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Precious Metals and Provenance Enquiries using LA-ICP-MS

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While the manufacture technology of archaeological gold and silver objects can often be explained by using classical analytical techniques, the origin of these precious metals remains difficult to determine. In most cases, several trace elements and/or lead isotope ratios must be measured in order to find the object to mine. Very few results are known in this kind of research: lead isotope ratios are often insufficient and trace elements are difficult to determine non-destructively at very low concentrations. Reaching detection limits below the ppm level and determining a wide range of elements, ICP-MS, either in liquid or laser ablation configuration, finds one of its most interesting applications here. Our aim is to present the possibilities and limitations of this technique for the pre-selection of lead isotope ratios groups in silver and for the characterization of several monetary gold ore sources.

Keywords: GOLD, SILVER, ICP-MS, LA, LEAD ISOTOPES, CHARACTERIZATION, PROVENANCE, SUDAN.

Introduction

Precious metals have always been a symbol of excellence and used as expression of status (Clark, 1986). Their role was very important in prehistoric societies and monetary silver and gold have always governed economies and led political systems. The study of precious metals is fundamental for the understanding of life in the past and to identify fakes.

The main questions in this field concern the manufacturing technology of the artefacts and the provenance of the ores. Some questions, which only need the determination of the major elements, may be quite simple, like the fineness of a certain coinage or the type of alloy used to manufacture an object. Also the study of soldering, gilding, blanching, plating and other manufacturing techniques may be done through the determination of major and sometimes minor elements using different kinds of analytical techniques. However, more elaborate questions concerning possible re-melting and changes in ore supplies may be posed.

Even after we had succeeded in the differentiation of the ore's supplies, the identification of the metals' origin, concerning the determination of trace elements or/and lead isotope ratios, remains a difficult question. The rarity or abundance of the ores' deposits, the high temperature required to purify the metals, and the re-melting and re-use of metals (Guerra, 1995), complicate the task.

However, a few examples were successful for a known mine (Guerra & Barrandon, 1997), as one trace element may be enough to identify the metal. Following In (measured by thermalized fast neutron activation analysis (TFNAA), Guerra & Barrandon, 1988), we dated the arrival of the Potosian silver (Guerra *et al.* 1991) to Spain and, following Pd (measured by proton activation analysis (PAA), Barrandon, 1986), the Brazilian gold (Barrandon *et al.*, 1993) to Portugal; also their influence and diffusion in the European economy of the 16–18th century were studied.

For all the other situations, trace elements and/or lead isotope ratio "fingerprinting" must be carried out (Hughes, 1991). Very few examples are known, even for native metals that suffer less processing; we can refer to the work of Gale & Stòs-Gale (1992) on lead isotope ratio databases for copper and silver and to Meyers (1969) on the trace element analysis of Sassanian silver by neutron activation analysis (NAA).

Identifying the origin of the archaeological ores is a very difficult analytical problem. Lead isotope ratios of silver may be determined. However, for pure and native gold, with a Pb content lower than 100 ppm (Morteani & Northover, 1995), we need a huge sample. That is why the determination of trace elements may be a solution to identifying the metals.

Trace elements in gold are difficult to measure. Particle induced X-ray emission (PIXE) and X-ray fluorescence (XRF) suffer the absorption of emergent X-rays, NAA needs very hard and expensive chemical separations and PAA only determines a few trace elements (Guerra, 1998). The low sensitivity of the classical techniques may explain the very few results in provenance research. The determination of the platinum group element series (PGEs: ruthenium, rhodium, palladium, osmium, iridium, platinum), as well as other representative elements (tin, antimony, indium, . . .) under the ppm level, increases the inter-element associations and so the possibility of providing a unique fingerprint.

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Table 1. LA-ICP-MS operating conditions and data collection parameters

ICP-MS instrument	
Instrument	Fison Elemental PlasmaQuad PQXS
Plasma	argon
Forward radio frequency power	1·350 kW
Reflected radio frequency power	<2 W
Coolant gas flow	14·0 l min^{-1}
Carrier gas flow	1·1 l min^{-1}
Auxiliary gas flow	1·4 l min^{-1}
Sampling cone	Ni 0·9 mm orifice
Skimmer cone	Ni 0·7 mm orifice
Data collection parameters	
Acquisition mode	pick jumping, 3 points per peak
Dwell time per channel	10·24 ms
Ion lens tuning	5×10^5 for ^{115}In in NIST612
Acquisition time	60 s and 10 s pre-ablate
Laser operating parameters	
Laser type	VG Nd:YAG (continuum)
Maximum output	2 mJ
Fundamental wavelength	266 nm
Laser operating mode	switched-Q
Number of shots per site	3
Shot repetition rate	6 Hz
Site pattern for each analysis	3 × 3 raster, i.e., 9 sites per analysis

Table 2. Isotopes used for LA-ICP-MS measurements

Isotopes		
Ti48	Ru102	Os189
Cr52	Rh103	Os192
Co59	Pd105	Ir191
Ni60	Pd106	Ir193
Cu65	Pd108	Pt195
Zn66	Cd111	Hg202
Ga69	In115	Tl203
Ga71	Sn118	Tl205
Ge70	Sn120	Pb208
Ge73	Sb121	Bi209
As75	Te125	Th232
Se82	Te126	U238
Ru99	Sm147	
Ru101	Rd185	

Inductively coupled plasma mass spectrometry (ICP-MS), owing to rapid collection, simple spectra, high sensitivity, low background and sub ng/ml detection limits and broad linear dynamic range, is a powerful technique for the characterization of materials. If the sample's introduction in liquid mode requires a difficult and expensive chemical dilution (Tykot & Young, 1996), the laser ablation (LA) introduction for direct analysis of solid samples needs no preparation and makes a virtually non-destructive analysis. Metal sampling is of about 1 µg (100 µg for Gordus' (1972) drilling). The few interferences may be predicted and in most cases solved.

Table 3. Certified composition of high-purity gold NBS SRM685 standard

Element	Concentration (ppm)
Cu	0·10
In	0·01
Fe	0·20
Ag	0·10
Sn	<0·07
Zn	<0·04
Ni	0·05

Table 4. LA-ICP-MS and PAA LoD values for main elements in ppm

Element	SRM685	Blanks	PAA
Ti	0·03	0·1	1
Co	0·03	0·03	–
Ni	3	0·7	–
Cu	1	0·1	1
Zn	0·3	0·02	5
Ga	0·1	0·04	10
Ge	0·01	0·01	1
As	0·1	0·05	1
Ru	0·004	0·004	2
Rh	0·002	0·004	1000
Pd	0·03	0·01	2
Cd	0·2	0·003	5
In	0·0002	0·0004	10
Sn	0·1	0·02	2
Sb	0·01	0·005	1
Te	0·05	0·03	1
Re	0·02	0·07	5
Os	0·02	0·01	20
Ir	0·04	0·01	20
Pt	0·01	0·01	1
Hg	2	1	3
Pb	0·5	0·005	1
Bi	0·01	0·001	–
U	0·04	0·02	–

For LA-ICP-MS both blanks fluctuation and high purity gold standard techniques were used. High Ni concentration is due to cone composition.

We made a first attempt to differentiate precious metals from several origins using our new analytical facilities: Fisons PlasmaQuad PQXS is combined with a 2 mJ pulsed VG Nd:YAG laser quadrupled to work at the UV wavelength of 266 nm with a maximum shot frequency of 10 Hz.

Tracing Gold with LA-ICP-MS

LA-ICP-MS has already been used for the analysis of industrial and geological gold (Kogan, Hinds & Ramendik, 1994; Watling *et al.*, 1994). The most encouraging case concerns the differentiation of several gold ores from western Australia (Watling *et al.*, 1994) on the basis of the gold ore trace elements signature. However, contrary to geologists, we analyse purified metals. A recent study (Geertsen *et al.*, 1994)

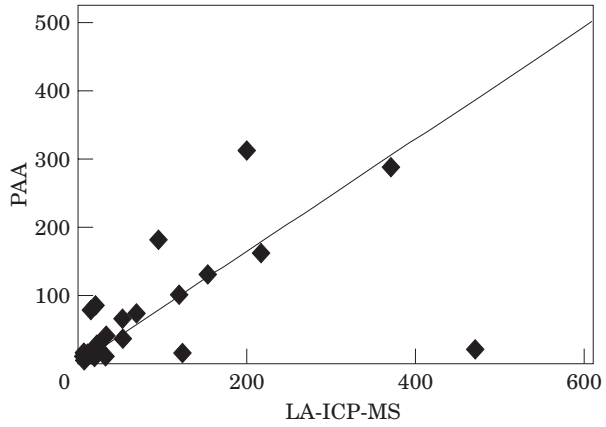

Figure 1. Comparison of Zn values by LA-ICP-MS and PAA in ppm. For several samples, some more volatile elements show good sensitivity but poor reproducibility.

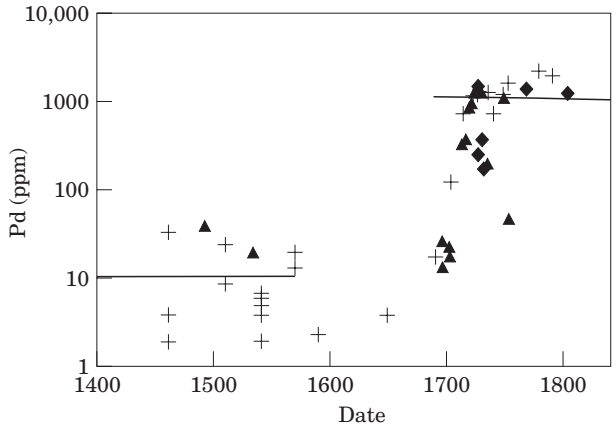

Figure 2. Palladium concentrations of Portuguese (+), Brazilian (◆) and English (▲) coins as a function of the date of issue, showing the date of arrival of the Brazilian gold to Europe.

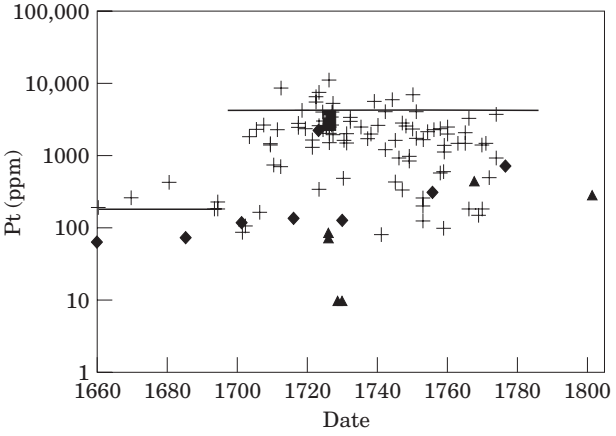

Figure 3. Platinum concentrations of French (+), Brazilian (▲) and Russian (◆) coins as a function of the date of issue, showing the date of arrival of the Brazilian gold to Europe. There is a mixture of Brazilian gold with another gold ore, which does not come from Russian mines.

comparing UV and IR lasers for sample introduction into the ICP, shows that UV prevails.

The optimized ICP-MS operation conditions give the maximum analyte sensitivity for a minimum interference from polyatomic and refractory oxide ions. For the optimization of LA, a certain number of parameters were controlled, such as the mode of laser operation, the number of shots per site and the number of replicate analyses.

The system was operated in Q-switched mode in order to have a more reproducible transport effect (Kogan, Hinds & Ramendik, 1994). The protocol was adopted to have a sampling representative of the object and small enough to allow multiple determinations, high sensitivities (mostly for PGE) and good reproducibility.

Optimized data collection parameters and instrument operating conditions are shown in Table 1. The isotopes used are shown in Table 2: the most abundant isotope free from isobaric overlap was chosen, otherwise interference was evaluated. The largest collimator was used and crater dimensions were measured: about 40 μm diameter and 130 μm depth. Nevertheless, samples must fit inside the 5-cm diameter ablation chamber.

The facilities of the cyclotron from the CERI/CNRS laboratory were used to produce gold certified standards by activation analysis, as reference materials for calibration. However, the limited number of measured elements requires the use of interpolation calibration. As the sensitivity from one analyte to another may vary by as much as 50%, both between samples and within a single sample (Jarvis *et al.*, 1995), internal standard correction was used for accurate quantitative analysis. It improves the reproducibility of the measurements and corrects for instrumental drift. Internal standard must be present at constant (or known) concentrations and its behaviour during ablation must be representative of the other elements. Only gold corresponds to these characteristics; as it has no low abundance isotope, we used one of the argon species ($AuAr^+$) generated in the plasma.

For the determination of the limits of detection (LoD), a certain number of methods have been proposed (Kogan, Hinds & Ramendik, 1994; Williams & Jarvis, 1993). The one most frequently used considers the LoD as the concentration equivalent to three times the standard deviation of 10 replicate analyses of blanks. However, during laser fire a background appears with the change in the plasma. We used a high-purity gold NBS RMS685 (Table 3 gives standard composition) to evaluate the LoD, assuming a perfectly homogeneous distribution of the analytes, and we considered the LoD to be the concentration equivalent to three times the standard deviation of three replicate analysis. Table 4 shows the LoD measured by both techniques for the most important elements. The difference may attain a factor of 10. Elements like Cu,

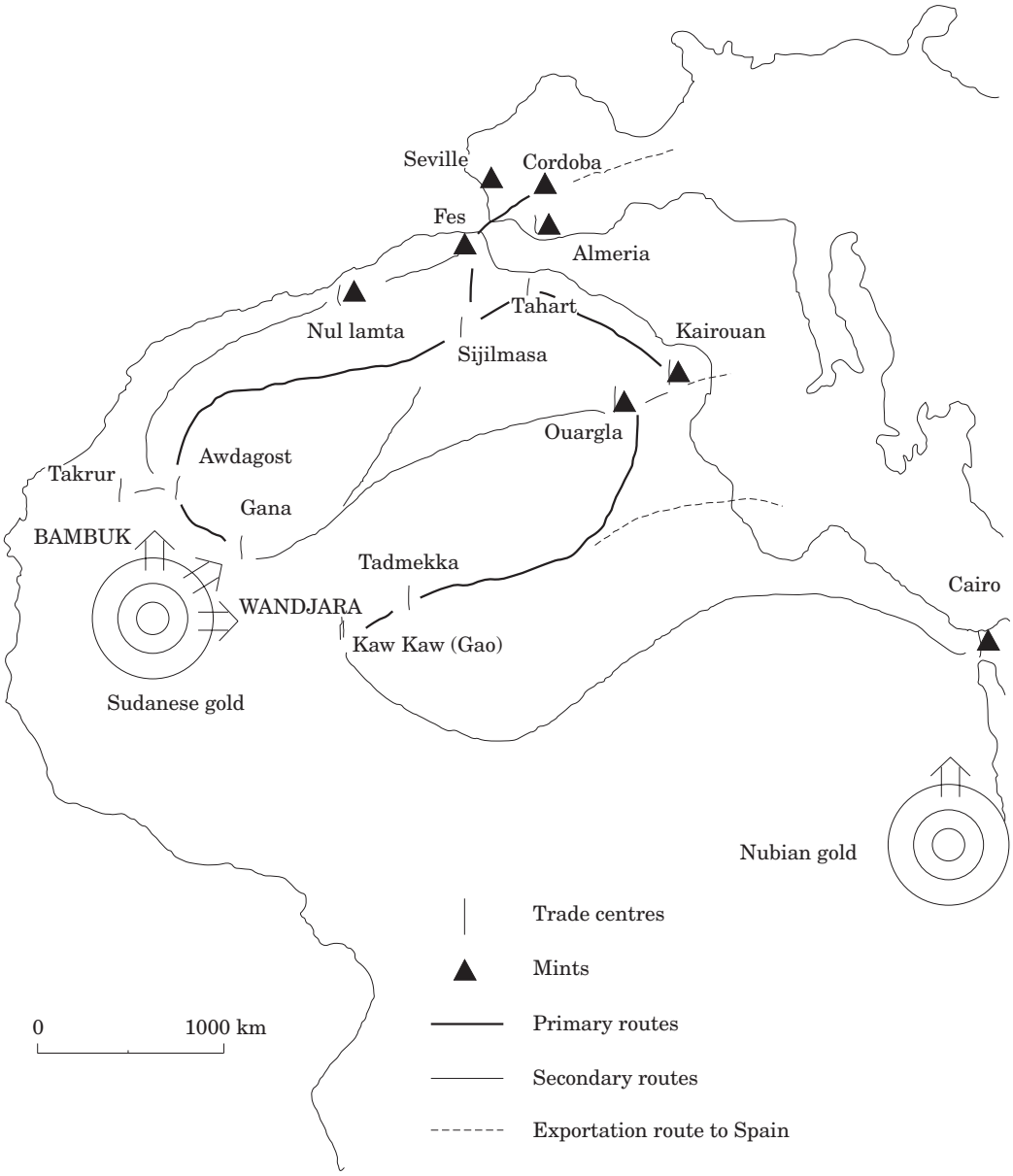

Figure 4. Gold trade routes in the occidental Muslim Empire (8–11th century).

Zn or Sn are present in the NBS composition and influence the LoD. We also notice that they are better by factors of 10 to 100 than for PAA. Certain more volatile elements such as Zn may present very good sensitivity but poor reproducibility (Figure 1). One of the worst elements is Pb which can show relative errors of more than 70% for silicates (Williams & Jarvis, 1993) and be quite random for gold matrices.

Applications to Archaeological Gold

In order to test the possibilities of the technique, several provenance problems have been considered. The first results for two monetary gold problems have already been published (Gondonneau, Guerra & Barrandon, 1996). One concerns the first coins struck in Gaul which were copies of the Philip II of Macedonia stater (356–336 BC). Coupling PAA with LA-ICP-MS, we showed that Gaul and Greek gold ores are different. Later degenerated imitations of the stater are also made with gold ore from Gaul. More recent results confirm these conclusions.

The second problem concerns the gold struck in Europe in the 18th century. Geochemical data showed that the gold ores from Minas Gerais (Brazil) are characterized by Pd. Using PAA, 1702 was determined to be the date of arrival of Brazilian gold to Portugal (Figure 2) and between 1703 and 1713 (any coin between) to England. The same study was made for

coins struck in France, where Brazilian gold arrived in 1705, and an estimate of the amount of Brazilian gold minted in France was carried out (Barrandon *et al.*, 1993).

However, contrary to Brazilian gold, French and English coinages have high contents of Pt, which means that a mixture of two different ores were used to make the coinages. As Oural gold was exploited at the same period and had high contents of Pt, we analysed some Russian coins. Figure 3 shows that Pt concentration is too low to be considered as the second gold source in Europe. As Colombia is a known origin of platinum (Scott & Bray, 1994), we should analyse coins struck in South America and in Spain during the 17th and the 18th century and try to differentiate several South American gold ores.

The Muslim Gold of West Africa (8th–11th Century)

The encouraging results obtained on the two preceding questions stimulated us to approach the importance of African gold in the economic history of the occidental Muslim Empire after the 8th century. Muslim sources from the Middle Ages presented Sudanese gold (now Mali, Mauritania, Niger, etc.) as the main factor in trans-Saharan commercial relations. However, only official documents describing the Arabic Occident Caliphates dinars after the Muslim conquest, numismatic research and the composition of the dinars may solve the problem. Several authors (Ehrenkreutz, 1959, 1963; Messier, 1973; Oddy, 1980) have studied the devaluation of the dinars during a few periods or dynasties. This is the first study, coupling PAA with LA-ICP-MS, of the manufacture technologies of the coinages and of the provenance of the ores.

Fomin (1990) says "The route to the wealth of the fabulous Ghana ran across Tahert, Wargla, Tadmekka and Sijilmasa". Arab literary sources show that in the 9th century two main routes from al-Qayrawan (capital of the north of Africa) passed through those trade centres: one via Awdghust to Soninke, capital of the Ghanan empire, and the other to the state of Gao (Figure 4). Messier (1973) affirms that Idrisi describes Wangara as "the country of gold, which is thus renowned because of the quality and quantity of the gold it produces". Meniaud's (1912) analysis gave 92% gold for Sudanese ore.

Following Bates' (1992) chronological sequence for the coins struck in Ifriqiya, the early solidi have Byzantian images suggesting that people working in the Arab mint of Carthage were the same as those under the Byzantines. After the introduction in 697–699 AD of the new Arab Islamic coins containing the "shahada", only abbreviated Latin translations appear on the solidi of Carthage (Morrisson *et al.*, 1982) which kept a small and thick blank. Inscriptional types in Latin were struck until 715 AD when the eastern Muslim dinar began to be struck (Bates, 1995).

Table 5. PAA results for major elements in % and lead in ppm

Reference	Date AH	Au (%)	Ag (%)	Cu (%)	Pb (ppm)
Byzantine					
1968/798	38–40	98·3	1·4	0·3	47
Sch2831	47–53	95·5	3·7	0·8	<1
Af725	54–58	96·7	2·6	0·7	95
Arab/Latin					
L109	85–87	88·6	10·4	3·0	125
L110	87–88	90·5	7·6	1·8	121
L111bis	90–91	84·9	12·0	3·2	84
L114	98	60·6	37·4	2·0	<1
Umayyad					
1978·51	101	98·8	1·0	0·04	<1
L408bis	101	98·7	1·1	0·1	18
1966·341	102	98·8	1·1	0·04	<1
L425	103	99·6	0·4	0·01	<1
1978·52	104	99·0	0·8	0·2	<1
L464	114	98·8	1·0	0·1	15
L465	117	98·4	1·2	0·2	21
Aghlabid					
L823	191	93·8	5·7	0·4	<1
L830	199	98·2	1·6	0·05	372
1972·1319	200	97·7	2·1	0·1	235
L836	213	97·2	2·5	0·2	61
1974·32	222	97·4	1·8	0·2	638
L845	199	99·1	0·8	0·05	133
1972·1321	236	98·2	1·3	0·3	<1
1978·53	242	98·2	1·2	0·5	37
1974·36	250	98·7	0·8	0·3	<1
1970·269·2	253	97·9	1·5	0·5	751
1967–210	269	98·6	0·8	0·5	<1
Low867	276	98·4	1·0	0·3	<1
1976–189	282	98·4	1·4	0·1	<1
L883	290	98·4	1·2	0·3	126
Fatimid					
1977·51	297	99·0	0·8	0·1	<1
1972·1332	309	97·7	1·9	0·3	267
1975·12	318	93·9	4·3	1·7	99
1970·209·5	325	97·9	1·5	0·6	<1
1975·13	333	98·3	1·4	0·1	29
Low·87	335	98·7	1·1	0·1	60
Low·91	340	98·9	0·9	0·05	59
L120	343	97·4	2·0	0·4	137
Low96bis	345	97·7	1·7	0·4	90
Low·108	351	97·7	2·0	0·1	194
Low96(5)	364	97·8	1·6	0·4	85
1974–1162	373	97·7	1·8	0·3	<1
Almohad					
1966·275	550	99·0	0·9	0·2	45
L729	580	99·2	0·7	0·01	19
1968·796	554–558	99·4	0·6	0·01	15
1967·142·1	870?	99·0	0·9	0·1	19

All coins belong to the Bibliotheque nationale of France collection.

Proton activation analysis, determining the major as well as some trace elements like lead, demonstrated the dinars fineness evolution and the alteration of gold by voluntary addition of silver or by using non-purified native gold. The elements which show the changes in the gold ore supplies were determined by LA-ICP-MS.

Table 6. LA-ICP-MS results for the main trace elements in ppm

Reference	Date AH	Ga	As	Ru	Pd	Rh	Sn	Sb	Os	Ir	Pt	Bi
Byzantine												
1968·798	38–40	2	3	1	16	0·2	52	4	1	9	320	0·2
Sch2831	47–53	3	5	0·5	12	0·1	183	18	1	8	252	2
Af725	54–58	1	2	1	21	2	35	2	4	17	371	1
Arab/Latin												
L109	85–87	2	1	1	24	5	77	11	6	10	344	10
L110	87–88	1	2	0·3	18	1	56	6	0·4	5	284	3
L111bis	90–91	2	3	1	31	2	53	8	1	10	308	3
L114	98	8	7	0·1	8	0·2	345	9	<0·02	1	92	19
Umayyad												
1978·51	101	2	1	0·2	18	1	17	1	0·1	4	312	0·2
L408bis	101	2	1	0·3	19	1	12	1	0·04	6	318	0·2
1966·341	102	0·4	1	0·3	33	2	6	0·3	0·2	6	312	0·03
L425	103	0·5	1	0·1	12	0·4	72	1	0·3	2	269	0·1
1978·52	104	1	1	0·4	19	1	23	1	1	5	301	0·3
L464	114	3	13	0·2	17	1	33	2	0·2	4	291	1
L465	117	<0·3	<0·2	1	18	2	<0·005	<0·005	1	13	409	<0·001
Aghlabid												
L823	191	12	3	0·1	2	0·3	14	3	0·5	1	30	0·5
L830	199	17	1	0·2	2	0·1	3	1	0·2	2	26	1
1972·1319	200	3	4	0·3	9	0·6	7	1	0·3	5	139	2
L836	213	22	1	0·3	9	1	5	3	1	3	117	0·4
1974·32	222	20	1	0·1	2	0·2	16	3	0·1	1	21	1
L845	230	25	1	0·01	0·2	<0·003	2	0·5	0·04	0·01	0·1	0·1
1972·1321	236	22	2	0·01	0·4	0·01	2	1	0·04	0·003	0·2	0·1
1978·53	242	78	2	0·03	1	0·01	3	2	0·1	0·01	2	0·1
1974·36	250	27	2	0·03	0·2	0·02	5	1	<0·02	<0·02	0·3	0·1
1970·269·2	253	23	0·5	0·02	0·4	0·01	1	0·1	<0·02	0·01	0·4	0·1
1967·210	269	126	2	0·03	0·3	<0·003	3	1	0·1	0·04	2	0·2
Low867	276	44	1	0·05	0·4	0·1	5	1	0·1	0·03	4	0·3
1976·189	282	7	1	0·1	9	0·2	0·5	0·2	0·3	2	95	0·1
L883	290	2	1	0·1	5	0·4	3	1	0·4	2	55	1
Fatimid												
1977·51	297	2	1	0·1	13	0·4	7	2	0·4	2	66	0·2
1972·1332	309	9	2	0·1	4	0·2	3	0·2	0·1	2	86	0·1
1975·12	318	31	4	0·2	11	0·4	15	2	0·2	2	38	2
1970·269·5	325	63	1	0·01	22	0·3	7	1	<0·02	0·01	3	0·2
1975·13	333	14	0·5	0·3	34	1	18	0·0	<0·02	1	86	2
L87	335	19	1	0·1	6	0·2	4	0·4	0·3	2	58	0·2
L91	340	21	1	0·05	4	0·1	1	0·1	0·004	1	28	0·1
L120	343	21	4	0·2	13	0·4	6	1·5	2	2·5	71	<0·001
L96bis	345	42	4	0·04	7	0·2	10	1	0·003	1	51	1
L108	351	28	1	0·004	1	0·03	4	<0·005	0·01	0·01	2	0·1
L96(5)	364	52	2	0·03	4	0·1	4	1	0·1	1	38	1
1974·1162	373	45	1	0·1	18	0·3	9	0·2	0·1	1	19	0·1
Almohad												
1966·275	550	1	0·4	<0·01	5	0·03	22	1	0·02	<0·02	1	0·04
L729	580	1	2	<0·01	14	0·02	10	1	<0·02	<0·02	2	0·1
1968·796	556	0·4	0·3	0·03	20	0·002	5	0·001	<0·02	<0·02	1	<0·001
1967·142·1	870	1	0·4	0·004	104	0·1	85	3	1	1	53	0·04

All coins belong to the Bibliothèque nationale of France collection. We thank Michel Amandry and François Thierry for their help.

We studied the manufacturing techniques and tried to characterize gold from Sudan and to differentiate it from other minted golds.

We analysed Byzantine and Arab/Latin solidi minted in Carthage and dinars minted in Ifriqiya after the Umayyads. Between the end of the Umayyads and the Aghlabids no gold coins were struck. The results for the major and trace elements can be found in Tables 5 & 6.

If we consider the fineness evolution with the date of issue, we can see that, except for Arab/Latin solidi, all coins have a high fineness standard. Coin 1975·12 struck in 318 AH confirms Oddy's (1980) results for this period. To cite Ehrenkreutz (1959, 1963), even the rising dynasty of the Fatimids was supplying the western regions of the Muslim empire with excellent gold coinage, continuing the monetary traditions of the Aghlabids in the north of Africa.

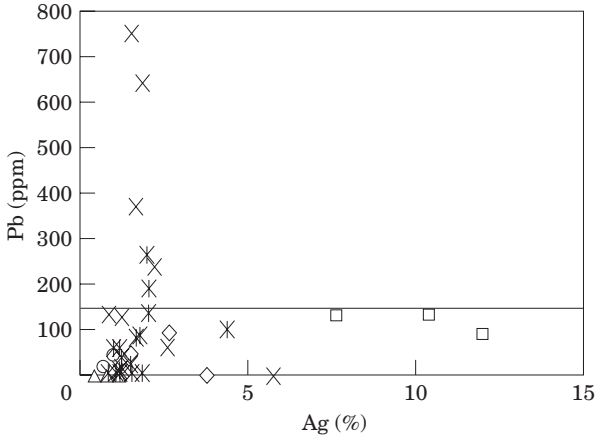

Figure 5. Lead concentration as a function of silver concentration for all the solidi and dinars, showing that most of the coins were struck with native gold. Some Aghlabid and Fatimid coins, which may be devaluated by the voluntary addition of silver, have an unusually high lead concentration. ◇, Byzantine; □, Arab-Latin; △; Umayyad; ×, Aghlabid; ×, Fatimid; ○, Almohad.

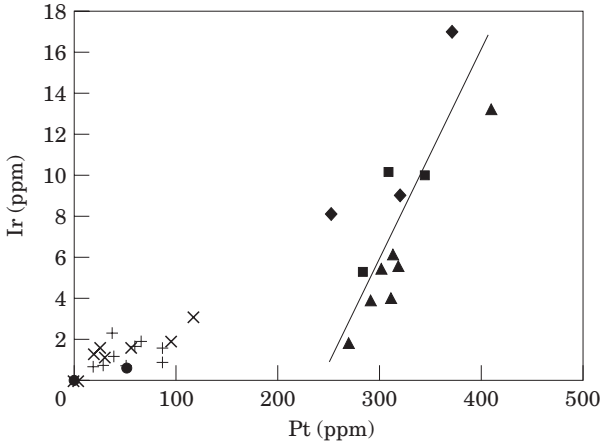

Figure 6. Iridium concentration as function of platinum concentration showing that the Byzantine and Arab-Latin solidi and Umayyad dinars were struck with the same gold. ◆, Byzantine; ■, Arab/Latin; ▲, Umayyad; ×, Aghlabid; +, Fatmid; ●, Almohad.

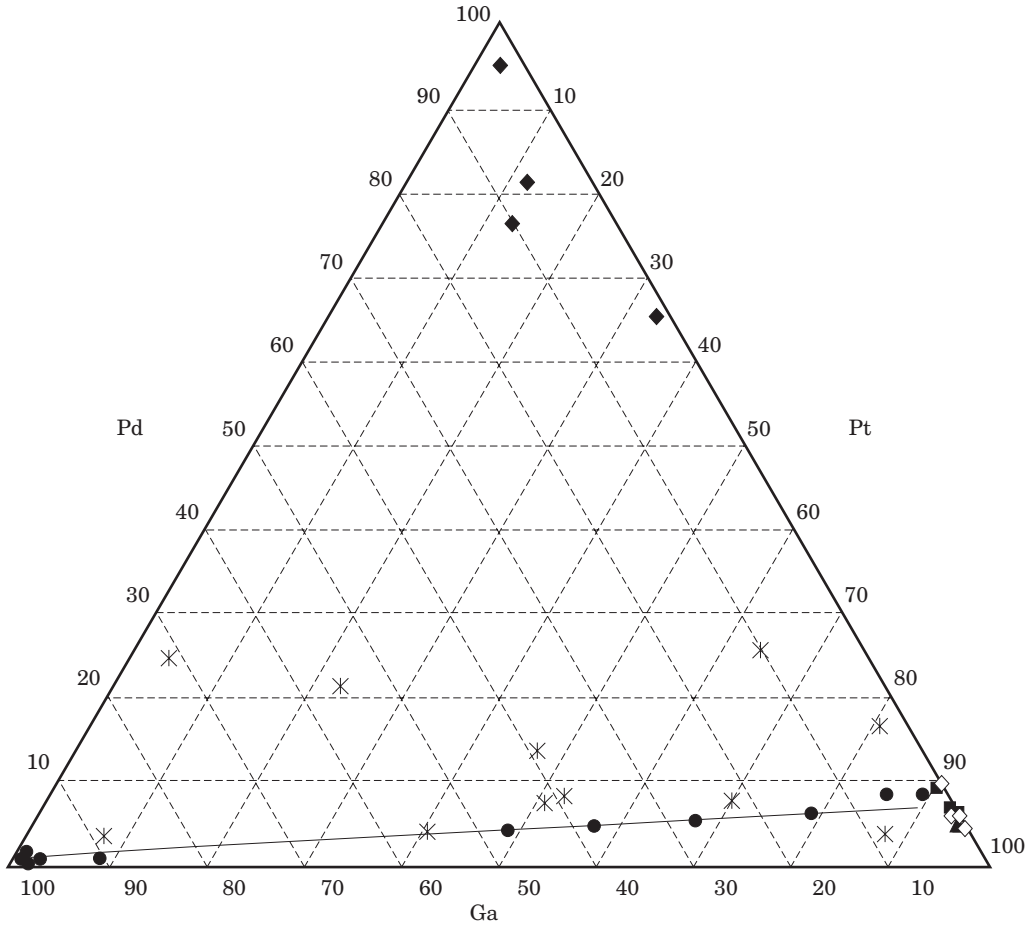

Figure 7. Pd–Pt–Ga ternary diagram for the Muslim and Byzantine coins. ▲, Byzantine; ■, Arab-Latin; ◇, Umayyad; ●, Aghlabid; ×, Fatimid; ◆, Almohad.

If we take the concentration of Ag as a function of Pb, as in Figure 5, we notice that most of the coins were made with native gold, except the group with a high concentration of lead and high fineness. For this group there is a correlation between silver and lead, thus we surmise that devaluation was due to the addition of silver with a high content of lead (about 5%). More coins from these periods will be analysed in order to understand this unusual phenomenon.

The concentration of Ir as a function of Pt, in Figure 6, separated the coins into two main groups. One, with Ir/Pt correlation, contained Byzantine, Arab/Latin solidi and Umayyad dinars.

If we consider the ternary diagram of Pd–Pt–Ga (Figure 7) we can see several phases:

- Byzantine and Umayyad Arab/Latin solidi and dinars are made with the same gold, confirming Bates' (1995) theory on Carthage mint as well as the results shown in Figure 5;
- gold supply changed under the Aghlabids, as the concentration of Ga suddenly increases and that of Pt decreases, PGE elements show very low concentrations;
- under the Fatimids two groups seem to appear: one with Ga concentrations similar to the Aghlabids' coins and another showing either remelting or a different gold source (note that Fatimids only possessed the east gold routes);
- a decrease of Pt and absence of Ga for the Almohad coins. Almohad gold seems to be different from the others but it was struck much later. Analysis of the Bibliothèque nationale of France collection (Lavoix, 1891) considering other periods and mints will allow us to confirm these first results and to extend this study to other regions.

Muslims arrived in Europe and, after the Poitiers defeat, settled in al-Andalous in the south of Iberia. Spufford (1994) writes: "At the end of the 10th century the key route ran due north across the western Sahara from the gold fields of Bambuk and Bure to Sijilmasa, and then through the Atlas Mountains to Fez and finally to the caliphate of Cordoba in southern Spain". Hence, we started the analysis of Iberian gold Muslim coinages in order to establish the historical and economical relation between Ifriqyiya and al-Andalous. A connection with the oriental caliphates will also be investigated by studying the gold from Nubia. The study of the three occidental Muslim possessions will give us an idea about the commercial exchanges in the Mediterranean basin during the Middle Ages.

Conclusion

LA-ICP-MS with very low LoD and rapid data collection in direct analysis of solids with such a small amount of sample ablated that it is considered as non-destructive, satisfies the importance in archaeology of assemblages of artefacts rather than the study of individual objects. The use of LA reduces (eliminates) problems associated with liquid solutions such as potential contamination and sample dilution below LoD. The possibility of determining a fingerprinting association for ores, places this technique as one of the most powerful for solving questions on the provenance of archaeological gold.

The application to Muslim coinages showed that solidi and dinars struck in the Carthage mint were made with the same gold. During and after the Aghlabids (9th century) other gold sources were used in the north African mints. This evolution agrees with the chronology and seems to reveal the arrival of the trans-Saharan Sudanese gold to the Ifriqiya economy. Our analysis also revealed an unusual phenomenon of manufacture technology: high lead content. This shows the importance of the study of the Muslim silver coinages.

The further study of coins from Ifriqyiya, Spain and Egypt, will allow the study of the occidental Muslim economy of the Middle Ages. A parallel investigation into the European Christian economy ("barbarian" coinages) will also be carried out.

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Appendix: Lead Isotope Ratios of Silver by ICP-MS

In order to have at our disposal as much information as possible on the metals, we are developing an ICP-MS technique for the characterization of archaeological silver by both trace element (using LA) and lead isotope determination. Here we tested the latter technique's possibilities for making a pre-selection of silver samples. Note that with Fisons PlasmaQuad it is impossible to reach the accuracy of TIMS and, at the present, we cannot avoid environmental pollution.

Considering the simultaneous measurement of Pb masses by TIMS, we tried to minimize the time between each isotope measurement. A first attempt was made using a Nd:YAG laser at 1064 nm for sample introduction. The precision obtained was too poor, even for a pre-selection: 0·01 for 207/206 and 0·03 for 208/206.

We tried the liquid mode for the sample introduction with 10 ppb lead solutions to optimize the stability parameters. The experimental conditions are: pick jumping detection mode and 2·5 ms dwell time. In order to use only 1 point per peak, the shape of the Pb peaks was optimized.

We performed 100 acquisitions of 45 s each on samples from two silver Greek coins having 1·14 and 0·37% of Pb. For these first experiments, neither Tl internal standard nor Hg correction were used, nor also NBS981 standard for ratio corrections (Walder *et al.*, 1993). In a first approach we excluded the values of $\pm 2\sigma$ and then we excluded those of $\pm 1\sigma$. Most of the points were kept even for the last situation (see Table 7).

Table 7. Statistical results of lead isotope ratios of two silver coins by ICP-MS. The results are compared with those from Cevennes (France) silver ore using TIMS

Coin No.	Lead isotope ratios		
COIN 1	207/206	208/206	206/204
Mean value for 100 runs	0·840	2·042	15·860
σ	0·0041	0·0077	0·18
Mean value for 97 runs	0·8392	2·043	15·874
σ	0·0031	0·0059	0·14
Mean value for 84 runs	0·8391		
σ	0·0023		
COIN 2			
Mean value for 95 runs	0·867	2·003	15·310
σ	0·006	0·006	0·21
Cevennes/TIMS			
Mean value	0·8486	2·0903	
σ	0·0025	0·0025	

The low abundance of isotope 204 explains the bad results for the 206/204 ratio, but if we compare the standard deviations with those of TIMS (Table 7), for the other two ratios the results are good and show that we can make a pre-selection. However, we will try to compensate the low abundance of the 204 isotope by a higher dwell-time and use internal and NBS standards to test the reproducibility and the precision. We hope to apply this technique to the study of the silver Muslim coinages as well as other important ones.