

**AMINO ACID STABILITY IN THE EARLY OCEANS.** E. T. Parker<sup>1</sup>, K. L. Brinton<sup>2</sup>, A. S. Burton<sup>3</sup>, D. P. Glavin<sup>4</sup>, J. P. Dworkin<sup>4</sup>, and J. L. Bada<sup>5</sup>, <sup>1</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology (erictparker@gatech.edu), <sup>2</sup>School of Mathematics, Science & Engineering, Southwestern College, <sup>3</sup>Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, <sup>4</sup>Solar System Exploration Division, NASA Goddard Space Flight Center, <sup>5</sup>Geophysical Research Division Scripps Institution of Oceanography, University of California, San Diego.

**Introduction:** It is likely that a variety of amino acids existed in Earth's early oceans at the time of the origin and early evolution of life. "Primordial soup" [1]-, hydrothermal vent [2]-, and meteorite [3]-based processes could have contributed to such an inventory. Several "protein" amino acids were likely present. However, based on prebiotic synthesis experiments and carbonaceous meteorite studies, non-protein amino acids such as  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), which are rare on Earth today, were likely much more abundant. An important uncertainty is the length of time these amino acids could have persisted before their destruction by abiotic and biotic processes. Prior to life, amino acid concentrations in the oceans were likely regulated by circulation through hydrothermal vents. Today, the entire ocean circulates through vent systems every  $10^7$  years. On the early Earth, the turnover rate was likely much higher due to higher heat flow. Thus marine amino acid lifetimes would have been shorter. After life began, amino acids in the oceans could have been assimilated by primitive organisms.

**Original Experimental Setup:** To better constrain primitive amino acid lifetimes, Scripps Institution of Oceanography pier seawater and baked (500 °C in air) La Jolla beach sand were placed in a glass container in spring, 1992. The container was spiked with protein and non-protein amino acids that could have been present on the early Earth. These included D,L-alanine (Ala), D,L-valine (Val),  $\alpha$ -AIB, and D,L-isovaline (Iva). These amino acids were measured several times over a 700 day period using chiral derivatization with reverse phase high performance liquid chromatography-fluorescence detection (HPLC-FD) [4]. The experiment was then spiked with glycine and monitored for an additional 1550 days. The abundances of D,L-Ala, glycine, and L-Val were found to rapidly decrease, apparently by microbes in the mixture. Yet minimal degradation of non-protein amino acids, and surprisingly, D-Val, was observed, after 2250 days.

**Recent Sample Analysis:** The La Jolla beach sand/seawater experiment was re-visited in summer, 2012 to determine if amino acids were still present. Sample analysis was performed by HPLC-FD and a triple quadrupole mass spectrometer (QqQ-MS), based on methods outlined elsewhere [5]. Findings indicated  $\alpha$ -AIB, D,L-Iva, and D-Val were still present in high

abundances, yet protein amino acids were present in very low abundances, or were non-detectable, which is consistent with the analyses after 2250 days.

To confirm that viable microorganisms were still present, the beach sand/seawater mixture was again spiked with glycine after the 2012 analyses. Aliquots were then collected immediately after spiking and at 5- and 9-month intervals after glycine addition. Analyses were conducted in 2014 via HPLC-FD/QqQ-MS to determine if glycine was still present, while concomitantly analyzing these samples for non-protein amino acids to compare the varying resistivity to biological degradation of protein and non-protein amino acids.

**Results and Discussion:** Upon final analyses, only  $\alpha$ -AIB, D,L-Iva, and D-Val were above detection limits. The disappearance of glycine and D,L-Ala indicates that microorganisms still live in the mixture and are capable of readily consuming protein amino acids. These findings demonstrate that the non-protein amino acids initially added to the samples over 20 years ago are minimally affected by biological degradation and thus have very long lifetimes under these conditions.

**Conclusions:** These findings suggest that non-protein amino acids derived from prebiotic synthesis, or meteorite in-fall were likely far more resistant to degradation by primitive marine microorganisms, than protein amino acids. Such robust non-protein molecules could have accumulated in the early oceans and reached a steady state concentration dependent on the circulation of the oceans through hydrothermal systems, and input from various synthesis processes. We are presently trying to estimate this concentration.

**References:** [1] Miller S. L. (1953) *Science*, 117, 528–529. [2] Baross, J. A. and Hoffman, S. E. (1985) *OLEB*, 15, 327–345. [3] Kvenvolden K. et al. (1970) *Nature*, 228, 923–926. [4] Zhao, M. and Bada, J. L. (1989) *Nature*, 339, 463–465. [5] Glavin D. P. et al. (2006) *Meteoritics & Planet. Sci.*, 41, 889–902.

**Acknowledgements:** Marine Biology Laboratory NASA Planetary Biology Internship Program & NASA Astrobiology Early Career Collaboration Award funded research. A.S.B. funding: NASA Postdoctoral Program at Goddard Space Flight Center, administered by Oak Ridge Associated Universities through a contract with NASA. J.P.D., D.P.G. funding: Goddard Center for Astrobiology & NASA Astrobiology Institute.