ESRF	Experiment title: Probing the in-situ formation of degradation compounds in historical paintings by multi-modal XRD	Experiment number: HG159
Beamline: ID13/ID22	**Date of experiment**: from: 23/09/20 to 28/09/20 (ID13) from: 19/11/20 to 22/11/20 (ID22)	**Date of report**: 15/02/21
Shifts: 9 (ID13) / 6 (ID22)	**Local contact(s)**: ID22 : C. Dejoie / ID13 : M. Burghammer	*Received at ESRF:*

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This proposal aimed at realising a synergy among a team of (experienced) users working on different projects related to oil painting compositions and conservation, but sharing the same techniques, in view of implementing a Block Allocation Group (BAG) proposal system for this experiment types in the future. As a result, this proposal encompassed several sub-projects. While the studied materials were different for each sub-project (among them, lead phosphates; arsenic sulphide-pigments, copper acetate-based pigments…), the analytical objectives were identical : characterizing the composition, microstructure and stratigraphic distribution of each class of pigment and of their associated degradation products within historical paint down to the sub-micrometric scale. A combination of high-angular resolution XRD combined with Rietveld analysis (ID22) and high-lateral resolution µXRPD mapping (ID13) was applied to each materials. Due to the sanitary situation, all the experiments were performed in remote mode. Samples were shipped to the ESRF, and positionned for analysis on the beamline by beamlime staff. Users were able to carry out analysis remotely, access the electronic logbook and collect their data at the end of the experiment. Samples were then shipped back to users.

Experimental

A) High-angle resolution XRD (ID22)

The versatily of the ID22 HR-XRD beamline allowed us to select a wavelength of $\lambda = 0.354$ Å (35 keV). This wavelength was chosen after preliminaries tryouts on historical samples: it permited the obtention of a good compromise to render a good peak resolution, and a sufficient data collection. The detector was a 9-channel Si 111 multianalyzer stage. Beam size was 1x1 mm². This surface allowed a global analysis of the entirety of each sample, once they were corectly aligned with the beam. Each recording was constituted by an accumulation of succesive diffractograms, on an angular range [2°,20°(2θ)]. Analysis times extended from 1 to 4 hours, according to the amount of diffracting matter contained in the capillary (that is to say, the size of the sample).

B) High-lateral resolution XRD (ID13)

µXRD maps were acquired at the ID13 "microbranch" beamline (ESRF). Samples were either thin (10µm) sections or thick sections, of paint fragments embedded in resin. Samples were mounted vertically, perpendicular to the X-ray beam. The energy of the incident beam was 13.0 keV. The beam was focused to 2x2 µm². XRD maps were obtained by raster scanning the samples and collecting XRD 2D patterns, in transmission, with the Dectris Eiger 4M single photon counting. A dwell time of 25ms/pixel was selected. 2D XRD patterns were azimuthally integrated using the PyFAI software package and XRD maps were analysed with the XRDUA and the PyMca ROI imaging software packages.

Results

As this proposal involved several research teams, each one of them presents here the results they gathered on beamline(s) ID13 and/or ID22.

Sub-project 1

Research group, Principal investigator and collaborators

- Marta Ghirardello, Politecnico di Milano, Milano, Italy
- Daniela Comelli, Politecnico di Milano, Milano, Italy,
- Douglas MacLennan, Getty Conservation Institute, Los Angeles, USA
- Catherine Patterson, Getty Conservation Institute, Los Angeles, USA
- Austin Nevin, Courtauld Institute of Art, London, UK
- Victor Gonzalez, Rijksmuseum, Amsterdam, Netherlands
- Letizia Monico, CNR SCITEC, Perugia, Italy

Context and motivation of the research

Pablo Picasso's painting *Femme* (1907, Fondation Beyeler, Riehen/Basel, Switzerland) contains two different *Cadmium Yellow* paints (CdY, based on CdS), preserved and degraded. The degraded paint exhibits a bright and unusual red photoluminescence (PL) emission, which we hypothesize can be ascribed to a higher density of surface crystal defects in CdS and could be linked to the presence of CdS nanoparticles. Moreover, PL micro-imaging performed at SOLEIL synchrotron has revealed a spatial heterogeneity of the PL emission at the microscale. SR μ-XRD analyses of paint cross-sections were performed in order to evaluate the crystal phase and crystallite size of CdS pigment and associate the heterogeneity of the μ-PL emission to the distribution of crystalline phases (emitting CdS and/or other paints components).

Analysed samples

Two cross-sections, taken from the well-preserved and altered CdY paints, were analysed. The cross-sections were embedded in resin and polished to obtain 1 mm thick resin slice. Results of the preliminary in-laboratory characterization are reported in table 1.

Sample name	CdY paint composition
Femme – CS3 preserved	$CdSO_4$[a], CdS[b], $(PbCO_3)_2 \cdot Pb(OH)_2$[b], $BaSO_4$[b], HgS[b], Si[c], Al[c]
Femme – CS5 altered	CdS, $CdCO_3$[a], $CdSO_4$[a], CdC_2O_4[a], $BaSO_4$[b], Al[c], Cl[c]

Table 1 - Samples overview. Compound/element detected with [a]μ-FTIR, [b]μ-Raman and [c]SEM-EDS.

Status of the data processing

Phase identification and mapping were performed on the two micro-cross sections. Identification of minor phases are currently under investigation and correlation of μ-XRD results with μ-PL and μ-XRF/XANES (performed at ESRF) are in progress.

Main results obtained

μ-XRD analyses have allowed to determine the presence of crystalline CdS only in preserved layer (in both crystalline forms, cubic and hexagonal). No diffraction peaks associated to CdS were found in the altered sample. This finding has allowed us to provide a first evidence of the different crystallinity of the CdS present in the preserved and degraded layer and could validate the hypothesis that the degraded CdY is composed of poorly crystalline or nanometric CdS. In addition to the paint components already identified, μ-XRD analyses detected $PbSO_4$, ascribed to lead white degradation, and Cd-Cl compounds. This latter were found in different chemical species between the paints, $CdCl_2$ in the preserved and $Cd(OH)Cl$ in the degraded.

The comparison between the distribution of crystalline compounds and PL measurements did not highlight any evident spatial correlation between the peculiar red PL emission observed in the degraded CdY paints and the distribution of crystalline compounds. Since this PL emission can be related to the presence of nano-CdS, not mapped by μ-XRD, other results obtained with μ-XRF/XANES maps will help to clarify this issue.

Eventual communication of results (manuscript in preparation, conference…)

Results obtained, combined with SR-μ-PL (SOLEIL synchrotron), μ-XRF and μ-XANES analysis (ESRF synchrotron) will be published in a manuscript in preparation.

Sub-project 2

Research group, Principal investigator and collaborators

- Nati Salvadó Departament d'Enginyeria Química. Universitat Politècnica de Catalunya·BarcelonaTech (UPC).
- Salvador Butí, Departament d'Enginyeria Química, UPC.
- Núria Oriols, Departament d'Enginyeria Química, UPC and Museu Nacional d'Art de Catalunya, Barcelona
- Trinitat Pradell, Departament de Física, Centre de Recerca en Ciencia i Enginyeria Multiescala de Barcelona, UPC.

Context and motivation of the research

The influence of magnesium in the process of carbonation of a dolomitic mortar modifies the morphology of the carbonate particles formed and, consequently, the mechanical and chemical properties of the mortar layer and the final aspect of the wall painting.

The chemical interactions in the system $CaO/MgO/H_2O/CO_2$ make its study of especial interest. In particular, the influence that magnesium alone may have in the carbonation process without considering the role of the other components present in the mortar may have. The low degree of carbonation of magnesium hydroxide attained and the wide diversity of the amorphous and crystalline carbonate phases obtained during the drying of the dolomitic mortar is, a priori, heavily conditioned by the reaction conditions (pH, evaporation rate???).

This research forms part of a thesis of N. Oriols.

A series of laboratory mock-ups of the process of carbonation of a dolomitic mortar in *fresco* paintings, as well as, of dried magnesium hydroxide and dolomitic lime water drops simulating the different states in the evolution of the drying process are analysed.

Analysed samples

2 samples: Micrometric painting fragment from fresco painting mockups, embedded in resin and cut as thin sections, mounted on tape.

5 samples: powder and film mortar from dried magnesium hydroxide water drops and dolomitic lime-water drops simulating the different states in the evolution of the drying process and mounted on tape.

Status of the data processing

The data obtained from the dried drops 5 samples are already processed, while these from the thin sections are still in process as it has to be related to the data obtained with other analytical techniques results.

Main results obtained

The carbonation phases formed in the dried magnesium water drops identified include several magnesium hydroxide carbonates, Hidromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ and Giorgiosite, $Mg_5(CO_3)_4(OH)_2 . 5H_2O$ while Brucita, $Mg(OH)_2$ is still present. On the contrary, the dried dolomitic lime-water drops show the presence of Brucite, $Mg(OH)_2$, absence of magnesium carbonates and the formation of calcium carbonates including Calcite, $CaCO_3$ and Aragonite, $CaCO_3$. These results are important for the determination and understanding of the role which Mg has in the carbonation process of a dolomitic mortar.

Eventual communication of results (manuscript in preparation, conference…)

Currently we are writing an article including the data obtained so far, on the influence of Magnesium in the carbonation of wall paintings.

Sub-project 3

Research group, Principal investigator and collaborators
- Koen Janssens, University of Antwerp, Belgium
- Frederik Vanmeert, University of Antwerp, Belgium
- Ermanno Avranovich Clerici, University of Antwerp, Belgium

Context and motivation of the research
The darkening of historic lead white, mostly hydrocerussite, in areas of wall paintings by famous (Italian) artists such as Cimabue, Baldovinetti and Signorelli is a phenomenon that can be attributed to the spontaneous formation of black plattnerite(β-PbO_2) from hydrocerussite($2PbCO_3.Pb(OH)_2$), that was originally present in the paintings. The main hypothesis is that the conversion of lead white to β-PbO_2 proceeds in two consecutive parts, with phosgenite($PbCO_3.PbCl_2$) as an intermediate step.

    (A) Phosgenite formation by partial CO_2 and H_2O removal, and reduction of Cl_2 to Cl^- in situ formation of O_2:

$$2(2PbCO_3.Pb(OH)_2) + 3Cl_2 \rightarrow 3\ PbCO_3.PbCl_2 + CO_2 + 2H_2O + O_2$$
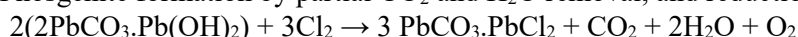
    (B) Secondary oxidation of phosgenite to mixtures of cotunnite($PbCl_2$) and plattnerite:

$$2\ PbCO_3.PbCl_2 + Cl_2 \rightarrow PbO_2 + 3PbCl_2 + 2CO_2$$
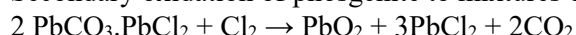
In order to verify this hypothesis, powdered lead white has been prepared and exposed to a Cl_2 rich environment aiming to understand the oxidation of lead white to plattnerite by chlorine and light.

Analysed samples
A fixed amount of lead white in powder form was exposed to Cl_2-rich atmosphere. This procedure was repeated three times employing three different time lengths: 1 hour, 2 hours and 3 hours. Three different samples were obtained in this way.

- One sample containing powdered lead oxide from Aldrich, observed to be mostly rich in massicot and with presence of hydrocerussite plumbonacrite and litharge was exposed to cycles of UV light and darkness in a high humidity environment to verify the possible formation of Pb^{4+} species.
- Two samples containing an unknown compound obtained through interaction of powdered cerussite and powdered hydrocerussite with hydrogen peroxide. The unknown compound has been observed to form Pb^{4+}.

Glass capillaries were filled with the exposed/reacted powders before being sent to ESRF for analyses at ID22.

Status of the data processing
The main crystalline compounds in the samples were identified and the structure of the unknown compound is being refined.

Main results obtained
Formation of **plattnerite** was identified along with the formation of **phosgenite** and **cotunnite**. These results confirm the initial hypotheses. Furthermore, unreacted **hydrocerussite** is still present, see Figure 1.

Figure 1: High resolution 1d pattern of lead white after exposure to a Cl_2 rich environment for three hours.

Eventual communication of results (manuscript in preparation, conference…)
The data collected will be employed to submit a manuscript defining the factors triggering the oxidation of lead white.
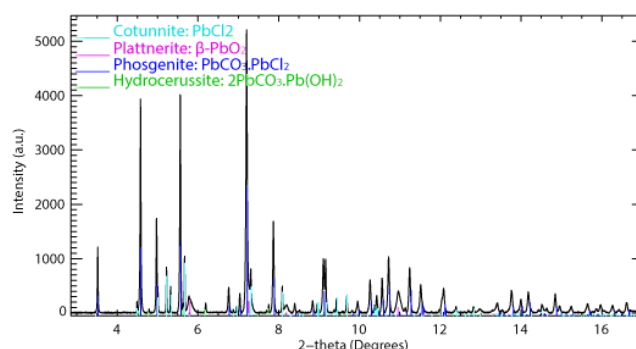
Sub-project 4

Research group(s), Principal investigator and collaborators

- Letizia Monico, CNR-SCITEC, Perugia, Italy
- CNR-SCITEC (Perugia) and University of Perugia
- Claudio Costantino, University of Perugia and CNR-SCITEC, Perugia, Italy
- Aldo Romani, University of Perugia, Perugia, Italy
- Marine Cotte, ESRF, Grenoble, France
- Victor Gonzalez, Rijksmuseum, Amsterdam, Netherlands

Context and motivation of the research.

The formation of crystalline Pb-Ca phosphates has been recently observed in several historical objects, including a masterpiece by L. da Vinci. [1] However, the source of P ions and the pathways of formation of Pb-Ca phosphates in paint layers are still issues which remain poorly understood. In order to obtain a more in depth characterization of the chemical nature of Pb-Ca phosphates already identified in cultural heritage objects, as a first step of the research a series of commercial/in-house synthesized powders of hydroxyapatite [$Ca_5(PO_4)_3OH$], Pb-Ca hydroxyapatite solid solutions [$Ca_{1-x}Pb_x(PO_4)_6(OH)_2$, with $0.1 \leq x 0.8$], and hydroxylpyromorphite [$Pb_5(PO_4)_3OH$] have been analyzed at beamlines ID13 (µ-XRPD mapping) and ID22 [high angular resolution (HAR) XRPD]. Such investigations aimed at determining the Ca:Pb stoichiometry and microstructural properties of each material.

Analysed samples

Powders were in-house synthesized by following the procedures reported in the literature. [2] A list of the analyzed samples along with their chemical formula is reported in Table 1.

Table 1. List of $Ca_{1-x}Pb_x(PO_4)_6(OH)_2$ [with $0 \leq x \leq 1$] powders analyzed at beamlines ID13 and ID22.

Sample	Chemical formula	source
Hydroxyapatite (HA)	$Ca_5(PO_4)_3OH$	commercial, Sigma-Aldrich
PbHA10	$(Pb_{0.1}Ca_{0.9})_5(PO_4)_3OH$	in-house synthesized
PbHA20	$(Pb_{0.2}Ca_{0.8})_5(PO_4)_3OH$	in-house synthesized
PbHA40	$(Pb_{0.4}Ca_{0.6})_5(PO_4)_3OH$	in-house synthesized
PbHA50	$(Pb_{0.5}Ca_{0.5})_5(PO_4)_3OH$	in-house synthesized
PbHA70	$(Pb_{0.7}Ca_{0.3})_5(PO_4)_3OH$	in-house synthesized
PbHA80	$(Pb_{0.8}Ca_{0.2})_5(PO_4)_3OH$	in-house synthesized
Hydroxylpyromorphite (HPy)	$Pb_5(PO_4)_3OH$	in-house synthesized

Main obtained results and status of the data processing

Powders were investigated at beamlines ID13 (Energy=13 keV, beam size 2.5×2.5 µm^2) and ID22 (Energy=35 keV, beam size: 1.0x1.0 mm^2) by µ-XRPD mapping and HR-XRPD respectively.

ID13-XRPD patterns (Figure 1a) were obtained as average of single-pixel XRPD patterns recorded from a map of 200×200 µm^2 size (step size: 2×2 µm^2; exposure time: 25 ms/pixel). ID22-XRPD data were combined into 0.002° bins (Figure 1b).
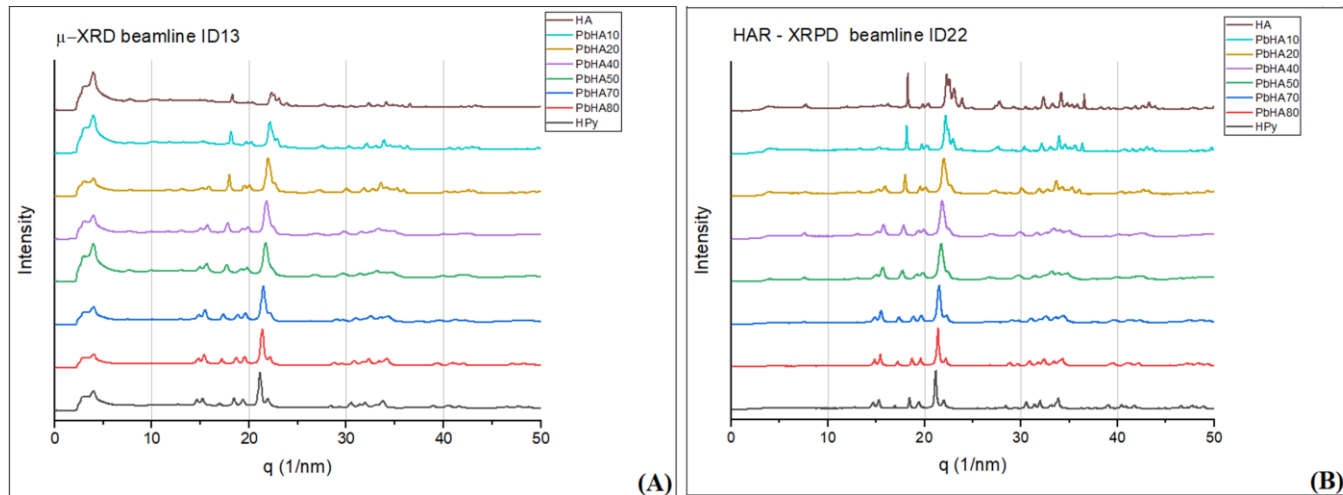
The XRPD patterns obtained at each beamline are comparable, showing a clear progressive shift of the peaks towards lower q values with increasing of Pb molar fraction in the $Ca_{1-x}Pb_x(PO_4)_6(OH)_2$ solid solution. ID22-XRD patterns present sharper peaks than the equivalent ID13-ones, as result of the higher angular resolution of the ID22 set-up. Data recorded at both beamlines are in line with those acquired by the laboratory XRD device. Rietveld refinement of each XRD pattern is ongoing in order to determine the exact stoichiometry and microstructural properties of the analyzed compound. This will also permit to more accurately/quantitatively assess eventual differences between ID13- and ID22-datasets.

Eventual communication of results (manuscript in preparation, conference…)

The collected data will be published soon in a paper that is in preparation.

References

[1] M. Eveno, Study report, C2RMF, **2007**.

[2] Y. Zhu & B. Huang, Characterization, dissolution and solubility of the hydroxypyromorphite–hydroxyapatite solid solution [(Pb$_x$Ca$_{1-x}$)$_5$(PO$_4$)$_3$OH] at 25 °C and pH 2–9, Geochem. Trans. **2016**, 17: 2.

Sub-project 5

Research group, Principal investigator and collaborators
- Marine Cotte, Beamline scientist, ESRF, Grenoble, France
- Victor Gonzalez, Rijskmuseum and UVA, Amsterdam, The Netherlands

Context and motivation of the research
The development of oil painting fundamentally relied on the use of metallic driers, in particular PbO. When mixed with oil, PbO will form lead carboxylates and will increase the speed of curing reactions. However, unreacted PbO can also react with environmental CO_2 and H_2O leading to the formation of lead carbonate and hydroxide groups. These reactions may explain the presence of plumbonacrite ($Pb_5(CO_3)_3O(OH)_2$) as observed in major artworks [1]. This research project aims at better understanding these concomitant reactions and assessing their speed.

Analysed samples
Model paints were prepared to mimic lead-based paint media (cooked oil, named PaWe) mixed with lead white pigment (hydrocerussite rich, LW or cerussite rich, Ce) and unreacted PbO particles (Li), and aged for months at room temperature and at 60°C. Thin sections were prepared to map the distribution of crystalline phases, from the core PbO to the paint film.
During this beamtime, 4 maps were acquired at ID13, on two samples: PaWeLiCe and PaWeLiLW. There was no analysis at ID22 for this project.

Status of the data processing
The azimuthal integration was performed with PyFAI. The data was analysed using PyMca and XRDUA.

Main results obtained
For these samples, no particular concentration of plumbonacrite or neo-formed hydrocerussite was observed in the vicinity of PbO. This would tend to show that the presence of LW affects the carbonation of PbO.
Surprisingly, an unusual lead carbonate oxide, $Pb_3C_2O_7$ has been detected.

Eventual communication of results (manuscript in preparation, conference…)
These results are part of a wider project, which should be presented in a manuscript in preparation about Leonardo da Vinci's paintings techniques.

References
[1] V. Gonzalez et al., Unraveling the Composition of Rembrandt's Impasto through the Identification of Unusual Plumbonacrite by Multimodal X-ray Diffraction Analysis, Angew. Chem. Int. Ed. **2019**, 58(17): 5619.

Sub-project 5

Research group, Principal investigator and collaborators

- Christelle Chauffeton, Institut de Recherche de Chimie Paris, Paris Sciences et Lettres, Paris, France
- Gilles Wallez, Institut de Recherche de Chimie Paris, Paris Sciences et Lettres, Paris, France

Context and motivation of the research

When introducing a $Co_{1-x}Al_{2+2x/3}O_4$ ($0 \leq x \leq 1$) spinel pigment in a porcelain glaze, the pigment reacts with the vitreous matrix and gets partially dissolved, changing the chemistry of the glaze, the crystal phases present and the resulting colour and possibly causing the devitrification of the glaze. This work aims at better understanding the reactions that take place and how to avoid them.

Analysed samples

$Co_{1-x}Al_{2+2x/3}O_4$ ($0 \leq x \leq 1$) pigments were prepared and introduced into porcelain glazes. Powder samples of the pigments and glazes were analysed at ID22. Thin sections of glazes painted on porcelains were prepared and mapped at ID21. Seven maps were acquired at ID13 for the samples: P01400, P05100, P05120, P25100, P25120, P75100, P75120. 15 powder samples were analysed at ID22.

Status of the data processing

The maps were analysed with PyMCa and the powder diffraction with FullProf Suite.

Main results obtained

The $Co_{1-x}Al_{2+2x/3}O_4$ pigment has a spinel structure with a tetragonal distortion. Once in the glaze, the pigment is recrystallised and a distortion-free $CoAl_2O_4$ spinel is observed. Pigments are observed on the upper part of the glaze, being less dense than the PbO-rich vitreous matrix. Part of the cobalt diffuses inside the glass, however the XRF Co map matches the map of spinel phase, meaning that the Cobalt that gets dissolved inside the glass stays localised around the pigment grains and does not diffuse further down the layer. Some sample show the presence of α-Al_2O_3, with grains mainly localised near the surface of the glaze, meaning they could be related to a high reflectivity and to the crackling of the glaze. Sample P75100 shows the case of the excessive Al^{III} reacting with the boron oxide of the matric to form $Al_4B_2O_9$ crystals. The XRD map shows that these crystals are mainly present above the spinel phase inside the layer.

Eventual communication of results (manuscript in preparation, conference…

This work is part of a PhD project and will be presented in a paper about the reactivity of Thénard Blue pigments in a porcelain glaze.

Conclusion and perspectives

This experiment succesfully paved the way for the establishment of a BAG mode of access for structual analysis of historical materials at the ESRF. Indeed, several key points were proven:

i) Remote operations are feasible : all the samples were shipped to the ESRF, and experiments followed using the Guacamole software. Users were then able to collect their respective data and work from their home institutions ;

ii) A large volume of data was gathered for 8 European teams, in only 12 shifts at ID13 and 9 shifts at ID22. What would have required multiple proposals in competition was achived in only two beamtimes, during which all users collaborated efficiently with the ESRF staff

iii) High quality datasets were obtained, permiting us to gain new insights into the artistic process of Old Masters, the conservation state of historical materials, and yielding precious assets for the long-term preservation and conservation of artworks.

We are thus confident that the submission of a BAG for the heritage science community could fundamentally increase the impact of the combination HR-XRD/μXRD for the study of historical materials at the ESRF.