Red "Staining" on Marble: Biological or Inorganic Origin?

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Brightly colored "stains" on white marble at the Memorial Amphitheater at Arlington National Cemetery prompted a scientific investigation to determine their origin.

Introduction

In 2004 "stains" colored red, orange, yellow, and brownish purple were brought to the attention of the Smithsonian's Museum Conservation Institute as a biological problem on the Memorial Amphitheater at Arlington National Cemetery near Washington, D.C. (Fig. 1). Similar phenomena have been observed on marble monuments in Europe, particularly in Italy. Red stains documented as early as 1844 on the Certosa of Pavia have been the subject of at least four papers over the past 20-odd years,[1] and such stains have been reported on the Fountain of Galatea at Villa Litta near Milan,[2] the Labyrinth Fountain in Florence,[3] and cathedral facades in Orvieto[4] and Siena.[5] In Copenhagen bright orange stains appeared on the pedestal of an eighteenth-century bronze equestrian statue soon after its marble facing was replaced.[6]

Fig. 1. Memorial Amphitheater, Arlington National Cemetery, view from the mast of the USS *Maine* Mast Memorial, probably at the dedication of the memorial in 1920. Library of Congress, Prints & Photographs Division, Theodor Horydczak Collection.

At first, researchers attributed stains on most of these monuments to biological sources. In most cases, however, subsequent microbiological analyses detected only small amounts or the absence of the expected carotenoids and/or other red-pigmented microorganisms. In 1986 the identification of lead compounds on the Labyrinth Fountain led to the conclusion that staining was instead caused by the oxidation of lead.[7] With the exception of stains reported on the Cathedral of Siena, later testing on the European monuments showed that the colored stains consist of the oxides of lead derived from lead used for roofing, gutters, fountain-basin liners, and plumbing or for spacers, cushions, fillers, or waterproofing membranes placed between marble blocks. Alkaline mortar,[8] acidic water,[9] atmospheric agents,[10] microorganisms,[11] and possibly bacteria[12] have been proposed as contributors to the process.

Initially, researchers at the Laboratory of Applied Microbiology at Harvard University attributed colored staining on the Memorial Amphitheater at Arlington Cemetery to a biological source. This team isolated red-pigmented bacteria from amphitheater samples and proposed that they stained the marble much as the bacterium *Serratia marcescens* had stained Isamu Noguchi's white marble Slide Mantra in Miami.[13] When biologists from the Museum Conservation Institute at the Smithsonian examined stained areas on the amphitheater, however, they noted that many locations that remained unstained would provide significant food for biological organisms, especially areas most exposed to rainwater. Subsequently, the

Fig. 2. Memorial Amphitheater, exterior portico. The largest areas of colored stains are on paving blocks between columns outside the balustrade on the exterior portico (type 1 stains). Photographs taken by the authors in 2008, unless indicated otherwise.

Harvard research team determined that the pigmented organism comprised a relatively small percentage of the bacterial community on the stained stone and was not the source of its coloration.

As other explanations for the staining were sought, bright orange-red material was observed on lead-coated copper sheet metal under viewing-box pavers, and analysis showed that it consisted of minium (Pb_3O_4), also known as red lead (see Table 1 for formulae of colored lead oxides). This mineral is so intensely colored that it has been used as an artist's pigment since at least the fifth century BCE.[14] Further testing showed that orange and yellow stains on the building contain the lead compound αPbO and probably, ßPbO, which have been used as the artists' pigments litharge and massicot, respectively. Brownish purple staining likely contains the brown mineral scrutinyite (αPbO_2) and/or its polymorph, the black mineral plattnerite (βPbO_2). (The coloration of these relatively rare minerals makes them unsuitable for use as artists' pigments, but lead dioxides have been found on wall paintings as alteration products of the pigments minium and white lead[15]; in one case plattnerite was identified[16]). Stains from the corrosion of iron, which was not found in the analyses at the amphitheater, could be confused with that of lead compounds, but iron stains tend to be more brownish orange in color.

Once alerted to the existence of these stains, conservators found other examples on marble buildings in the greater Washington area. Deposits of minium between crystal grains can be seen with the naked eye on the large-grained marble quarried at Texas, Maryland, that was used for two structures: the U.S. Patent Office Building (seat of the Smithsonian American Art Museum and National Portrait Gallery) and the Washington Monument, where yellow washes are also present. Lead wool placed between marble blocks during the 1940s has been identified as the source for lead-containing red stains on the dome of the District of Columbia World War I Memorial.[17] Yellow, orange, and red stains on the Carrara marble of the Tripoli Monument at the U.S. Naval Academy in Annapolis, Maryland, contain substantial quantities of lead, apparently derived from lead that was used to seal joints and embed iron elements on the monument.

Fig. 3. Base of the two right arches, 2009. Sweeps of a water-washing wand can be seen in the encircled area, with the arrow indicating their direction.

Fig. 4. Corner post of an exterior stairway (type 2 stains). Staining appears unchanged since photographs were published by Einhorn Yaffee Prescott in 1998.

Fig. 5. Stained corners on column-base blocks near the stage of the amphitheater (type 3 stains).

Fig. 6. Detail of corner block shown in Figure 4, photographed in 2004.

Fig. 7. Detail of same area shown in Figure 6, photographed in 2009, showing the outward migration of stains. The ring of dots indicates the previous inner perimeter of staining on the lower block.

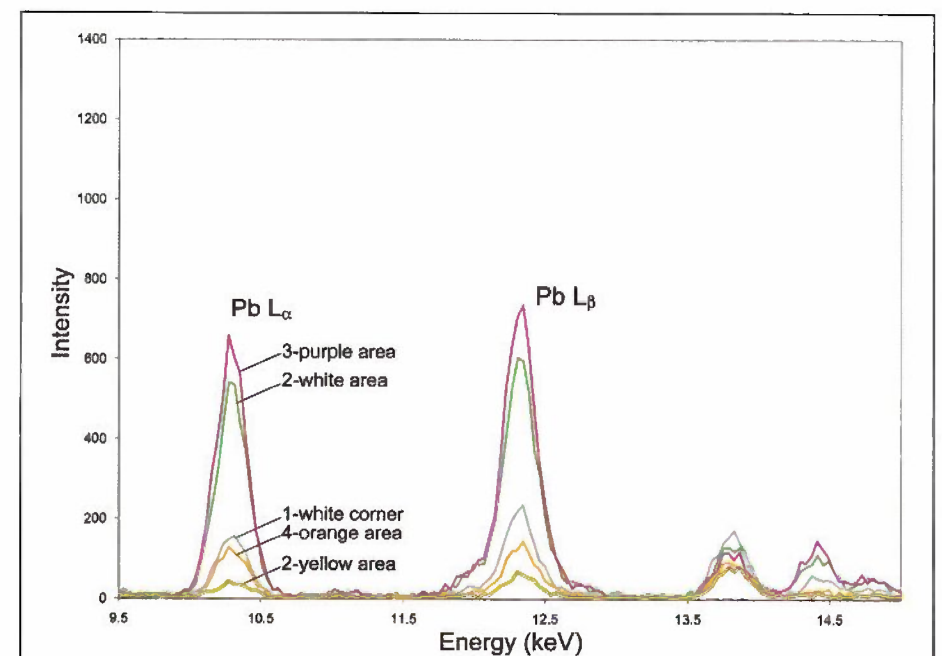

Fig. 8. X-ray fluorescence analyses of five areas on column-base blocks; the locations of the areas analyzed are indicated in Figure 9. The highest concentrations of lead were measured on white and purple surfaces (areas 2 and 3 respectively). Orange and yellow areas showed less lead, as did the damaged corner.

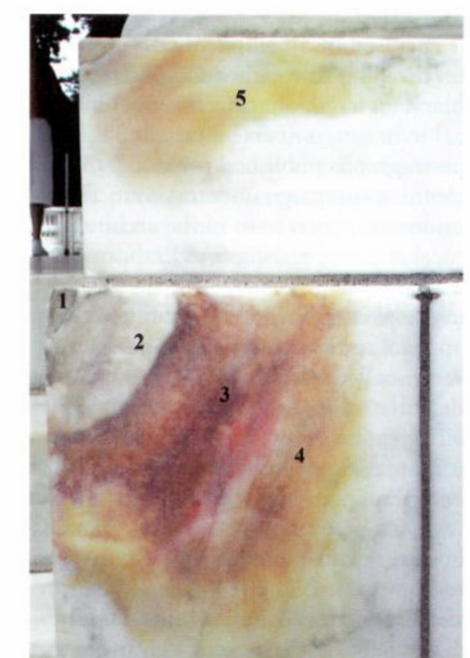

Fig. 9. Detail of the corner block showing the location of each analysis graphed in Figure 8.

Table 1. Colored Lead Oxides

Mineral	Common name	Chemical formula	Color	Increasing oxidation/ decreasing Pb
litharge massicot		α-PbO ß-PbO	yellow orange	↓
minium	red lead	Pb_3O_4	red	
scrutinyite plattnerite		α-PbO_2 ß-PbO_2	brown black	
hydrocerussite cerussite	white lead	$2PbCO_3Pb(OH)_2$ $PbCO_3$	white white	

To date, publications on American buildings have not described this phenomenon, and one goal of this paper is to raise awareness of lead staining and elicit further examples. This paper also describes six types of colored stains found on the Memorial Amphitheater, assesses methods of identifying lead-containing colored stains on monuments, details conditions necessary for staining, and considers some methods of remediation.

Staining at the Memorial Amphitheater

The Memorial Amphitheater at Arlington National Cemetery was constructed of Mountain White–grade marble from Danby, Vermont, from 1915 to 1920 to designs by the New York–based architectural firm of Carrère and Hastings. The amphitheater's central seating area is enclosed by an elliptical portico open on the sides to weather. Considerable black material, almost certainly biological in origin, is visible on the building in photographs published prior to a major cleaning campaign undertaken in 1996 under the supervision of the architectural and engineering firm Einhorn Yaffee Prescott (EYP).[18] Far less black material is visible today, although it appears to be accumulating again on water-collecting areas, such as steps. Brightly colored orange-red stains visible in EYP's before-treatment photographs, on the other hand, appear to be unchanged since the photographs were taken, except where blocks have been replaced. Comparison of photographs taken in 2004 and 2009 also show that most colored stains did not change over the course of that five-year period. Physical evidence of attempts to remove the colored stains suggests past use of mechanical cleaning devices (grinders or sanders), pressurized water washing, and chemical cleaners such as Clorox bleach (NaClO) and phosphate-containing solutions, as will be detailed below.

Analyses conducted by the Smithsonian's Museum Conservation Institute showed definitively that lead is present in highly colored areas on the amphitheater, while it is absent from unstained stone (with one exception noted below). Lead-containing construction materials were found in the vicinity of some stains, and it seems likely that lead is present near where other stains occur, almost certainly in joints where the lead is obscured by mortar and marble. Only disassembly of the monument, however, is likely to reveal its existence conclusively.

To provide a better understanding of the staining, the colored stains on the amphitheater are grouped in six categories, each with somewhat different characteristics, described as follows:

Type 1 stains: on marble pavers between external columns of the building's portico. In contrast, staining is absent on adjacent blocks below the columns (Figs. 2 and 3). These pavers are by far the most common location for colored stains on the building. Close scrutiny of the photograph taken around 1920 indicates that the stains were already present then, suggesting that they had formed almost immediately (Fig. 1).

Today the stains are characterized by red spots and yellow washes on horizontal surfaces of the pavers, which slope away from the marble balustrade of the portico. Evidence of water washing is visible as light streaks noted in Figure 3, apparently from the strokes of power-washing equipment; although some soiling on top of the colored stains was removed by the washing, the stains themselves appear to have been unaffected. More densely colored red and brownish purple areas are predominant on exterior vertical surfaces of these pavers, apparently as a result of thicker deposits of the staining material. X-ray fluorescence analysis (XRF) confirmed higher concentrations of lead on more densely colored vertical surfaces than on horizontal surfaces of the same blocks (see the XRF section below for details of the technique). Energy-dispersive spectroscopy (EDS) showed the presence of a significant quantity of phosphorus atop lead-containing particles on one brownish purple sample, most likely residue of a phosphate-containing cleaning agent (see section on SEM-EDS below for details of the technique). Brownish purple areas are also associated with significant stone erosion, and they are furthest from the probable source of lead.

The most likely source of lead for these stains would be lead under the balustrade; this source would also explain the absence of stains on adjacent blocks below columns. Gravity probably washed water containing small amounts of dissolved lead over the outwardly sloping pavers and down the exterior faces of the blocks. Although lead could not be seen under the balustrade, changes made during construction that would affect drainage include omission of pairs of scuppers in the bottom horizontal member of the balustrade.[19] Lead sheet might have been installed during construction in lieu of the scuppers.

Type 2 stains: on a single base block of a stairway corner post outside the portico leading to the Memorial Display Room north of the theater's stage. This spot is arguably one of the most disfigured areas on the monument, in part because its intensely colored stains are found on an otherwise pristine staircase (Fig. 4). Bright orange-red areas are concentrated next to spalled-off corners and along crevices. Minium has been identified in samples by X-ray diffraction analysis (XRD) and Raman spectroscopy (see the XRD and Raman sections below for details of the techniques). Black *Verrucaria* lichens, visually identified by Smithsonian lichenologist Paula DePriest, are also associated with the crevices but appear to be unconnected with staining, apart from the fact that both depend on moisture. Orange and yellow washes appear further from the corner. The source of lead is apparently sheet lead in the joint above the block: a positive test for lead at a pointing loss was produced using Plumbtesmo test strips (see the microchemical-testing section below for details). EYP photographs reveal that Clorox was tested to decolorize stains on this block, apparently without any effect, since they appear the same today.[20] Another EYP photograph shows corner-post blocks that exhibit similar but more severe staining on the same stairway; they have since been replaced with new blocks.

Type 3 stains: on column and pilaster bases at an entrance to the portico just north of the stage. Corners and high-relief areas are generally brownish purple, with other colored stains (red, orange, and yellow) at their perimeters (Fig. 5). No sources of lead could be seen, but sheet lead is likely present in joints above stained areas, where it was used for cushioning or shimming the columns or pilasters.

One fascinating block in this area features a unique example of change over the past five years (Figs. 6 and 7). Comparison of photographs taken in 2004 and 2009 show that brownish purple, orange red, orange, and yellow stains have migrated downward and outward over this period, with marked expansion of the area of yellow wash. These changes in staining may have been accelerated by a large number of wet-dry cycles from exposure to sun, wind, and rain. Higher evaporation rates are well known to occur on corners of stone blocks, and the location of this particular block at an entrance to the portico increases its exposure to wind. One side of the block also faces west, the prevailing direction from which rain arrives in the Washington area. Finally, this area is a primary entry point to the amphitheater from the much-visited Tomb of the Unknowns, and, as a result of its prominent location, stains have no doubt been subjected to attempted cleaning. Circular marks left by a grinder or sander on the surface of the block attest to heavy-handed attempts at stain removal. Cleaning solutions may also have increased the formation, dissolution, and redistribution of lead compounds, although documentation of cleaning is not presently available.

XRF analyses on the block found that the purple stain had the greatest amount of lead (Figs. 8 and 9). The adjacent white area, which had been purple in 2004, was found to have nearly as much lead, probably because of the formation of white lead compounds. The most likely candidates are cerussite (lead carbonate) and hydrocerussite (lead carbonate hydroxide), since carbonates are readily available from the marble and produce these stable white minerals. XRF showed the least lead in orange and yellow areas further from the probable source of lead. These areas almost certainly contain one or both of the polymorphs of PbO, which are somewhat soluble in acidic, neutral, and slightly alkaline solutions.[21]

Type 4 stains: adjacent to a lead-containing moisture barrier placed underneath the viewing-box pavers. The exposed lead-coated copper drip edge of the moisture barrier has deposits of bright orange-red and yellow material on and near it (Fig. 10). XRD confirmed the presence of minium in a sample taken from the metal sheet and of litharge in a sample from an adjacent yellow wash. The lead-coated copper sheets were almost certainly installed to prevent water penetration into basement rooms under the viewing boxes. Stalactites and water droplets on the drip edge, as well as rivulets of calcium deposits on the wall below, attest to copious amounts of water running off the barrier. Yellow and orange staining above the copper sheets reflects capillary rise of the lead oxides.

Type 5 stains: on opposite sides of a viewing box enclosure stone. Matching orange patches on opposite faces of one block are unique at the amphitheater (Fig. 11). XRF analysis showed that lead is present in stained areas but absent from adjacent white areas like the one being tested in the photograph. No lead is visible at the joint. However, the location of the stains near it suggests that the source of lead is likely related to the attachment of the block to the adjacent stone, possibly by an iron cramp that was set with hot lead or lead wool to inhibit corrosion of the iron. Cracks next to the joint retain moisture that probably contributes to staining.

Type 6 stains: around bronze electrical sockets. Red stains are found around bronze fittings set into holes in paving stones with lead sheet, indicated by an arrow in Figure 12. The slight recess of the socket in the floor almost certainly contributed to retention of moisture and subsequent staining.

Identification Techniques

X-ray fluorescence analysis (XRF). A Bruker Tracer III-V handheld energy-dispersive X-ray fluorescence spectrometer with a spot size of 4 mm was used for nondestructive elemental analyses at the Memorial Amphitheater (Fig. 11). The instrument is equipped with a rhodium tube and a SiPIN detector with a resolution of approximately 170 eV FHWM for 5.9 keV X-rays (at 1000 counts per second) in an area of 7 mm^2. The X-ray tube was operated at 40 keV and 15 μA, with an aluminum (12 mil)/titanium (1 mil)/copper (1 mil) filter placed in the X-ray path. All analyses were conducted for a 60-second live-time count. Lead fluoresces readily by XRF and can be detected in a marble matrix at concentrations well below 100 ppm.

This technique confirmed the presence of lead and calcium in all highly colored areas tested on the amphitheater. By contrast, lead was not found in significant quantities on unstained stone, except in the white area that had been brownish purple five years earlier (see type 3 stains). XRF also provided useful information about concentrations of lead, as shown in Figure 8. It must be noted that dull brown stains on amphitheater paving apparently stem from another source: XRF on brown-stained stage and portico pavers (not pictured) showed only calcium and the small amounts of strontium present in the marble. XRF testing on the Tripoli Monument in Annapolis also showed substantial quantities of lead on stained marble. Overall, portable XRF equipment proved to be the simplest way to identify the presence of lead in colored stains on the amphitheater, as well as its absence from unstained areas.

Fig. 10. Yellow and red staining related to lead-coated copper sheet in a joint (type 4 stains). The water droplets visible in the photograph reflect the large amount of water shed by this membrane, resulting in thick calcium incrustations from dissolved marble coating the sheet and running down the marble face.

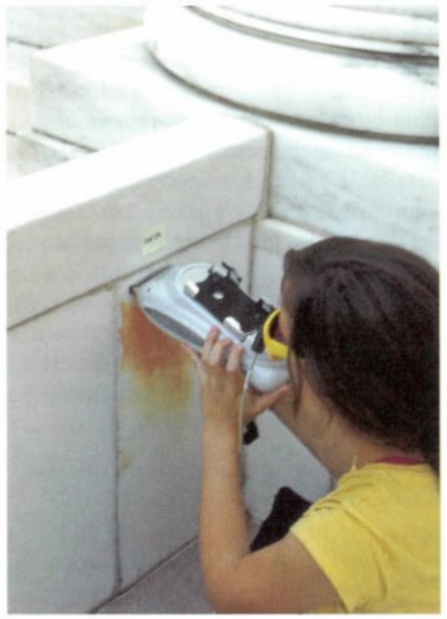

Fig. 11. Stone from the viewing-box enclosure with identical stains on opposite faces (type 5 stains). Vertical cracking of the stone next to the joint probably contributed to staining by its retention of moisture. X-ray fluorescence analysis performed on stone above the stain showed no lead, while the stain itself did.

X-ray diffraction analysis (XRD). Micro-X-ray diffraction analysis using a Rigaku D/Max Rapid confirmed the presence of minium, litharge, massicot, and plattnerite in reference mineral specimens obtained from the Smithsonian's National Museum of Natural History, as well as hydrocerussite in white lead pigment. On samples collected from the amphitheater, XRD successfully confirmed the presence of minium and litharge, as well as minium in samples from the Patent Office Building and the Washington Monument. A number of attempts at XRD analysis proved unsuccessful in identifying lead components in samples taken from the amphitheater that were thought to contain the less highly colored yellow massicot and brown scrutinyite, although lead was confirmed to be present in those samples by XRF and SEM-EDS analysis. This inability to identify some lead species by XRD may be attributed in part to the small size of lead-containing particles (generally less than 30µm across, according to SEM) compared to the significant amount of calcite in the samples. Lead particles less highly colored than minium are also more difficult to locate in a sample and mount for analysis.

Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS). Using the energy-dispersive spectrometer accompanying a Hitachi S-3700N scanning electron microscope, lead-containing particles were identified in amphitheater samples. SEM showed that lead particles collect at grain boundaries of the calcite and revealed considerable diversity in their shape, size, distribution, and grayscale. In backscattered SEM images, lead particles were easily distinguished from those containing calcium, because the lead particles appear brighter than those of calcium, in agreement with lead's higher atomic weight. Grayscale in backscattered electron images may also provide an indication of specific lead compounds, in accordance with the relative amount of lead in the compound: PbO (litharge and massicot) > Pb_3O_4 (minium) > PbO_2 (plattnerite and scutinyite) > $PbCO_3PbOH$ or $PbCO_3$ (hydrocerussite or cerussite) (Table 1).[22] Since PbO has more lead than Pb_3O_4, for example, "lighter" crystals may correspond to litharge or massicot and "darker" crystals to minium in a light orange sample taken from the stairway corner post (type 2 stains).

Raman spectroscopy. An Almega XR Dispersive Raman spectrometer, made by Thermo Fisher Scientific, with 532 and 785 nm excitation identified minium in samples taken from the bright orange-red area on the stairway corner post (type 2 stains). Although Raman is capable of distinguishing among different oxides of lead, no other oxides were identified on samples from the amphi-

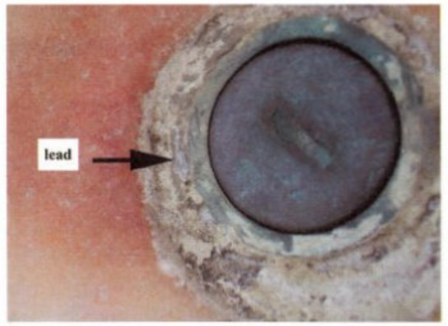

Fig. 12. Red staining surrounding a bronze electrical socket set with lead in paving (type 6 stains).

theater. The presence of unidentified peaks in the distinguishing region, however, suggests that intermediate lead compounds may be present. Some lead oxides, such as plattnerite, are also known to be weak Raman scatterers.[23] On-site use of a portable Raman (First Defender by Ahura Scientific, Inc.) was attempted, but lead compounds were not identified due to high instrument and matrix backgrounds, i.e., the calcium carbonate of the marble overwhelmed the instrument's detector.

Polarized-light microscopy (PLM). Using a Leitz Laborlux 12 POL 8 microscope, PLM was used to test a red-stained marble sample taken from the Washington Monument. The sample was ground, mounted in Cargille's Melt Mount, and compared using the microscope to a reference sample of minium pigment. The test sample was identified as minium on the basis of the mineral's highly characteristic blue-green interference between crossed polars. Other samples from the compounds being tested were not subjected to PLM examination, but it is likely that the difficulty of finding and mounting the less highly colored lead-containing compounds would make their identification more difficult by this method.

Microchemical testing. Microchemical testing is an inexpensive means of establishing the presence of lead oxides in samples taken from monuments. Such tests make use of acids to dissolve the lead compounds; thus, testing should be done on samples rather than in situ, since acids etch marble.

Commercial products for lead testing are useful (e.g., Lead Check, marketed for detection of lead in house paint, and Macherey-Nagel's Plumbtesmo test strips, sold for detection of lead on metal surfaces, ceramics, and toys). Both contain sodium rhodizonate ($C_6Na_2O_6$) in acidic solutions that etched test marble[24]; in use, the lead-containing particles turn cranberry red. The classic conservation test for lead can also be employed: dissolution of a sample in dilute nitric acid, followed by the addition of potassium iodide (KI) to form hexagonal yellow crystals of lead iodide (PbI_2).[25] All three methods worked well when tested on mineral and pigment samples, although positive tests for minium using the sodium rhodizonate indicators were sometimes difficult to differentiate from undissolved orange-red minium particles. Use of a low-power microscope (approximately 10x) proved necessary to confirm results on samples taken from stained marble due to the small particle sizes of the lead compounds.

Exclusion of the possibility of biological staining. Most biological staining is green or black. Red, brownish purple, orange, and yellow stains from biological substances are relatively rare, although discolorations on Noguchi's Slide Mantra indicate that red staining can occur from biological substances in a tropical environment. Lead-resistant microorganisms have been found with lead compounds on marble, but it remains unclear to what extent, if any, they play a role in the formation of those compounds.[26] Caution must be exercised if biological matter is found on stained marble, since microorganisms are ubiquitous in nature and may not be the source of coloration. Two pigment-producing fungi (*Epicoccum nigrum* and *Drechslera* sp.) were previously identified as causing discolorations on the Tripoli Monument at Annapolis,[27] for example, but XRF testing indicates instead that the staining is almost certainly caused by lead compounds.

Visual examination can often eliminate the possibility of biological origin for staining. Biological deposits are heaviest where food sources are maximized, most often associated with areas of greatest moisture. Lead stains are also associated with moisture, but they tend to be more localized. In the case of the Memorial Amphitheater, for example, photographs showed that black biological stains were heavy on horizontal surfaces of steps prior to the 1996 cleaning but that colored stains were absent from the steps. Another example is the red staining found on pavers between columns (type 1 stains). If that staining were biological in origin, it would likely be present on adjacent stones below the columns as well.

Successful decolorization of stains with substances used for removing biological stains could differentiate them from lead-based stains. If a stain decolorizes following application of a cotton poultice of hydrogen peroxide (H_2O_2), for example, the stain is almost certainly biological in origin. Application of biocides, such as alcohol or quaternary ammonium compounds, can also kill many biological organisms but may be too slow as a diagnostic technique. Indeed, the red stains on Noguchi's Slide Mantra were found to be difficult to remove or decolorize using a biocide. Harvard University researchers successfully used the enzyme laccase in the laboratory to decolorize the red *Serratia marcescens* identified as the source of staining on the Noguchi sculpture, but the technique is experimental and would likely be expensive and difficult to implement in the field as a diagnostic technique.

Summary of techniques for positive identification of lead compounds. For an architect or architectural conservator encountering red stains on a building or monument, the best technique for positive determination that lead compounds are present is portable XRF. This non-destructive technique can measure the small particles of lead without difficulty, because lead fluoresces readily and is measurable in low concentrations in stone matrices. Stained areas can be quickly and easily tested, and results can be compared to those obtained for unstained areas. XRF cannot identify the exact lead compound, but showing that lead-containing compounds are present is sufficient for most purposes. While the cost of portable XRF equipment is not inconsequential, such equipment is increasingly available for use at museums, by archaeometrists, and in the mining and metal-recycling industries.

If XRF equipment is not available, microchemical testing would be the next choice. Such testing does not require special expertise or equipment, and the test chemicals or products can be easily purchased. Microchemical testing requires sampling, however, and there is some possibility that samples would not contain the tiny lead-containing particles, especially when the particles are less highly colored.

PLM requires more expensive equipment and skill than microchemical testing and is considered unsatisfactory as a diagnostic technique. PLM also requires sampling and poses some of the same difficulties as XRD testing in terms of mounting less highly colored lead-containing particles.

The three other instrumental techniques used for analysis (SEM-EDS, XRD, and Raman) provided additional information for this study. They require a well-equipped laboratory, however, and are mainly of interest for research purposes. Micro-XRD proved to be best for identifying specific lead compounds in reference materials, but it failed to provide results other than calcium carbonate for a number of samples, apparently due to the small sizes and amounts of lead-containing particles present in the samples. SEM-EDS shows potential for studying particle shapes and crystal formation, and specific compounds may be identified based on gray scale, in combination with XRD analyses. Raman proved to be the least successful instrumental technique, as described above.

Causes of Lead Staining

A search of the literature found that staining of marble from lead was far from unknown in the past. In 1925, for example, the Vermont Marble Company warned against the use of lead in a promotional publication, *The Book of Vermont Marble: A Reference for Architects and Builders*, with this statement: "If cushions have to be used under heavy pieces, these should be of block tin or zinc. Lead is the material often used, but our experience has been that under certain conditions this causes stains."[28] Although the company supplied marble for the Memorial Amphitheater and published two photographs of the building in the book, apparently its advice was unheeded by the architects or builders.

In terms of laboratory research in this area, F. L. Brady's 1934 publication by the Building Research Board in England is seminal.[29] Brady focused on the important role of alkaline mortars in producing lead corrosion, especially those containing portland cement. His tests showed that portland cement produced much more severe corrosion than high-alumina cement and lime mortar. Fresh portland cement typically produces pH values up to 13.5, increasing the dissolution of lead substantially more than saturated lime water, with a pH of 12.5.[30]

Portland-cement mortar is a likely factor in staining on the amphitheater, although the composition of the original mortar is unknown. Both the hardness of the present mortar and the analysis of a mortar sample[31] indicate that portland cement is a major component of mortar used during pointing work done in 1996. The close proximity of mortar containing portland cement to lead located in joints should facilitate staining. A related example is the bright orange-red staining on the pedestal of the equestrian monument in Copenhagen noted in the introduction. It appeared only after the original gap between the marble facing and the pedestal's core was filled with alkaline hydraulic mortar.[32]

Moisture is critical for the formation of stains as the vehicle for dissolving lead and distributing lead ions and compounds. Stone would have been more exposed to rainwater during construction and prior to cleaning, reroofing, and repointing of the Memorial Amphitheater by EYP in 1996; moisture penetration in the building is reported to have been a serious problem.[33] Water washing in attempts to keep the building pristine may also have served to increase colored stains. The association of moisture and lead staining on the building is demonstrated by type 1 and 6 stains: they are located on horizontal surfaces with significant water runoff or in areas where water would collect. Heavy deposition of colored compounds on more deteriorated vertical surfaces of the paving blocks between columns may also be related to greater moisture retention in those areas. Even when the rest of the building appears dry, water runs down vertical surfaces below the lead-coated membrane under viewing boxes, creating the type 4 stains. Marble itself may play a role in staining because of the way its fine pores retain moisture: lead-based staining has not been reported on limestone, which is more porous.

It is probably not a coincidence that a number of examples of lead staining are found in Washington, D.C., which is noted for its high humidity. For example, excess moisture is clearly present on the dome of the District of Columbia World War I Memorial, evidenced by the presence of significant amounts of black biological material along with lead-containing red stains. Similar black deposits on the Tripoli Monument were already visible in a historic photograph taken before 1860 (when the monument was at the U.S. Capitol),[34] and black biological staining is present today, despite recent cleaning.

Prevention of Lead Staining

Lead, high alkalinity, and water are essential for the formation of lead-derived stains on marble, and staining can be prevented in the absence of any one of these elements. Minimizing them will also slow the rate of formation of stains. In marble construction, materials other than lead should be used for plumbing, cushioning or shimming stone, waterproofing membranes, corrosion-prevention for iron, and setting bronze. When lead is present and cannot be removed, use of lime-based mortar is advisable for repointing, since the higher alkalinity of portland-cement mortar contributes to the dissolution of lead and formation of colored stains. Reasonable efforts should be made to avoid exposure of monuments to excess water if lead is known to be present.

Removal of Lead-based Colored Stains

The prognosis for removal of colored stains from white marble is poor, because lead oxides are relatively stable. The most highly colored oxides are insoluble at pHs between about 5 and 10, requiring marble-damaging acidic or extremely alkaline solutions to dissolve them.[35] Clorox bleach, which photographs reveal was tested on the corner post at the Memorial Amphitheater,[36] was clearly ineffective. Indeed, bleach could be harmful, since it tends to render the environment more oxidizing, which would enhance the stability of the lead oxides. Other popular marble cleaning agents, such as hydrogen peroxide (H_2O_2, another powerful oxidizer) and ammonium citrate solutions, also proved ineffective in this testing. The most promising avenue for further investigation would be research into the transformation of colored to white compounds, as seems to have occurred on the singular block described in the type 3 stain section. At present, disguising the stains by overpainting or replacement are the only alternatives in the case of severe lead staining.

Conclusion

Red, yellow, and brownish purple "stains" on white Vermont marble were definitively found to consist of lead compounds at the Memorial Amphitheater at the Arlington National Cemetery and other monuments in the greater Washington, D.C., area. Use of a portable X-ray fluorescence unit proved particularly useful in determining that lead was present on stained marble in situ. Minium and litharge were identified by X-ray diffraction analysis of samples taken from the monument, and minium was also found using Raman spectroscopy in the laboratory. Other methods for identification of lead, such as microchemical tests, can also be successful. Prevention of staining requires elimination of any of the elements necessary for its formation: excess water, lead, and high alkalinity, such as that produced by portland-cement mortar. Methods of remediation are unlikely to be successful, beyond overpainting or replacement of stone.

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Fire Protection of the Las Flores Adobe in San Diego, California

DOUGLAS PORTER AND NICK ARTIM

This article explores the application of recently developed technology in designing and installing fire-detection and fire-suppression systems that meet fire-safety and historic-preservation goals.

History and Significance

Located on Camp Pendleton, near Oceanside, California, the Las Flores site has been an important center of human activity for at least 2,000 years. At the time of Spanish settlement in the late eighteenth century, a *Luiseno* pueblo already existed at Las Flores, and an *Asistencia*, or mission outpost, was established in 1823. In 1841 Pio Pico, the last Mexican governor of Alta California, received a grant for a vast tract of land lying adjacent to the pueblo at Las Flores.[1] In 1843 Las Flores was added to his holdings to form the *Rancho Santa Margarita y Las Flores*; Pico's tract ultimately exceeded 130,000 acres.[2]

In 1864 Pico sold the *rancho* to his brother-in-law, Don Juan Forster, to avoid foreclosure on the property.[3] Forster built the adobe ranch house at Las Flores as a wedding present for his son, Marcus, in 1868.[4] Probably one of the last traditional adobe ranchos constructed in California, the house is unusual in that it incorporates the vernacular architectural traditions of the hacienda with the more formal detailing of the Monterey-style main block. Following the deaths of their parents in 1882, Marcus and his brothers were forced to sell Santa Margarita y Las Flores to pay family debts.[5] San Francisco business partners James Flood and Richard O'Neill bought the property and leased the Las Flores adobe and 1,500 acres to the Magee family in 1888.[6]

The Magee family farmed about 3,000 acres of the property, and in the early-twentieth century the farm was one of the major producers of lima beans in the U.S.[7] Architect Cliff May was a frequent visitor, and the Las Flores adobe was featured in his 1946 book entitled *Western Ranch Houses* as an example of the Hispanic California architecture that inspired his incredibly popular "ranch-style" designs.[8] The United States Marine Corps acquired Las Flores in 1942, just after the U.S. entered World War II, and President Franklin Delano Roosevelt granted a life estate to the Magee family.[9] The last surviving family member died in 1968, leaving the ranch house unoccupied.[10]

Fig. 1. The Las Flores Adobe, a nineteenth-century adobe rancho on U.S. Marine Corps Base Camp Pendleton in north San Diego County, 2006. The building is associated with the historic *Rancho Santa Margarita y Las Flores* and is a National Historic Landmark. All images courtesy of the authors, unless otherwise noted.

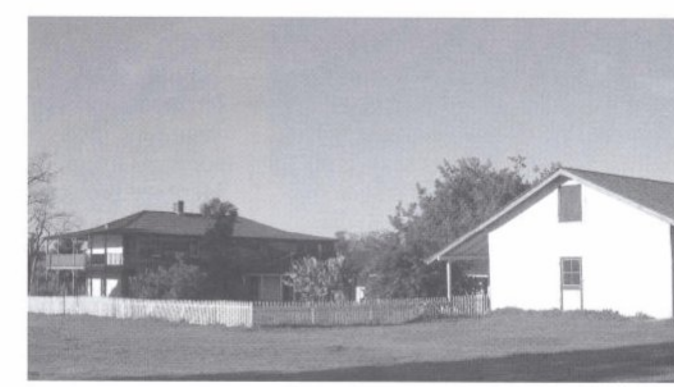

Fig. 2. Courtyard enclosed by the Monterey block (left) and the gable-roofed carriage barn (right).