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Why have Murillo's skies turned grey?

Smalt was commonly used as a pigment by artists between the 16th and 18th centuries. Unfortunately the pigment has frequently degraded causing the paint to appear brown or grey. Researchers from the new European platform for research on ancient materials (IPANEMA)¹, the SOLEIL synchrotron (CNRS/CEA), the National Gallery, London² and the C2RMF (CNRS/Ministère de la culture et de la communication)³ found the key of this discoloration, 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 LUCIA⁴ 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.

¹ IPANEMA, UPS 3352 of the CNRS, at SOLEIL synchrotron, is a platform developed jointly by the CNRS, The Ministry of Culture and the French Museum of Natural History. This platform is constructed under CPER 2007-2013 by the State and the Île-de-France Region. IPANEMA, the National Gallery, London and C2RMF are members of the European Commission's CHARISMA project.

² The Scientific Department in the National Gallery, London

³ The Center for Research and Restoration of Museums of France (C2RMF), UMR171 of CNRS, is one of the main participants in the Ministry of Culture research program on heritage works.

⁴ The experimental station LUCIA is one of the 26 beamlines of the SOLEIL synchrotron, dedicated to micro-absorption and micro-fluorescence experiments in the "tender" X-ray domain.



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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.

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Bibliography

"Investigation of the discoloration of smalt pigment in historic paintings by micro X-ray absorption spectroscopy at the Co K-edge", Laurianne Robinet, Marika Spring, Sandrine Pagès-Camagna, Delphine Vantelon and Nicolas Trcera, *Analytical Chemistry*. (2011) - <http://pubs.acs.org/doi/abs/10.1021/ac200184f>

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