Deterioration of Stone and Mineral Materials from the Roman Imperial “Villa of the Antonines” at Ancient Lanuvium

Gregory A. Pope, Deborah Chatr Aryamontri, Laying Wu, and Timothy Renner

Abstract
The “Villa of the Antonines”, located at the 18th mile of the ancient Via Appia, is so far the least explored of the ancient Roman imperial residences in the area of the Alban Hills. Excavations at “Villa of the Antonines” permit an investigation of subsurface deterioration of cultural stone, addressing two primary questions: (1) What are the deterioration processes in the soil and sediment environment, and how do these compare to subaerial deterioration processes? (2) How might the deterioration impact other methodologies reliant on the analysis of the material, such as use and wear analysis, dating techniques, and provenience by chemical tracers? The deterioration characteristics of materials recovered thus far can be visually described. Marbles are discolored and exhibit a loss of polish and partial to extensive granular disintegration and powdering. Brick varies in color and composition due to manufacturing and material differences, but may also exhibit within-soil alteration. Glass tesserae exhibit frosting and pitting from chemical solution. Scanning electron microscopy (SEM) reveals surface microdeterioration such as pitting, etching, and glazing. Qualitative backscatter electron microscopy (BSEM) and energy dispersive spectroscopy (EDS) indicate the distribution of elements, including byproducts of chemical deterioration, likely within the soil environment.

87.1 Introduction
In 2010, Montclair State University began investigation of archaeological remains at the 2nd Century Roman imperial “Villa of the Antonines”, at the 18th mile of the ancient Via Appia near Genzano di Roma, Italy (Fig. 87.1). This imperial residence spread over a considerable extent, but remained largely unknown apart from the massive concrete remains of the bath complex and the partially excavated adjacent amphitheater (Chatr Aryamontri et al. in press; Chatr Aryamontri and Renner 2010, 2011, 2012; Cassieri and Ghini 1990). The villa has been neglected and poorly explored, as well as subject to looting, vandalism, and decay. Nevertheless, the lavish decoration of the complex is apparent in the large quantity of fragments of decorative white and colored marble and the thousands of multi-colored glass tiles (tesserae) used for flooring or wall decoration. Many of the construction and decorative materials that once were an integral part of the buildings of the villa lie loose...
and scattered everywhere on the site, some in a sub-aerial setting, but the majority of them buried underground. The artifacts excavated from soil and sediment, especially fragments of brick, white marble, and the mosaic glass tesserae, have undergone differing levels of deterioration or corrosion.

The purpose of this paper is to provide an initial assessment of the deterioration of stone and mineral materials recovered from “Villa of the Antonines.” Deterioration in the soil matrix presents different weathering environments than the more-commonly understood subaerial deterioration. With a better understanding of stone deterioration in the soil matrix, researchers will be in a better position to assess sources of the materials, their working and production, and their eventual conservation. This goal is heightened at the “Villa of the Antonines” given the poor state of site preservation. With special permission from Italian authorities, the authors were able to obtain a number of stone, brick, and glass fragments, on loan, for this preliminary study.

### 87.2 Methods

Specimens were selected among existing recovered artifacts of the “Villa of the Antonines” site, by purposely choosing samples that demonstrated observable deterioration as well as less-deteriorated samples for comparison. Details of the ongoing excavation can be read in Chatr Aryamontri et al. (in press, 2013), Chatr Aryamontri and Renner (2010, 2011, 2012), and Cassieri and Ghini (1990).

Analysis presented for this paper relies on the capabilities of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) at the Microscopy and Microanalysis Research Laboratory at Montclair State University. Glass samples were mounted on aluminum stubs, fixed with carbon tape, and coated with a thin layer of gold film in a Denton Desk IV Sputter Coater. In the case of marble and brick, samples were mounted in the same manner but coated with a thin film of carbon. The samples were imaged by a Hitachi S-3400 N SEM, under a high vacuum system, 15 kV, ~10 mm working distance, spot size 30, and objective aperture size 2. Qualitative EDS spectrum analysis on the specimen surface was conducted at 15 kV accelerating voltage, beam spot size 70, and objective aperture size 2, working distance equal/close to 10 mm.

### 87.3 Results

#### 87.3.1 Brick

Brick fragments at the study site varied in the degree of deterioration, some in good condition, others intact but soft and capable of being scratched with a fingernail. Samples recovered from the study site, all from the soil matrix, were deteriorated samples. The surface was dark brown in color, while the interior was yellow-tan. Samples analyzed were damp.

At the macroscopic scale, a cross-sectioned brick fragment exhibited a distinct discolored rim along the perimeter of the fragment surface, approximately 1 mm in width. This rind was a post-burial formation, developing parallel to the fragmented surface, not related to the original surface of the fired brick. Oxidation was probably involved; elucidation of other chemical alteration processes to the clay minerals will await further microanalysis.

One brick fragment was imaged with SEM, BSEM, and qualitative element mapping (EDS) (Fig. 87.2). At magnifications ~200–2000x, the surface appeared granular, with aggregate particles ~5–20 µm in diameter. Fissures ~20 µm wide and up to several 100 µm in length crossed the soft material, probably the result of wetting and drying cycles (Lopez-Arce and Garcia-Guinea 2005). EDS indicated elements expected for clay minerals: Si, Al, Ca, K, Mg, in homogeneous distribution. Iron was also present (visible in element mapping and likely visible as brighter areas in BSE images), contributing to the oxidized surface over ~20 % of the fragment surface.
87.3.2 Marble

Four marble fragments have been analyzed thus far, three from the “Villa of the Antonines” (from the soil matrix) and one a fresh-cut modern marble (Table 87.1).

Like the brick, marble fragments at the study site varied in the degree of deterioration, including some that retained polish. None of the “Villa of the Antonines” marble samples recovered from the soil retained any glassy polished surface, though they are presumed to have been polished at one time. The marbles did retain flat faces, often with granular disintegration. For comparison, the modern marble (M1) did have a polished surface evident at the macroscopic scale, while SEM revealed a polished surface covered with shallow roughness interspersed with striated smooth glazing (Fig. 87.3 upper). No cracking or deep intergranular pitting was seen in M1.

The granoblastic M2 sample was composed of elements consistent with calcitic and dolomitic marble, with prominent amounts of both Ca and Mg. M2 exhibited extensive surface weathering features. A relatively smooth area (Fig. 87.3 middle) showed an etched surface of shallow, oriented crystal points (<10 µm in relief) split by several parallel fissures 5–10 µm wide and ~100 µm long. The etching was a product of chemical solution, while the cracking may have been the result of one or more agents: calcite crystal thermal expansion, salt crystal growth, fire, or physical stress on the stone (Rapp 2002). Elsewhere on the same sample, the surface was deeply pitted, resembling “grikes and clints” karst topography (Fig. 87.3 lower).

Under SEM analysis, marble sample M3 appeared the least-weathered of the analyzed samples. While not retaining polish, original surfaces had minimal relief, resembling the modern marble. Calcite crystals were in good condition, with little intergranular weathering. The weakest locations of the sample were associated with the gray stripe. SEM/EDS revealed this to be a type of mica mineral (probably biotite, given the Mg and Fe present), with fractures parallel to the phyllosilicate plates.

Sample M4 had a green-colored exterior that was lighter in color in the interior. Its composition was more heterogeneous than the other marbles, with inclusions of aluminosilicate minerals, some of these also containing Fe and Mg or K. There was minimal surface deterioration: some flaking and granular loss, but no deep pitting and no cracking.

87.3.3 Glass Tesserae

Four of the glass tesserae were analyzed thus far (Table 87.2), two each of green or red color, specifically selecting examples of both more and less deterioration. A general state of deterioration was visible at the macroscopic level. These macroscopic observations translated to later microscopic analysis (Fig. 87.4).

The chemical composition of the tesserae was variable. The major components of silica, calcium, and soda (Na) were apparent. Minor peaks of iron and chlorine were detected in some locations, due to impurities, colorants (Croveri et al. 2010; Fleming 1997), or possible use of evaporite salts for flux. Most components were homogenous throughout with the exception of T2, which gave indications of element segregation (Fig. 87.5).
The glass tesserae exhibited a variety of deterioration features including surface overgrowths, shallow pitting or cratering, linear and polygonal cracking, and surface flaking. The environment in which this deterioration occurred is uncertain, though burial in the soil is potentially responsible for much of the deterioration. Manufacturing features are also apparent, such as bubbles and striations, both contributing to later deterioration. Since the specimens of the same kind clearly presented different stages of deterioration, it is clear that the degree of deterioration is not reliant on the manufacturing process. We hypothesize the resulting order of deterioration of the tesserae as follows, in first to last order: (1) manufacturing faults (bubbles, striations); (2) pitting and cratering; (3) fine polygonal cracking and overgrowths; (4) large cracking; (5) flaking, biotic growth.

The most common features of the tesserae were shallow circular pits or craters, occasional on some surfaces such as T1 but ubiquitous and extensive on other surfaces, such as T3 and T4 (Fig. 87.4 lower right). The craters ranged in size from 20–80 µm in diameter and in depth <5 µm. We interpret these to be weathering features as they were limited to exposed surfaces and appeared to overlay manufacturing features, such as the striae. Cratering is probably related to chemical dissolution, described by Branda et al. (1999). Craters are not to be confused with often larger and deeper circular vesicles, interpreted as being bubbles in the glass, a product of manufacturing (Croveri et al. 2010). Bubbles do play a role in the surface deterioration, however. In the T1 sample, organic material filled several of these bubbles, which act as a protective location but also serve to retain biological weathering agents. (Fig. 87.4 upper right). In T3, an 80 µm bubble was completely filled with a flaked material, probably now clay (Fig. 87.4 lower left). This may have been an unmelted inclusion in the glass, perhaps of the sodic flux added to the raw material. It weathered into plates concentric to the circumference of the bubble.

Three types of cracking or fissuring were noted on the tesserae: small polygonal cracking; larger angular area cracking; and fine linear cracks. All represent mechanical

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description and macroscopic condition</th>
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<tbody>
<tr>
<td>T1</td>
<td>Green colored, good condition</td>
</tr>
<tr>
<td>T2</td>
<td>Red colored, good condition</td>
</tr>
<tr>
<td>T3</td>
<td>Red colored, poor condition</td>
</tr>
<tr>
<td>T4</td>
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surface stress, but from various causes. The smallest cracks define small (<20 µm) polygonal flakes, best seen on T3 (Fig. 87.4 lower left) and T4, but not observed on T1 and T2 (concordant with the visibly better condition of T1 and T2). The cracks and polygonal flakes are shallow surface features. Likely, polygonal cracking is a result of glass corrosion in either a subsoil or subaerial environment, described by Römich (1999). Atmospheric or soil acids are capable of leaching the alkaline elements of the sodic components. While SEM-EDS identified the presence of alkaline elements on the glass surface (Fig. 87.5), specific element loss (compared to the interior of the specimen) awaits cross-sectional microanalysis.

Fine polygonal cracks were in some instances contained within angular surface blocks, defined by larger cracks up to 20 µm wide. On the T4 specimen, these larger cracks cut through shallow craters or pits (Fig. 87.4 lower left and lower right). The crack-defined areas, ~100–500 µm in diameter, resemble macroscopic exfoliation seen on rock surfaces, and may be caused by temperature stress, salt crystal growth, hydration or dehydration of glass (which may originally contain up to 20 % water, Römich 1999), or clay hydration from the soda component (Ganio et al. 2012). The larger cracks would also allow deeper penetration of further weathering agents.

The third type of cracking, linear cracks (Fig. 87.4 upper left), appeared parallel to striations. We believe the striations, hundreds of µm long and 5–10 µm wide, to be manufacturing artifacts, possibly from irregular cooling or mixing of raw material, from cutting the glass into tesserae, or from polishing the glass. Striations were not apparent on all surfaces, and linear cracking not apparent on all striations. The linear cracks, ~0.5 µm wide, formed in the “troughs” of the striations. Linear cracks may be the result of cooling and shrinking during manufacture, from post-manufacture exposure to temperature extremes, glass hydration/dehydration, clay expansion, or salt crystal growth below the plates (given the presence of Cl, Na, and K identified within the glass matrix, Fig. 87.5). The linear cracks are likewise large enough to allow entry for weathering agents, extending the deterioration feedback. Thin overgrowths or coatings were identified on flat surfaces, particularly on striated surfaces. These overgrowths are probably secondary deposits of silica.
Conclusions

All samples analyzed thus far exhibited a degree of deterioration consistent with burial in a cyclically wet-dry soil environment. Soil moisture suitable for chemical weathering likely contributed to the oxidation and softening of brick, solution and disintegration of marble, and pitting and micromosaic cracking of glass tesserae. Mechanical weathering processes were also important, exerting physical stress to produce cracks in the materials, attributed to anisotropic mineral stress, wetting and drying of clays, and possibly thermal stress.

Our study of the recovered artifacts is ongoing, and better detail of the deterioration process as well as the nature of the materials is forthcoming. Cross-sectional backscatter SEM and EDS will be able to discern the extent of physical stress into the interiors of the samples, as well as determine the loss (or addition) of elements from surface to interior during the chemical weathering process. Continued study of additional specimens will expand the data set, including different varieties of marble and tesserae. With scrap and leftover material, we will also attempt to assess bulk chemistry of the major and trace elements in the brick, marble, and glass. The composition analysis may assist in the establishing the provenance of the materials used, while also establishing the degree of loss of key elements (by weathering) that would render provenance comparisons uncertain. The assessment of the decorative and architectural materials from the “Villa of the Antonines” provides an unexpected, albeit fragmentary window into technological aspects of the Roman Imperial period.

References

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