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Ancient procedures of gold cementation and gold scorification: considerations on their reliability through experimental archaeology, interpretation of chemical reactions and thermodynamics

Starověké postupy zlaté cementace a scorifikace zlata: úvahy o jejich spolehlivosti pomocí experimentální archeologie, interpretace chemických reakcí a termodynamiky

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Abstract: Reproductions of ancient gold-silver parting procedures were carried out following experimental archaeology protocols and interpreted in the light of the analytical characterization of reagents and products, aimed to define the chemical reactions involved, in order to prepare and execute the thermodynamic validation of them. Analyses were conducted by the authors on different kinds of ancient recipes, coming from textual evidence of a wide chronological range, involving the use of different cementation components. Initial archaeological experiments were conducted using a cement based on a recipe of Pedanius Dioscorides (I century AD) for the production of ios scolekos. Afterwards, the use of brick powder and salt, a procedure described for example in Theophilus, was reproduced and interpreted through the identification of reagents and products involved in the pyrometallurgical processes. A new set of experiments was then designed and carried out with cements containing the natural weathered mineral complex called "misy", following descriptions given by Galen (II century AD), Dioscorides and Georgius Agricola (XVI century). Other experiments reproduced the description of gold separation and collection made by Agatharchides of Cnidus (II century BC), after his direct observations made in the Nubian gold mines. The aims of these studies are to enlighten and classify the technical processes, to evaluate the reliability and the parameters of the procedures (e.g. temperature, atmosphere, and duration) and the characterization of products: this information contributes to new insights in the study of the ancient production of gold and precious metal artefacts.

Keywords: gold, cementation, scorification and collection, ancient recipes, experimental archaeology, analytical characterization, identification of chemical reactions, thermodynamics of reaction

INTRODUCTION

In this article the results of a long lasting interdisciplinary research on ancient gold purification is summarized, focusing on the interpretation of the *chaînes opératoires* applied in some common and less common procedures for gold parting and separation used in ancient times, and on their reliability using apparatuses and skills available in the relative chronological context. Four different procedures have been studied, three of them directly classifiable as cementation processes and the last, whose interpretation and classification is more complicated. A first experimental approach to the purification of gold through cementation, using this interdisciplinary approach, followed the recipe of the physician, pharmacologist and botanist Pedanius Dioscorides, who in his De Materia Medica, describes the production of *ios scolekos* cement. *Scolekos* is a hand-rolled cement (as from the translation conducted by David Loepp and Silvia Ronchey of the procedure in De Materia Medica) made of salt, alum, copper acetate and urine. The experiment proved to be successful and the thermodynamic interpretation of this first procedure was the basis on which a new experiment was designed and carried out, this time for the interpretation of cements containing the natural compound that was known under the name of *misy*, as it is described by Galen (while describing his trips in Cyprus and the visit to the Soli Mine – Skouriutissa, in his *De simplicium medicamentorum temperamentis ac facultatibus*, translated by C. G. Kühn, 1826), in Dioscorides (as from the translation reported in the Discorsi of P. A. Matthioli, 1544 and in Beck's translation, 2005), in Georgius Agricola (Bandy et Bandy 2004)), just to mention some of the better known authors that wrote on this subject. In this case the study focused on the identification of *misy* as a mineral compound and the chemistry that determines its function as a parting cement. The preparation of the cement mixture followed recipe 24 in the Leyden Papyrus, III–IV centuries AD (with *misy*, salt and vinegar as components). The experiment succeeded in the almost total elimination of silver and other metallics from the gold, as evidenced by SEM-EDS analyses of the gold leaves. This experiment supports our hypothesis on the identification of the natural mineral complex named *misy*, as well as the reliability of the process at temperatures attainable in ancient furnaces. The third set of experiments concerns the use of powdered brick and salt, as described by Theophilus Presbyter in his De Diversibus Artibus (XII century), an apparently common procedure in the medieval period. The last procedure is a controversial text of Agatharchides of Cnidus, a II century BC Greek historian and geographer. In the text *On the Erythraean Sea* (as recopied by Diodorus Siculus and the later Photius) he described a different purification process, consisting of the use of salt, tin, lead and sorghum flour, that has raised problems in its interpretation and reproduction. These four gold procedures herein proposed will be examined, starting from the interpretation of the ancient textual sources, through the reproduction in experimental archaeology, ending with a chemical-physical interpretation of the reactions and, for the first experiments involving the *ios scolekos* cement, a thermodynamic interpretation. Additional calculations for the thermodynamic validation of the other three sets of experiments will be executed in the future. The final purpose that this research is pursuing is to propose a clear idea of how a workshop for the production of refined gold would look and should be considered during archaeological field work, what samples are to be collected during the excavation of gold workshops or during the micro-excavations of furnaces and crucibles. Experimental reproduction produces a series of pictures and data to be used as means of comparison during the interpretation of ancient procedures for the production of artifacts, whether excavated or existing in museum collections. The selection of these four procedures was done in order to cover as much as possible the panorama of ancient gold procedures and characterize the various chemical reactions that promote the purification of gold.

At this point, a short overview of the history of ancient goldsmith's techniques is due, in order to give an idea of its chronological development. Melting and annealing, as they consist of simple metallurgical methodologies, were commonly used from the earliest phases of development of metalwork while more complex pyrotechnical operations, that involved changes in the composition of gold alloys may have been applied by the end of the IV millennium BC, possibly appearing together with casting and brazing (Duval et al. 1985, Eluère 1990). Textual evidence from Middle Eastern and Egyptian sources, dating from the late third to second millennium, indicate that ancient cultures were well aware of differences in alloy composition although direct, unequivocal material evidence that gold was refined before the seventh century BC continues to be debated (Craddock et Ramage 2000, Eluére 1990, Halleux 1974). Klemm et Klemm have recently reported studies of Egyptian pure gold used in the treasure of Tutankhamen, that show evidence of cementation. In the ancient Near East, from Sumerian, and more clearly in Acadian and Egyptian written documentations, as reported in Forbes' studies (1964), the knowledge of gold colouring is evident, from the use of a variegated nomenclature for gold, that is, a list of terms that define the aesthetic qualities of colour. Later texts, such as recipe books, manuals on empirical arts, medical compendia and natural treatises, contain indications for the purification of gold through the use of combinations of different mineral complexes and known reagents that were often used as well for the treatment of diseases or as dyes and pigments. Most of these texts use terms whose identification is problematic. Rare accounts of procedures for preparing the compositions, as well as their use during pyrotechnical processes are usually rudimentary or second-hand, necessitating a critical appraisal of previous translations, and a comparative analysis of all textual documents, including medieval and Renaissance sources, in light of present day archaeological evidence. The necessity to apply these procedures to cleanse the gold of impurities lay in the nature of gold itself. In fact, it is important to state that the presence of impurities is usual both in native and alluvial gold. Native gold from primary deposits and placers is naturally alloyed with silver in variable percentages, at times exceeding 20 %, occasionally with copper and/or iron that rarely exceed 1,5 %, as well as traces of platinum group elements (PGE). In the primary reservoirs gold is deposited through precipitation from hydrothermal fluids circulating in the embedding rock. It can be found in veins as prills within quartz matrix. It may be associated with sulphides or tellurium minerals. In the placers, or the secondary deposits, water disperses the lighter components of primary rock, while the very stable and heavy gold, platinum and palladium collect in the sands and alluvial deposits. In both cases impurities are present and were to be removed in the case pure gold was required.

CLASSIFICATION OF ANCIENT GOLDSMITH'S PROCEDURES

The basic strategies of extracting metallic concentrates from their natural environments remain the same since antiquity, that is mining, crushing, grinding, sifting and separation through hand picking and elutriation (Neesse 2014). A secondary source of considerable amounts of gold was scrap recovery from manufacturing processes and the recycling of old material. In order to win gold from both primary and secondary sources the ancient craftsman developed a number of procedures that are still used to this day, although now categorized as assaying techniques, while actual refining is now carried out by wet processing and electrolytic methods. There are three main methods of fire processing gold alloys and metallic concentrates for their values known in antiquity, based on lead processing, salt mixtures or mercury amalgamation. This article will focus on the first two groups for which there is both material and textual evidence. There are two lead-based procedures: scorification and cupellation. Scorification, or liquation according to Forbes (1964), is used primarily to collect metallic values through the mixture of lead or litharge and fluxes with high metallic concentrates recovered from primary and secondary deposits, placed in a crucible. The crucible is then sealed with a salt or borax plug and fired. The lead acts as a collector during the temperature ramp by separating metal from the gangue, forming slag at high temperature. The slag is removed by skimming. Once the charge is brought to 1000 °C and slightly cooled, the mass is oxidized by exposing it to blasts of air, thus removing metal oxides either through volatilization or absorption by the crucible matrix. The production of slag during scorification is of interest and shall be stressed as additional evidence for the identification of certain gold metallurgical processes. This slag generally consists of lead silicate and base metal oxides, as well as residual prills of the alloyed precious metals. A similar indication of slag production in connection to the treatment of gold pyritic ores can be found in the description of Claude Domergue and Hans Gert Bachmann concerning Tres Minas in Portugal (Domergue 1990, Bachmann 1993, 1995). Craddock also reviews the matter in relation to evidence found at Sardis (Craddock et Ramage 2000). Cupellation differs slightly in that metal is processed instead of an admixture of gangue and metallics. Consequently, no flux is necessary nor does any appreciable slag form. Cupellation refers to the property of the cupel to absorb high quantities of metal oxides, mostly litharge. Cupels are generally made of bone ash or similar materials. Although described by Pliny (Rackham 1934) as being made of a special refractory material, tasconium, the earliest bone ash cupels excavated at present date to the Medieval period. In this special porous cupel lead is added to the gold and the temperature is raised and maintained for a brief period at circa 1000 °C. The second step is to blow air on the surface of the metal bath, in order to get a strong oxidizing atmosphere that can oxidise the base metals, that are then absorbed by the cupel, while silver, gold and most PGE remain. The process is described in the Arthasastra (Indian treaty of the IV century BC) and as well in Theophilus' manual. All these indications on lead's possible uses are useful for the interpretation of the fourth procedure we experimented directly, the process described by Agatharchides of Cnidus.

The use of mercury amalgamation to extract values from gangue minerals was first described in detail by the Persian al-Hamdani in 942 AD (Allen 1979), although the process certainly dates earlier. The amalgamation method basically consists of recovering metal values from ore concentrates with mercury, panning out the gangue with water, extracting the excess mercury by squeezing the residual mass through leather, and heating the remaining amalgam to vaporize the mercury. The recovered values would then be processed by cementation to recover pure gold. While there is evidence of a large-scale production of mercury in Vinca in Roman times (Forbes 1964), this is not sufficient evidence that mercury amalgamation was used in winning precious metals. The passages in Pliny and Vitruvius most likely refer to the recovery and use of gold in the applied arts, rather than mining. Their descriptions contain some errors such as the assertion that one only need squeeze the amalgam through leather to produce gold in a pure state. Neither author mentions that the amalgam must be then heated to vaporize the mercury.

Scorification, cupellation and amalgamation result in a metal button containing gold, silver and most PGE, where present in the original charge. This brings us to the next step, the parting of gold and silver, or the final refining by ancient standards, through the process of cementation. Bullion is hammered to fine sheet and torn into small pieces. The metal is then layered alternately with cement in a crucible, sealed and fired. There are two types of cement composed either of salt and sulfur compounds or salt and brick dust. All ancient sources describe the former cement mixture. It is not until Theophilus in the XII century that we have a description of the salt and brick dust cement. The sulfates as minerals are of course not mentioned in the recipes, but less understandable terms such as *scolekos* or *misy* were used by ancient authors. The three reproduction processes we made are all referable to this class of methods. There are some procedures described in ancient texts that still need further interpretation; for example, the interesting description of *dawa,* a cement composed of salt, baked brick and pyrites (Allen 1979). It is not clear if these pyrites are sulphidic compounds or sulphates as Allen reports in the translations, indicating that some of these pyrites are actually sulphates, as one type is literally identified as white lead sulphate. We can hypothesize at this point that, in the case this translation is correct, the cement would be made of $PbSO_4$, lead (II) sulphate. This sulphate could play an analogous role as the copper and iron sulphates in *ios scolekos* and in *misy*, as it will be explained in detail in the dedicated paragraphs. In the case the pyrites hint to the use of sulfidic compounds as cementation agents, this would anticipate by two centuries the use of sulfides as purifiers of gold, such as stibnite, described in later scripts by Theophilus, Biringuccio and Agricola, whose use is mentioned, according to Forbes (1964), as the Sulphur Process. It consists of the use of sulphur compounds and charcoal instead of salt. Also described by Ammen (1997), sulfides, such as stibnite, are able to attack silver to create a very stable compound, silver sulfide. Forbes suggests that possibly the procedures involving *misy* can be ascribed to this group but our direct study and experience on this compound disprove this interpretation. Reconsidering al-Hamdani's text at this point, if we follow the translation that interpret his pyrites as sulfidic ores and considering that sulfides themselves can be enough to purify gold from silver, because of the production of silver sulfide, it has to be noted that in the *dawa* cement two different cements are added: the sulfide cement and the salt-brick dust cement. For any further consideration, we rely on future experimental trials. A final consideration is warranted: Davies evaluated the procedure with stibnite as datable back to an ancient period, suggesting its possible use in Egypt and the Ancient Near East (Davies 1935, where he describes a specimen of gold from the II Dynasty Egypt containing antimony). This classification is not exhaustive and, as we will see, procedures may have been combined together, as Agatharchides' description appears to testify, where apparently crucible scorification is followed by cementation, as will be discussed later in the discussion of the fourth experimental trial.

MATERIALS AND METHODS

In order to fully understand how these ancient pyrometallurgical procedures worked, based on the study of historical sources, it was decided to operate reproduction trials in experimental archeology. All the experiments reported below have been conducted in the Center of Experimental Archaeology Antiquitates (Civitella Cesi, Blera – Italy), by using only materials and methods analogous to those used in the contemporary era to the text describing the recipe. The furnaces, the crucibles, the bellows used were produced following the methods used in antiquity between the 2nd and the 1st millennium BC. The furnace used for experiments with *ios scolekos* and brick dust follows the models used in Sardis around the 6th century BC (made of lute – a mixture of clay, earth, stones, refractory soil and straw), while the oven used for the *misy* experiment and the latter following the Agatharchides' procedure make use of a furnace built following the archaeological evidence found in the workshops of Pyrgos in Cyprus (built with stones and clay). The furnace was supplied with various types of wood with various moisture content; the oven temperature controlled by a Chromel / Alumel thermocouple sensitive to variations of 0.5 °C in the temperature range of 200/900 °C. Generally, to prevent heat leakage or, in extreme cases, the collapse of the furnace, it was necessary to repair the cracks that were formed on the walls with clay slurry. The crucibles used were small, lidded terracotta containers of a diameter of about 6–7 cm and a height of about 7–8 cm. In the experiments in which the use of gold foil was requested, samples consisted of small laminae of non-constant area and a thickness of 1 to 2 tenths of a millimeter, produced by hammering long strips of gold-copper-silver alloys (whose compositions are given in the detailed section dedicated to each experiment) that were then cut into quadrangular sheets, marked with a punch with univocal marks. The practical work followed several steps carried out mainly as follows: the preparation of the cements and the run of the experiments in the furnace was conducted by Mr. D. Loepp and Dr. A. Celauro, under the supervision of D. Loepp, who prepared the gold samples and the copper tools as well, as it will be discussed further; diagnostic tests executed on the cements, the gold alloys and the crucibles (SEM-EDS) were conducted at the CNR – Nanostructured Materials Research Institute (ISMN)/ Department of Chemistry of La Sapienza University of Rome by Dr. D. Ferro and Dr. A. Celauro under the supervision of Dr. D. Ferro; XRD and Knudsen Cell Coupled Mass Spectrometry at the Diffractometry Laboratory of the Department of Chemistry of La Sapienza University of Rome were carried out from Dr. S. Brutti, and partially from 2016 in the SEM-EDS and XRD laboratories of the Deutsches Bergbau Museum-Bochm (Germany) by Dr. Stephen Merkel, Dirk Kirchner and Jan Sessing (DBM).

THE RECIPES, THE EXPERIMENTS AND THEIR INTERPRETATIONS

1. FIRST SET OF EXPERIMENTS ON THE PRODUCTION AND USE OF IOS SCOLEKOS IN GOLD CEMENTATION

1.1. TEXTUAL SOURCE

The first procedure was tested between 2004–2006 and was published in Ferro et al. 2011, and it will be described in the forthcoming article of Loepp et al. (forthcoming). Here the summary of the most important results obtained and the most important observations made are reported, in order to show the logical development of this research from its beginning. This first trial was a reproduction of a salt and sulfate cement, which was initially based on a formulation described in the Dioscorides' De Materia Medica (Wellmann 1958) from the I century of the current era. The cement is described by the author as a pharmaceutical simple for the cure of eye disease but the author mentioned it as well as a compound used by goldsmiths. The same reagents are proposed by other authors such as Bolos, Pliny, Zosimos, Ottavio Brembato and in the Mappae Clavicula (Smith et Hawthorne 1974) as a cement for gold parting, although often described in oblique terms. The translation here presented was reevaluated by Mr. David Loepp and by Prof. Silvia Ronchey after a rereading in the light of the practitioner's experience. This retranslation is reported here as in Ferro et al. 2011:

"There exist two types of ios scolekos.

The first is of extraction while the other is prepared as follows: in a pure copper mortar whose pestle is made of the same material, add half a cotyle of strong white vinegar and work it with the pestle until it becomes dense and sticky. Then add four drachme of best quality alum and transparent rock salt or sea salt, in which case as white and hard as possible, otherwise in alternative the same quantity of natrum. Then let it macerate under a very hot sun when the Dogstar rises until it assumes a greenish colour and a sticky consistency.

Fig. 1. a) vinegar poured in the copper vessel and stirred with a copper pestle under the summer sun develops a green tinge, indication of the release of copper ions to the solution; b) the addition of aged urine causes the development of effervescence; c) the mixture, after the addition of alum and salt, becomes a green sticky paste.

Obr. 1. a) ocet nalitý do měděné nádoby a míchaný měděným tloukem v záři letního slunce vytváří nazelenalé zbarvení, které je známkou uvolňování iontů mědi do roztoku; b) přidání odstáté moči vyvolává šumění; c) směs se po přidání kamence a soli promění v zelenou lepivou pastu.

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Fig. 2. The cement is then hand-rolled into green filaments that dry fast into thin, pale green cylindric sticks, resembling rose worms (sawfly larvae).

Obr. 2. Cement je poté ručně vyformován do tenkých zelených válečků, které rychle schnou a utvoří světle zelené tyčinky podobné červům.

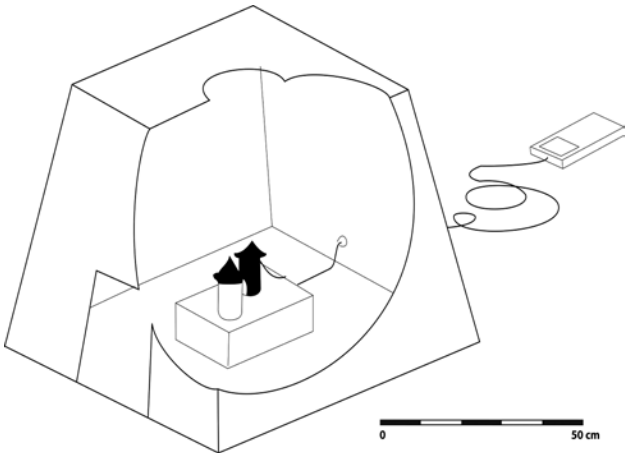

Fig. 3. Drawing of the experimental furnace with the setting of the two crucibles on a small plinth, and the thermocouple sensors located in the inside of the furnace, in direct contact with the crucibles.

Obr. 3. Kresba experimentální pece se dvěma tyglíky na malém podstavci a termoelektrickými senzory umístěnými uvnitř pece, v přímém kontaktu s tyglíky.

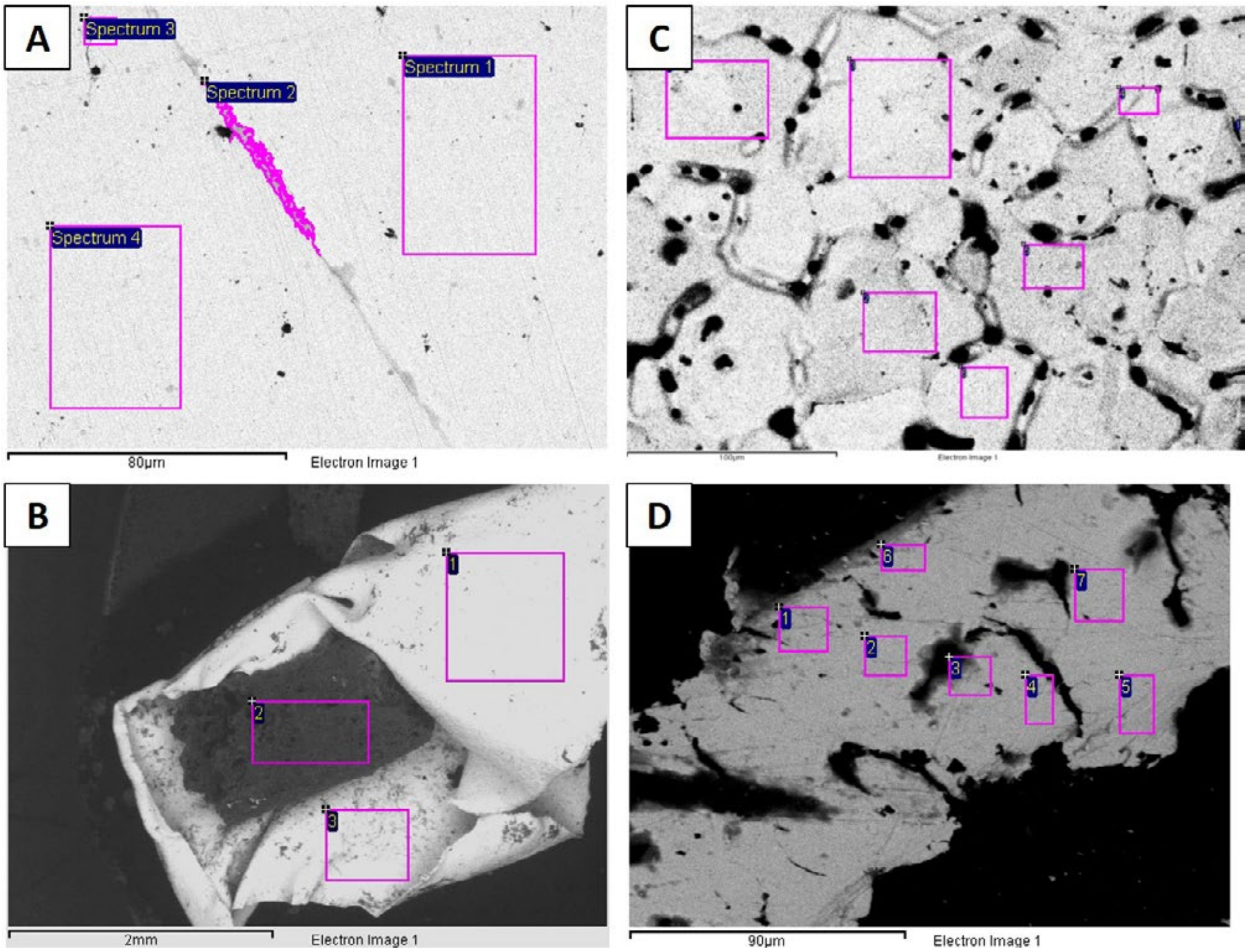

Fig. 4. SEM images in backscattered electrons of the gold laminae, before (A) and after (B, C and D) the experiment. In detail, in figure B the lamina is curled around a residual of *ios scolekos*; in figure C the gold leaf shows the typical porous structures induced by the cementation; in picture D the lamina is analysed in its cross-section, after embedding in resin.

Obr. 4. SEM snímky zlatých plátků ve zpětně odražených elektronech před (A) a po (B, C a D) experimentu. Na obr. B je plátek zkroucený kolem zbytku ios scolecos; na obr. C je na zlatém plátku vidět typická porézní struktura způsobená cementací; na obr. D je plátek analyzován v příčném řezu, po zalití pryskyřicí.

Tab. 1. EDS compositional table of the gold laminea before (A) and after the cementation (B,C and D) (all results in weight percentage).

Tab. 1. Tabulka složení zlatých plátků na základě EDS před (A) a po cementaci (B, C a D) (všechny výsledky jsou uvedeny v hmotnostních procentech).

Spectrum	Cu	Ag	Au
A.1	1,90	25,71	72,39
A.2	1,79	24,21	74,01
A.3	1,70	25,02	73,28
A.4	1,81	24,59	73,60
B.1	0,35	0,00	99,65
B.2	47,25	2,43	50,32
B.3	0,33	0,00	99,67
C.1	0,00	0,00	100,00
C.2	0,07	0,00	99,93
C.3	0,00	0,00	100,00
C.4	0,12	0,70	99,18
C.5	0,03	0,23	99,73
C.6	0,18	0,00	99,82
C.7	0,00	0,13	99,87
D.1	0,00	0,33	99,67
D.2	0,10	0,35	99,55
D.3	0,36	0,14	99,50
D.4	0,31	0,02	99,67
D.5	0,14	0,99	98,87
D.6	0,24	0,00	99,76
D.7	0,00	0,36	99,64

At this point work the paste [with your hands] so as to form small worms similar to those that infest roses and let them rest. The mixture comes out a stronger green and is more efficacious if one uses one part of vinegar and two parts of aged urine and proceed for the rest as described above. Some mix the product with gum Arabic shavings but this system is to be deplored as fraudulent. There is also a verdigris used by goldsmiths, always with a pure copper mortar and pestle, but with child's urine, with which they glue gold. The abovementioned varieties of verdigris are similar to burned copper, but they are stronger and more efficacious.

But one must know that mined scolekos is the best, then followed by the scraped kind and the prepared. The natural kind acts better as a mordant and is more astringent, while that of the goldsmiths is equivalent to the scraped kind."

At this point some comments to the recipe are in order. The recipe describes the production of the cement by mixing strong, aged vinegar in a copper mortar, stirred until it thickens. The addition of same quantity of salt and alum and aged urine, and the maceration under the hot summer sun results in a greenish cement. The addition of urine develops an effervescency (Fig. 1). Urine is a source of alkaline phosphates and ammoniac. It is therefore a degreasing and fixing agent used widely in ancient techniques (such as dyeing) and may be used as a pickle for metals. It is better to first stir the vinegar in a pure copper mortar under strong summer sunlight, as the Dogstar, Sirius, appears around July 26th (this tool was first reported by Theophrastus in the IV century BC and described as a tool used to extract metallic mercury by grinding cinnabar and vinegar together, in Caley et Richards 1956). In the Loepp-Ronchey translation, the compound is to be worked by hand to form small worm-like filaments (Fig. 2), while in most translations the worms presumably form by themselves, an assertion not supported by practical evidence. Dioscorides mentions the use of a related compound for gold processing (in this case soldering). Dioscorides finally suggests that there is a compound found in nature, of very good quality, also used by goldsmiths. This final indication of the good quality of the mined *scolekos* suggests the existence of a natural compound similar to *ios scolekos*. This indication has to be kept in mind as it will be the starting point for the second salt-sulfate formulation that will be discussed later. It is important to focus first on the production of the artificial *scolekos*, as the results obtained during the experimental trials of 2004–2006 will allow the setting of the second procedure on the use of *misy*, that follows in the section dedicated to the related experiments.

1.2. Experimental

The experimental part consisted of several steps. First the production of a pestle and mortar in copper was made with the lost wax technique. The furnace (Fig. 3) was built with semi-dried bricks of clay, silt, gravel, and straw, following the models of the metallurgical workshops in Sardis dated back to around the VI century BC (Craddock et Ramage, 2000).

Small gold foils (Fig. 4A) were prepared in two different ways, with quantities of gold that varied between 72.4 % and 93.1 %, were prepared (the lamina in Fig. 4A, Tab.1 has an amount of about 72–74 % Au). One group is composed of a gold, copper and silver alloy of about 73 % of gold, 25 % silver and 2 % copper, and a group made of previously cemented alloys with values of gold between 80 % and 93 %. The two groups are recognizable and distinguished by identification codes punched on their surface. All the gold leaves were placed in the same crucible, the identification marks easily distinguishing the different sets of samples.

Copper acetate was produced by mixing strong vinegar with a copper pestle and mortar under intense sunlight. The ultraviolet range of the solar spectrum seems fundamental for the reaction to occur, as other experiments made by the mean of infrared lamps did not produce similar results. Aged urine was added, provoking a characteristic effervescence. Alum and natural sea salt were mixed in equal portions. The paste obtained was then dense enough to be easily hand rolled into small filaments about two centimeters that actually resemble "rose worms" of a very vivid green tint (Fig. 1 and 2). In this form, each unit dries quickly and offers the maximum reactive surface per volume without increasing too much the time necessary for their preparation. Gold foils and cement "rose worms" were then placed in alternating layers in a vessel. The vessel, lidded and sealed with clay, was left overnight in water in order to guarantee a moist environment inside. The vessels were then fixed inside the furnace with clay and heated for 19 hours in the furnace. For

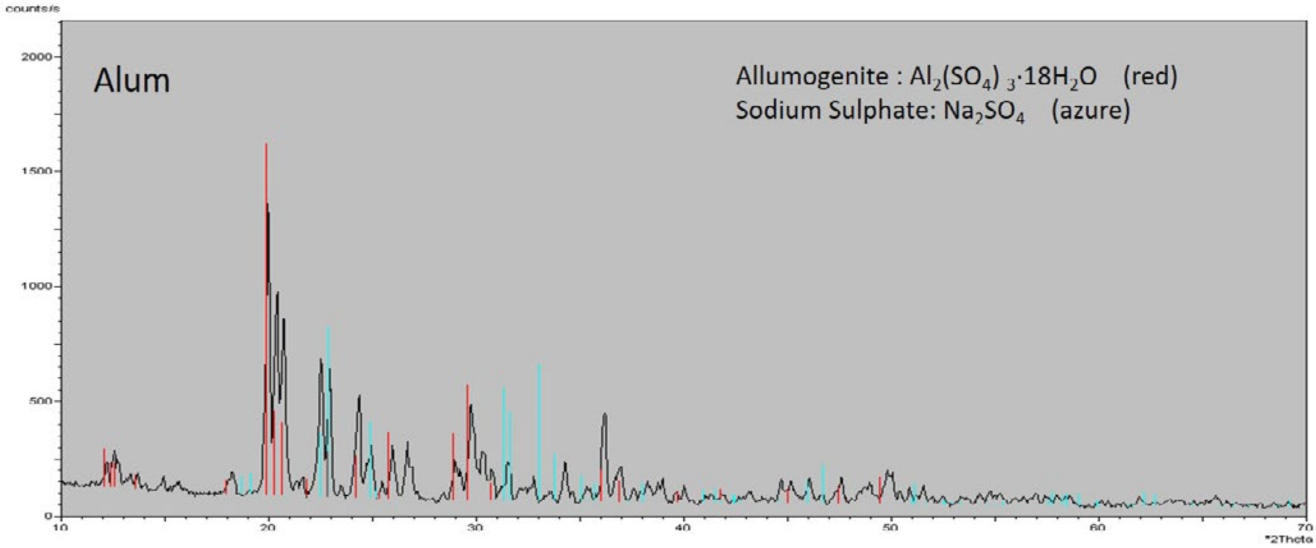

Fig. 5. XRD spectrum of alum.
Obr. 5. RTG difrakční spektrum kamence.

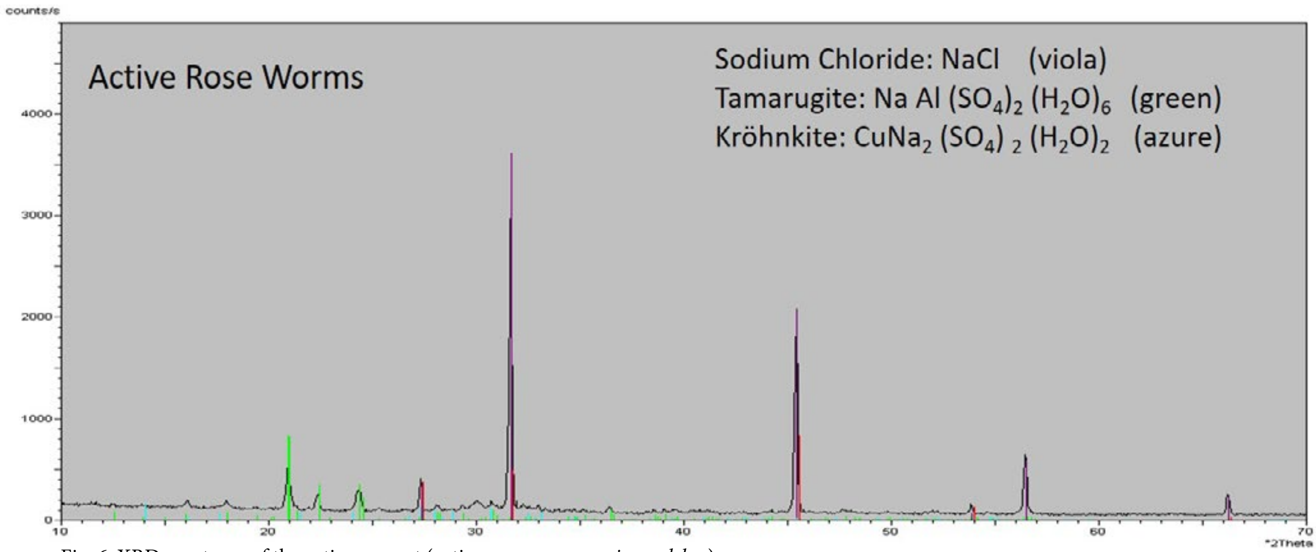

Fig. 6. XRD spectrum of the active cement (active rose worms or *ios scolekos*).
Obr. 6. RTG difrakční spektrum aktivního cementu (ios scolecos).

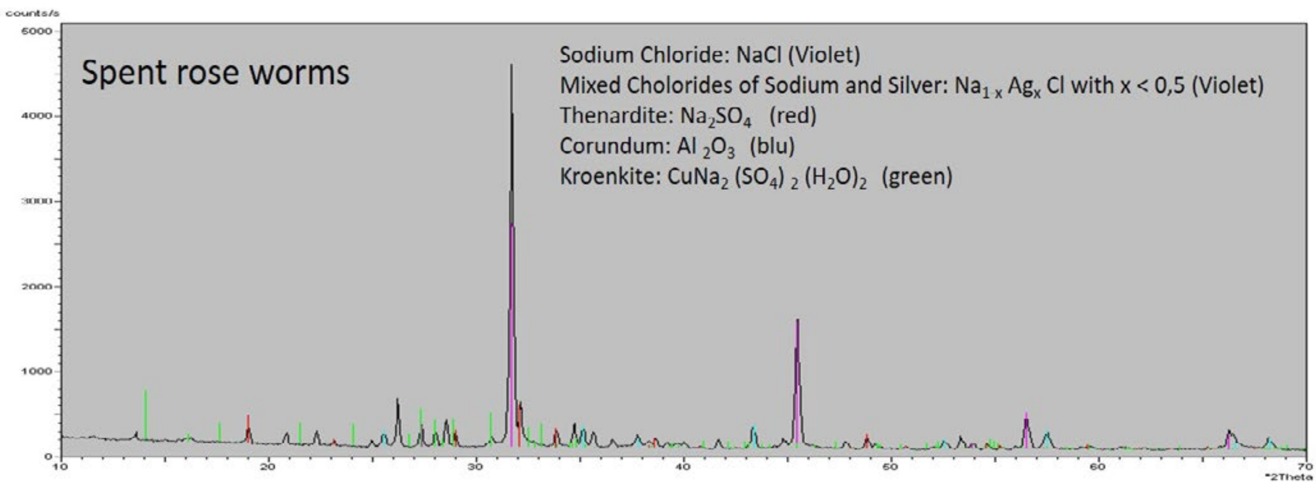

Fig. 7. XRD of the spent cement sampled after the experiment.
Obr. 7. RTG difrakce vzorků použitého cementu odebraných po skončení experimentu.

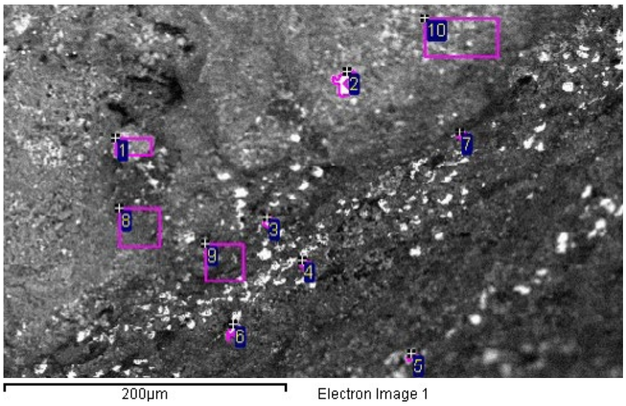

Fig. 8. SEM images in backscattered electrons of a cross-section of the crucible wall after the experiment.

Obr. 8. SEM snímky příčného řezu stěnou tyglíku ve zpětně odražených elektronech po skončení experimentu.

Tab. 2. EDS compositional table of the section of crucible walls (all results in weight percentage)

Tab. 2. Tabulka složení řezu stěnou tyglíku na základě EDS (všechny výsledky jsou uvedeny v hmotnostních procentech).

Spectrum	**Cl**	**Cu**	**Ag**	**Au**
1	69,81	7,65	16,67	5,87
2	23,01	16,55	1,89	58,56
3	34,66	47,94	6,02	11,38
4	44,81	23,52	7,96	23,70
5	46,55	19,98	0,00	33,47
6	57,61	22,28	4,67	15,43
7	55,74	24,43	11,25	8,59
8	41,50	38,70	19,80	0,00
9	41,78	42,49	9,16	6,58
10	42,54	41,90	11,35	4,21

Tab. 3. $\Delta_r G^0_t$, the equilibrium constants from partial pressure Kp, the partial pressures of gaseous species p and the ΔG calculated for the hypothesized reaction 1 to 5 (partially published in D.Ferro et al. 2011).

Tab. 3. $\Delta_r G^0_t$ v kJ mol^{-1}, rovnovážné konstanty vyjádřené pomocí parciálního tlaku Kp, parciální tlaky plynů p a ΔG vypočtené pro hypotetickou reakci 1 až 5.

1) $Al_2(SO_4)_3(s) \rightarrow Al_2O_3(s) + SO_3(g)$

T/K and °C	$\Delta_r G^0_t$ / kJ mol^{-1}	K_p / bar
800 ~ 527°	160,5	3,3E-11
900 ~ 627°	118,9	1,3E-07
1000 ~ 727°	78,4	8,1E-05
1100 ~ 827°	37,1	1,7E-02
1200 ~ 927°	-3,9	1,5E+00

2) $CuSO_4(s) \rightarrow CuO(s) + SO_3(g)$

T/K and °C	$\Delta_r G^0_t$ / kJ mol^{-1}	K_p / bar
800 ~ 527°	70,3	2,6E-05
900 ~ 627°	52,9	8,5E-0,4
1000 ~ 727°	35,8	1,3E-02
1100 ~ 827°	18,9	1,3E-01
1200 ~ 927°	2,2	8,0E-01

3) $SO_3(g) \leftrightarrow SO_2(g) + 1/2\ O_2(g)$			**$CuSO_4(s)$**		**$Al_2(SO_4)_3(s)$**	
T/K and °C	$\Delta_r G^0_t$ / kJ mol^{-1}	K_p / $bar^{1/2}$	$p(O_2)$ / bar	$p(SO_3)$ / bar	$p(O_2)$ / bar	$p(SO_3)$ / bar
800 ~ 527°	23,6	2,9E-02	3,2E-10	2,6E-05	4,7E-19	3,3E-11
900 ~ 627°	14,2	1,5E-01	7,1E-07	8,5E-04	1,3E-12	1,3E-07
1000 ~ 727°	4,9	5,5e-01	3,2E-02	1,3E-02	1,5E-07	8,1E-05
1100 ~ 827°	-4,3	1,6E+00	4,5E-02	1,3E-01	2,3E-03	1,7E-02
1200 ~ 927°	-13,5	3,9E+00	2,7E+00	8,0E-01	6,9E+00	1,5E+00

4) $2NaCl(s) + SO_3(g) + 1/2\ O_2(g) \rightarrow Na_2SO_4(s) + Cl_2(g)$			**From $CuSO_4(s)$**	**From $Al_2(SO_4)_3(s)$**
T/K and °C	$\Delta_r G^0_t$ / kJ mol^{-1}	K_p / $bar^{-1/2}$	$p(Cl_2)$ / bar	$p(Cl_2)$ / bar
800 ~ 527°	-73,1	6,0E+04	2,7E-02	1,4E-15
900 ~ 627°	-63,3	4,7E+03	3,4E-01	6,7E-10
1000 ~ 727°	-53,7	6,4E+02	1,5e-01	2,0e-05
1100 ~ 827°	-42,9	1,1E+02	2,9E+00	9,0E+02
1200 ~ 927°	-29,4	1,9E+01	2,5E+00	7,4E+01

5) $Cl_2(g) + 2Ag(s) \rightarrow 2AgCl(s)$		**from $CuSO_4(s)$**	**from $Al_2(SO_4)_3(s)$**
T/K and °C	$\Delta_r G^0_t$ / kJ mol^{-1}	$\Delta_r G_t$ / kJ mol^{-1}	$\Delta_r G_t$ / kJ mol^{-1}
800 ~ 527°	-171,8	-101,9	55,9
900 ~ 627°	-166,7	-124,1	-8,7
1000 ~ 727°	-161,9	-146,3	-71,8
1100 ~ 827°	-157,2	-167,1	-135,2
1200 ~ 927°	152,8	-184,9	-195,7

the first three hours, the temperature was held at 300 °C, after which the temperature was raised to 700 °C with brief peaks at 850–900 °C. At the end of the procedure all the reagents and the products were analyzed in order to hypothesize the outcome of the cementation. In that period, the analytical protocol consisted of the use of SEM-EDS and XRD for the analyses of reagents and products. This simple set of operations allowed the interpretation of the chemical reactions that lead to the purification of gold from silver and base metals. XRD on alum revealed the presence of aluminogenite and sodium sulphate (Fig. 5).

The vinegar left in the copper mortar under strong sunlight produced a green solution of pH 5, of copper acetate where copper is brought into the solution by the vinegar from the copper and pestle. The addition of urine to the copper acetate modified the pH of the paste, previously acidic due to the presence of copper acetates, and favoured the dissociation of the various compounds. XRD spectrum of a "rose worm" filament showed that the sample was formed prevalently of sodium chloride with lesser quantities of tamarugite and kröhnkite (Fig. 6).

Copper acetate and the alum components, allumogenite and sodium sulfate, reacted thus producing tamarugite and kröhnkite, whereas NaCl remained unaltered.

$2NaAl(SO_4) \rightarrow Al_2(SO_4)_3 + Na_2SO_4$

$CuNa_2 (SO_4)_2 \rightarrow CuSO_4 + Na_2SO_4$

After the experiment samples of gold foils as well as the residual filaments and the vessel were collected in order to individuate changes in composition and structure.

The XRD analyses of the spent cement showed the presence of sodium chloride, mixed chlorides of sodium and silver, thenardite, corundum and kröhnkite (Fig. 7), supporting the hypothesis that tamarugite and kröhnkite present in the active filaments, dissociate, during the thermal treatment, into copper sulfate, aluminium sulfate and sodium sulfate.

1) $Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$

2) $CuSO_4 \rightarrow CuO + SO_3$

3) $SO_3 \leftrightarrow SO_2 + 1/2\ O_2$

4) $2NaCl + SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4 + Cl_2$

The dissociation of sulfates of copper and aluminium in aluminium oxide (corundum), copper oxide and sulphur trioxide occurs at $T \approx 516$ °, 586 °C respectively. The sulphur trioxide also dissociated into its dioxide and oxygen. Sodium chloride and sulphur trioxide reacted producing molecular chlorine, the active agent in cementation. SEM-EDS analysis of the gold foil coming from both of the sample groups (non-cemented and partially cemented) indicate that in both cases the gold had attained a very high grade of purity of about 99,7 % as mean value (Fig. 4 and Tab. 1), thus confirming the hypothesis that molecular chlorine oxidized the silver producing silver chloride.

5) $Cl_2\ (g) + 2Ag\ (s) \rightarrow 2AgCl(s)$

The inner walls and cross-sections of the vessel were analysed and the results (Fig. 8, Tab. 2) evidenced a partial absorption of silver chloride (but it documents a small loss of gold as well). A thermodynamic analysis was carried out in order to investigate the reaction pattern that leads to the refining of a gold alloy with a large silver content, considering the EDS and XRD determinations of the solid phases involved in the process. First of all, a preliminary analysis of the gaseous phase developed during the experiment in a range of temperatures between 263° and 940 °C with mass spectrometry coupled with a Knudsen cell confirmed the production, among other gaseous phases, of Cl_2(g) and the presence of SO_3, SO_2, O_2, and Cu_3Cl_3. Each single reaction from 1 to 5 has been studied in order to consider the chemical equilibrium. In order to predict the feasibility of a reaction, the Gibbs free energy G, defined as the amount of energy that the system can use to perform work, and the ΔG, that quantifies the overall change in free system energy due to a reaction (passing from a first state G1 to a second state G2), have to be evaluated. The ΔG is equal to $\Delta_r G^0_t + RT\ln K$ (where R is the gas constant, T is the temperature in Kelvin, while $\Delta_r G^0_t$ considers the standard free Gibbs energy, and is a value obtainable in specific literature). It is necessary to evaluate the equilibrium partial pressure as well, in order to consider the effectiveness of the reactions: the equilibrium constant Kp is the constant in terms of partial pressure p. The standard Gibbs energy and the equilibrium partial pressure are the pivotal elements of evaluation of the reliability of a process. In order to understand if a reaction is spontaneous and proceeds to the right, so that the products are favoured, the partial pressure of the reagents has to be bigger than one of the products and the $\Delta G < 0$. By the calculation of them for each reaction, it can be state that the reactions hypothesized are possible. A summary of the $\Delta_r G^0_t$, the Kp and the p of the gaseous species involved, and the ΔG calculated for the hypothesized processes are presented in table 3.

From these data, it is interesting to note that the sulphur oxide SO_3, fundamental for the production of chlorine and an active agent in the process of purification, occurs at lower temperatures from the dissociation of copper sulphate (at 800 K – about 527 °C) and for higher temperatures from both the dissociation of copper and aluminium sulphate (> 900 K). Further indications on the thermodynamic interpretation are reported in Ferro et al. 2011 and Loepp et al. (forthcoming). The most surprising result is that in this recipe the ingredients are combined in order to cause at least one agent to trigger the production of molecular chlorine over a wide temperature range. This chemical interpretation is to be considered valid for analogous recipes based on sulphates, with minor differences in the temperatures of reaction. In this way, we used the interpretations obtained in this experiment as a parameter of evaluation for other procedures.

2. On the use of misy in ancient gold cementation

2.1. Textual sources

Having demonstrated the efficacy of sulfate-salt cements, the research focused on individuating sulfates in ancient terminology identifying minerals found in nature, similar to artificial, man-made *ios scolekos,* as explained previously

Tab. 4. list of descriptive characteristics on misy, calchitis, chalcanthos, melanteria, sory, coming from written documentations of Galen, Pliny, Agricola, Matthioli, J.C. Valmont de Bomare.

Tab. 4. Seznam deskriptivních charakteristik látek misy, calchitis, chalcanthos, melanteria a sory na základě písemných zmínek u Galéna, Plínia, Agricolu, Matthioliho a J. C. Valmonta de Bomare.

	Misy	**Calchitis**	**Calchantos**	**Melanteria**	**Sory**
Colour	Yellow[4], golden[4], gold and shining like a star [2, 3], once broken, sparkling[4]	Similar to copper, red[2, 3, 4], with long gold veins [2, 3, 4]	Blue-grey with green and yellow stains[3]	Grey-black[4], the best is the one with the colour of sulfur[2,3]	Grey black[4], black[2, 3, 4], shiny as misy[2,3]
Position in the stratigraphy	Top, superficial [1]	Middle position [1]	Coming from the secretions that drip in some caverns [2, 3]	Inferior[1]	Inferior[1]
Consistence, texture	Fine[1, 4], nodular[4]	Not fine like misy and not stony like sory[1, 4], friable, like compressed wool [4], fragile[2,3]	Like a soft condensed soil[2, 3]	Smooth and hard[2, 3, 4], like wool[4], nodular[4]	Divided in bigger parts[1], stonier, nodular but it can be porous [4] and spongy[2, 3]
Corrosiveness	Less corrosive (if in contact with flesh)[1]	Not described	Not described	Not described	The most corrosive (if in contact with flesh) [1]
Behaviours after burning	Difficult to be burnt[1], crust /loss of volume[1], it becomes calchitis[4]	Crust and loss of volume[1], it becomes copper[4]it easily burns[1]	Not described	Not described	Crust and loss of volume[1], it burns hardly[1]
Melting property	During the artificial production of misy, it undergoes heating, so it is too dry to be easily melted again[1]	Very easily melted[1]	Not described	Not described	Too hard to be melted[1]
Location of finding	Very good from Cyprus[1,4], in Cyprus it looks similar to gold[2, 3] – in association with vitriols in Goslar[4], Fahlun, and Massa Marittima (hypothesis)[3]	Cyprus[1], Germany [3]	The Roman variety (copparosa) is the best, the Cypriot and German is blue, there are caves for its extraction in Massa Marittima[3], the one from Cyprus is famous[1], produced in Spain[2,3], Goslar and Falun[4]	Cilicia[2, 3]	The best is from Egypt[2,3,5] but it is found as well in Lybia[5], Spain[4], Cyprus [1-5] and Germany[3]
Smell	Sulfur[1,4]	Sulfur[1, 3, 4]	Sulfur[1, 3]	Sulfur[4]	Very sulfuric, it is the most penetrating[4], causes nausea [2, 3, 4]
Origin	Misy originally was calchitis [1], it is native[4], misy effloresces from sory, calchitis and melanteria[4]	It is the "mother" of sory and melantheria[4], it becomes misy [1, 3], vitriols[4] derive from calchitis, it is native[1,3]	It easily transforms into misy.[1,3] It transmutes to calchitis in 20 years [1, 3], it is native[4]	It congeales at the entrance of copper mines[2,3], it surrounds the granules of pyrite[4], vitriols[4] derive from melanteria, it is native[4]	Sory becomes calchitis after a long period[1], it surrounds the granules of pyrite[4], vitriols[4] derive from sory, it is native[4]
Proposed composition	Yellow vitriol[5], it contains copper, misy and sory, it is known as *atramentummetallicum*[4]. In Bandy & Bandy (2004) the hypothesized composition is metavoltine and copiapite.	Red vitriol[5], it contains copper, misy, sory[4], it is copper pyrite[4], in Bandy & Bandy (2004) the hypothesized composition is romerite and botryogen	It contains misy, calchitis, sory and copper.[3] It is popularly called vitriol[3]	In Bandy & Bandy (2004) the hypothesized composition is melanterite	Grey vitriol[5], in Bandy & Bandy (2004) the hypothesized composition is voltaite, melanterite and pyrite
Water interaction	Not described	Not described	Calchanthos comes from the condensation of the water collected in green lakes in the depressions of copper mines such as in Solis, Cyprus[1, 3]	It becomes black[2, 3, 4]	Not described

[1]Galen, [2]Dioscorides, [3]Matthioli, [4]Agricola, [5]J.C.Valmont de Bomare

and described by Dioscorides as mined *scolekos.* The study of the corpus of ancient recipes related to the bettering and colouring of gold, clearly indicates the use of sulfates and salt as the primary cementation reagents. In the chapter on *ios scolekos* Dioscorides refers to the previous recipe that discusses verdigris and burned copper, the former consisting of copper acetate and carbonates, the latter of copper oxides. It would appear therefore that Dioscorides is only referring to his second recipe which is effectively a combination of carbonates and copper acetate, while the principle recipe, composed of sulphates and salt, only shares a number of descriptive qualities with the second. If the judgment shall come from the name, "rose worm mordant", it can be expected to be a corrosive yellowish to green mud formed in mines that can be opportunely shaped into putty-like filaments resembling rose worms. The most frequently cited mineral is *misy*. *Misy* is mentioned in Bolos, Dioscorides, Pliny, Galen, in the Leyden Payrus, in the texts of Zosimos, in the Mappae Clavicula and in De Re Metallica of Agricola, just to make some examples. Its identification as a mineral is not easy, as it is mentioned in many texts, sometimes in mutual contradiction. Many sources give a colorful description of the mineral and mining locations. From these clues and by performing a cross-check of the descriptions, and a confrontation with the common interpretations of other authors, such as Bandy et Bandy (2004), Hoover et Hoover (1950), Forbes (1964) and Craddock (Craddock et Ramage 2000), an identification of the mineral nature of *misy* has been attempted. The decision to use the texts by Galen (Kühn 1826) came by the fact that, while describing his trip to Cyprus and his visit to the Soli Mine- Skouriutissa he often mentioned *misy, sory* and *calchitis* (Kühn 1826, Matthioli 1544, Bandy et Bandy 2004). Just at the entrance walls of the mine he described the presence of three long, overlapping stripes, the inferior one was the so-called *sory*, the highest was *misy* and in the middle a layer of *chalcitis* was to be found. The area of Soli, in Cyprus, is known to be an ancient zone of exploitation of copper sulfides, which suggests that Galen was describing the layering of oxidized minerals weathered from sulfides to sulfates and oxides of the superficial gossan. It is noteworthy that, after having taken samples of the three compounds, *misy*, *sory* and *calchitis*, Galen discovered that *sory* eventually changed into *chalcitis*, and the latter developed a crust of *misy* on the surface. That could be explained considering the three compounds as belonging to the same chain of oxidation. In Matthioli's commentary to Dioscorides there is a very detailed description of *calcanthos* or *atramentum sutorium*, or vitriol as it was popularly called. Concerning a kind of vitriol of very good quality, copparosa, Matthioli declares that the best can be found in the mines of Cyprus, in Goslar (Germany), and in Italy in the mines of Massa Marittima. These sites are interested both by mining activity on polymetallic sulphides, a second indication. The final indication is given when Matthioli reported that *calcanthos* turns into calchitis by a natural transmutation, just natural as the transmutation of *calchitis* into *misy*. Galen, as reported in Matthioli (1544), further describes another area of the Soli mine, a cavern where a green lake was found. The water drops from the walls from cracks in the rock, the atmosphere is oppressive, it is difficult to breath, and it is very warm. Candles extinguish very quickly. All these elements described by Galen can be interpreted as a natural lake formed from acid rock drainage containing sulfides and sulfates. The atmosphere described appears to be poisoned by sulfur dioxide, which obliged the forced labor to collect the green water of the lake as fast as possible. Another term used by Dioscorides is *melanteria*, described as another compound that solidified as a salt at the entrance of copper mines or was found on the walls of these caves. In Agricola (Hoover et Hoover 1950, Bandy et Bandy 2004) there are many detailed descriptions of mineral outcrops, of course not as a clear description but as a collection of organoleptic and aesthetic characteristics that cannot be briefly listed, but that can be summarized in a table (Tab. 4), together with the indications from Galen (Kühn 1826) as reported in Dioscorides and Matthioli (1544) and from some direct descriptions given by J. C. Valmont de Bomare (1762).

All the descriptions suggest that the authors describe the natural weathering and oxidation of pyrite to vitriols. The steps of oxidations would therefore be: pyrite, *sory* – *melanteria*, *calchitis*, *misy*, vitriol. Now it is important to understand what specifically the species are. The sulfur number of oxidation changes between -2, +2, +4, +6 in relation to the oxidation states. There can be as well a change in the number of water moles. What seems to be the more probable hypothesis is that *misy* is the oxidation and weathering product of a sulfur mineral that could be pyrite or chalcopyrite and that can be found in the gossan of sulfur mines. This hypothesis matches well with the description of the sulfurous smell of the compound that would not be explained with a normal gossan of limonite or other oxides. These compounds are described as present in the mines of Cyprus (Skourioutissa), of Germany (Goslar), Italy (Massa Marittima), Egypt, Lybia, Cilicia (Hoover et Hoover 1950). In the translation with commentaries of De Natura Fossilium of Agricola (Bandy et Bandy 2004) *misy* is interpreted as copiapite and metavoltine (as in Tab. 4). In order to clarify doubts concerning these descriptions it was decided to conduct archaeological experimentation with a sample of the gossan yellowish compounds found in the most easily reachable mining area, Massa Marittima in Tuscany (Fig. 9).

2.2. Experimental

The experiments were prepared and carried out in order to use samples of "*misy*", in the simplest combination possible as exemplified for example in recipe XXIV of the Leyden Papyrus (Halleux 1981), reported below:

Leyden Papyrus – Recipe XXIV

Layer of Gold, or in other words on the purification of gold brilliance. Four parts of misy; Four parts of alum; Four parts of salt. Stir in the water, cover the gold, put it in a oven in an earthenware vessel. Seal it with lute until the mixture is consumed, then remove it and wash it with fresh water.

The experiment followed this proportion: *Misy* (a yellow mineral from the Massa Marittima mine) and salt in a ratio of 1:1; vinegar, as much as it is necessary to have a sticky cement, and make the stirring of the minerals as easy as possible. We avoided the use of alum in order to check the behavior of the sole yellow mineral.

In a mortar, the yellow mineral was ground, and the vinegar was added to this mixture. The foils of gold, cut from a strip in the form of small rectangles or squares, were added to the mixture inside the crucible. The composition of the gold leaves were for the most part 62 % gold and 38 % of silver (Fig. 10 A, Tab. 5). The crucible was closed and sealed with fresh clay. The furnace was charged with dry wood and burned for a cycle of about 20 hours. The temperature was maintained at 400 °C for the first two hours and then raised in the range between 500°/ 800 °C for the rest of the experiment with some peaks touching 900–915 °C. Once the crucible was opened, a very vivid red color was at first noticed in the inside. The pinkish-purple discolouration of the processed vessels is a typical indication of the salt cementation process which removes iron from the clay as ferric chloride that is in its gaseous phase at the temperature of the procedure (as described by Percy, reported in Craddock et Ramage, 2000). At the base of the crucible, inside, a glossy, mirror-like encrustation was visible, which could be interpreted as silver chloride (Fig. 11).

In order to evaluate the result of the experiment all products were analyzed. The original gold leaves were made of an alloy of electrum composed of gold for about 62 % and silver for 38 % as previously described (Fig. 10, Tab. 5). After the experiments, the silver decreased to 0.3 % (Fig. 10 B and C and Tab. 5) in the alloy, the rest dispersed as AgCl mainly in the crucible matrix (Fig. 11).

From the XRD analyses it appears that the mineral from the Massa Marittima gossan is composed mainly of copiapite, coquimbite and quartz (Fig. 12) in accordance with the

Fig. 9. Sample of a yellow compound coming from the gossan of Massa Marittima-Italia.

Obr. 9. Vzorek žluté sloučeniny pocházející z gossanu z Massa Marittima v Itálii.

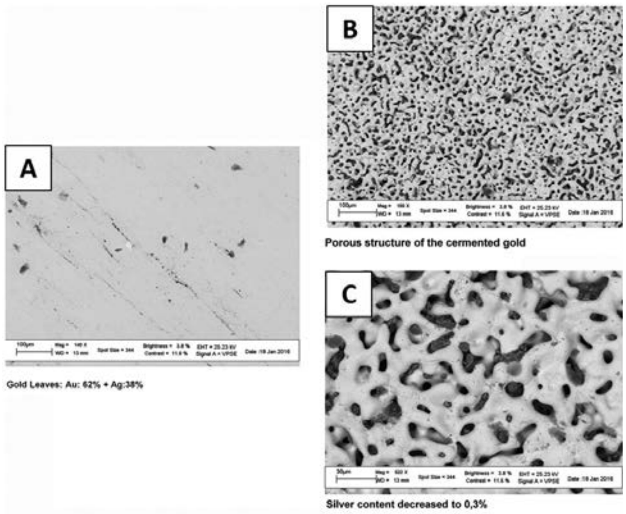

Fig. 10. SEM images in backscattered electrons of the gold, before (A) and after the experiment (B and C).

Obr. 10. SEM snímky zlata ve zpětně odražených elektronech před (A) a po experimentu (B a C).

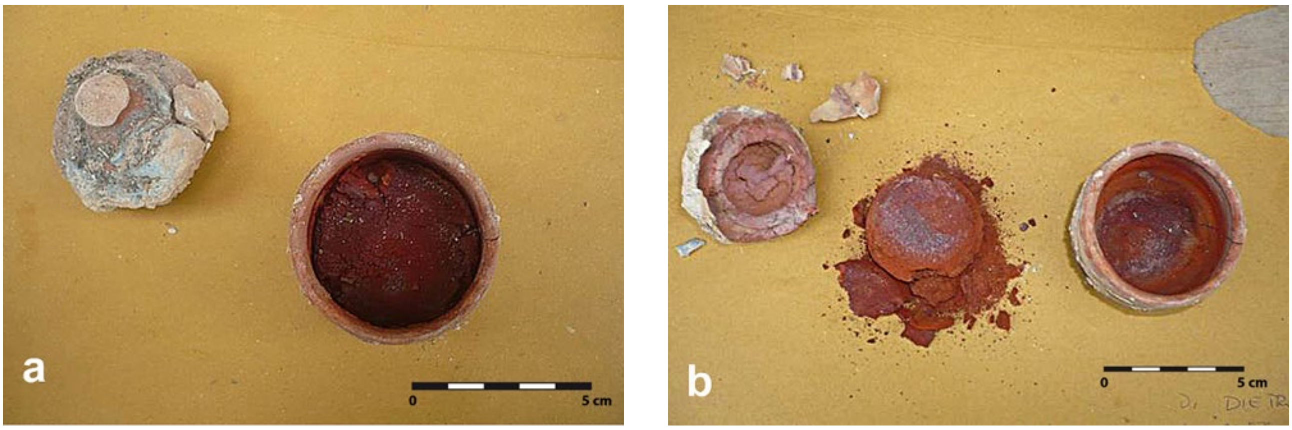

Fig. 11. a) crucible after the experiment with all its content, b) the emptied crucible shows a reddish tinge and a silvery encrustation.

Obr. 11. a) tyglík i s obsahem po skončení experimentu, b) prázdný tyglík se stopami načervenalého zbarvení a stříbřité krusty.

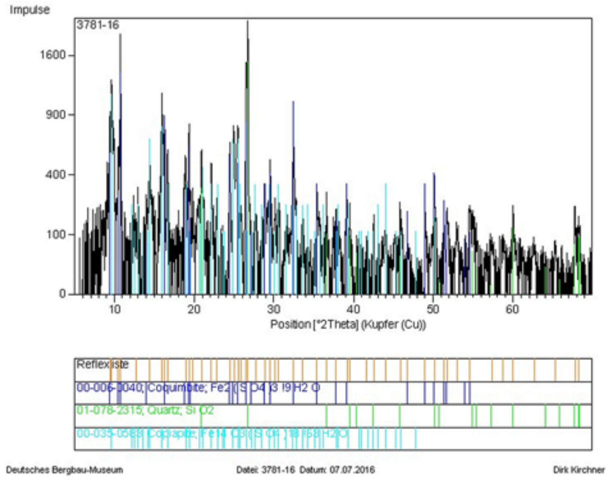

Fig. 12. XRD of the yellow mineral from Massa Marittima.

Obr. 12. RTG difrakce žlutého minerálu z Massa Marittima.

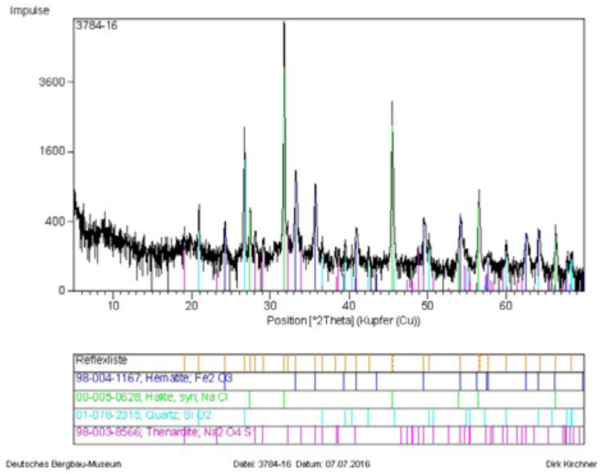

Fig. 13. XRD of the spent cement.

Obr. 13. RTG difrakce použitého cementu.

Tab. 5. EDS compositional table of the laminae in fig. 10 before (A) and after cementation (B and C)

Tab. 5. Tabulka složení plátků na základě EDS před (A) a po cementaci (B a C).

Spectrum	**Cu**	**Ag**	**Au**
A. mean area	0,00	38,7	61,3
B. mean area	0,00	0,36	99,64
B. mean area	0,00	0,00	100,00
B. mean area	0,00	0,00	100,00
C. mean area	0,00	0,00	100,00
C. mean area	0,00	0,00	100,00

indications given for *misy* in Bandy et Bandy (2004) and C. S. Smith (1977). Because of the weathered condition of those gossan samples, the mineral phases are not well maintained, as can be seen in picture 12.

Copiapite ($Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2{\cdot}20H_2O$) and coquimbite ($Fe_2^{3+}(SO_4)_3{\cdot}9H_2O$) are hydrated iron sulphates of the same typology of the tamarugite and kröhnkite present in *ios scolekos*. The decomposition in Fe_2O_3, FeO and SO_3 is balanced for coquimbite in the following reaction. Sodium sulfate or thenardite and hematite were present in the spent cement (Fig. 13), as again analogous to the previous experiment. As well in the XRD of the spent cement, the mineral phases are not well formed.

The hypothesized reactions for dehydrated copiapite is analogous to the one for the decomposition of dehydrated coquimbite, as follows:

$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$

$SO_3 \leftrightarrow SO_2 + 1/2\ O_2$

$2NaCl + SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4 + Cl_2$

with a final production of molecular chlorine. Starting from the consideration made for the first procedure, we can conclude that natural *misy* works as the active agent in the purification of gold because it dissociates during the thermal treatment to its oxides. Again, this gaseous compound reacts with salt producing a very stable thenardite and releasing molecular chlorine, which in turn oxidizes the silver, removing it from the alloy. This procedure can be ascribed to the group of the sulfate and salt-based procedures. Previous researchers had already hypothesized that *misy* was identifiable as a sulfate or a mixture thereof but our endeavor represents a first attempt to collect a possible sample, following the indications of ancient documentations, and to use it for the production of a cement. It is to be noted that the difference between the first and second procedure is the presence of iron (III) instead of copper which, as it will be explained in the next paragraph, can be an important agent in the cementation of gold.

3. On the use of brick powder in ancient gold cementation

3.1 Textual sources

The third set of experimentation concerns the use of powdered brick and salt, which was first described by Theophilus Presbyter in his De Diversibus Artibus (Craddock et Ramage 2000), presently dated in the XII century.

Break into tiny pieces a tile or piece of burnt and reddened furnace-clay and when it is powdered, divide it into two equal parts by weight and add to it a third part of salt of the same weight. It should then be likely sprinkled with urine and mixed so that it does not stick together but is just moistened.

The use of powdered brick cement was common in medieval times. The production of a purifying cement composed of pulverised brick, salt and urine or vinegar is also described in De Perfecto Magisterio, in the Pirotechnia of Biringuccio, in Agricola's De Re Metallica (Hoover et Hoover 1950), in Lazarus Ercker's Beschreibung der allerfürnemsten Mineralischen Ertzt und Bergwerksarten (1574, that not only mentioned the use of brick dust cement but verdigris and vetriols as well for the purification of gold), just to make some examples. This type of salt parting is the only one reproduced in previous experimentation with modern apparatus by D'Elhuiar, Boussingault, Percy, Hall, Notton and more recently by Craddock. These experiences have produced a large amount of comparative data. In the XIX century, it was believed that the mixing of salt and brick dust caused the development of HCl that removes silver as a chloride, but from daily experience with the use of an HCl solution for the cleaning of gold alloys, it is evident that only copper is removed in an appreciable way, even when the gold artefact is heated and emerged.

3.2. Experimental

Two experiments were undertaken: one was conducted together with the trial with *ios scolekos*, thus sharing the same thermal ramp, the same timing, the same type of equipment and the same kind of gold alloy as testers, while the other experiment was set at a lower temperature, in order to gain more information on temperature-dependant factors. The cement was prepared by mixing one part of natural salt to one part of powdered brick, not following to the word the indications of Theophilus, that states the use of two parts of brick dust and one of salt. In fact, from the evaluation of other textual sources such as, for example, the De Perfecto Magisterio (Craddock et Ramage 2000), where the advice is to use two parts of salt and one of brick dust and from the consideration of other experiments previously executed with the use of different combinations in quantity of reagents, it is possible to state that the cementation works always, as long as the presence of the active agents, brick dust and salt, is assured in sufficient quantity. For instance, D'Elhuiar in the eighteenth century (Craddock et Ramage 2000) ran experiments consisting in the heating of a clay crucible containing salt alone and noticed the development of a reaction between the salt and the crucible walls. The gold leaves, identical to the ones used with the *ios scolekos* cement, were prepared by cutting small squares from the same gold ribbons. The amount of silver in the gold alloy varied between 7 and 25 % in weight, identical to the other crucible. The XRD of the brick powder is reported in Fig. 14 and the EDS results are in weight percent in Tab. 6. The brick dust is mainly composed, as evidenced by the XRD analysis, of quartz and the high temperature phase cristobalite, diopside and by hematite, albite and gehlenite. These mineral phases are common in pottery that underwent heating during cooking. In fact, clay minerals, mainly composed of phyllosilicates, that contain hydrogen and oxygen in the form of hydroxyl, expel the water over 550–600 °C. Over 1000 °C the phyllosilicates decompose in silica (quartz and cristobalite), alumina and sodium and aluminum silicate such as albite, gehlenite and diopside (by interpreting the results obtained from XRD, Fig. 14, kyanite was detected as well from additional XRD analyses).

The crucible was filled with alternating layers of cement and gold leaves and the last layer was moistened by aged urine and sealed. After the thermal treatment of 19 hours all the reagents and products were analysed. The processed gold foils (Fig. 15, Tab. 7) was refined to 99,2 to 100 %, with silver presence for a maximum of 0,12 % in weight (considering as well copper residuals). XRD analysis of the spent cement indicated the presence of albite with quartz and hematite (Fig. 16). A SEM-EDS analysis of the crucible walls again showed that silver chloride was absorbed by them (Fig. 17, Tab. 8). Again, the analyses are confirmed by the XRD spectrum of the powdered walls and base of the crucible (Fig. 18), where the mixed chloride of silver and sodium has been evidenced. The possible interpretation of the results is proposed as follows:

1) by mixing the brick dust with the sodium chloride in a wet environment (due to the urine and the water used to moisten the crucibles overnight), over 650 °C the silica acts as a catalyst in the pyrohydrolysis of sodium chloride (Zhou et al. 2016):

$2NaCl + SiO_2 + H_2O \rightarrow Na_2O{*}SiO_2 + 2HCl$

It is hypothetically stated that alumina (not present in the XRD spectrum in Fig. 14 but whose presence is realistic because of the thermic decomposition of clay minerals during brick cooking) as well can have a role: in fact, NaCl and alumina react in a similar way as NaCl and SiO_2, by giving sodium aluminate and HCl (Clews 1925).

We then propose that albite is as well a product of this reaction, as follows:

$2NaCl + 6SiO_2 + Al_2O_3 + H_2O \rightarrow 2NaAlSi_3O_8 + 2HCl$

2) It can be assumed that the silica can be re-formed partially by the reaction of the produced albite and calcium carbonate:

$2NaAlSi_3O_8 + CaCO_3 \rightarrow CaAl_2Si_2O_8 + Na_2CO_3 + 4SiO_2$

We hypothesize that this reaction could take place because the reagents are present in the brick dust (calcite and albite) and the products can be obtained on heating, but the effective occurrence is theoretical, as these products are only partially observed in the XRD spectrum (silica):

3) The reaction between iron oxide (hematite in the brick dust) and HCl can be defined as a chlorination:

$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$

4) From thermic decomposition and dehydration that starts at 500°C (Moody 1991) the molecular chlorine is released (reaction described as well in Craddock and Ramage 2000: 181, with a starting temperature of 700–800 °C):

$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$

1*) Alternatively, the production of iron chlorides can take place as well without considering the formation of HCl, but involving a direct reaction between the reagents at temperatures higher than 801°C because sodium chloride, that is in molten state at that temperature, can react with iron oxides inducing a spontaneous volatilization of chlorination products ($FeCl_3$). In fact, at temperature higher than 801 °C, in the case of the reaction between goethite and sodium chloride, the ΔG^0 began positive, while for lower temperatures it stays negative (as in Zhou et al. 2016).

$FeO\ (s) + 2NaCl\ (l) \rightarrow Na_2O(s) + FeCl_2\ (g)$

Beside the production of $FeCl_2$, a reaction is as well proposed for hematite as follows:

$Fe_2O_3\ (s) + 6NaCl\ (l) \rightarrow 3Na_2O(s) + 2FeCl_3\ (g)$

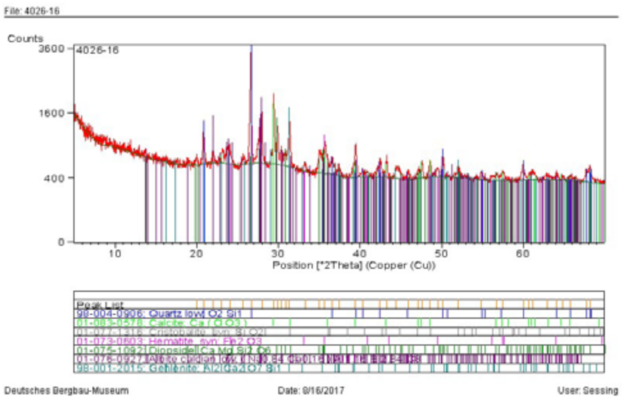

Fig. 14. XRD of the brick dust.

Obr. 14. RTG difrakce cihlového prášku.

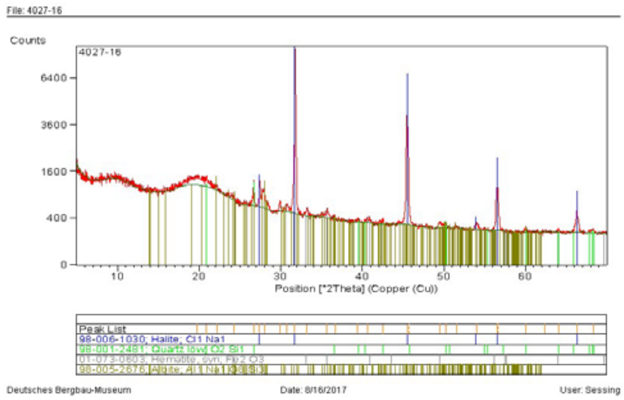

Fig. 16. XRD spectrum of the spent cement.

Obr. 16. RTG difrakční spektrum použitého cementu.

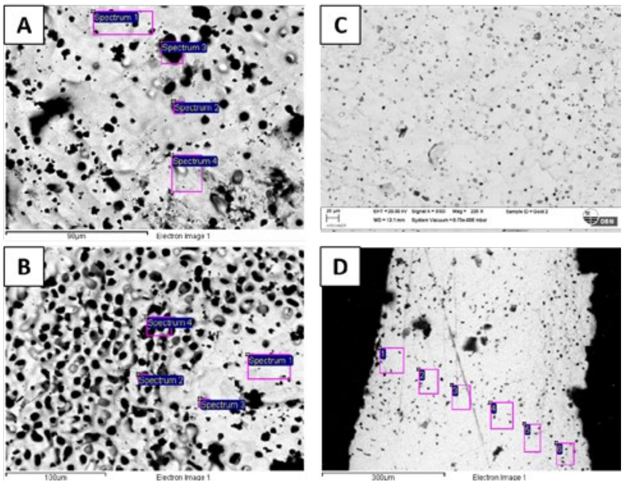

Fig. 15. SEM images in backscattered electrons of the gold, after the experiment (A, B and C) and a cross-section of a gold leaf embedded in resin after the experiment (D).

Obr. 15. SEM snímky zlata ve zpětně odražených elektronech po skončení experimentu (A, B a C) a snímek příčného řezu zlatým plátkem zalitým pryskyřicí po skončení experimentu (D).

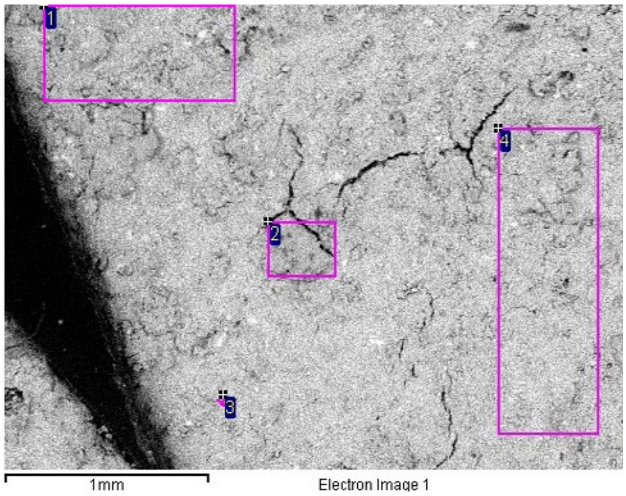

Fig. 17. SEM image in backscattered electrons of the crucible section after the experiment.

Obr. 17. SEM snímky řezu tyglíkem ve zpětně odražených elektronech po skončení experimentu.

5) $FeCl_3$ decomposes in molecular chlorine and iron chloride that volatilizes at that temperature (the development of iron chlorides in gas form was, as well, inferred by the yellow ejection of gases coming from the crucible, and the absence in the XRD spectrum is explained by their total development in gas form at the temperature of operation). The molecular chlorine is then the active agent of the reaction of silver oxidation. The Na_2O produced as well in this reaction can react again with SiO_2 producing a sodium silicate (Zhou et al. 2016).

It is possible to infer a direct reaction as well of residual lepidocrocite (coming from the clay minerals composing the brick dust and the crucible) with salt and silver in the cement and the function of Fe as the oxidizing agent of silver, following the hypothesis of the chemical phenomena involved as follows:

1) The pulverized baked brick is composed of phyllosilicates. The general formula is: $A_3Si_2O_5(OH)_4$ or $A_3Si_4O_{10}(OH)_2$, where A = (Mg, Ca Na, K, Fe, Al).

2) In the phyllosilicates, the iron can be a redox agent. It is thermodynamically sound the hypothesis that iron (III) acts as the oxidizing agent of Ag (0) in the presence of chlorides.

3) In phyllosilicates, the state of oxidation of iron varies from +2 to +3 without altering its structure significantly (so long as it compensates the charge with other ions, in this case sodium.) Therefore, the reaction that the procedure shall follow could be hypothesized as below:

x Ag + x NaCl + A_3-yFe(III)y$Si_2O_5(OH)_4$ → x AgCl + A_3-yFe(III)y-xFe(II)yNax$Si_2O_5(OH)_4$

In this case, high temperature is a necessary condition to activate the kinetics of the process, since the reaction is hypothesized to occur in solid-state. In order to verify fully all the gaseous species developed and the reliability of the reactions proposed, a further experiment conducted by using mass spectrometry coupled with Knudsen cell and the evaluation of enthalpy and free energy is desirable in the future. Other indications can be obtained by other trials made with the brick dust process, that warrant the conclusion that

Tab. 6. EDS compositional table of the brick powder (all results in weight percentage).

Tab. 6. Tabulka složení cihlového prášku na základě EDS (všechny výsledky jsou uvedeny v hmotnostních procentech).

Spectrum	Na-K	Mg-K	Al-K	Si-K	P-K	S-K	Cl-K	K-K	Ca-K	Ti-K	Fe-K
Brick powder	0,73	2,57	14,45	40,51	0,73	0,10	0,13	2,87	27,74	0,90	9,28

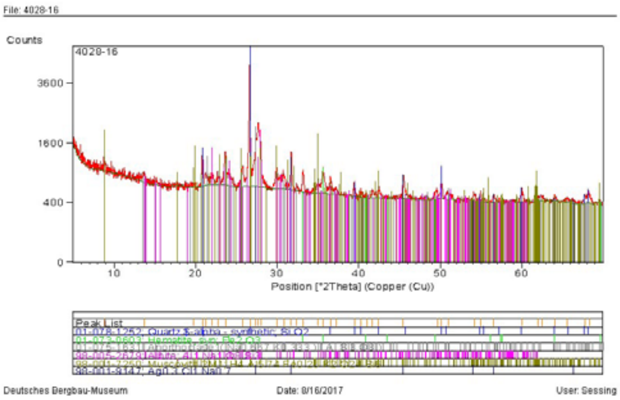

Fig. 18. XRD spectrum of the crucible after the experiment.

Obr. 18. RTG difrakční spektrum tyglíku po skončení experimentu.

Tab. 7. EDS compositional table of the laminae after the cementation (A, B, C) and a section of a refined leaf (D) of fig. 15 (all results in weight percentage).

Tab. 7. Tabulka složení plátků po skončení cementace (A, B, C) a řezu vyčištěným plátkem (D) na základě EDS (všechny výsledky jsou uvedeny v hmotnostních procentech).

Spectrum	Cu	Ag	Au
A.1	0,24	0,00	99,76
A.2	0,00	0,37	99,63
A.3	0,63	0,00	99,37
A.4	0,00	0,00	100,00
B.1	0,32	0,00	99,68
B.2	0,03	0,00	99,97
B.3	0,23	0,00	99,77
B.4	0,40	0,00	99,60
C. mean area	0,33	1,05	95,58
D.1	0,21	0,15	99,64
D.2	0,00	0,23	99,77
D.3	0,14	0,00	99,86
D.4	0,31	0,01	99,68
D.5	0,00	0,09	99,91
D.6	0,00	0,03	99,97

Tab. 8. EDS compositional table of the section of crucible wall in fig. 17 (all results in weight percentage).

Tab. 8. Tabulka složení řezu stěnou tyglíku na základě EDS (všechny výsledky jsou uvedeny v hmotnostních procentech).

Spectrum	O	Na	Al	Si	Cl	Fe	Ag
1	49,74	4,53	9,21	28,73	1,47	6,18	0,14
2	49,57	4,68	9,67	29,64	1,16	4,9	0,38
3	40,28	11,56	6,53	19,96	14,9	5,90	0,87
4	49,22	4,59	9,45	30,17	1,16	5,35	0,06

high temperatures are a necessary condition to activate the kinetics of the process which in the case it occurs in a solid state, is fairly slow. In fact, two additional trial runs experiments have been executed: in one the temperature was kept no higher than 550–650 °C for 17 hours and in the second trial an electric oven was used as a comparison with the use of the furnace. In both cases gold purity did not exceed 92 %, indicating that a higher temperature is fundamental to the success of the total purification of gold within that time range. As some ancient sources indicate longer and repetitive processing, this lower temperature range would account for it. However, very high temperatures may disperse gold within the matrix, as evidenced in the use of sulfate-chloride compositions, making recovery of pure values more complicated. A further issue is the resistance of coarseware vessels to high temperatures. It is important to note that NaCl will not dissociate spontaneously at high temperature but necessitates an agent to trigger the thermodynamic reaction, in this case the presence of silicate, alumina or phyllosilicates.

4. On the controversial description of Agatharchides of Cnidus on gold mining and metallurgy

4.1. Textual sources

In conclusion, a very intriguing text describes a method which for the moment has raised several questions and doubts on its reliability, as none of the past experiments has succeeded in its reproduction. The text is the very detailed description of the mining and metallurgy of gold given by Agatharchides of Cnidus (On the Erythraean Sea, 169 BC) as reported in the texts of Diodorus Siculus and Photius (Translation with comments by Burstein, 1990). The whole passage concerns gold production in Egypt, in the gold-bearing regions between the coast of the Red Sea and the Nubian Wadi. The two authors do not differ substantially in their descriptions of the smelting process. The more familiar passage from Diodorus Siculus (Burstein 1990, right column):

Finally other technicians gather up the gold that has collected, and pack it according to a fixed measure and weight into pottery vessels. They mix in a lump of lead of a size proportionate to the amount of gold and pieces of salt and, in addition, they add a little tin and barley bran. Having covered it with a close fitting lid and thoroughly sealed it with clay, they bake it in a kiln for five days and an equal number of nights continuously. Then, after allowing it to cool, they find in the jars none of the other substances, but they obtain pure gold with only a small amount having been lost.

And Photius (Burstein 1990: left column):

After, thus, completely separating out the gold nuggets, the Selangeus turns them over to the smelters. These take up the ore by set amount and weight and place it in a pottery vessel. Then, after adding in accordance with a fixed proportion a lump of lead, grains of salt and a little tin and barley bran, *they put on a close fitting lid, seal it all around and smelt it continuously in a kiln for five days and an equal number of nights. On the next day, after cooling the smelted ore slightly, they pour it out into a vessel and find that of what was put in with gold nothing remains, but of gold there is a solid mass, albeit slightly reduced in mass because of the dust.*

The historian described the gold refining process after a detailed account of the operations of fire-setting and of concentrating gold-rich metallics through labour intensive mechanical procedures ("on dry winnowing" and "wet beneficiation" see Neesse 2014), aimed at reducing the gangue. Agatharchides then discussed the heat processing of the gold powder by the addition of salt, tin, lead and sorghum flour, determined by specialized workers, in definite proportions and sealed in one or more earthenware jars. The jars were then fired at unreported temperatures for five days and five nights. According to the English translation in the Loeb Classical Library (1893) after the cooling of the jars, the only residual matter inside it was purported to be pure gold (the translation of course can be debatable on some points).

Notton in the '70's (Notton, 1974) reproduced it, by dividing the process into several tests. In each test Notton added a component of the procedure per trial. He made first a trial charged with salt alone in a sillimanite crucible. He deemed the experiment successful (it is believable that he used brick dust as well in his mixture). Lead is mentioned then as a possible fluxing agent to remove the traces of siliceous gangue (Notton 1974, Craddock et Ramage 2000). Notton then interpreted the presence of sorghum, or barley bran, as a reducing agent- correctly in our view- and substituted the flour with the addition of charcoal to the crucible charge. The addition of charcoal reduced the refined product to 80 % gold. The addition of lead and especially tin reduced even more the results, leading Notton to speculate that Agatharchides' interlocutors may have misled him concerning the addition of tin. Regardless the degree of success, experimentation produces results and data of value for subsequent trials. Although Notton used gold foil, he mentioned the possible use of lead as a scorifier of the residual gangue (Notton 1974), and, as well, Craddock considers the processing of gold dust instead of gold leaves (in Craddock et Ramage 2000). Yet throughout his experiment Notton did not consider processing a charge containing gangue nor did he use porous coarseware vessels with a high iron content, common to ancient usage. Craddock's appraisal of Notton's experiments focused on the possible presence of traces of ferric oxide in the sillimanite crucibles and the likely presence of water vapor in ancient furnaces that would have facilitated the formation of free chlorine necessary to oxidize the silver.

4.2. Experimental

Three sets of experiments have been conducted since 2008, the last in 2016. Results were discouraging largely due to the difficulty of duration (five full days), as well as the two initial failures. In fact, five days at high temperatures implied an enormous waste of energy resources, which is why we elected to curtail experiments earlier to gather preliminary evidence. The initial approach in 2008 was a replica of Notton's experiment with gold alloy foil, however using coarseware vessels instead of sillimanite and wood rather than electricity as fuel. The furnace used was the same built based on archaeological evidence found at Sardis and used for the experiments of *ios scolekos* and brick dust. In the first experiment, gold foils were put in a crucible with metallic lead and tin, salt and barley bran and heated for 15 hours at 500 °C. The experiment was unsuccessful as far as cementation was concerned, as the gold alloy appeared unaffected by the addition of the reagents (copper and silver remained alloyed to the gold as is visible from the SEM-EDS analyses). In 2015, we considered that the lead and tin served as a collector of metallic values in a first stage of the process. We therefore substituted the gold leaves with gold laboratory sweepings mixed with cement made of lead, tin, salt and coarse ground durum wheat. Once again the duration was limited to 17 hours at temperatures in the 800–900 °C range. At the end of the procedure it was evident that the procedure had not succeeded. From the SEM-EDS analyses it was clear that salt became a fused mass which did not participate in any reaction, while the tin and lead had effectively collected all metallics deposited at the bottom of the crucible, forming a low-melting alloy of gold, silver, copper, lead and tin. The ground durum was found carbonized on top of the charge. From this point on, we focused on resetting the interpretation of the procedure aimed at a new set of experiments.

The following considerations were formulated before the reproduction of the third set of experiments. Since the text of Agatharchides first describes the mining and extractive processes conducted in the Nubian mines, it is apparent that the charge to be processed consists of metallic concentrates with gangue in the form of dust, for no matter how meticulous mechanical separation is undertaken, gangue cannot be totally eliminated. According Klemm et al. (2001), the gold in the area described by Agatharchides was associated with sulfidic ores in quartz. It appears that the flux described by Agatharchides was an all-purpose flux. One would consider the method as crucible scorification coupled with salt cementation. In crucible scorification the mixture of lead, tin, flour and salt would initially act as a collector of metallic values and the production of slag with the gangue. The slag would be removed by skimming and the liquid metal would then be subject to strong drafts to oxidize all metals other than gold, silver and possible PGE, as previously described. The flour would act as a reducing agent, benefiting the collection of metallics from the gangue. However, the method described by Agatharchides excludes the possibility that the slag was removed or that the lead was oxidized since the vessel was reportedly sealed throughout the process. It therefore appears that an initial phase consisted in collection and scorification followed by a lengthy process of cementation, provided there was sufficient salt and possibly sulfuric compounds, as characteristic of gangue in that area. We considered that the presence of lead and tin would hamper cementation by forming a liquid alloy at the bottom of the crucible. A further difficulty was to hypothesize possible temperature ramps for the conflation of two processes that, taken separately, work egregiously in lesser time cycles that would require no more than 30 hours at the most to produce pure gold. After these considerations, a new set of experiments was set as follows: the low-melting point alloy obtained during the last experiment was placed in the crucible, covered by an additional amount of gold and silver dust, sorghum flour and a compound produced by adding ground sulfidic ores (mainly galena) in quartz and limestone as a simulation of the gangue. Natural salt was then added to fill the crucible. Two crucibles were filled with this mixture, closed with a close-fitting lid and sealed with high-temperature resistant lute (clay mixed with animal hair and straw) and then placed for 19 hours in the circular oven built in the shape of a small chamber of round shape and 70 cm in diameter. The temperature was kept in the range of 700–900 °C and during the final half an hour raised over 1100 °C by the combined use of two bellows. After removing the crucibles from the furnace, the presence of fused material that had seeped out of the crucibles was noted. The lute was then broken off and the contents of the two crucibles were reversed onto a flat stone surface. The material was primarily composed of residuals of carbonized sorghum flour, while the residual material adherent on the inside wall of the crucible, closely resembled what Agatharchides described in his passage: a button of gold in the middle of the crucible, surrounded by slag partially absorbed in the crucible. From this long-lasting and fascinating challenge and especially from these final results we believe Agatharchides' account is to be vindicated as his description actually matches well with experimental results. After these positive experimental results, the crucible was cut in two parts in order to allow macroscopic observation and a simple execution of SEM-EDS analyses of the inside (Fig. 19, Tab. 9).

The gold button was cut in half and analysed. The results show that lead and tin are present in a minimum amount, especially in the encrusted areas where the salts attached to the surface of the button that is mainly composed of gold and silver (Fig. 20 and Tab. 10).

From direct observation, we noted the presence of slag-like material encrusted on the outside and inside of the crucible. The inside slag seemed to bear several millimeter and sub-millimeter gold droplets, while the button of gold in the center looked pale in color, suggesting the presence of silver in the alloy. From these considerations, some hypotheses were elaborated and then validated by comparison with analytical results. The hypothesis that this passage of Agatharchides was not describing a cementation procedure but a combination of scorification or collection of gold and then a subsequent cementation is likely to be realistic, as can be deduced from the SEM-EDS analyses. The slag encrustation on the outer surface of the crucible, starting at the crucible lip, probably leaked from the inside of the crucible by a fracture in the sealing lute. It has a composition that matches well with the composition of the simulated gangue and a minimum quantity of salt. Moving the electronic beam inward, the crucible wall was crossed and analyzed. In the ceramic matrix (in the dark gray area in the picture), frequent needles of what is interpreted as a mixed chloride of lead and sodium were encountered. The stoichiometric calculations of relative atomic percentage confirm the hypothesis, but an XRD analysis will be required in order to confirm the thesis. The slag in the inside of the crucible is mainly composed of mixed chlorides of tin, lead and sodium, finely dotted with gold microglobules alloyed with silver. The button in the center of the crucible is composed of an alloy of silver and gold, with minimum traces of lead and lesser of tin. In some areas, the button is encrusted with chlorides of lead, tin and sodium. In conclusion, from the evidences produced during the experiment and coming from the direct observation of the crucibles and under the scanning electron microscope it is possible to deduce the following:

The procedure described by Agatharchides is a combined process of scorification and collection of the precious metal coming from mining extraction and beneficiation of the gold-silver alloy from the gangue through mechanical separation and selection. In this case the lead and tin were added in order to scorify the gangue by the reaction of the quartz and limestone present in the simulated gangue.

The lead and tin alloy with the higher melting metallics thus forming a low melting alloy that gradually collects at the bottom of the crucible.

The barley bran has two possible functions that are reported here as hypotheses: the bran once carbonized, favors the reduction of the mass; moreover, the bran, which, with its combustion increases the reducing power of the atmosphere inside the oven, to facilitate the alloying of gold with lead, before the latter oxides, such as would normally occur in an oxidizing atmosphere.

The galena and the quartz, added to simulate the gangue, react giving a low melting lead silicate slag while the sulphur volatilizes and may be implicated in the production of molecular chlorine (consideration that has still to be proved). The production of molecular chlorine in this case could be replaced by the reaction between salt with the SiO_2 of the gangue and the iron silicates of which the crucible is composed, as explained in the paragraph dedicated to the use of brick powder and proven by experiments of gold cementation with the sole use of salt in the crucible (the crucible's walls are active agents as in D'Elhuiar's experiments in the eighteenth century).

Galena can undergo a non-oxidative leaching by HCl producing lead chloride $PbCl_2$ and hydrogen sulfide.

$PbS + 2HCl \rightarrow PbCl_2 + H_2S$

As well, tin at about 150°–250 °C can be chloritized to stannous chloride $SnCl_2$ or to stannic chloride $SnCl_4$. The thermal decomposition over 623 °C of stannic chloride to stannous chloride can be a hypothetic source of molecular chlorine (indicated in Lewis 1996, as toxic, after thermal

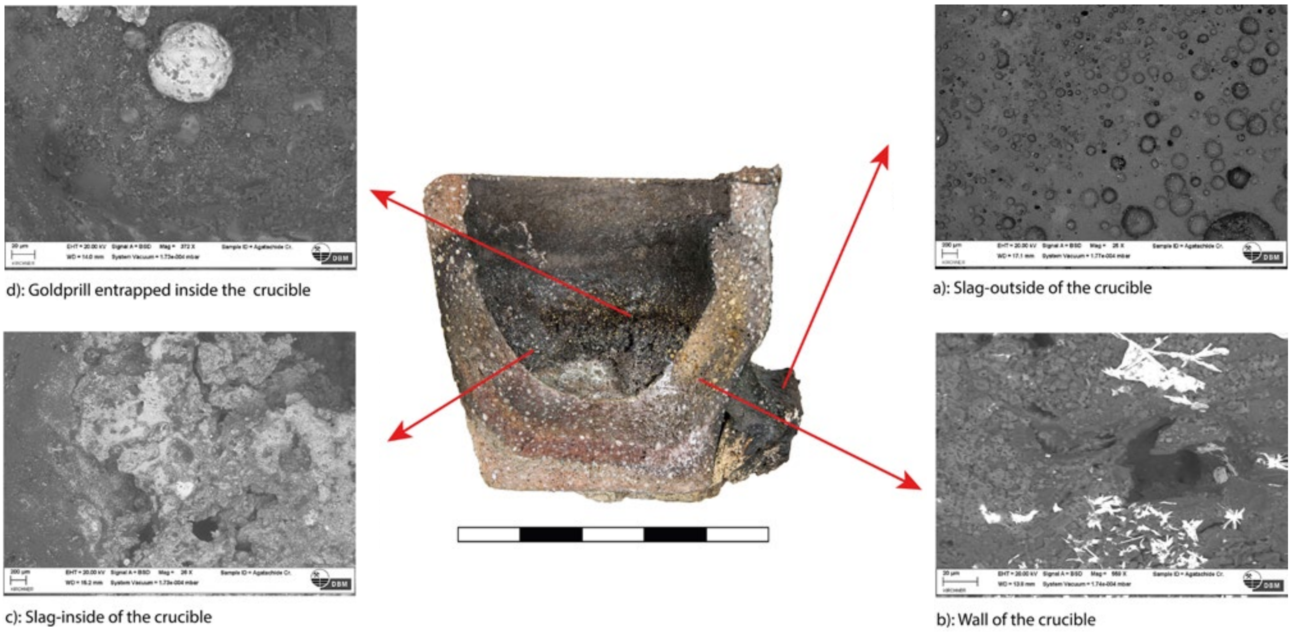

Fig. 19. Cut section of the crucible and SEM images of distinguished areas.
Obr. 19. Řez tyglíkem a SEM snímky vybraných částí.

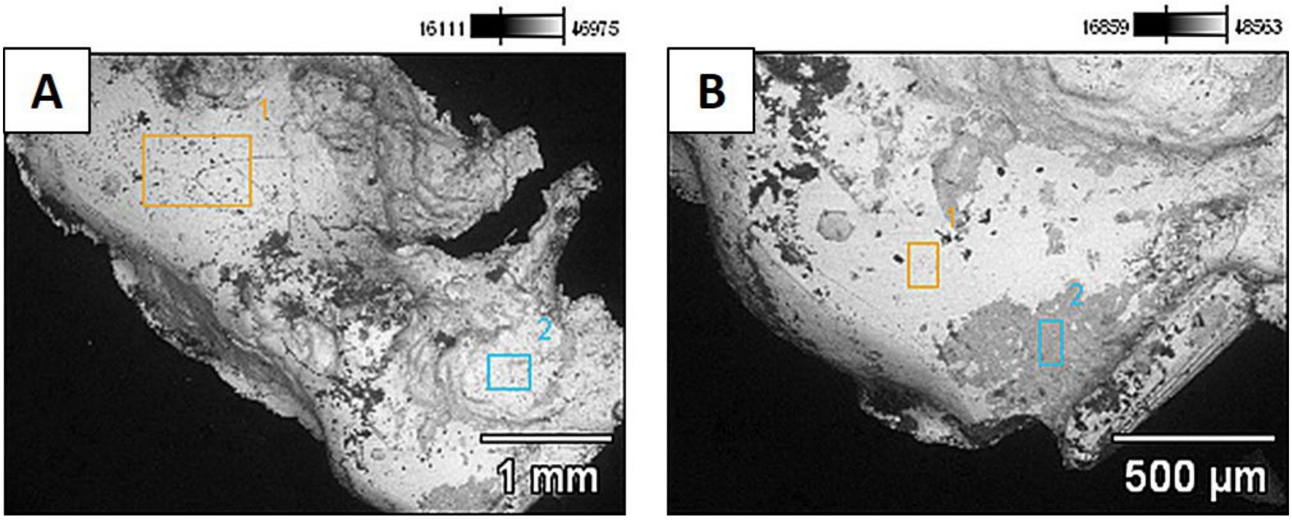

Fig. 20. SEM images in backscattered electron of the gold button.
Obr. 20. SEM snímky zlatého knoflíku ve zpětně odražených elektronech.

decomposition for the development of fumes of chlorine). This hypothesis needs to be proven by the use of mass spectrometry coupled with a Knudsen cell.

Lead chloride, $PbCl_2$, melts at 501 °C and is absorbed by the slag and crucible walls or partially lost in its gaseous phase that develops at 950 °C. In fact, this compound is found in the crucible walls and in the inner slag. A similar reaction regards tin as well, oxidized by molecular chlorine to $SnCl_2$ that melts at 247 °C and evaporates at 623 °C. The lower temperature of the gaseous phase could explain the reason why its presence is scarce in comparison to the presence of lead chloride. It has to be noted that the gold-silver button is almost totally lead and tin free, so that the function of these components is only to collect the precious metals, and then separate from it after oxidation with chlorine.

A further role of $SnCl_2$ at moderate temperatures could be to facilitate the precipitation of metallic values from their salts which would be favorable in the case of possible gold compounds but a hindrance to the production of $AgCl_2$ until the complete removal of tin from the reactive vessel.

As evidence suggests the formation of molecular chlorine in the crucible, we may assume that by following the Agatharchides process as described for the full duration of five days and five nights, it would be possible to remove the silver from the gold button. So, in this case the procedure should not conflate two different processes (Healy 1993) but describes a delicate procedure consisting of two different

Tab. 9. EDS compositional table of the slag outside the crucible, the slag inside the crucible, the crucible section walls and gold prills in the slag inside the crucible in fig. 19 (all results in weight percentage).

Tab. 9. Tabulka složení strusky vně tyglíku, strusky uvnitř tyglíku, řezu stěnou tyglíku a zlatých krystalků ve strusce uvnitř tyglíku na základě EDS (všechny výsledky jsou uvedeny v hmotnostních procentech).

Spectrum	Na-K	Mg-K	Al-K	Si-K	P-K	S-K	Cl-K	K-K	Ca-K	Ti-K	Fe-K	As-K	Cu-K	Ag-L	Sn-L	Au-L	Pb-L
A) Slag outside the crucible (mean area)	6,14	1,86	6,59	23,82	0,18	0,22	5,10	1,92	14,89	0,36	3,47	0,00	0,00	0,00	0,00	0,00	35,45
A) Slag outside the crucible (mean area)	2,36	3,27	10,21	33,75	0,39	0,22	0,95	2,52	28,38	0,49	5,32	0,00	0,00	0,00	0,00	0,00	12,13
B) Wall of the crucible (white area)	6,99	0,28	5,80	14,11	0,24	0,23	20,38	0,83	1,10	0,23	2,21	16,73	0,00	0,00	0,00	0,00	30,87
A) Slag outside the crucible (mean area)	6,14	1,86	6,59	23,82	0,18	0,22	5,10	1,92	14,89	0,36	3,47	0,00	0,00	0,00	0,00	0,00	35,45
A) Slag outside the crucible (mean area)	2,36	3,27	10,21	33,75	0,39	0,22	0,95	2,52	28,38	0,49	5,32	0,00	0,00	0,00	0,00	0,00	12,13
C) Slag inside the crucible (white areas)	4,75	0,08	0,83	2,10	0,00	0,53	5,59	0,04	0,63	0,06	0,61	0,00	1,99	17,10	0,00	63,01	2,68
C) Slag inside the crucible (medium gray)	24,84	0,52	2,23	5,38	0,00	0,26	30,54	0,17	1,88	0,06	4,62	0,00	0,00	2,71	0,00	0,00	26,79
C) Slag inside the crucible (white areas)	5,08	0,11	0,86	2,38	0,00	0,32	3,56	0,00	1,24	0,15	0,28	0,00	0,93	42,69	0,00	42,40	0,00
C) Slag inside the crucible (medium gray)	20,86	0,22	1,18	3,49	0,13	0,21	28,67	0,17	1,24	0,05	0,93	0,00	0,00	8,19	4,17	0,00	30,49
C)Slag inside the crucible (medium gray)	13,98	0,01	1,95	6,74	0,03	0,00	17,44	0,25	2,29	0,18	0,96	0,00	0,00	0,00	16,84	0,00	39,32
D) gold prills in the slag (light gray)	10,54	0,38	3,63	8,51	0,05	0,12	10,35	0,35	0,61	0,13	1,83	0,00	1,35	5,80	0,00	55,08	1,28
D) gold prills in the slag (white)	6,06	0,20	3,10	7,84	0,00	0,39	6,77	0,41	0,68	0,16	1,52	0,00	1,33	12,04	0,00	57,05	2,46

Tab.10. EDS table of the gold button in fig. 20 (all results in weight percentage).

Tab. 10. Tabulka složení zlatého knoflíku na základě EDS (všechny výsledky jsou uvedeny v hmotnostních procentech).

Spectrum	**Na-K**	**Mg-K**	**Al-K**	**Si-K**	**S-K**	**Cl-K**	**Ca-K**	**Ti-K**	**Fe-K**	**Ag-L**	**Sn-L**	**Au-L**	**Pb-L**
A.1	1,93	0,14	1,14	0,42	0,44	2,77	0,00	0,11	0,36	40,71	0,00	50,43	1,40
A.2	1,28	0,15	1,35	2,18	0,33	2,87	0,34	0,00	0,71	27,06	6,59	48,07	8,91
B.1	0,62	0,11	1,45	0,39	0,23	1,71	0,17	0,00	0,17	30,75	0,78	62,76	0,66
B.2	2,84	0,22	1,67	1,00	0,00	12,51	0,36	0,00	0,15	28,48	35,87	8,18	8,36

and subsequent steps. In this case it may be necessary to use a larger quantity of salt, in order to completely oxidize the lead, tin and, subsequently, the silver.

This assumption has to be further confirmed by the XRD analyses of the slag residuals and the crucible walls, and the gaseous phases has to be detected with Knudsen cell Mass Spectrometry, in order to definitively interpret this complex procedure. However, the process reproduced in experimental archeology precisely follows Agatharchides' description also in the results obtained. The scorification and collection procedure is guaranteed by this mixture of compounds, that, put together, allow this fine and delicate reaction to take place.

CONCLUSIONS

This excursus of ancient recipes and reproductions in experimental archeology and their analytical characterization had the scope to identify the active reagents and products in different kind of procedures involving gold purification and collection. From the direct experience of combining these different approaches of research it can be stated that the evidence, garnered by observations made during the direct reproduction of pyrometallurgical processes, provide insights which allow the formulation of hypotheses for the interpretation and understanding of archaeological evidence, ranging from the workshops and furnaces to the characterization of waste materials and artifacts. Beside this, many aspects of ancient metallurgical procedures are fraught with unknowns and, due to the lack of practical knowledge, interpretations are often misleading. The wide variety of ancient procedures has yet to be tested and characterized in its many possibilities. This text therefore has reported results from procedures arranged chronologically and geographically in order to have as much as possible a picture of the panorama of the gold metallurgy in the course of its development. These processes, as regards cementation, invariably have been used, in different scales, until the advent of the acid purification methods. The necessity to go on with this kind of experimental approach lies in the need to have controlled and standardized replicas of each step of the procedures that can be used as comparisons in the study of archaeological evidence, such as artifacts, crucibles, slags and so on. For example, the experimentation of sulfides such as stibnite as the sole active agent of cementation, without the addition of salt, may be necessary to fulfill the intent to have a whole idea of the possibilities in gold cementation. This process is described in the Probierbüchlein, a short practical manual published first in 1524, but whose possible usage may be assigned to the Ancient Egypt as well (Davies 1935). The retranslation of some of the textual evidences could give new insights and clues in the development of this branch of research.

SUMMARY

Gold occurs in nature principally as a native metal and as an alloy with variable quantities of silver, copper, nickel and platinum group elements, present in relation to their origin from primary or secondary deposits. Mineral inclusions, such as quartz and pyrites, and other impurities are not uncommon. These variations in composition of the raw material are reflected in the physical properties, possible defects and consequential workability, that necessitated beneficiation processes at an early stage of gold's exploitation. The knowledge of gold colouring, that implies the voluntary control of gold alloying for technical and aesthetic reasons, is suggested by evidence, such as the use in the earliest period (III-II millennium BC in the ancient Near East) of a complex and specific terminology concerning different types of gold, based on the aesthetic qualities of colour. Other evidence indirectly hints to the pyrometallurgy of gold, yield from mining extraction and trade of semi-finished products. Later texts, such as recipe books and natural treatises describe the use of cements for gold and their use as purification agents. Other operations that recall recent methods of assaying are present as well in ancient texts, as the first documentation of the separation of gold from its gangue, its collection and the scorification of waste residuals. The study of gold scorification and cementation is warranted by the need to gather unequivocal features in archaeological gold artifacts as well as in crucibles, slag fragments and furnaces, of the different processes involved in its production.

This study will be composed of an in-depth textual analysis of ancient recipes and their subsequent reproduction following experimental archaeology protocols; the analysis of reagents and products in their principal and trace elements, used and produced during gold cementation, scorification and cupellation, allows then the interpretation of chemical reactions that occur during thermal ramps and the necessary duration of those processes. The characterization of the reagents and products obtained during the experiments has been accomplished through the use of SEM-EDS, XRD and, in the case of *ios scolekos* cement, Mass Spectrometry coupled with Knudsen Cell, that allowed the detection of the gaseous phases developed from the crucibles, leading to a full interpretation of the thermodynamic parameters involved.

The recipes studied and reproduced were selected in order to broadly cover the panorama of possible options in gold fire processing, that is the use of lead based procedures of scorification/cupellation and cementation using two important methods based on salt and sulphate mixtures or salt and brick dust. The textual evidence used is the following:

1. Dioscorides' *De Materia Medica*, Book V, describes the artificial production of *ios scolekos*, a mixture of alum (sodium sulfate and allumogenite), salt (NaCl) and copper acetate in urine that causes, at specific temperatures, the evolution of sulphur oxide and dioxide that in their gaseous phases produce molecular chlorine in reaction with NaCl;
2. The Leyden Papyrus, recipe 24, describes the use of a *misy*-salt-alum-vinegar mixture, with a preliminary interpretation of *misy* as the natural-compound version of man-made *scolecia*, as discussed in Galen, Dioscorides and Matthioli. After the study of the perceptible features described in the ancient sources such as color, smell, and consistency, as well as its origin and location in geological stratigraphy, a yellow compound obtained from the gossan of the Massa Marittima sulphide mine, resembling the description, was sampled and used as a cement, proving suitable in the near total removal of silver from gold after one heating cycle. The interpretation of chemical reactions involving copiapite-coquimbite, of which this *misy* specimen is composed, is analogous to the interpretation of the *ios scolekos* cement;
3. Theophilus' *De Diversibus Artibus* reports the brick and salt cement, which on heating triggers the reaction between silica, salt and iron oxides and the function of Iron(III) on the oxidation of silver from the alloy silver-gold to silver chloride, together with the probable direct reaction of residual phyllosilicates with silver alloyed with gold and its oxidation;
4. Agatharchides' On the Erythrean Sea details mining exploitation in the Nubian area and a heating process, lasting five days and nights, with a cement composed of salt, tin, lead, barley bran, of difficult interpretation and experimentation, replicated successfully in 2016 once re-evaluated as a scorification-cupellation process aimed at the removal of the siliceous gangue and associated sulfides (gold mined in the area of Wadi Amammat is in quartz veins together with pyrite, sphalerite, galena, chalcopyrite and other sulphides) and subsequent cementation. The salt in the recipe suggests that the procedure was finalized to refine gold through cementation by chloridizing successively all the base metals, both added or native, through the exceptional length of the pyrotechnical process.

Material manipulation which is the basis of experimental archaeology, produces knowledge by its very action and can limit or disprove the hidden premises that are sometimes present in archaeometric conjectures. Once the experimental trials are coupled with thermo-chemical analyses, they contribute with new insights to the interpretation of archaeological evidence: in this way, experimental archaeology can enrich the discussion of archaeometric results. Micro-analyses are invariably used to hypothesize processes, a sort of reverse engineering based on the final state of things, whether an artifact in its context or the excavation itself, that may lead to erroneous assertions on how things are done or made. Experimental archaeology proceeds from the other direction by exploring probable chaines opératoires that produce information, be it transient, transitional or conclusive, thus discovering or predicting further data, often difficult to deduce from the archaeological record, to formulate new hypotheses. The materials and tools involved in experimentation, such as gold artefacts, reagent mixtures and their products, slag fragments connected to gold production, crucibles, copper pestles and mortars, may be considered as replicas that constitute a valid comparison in the interpretation of their archaeological correspondents. Additional deduced information such as technological skill, invested resources, rendering, and even decorative style choices can be attained from this approach. Furthermore, experimental archaeology coupled with chemical and thermodynamic interpretations, provides information that may be used to plan special procedures of archaeological excavation in gold workshops and micro-excavation of furnaces and crucibles.

SOUHRN

Zlato se nachází v přírodě v zásadě jako nativní kov a jako sloučenina s proměnným obsahem stříbra, mědi, niklu a platiny, s původem v primárním nebo sekundárním nalezišti. Běžné jsou i nerostné příměsi jako křemen a pyrit a další nečistoty. Tyto rozdílnosti ve složení suroviny se odrážejí ve fyzikálních vlastnostech, možných vadách a následné zpracovatelnosti, které vyžadovaly hned od začátku těžby zlata proces zlepšování fyzikálních a chemických vlastností (obohacování) suroviny. Znalost zbarvení zlata, k níž patří úmyslné slévání zlata pro technické a estetické účely, jsou prokázány už v nejranějším období (3. – 2. tisíciletí před naším letopočtem na starověkém Blízkém Východě), kdy byla používána složitá technologie zpracování různých druhů zlata na bázi estetické kvality jeho barvy. Jiné důkazy nepřímo ukazují na pyrometalurgii zlata, zisk z těžby a obchodování s polotovary. Pozdější texty, jako receptáře a traktáty z oblasti přírodních věd, popisují použití tmelu ve spojení se zlatem jako purifikačního činidla. Jiné postupy připomínající dnešní metody ověřování ryzosti zlata a přítomné již ve starověkých textech zahrnují například první zdokumentování separace zlata od jeho hlušiny, jeho shromažďování a struskování odpadních zbytků. Studie struskování a tmelení zlata vznikla z potřeby popsat jednoznačně prvky zlatých archeologických artefaktů, tyglíků, zlomků strusky a pecí a různých procesů tvořících součást jejich výroby.

Tato studie bude obsahovat hloubkovou textovou analýzu starověkých receptur a jejich následné reprodukce podle experimentálních archeologických protokolů; analýzu činidel a produktů a jejich základních a stopových prvků, a interpretaci chemických reakcí tmelení zlata, struskování a kupelace, které by umožnily výklad chemických reakcí, které nastávají během termodynamických procesů, a potřebných dob jejich trvání. Charakteristika činidel a produktů provedených experimentů byla provedena pomocí SEM-EDS, XRD a v případě tmelu *ios scolekos* pomocí hmotové spektrometrie ve spojení s Knudsenovou celou, které umožnily detekci plynné fáze stoupající z tyglíků a napomohly vyčerpávajícímu výkladu termodynamických parametrů těchto procesů.

Studované a reprodukované receptury byly vybrány tak, aby pokrývaly celé panorama možností tepelného zpracování zlata, tj. použití elektrodového struskování/kupelace a tmelení dvěma důležitými metodami založenými na solných a síranových směsích nebo solném a cihlovém prachu. Použité textové doklady byly následující:

1. Dioscoridesův spis *De Materia Medica*, Kniha V, popisuje výrobu umělého tmelu *ios scolekos* jako směsi kamence (síran sodný a alumogenit), soli (NaCl) a měděného acetátu v moči, která za daných teplot způsobuje vývoj oxidu sirnatého a siřičitého, které ve své plynné fázi produkují molekulární chlór v reakci s NaCl;
2. Leydenův papyrus, receptura 24, popisuje použití směsi soli, kamence a octa s *misy* jako přírodní variantou umělého *scolecia*, jak uvádí Galen, Dioscorides a Matthioli. Po studiu zjistitelných vlastností popsaných ve starověkých pramenech, jako je barva, zápach a konsistence, spolu s původem a umístěním v geologických souvrstvích, byl v síranovém dole Massa Marittima odebrán vzorek žluté sloučeniny, která tento popis připomínala, a použit jako tmel, který se projevil jako velmi účinný při odstranění téměř veškerého stříbra ze zlata po jediném zahřívacím cyklu. Výklad chemických reakcí s copiapitem--coquimbitem, z nichž je tento vzorek *misy* složen, je analogický s výkladem tmelu *ios scolekos*;
3. Theophilův spis *De Diversibus Artibus* popisuje tmel z cihel a soli, který po zahřátí spouští reakci mezi oxidem křemičitým, solí a oxidy železa, a funkci železa (III) při oxidaci stříbra ze sloučeniny stříbra a zlata na chlorid stříbrný, společně s pravděpodobnou přímou reakcí zbytkových fylosilikátů se stříbrem ze sloučeniny se zlatem a jeho oxidaci;
4. Agatharchidův spis O Rudém moři popisuje těžbu v Núbii a proces zahřívání trvající pět dní a pět nocí, s tmelem složeným ze soli, cínu, olova, ječných otrub, který se těžko popisuje a zkouší a byl úspěšně replikován až v roce 2016, po přehodnocení na proces struskování-kupelace s cílem odstranit křemičitou hlušinu a související sulfidy (zlato bylo vytěženo

v oblasti Wadi Amammat z křemenných žil společně s pyritem, sfaleritem, galenitem, chalkopyritem a dalšími sulfidy) s následným tmelením. Sůl v receptuře naznačuje, že proces byl zakončen rafinací zlata tmelením chlorací postupně všech základních kovů, přídavných i nativních, mimořádně dlouhým pyrotechnickým procesem.

Manipulace s materiálem, která je základem experimentální archeologie, přináší poznatky při samotném provádění a může omezit nebo vyvrátit skryté předpoklady, které jsou někdy přítomny v archeometrických hypotézách. Ve spojení experimentálních pokusů s termochemickou analýzou může přinést nové pohledy na výklad archeologických důkazů. Tímto způsobem může experimentální archeologie obohatit diskusi o archeometrických výsledcích. Pro hypotetizaci procesů se pravidelně používaní mikroanalýzy jako druh reverzního inženýrství vycházejícího z konečného stavu věcí, ať už artefaktu ve svém kontextu nebo vykopávky samotné, které mohou dát vnik chybným předpokladům o tom, jak věci vznikly nebo byly udělány. Experimentální archeologie postupuje opačným směrem, když zkoumá pravděpodobné řetězce chaines opératoires, které produkují informace, ať už pomíjivé, dočasné nebo přesvědčivé, a tím objevují nebo předvídají další údaje, které je často obtížné odvodit z archeologických záznamů, využitelné pro formulaci nových hypotéz. Materiály a nástroje používané pro experimenty, jako jsou zlaté artefakty, směsi činidel a jejich produkty, úlomky strusky související s výrobou zlata, tyglíky, měděné hmoždíře a drtiče, mohou být považovány za repliky umožňující platné srovnání pro výklad jejich archeologických původců z dávné minulosti. Z tohoto přístupu mohou vyplynout i další odvozené informace jako jsou technické dovednosti, investované zdroje, výklad a dokonce volby dekorativních stylů. Navíc experimentální archeologie ve spojení s chemickou a termodynamickou analýzou poskytuje informace, které lze využít pro plánování zvláštních postupů výroby archeologických vykopávek ve zlatnických dílnách a mikro vykopávek pecí a tyglíků.

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BIBLIOGRAPHY

Allen J. W. (1979): Persian Metal Technology 700–1300 AD. London.

Ammen C. W. (1997): Recovery and Refining of Precious Metals. London and New York.

Bachmann H-G. (1993): Zur Metallurgie der römischen Goldgewinnung in Tres Minas und Campo de Jales in Nordportugal, in *Montanarchäologie in Europa,* ed. H. Steuer and U. Zimmermann, 153–60. (Sigmaringen).

Bachmann H-G. (1995): Sophisticated Roman Recovery Techniques for Gold. – Institute for Archaeo-Metallurgical Studies, 19: 7–9.

Bandy C. M. et Bandy J. A. (2004) trans.: Agricola G. (1546) – De Natura Fossilium, Mineola, New York.

Beck L. Y. (2005) trans.: Pedanius Dioscorides – De materia medica XXVIII, Zürich, NewYork.

Burstein M. (1990) trans.: Agatharchides of Cnidus – On the Erythraean Sea, London.

Caley E. R. et Richards J. C. (1956): Theophrastus on Stones, Columbus, pages 204–205.

Clews F. H.(1925): The interaction of sodium chloride and alumina. – Journal of the Chemical Society, Transactions, 127: 735.

Craddock P. T. et Ramage A. (2000): King Croesus' Gold: excavations at Sardis and the history of gold refining, London.

Davies O. (1935) : Roman Mines in Europe, Oxford.

Domergue C. (1990): Les Mines de la Péninsule Ibérique dans el'Antiquité Romaine, Rome.

Duval A. R., Eluère C., Hurtel L., Tallon F. (1985): La pendeloque au petit chien de Suse (Iran), étude d'une brasure antique en laboratoire, Paris.

Eluère C. (1990): Les secrets de l'or antique, Paris, 163–69.

Ercker L. (1574): Beschreibung der allerfürnemsten Mineralischen Erzt und Bergwerksarten, Prague.

Ferro D., Loepp D., Brutti S., Celauro A. (2011): Characterization and Thermodynamic Interpretation of Ancient Gold Refining Processes based on Dioscorides Recipe. — A. Macchia, E. Greco, B. A. Chiarandà, N. Barbabietola, YOCOCU: Contribute and Role of Youth in Conservation of Cultural Heritage. Rome: 131–140.

Forbes R. J. (1964): Studies in ancient technology. Volume VIII, Leiden.

Halleux R. (1974): Le problème des métaux dans la science antique, Paris.

Halleux R. (1981) : Les alchimistes grecs, Tome I, Papyrus de Leyde, Papyrus de Stockholm. Fragments de recettes, Paris.

Healy J. F. (1993): Miniere e metallurgia nel mondo greco e romano. Rome.

Hoover H. et Hoover L. H. (1950) trans.: Agricola G. (1556) – De Re Metallica, New York.

Klemm D., Klemm R. et Murr A. (2001): Gold of the Pharaohs – 6000 years of gold mining in Egypt and Nubia. — African Earth Sciences, 33: 643–659.

Kühn C. G. (1826) trans. and ed. : Claudii Galeni Opera Omnia, Leipzig.

Lewis R. J. (1996): Sax's Dangerous Properties of Industrial Materials. 9th ed. Volumes 1–3. New York, NY.

Loepp D., Ferro D., Celauro A., Brutti S. (2015): Archaeological Experimentation and Thermodynamic Interpretation of Chloride-Sulphate Gold Cementation Based on Ancient Texts and Evidence from Sardis, in the proceedings of the 1st ICA – International Conference On Archaeometallurgy @ Brussels Museum – 3.–4. October 2015. The article is in review phase.

Matthioli M. P. A. (1544): I discorsi di M. Pietro Andrea Matthioli…nelli sei libri de Pedacio Dioscoride Anarzabeo della Materia Medicinale. Book 5, Venice, reprinted in 1970, Rome.

Moody B. (1991, 3rd ed.): Comparative inorganic chemistry, Great Britain.

Neesse T. (2014). Selective attachment processes in ancient gold ore beneficiation. – Minerals Engineering, 58: 52–63. DOI: 10.1016/j.mineng.2014.01.009.

Notton J. H. F. (1974): Ancient Egyptian gold refining – a reproduction of early techniques, in: Gold Bulletin, 7: 50–56 (Issue 2).

Rackham H. (1934) trans.: Pliny – Natural History, Volume IX, Books XXXIII-XXXV, Cambridge.

Smith C. S. (1977), Some Construtive Corrodings, in Brown et al., Corrosion and Metal Artifacts – A Dialogue Between Conservators and Archaeologists and Corrosion Scientists, Washington, 143–154.

Smith C. S. et Hawthorne J. G. (1974): Mappae Clavicula: A Little Key to the World of Medieval Techniques, Philadelphia.

Valmont de Bomare J. C. (1762): Mineralogie ou nouvelle exposition du regne mineral, Paris.

Wellmann M. (1958) trans.: Pedanii Dioscuridis Anazarbei – De Materia Medica Libri Quinque, Berlin.

Zhou S., Wei Y., Wang H., Ma B., Wang. C (2016): Mechanism of Sodium Chloride in promoting reduction of high-magnesium low-nickel oxide ore, in Nature, Scientific Reports, 6: 29061, 1–12.