Bioaccessibility and bioavailability of arsenic-bearing mine wastes via the inhalation pathway

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Due to extensive processing of ore from gold and silver mines in the Mojave Desert, CA, elevated concentrations of associated toxic metal(loid)s including arsenic (As) are often mobilized by the transport of mine wastes into surrounding communities. The fine-grained fraction of mine waste particles can readily become airborne and inhaled. making their bioaccesibility and bioavailibility extremely relevant.

Bulk samples were collected from a number of mines throughout the Mojave Desert and sieved to obtain fine size fractions. The size fraction was then ground using a ball mill to a size fraction (≤2.5 μm in particle diameter). The bioaccessibility of As as a function of pH was examined in phagolysosomal simulant fluid (PSF) Finally, the bioavailability of As was analyzed *in vivo* by intratracheally instilling the material.

Results from four different mine sites indicate that the mine wastes showed similar trends of arsenic dissolution within PSF, with the percent As released decreasing from pH 1.8-4.2 and then slightly increasing pH 5 (Figure 1). The As solubility at low pH is likely due to the dissolution of As-bearing mineral phases while the solubility at higher pH is likely due to the desorption of As sorbed to Fe-oxides. The *in vivo* studies will provide organ-specific bioavailability information which can be correlated with results from the PSF experiments.

This information will help to determine the operational pH for a PSF extraction that most accurately the *in vivo* outcome, with the eventual goal of developing a predictive bench-top bioaccessibility assay that can be used to estimate bioavailability of arsenic in mine wastes as introduced through the inhalation pathway.

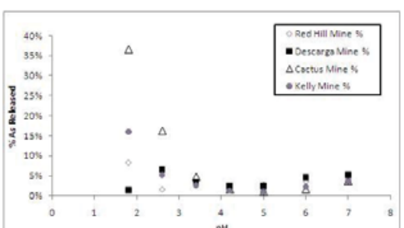

Figure 1: Percentage As released vs. pH

Extensive life on land ~1.1 Ga ago

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The precise timing of life's move onto land in the Precambrian, along with the extent of the terrestrial biosphere, is poorly constrained, with only a sparse record before the Neoproterozoic, known primarily from paleokarsts [1]. A recent study by Strother and colleagues [2] described the earliest non-marine eukaryotes from the ~1 Ga old lacustrine Diabaig Formation (Torridon Group, Scotland). Penecontemporaneous lakeshore and alluvial deposits well away from marine shorelines from Scotland also record microbially induced sedimentary structures [3]. Thus, at least locally, a significant and potentially diverse terrestrial biosphere was present, but the extent of the Mesoproterozoic terrestrial biosphere remains an open question.

Here, we present sedimentological and isotopic evidence for an extensive terrestrial biosphere preserved in sediments that are part of the ~1.1 Ga old Midcontinent Rift (MCR) of North America. The active rifting phase of the MCR was short-lived, from 1109 to 1087 Ma [4], and clastic sediments were deposited both as intrabasaltic units and as post-emplacement units. Rifting ceased due to Grenvillian compression to the East, which resulted in a partial re-closure of the rift. Penecontemporaneous intrabasaltic units from both sides of the rift in Minnesota and Michigan record a variety of sedimentary environments including paleosols [5-6], braid plains, alluvial fans, and lacustrine units; sites are currently >150 km apart, a distance that would have been significantly larger prior to the tectonic reversal caused by the Grenvillian compression. The sedimentary units have never been deeply buried or experienced any significant metasomatic alteration [5-6]. Microbially induced sedimentary structures including abraded Kinneyia, pustulose mound structures, multi-directional wave ripples, textured bedding planes, and stromatolites were recently documented [7]. Organic matter is also preserved on both sides of the rift in paleosols and microbial mat structures, as detrital carbon in laminated fluvial sediments, and occluded with the carbonate of lacustrine stromatolites in Michigan. "Clumped isotope" (Δ_{47}) analyses of stromatolitic carbonate range from 0.513–0.603 (± 0.004), which indicates carbonate formation temperatures of 35–60°C (±4°C), and that there was no significant post-burial heating of the preserved organic matter. $\delta^{13}C_{org}$ values range from -29.6 to -24.0‰, suggesting C fixation by photosynthesis. Some $\delta^{13}C_{org}$ depth profiles through paleosols indicate diffusive enrichment comparable to modern soils, which suggests that the microbial communities were present both at the soil surfaces and subsurface. Together, these various lines of evidence indicate an extensive terrestrial biosphere by ~1.1 Ga ago.

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