

Manganese oxides as biominerals in a granitic subterranean environment

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Abstract

Black coatings were detected on granite surfaces in groundwater catch work tunnels from Porto city (NW Portugal). The surveyed tunnels were dug throughout the granitic hard rock mass during the 16th century to facilitate transportation, drainage and water supply for the population. These tunnels have 3.3 km long and a maximum depth of 21 m b.g.l.. Rock fragments covered with black coatings were sampled on granite surfaces where groundwater seeps from sub-horizontal granite fractures.

XRD, FTIR, Micro-Raman, ICP-MS, TEM-EDS, SEM-EDS and SEM-FIB were the analytical procedures carried out to investigate the origin of the black coatings. In this subterranean environment, the enrichment in metals and other trace elements, such as Mn and Fe, and clay minerals characterize the black microbial mats, mainly composed of Mn/Fe-oxidising bacteria. Manganese and iron oxide nanoparticles were associated with large amounts of extracellular polymeric substances (EPS) exuded by bacterial communities. Birnessite and todorokite were the manganese oxides identified, which were associated with small quantities of clay minerals like montmorillonite. Microscopic observations conducted to propose that EPS served as nucleus for preferential precipitation of Mn and Fe oxides. These oxides grow within the microbial polysaccharides excreted by the cells and can provide sites for biominerals formation.

Keywords – manganese oxides, biominerals, black coatings, granitic subterranean environment