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Experimental reproduction of artificially patinated alloys, identified in ancient egyptian, palestinian, mycenaean and roman objects

Riassunto

Leghe a base di rame identificate in oggetti antichi, patinati artificialmente e ageminati con metalli in colore contrastante, sono state riprodotte in laboratorio. Gli oggetti antichi per i quali questi materiali sono stati impiegati provengono da diversi contesti archeologici, quali ad esempio l'antico Egitto, la Palestina, Micene ed i territori dell'impero romano, ma simili leghe, più recenti, sono note, da alcuni paesi dell'Asia.
Durante gli esperimenti sono state riprodotte leghe di composizione diversa e sono state trattate seguendo ricette e indicazioni tramandate da vari testi antichi. In molti casi le informazioni ottenute in Cina ed in Giappone, studiando gli oggetti, le tradizioni popolari e i consigli offerti dagli specialisti locali sono stati di grande aiuto per la comprensione di testi di difficile interpretazione. I risultati degli esperimenti sono illustrati nella relazione.

Parole chiave: *Patinatura artificiale, Corinthium aes, Hmty km, Shakudo, Kyanos*

1. Introduction

In 1993 the first detailed scientific studies on the discovery of *shakudo*-type alloys in the Classical World (GIUMLIA-MAIR, CRADDOCK 1993a; b; CRADDOCK, GIUMLIA-MAIR 1993) were published in German and English and followed an earlier short paper by Craddock (1982), on the analysis of the very first ancient object made of this material, which had been scientifically identified.
Before this discovery, all black decorations on metal were indiscriminately considered to be *niello*, a glassy, decorative black material consisting of different kinds of metal sulphides, used as inlays on metal objects. However the earliest examples of *niello* are dated to the 5th-4th c. BC (cfr. GIUMLIA-MAIR, LA NIECE 1998; GIUMLIA-MAIR 1998a; 1998b; 2000a), this material became common only in Roman times (MOSS 1953; MARYON 1954, pp. 161-165; SCHWEIZER 1993, pp. 171-184; LA NIECE 1983) and its nature is very different from that of the patinated alloys investigated here. The distinctive material discussed in this paper is a copper-based alloy with small amounts of gold, silver and often arsenic and iron, which, after a patination treatment, acquires a permanent, shiny and compact purple-black patina and it is very similar to the most famous Japanese *irogane*-alloys: the blue-black or purple-black *shakudo*. The first studies mentioned before, identified it as the metal employed for several Egyptian, Mycenaean and Roman objects, however the earliest instances of *shakudo*-type objects, identified later, are Egyptian and Palestinian and are dated around the mid 19th c. BC (GIUMLIA-MAIR 1995; 1996a; 1996b; 1997; GIUMLIA-MAIR, QUIRKE 1997; GIUMLIA-MAIR, RIEDERER 1998). The technique spread in later centuries all over the Roman Empire and desappeared at some point in Late Antiquity.
After the publication of the first discoveries on black patinated objects the interest of more scholars in this material was awakened and several analyses of black decorations were published in the last few years (PHOTOS JONES *et Alii*, 1994; DEMAKOPOULOU *et Alii*, 1995; STAPLETON *et Alii*, 1995; GIUMLIA-MAIR 1995; 1996a; 1996b; 1997; 1998; 2000b; GIUMLIA-MAIR, LEHR 1998a; 1998B; CRADDOCK 1998). These studies demonstrated the existence of black patinated copper-based alloys with small quantities of gold and silver in the West, from the middle of the beginning of the second Millennium BC to the Medieval Period. Further, several ancient fakes or imitations of the original precious material have been scientifically determined (GIUMLIA-MAIR in print). These are dated mainly to Roman times.

2. Aim of the experiments

As mentioned before, the earliest objects made of this material, scientifically determined up to now, are dated to the mid 19th c BC. These

are a statuette of the pharao Amenemhat III and a crocodile statuette, both found at el-Faiyum and the slightly later scimitar from Balata Shechem (Palestine) in the Ägyptische Sammlung München (GIUMLIA-MAIR 1996 a; 1996b). The statuette of Amenemhat III in the Ortiz collection in Geneva (ORTIZ 1994 and 1996, N° 37) contains small amounts of gold, but also of other metals. The recently cleaned portrait of the pharao shows a purple-black, iridescent and shiny patina; without any doubt it is the best preserved seen by the authors up to now on ancient objects. The statuette is also the largest (H.: 26.5 cm) ancient object of this material discovered up to now. Other examples are mostly of relatively small size and inlaid with other metals in contrasting colours or, in some cases, the objects are of copper-based alloys, inlaid with the artificially patinated alloy, which was obviously a rare and precious material.
The bronze crocodile from el-Faiyum, also dated to the 19th c.BC (Ägyptische Sammlung Munich, 6080), has a deep black colour, is inlaid with electrum and contains gold and small amounts of other metals (GIUMLIA-MAIR 1996a; 1997). Also this exceptional piece has been recently and carefully cleaned.
It is important to note, that most ancient objects made of this material were found several decades ago and there is often no way to know which sort of cleaning and conservation treatments were carried out on their surface (cfr. also CRADDOCK, GIUMLIA-MAIR 1993b). Former, not documented, or insufficiently documented conservation might have changed the appearance of the surface. Therefore it is always uncertain if we are dealing with the original patina or not. However in the case of the Amenemhat III statuette and of the crocodile from el-Faiyum the cleaning processes are clearly documented in all stages and we can be sure, that what we see now is indeed the original patination.

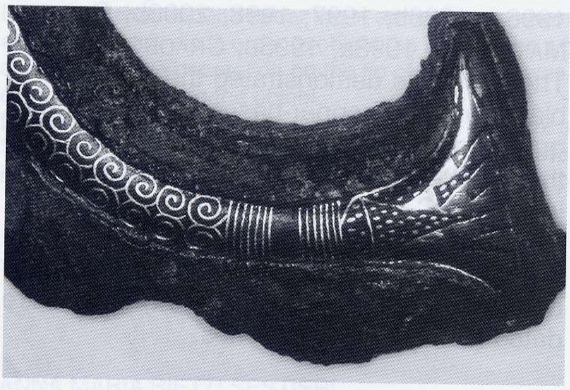

Fig. 1 The Syro-Palestinian sword from Balata Shechem Ägyptische Sammlung Munich (inv. 2907), ca. 1750 BC, is one of the 3 most ancient pieces made of a shakudo-type alloy (Photo Giumlia-Mair)
La spada siro-palestinese da B.S., ora nell'ÄSM è uno dei 3 pezzi più antichi prodotti in una lega di tipo shakudo

The broadly contemporary Syro-Palestinian sword from Balata Shechem, now in the Ägyptische Sammlung Munich (inv. 2907) *(fig. 1)* is of particular interest, because of the clear differences in the composition of the blade of bronze (with around 12% Sn, no Au and only very low traces of other metals) and the blue-black midrib, with 0.5% Au and noticeable amounts of other metals (in particular around 3% As) (GIUMLIA-MAIR 1997; GIUMLIA-MAIR, RIEDERER 1998).
The differences in composition and the presence of low amounts of non-precious metals in the patinated alloy suggested that these small amounts were deliberate additions and induced to wonder wether the ancient artisans were able to control the colour nuances of the patina by adding small amounts of metals (other than gold and silver) to their alloys.
In earlier years, the Japanese scholar Denzo Uno (1929) had carried out several patination experiments on the Japanese alloy *shakudo*, which had evidenced the importance of the low percentages of gold in the formation of the patina. Only alloys containing gold developed a deep black, shiny, resistant and compact patina. He produced a large number of test alloys, containing copper, around 3-5% Au, and different amounts of other metals, and treated them with several aqueous solutions containing different salts. His experiments seemed to indicate that the presence of minor alloying elements might influence the colour nuances of the patina.
The interesting results of his work, published in German, in an old metallurgical review dedicated to corrosion and corrosion protection, and quite difficult to find, seemed to confirm the observations, which resulted from the analyses of ancient works of art.
The authors decided to continue his research by applying similar methods of approach.
Several studies on *shakudo* and other *irogane*-alloys, were published in the last decades, (NOTIS 1988, MURAKAMI *et Alii* 1988; LA NIECE 1990, 87-94; MURAKAMI 1993 with further bibl.), how-

ever, after Denzo Uno, nobody had ever tried out a docimastic approach to the problem. Further, no experiments had ever been carried out on alloys similar to those determined in ancient objects (which are partly slightly different from the oriental alloys. In particular the amount of Ag and Au are normally lower) and, by using the methods described by ancient authors and in different texts, belonging to different civilisations and periods.
The authors reproduced binary, ternary and polimetallic copper alloys containing small amounts of Au, Ag, As, Fe, Sn and Pb, similar to the ancient alloys and tried out different working processes, chemical baths with solutions of different composition and several patination processes, as they can be drawn or inferred from Egyptian, Greek, Latin and later sources, which discuss or mention the production of black bronzes.

Fig. 2 Egyptian black patinated statuette, most probably a pretty example of "black copper" (hmty km) with gold inlays (Photo Los Angeles County Museum of Art, Courtesy of P. Meyers)
Statuetta egizia patinata di nero, probabilmente un grazioso esempio di "rame nero" (hmty km), con agemine in oro

3. Early evidence and ancient texts

The information we can gather from the archaeological material and the literary sources is thinly spread and has to be looked for in the strangest places and texts, because only very few ancient documents really give technical details on metals and alloys: the topic was not considered worth of being mentioned and most artisans were illitterate anyway. The only real metallurgical recipes we know from antiquity are the texts of the alchemists (BERTHELOT 1888) and the Leyden and Stockholm italies (HALLEUX 1981), with short notes and workshop recipes of Egyptian artisans.
The earliest references to a material named in Egyptian *hmty-km* "black copper", our material, *(fig.* 2*)* occur in the hieroglyphic inscriptions of kings and the highest officials during the mid-Eighteenth Dynasty, 15th c.BC (cfr. GIUMLIA-MAIR 1995, GIUMLIA-MAIR, QUIRKE 1997); such inscriptions are almost entirely lacking for the late Middle Kingdom, whereas they are abundant from the 18th Dynasty, beginning particularly in the reign of Thutmose III. To the latter reign belong two texts, which give a provenance for objects made of "black copper": a vessel of silver, gold and "black copper" is among items brought by men in Aegean garb from a place named Keftiu, generally identified as Crete (Urk. IV 1090, tomb-chapel of the first minister Rekhmira; Schoske 1984.); and the campaign annals inscribed in Karnak temple record for items brought from Syria -Palestine, in his 23rd year, objects of "black copper" among other precious materials (Urk. IV 744). These two references indicate a wide Eastern Mediterranean distribution of the finished products in the material "black copper" by the second half of the 15th c. BC. This also reflects the general knowledge we can gather for example from the archaeological finds at Ugarit, the archives at Mari and the linear B texts, which testify close trade- and cultural connections between the Aegean and the Near Eastern populations (for example THIMME *et Alii* 1980, 143-155).
Most texts on archaeology and history of art suggest that this technique came in the time around the middle of the 2nd Millennium BC from the Near East, Syria or Mesopotamia (COONEY 1966; 1968; HIGGINS 1974, pp. 140-141; HOOD 1978, pp. 178-181; LAFFINEUR 1990-91; DICKINSON 1994), but now the analy-

Fig. 3 Spring Peirene at Corinth: Pausanias (2, 3, 3) stated in the 2nd c. AD, that Corinthian bronze was patinated in its water (Photo Lehr)
Fonte di Peirene a Corinto: Pausania (2,3,3) scrisse nel II sec. d.C. che il bronzo corinzio veniva patinato in quest'acqua

ses of the Amenemhat III and of the crocodile statuette have shown the early use of black-patinated alloys. The absence of earlier mentions of *hmty-km* in Egyptian texts must be due to the lack of descriptions of material and not to the absence of black patinated objects of *shakudo*-type. This shows again quite clearly that negative evidence in archaeology cannot be taken as a proof for the non-existence of any archaeological material.
A few passages in ancient texts dated to various periods give us some hints about the patination processes and the composition of the metal, but all of them, with one exception, are rather vague, seem to describe materials and processes, which partly differ from those of the Japanese production and, before the experiment, it was impossible to understand what they meant.
One of the most important ancient mentions of this material, is dated to the 2nd c. AD and is found in the "description of Greece" by Pausa-

Fig. 4 Jacobite Syriac translation of the texts of the Egyptian alchemist Zosimos, 2nd c.AD, with several variations of recipes for the production of shakudo-type alloys (Photo Univ. Library Cambridge)
Traduzione giacobita in siriaco dei testi dell'alchimista egiziano Zosimo (II sec. d.C.) con diverse varianti di ricette per la produzione di leghe di tipo shakudo (foto dell'Università di Cambridge)

nias (ΕΛΛΑΔΟΣ ΠΕΡΙΗΓΗΣΙΣ, 2,3,3). The Greek author visited Corinth in 165 AD and stated that "Corinthian bronze, made red hot and incandescent is dyed by means of the water of the spring Peirene" *(fig. 3)*.
In the Japanese treatment the objects are put into a hot aqueous solution instead.
Clemens Alexandrinus, a Roman Egyptian scholar describes the statue of the god Serapis in Alexandria and states that the artist Bryaxis employed an alloy containing gold filings, silver, copper, iron, lead and tin and that "*...after the polishing and assembling of all parts he dyed it with kyanos and, for this reason, the colour of the statue is almost black*". (Protr. 4, 43P; authors transl. Cfr. GIUMLIA-MAIR 1997, pag. 12).
Some of the Japanese recipes recommand to carefully avoid contamination with iron, but here iron is mentioned as element of the alloy.
The medieval scholar Bar Bahlul, collected alchemistic texts and wrote an alchemistic Lexicon in Syriac. He also gives lists of metals, alloys and other substances and describes briefly their composition (BERTHELOT 1893, II, XVI, 1 pag. 23). Among other alloys there are also more definitions of Corinthian bronze (the name of these alloys in Roman times). One states that it is an "*alloy of iron and other kinds (of metals)*", a second one that it is "*a mixture of gold, silver, iron and other things*" (I, *Kings*, VII, 45).
Here iron is mentioned twice and indeed, in

most ancient objects analysed, some iron was present in the alloy.
Chinese descriptions of the production of *wu tong*, the Cinese name for this material, describe a patination method, carried out just by holding the objects in the hands (GIUMLIA-MAIR, CRADDOCK 1993a; CRADDOCK 1996, pp. 81-82), however in most descriptions of the Japanese process the artisans are warned NOT to touch the surface with the hands, because it would spoil the formation of the patina. In the same way Japanese collectors prefer not to touch their pieces with bare fingers.
Latin texts mention that collectors of Corinthian statuettes used to carry them around (PLINIO, Naturalis Historia, 34, 48) and spent most of their days with their "rusty metal sheets" (*in aeruginosis lamellis*) (SENECA, *De Brevitate Vitae*, 12,2). The emperor Nero carried about an Amazon statuette and G. Cestius had his statuette with him even in battle (PLINIO, *Naturalis Historia*, 34, 48). Apparently they had no problem in handling their beloved statuettes.
As mentioned before only one text gives an exact description of the process. *(fig. 4)* This is the Syriac translation of recipes of the Egyptian alchemist Zosimos from Panopolis, who lived in Alexandria in Egypt in the 2nd c.AD. One of the authors came by chance across the French translation by the great French chemist and humanist Berthelot (BERTHELOT 1893, II, pag. 223) and is now, since several years, studying the text in detail together with E. Hunter, Cambridge University. Part of this study is going to be published shortly (GIUMLIA-MAIR in print b; HUNTER in print). Some passages, which are important for the experiments should be quoted in this paper.
The first line says that the recipe is for preparing "*Corinthian bronze or black metal stripes*". The text gives in weight the exact recipe (1 mina of Cu, 8 drachmas of Au and 8 drachmas of Ag = 82,6% Cu, 6.9% Au, 6.9% Ag) for the preparation of the copper *"which is used for the process of colouring"*. A complex process, involving several stages is described in the following lines. Among other things, the copper should be mixed with sulphur to form a black compound and then reverted to metal, by strongly heating the mixture to get rid of the sulphur. A process of this kind is not mentioned in any other text on the production of *shakudo*-type alloys. In the Syriac text there are also many more recipes for alloys containing gold and silver but also different amounts of other metals, such as lead, arsenic (in form of realgar or orpiment) some iron compound and tin, which are not mentioned in any other description.

Fig. 5 Chemical baths employed in the experiments for the reproduction of patinated alloys, containing gold, silver and other metals (Photo Giumlia-Mair)
Soluzioni chimiche usate negli esperimenti di riproduzione di leghe patinate, contenenti oro, argento e altri metalli (foto Giumlia-Mair)

4. Experimental procedure

The experiments described in this section were carried out in the workshop of the Gold-und Silberschmiedeklasse, Akademie der Bildenden Künste, Nürnberg and in the laboratories of the Department of Materials Engineering and Applied Chemistry of the University of Trieste. The authors decided to start with the easiest steps, i.e. to try out the Japanese recipes as they are given in modern metallurgy texts on Japanese techniques (BUCHNER 1914, pp. 196-197; KRUPP 1922, pp. 378-379; UNO 1929; UNTRACHT 1982; LA NIECE 1990, pp. 87-94) and the recipes, which were described in detail to the authors by Japanese specialists at the Tokyo University and at the Kyoto Academy of Art. They are reported in the next paragraphs. *(fig. 5)*

Modern Japanese recipes:

Rokusho 1

Copper acetate	$Cu(C_2H_3O_2)_2 \times CuO$	6 g
Calcium carbonate	$CaCO_3$	2 g
Sodium hydroxide	$NaOH$	2 g

Dissolve in 150 ml aq. dest. in a pyrex container and allow the solution to stand ummolested for a week or more. Siphon off the clear liquid on the top and add one liter aq. dest. Mix and store sol. for future use. When ready for use add 2 g of copper sulphate to this amount.

Rokusho 2
Cu acetate, Cu nitrate, cupric chloride, copper sulphate,

Rokusho 3
Cupric acetoarsenate, Copper sulphate, Dest. Water

Rokusho 4

Copper acetate	$Cu(C_2H_3O_2)_2 \times CuO$	60g
Copper sulphate	$CuSO_4 \times 5H_2O$	60g
Acetic acid	CH_3COOH	½ gallon

Use vinegar diluted 4,5 - 12 % with water.

Rokusho 5

Copper sulphate	$CuSO_4 \times 5H_2O$	60g
Salt:	NaCl	22 grains
Water		2 ½ oz

Boil these together than cool the solution before use. The metal must be absolutely clean and polished as before gilding. After the cleaning operations boil the work in water, rinse in pickle, than in running water or dest. water. Rub the surface with fine pumice by using a clean bristle brush. Rinse. Do not touch it with the fingers. Attache a copper wire for handling. Place in destilled water. Use only wood, copper, glas, plastic. No iron!!

Mix all ingredients until they are all well dissolved and work at suggested temperatures. Worked metal colours more easily than cast metal.Grate about 1 pound of daikon (Japanese horse radish), save the juices add 5 parts of water. Heat rokusho in large and deep Cu pot to about 37,7°. Do not let it boil!

Move the piece constantly, check it, never let it get dry. Remove after 10 min. and immediately cover surface with *daikon* and rub gently. Than rinse, rub with baking soda, then with pumice and rinse again. To deepen the colour return the object to solution. Remove after a minute, rinse and repeat several times. Finally bring solution to boil and leave obj. suspendend in solution until it achieves the desired colour. Remove, rinse, dry. Coat surface with oil or hot wax. Rub off the surplus with a soft cloth.

5. Experiments (see also Table)

The first try was carried out on samples of 4 different alloys:

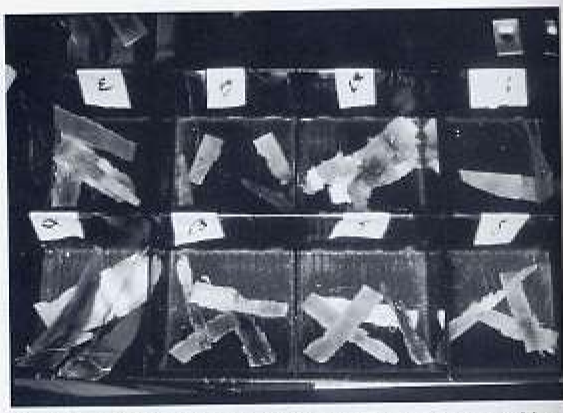

Fig. 6 Batches of samples of different composition, worked in different ways and marked with Greek letters to distinguish the various treatments. Some are already patinated (Photo Giumlia-Mair)
Gruppi di campioni di composizione diversa, diversamente lavorati e contrassegnati da lettere greche per distinguere i vari trattamenti. Alcuni sono già patinati

1% Au - 99% Cu
1% Au - 1% Ag - 98% Cu
3% Au - 97% Cu
3% Au - 1% Ag - 96% Cu

The alloys were prepared on a hollowed piece of charcoal, sprinkled with borax, melted down, cooled in water. The samples were cleaned in nitric acid, hammered and annealed several times and than rolled. This is the reason of the parallel lines sometimes visible on the back of the experimental specimens. This procedure is not recommended for decorative objects, but is sufficient for experiments. Part of the specimen were annealed as last working stage, a batch of samples was also cooled in water, to check the behaviour of pieces worked in different ways. *(fig. 6)*

The pieces of sheet were cut into stripes to be treated in different solutions and with diffferent methods. The first batch of specimens was cleaned by rubbing it with finely grinded marble powder mixed with *diatomeae* and not polished. At the end of the experiment the surface of the unpolished samples was rough and irregularly stained. Other specimens were polished as it was done in antiquity, by using a smooth piece of carnelian (of course any piece of compact and polished ornamental stone of the quarz group or for example a piece of haematite, would be suitable), the rest was mechanically polished with common jeweller's instruments.

The solutions used were taken from Japanese recipes, but also water fom the spring Peirene was brought to Nuremberg and used for what we called the "Greek method". A further solution recipe was taken from the Syriac text: about 10 gr verdigris were dissolved in apple vinegar. This was called "Zosimos' method". For the "Greek method" a second batch of samples with both, the same composition of the first samples, but also with new alloys containing small amounts of other elements identified in the ancient pieces (i.e. Fe, As, Pb, Sn), were prepared to be treated in the water of the spring, expressly brought from Corinth, to try out Pausanias' recipe. Samples with the same composition of those of the first group were

Sample Nr.	Composition									
	Cu	Au	Ag	As	Sn	Fe	Pb	Workability	Colour after 1/2 hour	Colour after 1 hour
1	99,0%	1,0%						cracks and casting faults	black purple	black purple, blue iridescent
2	97,0%	3,0%						good malleability	grey-brown	dark grey-black, purple-blue iridescent
3	80,0%	20%						high malleability	no patination	brightly coloured iridescence after heating
4	99,0%		1,0%					malleable	brown	dark brown, purple-blue iridescent
5	97,0%		3,0%					good malleability	grey-green	dark grey, purple iridescent
6	99,5%			0,5%				brittle, with cracks	reddish and light blue iridescent	brownish-red and bluish iridescent, patchy
7	99,0%			1,0%				patchy, porous, cracks under hammer	brown	dark brown and slightly iridescent blue
8	98,0%				2,0%			good malleability	reddish	dark orange-red
9	99,5%					0,5%		malleable with some casting faults	reddish-brown	porous, red-purple
10	98,0%						2,0%	porous, patchy	coppery red	brownish red
11	98,0%	1,0%	1,0%					malleable but some cracks under hammer	purple-black	purple-black, blue indescent
12	96,0%	3,0%	1,0%					low malleability, cracks and casting faults	purple-black with some iridescent green	blue-black, silvery
13	98,5%	1,0%		0,5%				malleable, but some cracks	purplish	dark purplish-black and bluishiridescent
14	98,5%		1,0%	0,5%				some cracks, fair malleability	grey-blue	dark blue, silvery iridescence
15	97,5%	1,0%	1,0%	0,5%				malleable, but some cracks	dark grey and silvery iridescent	dark blue and silvery iridescent
16	96,0%	1,0%	1,0%		2,0%			excellent malleability	homogeneous, black-purple	shiny, compact; black-purple iridescent
17	96,5%	0,5%	1,0%		2,0%			high malleability	deep black	deep black, slight blue iridescence
18	94,0%	3,0%	1,0%		2,0%			lower malleability, tends to spatter, brittle	speckled, purple-black	purple-black, blue iridescence
19	95,0%	1,0%	1,0%		3,0%			good malleability	grey	dark grey, greenish iridescence
20	94,0%	1,0%	1,0%		4,0%			good malleability	dark grey	dark purple grey, blue iridescence
21	86,0%	1,0%	3,0%		10,0-%			good malleability, increased working time	dark grey	deep black,matt
22	97,5%	1,0%	1,0%			0,5%		fairly malleable, some casting faults	speckled, brown - purple	irregular patina, purple -grey, silvery
23	95,5%	3,0%	1,0%			0,5%		brittle, fragile, not workable	purplish	dark silvery black
24	95,5%	1,0%	1,0%	0,5%	2,0%			high malleability	dark purple and pale blue iridescent	dark purple and blue iridescent
25	96,0%		1,0%	1,0%	1,0%		1,0%	fair malleability	greyish	purple grey, purple blue iridescence
26	96,0%		1,0%		1,0%	1,0%	1,0%	low malleability, cracks, casting faults	yellowish green	shiny, light purple red
27	95,0%	1,0%	1,0%	0,5%	2,0%	0,5%		good malleability	light purple and blue iridescent	purplish and silvery-blue iridescent
28	93,5%	1,0%	1,0%	0,5%	2,0%		2,0%	high malleability	irregular dark patina, patchy	purplish and blue black iridescent

also prepared, to be treated red hot in the cold solution employed for the "Zosimos method".
A batch of alloys, containing only different amounts of Au were also prepared, to be patinated by the "Chinese method": 15 persons of different age, from 6 to 75, held the samples in their hands for several hours.
3 samples made of unalloyed copper and of alloy nr. 2 (see table) were also treated with lanoline mixed with verdigris, to try out a further method by Zosimos in which an "ointment" spread on the surface of the objects is involved. By all other methods we were able to achieve an acceptable patination, but not in this case. Samples containing gold became only grayish and spotty, while copper did not show any "blackening" on the surface. Most probably better results might be achieved by this method, by trying out mixtures in other concentrations or by varying the patination time and the ingredients, but many more experiments would be necessary.

6. Discussion of result

The best patination results were achieved in general on repeatedly hammered and annealed pieces. As mentioned before, rolled specimens showed irregularly patinated stripes.
The polishing of the surface is an important phase of the process: not polished samples

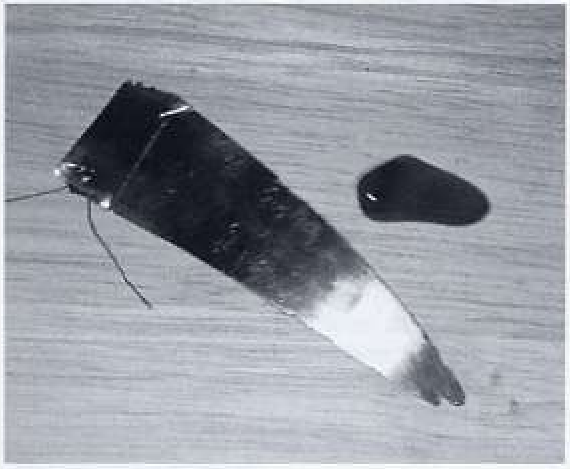

Fig. 7 One of the lab specimens polished as in antiquity with a smooth piece of carnelian. This working stage is very important for the development of a shiny and compact patina (Photo Giumlia-Mair)
Uno dei campioni da laboratorio lucidato come nell'antichità con un pezzo levigato di corniola. Questa fase di lavorazione è molto importante per lo sviluppo di una patina lucente e compatta

resulted black, after the chemical bath, only on the numbers and letters scratched or punched on the surface, to distinguish the different alloys; i.e. without some degree of work on the surface no patination happens. The polishing method does not seem to be important: no difference was noticeable between samples polished by hand with a semiprecious stone, as in antiquity, and samples polished by means of modern jeweller tools. *(fig. 7)*
The addition of small amounts of silver and non precious metals affects the properties of the alloy in different ways, depending on the amount of other elements present in the alloy (see table). In general, the addition of other metals reduces the crystal size after repeated hammering and annealing and this, together with an abrasive finishing of the surface improves and speeds up the formation of the patina. After each immersion in the hot solution (not boiling as stated in several texts!) each piece was energically brushed with a rough synthetic sponge to remove the loose layer of black tenorite and allow a regular "growth" of the shiny and compact patina underneath.
Alloys with more than 3% Au were not employed for the experiments, except in one particular case, because higher amounts of precious metal were never identified in ancient objects, which had been analysed with reliable methods.
It is important to note that surface analysis methods, such as XRF and SEM/EDX, tried out on patinated samples, gave mostly distorted results, which could vary on the same piece from 0 to very high percentages, much higher than the percentages actually present in the alloy. Bulk analyses by AAS were also carried out on the same samples. As expected, no variation in the composition of the patinated samples was noticed after treatment. Too high or too low results were clearly due to the inadequacy of surface analysis methods.
Metallographic samples were taken from several differently worked, patinated specimens. The structures did not show any anomalies, but were those, typical of respectively hammered, hammered and annealed, rolled or simply cast copper alloys.
The low amount of tin present in the alloys is already sufficient to give better working and casting properties to the metal, but does not change the colour of the copper before patination. This readily explains the Egyptian appel-

Fig. 8 The grandson of Su Jincheng, last famous wu tong worker, in his house with his own grandson, in the town Shiping (Yun Nan, China) (Photo Giumlia-Mair)
Il nipote di Su Jincheng, l'ultimo famoso artigiano del wu tong, nella sua casa, nella città di Shiping (Yun Nan, Cina)

lation *hmty km* - black copper, (not bronze) - for the material.
The presence of silver in the Japanese *shakudo* alloy has often been discussed and it has long been established, that this element is present in the alloy as a deliberate addition, but without understanding its significance. Similarly the low percentages of arsenic in the objects were explained as the consequence of the use of *shirome* (a speiss containing copper, lead, arsenic and antimony) or *yamagane* (natural impure copper containing arsenic) (GOWLAND 1894, WAKAYAMA, SATO 1974), but the rather pure copper used for many *shakudo* objects did not seem to confirm this hypothesis (LA NIECE 1990). The low iron content has been explained as impurity present in *shirome* or simply ignored.
The low lead content influences the properties of the alloy, as already very little amounts of this element dramatically improve the casting properties of the metal. In particular the fluidity of the alloy in molten state reaches its maximum point with only 2% Pb. Small amounts of lead can also come as an impurity from the copper ore, but the purity of the metal employed for other, not patinated parts of the objects seem to confirm that the presence of the lead in the alloy was deliberate.
Silver, tin, arsenic and lead affect the colour of the patina. Higher amounts of these elements only deteriorate the patination properties of the alloy. In particular an iron content over 5% considerably slows down the patination process. Annealed objects with large grains cannot be as easily patinated as objects with a more homogeneous and finely recrystallized metallographic structure; their patina is irregular and scales off easily. An addition of 1% of silver changes the colour from black to purple, as does an addition of 1% of arsenic. An addition of 1% of iron changes the colour to blue, but can affect the texture of the patina. The addition of 1% of tin blackens the patina. By higher percentages of the same elements there are further changes in the colour of the patina and in its properties. The addition of 5% of silver turns the colour to brownish, while 5% of arsenic turns it to blue. The addition of 5% of tin can produce a brownish patina, if the metal has been annealed and the grains are large, but a cold worked alloy is deep black. Of course the addition of higher arsenic percentages also renders the alloy fragile and difficult to work. The alloys, which have been extensively cold worked before patination and are more homogeneous, tend to achieve a lighter shade of colour. The reason for the presence of minor amounts of silver, arsenic, iron and probably also of tin in ancient artefacts, is manifestly due to the wish to achieve different shades of patination.
The most important data, we were able to collect from our experiments are doubtless those which can explain obscure passages in ancient texts. By trying out the "Greek" patination method described by Pausanias, all samples were made red hot and then dipped into the water of the spring Peirene and into the solution described in Zosimos'text. Some of the samples became immediately dark patinated, particularly in Zosimos'soluton, while for other ones the process had to be repeated several times. Among the alloys, which very quickly developed a dark patina, were those containing iron (in this case 0.5% Fe) and the alloys with 1% Au and 1% Ag, and with 1% Au and 0.5% As. These are the compositions which are also more commonly found in ancient objects. It is quite clear, that the small amounts of iron present in the alloy improve the colour, but also speed up the patination with the "Greek method", which was apparently the one employed by the specialized workshop in Corinth in Roman times. The slowest patination process was observed on alloys containing tin, but this was the case only by applying the "Greek method", not if the solution was hot.
The Chinese patination method, carried out just by holding the objects in the hands (GIUMLIA-MAIR, CRADDOCK 1993A), which was previously thought to be "inherently unlikely" (CRADDOCK 1996, pag. 82) represented a real surprise: it works perfectly well and amazingly fast. *(fig. 8)* Samples handled by children and by young people developed a fine patina in only one or two hours. The patination time increased by increasing age; it did not work at all with two older people. This depends clearly on the perspiration and on the skin quality and of course the skin was stained after some time, but the dark spots were easily removed with normal soap. We also discovered that pieces patinated by other methods, when scratched, redeveloped very quickly a fine patina just by handling, i.e. paradoxically, in this case, handling ancient pieces can represent an excellent restauration and conservation method. This also explains why ancient collectors used to carry

their Corinthian bronze statuettes around with them: keeping them in their hands enhanced the beauty of the pieces and restored the patina, when damaged. Japanese objects have often particular surface treatments or a special finishing, which can give a particular sheen or a velvety appearance to the surface. Bare fingers might live visible spots on it and this is most probably the reason, why some of the *shakudo* objects should not be touched.
Another important knowledge, which could be achieved by experimenting with this fascinating material, was the discovery that the patina develops much easier with lower amounts of precious metals in the alloy. In general it was observed that already a content of 3% of Au considerably slows down the patination. Only in the case of the Greek treatment samples containing 3% Au in combination with tin developed a good patina. Higher amounts of gold or of any other metal in the alloy delay the formation of the patina. The logical question was: Why should anybody use higher amounts of precious metals in the alloy, if better results could be achieved with much less? And why did Zosimos give such high gold weights as ingredients of his alloy in his recipe?
The answer could be found in Zosimos' text.
In the first paragraphs of the book Zosimos specifies *"the primary dyes are ripened from gold, silver and copper"* and are used, depending on the quantity, for the doublement, the multiplying, the softening and stretching of gold, silver and copper. This is clearly the description of the substance called by alchemists "the ferment of gold". One of the most important principles of alchemy is "what has been dyed will dye" (BERTHELOT 1888, 3, pag. 160; III, XIX, 1, 170). It is quite clear that here an alchemistic "preparation" is meant, because the first stage of the process involves the blackening or *"melanosis"*, by breaking down the copper with sulphur, then reverting it to metal, as some sort of rebirth and purification of the material. Apparently the normal procedure was to prepare a larger amount of treated alloys of different composition, which were then divided into the portions necessary to obtain the best patination results and different hues by adding them to unalloyed copper. This method was of course much simpler and quicker, than having to deal with tiny amounts of the different elements (as identified in the ancient alloys) to obtain the desired colour. The alchemist just took the right amount of metal from the treated alloy and therefore the percentages given in the recipe would result much lower. In a further passage Zosimos recommends to add the "preparation" to the same amount of copper (f.33r., 1.17). This reduces the percentage of precious metals to about 3%. Elsewhere (f.34r.1.2) one part of ten of the "preparation" is prescribed, i.e. about 0.7% of Au and Ag would be present in the alloy. The analyses of several ancient objects gave as result very similar percentages. This interpretation is supported by an entry on Corinthian bronze in the Lexicon of Bar Bahlul (BERTHELOT, 1893, II, pag. 123) in which he describes it as *"copper, alloyed with gold and silver and with copper"*, referring clearly to exactly this procedure and to the use of the alchemistic preparation as a dyeing substance for copper.
The Syriac text confirms also the deliberate addition of other metals to the "preparation" with the purpose of achieving particular effects.: in the same section there are many more recipes for alloys containing gold and silver, but also different amounts of other metals, such as lead (cfr. for example f.34v.1.9; 1.16; 1.20), arsenic (cfr. f.33v., 1.10; f.34v., 1.17; f.34+r., 1.5; 1.6), in form of realgar or orpiment, some iron compound (f.33v.1.5; f.34+r., 1.6) and tin (f.34+r., 1.3). In the case of the first recipe Zosimos states very clearly that the alloy thus produced is suitable for "stripes", i.e. for producing sheet metal to be used as inlays on a different copper alloy. In another section (f.34 + recto,II.1-22) also an alloy for casting statuettes, this time with lead, tin and some arsenic sulphide, is clearly defined and described.

7. Conclusion

The difficult task of interpreting in the correct way the fragments of knowledge, which arrived through 4 millennia to us, on this very special ancient alloy, has been greatly helped by experimenting with the material. Without practical work it would have been impossible to gain more knowledge on several of the many facettes of this almost magic alloy.
However several important questions concerning the history of this material through the millennia remain still unanswered and will require more researches. The certain identification of

all different *irogane*-type alloys in Roman times, the possible existence of this alloy in Persia and in India, the date of its appearance in China, as well as the question, if in Japan there was an indipendent development of this technique or a diffusion from the West, remain open and are still to be investigated.

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