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Mn-rich Black Patina Formation on Built Heritage in Humid Areas

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This study aims to characterise the decay due to black patinas of Santalla de Bóveda Monument (Lugo, Northwest of Galicia, Spain).

Manganese is one of the most abundant elements on Earth, and the granite on which Santalla de Bóveda Monument was built (used as building material of the monument) has considerable amounts of Manganese. This monument shows black patinas on the surface of its building materials (mortars and granites).

Mortars and granite with Mn-rich black patinas were analysed in their chemical, mineralogical and petrographical properties (polarizing and scanning electron microscopes, X-ray diffraction and X-ray fluorescence). In addition, the water from springs near the monument was analysed.

According to the experimental study results, it was observed that rich Mn-oxide crusts are presumably induced by bacteria. That is, the oxidation of Mn fuels the growth of chemolithoautotrophic microorganisms, which need water to live. These patinas of biogenic Mn-oxide minerals presented different shapes, nano-dimensions, with low degree of crystallinity, and appear to be composed of manganese oxides such as birnessite, ramsdellite and groutellite. They were associated with large amounts of extracellular polymeric substances exuded by filamentous bacterial communities, which serve as nuclei for preferential precipitation of manganese oxides on the extracellular sheaths, as seen in scanning electron microscope analyses.

Mn required for patina formation likely derives from the reductive dissolution in water of Mn-rich minerals, as suggested by the mineralogy and chemistry of Mn-rich phases present in the building granite and mortars. Mn migrates to the exposed surface of building materials, where they are re-oxidized via biological processes. Patinas developing over time result from the alternation of wetting-reducing and drying-oxidizing cycles.

Water absorption, dampness and black patinas are among the most common and critical

problems when it comes to decay of both cultural heritage and modern buildings. The climate and specifically the humidity are determinant for the development of Mn-rich black patinas. Results revealed that chemical composition and porosity played a major role in the development of biological activity that generates the black patinas of manganese oxides on mortars and granite.