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PRACTICAL EVALUATION AND APPLICATION OF CLEANING TECHNIQUES FOR MARBLE SCULPTURE

RAINA CHAO

Cleaning marble is an involved process that can require complex decision-making along with multiple tests and treatment steps to arrive at the desired outcome. The type of object, source of soiling, desired appearance, manner of carving and finishing, and even the properties of the stone itself are factors affecting treatment choices and results. There are many treatment options for cleaning marble that can be tailored to the specific needs of an object, including vinyl erasers, aqueous solutions, chelators, surfactants, poultices, solvents, and lasers. This article will explore the advantages and limitations of these techniques, which were investigated in preparation for the treatment of *La Première Pose* (1873–1876) by Howard Roberts, a life-size marble figure in the collection of the Philadelphia Museum of Art. This case study will be contextualized by a literature review of published cleaning techniques. While the treatment of *La Première Pose* necessitated a combination of cleaning methods executed in sequence, additional treatment examples that used different methodologies will also be discussed, highlighting the complex nature of the decision-making process.

KEYWORDS: Marble, Cleaning, Erasers, Lasers, Poultices, Surfactants, Methyl cellulose, Agar, Citrate, Diethylenetriaminepentaacetic acid (DTPA), Ethylenediaminetetraacetic acid (EDTA)

1. INTRODUCTION

In 2014, the Philadelphia Museum of Art reinstalled two of its galleries of American Art, prompting the treatment of two large-scale white marble sculptures, Howard Roberts's *La Première Pose* (fig. 1) and Randolph Rogers's *The Lost Pleiad.* The bulk of the treatment needed for both sculptures was cleaning to remove or reduce surface grime and accretions accumulated over approximately 80 years of display and handling. The timescale for the treatments and extent of surface area to be cleaned prompted an investigation into the best and most efficient method for cleaning these marble surfaces. After literature review and consultation with colleagues, numerous cleaning methods—including organic solvents, mechanical action, aqueous solutions, gelled aqueous systems, and lasers—were tested on Howard Roberts's *La Première Pose*. The testing and evaluation of multiple cleaning options not only aided the determination of a treatment methodology for *La Première Pose* but also helped inform subsequent marble cleaning projects and form the basis for this article. This article will present observations on the strengths and weaknesses of the cleaning techniques and illustrate the decision-making process through case studies.

2. CLEANING METHODS IN THE LITERATURE

The following review of published marble cleaning methods was done in preparation for the treatment of *La Première Pose* and other case studies discussed in this article. While it includes a variety of publications and cleaning methods, it should not be considered a comprehensive study of all publications on the subject.

2.1 Aqueous Cleaning

When approaching aqueous cleaning of marble, the effect of water alone on the marble itself must be considered. Marble is primarily calcite ($CaCO_3$), which is somewhat soluble in water alone and soluble in dilute acidic solutions (Lide 2005, 4–54). For these reasons, a saturated calcium carbonate solution at elevated pH (~ pH 9) is recommended in lieu of deionized water for surface cleaning or clearance to

Fig. 1. Before treatment, Howard Roberts, *La Première Pose*, 1873–1876, marble, 133 × 76 × 66 cm. Philadelphia Museum of Art, Gift of Mrs. Howard Roberts, 1929-134-1 (Courtesy of Philadelphia Museum of Art, photograph by Joe Mikuliak)

protect the surface of the marble from dissolution and etching. Gervais et al. describe the preparation of such a solution (2010, 172). In addition to protecting the marble surface, solutions at an elevated pH also tend to be more effective for the removal of aged and oxidized soiling (Stavroudis, Doherty, and Wolbers 2005, 18).

Aqueous cleaning methods for marble can be tailored to the specific condition issues of an object. Incorporation of chelators to aid in the removal of surface soiling and reduce staining plus surfactants to remove soiling, particularly greasy handling grime, is often necessary. The Modular Cleaning Program (MCP) developed by Chris Stavroudis and colleagues provides a useful tool for determining an appropriate aqueous cleaning system. The program aids in formulating and testing aqueous solutions accounting for variables such as pH, established with buffers, and the addition of chelators and surfactants (Stavroudis, Doherty, and Wolbers 2005).

2.1.1 Chelators

Chelating solutions have been shown to effectively remove surface soiling. A helpful discussion of chelators used on marble is provided by the 2010 article entitled "Cleaning marble with ammonium citrate," by Gervais et al. While the authors focus on ammonium citrate, another common chelator, ethylenediaminetetraacetic acid (EDTA) is also discussed. As both citrate and EDTA are known to chelate calcium ions (Gervais et al. 2010, 165), the study focused on the effect of chelating solutions of different formulations on marble. The authors found that elevated pH, lower concentrations of ammonium citrate, and reduced airflow caused the least damage to the marble surface. Multiple cleanings in succession showed more damage than a single cleaning, and EDTA proved more harmful than citrate even under ideal conditions (Gervais et al. 2010, 170–171).

2.1.2 Surfactants

Surfactants can help remove surface soiling—particularly nonpolar, greasy soiling that could result from handling or applied coatings. Stavroudis's 2009 article "Sorting out surfactants" gives a useful overview of surfactant chemistry and comments on the properties and potential applications of individual surfactants. The surfactants discussed fall into one of two categories: nonionic surfactants that are usable at any pH and anionic surfactants that are usable at elevated pH. Thus, they are suitable for aqueous cleaning of marble that should, ideally, occur at an elevated pH. Additionally, aged and oxidized material is typically more readily removed at an elevated pH (Stavroudis, Doherty, and Wolbers 2005, 18).

Chelators, surfactants, and other additives to water have the potential of crystallizing on the surface if residues of solutions remain and are allowed to dry. Marble surfaces should always be cleared after aqueous cleaning but clearance solutions should also account for the solubility of marble. The carbonate-saturated water discussed earlier or pH-adjusted water, a solution whose pH is set with volatile components and therefore leaves no residue (Stavroudis 2016), are both viable options.

2.2 Gels

Gelled aqueous formulations have also been used as poultices to clean marble, offering extended dwell time and uniformity in cleaning that can be applied overall or in specific passages. These poultices can be removed while still wet or allowed to dry completely before removal. Since a gel is a thickened aqueous solution, the same parameters discussed for designing aqueous cleaning solutions must be considered. In addition to the action of the aqueous solution in the gel, alteration of the marble surface due to mechanical removal of crystals attached to the poultice film is also a concern, particularly with methyl cellulose-based poultices.

2.2.1 Methyl Cellulose

Useful discussions of methyl cellulose based poultices are offered by Goldberg's 1989 article "A fresh face for Samuel Gompers: Methyl cellulose poultice cleaning" and Lauffenburger, Grissom, and Charola's 1992 article "Changes in gloss of marble surfaces as a result of methylcellulose poulticing." The primary concern addressed by both sources is alteration of the marble surface due either to mechanical removal of crystals attached to the poultice film or to etching of the stone by the aqueous solution itself. Lauffenburger, et al. tested a variety of poultice formulations and their effects on marble surfaces when removed wet or dry. The authors found that poultices removed while still wet generally exhibited less etching of the marble surface than those allowed to dry fully, likely due to the mechanical adhesion of calcite crystals to the dried films (Lauffenburger, Grissom, and Charola 1992, 159-160). Calcite crystals were detected on removed poultice films by touch, sight, and SEM by Lauffenburger, et al. (Lauffenburger, Grissom, and Charola 1992, 160) and with PLM and SEM by Goldberg (21–22). In addition to removing poultices while still wet, Goldberg successfully used additives such as bulking agents and plasticizers to prevent damage due to mechanical adhesion when using methyl cellulose (1989).

2.2.2 Agar

Another aqueous gel option is agar or agarose gel applied as precast sheets of gel or as a molten liquid that cools and conforms to an object's surface. Much of the literature on the use of agar in objects conservation is devoted to treating plaster. The 2013 article, "Cleaning plaster surfaces with agar-agar gels: evaluation of the technique," by Tortajada Hernando and Blanco Dominguez, provides a useful discussion of agar and its application (Tortajada Hernando and Blanco Dominguez 2013). Cindy Lee Scott, who recently used agar gels to clean a marble sculpture at the Detroit Institute of Arts (Detroit Institute of Arts 2013), discusses agar more generally in her 2012 article entitled "The use of agar as a solvent gel in objects conservation." Scott explores the use of agar gel with a range of aqueous solutions and added solvents, finding that agar behaves well under most aqueous conditions, including solutions with elevated or depressed pH and incorporating oxidizers and chelators; however, the addition of surfactants caused the gel to dissociate (76). One benefit of agar over other aqueous gels is the ease of clearance. Regardless of the mode of application, the agar gel is not adhered to the surface and can be easily peeled away without the concern of mechanical damage to the surface (78–79). Though the gelling agent (agar) appears to leave no residues, it should be noted that the aqueous solution employed within the agar might still require clearance.

2.3 Mechanical Cleaning—Vinyl Erasers

Mechanical surface cleaning of marble using vinyl erasers is also an option. Eraser cleaning can be executed dry on objects for which aqueous cleaning may pose a concern as well as in combination with other cleaning techniques. Using erasers, the cleaning can be easily controlled as the results are readily apparent, allowing for discrete control over extent of cleaning and enabling selective cleaning of variable surfaces (Williams and Lauffenberger 1996). These strengths have recently been demonstrated on the cleaning of *Adam*, by Tullio Lombardo (ca. 1455–1532), at the Metropolitan Museum of Art, where vinyl eraser strips were used in combination with saliva (Riccardelli et al. 2014, 103–104).

Despite these strengths, there are some potential drawbacks to cleaning with vinyl erasers, specifically concerns about residue deposition and abrading the surface. These issues were investigated by Williams and Lauffenberger in their 1996 article entitled "Testing erasers used to clean marble surfaces." In the article, surfaces cleaned with a variety of erasers are evaluated using specular gloss measurements, magnification with a binocular microscope, and SEM to gauge surface abrasions; and SEM-EDS, FTIR, and longwave UV to investigate potential residues. Though no residues were identified by the methods employed, the authors observed that areas treated with vinyl erasers did have a higher surface tension than untreated areas, suggesting that there may, in fact, be a minute amount of residue (121). Nevertheless, vinyl erasers behaved well, were recommended by the authors for cleaning marble, and have many strengths, as noted earlier.

2.4 Laser Cleaning

There are numerous articles that discuss laser cleaning of marble surfaces, many of which focus on the removal of encrustation from outdoor marble, the impetus behind the development of the type of laser most familiar to conservators, the Nd:YAG (neodymium-doped yttrium aluminum garnet) laser (Cooper 1998, 57). Laser cleaning, when using a properly configured unit, has many strengths, including the ability to selectively limit what is removed from the surface, instantaneous results, speed, and lack of mechanical action on the surface (62). Wetting the surface prior to laser cleaning can also improve the results and is sometimes referred to as “steam laser cleaning” (48–49).

The main concern regarding the laser cleaning of marble, aside from the obvious issue of access to an instrument, is the potential yellowing of marble surfaces after laser cleaning. There are a variety of possible causes for this phenomenon, including light scattering from voids, staining from organic compounds, and the transformation of iron-containing components within the stone (Pouli et al. 2007, 106; Vergès-Belmin and Labouré 2007, 116–117). While there is investigation into methods that would prevent this issue (Pouli et al. 2007), aqueous poultices have also been used to mitigate or remove the yellowing (Vergès-Belmin and Labouré 2007).

3. THE FIRST CASE STUDY

After review of published treatment techniques, cleaning tests were performed on the back of *La Première Pose* to determine the most effective way to remove soiling from the sculpture (fig. 2). The sculpture’s composition fortuitously provided a relatively flat, evenly soiled surface—the back of the chair—on which to compare and contrast the cleaning techniques (fig. 3). After initial testing, promising methods were tested in additional locations to ensure that an even overall cleaning could be achieved and to assess their efficacy on different types of soiling.

La Première Pose’s surface exhibited two types of soiling: overall darkening from accumulated grime and an uneven, yellow, and glossy appearance in distinct areas produced by repeated handling. The goal of the treatment was to remove these layers as completely as possible in order to present the sculpture close to its originally intended appearance. To this end, numerous cleaning methods—including organic solvents, vinyl erasers, lasers, and aqueous solutions—were tested on both types of soiling.

3.1 Cleaning Tests and Observations

3.1.1 Solvents

Polar and nonpolar organic solvents were tested first, as marble surfaces can have applied coatings that are not readily apparent under examination with visible or UV light. The solvents tested had no effect on either type of soiling, nor did the tests indicate the presence of a surface coating that could be holding grime onto the surface. Saliva also had no appreciable effect on either type of soiling.

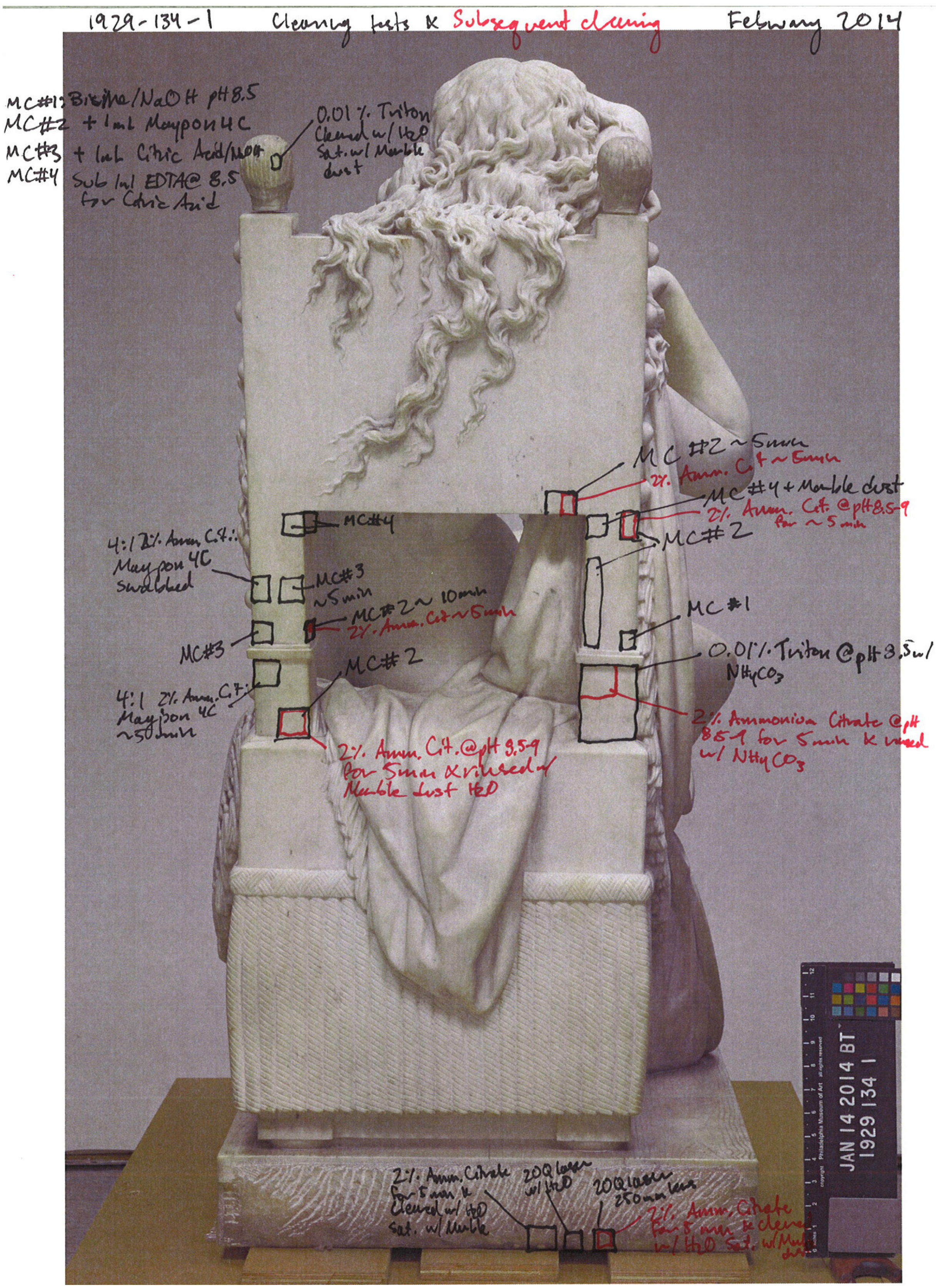

Fig. 2. Diagram of cleaning tests for *La Premire Pose* (Courtesy of Philadelphia Museum of Art)

Fig. 3. Detail of cleaning test results on the back of *La Première Pose* (Courtesy of Philadelphia Museum of Art, photograph by Raina Chao)

3.1.2 Aqueous Cleaning

As a complete, overall cleaning of the marble was desired, aqueous solutions formulated for the particulars of the surface soiling were a good option, and the challenge of limiting the cleaning to a specific area was not a concern. Various aqueous solutions were tested to gauge the efficacy of different chelators, surfactants, application methods, and dwell times, as well as their effects on the marble surface.

Table 1 summarizes the aqueous cleaning tests. From review of the literature and observations on the nature of the soiling, testing focused on chelators and surfactants. The tests moved from less aggressive to more aggressive in terms of components, concentration, and dwell time. Some of the solutions tested were prepared following the MCP, while others were custom mixed for the cleaning tests. In general, custom solutions were prepared with ammonium carbonate and ammonium hydroxide to prevent dissolution of the marble surface by saturating the solution with carbonates and raising the pH to 8 to 9. Solutions prepared using the MCP were buffered to pH 8.5 with bicine and sodium hydroxide. In order to assess the differences between modes of application and dwell time, solutions were tested up to three ways depending on results: (1) swabbed, (2) applied to the surface on a saturated pad for dwell times of 5 minutes, and (3) applied to the surface on a saturated pad for dwell times of 10 minutes.

All cleaning solutions were cleared with "carbonate-saturated water," a solution of ammonium carbonate adjusted to approximately pH 9 with ammonium hydroxide and added marble dust to saturate it with calcite

Table 1. Aqueous Solutions and Application Methods Tested on *La Première Pose*

	Major Components of Test Solutions	Application Method: Swabbed	Saturated Pad (5-min dwell)	Saturated Pad (10-min dwell)
1	0.01% Triton XL-80N[a]	x		
2	3.2% Maypon 4C[b]	x	x	x
3	2% ammonium citrate[a]	x	x	x
4	5% ammonium citrate[a]	x	x	x
5	1% citric acid + Maypon 4C (3.2%)[b]	x	x	
6	~2% ammonium citrate + Maypon 4C (3.2%)[a]	x	x	
7	1.5% EDTA + Maypon 4C (3.2%)[b]	x	x	

[a]Solution prepared with $(NH_4)_2CO_3$ and NaOH and set to pH 8–9
[b]Solution buffered to pH 8.5 with bicine and NaOH according to the MCP

and prevent dissolution of the marble surface (a detailed recipe can be found in appendix 1). This solution performed the same function as the one described by Gervais et al. (172); however, by using more readily soluble chemicals—ammonium carbonate and ammonium hydroxide—as the primary sources for carbonate ions and pH adjustment, the solution could be mixed more quickly than by using marble dust alone.

Of the two surfactants tested, Maypon 4C, an anionic surfactant, proved much more effective in removing greasy soiling than the nonionic surfactant, Triton XL-80N. Application on a saturated pad with a dwell time of approximately 5 minutes provided more complete cleaning than swabbing alone; however, no appreciable improvement was achieved by increasing the dwell time further to 10 minutes. Because the nonionic surfactant demonstrated minimal efficacy when swabbed, it was not tested at longer dwell times.

From the chelating solutions tested, the EDTA-based cleaning solutions—both swabbed and applied on a saturated pad—overcleaned the surface, leaving a bright white but raw surface likely due to dissolution of marble. The citrate-based chelating solutions proved successful in removing the accumulated grime without any perceptible adverse effects on the marble surface. The extent and efficiency of cleaning could be altered by changing concentration of the chelator and dwell time. Lower concentrations of citrate required longer dwell times to be as effective as a more concentrated solution at shorter dwell time. While vinyl erasers had previously been tested on their own or with saliva and proved minimally effective, they quickly rolled up soiling after application of a citrate solution.

3.1.3 Laser Cleaning

The Philadelphia Museum of Art owns a laser, which removed the major obstacle to laser cleaning. Tests were undertaken using a CleanLaser 20Q backpack laser (1062-nm wavelength) with a 250-mm lens on a small area on the back of the base. Two distinct areas were laser cleaned, one dry and one pre-wet with carbonate-saturated water for steam laser cleaning. An adjacent patch of surface was cleaned aqueously with the 2% ammonium citrate solution for comparison (fig. 4).

Laser cleaning removed the soiling quickly but left a yellow appearance when compared with the adjacent aqueously cleaned area. Steam laser cleaning resulted in less yellowing than laser cleaning the dry surface,

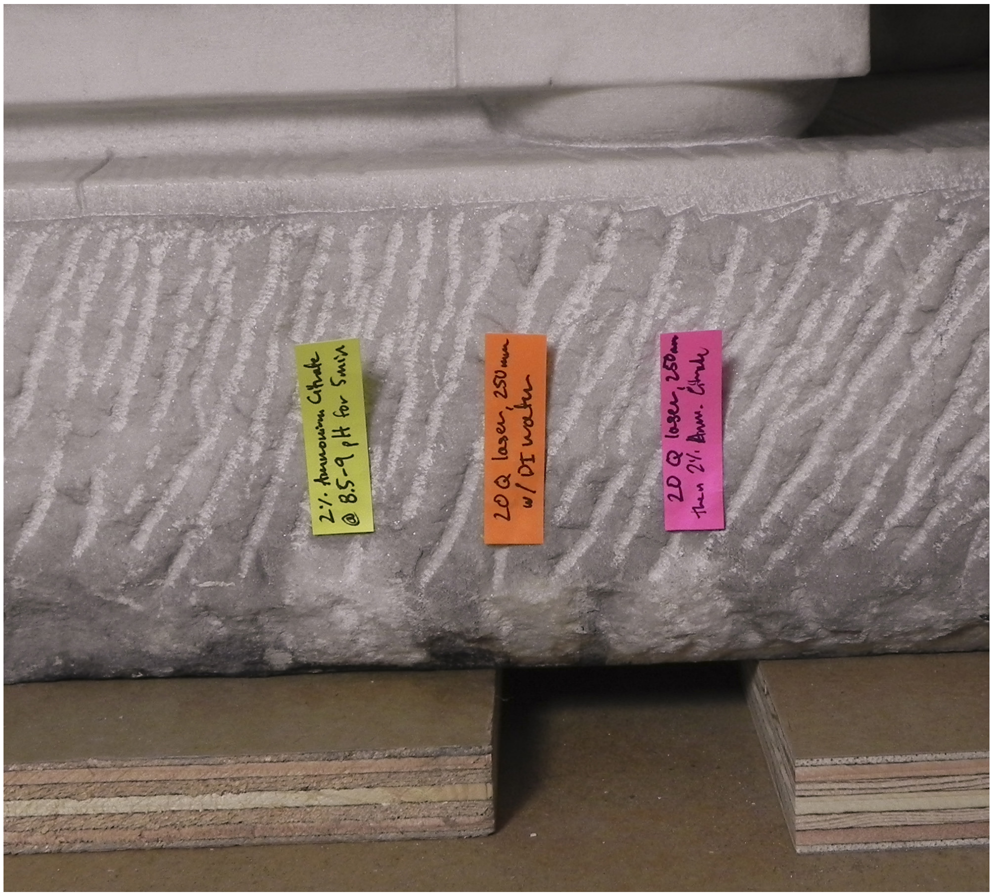

Fig. 4. Detail of laser-cleaning tests on *La Première Pose*, left to right: aqueous cleaning, steam laser cleaning showing yellowed surface, laser-cleaned area after subsequent aqueous cleaning to remove yellowing (Courtesy of Philadelphia Museum of Art, photograph by Raina Chao)

but was still noticeably more yellow than the aqueously cleaned area. The yellowing effect was easily removed with a subsequent aqueous treatment with the 2% ammonium citrate test solution described earlier. Laser cleaning was not tested on an area of particularly heavy handling residues.

3.2 Treatment

Based on these tests, aqueous solutions were chosen as the most efficient and safest method for cleaning *La Première Pose*. Citrate-based solutions were very effective in reducing the overall grime but less so on areas with greasy residue. The residue appeared to act as barrier to the chelating solution, preventing it from effectively and uniformly accessing the soiled surface and producing an unevenly cleaned surface. This result was found in areas of greasy residue even when a surfactant was added to the solution. Similarly, the anionic surfactant was successful in removing the greasy residue but the resultant surface still had a darkened appearance from accumulated grime. Therefore, a two-step treatment process was devised.

First, a buffered detergent solution consisting of 3.2% Maypon 4C solution at pH 8.5 (Solution 2 from table 1) was applied on a saturated pad for approximately 5 minutes. Maypon 4C was later replaced with sodium lauryl sulfate, another anionic detergent, as finding a supplier for a reasonable quantity of Maypon 4C proved difficult. Tests showed that a 1% buffered solution of sodium lauryl sulfate behaved similarly to the 3.2% Maypon 4C and the substitution proved satisfactory.

Second, a saturated pad of 2% ammonium citrate solution (Solution 3 from table 1) was applied to the surface with a stencil brush for 5 to 10 minutes, depending on the extent of soiling in that area. The soiling was then rolled off with a vinyl eraser and/or cotton swabs and the surface cleared with carbonate-saturated water after both steps. More tenacious soiling was removed with longer dwell times during the second (chelating) step and/or a more concentrated chelating solution of 5% ammonium citrate (Solution 4 from table 1). Detailed recipes for the aqueous solutions used in the treatment are included in appendix 1.

3.2.1 Protecting the Surface with Marble Dust

In addition to the ammonium carbonate added to these chelating solutions to prevent the dissolution of the marble surface, marble dust was added to the bulk solutions used for cleaning. The amount of marble dust varied but was always in excess of that needed to fully saturate the solution, and a layer of marble dust was visible at the bottom of the jar. This addition was intended to provide a more readily accessible source (due to the high surface area of a powder) of calcium to fill the chelating site on the citrate ion that could otherwise cause damage to the marble surface. The formation constants for citrate complexes indicate that their affinity for calcium is lower than for many other ions (Gervais et al. 2010, 165). Therefore, theoretically, the calcium ion could be displaced by other ions within the soiling for which citrate had a higher affinity. The treatment was successfully carried out without any perceptible alteration to the surface from the chelating solution; however, it is unlikely that the addition of marble powder contributed to this result as intended.

It was learned after treatment that the calcium citrate complex is minimally soluble in water (Lide 2005, 3–84) and therefore forms a precipitate, effectively removing citrate from the solution rather than allowing it to preferentially chelate for other ions within the soiling. This also retroactively explains a light-colored precipitate that seemed to form in older solutions directly above the marble dust. At the time, the precipitate was thought to be biological growth and the solutions were discarded. Nevertheless, though the addition of marble dust to the chelating solution did not achieve its intended purpose, it did not adversely affect the cleaning. Thus, the concept of preventing the chelation of calcium from the marble surface by loading the solution with calcium remains viable for other chelators, as discussed later.

3.2.2 Reduction of Yellowing with Methyl Cellulose Gels

The sculpture was treated overall with the procedure described earlier, generally producing an even, dramatically brighter surface (fig. 5). Some areas of greasy residue remained yellowed after overall cleaning, likely due to greater penetration of discolored oils from handling. This yellowing was reduced with methyl cellulose poultices consisting of approximately 10% (w/v) Methocel A4C in carbonate-saturated water. Poultices were applied to the surface, allowed to dry fully, peeled away, and the surface cleared with carbonate-saturated water. The dried poultice films were examined under magnification to ensure that no marble crystals were being removed from the surface, and the marble surface was not perceptibly altered by this treatment. Remaining yellowing was further reduced with a methyl cellulose poultice consisting of approximately 10% to 15% (w/v) Methocel A4C in the 2% ammonium citrate solution. The poultices were applied and cleared in the same manner.

The addition of the chelator to the methyl cellulose poultice had two observable effects: it took more methyl cellulose to reach a similar viscosity than without the chelator, and the dried poultice did not form a coherent film and sprang away from the surface upon drying (fig. 6). Though the incoherent dried films could not be examined for the presence of marble crystals, no alteration of the surface was observed visually or by touch after two applications. Following the third application, a slight alteration in the surface texture was noted by touch, but not visually, and the treatment was halted.

Fig. 5. Details showing progression of cleaning on *La Première Pose,* left to right: before, during, and after treatment (Courtesy of Philadelphia Museum of Art, photograph by Joe Mikuliak)

Despite the yellowish cast that remained in some areas, the marble's surface appeared much improved and homogenous overall (fig. 7).

4. CONTINUING CASE STUDIES

The literature review, in-depth cleaning tests, and observations made during the treatment of *La Première Pose* provided a foundation of experiential knowledge and a methodological template that influenced subsequent marble treatments undertaken by the author. The following case studies illustrate how this methodology was applied, adapted, and expanded for the specific parameters of each project. The features that affect the decision-making process include the type of soiling, level of carving and finish of the marble, the circumstances of its manufacture and intended appearance, and the context of its display.

4.1 Case Study: The Effect of Carving and Finish

Randolph Rogers's *The Lost Pleiad* (fig. 8) was treated immediately after *La Première Pose* for installation in the same gallery. The sculptures have a number of formal similarities, are roughly contemporary in manufacture, and were to be in close proximity. Thus, there was a desire for consistency in their appearance. *The Lost Pleiad* also had similar condition issues to *La Première Pose*—an overall layer of accumulated grime on its surface and yellow, greasy residues from repeated handling. In this case, the residues were restricted to localized areas on the base, likely due to the sculpture's elevated display height.

Due to the similarities between the sculptures, soiling, and their display contexts, testing for *The Lost Pleiad* focused on aqueous methods. The cleaning tests were similar to those executed as described earlier, except that they replaced Maypon 4C with sodium lauryl sulfate and were expanded to include methyl cellulose poultices. Following the relatively successful application of methyl cellulose poultices in the treatment of *La Première Pose*, these tests attempted to determine how effective and efficient poultices

Fig. 6. Dried methyl cellulose poultice on the foot of *La Première Pose* illustrating film disruption from addition of a chelator (Courtesy of Philadelphia Museum of Art, photograph by Raina Chao)

Fig. 7. *La Première Pose* after treatment (Courtesy of Philadelphia Museum of Art, photograph by Joe Mikuliak)

Fig. 8. Before treatment, Randolph Rogers, *The Lost Pleiad,* c. 1874–1882, marble, 173 × 113 × 91.5 cm. Philadelphia Museum of Art, Gift of Lydia Thompson Morris, 1929-162-1 (Courtesy of Philadelphia Museum of Art, photograph by Joe Mikuliak)

would be on a soiled, rather than a precleaned, surface. The solutions and gels tested are summarized in table 2 and results are shown in figure 9. All cleaning tests were cleared with carbonate-saturated water.

It was found that a methyl cellulose poultice without an added chelator did not fully clean the surface, while the poultice with a chelator appeared to overclean the surface (fig. 10). Subsequent applications of the same gel over the same areas did not produce any further visible change. Otherwise, the results of aqueous cleaning tests were similar to those of *La Première Pose.*

As methyl cellulose poultices proved unsuitable, a protocol similar to that used on *La Première Pose* was devised, but modified to suit the particulars of *The Lost Pleiad*'s condition. The greasy residues, more minimal in location and extent, could be addressed by swabbing with the anionic surfactant solution (Solution 4 in table 2), only in areas that were visibly yellowed and glossy. Then a 2% ammonium citrate solution (Solution 2 in table 2) was applied overall on saturated pads for 5 to 10 minutes and the soiling rolled off with a vinyl eraser and/or cotton swabs. Recesses and areas of complex carving retaining more tenacious soiling were addressed with the 5% ammonium citrate solution (Solution 3 from table 2) on cotton swabs. The surface was cleared with carbonate-saturated water after all treatment steps. Detailed recipes for the aqueous solutions used in the treatment are included in appendix 1.

During the cleaning, it was noted that the accumulated soiling was generally easier to remove from *The Lost Pleiad* than from *La Première Pose*. This was particularly noticeable in areas of higher polish and simpler carving. As most sculptures have some degree of variation in the complexity of their carving and finish of the marble surface, this was a useful reminder that these differences can be a factor in the extent and uniformity of cleaning achievable on a piece. In this case, the variations influenced the ease or difficulty of cleaning but did not impair the ability of the treatment to achieve a homogenously clean overall appearance that was consistent with that of its neighbor, *La Première Pose* (fig. 11).

4.2 Case Study: Using Agar Gels

In 2016, the Saint Louis Art Museum reinstalled its galleries of American art, prompting the treatment of a marble bust, *Joan of Arc Listening to the Voices* by Robert Porter Bringhurst (1855–1925; fig. 12). Records indicated that the marble bust had previously been treated to remove superficial surface soiling; however, the surface remained yellowed, particularly on the high points, and dark soiling remained trapped in point defects and cracks. Though the surface was not dramatically soiled, there was a desire to reduce the yellowing to better meld with adjacent works in marble.

Table 2. Aqueous Solutions and Application Methods Tested on *The Lost Pleiad*

		Application Method		
Major Components of Test Solutions		Swabbed	Saturated Pad (5-min dwell)	Methyl Cellulose Gel (removed dry)
1	Carbonate-saturated water	x	x	x
2	2% ammonium citrate[a]	x	x	x
3	5% ammonium citrate[a]	x	x	
4	1% sodium lauryl sulfate[b]	x	x	

[a]Solution prepared with $(NH_4)_2CO_3$ and NaOH and set to pH 8–9
[b]Solution buffered to pH 8.5 with bicine and NaOH according to the MCP

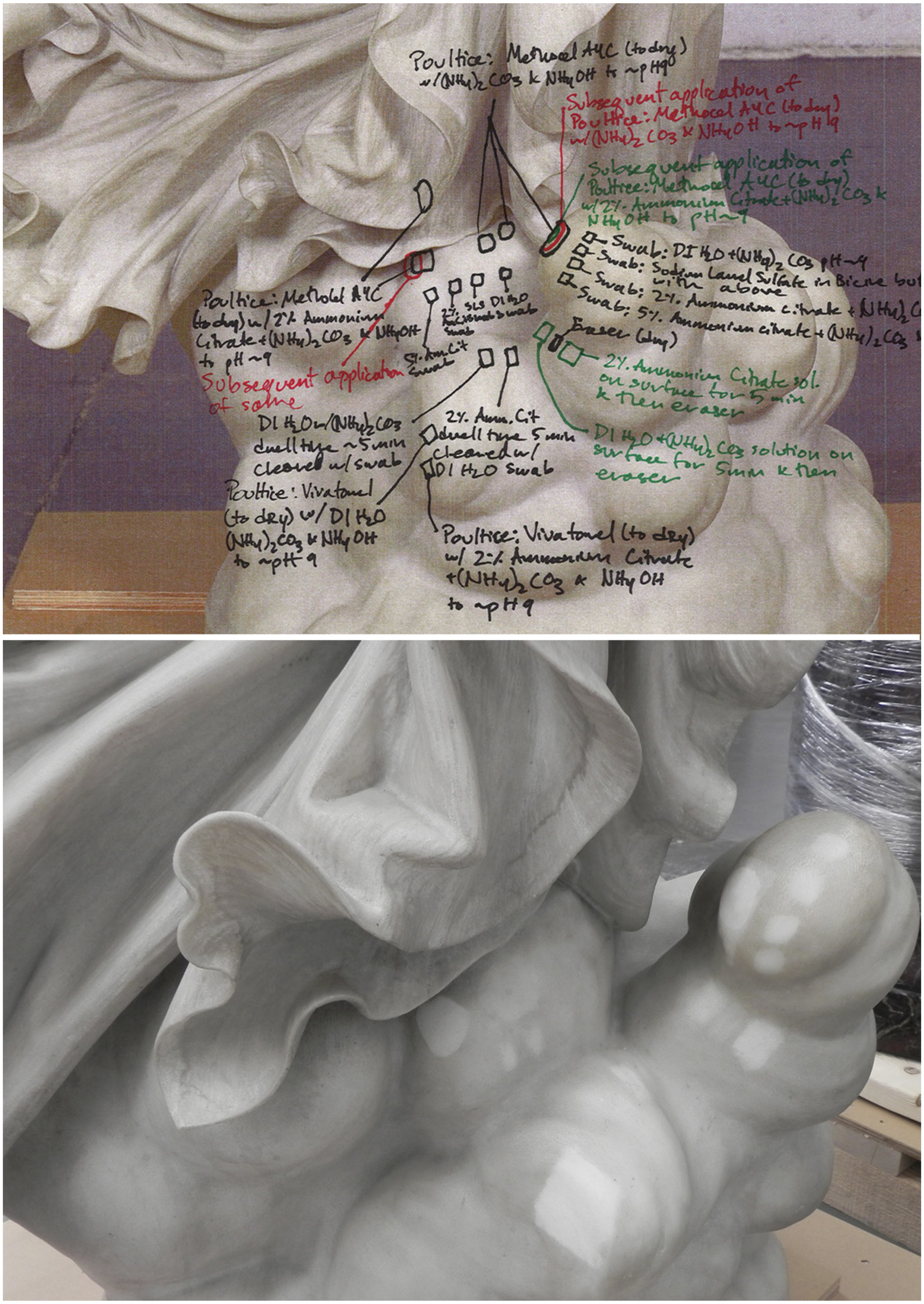

Fig. 9. Detail of cleaning tests conducted on *The Lost Pleiad*, diagram (top) and results (bottom) (Courtesy of Philadelphia Museum of Art, photograph by Raina Chao)

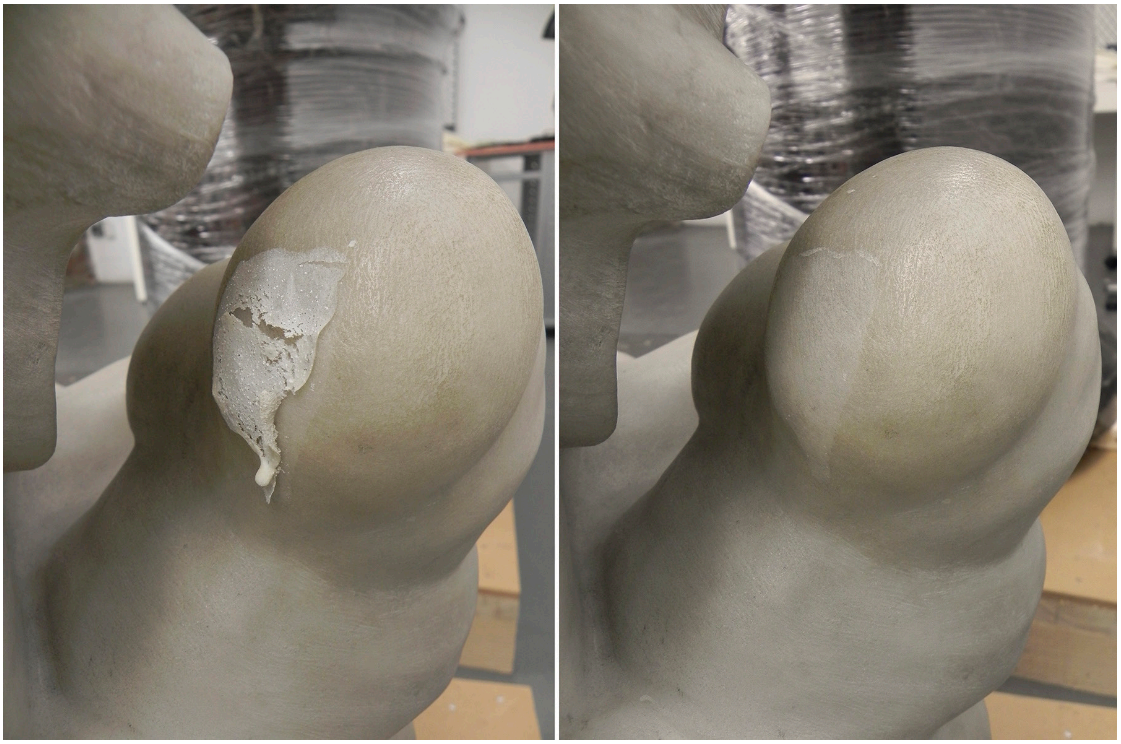

Fig. 10. Detail of methyl cellulose poultice tests on *The Lost Pleiad* (Courtesy of Philadelphia Museum of Art, photograph by Raina Chao)

The successful reduction of tenacious yellowing on areas of *La Première Pose* indicated that poultices of aqueous solutions might be effective in reducing the yellowing. However, because of the risk of damaging the marble surface and the chelator's observed disruption of the methyl cellulose gel, a different type of poultice was preferred. Therefore, the use of agar gels was explored since, as discussed earlier, agar gels are

Fig. 11. Progression of cleaning on *The Lost Pleiad*, left to right: before, during, and after treatment (Courtesy of Philadelphia Museum of Art, photograph by Joe Mikuliak)

Fig. 12. Robert Porter Bringhurst, *Joan of Arc Listening to the Voices*, 1885, marble, 38.1 × 19.7 × 19.1 cm, Saint Louis Art Museum, Gift of Friends of the Artist, 50:1924 (Courtesy of Saint Louis Art Museum, photograph by Jean-Paul Torno)

compatible with chelators and are not adhered to the marble surface, alleviating concerns about mechanical damage to the marble surface.

In order to assess the effect of an agar gel on the surface, a 2% (w/v) agar gel in pH-adjusted water at pH 8.5 was prepared, applied to the surface molten, and removed after 30 minutes. The gel successfully removed trapped soiling but had little effect on the yellowing. A 2% (w/v) agar gel made with 2% citrate solution in deionized water adjusted to a pH of 8.5 with ammonium hydroxide proved more effective in reducing the yellowing when allowed to dwell on the surface for approximately 15 minutes. Once the gel was removed, the area was cleared with pH-adjusted water at pH 8.5. The gel was applied to yellowed areas 1 to 2 times to achieve an even surface overall.

The treatment was successful, but improvement in the surface was relatively subtle and achieved slowly through multiple applications of agar gel (fig. 13). A batch of agar was made up by dispersing the dry agar in the intended cleaning solution; then, it was heated in a microwave until the agar dissolved and a molten solution was formed. The solution was applied molten to the marble surface, where it quickly formed a rigid gel upon cooling. After the designated dwell time, the agar was easily peeled off the surface along seams cut with a wooden skewer.

To reduce waste, the remaining gel that was not applied to the surface could be subsequently reheated and used for treatment. It was observed that the reheated gels containing the chelator were sometimes more effective than the gel as first applied, likely due to an increase in the concentration of the chelator from water evaporating during reheating. Evaporation during reheating is variable; thus, the concentration of chelator is difficult to quantify after reheating. Though it did not pose a problem in this treatment, the variability could be eliminated by always using newly mixed solutions or by adding the chelator or other additional components after the agar is molten, as recommended by Scott (2012, 73).

4.3 Case Study: Nuanced Partial Cleaning

In early 2017, the Saint Louis Art Museum installed the exhibition *Learning to See: Renaissance and Baroque Masterworks from the Phoebe Dent Weil and Mark S. Weil Collection*, a show primarily composed of promised gifts of prints and sculpture. One of the sculptures, a monumental white marble bust of the Roman emperor Marcus Aurelius (fig. 14), was cleaned in preparation for exhibition.

The *Bust of Marcus Aurelius*, as an earlier work reflective of antiquity, required a different type of treatment methodology than that presented in the other case studies. The goal of the treatment was to reduce and even out the overall soiling accumulated on the surface, but not to remove it completely. After discussion with the lender and curators, it was deemed most appropriate to retain some of the surface soiling as an indicator of age and the sculpture's history.

In order to accomplish this goal, cleaning tests focused not on how to most effectively clean the marble but rather on determining the most controllable method to execute a nuanced cleaning of the surface.

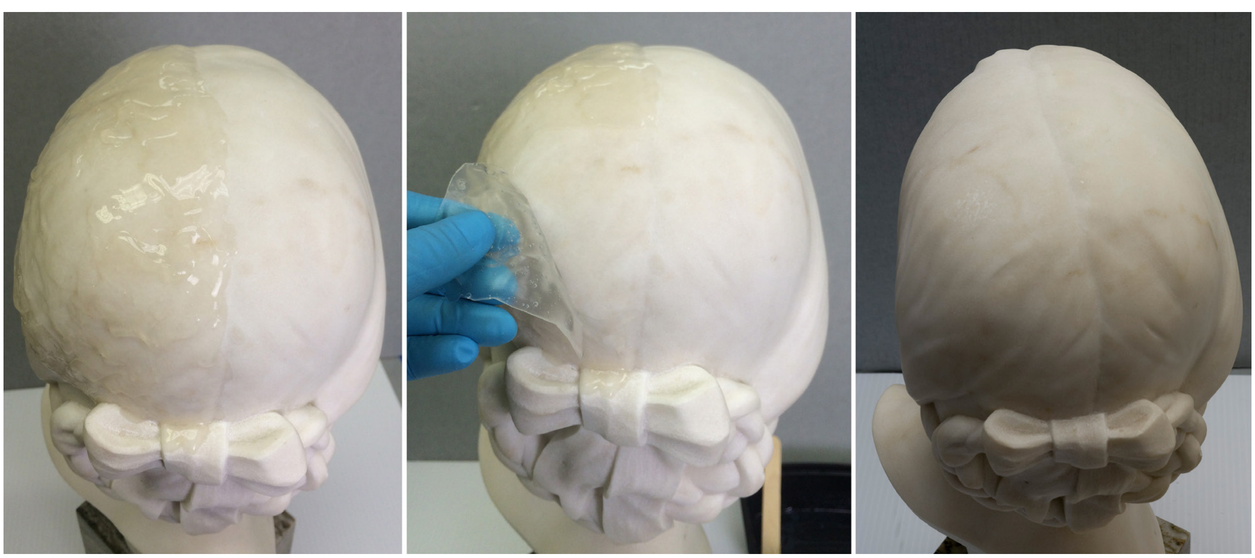

Fig. 13. During treatment details of *Joan of Arc*, left to right: agar gel applied to the proper left side, agar gel being removed, image of the partially cleaned surface, showing subtle reduction of yellowing (Courtesy of Saint Louis Art Museum, photograph by Raina Chao)

Fig. 14. Unknown Italian Artist, *Bust of Marcus Aurelius*, late 18th–early 19th century, marble, 80.6 × 40 × 37.9 cm, Private Collection, Promised gift of Phoebe Dent Weil and Mark S. Weil to Saint Louis Art Museum, 2016.21 (Courtesy of Saint Louis Art Museum, photograph by Jean-Paul Torno)

Tests performed on the back of the sculpture indicated that vinyl erasers and saliva produced the most controllable cleaning (fig. 15). However, as cleaning commenced and extended beyond the back of the sculpture, the efficacy of cleaning with this method decreased dramatically. More conspicuous areas of the sculpture appeared to have a protective layer, preventing the saliva and erasers from cleaning effectively. Solvent cleaning with odorless mineral spirits readily removed this layer (likely wax) and the dark soiling above it, greatly improving the appearance of the surface. After solvent cleaning, saliva and erasers were successfully used to reduce more entrenched soiling and even out the surface (fig. 16).

This case study highlights the importance of testing treatment methods in more than one area, as variations in soiling or surface treatment can lead to diverse responses to the same treatment method. Such unexpected results are particularly problematic in cases such as this in which a nuanced partial, rather than complete, cleaning is desired.

4.4 Case Study: New Methods

The case studies presented contain observations on the use and adaptation of published techniques tailored to the needs of specific objects. Yet, there are also new techniques that could be applied in marble treatments, if appropriately tested.

One such innovative approach to the use of chelators to treat marble was presented by Chris Stavroudis during the Modular Cleaning Program workshop held at the Saint Louis Art Museum in March 2017. As described earlier, the attempt to prevent citrate ions from chelating calcium from the

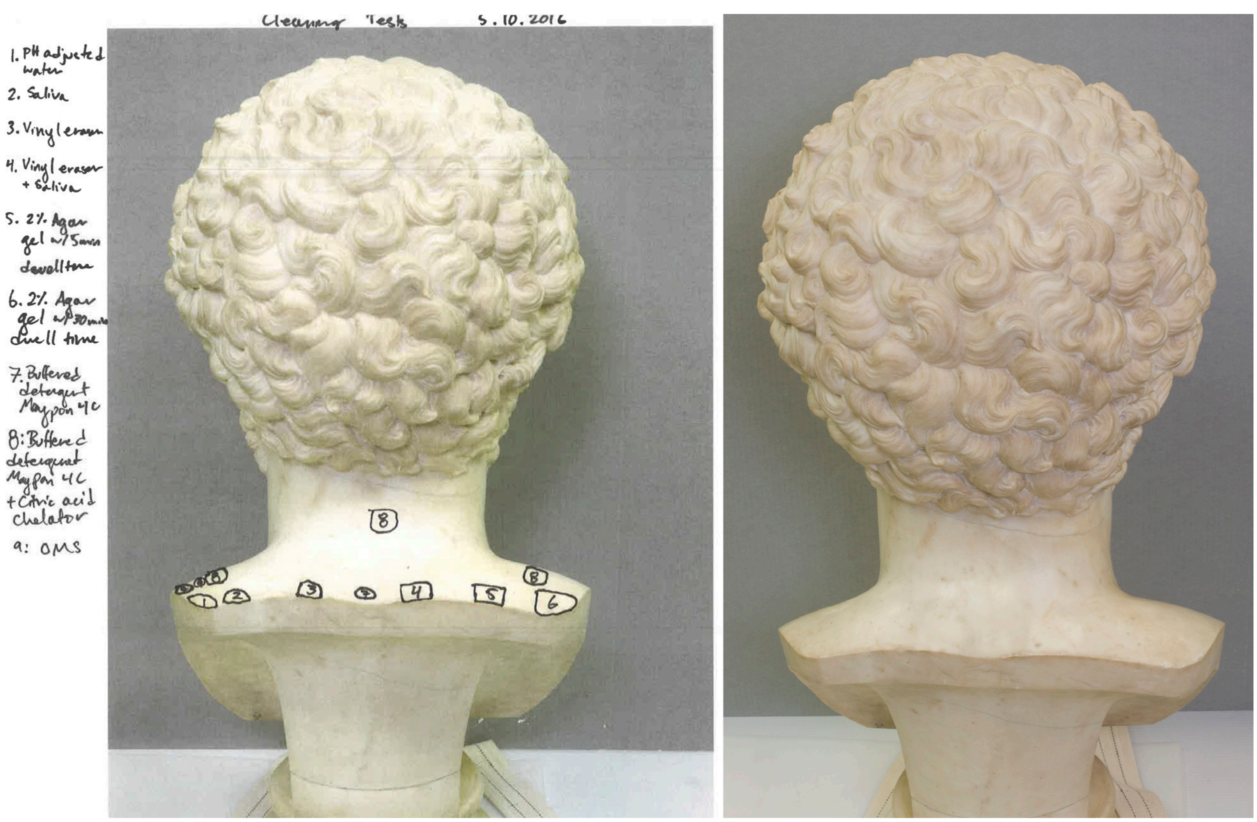

Fig. 15. Detail of cleaning tests on *Marcus Aurelius*. Left: diagram. Right: results. (Courtesy of Saint Louis Art Museum, photograph by Raina Chao)

Fig. 16. *Marcus Aurelius*. Left: partially solvent cleaned. Right: after treatment. (Courtesy of Saint Louis Art Museum, photograph by Raina Chao)

marble surface by adding a source of calcium to the solution was not effective. However, other chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), form soluble complexes with calcium, allowing the calcium-chelator complex to remain in solution. The calcium-chelator complex in solution remains capable of effectively solubilizing other ions from the soiling layer, which will then displace the calcium. Through this method, it is possible that EDTA and DTPA, previously shown to cause damage to marble surfaces, could be safely used for aqueous cleaning of marble.

To investigate this possibility, several aqueous solutions at pH 8.5 containing EDTA and DTPA with and without a reserve of calcium (from calcium hydroxide) were placed on a highly polished marble surface for 15 and 30 minutes (solutions and results are summarized in table 3). As shown in

Table 3. Observations of the Effect of Chelating Solutions Tested on Polished Marble

Solution	Effect after 15 Minutes	Effect after 30 Minutes
Deionized water	None	Not tested
pH-Adjusted Water (pH 8.5)	None	Surface slightly matte Notable change in texture
pH 8.5 EDTA[a]	Matte surface Slightly rough texture	Very matte surface Rough texture
pH 8.5 EDTA + $Ca(OH)_2$[a]	Barely noticeable Minimal texture change	Surface slightly matte Notable change in texture
pH 8.5 DTPA[a]	Matte surface Slightly rough texture	Very matte surface Rough texture
pH 8.5 DTPA + $Ca(OH)_2$[a]	Barely noticeable Minimal texture change	Slightly noticeable Minimal texture change
pH 8.5 Citric acid[a]	Slightly noticeable Minimal texture change	Matte surface Slightly rough texture

[a] Solution buffered to pH 8.5 with bicine and NaOH according to the MCP; recipes in appendix 1

figure 17, the chelating solutions without added calcium visibly etched the surface, but the solutions with calcium showed almost undetectable etching at 15 minutes. At 30 minutes, EDTA with added calcium appreciably etches the marble surface while the DTPA still has a barely perceptible effect on the surface.

When compared with citric acid, at 15 minutes the EDTA and DTPA solutions with calcium have similar or less effect on the surface. However, at 30 minutes, the DTPA with added calcium

Fig. 17. Test results showing effects on a polished marble surface by buffered pH 8.5 chelating solutions with and without added calcium hydroxide at dwell times of 15 and 30 minutes

performs much better than citric acid. Disturbingly, pH-adjusted water at pH 8.5 also seemed to etch the surface after 30 minutes (though it had no effect after 15 minutes), indicating that it may be prudent to investigate the inclusion of calcium or carbonates to further discourage dissolution of the marble surface for longer dwell times. This preliminary test indicates that the technique, particularly used with DTPA, shows great promise and could, after further investigation with more detailed and rigorous experiments, become a useful addition to the arsenal of marble cleaning options.

5. CONCLUSIONS

The literature review and initial case study of *La Première Pose* presented in this article informed and heavily influenced subsequent marble treatments undertaken by the author. Though the process of assessment and testing to determine the desired treatment methodology remains the same, individual treatment procedures are continually adapted to suit the specific needs of each object and as new treatment approaches arise. New techniques, such as the addition of calcium or carbonates to cleaning and clearance solutions, can be easily incorporated into the testing framework but should first be tested more thoroughly on samples and evaluated for their suitability for use on marble.

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APPENDIX 1: Recipes for Solutions

La Première Pose and *The Lost Pleiad*

Carbonate-Saturated Water

Deionized water adjusted to ~ pH 9 with ammonium carbonate and ammonium hydroxide with added marble dust

Recipe for a final volume of 200 mL
200 mL deionized water
6 g ammonium carbonate
~ 1.5 mL ammonium hydroxide
Marble dust

Buffered Detergent Solution
0.8% (0.5 M) bicine/sodium hydroxide pH 8.5 buffer
3.2% Maypon 4C

Recipe for a final volume of 200 mL
200mL deionized water
1.6 g bicine
6 mL Maypon 4C
Adjust to pH 8.5 with 1 M sodium hydroxide

Adjusted Buffered Detergent Solution
0.8% (0.5 M) bicine/sodium hydroxide pH 8.5 buffer
1% (0.355 M) sodium lauryl sulfate

Recipe for a final volume of 200 mL
200 mL deionized water
1.6 g bicine
2.1 g sodium lauryl sulfate
Adjust to pH 8.5 with 1 M sodium hydroxide

2% Ammonium Citrate Solution
2% (w/v) ammonium citrate in deionized water adjusted to ~ pH 9 with ammonium carbonate and ammonium hydroxide

Recipe for a final volume of 200 mL
200 mL deionized water
4 g ammonium citrate
6 g ammonium carbonate
~ 1.5 mL ammonium hydroxide
Marble dust

5% Ammonium Citrate Solution
5% (w/v) ammonium citrate in deionized water adjusted to ~ pH 9 with ammonium carbonate and ammonium hydroxide

Recipe for a final volume of 200 mL
200 mL deionized water
10 g ammonium citrate
6 g ammonium carbonate
~ 1.5 mL ammonium hydroxide
Marble dust

Joan of Arc Listening to the Voices
2% Agar Gel with 2% Ammonium Citrate
2% (w/v) agar dissolved in 100 mL of 2% (w/v) citric acid solution adjusted to ~ pH 8.5 with ammonium hydroxide

Recipe for a final volume of 100 mL
100 mL deionized water
2 g agar
2 g citric acid
Ammonium hydroxide to pH 8.5

2% Agar Gel with pH 8.5 Adjusted Water
2 g agar in 100 mL of pH 8.5 adjusted water

Recipe for 3000 mL of pH 8.5 adjusted water (Stavroudis 2016)
1 mL glacial acetic acid
3000 mL deionized water
Set pH to 8.5 with 10% ammonium hydroxide (~ 14 mL)

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SOURCES FOR MATERIALS

Agar-Agar

Myco Supply
PO Box 15194
Pittsburgh, PA 15237
888-447-7319
www.mycosupply.com

Ammonium Carbonate [$(NH_4)_2CO_3$], CAS Number 506-87-6; Ammonium Hydroxide (NH_4OH), CAS Number 1336-21-6; Calcium hydroxide [$Ca(OH)_2$], CAS Number 1305-62-0; Diethylenetriamine-pentaacetic Acid (DTPA; $C_{14}H_{23}N_3O_{10}$), CAS Number 67-43-6; Glacial Acetic Acid ($C_2H_4O_2$), CAS Number 64-19-7; Sodium Hydroxide (NaOH), CAS Number 1310-73-2; Sodium Lauryl Sulfate ($C_{12}H_{25}NaSO_4$), CAS Number 151-21-3

Fisher Scientific
Fair Lawn, NJ 07410
201-796-7100
www.fishersci.com

Ammonium Citrate Tribasic ($C_6H_{17}N_3O_7$), CAS Number 3458-72-8; Bicine ($C_6H_{13}NO_4$), CAS Number 150-25-4; Citric Acid ($C_6H_8O_7$), CAS Number 77-92-9

Sigma-Aldrich
3050 Spruce St.
St. Louis, MO 63103
800-325-5832
www.Sigma-aldrich.com

Ethylenediaminetetraacetic acid (EDTA; $C_{10}H_{16}N_2O_8$), CAS Number 60-00-4

Bioland Scientific, LLC
14925 Paramount Blvd. Suite C
Paramount, CA 90723
562-602-8882
www.bioland-sci.com

Maypon 4C
Inolex Chemical Company
2101 S. Swanson St.
Philadelphia, PA 19148
215-271-0800
www.inolex.com

Methocel A4C; Triton XL-80N
The Dow Chemical Company
2030 Willard H. Dow Center
Midland, MI 48674
800-258-2436
www.dow.com

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