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# The *al*chemy of red mercury sulphide: The production of vermilion for medieval art

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## ABSTRACT

Vermilion red, mercury sulphide ($\alpha$-HgS), was one of the most important reds in art and its use as a pigment dates back to Antiquity. In medieval Europe, it could be mined as cinnabar, or produced as vermilion by heating mercury with sulphur. This work aims to study the production of synthetic vermilion as a medieval pigment and to confirm which was the source (mineral or artificial) of the reds used in Portuguese medieval illuminations. The production of synthetic vermilion was based on the process described in the Judaeo-Portuguese medieval treatise "The book on how to make colours", using materials and technologies as close as possible to the medieval ones. The reaction mechanism was studied by following the heating process by X-ray diffraction, and it was possible to conclude that the transformation from black cubic $\beta$-HgS into red hexagonal $\alpha$-HgS is a solid-state phase transition, occurring at 235 °C. This result is contrary to what published in technical art literature, in which this process is described as a sublimation. Moreover, Scanning Electron Microscopy evidenced a sinterization effect on the artificial vermilion, not found in medieval original samples nor in paints prepared with mineral cinnabar from Almadén (Spain). Red mercury sulphide, natural and synthetic, was then prepared as a parchment-glue paint and compared to proteinaceous red paints from 12th–13th century miniatures produced in important medieval monasteries, previously fully characterized by a multi-analytical approach ($\mu$-Energy dispersive X-ray fluorescence, $\mu$-Fourier Transform Infrared Spectroscopy, Raman microscopy). A comparative Electron probe microanalysis of the red paints point to a mineral provenance for medieval vermilion found in Portuguese illuminations.

## 1. Introduction

Red mercury sulphide was considered "the red" of artists' paints. Its use dates back to Antiquity, and it was the inorganic red *par excellence* of Medieval Illumination. It has been identified in all sorts of masterpieces, in Egyptian and Roman wall-paintings, Chinese lacquer objects attributed to the 1st millennium B.C., altarpieces, canvas paintings, etc [1,2]. In medieval Europe, it could have been mined or artificially produced. As an artist pigment, when obtained by synthesis, red $\alpha$-HgS is usually named vermilion[1] (to distinguish it from the mineral cinnabar). Cinnabar could be mined in China, Iran and Ethiopia, but the product coming from Almadén in Spain was considered of superior quality [1–5]. Pliny (1st century) refers its economic value, which was the reason why its purification was carried out in Rome, where *circa* of two thousand pounds (~900 kg) of cinnabar were carried *per year* [3,5]. Typically, cinnabar originates in veins associated with volcanic activity and hot spring action, often replacing quartz and other sulphide minerals [1,6]. It is formed with impurities as stibnite ($Sb_2S_3$), pyrite ($FeS_2$), marcasite ($FeS_2$), gypsum ($CaSO_4$), quartz ($SiO_2$), calcite ($CaCO_3$), aluminosilicate minerals and other clay minerals [1,6]. In Almadén, it is commonly found as veins in quartzite [6].

### 1.1. Configuration of HgS

$\alpha$-HgS, with an octahedral coordination, presents a hexagonal $P3_121$ structure [7,10]. The $(HgS)_x$ chains are ordered so that each S

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[1] Cinnabar was consistently referred to as *minium* in Roman literature (currently, the common name for red lead, $Pb_3O_4$), which caused numerous misunderstandings throughout the ages.[5]

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atom is bind to Hg with three different Hg–S distances: two S atoms at 2.36 Å as part of chains that define the structure, two S atoms at 3.10 Å and two S atoms at 3.30 Å $\beta$-HgS has a $F43m$, zincblende structure with a tetrahedral coordination, leading to a cubic phase system (four S atoms co-ordinated to Hg with the same Hg–S distance of 2.53 Å) [7–10].

The basis for the understanding of the Hg–S system may be found in the equilibrium phase diagram described by Sharma and Chang in 1993 [11]; HgS exists in at least two crystalline modifications[2]: cinnabar ($\alpha$-HgS) and metacinnabar ($\beta$-HgS), eq. (1). Red $\alpha$-HgS is stable at lower and black $\beta$-HgS at higher temperatures (above 370 °C).

$$\beta - \mathrm{Hgs}\ \ (\mathrm{black}) \underset{\Delta'}{\overset{\Delta}{\rightleftarrows}} \alpha - \mathrm{Hgs}\ \ (\mathrm{red}) \quad \text{where } \Delta' > \Delta, \tag{1}$$

The reverse reaction, eq. (1) [8,12–14], and the “transformation temperature” has been reasonably identified with values that range from 386 °C [13] to 335 °C [8]; including values of 345 °C [8], 344 °C [14] and 377 °C [8]. Important to get insight into the complexity of the reaction depicted in eq. (1) is the contribution of Munir et al. in 1973 [8], by differential thermal analysis, these authors concluded that “the transformation of the red to black takes place with relative ease and is reproducible at temperature above the transformation temperature, but that the black to red transformation is exceedingly sluggish at temperatures below the transformation temperature, i.e., in the region where the red modification is stable”. Moreover, the authors describe an experiment[3] where metacinnabar was completely transformed in vermilion, within a few hours at 250 °C, but they were not able to determine the external(s) factor(s) responsible for this efficient transformation (it was neither pressure nor light).

More recently, Bell et al. studied the structural evolution of mercury sulphide precipitates by *in situ* high-temperature energy-dispersive X-ray powder diffraction (EDXRD) and characterize an unknown phase, designed as XHgS, that transforms to red HgS [15]. This intermediate was formed, in the temperature range 194–249 °C, from a “pseudocubic” metacinnabar phase.[4] The XHgS phase disappears and cinnabar develops at 269 °C, continuing to increase up to 374 °C [15].

### 1.2. Medieval vermilion

It is currently accepted that the know-how for vermilion’s production was brought into Europe by the Arabs who had already mentioned the reaction of sulphur with mercury to produce a red compound in the 8th–9th century [5]. The recipes for making vermilion, by heating mercury with sulphur, are frequent in medieval treatises [16–21]. In all the processes, vermilion is produced by what is commonly known as the *dry method*. Vermilion may also be produced by a *wet process*, which is much more easy than the *dry method* described in the medieval treatises aforementioned. With one exception, the procedures described in the treatises are often obscure, or incomplete or make use of a large excess of sulphur. The exception is *The book on how to make colours* where a stoichiometric proportion is recommended and detailed instructions are given [22]. This is the reason why we have selected this recipe as representative for the medieval production of vermilion. *The book on how to make colours* is the oldest known Judaeo-Portuguese treatise on the art of illumination, written in Portuguese, but using the Hebrew alphabet, of which the first version could date from the 14th century [23,24].

The Judaeo-Portuguese dry process starts with the production of black $\beta$-HgS that is then converted into red $\alpha$-HgS by heating, eq. (1). We have recently proposed that black $\beta$-HgS is a kinetic product that results from a complete grinding of S with Hg [5,25]. Taking into account what described by Munir et al. [8], one may anticipate that the second step, the direct reaction that leads to the formation of vermilion, will be complex and temperature control will be crucial as the kinetic barrier that must be overcome for the conversion of $\beta$- into $\alpha$-HgS requires a temperature similar to what is necessary to trigger the reverse reaction, eq. (1) [11].

The *wet process* also starts with black $\beta$-HgS, the kinetic product formed by the reaction of sulphur with mercury or mercury salts [5,13,15]. Contemporary reconstructions of the *wet process* evidenced that the complete conversion of metacinnabar to vermilion, requires strong basic media (e.g., NaOH 4M) and rather moderate temperature (e.g. 60 °C). The fact that such strong alkaline solutions were possibly not easily available in medieval Europe, restricts the medieval processes for producing vermilion to the *dry method*, in agreement to what described in medieval written sources [5,25]. According to Kopp [1], the *wet process* was discovered in 1687 by the German chemist Gottfried Schulz, who first converted black mercuric sulphide to vermilion by heating it in a solution of ammonium or potassium sulphide [1].

### 1.3. HgS in art

In this work, the *dry process* was accurately reproduced following the instructions of the medieval author, and XRD was used to characterize the phase transition profile of the solid-state reaction. SEM–EDS studies compared the pigment composition and morphology with original micro-samples from 12 to 13th manuscripts produced in the medieval monasteries of Lorvão, Santa Cruz de Coimbra and Santa Maria de Alcobaça[5] as well as with paints prepared with *wet process* vermilions and cinnabar from Almadén mines [26]. The selected original paint samples, have been previously fully characterized by EDXRF, microRaman and microFTIR, and are essentially made of red mercury sulphide in a proteinaceous binding media, usually a mixture of collagen with egg white [27–32].

## 2. Experimental

### 2.1. Methods

Unless otherwise specified, all reagents used were of analytical grade. Spectroscopic or equivalent grade solvents and Millipore filtered water were used.

#### 2.1.1. Metacinnabar synthesis

For both *wet* and *dry synthesis* metacinnabar was produced by thoroughly grinding an equimolar amount of sulphur and mercury on an agate mortar with an agate pestle. The process was completed when no mercury could be seen with the naked eye, which usually occurred after grinding the mixture for *circa* 1 h. Grinding sulphur with mercury revealed to be a crucial step, and

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[2] That may be described as polymorphs if the compounds stoichiometry is maintained.

[3] In these experiments they were heating samples of pressed wafer pellets instead of the powder.

[4] A black HgS that did not display a well defined crystalline cubic phase.

[5] St. Mamede of Lorvão, Holy Cross of Coimbra, St. Mary of Alcobaça.