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RESEARCH ARTICLE

Amino acid dipeptide formation induced by experimental irradiance of a solar flare power

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Abstract

The experimental study aimed to select the spectrometric results of the solar flare that meet the mathematical conditions for integration, to measure the *power* of this integrated flux, and to test the integrated power, whether it is able to form a peptide bond between two molecules of selected amino acids on the Earth's surface. Results show that the radiation power of the X17 solar flare scanned by the SOLSTICE and SIM spectrometers aboard the NASA SORCE spacecraft, when used for experimental irradiance of the same parameters, is sufficient to form methionine, alanine, glutamine and proline dipeptides in aqueous solution with pyrophosphate or carbonyl sulphide at laboratory temperature. The experiments, with their successful outcome, provide insight into the *biological significance* of the narrowband solar flare anchored in the broadband UV solar radiation.

Contents

Introduction

The *quantitative* behaviour of atoms, from the formation of elements in the gravitation of massive stars (Rubenstein *et al*., 1983) to the synthesis of amino acids in space (Elsila *et al*., 2009), is often referred

to as so-called 'chemical evolution'. The syntheses, mimicking possible natural prebiotic processes in the laboratory, have achieved the complete set of nucleobases of RNA, DNA and three amino acids molecules (Saladino *et al*., 2015). A large number of authors of these experiments with a mixture of elementary substances demonstrate the formation of amino acids and nucleotides under a sufficiently high energy. The energy of various forms (spark discharges, UV radiation of a whole Sun, volcanic heat, terrestrial radioactivity, meteorite impacts) has been used for their formation. The mentioned results thus prove that amino acids and nucleotides represent the edge of chemical evolution controlled by the quantum mechanics of atoms. Further accumulation of these results, same as their discussion, is beyond the focus of this study, because it looks for some additional way in which the assembly of protein and nucleic acid molecules is achieved.

'Biological evolution', a *qualitative* conception, is most commonly believed to be the organizing principle involved in the origin of life and species on Earth. In contrast, scientific advances offer basic results made in cosmology, physiology, molecular biology and genetics that, due to their intrinsic essence, are unable to be reconciled with a paradigm. The paradigm of continuous biological evolution based on the natural selection of random mutations and their accumulation in the offspring. If we accept 20 amino acids as a result of chemical evolution, but reject the continuation by the combinations of randomness mutations and their natural selection, then we have to find the principle according to which individual amino acids are assembled into peptides, and a tangible, physically measurable means of operation. Hard science has to be addressing the basic biological question of *the origin of life and species*. This is a challenge not only for our study. Amino acids absorb the radiation energy to the maximum extent in a very narrow wavelengths' band λ_{max}, specific and selective for each type of their molecules. The close absorbance maxima λ_{max} for the amino acids used in this study offer a possible formation of their dipeptides, if an irradiated flare power is sufficient for peptide bond formation. In a broader perspective, the variable anchoring of narrowband flares into the broad-band UV radiation of the whole sun could form the *specific patterns of radiation* (Mejsnar, 2014) for the assembly of the corresponding amino acids into di-/poly-peptides.

Material and methods

An instrumental setup (Ocean Optics, Inc.: DT-MINI-2-GS light source, UV-VIS XSR optical fibre with a 200 µm diameter, CUV-UV 1 cm cuvette holder, 500 µm diameter UV/SR-VIS optical fibre, USB 4000-XR1-ES spectrometer) was used for the spectral absorption measurements of four amino acids: Met (Fluka AG/Sigma-Aldrich, Seelze, Germany), Pro (Iris Biotech GmbH, Marktredwitz, Germany), Ala (Fluka AG, Seelze, Germany) and Gln (Iris Biotech GmbH, Marktredwitz, Germany). All samples were sterilized by a 0.20 µm filter.

Power of flare-photons flux scans and its centroid transposition to wavelength of 228 nm

During the solar storms between 18 October and 5 November 2003, there were eleven large X-class flares, including the X17 flare on 28 October 2003 (Woods *et al*., 2004). This flare, used for our experiment, was observed by the instruments aboard the NASA Solar Radiation and Climate Experiment (SORCE) satellite mission that provided state-of-the-art measurements of solar irradiance. Time series of the irradiated energy before and during the flare were measured by the Solar Stellar Irradiance Experiment (SOLSTICE) and Spectral Irradiance Monitor (SIM) spectrometers.

The SORCE SOLSTICE spectrometer, during observation of the X17 flare, scanned the time series in 21 moments (from 10:37:33 to 11:24:29 UT) of mini scan data from 276.15 to 283.64 nm (with a step size of cca 0.032 nm). In this way, the extensive collection of irradiance scans comprised 5040 values (in units of photons s^{-1} cm^{-2} nm^{-1}), arranged in a table consisting of 240 wavelength columns and 21 time rows. From this collection, the column of photon scans at 279.575 nm was selected for evaluation of the power data. Multiplication by the photon energy at this wavelength (using the Planck–Einstein equation $\varepsilon = hv$, where ε is the photon energy, h is the Planck constant, v is the

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frequency, and with a substitution for v), being equal to 7.11×10^{-19} J, yields the power at this wavelength. Integration was performed over wavelengths within the 0.1 nm band (over three 0.032 nm bins that span 279.543–279.688 nm as their full width), times 10 within the 1 nm band. Multiplication by the photon energy evaluates the power of the flare, the time course of which was transported to 228 nm. The SORCE SIM spectrometer allowed this transposition offering the collection of data measured at a lower resolution with a 1 nm step size comprising 4628 values, ranging from 220.50 to 285.13 nm. The photon flux power integration included ten 1-nm bins from 223.50 to 232.50 nm, giving thus pre-flare data at 228 nm (Woods *et al*., 2006).

Light source for UV irradiance

The four amino acids were exposed to the experimental irradiance of the parameters presented in Fig. 1, with HAWN. The results were observed with mass spectrometry (MS). The final HAWN setup for photoexcitation (following two prototypes to *increase* the required power, in contrast to the commercial development, *reducing* the light sources power while increasing the sensitivity of the detectors) was as at Home Arranged Wasserstofflampe Narva with the $D_2E/1$ deuterium bulb (Carl Zeiss Jena), a mechanical diaphragm (Meopta, with a 5–21 mm diameter aperture), a 228 nm optical bandpass filter (Andover Corporation, 228FS25-12.5) and a directly-attached cuvette holder (of our provenance). The photoexcitation output power over the full wavelength spectrum was ≈7.35 W. The 'preflare' irradiation power in experiments was universally equal to 806 μW cm^{-2}, as the increased natural irradiance power 47.62 μW cm^{-2} (Fig. 1) was proportional to the *measured* loss (in filter/cuvette holder + through a proximal cuvette wall) and to the *calculated* higher amount of amino acids. The irradiance intensity was calibrated in counts (Ocean Optics Spectrometer), in μW cm^{-2} (Light Meter, Lutron Electronics) and checked by the Czech National Standard of Total Flux of UV Radiation at 228 nm.

The irradiance of an Ala solution with pyrophosphate

The function of linear polyphosphates in promoting the condensation of amino acids has been shown by several authors; diglycine formation and, similarly, the formation of dialanine in the presence of sodium pyrophosphate required 14 days (336 h reaction) to reach a 0.7% yield of the dipeptide (Rabinowitz *et al*., 1969). Calcium chloride had to be added, as a protecting catalyst of the acyl group (Di Sabato and Jencks, 1961), and of the ionized amino acid carboxylate group, due to the proposed chelation of Ca^{++} to both oxygen atoms (Qin *et al*., 2014). The pyrophosphate method involved a number of complications, starting with the spontaneously created balance between dibasic and tetrabasic sodium pyrophosphate; dibasic pyrophosphate as the input solute (onset pH: approximately 3.6) forms tetrabasic pyrophosphate, and *vice versa*, tetrabasic sodium pyrophosphate as the input (onset pH: approximately 8.9) forms dibasic pyrophosphate. However, both directions tend towards equilibrium with varying formation of subsequent ionically bound adducts in solution. Ala-Ala dipeptide formation by irradiance was achieved only in experiments with tetrabasic pyrophosphate. In addition to the Ala-Ala dipeptide (Fig. 2), we explicitly identified: sodium alaninate, monosodium pyrophosphate, alaninium monosodium salt dibasic pyrophosphate and alaninium disodium salt dibasic pyrophosphate.

The irradiance of Met, Gln and Pro solutions with COS

Another type of irradiance-stimulated formation consists of the prior synthesis of a small amount of a dipeptide by carbonyl sulphide (COS) (Leman *et al*., 2006), serving as a kind of 'primer' (with apologies for the lame metaphor of primers as the starting material for the synthesis of a new DNA). Figure 3 shows, as an example the Met-Met dipeptide formation in this way.

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Mass spectrometry (MS)

MS of the four amino acids, dipeptides and all solute chemicals was performed, using Solarix^{XR} – the eXtreme Resolution mass spectrometer (Bruker Corporation, Billerica, MA, USA), provided with 12T and 15T magnets for informative and experimental MS, respectively. The mass spectrometer was used in ESI (electrospray ionization) mode in all experiments.

Statistical information

The dipeptides formed in this work (and all other solutes) were analysed by MS. The method is extremely sensitive to the detection of solutes (dipeptides) in a solution, and was chosen for this purpose. The professional rule is that the mass deviation of an analysed (and ionized) solute is permitted to the fifth and maximally to the fourth decimal place, with respect to the theoretical value. For example, the mass deviation of: 123.45678 versus 123.45681 = ± 0.00003, which is a difference of 3×10^{-5} units. Following the abovementioned rule, the ten Ala-Ala dipeptides (one shown in Results, Fig. 2) were recorded as ten signals independently measured in independent solutions, with a deviation of: $10^{-5} \leq \text{dev} \leq 10^{-4}$. All other experiments resulting in a deviation ≥0.001 (i.e. 1/1000 of a proton mass!) had to be rejected. This *binary* evaluation did not require statistics. In this way, however, regarding statistical reasoning, we could have obtained false-negative results when rejecting a dipeptide signal. In view of this risk of false-negative reporting, the rule places great demands on dipeptide confirmation.

Results

Amino acids absorbance

Four amino acids were chosen, proline (Pro), glutamine (Gln), methionine (Met) and alanine (Ala), and their absorption spectra were collected within the near-ultraviolet range from 200 to 260 nm. The amino acids absorb radiation to the maximum extent (representative of the respective acid) at the following wavelengths: λ_{max} for Pro = 206 nm, for Gln = 216 nm, for Met = 228 nm and for Ala = 216 nm. The energy of photons at these wavelengths (see Methods) for absorbance maxima λ_{max} is: $[\varepsilon_{Pro} = 9.65,\ \varepsilon_{Gln} = 9.21,\ \varepsilon_{Met} = 8.72,\ \varepsilon_{Ala} = 9.21] \times 10^{-19}$ J. The close absorbance maxima for the presented amino acids offer a possible formation of their dipeptides, if an irradiated flare power is sufficient for peptide bond formation. For such a purpose, the irradiated flare power has to be defined.

Solar flare definition

The definition (quantitative) of the X17 flare used in this study is presented in Fig. 1.

The peak maximum equals an increase by 25.7% (Fig. 1, Trace A) at 279.575 nm. For experimental photoexcitation, however, we needed the integrated form of this photon flux. The integration of Trace A (using the values measured within three 0.032 nm bins, i.e. over the cca 0.1 nm band) decreases its peak maximum to 15.2%. This integrated power with respect to time was transposed into 228 nm, using pre-flare data, scanned by the SIM and integrated over the 223–233 nm band with ten 1 nm bins (Fig. 1, Trace B).

For calculation details of the figure, see Methods. For an informative conception, an amino acid amount of 20 µmol (considered as a 0.05 M solution in a cuvette volume of 0.4 ml for experimental irradiance) needs half as much peptide bond formation (10 µmol), and an energy of approximately 55 mJ, if we consider the original estimation to be 5.44 kJ mol^{-1} (Haugaard and Roberts, 1942), taken from Borsook (1953). For the size estimation of natural flare integrated power in Fig. 1, it should be informative that its maximum power of 54.86 µJ s^{-1} cm^{-2} provides this energy within 16 minutes.

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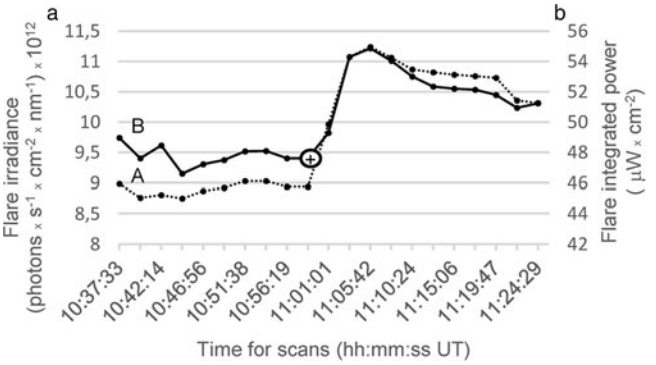

Fig. 1. *Definition of a solar flare. Trace A: time series of the SOLSTICE scan(photons.* s^{-1} cm^{-2} nm^{-1}*)* measured *at 21 UT moments (from 1 = 10 :37 :33 to 21 = 11:24:29) at 279.575 nm. Trace B: time series of the* calculated *flare power, integrated over the 223–233 nm band, and transposed into the* measured *pre-flare SIM scans (marked by +).*

The narrowband solar flare anchored in the broadband UV solar radiation

The scanned *record* shows why the correct interpretation of our flare experiment requires a new perspective. The current one compares the slight power of the flare to the huge power of the whole sun, and says that *'there is solar extreme ultraviolet…radiation all of the time…so this photochemistry is always happening. That is, a flare is not required for the photochemistry process to start'*. Let us follow the general information. The wavelengths of the solar UV radiation range in length from 400 nm (UVA) to about 280 nm (UVB) and a little to 100 nm (UVC). The SOLSTICE spectrometer, aboard the spacecraft, scanned the data from 276.147 to 283.644 nm (see Methods). In this interval, two flares centred at 279.575 and 280.265 nm were recorded. The former one was chosen to quantify the power of the flare (see Methods). If we sum up the number of photons forming the solar radiation within the whole range, we get a huge number, and with respect to time a huge power. However, the amino acid molecules cannot capture this enormous power, because they absorb the irradiance energy in a very narrow range of wavelengths λ_{max} (see Results, the first paragraph).

Actually, the ratio of the flare's 'slight' power to the power of the whole sun depends on the size of the solar integrand, i.e. on the range of the definition field of function under the integration sign. We narrow the range of solar UV radiation to a small one, from 277.186 to 279.763 nm, containing in its centre the centroid wavelength 279.575 nm of the selected flare. Thus the following *record* indicates the solar UV radiation scanned at seven wavelengths around the radiation of the studied flare (at 279.575 nm). Presented results are shaped as wavelength / photons . s^{-1} . cm^{-2} . nm^{-1} and the seven wavelengths mean: (1) the end of the *all of the time solar radiation* → (2, 3) the first minimum → (4) the value of the whole sun radiation upon which the flare is imposed → (5, 6) the second minimum → (7) return to the *all of the time solar radiation*. The radiation is as follows:

(1) 277.186 / 4.35450E + 13 → (2,3) 279.512 / 6.34374E + 12 and 279.543 / 5.89565E + 12 → → (4) 279.575 / 8.98308E + 12 → (5,6) 279.732 / 5.77242E + 12 and 279.763 / 6.72078E + 12 → → (7) 283.051 / 5.32228E + 13.

The intensity No. 4, pertaining to the photons flux 8.98308E + 12 is identical, by definition, to the first point of the Trace A in Fig. 1; it is therefore the first point of 'pre-flare' intensity. As it is shown in Fig. 1, the time course of the integrated flux achieves an increase in pre-flare radiation by 25.7% due to the flare. The increase is sufficient to form dipeptides, as shown in the following subchapters of the Results. The overall point is that the flare irradiance is significant compared to the background solar radiation. In addition, the control by flares appears more delicate and aimed in comparison with the long-lasting UV radiation of the whole sun.

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The irradiance of an Ala solution with pyrophosphate

The recent discovery of photosynthetic bacterial membrane-bound pyrophosphatase (catalysing light-induced phosphorylation of orthophosphate to pyrophosphate) is considered in association with geochemistry of the Earth surface at the time of the origin and early evolution of life (Holm and Baltscheffsky, 2011). Together with older pyrophosphate experiments (see Material and methods), it was logical to determine first and foremost whether solar flare power is sufficient to form the dipeptide of the simplest amino acid (with the asymmetric alpha carbon atom), i.e. alanine. The centroid mass spectra of alanine were highly complex; assigning peaks in the full spectrum is difficult even for experimentalists. Thus, Fig. 2 shows, as an example, the m/z details of the MS intensity obtained for the Ala-Ala dipeptide in an irradiated alanine solution. Complementary to this figure in addition to H^+ ionization, the same result was obtained, using ionization with Na^+. Due to 'flare' irradiance, the dipeptide was identified in ten samples, in four experiments, with different solute proportions and pH values. The results prove solar flare power to be sufficient for peptide bond formation between terrestrial alanine molecules.

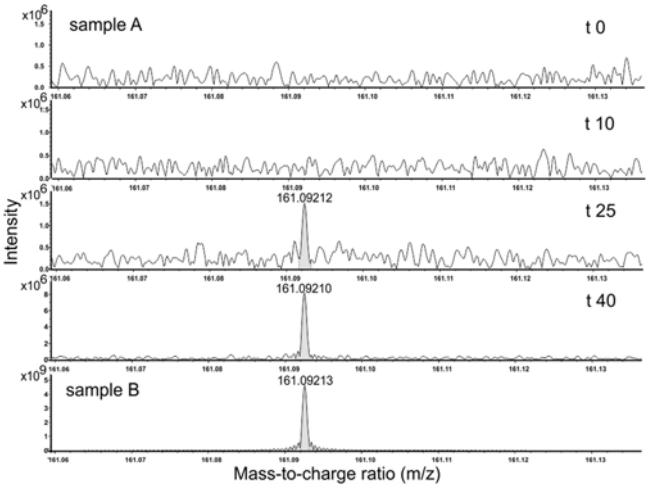

Fig. 2. *The MS intensity and m/z details indicating the formation of an Ala-Ala dipeptide. Samples A of the aqueous alanine solution containing pyrophosphate, was taken before and during irradiance. Sample A: A volume of 1 µl was withdrawn in time [minutes]:* t *0 (the start),* t *10 (the end of the 'pre-flare' irradiance intensity),* t *25 (15 min of 'flare' irradiance) and* t *40 (the end of irradiance). Sample B: non-irradiated Ala solution with the extrinsically supplied Ala-Ala dipeptide. The peaks were assigned to the Ala-Ala dipeptide according to the theoretical m/z value: Ala-Ala [M + H$^+$] = 161.09207.*

The irradiance of Met, Gln and Pro solutions with COS

Another type of irradiance-stimulated formation (see Methods) consists of the prior synthesis of a small amount of a dipeptide by COS. Figure 3 shows, as an example, the m/z details of the MS intensity obtained for the Met-Met dipeptide formed in this way.

The comprehensive results of Met, Gln and Pro dipeptide formation in this manner are shown in Table 1.

The dipeptide formation by COS (used in 1.02-fold mass excess of COS relative to the corresponding amino acids) decreased with the amino acid λ_{max} wavelength, and Pro-Pro was not detectable. The utility of irradiance decreased from the MS intensity of 17×10^7 to 1×10^6 for $[M + H^+]$ and from 15×10^7 to 2×10^6 for $[M + Na^+]$ for two agonistic reasons. Primarily, the energy demand of the three amino acids increased inversely in proportion to the λ_{max} wavelength, and secondarily, the HAWN Light

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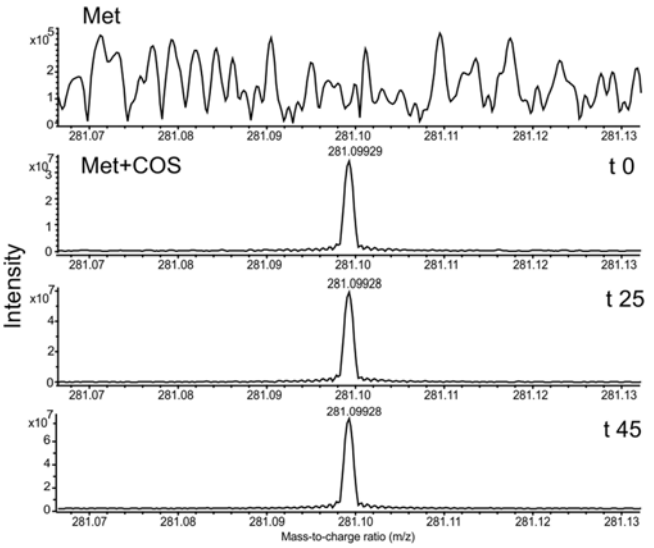

Fig. 3. *The MS intensity and m/z details indicates the formation of the Met-Met dipeptide. Samples of aqueous methionine solutions were taken before and after (*t *0) administration of COS. The subsequent dipeptide increase by irradiance was observed in samples withdrawn at* t *0,* t *25 and* t *45 min of irradiance. The peaks were assigned to the Met-Met dipeptide according to the theoretical m/z value: Met-Met* $[M + H^+] = 281.09881$.

Table 1. *MS intensity of previously-synthesized dipeptides by COS and by irradiance.*

Dipeptide		MS intensity		Increase
Met-Met ($N = 3$)		IRR 0 min	IRR 45 min	%
	A	7.87×10^7	17.43×10^7	222
	B	6.73×10^7	15.00×10^7	223
Gln-Gln ($N = 4$)				
	A	2.76×10^6	4.54×10^6	165
	B	11.30×10^6	17.30×10^6	153
Pro-Pro ($N = 3$)				
	A	–	1.45×10^6	–
	B	–	2.13×10^6	–

Each dipeptide was enumerated as the average of N experimentally independent values. A and B indicate $[M + H^+]$ and $[M + Na^+]$ ions, respectively.

Source is designed and calibrated for the Met λ_{max} 228 nm, with a permanent decrease in power towards shorter wavelengths. For comparison, the original study (Leman *et al.*, 2004) showed the utility of COS (added in eightfold mass excess) in promoting phenylalanine dipeptide formation in a reaction mixture that had stood for 56 h under argon at 25°C, which provided only a 6.8% yield.

Discussion

The study was limited by two inconvenient problems. First, the definition, i.e. quantitative expression of the X17 flare, valid in the range of λ_{max} for the tested amino acids. Second, from an organic chemistry standpoint, amides (in our case resulting from the connection of acyl and amino groups of two amino acids) are 'the least reactive acyl compounds known; and undergo hydrolysis and condensation,

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for example, only under fairly vigorous conditions' (Lewis, 1996). This is beneficial to stability of proteins in the live body (all of which are amides), i.e. to life, but certainly do not benefit the experimental synthesis of a peptide bond. In the course of the project, we found 'fairly vigorous' promotion of the condensation reaction in aqueous solution with pyrophosphate (a metabolite from cyanobacteria important to humans) or COS (a component of volcanic gas emissions).

In these experiments, God is thrifty, nature is thrifty, the flare is thrifty or the amino acid reaction under photoexcitation is thrifty; that is, the irradiance energy added to the amino acids molecules was not fully dissipated into their surroundings, absorbed within a rotation of molecules or a vibration of their parts, nor in the case of higher energies, within a transition of electrons between energetic states, but the energy could be utilized for peptide bond formation and peptide synthesis.

How realistic the experimental study is, where and when would similar conditions exist in nature? If we ask after the *origin of life*, the formation of the first dipeptides in prebiotic condition is essential, as it is for the *origin of species* later after geological disasters. For a broader discussion, we need the Geologic timescale to know that biological evolution is far away from being continuous. The development of life on Earth is not continuous, but discontinuous, realized in *stages*, separated by constraints, called *latent periods* (Mejsnar, 2014). Direct evidence of the oldest fossil bacteria (photosynthesizing cyanobacteria) has been found in Precambrian sediments as old as 2.5 billion years (Summons *et al*., 1999). This discrete first stage, the origin of life, required an introductory latent period, during which chemical evolution had to provide the same 20 amino acids we need today to compose proteins, five bases (in Precambrian Period identical to ones at the present time) to compose nucleic acid DNA, RNA and the 'Universal genetic code', the same genetic code in cyanobacteria as in modern humans. Considering that Earth surface remained molten rock for almost 1 billion years, there is a relatively short time left for the latent period. Moreover, its short time was largely filled by chemical evolution. So the principle of protein formation, starting with condensation of two amino acids into dipeptide, had to be pre-prepared and time-saving. A connection of this study to the origin of life could have different simulated scenarios; e.g. during the volcanic explosion, the gas cloud could easily reach a lake surface, and later on dissolved COS and amino acids can be irradiated by a solar flare.

Continuing the answer to the question posed, recurring mass extinctions of species cannot be neglected, being not evolutionary, but revolutionary steps in the history of life on Earth. The history contains five catastrophes (standing the end of the Geological Periods: (1) Ordovician, (2) Devonian, (3) Permian, (4) Triassic and (5) Cretaceous) which practically destroyed life. Take the Permian disaster as an example. Geologists and palaeontologists have worked hard and respectably, to find the extinction of 95% of the species that had accumulated before the catastrophe, and a fossil-free void space beyond the bounds of the Triassic Period. They explain the origin of species during their subsequent 'explosion' (with knowledge of climate change) logically by the adaptation to environmental changes. From molecular biology, genetics and physiology standpoint, the creation of such a large number of new genomes (genome = DNA containing the entire genetic information of a species) due to an increase of variations in new environmental conditions, and accumulated by 'natural selection', does not fit in the essential points. The synthesis of new proteins requires a different mechanism, but it always starts with the dipeptide formation. Volcanic activity at the end of Permian Period heated the surface upto 1200°C; however, in the new Geological Period, it could function according to the scenario presented above.

In astronomy, the *optical window* is the portion of the electromagnetic spectrum that passes through the atmosphere all the way to the ground. This window currently runs from approximately 300 to 1100 nm. As it appears, the wavelengths utilized in our experiments are slightly past at the short end of this range. Essentially, photoexcitation at these wavelengths allows for possible control of peptide bond formation, because this reaction can also take place at an upper atmospheric layer. The computational study of peptide bond formation between two glycine molecules in the gas phase reveals a relatively small energy barrier (Redondo *et al*., 2013). Moreover, the composition of atmosphere, i.e. the window's range, has changed in the past. Two and half billion years ago, the ancient Earth's atmosphere consisted mainly of water vapour, carbon dioxide, methane and ammonium (Petit *et al*., 1999).

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Quantitative models of atmosphere composition show a significant and sharp oscillation of carbon dioxide and oxygen concentration for the whole Phanerozoic time (Budyko *et al*., 1987).

Supplementary material. The supplementary material for this article can be found at https://doi.org/10.1017/S1473550422000118.

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Conflict of interest. None.

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