ENHANCED RESOLUTION OF CHIRAL AMINO ACIDS WITH CAPILLARY ELECTROPHORESIS FOR DETECTION OF BIOSIGNATURES IN EXTRATERRESTRIAL SAMPLES. J. S. Creamer, M. F. Mora, and P. A. Willis. Jet Propulsion Laboratory, California Institute of Technology. 4800 Oak Grove Dr. Pasadena, CA 91109. jessica.creamer@jpl.nasa.gov

Introduction: Amino acids occur throughout the solar system as a byproduct of abiotic reactions and they are also a necessary building block for life on Earth. However, between samples containing amino acids of abiotic vs biotic origins the distribution and abundances of specific amino acids is markedly different. Presumably, this is because as complex life evolved on Earth, the chemical abundances of organic molecules changed to reflect the needs of biotic reactions. For example, out of the hundreds of possible amino acid configurations seen abiotically, terrestrial proteins use an "alphabet" of only twenty. Furthermore, while abiotic reactions generate a racemic mixture of amino acids, homochirality is necessary for proper protein folding and life on Earth uses exclusively left-handed amino acid enantiomers.

In the search for extraterrestrial life it is reasonable to expect that a similar diversion from an abiotic chemical inventory could occur on other planetary bodies as life established itself. Therefore, in order to determine the presence or absence of biotic processes it is possible to look at the chemical distributions within a population of amino acids to identify three unique patterns: 1) which amino acids are present; 2) the relative abundance of those amino acids to glycine; 3) the presence of an enantiomeric excess.

However, the in situ analysis of amino acids in extraterrestrial environments remains a challenge. Because of the low expected abundances of organics in planetary samples (amino acid content in terrestrial soil and oceans can be part-per-billion or lower) in situ sampling techniques are preferable over optical ones because they provide increased sensitivity [1]. Capillary electrophoresis (CE) is an extremely promising analytical technique for the in situ analysis of low-abundance polar organics in environments where water and salts are present.

Here, we present two CE methods capable of resolving 17 amino acids labeled with 5-carboxyfluorescein succinimidyl ester (CFSE) for detection limits down to 5 nM. These 17 amino acids (seven enantiomer pairs D/L -Ala, -Asp, -Glu, -His, -Leu, -Ser, -Val and the achiral Gly, β-Ala, and GABA) represent amino acids found in high abundance in biotic and abiotic samples and form what we are calling the Signature17 standard.

These methods were then used to label and detect amino acids in high salinity samples from Mono Lake, CA (Figure 1). The hypersaline lake water samples were analyzed by simply mixing 1:1 with a tetraborate buffer and then adding CFSE for derivatization. No desalting or preconcentration was necessary.

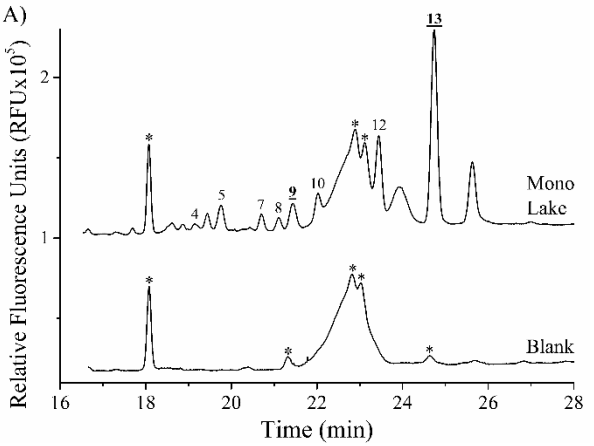

Figure 1: Electropherogram of the analysis for the Mono Lake sample compared to the blank. Separation conditions optimized for neutral amino acids, BGE: 80 mM sodium tetraborate pH 9.2, 30 mM γ-CD, 30 mM STC, and 5% v/v ACN. 40 cm effective length channel with a 25 kV separation voltage. Peaks: 4. L-His; 5. L-Leu; 7. GABA; 8. L-Val; 9. D-Ala; 10. L-Ser; 12. L-Ala; 13. Gly; *dye side products, peak numbers bolded and underlined denote amino acid species which comigrate with dye side product peaks, unmarked peaks are unidentified. Inset: Photo of the Mono Lake sample site (37.977999, -19.128618) [2].

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References: [1] Willis, P. A., Creamer, J. S., Mora, M. F. (2015) *ABC*, 23, 6939-6963. [2] Creamer, J. S., Mora, M. F., and Willis, P. A. (2017) *Anal Chem.*, 89, 1329-1337.