Gold to purple
Violet traces on Antique Marble

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In ancient times the colour purple or violet is usually associated with nobles and extravagance. To produce a "purple" colour various colorants like haematite, caput mortuum or – if affordable - purple of Tyros[1] was used. In some cases the colour "purple" was used to enhance the value of an artefact[2]. However, a violet or purple colour can be present on an artefact for rather unexpected reasons.

Researching colour in cooperation with Jan Stubbe Østergaard at the Ny Carlsberg Glyptotek, traces of a violet colour found on the sculpture "Artemis of Copenhagen" (c.125 BC) became the focus of interest. These traces did not seem to be associated with the former polychromy of the sculpture (Fig. 1; 2). These traces showed some similarity to those on an antique ivory relief from the Liebieg Haus in Frankfurt (Fig. 3; 4).

Fig. 1: Artemis of Copenhagen

Fig. 2: Detail of the violet traces

[1] Tyrian Puple, 6,6-Dibromoindigo, extract of *Hexaplex trunculus*
[2] Piening, H.: Mobile UV-VIS-Spectrometry – Investigations in the Alexander-Sarcophagus in Istanbul, in: Büyüköztürk, O., Tasdemir, M.A.Ed. Nondestructive Testing of Materials and Structures, Proceedings of NDTMS-2011 Istanbul, Heidelberg, London, New York 2013

The questions were: What caused these violet traces? Are they relicts of the original polychromy? Are there other causes?

Some basic considerations:
What produces colours on marble?

- 1. The marble has a natural colour caused by various finely distributed minerals
- 2. Corrosion products of mineral traces in the marble function as an natural ochre, for example limonite
- 3. Paint on marble as a decorative element of the art object.
- 4. Secondary staining, for example caused by handling the object or by paint drips caused when the room was decorated.

Causes of colour

The visual effect of seeing colours is complex and every person will see colours more or less differently. Therefore the eye is not a very precise instrument to assess colour. Colour measurement for the identification of colorants is completely different. Colours appearing similar often have different causes of colour and produce different spectra. Fifteen causes of colour[3] can be described in general by physical effects. Six of these causes are of interest for the analysis of colorants. Most of these produce spectra with a distinct contour.
For colour research mobile UV-VIS- spectrometry is used. With this method it is possible to identify nearly 90% of the commonly used pigments and ca. 80 % of the dyes[4] used. The method is non-invasive.

Two ivory miniatures

The Liebighaus in Frankfurt owns two ivory miniature reliefs ca. 600 BC and located to Laconia (Fig. 3; 4). The miniature reliefs were formerly parts of a necklace, now lost. On one relief miniatures Heracles, struggling with a lion and on the other one Gorgo are depicted[5]. On both reliefs remains of gold leaf and violet shades are visible.

[3] Nassau, Kurt, The fifteen causes of color, in: Nassau, Kurt (ed.) Color for science, art and technology, Amsterdam, Lausanne, New York 1998, p.123-168
[4] Piening, H.: From scientific findings to reconstruction – The technical background of the reconstruction of colours, in: Brinkmann, V.; Primavesi, O.; Hollein, M. (Hrsg): CIRCUMLITIO The Polycormy of the Antique and Medeaval Sculpture, Liebieghaus Frankfurt 2010, S. 108-113
[5] Liebieg-Haus Frankfurt, Inv. Nr. 1571

Fig.3: Ivory miniature with traces of violet

Fig. 4: Ivory miniature

The analysis of the UV-VIS- spectrum of the violet traces shows a high similarity to purple of Tyros (fig.5). Purple of Tyros is the natural dyestuff of a marine mollusc. Chemically this dyestuff is 6,6´-dibromoindigo. In ancient times purple of Tyros was rather expensive and it seems to be rather extravagant to use purple as an undercoat for gilding.

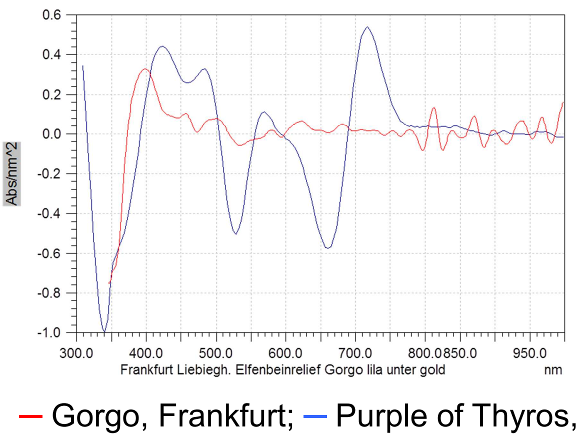
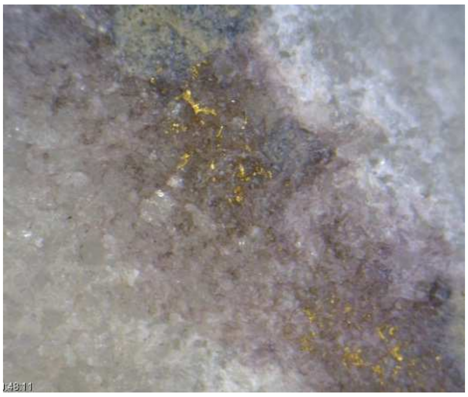


Fig. 5: Comparison of the spectra of the violet traces on the ivory miniature "Gorgo" and the spectra of purple of Tyros.

The Artemis of Copenhagen

As described before, some shades of violet are visible on the robe of the Artemis of Copenhagen. The violet colour looks diffuse and does not correspond to the former polychrome painting. On closer examination, more details of the former polychromy are visible. However, no reason for the violet colour can be detected. Investigations of the violet colour using XRF-technologies produced no clear results regarding the elements responsible for the colour. Conspicuous are some very small gold particles without any undercoat. The gold was placed directly onto the marble surface, encased into remains of a transparent media (Fig. 6).



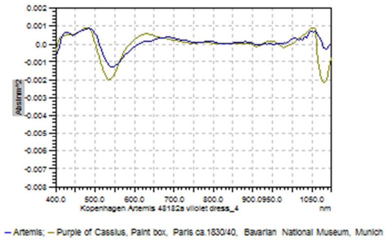


Fig. 6: Traces of Gold on the marble

Fig. 7: Comparison of the violet spectra of the marble with a spectra of gold purple

The comparison of the UV-VIS- spectrum of this violet with spectra in several different data libraries lead to a first hint at the unknown material. This UV-VIS-spectrum (Fig. 7) seemed not to be produced by a dyestuff but showed a remarkable similarity to gold purple, a pigment made of gold and tin, which is known as “Purple of Cassius”. “Purple of Cassius” is a synthetic pigment. Could gold purple be present here, and if so, why?

Carefully comparing the spectrum of the violet colour found on the Copenhagen Artemis to the spectrum of that found on the ivory relief in Frankfurt the differences became obvious (Fig. 8): the purple colour on each artefact is clearly caused by a different material.

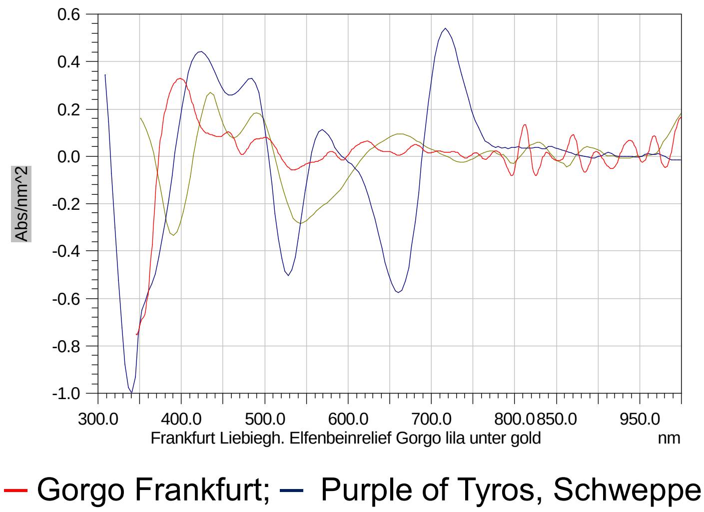


Fig. 8: Comparison of the spectra of the violet of the “Gorgo”, purple of Tyros and gold purple. The spectra of gold purple do not compare with the spectra of the “Gorgo”

About gold purple

Gold purple has been known for more than 2700 years. It was first mentioned in the archives of Ashurbanipal, 6400 BC in Ninive. The text found there describes how glass was given a violet colour using gold particles[6].

A similar technique was used for the production of the famous Lycurgus cup (400 A.C.). This is one of the most impressive masterpieces of roman artistic glass work and can be admired in the British Museum. The colour is caused by small traces (30-70nm) of gold within the glass matrix.

In the publication of Andreas Cassius, a medical doctor in Leiden (NL) and Hamburg, 1663 (?) the production process of the violet pigment "gold purple" is described. Cassius dissolved gold in aqua regia and added some tin chloride. He described that only when both solutions are of a very low concentration, violet gold purple will be produced. At higher concentrations the reaction product will turn black.

Michael Faraday specified gold purple in 1857[7] and concluded from the observations he made that the gold particles must be very small and the colour has to be caused by a scattering effect.

In 1908 Gustav Mie[8] described the purple colour as based on a nano size effect. Finally, since 1982 the colour effect has been described as a quantum- size-effect[9].

As good as gold?

Normally gold is considered to be extremely stable and only soluble in aqua regia, a mixture of hydrochloric acid and nitric acid. In fact, only the chloride ions of aqua regia react with gold[10].

At times gold corrosion can occur "naturally" and this is the case for some of the purple areas which can be found on antique marbles like the Copenhagen Artemis.

To trigger the corrosion process of gold, special conditions are necessary: the presence of water or wetness and the presence of chloride or other halogen ions.

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[6] Thompson, R.C.: A Dictionary of Assyrian Chemistry and Geology, Oxford 1936

[7] Faraday, M. : The Bakerian Lecture.–Experimental Relations of Gold (and other Metals) to Light. In: Philos. Trans. R. Soc. London. 147 (1857), S. 145–181in: Bücking, W. Untersuchung von mesoskopischen Eigenschaften von Nanopartikeln mit elektroanalytischen Methoden, Diss. Freiburg 2006

[8] Mie, G. : In: Ann. Phys. 25 (1908), S. 329, 181in: Bücking, W. Untersuchung von mesoskopischen Eigenschaften von Nanopartikeln mit elektroanalytischen Methoden, Diss. Freiburg 2006

[9] Ekimov, A. I.; Onushenko, A. A.: Quantum size effect in three-dimensional microscopic semiconductor crystals. In: J. Exp. Theor. Phys. Lett. 34 (1982), Nr.6, S. 346–349, in: 181in: Bücking, W. Untersuchung von mesoskopischen Eigenschaften von Nanopartikeln mit elektroanalytischen Methoden, Diss. Freiburg 2006

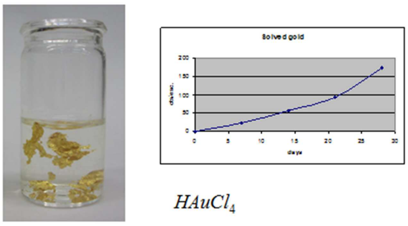
[10] About gold corrosion: Craig, Bruce D.: Handbook of corrosion data., 2nd Ed. ASM International 1997, P. 76, Tab. 21

Water is the basic medium for every process for dissociation. Chloride ions can be delivered by sodium chloride or other salts, for example from the sea. An alloy of gold and copper or silver will corrode faster than pure gold because of internal electrochemical processes.

The process of gold corrosion can proceed extremely slowly as it needs time to solve the gold ion by ion.

Corrosion test

In order to show how gold can be corroded by sodium chloride, flakes of gold leaf[11] were mixed with a highly concentrated solution of sodium chloride in water. The test material was sampled under room conditions. Samples were taken out once a week and analysed by XRF[12]. Gold particles were detected in the solution, which means that the gold flakes slowly dissolved. This means that gold can be dissolved in a slow but very simple process. (Fig. 9, 10)



$HAuCl_4$

Fig. 9: *Fig. 10*

Figure 9: Gold leaf flakes in sodium chloride. The graph shows the rising gold concentration in the solution

Figure 10: Dissolved gold chloride (left) and gold flakes in sodium chloride

The reaction scheme[13] shows that only the energy of other dissolved metals like tin or magnesia is necessary to reduce gold chloride to gold. This reaction will take place only in low ion concentrations (< 0.001%).

A second test was carried out in order to visualize that reactive gold is dissolved in the test solution. Small amounts of the solution are mixed with tin and magnesia chloride solution in low concentration (<1%). As shown in Fig. 11 both tests produce a positive result with a violet colour of gold purple.

The colour shade of gold purple depends on the size of the gold particles. The colours vary from orange to deep violet with rising diameter as can be seen in Fig. 12.

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[11] Khüny Blattgold, Augsburg, Gold alloy Au 93%, Ag 3.3%, Cu 2,6%, Zr 0,22%; Os 0,21%

[12] ARTAX 200, Bruker, Berlin

$Sn_2 + H_2O \rightarrow SnO_2 + 4H \rightarrow +2e$

[13] $Au3^+ + 3e \Rightarrow Au$ Siehe: http://www.chymiatrie.de/index.php/component/content/article/144?706f731382de41afc74bf3318b9a3234=7f2e4fe64fca93bf6f1d15ae708536dd 11.02.2013

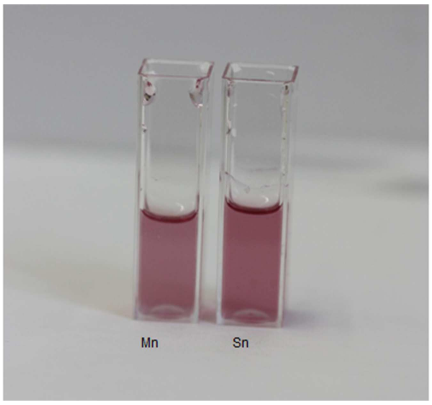

Fig.11

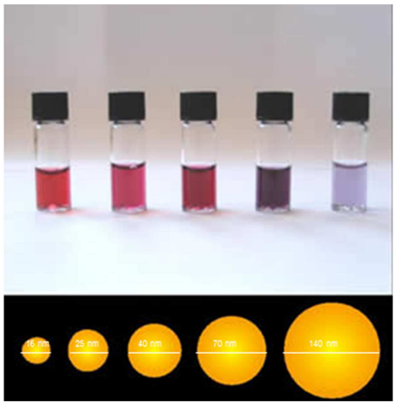

Fig. 12

Fig. 11: Gold purple as a reaction product of gold chloride with magnesia chloride (left) and tin chloride (right).
Fig. 12: Relation between grain size of the nano gold and the colour

It seemed obvious that gold of Cassius was not only used as a synthetically produced pigment but occurred naturally on marble surfaces in the course of a long-lasting corrosion process. This had to be triggered by magnesia or tin which are trace elements in the marble (Fig. 13).

The table shows trace elements of different kinds of marble. All marble samples contain magnesia and tin in various concentrations. So if the humidity or wetness on the marble is high enough, tin or/and magnesia can be dissociated and triggers the production of nano gold.

Gold purple on marble

To test the reaction of dissolved gold on marble a sample of marble of Paros is used[14]. The marble contains tin and magnesia naturally. However, for a better visualisation a drop of low concentrated magnesia chloride solution is placed onto the marble. After application of a drop of gold chloride the violet colour of gold purple becomes visible. The sample clearly shows the relationship between intensity of the colour and the concentration of magnesia. The drop of magnesia chloride was spread via capillary forces (similar to thin layer chromatography on paper). The magnesia concentration in the centre was much higher than in the outer circles. Accordingly, the shade of the Gold of Cassius was more intense in the centre and lighter in the outer circles (Fig. 14).

[14] A similar test was described by F. Wöhler: Berzelius, Jacob, Jahres-Bericht über die Fortschritte der physikalischen Wissenschaften, übersetzt aus dem schwedischen von F. Wöhler, Tübingen 1833, S. 114-115

Trace elements in marble

Element	Paros	Thassos	Mamara
Ca	116386	59920	91874
Mg	148	22	193
Fe	21	94	469
Zn	55	297	443
Sr	1463	451	1182
Sn	462	244	361

Unit: cts/sec.

Fig. 13: Trace Elements in different marbles

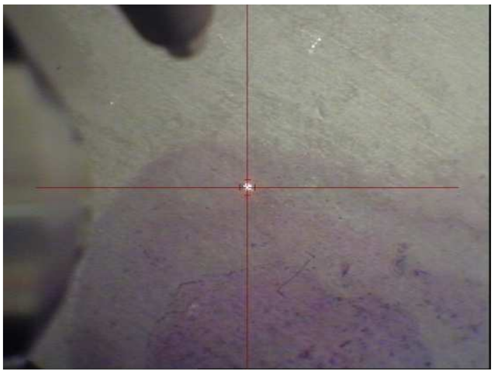

Fig. 14: Gold purple on marble

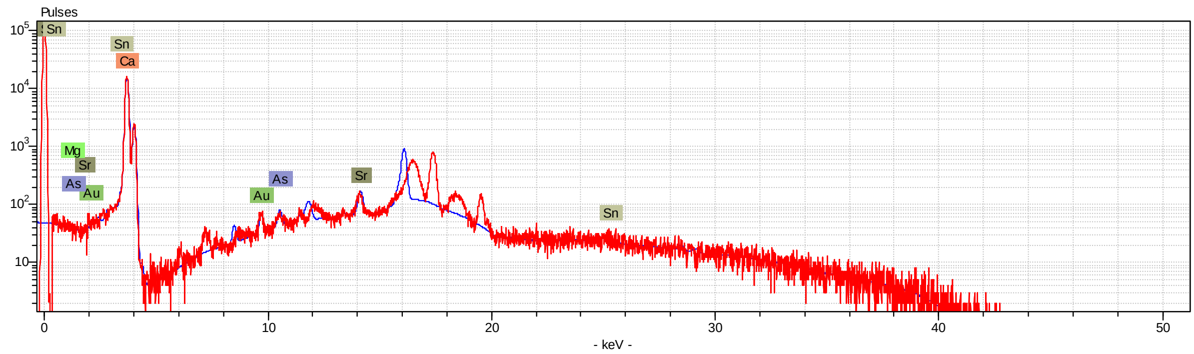

Fig.15: XRF-Spectra of gold purple on marble (Fig.14). The net count rate of 606 cts/sec is very low in the relation of the colour effect of the gold purple.

A third test is made on ivory. Ivory contains magnesia as a natural mineral at a concentration of ca. 2.1%, which is three times higher than in human dentine[15]. As shown in Fig. 16, all samples of dissolved gold (gold with NaCl, gold chloride from aqua regia, either a100% solution or solutions of lesser concentration) show colours of reduced gold. The various colours correspond to the different particle sizes of the nano gold.

[15] Fischer, F.G.; Bohn, H.: Zusammensetzung des Elfenbeins, in: Biological Chemistry, Bd. 302/1955, P. 283

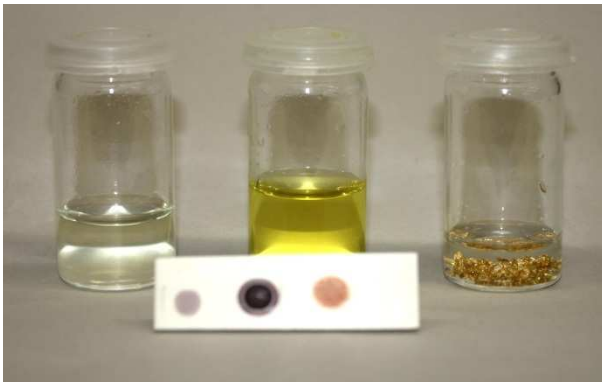

Fig. 16: Nano gold on ivory: very low concentrated dissolution of gold chloride, concentrated dissolution of gold chloride, gold flakes in sodium chloride. The colour depends on the different concentration of the dissolved gold.

Seen with the naked eye the purple on the Copenhagen Artemis is obviously very similar to the one on the marble sample (Fig. 17).

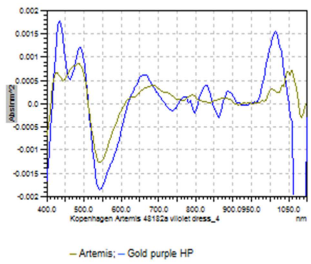

Fig. 17

Fig. 18

Fig. 17: Visual comparison of the violet of the Artemis of Copenhagen with the reconstructed gold purple on marble. Fig. 18: UV-VIS-spectra of the violet of the Artemis and the reconstructed gold purple on marble.

The XRF diagram (Fig. 15) shows that there is only a very low concentration of gold in the purple of the sample. On the one hand this means that the strong colour effect is caused by only small traces of gold. On the other hand it explains why the gold traces can be hard to detect using XRF.

In order to proof that gold corrosion can produce the same colour effect on ancient marbles as on the sample the UV-VIS-spectra of the purple on the Artemis and on the sample were compared. Both spectra show a high similarity leading to the conclusion that gold corrosion can be the cause of a purple colour effect on marble surfaces (Fig. 17, 18).

Conclusion

As shown, traces of a violet colour on marble can be caused by the corrosion of gold in combination with different trace elements contained in the marble. The gold corrosion is a long term, but very simple process taking place under conditions naturally to be found in underground storage. Depositions near the sea side will further the corrosion process.

A non-destructive proof of nano gold on marble is difficult because of the size and concentration of the colour producing particles. UV-VIS-spectroscopy delivers a clear spectrum of a quantum-size-effect which is different from other material spectra. It is therefore possible to identify nano gold such as the purple of Cassius. Mobile RAMAN-spectroscopy[16] show a specific peak for nano gold, but it is quite possible to damage the sample by the excitation laser.

Photos:
Fig. 1; 2; 6: Jan Stubbe Østergaard, Ny Carlsbeg Glyptotek, Copenhagen
Fig. 3; 4: Vinzenz Brinkmann, Liebieghaus, Frankfurt
Fig. 12: www.webexhibits.org/causesofcolor/9/html 28.02.2013
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