

Arsenic accumulation in microbial mats and the interpretation of signals of early arsenic-based metabolisms

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Organic inclusions that are enriched in arsenic are present in microbialites as old as 3.5 Ga and some modern microbialites, suggesting accumulation of As by carbonaceous matter throughout Earth history. At present, it is unclear if this accumulation is a consequence of microbial metabolisms or passive *post-mortem* binding of arsenic by organic matter during diagenesis in volcanically-influenced environments. Here, we address this uncertainty by evaluating the absolute concentrations, speciation and detectability of As in active or heat-killed biofilms formed by cyanobacteria or anoxygenic photosynthetic microbes exposed to environmentally relevant concentrations of As(III) or As(V) (50 μ M to 3 mM). Biomass accumulates As from the solution in a concentration-dependent manner and with a preference for oxidized As(V) over As(III). Autoclaved biomass accumulates As more strongly than active biomass, suggesting a reduced accumulation in the presence of As removal and detoxification processes in the living biofilms. Active biofilms oxidize and reduce As and accumulate both As(III) and As(V), whereas As that is passively bound to heat-inactivated biomass contains primarily the redox species that is present in the solution. These findings enable the reconstruction of past active metabolisms and passive interactions of microbial biomass with arsenic in fossilized microbial biofilms and microbialites from the early Earth. These mechanistic insights are now used to reconstruct biological and abiotic processes that shaped the distribution and speciation of As in drill core and outcrop stromatolite samples from the ~2.7 Ga Tumbiana Fm. In these samples, As enrichments are limited to micrometer-sized particles of As(III)-sulfide, most consistent with the presence of As-rich pyrites originating during diagenesis.