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Bacterial biomineralizations as natural attenuation processes

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Surface geological processes ruling the precipitation of minerals are often influenced by biological activity of microorganisms and plants that can mediate the formation of new mineral phases. Some living organisms can live in extreme environments (e.g. very acidic or basic conditions, very high temperatures, high content in salts, polluted environments) and can incorporate toxic elements in their tissues or in biominerals, affecting the biogeochemical cycle of elements and contributing to regulate metal mobility and their dispersion in water and soils.

More than 70 different types of biominerals have been identified from the continental to the marine environments in the Earth system. Here we report some results of our researches performed in abandoned mining areas (Zn-Pb mines), located in the SW Sardinia (Italy). We adopted a multi-technique (chemical analysis, X-ray diffraction, X-ray absorption spectroscopy, and electron microscopies) and interdisciplinary approach to investigate metal immobilization by microorganisms growing in an extreme environment. Specifically, we illustrate biomineralizations mediated by the cyanobacteria *Scytonema* sp and *Leptolyngbya frigida* along the Naracauli stream located in the abandoned mining area of Ingurtosu. *Scytonema* sp is responsible for the formation of bio-hydrozincite, $Zn_5(CO_3)_2(OH)_6$, that precipitates around the bacterial filaments forming globules (30-50 μm in diameter), usually in late spring and early summer. It is a composite material made up of an organic matrix, mainly composed by extracellular polymeric substances, and nano-scale crystalline hydrozincite. *Leptolyngbya frigida* mediates the precipitation of an amorphous Zn-silicate mainly in late summer. The Zn-silicate precipitates on the bacterial sheaths resulting in microtubules having a mean diameter of 2 μm, and it is characterized by an hemimorphite-like structure as demonstrated by the XAS analysis.

The application of hydrological tracer techniques along the Naracauli stream waters demonstrated that both biomineralizations control the mobility of Zn resulting in a natural decrease in its load. Specifically, mass-load calculations, derived from the tracer experiment, showed that about 1.2 kg/day of Zn is sequestered in hydrozincite, representing nearly 90% removal of Zn, and 0.7 kg/day Zn are sequestered in the amorphous Zn-silicate.

Achieved results are relevant to clarify biomineralization processes, and their understanding represents a useful tool both to explain the natural attenuation mechanisms in polluted environments and to apply them in bioremediation actions through the use of recent scientific and technological advances.