ESRF	**Experiment title:** Alteration of vivianite pigments in paint layers of 17th century oil paintings	**Experiment number**: ME-1199
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Report:

Alteration and degradation of pigments on art works are important problems in the conservation of cultural heritage. Such alterations, caused by environmental influences or by chemical reactions within the painting layers, can lead to significant colour changes of an object. To elucidate those processes, knowledge of the exact chemical and structural composition of the affected pigments is essential. It is evident that taking samples from paintings is highly restricted. Therefore, novel and non-destructive micro methods especially for structural analyses on cross sections are of major importantance. In the present study the alteration of the blue pigment vivianite ($Fe_3^{2+}(PO_4)_2 \cdot 8H_2O$) is investigated using scanning SR micro diffraction. It is part of a long-term cooperation of the Technische Universität München, the Doerner Institut, Munich, and the University of Applied Sciences, Cologne.

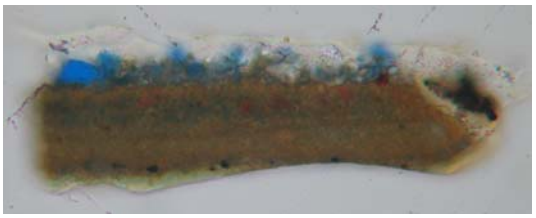
Until recently, the use of vivianite as a blue pigment was known only in the 12/13th centuries in art works mainly from Germany and the British Isles. The vivianite pigments on Medieval objects often remained unchanged until today. Recently, iron-phosphorus compounds have been identified (SEM/EDX) also on 17th century Dutch paintings (for example: Johannes Vermeer's famous painting *The Procuress* (1656)). In all these oil paintings the pigment underwent a striking change: it looses its colour and the originally blue or greenish pigment is now greyish or brownish.

The aims of the study was to find out if

- the pigment is the supposed vivianite or any other iron-phosphorus mineral (there are at least eight Fe-P minerals described in the literature)
- alteration products of the main phase can be identified to clarify the ageing mechanism. In literature the transformation from vivianite to metavivianite $Fe_{3-x}^{2+}Fe_x^{3+}(PO_4)_2(OH)_x \cdot (8-x)H_2O$ is stated.

Cross sections of three samples taken from paintings by Jan Vermeer (see above), Gerard Dou (The praying anchorite, 1646) and Cornelisz van Poelenburgh (Adoration of the shepherds, around 1650) has been investigated. All iron-phosphorus painting layers showed a loss of colour. In comparison, a fourth sample from a Medieval cross from Soest (Westphalia, Germany, around 1200) with an unchanged layer of vivianite (and orpiment) in egg tempera has been investigated. The samples were all embedded in epoxy resin, and

thin layers, mounted on glass, were prepared. The thin layers were investigated using a SR beam with λ = 0.9840 Å and a diameter of ca. 350 nm. SR micro diffraction easily allowed to examine single pigment particles in every painting layer individually.



Cornelisz van Poelenburgh (1586-1667*), Adoration of the Shepherds*; (Fig. 1, left). The robe of Virgin Mary is bleached by an alteration of vivianite and ultramarine pigments. The cross section (Fig. 2, right) shows the paintning`s startigraphy in the affected area (two underlayers of altered, changed vivianite and an upper blue ultramarine layer).

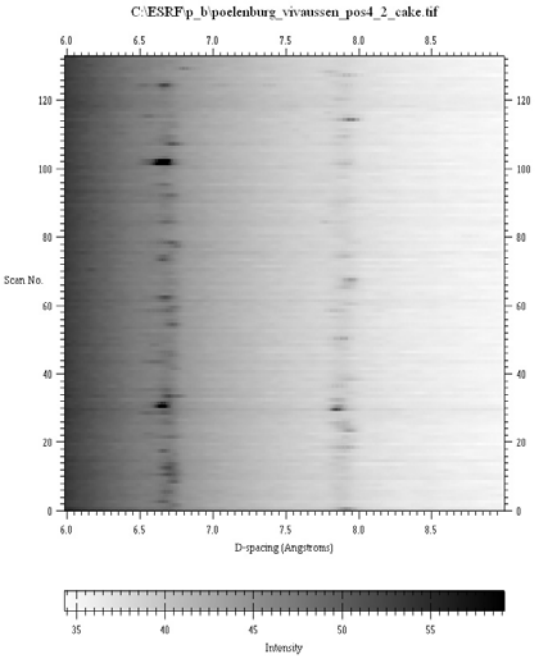


Fig. 3:
All single measurements of a line scan or a mesh scan through one layer were comprehended in a survey (left). This allows a reliable and quick inspection of the mineral phases present in the layer.The images shows the two most intense marker reflexes of vivianiteat d=6,73 and 7,93. Averaging of the single measurements and integration leads to a conventional plot of the pattern. Phases were identified by comparing with reference samples of iron phosphate minerals after geometry calibration with corundum.

First results

- µXRD was shown to be feasible for pigment identification on painting cross sections without damage of the probes by the SR beam. Further experiments on other pigments will be proposed, also with respect to optimized sample preparation and supports.

- The colour-changed iron phosphates could unambigously be identified as vivianite. Only one reference mineral from a fen in Northern Germany and, interestingly, the unaltered Medieval sample contained metavivianite beside vivianite. In addition, other pigments such as lead white and calcite could also be detected in the painting layers.

- The hypothese, that degradation and fading of vivianite in painting layers is exclusively caused by a transformation into metavivianite could not be confirmed by our study. Apparently, in oil paint a colour loss due to a $Fe^{2+} \rightarrow Fe^{3+}$ oxidation is also possible without destabilization of the vivianite structure.

Publication of this novel method and its first results is in preparation (*Studies in Conservation*).

Acknowledgements

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