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Micro-XRD analysis of reaction compounds of oil and egg tempera Gothic paintings

The drying oils used in the 15th century are either linseed or walnut oils. They include two poly-unsaturated fatty acids containing 18 carbon atoms, linoleic and linolenic acids, as well as, the mono-unsaturated oleic acid. They contain also about 8% of saturated acids, palmitic and stearic (C16 and C18 straight-chain monocarboxylic fatty acids). The drying and aging process results in a polymerisation by uptake of oxygen that free fatty acids may be produced.

Dried egg yolk contains two thirds of lipids and one third of proteins, resulting in different drying and aging processes from those that work with oil. The lipids are made up of one third phospholipids and two thirds triglycerides. These triglycerides contain two thirds unsaturated acids (~60% oleic, ~25% linoleic) and one third saturated acids, such as stearic and palmitic acids. Aging of the lipids in the egg yolk is the same as in the drying oil; an oxidative polymerization and, consequently, similar reaction compounds are formed. Consequently, drying and aging will produce similar free fatty acids in the egg yolk and in the drying oil.

The simultaneous presence of free fatty acids in the binders and metals, such as lead, calcium, copper or tin from the pigments and ground layers makes the formation of metal soaps predictable. In fact they are part of the drying process of the paint and therefore, they are always expected to form. In some cases those compounds affect the artwork to a large extend, (formation of protrusions) and it is in these cases that they have been identified. However, in most of the cases, and in particular, when they are not aggregated, their presence is hard to detect. In this study we identify the metallead, calcium and copper carboxylates formed in the different paint and ground layers from both 15th century paintings both with egg yolk and oil based binders. The presence of metal carboxylates has been reported in other studies, in particular in oil painting, in this study they have been non destructively identified and isolated in ancient egg yolk paintings. Moreover, it is the first time that these compounds have been identified by means of micro-XRD directly on ancient painting layers.

Oxalates are a type of salts usually found on the surfaces of artworks. However, their relationship to the degradation/weathering processes, although suspected, is still unknown. In this study, we determine the nature of the oxalates formed, in particular of oxalates of metals lead and copper apart from calcium and their distribution in the different chromatic, preparation and alteration layers. This is the first step necessary in order to ascertain origin of there oxalates and to establish the mechanisms responsible for their development and to relate their presence to specific degradation processes.

The samples analysed belong to altarpieces painted by the most important masters of the Crown of Aragó: Sant Vicenç de Menàrguens dated 1438-1440 by Bernat Martorell (1400?-1452), Sant Vicenç de Sarrià dated between 1455-1460 and El Conestable dated 1464 both by Jaume Huguet (141?-1492), La Mare de Déu dels Consellers dated 1443-1445 by Lluís Dalmau's (1428-1461) and L'aparició de la Mare de Déu a Sant Francesc a la Porciúncula by Mestre de la Porciúncula dated around 1450. They are on exhibit at the Museu Nacional d'Art de Catalunya in Barcelona. Finally, the altarpiece El

Conestable dated 1464 by Jaume Huguet is placed in the chapel of Santa Àgata in Barcelona.

The formation of calcium, lead and copper carboxylates in oil and egg yolk tempera from 15th century paintings has been demonstrated. These substances are part of the expected evolution and reactivity of the materials in the paintings. The non destructiveness, high brilliance and small footprint of Synchrotron Radiation and the combination of μ-SR-FTIR and μ-SR-XRD techniques have demonstrated to be particularly powerful for the study. Copper carboxylates are formed in copper based green paint layers, lead carboxylates in all lead containing paints and calcium carboxylates only when both, copper and lead are absent. The lead and calcium carboxylates formed are more crystalline with the egg yolk than with the drying oil.

The same metals, calcium, lead and copper also produce oxalates. Calcium oxalates are widespread on the surface, in the paint and ground layers. Their presence may be related to the degradation of the organic matter and reaction with the calcium from the environment or ground layer. Lead oxalates are formed in the yellow paints and copper oxalates in the green paints and, to a lesser extent, in the copper blue paint layers; they are also crystalline. The possible connection between their development and the formation of the corresponding carboxylates is still not clear. What is demonstrated is that calcium, copper and lead are the most reactive elements of the paint layers, forming both carboxylates and oxalates. The location, type and amount of carboxylates formed are consequence of the natural drying out of the paint. However, if a link between the formation of carboxylates and of oxalates is demonstrated, it may be one of the mechanisms of degradation that affects the paint preservation.

“Identification of reaction compounds in micrometric layers from gothic paintings using combined sr-xrd and sr-ftir “
Nati Salvadó, Salvador Butí, James Nicholson, Hermann Emerich, Ana Labrador, Trinitat Pradell
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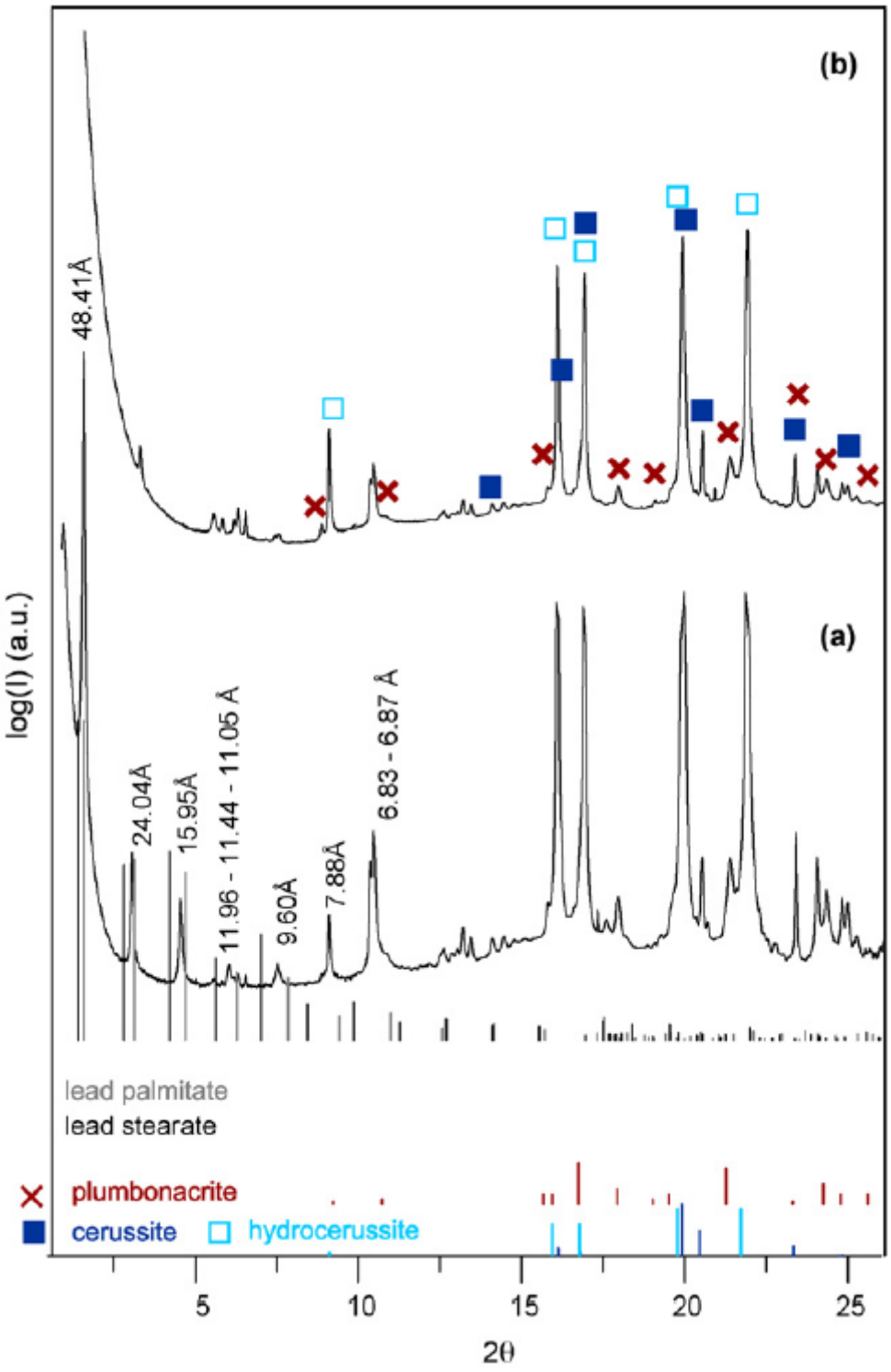
(b)
(a)
48.41Å
24.04Å
15.95Å
11.96 - 11.44 - 11.05 Å
9.60Å
7.88Å
6.83 - 6.87 Å
log(I) (a.u.)
lead palmitate
lead stearate
plumbonacrite
cerussite
hydrocerussite
5
10
15
20
25
2θ