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# Aging of the paint palette of Valerio Castello (1624–1659) in different paintings of the same age (1650–1655)

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**Abstract** It is well known, from ancient Egypt, that some pigments and colourants can change with time for light effect or chemical attack. *Cennino Cennini* in the fifteenth century in his book "Il libro dell'arte o trattato della pittura" describes the use of many pigments and their degradation. He was aware of the problems and was able to suggest the answers in the use of pigments on several supports, but he could not understand the physical–chemical reason of the alteration processes. In this study, we point out the aging effects in seven paintings, practically of the same period (1650–1655). We considered in particular green, white and blue pigments of the palette of Valerio Castello. About 150 spots were selected on works painted on four different supports, canvas, wood panel, copper and slate. For each point, several determinations were carried on the pigments and decomposition products, aiming to determine the state of conservation of the paintings, the nature of the pigments, their alteration and if the support can affect the kinetics of degradation.

**Keywords** Painting · Pigments · Alteration · Thermodynamic stability

## Introduction

An exposition of paintings of Valerio Castello took place in the year 2008 at the *Palazzo Reale* in Genoa, Italy [1]. At that time we carried out our study. The works of art considered were:

1. *Ratto di Proserpina*, oil on canvas, early work (ca. 1650).
2. *Ratto di Proserpina*, oil on canvas (1654–1655).
3. *Ratto di Elena* (or Ecuba), oil on canvas (ca. 1654).
4. *Madonna con Bambino e Santi Antonio e Martino*, oil on wood panels (ca. 1650).
5. *S. Francesco riceve le stimmate*, oil on copper support (1653).
6. *S. Chiara in adorazione del SS. Sacramento*, oil on copper support (1653).
7. *Madonna con Bambino e S. Luca*, oil on slate (1655).

## Experimental section

Our study was focused initially on the recognition of the painter's palette, the technique of preparation and previous restorations.

For this purpose, we used non-destructive methods of investigation, such as X-ray fluorescence and UV fluorescence, "visible fluorescence generated by ultraviolet excitation" and reflection spectrophotometry in visible light.

### X-ray fluorescence spectrometry

Elemental analysis was performed by using a Lithos 3000 portable equipment and an apposite Lithos program from Assing to elaborate the data. It consists of a molybdenum tube, a zirconium filter and a semiconductor silicon detector cooled by Peltier effect. Spectra were recorded with a collection time from 120 to 200 s, the current tube was 300 mA and the voltage was 25 kV.

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### Reflection spectrophotometry by visible light

Colour measurements have been performed on homogeneous spot areas of about 3 mm in diameter by using a Minolta CM-2600 portable spectrophotometer provided with a Xenon lamp to pulsate the light on sample surface and with an integrative sphere inside of the apparatus. The light is reflected by the pigment with d/8° geometry. It is captured by a silicon (Li) photodiode that permits to obtain the spectrum included between 360 and 740 nm with an interval of 10 nm. The colour coordinates are based on CIEL*a*b* system using an illuminant D65 with an observer angle of 10°. In this system L* is correlated with colour lightness while a* and b* are the coordinates of chromaticity. The coordinate $+a^*$ and $-a^*$ indicate red and green values while $+b$ and $-b$, respectively, indicate the yellow and blue values.

The spectra were compared with those of a data bank collected in our laboratories.

Some areas, considered representative for the analysis, were chosen to collect micro-samples in order to get information on the painting layers and preparative technique.

### Investigated areas

The analysis spots were chosen on the basis of their colours in different paintings. As an example, the work, *Ratto di Proserpina*, an early Valerio Castello's painting, made on canvas, is reported in Fig. 1. The numbers indicate the investigated areas. The results we obtained for each painting were compared between them. As already remarked, the works were painted on different supports and by different techniques in a period of time ranging from about 1650–1655.

**Fig. 1** *Ratto di Proserpina*, ca. 1650, oil on canvas, 148 × 217 cm, Genova, Museo di Palazzo Reale

## Results and discussion

The inorganic pigments used in the examined paintings by Valerio Castello could be identified by means of the principal characteristic elements, by observing the behaviour under UV radiation and by comparing the reflection spectra in the visible light. The results can be summarised on the basis of the different colours.

### White pigment

The lead white ($2PbCO_3 \cdot Pb(OH)_2$) was used as white pigment and in mixture with other colours and in the filling layer [2, 3].

### Red pigments

In these paintings, the hue range of red pigments varies from orange to dark-red. The red pigments were cinnabar, $\alpha$-HgS [4], red ochre ($Fe_2O_3$) [5], and lakes. In some cases red tonalities were obtained by appropriate mixtures of these pigments.

### Blue pigments

Natural Ultramarine (sodium silico-aluminate containing sodium sulphide and, as contaminants pyrite and carbonates) [6], azurite ($2CuCO_3 \cdot Cu(OH)_2$) [7] and cobalt smalt (potassic glass containing CoO, and sometimes, as contaminants, As and Bi oxides) [8].

### Brown pigments

*Terra d'ombra* [5] containing iron and manganese oxides.

### Green pigments

Besides green earth [9], Valerio Castello used copper resinate [10], in all the examined paintings.

### Thermodynamic considerations

Initially, we started our study evaluating the thermodynamic stability both of some pigments—namely azurite, cobalt smalt, white lead and copper resinate—that appeared in some cases altered, both of alteration products detected.

The effects of various factors on the transformation and kinetics of transformation of some of these pigments, or the polymerization reactions of binders are subject of different studies, but rarely have been studied thoroughly in terms of thermodynamic and kinetic laws.

With the present study, we have highlighted specially three critical points of Valerio Castello, related to technical and pictorial use of some components:

1. The use of a green copper-based, the copper resinate, which easily undergoes changes more or less deeply due to direct illumination [10].
2. Cobalt smalt: its use in contact with drying oils causes a dual effect of alteration, a yellowing of the binding media and a discoloration of the blue glass, with an overall effect of chromaticity loss [8].
3. Lead white may be altered in two different ways: the presence of sulphides or hydrogen sulphide, as air pollutant [11]; produces a darkening effect due to lead sulphide formation; the oxidation of lead from bivalent to tetravalent, forming brown-black lead dioxide. The reactions are as follow:

$$2\,PbCO_3 \cdot Pb(OH)_2 + 3H_2S \rightarrow 3\,PbS + 2CO_2 + 4H_2O$$

$$2\,PbCO_3 \cdot Pb(OH)_2 + 2O_2 \rightarrow 3\,PbO_2 + 2CO_2 + 2H_2O$$

Besides these two phenomena, known in the literature, but not clarified in their twofold aspect of kinetic and thermodynamic stability, other pigments, among those most used by Valerio Castello, are susceptible to structural alterations and colour; for example the azurite, that, depending on the media of painting and environmental conservation, can easily give changes to the green colour; cinnabar in its form $\alpha$-HgS, red, may present darkening phenomena linked to transformation in solid state form $\beta$, metacinnabar [12, 13].

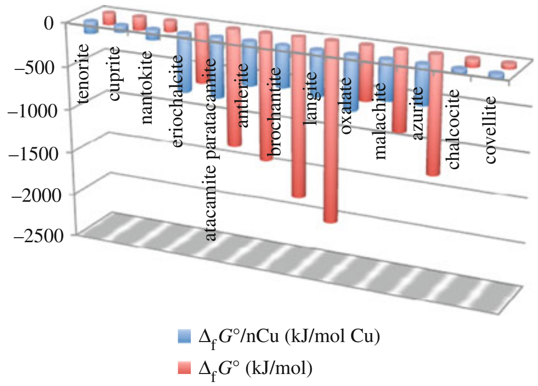

**Fig. 2** Graphical presentation of the thermodynamic stability of some copper compounds

In this study, we investigated the main thermodynamic aspects of processes to obtain a direct comparison of stability for some of the compounds of alteration and copper alloys, as well as for copper-based pigments such as malachite, azurite, copper acetate, copper resinate, etc. We have considered the reactions of formation for the individual compounds, referred to a number of copper units. Reactions of formation were then written as in Table 1.

As we can see, from the Table 1 and from the plot of Fig. 2, the major stability is to be ascribed to atacamite (and paratacamite) and eriochalcite, that are hydrossi-chloride and chloride of copper, followed by different sulphates and oxalate. The hydrossi-carbonates as malachite and azurite are thermodynamically less stable than these other categories of compounds (see last column of Table 1). The entropy factor, linked to the complexity of the molecule, plays a very important role in stabilizing these compounds. But we have always to consider that these stability values are evaluated referred to standard

**Table 1** Thermodynamic data for some Cu compounds [14]

| Standard reaction of formation 298.15 K, 0.1 MPa | Mineral | Colour | $\Delta_f G°$/ kJ mol$^{-1}$ | $\Delta_f G°$/nCu/ kJ mol Cu$^{-1}$ |
|---|---|---|---|---|
| $Cu + 1/2O_2 \rightarrow CuO$ | Tenorite | Black | −129.7 | −129.7 |
| $2Cu + 1/2O_2 \rightarrow Cu_2O$ | Cuprite | Red | −146.0 | −73.0 |
| $Cu + 1/2Cl_2 \rightarrow CuCl$ | Nantokite | Green | −119.86 | −119.86 |
| $Cu + Cl_2 + 2H_2O \rightarrow CuCl_2{\cdot}2H_2O$ | Eriochalcite | Greenish blue | −655.9 | −655.9 |
| $2Cu + 1/2Cl_2 + 3/2H_2 + 3/2O_2 \rightarrow CuCl(OH)Cu(OH)_2$ | Atacamite paratacamite | Bright to dark green | −1339.72 | −669.86 |
| $3Cu + 1/8S_8 + 2H_2 + 4O_2 \rightarrow CuSO_4{\cdot}2Cu(OH)_2$ | Antlerite | Blackish to light green | −1446.6 | −482.2 |
| $4Cu + 1/8S_8 + 2H_2 + 4O_2 \rightarrow CuSO_4{\cdot}3Cu(OH)_2$ | Brochantite | Blackish to pale green | −1817.7 | −454.4 |
| $4Cu + 1/8S_8 + 2H_2 + 4O_2 + H_2O \rightarrow CuSO_4{\cdot}3Cu(OH)_2{\cdot}H_2O$ | Langite | Bluish green | −2044.0 | −511.0 |
| $Cu + 2C + 2O_2 \rightarrow CuC_2O_4$ | Oxalate | Green | −608.7 | −608.7 |
| $2Cu + C + 5/2O_2 + H_2 \rightarrow CuCO_3{\cdot}Cu(OH)_2$ | Malachite | Green | −893.6 | −446.8 |
| $3Cu + 2C + 2O_2 + H_2 \rightarrow 2CuCO_3{\cdot}Cu(OH)_2$ | Azurite | Blue | −1315.5 | −438.5 |
| $2Cu + 1/8S_8 \rightarrow Cu_2S$ | Chalcocite | Black | −86.2 | −43.1 |
| $Cu + 1/8S_8 \rightarrow CuS$ | Covellite | Indigo-blue | −53.6 | −53.6 |

The above data are presented in Fig. 2 in graphical form to get a better view of comparing thermodynamic stability of the different compounds

**Table 2** Thermodynamic data for some Pb compounds [14]

| Standard reaction of formation 298.15 K, 0.1 MPa | Mineral | Colour | $\Delta_f G^o$/kJ mol$^{-1}$ | $\Delta_f G^o$/nPb/kJ mol Pb$^{-1}$ |
|---|---|---|---|---|
| $Pb + 1/2O_2 \rightarrow PbO$ | Litharge | Yellow | −187.9 | −187.9 |
| $3Pb + 2O_2 \rightarrow Pb_3O_4$ | Minium | Orange-red | −601.2 | −200.4 |
| $Pb + O_2 \rightarrow PbO_2$ | Lead dioxide | Brown-black | −217.4 | −217.4 |
| $3Pb + 2C + 2O_2 + H_2 \rightarrow 2PbCO_3{\cdot}Pb(OH)_2$ | Hydrocerussite | White | −1699.8 | −566.6 |
| $Pb + C + 3/2O_2 \rightarrow PbCO_3$ | Cerussite | White | −1315.5 | −1315.5 |
| $Pb + 1/8S_8 \rightarrow PbS$ | Galena | Black | −98.7 | −98.7 |

These data are presented in the Fig. 3, in graphical form

conditions; changing the concentrations of pollutants and the physical variables temperature and pressure, for example, we can easily stabilize one compound or another as shown by the graphics of Pourbaix [15].

In order to understand the processes of alteration of the pigments we have to consider all the factors involved, such as air pollution, lighting (the free radicals action is surely of great relief in pigment alteration), temperature, humidity, presence of catalysts (e.g. lead or other heavy metals in atmospheric dust) [16]. Therefore, the thermodynamic stability factor should be seen in light of all the reactions involved and kinetic factors that govern them. Let we consider, for example, the alteration of azurite in malachite in presence of alkali: depending on the pollutants, instead of the copper hydrossi-carbonate, we get the formation of various compounds as copper oxalate or oxy-chlorides [17], with the consequent discoloration.

Similar considerations can be carried on as it regards the compounds of lead (Table 2).

From the above data, we can derive that the major relative stability regards the carbonates of lead. However, it is well known that in the presence of other, less stable sulphides, the conversion reaction of lead white, for example, occurs very easily to lead sulphide, as already remarked by [13]. Thermodynamically this is a consequence of the formation of some very stable compounds as water or carbon dioxide. Moreover, the equilibrium can move towards the reaction products, due to the formation of these last volatile compounds.

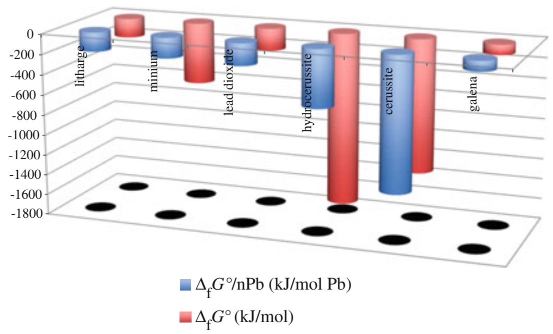

**Fig. 3** Graphical presentation of the thermodynamic stability of some lead compounds

## Conclusions

We have identified by non-destructive and micro-destructive methods the colour palette used by Valerio Castello in his paintings pointing out the use, besides many precious pigments, of two artificial pigments cobalt smalt and copper resinate. They presented alterations in all the works analyzed independently on the support used. Such alteration seems linked mainly to the purity of compound employed as pigment than to environmental factors.

In order to understand these phenomena, we evaluated thermodynamic data that represent the stability of the phases. This is the first step that can give reason of alteration effects. The second step will be the presence of particular substances in the painting, for example arsenic in the smalt, residue of the smelting extraction of cobalt from its minerals or of the fabrication process of glass itself. To obtain this information we are carrying out experiments on different cobalt smalt samples containing various well known amounts of arsenic, in contact with different kinds of medium. The pigment, laid on a support of alumina in thin layer, is put in a climatic room in order to observe the colour alteration, via spectrophotometric measurements, in different environmental conditions. We are so aimed to determine the role of the presence of arsenic in the discoloration of the paintings containing cobalt smalt.

As it regards copper resinate many efforts have been made in order to understand its darkening, which become more evident in the sections of painting exposed to the light. Probably a large number of factors can induce this discoloration, as the formation of more stable black copper oxide and the presence of free acids residues of the preparation reactions.

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