2016

An Evaluation of Laser Ablation Cleaning on Surficial Black Crust on Pennsylvania Marble: A Case Study of the Hood Cemetery Gate, Germantown, Philadelphia, PA

Xinhui Yang

University of Pennsylvania

Follow this and additional works at: http://repository.upenn.edu/hp_theses

Part of the Historic Preservation and Conservation Commons

http://repository.upenn.edu/hp_theses/602

Suggested Citation:

This paper is posted at ScholarlyCommons. http://repository.upenn.edu/hp_theses/602
For more information, please contact repository@pobox.upenn.edu.
An Evaluation of Laser Ablation Cleaning on Surficial Black Crust on Pennsylvania Marble: A Case Study of the Hood Cemetery Gate, Germantown, Philadelphia, PA

Abstract
Black crust, or gypsum crust, is a surficial accumulation of atmospheric deposits in a gypsum matrix, which is often firmly bonded to the substrate. This condition is ubiquitous on marble buildings, not only threatening the historic fabric, but also leading to aesthetic damage. Laser ablation cleaning has become a popular method to remove black crust from masonry surface. This study focuses on the evaluation of laser ablation cleaning on the Pennsylvania marble of the Hood Cemetery Gate, which locates in Germantown, Philadelphia, PA. In advance of cleaning, the marble and the black crust was characterized through petrographic thin-sections, X-Ray Diffraction, and Scanning Electron Microscopy to understand the micro-structure and chemical composition of the materials. A low power portable fiber laser was used for cleaning and evaluation. Laboratory cleaning tests on small samples were conducted to determine the effective parameters, in dry and wet conditions. The cleaned area was examined with a spectrophotometer, Scanning Electron Microscopy, and Raman spectroscopy to detect potential changes in, surface morphology, and chemical composition. In situ cleaning test was conducted using the optimal parameters based on the results of laboratory tests, and the outcome was evaluated in terms of color change. In conclusion, laser ablation cleaning was generally effective on the marble of the Hood Cemetery Gate. In wet condition, it resulted in a satisfying removal of the black crust without causing micro-scale damage or undesired discoloration.

Keywords
fiber laser, gypsum, petrography, SEM, color changes

Disciplines
Historic Preservation and Conservation

Comments
Suggested Citation:


This thesis or dissertation is available at ScholarlyCommons: http://repository.upenn.edu/hp_theses/602
AN EVALUATION OF LASER ABLATION CLEANING ON SURFICIAL BLACK CRUST ON PENNSYLVANIA MARBLE: A CASE STUDY OF THE HOOD CEMETERY GATE, GERMANTOWN, PHILADELPHIA, PA

Xinhui Yang

A THESIS in Historic Preservation

Presented to the Faculties of the University of Pennsylvania in Partial Fulfillment of the Requirements of the Degree of

MASTER OF SCIENCE IN HISTORIC PRESERVATION

2016

______________________
Advisor
Reza Vatankhah
Lecturer in Historic Preservation

______________________
Program Chair
Randall F. Mason
Associate Professor
Acknowledgements

I would like to express my deepest gratitude to Adam Jenkins, who not only provided the laser system and great information for the aim of my research, but also patiently helped me with operating the laser for the testing in laboratory and in-situ. Without you this thesis would not have been possible.

I am very appreciative to Prof. Frank Matero and Dr. Reza Vatankhah, who supported me constantly throughout my thesis process. Thank you for advising me on my thesis topic, for arranging the site-visits and appointments for laboratory analysis, and your suggestions and comments for my writing.

My special thanks go to Dr. Marie-Claude Boileau for sharing her great knowledge on petrography, Catherine Matsen for her expertise on Raman spectroscopy analysis, and Steve Szewczyk for his patient guidance on XRD analysis. To Courtney Magil, thank you for all the help with the laboratory equipment and software.

My appreciation goes to thank Mark Sellers and the Friends of Hood Cemetery, who helped me greatly during my site-visits by providing a ladder, scaffolding, and a generator. Your support was indispensible.

Finally, to my family and friends, thank you for all your encouragement and love throughout the entire process.
# Table of Contents

Acknowledgements ........................................................................................................... i
Table of Contents ............................................................................................................ iii
List of Figures .................................................................................................................... v
List of Tables ...................................................................................................................... viii
Chapter 1: Introduction ................................................................................................... 1
Chapter 2: Background and Building Conditions ........................................................... 5
  2.1 Historical Background ............................................................................................. 5
  2.2 Building Description ............................................................................................... 9
  2.3 Masonry Conditions and Diagnosis ......................................................................... 10
Chapter 3: Black Crust on Calcareous Stones ............................................................... 14
  3.1 Definition, Nature, Where It Occurs ...................................................................... 14
  3.2 Formation Mechanism ............................................................................................ 17
    3.2.1 Dissolution Reactions ....................................................................................... 17
    3.2.2 Thermally Induced Micro-cracking of Marble ................................................ 20
    3.2.3 Layering of Black Crust and Gypsum Crystallization ....................................... 21
Chapter 4: Laser Ablation Cleaning on Stone ................................................................. 26
  4.1 Principles of Laser .................................................................................................. 26
  4.2 Laser Ablation Cleaning ......................................................................................... 29
    4.2.1 Principles ......................................................................................................... 29
    4.2.2 Advantages ..................................................................................................... 32
    4.2.3 Major Disadvantage: Discoloration Effect ....................................................... 35
  4.3 Studied Parameters and Conditions of Laser Cleaning on Stone ....................... 38
    4.3.1 Wavelengths .................................................................................................. 38
    4.3.2 Operating Mode/ Pulse Duration ................................................................. 42
    4.3.3 Fluence (Power Density) .......................................................... ......................... 44
    4.3.4 Wet/Dry Condition ....................................................................................... 45
Chapter 5: Material Characterization ............................................................................. 47
  5.1 Overview ............................................................................................................... 47
  5.2 Background of Pennsylvania Marble ..................................................................... 48
  5.3 Methodology ......................................................................................................... 50
List of Figures

Figure 1.1: The south façade of the Hood Cemetery Gate (Author 2016).................. 1

Figure 2.1: Site map of the Hood Cemetery (the yellow dot indicates the gate), created from
Google Earth................................................................. 5
Figure 2.2: A view inside the cemetery, looking east (Author 2016)............................ 7
Figure 2.3: The inscription under the arch (Author 2016)........................................ 8
Figure 2.4: The back. The skull and cross-bones has been damaged. Horizontal and diagonal
streaks can be seen on the marble blocks around the arch, indicating the foliation planes (Author
2016).................................................................................. 13

Figure 3.1: Above: Biological colonization “crust” showing some patterns (Siegesmund and
Snethlage ed., Stone in Architecture, 298). Below: Iron-rich patina on sandstones (Vergès-Belmin,
Illustrated Glossary, 59).............................................................................................................. 15

Figure 4.1: Schematic representation of a flashlamp-pumped Nd:YAG laser (drawing by author
after Cooper). ........................................................................................................................................ 28
Figure 4.2: A simplified schematic of the interaction of long-pulse laser radiation with black crust,
from Lazzari and Asmus “The Application of Laser Radiation,” 46. .................................................. 29

Figure 5.1: Above: The urn to the east of the gate. Below: The broken piece. The white rectangular
frame indicates where the sample was taken. .................................................................................. 56
Figure 5.2: Sample #1, white marble with biological colonization on surface......................... 57
Figure 5.3: Looking at the cornice from the northwest corner. The white rectangular frame
indicates where Samples #2, 3, and 4 were taken. ........................................................................... 57
Figure 5.4: Sample #2, the framboidal black crust of spherical shape, with disaggregated substrate.
......................................................................................................................................................... 58
Figure 5.5: Sam ple #3, black crust on a solid substrate................................................................. 59
Figure 5.6: Sample #4, a very thin piece with yellowish surface, partially covered by thin black
crust. .................................................................................................................................................. 60
Figure 5.7: Photomicrograph of Sample #2, looking at the section, 25x magnification. A change of
color from white (substrate) to black (outer crust) is visible.......................................................... 60
Figure 5.8: Photomicrographs of Sample #2. Above: looking at the black crust surface, 12.5x magnification. Below: looking at the cracked crust and disaggregated marble (yellowish color) from the bottom, 2.0x magnification.

Figure 5.9: Photomicrographs of Sample #3. Above: The morphology of the crust changes from relatively smooth to framboidal, 10x magnification. Below: The marble substrate with black inclusions, yellowish stains and greyish grains, 25x magnification.

Figure 5.10: Photomicrograph of Sample #4. A yellow layer underlying the black crust is visible, 20x magnification.

Figure 5.11: Grain size distribution of Sample #1 (marble). The longest dimension of each grain was measured and rounded to the closest number (100 μm interval). Grains smaller than 50 μm are mostly inclusions, thus they are not included in this chart.

Figure 5.12: Thin-section of the marble in PPL (above) and XPL (below), at 40x magnification.

Figure 5.13: Thin-section of the framboidal black crust in PPL (above) and XPL (below), at 40x magnification. Clear gypsum is visible between the calcite grains.

Figure 5.14: The framboidal black crust in PPL (above) and XPL (below), looking at euhedral gypsum crystals, at 100x magnification.

Figure 5.15: The inclusions in the outer crust, possibly carbon particles, organic flakes, and small mineral grains, at 400x magnification.

Figure 5.16: The framboidal black crust in PPL (above) and XPL (below), looking at the brownish stains around calcite crystals, at 40x magnification.

Figure 5.19: SEM image of Sample #3, showing crystals and air-borne particles.

Figure 5.20: SEM image of Sample #4, showing tabular gypsum crystal growing with eroded calcite grains.

Figure 5.21: Elemental mapping of an area on Sample #4, at 100x magnification. High concentration of Ca, S, and O indicates the prevalence of gypsum. See Appendix B for the full report generated from the software.

Figure 6.1: The CL 20 Q Laser backpack (Author 2016).

Figure 6.2: The laser scanning head (Author 2016).

Figure 6.3: Different operating modes of a Nd:YAG laser (left) and a fiber laser (right). From Hildenmann and Dickmann, “Comparative Studies: Nd:YAG vs. Fibre,” in LACONA VIII, 120.

Figure 6.4: Sample #3 after cleaning with the surface dry (above) or wet (below), at 20 W. The dried-cleaned area (left) exhibits much darker color when wetted.

Figure 6.5: A fragment of Sample #4 after dry-cleaning at 10 W.
Figure 6.6: The scaffolding prepared for in-situ cleaning test (Author 2016). ................................. 82
Figure 6.7: The testing area before and after cleaning, view from the northeast corner. The cleaned surface exhibited a similar color to the marble on the north side of the pillar. ................................. 84
Figure 6.8: A comparison of the testing area before and after cleaning, view from the front. The thick crust on the middle molding was only partially removed. ............................................... 85

Figure 7.1: Photomicrograph of Sample #3, after dry cleaning (right), 20x magnification .......... 96
Figure 7.2: Photomicrograph of Sample #3, after wet cleaning (right), 20x magnification. .......... 96
Figure 7.3: Photomicrograph of Sample #3, comparing dry-cleaned (left) and wet-cleaned surface (right), 20x magnification. ......................................................................................................................... 97
Figure 7.4: Surface before (left) and after (right) in-situ cleaning test, 10x magnification. .......... 97
Figure 7.5: Surface after in-situ cleaning test, 10x magnification, showing a yellowish layer .......... 98
Figure 7.6: The locations of color measurements for in-situ cleaning test: 1 - Yellow area before; 2- Dark area before; 3 - Yellow area after; 4 - Dark area after; 5 - Fresh marble; 6 - Weathered marble. ............................................................................................................................................................................................ 98
Figure 7.7: Results of color measurement on laboratory samples. Above: Data plotted in a*/b*. Below: Data plotted in L*/b*. Diamond- Marble. Round- Before cleaning. Square- After cleaning. ............................................................................................................................................................................................ 99
Figure 7.8: Results of color measurement for in-situ cleaning test. Above: Data plotted in a*/b*. Below: Data plotted in L*/b*. Diamond- Marble. Round- Before cleaning. Square- After cleaning. ............................................................................................................................................................................................ 100
Figure 7.9: SEM images of Sample #3, 100x magnification. Above: dry-cleaning. Below: wet-cleaned. ............................................................................................................................................... 101
Figure 7.10: SEM images of Sample #3, 500x magnification. Above: before cleaning. Below: wet-cleaned. ............................................................................................................................................... 102
Figure 7.11: SEM images of Sample #4, 100x magnification. Above: before cleaning. Below: dry-cleaned. ............................................................................................................................................... 103
Figure 7.12: SEM image of Sample #4, 500x magnification, wet-cleaned. ........................................ 104
Figure 7.13: Raman spectra (partial) overlay of dry-cleaned samples (green), wet-cleaned samples (red), gypsum (blue), and anhydrite (purple). ............................................................................................................................................................................................ 104
Figure 7.14: Full Raman spectra of dry-cleaned samples (above) and wet-cleaned samples (below), compared with anhydrite (purple) and gypsum (blue), respectively. ............................................................................................................................................................................................ 105
List of Tables

Table 1: A summary of previous studies, in which laboratory experiments were performed to observe the forming process of black crust. .................................................................25
Table 2: Reported ablation thresholds and damages thresholds in literature. QS = Q-switched; LQS = Long Q-switched; SFR = Short free running; NFR = Normal free running. ......................45
Table 3: The specifications of CL 20 Q laser ........................................................................75
Table 4: Fluence calculations. Peak power indicates the maximum occurring power of a laser pulse. .......................................................................................................................... 86
Table 5: Color measurements on the laboratory samples, after cleaning. .................................92
Table 6: Color measurements for the in-situ test, before and after cleaning. .........................93
Chapter 1: Introduction

The Hood Cemetery Gate, located at 4901 Germantown Avenue in Philadelphia, PA, is a marble building carved by William Struthers, one of the most significant stonemasons in the nineteenth century in the United States (Figure 1.1). It is now over 150 years old and exhibits a variety of conditions. Recently, a masonry conservation program, sponsored by the Friends of Hood Cemetery, was proposed to preserve the historical fabric and recover the appearance, which is primarily affected by black crust and yellow staining (common on marble buildings). Given the complicated pattern of conditions on this building, a satisfying restoration can only be achieved by applying multiple treatments in a certain sequence. In terms of cleaning, black crust should take the first priority because it is the most damaging surficial condition.

Figure 1.1: The south façade of the Hood Cemetery Gate (Author 2016).
Marble, one of the most important building materials since the ancient time, has been suffering from severe deterioration caused by atmospheric pollutants, particularly in the last two centuries due to the industrial development. The formation of black crust is ubiquitous on marble surface. Gypsum, which forms the matrix of the crust, is originated from sulfating process of calcite; the dark color of the crust results from embedded particles. The crust is potentially damaging since it is often dense and compact while the substrate is often deteriorated; therefore, spallation of stone is commonly observed where black crust occurs. Importantly, it affects severely the appearance of decorative marble, which is usually light-colored. Extensive research has been done to reveal the nature of black crust and its formation mechanism, allowing for rational decisions in selecting treatments.

In the early 1970s, laser ablation was introduced as a cleaning method specifically aiming at dark-colored pollutants on light-colored marble surface. Based on its cleaning mechanism, laser is considered particularly suitable for this kind of conditions. It can differentiate black crust from marble, potentially leaving no damage or little compared to conventional cleaning methods (such as chemical cleaning). Laser ablation cleaning has been used for outdoor cleaning since the 1990s and was proved successful in many cases. However, given the great variation of stones, black crusts, and laser systems, it should be performed carefully although it is relatively “safe”. In order to achieve the best cleaning outcome, it is necessary to conduct a close investigation on the properties of the crust and the substrate, and cleaning trials on sample areas should follow.
The building material of the gate, the Pennsylvania marble, was a local stone quarried from Montgomery County. It was used on numerous important buildings in Philadelphia, including the Second Bank of the United States and the Philadelphia Merchants’ Exchange. The marble of these buildings has been characterized, and a variety of treatments have been tested for the earlier restoration campaigns. Laser ablation cleaning is now commonly used in the United States, and a few large-scale projects have been done successfully on stone buildings. These studies are very informative, but unlike some famous European marbles (such as the Carrara marble) that have been investigated for many years, there is no publication yet focusing on the application of laser cleaning on the Pennsylvania marble.

This thesis aims to evaluate the effectiveness of laser cleaning on the surficial black crust identified from the Hood Cemetery Gate. The methodology of study will involve literature review, laboratory analysis and in-situ testing. First, a review of technical literature will help to understand the variation, composition and microstructure of black crust and its developing process on the surface of calcareous stones, including marble. The following will be a summary of the principles of laser ablation cleaning, and a general discussion of the adjustable parameters widely studied in the field in the last two decades. Possible laser-induced alterations on black crust and marble surface, both positive and negative, will be taken into consideration. This part of research will provide background knowledge for analysis and testing.

Laboratory analysis will be conducted on samples taken from the Hood Cemetery Gate to
characterize the black crust and the marble substrate on this specific building. The aim is to identify potential vulnerability of the stone under laser irradiation, and to build up a general expectation of the cleaning effects by comparing the sample to some others from previous cases. The investigation will involve analytical techniques including petrography, X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Some information gained from this step will be used for before- and after-cleaning comparison to identify possible damage.

A portable fiber laser system, the CL 20 Q backpack, will be used for cleaning test. It has not yet been widely employed in architectural conservation, and this thesis will provide some new insights concerning this specific system. The first stage will be laboratory test on small samples, and the second stage will be in-situ test on a larger area. The evaluation will emphasize on color change, chemical alteration, and general surface morphology after cleaning (although some other topic has also been studied, such as cleaning rate). Spectrophotometer, SEM and Raman spectroscopy will be employed. Finally, a recommendation will be provided based on the results of evaluation.
Chapter 2: Background and Building Conditions

Figure 2.1: Site map of the Hood Cemetery (the yellow dot indicates the gate), created from Google Earth.

2.1 Historical Background

Germantown is a neighborhood in the northwest section of Philadelphia, PA. Less than a year after William Penn’s arrival, thirteen German farmer families settled here as an independent borough on October 6th, 1683. The township was incorporated into the City of Philadelphia in 1854 and became a part of the Six Ward.¹ The settlement developed along Main Street, now Germantown Avenue, which connects this area to the city center.

The Hood Cemetery, originally known as the Lower Burying Ground, is located at 4901 Germantown Avenue (Figure 2.1), i.e. the northeast corner of the avenue’s intersection with East

¹ Naaman H. Keyser et al., History of Old Germantown (Germantown, Philadelphia: H.F. McCann, 1907), 28-9, 85.
Logan Street (historically Fisher’s Lane). Opened in 1693, it is one of the city’s oldest burying grounds. In February 1692, one half-acre of land was conveyed by Leonard Arets to Paul Wulff (both were inhabitants of Germantown) to be used “in no way other than a burying place”. Thereafter, Wulff deeded the land and another half-acre of his own (later became the Upper Burying Ground) to the Commonalty of Germantown in March of the same year, and received a quarter acre in return. The premises have been enlarged through further purchasing, and the cemetery now encompasses about two acres of ground enclosed by stonewalls. The oldest tombstone dates to 1708, and many veterans, from the Revolutionary War to the First World War, are buried here (Figure 2.2).

The cemetery received its current name in honor of William Hood, a former local resident who earned a great fortune in Cuba. In 1847, Hood offered to erect a marble entrance for the cemetery if he could be allowed to built a vault near the front gate. The trustees, who have been managing the cemetery, accepted this proposal. The gate was designed by architect William Johnston and was built by marble mason William Struthers in 1849, as inscribed under the arch of the gateway (Figure 2.3). Hood died in 1850 in Paris and was buried at the chosen location. In 1866, the trustees obtained a charter under the title of the Hood Cemetery Company and received

---

1 The original document was written in Germany as *Germantown Grund und Lager Buch*, and was translated to English. Leonard Arets (whose name appears in different ways in literature) was one of the first settlers in Germantown. In 1683, a large area of land was granted to him by deed of William Penn’s. See Ibid, 227-30.
2 A magazine article from 1881 indicates that the front was about 180 feet and the depth was 350 feet. See Townsend Ward, “The Germantown Road and Its Associations: Part Third,” *The Pennsylvania Magazine of History and Biography* 5, no. 3 (1881): 241.
the property in 1868, since when the cemetery was known for its current name.4

Figure 2.2: A view inside the cemetery, looking east (Author 2016).

The architect William L. Johnston (1811-1849), a Philadelphia local, started his career as a “house carpenter” and later as an architect. He designed houses, churches and public buildings in the city, and also taught architectural drawing at a school run by the Carpenter’s Company of Philadelphia. His best-known work is the Jayne Building, an eight-story building (with a two-story gothic tower on top) completed in 1850 (after the death of Johnston, architect Thomas U. Walter took over the project) that is often described as the first “skyscraper” in Philadelphia.5

He was also a contributor for The Carpenter’s New Guide: Being a Complete Book of Lines for

---

Carpentry and Joinery, of a few plates demonstrating joinery, staircase and hand-railing.\(^6\)

Figure 2.3: The inscription under the arch (Author 2016).

The marble mason William Struthers (1812-1876), following his father John Struthers (1786-1851), was successful as a stonecutter and businessman. The elder Struthers, descendant of a long-line Scottish stonemason family, immigrated to Philadelphia in 1816 and founded his company. He supplied the marble work for many distinguished public buildings in the city, including the Second Bank of the United States (1818-1824), the United States Naval Asylum (1827-1833) and the Philadelphia Merchant’s Exchange (1832-1834). He was associated with architects working in the city, such as William Strickland and Thomas U. Walter.\(^7\) William Struthers was born in the town of Irvine in Scotland. He joined the company around 1840 and


gained his reputation for the Farmers’ and Mechanics’ Bank (1853-1855) on Chestnut Street. In the 1870s, he received the marble commission of Philadelphia City Hall. By that time, the five-million-dollar contract was one of the largest ever. He was interested in public affairs, being “a treasurer of the Pennsylvania Academy of Fine Arts, a member of the Historical Society, the Franklin Institute, and the Academy of Natural Sciences”.  

2.2 Building Description

The cemetery gate is located at the middle of the south wall, facing the southwest. In 1973, Historic American Buildings Survey (HABS) photo-documented the gate (see Appendix D) and described it as: “Marble, approx. 147” front, horseshoe-arch entry between engaged Corinthian columns and beneath bracketed round-arch with cartouche, balustraded front wall.” Since the cemetery ground is higher than the grade of the streets, the entire structure stands on two courses of base stone. Five steps lead to the gateway and connect to a path, which divides the cemetery into halves. The total height of the gate is about 20 feet from the cemetery ground (or 23 feet from the pavement), and the width of the gateway is 6 feet 6 inches. The design is of Neo-Baroque style, with scroll buttresses flanking the gate, ending with an ornamental urn on each side; however, the

---


horseshoe-arch indicates an Islamic influence. The cartouche is decorated with a winged hourglass in the front (Figure 2.4), and with a skull and cross-bones at the back. Both symbols are commonly employed in funerary iconography.

The gate is composed of solid marble blocks, carefully finished on both sides with various tooling marks: patent hammered or bush hammered on the base, and rubbed on the main structure. By visual examination, the upper part of the structure is made of a fine-grained marble, presumably required by the sculptural detailing, while the base part is made of a coarser-grained marble. The foliation planes of the marble are evident at some locations. The blocks are either face-oriented or edge-oriented (horizontal, vertical, or diagonal), and some of them seems to be placed intentionally to achieve certain visual effect (Figure 2.5).

2.3 Masonry Conditions and Diagnosis

The Hood Cemetery Gate does not exhibit structural failure and the marble blocks are generally sound. However, a variety of deterioration forms are evident on the building, particularly on the carved details, severely damaging the aesthetic value. In 2012, Yun Liu and Tingting Weng, students from the University of Pennsylvania, have completed a condition report

\[10^\text{The source of these marbles was found through archival research. Their properties will be further discussed in Chapter 5.}\]
(unpublished) for the gate.\textsuperscript{11} Basic photograph comparison indicates that the conditions generally remain the same as four years ago, although there are some minor differences.

A few conditions, including spallation, dimensional loss and cracking, are triggered by the incipient stress of the structure. There can be various source of the stress, such as differential settlement, vibration (resulting from traffic or construction), thermal expansion and contraction of the material, etc. Moderate cracks are concentrate at the lower part of the structure. Some develop along the foliation planes of the marble blocks, as the binding between the layers is usually weaker than within a layer, others may be caused by compression load. For similar reason, partial detachment of the stone occurs at the column base, and previous mortar repair is visible. A major crack has been identified on the east column in the front, possibly caused by shear force. It locates at the connection between the column and the main body, penetrating the entire shaft. The medallion (in the middle of the cartouche) shows significant dimensional loss at the left bottom and a crack on the right. These conditions can be attributed to the volume expansion of the rusted iron anchor, which ties the medallion to the back stone.

Other conditions, such as flaking, erosion, staining and encrustation, generally result from chemical changes beginning with dissolution of calcite grains. Some mechanical processes, such as freeze-thaw cycles, are also involved. Large part of the structure exhibits crumbling surface, and many carved details of the capitals show localized loss or reduction. Yellow staining, often

attributed to atmospheric iron, follows a run-down pattern independent of the surface configuration. Black encrustation, presumably consisted of gypsum and dark air-borne pollutants, intensively develops on area sheltered from running water. The above conditions, as exhibited on many marble structures around Philadelphia, are clearly related to the urban and industrial context of the building, given that Germantown was a manufacturing center and a large industrial town by the end of the 19th century and the beginning of the 20th century. Besides, the site has been exposed to heavy traffic of Germantown Avenue. These environmental factors probably have accelerated the deterioration.

Biological growth was identified on the building, particularly on the north side, where there is less direct sunshine due to the orientation and the tree shades in the cemetery. On the other hand, efflorescence occurs mainly on the front surface, probably due to higher evaporation rate on this side. The salts may come from the cemetery soil and de-icing salts on the street. These two conditions are subject to seasonal change in terms of precipitation and evaporation. The HABS photos in 1973 reveal graffiti on the base, which was covered through repainting in the 1980s (the solid wall around the gate in the front was all painted). The repointing work was done in the same period, but some joints are currently open.
Figure 2.4: The cartouche is significantly deteriorated; this area exhibits spallation, cracking, black crust and yellow staining. The shape of the hourglass is still visible (Author 2016).

Figure 2.4: The back. The skull and cross-bones has been damaged. Horizontal and diagonal streaks can be seen on the marble blocks around the arch, indicating the foliation planes (Author 2016).
Chapter 3: Black Crust on Calcareous Stones

3.1 Definition, Nature, Where It Occurs

Black crust, also referred as gypsum crust, is a surficial accumulation of atmospheric deposits in a gypsum (CaSO₄·2H₂O) matrix, which is often firmly bonded to the stone substrate.¹² On buildings and monuments, it generally develops on surfaces sheltered from running water. The dark color is given by the embedded particles, which may include mineral dust, coal ash, iron oxides and other organic pollutants, although the crystallized gypsum is transparent to opaque white by itself. Thickness of the crust can be homogeneous or not, following or disturbing the shape of the architectural component on which it occurs. The crust may detach spontaneously from its substrate, resulting in loss of historic material. Besides, it often leads to aesthetic damage on monuments.

By visual inspection, black crust may be confused with other types of black layers on stone surface, such as biological colonization and patina (Figure 3.1). Lichens, which commonly grow on calcareous stone around the world, can from a dark colored “crust”. However, it does not preferentially occur on rain-protected surface. In many cases, the biological crust shows a “landscape” pattern and some color variation, differentiating it from gypsum crust that exhibit a more uniform color. On the other hand, lichens are sensitive to industrial pollutants, so this

condition occurs more extensively in rural environment (opposite to black crust). Another example, iron rich patina, may also appear dark-colored, but it develops on exposed surface and does not have a perceivable thickness as gypsum crust does. In fact, marble and limestone are more associated to brown to orange patina containing calcium oxalates (CaC₂O₄), while black patina is often identified on sandstones.

---

Figure 3.1: Above: Biological colonization “crust” showing some patterns (Siegesmund and Snethlage, *Stone in Architecture*, 298). Below: Iron-rich patina on sandstones (Vergès-Belmin, *Illustrated Glossary*, 59).

---


Two types of black crusts are identified according to their morphology: laminar crusts and framboidal crusts. The former, often found on vertical or sub-vertical architectural components, is relatively thin (a few millimeters) and has smooth surface. The latter type, also referred as globular crust, can reach a thickness of a few centimeters. The laminar type is generally rigid, while blistering and scaling are more common on the framboidal type. The former can develop into the latter.\textsuperscript{15} However, this classification is macroscopic and does not indicate the crystal habit of gypsum.

Black crust occurs on various types of stone: marble, limestone, sandstone and granite.\textsuperscript{16} In the past decade, a variety of examples have been well studied for the restoration campaigns, including: in Europe, the marble on the Milano Cathedral;\textsuperscript{17} the oolitic limestone and travertine used on buildings in Budapest;\textsuperscript{18} the “Drachenfels” trachyte used as building material in medieval time on the Cologne Cathedral;\textsuperscript{19} the limestone on the Chartres Cathedral in France;\textsuperscript{20} and in the United States, the marble at the Philadelphia Merchants’ Exchange Building.\textsuperscript{21}

\textsuperscript{16} On granite and sandstone that are not calcite-cemented, the formation mechanism is not the result of substrate deterioration as on calcareous stones. See Siegesmund and Snethlage, \textit{Stone in Architecture}, 261.
3.2 Formation Mechanism

Over the past few decades, an extensive amount of work has been done to reveal the formation mechanism of black crust, especially in urban areas. The formation process is complex, involving a sequence of physical and chemical changes. As thorough introduction to the properties, deterioration and conservation of stone, E. M. Winkler’s *Stone in Architecture: Properties, Durability* (1994) and the later version (2011) edited by Siegesmund and Snethlage have summarized the general process of gypsum crust formation and the effects of air pollutants. Dario Camuffo’s *Microclimate for Cultural Heritage* (2014) investigates the causality between acid rain and crusts. Alison Henry’s *Stone Conservation: Principles and Practice* (2006) refers to gypsum crust as a major deterioration type of limestone and marble.

3.2.1 Dissolution Reactions

For all calcareous stone, the entire chemical deterioration process similarly begins with dissolution reactions. Calcium in gypsum originates from dissolution reactions of the rock forming minerals, such as calcite (CaCO$_3$) and dolomite (CaMg(CO$_3$)$_2$), when the surface is in contact with water exhibiting acidity.\textsuperscript{22} Although the solubility of these minerals is very low in pure water, the process can be accelerated with the presence of carbon dioxide alone. Other

---

atmospheric weathering agents from the combustion of fossil fuels, such sulfur dioxide and nitrogen oxides, can cause a significant decrease in pH. These agents arrive at stone surface by either dry deposition, i.e. setting as particulates, or wet deposition, i.e. acid rain.  

The formation of gypsum is mainly attributed to SO\textsubscript{2}. The gas dissolves in water layer at stone surface and produces sulfurous acid, which reacts with calcite and produce calcium sulfite (CaSO\textsubscript{3}). The product can be further oxidized and bonded with water to form gypsum. CaCO\textsubscript{3} can also directly react with sulfuric acid. Availability of liquid water is essential to these reactions, but direct exposure to running water can remove CaSO\textsubscript{4}, which has a much higher solubility than calcite and dolomite.  

The reactions are indicated by the following formulas:

\[
\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \\
\text{H}_2\text{SO}_3 + \text{CaCO}_3 \rightarrow \text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O} + \text{CO}_2 + \frac{1}{2} \text{H}_2\text{O} \\
2\text{CaSO}_3 \cdot \frac{1}{2} \text{H}_2\text{O} + \text{O}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \\
\text{H}_2\text{SO}_4 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CO}_2
\]

Laboratory tests conducted by Elfving et al. suggests that molecular O\textsubscript{2} alone is too weak to oxidize S (IV) to S (VI). However, the presence of ozone and nitrate dioxide can lead to rapid oxidation. Calcite was exposed in air with SO\textsubscript{2} alone or with O\textsubscript{3} or NO\textsubscript{2} added, in humid and dry conditions, respectively. The results indicate that O\textsubscript{3}, as a strong oxidant, can react with

\[23\text{ Siegesmund and Snethlage, } \textit{Stone in Architecture}, \text{ 259.}\]
ready-formed sulfite with or without moisture, while NO₂ acts as catalyst in the presence of O₂ and moisture.²⁵ The experiment performed by McAlister et al. reveals that transition metals, such as Fe, Mn, and Zn, can also act as catalyst in the oxidation of S (IV). Dust samples were collected from a building at various heights and locations exposed, moderately and highly sheltered. Selective extraction studies showed that dust accumulated at sheltered surface shows a higher concentration of transition metals in their soluble phase. The mobility of metal ions allows them to participate in surface reaction.²⁶

Many studies have focused on acid deposition on calcareous stones, attempting to draw correlation between microclimate and sulfation rate. A very common method is to compare the chemical composition of the incident rain and the runoff solutions from monuments. Using this method, Dolske performed experiments at two sites in Pennsylvania: the Gettysburg National Military Park and the Merchants’ Exchange Building in Philadelphia. Two marbles, Carrara and Pennsylvania Blue, were investigated. The result of Gettysburg suggests that the rate of calcium loss is more dependent on the shape of the monument than the type of marble. Rougher surface and more complex shape can enhance sulfur deposition. By monitoring the microclimate at two capitals of the Merchants’ Exchange, the data suggest that sulfur concentration increases with

longer duration of wetness and exposure to wind.\textsuperscript{27}

### 3.2.2 Thermally Induced Micro-cracking of Marble

Thermal micro-cracking is another type of condition commonly identified on marble. Formed from a physical process, it is not the immediate cause of gypsum formation. However, if it occurs simultaneously with acid deposition, it clearly can accelerate the dissolution reactions by increasing surface area in contact with acid. On marble, micro-cracking may readily occur when the stone surface temperature reaches 40-50°C, which is not difficult during summer, particularly when the surface is directly exposed to sunlight.\textsuperscript{28}

Marble is more susceptible to temperature change than other rocks due to the thermal behavior of calcite crystal. Upon heating, most minerals expand in both directions, along or perpendicular to the c-axis (the principal axis in uniaxial minerals), while calcite only expands along the c-axis and contracts in the other axes. Upon cooling, calcite only contracts along c-axis and expands in other directions. Compared with calcite marble, dolomite marble may be more resistant to thermal cycles. However, their vulnerability to thermal-induced deterioration also depends on the texture and the nature of residual strain, i.e. the permanent change of length after thermal cycles.\textsuperscript{29}

\textsuperscript{28} Siegesmund and Snethlage, \textit{Stone in Architecture}, 233.
\textsuperscript{29} Ibid, 146-7, 232-5.
3.2.3 Layering of Black Crust and Gypsum Crystallization

Some characteristics of gypsum are essential to the formation of the crust. For example, its low solubility results in low mobility in stone, that is, even if the stone is fully saturated, little gypsum can be dissolved and transported away. Thus, it tends to accumulate over time. Occurring at the evaporation front, the accumulation of gypsum can clog the pores and reduce the evaporation rate. As the substrate remains damp for longer period, there is more chance for surface reactions that increase the acidity. Gypsum is able to generate his crystallization pressure in stone. Growing in micro-cracks and between large crystals, it induces a wedge action that can enlarge the cracks. On the other hand, gypsum can dehydrate to the hemihydrate (CaSO₄·0.5H₂O) at 42°C, but this process rarely occurs in nature since it requires high temperature and very low humidity. Therefore, although the hydration and dehydration of CaSO₄ lead to expansion, it is usually not the cause of deterioration.³⁰

Petrographic investigation of marble covered by black crust often reveals a thin clear layer of gypsum between the dark-colored crust and the unaltered stone substrate. The clear layer is formed through pseudomorphism process, which refers to, in this case, the “transformation of calcite into gypsum without any change in shape or volume of the crystals.”³¹ Frequently seen in igneous and metamorphic rocks, this process is featured by an inward development of new

---

minerals. In a highly metamorphosed marble, it begins with formation of gypsum rims around the original grains, then the formation of boxwork, i.e. a hollow crystalline structure that occupies the space of the parent crystal as the calcite dissolves in acidic environment. Finally, the voids are filled by precipitation of gypsum. As stated above, dissolution reaction of marble not only occurs at the stone surface, but also within the stone, around the crystal boundaries and cleavages. Therefore, pseudemorphic gypsum can develop across several layers of crystal near the surface. Formed simultaneously with the outer dark layer, this gypsum layer remains clear since it is not in direct contact with the atmosphere particles deposited on the stone surface.

Toniolo et al. investigated four black crust samples on marble substrate dated to various periods (old or recent repair) from the Milan Cathedral. The petrographic and chemical analyses suggest that these crusts formed through different processes, despite that they appear similar and all contain gypsum. The thick and dark crust on a nineteenth-century marble exhibits an incompact texture, with gypsum crystals growing in “desert rose” pattern. The transition area between the crust and the substrate, in this sample, is an irregular layer containing detached calcite crystals. This black crust seems to be the most typical kind. Another crust, developed since the 1930s, clearly exhibits two parallel layers consisting of tabular gypsum crystals. While the inner layer is similar to the old sample, the outer layer is transparent with fewer particles

embedded. The crystal form suggests a low forming rate and the layering may be caused by application of acrylic treatment. A crust sample regarded as “compact deposit” has a sound substrate (owing to a protective layer), indicating that gypsum can also be exogenous (although in most cases it is from the weathered marble).\textsuperscript{33}

In terms of limestone, similarly, a transition layer can often be observed between the substrate and the surficial crust. The texture and composition of all the three layers may appear significantly different depending on the case. For example, Belfiore et al. investigated black crust on three historical buildings in Italy, Belgium and France. The samples from Italy are covered by thin crust (about 200 \(\mu\)m) solidly attached to the substrate, which is not significantly altered. The samples from the other two sites both show high secondary porosity of the substrate, with microcrystalline gypsum developing in the fractures.\textsuperscript{34} Fontaine et al. characterized and compared thick and thin (or “film”) black crust on the limestone from the Tournai Cathedral, Belgium. The substrate of the thick crust is fragmented, and the transition layer, consisting of stone remnants and a weakly cohesive matrix, can be several millimeters thick. In contrast, the transition layer is very thin in the film type. While the original texture of stone is preserved, the matrix is replaced by gypsum.\textsuperscript{35}

\textsuperscript{33} Toniolo et al. “Black Layers on Historical Architecture,” 224.
\textsuperscript{34} C. M. Belfiore et al., “Application of Spectrometric Analysis to the Identification of Pollution Sources Causing Cultural Heritage Damage,” \textit{Environmental Science and Pollution Research} 20, no. 12 (2013): 8848–59.
Carbonaceous dust plays an important role in the nucleation of gypsum crystals. Dust particles are usually round and have porous morphology. Several research groups conducted laboratory tests on limestone to observe the gypsum crystallization process, using simulation chambers filled with SO$_2$ or SO$_3$ and controlled under a high relative humidity. Micrographs clearly showed that gypsum grew into acicular or tabular crystals on surface exposed to particulates. Crystals developed at the interface of the particles and the substrate, acting as “anchor”. On the other hand, without particulate matter, the growth of gypsum crystal was less intense or even excluded, depending on the experiment materials and conditions (as listed below in Table 1). Some of these experiments also highlight that pollutants from fossil fuel exhaustion, containing metallic particulates, can accelerate gypsum growth. In laboratory condition, a much higher concentration of SO$_2$ (at around 100 ppm level, while in real urban environment it is usually at ppb level) was often used (except by Ausset et al.). In these conditions, the gypsum grew at an extremely fast speed, but the crystal habit was not affected.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Materials and Conditions</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rodriguez-Navarro and Sebastian (1996)$^{36}$</td>
<td>Tortonian limestone, high porosity (average 32%) SO$_2$ initially 100 ppm (much higher than real situation), 30°C, 100% RH Samples: fresh, coated with dust, gasoline exhaust particulates, diesel exhaust particulates</td>
<td>Fresh: no gypsum after 48 h Dust (after 48 h): Fungi, under which small gypsum crystals, star- or needle-shaped Gasoline (after 48 h): incipient growth, amassed in globular aggregates Diesel: Crystals seen after 24 h on etched</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Study</th>
<th>Material Type</th>
<th>Conditions</th>
<th>Description</th>
</tr>
</thead>
</table>
| Ausset et al. (1999)37        | Jaumont limestone              | SO₂ 125 ppb; NO₂ 50 ppb (close to real situation), using Lausanne Atmospheric Simulation Chamber (LASC); 13°C; 79% RH | Naked: presence of small acicular gypsum crystals, but did not cover the whole surface even after 12 months  
Sprinkled: area not in direct contact with ash was similar to naked; acicular, tabular or “desert rosette” crystals on and between dust particles, significant after 3 months |
| Cultrone et al. (2004)38      | Tortonian limestone (Same type as investigated in 1996) | SO₂ 50-400 ppm; 25°C; 100% RH                                                | Fresh: no gypsum after 48 h  
Dust: significant growth of star- or needle-shaped crystals after 48 h  
Gasoline and diesel: Incipient growth similar to dust coated one, finally covered with interwoven crystals |
| Gomez-Heras et al. (2007)39    | Jurassic limestones used in Oxford | Pre-contaminated by SO₃ or placed in flowing SO₃ | In airflow, no particulates: showed discontinuous development of gypsum on the surface  
With particulates: whole surface covered by a grey layer of gypsum cementing the particulates |

Table 1: A summary of previous studies, in which laboratory experiments were performed to observe the forming process of black crust.

---

Chapter 4: Laser Ablation Cleaning on Stone

Since the invention of the first laser equipment in 1960, this technology was soon employed in conservation. In 1973, Lazzarini and Asmus conducted the earliest test of laser ablation cleaning on historic stone material. 40 However, due to the high expense and low portability of the early laser system, this method was limited to indoor work until the 1990s. The first international conference LACONA (Lasers in the Conservation of Artworks) was held in 1995 to promote cooperation between scientists and conservators. 41 Since then, a great amount of studies have been done to improve the reliability (to avoid undesirable alteration), and efficacy (to achieve complete cleaning), and to overcome the disadvantages of this method. This chapter will introduce the principles and properties of laser ablation cleaning, as well as the parameters widely investigated in the conservation field, in order to develop the testing methodology for the Hood Cemetery Gate.

4.1 Principles of Laser

LASER is an acronym for Light Amplification by Stimulated Emission of Radiation. It is “an extremely intense form of monochromatic light which is emitted in a highly collimated beam.” 42

---

Unlike radiation from conventional light sources (such as the sun and light bulbs), which undergoes a random process in an atomic system, laser is triggered by a stimulating wave with specific energy. The process, called “stimulated emission”, produces photons that are coherent, that is, all identical to the incident one, exhibiting the same wavelength, phase and direction. In this way, the incident light is amplified. Stimulated emission usually occurs at low possibility. Thus, the generation of laser requires an atomic system in which more electrons are at higher energy level.

A laser generating equipment contains three important parts: a lasing medium, which provides the atomic system, a pumping source providing sufficient energy, and an optical cavity forming a feedback system (Figure 4.1). Various materials (in gas, liquid, or solid state) can be used as the medium, and their diverse properties can result in unique features of each type. Nd:YAG (yttrium aluminum garnet doped with neodymium) laser, giving a near infrared wavelength of 1064 nm, is now the most commonly employed type in conservation. Other common laser types for stone cleaning include: 1) Er:YAG (erbium doped, solid-state), $\lambda = 2940$ nm; 2) Fiber laser (optical fiber doped with rare-earth elements), which produces various wavelengths; 3) Excimer (gas) lasers, such as KrF (krypton fluoride) and XeCl (xenon monochloride), producing ultraviolet radiation.43

Properties of laser radiation include directionality, brightness, purity and tunability. Directionality is described by the divergence of light beam, usually measured by the increase in beam diameter over a certain distance (e.g. ten meters). Smaller divergence means that the laser can be operated more precisely. Brightness of laser, same as the other kind of light, is defined as the power per unit area per unit solid angle. Purity indicates the degree of coherence of the emitted light. A “tunable” laser suggests that this type of system allows the generation of a wavelengths range, or harmonics. For example, Nd:YAG laser, which generates a fundamental radiation of 1064 nm (the first harmonic), may also produce 532, 355 and 266 nm wavelengths (called the second, third and fourth harmonic respectively).  

Figure 4.1: Schematic representation of a flashlamp-pumped Nd:YAG laser (drawing by author after Cooper).


Cooper, Laser Cleaning in Conservation, 32-8.
4.2 Laser Ablation Cleaning

4.2.1 Principles

Laser ablation, i.e. the removal of material from a solid surface by laser irradiation, can be either a photothermal or a photochemical process. In essence, the photothermal process is the selective ejection or vaporization of material based on the differential absorption of radiation by dark-colored and light-colored surfaces. Lazzarini and Asmus provide simplified schematics in their publication, showing the interaction of long-pulse laser radiation with dark encrustation on white marble: the laser beam vaporize the highly absorbing encrustation by inducing heat, but is reflected by the marble surface without causing damage (Figure 4.2). This phenomenon is significant for infrared laser, but not for ultraviolet laser radiation, which is almost equally absorbed by dark- and light-colored surfaces. As UV radiation has higher energy than IR

radiation, it may directly break covalent bonds in the surficial material without producing heat.\textsuperscript{46}

Laser can be operated in various modes. In stone conservation, the most commonly applied modes are Q-switched (QS) and short free running (SFR). In an Nd:YAG laser system, the pumping source, i.e. a flashlamp, can only last a short time. Therefore, the laser output appears in pulses, which can be characterized by duration (or pulse length) and repetition rate.\textsuperscript{47} The short free running mode produces normal pulses of duration at microsecond level, while the QS mode produces pulses of much shorter duration (typically around 10 ns) by operating a shutter within the optical cavity.\textsuperscript{48}

In the photothermal process, the surface temperature rise induced by long-wave laser is dependent on material properties and the surface power density of the laser beam \( I \), i.e. pulse energy/ (pulse duration \( \times \) beam size), measured by W/cm\textsuperscript{2}. Within a certain period of time \( t \), the approximate temperature rise is given by:

\[
T(t) = \frac{2aI}{K} \sqrt{\frac{kt}{\pi}}
\]

In the above equation, \( a \) is the absorptivity of the surface at the wavelength of the incident radiation and \( K \) is thermal conductivity. The value \( k \) represents thermal diffusivity, which is dependent on density \( (\rho) \), specific heat capacity \( (c) \) and \( K \). It is defined by:\textsuperscript{49}

\textsuperscript{46} Cooper, Laser Cleaning in Conservation, 42.
\textsuperscript{47} A continuous laser output can be achieved by using other pumping sources, such as quartz-halogen lamps. Ibid, 31.
\textsuperscript{48} Pulse duration varies between laser systems and manufacturers. See section 4.3.3 for examples.
\textsuperscript{49} Cooper, Laser Cleaning in Conservation, 42-3.
Surface power density (SPD) is in reverse proportional to pulse duration. Thus, due to the short pulse duration of QS mode laser, it is able to deposit energy very rapidly and little heat can be conducted away through the material within such a short time. While the SPD of normal pulse can only reach $10^3$ to $10^5$ W/cm$^2$, the concentrated radiation released by QS mode can reach $10^7$ to $10^{10}$ W/cm$^2$, leading to a much higher maximum temperature.\textsuperscript{50}

In the cleaning of black crust on marble, if a low SPD is employed, the thermal expansion of the heated crust will cause stress and strain within itself. By increasing the SPD, the stress will exceed the yield strength of the crust and spallation begins. The energy at this point can break bonds within the crust and between the crust and the substrate. An ejection of particulates from the surface may occur. When the SPD becomes sufficiently high, ablation may take place in the form of explosive vaporization. However, extremely high power density can lead to plasma formation, in which material ejected from the surface will be iodized. This phenomenon is evident with the presence of flashes of light and snapping sound, which corresponds to shock waves. A few authors suggest that this phenomenon should be avoided in conservation because plasma cannot discriminate between the crust and the substrate, leading to aggressive ablation.\textsuperscript{51}

Laser cleaning may have a “self-limiting” nature. Ideally, it means that once the dirt layer or

\[
k = \frac{K}{cP}
\]
crust is removed, the substrate will not be damaged by further exposure to the radiation. But this only exists in theory when the dark layer is perfectly absorbing and the substrate exhibits perfect reflection. In reality, any substrate will absorb a little amount of energy, thus a high radiant fluence (or energy density, measured in J/cm²) can result in undesired damage. In order to control the fluence in laser ablation cleaning, many studies aimed at determining the ablation threshold, i.e. the lowest fluence above which the ablation is enabled. The threshold is dependent on the laser system, the properties of the surface pollution, as well as the substrate. Cooper and Larson’s research, using a 1064 nm Nd:YAG laser, shows that a polluted surface of Carrara marble has an absorptivity of 0.9, while the value of a fresh surface is only 0.25. In fact, IR wavelength shows the largest gap between the ablation thresholds of crust and marble, although the self-limiting process can also be observed at other wavelengths. The gap indicates that damage to the substrate can generally be excluded, but trials and adjustments are still necessary in practice due to the heterogeneity of the materials.

4.2.2 Advantages

Laser ablation cleaning has gained attention, as conventional cleaning methods are unable to clean an object completely without causing damage. Although some damage is at microscopic scale, it may result in a surface more susceptible to future deterioration. For example,

52 Ibid, 54-8.
micro-abrasive cleaning usually removes the encrustation with part of the weathered substrate, as the latter is typically softer than the former. On stone, this indicates exposure of a crumbling surface that is very sensitive to weathering agents. Water-based methods will cause mobilization of soluble salts in the masonry body. The subsequent salt crystallization can be very damaging. Chemical treatments may etch the minerals at the stone surface, and a deep penetration can lead to staining and bleaching in the long term.\textsuperscript{54}

Laser is favored for its high precision and selectivity with appropriate parameters. It is supposed to discriminate between the black crust/soling and the light-colored substrate without leaving undesired alteration. In order to validate the cleaning effect of laser, conservators have conducted many tests in laboratory or in situ, comparing laser to some conventional methods. Appolonia et al. applied ion exchange resins, air-abrasive cleaning with pumice powder, and QS Nd:YAG laser at 1064 nm on the brickwork of St. Orso Priory in Italy. The colorimetric measurement with CIE-$L^*a^*b^*$ and CIE-$L^*C^*H^*$ systems suggests that, among the three methods, laser showed the most homogeneous cleaning effect ($\Delta E^*$) in different areas and resulted in the least change in tone ($C^*$ value).\textsuperscript{55}

In 2000, Salimbeni et al. reported the state of stone surfaces on three buildings cleaned in the 1970s and 80s. All the three were cleaned by Nd:YAG laser and micro-sandblasting in different areas, and one of them was also partly cleaned by chemicals. The laser-cleaned samples remained

\textsuperscript{54} Cooper, Laser Cleaning in Conservation, 3-7.
smooth without evidence of newly formed black crust, while the micro-sandblasted samples exhibited micro-cavities, craters, and disaggregation. Laser ablation cleaning seems to have minimized impact on stone substrate and do not exhibit damage even after a long period. However, since most large-scale laser cleaning projects were performed recently, its long-term effects on different stone types need more careful investigation.

Gaspar et al. compared laser cleaning to abrasive, chemical, and steam cleaning, using topographical assessment method. The result on marble suggests that laser cleaning has a potential to induce more severe alterations in surface topography, i.e. to increase surface roughness, and the phenomenon seems related to spallation of calcite crystals. However, the other methods induced erosion or dissolution of calcite grains (probably smoothing the surface), and exhibited a potential to leave residual products on the surface. There was no evidence that laser was more harmful than the other methods.

There are other advantages of laser ablation cleaning. It does not involve direct contact with the object. Thus, skilled conservators are able to remove accretions from a crumbling stone surface. Besides, this method allows immediate control and feedback. Conservators can get real-time visual information during cleaning and stop the cleaning at any moment. Additional on-line monitoring techniques, such as Laser-induced Breakdown Spectroscopy (LIBS), can be

---

incorporated with cleaning system.  

4.2.3 Major Disadvantage: Discoloration Effect

Discoloration or “yellowing” effect is probably the most significant disadvantage of cleaning by Nd:YAG laser at 1064 nm. Since the restoration of Amiens Cathedral in 1993, this phenomenon has been observed on stone and other substrates during encrustation/soiling removal. Many studies have reported colorimetric data in the CIE-L*a*b* color system, comparing the laser-cleaned surface with black crust, fresh stone, or surface cleaned by other methods. A significant increase of the b* value, observed by different researchers, confirms the yellowing effect. For example, Klein et al. reported the average b* values, 9.77 (10 pulses) and 7.34 (20 pulses), on the cleaned marble surface, in contrast to -0.6 of the fresh marble and -1.93 of the crust. Pouli et al. reported a b* value of 19.23 on cleaned marble (originally covered by thin crust). It is also much higher than 1.98 of the bare stone and 12.24 of the crust. There are different explanations for the yellow discoloration, as listed below:

1) The removal of black crust may reveal an early-formed yellowish patina, which is usually rich of calcium oxalates. The patina can be naturally formed by exposure to the outdoor

environment. Valls del Barrio et al. characterized an orange patina on dolostone and attribute the color change to bioactivity.\textsuperscript{62} Besides, the patina can be an intentionally applied layer on the stone surface, either to protect the surface (using oil, waxes, etc.), or as primer for painted decoration. For example, patinas on marble from Acropolis contains considerable amount of Si or Pb. This is corresponding with historical archives, indicating the use of alkali silicates and ochre paints. In this case, the patina should be preserved as it demonstrates ancient treatments.\textsuperscript{63}

2) Soluble yellow fractions embedded in the black crust may migrate inward and deposit under the crust. Gaviño et al. extracted various organic compounds (including aliphatic and aromatic carboxylic acids and phenols) originated from atmospheric pollution in black crust samples. These organic matters, which impregnate the epigenic gypsum layer under the crust, showed resistance to 1064 nm laser irradiation.\textsuperscript{64}

3) The discoloration effect may be attributed to the thermally induced chemical change of iron particulates in the stone or the crust. Klein et al. and Gracia et al. performed cleaning tests on model samples, in which the crust contained iron (Fe\textsubscript{2}O\textsubscript{3}) and the substrate did not. In the former case, using SEM-EDX, iron could be identified from sample cleaned by 1064 nm laser (showing intense yellowing), but not for 355 nm. In the latter, 1064 nm laser irradiation led to reduction of

\textsuperscript{64} Artificially samples, stained with the yellow fractions extracted from natural samples, were used to test the effect of laser irradiation. M. Gaviño et al., “Black Crust Removal: The Effect of Stone Yellowing and Cleaning Strategies,” in \textit{Air Pollution and Cultural Heritage}, 239.
Fe$_2$O$_3$ to Fe$_3$O$_4$ and other chemical changes (detected by XRD).\textsuperscript{65} Pouli et al. also note that the fluences employed in these two cases are close to the ablation threshold, so “thermally induced dissolution processes” may be favored instead of complete ablation.\textsuperscript{66}

4) The perception of yellowish hue may be the result of differential scattering of light at various wavelengths. Zafiropulos et al. suggest that, if a low fluence (lower than the spallation threshold of the crust) is used, the dark particles embedded in the crust can be vaporized, leaving some voids, but the gypsum layer may remain. Because of the voids, visible light of shorter wavelength may scatter back and be absorbed by the material, while long-wave light (red, orange, and yellow) tends to escape.\textsuperscript{67}

In most of the practical cases, particular for monuments built with white marble, the yellowish appearance is very undesirable and needs remedies. Based on the above theories, Vergès-Belmin and Labouré proposed poultices as a subsequent treatment for the discolored marble surface after laser ablation.\textsuperscript{68} In the cleaning campaign of Philadelphia Merchants’ Exchange, laser failed to remove the orange-colored gypsum layer underneath the dark soiling, but alkaline poultices plus mechanical removal (with soft/medium bristle brushes) was successful.

\textsuperscript{68} Vergès-Belmin and Labouré, “Poultices as a Way to Eliminate the Yellowing Effect,” in \textit{LACONA VI}, 115.
as follow-up methods. In addition to chemical methods, many investigations are focusing on the laser itself, attempting to eliminate the yellowing effect by adjusting parameters (to be further explained in the following section).

4.3 Studied Parameters and Conditions of Laser Cleaning on Stone

Although laser ablation is regarded as promising cleaning method, its high precision and selectivity can only “be realized just in a given range of values of the main irradiation parameters: fluence, pulse duration, and pulse frequency rate”. These parameters are related to the power and operation mode of the equipment. In addition, surrounding media, particularly water on the surface, can affect the damage thresholds. Furthermore, the cleaning effect (especially the change of color tone) also depends on different wavelengths (IR, UV, or visible light) given by a single laser system (adjusted) or different systems. In present day, these factors are widely studied to optimize the cleaning method in each case.

4.3.1 Wavelengths

As mentioned above, cleaning by the fundamental wavelength of Nd:YAG laser (1064 nm) leads to significant yellowing of stone surface. To overcome this effect, conservators and laser

---

69 The alkaline solution used for poulticing contains ammonium bicarbonate, sodium bicarbonate, EDTA acid, and distill water. The mechanical cleaning did not lead to damage evident to naked eyes. See Hall and Matero, “Carrara Marble Capitals of the Philadelphia Merchants’ Exchange,” 146.

technicians have carries out many laboratory tests to compare various laser types with different wavelengths, as well as other harmonics (second and third) produced by this laser. Particularly, the use of UV radiation is widely considered as it involves a different cleaning mechanism (bond-breaking), which can be effective in removing organic compounds.

Excimer lasers were investigated due to their UV wavelengths. Maravelaki-Kalaitzaki et al. tested 308 nm XeCl and 248 nm KrF lasers on marble with various encrustations. On dendritic black crust, KrF laser cleaning did not exhibit the “self-limiting” process due to the marble’s high absorption rate of 248 nm radiations. On the other hand, XeCl laser resulted in an acceptable cleaning effect. Both lasers could remove thin compact crust, soiling and biological crust within a certain range of fluence. Marakis et al. also studied these two lasers, in comparison to the first and third harmonics of Nd:YAG laser. On sandstone, the measured gaps between the ablation and damage thresholds were significant for the 1064 and 308 nm lasers, but there was almost no gap for the 248 nm laser. This result is in good agreement with the former one.

Er:YAG (λ= 2940 nm) was first evaluated for cleaning of painted surfaces. The experiment done by deCruz et al. proves that Er laser can selectively remove atmospheric deposit from stone sculptures with polychrome paints or patina. Sansonetti et al. performed tests using Nd:YAG, Er:YAG and XeCl lasers on two lithotypes: Carrara marble and Verona red limestone (which

---

contains iron and is very sensitive to laser irradiation), both covered by artificial thick soiling.

Damage thresholds were determined for each lithotype and each laser. The Nd and Er lasers exhibited good cleaning efficacy on Carrara marble with a fluence well below the damage thresholds, but there was little gap between the cleaning and damage thresholds on the dark areas of the limestone. The Excimer laser failed to remove the thick soiling.\textsuperscript{74}

However, none of the studies above employed colorimetric measurement for surface cleaned by Excimer lasers, even though XeCl laser has some potential to eliminate the yellowing effect. Marakis et al. point out that Excimer lasers are more difficult to handle in practical stone cleaning.\textsuperscript{75} This may explain why most recent studies still emphasize on Nd:YAG laser.

Klein et al. investigated Nd:YAG laser’s cleaning effect at $\lambda =1064, 532$ and 355 nm on a biogenic encrusted marble. This research aimed to evaluate the overall results of cleaning, with color measurement using CIE-$L^*a^*b^*$ system. For each wavelength, a relationship was drawn between the fluence and the color difference between the fresh marble and the cleaned areas. Shorter the wavelength, lower the fluence is required for similar result (lightness). The color tone after cleaning by either 532 or 355 nm lasers was very close to fresh marble. However, 532 nm seemed unable to completely remove the crust (the area showed much lower lightness).\textsuperscript{76}

Marakis et al. performed cleaning tests, using 1064 and 355 nm, on marble pieces covered

\textsuperscript{74} A. Sansonetti et al., “Nd, Er and Excimer Laser Sources: Laboratory Evaluation of Cleaning Efficacy and of Interaction with Substrate”, in LACONA V, 364-7.
\textsuperscript{75} See note 72 above.
with three different types of crust: thick or thin compact gypsum crust and biological crust. The 1064 nm laser could easily remove the former two, but had significant yellowing effect; it failed to remove the biological crust. On the other hand, the 355 nm laser performed well on the thin crust and biological crust, with no yellowing effect observed.\textsuperscript{77}

Zafiropulos et al. point out the risk of using UV laser only despite of its advantages. On an inhomogeneous crust (which is usually the case), the spallation threshold may change from point to point, increasing the chance of over-cleaning.\textsuperscript{78} Also, UV laser was sometimes insufficient to remove pollution crust. Base on these, researchers proposed and validated new cleaning methods using both 1064 and 355 nm wavelengths, either sequentially (SQ) or synchronously (SN), in order to compensate the drawbacks of each wavelength.

Pouli et al. published a series of testing results on this topic. The first test was using the SN method on the west frieze of Parthenon. Colorimetric measurements and microscopy revealed that, at relatively low fluence with moderate number of pulses, the combined laser was very successful on compact crust. But still, the dendritic crust could only be removed by IR laser at higher fluence.\textsuperscript{79} Later tests were conducted on limestone with thick pollution crust, marble and gypsum with thin pollution. The test started at the ablation threshold of each radiation and the fluence was increased little by little. On all the three surfaces, both SQ and SN mode resulted in

\textsuperscript{77} Photo documentation in this research showed the color change, but quantitative color measurement was lacking. See G. Marakis et al., “Comparative Study on the Application of the 1st and the 3rd Harmonic of a Q-switched Nd: YAG Laser System to Clean Black Encrustation on Marble,” Journal of Cultural Heritage 4 (2003): 83s–91s.

\textsuperscript{78} Zafiropulos et al., “Synchronous Use of IR and UV Laser Pulses,” 316.

efficient removal without inducing chemical alteration, and the yellowing effect was either avoided or corrected (UV after IR). Still, the SN mode was considered superior as it led to more homogenous color and surface morphology, while the SQ mode led to an uneven surface.  

4.3.2 Operating Mode/ Pulse Duration

As an alternate to Q-switched laser, short free running (SFR) Nd:YAG laser systems with pulse duration of 20 μs were developed in the late 1990s. It was reported that QS laser, although allowing high ablation rate, caused micro-cracking and spallation on stone surface while removing the thick crust. On the other hand, normal free running (NFR or FR) laser removes the crust through slow vaporization, leading to thermal side effects (based on Siano’s model). Thus, SFR laser is aiming to merge the advantages and compensate the drawbacks of QS and FR lasers.  

Later, SFR laser systems that could produce 20-150 μs pulses, and long Q-switched (LQS) lasers with 60 and 120 ns pulse duration were introduced to conservation. Some studies focused on comparing different operating modes or pulses durations.

Since 2008, Siano et al. conducted a series of laboratory tests, aiming to draw the correlation between pulse duration and ablation rate ($z_{ab}$), which is associated with fluence (F) and defined as

---

80 See notes 61 and 66 above.
“the depth produced by a number of pulses.” The authors simulated black crust on marble and sandstone substrates, which were subjected to ablation tests using 1064 nm Nd:YAG laser systems of QS, LQS, or SFR mode. The results indicate that the ablation threshold increases with pulse duration and exhibits a significant variation within the SFR regime (40 to 155 μs for this investigation). The ablative efficiency $$(z_{ab}/F)$$ was also evaluated. The QS laser shows higher efficiency below 1 J/cm² while the LQS becomes more efficient at higher fluences. From the practical aspect, although SFR requires much higher fluence (often higher than 8 J/cm²) than QS and LQS, it shows a very large gap between the ablation and damage thresholds, providing greater operative domains. In the case of San Ranieri in Pisa, SFR laser preserved the most internal calcium oxalate layer, while QS was found too invasive.83

Vergès-Belmin et al. evaluated the cleaning outcomes of LQS (100 ns) and SFR (100 μs) lasers on limestone. The color measurement suggests that cleaning by SFR laser resulted in a darker but less yellow surface than by LQS laser. Examination on the surface microstructure indicates that both lasers did not remove the oxalate layer beneath the black crust, but only LQS removed the crust completely (this result is generally in consistent with Siano’s). From practical aspect, SFR was found slower than LQS, particularly on thicker crust. This should be taken into account in large-scale cleaning project.84

83 Ibid.
4.3.3 Fluence (Power Density)

Ablation and damage thresholds are critical in laser cleaning. Only when the energy (over per unit area) given by each laser pulse, i.e. the fluence, lies between the two thresholds that the surface can be completely cleaned without damage. To determine the thresholds, experiments are usually conducted by cleaning a number of test spots with gradually increased fluence, and examine the cleaned spots with microscopy and other methods. Experiments have been done using Nd:YAG laser on various stone samples, and some examples are listed in Table 2.

Number of pulses does not determine whether the crust can be removed or not, but it does affect the result of cleaning. Due to the heterogeneous morphology of encrustation (particularly for the framboidal black crust), some area requires much higher number of pulses to remove the crust completely. In literature, depending on the aim of the authors, in some experiments a constant number of pulses were applied on different test spots, while in other experiments the surface was cleaned to a visually satisfying degree.\(^{85}\)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Pulse Duration</th>
<th>Wavelength (nm)</th>
<th>Material</th>
<th>Ablation Threshold (J/cm(^2))</th>
<th>Damage Threshold (J/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maravelaki et al. (1997)</td>
<td>15 ns QS</td>
<td>1064</td>
<td>Marble</td>
<td>1.8</td>
<td>3.5</td>
</tr>
<tr>
<td>Siano et al. (1997)</td>
<td>6 ns QS</td>
<td>1064</td>
<td>Carrara marble with artificial patina and</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>20 μS FR</td>
<td>1064</td>
<td></td>
<td>5</td>
<td>10-20</td>
</tr>
</tbody>
</table>

\(^{85}\) For example, Pouli et al. applied 50 or 10 pulses in their experiment. However, only a laser system in which the pulse frequency can be turned down (sometimes to 1 Hz) allows this well-controlled test. See notes 61 and 66 above.
<table>
<thead>
<tr>
<th></th>
<th>200 μs NFR</th>
<th>1064</th>
<th>gypsum crust</th>
<th>14</th>
<th>30-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabatini et al. (2000)</td>
<td>20 μs SFR</td>
<td>1064</td>
<td>Marble from Logge del Papa</td>
<td>1.2</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Marble from the portal of the Baptistery</td>
<td>1.5</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Marble from a cornice of the Capella di Piazza</td>
<td>2</td>
<td>--</td>
</tr>
<tr>
<td>Marakis et al. (2000)</td>
<td>5-7 ns QS</td>
<td>1064</td>
<td>Sandstone from Dresden Zwinger</td>
<td>0.85</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td></td>
<td></td>
<td>0.89</td>
<td>0.95</td>
</tr>
<tr>
<td>Pouli et al. (2003)</td>
<td>6.5 ns QS</td>
<td>1064</td>
<td>Excavated marble with inorganic crust</td>
<td>1.92</td>
<td>3.77</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td></td>
<td></td>
<td>0.9</td>
<td>--</td>
</tr>
<tr>
<td>Marakis et al. (2003)</td>
<td>5-7 ns QS</td>
<td>1064</td>
<td>Marble, dendritic crust</td>
<td>0.7</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td></td>
<td>Thin compact crust</td>
<td>0.2</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dendritic crust</td>
<td>0.6</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Thin compact crust</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>Pouli et al. (2008)</td>
<td>5-15 ns QS</td>
<td>1064</td>
<td>Thin soiling layer on Pentelic Marble</td>
<td>0.8</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td></td>
<td>Pentelic Marble</td>
<td>0.35</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td></td>
<td>Thick pollution crust on limestone</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>355</td>
<td></td>
<td>limestone</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Siano et al. (2009)</td>
<td>QS</td>
<td>1064</td>
<td>Artificial gypsum crust on sandstone</td>
<td>0.28</td>
<td>1-1.5</td>
</tr>
<tr>
<td></td>
<td>LQS</td>
<td></td>
<td></td>
<td>0.56</td>
<td>3-4</td>
</tr>
<tr>
<td></td>
<td>SFR</td>
<td></td>
<td></td>
<td>2.2</td>
<td>20-30</td>
</tr>
</tbody>
</table>

Table 2: Reported ablation thresholds and damages thresholds in literature. QS = Q-switched; LQS = Long Q-switched; SFR = Short free running; NFR = Normal free running.

4.3.4 Wet/Dry Condition

Many authors have reported the improvement of laser ablation with the presence of a water film, which not only increases the ablation rate, but also reduces the laser-induced surface alteration. In general, water can significantly affect the optical properties at the surface of a porous material. It reduces the reflectance of both the black crust and the substrate, thus more energy can penetrate into the bulk. Water has a much higher specific heat capacity than stone, so the average
temperature of the irradiated area will be much lower with water. The cleaning efficiency is enhanced due to the water vapor generated inside the pores of the black crust, leading to “impulsive removal” of the material.86

In literature, the efficiency of laser ablation is denoted in different ways. For example, Labouré et al. reported the overall cleaning speed in m²/h, which is important for large-scale restoration projects.87 Bartoli et al. measured the etch depth (μm/pulse) different lasers at various fluence.88 Zhang et al. evaluated the cleaning rate by ablated weight (μg/pulse).89 Whatever method was used, these studies confirmed the positive effect of using water regardless of wavelength (IR or UV) and pulse duration. The last publication also points out that some liquids with lower boiling point than water, such as acetone and ethanol, can enhance the ablation rate even more significantly. However, the potential hazard of using these liquids should be considered in practice.

The cooling effect of water can prevent the reduction of hematite (Fe₂O₃) by graphite, as these two substances may co-exist in the black crust. Besides, the spallation of the crust occurs more thoroughly with water vapor, so the iron can be taken away without leaving traces.90 This well corresponds to one of the theories for yellow discoloration (see section 4.2.3).

86 Siano et al., “Laser Cleaning of Stones,” 34.
90 Ibid.
Chapter 5: Material Characterization

5.1 Overview

This chapter will focus on the characterization of the marble and the black crust from the Hood Cemetery Gate. As mentioned in Chapter 3, marble is more susceptible to thermal micro-cracking than other stones due to the nature of calcite. Although each laser pulse only affects the surface for a very short period, the temperature will considerably increase (may reach a few hundred degrees Celsius). Not only the mineralogical composition (calcite or dolomite), but also the texture of the marble influences its vulnerability in high temperature. Rodriguez-Navarro et al. conducted laser irradiation on two marbles (with polished surface) and single-crystal calcite and examined the surface. Greater damage was observed on the finer-grained marble due to spallation of grains, while exfoliation occurred more frequently on marble with strong crystallographic preferred orientation. Thus, it is necessary to understand the microstructure of the marble before laser ablation cleaning.

Characterization of black crust provides information of its composition, which may be closely related to the discoloration effect after cleaning. Care should be taken if the crust contains iron oxides and calcium oxalates. Layering within the crust may reveal previous treatment (ancient or relatively recent from restoration campaigns, including waxing, painting, coating, etc.).

---

91 See note 71 above.
A close examination of the embedded particles can reveal the source of pollutants, although this is not the aim of this thesis.

5.2 Background of Pennsylvania Marble

Archival research reveals that the Hood Cemetery Gate is built of Pennsylvania marble quarried from two locations in Montgomery County: the base marble was from the quarry of D. O. Hitner, Esq. in Marble Hall, and the above part was from the quarry of Mr. Brooks in Upper Merion.93 In Montgomery County, a variety of limestones (either metamorphosed or not) underlie Whitemarsh Valley and Chester Valley. In the nineteenth century, the stones were quarried for different uses, but those capable of taking high polish were extensively used as building and ornamental material in Philadelphia and other places.

The commercial name “Pennsylvania marble” refers to either limestone or genuine marble from the same geological formation. There is no hard distinction between the White and the Blue (often referred to as the two major types of Pennsylvania marble), but the rock may have some features depending on its location. The limestone can be grayish blue, pale yellow, or white, sub-crystalline or purely sedimentary in texture. The true marble, white, grey or streaked, is

93 Unknown. “Germantown Cemetery,” Germantown Telegraph, April 18, 1849. See Appendix D for the excerpt.
highly crystallized and occasionally contains graphite, pyrite, talc and mica. Although Pennsylvania marble is often considered rich in magnesium, there are some low-magnesium examples. Specifically, the marble produced from Hitner’s quarry was reported, according to the geological information obtained in 1853, as pure white or clouded, devoid of fossils.

Some research has been done concerning the petrography of the Pennsylvania marble. Elaine S. McGee of the United States Geological Survey completed a report for the marble of Philadelphia Merchants’ Exchange. The examined marble is weakly metamorphosed, dominant by light blue gray calcite grains (nearly pure CaCO$_3$), angular and sub-rounded in shape. It contains muscovite and apatite as inclusions. Jocelyn Kimmel investigated the building stone of the Second Bank of the United States. Three samples were examined in thin-section, and the petrography suggests that they are somehow different in texture and mineral content. But in general, all the samples mainly consist of calcite (over 90%), containing dolomitic alterations and inclusions such as muscovite and graphite (in the medium grey sample). Given that the marble of these two buildings was quarried from the same area, these samples may have some similarities to those from the Hood Cemetery Gate.

---

95 F. Bascom made the following description: “Overlying the Beckmantown is a more or less persistent band of marble which consists of coarsely crystalline gray marble, low in MgCO$_3$, interbedded with highly magnesian stone, much finer in texture and a great deal harder.” See Benjamin L. Miller, Limestones of Pennsylvania (Harrisburg: Department of Internal Affairs, Topographic and Geologic Survey, 1934), 565, 576.
5.3 Methodology

Thin-section microscopy, X-Ray Diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) have become conventional methods in the analysis of black crust. Thin-section microscopy is useful to identify the “strata” of the crust at lower magnification (40x), and the mineralogical composition at higher magnifications. In the case of marble, XRD is helpful to differentiate calcite and dolomite, as these two minerals look very similar in thin-sections. Some common inclusions in the marble or the crust, such as quartz, mica, and feldspar, can also be identified using this technique. SEM is able to demonstrate the three-dimensional surface morphology. Besides, observation under stereoscope can reveal the general condition of the samples.

Four samples were used for material characterization. Ideally, the samples should be taken from the upper part of the gate since it is where the black crust occurs. However, because bulk sampling is undesirable on the main structure, a stone sample (Sample #1) was taken from the already broken part of a finial that has fallen off from the urn located to the east of the gate (Figure 5.1, 5.2). Three samples (Samples #2, 3, 4) covered by black crust (thick or thin) were taken from the north elevation (back) of the main structure, around the west cornice (Figures 5.3, 5.4, 5.5, and 5.6). Petrographic thin-sections (about 30 μm thick) were made from two samples: Sample #1, white marble with some biological growth at the surface, and Sample #2, a piece of framboidal black crust in semispherical shape, adhering to some marble substrate. X-Ray
Diffraction powder samples were separately done the crust and the substrate of Sample #2, and SEM was conducted on both Samples #3 and #4.

5.4 Analysis

5.4.1 Optical Microscopy

The black crust samples were observed under a Leica MZ16a stereomicroscope and the photographs were taken with a Nikon DS Fi-1 Camera with NIS Elements BR software. Magnifications from 1.0x to 5.0x were used. The marble substrate of Sample #2 (Figures 5.7 and 5.8), the framboidal crust, is significantly disaggregated and shows yellow orange color at some locations. The crust is generally solid, but shows some cracking. Compare to the very irregular outside, the inner side of the crust (where it adheres to the substrate) seems smooth. Sample #3 (Figure 5.9) has a “platform” of relatively smooth growth of black crust and framboidal growth on sides. A fresh marble surface is exposed at the back of this sample, generally white in color, but also showing bluish-grey clouds and containing some dark particles. Sample #4, a thin sample with uneven growth of crust, exhibits a yellow orange layer beneath the dark crust (Figure 5.10).

5.4.2 Thin-Section Microscopy

The two thin-sections were examined with a Nikon Alphaphot-2-YS2 compound microscope under plane-polarized light (PPL) and cross-polarized light (XPL), with
magnifications from 40x to 400x. For each view, photographs were taken with the above-mentioned camera under both PPL and XPL for comparison. For the marble sample, the longest dimension of about 200 grains (in the unweathered core) was measured in micrometer to understand the grain size distribution.

Sample #1 is a crystalline white marble, fine-grained with grain size ranging from 100 to 800 μm, but mostly under 500 μm with an average about 300 μm (Figures 5.11 and 5.12). It exhibits a granoblastic (or crystalloblastic) texture, mainly composed of subhedral calcite crystals, angular to sub-rounded in shape. The grains show high relief (but changes with rotation of the stage), rhombic cleavage and evident deformation twinning (usually with lamellae parallel to cleavage). The birefringence color of calcite is in high order (creamy or pinkish), but the twinning often exhibits second or third order colors (highly saturated). Some inclusions are visible within the calcite grains. This marble sample rarely contains foreign (non-carbonate) materials. The only identifiable one is quartz, showing first order interference colors (which differentiates it from calcite) and shadowy extinction under XPL. Some little flakes of opaque mineral are also visible, but could not be identified with this method. In general, this marble exhibits a similar texture to the previously studied examples of Pennsylvania marble. It is potentially susceptible to disaggregation caused by laser irradiation due to the fine grain size.

The substrate of Sample #2 is extremely disaggregated, making it impossible to understand the porosity of weathered stone, but sample provides great information of the gypsum crust. The
substrate contains many partially dissolved or cracked calcite crystals, with clear gypsum developing around the grains and at the presumably original stone surface (Figure 5.13). In this layer, the gypsum crystals are small and do not exhibit clear boundary in PPL. In contrast, gypsum grows aggressively in the outer layer, i.e. the real “black” crust, which is 300-500 μm thick in general, but at most can reach over 2000 μm (2 mm) at the framboid part. Many crystal druses of gypsum are visible at the surface of the crust, showing birefringence of first order colors and twinning in XPL (Figure 5.14). A large amount of small particles (usually 20-50 μm in diameter), most of which are opaque but some are brown orange, are embedded in the crust (Figure 5.15). Some opaque particles are probably carbonaceous fly-ash, as they are round in shape and some are spongy-looking (this appearance matches the fly-ash particles examined in literature).\footnote{Ausset et al., “Embryonic Sulphated Black Crusts on Carbonate Rocks,” 1527.} A small, isolated particle was found exhibiting birefringence of high order colors. It can possibly be a single anhydrite crystal altered from gypsum. In some areas, a brownish stain is visible around calcite crystals, possibly clay minerals (Figure 5.16). No evident layering can be identified from this sample, suggesting that there is no previous treatment. The porosity within the crust is low.

5.4.3 X-Ray Diffraction

X-Ray Diffraction was conducted on a Rigaku Powder X-Ray Diffratometer set at 40 kilovohms and 30 milliamperes. Each sample was ground with mortar and pestle, and the powder was
placed onto a recessed cavity holder. Both samples were first analyzed at a speed of 15° per minute with a 2θ reflection angle started from 2° to determine the 2θ range of interest. Based on the preliminary result, the marble sample was re-analyzed from 5° to 75°, and the black crust from 10° to 75°, at a lower speed of 5° per minute to obtain higher accuracy.

Calcite and muscovite mica were identified from the marble sample. This result consists with the information from the geological survey report. A little amount of gypsum and magnesium chloride (MgCl₂) also exists in this sample, presumably due to deterioration as the marble grains were obtained from the weathered substrate (Figure 5.17). The result for the black crust confirms gypsum as the main component and also indicates the presence of quartz (SiO₂), which may be originated from the marble (Figure 5.18).

5.4.4 Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy

The SEM examination was carried out on thin and framboidal black crust, using a FEI Quanta 600 FEG Mark II Environmental Scanning Electron Microscope, analyzed with XT Microscope Control software. It was run at a chamber pressure of 1 torr with a spot size of 3.0 nm, and the excitation energy was set to 20 kV. At low magnification (100x), the crust surface showed extensive growth of gypsum crystals (slightly uneven) and a large amount of small particles (Figure 5.19). At higher magnification (500x), some areas exhibited a full-coverage by tabular (or lamellar) gypsum crystals (Figure 5.20).
Elemental mapping with EDS (Figure 5.21) confirmed the general presence of gypsum with the overlap between calcium, oxygen and sulfur. The overlap between potassium, aluminum and silicon, or the latter two at some locations indicates the presence of muscovite (KAl₂(AlSi₃O₁₀)(F,OH)₂) or K-feldspar (KAlSi₃O₈), and kaolinite (Al₂Si₂O₅(OH)₄) as well. Iron was also identified from the surface, and some locations seem independent from K, Al, Si and Mg, suggesting that it may exist in the form of oxides.
Figure 5.1: Above: The urn to the east of the gate. Below: The broken piece. The white rectangular frame indicates where the sample was taken.
Figure 5.2: Sample #1, white marble with biological colonization on surface.

Figure 5.3: Looking at the cornice from the northwest corner. The white rectangular frame indicates where Samples #2, 3, and 4 were taken.
Figure 5.4: Sample #2, the framoidal black crust of spherical shape, with disaggregated substrate.
Figure 5.5: Sample #3, black crust on a solid substrate.
Figure 5.6: Sample #4, a very thin piece with yellowish surface, partially covered by thin black crust.

Figure 5.7: Photomicrograph of Sample #2, looking at the section, 25x magnification. A change of color from white (substrate) to black (outer crust) is visible.
Figure 5.8: Photomicrographs of Sample #2. Above: looking at the black crust surface, 12.5x magnification. Below: looking at the cracked crust and disaggregated marble (yellowish color) from the bottom, 20x magnification.
Figure 5.9: Photomicrographs of Sample #3. Above: The morphology of the crust changes from relatively smooth to frambooidal, 10x magnification. Below: The marble substrate with black inclusions, yellowish stains and greyish grains, 25x magnification.
Figure 5.10: Photomicrograph of Sample #4. A yellow layer underlying the black crust is visible, 20x magnification.

Figure 5.11: Grain size distribution of Sample #1 (marble). The longest dimension of each grain was measured and rounded to the closest number (100 μm interval). Grains smaller than 50 μm are mostly inclusions, thus they are not included in this chart.
Figure 5.12: Thin-section of the marble in PPL (above) and XPL (below), 40x magnification.
Figure 5.13: Thin-section of the frambooidal black crust in PPL (above) and XPL (below), 40x magnification. Clear gypsum is visible between the calcite grains.
Figure 5.14: The framboidal black crust in PPL (above) and XPL (below), looking at euhedral gypsum crystals, 100x magnification.
Figure 5.15: The inclusions in the outer crust, possibly carbon particles, organic flakes, and small mineral grains, 400x magnification.
Figure 5.16: The frambooidal black crust in PPL (above) and XPL (below), looking at the brownish stains around calcite crystals, 40x magnification.
Figure 5.17: XRD analysis of the finer fraction of the marble. Calcite and muscovite were found.
Figure 5.18: XRD analysis of the finer fraction of the black crust. Gypsum and quartz were found.
Figure 5.19: SEM image of Sample #3, showing crystals and air-borne particles.

Figure 5.20: SEM image of Sample #4, showing tabular gypsum crystal growing with eroded calcite grains.
Figure 5.21: Elemental mapping of an area on Sample #4, at 100x magnification. High concentration of Ca, S, and O indicates the prevalence of gypsum. See Appendix B for the full report generated from the software.
Chapter 6: Laser Cleaning Tests

The laser equipment used for this thesis is a Clean Laser System CL 20 Q backpack with a scanning optic, manufactured in Germany in 2006 (Figure 6.1). It emits infrared radiation of about 1062 nm wavelength; the adjustable parameters include power, pulse frequency, scan frequency and scan width. In conservation field, this portable laser system is not as commonly used and studied as studio-based Nd:YAG systems, and it clearly has some differences in regard to operation. The first section of this chapter will review the laser system in detail.

Laser cleaning test was conducted first in laboratory to understand this laser system’s
general performance on the black crust samples from the Hood Cemetery Gate. In-situ test followed with appropriate parameters based on the laboratory results. All the tests were conducted with the help from experienced conservator Adam Jenkins, who performed laser cleaning on the terracotta ornaments of the Philadelphia Museum of Art and on the marble capitals of the Philadelphia Merchants’ Exchange using the same equipment.

6.1 Laser Equipment

The CL 20 Q system is a diode pumped, Q-switched, ytterbium fiber laser, delivering laser pulses at approximately 1062 nm infrared wavelength. The system operates with 115 V input at a maximum power of 20 W (average power), which can be stepped down to 50%, 25% and lower. The laser is equipped with an OSH 20L scanning head (Figure 6.2). Two alternative focusing lenses, 120 mm and 250 mm, determine the working distance, and the former provides higher power density. It produces a linear beam (instead of a round spot by typical Nd:YAG systems) on the surface under cleaning. The pulse frequency (PF), scan frequency (SF), and the scan width (SW) are adjustable through three knobs on the scanning head. The knobs are marked with scale from 0 to10, but in fact the adjustment is continuous. In this laser system, higher power density is given by PF at lower number, while the effect of SF and SW is negligible. The specifications of the laser system are listed in Table 3.
Table 3: The specifications of CL 20 Q laser

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan width</td>
<td>4-25 mm (120 mm lens, at scale 1-10)</td>
</tr>
<tr>
<td>Scan frequency</td>
<td>30-180 Hz</td>
</tr>
<tr>
<td>Focal Diameter</td>
<td>55 μm (120 mm lens)</td>
</tr>
<tr>
<td>Pulse frequency</td>
<td>40-100 kHz</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>0.2-0.5 mJ (20 W)</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>100 ns</td>
</tr>
<tr>
<td>Fluence range</td>
<td>8.42–21.05 J (20 W); 4.21-10.52 J (10 W)</td>
</tr>
</tbody>
</table>

Fiber laser is not as widely used as Nd:YAG laser in laboratory test for art conservation. In 2011, Hildenhagen and Dickmann published their investigation on a fiber laser system (power of...

---

99 All the information was provided by the manufacturer except for scan width. For this study, the scan width at level 1 and 10 (maximum) was measured using a digital caliper, on a rusted metal piece cleaned using the 120 mm lens.
20 W, with 250 kHz pulse frequency and 0.04 mJ pulse energy), comparing it to a Nd:YAG laser. In terms of the temperature change after laser irradiation, a simulation suggests that the accumulation of heat is more significant during fiber laser cleaning. This is probably due to its lower peak power and high repetition rate (Figure 6.3), distinct from common Nd:YAG systems, which may emit 100-1000 mJ in one pulse, at a repetition rate of 1-30 Hz.\(^\text{100}\) Scanning Electron Microscopy reveals a significant difference between marble surface cleaned with the two lasers. The Nd:YAG laser resulted in more exposure of calcite grains, while fiber laser left more residual. However, the “cleaner” surface may indicate a more aggressive cleaning. Another problem of fiber laser is concerning the linear scanning routines, which may result in over-heated spots (hot spots) on both sides of the beam. This can be reduced with a circular routine. Finally, the authors suggest than the current fiber laser system is not an adequate alternative for Nd:YAG laser.\(^\text{101}\)

Despite of its disadvantage, the application of scanning head is crucial in large-scale building conservation work to increase the efficiency. The restoration of the Nickerson Mansion (built 1883) in Chicago, IL, done by 2005, is the first completed example of laser cleaning on an entire building in the United States. The CL 120 Q system, with pulse frequency of 8-35 kHz and scan frequency of 50–150Hz, was used in this project. Dajnowski discussed the practical aspects including the speed of cleaning and the issue of hot spots. It requires constant moving of the


scanning head in an irregular way to eliminate higher ablation impact at certain locations.  

The CL 20 Q is the only available laser system for this thesis, and indeed it has many limitations. As some authors point out that fiber laser is favored for the compact construction and cost-effectiveness, this kind of system is popular with industries, but less precise than many systems designed for conservation. The CL 20 Q does not allow an accurate calculation of the power density at the surface (an estimation will be given in section 6.4) by knowing the scale of each adjustable parameter. Since it is designed to be portable, it operates at low power, leading to a low cleaning rate, which limits the scale of testing (the laser systems used for large-scale

---


103 To determine the actual fluence, it is necessary to measure directly at the optic using a laser power meter, which cannot be obtained for this thesis.
projects can be up to 1000 W). On the other hand, in terms of wavelength, it is highly comparable to Nd:YAG laser at 1064 nm.

6.2 Laboratory Test

The cleaning test started at 25% of power, with a scan width at 4 (about 14 mm), using the 250 mm lens on a very small area of Sample #3 in dry condition. The power was gradually turned up to determine the lowest point by which the laser beam could started removing the black crust. Similar trials were also done using the 120 mm lens. After a few attempts, it appeared that only at full power (20 W) with the 120 mm lens the change on the black crust was evident (the color turned lighter with particulates ejected from surface). This was possibly due to the density of the crust on this sample. The cleaning effect seemed more significant with a little water brushed on the surface (this is consistent with the observation from the case of the Philadelphia Merchants’ Exchange).

Based on preliminary test, two larger areas (approximately 1 inch by 3/4 inch) were cleaned at full power using the 120 mm lens. One testing area was done in dry condition first, and the other in wet condition later. The sample was partially covered with aluminum foil during cleaning, so only the desired area was exposed to laser irradiation. The scan width was kept at 4; the pulse frequency and scan frequency were set at 5 for most of the time, but turned to 2 (higher fluence/surface power density) in order to finalize the cleaning at certain locations where the crust was
thicker than average. For the wet condition, as water evaporated very quickly due to the laser-induced heat, the surface was irradiated until it dried out, and the laser was paused to allow surface to be wetted again.

The cleaning was stopped when visible change no longer occurred on the surface. In both dry-cleaned and wet-cleaned area, the crust surface exhibited a significant lightening of color. When the entire sample was dry, there was only a slight difference between the two areas. However, the dry area turned much darker when it was wetted (Figure 6.4). Besides, calcite crystals can be seen by naked eyes on the wet-cleaned area, but not the dry-cleaned area. These observations indicated that the cleaning was in fact incomplete, that is, the gypsum was not removed or only partially removed from the surface. Further investigation aiming to reveal the actual change of the crust will be discussed in the following Chapter 7.

During cleaning, when the laser was in focus, flashes of light were clearly visible on the surface, indicating the formation of plasma. Although plasma was suggested to be a possible cause of laser-induced damage, it was probably not in this case if the inner layer of gypsum was preserved and could protect the calcite. The sample was significantly warmed during cleaning in both dry and wet condition. However, it is possibly due to the small size of the sample, and may be less significant on a building, which can conduct away much more heat. The micro-scale behavior of the calcite crystals is not detectable in this research, but no immediate loss of the grains was observed from the surface.
Figure 6.4: Sample #3 after cleaning with the surface dry (above) or wet (below), at 20 W. The dried-cleaned area (left) exhibits much darker color when wetted.

Similar test was then performed on Sample #4. Considering that the crust on this sample was much thinner, the laser power was turned down to 50% (10W) but the other parameters remained the same (SW at 4, PF and SF at 5). This sample was irradiated under dry and wet condition as on
Sample #3. Both areas exhibited much lighter color after irradiation, indicating at the cleaning was effective (Figure 6.5). However, it was observed during cleaning that the sample, originally thin and fragile, fell apart due to moisture and brushing, although the laser did no harm to it. Spraying water instead of brushing will be a proper alternative to avoid direct contact. A careful control of the amount of water is also very important, but this is clearly dependent on the experience and skill of the conservator.

Figure 6.5: A fragment of Sample #4 after dry-cleaning at 10 W.

6.3 In-situ Test

The in-situ laser-cleaning test was performed on March 29, 2016. The testing location was pre-determined to be on the back (north) of the gate, near the cornice where the black crust
samples were taken, so the characteristics of the black crust in this area were presumably similar to the samples. Scaffolding was set up in advance to the north of the gateway (Figure 6.6), and a 1200 W generator was used as power supply for the laser.

Figure 6.6: The scaffolding prepared for in-situ cleaning test (Author 2016).

Given that a large area was covered by black crust around the cornice, the exact cleaning location was selected for two reasons. The first consideration was the accessibility from the scaffolding and a relative comfortable working height, so there would be no need of holding the scanning head too high or crouching during the work (although in practice there must be some situations that the conservator has to work from an uncomfortable position). The second
consideration was the pattern of black crust. The selected area exhibited some variations of black crust in terms of thickness and surface morphology. Besides, a yellowish layer seemed to underlie the crust as it was partially exposed on the plane surface where the crust was generally thin (Figure 6.7). As literature often suggests that laser cleaning can preserve (or fail to remove, depending on if the layer is worth preserving), testing at this location could potentially confirm this or provide other information.

The testing area was two plane bandings (with the upper and lower boundaries readily defined) with a molding in the middle. It was located at the corner, so only the left side of the area was taped for the convenience of visual examination. The upper plane area was about 4 inches by 3 inches, and the lower plane area was 3 inches by 2 inches. The molding, 3 inches long and 1 inch high, was significantly deteriorated with some spallation around the corner.

The surface was cleaned in wet condition, as the cleaning effect was found enhanced by water in the laboratory test. The cleaning was performed with water sprayed onto the surface (more efficient than brushing). The first setup of the parameters referred to the cleaning setup of Sample #3, with scan width at 5, both scan frequency and pulse frequency at 2. Later, it was changed to SW at 3, both SF and PF at 1 to acquire higher power density.

The cleaning process lasted about an hour and fifteen minutes. A significant cleaning effect was observed in the first ten minutes of cleaning, but the process gradually slowed down. Laser irradiation resulted in a relatively homogeneous color on plane surface, but exhibited some
difficulty in removing the black crust around the corner and the molding even if these locations were particularly cleaned using the highest fluence (PF at 1) for many passes (Figure 6.8).

Figure 6.7: The testing area before and after cleaning, view from the northeast corner. The cleaned surface exhibited a similar color to the marble on the north side of the pillar.
Figure 6.8: A comparison of the testing area before and after cleaning, view from the front. The thick crust on the middle molding was only partially removed.

6.4 Discussion on Power Density

For each setting used in laboratory or in-situ test, the fluence was calculated using a Microsoft Excel file (named CL20-OSH20 Beam Energy Calculator) provided by the manufacture. For the CL 20 Q laser system, the fluence is essentially dependent on the power (controlled through the backpack), the focal diameter of the lens (55 μm), and pulse frequency (controlled through the scanning head). The pulse frequency at 1, 2 and 5 are about 40.0, 46.7 and 66.7 kHz, respectively. These values were input into the Excel file and the results are presented in Table 4.

The fluence values are only estimation for several reasons. First, since the scale is actually
continuous, only the values at 1 and 10 are accurate, while those above 1 and below 10 are estimated because the knob might not be turned to the very exact place. Second, the optic can be frequently out of focus during cleaning, as the operator’s hands cannot be perfectly stable. If the difference is slight, the ablation may still occur, but the power will be lower than the estimated value. Third, the ageing of the laser equipment may result in significantly lower fluence. Given that the laser was manufactured about ten years ago and has been used on a few large-scale projects, it should not be expected to function as new equipment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Focal Diameter (μm)</th>
<th>Power (W)</th>
<th>Pulse Frequency (kHz)</th>
<th>Peak Power (kW)</th>
<th>Pulse Intensity (W/cm²)</th>
<th>Fluence (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td># 3 thick crust</td>
<td></td>
<td>20</td>
<td>66.7 (5)</td>
<td>3.0</td>
<td>1.3×10⁸</td>
<td>12.6</td>
</tr>
<tr>
<td># 4 thin crust</td>
<td></td>
<td>20</td>
<td>46.7 (2)</td>
<td>4.3</td>
<td>1.8×10⁸</td>
<td>18.0</td>
</tr>
<tr>
<td>In-situ (1)</td>
<td></td>
<td>10</td>
<td>66.7 (5)</td>
<td>1.5</td>
<td>6.3×10⁷</td>
<td>6.3</td>
</tr>
<tr>
<td>In-situ (2)</td>
<td></td>
<td>20</td>
<td>40.0 (1)</td>
<td>5.0</td>
<td>2.1×10⁸</td>
<td>21.0</td>
</tr>
</tbody>
</table>

Table 4: Fluence calculations. Peak power indicates the maximum occurring power of a laser pulse.

The CL 20 Q may be regarded as a Long-Q-switched-mode laser for its 100 ns pulse duration. The surface power density (or pulse-intensity) is at the level of 10⁸ W/cm², which is also consistent with common QS lasers. However, due to the significant differences in other operating parameters (particularly the beam size and pulse frequency), its irradiation did not react with the black crust in the same way as typical LQS Nd:YAG lasers. Although the fluence was estimated, it is certain that this laser system gives much higher ablation and damage thresholds than QS and
LQS Nd:YAG lasers (around 10 J/cm² versus 3-4 J/cm² in terms of ablation threshold). Its cleaning effect seems more similar to free-running lasers.

As pointed out by Graue et al., for a Nd:YAG laser, the SPD can be regulated by flashlight current, repetitions rate and optic, while for a fiber laser, the contributing factors include power, scan width, scan frequency, repetition rate and number of passes. In this calculation, the scan frequency and scan width do not affect the fluence, which is regarded as the effect of individual pulses. But the distribution of laser energy on the surface and over time is clearly dependent on these two parameters. For example, a lower scan frequency indicates that within one scan, the laser beam stays longer at a location. If the scan width is very small (such as 4 mm), the two hot spots can be very close to each other. Thus, SF and SW still affect the overall SPD although they are less significant.
Chapter 7: Evaluation

7.1 Methodology

In the field, there are several major focuses for the evaluation of laser cleaning with some corresponding analytic methods. The following three aspects are most important for the aim of this thesis. First, the color differences between the cleaned area, the black crust and the fresh marble substrate indicate the overall effectiveness of cleaning. Since perception of color can vary significantly depending on the light source, the surface texture, and the viewer, the CIE 1976 L*a*b* system is commonly utilized for color measurements. The CIE 1976 L*a*b* color space is “an approximately uniform color space based on nonlinear expansion of the tristimulus values and taking differences to produce three opponent axes that approximate the percepts of lightness-darkness, redness-greenness and yellowness-blueness.” A spectrophotometer using this color system can provide quantitative data that are easy to compare. The relative differences between the color of each testing area and a chosen reference are estimated through calculating the ΔE*, defined as:

\[ \Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \]

Second, the change in surface morphology is important since it reveals the degree of cleaning.

---

104 Based on previous studies, it is not likely that the surface can return to the color of the fresh substrate, but a similar color is usually considered satisfying. In fact, for historical buildings, maintaining a slightly weathered appearance after cleaning is often preferred.

As mentioned in Chapter 5, surficial gypsum and calcite have very different crystal shapes, thus the removal of gypsum should be visible using Scanning Electron Microscopy. Besides, SEM can also reveal micro-cracking (which probably indicates over-cleaning) or other potential damage on the calcite grains if they come to exposure after cleaning.

Third, chemical alterations of the black crust (including the outer crust and the layer adjacent to the substrate) can potentially occur due to high temperature, particularly in the dry-cleaning condition. Gypsum can be converted into anhydrite, leading to a more porous surface layer than its previous state, and the hydration process may accelerate deterioration.\(^{106}\) The presence of anhydrite is detectable using Raman spectroscopy, which is also capable of identifying small amount of chemicals (iron oxides and calcium oxalates) that are usually responsible for the discoloration effect.

Admittedly, the properties of the black crust on the Hood Cemetery Gate and the available laser system did not allow many variations of the parameters to be tested, and this testing project may not be able to determine the optimal parameters for practical use. However, the full evaluation process on the laboratory samples (Samples #3 and #4) can still throw light on the dry and wet cleaning, as the differences between these two conditions are already evident. If no evident damage occurs on the laboratory samples, the parameters will be considered appropriate, and color change will be the major concern for the in-situ testing.

Also, note that the desirable of cleaning does not require a complete removal of gypsum from the marble surface. Some authors argue that the clear gypsum layer should be left intact because it can protect the eroded calcite.\textsuperscript{107} Based on the observations of the black crust from the Hood Cemetery Gate, if the clear gypsum layer is removed, a loss of disaggregated grains seems inevitable. In practice, pre-consolidation may be applied but this will increase the difficulty in removing the black crust, as well as the cost. Therefore, the cleaning outcome may be considered satisfying with some gypsum remains observed on after-cleaning surface.

### 7.2 Evaluation

#### 7.2.1 Preliminary Examination

After cleaning in laboratory, the Samples #3 and #4 were examined under the Leica MZ16a stereomicroscope, with 20x magnification. On the dry-cleaned areas (Figure 7.1), the surface texture remains similar to the black crust. There was no evident recess from the original surface. In contrast, on the wet-cleaned areas (Figure 7.2), the texture was significantly altered; some calcite grains were exposed, but still bound by a layer of translucent material (presumably gypsum). Comparing the dry-cleaned and the wet-cleaned areas (Figure 7.3), it is evident that the crust material has been removed from the latter. After the in-situ test, the surface was examined.

using a 10x loupe. There was no significant change before and after cleaning in terms of the surface texture, which seemed to be a result from the yellowish layer beneath the dark crust or soiling (Figures 7.4 and 7.5).

7.2.2 Color Measurement

A Konica Minolta Spectrophotometer CM-2500d was used to evaluate changes in color. Each area of interest was measured three times at slightly different locations to obtain average results. On Sample #3, given that the thick black crust was homogenous in color, one group of measurement was conducted before cleaning (labeled “thick crust”); two groups were on the dry- and wet-cleaned areas, respectively. On Sample #4, four groups of readings were taken: two (before and after) on the yellowish area, which was then cleaned with water, and the other two on the dark area, which was then cleaned in dry condition. In addition, one group was taken on the slightly weathered marble (exhibiting a yellowish tone) at the back of Sample #3; then the surficial layer was removed to determine the color of the fresh marble. For in-situ cleaning test, as the testing area exhibited light yellowish and dark colors, four groups of measurements were done following the same procedure as on Sample #4; another two groups were taken on weathered marble (without black crust, but the color was different from fresh marble due to slight sulfation) near the testing area, and at the corner of a molding that exhibited fresh spallation. The locations are indicated in Figure 7.5.
In general, for the laboratory samples, all the areas exhibited similar colors (as represented by square markers in Figure 7.6) after cleaning regardless of their original colors (round markers). All of the nine readings are close in terms of a* (varying within 4.5), thus L* and b* are the actual significant indicators of the color differences. For Sample #3, the thick black crust showed a similar color tone to the fresh marble, and so did the dry-cleaned area. However, the wet-cleaned area exhibited a color change towards yellow (although not very significant) as observed in many previous cases. Correlating the fact that the color turned towards the weathered marble and the observations in section 7.2.1, this yellowing effect probably resulted from the exposure of the gypsum layer beneath the outer crust. For Sample #4, at both locations, the cleaning led to significantly lower values of b*, as well as lower values of a*. This change, easily recognized by naked eyes, probably suggests a successful removal of the yellow and brown particles embedded in the crust. Comparing the two cleaning conditions, on both samples, the wet-cleaned areas exhibited higher L* values (closer to the fresh marble) but more red and yellow tone than the dry-cleaned areas. The calculated ΔE* values between cleaned areas and the fresh marble, as shown in Table 5, suggest better clean results in wet condition.

<table>
<thead>
<tr>
<th></th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
<th>ΔL*</th>
<th>Δa*</th>
<th>Δb*</th>
<th>ΔE*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Marble</td>
<td>69.81</td>
<td>-0.07</td>
<td>7.30</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Sample #3 Dry</td>
<td>56.62</td>
<td>0.72</td>
<td>6.28</td>
<td>-13.19</td>
<td>0.79</td>
<td>-1.02</td>
<td>13.25</td>
</tr>
<tr>
<td>Sample #3 Wet</td>
<td>60.29</td>
<td>0.94</td>
<td>9.84</td>
<td>-9.52</td>
<td>1.01</td>
<td>2.54</td>
<td>9.90</td>
</tr>
<tr>
<td>Sample #4 Dry</td>
<td>51.33</td>
<td>0.86</td>
<td>6.99</td>
<td>-18.48</td>
<td>0.93</td>
<td>-0.31</td>
<td>18.51</td>
</tr>
<tr>
<td>Sample #4 Wet</td>
<td>59.75</td>
<td>1.36</td>
<td>8.97</td>
<td>-10.06</td>
<td>1.43</td>
<td>1.67</td>
<td>10.29</td>
</tr>
</tbody>
</table>

Table 5: Color measurements on the laboratory samples, after cleaning.
The measurements for the in-situ cleaning test, just as on the laboratory samples, showed little difference in $a^*$ value among all the readings. After cleaning, higher values of $L^*$ were observed on both the yellowish and the dark areas; however, the darker area exhibited a lower $b^*$ value, while on the yellowish area the tone was intensified. With current information, it is difficult to know the exact process causing this phenomenon, but two hypotheses are given as follow: 1) It is possible that the sulfated marble surface in fact had uneven color beneath the outer black layer (as a very different color of weathered marble was observed nearby, shown in Table 6), and the different after-cleaning tones only resulted from the removal of dark particles and the exposure of the color underneath; 2) The discoloration can potentially caused by the melting of yellowish and brownish particles embedded in the crust, as observed in the thin-section (see section 5.4.2). The overall evaluation by $\Delta E^*$ suggests that laser cleaning did not make a significant difference on the yellowish area (this accords with the common observation in the field), but a good result was achieved on the dark area.

<table>
<thead>
<tr>
<th></th>
<th>L*</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>$\Delta L^*$</th>
<th>$\Delta a^*$</th>
<th>$\Delta b^*$</th>
<th>$\Delta E^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh Marble</td>
<td>63.98</td>
<td>0.27</td>
<td>5.59</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Yellow area before</td>
<td>47.75</td>
<td>2.35</td>
<td>16.55</td>
<td>-16.23</td>
<td>2.08</td>
<td>10.96</td>
<td>19.69</td>
</tr>
<tr>
<td>Yellow area after</td>
<td>59.03</td>
<td>3.11</td>
<td>21.17</td>
<td>-4.95</td>
<td>2.84</td>
<td>15.58</td>
<td>16.59</td>
</tr>
<tr>
<td>Dark area before</td>
<td>20.57</td>
<td>2.26</td>
<td>15.38</td>
<td>-43.42</td>
<td>1.99</td>
<td>9.79</td>
<td>44.55</td>
</tr>
<tr>
<td>Dark area after</td>
<td>53.68</td>
<td>1.14</td>
<td>11.02</td>
<td>-10.31</td>
<td>0.87</td>
<td>5.43</td>
<td>11.68</td>
</tr>
</tbody>
</table>

Table 6: Color measurements for the in-situ test, before and after cleaning.
7.2.3 Scanning Electron Microscopy

After cleaning, Samples #3 and #4 were examined with SEM using the same setting as mentioned in section 5.4.4. The observations were consistent with the results of preliminary examination. On Sample #3, the areas cleaned in dry or wet conditions exhibited very different surface morphology (Figure 7.8). Dry-cleaning was able to remove the tabular gypsum crystals forming at the surface, but the depth of cleaning effect was very limited and the crust generally retained its original morphology (somewhat framboidal). In contrast, the wet-cleaned area was “smoothed”, showing a relatively even surface. At high magnification (Figure 7.9), the surface seemed porous; neither gypsum nor calcite crystals can be recognized. This morphology suggests a complete removal of the outer crust without over-cleaning (in which state the calcite grains will be exposed). On Sample #4, a similar result was observed on dry-cleaned area (Figure 7.10). But wet cleaning left a seemingly more aggressive effect on this sample than on Sample #3 with some exposure of calcite grains (Figure 7.11). This could be explained by the fact that this area was only exhibited a thin layer of gypsum before cleaning.

108 The wet-cleaned surface seems similar to the sample cleaned with fiber laser by Hildenhagen and Dickmann. An example of higher degree of cleaning achieved by Nd:YAG laser is also given. However, the original condition of the marble used for their test was not specified (the authors only mentioned that it was weathered). See Hildenhagen and Dickmann, “Comparative studies: Nd:YAG vs. Fibre”, in LACONA VIII, 120.
7.2.4 Raman Spectroscopy

The samples were analyzed with the Renishaw Invia Raman spectrometer (785nm diode laser) in conjunction with WiRE 3.4 software with extended scan from 200-2200cm\(^{-1}\), 50X objective lens, exposure time of 30 or 60 seconds/scan for one accumulations, and 5% laser power. Analysis was performed by Catherine Matsen, Associate Scientist, Winterthur Museum. As hypothesized, on both samples, an alteration of gypsum to anhydrite was observed on the dry-cleaned areas, while the gypsum on the wet-cleaned areas primarily remained the same (Figure 7.12). On the other hand, although iron was identified from the black crust with SEM-EDS, the Raman analysis did not reveal the presence of typical materials that could potentially lead to discoloration, and indeed the yellowing effect was only in little extent as discussed in section 7.2.2. On the wet-cleaned area, this could be explained by a complete ejection of the outer crust without significant melting of brownish particles. However, since dry-cleaning failed to remove the major part of the crust, melting may have occurred beneath the surface but was not detectable with current methods.
Figure 7.1: Photomicrograph of Sample #3, after dry cleaning (right), 20x magnification.

Figure 7.2: Photomicrograph of Sample #3, after wet cleaning (right), 20x magnification.
Figure 7.3: Photomicrograph of Sample #3, comparing dry-cleaned (left) and wet-cleaned surface (right), 20x magnification.

Figure 7.4: Surface before (left) and after (right) in-situ cleaning test, 10x magnification.
Figure 7.5: Surface after in-situ cleaning test, 10x magnification, showing a yellowish layer.

Figure 7.6: The locations of color measurements for in-situ cleaning test: 1- Yellow area before; 2- Dark area before; 3- Yellow area after; 4- Dark area after; 5- Fresh marble; 6- Weathered marble.
Figure 7.7: Results of color measurement on laboratory samples. Above: Data plotted in $a^*/b^*$. Below: Data plotted in $L^*/b^*$. Diamond- Marble. Round- Before cleaning. Square- After cleaning.
Figure 7.8: Results of color measurement for in-situ cleaning test. Above: Data plotted in $a^*/b^*$. Below: Data plotted in $L^*/b^*$. Diamond- Marble. Round- Before cleaning. Square- After cleaning.
Figure 7.9: SEM images of Sample #3, 100x magnification. Above: dry-cleaning. Below: wet-cleaned.
Figure 7.10: SEM images of Sample #3, 500x magnification. Above: before cleaning. Below: wet-cleaned.
Figure 7.11: SEM images of Sample #4, 100x magnification. Above: before cleaning. Below: dry-cleaned.
Figure 7.12: SEM image of Sample #4, 500x magnification, wet-cleaned.

Figure 7.13: Raman spectra (partial) overlay of dry-cleaned samples (green), wet-cleaned samples (red), gypsum (blue), and anhydrite (purple).
Figure 7.14: Full Raman spectra of dry-cleaned samples (above) and wet-cleaned samples (below), compared with anhydrite (purple) and gypsum (blue), respectively.
Chapter 8: Conclusions and Recommendations

The tests and the analyses performed on the marble of the Hood Cemetery Gate have served to obtain a better insight into the characteristics of the gypsum crust on Pennsylvania marble, and the ablation cleaning method using a low-power fiber laser system. In both the laboratory and the in-situ tests, the results of laser cleaning were in general satisfying, with a better performance in wet condition. First, as indicated by the color measurements, the overall appearance of the laser-cleaned areas was significantly improved by a primary change in lightness despite that some yellowing effect was observed. Second, SEM and Raman analyses revealed no damage to the substrate, and in effect the clear gypsum layer, which plays an important role in binding the disaggregated marble surface, was successfully preserved. Third, in wet condition, a considerable part of the outer crust can be removed, thus the chance of further spallation (due to the density of the crust) can be reduced.

In this case, laser ablation cleaning also exhibited the advantage that it allows any following treatments. Given current conditions of the Hood Cemetery Gate, a complex series of treatments, which will be conducted in multiple phases, is necessary for full restoration of this building. Therefore, the sequential compatibility and retreatability provided by each method should be carefully considered. Laser cleaning, unlike chemical or micro-abrasive cleaning methods, leaves no residue on the surface. Furthermore, in wet condition, chemical alteration is not likely to occur within the gypsum crust itself.
However, the CL 20 Q backpack laser system is not the optimal equipment in practice for the Hood Cemetery Gate. Probably due to its operation mode (low energy per pulse and high repetition rate), this laser system exhibited low efficiency in removing thick black crust (as observed in laboratory on Sample #3 and in-situ around the molding) even if the cleaning was performed with a high power density (compared with common Q-switched Nd:YAG lasers) and at full power of this system. Therefore, although the building can be cleaned with great caution with the current laser system, this approach is not recommended in regard to cost-benefit ratio. Using another laser system with higher power or a different operation mode can be an alternative, but its performance needs to be tested on laboratory samples and small areas in-situ before implementation.

Although Scanning Electron Microscopy is probably the best analytic method to reveal change in surface morphology after cleaning, it can only be conducted on laboratory samples, and may require a considerable cost. For future in-situ cleaning test, examination with a loupe of 10x (or above) magnification is recommended. This low-cost and convenient method can still provide better information than naked-eye examination.

In terms of color change, using a spectrophotometer for quality control is recommended. A comparison among the cleaned area, the black crust (or soiling), and the fresh stone, can reveal the degree of cleaning and potential discoloration effect (which may suggest alternative methods or remedies). If cleaning tests are to be conducted using different parameters on multiple areas,
one of the areas may be considered exhibiting the most satisfying color after cleaning. This color can be determined as the “target” in spectrophotometer, and the color of the black-crust areas can be measured frequently during cleaning until the ΔE* is reduced close to zero.

There are other practical issues related to laser cleaning. For example, laser cannot be operated in rain. Laser operation also requires special eye-protection with safety glasses designed for certain wavelengths. Working on site, the infrared or ultraviolet irradiation emitted by a laser may be hazardous to pedestrians. It is crucial in this case since the cemetery gate is adjacent to the sidewalk of Germantown Avenue, and the working location is not very high from the ground. From these perspectives, it is necessary to set up an enclosure on site for laser cleaning.
Bibliography

Books


**LACONA Proceedings**


**Articles from LACONA Proceedings**


Journal Articles


**Papers from Conferences and Special Publications**


Other References


Unknown. “Germantown Cemetery,” *Germantown Telegraph,* April 18, 1849.
Appendix A: Working Photos during Cleaning Tests

In laboratory cleaning test, the sample was partially covered by reflective tape for preliminary test.

Cleaning a piece of metal in order to measure the scan width (laser operation by Adam Jenkins, photo by author).
During in-situ cleaning test, the surface was wetted and appeared dark (above), but whitened as the water vaporized (laser operation by Adam Jenkins, photo by author).
Appendix B: Original Report of SEM-EDS Elemental Mapping

EDAX TEAM

Hood Cemetery Gate

Author: Xinhui YANG
Sample Name: Sample #4
Area 1

Live Map 2

Notes:

Image

[Color legend with percentages and elements listed]
**EDAX TEAM**

**Phase:** SiK/O K/s K/CaK/AIK

![Graph showing elemental analysis results](image)

**eZAF Smart Quant Results**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
<th>Kratio</th>
<th>Z</th>
<th>R</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>3.03</td>
<td>5.06</td>
<td>59.50</td>
<td>30.28</td>
<td>0.0053</td>
<td>1.0928</td>
<td>0.9507</td>
<td>0.1603</td>
<td>1.0000</td>
</tr>
<tr>
<td>O K</td>
<td>53.89</td>
<td>67.47</td>
<td>4675.50</td>
<td>9.19</td>
<td>0.1402</td>
<td>1.0470</td>
<td>0.9724</td>
<td>0.2485</td>
<td>1.0000</td>
</tr>
<tr>
<td>NaK</td>
<td>0.70</td>
<td>0.61</td>
<td>130.70</td>
<td>20.28</td>
<td>0.0023</td>
<td>0.9520</td>
<td>0.9985</td>
<td>0.3401</td>
<td>1.0048</td>
</tr>
<tr>
<td>MgK</td>
<td>2.59</td>
<td>2.13</td>
<td>931.40</td>
<td>8.42</td>
<td>0.0126</td>
<td>0.9685</td>
<td>1.0061</td>
<td>0.4976</td>
<td>1.0081</td>
</tr>
<tr>
<td>AIK</td>
<td>5.68</td>
<td>4.22</td>
<td>2524.40</td>
<td>5.93</td>
<td>0.0336</td>
<td>0.9328</td>
<td>1.0132</td>
<td>0.6257</td>
<td>1.0113</td>
</tr>
<tr>
<td>SiK</td>
<td>12.42</td>
<td>8.86</td>
<td>6105.20</td>
<td>4.70</td>
<td>0.0838</td>
<td>0.9534</td>
<td>1.0199</td>
<td>0.7011</td>
<td>1.0093</td>
</tr>
<tr>
<td>S K</td>
<td>8.04</td>
<td>5.02</td>
<td>3559.50</td>
<td>4.10</td>
<td>0.0602</td>
<td>0.9339</td>
<td>1.0322</td>
<td>0.7917</td>
<td>1.0136</td>
</tr>
<tr>
<td>K K</td>
<td>1.76</td>
<td>0.90</td>
<td>681.40</td>
<td>7.40</td>
<td>0.0149</td>
<td>0.8844</td>
<td>1.0481</td>
<td>0.6172</td>
<td>1.0421</td>
</tr>
<tr>
<td>CaK</td>
<td>10.34</td>
<td>5.17</td>
<td>3395.60</td>
<td>2.91</td>
<td>0.0882</td>
<td>0.9006</td>
<td>1.0528</td>
<td>0.5406</td>
<td>1.0181</td>
</tr>
<tr>
<td>FeK</td>
<td>1.55</td>
<td>0.56</td>
<td>260.10</td>
<td>15.24</td>
<td>0.0134</td>
<td>0.8032</td>
<td>1.0729</td>
<td>0.6947</td>
<td>1.0796</td>
</tr>
</tbody>
</table>
**Phase:** S K/CaK/O K

![EDAX TEAM](image)

**eZAF Smart Quant Results**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
<th>Kratio</th>
<th>Z</th>
<th>R</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>2.73</td>
<td>4.91</td>
<td>42.20</td>
<td>16.51</td>
<td>0.0050</td>
<td>1.104</td>
<td>0.9389</td>
<td>0.1665</td>
<td>1.0000</td>
</tr>
<tr>
<td>O K</td>
<td>49.06</td>
<td>66.17</td>
<td>2047.20</td>
<td>9.63</td>
<td>0.0819</td>
<td>1.0585</td>
<td>0.9613</td>
<td>0.1577</td>
<td>1.0000</td>
</tr>
<tr>
<td>NaK</td>
<td>0.06</td>
<td>0.06</td>
<td>7.90</td>
<td>64.91</td>
<td>0.0002</td>
<td>0.9631</td>
<td>0.9883</td>
<td>0.3124</td>
<td>1.0041</td>
</tr>
<tr>
<td>MgK</td>
<td>0.11</td>
<td>0.10</td>
<td>26.60</td>
<td>18.56</td>
<td>0.0005</td>
<td>0.9600</td>
<td>0.9962</td>
<td>0.4691</td>
<td>1.0076</td>
</tr>
<tr>
<td>AlK</td>
<td>0.97</td>
<td>0.78</td>
<td>327.00</td>
<td>6.11</td>
<td>0.0058</td>
<td>0.9441</td>
<td>1.0036</td>
<td>0.6225</td>
<td>1.0133</td>
</tr>
<tr>
<td>SiK</td>
<td>0.64</td>
<td>0.49</td>
<td>256.50</td>
<td>5.93</td>
<td>0.0047</td>
<td>0.9651</td>
<td>1.0106</td>
<td>0.7421</td>
<td>1.0222</td>
</tr>
<tr>
<td>S K</td>
<td>19.04</td>
<td>12.62</td>
<td>7368.40</td>
<td>2.20</td>
<td>0.1663</td>
<td>0.9457</td>
<td>1.0234</td>
<td>0.9039</td>
<td>1.0216</td>
</tr>
<tr>
<td>K K</td>
<td>0.17</td>
<td>0.09</td>
<td>51.00</td>
<td>14.29</td>
<td>0.0015</td>
<td>0.8959</td>
<td>1.0402</td>
<td>0.6177</td>
<td>1.0804</td>
</tr>
<tr>
<td>CaK</td>
<td>26.76</td>
<td>14.41</td>
<td>6090.80</td>
<td>1.81</td>
<td>0.2343</td>
<td>0.9124</td>
<td>1.0452</td>
<td>0.9478</td>
<td>1.0124</td>
</tr>
<tr>
<td>FeK</td>
<td>0.44</td>
<td>0.17</td>
<td>53.90</td>
<td>14.76</td>
<td>0.0037</td>
<td>0.8143</td>
<td>1.0670</td>
<td>0.9769</td>
<td>1.0636</td>
</tr>
</tbody>
</table>
**Phase:** S K/CaK/O K

![Graph showing element percentages and atomic weights](image)

**eZAF Smart Quant Results**

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
<th>Kratio</th>
<th>Z</th>
<th>R</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>3.27</td>
<td>5.47</td>
<td>72.60</td>
<td>16.26</td>
<td>0.0066</td>
<td>1.0915</td>
<td>0.9477</td>
<td>0.1836</td>
<td>1.0000</td>
</tr>
<tr>
<td>O K</td>
<td>57.39</td>
<td>72.11</td>
<td>3634.90</td>
<td>9.21</td>
<td>0.1163</td>
<td>1.0460</td>
<td>0.9695</td>
<td>0.1937</td>
<td>1.0000</td>
</tr>
<tr>
<td>NaK</td>
<td>0.69</td>
<td>0.60</td>
<td>115.40</td>
<td>10.82</td>
<td>0.0020</td>
<td>0.9512</td>
<td>0.9959</td>
<td>0.3084</td>
<td>1.0037</td>
</tr>
<tr>
<td>MgK</td>
<td>0.39</td>
<td>0.32</td>
<td>139.20</td>
<td>9.59</td>
<td>0.0018</td>
<td>0.9670</td>
<td>1.0036</td>
<td>0.4608</td>
<td>1.0088</td>
</tr>
<tr>
<td>AlK</td>
<td>1.03</td>
<td>0.77</td>
<td>444.10</td>
<td>6.02</td>
<td>0.0050</td>
<td>0.9322</td>
<td>1.0108</td>
<td>0.6124</td>
<td>1.0118</td>
</tr>
<tr>
<td>SiK</td>
<td>0.78</td>
<td>0.56</td>
<td>400.60</td>
<td>5.17</td>
<td>0.0056</td>
<td>0.9529</td>
<td>1.0175</td>
<td>0.7335</td>
<td>1.0194</td>
</tr>
<tr>
<td>S K</td>
<td>15.43</td>
<td>9.67</td>
<td>7713.60</td>
<td>2.26</td>
<td>0.1320</td>
<td>0.9335</td>
<td>1.0300</td>
<td>0.8986</td>
<td>1.0199</td>
</tr>
<tr>
<td>K K</td>
<td>0.13</td>
<td>0.07</td>
<td>50.80</td>
<td>15.36</td>
<td>0.0011</td>
<td>0.8841</td>
<td>1.0461</td>
<td>0.9308</td>
<td>1.0731</td>
</tr>
<tr>
<td>CaK</td>
<td>20.50</td>
<td>10.28</td>
<td>6754.60</td>
<td>1.73</td>
<td>0.1794</td>
<td>0.9003</td>
<td>1.0509</td>
<td>0.5554</td>
<td>1.0140</td>
</tr>
<tr>
<td>FeK</td>
<td>0.40</td>
<td>0.14</td>
<td>64.90</td>
<td>11.77</td>
<td>0.0034</td>
<td>0.8031</td>
<td>1.0714</td>
<td>0.6865</td>
<td>1.0714</td>
</tr>
</tbody>
</table>
Phase: CaK/S K/O K

eZAF Smart Quant Results

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
<th>Kratio</th>
<th>Z</th>
<th>R</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>2.38</td>
<td>4.31</td>
<td>31.10</td>
<td>18.83</td>
<td>0.0049</td>
<td>1.1058</td>
<td>0.9376</td>
<td>0.1845</td>
<td>1.0000</td>
</tr>
<tr>
<td>O K</td>
<td>48.99</td>
<td>66.64</td>
<td>1513.40</td>
<td>9.77</td>
<td>0.0794</td>
<td>1.0603</td>
<td>0.9600</td>
<td>0.1528</td>
<td>1.0000</td>
</tr>
<tr>
<td>NaK</td>
<td>0.03</td>
<td>0.03</td>
<td>3.10</td>
<td>72.40</td>
<td>0.0001</td>
<td>0.9649</td>
<td>0.9872</td>
<td>0.3068</td>
<td>1.0039</td>
</tr>
<tr>
<td>MgK</td>
<td>0.13</td>
<td>0.12</td>
<td>25.40</td>
<td>21.75</td>
<td>0.0006</td>
<td>0.9810</td>
<td>0.9951</td>
<td>0.4623</td>
<td>1.0073</td>
</tr>
<tr>
<td>AlK</td>
<td>1.42</td>
<td>1.14</td>
<td>359.00</td>
<td>6.02</td>
<td>0.0083</td>
<td>0.9459</td>
<td>1.0025</td>
<td>0.6153</td>
<td>1.0124</td>
</tr>
<tr>
<td>SiK</td>
<td>0.81</td>
<td>0.63</td>
<td>243.10</td>
<td>5.83</td>
<td>0.0058</td>
<td>0.9670</td>
<td>1.0095</td>
<td>0.7317</td>
<td>1.0206</td>
</tr>
<tr>
<td>S K</td>
<td>15.67</td>
<td>10.63</td>
<td>4603.40</td>
<td>2.37</td>
<td>0.1362</td>
<td>0.9475</td>
<td>1.0224</td>
<td>0.8958</td>
<td>1.0249</td>
</tr>
<tr>
<td>K K</td>
<td>0.21</td>
<td>0.12</td>
<td>50.80</td>
<td>13.78</td>
<td>0.0019</td>
<td>0.8976</td>
<td>1.0393</td>
<td>0.6284</td>
<td>1.0032</td>
</tr>
<tr>
<td>CaK</td>
<td>29.69</td>
<td>16.12</td>
<td>5718.00</td>
<td>1.76</td>
<td>0.2626</td>
<td>0.9142</td>
<td>1.0443</td>
<td>0.5559</td>
<td>1.0123</td>
</tr>
<tr>
<td>FeK</td>
<td>0.67</td>
<td>0.26</td>
<td>62.60</td>
<td>15.07</td>
<td>0.0056</td>
<td>0.8160</td>
<td>1.0663</td>
<td>0.9752</td>
<td>1.0616</td>
</tr>
</tbody>
</table>
# Appendix C: Color Measurement Data

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Material</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample #3</td>
<td>Black Crust</td>
<td>41.75</td>
<td>0.78</td>
<td>6.06</td>
</tr>
<tr>
<td></td>
<td>S3B_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S3B_2</td>
<td>38.13</td>
<td>1.20</td>
<td>8.33</td>
</tr>
<tr>
<td></td>
<td>S3B_3</td>
<td>41.55</td>
<td>1.15</td>
<td>7.76</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>40.48</td>
<td>1.04</td>
<td>7.38</td>
</tr>
<tr>
<td>Sample #4</td>
<td>Yellow Area</td>
<td>24.48</td>
<td>4.46</td>
<td>28.77</td>
</tr>
<tr>
<td></td>
<td>S4Y_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S4Y_2</td>
<td>24.06</td>
<td>4.23</td>
<td>27.58</td>
</tr>
<tr>
<td></td>
<td>S4Y_3</td>
<td>23.45</td>
<td>4.55</td>
<td>29.01</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>24.00</td>
<td>4.41</td>
<td>28.45</td>
</tr>
<tr>
<td>Sample #4</td>
<td>Black Area</td>
<td>15.11</td>
<td>2.47</td>
<td>13.44</td>
</tr>
<tr>
<td></td>
<td>S4B_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S4B_2</td>
<td>14.99</td>
<td>3.08</td>
<td>16.01</td>
</tr>
<tr>
<td></td>
<td>S4B_3</td>
<td>13.11</td>
<td>4.10</td>
<td>18.16</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>14.40</td>
<td>3.22</td>
<td>15.87</td>
</tr>
<tr>
<td>Sample #3</td>
<td>Dry Cleaning</td>
<td>58.05</td>
<td>0.66</td>
<td>6.67</td>
</tr>
<tr>
<td></td>
<td>S3D_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S3D_2</td>
<td>55.41</td>
<td>0.97</td>
<td>6.09</td>
</tr>
<tr>
<td></td>
<td>S3D_3</td>
<td>56.40</td>
<td>0.52</td>
<td>6.09</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>56.62</td>
<td>0.72</td>
<td>6.28</td>
</tr>
<tr>
<td>Sample #3</td>
<td>Wet Cleaning</td>
<td>59.01</td>
<td>0.89</td>
<td>10.16</td>
</tr>
<tr>
<td></td>
<td>S3W_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S3W_2</td>
<td>61.17</td>
<td>1.16</td>
<td>9.43</td>
</tr>
<tr>
<td></td>
<td>S3W_3</td>
<td>60.70</td>
<td>0.76</td>
<td>9.92</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>60.29</td>
<td>0.94</td>
<td>9.84</td>
</tr>
<tr>
<td>Sample #4</td>
<td>Dry Cleaning</td>
<td>51.58</td>
<td>0.85</td>
<td>6.85</td>
</tr>
<tr>
<td></td>
<td>S4D_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S4D_2</td>
<td>51.12</td>
<td>0.90</td>
<td>7.26</td>
</tr>
<tr>
<td></td>
<td>S4D_3</td>
<td>51.28</td>
<td>0.82</td>
<td>6.86</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>51.33</td>
<td>0.86</td>
<td>6.99</td>
</tr>
<tr>
<td>Sample #4</td>
<td>Wet Cleaning</td>
<td>57.08</td>
<td>1.49</td>
<td>9.93</td>
</tr>
<tr>
<td></td>
<td>S4W_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S4W_2</td>
<td>64.76</td>
<td>1.17</td>
<td>7.45</td>
</tr>
<tr>
<td></td>
<td>S4W_3</td>
<td>57.42</td>
<td>1.42</td>
<td>9.52</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>59.75</td>
<td>1.36</td>
<td>8.97</td>
</tr>
<tr>
<td></td>
<td>LFM_1</td>
<td>LFM_2</td>
<td>LFM_3</td>
<td>Average</td>
</tr>
<tr>
<td>------------------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>Fresh Marble</td>
<td>69.29</td>
<td>71.43</td>
<td>68.71</td>
<td>69.81</td>
</tr>
<tr>
<td>Weathered Marble</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LWM_1</td>
<td>65.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LWM_2</td>
<td>67.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LWM_3</td>
<td>64.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>65.89</td>
<td></td>
<td></td>
<td>65.89</td>
</tr>
<tr>
<td>In-Situ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IYB_1</td>
<td>48.47</td>
<td>48.15</td>
<td>46.64</td>
<td>47.75</td>
</tr>
<tr>
<td>IYB_2</td>
<td></td>
<td></td>
<td></td>
<td>47.75</td>
</tr>
<tr>
<td>IYB_3</td>
<td></td>
<td></td>
<td></td>
<td>47.75</td>
</tr>
<tr>
<td>Average</td>
<td>47.75</td>
<td>47.75</td>
<td>47.75</td>
<td>47.75</td>
</tr>
<tr>
<td>Black Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBB_1</td>
<td>20.73</td>
<td>21.62</td>
<td>19.35</td>
<td>20.57</td>
</tr>
<tr>
<td>IBB_2</td>
<td></td>
<td></td>
<td></td>
<td>20.57</td>
</tr>
<tr>
<td>IBB_3</td>
<td></td>
<td></td>
<td></td>
<td>20.57</td>
</tr>
<tr>
<td>Average</td>
<td>20.57</td>
<td>20.57</td>
<td>20.57</td>
<td>20.57</td>
</tr>
<tr>
<td>In-Situ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IYA_1</td>
<td>57.75</td>
<td>60.43</td>
<td>58.92</td>
<td>59.03</td>
</tr>
<tr>
<td>IYA_2</td>
<td></td>
<td></td>
<td></td>
<td>59.03</td>
</tr>
<tr>
<td>IYA_3</td>
<td></td>
<td></td>
<td></td>
<td>59.03</td>
</tr>
<tr>
<td>Average</td>
<td>59.03</td>
<td>59.03</td>
<td>59.03</td>
<td>59.03</td>
</tr>
<tr>
<td>Black Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBA_1</td>
<td>54.73</td>
<td>51.98</td>
<td>54.32</td>
<td>53.68</td>
</tr>
<tr>
<td>IBA_2</td>
<td></td>
<td></td>
<td></td>
<td>53.68</td>
</tr>
<tr>
<td>IBA_3</td>
<td></td>
<td></td>
<td></td>
<td>53.68</td>
</tr>
<tr>
<td>Average</td>
<td>53.68</td>
<td>53.68</td>
<td>53.68</td>
<td>53.68</td>
</tr>
<tr>
<td>In-Situ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fresh Marble</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IFM_1</td>
<td>60.87</td>
<td>67.30</td>
<td>63.78</td>
<td>63.98</td>
</tr>
<tr>
<td>IFM_2</td>
<td></td>
<td></td>
<td></td>
<td>63.98</td>
</tr>
<tr>
<td>IFM_3</td>
<td></td>
<td></td>
<td></td>
<td>63.98</td>
</tr>
<tr>
<td>Average</td>
<td>63.98</td>
<td>63.98</td>
<td>63.98</td>
<td>63.98</td>
</tr>
<tr>
<td>Weathered Marble</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IWM_1</td>
<td>43.27</td>
<td>43.29</td>
<td>44.18</td>
<td>43.58</td>
</tr>
<tr>
<td>IWM_2</td>
<td></td>
<td></td>
<td></td>
<td>43.58</td>
</tr>
<tr>
<td>IWM_3</td>
<td></td>
<td></td>
<td></td>
<td>43.58</td>
</tr>
<tr>
<td>Average</td>
<td>43.58</td>
<td>43.58</td>
<td>43.58</td>
<td>43.58</td>
</tr>
</tbody>
</table>
Appendix D: Archival Materials

Excerpt from *Germantown Telegraph*, April 18, 1849:

**Germantown Cemetery.**

For some weeks we designed to say something in relation to the elegant and costly improvement which is about being made to the “Germantown Cemetery,” commonly known as the Lower Burying Ground, corner of Main and Logan streets, by WILLIAM HOOD, Esq., of Philadelphia. The preparation of the material has been in hand for some time, and the whole is expected to be completed in August or September. It will be a highly ornamental work, and will add greatly, not only to the appearance of the Cemetery itself, but to the lower part of the borough generally. The structure will be composed entirely of solid blocks of marble of the best description, dressed on both sides. The base course will be from the quarry of D. O. HITNER, Esq., Marble-Hall, Montgomery county; and all above from the quarry of Mr. BROOKS, west-side of the Schuylkill, in Upper-Merion.

The Architect is WILLIAM JOHNSTON, Esq., of Philadelphia, who stands at the top of his profession; and the Marble Masons are Messrs. JOHN STRUTHERS & SON, who are too well known to need a word of commendation.

The following dimensions of the New Front, has been kindly furnished to us by Mr. PETER M’MORLAND, the intelligent foreman of the Messrs. STRUTHERS. It will no doubt be read with interest by people of the borough: —

The whole length of the wall to be 149 feet 6 inches; height of wall at Logan street, from pavement to top of baluster rail, 6 feet 6 inches; and at the other corner on Main street, 10 feet 7 inches. The thickness of wall will be, corner posts at base 3 feet square, and at top 2 feet square, to finish with urns, and 11 intermediate posts each to be 2 feet 8-1/2 inches square at base, and at top 1 feet 9 inches square, all to finish with urns. The pannels between posts will be 2 feet 5 inches thick at base, and at top 1 foot 5 inches. The front will have nine pannels filled with balusters, six pannels between Logan street and gate, and three from gate to the other corner; beside these there will be a solid panel to each side of the gate with heavy carved trusses on top, to form an abutment to the arch over the gate. The size of gate will be, width in clear 6 feet 5 inches, height from pavement to lower side of arch 17 feet, and to the crown of arch 23 feet. The keystone of arch to be in the form of a shield in front, with scull and cross-bones carved on it. The whole of gateway, including arch, to be richly ornamented.

We learn that in addition to this, other portions of the cemetery are to be modernised so that this ancient and venerated place of the dead is at last, through the liberality of a citizen of Philadelphia, deeply attached to the land of his fathers, to rise up and smile in its old age, in the midst of the gloom that surrounds it.
Index

CIE-L*a*b* .......................................................................................................................... 33, 35, 40, 88
Discoloration/ Yellowing ..................................................................................................... 35, 36 38, 40-42, 92, 95, 106
Fiber laser .......................................................................................................................... 4, 27, 74-77, 87, 106
Fluence/ Power density ...................................................................................................... 30-32, 37-44, 46, 74-78, 83-87, 107
Gypsum ................................................................................................................................. 2, 12, 14-18, 20-25, 36, 37, 41, 45, 52-55, 79, 90, 92, 95, 106
Laser ..................................................................................................................................... 2-4, 26-47, 53, 73-83, 85-89, 93, 95, 106-108
Morphology ............................................................................................................................ 4, 16, 24, 42, 44, 50, 83, 88, 94, 107
Particles/ Particulates .......................................................................................................... 2, 14, 18, 22, 24, 25, 31, 37, 50, 51, 53, 54, 78, 92, 93, 95
Pennsylvania marble ........................................................................................................... 3, 19, 48, 49, 52, 106
UV/ 355 nm (wavelength) .................................................................................................. 27-29, 36, 38-42, 45, 46, 108
Wet condition ....................................................................................................................... 45, 46, 78-80, 83, 89-92, 94, 95, 106