

DECOMPOSITION OF AMINO ACIDS IN WATER WITH APPLICATION TO ENCELADUS AND EUROPA. N. Truong^{1,2}, A. A. Monroe³, A. D. Anbar^{3,4}, J. I. Lunine^{1,5}. ¹Cornell Center for Astrophysics and Planetary Science, Cornell University, Ithaca, NY 14850, ntruong@astro.cornell.edu, jlunine@astro.cornell.edu, ²Department of Earth and Atmospheric Sciences, Cornell University, ³School of Earth and Space Exploration, Arizona State University, PO Box 871404, Tempe, AZ 85287, aamonroe@asu.edu, anbar@asu.edu, ⁴School of Molecular Sciences, Arizona State University, ⁵Department of Astronomy, Cornell University.

Introduction: Amino acids, the building blocks of proteins, are key biosignatures in the search for life. However, amino acids can also be synthesized from abiotic processes and preserved in a range of primitive materials and glycine was found in the coma of comet 67P/Churyumov-Gerasimenko [1]. Thus, even if amino acids can be detected on Enceladus or Europa, they might be formed by other processes not related to biology such as 1) Primordial processes on planetesimals or ice photochemistry or 2) Geochemically related processes. Therefore, a major challenge in using amino acids as biosignatures is to determine whether amino acids are being actively produced by biological processes. This requires understanding the source (what is the biotic vs. abiotic distribution of amino acids) and the sink – decomposition in aqueous solution absent a process to regenerate the amino acids. Here we extend previous work [2] to calculate the decomposition timescales of amino acids under two scenarios:

- 1) “Free dissolved” amino acids in the ocean.
- 2) “Mixing” amino acids concentrated in hydrothermal vent chimney.

Modelling methods: We attempted to collect *all* kinetics data published in the literature, e.g., from organics extraction processes using high-temperature, high-pressure water applied in industry and biotechnology, and also from experiments simulated hydrothermal vents on Earth [3,4,5,6]. To apply to Enceladus, we only choose kinetics data from experiments with conditions taken far below the critical point of water (in pressure condition smaller than 100 bar, given the low gravity of Enceladus [7] and as a result, a low pressure in the seafloor). Thus, we eliminate from our consideration any kinetics data which was experimentally obtained at a higher pressure.

Extrapolating the rate constant to temperatures that not determined experimentally. For each amino acid, at least three data points or more were used, allowing us to fitted $\ln[k]$ vs. $1/T$ with least square fitting. All kinetics rate constants of all amino acids are well fitted to an Arrhenius relationship between rate constant and inverse temperature. This approach was used in several experiments to find the Arrhenius activation energy and the frequency factor (e.g. [3,5,6]).

The analytical solution to the decomposition timescale of amino acids. We define the decomposition

timescale of each amino acid as the time in which 99% of the initial concentration was destroyed by a first order process. A similar approach was used to estimate racemization timescale for meteoritic amino acid based on asteroidal parent body temperature [8]. We solve the kinetics equation with the corresponding kinetic rate constant collected above to calculate the destruction timescales.

Results and Discussions: The decomposition timescale of amino acids is very **sensitive** to ocean temperature.

1. “Free dissolved” amino acids decomposition timescale in the ocean. In this case, each amino acid is assumed to decompose individually in water. Gly, Ala, Val, Glu are decomposed to the least extent. They are destroyed very slowly, taking about ~ 10 Ga to be reduced to 1% of their initial value if the ocean temperature is 300K. Hydrothermally cycling water through the core produces the fluid temperature of at least 323K [9], but the ocean temperature is still unknown as no data for temperature profile in the ocean exists. Except for Gly, Ala, Val, Glu, most other amino acids decomposition timescales are *relatively short* compared with the age of the solar system.

Organizing the amino acids conventionally by the chemical identities of their R-groups (hydrophobic non-polar (Gly, Ala, Val, Leu, Ile, Met), hydropolar aliphatic (Ser, Thr, Pro), aromatic (Phe, Tyr), basic (Lys, Arg, His), acidic (Asp, Glu) allows some useful comparisons to the rates of decomposition.

Number of C in R-group. It seems that rate of decomposition increases with the length of C-chain in R-group. For Gly and Ala, they can quickly transform into more stable states through dimerization and then cyclization, especially in very alkaline water (pH=9.8), thus lower down the decomposition rate [10,11]. It also has been noted that longer elongation of R-groups leads to the weakening of hydrogen bond between amino acids and water molecules, and facilitate the decomposition process [12].

Effect of pH. We calculated amino acids decomposition timescale at 503K for different pH environments: acidic (pH 2.5), nearly neutral (pH 6.2), and alkaline (pH 10.5). Except for some basic amino acids, all other amino acids show an increase in the decomposition time when the ocean environment is more

alkaline. When the water is very alkaline ($\text{pH} > 10.5$) resembling what has been derived for Enceladus's ocean [13], *only* arginine and lysine decompose faster.

Effect of redox states. In some cases, the presence of aqueous H_2 in water may affect the decomposition: glutamic acid decomposition is inhibited in the solution containing 13 mM of H_2 in a lab experiment [14]. To evaluate the potential effect of aqueous H_2 in Enceladus's ocean for the decomposition process, we calculated the concentration of H_2 in the ocean based on the constraining value of H_2 molality [15]. As the H_2 concentration on Enceladus is on the range of 10^{-2} – 10^{-1} mM, far below the corresponding condition in the experiment (13 mM); the effect of aqueous H_2 would not significantly affect to the decomposition timescale of amino acids.

2. *Decomposition of "mixing" amino acids in hydrothermal vent chimney.* In hydrothermal vent setting, thermal gradients have been demonstrated theoretically as well as from lab experiments and observations of mineral chimneys as an efficient mechanism to concentrate highly single nucleotides into microscopic pore spaces in the chimney structure [16].

For "mixing" model, amino acids are assumed to be decomposed as "free dissolved" amino acids for ~1000 yrs, (a comparable value to the mixing time on Earth's ocean) [17] before they are trapped in the pore spaces of chimney structure and spend the rest of their lifetime here.

The timescale for the case of "mixing" of concentrated amino acids in hydrothermal vent chimney. When amino acids are concentrated in the pore spaces of chimney structure, amino acids are destroyed even *faster* than the one "free dissolved" in the ocean because of the interactions between amino acids in the mixture [3]. Their lifetime against decomposition of most amino acids considering in this study is *shorter* than the shortest plausible timescales of the Enceladus ocean (time to freeze, ~ 10^6 years) [18].

Effect of minerals. The presence of minerals affects to the reaction rates and in the decomposition pathway, either by direct catalysis by mineral surfaces or indirectly by contributing inorganics compounds that alter intermediate reaction pathways (e.g., dissolved sulfur species in minerals). Norvaline, a representative of alkyl- α -amino acid group, decomposed more rapidly in the assemblage of hematite-magnetite-pyrite (HMP) or pyrite-pyrrhotite-magnetite (PPM) than the one occurred in the absence of minerals. Also, the decomposition rate in HMP assemblage is much faster than in PPM assemblage because of the surface catalyst effect of magnetite, which has a surface area more than ten times pyrrhotite [19].

Conclusions:

1. The *relatively* short lifetime of most amino acids (except Gly, Ala, Val, Glu) in both scenarios, "free dissolved" in the ocean and "mixing concentrated" in chimney structures suggest that if amino acids can be detected on Enceladus, their origin should come from active production rather than primordial synthesis.

2. For amino acids concentrated in pore spaces of chimney structures, their lifetime is shorter than their "free dissolved" amino acids, and for most amino acids in this study, much shorter than the plausible timescale of Enceladus's ocean. It suggests that even if accumulation mechanisms on Enceladus are efficient enough to concentrate prebiotic molecules into pore spaces of chimney structures for a substantial amount of time, polymerization of peptides and nucleic acids face a challenge that thermal decomposition could destroy them before polymerization conditions are obtained.

3. As the decomposition timescale of amino acids is relatively short and in some special cases, even shorter than the timescale of ocean existing on Enceladus, any models considering the production of amino acids (both abiotic and biotic production) should take into account the effect of the decomposition process.

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