

**MODERN FRESHWATER MICROBIALITES, CUATRO CIENEGAS, MEXICO. II. DETAILED SPATIAL ANALYSIS OF GEOCHEMICAL SIGNALS LINKED TO MICROBIAL ACTIVITY AND CARBONATE PRECIPITATION.**

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The ability to accurately reconstruct chemical and biological processes using geochemical signals preserved in ancient microbialites relies on our understanding of the origin of these signals in biologically mediated carbonate minerals. The actively forming modern microbialites in the phosphorus-limited waters of the Cuatro Ciénegas Basin in northern Mexico provide a unique analogue to the ancient stromatolites of early Earth. A companion abstract (Breitbart et al.) on the Cuatro Ciénegas microbialites indicates that a complex aerobic and anaerobic, autotrophic and heterotrophic microbial community is associated with carbonate precipitation. However, to more precisely link the role of specific microorganisms, metabolic processes, chemical environments to carbonate precipitation, a more highly resolved spatial analyses of the microbialite are required. Visual and petrographic observation of the Cuatro Ciénegas microbialites reveals 5 visually distinct layers within the surface structure that spans 4-5 cm. This research utilizes stable isotopic, organic geochemical, and genomic techniques performed on the 5 individual layers to develop an understanding of the microbial community structure and how it directly relates to carbonate accretion within these freshwater microbialites. This research also provides insights into how geochemical signatures are formed and preserved during carbonate precipitation and whether, the geochemical signals at the base of the microbial accurately record the microbial community structure and chemical environmental conditions associated with carbonate precipitation.

Culture independent 16S rRNA gene analyses of bacteria and archaea have enabled us to construct a well-developed representation of the microbial community structure and function. Results depict a surface community dominated by cyanobacteria with an increase to heterotrophic proteobacteria at depth. This systematic change in microbial community from dominantly photoautotrophic to heterotrophic metabolism creates microenvironments favorable for carbonate precipitation and accretion. Stable isotopic analysis of the intra-crystalline organic matter reveals C, N, and S profiles that support the genomic work, further suggesting the co-occurrence of autotrophic and heterotrophic organisms and aerobic and anaerobic nutrient cycling processes, including denitrification and sulfate reduction. Molecular organic geochemical analyses of free lipids (hydrocarbon, fatty acids, sterols and hopanols) document the photoautotrophic production of biomass in the surface layers and its efficient consumption by aerobic and anaerobic heterotrophic bacteria in the lower layers. The formation of EPS at the surface of the microbialite is isotopically and molecularly distinct and provides a medium through which a strong chemical gradient can be developed and that supports a diverse community of microorganisms and microenvironments favorable to carbonate precipitation.

Compositional changes across the 5 layers comprising the microbialite show two spatially distinct zones of carbonate precipitation with multiple generations of carbonate mineral formations and accretion leading to increasing carbonate mineral concentrations and density.  $\delta^{13}\text{C}$  values of  $\text{CaCO}_3$  from the 5 layers decrease with depth reflecting the progressive incorporation of increasing amounts of respired carbon released during the remineralization of cyanobacterially-derived biomass. Based on mass balance calculations at the base of the microbialite we estimate that 55% of the carbonate is produced in regions dominated by autotrophic organisms and aerobic conditions and ~45% of the carbonate in layers dominated by heterotrophic organisms and sub-oxic to anaerobic conditions.

The interdisciplinary research provides a framework to relate microbial and chemical processes to the formation of carbonate minerals. This study further documents how stable isotopic (organic and inorganic) and molecular organic geochemical signals are formed through the complex interactions between autotrophy and heterotrophy under aerobic and anaerobic conditions and preserved within the successive generations of carbonate precipitation and microbialite formation. Additionally, in order to interpret the environmental and evolutionary significance of microbialites throughout the geologic record, it is vital to develop an integrated and comprehensive understanding of how chemical processes and microorganisms lead to the precipitation of modern microbialites. Integrating the results of this study with others on modern microbialites, we have developed a scheme called "CORPSE" to explain the precipitation of carbonate in modern microbialites and to interpret chemical and microbiological processes on early Earth. This CORPSE scheme provides a model to understand how the Chemistry of an environment define the presence of Organisms and the occurrence of Processes that form the geochemical Signals in organic matter and carbonates from which we can Extrapolate the chemical and biological conditions of ancient systems. More details of the CORPSE scheme will be presented.