

LEAD ISOTOPE CHARACTERIZATION OF COPPER INGOTS FROM SARDINIA (ITALY): INFERENCES ON THEIR ORIGINS

Pinarelli L.

CNR, Institute of Geosciences and Earth Resources, Section of Florence, Via La Pira, 4, 50121 Florence, Italy, lapina@igg.cnr.it

ABSTRACT

The provenance of the materials making up the metal artifacts represents a fundamental question for archaeological research. The complex processes necessary to extract the metals from the minerals cause considerable changes in their chemical composition. By contrast, the ratio of the different lead isotopes in artifacts is not influenced by metallurgic processes. Therefore, the raw mineral material and the extracted metal exhibit the same isotope "footprint".

Over the course of history, Sardinia has played a major role in maritime routes. Its considerably rich mineral resources, with copper, lead and iron mineralizations, moreover complemented its strategic importance. During the 10th and 9th centuries BC Sardinia, because of its strategic location, was to become directly involved in the "precolonial" Phoenician expansion.

Two repositories of copper ingots recovered at different levels within a nuragic village in north-west Sardinia, can be placed within this historical context of intense traffic and exchange of goods between native Sardinian and Phoenician communities. The ingots were made in different shapes: plane-convex, biconvex, truncated cone and irregular.

The analyzed ingots exhibit a considerable lead isotopic variability, although no systematic differences in isotope composition were revealed between the ingots from the two different repositories. Moreover, no systematic isotopic variations were observed between the different shapes in which the material was found.

Overall, the ingots exhibit a linear distribution in the lead/lead diagrams. The group of ingots with the lowest isotope ratios project onto the area defined by the northwestern Sardinian mineralizations. The ingot located on the other extreme end of the straight line in the Pb diagrams overlaps the area defined by the southern Sardinian deposits. The isotope footprints of the intermediate samples seem to indicate that they stem from the mixing of two components from two different mining areas of Sardinia, one in the north, the other in the south. Therefore, widespread exchange of metal must have taken place throughout the island, and such an exchange does not seem to have been hindered by the advent of the Phoenicians in Sardinia.

The results of the present investigation indicate that the majority of the examined ingots was produced with metal from the northwest of the island, and that these mines were therefore known and exploited in nuragic times. Such findings shed new light on the complex issues involved in proto-historic Sardinian metallurgy.

1 INTRODUCTION

Geographically, Sardinia is set at the crossroads between the eastern and western Mediterranean (Fig.1). Thus, over the course of history it has played a major role in maritime routes. Its strategic importance is moreover complemented by its considerably rich mineral resources, with copper, lead and iron mineralizations scattered throughout various parts of the island (Marcello et al. 1978, Garbarino et al. 1984, Cello & De Vivo 1988).

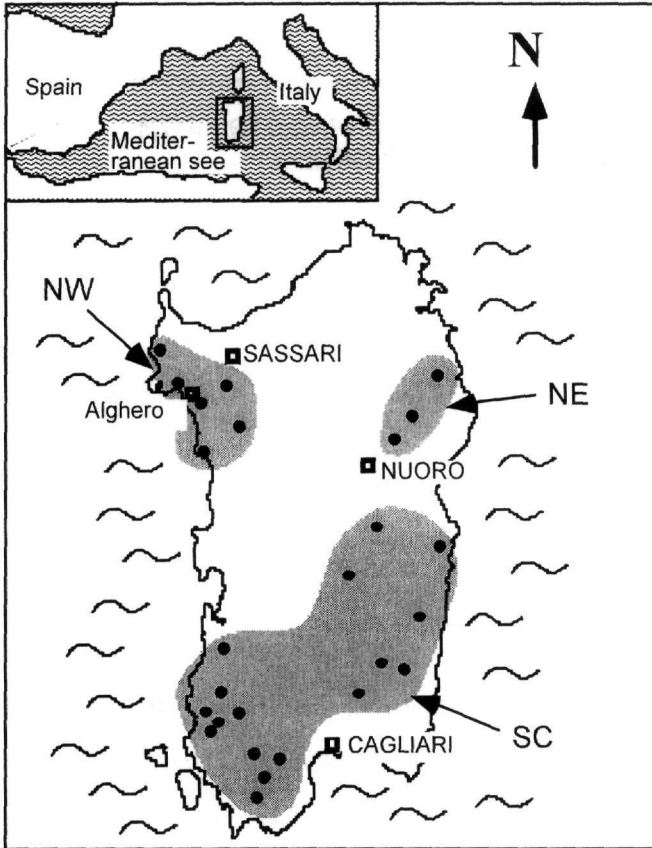


Figure 1. Sketch map of Sardinia showing the location of base-metal ores (black dots) grouped in three areas: Northeast (NE), Northwest (NW) and South-central (SC). Grouping is based on lead isotopic similarities, without considering genetical processes.

The earliest exploitation of these natural resources by local communities can be traced back to the late Neolithic Age (Lo Schiavo 1989). Metallurgical activities appear to have been particularly developed and widely practiced in Sardinia between the close of the Bronze Age and the beginning of the Iron Age. Particularly wide-spread testament of this period are present in the findings of repositories, collections of metal in the form of both whole or fragmented manufactured articles as well as ingots of varying types, though most commonly loaf-shaped. Thus, these sites represented true treasure chests: wealth accumulated in the form of metal, amassed and stashed away by local communities.

It is during this same period that the complex phenomenon of "precolonial" Phoenician expansion came about. In fact, during the 10th and 9th centuries BC, these middle-eastern peoples developed into a powerful economic and commercial force, whose sphere of influence spread outwards from the area of Syria and Palestine toward the regions of the central and western Mediterranean. Because of its strategic location, Sardinia was to become directly involved in their influence (Moscatti 1983, 1988, Bisi 1988, Godart 1988).

Within this historical context of intense traffic and exchange of goods between native Sardinian and Phoenician communities we can place the two hoards of copper ingots recovered at different levels within a nuragic village near Alghero, in northwest Sardinia (Fig.1). The first (Site-1) was unearthed beneath the floor of a nuragh, in a turned Phoenician amphora dated to between the late

8th and mid 7th century BC. The second (Site-2) was in a nuragic vase discovered beneath a layer containing a Euboic Skiphos dated to the early 8th century BC.

The two caches were deposited at the height of nuragic metallurgy, between the time of their earliest contact with the western world, in the 10th-11th century BC, and the colonization of Sardinia by the Phoenicians, from the 8th to the 7th century BC. It is thus interesting to investigate any influence the Phoenicians may have had on the metallurgical techniques and origins of the metals used.

2 THE ORIGIN OF THE METAL ARTIFACTS AND PB ISOTOPES

The origins of the raw materials, first amongst which the metal components, represents a fundamental question for archaeological research. Attempts to establish the origins of the copper in artifacts by comparing their chemical composition with that of cupriferous minerals have to date been unable to yield unequivocal results. Indeed, the metallurgical processes necessary to smelt the metal from the ore, and its subsequent refining, cause considerable changes in their chemical composition. For instance refining the copper can dramatically change the levels of iron, sulfur, arsenic and other elements (Tylecote et al. 1977).

In contrast to their chemical composition, the ratio of the different lead isotopes in artifacts is not influenced by metallurgical processes (Barnes et al. 1978). Therefore, the raw mineral material, the extracted metal and even the scoriae all exhibit the same isotope "footprint". The ubiquitous presence of lead in copper mineralizations therefore allows for characterizing the metals originating in different copper deposits, as well as the articles manufactured therefrom. Thus, artifacts can be linked to the deposits whence their constituent metals were drawn.

3 ANALYTICAL METHODS

The procedure used for the Pb isotope ratio analysis consists of two stages: firstly, the Pb is separated chemically from other elements; secondly, the pure element is analyzed via TIMS (thermal ionization mass spectrometry).

In detail, the chemical purification technique adopted is as follows: several mg of sample are purified of the oxidized parts via a Frantz isodynamic separator, then dissolved in aqua regia at 100°C in a Teflon-PFA beaker. The Pb is concentrated and separated from other interfering elements by passing the solution twice through anion exchange resins. A blank analysis is conducted for each sample series, that is to say, the complete chemical procedure is performed without the addition of any sample, thereby providing a test of the degree of contamination due to the reagents and materials used. During the current study, the blanks were about 0.4 ng.

Pb isotope ratios were measured on a Finnigan MAT 262 multicollector mass spectrometer. Two μl of the solution containing the sample were loaded onto a preheated Re filament using the silica gel-phosphoric acid loading technique. Stable beams of 10^{-11} Amps were obtained at filament temperatures of 1150-1180°C.

Each Pb isotope ratio reported in Table 1 represents the mean value of a series of 100 individual measurements. Within run errors were generally below 0.01% (2σ). A more realistic evaluation of the errors, however, ought to take into account the isotope fractionation that occurs at the high temperatures attained in the spectrometer source. The degree of fractionation was evaluated using the international standard for common Pb isotopic composition (NBS SRM-981). Standard samples were measured repeatedly in alternation with the unknown specimens, and the resulting sample isotope ratios were then normalized to the standard at the end of each measurement set.

The error reported in Table 1 for each isotope ratio includes both within run and fractionation errors. Such "total" values provide a measure of the precision with which the individual isotope ratios were determined and are represented graphically by means of the error bars.

Table 1. Lead isotope ratios of the analyzed copper ingots

Sample (shape)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
<u>Site-1</u>						
13 (plane-convex)	18.536	15.656	38.645	0.8446	2.0849	2.4685
23 (bi-convex)	18.287	15.632	38.437	0.8548	2.1019	2.4589
26 (truncated cone)	18.512	15.611	38.572	0.8433	2.0836	2.4708
28 (irregular)	18.288	15.553	38.421	0.8504	2.1009	2.4705
33 (plane-convex)	18.109	15.602	38.169	0.8618	2.1077	2.4463
<u>Site-2</u>						
17 (flat)	18.433	15.581	38.444	0.8453	2.0856	2.4674
30 (flat)	18.557	15.675	38.712	0.8447	2.0861	2.4696
50 (truncated cone)	18.243	15.590	38.290	0.8546	2.0989	2.4560
51 (truncated cone)	18.527	15.610	38.603	0.8426	2.0836	2.4728
59 (irregular)	18.536	15.614	38.621	0.8424	2.0836	2.4734
Error% (2σ)	0.08	0.09	0.10	0.05	0.05	0.09

4 RESULTS

Ten copper samples were analyzed (Tab. 1), five each from the two different hoards, Site-1 (13, 23, 26, 28, 33) and Site-2 (17, 30, 50, 51, 59). The five specimens for each site were drawn from different shaped ingots: plane-convex, truncated cone, flat, biconvex and irregular, in order to test for any possible differences in composition.

The Pb isotope ratios of the analyzed samples were plotted with the respective error bars in the variation diagrams in figure 2. The ratios $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ were used because they exhibited the lowest error (the error associated with $^{207}\text{Pb}/^{206}\text{Pb}$ is not visible in the graphs, as it is below the scale of the symbols). The diagrams can be looked at as the mirror image of groups of points in a three-dimensional space projected onto two planes at 90° one from the other. Each point is defined by three parameters: the ratios $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$; two points can be only considered equivalent if they coincide (within the limits of error) in both the diagrams.

Although the copper ingots exhibit a considerable degree of isotopic variability, no systematic differences in isotope composition were revealed between the different shapes in which the material was found (fig. 2a). Moreover, no systematic isotopic variations were observed between the ingots from the two different caches (fig. 2b and c).

The diagrams in figure 2 show that, overall, the samples exhibit a linear distribution. A group of isotopically homogeneous samples, highlighted by the stippled area, is made up of six ingots that are heterogeneous in both shape and site of origin. These ingots present the lowest $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios and the highest $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of all the analyzed samples and are all clustered on one end of the straight line defined by the other samples. It should also be pointed out that sample 17 falls within this group only in the $^{208}\text{Pb}/^{206}\text{Pb}$ vs $^{207}\text{Pb}/^{206}\text{Pb}$ diagram (fig. 2c), while its lower $^{206}\text{Pb}/^{204}\text{Pb}$ distinguishes it from the other samples, even if the error bars are taken into account (fig. 2d).

A linear distribution in the Pb variation diagrams may be indicative of a two-component mixing process: the pure components are found at the two extremes, while the hybrids produced by their blending in various proportions are lined up along the plot. This fact leads to the hypothesis that at least some of the copper ingots are the product of recasting.

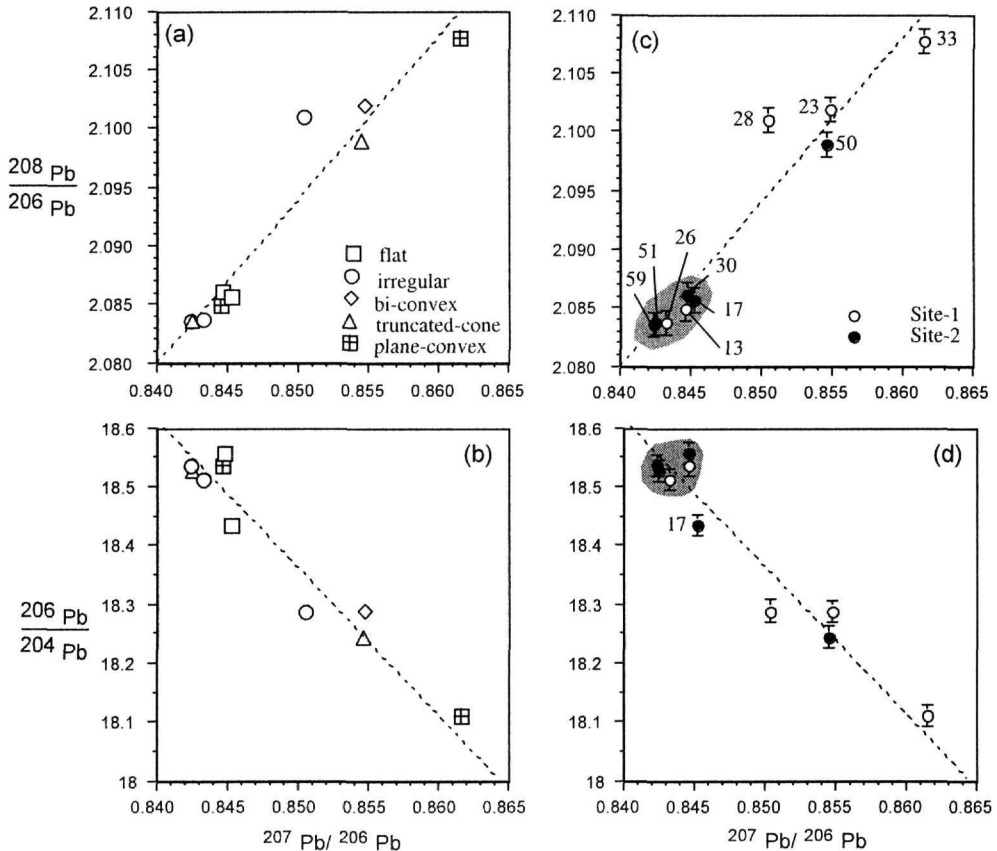


Figure 2. $^{208}\text{Pb}/^{206}\text{Pb}$ (a, c) and $^{206}\text{Pb}/^{204}\text{Pb}$ (b, d) vs $^{207}\text{Pb}/^{206}\text{Pb}$ diagrams. (a, b): the copper ingots are marked with different symbols indicating their shapes. (c, d): the two different repositories in which the ingots were found are distinguished. Error bars are according to the errors reported in Table1.

With the aim of determining the origins of the metal employed to produce the ingots, figure 3 shows the Pb isotope data drawn from the literature on the mineral deposits of Sardinia, Tuscany, Spain, Cyprus and Attica (Lavriion).

The homogeneous group of samples with the lowest $^{207}\text{Pb}/^{206}\text{Pb}$ project onto the area defined by the northwestern Sardinian deposits (Fig.3a, b), in particular near the mines of Calabona and Capo Marargiu (Fig.3c, d). The ingot located on the other extreme end of the straight line passing through the samples in the Pb diagrams, overlaps instead the South-central Sardinia field (Fig.3a b), in the area defined by the Montevecchio mine (Fig.3c and d).

As regards to the intermediate samples: i) sample 17, which in figure 3c plot near Calabona/Capo Marargiu mines, in figure 3d is displaced towards the lower $^{206}\text{Pb}/^{204}\text{Pb}$ values of Cyprus. ii) Sample 28 has $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ similar to those of the Canale Barisone mine (NE- Sardinia; fig. 3c), but distinctly lower $^{206}\text{Pb}/^{204}\text{Pb}$ (fig. 3d). iii) Both samples 23 and 50 lie within the field characteristic of the South-central deposits of Sardinia, though they plot rather towards the edge of the field.

As already mentioned, the diagrams in figure 3 are two-dimensional projections of a three-dimensional space, by which, two points can only be considered coincident if they overlap in both

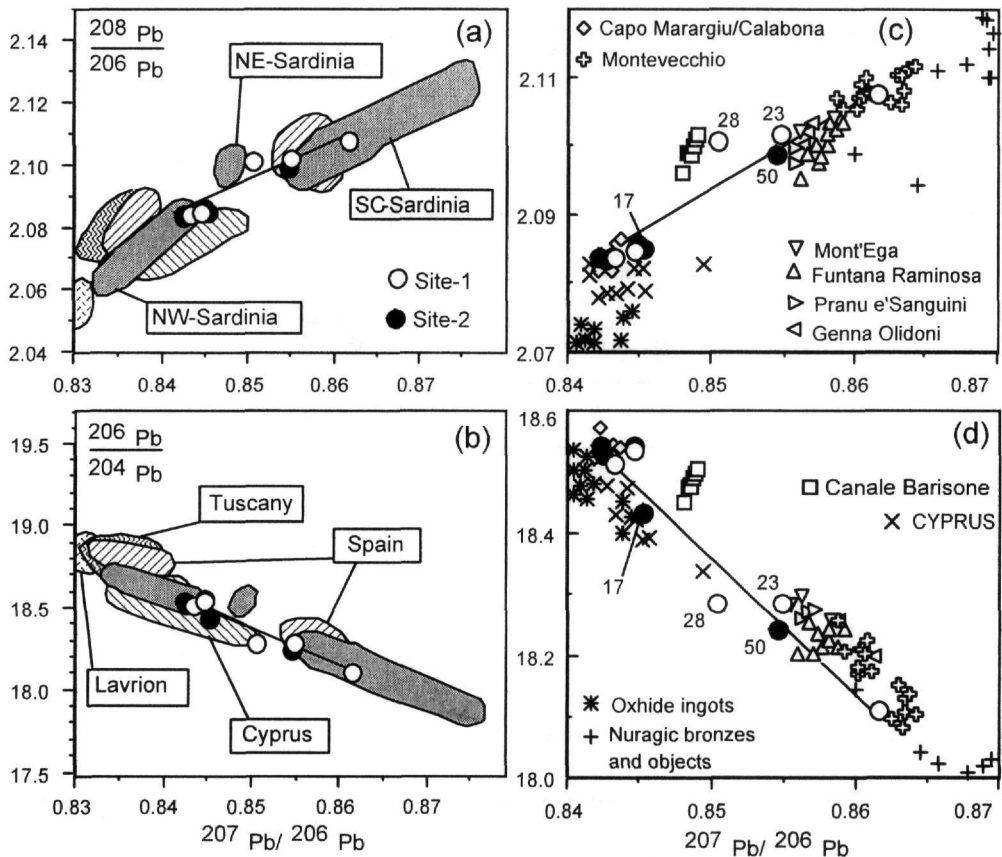


Figure 3. $^{208}\text{Pb}/^{206}\text{Pb}$ (a, c) and $^{206}\text{Pb}/^{204}\text{Pb}$ (b, d) vs $^{207}\text{Pb}/^{206}\text{Pb}$ diagrams. (a, b): Besides the analyzed copper ingots, the representative fields of Sardinian, Tuscan, Spanish, Cypriot and Attica (Lavrion) mining areas are also indicated. The areas of Sardinia are labeled according to Figure 1. (c, d): The data points of some specific Sardinian mines are reported, along with published data on some nuragic bronzes and objects, as well as copper oxhide ingots. (Data sources: Swainbank et al. 1982, Stos-Gale et al. 1986, Gale & Stos-Gale 1987, Ludwig et al. 1989, Sayre et al. 1992, Stos-Gale & Gale 1992, Stos-Gale et al. 1995, Stos-Gale et al. 1997).

diagrams. Thus, it follows that the material making up samples 17 and 28 do not originate directly from the Sardinian or Cyprus mines. The isotope footprints of these samples, and perhaps of 23 and 50 as well, instead seem to indicate that they stem from the mixing of two components from two different mining areas of Sardinia, one in the northwest, the other in the south.

Isotope studies conducted by Gale & Stos-Gale (1987) on bronzes from the cache of Santa Maria in Paulis, on some nuragic lead artifacts from the nuraghs Antigori (Cagliari) and Albucciu (Arzachena), as well as some copper bars from Baccu Simeone (Villanovaforru), have indicated their origins to be in the ore deposits of southern Sardinia (fig.3c, d). Some copper oxhide ingots found in various parts of Sardinia, analyzed by the same authors, have however shown ambiguous lead isotope characteristics. While their $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ (Fig.3d) were similar to those of the Cypriot mines, their $^{208}\text{Pb}/^{206}\text{Pb}$ (Fig.3c) were displaced towards rather low values, far from both the Cypriot or the Sardinian field.

The data presented in the foregoing support the existence of a second source of copper on Sardinia, in addition to the well known southern deposits: the northwestern deposits.

The utilization of metals of various origins (and therefore with varying isotopic characteristics) in the production of ingots fits in well with the metallurgic techniques in use in foundries of the Tyrrhenian area during the first Iron Age. Some circular plane-convex ingots from the Sicilian hoard of

Mendolito di Adrano (datable to the end of the first Italian iron age) bear incompletely melted fragments of objects, demonstrating that the ingots themselves were produced by re-utilizing metallic discards and remnants (Albanese Procelli 1993). Study of the composition of bronzes from the hoard of San Francesco in Bologna (early 7th century BC) has moreover revealed that in Emilia during Villanovan times valuable bronze objects were produced from pure copper, to which the necessary tin was added (Bietti Sestieri et al. 1998). It was therefore common practice to have two types of ingots, alloy bars and pure copper ones, distinguishable by their color, and to fuse together fragments of ingots having the same copper-red shade to guarantee a similar composition.

5 CONCLUSIONS

The results of the lead isotope study suggest a predominantly local origin for the copper making up the ingots from the two repositories near Alghero. It seems, in fact, to have originated to a large extent in the geographically nearby deposits of the northwestern Sardinia. However, there are also indications that copper from the south of Sardinia was utilized as well: it seems to have been mixed with the local metal to produce bars with intermediate Pb isotope compositions. Therefore, widespread exchange of metal must have taken place throughout the island, and such an exchange does not seem to have been hindered by the advent of the Phoenicians in Sardinia. Even the strengthening of ties with Villanova that came about in the first iron age (Lilliu 1988) does not appear to have translated into direct copper importation, at least based on the results of the reported analyses.

It should moreover be stressed that no difference in makeup of the ingots has been found which enable the metals from the two areas to be distinguished: either the plane-convex, the truncated-conical, and the irregular artifacts result to be products of both northern as well as southern copper.

In closing, the results of the investigations carried out on the caches near Alghero indicate that the majority of indigenous ingots were produced with metal from the northwest of the island, and that these mines were therefore known and exploited in nuragic times. Such findings shed new light on the complex issues involved in proto-historic Sardinian metallurgy.

AGKNOWLEDGEMENTS

The author is indebted to F. Lo Schiavo for providing samples of copper ingots from the two repositories near Alghero. She also is grateful to C. Giardino for useful discussions and comments.

This work is part of the CNR project "Mining and metallurgical production in the pre-roman Italy. Archeometry and experimentation" and was carried out at the "Istituto di Geocronologia e Geochimica Isotopica" of CNR (Pisa, Italy).

REFERENCES

- Albanese Procelli R.M. (1993). Ripostigli di bronzi della Sicilia nel Museo Archeologico di Siracusa. Palermo.
- Barnes I. L., Gramlich J. W., Diaz M. G. & Brill R. H. (1978). The possible change of lead isotope ratios in the manufacture of pigments; a fractionation experiment. *Archaeological Chemistry II. Advances in Chemistry*, 171, 273-279.
- Bietti Sestieri A. M., Giardino C. & Gigante G. E. (1998). L'alligazione del rame nella tarda preistoria, ovvero: l'antico metallurgista disponeva di ricettari? In M.-C. Frère-Sautot (ed), *Paléoméallurgie des cuivres. Actes du colloque de Bourg-en-Bresse et Beaune*, Montagnac, 165-172.
- Bisi A.M. (1988). Modalità e aspetti degli scambi fra Oriente e Occidente fenicio in età precoloniale. *Proceedings of the International Congress: Momenti precoloniali nel Mediterraneo antico. Questioni di metodo- Aree d'indagine. Evidenze a confronto*, Rome, 205-226.
- Cello G. & De Vivo B. (1988). Cenni sulle mineralizzazioni metallifere italiane. In C.F. Park & R.A. Mac Diarmind (eds), *Giacimenti minerali*, Napoli, 626-676.

- Gale N.H. & Stos-Gale Z.A. (1987). Oxhide Ingots from Sardinia, Crete and Cyprus and the Bronze Age Copper Trade: New Scientific Evidence. In M.S. Balmuth (ed), *Studies in Sardinian Archaeology III. Nuragic Sardinia and the Mycenaean World*, BAR Int. Series 387, Oxford, 135-178.
- Garbarino C, Grillo S. M., Marini C., Mazzella A., Melis F., Padalino G., Tocco S., Violo M. & Maccioni L., Fiori M. (1984). The Paleozoic metallogenic epochs of the Sardinian microplate (Western Mediterranean): an attempt of synthesis on geodynamic evolution and mineralizing processes. *Rend. Soc. Ital. Miner. Petrol.*, 39,1, 193-228.
- Godart L. (1988). Conclusioni. *Proceedings of the International Congress: Momenti precoloniali nel Mediterraneo antico. Questioni di metodo- Aree d'indagine. Evidenze a confronto*, Rome, 291-297.
- Lilliu G. (1988). La civiltà dei Sardi. Dal paleolitico all'età dei nuraghi (III ed.). Torino.
- Lo Schiavo F. (1989). Early Metallurgy in Sardinia. Copper Ox-Hide Ingots. In A. Hauptmann, E. Pernicka & G.A. Wagner (eds), *Archaeometallurgie der Alten Welt, Beitrage zum Internationalen Symposium "Old World Archaeometallurgy"*, Heidelberg, Der Anschnitt 7, Bochum, 33-38.
- 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.
- Marcello A., Pretti S. & Salvadori I., (1978). Carta Metallogenica della Sardegna. Firenze.
- Moscato S. (1983). Precolonizzazione greca e precolonizzazione fenicia. *Rivista studi fenici*, XI, 1, 1-7.
- Moscato S. (1988). Momenti precoloniali nel mediterraneo antico. *Proceedings of the International Congress: Momenti precoloniali nel Mediterraneo antico. Questioni di metodo- Aree d'indagine. Evidenze a confronto*, Rome, 11-18.
- Sayre E.V., Yener K.A., Joel E.C. & Barnes I.L. (1992). Statistical Evaluation of the Presently Accumulated Lead Isotope Data from Anatolia and Surrounding Regions. *Archaeometry*, 34, 1, 73-105.
- Stos-Gale Z.A. & Gale N.H. (1992). New Light on the Provenience of the Copper Oxhide Ingots Found on Sardinia. In R.H. Tykot & T.K. Andrews (eds), *Sardinia in the Mediterranean: A Footprint in the Sea*, Sheffield, 317-346.
- Stos-Gale Z.A., Gale N.H., Houghton J. & Speakman R. (1995). Lead Isotope Data from the Isotrache Laboratory, Oxford: Archaeometry Data Base 1, Ores from the Western Mediterranean. *Archaeometry*, 37, 2, 407-415.
- Stos-Gale Z.A., Gale N.H. & Zwicker U. (1986). The Copper Trade in the South-East Mediterranean Region. Preliminary Scientific Evidence. *Report of the Department of Antiquities, Cyprus*, 122-144.
- Stos-Gale Z.A., Maliotis G., Gale N.H. & Annetts N. (1997). Lead Isotope Characteristics of the Cyprus Copper Ore Deposits Applied to Provenience Studies of Copper Oxhide Ingots. *Archaeometry*, 39, 1, 83-123.
- 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.
- Tylecote R. F., Ghaznavi H. A. & Boydell P. J. (1977). Partitioning of Trace Elements between Ores, Fluxes, Slags and metal during the Smelting of Copper. *Jour. Archaeol. Sci.*, 4, 305-333.