Manganese oxides of caves: a multi-tool geomicrobiological approach to identify their origin and traits

Pellegrini M.*[1], Farda B.[1], Djebaili R.[1], Vaccarelli I.[1], Bernardini S.[2], Ercole C.[1], Bellatreccia F.[2] & Del Gallo M.[1]

[1] Dipartimento di Medicina Clinica, Sanità Pubblica, Scienze della Vita e dell'Ambiente, Università dell'Aquila.
[2] Dipartimento di Scienze, Università di Roma Tre.

Corresponding author e-mail: marika.pellegrini@univaq.it

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Manganese oxides (MnOx) are common and important geomaterials that regulate the availability of various elements and biogeochemical cycling (Bernardini et al., 2021). Among natural environments where MnOx can be found, caves are one of the most interesting ones in which they occur as black crusts or patinas, speleothem stains, or black sedimentary fill deposits (Hill & Forti, 1997). Both biogenic and abiotic models exist for MnOx formation. Different microbial groups can control Mn oxidation when conditions are favourable, competing with the abiotic process (Vaccarelli et al., 2021). Within this context, this study aimed to investigate the mineralogical, geochemical, and microbiological characteristics of caves' Mn patinas. Optical microscopy, SEM-EDS, XRF, XRPD, FT-IR, and Raman spectroscopy were used to determine the structure and characteristics of Mn patinas. SEM-EDS and 16S rRNA sequencing and metagenome function prediction was used to investigate the microbial role in the formation of these deposits and the biotic processes involved. Geochemical analyses revealed that patinas consist of Fe-lenses (fine-mixture of hematite, goethite, and detrital minerals) alternated to Mn-layers (with vernadite, todorokite, and/or ranciéite). An oscillatory Mn and Fe pattern was also observed along with patina growth, suggesting an alternating oxic and suboxic formation environments according to the different phases of the flood occurrences. Microbiological analysis showed the occurrence of *Bacillus, Flavobacterium*, and *Pseudomonas*, Mn^{2+}-oxidizing bacteria related to Mn-rich environments (Vaccarelli et al., 2021). Metagenome function analysis predicted the presence of cytochrome-c-oxidase (CcO), superoxide dismutase (SOD), and peroxiredoxin (POD). One of the primary enzymes involved in Mn(II) oxidation is CcO, while SOD and POD reduce the oxidative stress produced by bioreactions. Our results revealed interesting traits of Mn patinas and abiotic and biotic processes involved in their formation. The findings also confirmed the validity of such a multidisciplinary approach to clarify past hydrogeological, mineralogical, and biological processes.

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