Calcium oxalate formation in mural paintings: the case of three significative Catalan Romanesque churches (S.IX-XI)

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Introduction

Calcium oxalates are often found in most cultural heritage objects exposed at the open air. They form patinas, known as "oxalate patinas", mainly developed on marble and limestone [1-4]. A long and unsolved discussion arisen in the scientific community on the origin of such patinas. A set of researchers claim they have a biological origin by mineralisation and collapse of microorganisms while others consider oxalates as the remains of ancient treatments applied to the stone for protective and colouring purposes.

A third hypothesis considers a chemical origin as oxidation products of those organic substances applied as conservation treatments. It is well known that the degradation of organic compounds used as binding media and coating layers produce oxalic acid as one of the final by-products, which could react with calcium, already present in large amounts in the atmosphere, to produce calcium oxalate [2]. However, some authors believe less plausible to attribute oxalate formation to purely chemical reactions without any involvement of living-microorganism (lichens or fungi) [3].

Recent analyses made by this group based on X-ray diffraction using synchrotron radiation (Daresbury laboratory station 9.6) showed that calcium oxalates are also present in ancient paintings though they had always been kept inside a church or a museum [5]. In that case, as in Sant Benet del Bages, any effect of an ancient or present colonisation by microorganisms has been found on the painting layers. So that, it is really difficult to attribute the calcium oxalate to a bio-construction. Additionally, lichens produce calcium oxalate (always the di-hydrated form weddellite) that always appears as small well-shaped crystals (tetragonal pyramid and prismatic) sized from 5 to 10 microns [1,6]. On the contrary, calcium oxalates crystals found in patinas and painting samples are sized under the resolution of the Scanning Electron Microscope and both crystalline forms weddellite and whewellite can be found [2]. This suggests that they are not micrometric but nanometric. That would mean that calcium oxalate crystals are formed during the ageing process of the painting not as a methabolic product of lichens or fungi, as those products are above micrometers, but as decay product of the organic binding medium.

The challenge of the experiments was to obtain the spatial distribution of calcium oxalates and the distribution of organic material present in a set of selected samples of ancient paintings by means of SR-XRD and SIRMS to establish the relation between the presence of organic compounds and the formation of calcium oxalates. The key findings achieved by SR imaging techniques are that calcium oxalates present a differential distribution in each sample. Calcium oxalates appear in the layers in which some organic material have been reported or at least it would be supposed to be due to the know-how on painting techniques.

Experimental

The samples that were finally studied are described in the following table:

Sample	Characteristics	Description
SPT-B	Egyptian Blue ($CaCuSi_4O_{10}$) $CaCO_3$	Altarpiece of the Romanesque church of Sant Pere de Terrassa (Barcelona) S.X
SPT-O	yellow ochre ($Fe_2O_3.H_2O$) $CaCO_3$	
SQC-M	hematite (Fe_2O_3) $CaCO_3$	Mural painting of the Monastery of Sant Quirze de Colera (Girona) S.IX
SBB-A	gold $CaSO_4$	Cript of Sant Benet del Bages (Barcelona) S.XIII
SBB-B	azurite ($Cu_3(CO_3)_2(OH)$) Preparation layer: $CaSO_4$	
SBB-C	gold $CaSO_4$	

1. Imaging oxalate distribution by means of SR FTIR

A critical point in performing SR FTIR mappings in transmission mode is the sample preparation method as it is necessary to obtain samples thin enough to perform transmission experiments avoiding the complete absorption of the transmitted beam. Typical thickness for transmission measurements is 4-20 microns [7]. Few methods have been described to achieve such a thin painting sections. Among them, polishing a KBr pellet [8] and using a 5 steps method combining acrylic resin with epoxy one [9] have been reported recently. We tried by mounting the cross section in epoxy embedding media and then microtoming with a glass knife to produce a thin section that was placed directly (after being pressed between two diamond windows to flatten it) on a hole under the FTIR microscope. The experimental sample thickness was from 4 microns to 12 microns depending on the sample.

Synchrotron radiation Fourier transform infrared microspectroscopy (SR FTIR) was performed at the station ID21 at the European Radiation Synchrotron Facility (ESRF, Grenoble). Working conditions were modified depending on the sample thickness and absorption characteristics. Maps were recorded using 4 to 8 microns step and 50-40 scans for each spectrum. Aperture and resolution was were fixed at 8 x 8 μm and 8 cm^{-1}, respectively. In all cases the aperture and the step size chosen generates overlapping areas in order to increase the resolution of the components [7].

Synchrotron radiation source advantages for infrared microspectroscopy have been extensively and accurately described in bibliography [10-12]. However, this method requires an analysis window with a minimum size of 20x20 microns to acquire a spectra in the whole range 4000-350 cm^{-1}[7].

As we were mainly interested in the calcium oxalate distribution (and not in the characterization of the materials in each layer), we worked at 8x8 μm loosing the spectra under 1000 cm^{-1}.

Imaging of functional groups was determined by using OMNIC software (Thermo Nicolet Instruments) derived from the peak height of characteristic vibrational bands. Measuring peak heights or areas is the most straightforward way of identifying its location and concentration [12, 13]. However, as the spectra intensities of the characteristic peaks were clearly depending on the thickness of the sample, the multivariate methods of data analysis provided in the software were used to correct the maps obtained.

SR FTIR mappings of calcium oxalates were based on the distribution of the characteristic peak around 1320 cm^{-1} (OCO stretching). Few compounds exhibit such band [13] nor the epoxy resin thus (resin typical bands : 2958, 2932, 2871, 1738, 1458, 1408, 1380, 1256, 1161 cm^{-1}). In this case, to confirm the calcium oxalate identification, we could not image any other characteristic band attributed to calcium oxalate. The peak at 1620 cm^{-1} interfere with a band of gypsum and proteinaceous materials, and the characteristic band at 782 cm^{-1} was lost due to the aperture chosen.

Figure 1a shows a photomicrograph of the microtomed cross-section of SBB1 (12 μm). The rectangle marks the area selected to perform the FTIR mapping, b) chemical image of the oxalates band at 1320 cm^{-1} . The spectra have been recorded with a 8x8 μm aperture, 50 scans, 6μm step and 8 cm^{-1} resolution (area 102 x 174 μm). Calcium oxalates distribution in SBB1 seems to be restricted to the identified as mordant layers (layer 2,3) finishing at the beginning of the gypsum preparation layer (layer 1). On top of them there is a layer (layer 4) in between gold leaves.
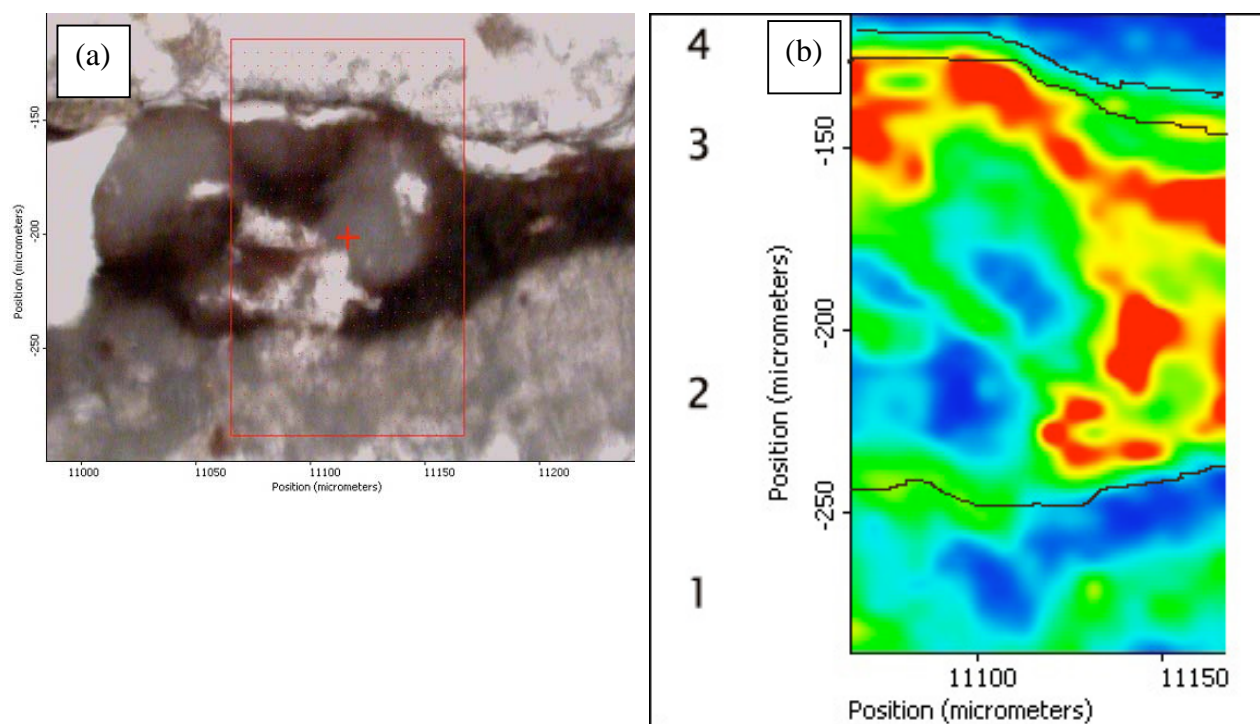

Fig 1.

2. Oxalate distribution in depth from SR XRD profiles

For SR XRD, sample preparation has been described in a previous work already published [5]: samples are embedded in polyester resin polymerised by a peroxic organic hardener under low humidity conditions and sectioned with a diamond saw of thickness 0,1 mm into a 200 microns thick slice.

SR XRD (Synchrotron radiation X Ray diffraction) patterns were acquired at station ID18F of the ESRF. A focal spot of 2,3 microns in the vertical direction and 11 microns in the horizontal one was chosen with steps of 2 microns in the vertical direction and 10 microns in the horizontal. A wavelength of 0,443A (28 keV) was selected and the acquisition time was 20seconds per pattern. The diffraction signal was recorded in transmission by means of a 2-dimensional CCD-based X-ray detector (refined detector distance 107,26 mm). The cross-section was placed into the focused beam with the paint layers oriented horizontally. In this position the sample was scanned both horizontally and vertically to obtain a map. Patterns were fitted with the ESRF FIT2D package [14].

DRX line scan on sample SBB1 is shown at figure 2. a) mineral phases distribution b) XRD patterns of scans 0, 10 and 30. (Gy) indicates gypsum [CaSO4·2H2O], (Min) minium [Pb3O4], (Wdd) weddellite [C2CaO4 ·2H2O], (HCer) hidocerussite [Pb3(CO2)2], (Rs) ramsdellite [MnO2], (Cer) cerussite [PbCO3], (Ill) illite [2K_2O ·3MgO · Al_2O_3 ·24SiO_2 ·12H_2O], (Mgh) maghemite [Fe2O3] and, finally, (AuM) gold metallic [Au].
There is a higher amount of calcium oxalates in the mordant layers (scan 10) and less in the preparation layer (scan 30). In the top gold-adhesive layer (layer 4) there is also weddellite but in less amount than in the mortdant layers, in agreement with the SR FTIR results.
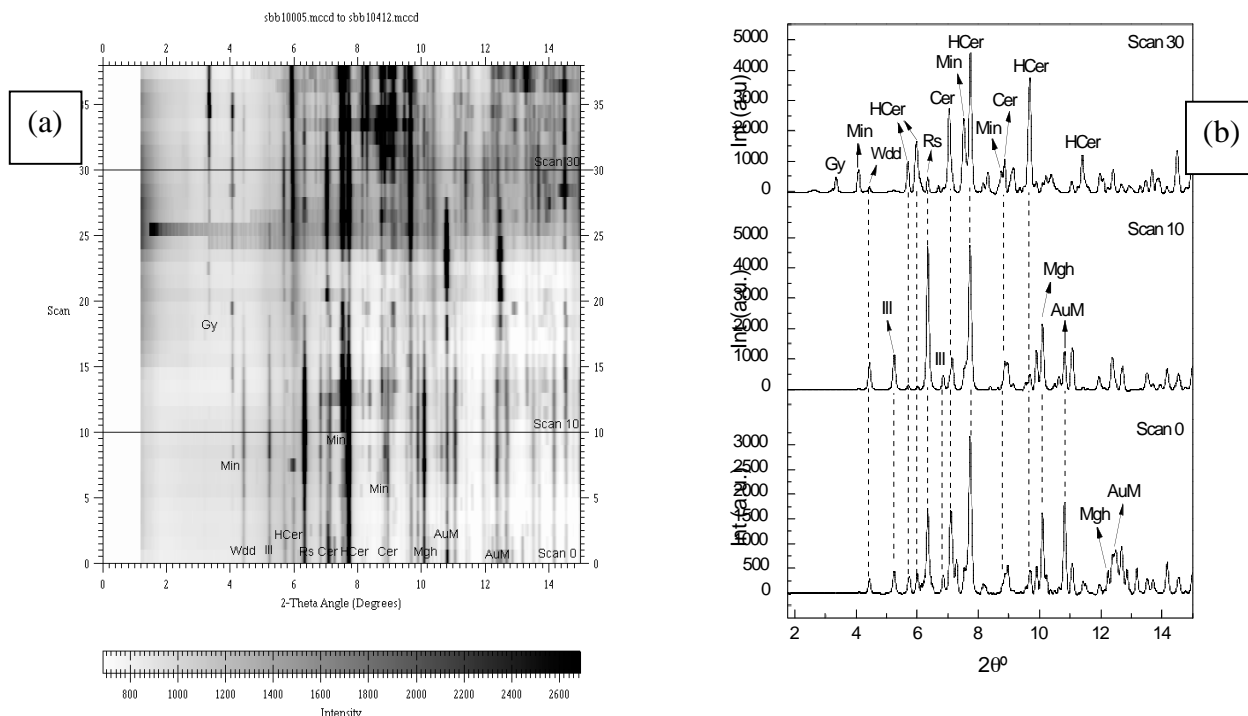

Fig 2

Results

SR FTIR mappings and SR XRD profiles allowed to obtain information on the distribution of compounds but also they add information to the standard characterisation results.

The use of SR XRD allows appreciating only the existence of the weddellite (calcium oxalate dihydrate [$CaC_2O_4 \cdot 2H_2O$]) by the presence of the peak 200. In those samples were there is a highest amount of calcium oxalate, both peaks 200 and 411 of weddellite pattern could be identified.

Calcium oxalates distribution seems to demonstrate the relationship between the presence of binding medium and their formation. It appears that the hypothesis considering calcium oxalates as a deposition of materials from the mineralisation and collapse of algae filaments from pollution can be discarded. They appear related to the presence of organic material.

Although resin peaks (2958, 2932, 2871, 1738, 1458, 1408, 1380, 1256, 1161 cm^{-1}) are distributed in all the range, some peaks of the main inorganic compounds such as gypsum or clays can also be distinguished. Apart from those inorganic components and the resin peaks, the absorption bands of the spectra are relatively broad and their intensity low. However, further examination of the spectrum obtained from some areas showed that it contained few additional bands (2850, 1715, 1548 cm^{-1}) that could be attributed to the organic materials already identified by conventional IR spectroscopy and were used to imaging those materials. Also, the typical distribution of the C-H st bands of the epoxy resin was sometimes altered indicating the contribution of other organic materials present.

The presence of other inorganic compounds is also easily identified and thus mapped. From these date the presence of copper oxalates and degradation products of pigments such as copper ones could be also be mapped.

Conclusions and future plans

It was impossible to embed the samples in a way that ensure the embedding agent not to penetrate in the painting layers avoiding contamination and erroneous spectra [10,17]. Although calcium oxalate can be easily differentiate as they have a very particular signal (around 1320 cm^{-1}), imaging the organic material present or just identifying it has been unachievable. Absorptions observed in our slices mainly correspond to inorganic compounds such as gypsum, calcite or kaolinite.

Another limitation of the technique is that a component cannot be reliably identified based on one IR absorption band. Thus, additional analyses (such as SR XRD or GC MS) are required to complement the map and provide interpretation [9].

Sample preparation process must be improved to obtain cross-sections with a bigger area avoiding holes, and thus more representative of the painting stratigraphy, at no more than 6 microns of width, and besides, avoiding resin penetration also. Then, the SR FTIR mapping mode would allow us to study calcium oxalates distribution and to relate it to the organic material distribution, obtaining the ratio of the organic bands and the calcium oxalate ones.

Finally, finishing the interpretation of all the data obtained and also the study of more samples by the techniques described above will be of interest to establish some kind of reliable hypothesis on

calcium oxalate origin and formation in painting samples. The analysis of more samples rich in oxalates will be the way to corroborate these first results and also to establish a general knowledge of oxalates distribution in all kind of painting samples.

As it has been already commented, new and complementary problematic have been established from the data obtained.

Publications

Some of the results obtained have been presented in the Synchrotron Radiation in Art and Archaeology congress (27-29 September 2006, Berlin).

A publication has been written based on the data obtained from the project EC38. The publication has been sent to the Journal of Applied Physics and has been accepted for publication. Other publications are still under preparation.

The title of the accepted paper is:

Weathering of gilding decorations investigated by SR: development and distribution of calcium oxalates in the case of Sant Benet de Bages (Barcelona, Spain)

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Abstract

On this paper gilding paintings of the 17th century decoration of the crypt of Sant Benet de Bages, a medieval monastery at the Catalonia region in Spain, near Barcelona, have been studied. Cross sections from two different gilded decorations have been studied by means of optical microscopy and electron microscopy and EDS to determine the statigraphy and elemental composition, and by means of FTIR coupled to a microscope to determine the binding media associated to each layer. These preliminary results demonstrated that a gilded area decorations were made by the application of a gold foil on a mordant substrate on a gypsum base, while the mouldings of the vaults seem to be gilding on a bol with a glaze on top of the gold leaf. It is interesting to notice that the first remained unaltered while the gilded vaults mouldings look almost black due to the darkening of the organic material. To elucidate the causes involved in the darkening of the sample from the vaults a set of Synchrotron μXRD and μFTIR experiments have been carried out on these samples at the ESRF (ID18F and ID21 respectively). High brightness and small spot working conditions, allowed revealing the development and distribution of calcium oxalates in the binding media, which seems to be responsible of the darkening. Results point out the fact that weddellite ($CaC_2O_4.2H_2O$) is the phase formed in those layers were organic material has also been identified or at least it would be supposed to be by bibliographic sources and not necessarily those superficial as it would have been suggested due to the similarities with patinas formation.

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