Experimental evaluation and archaeometric significance of lead isotope and chemical fractionation in metallurgical processes

A. Cincotti, U. Sanna, A. Rivoldini, A. Viola

An experimental investigation has been conducted for the purpose of assessing what influence, if any, the main metal working techniques have on the lead isotope composition. Smelting, whereby the lead is separated from the galena ore, prolonged melting and the segregation that accompanies the solidification of ingots, have been considered. Isotope ratios have been determined using the ICP-MS technique. The findings show that metalworking does not produce any significant changes in lead isotope ratios that might influence lead provenancing.

Key words: archeometallurgy, lead

INTRODUCTION

Lead isotope analysis by means of ICP-MS (inductively couple plasma-mass spectrometry) or TI-MS (thermal ionization-mass spectrometry) [1-3] is proving to be one of the most promising methods for identifying the mining region (or, at the best, the actual ore deposit in a given region) from which the raw material for making metal (lead, silver copper or bronze) artefacts originated [4-13]. The reliability of this method depends basically on two factors:

- the lead isotope composition ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ e $^{206}Pb/^{204}Pb$) is sufficiently constant and characteristic to allow to distinguish between minerals of different geographic origin and possibly between different ore deposits in the same region;
- the original isotope ratios do not change during metalworking, notably: smelting, melting e re-melting.

This paper aims at providing a contribution to the second of these. In fact, there is considerable disagreement among workers in this field as to the significance of possible alterations to the lead isotope composition induced by metallurgical processes. For instance, Barnes [14] ruled out that in the transition from galena to metallic lead and from metallic lead to lead oxides used for pigments any changes occurred in the lead isotope composition, beyond the limits of experimental error. More recently however, Budd [15] argued on theoretical grounds that appreciable alterations do take place, especially in metallurgical processes where the metal undergoes intense vaporization. Similar problems have been recently addressed by Gale [2] in regard to certain aspects of tin metallurgy.

In an attempt to elucidate this problem, lead isotope analyses have been performed on samples of lead taken during the following operations reproduced in the laboratory:

- smelting and hence the passage from galena to metallic lead;
- remelting of metallic lead in an airflow, thus with significant losses due to evaporation;
- ingotcasting, with possible segregation.

A. Cincotti, U. Sanna, A. Viola
Dipartimento di Ingegneria Chimica e Materiali, Università degli Studi di Cagliari

A. Rivoldini
Dipartimento di Georisorse, Geongegneria e Tecnologie Ambientali, Università degli Studi di Cagliari

Memoria pervenuta il 26 giugno 2000

EXPERIMENTAL

Metallurgical processes

Galena smelting - A well crystallized galena, fragmented into rough cubes was placed in an aluminium crucible. A galena and coal charge was used throughout, in successive stages. A Heraeus furnace was employed with Heraeus Thermicon P controller. Temperature was maintained at 700°C and measured with a thermocouple placed in the crucible. A constant airflow of 4300 ml/min was supplied and measured with a Gilmont Instruments Flowmeter, provided with steel float. The smelting process lasted four and a half hours with yield of 23%.

Lead melting and re-melting - Two experiments were carried out at temperatures of 550° and 950°C. Electrolytic lead, supplied by the SAMIM foundry at S. Gavino (Cagliari), was "contaminated" with various elements.

The first experiment was conducted in a steel crucible under constant airflow. Four samplings were done during the test which lasted 90 minutes. Lead loss by evaporation amounted to 7% of the metal introduced as charge.

In the experiment at 950°C, again on impure lead, the air supply was suspended as this would have immediately formed a thick and hard oxides layer on the surface, thereby reducing lead loss by evaporation. Six samplings were done during the experiment which lasted 70 minutes. Evaporation loss was 2%.

Ingot casting - Two castings were carried out, one using electrolytic lead, the other lead containing different proportions of impurities, for obtaining two ingots each, one moulded in a steel shell, the other cooled slowly in a mould of refractory material. The ingots were 95 mm high with diameter of 13 mm. They were sampled at three points along the longitudinal axis (bottom mid-height and top). The samples were then analyzed by means of ICP-MS for determining the isotopic ratios and the chemical elements Ni, Cu, Zn, As, Ag, Cd, Sn, Sb, Te, Cs, Tl, Bi.

ICP-MS analytic determinations

Samples weighing roughly 100 mg were dissolved in 4 ml of a solution containing 1:1 by volume of ultrapure ARISTAR BDH nitric acid and deionized distilled water (conductivity <0,08 μS). They were digested for 12 hours at 70°C in Nage Company Teflon FEP capsules covered with a watchglass. The solution was made up to 50 ml and then diluted to obtain a final concentration of about 100 μg/l Pb in water with 1%

HNO_3. This amount of lead allows to obtain counts of over 100,000 and consequently isotopic ratios with acceptable relative errors for the purpose of this work [3].
A standard NBS reference sample "Common Lead Isotopic Standard" (SRM 981) was solubilized following the same procedure and a blank was prepared. The laboratory materials were washed and conditioned using laboratory detergents and 1N HCl and HNO_3 solutions. A Perkin Elmer SCIEX ELAN 5000 ICP-MS was used for measuring isotopic ratios. Operating conditions and data acquisition modes are shown in Table 1.

Condition	Values
RF power	1100W
Nebulizer gas flow rate	0.85 l/min
Auxiliary gas flow rate	0.90 l/min
Plasma gas flow rate	15.00 l/min
Nebulizer type	Cross-Flow
Interface cones	Nickel
Dwell time	20 ms
Number of sweeps	1000
Number of replicates	3
Scan mode	Peak hopping

Table 1-Operating conditions and mass spectrometer settling for measuring Pb isotopes.

Tab.1-Condizioni oiperative e di acquisizione dati dello spettrometro di massa per la misura degli isotopi del piombo.

The lead isotope ratios of the different samples were standardized with the SRM 981 certified values introduced, after the blank, every five real samples .Short time accuracy was evaluated repeating measurements ten times on the same sample and expressed as percent relative standard deviation (RSD%), while long term accuracy was calculated measuring the same standard and calculating the RSD% (Table 2).

Isotopic ratios	RSD% (st)	RSD% (lt)	RSD% (st) *	RSD% (lt) *
208/204	0.223	0.242	0.10÷0.45	0.416
207/204	0.291	0.177	0.13÷0.57	0.175
206/204	0.398	0.097	0.10÷0.49	0.221

Table 2 - Isotopic ratios and RSD% over the short (st) and long (lt) term. For comparison, data reported in the literature [1] for a similar archeometrical use are shown.*

Tab.2 - Rapporti isotopici e RSD% per tempi brevi (st) e lunghi (lt). Per confronto sono riportati dati di letteratura [1] per un analogo uso archeometrico.*

RESULTS AND DISCUSSION

Smelting was carried out on a sample of galena from the Montevecchio mine, one of the traditional and oldest centres of the extractive industry in Sardinia. This particular ore is well characterized, the lead isotope ratios having been determined by a number of workers. Table 3 shows the isotopic ratios obtained during this experiment and those of the metallic lead determined during the laboratory smelting test.The data obtained for the galena further confirm the lead isotope fingerprint of this ore deposit. Passing from galena to lead does not produce alterations such as to question the mineral provenancing,at least in a regional context, as can be seen from the data given in Table 4. Possible changes to isotopic ratios induced by prolonged melting of the metal have been studied at temperatures of 550 e 950°C.
Lead weight losses measured after heat treatment were 7% and 2% respectively.
The results are shown in Table 5, while Fig. 1 shows the lead isotope ratio 208/204, which have greater difference in mass, and can thus be taken as indicative of possible fractionation. Error bars of measures are shown.

Data source:	208/207	207/206	206/204
Galena, our data	2.1103 ± 0.0091	0.8593 ± 0.0031	18.2094 ± 0.0693
Metal, our data	2.1090 ± 0.0082	0.8640 ± 0.0027	18.0680 ± 0.0589
Galena, [19]	2.1082 ± 0.0009	0.8610 ± 0.0005	18.1865 ±0.0106
Galena, [10]	2.1073 ± 0.0022	0.8616 ± 0.0018	18.1546 ± 0.0499
Galena, [21]	2.1091 ± 0.0014	0.8613 ± 0.0017	18.1908 ± 0.0481
Galena, [22]	2.1113 ± 0.0014	0.8623 ± 0.0003	18.1580 ± 0.0057

Table 3 - Lead isotope composition of Montevecchio galena and the lead obtained in the laboratory.

Tab. 3 - Composizione isotopica della galena di Montevecchio e del piombo ottenuto in laboratorio.

Country	Region	208/207	207/206	206/204
Italy	Sardinia (Arburese)	2.1077+0.0026	0.8613 0.0016	18.1749 0.0470
"	Sardinia (Barbagia)	2.1000 0.0030	0.8577 0.0017	18.2275 0.0429
"	Sardinia (Barb/Gerrei)	2.1011 0.0049	0.8564 0.0011	18.3057 0.0150
"	Sardinia (Baronia)	2.0992 0.0061	0.8496 0.0023	18.4551 0.0961
"	Sardinia (Fluminese)	2.1160 0.0065	0.8686 0.0041	18.0211 0.0742
"	Sardinia (Iglesiente)	2.1084 0.1422	0.8715 0.0072	17.9577 0.1537
"	Sardinia (Oridda)	2.1163 0.0052	0.8684 0.0038	18.0258 0.0807
"	Sardinia (Sulcis)	2.1030 0.0072	0.8594 0.0052	18.2174 0.1173
"	Tuscany	2.0821 0.0092	0.8374 0.0009	18.7499 0.0285
Spain	Almeria	2.0713 0.0034	0.8344 0.0015	18.7934 0.0511
"	Andalusia (Alham.)	2.1049 0.0060	0.8560 0.0018	18.3330 0.0144
"	Andalusia (Almagr.)	2.0795 0.0014	0.8361 0.0002	18.7524 0.0156
"	Huelva	2.1021 0.0013	0.8596 0.0004	18.1924 0.0101
"	Murcia (Cartagena)	2.0857 0.0022	0.8383 0.0008	18.7368 0.0287
"	Murcia (Mazzaron)	2.0807 00020	0.8366 0.0004	18.7326 0.0163
"	Seville	20999 00023	0.8595 0.0006	18.1773 0.0313
Greece	Cicladi	20785 00017	0.8354 0.0007	18.8169 0.0334
"	Northern Aegean	20695 00014	0.8342 0.0006	18.7812 0.0177
	Laurio	20592 00023	0.8315 0.0005	18.8544 0.0309

Table 4 - Average lead isotope ratios for different mining regions of Sardinia and nearby Mediterranean regions. [1,4,6,7,9,10,11,17,18,19,20,21,22]

Tab.4 - Medie dei rapporti isotopici del piombo per differenti zone mineralogiche della Sardegna e delle vicine regioni del Mediterraneo [1,4,6,7,9,10,11,17,18,19,20,21,22]

Temp. °C	Time, min	208/206	207/206	206/204
550	1	2.0832	0.8636	18.1208
"	55	2.0896	0.8640	18.1259
"	65	2.0866	0.8646	18.0939
"	75	2.1014	0.8633	18.0934
"	90	2.0948	0.8685	18.0778
950	2	2.0898	0.8607	17.8419
"	10	2.1050	0.8606	18.0853
"	25	2.0966	0.8662	17.9112
"	35	2.1003	0.8649	17.9447
"	45	2.0941	0.8637	17.9409
"	70	2.0951	0.8636	17.9579

Table 5 - Isotopic ratios of samples subjected to prolonged melting.

Tab 5 - Rapporti isotopici di campioni sottoposti a fusione prolungata.

Here too, the variations in the data characterizing the lead isotope composition were found to be insignificant as far as metal provenancing is concerned.
As for the differences observed on the samples removed from the longitudinal axis of a cylindrical ingot, the results are shown in Table 6.
Again the values never vary to the extent that they might influence identification of the source of the metal.
Table 7 gives the chemical composition of the elements present in proportions greater than 10 ppm determined for samples removed from the longitudinal axis of the ingot cooled slowly.
The percent variation with respect to the top of the ingot, taken as 100, is also shown.
Some physical properties of the trace elements significant for the discussion are shown in Table 8. The mean atomic weight of lead is 207.2 while its density in the liquid state is 10.7 g/cm^3 at 327 °C and 10.1 g/cm^3 at 80°C. Obviously, the chemical elements having atomic weight and density close to those of lead (Tl and Bi) will not be subject to gravity segregation. Only those elements much lighter than lead (Ni, Cu and Ag) will undergo significant variations in concentration, being enriched in the upper part of the ingot and decreasing down the ingot. On the other hand Sb undergoes fractionation because, in spite of its relatively high specific weight, its density in the liquid state is rather low.
These data are interesting not only in relation to the correct interpretation of the analytic data determined for the necessarily small samples that can usually be removed from archaeological finds, but they also further substantiate the conclusion that fractionation based on the slight differences in mass attributable to the different lead isotopes, can be

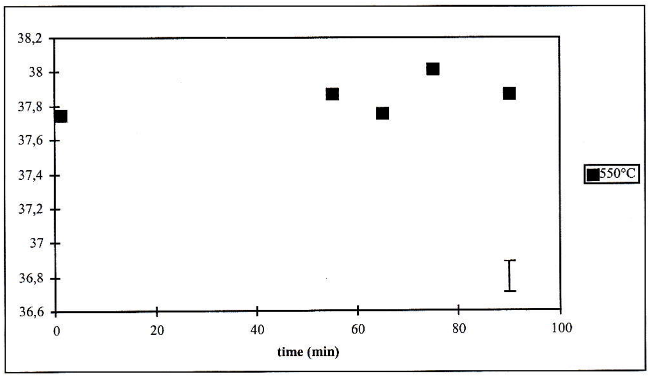

Fig. 1a - 208/204 ratio as indicator of possible fractionation fro the experiments at 550 °C.

Fig. 1a - Rapporto 208/204 quale possibile indicatore del frazionamento per gli esperimenti a 550 °C.

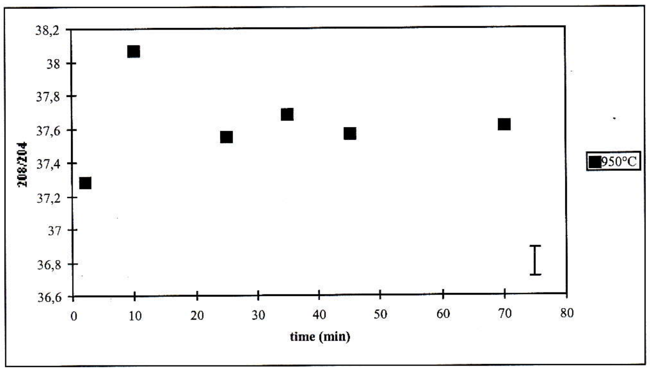

Fig. 1a - 208/204 ratio as indicator of possible fractionation fro the experiments at 950 °C.

Fig. 1a - Rapporto 208/204 quale possibile indicatore del frazionamento per gli esperimenti a 950 °C.

considered uninfluential in identifying the source of the galena employed.

CONCLUSIONS

The findings of the present study indicate that metalworking (galena smelting, lead melting and remelting, ingot casting) does not have any appreciable effect on lead isotope ratios. In particular, during smelting no significant changes have been observed in the isotopic ratios in the passage from galena to the metal. A slight alteration in the 208Pb/204Pb ra-

Table 6 - Isotopic composition of the samples removed from the longitudinal axis of the ingots (RC: rapid cooling, SC: slow cooling).

Tab.6 - Composizione isotopica di campioni prelevati lungo l'asse longitudinale dei lingotti (RC; raffreddamento rapido; SC: raffreddamento lento).

Position	Type	Cooling	208/207	207/206	206/204	208/204
top	Electrolytic	RC	2.1074	0.8540	18.0967	38.1364
		SC	2.1072	0.8519	18.0967	38.1326
	Impure	RC	2.0985	0.8517	18.0511	37.8808
		SC	2.0963	0.8544	18.0071	37.7491
middle	Electrolytic	RC	2.1135	0.8527	18.1084	38.2714
		SC	2.1139	0.8520	18.0846	38.2284
	Impure	RC	2.1074	0.8545	18.1979	38.3494
		SC	2.1061	0.8543	18.1985	38.3270
bottom	Electrolytic	RC	2.1133	0.8525	18.1084	38.2676
		SC	2.1079	0.8562	18.0369	38.0197
	Impure	RC	2.1110	0.8563	18.1657	38.3485
		SC	2.1097	0.8501	18.1675	38.3288

Position	Ni	%	Cu	%	Ag	%	Sb	%	Tl	%	Bi	%
top	440	100	516	100	143	100	468	100	62	100	24	100
middle	417	95	508	98	105	73	375	80	61	98	24	100
bottom	266	60	463	90	104	72	117	25	61	98	24	100

Table 7 - Composition (ppm) and percent variation respect to the top of the ingot of trace elements determined in samples removed from the longitudinal axis of the ingot.

Tab.7 - Composizione (ppm) e variazione percentuale degli elementi in tracce di campioni prelevati lungo l'asse longitudinale del lingotto rispetto alla parte sommitale.

	Ni	Cu	Ag	Sb	Tl	Bi
Atomic Weight	58.7	63.5	107.9	121.2	204.4	208.9
Density in liquid state (g/cm^3)	7.8 1454 °C	7.94-7.62 1100 - 1300 °C	9.22-9.04 1100 - 1300 °C	6.44-6.32 728 - 917 °C	11.1-10.8 412 - 651 °C	9.78-9.30 500 - 900 °C

Table 8 -Physical properties of significance for the discussion (CRC, 1970).

Tab.8 - Proprietà fisiche significative per la discussione (CRC, 1970).

tio, adopted as an index of fractionation during prolonged melting experiments, has been observed at 550°C, probably close to the temperature at which ancient metalsmiths remelted lead. At 950°C on the other hand, the ratio remains practically constant, demonstrating that no fractionation takes place under these conditions. Although some fractionation has been observed in the samples removed from the longitudinal axis of cylindrical lead ingots cooled in two different ways, but not to the extent that it could mislead metal provenancing.
The distribution of the chemical elements accompanying lead in ingot casting suggested that if it does take place, fractionation is essentially due to the laws of gravity and to the density in the liquid state.

ACKNOWLEDGEMENTS

This research has been conducted within the framework of the Target Project "Cultural Heritage", funded by the Italian Research Council (CNR). Work group coordinated by Prof. Ulrico Sanna.

REFERENCES

[1] N.H.Gale, The isotopic composition of tin in some ancient metals and the recycling problem in metal provenancing, Archaeometry, 39, 1,1997, pp.71-82.
[2] S.M.M.Young,.P.Budd, R.Haggerty, and A.M.Pollard, Inductively coupled Plasma-Mass Spectrometry for the analysis of ancient metals, Archaeometry, 39, 2, 1997, pp.379-392.
[3] A.M.Ghazi, Lead in archaeological samples: an isotopic study by ICP-MS, Applied Geochemistry,. 9, 1994, pp. 627-636.
[4] I.L.Barnes, W.R.Shields, T.J.Murphy, and R.H.Brill, Isotopic Analysis of Laurion Lead Ores, Archaeological Chemistry, Hrsg, C.W. Beck, American Chem. Soc., 1974, pp. 1-10.
[5] P.Budd, D.Gale, A.M.Pollard, R.G.Thomas, and P.A.Williams, Evaluating lead isotope data: Further observations, Archaeometry, 5, 2, 1993, pp. 241-247.
[6] S.Chalkias, M.Vavelidis, S.Schmitt-Strecker, and F.Begemann, Geologisch interpretation der bleiIsotopen-verhältnisse von Erzen der Insel Thasos, der Ägäis und Nordgriechenlands, in Antike Edel- und Buntmetallgewinnung auf Thasos. Eds. G.A. Wagner and G. Weisgerber, Suppl. 6, 1988, pp. 59-74.
[7] N.H.Gale and Z.A.Stos-Gale, Oxhide ingots from Sardinia, Crete and Cyprus and the Bronze Age Copper Trade: New Scientific Evidence, in Studies in Sardinian Archaeology, Ed. Balmuth, III, B.A.R., 1987, pp. 135-176.
[8] E.V.Sayre, K.A.Yener, E.C.Joel, and I.L.Barnes, Statistical evaluation of the presently accumulated lead isotope data from Anatolia and surrounding regions, Archaeometry , 34, 1, 1992, pp. 73-105.
[9] Z.A.Stos-Gale and N.H.Gale, New Light on the provenience of the Copper Oxhide Ingots found on Sardinia, Sardinia in the Mediterranean., Sheffield Academic Press, 1992, pp. 317-341.
[10] Z.Stos-Gale, N.H. Gale, J.Houghton and R.Speakman, Lead isotope data from the isotrace laboratory, Oxford: Archaeometry Data Base 1, Ores from the Western Mediterranean, Archaeometry , 37, 2, 1995, pp. 407-415.
[11] Z.Stos-Gale, N.H.Gale and N.Annetts, Lead isotope data from the isotrace laboratory, Oxford: Archaeometry Data Base 3, Ores from the Aegean, part 1, Archaeometry , 38, 2, 1996, pp. 381-390.
[12] Z.Stos-Gale, N.H.Gale and N.Annetts, Lead isotope data from the isotrace Laboratory, Oxford: Archaeometry Data Base 3, Ores from Cyprus, Archaeometry , 39, 1, 1997, pp. 237-246.
[13] M.Vavelidis, I.Bassiakos, F.Begemann, K.Patriarcheas, E.Pernicka, S.Schmitt-Strecker and G.A.Wagner, Geologie und erzvorkommen der insel sifnos, in Silber. Blei und Gold auf Sifnos. Prähistorische und antike Metallproduktion., Eds..G.A. Wagner and G. Weisgerber, Suppl.3, 1985, pp. 45-81.
[14] I.L. Barnes, J.W. Gramlich, M.G. Diazand and R.H Brill, The possible change of lead isotope ratios in the manufacture of pPigments: A Fractionation Experiment, Archaeological Chemistry IV, G.F. Carter Editor, Advances in Chemistry series 171, American Chemical Society, 1978, pp. 273-277.
[15] P.Budd, A.M. Pollard, B. Scaife, and R.G. Thomas, The possible fractionation of lead isotopes in ancient metallurgical processes, Archaeometry, 37, 1, 1995, pp. 143-150.
[16] A.Jr.Arribas and R.M. Tosdal, Isotopic composition of Pb in ore deposits of the Betic Cordillera, Spain: Origin and relationship to the other european deposits, Economic Geology, 89, 1994, pp. 1074-1093.
[17] M. Boni and V. Koeppel, Ore-lead isotope pattern from the Iglesiente-Sulcis area (SW Sardinia) and the problem of remobilization of metals, Mineralium Deposita, 20, 1985, pp. 185-193.
[18] C.Caron, J.Lancelot and J.J.Orgeval, Hétérogénéités isotopiques du plomb dans les amas sulfurés à encaissant carbonaté Cambrien inférieur de l'Iglesiente (Sud-Ouest Sardaigne): effets de mélange entre sources crustales diffé-

renciées, C.R. Acad. Sci. Paris, t. 317, Sèrie II, 1997, pp.1073-1080
[19] C.Caron, J.Lancelot, P.Omenetto and J.J.Orgeval, Role of the Sardic tectonic phase in the metallogenesis of SW Sardinia (Iglesiente): lead isotope evidence, European Journal of Mineralogy, 5, 1997, pp. 1005-1016.
[20] P.Lattanzi, W. Hausmann and V.Koeppel, Preliminary data on the Pb-isotope composition of mineral deposits in southern Tuscany, Italy, in Source, Transport and Deposition of Metals, M. Pagel and L. Levoy, 25 years SGA Anniv Mtg, Balkema, 1991, pp. 317-320.
[21] K.R.Ludwig, R.Vollmer, B.Turi, K.R.Simmons and G.Perna, Isotopic constraints on the genesis of base-metal ores in southern and central Sardinia, Eur. J. Mineral., 1, 1989, pp. 657-666.
[22] I.G.Swainbank, T.J.Shepherd, R.Caboi and R.Massoli-Novelli, Lead isotopic composition of some galena ores from Sardinia, Periodico di Mineralogia., Roma, Anno 51, 1982, pp. 275-286.

ABSTRACT

VALUTAZIONE SPERIMENTALE E RILEVANZA ARCHEOMETRICA DEL FRAZIONAMENTO ISOTOPICO E CHIMICO IN OPERAZIONI DELLA METALLURGIA DEL PIOMBO

La determinazione dei rapporti isotopici del piombo, tramite ICP-MS o TI-MS [1-3] si sta rivelando uno dei metodi più promettenti per riconoscere l'area mineraria (o persino, nei casi più favorevoli, il singolo giacimento di una regione mineraria) dalla quale deriva la materia prima impiegata per la realizzazione dei manufatti metallici (in piombo, argento, rame o bronzo). Particolarmente intenso è il lavoro di ricerca ed il dibattito concernente la preistoria del Mediterraneo [4-13] Due sono i principali fattori alla base della affidabilità di questo metodo:

- *l'esistenza di un set di rapporti isotopici del piombo ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ e $^{206}Pb/^{204}Pb$) sufficientemente costante e distintivo tra le diverse aree minerarie (ed eventualmente anche tra singoli giacimenti);*
- *la conservazione dei rapporti isotopici originari nel corso delle operazioni metallurgiche: smelting, melting e re-melting.*

La presente comunicazione intende fornire un contributo riguardo la conoscenza di questo secondo fattore. Sono infatti presenti in letteratura alcune valutazioni decisamente discordanti riguardo alla significatività di eventuali modificazioni indotte dalle operazioni metallurgiche sul set dei rapporti isotopici del piombo. Ad esempio, mentre Barnes[14] escludeva che nelle operazioni di passaggio dalla galena al piombo metallico e da questo all'ossido impiegabile come pigmento vi fossero modificazioni dei rapporti isotopici, entro i limiti dell'errore sperimentale, più recentemente Budd [15] ritiene, sulla base di alcune considerazioni teoriche, che queste modificazioni siano viceversa apprezzabili, soprattutto considerando quelle lavorazioni nelle quali ritiene che il metallo sia soggetto ad intensa vaporizzazione. Problemi analoghi sono stati recentemente affrontati da Gale [2] per quanto concerne alcuni aspetti della metallurgia dello stagno.

Per fornire un contributo a dirimere questi problemi, in questo lavoro sono state eseguite determinazioni di rapporti isotopici su campioni di piombo prelevati nel corso delle seguenti operazioni simulate in laboratorio:

- *l'operazione di smelting e quindi il passaggio da galena a piombo metallico;*
- *la rifusione del piombo metallico in condizioni di corrente di aria e quindi di forte perdita per evaporazione*
- *il getto in lingotti, con l'eventuale segregazione.*

Le dimensioni dei lingotti sono state: altezza 95 mm e diametro 13 mm. I lingotti sono stati campionati lungo l'asse longitudinale a tre altezze: fondo, metà altezza e sommità. I campioni così ottenuti sono stati analizzati tramite ICP-MS per la determinazione dei rapporti isotopici e degli elementi chimici: Ni, Cu, Zn, As, Ag, Cd, Sn, Sb, Te, Cs, Tl, Bi.

Le condizioni operative e di acquisizione dati sono riportate in tabella 1

Le operazioni di smelting sono state condotte su un campione di galena della miniera di Montevecchio, uno dei centri tradizionali e più antichi della attività estrattiva della Sardegna, che attualmente risulta essere ben caratterizzata da diversi ricercatori, quanto a rapporti isotopici del piombo. La tabella 3 riporta i rapporti isotopici ottenuti nel corso di questa sperimentazione e quelli del campione di piombo metallico ottenuto nel corso della operazione di smelting condotta in laboratorio.

I dati sulla galena confermano ulteriormente la caratteristica isotopica di questo giacimento. Il passaggio galena → piombo non risulta avere comportato modificazioni tali da far insorgere dubbi sulla provenienza del minerale, perlomeno per quanto riguarda l'ambito regionale, come può constatarsi considerando i dati riportati nella tabella 4.

Il fenomeno della eventuale modificazione dei rapporti isotopici durante fusione prolungata di metallo è stato convenientemente studiato alle temperature di 550 e 950°C. Le perdite in peso registrate alla fine del tempo di trattamento sono risultate, rispettivamente, del 7% e del 2%. I risultati ottenuti sono riportati nella tabella 5, mentre la fig.1 riporta l'andamento del rapporto tra gli isotopi 208 e 204, caratterizzati dalla maggiore differenza di massa, e quindi assimilabile ad indice dell'eventuale frazionamento.

Anche in questo caso è quindi possibile riscontrare che le modificazioni indotte sul set dei valori caratterizzanti la composizione isotopica del metallo sono del tutto irrilevanti per quanto concerne la valutazione della sua origine

Per quanto concerne le differenze riscontrabili sui campioni prelevati lungo l'asse longitudinale di un lingotto cilindrico, si sono riscontrati i risultati riportati nella tabella 6. Si constata che le variazioni non sono mai di entità tale da alterare una aggiudicazione di provenienza.

La tabella 7 riporta la composizione chimica degli elementi presenti in tenore > 10 ppm, da campioni prelevati lungo l'asse longitudinale del lingotto raffreddato lentamente. È riportata anche la variazione percentuale assunta pari a 100 il valore della parte alta, ed alcuni dati fisici rilevanti per la discussione. Il peso atomico medio del piombo è 207.2, mentre la sua densità allo stato liquido è 10.7 g/cm^3 a 327 °C e 10.1 g/cm^3 a 80°C. È evidente che gli elementi chimici che presentano peso atomico e densità prossimi a quelli del piombo (Tl e Bi) non sono soggetti ad alcun fenomeno di segregazione gravitativa. Solo gli elementi decisamente più leggeri del piombo (Ni, Cu, e Ag) sono soggetti a significative variazioni di concentrazione, con arricchimento nella parte alta del lingotto e conseguente impoverimento in quella bassa. L'Sb è invece soggetto ad un netto frazionamento in quanto pur avendo un peso specifico relativamente alto ha comunque un valore piuttosto basso della densità allo stato liquido.

Questi dati, oltre all'evidente interesse connesso alla corretta interpretazione dei dati analitici di campioni necessariamente limitati che è ordinariamente possibile prelevare dai reperti archeologici, supportano ulteriormente la conclusione che un frazionamento basato sulle lievi differenze di massa associabili ai differenti isotopi del piombo è da ritenersi non rilevante ai fini della associazione di reperti di questo genere con la fonte della galena.