

## Biogenic Carbonate Precipitation by a Planktonic Microbial Population

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After operation of the carbonate-hosted Piquette Pb,Zn mine (Tennyson, Wisconsin) ceased ~ 30 years ago, the mine was flooded (water temperature ~10 °C, pH ~ 7.5 to 8.5). Water, rock, and biofilm samples were collected by scuba divers (TTE and colleagues) and examined by optical, electron, and X-ray microscopies. Regions of the flooded tunnels exhibit distinctive zones of clear (upper) and cloudy or turbid (lower) water which corresponds to redox gradients (rusty iron staining to grey) on the tunnel walls. Water chemistry reflects dissolution of the host rock and is approximately 2.7 mM Ca, 2.3 mM Mg, 0.6 mM Na, 0.05 mM K, 1.2 mM Cl, 1.2 mM sulphate, 0.05 mM nitrate and pH = 8. Major ion chemistry in the water column is not significantly different between the clear and turbid zones in the water column. Solubility calculations using PHREEQC show that the water is slightly supersaturated with respect to calcite, aragonite, and dolomite. In spite of the abundant iron precipitates on the floor and walls of the tunnel, dissolved Fe is not detectable. Optical and epifluorescent characterisation of water samples revealed cell densities of approximately  $1.0 \pm 0.5 \times 10^6$  cells/ml the turbid zone and  $1.4 \pm 0.7 \times 10^6$  cells/ml in the clear zone. The cells in both the clear and turbid layers are predominately short rods. However, the cloudy layer also contains mineralised aggre-

gates (few micron size) that fluoresce with DAPI (a DNA stain) indicating the presence of mineralised micro-organisms. Isolation of heterotrophic bacteria was done on specific carbonate containing mineral agar medium, resulting in at least 16 pure cultures. Despite the different colony morphologies, cell morphologies were very similar to the short rods observed in the water samples. Investigation of colony forming units on the same agar medium revealed in a number of  $2.6 \times 10^4 \pm 4\%$  colonies per ml. Suspended particulate material from the turbid and clear layers were analysed by SEM, and TEM, and X-ray diffraction, SEM and TEM analysis of the turbid water reveals abundant mineralised filamentous micro-organisms. EDS analysis of the mineral material shows primarily Ca with variable amounts of Mg and Zn. The XRD analysis of particulates collected on a 0.2 micron filter from the turbid water show five broad peaks with d spacings that are consistent with calcite and a Ca-Mg-Zn carbonate of intermediate composition. Although cell abundance and major ion chemistry above the cloudy layer is similar to that below the interface, mineralised cells or other precipitates were not observed. The turbid zone in the water column is reminiscent of carbonate 'whittings' formed under different circumstances in other modern environments.