Excess of L-alanine in amino acids synthesized in a plasma torch generated by a hypervelocity meteorite impact reproduced in the laboratory ☆

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A R T I C L E I N F O

A B S T R A C T

We present a laboratory reproduction of hypervelocity impacts of a carbon containing meteorite on a mineral substance representative of planetary surfaces. The physical conditions of the resulting impact plasma torch provide favorable conditions for abiogenic synthesis of protein amino acids: We identified glycine and alanine, and in smaller quantities serine, in the produced material. Moreover, we observe breaking of alanine mirror symmetry with L excess, which coincides with the bioorganic world. Therefore the selection of L-amino acids for the formation of proteins for living matter could have been the result from plasma processes occurring during the impact meteorites on the surface. This indicates that the plasma torch from meteorite impacts could play an important role in the formation of biomolecular homochirality. Thus, meteorite impacts possibly were the initial stage of this process and promoted conditions for the emergence of a living matter.

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1. Introduction

Homochirality is generally recognized as the most important structural feature of living matter, and a unique marker of life (Keszthelyi, 1995; Avetisov and Goldanskii, 1996; Barron, 2008). Its origin, however, remains unknown, and biochemical replication could not develop, and hence life could not arise, without it (Eigen and Schuster, 1979). Thus, homochirality must have originated in non-living matter. However, for 130 years, since Louis Pasteur (1884) discovered the chiral asymmetry of life, homochirality has remained the main obstacle for hypotheses about the genesis of living matter.

The consideration of the origin life from abiologic matter with the chiral asymmetry of enantiomers are connected to two major questions, which remained unanswered for a long time until today:

First: How could complex biochemical material, which is typical for life, arise in inanimate nature and what processes are responsible for that? In this work we present a preliminary answer.
Second: How did the sequence of amino acids able to replicate appeared for the first time? Was such sequence unique or not? We still don't know the answer.

The emergence of biologic matter in inanimate nature requires its existence in homochiralic form of the macromolecular

structures possessing high-precision, and "faultless" abiogenic assembly, characteristic only for biology. If the number of errors during the assembly of structures consisting of 10^6–10^8 elements exceeds 1, it could lead to casual generation of an arbitrary variation and to loss of the genetic information, or to "catastrophe of errors" according to (Eigen and Schuster, 1979).

It was shown that the explanation of the emergence of life based on processes of statistical sampling of monomers is impossible (Frank, 1953; Eigen, 1973; Prigogine, 1980; Goldanskii et al. 1987), and that the process of origin of life is significantly more difficult. So, by estimates of many experts the number of these samplings is so high that even possibilities of our entire Universe are not sufficient.

Experimental studies of the influence of a medium's chiral properties on the processes of oligomerisation showed that the initial organic compounds (OCs) must possess homochirality before the emergence of life (Joyce et al., 1984; Visser et al., 1984; Visser, 1986). The results of these studies revealed insurmountable difficulties for the origin of life in a medium based on chemical equilibrium. These authors reliably showed that for solving the origin of life problem a new natural environment with previously unknown properties must be found.

We were led to the problem of the origin of life research accidentally during research on laser-based mass spectrometry (MS). During the development of the laser ablation (LA) time-of-flight (TOF) MS LIMA-D and LIMA instruments mass peaks of multiply ionised hydrocarbons were registered, which were not observed earlier. In these experiments the observed OCs could only arise by synthesis in plasma torch itself. Later, such ions were discovered in other plasma processes as well.

The formation of OCs from a target composed of biogenic species and non-organic substances in a plasma torch produced by laser irradiation was reported for first time by Managadze (2001). At that time, laser-produced (Stamper, 1991) and impact-produced (Crawford and Schultz, 1999) plasma torches were already known to be highly similar in their physical parameters. Hence, emulating the impact plasma by high power laser pulses proved to be convenient and practical at the initial stage of laboratory studies of impact plasma properties (Managadze, 1992). Since the plasma formation, as well as chemical processes, molecule formation and destruction, are determined by physical properties of the plasma plume such as temperatures, densities, collision rates, and the expansion velocity the resulting chemical composition varies with the particle impact or laser conditions, respectively (e.g. Mocker et al., 2012; Fiege et al., 2014).

Mass-spectrometric analysis of the expanding plasma showed that laser plasma torches provided the synthesis of simple and complex OCs with molecular masses up to 6500 amu. (Managadze, 2003; Managadze et al., 2003). The comparison of results showed that the OCs synthesized in an impact produced plasma torch (Stubig et al., 2002) were remarkably similar to those synthesized in a laser-produced torch (Managadze, 2001). Hence, impact-produced plasma torches are also expected to be capable of abiotic synthesis of OCs.

Plasma–chemical reactions differ significantly from pure chemical ones. The high catalytic activity of ions and radicals created in the plasma increases the speed of chemical reactions by 10^6–10^8 times in the plasma compared to pure chemical reactions. For example, halogenides of inert gases and noble metal carbides can be easily synthesized in plasma–chemical reactions, however it is difficult or even impossible to do it in chemical reactions. Furthermore, the fast cooling of the plasma during the expansion of the torch strongly limits decomposition reactions of products in contrast to a pure chemical case. More detailed research of a plasma torch regarding of electromagnetic fields and the processes happening during scattering of plasma allowed coming to the

important conclusion that the electromagnetic fields of internal areas of a plasma torch are true local chiral fields (Managadze, 2005).

The influence of the local chiral field on enantiomers synthesized in a torch can lead to break of their mirror symmetry. New properties of plasma torch were discovered in experiments on modeling the meteorite impact by laser pulses, which resulted in the hypothetical "plasma scenario" for the emergence of living matter (Managadze, 2007). The important properties of plasma torch are:

- High initial density and temperature reaching up to 10^6 K (> 70 eV), which is rapidly decreasing after impact
- High speed of plasma–chemical reactions with rapid removal of the reaction products, resulting in an imbalance of the direct and reverse reaction rate
- Break of mirror symmetry of synthesized substances.

According to the plasma scenario, the plasma and plasma processes arising during adiabatic expansion of plasma torch could provide the formation of the homochiral macromolecular structures necessary for origin of a living matter.

For the confirmation of the validity of a plasma scenario, first of all, it was necessary to experimentally demonstrate the possibility the synthesis of OC and the breaking of their mirror symmetry directly in the plasma torch occurring in experiments reproducing the meteorite impact. This idea is based on experiments on emulating the hypervelocity impact by high-power laser pulse irradiation.

The plasma scenario introduced in this paper assumes that the synthesis of amino acids and breaking of their symmetry should occur in the impact plasma in analogy to the laser plasma (Managadze, 2005, 2007). The plasma torch has important features and particular characteristics because it is highly heated and therefore is a fully ionized gas. In that, the plasma environment radically differs from the chemical environment because of the high catalytic activity and the resulting high-speed chemical reactions in the plasma that are not possible for the chemical environment. In the impact plasma torch the formation of complex molecules, like amino acids and other biological matter, is realised in a very short time during the expansion of the torch.

Earlier studies carried out prior to our formulation of the plasma scenario are based on a chemical formation process instead of plasma formation process (Chyba and Sagan, 1992; Pizzarello, 2007). However, the plasma scenario is different from earlier well-known works such as (Chyba and Sagan, 1992; Pizzarello, 2007) considering the assumed chemical processes, which thus do not have relevance for plasma scenario. Therefore, in this work we considered only the works related to impact plasma processes (Martins, et al., 2013; Furukawaa et al., 2015).

At present there are two publications concerning laboratory reproductions of impacts where relative yields of glycine and alanine produced in impact processes are measured and there is no doubt about the purity of these experiments. Recent experiments of steel projectiles impacting on an ice mixture resembling cometary material showed the formation of several amino acids, however finding equal amounts of D- and L-enantiomers (Martins et al., 2013). The reported ratio of glycine to alanine yields was 9.45 in one of two measurements. In other recent impact experiments also the possibility of the synthesis of nucleobases and protein amino acids without mirror symmetry breaking was shown (Furukawaa et al., 2015). In these experiments the glycine to alanine yield ratio was 10.8 and 13.8 in 2 of 6 measurements, the other 4 measurements are far from these values. Based on these experimental reports we assume the glycine to alanine yield ratio is about 10 as the most reliable estimate of this ratio.

2. Experiment

We performed hypervelocity impact experiments using a ballistic launcher equipped with a light-gas gun (Skalkin et al., 2011). To improve throughput, the apparatus was adapted to launch a set of 20–50 projectiles at once with diameters ranging from 1.5 to 2.5 mm, at a flat multilayer target. Projectiles of pure ^{13}C synthetic diamond were used, which remained intact during acceleration. The ^{13}C served as isotopic marker to identify amino acids synthesized in the impact torch. In total six impact experiments were performed, with the last two experiments using the ^{13}C diamond impactors. The material produced in last experiment was used in the present analysis.

The target consisted of a high-purity sintered ammonium nitrate (NH_4NO_3) disk with a thickness of 15 mm and a diameter of 60 mm, placed above a hard 1.2-mm thick disk of pure standard graphite, followed by a steel plate with a thickness of 5 mm placed in a steel container. The carbon disk increased the efficiency of the interaction of the impactors with the target, since the sintered NH_4NO_3 disk was not hard enough by itself. A 50-mm diameter hole in the front butt of the steel container ensured that projectiles could access the ammonium nitrate target, and allowed impact products to be preserved inside the container.

During the impact, diamond projectiles interacted with the ammonium nitrate, the carbon plate, and the steel surface layer of the plate, to form, together with the target material and after their atomization and ionization, a plasma torch. The impact products from the plasma expansion were deposited on an internal surface of the clean container walls. To easily collect the products of the impact we inserted a titanium foil lining in the container, which easily separated from the container itself. The impact product was scraped from the lining surface and has the form of a dark gray fine powder, with sharp-edged grains ranging from μm to mm in size, and which was highly inhomogeneous in terms of its carbon isotopes distribution. The total mass of ^{13}C projectiles was 0.4 g. Due to the destruction of the carbon plate, the mass of the ^{12}C isotope inside the container was 5.6 g. Thus, the maximum $^{12}C/^{13}C$ ratio would be 14 if complete mixing occurred.

For our experimental conditions, a vertical impact at about 7 km/s and a projectile density of ~ 3.5 g/cm^3, the initial compression at the impact can reach about 170 GPa (Zel'dovich and Raizer, 2002), which is sufficient for heating the projectile and part of the target to temperatures of $(3–4) \cdot 10^4$ K. Such temperatures lead to complete chemical decomposition, actually atomization, of organic contaminants initially present in the interacting bodies. This is confirmed by numerical modeling of meteorite impacts (Pierazzo and Chyba, 1999). The survival of amino acids in hypervelocity impacts was studied recently where it was found that their survival declines steeply at compressions of 18 GPa and most of the amino acids were decomposed at 35 GPa, corresponding to impact temperatures of 420–840 K (Sugahara and Mimura, 2014). The heating ensures the formation of a plasma torch, the survival of synthesized organic compounds (OCs) in the expanding and cooling plasma, and break of chiral symmetry by the local physical chiral fields of the plasma torch.

2.1. Preparation of projectiles

Projectiles of pure synthetic diamond were grown from the ^{13}C isotope. The starting material consisted from ^{13}C of ISOTEC, Sigma-Aldrich, in the form of amorphous carbon with 99 at% of ^{13}C. The produced diamond projectiles have been washed two times in an ultrasonic bath with high-purity deionized water. Then, the projectiles have been placed in a plexiglas mini container (sabot) that has been entered into a barrel as a sub caliber shell. When departed from the barrel the sabot was disintegrated into four parts

and these parts hit the steel plate with the central hole. Projectiles, however, were flying through central hole and reached the target. At the same time the parts of container could not go through this hole. This completely excluded getting them onto the target.

2.2. Preparation of the target

The target was made of ammonium nitrate from Acros Organics (Thermo Fischer Scientific) of purity of $> 99\%$ (for analysis). The target was mixed in a sterile cylinder and baked at a temperature of 170 °C, which caused melting of ammonium nitrate.

The internal surface of the titanium lining was carefully cleaned before the impact experiment: The cleaning procedure included washing the liner twice in an ultrasonic bath with de-ionized water and subsequent baking of the lining at 600 °C. Subsequent analysis of this lining using a laser ablation time-of-flight (TOF) mass spectrometer was carried out, which assured that the amount of contamination on the lining surface after cleaning was below 1 ppm.

2.3. Cleanliness measures

In the present experiment all necessary measures were taken to avoid contamination at the stages of target and projectile preparation, and carrying out the experiment and sample collection. For this purpose:

1. All parts of the container and a target were produced from stainless steel. Before assembly of the container and installation of the substrate for a target all mechanical elements have been cleaned two times in an ultrasonic bath, dried at a temperature of 200 °C for 3 h, and finally they have been annealed up to the temperature of 600° C.
2. Prior to the final assembly of the target container with the target, mass-spectrometric measurements were performed from the target mixture by a laser mass spectrometer, LASMA, with a sensitivity of about 1 ppm. The same analysis was done using a Bruker Daltonics flexAnalysis instrument searching for organic contamination.
3. In case of no detection of contamination, the target container closed hermetically with the target material inside, and was transferred to the ballistic launcher for installation in the vacuum chamber. The hermetic cover, that closes the hole for impactors entrance, was removed before vacuum pumping.
4. All the internal surfaces of the target container and of the entrance tube have been covered by a titanium foil, a lining that allowed collecting the sample generated during the impact without contamination.
5. The products of the impact were collected observing all well-known and necessary measures of sterility, have been were washed away or scratched out from the titanium foil and distributed into Eppendorf tubes. Then they have been delivered to different laboratories for analysis.

3. Results

We analyzed the impact products using three separate analytical techniques with different strengths, limitations, and detection limits: a matrix assisted laser desorption ionization (MALDI) TOF instrument, a laser desorption TOF instrument, and a GC–MS instrument. In each measurement an aliquot of the impact sample was used.

A MALDI TOF–TOF Bruker Autoflex Speed (Goddard Space Center, NASA) was used in this work for the analysis of samples synthesized in plasma torch of the impact. This complex and

multifunctional instrument possesses a several important analytical and technical characteristics for investigation of biological macromolecules. In standard configuration this instrument desorbs and ionizes the sample by 337 nm laser with up to 2 kHz repetition rate, focal spot ranges from 10 to 100 μm. The instrument has mass resolution in the range up to 26,000, while the maximum registered mass can reach > 500,000 u/e. Usually the sample is applied together with a matrix on a plate with a 800×800 μm square cells, and after evaporation of solvent is introduced into the vacuum chamber. The presence of the matrix improves the ionization of large sample molecules during the laser irradiation (MALDI process). Ablated ions are accelerated into the drift tube, pass through the ion reflector and again through drift tube until they are registered by a detector. An important design feature of this instrument is the vertical orientation of TOF analyzer to ensure the horizontal position of the sample. This feature of the device significantly simplifies the analysis of unconsolidated samples, like powders.

In the present investigation we used the simplest functional capabilities of the Bruker Autoflex Speed to record the mass spectra shown in Figs. 1 and 2A and B. For the measurement of the molecular composition of the impact sample we analyzed a pure sample without the matrix after its slight compression on the standard sample holder. The measurements were made at 500 Hz laser pulse repetition rate and a laser power density of about 10^6 W/cm^2 (laser desorption mode). The omission of the matrix for sample analysis allows also for registering light ions; when using a matrix the light ions are usually masked with matrix ions.

It provided mass coverage for positive and negative molecular ions with a sensitivity of 10 ng/g in the MALDI mode. However, we registered mass spectra without matrix, directly from the pure powder of the impact samples (Figs. 1 and 2). Unlike MALDI, such an approach allowed registering also mass peaks of light organic compounds, including amino acids. As can be seen from the presented mass spectra, the signal to noise ratio is more than sufficient for identifying mass peaks of organic compounds with high reliability in the impact samples, and the mass resolution allowed their accurate identification. We have many more of such mass spectra, obtained by direct measurements without matrix, which are at the stage of processing and interpretation at the present moment.

Mass spectra of impact samples are shown in Figs. 1 and 2 which demonstrate that during the synthesis of OCs the ^{13}C

isotope has been involved. However, the stepping structure equaling to 13 amu the range presented in Fig. 1 shows that synthesis of linear carbon chains was carried out on ^{13}C (negative ion mode). During the analysis of these mass spectra it is necessary to consider that results of these measurements have qualitative character. The peak heights can vary considerably because of the significant heterogeneity of the produced impact samples, which is a result of the stochastic nature of synthesis in the plasma torch.

The mass spectrum presented in Fig. 2A shows groups of mass peaks around mass 1300 u/e with mass differences between the groups corresponding to the masses of glycine, alanine, and serine, indicating the formation of simple peptides during the impact. For comparison, the MALDI-TOF spectrum shown in Fig. 2C of a synthetic polypeptide built of 9 amino acids (Cotter 1997, Fig. 10.7) has high similarity with a spectrum presented in Fig. 2A, which shows the peptide nature of some OCs contained in our impact sample. This result is of interest because short peptides synthesized in impact processes might be precursors of enzymes possibly formed later. It is expected that with increasing size of the projectiles the produced polypeptides will become more complex. The distribution of peaks in a group of mass peaks in the mass spectrum presented in Fig. 2A is shown in Fig. 2B. It results from the ^{12}C and ^{13}C isotopes in the analyzed sample and can be explained by having about equal quantities of ^{12}C and ^{13}C isotopes, which were mixed even before synthesis of amino acids. The carbon isotope distribution resulted in the presence of two mass-to-charge peaks for each amino acid (positive ion mode).

Splitting of peaks, into a series of ^{12}C/^{13}C peaks, of the amino acids (see Fig. 2B), which are in the structure of a fragment of a short peptide shows that the peptide and amino acids with high reliability arose in the plasma torch, and that these compounds are not the result of contamination. The degree of involvement of the two carbon isotopes in the synthesis of protein amino acids (Fig. 3) is shown in the laser desorption mass spectra of the extracted OC of the impact sample. Organic material was extracted from the impact sample (2 mg) by dissolving the organics in 2 M hydrochloric acid (for 24 h, at 150 °C), which gave 40 pmol. The extract was put on an Au sample holder of the laser mass spectrometer, the solvent was dried off in a vacuum furnace (24 h), and only the organic residue remained on the sample holder for analysis.

In the laser desorption measurement a laser is used for removing material from the extract sample, which is ionized at the
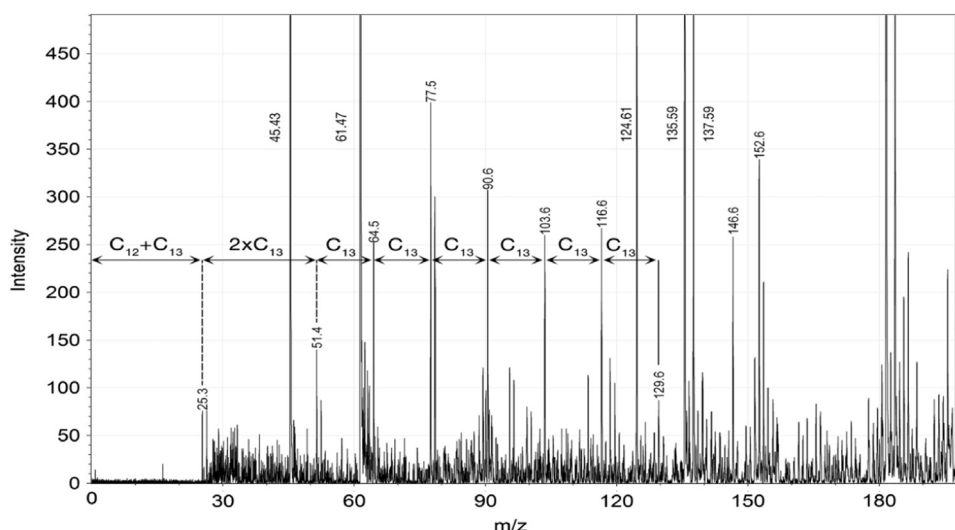

Fig. 1. Mass spectrum recorded with the MALDI TOF/TOF instrument in negative ion mode. It shows that linear-chain carbon compounds were synthesized from ^{13}C atoms. This is evidenced by the 13 amu period of the carbon structures, which is observed for the first time for impact-produced material.
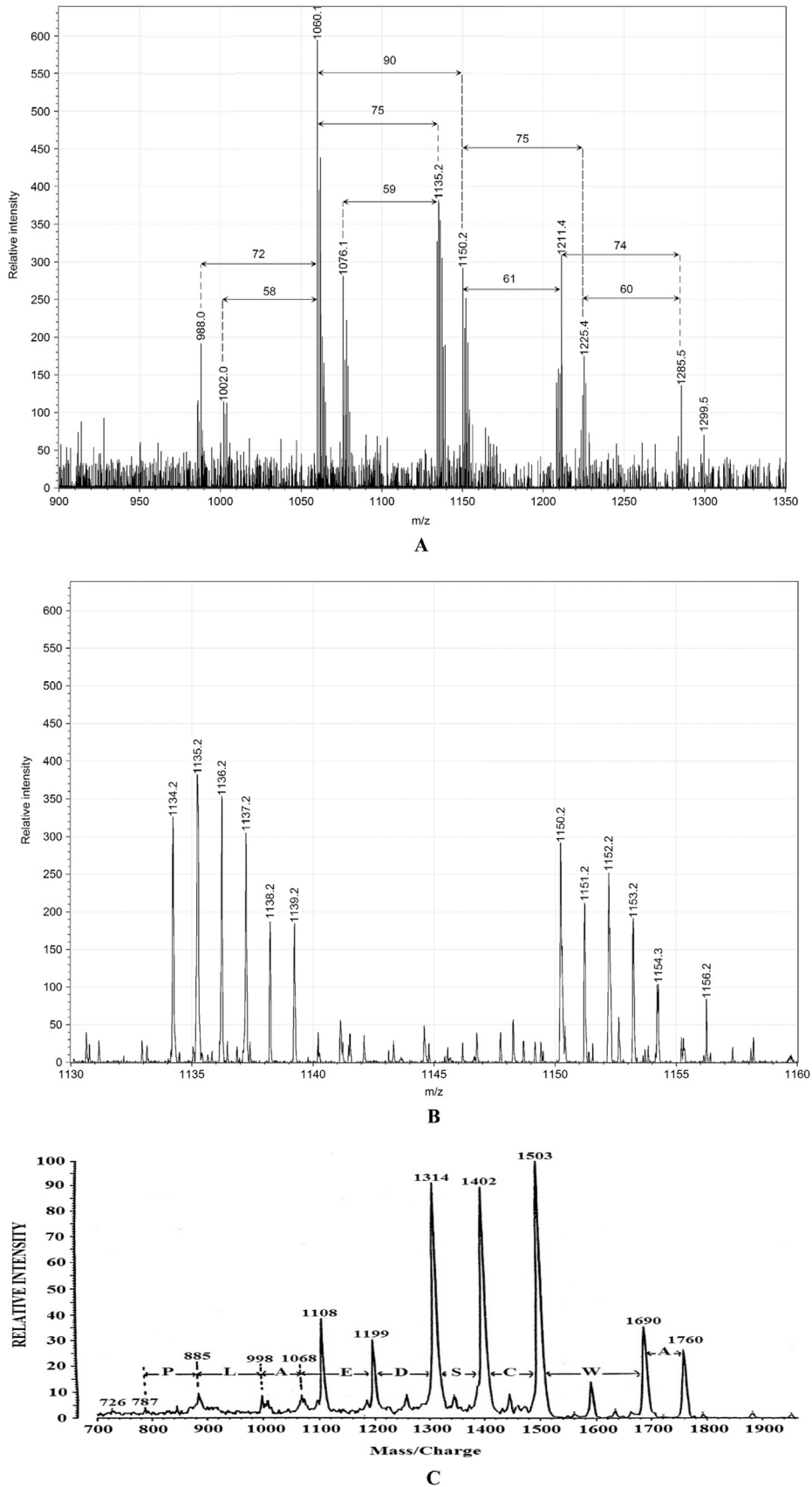
Fig. 2. (A) Mass spectrum recorded with the MALDI TOF/TOF instrument in positive ion mode. It shows a section of the mass spectrum of OCs with a molecular mass around 1300 amu. The arrangement of groups of peaks 1 amu apart is periodic with the periods corresponding to the masses of glycine, alanine, serine and their fragments. (B). Mass spectrum recorded with the MALDI TOF/TOF instrument in positive ion mode. It shows the fine structure of a group of mass peaks, which depends on the number of carbon atoms in the amino acids forming the protein. (C). For comparison, MALDI-TOF mass spectrum of an artificial polypeptide with a molecular weight of 1800 amu, which includes 17 protein amino acids (AWCSDEALPPGSPRCDG) (from Cotter, 1997, Fig. 10.7).
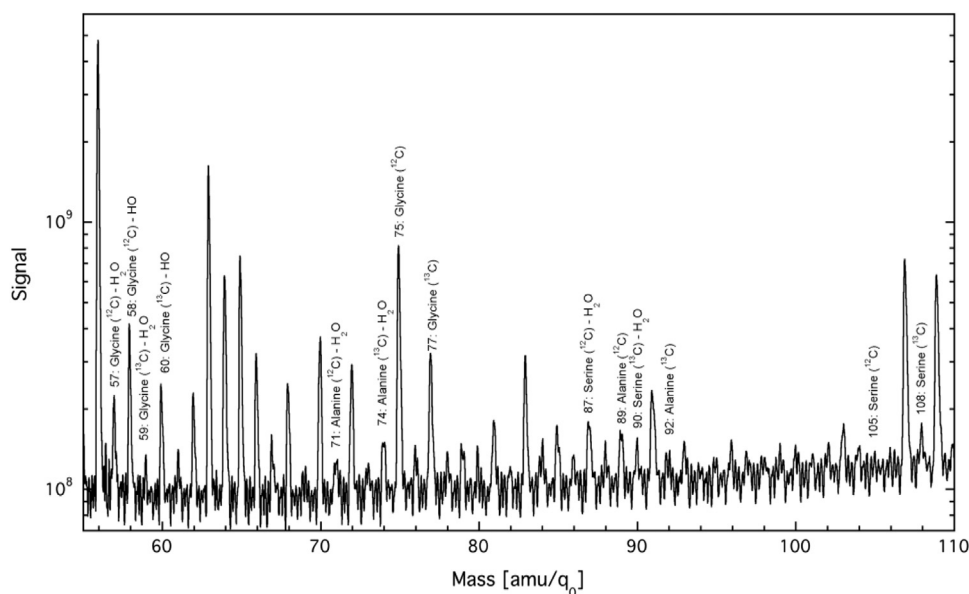
Fig. 3. The mass spectrometric measurements of the extract of organic compounds (see main text) from the produced impact samples were performed with a laser-based mass spectrometer operating in the desorption mode (Riedo et al., 2013).

same time (Wurz et al., 1992). We used a pulsed laser at 775 nm wavelength with 190 fs pulses at a repetition rate of 1 kHz and the desorbed ions are mass-analyzed by a TOF mass analyzer (Riedo et al., 2013). In desorption mode the laser pulse power is kept low enough to desorb molecules intact and to avoid formation of molecules in the laser torch.

The peaks corresponding to glycine, alanine, serine, and their fragments are marked accordingly (Fig. 3). Amino acid peaks were identified by the presence of the parent peak and the simultaneous presence of its largest fragment, i.e., having lost OH, in the mass spectra. This mass spectrum for Fig. 3 corresponds to the case when synthesis of amino acids happened before the mixing of carbon isotopes occurred. Thus, despite the initial carbon isotope ratio of 14 for the amount of graphite and the impactors, the final ratio for glycine was 3.1. This can be explained by the high efficiency of involvement of ^{13}C from the impactor in contrast to the low involvement efficiency of ^{12}C coming from the graphite plate located deep inside the target below the ammonium nitrate layer, thus also contributing at a later time to the material in the plasma torch. Mixing of species with different carbon isotopes occurred after the peptides formed in the plasma torch at cooler temperatures.

It is evident in Fig. 3 that the amplitudes of amino acid peaks decrease with increasing mass (i.e., with increasing chemical complexity). This fact is indicative of the absence of amino acid contaminants, which would have a different the pattern. Thus, it can be reasonably concluded that amino acids, which contain ^{12}C, like those containing ^{13}C, were synthesized in the impact torch. They can therefore be considered equally significant.

Experimental values of relative yield of amino acids synthesized in plasma torch versus their chemical complexity can be treated as a criterion for experiment purity estimation. According to our measurements ratio of the relative yield of glycine to alanine is 11.8 by mass-spectrometry (see Fig. 3) and 12.1 by our chromatography measurements, they are close to mentioned above ratio estimated as 10.

The impact sample was crushed using a mortar and pestle to increase its surface area. Next, the sample was placed in a clean 25 ml Pyrex glass tube. Five milliliters of distilled water was added to the tube and the tube was sealed, placed in an oven and heated for 8 h at 100 °C. Next, the tube was allowed to cool to room temperature and then the water and mineral slurry was passed through a Millipore (0.22 μm) glass fiber filter. The water extract was transferred to a clean, 25 ml Pyrex glass tube and evaporated to dryness under N_2. One milliliter of 6 M HCl was added to the dried residue. The tube was sealed under N_2 and the sample was hydrolyzed for 24 h at 100 °C. Next, the tube was allowed to cool to room temperature and then the acid hydrolyzate was transferred to a clean 4 ml glass vial and evaporated to dryness under N_2.

The glass fiber filters are cleaned before use by passing 50–100 ml of distilled water through them. The Pyrex tubes are thoroughly cleaned by washing in a soap solution (Sparkleen), rinsed several times with distilled water, and then heated in a furnace to approx. 550 °C for 2 h. All of the glassware that comes in contact with samples was treated this way prior to use, including all beakers, flasks, etc.

Esterification: A 0.3 ml aliquot of acidified (3 M) isopropanol was added to the dried acid hydrolyzate. The tube was sealed and heated at 110 °C for 1 h. Next, the tube was cooled to room temperature and the excess isopropanol was removed by careful evaporation under N_2.

Acylation: A 0.5 ml aliquot of dichloromethane and 0.2 ml of trifluoroacetic anhydride were added to the residue. The tube was sealed under N_2 and heated at 110 °C for 10 min. The tube was cooled to room temperature and then the sample was carefully evaporated to dryness. Approximately 1 ml of dichloromethane was added to the trifluoroacetyl isopropyl ester amino acid derivatives.

The extracted amino acids were analyzed using a Hewlett Packard 5890 gas chromatograph (GC) equipped with a 50 m × 0.25 mm (internal diameter) fused silica capillary column coated with an optically active stationary phase (Chirasil-Val) purchased from Alltech (Deerfield, IL, USA). The GC was interfaced to a Hewlett Packard 5972 mass selective detector (MSD) for GC/MS analysis. The original total ion chromatogram and selective ion monitoring (SIM) mode chromatogram show the presence of glycine and D- and L-alanine in the impact sample (Fig. 4). The GC/MS conditions have been previously reported (Engel and Macko, 1997). A control sample consisting of a procedural bank is run in which a 5 ml sample of distilled water is taken through the entire procedure that the sample would be exposed to. Only two protein
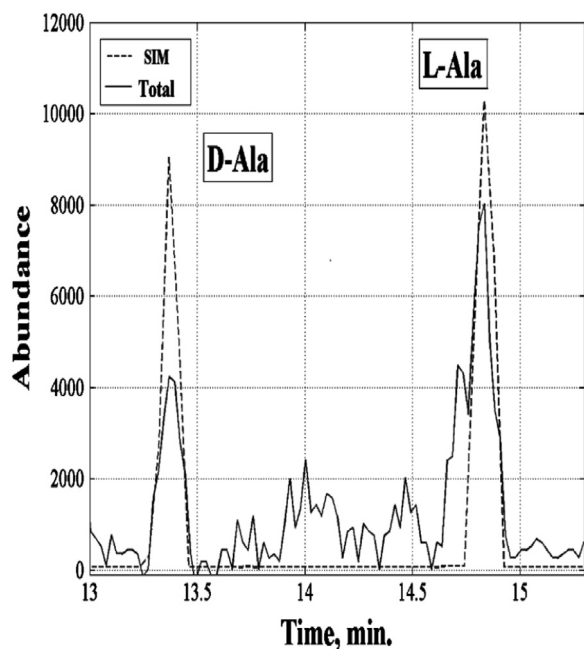
Fig. 4. Section of the total ion and SIM chromatograms of amino acids extracted from the impact sample (N-trifluoroacetyl, isopropyl esters), with the retention times for D-Ala and L-Ala at 13.3 s and 14.7 s, respectively, derived from SIM mode measurements. Comparison of chromatograms in SIM mode and total ion mode to verify the retention times for D-Ala and L-Ala. In SIM mode the mass 140 amu was used for D-Ala and L-Ala.

amino acids, glycine and alanine, were detected by this method. The absence of the other 18 protein amino acids in the GC/MS analysis clearly indicates that contamination did not occur, or was below detection. The glycine peak exceeds the peak of L-alanine by 4.75 times.

The peaks of L- and D-alanine (Fig. 4) are shown in the SIM and total ion modes. This measurement enabled us to calculate L/D values for alanine based on peak integrals and peak amplitudes in both the SIM and total ion modes. Using SIM data, the values for alanine are L/D = 1.15 based on the peak amplitudes and L/D = 1.68 from evaluating the integrals of peaks. For the total ion mode, the values for alanine are L/D = 2.5 for the peak amplitudes and L/D = 2.4 for integrals of peaks. Given the unavoidable background noise in the total ion mode, the L/D values obtained for the SIM mode should be considered more reliable. Thus, the violation of symmetry could be in the range from 1.15 to 1.68.

The results of our impact experiments can be summarized as follows: the plasma expansion of the impact-produced plasma torch results in:

1. The synthesis of the protein amino acids glycine and alanine, which were discovered using GC–MS, and confirmed by laser-MS, and the additional detection of serine by laser-MS.
2. The synthesis of organic compounds with mass around 1300 amu containing fragments of artificial (synthetic) polypetides composed of glycine, alanine and serine.
3. The excess of L-alanine over D-alanine determined in the SIM mode by amplitudes and integrals of peaks could be from 1.15 to 1.68.
4. The "sign" of asymmetry coincides with the bioorganic world.

The analysis of the impact experiments also show that the samples contain no amino acid contaminants.

4. Discussion

We find the same sign of chiral asymmetry and the magnitude of enantiomers excess being similar to what is observed in meteorites, in particular compared to the Murchison carbonaceous chondrites (Engel et al., 1990; Engel and Macko, 1997). More recently, a pronounced excess of the L-enantiomers in a recent fall of the Tagish Lake meteorite, a carbonaceous meteorite was also shown to be of extraterrestrial origin (Glavin et al., 2012). According to Fedkin and Grossman (2013), such impacts occurring during the geological history of chondrites could be responsible for the formation of chondrules.

Circularly polarized light (CPL), as is generated in a plasma torch, forms truly local chiral physical fields (Barron, 1986; Avalos et al., 1998). CPL can cause the observed chiral symmetry breaking of amino acids (Bonner, 1991; Meierhenrich et al., 2005). CPL and systems far away from thermodynamic equilibrium have been recognized as advantage factors to cause chiral symmetry breaking (Gol'danskii and Kuz'min, 1989; Avetisov and Goldanskii, 1996).

To demonstrate the reliability of our results, compelling evidence is required that the amino acids found are not contaminants, but were synthesized in the plasma torch. For laboratory impact experiments it is necessary to develop procedures of cleanliness, as discussed above, and its realization because substances used in the experiment cannot always be subjected to prior analysis of purity. The experiments were all performed very carefully to avoid contamination. Based on the methods currently available we assured that the products of the experiments were pristine. The obtained mass spectra contain mass peaks that do not correspond to amino acid contaminants. The glycine and alanine abundances are inversely proportional to the complexity of their chemical structure. These OCs are the first to form in all known natural processes of abiotic synthesis. The central evidence for plasma torch synthesis of amino acids is the extremely high percentage (40%) yield of ^{13}C-enriched alanine. This implies efficient production of CN bonds from the impacting projectiles and the ammonium nitrate target, and subsequent quench synthesis of amino acids and residues from these precursors in the plasma torch. The 60% of ^{12}C containing amino acids should also have been synthesized in the plasma torch given the absence of other mechanisms.

The physical properties of the investigated plasma torch are (i) an enormous energy density (of the order of 10^{10} J/m^3), (ii) rapid plasma expansion causing non-equilibrium chemical reactions, which are characteristic of impact processes, and (iii) chiral physical fields that allow the asymmetric synthesis of the evolving chemical products far from the thermodynamic equilibrium.

The possibility of a symmetry breaking in chemical processes was considered in a number of studies (Frank, 1953; Kondepudi and Nelson, 1985). An analysis of this problem in terms of the concept of dissipative structures was previously reported (Prigogine and Kondepudi, 1998). The most important consequence of these processes is their dualistic irreversibility: they break the order near equilibrium and create it far from equilibrium.

Plasma torches are an efficient approach to study catalytic properties of systems outside thermodynamic equilibrium. For modeling of plasma torches, researchers use the gas approximation to describe all components of the medium including ionized particles. This is a common practice despite the fact that powerful currents of charged particles generate strong spontaneous electromagnetic fields and plasma instabilities (Stamper, 1991). The high energy density characteristic of impact processes drives the asymmetric synthesis of the medium if the pressure exceeds 100 GPa. Note that pressures of only 50 GPa were reached in the earlier experiment where racemic mixtures of two amino acids were reported (Martins et al., 2013). Certainly, the high energy

density produced in the compression by the impact is initially concentrated in the radiation pressure (Zel'dovich and Raizer, 2002). At the initial stage of plasma expansion, and thus of plasma cooling, the compressed plasma is dominated by atoms and ions in highly excited states (Nektarov et al., 1999). This presence of chemical radicals ensures extremely high catalytic activity of the atoms and evolving molecules in the expanding plasma, which may bring about further strong asymmetric synthesis of enantiomers and the formation in the plasma torch of isolated areas having close to chiral pure properties.

5. Conclusions

Our experiments show that the plasma processes naturally arising in a plasma torch during hypervelocity impact of meteorites can provide synthesis of protein amino acids and other OCs, and can generate moderate break of their mirror symmetry with a sign coinciding with bioorganic world, which is a prerequisite for the homochirality of life. Moreover, we observe the formation of simple polypeptide molecular structures formed from protein amino acids that were synthesized in the impact plasma torch. The formation of such molecules in the plasma torch of a meteorite impact overcomes a number of obstacles connected with the conditions for emergence of a live matter.

As stated above this gives us the possibility to make the following conclusion, which we have shown experimentally

1. The formation of non-racemic matter in impact plasma from inanimate abiological matter with chiral asymmetry identical of the biochemical is demonstrated.
2. Our experiments suggest that the sign of chiral asymmetry of the produced matter is controlled by the local chiral fields of the torch.
3. The produced plasma medium has a very large energy density, promoting high velocity of plasma chemical reactions, with a high level of catalytic activity, and the possibility of the formation complex OC synthesis including polypeptides.
4. This unique matter, in the process of further evolution, hypothetically may be favorable for assembly of homochiralic amino acids chains with a sequence of monomers able to replicate in limited time and formation of the simplest genetic code.

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