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Test Report No 450'588-2

Test assignment:	**Expertise based on technical (CT, SEM/EDX, morphology) and chemical analyses (LA-ICP-MS, U, Th, -^{4}He dating method)**
Client:	Marco Grandi
Test object:	Gold figurine produced by granulation technique
Client's ref.:	E-mail, September 2008
Order dated of:	End of September 2008
Test object received:	September 2008
Test performed:	September 2008, January / February 2009
Number of pages:	10
Attachments:	-

Swiss Federal Laboratories for Materials Testing and Research
Dübendorf, 14. Mai 2012

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Accreditation
STS 137

ISO / IEC 17'025

1 General information of the customer

The figurine is in possession of the owner complying with legal requirements. German public authorities did confirm that. It was possible to have a look at the according documents. The figurine had been analysed by others in the past.

Fig. 1. Front and lateral view of the golden figurine.

2 Physical characteristics of the golden figurine

The figurine’s weight today is 24 g at a height of 7.3 cm (Fig. 1). Looking at the front side of the figurine its left shoe is broken off.

The figurine is entirely manufactured by the granulation technique. A view on the underside of the broken shoe reveals details of the manufacturing process. The metal substrate of the shoe is built of tubes soldered to a sheet. A ring consisting of six gold granules was soldered on the tubes (Fig. 2-4).

Fig. 2.Underside of the broken off shoe consisting of tubes and a sheet.

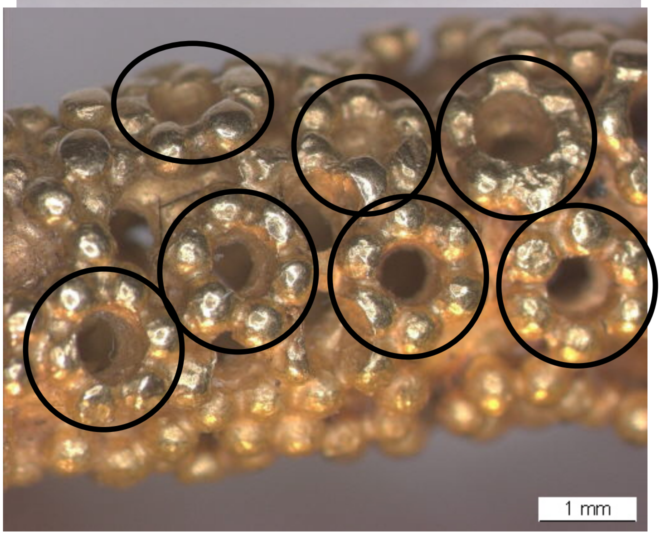

Fig. 3. Detail of the arm showing soldered groups of six gold granules.

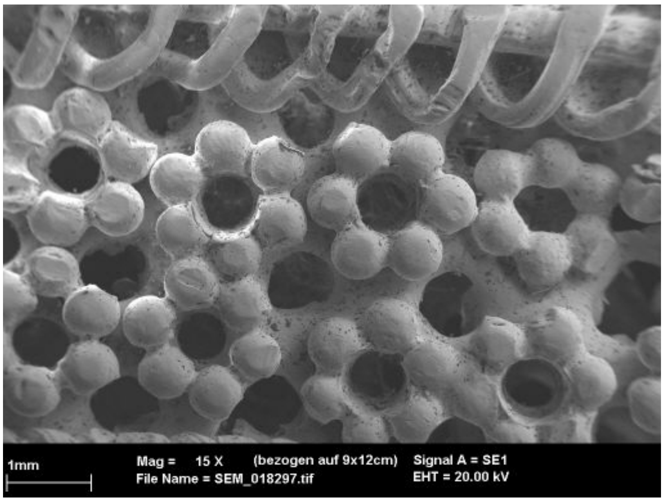

Fig. 4. Detail of the garment with middle fastener. Groups of six granules on a punched sheet. The fastener is manufactured from a wire lying about a wire (SEM-picture, SE-mode).

The figurine is damaged at various locations and partly broken off (Fig. 5). Computer tomography makes visible that the head and the right shoe are attached to the body. Reinforcing sheets become visible in the neck and between the shoe and the leg (Fig. 5-7).

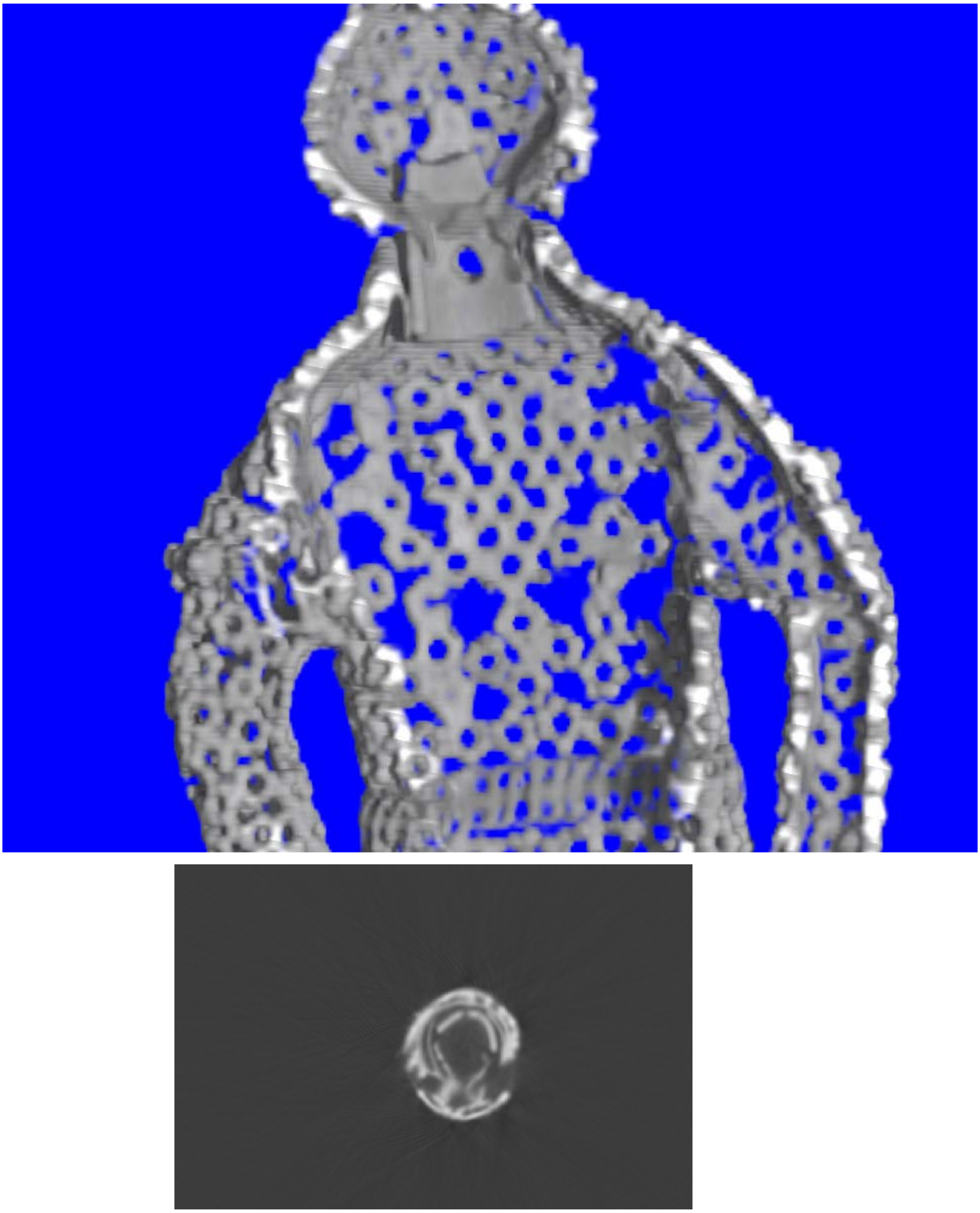

Fig. 5. Above section through a 3D reconstruction by computer tomography of the figurine. Bottom axial section through the neck.

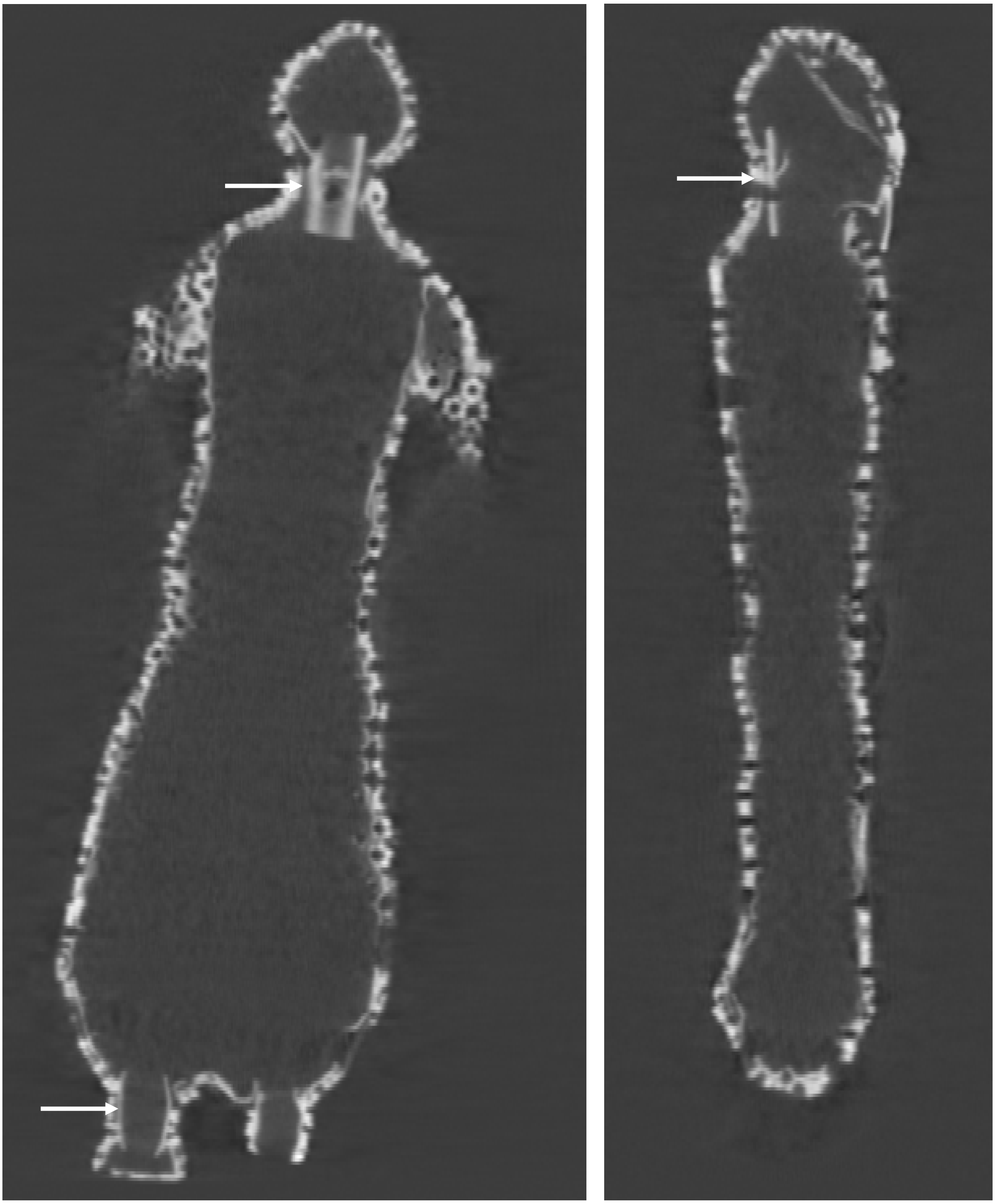

Fig. 6. Frontal and sagittal section through the figurine by computer tomography. A fixation sheet is visible between the spine and the back of the head. A second one is visible between the right shoe and the trousers.

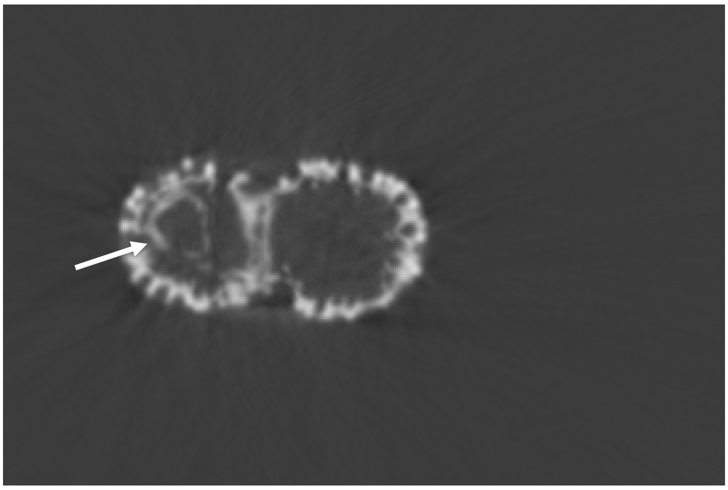

Fig. 7. Axial section through the leg by computer tomography. On the left side, a tubular sheet is visible connecting the feet and the trousers.

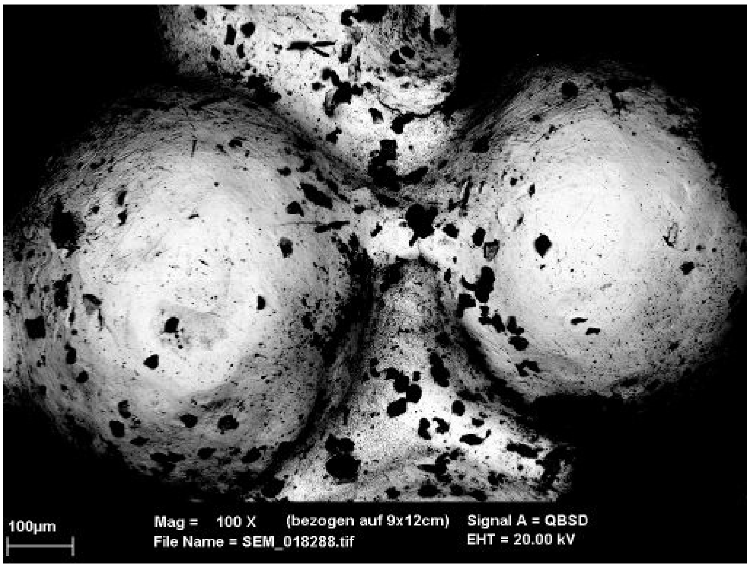

Fig. 8. The entire figurine is covered by an organic precipitate. The SEM picture in the back scattered electron mode (BSDE) indicates heavy elements in white colour and light elements in black colour. The metal alloy is white in this picture and the precipitate consisting of carbon and oxygen is black.

The figurine was also analysed by scanning electron microprobe (SEM; fig. 4 and 8). By this method a dark precipitate was detected covering the figurine. The elemental analyses did show carbon and oxygen (method energy dispersive x-ray EDX). Presumably the precipitate consists of an organic material.

3 Chemical analyses by laser-ablation with inductively coupled plasma-mass-spectrometry (LA-ICP-MS; Robert Kovacs, Prof. Detlef Günther, ETH Zurich)

Only the broken off shoe of the figurine was analysed with a Nd:YAG-Laser (Laser settings: Nd:YAG 213 nm, 4ns pulse width, fluence: 10 J/cm^2) coupled to an ICP-MS (Perkin Elmer SCIEX ELAN 6100 DRC II). In a first step a surface of 100 µm was pre-ablated. For elemental analysis, a lower surface of 50 µm was ablated.

Analysed site	Type of result	Cu	Ag	Au	Fe	Pb	Pt	Sn	Sb	Ni	Zn	As	Mn	Pd	Bi	Co
		%mass			mg/kg (ppm)											
granules (n=3)	Mean 1	7.1	15.2	77.3	4600	560	120	180	40	80	100	70	40	20	8	2
soldering (n=3)	Mean 2	7.9	17.3	74.3	3000	700	100	200	50	90	60	20	10	30	7	2
metal 1 (n=6)	Mean 3	6.8	15.8	77.1	3000	570	120	200	40	60	60	50	20	20	7	1
metal 2 (n=5)	Mean 4	6.5	18.4	74.8	700	1100	90	400	60	70	40	40	3	20	9	1
	RSD1 %	5	3	0.2	10	9	11	8	13	9	10	4	41	7	7	8
	RSD2 %	18	6	2	73	62	22	47	48	25	55	57	63	18	59	31
	RSD3 %	4	5	1	22	9	6	17	10	7	27	47	21	7	14	16
	RSD4 %	27	6	2	21	15	7	27	14	37	17	67	22	2	18	26

Tab. 1 Mean composition of the figurine’s parts analysed by LA-ICP-MS (n = number of analyses per mean, RSD relative standard deviation).

Besides the reported elements in Tab. 1 tellurium, selenium, cadmium, titanium and chromium were analysed as well. None of these elements could be detected at limits of DL in mg/kg Te <2, Se <5, Cd <2, Ti <2, Cr <4. The granules, the soldering joints between granules and metallic substrate and the metallic substrate itself were analysed several times. Totally 16 analyses were carried out. One data set is included in two mean values (mean 2, mean 4). The granules and the substrate metal 1 had a lower silver content than the soldering joints and metal 2, an other part of the substrate. The copper content in the soldering joints is only faintly higher than in the rest of the metal. The lead content increases with the silver content. The composition of metal 2 differs from that of metal 1, granules and soldering joints. Probably more than one starting metal was used for the manufacturing of the figurine.

4 Interpretation of the gold composition

In modern, well refined gold, the major impurities of silver, copper, palladium and iron exist at trace element level (Kinneberg et al. 1998). In the analysed gold figurine, the major impurities at trace element level are iron, lead, tin and platinum. The tin and platinum contents in the figurine are higher than in refined, modern gold (Sn typically at 10 mg/kg, Pt below detection limit). Silver is a main element in alluvial gold, but also tin and platinum are often found in it. Typical impurities are copper, tellurides and sulphides

(Chapman et al. 2002). Tin contents of several hundred mg/kg are typical for alluvial gold. With these findings, one can conclude that the figurine is probably manufactured from native or alluvial gold.

To further interpret the chemical composition of the metal, it is also necessary to discuss the manufacturing process. The gold granules are melted from gold particles and can be rather small (Wolters 1981). The process is based on the property that small metal particles tend to adopt a spherical shape by melting. The actual granules of the figurine have a diameter of 0.5 mm. This is a mean diameter compared to other granules varying between 0.14 and 2 mm. The granules were fixed by a glue (flour, gum arabicum or fish glue) on the metal substrate. The soldering is carried out by mixing the glue with a copper oxide. At temperatures of 850 to 950°C the copper is reduced and enriched in both, the gold or silver compound of the alloy (melting point gold 1063°C). During repeated heating the copper is dissolved uniformly in the gold alloy. In the end, the soldering joints have a similar composition like the rest of the metal. This process is called reaction soldering. A gold alloy with some silver content or mint silver are often used as starting material.

The oldest artefacts made with such granulation technique came from the city of Ur in Mesopotamia and date back to 2500 BC. Early objects are made of silver-rich granules on a copper-rich metal substrate (2nd millennium BC), while younger European objects (7th cent. BC, Etruscan) show a uniform distribution of all the elements gold, silver and copper (65-70 %mass gold, 30 %mass silver 5-8 %mass copper, 2 %mass others). There are no colour differencies of the substrate, the soldering joints and the granules of the examined figurine. This is confirmed by the scanning electron microprobe pictures in the BSDE-mode. The used BSDE-mode differentiates between heavy and light elements. The alloy of the figurine is similar to that of younger, European objects.

Comparing the chemical composition of the figurine and of gold coins from the Arab Empire (North Africa, Egypt, Near East) dating between 660-1170 AD no complete correlation can be found (Gondonneau and Guerra 2002). The gold content of the figurine varies between 80-84 %mass, if the copper content is subtracted. The Arabic gold coins, on average have a higher gold content, except few coins. There is a certain similarity with Abbassid gold coins from Bagdad, Iraq with comparable Pb-, Pt- and Zn-contents and from different Syrian mints which had comparable As-, Pd-, Pt- and Zn-contents. The comparison is based on the elements As, Pb, Pd, Pt, Sb, Sn and Zn.

5 Dating of the gold by the uranium, thorium-^{4}helium method (Prof. Otto Eugster, University of Bern)

To date the figurine, two samples (IG 1 and IG 2) of 20 mg were chosen. IG 1 was taken between the legs of the trousers, IG 2 on the spine of the figurine.

The dating method is based on the known decay rate of uranium, thorium, and samarium to ^{4}Helium (Eugster 2008). All native gold alloys contain uranium and thorium. Certain uranium isotopes decay to lead via emission of alpha-particles (^4He). The samarium-isotope ^{147}Sm is, to some restricted degree, also involved in the formation of ^4He. The helium isotope is collected in the gold till melting is taking place. When the metal becomes liquid, helium escapes and the decay restarts.

A 10 mg sample was etched by aqua regia to extract pollution before analysing helium in the physical institute of the University of Bern. Subsequently the sample was rinsed with acetone and dried. The helium analysis was carried out with a mass spectrometer type SPECTRON, St. Petersburg, adapted to analyse the small quantities of helium. The uranium, thorium and samarium contents were obtained on 5 mg samples in three different laboratories (see table 2) with inductively coupled plasma mass spectrometry (ICP-MS).

Sample	helium concentration 10^4 atoms/mg gold	uranium µg/kg (ppb)	thorium	samarium	age years
IG 1 received aug. 2008	0.85 ± 0.50	0.9	0.8	300	1800 ± 1000
IG 2 received jan. 2009	2.0 ± 1.0	6.2	126	20.5	170 ± 100

Relative standard deviation of the U, Th and Sm analyses ca. 30%.

Helium analyses: Otto Eugster, Physical Institute of the University of Bern

Uranium, thorium and samarium analyses: Stefan Röllin, AC Zentrum Spiez
Jan Kramers, Geological Institute University of Bern
Valerie Olive, SUERC Kilbride Schottland

Tab. 2 Results of dating by U/Th-^4He method of two samples of the Islamic golden figurine.

6 Judgement of the golden figurine

The present study based on natural scientific analyses confirms the manufacturing of the gold figurine from a native gold-silver alloy using copper oxide as soldering material. The measured alloy compositions of the shoe vary considerably. We therefore assume that at least two starting materials were used. Based on the composition of the trace elements one can assign the figurine to the area of Iraq and Syria. The dating of the figurine gives two data, one in the period of 2800-800 BP (before present) and a second from the period 270-70 BP. The younger materials belong to the sample taken from the spine. The spine of the figurine is strongly damaged (Fig. 5), while the region between the legs of the trousers, where the other sample was taken, is well preserved. It can be imagined that some repairs were carried out on the damaged spine in younger time. In this context the question arises if the fixation sheets of the head and the shoe made visible by computer tomography were repairs with a similar dating (fig. 5-7).

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