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SOLID-STATE NMR STUDIES REVEAL WHY ULTRAMARINE BLUE FADES

The 20-year restoration of Michelangelo's frescoes on the ceiling of the Sistine Chapel has left visitors in awe of the work's original majesty--notably the brilliance of the blue that graces the Last Judgment's sky. Recent investigations into this shade of blue--ultramarine blue--have brought to light the pigment's tendency to fade. Is it possible that the longevity of such a masterpiece as the Last Judgment could be in peril?



Figure caption:

The Sistine Chapel's "Last Judgement" Ultramarine pigments have been used pervasively by artists starting in the late 13th century. Jerschow, Del Federico and coworkers provide key insight on why and how color fades in ultramarine pigments.

Researchers at New York University and Pratt Institute now have the answer to why it fades, which gives the art world direction on how to protect the works of past and future masters.

The natural ultramarine pigment, obtained from the semi-precious stone lapis lazuli, has been one of the most valued pigments by European painters since the late 13th century. Before the 19th century, the only known source of lapis lazuli was in the quarries of Badakhshan (northeastern Afghanistan), a site visited and described by Marco Polo. He wrote: "There is a mountain in that region where the finest azure [lapis lazuli] in the world is found. It appears in veins like silver streaks." Lapis lazuli provided not only a vibrant blue color unmatched by any other pigment available at the time, but it added a divine nature to the artwork in which it was used. Since it was valued more highly than gold, its use typically conveyed the high status of a work's commissioner. Ultramarine was the pigment often reserved to paint the mantle of the Virgin Mary.

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Instances of fading of ultramarine pigments are known, but the mechanism of color alteration of the pigments is not understood--a process that served as the focal point of the researchers' study. In their work, Alexej Jerschow, an assistant professor of chemistry at NYU, Eleonora Del Federico, an associate professor of chemistry at Pratt Institute, and their co-workers examined ultramarine pigments, which are made up from frameworks of aluminum and silicon atoms. The intense blue color is formed by small molecules made up from sulfur trapped within this framework. The researchers found that upon color degradation the framework breaks apart and releases the color-forming molecules.

The research team reached this conclusion by measuring the nuclear magnetic resonance (NMR) signals of the aluminum and silicon atoms in the framework. This method is akin to magnetic resonance imaging, but is used by chemists to understand the structure and geometry of molecules and materials. This procedure allowed the researchers to determine the concentration of these color-forming molecules. Similar analysis prepared in conjunction with Prof. Licio Isolani from the Department of Fine Arts at Pratt of fresco samples stored under accelerated degradation conditions revealed that the ultramarine pigment framework structures break apart and set free the color-forming molecules. Understanding the process by which ultramarine blue fades will allow further research to identify proper art conservation techniques.

“Apart from the scientific interest in this work, these activities have created an exciting opportunity for both science and arts students to transcend discipline boundaries,” said Jerschow. “These unique investigations promise to have tremendous impact on our understanding and prevention of the chemical processes that underlie the slow—often irreversible—decay of our cultural heirlooms.”

The research on ultramarine pigments is part of a larger collaborative initiative among the NYU Chemistry Department, Pratt Institute, and the Metropolitan Museum of Arts' associate research scientist Dr. Silvia Centeno. The research team is currently also investigating the origin of lead-white flaking in illuminated manuscripts and lead-soap formation in traditional oil paintings.

An important aspect of this work is related to bringing the experimental techniques right into museums, a revolutionary step that will allow researchers to analyze delicate material onsite so as to maximize conservation while protecting unique works of art.

With funds from the Alfred P. Sloan Foundation, Pratt Institute acquired a portable NMR micro-spectrometer for on-site analysis both at Pratt and at the Met under the supervision of Del Federico and Centeno. While the technical capabilities of this instrument are more limited than for regular NMR spectrometers, the portable device allows one to investigate artwork non-invasively. In-situ NMR analysis will be conducted on the Metropolitan Museum of Art's collection beginning this fall under the supervision of Centeno. This component will investigate this new technology's potential application to the study of ink and paint materials in paper and parchment, as well as its ability to characterize the degradation processes.

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