ISOTOPIC LEAD RATIO ANALYZED BY ICP-MS IN SOME METALLIC SLAGS COMING FROM LOCRI EPIZEPHIRI (MAGNA GRAECIA, SOUTH ITALY)

G. Moretti , C. Barbante , W.R.L. Cairns , F. Guidi, F. Fanari, M. Rubinich

The lead isotopic composition of samples of iron slags recovered from two archaeological sites in Locri Epizephiri (Italy - Calabria) were analysed for the first time by ICP-MS. The 204Pb, 206Pb, 207Pb and 208Pb content of traces of lead present in the slags are reported. The analysis allows some preliminary conclusions on the different origins of iron slags and on the metallurgical processes that they had undergone to be made. The two archaeological sites are different by excavated extension, chronology and position in the ancient town: the first one shows that, in the 6th cent. B.C. the activity was mostly a reduction of minerals probably not coming from a single unique source of ore or an individual mine; the latter, with slags coming from a foundry in a main sanctuary of Locri Epizephiri, indicates that, in the 5th - 4th cent. B.C., the metalworking used ingot or bloom, probably obtained from ores retrieved from mines sited near the city.

KEYWORDS: Locri Epizephiri (Italy); 6th - 4th cent. B.C.; Magna Graecia; Metallic slags; Lead isotope analysis; Metalwork; Ironmaking.

INTRODUCTION

Locri Epizephiri is one of several towns founded by the Greeks in Southern Italy (Magna Graecia) and in Sicily between the 2nd half of the 8th and the 7th cent. B.C. Locri was founded at the end of the 8th cent. B.C. on the Ionian coast of Calabria [1] and rapidly became renowned for its sanctuaries (dedicated to Persephone, Aphrodite, Zeus Olympios, etc.) and for its handicraftsmen, who worked clay and metals (in particular: bronze) producing votive objects, such as statuettes, vases, mirrors, furniture decorations and personal ornaments. From the mid 6th cent. B.C., bronze mirrors with decorated joints or decorated handles are typical of female grave-goods found in Locri. These mirrors were certainly produced by local craftsmen, but we don't know where their smithies were located [2]. Our knowledge of the metallurgical workshops in Locri was practically inexistent until now, even though we know that a lot of metal (bronze and iron) objects were made locally, because they were essential to everyday life (for instance nails, fish-hooks, arrow-points, weapons, tools, building-cramps, coins, etc.). Other ancient Greek towns in Magna Graecia and in Sicily show a similar range of activities.

In fact - and unfortunately - only metallic slags and remains of smelting or forging operations are found in archaeological sites, because the metalworking usually was carried out in small and local smithies that were destroyed after each job. The ruins of these small furnaces, and in particular the slag analysis, in any case can give us information on the technology level reached by the artisans of that time. They constitute the most evident proof of metallurgical activities in the Locri archaeological sites.

In particular, recent excavations in Locri Epizephiri (2002-'06) brought to light two areas (Dromo Area and Marasà-Temenos), in which metallic slags were found.

The Dromo Area, from where the samples A1 → 3S-06, A2 → 4S-06 and A3 → 6S-06 come from (Tab. 1), is a small archaeological site found during the renovation of eighteenth-century buildings: under some Roman walls, the archaeologists found the remains (especially iron slags) of metallurgical activity that may be dated to the 2.nd half of the 6th cent. B.C..

On the contrary, the Marasà-Temenos site showed clear evidence of smelting and forging operations, and is located by the side of the Marasà sanctuary, one of the main urban sacred areas of Locri Epizephiri [3]. The Marasà smithy was built immediately inside the ancient city walls and probably was active between the 2nd half of the 5th and the mid 4th cent. B.C..

The Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

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Site	Samples	Weight (g)	Density (g/cm³)	Magnetism test	Origin*
Dromo Area (VI° c. B.C.)	A1 → 3S-06	12,8836	2:01	weakly magnetic	reduction**
	A2 → 4S-06	14,6075	2:04	no	reduction
	A3 → 6S-06	29,0767	3:02	quite magnetic	smithy***
Marasà-Temenos (V-IV° c. B.C.)	B1 → 13S-02	138,3	6:09	very magnetic	smithy
	B2 → 26S-02	3,9619	2:00	quite magnetic	smithy
	B3 → 38S-02	2,8652	2:09	weakly magnetic	smithy
	B4 → 44S-02	4,6357	2:03	no	smithy

*: see the discussion of the results; **: reduction: indicate slags coming from ore working;
***smithy: indicate slags coming from metalworking of ingot or bloom.

Tab. 1
Slag samples coming from Locri Epizephiri.
Scorie provenienti da Locri Epizephiri.

Instrumental Conditions	
Rf power	1450 W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Nebuliser gas flow rate	1.2 L min^{-1}
Sample uptake rate	0.5 ml min^{-1}
Spray chamber temperature	2 °C
Acquisition Parameters	
Isotope ratio analysis (3 points per peak, 5 replicates)	
Mass	Integration time per point (sec)
204	19
206	1,1
207	1,2
208	0,5

Tab. 2
ICP-MS operating conditions.
Condizioni di lavoro nell'utilizzo dell'ICP-MS.

measurements made on these slags are absolutely the first ones carried out on finds of this kind.
First of all, it can be said that natural lead consists of four isotopes, 204Pb, 206Pb, 207Pb and 208Pb. Only the last three isotopes derive from radioactive decay of the nuclides of uranium (238U and 235U) and thorium (232Th), while the first one, 204Pb, is not radiogenic and therefore its concentration is constant in time.
It is well known that the use of this element for provenance investigations depends on two parameters, one geological (that lead is one of the few elements which varies significantly in its isotopic composition) [4] and one historical. From this last point of view, lead was among the first metals extracted from ores by man, and because it is abundant in nature and its extraction is not particularly difficult, it is found in many archaeological sites [5].
The isotope ratio technique for the determination of the origin of samples is based on the comparison between data acquired during the analysis of lead within the sample and well characterised geological ore samples.
Starting by the fact that an archaeological metal object rarely is made up of a chemically homogeneous material, isotope abundance ratios can be a useful tool to try to establish the provenance of an ancient metallic object [6-8].
The chemical composition of a sample can furthermore be influenced by impurities due to the addition of fluxes in the smelting process or in fractionation of main and trace elements during the cooling process [9].
Constraints on the use of lead isotope data for provenance are given by the potential blending of the raw products, which might originate from different sources. It is well known, in fact, that in the ancient past, many metallic objects of different origins were re-utilized by the craftsmen of the metallurgical art.
Further, a full separation of the origin for lead isotope ratio ore field data is not given in any case, so, for example, a metal object can not be traced to one specific origin [5].
As with the variability of the isotope ratios of a given ore field, a further contribution has to be considered; that the lead isotope ratios are not noticeably altered by processing of the ores or during refining of the product [10]. This is a basic condition when using lead isotope abundance ratios for provenance studies, and therefore the comparability of results for different investigated objects is guaranteed.
The discovery of ancient metalwork-areas is not very frequent and the analyses of slag are still rather rare [11].
In this work the isotopic composition 204Pb, 206Pb, 207Pb and 208Pb of traces of lead present in slags coming from Locri Epizefiri is reported.
Unfortunately, it was not possible to find similar data on the archaeological ores or mines of the Calabria Region: so in this work the Locri Epizephiri data were compared with those found in the recent literature.

EXPERIMENTAL PART

Slag samples

Seven ancient metal slag samples were chosen (Tab. 1).
According to the archaeological evidence, all samples are dated from VI to IV c. B.C. . The samples were categorized in two distinct groups: the first one including those slags coming from the Dromo Area (VI cent. B.C.), the second those found in the Marasà-Temenos (V-IV c. B.C.). From these two groups of slags, the samples were cut and used first of all for the preliminary analyses (see below), and then were digested for the ICP MS analysis.

Instrumentation, reagent and standards

ICP-MS analyses were carried out on an Agilent 7500i ICP-MS (Agilent Technologies, Yokogawa Analytical Systems, Tokio, Japan) with a quartz double pass spray chamber, thermostatted to 2°C, and fitted with a PolyPro concentric nebuliser (free aspiration rate <500µl min-1) (Elemental Scientific, Inc, Omaha, USA). High purity de-ionized water (18 MΩ cm-1 resistivity; Purelab Ultra, Elga, High Wycombe, UK) was used. A solution of SRM 981 Common Lead Isotopic Standard (NIST, Gaithersburg, MD, USA) was used as a mass bias correction solution for isotope ratio analysis. A sample of SRM 981 Common Lead Isotopic Standard (NIST, Gaithersburg, MD, USA) was dissolved in cold nitric acid (Suprapur grade, Merck, Darmstadt, Germany) and was serially diluted to give a final concentration of 10 µg l-1 (total Pb), and was used as a mass bias correction solution for isotope ratio analysis. The instrumental operating conditions are reported below in Tab. 2.

Analytical procedure

All samples were analysed using the isotope analysis acquisition parameters for isotope ratio analysis, the instrumental operating conditions are reported in Tab. 2.

For isotope ratio analysis, the number of scans is pre-set to 1000 in the ICP-MS software [12], so only three parameters can be optimised, the points per peak, the integration time per measurement and the number of replicates. The integration times were set to give similar count rates for the 4 isotopes studied (204Pb, 206Pb, 207Pb and 208Pb) based on their mean isotopic abundances [13] to obtain a similar measurement precision for each isotope. Three points per peak were chosen as this gives the best precision for quadrupole instruments [12] and 5 replicates were chosen to give a total analysis time of 327 seconds. Samples were diluted so that all the isotopes were acquired in pulse counting mode, as this ensures that the same integration time is used throughout the measurement. After each sample the common lead isotopic standard was run to correct for any drift in mass bias.

Sample preparation

About 1g of each slag sample was dissolved in an acid cleaned glass beaker, after the addition of 30ml of hydrochloric acid and 10 ml of nitric acid, on a hotplate. Once dissolved, solutions were allowed to cool, were filtered and then made up to 100 ml with ultra pure deionized water.

After a previous determination of the amount of lead in the solutions (by a semi-quantitative ICP-MS analysis), aliquots of the principal solutions were diluted to obtain solutions with a lead content of <10 µg/L, so that all the isotopes were acquired in pulse counting mode.

All samples were analyzed using the isotope analysis acquisition parameters for isotope analysis as reported above.

Other support analyses

Before carrying out the ICP MS analyses, some other analytical techniques were used and the results were integrated with these results. For the SEM analyses a JEOL JSM-5600 LV device was used coupled with an Oxford LINK ISIS Series 300 electronic spectrometer. A Perkin Elmer 3100 AAS was used for the AA analysis, and a Philips PW1050 system for XRD characterisation.

RESULTS AND DISCUSSION

In any archaeological metallurgical research, the metallic slags are usually the most evident - often the only - proof of the ancient metalworking. From these kinds of materials it is possible to draw out a significant number of data, useful for defining the economical and social context of the analyzed site, along with the technological one.

Beyond the results of the usual analyses (i.e.: optical microscopy, AAS, SEM, XRD, etc.), it is well known that some indexes revealed by ICP-MS analyses often permit the definition not only of the ores or mines of origin of these slags, but also the technology used and its evolution in time.

The precision of the data obtained with a quadrupole ICP-MS instrument with one detector is not as high, as could be obtained by, for example, by a double-focusing mass spectrometer multicollector instrument, but it is accurate enough to reveal a reliable trend or fields of isotope ratios, as demonstrated by the results of repeated distinct measurements carried out by other authors [14].

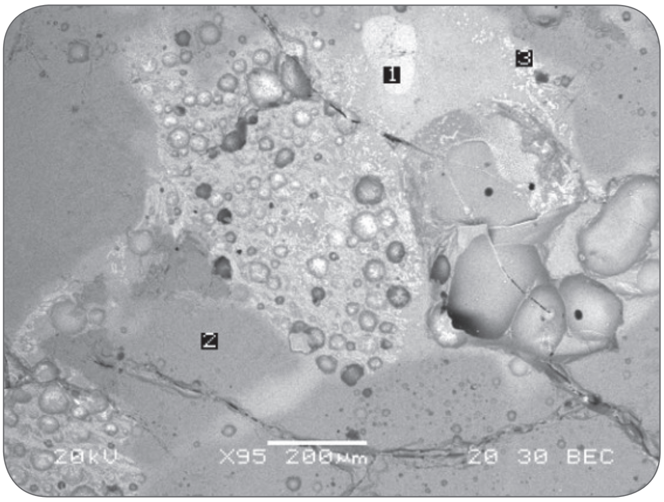

Fig. 1

Sample 3S-06 (95x). The analyses resulted in a structure rich in SiO_2 and Al_2O_3, with a marked presence of Na and K (point 1); in others the iron is present as an oxide or Fe_2SiO_4 (point 2). The iron is present also in dendrite form, where Ti can often be found (point 3).

Campione 3S-06 (95x). Si notino la struttura ricca in SiO_2 e Al_2O_3, con forte presenza di Na e K (punto 1); nelle altre zone il Fe è presente sottoforma di ossido o di Fe_2SiO_4 (punto 2). Il Fe è, inoltre, presente in forma di dendrite, dove è possibile trovare spesso anche il Ti (punto 3).

This first study on Locri Epizefiri slags is concerned with almost the same period of time - in the archaeological sense: for this reason, it is not possible to distinguish between different technological levels in the iron making from the different slag analyses. In fact, the technological revolution had already occurred: for instance, iron making in Magna Graecia has already been testified in the mid of VIII cent. B.C.. However, these two groups of slags were chosen because of their different origin. In fact, the discovered foundry and the relative metallurgical activity - near the Temenos of the Ionic temple - presumably finished their activity around the mid IV cent. B.C., while the ritual activity in the nearby temple took place and developed since the end of VII cent. B.C..

The various metallurgical holes found here were filled with sacrifices such as remains of burnt animal bones, charcoal and shards of votive pottery (black glazed cups and plain vases), and then were sealed with cobbles and tile fragments. In short, the smithy was sacralized, the holes transformed into proper votive deposits (bothroi), and the ground levelled with the same manufacturing rejects, charcoals and iron slags [3].

Accordingly, the slags were initially classified using usual archaeometric techniques (optical microscopy, AAS, SEM, XRD).

From this part of the work one can summarize the following:

1. The sample 3S-06 and 4S-06 coming from the Dromo Area (Tab. 1) are slags of a reduction process. In fact both of them are constituted of a glassy background (see, for ex., the SEM reported in Fig. 1), formed by the oxides SiO_2 and Al_2O_3. The Fe is present as

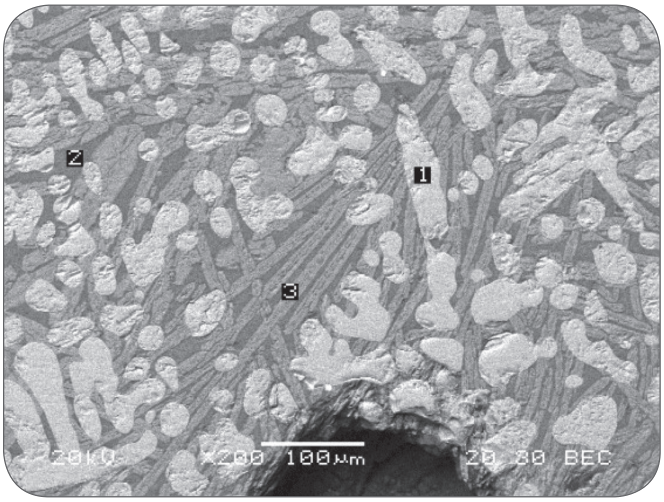

Fig. 2

Sample 6S-06 (200x). The analyses showed a structure rich in SiO_2 and Al_2O_3, with the presence of Fe, K e Ca (point 2). The acicular crystals are of Fe_2SiO_4 (point 3). The white zones (point 1) consist almost entirely of FeO.

Campione 6S-06 (200x). L'analisi mostra una struttura ricca in SiO_2 e Al_2O_3, con la presenza di Fe, K e Ca (punto 2). I cristalli aciculari sono formati da Fe_2SiO_4 (punto 3). Le aree bianche (punto 1) sono costituite quasi interamente da FeO.

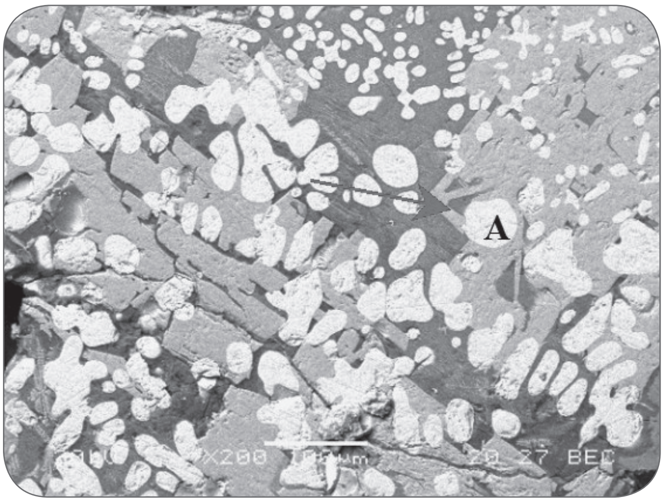

Fig. 3

Sample 13S-02 (200x). As in Fig. 2, the white parts (point A) are almost entirely of FeO. The process was not perfectly optimized because of the internal temperature of the furnace, which did not reached that of the formation the fayalite (1100°C), even if it permitted the exit of the slags from a suitable hole in the furnace.

Campione 13S-02 (200x). Come in Fig. 2, le aree bianche (punto A) sono costituite quasi interamente da FeO. Il processo che ha portato alla produzione di tale scoria non è stato perfettamente ottimale a causa della temperatura interna della fornace, la quale non ha raggiunto il punto di formazione della fayalite (1100°C), anche se ha permesso l'evacuazione della scoria da un apposito foro di scolo presente nella fornace stessa.

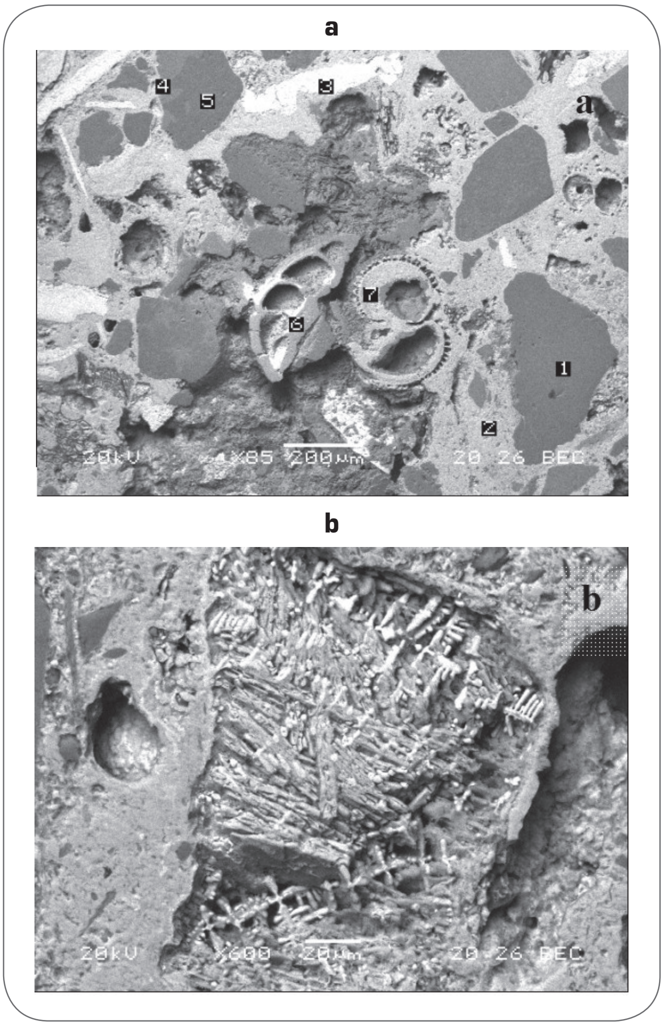

Fig. 4

Sample 26S-02. a) (85x). The presence of shell remains are evident, as they were probably used during the metalworking process. The white parts [a) point 3] consist of FeO. b) (600x). The presence of iron dendrites can be noted.

Campione 26S-02. a) (85x). La presenza di gusci di conchiglie è ben evidente, provenienti presumibilmente dall'aggiunta di sabbia durante il processo metallurgico. Le aree bianche [a) punto 3] sono costituite da FeO. b) (600x) Si osserva la presenza di dendrite di Fe.

FeO e Fe_3O_4: the creep trace evidence confirms that these slags were produced by a reduction process of a Fe ore containing ilmenite ($FeTiO_3$) as a secondary ore;

2. The other sample 6S-06 derived from metalworking of ingot or bloom: for example, in Fig. 2 the reported SEM image permits the recognition of the typical structures of fayalite and wustite, beyond the clear traces of metallic iron;

3. All the other samples (13S-02, 26S-02, 38S-02 and 44S-02), come from the Marasà-Temenos, they are slags deriving from the metalworking of ingot or bloom. In Fig. 3, for example, a structure is shown that is very similar to that of the sample 6S-06 of Fig. 2, while in the Fig. 4a) shell remains, used during the process of metalworking, are evident; furthermore, in Fig. 4b) one can note the presence of iron dendrites, that are typical for this kind of slag [15].

Isotope ratios are usually used to make plots with two comple-

Sample	$^{206/207}Pb$	$^{208/207}Pb$	$^{207/204}Pb$	$^{206/204}Pb$	$^{208/206}Pb$	$^{207/206}Pb$
A1	1.143 ± 0.006	2.422 ± 0.016	13.89 ± 0.35	15.87 ± 0.39	2.119 ± 0.011	0.8750 ± 0.0042
A2	1.130 ± 0.006	2.411 ± 0.017	3.41 ± 0.02	3.85 ± 0.04	2.134 ± 0.015	0.8849 ± 0.0047
A3	1.135 ± 0.003	2.421 ± 0.008	13.22 ± 0.15	15.00 ± 0.16	2.134 ± 0.007	0.8813 ± 0.0022
B1	1.136 ± 0.004	2.421 ± 0.006	16.13 ± 0.06	18.33 ± 0.10	2.130 ± 0.007	0.8799 ± 0.0031
B2	1.154 ± 0.005	2.435 ± 0.007	16.37 ± 0.08	18.88 ± 0.17	2.111 ± 0.008	0.8669 ± 0.0040
B3	1.127 ± 0.004	2.407 ± 0.009	16.26 ± 0.04	18.32 ± 0.08	2.136 ± 0.004	0.8876 ± 0.0034
B4	1.175 ± 0.002	2.447 ± 0.008	16.70 ± 0.05	19.62 ± 0.09	2.082 ± 0.008	0.8511 ± 0.0016

Tab. 3

Lead isotope ratios for the Locri Epizephiri samples analyzed. To simplify all the graphs: A1 → 3S-06, A2 → 4S-06, A3 → 6S-06, B1 → 13S-02, B2 → 26S-02, B3 → 38S-02, B4 → 44S-02.

Rapporti isotopici del piombo per i campioni analizzati provenienti da Locri Epizephiri. Per semplificare i grafici i campioni vengono riportati secondo la seguete dicitura: A1 → 3S-06, A2 → 4S-06, A3 → 6S-06, B1 → 13S-02, B2 → 26S-02, B3 → 38S-02, B4 → 44S-02.

mentary variables where one can put all isotopic abundance experimental data, to identify a field of values representative of an ore-lead containing region.
As similar data for the Calabria Region on archaeological ores or mines does not yet exist, we proceeded by comparing our data with other literature data from analyses of European ore fields.
For example, Rosman used 206/207Pb vs. 208/207Pb plot to define ores into Aegean, British, German, Greek and Spanish regions [7]; similarly, Stos-Gale [16, 17] and Rhol [18] used 208/206Pb vs. 207/206Pb to plot ores of western Mediterranean, Aegean, Britain, and Ireland. Finally, Boni [19] reported 207/204Pb vs. 206/204Pb plots from Pompeii (Italy) while Fortunato [5] also reported other data from Italy.
In Tab. 3 the lead isotopic ratios (together with the standard deviation of the five different measurements on the same specimen) of the samples are reported.
In Fig. 5 the experimental data of the ratio 206/207Pb vs. 208/207Pb of the examined samples are reported.
One can see that the Dromo Area and the Marasà-Temenos data lie in two areas confined by an ellipse.

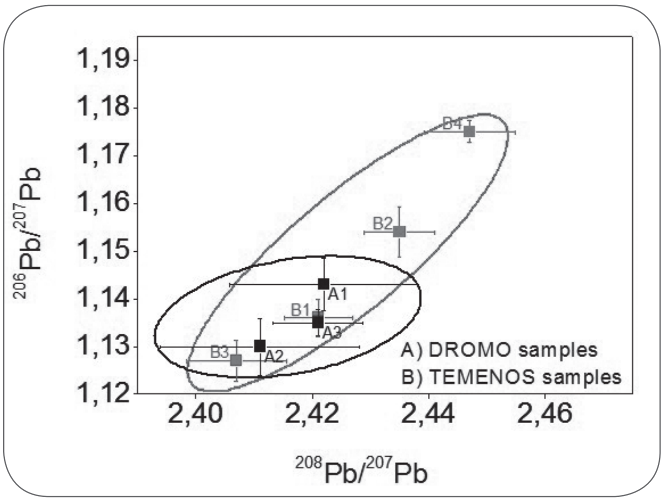

Fig. 5

The trends of the lead isotopic ratios $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ for the Locri Epizefiri samples.

L'andamento dei rapporti isotopici $/^{207}Pb$ vs $^{208}Pb/^{207}Pb$ nei campioni provenienti da Locri Epizephiri.

The isotopic ratio of slags coming from the Dromo Area are closed in an area between 206/207Pb ≈ 2.41 ÷ 2.42 vs. 208/207Pb ≈ 1.13 ÷ 1.14, thus indicating that, even if only the samples A1 → 3S-06 and A2 → 4S-06 are slags coming from a reduction process, their ore or mine origin, at a first sight, would seem to be the same.
Different trends can be drawn from the Marasà-Temenos data: in this case a clear differentiation can be noted between these and those of the Dromo Area: in fact these ratios are lying in a more wide range (206/207Pb ≈ 2.41-2.45 vs. 208/207Pb ≈ 1.12-1.17).
From Fig. 5 seems likely that the area of the Marasà-Temenos samples that of the Dromo Area.
Superimposing these data onto those reported by Rosman (Fig. 6) one can note that there is no correspondence with those coming from the Aegean and Greece (Laurion), and it is doubtful that the lead is British or European in origin.
If we superimpose our data onto those of Stos-Gale [16, 17] we

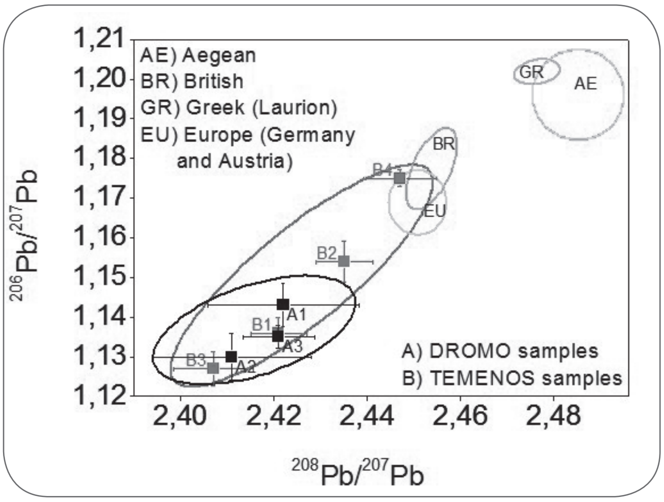

Fig. 6

Experimental data of Dromo Area (A) and Marasà-Temenos (B) superimposed onto the Rosman plot [7] ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$).

Dati sperimentali relativi ai campioni raccolti nell'Area Dromo (A) e in quella del Temenos di Marasà (B) sovrapposti ai dati raccolti da Rosman [7] e riportati nel grafico $^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{207}Pb$.

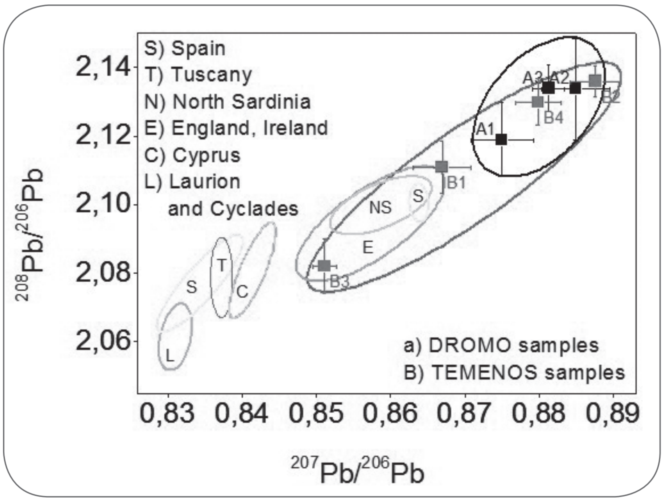

Fig. 7

The lead isotopic ratios $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ for the data of Dromo Area (A) and Marasà-Temenos (B) superimposed to the data of Stos-Gale [16, 17].

I rapporti isotopici $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ dei campioni provenienti dall'Area Dromo e dal Temenos di Marasà, confrontati con i dati raccolti da Stos-Gale [16, 17].

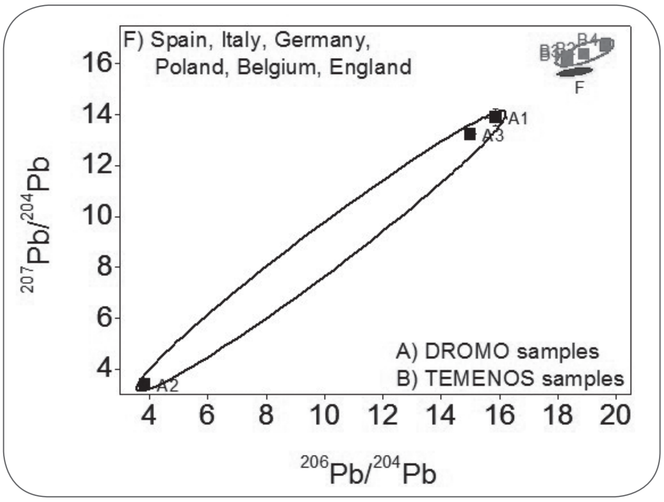

Fig. 8

The trends of the lead isotopic ratios $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ for the data of the Dromo Area (A) and Marasà- Temenos (B) superimposed onto the data of Boni [19] and Fortunato [5].

IL'andamento dei rapporti isotopici $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ per i campioni provenienti dall'Area Dromo (A) e dal Temenos di Marasà sovrapposti ai dati elaborati da Boni [19] e Fortunato [5].

obtain the graph 208Pb/206Pb vs 207Pb/206Pb of Fig. 7, in which it is possible to compare the data of Dromo Area (A) and Marasà-Temenos (B) with those of Spain, Tuscany (Italy), Northern Sardinia (Italy), England and Ireland, Cyprus and Greece (Laurion).
A slight correspondence can be noted between the Marasà-Temenos data and those obtained from measurements on samples coming from Spain, England and North Sardinia (Italy).
This could be in agreement, for example, with the historical memory of commercial trade by the people of Magna Grecia and the mining areas of southern Spanish regions. During more recent times, especially near the IV c. B.C., trade was probably more frequent, and so it is possible to hypothesize also exchanges of metal ingot between some Mediterranean regions and the Locri Epizephiri. But this hypothesis can be sustained only by studies on local, archaeological mines, that up to today are unavailable.
In Fig. 8 the experimental data of the ratio 207/204Pb vs. 206/204Pb of the Dromo Area and Marasà-Temenos, superimposed onto that reported for Italy finds by Boni [19] and Fortunato [5], are reported.
Also in this case two areas can be identified, both well distinct and different in their variation ranges, and with a - more evidenced - linear trend.
In this case only the slags coming from Marasà-Temenos could seem to be of the same ore origin, while those from the Dromo Area - especially as the A2 → 4S-06 is concerned - are completely different. Furthermore, the nearness of the Marasà-Temenos data to the area of those reported in Fig. 8 would seem to indicate an Italian origin of the slag ores from which they come from: this may also be true also for the Dromo Area ones, excluding sample A2 → 4S-06, which indicates that there may have been another as yet unknown source.
Nevertheless, it is more likely that the Locri craftsmen were able to retrieve the indispensable iron ores from mines near the city. In favour of this hypothesis, are some historical facts that can be found: for example, the Stilaro mines, known as archaeological mines, are in the area of Kaulonia, another Greek colony contemporary to Locri, but under the influence of Crotone, at least until the mid of VI cent. B. C., the period of time in which Kaulonia and its mines probably came under Locri jurisdiction.

CONCLUSIONS

The conclusions of this work can be summarized as follows:
1) The iron slags coming from Locri Epizephiri were distinguished by means of the usual analytical techniques into two groups:
a. One coming from the Dromo Area (VI c. B.C.), in which two slags (A1 → 3S-06 and A2 → 4S-06) were obtained by a process of ore reduction, probably coming from a nearby mine, and one slag (A3 → 6S-06) from the metalworking of ingot or bloom; the reduction occurred in a continuous furnace, because the slags came out from a hole at the bottom of the oven, proving that the technological level reached by the Locri craftworks was already enough advanced;
b. The second group came from Marasà-Temenos (V-IV c. B.C.): all slags derive by ingot or bloom metalworking; in this case the ironworking was certainly subsequent to reduction processing of the ores: the technique foresaw the addition of different materials to the ore charge, as different kind of sands mixed with triturated shells used as anti-oxidizing crusts during the successive reduction operations.
2) These slags were analyzed for the first time by ICP-MS to investigate their origin: because of the unavailability of other Calabria Region data, the comparison was made with other Mediterranean and/or European data. Even if these first results indicate no real superimposition areas, but only a nearness of those of Marasà-Temenos (V-IV c. B.C.) with the Spanish or Italian data, we can conclude the followings:
a. Two slags (A1 → 3S-06 and A3 → 6S-06) coming from the Dromo Area (VI c. B.C.) probably have the same local ore origin, even if we can distinguish two different processes that produced them;

b. On the Marasà-Temenos slags (V-IV c. B.C.) we can only indicate a different origin of the start materials: in fact, only in the Fig. 8 - that reported the data of Boni [19] and Fortunato [5], the results seem to indicate a very similar origin to that of the start ores;
c. From these first two conclusions and by the comparison with the data of different authors it is more likely that the Locri craftsmen were able to retrieve the indispensable iron ores from mines near the city. This is supported by some historical facts: for example, the Stilaro mines - a valley that is at 20 km from Locri Epizephiri [20], also near to the area of Kaulonia and its mines - was conquered by Locri in the beginning of IV cent. B. C. .

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ABSTRACT

I RAPPORTI ISOTOPICI DEL PB RICAVATI MEDIANTE ICP-MS IN ALCUNE SCORIE METALLICHE PROVENIENTI DA LOCRI EPIZEFIRI (MAGNA GRECIA, SUD ITALIA)

Parole chiave: storia della metallurgia, caratterizz. materiali, microscopia elettronica, processi

La composizione isotopica dei campioni di scorie di materiale ferroso, rinvenute in due scavi archeologici effettuati a Locri Epizephiri (Calabria), è stata analizzata per la prima volta con ICP-MS: in particolare si riporta il contenuto in 204Pb, 206Pb, 207Pb e 208Pb delle tracce di piombo presenti nelle scorie. Le analisi hanno permesso di fare alcune considerazioni preliminari sulla diversa origine delle scorie in ferro e sui processi metallurgici che hanno portato alla loro produzione. I due siti archeologici si differenziano per l'estensione dello scavo, per la cronologia e per la loro posizione all'interno dell'antica città: il primo mostra che, nel VI° secolo a.C., l'attività era incentrata anche sulla riduzione del minerale, probabilmente non proveniente da un solo tipo di minerale o da un unico giacimento; le scorie provenienti dal secondo sito sono state prodotte da un'officina metallurgica sita nelle strette vicinanze di uno dei principali santuari di Locri Epizephiri e indicano che nel V° - IV° secolo a.C. gli artigiani utilizzavano lingotti o blume di ferro, probabilmente ottenuti da minerali estratti dalle miniere situate nei pressi della città.