CHARACTERIZING ORGANIC CARBON COMPOSITION IN TERRESTRIAL HYDROTHERMAL SYSTEMS THROUGH 3D FLUORESCENCE SPECTROSCOPY. Joshua J. Nye¹ and Hilairy E. Hartnett^{1,2}, ¹School of Molecular Sciences, Arizona State University, 551 E University Dr., Tempe, AZ 85281. ²School of Earth and Space Exploration, Arizona State University, 781 S. Terrace Rd., Tempe, AZ 85281.

Introduction: Hydrothermal systems host some of the earliest microbial lineages on Earth and are theorized to be where life first arose [1]. Carbon is a life essential element; studying the carbon cycle in these systems provides information about how organic molecules are used and transformed by extremophiles. However, a detailed understanding of the carbon cycle in hydrothermal systems is limited not only by our ability to sample them, but also by the complexity of the thousands of different organic compounds present in these environments.

3D Fluorescence spectroscopy has become a routine tool used to assess the composition of the bulk Dissolved Organic Matter (DOM) pool [2]. This technique provides a chemical fingerprint of a portion of the organic carbon pool, but has largely been applied to study carbon in surface water systems, such as lakes and rivers [2,3,4]. This research presents the first application of 3D fluorescence spectroscopy to the characterization of DOM from terrestrial hot springs.

Research Findings: Hot spring water samples (n=222) collected from hot springs in Yellowstone National Park, Wyoming, USA and the Yunnan Hydrothermal Region, Tengchong Province, China were analyzed using 3D fluorescence spectroscopy. Excitation-Emission Matrices (EEMs) were generated (ex: 240-450 nm; em: 300-550 nm), blank corrected, and normalized to the Raman intensity of deionized water each day. Parallel Factor (PARAFAC) analysis [5] was employed to deconvolute the fluorescence signals in the EEM data set into a five component model. This model was validated by split half validation. Four of the components in this model correspond to components that appear in literature PARAFAC models for surface waters; these components include: 3 humic components (terrestrial organic matter) and 1 protein-like component (tyrosine; microbial organic matter). A previously undescribed component was also produced. This uniquely hydrothermal component only appears in acidic (pH < 4) springs. It bears spectral similarities to tryptophan components in the literature (both the free amino acid and protein-bound moeties; [2-4,6]) with an emission maxima at ~350 nm; however, its excitation maxima at 250 nm sets it apart from these components. Additionally, lab experiments show that the fluorophores responsible for this component can be precipitated out of solution at $pH \ge 7$.

This new fluorescence model is being used to assess the organic composition of dissolved matter from terrestrial hot springs over a wide range of geochemical environments as well as changes in organic composition along individual hot spring flow paths.

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