Depth profile LA-ICP-MS Analysis of Ancient Gold Coins

Maryse Blet-Lemarquand, Sylvia Nieto-Pelletier, Bernard Gratuze

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Metallurgy in Numismatics 6

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Ancient World Studies in Science, Archaeology and History

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PREFACE

The papers in this volume in part stem from a conference that was conceived and organised by the Australian Centre for Ancient Numismatic Studies (Macquarie University) and the Epigraphical and Numismatic Museum, Athens. The conference, held at the Iliou Melathron in Athens from 20-22 April, 2015, was entitled ‘Mines, Metals and Money in Attica and the Ancient World’. One of its goals was to survey the applications and current state of non-destructive metallurgical analyses in Greek numismatic study. In recent years, progress in these areas has been rapid; and as laboratory instrumentation and techniques have continued to multiply and expand, the topic could not be more timely. The other work that the conference and now this volume addresses is the renewed interest of geologists and archaeologists in further exploiting the evidence on the ground for reconstructing the silver mining and processing industries in Southeastern Attica and Northern Greece. Accompanying these studies are papers from the staff of the Numismatic Museum on the museum’s program of testing new acquisitions and on the study of two hoards excavated in Athens.

Altogether, the articles trace precious metal in the Greek world from the extraction of ore in antiquity to museum artifacts of today. Expanding on previous volumes of the Royal Numismatic Society’s *Metallurgy in Numismatics* series, the present contributions range from numismatic metallurgy in its traditional laboratory context to metallurgy in the broader, historical sense of ancient metal working in general. In what is probably the most significant achievement, a core of the papers present abundant, fresh evidence for the tremendous scale of long-distance trade in silver from a handful of sources in the Aegean to the great number of Greek city-states around the Mediterranean that began to coin in the late archaic period, including even the cities of Southern Italy and Sicily.

While this volume will be welcomed for its many such findings, its value rests also on the editors’ foresight that by inviting these contributions and bringing them together in one place, the studies will become more accessible and prominent than if they had been published separately.

J. H. KROLL

FOREWORD

As Director of the Numismatic Museum at Athens, I am proud of our longstanding numismatic and scientific collaboration with the Australian Centre for Ancient Numismatic Studies (ACANS) at Macquarie University, Sydney. Many Australian researchers, including the two editors of this volume, have spent extensive periods researching at the museum over many years to our mutual benefit. Together we organised the major international conference entitled *Mines, Metal and Money in Attica and the Ancient World* hosted at the museum from 20-22 April, 2015 which formed the genesis of this volume.

The themes of the conference focused on archaic Greek coinage, methods of mining precious metals, and on the historical and institutional framework of the Archaic period in which the conventions for the organisation and control of mining were developed, and through which the commercial distribution of precious metals was carried out. The conference themes also embraced studies of coin production, and technological and research methods for the analysis and conservation of metals that reliably help authenticate ancient coins. In these themes the conference successfully brought together scientists from all over the world.

At the end of the Conference, the temporary exhibition, *When Silver was Born. Archaic Coinage of Athens, Mines, Metals and Coins*, was inaugurated. The exhibition was displayed in the Great Gallery of temporary exhibitions of the Iliou Melathron, the Library of Heinrich Schliemann, on 28 May 2015. It took as its subject the coinage of the Archaic period, an era during which profound changes occurred in politics, the arts, and in society more generally. The exhibition, which was the conclusion of the very fruitful co-operation of our Museum with our colleagues from Australia, exhibited 263 artifacts, most of them for the first time. The objects displayed included acquisitions by Museums and Ephorates of Antiquities, and objects from the Collection of the Alpha Bank. We thank and acknowledge the Alpha Bank for sponsoring the exhibition, and the Australian Research Council of the Australian Government for sponsoring the Conference.

GEORGE KAKAVAS

13. DEPTH PROFILE LA-ICP-MS ANALYSIS OF ANCIENT GOLD COINS

Maryse Blet-Lemarquand, Sylvia Nieto-Pelletier, Bernard Gratuze

ABSTRACT

This paper presents use of the Depth Profile mode coupled with LA-ICP-MS for analysing ancient gold coins. It explains how this mode can improve the characterisation of coins for the following difficult analytical problems: surface gold enrichment, low fineness gold alloys, localised enrichments in platinum and palladium and inclusions of platinum group elements.

INTRODUCTION

LA-ICP-MS (Laser Ablation Inductively coupled Plasma Mass Spectrometry)[1] is an elemental analytical method which has proved its worth for analysis of silver and gold coins.[2] Two or more micro-samplings are taken starting from the surface of the coin using the laser ablation process with diameters so small as to be practically invisible to the naked eye. The elemental composition of these samples is assumed to be representative of the metal worked in the mint, an hypothesis which has to be demonstrated for each alloy.

The Depth Profiling (DP) mode enables determination of the depth composition from the surface to the interior of the coin, and is particularly useful for artefacts that show composition gradients from their surface to their core. It has been studied for multi-layered industrial samples and for depth-heterogeneous minerals (Mason and Mank 2001; Woodhead *et al.* 2008). Its application to cultural heritage artefacts was first tested and validated for silver-copper alloy coins which often present significant silver enrichment on their surface due to a depletion of the copper (Sarah *et al.* 2007; Sarah and Gratuze 2016).[3]

Gold alloy artefacts, including coins, may be enriched in gold on their surface as a result of depletion-gilding processes by goldsmiths done to enhance the gold colour, and also from corrosion developed post deposition.[4] More generally, ancient gold artefacts can sometimes appear to be 'heterogeneous' at the scale of the tiny laser micro-sampling. Our article assesses, from various case studies, how the DP mode can contribute to improve the characterisation of gold coins. It aims to describe the consequences for numismatic studies of the following analytical problems: surface gold enrichment of coins, low fineness gold alloys, localised enrichments in platinum and palladium and inclusions of platinum group elements.

THE DP-LA-ICP-MS METHODOLOGY

LA-ICP-MS presents many advantages for analysing ancient gold coins in order to discuss archaeological, numismatic and historical questions (Dussubieux and van Zelst 2004; Gratuze *et al.* 2004; Blet-Lemarquand *et al.* 2009).[5] The damage left by the laser ablation is virtually invisible to the naked eye as the diameter of the crater is usually tuned to around 80 micrometres (Fig. 1). The contents of a very large number of elements are determined with detection limits reaching the sub-ppm level: gold, silver, copper and the whole set of the trace elements that could characterise these metals can be studied (notably Pb, Bi, Sn, Pt, Pd, etc.). More than 10 coins can be analysed per day and the compositions determined in the course of the analytical session.

[1] For a recent general presentation: Fricker and Günther 2016.
[2] See for instance studies quoted in the last editions of the *Survey of Numismatics Research* (Blet-Lemarquand and Ponting 2009; Blet-Lemarquand and Nieto-Pelletier 2015).
[3] The question of the surface enrichment of ancient silver-copper alloy coins and the impacts of this phenomenon for metallurgical analysis have been much discussed. See especially Ponting 2012; Sarah and Gratuze 2016.
[4] Examples of depletion gildings: Blakelock *et al.* 2016; Bray 1993. On the corrosion of gold alloys: Scott 1983.
[5] Recent review of the constraints when analysing precious metal coins in Blet-Lemarquand *et al* 2014a; recent summary of the difficulties faced when provenance studies of gold objects in Pernicka 2014, 260.

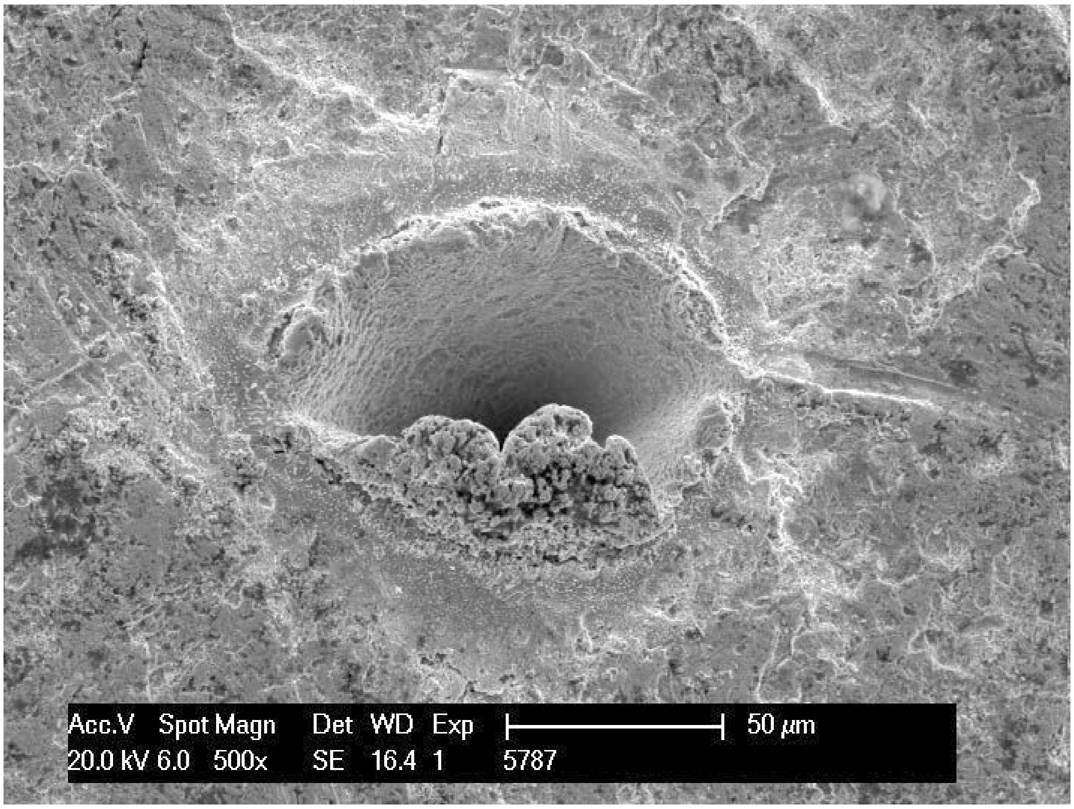

Figure 1. SEM images of laser ablation craters made on prehistoric gold artefacts using the two laser equipment available in the IRAMAT-CEB: (a) Nd:YAG; (b) ArF-excimer. © CNRS IRAMAT-CEB

However, there are challenges to solve that are specific to the analysis of archeomaterials and to the use of LA-ICP-MS on metals. Gold alloy coins and artefacts in general cannot be systematically regarded as homogeneous materials at the scale of micro-sampling mainly because of possible surface enrichment in gold. However, it seems that above 50 atomic percent gold corrosion will be very limited (Scott 1983); this level corresponds to 76 weight% and 65 weight% respectively in binary gold-silver or gold-copper alloys. To solve the problem of corrosion, the gold artefacts are analysed with LA-ICP-MS using the Depth Profiling (DP) mode with a procedure that directly derives from the investigations carried out on silver coins (Sarah *et al.* 2007; Sarah and Gratuze 2016). With this procedure, the transient signal generated from the LA-ICP-MS is recorded each time slice the laser drills down into the sample at one spot. Thus, it is possible to determine variations in the elemental concentration starting at the surface of the coin (see for example Figs. 3, 4 and 6). When the signals plateau, it indicates that intact material is being sampled. This metal, that has neither been deliberately enriched in gold, corroded nor contaminated, reflects the metal worked in the mint to produce the blank, and for which composition is meaningful. Two to three laser ablations are generally carried out on each coin and the compositions are averaged.

The depth of the crater is around 200-250 micrometres after 3,000 laser shots in the operating conditions fixed for the ArF-excimer (Table 1, diameter 80 μm, laser energy 6 mJ, irradiance 0.4 $GW.cm^{-2}$).[6] The crater is cylindrical near the surface and ends with a conical shape at its bottom (Eggins *et al.* 1998). This geometry is consistent with the evolution of the ablation efficiency with depth. It is maximum at first when the laser is started because ablation takes place at the focus point of the laser, and then there is a drop in efficiency with depth as ablation proceeds further away from the focus (Mason and Mank 2001, 1384). The raw transient signal obtained for a gold standard shows a similar evolution (Fig. 2); it is reduced by a factor of five after 3,000 laser shots for the considered analysis. Its decrease with depth has different consequences for the analysis; as the sensitivity decreases with time, the error made on the calculation of the contents increases and finally the detection limits increase. However, this loss of sensitivity does not limit the detection of trace element in ancient gold artefacts. In fact, at the end of this analysis, after 200 or 300 seconds of laser

Table 1. Instrumental parameters for the laser devices and the ICP-MS available at the IRAMAT-CEB. *usual operating conditions

Laser System	*1*	*2*
Laser Type	VG UV Microprobe (*VG Elemental*)	Resolution M-50-E (*Resonetics*)
Lasing source	Nd:YAG	ArF-excimer
Wavelength (nm)	266	193
Output energy (mJ)	4	240
Ablation rate (Hz)	1-10; 6-8*	1-300; 6-8*
Pulse duration (ns)	3-5	6-8
Laser spot diameter (μm)	About 30; 60; 90; 200	2-100; 80*
Ablation cells	*VG* cell + in-house cells designed for big objects	S-155 (*Laurin Technic*) + in-house cells designed for big objects
Carrier gas	Ar	Mixing of Ar and He or Ar
ICP-MS type	Element XR (*Thermo Fisher*)	
RF forward power (W)	1,350	
Sampling cone (mm)	1.0 Ni	
Skimmer cone (mm)	0.7 Ni	
Detector	Faraday Cup + Secondary Electron Multiplier	

[6] The laser ablation efficiency depends on many parameters (composition and microstructure of the metal, focus of the laser beam, power density...) that can change in the course of the ablation realized at one spot and from an analytical session to another. The rate of ablation per laser pulse is ranging from 0.1 to 2 micrometres (Mason and Mank 2001).

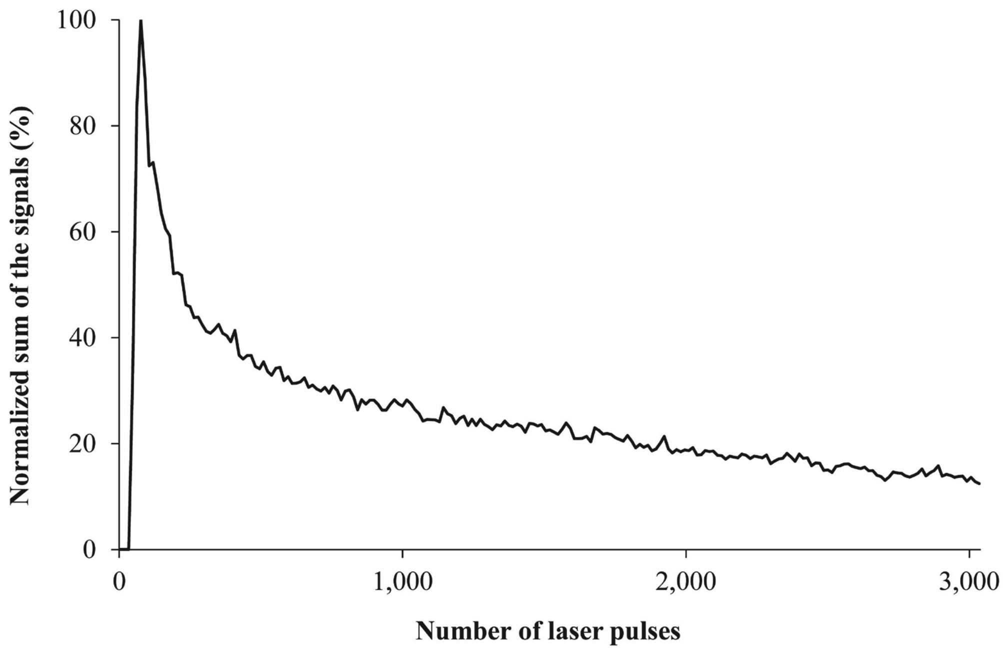

Figure 2. Normalised LA-ICP-MS response of laser ablation of the certified reference gold material RAuP7. Average of 4 analyses carried out in the course of an analytical session. Normalisation to the highest signal. ArF-excimer laser. Laser spot diameter fixed at 80 micrometres.

Table 2. Sensitivity of the DP-LA-ICP-MS calculated for the main trace elements in ancient gold from the analysis of the certified reference gold material RAuP7.

Isotope	Zn66	Rh103	Pd108	Sb121	Pt195	Pb208	Bi209
Isotopic abundance	28%	100%	27%	57%	34%	52%	100%
Element	**Zn**	**Rh**	**Pd**	**Sb**	**Pt**	**Pb**	**Bi**
Background (counts rates)	180	52	20	214	0	305	134
Time of laser ablation (s) / Number of laser pulses for 1 ppm of element	**Net intensity counts rates corrected for isotopic abundance**						
	Zn	**Rh**	**Pd**	**Sb**	**Pt**	**Pb**	**Bi**
3 / 29	20,219	5,814	6,955	7,008	6,221	14,343	10,603
50 / 505	2,441	2,457	2,872	2,907	2,329	3,724	3,800
100 / 996	1,898	2,236	2,411	2,457	1,774	3,138	3,385
201 / 2,006	1,221	1,794	1,798	1,772	1,432	2,488	2,026
297 / 2,972	890	1,128	920	1,038	908	1,402	1,435

ablation (shots), the net intensity counts rates for 1 ppm are ranging from 1,000 to 1,500 for the main trace elements, and the corresponding background intensities are less than 300 counts (Table 2).

Previous studies have investigated different parameters in order to achieve maximum depth resolution (Mason and Mank 2001). They came to the conclusion that a small depth/diameter ratio for the ablation crater was the best for determining the composition of thick layers in multi-layered samples. In other words this would correspond to a wide but shallow ablation crater. However, other parameters have to be taken into account for analysing ancient gold artefacts. We have on the one hand to limit the diameter of the crater ablation for conservation purposes, and on the other hand we wish to reach the deepest zone possible when analysing low gold content coins (see below application on Late Celtic coins). A compromise has to be made between all these constraints. The depth resolution reached with 80 micrometre wide craters that are as deep as possible seems sufficient for our studies. It allows in nearly all the cases to reach a plateau of stable composition showing good reproducibility for a minimum of two micro-samplings carried out at different places on the artefacts.

Elemental fractionation is a problem ruled by many parameters peculiar to metals (Cromwell and Arrowsmith 1995; Russo *et al.* 2002; Dussubieux 2016). It concerns metals having a low melting point (e.g. Pb and Zn) when they are present in large quantities. This may cause their preferential volatilisation during ablation, leading to non-representative subsampling. Standardisation with matrix-matched standards is an efficient solution to correct this problem in brass (Flament 2017). Elemental fractionation does not happen for ancient gold artefacts analysed with our analytical conditions (table 1) mainly because both lead and zinc are only present at low levels.[7]

The signals yielded by the LA-ICP-MS are standardised using matrix-matched standards that are analysed several times during each analytical session. Some of these standards are certified reference materials: high purity gold doped with trace elements at the 100-200 ppm or 15-30 ppm concentration levels (RAuP3 and RAuP7, Rand Refinery Ltd, South Africa) and standards made for XRF analysis (Comptoir Lyon-Alemand, Louyot et Cie, France). Others are in-house standards: Au-Ag-Cu alloys doped or not with tin and lead which were manufactured at our request, or ancient gold coins previously analysed by other methods.[8] The calculation procedure normalises the sum of the elemental contents to 100 weight%, and derives from the procedure previously developed for archaeological glass samples (Gratuze 2016). This standardisation procedure and the LA-ICP-MS analysis of gold as a whole were validated comparing the results obtained for different types of gold coins with their compositions obtained performing PAA (Blet-Lemarquand *et al.* 2009; Blet-Lemarquand *et al.* 2014a; Blet-Lemarquand *et al.* 2015).

HETEROGENEITIES IN ANTIQUE GOLD COINS

Gold enrichment of the surface

Some coins made of gold-silver binary alloys show strong enrichment of gold on their surface.[9] An antique Greek coin from Boeotia provides a typical example (Fig. 3).[10] Its worn reliefs are whitish while the rest of the surface is golden. The DP-LA-ICP-MS analysis shows that the surface is heavily enriched in gold to the detriment of silver and copper compared with the alloy beneath the surface. The gold content is about 90 % at the surface of the coin, then it decreases rapidly and stabilises at about 61 % after 40 seconds of laser shots. It is assumed that the composition is then representative of the inner part of the coin. In parallel, the silver concentration increases from the surface to about 37 % in the original alloy. The thin golden layer[11] of this coin results from metallurgical treatments carried out to disguise the low fineness of the gold alloy. The DP mode informs us about the enrichment and yields the compositions in major, minor and trace elements of the original alloy.

[7] Elemental analysis carried out for years on gold coins dating back from the antiquity to the modern period at the IRAMAT-CEB gives us an overview of the compositions. 0.1 % appears to be a maximum for the zinc contents in gold coins (see especially Merovingian gold coins: Blet-Lemarquand *et al.* 2010). Lead concentrations depend mostly on the proportion of silver added to debase gold. They can reach 0.3 % (see Celtic coins: Barrandon *et al.* 1994 and Byzantine coins: Morrisson *et al.* 1985).

[8] ICP-MS in liquid mode: Dussubieux and van Zelst 2004; PAA (Proton activation analysis): Gratuze *et al.* 2004; cupellation, ICP-OES.

[9] Examples of surface gold-enriched coins: Lehrberger and Raub 1995; Gruel *et al.* 2010; Araújo *et al.* 1993; Beck *et al.* 1991; Travaini 1998; Blet-Lemarquand *et al.* 2010; Artru 2015.

[10] FG 635, MMA BnF http://catalogue.bnf.fr/ark:/12148/cb418141891. This coin has been analysed in the framework of the AUREUS research project funded by the French Région Centre-Val de Loire. We owe a special thanks to Arnaud Suspène and Benjamin Gehres for allowing us to use this analysis.

[11] Fig. 3 shows that it took 44 seconds (352 laser shots) for the Au signal to decrease from 61 % to 30 %. This delay depends not only on the thickness of the golden layer but also on the aerosol washout time. This parameter is about 20 seconds for the S-155 cell used to analyse this coin.

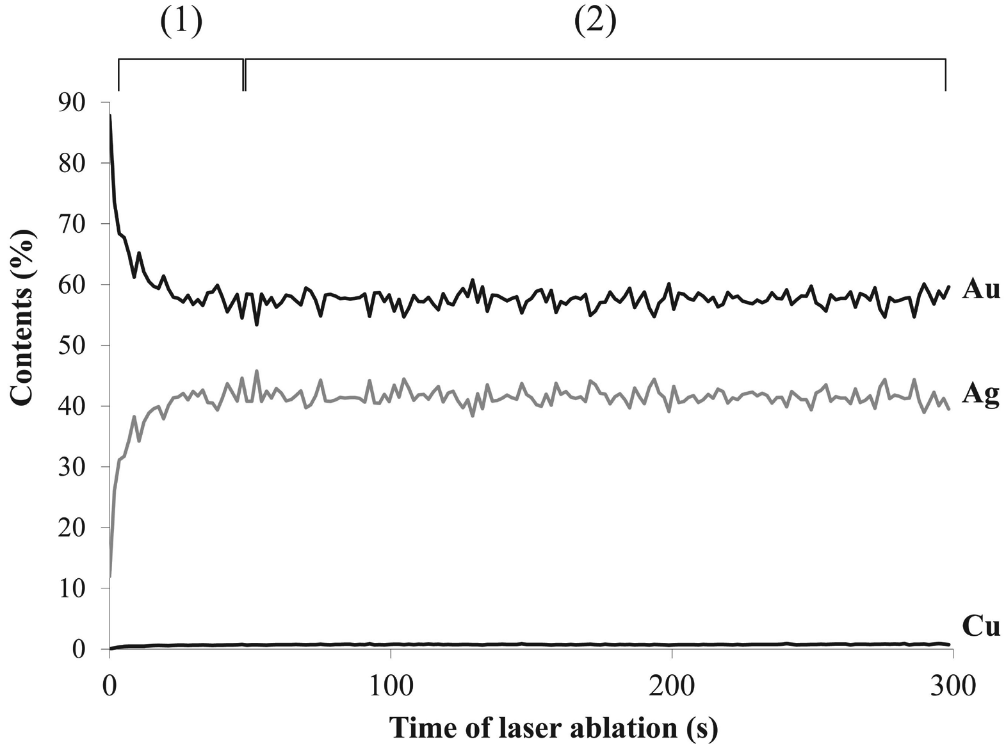

Figure 3. Concentrations profiles for gold, silver and copper versus the time of laser ablation obtained by DP-LA-ICP-MS for a Greek gold coin (FG 635, MMA BnF). (1) Gold enriched surface; (2) original alloy.

Ternary gold-based alloy coins[12]

LA-ICP-MS analyses were made on Celtic coins some years ago when the DP mode could not be performed with the available instrumentation (Blet-Lemarquand *et al.* 2009; 2014a). Before starting the analysis, a 20 second pre-ablation was first performed to remove potential corrosion and contamination, and then the transient signal obtained from 40 seconds of ablation was integrated to calculate elemental concentrations. For some coins noticeable variations could be obtained for the copper contents between the three micro-samplings (Blet-Lemarquand *et al.* 2009; 2014a). Could the DP mode improve the quality of analysis and reduce these variations?

An analytical program using the DP mode was undertaken on a representative set of 150 Late Celtic gold coins from the Laniscat hoard and providing the opportunity to test this question (Nieto-Pelletier *et al.* 2011).[13] Three types of depth-profiles were obtained (Fig. 4). For a minority of coins, gold, silver and copper signals are relatively constant from the surface to the core of the coins (Fig. 4a). Certain coins have a surface layer mainly enriched in gold but also slightly in silver to the detriment of copper (Fig. 4b). Other coins gave very irregular signals which eventually stabilized (Fig. 4c). However, in some cases the alloy appeared to be too heterogeneous to calculate a reliable composition. These fluctuations could be due to corrosion phases. Generally speaking, the elemental analyses showed that the coins contain about 18 % gold, 5-35 % silver and 42-78 % copper. The DP mode appeared to be the only way of producing reliable composition data using the LA-ICP-MS method.

[12] It has already been shown that DP-LA-ICP-MS was suitable for analysis of binary gold-silver alloy coins like the early electrum coins made from weakly homogenised alloys (Blet-Lemarquand and Duyrat 2020).
[13] All the coins contained in this hoard are attributed to the *Osismii*.

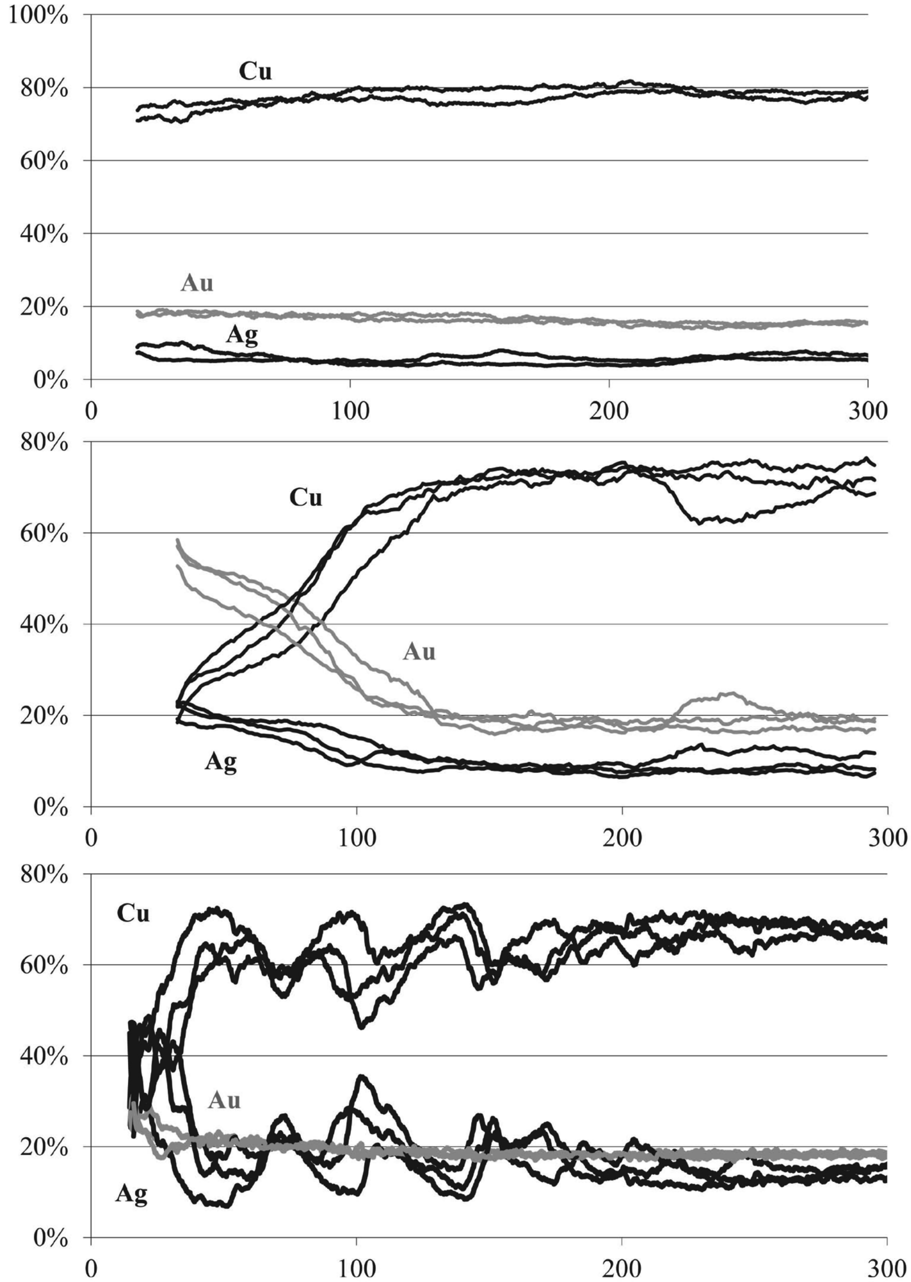

Figure 4. Concentrations profiles for copper, gold and silver, obtained by DP-LA-ICP-MS versus the time of analysis in seconds, for three different Late Celtic coins from the Laniscat hoard. Two or three different laser micro-samplings were made per coin. From top to bottom: (a), (b), (c).

Localised enrichments in platinum and palladium

Platinum and palladium are impurities of gold that are of prime importance for provenance studies (Blet-Lemarquand *et al.* 2014b; Blet-Lemarquand *et al.* 2017; Duyrat and Blet-Lemarquand this volume). These elements are soluble in gold (Ogden 1977) and most of the time, using LA-ICP-MS, their contents are indeed uniform all over a coin. This is the case for a set of 12 Augustus' gold coins (Table 3). The relative standard deviations calculated for the three laser micro-samplings are usually below 10 %. It should be noted that the Pt/Pd ratios are always less variable than the platinum and palladium contents with the exception of coin BNC 330 for which palladium level is near the detection limit (Table 3).

Table 3. Partial results of the LA-ICP-MS analysis of 12 Augustus' gold coins for platinum and palladium (contents and ratios). The arithmetic means (AM) and relative standard deviations (RSD) are calculated from three laser micro-samplings. The contents are expressed in ppm. From Blet-Lemarquand *et al.* 2015.

		BNC 83	*BNC 86*	*BNC 106*	*BNC 107*	*BNC 108*	*BNC 109*	*BNC 110*	*BNC 111*	*BNC 220*	*BNC 330*	*BNC 531*	*BNC 1281*
Pt	AM (ppm)	103	138	150	114	113	99	138	105	77	1.8	125	5.5
	RSD	3%	2%	10%	7%	2%	1%	17%	12%	18%	3%	3%	4%
Pd	AM (ppm)	35	45	14	27	22	27	40	25	23	0.7	38	5.9
	RSD	5%	5%	4%	5%	7%	5%	21%	16%	21%	23%	6%	3%
Pt/Pd	AM	2.9	3.1	10.4	4.2	5.2	3.6	3.4	4.2	3.4	2.7	3.3	0.9
	RSD	3%	3%	7%	4%	5%	1%	5%	4%	3%	26%	4%	2%

Table 4. Platinum and palladium concentrations and platinum to palladium ratios determined for a Lysimachus gold coin (MMA BnF, Luynes 1808).[14] Four laser micro-samplings were carried out. AM: arithmetic mean; SD: standard deviation; RSD relative standard deviation.

	No. 1	*No. 2*	*No. 3*	*No. 4*	*AM*	*SD*	*RSD*
Pt (ppm)	503	502	276	95	344	197	57%
Pd (ppm)	23	23	12	3.4	15	10	62%
Pt/Pd	21	22	23	28	24	3.1	13%

Sometimes significant variations in platinum and palladium can be observed among the micro-samplings. Table 4 presents the contents in both these elements obtained for a Lysimachus coin with four laser micro-samplings that led to three different concentrations. Despite these variations, the Pt/Pd ratio is essentially the same. Localised enrichments in platinum and palladium can be shown in the gold with the DP-LA-ICP-MS analysis. They are likely the result of platinum elements inclusions associated with gold flakes in the gold placer.

What are the consequences of these variations in the platinum and palladium contents? The Pd/Au and Pt/Au ratios of seven different Lysimachus gold coins classified into different groups are plotted on a binary graph (Fig. 5). The relative standard deviations for each element are reported as errors. This graph can be compared with the one showing all the available data for Lysimachus gold (Duyrat and Blet-Lemarquand this volume; Fig. 3). Moreover, it leads to the same conclusions between two groups of coins: the Mithridatic Wars Lysimachi can be distinguished from the other groups of Lysimachus coins. This means that the gold they are made of is different from the gold used for the lifetime or posthumous Lysimachi. Thus, the micro-sampling does not limit the provenance studies on gold coinages.

The PGE inclusions

Platinum group elements (PGE) inclusions can be observed at the surface of certain ancient gold coins. Most of these inclusions are made of osmium-iridium-ruthenium alloy (Meeks and Tite 1980; Ogden 1977) but noticeable contents of platinum were sometimes reported for some of them (Blet-Lemarquand and Duyrat 2020; Lemasson *et al.* 2015) and could perhaps account for the platinum content of the gold.

[14]See Duyrat and Blet-Lemarquand this volume. Values from No. 4 micro-sampling were discarded from the calculations because they were too low.

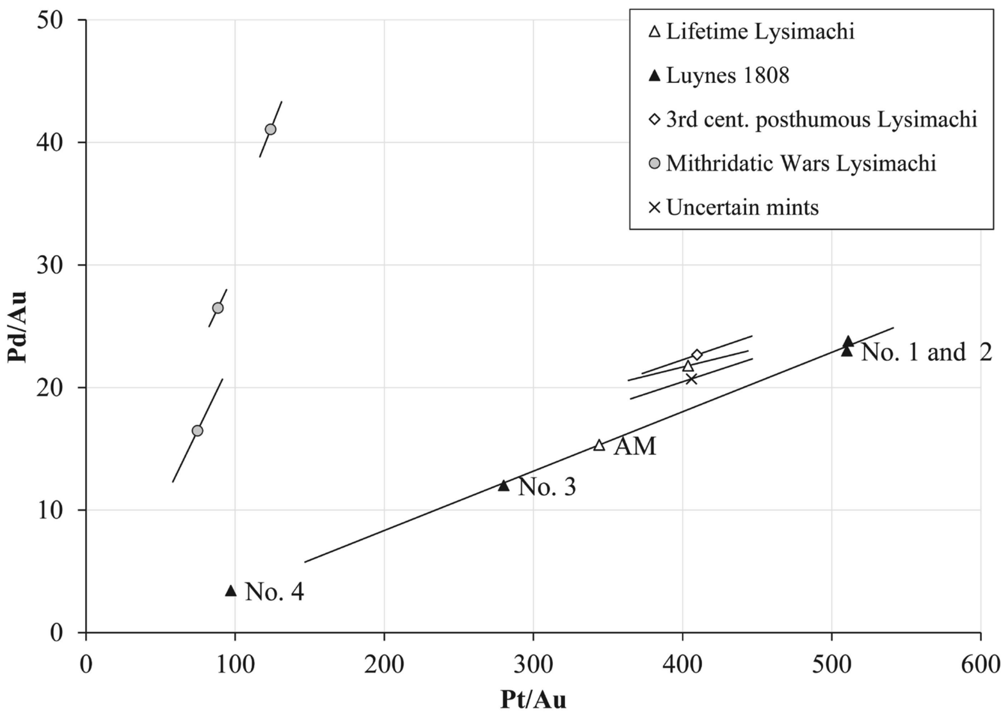

Figure 5. Scatterplot of the ratios of palladium and platinum to gold for seven Lysimachus gold coins.[15] The errors derive from the standard deviations calculated from the three (or four) different laser micro-samplings made per coin and take into account the fact that the platinum to palladium ratios remain constant for a coin. The four results obtained for Luynes 1808 (MMA, BnF) are made distinctive (see Table 4).

An inclusion was fortuitously analysed in the course of the LA-ICP-MS analysis of an early electrum coin (Fig. 6). The osmium, iridium and ruthenium contents dramatically increase from 100 seconds onwards whereas the platinum and palladium concentrations remain stable during the sampling. The profile graph clearly establishes that a PGE inclusion has been sampled and that it is of no consequence on the platinum and palladium content of the gold. As gold and PGE inclusions are only very rarely associated in primary deposits (Ogden 1977), it can be hypothesised that this coin was very likely manufactured from gold coming from a placer deposit containing both gold particles and PGE inclusions.

Conclusions

Depth profile analysis mode represents a real improvement compared with average quantitative analysis for gold coins. Different microstructural data can be obtained such as PGE inclusions, enrichment or depletion phenomena and so forth. It enables the researcher to characterise the alloy beyond enrichment and contamination layers leaving minor damage almost invisible to the naked eye. However, it seems that DP-LA-ICP-MS is not suitable for certain coins made of highly debased and corroded gold. Some elements may appear to be inhomogeneous at the scale of the micro-sampling (e.g. Pt, Pd and Pb). As a consequence, their contents have a higher degree of uncertainty than other elements. These limitations do not adversely impact the conclusions concerning the manufacture of coins or the provenance of metals.

[15]For explanations on the different groups, see Duyrat and Blet-Lemarquand this volume.

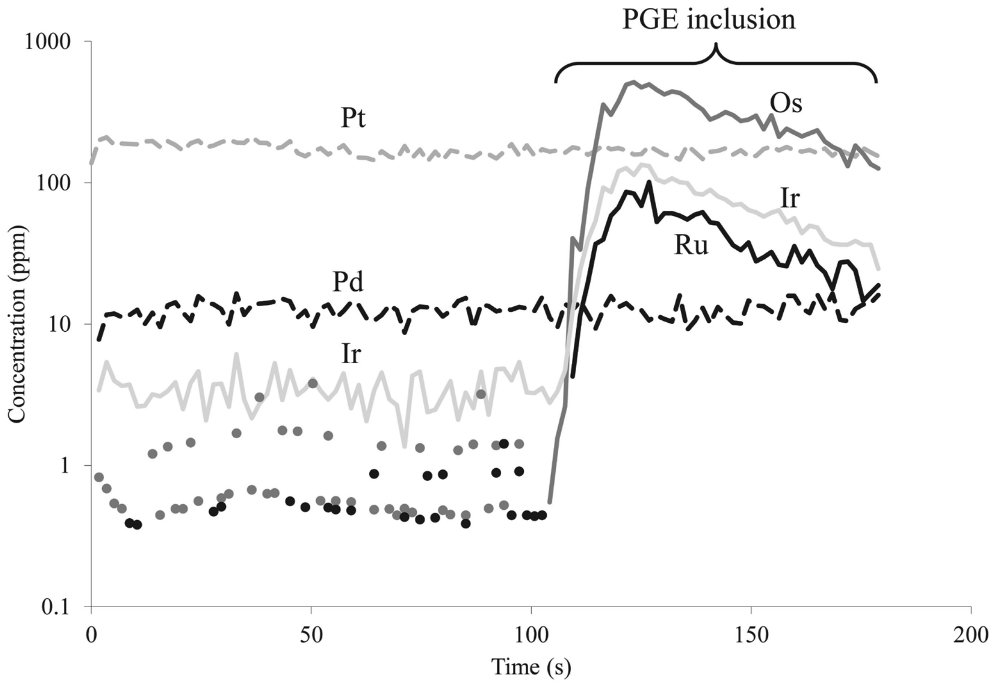

Figure 6. Concentrations profile for the main platinum elements versus the time of laser ablation obtained by DP-LA-ICP-MS for an early electrum coin (Luynes 2625, MMA BnF).[16]

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[16] From Blet-Lemarquand and Duyrat 2020.

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