CASE STUDY: RED STAINING ON MARBLE

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Extended Abstract

Red stains were observed on the marble of the Certosa of Pavia in Italy as early as 1844 (Realini and Sorlini, 1988), and they have since been found on other marble monuments, such as the Cathedral of Orvieto, the *Fountain of Galatea* at Villa Litta north of Milan, the *Fountain of the Labyrinth* in Florence, and the pedestal of an equestrian statue in Copenhagen. Microbiological analyses carried out on stained marble samples have sometimes detected carotenoids and red-pigmented organisms. On the other hand, the presence of minium (Pb_3O_4, with a bright red color) on the aforementioned monuments suggests that these red stains can also be caused by the corrosion and oxidation of lead present in gutters, fountain plumbing pipes, or between marble blocks. Up to now there is no clear explanation of how the corrosion of lead and formation of minium occur. Hypotheses include corrosion of lead gutters by acidic water (Zanardini et al, 1994); oxidation of lead salts derived from atmospheric attack of lead building components (Realini and Sorlini, 1988; Bruni et al., 1995); attack of lead by alkaline water that percolated through non-carbonated mortar (Bredal-Jørgensen et al., 2008); production of hydrogen peroxide by micro-organisms (Petushkova and Lyalikova, 1986); and possibly oxidation of lead by bacteria (Realini et al., 2005).

The Memorial Amphitheater at Arlington National Cemetery, made of Danby Vermont marble (Mountain White grade) and constructed between 1915 and 1920, presents another example of red staining. Preliminary microbiological analysis resulted in the isolation of a red pigmented bacterium (Figure 1). However, in all cases the stains have been found to contain lead corrosion products, in particular the bright red minium. Scanning electron microscopy (SEM) accompanied by energy dispersive spectrometry (EDS), X-ray diffraction (XRD) analyses, X-ray fluorescence spectroscopy (XRF), and Raman spectroscopy revealed considerable diversity of lead compounds in the stains, as well as in their shapes, sizes, and distribution.

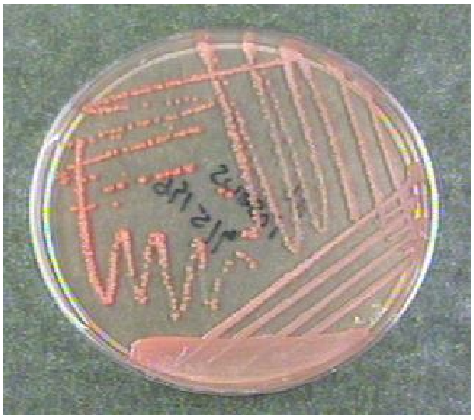

Figure 1. A red pigmented bacterium isolated from stained areas in Memorial Amphitheater.

The staining at Arlington National Cemetery, which also varies significantly in color and appearance (Figure 2), occurs at discrete locations. Most often it is found on marble paving blocks between external columns of the amphitheater, particularly between the east and north entrances. Located on contiguous horizontal and vertical surfaces of the same blocks, these stains generally appear as agglomerations of small red spots on horizontal surfaces, brown-purple stains on vertical edges, and yellow washes underneath. In-situ XRF analysis confirmed that lead is present in all stained areas, with higher concentrations in purple areas. Staining is mainly concentrated in the middle of the blocks and never continues over vertical joints, as staining of biological origin likely would.

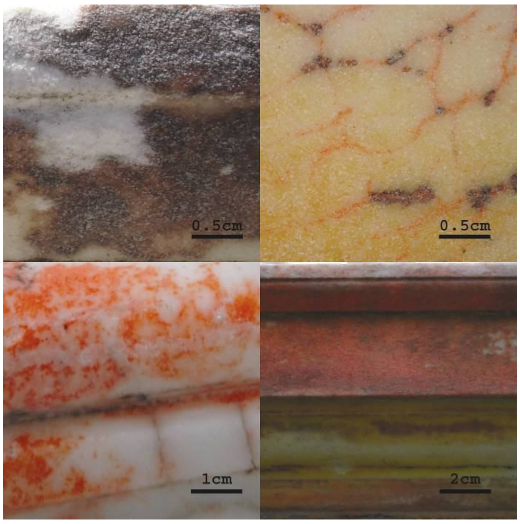

Figure 2. Typical colors and textures of colored stains observed at the Memorial Amphitheater (scale is approximate). Clockwise starting from top left: (i) purple stains, sometimes very dark and almost brown, often thickly incrusted, found mainly between the columns; (ii) yellow thin washes on a stairway corner post with red stains along fissures (note the presence of black Verrucaria lichens); (iii) typical staining of vertical areas on marble blocks between columns, with presence of dark crusts, red stains, and yellow washes, (iv) patchy orange-red stain on the stairway corner post.

A second striking example of staining is located on the outer corner of a column base to the left of the amphitheater's stage. This area features a Liesegang-ring-like pattern, with purple, coral red, orange, and yellow areas located sequentially outward from the white corner. Comparison of photographs taken in 2004 and 2008 shows a net progression of staining, with migration away from the corner and expansion of the area of yellow washes (Figure 3). In-situ XRF analysis confirmed the presence of lead in all pigmented areas, as well as in the white area between the missing corner (apparently replaced with a mortar repair, now also missing) and purple stain (Figure 4). The largest quantity of lead was found in white and purple stains (regions 2 and 3).

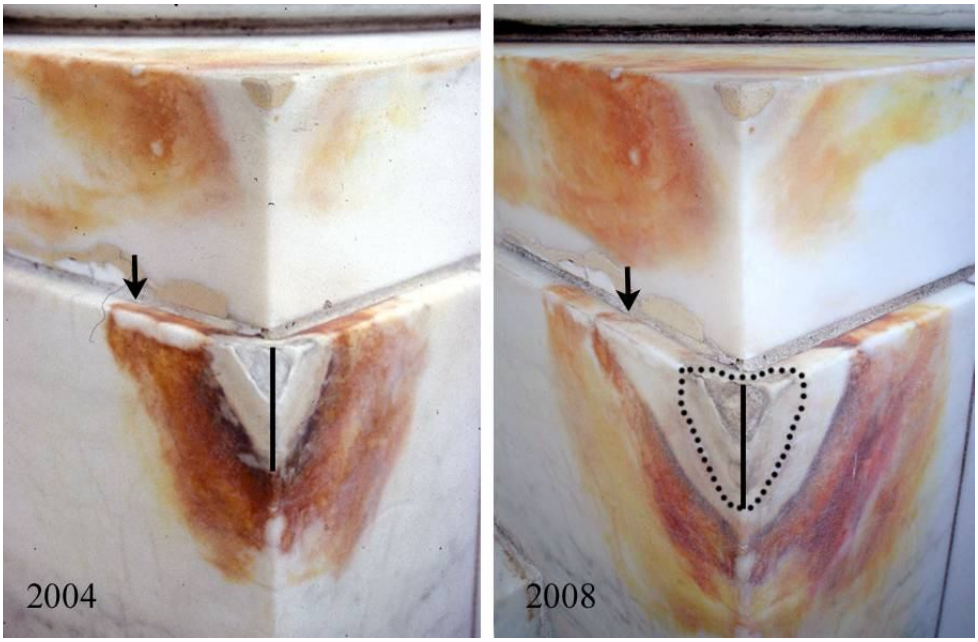

Figure 3. Evolution of the red staining between 2004 and 2008. The dotted line indicates the inner edge of the 2004 stain, and the black arrow indicates its outer limit. Vertical black lines reflect the same locations in each photograph.

Finally, a stairway post behind and to the left of the stage exhibits bright red spots around partially spalled-off corners and along crevices, as well as yellow washes. A lead sheet was detected in the joint above the stained block. XRF analysis confirmed lead in all pigmented areas, and both Raman spectroscopic and XRD analysis found minium in one of the bright orange-red corners. Identification of compounds in the yellow washes proved more difficult. Samples contained a mixture of red minium particles and tiny yellow particles that did not yield identification by XRD or Raman spectroscopy (possible causes can be respectively a poor crystalline state or a scarce amount of corrosion products for XRD, and low scattering of lead oxides for detection by Raman). SEM-EDS also showed two lead-containing compounds with different crystal sizes and shapes. Although precise characterization of the two compounds is not possible because of topographic and thickness variations, one might reasonably assume that the compounds correspond to the red Pb_3O_4 and to one of the two yellow polymorphs of PbO (either litharge or massicot) based on their gray values in secondary electron SEM images (Aze, 2005).

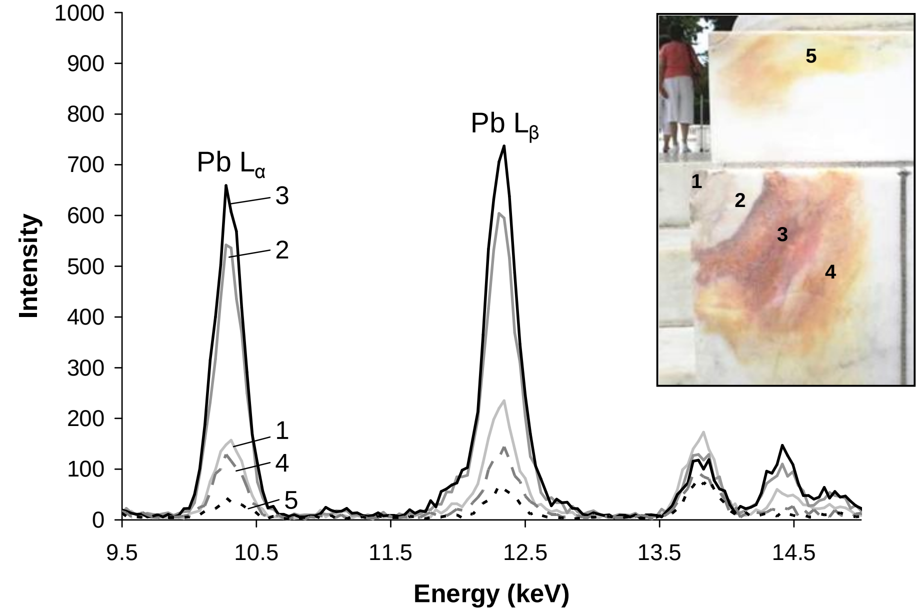

Figure 4. X-ray fluorescence analysis of the corner showing highest concentrations of lead in white and purple areas (regions 2 and 3).

Possible sources of lead in stained areas include the lead sheet found in the joint above the stairway block and a lead drip edge observed to the right of the stage on the interior of the amphitheater. The drip edge is heavily corroded, with minium found in red corrosion products by XRD analysis, and the vertical wall underneath also presented yellow washes similar to those observed on stained corners. In this case lead sheets were almost certainly used to prevent water penetration into basement rooms. Finally, lead sheets are likely to be present at floor level under the balustrade between the exterior columns, although none were observed. Regular water washing of the pavement in combination with rain has likely contributed to the severe red staining of the external paving blocks between the columns.

Lead sheets corrode rapidly in the presence of Portland cement and lime water (Brady, 1934). Typically, fresh Portland cement can give rise to pH values in the pore-water up to 13.5 (in comparison, saturated lime water has a pH of 12.5). At this very high pH, PbO becomes a stable oxide, as does Pb_3O_4 when the environment is slightly oxidizing (i.e., in the presence of oxygen). Although it has not yet been confirmed, it appears that Portland cement may have been used for both pointing and mortar repairs at the Memorial Amphitheater. With that in mind, it is not surprising to find examples of red staining consisting of lead corrosion products.

Despite the presence of red-pigmented bacteria isolated from the Memorial Amphitheater, the staining observed on the marble is caused by lead oxides. In this case, we believe that the pigmented organism comprises a relatively small percentage of the bacterial community on the stone and that biases introduced by culturing caused large numbers of this bacterium to be isolated. However, the etiology of red staining on stone structures does not appear limited to lead oxides. Konkol et al. (Konkol, 2009) found red stains on a marble sculpture produced by *Serratia marcescens*. The stains were caused by an organic pigment, and no lead was used in construction of the sculpture. Careful analysis of red stains is needed to ascertain the cause of the staining and determine appropriate solutions.

Acknowledgments

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FIGURE CAPTIONS

Figure 1. A red pigmented bacterium isolated from stained areas in Memorial Amphitheater.

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Figure 4. X-ray fluorescence analysis of the corner showing highest concentrations of lead in white and purple areas. For regions 1, 2, and 3, spectra exhibit peak height ratios $L\beta/L\alpha$ slightly more than one, which indicates that the concentration of lead is higher inside the marble than at the surface.