

## **Annual Report for project EC-69:**

### **Influences between European regions in the transition from Gothic to Renaissance: SR analysis of submillimetric complex mixtures of compounds in medieval paintings**

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#### **Project objects.**

This project has two main objects: historical and scientific.

The historical goal of this proposal is to obtain scientific proofs of the relationship between the different painters and schools during the transition from Gothic to Renaissance in the critical 15<sup>th</sup> AD century in Catalonia, finding out the influences and connections with other European regions. The study includes the investigation of a selection of master artworks belonging to the MNAC (Museu Nacional d'Art Nacional de Catalunya) by means of the analysis of pigments, binders, preparation layers and reaction/aging compounds.

The scientific goal is threefold: First, to establish a methodology including specific sample preparation and the selection of adequate chemical and structural analytical techniques with ten micron resolution for the full identification of submillimetric mixtures of compounds.

Secondly, to produce a database including all the information obtained from the pigments, reaction, alteration and aging compounds for use in future studies. The reproduction of the processes of synthesis following medieval treatises will be one of the keys of the study allowing a full and unambiguous characterization of the original materials. In order to study reaction (drying) and alteration and aging compounds, natural and artificial process will be induced to determine the physical and chemical mechanisms responsible.

Thirdly, a substantial upgrade of the beamline, due to the implementation of a focusing device (10 to 50 micron spot size) allowing for (quasi-) simultaneous micro-XRF, micro-HRPD and possibly Raman spectroscopy.

#### **Report of Year 1 work.**

During this first year the following tasks have been fully developed:


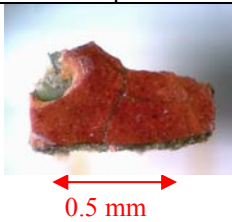
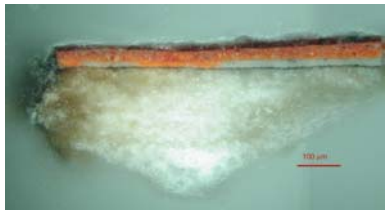
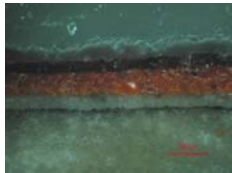
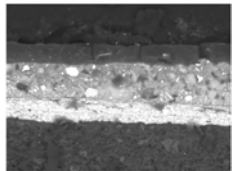
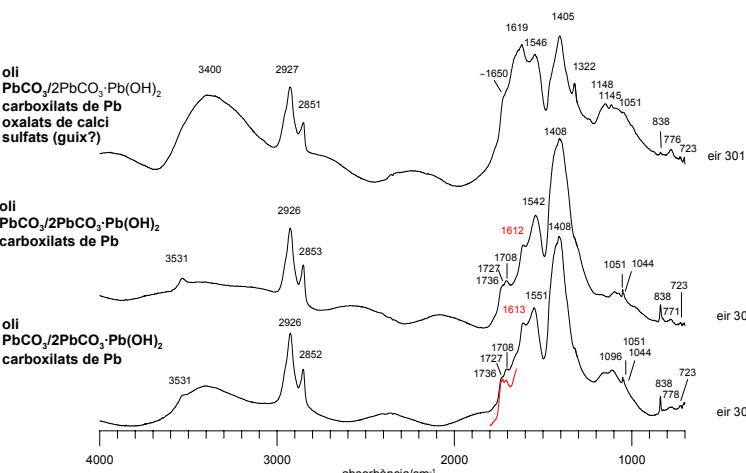
##### ***1- Selection and preparation of ancient paintings***

Selection of the 15<sup>th</sup> century AD painters, from each of them one altarpiece produced after year 1440 was selected, samples were extracted and specific preparations were made. Optical Microscopy and Scanning Electron Microscopy were performed in our laboratory. SR-FT-IR was performed through a European funded project in SRS-Daresbury Laboratory (UK). SR-FTIR is especially important for the identification of organic compounds, that is, the binders, varnishes and glues used. The altarpieces and samples selected and analysed up to now are indicated in Table 1. An example of the samples' preparations and some of the previous analysis is shown in Figure 1.

Table 1.

author	Altarpiece an wood carvingd	Year	Samples
Lluís Dalmau, ?-1460	La Mare de Déu dels Consellers	1443	D1 to D8
Jacomar (Jaume Baço), 1410-1461	L'aparició de la Mare de Deu a Sant Francesc a la Porciúncula	c. 1440	J1 to J6
Bernat Martorell, 1390-1452	Sant Vicenç de Menargues	1438-1440	BM1 to BM7
Jaume Huguet, 1412-1492	Sant Vicenç de Sarrià	c. 1440	JH1 to JH8
Anonymous	Museu Diocesà de Lleida	Last years 15 <sup>th</sup> century AD	MDL1 to MDL8
Anonymous	Saint John's sculpture carved on wood, plastered and painted.	Last years 15 <sup>th</sup> century AD	SJ1 to SJ6

Figure 1

Sample D8	Sample extraction	Sample	
Red			
Cross section			Optical Microscopy
			Scanning electron Microscopy
	LLUÍS DALMAU MNAC vermell 8		

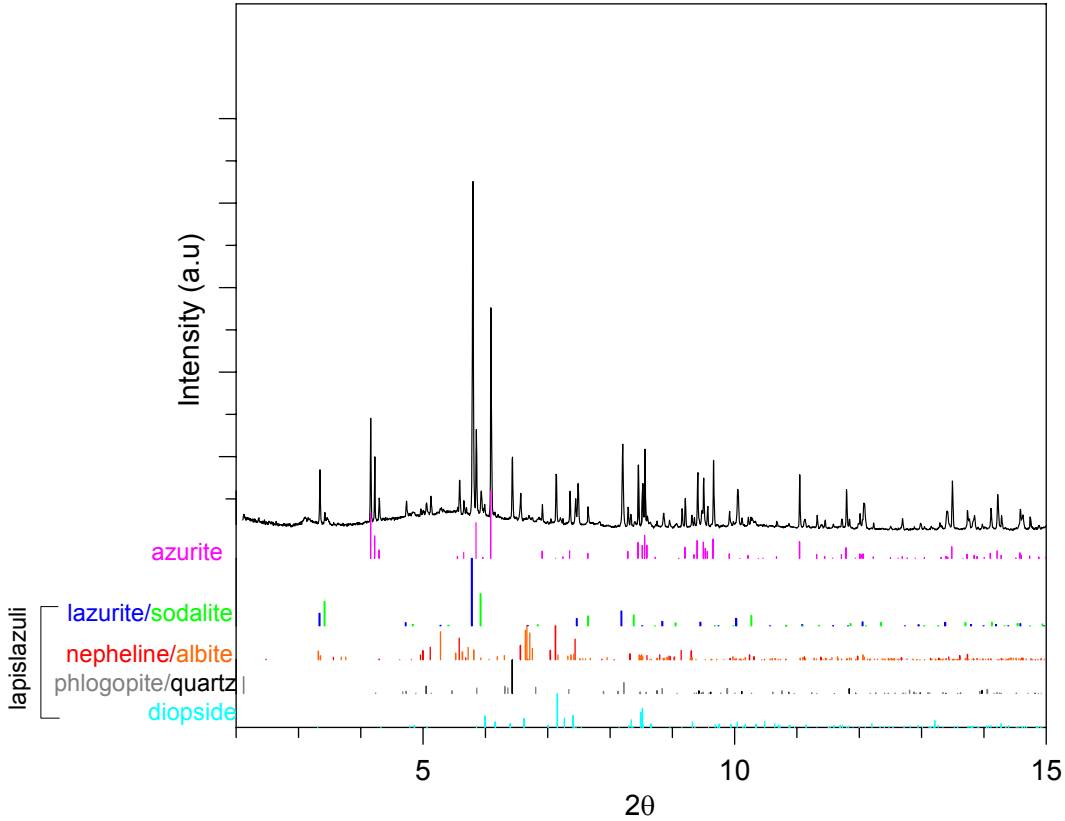
## 2. High resolution X-ray Powder Diffraction and X-ray Fluorescence of the ancient samples.

In the beamtime allocations we have performed High Resolution X-ray powder Diffraction of the samples. The high resolution of the detector has been fundamental in order to discriminate between the complex mixtures of compounds forming the paintings. The X-Ray Fluorescence detector has been also attached during the measurement and simultaneous Fluorescence analyses have also been obtained from the same samples.

As an example of the identification of compounds in the samples in Figure 2 we present the low angle region corresponding to the HR-PD from sample D3. This is a blue pigment formed by two successive layers of two different blue natural pigments: azurite, a copper basic carbonate  $\text{-Cu}_3(\text{CO}_3)_2(\text{OH})_2\text{-}$ , and lapis-lazuli, a blue rock formed by a mixture of minerals. In

our case we have unambiguously identified for the lapis lazuli, lazurite -  $\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2$ -, sodalite -  $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2(\text{H}_2\text{O})_2$ -, a Na rich nepheline -  $(\text{KNa})_3\text{Al}_4\text{Si}_4\text{O}_{16}$ -, albite -  $\text{NaAlSi}_3\text{O}_8$ - some quartz -  $\text{SiO}_2$ - and phlogopite -  $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$ -.

Figure 2.



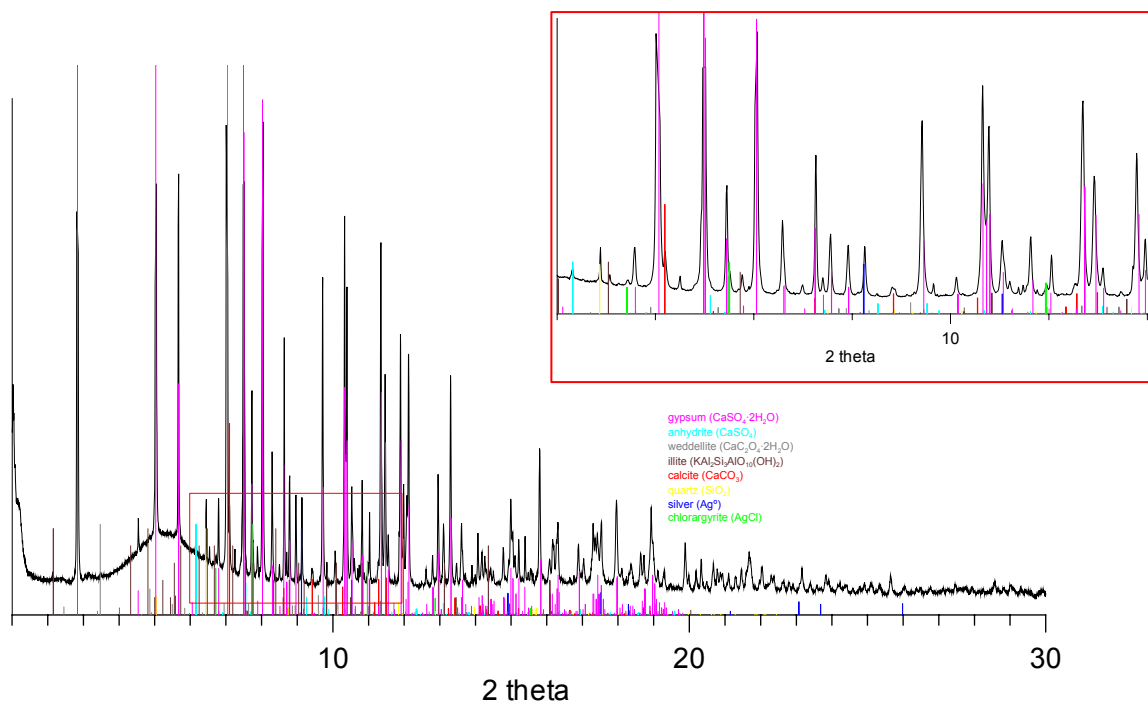
This mixture is characteristic of the lapis-lazuli natural deposits, for example from Afghanistan. Thanks to the high resolution of the detector it has been possible to

unambiguously identify the mixture of compounds. The quality of the data is high enough to Rietvelt refine it in order to determine the crystallographic parameters of the phases present and also their relative amounts, this is important allow us to compare to the natural lapis lazulis studied from the different geographic regions and therefore to relate the pigment to a source region.

Apart from the pigments, compounds associated to the pigments and present in very small amounts could also be identified. This is very important, because it can help in determining original sources if the pigments are natural, or the processes followed in their synthesis if the pigments are synthetic. The other pigments corresponding to the samples studied until now have also been identified. This will be published in a series of papers for the Museum Bulletin concerning each of the altarpieces studied (1,2). There, the identification of the pigments and binders is shown. This series of papers are dedicated to the Art Historians and Conservators. The first paper will appear in the next number of the Bulletin of the Museum and corresponds to the “Mare de Deu dels Consellers” from Lluís Dalmau. (1)

Moreover, the high resolution of the detector has been fundamental in determining not only the pigments but also reaction and aging compounds. The identification of reaction and also of aging compounds that appear in extremely small amounts is very complex, because the difficulties involved in their identification. There are no previous references on this subject in the literature, and we are writing a publication for a journal dedicated to Analytical Chemistry (3). Moreover, it is also very important for the Conservation of the art works. Figure 3 shows an example of the identification of the alteration compounds, it corresponds to the armour of one of the knights represented in the “Retaule de Sant Vicenç” from Jaume Huguet. The armours are plated with silver which appears completely altered. The presence of chlorargyrite (AgCl) as main alteration compound and other compounds has been possible thanks to the high resolution and sensibility of the detector.

Figure 3.



### 3- Reference materials. Aged compounds. Synthetic and reactions compounds.

A second objective of this first year was to measure a complete collection of reference materials, aged materials and synthetic materials produced in the laboratory but following ancient recipes. We have measured the whole set prepared up to now. We have also initiated

the production of reaction compounds. Some of the reference materials have been mixed with different binders (egg and oil) to study the reaction compounds formed during drying. We have already observed some significant differences in the reaction compounds formed using the different binders although the full drying process has not yet been accomplished. Therefore, new analyses will be performed during the next year in order to follow the drying process and the development the reaction compounds. Although some first results have already been obtained, this is a long term task; we expect to collect the three years data and obtain the reactivity of the pigments with the different binders and the resulting reaction compounds.

#### **4. Technical aspects.**

Up to now we have performed simultaneous high resolution powder diffraction and X-ray fluorescence measurements of submillimetric samples. We already performed some first tests to incorporate the Raman spectrometer to the beamline in order to perform simultaneous Raman Spectroscopy. Some modifications in the setup of the experiment have to be performed in order to incorporate the Raman spectrometer; we plan to do this next year. A second improvement will be the incorporation of a focusing device that will improve the sensitivity of the measurements because it will allow to measure small areas of the samples. This will also be implemented in the future.

#### **Publications:**

- (1) Nati Salvadó, Salvador Butí, Francesc Ruiz-Quesada, Hermann Emerich, Trinitat Pradell. **“The Madonna of the Councillors from Lluís Dalmau. A New painting technique for a singular Art work”**, Bulletin from The Museu Nacional d’Art de Catalunya (MNAC), *in press*.
- (2) Nati Salvadó, Salvador Butí, Francesc Ruiz-Quesada, Hermann Emerich, Trinitat Pradell. **“The altarpiece of Sant Vicenç from Menargues from Berant Martorell. The Florentine influence in the painting technique”**, Bulletin from The Museu Nacional d’Art de Catalunya (MNAC), *in preparation*.

And a series of three more papers concerning the other altarpieces that we will prepare sequentially.

- (3) Nati Salvadó, Salvador Butí, Hermann Emerich, Trinitat Pradell. **“Identification of reaction and aging compounds in submillimetric samples from 15<sup>th</sup> century gothic paintings”**, Analytical Chemistry, *in preparation*