A STUDY OF CINNABAR BLACKENING: NEW APPROACH AND TREATMENT PERSPECTIVE

Vanessa Terrapon[1] and Hamdallah Béarat[2*]

[1]*Rue des Epouses 9, CH-1700 Fribourg, Switzerland,* vanessa.terrapon@gmail.com
[2] *School for Engineering of Matter, Transport & Energy, Arizona State University, Tempe, AZ 85287-6106, USA[1]*,hamdallah.bearat@asu.edu

ABSTRACT

Blackening of cinnabar or vermilion has always been a dilemma. The hexagonal mercury sulfide pigment, often of mineral origin, has an intense red color. For long, cinnabar has generated large interest among mural painters, artists, and alchemists in antiquity as well as nowadays conservation scientists and restorers, who are anxious to restore the color of paintings seriously affected by blackening of the pigment, often qualified as dramatic and irreversible. However, if particular attention has been given to the study of such phenomenon since the beginning of the 20th Century, conservation of this color still presents numerous difficulties. Light has for long time been considered the cause of the color change. The Romans recognized this color change and utilized the pigment for inside painting away from direct sun light. The principal factors to cause or accelerate this specific alteration are solar radiation, atmospheric agents and associated pollutants, relative humidity as well as soluble salts and organic compounds. Yet, no viable solution of preventive conservation at excavations or restoration of altered vermilion has been proposed. Lately, research has shown that blackening is associated with an amorphous phase, forming as a coating on the exposed grains, and not due to transformation of cinnabar into the black cubic sulfide phase. This study aims at isolating the factors responsible of blackening in order to evaluate the most significant effects on the preventive conservation of the pigment. In this perspective, artificial weathering (aging) experiments were carried out by exposing modern and archaeological samples to direct sun light, or in the shade, with distinct conditioning. All were covered with optical filters transmitting only certain frequencies of light spectrum to determine the wavelengths the most detrimental on the stability of pigment and which conditions mostly favor the alteration. Progress of alteration was monitored and analyzed prior and after irradiation, using scanning electron microscopy, energy dispersive spectroscopy, particle-induced X-ray emission spectroscopy, and colorimetric methods. Data obtained show that the different wavelengths transmitted have different effects on cinnabar. The chromatic change can be accelerated also by higher relative humidity and by certain atmospheric pollutants, which may induce formation of gypsum by sulfate attack of calcium-rich phases present. This study, while providing a better understanding of the mechanism of alteration process of pigment under external conditions, allows for a cost-effective method of preventive conservation during excavation wherever cinnabar is being used as pigment in wall paintings.

Keyworeds: Cinnabar blackening, amorphization, sunlight effect on cinnabar, wall painting, preventive conservation

*Corresponding author

INTRODUCTION

From immemorial time, people have had a taste for color. They have tried to find necessary pigments and techniques for parietal decoration, thus transmitting the testimony of their secular traditions. Amongst these pigments, cinnabar was used as prestigious pigment in different cultures. For instance, it was employed by Roman elite [1,2,3,4], especially in the Second Pompeian Style (1st Century BC) wall painting. Its associated alteration was already known in Antiquity [1,2,3]. Some of these frescoes, famous by the intensity and depth of their red color, were protected from alteration due to their burial conditions. As soon as they are uncovered, the paintings suffer from a fast darkening reaction, an effect which seems to be induced by solar irradiation and considered as irreversible [5-10]. For long, it has been claimed that the color change is due to transformation of red hexagonal cinnabar (α-HgS) into the black cubic metacinnabar (ß-HgS). However, the required temperature for cinnabar-metacinnabar phase change is above 300°C [11-15]. Moreover, since metacinnabar has never been detected in analyses [8,15,16], the crystallographic change (α to ß) cannot explain cinnabar color change observed at low temperatures. Since 1950, restoration treatments involved chemical dissolution of altered pigment [5,17] or mechanically scratching of blackened surface. Recently, laser cleaning of cinnabar-containing paintings has induced a surface blackening of the paint which can proceed to its decomposition, causing volatilization of both mercury and sulfur [15,18-20] .

Blackening process of cinnabar pigment is controlled by different factors. Exposure to direct sunlight coupled with the others factors, such as water, alkali salts, halogens, organic compounds (DOM: Dissolved organic matter), or atmospheric gases (oxygen in particular) can accelerate the blackening effect [8,15,16,21-28]. The mechanism given here to explain the cinnabar blackening is a change in mercury sulfide stœchiometry induced by the solar radiation [9,29], leading to an excess in mercury or sulfur on pigment grain surfaces and thus producing an amorphous layer on the surface (α'-HgS) [8,15,27,30]. Given that amorphous mercury sulfide is metastable [8,12,15,16,31-34], new perspectives are opened for restoration treatments of altered cinnabar.

OBSERVATIONS AND REPORTS ON FIELD AT OSTIA

Excavations of the *Schola del Trajano* at Ostia (ancient port of Rome) revealed vestiges of a late republican building: the *domus dei Bucranes*. It shows spectacular wall paintings, in particular the oecus 101[35], presenting large orthostats painted with cinnabar (Fig. 1) as well as numerous fresco fragments. The ornamental wall, preserved *in situ*, was discovered in an exceptional state of preservation. During the period preceding its removal, the painting was kept in the shade for as much as possible. A rapid and progressive blackening developed in the zones bearing salt efflorescence (Fig. 1). In summer time, seven days, at approximately 3 hours of daily exposure to direct solar radiation, were sufficient to modify the color of the painted surface (Figure 2). Diminishing of the color alteration following reburial in winter time could be connected with a chemical process involving dissolution of altered cinnabar product in soil solution [28]. A painting fragment from the same context, kept dry and exposed to direct solar radiation, has blackened from its peripheral zones and alteration has extended inward over its whole surface within three months. Zones with no salt efflorescence have shown less marked but progressive blackening phenomenon (Fig. 3). No color change has developed on fragments preserved in the restoration laboratory, where light intensity had not exceeded 620 lux (Fig. 4).

Figure 1*: Schola del Trajano excavations, Oecus 101 a wall painting from the Domus dei Bucranes in September 2005 (up) and October 2006 (down): darkening of a red orthostate. Alteration started in interface or mortar break line (up) and increased in wet areas showing salt crystallization (down).*

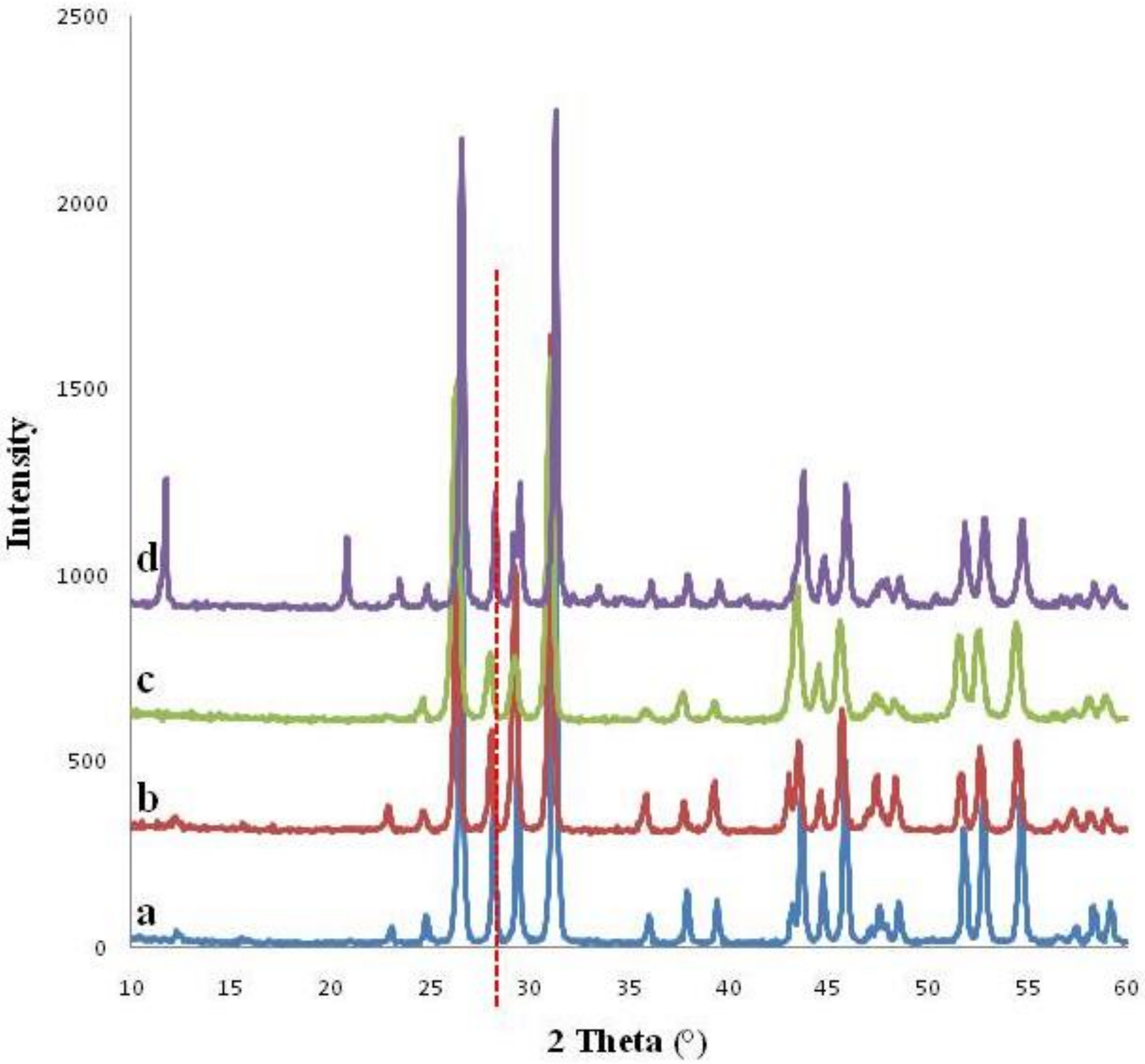

Figure 2*: X-ray diffraction patterns for: (a) modern sample kept in the shade without packaging; (b) modern sample exposed to sun light without packaging; (c) non-altered reference archaeological sample; (d) altered archaeological sample exposed outdoor for 10 months. Note the absence of the characteristic X-ray reflection peak of metacinnabar in the blackened samples, the position of which is indicated by the red dashed line.*

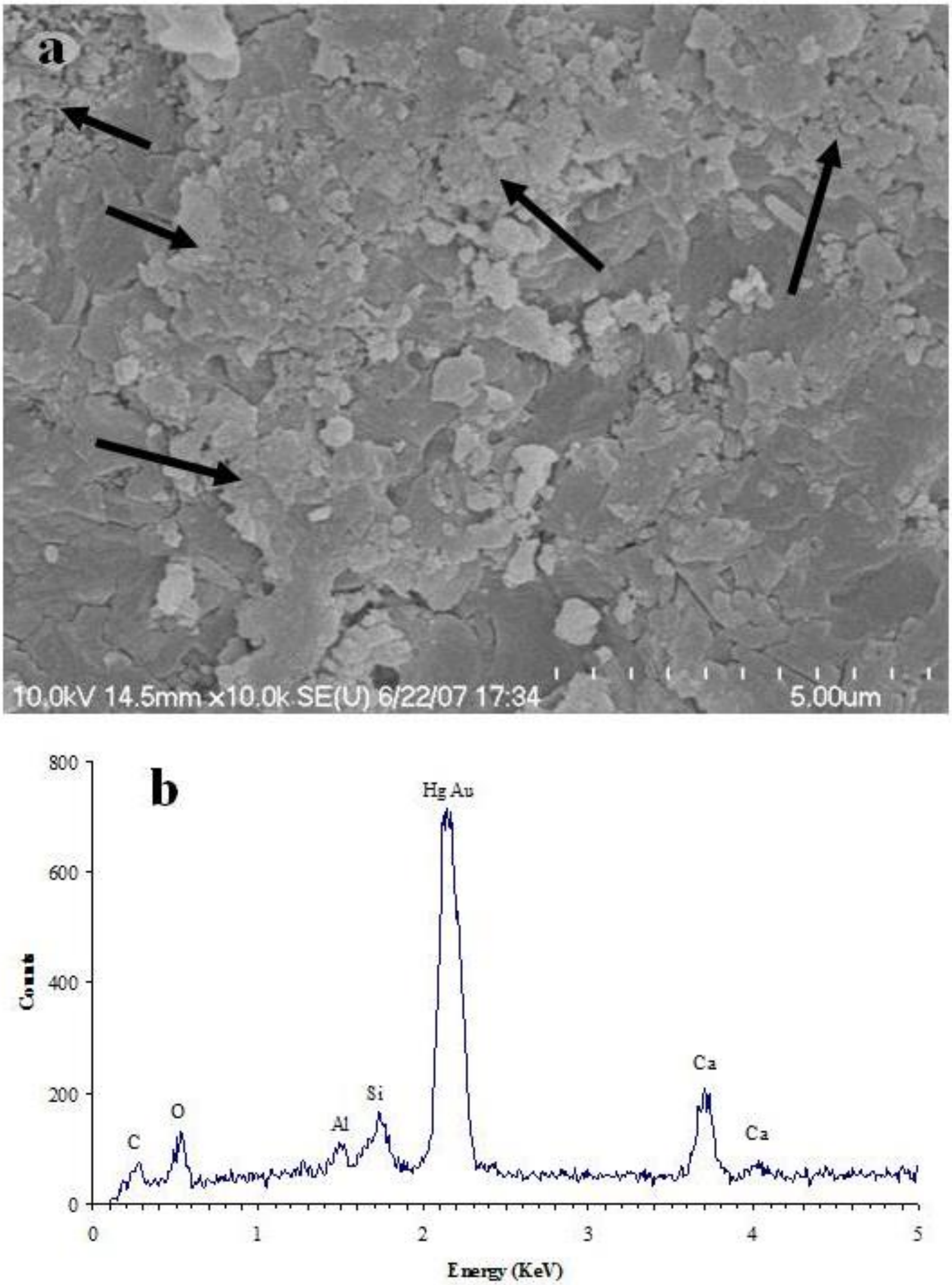

Figure 3: *Secondary electron image (a) and energy dispersive spectrum (b) of an altered (blackened) archaeological sample of wall painting cinnabar sample. One notes in (a) the thin amorphous layer (indicated by the arrows) which formed on the surface after exposure to sun light. In (b) one notes the major presence of mercury in the amorphized areas of the painting. The characteristic X-ray line of sulfur (~2.3keV) is not seen here, indicating depletion of sulfur in the altered areas. Gold was used as a coating to render the sample conductive and avoid charging effects under the electron beam.*

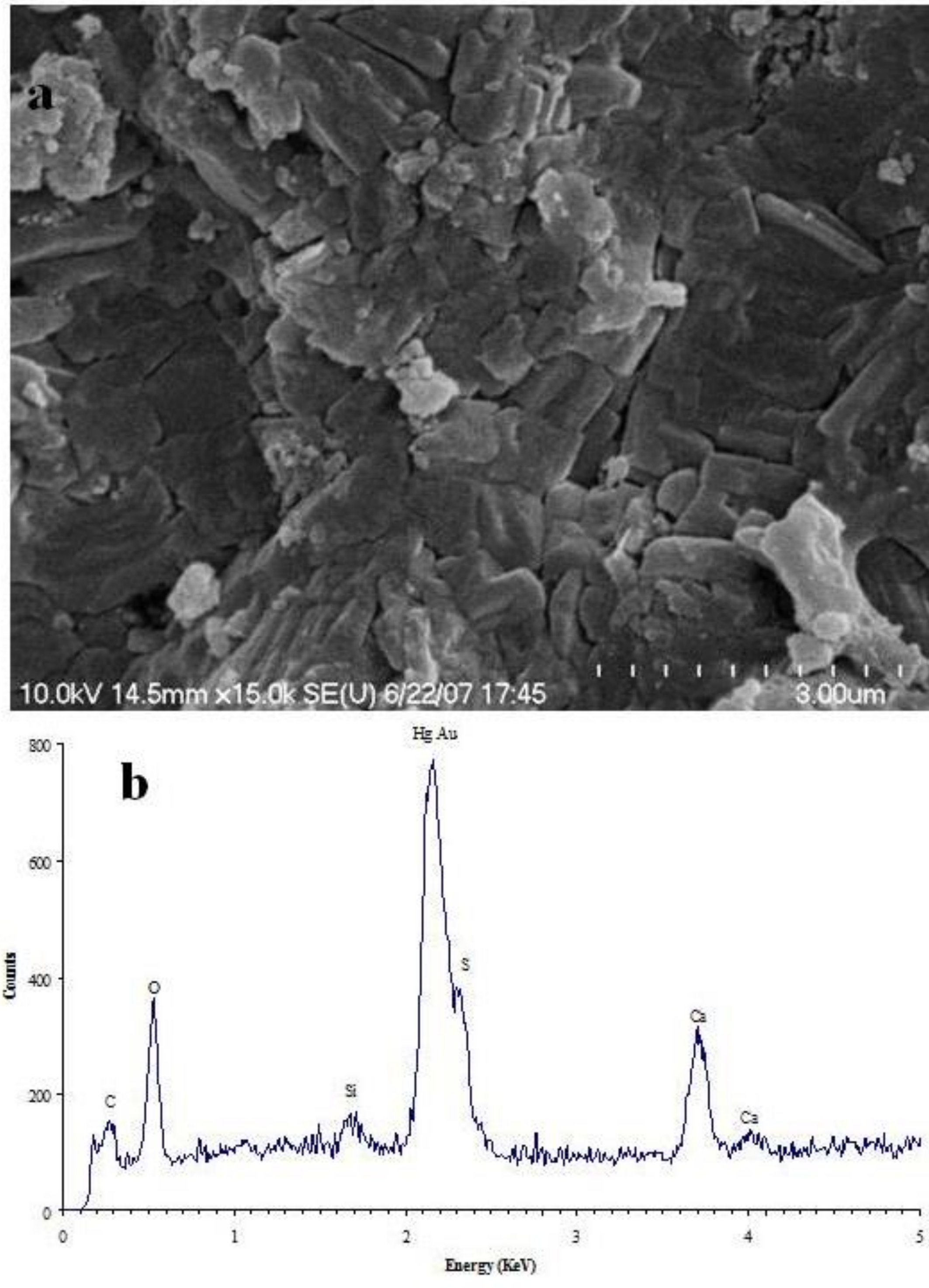

Figure 4*: Secondary electron image (a) and energy dispersive spectrum (b) for a non-altered archaeological wall painting sample of cinnabar. One notes in (a) the crystalline nature of the paint layer. In (b) one notes the major presence of mercury in the pigment as well as the sulfur characteristic X-ray line (~2.3keV). Gold was used as a coating to render the sample conductive and avoid charging effects under the electron beam.*

OBSERVATION IN ARIZONA DESERT CLIMATE

Modern and archaeological fresco samples were tested in Arizona. The samples were exposed to direct sun light or in the shade under blue, green, yellow and red emission filters. A set of samples were also packaged at 90 % of relative humidity (RH). The color change in samples was measured with a Pantone® colorimeter as a function of light wavelength, luminous intensity, relative humidity, and ambient temperature.

The color change began within 7 days in all moderns samples exposed to solar radiation (290-700 and 400-700nm with UV filter), under yellow filter (which transmits light between 500-700 nm). Then, blackening began later under green filters (475-575nm) and blue (400-575nm) and lastly under red filter (575-700nm). Color change of samples packaged in humid environment (90 % RH) was more noticeable. Archaeological fragments with polished and smooth surface have shown better resistance to alteration than the modern fresco samples which had slightly rough surfaces. No alteration has been observed in the samples that were tested in the shade (less than 2450 lux).

During the study, the pigment darkened slowly and suddenly became redder before a new process of darkening. Suspecting a loss of substance, 6 samples of pure cinnabar pigment were prepared on microscope slides and covered with thin glass sheet. The preparations were weighed and were exposed to direct sunlight and in the shade. After 7 days, a small and identical weight loss of (0.0003g) where measured on all preparations exposed to the sun. This phenomenon is provoked by photo radiation and can be explained by a disproportion of the ratio Hg/S. The change mechanism suggested here is that first, as the pigment darkens, sulfur contained in the crystal lattice is lost through oxidation and volatilization, leaving behind excess elementary mercury (Hg^0) [15]. Then for the tint to become red again the excess elementary mercury must volatilize, allowing thus rebalance of the crystal composition.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

Different frequencies of visible light have different effects on cinnabar (Fig. 5). In a desert environment, the color change first begins in samples exposed to visible light (290-780 nm), visible light without UV (400-700 nm), and then under yellow filter (500-700 nm). The time needed to observe color change under the green filters (475-575nm), blue (400-575nm), and red (575-700nm) is double. The blackening process must be facilitated by exposure light between 500 and 575 nm, region where cinnabar absorbs the light. The yellow radiation could present more risks in the deterioration process. To confirm such conclusion, it would be convenient to expose cinnabar samples to various monochromatic light emissions.

Frescoes painted with cinnabar and preserved *in situ* in damp and polluted environment undergo fast chemical reactions. The latter increase the speed of cinnabar blackening. In areas with salt crystallization, black gypsum forms a layer as a result of the sulfate attack of adjacent calcareous materials (calcium carbonate within the mortar). Water plays an important role in the reaction processes, whether chemical or biological. Black gypsum formation on the amorphous altered cinnabar surface results in a distinct form of dark spots or islands. The noticeable weight loss when sun light strikes cinnabar could be a phenomenon of photo-induced oxidation-reduction caused by solar radiation. It is suggested that a change in cinnabar stœchiometry resulting in formation of an amorphous layer of mercury sulfide on the outer surface of the mineral grains, which advances from the fragment periphery inward in a progressive manner and without formation of gypsum the change is less marked but

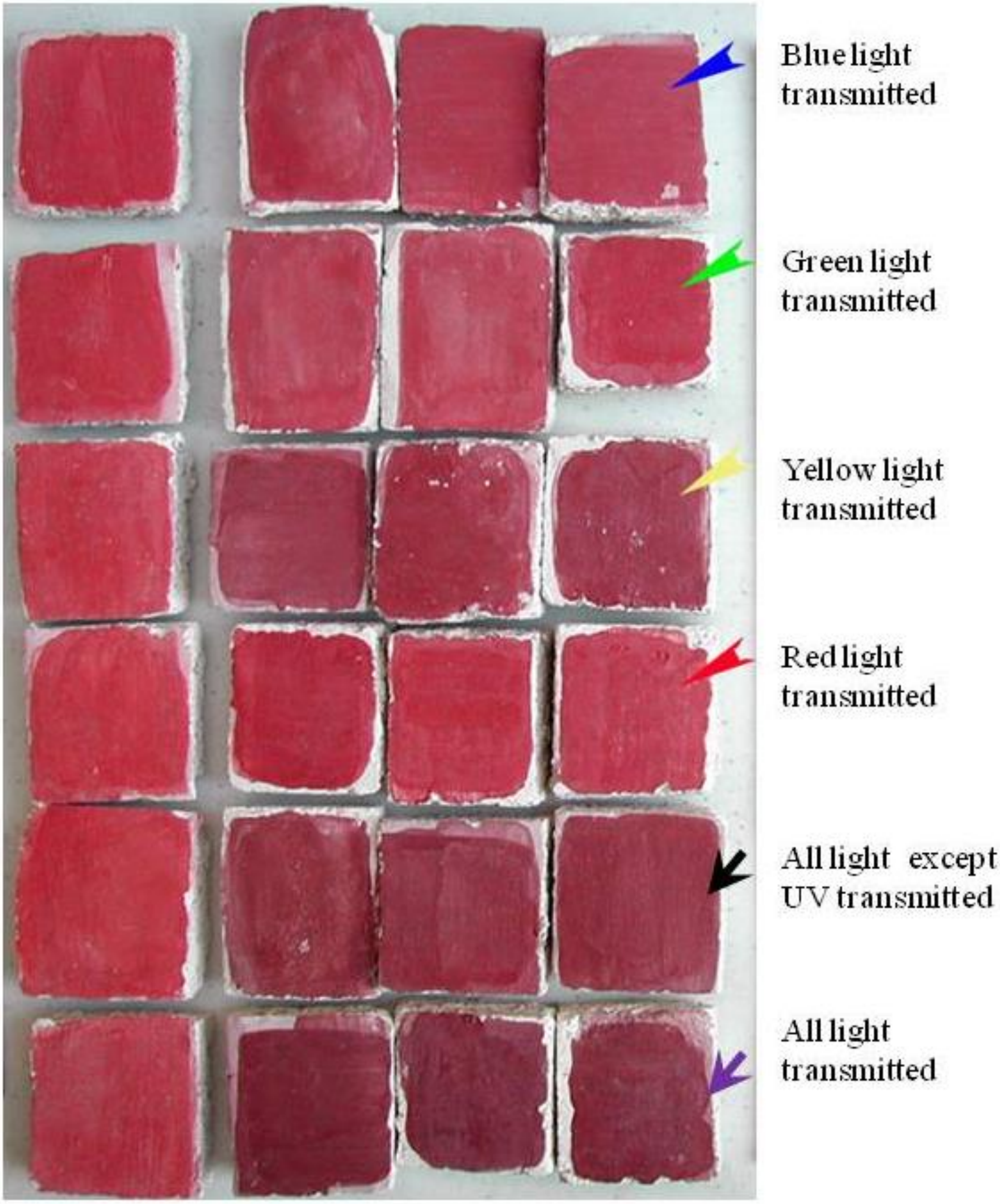

Figure 5: *cinnabar paints exposed to different types of light. Triplet samples to the right were packaged and exposed to the respective type of light radiation. Samples in the left column were contained in the same package conditions, but kept in the shade. Note that blackening is mostly induced by the yellow radiation. The last two rows show the summed effect of all light frequencies with and without UV.*

evolutionary. By keeping the in situ frescoes strictly in absolute shade during excavation, one would protect this photosensitive pigment from amorphization and fast sulfate reactions.

The blackening problem of cinnabar in wall paintings remains an opened question. The research still needs refinement on several axes. Some aspects were left aside in this study such as the crystallization of soluble salts, which catalyzes and amplifies the cinnabar alteration process. It would be suitable to identify them and to estimate the critical threshold concentration in mortars. Also, the role of soil solution pH in the alteration processes was not tackled here. It would be important to identify with accuracy the mechanisms of sulfate reactions induced by atmospheric agents and the exact role that bacterial activities can have on cinnabar stability. Irradiations with monochromatic lasers would allow identifying the kind of photon the most detrimental to the pigment. The contribution of such new research relative to the mechanisms of phase change of this pigment would allow developing and applying physical methods of restoration such as thermal activation/deactivation of pigment in altered paintings.

ACKNOWLEDGMENT

The authors would like to thank LeRoy Eyring Center for Solid State Science at Arizona State University for using the different analytical facilities; the *Schola del Trajano* excavation team at Lyon 2 University; Noé Terrapon, Christophe Bocherens and Nicholas E. Kendall for their help.

REFERENCES

[1] Vitruvius. *The Ten Books of Architecture*, VII, French translation, Liou B. and Zuinghedau M. (Ed.), Les Belles Lettres, Paris (1995).

[2] Pline The Elder. *Natural History,* XXXIII, French translation, Zehnacker H. (Ed.), Les Belles Lettres, Paris (1999).

[3] Pline The Elder. *Natural History,* XXXV, French translation, Ernout, A. (Ed.), Les Belles Lettres, Paris, (1997).

[4] A. Barbet, 2002, L'emploi des couleurs dans la peinture murale romaine antique, "marqueurs" chronologiques et révélateurs du "standing" social? In *: Pigment et Colorants, de l'Antiquité et du moyen age*, Colloque International du CNRS, Paris, 255-271.

[5] S. Liberti, 1950, Ricerche Sulla Natura E Sulla Origine Delle Alterazioni del Cinabro. *Bollettino dell'Istituto Centrale del Restauro, ICR, Boll*. 3-4, 57-60.

[6] R. J. Gettens, R. L. Feller , W.T. Chase, 1972, Vermilion and Cinnabar. *Studies in Conservation* 17 (2), 45-69.

[7] P. Mora, L. Mora, P. Philippot, 1977, French translation, *La conservation des peintures murales*. Centre international d'études pour la conservation et la restauration des biens culturels. Editrice Compositori, Bologne, 82.

[8] Daniels, Vincent, 1987, The Blackening of Vermilion by Light. *Recent Advances in the Conservation and Analysis of Artifacts.* Summer Schools Press, London, 280-282**.**

[9] R. J. Gettens, R. L. Feller, W. T. Chase, 1993, Vermilion and Cinnabar. In Ashok, Roy (ed.). *Artists' Pigment, A Handbook of Their History and Characteristics*, Vol. 2. Oxford University Press, New York, 159-182.

[10] Zuppiroli, Liberto, M-N. Bussac, 2001, *Traité des couleurs*. Presses Polytechniques et universitaires romandes, Lausanne, 100.

[11] J. Lamure, H. Brusset, 1962, Mercure. In : *Nouveau traité de chimie Minérale*, **Tome V**, Pascal P., Ed., Masson et Cie, Paris, 733-797.

[12] Potter, W. II Robert, H.L. Barnes, 1978, Phase relations in the binary Hg-S. *American Mineralogist* 63, 1143-1152.
[13] W. Paszkowitz, W. Szuszkiewicz, E. Dynowska, J. Domagala, B. Witkowska, M. Marczak, P. Zinn, 1999, High-pressure-high-temperature study of $Hg_{1-x}Mn_xS$. *Journal of Alloys and Compounds* 286, 208-212.
[14] A. K. Mahapatra, A. K Dash, 2006, α-HgS nanocrystals: Synthesis, structure and optical properties. *Physica E* 35 (1), 9-15.
[15] H. Béarat, A. Chizmeshya, R. Sharma, A. Barbet, M. Fuchs, 2004, Mechanistic and computational study of cinnabar phase transformation: Applications and implications to the preservation of this pigment in historical painting. In: *The 3rd International Conference on "Science and Technology in Archaeology and Conservation", (December, 7-11 2004, Jordan).* Editor: T.S. Akasheh, Foundation El Legado Andalusi, Spain, 2008, 53-70.
[16] M. Cotte, J. Susini, N. Metrich, A. Moscato, C. Gratziu, 2006, Blackening of Pompeian Cinnabar paintings: X-ray micro-spectroscopy analysis. *Analytical Chemistry* 78 (21), 7484-7492.
[17] S. Liberti, 1951, Ricerche Sulle Alterazioni del Cinabro (II). *Bollettino dell'Istituto Centrale del Restauro, ICR, Boll.* 5-6, 45-64.
[18] P. Pouli, D. C. Emmony, C.E. Madden, I. Sutherland, 2001, Analysis of the Laser-Induced Reduction Mechanisms of Medieval Pigments. *Applied Surface Science* 173, 252-261.
[19] P. Pouli P., D. C. Emmony, C. E. Madden, I. Sutherland, 2003, Studies towards a thorough understanding of the laser-induced discoloration mechanisms of medieval pigments. *Journal of Cultural Heritage* 4, 271-275.
[20] V. Zafiropulos, C. Balas, A. Manousaki, Y. Marakis, P. Maravelaki-Kalaitzaki, K. Melesanaki, P. Pouli, Th. Stratoudaki, S. Klein, J. Hildenhagen, K. Dickmann, Luk'Yanchuk, S. Boris, C. Mujat, A. Dogariu, 2003, Yellowing effect and discoloration of pigments: experimental and theoretical studies. *Journal of Cultural Heritage* 4, 249–256.
[21] R. S. Davidson, C.J. Willsher, 1981, The light-induced blackening of the red mercury (II) sulfide. *Journal of the Chemical Society* 3, 833–835.
[22] R. M. Dreyer, 1938, Darkening of cinnabar in sunlight. American Mineralogist 23, 457-460.
[23] R. L. Feller, 1967, Studies in the darkening of vermillon by light. *Report and studies in the history of Arts*. National Gallery of Art, Washington D.C., 99-111.
[24] S. Edholm, T. Wilder, 1998, The dirt on colors : a mineral pigment primer. *Bulletin of primitive technology* 15, 20-24.
[25] M. Ravichandran, G. R. Aiken George, M. M. Reddy, J. N. Ryan, 1998, Enhanced Dissolution of Cinnabar (Mercuric Sulfide) by Dissolved Organic Matter Isolated from the Florida Everglades. *Environ. Sci. Technol.* 32 (21), 3305 -3311.
[26] J. K. McCormark, F. W. Dickson, M. P. Leshendok, 1991, *American Mineralogist* 76, 1715-1721.
[27] J. K. McCormack, 2000, The darkening of cinnabar in sunlight. *Mineralium Deposita* 35, 796-798.
[28] J. S. Waples, K. L. Nagy, G. R. Aiken, J. N. Ryan, 2005, Dissolution of cinnabar (HgS) in the presence of natural organic matter. *Geochimica et Cosmochimia Acta* 69 (6), 1575-1588.

[29] M. S. Gustin, H. Biester, C. S. Kim, 2002, Investigation of the light-enhanced emission of mercury from naturally enriched subtrates. *Atmospheric Environment* 36 (20), 3241-3254.

[30] L-F. Jéhan, 1851, *Dictionnaire de chimie et de minéralogie*. Encyclopédie théologique, Tome 46. Aux ateliers Catholiques du Petit-Montrouge, Paris, 122.

[31] F. W. Dickson, G. Tunell, 1954, The Saturation Curves of Cinnabar and Metacinnabar in the System HgS-Na2S-H2O at 25°C. *Science* 119 (3093), 467-468.

[32] A. A. Kelsey, G. J. Ackland, S. J. Clark, 1998, Stability and Electronic Structure of the Cinnabar Phase in GaAs. *Physical Review B: Condensed Matter* 57 (4), 2029-2032.

[33] J-H. Zeng, J. Yang, Y-T. Qian, 2001, A novel morphology controllable preparation method to HgS. Materials Research Bulletin 36 (1), 343-348.

[34] L. V. Mel'chakova, I. A. Kiselyova, 2002, *Cinnabar to metacinabar phase transition : The enthalpy, temperature, and specific heat of the transition*. Division of Geology, Moscow State University, Vorob'evy gory, Moscow, unpublished.

[35] N. Terrapon, 2007, Les enduits peints du péristyle et de l'oecus 101 de la Domus aux Bucranes : observations techniques, In : Villas, maisons, sanctuaires et tombeaux tardo-républicains : découvertes et relectures récentes. Actes du colloque international de Saint-Romain-en-Gal en l'honneur d'Anna Gallina Zevi, Vienne-St Romain-en-Gal, 8-10 février 2007, Bertrand Perrier (Ed.), Edizioni Quasar, Rome, 81-98.