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The Rio Naracauli, Sardinia, hydrozincite biomineral: factors affecting precipitation

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Hydrozincite, $Zn5(CO_3)2(OH)6$, biomineralization controls the mobility of Zn, Pb, Cd, Cu and Ni in the Rio Naracauli stream waters (SW Sardinia, Italy). The process occurs in late spring and early summer, and is promoted by a microbial community made up of a filamentous cyanobacterium (Scytonema sp.) and a microalga (Chlorella sp.). Confocal Laser Microscopy (CLM) and Scanning Electron Microscopy (SEM) images show that Naracauli bio-hydrozincite precipitates around the bacterial filaments forming globules. Hydrozincite is a composite material made up of an organic matrix, mainly composed by extracellular polymeric substances (EPS), and nano-scale crystalline mineral.
A morphological study on Naracauli hydrozincite showed the influence on biomineralization morphology of environmental conditions. Optical Microscopy (OM) and SEM images show that variations of hydrozincite morphology depend on the development of biofilms grown under different environmental conditions. Changes were observed between samples collected in late spring and samples collected in summer, and among samples precipitated under different water flow conditions. These variations can be ascribed to a difference in the production of external mucilage sheaths by cyanobacteria, and to a different development of biofilms depending on parameters such as pH, temperature, water composition, and flow conditions.
In agreement with field observations, speciation and equilibrium calculations show that Zn content, pH, alkalinity, and hydrozincite Saturation Index (SI) values play a relevant role in the biomineralization efficiency. The optimum condition for hydrozincite precipitation occurs in late spring of rainy years, when the hydraulic regime in the stream reaches steady state conditions, i.e. weeks after abundant rainfall. In these conditions, pH and SI values with respect to hydrozincite reach the highest values, in agreement with the higher stability of hydrozincite in contact with slightly alkaline waters. Concomitantly, $Zn2+/CO_32-$ molar ratio reaches values close to 1, suggesting that this value might correspond to the most favourable conditions for activating hydrozincite precipitation. Conversely, heavy rain events occurring in late spring appear to inhibit biomineralization, likely due to the decrease in the SI values resulting from the dilution effect of rain water.
Hydrozincite bioprecipitation represents a potentially useful bioremediation strategy for remediation of Zn-contaminated waters. In this respect, solubility product (Ksp) is a key factor, because it is a measure of the degree to which a mineral dissolves or precipitates in waters. Solubility experiments in MilliQ water were performed at 298 K on three different types of samples: Naracauli bio-hydrozincites, supergene hydrozincite (of presumably abiotic origin) from the Malfidano Zn deposit, and synthetic hydrozincites. Equilibrium calculations gave the following apparent logKsp (for the reaction: $Zn5(CO_3)2(OH)6+8H+ => 5Zn2++2HCO_3-+6H_2O$):
Naracauli hydrozincite 29.7 ± 0.1, synthetic 28.1 ± 0.4, and Malfidano 26.9 ± 0.6. The biomineral thus is slightly less soluble than synthetic and natural abiotic samples.