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, and such stains have been reported on the Fountain of Galatea at Villa Litta near Milan, the Labyrinth Fountain in Florence, and cathedral facades in Orvieto and Siena. In Copenhagen bright orange stains appeared on the pedestal of an eighteenth-century bronze equestrian statue soon after its marble facing was replaced.

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. 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, gutter, fountain-basin liners, and plumbing or for spacers, cushions, fillers, or waterproofing membranes placed between marble blocks. Alkaline mortar, acidic water, atmospheric agents, and possibly bacteria 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. 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...
Harvard research team determined that the pigmented organisms 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 (Pb₃O₄), 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. Further testing showed that orange and yellow stains on the building contain the lead compound aPbO and probably, bPbO, which have been used as the artists’ pigments litharge and massicot, respectively. Brownish purple staining likely contains the brown mineral scrutinyite (cPbO₂) and/or its polymorph, the black mineral platteinite (dPbO₂). (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; in one case platteinite was identified). Stains from the corrosion of iron, which was not found in the analyses at the amphitheater, could be confounded 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. 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.
Table 1. Colored Lead Oxides

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Common name</th>
<th>Chemical formula</th>
<th>Color</th>
<th>Increasing oxidation/ decreasing Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>litharge</td>
<td>a-PbO₂</td>
<td>Pb₂O₃</td>
<td>red lead</td>
<td></td>
</tr>
<tr>
<td>massicot</td>
<td>PbO</td>
<td>PbO₂</td>
<td>yellow</td>
<td></td>
</tr>
<tr>
<td>litharge</td>
<td>a-PbO</td>
<td>PbO₂</td>
<td>orange</td>
<td></td>
</tr>
<tr>
<td>brown stone</td>
<td>PbO₂·2PbO₃</td>
<td>PbO₂·2PbO₃·1/4P₂O₅</td>
<td>brown</td>
<td></td>
</tr>
<tr>
<td>cerussite</td>
<td>PbCO₃</td>
<td>PbCO₃</td>
<td>yellow</td>
<td></td>
</tr>
<tr>
<td>white lead</td>
<td>Pb₃O₄</td>
<td>Pb₃O₄</td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>red oxidation Pb</td>
<td>PbO₂</td>
<td>PbO₂</td>
<td>red lead</td>
<td></td>
</tr>
</tbody>
</table>

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...
X-ray diffraction analysis (XRD). Micro-X-ray diffract analysis using a Rigaku DMax Rapid confirmed the presence of minium, litharge, and massicot, and plattnerite in reference mineral samples obtained from the Smithsonian's National Museum of Natural History, as well as hydrocerussite in white lead pigments. On samples collected from amphitheater, XRD successfully confirmed the presence of minium and litharge, as well as hydrocerussite, although lead samples were easily distinguished from litharge or massicot and "darkcr" crystals to minium in a light orange sample from the stairway corner post (type 2 stains). Ramon spectroscopy. An Almega XR dispersing 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 Ramon is capable of distinguishing among different oxides of lead, no other oxides were identified on samples from the amphitheater. 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. On-site use of a portable Ramon (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 mi-croscope, PLM was used to test a red-stained marble sample taken from the Washington Monument. The sample was ground, mounted in Carpyell'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 exam-ination, but it is likely that the difficulty of finding and mounting the less highly colored yellow massicot (plattnerite and 3) would make their identification more difficult by this method.

Microchemical testing. Microchemical testing is a method 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 Maderian's Plumbemos test strips, sold for detection of lead on metal surfaces, ceramics, and toys). Both contain sodium dihydrogen phosphate (Na2HPO4) in acidic solutions that etched test marbles, but in use, the lead-containing particles remained red. The classic color test for lead can also be employed: dissolution of a sample in dilute nitric acid, followed by the addi-tion of potassium iodide (KI) to form hexagonal yellow crystals of lead iodide (PbI2). Since PbI2 has more lead than PbO4, 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). Scanning electron microscopy with X-ray fluorescence (SEM-EPS) scanning electron microscopy (SEM). Using the energy dispersive spectrometer accompanying a Hitachi S-3700N scanning electron microscope, lead-containing particles were identified in amphibolite samples. SEM showed that lead particles collect at grain boundaries of the rock and revealed considerable diversity in their shape, size, distribution, and gray scale. 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. Gray scale 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) > PbO2 (minium) > PbO (plattnerite and cerussite) > PbCO3 (hydrocerussite or cerussite) (Table 1). Since PbCO3 has more lead than PbO2, 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).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 (H2O2), for example, the stain is almost certainly biological in origin. Application of biocides, such as alcohol or quaternary ammonium compound, can 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 exercised if biological matter is found when tested on mineral and pigment samples, although positive tests for lead compounds may be present. Some lead compounds may be present on adjacent stones below the amphitheater. The presence of unidentified when tested on mineral and pigment compounds, in accordance with the least highly colored yellow massicot (plattnerite and 3) would make their identification more difficult by this method. 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. 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as a diagnostic technique. PLM also requires sampling and poses some of the difficulties in terms of mounting less highly colored lead-containing particles.

The three other instrumental techniques used for analysis (SEM-EDS, XRD, and Raman) provide additional information for this study. They require well-equipped laboratories, 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 by lead is not uncommon but seems to be little understood. Although the causes of the original mortar is unclear, both the hardness of the material and the presence of a large sample is important that portland cement is a major component of mortar used during pointing work done in the 1950s. 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. As noted in the introduction, it appeared only after the original gap between the marble face and the pedestal’s core was filled with alkaline hydraulic mortar.

Moisture is critical for the formation of stains as the vehicle for dissolving lead and distributing lead ions and compounds. Stains would have been more exposed to moisture during cleaning, prior to being coated. After cleaning, exposed areas are located on horizontal surfaces with significant water runoff or in areas where the capillary water would collect. Dissolution of colored compounds on more deteriorated vertical surfaces of the monument blocks between columns must also be related to greater moisture retention in those areas. Even when the rest building appears dry, water runs down the vertical surfaces. If the coating mix is not coated membrane under viewing boxes, creating the type 4 stain. Marble itself may play a role in staining because of the way its fine pores retain moisture, but 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 were found in Washington, D.C., which is noted for its high humidity. For example, excessive moisture is clearly present on the dome of the District of Columbia World War I Memorial. High moisture incident on 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), 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 shielding stone, waterproofing membranes, corrosion-prevention for iron, and setting bronze. When lead is present and cannot be reduced, the use of lime mortar is advisable for repointing, since the higher alkalinity of portland-cement mortar is beneficial 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-colored Stains

The proposal for removal of stains from white marble is poor, because lead oxides are relatively stable. The most highly colored oxides are insoluble in water and at pH 10, regardless of the material, and all types of cleaning agents dissolve them. Clorox bleach, which photograph revealed was tested on the corner post at the Memorial Amphitheater in Washington, D.C. This stain, which was not clearly visible, bleach could be harmful, since it tends to render the environment more oxidizing and dissolve organic material from the surface of the lead oxides. Other popular marble cleaning agents, such as hydrogen peroxide, can be harmful and destroy the fabric of the lead oxides. A more promising avenue for further investigation would be research into the transformation of colored to white material or into a more stable form such as 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.

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Notes


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 Indian pueblo already existed at Las Flores, and an assistance, or mission outpost, was established in 1823. In 1843 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. In 1843 Las Flores was added to his holdings to form the Rancho Santa Margarita y Las Flores, Pico's tract ultimately exceeded 200,000 acres, and in 1864 Pico sold the ranch house tin occupied. In 1864 Pico sold the ranch house to his brother-in-law, Don Juan Forster, to avoid foreclosure on the property. Forster built the adobe ranch house at Las Flores as a wedding present for his son, Marcus, in 1868. 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. 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 1884. 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. 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. 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. The last surviving family member died in 1968, leaving the ranch house unoccupied.