DEPARTMENT OF THE INTERIOR

U. S. GEOLOGICAL SURVEY

Philadelphia Merchants' Exchange Conservation Strategy: Marble Characteristics and Deterioration

by

Elaine S. McGee

U. S. Geological Survey, Mail Stop 953, Reston VA 22092

Open-File Report 96-579

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards. Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S.G.S.

1996

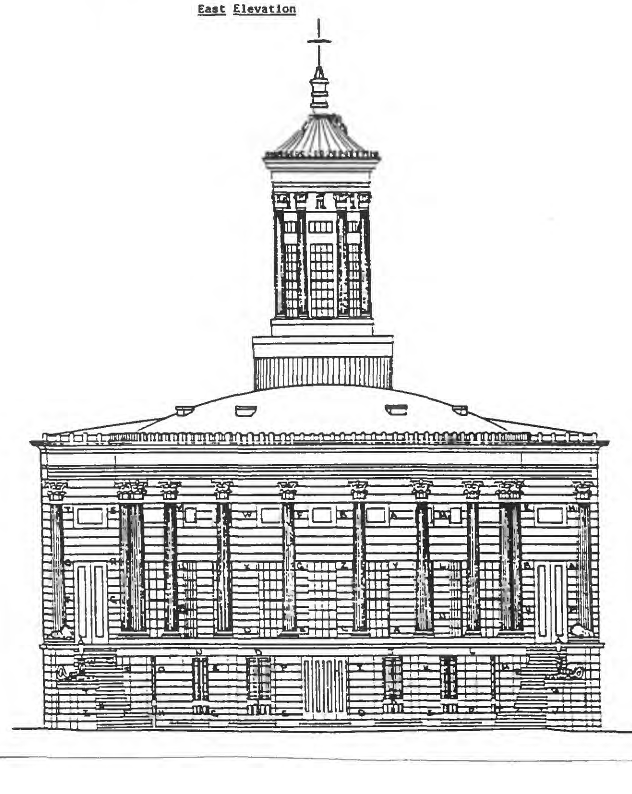
Philadelphia Merchants' Exchange Conservation Strategy:
Marble Characteristics and Deterioration

INTRODUCTION

The Philadelphia Merchants' Exchange was built in 1834 for the Philadelphia Exchange Company. For many years the classically designed marble building was used for various commercial purposes, and a number of modifications were made to William Strickland's original design. In 1952, the building was purchased by the National Park Service and it is now a part of Independence National Historic Park in central Philadelphia.

One of the park's objectives for the building is to preserve the historic structure and to interpret its historical and architectural significance to park visitors. In 1986 the park began a detailed study of the building in order to develop a strategy for preserving and restoring the building. A multifaceted study was carried out by a group of researchers who documented and monitored conditions at the building. In 1992 a Conservation Strategy Meeting was held to present the results of the various studies to a panel of conservation experts and National Park Service managers. One aim of the meeting was to develop a plan, based on the research, that would help the park preserve this historic structure. A draft document was prepared for participants at the meeting. The document covered the following topics: Building History and Alterations; Marble Characteristics and Deterioration; Photogrammetric Description of Marble Decay; Environmental Exposure; Implications of Building History, Exposure and Weathering Patterns; and Conservation Treatment Options. The intent was that after the meeting, when a specific plan had been developed, the document prepared for the meeting would be published, along with the plan for addressing the conservation issues at the building. This paper is the chapter (and related appendix) from the draft document, which describes the marble and its deterioration at the Merchants' Exchange.

East Elevation



Chapter 2: MARBLE CHARACTERISTICS AND DETERIORATION

by Elaine S. McGee

The chemical and physical characteristics of the stone used in a building influence the nature and rate of deterioration and are important in choosing appropriate treatments for deteriorated stone. The Philadelphia Merchants' Exchange is composed of three marbles. A local marble from Pennsylvania and Carrara marble from Italy were used in original construction. A marble from Georgia was used in the 1960s restoration. While the marbles are predominantly composed of calcite, they differ in the amount and type of inclusions, grain size distribution, and original stone fabric. These characteristics may influence the manner in which the marbles deteriorate and may also influence the effectiveness of treatments that may be applied to the deteriorated stone.

The form of visible deterioration of the marble varies. The architectural features have weathered differently; sheltered and exposed areas show pronounced contrast in the form of deterioration, and some of the decay appears to correlate with position around the building. The varied types of deterioration suggest that specific treatments are required for each particular type of stone deterioration.

DESCRIPTION OF THE STONE

Most of the Merchants' Exchange is blue-gray marble from Pennsylvania, but the more intricately carved column and pilaster capitals are made of marble imported from Carrara, Italy. Marble from Georgia that has a mottled appearance somewhat similar to the Pennsylvania marble was used for the replacement stairs on the east facade during the building renovation in 1964. This study has focused only on the characteristics and deterioration of the original Pennsylvania and Carrara marbles. Both of these marbles show dramatic deterioration.

Marble is a metamorphic rock, predominantly composed of the mineral calcite (calcium carbonate). Three characteristics of marble may contribute to variations in the appearance and durability of different marbles: 1) the presence of mineral inclusions, 2) the grain size of the calcite, and 3) how strongly the marble was metamorphosed (recrystallized) during its original formation. Inclusions in marble occur as isolated grains or as clusters that form streaks or swirls of contrasting color in the stone. Mineral inclusions tend to weather differently than the calcite. The boundaries between calcite grains and inclusions may also permit easier penetration of water into the stone than inclusion-free areas, and thus contribute to the stone deterioration. Grain size and texture of the marble reflect its formation; weakly metamorphosed stone will have a range of grain sizes and shapes resulting in a loose texture, with many inclusions, whereas more strongly metamorphosed marble will be tightly compacted and the recrystallized calcite will be tightly locked together. Although fine grain size presents more surface area in the stone, coarse grain size has been cited as contributing to marble deterioration (Julian, 1884), possibly because loose-textured, coarse-grained marbles permit greater accessibility of water than fine grained marbles (Dale, 1912).

Pennsylvania Marble

The Pennsylvania marble was quarried in nearby Montgomery County, of southeastern Pennsylvania, from the Conestoga Limestone which ranges in age from Middle Cambrian(?) to Early Ordivician(?). Trade names "King of Prussia marble" or "Pennsylvania Blue marble" were used for this stone. The quarries were opened around the time of the American Revolution and the marble was used widely for buildings in and around Philadelphia until about 1840, when marbles from other eastern states became more readily available (Merrill, 1889). Both white and blue marbles were quarried near King of Prussia, Pennsylvania (Stone, 1932). Marble from these quarries has been described as "beautiful coarse grained marble, white, gray, blue and mottled" (Miller, 1934) and "...light blue, semi-crystalline texture, with signs of irregular stratification, evenly bedded, and in medium to thick courses" (Census, 1884). Bascom and others (1909) describe the marble as a white or blue magnesian limestone that is highly siliceous. It varies from blue to white within one quarry, contains disseminated inclusions of quartz, feldspar, phlogopite, graphite, pyrite, and siderite, and it may have calcite and quartz veins (Bascom et al, 1909). Marble from Montgomery County quarries is described in the 10th U.S. Census Report (Census, 1884) as "distinguished from other marbles in use here [Philadelphia] by its bluish color and coarser texture...". Some of the many public buildings constructed in Philadelphia of Montgomery County marble include Girard Bank (1798), United States Custom-House (1819), United States Mint (1829), United States Naval Asylum (1830), Philadelphia Merchants' Exchange (1832), and Girard College (1833). After 1840, the stone was used mostly for sills, ledges, and curbing in the Philadelphia area.

Park archives contain the business records of the Henderson Quarry. They document that the marble used in the Exchange came from the Henderson Quarry, located west of the Schuylkill River near King of Prussia; about one half mile south of Henderson Station in Montgomery County, Pennsylvania. The Henderson Quarry was one of the principal quarries in the marble beds located in Upper Merion Township of Montgomery County (Hall, 1881). The marble beds are located near the southern margin of the limestone area and near an area of slate and limestone alternations (Hall, 1881). Miller (1934) gives the following description of the stone from the Henderson Quarry:

> The stone in this property consists of interbedded coarsely crystalline white to white and light blue banded or mottled marble in parallel beds interbedded with dark blue to black hard silicious dolomite. The strata have a strike of approximately east-west and dip about 60° S. The largest and most southern bed worked varies from 20 to 25 feet in thickness. It is underlain by 30 feet of silicious dolomite and then the second marble bed formerly worked is found. It is similar to the first marble band; but only 10 to 12 feet thick.

The Pennsylvania marble used in the Exchange is predominantly blue gray in color but in some areas it has a mottled, streaked appearance of light gray or blue gray areas with white. There is no regularity to the streak pattern and generally the mottling is neither large nor continuous, but streaks are more apparent on flat wall areas than on carved features. The stone is weakly metamorphosed; it contains abundant micaceous inclusions and the calcite is not strongly recrystallized. The marble is loosely textured, with a marked foliation (or planar) fabric forming a series of parallel planes that are weakly held together. The loose texture and pronounced foliation of this marble have been accentuated by exposure, as weathering and deterioration have concentrated at weak points in the stone. Light blue gray calcite is the dominant mineral in this stone; the longest dimension of the grains range from about 40 mm to 1060 mm, but most grains are 100 to 400 mm (Figure 14). The calcite grains are angular to subrounded in shape (Figure 15a) and are nearly pure $CaCO_3$, with minor amounts of magnesium and a trace of iron (Table 1). Muscovite (a mica) 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. Muscovite occurs as small (10-50 mm) isolated grains and in linear clusters, often with apatite. Small grains of muscovite are commonly found still attached to loose grains of calcite (Figure 16) that have disaggregated from exposure. Minor pyrite, sphene, zircon, and tourmaline are also present in inclusion rich areas.

Carrara Marble

Carrara marble from the Adriatic coast in northern Italy has been widely used for statuary and buildings since Roman times. The marble, produced by a number of quarries near the town of Carrara, is varied in appearance and abundant (Merrill, 1889). It has been noted and admired for its appearance, particularly for the fine grained and lustrous varieties that could be delicately carved. Many descriptions of marble in the literature compare the qualities of other marbles to marble from Carrara, but few are able to measure up to it, as illustrated by the following quote from Burnham (1883, p. 49). "The white, statuary marble of this State [Vermont] has been compared to the Carrara of Italy, but any marble-worker knows that the latter is greatly superior to the former for art purposes. It is softer, more translucent, and freer from siliceous and other foreign substances."

The Carrara marble used in the Philadelphia Merchants' Exchange is quite homogeneous in texture and mineralogy, although weathering has obscured the original character. It is even grained and tightly textured, suggesting that it was strongly metamorphosed. The Carrara marble consists almost entirely of calcite with a few rare inclusions of muscovite mica that form thin, light gray veins. The calcite is of nearly pure $CaCO_3$, containing only minor amounts of magnesium (Table 1). The calcite is beige to light buff in color but it was probably originally white (Dean, 1988). The grains are angular to subrounded in shape (Figure 15b), and vary in size from about 60 mm to 1120 mm in diameter, with most grains between 200 and 500 mm in diameter (Figure 14). The stone has a slight, subtle foliation, reflected in the alignment of the slightly elongate calcite grains. The foliation, however, does not appear to be significant in the weathering response of the stone; the Carrara marble has weathered evenly but shows pronounced deterioration effects from extremes in exposure to and sheltering from water.

DETERIORATION OF MARBLE

When stone is exposed to the effects of wind, rain, and temperature, weaknesses in the stone are attacked by a combination of chemical, physical, and biological processes. In an urban setting, these deterioration processes may be exaggerated by contributions from pollutants. Marble is particularly susceptible to the effects of both weather and pollutants because it is predominantly composed of the mineral calcite (calcium carbonate). Calcite readily dissolves in weak acids such as carbonic acid (that forms from carbon dioxide plus water in air) and sulfuric and nitric acids. Calcite will also react with sulfur dioxide gas and moisture in the air to form the alteration mineral phase, gypsum (hydrated calcium sulfate). Two forms of pollutant-accelerated decay are recognized on marble buildings; those resulting from dissolution, and those resulting from chemical alteration of the stone. Dissolution effects are seen in stone exposed to washing by rain. Because gypsum is very soluble in water, it does not tend to accumulate where it is exposed to water; thus surficial alteration crusts tend to form in rain-sheltered areas (Amoroso and Fassina, 1983).

Carved details are particularly vulnerable to dissolution deterioration because of the number of facets and sharp edges presented to rain. The edges are readily rounded as water flows over the stone; here the loss of individual grains is most likely to occur. The carved surfaces also experience more turbulent flows around the edges and over the surface of the stone, thus increasing the impact of dissolution to the stone (Sherwood et al, 1990). The effects of dissolution are visible in the loss of sharp edges, softening of carved details, and sugaring (a loosening of individual grains) and subsequent loss, making the surface rough. Two other forms of deterioration which may begin with dissolution of the calcite grains and then be exacerbated by temperature and freeze-thaw cycles include splitting of the stone along foliation planes and loss of partial or entire architectural details.

Carved details are also particularly vulnerable to alteration deterioration because the shape of the surface (with nooks and crannies) allows moisture to linger, and thus promotes gypsum growth in the restricted and protected areas. As the alteration crusts grow thicker, cracks are likely to develop. When portions of the encrusted features crack, there is significant and irreparable loss. The process by which the stone beneath these crusts disaggregates is not yet understood, but the thickest crusts seem to cover the most severely affected stone.

Dissolution

Various architectural details at the Exchange have suffered from dissolution deterioration that varies with the exposure to rain. The antefixes are the architectural detail most fully exposed to rain. Roughened surfaces and loss of much of the carved detail on the antefix faces (see Plate 9) are typical features of dissolution deterioration that result from the full exposure as well as from characteristics of the stone. Although some antefixes show preferential weathering around inclusions (see Plate 9), most have suffered from a more general loss of stone material. The natural foliation of the marble has led to a common form of antefix deterioration; thin layers of stone spalled along weakened foliation planes on the backs of the antefixes (Figure 17).

The columns and capitals show the most dramatic deterioration (Figure 18). Many of the exterior volutes on the east facade column capitals are missing, as are much of the carved details between the volutes. Where the volutes are fully exposed to washing from rain, the surface is whitened and covered with loosened grains of calcite. The Carrara marble in the capitals has weathered homogeneously with no indication of preferential loss of inclusions. The

Pennsylvania marble columns have nearly all lost the upper edge of the flutes in exposed areas. On the outward facing sides of the column shaft, the arrises no longer have smooth surfaces or sharp edges; the surface is sugared and rough, and the arrises are rounded or wavy where the stone has split along the foliation that runs vertically in the column (Figure 19). Around a given column, the impact from dissolution on the stone integrity is quite notable; zones of rain-exposed and rain-sheltered flutes can be readily identified (Figure 20) and mapped (see Chapter 5). Dissolution effects on the column bases are far less pronounced than on the shafts, possibly because on the bases the foliation in the stone is horizontal or because there may be less variation in the stone selected for bases.

In contrast to the other fully exposed marble at the Exchange, the condition of the lion statues is quite good. Carved details are softened but recognizable. The stone surface is slightly roughened but is not as markedly sugared as the columns. This apparent resistance to dissolution effects may be due to difference in stone characteristics; the stone from which the lions were carved has a tighter petrographic fabric than some of the other stone in the Exchange. In addition, the lions may also have had a more limited exposure to the elements.

Dentils and the upper sections of walls are partially sheltered by the roof overhang and thus show little evidence of dissolution deterioration. Dentils on the east facade, however, have slightly rounded edges and very rounded lower corners and have lost tooling marks in some cases. The walls show little impact from dissolution, except perhaps for a slight rounding of the original tool marks on the stone.

Alteration

Chemical alteration of the Pennsylvania and Carrara marbles at the Exchange is manifested by the blackening or discoloration of the surface. The alteration crusts vary in appearance from soft thin orange crusts (Figure 21) to thick, hard black crusts (Figure 22). Under the microscope, the thinnest crusts appear as an opaque orange glaze that obscures the underlying marble; randomly scattered fine black particles on the surface of the glaze are the only discernible feature. Black crusts appear as rough hummocky surfaces covered by fine black particles; the marble is fully obscured by the dirt. X-ray diffraction and scanning electron microscopy with energy dispersive X-ray analysis show that both types of crusts are predominantly composed of gypsum (Appendix A). The gypsum in the alteration crusts consists of elongate crystals that range in shape from blocky, rectangular blades to thin needle-like crystals (Figure 23a). The elongate crystal habit and the random orientation of the gypsum crystals on the marble surface forms a mat that traps airborne particles (Figure 23b) giving a blackened appearance to the crust.

The major difference between the orange and black crusts is in the abundance and diversity of particles trapped in the network of gypsum crystals. X-ray diffraction analysis showed gypsum, calcite, and quartz present in the black crusts and gypsum, calcite, and fluorite(?) (a possible residue from cleaning) present in the orange crusts (Appendix A). Scanning electron microscopy reveals an abundance of mineral fragments, organic material (e.g., pollen), dirt, and pollutant particles trapped in the black crusts. There are fewer particles overall and less dirt in the orange crusts. The gypsum in orange and black crusts also differ. The gypsum crystals in the black crusts are 10 - 15 mm long and 1 - 2 mm wide, and they have grown at random angles forming a crisscross network of openings. In orange alteration crusts, the gypsum crystals are generally shorter, broader, and poorly defined. Where they can be measured they are 8 - 10 mm long and ~5 mm wide. Many gypsum crystals in the light crusts are rounded and uneven or covered by a very fine-grained coating. The crystal habit suggests that the smaller, less defined crystals in the orange crusts have experienced repeated cycles of dissolution and precipitation.

The black crusts at the Exchange are located on the inward facing sides of the columns and capitals. The thickness 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. The thickest alteration crusts have accumulated on the inside of column capitals. Slightly thinner, less pronounced darkened crusts on the sides of the capitals that receive occasional washing from rain appear as a gradual zone of transition from exposed to sheltered stone and unaltered to greatly altered surfaces.

The second floor portico column shafts also have tough black crusts on the inside. The black crusts form in visible zones on the columns, prominent in the sheltered areas but becoming thinner where there is occasional rain washing (Figure 20). The crusts are particularly striking on the arrises of the column flutes. Some of these crusts are cracked and fractured parallel to the stone foliation, and while they appear fragile, pieces of the blackened layers are very difficult to remove. Thinner, orange crusts have accumulated on the sides of the arrises and in the flutes. The orange and black crust distribution on the column shafts reflect the presence of moisture, evaporation, and pollutant exposure. Because they are more protected, the troughs of the flutes probably retain surface moisture from condensation longer than the arrises, resulting in longer cycles between dissolution and reprecipitation of gypsum. The darker appearance of the arrises may reflect that the deposition here is enhanced relative to that on the flutes.

Black crusts on the ground level columns are concentrated where the stone faces the building, but outward facing areas close to the street are also black. 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 have blistered in patches (Figure 24) and have exposed crumbling stone underneath the crust.

In contrast to the columns, the walls of the building have only minimal alteration crusts. Two light colored gypsum crusts have formed here; one is orange, soft, and easily scraped off the wall; the other crust is light yellow, tough, and tightly adhered to the stone surface. Both types of crusts are gypsum with trapped particles. Systematic sampling and analysis of these alteration crusts on the second level east facade wall (Appendix A), found a variation in the abundance of the gypsum, calcite, and fluorite(?) in each sample collected around the facade. The presence and distribution of fluorite(?) in the crusts was unexpected, and may reflect an early attempt at cleaning the building. In contrast to the dark crusts, the stone underneath the thinner light crusts is intact and does not show signs of beginning disaggregation. These light crusts may represent an early stage of decay, with disaggregation beginning when the crusts reach a certain thickness or density. Alternatively, the light colored crusts may reflect an undocumented treatment.

Disaggregation

While the colored alteration crusts appear to preserve the original detailed features of the carved stone, the marble can be severely disaggregated underneath (Figure 22). The black crusts on the Carrara marble consist of a distinct black outer layer (about 0.1 mm thick) underlain by a dense light-colored transition zone (up to 0.6 mm thick) under which the marble is disaggregated. Some new gypsum crystals are found in the disaggregated zone (Figure 25), but it is not clear whether these small intergranular gypsum crystals formed before or after the disaggregated marble was exposed. The black crusts on the Pennsylvania marble are thinner and consist of a black layer (0.03 mm to 0.07 mm thick) with no discernible transition layer. The marble appears more intact under these thinner black crusts. While it appears that the Carrara marble is more susceptible to disaggregation beneath the alteration crusts than the Pennsylvania marble, the integrity of the underlying marble may in part reflect their relative exposure, rather than the original petrographic character.

Although it appears that the Carrara marble is more susceptible to disaggregation under the alteration crusts than the Pennsylvania marble; the crusts on these marbles have developed in areas of slightly different exposure to water, so the integrity of the underlying marble may in part reflect their relative exposure. Where the Carrara marble is more sheltered, slow evaporation of surficial moisture and the relatively tight texture of the Carrara marble may trap water that later disaggregates the stone. Possibly, the foliation of the Pennsylvania marble permits greater movement of moisture in the stone, and thus helps to minimize disaggregation of the stone under the alteration crusts. If little water is trapped in intergranular spaces prior to the accumulation of an impenetrable alteration crust, then the effect of temperature cycles or salts precipitating in intergranular areas would be reduced, resulting in less disaggregation of the encrusted marble.

COMPARISON OF THE WEATHERING OF THE MARBLES

Variations in inclusions, texture, and grain characteristics are the most striking difference between the Pennsylvania and Carrara marbles. The disaggregated grains of the two marbles are visibly different in color; Carrara marble grains are yellow to beige, while Pennsylvania marble grains are blue to gray in color. The composition of the calcite from both marbles, however, is very similar (Table 1). Although the grains in the Pennsylvania marble sample appear smaller than those in the Carrara marble sample, grain measurements indicate that their size ranges overlap (Figure 14). Calcite grains from the Carrara marble are mostly rounded to slightly angular (Figure 15b); in rare cases a minor inclusion phase may be attached to the calcite grain. Calcite grains from the Pennsylvania marble are also rounded to slightly angular, but many individual grains have abundant inclusions of muscovite and apatite (Figure 16).

Many of the Pennsylvania marble calcite grains have a rough, dog-toothed surface suggestive of an etched surface which contrasts with the smooth surfaces of the inclusion minerals dominating the grains in the Carrara sample. Amorphous looking "plates" that contain calcium and phosphorous cover the surface of many Pennsylvania marble grains that were taken from the partially sheltered wall on the east facade portico. Although the plates look like a precipitate that has formed on the grain surface, their source is unknown. A significant number of Carrara calcite grains collected from under a thick black alteration crust have surficial gypsum crystals (Figure 25). It is unclear, however, whether this intergranular gypsum developed after the stone was significantly disaggregated, or whether early growth of the gypsum was the mechanism that caused the disaggregation. It is possible that the intergranular crystals are an artifact, because accumulation of gypsum crystals is predominantly a surficial phenomenon. Analysis and examination of limestone from an older building has shown that although elevated levels of sulfate are detected for some distance into the stone, gypsum in crystal form is restricted to the near surface area (McGee and Mossotti, 1992).

Texture differences are reflected on a visible and a microscopic scale. In contrast to the Carrara marble, the pronounced foliation of the Pennsylvania marble is a major weakness that has been visibly accentuated by exposure. But on a microscopic scale, within the planes of foliation, intergranular gaps are narrower in the Pennsylvania marble than in the Carrara marble. Polished thin sections of poorly consolidated samples of Carrara and Pennsylvania marble allow a comparison to be made of the grain boundary and pore structure characteristics of these two marbles (Figure 15).

The grain boundaries of the Pennsylvania marble sample are fairly thin, typically 5mm wide, with some boundaries at about 10 mm. In contrast, the Carrara marble grain boundaries are fairly wide; typically 20 to 30 mm, ranging from 5 mm to 60 mm. Further, the area occupied by stone versus pore space differs and may be significant in choosing treatment actions. On average, for a 1.8 x 1.7 mm area in a SEM photograph, 2.9% of the Pennsylvania marble sample is pore space (92.9% is calcite grains) compared to 12.2% pore space in the Carrara marble (83% calcite grains).

SUMMARY

In general, the Pennsylvania marble has suffered more from dissolution deterioration whereas the Carrara marble shows more pronounced effects from alteration. The abundant inclusions and foliated texture of the Pennsylvania marble may make it more susceptible to dissolution deterioration because water can readily penetrate along inclusion-calcite boundaries and along the pronounced foliation planes in the marble. The Carrara marble may be particularly susceptible to alteration deterioration because thin films of surficial moisture cannot readily be absorbed by the relatively impervious stone, and thus remain on the stone surface longer, enhancing sulfur deposition and promoting growth of surficial gypsum.

REFERENCES

Amoroso, G. and Fassina, V., 1983, Materials Science Monographs, no. 11, Stone Decay and Conservation, Elsevier, New York, 453 p.

Bascom, F., Clark, W.B., Darton, N.H., Dummel, H.B., Salisbury, R.D., Miller, B.L., and Knapp, G.N., 1909, Description of the Philadelphia area, Pennsylvania-New Jersey-

Delaware. Geologic Atlas of the United States, Philadelphia Folio No. 162, U.S. Geologic Survey, 35p.

Burnham, S.M., 1883, History and Uses of Limestones and Marbles, S.E. Cassino and Company, Boston, 392 p.

Census, 1884, Report on The Building Stones of the United States, and Statistics of the Quarry Industry for 1880, 410 p.

Dale, T.N., 1912, The Commercial Marbles of Western Vermont, U.S. Geological Survey Bulletin 521, 170 p.

Dean, Nancy E., 1988, Geochemistry and Archaeological Geology of the Carrara Marble, Carrara, Italy, in: N. Herz and M. Waelkens (eds.), Classical Marble: Geochemistry, Technology, Trade, Kluwer Academic Publishers, p. 315-323.

Hall, Charles E., 1881, The Geology of Philadelphia County and of the Southern Parts of Montgomery and Bucks. Second Geological Survey of Pennsylvania: Report of Progress C^6. Board of Commissioners for the Second Geological Survey, Harrisburg, Pennsylvania, 145 p.

Julian, Alexis, A., 1884, The Durability of Building Stones in New York City and Vicinity, in: Census, 1884, Report on The Building Stones of the United States, and Statistics of the Quarry Industry for 1880, p. 364-393.

McGee, Elaine S. and Mossotti, Victor G., 1992, Gypsum Accumulation on Carbonate Stone, Atmospheric Environment, v26B, p. 249-253.

Merrill, George P., 1889, The Collection of Building and Ornamental Stones in the U.S. National Museum: A Handbook and Catalogue, from: Report of the Smithsonian Institution, 1885-86, Part II, p. 277-648.

Miller, Benjamin, L., 1934, Limestones of Pennsylvania, Pennsylvania Geological Survey, Fourth Series, Bulletin M 20, 729 p.

Sherwood S.I., Gatz, D.F., Hosker, R.P., Jr., Davidson, C.I., Hicks, B.B., Linzey, R., McGee, E.S., Schmiermund, R.L., Dolske, D.A., Langmuir, D., Lipfert, F.W., Mossotti, V.G., and Spiker, E.C., 1990, State of Science & Technology, Report No. 20: Processes of deposition to structures. National acid Precipitation Assessment Program, Washington, D.C., 145 p.

Stone, Ralph W., 1932, Building Stones of Pennsylvania, Pennsylvania Geological Survey, Fourth Series, Bulletin M 15, 316 p.

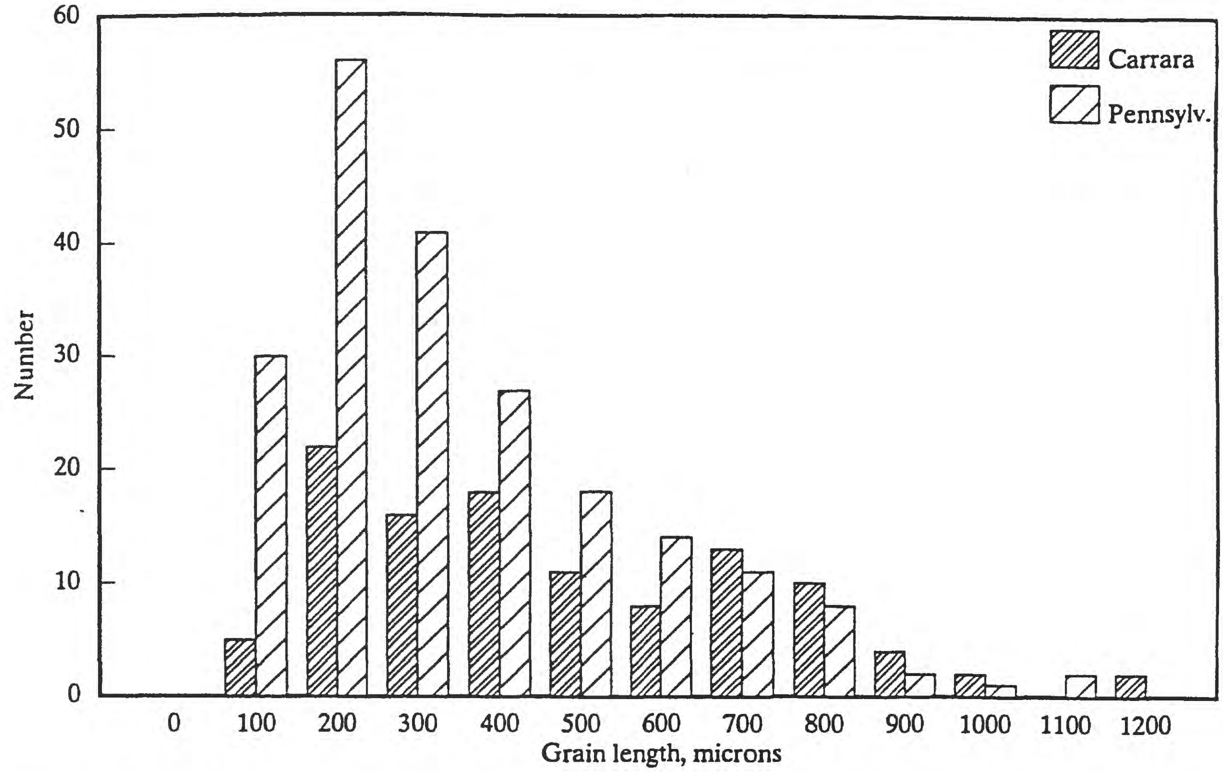


Figure 14. *Calcite grain size for Pennsylvania and Carrara marble samples; longest dimension of grains measured in microns vs. number of grains in each size range.*

Table 1. Calcite composition

Pennsylvania marble

	Average	Minimum	Maximum
CaO	56.22	55.90	56.60
MgO	0.25	0.14	0.32
MnO	0.00	0.00	0.00
FeO	0.08	0.01	0.13
SrO	0.00	0.00	0.02
BaO	0.01	0.00	0.06

Carrara marble

	Average	Minimum	Maximum
CaO	55.89	54.78	56.78
MgO	0.19	0.10	0.26
MnO	0.00	0.00	0.00
FeO	0.05	0.00	0.13
SrO	0.00	0.00	0.03
BaO	0.02	0.00	0.43

A.

B.

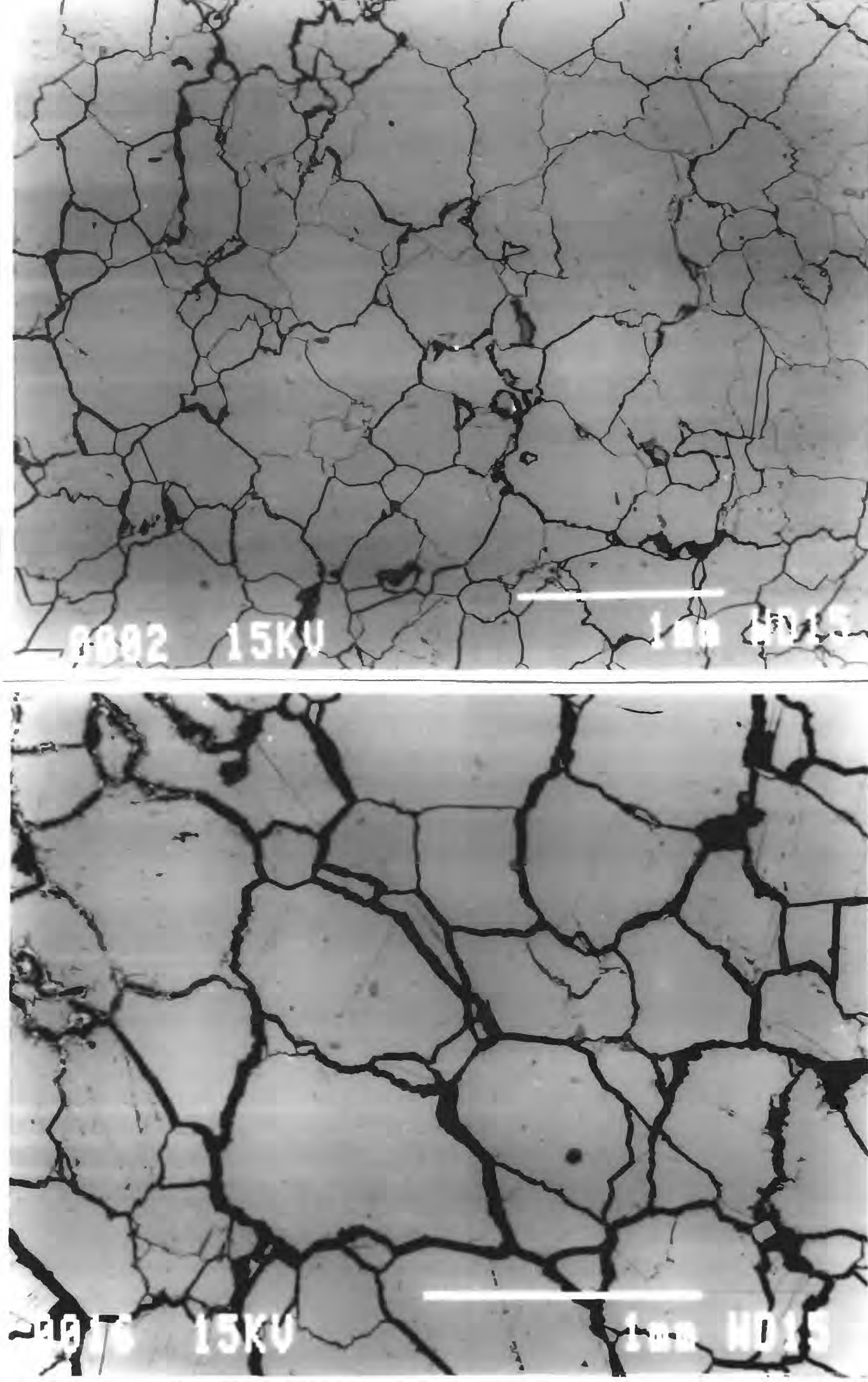


Figure 15. Typical grain shapes and boundaries in a) Pennsylvania marble and b) Carrara marble. The Pennsylvania marble sample is from a small spalled piece on the wall of the east facade portico with no visible alteration crust; the Carrara marble sample is a cross section of an alteration-covered carved piece that fell from an east facade column capital. Photos are scanning electron micrographs from polished sections; scale at lower right.

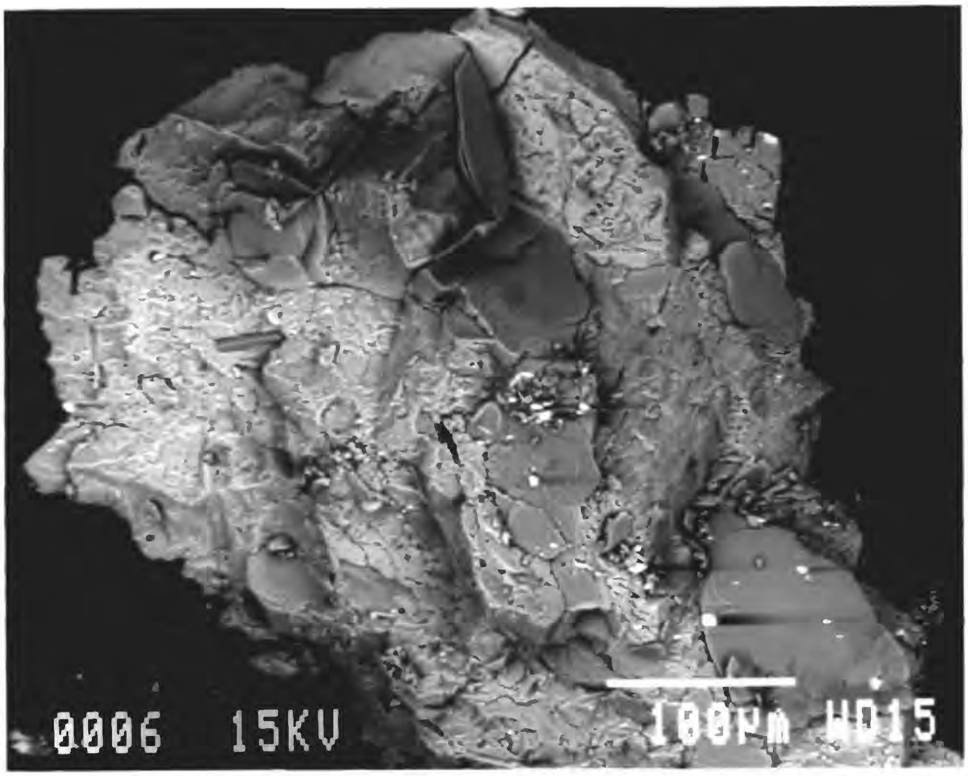


Figure 16. Backscattered electron image of a Pennsylvania marble calcite grain with attached (platy, darker gray) muscovite grains. Small bright white dots are apatite grains. The sample is from an antefix.

Figure 17. Weathering has accentuated the natural foliation (planar texture) of the Pennsylvania marble and resulted in spalling and loss of layers of stone material on this antefix.

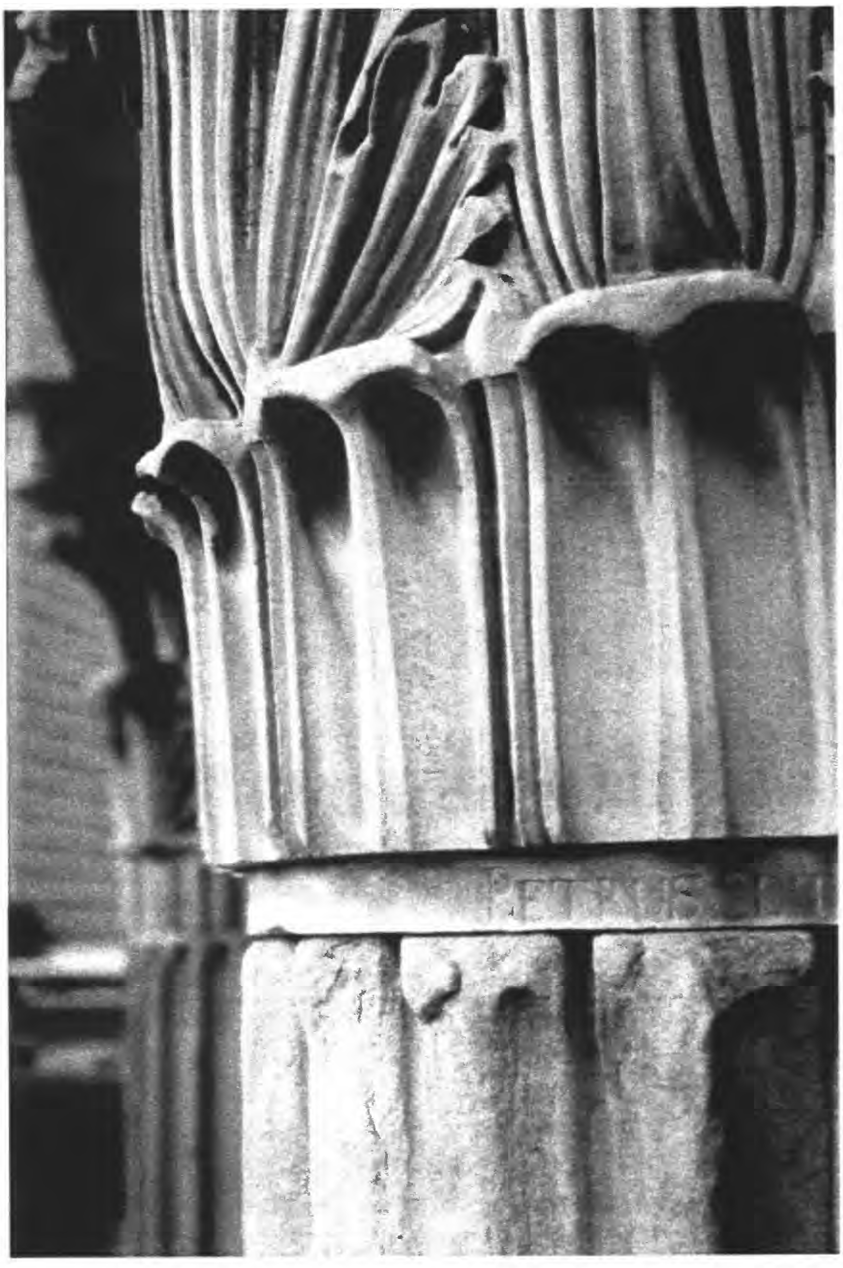


Figure 18. The Pennsylvania marble in the column shafts is grainier and has lost more of the original carved details compared to the similarly-exposed Carrara marble.

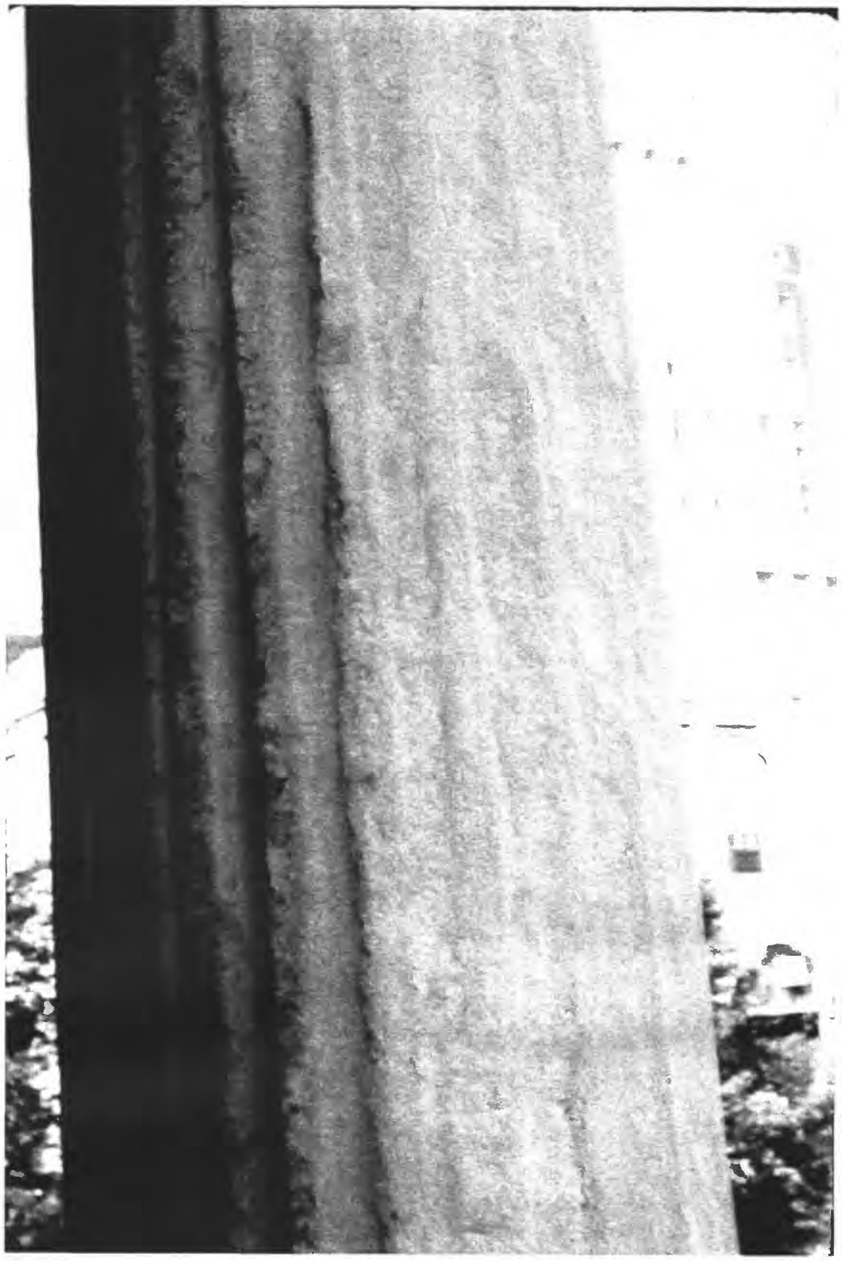


Figure 19. Column shafts of Pennsylvania marble on the east facade have developed rounded, wavy edges. Where the foliation of the original stone lies parallel to the exposed stone surface, the arrises are almost completely gone.

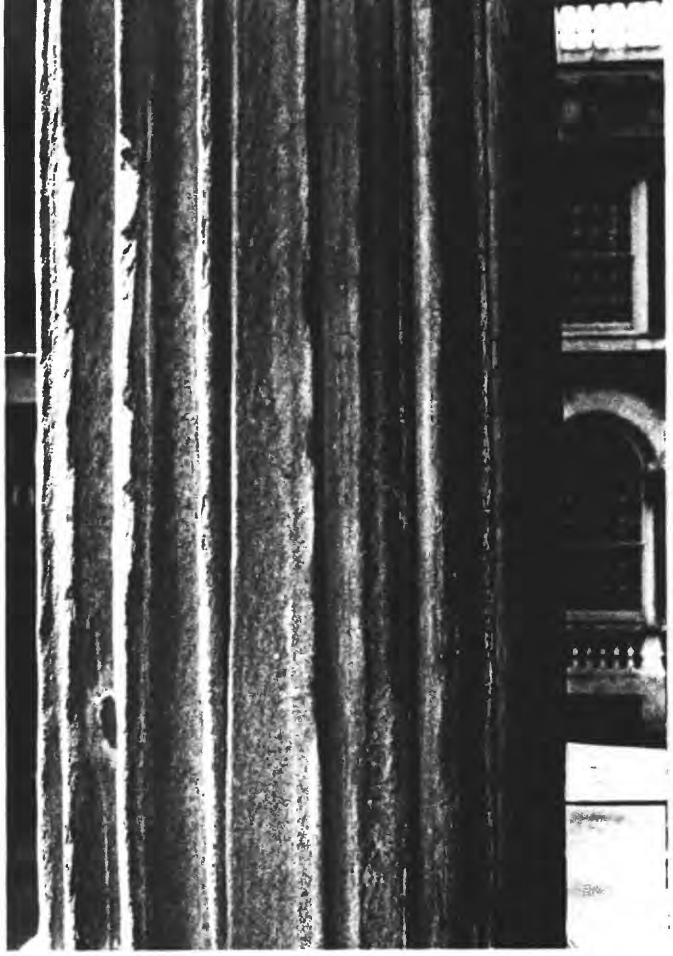


Figure 20. Pennsylvania marble column shaft on the east facade shows a transition from exposed to sheltered areas marked by the accumulation of black alteration crusts in the sheltered area.

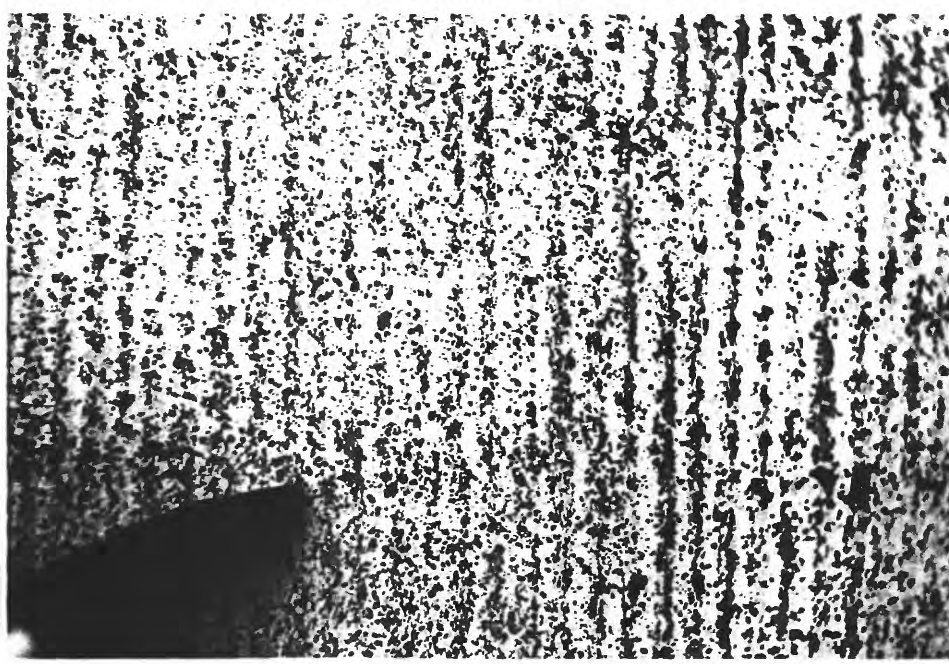
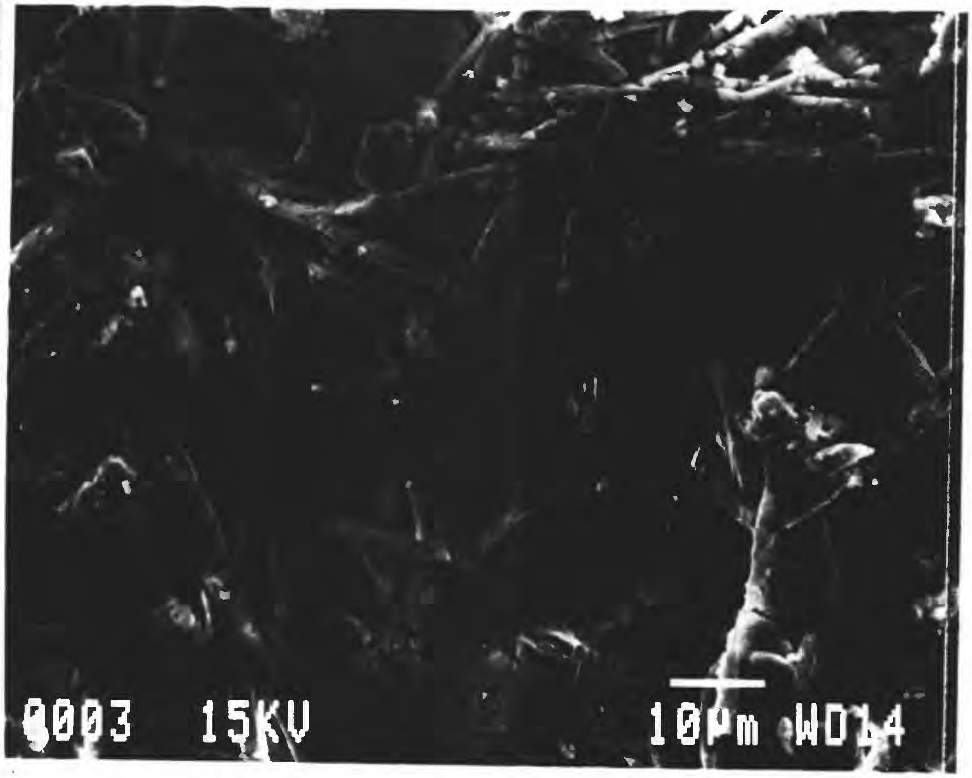


Figure 21. Orange alteration crust on the east facade portico wall made from Pennsylvania marble partly obscures the original tool marks. Pen cap in lower left is for scale.

Figure 22. Carrara marble underneath a black alteration crust on the east facade is completely disaggregated into loose grains, seen on a knife blade.

A.



B.

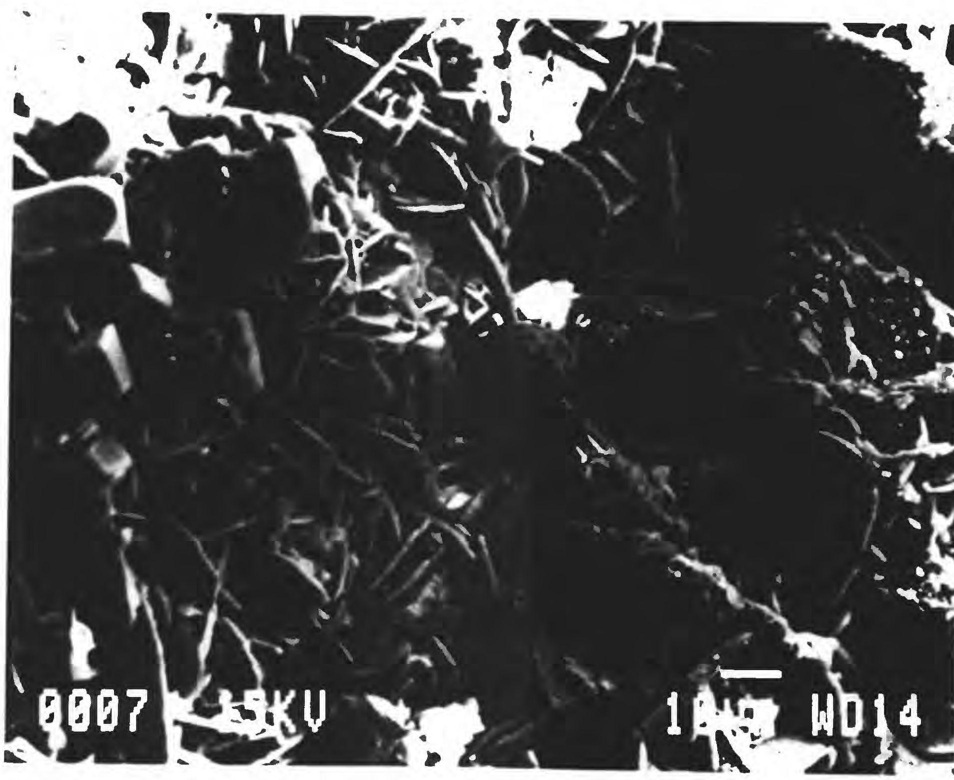


Figure 23. Scanning electron micrograph of black alteration crusts on Pennsylvania marble of Column 14; a) bladed gypsum crystals form a network that covers the stone surface and b) pollutant particles (center), dirt, and salt crystals (cube, left-hand side) are readily trapped by the open network formed by the gypsum crystals.

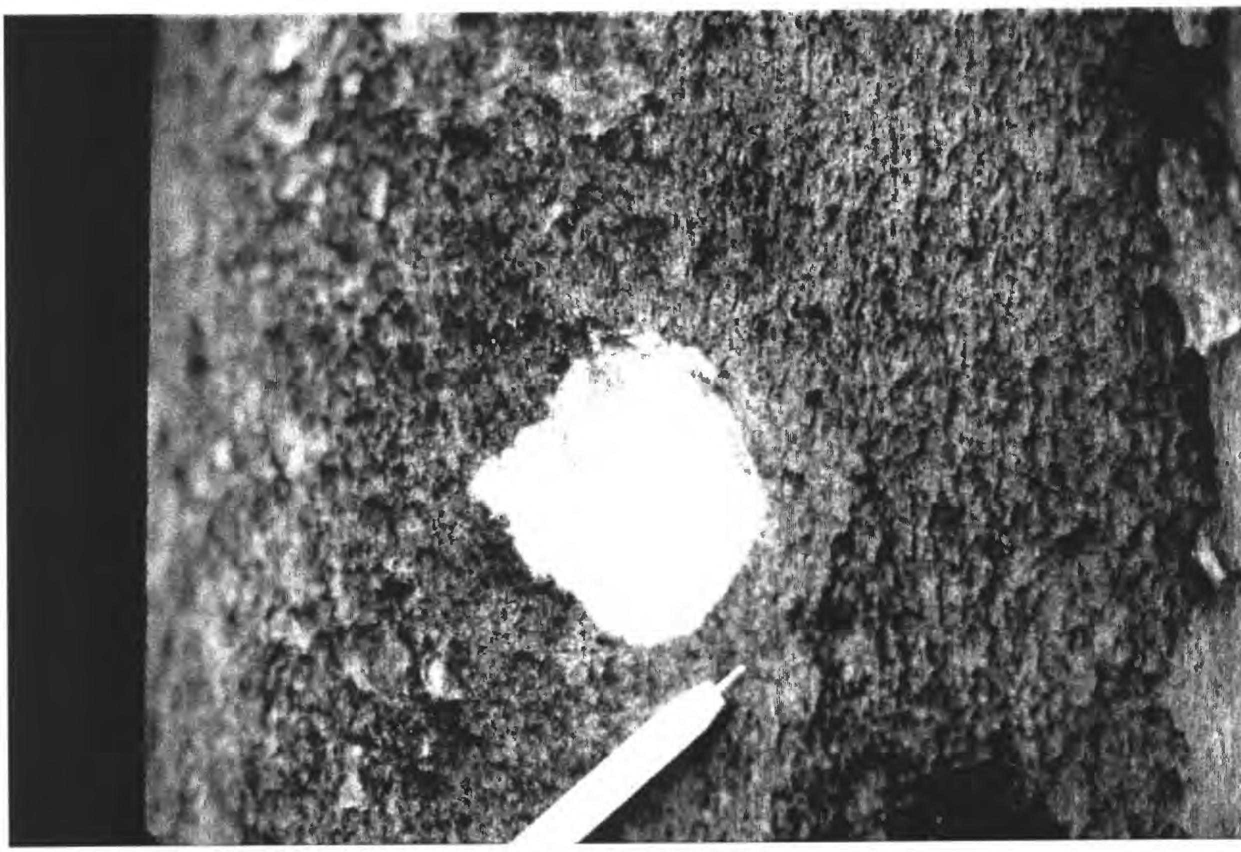


Figure 24. The blackened alteration crust on a ground level column on the west facade has blistered off, exposing white, newly-revealed and disaggregated Pennsylvania marble underneath. Smooth area on right appears to be the original surface of the column.

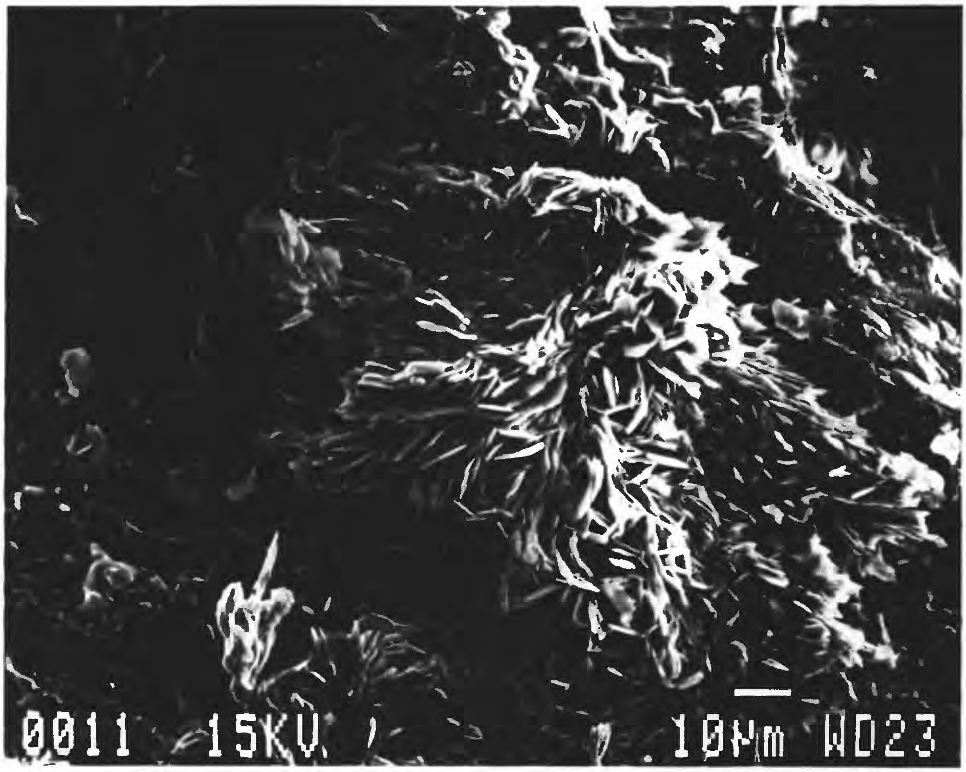


Figure 25. New gypsum crystals (white, fine grains at center) have formed on a calcite grain (dark grain in background) that was underneath a black alteration crust on a Carrara marble capital on the east facade.

APPENDIX A:

X-ray and Scanning Electron Microscopic Study of Alteration Crusts

We began a systematic examination by sampling and analyzing the alteration crusts on the east facade of the Exchange, and then collected additional samples on the west facade. Although samples of alteration crusts had previously been collected and examined with scanning electron microscopy, there was not enough material available from those samples to perform X-ray diffraction analysis. We also sought to systematically observe both the distribution and characteristics of the various crusts around the facade, in order to document characteristics that might reflect exposure of the stone, or the nature of the crusts.

Samples of light and dark colored crusts were collected from the east and west facade portico walls, and from column shafts on the east and west facades. All of the samples were collected on the second floor portico level and the crusts were all on Pennsylvania marble. Specific locations of the samples are described in Table A-1, and are shown in Figures 47 and 49. Samples were collected by scraping a small amount of the crust with a knife blade. We described the appearance of the crust on the building, observed characteristics of the crust during the sampling (eg. how soft, how tightly adhered to the underlying stone), and the appearance of the resulting (powder) sample. A small portion of each sample was reserved for examination with the scanning electron microscope (SEM) and the remainder was ground in an agate mortar with acetone and mounted for powder X-ray diffraction. Major and minor peaks on the X-ray diffraction patterns were identified and visual estimates were made of the proportion of each mineral phase in the sample. Portions of each sample were examined using the SEM to see how the mineral phases, that were detected with X-ray diffraction, occur in the sample.

Using the SEM we are able to see many of the phases that are present in the sample, but SEM identification does not give us an adequate representation of the abundance of the phases. X-ray diffraction gives more of a bulk identification of phases in the sample; it will detect phases with a crystalline structure that constitute at least 10% of the sample. Table A-1 summarizes the phases identified in each sample. The crusts consist of calcite, gypsum, quartz, and fluorite(?). We did not detect any oxalates in the samples that we analyzed. The main constituent of the crusts is either calcite or gypsum. In some cases, especially where the proportion of calcite is high, we suspect that part of the calcite that was detected is grains of the underlying marble that came off when the alteration crust was sampled. The SEM images substantiate this explanation, as seen in sample MX210-4, where grains of calcite have thin crusts of gypsum crystals (Figure A-1). Quartz is an accessory phase, present mainly in the black alteration crusts and seen in the SEM as individual grains sitting in the network of gypsum crystals (Figure A-2).

The presence of fluorite(?) was a surprise, in part because it seemed at first to be an unlikely alteration phase. The Pennsylvania marble does not contain any fluorite (CaF_2) as an accessory mineral phase, so we did not think that we were detecting a portion of the underlying stone in those samples where the X-ray pattern seemed to indicate fluorite. The peaks we identified as fluorite(?) on the X-ray diffraction patterns do not coincide with any of the calcite, gypsum, or quartz peaks (phases typically found in alteration crusts); likewise, the peaks do not coincide with peaks of accessory phases in the Pennsylvania marble. So, the fluorite(?) peaks are not likely to be from overlaps of phases that we expected to find in the samples of alteration crusts. The fluorite(?) peaks are indistinct in shape and thus may indicate that the phase is not well crystallized. Optical examination of the fluorite(?) rich samples showed that they all contained some "fluffy" material, which may also indicate the presence of a poorly crystalline phase. We attempted to confirm the identification of fluorite by examining some of the puzzling samples on the SEM with energy dispersive X-ray analysis. To improve our chances of finding the phase in question, we examined samples that appeared to have the highest fluorite(?) content. Although we detected some fluorine in these samples, we did not find any distinct grains that contained calcium and fluorine, as a fluorite (CaF_2) sample would. Where F was detected in the samples, the grains had an indistinct morphology, perhaps suggesting a precipitate rather than a crystalline phase, and we found phosphorous was a significant component in the analysis (Fig. A-3). The chemical analysis and indistinct crystal habits in these fluorite(?) bearing samples suggest that some of the sample material might be a residue from a cleaning treatment used on the building. The Exchange was cleaned in the early 1960's (see Chapter 1) and the Historic Structures Report (Petrak 1963) recommended cleaning the stone with fluoride and water solution. Although we are not sure whether the building was cleaned with fluoride, some testing may have been done and the fluorite(?) phase might be a residue that formed from or was left on the stone after cleaning. The distribution and abundance of fluorite(?) in our samples (Figure 47) suggests that treatment may have been concentrated in the north facing section of the east facade.

Reference

Petrak, J., 1963, Historic Structures Report Part II Supplement I, Architectural Data Section, Restoration and Reconstruction on Merchants' Exchange. Independence National Historical Park, Philadelphia, November 1963.

Mary Woodruff is acknowledged for her assistance collecting samples and for obtaining the powder X-ray diffraction patterns for the samples.

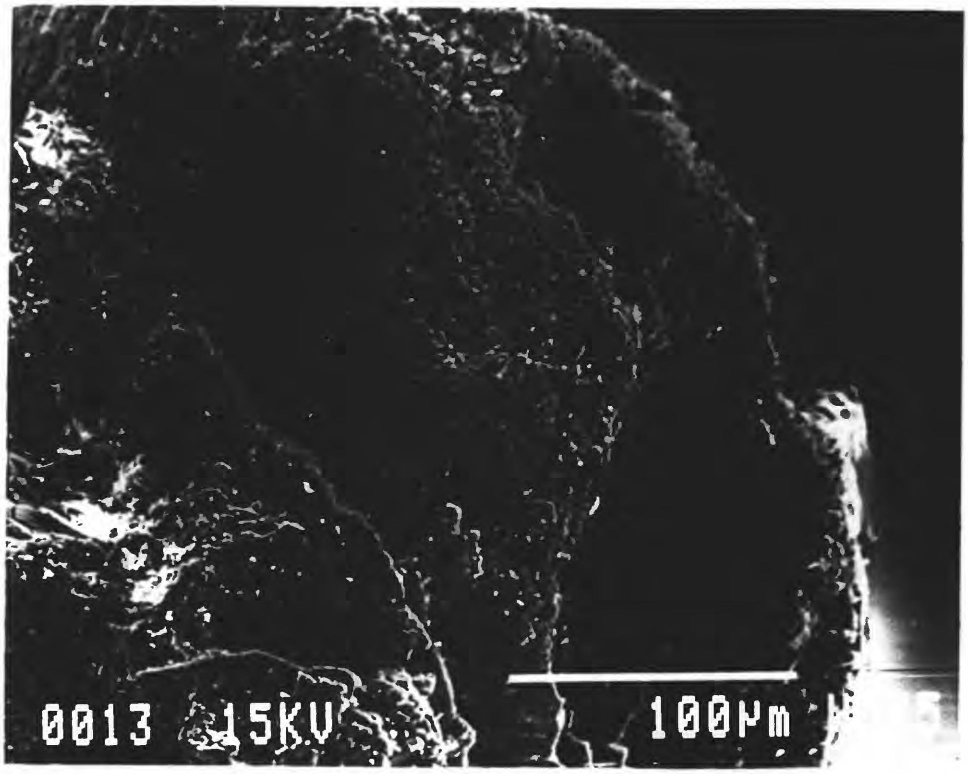


Figure A-1. Scanning electron micrograph (SEM) of alteration crust sample MX210-4. Gypsum crystals cover only a small portion of a calcite grain from the underlying marble; this relative proportion is reflected in the estimated abundance of these phases from the X-ray diffraction pattern.

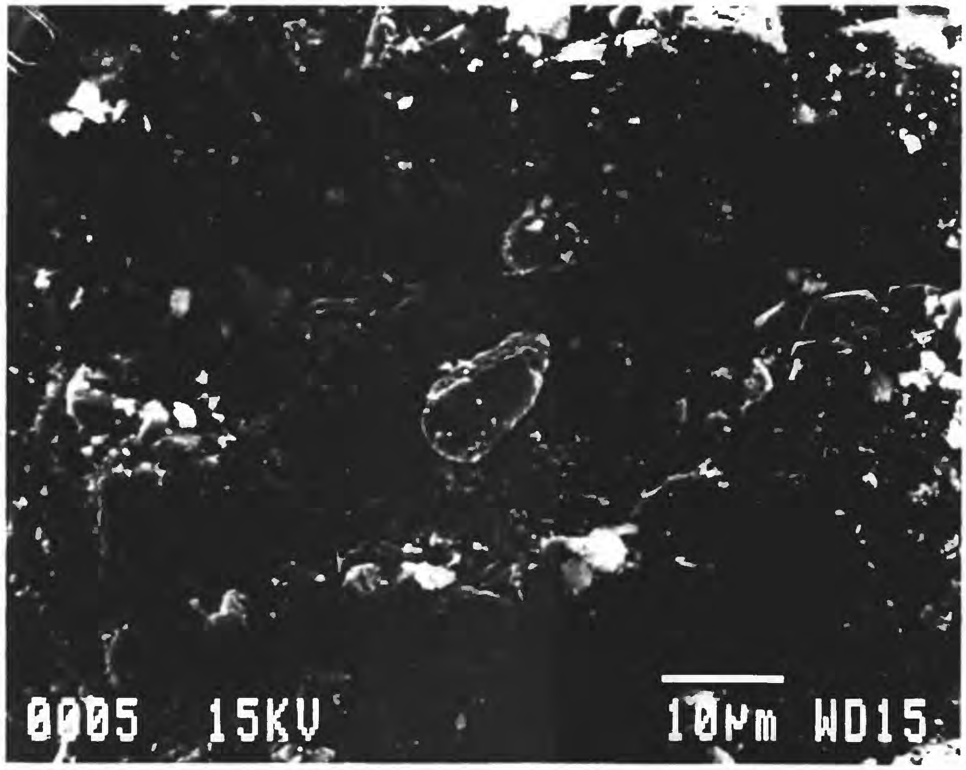


Figure A-2. SEM micrograph of a typical quartz particle in an alteration crust sample.

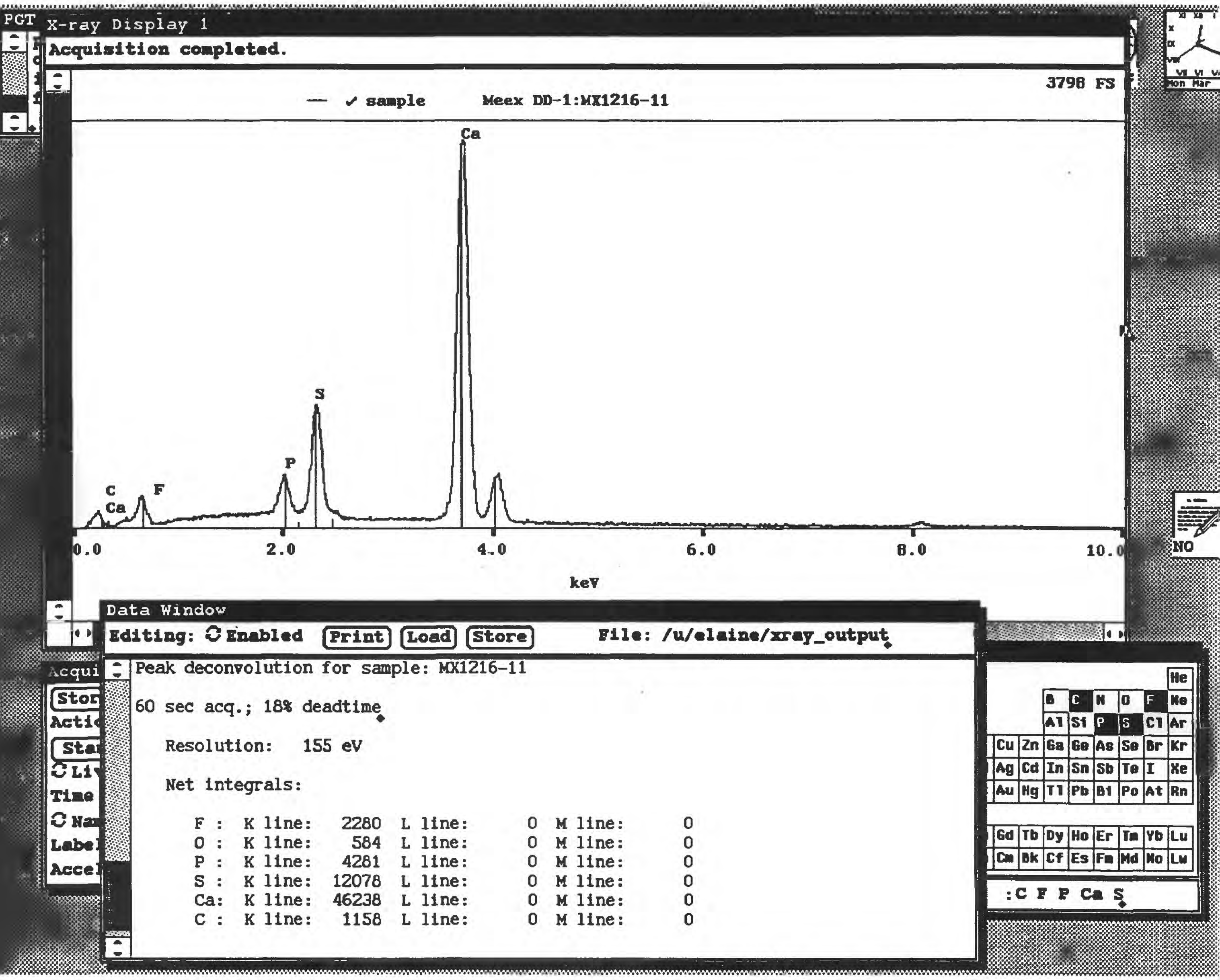


Figure A-3. Energy dispersive X-ray analysis spectrum from a fluorite(?) rich sample (MX1216-11). The spectrum represents a qualitative analysis, but the relative peak heights indicate the approximate relative abundances of each of the elements shown. Note that while the sample does contain fluorine (F), phosphorous (P) appears to be a significant component of the phase that was analyzed. [The apatite, $Ca_5(PO_4)_3(OH,F,Cl)$, which occurs as an accessory mineral phase in the Pennsylvania marble, does not contain any significant amount of F.]

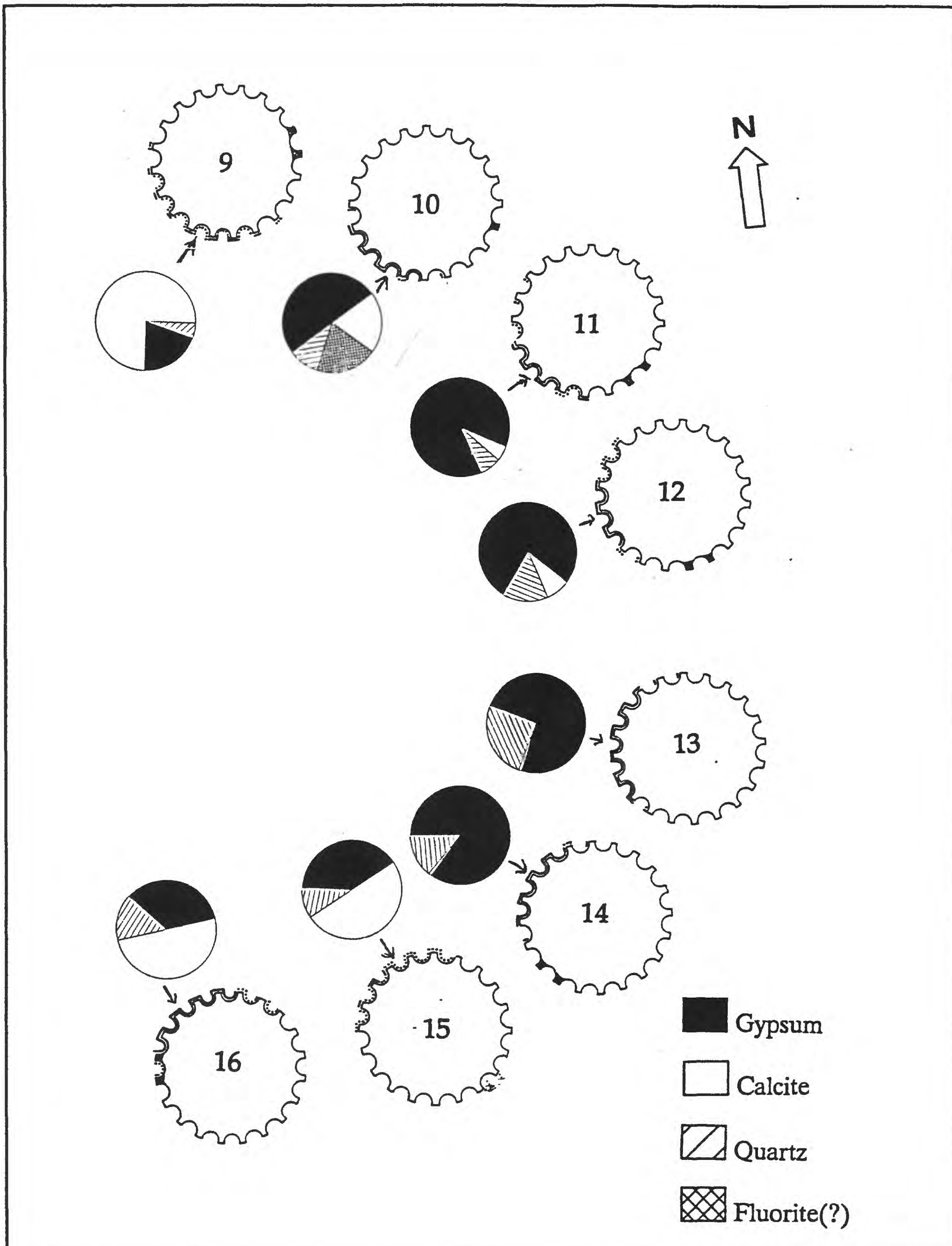


Figure 47. Encrustation on columns; distribution and composition.

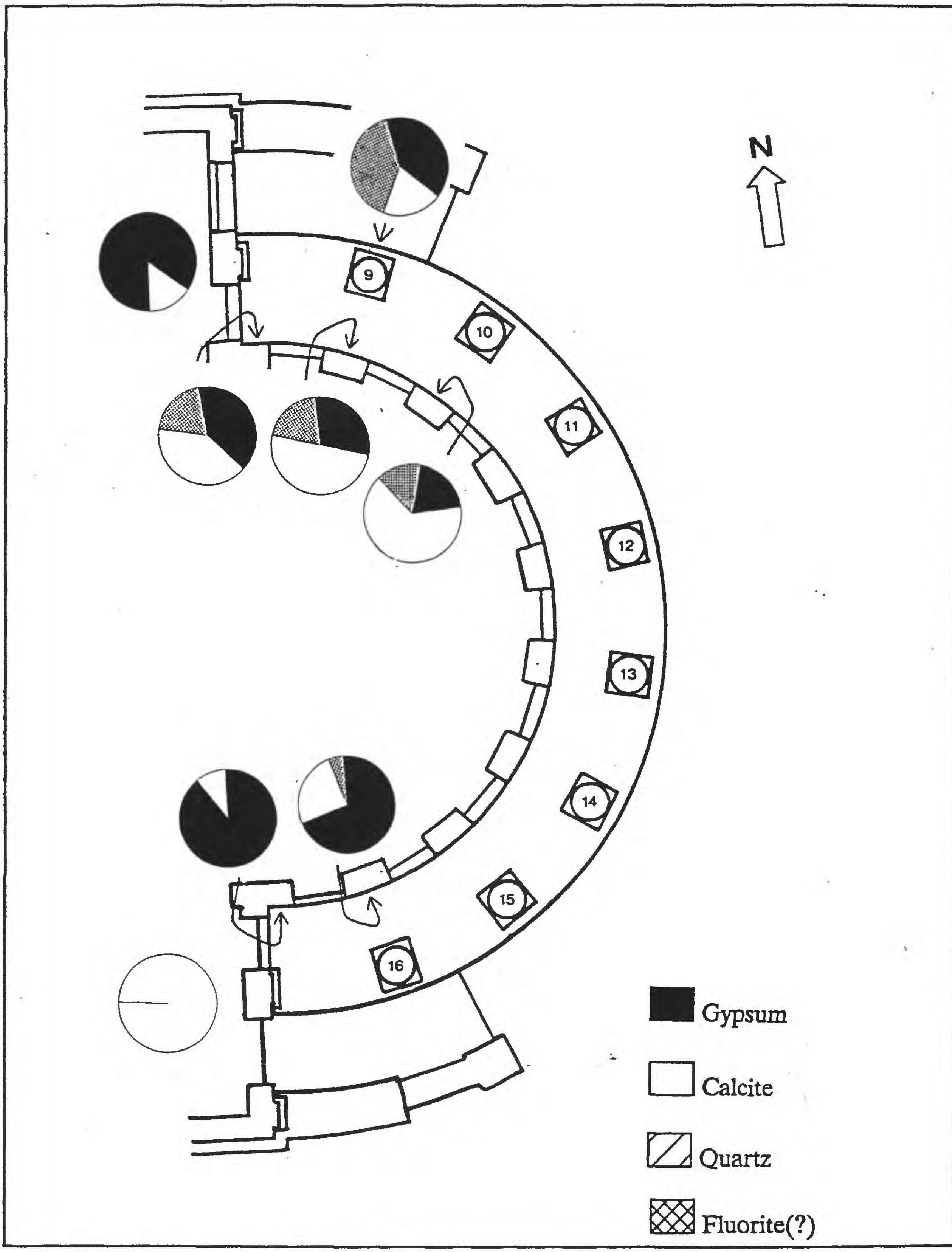


Figure 49. Composition of crusts on east portico walls.

PLATE 9

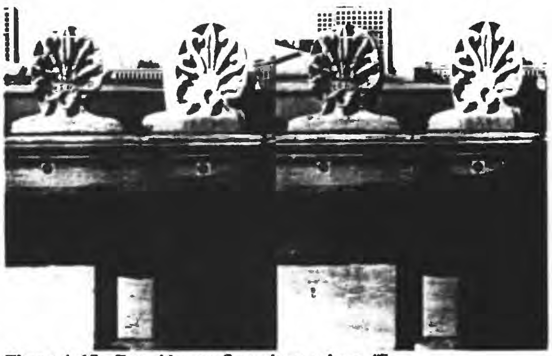


Figure A-15. East side, antefixae above column #7.

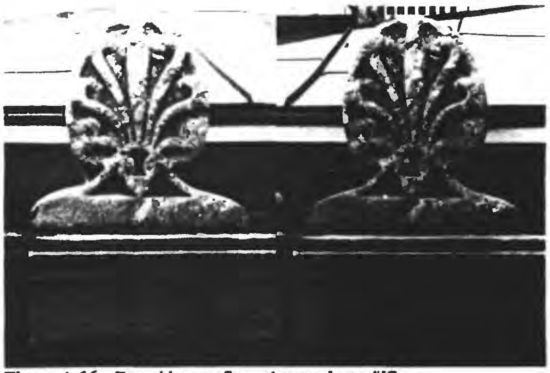


Figure A-16. East side, antefix above column #17.

Plate 9.

Table A-1. Summary of the Merchants' Exchange Alteration Crust Samples

Number	Sample	Area	Field Description	Phases
MX210-1	E-lc-w-8	4 blocks above porch	light orange, hard to scrape off	Calcite 40%, Gypsum 40%, Fluorite(?) 20%
MX210-2	E-lc-w-9	3 blocks above floor	orange-yellow, thick, came off easily	Calcite 50%, Gypsum 30%, Fluorite(?) 20%
MX210-3	E-lc-c-10	in flute facing wall, ~4.5' up	orange-yellow, scraped off easily	Calcite 20%, Gypsum 50%, Quartz 10%, Fluorite(?) 20%
MX210-4	E-lc-c-10	side of flute, near 210-3	yellow, open network, scraped off easily	Calcite 85%, Gypsum 5%, Fluorite(?) 10%
MX210-5	E-lc-w-10	4th block up	yellow, open network, came off easily	Calcite 65%, Gypsum 20%, Fluorite(?) 15%
MX210-6	E-lc-w-16	3rd block up	white, hard to remove	Calcite 25%, Gypsum 70%, Fluorite(?) 5%
MX210-7	E-lc-w-17	4th block up	pale orange, pervasive, hard to remove	Calcite 10%, Gypsum 90%
MX210-8	E-dc-c-15	edge of flute, facing wall	black, scraped fine powder	Calcite 50%, Gypsum 40%, Quartz 10%
MX210-9	E-dc-c-13	top of arris facing wall	black, easily pried spall pieces, hard to scrape	Calcite 10%, Gypsum 40%, Quartz 50%
MX210-10	E-lc-w-9	under overhang, by grd level steps	white, scraped easily	Calcite 20%, Gypsum 40%, Fluorite(?) 40%
MX1216-1	E-dc-c-9	arris - flat edge, ~1' abv col base	black, heavy accuml, scraped easily, sm bit pried off	Calcite 70%, Gypsum 20%, Quartz 10%
MX1216-2	E-lc-c-9	flute- near edge of blk zone; ~2' abv col base	yellow, scraped, light & powdery	Calcite 59%, Gypsum 40%, Quartz 1%
MX1216-3	W-lc-w-1	corner, left & below window	orange, hard to scrape, powdery	Calcite 47%, Gypsum 45%, Quartz 3%, Fluorite(?) 5%
MX216-4	W-lc-w-3	near window	white, scraped, powdery	Calcite 30%, Gypsum 65%, Fluorite(?) 5%
MX1216-5	W-dc-c-2	arris- flat face, S side col, 4 ft. above base	black, spalled piece	Calcite 86%, Gypsum 6%, Quartz 5%, Pholgopite 3%
MX1216-6	W-dc-c-3	inward side arris, S side col	black, scraped, mostly powder	Calcite 55%, Gypsum 30%, Quartz 7%, Muscovite 8%

Number	Sample	Area	Field Description	Phases
MX1216-7	W-lc-c-3	edge of arris - side of flute, near? 1216-6	yellow, scraped easily	Calcite 70%, Gypsum 7%, Quartz 7%, Fluorite(?) 1%, Muscovite 15%
MX1216-8	W-dc-c-4	edge of arris, S side col	black, thick, scraped	Gypsum 55%, Quartz 45%
MX1216-9	W-lc-c-4	in flute, near 1216-8	yellow, scraped	Calcite 79%, Gypsum 15%, Quartz 2%, Fluorite(?) 4%
MX1216-10	W-dc-c-5	side of arris, facing bldg	black, spalled pieces, friable	Calcite 91%, Gypsum 4%, Quartz 5%
MX1216-11	W-lc-w-1	~3' abv floor	white	Calcite 65%, Gypsum 5%, Fluorite(?) 30%
MX1216-12	W-dc-c-5	side of arris, S side col	black, powdery, scraped easily	Gypsum 40%, Quartz 60%
MX1216-13	W-lc-c-5	flute, beside 1216-12	yellow, thin, scraped	Calcite 97%, Gypsum 2%, Muscovite 1%
MX1216-15	E-dc-c-16	arris -flat face, toward bldg, ~3' from base	black, scraped easily	Calcite 50%, Gypsum 35%, Quartz 15%
MX1216-16	E-lc-c-16	in flute near 1216-15	brown, scraped easily	Calcite 70%, Gypsum 9%, Quartz 12%, Muscovite 9%
MX1216-17	E-lc-c-12	flute facing bldg	scrapes off easily	Calcite 8%, Gypsum 70%, Quartz 2%, Fluorite(?) 20%
MX1216-18	E-dc-c-14	edge of arris, near 1216-17	black, thin outer layer of crust	Calcite 1%, Gypsum 85%, Quartz 14%
MX1216-19	E-lc-c-13	flute facing bldg	orange, scraped surficial material only	Gypsum 60%, Quartz 2%, Fluorite(?) 38%
MX1216-20	E-dc-c-13	edge of arris, near 1216-19	black, scraped surficial material only	Calcite 1, Gypsum 74%, Quartz 25%
MX1216-21	E-dc-c-9	edge of arris, W side of col	black, scraped surface w/few grns	Calcite 75%, Gypsum 20%, Quartz 5%
MX1216-22	E-dc-c-11	edge of arris, facing bldg	black, surficial, scraped easily	Calcite 5%, Gypsum 88%, Quartz 7%
MX1216-23	E-dc-c-12	edge of arris, facing bldg	black, scraped	Calcite 8%, Gypsum 77%, Quartz 15%
MX1216-24	E-lc-p-17	side of flute	white, scraped	Calcite 100%
MX1216-25	E-lc-p-8	flute, ab middle of plstr	orange-white, scraped	Calcite 15%, Gypsum 85%

In the sample column: E = east facade, W = west facade, lc = light crust, dc = dark crust, w = wall, c = column, p = pilaster, # = number of column (or column closest to the wall area sampled).
Abbreviations: grd = ground, abv = above, accuml = accumulation, sm = small, col = column, ab = about, plstr = pilaster.
Phases column shows estimate from X-ray diffraction analyses of relative abundances of the phases in each sample.