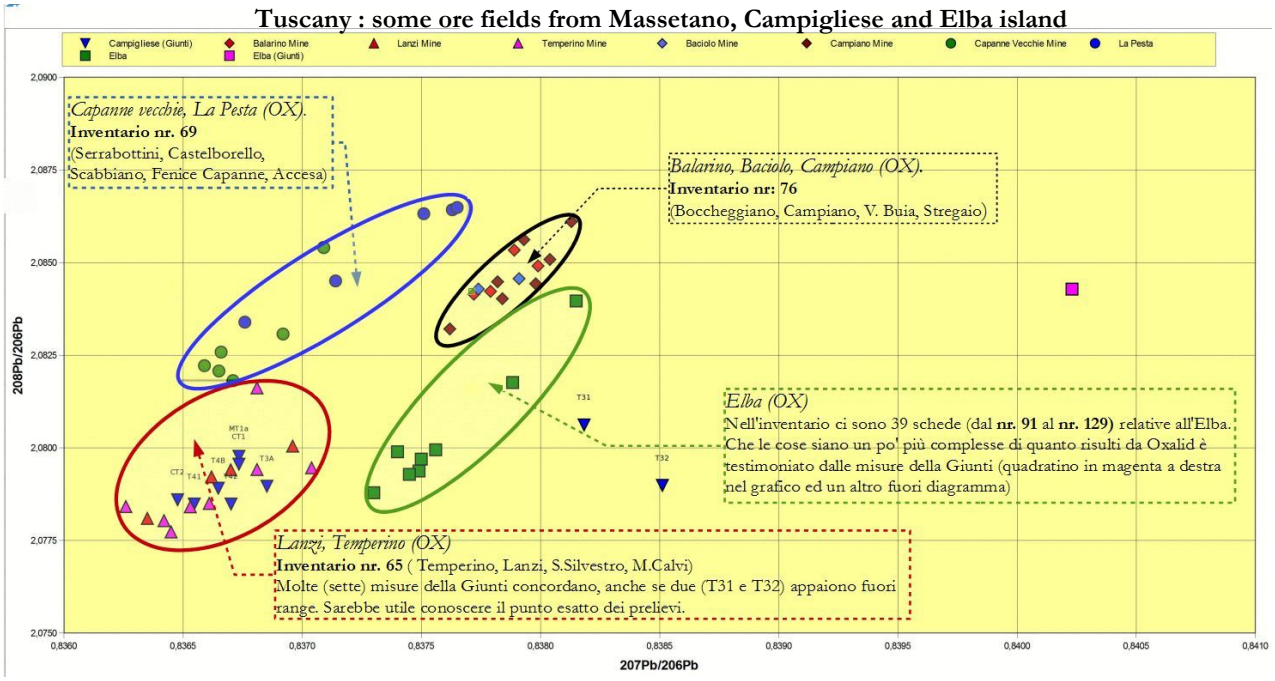
Another problem to consider and not least is the one relating to the correct identification and characterization of each mining field. The "Inventories" we have available are a necessary first step but it is not enough yet. The University of Siena (Francovich and Dallai) is engaged in capillary surveys on the territory for the primary purposes of investigations on the medieval front[68]. But of course, as a relapse, all the data on much older temporal horizons are documented.

By way of example, we consider the sheet 69 taken from the 1991 inventory previously mentioned, which we reproduce in part along with the corresponding card 179 instead of that of 2011. The sheet identifies the main mining area of the municipality of Massa Marittima, which includes the mines of[69]: Serrabottini Sud[70]; Castelborello (near Serrabottini); La Speziala (not mentioned) near Castelborello; Fenice Capanne[71] with cupriferous and lead-zinc minerals extracted from this mine in the years 1950 to 1980[72]; La Pesta for the extraction of copper and lead-zinc ore[73]; Scabbiano (Scabiano) with modest mineralizations of mixed pyrites and sulphides.

Between the old names and the recent ones there is a great confusion: what is called by the workmen as a well no. 4, is sometimes labelled as La Pesta mine.

It is actually part of the mineralization of Serrabottini, as Castelborello, La Speziala and Scabbiano. It seems that in ancient times copper was mainly extracted: there are several plano-convex ingots found in the area and dated back at least to EBA[74]. Secondly, silver was extracted in the Bronze Age and then iron. In the Middle Ages copper, silver and iron.

In recent times copper, lead, zinc and pyrite have been extracted. An interesting fact is that if you



compare the isotopic signatures on Oxalid they appear grouped according to the mining fields on

68 Cf. Aranguren, Dallai (2007)

69 For the mapping of the ancient mines see: Gaetano Badii: «*Le antiche miniere del massetano*». *Studi Etruschi*, v (1931)

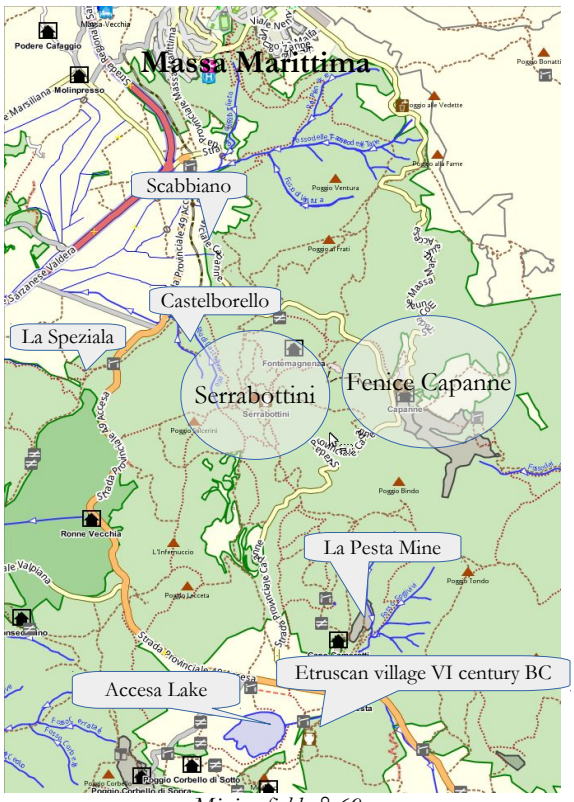
70 Today what Badii has called Serrabottini Sud is simply called Serrabottini; while what the same author calls Serrabottini Nord is Le Bruscoline.

71 The unique "Fenice Capanne" diction is probably due to the fact that in 800 there were two companies exploiting the mines in the area: Capanne Vecchie and Fenice Massetana to which Montecatini then succeeded, which gave a new impetus to all the mines of Tuscany.

72 As appears from various documents of the Tuscany region.

73 Ibid.

74 Both Serabottini's (see Aranguren - 2005) and those of La Speziala (cf. Aranguren - 2006)



Mining field n° 69

inventories.

Once the Data Base is completed and the correct groupings are made for each mineralogically homogeneous area, it will be possible to build clusters that could be very useful to try to change the classification method: from Minimum Distance to Mahalanobis Distance[75], if not to Maximum Likehood.

Accesa Lake

[75] With each cluster featuring a centre of gravity and a covariance matrix

Località: **SERRABOTTINI - S. CASTELBORELLO-SCABBIANO-FENICE CAPANNE-ACCESA**

Emergenza Mineralogica: sì *Emergenza Mineraria*: sì *Attiva:* no

Mineralogia: blenda, galena, calcopirite, pirite, tetraedrite, stibina, arsenopirite, pirrotina, bismutina, magnetite, ematite, limonite, bornite, calcosina,

Sostanze Estratte: Pb (Piombo), Ag (Argento), Cu (Rame), Zn (Zingo), Sb (Antimonio) (?), Au (Oro) (?), Alu (Alunite), Vet (Vetriolo).

Descrizione Naturalistica: importante mineralizzazione filoniana a solfuri misti in ganga prevalentemente quarzosa, ma anche calcitica e a skarn, localizzata entro una serie di faglie appenniniche interessanti i flysch liguridi, il Calcare Cavernoso e le filladi del basamento. I filoni mostrano frequenti restringimenti e allargamenti ed una zonalità mineralogica. I filoni sono interessati da un alone di alterazione con fenomeni di silicizzazione, silicatizzazione, e alunitizzazione. Di interesse mineralogico i quarzi ametistini dell'Accesa.

Interpretazione Geologica: vedere la scheda relativa n. 77 a Montieri (GR).

Descrizione Storica: si tratta di un'ampia area interessata da mineralizzazioni a solfuri misti nella quale si trovano tantissime tracce di escavazioni antiche per l'estrazione di rame e piombo argentifero; a Serrabottini (Mons de Buctinis o de Poczorio) vi sono oltre 200 pozzi, tra aperti e chiusi alcuni dei quali ben conservati con profondità variabile dai 40 agli 80 m., rivestiti in pietra e disposti a distanza di circa 25 m. l'uno dall'altro; a Castelborello ve ne sono una quarantina per lo più franati. Più ad est vi sono coltivazioni moderne e contemporanee.

Sheet 69 of the Tuscany Region Inventory (partial)

Codice Miniera: MIN_179
SERRABOTTINI – S. CASTELBORELLO – SCABBIANO – FENICE CAPANNE – ACCESA - P. GUARDIONE

Morfologia	Dati Economici
filoniana - *veins*	giacimento grande non più in coltivazione *large deposit, abandoned*
Tessitura	**Coltivazione**
massiva - *massive*	
Processo Genetico	**Età minerogenesi**
idrotermale, alterazione ipogenica *hydrothermal, hypogenic alteration* metasomatico - metasomatic	Terziario - *Tertiary*
Elementi e Minerali	
Zn Pb Ag Cu Sb Au	
Chimismo	**Ganga**
z - solfuri e combinazioni affini	carbonatica - *carbonatic* silicatica - *silicatic*

Sezione CTR: 306150-318030
Area Protetta: no/si
Attiva: no
Provincia: GR
Comune: Massa Marittima

Mineralogia: blenda, galena, calcopirite, pirite, tetraedrite, stibina, arsenopirite, pirrotina, bismutina, magnetite, ematite, limonite, bornite, calcosina.

Sostanze Estratte: Pb (Piombo), Ag (Argento), Cu (Rame), Zn (Zinco), Sb (Antimonio), Au (Oro), Alu (Alunite), Vet (Vetriolo).

Descrizione del giacimento:
importante mineralizzazione filoniana a solfuri misti in ganga prevalentemente quarzosa, ma anche calcitica e a skarn, localizzata entro una serie di faglie appenniniche interessanti i flysch liguridi, il Calcare Cavernoso e le filladi del basamento. I filoni mostrano frequenti restringimenti e allargamenti ed una zonalità mineralogica. I filoni sono interessati da un alone di alterazione con fenomeni di silicizzazione, silicatizzazione, e alunitizzazione. Di interesse mineralogico i quarzi ametistini dell'Accesa.

Sheet 179 of the Lamma-CNR Inventory(partial)

The total absence of "coverage" of the fields

The mines in the subalpine area

Oxalid's major deficiency is that it does not include data on any mineralization of subalpine Italy[76]. We have seen how it is deficient in number and in the geographic coverage of Tuscany, that is, the most important mining area of Italy but the fact that are no sample from the subalpine regions (Piedmont, Lombardy, Trentino-Alto Adige, Veneto and Friuli) is even more serious.

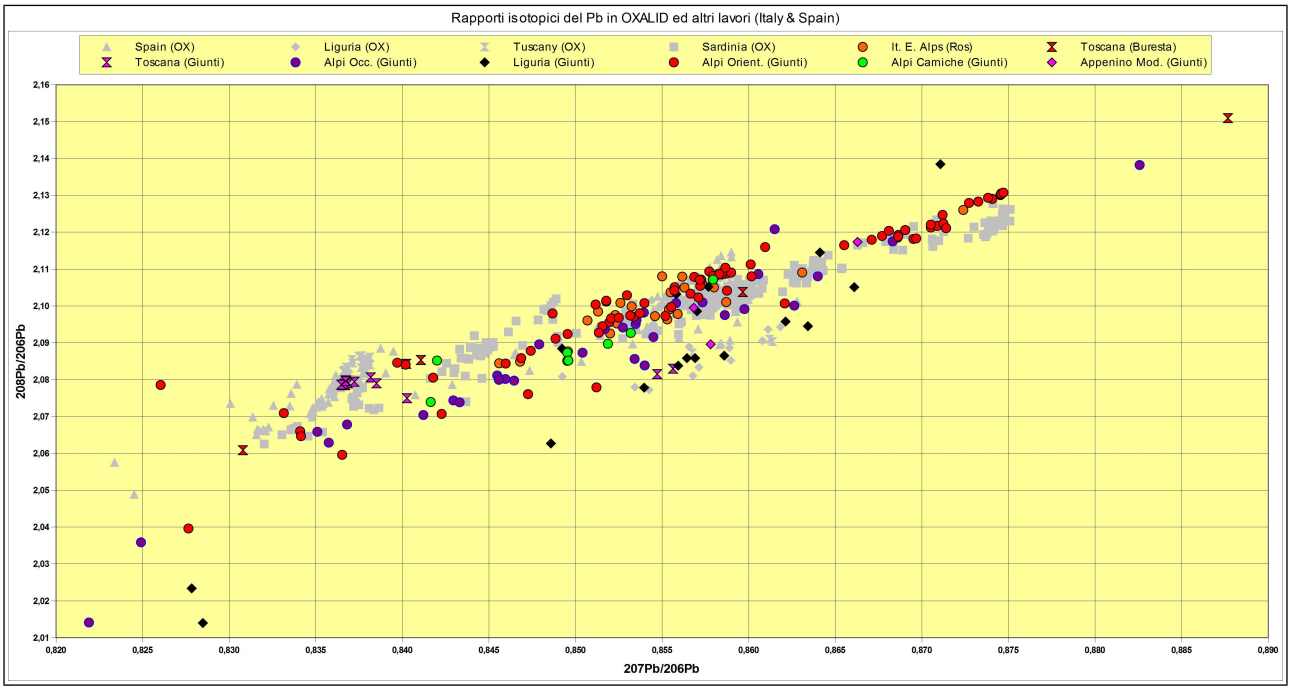
Oxalid	miniere	campioni
Liguria	7	13
Sardegna	68	250
Toscana	10	49
Totale	**85**	**312**
Giunti/Ros/Buresta	miniere	campioni
Alpi occidentali	18	35
Appennino ligure	5	18
Toscana SW	4	18
Appenino modenese	1	3
Alpi centro-orientali	21	113
Totale	**49**	**187**

Italy: the new isotopic signatures

Fortunately, in recent years, research and doctoral dissertations have been carried out, covering at least part of this gap. Two in particular are to be mentioned: that of Ilaria Giunti (2011)[77] for the Ph.D. in Earth Sciences of the University of Padua supervised by the director Gilberto Artioli and Veronica Ros (2009) for the degree in Chemistry at Ca 'Foscari University of Venice supervised by Carlo Barbante.

In particular, the two theses, in addition to expanding the Oxalid Data Database, make it possible to achieve a more homogeneous geographical coverage, although many mining areas are still lacking.

The result is visible in the following graph, where the data currently present on Oxalid appears in grey, while the ones related to the new isotopic signatures are coloured. Obviously there are areas of marked overlap between the signatures of the alpine mines and those of some Spanish and Sardinian mines.

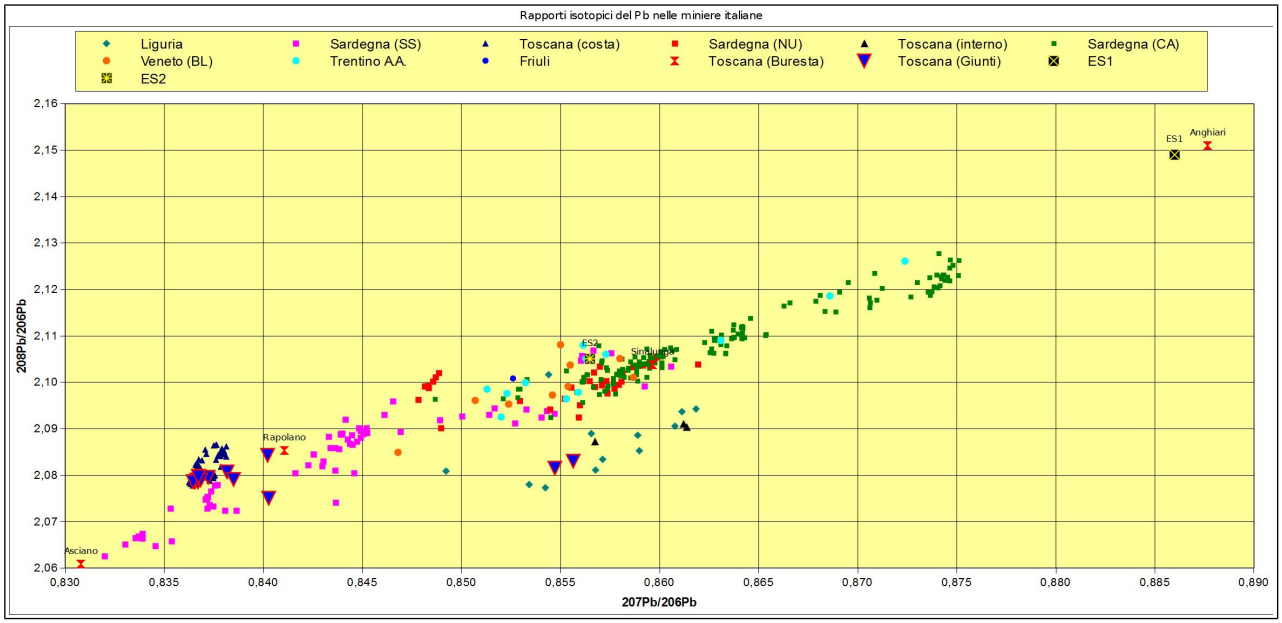


[76] Jung (2011) says: *"Unfortunately, chemical and isotopic analysis from the northern Italian ores deposits in Trentino and Alto Adige/Sudtirol are not yet available"*

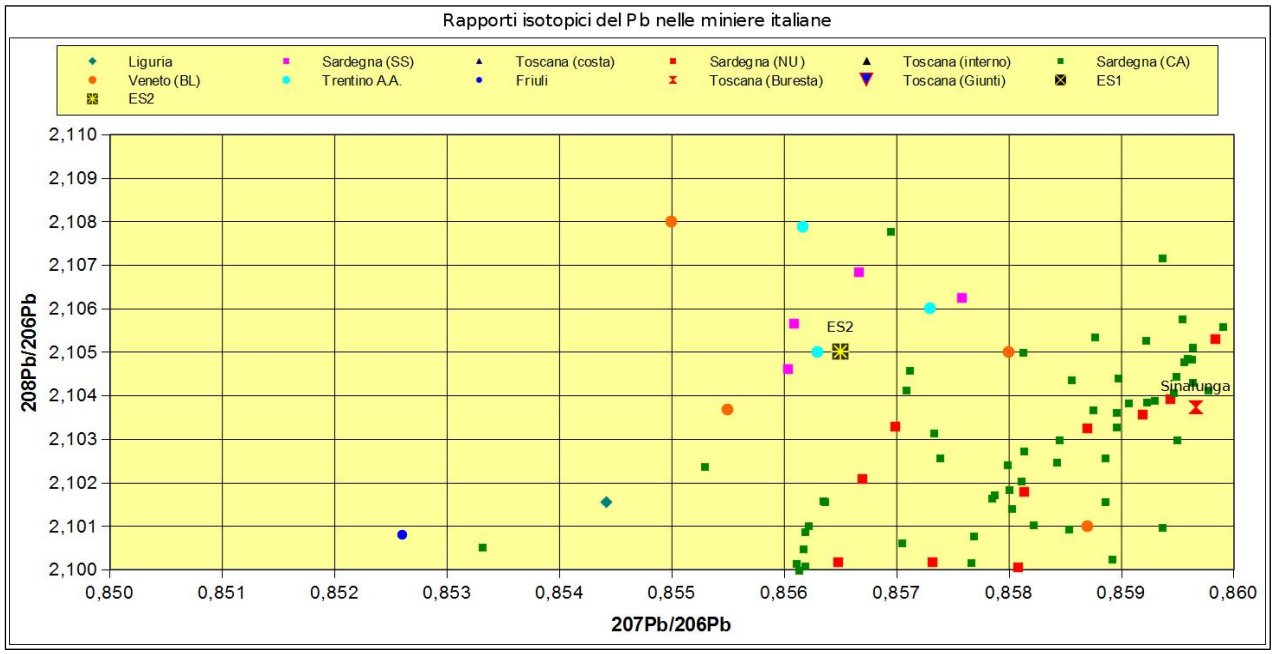
[77] http://paduaresearch.cab.unipd.it/3982/

Errors caused by an incomplete DataBase

When trying to classify a finding using LIA, the Euclidean minimum distance technique is used, that is, assigning the object under consideration (represented in a 3D space by its isotopic $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, and $^{206}Pb/^{204}Pb$) to that mineral source present on the reference DataBase and showing a minimum Euclidean distance. For example, if we had a search with $^{208}Pb/^{206}Pb$ of 2.149 and $^{207}Pb/^{206}Pb$ of 0.886 (ES1 on the graph simplified with a single 2D chart), in the case of Oxalid, we will have to assign it to Sardinia[78] while it is actually more likely to be attributed to the copper quarry in the serpentine of Monti Rognosi near Anghiari (Montauto).



The same is true for the most common isotopic $^{208}Pb/^{206}Pb$ ratios of 2.105 and $^{207}Pb/^{206}Pb$ of 0.8565 (see ES2 point) that using only Oxalid would be attributed to a Sassarese (magenta) or Cagliaritan (green), while in all probability, it comes from one of Trentino AA (Cyan).

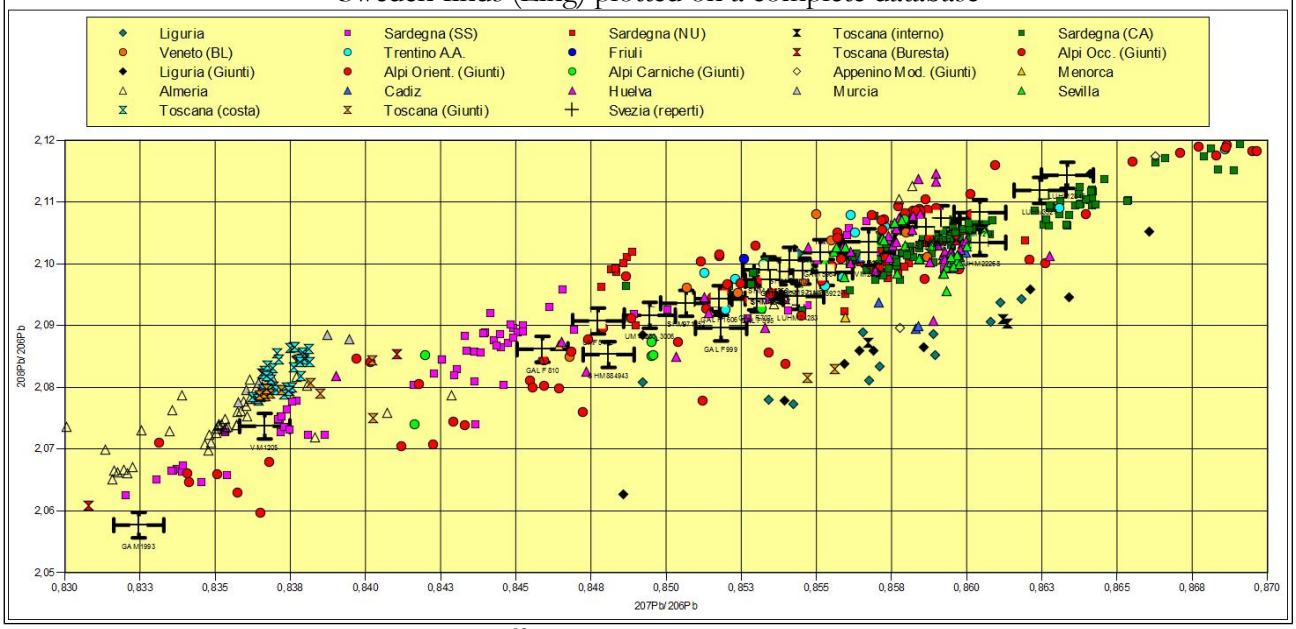


[78] If the "minimum Euclidean distance" is equal to the instrumental error or half as provided by Stos-Gale & Gale (2009), there would be no attribution.

Also by way of example we see how some attributions of Ling[79] can be questioned by adding isotopic mining signatures not yet present on Oxalid.

From these few examples, we can safely say that some recent surveys that have given inconclusive results due to lack of information on mineral sources[80] or results that are baffling as the one mentioned in the aforementioned Ling will surely benefit from the increase in Geographic coverage of mining sources, in particular those of the Alpine chain carried out by Gilberto Artioli's group at the Department of Geosciences of the University of Padua[81].

Sweden finds (Ling) plotted on a complete database



The same can be said of the Buresta[82] surveys. Perhaps, there were no specimens from other copper deposits such as Murlo[83] or Roccatederighi[84], Monte Vaso[85], Monte Noccola[86], Il Terriccio[87], or Pomaia[88]. Not to mention the mines of Massa Marittima: one is the only mining field on Oxalid: the aforementioned 69 (179) with data from La Pesta and Capanne Vecchie which obviously have very close isotopic signatures. Nothing is said about other important mines in the municipality of Massa, that is, Prata and Ritorto which were active for Cu and Fe in the Middle Ages; Niccioleta, Val Castrucci, Poggio al Montone, Rocchette and Cugnano[89]: the latter also active in the Bronze Age.

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79 Ling et alii (2014)

80 Cf. Jung, Mehofer, Pernicka (2011)

81 http://geo.geoscienze.unipd.it/aacp/welcome.html Cf. Artioli (2014)

82 The same researcher hopes for a more extensive sampling of neighboring fields and of Tuscany in general.

83 Sheet no 74 from the Inventory of the Tuscany Region, which reports mineralization of native copper, in addition to chalcopyrite, bornite, blend, galena, covellite, manganite etc.

84 Sheet No. 80 with cupriferous minerals (chalcopyrite, bornite, calchocite) concentrated between serpentinites and basalts. Despite being exploited in medieval times, however, Simonin in the 1800s found traces of ancient workmanship.

85 Sheet No. 38. Municipality of Chianni in Val d'Era. Mineralization of chalcopyrite, native copper, bornite, malachite, azurite, dialect, aragonite, quartz

86 Sheet n ° 39 in the municipality of Castellina Marittima. Cupriferous minerals in the ophiolites. Cultivated at least from the Etruscan age.

87 Sheet n° 40 in the municipality of Castellina Marittima. Mineralization of chalcopyrite, native copper, bornite, malachite, azurite, calchocite

88 Sheet n° 41 in the municipality of Castellina Marittima. Cupriferous minerals (chalcopyrite, cuprite, bornite) in serpentine or in contact with basalt

89 Sheet No. 60. Mineralization of galenas, chalcopyrite, blend, pyrite, tetrahedrite, limonite, azurite, silver, malachite.

What the archaeologists say

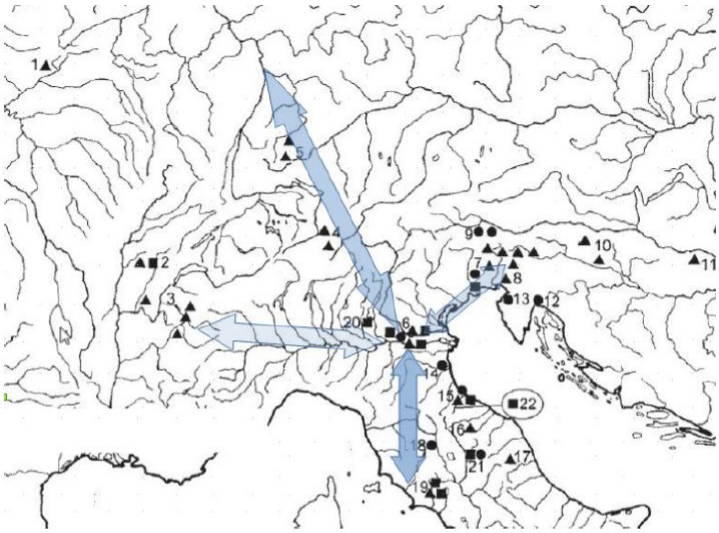
From protohistory scholars

A. Zanini (1999):

"With regard to raw material supply sources, it has been repeatedly stressed, in relation to trade with the Venetian area, as Tuscany was in the Protohistory an area of extraction and first processing of minerals[90]*. An obvious reflection is that of the spreading of pick-ingots and socketed shovels between Etruria, Veneto, Friuli, Istria and more west the Alpine arch. The metallurgical models and widespread artefacts are also a further indication. This can be interpreted as proof that even more areas of supply and multiple distribution areas were within the same time frame that were equally accessible. For mineral resources, Frattesina is in fact connected to one side by the Adige valley with the Mitteleuropean areas, on the other in close ties with the Middle-Tyrrhenian area. "*

After a few years, Zanini himself tries to clarify (2012):

"It seems to read, to the central stage of the final Bronze, a director heading that from the north move to the south, linked also to metallurgical circulation, as testified by the evidences that from Frattesina through Romagna and the Apennines arrive in northern Etruria, towards the Tuscan metallic resources. It is in the advanced moment of the Final Bronze (BF3) which, however, is well perceived by the role of southern Etruria, which, through a direction that now seems to go south to the north, typically draws Protovillanovian influences down to the bottom necropolis Zanotto and Narde 2, in the Polesine, and is part of the central-northern metallurgical circuit. "



Ingots types: ▲pick-ingot; ■socketed-shovel; ● axe Ponte S. Giovanni

From Bellintani (2008) with some modifications

1) Caix 2) Larnaud 3) Laigneu, Albertville, Goncelin 4) Schiers, Filisur 5) Beuron, Pfiffingen 6) Frattesina, Villamarzana, Montagnana, Fondo Paviani 7) Porpetto, Madriolo, Cividale del Friuli, Redipuglia, Purgessimo, Nimis 8) Kanalski Vhr, Veliki Otok, Dragomelj 9) Fresach-Mittemberg e località sconosciuta (Austria) 10)Milijana, Ivanec Bistranski 11) Kapelna 12) Rijeka (Fiume) 13) Buje 14) Casalecchio 15) Poggio Berni 16) Chiuse al Frontone 17) Marsia 18) Ponte San Giovanni 19) Manciano, Sorgenti della Nova 20) Turbine di Gazzo veronese, Sabbionara, Calcinato Ponte S. Marco 21) Monte Ansciano e Monte Ingino (Gubbio) 22) San Marino

Bellintani (2008)[91]:

"Metallurgy in Northern Italy, closely linked to transalpine models in the early stages of the Bronze Age (XXI - XVII century BC) During the second half of the II millennium BC also processes its own and innovative elements, such as some types of needles, fibulae and daggers that penetrate the peninsula, especially along the Adriatic. During the Recent Bronze, productive expansion is linked to a more systematic exploitation of mineral resources such as those in Trentino-Alto Adige, where dozens of smelting areas have been recognized, with the presence of melting furnaces for the reduction of the local cupriferous mineral. In the Bronze Finale, the site where metallurgical production is more accurately evidenced is that of Frattesina. Here, in addition to hundreds of

[90] See A. M. Bietti Sestieri various works.

[91] P. Bellintani, L. Stefan - "Protovillanoviano in S. Marino" in Bottazzi G., Bigi P. (edited by), *First Settlements on Mount Titano. Excavations and Research* (1997-2004), Catalog of the exhibition, State Museums of San Marino - 2008

finished objects that point to a wide range of traffic (from Aegean to Sicily, to the Balkans, to central-northern Europe) but above all to central Italy, an extremely large number of matrices for melting and a group of 'casting' responses, currently four concentrated in a well-defined area in the central part of the town. From the same area are also the main evidences of another important pyrotechnic activity, that of glass for pearl production, still the leading glass processing of the European Bronze Age in the north of the Aegean. In addition to glass and metal, Frattesina had worked large-scale deer horn (local), but also elephant ivory. The latter, along with 'Mycenaean' ceramics and ostrich egg shells, could have been brought to the Adriatic by Cypriot or Phoenician merchants in search of metals (those of the alpine and mineral deposits) and of an other particularly precious material: amber. The Baltic Sea, which is not the only one to travel in Italy at an early age as it was often thought to be, was crisscrossed through the Middle Eastern Alps, at least in part, had to be worked on Frattesina, forerunner of Verucchio in the Villanovian age. In the peninsular area, at the beginning of the Bronze Finale, there is for the first time a substantial metallurgical activity that will take on about three centuries ever more peculiar and distinctive features of regional metallurgical circles. This is mainly the case with Etruria Mineraria, which is a sign of the systematic exploitation of the mineral resources of Tuscany from this stage."

According to Bietti-Sestieri[92], it is with Frattesina that the supply of minerals in North-East Italy that, before the Bronze Finals, was completely coming from the alpine mines, moves in the direction of *Etruria Mineraria*. Already Pearce[93] had suggested that the main causes of this shift had been the difficulty of coping with a growing demand, which was not dependent on seasonality, and the fact that *Etruria Mineraria*, in addition to copper, could also provide tin. There are unfortunately still read waggeries about the tin as follows: "*There are some reports of tin ores in Tuscany, but no indication of prehistoric exploitation.*"[94] and also *"Tin ores are also present on Sardinia but it is not confirmed that they were exploited in the prehistoric times.* " The facts are:

1. Considering that many Tuscan mines have been exploited from Eneolithic or at least from the EBA with the complete destruction of the old excavations[95], the phrase "no indication of prehistoric exploitation" is true but at the same time it is devoid of real meaning.
2. The difference between the tin mines of Tuscany[96] and those of Sardinia is in quantity and quality:
   A. the amount of metallic tin excavated in ancient times (before the Middle Ages) only in the Monte Valerio[97] mines is found to be at least 3,400 tonnes[98];
   B. Sardinian tin was not exploitable in ancient times due to the low percentage of rock visible only to the microscope[99], while the average content of cassiterites in the rock of the Cento

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92 A. M. Bietti-Sestieri "L'Italia nell'età del bronzo e del ferro" - Carocci editore - 2010

93 M. Pearce - "Bright Blades and Red Metals. Essays on North Italian Prehistoric Metal work" - London - 2007

94 Ling et alii (2014) cit.; M. R. Jones (2007)

95 Cf. Giardino: *"Rebuilding ancient mining landscapes is a very difficult task. The exploitation of subsoil resources aimed at achieving the maximum benefit has often been achieved through the multi-century work of the works, especially after the introduction of modern excavation technologies, the upheaval of the environment and almost complete obituaries of evidence related to the oldest Mining activities, with the disappearance of whole portions of territory " in* Paesaggi minerari dell'Etruria pre-protostorica - Centro Studi di Preistoria e Protostoria - 2008

96 Cf. Giardino (2008): *"Northern Etruria also owns the main tin deposits of the central Mediterranean, located in the area of Monte Valerio and Monte Rombolo, in the municipality of Campiglia Marittima."*

97 Not taking into account the mines of Monte Rombolo, which were also excavated in ancient times.

98 Cf. A. Pampaloni - "The tin from Campigliese: 40 century of usage"

99 Cfr. Valera e Valera (2005) And also N. H. Gale (2006), who states by recounting the quoted Valera: "*confirm our own observations that there is no source of lead containing tin in Sardinia available in the Bronze Age, and indeed that the tin occurrences in Sardinia are mostly mineralogical occurrences only,'with the only hypothetical possibility, though very weak, of a Sardinian tin beneficiation being offered by an eventual small "placer" from the Perdu Cara mineralisation'".* The mining area of Perdu Cara has been the subject of research in the 20th century for several minerals including cassiterites. All the researches failed.

Camerelle mine was 85%[100], with a 66% of the extracted material, thus of exceptional quality[101].

Frattesina: the most important trading hub in the Bronze Finale

Frattesina was a village with an industrial and commercial vocation of over 20 hectares born in the XIII century BC and which had the highest flowering in the following two centuries. Apart from the two necropolis of Narde and Fondo Zanotto, there are two other neighbouring sites to be mentioned, namely Montagnana (EIA) and Campestrin which date back to the first phase of Frattesina, that is to the thirteenth century and is a site entirely dedicated to Amber processing[102].

A.M. Bietti-Sestieri (2001):

"The most element of interest in this complex is the very exceptional features of its economy: it is a real industrial centre, where large quantities of vitreous pasta, bone and horn of deer, ivory, bronze and other metals, perhaps amber. Some of the handicraft activities that took place in the town, and the materials found less frequently, indicate systematic transmarine connections, probably with the area of the Eastern Mediterranean. The work of elephant ivory was certainly on the spot, as is indicated by the abundance of finished objects and machining waste... Long distance connections with the whole Italian territory and with the major islands are indicated by the wide distribution of some of the main types known to Frattesina (pearls of vitreous and amber pearls, ivory combs) in numerous contemporary complexes; furthermore, metallurgical production shows a close relationship with the metallurgy zone of Etruria. The whole set of features of the Frattesina complex indicates its specific role, so far unmatched, in the field of craftsmanship and trade in Italy between the late Bronze Age and the Iron Age. "

Bellintani (2011):

"... the distribution of Frattesina type glass beads, in fact, seems to remind and expand, especially towards the north, already active paths in the final phase of the terramare facies and probably linked to the exchange of the alpine copper and the supply of Baltic amber. "

Negroni Catacchio (2014):

"Once again, the importance of the high-Adriatic area as a point of arrival of the amber road is to be emphasized first through probably the passage of the Resia and the Adige valley and later in the Final Bronze through probably the Tarvisio ghat and the Soča course. Here, first in Campestrin and then in Frattesina, the amber was sent to one side towards the Italian peninsula and the Tyrrhenian islands (Elba, Sardinia, Lipari) and the other towards the Adriatic, the Balkans and the Eastern Mediterranean.

At Frattesina were realized the pick-ingots and all other forms depending on the customer's preferences, such as bar and tongue ingots.[103] Among the findings in our possession that have been analysed, despite expected cases there are also some surprises. The same can be said of pick-ingots: the majority is alligated with tin, at different percentages[104], but there are also exceptions.

The vast majority of bronze found in Frattesina and belonging to the last period of the Bronze Finale (¾ of the XI century BC) and in contexts that we can indicate as contiguous or in relation, shows a

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[100] Numerous analysis carried out at the end of 800 by Simonin and Blanchard on what remained of ancient cultivations.

[101] As a curiosity it is reported that in the XIX-XX centuries were extracted in Italy ca. 1,604 tons of tin and all of the mines of the Campigliese. No other mine in Italy produced tin in the period indicated.

[102] At Campestrin many necklace circlets Tirinto type have been found in the process and *"not only indicates local processing in an unequivocal way, but it makes the northern Italian origin of this typology even more likely." (Bellintani - 2010)*

[103] Cf. D. Girelli (2009)

[104] Pick-ingots have been found with tin percentage of 5%, i.e. low. It could be a destination for simpler use (hammers and shredders) or for particular customers (local or remote).

high tin content, much higher than the bronzes of other areas of Italy unrelated to the Protovillanovian culture. Which means that the Protovillanovians had considerable amounts of tin available.

In the Recent Bronze Age, Campiglia's tin was the only one available in the Mediterranean. It would not have been for a long time. Soon, the tin from the Iberian peninsula would soon arrive. For that, Cornwall would take more time and much more for that by the Erzgebirge[105] [106].

In the past many authors have argued that the Mediterranean tin between the Medium and Recent Bronze Age was from Afghanistan[107], Cornwall, the Iberian peninsula, etc.

Indeed today we know that the tin of the Cornwall mines had been extracted in quantities only since the 1st century AD; that the tin from the Iberian Peninsula and Brittany had crossed the local boundaries only from the Bronze Finale and finally that many supposed fields that could be theoretically usable could not be due to the low percentage of cassiterite in the rock[108].

We do not know for what precise reason the Frattesina residents were addressing to *Etruria Mineraria* and if they really did it[109].

If for reasons not only seasonal[110] of copper, whether by the fact that with copper they also received tin, or because they shared roughly the same material culture or, as hypothesized by Bietti-Sestieri[111], they spoke the same language.

But what could be the forms used for transport, especially long distance ones?

What can we mean by plano-convex ingots, pick-ingots, socketed shovels and axes?

In the past, some scholars[112] have assumed that the pick-ingots were objects for trade and made in the sorting sites, starting from the plano-convex ingots that were merged with the mine. This at least in Frattesina[113] where all kinds of objects supposed to trade and produce bronzes coexist.

Minerals sent from *Etruria Mineraria* to Frattesina[114] are certainly copper and tin plano-convex ingots. We can not say any more: nor did the pick-ingots go, and nothing can be said on the plano-convex ingots as an indispensable instrument for metallurgical activity[115] and axes, even though of long

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105 G. Rapp (2009): *"The first direct evidence for mining in the Erzgebirge dates to the close of the 12th century. Penhallurick (1986) addresses the question by stating, '...but tin mining there must have been in the Erzgebirge during the Bronze Age, for without it, the achievements of Europeans metallurgist before the discovery of Cornish ores cannot be explained'"-*

106 Cf. E. Niederschlag, E. Pernicka, T. Seifert, M. Bartelheim (2002)

107 Cf. Cleuziou-Berthoud (1982), but with little certainty about the tin. Even recent surveys (the Sistan basin) indicate tin only in ppm.

108 Like in many of Anatolia's mineral deposits and in all those of Sardinia. Cf. Valera: "*cassiterite is finely intergrown with major zinc and lead sulfides, and it is only visible under the microscope"* (2005).

109 Cf. Leonardi (2013)

110 Cf. A. M. Bietti Sestieri (2010) pag. 35 e A. De Guio (2012)

111 Ibid. A. M. Bietti Sestieri

112 Cf. Borgna, Turk and also Pernicka, who does not find the proposal foolishly. See also F. Cattin e M. Villa (2014)

113 More than 70 melting matrices were found in Frattesina.(Cfr. Le Fevre 1992 - Bellintani 2008)

114 The writer is not sure of the fact given for sure by Pierce and also by Bietti-Sestieri. We do not forget that Pierce was completely wrong (perhaps dazzled by the Bell-Beaker myth) in pointing the direction of the introduction of metallurgy in Italy. But the Bietti-Sestieri is hardly mistaken. However, it is necessary to verify that only new finds or even archaeometallurgical investigations have been extended to all that we have, to confirm the hypothesis.

115 I agree with A. M. Bietti Sestieri about the primary function of the blades that is to act as scrapers. I also add that, in addition to the obvious and apparent function of the fireplace accessory, there were scrapers for different uses but mainly for braziers and crucibles, that is, they needed to remove all the residues of combustion and fusion. The fact that there is an asymmetric consumption, which is unlikely to be used only for the hearth, is perhaps due to the force needed to scrape: a right-hander in the use of the shutter lever lever on the left side of the blade, while a left 'opposite. It would be useful to compare the few intact pieces of evidence in our possession, where it is possible to read the wear (17 according to the list of Bellintani cit.), If the percentage of wear between the two sides can be compatible with that of the population (typically 90 % -10%).

tradition in central Tyrrhenian Italy. In any case, the pick-ingots, the socketed shovels[116] and the axes of Ponte S. Giovanni type were undoubtedly produced in Frattesina[117].

We have no details about the chemical composition of all plano-convex ingots found. The jobs are partial, that is, they refer to one or more hoards.

Not having an all-encompassing vision we do not know if they were all copper, then accompanied by other tin plano-convex ingots. In fact, there are also exceptions: two plano-convex ingots of Madriolo, for example, contain high tin percentages[118].

Of course all of the bronzes are axes and socketed shovels, as shown by the analysis. They also tell us that the percentage of tin in bronze is higher in the direction from Frattesina going North than to the East.[119]

We do not know whether this is due to purely aesthetic reasons, or to the closer relations between the Protovillanovians and the Rhaetian[120].

Looking at the bulk of the finds and ignoring the exceptions for the time being, it would seem reasonable to think that the bronze pick-ingots "*represent a second step of ingots production, in which copper of plano-convex ingots was cast into pick-ingots*" [121].

If this corresponds to reality and it may be at least for the majority of situations, we can not exclude the fact that more plano-convex ingots were used to make pick-ingots.

And in all likelihood it may have happened that plano-convex ingots from several mining fields contributed to the fusion of a pick-ingot.

Which leads us to conclude that, in all likelihood, at least as far as the Final Bronze horizon is concerned, the use of the LIA technique should be used with great caution because it could be dangerously misleading.

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116 Socketed shovels type "Fondo Paviani" (FP) found in Frattesina. The typology is the oldest (beginning of the 11th century), so it is likely that FPs were originally produced in Frattesina. Then, from the end of the century, the type "fra Manciano and Semprugnano" (MS) was also imported from Etruria. The diffusion of this type of artefacts is illustrated in the figure. The MS socketed shovels found in Etruria have a tin content of 15%.

117 From the chemical analysis of the socketed shovels (see Zaghish-2000) there is a wide variability in the composition of the MS socketed shovels of Frattesina hoards. If 2/3 of the socketed shovels analyzed are made of copper with a tin content between 6% and 12% (with an average of 9.85%), there are some samples in which the tin is almost absent, copper very low (20-26%) and the alloy is predominantly composed of Ni (18-19%), As (16%), Sb (23-27%) and Pb (3-9%).

118 Between the 12 and the 15%.

119 Cf. Giumlia-Mair (2009)

120 Cf. A. Pampaloni: "Sull'antica Lupatia" (2014)

121 Borgna e Turk (1996) quoted by Jung, Mehofer, Pernicka (2011)

Conclusions

When it comes to protohistory, there are few certainties and many doubts. In this case, thanks to the archaeometallurgical approach, we have little certainty. Among these:

1. With regard to the LIA technique:
   A. It is to be hoped that it will be used by reference to a geographic and exhaustive Geographic Data Base as far as the ratio of copper isotopes and component chemical analyses, including rare earths, is concerned;
   B. To carry out investigations, without having the information indispensable for the purposes such as those relating to the isotopic signatures of sub-alpine mines[122], means:
      1. In the case of Jung, Mehofer, Pernicka (2011) they did not come to conclusions because the authors realized the problem;
      2. In the case of Ling (2014) hasty conclusions were given since many Spanish and Sardinian mines (referred to as metal sources) have isotopic signatures very close to those of the sub-alpine mines. We do not forget that, at least in the Bronze Finale, the central place for both metal and amber trade between North Europe and the Mediterranean was Frattesina, a place close to the sub-alpine arc.
2. About the tin:
   A. Throughout the period between the Middle and Recent Bronze Age (1,700-1,200 BC), the only source of tin that was actually used in the central Mediterranean[123] was the ores of Campigliese[124] and Mount Cer in Serbia[125];
   B. Using the LIA technique on the tin does not seem right. Many cassiterite mineralizations do not contain lead even in ppm[126]. The only possible technique is that of the isotopes of tin[127].
3. With regard to amber:
   A. Baltic amber (succinite) arrives in Northern Italy[128] at the end of EBA (about 1,800 BC) and through the "Adriatic corridor" reaches the MBA in Puglia as well as the Ionian coasts and subsequently is present throughout the peninsula[129], reaching Sardinia only in the Bronze Finale[130]. This is something that contributes to raising doubts about Ling's proposal (2014),

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122 How does Bellintani look (2014): "*no attention has been paid to the ore outcrops located on the southern side of the Central and Eastern Alps, especially those from Trentino*"

123 Wiman says about the Cento Camerelle mine: *"The mineral deposits were among the wealthiest in the whole of the Mediterranean"*. Cfr. I. M. B. Wiman (2013)

124 Cf. Pampaloni (2016)

125 Cf. Huska (2014)

126 In the analysis of the "tout venant" extracted from the mines of Monte Valerio (Cento Camerelle and Cavina) there are no traces of lead; while in those of Monte Rombolo/Campo alle Buche cassiterite appears red because it is mixed with lead arsenic and iron sesquioxides.

127 Cf. Haustein (2010)

128 Cf. Bellintani (2005, 2010)

129 From Bellintani (2005): "*Within the eastern Alps, the Adige Valley is interesting because it shows a good concentration of amber finds in the MBA and because of the strategic importance of this ancient trade route in the Alpine region. All amber samples from the area are succinite, pointing to the fact that the valley, which is related to the Resia and Brennero Alpine passes, represented a preferential access route for the trade of Baltic amber in the Italian peninsula.*"

130 In fact, the first amber appears in Sardinia in the Recent Bronze (Bellintani 2009) but are clearly of North-Italian origin because of the fact that they are associated with glassy material, predominantly faïence, and because the shape recalls the

then resumed by Earle (2015), which uses very old references instead of up-to-date data [131].

B. At least at the end of the Recent Bronze and in the Final, raw amber comes to Northern Italy and is worked at Campestrin. It is therefore highly probable, that is to say, that the raw amber was exchanged with raw metal of Alpine or Tuscan origin or a combination of the two. Another factor contributing to sinking Ling's (2014) and Earle's (2015) hypotheses.

C. The most likely hypotheses based on many elements about the amber routes are:

1. For the entire MBA: Scandinavia → Tyrol → North-Italy → Adriatic Corridor → Eastern Mediterranean.
2. For the RBA-FBA period: Scandinavia → Austria → North-Italy (Frattesina area) then on the same time:
   I. Central Tyrrhenian Italy → Sardinia → Western Mediterranean;
   II. Adriatic Corridor → Eastern Mediterranean.

Among doubts and bewilderments:

I. We do not know if the metal sources in Frattesina were mines of the Etruria Mineraria or those of the Sub-alpine arc or a combination of the two. There is no comparative analysis of all the findings at our disposal in order to conceive anything.

II. Such analyses will also allow you to test the production process. That is, if the pick-ingots were made from plano-convex ingots. In this case, I fear that the LIA technique is no longer applicable and is valid as Pernicka said: "*Today we realize that the mixing of metals from different sources destroys the information of origin of each component completely*" [132]

III. The Optimal Data Base for a proper and complete LIA analysis, as well as ensuring the geographical coverage of the territory and to be accompanied by other information as indicated in the text, should be more precise with regard to the quantity and exact location of each sampling point for a more accurate relevance to the various possible mineralizations.

IV. It is obvious that the LIA technique searches for lead, but is mainly used for copper. Taking samples from a rich but lead-free area is nonsense. Also believing that the LIA signature is always absolutely meaningful for a particular field is a risky statement that can lead to unexpected results. It can happen that inside a field there are, as foreign bodies, mineralizations that have undergone different para-genesis and are thus liable to have different LIA signatures from the main mineralization.

V. I share the doubt reported by Bellintani (2009-2012) about Sardinia: "*As far as BF is concerned, the absence of mixed alkaline glasses, typical of north-eastern Italy, and present in many contexts on the peninsula, Faced with the massive attestation of amber of types of clear peninsular derivation.* "

VI. As far as relations between continental Italy and Scandinavia are concerned, we have no clues about a two-way exchange in the Bronze Finale. Shortly after, however, the villanovian cups Stillfried-Hostomice, are found in the south of Sweden[133].

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relatively frequent elongated Terramare vase in the recent Bronze.

131 Earle's work has created many perplexities. Starting from the copper of Sardinia indicated as a resource exported where it has never been proven to leave the island contrary to that of the Etruria Mineraria not even mentioned; the continued use of Ling's hypotheses (2014) which are not really a starting point, but should be what is to be demonstrated.

132 Cf. Pernicka (2014) with the exceptions cited below by the author.

133 Cf. A. Nijboer (2010)

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