ArcheoSciences
Revue d'archéométrie

33 | 2009
Authentication and analysis of goldwork

Helium, uranium and thorium analyses of ancient and modern gold objects: estimates of their time of manufacturing

Analyse de l'hélium, de l'uranium et du thorium dans des objets anciens et modernes en or : estimation de leur date de fabrication

Otto Eugster, Ernst Pernicka, Michael Brauns, Alex Shukolyukov, Valerie Olive and Stefan Roellin

Helium, uranium and thorium analyses
of ancient and modern gold objects: estimates
# of their time of manufacturing

Analyse de l'hélium, de l'uranium et du thorium dans des objets anciens et modernes en or : estimation de leur date de fabrication

Otto Eugster*, Ernst Pernicka**, Michael Brauns**, Alex Shukolyukov***, Valerie Olive**** and Stefan Roellin*****

Abstract: Authenticating archaeological gold objects is a major problem, as gold is probably the most difficult material in terms of detecting modern forgeries. In 1996 we published the results of the study of faked and genuine gold crystals from the Santa Elena gold mine in Venezuela, and demonstrated that the U/Th – He dating method is a powerful tool for detecting forgeries among gold objects. U and Th decay by emitting He atoms that remain stored in gold. By measuring U, Th, and He, the time when the He trapping process started can be determined. In the 1996 publication we also mentioned that the same method can be applied to ancient gold objects, in order to determine the time when they experienced their last melting process and, thus, to verify their antiquity. In the present work we report on a systematic and quantitative study of He, U, and Th in a large number of ancient and modern gold objects.

Résumé : L'authentification d'objets en or est un problème majeur, car l'or est probablement le matériau le plus difficile quand il s'agit de détecter des contrefaçons modernes. En 1996 nous avons publié les résultats d'une étude de cristaux d'or faux et authentiques de la mine d'or de Santa Elena, au Venezuela, et nous avons montré que la méthode de datation U/Th – He est un outil puissant pour détecter les contrefaçons dans le cas des objets en or. La décroissance de l'U et du Th se fait par émission d'atomes d'He qui restent stockés dans l'or. La mesure de l'U, du Th et de l'He permet de déterminer le moment de départ du processus de piège de l'He. Dans notre publication de 1996, nous avons aussi mentionné que cette même technique peut être appliquée aux objets d'or anciens, de façon à déterminer le moment correspondant à leur dernière fonte et ainsi de vérifier leur ancienneté. Dans cet article nous présentons une étude systématique et quantitative de l'He, de l'U et du Th dans un large nombre d'objets d'or anciens et modernes.

* Physics Institute, University of Bern – Sidlerstrasse 5, 3012 Bern, Switzerland. (eugster@space.unibe.ch)

** Curt-Engelhorn-Zentrum Archäometrie – C5, Zeughaus, 68159 Mannheim, Germany. (ernst.pernicka@cez-archaeometrie.de), (michael.brauns@cez-archaeometrie.de)

*** Scripps Institution of Oceanography, UCSD – 9500 Gilman Drive, La Jolla, CA 92093, USA. (ashukolyukov@ucsd.edu)

**** SUERC – Ranking Avenue, East Kilbride G75 0QF, Scotland. (v.olive@suerc.gla.ac.uk)

***** Bundesamt für Bevölkerungsschutz – Labor Spiez, 3700 Spiez, Switzerland. (stefan.roellin@babs.admin.ch)

1. Introduction

When gold crystals are formed in the Earth's crust, other elements, such as U, are incorporated into the crystal lattice. Thus, gold from mines and from river beds always contains traces of U and Th. The three long-lived isotopes ^{238}U, ^{235}U, and ^{232}Th decay to Pb by emitting α-particles. An α-particle is the nucleus of the ^{4}He atom, so when two electrons combine with an α-particle, a ^{4}He atom is formed. The ^{4}He atoms remain stored in the metal. A fourth long-lived radionuclide, ^{147}Sm, also disintegrates by α-decay, but contributes in antique gold objects only a few percent to the total radiogenic (produced by radioactive decay) ^{4}He. Because gold is highly retentive of this gas up to about 500 °C, the He atoms remain trapped in the metal. Beginning with 1992, we have studied these characteristics in numerous natural gold samples from all over the world (for references, see Eugster *et al.*, 2009). In Table 1, the data on He, U, and Th obtained for placer gold samples are provided.

In a subsequent work (Eugster, 1996), we presented results on the study of genuine and faked gold crystals (Fig. 1) from the Santa Elena gold mine in Venezuela. The data for the genuine samples provided in the aforementioned paper and new data obtained for three samples of genuine crystals analyzed recently (Table 1) yield an estimated age of 240 million years (Ma). This time may be consistent with the Palaeozoic-Mesozoic (542 – 65.5 Ma) intrusive rocks of the gold mineralisation (Beda Hofmann, private communication). In Eugster (1996), we also presented He, U, and Th data for faked gold crystals that appeared on the mineral market. These data, complemented with two new He analyses and Th concentrations obtained recently, demonstrate that the fake crystals are undatably young, the He concen-

Figure 1: Faked octahedral gold crystals of up to 30 grams, purported to originate from the Santa Elena gold mine (Venezuela).
Figure 1 : Faux cristaux en or octogonal de plus de 30 g, dont la provenance supposée est la mine d'or de Santa Elena (Venezuela).

trations being below the detection limit of the mass spectrometer.

The He quantities in samples of art objects are extremely small for two reasons: (1) the time during which He has accumulated is usually only a few thousand years, in contrast to geological gold that formed millions of years ago; (2) only very small samples of a valuable object are available for the analyses. Inspired by our initial publications, specialists in the scientific investigation of ancient metals saw the potential for additional authenticity studies. Kossolapov *et al.* (1999) and Kossolapov and Chugunova (2002), working at the State Hermitage Museum in St. Petersburg, Russia, collaborated with the company SPECTRON ANALYT in St. Petersburg to build a highly sensitive mass spectrometer and measured the He concentrations in a selection of ancient gold objects.

The present work is a continuation of our earlier investigation of a number of antique gold objects (Eugster *et al.*, 2009). Some objects described in this earlier publication are also included in the present work, because we obtained additional He data for them, and, in particular, because U and Th analyses were performed for these objects, for which, in our earlier investigation, we had to employ average U and Th values.

2. Investigated objects

Test objects of modern manufacture

In the course of our experimental work, we repeatedly analyzed samples from gold objects of modern manufacture to verify the absence or low abundance of radiogenic He expected for the short time of U and Th decay since their manufacture. Table 2 lists the three objects used for this purpose. Results for these objects have already been reported in our earlier publication (Eugster *et al.*, 2009). Because in the meantime additional He results were obtained and the U and Th measurements had not been completed earlier, we will discuss the results for these objects. The He concentrations in eight samples of typically 10 mg of a gold coin Napoléon III, minted in 1857, were measured. New results for a wedding ring of 1886 are presented, as U and Th concentrations are now known, allowing us to verify the recent date of manufacture. Finally, we intended to confirm the absence of He in 11 samples of a commercial gold wire, and we also determined its U and Th concentrations.

	⁴He 10¹⁰ atoms/g	²⁰Ne 10¹⁰ atoms/g	U ppb	Th ppb	Estimated [6] U,Th – ⁴He age (million years)
Placer gold Grosse Fontanne river Switzerland	75 000 [1]	0.48	220	220	850
Gold crystal, genuine Santa Elena gold mine (Venezuela)	17 000 [2,3]	0.054 [2,3]	12.1 [3]	40 [5]	240
Gold crystal, fake purported to originate from the Santa Elena gold mine	< 0.003 [4]	0.027 [2,3]	8.5 [3]	30 [5]	< 0.001

Table 1: Noble gases, U and Th concentrations and estimated ages of geologic gold samples.
Tableau 1 : Gaz rares, concentrations d'U et Th, et âges estimés d'échantillons géologiques en or.

Experimental error of placer gold and genuine Santa Elena gold: 5-10%; of fake gold: 30%.
[1] Average of 4 analyses; [2] average of 3 analyses; [3] Eugster (1996); [4] average of 2 analyses; [5] adopted value; [6] due to sample inhomogeneities, the ages are only estimates.

Table 2: Test objects of modern manufacture.
Tableau 2 : Objets de test de fabrication moderne.
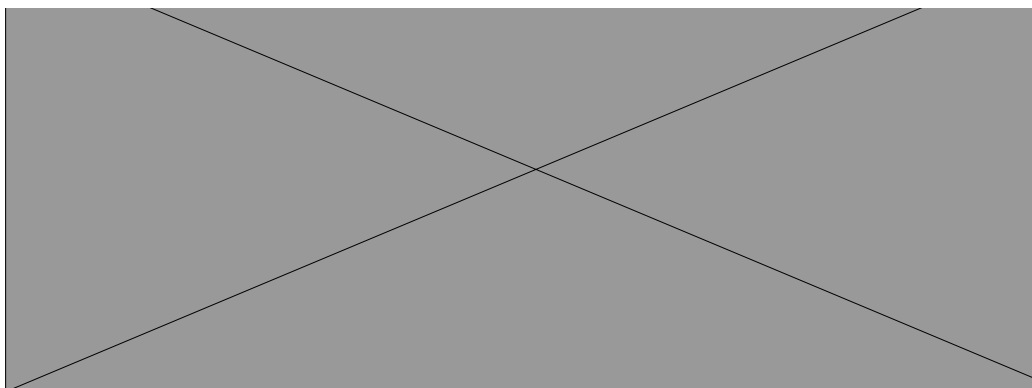
Gold objects to be tested for their antiquity

The objects to be tested in this study are listed in Tables 3 and 4. In most cases, the purported origin and age have been indicated by the owners of the objects. There are three objects that deserve to be described in more detail: (i) A gold torc (Fig. 2), purported to originate from the Hallstatt/La Tène transition period, about 5th century BC. Its diameter is 16.5 cm; X-ray fluorescence analyses yielded 8% Ag and 1% Cu; the object is said to originate from southern Germany. The torc was obtained from Dr. Pieter Meyers, Los Angeles County Museum of Art, on behalf of a client. (ii) A figurine made by an extremely fine granulated golden openwork technique. The surface is strengthened by golden wires, which form the basic structure of this figurine (Fig. 3). It is damaged and repaired at various locations. The present weight is 24 g at a height of 7.3 cm. Appearance and manufacturing techniques were discussed by Shalem (2002).

According to this author, decorating jewellery pieces with gold granules of various sizes was probably known in the early mediaeval Islamic world. However, the earliest visual material of Islamic gold jewellery with granulated openwork presently known is usually datable to and associated with the Fatimid period (Fatimid dynasty of Egypt, 969-1171 AD). An expertise based on technical (CT, SEM/EDX), chemical (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry, LA-ICP-MS), and our He, U, and Th analyses has been compiled by Senn *et al.* (2009). (iii) A signet ring with the picture of a male bust in side-view and an inscription in reflected face 'HILDEB ERTISREGIS' (Fig. 4). In a comprehensive study of this ring, Weber (2007) concluded that it can be attributed to one of the two kings Childebert I or II, of the sixth century Merovingian dynasty of Western Europe. The weight of this gold ring (40.56 g) corresponds almost exactly to the weight of nine Byzantine *solidi* (gold

Figure 2: (See colour plate) Gold torc purported to originate from the Hallstatt/La Tène transition period (5th century BC). Diameter: 16.5 cm.
Figure 2 : (Voir planche couleur) Torque en or supposément attribué à la période de transition Hallstatt/La Tène (ve siècle av. J.-C.). Diamètre : 16,5 cm.
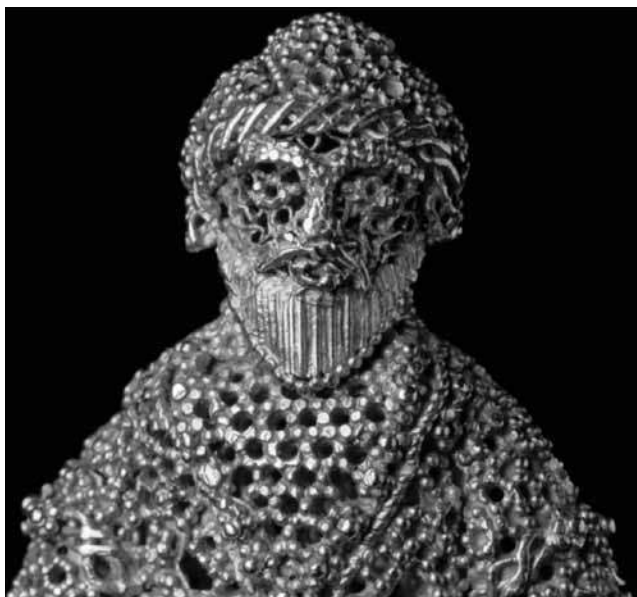

Figure 3: (See colour plate) Golden figurine decorated with granulation. Possible origin: Iran or central Asia (11th or 12th century AD). For size, see text.
Figure 3 : (Voir planche couleur) Figurine en or décorée de granulation. Origine possible : Iran ou Asie centrale (xie ou xiiie siècle). Pour les dimensions voir texte.

coins), indicating that coins of this type were used by the goldsmith to manufacture the royal ring. Regarding the chemical composition of the gold in the Childebert ring, we refer to Weber (2007), who discussed the results that were

Figure 4: (See colour plate) Signet ring attributed to kings Childebert I or II, of the sixth century Merovingian dynasty of Western Europe.
Figure 4 : (Voir planche couleur) Bague à sceau attribuée au roi Childéric I ou II, de la dynastie Mérovingienne d'Europe Occidentale, vi[e] siècle.

obtained at the Curt-Engelhorn-Zentrum Archäometrie in Mannheim using LA-ICP-MS. In the present work, we report additional data, in particular the U and Th concentrations for the Childebert ring, which were not yet available for our previous publication.

3. Experimental methods

For the details of sample preparation and He analyses we refer to our earlier publication (Eugster *et al.*, 2009). The U and Th analyses used in this work were performed by six different laboratories. In most cases, multiple analyses for a particular gold object, and numerous tests and blank measurements had to be carried out. Therefore, the work load would have been too large for a single laboratory, as the U and Th analyses of gold objects were not the main priority of the respective scientists' activity. Furthermore, two of the collaborators went into retirement in the course of the present work. The following laboratories were involved in this study: (i) Curt-Engelhorn-Zentrum Archäometrie, Mannheim (Ernst Pernicka, Michael Brauns, Boaz Paz), using quadrupole inductively coupled plasma mass spectrometry after electrolytic separation of U and Th from Au and other metals on graphite electrodes; (ii) Scripps Institution of Oceanography, UCSD, La Jolla, CA (Alex Shukolyukov, Paterno Castillo), using an inductively coupled plasma mass spectrometer (ICP-MS) after chemical separation of U and Th from Au and other metals; (iii) Labor Spiez (Stefan Röllin), digestion of Au samples in aqua regia, direct analy-

sis of U and Th with an ICP-MS; (iv) Scottish Universities Environmental Research Center (Valerie Olive), using an ICP-MS after chemical separation of U and Th; (v) Institute of Geology, University of Bern (Jan Kramers), using a multi-collector inductively coupled plasma mass spectrometer with desolvating nebulizer, after chemical separation of U and Th and addition of a ^{236}U and a ^{229}Th spike; (vi) Department of Chemistry and Biochemistry, University of Bern (Urs Krähenbühl), using an ICP-MS after chemical separation of U and Th.

For an inter-laboratory comparison, a large number of different samples of object DL 807 (Table 3) were prepared. In five different laboratories, samples of this ancient gold object were measured for their U concentration, the most important element for He production. The following results were obtained (in case of multiple analyses, the average values are given): 0.9 ppb (laboratory (i), as indicated above), 3.5 ppb (ii), 1.9 ppb (iii), 5.5 ppb (v), 12.8 ppb (vi). The differences in the U concentration obtained by these laboratories are presumably due to sample inhomogeneity. This shows that it is important to analyze the He, U, and Th concentrations in the same section of the sample.

4. Results and discussion

Objects of modern manufacture

The results are given in Table 2. The He concentrations for the three objects are extremely low; for the wedding ring of 1886 and the commercial gold wire, they are at or below the detection limit of the mass spectrometer. For the Napoléon coin, we used typically 10 mg of gold material (after etching) to obtain a reliable signal. The age estimate is consistent with the time when the coin was minted.

Object and origin (sample Nr.)	Obtained from	Reported century *	He 10^4 atoms/mg	U ppb	Th ppb	Estimated U,Th – ^{4}He age (years)
Signet ring of Merowingian king France (MR 1)	1	6th AD	10.7	3.4 [9]	79 [9]	1460 ± 400
Celtic torc, Southern Germany (CT 1)	2	5th BC	18.5	15 [10]	45 [10]	2200 ± 1100
Belt chain, Balkan (DL 807)	3	2nd AD	16.8	9.2 [11]	28.6 [11]	3200 ± 1600
Ring Arjhan II tomb, Scytia (Scyt 1)	4	7th BC	21.3	15 [10]	45 [10]	2500 ± 1200
Gold object, Black Sea, Russia (JDM 2)	5	6th BC	16.1	4 [9]	69 [9]	2400 ± 1200
Glazed ceramic box, Liao dynasty, China (083108-8)	2	10 – 12 AD	12.7	7.9 [12]	128.5 [12]	1010 ± 500
Gold cup with boar-shaped handle Outer Mongolia (2032)	6	1st AD	1.2	0.4 [13]	0.2 [13]	4500 ± 3000
Chain, Balkan (DL 808)	3	4th AD	1.2	0.8 [15]	<0.8 [15]	2700 ± 1300
Gold bowl, origin u.k. (AA)	5	3-4th BC	8.0	6.3 [11]	35 [11]	1650 ± 800
Golden figurine, Islamic (IG 1)	7	11-12th AD	0.85	0.9 [14]	0.8 [14]	1800 ± 1000
Golden figurine, Islamic (IG 2)	7	11-12th AD	2.0	6.2 [12]	126 [12]	170 ± 100

Table 3: Ancient gold objects
Tableau 3 : Objets en or anciens

* Time of manufacture adopted before U;Th – dating (BC: before Christ, AD: after Christ); u.k. : origin unknown to us.

Samples of the gold objects were obtained from: 1 private ownership; 2 Pieter Meyers (see Table 2), on behalf of a client;

3 Dieter Willers; 4 Alex Kossolapov; 5 Jack Ogden, on behalf of a client; 6 Melanie Roy; 7 Marianne Senn, on behalf of a client; 8 Ernst Pernicka, on behalf of a client.

U and Th measurements performed by: 9 Urs Krähenbühl (see Table 2); 10 adopted values (Eugster et al., 2009); 11 average values from Urs Krähenbühl and Jan Kramers; 12 Valerie Olive; 13 Ernst Pernicka; 14 Jan Kramers; 15 Stefan Röllin.

Ancient gold objects

The gold objects that could be confirmed to be ancient are compiled in Table 3. Based on the ^{4}He, U, and Th concentrations, their ages were calculated using the formula

$$T = [\,^4He\,] / (3.24 \times 10^6 [\,U\,] + 7.70 \times 10^5 [\,Th\,] + 4.02 \times 10^3 [\,Sm\,])$$

where ^{4}He is expressed in atoms per g and U, Th, and Sm in ppm. The U, Th – He age results are in years. For the derivation of this formula and for the decay constants of the radionuclides and their relative abundances we refer to our previous publication (Eugster *et al.*, 2009). Usually the main contribution of ^{4}He comes from U, whereas Sm contributes only a few percent to the total He. The estimated U, Th – He ages are consistent with the presumed date of manufacture of these gold objects. The experimental errors are up to 50% because in most cases the He, U, and Th concentrations are very low. The counting statistics for the measurements for each of these elements lead to an uncertainty of about 30%.

In the following, we discuss two objects in more detail: (i) as mentioned in section 2, the result for the signet ring of a Merovingian king was already presented in Eugster *et al.* (2009). In the present work, we obtain a more reliable age of 1460 ± 400 years, because U and Th concentrations are now available. This age is in good agreement with the time when the kings Childebert I and II lived. (ii) Two different samples of the Islamic figurine were analyzed for He and chemical elements, and two different U, Th – He ages were obtained. As outlined by Senn *et al.* (2009), the figurine is characteristic for the Islamic tradition and dated to the 11th or 12th century AD. Based on the trace element pattern, it can be inferred that the figurine derives from the area of Iraq

and Syria. The figurine is manufactured from a native gold-silver alloy, using copper as soldering material. The measured alloy compositions of the feet vary considerably. Therefore, it can be assumed that at least two different materials were used to manufacture the figurine or to repair it. Our dating of the figurine provides two dates, one to the period of 1800 ± 800 years ago, and a second one 170 ± 100 years ago (Table 3). The older material belongs to a sample taken from an area between the legs of the trousers, a section of the figurine that is well preserved. The younger material was taken from the spine, where the figurine is strongly damaged and where the elemental composition differs from that of the undamaged parts. It appears that repairs were carried out on the damaged spine in more recent times. In general, the natural scientific study confirms the results of the stylistic study (Senn *et al.*, 2009).

Modern and undatable gold objects

In Table 4, gold objects are listed that turned out to be modern or were undatable due to a He excess of unknown origin. For three objects, the He concentration was below the detection limit or extremely low, resulting in a modern date. One of these three objects is not specified in Table 4, as the owner did not give the permission to mention the details in this paper. Some objects yielded He concentrations, for which, together with the U and Th concentrations, an unreasonably high U, Th – He age was obtained. These objects must contain helium that was not completely outgassed when the object was manufactured. Among these objects are samples Java 1-4, for which, in an earlier report to the owners, we estimated an ancient origin. A more critical interpretation, after having found more similar cases

Object and origin (sample Nr.)	Obtained from *	Adopted century *	He 10^4 atoms/mg	U ppb	Th ppb	Estimated U,Th – He age
Large golden plate, origin u.k. (MG 4)	5	u.k.	b.d.	0.5 [14]	0.7 [14]	modern
Large plate with 10 human figures Liao dynasty, (083108-1)	2	10-12th AD	1.8	11 [12]	88 [12]	modern
Undatable objects, due to He rich inclusions						
Gold object JDM 1, Black Sea, Russia (JDM 2)	5	6th BC	860	5.4 [9]	69 [9]	-
Gold inlaid leopard, China (080406)	2	u.k.	400	12 [15]	3.9 [15]	-
Necklace of 32 gold beads, Outer Mongolia (3101)	6	4th BC	24	0.8 [13]	0.3 [13]	-
Buddha statue Avelokateshvara, Java (Ave 1-4)	p.c.	13th AD	7 – 5000	0.3 – 0.8 [13]	0.3 – 0.7 [13]	-
Gold objects (Java 1-4)	8	u.k.	6 – 24	0.14 – 7.12 [13]	0.38 – 12.2 [13]	-

Table 4: Modern and undatable gold objects
Tableau 4 : Objets en or modernes et non datables

Remarks: * see remarks to Table 4; u.k. unknown to us; b.d. below detection limit; p.c. private client.

of He excesses, led us to the conclusion that the Java 1-4 samples are undatable. This leads us to acknowledge that the U, Th – He dating method presented in this work for detecting forgeries in the market of antique gold objects is still far from being a reliable dating method. The reason for this are the extremely low He, U and Th concentrations, which are at the limit of being precisely determined by the presently available techniques. We observed that some antique gold objects contain inclusions, such as micron sized quarz and feldspar grains that did not completely release all He when the gold object was manufactured. Therefore, we plan to search for inclusions by electron microscopic investigations. On the other hand, it appears that in cases where the original material for the production of the gold object was already processed before, the dating method works fine. Examples are the Childebert signet ring, probably produced from Byzantine *solidi*, and the Napoléon gold coin. Knowing that gold is very often recycled, the determination of its chemical composition is not a final test for authenticating an ancient object, and dating, performed using the method presented in this work, may be necessary.

Acknowledgements

References

Eugster, O., 1996. Applications for noble gas analyses of gold. *Gold Bulletin* 29(3): 101-104.

Eugster, O., Kramers, J. and Krähenbühl, U., 2009. Detecting forgeries among ancient gold objects using the U,Th – ⁴He dating method. *Archaeometry* 51(4): 672-681.

Kossolapov, A.J. and Chugunova, X.S., 2002. Authenticating ancient gold using the U-He radiogenic clock, in R. Van Grieken, K. Janssens, L. Van't Dack, G. Meersman (eds.), *Proceedings ART 2002, 7th International Conference on Non-destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, 2-6 June 2002, Congress Centre Elzenveld, Antwerp, Belgium.* Antwerp, University of Antwerp, CD-ROM.

Kossolapov, A.J., Ivanov, A.P. and Kuznetsov, P.B., 1999. Helium radiogenic clock for dating of archaeological gold, in W. Mc Crone, D.R. Chartier, R.J. Weiss (eds.), *Proceedings SPIE, v. 3315, Scientific Detection of Fakery in Art.* San Jose, CA, SPIE, 16-20.

Senn, M., Flisch, A., Eugster, O., Günther, D. and Vonmont, H., 2009. Test report No. 450'588, EMPA Ueberlandstrasse 129, Dübendorf, Switzerland.

Shalem, A., 2002. A note on a unique Islamic golden figurine. *Iran* 40: 173-180.

Weber, A.G., (ed.), 2007. *Der Childebertring und andere frühmittelalterliche Siegelringe.* Köln, Weber.