Natural Attenuation of heavy metals via secondary hydrozincite precipitation in an abandoned Pb-Zn mine in the Arán Valley, Spain

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INTRODUCTION

The Arán Valley has a long history of mining activities (~1740-1950). Many of the abandoned mining sites such as tunnels and processing facilities have not been properly reclaimed. Further, these sites can often be characterized by elevated levels of heavy metals due to the dissolution of left-over ore material (Marguí et al., 2006). This in turn, may pose an environmental risk to the adjacent ecosystem.

The Victoria Mine in the Aran Valley was active until 1950. The underground mine targeted sphalerite (ZnS) although limestone is present in abundance. Today the relict tunnels and shafts are exposed to air and flowing water provoking oxidative dissolution and contemporary microbial activity alongside secondary precipitation of minerals. Surface waters within and below the mine would be considered dangerous if consumed by humans due to elevated levels of Cd (up to ~28 ppb). The source of dissolved Cd is almost certainly the solid ZnS, which is abnormally rich in Cd (upwards of ~5000 ppm).

Biomineralization of hydrozincite has been demonstrated as a naturally occurring process in the presents of abundant dissolved zinc, carbonate, and sunlight (De Giudici et al., 2009; Medas et al., 2012; Podda et al, 2000). However, biomineralization of hydrozincite without sunlight has yet to be discovered. Further, this mineral can act as a sink for Cd (Lattanzi et al., 2010), therefore understanding the controls of its formation can be useful for predicting heavy metal availability.

METHODS

Two sampling campaigns have been carried out (October 2019 & July 2020) to examine dissolved species concentrations, pH, alkalinity, and conductivity the mine water. These samples were taken at known distance intervals beginning with the opening of the mining tunnel until ~350 meters into the mine where the tunnel because inaccessible. Additionally, associated sediment samples were frozen in liquid nitrogen to later analyze for 16s ribosomal ribonucleic acid (rRNA) to characterize the microbiological species and look for potential organisms that could contribute to any potential biomineralization. Solid samples of the hydrozincite from the mine were using a Scanning Electron Microscope (SEM (Figure 1) and underwent microprobe analysis to investigate compositional changes within the minerals.

RESULTS

The obtained data from within the Victoria Mine demonstrate (1) abundant precipitation of hydrozincite, a zinc-carbonate mineral, (2) several structural forms of this mineral, and (3) that the mine is at a steady state as concentrations from the two sampling campaigns were very similar. Digestions of hydrozincite show elevated concentrations of Cd. DNA sequencing shows a diverse microbiological community living within the tunnels and some species have the potential to influence biomineralization.

CONCLUSIONS

The outflow water of the Victoria Mine poses an environmental risk due to the elevated concentrations of Cd (27.5 ± 6.5 ppb), however, these concentrations would be higher if hydrozincite was not forming and acting as a sink for the cadmium. Biomineralization of hydrozincite by microorganisms, though no proven at present, could be possible because (1) microorganisms consistent with biomineralization of calcite found in the DNA analysis and (2) the variable morphologies of hydrozincite which indicate there is more than one avenue for precipitation.

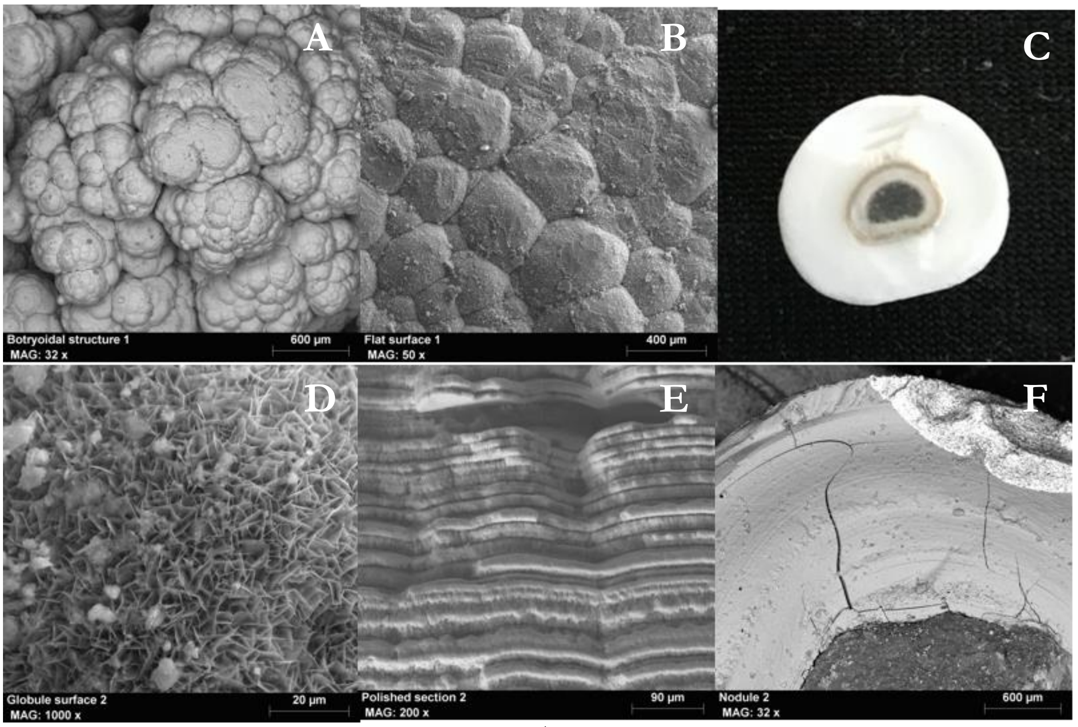

Figure 1. *SEM images of three morphologies (botryoidal, smooth/layered, and nodular) of hydrozincite. Images A and D show the botryoidal morphology, Images B and E show the smooth layered morphology, and images C and F show the nodules. The nodule (C) is approximately 1.0 cm across. Images were taken by Ignasi Queralt.*

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