Scientists develop a new approach to help optimize marble conservation

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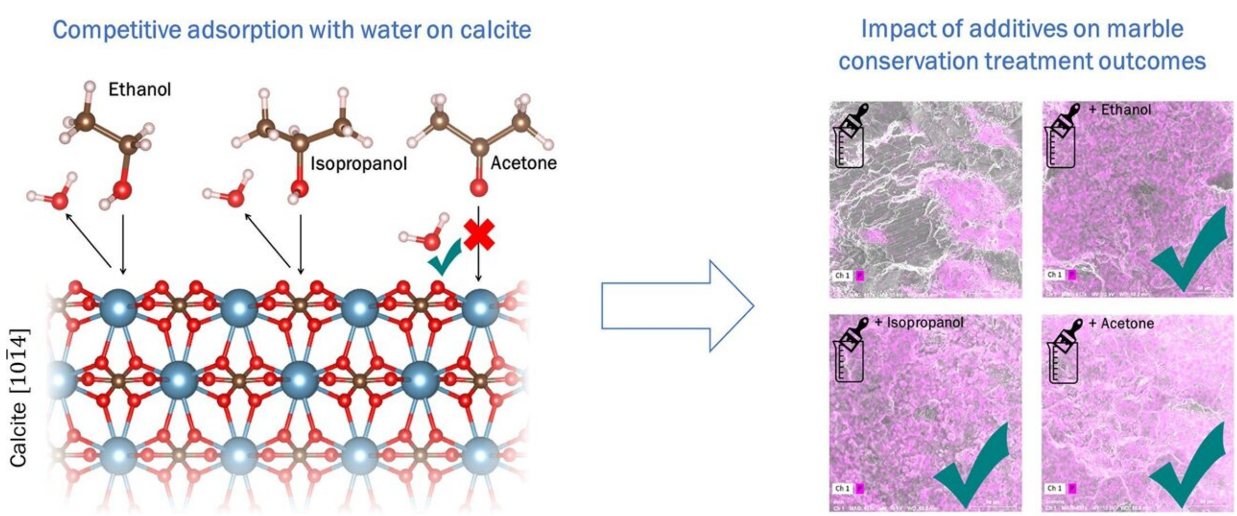

Graphical abstract. Credit: *Applied Surface Science* (2023). DOI: 10.1016/j.apsusc.2023.156438

Scientists have used a novel approach that could improve how artifacts made from marble are preserved.

In the study, published in *Applied Surface Science*, a team from UNSW Sydney and The University of Bologna, Italy combined computational modeling with experimental methods to measure whether different organic solvents like alcohol could improve a protective treatment used for marble preservation. They found that while the range of solvents behaved differently on the marble surface, all enhanced the treatment similarly.

Among calcite-based materials, marble is coveted for its aesthetic qualities. It has been used in many artifacts of cultural significance worldwide, from the statue of David by Michelangelo in Florence to the famous columns of the Parthenon in Athens. But when exposed outdoors, marble works are prone to deterioration from the rain.

"Most of us are familiar with some iconic marble works of great historical and cultural significance. We're working to find ways to help preserve these works for future generations so they can have the chance to enjoy and appreciate them just like us," says Dr. Martina Lessio, lecturer in the School of Chemistry at UNSW Science and a senior author of the study.

In recent years, a promising new treatment has been developed by conservation scientists to improve the resistance of marble to rain. This treatment works by forming a durable protective coating on the marble surface composed of calcium phosphate (CaP), or hydroxyapatite—a naturally occurring mineral also found in our teeth and bones. Unlike other treatments, it causes no discolouration or aesthetic change to the marble.

Previous research has shown adding organic solvents such as alcohol to this treatment helps improve the ability of the hydroxyapatite layer to protect the marble, but the reasons for the observed improvement were not exactly clear.

"Finding out the reason it's behaving this way is critical to be able to select the best possible solvent for the treatment and maximize the protective efficacy," Dr. Lessio says.

"Computational tools allow us to investigate the fundamental chemistry behind these observations.

"Combined with experimental insights, we can better understand how these organic solvents work at the molecular level and develop a rational design for the marble conservation treatment."

Optimizing marble treatment

For the study, the researchers tested the adsorption of ethanol, isopropanol and acetone on the calcite surface of a Carrara marble sample—a type of marble widely used in sculpture and architecture. Adsorption (not to be confused with absorption) refers to the accumulation of molecules, atoms or ions on surfaces, like in small pouches of silica gel that help hold water vapor and keep things dry.

To gauge suitability, the researchers first simulated the interaction between the different solvents (both in pure form and mixed with water) and the calcite surface of the marble using computer modeling. In their experiments, they tested four different conditions—one using water exclusively as a solvent and the remaining three using the additives. The marble samples were treated by immersion in separate beakers containing 100 mL of an aqueous solution of a phosphate precursor, with and without the organic additives.

The different organic solvents displayed different behaviors when they approached the marble surface in the modeling. The alcohols formed a water-repellent layer on calcite, while the acetone formed a mixed, dynamic layer. But interestingly, each solvent improved the protective performance of the treatment without any significant differences between them in the experiment.

"It was surprising and intriguing to us that all solvents favor the formation of a protective calcium phosphate layer, particularly acetone, which has very different chemical properties from the other solvents tested," Dr. Lessio says. "It suggests when selecting a solvent to optimize the marble conservation treatment, the solvent behavior at the surface is not a critical factor to consider like we thought."

In the next stage of the research, the team plan to test whether factors other than adsorption are responsible.

"So far, we have only investigated one aspect—the behavior of the solvent at the surface. But other factors need to be investigated, like the behavior of the solvent in solution, and computational work is currently in progress in our group to uncover this," Dr. Lessio says.

More information: Antonia E. Papasergio et al, Adsorption of water and organic solvents on the calcite [101¯4] surface: Implications for marble conservation treatments, *Applied Surface Science* (2023). DOI: 10.1016/j.apsusc.2023.156438

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