EFFECTS OF RADIATION ON THE STABLE ISOTOPE COMPOSITION OF GLYCINE: IMPLICATIONS FOR INTERPRETING EXTRATERRESTRIAL ISOTOPE SIGNATURES

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The inventory of organic compounds that preceded the origin of life on Earth is unlikely to be determined by direct analysis of terrestrial materials. This is because life as we know it appears to have existed on Earth for approximately as far back in time as the rock record itself (~3.8 to 4.0 Ga). The lack of appropriate terrestrial rock samples for organic compound analysis that span the first five hundred million years of Earth's history has led to alternative, indirect approaches to resolve this question. Starting with the experiments Miller (1953), there have been a multitude of attempts to simulate the prebiotic synthesis of organic compounds under early Earth conditions (e.g., Engel, 2011 and references therein). An alternative approach has been the analysis of extraterrestrial materials that contain organic matter from the time and perhaps prior to the formation of our solar system. Carbonaceous meteorites have been the primary focus of this type of research (e.g. Glavin et al., 2012 and references therein).
Approximately 10 of the 20 protein amino acids that are common to all life on Earth have been observed in carbonaceous meteorites. Thus, a challenge has been to find ways to determine if the amino acids in the meteorites were unequivocally extraterrestrial in origin rather than being derived via contamination during and/or subsequent to impact. This question has to some extent been resolved by the discovery that amino acids in meteorites are moderately to substantially enriched in ^{13}C, ^{15}N and ^{2}H relative to terrestrial amino acids of biological origin (e.g. Engel et al., 1990; Glavin et al., 2012). This stable isotope approach has also been used to confirm the extraterrestrial origin of glycine in cometary dust (Elsila et al., 2009).
The robustness of stable isotope analysis for determining the authenticity of amino acids in meteorites hinges on the assumption that these isotopic signatures have not been altered by diagenetic processes subsequent to synthesis. Kminek and Bada (2006) and more recently Matthewman et al. (2016) have conducted simulation experiments to assess the stability of amino acids exposed to ionizing radiation on Martian and lunar surfaces. De Gregorio et al. (2010), Le Guillou et al. (2013) and Laurent et al. (2014) have reported stable isotope fractionations resulting from the irradiation of kerogens and kerogen like materials. Large and small bodies alike are continuously exposed to cosmic radiation, which consists of high energy protons.

In the present study we report the effects of cosmic radiation on the stable isotope composition of glycine. Powdered samples of glycine were mounted on 10 mm diameter glass fibre filters which were loaded into an aluminium sample holder. The targets were exposed to a 1.7 MeV proton beam generated by a Van de Graaff accelerator. The target samples were irradiated for up to 10 minutes at beam currents of 20, 40 and 60 nA. The centres of the targets directly impacted by the beam were depleted in ^{13}C by up to 3 ‰ relative to the starting material, whilst the outer rims of the targets retained stable carbon isotope values close to that of the original glycine. A series of experiments were also performed to determine whether this isotope depletion effect was a direct consequence of a nuclear reaction and/or the result of, for example, thermally induced decarboxylation. Quantitative recovery of the carboxyl carbon of glycine via the ninhydrin reaction performed under vacuum indicated that the carboxyl carbon was approximately 3.5 ‰ enriched relative to the bulk $\delta^{13}C$ value for glycine prior to irradiation.

Thus, thermal effects resulting in decarboxylation of glycine from the radiation experiment may have contributed to the observed stable isotope depletion for the residual target samples. Possible implications of cosmic-ray induced isotope effects for interpreting the stable isotope compositions of amino acids in carbonaceous meteorites are discussed.

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