SR µ-XRF and SR µ-XANES Analyses on degraded Cadmium Sulphide Paint Samples

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The paintings of the end of the 19th-C and the beginning of the 20th-C form an interesting field of research as numerous new pigments were developed by the emerging chemical industry at that time. These new painting materials often out-classed the traditional pigments with regards to colouring intensity, purity, cost price, covering power, etc. These innovative, bright pigments opened up new stylistic possibilities and were soon picked up by progressive artists. In combination with some other technical improvements like the aluminium paint tube, this resulted in a new art movement characterised by clear, vibrant colours and live, outdoor painting. This movement, which was the direct result of interplay between artistic and scientific progress, is now known as impressionism.

However, not all of these modern pigments appeared to be chemically stable on the long term. This seems for instance the case for cadmium yellow, a cadmium sulphide compound invented by Stromey in 1818 and commercialised around the middle of the 19th-C. This pigment was initially produced from cadmium impurities which were derived from zinc ores. There were two processes known to synthesise CdS. The first one was a dry process during which Cd, CdO or $CdCO_3$ was heated together with sulphur. The result is CdS + SO_2 (in case of CdO) +CO_2 (in case of $CdCO_3$). The alternative was a wet process during which cadmium sulphide was precipitated from the reaction between a cadmium salt (chloride, nitrate, sulphate or iodide) with a soluble sulphide (H_2S, Na_2S or BaS).[1] Fading of the yellow colour and loss of adhesion has been reported by several authors, but the exact deterioration process remains a point of discussion[2,3].

Both in the Royal Museum of Fine Arts of Antwerp and in the Kroeller-Mueller Museum, degraded cadmium yellow was found on paintings of the Belgian avant-garde artist James Ensor (1860-1949). The surface of the yellow paint looks dull and flaky, has become brittle and displays cavities. However, the most striking feature is the formation

[1] Fiedler I. and Bayard A.B. 'Cadmium Yellows, Oranges and Reds'. *Artists' Pigments. A Handbook of their History and Characteristics. Volume 1*. National Gallery of Art, p.65-105.
[2] Fiedler I. and Bayard A.B. 'Cadmium Yellows, Oranges and Reds'. *Artists' Pigments. A Handbook of their History and Characteristics. Volume 1*. National Gallery of Art, p.65-105.
[3] Bronwyn, L., Burnstock, A., e.a. 'The Deterioration of Cadmium Sulphide Yellow Artists' Pigments'. *ICOM 14th-Triennial Meeting, The Hague*. 12-16 September 2005, p.803-812.

of whitish, semi-transparant protrusions on the surface. The chemical characterisation of both the white globules and the overall degradation process is obviously of great interest to conservators.

The conservators of both museums supplied scrapings of the surface of the paint containing white globules and some yellow paint. In the course of 2007, these samples were examined at the ESRF by means of SR µ-XRD at ID18F and SR µ-XRF and SR µ-XANES at ID21.

In Fig.1a, an example of the results obtained via combined µ-XRD and µ-XRF at ID18F is shown. It shows the distribution of anglesite ($CdSO_4$.H2O), otavite (CdCO3) and greenockite (CdS) throughout an assembly of grains isolated from one of the paint scrapings. The optical photograph of this scraping, shown on the right in Fig. 1 reveals that the yellow parts is where the original yellow CdS is remaining; also the otavite is present in this area. By contrast n the whitish/transparant grains, the CdS has transformed to $CdSO_4.H_2O$ via UV-licht induced oxidation in the presence of moisture.

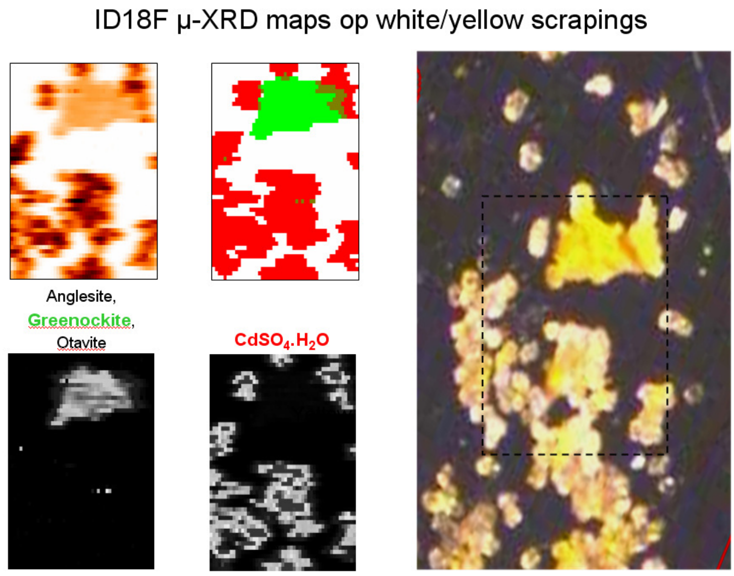

Fig. 1a: Left: intensity maps of different crystalline phases identified in yellow and white coloured areas of paint scrapings examined with scanning µ-XRF/µ-XRD. Right: optical photograph of paint scrapings.

Fig. 1b shows a number of XRPD spectra obtained locally at several positions within the scrapings. Next to greenockite ($CdSO_4.H_2O$) also another sulphate, nl . $(NH_4)_2Cd_2(SO_4)_3$ was found to be present in the oxidized areas.

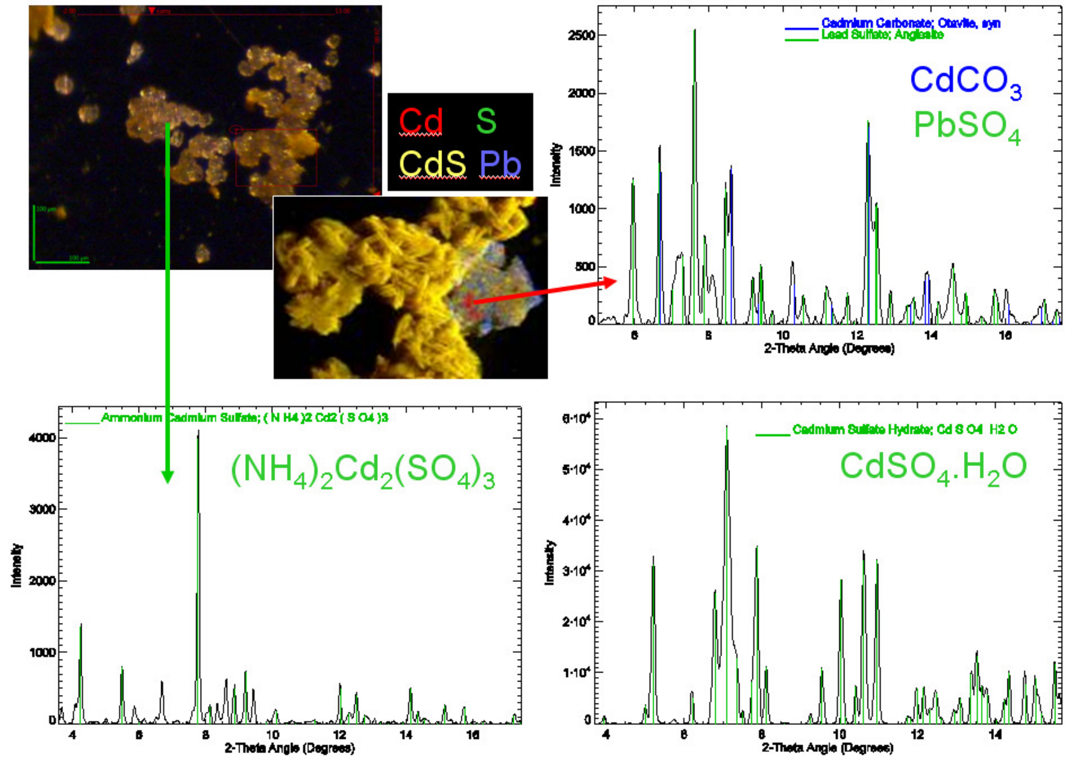

Fig. 1b: XRPD spectra from the indicated position in the yellow/white paint scraping indicating the presence of several crystalline phases apart from greenockite (CdS).

On the basis of these findings, already the major mechanism for colour change of the yellow CdS could be identified, i.e.:

$CdS + O_2 + H_2O \rightarrow CdSO_4.H_2O$

The XANES and XRF maps collected ina second phase at ID21 confirmed this hypothesis and allowed us also to obtain information on the depth of the oxidation front.

As Fig. 2 illustrates, elemental XRF maps on the scrapings demonstrated a homogeneous distribution of both S and Cd in the globules. Apart from Cd and S, the yellow parts also display Pb-rich zones. The Pb content is most probably due to the use of lead white, a lead carbonate which was commonly mixed with other pigments in order to lighten the hue of a colour.

In addition, the yellowish part of the scrapings also displayed small areas were Cd was detected in absence of S or Pb (red colour in the SR µ-XRF sum imag. SR µ-XANES analyses measured around the Cd-L3 edge, identified these Cd- rich parts as a cadmium carbonate, as demonstrated by Fig. 3. The presence of cadmium carbonate could be a residue of the starting product of the production process, provided that $CdCO_3$ was used as raw material to produce the CdS (see above).

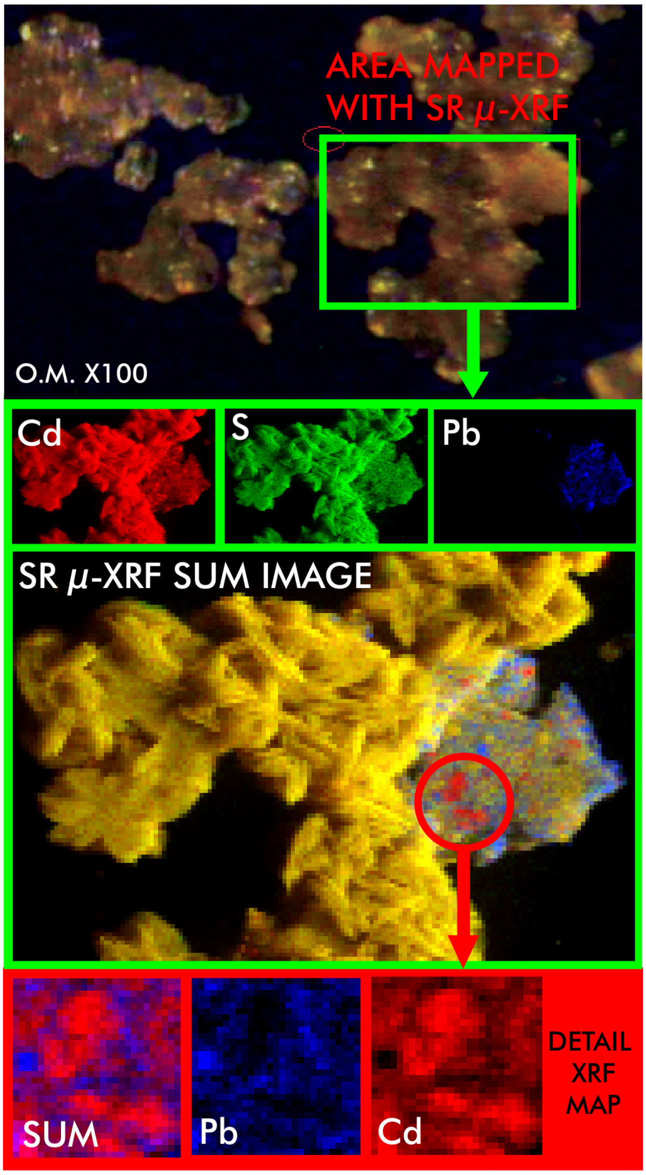

Fig. 2: top: Detail of the paint scrapings, optical microscope X100. An area containing both semi-transparent globules and yellow paint was mapped by means of elemental SR µ-XRF. below: the elemental SR µ-XRF maps. Cd and S seems homogeneous distributed in the globules, whereas the yellow paint area displays Pb and Cd rich parts.

In addition, SR µ-XANES spectra were recorded around the S-K edge with the aim of establishing the chemical state of sulphur. The spectra of the semi-transparent globules matched the reference spectrum of cadmium sulphate, which suggests that the degradation process is actually an oxidation of the CdS. The characteristic sulphate peak was also observed in the spectra derived from the yellow paint parts, but this was accompanied by a sulphide peak. This indicates that the yellow part still contains the original CdS, but is nevertheless degraded to some extent. In addition a degraded, yellow paint sample was cut in two, in order to allow analysis on a fresh cross-section. In this way it was possible to study the thickness of the degraded layer. The XANES map in Fig. 4 established the presence a layer of $CdSO_4$ of ca. 1-2 µm on top of the unaltered CdS bulk.

Although this research allowed determining the chemical state of the whitish protrusions on the surface, the exact mechanism of the degradation process remains unclear. For

that reason some samples were exposed to artificial ageing in order to study the formation of degradation products.

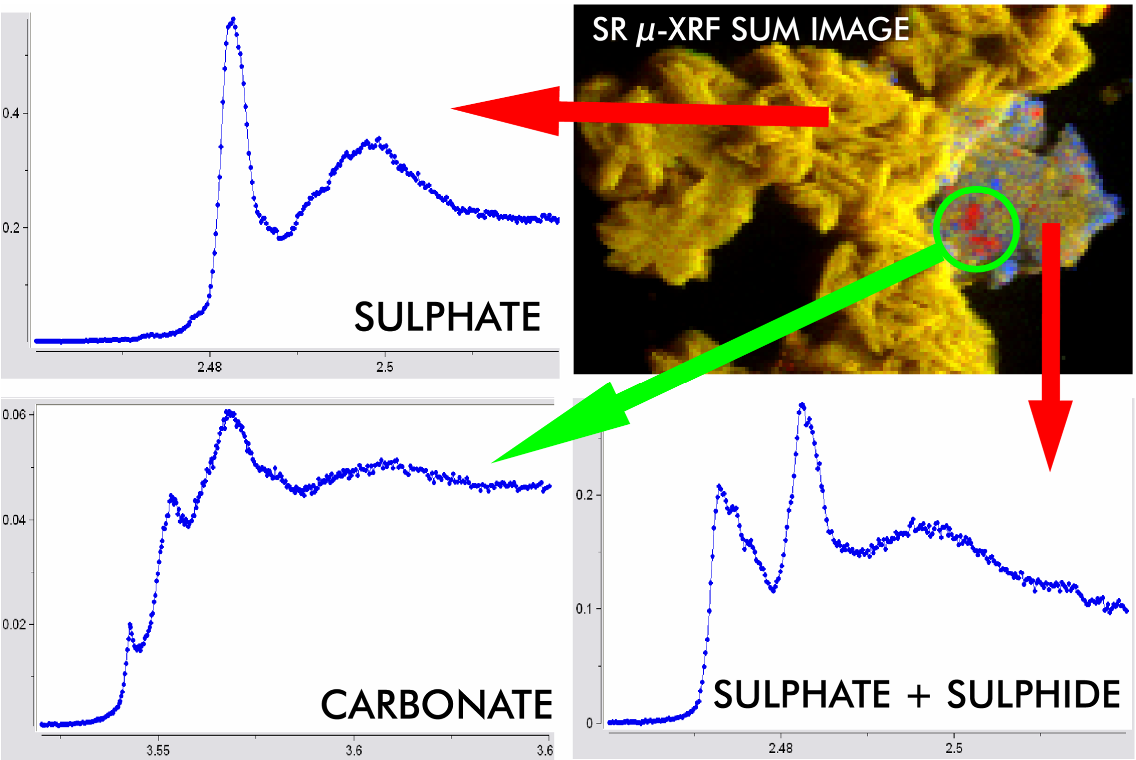

Fig.3: SR µ-XANES spectra demonstrate the presence of a sulphate in the semi-transparant globules (yellow on the SR µ-XRF sum image), a sulphate + sulfide in the yellow paint (right part of the SR µ-XRF sum image), and a cadmium carbonate in the areas where only Cd was detected (red areas in the SR µ-XRF sum image).

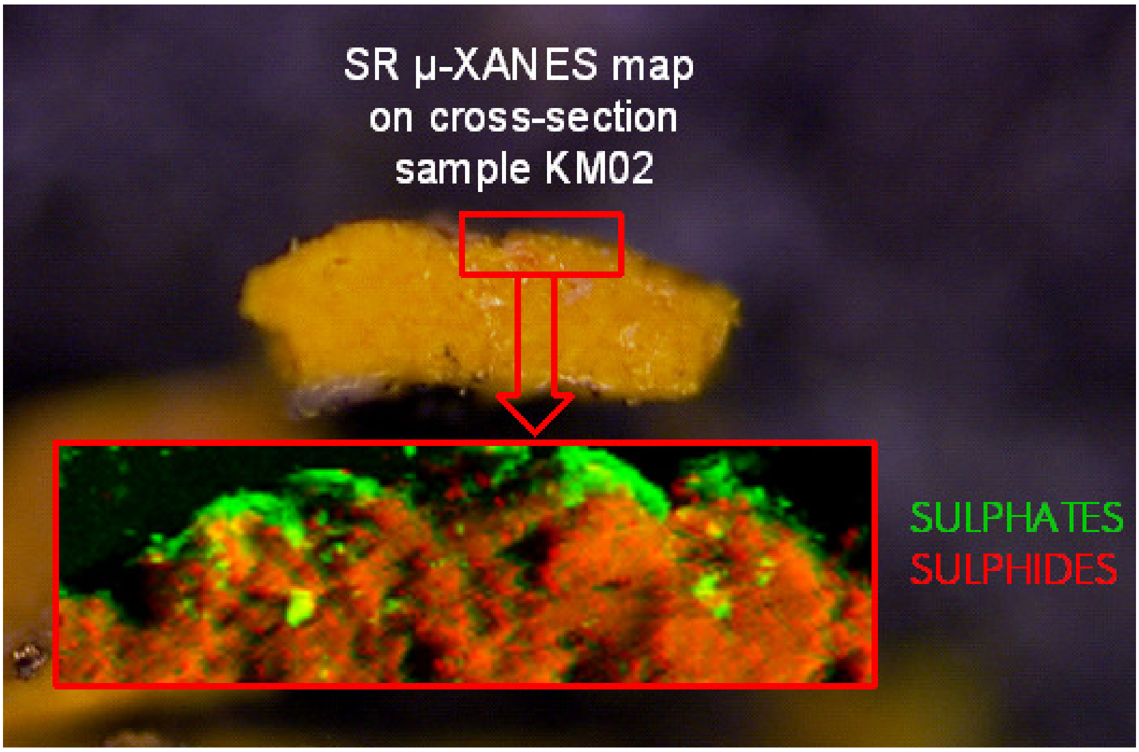

Fig. 4: SR µ-XANES map of a cross-section of a degraded paint sample. The degradation product (=$CdSO_4$) is limited to the upper micrometers of the paint layer.