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Microscopy AND Microanalysis

Monet's Painting under the Microscope

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Abstract: An oil painting by Claude Monet, *Port-Goulphar, Belle-Ile* 1887 (collection of the Art Gallery of New South Wales), was examined to determine both the identity of the pigments used by the artist in this painting and his technique of mixing colors and laying paint on the canvas. The extremely complex construction of the painting was revealed by optical microscopy, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDS), and X-ray mapping (XRM) analysis of cross sections of paint flakes excised from damaged regions of *Port-Goulphar, Belle-Ile*. Nine different pigments were found on the painting. Many of the identified colors were modern pigments that became available only late in the 19th century as a result of scientific advances in pigment chemistry. Although similar colors were available in a natural mineral form, they lacked the vivid color of their manufactured counterparts. The use of these new synthetic metallic oxide colors by Monet accounts for the brilliance of his paintings. In addition, a separation between successive paint layers was observed in some areas of paint chip cross sections, indicating that oil-based paint was applied to paint that had dried, and consequently, *Port-Goulphar, Belle-Ile* was painted over a long period of time. This observation is contrary to the general perception of Monet's technique of painting freely and quickly.

Key words: Claude Monet, optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, X-ray mapping

Introduction

The Art Gallery of New South Wales is conducting a comparative study of the painting techniques of Claude Monet (1840–1926), John Russell (1858–1930), and Henri Matisse (1869–1954). This work has focused on two artistic encounters between these three painters; the first in 1886, when John Russell met Claude Monet while they were both painting at Belle-Ile, an island in Brittany off the northwest coast of France, and the second in 1896–1897, when the young Matisse visited Belle-Ile and was befriended by John Russell, who moved permanently to the island in 1887. The aim of our on-going study is to determine if these two encounters between the painters influenced the painting style and technique of each painter.

The Art Gallery of New South Wales has a number of works by John Russell in its collection which have been previously studied, as well as a painting by Claude Monet, *Port-Goulphar, Belle-Ile* (Fig. 1). It is this painting by Monet which is the subject of this collaborative research project by the authors.

Energy dispersive X-ray spectrometry (EDS) is an established technique for the analysis of the chemical composition of paint layers in a scanning electron microscope (SEM). X-ray mapping (XRM) is the collection of character-

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Figure 1

Figure 2

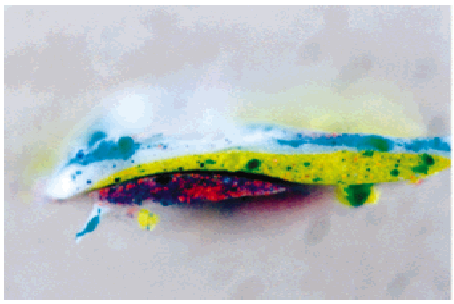
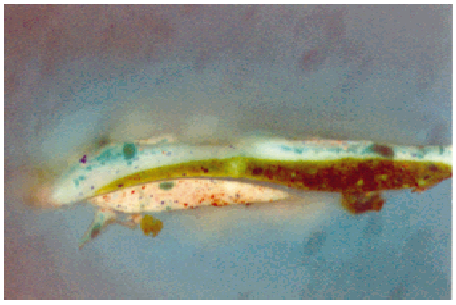


Figure 3



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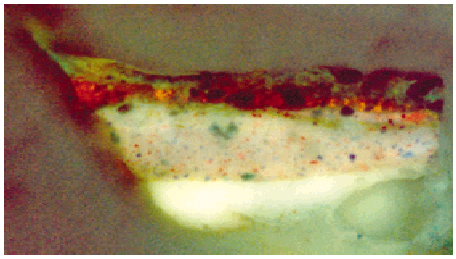

Figure 5

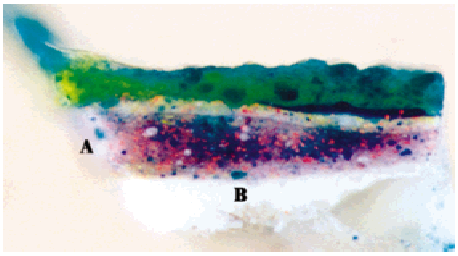

Figure 6

Figure 1. *Port-Goulphar, Belle-Ile* painted by Claude Monet in 1887 from the collection of the Art Gallery of New South Wales.

Figure 2. A magnified section of the lower right-hand side of the painting in Figure 1 showing the complexity of color used by Monet in this painting.

Figure 3. Optical micrograph with visible incident illumination of the cross section of a paint chip excised from the rock in the lower right-hand corner of the painting in Figure 1. Width of field is 360 μm.

Figure 4. Optical micrograph of the same paint chip in Figure 3 with ultraviolet incident illumination. Width of field is 360 μm.

istic X rays as a function of the position of the scanning electron beam on the specimen. This analysis provides a high magnification image related to the distribution and relative abundance of elements within a given specimen. This capability makes X-ray mapping particularly useful to (i) identify the location of individual paint layers, and (ii) map the spatial distribution of specific paint pigments within each layer.

Materials and Methods

Sample Preparation

Samples of the painting were taken from the edges of preexisting damaged regions. Tiny paint chips (approximately 400 μm in diameter) were embedded in polyester resin (Struers Serifix), matching the hardness of an aged oil paint film. These were sectioned with a microtome to reveal a cross section through all the paint layers.

Optical Microscopy

A high magnification light microscopy image (Fig. 2) of the lower-right area of the *Port-Goulphar, Belle-Ile* reveals the enormous variety of color within a small area of the painting. The exposed sections were examined by optical microscopy under both incident visible and ultraviolet illumination (Leitz Laborlux 12 Pol X; see Figs. 3 to 6).

The light microscopy study shows that some colors are mixed from a number of different pigments, while others are laid onto the canvas straight from the paint tube. For example, under normal visible (incident illumination) microscopy, the two types of blue used by Monet cannot be distinguished (Fig. 5). However, through the use of ultraviolet illumination, the two types of blue can be distinguished due to each blue pigment having its own characteristic fluorescence. For example, in Figure 6, French ultramarine appears very dark (area A), while cobalt blue appears pale in color (area B).

Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis

Prior to imaging and analysis in the SEM, the microtomed resin blocks containing the cross section of each paint chip were coated with 30 nm of carbon to prevent localized charging under the electron beam, using a Balzers CEA010 carbon thread evaporation attachment connected to a Balzers SCD020 sputter coating unit.

Each specimen was analyzed using a JEOL 6300F field emission gun (FEG) SEM equipped with a thin window Kevex light element EDS X-ray detector with Moran Scientific X-ray analysis and mapping system. Backscattered electron mode imaging at 25 kV was used to locate each paint layer as well as the various pigments within each layer. Quantitative EDS spot-mode X-ray analysis was used to identify each pigment type (Feller, 1986; Fitzhugh, 1997; Roy, 1993).

All X-ray maps were acquired at 25 kV in the JEOL 6300 FEG SEM. The beam current was set at 0.15 nA, providing a total X-ray count rate of 3000 cps. The FEG tip was "flashed" (cleaned) and allowed to stabilize for 20 min prior to the collection of each map. The probe current was measured before and after each X-ray acquisition to ensure that a relative change of less than 10% in the beam current was observed. X-ray maps were collected with 256 $\times$ 256 pixel resolution and a dwell time per pixel of 100 ms to obtain good counting statistics within the required beam stability requirement.

Results and Discussion

An optical image (visible incident illumination) of the cross section of the Monet painting sample is shown in Figure 3. The optical cross section reveals that this section of painting was painted by applying wet paint over dry paint, as revealed by the separation at the interface between the two

Figure 5. Optical micrograph with visible incident illumination of the cross section of a paint chip excised from the rock in the lower right-hand corner of the painting in Figure 1 from a region close to the paint flake in Figure 3. Note the noticeable difference in pigment distribution. Width of field is 360 μm.

Figure 6. Optical micrograph of the same paint chip in Figure 5 with ultraviolet incident illumination. Utraviolet illumination shows the presence of two different blue pigments, French ultramarine (region A) and cobalt blue (region B). Width of field is 360 μm.

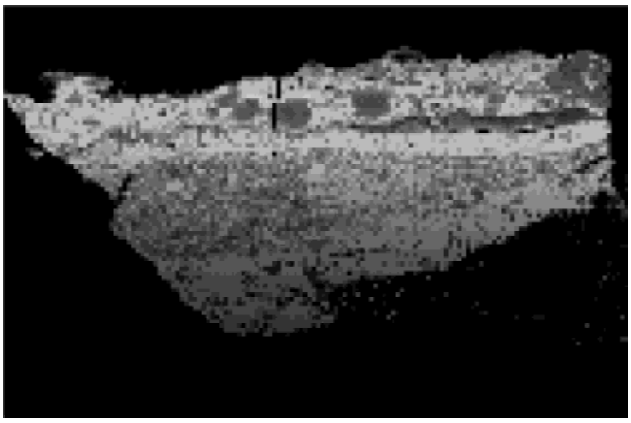

Figure 7. A backscattered electron image of the paint chip cross section excised from the lower right-hand corner of the painting showing the abundance of pigments used by Monet in this work. Width of field is 340 μm.

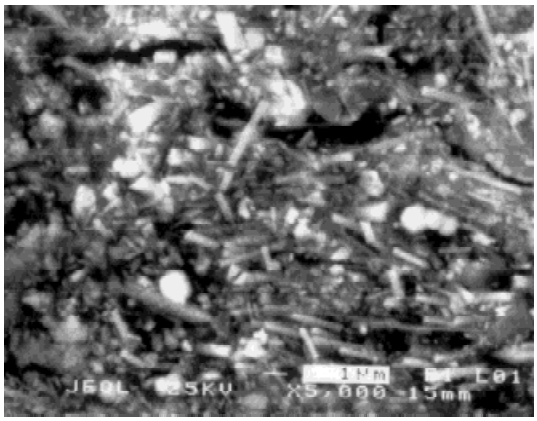

Figure 8. Backscattered electron image of a yellow section of the painting containing a rodlike pigment known as chrome yellow, a lead chromate ($PbCrO_4$ and $PbCrO_4 \cdot PbSO_4$). Width of field 23 μm.

layers. This observation indicates that Monet worked on this painting over a long period of time, as oil paints take a long time to dry, and this is contrary to the generally held belief that Monet painted quickly and freely. However, the optical images (Figs. 3, 4, 5, and 6) also show regions with no separation between the paint layers, indicating that these areas were painted wet paint over wet paint, while mixing the paints directly on the canvas.

A SEM backscattered electron image (Fig. 7) of a paint cross section shows the abundance of pigments used within a small section of painting. A high magnification backscattered electron image of a yellow region of the painting reveals that the areas contain rod-like pigments (Fig. 8), which contain lead, chromium, and oxygen. This pigment is known as chrome yellow, a lead chromate ($PbCrO_4$ and $PbCrO_4 \cdot PbSO_4$). Interestingly, the chrome yellow pigment was replaced by cadmium yellow late in the 19th century. However, *Port-Goulphar, Belle-Ile* seems to have a mixture (blended) of the two types of yellow pigment (chrome and cadmium).

Background corrected X-ray maps for aluminium, silicon, calcium, chromium, cobalt, copper, cadmium, mercury, and lead from a representative paint chip are shown in Figure 9. These maps, as well as extensive spot mode EDS analysis, were used to identity the following pigments: lead white [basic lead carbonate $2PbCO_3 \cdot Pb(OH)_2$], vermilion [mercuric sulphide HgS], cadmium yellow [cadmium sulfide CdS], chrome yellow [lead chromate $PbCrO_4$ and $PbCrO_4 \cdot PbSO_4$], viridian [hydrated chromium oxide $Cr_2O_3 \cdot 2H_2O$ or $Cr_2O(OH)_4$], emerald green [copper acetoarsenite $3Cu(AsO_2)_2 \cdot Cu(CH_3COO)_2$], cobalt blue [cobalt aluminate $CoO \cdot Al_2O_3$], and French ultramarine [approximately $Na_{6-10}Al_6Si_6O_{24}S_{2-4}$]. The complex distribution of these pigments within a paint chip cross section from the painting is shown in Figure 10.

Two organic lake colors (a dye precipitated onto an inert base) were also found in *Port-Goulphar, Belle-Ile*; a red lake (presumably madder) on an aluminium hydroxide base, and a yellow lake (unidentified) on a base of natural chalk sphericals.

This present work shows that Monet worked on *Port-Goulphar, Belle-Ile* with a limited number of pigments; two reds, three yellows (the yellow lake may be an impurity added by the color merchant to enhance the color of the cadmium yellow), two blues, two greens, and white. These pigments were premixed in an impressive number of combinations to give enormous variation in color on the painting. Some single brush strokes, such as those in the dark rocks, contained all 10 pigments mixed together. Subtle variations in color were achieved by slight alterations in the proportions of each pigment in the paint mix.

Conclusions

The combination of these microscopy methods used in this study enabled (a) the identification of each of the pigment types used in the painting, and (b) an insight into the paint application techniques used by Monet, in particular whether the paint was premixed or applied pure from the tube and mixed wet-in-wet on the canvas. The complex construction of the paint layers studied in this work confirmed that

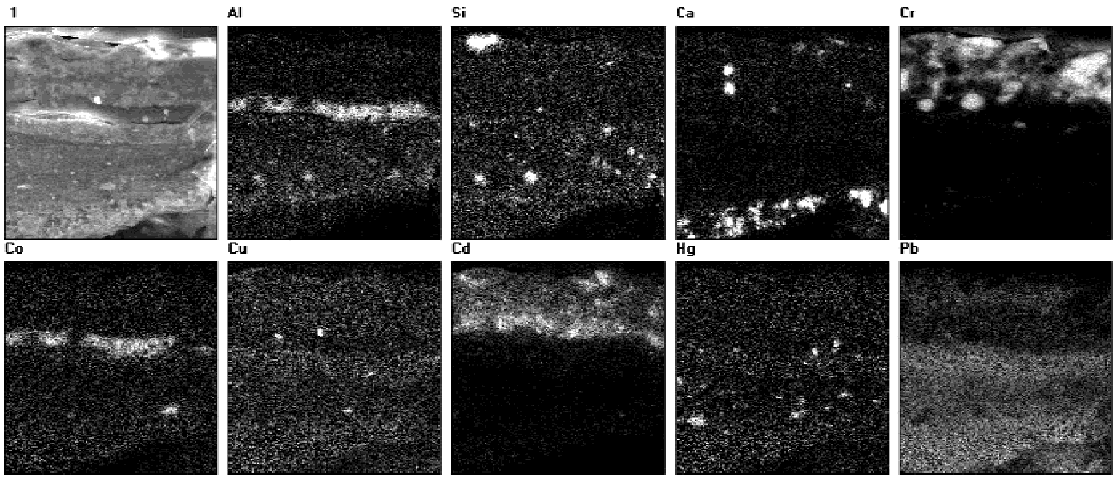

Figure 9. X-ray maps (XRM) for aluminum, silicon, calcium, chromium, cobalt, copper, cadmium, mercury, and lead from a representative paint chip cross section. Maps were collected at an accelerating voltage of 25 kV, beam current of 0.15 nA, 256 × 256 pixels and a dwell time per pixel of 100 ms. Width of field, 110 μm.

Figure 10. Optical micrograph image showing the complex distribution of pigments identified using EDS spot mode analysis. Width of field 50 μm.

Monet possessed a mastery of color through a deep understanding of the pigments available at that time. In addition, contrary to popular belief, certain sections of *Port-Goulphar, Belle-Ile* were painted over intervals long enough for the previously painted area to dry.

Acknowledgments

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