

Why have Murillo's skies turned grey?

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The Heavenly and Earthly Trinities ('The Pedroso Murillo') the work of Bartolomé Estaban Murillo, one of the paintings from which micro-samples were taken for this study. The samples were taken from an area to the right of the child's head, in the middle of the painting. Credit: National Gallery, London

Smalt was one of the blue pigments the most commonly used by the artists between the 16th and 18th centuries. Unfortunately, this pigment is unstable and tends to fade with time. Researchers from the new European platform for research on ancient materials, the SOLEIL synchrotron, the National Gallery, London and the C2RMF found the key of this fading, described for four centuries. These results, obtained through the synchrotron analysis of microsamples of paint from works

by Baroque painter Murillo and other artists, have been published in the journal *Analytical Chemistry*.

Smalt is a pigment that was widely used by artists between the sixteenth and eighteenth centuries, among which were the painters Veronese and Murillo. To produce this pigment, a mixture of [cobalt](#) ore, [silica](#) (e.g. sand) and potash was fired to form a deep blue glass, which was then ground to a powder. The intensity of the blue colour depended on the fineness of the pigment particles and the cobalt content.

This pigment tends to lose its colour with time, resulting in drastic changes in the appearance of art works – a blue sky turned grey can completely distort the interpretation of a painting. By the end of the eighteenth century smalt was less commonly used, perhaps because other more stable artificial blue pigments had become available. To explain this discoloration phenomenon, described since the seventeenth century, several hypotheses have been advanced, but the exact physicochemical origin of this colour change has until now remained uncertain.

An original analytical approach to this question was developed by scientists at the CNRS, the SOLEIL synchrotron, the National Gallery and the C2RMF under the auspices of IPANEMA, the European research platform for ancient materials. This pigment discoloration is due to a change in the environment of the cobalt ions, which are responsible for the colour. These new results show that there is a direct link between the migration of potassium ions out of the [pigment](#) particles, a common process in glass alteration, and this change in coordination of the cobalt ion resulting in loss of the blue colour.

These results were obtained by analysis of microsamples from works in the [National Gallery](#) and the Louvre by X-ray absorption spectroscopy on the LUCIA beamline at SOLEIL synchrotron. The unique combination of the micron-sized X-ray beam delivered by LUCIA and

its broad energy range has been crucial in allowing individual smalt particles to be probed in the paint samples and as a result putting an end to an old mystery.

More information: “Investigation of the discoloration of smalt pigment in historic paintings by micro X-ray absorption spectroscopy at the Co K-edge”, Laurianne Robinet, et al., *Analytical Chemistry*. (2011)

Provided by CNRS

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