Abiotic synthesis of peptides driven by the solar energetic particles in early Martian and terrestrial atmospheres

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The origin of amino acids, peptides, proteins, and their precursors is the most important issue for elucidating the origin and evolution of life on planets with the atmosphere and ocean. It has been theoretically predicted that these prebiotic substances are synthesized abiotically from atmospheric molecules by any energy injections: e.g., lightning discharge, solar ultraviolet photon, and Solar Energetic Particles (SEP). Many laboratory experiments have been conducted for the abiotic synthesis of prebiotic substances from the atmosphere by various energy injections [e.g., Miller, 1953]. Most of these laboratory experiments modeled the early Martian and terrestrial environments with mildly reduced (CO or CO_2, H_2O, N_2) and strongly reduced (CH_4, H_2O, NH_3) atmospheres. Proton irradiation experiment for modeling the solar energetic particle (SEP) injections most effectively produced amino acids and their bound macromolecules called tholins [Sagan and Khare, 1979] from both the mildly and strongly reduced atmospheric molecules [Kobayashi et al., 1989]. However, because only the amino acids and tholins were synthesized in the previous studies, the formation of peptides from amino acids bounding and abiotic evolution to the protein have been not evaluated yet.
Here we focused on the sulfuric gas, which is abundant around the volcanoes on ancient Mars and Earth and highly reactive for the chemical process in the atmosphere. With the assumption that the sulfur-containing amino acid was abiotically synthesized from the volcanic atmosphere as well as the non-sulfuric amino acids, we evaluated the abiotic synthesis of peptides from these mother substances based on the laboratory plasma irradiation experiment. We irradiated a powder sample of non-sulfuric amino acids composed of 74.6% glycine, 19.9% alanine, and 5.49% serine, and a sample with sulfur-containing amino acid (cysteine) composed of 73.3% glycine, 19.6% alanine, 5.39% serine, and 1.77% cysteine with hydrogen ions at 10 keV with a beam current of 7 μA for an hour. Based on the high-performance liquid chromatographic analysis, we detected macromolecular organic compounds only from the sulfur-containing amino acid sample. The N-terminal amino acid sequence analysis of the macromolecular materials showed that the detected macromolecules have multiple peptide bonds, which indicates that the peptide was synthesized in the sample. It was confirmed that formed peptides were mainly composed of glycine and alanine by mass spectrometry. Non-proteinogenic amino acids were also found in the peptides. This demonstrated that sulfur-containing amino acids promote the bonding of amino acids to form peptides under hydrogen irradiation. These results suggest that the peptides were abiotically synthesized in the atmosphere around the volcanoes on ancient Mars and Earth. We are going to address the structural analysis of the peptide, and abiotic synthesis of peptide and protein from gases by High-energy proton irradiation of atmospheric molecules containing sulfur.

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