

CHARACTERIZATION AND THERMODYNAMIC INTERPRETATION OF ANCIENT GOLD REFINING PROCESSES BASED ON A DIOSCORIDES RECIPE

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Abstract

The chemical processes involved in ancient gold refining are investigated based on textual analysis and current archaeological evidence. Ancient cementation recipes in most cases are composed of sulphates and chlorides. Experimentation based on sulphates of a single divalent metal were preferred, in this case a recipe of Dioscorides aimed to imitate the oxidation of a natural sulphide mineral complex reportedly used in ancient gold processing. Experimental archaeology has been employed to reproduce the whole cementation process step by step in order to analyse the composition of the products obtained for each specific chemical equation. Thermodynamic considerations indicate the reliability of the chemical processes over a wide temperature range.

Keywords: Cementation, Experimental Archaeology, Thermodynamics

INTRODUCTION

Gold artefacts have been systematically produced as far back as 6500 years, making it 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. More complex pyrotechnical operations that involved the recognition and transformation of gold alloys may have been developed by the end of the IV millennium BC, perhaps in coincidence with the emergence of manufacturing techniques such as casting and brazing (1), (2), while the possibility of intentional gold refining before the first millennium BC is still open to debate (2); (3); (4). The aim of the present work is to study a possible metal processing recipe based on a passage by Dioscorides (I century b. C.). After each experimental procedural step, materials involved in the chemical process were characterized by micro-chemical analyses (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. A new translation from the ancient Greek source has been attempted (5). The English translation of the Dioscorides recipe for the production of *ios scolecos* is reported below:

There exist two types of ios scolecos. 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. 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...

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 IV century BC as used to extract metallic mercury by grinding cinnabar and vinegar together (7). Further, it is better to first stir the vinegar in the mortar under strong summer sunlight (the Dogstar, Sirius, appears around July 26th) so as to facilitate the release of copper cations, a process evidenced by the greenish tinge the liquid develops. In light of Pliny's elliptic phrasing (*Naturalis Historia*, book XXXIV, 116, in ref. 6,) and Matthioli's use of reflexive verbs in his 1586 Italian translation of Dioscorides, it is difficult to understand how the "worms" are formed (8). One is not quite sure that the "worms" form of themselves or are formed by an agent, a matter easily resolved by workshop trials.

MATERIALS AND METHODS

On the basis of experiments carried out in the eighteenth and nineteenth centuries with the proposal of elucidating the chemical processes involved in salt cementation (4) 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 (VI century BC)(4);
- 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 coarseware 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 4mm to 6 mm, a measure adopted to contrast observed fast wear. Coarseware vessels and lids were fabricated to specification by a traditional potter in local prospected clay body to resist high temperatures. 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 VI century BC (pp. 83-86 in ref. 4). The square draft furnace was 68 cm. high, 76 cm wide, broad at the bottom, slightly narrowing at the top. The walls averaged 15 to 20 cm thick. A rectangular mouth or door was provided for at floor level that served both for draft and for stocking wood. The preferred fuel was a combination of well-seasoned and partially seasoned young wood (pp. 179-181 in ref. 4).

Small gold foils, with unknown quantities of gold that varied between 72.8% and 93.1%, according to subsequent EDS analyses, with a variable area of around 1,2 cm², and a thickness of 0,03 to 0,1 mm, were prepared by tearing or cutting snippets from hammered gold alloy strips. The cement, which is the object of the present paper, was made according to the procedure related by Dioscorides in which the following compounds had been individuated (book V, 79 in ref. 5); (9):

- Alum (50.019 g)
- Traditionally prepared natural sea salt (50.164 g)
- Aged urine (40 ml)
- Solution of copper in concentrated vinegar (46.5 ml, after evaporation).

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 effervescence (10). The compost quickly became a dense, green putty, oily to touch, under the combined effects of sunlight, heat and stirring. The paste obtained was then hand rolled into small filaments resembling “rose worms” (Fig. 2) 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 coarseware vessel, assuring contact between the gold foil and the cement. The vessel, lidded and sealed with clay, was left overnight in a plate of water to allow water to penetrate. The vessels were set in a lump of wet clay placed inside the furnace on two parallel heat-resistant plinths. To avoid the loss of heat or even the collapse of the furnace, continuous maintenance was necessary, filling the cracks with semi-liquid clay. The furnace remained active for 19 hours. The temperature, controlled in antiquity by observing colour



Fig. 1: Image of the used furnace. In the insert a drawing of the furnace and thermocouple inserted below the vessel is showed.



Fig. 2: Dioscoride's rose worms before pyrotechnical processing.

changes assumed by the vessel and the inner furnace walls, 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° occurred despite efforts to avoid high temperatures. Concluded the firing cycle, observation with a binocular optical microscope at 40x have been carried out, showing that the gold precipitate within the filaments and on the inside surface of the vessel consisted of micrometric crystallites. 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.%. To verify the presence of a specific compound produced in the different phases of the process, samples were analyzed with the x ray powder diffraction by 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 (11). As a final check of the validity of the proposed chemical process, a thermodynamically valid modelling and a MSKC (Mass Spectrometry-Knudsen Cell) (22) high temperature experiment was carried out on the “rose worms” sample. in order to propose a thermodynamically valid modelling compatible with experimental conditions.

RESULTS AND DISCUSSION

The reactions that occur during cementation may be understood by analyzing the initial materials and their products in each phase of the process. 39 samples were analyzed with SEM and EDS and 8 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 aluminogenite ($\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$) 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 was to draw into solution the copper ions that compose the mortar and pestle, leading to the formation of $\text{Cu}(\text{CH}_3\text{COO})_2$, salt and alum, followed by aged urine, were mixed into the solution, quickly forming a green compost with a plastic, greasy consistency. The addition of urine apparently has the function of amalgamating the cement components, modifying the pH of the paste, previously acidic due to the presence of copper acetates, and favouring the dissociation and re-precipitation of the various compounds. 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. 3 and Tab. 1) are oxygen, chlorine, copper, sodium, aluminium and sulphur. XRD spectrum showed that the sample was formed of tamarugite, ($\text{NaAl}(\text{SO}_4) \times (\text{H}_2\text{O})_6$), kroenkite ($\text{CuNa}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2$), 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

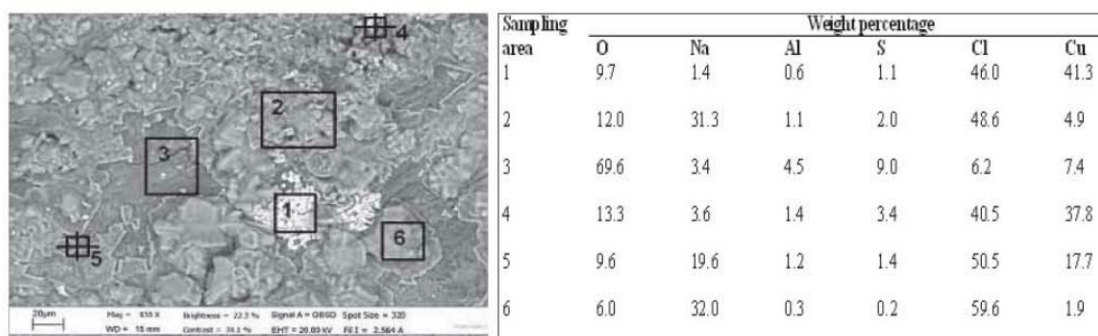


Fig. 3, Tab. 1: SEM image of an active “rose worm and SEM-EDS composition table of the sample.

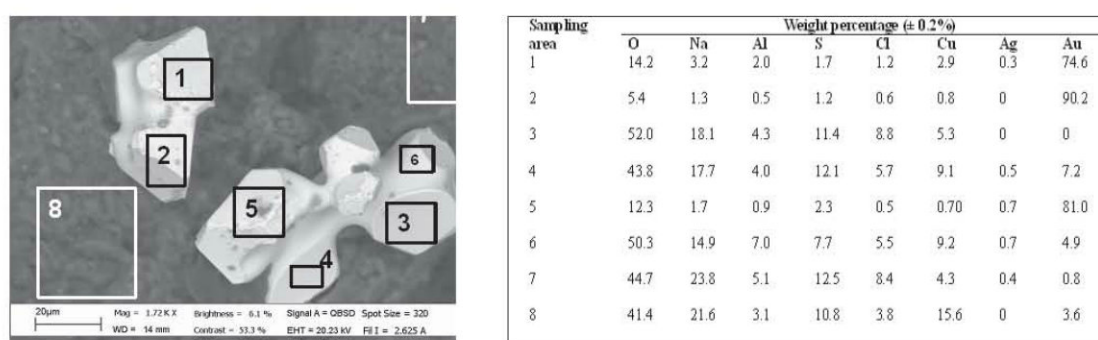
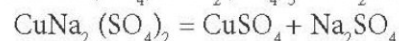
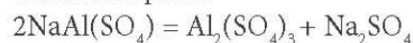
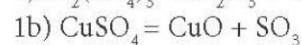
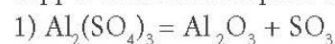


Fig. 4, Tab. 2: SEM image of a spent rose worm and SEM-EDS composition table of the sample.

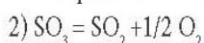
that a reaction occurred between the copper acetate and the alum components, allumogenite and sodium sulphate, thus producing tamarugite and kroenkite, whereas NaCl remained unaltered. After thermal treatment the gold foil was analysed to determine the degree of purity, as well as the residual filaments and the vessel in order to individuate eventual changes in composition and structure. SEM analysis of the “rose worms” (Fig. 4 and Tab. 2) after pyrotechnical treatment indicated the presence of silver, as well as oxygen, sodium, aluminium, sulphur and copper, present in a higher percentages 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 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), tenardite (Na₂SO₄), corundum (Al₂O₃) and kroenkite (CuNa₂(SO₄)₂(H₂O)₂). 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:



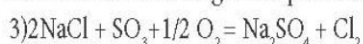
The sulphates of copper and aluminium then dissociate into aluminium oxide (corundum), copper oxide and sulphur trioxide at T ≈ 516, 586°C, respectively (23):



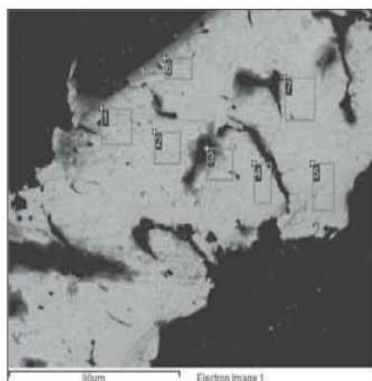
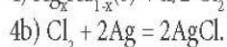
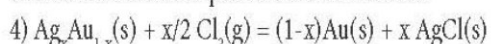
The sulphur trioxide also dissociated into:



The reaction between sodium chloride, a compound that had not previously participated in any reaction, and sulphur trioxide produces molecular chlorine, the active agent in cementation according to the previous studies by Craddock (4).



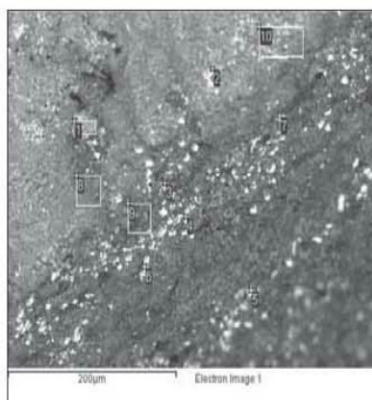
SEM-EDS analysis of the gold foil (Fig. 5 and Tab. 3) indicate that the gold had attained a very high grade of purity, thus substantiating the hypothesis that molecular chlorine oxidized the silver to produce silver chloride:



Sampling Area	Weight percentage ($\pm 0.2\%$)		
	Cu	Ag	Au
1	0	0.36	99.64
2	0	0	100
3	1.37	0	98.63
4	0.37	0	99.63
5	0	0	100
6	0	0	100
7	0	0.56	99.44

Fig. 5 Tab. 3: SEM image of a transversal section of a purified gold leaf and SEM-EDS normalized composition of the same sample

Analyses conducted on the inner walls and cross-sections of the earthenware jar established that there was a strong absorption of silver chloride. In fact, the vessel, after 19 hours of thermal treatment in close contact with the gold alloy leaves and the cement, shows the presence of white to pale green concretions and a golden dust on the lower inside surface of the vessel. Analysis of the inner surface of the vessel revealed the presence of gold and silver,



Sampling area	Weight percentage ($\pm 0.2\%$)			
	Cl	Cu	Ag	Au
1	68.1	8.7	23.3	0
2	30.1	16.7	2.2	51.0
3	39.1	54.0	7.0	0
4	56.0	32.6	11.4	0
5	66.7	33.3	0	0
6	65.9	29.2	4.9	0
7	57.8	28.1	14.1	0
8	40.6	36.5	23.0	0
9	44.0	45.9	10.0	0
10	43.0	43.6	13.4	0

Fig. 6, Tab. 4: SEM image of a transversal section of an inner wall of the jar and SEM-EDS composition of the same sample.

while analysis of a transversal section (Fig. 6 and Tab. 4) established the depth of absorption of the two elements. 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” (see Fig. 4 and Tab. 2) may be caused by the local formation of the eutectic Au-Ag-Cu.

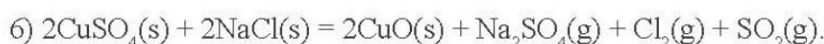
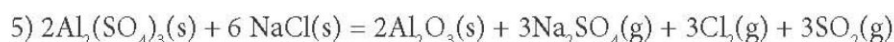
Thermodynamic methods for the analysis of the high temperature refining process

A thermodynamic analysis, 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, considering the EDS and XRD determinations of the solid phases involved in the process. The active “rose worms”, analysed before the high temperature cementation, consisted in 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, $\text{Na}_{1-x}\text{Ag}_x\text{Cl}$, Na_2SO_4 , Al_2O_3 , Au and the mixed copper-sodium hydrated sulphate. A summary of the standard Gibbs energy of reaction for processes 1-1b-2-3-4b are presented in Table 5. These data were retrieved from SGTE (1994) and Ivtan (24).

Tab. 5 Standard Gibbs energy of reaction [kJ mol^{-1}] for the high temperature processes 1-1b-2-3-4b

Reaction	$\Delta_r G_{T/K}^\circ$				
	800K	900K	1000K	1100K	1200K
(1) $\text{Al}_2(\text{SO}_4)_3(\text{s}) = \text{Al}_2\text{O}_3(\text{s}) + 3\text{SO}_3(\text{g})$	160	119	78	37	-4
(1b) $\text{CuSO}_4(\text{s}) = \text{CuO}(\text{s}) + \text{SO}_3(\text{g})$	70	53	36	19	2
(2) $\text{SO}_3(\text{g}) = \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$	24	14	5	-4	-14
(3) $2\text{NaCl}(\text{s}) + \text{SO}_3(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{Na}_2\text{SO}_4(\text{s}) + \text{Cl}_2(\text{g})$	-73	-63	-54	-43	-29
(4b) $\text{Ag}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) = \text{AgCl}(\text{s})$	-86	-83	-81	-79	-76

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 $\text{Cl}_2(\text{g})$ produced by the “worms” (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. $\text{AgCl}(\text{s}) = \text{Ag}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g})$). 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:



From data reported in Table 2 the equilibrium partial pressure of gaseous molecular chlorine can be calculated by the formulas $p_{\text{Cl}_2} = \sqrt{e^{-\Delta_r G_{T/K}^\circ(n)/RT}}$ in which R is the gas constant, $\Delta_r G_{T/K}^\circ(n)$ are the standard Gibbs energy of reaction (5) and (6) that can be calculated by data reported

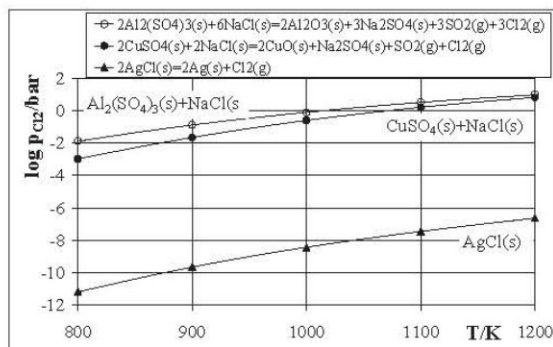


Fig. 7: Calculated partial pressure of Cl₂(g) in equilibrium over the various different systems considered.

in table 5 by summing the Gibbs energy of reaction 1-2-3 and 1b-2-3, respectively. Similarly the equilibrium Cl₂(g) partial pressure for reaction 4b is calculated by the equation $p_{Cl_2} = e^{\Delta_r G_{T/K}^\circ(4b)/RT}$, in which $\Delta_r G_{T/K}^\circ(4b)$ is the corresponding Gibbs energy of reaction. The calculated partial pressures of Cl₂(g) are shown in Fig. 7. The equilibrium partial pressure of gaseous chlorine produced by the interaction of the sulphates with NaCl(s) at high temperature are several order of magnitudes larger than the equilibrium pressure

of Cl₂ 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 800-1200 K the Gibbs energy of reaction 4b, (given by the equation

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

in which $\Delta_r G_{T/K}^\circ(4b)$ 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 term of the smaller silver content in the Au-alloy that will result in a null Gibbs energy of reaction 4b. In figure 8 the driving force for reaction 4b at 1100 K is plotted in function of the silver content in the Au-alloy. From a thermodynamic point of view SO₃ is produced both at lower temperatures (< 900°K) by Al-sulphates, and at higher temperatures (> 900°K) by Cu sulphates. In both cases, by using aluminium or copper sulphates-NaCl mixtures, the

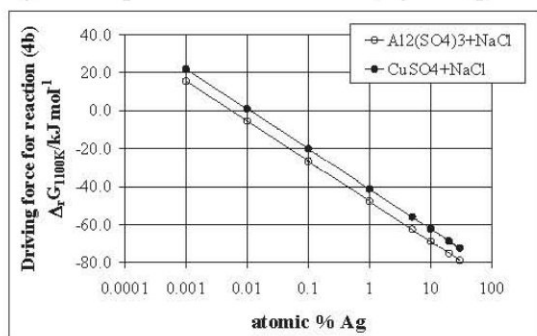


Fig. 8: Driving force for reaction 4b at 1100K plotted in function of the silver content in the Au-alloy.

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 Cl₂(g) partial pressures that are sufficient to oxidise the metallic silver in the gold alloy to

give AgCl(s). To identify the presence of the gas phase and to measure their vapour pressure an experiment has been carried out by using the Knudsen Cell-Mass Spectrometry method (25). 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. Apparently around 200-300°C 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 414°C this first decomposition stage is apparently ended. Around 650°C the production of gaseous chlorine is observed together with SO₃ and SO₂. This experimental evidence confirms the reliability of the thermodynamic model presented in the previous section: indeed the evolution of Cl₂ due to the equilibrium between SO₃/SO₂ and the condensed phases, is the driving force that promote the extraction of silver from the gold alloy to give AgCl. At higher temperature the reaction slowly ended. Owing to this we consider reliable for the interpretation of the occurring decomposition process only data below 700°C.

In summary the mass spectrometric experiment confirmed that at high temperature the “rose worms” decompose giving a mixture of SO₃/SO₂/Cl₂ vapours that are available to promote the oxidation of silver from the gold alloy to give the corresponding chloride.

CONCLUSIONS

The innovative findings of this experiment are to be ascribed to the relevance given to each possible point of view under which the refining process could be evaluated. The most surprising result is that ancient recipes based on sulphates and chlorides point to a refining methodology in which ingredients are combined in order to cause at least one agent to trigger the production of molecular chlorine over a wide temperature range. It should be supposed that these skills were not simply based on casual or coincidental approach, but on acquired knowledge based on acute observations. Another valuable aspect of this work is that the analytical protocol tested in this experiment has given optimal results and could be applied in further analyses with similar targets. A further consideration is that the compounds and characteristic “fingerprints” developed during this process may be considered as markers for the presence of identical or similar processes on archaeo-metallurgical sites.

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REFERENCES

1. Duval A. R., Eluère C., Hurtel L. & Tallon F., , *La pendeloque au petit chien de Suse (Iran), étude d'une brasure antique en laboratoire*, Revue du Louvre, 1985.
2. Eluère C., *Les secrets de l'or antique*, La Bibliothèque des Arts, 1990, Paris, pp. 163-169.
3. Halleux R., *Le problème des métaux dans la science antique*, Les Belles Lettres, 1974, Paris.
4. Craddock P. T. & Ramage A., *King Croesus' Gold: excavations at Sardis and the history of gold refining*, published for the Trustees of The British Museum by British Museum Press, 2000, London.
5. Wellmann M., *Pedanii Dioscuridis Anazarbei*, De Materia Medica Libri Quinque, 3 vols, 1958.
6. Rackham H., *Pliny: Natural History*, IX, Books XXXIII-XXXV, Loeb Classical Library, 1934.
7. Caley E. R. & Richards J. C., *Theophrastus on Stones*, Columbus, 1956, pp. 204-205.
8. Matthioli M. P. A., *I discorsi di M. Pietro Andrea Matthioli...nelli sei libri de Pedacio Dioscoride Anazarbeo della Materia Medicinale*, Book 5, 1586, Venice, reprinted in 1970, Rome.
9. Beck L. Y., (trans.), *Pedanius Dioscorides of Anazarbus*, XXVIII, Olms-Weidmann (eds), Hildesheim, 2005, Zürich, New York.
10. Berthelot M., , *Introduction à l'étude de la chimie des anciens et du moyen âge*, 1889, Paris.
11. Blanton T. N., Schreiner W. N., Dann J. N., Hamill G. P. & Amilton R. F., *JCPDS—International Centre for Diffraction Data statistical process control method development*, Powder Diffraction, Issue 4, December 1993 –8, pp. 229-235.
12. Drowart J., Chatillon C., Hastie J. & Bonnel, D., , *High Temperature Mass Spectrometry: instrumental techniques, ionization cross-sections, pressure measurements and thermodynamic data*, Pure and Applied Chemistry, 77, 2005, pp 683-737.
13. Tagawa H., *Thermal dissociation of metallic sulphates*, Thermochemica Acta, 80, 1984, pp. 23-33.
14. Gurvich L. V., Iorish V. S. et al., *IVTANTHERMO database of thermodynamic properties of individual substances*, Thermocentre of the Russian Academy of Science, 1993, New York.
15. Balducci G., Brutti S., Ciccio A., Gigli G., Trionfetti G., Palenzona A. & Pani M., , *Vaporization thermodynamic of the Sr-Si phases Intermetallics*, 14, 2006, pp. 578-583 and references cited therein.