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STUDIES IN EXPERIMENTAL ARCHAEOMETALLURGY
METHODOLOGICAL APPROACHES FROM NON-FERROUS METALLURGIES

eds. Georges VERLY, Frederik W. RADEMAKERS and Florian TÉREYGEOL

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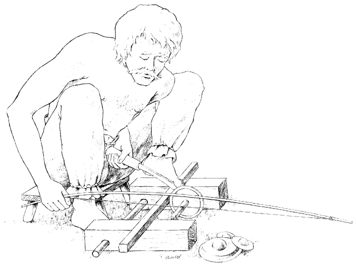

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PREFACE

This volume brings together a range of methodological approaches to the study of ancient metallurgy, all of which draw on experimental archaeology to an important degree. The integration of archaeological excavation, archaeometry and experimental archaeology in a holistic research framework for archaeometallurgy is thus developed from different perspectives to illustrate its potential as a research tool in ancient technology studies.

This publication was prompted by the first International Conference on *Non-Ferrous Metal Metallurgy and Experimental Archaeology – Métallurgie des non-ferreux et archéologie expérimentale ICA I*, held in Brussels on 3 and 4 October 2015 and jointly organized by the EACOM « Egyptian and African Copper Metallurgy » project (BELSPO-BRAIN), the Museum of Art and History, Brussels and the FNRS « Arts et techniques métallurgiques pré-industriels. Étude et conservation » project.

The first two articles of this volume present methodological frameworks for applying experimental archaeology from a general perspective (Verly & Longelin) and in archaeometallurgy more specifically (Téreygeol). Together they set the stage for a range of archaeological case studies presented in the following chapters.

Gauthier *et al.* (Chapter Three) discuss ongoing research at Castel-Minier (France) on the *chaîne opératoire* of silver production during the 14th and 15th century, while Flament & Téreygeol cover copper metallurgy at the same site, drawing on 16th century sources (Chapter Four). Both studies exemplify the integration of experimental archaeology and archaeometry, complemented by contemporary written sources, in a broader archaeological research project on historical metallurgy in Europe.

Loepp *et al.* similarly make use of written sources to set up experimentation around a specific archaeological context : gold cementation at Sardis (Chapter Five). Furthermore, their research highlights the application of thermodynamic models in testing the reliability of inferred interpretations of ancient chemical processes.

The study presented by Verly *et al.* in Chapter Six was prompted by an unusual Bronze Age find in Belgium, requiring insights from experimental archaeology to obtain a coherent interpretation.

The following chapters focus on case studies in ancient Egyptian metallurgy. In Chapter Seven, Faucher discusses the production of gold in Ptolemaic Egypt, employing experimental and archaeometric evidence to understand its exploitation in the Eastern Desert.

In Chapter Eight, Verly *et al.* zoom in on the intersection of ancient mining and metal studies. Drawing on evidence from Dayr Abu Hinnis (Egypt) and Timna (Israel), the use of copper alloy tools for New Kingdom quarrying and mining is considered from different perspectives, highlighting the essential interaction between experimental archaeology and archaeological documentation in such contexts.

Auenmüller *et al.* present the most recent insights into Late Period bronze casting techniques in Chapter Nine. An extensive experimental programme has generated an improved understanding of the functionality of casting moulds and illustrates how an iterative approach to archaeometry and experimentation can generate a more detailed picture of intricate ancient technologies.

Finally, Téreygeol presents experiments on crucibles from Bouto (Egypt, 3rd c. CE) showing the ability of metallurgists to adapt their savoir-faire in relation to their environment. They reinvented an old process following the constraints of the site.

We hope that this volume, through its mixture of more theoretical discussion as well as specific case studies, can inspire readers with a wide variety of backgrounds and interests. In particular, we aim to convince our colleagues in ancient metallurgy studies – working in the field, lab, library and beyond – who have not yet considered experimental archaeology in their protocols to integrate this powerful research tool in their ongoing and future work.

The editors

All images presented in this volume are available on the publisher website, in high definition, along with video footage for article chapter 9 (Auenmüller et al.).

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5/ ARCHAEOLOGICAL EXPERIMENTATION AND THERMODYNAMIC INTERPRETATION OF CHLORIDE-SULPHATE GOLD CEMENTATION BASED ON ANCIENT TEXTS AND EVIDENCE FROM SARDIS

David Loepp, Daniela Ferro, Angela Celauro & Sergio Brutti

1) INTRODUCTION

Gold artefacts have been systematically produced for 6500 years, making gold one of the first mechanically processed metals. Simple pyrotechnical operations such as melting and annealing were likely practiced at a very early stage in metalwork, entailing the necessity of surface enhancement to remove oxides. More complex pyrotechnical operations that involved the recognition and transformation of gold alloys may have been developed by the end of the 4th millennium BCE, perhaps coinciding with the emergence of manufacturing techniques such as casting and brazing (Duval *et al.* 1985, Eluère 1990), while the possibility of intentional gold refining before the first millennium BCE remains open to debate (Halleux 1974, Eluère 1990, Ramage and Craddock 2000).

Ancient chemical processes were most likely developed to maximize preferred physical and aesthetic characteristics and eliminate damaging contaminants without unduly reducing material weight, rather than knowingly upgrade gold content in alloys. Combinations of simple reagents such as salt, sulphates and alums, *natron*, vinegar and urine likely absolved many of these corrective functions at a very early stage, the only difference being the dosage of ingredients and the different procedures.

The excavation of an ancient gold refinery in Sardis (Ramage and Craddock 2000) and the analyses of its materials offered an opportunity to characterize ancient processes through experimentation based on archaeological evidence. While Craddock (Ramage and Craddock 2000: Chapter 8) acknowledged that ancient recipes were based on admixtures of sulphates and salt, he replicated a medieval recipe comprised of salt and powdered brick using modern alumina crucibles and an electric oven, as both Notton (1974) and Hall (1953) had previously done. In order to characterize the chemical reactions, Craddock summarized the history of silver chlorination through the experiments of D'Elhuyar (1790), Boussingault (1833) and Percy (1880 : 390-397) which proved that chlorine, the active agent in oxidizing metallic silver, could be generated by heating to red heat cements based on common salt and materials such as crushed quartz, marble or sulphates. Boussingault (1833) determined the essential role of water, whether bond or atmospheric, in triggering the reaction. D'Elhuyar's observation that a substance within the crucible matrix played a role in the reactions in the presence of salt alone lead Percy to focus on the phenomena. Percy concluded that iron salts played a role in the production of chlorine. Following the experiments conducted by Craddock, results were compared to the archaeological evidence. Craddock raised a number of questions such as the roles of coarse-ware vessels and the furnace environment, and the effective parameters of the refining cycles. He also noted the absence of salt glazing on ancient coarse ware vessels used for cementation in contrast to modern experiments conducted by Notton (1974), Hall (1953) and Craddock (Ramage and Craddock 2000), as well as the absence of finely ground brick on the Sardis site. The experiment provided no comparative material products other than the gold foils in various stages of refinement.

The wealth of material evidence and the questions left open by researchers in Sardis provided the opportunity to undertake a long-term program of experimental archaeology conducted at the Antiquitates Center for Experimental Archaeology in Civitella Cesi in collaboration with the Department of Chemistry at the University la Sapienza in Rome, Italy.

In order to simplify the task of characterization and thermodynamic modelling, we initially sought a recipe that was clear, easy to reproduce and limited to single divalent metal compounds likely known in antiquity. Most ancient recipes contain an excess of ingredients, difficult to collocate in modern categories, listed with rudimentary instructions for production and use, if at all. A recipe of Dioscorides (cfr. below), although not specifically contextualized as a gold cementation formula by the author, was preferred, as it not only consisted of reagents found in more sketchy recipes but had been associated in literature with natural mineral aggregates used for gold refining. Once a certain degree of expertise had been consolidated through progressive iterations of the procedure based on analyses and feedback, a chemical composition extrapolated from Pliny and the Leiden Papyrus was experimented. Other than the two recipes used as cements, all pertinent procedures described in ancient texts have been carried out by experimental archaeology. After each experimental procedural step, materials involved in the chemical process were characterized by micro-chemical analyses (SEM-EDS) and physical-chemical methods, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Thermodynamic evaluation of all chemical processes involved in the entire gold refining procedure were carried out for a correct interpretation of the complex phenomena involved.

2) ANCIENT RECIPES

Cementation and depletion gilding recipes from extant classical sources are for the most part based on an admixture of sulphates and chlorides, starting chronologically with Bolos' second recipe, lines 195-198 (Berthelot 1889, Betz 1996, Halleux 1981, pp.163-166), Pliny (XXXIII: 84, XXXIV: 121 in Rackham 1934), and recipes 14 and 24 of the Leiden Papyrus (Halleux 1981, Berthelot 1889, Caley 1926). In our era the recipes are generally more detailed while the reagents remain substantially the same, such as the medieval *Alchimie Syriaques* (Berthelot 1893), recipes 19 and 100 of the later Mappae Clavicula (Smith and Hawthorne 1974), and medieval and Renaissance recipes reported by Albertus Magnus (1569), Agricola (Hoover and Hoover 1912), Ercker (1574; Sisco and Smith 1951), Biringuccio (1540; Smith and Gnudi 1942) and Brembato (1663). This preferred combination of reagents is confirmed by continuous use throughout history.

Ancient nomenclature presents a hurdle to identifying substances based on physical descriptions. Most chloride-sulphate recipes call for the use of *misy*, and at times *sory* and *calchitis*, on which ancient authors slightly diverge in their descriptions. Pedanius Dioscorides, Pliny and Galen are to be noted as the most exhaustive and influential ancient scholars on minerals, their use and winning. Dioscorides' *Materia Medica* (Beck 2005, Matthioli 1586, Wellmann 1958) is the work of a practitioner who spares no effort in clarity in his description of plants, animals and minerals as well as procedures. Despite his focus on medicine, his description of minerals would become a standard reference for the later Greek technical manuals, such as the verbatim description of reagents used in technical processes extraneous to medicine found at the end of the Leiden Papyrus, a compilation of technical recipes dating from the late 3rd century CE (Von Lagercrantz 1913, Berthelot 1889, Caley 1926, Halleux 1981). Pliny on the contrary produced his work, *Historia Naturalis* (Rackham 1934), for a discerning Roman public at the apogee of Roman power. His text is rich in anecdotes and digressions. Both Pliny and Dioscorides declare in certain passages to have consulted several authors in compiling their respective works on metals and minerals. It is however difficult to assess the extent of their first-hand knowledge of mining technology beyond that of acute observers. Nonetheless, both authors demonstrate sufficient familiarity with metals, minerals and mining to arbitrate between sources. Approximately 50 years after Dioscorides' text, Galen visited the Skouriotissa mine at Solis, Cyprus, offering unequivocal first-hand testimony on metals, mining and minerals (Kühn 1826). His description of mining appears to be the first detailed account of deliberate human exploitation of the weathering effects of rain or ground water on sulphides within adits (Bruce 1937, Coghlan 1975, Costantinou 1982).

Pliny describes *calchitis* as a subterranean source of copper, *misy*, and *sory* excavated in mine adits or galleries, friable, subject to weathering, and associated with native copper oblong veins (XXXIV: 117-118 in Rackham 1934). Pliny further asserts that natural *scolex* is obtained from *calchitis* (XXXIV: 116). This same substance, *ios scolekos* in Greek, is described in near identical terms by Dioscorides, suggesting a common source. In a pertinent passage Galen locates *calchitis* in long veins starting at a mine entrance on the mountains above Solis in which the various minerals, *sory*, *calchitis* and *misy*, are clearly stratified in ascending order (Kühn 1826, pp. 226-229). Galen, who kept specimens for thirty years, details the transformation of *calchitis* into *misy*, noting intermediate phases, and speculates that *sory* may change into *calchitis* over a long period. Pliny, on the contrary, asserts that it is *calchitis* that changes into *sory*. Dioscorides' description of the minerals is minimal in comparison (V: 99, 100 and 102, in Wellman 1958, Beck 2005). He makes no note of mineral transformation although he points out that *calchitis* is easily crumbled while *misy* is hard and breaks with a gold yellow cleavage (Wellman 1958, Beck 2005). In the 16th century CE, Agricola discussed the three substances at length in *De Natura Fossilium* (Bandy and Bandy 1955, pp 47-56, Hoover and Hoover, 1950, pp. 572-574), while Matthioli located *misy* in a mine near Levico di Val Sugana (Matthioli 1970, p. 1426). Both renaissance authors associated the minerals with European vitriol production. Modern commentators have suggested that *misy* is primarily ferrous sulphate (Bandy and Bandy 1955, Hoover and Hoover 1950), decomposed cuprous pyrites (Rackham 1934) or cuprous and ferrous sulphate (Berthelot 1889, Smith and Hawthorne 1974). Despite the minor anecdotal divergences in the descriptions, it is apparent that these mineral assemblages are due to the exceptional dynamism of *in situ* sulphide reactivity coupled with exposure to weathering (Alpers *et al.* 1994, Jambor *et al.* 2000). What little difference there may be in reactivity of these mineral assemblages, it appears that the preference for *misy* in most ancient formulations was due more to its yellow color than any other factor, in the belief that a property such as colour can be transferred to other materials through certain processes.

Although not the object of the present review, there is a complex recipe that appears to combine collection, scorification and cementation into one procedure. The recipe is Agatharchides' description of gold processing with lead, tin, flour and salt, as transmitted by Diodorus Siculus (Oldfather 1935, pp. 115-123, Burstein 1970) and Photius (Henry 1974, pp. 152-156, Burstein 1970). It had been previously experimented by Notton (1974) (also Halleux 1975, 1979, Ramage and Craddock 2000), based on his interpretation of the text, with modern equipment. Notton then experimented a medieval recipe, first described by Theophilus Presbyter, composed of two parts of powdered brick and one of salt. It is this latter recipe that was replicated by Hall (1953) and Craddock (Ramage and Craddock 2000).

Ios scolekos has been preferred in the first set of experiments as it can be unequivocally identified and characterized in modern chemical terminology and is representative of the sulphate assemblage used to refine gold according to classical textual sources, as well as Renaissance recipes. Following this first set of experiments, for which the thermodynamic process was characterized (see below), a second set of experiments (Celauro *et al.* 2017) was conducted using weathered yellow mineral assemblages, collected at Le Roste near Massa Marittima, Italy (a location mentioned by Matthioli for natural compounds related to *misy* such as vitriols or *calcanthos*), that best corresponded to ancient description.

A translation from the ancient Greek source (Wellman 1958) was undertaken by one of the authors in collaboration with two philologists, to resolve ambiguities found in English translations. Our English translation of the Dioscorides recipe for the production of *ios scolekos* is reported in the following paragraph, divided in steps with commentary.

« There exist two types of *ios scolekos*. The first is of extraction while the other is prepared as follows: »

There exist two types of *ios scolekos*, one of the active components of the mixture used by us for gold-refining. One is mined while the other is prepared following the Dioscorides recipe. While Dioscorides does not indicate what natural *ios scolekos* is, Pliny (XXXIV: 116, in Rackham 1934) describes mined *scolekos* as a product derived from subterranean *calchitis*. There is no indication of the colour or form of natural *ios scolekos*, which is only characterized by its properties, but one might presume that it is similar in colour and form to the man-made variety.

"[...] 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 drachmae of best quality alum and transparent rock salt or sea salt, in which case as white and hard as possible, or in alternative the same quantity of *natrum*."

Both Pliny and Dioscorides call for the use of a single purpose tool, a mortar and pestle in pure copper. The tool is first described by Theophrastus in the 4th century BCE as used to extract metallic mercury by grinding cinnabar and vinegar together (Caley and Richards 1956). Bailey's experiment, described by Caley and Richards (1956, pp. 204-205) and Halleux (1974, p. 184), on the validity of the process found that heat was indispensable, a parameter clearly expressed by both Pliny and Dioscorides in their respective recipes. Further, it is better to first stir the vinegar in the mortar under strong summer sunlight so as to facilitate the release of copper cations, a process evidenced by the greenish tinge the liquid develops. The mortar and pestle were likely used to produce consistent quality, high-grade copper compounds and copper-based mixtures initially associated with metallurgical processes. The versatility of the tool and its light weight would make it convenient for transportation, a reliable tool where availability and purity of minerals could not always be guaranteed.

Two variants of the mixture are detailed here. One that contains equal portions of alum and salt and another that may be read as composed of equal quantities of alum and *natrum*, generally understood as a natural carbonate of soda.

"Then let it macerate under a very hot sun when the Dog star rises until it assumes a greenish colour and a sticky consistency. 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."

The Dog star, Sirius, appears around July 26th, and is therefore associated with the hottest period of the year. In light of Pliny's elliptic phrasing (XXXIV: 116, in Rackham 1934) and Matthioli's use of reflexive verbs in his translations of Dioscorides, it is difficult to understand how the "worms" are formed (Matthioli 1548). One is not quite sure that the "worms" form of themselves or are formed by an agent, a matter easily resolved by workshop trials.

"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."

Dioscorides does not specify what formula is used by gold workers, nor does he appear to be interested in specifying precisely its usage beyond "with which they glue gold." The phrase is best understood as gold «solder», as in a similar passage in Pliny that identifies *natrum* as the sole additive to the basic recipe, a variant called santerna (XXXIII: 93; XXXIV: 116, in Rackham 1934).

"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, followed by the scraped kind and the prepared. The natural kind acts better as a mordant and is more astringent, while that of goldsmith is equivalent to the scraped kind."

While all verdigris formulations are considered stronger than burned copper in their strength and effect, mined *scolekos* is singled out as the best of all. However, as far as natural *scolekos* is concerned, the specific environment under discussion suggests the formation of sulphates that, according to Pliny, must be scraped from *calchitis* (XXXIV: 116, in Rackham 1934).

3) EXPERIMENTAL MATERIALS AND METHODS

Experimentation was conducted based on prior operational parameters hypothesized at Sardis (Ramage and Craddock 2000, pp. 200-210), working knowledge acquired through experimental archaeology, the collaboration of single specialists, and the exclusive utilization of materials known in antiquity. The following schema was observed:

- Fabrication of tools, vessels and materials in accordance with archaeological evidence or ancient descriptions;
- Construction of a furnace in mud bricks and surface clay mortar according to the ancient typology found at Sardis (4th century BCE);
- Preparation of thin, hammered gold foils with variable silver-copper content;
- Preparation of the cements based on ancient textual sources and previous experimentation;
- Placement of the foils in contact with the cement in a fired coarse-ware vessel;
- Reproduction of the experiment by introducing the vessel in the furnace at increasing stepped temperatures (maximum 800°C) over a period of time.

A pestle and mortar were fabricated in pure copper with the lost-wax process. The wall thickness of the mortar ranged from 4 to 6 mm, a measure adopted to contrast observed fast wear. Coarse ware vessels and lids were fabricated to specification by a traditional potter in local prospected clay body to resist high temperatures. The vessels were small by comparison to the parting vessel found at Sardis so as to process small charges of gold. Lute containing organic fillers, often called the "lute of wisdom", was used (Colinet 2002, p. 65) to seal the containers.

The furnace (Fig. 1) was built with semi-dried bricks of coarse surface clays, gravel, and straw, luted with the same material, following the models adopted in Sardis around the 4th century BCE (Ramage and Craddock 2000, pp. 83-86).

Similar furnaces have been described by Theophilus Presbyter (Book III: 33, in Dodwell 1961, Smith and Hawthorne 1974), Agricola (Hoover and Hoover 1912, p. 455), Biringuccio (Smith and Gnudi 1942), and Brembato (1991, pp. 53-60). The square draft furnace was circa 65 cm high, 75 cm wide, broad at the bottom, slightly narrowing at the top. The walls averaged 15 to 20 cm in thickness. A rectangular mouth or door was provided at floor level that served both for draft and for stocking wood. After a series of trial runs, it was concluded that the furnace functions much better if there is a removable lid as described by Theophilus Presbyter (Dodwell 1961, Smith and Hawthorne 1974). By closing the furnace there is a noteworthy economy of wood as well as a major control of temperature. A circle-shaped vent, 20 cm in diameter, was made in the lid for this particular experiment although more rudimentary alternatives have been used with success. By adapting a single large vent, it is possible to stock the furnace from above as well as control the condition of the vessels. The preferred fuel was a combination of well-seasoned and partially seasoned young wood (Ramage and Craddock 2000, pp. 179-181).

Small gold foils with a variable area of around 1.2 cm^2 and a thickness of 0.03 to 0.1 mm were prepared by tearing or cutting snippets from hammered gold alloy strips.

One binary and three ternary gold alloys were prepared, containing gold that varied between 72.8% and 93.1%, according to EDS analyses. Copper content did not exceed 1.5%.

All of the samples were code marked to facilitate comparison between samples: a group was treated with the cement and the other set aside as a control group.

In this first set of experiments the cement was made according to Dioscorides' first recipe variant for *ios scolekos* (V: 79, in Wellmann 1958, Beck 2005). In a copper mortar strong vinegar was continuously mixed with a copper pestle under intense sunlight, thus producing copper acetate. Alum and natural sea salt were added in equal portions and stirred until the compost became dense. Aged urine was then added, provoking a characteristic reaction (Berthelot 1889). The compost quickly became a dense, green putty, oily to touch, under the combined effects of sunlight, heat and stirring (Fig. 2). The paste obtained was then hand rolled into small filaments resembling « rose worms » (Fig. 3) as instructed in the recipe thus producing convenient homogenous units that dry quickly and offer the maximum reactive surface per volume. Small gold foils and cement « rose worms » were then placed in alternating layers in a coarse ware vessel, assuring contact between the gold foil and the cement.

The vessels were set in a lump of clay placed inside the furnace on two parallel terracotta plinths. The furnace remained active for 19 hours. The temperature was measured with a Cr-Alumel thermocouple inserted below the vessels. For the first three hours the temperature was raised to and held at 300°C, after which the temperature was gradually raised to and kept at 700°C. Temporary peaks of over 800°C, the maximum 940°C, occurred despite efforts to avoid high temperatures.

Concluded the firing cycle, preliminary observations of the vessel containing the «rose worm» cement revealed a compact mass of pale green to ash white filaments, reduced in volume. Closer scrutiny revealed the presence of gold within the interstices of the filaments as well as on the inner surface of the vessel, concentrated at the bottom of the vessel. The gold foils within the mass of filaments remained intact with evident visible signs of corrosion (Figs. 4 and 5).

Observation with a binocular optical microscope at 40x showed that the gold precipitate within the filaments and on the inside surface of the vessel consisted of micrometric crystallites (Figs. 6, 9 and 12). All the parts of the vessel and its contents of cement and gold foil were analyzed by SEM-EDS and XRD techniques. SEM observations were conducted with a LEO 1450VP operating in high to low vacuum, with a tungsten wire as electron source, equipped with detectors for secondary and backscattered electrons, with a resolution of 4 nm. Microanalysis with EDS INCA 300 allows elemental detection starting with boron with a detection limit of 0.2 wt%.

The use of an instrument that allows observation of non-conductive samples without carbon coating was crucial in the investigation of the cements and of the vessel parts. The use of the detector for backscattered electrons is a valid tool for the selection of micro-areas to be investigated by EDS. In fact, the difference of contrast due to the difference of atomic number, leads to the selection of areas with the same composition without the interference of neighbouring areas. In this way it is possible to compare different micro-areas in the same sample or among different samples as the investigation progresses. An example of this is shown in Figure 6 where the brighter contrast indicates the presence of elements with a high atomic number, thus making it easy to define the presence and position of metals. By comparing with standards, it is possible to establish the existence of probable compositional correlations among elements from the values of wt% composition.

To verify the presence of a specific compound produced in the different phases of the process, samples were analyzed by X-ray powder diffraction using a Philips X Pet Pro diffractometer. The analyses of the obtained spectra and of the phases were conducted with X Pert data analyzer software, connected to the Powder Diffraction file data base edited by JCPDS (Blanton 1993).

As a final check of the validity of the proposed chemical process, an MSKC (Mass Spectrometry-Knudsen Cell) (Drowart *et al.* 2005) high temperature experiment was carried out on the « rose worms » sample. The analysis of the process of refining initiated with EDS and XRD compositional data in order to propose a thermodynamically valid modelling compatible with experimental conditions.

4) ANALYSIS RESULTS

The reactions that occur during cementation may be understood by analyzing the initial materials and their products in each phase of the process. Thirty-nine samples were analyzed with SEM and EDS and eight with XRD for which the more useful and representative results are here presented.

A sample of alum was analysed by XRD and revealed the presence of alunogen ($Al_2(SO_4)_3 \cdot 18H_2O$) and sodium sulphate ($Na_2SO_4$). The vinegar stirred in the copper mortar under strong sunlight produced a green solution, pH of 5. The acetic acid contained in the vinegar reacted with the copper that composed the mortar and pestle, leading to the formation of $Cu(CH_3COO)_2$.

A small sample of the dry active « rose worms » was submitted to SEM and XRD analyses. The elements found in detectable quantities by SEM (Fig. 7 and Tab. 1) are oxygen, chlorine, copper, sodium, aluminium and sulphur. XRD (Fig. 8) showed that the sample was formed of tamarugite ($NaAl(SO_4)_2 \cdot 6H_2O$), kroenkite $Na_2Cu(SO_4)_2 \cdot 2H_20$, while the sodium chloride remained unaltered, not having taken part in any reaction during this step. Given that the spectrum of alum does not coincide in any portion with the spectrum of the filaments, results suggest that a reaction occurred between the copper acetate and the alum components, alunogen and sodium sulphate, thus producing tamarugite and kroenkite, whereas NaCl remained unaltered.

Sampling area	Weight percentage					
	O	Na	Al	S	Cl	Cu
1	9.7	1.4	0.6	1.1	46.0	41.3
2	12.0	31.3	1.1	2.0	48.6	4.9
3	69.6	3.4	4.5	9.0	6.2	7.4
4	13.3	3.6	1.4	3.4	40.5	37.8
5	9.6	19.6	1.2	1.4	50.5	17.7
6	6.0	32.0	0.3	0.2	59.6	1.9

Table 1: SEM-EDS composition of an active " rose worm". Sampling areas are shown in Figure 7.

After thermal treatment the gold foil was analysed to determine the degree of purity, as well as the residual filaments and the vessel in order to individuate eventual changes in composition and structure. SEM analysis of the « rose worms » (Fig. 9 and Tab. 2) after pyrotechnical treatment indicated the presence of silver, as well as oxygen, sodium, aluminium, sulphur and copper, present in higher percentage with respect to the active filaments. The only element present in a lesser percentage in comparison with the active filaments was chlorine. The XRD analyses of the spent cement (Fig. 10) revealed the presence of sodium chloride (NaCl), mixed chloride(s) of sodium and silver ($Na_{1-x}Ag_xCl$ with $x < 0,5$, i.e. silver is up to 50% present), thenardite (Na_2SO_4), corundum (Al_2O_3) and kroenkite $Na_2Cu(SO_4)_2 \cdot 2H_20$.

Sampling area	Weight percentage							
	O	Na	Al	S	Cl	Cu	Ag	Au
1	14.2	3.2	2.0	1.7	1.2	2.9	0.3	74.6
2	5.4	1.3	0.5	1.2	0.6	0.8	0	90.2
3	52.0	18.1	4.3	11.4	8.8	5.3	0	0
4	43.8	17.7	4.0	12.1	5.7	9.1	0.5	7.2
5	12.3	1.7	0.9	2.3	0.5	0.7	0.7	81.0
6	50.3	14.9	7.0	7.7	5.5	9.2	0.7	4.9
7	44.7	23.8	5.1	12.5	8.4	4.3	0.4	0.8
8	41.4	21.6	3.1	10.8	3.8	15.6	0	3.6

Table 2 : SEM-EDS composition of a spent "rose worm". Sampling areas are shown in Figure 9.

The results support the hypothesis that tamarugite and kroenkite, present in the active filaments, dissociate during thermal treatment, producing copper sulphate, aluminium sulphate and sodium sulphate :

$$2NaAl(SO_4)_2 \rightarrow Al_2(SO_4)_3 + Na_2SO_4$$

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

The sulphates of copper and aluminium then dissociate into aluminium oxide (corundum), copper oxide and sulphur trioxide at $T \approx 516°$, 586°C, respectively (Tagawa 1984) :

$$Al_2(SO_4)_3 \rightarrow Al\,_2O_3 + 3SO_3$$

$$CuSO_4 \rightarrow CuO + SO_3$$

The sulphur trioxide also dissociated into:

$$SO_3 \leftrightarrow SO_2 + \tfrac{1}{2}\,O_2$$

The reaction between sodium chloride, a compound that had not previously participated in any reaction, and sulphur trioxide produces molecular chlorine.

$$2NaCl + SO_3 + \tfrac{1}{2}\text{-}\,O_2 \rightarrow Na_2SO_4 + Cl_2$$

SEM analysis of the gold foil (Fig. 11 and Tab. 3) indicate that the gold had attained a very high grade of purity, thus substantiating the hypothesis that molecular chlorine oxidized the silver to produce silver chloride :

$$Cl_2 + 2Ag \rightarrow 2AgCl$$

Sampling area	Weight percentage		
	Cu	Ag	Au
1	0.07	0	99.93
2	0	0	100.00
3	0.12	0.7	99.18
4	0.03	0.23	99.73
5	0	0.13	99.87

Table 3 : SEM-EDS analysis results of sampling areas in Figure 11, normalized for copper, silver and gold.

Analyses conducted on the inner surface and cross-sections of the coarse ware vessel established that there was strong absorption of silver chloride. In fact, concluded thermal treatment, while to pale green accretions were observed on the upper inner surface of the vessel. On the lower inside surface a faint, mottled gold film had formed, as previously mentioned. In Figure 12, SEM imaging with backscattered electrons evidences the distribution of metallic particles, thus allowing spot analysis on specific micro-areas. Area 2 was identified as gold, while in areas 3 to 7 the presence of silver and chlorine predominated. The darker areas 8 to 10 contain compositional information typical of clays.

The absorption of the silver chlorine takes place also on the surface of the rose worms while the major presence of gold in certain zones of the spent «rose worms» (Tab. 2) may be caused by the local formation of the eutectic Au-Ag-Cu: if a notable quantity of copper was present at the point of contact between the «rose worm» and the gold foil, the eutectic formed thus melting at a temperature below that of the individual elements. The silver and copper would thus be segregated and absorbed by the «worm» while pure gold re-crystallized on the surface or within micro-spaces of the filament.

The reactions which take place during the refining process are summarized in Table 4.

STEP	PROCESS	REAGENT	PRODUCT
1	Vinegar stirred in a copper mortar, under UV emission.	$H_3C\text{-}COOH$ Cu	$Cu(CH_3COO)_2$
2	Addition of alum.	$Cu(CH_3COO)_2$ $(Al_2(SO_4)_3{\cdot}18H_2O$ Na_2SO_4	$(NaAl(SO_4){\cdot}(H_2O)_6$ $(CuNa_2(SO_4)_2(H_2O)_2)$
3	Addition of salt.	$(NaAl(SO_4){\cdot}(H_2O)_6$ $(CuNa_2\,(SO_4)_2(H_2O)_2)$ NaCl	$(NaAl(SO_4){\cdot}(H_2O)_6$ $(CuNa_2(SO_4)_2(H_2O)_2)$ NaCl
4	The addition of urine has the main function of favouring the disassociation of tamarugite and kroenkite.	$NaAl(SO_4)_2{\cdot}(H_2O)_6$ $Na_2Cu(SO_4)_2{\cdot}2H_2O$	Na_2SO_4 $Al_2(SO_4)_3$ $CuSO_4$
5	Dissociation of sulphates of copper and aluminium.	$Al_2(SO_4)_3$ $CuSO_4$	Al_2O_3 CuO SO_3
6	Dissociation of sulphuric trioxide.	SO_3	O_2 SO_3
7	Reaction between sodium chloride and sulphur trioxide.	NaCl O_2 SO_3	$Na_2\,SO_4$ Cl_2
8	Reaction between molecular chlorine and the silver contained in the impure gold leaf.	Cl_2 Ag	AgCl Silver chloride is absorbed in the inner walls of the vessel and in the spent cement.

Table 4: Summary of the reactive steps that take place during a refining process.

A second set of experiments (Celauro *et al.* forthcoming) focused on the probable identification of *misy* and its use in ancient recipes as evinced from recipe 24 of the Leiden Papyrus (Halleux 1981) and Pliny (XXXIII: 84-5). The cement was composed of equal parts of salt and *misy* combined with water or vinegar. Alum, present in recipe 24, was omitted in order to simplify the composition of the cement. 62 wt% gold alloy foils were processed as the previous set of experiments for 19 hours at temperatures generally in the range of 700°C, with rare, brief peaks at 900°C. XRD analyses, in the XRD laboratory of the Deutsches Bergbau-Museum Bochum, determined that the yellow efflorescence collected at Le Roste consisted of copiapite, coquimbite and quartz. Copiapite and coquimbite are hydrated iron sulfates of the same typology of tamarugite and kroenkite present in *ios scolekos*. The dissociation of copiapite ($Fe^2+Fe_4^3+(SO_4)_6(OH)_2\cdot 20H_2O$) and coquimbite ($Fe_2^3+(SO_4)_3\cdot 9H_2O$) results in thenardite, hematite and sodium chloride, recognized in the spent cement (Fig. 13), analogous to the previous experiment. The reaction reported below describes the dissociation of dehydrated coquimbite, which likewise takes place for the copiapite (Celauro *et al.* 2017):

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

$$SO_3 \leftrightarrow SO_2 + \tfrac{1}{2}\, O_2$$

$$2NaCl + SO_3 + \tfrac{1}{2}\, O_2 \rightarrow Na_2SO_4 + Cl_2$$

$$Cl_2 + 2Ag \rightarrow 2AgCl$$

Again, this gaseous compound reacts with salt producing thenardite and releasing molecular chlorine, which in turn oxidizes the silver, removing it from the alloy. 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 documentation, 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, both important agents in the cementation of gold.

5) THERMODYNAMIC METHODS FOR THE ANALYSIS OF THE HIGH TEMPERATURE REFINING PROCESS

A thermodynamic analysis of the high temperature process has been carried out in order to investigate the reaction pattern that leads to the refining of a gold alloy with a large silver content.

The thermodynamic study is split in two parts:

(1) A thermodynamic analysis in which a description of a simple and schematic reaction pattern coherent with the experimental observations and the corresponding thermo-chemistry is presented (standard thermodynamic analysis approach);

(2) A thermodynamic modelling where multi-equilibrium thermodynamic calculations, carried out starting from physical and chemical conditions (pressure, temperature, composition) similar to those realized in the experiments, are discussed (multi-equilibrium thermodynamic modelling approach).

For further details about approach 2, see appendix.

5.1) Thermodynamic analysis: standard approach

By considering the EDS and XRD determinations of the solid phases involved in the process (see Tables 1-3) a simplified ensemble for the reagents and products can be outlined and used as the starting point for the thermodynamic analysis. The active «rose worms», analysed before the high temperature cementation, consisted of a complex matrix that is mainly formed by NaCl(s) and two mixed aluminium-sodium and copper-sodium hydrated sulphates. The second starting material is the Ag-Au alloy. The reaction products are apparently NaCl, $Na_{1-x}Ag_xCl$, Na_2SO_4, Al_2O_3, Au and the mixed copper-sodium hydrated sulphate. This ensemble can be simplified by assuming the reagents and products summarized in Table 5.

Reagents		Products
$NaCl(s)$; $CuSO_4(s)$; $Al_2(SO_4)_3(s)$; $Na_2SO_4(s)$; Ag_xAu_{1-x}	→	$Na_2SO_4(s)$; $Al_2O_3(s)$, AgCl, Au

Table 5: Chemical species involved in the process reactions.

Starting from this simplified ensemble a schematic reaction sequence can be drawn out:

(1) $Al_2(SO_4)_3(s) = Al_2O_3(s) + 3SO_3(g)$

(2) $SO_3(g) = SO_2(g) + ½\ O_2(g)$

(3) $2\ NaCl(s) + SO_3(g) + ½\ O_2(g) = Na_2SO_4(s) + Cl_2(g)$

(4) $Ag_xAu_{1-x}(s) + x/2\ Cl_2(g) = (1-x)Au(s) + x\ AgCl(s)$

(1) is the aluminium sulphate decomposition to give alumina, $Al_2O_3(s)$, and sulphur (III) gaseous oxide, $SO_3(g)$. Reaction (2) is the gaseous high temperature $SO_3(g)$ decomposition equilibrium. Reaction (3) is the oxidation of the sodium chloride to give molecular chlorine and sodium sulphate. Reaction (4), that is the true refining step, is the oxidation of the silver in the gold alloy to give AgCl and purified Au. This reaction can be further simplified by considering the direct reaction of silver with gaseous molecular chlorine:

(4b) $Ag(s) + ½\ Cl_2(g) = AgCl(s)$

Reaction (4b) can easily mimic reaction (4) by assuming an Ag(s) thermodynamic activity smaller than unity.

Before continuing it is to be noted that a similar reaction scheme can also be written starting with copper sulphate. In this second case whereas reactions (2-3-4) are unaltered, reaction (1) is modified:

(1b) $CuSO_4(s) = CuO(s) + SO_3(g)$

In the XRD analysis of the reaction products apparently no traces of copper (II) oxide, CuO(s), were observed. However, for the sake of completeness the thermodynamic analysis presented also considered this second case in order to check the possible role of copper in the assumed refining process.

A summary of the standard Gibbs energy of reaction for processes 1-1b-2-3-4b are presented in Table 6. These data were retrieved from SGTE (1994) and Ivtan (1993).

Reaction		$\Delta_rG°_{T/K}$				
		800K	900K	1000K	1100K	1200K
(1)	$Al_2(SO_4)_3(s) = Al_2O_3(s) + SO_3(g)$	160	119	78	37	-4
(1b)	$CuSO_4(s) = CuO(s) + SO_3(g)$	70	53	36	19	2
(2)	$SO_3(g) = SO_2(g) + ½\ O_2(g)$	24	14	5	-4	-14
(3)	$2NACl(s) + SO_3(g) + ½O_2(g) = Na_2SO_4(s) + Cl_2(g)$	-73	-63	-54	-43	-29
(4b)	$Ag(s) + ½\ Cl_2(g) = AgCl(s)$	-86	-83	-81	-79	-76

Table 6: Standard Gibbs Energy of reaction (kJ mol^{-1}) at different temperatures (in Kelvin) for the reaction involved in the process.

In order to verify the effectiveness of the considered reaction sequences to refine gold through the precipitation of silver chloride, it is necessary to check if the equilibrium partial pressure of $Cl_2(g)$ produced by the « rose worm » (reactions 1-2-3 or 1b-2-3) is larger than the equilibrium partial pressure of gaseous chlorine in the high temperature decomposition of AgCl(s) (the reverse of reaction 4b, i.e. $AgCl(s)=Ag(s)+½Cl_2(g)$). Indeed, in this case a driving force, represented from a thermodynamic point of view by the Gibbs energy of reaction, allows reaction (4b) to occur.

By considering together the reaction sequences 1-2-3 and 1b-2-3, the two different possible ways to produce Cl_2 are:

(5) $2Al_2(SO_4)_3(s) + 6\ NaCl(s) =$
$2Al_2O_3(s) + 3Na_2SO_4(g) + 3Cl_2(g)$
$+ 3SO_2(g)$

(6) $2CuSO_4(s) + 2NaCl(s) =$
$2CuO(s) + Na_2SO_4(g) + Cl_2(g)$
$+ SO_2(g)$

From data reported in Table 2 the equilibrium partial pressure of gaseous molecular chlorine can be calculated by the formulas $p_{Cl_2} = \sqrt{e^{-\Delta_r G°_{T/K}(n)/RT}}$, in which R is the gas constant, $\Delta_r G°_{T/K}(n)$ are the standard Gibbs energy of reaction (5) and (6) that can be calculated by data reported in Table 6 by summing the Gibbs energy of reaction 1-2-3 and 1b-2-3, respectively. Similarly, the equilibrium $Cl_2(g)$ partial pressure for reaction 4b is calculated by the equation $p_{Cl_2} = e^{\Delta_r G°_{T/K}(4b)/RT}$, in which $\Delta_r G°_{T/K}(4b)$ is the corresponding Gibbs energy of reaction. The calculated partial pressures of $Cl_2(g)$ are shown in Figure 14.

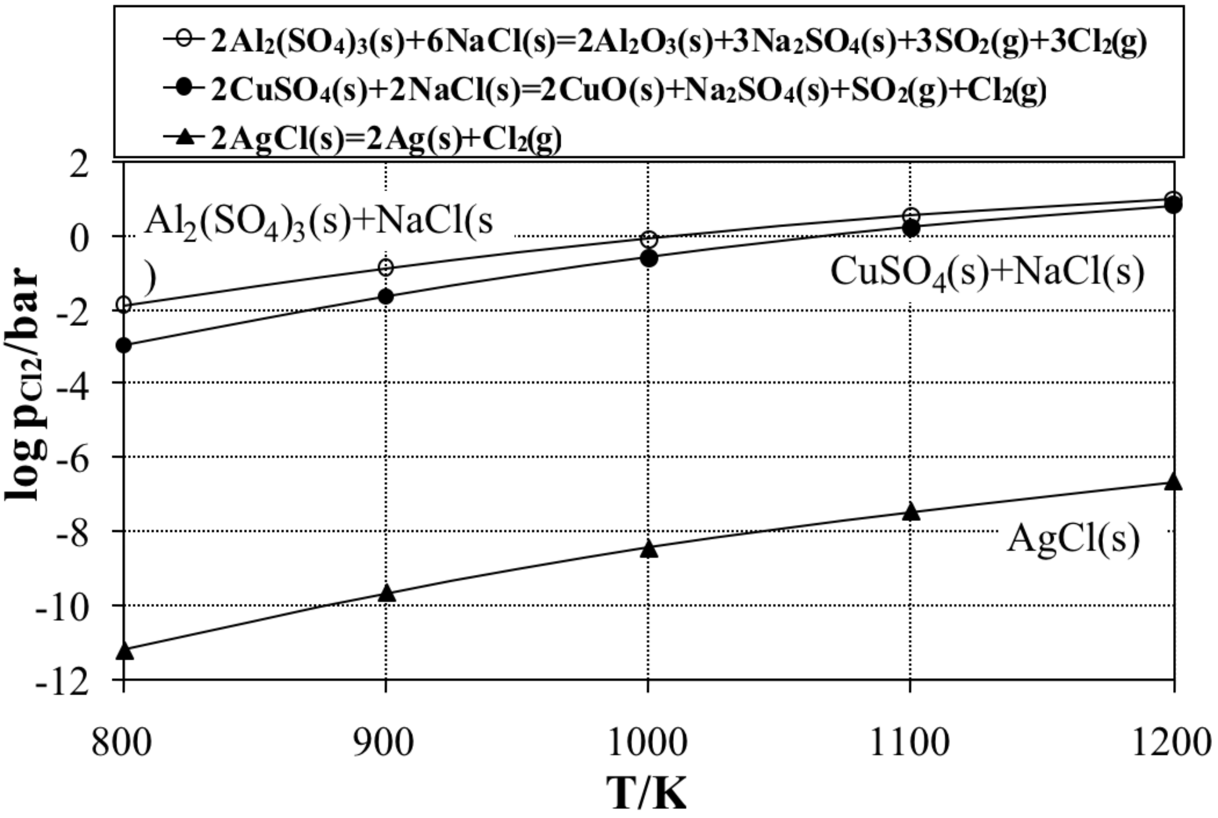

Figure 14: Calculated partial pressure of Cl_2 (g) in equilibrium over the various different systems considered.

The equilibrium partial pressure of gaseous chlorine produced by the interaction of the sulphates with NaCl(s) at high temperature are several orders of magnitude larger than the equilibrium pressure of Cl_2 in the decomposition of AgCl(s). In the experimental condition realized in the reactor this is reflected in a driving force that allowed reaction 4b to take place. Indeed in the temperature range 800-1200K the Gibbs energy of reaction 4b, $\Delta_r G_{T/K}(4b)$, given by the equation

$$\Delta_r G_{T/K}(4b) = \Delta_r G^\circ_{T/K}(4b) + RT \cdot \ln\left(\frac{1}{a_{Ag(s)} \cdot p_{Cl_2(g)}}\right)$$

in which $\Delta_r G^\circ_{T/K}(4b)$ is the standard Gibbs energy of reaction 4b, $a_{Ag(s)}$ is the thermodynamic activity of solid silver and $p_{Cl_2(g)}$ is the chlorine partial pressure produced by equilibrium 5 or 6, is negative, providing the reaction to occur. It is to be noted that thermodynamic activities smaller than the unity for the solid Ag reflect in a reduction of the driving force, as can be easily derived by the above equation. By assuming that the silver activity in the Au alloy is equal to its molar fraction, it is possible to predict the Ag thermodynamic refining limit in terms of the smaller silver content in the Au-alloy that will result in a null Gibbs energy of reaction 4b. In Figure 15, the driving force for reaction 4b at 1100 K is plotted in function of the silver content in the Au-alloy.

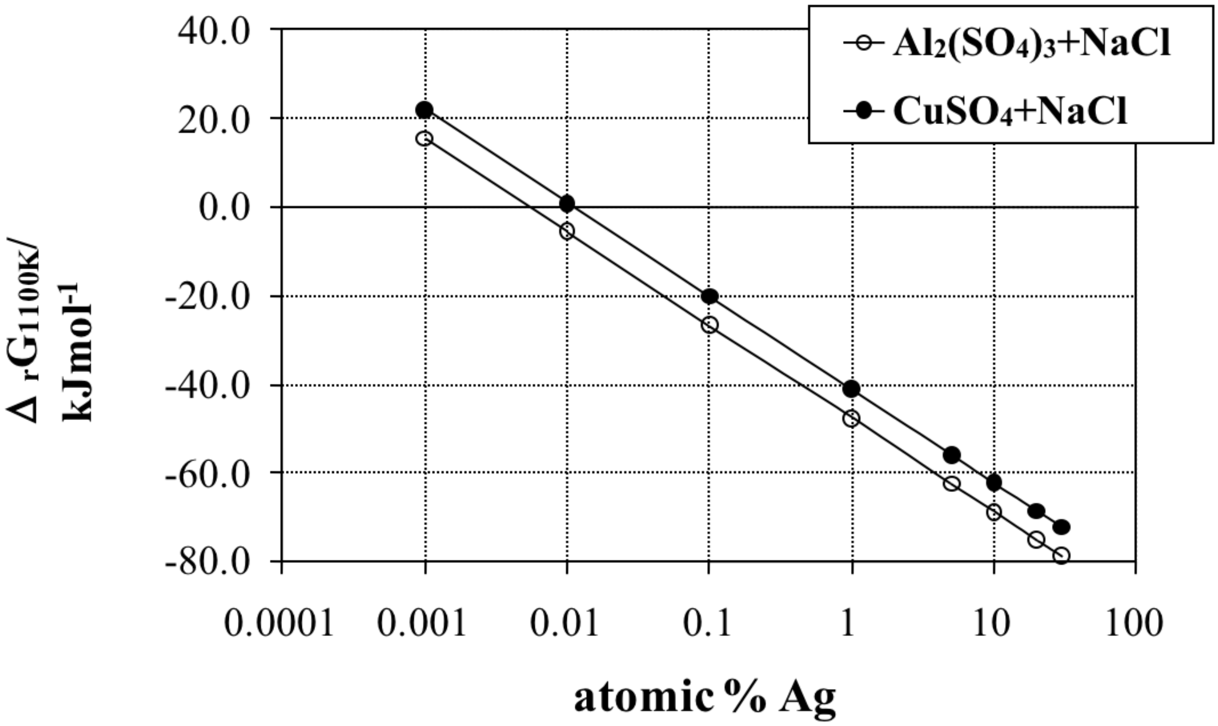

Figure 15: Driving force for reaction 4b at 1100 K plotted in function of the silver content in the Au-alloy.

From a thermodynamic point of view in both cases, by using aluminium or copper sulphates-NaCl mixtures, the cementation processes for the gold refining are apparently able to purify Au by reducing the residual Ag content in the alloy below the limit of 0.01 atomic percent.

In summary, the thermodynamic analysis confirms the assumed simplified reaction sequences: the cements, formed by Cu or Al sulphates and NaCl(s), at temperatures 800-1200K decompose by producing equilibrium Cl_2(g) partial pressures that are sufficient to oxidise the metallic silver in the gold alloy to give AgCl(s).

5.2) Thermodynamic modelling

The thermodynamic modelling has been carried out by fixing the composition of the system, the temperatures and pressure in order to mimic the experimental conditions realized in the crucible.

The main advantage of this thermodynamic approach is the lack of any postulation for the chemical process sequence to accomplish the refining. Indeed, starting from fixed p-T-c (pressure-temperature-composition) conditions, the modelling provides the resulting equilibrium state in terms of stable solids and gas phase composition. In view of this, the modelled system has been assumed to have a starting composition fixed by the following molar ratios NaCl(s) : $NaAl(SO_4)_2$• 12H2O : $Na_2Cu(SO_4)_2$• $2H_2O$: Au : Ag, being 100 :10 :5 :20 :10, respectively.

This composition set has been derived on the basis of the original Dioscorides procedure and the XRD analysis. The pressure was fixed at 1 bar and the temperatures were ranged between 900 and 1200K. The thermodynamic modelling was applied to two systems: the first by fixing as null the amount of silver and gold and the second including the Au-Ag alloy. In Table 7, the results of the modelling are presented by summarizing the stable condensed phases and the major gaseous species computed in each considered thermodynamic state. The resulting equilibrium composition of the condensed phases confirms that the Cu and Al sulphates are not stable under the modelled p-T conditions, regardless of the Au-Ag alloy, with Na_2SO_4(s,l) being the only predicted stable sulphate. In summary the results of the modelling, apart for the formation of the unexpected $CuAl_2O_4$(s) phase, match well with the XRD data, predicting the formation of the observed Al_2O_3(s), Na_2SO_4(s), Au(s) NaCl(s) and AgCl(s) phases (the latter only for modellings where the Au-Ag alloy was considered). It is to be noted that the chlorides where identified in the XRD patterns as solid solution and not as individual phases. However, the diffraction lines of the two compounds may be overlapping, therefore not allowing for an independent identification. Moreover, in the database the $Ag_xNa_{1-x}Cl$ solid solution phase was not included due to the lack of any reference data. Due to this, the modelling could not verify whether the solid solution was formed. In all cases this aspect is only marginal in the description of the cementation process.

Composition		Computed thermodynamic states			
		900K	1000K	1100K	1200K
$NaCl(s) : NaAl(SO_4)_2 \bullet 12H_2O :$ $Na_2Cu(SO_4)_2 \bullet 2H_20$ respectively inb the ratio 100 : 10 : 5	Solid phases	$Al_2O_3(s)$ $NaCl(s)$ $Na_2SO_4(s)$ $CuAl_2O_4(s)$		$Al_2O_3(s)$ $NaCl(s)$ $Na_2SO_4(s)$ $CuAl_2O_4(s)$	$Al_2O_3(s)$ $NaCl(s)$ $Na_2SO_4(s)$ $CuAl_2O_4(s)$
	Major gaseous species	H_2O, HCl, SO_2, NaCl, O_2, Cl_2			
$NaCl(s) : NaAl(SO_4)_2 \bullet 12H_2O :$ $Na_2Cu(SO_4)_2 \bullet 2H_2O : Au : Ag$ respectively in the ratio 100 : 10 : 5 : 20 : 10	Solid phases	$Al_2O_3(s)$ $NaCl(s)$ $Na_2SO_4(s)$ $CuAl_2O_4(s)$ Au(s) AgCl(I)		$Al_2O_3(s)$ $NaCl(s)$ $Na_2SO_4(s)$ $CuAl_2O_4(s)$ Au(s) AgCl(I)	$Al_2O_3(s)$ $NaCl(s)$ $Na_2SO_4(s)$ $CuAl_2O_4(s)$ Au(s) AgCl(I)
	Major gaseous species	H_2O, HCl, SO_2, NaCl, AgCl, O_2, Cl_2			

Table 7 : Thermodynamic modelling results (p = 1 bar).

The modelling also provides information about the composition of the equilibrium gaseous phase. The partial pressures of the major gaseous species are presented in Figures 16 and 17 for the two systems.

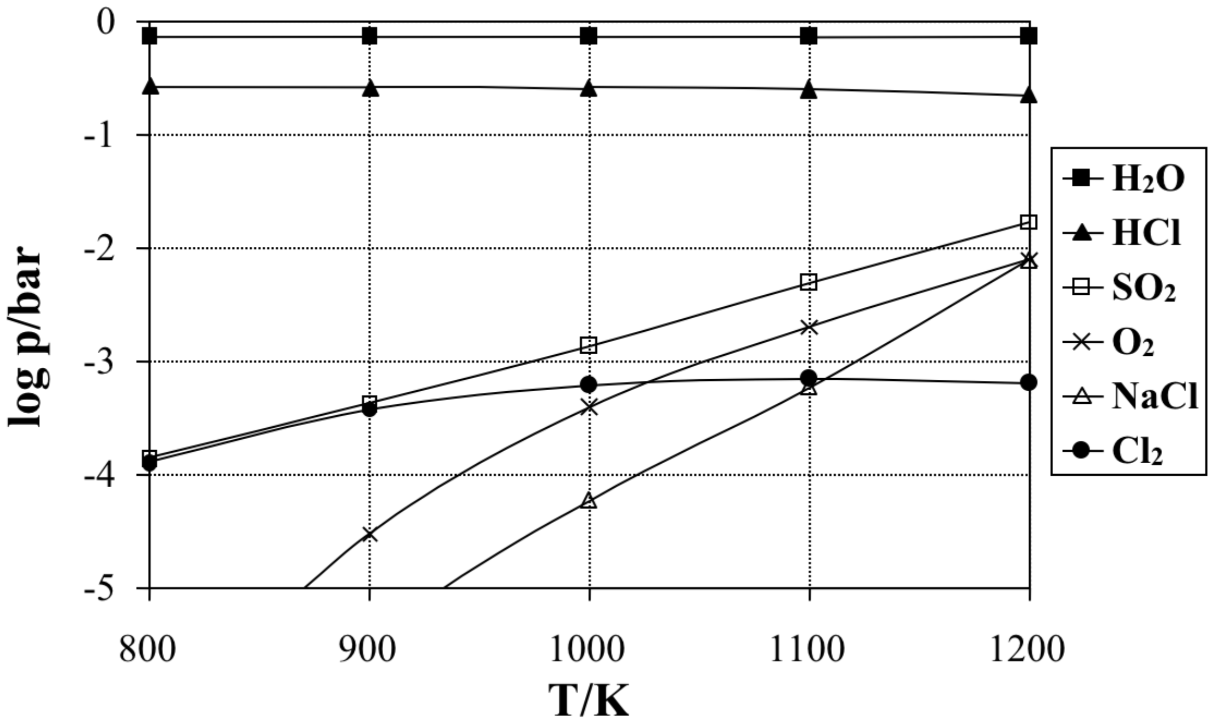

Figure 16 : Equilibrium partial pressures computed in the modellings performed without including the Ag-Au alloy.

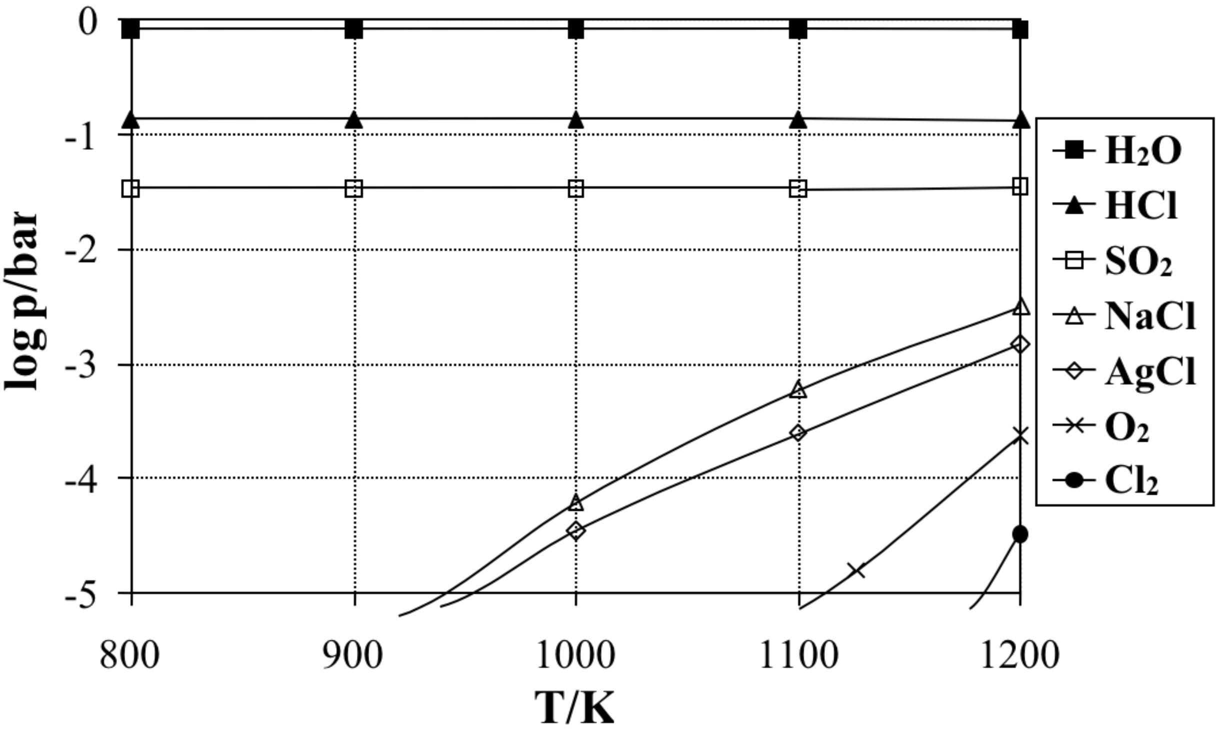

Figure 17 : Equilibrium partial pressures computed in the modellings performed including the Ag-Au alloy, therefore simulating the complete refining process.

The analysis of the partial pressures of the major constituent of the gas phases in the sets of thermodynamic modellings predicted that the decomposition of the hydrated sulphates leads to large concentrations of H_2O and SO_2 molecules in the gas phase but also the formation of HCl. The main difference between the gas phases modelled without including or considering the Au-Ag alloy in the starting composition set is the reduction in the second case (Fig. 8) of the partial pressure of Cl_2(g). From these predictions, apparently, this molecule acts as the oxidant agent for the metallic silver in the Au-alloy.

In conclusion, the thermodynamic modelling results are consistent with the experimental evidence and confirm the reliability of the reaction pattern proposed in the thermodynamic analysis to simply explain how the cementation process occurs.

5.3) Vapour pressure measurements

Knudsen Cell-Mass Spectrometry measurements have been carried out in order to check the occurrence of the chemical species necessary to promote the above described gold refining process. Indeed, this technique allows us to measure the composition of the gas phase in equilibrium above a condensed state sample at high temperature in vacuum conditions (10^{-6}-10^{-8} mbar). Technical details about this experimental methods and apparatus can be found elsewhere (Balducci 2006 and references cited therein).

In order to derive a qualitative description of the gas phase composition provided by the decomposition at high temperature of the refining cement, we have submitted the active « rose worms » to high temperature treatment in a tantalum Knudsen cell: the effusing vapours and gaseous species were detected and monitored by mass spectrometry. The collected results are reported in Table 8 in terms of relative ion intensities recorded by the mass spectrometer. The values of the ion intensities are correlated to the vapour pressure of each molecule formed by the vaporization process. From these data we can depict a qualitative trend of the occurring decomposition of the « rose worms » at the various high temperatures.

T/K	Relative ionic intensities for each mass/charge (m/q) signal											Total pressure / mbar
	17 NH_3	18 H_2O	28 CO	32 O_2	44 CO_2	58 NaCl	60 CH_3COOH	64 SO_2	70 Cl_2	80 SO_3	296 Cu_3Cl_3	
553	93	571	43		310						1	0.057
687				1							56	0.001
916		3				11		12	21	1	53	0.008
972				1		25		4	7	0.3	2	0.004
1053				1		130		9				0.011
1115				1		3		3				0.004

Table 8: High temperature vaporization of the "rose worms": Knudsen-effusion Mass-spectrometry experimental results.

Apparently, around 473-573 K the cement degradation leads to the evolution in the gas phase of ammonia, water, carbon monoxide and dioxide: these are the main constituents of the organic part of the cement. At 687 K this first decomposition stage is apparently ended. It is to be noted that even at this moderately high temperature an unexpected Cu_3Cl_3 gas species was observed. It is probably formed by the direct interaction of the sulphates with the sodium chloride. However, the surprising oxidation state of Cu (+1) suggests that in the condensed phase some more complex oxidation-reduction reactions have been taking place. This gas species may be primarily responsible for the migration of copper onto the gold foils, allowing the local formation of the observed Cu-Ag-Au eutectic alloys.

At around 923 K the production of gaseous chlorine is observed together with SO_3 and SO_2. This experimental evidence confirms the reliability of the thermodynamic model presented in the previous section: indeed, the evolution of Cl_2 due to the equilibrium between SO_3/SO_2 and the condensed phases is the driving force that promotes the extraction of silver from the gold alloy to give AgCl. At higher temperature the reaction slowly ended: however, this behaviour is only apparent. Indeed, as each temperature in the vaporization experiment was kept for approximately 2 hours, the sample at the end of the entire run appeared to be completely exhausted due to the mass loss via the gas phase. Owing to this, we consider reliable for the interpretation of the occurring decomposition process only data below 972 K.

In summary, the mass spectrometric experiment confirmed that at high temperature the « rose worms » decompose, giving a mixture of $SO_3/SO_2/Cl_2$ vapours that are available to promote the oxidation of silver from the gold alloy to give the corresponding chloride.

6) CONCLUSIONS

This review has focused on the replication in experimental archaeology and the thermodynamic characterization of ancient gold refining in light of the data collected at the Sardis gold refining site. Further research into ancient literary sources provided sufficient input to formulate and test cements. We have found that ancient recipes based on sulphates and chlorides point to a refining methodology in which ingredients are combined in order to cause different reagents to trigger the production of molecular chlorine over a broad temperature range. De-alloying begins at a much lower temperatures than previously hypothesized, establishing that the entire process can be conducted well below 973 K. This would exclude the formation of vitreous residues and slags in accordance with archaeological evidence. Initial experiments conducted at higher temperatures produced gold crystallites within the coarse-ware matrix, suggesting that ancient craftspeople may have sought to avoid higher temperatures due to the extra effort needed to recover precious metal values. A large number of fired sherds excavated at Sardis contain gold residues in the form of fused spheres which may have been gold crystallites formed through repetitive work cycles in which higher temperatures were accidentally attained. The high temperature firing of the broken sherds could therefore represent attempts at recovery of gold values rather than periodical assaying, as suggested by Craddock (Ramage and Craddock 2000).

The research has opened further avenues of experimentation on gold processing at Sardis suggesting different hypotheses concerning the material evidence, as well as consolidating a research protocol for the archaeological experimentation of other ancient and medieval gold processing recipes, such as Agatharchides' description (Burstein 1990, Celauro *et al.* 2017). Further questions remain open, such as the possible recovery of silver values from the used cements and coarse ware vessels. AgCl has been confirmed to be a durable fingerprint while this study suggests that most reagents involved in the reactions either volatilize, as in the case of sulphur, or decompose. The work provides a reference for the possible identification of gold processing on future excavations.

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APPENDIX. THE MULTI-EQUILIBRIUM THERMODYNAMIC MODELLING

The multi-equilibrium thermodynamic modelling approach has the advantage, with respect to the standard thermodynamic approach (see text), to avoid the postulation of a sequence of reactions: the overall behaviour of the high temperature system is calculated directly starting from the thermodynamic properties of the individual species considered and the starting conditions of composition (c), pressure (p) and temperature (T). Indeed, a thermodynamic modelling computes a chemical system by considering all the possible equilibria that involve all the phases and gaseous species that can be formed by the initial constituent elements in a fixed c-p-T condition. Each resulting computed thermodynamic state consists of the stable set of condensed phases and the corresponding equilibrium gaseous phases, each component's amount being determined. In view of this, by choosing appropriate starting c-p-T conditions, it is possible to describe a thermodynamic system by analysing the equilibrium composition of the condensed and gaseous phases and by verifying the occurring processes without postulating any arbitrary chemical reactions.

Athermodynamic modelling requires a large thermodynamic database: in our case it has been built starting from the SGTE database of the individual substances [SGTE] by including all the species (condensed or gaseous) formed by the combination of the following nine atomic types: Ag, Al, Au, Cl, Cu, H, Na, O, S. In summary the database includes 110 condensed phases, i.e. Ag(s), Ag(l), AgCl(s), AgCl(l), $AgClO_3$(s), Ag_2O(s), Ag_2O(l), Ag_2SO_4(s) Ag_2SO_4(HT-s), Ag_2SO_4(l), Ag_2S(s), Ag_2S(HT-s), Ag_2S(HT-s2), Ag_2S(l), Al(s), Al(l), AlClO(s), $AlCl_3$(s), $AlCl_3$(l), $AlCl_3 \cdot 6H_2O$(s), $NaAlCl_4$(s), Na_3AlCl_6(s), AlH_3(s), $Al(OH)_3$(s), $NaAlO_2$(s), $NaAlO_2$(HT-s), $CuAl_2O_4$(s), Boehmite-AlO(OH), Diaspore-AlO(OH), Bayerite-$Al(OH)_3$, Gibbsite-$Al(OH)_3$, α-Al_2O_3(s), Al_2O_3(l), δ-Al_2O_3(s), γ-Al_2O_3(s), κ-Al_2O_3(s), $Al_2(SO_4)_3$(s), Al_2S_3(s), Al_2S_3(HT-s), Al_2S_3(l), Au(s), Au(l), AuCl(s), $AuCl_3$(s), $Au(OH)_3$(s), Au_2O_3(s), CuCl(s), CuCl(l), NaCl(s), NaCl(l), $NaClO_4$(s), $NaClO_4$(HT-s), $CuCl_2$(s), $CuCl_2$(HT-s), $CuCl_2$(l), Cl_2S_2(l), Cu(s), Cu(l), $CuSO_4 \cdot 5H_2O$(s), $Cu(OH)_2$(s), $CuSO_4 \cdot H_2O$(s), $CuSO_4 \cdot 3H_2O$(s), CuO(s), $CuSO_4$(s), CuS(s), Cu_2O(s), Cu_2O(l), Cu_2SO_4(s), $CuO \cdot CuSO_4$(s), Cu_2S(s), Cu_2S(HT-s), Cu_2S(HT-s2), Cu_2S(l), $H_2SO_4 \cdot 4H_2O$(l), $H_2SO_4 \cdot 6.5H_2O$(l), NaH(s), NaH(l), NaOH(s), NaOH(HT-s), NaOH(l), H_2O(l), H_2O_2(l), H_2SO_4(l), $H_2SO_4 \cdot H_2O$(l), $H_2SO_4 \cdot 2H_2O$(l), $H_2SO_4 \cdot 3H_2O$(l), Na(s), Na(l), NaO_2(s), NaS(s), NaS(l), NaS_2(s), NaS_2(l), Na_2O(s), Na_2O(HT-s), Na_2O(HT-s2), Na_2O(l), Na_2O_2(s), Na_2S_2(HT-s), Na_2O_2(l), Na_2SO_4(s), Na_2SO_4(HT-s), Na_2SO_4(HT-s2), Na_2SO_4(l), Na2S(s), Na_2S_3(s), Na_2S_3(l), S(s), S(HT-s), S(HT-s2) (s = solid phase, l = liquid phase, HT-s = high temperature solid phase, HT-s2 = second high temperature polymorphic solid phase) and 112 gaseous species, i.e. Ag, AgCl, AgO, AgS, Ag_2, Ag_2S, Al, AlCl, AlClH, AlClOH, $AlClH_2$, $AlCl(OH)_2$, AlClO, $AlCl_2$, $AlCl_2H$, $AlCl_2OH$, $AlCl_2O$, $AlCl_3$, AlCu, AlCuS, $AlCuS_2$, AlH, AlOH, HAlO, AlO_2H, AlH_2, $Al(OH)_2$, AlH_3, $Al(OH)_3$, AlO, AlO_2, AlS, AlS_2, Al_2, Al_2Cl_6, Al_2O, Al_2O_2, Al_2O_3, Al_2S, Al_2S_2, Au, AuO, AuS, Au_2, Cl, CuCl, HCl, HClO, $HClSO_3$, NaCl, ClO, ClO_2, ClS, ClS_2, Cl_2, $CuCl_2$, $CuCl_2$, Na_2Cl_2, Cl_2O, Cl_2SO, Cl_2SO_2, Cl_2S, Cl_2S_2, Cu_3Cl_3, Na_3Cl_3, Cu_4Cl_4, Cu_5Cl_5, Cu, CuH, CuOH, CuO, CuS, Cu_2, Cu_2S, H, NaH, NaOH, OH, HSO, SOH, HO_2, HS, $(NaOH)_2$, H_2O, H_2SO, HSOH, H_2O_2, H_2SO_4, H_2S, H_2S_2, Na, NaO, Na_2, Na_2O, Na_2O_2, Na_2SO_4, O, SO, SO_2, SO_3, O_2, O_3, S, S_2, S_3, S_4, S_5, S_6, S_7, S_8. The thermodynamic modelling calculations were carried out by the Thermocalc software [Thermocalc] by fixing the initial composition of the system, the pressure (1bar) and the temperatures.

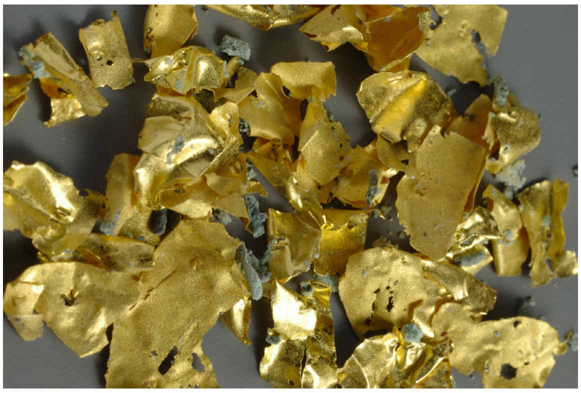
LIST OF FIGURES


1


2


3


4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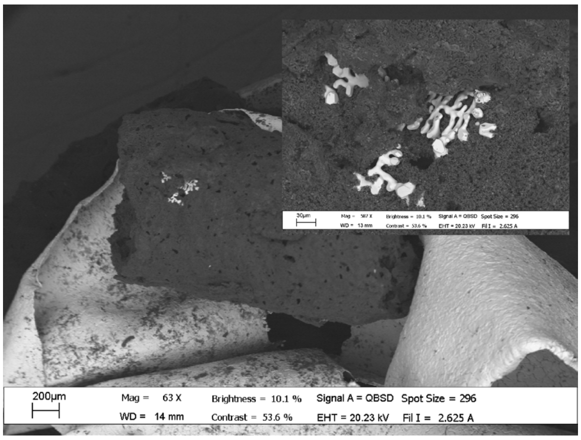
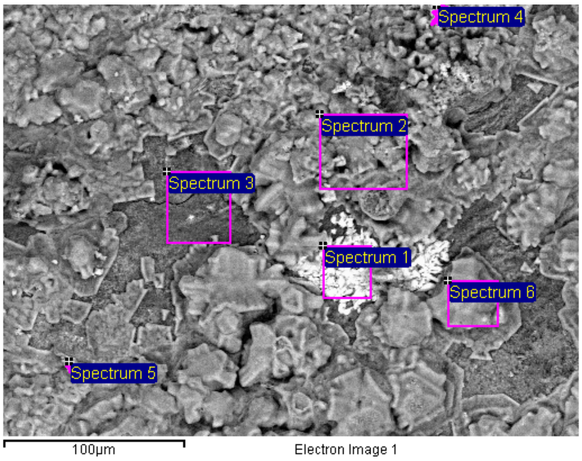
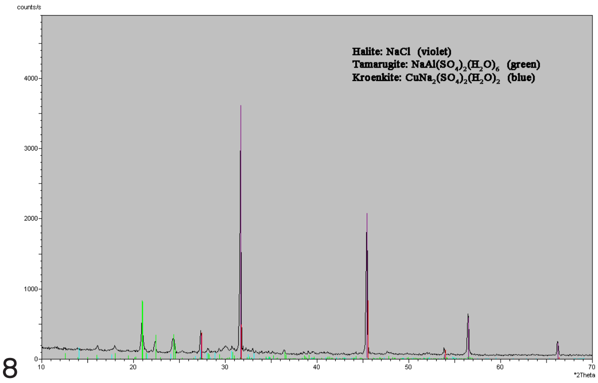

6

200μm
Mag = 63 X
WD = 14 mm
Brightness = 10.1 %
Contrast = 53.6 %
Signal A = QBSD
EHT = 20.23 kV
Spot Size = 296
Fil I = 2.625 A

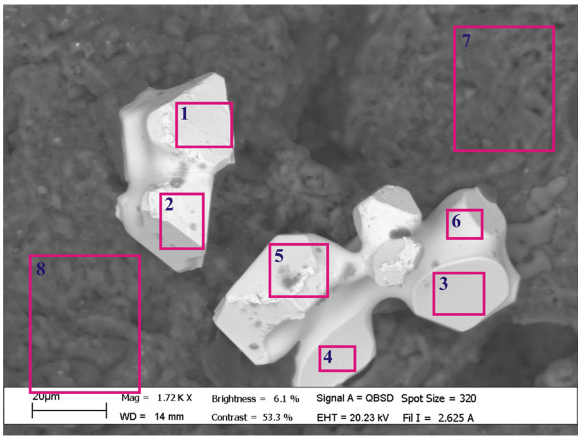

7

Spectrum 4
Spectrum 2
Spectrum 3
Spectrum 1
Spectrum 6
Spectrum 5
100μm
Electron Image 1

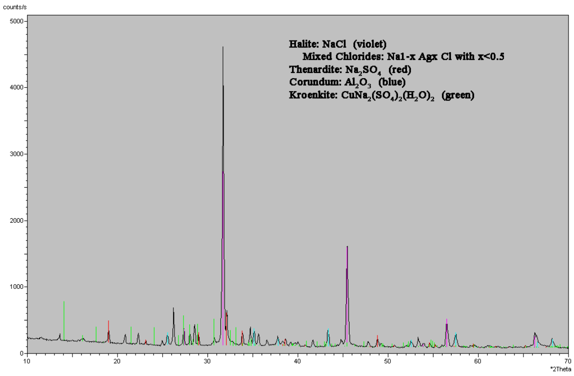

8

counts/s
Halite: NaCl (violet)
Tamarugite: $NaAl(SO_4)_2(H_2O)_6$ (green)
Kroenkite: $CuNa_2(SO_4)_2(H_2O)_2$ (blue)
0
1000
2000
3000
4000
10
20
30
40
50
60
70
°2Theta

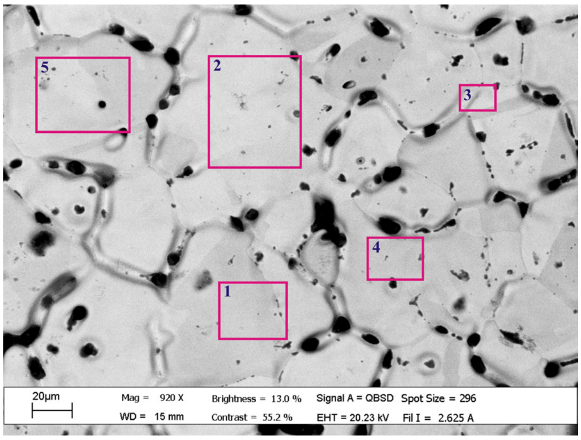
LIST OF FIGURES


1
2
3
4
5
6
7
8
20µm
Mag = 1.72 K X
WD = 14 mm
Brightness = 6.1 %
Contrast = 53.3 %
Signal A = QBSD
EHT = 20.23 kV
Spot Size = 320
Fil I = 2.625 A

9


counts/s
5000
4000
3000
2000
1000
0
10
20
30
40
50
60
70
°2Theta
Halite: NaCl (violet)
Mixed Chlorides: Na1-x Agx Cl with x<0.5
Thenardite: Na2SO4 (red)
Corundum: Al2O3 (blue)
Kroenkite: CuNa2(SO4)2(H2O)2 (green)

10


1
2
3
4
5
20µm
Mag = 920 X
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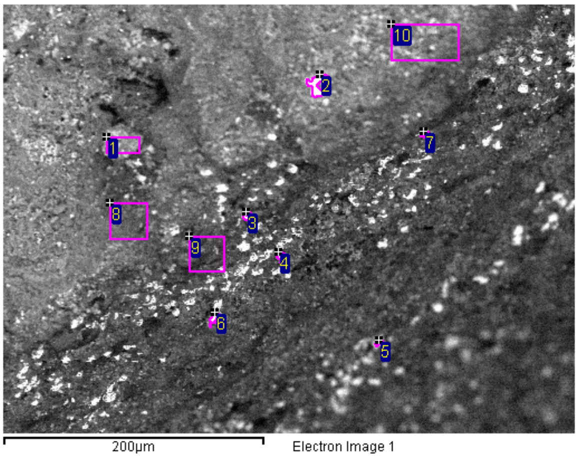
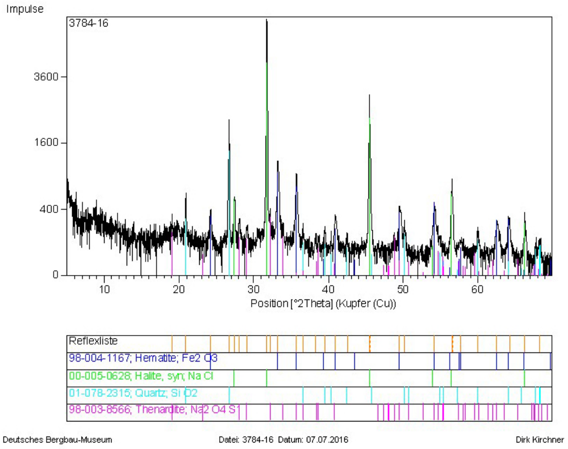
Contrast = 55.2 %
Signal A = QBSD
EHT = 20.23 kV
Spot Size = 296
Fil I = 2.625 A

11


1
2
3
4
5
6
7
8
9
10
200µm
Electron Image 1

12


Impulse
3784-16
3600
1600
400
0
10
20
30
40
50
60
Position [°2Theta] (Kupfer (Cu))
Reflexliste
98-004-1167; Hematite; Fe2 O3
00-005-0628; Halite, syn; Na Cl
01-078-2315; Quartz; Si O2
98-003-8566; Thenardite; Na2 O4 S1
Deutsches Bergbau-Museum
Datei: 3784-16 Datum: 07.07.2016
Dirk Kirchner

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