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Characterization of Dissolved Organic Matter via High-Resolution Mass Spectrometry of Axel Heiberg Island Perennial Springs: Investigation of a Martian Analogue

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The perennial, sub-zero hypersaline springs of Axel Heiberg Island (AHI) represent excellent terrestrial analogs for subsurface Martian environments. While prior studies have identified active chemolithoautotrophic communities driven by sulfur and methane cycling within these brines, the organic carbon cycle has remained poorly unconstrained. Historically, the combination of extreme salinity and vanishingly low dissolved organic carbon has precluded the accurate quantification and molecular characterization of Dissolved Organic Matter (DOM). However, understanding this organic pool is critical for astrobiology because anoxic, high-ionic-strength environments with active evaporite mineral co-deposition have been hypothesized to represent a refuge for life on Mars and/or an ideal environment for biosignature preservation. In this study, we used negative electrospray ionization paired to Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) to establish the first comprehensive molecular baseline of AHI DOM. By reverse-calculating volumetric concentration factors against the optimal carbon mass thresholds required for FTICR-MS performance, we established a first-order quantitative estimation of the overall dissolved organic carbon (DOC) pool, placing it between 30 and 300 ppb. We evaluated the structural diversity of the DOM pool across several spring sites including Wolf Spring (Lost Hammer), Gypsum Hill's Little Black Pond, and Colour Peak, the outflow paths downstream, as well as two ice-dammed lakes (Astro and Phantom Lakes) previously hypothesized as water sources for the groundwater feeding the springs. The springs exhibited a diverse DOM pool, containing between ~5,000 and 8,000 unique chemical formulas, whereas the ice-dammed lakes displayed minimal diversity (<700 unique formulas). Peak chemodiversity occurred at Wolf Spring, followed by Little Black Pond and Colour Peak. Across all samples, of the compounds detected the DOM signature was dominated by CHON, CHOS, and CHO which were further characterized as lipid, lignin, and condensed aromatic compounds. Signatures of the top classes contained multiple heteroatoms. Primarily N_3, N_1O_5, N_2O_1, N_2, and O_4. If Astro and Phantom lakes are indeed water sources, these results indicate addition of significant concentration and chemical diversity through the groundwater flow system. Ongoing work has the goal of assessing the role of geologic matrix carbon sources and extent of microbial cycling occurring within the groundwater system.