Diagenetic Changes in Microstromatolites from a Modern Cool-Water Travertine Spring.
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Introduction: Located along the banks of the Green River in Utah, Crystal Geyser is a saline and mildly acidic cool-water geyser that has formed a spectacular terraced travertine mound. Terraces are comprised of smaller microterracette ponds that range from one to several cm deep and contain a variety of microscale columnar stromatolite forms, as well as other potential morphological biosignatures [1]. Each terracette pond records changes between subaerial and subaqueous microenvironments and are inhabited by a variety of microorganisms including cyanobacteria, α-proteobacteria, and δ-proteobacteria among others [2]. The typically rapid rate of carbonate precipitation from Crystal Geyser promotes the capture and preservation of morphological and chemical biosignatures within the finely laminated stromatolitic framework.

This cool-water carbonate spring represents a unique environment where modern microstromatolites actively form. These features may be analogs for yet to be discovered travertine spring deposits on Mars. The young age (<80 yr) of the Crystal Geyser deposits provides an opportunity to constrain early taphonomic and diagenetic processes. Furthermore, older travertine deposits located in close proximity to Crystal Geyser provide an opportunity to observe late stage diagenetic changes in travertine deposits from similar depositional environments that formed over a much longer period, perhaps thousands of years.

Methods: Mineralogy and microtextural features of samples were observed in 30μm thick thin-sections viewed through a standard petrographic microscope. Further mineralogical characterization was carried out using X-Ray Powder Diffractometry (Siemens D5000 and Panalytical X'Pert Pro instruments). Additional compositional information (mineralogy and fossil kerogen) was obtained using 532 nm Raman laser spectroscopy with a spatial resolution of 15 microns.

Microstructure was also studied using a Leica SP5 confocal imaging system and an XL30 ESEM-FEG Scanning Electron Microscope. Travertine samples were etched in a 5% HCl dilution, and a 30 second Au/Pd coating was applied. Samples were mounted onto SEM stubs using colloidal silver. Spot elemental composition was acquired using the EDX capabilities of the ESEM-FEG.

Micro-cores of the travertine were sent to the University of Arizona Environmental Isotope Laboratory for $\delta^{13}C$ measurements. Finally, in an effort to characterize near-IR spectral characteristics of the Fe-bearing travertine samples, infrared spectra were analyzed via ASD Fieldspec 3 Portable Spectroradiometer.

Results: Branching, microdigitate stromatolites were observed in sample cross-sections, where they formed regular, repeating depositional cycles underlain by flat laminae. Stromatolitic intervals were succeeded by porous layers infilled by sparry calcite. Within stromatolites, the relief of columns and lamina definition appeared to decrease down-section and was eventually replaced by zones of amorphous, amber globules faintly representing their original microdigitate form. Despite fluorescence effects, kerogen was identified by Raman spectroscopy in both relatively pristine and degraded stromatolite forms. Kerogen was rarely preserved as cellular forms, but mostly occurred in a degraded, particulate form.

The Crystal Geyser travertines are composed primarily of calcite and aragonite. However, orange laminae inferred to be enriched in amorphous ferrihydrite were also identified in thin section and confirmed by VNIR. SEM images showed abundant filamentous structures as well as extracellular polymeric substances (EPS) embedded within carbonate lamina. EDX measurements of these structures also showed elevated carbon concentrations. Carbon isotope measurements of microcores taken in both microstromatolitic regimes and sparry calcite regimes show high $\delta^{13}C$ enrichments from +7.38‰ to +8.24‰, likely an effect of rapid CO_2 degassing.

Discussion: Previous work at Crystal Geyser [2] suggested that micritic laminae bands comprising the stromatolites precipitate during daylight hours following geyser eruptions. Conversely, sparry calcite cements appearing as porous basal laminae have been shown to grow during nighttime eruptions when photosynthesis is inactive [2]. Once the travertine accumulates to a few centimeters thickness, the stromatolite forms begin to degrade quickly as a result of the onset of diagenesis. Despite morphological degradation, chemical signatures of life in the form of kerogen can still be detected with Raman. A key mechanism for the degradation of these stromatolites may be the mineralogical transformation from metastable fibroradial aragonite to microgranular calcite.

References:

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