Mössbauer spectroscopy of iron phosphate Fe$_3$(PO$_4$)$_2$(H$_2$O)$_n$ pigments

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Mössbauer spectroscopy of iron phosphate Fe₃(PO₄)₂(H₂O)₈ pigments

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Abstract. In this work the Fe₃(PO₄)₂(H₂O)₈ pigment was synthesized from a FeSO₄·7H₂O and digested during some time in a solution of hydrogen ammonium phosphate at 75°C. This compound of a light blue colour was heated at 200°C, 300°C and 800°C, changing their colour and characterized by X-ray diffraction, scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and Mössbauer spectroscopy. The Mössbauer results of the compound subjected to thermal treatment show only the occurrence of Fe (III).

1. Introduction
Commercial phosphates based pigments are widely used by art painters. The iron phosphate Fe₃(PO₄)₂(H₂O)₈ is used as oil, acrylic, temple and aquarelle pigment. It is a mineral that occurs naturally in the form of light blue-green crystals [1,2] There are different hydrated compounds of iron (II) phosphate. The blue pigment Fe₃(PO₄)₂(H₂O)₈ occurs as the vivianite mineral but, due to a progressive loss of water, Fe₃(PO₄)₂0(H₂O)₄ ludlamite, Fe₃(PO₄)₂(H₂O)₃ phosphoferrite and a monohydrate compound Fe₃(PO₄)₂H₂O are usually also formed[2, 3]. Alternatively, the vivianite may change to various other mineral species namely hydroxi phosphates, by an oxidation process, metavivianite or kertschenite Fe₂⁺Fe³⁺(PO₄)₂(OH)(H₂O)₂, ferrostrunzite Fe²⁺Fe³⁺(PO₄)₂(OH)₂(H₂O)₈ and allanpringite Fe³⁺(PO₄)₂(OH)₃(H₂O)₉ [2]. At this stage of chemical change all divalent iron is oxidized. Some of these chemical species have been early prepared and characterized by Mössbauer spectroscopy [4 – 6].

In this work a vivianite pigment was prepared and processed at 200°C, 300°C and 800°C and the following studies to the samples: structure X-ray diffraction, (EDX), microstructure and morphology, with scanning electron microscopy (SEM) and Mössbauer spectroscopy.

2. Experimental
The laboratory synthesis of vivianite was from a soluble iron compound, FeSO₄·7H₂O, and hydrogen ammonium phosphate (NH₄)₂HPO₄, made by starling digested in a solution at 75°C, for 30 minutes. The compound so obtained was a light blue precipitate in the form of crystals, formed under stirring. Crystals were washed with distilled water and dried at room temperature. The purity of this iron phosphate Fe₃(PO₄)₂(H₂O)₈ was checked by X-ray diffraction and elemental chemical analysis. The sample, then was heated at 200° C, 300° C and 800° C. The initial product obtained was of a light blue colour and during the thermal process there was a progressive change of colour in the following sequence: green, dark orange and light yellow.
The X-ray diffraction shows intermediate amorphous products at 200°C and 300°C due to a chemical alteration until a crystalline phase of ferric phosphate at 800°C was obtained. X-ray diffraction patterns were recorded using a Siemens D500 diffractometer and Cu Kα radiation. The study of the microstructure and morphology as well as the energy dispersive X-ray (EDX) analysis of the composition elements of these pigments was done with a scanning electron microscope (SEM) Jeol model JSM-5900LV.

Mössbauer spectra were obtained at room temperature using a constant acceleration Austin Scientific Associates S-600 spectrometer and a 370 MBq (10 mCi) ⁵⁷Co/Rh source; calibration was carried out using a natural iron foil and the spectra were fitted by using the NORMOS program [7].

3. Results and Discussion
The examination of the X-ray diffractograms revels the following evidences: vivianite is synthesized at 75°C, as a blue pigment, (Figure 1) and corresponding chemical formula is Fe₃(PO₄)₂.(H₂O)₈ indicates only the Fe²⁺ presence. However, Mössbauer spectroscopy shows two oxidation states due to the iron partial oxidation. This situation agrees with its chemical change by exposing the material to air or light, meaning the occurrence of in the chemical structure. [1].

![Figure 1. X-ray diffractogram of vivianite.](image1)

![Figure 2. X-ray diffractogram of ferric phosphate.](image2)

At 200°C vivianite completely disappears and the pigment becomes green at 300°C it changes to a dark orange colour and the corresponding X-ray pattern shows evidences of amorphous products with short range order and finally the sample processed at 800°C shows only a light yellow ferric phosphate, FePO₄, see figure 2. This means a chemical alteration during the thermal process. In these samples the divalent iron has been oxidized to trivalent iron. This is confirmed by Mössbauer spectroscopy, see figure 3. Some changes in vivianite are due to the partial oxidation of Fe²⁺ to Fe³⁺ by being exposed to air and light but with the thermal treatment total oxidation occurs.
Previous studies report that the laboratory synthesis of vivianite is complicated by the large number of Fe$^{2+}$ hydrates phosphates phases: ludlamite ($n = 4$), phosphoferrite ($n = 3$), two anhydrous forms, sarcopside and graphonite; one acidic ferrous trihydrate and two basic ferrous species [1, 3] with the tendency of solutions and powdered products to be promptly oxidize in air [2-6]. According to Matievich, it is relatively easy to prepare vivianite by various methods, particularly by the Evans [8] method, in which preparation usually avoids any contact with air. Nevertheless our synthesis, similar to the Evans method, was done in contact with air. In opinion of Rouzies and Millet [6] the concentration of approximately 50% of Fe$^{3+}$ corresponds to the limit of stability of the vivianite structure after 375 days.

Table 1. Mössbauer parameters at room temperature of vivianite synthesized and samples of thermal process.

| Compound                  | IS (mm/s) | QS (mm/s) | Spectral area (%) | Oxidation state |
|---------------------------|-----------|-----------|-------------------|-----------------|
| Fe$_3$(PO$_4$)$_2$.8H$_2$O| 1.102±0.05| 2.856±0.1 | 45.9              | Fe$^{3+}$       |
|                           | 0.317±0.01| 0.607±0.03| 54.1              | Fe$^{3+}$       |
| 200°C                     | 0.010±0.003| 0.622±0.03| 17.0              | Fe$^{3+}$       |
|                           | 0.351±0.01| 0.751±0.04| 83.0              | Fe$^{3+}$       |
| 300°C                     | 0.292±0.01| 1.146±0.06| 50.0              | Fe$^{3+}$       |
|                           | 0.310±0.01| 0.728±0.04| 50.0              | Fe$^{3+}$       |
| Fe PO$_4$                 | 0.011±0.003| 0.861±0.04| 9.0               | Fe$^{3+}$       |
| 800°C                     | 0.191±0.01| 0.623±0.03| 91.0              | Fe$^{3+}$       |

The Mössbauer parameters at room temperature, from table 1 show that the vivianite synthesized at 75°C contains 54% of high spin Fe$^{3+}$ and 46% of Fe$^{3+}$, the values for IS and ΔQ indicate that the Fe$^{3+}$ and Fe$^{2+}$ ions are in an octahedral or distorted octahedral coordination, also not having an internal magnetic field, vivianite is considered paramagnetic. In opinion of Mattievich [3] a precise structure determination reveals an extraordinarily complex atomic arrangement and the spectra differ notably from those of all the other ferrous phosphates an indicate the presence of Fe$^{2+}$ occupying three non equivalent sites in the crystal, the environment of two sites are distorted octahedral and the one is a
very distorted tetragonal pyramid. The Mössbauer results at room temperature, from table 1, after the thermal process at 200°C, 300°C and 800°C show only Fe³⁺ figure 4.

The blue coloration of partially oxidized vivianite is attributed to the Fe²⁺ → Fe³⁺ electron transition [1-3]. The vivianite blue pigment has been used by dipping it in to oil or sealing it with a thin coat of lacquer. It has been reported that the bulk of vivianite is more resistant to oxidation than the surface region. Figure 5, shows SEM microstructure of the blue pigment as agglomerates of fine particles and finally Energy dispersive X-ray (EDX) analysis on the vivianite, see figure 6, confirms the assumptions made from the X-ray diffraction pigment results.

![Figure 5. Microstructure of blue pigment (vivianite).](image)

![Figure 6. X-ray energy dispersive analysis of vivianite.](image)

4. Conclusions.
X-ray diffraction pattern corresponding to a blue vivianite pigment structure. Results by Mössbauer spectroscopy show partial oxidation, 54% of Fe³⁺ and 46% Fe²⁺. In the thermal process, the total oxidation occurs from 200°C to 800°C. Loss of water and reorganization of the chemical elements at 800°C results in a ferric phosphate structure. The microstructure of the blue pigment show fine particle size appropriate to be used by art painter.

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