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Technical Note

X-Ray Fluorescence and Laser-Induced Breakdown Spectroscopy analysis of Roman silver denarii

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ABSTRACT

In this paper we present the results of a study performed on a large collection of silver Roman republican denarii, encompassing about two centuries of history. The joint use of Laser-Induced Breakdown Spectroscopy (LIBS) and X-Ray Fluorescence (XRF) spectroscopy allowed for an accurate determination of the coins' elemental composition; the measurements, performed mostly in situ at the 'Monetiere' in Florence, revealed a striking connection between the 'quality' of the silver alloy and some crucial contemporary events. This finding was used to classify a group of denarii whose dating was otherwise impossible. The comparison with other contemporary denarii disproves a recent theory on the origin of the so called 'serrated' denarii (denarii showing notched chisel marks on the edge of the coin).

1. Introduction

Numismatics is a science encompassing a number of disciplines, starting from Economy to History, Archaeology, Art and, the last but not the least, Metallurgy. The analysis of the metal alloy of the coin can be invaluable for understanding the techniques used for its realization, as well as the effect that time and the environment produced on it. Moreover, although indirectly, dating of the specimen can be done and an indication of its origin could be given, through the study of the bulk metal and the corrosion patina.

A metallurgic analysis of ancient coins could give a sound basis for historical, archeological and numismatic studies. At the present time, a non-destructive analysis on coin patina and bulk is extremely challenging. A number of well assessed non-destructive techniques, such as X-Ray Fluorescence (XRF) [1–4] and micro-Raman analysis [5], can be used for characterizing the surface of the coin, while in depth analysis can be performed using other techniques, such as Laser-Induced Breakdown Spectroscopy (LIBS) [6,7]; however, LIBS is micro-destructive since a small amount of the material is removed, under the effect of the laser. The great majority of studies published up to now, however, are based on destructive methods that are obviously unacceptable for the analysis of numismatically valuable coins.

Most of the applications reported in the literature for the elemental analysis of ancient metals refer to laboratory measurements, which in general employ the transfer of the object to the laboratory and/or sampling. This procedure may have important disadvantages: depending on the circumstances, the artistic relevance of the object may forbid sampling, as well as its fragility and/or its dimensions may forbid transportation. The use of portable, instrumentation for in situ micro-analysis appears the most straightforward solution to the above-mentioned problems. In particular, the joint use of portable XRF and LIBS instrumentation has already been demonstrated as a particularly effective approach to the analysis of ancient artifacts [8]. In fact, it is well known that the presence of surface deterioration layers affects XRF measurements and prevents a reliable achievement of the bulk composition [4]. Although LIBS measurements of the bulk composition are possible, deeply corroded objects may require protract ablation to reach the bulk, which would result in greater damage to the piece. Thus it is important to devise a method that would be benefitted by both the intrinsic non-destructivity of the XRF technique, and by the capability of LIBS performing true bulk composition measurements even in the presence of heavy surface

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deterioration. The results presented in this communication will show that through a careful cross-validation of the two techniques, significant information can be gathered with respect to such aspects as fabrication context and technology, and deterioration mechanisms of archeological and historical metals, guaranteeing at the same time a substantial reduction of the overall number of ablations. Consequently, the impact on the piece is reduced as well.

2. Experimental setup

The LIBS measurements were performed using the Modì Smart spectrometer developed by the Applied Laser Spectroscopy Laboratory at CNR in Pisa, in collaboration with Marwan Technology s.r.l. [9]. Modì is a transportable LIBS instrument, already widely tested for in-situ analysis of art and archeological objects. It has a double-pulse collinear Nd:YAG laser, emitting at a wavelength of 1064 nm and is able to deliver on the target up to 80 mJ per pulse (8 ns FWHM) at a maximum repetition rate of 10 Hz. The short term pulse-to-pulse stability of the laser energy is ±4%, with a long term drift<5%. The laser beam was focused on the target by a f=150 mm converging lens; the plasma emission was collected by an optical fiber, placed at a 45 degree angle 1 cm from the laser spot on the surface. In the 'Smart' Modì model, the fiber conveys the optical signal to a dual-channel broadband Avantes mini-spectrometer, covering the spectral range between 200 and 900 nm with a resolution of 0.1 nm in the range 200–430 nm and 0.3 nm from 430 to 900 nm. The LIBS spectrum acquisition was triggered 2 μs after the second laser pulse; the acquisition time was about 2 ms. The LIBS spectra were finally analyzed with the proprietary LIBS++ software, which allowed for the automatic identification of the elements in the sample and their quantification [10].

The XRF measurements were carried out using a highly performing portable device developed at the Institute for Technologies Applied to Cultural Heritage of CNR [11]. The system is equipped with an X-ray tube, working at 60 kV, 1.5 mA (though not essential in the present work, the system is therefore capable of efficient excitation of the K-lines of Ag); the detector is a Si-Drift produced by Ketek (area=10 mm^2, thickness=450 μm, FWHM=165 eV at 5.9 keV) and the spot diameter at the measurement point is about 2 mm. A set of 9 standard Ag–Cu–Au alloys was used to calibrate the system; the mean relative deviation between measured and nominal compositions $(C_{meas}-C_{nom})/C_{nom}$ is 13% for Cu and 11% for Au, whereas estimated detection limit, calculated with the single standard method, is 0.06% for Cu K_α and 0.04 for Au L_α; detection limit for Pb L_α is assumed in the same range. Quantitation was carried out by the fundamental parameter software package PyMCA [12], using the K-lines of Cu and Ag and the L-lines of Pb.

The measurements were performed mostly at the Monetiere of the Archaeological Museum in Florence, which hosts one of the largest collections of ancient coins in Europe, including many republican denarii.

3. Results and discussion

The measurements were performed on more than 100 republican denarii, issued in a time span encompassing about two centuries of Roman history. The debate about the date of issuing of the first Roman denarius is still a controversial issue among numismatics [13–15]; according to several authors, the denarius was first introduced in the year 211 BC, after the sack of Syracuse which made a large amount of silver available to the Roman republic. The republican denarius was issued from that date to the end of the republic, which is conventionally related to the battle of Actium (31 BC), which brought the defeat of Mark Antony and Cleopatra and the beginning of the Principate of Octavian Augustus. During these years, the weight and value of the republican denarius changed several times; however, it is widely believed that the silver alloy of the denarius was always maintained at silver concentrations higher than 95% in weight, with the exception of the late Mark Antony 'legionary' denarii which were coined on debased silver flans during the civil war against Octavian. To the best of our knowledge, no systematic metallurgic studies were performed on a statistically significant number of republican denarii for assessing their 'quality' in the course of those years. The use of portable instrumentation for in situ micro-analysis, in conjunction with the availability of a large number of republican coins at the Monetiere in Florence, allowed us to test a statistically significant sample of coins, determining precisely their elemental composition and, for the first time, correlating the silver content of the coins with important historical events. The demonstration that critical political or military situations would have justified the issuing of coins with intrinsically lower value (because of the lower silver content) is particularly important since it could help in dating, although indirectly, coins which would not be possible to date otherwise. Such an example can be given in the case of the Mark Antony 'legionary' denarii.

The first measurements performed were aimed at cross-validating the LIBS and XRF results. In recent years, the authors of this communication developed an experimental strategy involving the joint use of XRF and LIBS [8]. Both these techniques are characterized by the easy transportability of the instrumentation and their ability to provide quantitative analytical information in very short measurement times. However, in the presence of heavily corroded surfaces – quite common in bronze archeological artifacts, for example – it has been pointed out that such quantitative information may not coincide with the bulk composition that, in principle, is what one is looking for. In the case of silver coins, the use of surface information for deducing bulk composition has led in the past to incorrect deductions, as in the case of Roman 'Antoniniani' (debased silver coins which were treated to develop a thin silver-enriched layer at the surface). Well assessed theories on the process leading to the silver surface enrichment of those coins, based on the early XRF results obtained by Walker [16] in the seventies, are now being challenged by new, in depth analysis [17].

To determine the capability of XRF analysis for the determination of the bulk composition of the silver coins under analysis, we selected a limited – although significant – set of coins on which we performed in depth LIBS analysis. The coins were selected to be representative of the different conservation status and colors of the patina of the whole set of denarii. The energy of the laser and the number of laser shots on the same spots were chosen with the aim of obtaining a readable LIBS spectrum of the silver flan under the patina and, at the same time, avoiding the formation of a large crater at the coin surface. It turned out that three double pulses with an energy of 50 mJ each were able to pass through the surface patina with very limited damage to the surface of the coin. The diameter of the laser-induced microcrater on the coin surface was around 200 μm and the depth, estimated from optical microscopy, was around 4 μm (See Fig. 1).

Fig. 3 shows the comparison of the line intensities of the major elements of the alloy (normalized to the background) measured by LIBS with those obtained with XRF for the same elements. In order to minimize enrichment, patina and geometry effects, XRF data were obtained by averaging two measurements carried out on the most worn out areas of each side of the coin.

The close correlation found between the LIBS and XRF results (R=0.96 for Cu and R=0.98 for Pb), obtained despite of the different spot sizes (200 μm for LIBS vs 2 mm for XRF) and penetration lengths (the LIBS analysis is performed between 3 and 4 μm under the surface, while the maximum XRF signal comes from the sample surface, down to about 10 μm under the surface) and not considering possible self-absorption effects in LIBS analysis, suggested the possibility of measuring the composition of the rest of the coins using XRF only, in order to avoid even a minimal surface damage produced by the LIBS analysis. Fig. 4 shows the copper percent weight concentration measured by XRF solely on the silver denarii, as a function of the emission date of the coin; again copper concentration results from averaging two measurements

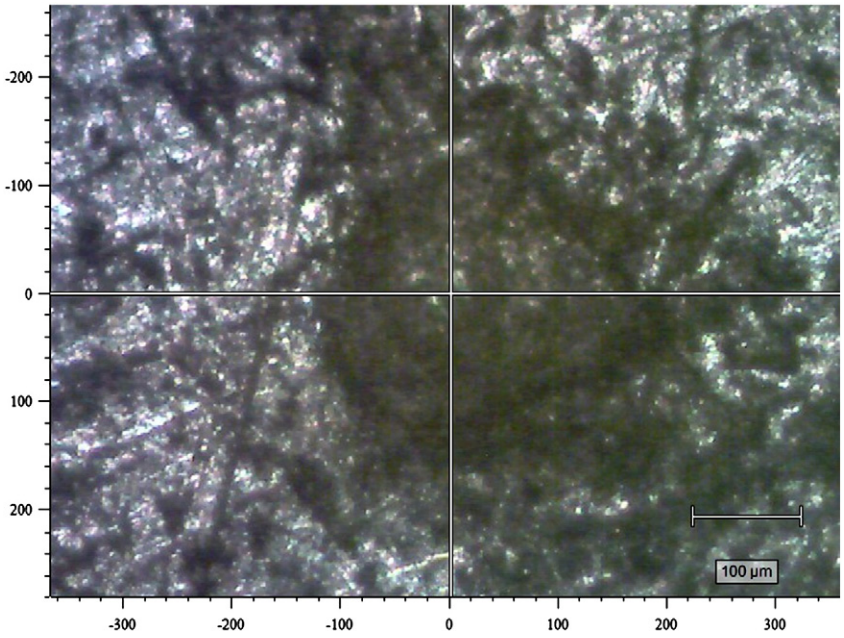

Fig. 1. Laser-induced microcrater at the coin surface. A typical LIBS spectrum of a republican silver denarius is shown in Fig. 2.

carried out on the most worn out areas of each side of the coins. The silver content of the coins can be determined by difference (%Ag ≅ 100% − %Cu, since silver and copper are the main components of the republican denarii, while lead is present in traces); this determination is more precise than the direct measurement of the silver content, since the silver concentration is always larger than 90% in weight and the experimental error in the silver determination (around 10%) is of the same order of the variations to be measured.

Scholars are not unanimous in the dating of the denarii; the chronology proposed by Crawford [14], which is the most assessed at present time, was used in this study.

From Fig. 4, a striking correlation can be seen between the increase in the copper content (and, thus, the reduction of the silver) in the coins, in correspondence with the most critical events in the Roman history of the time (the Jugurthine War, the Social War, the Uprising in Spain with the associated possible shortages of silver supplies, the War against Pompey and, finally, the Civil War between Octavian and Mark Anthony). Moreover, the first 5 denarii considered, issued between 180 and 150 BC according to Crawford [14], should be placed around the year 200 BC according to other scholars, at the time of the Second Punic War [13]. This dating would be concurrent with the fact that the silver content of these coins is, in fact, lower than the average.

The results described could sustain the hypothesis that in time of crisis, the silver content of the denarii would be reduced in order to

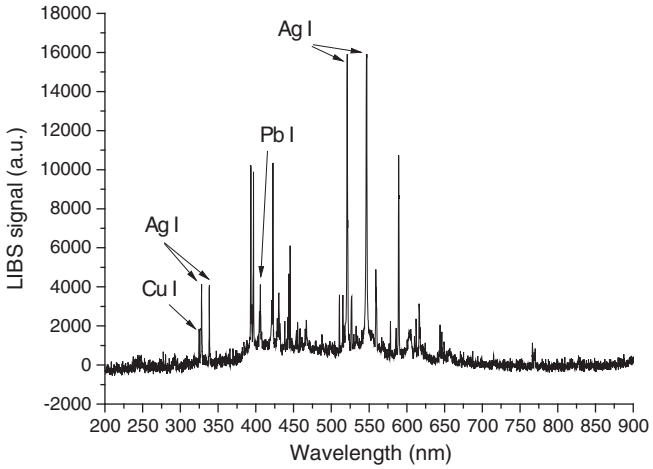

Fig. 2. LIBS spectrum of a republican denarius.

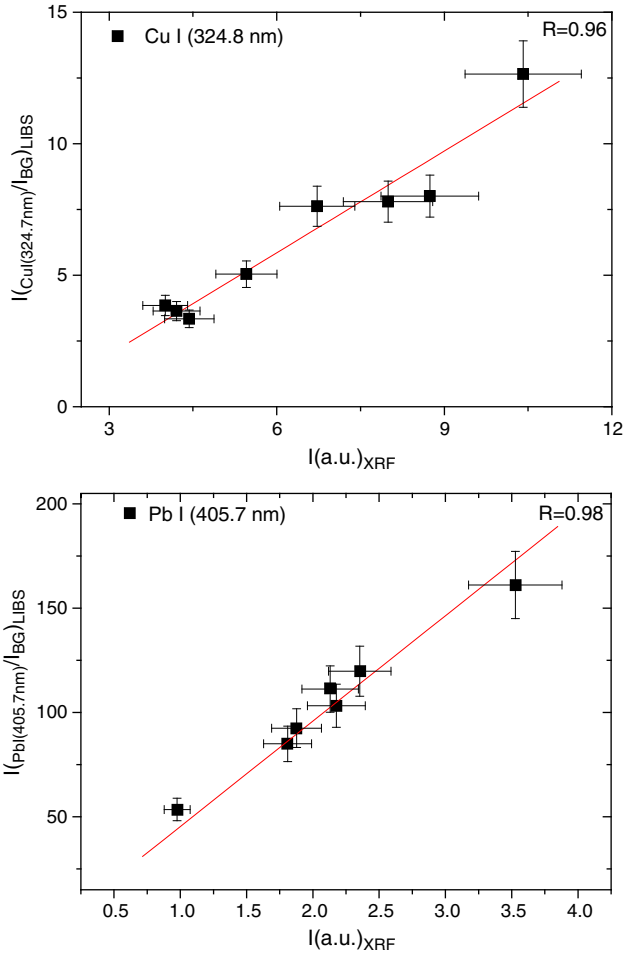

Fig. 3. Correlation between LIBS and XRF signals for copper (left) and lead (right).

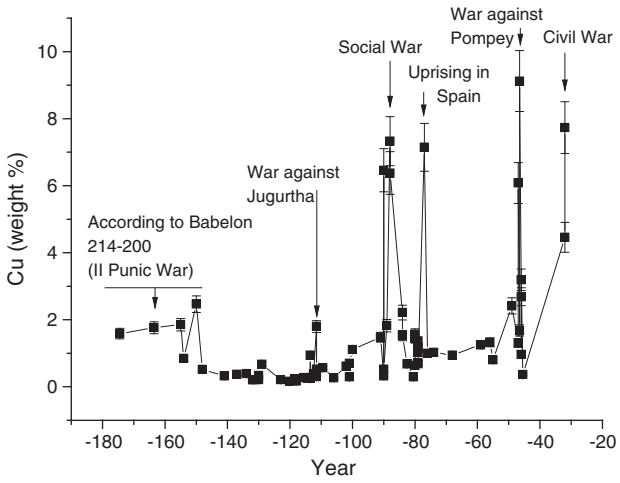

Fig. 4. Time evolution of the copper content in silver denarii.

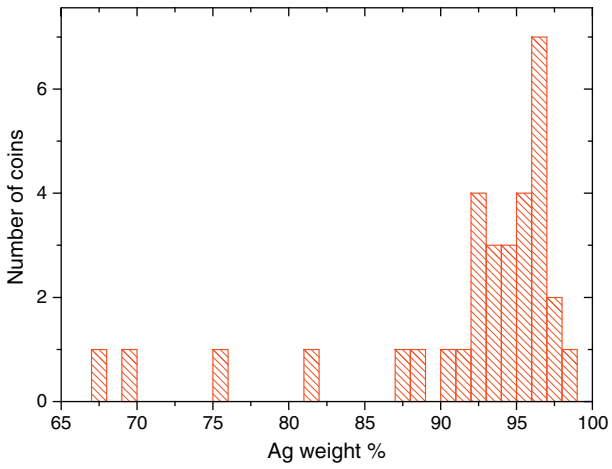

Fig. 6. Histogram of the silver content in the denarii analyzed (weight percent).

save on the coin value that, at the time, coincided with the value of the precious metal in the alloy.

3.1. The Mark Antony 'legionary' denarii

If the previous hypothesis is accepted, it would be possible to suggest a dating for some coins that would be otherwise impossible. This was the case with the Mark Antony 'legionary' denarii. These denarii were issued by Mark Antony during the Civil War against Octavian from 32 to 31 BC and probably coined by a traveling mint following the Mark Antony legions. This is the reason why they are commonly called 'legionary' denarii. They are all identical at the obverse, depicting a Roman galley with the prow on the right and standards on the mast; the legend reads ANT AVG III VIR R P C (*Antonius augur triumvir reipublicae constituendae*). The reverse was very similar, too, showing the legionary eagle between two standards and the number (in four cases the full names) of the legion to be paid (see Fig. 5).

From a stylistic point of view, it is impossible to distinguish a legionary denarius issued at the beginning of the war (32 BC) from the same denarius issued at its end (31 BC), so that these denarii are always dated 32/31 BC. However, the analysis performed on 35 'legionary' coins clearly shows the distinction between the regular denarii – probably issued at the beginning of the war – and the denarii with much lower silver content, probably issued when the fate of the war was already against Mark Antony and Cleopatra.

In fact, the measurement of the composition of the legionary denarii revealed that most of them had a silver content corresponding to about 95% in weight, a value compatible with the war-time situation in which they were issued [18]. However, about 10% of the coins analyzed showed a silver content lower than 85%, with a minimum silver content of around 65% (see Fig. 6). It is reasonable to hypothesize that these coins were issued in the last months of the war, when the Mark Antony silver supplies were probably near the end.

3.2. The serrated denarii

The *serrati* were denarii whose edge was regularly notched resembling the teeth of a saw, from which came the name (*serra*, in Latin, means *saw*). One of the serrated denarii analyzed in this work is shown in Fig. 7.

From a technological standpoint, it is quite certain that the notches were produced by vertically striking the flan edge before the actual coinage [19]; however, at the present time, the true reason for doing that is not yet fully known. The most accepted theory is that the serration of the denarii was an anti-counterfeit measure, to show the inner part of the coin and thus avoiding the possible circulation of silver-plated fake coins (known as *suberati*) [20]. There are, however, a number of convincing arguments against this theory; Bahrfeldt [21] and Crawford [14], for example, maintained that the serration of the denarii had a merely esthetic value, starting from the consideration that in Greek coinage several bronze coins were actually serrated. Obviously, there was no reason of applying an anti-counterfeit measure for a bronze coin. However, the Greek serrated coins were stricken on blanks already prepared in the serrated form, while the Roman *serrati* were produced by hand, one by one. In most cases the dents are irregularly spaced and with variable depth, giving an esthetic result which was not completely satisfactory. Among the different hypotheses, a recently proposed theory by De Caro and Ingo [22,23] seems to be particularly interesting. This theory is based on metallurgic considerations and, therefore, it can be maintained or disproved by further analysis. De Caro's and Ingo's idea is that the serration of the blank was introduced

Fig. 5. The Mark Antony 'legionary' denarius (Legio V).

Fig. 7. One of the 12 serrated denarii analyzed (Gens Papia, Crawford 384/1).

Table 1
The serrated denarii analyzed in this study.

Moneyer	Classification [13]	Year	Cu (mass%)	Pb (mass%)
L. Pomponius Cnaeii filius	Crawford 282/4	118 BC	0.2 ± 0.2	0.2 ± 0.2
L. Cornelius Scipio Asiagenus	Crawford 311/1	106 BC	0.3 ± 0.2	0.5 ± 0.2
Q. Antonius Balbus	Crawford 364/1	83/82 BC	0.7 ± 0.2	0.4 ± 0.2
L. Procilius	Crawford 379/2	80 BC	0.6 ± 0.2	0.3 ± 0.2
Ti. Claudius Nero	Crawford 383/1	79 BC	1.2 ± 0.2	0.5 ± 0.2
Ti. Claudius Nero	Crawford 383/1	79 BC	1.0 ± 0.2	0.6 ± 0.2
L. Papius	Crawford 384/1	79 BC	1.1 ± 0.2	0.9 ± 0.2
L. Papius	Crawford 384/1	79 BC	0.7 ± 0.2	0.9 ± 0.2
L. Papius	Crawford 384/1	79 BC	1.4 ± 0.2	0.8 ± 0.2
Cn. Naevius Balbus	Crawford 382/1b	79 BC	0.7 ± 0.2	0.7 ± 0.2
Cn. Hosidius Geta	Crawford 407/1	68 BC	0.9 ± 0.2	0.2 ± 0.2
L. Roscius Fabatus	Crawford 412/1	59 BC	1.3 ± 0.2	0.7 ± 0.2

to improve the mechanical resistance of the flan when a nearly pure silver alloy, intrinsically brittle due to the presence of lead, was used. The authors based their theory on the analysis of four serrated denarii; unfortunately, the authors did not mention in their paper which kind of serrated denarii were analyzed, so that a direct comparison with our results was impossible. However, our measurements on 12 serrated denarii (see Table 1) showed that the Cu concentration of the *serrati* was very similar to that of the coeval denarii, and in most of the cases this concentration was not negligible (see Fig. 8).

Also the lead concentration of the *serrati* was very similar to the standard denarii and around 0.5/1% in weight (see Fig. 9).

Our measurements, therefore, do not support the De Caro/Ingo theory. We can then conclude that the true reason for the issuing of serrated denarii, at the present, is still unknown.

4. Conclusion

The results reported demonstrate the possibility of analyzing in short time and in situ a statistically significant number of coins. Useful information can be obtained about the coin composition, both for main components and traces that could be used for classifying the coins in groups, according to different levels of concentrations of the detected elements. This information can be used for dating and authentication. The results obtained suggest the possibility of extending the methodology used for this study to other types of coins.

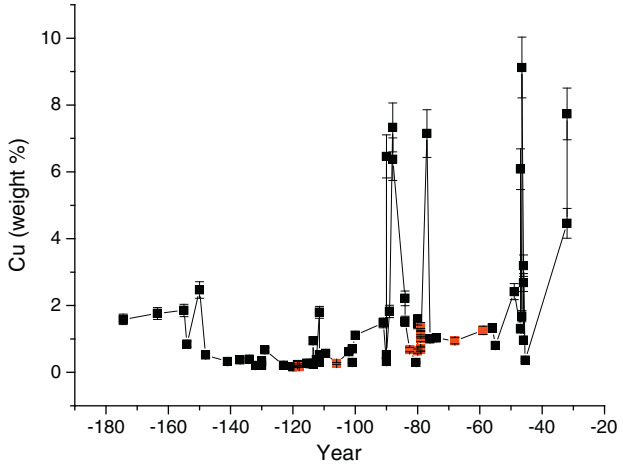

Fig. 8. Time dependence of the Cu mass% content in the serrated denarii considered (in red) compared with the standard denarii (in black).

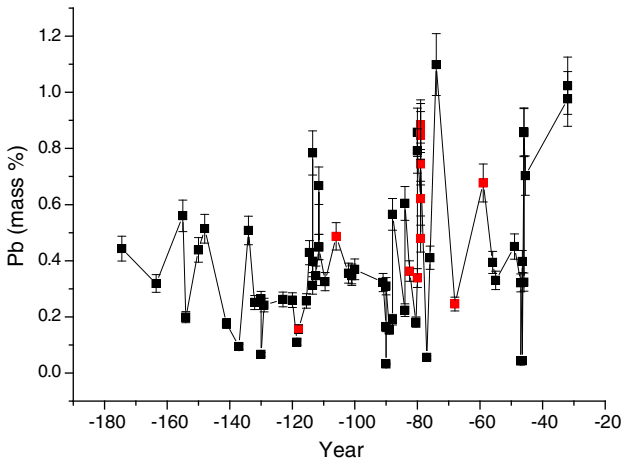

Fig. 9. Time dependence of the Pb mass% content in the serrated denarii considered (in red) compared with the standard denarii (in black).

Acknowledgments

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