Geochemistry of arsenic in microbial mats and sediments in El Tatio Geyser Field, Chile

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Abstract: El Tatio geyser field (ETGF), located in the Altiplano-Puna Volcanic Complex in northern Chile, is one of the largest geothermal fields in the world. ETGF is a natural source of toxic metalloids, like arsenic (As), that locally impact regional water quality, policy, and agricultural commerce. At ETGF, metalloid behavior is influenced by water temperature, UV radiation, adsorption onto ferric oxyhydroxides, and microbial metabolism. In the circumneutral pH waters, arsenite [As(III)] is found upstream while arsenate [As(V)] is predominant several meters downstream. As(III) oxidation occurs during the day and night indicating limited to no photic oxidation, but As(V) reduction may be linked to photosynthesis due to higher reduction rates during the day than at night. To characterize these microbial processes, the diversity of the microbial mats was evaluated based on 16S rRNA and arsenite oxidase (*aro*A) gene sequences. The most prevalent *aro*A genotypes belonged to the *Chloroflexi* and *Proteobacteria*. This expands our understanding of the types of microbes linked to As(III) oxidation, as *Chloroflexi* have not been previously linked to As(III) oxidation in geothermal habitats. Using XANES and ATR-FTIR, As speciation within the microbial mats and sediments differed between upstream and downstream samples. Downstream samples show As(V) possibly associated with ferric oxyhydroxides and accumulated organic matter (i.e. microbial mats). The interaction between As and organic matter was evaluated from experiments using Tryptone and Pony Lake Fulvic Acid combined with As_2O_3 and artificial UV radiation to mimic UV exposure at ETGF and fluorescence spectroscopy analyses. Microbes release protein-like dissolved organic matter that interacts with As, with the presence of As influencing the fluorescence of humic-like (Pony Lake Fulvic Acid) but not protein-like (Tryptone) components. This suggests that the interactions between organic matter and As may be due to a photosensitive ligand-metal complex. Although the identity of this complex is not known, ATR-FTIR may indicate that downstream oxidation of As might be due to the increasing presence of organic matter and possibly differential adsorption to ferric oxyhydroxides. Continued investigation of As behavior, habitat geochemistry, and microbial diversity at ETGF may reveal novel metal transformation processes that could benefit As remediation efforts.