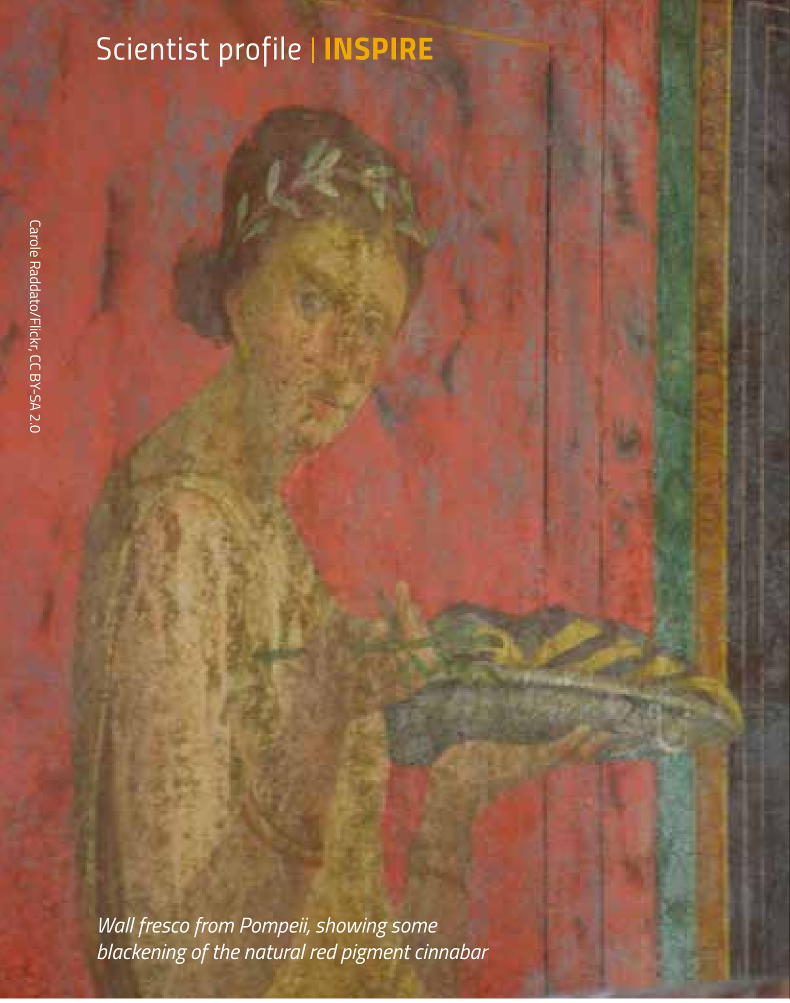
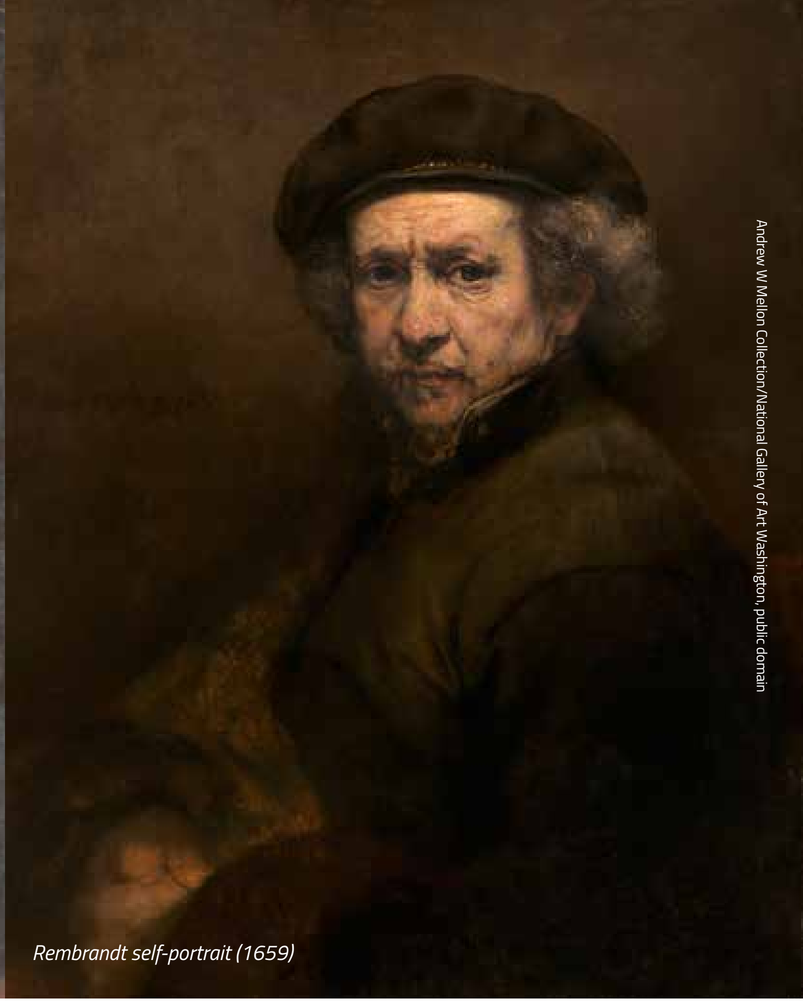


Wall fresco from Pompeii, showing some blackening of the natural red pigment cinnabar



Rembrandt self-portrait (1659)

Art and science from Pompeii to Rembrandt

Applying high-tech science to the study of ancient art and famous paintings has been a rewarding career choice for synchrotron scientist Marine Cotte.

By Montserrat Capellas Espuny

We sometimes think of art and science as two quite different areas of endeavour. But one person whose career challenges this view is Dr Marine Cotte, a scientist at the European Synchrotron Radiation Facility (ESRF)[w1] in Grenoble, France. Marine has always been fascinated not only by science but also by cultural heritage, and this has influenced her career from the very start. After studying chemistry at the prestigious Ecole Normale Supérieure de Lyon, for her PhD research she moved not to a university but instead to the Louvre Museum in Paris. In 2001, at the Centre of Research and Restoration of French Museums, situated in the basement of the Louvre, she began her research studies.

Ancient materials

As part of her thesis, Marine used advanced scientific techniques to study tiny fragments of ancient materials in some of the Louvre's collections. "Surprisingly, many of the antique cosmetics pots which are stored and exhibited at the Louvre Museum are made of lead compounds", she says. While today people would not like to find lead in their make-up, in earlier periods it was a common practice to use lead-based ingredients to prepare cosmetics – and also in pharmaceutical products. For example, the black eye make-up used by ancient Egyptians was generally made of galena (a lead sulfide mineral). And until the beginning of the 20th

Chantal Argoud/ESRF

Synchrotron scientist and art conservation researcher Marine Cotte

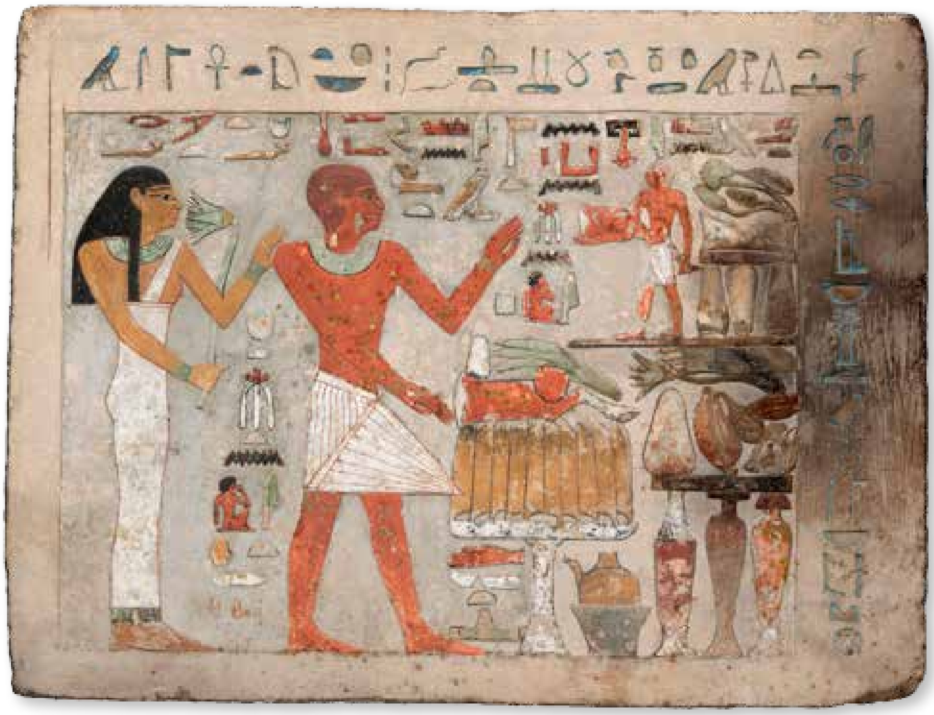
century, pastes used to treat burns or wounds were made by mixing fat or oil with a lead compound and various additional ingredients.

One technique Marine brought to her research at the Louvre was a new type of X-ray microscopy, carried out using the high-powered beam produced by a synchrotron – a very narrow, intense light beam ranging from infrared to X-ray wavelengths, produced in a dedicated research facility. Using synchrotron microscopes to study ancient materials was a rare approach in those days, but one Marine has carried on using with great success. She continued to study ancient arts for her postdoctoral research, moving to ESRF in 2004. While she has been based at ESRF ever since, her research has been truly international.

In one of her first research projects at ESRF, Marine joined forces with researchers from Paris and Pisa, Italy, to study the degradation of wall paintings in a house near the ancient city of Pompeii, which was buried when the volcano Vesuvius erupted in 79 AD. Scientists have been wondering for many years why the red paintings on the walls of Pompeii, made using the natural pigment cinnabar, turned black. This colour change was familiar even to the ancients: they attempted to prevent the problem by applying a protective varnish based on a substance called 'punic wax'.

Until Marine's research, the most widely accepted explanation was that, when exposed to light, cinnabar undergoes a change in crystal structure into metacinnabar, which is black. However, the experiments – performed on an X-ray microscopy beamline at ESRF – showed that this structural change did not happen: instead, the team found that two chemical reactions (one involving chlorine) were the cause of the blackening (Cotte et al., 2006). Ironically, the punic wax varnish may have hastened this change. "Chlorine probably comes from the neighbouring Mediterranean Sea and might even have been applied by painters, since punic wax was made using sea water", explains Marine.

"Rembrandt revolutionised painting with a technique called *impasto*, where thick paint makes parts of a painting protrude from the surface."



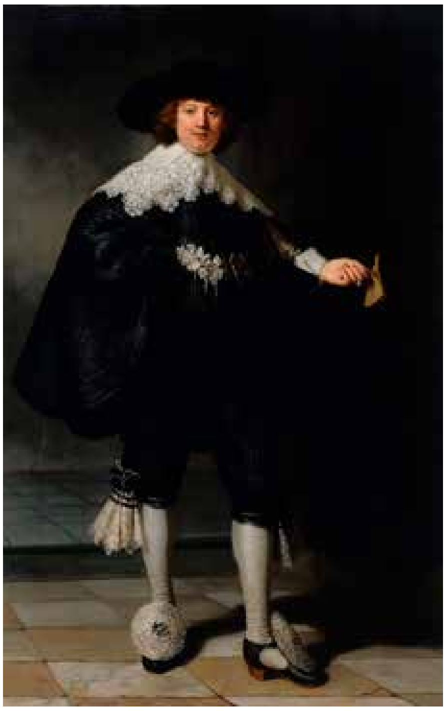
Museum Purchase Fund/Art Institute of Chicago, CC0 1.0

Amenemhat and his wife Hemet, c. 1900 BCE. Both the male and female figures depicted in this ancient Egyptian painting wear striking lead-based eye make-up.

Fine art investigations

The quest for what makes old and valuable paintings degrade has always been at the top of Marine's goals in her research. Such a question is fundamental if we want to preserve our artistic heritage in the best state for future generations, because understanding the chemistry involved can help conservators to minimise degradation. In 2010, Marine joined a collaboration with researchers at the University of Antwerp, the University of Perugia and the Van Gogh Museum in Amsterdam to study how the chrome yellow pigment has changed in van Gogh's paintings, especially in the *Sunflowers* series[w2] (Dik et al., 2008).

The Dutch connection did not stop there. In 2018, Marine began working on the paintings of the 'old master' painter Rembrandt, who epitomised the Dutch Golden Age of painting. Rembrandt revolutionised painting with a technique called *impasto*, where thick paint makes parts of a painting protrude



Rijksmuseum/ Musée du Louvre, public domain

Portrait of Marten Soolmans *(1634). Samples from this Rembrandt painting were used to study Rembrandt's* impasto *technique.*

from the surface, creating a three-dimensional effect and increasing the light-reflecting and textural properties of the painting. Rembrandt achieved the *impasto* effect by using materials traditionally available on the 17th century Dutch colour market – namely, the lead white pigment (a mixture of hydrocerussite, $Pb_3(CO_3)_2{\cdot}(OH)_2$, and cerussite, $PbCO_3$) and organic media (mainly linseed oil). However, the precise recipe of his *impasto* was unknown.

Marine assisted Victor Gonzalez, a researcher from the Rijksmuseum and the Delft University of Technology, to analyse tiny fragments from three of Rembrandt's masterpieces: *Portrait of Marten Soolmans*, *Bathsheba* and *Susanna*. Using ESRF's beamlines, they investigated the structure and composition of the *impasto* material on the micron scale. The outcome was the discovery that the *impasto* layers contained plumbonacrite, $Pb_5(CO_3)_3O(OH)_2$ – a lead compound that is extremely rare in historical paints, thus providing a distinctive chemical 'signature' of the material that Rembrandt used (Gonzalez et al., 2019).

"This was a real surprise because, before starting the experiments, we had absolutely no clue that our technique would detect any particular signature in the *impasto*", says Marine.

Prizewinning research

Beyond such important results for the art world, Marine's extensive international research has paid further dividends: in November 2018, she was awarded the Descartes-Huygens Prize, an award created in 1995 by the French and Dutch governments to strengthen Franco-Dutch scientific cooperation. The prize is awarded each year to two researchers – one in France, the other in the Netherlands – for their outstanding work and contribution to the two countries' bilateral relationship.

This award now allows Marine to travel regularly to the Netherlands – which is excellent timing, due to the current temporary shutdown of ESRF for an upgrade. "2019 is the perfect year to organise stays in the Netherlands and strengthen our collaborations there", says Marine. In addition to her ongoing research on painting techniques, she will be involved in the design and construction of a small, transportable 'table-top' synchrotron currently being built for use in the Netherlands.

> **"The outcome was the discovery of a distinctive chemical 'signature' of the material that Rembrandt used."**

Marine is also on a mission to convince members of the art world of what synchrotron science can do for them. "With my collaborators from Amsterdam and Delft, we hope to raise the awareness of Dutch cultural heritage actors – academics, museum scientists, curators, conservators, art historians – about the assets of synchrotron radiation techniques to study works of art", she says. As well as following up the research on Rembrandt and plumbonacrite, Marine and her colleagues hope to reveal the material secrets of other master painters – including the enigmatic Leonardo da Vinci – in their future research.

References

Cotte M et al. (2006) Blackening of Pompeian cinnabar paintings: X-ray micro-spectroscopy analysis. *Analytical Chemistry* **78**: 7484-7492. doi: 10.1021/ac0612224

Dik J et al. (2008) Visualization of a lost painting by Vincent van Gogh using synchrotron radiation based X-ray fluorescence elemental mapping. *Analytical Chemistry* **80**: 6436-6442. doi: 10.1021/ac800965g

Gonzalez V et al. (2019) Unraveling the composition of Rembrandt's impasto through the identification of unusual plumbonacrite by multimodal X-ray diffraction analysis. *Angewandte Chemie International Edition* **58:** 5619-5622. doi: 10.1002/anie.201813105

Web references

w1 Situated in Grenoble, France, ESRF operates the most powerful synchrotron radiation source in Europe. See: www.esrf.eu

w2 Learn how the X-ray techniques of ESRF explain the darkening of rich yellow in van Gogh's paintings. See:
Brown A (2011) Van Gogh's darkening legacy. *Science in School* **19:** 19-25. www.scienceinschool.org/2011/issue19/vangogh

Resources

Find out more about the study that revealed the secret of Rembrandt's *impasto* in this article on the Phys.org website. See: https://phys.org/news/2019-01-secret-rembrandt-impasto-unveiled.html

Read a press release announcing Marine Cotte as a recipient of the 2018 Descartes-Huygens Prize on the Koninklijke Nederlandse Akademie van Wetenschappen website. See: www.knaw.nl/en/news/news/descartes-huygens-prize-for-art-conservation-researcher-and-literary-scholar

Montserrat Capellas Espuny is a senior science communicator at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France.