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Quantitative Analysis and Treatment of Pennsylvania Blue Marble at the Philadelphia Merchants' Exchange

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Presented to the Faculties of the University of Pennsylvania in Partial Fulfillment of the Requirements for the Degree of Master of Science in Historic Preservation.
Advisor: A. Elena Charola

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QUANTITATIVE ANALYSIS AND TREATMENT OF PENNSYLVANIA BLUE MARBLE AT THE PHILADELPHIA MERCHANTS' EXCHANGE

Felicia Lyles McBratney

A THESIS

in

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CHAPTER 1: INTRODUCTION

1.1 Project Background

Pennsylvania marble, also known as Pennsylvania blue or Montgomery County Marble, was an important regional building stone for public and domestic structures during the first half of the nineteenth century. However, by mid-nineteenth century the use of Pennsylvania marble as a building stone declined because of its poor weathering properties and competition from other domestic quarries. Its short-lived fame and restricted use have resulted in the limited scientific study of its deterioration and responses to conservation treatments.[1]

Over the past ten years the University of Pennsylvania's Architectural Conservation Laboratory along with the National Park Service have been involved in the documentation of Pennsylvania blue marble buildings in Independence National Historical Park, including the Second Bank of the United States and the Philadelphia Merchants' Exchange, named the *Pennsylvania Blue Project,* The objectives of the program are to characterize the stone and identify conservation needs and issues for treatment research.

The program has begun with the development of a multi-phased conservation plan beginning with a detailed CAD/GIS-based survey of the exterior masonry conditions of the Second Bank of the United States, which was completed in 2004. This was followed by a study of mechanical repair options for detached areas of marble, also completed in 2004.[2]

During the summer of 2004, the *Pennsylvania Blue Project* was expanded to include the Philadelphia Merchants' Exchange. Phase I of the condition survey was begun with the intent of preparing a detailed CAD/GIS-based survey of the exterior masonry conditions.

1.2 Introduction to Current Research

This thesis is a continuation of the conditions survey. The goal of the thesis is to study the deterioration of the Pennsylvania blue marble used on the first floor columns of the Philadelphia Merchants' Exchange and to recommend eventual conservation treatments that would be applicable.

The first phase of the thesis was to review the historical information, past treatments, and past analysis, which is an essential part in studying any deterioration mechanisms. The historic information and evaluation of past treatments gives a clear context to building and material performance, which can help in determining the source of the deterioration. If the source is not identified prior to treatment and is not mitigated, it is likely that further deterioration will occur. It is also important to review the past analyses to determine the rationale for previous treatments or interventions. This also helps in determining the state of the marble deterioration at specific points in time. This phase in particular included researching the history and past use of barium hydroxide as a conservation treatment.

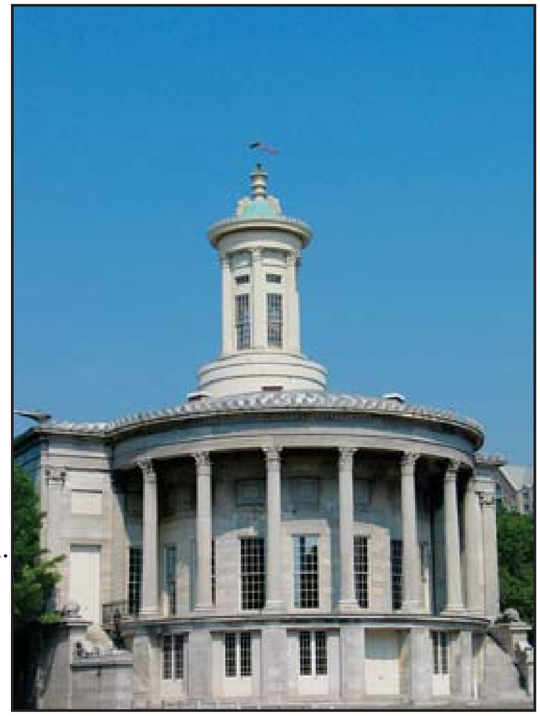

Figure 1.1: Philadelphia Merchants' Exchange, East elevation, summer 2004

Phase II of the thesis consisted of surveying and documenting the current condition of the stone of the first floor columns of the Philadelphia Merchants' Exchange. The twenty-four columns on the first floor were analyzed to understand the current conditions as functions of their geology, location, orientation, past treatments, and other recorded conditions. In addition, a comparative analysis of historical photographs to current photographs was conducted to determine the stone's deterioration over time.

1.3 The Current Program

As a result of the condition survey, two major deterioration factors were identified. These are the presence of acid air pollutants and freeze-thaw cycles. The presence of air pollutants, originating from vehicular traffic and nearby local industry, result in the formation of black crusts, characteristic of marble decay in urban areas. The reaction of the pollutant gases, primarily sulfur oxides, with the marble leads to the formation of gypsum, a slightly soluble salt. The surface blackening is due to the deposition of dirt, fly ash, and carbon particles that are trapped on the surface and incorporated into the gypsum crust, as seen in Figure 1.2.

Figure 1.2: West Elevation, column 3, summer 2004

Freeze-thaw action occurs preferentially in the capillary spaces between mica inclusions inherently present in the stone or accessory minerals. When water enters these spaces and freezes, the resulting expansion causes the stone to delaminate along these veins. This process results in the exposure of new marble surfaces that are exposed to the attack of air pollutants with the consequent formation of more gypsum, as shown in Figure 1.3.

Although gypsum is not a highly soluble salt, over time changes in humidity and wet-dry cycling will induce cycles of dissolution and re-crystallization of this salt leading to mechanical damage. Therefore, it is to be expected that this slow process will continue and possibly escalate over time.

Figure 1.3: North Elevation, columns 7 and 8, summer 2004

Phase III focused on mitigating the long-term problem posed by the presence of gypsum on the surface and subsurface of the marble. A powdering and delaminating surface needs a consolidation treatment to preserve it. However, the presence of soluble salts, such as gypsum, interferes with any consolidation attempt. Since extraction of the slightly soluble salt would result in a significant surface loss -presently the surface is held together by the growth of gypsum crystals- a possible solution is to immobilize this salt by converting it into an insoluble compound. This can be achieved, in principle, by the use of barium hydroxide resulting in the formation of the extremely insoluble barium sulfate. Given its insolubility, this salt will not re-crystallize over time thus reducing the damage resulting from soluble salt re-crystallization. Test treatments were applied *in situ* for evaluation.

For this purpose, small samples both pre- and post-treatment were analyzed in thin section using polarized light microscopy and by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) dot mapping to evaluate the effects of the treatment.

[1] Matero, F. et al. *Documentation and Conditions Survey of the Exterior Marble Masonry: Second Bank of the United States, Philadelphia, Pennsylvania*. Unpublished Report. 2004. 1.

[2] Matero, F. et. al.. 2-3.

CHAPTER 2: BUILDING HISTORY AND ALTERATIONS

The Philadelphia Merchants' Exchange was built in 1834 by Philadelphia architect, William Strickland, on the triangular lot bordered by Third, Walnut, and Dock Streets. The building is a free standing monumental structure in the Greek revival style, with the main entrance facing toward Dock Street.[1] According to Brookover, over 30,000 cubic feet of marble were delivered from Montgomery County during construction. John Struthers and his Italian masons were "hired to put up the marble façade on the building's thick brick walls, and to carve embellishment at the cornice, the water belt, the portico, and west façade."[2]

Figure 2.1: The Maritime Exchange Building, Philadelphia, PA, circa 1890. *From the INHP Archives, from Historical Society of Philadelphia.*

Samuel Henderson and Son supplied the marble from their quarry in Upper Marion Township, which was one of the principle quarries in Montgomery County. "This quarry produced mostly blue marble, but also some pure white. The belt of Pennsylvania marble in nearby Montgomery County is described as limestone in 19th century geological literature. David Henderson is listed as the marble quarrier on the cornerstone."[3] The Corinthian column capitals were carved in Italy of Carrara marble and in 1838 the marble lions were added on the east portico.[4]

"Until the Civil War the Exchange served its original purpose as a center for commerce as well as a home for the Philadelphia Post Office."[5]As Commerce moved to the west, away from the Delaware River, the Exchange suffered increasing neglect and "in 1900 a group of capitalists purchased the building and donated it to the Philadelphia Stock Exchange Company."[6]

In 1901, Louis C. Hickman won a competition for the alterations required by its new use. The design entailed removing the roof and lantern and much of the original interior. The interior was gutted, and new roof and tower of different design and placement were added. The main entrance was shifted to the west, and "round piers and a recessed entry" were added. [7] A new window configuration for the west façade behind the portico was designed and the outermost marble panels on the east portico were replaced with windows.[8]

Figure 2.2: (left) Merchants' Exchange, 1900-1922. *From the INHP Archives; from Hugh Moore Park Collection, Canal Museum, Easton, PA.*

Figure 2.3: (right) Merchants' Exchange, 1900-1922. *From the INHP Archives; from Hugh Moore Park Collection, Canal Museum, Easton, PA.* (originally Printed backward)

S.W. Hollowell purchased the building in 1922, when it was converted to a produce market. More alterations were made including the addition of metal awnings and produce stalls on the east and north elevations. Alterations to the interior were also made.

Windows were “inserted in place of the recessed marble panels along the third floor of the east portico.”[9] Cuts were made into the shafts of the far northernmost columns on the east portico to receive iron straps and rods to support the produce shed roofs below. Prior to 1947, copper bird netting was added around the west and east column capitals. The stairs flanking the east portico were demolished and the 1838 lions were moved to the Philadelphia Museum of Art.[10]

Figure 2.4:(left) Merchants’ Exchange, 1947. *From the INHP Archives.*
Figure 2.5: (right) Merchants’ Exchange, September 1950. *From the INHP Archives.*

In 1950, drawings were produced by Charles Oeslanger to document the existing structure and during the summer of 1951 the Historical American Buildings Survey produced architectural drawings of the building. Shortly after in 1952, the National Park Service purchased the building as part of its plan for the creation of Independence National Historical Park. Between May and December 1953, the produce sheds were demolished. “As a part of the restoration of the building, the National Park Service cleaned the exterior masonry. Several different methods were sampled on the building. First floor columns on the north

Figure 2.6: Merchants’ Exchange: Wrecking of Produce Stalls, September 16, 1953. *From the INHP Archives.*

side of the building were re-carved in May 1953 and sandblasting in December 1953."[11] Historic photographs indicate that one column was recarved and two were sanblasted.

"Both of these methods were determined to be unacceptable. Instead the entire building was cleaned using high pressure water spray for lengthy periods of time (24-36 hours). The work was undertaken by the Day Labor force of Independence Nation Historical Park. The Weekly Field Reports and Day Labor Logs document the cleaning process but do not specify the pressure of the water spray. The day labor carpenters put up the scaffolding while the painters did the cleaning, and the masons did the pointing work following the cleaning. A Memorandum from August 22, 1963, in the park's correspondence file describes a program of cleaning and pointing and waterproofing to start that year. No reference has been found in the available files to clarify what was intended as waterproofing, or that waterproofing was actually carried out."[12] Most likely the term "waterproofing" implies that the building was made water tight. There is no indication of a protective water

Figure 2.7: Merchants' Exchange: Re-carving of North elevation column by Milione, May 1953. *From the INHP Archives.*

Figure 2.8: Merchants' Exchnage, after restoration, northwest façade, July18, 1966. *From the INHP Archives.*

repellant product applied to the stone at this time and no physical evidence suggests that this was done. The cleaning continued into 1965. The copper bird netting was also removed at this time.[13]

In the early 1980s, chemist Seymour Lewin was hired to develop a conservation study and treatment strategy for the facades of the historic buildings in Independence National Historical Park. The Merchants' Exchange Building was included as a part of this conservation study. The aim of the study was:

> A. to sample, chemically analyze and determine the microscopic, petrographic and morphologic character of the façade materials (exterior stone masonry) of the Merchants' Exchange
> B. develop and test in situ procedures for removing deleterious resinous substances from these facades
> C. develop and test in situ the most appropriate technique for the consolidation and preservation of the marble surfaces
> D. Carry out periodic sampling and analyses of the test areas during a one year period of natural weathering to assess the efficiency and safety of the techniques employed.
> E. Devise and recommend a protocol for a large-scale preservative treatment of the three facades.[14]

The study briefly overviews the historical development of the building and acknowledges that the

> search of the historical records shows no other indication of large-scale work on the building façade. On several occasions, small test areas were treated with proprietary materials, at the suggestion of entrepreneurs. These were claimed to be useful for cleaning and/or preservation purposes. The tests sought to determine whether such treatments were in fact both safe and effective. None of these tests was followed by the adoption of the proposed treatments.[15]

During Lewin's study, forty samples were taken for analyses in order to characterize the types of stone and to establish a range of variability. The samples generally came from detaching flakes or spalls. Core samples were not taken thus the

> samples tend to contain much more gypsum than would be characteristic of the bulk of the stone. However, the gypsum content tells much about the susceptibility of the stone of that type and in that location to attack by air pollutants, and the minor mineral constituents still serve to establish the stone type.[16]

Each sample underwent several types of analyses including x-ray diffraction (XRD), scanning electron microscopy (SEM), and wet micro chemical analysis. The samples taken from the ground floor columns on the north, west, and east elevations are numbered and identified on photographs.[17] The mineralogical compositions are given, as well as indurations and texture of the Pennsylvania blue marble samples. [18]

The state of the stone was also discussed as a part of the analyses. The stone decay problems afflicting the façade of the Merchants' Exchange building were described as originating from three main sources. The first source was that two of the facades, south and west, are exposed to heavy traffic and to high concentrations of automotive exhaust. This was described subsequently as causing the marble to be heavily encrusted with gypsum. The black crusts were soft and blistering, and were considered a danger to the stone.[19] The black crusts are "the cause of progressive decay of the underlying stone, over and above the eating away of the marble by the acidic pollutants that give rise to the gypsum in the first place."[20]

The second source was described as the "veined micaceous stratifications which, although originally prized because of their attractive appearance, are now the cause of serious deterioration…most strikingly the case for some of the ground level columns of the south and north facades."[21] The third principal source of decay described does not apply to the ground floor columns.[22]

Conservation treatment tests were also undertaken by Lewin. Due to the substantial amount of gypsum crusts present cleaning tests were performed. This established whether the gypsum could thoroughly be removed without "resorting to heroic measures" and to reveal the condition and degree of soundness of the underlying stone.[23] Two of the most heavily sulfated ground floor columns were selected for the test cleaning[24] "Philadelphia city water was allowed to drip slowly and continuously over the stone surface for 6-8 hours."[25] Analyses of the stone surface pre and post treatment was conducted. Post treatment analyses showed that 90 to 95% of the gypsum had been

 

Figure 2.9: (left) Merchants' Exchange, South elevation – cleaning of column 2, circa 1984. *From INHP Archives.*
Figure 2.10:(right) Merchants' Exchange, South elevation – after cleaning of column 2, circa 1984. *From INHP Archives.*

removed as a result of the treatment. However, there is no mention in the report of how this analysis was conducted. This technique was described as representative of the mildest and safest technique for cleaning and removing surface encrustation.[26] "An additional 12 hours of this type of water flow over the surface served to leach out the remainder of the gypsum."[27] The stone surface after cleaning was described as friable to a depth of 1 to 2 millimeters.

More relevant to this thesis is the test performed "to evaluate the effectiveness of the barium hydroxide-urea technique for consolidating the friable weathered surface and preserving the stone against renewed attack by air pollutants."[28] The lower half of the ground floor column identified as south column 2, after the above-described cleaning was completed, was selected for this test. Recommendations for the façade of the Merchants' Exchange were also made as a part of this analysis. These included cleaning and consolidation treatment with barium-hydroxide urea. [29]

In a report dated March 5, 1984, Tom Davies of Independence National Historic Park analyzed the current state of the Pennsylvania blue marble of the Merchants' Exchange building. His analyses concluded that the marble was displaying serious deterioration and was in need of major conservation work. One of the three major deterioration categories defined was deterioration caused by atmospheric pollution which was causing gypsum encrustation and surface deformation as already discussed by

Lewin.[30]

In 1992, the National Park Service devised a conservation strategy for the Merchants' Exchange Building. As a part of the Conservation Strategy, geologist Elaine McGee conducted a study on the marble characteristics and deterioration mechanisms occurring on the marble at the Merchants' Exchange.[31] Three different types of marble were identified, local Pennsylvania marble (Pennsylvania blue), Carrara marble from Italy, and Georgia marble.[32]

This analysis confirmed that while "the marbles are composed primarily of calcite, they differ in the amount and type of inclusions, grain size distribution, and original stone fabric." These characteristics are important to understand because they "influence the manner in which the marbles deteriorate and …influence the effectiveness of treatments that may be applied to the deteriorated stone."[33]

The Pennsylvania blue marble used was quarried from "the Conestoga formation of Cambro-Ordovician age in southeastern Pennsylvania. Marbles from these quarries have been described as "'beautiful coarse grained marble, white, gray, blue, and mottled' and '…light blue, semi-crystalline texture, with signs of irregular stratification, evenly bedded, and in medium to thick courses."[34]

"The Pennsylvania blue marble used at the Merchant's Exchange is predominately blue gray in color but in some areas it has a mottled, streaked appearance of light gray or blue gray areas with white;" however, it does not display a regularly streaked pattern and the mottling is neither large nor continuous.[35] "Pennsylvania blue marble is weakly metamorphosed and contains abundant micaceous inclusions.[36] It is loosely textured, with a marked foliation fabric forming a series of parallel planes that are weakly held together. The texture and pronounced foliation of this marble have been accentuated by exposure, as weathering and deterioration have concentrated at weak points in the stone."[37]

Light blue gray calcite is the dominant mineral in the Pennsylvania blue marble. The calcite grains range in size from 40-1060µm, however most grains are 100 to 400µm.

"The calcite grains are angular to subrounded in shape and are nearly pure $CaCO_3$, with minor amounts of magnesium and a trace of iron. Muscovite and apatite, a calcium phosphate, are common inclusion phases in the marble, visible with the scanning electron microscope (SEM) but difficult to see visually or optically because they are small and similar in color to the calcite. Minor pyrite, sphene, zircon, and tourmaline are also present in inclusion rich areas."[38]

Several different types of deterioration were identified during McGee's analysis including dissolution, chemical alteration, and disaggregation. However, these terms were not extensively defined, only briefly described in the overview of deterioration. Not all of these mechanisms were discussed in relationship to the first floor columns. It seems as if the analysis was mainly focused on the deterioration of the Corinthian columns and capitals.[39]

As far as McGee's analysis, dissolution was not found on the ground floor columns. The major deterioration occurring on the ground floor columns was defined as chemical alteration. Chemical alteration is identified by McGee as the sulfation of marbles due to pollutants in the air resulting in the formation of gypsum crusts which trap dirt, fly ash and other particles causing the darkening and discoloration of the stone surface.[40] The black crusts were described as: "rough hummocky surfaces covered by fine black particles; the marble is fully obscured by dirt." The black crust sample taken for analysis came from column shafts on the east portico. While these are exposed to different conditions, the analyses of the black crusts are comparable to those on the ground floor columns.[41]

X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM-EDS) determined that the crusts were predominantly composed of gypsum. The analysis confirmed that "the gypsum in alteration crusts consist of elongate crystals that range in shape from blocky, rectangular blades to thin needle-like crystals. The elongate crystal habit and the random orientation of the gypsum crystals on the marble surface form a mat that traps airborne particles giving a blackened appearance to the crust."[42] XRD found gypsum, calcite, and quartz in the black crusts and SEM revealed an abundance of mineral fragments and organic materials such as pollen, other particles such as dirt, and pollutant particles.[43]

"The thicknesses of the gypsum crusts vary with their location on the building; the thickest crusts are in areas that have probably never been washed, while similar but thinner crusts have accumulated where the stone is occasionally wet."[44] Black crusts on the ground level columns were described as "being concentrated where the stone faces the building, but outward facing areas close to the street are also black."[45] "The impact of traffic is evident in the abundance and type of particles in the crusts. Particles from auto emission are common, as are salt (NaCl) crystals. These crusts are particularly notable because although they are thin (0.03 – 0.07 mm), the crusts on the originally smooth surface of the column shafts have blistered in patches exposing newly reveled, crumbling stone underneath."[46]

"While the colored alteration crusts appear to preserve the original detailed surface features of the carved stone, the marble can be severely deteriorated underneath."[47] Disaggregation was discussed as a mechanism which was occurring underneath the black crusts. Comparisons of the weathering marbles were also analyzed, comparing deterioration of the Carrara marble and the Pennsylvania blue marble.[48]

As a part of the Conservation Plan, a photogrammetric description of marble decay was done by Victor G. Mossotti and A. Rauf Eldeeb. This was however only done on the Corinthian columns and capitals on the east and west elevations.[49] Environmental exposure analysis was also conducted by Donald A. Dolske and Susan I. Sherwood. The purpose of this aspect of the project was to determine relative exposure to weathering agents, such as rain, pollutants, moisture, and temperature. The information was used to help explain the observed variations in marble deterioration.[50]

Also as a part of the conservation strategy, conducted by Susan I. Sherwood was a section on the "Implications of Building History, Exposure, and Weathering Patterns." This was "an introductory attempt to relate the historical and physical evidence to the current condition of the marbles, and to consider the implications of this evidence for the selection of conservation strategies. Preliminary information that speaks to particular conservation questions is presented to highlight the need for further discussion and interpretation."[51]

Deterioration cause and effect relationships were outlined. These conclusions were however very preliminary and need to be reexamined for use in further conservation intervention. Additional information needs and implications for stone conservation were also outlined, including conservation treatment options. [52] The current study is responding to this need; however it focuses only on the ground floor columns, which are exhibiting some of the most severe deterioration.

[1] Brookover, William D. "Building History and Alterations" in *Philadelphia Merchant's Exchange Conservation Strategy*. National Park Service. Preservation Assistance Division: Washington, DC, 1992. 5.
[2] Ibid.
[3] Ibid.
[4] Ibid.
[5] Ibid.
[6] Ibid.
[7] Brookover, 6.
[8] Ibid.
[9] Ibid.
[10] Ibid.
[11] Ibid.
[12] Ibid. Other primary records document estimates proposed for the waterproofing of the building, however, no records detail whether this was ever carried out.
[13] Brookover, 9. "A restoration program was developed to return the architectural emphasis of the building to its east or portico end…Under a separate construction contract, the east stairs flanking the portico were rebuilt, stone columns damaged where iron straps had been cut into the stone were repaired with epoxy patches, the tar was removed from the portico flooring and replaced with new marble, and the roof with its lantern was restored to the building. The lions were moved back into position on June 3, 1965."
[14] Lewin, S.Z. "Conservation of the Facades of Historic Buildings at Independence National Historic Park – Final Report." *NPS Contract 4000-1-0055.* INHP Archives: Philadelphia, PA. 1984. 1-2.
[15] Lewin, 22.
[16] Lewin, 23.
[17] Ibid.
[18] Ibid. Sample compositions are shown in Table II of the contract document on page 27 and Lewin, 28, Table IIA.
[19] Lewin, 29. The darkening of the surface is caused by grime, fly ash, soot, and hydrocarbons that are getting trapped in the interstices of the gypsum crystals.
[20] Ibid.
[21] Ibid.
[22] Lewin, 36.
[23] Lewin, 37.
[24] Ibid. These are the southernmost ground level column on the west face, and the second column from the west corner of the south side. These are currently identified as west elevation column 4 and south elevation column 2.
[25] Ibid.
[26] Lewin, 37.
[27] Ibid.
[28] Ibid.
[29] Lewin, 39 and 41.
[30] Davies, Tom. *Independence National Historic Park Masonry Report*. Unpublished. 1984.
[31] McGee, Elaine. "Marble Characteristics and Deterioration" In *Philadelphia Merchant's Exchange Conservation Strategy*. National Park Service. Preservation Assistance Division: Washington, DC, 1992. 13.
[32] Ibid. The 1960's replacement stone was Georgia marble. Pennsylvania marble is also known as Pennsylvania blue or King of Prussia marble.
[33] Ibid.
[34] Ibid.
[35] McGee, 14.
[36] Ibid. The calcite has not strongly re-crystallized. Thus it is considered to be a crystalline limestone.
[37] Ibid.
[38] Ibid.

[39] McGee, 18. Note: Corinthian columns- bases as shafts are constructed of Pennsylvania blue marble; the capitals are carved of Carrara marble.
[40] Ibid.
[41] McGee, 22-24.
[42] McGee, 24.
[43] Ibid.
[44] Ibid.
[45] Ibid.
[46]Ibid. The basis for this conclusion, as far as analysis technique, was not discussed. However, this is one of the main deterioration phenomenon that is currently evident on the stone column surface. The gypsum encrustation was also confirmed using XRD and SEM-EDS.
[47] Ibid.
[48] Ibid.
[49] Mossotti, Victor G. and A. Rauf Eldeeb. "Photogrammetric Description of Marble Decay" in *Philadelphia Merchant's Exchange Conservation Strategy*. National Park Service. Preservation Assistance Division: Washington, DC, 1992. 29-41.
[50] Dolske, Donald A. and Susan I. Sherwood. "Environmental Exposure Analysis" in *Philadelphia Merchant's Exchange Conservation Strategy*. National Park Service. Preservation Assistance Division: Washington, DC, 1992. 42-66.
[51] Sherwood, Susan. "Implications of Building History, Exposure, and Weathering Patterns" in *Philadelphia Merchant's Exchange Conservation Strategy*. National Park Service. Preservation Assistance Division: Washington, DC, 1992. 67-77.
[52] Sherwood, 65.

CHAPTER 3: STONE DECAY MECHANISMS: AN OVERVIEW

Several different stone decay mechanisms have previously been mentioned as causes for deterioration on the first floor columns of the Philadelphia Merchants' Exchange. This chapter aims at providing a thorough but brief explanation of these deterioration phenomenons.

Stone deterioration results from many interacting conditions thus it is difficult to determine the extent of deterioration as a result of any one deterioration mechanism. Some are a result of inherent stone characteristics in relationship to weathering and others are a result of atmospheric pollution in contact with a substrate.

3.1 Acid Deposition

Calcareous stones are susceptible to deterioration from chemical attack by acidic pollutants.

> The stone itself is an active partner in the reaction, and thus different stones behave differently. The degree of damage due to acid deposition depends on the nature of the stone and the presence of moisture…both porosity and texture play an important role in determining the type and extent of deterioration.[1]

The important role of acid deposition on calcareous stones ultimately results in the formation of gypsum and "carbonaceous particles are very active in forming black crusts when they are wet, because they contain both sulfurous compounds and catalysts."[2] Calcareous materials absorb "sulfur dioxide from the atmosphere and can serve to nucleate gypsum crystals. Thus the gypsum in the crust is partly due to the transformation of the calcareous surface and partly contributed from particle deposition and nucleation."[3] In exposed areas, sulfation is "practically absent because the deterioration products formed on the stone surface are removed by the mechanical action of rain."[4] This is due to the solubilization of gypsum formed.[5]

Acid precipitation originating from air pollution can occur both as wet and dry deposition.[6] In polluted areas, dry deposition is "more important than wet deposition as a source of stone decay."[7] Charola and Ware describe dry deposition as resulting from "the transfer of pollutant gases and/or particles, including aerosols, from the atmosphere to a surface in the absence of rain. In general, dry deposition originates from nearby sources and is therefore called short-range deposition."[8]

Gases are the most important contributors and can react with both the surface of the stone and other aerosol particles. The deposition occurs in the boundary layer at the surface of the stone and is influenced by "the nature of the substrate, its surface conditions, and its micro-environment."[9] The rate of deposition is affected by the concentration of these gases and particles in the boundary layer, which is enhanced by "an increase in concentration of the pollutants, air turbulence, roughness and heterogeneity of the receiving surface, chemical affinity of the surface for the pollutant, and surface moisture."[10] The most damaging of the pollutants found in the atmosphere is sulfur dioxide, which is created by the combustion of fossil fuels such as, coal, oil and natural gases.[11]

Wet deposition is of lesser importance than dry deposition and only affects the "exposed surfaces of a building, while dry deposition can affect all surfaces of a building."[12] "Wet deposition is concerned with the incorporation of pollutant substances in cloud droplets, i.e. rain-out, and by entrapment during their fall, i.e. wash-out. The combined effect of rain-out and wash-out is called 'acid rain."[13]

Domaslowski describes the effects of air pollution and the formation of gypsum and the ensuing effects of gypsum crystallization.[14] Torraca highlighted that the formed gypsum crusts "are seldom continuous and impervious to water because cracks traverse them frequently; they do not constitute a protective layer. Deterioration may continue behind the crust which is often found lying over incoherent; disintegrated material."[15] There are also different types of crusts that can form on the surface. Amoroso and Fassina also studied the deterioration associated with stone surface crusts. They state that “a careful examination of crusts which do not seem to have affected stone, often show that decay processes have already occurred and have cause irreversible damage,” such as flaking or exfoliation of the stone surface and subsurface. [16]

The gypsum crystals themselves incorporate and trap “airborne clay, sand, soot, tar, and fly-ash particles,” causing the surface to darken and become black in appearance. [17] The formation of gypsum crusts also causes surface discoloration.

Török studied these different types of crust formations on limestone buildings in Budapest. His study describes six different types of crusts. Included in these six types of crust formations are thick hard white crusts, thin blistering white crusts, thin surface parallel laminar black crusts, thick laminar black crusts, framboidal black crusts, and grey dust crusts. Török defines each and provides information on the protective or destructive role of the crust on the substrates and discusses the stability and adherence of the crusts to the substrate.[18]

3.2 Wetting and Drying Cycles

Porous materials “exhibit both hygric and hydric dilation and contraction as a result of moisture changes.”[19] “When porous materials absorb moisture or liquid water, they expand. This effect is known as hydric dilation, when moisture is absorbed or hygric dilation, when it is produced by liquid water.” [20]

Although these cycles alone are reversible, there is possible material fatigue under numerous wetting-drying cycles.[21] “The presence of soluble salts changes this behavior significantly and irreversibly.”[22]

3.3 Salts and Stone Deterioration

It is known that the crystallization of salts will cause stone damage, especially when they are highly soluble or hydrate forming.[23] "The deterioration of materials is often simplistically attributed to 'the presence of salts' or, at best, to the crystallization—or hydration pressure of a particular salt."[24] There are however "many mechanisms that are involved in the deterioration of porous materials by salts." [25]

Moisture and salts impact porous materials together.[26] Thus "for damage to occur, salts must move into and within the porous bodies, a process that requires the presence of water (liquid) and/or moisture (water vapor)."[27] "Salts can enter and move through porous bodies only when dissolved in water," which can enter either as a liquid or vapor.[28]

According to Charola, two mechanisms can be operative when water enters in the liquid state: capillarity and/or infiltration. "While the first is the result of the attraction of the water and the capillary material as well as the surface tension of the liquid, the latter requires a hydrostatic pressure and depends on the permeability of the material."[29] Condensation and hygroscopicity are the mechanisms in which water in the vapor state can enter a porous material. When discussing condensation, "two types of condensation should be distinguished: surface condensation and micro-condensation (or capillary condensation) in pores."[30]

Once inside a porous material, water can move in several different ways. It can move as a liquid with the ability to transport salts, or as a vapor which salts will retain through hygroscopicity.[31] If moving as a liquid, "the mechanism relies on capillarity."[32] If moving as a vapor, the mechanism relies on diffusion.

The presence of salts will increase the amount of water in the material, "partly by enhancing capillary rise … and because of hygroscopicity."[33] "Once a salt is in a porous material, its movement will be strongly dependent on ambient conditions –i.e. temperature and relative humidity – as well as the presence of other salts. Changes in relative humidity result in its partial crystallization and dissolution."[34]

A salt solution containing different salts will have a wider range of relative humidity. “The effect of a wider RH range of a mixed solution within the pore system of a material will be compounded by the hygroscopicity and capillary condensation capability of the latter, increasing the deterioration potential of the salt.”[35]

Damage generally occurs in the zone of maximum moisture content. The type of resulting damage will depend on where this zone is located in the stone. Snethlage and Wendler state, regarding the degradation of sandstone, that “if this zone is located on the surface, the damage type that forms will be sanding off; if it is very close to the surface (e.g. 1 or 2 mm), a thin scale will form; if it is deeper in the stone, a scale of 1 or 2 cm will form.”[36] “The detachment of black crusts can also be explained by the same model.”[37] When exfoliations occur parallel to the layering of the stone, the weak boundary layers favor their detachment.[38]

There are several different deterioration mechanisms associated with the presence of salts including, hydrostatic crystallization pressure, linear crystal growth pressure, and hydration pressure. Deterioration mechanisms vary between different materials and among salts of different solubilities. [39]

“Hydrostatic crystallization pressure can develop when a supersaturated solution occupies a smaller volume than the precipitating crystals plus the residual saturated solution.”[40] Hydration pressure is “pressure developed by volume increase upon hydration of a salt.”[41] There are still, however, questions concerning this hypothesis regarding crystallization and hydration pressure.[42]

Snethlage and Wendler describe the effects of hydric dilation in the presence of gypsum in sandstones, as not only enhancing the decay but causing the detachment of the scales as a result of its crystallization pressure.[43] Charola also considers that the precipitation of less-soluble salts exert a mechanical wedge action, which contributes to the irreversibility of the dilation pressure. [44]

3.4 Freeze- Thaw Cycles

The nature of the stone itself plays an important role in its deterioration. Not only in its susceptibility to deterioration caused by acid deposition, but in its inherent stone characteristics such as mineral inclusions. These mineral inclusions can cause stress on the surrounding stone during freeze-thaw cycles.

Lewin described it as follows: "It is the capillary spaces between the mica platelets, and the fissures along the interfacial planes where the micaceous strata meet the [calcite crystals] that provides places for the tenacious retention of imbibed water."[45] When the water freezes, the resulting expansion causes the stone to crumble along these veins and interfaces. "Once the decay has gained foothold, the fissures progressively widen and deepen. This decay process and others as well, can proceed more and more rapidly as time goes on. Thus, the opening up of the stone at the boundaries of the foreign inclusions facilitates the attack of air pollutants, salt re-crystallization, and mechanical damage. The rate of decay, and the contribution to it from all the variety of decay mechanisms, increases as the amount of decay grow."[46]

Lewin and Charola described stone decay due to mineral inclusions as resulting from the "freezing of retained water in the interlaminar and interfiber spaces of the inclusions."[47] "When platy or fibrous inclusions occur at, or just below the exposed surface of a building stone, it serves as a trap for liquid water."[48] These types of inclusions exert a strong "wicking" effect. When the retained water freezes, the inclusions and any thin skin of the matrix stone that might be covering it will rupture. The ruptured stone surface can appear as a blistered, pitted, or pock-marked surface. [49] This type of deterioration can be also compounded by the presence of salts.

[1] Charola, A. Elena and Robert Ware. "Acid Deposition and the deterioration of stone a brief review of a broad topic" in *Natural Stone, Weathering Phenomena, Conservation Strategies and Case Studies.* Ed. by Siegesmund, St. Weiss, T. and Vollbrecht, A. Geological Society, London. Special Publications. 2002. 399.
[2] Ibid.
[3] Ibid.
[4] Amoroso, G.G., and V. Fassina. *Stone Decay and Conservation: Atmospheric Pollution, Cleaning, Consolidation and Protection*. New York: Elsevier, 1983. 148.
[5] Ibid.
[6] Charola and Ware, 393.
[7] Ibid.
[8] Ibid.
[9] Charola and Ware, 393-394.
[10] Charola and Ware, 394.
[11] Torraca, G. *Porous Building Materials: Materials Science for Architectural Conservation, Second Rev. Ed.* Italy: ICCROM. 1982. 40.
[12] Charola and Ware, 395.
[13] Charola and Ware, 397-398.
[14] Domalslowski, Wielaw. *La conservation préventive de la Pierre. Imorimeries Populaires, Arts graphiques, Genéve.* 1982.
[15] Torraca, 41.
[16] Amoroso and Fassina 149-150.
[17] Amoroso and Fassina. 263.
[18]Török, A. "Gypsum – Induced Decay and Weathering Crusts on Limestone Buildings in Urban Environment of Budapest." *In Proceedings from the Sixth International Symposium on the Conservation of Monuments in the Mediterranean Basin*. 2003. 211-215.
[19] Snethlage, R. and E. Wendler. "Moisture Cycles and Sandstone Degradation" In *Saving Our Architectural Heritage: The Conservation of Historic Stone Structures.* Ed. N.S. Baer and R. Snethlage. Berlin, March 3-8, 1996. 9.
[20] Charola, A. Elena. "Salts in the Deterioration of Porous Materials: An Overview." JAIC 39(2000):327-343. 329.
[21] Snethlage and Wendler, 9.
[22] Charola, "Salts in the Deterioration of Porous Materials: An Overview." 336.
[23] Charola, "Salts in the Deterioration of Porous Materials: An Overview." 328.
[24] Ibid.
[25] Ibid.
[26] Snethlage, R. and E. Wendler. "Moisture Cycles and Sandstone Degradation" In *Saving Our Architectural Heritage: The Conservation of Historic Stone Structures.* Ed. N.S. Baer and R. Snethlage. Berlin, March 3-8, 1996. 9.
[27] Ibid.
[28] Ibid.
[29] Ibid.
[30] Ibid.
[31] Charola, "Salts in the Deterioration of Porous Materials: An Overview." 329.
[32] Ibid.
[33] Ibid.
[34] Ibid.
[35] Charola, "Salts in the Deterioration of Porous Materials: An Overview." 330.
[36] Snethlage and Wendler, 17.
[37] Snethlage and Wendler, 18.
[38] Snethlage and Wendler, 17.
[39] Charola, "Salts in the Deterioration of Porous Materials: An Overview." 335.
[40] Charola, "Salts in the Deterioration of Porous Materials: An Overview." 332.

[41] Ibid.
[42] Snethlage, R. and E. Wendler, 15.
[43] Snethlage, R. and E. Wendler, 7
[44] Charola, "Salts in the Deterioration of Porous Materials: An Overview." 336.
[45] Lewin, S.Z. "Conservation of the Facades of Historic Buildings at Independence National Historic Park – Final Report." *NPS Contract 4000-1-0055.* INHP Archives: Philadelphia, PA. 1984. 29.
[46] Lewin, 36.
[47] Lewin, S.Z. and A.E. Charola. "Stone Decay Due to Foreign Inclusions" In *The Conservation of Stone II: Preprints of the Contributions to the International Symposium, Bologna. 27-30 October 1981.* Edited by Rafaela Rossi-Manaresi. Bologna Italy: Centro Per La Conservezione Delle Sculpture All'Aperto. 1981. 205.
[48] Lewin and Charola, 210.
[49]Ibid.

CHAPTER 4: CURRENT STATE OF DETERIORATION AND SEMI-QUANTITATIVE ANALYSIS

4.1 Introduction

Two approaches were taken in order to understand the current state of deterioration. The first approach was to conduct a condition survey of the columns to create condition drawings in order to quantify particular conditions. The second approach was to analyze comparative photographs of historical and current conditions in order to determine deterioration over time.

The conditions from the original project glossary were narrowed down to a selected number of deterioration mechanisms. This was done based on a brief examination of the most prominent conditions occurring on the columns. A glossary was then developed with field conditions and an in depth guide to understanding them including site identification. The glossary created ranged from conditions of flaking to stone orientation.[1]

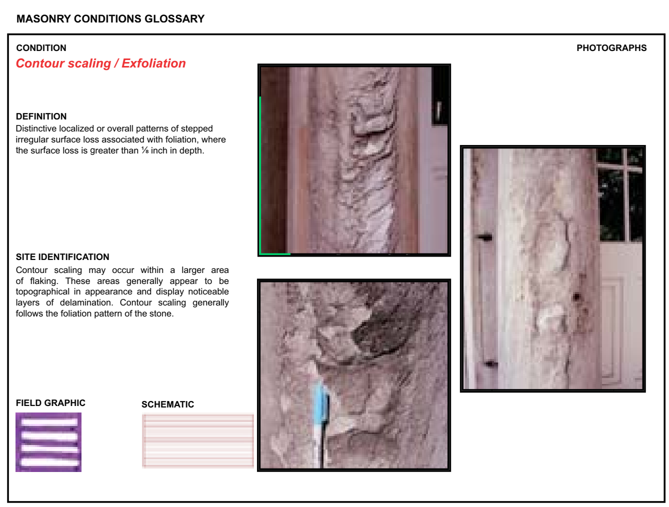

Figure 4.1: Sample page from the Conditions Glossary, *See Appendix A for complete version.*

The first floor columns are monolithic columns carved of Pennsylvania blue marble. They are approximately nine feet tall with a base circumference of approximately 44 inches (111.76 cm) and a top circumference of approximately 38.5 inches (97.79 cm). Because of the absence of arises, which would have provided an easy reference for recording, a grid was created that could be wrapped around the column to create uniform divisions for ease of recording. The grid was divided into eight sections. AutoCAD drawings were created based on the grid so the columns could be recorded as a one dimensional flat surface. The grids were numbered and placed in the same position on each column to keep uniformity, so each column unravels in drawing at the same position.

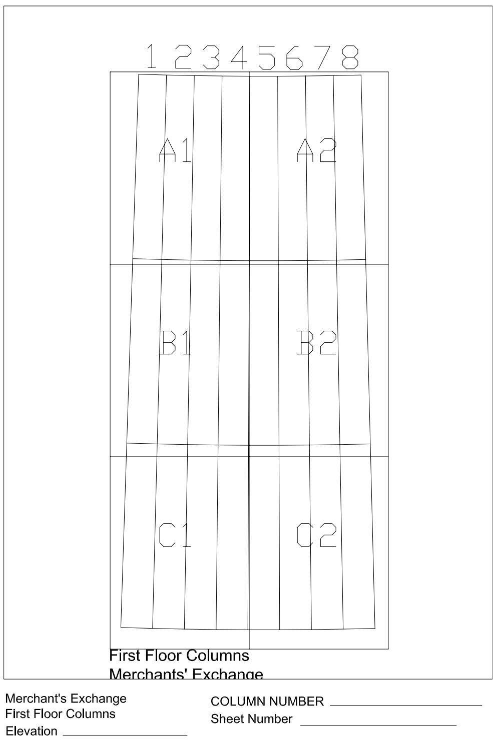

Figure 4.2: (right) Grid applied to column for recording
Figure 4.3: (lower right) Grid placement detail
Figure 4.4: (left) AutoCAD Base drawing used for recording

The drawings were then inserted into acetate sleeves and conditions were recorded based on a set of field symbols developed earlier as a part of the summer internship project. The drawings were then scanned and combined to create a digital montage in Photoshop. These digital montages were then imported into AutoCAD and traced to produce a digital drawing representing the column conditions. The AutoCAD drawings were then exported into Arc View to create a GIS map. This enabled conditions to be quantified and questions to be answered concerning the relationship between different conditions, their frequency, location on the column, and location on the building.

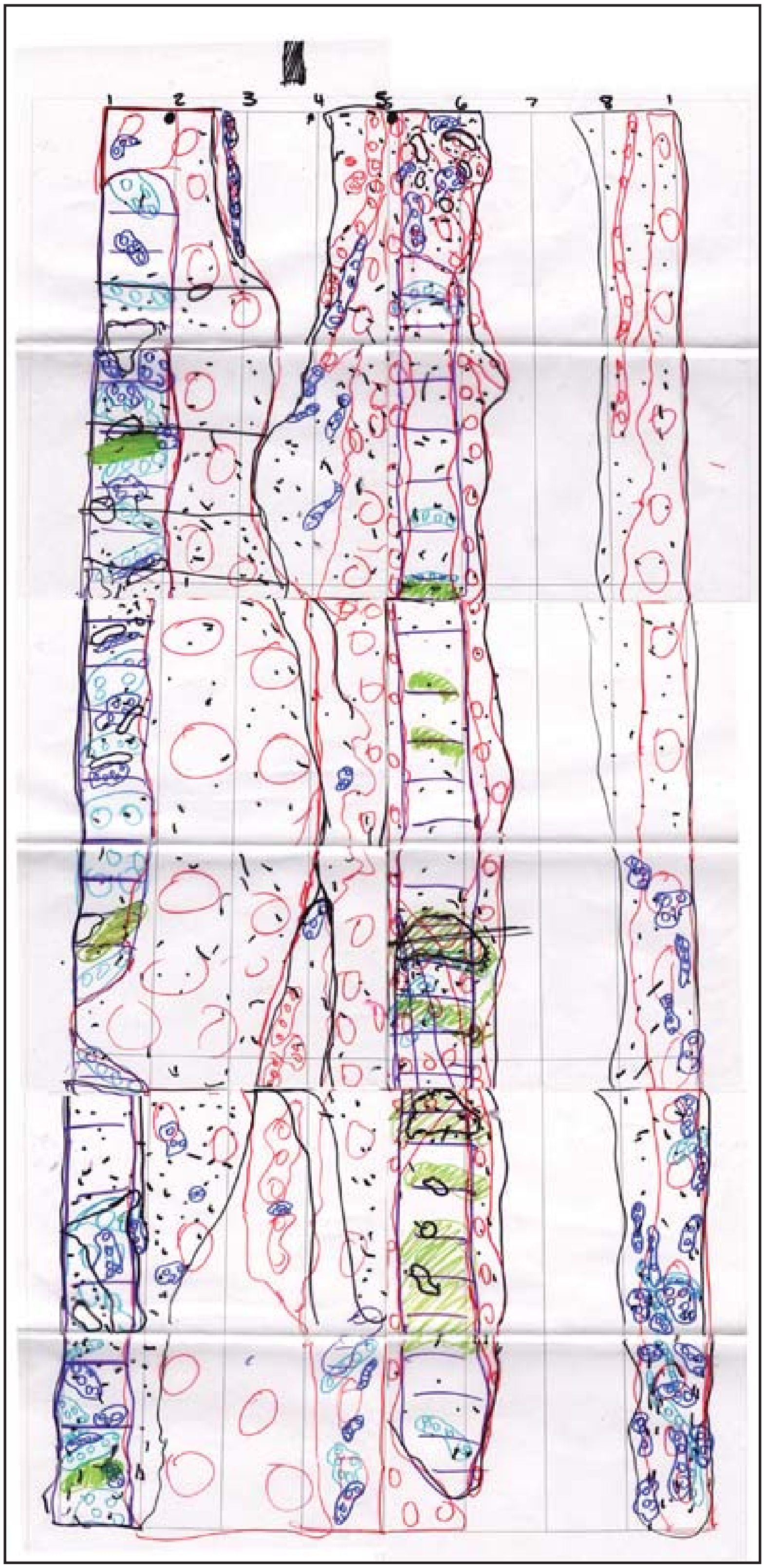

Figure 4.5: Scanned conditions drawing, column montage; South elevation, column 5

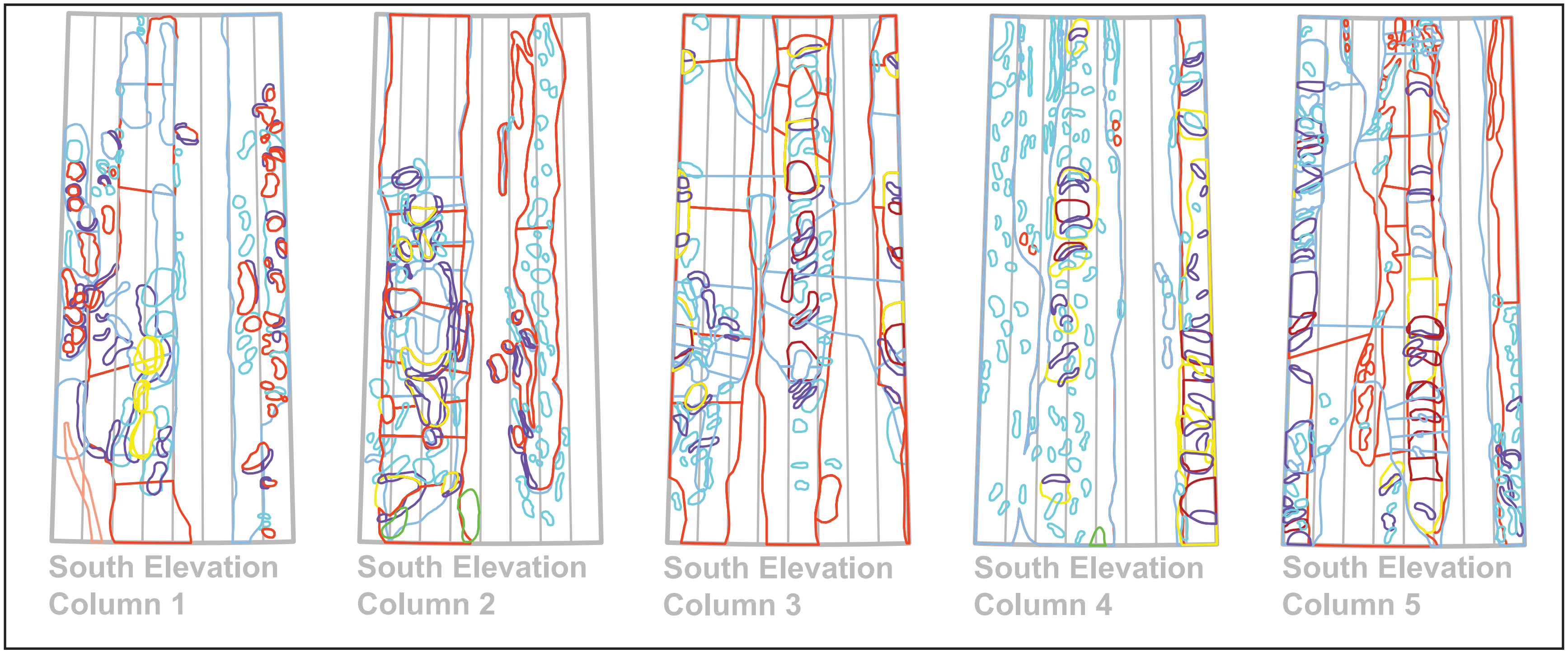

Figure 4.6: CAD drawing produced from field drawings; South elevation, columns 1-5

4.2 Surrounding Environment

There are several different levels of building analyses to conduct in order to determine the cause of deterioration and a suitable intervention. The Philadelphia Merchants' Exchange is located in Independence National Historical Park within the city of Philadelphia. It is bordered on the north and east by Dock Street, on the south by Walnut Street, and on the west by Third Street. Traffic is no longer permitted on Dock Street. Both Walnut and Third Streets have heavy traffic frequented by both SEPTA and tourist buses, which tend to be heavier during certain times of the year due to the increased influx of tourists. There is a light at the intersection of Walnut and Third Streets, which increases idling time of cars and buses and the building is thus exposed to longer periods of pollution on the south and southwest corner. There are sidewalks located around the perimeter of the building. The twenty fours columns are located on the north, south, and west elevations at ground level with an overhanging cornice.

Although there are fewer industries near the city of Philadelphia and the quality of air and amount of acid rain has improved, pollution continues to be a problem due to the proximity of oil refineries to the city of Philadelphia.

The average temperature in Philadelphia during a normal year ranges from an average low of 27 degrees Fahrenheit (2.78 degrees Celsius) during the winter months, with record lows between 1-10 degrees Fahrenheit (12.22-17.22 degrees Celsius) to an average high of 86 degrees Fahrenheit (30 degrees Celsius) during summer months with record highs in the upper 90's and lower 100's degrees Fahrenheit (32.22-37.78 degrees Celsius). [2] The normal precipitation ranges from 2.75 inches (6.985 cm) during a dry summer month to 42 inches (106.68 cm) during a wet winter month.[3] The wide range of temperatures and the increased liquid water precipitation increases freeze-thaw cycling and wetting drying cycles, which contributes to the advanced deterioration of the marble as discussed in Chapter 3. [4]

The average relative humidity (RH) recorded over the past 45 years through 2004 ranges from 70% to 80% in the morning to 50% to 60% in the afternoon. The high percent RH increases the amount of acid deposition on the surface of the stone as does the amount of precipitation, which leads to significant stone deterioration. The average wind speed ranges from 8-11 mph (12.875-17.703 km/h), with the highest wind gusts recorded from the south and southwest, which can also contribute to stone weathering.[5]

The east elevation of the building is exposed to sunlight during the morning and the west during the afternoon. The south façade is in direct sunlight most of the day. The north thus has little exposure to direct sunlight, therefore when the stone is wet it dries less quickly than on the other three elevations.

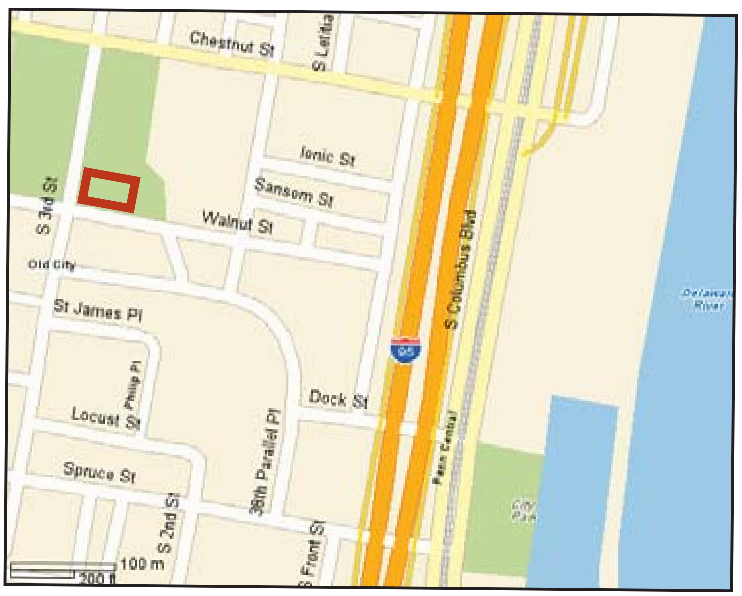

Figure 4.7: Location of the Merchants' Exchange in relationship to Interstate 95 and the Delaware River. *From Yahoo Maps.*

The Delaware River is located approximately 0.341 miles (1800 feet, 548.79m) to the east of the Merchants' Exchange, with an active port on both the east and west banks of the river. Interstate 95 lies approximately 0.256 miles (1350 feet, 411.99 m) to the east of the building. Both of which influence the surrounding environment, contributing to the salts and sulfur oxides in the air.

4.3 Deterioration Patterns at the Merchants' Exchange

The twenty-four columns on three different facades were analyzed to understand the current conditions as a function of location, past treatments, and other recorded conditions. The GIS maps which were created from the AutoCAD conditions drawings, served to process this information.[6] There are two types of GIS maps. The first is the condition survey of the columns, which shows the major deterioration types of symptomatic deterioration and their pattern on the stone surface. The second type are drawings based on calculated areas of conditions. The area in inches of the conditions were calculated for each column and the drawings produced represent the columns ranked in relationship to those having the highest area of a certain condition to those with the lowest.

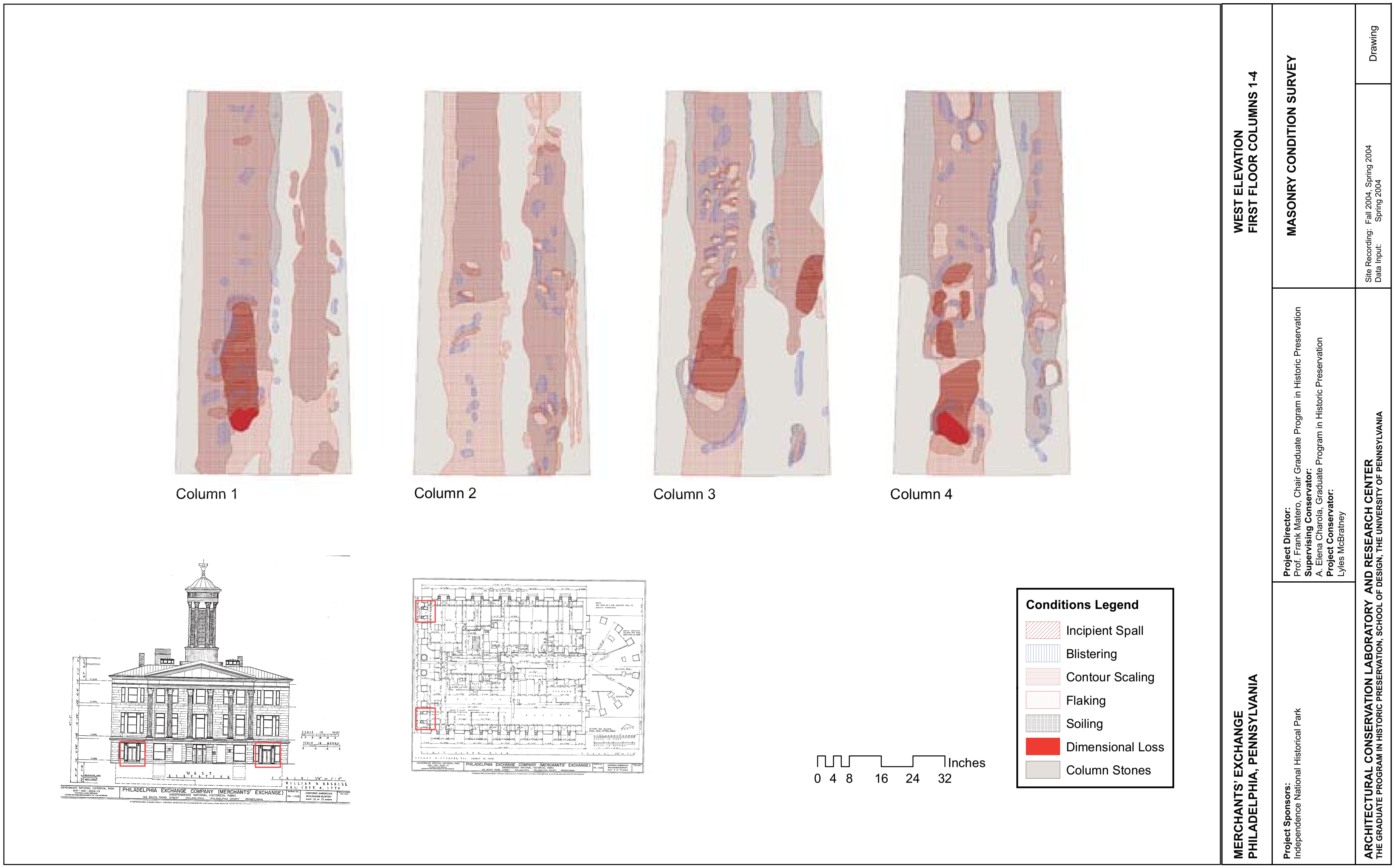

Figure 4.8: GIS Masonry Condition Survey Drawing: Type I.

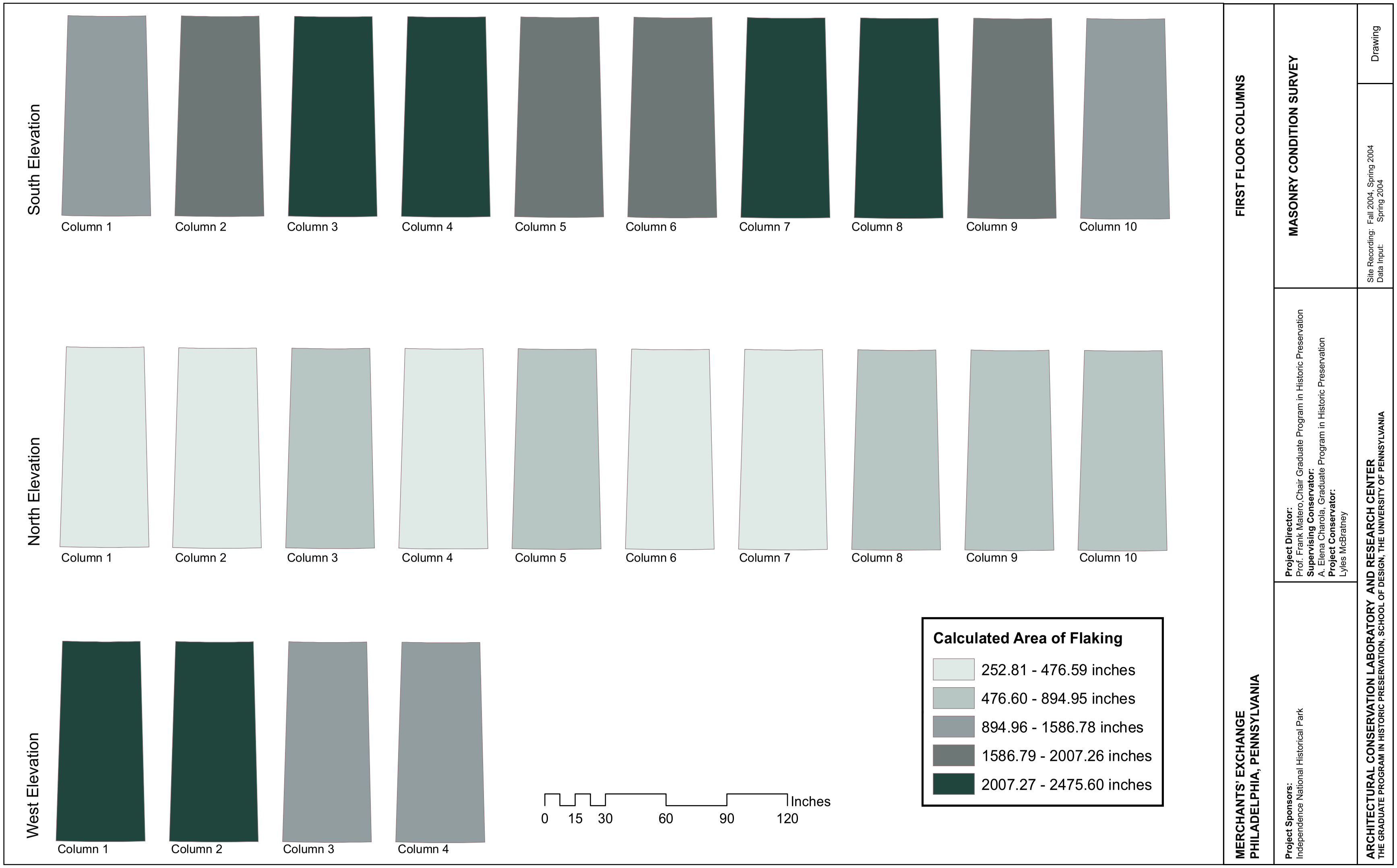

Figure 4.9: GIS Masonry Condition Survey Drawing, Type II. Calculated surface area of flaking on all columns, indicating larger areas of flaking on the south and west elevation columns.

4.3.1 Recorded Deterioration Mechanisms

Orientation of foliation planes is one of the most significant indicators of the stones' performance. Damage generally occurs where mineral inclusions have been exposed and the deterioration is the result of freeze thaw action, which is compounded by the presence of gypsum. The deterioration that results from this are flaking and contour scaling, which are described more in depth below. Their patterns, as described in 1980 by Seymour Lewin, directly correlate to the orientation of foliation planes. Because of this, patterns of deterioration can be predicted based on the stones' orientation. In general face oriented and obliquely oriented areas of the stone tend to be more susceptible to deterioration. It is important to recognize that because of the way the stone was originally carved there are both face or obliquely oriented areas of the stone and vertical or diagonally oriented areas of the stone. None of the stones were carved with horizontally edge oriented foliation. Orientation in some cases was hard to determine due to heavy soiling, however, patterns of deterioration follow foliation patterns so conclusions can be made regarding the stones' orientation.

Two of the most prominent conditions occurring on the columns are blistering and flaking. Blistering is defined as distinctive deformation of the stone surface. They appear as small or large-scaled swelling and/or rupturing of a uniform layer. They can be intact or in the early stages of rupture. Active blistering results in a fresh clean whitish appearance, while those that have not popped are generally soiled. Overlaps of incipient spalls and soiling serve as indicators of activity.

(a) Blistering can occur within larger areas of flaking and contour scaling. They have been recorded as those that have not yet popped or are in the early stages of popping. The south and west elevations tend to have more freshly popped blisters which can be partly attributed to mechanical damage from people passing by the building possibly touching the columns.

These blisters are generally caused by gypsum formation and can be distinguished by surface deformation. Surfaces heavily encrusted with gypsum also tend to darken over time due to the collection of dirt, fly ash, dust and other airborne particles that become trapped within the gypsum crusts. On the Merchants' Exchange, this type of stone deterioration is most prevalent on the west and south facades, due in part to heavier vehicular traffic.

(b) Blistering will also occasionally occur along micaceous mineral inclusions leading to flaking and eventually contour scaling.

Generally, when a blister is popped, underneath the surface is a powder-like substance, which was described as disaggregation in previous reports. These areas are only recorded as blistering in this survey. After the powder substance is brushed away, the remaining surface generally appears as flaking which is described below.

Flaking areas are described as surfaces that display active thin lamellar detachment of even thickness or past evidence of such. There tends to be several causes of this type of deterioration mechanism.

(a) When blistering occurs and the surfaces of blisters rupture what remains underneath is an area of flaking. This area can then develop more blisters exhibiting more advanced flaking which will eventually lead to contour scaling.

(b) General areas flaking are also present apart from those associated with blistering. These areas can be attributed to the presence of salts and their ensuing effects, as discussed above in the overview of deterioration mechanisms.

(c) Another pattern tends to be created by mineral inclusions -- generally mica minerals -- due to freeze-thaw cycles. This type of flaking generally progresses into contour scaling, which is closely related to stone orientation, occurring on face oriented or diagonally oriented stone surfaces. They appear as U-shaped or up-side-down U-shaped scales, generally with corresponding incipient spalls.

Contour scaling is defined as distinctive localized or overall patterns of stepped irregular surface loss associated with foliation where the surface loss is greater than 1/8" in depth. Contour scaling may occur within a larger area of flaking. These areas generally appear to be topographical in appearance and display noticeable layers of delamination. Contour scaling generally begins as flaking or blistering and can eventually result in significant stone loss. Contour scaling generally follows the foliation pattern of the stone, "the working of the stone into a cylindrical shape has produced chevron-shaped veining at the surface."[7] The u-shaped scales also serve to hold water at the exposed surface, increasing the possibility for further deterioration due to freeze-thaw cycles and the presence of salts.[8]

Incipient spalls are described as surface planar discontinuities of any size that have become partially detached from the stone, usually lens shaped in section. The detached area can be detected visually or audibly by sounding. The angle of separation will be approximately 0-60^{o} from the surface plane of the surrounding stone and usually in association with foliation. Incipient spalls are generally found in areas of contour scaling, flaking, and blistering and are closely related to these recorded conditions.

Dimensional loss is described as localized stone loss greater than 2 square inches in area and at least ½ inch in depth as measured in plane with the surrounding stone surface. Dimensional loss may be associated with other conditions.

In the case of the Merchants' Exchange columns, there is a progression of deterioration patterns that ultimately leads to dimensional loss. These include, blistering → flaking → contour scaling→ incipient spalling → dimensional loss; or, flaking→ contour scaling → incipient spalling → dimensional loss.

Differential erosion is defined as surface weathering described by: (a) large areas of coarse texture (this is a very loose definition), (b) localized loss greater than 1/8" in depth (i.e. along foliation planes or inclusions), or (c) the reduction of surface details (e.g. weathered arises or edges). Differential erosion has not been observed on any of the surfaces recorded, but are evident on the corners of the bases of the columns.

Soiling is recorded on a relative scale and is described by the dark grey and black surface deposits, which cause darkening of the stone surface. Soiling also tends to occur in areas not washed by rain. Light soiling due to normal weathering and exposure was not recorded, the darker heavier soiling which indicated the presence of gypsum and advanced soiling was recorded. Soiling generally coincides with blistering, flaking, and contour scaling. The above cornice prevents the columns from being washed by rain. Heavier soiling tends to occur on the south and west facades due to nearby vehicular traffic.

Stones may display large mineral inclusions as veins or phenocrysts. Recorded inclusions are at least ¼ inch in width and noticeably larger than prevailing foliation patterns. They are typically raised in relief or weathered out and distinctive in color and texture from the surrounding stone matrix. Some are recorded, however many were hard to determine due to the level of soiling.

Gypsum encrustation is marked by the formation of grey to black crusts in protected areas that are noticeably more concentrated than the prevailing soiling patterns. They appear to be gritty bumpy textured framboidal crusts. Surfaces on the south and the west have most prevalent evidence of gypsum formation; however, it has not been recorded as gypsum encrustation since they are not the framboidal crusts, like those located on the underside of cornices and drip edges. The presence of gypsum is however marked by other deterioration mechanisms such as blistering and flaking, and was confirmed by XRD and optical, as well as SEM microscopy.

4.3.2 Conclusions

Based on the conditions drawings the most prominent conditions occurring on the first floor columns are flaking and soiling. The areas of flaking can lead to contour scaling and dimensional loss, thus areas of contour scaling and dimensional loss occur within areas of flaking. Soiling also overlaps with areas of flaking and contour scaling. Based on the area of flaking calculated for each column, as seen in the second set of condition drawings, the largest areas of flaking occur on columns located on the south and west elevations. In particular, south elevation, columns 3, 4, 7 and 8 and west elevation columns 1 and 2, exhibited the largest calculated area of flaking. There are also larger areas of soiling on the south and west elevations. In particular, south elevation columns 4 and 5, show the largest calculated area of soiling. South elevation columns 4, 5, 6, and 8 exhibit larger calculated areas of contour scaling.

Dimensional loss and incipient spalls also follow the same pattern, they occur in larger areas on the south and west elevations. South elevation, column four has the largest area of dimensional loss, indicating that its condition is more severe than that of the other columns. The calculated area of incipient spalls is largest on south elevation, columns 1, 5 and 8, indicating that the most active deterioration is occurring on those particular columns. There are larger areas of blistering on south elevations columns 1, 3, 6, and 8 and on north elevation column 1. The location of the blisters on north elevation, column 1 follow the pattern of the mica mineral inclusions unlike those on the south and west elevation columns that tend to occur in with areas of flaking, primarily caused by the presence of gypsum.

After reviewing the calculated area drawings, each range of area for each drawing was assigned a numerical value, with 5 representing the largest range of area and 1 representing the smallest range of area for each drawing. The values were then totaled. The columns that scored the highest represent those that are in the worst condition and those with the lowest values represent those in the best condition.[9] The following table shows the total values for each column.

Table 1: Semi-quantitative analysis of conditions as determined from assigned numerical values.

Column ID	Flaking	Soiling	Contour Scaling	Blistering	Dimensional Loss	Incipient Spall	TOTAL
S1	3	2	1	5	1	5	17
S2	4	2	2	4	1	4	17
S3	5	4	3	5	4	4	25
S4	5	5	4	4	5	4	27
S5	4	5	5	3	4	5	26
S6	4	4	4	5	1	4	22
S7	5	2	2	2	1	3	15
S8	5	4	5	5	3	5	27
S9	4	4	3	4	2	4	21
S10	3	2	1	4	1	2	13
W1	5	4	3	3	2	3	20
W2	5	3	1	3	1	3	16
W3	3	3	3	4	1	3	17
W4	3	4	3	4	3	4	21
N1	1	1	1	5	1	2	11
N2	1	2	1	1	1	2	8
N3	2	1	1	3	1	1	9
N4	1	2	3	2	1	2	11
N5	2	1	2	2	1	3	11
N6	1	1	1	3	1	1	8
N7	1	1	1	1	1	1	6
N8	2	1	1	3	1	2	10
N9	2	1	3	2	1	3	12
N10	2	1	1	3	1	2	10

This table paired with the information shown in the surface area drawing is a valuable resource in identifying the columns in the worst condition. Overall the columns in the worst condition are located on the south and west elevations, in particular south elevation columns 3, 6, 5, and 8 and on the west elevation, columns 1 and 4.

The average score (and standard deviation) of south elevation columns is 21 (± 5.2), while the average score of the west elevation columns is 18.5 (± 2.4), and the north elevation columns' average score is 9.6 (± 1.8). The average calculations show that the south elevation columns are in worse condition and that the deterioration intensity has a wider range than the west and north elevation columns respectively. The north elevation column are in best condition and have a lower range of deterioration intensity.

The patterns of deterioration indicate that the deterioration is active and subject to further stone loss. As discussed previously and confirmed by this analysis and the following photographic analysis, vehicular traffic is responsible for the deterioration on the south and west. This is exemplified by the condition of the columns on the north elevation, where with the elimination of this factor the deterioration is less active than that of the south and west elevation columns. The highest recorded wind gusts were recorded from the south and southwest. The winds from this direction with average wind speeds ranging from 8-11 mph (12.875-17.703 km/h) also contribute to the larger condition intensity on the south elevation columns as compared to the deterioration intensities of the west and north elevation columns.

4.4 Comparative Photograph Analysis

The second approach in understanding the deterioration of the first floor columns of the Merchants' Exchange was conducting a semi-quantitative analysis describing current conditions as compared to historic conditions documented in historic photographs. The aim was to determine if it were possible to differentiate deterioration rates between columns. The descriptions and illustrations give a general sense of the rate of decay, which can then be correlated to the conditions drawing created and related to previous alterations or treatments that may have had an impact on the stone surface, such as cleaning, re-carving, traffic, etc.

To allow the comparison to be carried out the following dates need to be taken into account: the building was constructed in 1834. Because of the heavy soiling, three columns were “cleaned” in 1953: a pair was sandblasted and a single one was re-carved in 1953. Ten years later, between 1963 and 1965, the whole building was cleaned by high pressure water spray.

For identification purposes, all columns were numbered:

- North façade: numbers #1-10 run from east to west (facing the building the numbers run from left (E) to right (W)).
- West façade: numbers #1-4 run from north to south (facing the building the numbers run from left (N) to right (S)).
- South façade: numbers #1-10 run from west to east (facing the building the numbers run from left (W) to right (E)).

A good first impression can already be obtained by comparing Figures 4.10 and 4.11. These photographs show the west façade of the building in 1959 (25 years after construction) and in 1965, soon after cleaning. Although the pictures are not taken from the same angle, it is easy to see the difference in appearance of the whole façade. The older pictures show the black deposit on the columns—really evident on those on the second floor. And careful analysis of the photograph shows that the four bottom columns are equally soiled.

The following paragraphs will analyze in more detail some of the columns to allow correlation of soiling with conditions and previous treatment history.

4.4.1 Comparisons

- West Façade: Figures 4.12 and 4.13; 4.14 and 4.15:

Columns 3 and 4 on the west elevation, exhibit the typical deterioration of soiling, blistering, flaking, and contour scaling with lighter areas where blisters have spalled off. A significant increase in soiling can be seen in the later photograph (Fig. 4.13, 2004 – 39 years after cleaning) as compared to the earlier one (Fig. 4.12, 1958—24 years after construction).

Another set of close-up photographs of these same columns is shown in Figures 4.14 and 4.15. Figure 4.14 was taken in 1984, twenty years after the cleaning of the building, while Figure 4.15 was taken 20 years later. The latter shows significant soiling and fresh blistering and flaking. This heavy soiling can be attributed to the continual exposure of the columns to vehicular traffic along Third Street, which is an important emission source for carbon and other particles in the emission of motor vehicles.

- South Façade: Figures 4.16; 4.17, 4.18 and 4.19 ; 4.20, 4.21 and 4.22.

Figure 4.16 shows the general appearance of this elevation prior to cleaning in an undated photograph. Figure 4.17 shows columns 9 and 10 on the south elevation as they appear currently. The comparison of the lower part of these columns can be made between a photograph of 1961 (27 years after construction) (Fig. 4.18) and that taken in 2004 (39 years after cleaning) (Fig. 4.19). What is evident is that there has been a decrease of soiling in the years after the cleaning. However, deterioration has continued, as can be observed in the highlighted areas on column 9 in Figures 4.18 and 4.19 that shows an area with more loss than it had 43 years previously. Differences in deterioration between paired columns can be attributed to variations in the amount and distribution of the inclusions in the marble and which determine their sensitivity to freeze-thaw damage. Thus, column 9 shows more deterioration than column 10. And this difference is maintained over time.

Figure 4.20 shows columns 7 and 8 of the same elevation in 2004. Detail of the lower center part of column 8 can be compared in photographs from 1952 (Fig. 4.21) and 2004 (Fig. 4.22). Again it can be observed that the soiling has decreased, 18 years of earlier soiling were far heavier than twice the amount of years after cleaning.

- North Façade: Figures 4.23 and 4.24; 4.25, 4.26; 4.27 and 4.28; 4.29; 4.30 and 4.31

Figure 4.23 shows a general view of the north elevation of the building a few years before its cleaning. Clearly visible are the service station, which was located right across it and the allowed parking of cars and trucks. Figure 4.24 shows columns 7-10 in more detail in a picture taken prior to cleaning.

Figures 4.25 and 4.26 show the section with columns 5-10 on the north façade. Columns 5 and 6 were sandblasted in 1953 and column 7 was re-carved in 1953, removing all soiling thoroughly, and in the case of column 7, refinishing the surface. All three of them were also cleaned again in 1964-65 with high pressure water spray. The current state of these columns, as shown in Figure 4.26 , shows that these 3 columns would appear cleaner and columns 8, 9 and 10 which were cleaned by high pressure water spray in 1963-65. However, closer photographs of the pair of columns 7 and 8 show that photographs can be misleading as seen in Figures 4.28 and 4.29. These were taken in 1983 and 2004 respectively. And no significant soiling difference can be found between the re-carved (#7) and the washed (#8) column.

Figure 4.29 shows the pair of columns that was sandblasted and eventually washed in their present state. It is clear that there is a difference in deterioration that can be mainly attributed to differences in the nature of the marble. Column #5 shows a higher degree of deterioration than column #6.

The last example taken for discussion is column #9 shown prior to cleaning in Figure 4.30 and in its present state Figure 4.31. The deterioration evident in the historic photograph does not appear to have increased significantly. The soiling accumulated in the first 23 years is far more than that in the subsequent 39 years after cleaning. This is partly due to the improvement in the surrounding environment and conditions. Vehicular traffic was removed with the closing of Dock Street.

Figure 4.10:
West Elevation
Source: INHP Archives
Creator: W. A. McCullough
Date: October 1959

Figure 4.11:
West Elevation, after restoration
Source: INHP Archives
Creator: W. A. McCullough
Date: November 1965

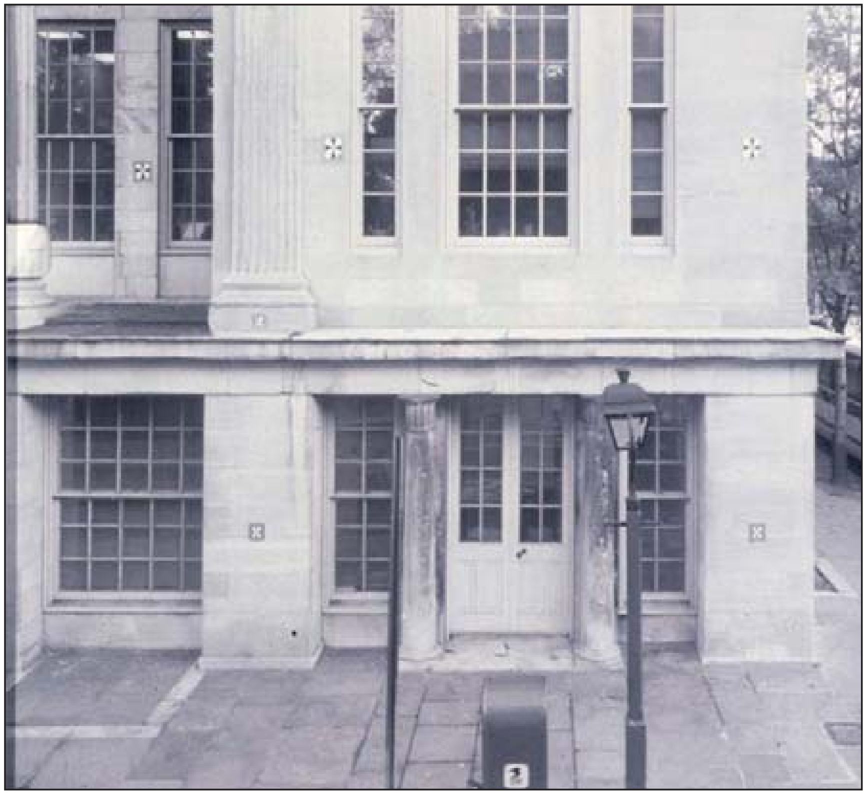

Figure 4.12:
West Elevation at south corner, columns 3 and 4
Source: INHP Archives
Date: October 30, 1958, W.A. McC.

Figure 4.13:
West Elevation, columns 3 and 4
Source: University of Pennsylvania
Date: Summer 2004

Figure 4.14:
West Elevation, columns 3 and 4
Source: INHP Architects' office
Creator: William Brookover
Date: March 3, 1984

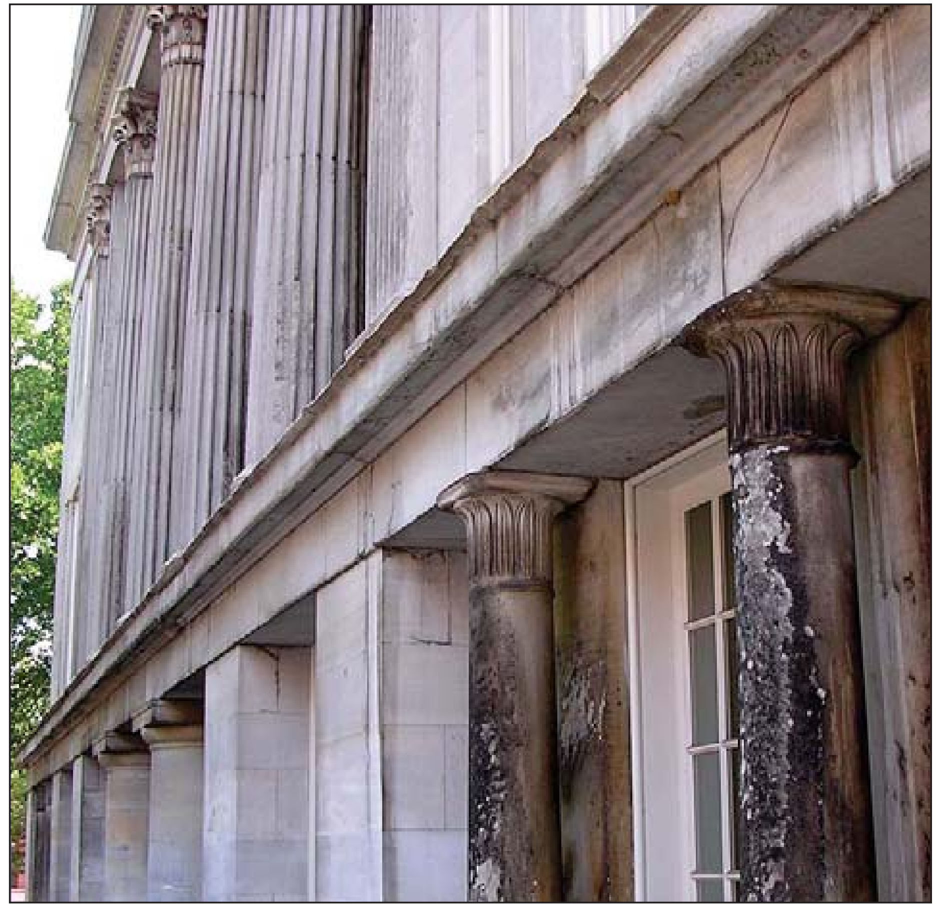

Figure 4.15:
West Elevation, columns 3 and 4
Source: University of Pennsylvania
Date: November 2004

Figure 4.16:
South Elevation, columns 4-10
Source: INHP Archives
Date: Unknown

Figure 4.17:
South Elevation, columns 9 and 10
Source: University of Pennsylvania
Date: Summer 2004

Figure 4.18:
South Elevation, columns 9 and 10
Source: INHP Archives
Caption: Merchants' Exchange marble deterioration
Creator: W. A. McCullough
Date: April 5, 1961

Figure 4.19:
South Elevation, columns 9 and 10
Source: University of Pennsylvania
Date: Summer 2004

Figure 4.20:
South Elevation, columns 7 and 8
Source: University of Pennsylvania
Date: Summer 2004

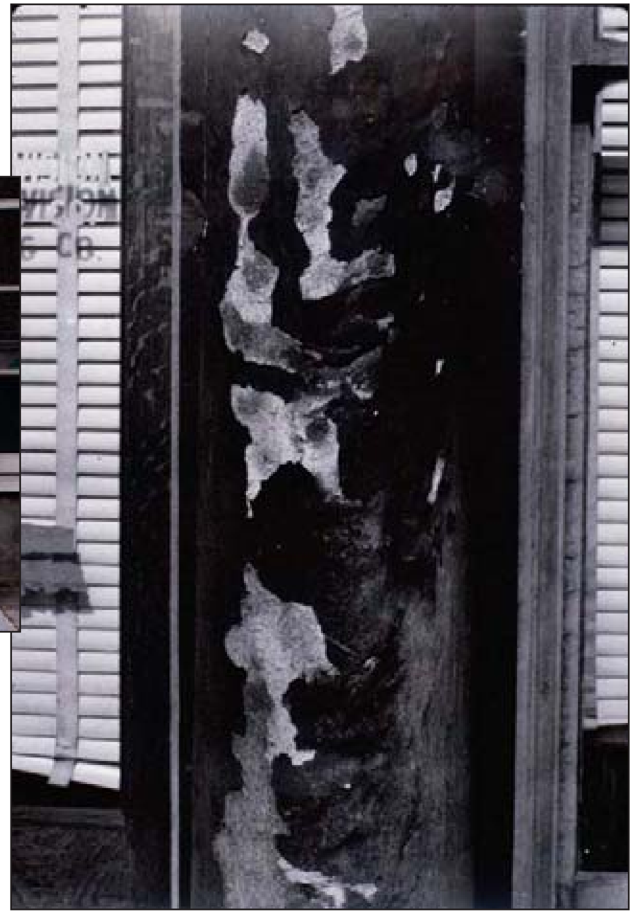

Figure 4.21:
South Elevation, second entrance from east,
detail of column 8
Source: INHP Archives
Date: March 20, 1952

Figure 4.22:
South Elevation, detail of column 8
Source: University of Pennsylvania
Date: Summer 2004

Figure 4.23:
North Elevation
Source: INHP Archives
Creator: C.E. Peterson
Date: April 19, 1960

Figure 4.24:
North Elevation, Columns 7-10
Source: INHP Archives
Creator: W. A. McCullough
Date: April 5, 1961

Figure 4.25:
North Elevation, columns 5-10
Source: INHP Archives
Date: December 2, 1953
Columns 5-6 was sandblasted, Column 7 was recarved

Figure 4.26:
North Elevation, columns 5-10
Source: University of Pennsylvania
Date: Summer 2004

Figure 4.27:
North Elevation, columns 7-8
Source: INHP Archives
Date:1983

Figure 4.28:
North Elevation, columns 7 and 8
Source: University of Pennsylvania
Date: Summer 2004

Figure 4.29:
North Elevation, columns 5 and 6
Source: University of Pennsylvania
Date: Summer 2004

Figure 4.30:
North Elevation, column 9
Source: INHP Archives, Historical Society of Philadelphia
Date: February 19, 1957

Figure 4.31:
North Elevation, column 9
Source: University of Pennsylvania
Date: Summer 2004

4.4.2 Conclusions

The examples discussed above allow us to draw some interesting conclusions which can be summarized in the following table.

Table 2. Semi-quantitative analysis of soiling and damage as determined from historic and current photographs. The number of years is computed from the last time the building was clean.

Façade	Columns	Date	Years	Soiling
W	#3 & 4	1958	24	+
W	#3 & 4	2004	39	+++
S	#9 & 10	1961	27	+++
S	#9 & 10	2004	39	++
S	#8	1952	18	+++
S	#8	2004	39	+
N	#7 & 8	1983	18	+
N	#7 & 8	2004	39	+
N	#9	1957	23	+++
N	#9	2004	39	+

It is evident that the closing of Dock street to traffic has diminished the rate of soiling (and pollution) that reaches the north façade. The heavy soiling that accumulated during the first 30 years of the building diminished significantly in the years after the cleaning. Thus, the soiling rate can be said to have decreased significantly.

The important contribution of vehicular traffic and in particular that driven by Diesel engines, can be seen on the west façade. There, soiling has increased considerably and that can be attributed to the increase of tour buses and regular traffic.

On the other hand, the south side, even though it continues to have traffic, shows a decrease in the rate of soiling. This is an unexpected result which could be explained by the shielding effect that the trees planted on that street have on that façade. These were probably planted around 1962 during the cleaning of the building and at the time Dock Street was closed and the cobblestones installed around the building. Changes in the neighborhood buildings, new construction or demolitions may have affected the local air flow on the south side of the building. For example the construction of a private residence on the southeast corner of Third and Walnut Streets has replaced a parking lot, which has lessened the impact of high gusts of south and southwest winds on the south elevation.

Figure 4.32: Merchants' Exchange, Northeast view, August 8, 1962. *From the INHP Archives.*

Figure 4.33: Merchants' Exchange, South elevation, 1963. *From the INHP Archives.*

4.5 Pre-Treatment Analyses

Additional analysis including X-Ray diffraction, scanning electron microscopy, and polarized light microscopy were conducted on small surface samples of columns on each elevation to determine the condition of the stone and the presence of other materials.

4.5.1 X-Ray Diffraction

The sample used for XRD was obtained from column four on the first floor of the west elevation of Merchants' Exchange building in Philadelphia, PA. It was a piece of a black encrusted flake of the column.

For XRD, a small amount of the sample was powdered using a mortar and pestle. The powder was then put onto a slide and evenly spread over the surface using a small amount of acetone. The sample was left to dry. Once dry, it was inserted into the diffractometer. Since the wave-lengths of X-Rays are in the same order as the distances between atoms in crystalline materials, these can act as diffraction gradings for X-Rays. Resulting patterns provide a means of identifying crystalline materials. The analyzed samples contained 82.3% calcium carbonate (calcite, $CaCO_3$) and 6.3% calcium sulfate dihydrate(gypsum, $CaSO_4.2H_2O$).

4.5.2 Scanning Electron Microscopy

Scanning electron microscopy was used as well to gather information about the morphology of the samples. Two samples from two elevations were examined: west elevation, column four and north elevation, column one.

The SEM photomicrographs from the sample obtained from west elevation, column four showed well formed gypsum crystals with some cubic crystals of sodium chloride. The surfaces of the calcite crystals showed etching with gypsum crystals forming on them. The photomicrographs from the sample obtained from north elevation, column nine showed interlocking gypsum crystals, soiling particles in between the calcite crystals and some biogrowth present. The presence of biogrowth on the north elevation can be attributed to the lower amounts of direct sunlight on this elevation.

4.5.3 Polarized Light Microscopy

Samples from the three columns selected for treatment (one from each elevation) were examined in thin section prior to the barium hydroxide application to determine the morphology of the stone and determine the extent of surface damage including the formation and location of gypsum crystals and micro-cracking, both of which contribute to stone disaggregation and flaking. One other sample was also examined in thin section from west elevation, column 2, to understand the extent of damage on the surface of one of the most deteriorated columns. The samples were obtained from small flakes detaching from the columns in soiled areas representative of the entire column. Samples were examined both stained with alizarin red stain for calcium carbonate and unstained under transmitted polarized light.

Both samples from the west elevation, from columns 2 and 4, had a layer of amorphous soiling on the external surface of the flake. Soiling also appeared on the internal surface of the flake and within the micro cracks of the flakes. Both samples displayed extensive microcracking and the calcite crystals on the external surface were extremely etched and eroded. The calcite grains are also loosely attached to one another which results in flaking and disaggregation and provides at a microscopic level pores for water and other foreign materials to dwell.

The sample obtained from north elevation, column nine showed much less soiling than that of the west elevation samples. This again can be attributed to the exposure of the columns. The west elevation columns are much more exposed to sulfur oxides and pollutant particles produced by traffic along the west elevation. Surface etching of the calcite crystals was also less prevalent on the north elevation. Extensive microcracking and loosely adhered calcite grains were also evident.

The sample obtained from south elevation, column 4 had heavy soiling as did the west elevation sample and exhibited grain boundary failure with loosely adhered calcite grains. However, the amount of surface etching was not as extensive as it was on the west façade. As explained, in the photographic comparison, the trees along the south may be acting a buffer from deposits of sulfur oxides settling on the stone surface.

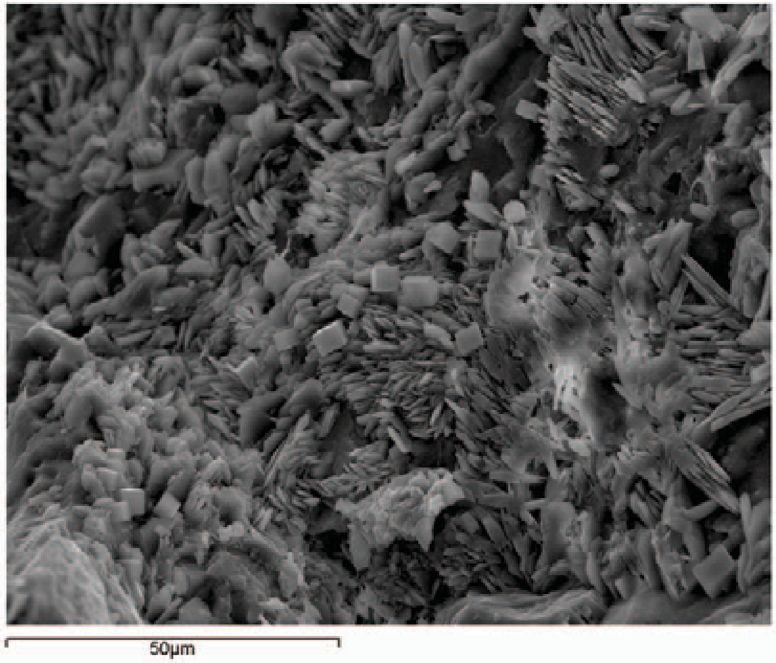

Figure 4.34:
Sample ID: W-4 Before Sample Location: West elevation, column 4
SEM Photomicrograph, 1000x, showing platey gypsum crystals and cubic halite crystals

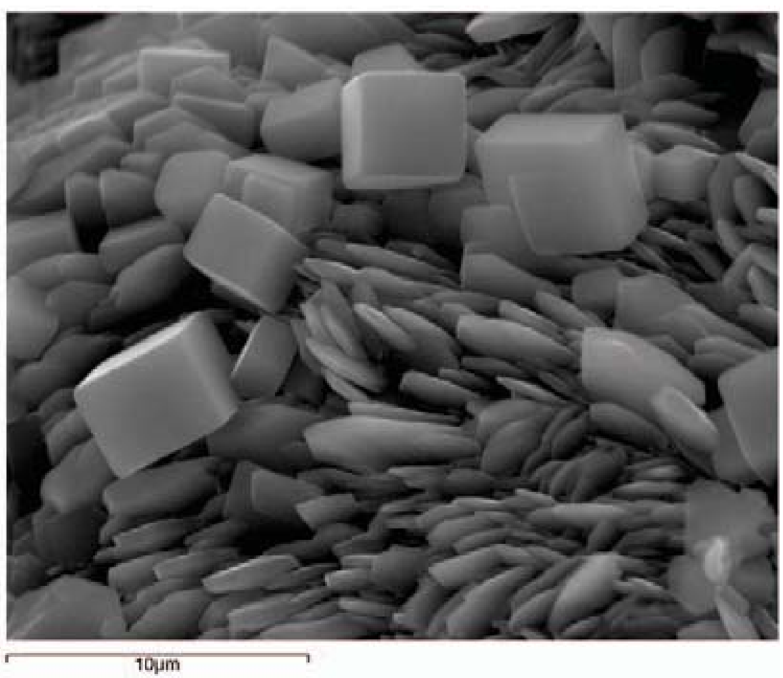

Figure 4.35:
Sample ID: W-4 Before Sample Location: West elevation, column 4
SEM Photomicrograph, 4500x, detail of the plately gypsum crystals and cubic halite crystals as seen in Figure 4.35

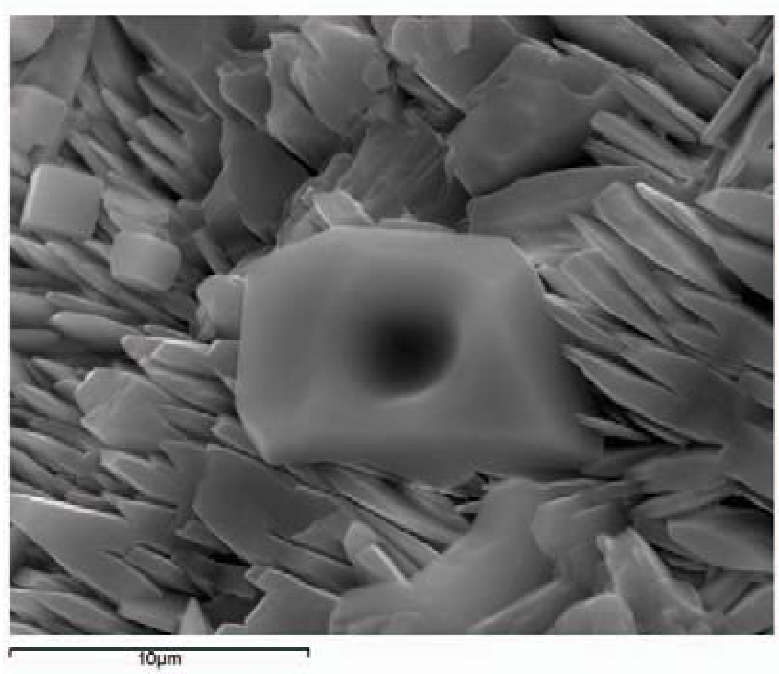

Figure 4.36:
Sample ID: W-4 Before Sample Location: West elevation, column 4
SEM Photomicrograph, 5000x, dissolution and recrystalization of salts are evident from the rounded shape in the center of the cubic halite crystal

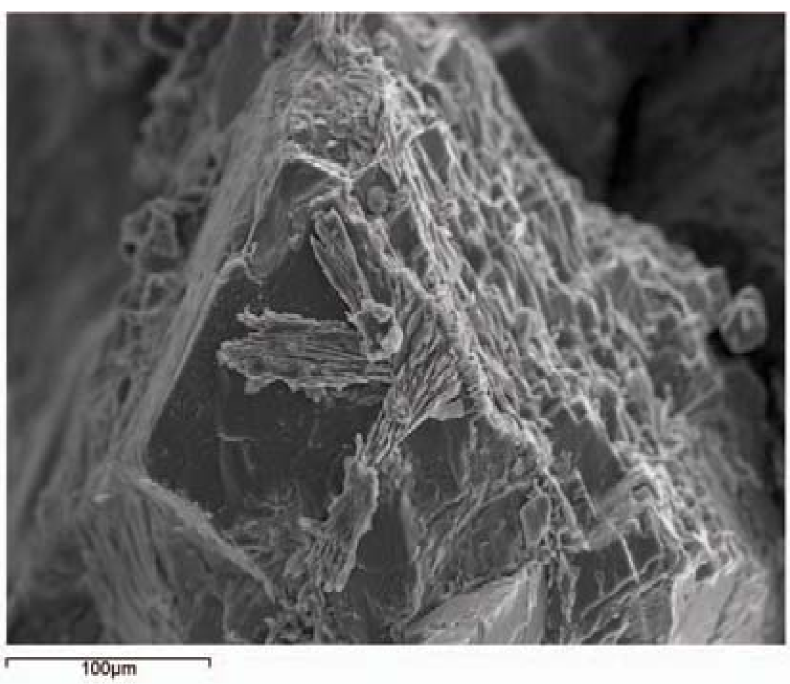

Figure 4.37:
Sample ID: W-4 Before Sample Location: West elevation, column 4
SEM Photomicrograph, 300x, low magnification photomicrograph showing the gypsum crystal growth of the surface of the marble calcite crystal

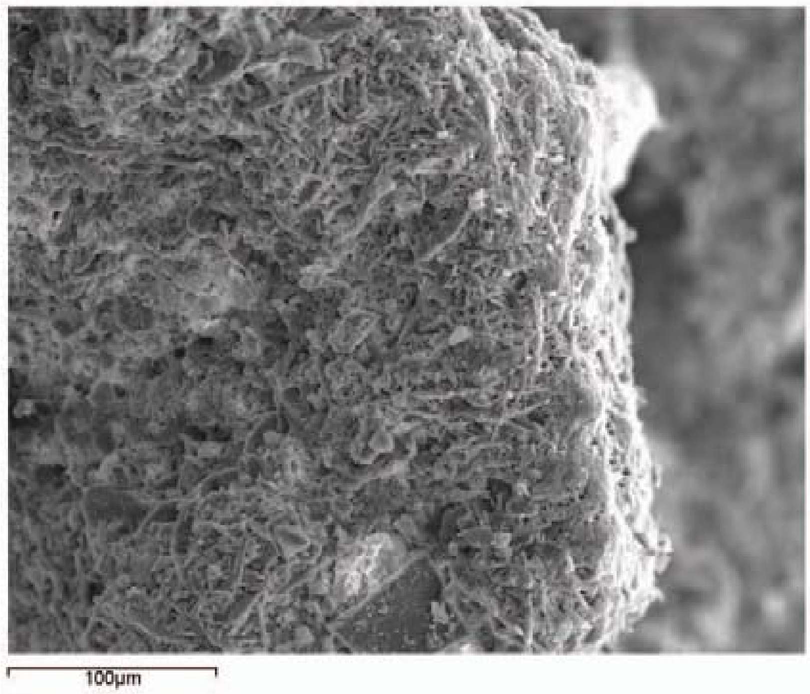

Figure 4.38:
Sample ID: N-9 Before Sample Location: North elevation, column 9
SEM Photomicrograph, 300x, low magnification photomicrograph showing external black crust attached to the underlying stone

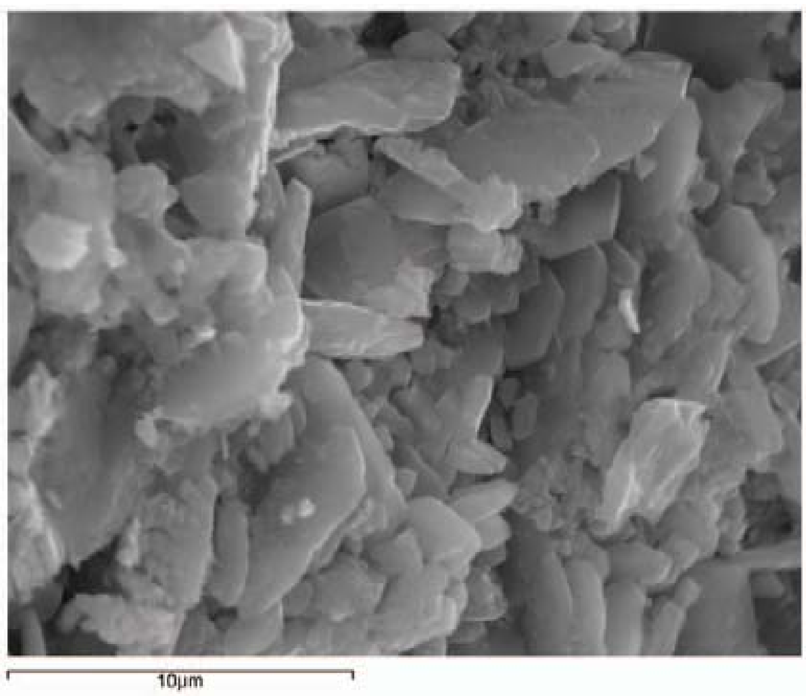

Figure 4.39:
Sample ID: N-9 Before Sample Location: North elevation, column 9
SEM Photomicrograph, 5000x, detail of the external black crust showing gypsum crystals and amorphous particles

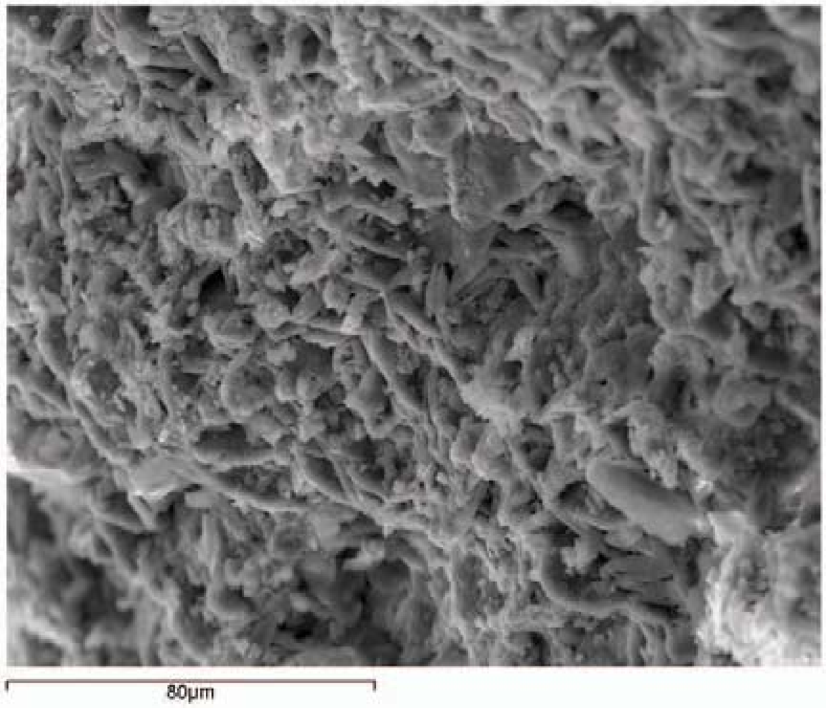

Figure 4.40:
Sample ID: N-9 Before Sample Location: North elevation, column 9
SEM Photomicrograph, 650x, another view of the external black crust on the surface of the stone

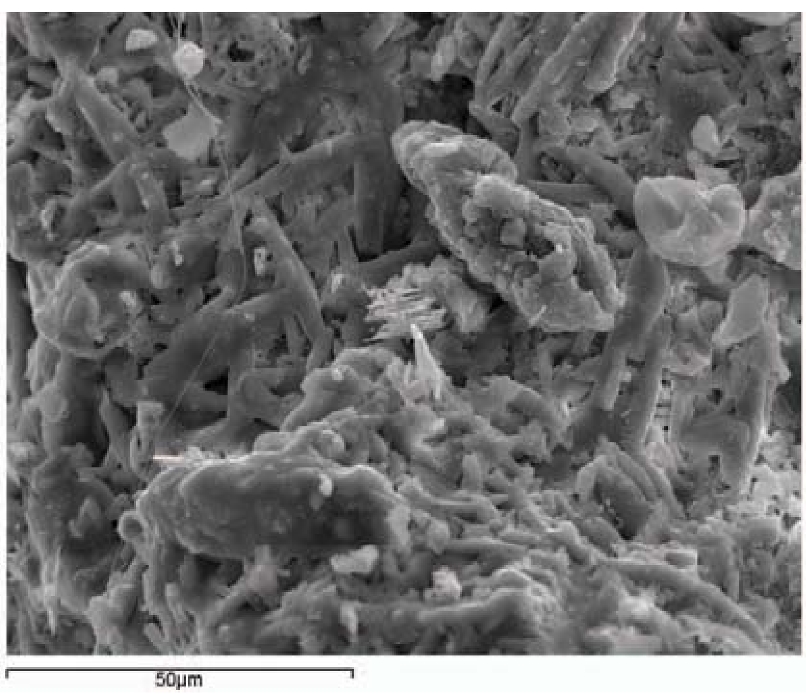

Figure 4.41:
Sample ID: N-9 Before Sample Location: North elevation, column 9
SEM Photomicrograph, 1000x, detail of the surface black crust as seen in Figure 4.40

PLM Pre-treatment Analysis:
PLM Photomicrographs
Nikon Optiphot 2-POL
Sample ID: W-2
Sample Location: West elevation, column 2
Comments: note the dark crust on the external surface of the stone (top) and microcracking near the surface of the stone

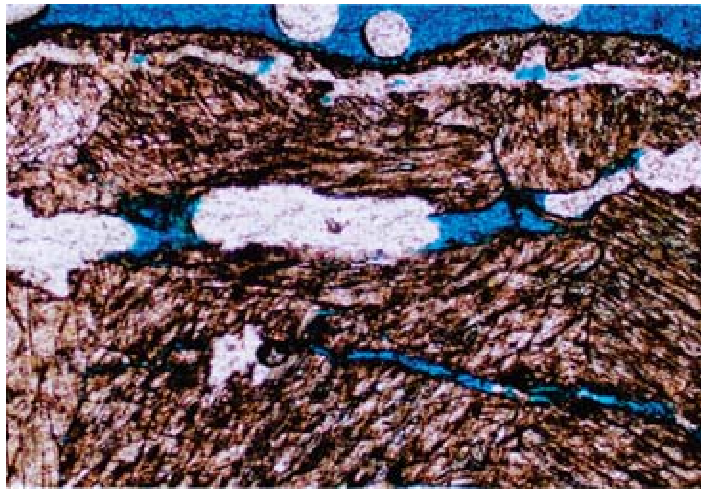

Figure 4.42: Plane Polarized Light, 10x

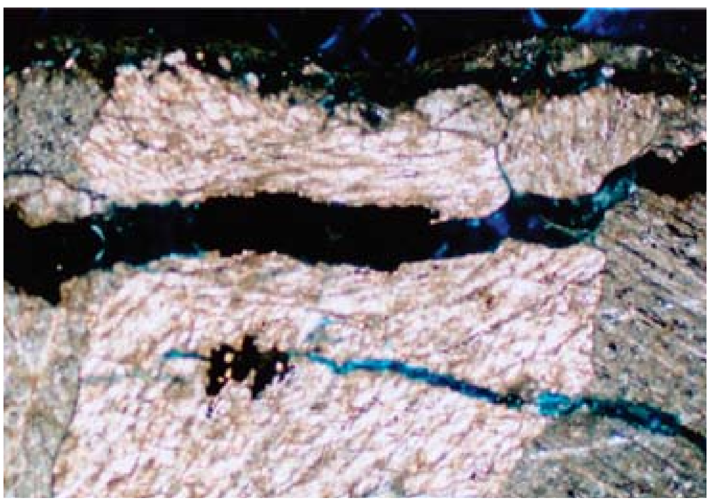

Figure 4.43: Cross Polarized Light, 10x

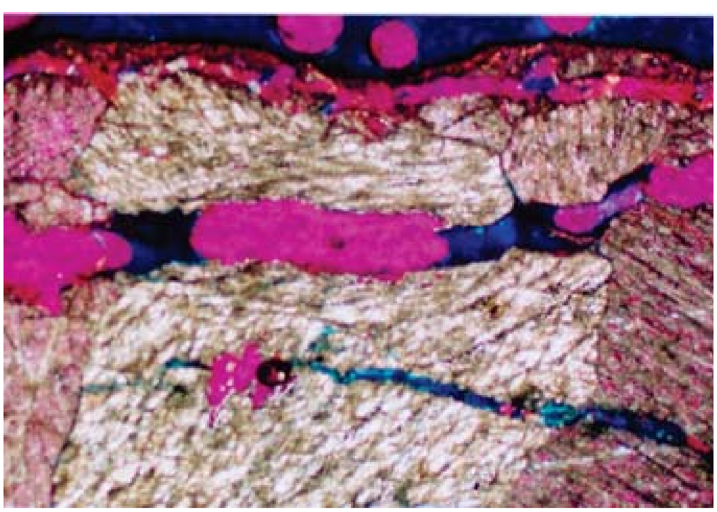

Figure 4.44: Cross Polarized Light, 10x

PLM Pre-treatment Analysis:
PLM Photomicrographs
Nikon Optiphot 2-POL
Sample ID: W-2
Sample Location: West elevation, column 2
Comments: note the dark crust on the external surface of the stone (top) and microcracking near the surface of the stone
(sample is stained with red alizarin stain for calcium carbonate)

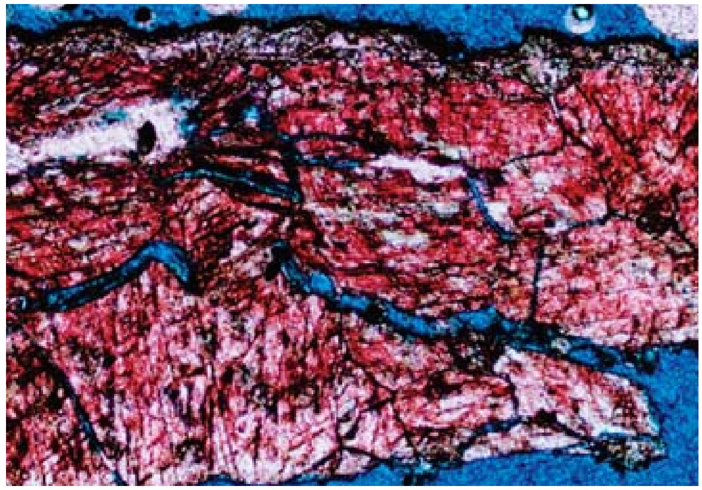

Figure 4.45: Plane Polarized Light Microscope, 10x

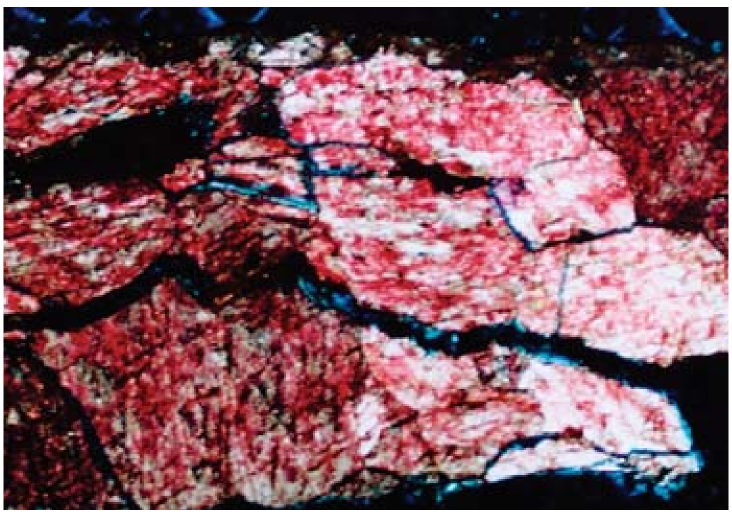

Figure 4.46: Cross Polarized Light, 10x

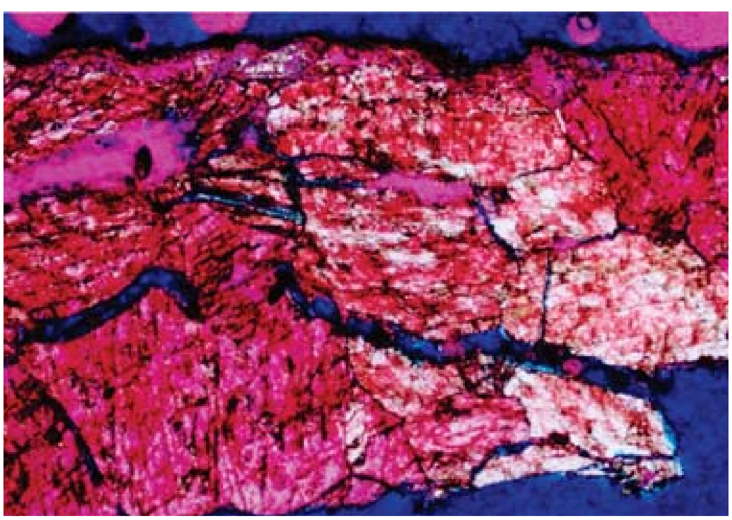

Figure 4.47: Cross Polarized Light, 10x

PLM Pre-treatment Analysis:
PLM Photomicrographs
Nikon Optiphot 2-POL
Sample ID: W-4 Before
Sample Location: West elevation, column 4
Comments: note the thick black surface crust on the external surface (top) and detached grain boundaries
(sample is stained with red alizarin stain for calcium carbonate)

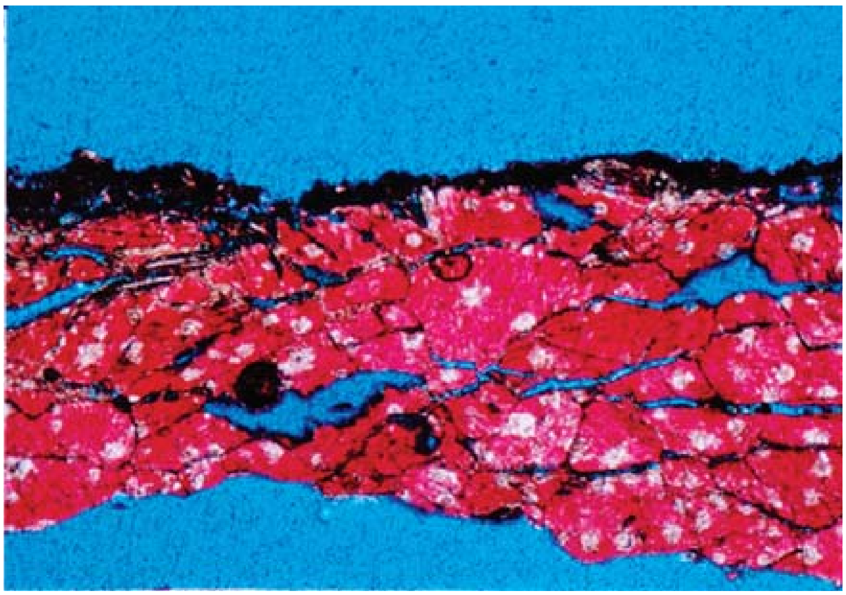

Figure 4.48: Plane Polarized Light, 5x

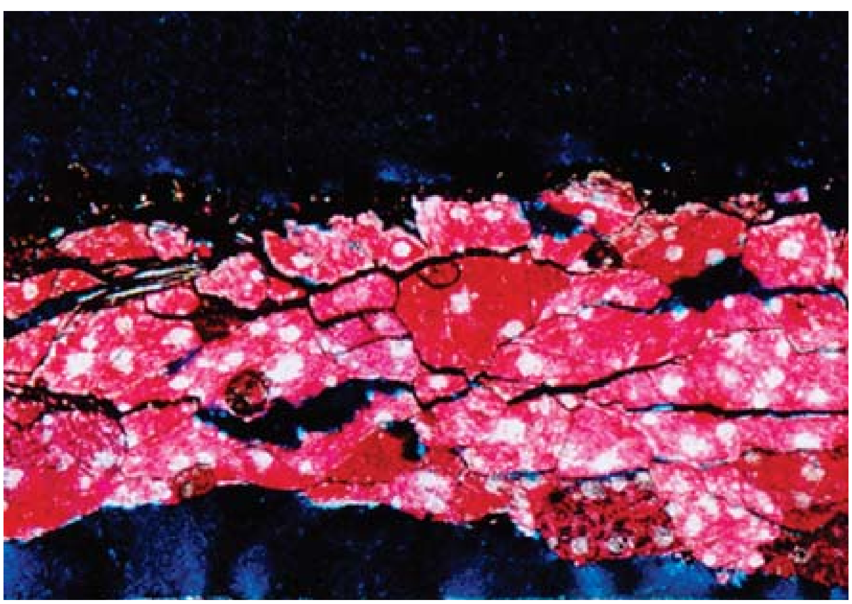

Figure 4.49: Cross Polarized Light, 5x

PLM Pre-treatment Analysis:
PLM Photomicrographs
Nikon Optiphot 2-POL
Sample ID: W-4 Before
Sample Location: West elevation, column 4
Comments: note the surface etching and black crust on the external surface of the stone (top). the sample also shows grain boundary detachments and microcracking

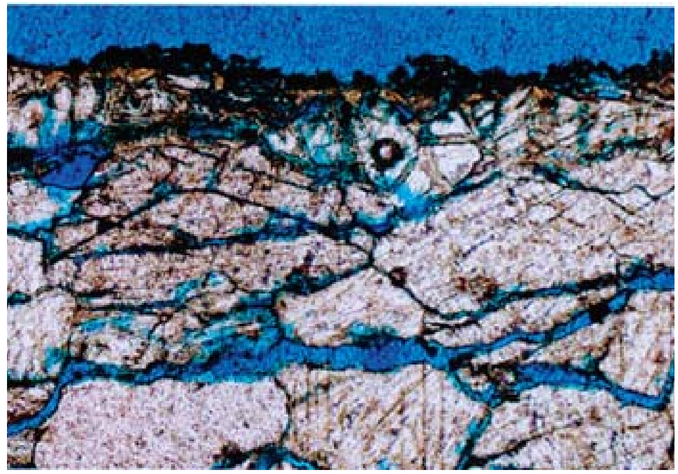

Figure 4.50: Plane Polarized Light, 10x

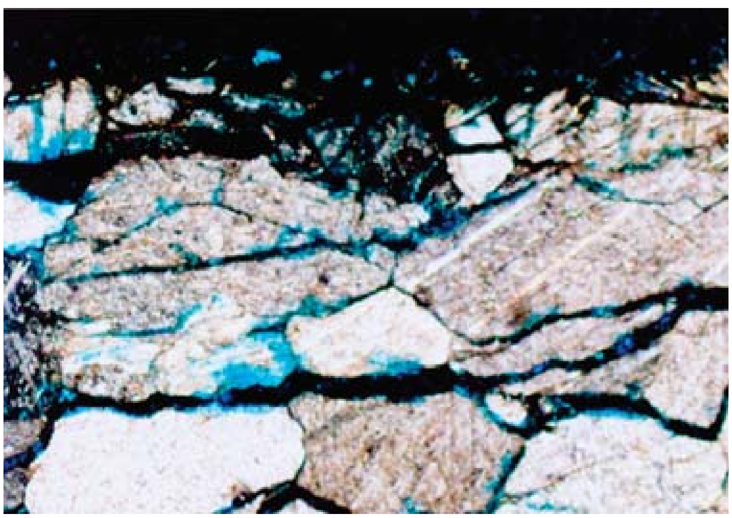

Figure 4.51: Cross Polarized Light, 10x

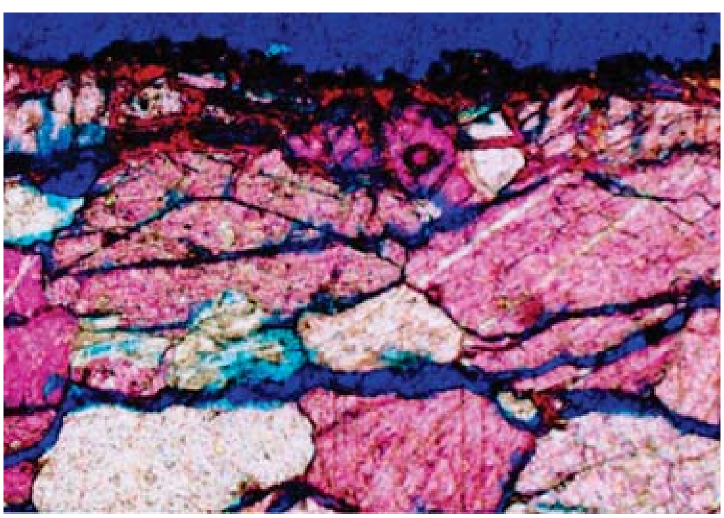

Figure 4.52: Cross Polarized Light, 10x

PLM Pre-treatment Analysis:
PLM Photomicrographs
Nikon Optiphot 2-POL
Sample ID: N-9 Before
Sample Location: North elevation, column 9
Comments: note the sample exhibits less black surface crust than the west and south column samples. also note the microcracking and surface etching (top) external surface of the stone sample

Figure 4.53: Plane Polarized Light, 10x

Figure 4.54: Cross Polarized Light, 10x

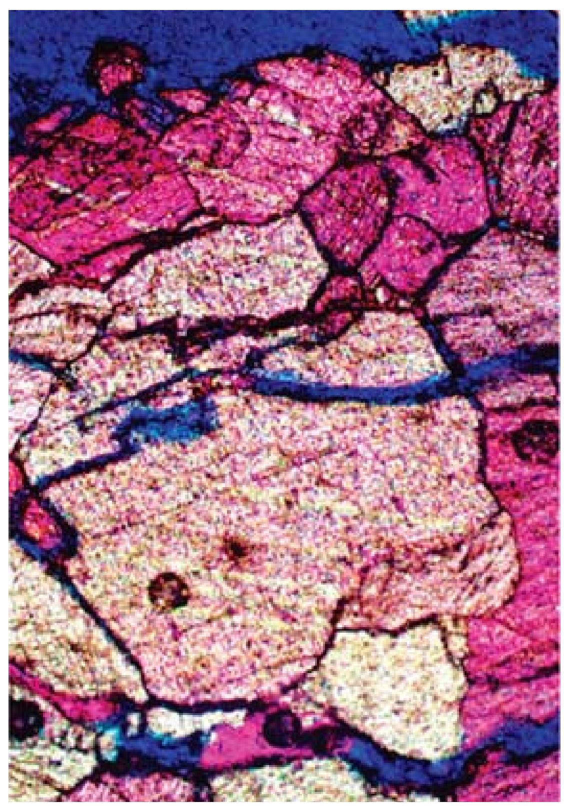

Figure 4.55: Cross Polarized Light, 10x

PLM Pre-treatment Analysis:
PLM Photomicrographs
Nikon Optiphot 2-POL
Sample ID: N-9 Before
Sample Location: North elevation, column 9
Comments: same sample as above shown under lower magnification; note the grain boundary detachment and microcracking; also note the less soiled surface than seen on the west and south elevation column samples

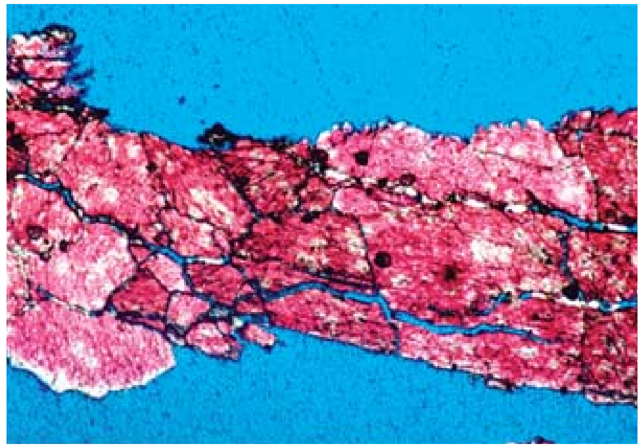

Figure 4.56: Plane Polarized Light, 5x

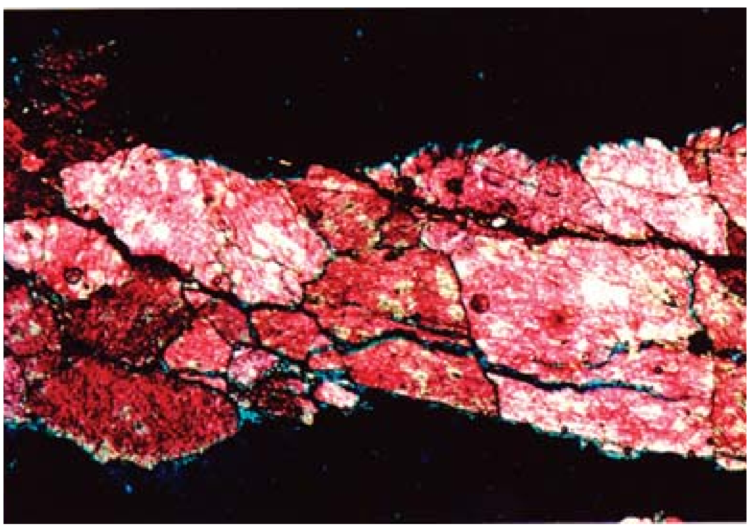

Figure 4.57: Cross Polarized Light, 5x

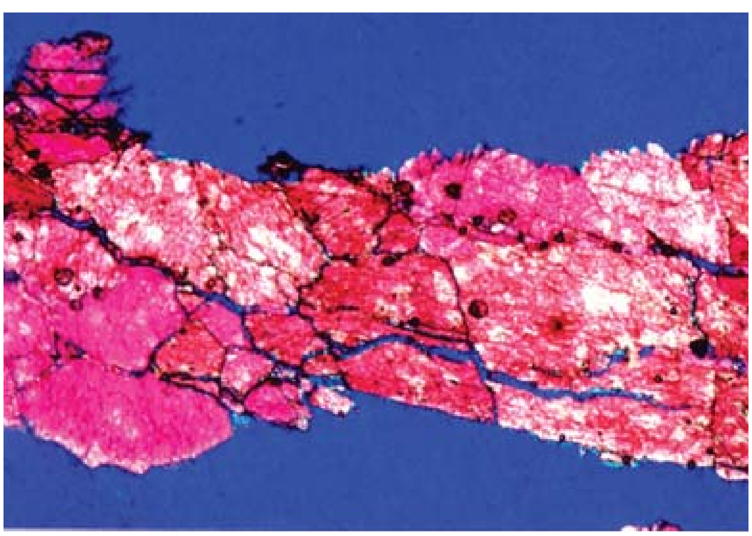

Figure 4.58: Cross Polarized Light, 5x

PLM Pre-treatment Analysis:
PLM Photomicrographs
Nikon Optiphot 2-POL
Sample ID: S-4 Before
Sample Location: South elevation, column 4
Comments: note the thin black surface crust on the external surface of the stone (top); severe grain boundary detachment

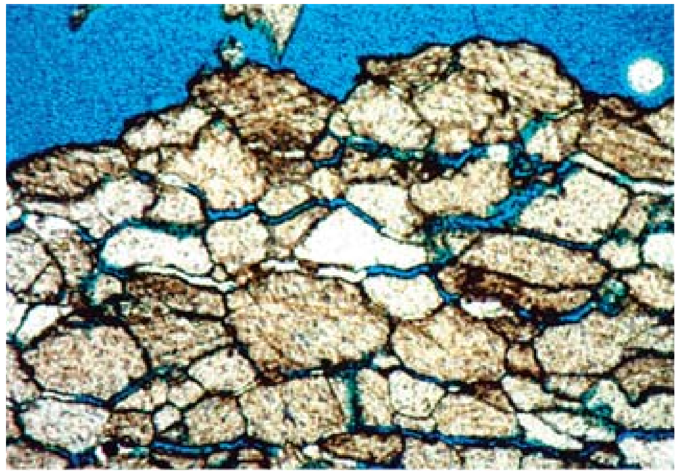

Figure 4.59: Plane Polarized Light Microscope, 5x

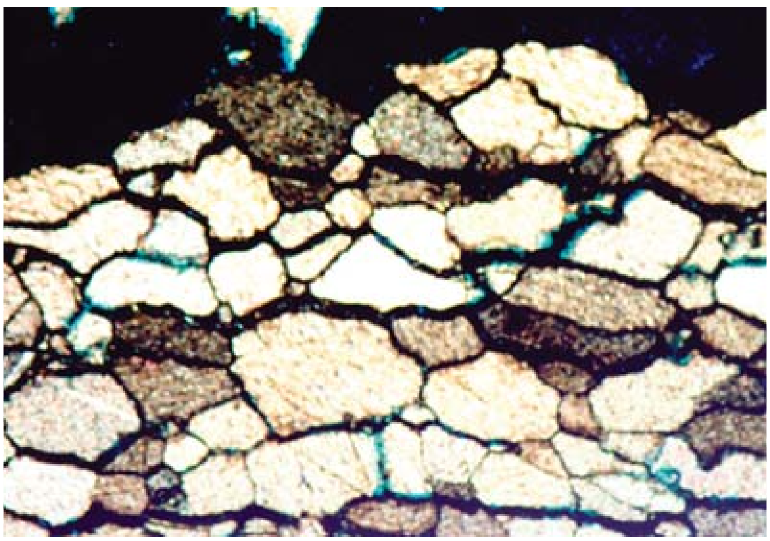

Figure 4.60: Cross Polarized Light , 5x

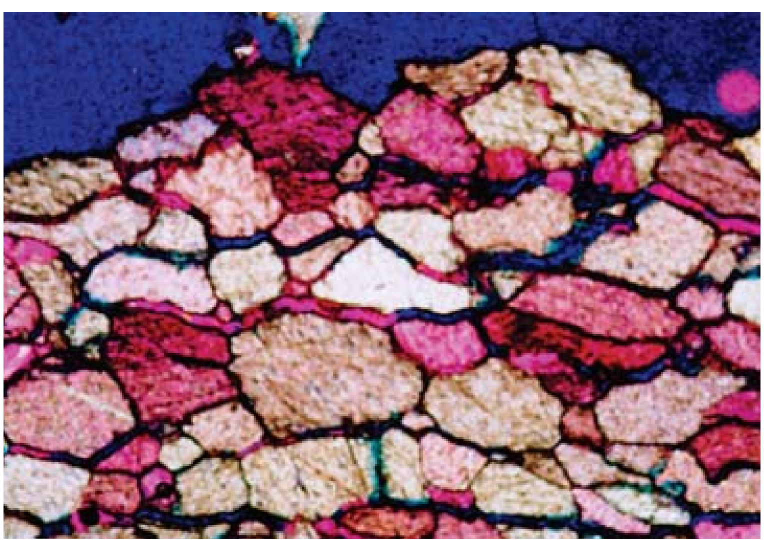

Figure 4.61: Cross Polarized Light, 5x

[1]See Appendix A: Conditions Glossary. University of Pennsylvania, Architectural Conservation Laboratory.
[2] NOAA Website, (http://www.erh.noaa.gov/phi/climate/phlclimate.html) Climate Data for Philadelphia, Pennsylvania.
[3] NOAA Website, (http://ols.nndc.noaa.gov/plolstore/plsql/olstore.prodspecific?prodnum=C00095-PUB-A0001#TABLES). The normal precipitation is the arithmetic mean for each month over the thirty year period, and includes the liquid water equivalent of snowfall.
[4] NOAA Website, (http://www.erh.noaa.gov/phi/climate/phlclimate.html) Climate Data for Philadelphia, Pennsylvania.
[5] NOAA Website, (http://www.erh.noaa.gov/phi/climate/phlclimate.html) Climate Data for Philadelphia, Pennsylvania.
[6] See Appendix B for conditions drawings.
[7] Lewin, S.Z. "Conservation of the Facades of Historic Buildings at Independence National Historic Park-Final Report." *NPS Contract 4000-1-0055.* INHP Archives: Philadelphia, PA. 1984. 29..
[8] Lewin, 29 and 36. This type of stone decay is observed in most of the Pennsylvania blue marble, for this stone owes its coloration to the presence of the foreign (micaceous) mineral inclusions. However, it is relatively minor where the mica grains are well dispersed in the marble matrix, and it is more pronounced, the more concentrated the mica is in veins and strata. Thus, the specific stone blocks originally selected for several of the ground level columns of the Merchants' Exchange are particularly susceptible to this decay process because of their special veining.
[9] See Appendix F: Assigned Numerical Values for Ranges of Calculated Area

CHAPTER 5: STONE CONSERVATION

5.1 Barium Hydroxide Treatment

Barium hydroxide is considered an inorganic consolidant. As noted in a recent review paper, inorganic consolidants in the past have not been well represented in literature, "despite their past use and potential usefulness."[1] The application of barium compounds such as barium hydroxide rely on chemical reactions, wherein "a material is precipitated from solution, some minerals are dissolved and others are precipitated in their place."[2]

Treatments using barium hydroxide have been given preference because of its ability to convert calcium sulfate dihydrate into a very insoluble salt, barium sulfate. [3] The application of barium hydroxide on gypsum encrusted stone results in its transformation into barium sulfate as expressed by the following reaction:

$$Ba(OH)_2 + CaSO_{4.}2H_2O \rightarrow BaS0_4 + Ca(OH)_2 + 2H_2O.$$

The calcium hydroxide obtained from this reaction will react with atmospheric carbon dioxide (CO_2), carbonating into calcium carbonate, expressed by the following reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3.$$ [4]

However, such treatments involve complex methodologies, not just simple chemical reactions. [5]

Barium hydroxide treatments have been used for their consolidating properties on carbonate materials since the second half of the 19th century.[6] According to Amoroso and Fassina, "they were particularly important in cases which involved transformation of calcium sulfate to insoluble sulfates, which are more resistant both to atmospheric erosion and being washed out by water."[7]

The earliest reference to the use of a barium compounds as consolidants appear in 1861, and correspond to Jesse Rust. Rust's process included the use of barium hydroxide and a fluorosilicic acid treatment, which was never patented. Around the same time J.C. Combe and J. Wright patented a similar fluorosilicic acid and baryta or lime water treatment.[8] The first barium-hydroxide treatment patented for stone was on January 28th, 1862 by Arthur Herbert Church for:

> Improvements in the Means of Preserving Stone, Brick, Slate Wood, Cement, Stucco, Plaster, Whitewash, and Colourwash form the Injurious Action of Atmospheric and other influences; also in the Application of Colours to the Surfaces of Stone, Brick, Slate, Wood Cement, Stucco, Mortar, Clay, Plaster of Paris, Plaster, Whitewash and Colourwash, and the Retention of such Colours thereon.[9]

Church's method was used in 1904 on calcareous sandstone. In the *Journal of the Society of Chemical Industry 23*, it was reported that:

> the remedy applied, consisted in repeated treatment of stone with a saturated aqueous solution of barium hydroxide, by means of a White's pneumatic diffuser, after cleansing the surface from dust by an air jet, applied for instance by a Fletcher foot-blower. The liquid penetrated the decayed stone for depth of several inches, but did not, until after several successive applications, form an impervious crust on the surface… The chemistry of the process consists in the conversion of the gypsum in the decayed stone into Barium sulfate, with the simultaneous production of calcium hydroxide, which, gradually absorbing carbon dioxide, reconstitutes calcium carbonate.[10]

The application described is different from the one patented, and is limited to the use on gypsum encrusted stone. This treatment was applied to the bays of the Chapter house of Westminster Abbey with successful results.[11] It was also used at a bell tower in Chichester, England and the five bays of the front elevation of Mercer's Hall in Cheapside, England.[12]

Other historical consolidation treatments using barium hydroxide or similar compounds are also documented, such as Frederick Ransome's treatment, which was patented in 1868. Ransome's treatment entailed applying a solution of baryta or similar substances and a solution of silica, primarily alkaline silicates.[13] However, there are no records of the implementation of this treatment.[14] Maximilian Dennstedt developed a barium hydroxide treatment which was patented October 17th, 1884, however, the treatment patented was impractical to the application on building stones.[15] These other treatments also did not acknowledge the application of these treatments to sulfated carbonate rocks.

"Although barium treatments for stone consolidation were sharply criticized in the early twentieth century, experimentation with barium compounds as consolidants persisted."[16] The resurgence of interest in the barium hydroxide treatment came during a presentation by Seymour Lewin at the *Conference on the Weathering of Stones in Brussels* on "The Conservation of Limestone Objects and Structures."[17] The treatment developed was modeled on Church's barium hydroxide treatment. "The fundamental difference between the two treatments is that Church's goal was reclamation of the calcium from gypsum by the formation of insoluble barium sulfate."[18] Lewin's process was aimed at the consolidation of stone through the deposition of barium carbonate, which would also "serve a protective function by decomposing to an insoluble salt, rather than to gypsum."[19]

The treatment patented by Lewin for the use on stone is similar to the historic treatment of frescoes using ammonium carbonate and barium hydroxide.[20] The Opificio delle Pietre Dure in Italy has used this process to conserve mural paintings. The frescoes on which it was experimented had been seriously damaged by sulfation. This methodology or "Florentine method" was developed particularly to address such problems.[21]

The treatment used is based on a two part system. The first entails cleaning using an ammonium carbonate poultice. The application of ammonium carbonate converts the gypsum (calcium sulfate dihydrate) into soluble ammonium sulfate:

$$CaSO_4.2H_2O + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O.$$[22]

The excess ammonium carbonate then decomposes and leaves the plaster within a few months:

$$(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O.$$

This treatment is then followed by the application of barium hydroxide, where the ammonium sulfate is definitively converted to the insoluble and inert salt, barium sulfate, thus preventing any further damage as shown by the following reaction:

$$(NH_4)_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2NH_3 + 2H_2O.$$[23]

Two consolidating mechanisms then occur. The carbonation of barium hydroxide

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

which "reestablishes micro-cohesion of the surface through the build up of a compact crystalline texture."[24] And also through the "reaction of barium hydroxide with calcium carbonate to produce barium carbonate and calcium hydroxide the latter then converting upon carbonation to calcium carbonate:"

$$Ba(OH)_2 + CaCO_3 \leftrightarrow BaCO_3 + Ca(OH)_2.$$[25]

As summarized in "A review of selected inorganic consolidants and protective treatments for porous calcareous materials," this action does not prevent the new sulfation caused by the dry deposition of SO_2 and the formation of gypsum. However, the surface-paint layer exhibits lower porosity and reduced roughness due to the formation of both barium carbonate and barium sulfate."[26] The reduced surface area would then reduce exposure to environmental pollutants causing sulfation.[27]

At the end of the 1960's, Professor Enzo Ferroni of the University of Firenze with the help of Professor Dino Dini, proposed and used a barium hydroxide treatment on frescoes damaged during the flood in 1966, which were strongly affected by the presence of gypsum. This included the treatment of "the splendid frescoes by Beato Angelico at San Marco in Florence (and particularly the well-known Crucifixion in the Chapter-hall), were taken into special account. Small, more or less evident flaking of the pictorial film appeared on the entire smooth and compact frescoed surface, together with small craters evidently formed as a final effect of this progressive flaking process."[28] The conservation treatment was aimed at the possibility of "retransforming" the gypsum into calcium carbonate.[29] The transformation would be possible through the application of ammonium carbonate. However, when ammonium carbonate is applied to calcium sulfate, the double exchange reaction causes the formation of ammonium sulfate through the following reaction:

$$CaSO_4 + (NH)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4.$$

This avoids leaving traces of ammonium carbonate, which could possibly lead to blooming thus altering the appearance of the fresco.

"It was therefore proposed to perform a second operation utilizing $Ba(OH)_2$, which is capable to block and turn the ammonium sulfate, which is both soluble and diffusible, into barium sulfate, which is both insoluble and inert. In order to ensure the physical cohesion of the system it was necessary to overcome the stoichiometric conditions, using concentrated solutions of $Ba(OH)_2$, well aware that an excess of this compound in the 'intonaco' would turn into barium carbonate, under the action of carbon dioxide present in the atmosphere."[30]

Many other frescoes besides Angelico's Crucifixion as mentioned above, were treated using the same conservation methods. They include Sogliani and Fra'Angelico's "decoration of all the cells only to remain in San Marco."[31] "The consolidation power of barium hydroxide was only subsequently recognized."[32]

In 1981, the findings of Ferroni and Dini in the treatment of frescoes along with their knowledge of the damage resulting from gypsum formation in marbles led to the experimentation of the treatment for stone as described for frescoes. The treatment again was concentrated on the retransformation of gypsum into calcium carbonate. The treatments were executed on marble statues at the Museum of San Marco in Florence, Italy and exhibited "very effective and encouraging results."[33]

Edward Sayre also discussed the use of a similar type of treatment for stone, based on its use on sulfated Italian frescoes. The method was based on the precipitation of barium sulfate from a homogeneous solution of barium ethyl sulfate and barium hydroxide within porous stones:

$$Ba(C_2H_5SO_4)_2 + Ba(OH)_2 \rightarrow 2C_2H_5OH + 2BaSO_4.$$

The ethanol produced will evaporate.[34] "Sayre's process is also derived from Arthur Church's, in that one desired result is conversion of calcium sulfate."[35] "Unlike Church, however, Sayre realized that treatment with barium hydroxide alone would have no binding effect, because 'barium and sulfate ions in solution react together almost instantaneously and precipitate as a finely divided powder'."[36] Because of this, the sulfate conversion is not sufficient to induce cohesive properties. Sayre discovered that the slow precipitation of barium sulfate resulted in the growth of well developed crystals which contributes to cohesion and also "tends to cover the chemically reactive carbonate particles with a protective inert coating."[37] The process developed by Sayre involved the facing of the surface of the fresco with paper followed by a poultice, keeping it moist with the barium ethyl sulfate-barium hydroxide solution for an extended period of time "in order for the reaction between the two materials to go to completion."[38]

According to Lewin's method, which was used primarily for consolidation, barium hydroxide could be used as a stabilization treatment for gypsum. The treatment was last patented with modifications for *in situ* treatment in 1971.[39] Lewin's barium hydroxide is used either by immersion or poulticing with a 25% w/v monohydrate in a solution of 25% v/v glycerin and 75% v/v water. If gypsum is present, barium hydroxide will combine with the calcium sulfate dihydrate, transforming the gypsum crusts into barium sulfate.

Reaction:

$$CaSO_4.2H_2O + Ba(OH)_2 + CO_2 \rightarrow BaSO_4\downarrow + CaCO_3\downarrow + 3H_2O.$$

If consolidation is required, then 10% w/v urea can be added prior to the application, which can be described by the following reactions:

$$CO(NH_2)_2 \text{ (urea)} + H_2O \rightarrow CO_2 + 2\ NH_3\uparrow,$$

followed by

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3.$$

The final product of barium carbonate is stable even when sulfur dioxide or sulfuric acid is introduced to the stone by the following reaction:

$$BaCO_3 + SO_3 + H_2O \text{ (air pollution) } \rightarrow BaSO_4 + CO_2.$$

Amoroso and Fassina stated that "Lewin modified the techniques so that the barium hydroxide solution he used remained in contact with the surface to be consolidated for a longer time. The product used for treatment consisted of barium hydroxide, urea and glycerin, and it produced good results on certain marbles and calcite limestones…"[40] Amoroso and Fassina also describe additives that can be added to the solution of barium hydroxide for application, such as the addition of glycerin. "Glycerin has a secondary role and prevents the formation of barium hydroxide crystals in the solution, whereas the urea facilitates deep penetration of the hydroxide and regulates pH and constitutes a source of carbon dioxide. The CO_2 produced by the hydrolysis of urea serves to consolidate the interior of the stone."[41]

In the early 1980's, Seymour Lewin was hired to develop a conservation study and treatment strategy for the Facades of the Historic Buildings in Independence National Park. The Merchants' Exchange Building was addressed as a part of this conservation study. The aim of the report was

> to develop and test in situ procedures for removing deleterious resinous substances from these facades; develop and test in situ the most appropriate technique for the consolidation and preservation of the marble surfaces; carry out periodic sampling and analyses of the test areas during a one year period of natural weathering to assess the efficiency and safety of the techniques employed; and to devise and recommend protocol for a large-scale preservative treatment of the three facades.[42]

Lewin used this opportunity "to evaluate the effectiveness of the barium hydroxide-urea technique for consolidating the friable weathered surface and preserving the stone against renewed attack by air pollutants."[43]

After cleaning was completed, the lower half of the ground floor column identified as south column was selected for testing. "A solution containing 20% barium monohydrate + 5% urea in a vehicle consisting of 20% glycerol + 80% water was worked into the surface by brush."[44] The application was repeated three times over a 48 hour period. "There was an 8-hour interval between the first and second brushings; and 40 hours was allowed to elapse between the second and third applications. This was for the purpose of allowing sufficient time for capillarity to draw the solution deeply into the interior intergranular channels of the stone."[45] The impregnated surface was covered in plastic for a two week period to prevent rain water washing of the chemically treated stone surface.[46]

The treated areas were examined at intervals during an eighteen month period. According to Lewin, these examinations showed "no evidence of any new decay and analyses of the surface show no gypsum formation. The treated surface, which had been friable prior to the application of the barium-hydroxide urea, had become consolidated after it, and remains, consolidated."[47] Although consolidated the "hardness is not much different from that of the untreated, aged but not decaying surfaces."[48] The barium hydroxide treatment binds the loose calcite grains of the marble back together while keeping the intergranular pores open for water vapor transmission and so that any moisture or salts in the pores are not trapped within the stone, behind the treated surface. Because of this effect the surface of the stone is not made harder than that of a "similarly porous, textured surface that is not undergoing progressive environmental attack."[49]

One of the most recent evaluations of Lewin's treatments was conducted in 1988, at Columbia University, by L. Schnabell.[50] The purpose of the analysis was to determine the depth of deposition of the barium compounds, to characterize the barium compounds deposited, and to determine the preliminary effectiveness of the treatment in consolidating the stone, as estimated by formation of bridges between adjacent grains.[51] It was concluded that it was not an effective treatment for consolidating marbles when applied by capillarity *in situ*. Schnabell described the distribution of barium carbonate deposits as being uneven. There was also little evidence that the barium carbonate deposits bridged intergranular spaces in the weathered marble. She also concludes that the potential for consolidation of limestone may be somewhat greater, depending upon the characteristics of the stone. The addition of urea to the barium hydroxide solution did not significantly alter the end result of the treatment.

Further studies or reports on case studies can be found elsewhere.[52] There are several reasons why these barium compounds are considered desirable as stone consolidants. They are highly durable and compatible with the substrate, satisfying these two very important conditions. They also minimally affect appearance; preserve and restore the original hydrophilic properties; are compatible with other consolidants and effectively transform gypsum, indirectly providing protection.[53] Another advantage is that barium hydroxide treatments are environmentally safe because they rely on “water-based systems, rather than organic solvents.”[54] The lack of current research and experimentation concerning the application of barium hydroxide as a stabilization treatment leads to the belief that this subject should be revisited as a viable treatment for gypsum encrusted stone.

5.2 Development and application of treatment

With stone surface conditions as seen on the columns, a consolidant would be preferable, however, the presence of soluble salts, such as gypsum, interferes with any consolidation attempt. Since extraction of the slightly soluble salt would result in a significant surface loss -presently the surface is held together by the growth of gypsum crystals- a possible solution is to immobilize this salt by turning it into an insoluble compound. This can be in principle easily achieved by the use of the barium hydroxide resulting in the formation of the extremely insoluble barium sulfate. Given its insolubility, this salt will not recrystallize over time thus reducing the damage resulting from soluble salt recrystallization.

There are several advantages to the use of barium hydroxide. While the application of barium hydroxide is not reversible, it results in the formation of an innocuous compound which will not stain or change the color of the marble, nor decompose over time (being a stable inorganic material). Moreover, it will not interfere with any possible future conservation treatment, be it cleaning or consolidation. It will stabilize the sulfates present in the stone preventing their recrystallization and the damage caused by this mechanism. However, it will not prevent new sulfur dioxide from depositing on the stone, reacting with the calcium carbonate forming more gypsum.

Furthermore, the treatment may have a slightly consolidating effect which may stabilize the stone surface and reduce stone loss that could occur through other treatment methods, such as cleaning with microabrasives.

However, the current treatment varied from that of Professor Lewin in that the aim of the treatment was the immobilization of the slightly soluble gypsum which is ubiquitous on the surface and subsurface of the columns and partly responsible for the observed damage. Therefore, urea was not added since the purpose of this compound is the liberation of carbon dioxide to enhance the formation of barium carbonate thus filling the spaces between calcite crystals in the marble and consolidating it. In the current variation, no barium carbonate could be expected but the release of the calcium ions from the gypsum result in the formation of new calcite which is redeposited on the existing calcite matrix of the stone thus achieving a minor consolidation effect.

The conservation treatment was tested *in situ* on three different columns, one on each elevation, to produce accurate results based on different variables in the different locations such as exposure to heat, amount of gypsum encrustation, and soiling. The columns were analyzed and three columns were selected for treatment testing, south elevation, column four; west elevation, column four; and north elevation, column nine.

The treatment was applied in a poultice which was spread in a relatively thick coating over Japanese paper to facilitate the removal of the poultice. The poultice consisted of paper pulp and a barium hydroxide solution.[55] The solution was prepared by heating 2.5 liters of deionized water to boiling point. 900 grams of $Ba(OH)_2$ and one liter of glycerin were added to the water while stirring. The solution was then filtered.[56] When cold it was diluted with deionized water to four liters. This formulation was based on Professor Lewin's recipe.

Eight liters or two gallons of solution were added to a five gallon bucket and these were tightly covered to prevent carbonation. When the poultice was to be prepared, the top liquid portion of the solution was poured into a separate bucket and then the paper pulp was added to form the poultice.[57]

The area of column to be treated was first spayed with the barium hydroxide solution and Japanese paper was applied. The poultice was then applied to the top six to nine inches of the three selected columns over the Japanese paper. The column was then wrapped with plastic film to prevent the washing of rain. To prevent drying out the poultice was sprayed every other day with the same solution and to extend the dwell time of the solution, allowing for improved conversion. The poultice was then removed after a one week period. After the stone dried, small samples from the test areas were taken for analyses.

Treatment Application

Figure 5.1: (top left) North elevation, column 9, Before treatment

Figure 5.2: (middle right) North elevation, column 9, Application of Japanese paper

Figure 5.3: (bottom left) North elevation, column 9, Application of barium hydroxide poultice

Figure 5.4: (top right) North elevation, column 9, Application of plastic wrap

Figure 5.5: (middle left) North elevation, column 9, One week after treatment application

Figure 5.6: (bottom right) North elevation, column 9, After removal of poultice

5.3 Post-treatment: SEM and Barium dot mapping (SEM-EDS) Analysis, Polarized Light Microscopy

Three samples were analyzed post treatment as well as two samples from south elevation, column 2, taken from areas treated by Seymour Lewin in the early 1980's to determine their morphology. Small flakes from the stone surface in the treated areas were taken for examination.

Small samples were analyzed in thin section pre- and post- treatment to evaluate the effectiveness of the barium hydroxide by optical microscopy and SEM-Energy Dispersive Spectroscopy (EDS). A comparison of thin sections by optical microscopy showed the degree of consolidation achieved, while SEM-EDS, through dot mapping, determined if all the sulfates present were bound by the barium ion.

5.3.1 SEM-EDS

The thin section samples were examined using a Scanning Electron Microscope (JEOL SEM 6400) with an Energy Dispersive Spectrometer. This measures the energy of the X-Rays released from the different elements in the sample as they are bombarded by electrons in the microscope. It also allows a dot mapping of these elements to be created in the area under examination. To obtain these maps, the EDS was run for 5 minutes to collect sufficient data to produce the maps, allowing the location of the different elements to be observed. The dot maps along with the SEM images can then be compared to determine the location of certain compounds.

Of the post-treatment samples examined, only one sample showed the presence of the barium ion. The presence of the ion occurred in the sample obtained from west elevation column 8. In this sample barium ion was identified in small microcracks near the external surface of the sample. Sulfur was also present in these same interstitial spaces indicating that the sulfur present was bound to the barium, leading to the conclusion that conversion of the gypsum (calcium sulfate dihydrate) to barium sulfate was successful. Although conversion does occur, the degree of conversion may vary depending on the texture and microstructure of the sample. These may be some of the reasons that explain why barium was only detected in one sample. It should also be noted that the barium ion was only detected at a high magnification, while at a lower magnification the barium signal was swamped by the higher amount of calcium present. The same sample was examined at a lower magnification and no barium was found. Sodium and chloride ions were detected as well, confirming the presence of sodium chloride, as observed in the pre-treatment SEM photomicrographs of similar samples.

The sample that had been treated by Prof. Lewin in the early 1980's, sample S-2 from south elevation, column 2, did not show the presence of the barium ion. Approximately 20 years have elapsed since the treatment was applied, mechanical wear may have eliminated some of it. The fact that no sulfur was detected in this sample supports this conclusion.

The other two samples analyzed from south elevation, column 4 (S-4, After) and north elevation, column 9 (N-9 After), did not show the presence of barium. At a magnification of 30x, sulfur was detected in sample N-9 After, located in the same position as the detected calcium ions, indicating the presence of calcium sulfate.

5.3.2 PLM

Samples were obtained from the treated areas and examined using transmitted polarized light microscopy. Three samples from the columns selected for treatment were examined in thin section post treatment to determine if any there were any visual changes in the morphology or appearance of the sample due to the applied treatment. This includes the formation of barium sulfate crystals in the interstitial spaces between calcite crystals or on the surface of sample and the appearance micro-cracking, both of which contribute to stone disaggregation and flaking. The samples were obtained from small flakes detaching from the columns in soiled areas representative of the entire column. Samples were examined both stained with alizarin red stain for calcium carbonate and unstained under transmitted polarized light. This analysis reveals at a microscopic level any changes taken place on the columns due to the applied barium hydroxide treatment.

The sample from the west elevation, column 4, had a layer of soiling on the external surface of the flake, as did the sample examined prior to treatment. Soiling also appeared on the internal surface of the flake and within the micro cracks of the flakes. The sample displayed extensive microcracking and the calcite crystals on the external surface were extremely etched and eroded. The calcite grains are also loosely attached to one another which results in flaking and disaggregation and provides at a microscopic level pores for water and other foreign materials to dwell. There does not seem to be much of a difference in appearance as compared to the sample examined prior to treatment.

The sample obtained from north elevation, column nine showed soiling like that of sample obtained from the west elevation. Surface etching of the calcite crystals is also present on the north elevation sample. Extensive microcracking and loosely adhered calcite grains were also evident. There is also the presence of small crystals near the surface, which can be seen under cross polarized light at a higher magnification.

The sample obtained from south elevation, column 4 had soiling similar to the west and north elevation samples and exhibited serious microcracking with loosely adhered calcite grains. Overall, there was not a large difference as seen using polarized light microscopy between those samples taken prior to treatment and those taken post treatment.

A sample from south elevation, column 2, was obtained. The sample was taken from the area documented as having been treated by S. Lewin. This sample did not appear to be that different from the sample obtained from south elevation, column 4.

The following photomicrographs show examples of the deterioration explained above.

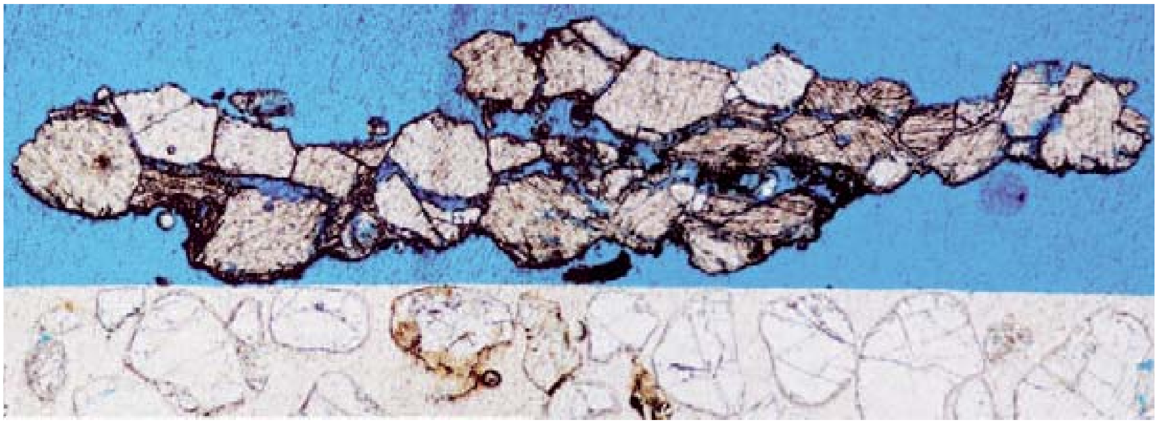

Figure 5.7:
Sample ID: W-4 After
Sample Location: West elevation, column 4, treated area
Nikon Optiphot 2-POL, Plane Polarized Light, 5x
Note the bottom of the sample is the external surface of the stone sample.

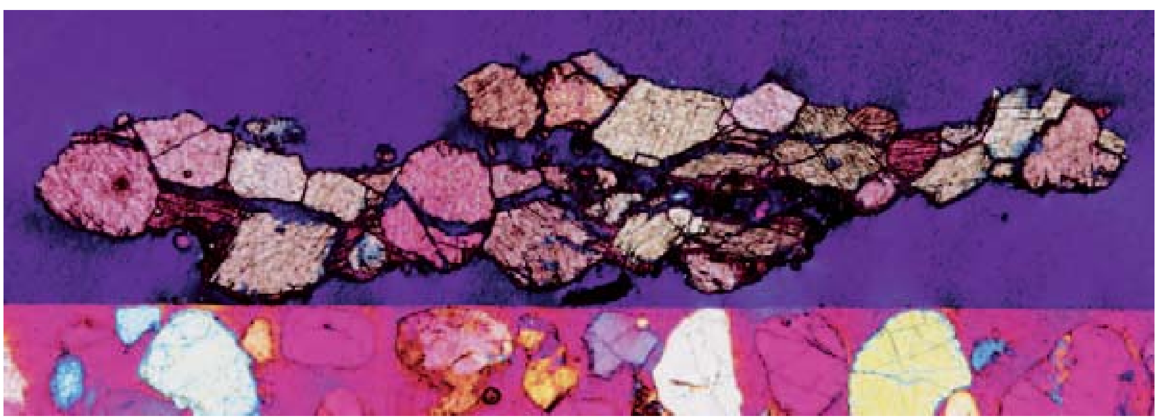

Figure 5.8:
Sample ID: W-4 After
Sample Location: West elevation, column 4, treated area
Nikon Optiphot 2-POL, Cross Polarized Light, 5x, note the grain boundary detachment

SEM-EDS Analysis:
SEM photomicrograph and Elemental Dot Maps
Magnification: 20x
Sample ID: W-4 After
Sample Location: West elevation, column 4, treated area
Comments: Note the concentration of calcium ions on the exterior surface (bottom) of the sample and also the presence of sulfur on the exterior surface. Note the detection of sodium and chloride ions on the exterior surfaces of some of the calcite grains, which may the presence of sodium chloride as seen in the pre-treatment SEM images.

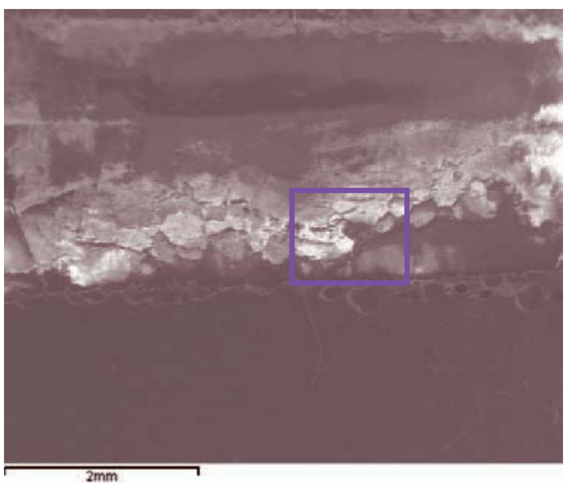

Figure 5.9: SEM photomicrograph, (note the bottom is the external surface of the stone)

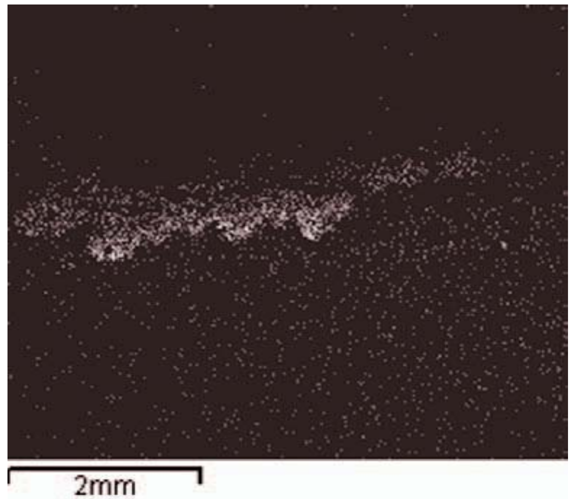

Figure 5.10: Dot Map for Calcium

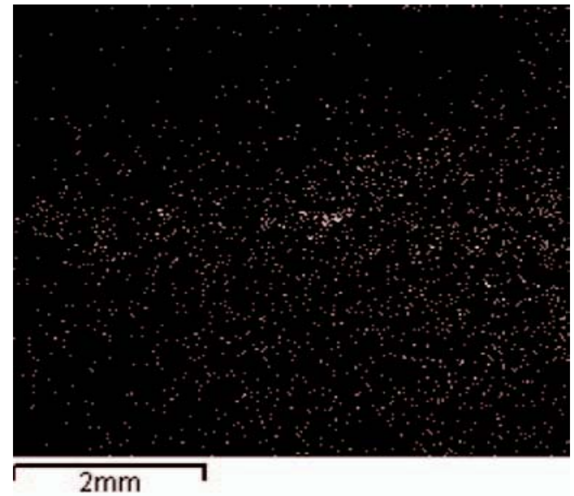

Figure 5.11: Dot Map for Sulfur

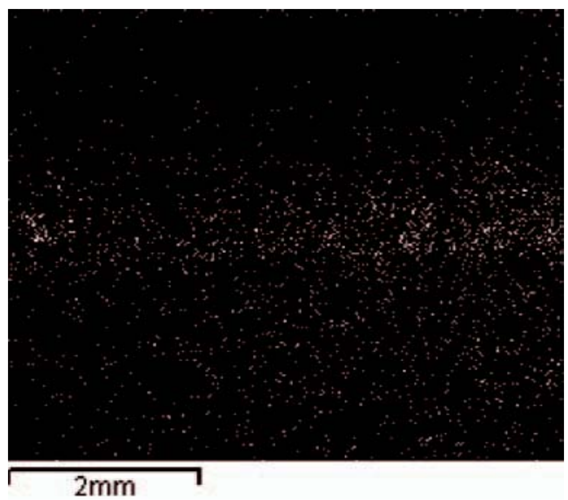

Figure 5.12: Dot Map for Chloride

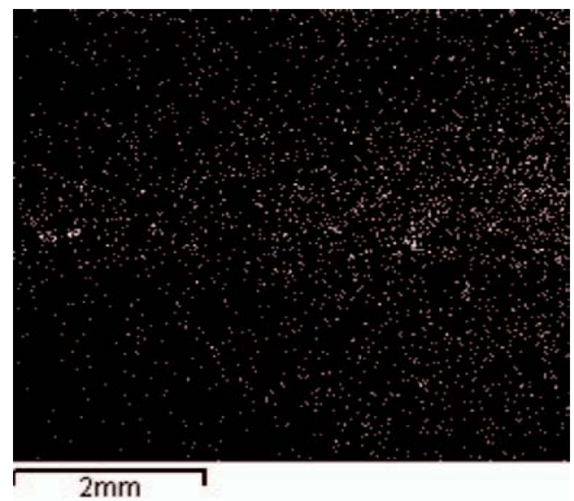

Figure 5.13: Dot Map for Sodium

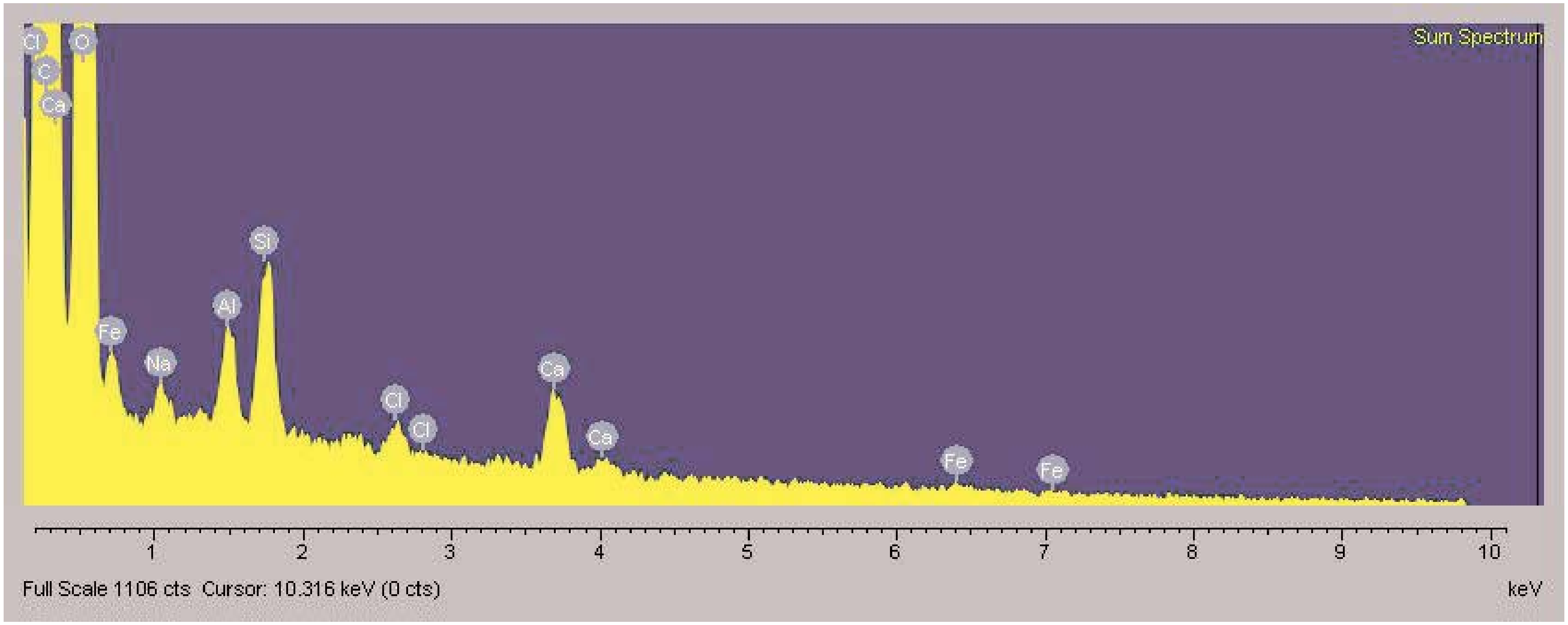

Figure 5.14:
Sample ID: W-4 After
Sample Location: West elevation, column 4, treated area
Elemental Spectrum derived from SEM-EDS Dot Mapping, 20x
Note the absence of sulfur (S) and barium (Ba) peaks as seen in the elemental spectrum of the same sample at a higher magnification.

SEM-EDS Analysis:
SEM photomicrograph and Elemental Dot Maps
Magnification: 100x
Sample ID: W-4 After
Sample Location: West elevation, column 4, treated area
Comments: Note the concentration of calcium ions on the exterior surface (bottom) of the sample and the pattern of sulfur and barium ions between the grain boundaries. Chloride ions were also detected between the grain boundaries of the calcite crystals.

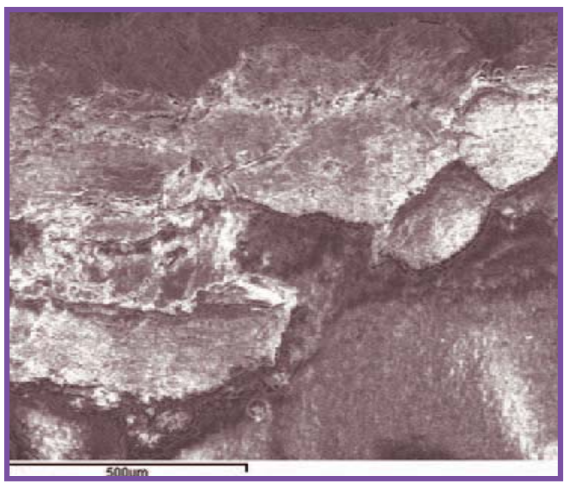

Figure 5.15: SEM Photomicrograph, (note the location of this area highlighted in blue in Figure 5.9)

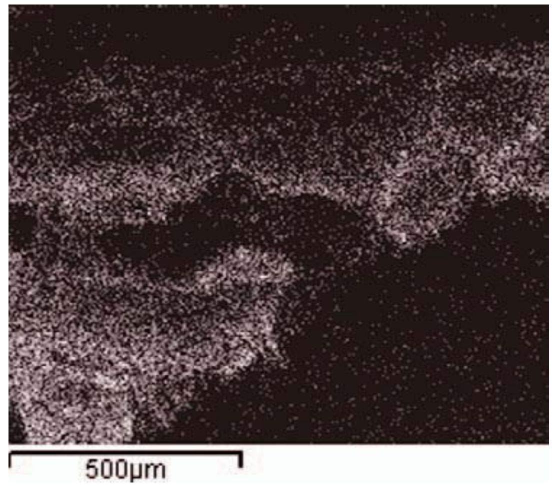

Figure 5.16: Dot Map for Calcium

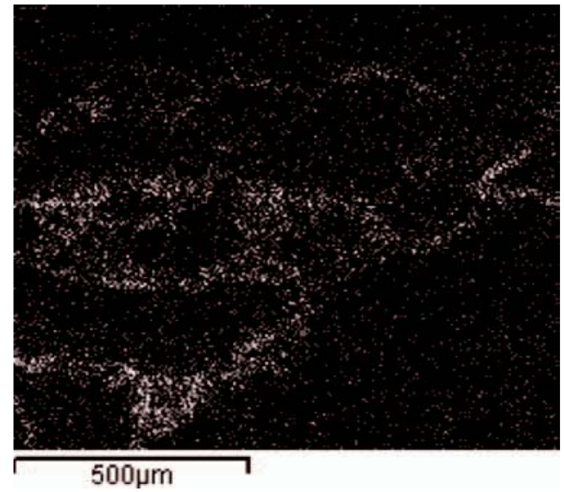

Figure 5.17: Dot Map for Sulfur

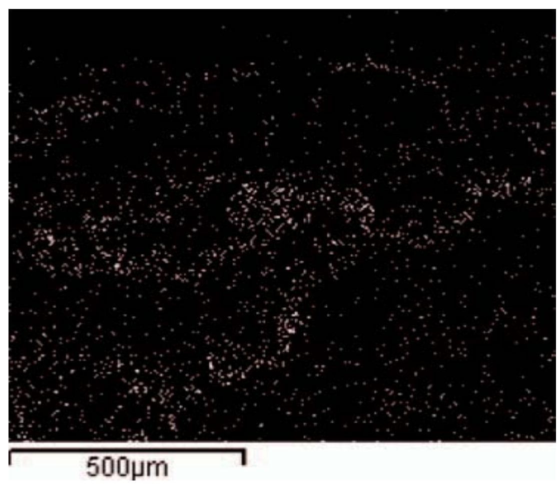

Figure 5.18: Dot Map for Barium

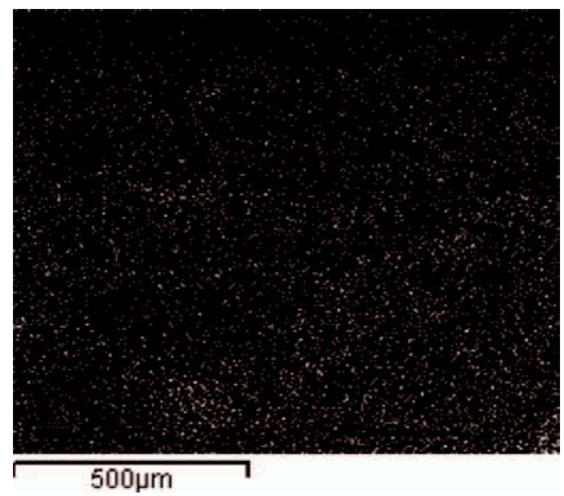

Figure 5.19: Dot Map for Chloride

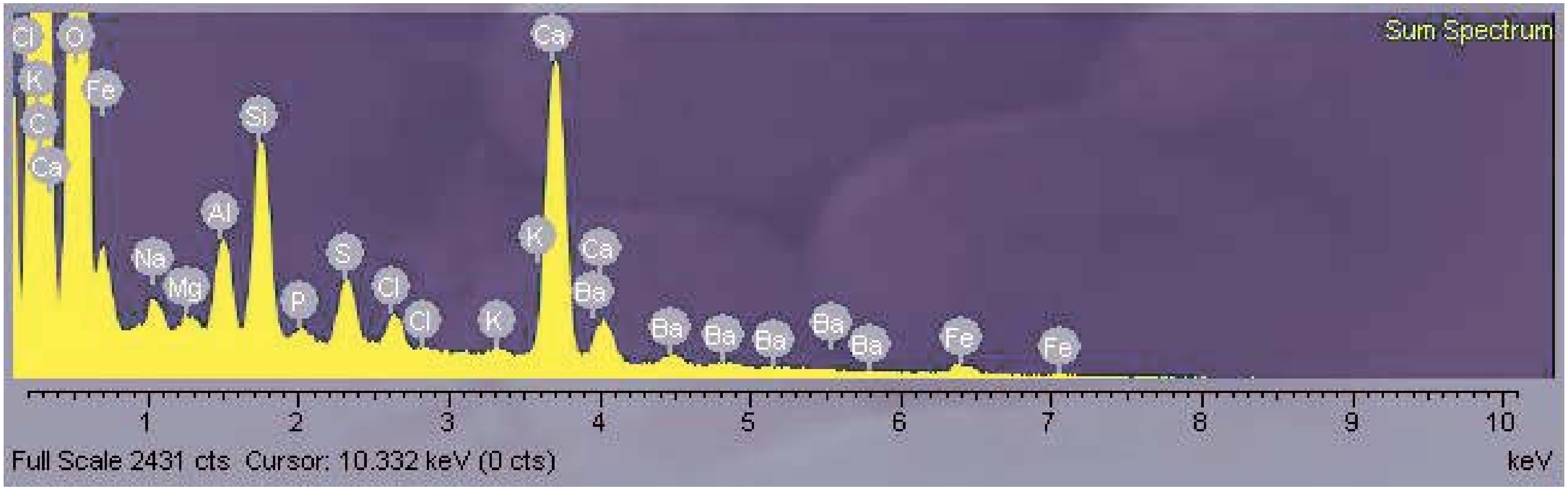

Figure 5.20:
Sample ID: W-4 After
Sample Location: West elevation, column 4, treated area
Elemental Spectrum derived from SEM-EDS Dot Mapping, 100x
Note the peaks of barium (Ba) and sulfur (S) indicating the presence of those elements.

PLM and SEM Analysis:
PLM and SEM photomicrographs
Sample ID: S-4 After
Sample Location: South elevation, column 4, treated
Comments: Note the microcracking and grain boundary separation. There is also a layer of amorphous particles on the external surface of the stone. The external surfaces of the calcite grains are also etched and rigid as compared to those on the internal surface. (the bottom is the external surface of the stone)

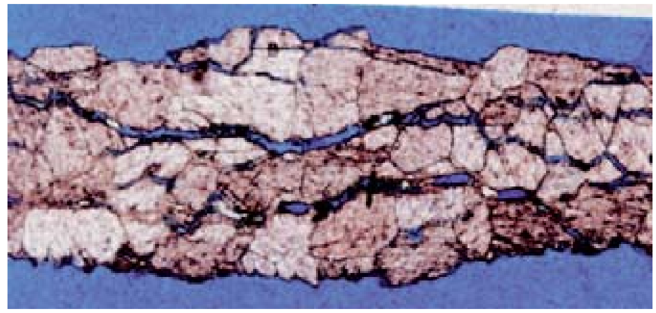

Figure 5.21: Nikon Optiphot 2-POL, Plane Polarized Light, 5x

Figure 5.22: Nikon Optiphot 2-POL, Cross Polarized Light, 5x

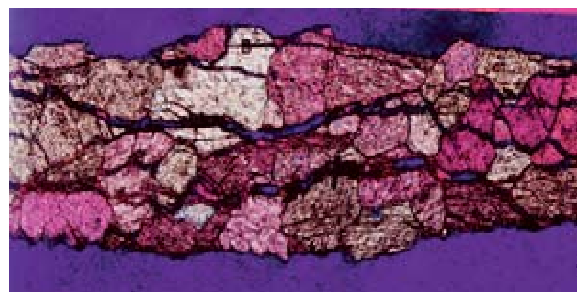

Figure 5.23: Nikon Optiphot 2-POL, Cross Polarized Light, 5x

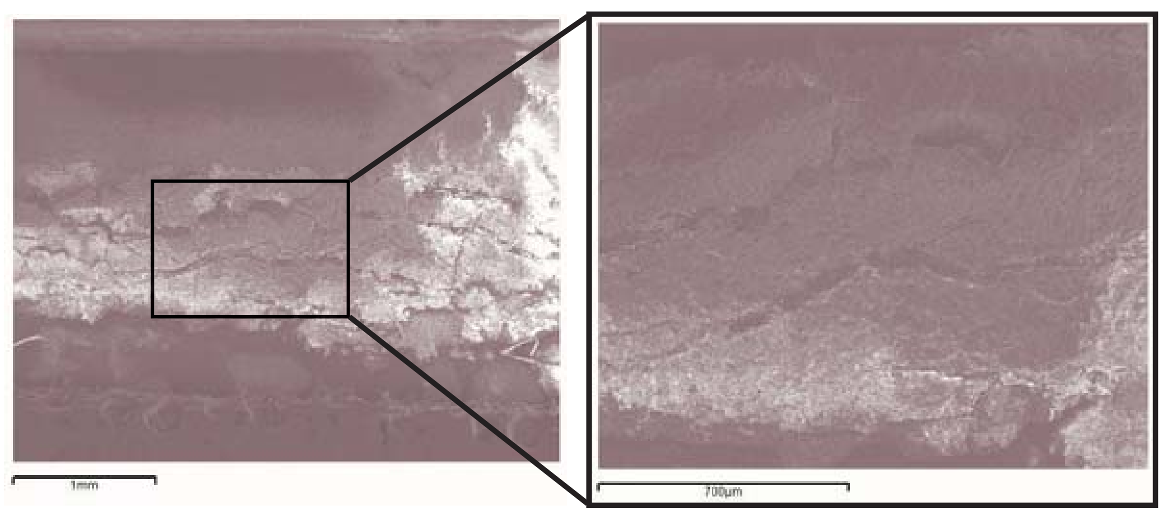

Figure 5.24: SEM Photomicrograph, 30x

Figure 5.25: SEM Photomicrograph, 75x

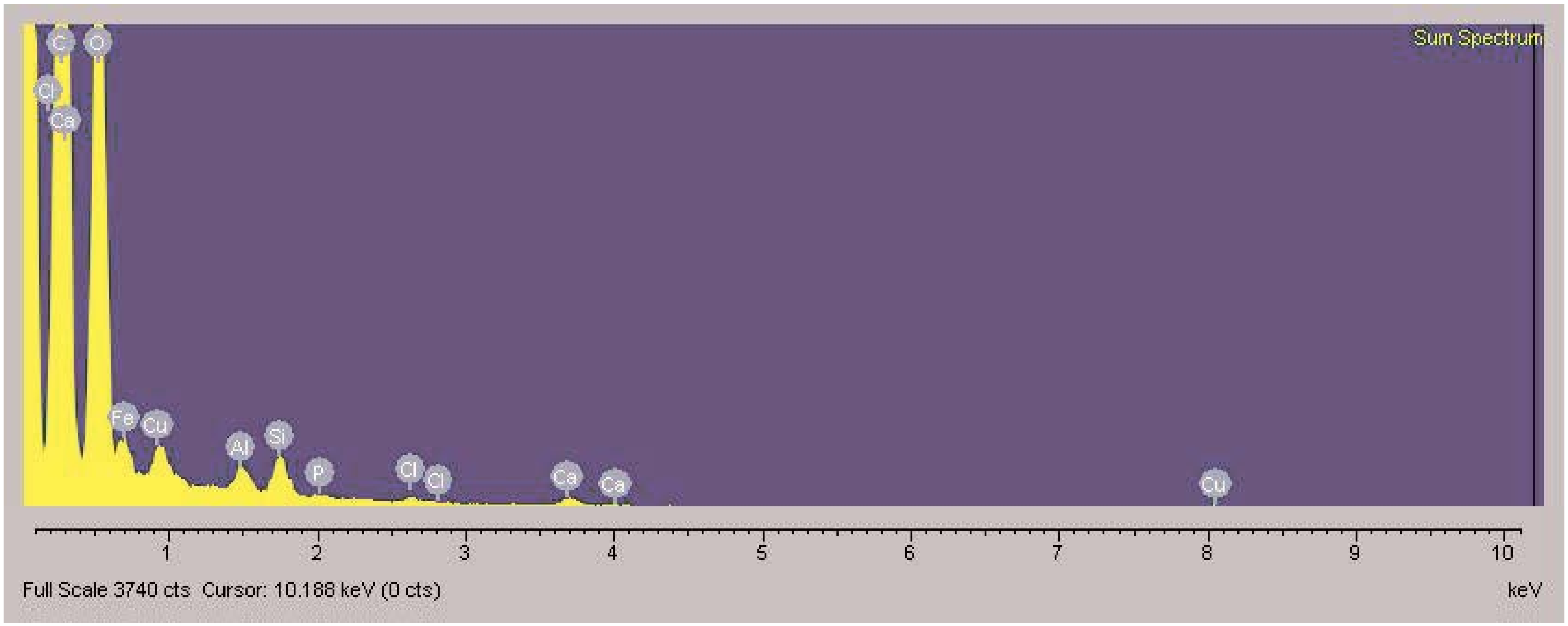

Figure 5.26:
Sample ID: S-4 After
Sample Location: South elevation, column 4, treated area
Elemental Spectrum derived from SEM-EDS Dot Mapping, 30x

PLM and SEM-EDS Analysis:
PLM and SEM photomicrographs
Sample ID: N-9 After
Sample Location: North elevation, column 9, treated area
Comments: Note the grain boundary detachment and the dark layer of soiling on the external surface of the stone sample. (the top is the external surface of the stone)

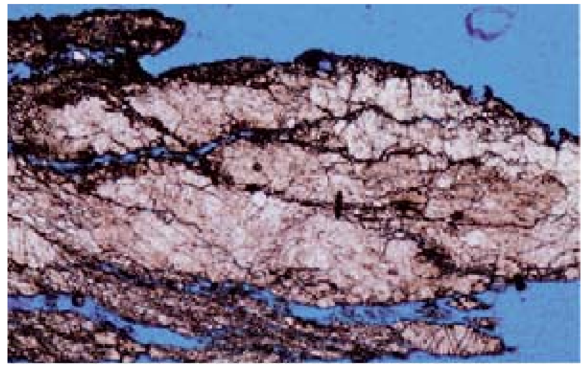

Figure 5.27: Nikon Optiphot 2-POL, Plane Polarized Light, 5x

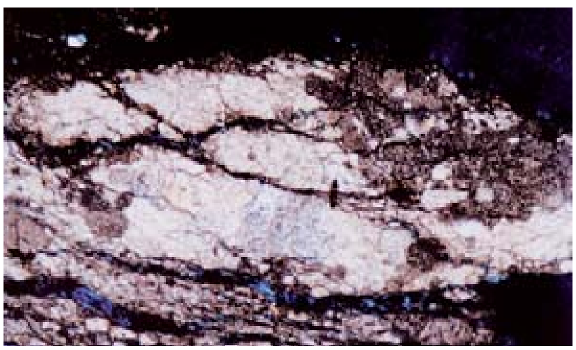

Figure 5.28: Nikon Optiphot 2-POL, Cross Polarized Light, 5x

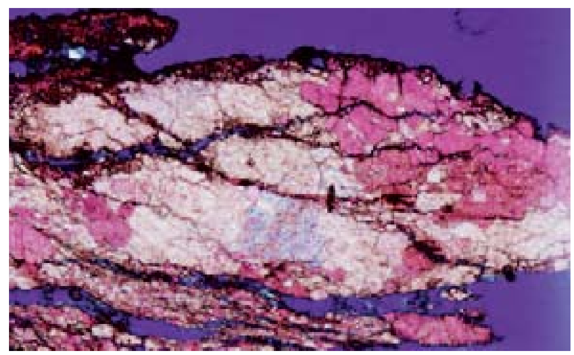

Figure 5.29: Nikon Optiphot 2-POL, Cross Polarized Light, 5x

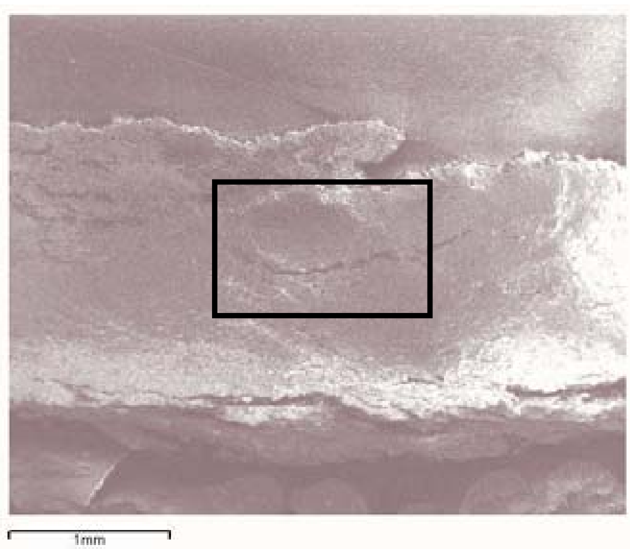

Figure 5.30: SEM Photomicrograph, 30x

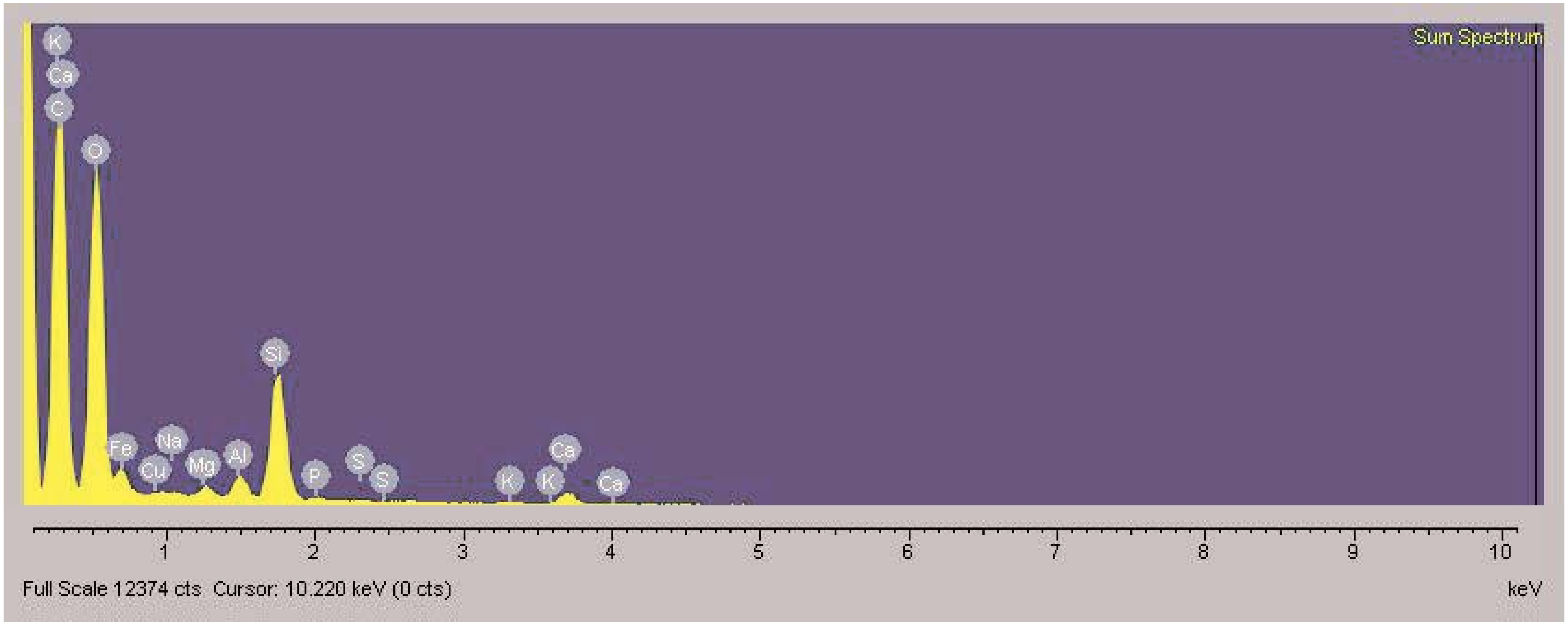

Figure 5.31:
Sample ID: N-9 After
Sample Location: North elevation, column 9, treated area
Elemental Spectrum derived from SEM-EDS Dot Mapping, 30x

PLM and SEM-EDS Analysis:
PLM and SEM photomicrographs
Sample ID: N-9 After
Sample Location: North elevation, column 9, treated area
Comments: Note the dark layer of amorphous particles attached to external surface of the stone (the top is the external surface of the stone)

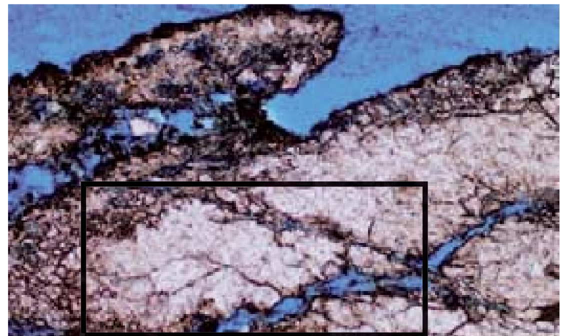

Figure 5.32: Nikon Optiphot 2-POL, Plane Polarized Light, 10x

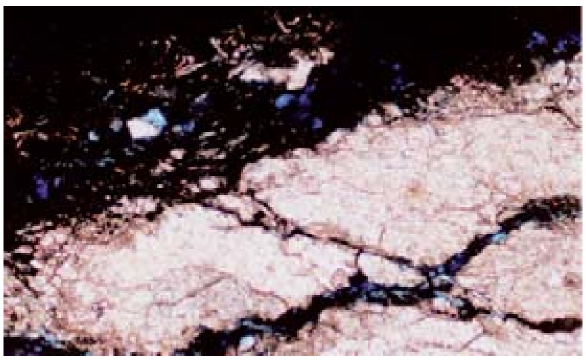

Figure 5.33: Nikon Optiphot 2-POL, Cross Polarized Light, 10x

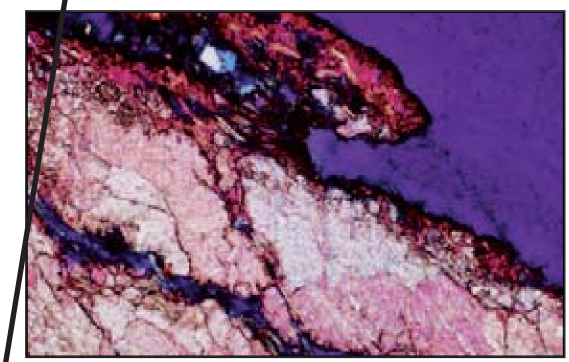

Figure 5.34: Nikon Optiphot 2-POL, Cross Polarized Light, 10x, sample rotated 45 degrees

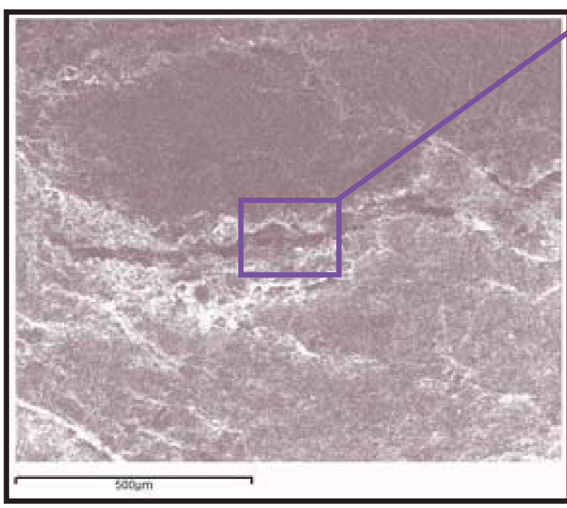

Figure 5.35: SEM Photomicrograph, 100x (note the location of this area highlighted in black in Figure 5.30 and 5.32)

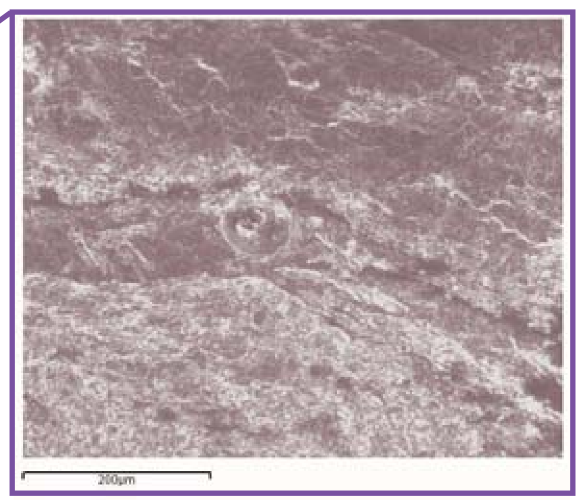

Figure 5.36: SEM Photomicrograph, 200x (note the location of this area highlighted in blue in Figure 5.35)

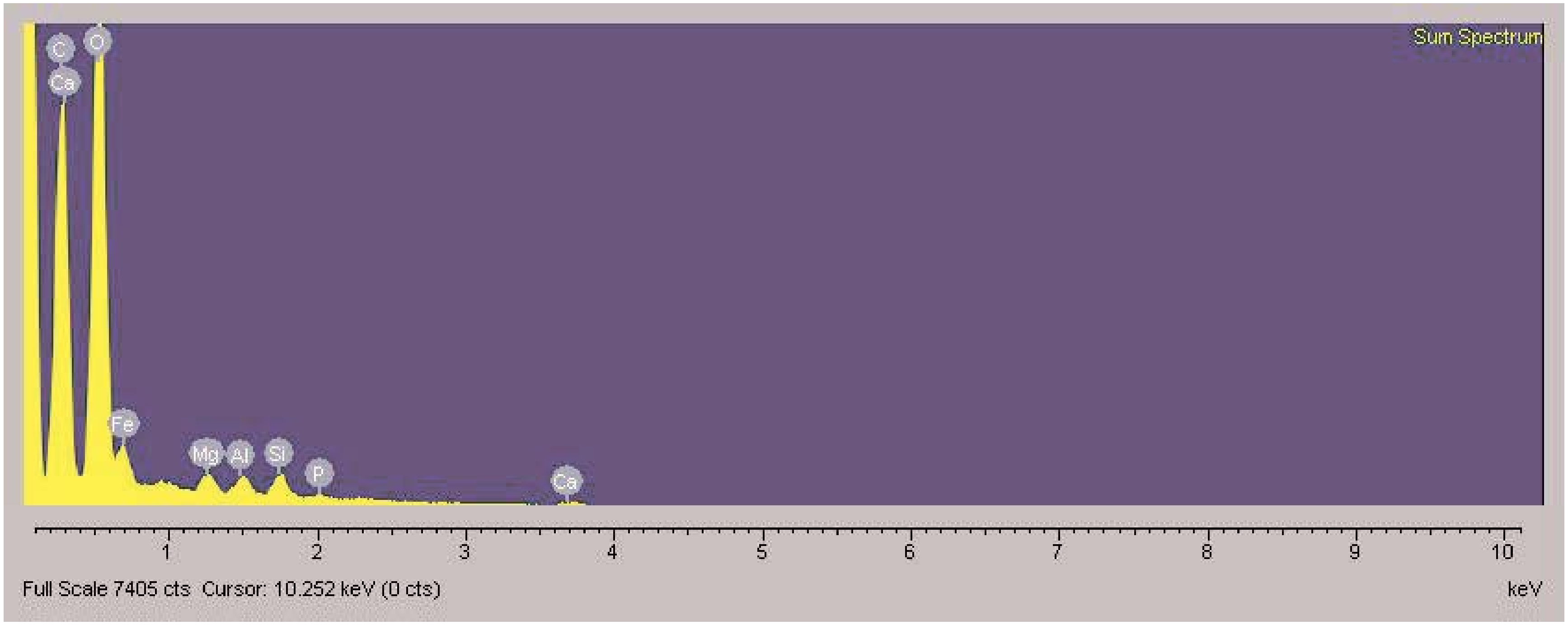

Figure 5.37:
Sample ID: N-9 After
Sample Location: North elevation, column 9, treated area
Elemental Spectrum derived from SEM-EDS Dot Mapping, 100x
Note the absence of sulfur and barium peaks as seen in the elemental spectrum from Sample W-4 After, examined under the same magnification.

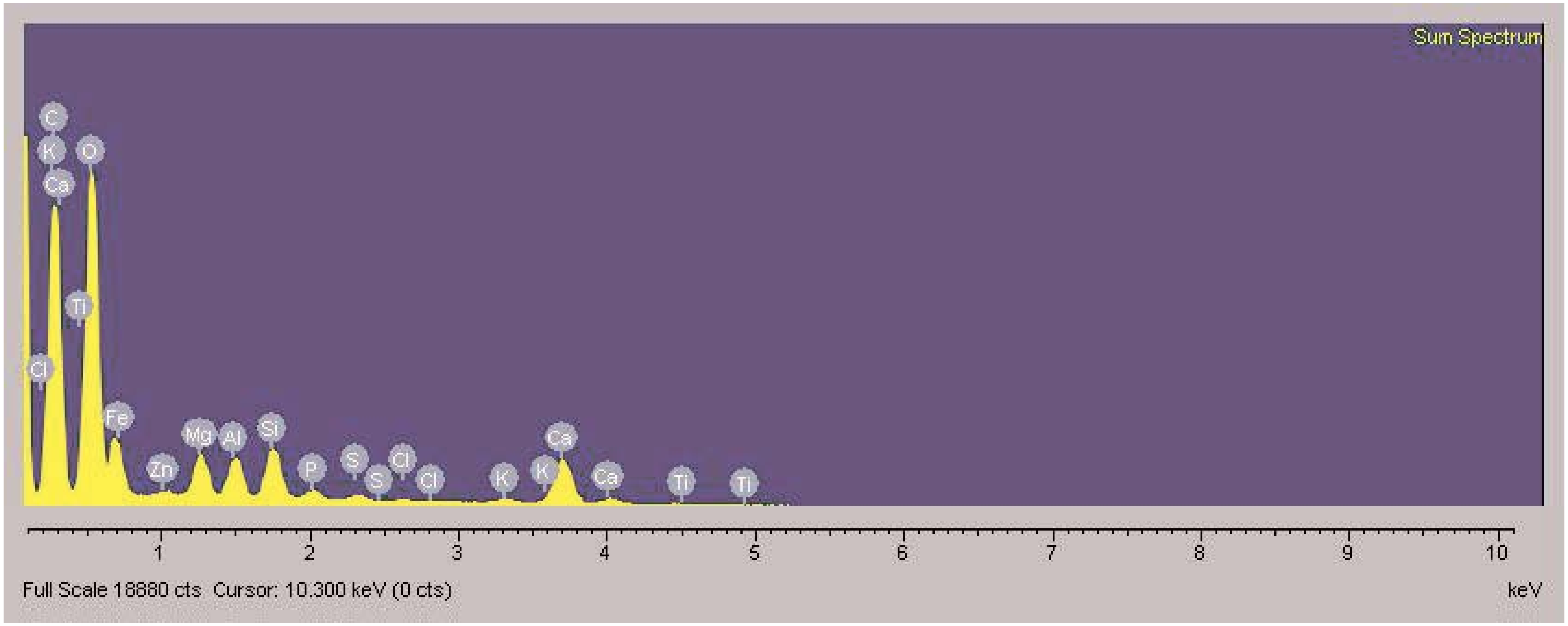

Figure 5.38:
Sample ID: N-9 After
Sample Location: North elevation, column 9, treated area
Elemental Spectrum derived from SEM-EDS Dot Mapping, 200x
This sample was also examined under 200x. Even at such a high magnification no barium (Ba) or sulfur (S) was detected in this sample.

PLM and SEM-EDS Analysis:
PLM and SEM photomicrographs
Sample ID: S-2
Sample Location: South elevation, column 4, Area treated by S. Lewin
Comments: Note the calcite grain detachment and the dark layer of surface soiling on the external surface of the stone sample.
(the bottom is the external surface of the stone)

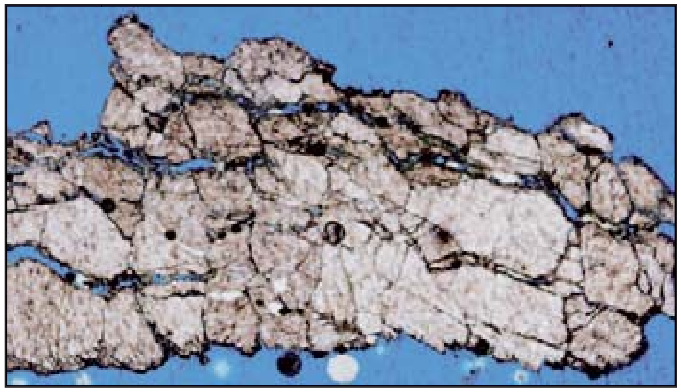

Figure 5.39: Nikon Optiphot 2-POL, Plane Polarized Light, 5x

Figure 5.40: Nikon Optiphot 2-POL, Cross Polarized Light, 5x

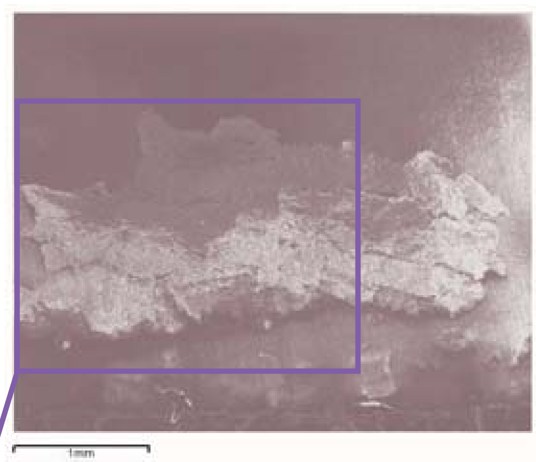

Figure 5.41: SEM Photomicrograph, 30x

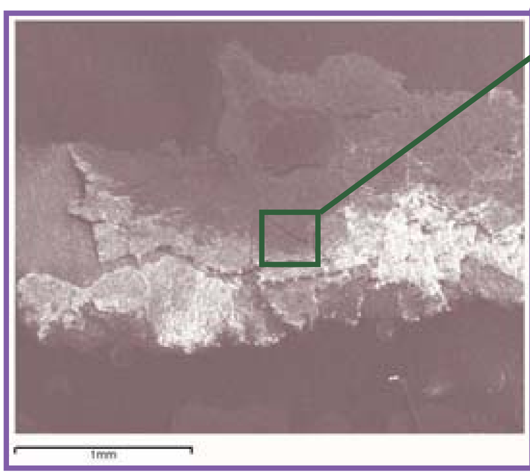

Figure 5.42: SEM Photomicrograph, 75x, (note this area highlighted in blue in the lower magnification image in Figure 5.41)

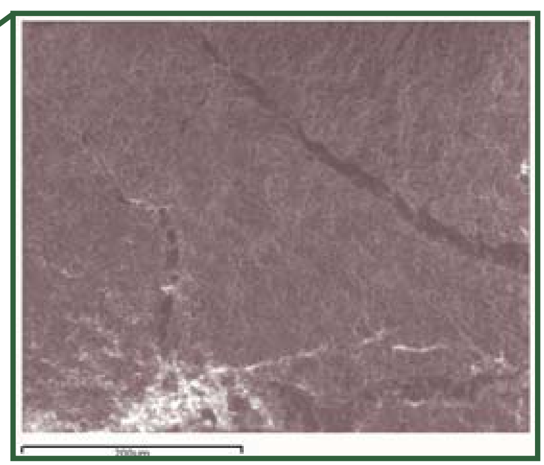

Figure 5.43: SEM Photomicrograph, 250x, (note this area highlighted in green in the lower magnification image in Figure 5.41)

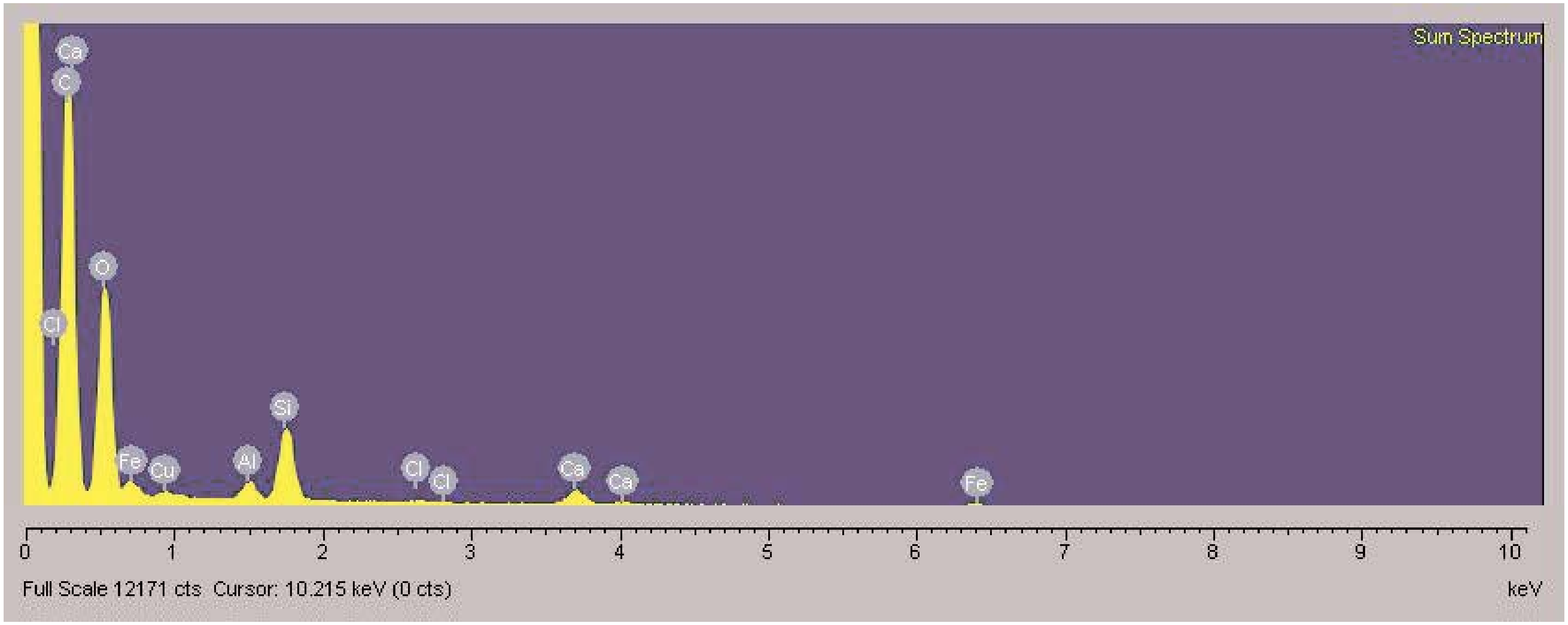

Figure 5.44:
Sample ID: S-2
Sample Location: South elevation, column 2, area treated by S. Lewin
Elemental Spectrum derived from SEM-EDS Dot Mapping, 30x

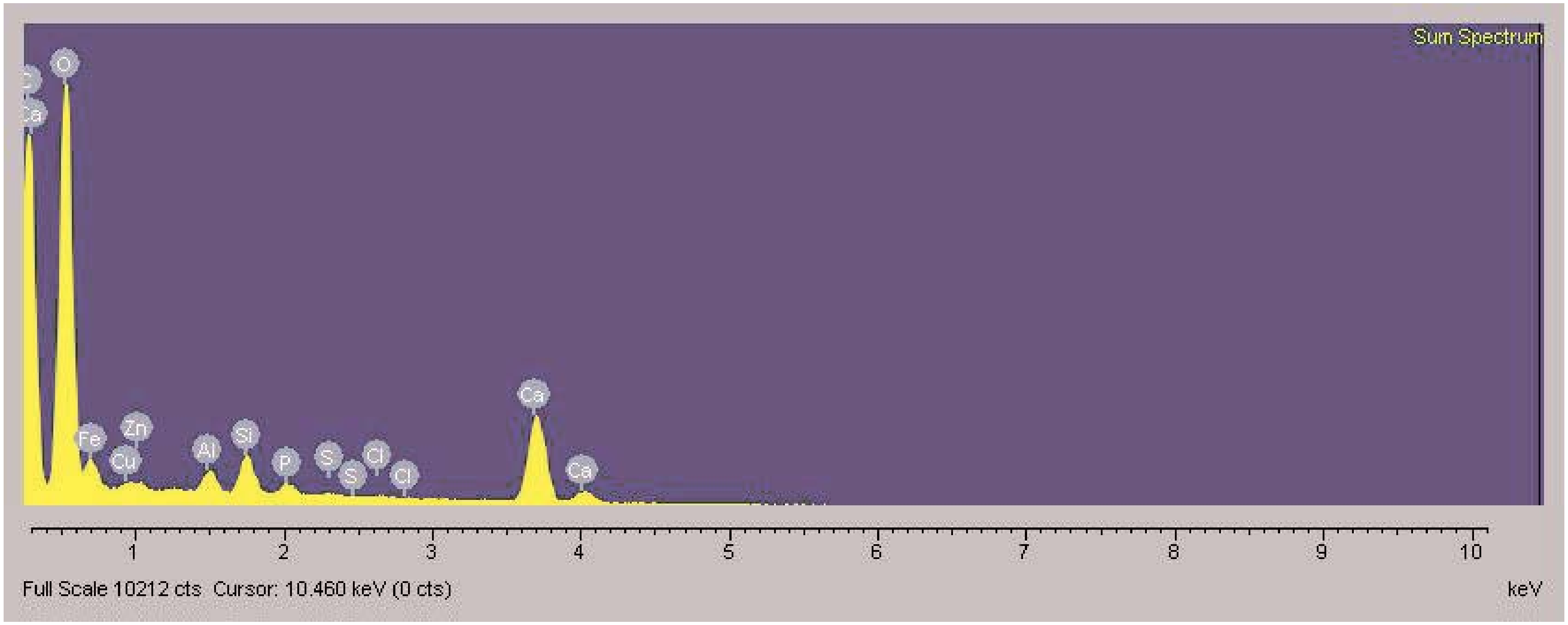

Figure 5.45:
Sample ID: S-2
Sample Location: South elevation, column 2, area treated by S. Lewin
Elemental Spectrum derived from SEM-EDS Dot Mapping, 250x
This sample was treated with Lewin's Barium hydroxide - Urea Treatment. No barium (Ba) was detected in this area, however small amounts of sulfur (S) were detected indicating the formation of gypsum.

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[2] Hansen, 15-16.
[3] Hansen, 18 - 19.
[4] Hansen, 13.
[5] Hansen, 14.
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[11] Ibid.
[12] Schnabell, 24.
[13] Schnabell, 25.
[14] Schnabell, 26.
[15] Ibid.
[16] Schnabell, 30.
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[18] Schnabell, 30.
[19] Ibid.
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[21] Ibid.
[22] Matteini, 143.
[23] Matteini, 144 and Hansen, 15. The Solubility of barium sulfate in water is 2 g/100 cc x 10^{-4}; Calcium carbonate's solubility is 14 g/100 cc x 10^{-4}; Barium carbonate is 22 g/100 cc x 10^{-4}; Calcium hydroxide is 1,850 g/100 cc x 10^{-4}; Calcium sulfate dihydrate is 2,410 g/100 cc x 10^{-4}. Note: the higher solubility # in g/100 cc x 10^{-4}, the more soluble it is in water.
[24] Matteini, 144.
[25] Hansen, 19.
[26]Ibid.
[27] Ibid.
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[29] Ferroni and Dini, 561.
[30] Ferroni and Dini, 562.
[31] Ferroni and Dini, 564.
[32] Lanterna, et. al., 388.

[33] Ferroni and Dini, 565.
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[35] Schnabell, 32.
[36] Ibid.
[37] Ibid.
[38] Ibid.
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[43] Lewin, 37.
[44] Ibid.
[45] Ibid.
[46] Lewin, 39.
[47] Ibid. The testing for effectiveness of the treatment in halting the formation of gypsum during weathering exposure was performed by analyzing for the gypsum content of scrapings taken from the exposed surface at intervals. Approximately 1 gram of the surface was scraped from an area of about 2 centimeters square. The surface hardness prior to the scraping was estimated by a scratch test with standard Mohs pencils. A different area was scraped in each test.
[48] Lewin, 39 and 41.
[49] Ibid.
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[53] Hansen, 19.
[54] Hansen, 13.
[55] The barium hydroxide solution is slightly caustic; therefore, protective gear, such as gloves and safety goggles, would be worn by the architectural conservators during application. Once applied to the surface the barium hydroxide solution quickly reacts with the calcium sulfate forming barium sulfate becoming innocuous.
[56] Filtration proved to be difficult, thus all of the solution was not filtered.

[57] Cotton linters were used for the paper pulp. The linter was prepared by adding water to the paper pulp and blending to refine the paper pulp and produce a smooth consistency.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

The present study has focused on a study of stone decay at the Merchant's Exchange and their present condition drawings using the 24 columns on the first floor to analyze the effect of location, changes in air pollution and environment as well as the effect of different cleaning techniques used on this building.

The semi-quantitative analysis conducted has shown that:

- Closing Dock Street to traffic on the north side of the building has significantly reduced the soiling rate;
- Soiling rate has increased on the west façade due to increased general and tourist traffic;
- Soiling rate has decreased on the south side, even though traffic has not decreased, but this decrease could be attributed to the shielding effect of the trees planted on that side plus changes in air circulation patterns due to changes in the buildings in that area.

The present condition survey will serve to allow performing an even better analysis of changes in deterioration rate in the future.

The damage suffered by these columns originates from a combination of air pollution and freeze-thaw cycling. The first causes soiling and the conversion of the marble surface to gypsum, with the consequent formation of black crusts which tend to detach in various patterns depending on location. Areas subject to direct wetting by rain do not accumulate soiling and the gypsum is mostly washed off. Protected areas can accumulate a heavy crust. Whether this crust will be firmly attached or tend to flake off, will depend on the amount of moisture that can accumulate on it. This will solubilize in part the gypsum, which will recrystallize and cause damage, when the water evaporates. The differences in moisture will therefore determine whether the surface will delaminate, flake or blister.

The second damage is the freeze-thaw cycling to which this particular marble is subject due to the micaceous inclusions it holds. As found through the analysis of the historic photographs, pairs of columns, with the same history and location show different degrees of deterioration due to the orientation these mineral veins have within the column. This damage is enhanced by air pollution by the compounding effect of salt crystallization.

To address the presence of gypsum, conversion of this mineral to the very insoluble barium sulfate may prove to be a viable approach to control damage. The treatment will immobilize the sulfate present and provide some consolidation that would allow localized cleaning of the most soiled areas. However, as has been shown, in practice the method depends on surface texture and exposure.. Therefore, more practical testing to improve penetration of the barium hydroxide solution may be required. For example, as in the case of consolidation with lime water, the treatment may have to be applied continuously for several hours. Or repeated poultices may be required to improve the effectiveness of the conversion.

Apart from the actual conversion, regular elimination of localized soiling would be desirable. And, after this has been achieved, reapplication of the barium hydroxide would serve to block any remaining sulfates that will surface during the drying out of the column after a cleaning by water spray.

Finally, the deterioration resulting from freeze-thaw cycling should be addressed. Since this problem is inherent to the stone, the only solution is to protect it from these temperature cycles. It is well known that stone statues in palatial gardens were wrapped up in straw during the winter months. This approach is currently being revived in France. A similar solution could be developed for these columns, particularly since they are readily accessible. And better materials than straw could be used for their protection. One can even consider having cylindrical boxes, fashioned so the outside represent the hidden column, to cover them up and protecting them with an insulating material.

The study has shown that a conditions survey analysis can provide a large amount of information concerning deterioration patterns and the actual amount of deterioration occurring on a certain element. It is especially valuable when trying to analyze a certain element of the same material exposed to different conditions. Conclusions regarding the deterioration patterns can then be drawn based on the elements location and exposure to different elements. Based on the conditions survey, including both sets of drawings, the stone on the north elevation columns is fairly sound, while those on the south and west elevation continue to actively deteriorate. The average score of south elevation columns is 21 (± 5.2), while the average score of the west elevation columns is 18.5 (± 2.4), and the north elevation columns' average score is 9.6 (± 1.8). These average calculations with the standard deviation indicate that the distribution of conditions is larger on the south elevation columns than on the west or north. This confirms that south elevation columns are in worse condition. The difference in the stone deterioration is primarily attributed to the presence of vehicular traffic, which has been eliminated from the north elevation.

The study has also shown that historic records are invaluable in assessing the degree of damage that a building shows and, in particular, the changes in deterioration rate that may occur. In combination, the condition survey drawings and photographic analysis will serve for a more thorough analysis in the future. In both cases, the analysis allows to develop tailored measures and treatments that will help preserve our built heritage.

SEM-EDS as explained previously showed that only one of the three samples analyzed showed the presence of barium ions in the location of sulfate ion, indicating the presence of barium sulfate. Anytime a conversion reaction is solely relied upon to occur it is impossible to predict whether or not full conversion will occur across the surface of a heterogeneous material. The presence of other substances, the environment, and microstructure can interfere with the chemical reaction.

The application method can be a possible explanation of the results. For example, there were very few gypsum crystals seen in the interstitial spaces in the micro-cracks of the samples as viewed using PLM. The poultice could have possibly extracted the gypsum on the surface with conversion occurring deeper within the stone or not at all. The excessive soiling and the types of gypsum crystal formation may also have contributed to the lack of consistent results. Samples taken in more frequent locations may have revealed more consistent or conclusive results.

The type of surface deterioration in the area in which the sample was taken may also contribute to the lack of conclusive results. For example, the amount of gypsum encrustation and soiling causing lower porosity could have prevented the solution to penetrate the surface thus enabling conversion.

Limited dwell time may also explain the amount of conversion. In this treatment testing, the treatment was only allowed to dwell for a one week period; however, a longer dwell time may have produced better results.

As noted in previous assessments of the barium-hydroxide treatment it is not a completely reliable method and practical results do not reflect the theoretical principle behind it. The present study confirms this conclusion. The *in situ* treatment proved to have some conversion effect however; the results leave much to be desired. The main problem being that the penetration of the barium ion appears to follow the micro-cracks present in the sample. Thus, to improve penetration, several successive applications may be needed and the actual application method still requires further testing.

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APPENDIX A: Condition Glossary

MASONRY CONDITIONS GLOSSARY

CONDITION

Orientation of foliation planes

DEFINITION

Stones display a pattern of weathering based on the orientation and exposure of their foliation planes. For edge-oriented stones, the position of these planes is perpendicular (90°) to the stone face and can be horizontal, vertical or at an angle (diagonal) to the ground. Edge oriented stones usually display a striated appearance. For face-oriented stones the position of foliation is parallel (0°) to the stone face. Face oriented stones are usually gray or white or mottled.

SITE IDENTIFICATION

Because of the way the columns were originally carved, there are both (c) edge-oriented vertical and (d)diagonal and (a) face oriented areas of the column stones. None of the stones were carved with (a) edge-oriented horizontal bedding. Patterns of deterioration, such as flaking and contour scaling, are often associated with face-oriented stones. Orientation in some cases was hard to determine due to heavy soiling, however, patterns of deterioration can help determine the stones orientation at a particular position on the column.

FIELD GRAPHIC

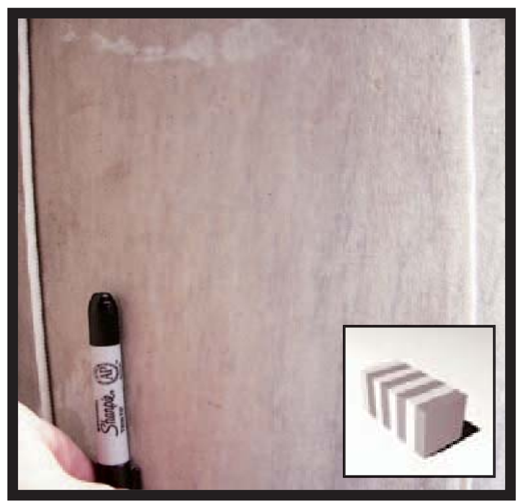
SCHEMATIC

Stone orientation is not represented on condition drawings.

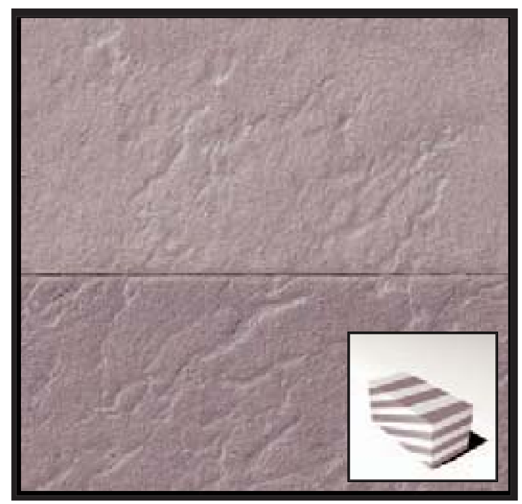
PHOTOGRAPHS

(a) edge-oriented horizontal

(b) face-oriented parallel



(c) edge-oriented vertical



(d) edge-oriented diagonal

MASONRY CONDITIONS GLOSSARY

CONDITION

Mineral Inclusions

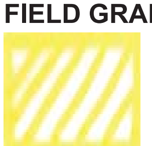
DEFINITION

Stones may display larger mineral inclusions as (a) veins or (b) phenocrysts. Recorded inclusions are at least 1/4 inch in width and noticeably larger than prevailing foliation patterns. They are typically raised in relief or weathered out and are often distinctive in color and texture from the surrounding stone

SITE IDENTIFICATION

Mineral inclusions are identified by a distinct physical boundary similar to that associated with a man-made patch. Mineral inclusions often occur as (d) single or multiple bands on edge-oriented stones. On face-oriented stones, areas with a web-like pattern of inclusions will sometimes be observed. An area that displays a (c) color change only is not considered to be a mineral inclusion. Inclusions are typically distinctive in texture (mineral grains of different size and shape) from the surrounding stone matrix.

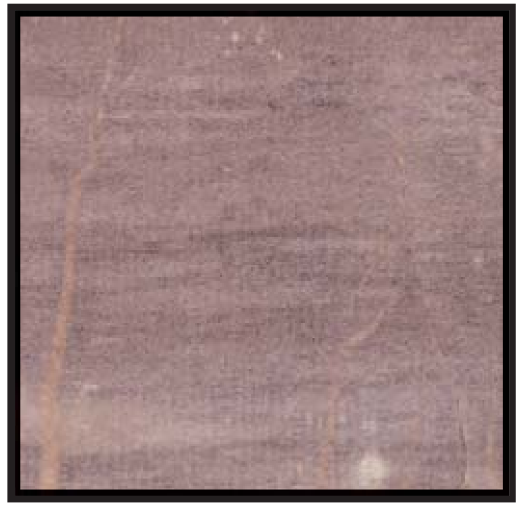
FIELD GRAPHIC



SCHEMATIC

Mineral inclusions are not represented on condition drawings.

PHOTOGRAPHS



(a) veining

(b) phenocryst

(c) color change only

(d) horizontal banding

MASONRY CONDITIONS GLOSSARY

CONDITION

Flaking

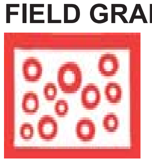
DEFINITION

Surfaces that display active thin lamellar detachment of even thickness or past evidence of such.

SITE IDENTIFICATION

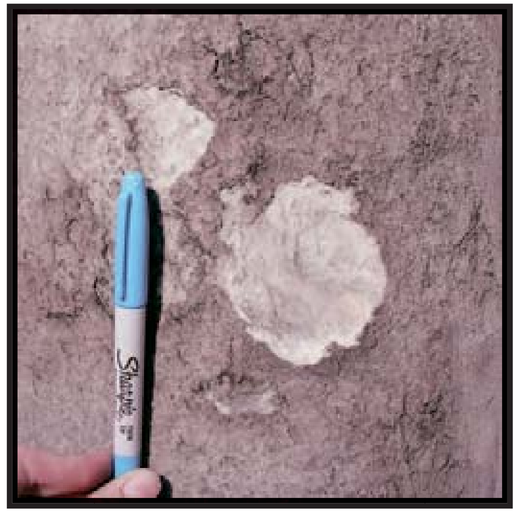
There tends to be several different causes of this type of deterioration mechanism: (a) Flakes resulting from popped blisters, associated with the presence of salts. (b) General areas of flaking attributed to the presence of salts not associated with blisters. (c) Flakes that are associted with mineral inclusions, compounded by the presence of salts.Thus flaking can occur alone or with other deterioration mechanisms such as blistering and contour scaling. Regardless of the cause, flaking is recorded with one field graphic and schematic.

FIELD GRAPHIC

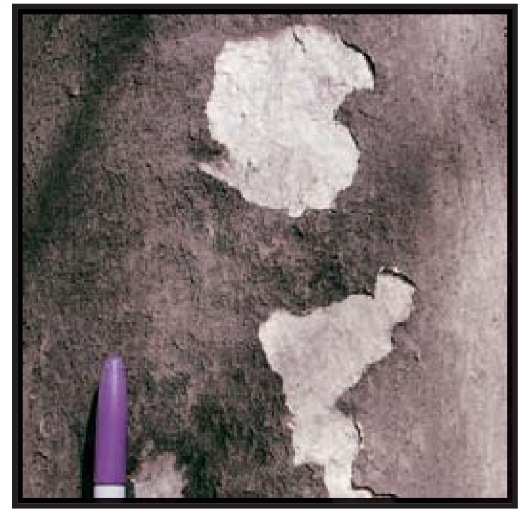


SCHEMATIC

PHOTOGRAPHS



(a) flaking resulting from popped blisters



(a) flaking resulting from popped blisters

(b) general area of flaking

(c) flaking associated with mineral inclusions

MASONRY CONDITIONS GLOSSARY

CONDITION

Contour scaling / Exfoliation

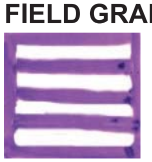
DEFINITION

Distinctive localized or overall patterns of stepped irregular surface loss associated with foliation, where the surface loss is greater than ⅛ inch in depth.

SITE IDENTIFICATION

Contour scaling may occur within a larger area of flaking. These areas generally appear to be topographical in appearance and display noticeable layers of delamination. Contour scaling generally follows the foliation pattern of the stone.

FIELD GRAPHIC



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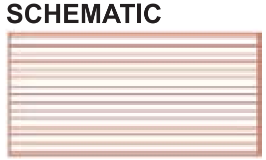


PHOTOGRAPHS

MASONRY CONDITIONS GLOSSARY

CONDITION

Incipient spalling

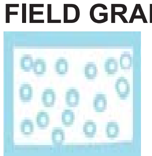
DEFINITION

Localized surface planar discontinuities that have become partially detached from the stone, usually lens-shaped in section. The partially-detached area can be detected visually and audibly by sounding. The angle of separation will be approximately 0-60° from the surface plane of the surrounding stone and usually in association with foliation.

SITE IDENTIFICATION

Incipient spalls are generally found in areas of contour scaling or blistering, as well as on the corners of stones, near cracks, and composite repairs. They are mostly visible on the cornices, drips, capitals and columns. However, when incipient spalls are not visually obvious, the area is tapped.
The hollow sound will indicate if the area is incipient.

FIELD GRAPHIC



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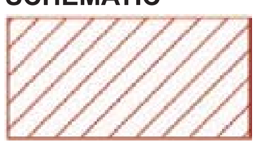
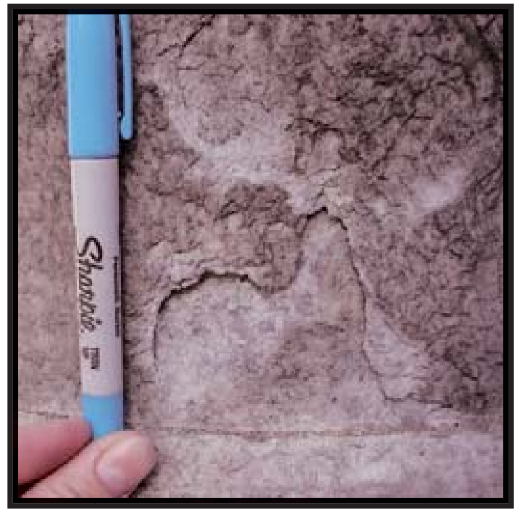


PHOTOGRAPHS



MASONRY CONDITIONS GLOSSARY

CONDITION

Dimensional loss

DEFINITION

Localized stone loss greater than 2 square inches in area and at least ½ inch in depth as measured in plane with the surrounding stone surface. Condition may be in association with conditions other than spall.

SITE IDENTIFICATION

Dimensional loss is most frequently associated with areas of contour scaling.

FIELD GRAPHIC

SCHEMATIC

PHOTOGRAPHS

MASONRY CONDITIONS GLOSSARY

CONDITION

Blistering

DEFINITION

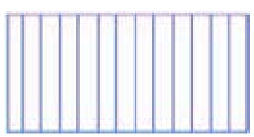
A distinctive deformation of the stone surface in the form of a blister. They appear as smal or large-scaled swelling and/or rupturing of a uniform layer. They can be intact or in the early stages of rupture.

SITE IDENTIFICATION

Active blistering results in fresh clean whitish appearance, while those that have not popped are generally soiled. Overlapping conditions, such as incipient spalls and soiling serve as indicators of activity. Blistering may occur within larger areas of flaking and contour scaling. Blistering is recorded as those blisters that have not popped and those that are in the early stages of popping. Blisters generally appear circular in shape. As with incipient spalling, when blistering is not visually obvious, the area is tapped. A hollow sound indicates if the surface is blistering.

FIELD GRAPHIC

SCHEMATIC



PHOTOGRAPHS

(a) blistering in areas of flaking and contour scaling

(b) blistering along mineral inclusions

small blisters detaching from stone surface

large blister detaching from stone surface

MASONRY CONDITIONS GLOSSARY

CONDITION

Soiling

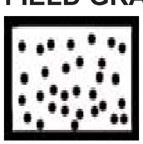
DEFINITION

Dark grey or black coloring of the stone surface.

SITE IDENTIFICATION

Soiling tends to occur in areas not washed by the action of rain. Light soiling due to normal weathering and exposure was not recorded, the darker grey and black soiling was recorded. Soiling generally coincides with other conditions such as blistering, flaking, and contour scaling where dust and other foreign particles are entrapped.

FIELD GRAPHIC



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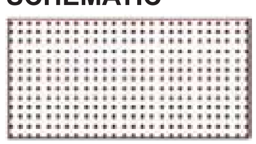

PHOTOGRAPHS

APPENDIX B: Condition Drawings


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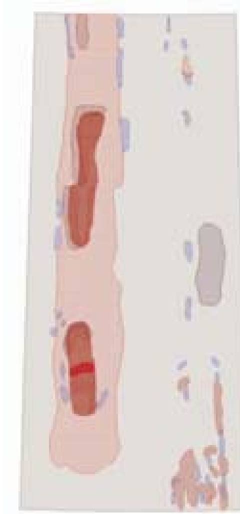
Column 2


Column 3


Column 4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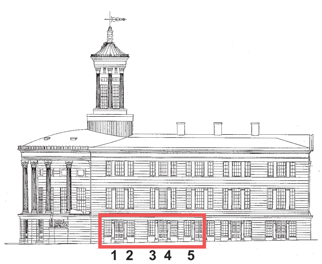

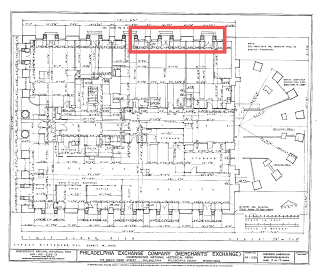

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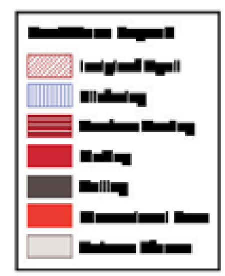

MERCHANTS' EXCHANGE
PHILADELPHIA, PENNSYLVANIA

NORTH ELEVATION
FIRST FLOOR COLUMNS 1-5

Project Sponsors:
Independence National Historical Park

Project Director:
Prof. Frank Matero, Chair Graduate Program in Historic Preservation
Supervising Conservator:
A. Elena Charola, Graduate Program in Historic Preservation
Project Conservator:
Lyles McBratney

MASONRY CONDITION SURVEY

ARCHITECTURAL CONSERVATION LABORATORY AND RESEARCH CENTER
THE GRADUATE PROGRAM IN HISTORIC PRESERVATION, SCHOOL OF DESIGN, THE UNIVERSITY OF PENNSYLVANIA

Site Recording: Fall 2004, Spring 2004
Data Input: Spring 2004

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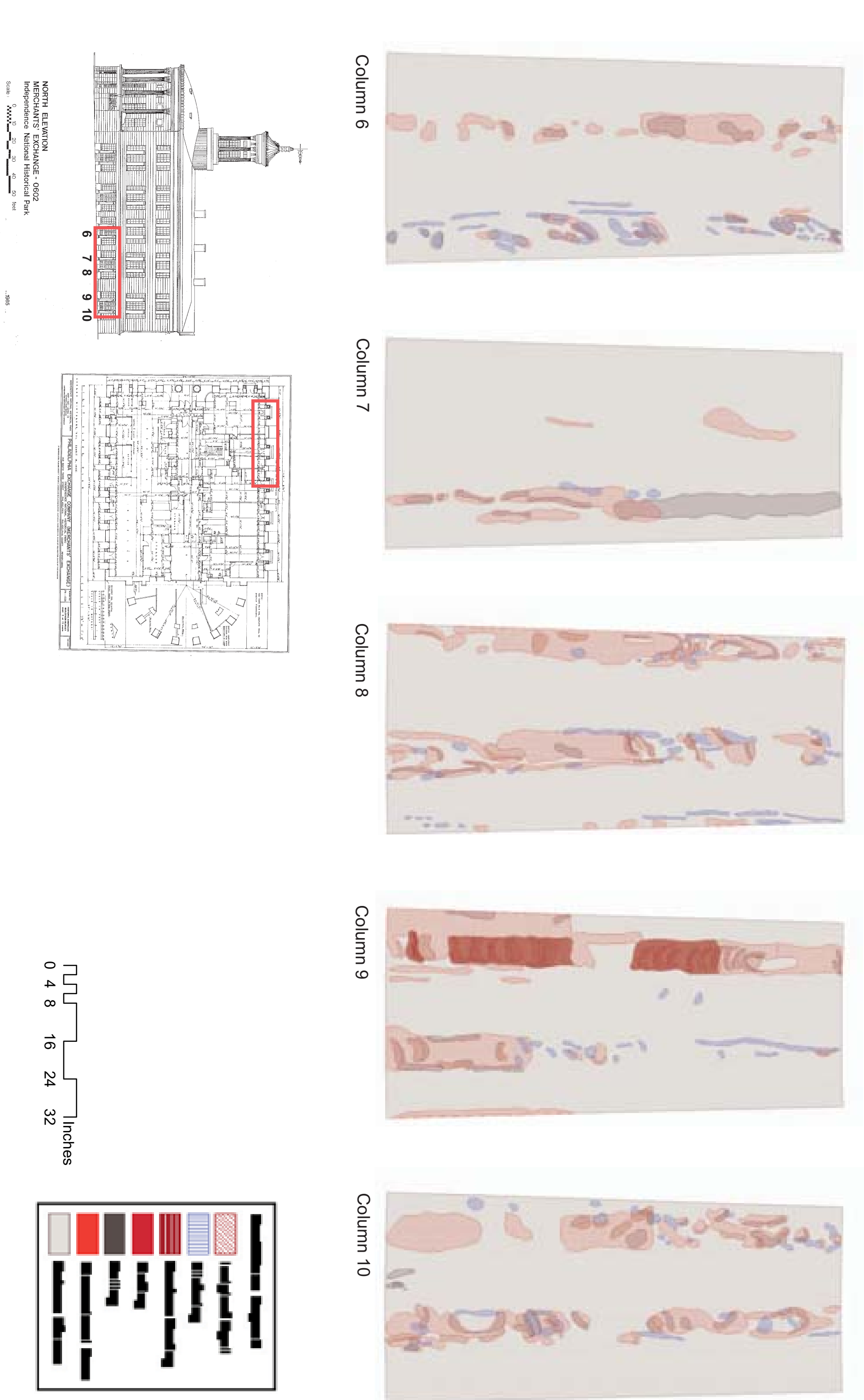

MERCHANTS' EXCHANGE
PHILADELPHIA, PENNSYLVANIA

NORTH ELEVATION
FIRST FLOOR COLUMNS 6-10

Project Sponsors:
Independence National Historical Park

Project Director:
Prof. Frank Matero, Chair Graduate Program in Historic Preservation
Supervising Conservator:
A. Elena Charola, Graduate Program in Historic Preservation
Project Conservator:
Lyles McBratney

MASONRY CONDITION SURVEY

ARCHITECTURAL CONSERVATION LABORATORY AND RESEARCH CENTER
THE GRADUATE PROGRAM IN HISTORIC PRESERVATION, SCHOOL OF DESIGN, THE UNIVERSITY OF PENNSYLVANIA

Site Recording: Fall 2004, Spring 2004
Data Input: Spring 2004

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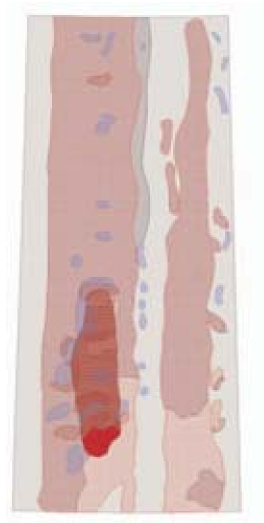

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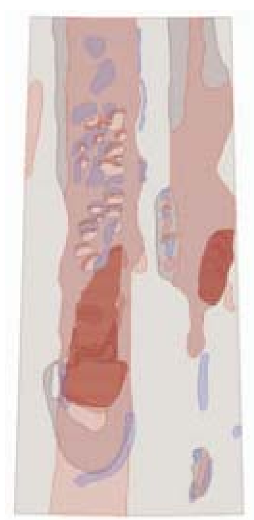

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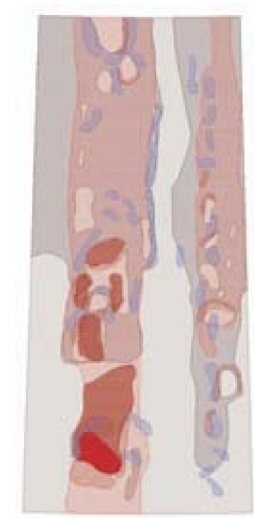

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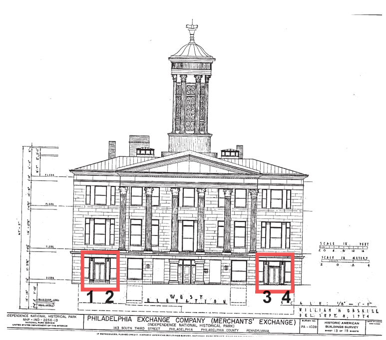

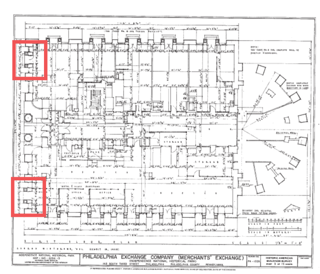

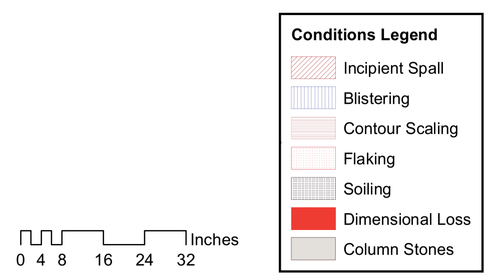

MERCHANTS' EXCHANGE
PHILADELPHIA, PENNSYLVANIA

WEST ELEVATION
FIRST FLOOR COLUMNS 1-4

Project Sponsors:
Independence National Historical Park

Project Director:
Prof. Frank Matero, Chair Graduate Program in Historic Preservation
Supervising Conservator:
A. Elena Charola, Graduate Program in Historic Preservation
Project Conservator:
Lyles McBratney

MASONRY CONDITION SURVEY

ARCHITECTURAL CONSERVATION LABORATORY AND RESEARCH CENTER
THE GRADUATE PROGRAM IN HISTORIC PRESERVATION, SCHOOL OF DESIGN, THE UNIVERSITY OF PENNSYLVANIA

Site Recording: Fall 2004, Spring 2004
Data Input: Spring 2004

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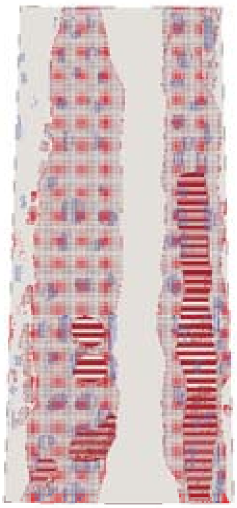
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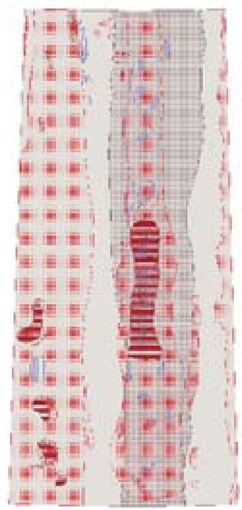
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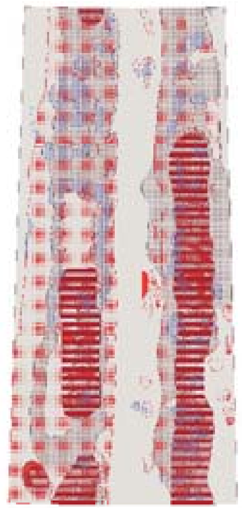
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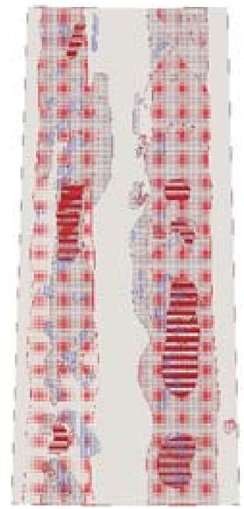
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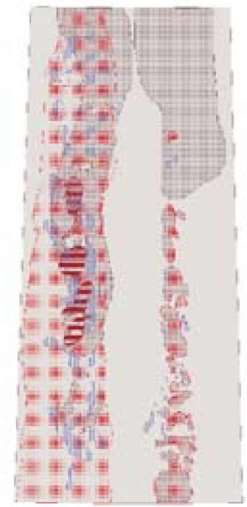
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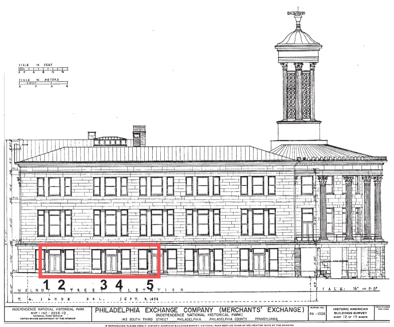
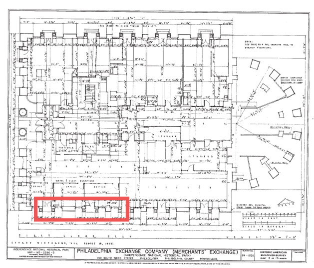
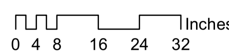






Conditions Legend

- Incipient Spall
- Blistering
- Contour Scaling
- Flaking
- Soiling
- Dimensional Loss
- Column Stones

MERCHANTS' EXCHANGE
PHILADELPHIA, PENNSYLVANIA

SOUTH ELEVATION
FIRST FLOOR COLUMNS 1-5

Project Sponsors:
Independence National Historical Park

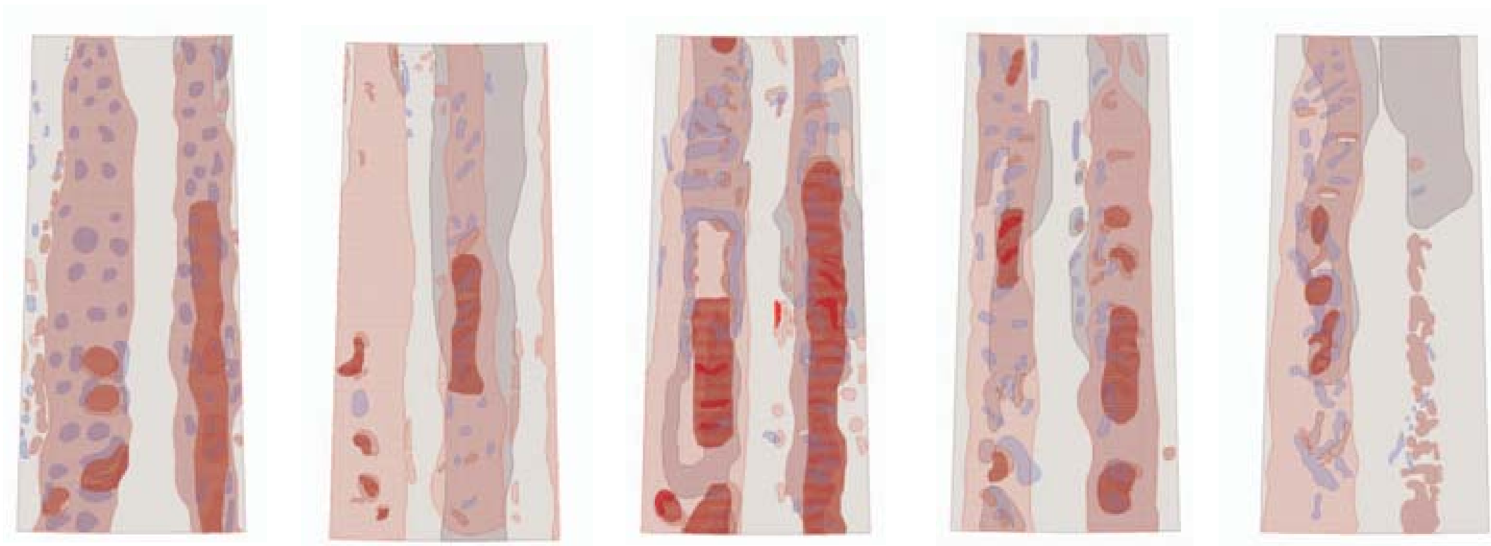
Project Director:
Prof. Frank Matero, Chair Graduate Program in Historic Preservation
Supervising Conservator:
A. Elena Charola, Graduate Program in Historic Preservation
Project Conservator:
Lyles McBratney

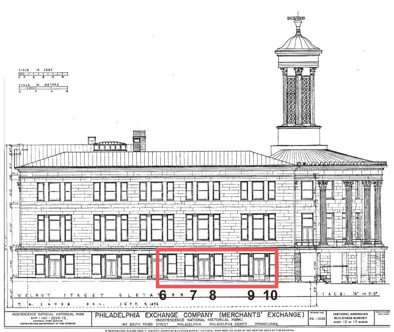
MASONRY CONDITION SURVEY

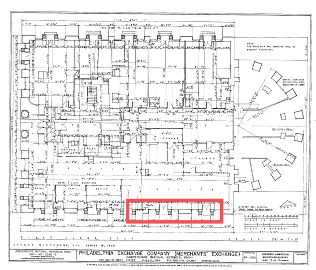
ARCHITECTURAL CONSERVATION LABORATORY AND RESEARCH CENTER
THE GRADUATE PROGRAM IN HISTORIC PRESERVATION, SCHOOL OF DESIGN, THE UNIVERSITY OF PENNSYLVANIA

Site Recording: Fall 2004, Spring 2004
Data Input: Spring 2004

Drawing







0 4 8 16 24 32 Inches

Conditions Legend

- Incipient Spall
- Blistering
- Contour Scaling
- Flaking
- Soiling
- Dimensional Loss
- Column Stones

MERCHANTS' EXCHANGE
PHILADELPHIA, PENNSYLVANIA

SOUTH ELEVATION
FIRST FLOOR COLUMNS 6-10

Project Sponsors:
Independence National Historical Park

Project Director:
Prof. Frank Matero, Chair Graduate Program in Historic Preservation
Supervising Conservator:
A. Elena Charola, Graduate Program in Historic Preservation
Project Conservator:
Lyles McBratney

MASONRY CONDITION SURVEY

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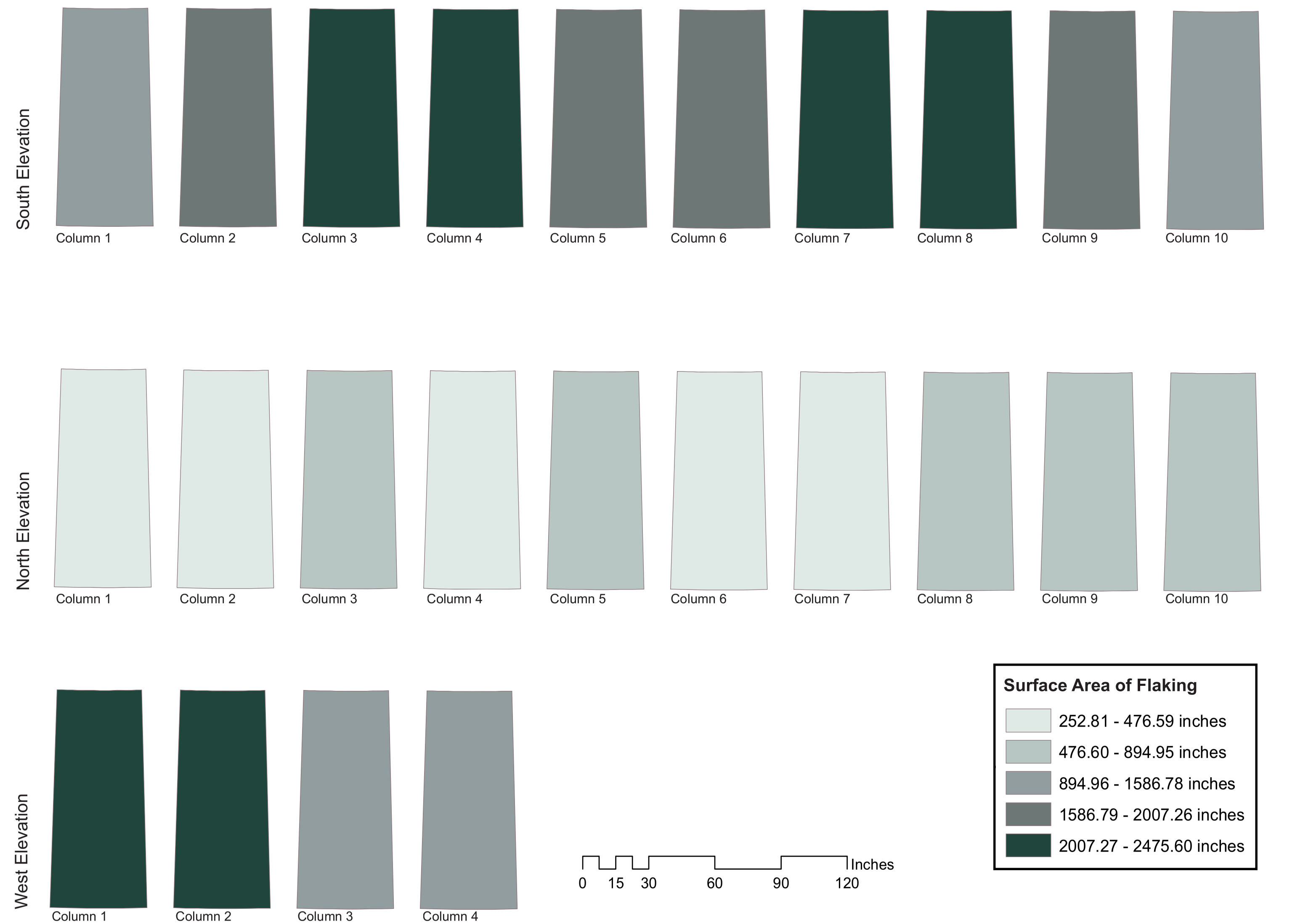
Site Recording: Fall 2004, Spring 2004
Data Input: Spring 2004

Drawing



FIRST FLOOR COLUMNS

MERCHANTS' EXCHANGE
PHILADELPHIA, PENNSYLVANIA

MASONRY CONDITION SURVEY

Project Sponsors:
Independence National Historical Park

Project Director:
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Chair Graduate Program in Historic Preservation
Supervising Conservator:
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Graduate Program in Historic Preservation
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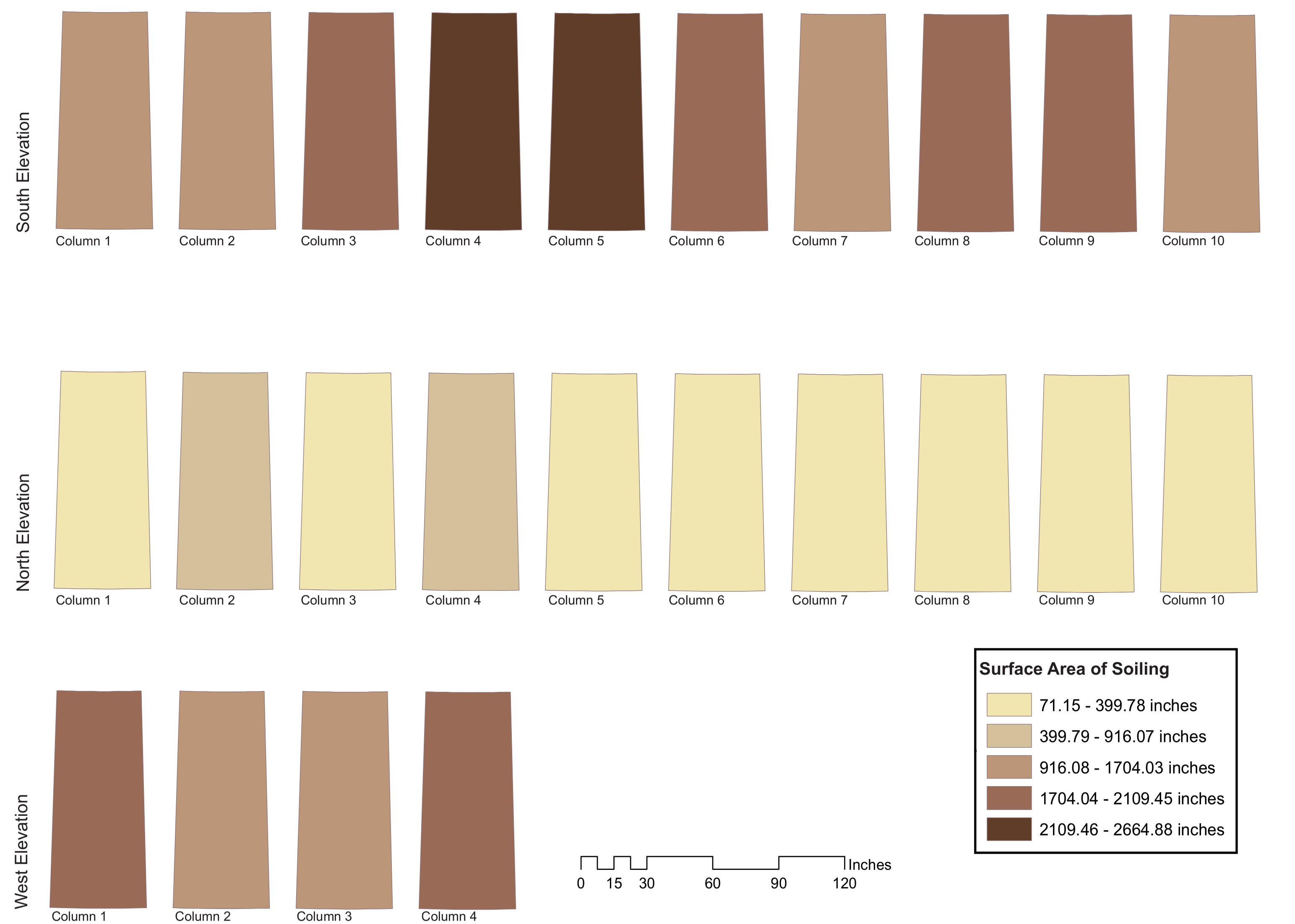
Data Input: Spring 2004

Drawing

ARCHITECTURAL CONSERVATION LABORATORY AND RESEARCH CENTER
THE GRADUATE PROGRAM IN HISTORIC PRESERVATION, SCHOOL OF DESIGN, THE UNIVERSITY OF PENNSYLVANIA



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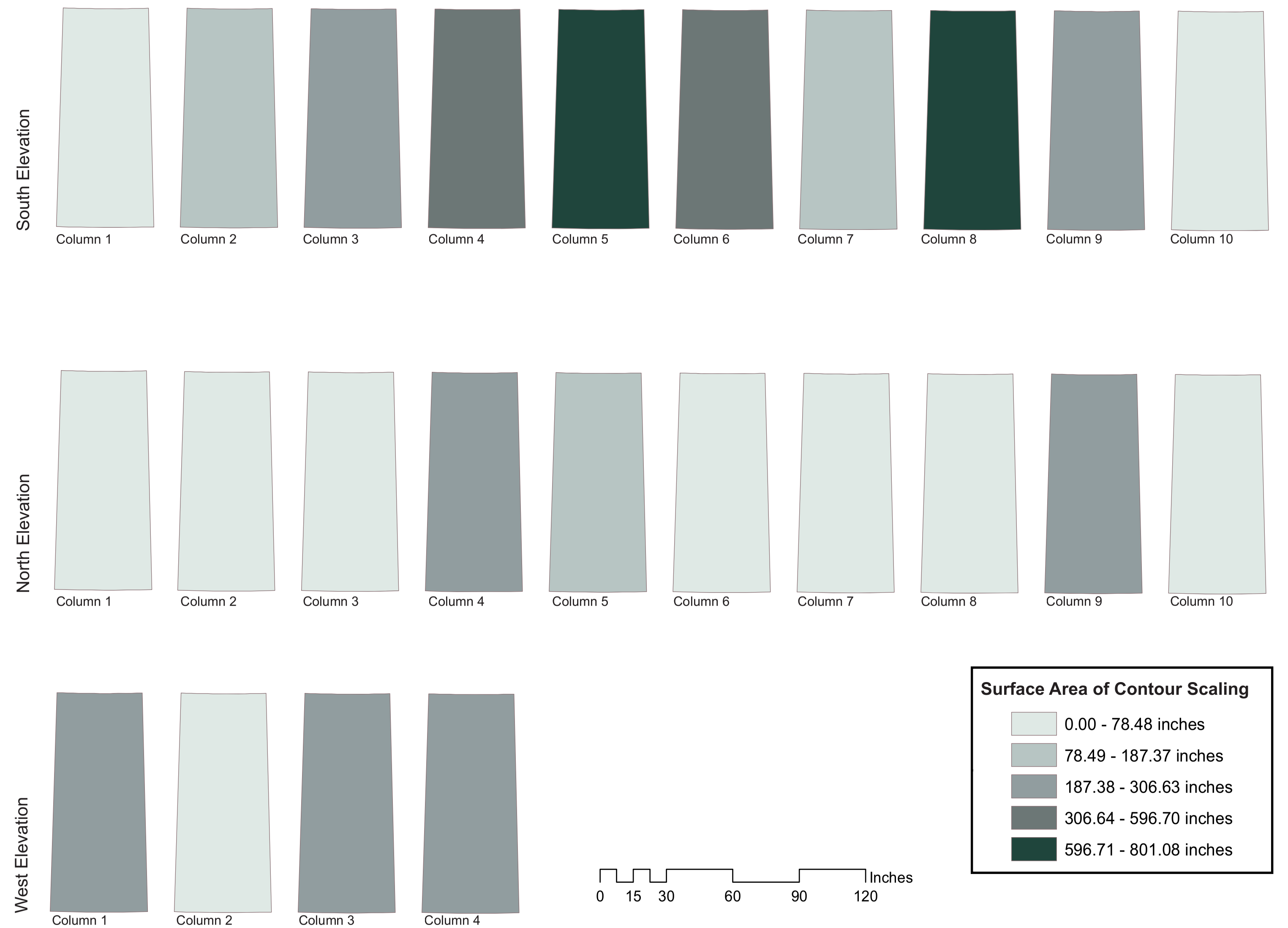

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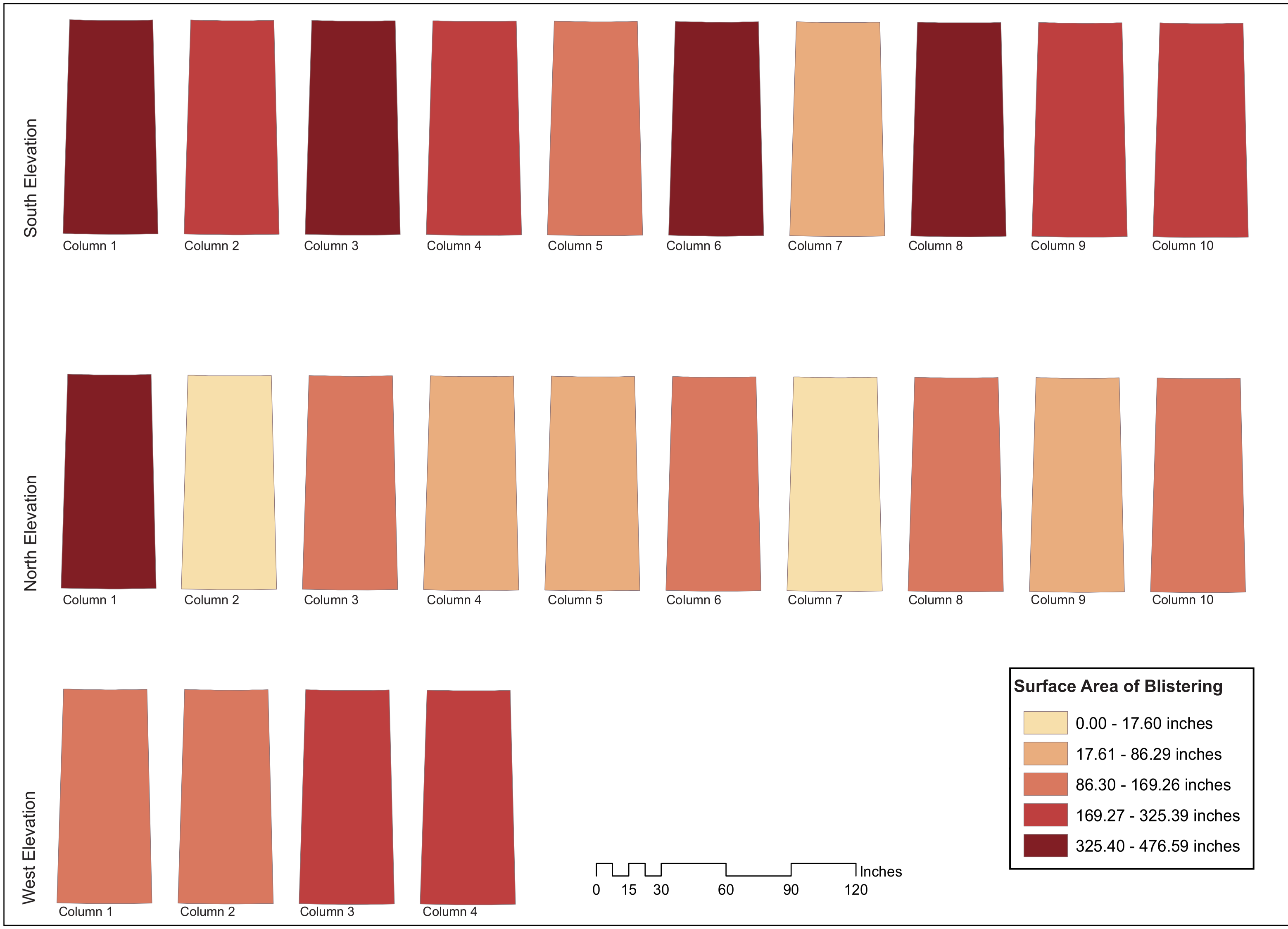

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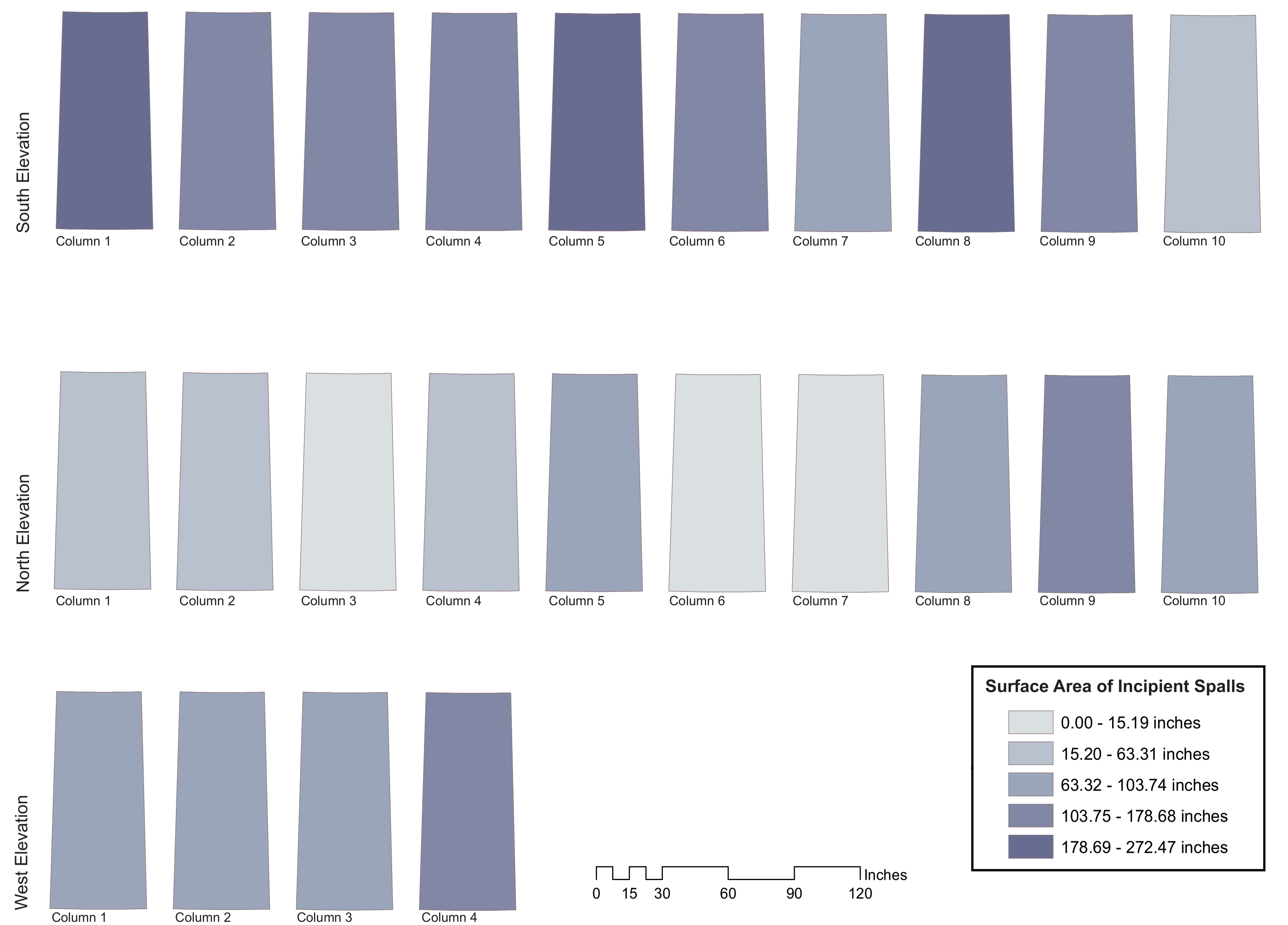

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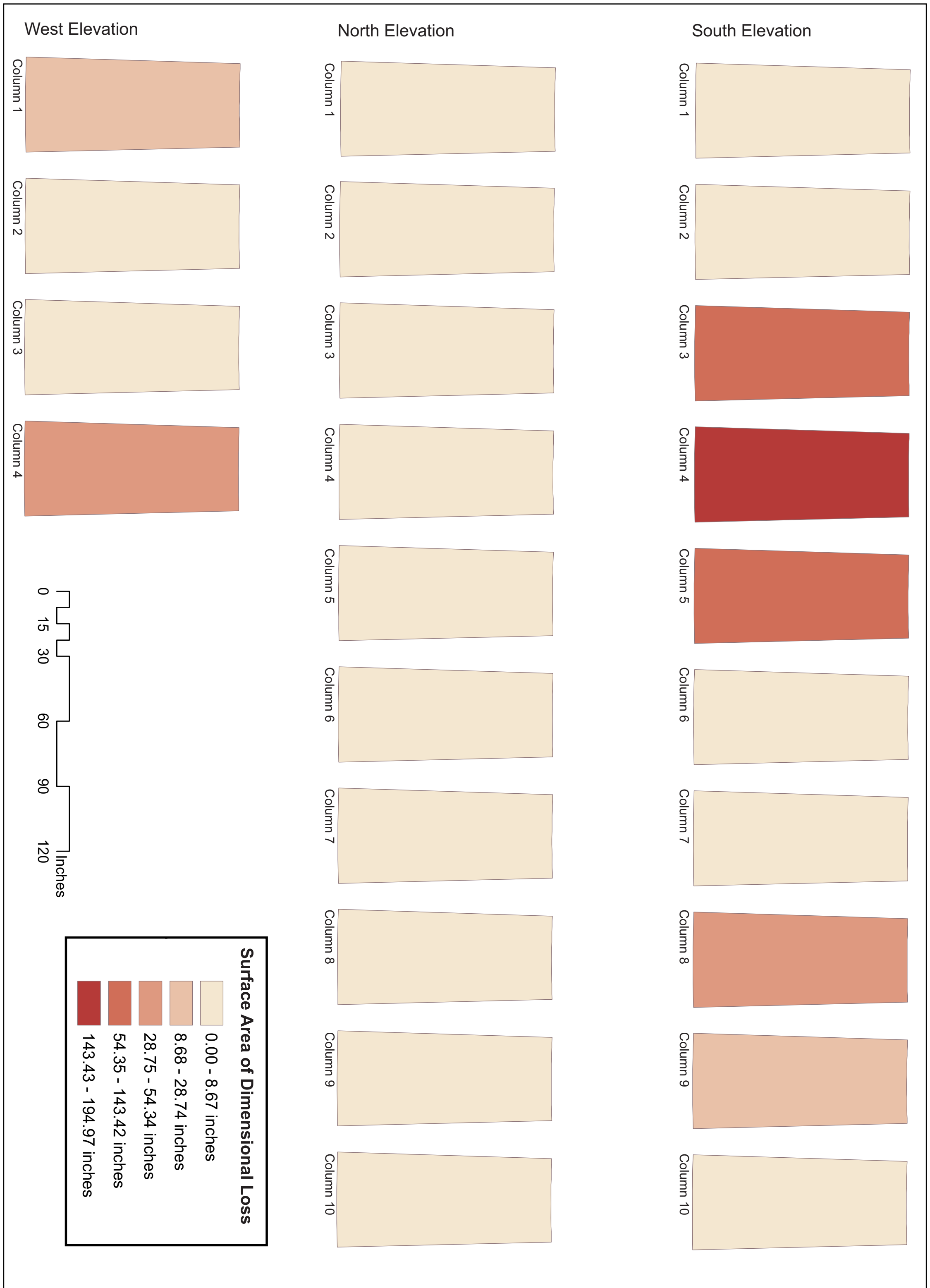

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Site Recording: Fall 2004, Spring 2004
Data Input: Spring 2004

Drawing

APENNDIX C: Additional Historic and Current Photograph Comparisons

Figure C.1:
North elevation , 1975
Source: INHP archives
Color enhanced

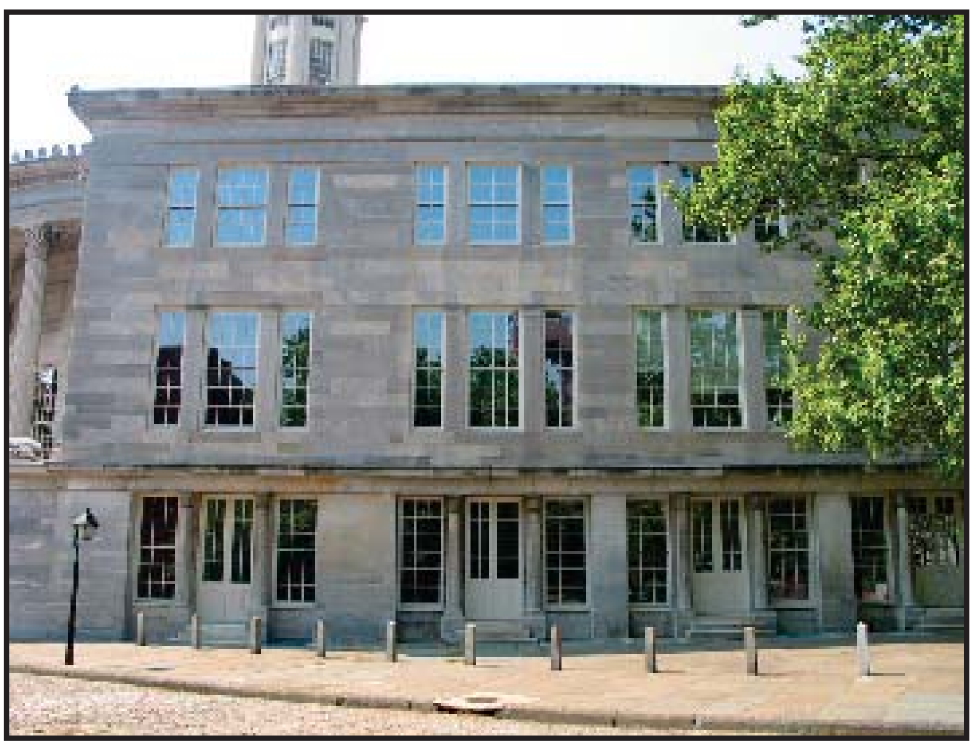

Figure C.2:
North elevation, Summer 2004
Source: University of Pennsylvania

Figure C.3:
North elevation April 1976
Source: INHP Archives

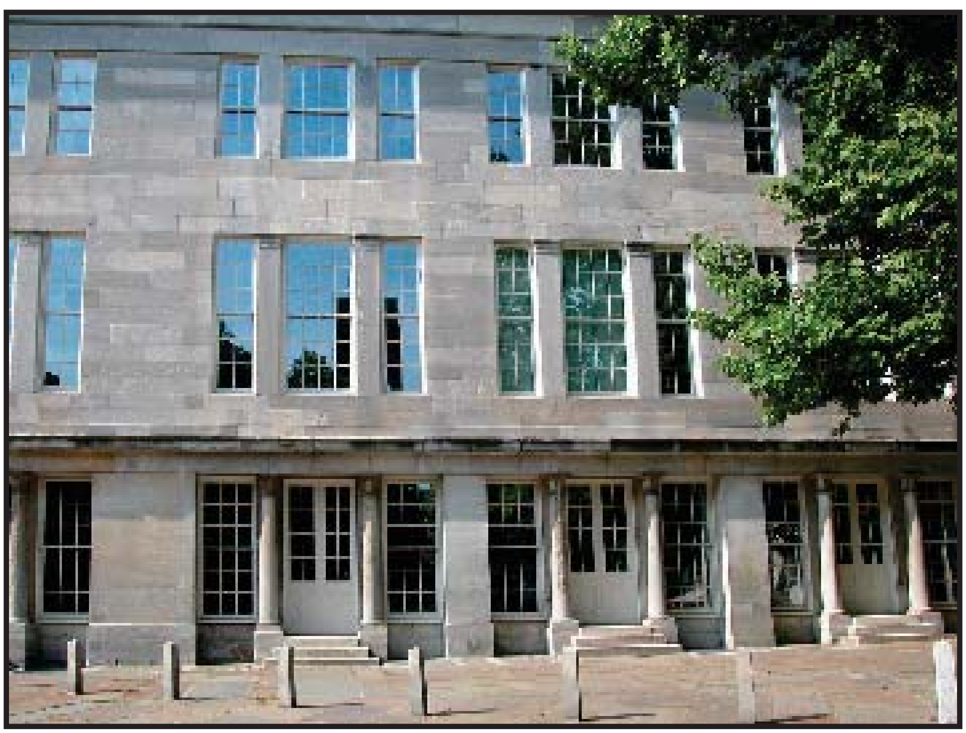

Figure C.4:
North elevation, Summer 2004
Source: University of Pennsylvania

Figure C.5:
North elevation, April 1976
Source: INHP Archives

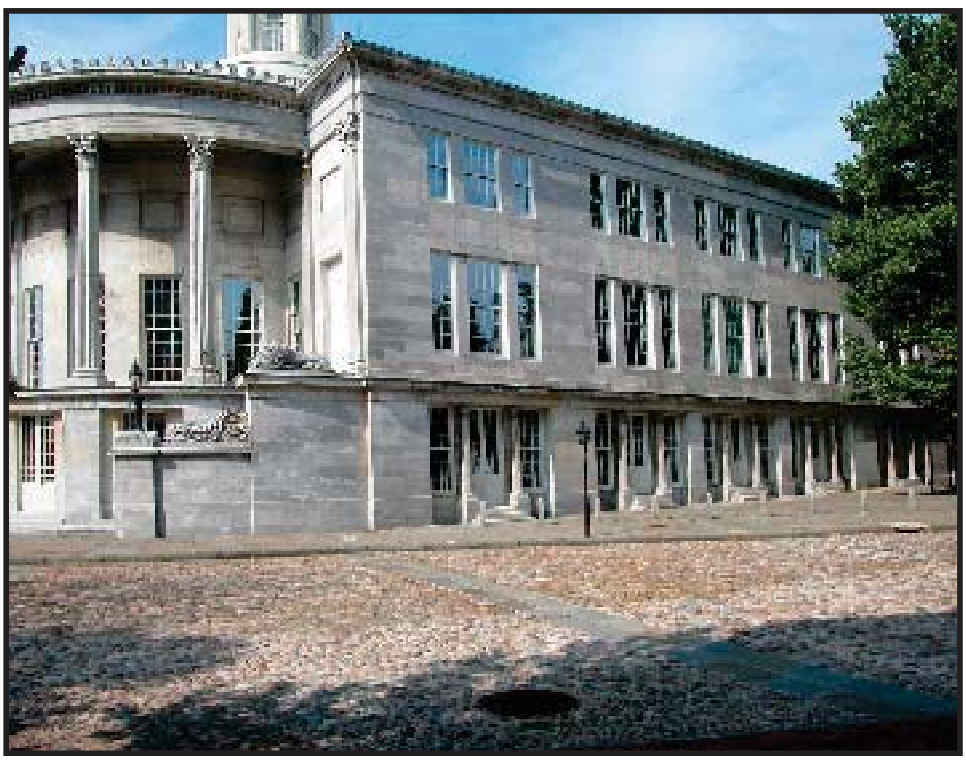

Figure C.6:
North elevation, Summer 2004
Source: University of Pennsylvania

Figure C.7:
North elevation, Ocotber 1975
Source: INHP Archives

Figure C.8:
North elevation, Summer 2004
Source: University of Pennsylvania

Figure C.9:
North elevation first floor, west bay, October 1975?
Columns 9 and 10
Source: INHP Archives

Comments: Column 9 exhibits contour scaling forming u-shaped scales along the length of the column with some mild soiling. Column 10 exhibits flaking and mild soiling in the areas of flaking.

Figure C.10:
North elevation, Summer 2004
Columns 9 and 10
Source: University of Pennsylvania

Comments: Column 9 still exhibits its contour scaling. The deterioration that has occured since 1975 is only slightly advanced.

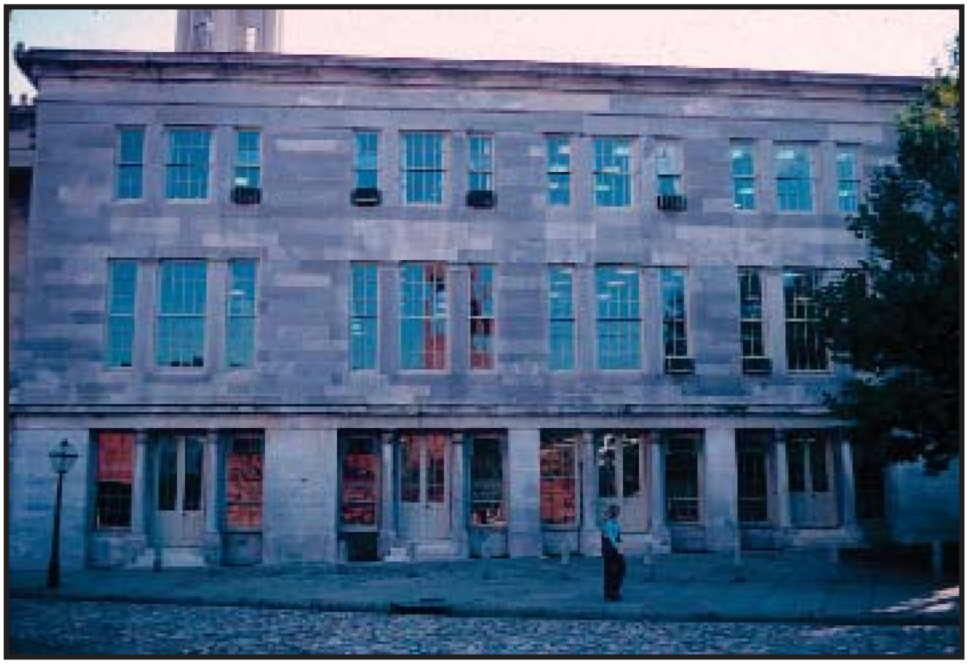

Figure C.11:
North elevation, October 1975?
Source: INHP Archives

Figure C.12:
North elevation, Summer 2004
Source: University of Pennsylvania

Figure C.13:
North elevation, contextual image Source:INHP Archives
Creator: C.E. Peterson Date: April 19, 1960

Figure C.14:
North elevation, Summer 2004
Source: University of Pennsylvania

Comments: The surrounding conditions on the north façade of the Merchants' Exchange have drastically changed. The historic photograph shows a darkened soiled façade behind a gas station with parking next to the building. The current photograph shows that these surroiunding conditions have been removed, Dock Street was blocked off in 1962 and the location of the gas station and parking has been filled with sidewalks and plantings.

Figure C.15:
North elevation, columns 5-10
Source: INHP Archives
Caption: Merchants' Exchange: 2 columns treated by sandblasting and 1 column carved by stone cutter
Creator: Paul J. F. Schumacher
Date: December 2, 1953

Figure C.16:
North elevation, columns 5-10
Summer 2004
Source: University of Pennsylvania

Figure C.17:
North elevation, columns 6-10
Source: INHP Archives
Caption: Merchants' Exchange: 2 columns treated by sandblasting and 1 column carved by stone cutter
Creator: Paul J. F. Schumacher
Date: December 15, 1953

Figure C.18:
North elevation, columns 6-10
Summer 2004
Source: University of Pennsylvania

Figure C.19:
North elevation, column 9
Source: INHP Archives, Historical Society of Philadelphia
Caption: Merchants' Exchange: north elevation, note: deterioration of stonework on column
Creator: PH
Date: February 19, 1957

Figure C.20;
North elevation, column 9
Summer 2004
Source: University of Pennsylvania

Figure C.21:
North elevation, columns 3 and 4 (second bay from the east)
Source: INHP Archives
Caption: Merchants' Exchange – bay deterioration
Creator: W. A. McCullough
Date: March 16, 1961

Figure C.22:
North elevation, columns 3 and 4
Summer 2004
Source: University of Pennsylvania

Figure C.23:
North elevation, columns 1 and 2 (first bay from the east)
Source: INHP Archives
Caption: Merchants' Exchange – bay deterioration
Creator: W. A. McCullough
Date: March 16, 1961

Figure C.24:
North elevation, columns 1 and 2
Summer 2004
Source: University of Pennsylvania
Note on column 1, a composite repair that runs diagonally across the the column that was not present in the historic photograph.

Figure C.25:
Norht elevation, columns 5-8
Source: INHP Archives
Caption: Merchants' Exchange – first level, second and third bays from west
Creator: W. A. McCullough
Date: March 16, 1961

Figure C.26:
Norht elevation, columns 5-8
Summer 2004
Source: University of Pennsylvania

Figure C.27:
North elevation, columns 6-10
Source: INHP Archives
Caption: Merchants’ Exchange – first level, first and second bays from west
Creator: W. A. McCullough
Date: March 16, 1961

Figure C.28:
North elevation, columns 6-10
Summer 2004
Source: University of Pennsylvania

Figure C.29:
North elevation, columns 1-10
Source: INHP Archives
Creator: W. A. McCullough
Date: April 5, 1961

Figure C.30:
North elevation, columns 1-10
Summer 2004
Source: University of Pennsylvania

Figure C.31:
North elevation, columns 7 and 8
Source: INHP Architects' office
Caption: Merchants' Exchange: north side, 2nd bay from street, left-hand capital shown in frames #4&5, shaft repairs also probably performed August 1953 by Louis Milione, see Solon Report Jan. 1978.
Date: November 1983

Figure C.32:
North elevation, columns 7 and 8
Summer 2004
Source: University of Pennsylvania

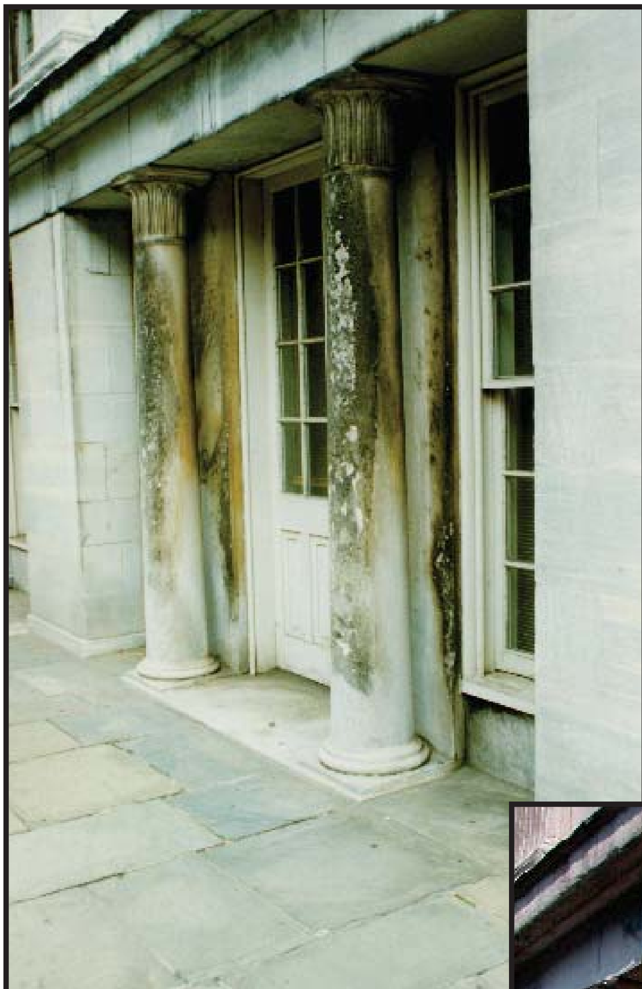

Figure C.33:
West elvation, columns 3 and 4
Source: INHP Architects' office
Caption: Merchants' Exchange: north elevation (not north elevation)
Date: August 1993

Figure C.34:
West elevation, columns 3 and 4
Summer 2004
Source: University of Pennsylvania

Comments: The current photograph appears to have larger area of fresh blistering and flaking that are marked by the absence of soiling on both columns 3 and 4. There seems to be advanced soiling, flaking, and blistering, which can be attributed to the continued vehicular traffic along the west elevation. On column 4, areas that were freshly flaking or blistering in the historic photograph have soiled.

Figure C.35:.
North elevation, columns 1-7, Wrecking of the Produce Stalls
Source:INHP Archives
Creator: Swallow Studios Date: September 24, 1953

Figure C.36:
North elevation, columns 1-7
Summer 2004
Source: University of Pennsylvania

Comments: Notice the re-carved column (#7) in the historic photograph. The produce stalls are being removed, changing the surrounding environmental conditions around the columns. During the wrecking of the produce stalls, possible mechanical damaged could have occurred. Notice the black soiling of the columns in the historic photograph has been removed.

Figure C.37:
South elevation, columns 9 and 10
Source: INHP Archives
Caption: Merchants' Exchange marble deterioration detail
Creator: W. A. McCullough
Date: April 5, 1961

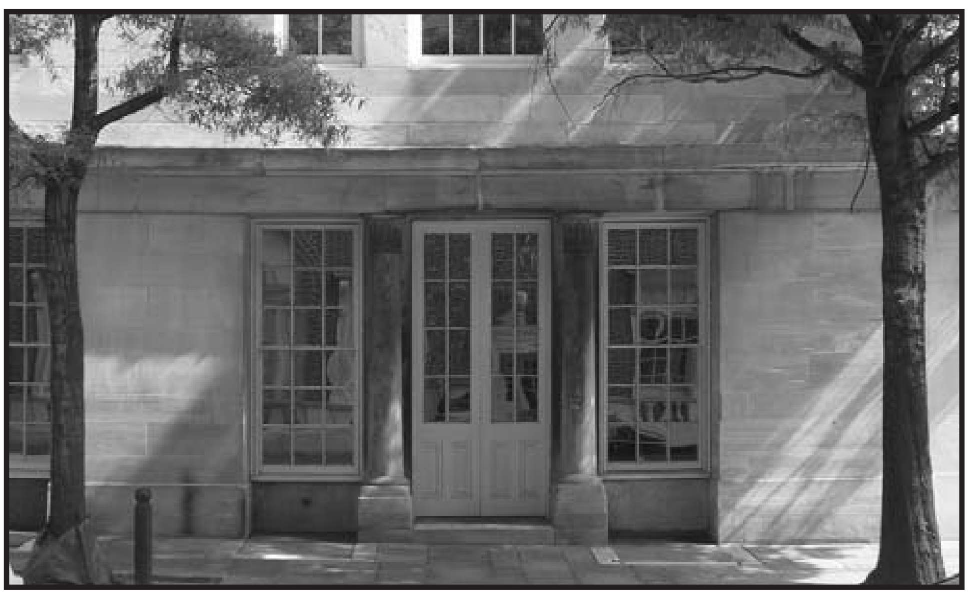

Figure C.38:
South elevation, columns 9 and 10
Summer 2004
Source: University of Pennsylvania

Figure C.39:
Source: INHP Archives; from Hugh Moore Park Collection, Canal Museum, Easton, PA
Creator: W.H. Rau
Date: 1900-1922
Other: original print was printed backward – corrected in photoshop 5/2004

Figure C.40:
Southwest view
Source: INHP Archives
Creator: Leonard Overturf
Date: Spring 1951

Figure C.41:
Southwest façade
Source: INHP Archives
Date: October 30 ,1958,
Creator: W. A. McCullough

Figure C.42:
South elevation
Source: INHP Archives
Date: May 17,1965, W.A.
Creator: McCullough

Figure C.43:
South elevation
Summer 2004
Source: University of Pennsylvania

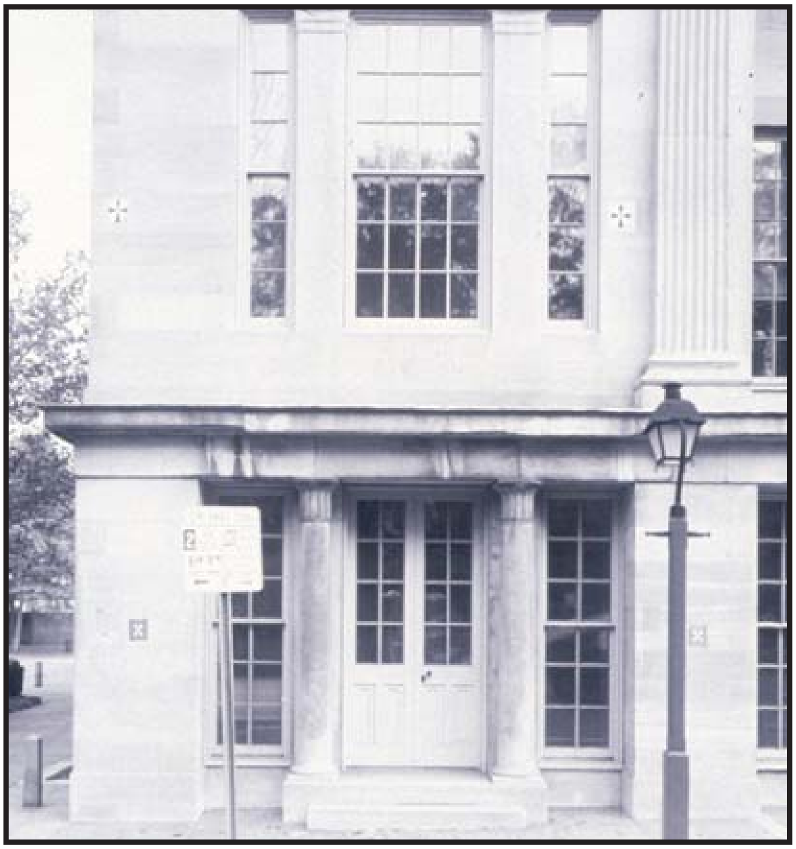

Figure C.44:
West façade at north corner, columns 1 and 2
Source: INHP Archives
Date: October 30, 1958
Creator: W.A. McC.

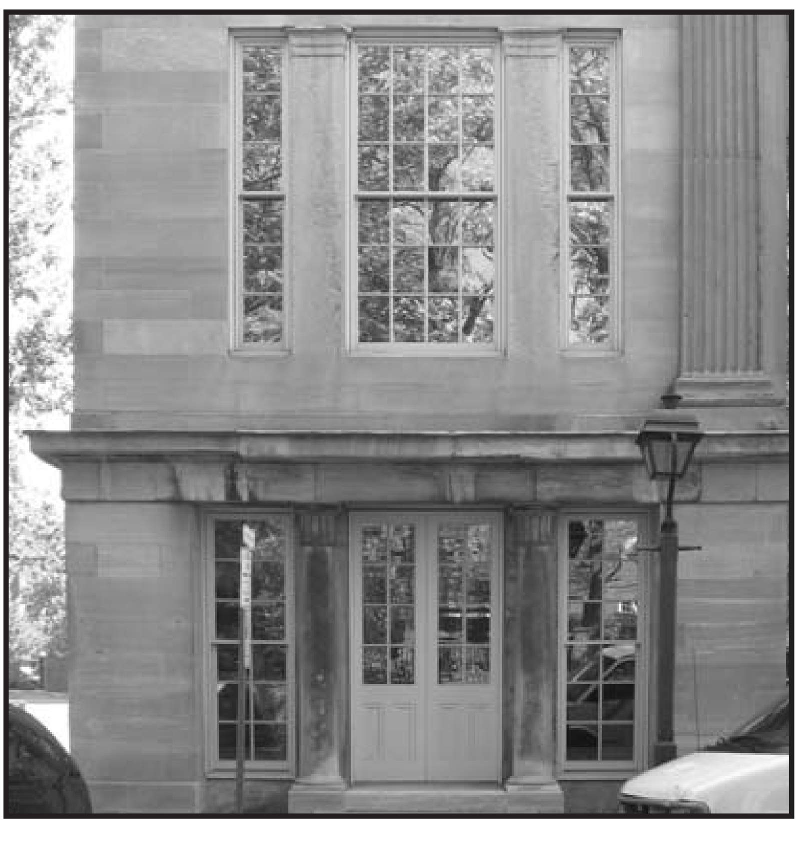

Figure C.45:
West elevation, columns 1 and 2
Summer 2004
Source: University of Pennsylvania

Figure C.46:
South elevation, column 2
Source: INHP Architects' office
Caption: Merchants' Exchange: south elevation column with marble decay and fill
Date: September 1993

Figure C.47:
South elevation, column 2
Winter 2005
Source: University of Pennsylvania

Comments: The most evident deterioration mechanisms shown in the historic photograph are contour scaling and demensional loss. The caption of teh photoraphs mentions a "fill", which is no longer present. There is a clear up-side-down u-shaped pattern of contour scaling which follows the stone's orientation and correlates to the location of mica mineral inclusions. The action of contour scaling is compounded by the presence of salts and freeze-thaw action. This deteriroation pattern is evident in both the historic and current photographs.

Figure C.48:
South elevation, columns 1-10
Source: INHP Archives
Creator: Knickerbocker, N.Y.
Date: March 20, 1952

Figure C.49:
South elevation, columns 1-10
Winter 2005
Source: University of Pennsylvania

The location of a structure on the corner prevented replicating the angle of the historic photograph.

Figure C.50:
South elevation, columns 3 and 4
Source: INHP Archives
Caption: Merchants' Exchange: South wall, second entrance from west end. Detail showing disintegration of first floor marble columns
Creator: Knickerbocker (Housam)
Date: March 20, 1952

Figure C.51:
South elevation, columns 3 and 4
Source: University of Pennsylvania
South wall, second entrance from west end.
Date: Winter 2005

Figure C.52:
South elevation, columns 1-10
Source: INHP Archives
Caption: Merchants' Exchange
Creator: W. A. McCullough
Date: March 16, 1961

Figure C.53:
South elevation, columns 1-10
Source: INHP Archives
Creator: W. A. McCullough
Date: April 5, 1961

Figure C.54:
South elevation, columns 1-10
Source: University of Pennsylvania
Date: Winter 2005

Figure C.55:
South elevation, column 1 and 2 south side – cleaning of column
Source: INHP Archives
Date: 1984?, cleaning of column 2
(The base of column 2 was also treated with barium hydroxide by S. Lewin.)

Figure C.56:
South elevation, column 1 and 2 south side – cleaning of column
Source: University of Pennsylvania
Date: Winter 2005

APPENDIX D: Products and Supplier List

Fisher Scientific

- Barium Hydroxide anhydrous
- Glycerin 83.5-88.5 wt% Aqueous solution

Michael's Craft Store

- Paper pulp: Cotton Linters

University of Pennsylvania Architectural Conservation Lab:

- Japanese paper (test the pH of the pulp in distilled/deionized water to make sure it is neutral) (can also be purchased from Talus supplies)

Home Depot

- Plastic funnels
- Five gallon buckets
- Spray bottles
- Plastic wrap

APPENDIX E: Calculations

Calculations for the preparation of the treatment are as follows:

Molecular weight of Barium Hydroxide octahydrate	315.47
Molecular weight of H_2O	- 144.00
Molecular weight of Barium hydroxide	171.50
Molecular weight of H_2O	+ 18.00
Molecular weight of Barium hydroxide monohydrate	189.50
Molecular weight of Barium hydroxide monohydrate	189.50 = 25 g
Molecular weight of Barium hydroxide anhydrous	171.50 = 22.6 g

226 g / liter x 4 = 900 grams of $Ba(OH)_2$

Based on 900 g $Ba(OH)_2$

2.5 liter of H_2O

900 g $Ba(OH)_2$

1 liter of glycerin

APPENDIX F: Assigned Numerical Values for Ranges of Calculated Surface Area

Flaking:

Calculated Range of Area in Inches	Assigned Numerical Value
252.81-476.59 inches	1
476.60-894.95 inches	2
894.96-1586.78 inches	3
1586.79-2007.26 inches	4
2007.27-2475.60 inches	5

Soiling:

Calculated Range of Area in Inches	Assigned Numerical Value
71.15-399.78 inches	1
399.79-916.07 inches	2
916.08-1704.03 inches	3
1704.03-2109.45 inches	4
2109.46-2664.88 inches	5

Contour Scaling:

Calculated Range of Area in Inches	Assigned Numerical Value
0.00-78.48 inches	1
78.49-187.37 inches	2
187.38-306.63 inches	3
306.64-596.70 inches	4
596.71-801.08 inches	5

Blistering:

Calculated Range of Area in Inches	Assigned Numerical Value
0.00-17.60 inches	1
17.61-86.29 inches	2
86.30-169.26 inches	3
169.27-325.39 inches	4

325.40-476.59 inches	5

Dimensional Loss:

Calculated Range of Area in Inches	Assigned Numerical Value
0.00-8.67 inches	1
8.68-28.74 inches	2
28.75-54.34 inches	3
54.35-143.42 inches	4
143.43-194.97 inches	5

Incipient Spalls:

Calculated Range of Area in Inches	Assigned Numerical Value
0.00-15.19 inches	1
15.20-63.31 inches	2
63.32-103.74 inches	3
103.75-178.68 inches	4
178.69-272.47 inches	5

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