MECHANISTIC AND COMPUTATIONAL STUDY OF CINNABAR PHASE TRANSFORMATION: APPLICATIONS AND IMPLICATIONS TO THE PRESERVATION OF THIS PIGMENT IN HISTORICAL PAINTING

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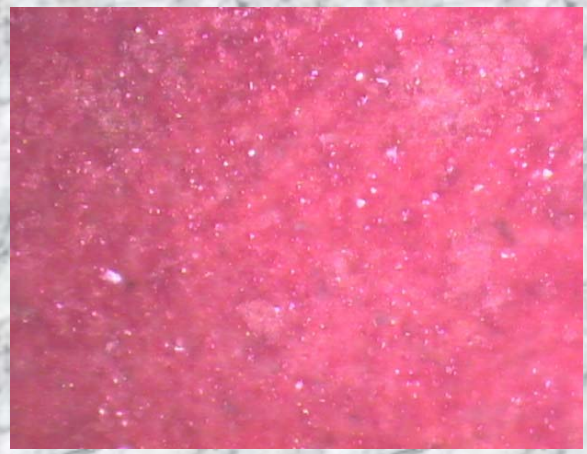
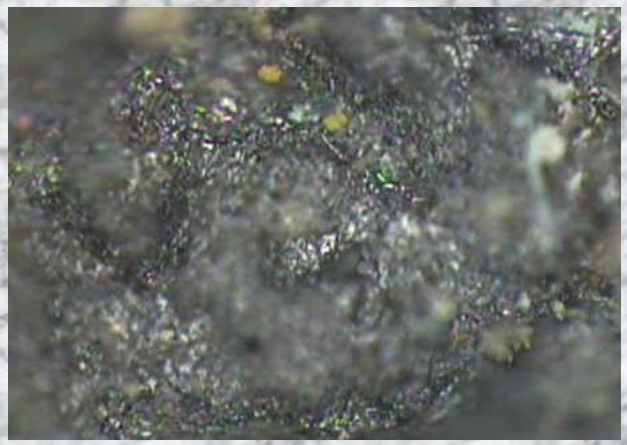
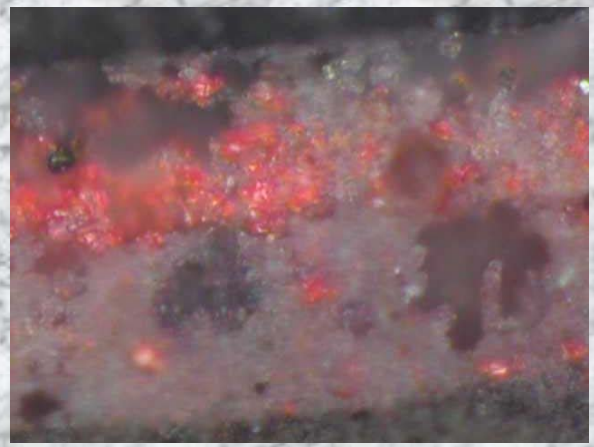
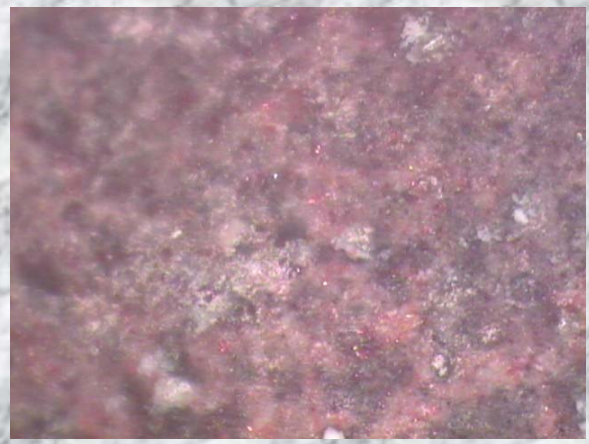
CINNABAR OR VERMILION IN ANTIQUITY

- **In general:**
  - **-What is cinnabar? Mercuric sulfide: α-HgS**
  - **-Terminology (cinnabar & minium)**
  - **-Origin (natural & synthetic)**
  - **-Use (pigment, ink, preservative, cosmetics, rituals)**
- **As a pigment**
  - **-Significance (socio-economic and artistic)**
  - **-Technology (extraction & application)**

What is the cinnabar problem?

The blackening!

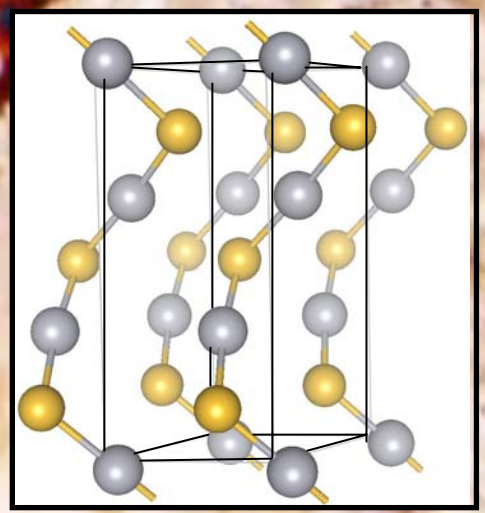


Structural models of HgS phases: cinnabar (left) and metacinnabar (right). The metacinnabar structure is given here in terms of a tripled cell (3C setting) of the conventional cubic structure (a=5.852 Å). The equivalent hexagonal cell has $a_H = a/\sqrt{2}$ and $c_H = a\sqrt{3}$.

α-HgS

β-HgS



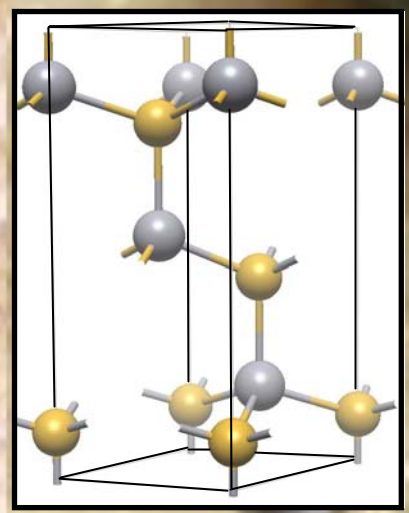
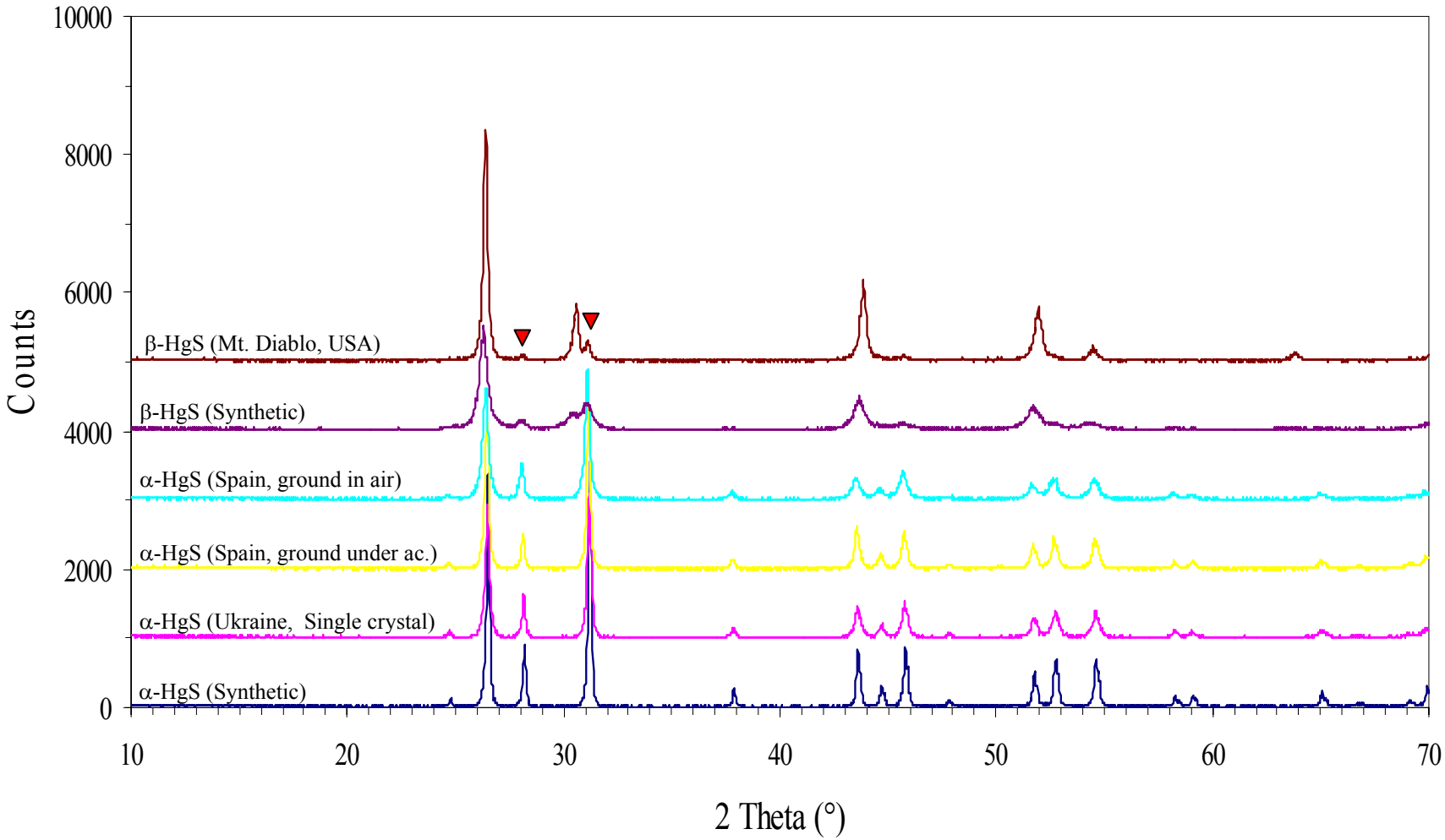


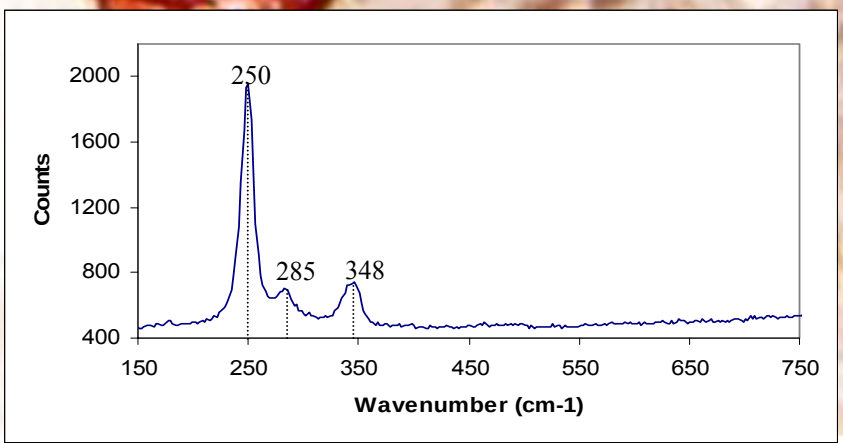
Table 1: List of raw samples studied with their origin, phase composition, and structural data obtained by XRD and cell refinement.

Sample	Origine	Description	System	Cell Parameters
Cinnabar 1 α-HgS	Synthetic	Pure red powder	Hexagonal S.G.: P3221	*a=4.147* *c=9.492*
Cinnabar 2 α-HgS	Nikitovka Mine Dombass, Ukrania	Pure red single crystals	Hexagonal S.G.: P3221	*a=4.149* *c=9.501*
Cinnabar 3 α-HgS	Al-Maden Mine, Spain	Polycrystalline ground under acetone; pure red	Hexagonal S.G.: P3221	*a=4.152* *c=9.502*
Cinnabar 3 α-HgS	Al-Maden Mine, Spain	Polycrystalline ground in air; dark brown	Hexagonal S.G.: P3221	*a=4.152* ***c=9.513***
Metacinnabar 1 β-HgS	Synthetic	Black powder (contains some cinnabar)	Cubic S.G. $F\bar{4}3m$	*a=5.853*
Metacinnabar 2 β-HgS	Mont Diablo Mine, CA, USA	Black polycrystalline	Cubic S.G.: $F\bar{4}3m$	*a=5.854*

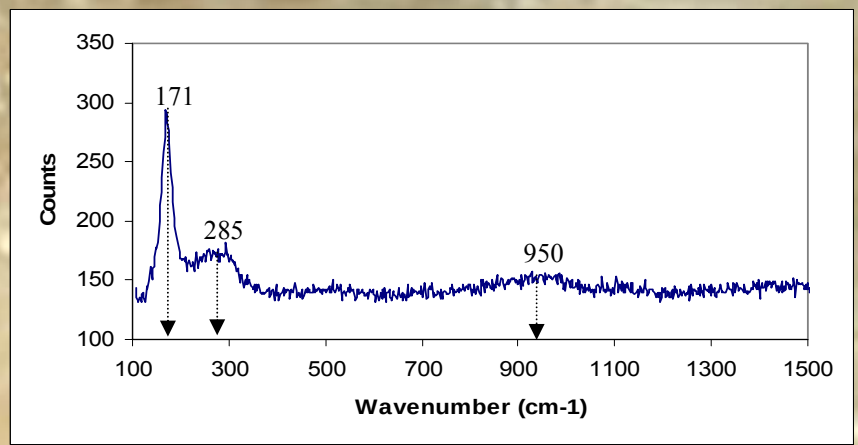
X-ray powder diffraction patterns for the the raw samples. While all cinnabar (α-HgS) samples are phase pure, both synthetic and natural metacinnabar (β- HgS) contain some cinnabar as phase impurity (reflections indicated with red triangles).



Raman spectrum obtained for cinnabar (α-HgS) single crystal from Ukrania using a green laser of λ=540 nm.

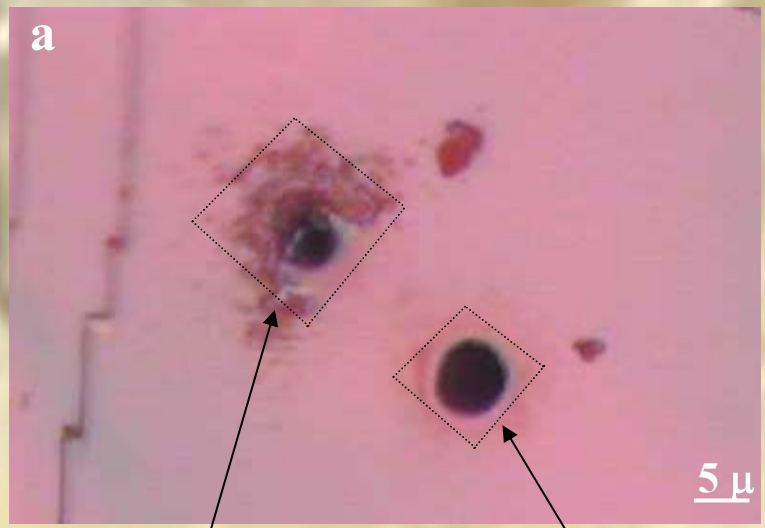


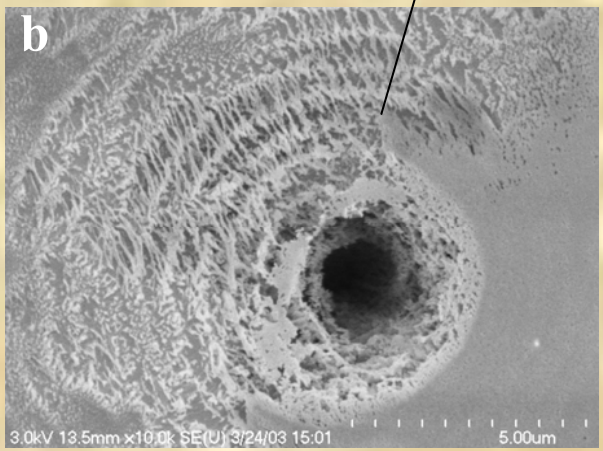
Raman spectrum obtained for metacinnabar (β-HgS) polycrystalline material from Mont Diablo, CA, USA using a green laser of λ=540 nm.

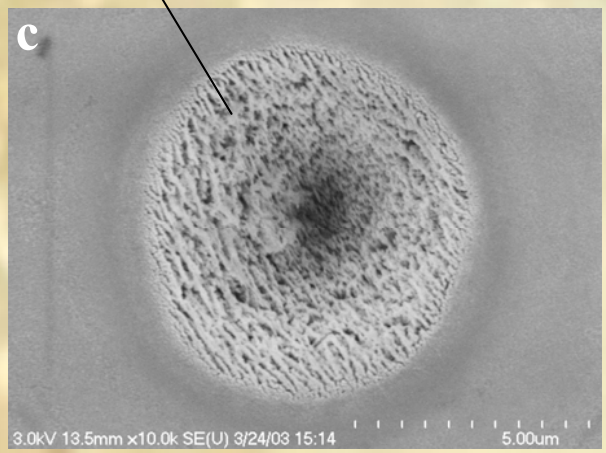


Blackening of cinnabar

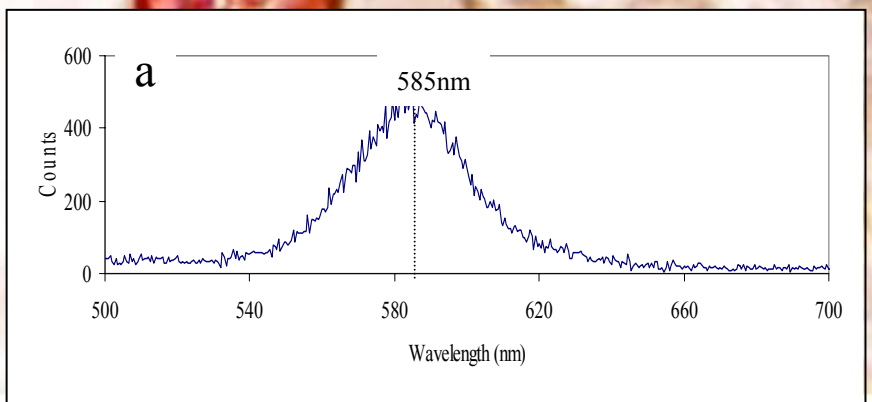
Effect of lasers and electrons

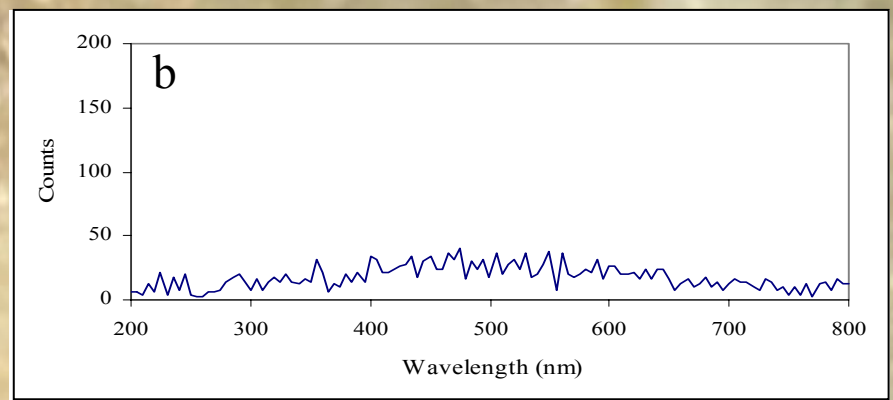






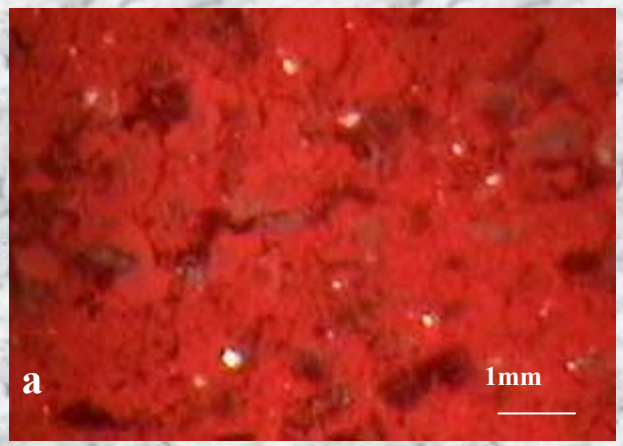
Cathodoluminescence spectra of (a) single crystal cinnabar from Ukraine, (b) polycrystalline metacinnabar from CA, USA.,

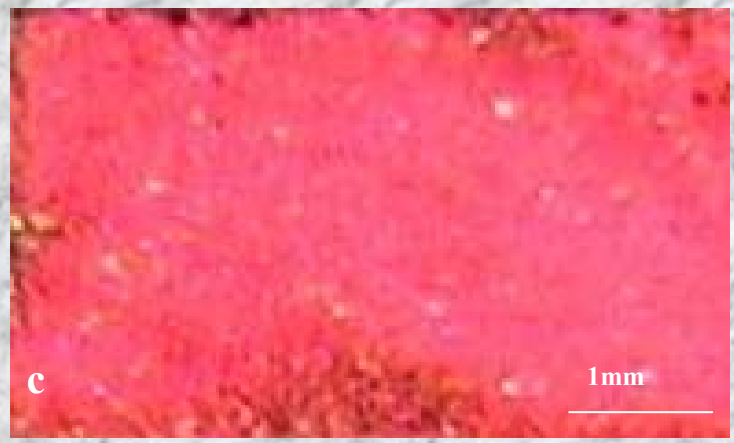


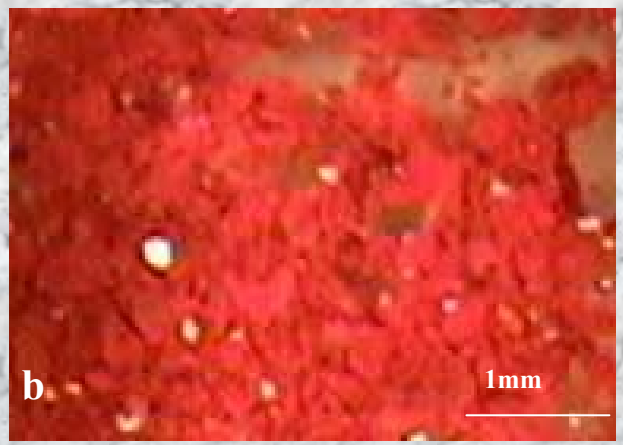


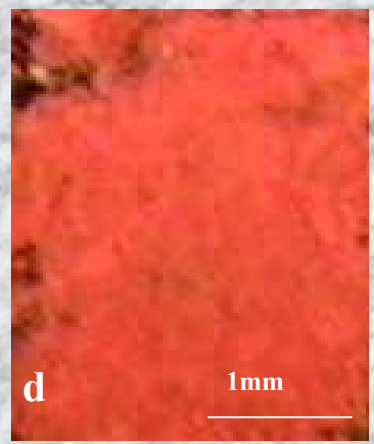
Effect of Grinding & heat treatment

(a) Single crystal cinnabar from Ukraine ground in air and (b) same sample after heat treatment at 100°C in air. Polycrystalline cinnabar from Spain, (c) ground under acetone, (d) ground in air, and (e) same sample in (d) after heat treatment at 100°C in air.

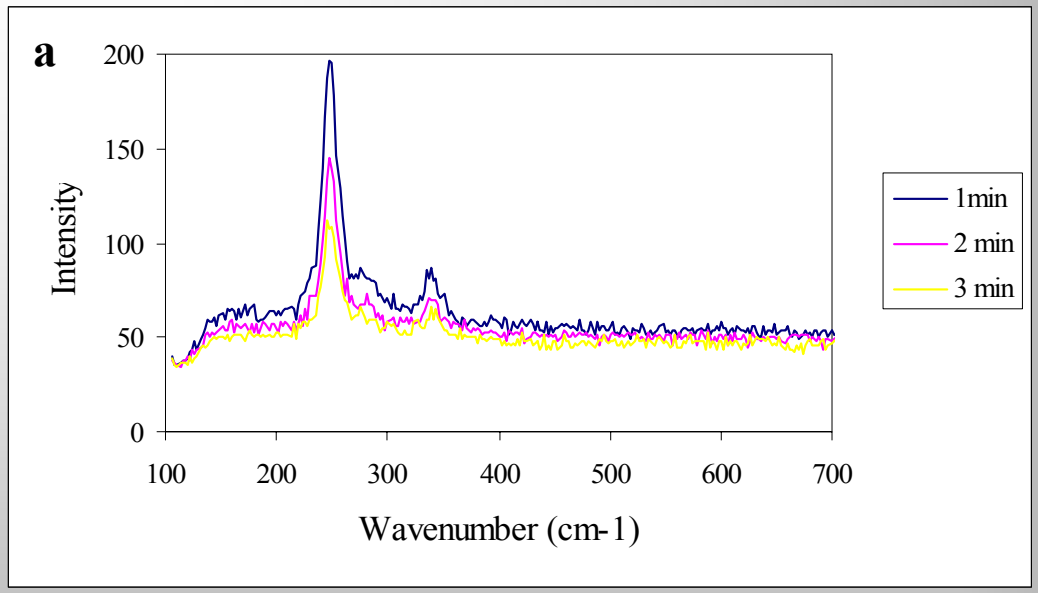




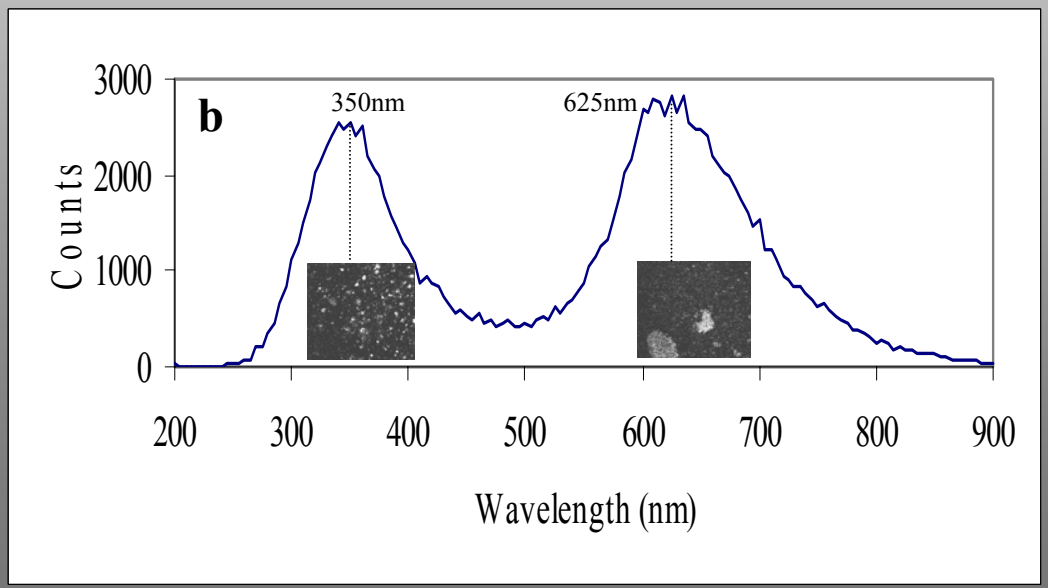




Raman & cathodoluminescencfe of blackened cinnabar

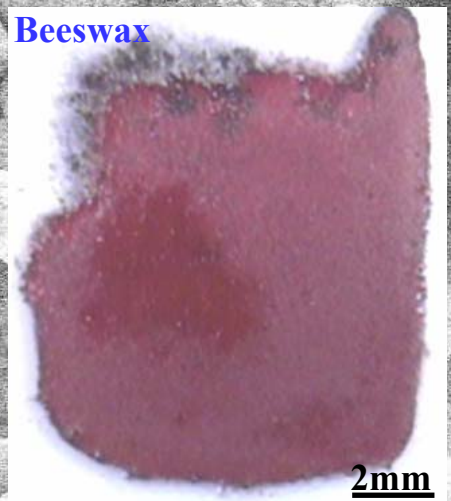


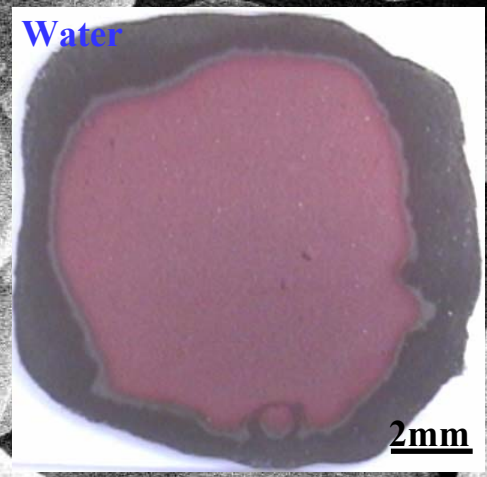
(a) Micro-Raman spectra of blackened cinnabar obtained by grinding cinnabar from Spain in air after 1, 2, and 3 minutes of exposure to the laser

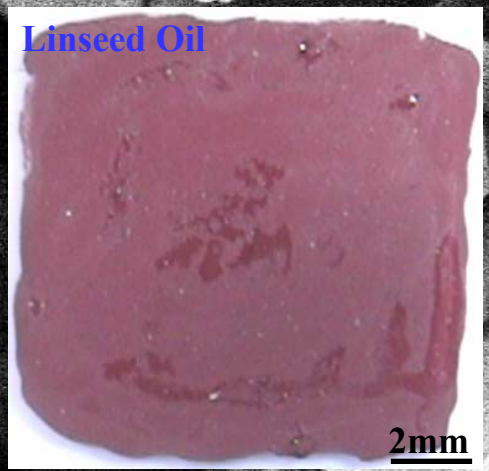


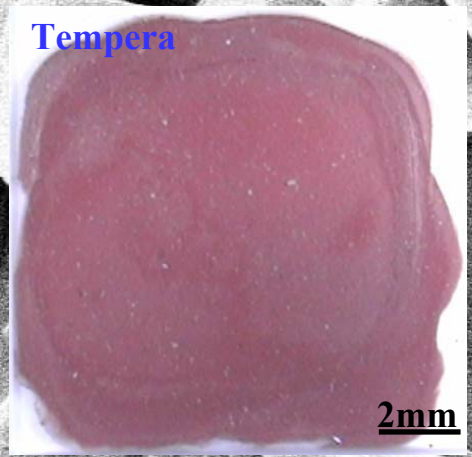
(b) cathodoluminescence spectrum of the same sample with CL images of the zones emitting in the UV (350nm) and in the red-orange (625nm).

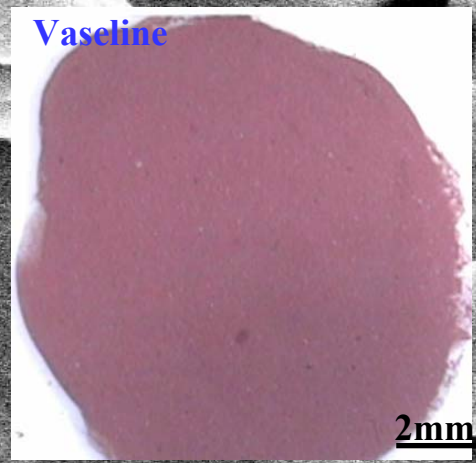
Effect of sunlight on the color of cinnabar paint films prepared with different media, exposed to direct Arizona sunlight for 8 months.





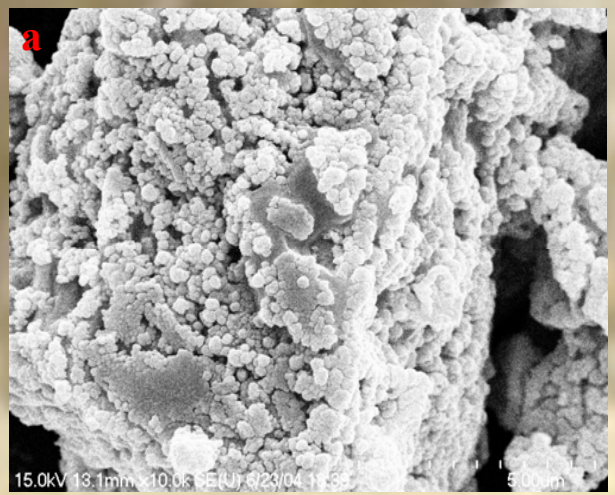


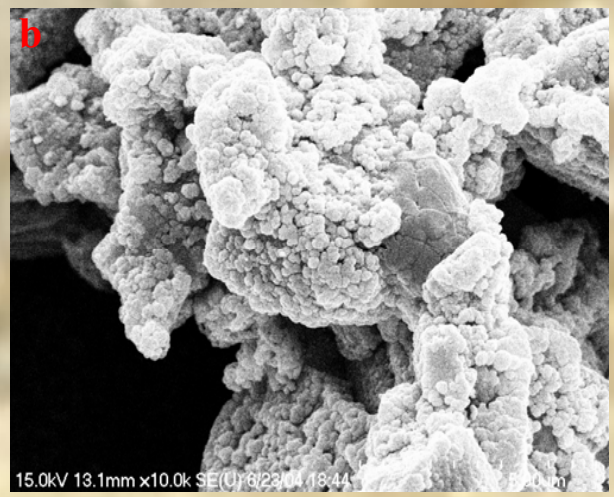


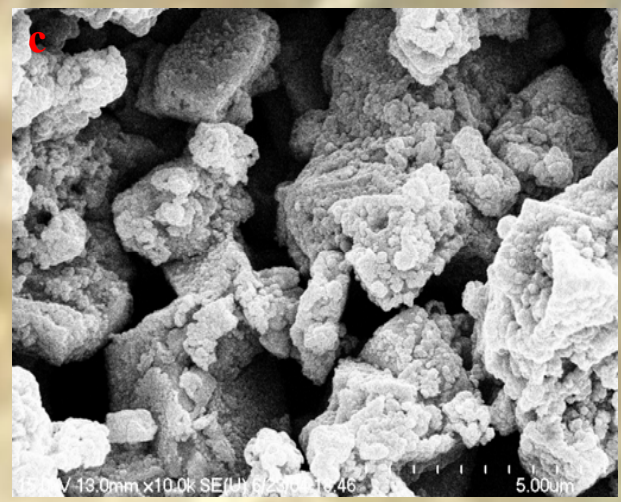


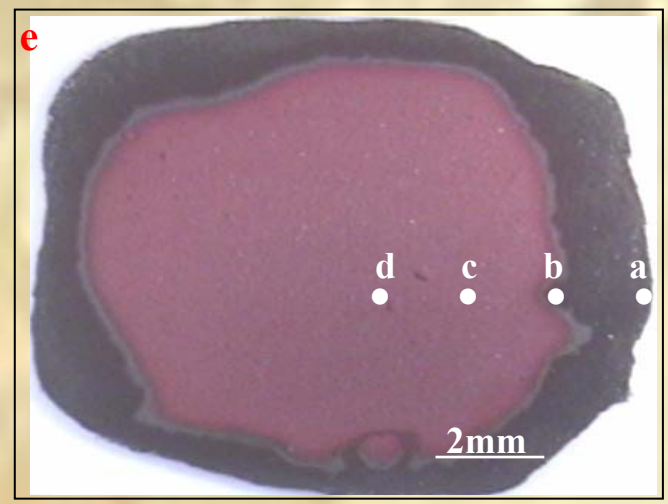
15.0kV 13.0mm x10.0k SE(U) 6/23/04 18:50 5.00um

Amorphization gradiant of cinnabar as a function of distance from the edge. Images a-d correspond to points a-d in image e. Pigment was prepared in water and exposed to Phoenix, Arizona sunlight for 8 months. Images a-d were obtained using a Hitachi 4700 Field Emission Scanning Electron Microscope (FESEM).









Comparison of XRD spectra of the red and black zones in the previous plate. The reflection given here is (104) of cinnabar. Note the shift of the d-spacing of this plane toward a higher value, which is closer to that of metacinnabar (2.92Å).

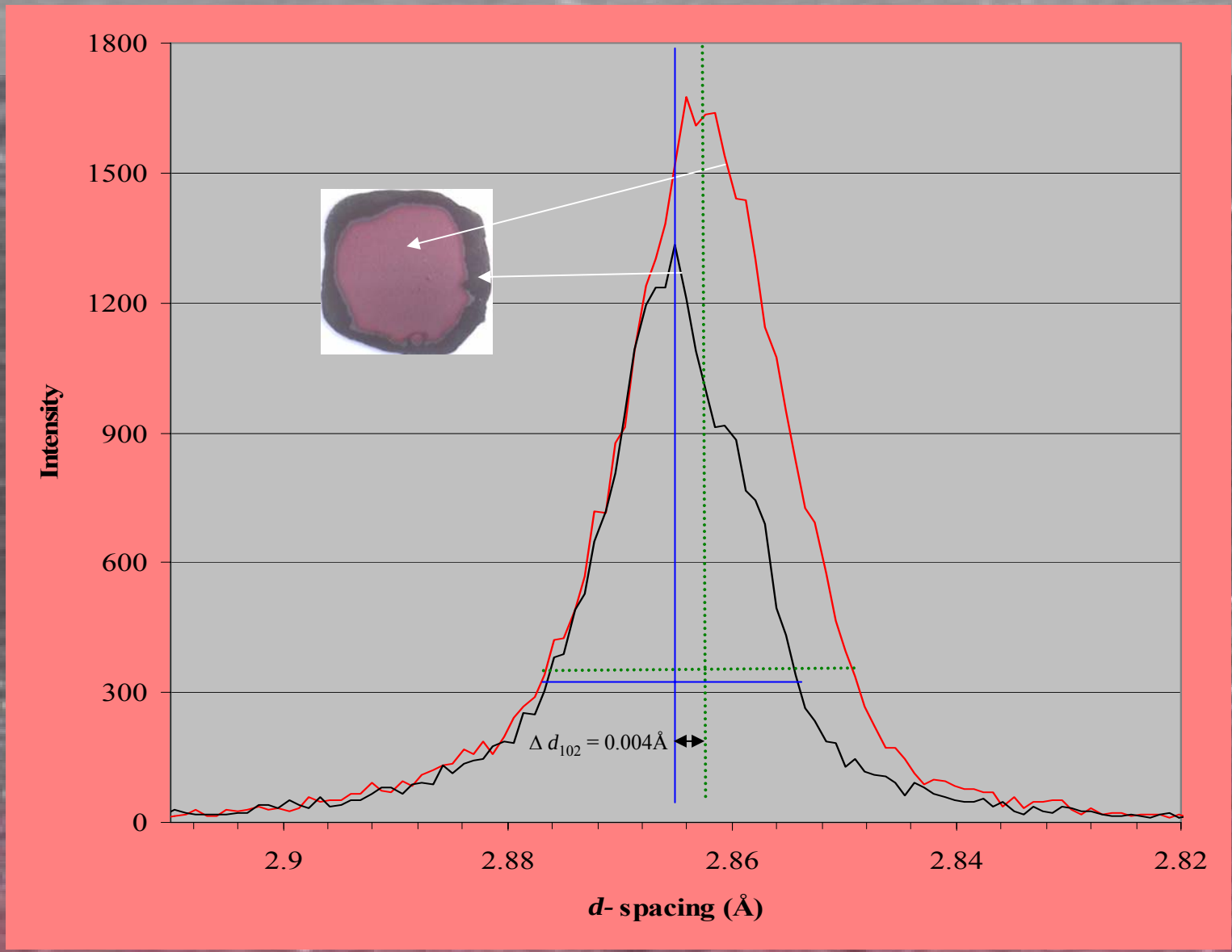


Table 2: Chemical composition (expressed in atomic %) of a black spot caused by irradiation with electrons (15KV, 10mA) as compared to that of a fresh zone.

	Fresh Zone	Irradiated Zone
Hg (Atomic %)	**45.80**	**50.83**
S (Atomic %)	**54.20**	**49.17**
Hg/S Ratio	**0.85**	**1.03**
% Sulfur Deficiency	0	**18.26**

CONCLUDING REMARKS

-Blackening of cinnabar is a physico-chemical & structural transformation process which is complex, but quite reversible.

-Several factors can induce the blackening of the pigment such as the radiation (electrons, lasers, sunlight) and by mechanical activation/amorphization.

-The blackening cannot be attributed to the formation of cubic metacinnabar, as very often speculated, but to an intermediate and amorphous phase. This was evidenced by the broadening of the XRD reflections, splitting of the band gap of the product, and by the SEM imaging.

-SEM images also show that the amorphous product forms a passivating layer around the cinnabar grains/crystals that may inhibit further transformation, and which is consistent with the observations made on historical samples.

-The red vermilion color can be restored by moderate thermal treatment of the blackened pigment in air. Further work is still required to validate this statement.