Early viridian pigment composition found in paintings by Van Gogh and contemporary artists

Chemical and morphological characterisation of a vitreous (hydrated) chromium oxide borate pigment

S. Zumbühl, N.C. Scherrer — Bern University of Applied Sciences, Art Technological Laboratory

U. Eggenberger — University of Bern, Institute of Geological Sciences

A. Berger — University of Copenhagen, Institute for Geography and Geology

M. Gross — Fondation Beyeler, Riehen/Basel

E.S.B. Ferreira — Swiss Institute for Art Research SIK-ISEA, Zürich

Abstract Pigment analyses on more than 90 paintings dating between 1885 and 1943 have revealed that the majority of samples with viridian contain a spectroscopically conspicuous by-product. This has been observed in paintings by Van Gogh, Jawlensky, Kandinsky, Hodler, Amiet and Klee, as well as in samples from different historic color swatch tables. With the aim of tracking down the origin of this component, the so-called Guignet green, a variation of viridian produced by calcination, was systematically synthesised under varying conditions. The resulting products were characterised with different analytical methods. The pigment composition was identified as an amorphous chromium oxide borate $Cr_2O_3 \cdot (xH_2O)$-Cr_3BO_6-polymorph with variable ratios of its components.

Introduction The characterisation of Guignet green is of interest because of its widespread use in the late 19th and early 20th century. In contrast to modern viridian, earlier products are often associated with a process related by-product. To reproduce this type of pigment, synthesis was run under variable conditions (T and t), according to historic recipes.

Methods The resulting intermediate and final products were characterised applying Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, electron microscopy (SEM-SE and SEM-BSE), electron probe micro analysis (EPMA), X-ray diffraction (XRD), thermogravimetric analysis (TGA), polarised light microscopy (PLM) and colorimetry.

Pigment synthesis The results show, that the composition and morphology of the final products strongly depend on the maximum temperature reached in the range from 550-750°C **(Fig. 1)**. Furthermore, the duration of calcination directly influences yields and ratios of the reaction products and consequently the color of the final product. At temperatures ≥ 650°C insoluble boron by-products are formed which remain in the final pigment product. Insoluble chromium borate develops as a matrix, enclosing particles of chromium oxide **(Fig. 2)**. This reduces the uptake of water during the rinsing procedure and leads to variable proportions in the final pigment product (ratio of Cr_2O_3:H_2O:Cr_3BO_6). Thus, Guignet green is not a pure chromium oxide hydrate. In extremis, the borate content may completely inhibit access to the chromium oxide nuclei and prevent their hydration to chromium oxide hydrate. The resulting pigment can be characterised as a low water-containing amorphous chromium oxide borate $Cr_2O_3 \cdot (xH_2O)$-Cr_3BO_6-polymorph. It can easily be identified applying FTIR, based on two very strong and sharp signals at 1288 and 1252 cm^{-1} **(Fig. 3)**.

A nearly water free chromium oxide borate was found in a green paint sample of the painting „Les meules de blé“ (F. 809) by Vincent Van Gogh from 1890, painted in Auvers-sur-Oise. Of particular interest is the large size of the pigment particles (Fig. 4), which corresponds to the observation made with the products synthesised at high temperatures (Figs. 1-3).

Vincent Van Gogh, „Les meules de blé“, 1890, ca. 50x100cm, located at the Fondation Beyeler, Riehen/Basel, Switzerland

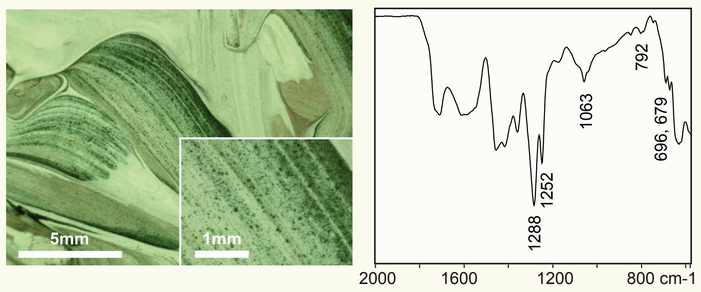


Fig. 4 Van Gogh „Les meules de blé“ 1890: Detailed view of coarse pigment (left) and FTIR spectrum identifying the green pigment as a Guignet green with a high chromium borate content (right)

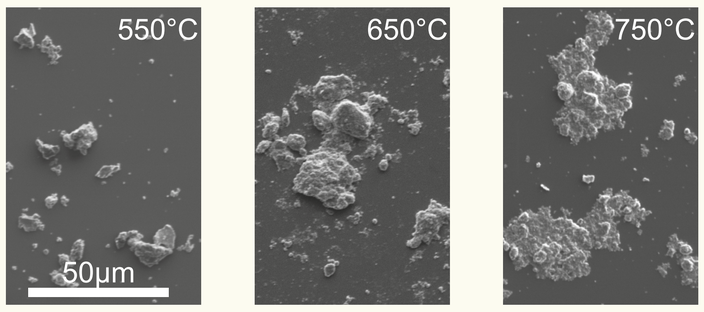


Fig. 1 Pigment morphology: increased cluster formation with rising calcination temperatures (SEM-SE)

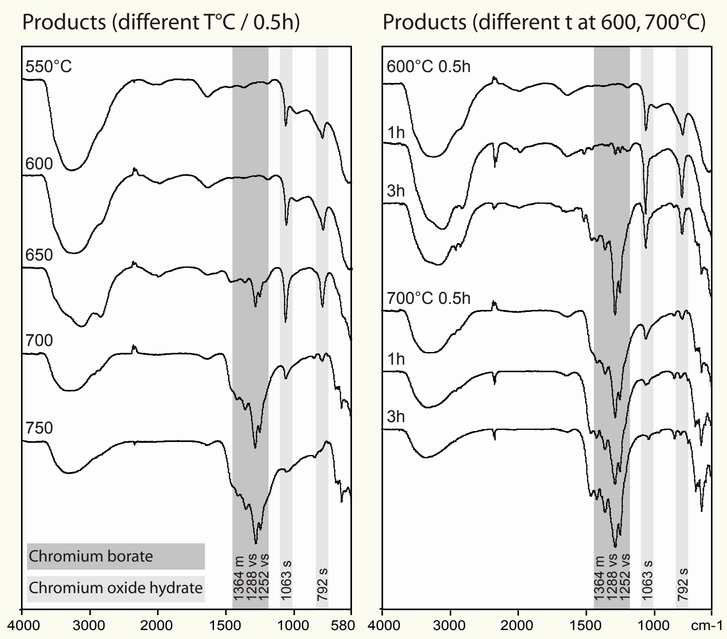


Fig. 3 Transmission FTIR-spectra series of the pigment products at different T°C and variable calcination times t

Findings in paint sample analysis Coarse chromium borate oxide pigment particles were found in a painting by Van Gogh **(Fig. 4)**. As it is associated with the manufacturing process, the documentation of the presence of the borate component in green samples can be extremely insightful. Studying the pigment composition of well dated paint samples may give quite specific answers to ancient pigment production. We have observed that calcination conditions in the past were highly variable. The current dataset is such that the use of paint from a specific production batch can be resolved in time, based on analyses of more than 60 samples taken from reference paintings of Jawlensky. Within the Jawlensky project this pigment information, in combination with other analytical and historical data, is being exploited for the authentication and dating of paintings.

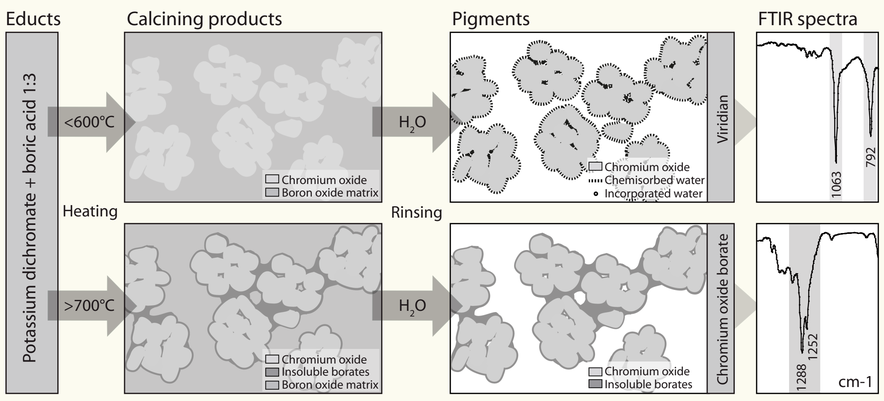
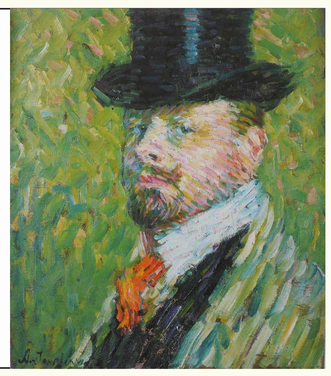


Fig. 2 Schematic diagram of the pigment formation process

Jawlensky Project

Alexej von Jawlensky (1864-1941) was a member of the „Neue Künstlervereinigung München“, the „Blue Rider“ and the „Blue Four“.

Since 2002 an independent and interdisciplinary Scientific Advisory Committee supports the Jawlensky Archive S.A. Locarno, Switzerland, to complete the Jawlensky Catalogue raisonné. So far, the data of 104 paintings has been collected of which over 60 have been specifically sampled with respect to Guignet green.



Bern University of Applied Sciences
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