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Temperature-related degradation and colour changes of historic paintings containing vivianite

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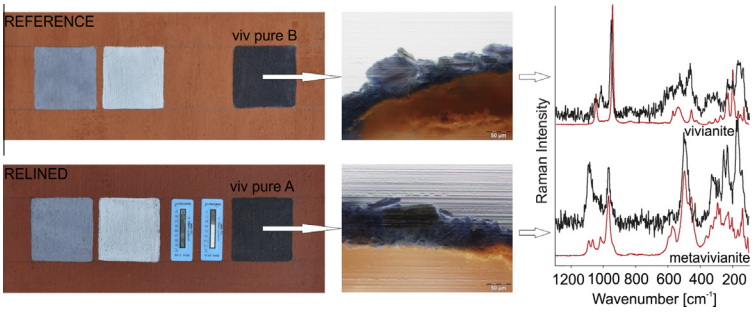
HIGHLIGHTS

- Temperature-related degradation of vivianite is presented.
- Already temperatures around 70 °C are harmful, 90 °C start vivianite's oxidation.
- At 80 °C, ground natural vivianite paint layer sample turns from blue to grey.
- The colour change corresponds with the one described in works of art.
- Conservation treatments using heat (like relining) should be performed with care.

GRAPHICAL ABSTRACT



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ABSTRACT

Temperature-related degradation of pure synthetic as well as partly oxidised natural vivianite has been studied by high-temperature X-ray diffraction (HT-XRD) covering the whole extent of the temperature-related stability of its structure. While temperatures around 70 °C are already damaging to vivianite, exposition to 160 °C results in complete amorphisation of both the vivianite and its oxidation products. As indicated by Mössbauer spectroscopy, temperature-induced oxidation of vivianite starts at 90 °C. To study the occurring structural as well as accompanying colour changes in more detail, model vivianite paint layer samples with different historic binders were prepared and subjected to increased temperatures. Exposition to 80 °C caused pronounced colour changes of all the samples: ground natural blue vivianite became grey – a colour change which has been described in actual works of art. Regarding the binders, the oil seemed to facilitate the transfer of heat to vivianite's grains. To simulate conditions of conservation treatment under which the painting is exposed to increased temperatures, oil-on-canvas mock-ups with vivianite were prepared and relined in a traditional way using iron. The treatment affected preferentially larger grains of vivianite; the micro-samples documented their change to grey, and their Raman spectra showed the change from vivianite to metavivianite.

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Introduction

Vivianite is a phosphate mineral ($Fe_3(PO_4)_2{\cdot}8H_2O$) with monoclinic crystal structure. In nature, it is found either in the form of crystals or various types of aggregates, commonly the earthy ones [1]. The colour of the crystals is often very dark with strong pleochroism [2], earthy vivianite ranges from light greyish green to saturated blue, frequently being light blue.

Vivianite has been used as a pigment for several centuries (documented usage in Europe ranges from 1050 to 1780) in various types of artworks: from polychromy on wood and stone to wall paintings, as well as paintings executed on wooden panels and canvases. The resulting colour of the paint with vivianite was usually blue (commonly in mixture with lead white, sometimes also with other blue pigments like azurite, smalt or ultramarine), more rarely green (e.g., in complex mixtures of pigments including yellow lake and yellow earth) [3].

Vivianite is a rare pigment and, so far, has been identified in only about eighty artworks; the majority of them originate in Germany and Austria. However, in the 17th century, the predominant country of origin of works with identified vivianite is The Netherlands, where this pigment was used e.g. in the famous workshops of Rembrandt van Rijn, Aelbert Cuyp or Jan Vermeer. Other documented works come from the Czech Republic (recently, vivianite was identified as a constant part of Jean George de Hamilton's palette – in seven of his canvas paintings), United Kingdom, Switzerland, Norway, Sweden, Lithuania and Romania [3–7].

In some of the artworks, vivianite has degraded and changed its colour to grey or yellowish brown. A pronounced colour change is described e.g., by van Loon [8] on the 17th century paintings located in the Oranjezaal in the Royal Palace of Huis ten Bosch (The Hague, The Netherlands) or by Spring and Keith [9] in the oil-on-canvas painting "The Large Dort" by Aelbert Cuyp (c. 1650).

So far, the external causes of the degradative changes of vivianite in the paintings have not been studied. It is known that the colour stability of vivianite is endangered by its tendency to oxidative degradation.

The current knowledge about vivianite's mineralogical oxidation series is following: vivianite (monoclinic) – metavivianite (triclinic) – Fe^{3+}-rich "metavivianite" (triclinic with different cell dimensions) – santabarbaraite (amorphous) [10]. This degradation is known to be accompanied by colour change from white to blue to, finally, yellowish brown; while white vivianite in pristine state in contact with air almost immediately starts to change to blue, it seems that the change to yellowish brown is a much longer process. The colour change can also be triggered by external conditions, e.g. increased temperature.

The temperature-related oxidation of vivianite can be profitably monitored by Mössbauer spectroscopy. One of the studies regarding vivianite as a pigment [11] describes the structural, colour and oxidation changes at the temperatures of 200, 300 and 800 °C. A more profound Mössbauer study of vivianite's oxidation by increased temperatures was performed by Hanzel et al. [12]. However, it is not clearly stated at which temperature vivianite starts to oxidise by temperature influence, a graph suggests value around 105 °C.

The structural changes of vivianite under increased temperatures were monitored e.g., by Tien and Waugh [13] in an X-ray diffraction (XRD) study of thermally treated vivianite. A high-temperature XRD (HT-XRD) study was undertaken by Poffet [14] in her thesis – she described the loss of intensity of the lines of vivianite diffraction pattern during storage at certain temperatures.

Based on the above-stated published data, it seems that temperatures around 70 °C may already be harmful for vivianite. Historic paintings containing this pigment can be exposed to such conditions, especially when inappropriately positioned on direct sunlight, or during relining – a common conservation treatment of canvas paintings, which consists of ironing a new canvas to the painting's degraded one from the back using, e.g., a mixture of wax and resin [15,16]. The wax-resin method has been widely used up to 1970s; since this period of time, the most wide-spread method of relining employed modern materials like BEVA 371 (a complex mixture of copolymers, synthetic resin and wax) or acrylic adhesives [17,18]. Nowadays, the traditional wax–resin or glue–paste relining whose side-effects may include canvas shrinkage (glue–paste) or darkening of the paintings (wax–resin) is applied more scarcely and in cases when the paintings have been previously relined by this method [18]. Unlike the hand irons, modern relining tables enable temperature control; however, earlier conservation treatments could exceed recommended temperatures. Furthermore, 70 °C is generally considered to be a safe temperature for the procedure [Igor Fogaš, restorer, pers. comm.].

To clarify the temperature-related behaviour of vivianite especially during the initial state of the changes, a high-temperature X-ray diffraction study was performed; the full range of the vivianite's structure temperature-stability is published for the first time. For this purpose, a synthetic vivianite was prepared by an adapted procedure. Subsequently, the damaging effect on vivianite of relatively low temperatures has been monitored by Mössbauer spectroscopy. Afterwards, experiments with vivianite model paint layer samples were carried out in order to study the dependence of changes of colour on structural changes that take place in the temperature interval up to 200 °C. To test and simulate the actual conditions that may cause vivianite's temperature degradation in works of art, oil-on-canvas mock-ups were prepared, and subsequently, relined in a traditional way. The changes were monitored by analysis of image histograms and micro-Raman spectroscopy.

Samples

Synthesis and reference vivianites

Synthetic vivianite for the experiments was prepared by a precipitation reaction. Since the reported procedures [19] led to multicomponent products (e.g., the recommended method of Evans resulted in a mixture of vivianite and spheniscidite, $(Fe_2(NH_4)(OH)(PO_4)_2{\cdot}2H_2O)$, the method has been adapted.

The precipitation reaction was carried out according to a general principle:

$$3Fe^{2+} + 3HPO_4^{2-} \rightarrow Fe_3(PO_4)_2 + 3H^+ + PO_4^{3-}$$

An appropriate amount of $FeSO_4{\cdot}7H_2O$ p.a. (Lachema Neratovice) was dissolved in 5 wt.% solution of H_3PO_4 (Merck) with a final molar concentration of Fe being 0.28 mol/l. A stoichiometric quantity of $Na_2HPO_4{\cdot}12H_2O$ p.a. (Lachema Neratovice) was dissolved in distilled water and added drop by drop by peristaltic pump (ca 3 ml/min) into the solution of $FeSO_4$ and H_3PO_4 under continuous magnetic stirring. The resulting mixture was then stirred until the following day under laboratory conditions. Subsequently, the bluish grey precipitate was left to settle for 24 h. The resulting product was separated by centrifugation and washed by distilled water. The centrifugation showed that the product is formed by whitish and blue precipitates with different density, therefore, they were separated by the centrifugation process. The final blue precipitate was left to dry on air under laboratory conditions and checked by X-ray diffraction as well as Mössbauer spectroscopy, which showed that it is phase pure vivianite with 15% of Fe^{3+}. The whitish by-product was found to be amorphous phosphate with 94% of Fe^{3+}.