An Experimental Investigation of Biomolecules under Impact Induced Shock

A thesis submitted in partial fulfilment of

the requirements for the degree of

Doctor of Philosophy

by

Surendra Vikram Singh

(Roll No. 16330003)

Under the guidance of

Dr. Bhalamurugan Sivaraman

Associate Professor

Atomic Molecular and Optical Physics Division

Physical Research Laboratory, Ahmedabad, India

Discipline of Physics

Indian Institute of Technology Gandhinagar, India

Dedicated to my family

Declaration

I declare here that this thesis report represents my own ideas in my own words and I have included others ideas with appropriate citations from original sources. I also declare that I have followed all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/fact/source/data in my submission. I understand that any violation of the above can cause disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

Surendra Vikram Singh

(Roll No.: 16330003)

Department of Physics

Indian Institute of Technology, Gandhinagar

Gandhinagar, Gujarat-382355

CERTIFICATE

It is certified that the work contained in the thesis titled **“An Experimental Investigation of Biomolecules under Impact Induced Shock”** by **Mr. Surendra Vikram singh** (Roll no: 16330003), has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

Dr. Bhalamurugan Sivaraman

(Thesis Supervisor)

Associate Professor,

Atomic Molecular and Optical Physics Division,

Physical Research Laboratory,

Ahmedabad, India

Acknowledgments

I would like to convey my heartfelt gratitude to Dr. Bhalamurugan Sivaraman, my Ph.D. supervisor, for his unwavering support of my Ph.D. study and associated research, as well as his patience, drive and enthusiasm. He always insisted on the importance of pursuing your curiosity wherever it might lead, even beyond the traditional boundaries. I am grateful to my co-supervisors, Dr. V Jayaram and Dr. T Vijay, for their continuous support and guidance that helped me to carry out various experiments and analyses. I am thankful to my DSC members Dr. Shashikiran Ganesh, Dr. Rajesh Kushawaha and Dr. Naveen Chauhan for their support, suggestions and encouragement during my Ph.D. period.

Further, I take this opportunity to thank the wonderful collaborators Dr. S Vijayan, Dr. B N Rajasekhar, Dr. R Thombre, Dr. M Muruganantham, Mr. Ambresh Mallaya, Ms. Haritha, Prof G Jagadeesh, Prof K P G Reddy, whose contribution to this research work has added great significance. I also thank Prof Mark Burchell and Prof Nigel Mason for their helpful discussions during my visit to the University of Kent and online meetings. I am thankful to have fantastic lab members Dr. Dipen Sahu, Dr. Rahul Kushwaha, Mr. Jaya K Meka, Mr. Utkarsh Deva, Mr. Arijit Roy, Mr. Shiva, with whom I had a pleasant time at Astrochemistry Lab PRL. I am also thankful to Mr. Sarvesh, Mr. Aravind and Mr. Chirag, who helped me carrying out initial shock experiments at IISc Bangalore. I am grateful to Mr. Mike Cole for his help carrying out impact experiments at the University of Kent.

Further, I express my sincere thanks to Prof R P Singh (Chairman AMOPH Division), Prof Anil Bhardwaj (Director PRL), Prof D Pallam Raju (Dean PRL), Academic Committee PRL, Dr. Bhushit Vaishnav (Head of Academic Services) for their continuous support at various occasion during my Ph.D. Also, I thank the PRL members from accounts, purchase, library, administration, computer center, canteen, CMD, dispensary, transport, and housekeeping sections for providing me a more accessible environment to work in.

I would like to extend my special thanks to Sir John and Lady Mason academic trust for funding this research. I thank PRL for financially assisting me in attending conferences/workshops, which significantly helped my research work. I would like to express my gratitude to all of the organizations that helped fund my research.

I especially thank my parents, my brother and sisters for the unconditional love, care, and sacrifices they have made for me. I am grateful to my brothers-in-law, who have been a continuous inspiration in this journey and help me always. I know I always have them to count on.

I am very much thankful to have amazing friends with whom I had a wonderful time in the last five years in Thaltej hostel. Many thanks to Sandeep, Abdur, Priyank, Harish, Nisha, Ayan, Deepika, Sajan, Somdutta, Avik, Sushree, Prabir for all the wonderful memories. Thank you Nisha for cooking for us delicious food that always felt like home, Deepika for all your PJs, Abdur for your special tea, Sandeep and Priyank I would never have played a game without you, Sana for your special coffee, Monika for all the laughs, Ankit for all the memes you shared that made my day, Rahul for all the help, Sushree for all the chats, Sarvesh for helping me always. I am thankful to all my amazing seniors and juniors, I am unable to list you all here, you all had made an impact on me, and I am grateful to you all.

Surendra Vikram Singh

Abstract

Amino acids, nucleobases, and sugar-related compounds are among the organic compounds found in primitive meteorites, which may be the potential building blocks of life. These organic compounds would have developed and evolved in a variety of environments. Many of these may have arrived on the early Earth in meteorites, comets, and interplanetary dust particles. The origins and evolutions of organic compounds are not well established despite numerous meteorite analyses and experimental studies. Sample return missions like Hayabusa2 and OSIRIS-REx are expected to provide more information about the origin, evolution, distribution, and delivery of prebiotic molecules. Under simulated prebiotic conditions, laboratory studies have shown the synthesis of almost all life's building blocks and polymers. On the primitive Earth, however, it is mysterious how these compounds spontaneously assembled to produce proto-biological functions (e.g., metabolism, replication). One of the most important and exciting challenges of our time is discovering pathways that led to the transition. While tremendous progress has been made in prebiotic chemistry since the famous Miller's experiments in the 1950s that revolutionized the field of prebiotic chemistry, there are still major challenges that remain in our understanding of the origin of life. Many of these studies have focused on the role of endogenous sources such as hydrothermal vents, synthesis in the primitive atmosphere, the importance of minerals surrounding, etc. However, given the intensity of impact bombardment on the early Earth, these environments are equally crucial in the prebiotic scenario for the studies on the origin of life. Impact induced shock provides a sharp increase in pressure and temperature due to shock compression and subsequent cooling due to expansion within a very short time scale. Such thermodynamic conditions can offer various pathways for molecules to react, thus can lead to the synthesis of a variety of molecules. Consequently, the studies herein investigate the fate of amino acids and nucleobases under high temperature heating effect of impact induced shock using laboratory techniques.

To simulate impact induced shock environment in the laboratory, an experimental set up of shock tube (HISTA) is designed and developed in Astrochemistry Lab PRL India. The shock tube setup is capable of providing a high temperature of approximately 8000 K maintained over a 2 ms time scale. Variety of amino acids were shock processed at various temperature ranges leading to the formation of a variety of complex structures,

including globules, threads, filaments, twisted and folded assemblies, tubular structures of various sizes ranging from micrometer to millimeter scale, as revealed from microscopic observation. Membrane-like structures were seen at the nanometer scale in TEM observations. Spectroscopic observations have shown the formation of the peptides in shock processed residue. Impact experiments were also performed using a light gas gun facility with high-speed bullet firing on the amino acid-water ice target, and ejecta coming out of target were collected and analyzed. Complex structures were observed in the ejecta similar to dendritic pattern and flower morphology. TEM observations of these ejecta have also shown membrane-like structures as we observed in shock processed residues. Further, mass spectrometry has shown that long polypeptide chains were synthesized in the ejecta. The formation of such peptides containing complex structures has important implications for the origins of life. Nucleobases, the basic component of informational polymers RNA and DNA, were also shock processed and formed long threads spanning up to mm scale.

Overall, in the present thesis, a novel method is designed for simulating the high temperature and pressure condition as achieved in natural impact events using high intensity shock tubes. The effect of high intensity shocks on amino acids and nucleobases is studied. This is the first report on the formation of complex macroscale structures due to impact induced shock conditions which provide pathways for the origin of life. Given the widespread record of impact events across the solar system bodies, hypervelocity impacts experiments are performed on icy mixtures of amino acids to simulate the impact on icy bodies of the solar system using a light gas gun, showing the formation of the long polypeptide chain in the impact ejecta. These results demonstrate that extraterrestrial impact provided necessary life ingredients and assisted in the formation of complex architecture that can form the basis for cellular life. Future research endeavors will focus on the various combination of biomolecules, including amino acids, nucleobases, sugars and fatty acids under impact shock conditions to resolve the complex pathways that lead to the origin of life.

Contents

List of Figures

List of Tables

Abbreviations

ESI	Electrospray Ionisation
HISTA	High Intensity Shock Tube for Astrochemistry
HPLC	High-Performance Liquid Chromatography
IR	Infrared
ISM	Interstellar medium
LC-MS	Liquid Chromatography Mass Spectrometry
LGG	Light Gas Gun
MS	Mass Spectrometer
MST1	Material Shock Tube
SEM	Scanning Electron Microscopy
UPLC	Ultra-Performance Liquid Chromatography
TEM	Transmission Electron Microscopy
TOF	Time of Flight

Chapter 1 Introduction

Chapter overview

This chapter provides a basic introduction and overview of the thesis. A brief introduction is provided that connects the link between the prebiotic chemistry, biomolecules and the origin of life. The role of various endogenous sources and exogenous delivery are discussed that are available on the prebiotic Earth and might have played an essential role in the origin of life. Much emphasis is given on the role of exogenous delivery as a variety of biomolecules are known to be delivered as a result of impact bombardment on early Earth intact. Thereupon an introduction is provided on the journey of molecules from interstellar space to impact bombardments on planetary bodies. Towards the end of the chapter, a summary of previous studies is provided that have been carried out to explore the role of impact bombardment in the origin of life. The chapter concludes with the objectives of the present work along with the organization of the thesis.

1.1 Life as we know it

The origin of life is one of the biggest unsolved mysteries. When, where and how did life originate on the Earth? These questions are still unanswered. The search for the origin of life is the most challenging and enthralling subject that requires an integrated understanding of the wide range of scientific disciplines, including biology, chemistry, physics, geology, astronomy, etc. There is no consensus on a common definition of life yet. As proposed by NASA, life is defined as "a self-sustaining chemical system capable of Darwinian evolution" (Benner, 2010). The most basic assumption about the origin of life on the Earth is that life emerged spontaneously and gradually from inanimate to animate matter with the increase in molecular complexity. It was not just a single step; instead, it was a sequence of physicochemical processes that guided the transition from prebiotic chemistry to biology leading to the emergence of the first cell (Luisi, 2016).

Life is generally specified by the three different functions (Kitadai and Maruyama, 2018)

(1) Compartmentalization: the ability to limit their extent to a definite space and separate from the rest of the environment.
(2) Replication: the ability to process and transmit heritable information to progeny.
(3) Metabolism: the ability to capture energy and material resources and staying away from thermodynamic equilibrium.

These three basic requirements are functionalized by biopolymers such as proteins, nucleic acids and phospholipids. Proteins are comprised of a long chain of amino acids joined together by peptide bonds. Amino acids are the building blocks of proteins consisting of an amino group and carboxylic group together with a side chain specific to each amino acid. The known life on Earth comprised proteins that essentially consist of the 20 standard amino acids. The nucleic acids, DNAs and RNAs are comprised of nucleotides (composed of sugar and nucleobases) bound by phosphodiester linkages. The nucleobases that are found in DNA and RNA are single ring and double ring molecules, namely adenine (A), cytosine (C), guanine (G), thymine (T) and uracil (U). A, C, G, and T appear in DNA, whereas T is replaced by U in RNA. Lipids are made of fatty acids esterified to a glycerol phosphate molecule. These vital biopolymers must have been available on the prebiotic Earth that accumulated, interacted and eventually evolved into a self-sustaining system that led to the emergence of life. The prebiotic chemistry and origin of life research encompass the exploration that led to these prebiotic steps. Various experimental and theoretical studies have been done to find these pathways. However, we still have much more to explore. One of the main challenges in this research is to find reaction pathways that might have led to the synthesis of biomolecules from their possible precursors on the prebiotic Earth. The Oparin's (Oparin, 1928) and Haldane's (Tirard, 2017) 'primordial soup theory' led to the discovery of the abiotic origin of life from the aggregation of simple molecules (Luisi, 2016, Lingam and Loeb, 2021). The experimental support of this theory provided by the famous Miller Urey experiments (Miller, 1953) led to the pathways for the synthesis of biomolecules necessary for the origin of life. Since then, a considerable number of studies have been done to find prebiotic steps that led to the synthesis of building blocks of life. These building blocks may have been provided from two main sources: endogenous synthesis and exogenous delivery i.e., synthesis of organics in various environments such as Earth's atmosphere, in primeval oceans and interstellar environments, under the influence of various energetic sources.

1.2 Energy sources

Table 1 summarizes the variety of energy sources and their relative amount that are available for the organic synthesis on present Earth, which includes solar radiation, electric discharge, thermal energy from volcanos and shocks, cosmic rays and radioactivity (**Figure 1.1**). It's reasonable to assume that similar energy sources existed 4 billion years ago when life first began (Deamer and Weber, 2010). The importance of a given energy source is determined by the product of energy available and its efficiency for the synthesis of organics. It should be emphasized that no single source can offer enough energy to account for all the organic compounds. A diverse setting is a must for the origin of life. The largest source of energy is clearly the UV solar radiation which was capable of performing photochemical reactions and thus considered as the most important source of energy on early Earth. Another important source is an electric discharge which was the most widely used source in the laboratory synthesis, starting from well-known Miller experiments on the synthesis of amino acids in the Earth’s primitive atmosphere. Electric discharges are an important source for the synthesis of hydrogen cyanide, where UV radiation seems to have poor results. HCN being an intermediate for the prebiotic synthesis of amino acids, as well as purines adenine and guanine, is an important candidate for the origin of life. The electric discharges have another advantage in that they would have occurred near the Earth’s surface. In contrast, UV would have been effective in the upper atmosphere where the photochemical reactions were dominant. The energies from radioactivity and volcanoes are minimal and not effective in organic synthesis, while energy from cosmic rays is almost negligible (Miller, 1974, Deamer and Weber, 2010).

Shock waves are also one of the important sources for the synthesis of prebiotic organics. Various sources of shock waves were available on the prebiotic Earth coming from the impact of extraterrestrial objects such as comets and meteorites. The role of shock processes in the prebiotic development of life will be discussed in detail in this thesis.

Table 1.1 Present sources of energy averaged over Earth (Deamer and Weber, 2010)

Sources	Energy (kilojoules m^{-2} yr^{-1})
Solar radiation (UV < 250 nm)	24000
Electric discharges	2.9
Radioactivity (to 1.0 km depth)	117
Volcanoes	5.4
Shock waves	200
Chemical energy	Not estimated

1.3 Endogenous synthesis

Various environments have been suggested as plausible sites for the origin of life, including the atmosphere, the water bodies, the interfaces and the hydrothermal systems. This section will briefly discuss the role of each geological setting in the origin of life one by one.

1.3.1 Atmospheric synthesis

Miller and Urey's experiment, first reported in 1953 (Miller, 1953), the synthesis of amino acids in Earth’s atmosphere triggered by lightning, revolutionized the field of prebiotic chemistry. An electric discharge was passed through a mixture of CH_4, H_2,

NH_3 gases mimicking the Earth's primitive atmosphere, resulting in the formation of several amino acids (Miller, 1953, Miller, 1955). The atmospheric composition determined the type of chemical reaction that would have happened. Along with the atmospheric synthesis, it also affected the type of radiation that reached the Earth's surface. The interaction of Earth's atmosphere with falling extraterrestrial objects would also have affected the prebiotic synthesis (McKay and Borucki, 1997, Bar-Nun et al., 1970, Briani et al., 2013).

1.3.2 Hydrothermal systems

Hydrothermal systems are considered ideal sites for the origin of life. These sites offer exceptional benefits for early life, such as protection from harsh UV radiation and impact bombardments, and provide a source of thermal and chemical energy and catalytic minerals for the origin of life (Kitadai and Maruyama, 2018). The gradient in temperature, chemical concentration, salinity and pH at these sites would be certainly relevant for chemical evolution and origin of life. An integrative approach of chemistry and geology is required to understand the role of various geological settings in prebiotic chemistry. Various experiments have been performed simulating the physiochemical conditions of hydrothermal vents relevant to prebiotic chemistry (Colín-García et al., 2018).

1.3.3 Earth surface environment

Various types of reactions are involved in the synthesis of organic compounds and their polymers from simple molecules such as condensation reaction, hydrolysis and redox reactions. Many of these reactions require a high concentration of reactants. In this regard, Earth's surface environments offered suitable sites for such reactions. Tidal pools, volcanic crates, lakes, sedimentary pores, and various other geological settings are the ideal sites to promote condensation type of reaction and increase reactants concentration (Dalai et al., 2016).

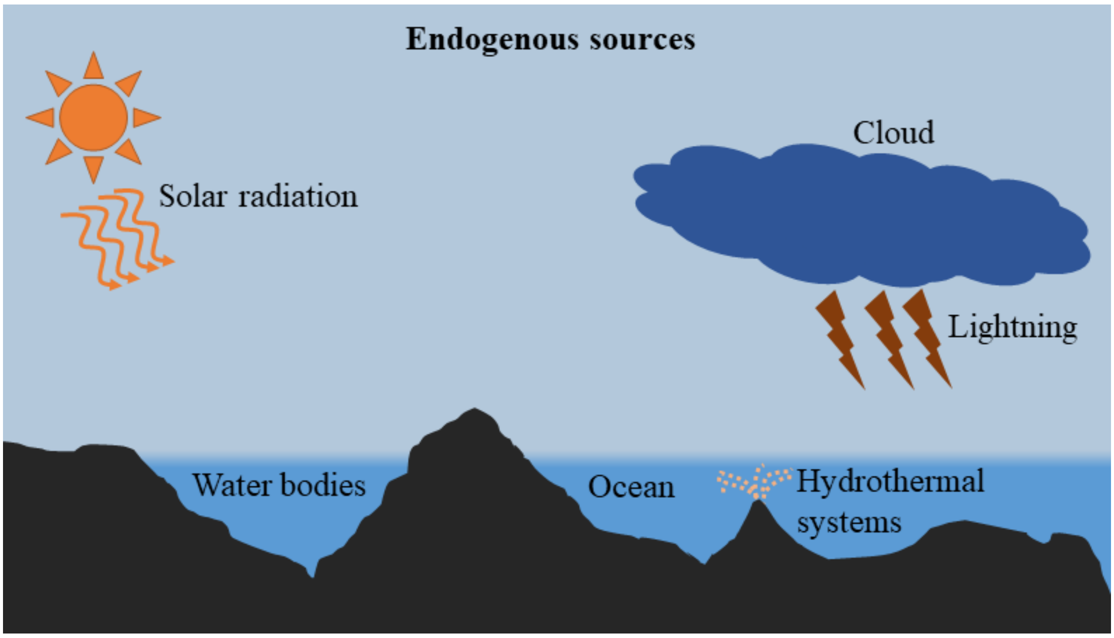

Figure 1.1 A schematic diagram of early Earth environment

1.4 Interstellar medium

The interstellar medium (ISM) is the region between the stars and is considered almost empty. The density in ISM is too low for any chemistry to occur. For a long time, the interstellar environment was suspected too harsh for the sustainability of molecular species. However, with the advancement in the ground-based and space-based observation capabilities, the search of interstellar molecules in the past few decades have shown the richness of the molecular content of the universe. A variety of molecules have been detected in different regions of interstellar environments. These interstellar regions are categorized into various groups depending on their size, density, temperature and chemical composition, as listed in **Table 1.2** (Kaiser, 2002). The observations at different ranges of wavelength ranging from radio to millimetre and submillimetre, and from infrared to visible domain have led to the discovery of over 200 molecules in various interstellar environments ranging from neighbouring objects in our solar system to distance sources in the universe (McGUIRE, 2021). Variety of organic molecules, including simple diatomic molecules to complex organic species such as hydrocarbons, alcohols, aldehydes, amines and many others are detected in various interstellar environments such as in dense clouds, in the diffuse interstellar medium, in planetary nebulae, and in hot molecular cores (Herbst and Van Dishoeck, 2009). The recent detection of larger polycyclic aromatic hydrocarbons such as C_{60} and C_{70} (Cami et al., 2010) provides evidence that large and complex molecules exist in extreme environments of the interstellar medium. Apart from this, laboratory analogue experiments and investigations on actual interstellar samples have significantly boosted our understanding of the molecular universe. Thus, the different regions of ISM are giant factories of a variety of molecular species. The question arises of how these molecules contributed to the origin of life on the Earth and what role do they play in prebiotic chemistry. To answer these questions, we must understand their journey from the interstellar environment to the prebiotic Earth. Many puzzles in this filed are still unsolved and mandatory to be resolved to understand the origin of life on Earth and search for its signature elsewhere.

Table 1.2 Physical parameters of different regions of the interstellar medium.

Region	**Density (cm^{-3})**	**Temperature (K)**
Diffuse interstellar medium	1-100	100
Translucent molecular cloud	10^2-10^3	50-100
Dense molecular cloud	10^2-10^4	10-15
Hot molecular cores	10^6-10^9	100-300
Circumstellar envelopes	variable	10-4500
Planetary nebulae	variable	200-300

1.4.1 The interstellar life cycle

These interstellar molecules synthesized as derivatives of various stages of the stellar evolution cycled through various phases, as shown in **Figure 1.2**, which start in the stars. The essential elements carbon, nitrogen, oxygen, sulphur and phosphorus are synthesized in the interior of the stars through the stellar nucleosynthesis process. These materials are thrown out in the surroundings of stars at the end of the star's lifetime during red giant, nova and supernova phases with a dispersion mechanism depending on the mass of the star (Ziurys, 2018). The nucleosynthesis process ceases at the end-stage as almost all its initial mass is blown off. These ejected materials disperse into the surrounding diffuse interstellar medium, where they mingle into diffuse clouds. Diffuse clouds have a density of 10 - 100 cm^{-3} and a temperature of 100 K. Initially, these ejecta is quite hot and all the material is in atomic form. In due course of this cycle, this material again accretes into denser clouds. Dense molecular clouds, categorized by their gas densities (10^4-10^6 cm^{-3}) and temperature, ranges from 10 – 100 K. As the gas cools, synthesis of molecules and grain production starts which are processed by various energetic processing such as ultraviolet irradiation, cosmic ray bombardment, interaction with dust surface and interaction with shock heating. Dense molecular clouds are home to rich chemistry and contain different molecular species. These clouds are dense enough to attenuate harsh interstellar radiation, allowing the synthesis of complex molecules. At the low temperature in these clouds, gas molecules condense into cold dust grains, which is the source of rich surface chemistry leading to gas-grain chemical reactions. Laboratory simulation studies on these icy mantles have shown evidence of rich chemistry when exposed to irradiation and thermal processing (Schutte, 1999). Apart from simple molecules, biomolecules relevant to the origin of life, such as amino acids and nucleobases, are known to be synthesized by such processes. Eventually, the evolution of their material in dense molecular clouds as the gravitational collapse dominates leads to the formation of new stars, protoplanetary disks and planetary systems. A wide range of chemistry occurs in these disks and varieties of species are discovered in these environments. The rich chemistry in the protoplanetary disk affects the composition of planetary systems that evolved from this. However, these studies are still in their infancy and require detailed investigations.

The synthesis of complex organic molecules in the interstellar medium has important consequences for the origin of life on Earth. It is widely accepted that the one possible inventory of organics on the Earth and other planetary bodies in the solar system is provided by extraterrestrial bombardments by comets, meteorites and interplanetary dust particles. Thus the organic materials from the interstellar medium are survived and are processed in the transition from one phase to another in this cycle before its incorporation into the planetary system during impacts.

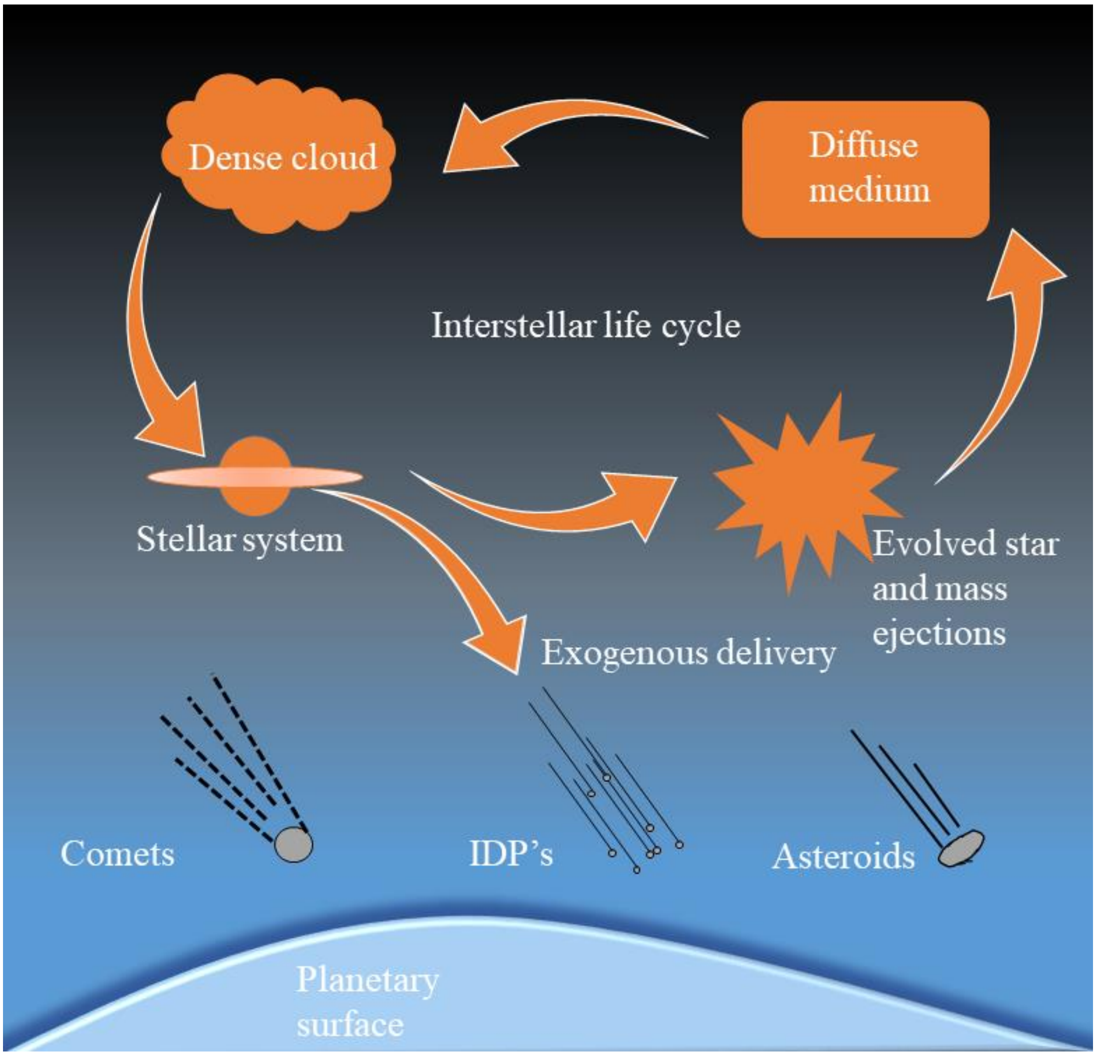

Figure 1.2 The interstellar life cycle, showing stellar birth and death. The material is evolving from one phase to another: from the interior of stars to diffuse medium, onto dense clouds and incorporated into planetary system through exogenous delivery.

1.5 Impacts in the solar system

Impacts are prevalent in the solar system shaping the formation of asteroids, planets and satellites. Impacts are instantaneous events leaving various characteristics features such as the formation of craters, ejecta and rays (Melosh, 1989a). Impact collisions between small bodies of the solar system lead to the growth of planetesimals and ultimately planets (Gerasimov et al., 1998). Impact craters are almost circular excavations on planetary surfaces marked by an impactor. **Figure 1.3** shows the variety of impact craters that are widely observed on the surface of planetary bodies showing evidence of impact activity in the past. Images obtained from various spacecraft illustrate that planetary bodies are carved by a large number of impact craters with sizes as large as a considerable fraction of their diameter. As an impactor strikes the surface of the planetary body, it generates a shock wave that expands out in all directions leading to the formation of craters and spread of ejecta, melting and vaporization of rocks. Thus, as a result of the impact, a tremendous amount of energy is released, leading to some global and local endogenic processes. The size and shape of the crater, as well as the amount of ejected materials, depend on several parameters such as velocity and mass of the impactor, angle of impact as well as the geology of impacting surface (Melosh, 1989a, Melosh, 2013). Impact craters are the most common geological structures that are observed on all the terrestrial planets and their satellites, as well as the surface of asteroids and icy and rocky satellites of Jupiter and Saturn. The craters formed by the impactors preserve the record about the age as well as the composition of the planet's surface at the time of formation of craters. While impacts are widespread, their records are not always safeguarded. On the Earth, which a result of impact activity, has a limited impact cratering record. Other activities such as volcanic resurfacing, tectonic movements, and erosions continuously wipe out the record of impacts signature. Only 200 impact structures are recognized on the Earth (Schmieder and Kring, 2020).

Similarly, impact records on Venus differ significantly, due to dense atmosphere and high temperature most of the impactor break off while some survived and produces craters. However, studies suggest that Venus had a thin Earth-like atmosphere, which might have a different effect on the crater population (Kreslavsky et al., 2015, Way et al., 2016). In comparison, Mercury and the Earth’s Moon both have surfaces heavily cratered, unlike Earth and Venus. Both planetary bodies lack liquid waters and atmosphere, so the erosion processes were not so dominant, and impact records are preserved. Impact cratering records had shown an era of Late Heavy bombardment 3.8 billion years ago when the magnitude of impact fluxes was much higher than the present (Ryder, 2002, Bottke and Norman, 2017). A high cratering record implies that the Earth must have been heavily bombarded by large impacts (Koeberl, 2006). This period of high impact flux seems to overlap with the oldest record of life on the Earth (Mojzsis et al., 1996). Thus, impact events have significant consequences for the origin of life. Impacts are believed to bring necessary life ingredients to Earth and create the catastrophes that caused biological extinction. A detailed investigation in this field is required to understand the relation of impacts and the origin of life.

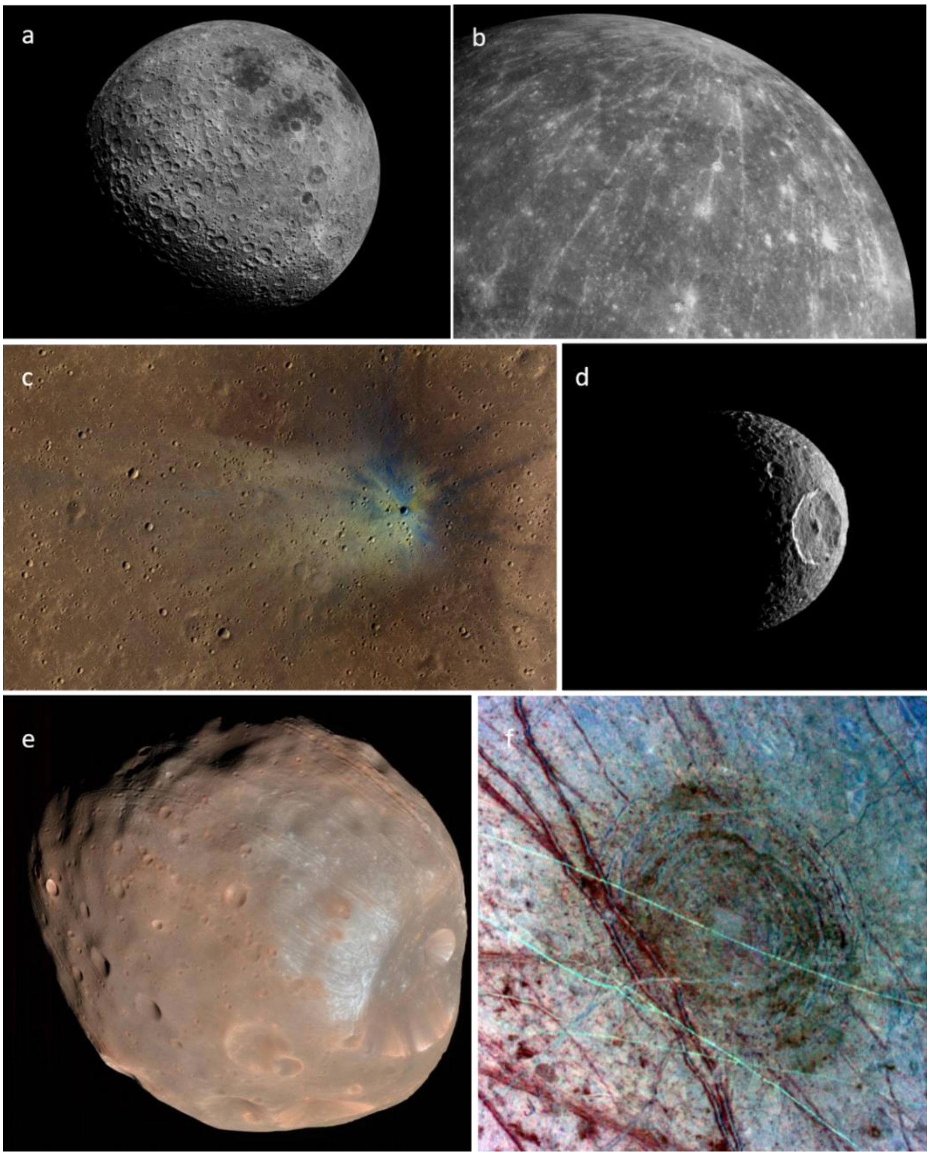

Figure 1.3 Variety of impact craters observed on the surface of solar system bodies, (a) Heavily cratered surface of Moon taken from Apollo 16 metric camera image, (b) impact craters on Mercury observed from MESSENGER spacecraft, (c) cratered surface of Mars observed from Mars Reconnaissance Orbiter, a distinctive colour region marks a new crater, (d) Herschel crater on Saturn's moon Mimas observed from the Cassini spacecraft, (e) cratered surface of Mars' moon Phobos as observed from Mars Reconnaissance Orbiter and (f) a 140 km wide impact crater on Jupiter's icy moon Europa recorded by the Galileo spacecraft.

1.5.1 Impact delivery of organic compounds to the early Earth

Availability of organics is a prerequisite for the origin of life. As previously discussed, endogenous production of organics was considered as one possibility that contributed to the Earth's organic budget. However, with the detection of organics in extraterrestrial environments, theories on exogenous impact delivery have been widely recognized. Comets, asteroids, meteorites and interplanetary dust particles are the sources of extraterrestrial sources that delivered important organics and volatiles to the early Earth (Chyba et al., 1990, Chyba and Sagan, 1992). These impact events were more frequent on the early Earth than today. Varieties of organic molecules are known to be abundant on these bodies. Given the ubiquity of impacts, this must have been the source of complex organic molecules on other solar system bodies. Several experiments were carried out to investigate the survivability of organics during impact. Results have shown that a significant amount of organics can survive these impacts (Blank and Miller, 1998, Blank et al., 2001, Burchell et al., 2014). A variety of objects ranging in size from micrometres to kilometres are responsible for impact delivery. The submicron-sized particles are the grains that are accreted directly from interstellar clouds. The small interplanetary dust particles of size approximately 10 microns are decelerated in the stratosphere and stopped there termed as "stratospheric IDPs" and slightly larger particles that reach the surface are micrometeorites. The meteorites are ranged from centimetres to decametres.

Comets and asteroids range from a few metre to kilometres. While small particles could softly have delivered to Earth intact, large objects size 1-100 meters can airburst in the atmosphere, for example, Tunguska event 1908, and have caused some catastrophic effects (Turco et al., 1982). The extreme condition of high temperature created in such impacts seems too improbable for the impact delivery of organics. However, results have shown that organics can be delivered intact in such events due to unheated interiors, atmospheric drag and uneven distribution of shock (Chyba et al., 1990). It is also suggested shock generated from impacts may have synthesized organics on early Earth (Gilvarry and Hochstim, 1963). Chyba and Sagan (Chyba et al., 1997) estimated possible synthesis of organics in the early Earth atmosphere due to impact shock and other endogenous sources as listed in Table 2. The detection of nonbiological amino acids α-amino-isobutyric acid and racemic isovaline in the Cretaceous/Tertiary (K/T) boundary sediments suggests that large impact deposited organics to the Earth (Zhao and Bada, 1989) or synthesized post-impact shock (Oberbeck and Aggarwal, 1991).

1.5.1.1 Comets

Comets are important candidates for the origin of life. Cometary nuclei contain the most pristine material that preserves the information from a range of processes that happened before its formation, thus connecting the link to proto nebula and interstellar clouds. Studies have shown a comparative molecular abundance of cometary ices with interstellar ices leading to the conclusion that provides a possible link between the two (Bockelée-Morvan et al., 2000, Ehrenfreund and Charnley, 2000, Despois and Cottin, 2005). The two key ingredients of life, water and carbon, are abundant in comets. Oró first proposed the idea of the interaction of comets with the early Earth that might have provided necessary biochemical compounds (Oró, 1961). Spectroscopic observations and in situ measurements have led to the discovery of a variety of extraterrestrial species in various comets (Mumma and Charnley, 2011). Amino acid glycine has been detected in the sample of comet Wild 2 from the Stardust mission marking the first detection of amino acid in a comet (Elsila et al., 2009). Amino acid glycine has also been detected in the coma of 67P/C-G along with methylamine, ethylamine and phosphorous (Altwegg et al., 2016). No other amino acids except glycine were observed in a comet; however, many carbon-rich species such as amines, nitriles, alcohols, etc. have been observed through remote observation and in situ measurements (Despois and Cottin, 2005, Crovisier et al., 2009, Wright et al., 2015, Goesmann et al., 2015, Altwegg et al., 2016). These results justify the significance of cometary impact delivery and the origin of life.

1.5.1.2 Asteroids

Organics are known to be abundant on asteroids as well. Recent results from various space missions have significantly improved our understanding of asteroids and their composition. Observation from the OSIRIS-Rex spacecraft has shown carbon materials on the asteroid Bennu (Simon et al., 2020). A recent result has revealed the organic composition of dust particles from near-Earth asteroids Itokawa collected by the Hayabusa mission (Chan et al., 2021). Organics have been detected on the surface of asteroid 24 Themis (Campins et al., 2010) and asteroid Cybele (Licandro, 2011). A higher abundance of organics is being expected on asteroid Ryugu (Potiszil et al., 2020) from which samples were returned to the Earth in December 2020, and analyses are in progress.

1.5.1.3 Meteorites

Meteorites are the remains of asteroids that have reached the Earth. These meteorites are categorized into many categories based on their elemental, isotopic and mineralogical composition (Weisberg et al., 2006). Most of them are carbonaceous chondrites, which are primitive and rich in soluble organics. Many organics relevant to the origin of life, such as amino acids, nucleobases and sugars, are found in meteorite samples. More than 80 amino acids have been detected in meteorites, and most of them are not linked to terrestrial biology, giving compelling evidence that they have an extraterrestrial origin. Also, the enantiomeric analysis of these meteorites has significance for the origin of life. Enantiomeric excess was found in some meteorites may have led to the initial asymmetry as observed in present biology (Cronin and Pizzarello, 1999, Burton and Berger, 2018). Further, isotopic ratios can help to assign the extraterrestrial origin of meteoritic amino acids (Chan et al., 2016).

1.5.1.4 IDP's and micrometeorites

Interplanetary dust particles (IDP) and micrometeorites are micron-size particles fragmented from comets and asteroids. IDP's are collected from stratospheres by aircraft and returned to the lab for analysis, while micrometeorites are collected from the ice field of the Antarctic. They are rich in organics such as aliphatic and aromatic hydrocarbons (Flynn et al., 2003, Flynn et al., 2008). Low contents of amino acids were also identified in micrometeorites (Glavin et al., 2004). The Antarctic micrometeorites are found to be high in nitrogen and deuterium-rich organic matter (Dartois et al., 2013). Most of the micrometeorites recovered from Antarctic ice lies in size range of a few hundreds of microns. The flux of micrometeorites of size 50-500 μm is 100 times higher than that found outside this size range (Glavin et al., 2004, Briani et al., 2013).

1.5.2 Survivability of organics

As it is clear that the Earth was hit by wide range of objects which were rich in organics and delivered necessary life ingredients that were required for the origin of life. However, the survivability of organics remains an essential question in this scenario. These organics must survive harsh UV radiation during their journey in the interstellar medium, the high temperature pyrolysis in the atmosphere and energy release upon impact when they hit the ground. Experiments have shown that amino acids are unstable to UV radiation; however, shielded environments such as those provided by minerals can stabilize their degradation (Ehrenfreund et al., 2001, Barbier et al., 2002). On the other side, in impact environments, they show greater stability as evident from various experimental and theoretical simulations on the survivability of organics in impact conditions (Peterson et al., 1997, Blank and Miller, 1998, Pierazzo and Chyba, 1999, Blank et al., 2001, Bertrand et al., 2009, Burchell et al., 2014, Umeda et al., 2016).

1.5.3 Impact-shock synthesis

Gilvarry and Hochstim (Gilvarry and Hochstim, 1963) first proposed the idea of shock synthesis of organic compounds from meteoroids. Hochstim (Hochstim, 1963) further developed this theory based on physical and chemical parameters associated with shock around a meteorite and suggested that complex chemical compounds could be synthesized due to meteorite impact. Thus shocks generated from meteors, airbursts and giant impact plumes could have produced large quantities of organics (Chyba and Hand, 2006). Bur-Nun et al. (Bar-Nun et al., 1970) demonstrated the shock synthesis of amino acids in simulated Earth's primitive atmosphere using the experimental setup of a shock tube. Since then, many experiments have been performed to understand the role of impact-shock chemistry using the various experimental design to simulate various impact environments as listed in Table 1.3. As a result of these investigations many biomolecules such as amino acids, nucleobases and fatty acids were known to be synthesized by impact generated shock and related processes. Molecular dynamics simulations have also shown complex chemistry can occur as a result of impact driven processes (Goldman et al., 2010, Goldman and Tamblyn, 2013). The shock wave generated from impacts can cause the material to experience various thermodynamical states. Shock waves provide a sharp increase in pressure and temperature due to shock compression and subsequent rapid cooling due to rarefaction. Under such conditions, various pathways are available for molecules to react, which can lead to complex chemistry (Goldman and Tamblyn, 2013). Thus extraterrestrial impact not only delivered the necessary life ingredients but also assisted in the synthesis of important prebiotic organics.

Table 1.3 Summary of the various experimental investigation carried out to explore impact-shock chemistry.

Initial composition	**Simulated environment**	**Experimental setup**	**Experimental parameter**	**Products**	**Reference**
CH_4, C_2H_6, NH_3, H_2O	Earth's primitive atmosphere	Shock tube	Shock temperature 2000 – 3500 K	Amino acids	(Bar-Nun et al., 1970)
Aqueous solution of amino acids	Comet impacts	Single stage propellant gun	Impact velocity ~ 0.5-1.9 km s^{-1}	Amino acid dimers, peptides	(Blank et al., 2001)
Solid carbon, Fe, Ni, H_2O, N_2 and NH_3	Impact of chondritic meteorites into an early ocean	Single stage propellant gun	Impact velocity ~ 0.9 km s^{-1}	Fatty acids, amines, amino acids	(Furukawa et al., 2009)
NH_4OH, CO_2 and CH_3OH ice	Impacts on icy bodies and rocky surface	Two stage light gas gun	Impact velocity ~ 7.15 km s^{-1}	Amino acids	(Martins et al., 2013)
Fe, Fe_3O_4, Ni, Mg_2SiO_4, NH_4HCO_3, H_2O, N_2	Impact of chondritic meteorites into an early ocean	Single stage propellant gun	Impact velocity ~ 0.8 km s^{-1}	Nucleobases, amino acids, amines	(Furukawa et al., 2015)
Alanine, water ice and silicates	Impact shock	Single stage propellant gun	Impact velocity ~ 0.2-1.4 km s^{-1}	Di and tri - Peptides	(Sugahara and Mimura, 2014)
Glycine, water ice and silicates	Impact shock	Single stage propellant gun	Impact velocity ~ 0.2-1.4 km s^{-1}	Di and tri - Peptides	(Sugahara and Mimura, 2015)
Fe, Ni, Mg_2SiO_4, H_2O, CO_2, and N_2	Meteorites/asteroids impacts on oceans with a CO_2 and N_2 atmosphere	Single stage propellant gun	Impact velocity ~ 0.9 km s^{-1}	Amino acids	(Takeuchi et al., 2020)
NH_3, CO and H_2O (Miller-Urey reducing atmosphere)	Asteroid shock wave impact plasma and electric discharge	High power laser	Temperature ~ 4500 K	Nucleobases	(Ferus et al., 2017)
Formamide	Shock wave impact plasma	High power laser	Temperature ~ 4500 K	Nucleobases	(Ferus et al., 2015b)
HCHO and N2	Plasma conditions mimicking an asteroid descent in an Earth-like atmosphere	High power laser	Temperature ~ 4500 K	Nucleobases, glycine, ribose	(Ferus et al., 2019)

*Shock experiments simulating high pressure condition observed in cometary impacts containing water

Apart from delivering and synthesizing necessary prebiotic organics on the early Earth, impacts contributed enormously to the origin of life. Impact events gave rise to several habitats that are sites for prebiotic chemistry and favourable for microbial colonization (Cockell et al., 2002, Cockell, 2006). Impact craters provided many geochemical environments such as hydrothermal vents, splash pools, shocked-rock habitat conducive for prebiotic reactions and the origin of life. Shocked surfaces of rocks have more pores and fracturing than the unshocked ones, which are ideal sites for microorganisms as they provide a shield from harsh UV radiation (Cockell, 2004). These shocked rocks are also suitable sites to trap organics (Cockell, 2006). Impact themselves have delivered important minerals which have catalysed a variety of chemical reactions leading to the formation of complex molecules as well as assisted polymerization (Goldman et al., 2018, Osinski et al., 2020, Chyba and Sagan, 1992). Hydrothermal systems generated from impact structures would also have been an ideal site for prebiotic reactions and microbial colonization (Osinski et al., 2020). Thus meteorite impacts are the essential geobiological process that led to the origin and evolution of life on the Earth. As impact craters are profound in the solar system bodies, these sites should be prime sites to search for extraterrestrial life (Osinski et al., 2020).

1.6 Overview of thesis

1.6.1 Motivation

Prebiotic chemical evolution that led to the emergence of life on the primitive Earth is deeply rooted with the delivery of organic material through the impact of comets, asteroids and meteorites, among others. The extreme thermodynamic condition that is achieved in these conditions has diverse effects. The motivation of the present work revolves around these aspects and unfolds the field of impact-shock chemistry. The motivation factors are summarized below:

- **The need to understand impact-shock chemistry**: The extreme condition of impact can offer enormous potential for the synthesis of molecules relevant to the origin of life. This field of impact shock chemistry has emerged as an essential topic of investigation, and there are many aspects that need to be explored.

- **The laboratory simulation of impact shock**: The high temperature and pressure conditions achieved in these environments are challenging to understand the phenomenon associated with impact shock. The novel experimental and theoretical approaches are required to tackle these issues. While previous attempts in the last few decades have provided the solutions to resolve these issues, experiments with shock tubes to simulate impact-shock environments are seldom reported. The experimental approach presented in this work offers a novel method and alternative technique to understand impact shock chemistry.

- **Impacts on icy bodies**: Impacts are prevalent in the solar system. Icy bodies of the solar system have cratered surfaces and harbour many organics. Impact-shock chemistry thus could be an important driving force for the synthesis of organics. These icy bodies have been suggested as a potential habitat for extraterrestrial life. An understanding of the roles of impact processes in such environments is necessary.

- **Pathways from molecules to life**: While many biomolecules are known to be synthesised from simple building block in various environments ranging from interstellar medium to solar system bodies and Earth’s surfaces. Accumulation of these biomolecules into organized assemblies is an important step in the origin of life. While endogenous sources such as hydrothermal systems and many others are suggested as important sites for the origin of life, the role of impact processes is equally important and worthy to explore.

1.6.2 Objectives

The fundamental goal of the present work is centered around the fate of biomolecules under impact induced shock condition and their significance for the origin of life on the Earth and with the ubiquity of impact events across other planetary bodies to search for its implications on other planetary bodies. The objectives have been listed below.

- To design and develop an experimental setup of shock tube for simulating high-intensity impact conditions in the laboratory
- To understand the effect of high-intensity shock on the building blocks of life, such as amino acids and nucleobases and their link to the prebiotic chemical evolution and the origin of life.

- To understand the role of impact induced synthesis on the icy bodies of the solar system by using experimental set up of light gas gun.

1.6.3 Structure of the thesis

The chapters in the thesis are organized in the following manner:

- Chapter 1 gives an outline of the present study. It provides a basic introduction to the subject and presents a review of the literature pertaining to this topic. It provides the motivation and objectives of the work.
- Chapter 2 gives relevant details related to shock waves and shock tubes.
- Chapter 3 gives the relevant details related to the experimental setup of shock tubes and light gas gun to simulate impact shock conditions in the laboratory. The capabilities and application of these devices are discussed to mimic the extreme condition of impact.
- Chapter 4 discusses the role of impact shock processes on the amino acids at various temperatures and the formation of complex structures as a result of impact shock and its implications for the origin of life.
- Chapter 5 discusses the role of impact shock processes on amino acids and its implications for microstructures observed in meteorites samples.
- Chapter 6 covers the role of impact shock synthesis using the experimental setup of the light gas gun to simulate hypervelocity impact on the icy mixture of amino acids.
- Chapter 7 covers the fate of nucleobases in impact induced shock conditions.

- Chapter 8, the final chapter of the thesis, provides a description of the findings from the present study. The concluding remarks are followed by directions for future studies.

Chapter 2 Shock Waves and Shock Tubes

Chapter overview

This chapter provides a basic introduction to shock waves and shock tubes. The diversity of shockwave research and the applications of shockwaves in different interdisciplinary fields are presented. The reasons for shock tubes' continued use as an effective and attractive single pulse shockwave generator are presented. A brief description is provided about meteoroid-generated shock and laboratory simulation of impact shock processes.

2.1 Shock waves

Any disturbance in a medium causes compression waves to propagate at the local speed of sound in the gas medium. Shockwaves are non-linear waves that form when several compression waves collide and travel above supersonic speeds (greater than the local speed of sound in the medium). Shock waves are characterized by energy dissipation, sharp (or instantaneous) changes in velocity, pressure, temperature, density and flow turning (Glass, 1977, Jagadeesh, 2008). Shock disruptions are widely observed during bomb blasts, earthquakes, hydraulic jumps, lightning strokes, meteorites impacts, etc. Shock waves are formed when different gas molecules travel in a medium with speed greater than the local speed of sound. While sound wave propagates in the medium in the form of weak isentropic adiabatic compression, a shock wave is an adiabatic but not an isentropic process. Unlike a sound wave, a shock wave is an irreversible process. Shock waves can be visualized as a very sharp and thin wavefront across which pressure, temperature, density, entropy and velocity of flow change abruptly. Shock waves are classified as either strong or weak based on the instantaneous changes in flow properties such as pressure and temperature that they cause in the medium of propagation. Any sudden release (few μs) of mechanical, chemical, nuclear or electrical energy in a limited space (ranging within the distance of the mean free path of the molecules) will result in the formation of a shock wave (Glass, 1977, Jagadeesh, 2008). Shockwaves do not propagate in a vacuum due to their dissipative nature. Various examples of shock waves are shown in **Figure 2.1**. Shockwaves are a common phenomenon that occurs in nature, and they can be caused by both natural and man-made phenomena. **Table 2.1** gives examples of shockwaves generated by various sources. A force capable of supersonic displacement of the gas is needed to create a shock wave. For example, in a violent explosion, a rapidly expanding gas deriving its momentum from chemical energy generates shock waves. In a closed shock tube, shock waves are generated by the sudden release of high-pressure gas into much low-pressure gas, an acoustic supersonic boom in supersonic spacecraft is due to the formation of shock waves in the air. Shock waves have both beneficial and harmful effects. A few examples of the destructive nature of shock waves are shown in **Table 2.1**, such as earthquakes, impacts, etc. Human-made sources of shock waves can also be problematic. However, shockwaves have been used in various new ways by researchers worldwide in a multidisciplinary context. The tree of shockwave applications is represented as a sapling to reflect the increasing interest in shockwave applications across various disciplines (Krehl, 2011, Subburaj, 2018).

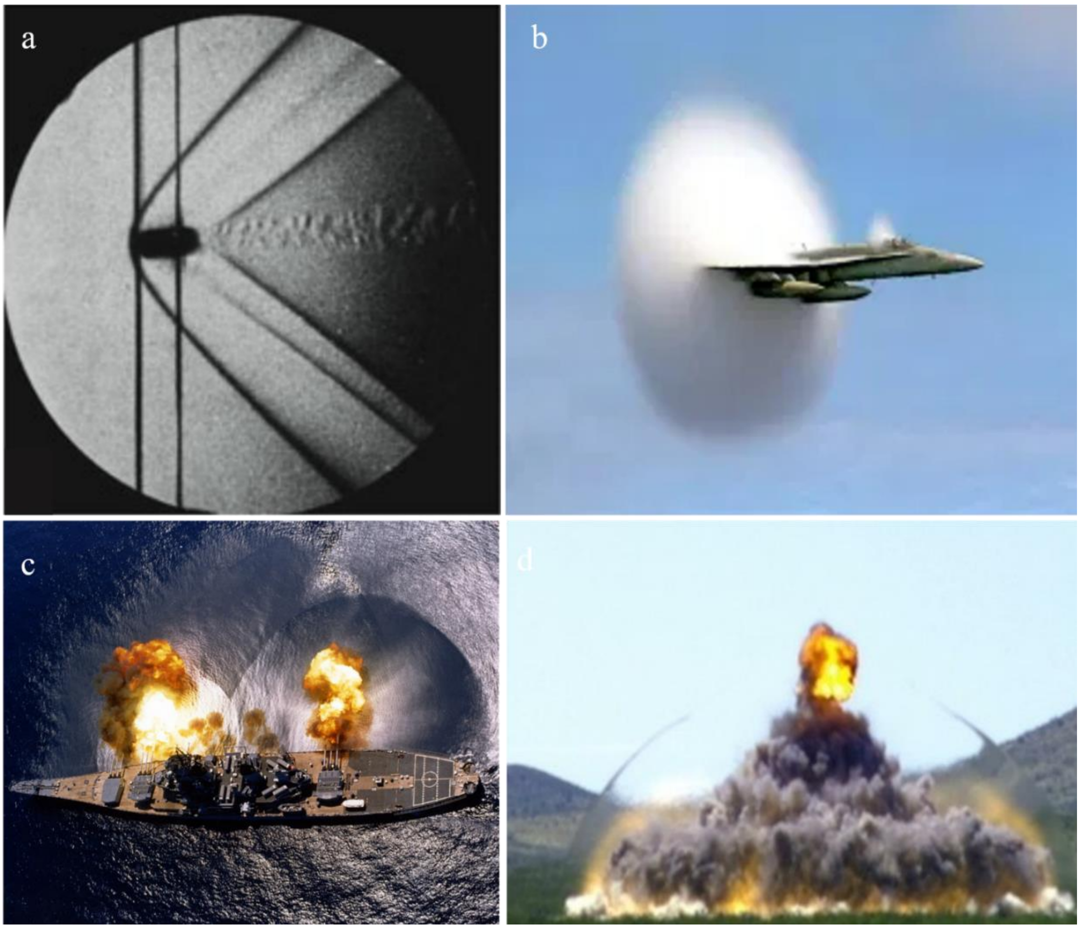

Figure 2.1 Shock waves observed from human-made sources, (a) shock wave around a supersonic brass bullet taken by Ernst Mach in 1888 using Schlieren photography (b) shock waves from the fighter jet as it breaks the sound barrier, a conical cloud is formed as the water vapour in the air is compressed due to shock wave (Jagadeesh, 2008) (c) expanding spherical shock waves observed on the surface ocean during USS Iowa firing in Puerto Rico 1984 (Jagadeesh, 2008) and (d) shock waves produced by the explosion (Hammond, 2010).

Table 2.1 Various sources of shock waves

Natural sources		Human-made sources
Terrestrial	**Extraterrestrial**	Shock tubes
Thunderclap	Supernova explosions	Explosives
Volcanic eruptions	Impact events	Whip-cracking
Earthquakes	CME's	Supersonic aircrafts
	Collision between molecular clouds	Supersonic/Hyperonic ballistic missiles
		Musical instruments
		Hand clapping

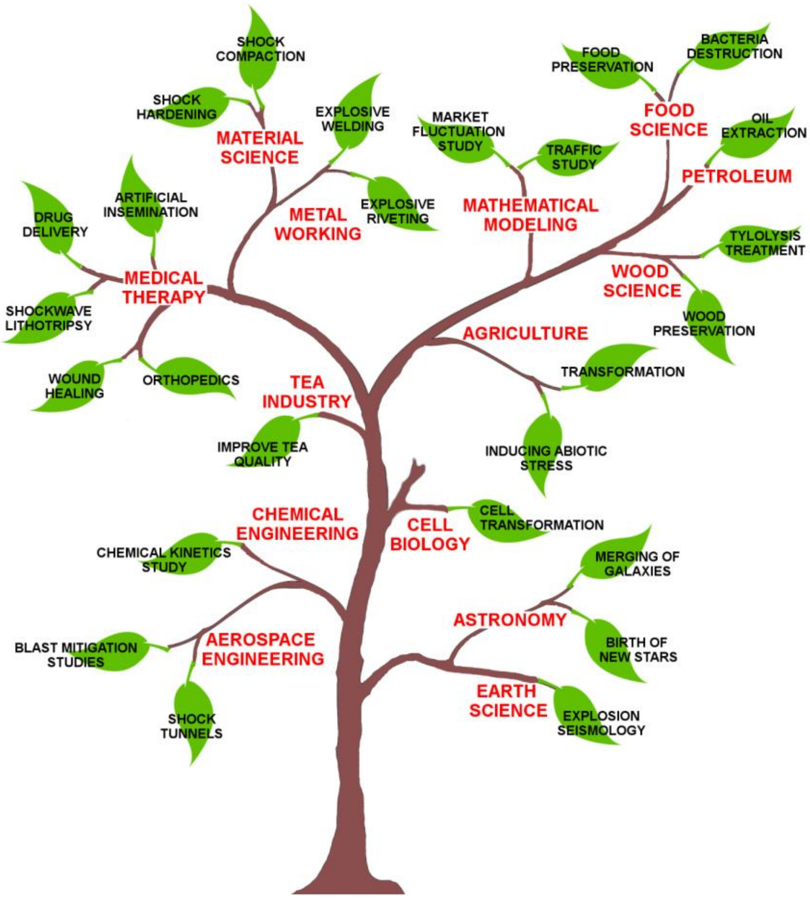

Figure 2.2 Application of shockwaves in various fields (Subburaj, 2018).

2.2 Shock tubes

With the invention of gunpowder and explosives, producing shockwaves of varying intensity became simple and straightforward. However, using explosives to produce shockwaves in an academic and research setting raised concerns about safety and replication. With the invention of the shock tube in 1899 by Paul Vielle, the safest and most reproducible method of producing shockwaves in the laboratory was achieved. A shock tube is a simple device to produce a plane shock wave by sudden bursting of a diaphragm which separates a high pressure and a low pressure section (Gaydon and Hurle, 1963). Over the last few decades, shock tubes have rapidly evolved as a research method for studying processes in high temperature gases and fast gas flow. A shock tube is a valuable ground testing facility for investigating physical and chemical processes at high temperatures. Various shock tube applications include the study of the combustion process, dissociation rates of various gases, supersonic and hypersonic flow, heat transfer and ablation of thermal protection system materials at high temperature, material properties at high temperature, etc. Depending on the needs of the study, shock tubes come in a variety of configurations that can be used for various applications. Some of them are listed as follows:

- Pressure driven shock tube: The high pressure gas in the driver section is used to drive the shock formation.
- Combustion driven shock tube: Such shock tubes are used to create stronger shock driven by the combustion of stoicheometric hydrogen and oxygen with a helium diluant.

- Explosive piston shock tube: In these shock tubes, high density shock can be generated by detonation of explosive surround a thin-walled pressurized tube.
- Free piston driven shock tube: Heavy piston is used to acquire sufficient momentum to compress driver gas.
- Variable cross section shock tube: In such shock tubes, shock wave strength can be drastically modified in a variable cross section channel.

In the present study, we used a pressure-driven shock tube which is the most basic and widely used shock tube.

2.2.1 The working principle of shock tube

The schematic diagram of a conventional shock tube is shown in **Figure 2.3.** It consists of high pressure driver section and a low pressure driven section separated by a metal diaphragm. The shock waves are generated by the sudden bursting of metal diaphragm mounted between these two sections. To obtain different reflected shock temperatures, diaphragms of varying thicknesses are used. The choice of material of diaphragm depends on the need of the experiments. The bursting pressure for a diaphragm for a particular material is directly proportional to its thickness and inversely proportional to the exposed diameter. For low pressure difference across the diaphragm, non-metallic materials such as Mylar can be used. Different diaphragm thicknesses will offer different bursting pressure resulting in different Mach number, depending on that shock parameters will be different (Gaydon and Hurle, 1963). A high pressure helium gas is filled with a high flow rate in the driver section until the diaphragm burst. The sudden bursting of the diaphragm results in the formation of a shock front, which travels in the driven section, compresses and heat the low-pressure test gas and simultaneously, expansion wave travels back to the driver side, known as the expansion fan. Behind the shock front, there exists a contact surface between driver gas and driven gas or test gas, which moves behind the shock front. The primary shock wave gets reflected from the end flange of the shock tube resulting in the formation of reflected shock travelling back in the driven section and resulting in a sudden increase in pressure and temperature at the end of the shock tube, as the velocity of gas molecules stop instantaneously. This pressure and temperature are maintained constant for a certain duration of time until the reflected rarefaction wave arrives and then drops suddenly. This time is known as dwell time or test time. An x-t diagram (distance-time) for a shock tube is presented in **Figure 2.3,** showing the propagation of shock wave, rarefaction fan, the contact surface and reflected shock and test time, adapted from Gaydon and Hurle (Gaydon and Hurle, 1963). The usually designated symbols for the different region of the shock tube are presented by numerical subscript: an initial pressure and temperature in the driven section are P_1 and T_1, the pressure and temperature in the region between front and contact surface are referred to as primary shock and denoted as P_2 and T_2, respectively. The pressure and temperature between the contact surface and the rarefaction fan are referred to as P_3 and T_3. The pressure and temperature in the high-pressure side driver section are referred to as P_4 and T_4. The pressure and temperature in the reflected shock region are denoted as P_5 and T_5. The test time is represented at the end of the x-t diagram as ΔT. The variation of pressure and temperature along the shock tube at a particular time is shown in **Figures 2.3(c)&(d)**, respectively.

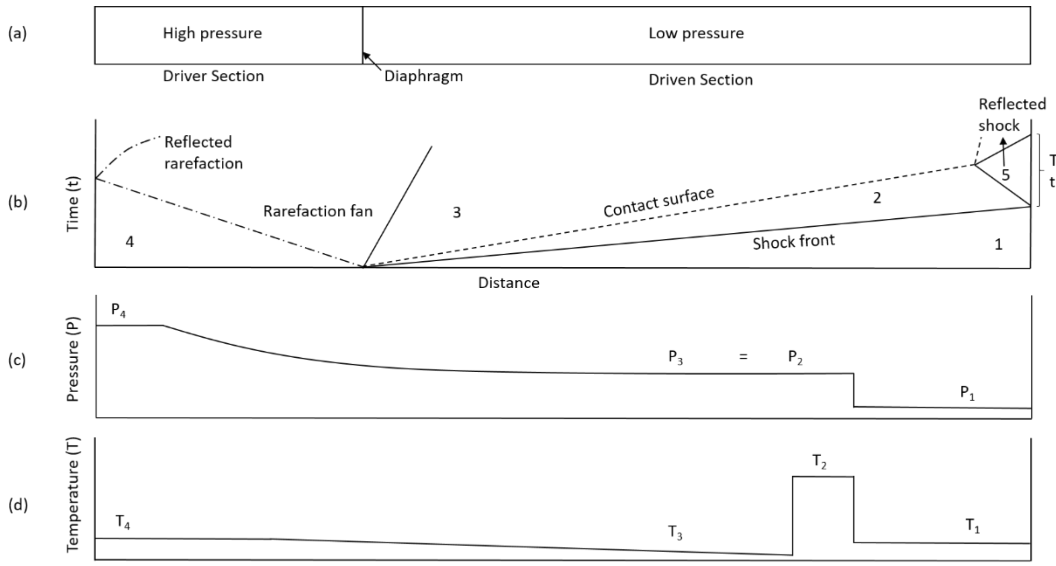

Figure 2.3 (a) The schematic of conventional shock tube, (b) the wave (x-t diagram showing the various regions in a shock tube, the distribution of (c) pressure and (d) temperature at time t along the x-axis of the shock tube.

2.2.2 Shock tube theory for ideal gas

Kinetic Energy of the test gas molecules in the driven section is very high as the gas molecules travel at high velocity (Vs), which instantaneously stops at the end flange of the driven section of the shock tube called as stagnation point condition or isotropic condition. The kinetic energy of gas molecules is converted to heat energy, so the pressure and temperature shoot up simultaneously at the end flange of the shock tube. Under this condition, the Rankine-Hugoniot relations are derived in a shock fixed coordinate system considering the passage of gas through the unit area of the shock front and applying the conservation of mass, momentum and energy across the shock front (Gaydon and Hurle, 1963). A corresponding pressure jumps (P_2/P_1), (P_5/P_1) and temperature jumps (T_2/T_1) and (T_5/T_1) for a given shock Mach number are estimated using the following equations,

$$\frac{P_2}{P_1} = \frac{2\gamma\,(M_S)^2 - (\gamma-1)}{\gamma+1} \tag{2.1}$$

$$\frac{T_2}{T_1} = \frac{\left(2\gamma\,(M_S)^2 - (\gamma-1)\right) - \lfloor(\gamma-1)(M_S)^2 + 2\rfloor}{(\gamma+1)^2 (M_S)^2} \tag{2.2}$$

Where γ=C_p/C_v specific heat ratio of test gas, C_p and C_v are the specific heat of the gas at constant pressure and volume, respectively. The pressure jump (P_5/P_1) across the reflected shock wave can also be estimated theoretically using the following equation:

$$\frac{P_5}{P_1} = \frac{2\gamma\,(M_S)^2 - (\gamma-1)}{\gamma+1} \left[\frac{(3\gamma-1)(M_S)^2 - 2(\gamma-1)}{(\gamma-1)(M_S)^2 + 2}\right] \tag{2.3}$$

The estimated temperature jump across the reflected shock wave (T_5/T_1) for the measured value of shock Mach number in the driven section is computed using the following equitation.

$$\frac{T_5}{T_1} = \frac{\{2(\gamma-1)(M_S)^2 + (3-\gamma)\}\{(3\gamma-1)(M_S)^2 - 2(\gamma-1)\}}{(\gamma+1)^2\,(M_S)^2} \tag{2.4}$$

Where P_1 initial test gas pressure in the driven section, P_2 primary shock pressure, T_1 is the ambient temperature for the test gas, T_2 primary shock temperature, T_5 reflected shock temperature. The shock speed and Mach number are measured experimentally using appropriate pressure sensors, as shown in the next chapter. The strength of shock waves depends upon pressure ratios applied across the diaphragm and the physical properties of the two gases used.

This one-dimensional shock tube theory is based on several assumptions as listed below. Due to these assumptions, the shock tube parameters in a practical scenario do not match with the predictions of the ideal shock tube theory.

- The theory predicts the behaviour of inert monoatomic gases upto high temperature of ~ 8000 K, above which the effect of electronic ionisation and excitation dominates. Gas molecules at high temperature (real gas effect) experience four types of internal energies like: translational, rotational, vibrational and electronic excitation energy, in addition to this, gas species undergo dissociation and ionisation occurs at elevated temperature. Hence these equations are inadequate to explain the behaviour.

- The theory assumes an inviscid gas with no boundary layer. Boundary layer disruptions behind incident shock waves are minor, but they are amplified in the post reflected-shock field, contributing to deviation from the ideal behaviour.
- The theory assumes the sudden bursting of the diaphragm, which is not an ideal case. The gradual opening of the diaphragm is not taken into account by the ideal shock tube theory. In practical situations, the time it takes for the diaphragm to open plays a significant role in the shock forming process.

2.2.3 Test time in shock tubes

Knowledge of test time (ΔT), i.e., the time available when the elevated pressure and temperature conditions are approximately uniform, is essential in shock tube studies. This test time is determined by the interactions of shock waves at the end flange of the shock tube, which are produced after the bursting of the diaphragm. This time is primarily constrained by the arrival of the contact surface at the end station of the shock tube. This time can be increased by increasing the distance between the diaphragm and the end station leading to the increase in separation of shock front and contact surface. From this perspective, it seems that a tube of sufficient length would suffice for the longer test time duration, but this fact is not true. The shock wave will exist as long as the driving force exists to drive it. This driving force is provided by the high pressure driver gas and as the gas expands and the pressure values go below the pressure of the shock wave, this force diminishes. This occurs when the contact surface is overtaken by the reflected rarefaction. This property depends on the initial conditions and shock tube dimensions, and by adjusting these quantities, test time can be controlled.

2.3 Shock waves from meteoroids

The space vehicles like space shuttles/spacecraft from orbits, ballistic missiles, etc., generate shock waves when they enter Earth’s atmosphere with 6-25 Mach number. When meteoroids enter Earth's atmosphere, they generate shock waves. However, these shock waves are very complex and differ from those caused by re-entry vehicles. Meteoroid generated shocks are significantly stronger due to high translational temperature and ablation. For the typical impact velocities, the kinetic energy of flow converted into internal energy of gas can generate very high temperature (> 10000 K) in the front shock layer with pressure and densities exceeding several orders of magnitude that of ambient air (Silber et al., 2018). A detailed understanding of physicochemical processes associated with meteoroid generated shock is required. A historical event, the Tunguska meteor, which exploded over Siberia in 1908, is a dramatic example of meteoroid generated shock. This event was accredited to an air bust of meteoroids of size tens of meters in radius entering at hypervelocity in Earth's atmosphere (Chyba et al., 1993). Though no impact crater was found at the impact site, impact-generated shock destroyed nearly two thousand square kilometers area of the forest when it exploded (Turco et al., 1982). The most recent event of extraterrestrial impact induced shock is the Chelyabinsk event which occurred over Russia in 2013. The object speed was estimated to be approximately 18 km s^{-1} which exploded at the height of 30 km, creating a bright flash and large shock wave (Brown et al., 2013, Popova et al., 2013). These events demonstrated the destructive nature of shock waves generated by the impact of large meteoroids and the significance of research on shock wave phenomena.

2.4 Laboratory simulation of impact-shock processes

Natural impact-shock processes are very complicated in terms of their physical and chemical characteristics. It is impossible to conduct a comprehensive investigation of the full-scaled effect of the impact process. So the laboratory investigations are focused only on a limited aspect of the impact process at a time. Most common impact experiments are performed using accelerating devices capable of firing millimetre-sized projectiles of a few grams with a velocity of few km s^{-1}. A wide variety of accelerating devices are available in the laboratory, such as single stage and two stage light gas gun, Titov gun and Van de Graaf accelerator, etc. (Gerasimov et al., 1998). A detailed description of two stage light gas gun is provided in chapter 3 as used in the present investigation. Such small-scale impact experiments are beneficial for the investigation of the physical aspect of impact events such as the formation of craters, dynamics of ejecta and others. Recent experiments as shown in **Table 1.3**, have demonstrated how hypervelocity impact experiments can be utilized to investigate chemical transformation associated with impact-shock processes. However, the problem exists with small-scale hypervelocity impact experiments when these results are applied to planetary scale. The effects from actual impact events would be more intense, significant and long-term, and a careful investigation is required for extrapolation of laboratory scale to planetary scale.

Another experimental setup is to use high explosive detonation as a source of energy to simulate the impact process. Such experimental techniques are helpful in the study of impact cratering mechanisms, such as the study of transient cavity growth and its modification (Oberbeck, 1971).

High temperature heating effect of the impact process can be simulated in the laboratory to investigate the chemical modification induced by impact. Such methods do not reproduce the actual impact process; instead, and they simulate characteristic temperature (thousands of Kelvin) to understand impact induced melting, vaporisation and chemical reactions at high temperatures. Among various sources, a powerful pulsed laser is a valuable tool for laboratory simulation of such processes. Though laser induced irradiation experiments do not reproduce the actual high pressure shock effect of impact, they are capable of simulation of high temperature thermal effect of impacts, when decompression occurs after impact and pressure value returns to normal. Thus they are a useful tool to investigate chemical processes that is induced as a result of the impact. Many laser experiments have been performed to investigate the melting and mixing process of projectile and target during meteorite impact and have shown similar results from natural impact events (Gerasimov et al., 2005, Ebert et al., 2017). A series of experiments have been performed using high intensity laser to explore impact induced shock chemistry as shown in **Table 1.3**.

The shock tube also offers interesting characteristics such as a sharp increase in temperature (thousands of kelvin) within a very short time scale and subsequent cooling, with the rate of millions of degrees per second. Such transient events are expected as a result of catastrophic impact events. Thus shock tubes offer a better analogue of natural impact induced shock processes. Apart from that, high temperature conditions are easily achieved in shock tubes which are otherwise difficult to achieve in other experimental facilities such as light gas gun. Also, shock tube offers a cleaner environment compared to other experimental facilities, which is necessary for chemical studies. However, shock tubes are seldom used for laboratory simulation of impact induced shock (Bar-Nun et al., 1970). The results presented in the thesis extends the application of shock tube to study impact induced shock processes and shock chemistry of interstellar environments in the laboratory. In the next chapter, we will discuss the detailed experimental setup of shock tubes and light gas guns as used in the present thesis.

Chapter 3 Instrumentation and Experimental Methods

Chapter overview

This chapter describes the instrumental description and various analytical techniques used in the present studies to perform novel experiments with the impact of the shock. The experiments described in this thesis were performed using shock tube facilities available at the Indian Institute of Science (IISc) Bangalore and Physical Research Laboratory (PRL) Ahmedabad and Light Gas Gun (LGG) facility at the University of Kent UK. A brief description of the instrumental methods is provided with their working principle, the methodology for calculating experimental parameters. Various analytical instruments like SEM, TEM, FTIR, LC-MS are used for the characterisation and analysis of both pre and post shock processed material samples.

3.1 Shock experiments

We performed shock experiments at the Material Shock Tube (MST1) facility in IISc Bangalore. Further, we established a similar shock tube setup at Astrochemistry Laboratory, PRL Ahmedabad, for the application of shock tubes mainly dedicated to research in planetary science, astrochemistry and astrobiology to investigate physical and chemical consequences of shock waves in interstellar and planetary environments.

We also utilized the Light Gas Gun (LGG) facility designed and developed at the University of Kent, Canterbury, to simulate the impact on icy bodies of the solar system. LGG is designed to study the hypervelocity impact phenomenon on the surface of solar system bodies and properties of material surfaces exposed to dust particles impact in space.

3.1.1 Material shock tube (MST1)

The shock tube MST1 is designed and developed by Dr. V. Jayaram, Solid State and Structural Chemistry Unit (SSCU), IISc Bangalore, to investigate the interaction of shock heated gases with materials in solid and powder form to study properties of materials at elevated temperature for various applications (Vishakantaiah, 2017). This is the first novel shock tube established to study multiphase systems. The schematic of the Material shock tube (MST1) as used in these experiments is shown in **Figure 3.1**. The shock tube consists of two sections, namely, a driver section and a driven section of the length of 2 meters and 5 meters, respectively. The tube has an inner diameter of 80 mm. These two sections are separated by an aluminium diaphragm of about 2mm thickness. Suitable V-grooves of length 85mm are made perpendicular to each other with a groove depth of one-third of the thickness of the used diaphragm; this becomes the weakest point to burst the diaphragm instantaneously. The pictorial representation of the diaphragm before and after bursting is shown in **Figure 3.2**. The driven section is filled with low-pressure test gas (P_1) and the driver section is filled with high pressure (P_4) gas until the diaphragm bursts instantaneously, producing shock waves in the driven section. For a fixed diaphragm thickness, the shock Mach number increases by decreasing test gas pressure in the driven section. Also, it is possible to increase the Mach number by increasing the thickness of the diaphragm material. Shock strength increases with an increase of the shock Mach number. At the end of the driven section, an arrangement is made to place the sample to study the interaction of shock wave with the powder test sample. The sample is mounted on a horizontal plate between a manually operated ball valve and the reaction chamber. The interaction of the strong shock heated gas with the sample occurs at the end flange of the 300 mm long reaction chamber. Three pressure sensors are mounted at the end of the driven section, each 0.5 meters apart to measure the shock speed and profile of primary and reflected shock at the end of the shock tube.

3.1.2 High intensity shock tube for astrochemistry (HISTA)

We have designed a new shock tube setup HISTA at Physical Research Laboratory Ahmedabad, dedicated to astrochemistry research to study shock processes in the interstellar and planetary environment. The MST1 and HISTA are similar in design and construction. The only difference between the two shock tubes is the techniques for placing the sample in the shock tube. In MST1 samples are places on a horizontal plate while in HISTA it is placed on sidewall of the shock tube. A detailed instrumental design of HISTA is shown in **Figure 3.3**, consisting of the driver section and driven section of length 2 meters and 5 meters, respectively. The inner and outer diameters of the shock tubes are 80 cm and 115 mm, respectively. The shock tube body is comprised of stainless steel with the suitable mounting ground. Three pressure sensors are mounted at the end driven section, each 0.15 meters apart. The sample is loaded at the end of the driven section. A pumping system is attached to the driven side. The laboratory setup of MST1 and HISTA is shown in **Figure 3.4**.

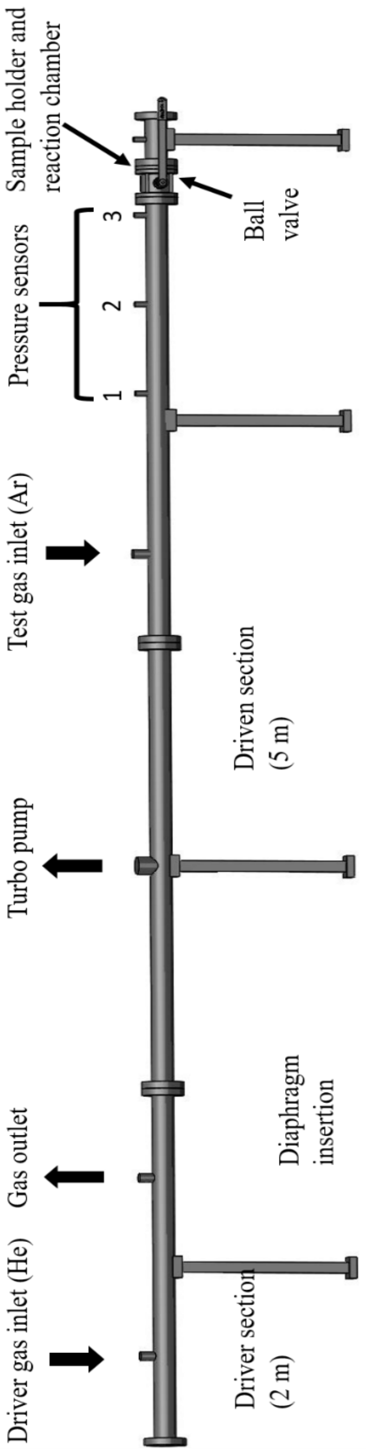

Figure 3.2 Schematic diagram of MST1.

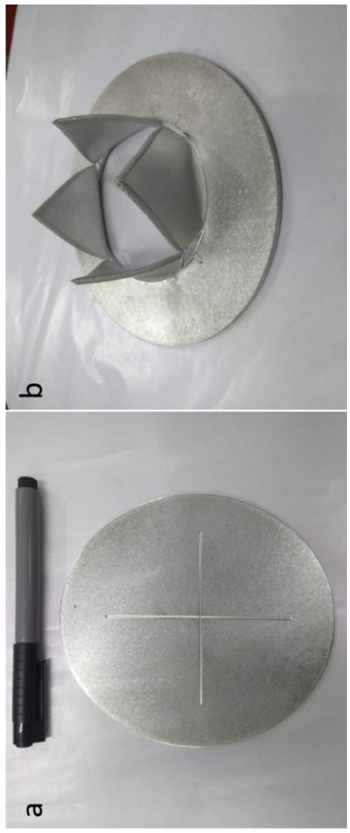

Figure 3.1 The 2 mm thick aluminium diaphragm with V-grooves cut on the surface.

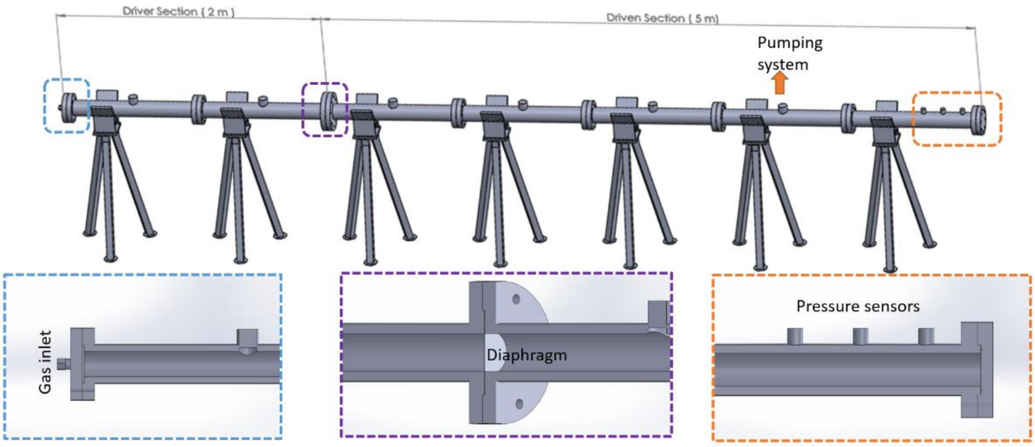

Figure 3.3 Experimental setup for HISTA, cross sectional views of different section are shown in respective coloured boxes.

Figure 3.4 (a) MST1 at IISc Bangalore and (b) HISTA at PRL Ahmedabad, single pulsed shock tube used in present study.

3.2 Experimental procedure of shock processing

Before starting the experiment, the complete shock tube is sterilized with acetone 3–4 times to avoid impurities from previous experiments. Powdered samples were uniformly distributed over the sample holder parallel to the flow of gas inside the shock tube (**Figure 3.5**). After the sample is loaded, the shock tube is closed tightly with end flange, the driven section of the shock tube is purged 2–3 times with ultra-high purity (UHP) argon (99.999%) to remove any residual gas impurity present inside the shock tube then pumped to vacuum down to 3×10^{-4} mbar using a turbo-molecular pumping system and then filled with UHP argon up to the desired pressure (pressure values are estimated before the shock, to produce a particular temperature) to perform different experiments. A rotary pump connected to a gas outlet port of the driver section is used to evacuate up to 0.01 bar. High-pressure helium gas is rapidly filled to the driver section at a very high flow rate until the burst of the aluminium diaphragm. The sudden bursting of the diaphragm results in the formation of a shock wave that travels through the driven section and is reflected from the end flange of the reaction chamber. The ball valve next to the reaction chamber is closed immediately after the rupture of the diaphragm. The sample experiences this reflected shock in the reaction chamber. After shock processing, the high-pressure gas inside the chamber is released slowly, and the solid residue left in the reaction chamber and from the end flange was collected in airtight vials and stored in a vacuum desiccator until further analysis. Three pressure sensors (PCB Piezotronics 113B22) surface mounted at three different locations, each 0.5 metres apart, on the driven section, were used to obtain a pressure signal recorded using a Tektronix digital storage oscilloscope (TDS2014B).

Figure 3.5 (a) The end flange, (b) the sample holder with a horizontal plate of length 8 cm and width 1 cm. (c) The sample holder flange mounted between the ball valve and the 300 mm long reaction chamber, which is terminated with blank end flange. This end is closed with an end flange.

3.2.1 Measurement of shock parameters

Three pressure sensors surface mounted at three different locations, each 0.5 meters apart, on the driven section were used to obtain a pressure signal, recorded using a Tektronix digital storage oscilloscope. The signals recorded from the oscilloscope show the signatures for both the incident and reflected shock pressure, as shown in **Figure 3.6**.

The shock speed (Vs) is calculated by finding the time taken (Δt) by the shock wave to travel the distance (Δx) between the pressure sensors with the help of the recorded pressure signal. The strength of shock is determined by Mach number (M_s). The Mach number is calculated using the relationship

$$\text{Shock Mach number (Ms)} = \frac{\text{Shock speed in the gas (Vs)}}{\text{Local speed of sound in the gas (a)}}$$

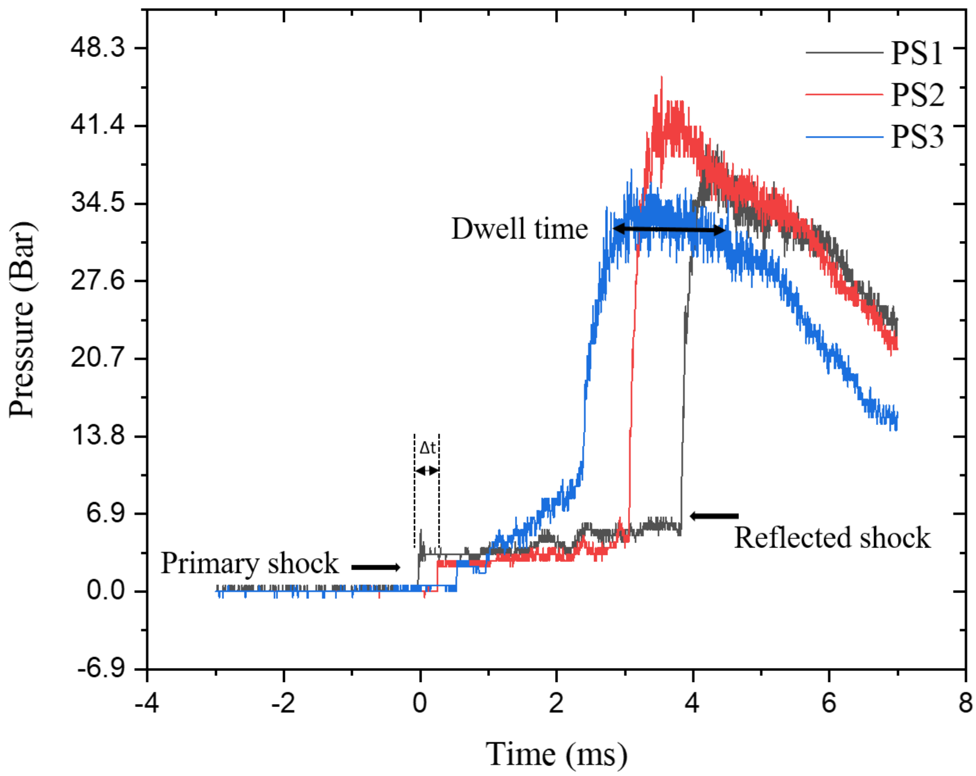

Figure 3.6 Pressure signal recorded from oscilloscope showing the profile of primary shock and reflected shock.

This Mach number is used to calculate the shock parameters using one-dimensional normal shock equations known as Rankine-Hugoniot relations shown in Chapter 2. Experimentally we measured reflected shock pressure (P_5) and estimated the reflected shock temperature (T_5) under isotropic conditions using Equation 2.4. It is difficult to measure actual shock temperature within the test time of 1-2 millisecond time scale. Using platinum resistance thermometer, we can only measure heat transfer rate, but not the actual temperature. Knowing the ambient temperature, it is possible to estimate the reflected shock temperature experienced by the test gas. Estimated reflected shock temperature is a function of M_s and γ of test gas and it is accurate up to 5% as we used monoatomic gases like He and Ar gas in the experiments. Powder sample loaded inside the shock tube experiences this stagnation pressure and temperature simultaneously at the end of the shock tube for a short duration. During this process, the sample experiences superheating and cooling at the rate of about 10^6 K s^{-1} at medium reflected shock pressure. Present experiments were performed with reflected shock temperatures ranging from 3000 K to 8000K (estimated) and reflected shock pressure of about 15-34 bar for 1-2 milliseconds timescale. This is the uniqueness of the experimental setup done to study materials under extreme thermodynamic conditions.

3.2.2 Safety aspects of shock tube

Shock tube operation requires specific safety guidelines as its deals with high pressure gas and bursting of the diaphragm. The following points are monitored during shock tube firing.

- Do not stand near the shock tube when it is being fired except for the helium tank and vacate the nearby area during operation and place the warning signboard in the lab area.
- Warn everyone before firing.
- Make sure that all bolts are thoroughly tightened.
- High pressure cylinders to be handled carefully, make sure there is no gas leakage, and gas regulators are working correctly.
- If the diaphragm does not burst at the required pressure, close all the valves and let the gas out immediately.

3.3 Two Stage Light Gas Gun

The two-stage light gas gun (LGG) was designed and developed at the University of Kent, Canterbury, UK. The details of instrumentation, experimental setup and recent upgrades are described in Burchell et al. (Burchell et al., 1999) and Hibbert et al. (Hibbert et al., 2017). The instrument is capable of firing projectiles of size 0.1 mm to 3.0 mm diameters in a velocity range of 0.3 to 7.5 km s^{-1}. The instrument is developed to understand the physical and chemical consequences of extreme pressure and temperature that are created during impact bombardment across the solar system. The impacts in such velocity range are labelled as hypervelocity impact and defined as any impact such as upon impact on any target material, the energy delivered is faster than energy dissipated. So the speed is also determined by the impactor and target material. Such hypervelocity impacts are widespread across the solar system bodies. Meteorites craters, as observed on many planetary bodies, are an example of hypervelocity impacts. LGG’s are a valuable tool to achieve such velocity in the laboratory to simulate impact events.

The two-stage LGG operates on the principle that a light gas (hydrogen/helium), highly compressed between a piston and a metal disc (diaphragm), is released suddenly by the sudden rupture of the diaphragm and the projectile attached ahead of it gets accelerated. The initial compression of gas is provided by propelling a piston by igniting the powder charge in the shotgun cartridge (first stage), which results in compression of the light gas (second stage). Expansion of light gas accelerates the projectile; hence the name two-stage light gas gun exists. Since the light gas having low molecular weight can be compressed easily to high pressure, they are used efficiently to achieve hypervelocity. **Figure 3.7** shows the schematic diagram and pictorial representation of the University of Kent's two-stage LGG as used for the present work in this thesis. In the present investigation, we impacted a spherical bullet (stainless steel 420) of size 1 mm at a velocity of approximately 5 km s^{-1} on amino acid-water ice targets.

The light gas gun consists of two sections, the pump tube and the launch tube of length 0.7 meters, each joint together by a central breech. These two sections are separated by a burst disc of diameter 12.7 mm attached at the end of the launch tube. The pump tube has a rifled barrel with a bore size of 12.7 mm. To achieve the speed of approximately 5 km s^{-1}, hydrogen gas is held at 40 bar through a connection hole in the pump tube. The launch tube has bore of 4.30 mm. Behind the burst disc at the breech end of the launch tube, a sabot is placed containing projectile (spherical stainless steel (SS 420) bullet of size 1 mm). A powder chamber is attached at other end of pump tube containing the cartridge. The cartridges are prepared in lab and contain standard shotgun cartridge (20 mm diameter), primer and gun powder (approximately 12 grams for 5 km s^{-1} speed). A nylon piston of length 8 cm and mass 12 g is placed in the cartridge end of pump tube. The piston has a dimeter of 12.7 mm same as the bore of the pump tube, so it is a tight fit. At both ends of the piston, circular grooves are cut to fit the O ring in each so that it fits the pump tube and makes it a gas-tight seal. The bore inside the pump tube is funnelled shaped at the breach section side to increase pressure and to stop the piston from hitting the launch tube.

To initiate the firing of gun, a firing pin is inserted in the base of the cartridge, which is held in the powder chamber at the end of the pump tube. A brass pendulum is suspended on a panel next to the firing pin at 50° from vertical and controlled by an electric switch remotely for safety purposes. By pressing the switch, the pendulum is released and it hits the firing pin with sufficient force, which ignites the primer and subsequently the cartridge.

The sabot used in the experiments is a four-way split sabot of size 0.175”. The sabot has approximately the same width as the bore of the launch tube to minimize the pressure lost while propelling. As the firing is triggered, the sabot containing the projectile is launched into a much wider blast tank and does not remain confined. In the blast tank, the sabot gets separated from the projectile path because of the spinning imparted due to the launch tube and travel off the gun axis, and is seized by the stop plate mounted at the exit of the blast tank. As the projectile exits the blast tank, it travels

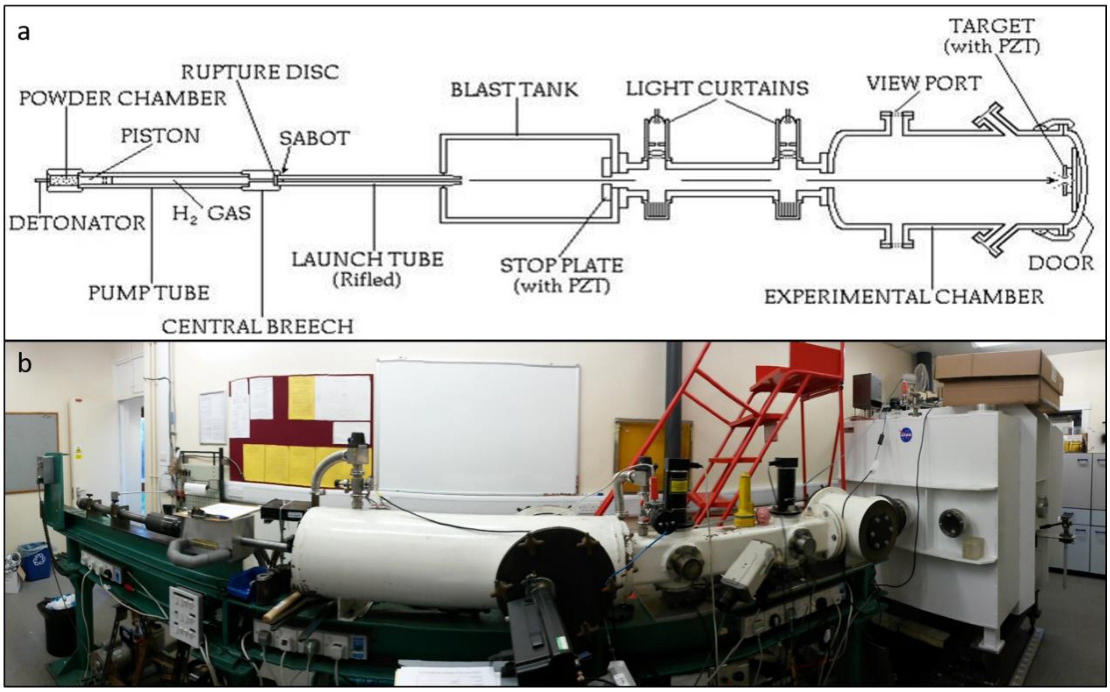

Figure 3.7 (a) Schematic diaphragm of two stage Light Gas Gun (b) panoramic view of laboratory setup at the University of Kent.

through two laser curtains (continuous wave, wavelength 633 nm) 0.499 meters apart. The laser curtains are created by broadening the laser beam by barrel lens and passing it through a slit. These beams are further focused on a photodiode with the help of another barrel lens at the bottom. The photodiodes are connected to a highly sensitive digital oscilloscope.

By measuring the time taken by the projectile to cross the known distance between the laser curtains through an oscilloscope, the speed of the projectile can be calculated with an approximate accuracy of ±1%. The end of the blast tank is attached to a cubical chamber (1.14 × 1.14 × 1.14 meters) which was lent to the University of Kent by NASA. The required target of study can be mounted in this chamber, and two viewports are available for visual inspection of the target. The speed of projectile achieved in a shot depends on various firing conditions such as the quantity of gunpowder used, the mass of the piston and sabot, the strength of the bursting disc, the type and amount of gas pressure filled in the pump tube for firing. These parameters are detailed in Burchell et al. (Burchell et al., 1999). In the present thesis, we have performed experiments at a single velocity of approximately 5 km s^{-1}. For which ~ 45 bar of hydrogen gas was used in the pump tube and 12 grams of gunpowder was used for propelling the piston. To start each new firing, the pump tube and the launch tube are cleaned after each shot.

3.3.1 Preparation of target

The amino acid embedded in water ice targets was prepared in the laboratory at the University of Kent. The single amino acids as well mixtures of amino acids were mixed in an equal weight ratio in the total weight of 3.5 grams and dissolved entirely in 150 ml HPLC grade water using a magnetic stirrer in a glass beaker and then cooled to 1.5°C. In a separate steel beaker, water ice is prepared frozen at -20°C. The solution of amino acid-water is poured into the beaker containing the water ice, and this whole mixture is cooled to 140 K in a freezer. Various steps to prepare the amino acid-water ice target are shown in **Figure 3.8**. The targets were kept in the freezer for almost 15-20 hours and removed from the freezer just before the firing to be mounted in the target chamber (**Figure 3.9a**). Chamber walls are covered with aluminium foil to collect the ejecta from the target after projectile impact (**Figure 3.9b**). Chamber is evacuated to 50 mbar before the firing of the gun. After the firing is done the ejected materials from the target are left on the aluminium foil in the chamber to be dried out entirely at room temperature and then collected for further analysis (**Figure 3.9e&f**). These residues were further analysed using SEM and LC-MS. Also, during target preparation, while dissolving the amino acid in the water, a small amount of solution was drop cast on aluminium foil to analyse sample using SEM and LC-MS before impact and to compare it with ejected material after impact.

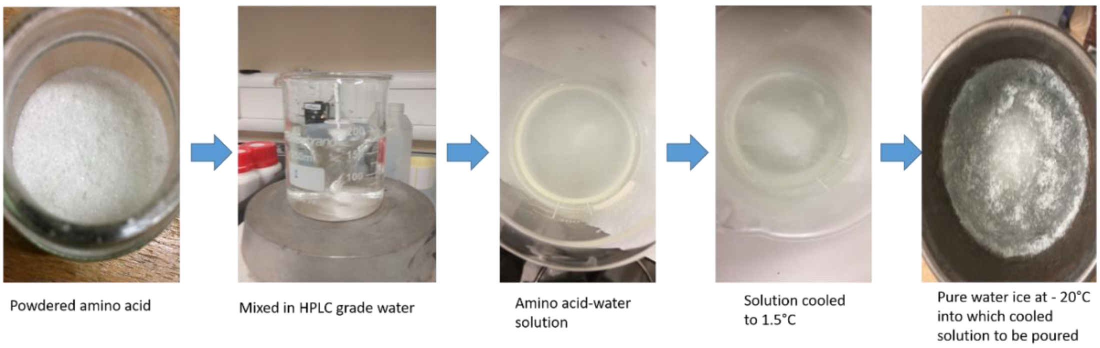

Figure 3.8 Step for the preparation of amino acid-water ice target.

Figure 3.9 (a) Target mounted at the door of the chamber, (b) chamber covered with aluminium foil to collects the ejecta after impact, (c) target before impact, (d) target after impact with projectile showing small crater in the center and (e&f) after impact white ejecta on the aluminium foil.

3.3.2 Calculation of peak pressure upon impact

The peak shock pressure in the impacts was calculated using planar impact approximation (Melosh, 2013). As the projectile impacts, the material of both objects compressed, generating shock waves. The strength of shock waves can be calculated using Hugoniot equations based on the conservation of mass, energy and momentum across the shock front. This method assumes a linear shock wave speed relationship of the form $U = C + S \times u$ for both materials, where C and S are material-specific empirical constant, U is the shock velocity, and u is the particle velocity (Burchell et al., 1999, Melosh, 2013).

3.4 Qualitative analysis

Various techniques were applied in the present investigation for analysis of the compounds obtained from different experiments. Microscopic techniques were applied to get the morphology of shock processed residues, FTIR spectroscopy and LC-MS were used to get the details of chemical modifications after impact-shock processing.

3.4.1 SEM and TEM

Microscopic techniques such as SEM, TEM, etc. provide great insights at micro and nano scale revealing the basic architecture, morphology, surface properties, microstructures and interfaces of biopolymers which is an essential tool to determine their ideal application (Venkateshaiah et al., 2020). The remarkable application of the microscopic technique in interpreting various self-assembling systems and its application in the origin of life research has also been discussed by Jia & Kuruma (Jia and Kuruma, 2019). Scanning electron microscope (SEM) imaging was performed to investigate the morphology of both unshocked samples and shock processed residue. Carbon tape was pasted on the SEM sample stub, on which sample was spread and then gold sputter coating was done on the top of the surface of the sample to avoid surface charging during SEM analysis. The SEM was conducted utilizing a ZEISS ULTRA 55 at an operating voltage of 5 kV at different magnifications ranging from 30× to 10000×.

Transmission electron microscope (TEM) analysis was also performed to investigate the internal structure of shock processed residual samples at higher magnification. The small quantity of sample was placed in 1.5 ml of acetone solvent in an Eppendorf tube and then kept in ultrasonic bath for sonication for 10-20 min. If the solution looks dark, the sample may agglomerate and it is not suitable to get good TEM images. Acetone is further added to make the solution more dilute and a micro pipette is used to collect the suspended particles from the dilute solution and a drop of this solution is dispersed on 200 mesh carbon coated copper grid. The sample is kept in vacuum desiccators before loading into the microscope**.** TEM studies were performed utilizing a Titan Themis from FEI, at an operating voltage of 300 kV and magnification of approximately 25000×.

3.4.2 Infrared (IR) spectroscopy

The shock-processed residues were further characterized by Infrared (IR) spectroscopy over a wave number range of 4000–500 cm^{-1}, using the Nicolet iS10 FTIR in ATR mode.

3.4.3 Liquid chromatography mass spectrometry (LC-MS)

We have followed the general protocol for LCMS (Stone, 2018). Samples from various experiments were analysed in the Waters Acquity UPLC-SYNAPT G2-S MS system. The ACQUITY UPLC H-Class performs both UPLC and HPLC functions, and can achieve high resolution, speed and sensitivity in liquid chromatography analysis, compared to conventional systems. The SYNAPT G2-MS is hybrid, quadrupole/orthogonal acceleration, time of flight mass spectrometer controlled by MassLynx software.

The tiny amount (typical concentration ~ 0.1-1 µg/ml) of residue was dissolved in HPLC-grade water. 100 µL of this sample was dissolved in 1 mL HPLC grade methanol to prepare a 100 µL/mL solution. The sample was injected at a flow rate of 0.05 ml/min into UPLC with an injection volume of 5 µL. The sample components were separated using a waters ACQUITY UPLC BEH C18 1.7 µm column, with dimensions 2.1×100 mm. The temperature of column, sample and room were maintained at 30°C, 20°C and 22°C respectively. The mobile phase consisted of (A) water containing 0.1% formic acid and (B) acetonitrile containing 0.1% formic acid. The gradient for the mobile phase started from 95% solvent A and 5% solvent B, decreasing linearly to 0% solvent A and 100% B in 20 minutes, at a flow rate of 0.4 mL/min. The sample was analysed by using a Lockspray source (Leucine, flowrate 0.3 ml/min), with ESI ionization and positive ion modes. The TOF mass range for the instruments is from m/z 50-2000. The analysis and assigning of peaks were carried out using the MassLynx software. Further, each m/z peaks corresponds to an $(M)^+$ or $(M+H)^+$ peaks were recorded using LC-MS.

Chapter 4 Shock Processing of Amino Acids: Part 1

Chapter overview

This chapter describes the experimental results obtained from shock processing of single amino acid glycine and mixtures of two amino acids glycine-glutamic acid and asparagine-glutamic acid. Shock experiments were performed using experiment setup MST1 as described in the previous chapter. Sample obtained after shock processing were analysed using SEM, TEM, IR spectroscopy and LC-MS. A detailed description is provided from the SEM and TEM observations on the formation of complex structures due to shock processing and analytical techniques revealed the chemical nature of shock processed residues.

4.1 Introduction

Impact delivery of organic compounds on planetary bodies such as the Earth is considered one of the possible methods for supplying prebiotic organics on the early Earth and thus may be significant in the origin of life (Chyba and Sagan, 1992, Osinski et al., 2020). Detection of biomolecules in meteorite samples has confirmed the abiotic origin of such molecules (Burton et al., 2012), with recent measurements confirming high abundances of amino acids (Glavin et al., 2020). The detection of simplest amino acid glycine from the sample return of stardust mission (Elsila et al., 2009) and further confirmation by ROSINA mass spectrometer in Comet 67P/C-G during the Rosetta mission (Altwegg et al., 2016) has also demonstrated that larger bodies in space can harbour important organics. Recent reports have suggested a mechanism of glycine formation in the interstellar medium without the presence of any energetic sources (Ioppolo et al., 2021). Studies have also shown chemical complexity in the interstellar environment due to shock compression resulting from icy dust collision (Cassone et al., 2018). The role of meteorites have been studied in assisting the synthesis of nucleosides and nucleotides (Ferus et al., 2015a, Bizzarri et al., 2020). Thus exogenous sources could have provided large quantities of biologically important organics and, therefore could have been a major source of the Earth's organic budget and may have played a crucial role in the origin of life (Ruf et al., 2018, McKay and Roth, 2021).

However, given the catastrophic nature of large-scale bolloid impact and its related events, the survival of organics in such extreme environments of high temperature and pressure remains uncertain. In addition, impact bombardment of comets and asteroids causes significant damage to the planetary surface upon impact, resulting in the formation of craters, melts and vapours (Melosh, 1989b). Impact induced shock provides a sharp increase in pressure and temperature due to shock compression and subsequent cooling due to expansion within a very short time scale which have the potential for driving complex chemical reactions (Blank et al., 2001, Goldman et al., 2010, Goldman and Tamblyn, 2013). Given the impact of extraterrestrial bodies on the prebiotic Earth during late heavy bombardment (LHB) approximately 4.0-4.2 to 3.5

billion years ago (Koeberl et al., 2000), though the timing, sources and mechanism are still debated (Bottke and Norman, 2017), and increasing evidence of the oldest form of life to be at or before approximately 3.8-4.0 billion years (Schidlowski, 1988, Mojzsis et al., 1996, Dodd et al., 2017, Lingam and Loeb, 2021), which coincides with the period of LHB, the role of impact bombardments in prebiotic chemistry and emergence of life on Earth must be explored (Chyba and Sagan, 1992).

As discussed in Chapter 1, many experimental and theoretical simulations are available in the literature that examines the role of impact processes in prebiotic chemistry and the origin of life. All of these studies have confirmed a wide number of biologically important molecules such as amino acids and nucleobases can be delivered or synthesized as a result of impact bombardment and related events. However, given the history of impact bombardment on Earth, these synthesized materials must have undergone multiple impact events. Studying the effect of sequential impact events and their influence on complex molecular synthesis remains in its infancy. Therefore, it is imperative to subject amino acids to impact-induced shock conditions if we are to understand the next step in the emergence of life after the formation of complex molecules. In the present study, we have investigated the effect of strong shock waves on amino acids in a shock tube. We exposed various amino acids to strong shock waves at temperatures of around 2500 K–8000 K. Our experimental conditions mimic a small portion ($<10^4$ K) of the extreme conditions experienced in real impact events.

4.2 Experimental Methodology

The simplest amino acid glycine and mixtures of amino acids asparagine-glutamic acid and glycine-glutamic acid were shock processed at various reflected shock temperatures using the experimental setup of MST1 as described in Chapter 3. The two combinations of amino acids (mixed in equal weight ratio) were selected as suggested by Miller & Orgel (Miller, 1974) that a sequence of positively charged, negatively charged and uncharged amino acids might have stereochemical basis. If a life based on proteins is possible only when random polypeptides can be synthesized from a small set of polypeptides that are capable of identical or complementary replication, so such combinations are possibly worthy for experimental study (Miller, 1974). Experimental parameters for the different experiments are detailed in **Table 4.1**. After shock processing the residue was left in the reaction chamber was collected and further analysed. Repeated experiments were performed to check the reproducibility of results. Initial experiments have shown that a very tiny amount of samples were recovered after shock processing, so we have to do repeated measurements at the same shock conditions many times to get sufficient samples for analysis and also, in some cases, we did a few experiments with a large amount of starting material. The quantity of samples for each run is shown in **Table 4.1**.

Table 4.1 Experimental shock parameters for different experiments.

S. No.	Run No.	Quantity (g)	Test gas pressure (Bar)	Shock Mach number	Reflected shock temperature (K)	Reflected shock pressure (Bar)
Glycine						
1	675	0.18	0.05	5.95	8080	28.4
2	677	0.18	0.154	4.67	5020	25.1
3	825	0.4	0.075	5.18	6150	25.3
4	826	0.4	0.05	5.55	7040	21.8
5	827	0.4	0.194	4.08	3870	16.3
Two mixture of amino acids (glycine & glutamic acid)						
6	823	0.4	0.075	5.25	6320	19.6
7	828	0.4	0.16	4.67	5020	16.8
8	829	0.4	0.029	5.80	7670	18.8
Two mixture of amino acids (asparagine & glutamic acid)						
9	696	0.2	0.25	4.21	4110	25.4
10	711	0.8	0.25	4.36	4410	25.1
11	726	0.5	0.25	4.27	4220	24.0
12	731	0.5	0.25	2.53	1570	3.2
13	830	0.4	0.075	5.20	6190	22.8
14	831	0.4	0.16	4.67	5020	22.0
15	832	0.4	0.029	5.80	7670	22.2

4.3 Results and discussion

4.3.1 SEM and TEM analysis

SEM observation of shock processed residues revealed a variety of complex microstructures in the residue synthesized as a result of shock processing. No such structure was observed in the sample before the shock. Unprocessed samples showed large micron-sized particles as shown in **Figure 4.1** for glycine and asparagine–glutamic acid mixture. The shocked sample of pure glycine revealed the formation of a distinct globule of ~ 45 to 50 μm diameter, with a smooth texture and a spongy appearance as shown in **Figure 4.2a**, showing resemblance with macrovesicle structures obtained from self-assembled peptide structures (Koley and Pramanik, 2012). Interestingly, a ribbon/thread structure stretching to a few tenths of a micron in thickness, was also observed (**Figure 4.2**). The length of these threads spans up to 100's of micrometre and a few of them spans up to millimeter length. These threads resemble fibril structures obtained from self-assembled peptide mixtures (Ridgley et al., 2012).

Further adding another amino acid, glutamic acid, in equal weight proportions with glycine, shows the formation of an entirely different macrostructure in the shocked sample. Small threads like structures and spherules were observed (**Figure 4.3a-c**). Floral patterns consisting of petals-like morphology were also observed in this mixture. These structures formed resemble hierarchical ordered floral structures viz. rose flower petals and shorter bunched threads. Similar hierarchically ordered structures, floral structures formed by diphenylalanine peptide, have been reported earlier with peony-like flower morphology (Su et al., 2010). A similar floral pattern was also observed in the shock processed mixture of asparagine and glutamic acid sample as shown in **Figure 4.4**. TEM observation of shock processes residues showed multi-layered porous structure with a membrane-like appearance in glycine as well as in two mixtures of amino acids (**Figure 4.5**). Thus a variety of micro and nanostructured materials such as fibrils, threads, macrovesicles, petals, and microporous structures were revealed as a result of shock processing of amino acids and some of them showing exciting resemblance with self-assembled peptide structures.

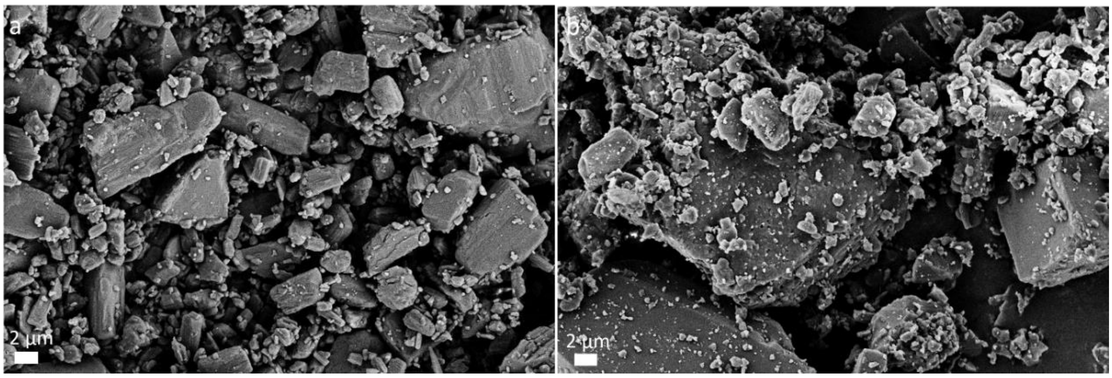

Figure 4.2 SEM micrograph of unprocessed mixture of (a) glycine and (b) asparagine-glutamic acid mixture.

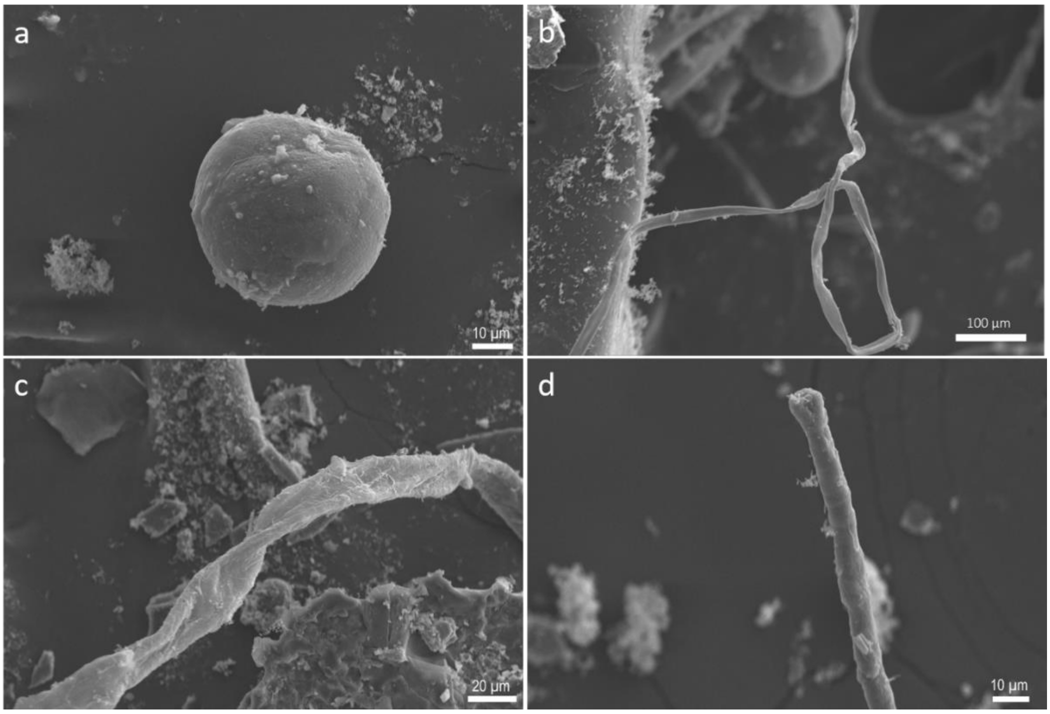

Figure 4.1 SEM micrograph of shock processed of glycine shows (a) globule structure, (b) fine filamentous thread structure, (c) magnified thread structure and (d) cylindrical fibril structure.

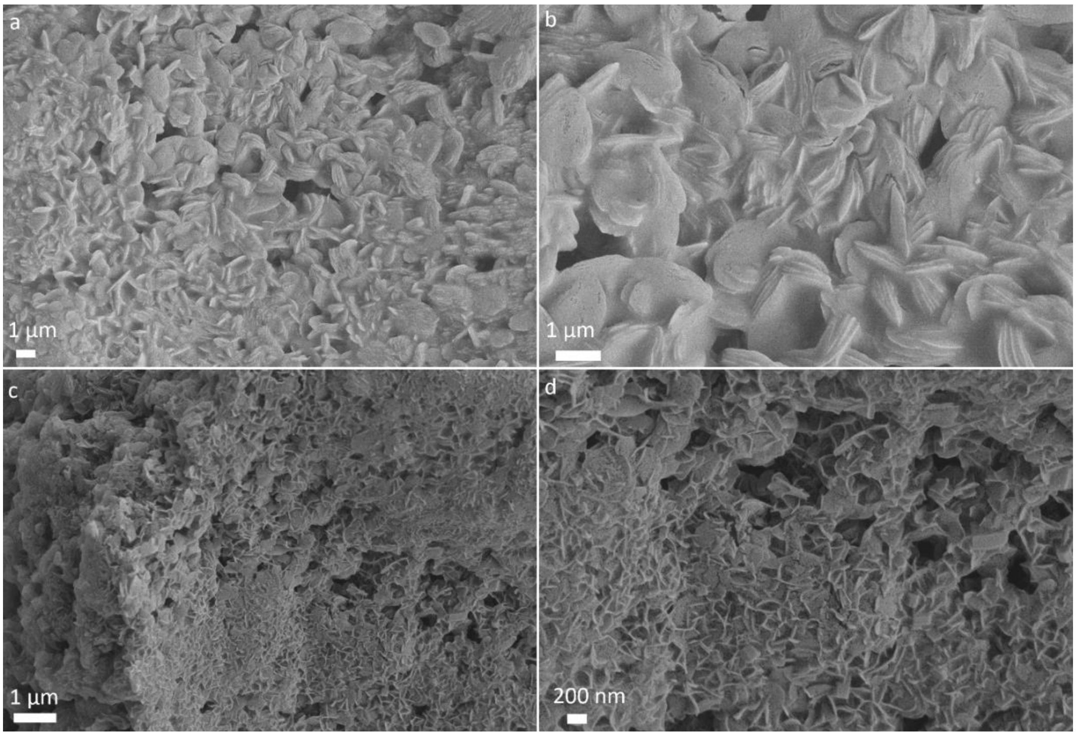

Figure 4.3 SEM micrographs of shock processed mixture of asparagine-glutamic acid mixture shows (a) petal like morphology, (b) petals at higher magnification and (c&d) aggregated fine threads at different magnifications.

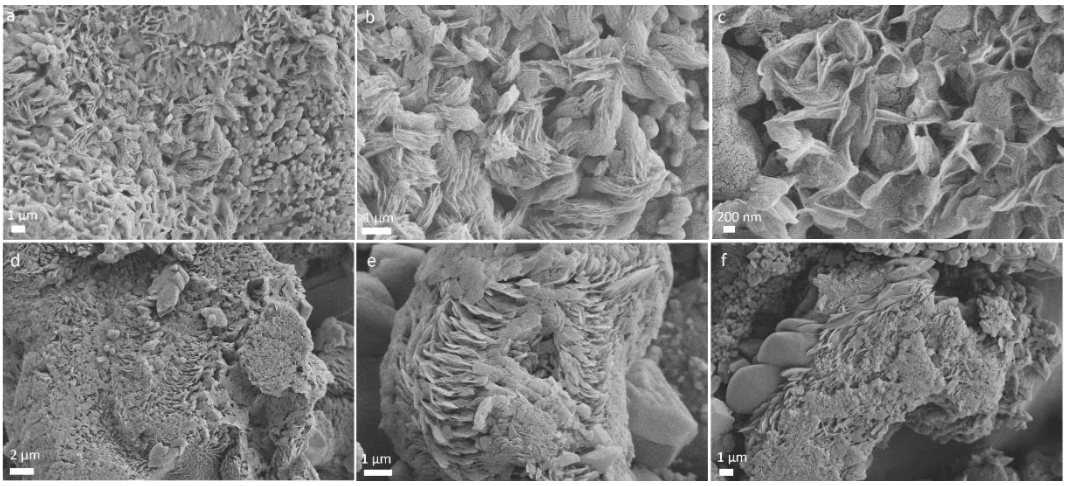

Figure 4.4 SEM micrographs of shock processed glycine- glutamic acid mixture shows (a) short threads and spherules, (b&c) fine structures at higher magnifications (d) floral patterns with petals and (e&f) various assembly of petals.

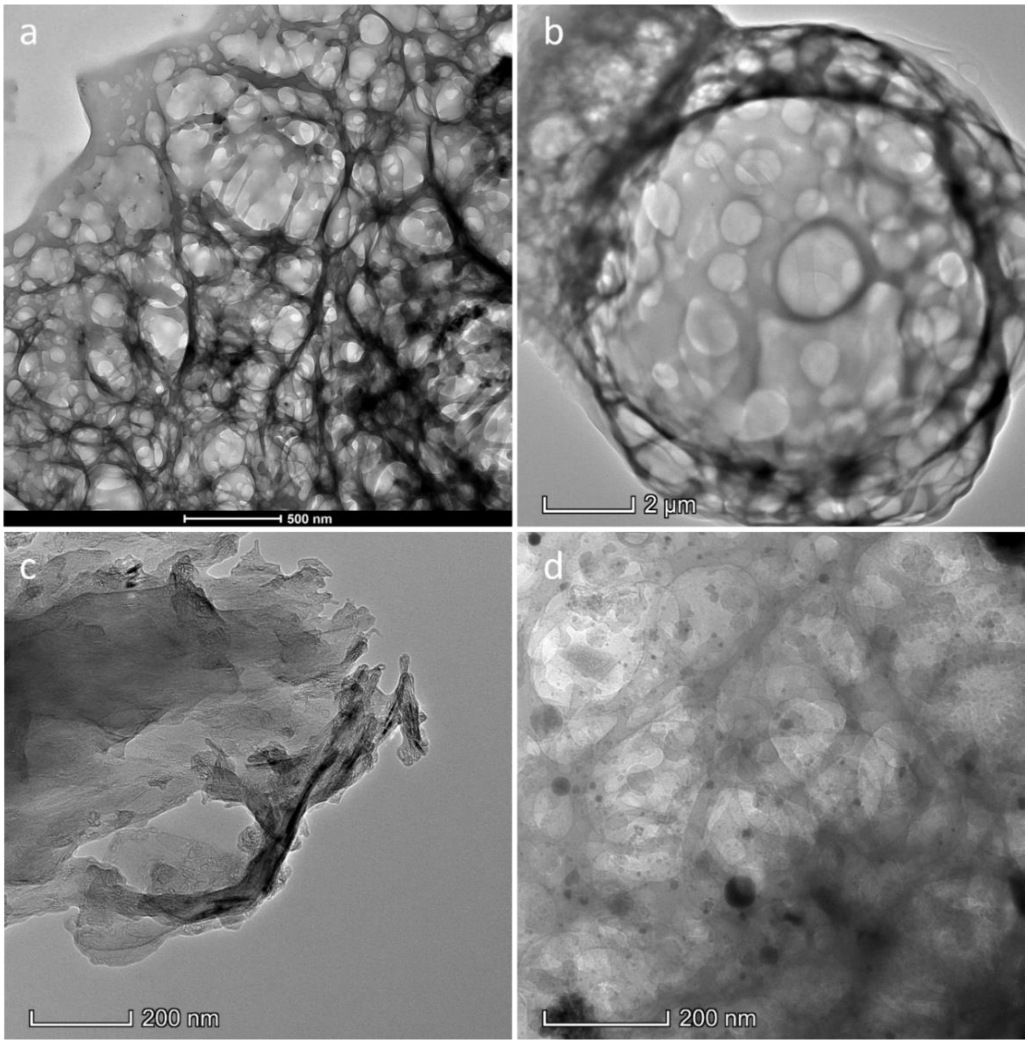

Figure 4.5 TEM micrographs of shock processed (a) glycine, (b) glycine-glutamine mixture and (c&d) asparagine-glutamic acid mixture

4.3.2 Infrared spectroscopy

IR spectroscopy was carried out for shock processed residue and unshocked sample as shown in **Figure 4.4**. Most of the peaks corresponding to various characteristic vibrational transitions can be seen in shock processed residue and unshocked samples. An additional weak absorption in 1750-1600 cm^{-1} can be seen in IR spectra of shock processed residue (red curve) corresponding amide I band, a signature of the peptide.

The absorption of amide I vibration (~1650 cm^{-1}) arises mainly due to C=O stretching vibration with a minor contribution from C-N stretching vibration (Barth, 2007).

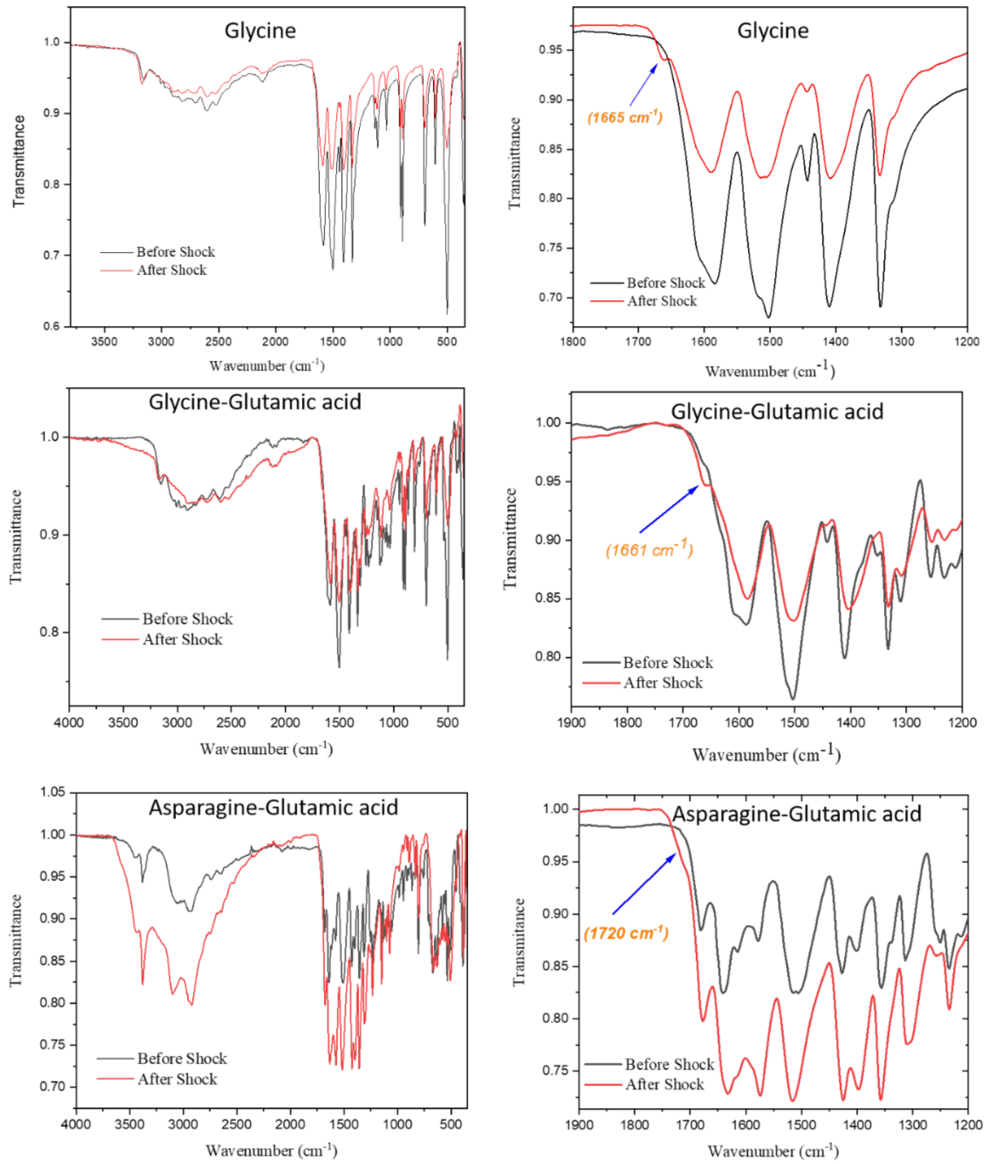

Figure 4.6 IR spectra of shock processed residue and unshocked sample of glycine, glycine-glutamic acid and asparagine-glutamic acid in full mid IR range (4000-500 cm^{-1}) and in 1900-1200 cm^{-1} range to see the signature of amide bands.

4.3.3 LC-MS analysis

We carried out mass spectrometry analysis of shock processed residue. The detailed methodology for LC-MS analysis is provided in Chapter 3. Various long polypeptides chains were identified in the mass spectra by comparing the theoretical value of peptides calculated from the peptide mass calculator by putting in the constituent amino acids (PeptideSynthetics). The identified peptides peaks from different samples and retention time are listed in **Table 4.2,** along with the calculated value and sequence from the peptide mass calculator.

Table 4.2 shows the mass number and retention time identified from the mass spectra, corresponding to the calculated mass and sequence of peptides obtained from the PeptideSynthetics peptide mass calculator.

Peak value (m/z)	Retention time (min)	Sequence	Calculated value
Glycine (G)			
474.8404	0.526	GGG	189.155
588.8224	0.526	GGGG	246.207
702.8044	0.526	GGGGGGGGGGGG	702.621
Asparagine (N)-Glutamic acid (E)			
133.0133	0.635	N	132.103
148.0091	0.635	E	147.115
262.9998	0.635	1 N & 1 E	261.218
277.0126	0.635	EE	276.230
391.1040	3.579	1 N & 2 E’s	390.334
649.2875	16.849	1 N & 4 E’s	648.564
Glycine (G)-Glutamic acid (E)			
148.0091	0.635	E	147.115
205.0119	0.635	1 G & 1 E	204.167
277.0125	0.635	EE	276.230

Shock processed glycine residue have shown the presence of long polypeptide chains in the residue. Among various peaks in mass spectra, we identified the polypeptide peaks corresponding to sequence to three, four and twelve glycines as sown in **Figure 4.7**. The mass spectra of shock processed mixture of two amino acids asparagine-glutamic acid sample is shown in **Figure 4.8 & 4.9**. Among various products, the presence of asparagine and glutamic acid was seen in the sample along with long polypeptides. This sample also showed different peptides chains of various sequences, as listed in **Table 4.2**. The mass spectra of shock processed glycine-glutamic acids are shown in **Figure 4.10**. Few peptides are also identified in these samples as listed in **Table 4.2.**

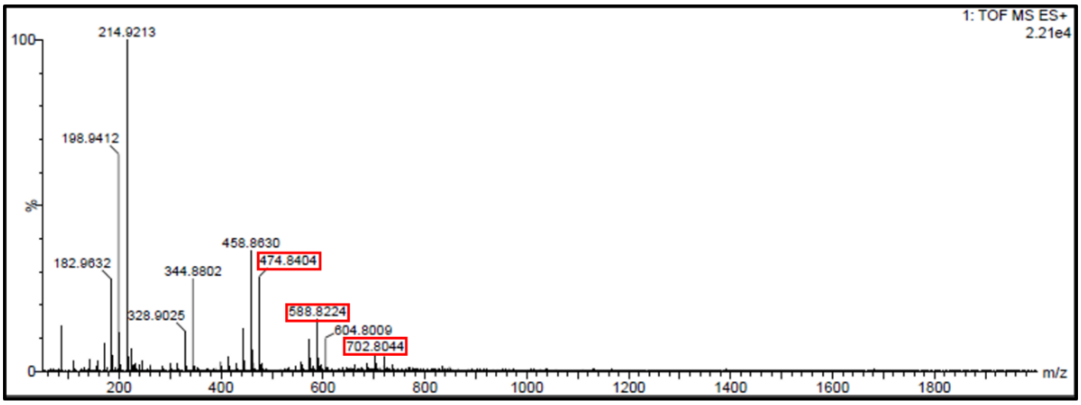

Figure 4.7 Mass spectra of glycine residue showing formation of long polypeptide chain, identified peaks 474.8404, 588.8244 and 702.8044 (corresponding to $[M]^{+}$) are shown in the red box.

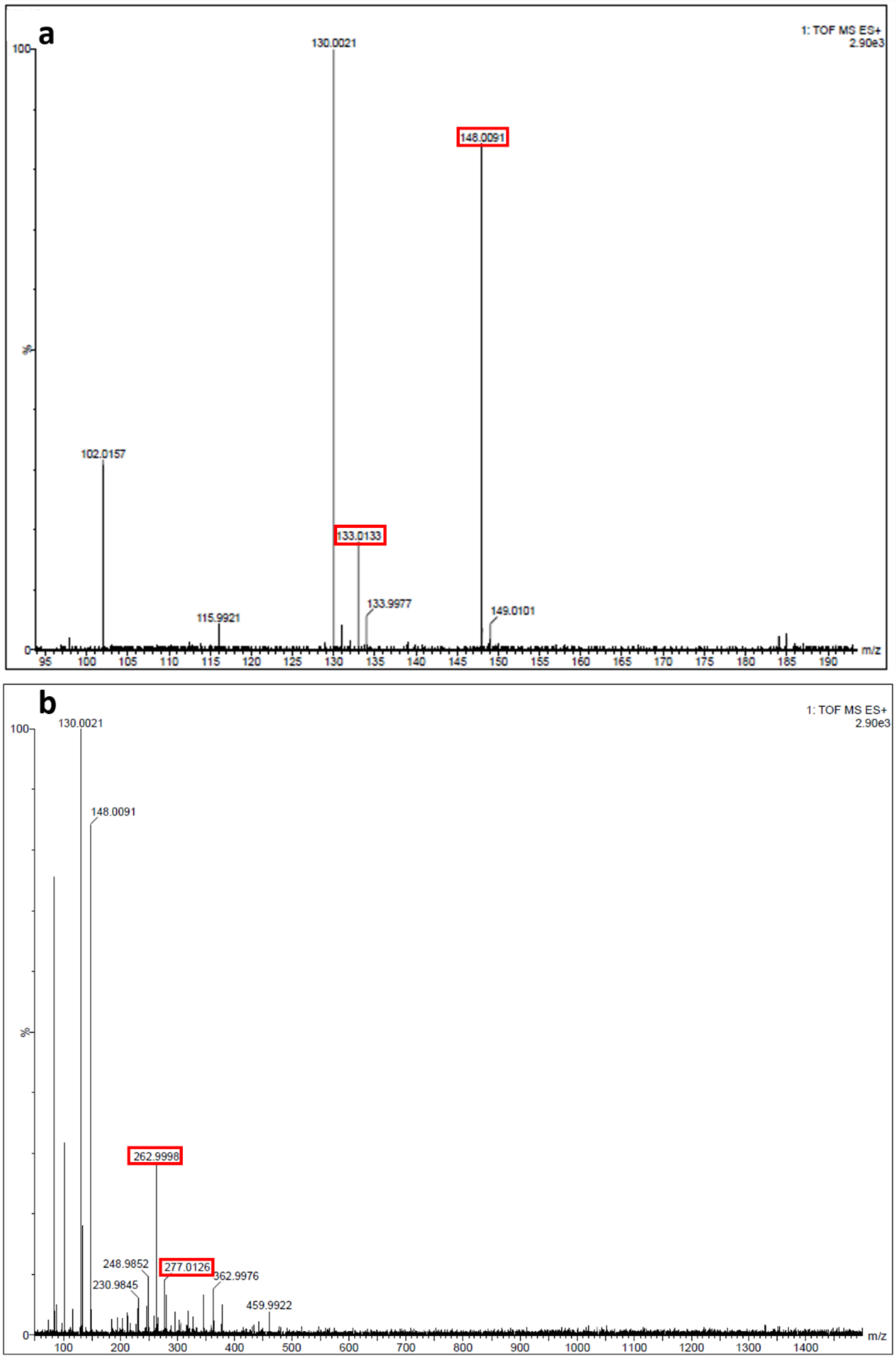

Figure 4.8 Mass spectra of mixture asparagine-glutamic acid residue showing formation of long polypeptide chain, identified peaks (corresponding to $[M+H]^+$) are shown in the red box. (a) 133.0133 & 148.0091 and (b) 262.9998 & 277.0126.

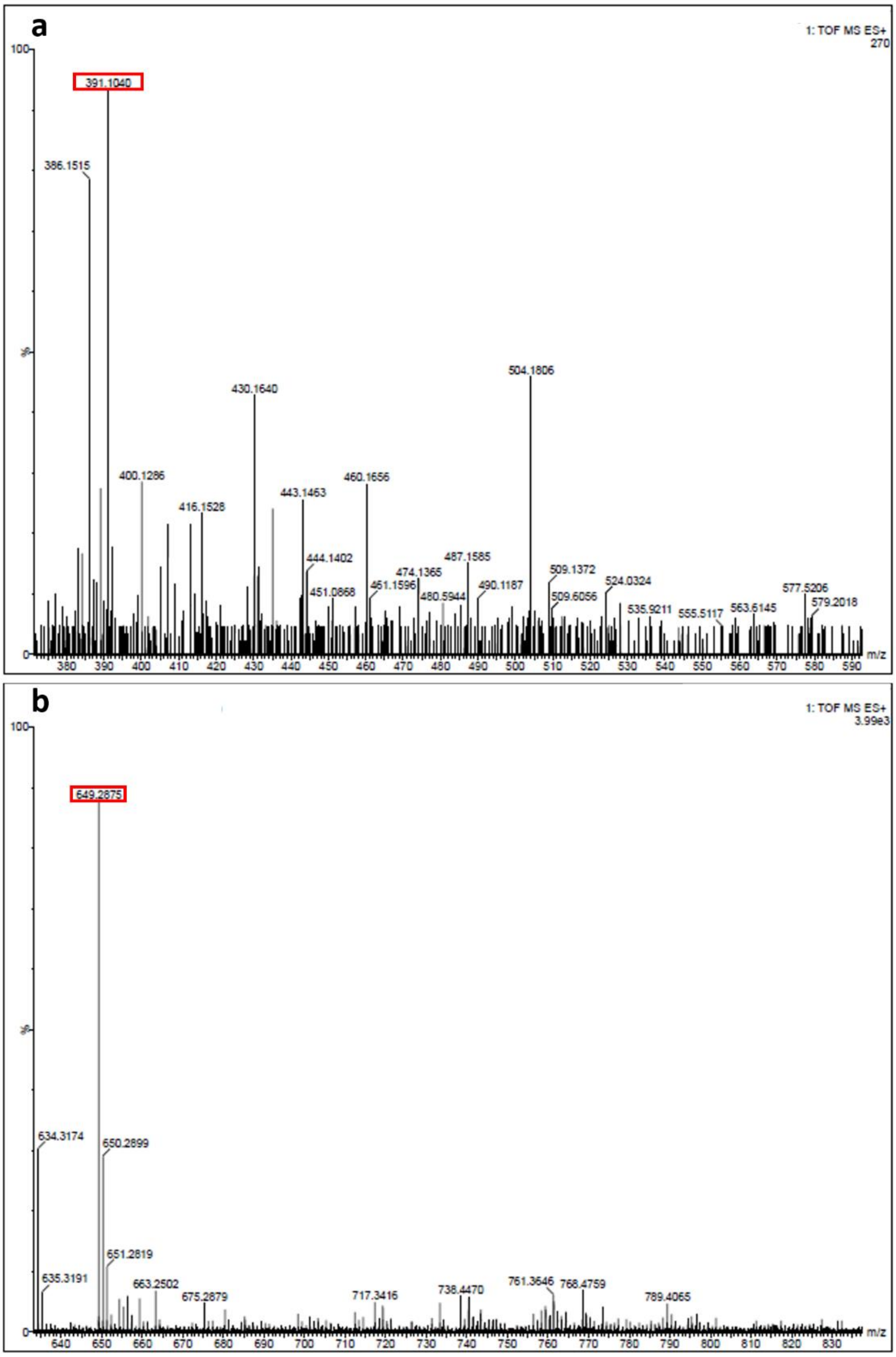

Figure 4.9 Mass spectra of mixture asparagine-glutamic acid residue showing formation of long polypeptide chain, identified peaks (corresponding to $[M+H]^+$) are shown in the red box. (a) 391.1040 and (b) 649.2875.

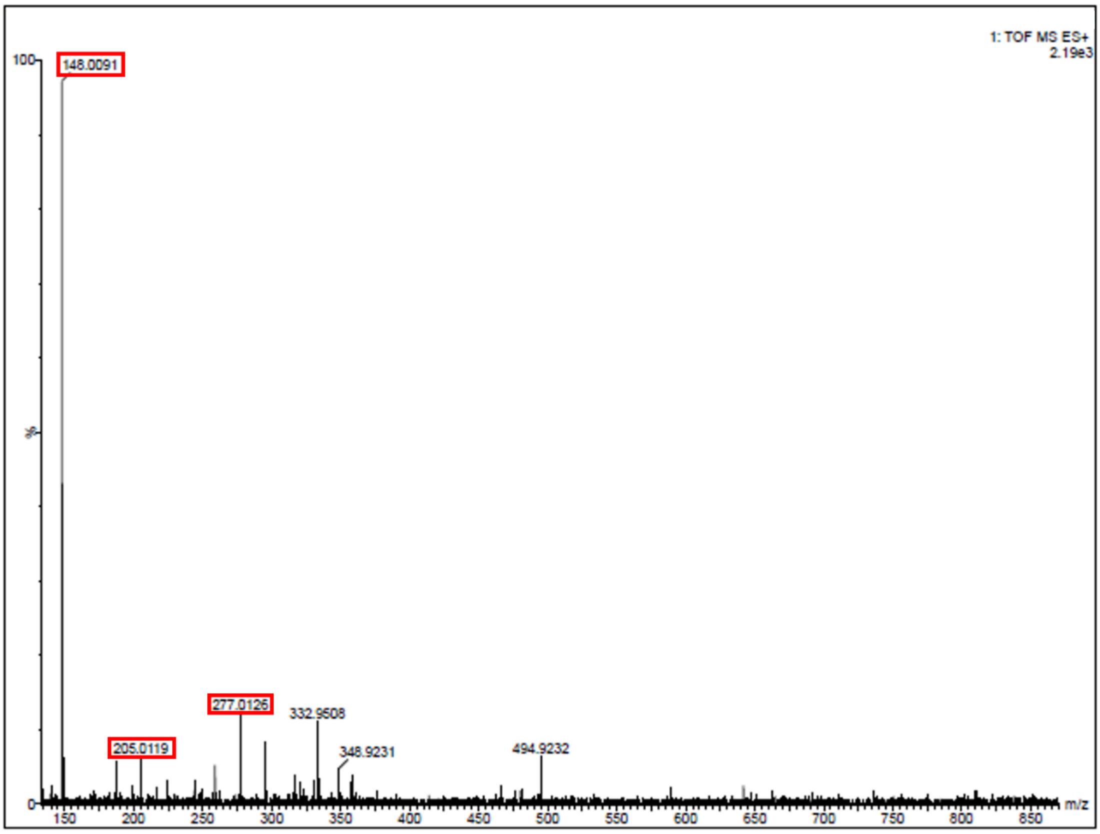

Figure 4.10 Mass spectra of mixture glycine-glutamic acid residue showing formation of peptide formation, identified peaks 148.0091, 205.0119 and 277.0125 (corresponding to $[M+H]^+$) are shown in the red box.

Proteins are an essential part of all living entities. The extant biology is characterized by an interconnecting network of biopolymers such as proteins, lipids, nucleic acids for their functioning, in which peptides play a central role in mediating these cellular networks because of their unique architecture and functionality and therefore considered as “molecular hubs in the origin of life” (Frenkel-Pinter et al., 2020). Abiotic synthesis of peptides is thus an essential step in the prebiotic chemistry that led to the emergence of life on primitive Earth. Various scenarios have been suggested on the synthesis of peptides on the prebiotic Earth which includes synthesis in hydrothermal vents and dehydrating conditions under dry and wet cycles (Lemke et al., 2009), synthesis triggered by activating agents (Deming, 2006, Huber and Wächtershäuser, 1998), presence of mineral catalysis (Danger et al., 2012, Lambert, 2008) and high energy protons and UV irradiation (Simakov et al., 1997, Tanaka et al., 2008). The experimental investigation carried out by Sugahara and Mimura (Sugahara and Mimura, 2014, Sugahara and Mimura, 2015) confirmed the amino acids oligomerized up to tripeptides when shocked at cryogenic condition simulating comet impacts (Sugahara and Mimura, 2014, Sugahara and Mimura, 2015). However, such long polypeptide chains have never been reported earlier, as revealed in these experiments with a combination of the same and different amino acids under impact induced shock conditions forming various architectures. More implications of these structures are discussed in the next chapter, where we have extended the experiments on shock processing to various other combinations of amino acids.

4.4 Conclusion

In this chapter, we have shown the formation of complex macroscale structures resulting from shock processing of amino acids, as revealed from microscopic observations. Single, as well as the mixture of amino acids, were shock processed at various temperatures showing a variety of structures. Infrared spectroscopy and mass spectrometry revealed that polypeptide chains are synthesized as a result of the shock processing of amino acids. These results elucidate our understanding of the role played by complex molecules and impact events in the origins of life.

Chapter 5 Shock Processing of Amino Acids: Part 2

Chapter overview

In this chapter, we have shown extended results on shock processing from the previous chapter to various other combinations of amino acids. Different combinations of amino acids were selected from the list of twenty proteinogenic amino acids and shock processed. Results from SEM analysis of shock processed residue are presented. A detailed description is provided on the microstructures observed in the meteorite samples from previous studies and its comparison with microstructures observed in shock processed residues.

5.1 Introduction

In the previous chapter, we have shown long polypeptide chains were synthesized as a result of shock processing of single amino acid glycine and combinations of two amino acids, glycine-glutamic acid and asparagine-glutamic acid, with the formation of complex structures revealed from microscopic observations. The spontaneous formation of these complex architecture from amino acids has important implications for the origin of life. Miller's experiments revealed that various amino acids were present in the prebiotic soup (Miller, 1953). Also, various amino acids were synthesized together from simple molecules due to impact shock processing (Bar-Nun et al., 1970, Martins et al., 2013). These findings suggest that the first polymers made from these building blocks must have a variety of amino acids and formed a complicated mixture. As different amino acids have different reactivity and some amino acids are more reactive than others, so the sequence would not have been completely random. It is known from the polymerization of amino acids that chances of having longer chain would have been difficult as the least stable peptides would have hydrolysed (Miller, 1974). So a steady state would have been achieved where synthesis and hydrolysis were balanced. At present, we do not entirely understand the nature of random polypeptides, which led to a steady-state mixture having a balance between synthesis and breakdown. Considering laboratory research into the fate of various combinations of amino acids in an impact-induced setting might be worthwhile to learn how such combinations may have evolved. Here we present result from many combinations of amino acids, shock processed at various reflected shock temperatures using experimental setup of MST1.

5.2 Experimental Methodology

The various combinations of amino acids (**Table 5.1**) were mixed in equal weight ratio and shock processed at various reflected shock temperatures using the experimental setup of MST1 as described in Chapter 3. The detailed experimental procedure is described in Chapter 3. Experimental parameters for the different experiments are detailed in **Table 5.1**.

Table 5.1 Experimental shock parameters for different experiments.

Run No.	Quantity(g)	Test gas pressure (Bar)	Shock Mach number	Reflected shock temperature (K)	Reflected shock pressure (Bar)
Sample 1 (Mixture of four amino acids) Lysine, Aspartic acid, Arginine, Glutamic acid					
694	0.2	0.1	5.34	6630	32.9
712	0.5	0.25	4.02	3770	19.5
819	0.5	0.20	4.32	4330	22.3
820	0.5	0.20	4.18	4020	17.6
833	0.5	0.075	5.09	5960	24.4
834	0.5	0.025	5.86	7850	20.1
Sample 2 (Mixture of eight amino acids) D-Alanine, L-Alanine, Glycine, DL –Valine, D-Norvaline, L-Norvaline, Aminobutyric acid, Aminoisobutyric acid					
719	0.4	0.25	4.20	4080	23
837	0.4	0.075	5.34	6540	24
838	0.4	0.1	4.92	5560	20.2
Sample 3 Mixture of seventeen amino acids (Glycine, Alanine, Valine, Isoleucine, Leucine, Proline, Serine, Aspartic acid, Glutamic acid, Isoleucine, Cysteine, Methionine, Asparagine, Glutamine, Arginine, Lysine, Histidine,)					
845	0.51	0.1	4.98	5700	26.4
Sample 4 (Mixture of 18 amino acids) (Glycine, Alanine, Valine, Leucine, Proline, Serine, Aspartic acid, Glutamic acid, Cysteine, Methionine, Asparagine, Glutamine, Arginine, Histidine, Phenylalanine, Lysine, Tyrosine, Tryptophan)					
676	0.186	0.055	5.63	7280	28.2
692	0.18	0.25	4.07	3850	22.2
814	0.5	0.25	4.22	4140	24.7
815	0.4	0.2	4.13	3970	15.5
835	0.54	0.075	5.29	6400	22.2
836	0.54	0.1	4.86	5430	22.8
Sample 5 (Mixture of 20 amino acids) Glycine, Alanine, Valine, Leucine, Proline, Serine, Aspartic acid, Glutamic acid, Cysteine, Methionine, Asparagine, Glutamine, Arginine, Lysine, Histidine, Phenylalanine, Tyrosine, Tryptophan, Isoleucine, Threonine					
727	0.5	0.1	4.89	5490	22.1
728	0.5	0.25	3.77	3820	19.7

A series of experiments were performed with different shock temperatures. These shock temperatures can be adjusted by changing the test gas pressure and bursting pressure by changing the diaphragm and groove thickness.

5.3 Results and discussion

5.3.1 SEM and TEM analysis

5.3.1.1 Sample 1

Sample 1, a mixture of four amino acids containing lysine-aspartic acid-arginine-glutamic acid mixed in equal weight ratios, was chosen based on a combination of positively charged, negatively charged and neutral amino acids, as suggested by Miller and Orgel (Miller and Orgel, 1974). They have suggested that a four letter system based on such combinations might have stereochemical basis. A series of experiments were performed with this combination of amino acids at different shock temperatures, as shown in **Table 5.1**. After shock processing, this mixture resulted in a dark black sticky residue. At a shock temperature of approximately 6630 K, SEM imaging of this sample showed long thick threads with irregular surface structures (**Figure 5.1a**) and a garden of tubular structures (**Figure 5.1b**) a much more surprising result, the formation of a porous cylindrical structure (**Figure 5.1c**), a few microns in diameter. Such porous and multi-chambered structures are feasible candidates for primitive abiotic cellularity due to their energy capture and conversion capacity (Zou et al., 2014). Various thread and folded structures were obtained at different temperatures and repeated experiments showed similar results.

5.3.1.2 Sample 2

In Sample 2, a mixture of eight amino acids was used, mixed in equal weight ratios and shock processed at various temperatures. These amino acids have all been shown to be synthesized together in the impact processing of a simple ice mixture (Martins et al., 2013). Given the possibility that all these amino acids can be synthesized together from simple molecules as a result impact induced reaction, we intended to investigate their fate under further impact-shock conditions. SEM observations of the shocked material showed entirely different structures. Long thick threads which span up to hundreds of microns with fine textures on the threads were observed, as shown in **Figure 5.2a**. These threads showed a twisted (**Figure 5.2b**) and folded (**Figure 5.2c**) appearance at various locations.

5.3.1.3 Sample 3

Sample 3 is a mixture of seventeen amino acids mixed in equal weight ratios. Among the twenty proteinogenic amino acids only seventeen amino acids were chosen, omitting the three amino acids containing a benzene ring (phenylalanine, tyrosine, tryptophan). Phenylalanine and tryptophan were shock processed individually, and they resulted in the formation of large quantities of soot formation. In SEM, these samples showed fine particles which are agglomerated together. When shock processed at a temperature of ~ 5700 K, this sample produced needle-type nanorod structures (**Figure 5.3a**), many of them locked together or branched from a common point (**Figure 5.3b**). Similar structures are shown in **Figure 5.3c**. In addition, many zigzag structures of varying sizes seem to be hanging with nanorods (**Figure 5.3c**).

5.3.1.4 Sample 4

By further increasing the number of amino acids to eighteen in the mixture (**Table 5.1**), mixed in equal weight proportion, a thick black sticky residue resulted and many different structures were observed, including threads and ribbons as well as twisted and cylindrical (**Figure 5.4**). Upon closer inspection, we could clearly see that the threads were made of small (about a micron size) features. The length of the threads formed was quite surprising as they spanned more than one mm. The formation of such long-range ordered structures from basic building blocks is crucial to complex biological systems with multiple functional properties (Liu et al., 2015). The twisted threads were observed to split (**Figure 5.4**), which is an indication of an even more complex structure. Most of the threads were observed to be solid; nevertheless, our visual inspections suggest tubular structures were also found (**Figure 5.4**).

5.3.1.5 Sample 5

Sample 5 was a mixture of all twenty proteinogenic amino acids being mixed in equal weight ratios and shock processed at a temperature of ~ 5490K. The shocked sample showed the formation of flat ribbon structures (**Figure 5.5a**), hollow tubular structures (**Figure 5.5b**) and folded sheet structures (**Figure 5.5c**).

So a variety of structures were observed when many amino acids were mixed and subjected to extreme shock conditions. As different amino acids possess different physicochemical properties, depending upon their size, charge and polarity of the side chain, etc., they can self-assemble into various structures depending upon the amino acid sequence (Mandal et al., 2014). The formation of these complex structures occurs as the shock heated gas interact with the sample in the reaction chamber within a ~ 2 ms time scale. The diverse range of morphological features was obtained from shock processing of amino acids of various samples. Overall, the effect of impact shock on amino acids resulted in residues that demonstrated the formation of structures that resembled supramolecular cellular structures, such as fibrils, α-helical peptides, thread like microfibrils and self-assembled hollow nanotubes. In nature, filamentous proteins, such as actin polymers, microtubules, etc. are composed of monomeric building blocks. These nanosized peptides assemble spontaneously or by other chemical attraction or bond formation processes to form fibers and filaments that are a few micrometers in length. These characteristic structures can be observed using electron microscopy.

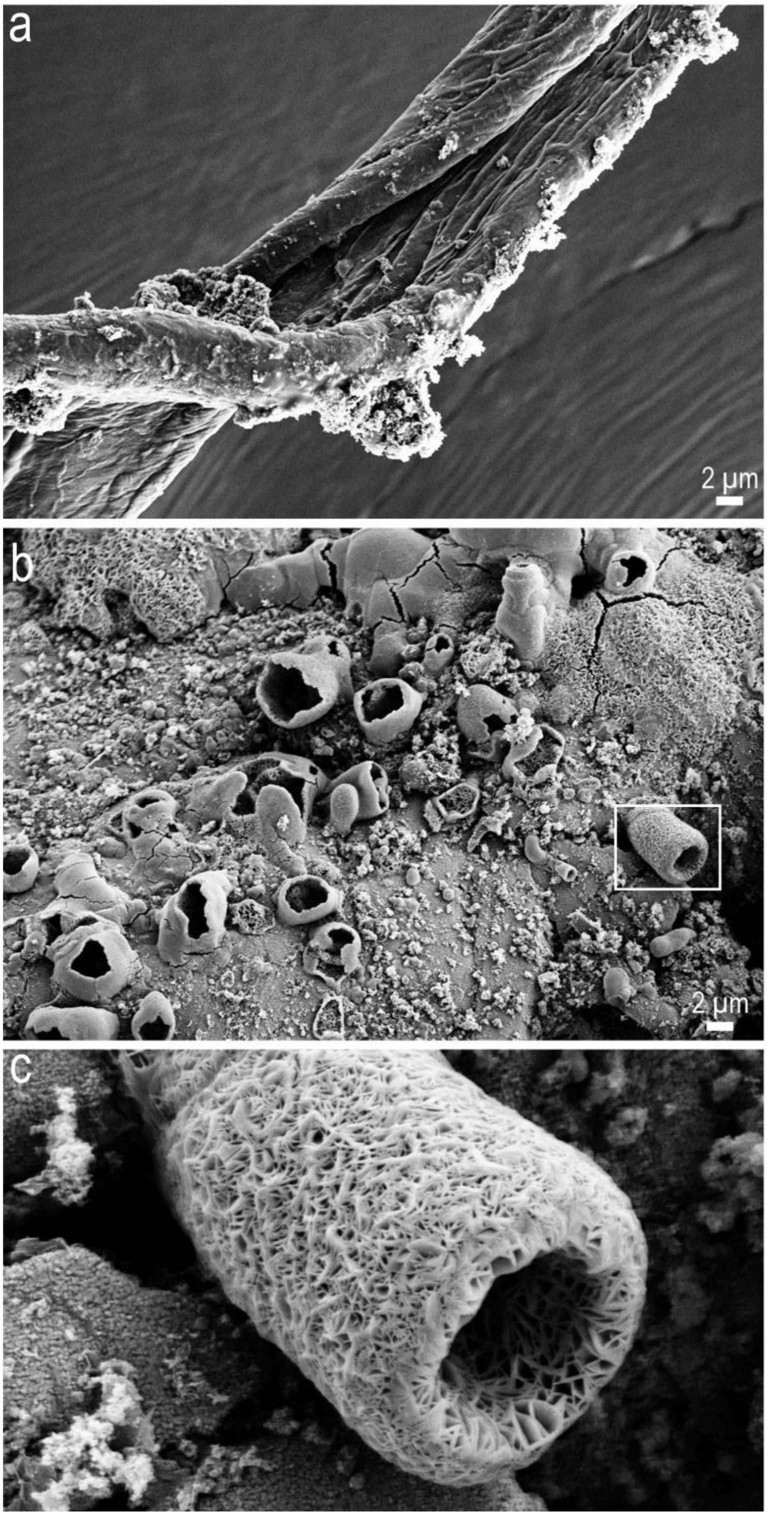

Figure 5.1 SEM images of residues obtained after shock processing of mixture of four amino acids (a) thick thread feature containing fine threads running all along, (b) shows many porous features and (c) the porous cylindrical feature.

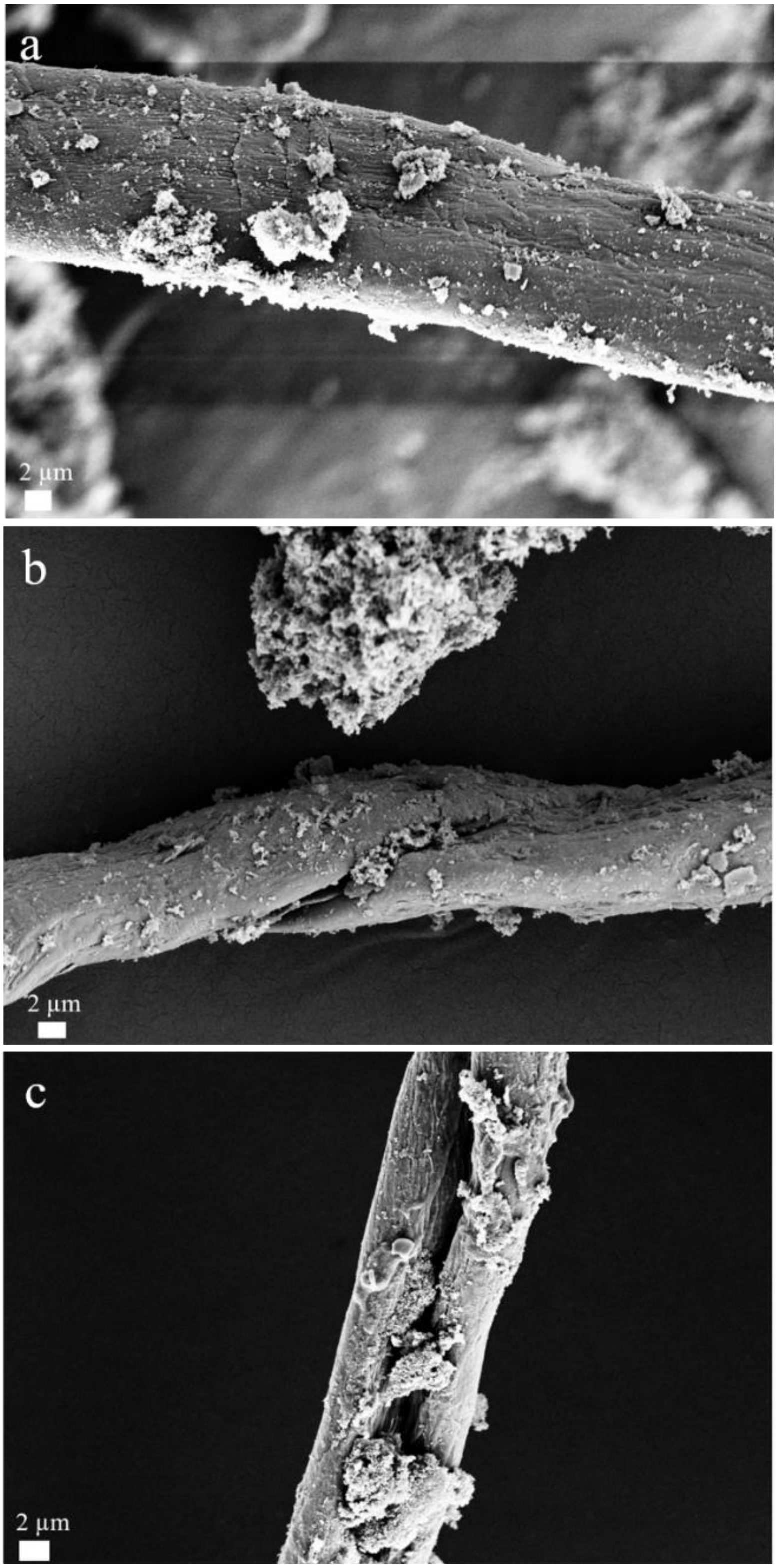

Figure 5.2 SEM micrograph of shocked sample 2 (containing eight amino acids) showing (a) Long thread morphology with fine surface texture, (b) twisted thread morphology and (c) folded threads.

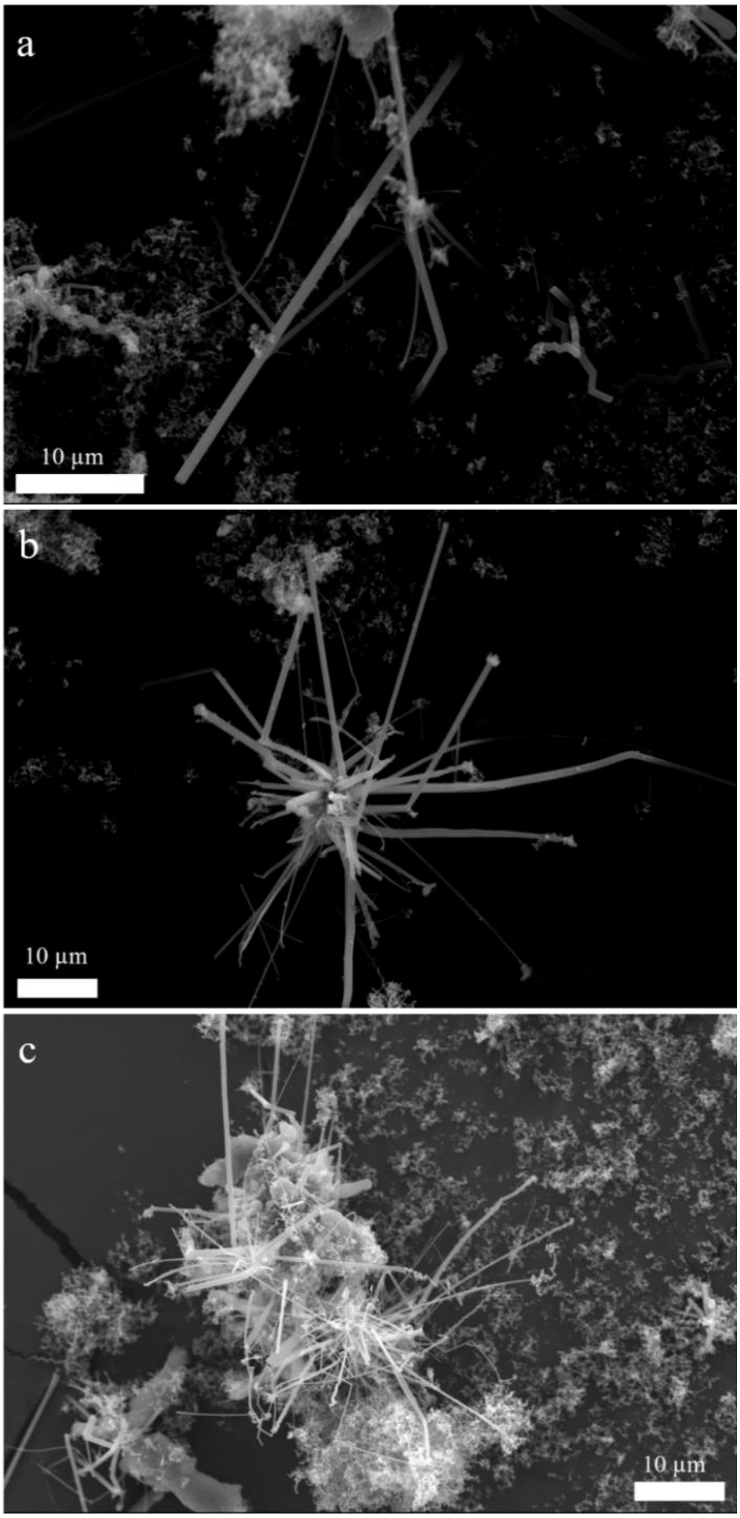

Figure 5.3 SEM micrograph of shocked sample 3 (containing seventeen amino acids) showing (a) Rod-like morphological structure, (b) branching structure and (c) zigzag structures at various length scale.

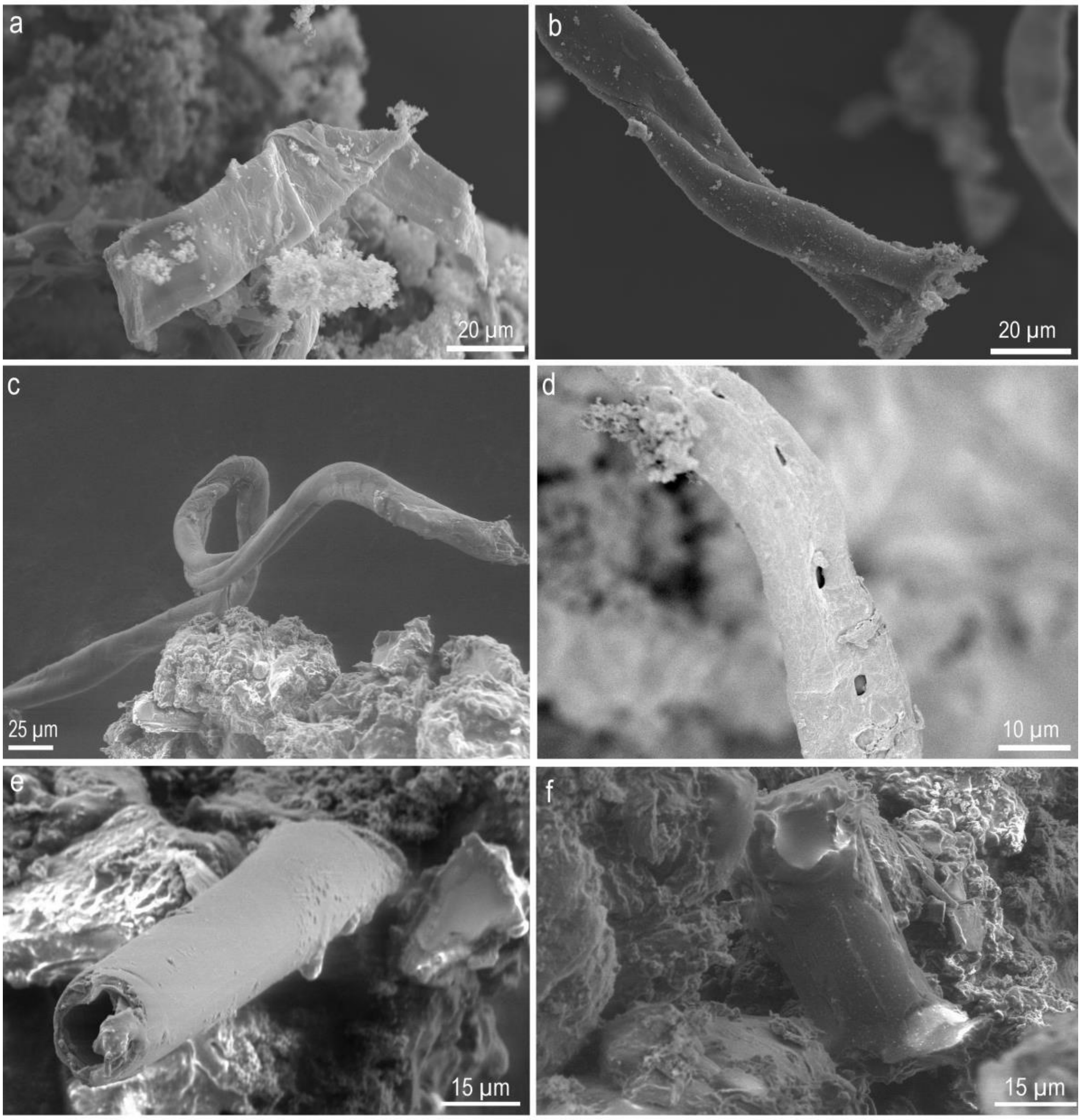

Figure 5.4 SEM images of the residue obtained after shock processing of sample 4 (mixture of eighteen amino acids). Several features, including (a) a thin ribbon, (b) a helical structure, (c) a branching filamentous thread and (d–f) hollow tubule structures, were observed.

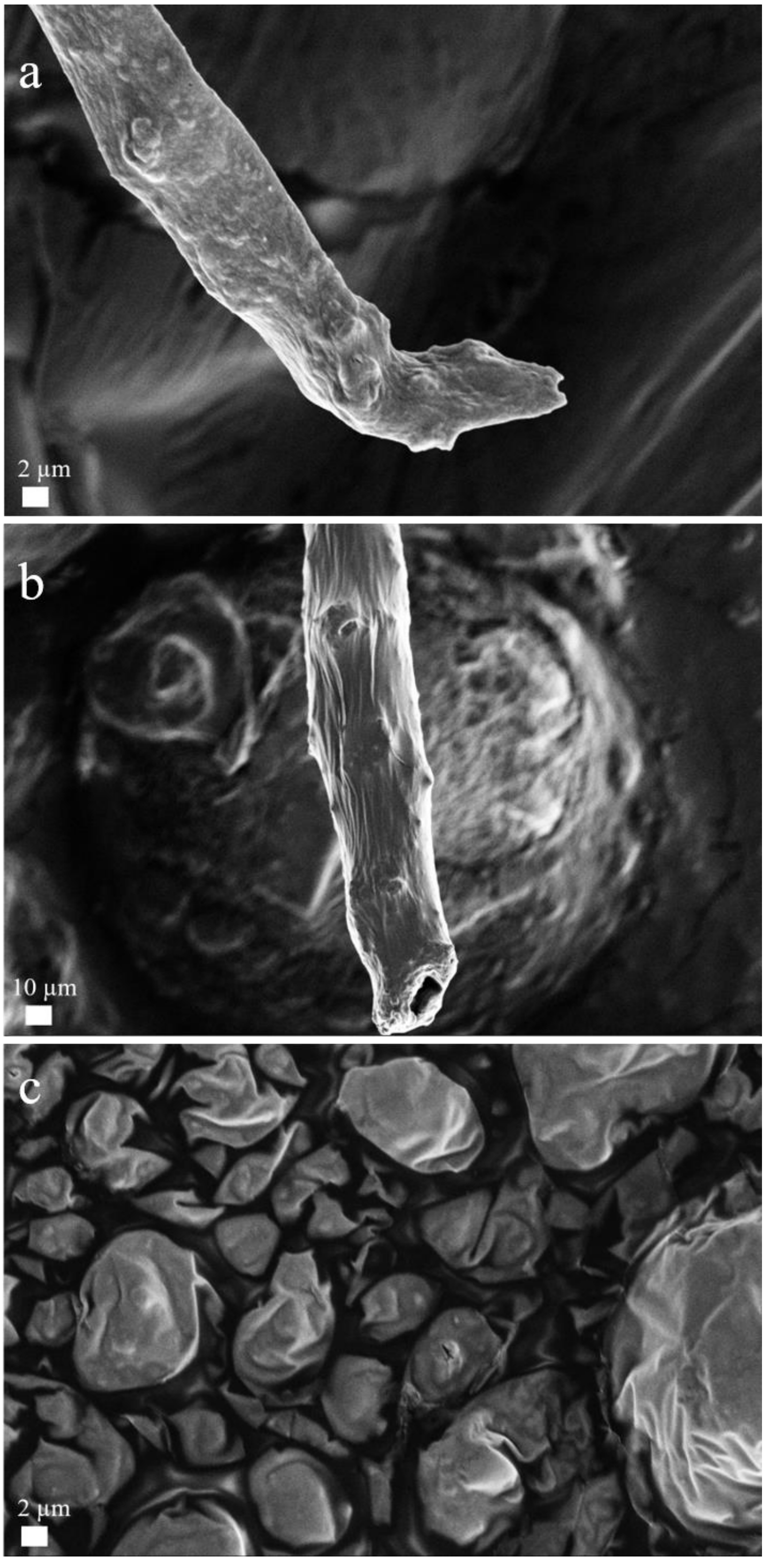

Figure 5.5 SEM micrograph of shocked sample 5 (containing twenty amino acids) showing (a) Micro-ribbon structure, (b) tubular structure, (c) folded sheet.

5.3.2 Microstructures and the origin of life

The first step among many challenges in the origin of life is to look for a simple structure formed by self-assembly, which is as complex as to take the properties of the biological system and how on the early Earth environment these processes happened. However, a great challenge remains on designing of such structural architecture from basic ingredients in the plausible prebiotic environment (Szostak et al., 2001, Szostak, 2009, Mann, 2012, Cardoso et al., 2020). The role of synthetic microstructures in the origin of life has been discussed previously, and various prebiotic conditions have suggested on the synthesis of such structures, which includes quenched spark discharge experiments (Folsome, 1976), formation of lipid-like structures (Simionescu et al., 1985, Simionescu et al., 1982, Simionescu et al., 1981), tubular structures in mineral surfaces (Parsons et al., 1998). Various protocellular structures were obtained from polypeptide formation from four amino acids simulating in hydration-dehydration cycle of the tidal pool (Yanagawa et al., 1988). Microspheres were synthesized from simple molecules under the simulated condition of prebiotic times (Valladas-Dubois and Prudhomme, 1983). Lipid-like self-assembling peptides were synthesised from amino acids forming tubular and vesicle structures (Zhang, 2012). The formation of complex organized structures, as revealed in the present investigation resulting from building blocks of life from impact induced processes, has significant implications for the origin of life. Such a rich abundance of structures revealed by microscopic technique seem to achieve the combination of two fundamental characteristics in the context of life, i.e., structural order and complexity (Mayer, 2020). It has already been shown that vesicle membrane like structures may be formed by exposure of irradiated prebiotic compounds to water (Dworkin et al., 2001). Electrostatic interactions induced by short, positively charged, hydrophobic peptides may then attach RNA to vesicle membranes and thus the first forms of life may have been simple cells containing systems of peptides and short strands of nucleic acid, such as RNA.

5.3.3 Implications to the microstructures observed in meteorites

The various features reported in our studies have a striking resemblance to microstructures observed in some meteorites (Claus and Nagy, 1961, Mamikunian and Briggs, 1963). These microstructures were titled as “organized elements” by Claus and Nagy, 1961 (Claus and Nagy, 1961), which resembled biological forms, but their biogenic origin was unknown, and they were also excluded as being of terrestrial contamination (Nagy et al., 1963). However, the existence of such structures in meteorites was discussed in detail and no convincing evidence was found concerning their origin (Anders and Fitch, 1962, Briggs, 1962, Fitch et al., 1962, Mueller, 1962). Further studies identified these structures as microfossil remains (Claus and Nagy, 1961, McKay et al., 1996, Nagy et al., 1962). Hoover et al. (Hoover et al., 2004) and Hoover (Hoover, 2011) also deciphered these elements as microfossils of extraterrestrial life forms, indigenous to the meteorite, by comparing these structures with living and fossilized cyanobacteria. However, our results on the creation of microstructures in shock processed amino acids give a more plausible explanation for the formation of these structures in meteorites when they are subjected to impact induced shock events. A comparison of the structures we have observed with similar structures in several meteorites is shown in **Figures 5.6-5.9**. The striking similarities between the two suggest that shock induced processing of amino acids, known to be present in meteorites, can lead to the formation of microstructures.

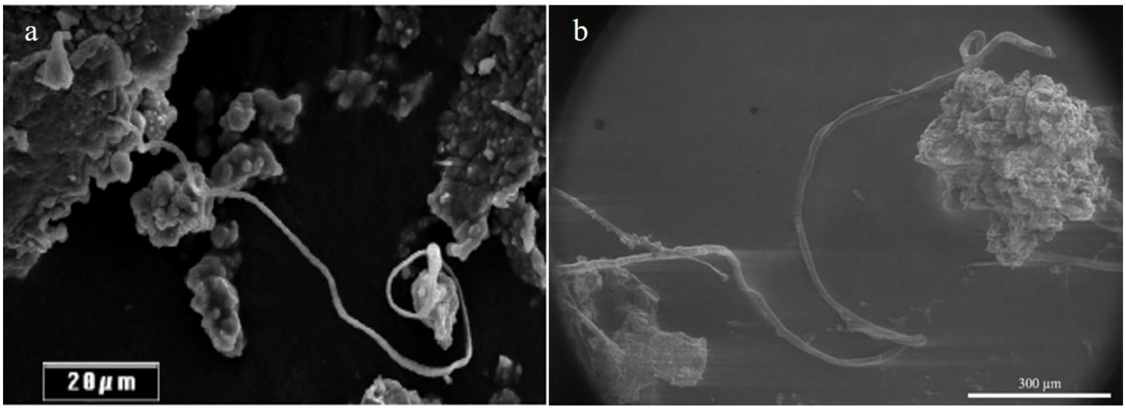

Figure 5.7 (a) A long helical coil observed in the Orgueil meteorite [32] and (b) a similar long thread seen in shock processing of amino acids.

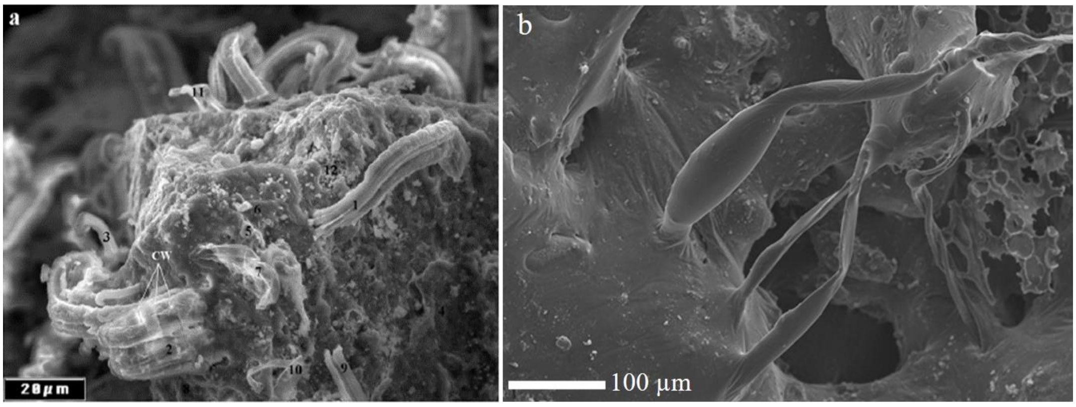

Figure 5.6 (a) Shows embedded filaments in freshly fractured fragment of Orgueil meteorite [32] and (b) Embedded filament observed in shock processed 18 mixtures of amino acid.

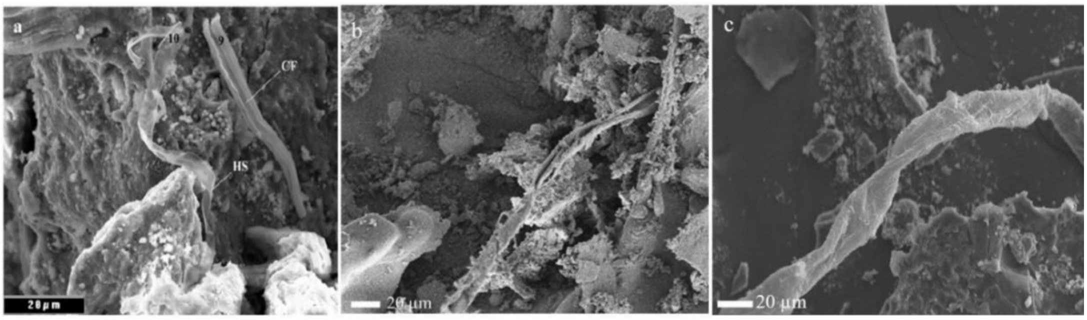

Figure 5.8 (a) Helical filament and collapsed filament in Orgueil meteorite [32], (b) Similar collapsed filament observed in after shock processing of glycine residue and (c) Twisted filament in glycine residue similar to filaments observed in meteorite.

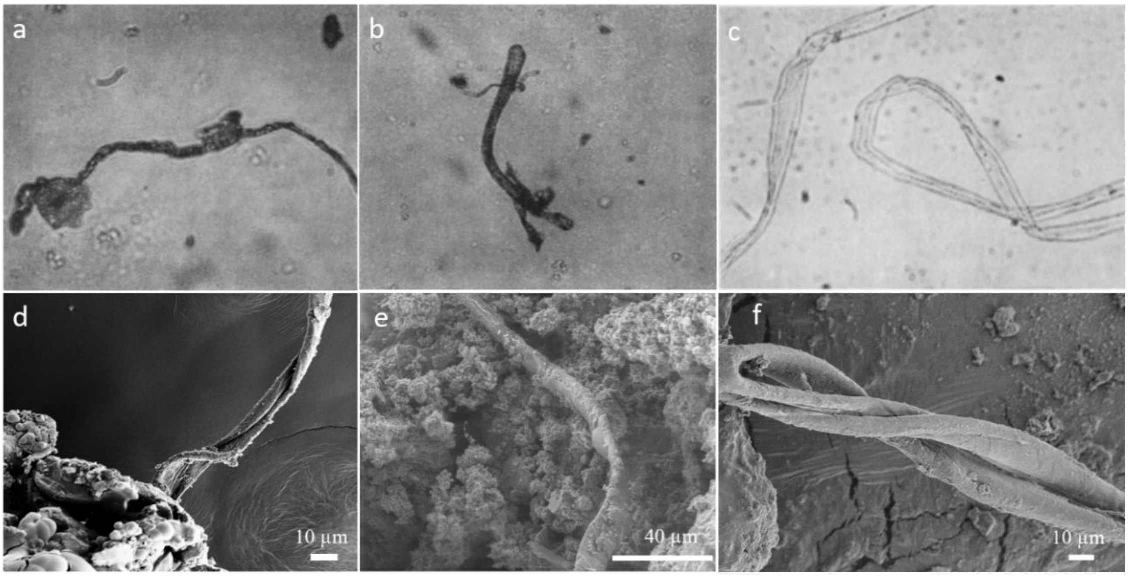

Figure 5.9 Photomicrographs of filamentous structures observed of size range ~ 20 μm in (a) Mighei meteorite, (b) Murray meteorite, (c) Dimmit meteorite [23] and (d–f) similar structures observed in SEM micrographs of shock processed residue of amino acid.

5.4 Conclusion

In this chapter, we have investigated the effect of strong shock impact at extreme thermodynamic conditions on the mixtures of several amino acids, which provides insight into the role of impact events in prebiotic evolution and origin of life. SEM analysis provided valuable insights into the self-assembled complex architectures. These structures resembled supramolecular cellular structures, such as fibrils, α-helical peptides, thread-like microfibrils, hierarchical ordered floral structures and self-assembled hollow nanotubes. Furthermore, microstructure analysis of the shock processed amino acids using electron microscopy revealed hierarchical formation and assembly of molecular structures that may be produced in impact shock to meteorites and may explain some of the structures revealed in some meteorite samples in response to impact shock in meteorites. In future endeavors, we expect this research work will expand towards the formation of more complex structures that are closer to biological architectures, not only in structural resemblance but also in performance, by considering the role of other functional biomolecules, such as nucleobases, fatty acids, nucleic acids, etc.

Chapter 6 Hypervelocity Impacts on Amino Acids Embedded in Water Ice

Chapter overview

This chapter reports the experiments in which we shocked ice mixture of amino acids analogous to those found in icy bodies of the solar system by firing a stainless steel projectile using the light gas gun facility to simulate hypervelocity impacts of icy bodies onto rocky surfaces and vice versa. Various batches of amino acids were shocked, and ejected material were analysed. Microscopic observations provided fine morphological details of ejecta. Mass spectrometry was applied for the inspection of the presence of long polypeptide chains. Results are discussed on the potential role of the impact process in the chemical evolution that led to the emergence of life on the Earth and applicability of these results to understand the impact shock chemistry on icy bodies of the solar system.

6.1 Introduction

Ices are widespread in the solar system. They have been detected on planetary surfaces such as Earth and Mars, planetary satellites such as satellites of Jupiter and Saturn, on small bodies such as comets and Kuiper belt objects. Water is most common among the various volatiles which has been detected in every planet and/or their satellites except Venus. Over the past few decades, ground and space-based observations have revealed a variety of ices composed of carbon, oxygen, nitrogen and sulphur bearing species are present on icy satellites (Clark et al., 2013). Icy satellites with primordial surfaces can reveal a lot about the status of the early solar system and the range of components there. Icy objects with more processed surfaces show how the initial compositions has changed over time. Ice composition varied because of various endogenic and exogenic processes. Exposure to UV photons and high-energy charged particles may modify the chemical composition of icy planetary, but impact bombardment may also play a role in chemical modification. As it is evident that impacts are widespread in the solar system and the record of impact craters are present on the icy satellites (Burchell, 2013), impacts may have played a crucial role in modifying the chemical composition of icy satellites at a larger scale (Nna-Mvondo et al., 2008). Here we perform a series of experiments related to impacts on icy bodies using LGG facility of the University of Kent as detailed in Chapter 3. These experiments simulate the impacts of icy bodies on the rocky surfaces (for example impact of icy comets onto the Earth) as well as impact of rocky bodies on icy surfaces (impacts on icy satellites) and results are applicable for both the scenario. The previous study has shown variety of amino acids can be synthesized as a result of such impact process (Martins et al., 2013). Simple ices and the organic precursors of the building blocks of life, such as amino acids, have been found on comets (Elsila et al., 2009, Altwegg et al., 2016). Thus it is imperative to understand the fate of amino acids in impact shock environments to explore further the role of impact processes in the prebiotic evolution.

6.2 Experimental methods

The hypervelocity impact experiments were performed utilizing a two-stage light gas gun facility at the University of Kent, as detailed in Chapter 3. In the present investigations, we impacted a spherical projectile, 1 mm in diameter, at a velocity of approximately 5 km s^{-1} on amino acid-water ice targets. The rationale for the choice of projectile velocity is to mimic maximally the physical condition observed in natural impacts. The average impact speed for the observed short period comets is approximately 24 km s^{-1} which generates a pressure of more than 200 GPa upon impact (Hughes and Williams, 2000). Such pressure values are clearly higher than the peak shock pressure (**Table 6.1**) observed in our experiments and nearly impossible to simulate in such experiments. However, there are several plausible scenarios where the pressure values in natural impacts can be reduced sufficiently, such as deceleration of comets due to atmospheric drag, airburst in the atmosphere, fragmentation and oblique impacts (Chyba et al., 1990, Bland and Artemieva, 2006). Further, in a single impact pressure values can differ significantly as pressure are distributed heterogeneously around various points of an impacting object (Pierazzo and Melosh, 2000). Thus a range of pressure values are offered in nature impacts and we have tried to simulate a part of such values in our experiments. The amino acid water ice targets were prepared in the laboratory, as detailed in Chapter 3. The amino acids were procured from Sigma Aldrich with purity level > 99%. Several ice batches are prepared with different compositions, as listed in **Table 6.1**. The experimental parameters for different experiments are also listed in **Table 6.1**. These ejected materials after impact, were left in the chamber to dry out completely and further collected. The foils containing the residues were sealed in boxes and transported to PRL Ahmedabad from the University of Kent. These residues were further analysed using SEM, TEM and LC-MS.

Table 6.1 Experimental parameters for each experiment.

Target	**Impact velocity (km s^{-1}) accurate to ±1%**	**Peak shock pressure (GPa)**	**Ejecta**
Pure water ice	4.80	29.06	No residue
Glycine	5.09	32.15	White ejecta
Glutamine	4.66	27.63	White ejecta
Glycine-Glutamine	4.77	28.75	White ejecta

6.3 Result and discussion

As revealed in previous chapters fascinating structures were produced by shock processing of amino acids, here also we explored intricate details of surface morphology and structures in the ejecta. Microscopic observations revealed that remarkable morphological features are present in the ejecta. Ejecta from different targets yielded unique morphological characteristics. Glycine ejecta showed the formation of large clumps, 100's of microns in size, in the ejecta, as shown in **Figure 6.1a**. More magnified images showed various sharp structures clumped together, as shown in **Figures 6.1b&c**. Ejecta from different places of foil showed similar results.

When observed using FESEM, ejecta from shocked glutamine revealed an entirely different pattern. Large dendritic structures with various branching features were observed with an upward orientation from nucleation points ranging in size up to few millimeters, as shown in **Figure 6.2a**. More magnified structures of these branching features are shown in **Figure 6.2b&c**. These dendritic structures resemble dendritic structures observed in the self-assembly of peptides (Konda et al., 2016). Apart from dendritic structures, a spherical assembly of rods was also found as shown in **Figure 6.2d**. More magnified images show these rods to have geometrical shapes and to be of varying size, typically tens of micrometres (**Figure 6.2e&f**). Images were from multiple sites on the aluminium foils were analysed in the SEM and similar structures were found.

Ejecta from the mixture of glycine-glutamine revealed large aggregates, ranging upto hundreds of microns (**Figure 6.3a**). More magnified images revealed nest-like intertwined organized structures formed by association of thin ribbons of length tens of micrometers (**Figure 6.3b&c**). Sample collected from another site on the foil for the same mixture, we found different structures as shown in **Figure 6.3d**. An array of needle-shaped fibres hundred micrometers in size were observed oriented in various directions. More magnified microstructures are shown in **Figure 6.3e&f**.

Ejecta residues were also subjected to a transmission electron microscope. TEM micrographs of glycine and glycine-glutamine samples are shown in **Figure 6.4**. TEM observation of both the samples showed a multi-layered porous structure with membrane-like appearances on the nanometre scale.

During target preparation for experiments, while dissolving the amino acid in the water, control samples were prepared by drop-casting the amino acid-water solution on aluminium foil. These samples, when analysed in the SEM did not show any such l organized structure formation as shown in **Figure 6.5**, only large clumps are observed with less apparent structures compared to the ejecta from impacts. This confirms that the organized structure that is observed in the ejecta materials results from impact induced processes.

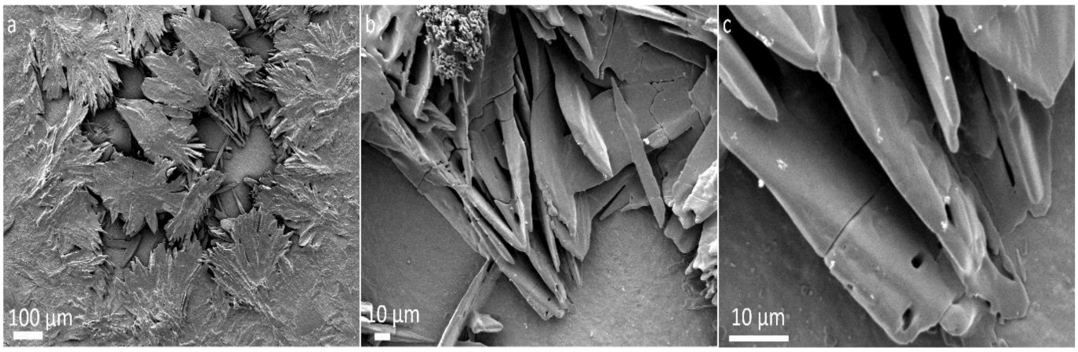

Figure 6.1 SEM micrographs of glycine ejecta after impact show (a) large clumped structures and (b&c) more magnified images reveal sharper structures.

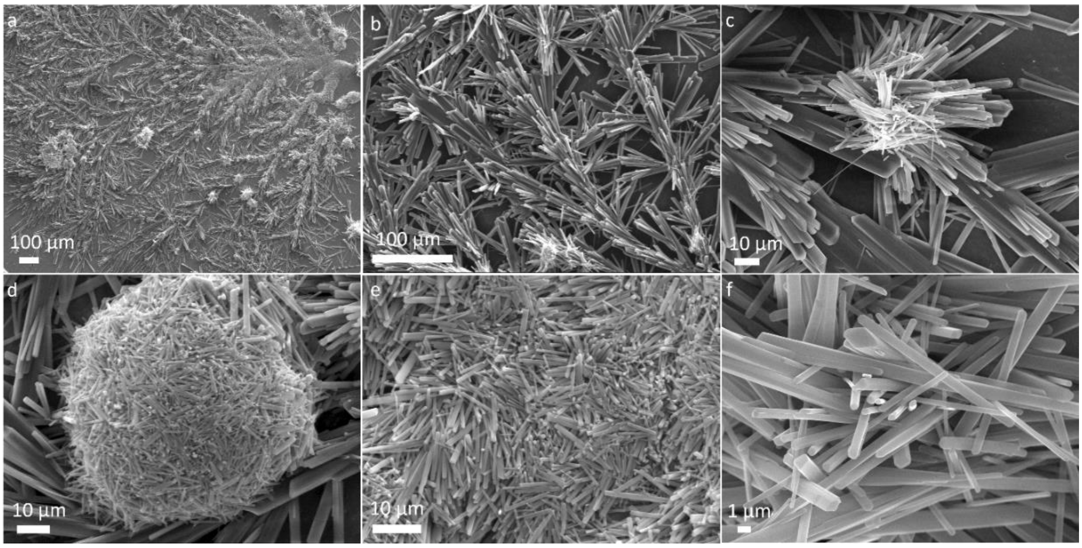

Figure 6.2 SEM micrographs of glutamine ejecta show (a) large dendritic structures, (b&c) more magnified images show branching features, (d) spherical assembly of nanorods and (e&f) more magnified images shows rod-like structures of various length.

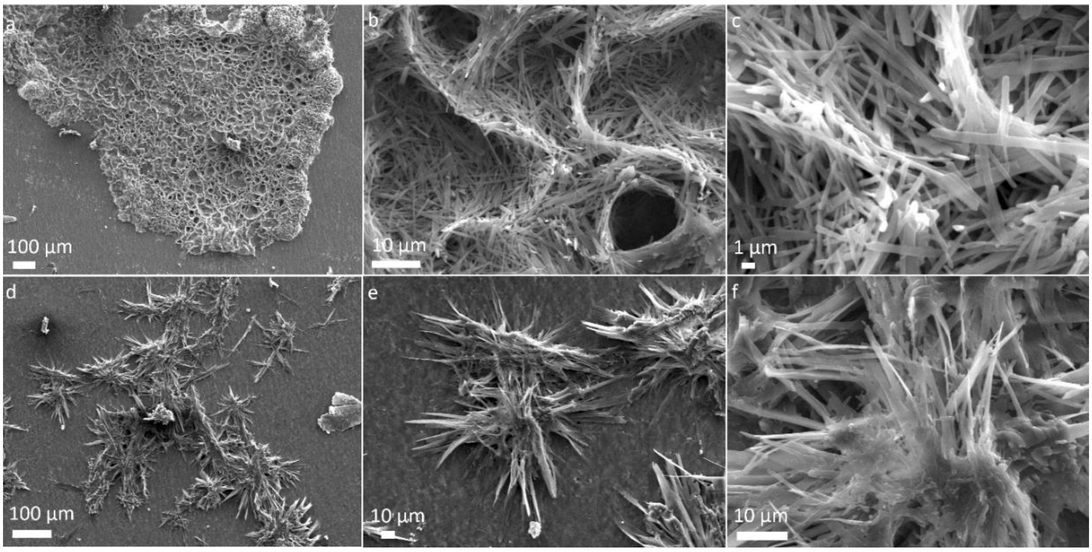

Figure 6.3 SEM micrographs of glycine-glutamine ejecta show (a) an array of large aggregates, (b&c) magnified images show organized structures made of micro-ribbons, (d) assembly of needle-shaped fibres and (e&f) more magnified microstructures.

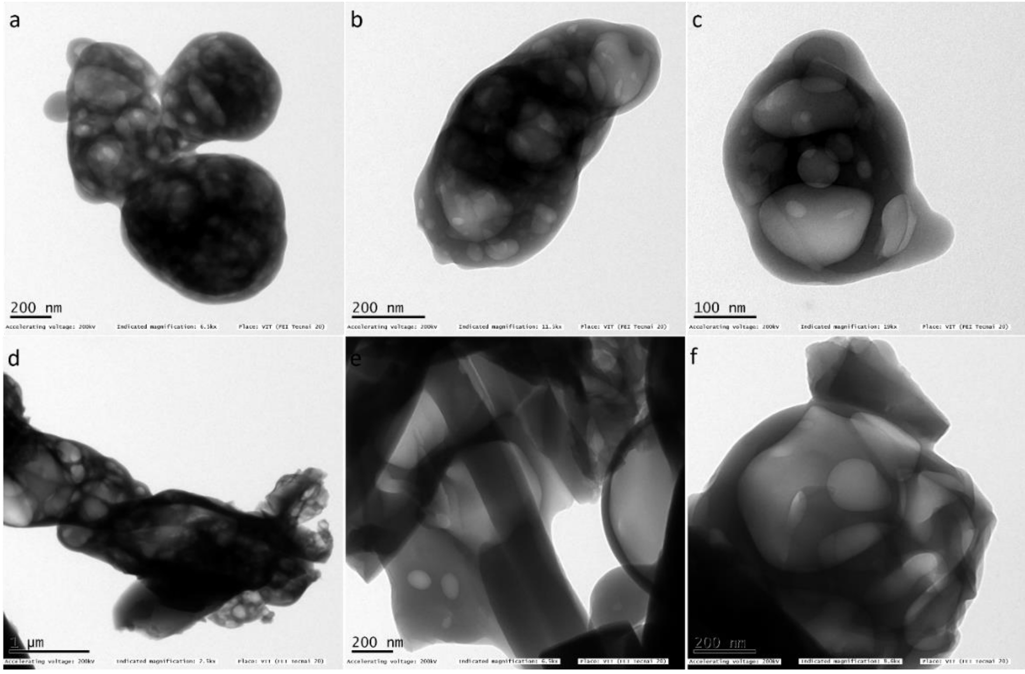

Figure 6.4 TEM micrographs (a-c) glycine ejecta and (d-f) glycine-glutamine ejecta.

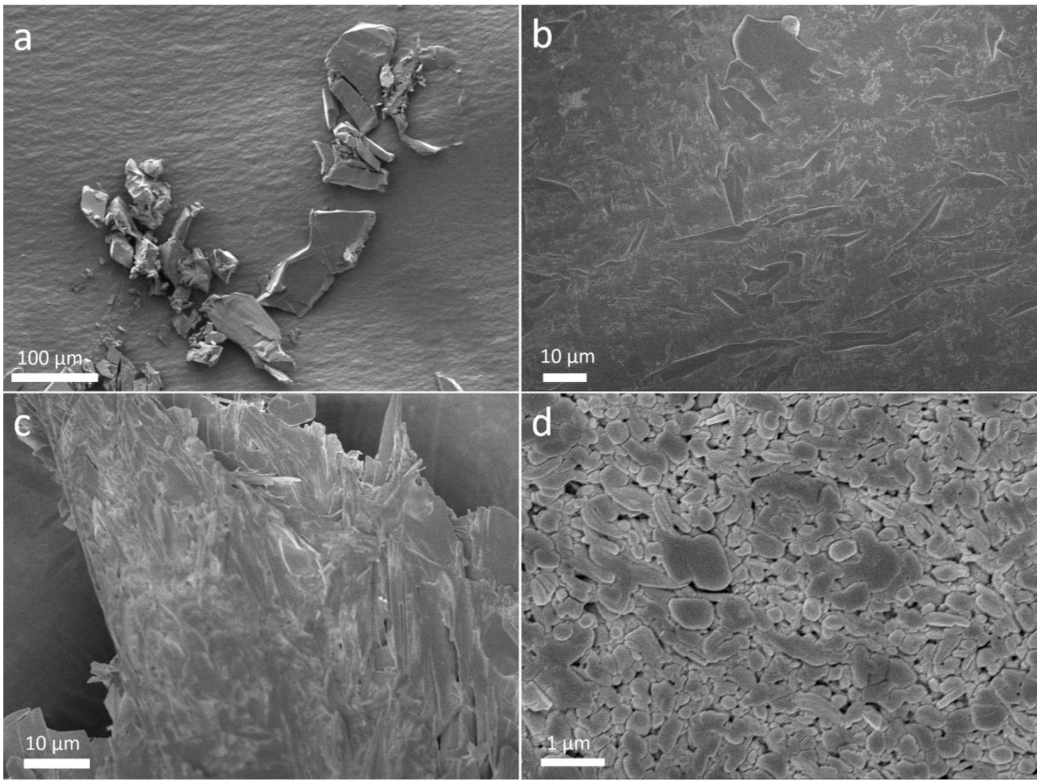

Figure 6.5 SEM micrographs of control showing large particles and aggregates.

6.3.1 Mass spectrometry analysis

Ejecta residue showing the complex macroscale structures were analysed using LC-MS. The appropriate steps taken for LC-MS analysis are provided in Chapter 3. The mass spectra from glycine, glutamine and glycine-glutamine mixtures are shown in **Figures 6.6-6.8**. Long polypeptide chains were identified in the ejecta by comparing the mass of peptides calculated from the peptide mass calculator by putting in the constituent amino acids (PeptideSynthetics). These values are listed in **Table 6.2** for all three samples. Ejecta from glycine showed that various polypeptides were synthesized as a result of the impact. The different peptide sequence which could be identified corresponds to the sequence of three, five, nine and twelve glycine as shown in **Figure 6.6**. Ejecta from the glutamine sample also showed long polypeptide chains as shown in **Figure 6.7**. The identified peptide sequence corresponds to the sequence of two, three and five amino acids. Glutamine was also identified in the ejecta (**Figure 6.7a**). Further, the mixture of glycine and glutamic also showed the synthesis of long polypeptide chains with various combinations of two amino acids as shown in **Figure 6.8** and corresponding sequences are listed in **Table 6.2**. These results prove that long polypeptide chains are synthesized in the ejecta as a result of their impact on amino acids.

There may be other products present in the ejecta that could not be found among the different products identified by LC-MS analysis. Also, the ejecta on the aluminium foils is scattered in various places in about one-meter square area of the aluminium foil.

Extensive analysis will be needed to scan the samples from multiple foil positions and identify those undetermined products.

Table 6.2 shows the mass number and retention time identified from the mass spectra corresponding to the calculated mass and sequence of peptides obtained from the Peptide Synthetics peptide mass calculator.

Peak value (m/z)	**Retention time (min)**	**Sequence**	**Calculated value**
	Glycine (G)		
189.0200	0.553	GGG	189.155
246.2485	4.63	GGGG	246.207
531.4402	13.094	GGGGGGGGG	531.466
702.9087	17.011	GGGGGGGGGGGG	702.621
	Glutamine (Q)		
147.0300	0.635	Q	143.130
275.0708	2.625	QQ	274.261
403.1232	9.447	QQQ	402.391
659.3535	15.439	QQQQQ	658.652
	Glycine (G)-Glutamine (Q)		
204.0777	8.389	1 G and 1 Q	203.182
332.2456	8.389	1 G and 2 Q’s	331.312
517.2334	9.675	2 G’s and 3 Q’s	516.495
773.6675	10.981	2 G’s and 5 Q’s	772.756

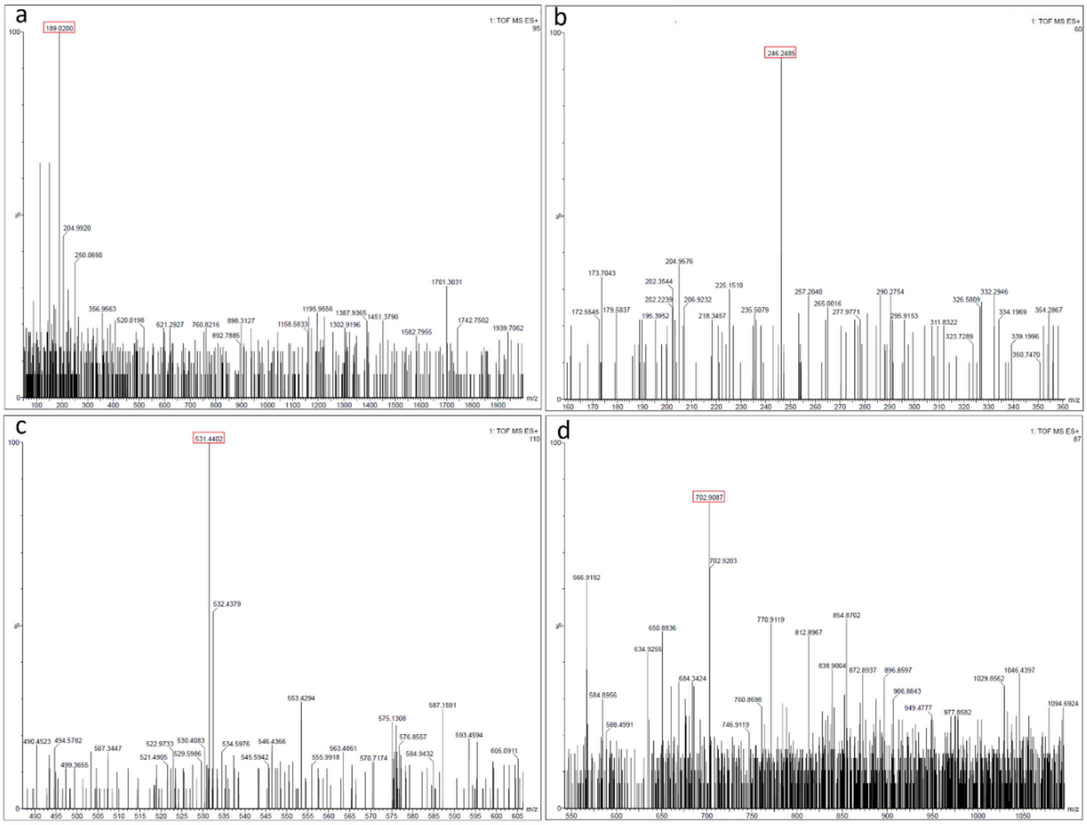

Figure 6.6 Mass spectra of glycine residue showing formation of long polypeptide chain in the ejecta, identified peptide peaks (corresponding to $[M]^{+}$) are shown in red box (a) 189.0200, (b) 246.2485, (c) 531.4402 and (d) 702.9087. Y-axis shows relative abundance.

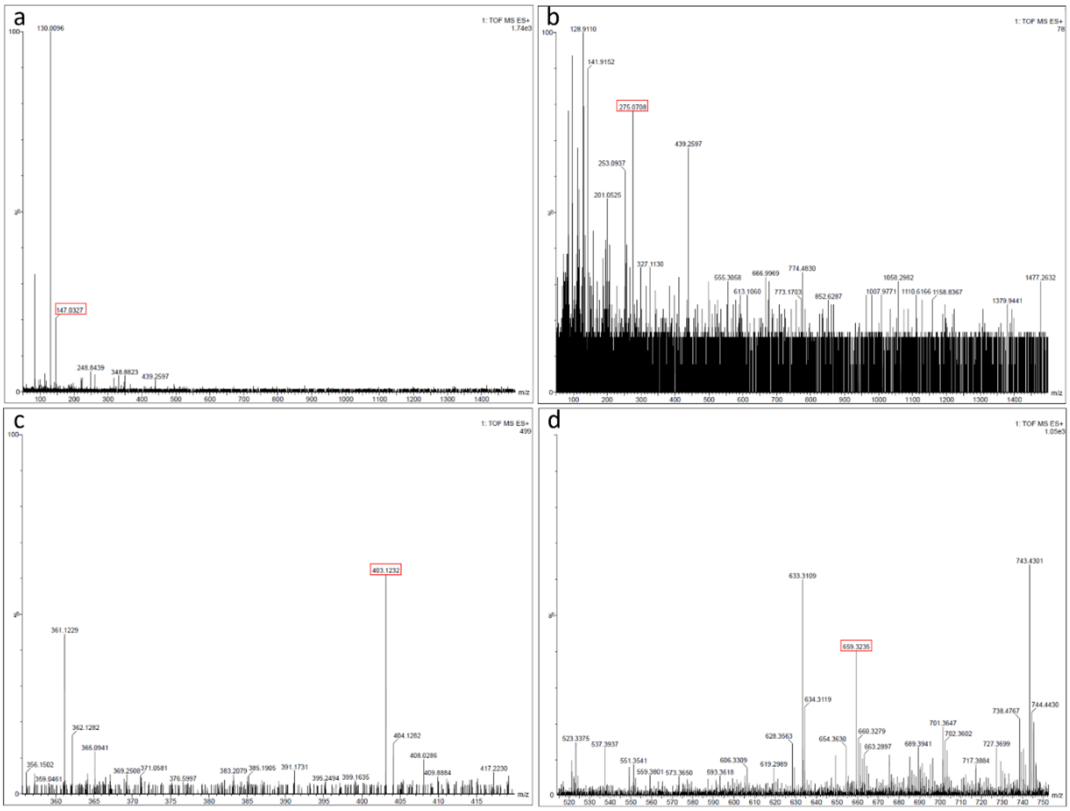

Figure 6.7 Mass spectra of glutamine residue showing signature of glutamine along with formation of long polypeptide chain in the ejecta, identified peptide peaks (corresponding to $[M+H]^+$) are (a) 147.0300 (b) 275.0708 (c) 403.1232 (d) 659.3535, shown in red box.

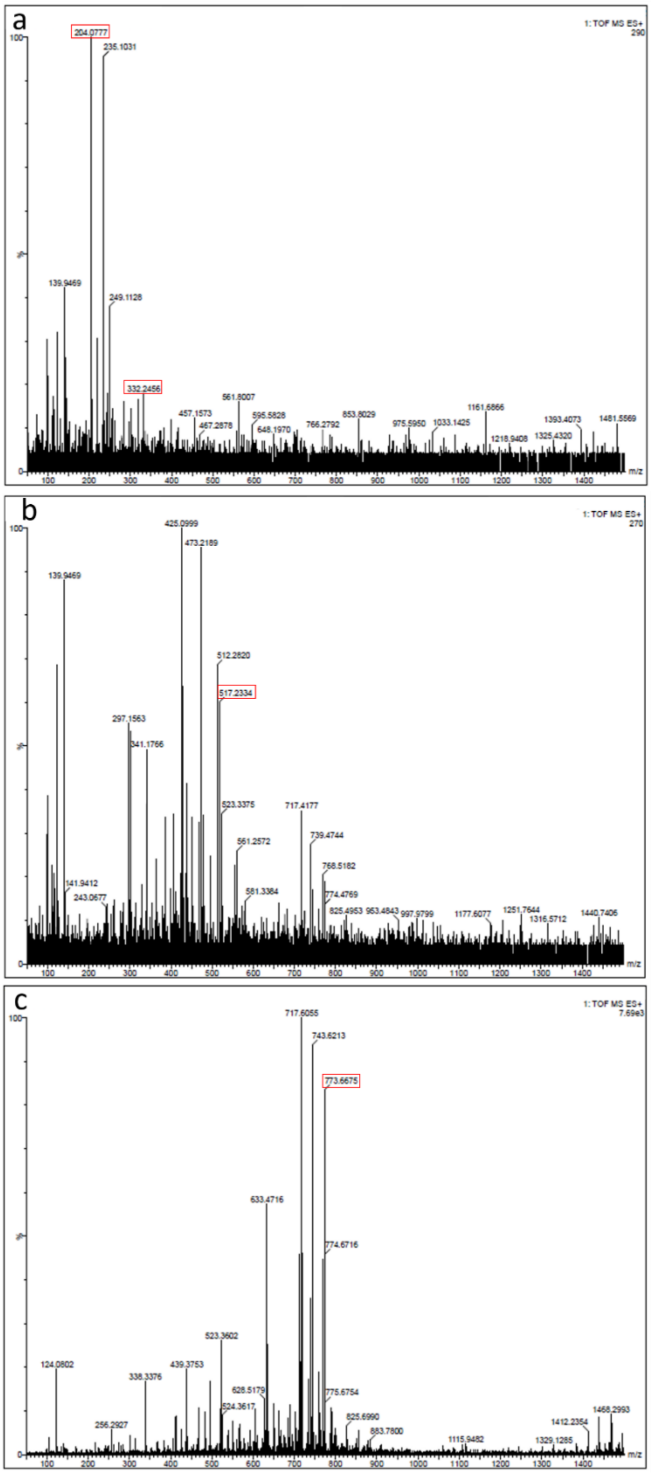

Figure 6.8 Mass spectra of mixture of glycine-glutamine residue showing signature of polypeptide with mix of glycine and glutamine, identified peptide peaks (corresponding to $[M+H]^+$) are shown in red box correspond to (a) 204.0777 and 332.2456, (b) 517.2334 and (c) 773.6675.

The results obtained from SEM and LC-MS analysis demonstrate that amino acids reacted strongly within a short time scale to form organized structures and long polypeptide chains due to the high pressures and temperatures incurred during the impact and in post-impact relaxation. The individual chemical composition of each structure is challenging to determine, however, their similarity with known structures obtained from various peptide self-assembly indicates that these structures can possibly arose as a result of the assembly of various polypeptides synthesized upon impact. These results have important implications for the prebiotic chemical evolution on the prebiotic Earth. These synthesized peptides further might have contributed for the synthesis of longer peptides as elongation of peptides is thermodynamically easier by addition of amino acids to peptides than the addition of various amino acids (Martin et al., 2008). Thus synthesis of peptides in an impacting event might have seeded the Earth with an ingredient that has triggered a nucleation event on early Earth for the synthesis of larger and complex molecules.

Given the ubiquity of impact events in the solar system, impact shock chemistry could be a significant source of chemical modifications on the planetary bodies. As discussed earlier variety of organic molecules can be delivered or synthesized as a result of impact-derived processes. The experiments described in this chapter are equally applicable to the other extraterrestrial bodies, such as impacts on Jovian and Saturnian satellites. These icy satellites are expected to have acquired a significant amount of cometary material during their formation (Canup and Ward, 2006). As a result, it can be anticipated that significant amounts of peptides can be generated during their formation by comet impacts. Furthermore, the Galilean satellites were bombarded intensely by comets, similar to impact bombardment on early Earth (Greeley et al., 2000). Thus it is highly probable that a significant amount of amino acids and peptides could have been derived from cometary impacts on these bodies.

Further, icy satellites such as Europa and Enceladus have subsurface oceans, and they offer potential energy sources for complex chemistry for such polypeptides. Thus they could be an ideal environment to search for extraterrestrial life in the future. Apart from this, impact craters have been suggested as excellent sites for prebiotic chemistry as they offer many exciting possibilities (Cockell, 2006). The present investigation indicates that if we look for the signature of precursors of life, the ejecta materials around the craters could also be an ideal place to search for them.

6.4 Conclusion

We have performed hypervelocity impact experiments on icy mixtures of amino acids as a simulation of a cometary impact. Our results demonstrate that complex macroscale structures were synthesized upon impact and can be observed in the ejecta. Mass spectrometric analysis shows the presence of many polypeptides in the ejecta. These results provide a pathway for the building blocks of life to evolve into complex organized structures, which has implications for the origin of life. This is the first report on the formation of long polypeptide chains to be synthesized under plausible prebiotic conditions with a combination of the same and two different amino acids. As impacts are widespread in the solar system, these results could be applied to the icy bodies of the solar system, such as the icy satellites of Jupiter and Saturn, to understand the chemical composition and evolution of icy surfaces. It is expected that these icy bodies must have been supplied with a significant amount of organics as a result of impact events and thus could possibly have synthesized peptides as well due to impact induced shock processes.

Chapter 7 Shock Processing of Nucleobases

Chapter overview

This chapter reports the experiments on shock processing of nucleobases using the experimental setup of the shock tube. A brief review is provided on the prebiotic synthesis of nucleobases, detection of nucleobases in meteorites sample and synthesis in interstellar ice analogous. Results are provided on the shock processing of single nucleobases as well as mixtures of four nucleobases using microscopic observations of shock processed residue and IR spectroscopy. A discussion is provided on the self-assembled complex structures and their implications for the origin of life.

7.1 Introduction

Nucleobases, the one ring (pyrimidines) or two rings (purines), are the key structural units of nucleic acids (DNA & RNA) that store genetic information. The five nucleobases – adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U) are termed as canonical, with AGCT are the constituents of DNA and AGCU are the constituents of RNA. Being the informational unit, nucleobases plays an essential role in prebiotic chemistry, leading to the origin of life. Many nucleobases have been detected in meteorite samples, confirming their extraterrestrial origin (Martins et al., 2008, Callahan et al., 2011, Burton et al., 2012, Martins, 2018). Ribose and related sugars have also recently been identified in primitive meteorites (Furukawa et al., 2019). Several experiments have been performed to investigate pathways for extraterrestrial synthesis of these molecules. As a result of these investigations, it is found that nucleobases can be synthesized in residues obtained from UV irradiated molecular ices containing simple molecules such as NH_3, H_2O, CH_3OH, etc. (Nuevo et al., 2009, Nuevo et al., 2012, Materese et al., 2017, Oba et al., 2019). Sugars and deoxysugar derivatives are also reported in residues of UV irradiated icy mixture of H_2O and CH_3OH and confirming their presence in astrophysical environments and carbonaceous meteorites (Nuevo et al., 2018). These results suggest the possible origin of these biomolecules in interstellar space, where ice-covered dust grains are illuminated by UV irradiation. Other mechanisms have been proposed that discuss the plausible prebiotic origin of nucleobases in Earth's primitive environment. These include synthesis of adenine from ammonium cyanide (Oró, 1960) and hydrogen cyanide (Oró and Kimball, 1961), UV irradiation of formamide solution (Saladino et al., 2006, Barks et al., 2010), UV irradiation of acetylene in a water/ice solution (Menor-Salván and Marín-Yaseli, 2013), and spark discharge of urea in water/ice solution (Menor-Salván et al., 2009). As already discussed in previous chapters, impact-induced shock may also serve as an essential source for large-scale molecular synthesis due to various chemical pathways of reaction available in the extreme thermodynamic conditions provided by impact events. Synthesis of various amino acids and nucleobases from simple molecules containing nitrogen, oxygen, carbon, and hydrogen in simulated impact shock conditions has already been discussed (Bar-Nun et al., 1970, Martins et al., 2013, Furukawa et al., 2015, Rios, 2015). Experiments have also shown the synthesis of nucleobases from formamide due to the plasma formed by high energy impact events (Ferus et al., 2014, Ferus et al., 2015b, Ferus et al., 2019). Ferus et al. (Ferus et al., 2017) have also demonstrated the formation of nucleobases as driven by impact plasma and electric discharge in a Miller Urey reducing atmosphere containing simple gases. Apart from amino acids and nucleobases, sugars are also synthesized in impact driven processes (Civiš et al., 2016). So, the routes by which prebiotic availability of nucleobase, either due to endogenous production or as a result of exogenous delivery, have been confirmed. The next key step in this process requires that these molecules had to be brought in closer proximity to facilitate the emergence of nucleosides, nucleotides and their oligomers (Menor-Salván, 2018). Given the possible synthesis of all the nucleobases together in impact-shock condition (Ferus et al., 2014, Ferus et al., 2015b) or synthesis in interstellar ice analogous (Oba et al., 2019) and their detection in meteorites samples (Callahan et al., 2011), and with evidence of intense impact events on Earth during the period of late heavy bombardment (Koeberl et al., 2000), these organics must have undergone multiple impact events leading to some destructive and some constructive consequences. So, it is necessary to further understand the subsequent fate of these nucleobases in extreme conditions of impact to understand the pathways to the origin of life. While amino acids are known to survive in such extreme condition and also resulted in formation of peptides as a result of impact driven shock processes, (Blank et al., 2001, Otake et al., 2011, Sugahara and

Mimura, 2014, Sugahara and Mimura, 2015), the fate of nucleobases in similar impact conditions remains largely unexplored.

7.2 Experimental Methods

To simulate the high-temperature heating effect of impact-induced shock, we have utilized MST1 and HISTA shock tube facility to simulate impact induced shock conditions. Single nucleobases adenine and cytosine, and the mixture of RNA and DNA bases mixed in equal weight ration were shock processes at various temperatures as listed in **Table 7.1**. The nucleobases samples were procured from Sigma Aldrich, having purity ≥ 99%. A comprehensive experimental procedure for shock processing, as well as measurements of shock speed, reflected shock temperature, and pressure are provided in Chapter 3. After the shock processing, the blackish residue left in the reaction chamber was collected and stored in inert condition until further analysis.

Table 7.1 Shock parameters for different experiments

Sample	**Quantity (g)**	**Diaphragm bursting pressure (Bar)**	**Test gas pressure (Bar)**	**Mach Number**	**Reflected shock temperature (K)**	**Reflected shock pressure (Bar)**
Cytosine	0.2	34.5	0.2	4.2	4050	17.0
Adenine	0.2	30.2	0.2	4.1	3910	16.0
AGCT	0.16	32	0.2	4.0	3740	15.0
AGCT	0.16	62.2	0.1	5.3	6360	29.0
AGCT+ Ribose	0.12	61.5	0.075	5.4	6900	34.0
AGCU	0.12	47.6	0.075	5.3	6320	17.0

7.3 Results

7.3.1 Microscopic analysis

The solid residue after shock processing was subjected to SEM to reveal the intricate details present in the residue. The SEM micrographs revealed that a variety of complex structures appeared after shock processing. No such structures were observed in the unshocked mixture of nucleobases. SEM observations of the mixture of nucleobases before shock only show some micron-sized particles in the sample as shown in **Figure 7.1**. These samples do not show the presence of any complex structures. As these samples showed very much charging in SEM, a thick coating was needed to apply on the top surface of samples to reduce charging. In these SEM images surface features are not much clear, however, it clearly shows micron sized particles are present in the sample.

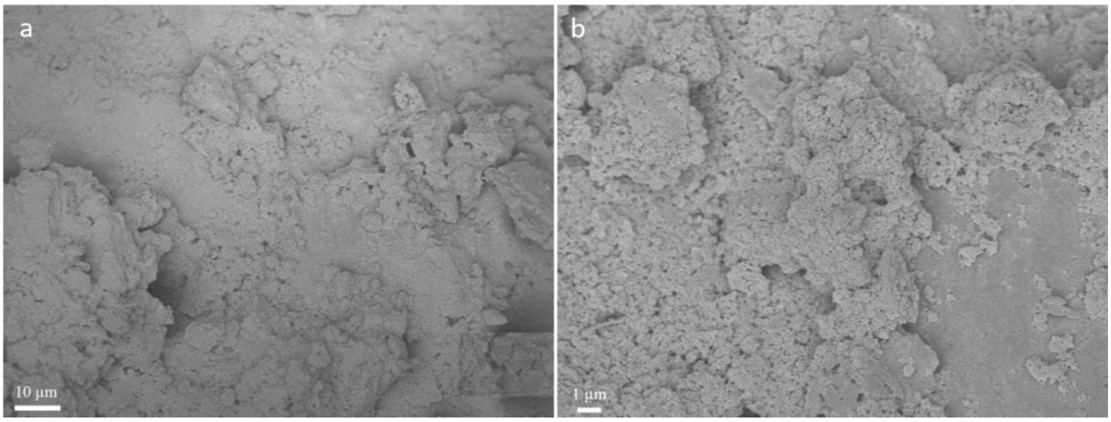

Figure 7.1 SEM micrograph of AGCT mixture before shock.

The SEM micrographs of a mixture of AGCT residue, shock processed at an approximate temperature of 3700 K, shows the formation of many smooth globule structures with a diameter of 30-50 μm as shown in **Figure 7.2** as well as the formation of long (~500 μm) periodically twisted filaments were seen in shock processed sample. Various long folded threads spanning up to a few mm length were also observed, as shown in **Figure 7.2d**. All these structure formations occur as the result of shock processing of a mixture of nucleobases as the shock heated gas interacts with the sample in the reaction chamber. The same mixture of nucleobases was further subjected to a higher reflected shock temperature of approximately 6360 K. Interestingly, variety of large-scale ordered structures were seen in shock processed residue (**Figure 7.3**), as were long threads of few mm lengths running along with a variety of structures were observed (**Figure 7.3**). The various features observed at higher magnification show that some threads are more twisted and folded.

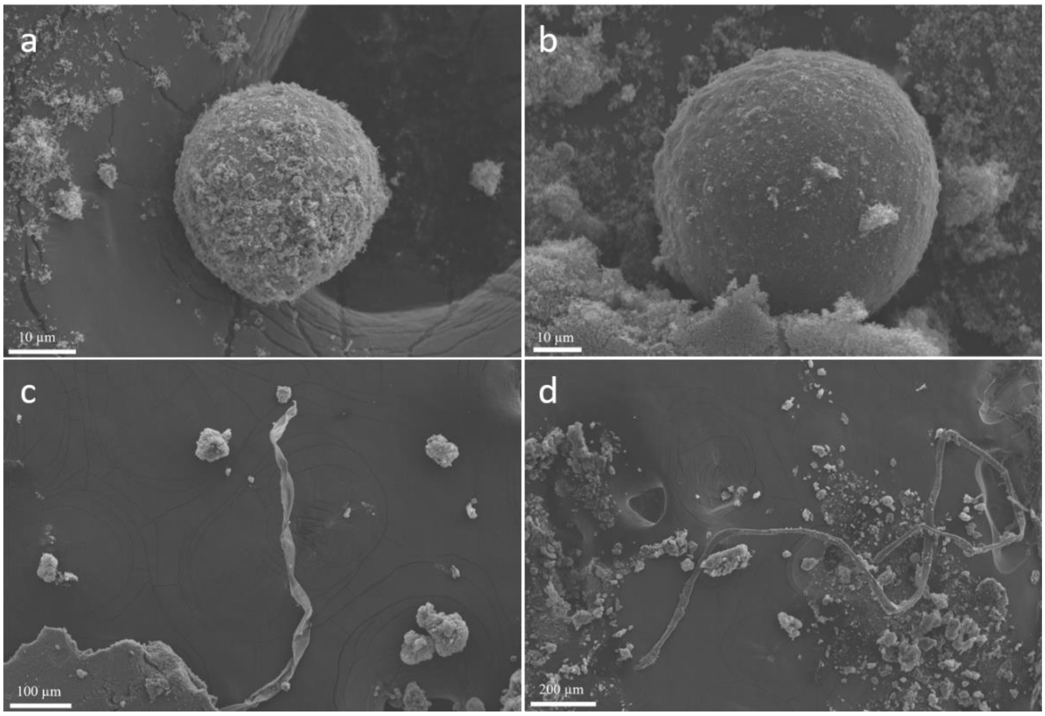

Figure 7.2 SEM micrographs of shock processed residue of AGCT mixture at temperature of ~ 3700 K reveals the (a&b) formation of globule features, (c) twisted filaments and (d) long folded threads.

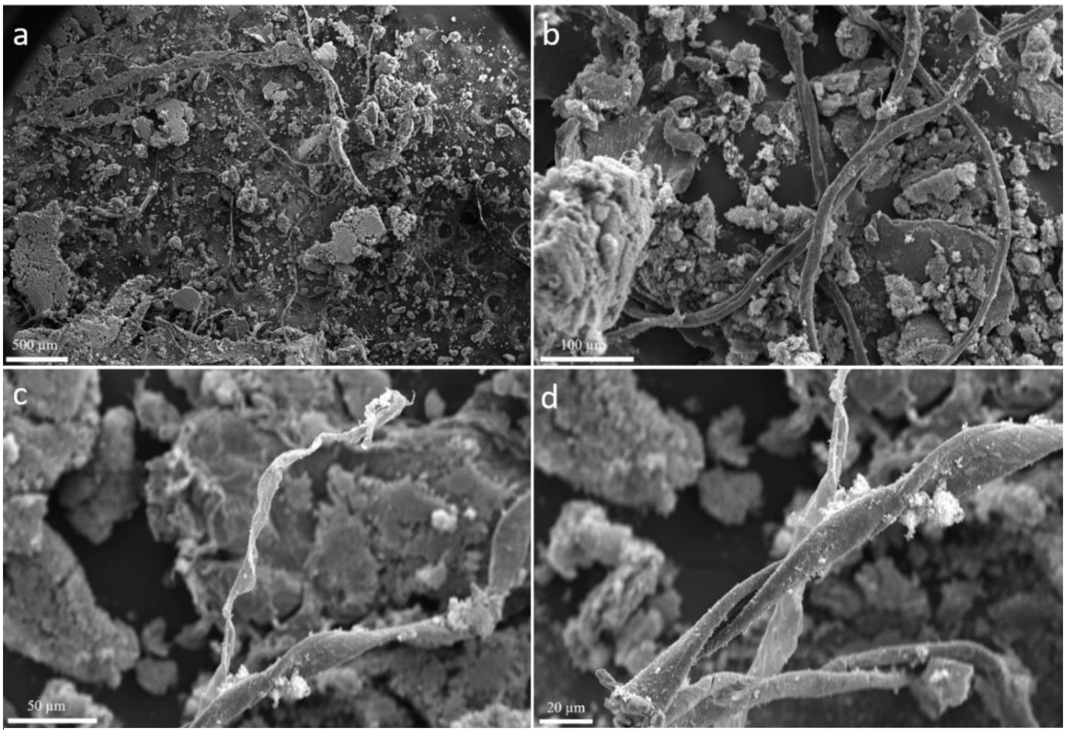

Figure 7.3 SEM micrographs of shock processed residue of AGCT at temperature of ~ 6360 K (a) long threads feature mm in length, (b) thread like structures can be seen at higher magnification, (c) twisted fine filaments and (d) helically twisted filaments.

Further ribose was added to the mixture of AGCT bases, all mixed in equal weight proportion (1:1:1:1:1), shock processed at a temperature of approximately 6900 K. The SEM micrographs of residues also shows the formation of long-range (few mm) threads along with large clumped structures. The threads were found to be twisted and folded, as shown in **Figure 7.4**. The structures as such did not show any significant change in morphology compared to the mixture of only AGCT. Further, the shock processed AGCT residue was subjected to TEM, which showed the presence of fine twisted and folded features at a nanometre scale, as shown in **Figure 7.5a&b.**

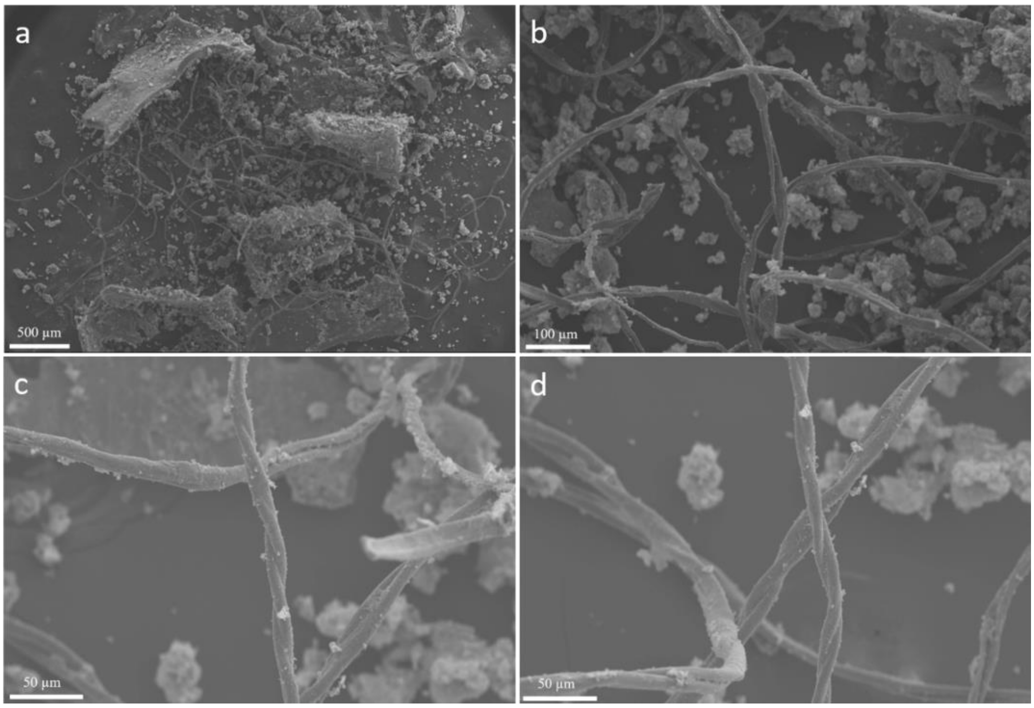

Figure 7.4 SEM micrographs of shock processed residue of nucleobases AGCT with ribose at a temperature of ~ 6900 K (a) long threads feature mm in length (b) various thread like structures can be seen at higher magnification (c&d) magnified image shows more twist.

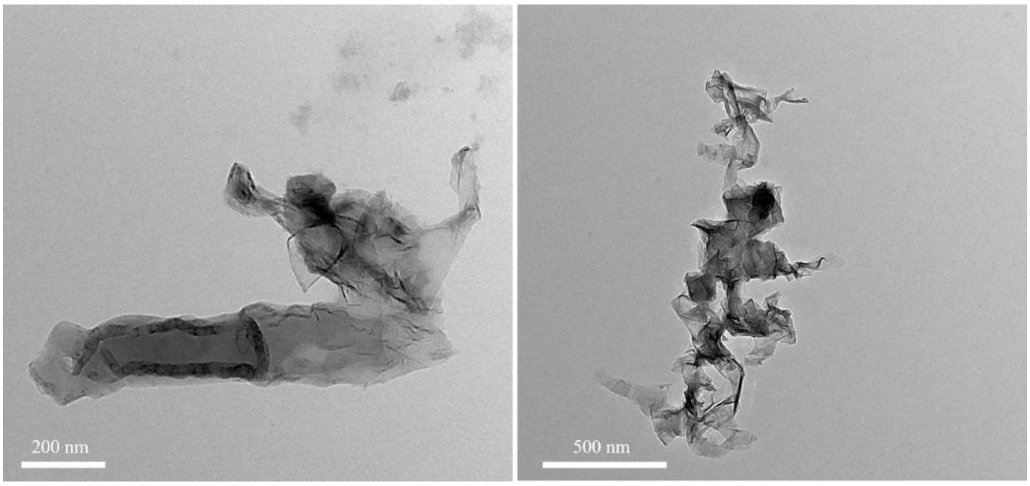

Figure 7.5 TEM micrographs of shock processed residue of AGCT at temperature of ~ 6360 K.

Mixtures of four RNA bases adenine, guanine, cytosine and uracil (AGGU) were also shock processed at temperature of approximately 6320 K. Various thread structures of size hundreds of micron were observed in SEM observation (**Figure 7.6).** However, the number of threads present in this sample was not as prominent as we observed in the mixture of AGCT also, these threads were not so twisted or folded compared to the mixture of AGCT and AGCT with ribose. TEM observation of this mixture showed few sheets some with uniform and some with twisted appearances at nanometre scale as shown in **Figure 7.7,** respectively.

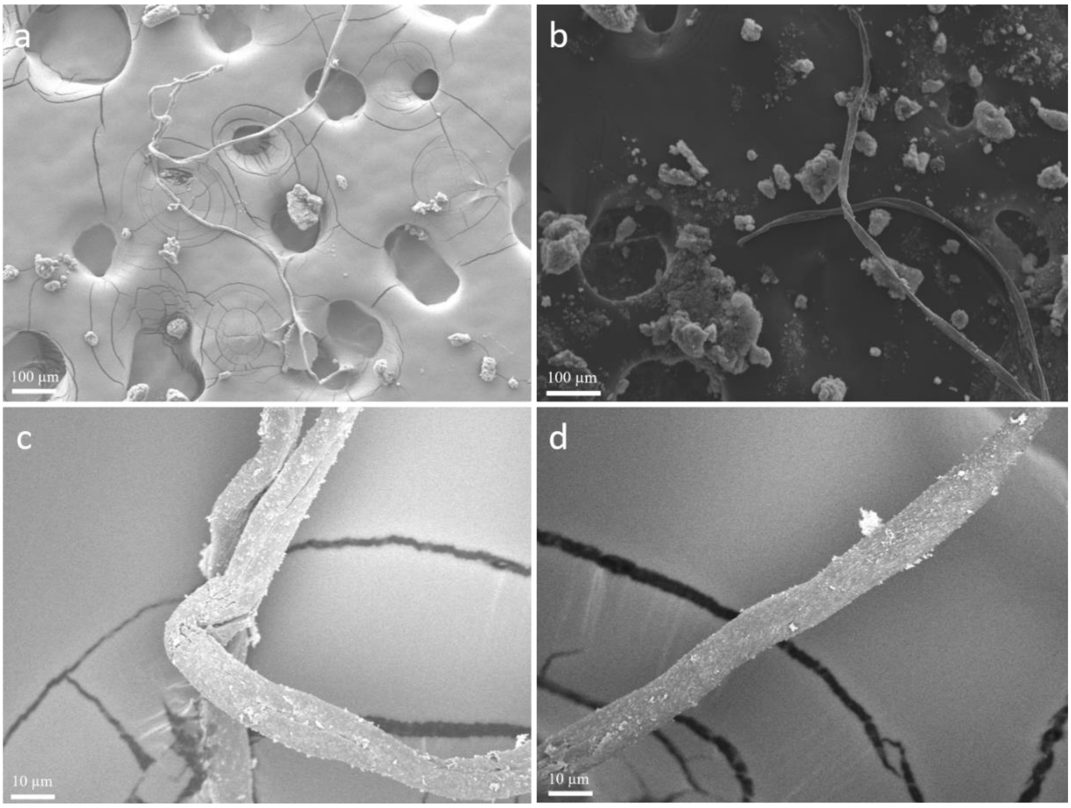

Figure 7.6 SEM micrographs of shock processed mixture of nucleobases AGCU at temperature of at temperature of ~ 6320 K (a&b) long threads and (c&d) threads at higher magnification.

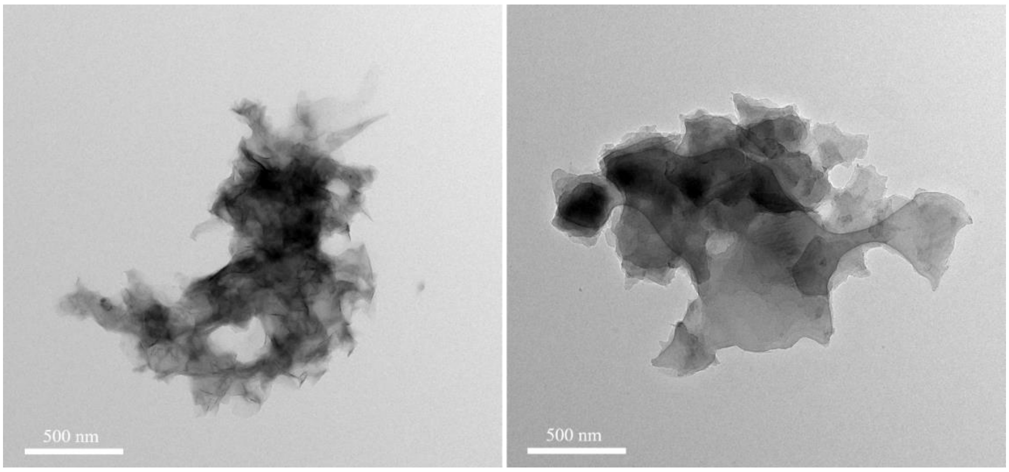

Figure 7.7 TEM micrographs of shock processed residue of AGCU at temperature of ~ 6320 K revealing twisted and folded ribbons and sheets at the nm scale.

Single nucleobase adenine and cytosine were also shock processed at a temperature of approximately 3800 K (**Table 7.1**). SEM observations of these shock processed residue did not show any complex structures as observed in the mixture of four nucleobases. Large particles of size few microns were observed, as shown in **Figure 7.8.**

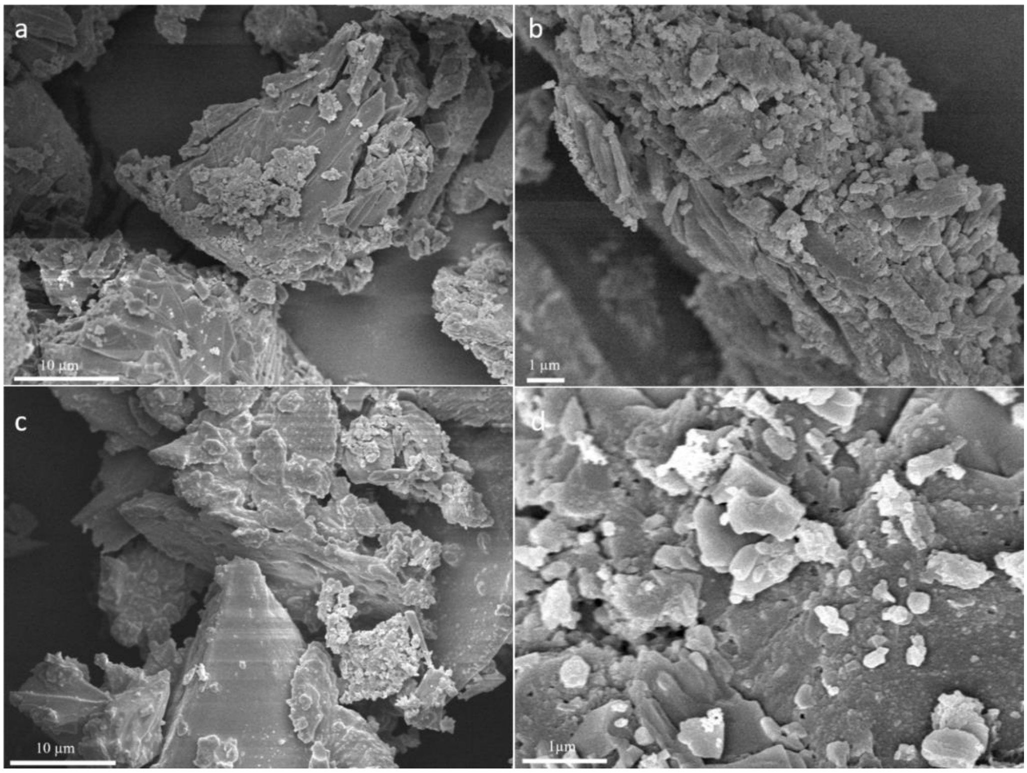

Figure 7.8 SEM micrograph of shock processed residue of single nucleobase (a&b) adenine and (c&d) cytosine.

7.3.2 IR spectroscopy of shock processed residues of nucleobases

The shock processed residues were further characterized by Infrared (IR) spectroscopy. IR spectroscopy of shock processed residue and unshocked sample were obtained for single nucleobases as well as the mixture of nucleobases over a wavenumber range of 4000-500 $cm^{-1,}$ as shown in **Figure 7.9**. Various characteristic peaks corresponding to vibrational modes of nucleobases can be seen in both the shocked and the unshocked samples. This indicates that nucleobases remain intact against the impact of the strong shock.

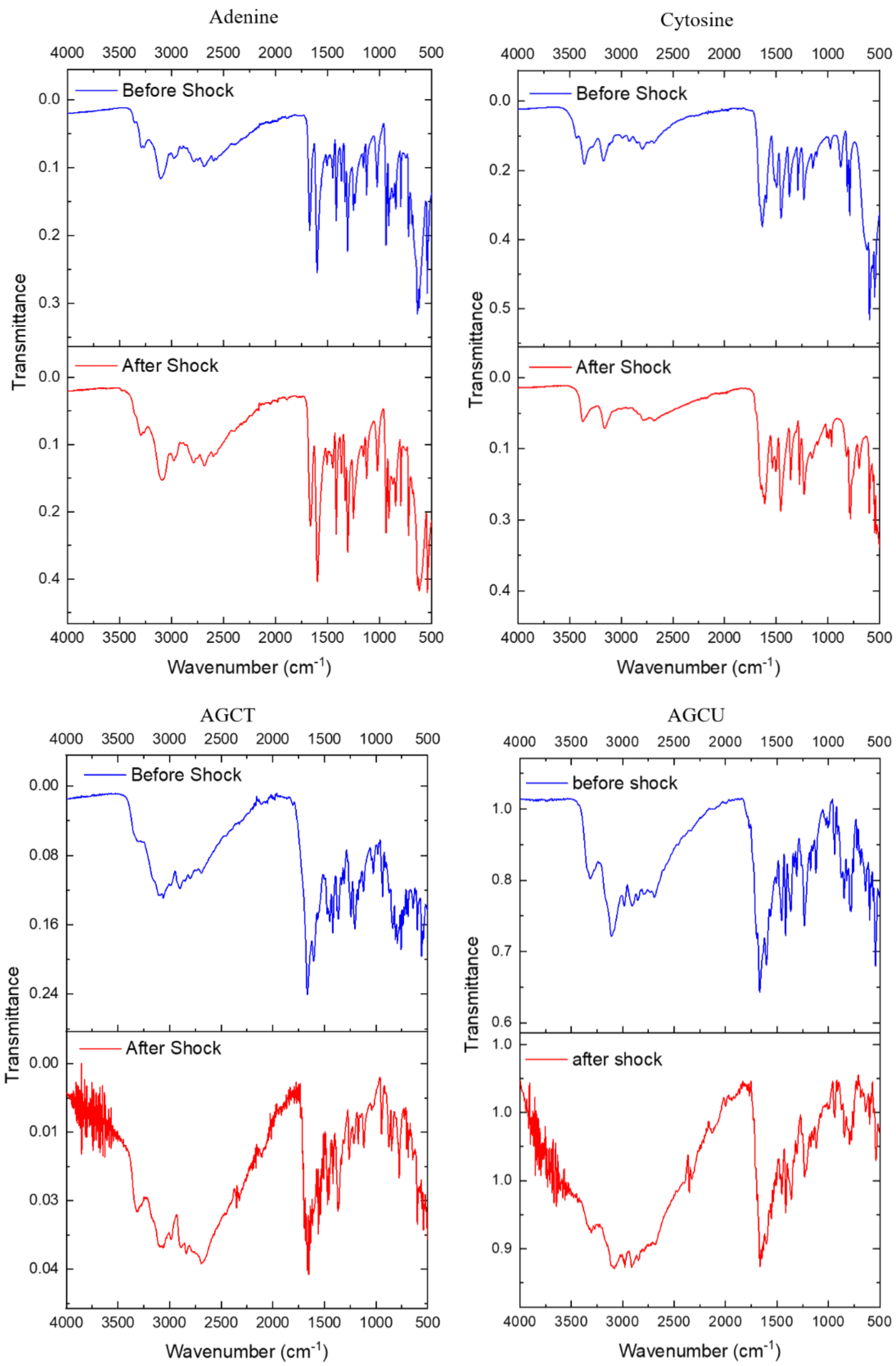

Figure 7.9 IR spectra of single nucleobases and mixture of nucleobases before and after shock processing.

Thus a variety of morphological features including long threads and ribbons, twisted and folded appearance, and globule structures, were observed in the shock processing of nucleobases. These observations indicate that the property of self-organization seems to be not profound in AGCU bases. Though a possible explanation on these results requires detailed investigation, a possible reason could be the presence of thymine instead of uracil providing more stability due to the presence of methyl group in thymine (Wärmländer et al., 2002, Marathe and Bansal, 2010). The self-organization property of the mixture of AGCT bases also favors the early role of DNA and their components in the prebiotic evolution of life, confirming the previously suggested theories on the origin of life that require heterogeneous genetic system made up of both RNA and DNA (Bhowmik and Krishnamurthy, 2019, Xu et al., 2020, Kim et al., 2020).

7.4 Discussion

While from the previous investigations, it is revealed that rich chemistry can occur at such extreme conditions, the formation of such microstructures were never revealed before. At present, the chemical composition of these microstructures is unknown. Given that nucleobases can still remain intact in the shock processed residue as revealed from IR data, these structures could be the outcome of the assembly of nucleobases. Such structures play an essential role in biological function because of their unique architecture. Self-organization of such complex structures on a macroscopic scale under simulated impact shock conditions is an important step in the prebiotic development of life. The formation of such long-range ordered structures in a prebiotic context has always been a difficult task. Life requires a high degree of structural order as well as complexity (Mayer, 2020). Any system which lacks one or another will lead to a dead-end, for example asphalt or tar (Benner et al., 2012) which is highly complex, conversely crystals that are highly ordered (Mayer, 2020). A mechanism of simultaneous increase in order and complexity will have significance for prebiotic chemistry. The complex ordered structures synthesized by shock processing of biomolecules which evolve from simple disordered structures to complex ordered structures, thus have an important consequence for the origin of life. Many attempts have been made on the synthesis of such microstructure in primitive Earth environments and justifying their importance for the origin of life studies (Fox, 1973, Folsome, 1976, Valladas-Dubois and Prudhomme, 1983, Simionescu et al., 1985, Yanagawa et al., 1988). Formation of such structures are not only limited to terrestrial environments but seem to be profound in interstellar space as well, with discoveries of self-assembled membranous structures observed in carbonaceous meteorites (Deamer and Pashley, 1989) and further confirmation by experimental investigation of similar self-assembled vesicles structures formed as a result of UV photolysis of interstellar ice analogs containing simple molecules (Dworkin et al., 2001). However, our method of shock processing of nucleobases provides a pathway by which these self-assembled organized structures could have appeared on the Earth, without the presence of any additional catalytic activity or atmospheric condition, only triggered by shock energy provided by impact events.

Many competing models are suggested to explain the origin of life, such as the RNA world, the compartmenlistic approach, the prebiotic metabolism approach and many others. There is still no united model available for the origin of life (Luisi, 2016).

However, the universal presence of cellular life on the Earth demands the emergence of cell-like architectures and functionality (Szostak et al., 2001, Mann, 2012). The first step in this process is to search for a system that can spontaneously organize itself into structures that can act as a prototype that mimics various characteristics of minimal cellularity (Mann, 2012, Zhang, 2012). The formation of complex structures as revealed in the present investigation is a possible answer to the first step in the path of prebiotic cellularity. Evidently, many profound challenges remain that need to be answered to search for the origin of life and find its signature elsewhere (Lingam and Loeb, 2021). In future endeavors, we will discuss physical and chemical characterises of these structures, which will provide significant elucidation of our understanding of the role played by complex molecules and impact events in the origin of life.

7.5 Conclusion

The novel shock tube method is used to produce extremely high shock temperatures (3500 K - 7000 K estimated) and pressure of (15-34 bar) for a small duration to interact with the nucleobases. The shock processing of nucleobases has shown a plausible pathway by which nucleobases can spontaneously be self-assembled in complex structures when subjected to impact shock conditions. SEM and TEM analysis of shock processed residue provides an insight into the synthesis of a variety of complex structures, including globules, long helical threads, and ribbons of up to millimeter length scale and twisted patterns at the nanometre scale. The formation of such structures in plausible prebiotic conditions implies their prebiotic significance in the subsequent stage of evolution; these structures may be incorporated with other prebiotic polymers in the right conditions and serve as the basis for the lifelike self-assembling system. In future work, we will pursue more experiments to investigate the chemical nature of these structures using characterization techniques.

Chapter 8 Summary and Future Work

Chapter overview

This chapter provides a concise overview of the whole work and focuses on the most important aspects of the current work. The closing remarks are accompanied by recommendations for future research.

8.1 Summary of the thesis work

Previously a number of attempts have been made to extend the boundaries of current knowledge of potential prebiotic polymerization of biomolecules to find pathways that led to the emergence of life. Impact bombardment has been shown to deliver biomolecules, and impact driven processes have also been shown to synthesize them. However, the further role of these biomolecules in the extreme condition of impact remains unexplored. The central theme of this study is to explore the fate of biomolecules under impact induced shock conditions, which has important consequences for prebiotic chemistry and the origin of life.

In chapter 3, we have provided details of the experimental setup of shock tubes (MST1 and HISTA) that is designed and developed to mimic impact induced shock conditions in the laboratory. An overview is also provided for the LGG facility that is capable of firing a projectile at a higher speed to simulate hypervelocity impacts. Impact processes are highly complex phenomena with respect to their physical and chemical aspects. Laboratory simulations of impacts conditions are challenging tasks and provide limited aspects of the impact process. Previous studies have shown various techniques for simulation of impact processes, such as including light gas gun, dynamic shock loading methods, explosive detonations, laser pulse heating, etc. While shock tube is widely used for different applications in various fields, there were limited application of shock tube for simulation of impact induced shock. Thus, the technique developed is novel and offers interesting characteristics for impact shock simulation in the laboratory and could be advantageous for the study of various shock induced chemistry in interstellar space.

In Chapter 4, we have the results from shock processing of single amino acids glycine and mixtures of two amino acids, glycine-glutamic acid and asparagine-glutamic acid. We have shown that shock processed residues tend to form varieties of complex structures. These structures show remarkable resembles to structures that results from peptides assembly. Results from IR observations have shown the formation of the Amide I band in the shock processed residue, a signature of peptide bond formation. LC-MS revealed the presence of long polypeptide chains in shock processed residue. Our results demonstrate how impact processes in prebiotic earth led to the synthesis of basic architectures from building blocks of life.

Motivated by seeing results as shown in Chapter 4, in Chapter 5, we explored other combinations of amino acids selected among the list of twenty proteinogenic amino acids. The combinations are chosen on the basis of their significance in prebiotic chemistry to explore order and complexity. The various architectures were revealed from microscopic observation of these shock processed mixtures. These results affirm the importance of shock processes in the synthesis of biomimetic structures. These results also enable the significance of nanoscience in prebiotic chemistry. We have also provided a possible explanation of microstructures observed in the meteorites samples by comparing them to the structures observed in shock processed residue. The structures in meteorites could possibly be synthesized as an aggregation of biomolecules by impact processes.

In Chapter 6, we explored impact shock processing on the icy mixture of amino acids. Icy bodies in the solar system may provide potential habitat for the extraterristrial life. Given the ubiquity of the impact process in the solar system, amino acids can be delivered or synthesized due to the impacts process. We showed the impact on the icy mixture on amino acids led to form the assembly of complex structures. We also found long polypeptide chains were synthesized in the ejecta as a result of impact-shock processing. These are the first report on forming long polypeptide chains with complex architecture in the impact ejecta.

Chapter 7, we explored the fate of nucleobases under impact shock processing. Nucleobases are building blocks of RNA and DNA. Impact synthesis of nucleobases is well known. They were also detected in meteorites samples. We show that impact shock processing of nucleobases leads to the formation of long helically twisted threads with twisted and folded appearance as revealed from SEM observations. TEM observations show the twisted and folded appearance at the nanometre scale. IR observations of shock processed residue of nucleobases show they remain stable under impact induced shock.

8.2 Future work

This thesis inspires a variety of prospective research directions, including experimentation, observation, and theory, as listed below.

- The experimental setup of shock tube is a novel method to simulate extreme thermodynamic conditions of shock in the laboratory. Shocks are common phenomenon in the interstellar medium emerging from violent events like supernova explosions. High temperatures in shocks can drive many chemical reactions, which are otherwise impossible in low temperatures. Among various processes in interstellar environments shock induced chemistry is the least understood subject. Several fundamental chemical processes have yet to be investigated under such conditions to better understand the chemical evolution. The shock tube designed in our laboratory can be a useful tool to explore the impact-shock chemistry of interstellar environments.
- The complex structures synthesized as a result of impact-shock processing of amino acids and nucleobases are novel and have important implications for the origin of life. There is a need to explore the shock processing of other class of biomolecules such as fatty acids, a crucial component of the early cell membrane. Various combinations of biomolecules can be explored under impact shock conditions to explore chemical complexity. Future experiments are expected to with various combinations of biomolecules like amino

acids, nucleobases and fatty acids for the understanding of the interaction among different classes of biomolecules. The presence of mineral components as catalysis under impact induces shock will enhance our understating of this subject. The further role of metals included in organic mixtures under shock conditions can be explored as metals have an important role in prebiotic chemistry and the origin of life.

- Further, to understand the structure and evolution of the solar system bodies, there is a need to investigate the properties of minerals at the extreme condition of temperature and pressure. Shock tubes can offer interesting capabilities to elucidate mineral activity under different thermodynamic conditions.
- Despite the methodological accomplishments achieved in this work, sophisticated analytical techniques are required to improve the chemical nature of organized structures. Further analysis is expected to study properties of these structures using CD spectroscopy to understand optical properties, AFM to reveal their mechanical properties and topography studies, NMR analysis to probe molecular structures.
- Previous theoretical results have demonstrated the formation of biomolecules like amino acids from their simple precursors under impact conditions using molecular dynamics simulations. Similar studies are desired for amino acids to understand the step-by-step processes that led to the formation of such structures.

- Various other pairs of nucleobases in various combinations can be tried to explore the nature of self-assembled structures. A detailed explanation is required on the formation of complex structures from shock processing of a mixture of nucleobases. These results provide a scope that is worthy of future investigation.

To conclude, the effects of impact shock are extensive, and much of it is unknown. Increasing experimental investigations are vital for the understanding of such processes. The role of impact processes has many important consequences in the field of astrobiology. For now, hopefully, the shock experiments carried out in this thesis will add one small increment in the step to solve the mysteries of the origin of life.

Bibliography

ALTWEGG, K., BALSIGER, H., BAR-NUN, A., BERTHELIER, J.-J., BIELER, A., BOCHSLER, P., BRIOIS, C., CALMONTE, U., COMBI, M. R. & COTTIN, H. 2016. Prebiotic chemicals—amino acid and phosphorus—in the coma of comet 67P/Churyumov-Gerasimenko. *Science advances,* 2**,** e1600285.

ANDERS, E. & FITCH, F. W. 1962. Search for organized elements in carbonaceous chondrites. *Science,* 138**,** 1392-1399.

BAR-NUN, A., BAR-NUN, N., BAUER, S. & SAGAN, C. 1970. Shock synthesis of amino acids in simulated primitive environments. *Science,* 168**,** 470-472.

BARBIER, B., HENIN, O., BOILLOT, F., CHABIN, A., CHAPUT, D. & BRACK, A. 2002. Exposure of amino acids and derivatives in the Earth orbit. *Planetary and Space Science,* 50**,** 353-359.

BARKS, H. L., BUCKLEY, R., GRIEVES, G. A., DI MAURO, E., HUD, N. V. & ORLANDO, T. M. 2010. Guanine, Adenine, and Hypoxanthine Production in UV-Irradiated Formamide Solutions: Relaxation of the Requirements for Prebiotic Purine Nucleobase Formation. *ChemBioChem,* 11**,** 1240-1243.

BARTH, A. 2007. Infrared spectroscopy of proteins. *Biochimica et Biophysica Acta (BBA)-Bioenergetics,* 1767**,** 1073-1101.

BENNER, S. A. 2010. Defining life. *Astrobiology,* 10**,** 1021-1030.

BENNER, S. A., KIM, H.-J. & CARRIGAN, M. A. 2012. Asphalt, water, and the prebiotic synthesis of ribose, ribonucleosides, and RNA. *Accounts of chemical research,* 45**,** 2025-2034.

BERTRAND, M., VAN DER GAAST, S., VILAS, F., HÖRZ, F., HAYNES, G., CHABIN, A., BRACK, A. & WESTALL, F. 2009. The fate of amino acids during simulated meteoritic impact. *Astrobiology,* 9**,** 943-951.

BHOWMIK, S. & KRISHNAMURTHY, R. 2019. The role of sugar-backbone heterogeneity and chimeras in the simultaneous emergence of RNA and DNA. *Nature chemistry,* 11**,** 1009-1018.

BIZZARRI, B. M., ŠPONER, J. E., ŠPONER, J., CASSONE, G., KAPRALOV, M., TIMOSHENKO, G. N., KRASAVIN, E., FANELLI, G., TIMPERIO, A. M. & DI MAURO, E. 2020. Meteorite-Assisted Phosphorylation of Adenosine Under Proton Irradiation Conditions. *ChemSystemsChem,* 2**,** e1900039.

BLAND, P. A. & ARTEMIEVA, N. A. 2006. The rate of small impacts on Earth. *Meteoritics & Planetary Science,* 41**,** 607-631.

BLANK, J. & MILLER, G. The fate of organic compounds in cometary impacts. Proceedings of the 21st International Symposium on Shock Waves, 1998. Panther Publishing Fyshwick, Australia, 1205-1210.

BLANK, J. G., MILLER, G. H., AHRENS, M. J. & WINANS, R. E. 2001. Experimental shock chemistry of aqueous amino acid solutions and the cometary delivery of prebiotic compounds. *Origins of Life and Evolution of the Biosphere,* 31**,** 15-51.

BOCKELÉE-MORVAN, D., LIS, D., WINK, J., DESPOIS, D., CROVISIER, J., BACHILLER, R., BENFORD, D., BIVER, N., COLOM, P. & DAVIES, J. 2000. New molecules found in comet C/1995 O1 (Hale-Bopp). Investigating the link between cometary and interstellar material. *Astronomy and Astrophysics,* 353**,** 1101-1114.

BOTTKE, W. F. & NORMAN, M. D. 2017. The late heavy bombardment. *Annual Review of Earth and Planetary Sciences,* 45**,** 619-647.

BRIANI, G., PACE, E., SHORE, S. N., PUPILLO, G., PASSARO, A. & AIELLO, S. 2013. Simulations of micrometeoroid interactions with the Earth atmosphere. *Astronomy & Astrophysics,* 552**,** A53.

BRIGGS, M. H. 1962. Properties of the organic microstructures of some carbonaceous chondrites. *Nature,* 195**,** 1076-1077.

BROWN, P. G., ASSINK, J. D., ASTIZ, L., BLAAUW, R., BOSLOUGH, M. B., BOROVIČKA, J., BRACHET, N., BROWN, D., CAMPBELL-BROWN, M. & CERANNA, L. 2013. A 500-kiloton airburst over Chelyabinsk and an enhanced hazard from small impactors. *Nature,* 503**,** 238-241.

BURCHELL, M. 2013. Cratering on icy bodies. *The Science of Solar System Ices.* Springer.

BURCHELL, M. J., BOWDEN, S. A., COLE, M., PRICE, M. C. & PARNELL, J. 2014. Survival of organic materials in hypervelocity impacts of ice on sand, ice, and water in the laboratory. *Astrobiology,* 14**,** 473-485.

BURCHELL, M. J., COLE, M. J., MCDONNELL, J. & ZARNECKI, J. C. 1999. Hypervelocity impact studies using the 2 MV Van de Graaff accelerator and two-stage light gas gun of the University of Kent at Canterbury. *Measurement Science and Technology,* 10**,** 41.

BURTON, A. S. & BERGER, E. L. 2018. Insights into abiotically-generated amino acid enantiomeric excesses found in meteorites. *Life,* 8**,** 14.

BURTON, A. S., STERN, J. C., ELSILA, J. E., GLAVIN, D. P. & DWORKIN, J. P. 2012. Understanding prebiotic chemistry through the analysis of extraterrestrial amino acids and nucleobases in meteorites. *Chemical Society Reviews,* 41**,** 5459-5472.

CALLAHAN, M. P., SMITH, K. E., CLEAVES, H. J., RUZICKA, J., STERN, J. C., GLAVIN, D. P., HOUSE, C. H. & DWORKIN, J. P. 2011. Carbonaceous meteorites contain a wide range of extraterrestrial nucleobases. *Proceedings of the National Academy of Sciences,* 108**,** 13995-13998.

CAMI, J., BERNARD-SALAS, J., PEETERS, E. & MALEK, S. E. 2010. Detection of C60 and C70 in a young planetary nebula. *Science,* 329**,** 1180-1182.

CAMPINS, H., HARGROVE, K., PINILLA-ALONSO, N., HOWELL, E. S., KELLEY, M. S., LICANDRO, J., MOTHÉ-DINIZ, T., FERNÁNDEZ, Y. & ZIFFER, J. 2010. Water ice and organics on the surface of the asteroid 24 Themis. *Nature,* 464**,** 1320-1321.

CANUP, R. M. & WARD, W. R. 2006. A common mass scaling for satellite systems of gaseous planets. *Nature,* 441**,** 834-839.

CARDOSO, S. S., CARTWRIGHT, J. H., ČEJKOVÁ, J., CRONIN, L., DE WIT, A., GIANNERINI, S., HORVÁTH, D., RODRIGUES, A., RUSSELL, M. J. & SAINZ-

DÍAZ, C. I. 2020. Chemobrionics: From Self-Assembled Material Architectures to the Origin of Life. *Artificial Life,* 26**,** 315-326.

CASSONE, G., SAIJA, F., SPONER, J., SPONER, J. E., FERUS, M., KRUS, M., CIARAVELLA, A., JIMÉNEZ-ESCOBAR, A. & CECCHI-PESTELLINI, C. 2018. Dust motions in magnetized turbulence: source of chemical complexity. *The Astrophysical Journal Letters,* 866**,** L23.

CHAN, Q., STEPHANT, A., FRANCHI, I., ZHAO, X., BRUNETTO, R., KEBUKAWA, Y., NOGUCHI, T., JOHNSON, D., PRICE, M. & HARRISS, K. 2021. Organic matter and water from asteroid Itokawa. *Scientific reports,* 11**,** 1-12.

CHAN, Q. H. S., CHIKARAISHI, Y., TAKANO, Y., OGAWA, N. O. & OHKOUCHI, N. 2016. Amino acid compositions in heated carbonaceous chondrites and their compound-specific nitrogen isotopic ratios. *Earth, Planets and Space,* 68**,** 1-13.

CHYBA, C. & HAND, K. 2006. Comets and prebiotic organic molecules on early Earth. *Comets and the Origin and Evolution of Life***,** 169-206.

CHYBA, C. & SAGAN, C. 1992. Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature,* 355**,** 125-132.

CHYBA, C. F., MCKAY, C. P. & THOMAS, P. J. 1997. *Comets and the Origin and Evolution of Life,* Springer New York.

CHYBA, C. F., THOMAS, P. J., BROOKSHAW, L. & SAGAN, C. 1990. Cometary delivery of organic molecules to the early Earth. *Science,* 249**,** 366-373.

CHYBA, C. F., THOMAS, P. J. & ZAHNLE, K. J. 1993. The 1908 Tunguska explosion: atmospheric disruption of a stony asteroid. *Nature,* 361**,** 40-44.

CIVIŠ, S., SZABLA, R., SZYJA, B. M., SMYKOWSKI, D., IVANEK, O., KNÍŽEK, A., KUBELÍK, P., ŠPONER, J., FERUS, M. & ŠPONER, J. E. 2016. TiO 2-catalyzed synthesis of sugars from formaldehyde in extraterrestrial impacts on the early Earth. *Scientific reports,* 6**,** 1-8.

CLARK, R. N., CARLSON, R., GRUNDY, W. & NOLL, K. 2013. Observed ices in the Solar System. *The science of solar system ices***,** 3-46.

CLAUS, G. & NAGY, B. 1961. A microbiological examination of some carbonaceous chondrites. *Nature,* 192**,** 594-596.

COCKELL, C. 2004. Impact-shocked rocks–insights into archean and extraterrestrial microbial habitats (and sites for prebiotic chemistry?). *Advances in Space Research,* 33**,** 1231-1235.

COCKELL, C. S. 2006. The origin and emergence of life under impact bombardment. *Philosophical Transactions of the Royal Society B: Biological Sciences,* 361**,** 1845-1856.

COCKELL, C. S., LEE, P., OSINSKI, G., HORNECK, G. & BROADY, P. 2002. Impact-induced microbial endolithic habitats. *Meteoritics & Planetary Science,* 37**,** 1287-1298.

COLÍN-GARCÍA, M., VILLAFAÑE-BARAJAS, S., CAMPRUBÍ, A., ORTEGA-GUTIÉRREZ, F., COLÁS, V. & NEGRÓN-MENDOZA, A. 2018. 5.4 Prebiotic chemistry in hydrothermal vent systems. *Handbook of Astrobiology; Kolb, V., Ed.; CRC Press: Boca Raton, FL, USA***,** 297-329.

CRONIN, J. & PIZZARELLO, S. 1999. Amino acid enantiomer excesses in meteorites: origin and significance. *Advances in Space Research,* 23**,** 293-299.

CROVISIER, J., BIVER, N., BOCKELÉE-MORVAN, D., BOISSIER, J., COLOM, P. & LIS, D. C. 2009. The chemical diversity of comets: synergies between space exploration and ground-based radio observations. *Earth, Moon, and Planets,* 105**,** 267-272.

DALAI, P., KADDOUR, H. & SAHAI, N. 2016. Incubating life: prebiotic sources of organics for the origin of life. *Elements,* 12**,** 401-406.

DANGER, G., PLASSON, R. & PASCAL, R. 2012. Pathways for the formation and evolution of peptides in prebiotic environments. *Chemical Society Reviews,* 41**,** 5416-5429.

DARTOIS, E., ENGRAND, C., BRUNETTO, R., DUPRAT, J., PINO, T., QUIRICO, E., REMUSAT, L., BARDIN, N., BRIANI, G. & MOSTEFAOUI, S. 2013. UltraCarbonaceous Antarctic micrometeorites, probing the Solar System beyond the nitrogen snow-line. *Icarus,* 224**,** 243-252.

DEAMER, D. & WEBER, A. L. 2010. Bioenergetics and life's origins. *Cold Spring Harbor perspectives in biology,* 2**,** a004929.

DEAMER, D. W. & PASHLEY, R. 1989. Amphiphilic components of the Murchison carbonaceous chondrite: surface properties and membrane formation. *Origins of Life and Evolution of the Biosphere,* 19**,** 21-38.

DEMING, T. J. 2006. Polypeptide and polypeptide hybrid copolymer synthesis via NCA polymerization. *Peptide hybrid polymers.* Springer.

DESPOIS, D. & COTTIN, H. 2005. Comets: potential sources of prebiotic molecules for the early Earth. *Lectures in astrobiology.* Springer.

DODD, M. S., PAPINEAU, D., GRENNE, T., SLACK, J. F., RITTNER, M., PIRAJNO, F., O'NEIL, J. & LITTLE, C. T. 2017. Evidence for early life in Earth's oldest hydrothermal vent precipitates. *Nature,* 543**,** 60-64.

DWORKIN, J. P., DEAMER, D. W., SANDFORD, S. A. & ALLAMANDOLA, L. J. 2001. Self-assembling amphiphilic molecules: Synthesis in simulated interstellar/precometary ices. *Proceedings of the National Academy of Sciences,* 98**,** 815-819.

EBERT, M., HECHT, L., HAMANN, C. & LUTHER, R. 2017. Laser-induced melting experiments: Simulation of short-term high-temperature impact processes. *Meteoritics & Planetary Science,* 52**,** 1475-1494.

EHRENFREUND, P., BERNSTEIN, M., DWORKIN, J., SANDFORD, S. & ALLAMANDOLA, L. 2001. The photostability of amino acids in space. *The Astrophysical Journal Letters,* 550**,** L95.

EHRENFREUND, P. & CHARNLEY, S. B. 2000. Organic molecules in the interstellar medium, comets, and meteorites: a voyage from dark clouds to the early Earth. *Annual Review of Astronomy and Astrophysics,* 38**,** 427-483.

ELSILA, J. E., GLAVIN, D. P. & DWORKIN, J. P. 2009. Cometary glycine detected in samples returned by Stardust. *Meteoritics & Planetary Science,* 44**,** 1323-1330.

FERUS, M., KNÍŽEK, A. & CIVIŠ, S. 2015a. Meteorite-catalyzed synthesis of nucleosides and other prebiotic compounds. *Proceedings of the National Academy of Sciences,* 112**,** 7109-7110.

FERUS, M., MICHALCIKOVA, R., SHESTIVSKÁ, V., ŠPONER, J. Í., ŠPONER, J. E. & CIVIŠ, S. 2014. High-energy chemistry of formamide: A simpler way for nucleobase formation. *The Journal of Physical Chemistry A,* 118**,** 719-736.

FERUS, M., NESVORNÝ, D., ŠPONER, J., KUBELÍK, P., MICHALČÍKOVÁ, R., SHESTIVSKÁ, V., ŠPONER, J. E. & CIVIŠ, S. 2015b. High-energy chemistry of formamide: A unified mechanism of nucleobase formation. *Proceedings of the National Academy of Sciences,* 112**,** 657-662.

FERUS, M., PIETRUCCI, F., SAITTA, A., IVANEK, O., KNIZEK, A., KUBELÍK, P., KRUS, M., JUHA, L., DUDZAK, R. & DOSTÁL, J. 2019. Prebiotic synthesis initiated in formaldehyde by laser plasma simulating high-velocity impacts. *Astronomy & Astrophysics,* 626**,** A52.

FERUS, M., PIETRUCCI, F., SAITTA, A. M., KNÍŽEK, A., KUBELÍK, P., IVANEK, O., SHESTIVSKA, V. & CIVIŠ, S. 2017. Formation of nucleobases in a Miller–Urey reducing atmosphere. *Proceedings of the National Academy of Sciences,* 114**,** 4306-4311.

FITCH, F., SCHWARCZ, H. P. & ANDERS, E. 1962. 'Organized elements' in carbonaceous chondrites. *Nature,* 193**,** 1123-1125.

FLYNN, G., KELLER, L., FESER, M., WIRICK, S. & JACOBSEN, C. 2003. The origin of organic matter in the solar system: Evidence from the interplanetary dust particles. *Geochimica et Cosmochimica Acta,* 67**,** 4791-4806.

FLYNN, G., KELLER, L., WIRICK, S. & JACOBSEN, C. 2008. Organic matter in interplanetary dust particles. *Proceedings of the International Astronomical Union,* 4**,** 267-276.

FOLSOME, C. E. 1976. Synthetic organic microstructures and the origins of cellular life. *Naturwissenschaften,* 63**,** 303-306.

FOX, S. 1973. Origin of the cell-Experiments and premises.

FRENKEL-PINTER, M., SAMANTA, M., ASHKENASY, G. & LEMAN, L. J. 2020. Prebiotic Peptides: Molecular Hubs in the Origin of Life. *Chemical Reviews*.

FURUKAWA, Y., CHIKARAISHI, Y., OHKOUCHI, N., OGAWA, N. O., GLAVIN, D. P., DWORKIN, J. P., ABE, C. & NAKAMURA, T. 2019. Extraterrestrial ribose and other sugars in primitive meteorites. *Proceedings of the National Academy of Sciences,* 116**,** 24440-24445.

FURUKAWA, Y., NAKAZAWA, H., SEKINE, T., KOBAYASHI, T. & KAKEGAWA, T. 2015. Nucleobase and amino acid formation through impacts of meteorites on the early ocean. *Earth and Planetary Science Letters,* 429**,** 216-222.

FURUKAWA, Y., SEKINE, T., OBA, M., KAKEGAWA, T. & NAKAZAWA, H. 2009. Biomolecule formation by oceanic impacts on early Earth. *Nature geoscience,* 2**,** 62-66.

GAYDON, A. G. & HURLE, I. R. 1963. *The shock tube in high-temperature chemical physics,* Chapman and Hall.

GERASIMOV, M., IVANOV, B., YAKOVLEV, O. & DIKOV, Y. P. 1998. Physics and chemistry of impacts. *Earth, Moon, and Planets,* 80**,** 209-259.

GERASIMOV, M., YAKOVLEV, O., DIKOV, Y. P. & WLOTZKA, F. 2005. Evaporative differentiation of impact-produced melts: Laser-simulation experiments and comparison with impact glasses from the Logoisk crater. *Special Paper of the Geological Society of America,* 384**,** 351-366.

GILVARRY, J. & HOCHSTIM, A. 1963. Possible role of meteorites in the origin of life. *Nature,* 197**,** 624-625.

GLASS, I. 1977. Terrestrial and Cosmic Shock Waves: Shock waves can create as well as destroy; they serve man in a variety of ways and may even have helped to form life itself. *American Scientist,* 65**,** 473-481.

GLAVIN, D., MATRAJT, G. & BADA, J. 2004. Re-examination of amino acids in Antarctic micrometeorites. *Advances in Space Research,* 33**,** 106-113.

GLAVIN, D. P., MCLAIN, H. L., DWORKIN, J. P., PARKER, E. T., ELSILA, J. E., APONTE, J. C., SIMKUS, D. N., POZARYCKI, C. I., GRAHAM, H. V. & NITTLER, L. R. 2020. Abundant extraterrestrial amino acids in the primitive CM carbonaceous chondrite Asuka 12236. *Meteoritics & Planetary Science,* 55**,** 1979-2006.

GOESMANN, F., ROSENBAUER, H., BREDEHÖFT, J. H., CABANE, M., EHRENFREUND, P., GAUTIER, T., GIRI, C., KRÜGER, H., LE ROY, L. & MACDERMOTT, A. J. 2015. Organic compounds on comet 67P/Churyumov-Gerasimenko revealed by COSAC mass spectrometry. *Science,* 349.

GOLDMAN, N., KROONBLAWD, M. & LINDSEY, R. Self-Assembly of Prebiotic Organic Materials from Impact Events of Amino Acid Solutions. APS March Meeting Abstracts, 2018. V38. 003.

GOLDMAN, N., REED, E. J., FRIED, L. E., KUO, I.-F. W. & MAITI, A. 2010. Synthesis of glycine-containing complexes in impacts of comets on early Earth. *Nature Chemistry,* 2**,** 949-954.

GOLDMAN, N. & TAMBLYN, I. 2013. Prebiotic chemistry within a simple impacting icy mixture. *The Journal of Physical Chemistry A,* 117**,** 5124-5131.

GREELEY, R., KLEMASZEWSKI, J. & WAGNER, R. 2000. Galileo views of the geology of Callisto. *Planetary and Space Science,* 48**,** 829-853.

HAMMOND, R. 2010. *http://news.bbc.co.uk/2/hi/sci/tech/8569953.stm*. [Online]. [Accessed].

HERBST, E. & VAN DISHOECK, E. F. 2009. Complex organic interstellar molecules. *Annual Review of Astronomy and Astrophysics,* 47**,** 427-480.

HIBBERT, R., COLE, M., PRICE, M. C. & BURCHELL, M. 2017. The Hypervelocity Impact Facility at the University of Kent: Recent Upgrades and Specialized Capabilities. *Procedia engineering,* 204**,** 208-214.

HOCHSTIM, A. R. 1963. Hypersonic chemosynthesis and possible formation of organic compounds from impact of meteorites on water. *Proceedings of the National Academy of Sciences of the United States of America,* 50**,** 200.

HOOVER, R. B. 2011. Fossils of cyanobacteria in CI1 carbonaceous meteorites. *Journal of Cosmology,* 13**,** 3811-48.

HOOVER, R. B., JERMAN, G., ROZANOV, A. Y. & SIPIERA, P. P. Indigenous microfossils in carbonaceous meteorites. Instruments, Methods, and Missions for Astrobiology VIII, 2004. International Society for Optics and Photonics, 1-17.

HUBER, C. & WÄCHTERSHÄUSER, G. 1998. Peptides by activation of amino acids with CO on (Ni, Fe) S surfaces: implications for the origin of life. *Science,* 281**,** 670-672.

HUGHES, D. W. & WILLIAMS, I. P. 2000. The velocity distributions of periodic comets and stream meteoroids. *Monthly Notices of the Royal Astronomical Society,* 315**,** 629-634.

IOPPOLO, S., FEDOSEEV, G., CHUANG, K.-J., CUPPEN, H., CLEMENTS, A., JIN, M., GARROD, R., QASIM, D., KOFMAN, V. & VAN DISHOECK, E. 2021. A non-energetic mechanism for glycine formation in the interstellar medium. *Nature Astronomy,* 5**,** 197-205.

JAGADEESH, G. 2008. Fascinating world of shock waves. *Resonance,* 13**,** 752-767.

JIA, T. Z. & KURUMA, Y. 2019. Recent Advances in Origins of Life Research by Biophysicists in Japan. *Challenges,* 10**,** 28.

KAISER, R. I. 2002. Experimental investigation on the formation of carbon-bearing molecules in the interstellar medium via neutral− neutral reactions. *Chemical Reviews,* 102**,** 1309-1358.

KIM, S. C., ZHOU, L., ZHANG, W., O'FLAHERTY, D. K., RONDO-BROVETTO, V. & SZOSTAK, J. W. 2020. A model for the emergence of RNA from a prebiotically plausible mixture of ribonucleotides, arabinonucleotides, and 2′-deoxynucleotides. *Journal of the American Chemical Society,* 142**,** 2317-2326.

KITADAI, N. & MARUYAMA, S. 2018. Origins of building blocks of life: A review. *Geoscience Frontiers,* 9**,** 1117-1153.

KOEBERL, C. 2006. The record of impact processes on the early Earth: A review of the first 2.5 billion years. *Geological Society of America Special Papers,* 405**,** 1-22.

KOEBERL, C., REIMOLD, W. U., MCDONALD, I. & ROSING, M. 2000. Search for petrographic and geochemical evidence for the late heavy bombardment on Earth in early Archean rocks from Isua, Greenland. *Impacts and the early Earth.* Springer.

KOLEY, P. & PRAMANIK, A. 2012. Multilayer vesicles, tubes, various porous structures and organo gels through the solvent-assisted self-assembly of two modified tripeptides and their different applications. *Soft Matter,* 8**,** 5364-5374.

KONDA, M., BHOWMIK, S., MOBIN, S. M., BISWAS, S. & DAS, A. K. 2016. Modulating Hydrogen Bonded Self–assembled Patterns and Morphological Features by a Change in Side Chain of Third Amino Acid of Synthetic γ-Amino Acid Based Tripeptides. *ChemistrySelect,* 1**,** 2586-2593.

KREHL, P. O. 2011. Shock wave physics and detonation physics—a stimulus for the emergence of numerous new branches in science and engineering. *The European Physical Journal H,* 36**,** 85-152.

KRESLAVSKY, M. A., IVANOV, M. A. & HEAD, J. W. 2015. The resurfacing history of Venus: Constraints from buffered crater densities. *Icarus,* 250**,** 438-450.

LAMBERT, J.-F. 2008. Adsorption and polymerization of amino acids on mineral surfaces: a review. *Origins of Life and Evolution of Biospheres,* 38**,** 211-242.

LEMKE, K. H., ROSENBAUER, R. J. & BIRD, D. K. 2009. Peptide synthesis in early Earth hydrothermal systems. *Astrobiology,* 9**,** 141-146.

LICANDRO, J. 2011. Cybele: Detection of small silicate grains, water-ice and organics. 2011. *Astron. Atrophys,* 525**,** A34.

LINGAM, M. & LOEB, A. 2021. Life in the Cosmos: From Biosignatures to Technosignatures. Cambridge: Harvard Univ. Press 2021.

LIU, K., XING, R., CHEN, C., SHEN, G., YAN, L., ZOU, Q., MA, G., MÖHWALD, H. & YAN, X. 2015. Peptide-Induced Hierarchical Long-Range Order and Photocatalytic Activity of Porphyrin Assemblies. *Angewandte Chemie International Edition,* 54**,** 500-505.

LUISI, P. L. 2016. *The emergence of life: from chemical origins to synthetic biology*, Cambridge University Press.

MAMIKUNIAN, G. & BRIGGS, M. H. 1963. Some microstructures of complex morphology observed in preparations of carbonaceous chondrites made under sterile conditions. *Nature,* 197**,** 1245-1248.

MANDAL, D., SHIRAZI, A. N. & PARANG, K. 2014. Self-assembly of peptides to nanostructures. *Organic & biomolecular chemistry,* 12**,** 3544-3561.

MANN, S. 2012. Systems of creation: the emergence of life from nonliving matter. *Accounts of chemical research,* 45**,** 2131-2141.

MARATHE, A. & BANSAL, M. 2010. The 5-methyl group in thymine dynamically influences the structure of A-tracts in DNA at the local and global level. *The Journal of Physical Chemistry B,* 114**,** 5534-5546.

MARTIN, W., BAROSS, J., KELLEY, D. & RUSSELL, M. J. 2008. Hydrothermal vents and the origin of life. *Nature Reviews Microbiology,* 6**,** 805-814.

MARTINS, Z. 2018. The nitrogen heterocycle content of meteorites and their significance for the origin of life. *Life,* 8**,** 28.

MARTINS, Z., BOTTA, O., FOGEL, M. L., SEPHTON, M. A., GLAVIN, D. P., WATSON, J. S., DWORKIN, J. P., SCHWARTZ, A. W. & EHRENFREUND, P. 2008. Extraterrestrial nucleobases in the Murchison meteorite. *Earth and planetary science Letters,* 270**,** 130-136.

MARTINS, Z., PRICE, M. C., GOLDMAN, N., SEPHTON, M. A. & BURCHELL, M. J. 2013. Shock synthesis of amino acids from impacting cometary and icy planet surface analogues. *Nature Geoscience,* 6**,** 1045-1049.

MATERESE, C. K., NUEVO, M. & SANDFORD, S. A. 2017. The formation of nucleobases from the ultraviolet photoirradiation of purine in simple astrophysical ice analogues. *Astrobiology,* 17**,** 761-770.

MAYER, C. 2020. Life in the context of order and complexity. *Life,* 10**,** 5.

MCGUIRE, B. A. The 2021 Census Of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, And Exoplanetary Molecules: What Are The Pressing Spectroscopic Needs From The Laboratory? , 2021. International Symposium on Molecular Spectroscopy.

MCKAY, A. J. & ROTH, N. X. 2021. Organic Matter in Cometary Environments. *Life,* 11**,** 37.

MCKAY, C. P. & BORUCKI, W. J. 1997. Organic synthesis in experimental impact shocks. *Science,* 276**,** 390-392.

MCKAY, D. S., GIBSON, E. K., THOMAS-KEPRTA, K. L., VALI, H., ROMANEK, C. S., CLEMETT, S. J., CHILLIER, X. D., MAECHLING, C. R. & ZARE, R. N. 1996. Search for past life on Mars: possible relic biogenic activity in Martian meteorite ALH84001. *Science,* 273**,** 924-930.

MELOSH, H. J. 1989a. Impact cratering: A geologic process. *icgp*.

MELOSH, H. J. 1989b. Impact cratering: A geologic process. *Oxford University Press New York*.

MELOSH, H. J. 2013. The contact and compression stage of impact cratering. *Impact Cratering: processes and products***,** 32-42.

MENOR-SALVÁN, C. 2018. *Prebiotic chemistry and chemical evolution of nucleic acids*, Springer.

MENOR-SALVÁN, C. & MARÍN-YASELI, M. R. 2013. A new route for the prebiotic synthesis of nucleobases and hydantoins in water/ice solutions involving the photochemistry of acetylene. *Chemistry–A European Journal,* 19**,** 6488-6497.

MENOR-SALVÁN, C., RUIZ-BERMEJO, M., GUZMÁN, M. I., OSUNA-ESTEBAN, S. & VEINTEMILLAS-VERDAGUER, S. 2009. Synthesis of pyrimidines and triazines in ice: implications for the prebiotic chemistry of nucleobases. *Chemistry–A European Journal,* 15**,** 4411-4418.

MILLER, S. L. 1953. A production of amino acids under possible primitive earth conditions. *Science,* 117**,** 528-529.

MILLER, S. L. 1955. Production of some organic compounds under possible primitive earth conditions1. *Journal of the American Chemical Society,* 77**,** 2351-2361.

MILLER, S. L. 1974. The origins of life on the earth. *Concept of Modern biology series*.

MILLER, S. L. & ORGEL, L. E. 1974. The origins of life on the earth. *Prentice Hall, New Jersey*.

MOJZSIS, S. J., ARRHENIUS, G., MCKEEGAN, K., HARRISON, T., NUTMAN, A. & FRIEND, C. 1996. Evidence for life on Earth before 3,800 million years ago. *Nature,* 384**,** 55-59.

MUELLER, G. 1962. Interpretation of micro-structures in carbonaceous meteorites. *Nature,* 196**,** 929-932.

MUMMA, M. J. & CHARNLEY, S. B. 2011. The chemical composition of comets—emerging taxonomies and natal heritage. *Annual Review of Astronomy and Astrophysics,* 49.

NAGY, B., CLAUS, G. & HENNESSY, D. J. 1962. Organic particles embedded in minerals in the Orgueil and Ivuna carbonaceous chondrites. *Nature,* 193**,** 1129-1133.

NAGY, B., FREDRIKSSON, K., UREY, H. C., CLAUS, G., ANDERSEN, C. A. & PERCY, J. 1963. Electron probe microanalysis of organized elements in the Orgueil meteorite. *Nature,* 198**,** 121-125.

NNA-MVONDO, D., KHARE, B., ISHIHARA, T. & MCKAY, C. P. 2008. Experimental impact shock chemistry on planetary icy satellites. *Icarus,* 194**,** 822-835.

NUEVO, M., COOPER, G. & SANDFORD, S. A. 2018. Deoxyribose and deoxysugar derivatives from photoprocessed astrophysical ice analogues and comparison to meteorites. *Nature communications,* 9**,** 1-10.

NUEVO, M., MILAM, S. N. & SANDFORD, S. A. 2012. Nucleobases and prebiotic molecules in organic residues produced from the ultraviolet photo-irradiation of pyrimidine in NH3 and H2O+ NH3 ices. *Astrobiology,* 12**,** 295-314.

NUEVO, M., MILAM, S. N., SANDFORD, S. A., ELSILA, J. E. & DWORKIN, J. P. 2009. Formation of uracil from the ultraviolet photo-irradiation of pyrimidine in pure H2O ices. *Astrobiology,* 9**,** 683-695.

OBA, Y., TAKANO, Y., NARAOKA, H., WATANABE, N. & KOUCHI, A. 2019. Nucleobase synthesis in interstellar ices. *Nature communications,* 10**,** 1-8.

OBERBECK, V. R. 1971. Laboratory simulation of impact cratering with high explosives. *Journal of Geophysical Research,* 76**,** 5732-5749.

OBERBECK, V. R. & AGGARWAL, H. 1991. Comet impacts and chemical evolution on the bombarded Earth. *Origins of Life and Evolution of the Biosphere,* 21**,** 317-338.

OPARIN, A. 1928. The origin of life. Translated by S. Morgulis. NY. *Y., Macmillan*.

ORÓ, J. 1960. Synthesis of adenine from ammonium cyanide. *Biochemical and Biophysical Research Communications,* 2**,** 407-412.

ORÓ, J. 1961. Comets and the formation of biochemical compounds on the primitive Earth. *Nature,* 190**,** 389-390.

ORÓ, J. & KIMBALL, A. 1961. Synthesis of purines under possible primitive earth conditions. I. Adenine from hydrogen cyanide. *Archives of biochemistry and biophysics,* 94**,** 217-227.

OSINSKI, G., COCKELL, C., PONTEFRACT, A. & SAPERS, H. 2020. The Role of Meteorite Impacts in the Origin of Life. *Astrobiology,* 20**,** 1121-1149.

OTAKE, T., TANIGUCHI, T., FURUKAWA, Y., KAWAMURA, F., NAKAZAWA, H. & KAKEGAWA, T. 2011. Stability of amino acids and their oligomerization under high-pressure conditions: implications for prebiotic chemistry. *Astrobiology,* 11**,** 799-813.

PARSONS, I., LEE, M. R. & SMITH, J. V. 1998. Biochemical evolution II: Origin of life in tubular microstructures on weathered feldspar surfaces. *Proceedings of the National Academy of Sciences,* 95**,** 15173-15176.

PEPTIDESYNTHETICS. *https://www.peptidesynthetics.co.uk/tools/* [Online]. [Accessed].

PETERSON, E., HORZ, F. & CHANG, S. 1997. Modification of amino acids at shock pressures of 3.5 to 32 GPa. *Geochimica et cosmochimica acta,* 61**,** 3937-3950.

PIERAZZO, E. & CHYBA, C. 1999. Amino acid survival in large cometary impacts. *Meteoritics & Planetary Science,* 34**,** 909-918.

PIERAZZO, E. & MELOSH, H. 2000. Hydrocode modeling of oblique impacts: The fate of the projectile. *Meteoritics & Planetary Science,* 35**,** 117-130.

POPOVA, O. P., JENNISKENS, P., EMEL'YANENKO, V., KARTASHOVA, A., BIRYUKOV, E., KHAIBRAKHMANOV, S., SHUVALOV, V., RYBNOV, Y., DUDOROV, A. & GROKHOVSKY, V. I. 2013. Chelyabinsk airburst, damage assessment, meteorite recovery, and characterization. *Science,* 342**,** 1069-1073.

POTISZIL, C., TANAKA, R., KOBAYASHI, K., KUNIHIRO, T. & NAKAMURA, E. 2020. The Albedo of Ryugu: Evidence for a High Organic Abundance, as Inferred from the Hayabusa2 Touchdown Maneuver. *Astrobiology,* 20**,** 916-921.

RIDGLEY, D. M., CLAUNCH, E. C. & BARONE, J. R. 2012. The effect of processing on large, self-assembled amyloid fibers. *Soft Matter,* 8**,** 10298-10306.

RIOS, A. C. 2015. Impact synthesis of the RNA bases. *Proceedings of the National Academy of Sciences,* 112**,** 643-644.

RUF, A., D'HENDECOURT, L. L. & SCHMITT-KOPPLIN, P. 2018. Data-Driven Astrochemistry: One Step Further within the Origin of Life Puzzle. *Life,* 8**,** 18.

RYDER, G. 2002. Mass flux in the ancient Earth-Moon system and benign implications for the origin of life on Earth. *Journal of Geophysical Research: Planets,* 107**,** 6-1-6-13.

SALADINO, R., CRESTINI, C., CICIRIELLO, F., COSTANZO, G. & DI MAURO, E. 2006. About a formamide-based origin of informational polymers: syntheses of nucleobases and favourable thermodynamic niches for early polymers. *Origins of Life and Evolution of Biospheres,* 36**,** 523-531.

SCHIDLOWSKI, M. 1988. A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature,* 333**,** 313-318.

SCHMIEDER, M. & KRING, D. A. 2020. Earth's impact events through geologic time: a list of recommended ages for terrestrial impact structures and deposits. *Astrobiology,* 20**,** 91-141.

SCHUTTE, W. 1999. Laboratory simulation of processes in interstellar ices. *Formation and Evolution of Solids in Space.* Springer.

SILBER, E. A., BOSLOUGH, M., HOCKING, W. K., GRITSEVICH, M. & WHITAKER, R. W. 2018. Physics of meteor generated shock waves in the earth's atmosphere–a review. *Advances in Space Research,* 62**,** 489-532.

SIMAKOV, M., KUZICHEVA, E., DODONOVA, N. Y. & ANTROPOV, A. 1997. Formation of oligopeptides on the surface of small bodies in solar system by cosmic radiation. *Advances in Space Research,* 19**,** 1063-1066.

SIMIONESCU, C., DENES, F. & TOTOLIN, M. 1985. The formation of some lipid-like structures under cold conditions. *Bioelectrochemistry and Bioenergetics,* 14**,** 429-437.

SIMIONESCU, C., DÉNES, F. & TOTOLIN, M. 1981. The synthesis of some lipid-like structures in simulated primeval Earth conditions. *Biosystems,* 13**,** 149-156.

SIMIONESCU, C., DÉNES, F. & TOTOLIN, M. 1982. Ordered protomembranes. *Bioelectrochemistry and Bioenergetics,* 9**,** 723-731.

SIMON, A. A., KAPLAN, H. H., HAMILTON, V. E., LAURETTA, D. S., CAMPINS, H., EMERY, J. P., BARUCCI, M. A., DELLAGIUSTINA, D. N., REUTER, D. C. & SANDFORD, S. A. 2020. Widespread carbon-bearing materials on near-Earth asteroid (101955) Bennu. *Science,* 370.

STONE, J. 2018. A practical guide to sample preparation for liquid chromatography-tandem mass spectrometry in clinical research and toxicology. *Article,* 30**,** 15-21.

SU, Y., YAN, X., WANG, A., FEI, J., CUI, Y., HE, Q. & LI, J. 2010. A peony-flower-like hierarchical mesocrystal formed by diphenylalanine. *Journal of Materials Chemistry,* 20**,** 6734-6740.

SUBBURAJ, J. 2018. *Investigations on Supersonic Flow in Miniature Shock Tubes.*

SUGAHARA, H. & MIMURA, K. 2014. Glycine oligomerization up to triglycine by shock experiments simulating comet impacts. *Geochemical Journal,* 48**,** 51-62.

SUGAHARA, H. & MIMURA, K. 2015. Peptide synthesis triggered by comet impacts: A possible method for peptide delivery to the early Earth and icy satellites. *Icarus,* 257**,** 103-112.

SZOSTAK, J. W. 2009. Systems chemistry on early Earth. *Nature,* 459**,** 171-172.

SZOSTAK, J. W., BARTEL, D. P. & LUISI, P. L. 2001. Synthesizing life. *Nature,* 409**,** 387-390.

TAKEUCHI, Y., FURUKAWA, Y., KOBAYASHI, T., SEKINE, T., TERADA, N. & KAKEGAWA, T. 2020. Impact-induced amino acid formation on Hadean Earth and Noachian Mars. *Scientific Reports,* 10**,** 1-7.

TANAKA, M., KANEKO, F., KOKETSU, T., NAKAGAWA, K. & YAMADA, T. 2008. Fragmentation and dimerization of aliphatic amino acid films induced by vacuum ultraviolet irradiation. *Radiation Physics and Chemistry,* 77**,** 1164-1168.

TIRARD, S. 2017. JBS Haldane and the origin of life. *Journal of genetics,* 96**,** 735-739.

TURCO, R. P., TOON, O., PARK, C., WHITTEN, R., POLLACK, J. & NOERDLINGER, P. 1982. An analysis of the physical, chemical, optical, and historical impacts of the 1908 Tunguska meteor fall. *Icarus,* 50**,** 1-52.

UMEDA, Y., FUKUNAGA, N., SEKINE, T., FURUKAWA, Y., KAKEGAWA, T., KOBAYASHI, T. & NAKAZAWA, H. 2016. Survivability and reactivity of glycine and alanine in early oceans: effects of meteorite impacts. *Journal of biological physics,* 42**,** 177-198.

VALLADAS-DUBOIS, S. & PRUDHOMME, R. 1983. Formation of microspheres from simple molecules under simulated primitive earth conditions; ultrasound and light radiation. *Experientia,* 39**,** 571-573.

VENKATESHAIAH, A., PADIL, V. V., NAGALAKSHMAIAH, M., WACLAWEK, S., ČERNÍK, M. & VARMA, R. S. 2020. Microscopic techniques for the analysis of micro and nanostructures of biopolymers and their derivatives. *Polymers,* 12**,** 512.

VISHAKANTAIAH, J. Experimental Investigation of Strong Shock-Heated Gases Interacting with Materials in Powder Form. International Symposium on Shock Waves, 2017. Springer, 727-734.

WÄRMLÄNDER, S., SPONER, J. E., SPONER, J. & LEIJON, M. 2002. The influence of the thymine C5 methyl group on spontaneous base pair breathing in DNA. *Journal of Biological Chemistry,* 277**,** 28491-28497.

WAY, M. J., DEL GENIO, A. D., KIANG, N. Y., SOHL, L. E., GRINSPOON, D. H., ALEINOV, I., KELLEY, M. & CLUNE, T. 2016. Was Venus the first habitable world of our solar system? *Geophysical research letters,* 43**,** 8376-8383.

WEISBERG, M. K., MCCOY, T. J. & KROT, A. N. 2006. Systematics and evaluation of meteorite classification. *Meteorites and the early solar system II,* 19.

WRIGHT, I., SHERIDAN, S., BARBER, S., MORGAN, G., ANDREWS, D. & MORSE, A. 2015. CHO-bearing organic compounds at the surface of 67P/Churyumov-Gerasimenko revealed by Ptolemy. *Science,* 349.

XU, J., CHMELA, V., GREEN, N. J., RUSSELL, D. A., JANICKI, M. J., GÓRA, R. W., SZABLA, R., BOND, A. D. & SUTHERLAND, J. D. 2020. Selective prebiotic formation of RNA pyrimidine and DNA purine nucleosides. *Nature,* 582**,** 60-66.

YANAGAWA, H., OGAWA, Y., KOJIMA, K. & ITO, M. 1988. Construction of protocellular structures under simulated primitive earth conditions. *Origins of Life and Evolution of the Biosphere,* 18**,** 179-207.

ZHANG, S. 2012. Lipid-like self-assembling peptides. *Accounts of chemical research,* 45**,** 2142-2150.

ZHAO, M. & BADA, J. L. 1989. Extraterrestrial amino acids in Cretaceous/Tertiary boundary sediments at Stevns Klint, Denmark. *Nature,* 339**,** 463-465.

ZIURYS, L. M. 2018. Interstellar Molecules and Their Prebiotic Potential. *Handbook of Astrobiology*. CRC Press.

ZOU, Q., ZHANG, L., YAN, X., WANG, A., MA, G., LI, J., MÖHWALD, H. & MANN, S. 2014. Multifunctional Porous Microspheres Based on Peptide–Porphyrin Hierarchical Co-Assembly. *Angewandte Chemie International Edition,* 53**,** 2366-2370.

List of Publications

1. **Singh, S.V.**, Vishakantaiah, J., Meka, J.K., Sivaprahasam, V., Chandrasekaran, V., Thombre, R., Thiruvenkatam, V., Mallya, A., Rajasekhar, B.N., Muruganantham, M., Datey, A., Hill, H., Bhardwaj, A., Jagadeesh, G., Reddy, K.P.J., Mason, N.J., Sivaraman, B. (2020). Shock Processing of Amino Acids Leading to Complex Structures—Implications to the Origin of Life. *Molecules*, *25*, 5634. (https://doi.org/10.3390/molecules25235634)
2. **Surendra, V. S.**, Jayaram, V., Muruganantham, M., Vijay, T., Vijayan, S., Samarth, P., Hill H., Bhardwaj A. & Sivaraman, B. (2021). Complex structures synthesized in shock processing of nucleobases–implications to the origins of life. *International Journal of Astrobiology*, 1-9. (https://doi.org/10.1017/S1473550421000136)
3. **Surendra, V. S.**, Jayaram, V., Meka J. K., Muruganantham, M., Vijay, T., Vijayan, S., Bhardwaj A. & Sivaraman, B. Three-dimensional complex architectures observed in shock processed amino acid mixtures **(Accepted for publications in Experimental Results)**
4. **Surendra, V. S.**, Haritha, D., Meka, J. K., Vijay, T., Jayaram, V., Muruganantham, M., Vijayan, S., Rajasekhar B. N., Bhardwaj, A., Mason, N.J., Burchell, M. & Sivaraman, B. New signatures of bio-molecular complexity in the hypervelocity impact ejecta of icy moon analogues **(under review)**
5. **Surendra, V. S. et al**., Synthesis of polypeptides in shock processing of amino acids (**under preparation**)
6. Shivakarthik, E., Meka, J. K., Harish, **Surendra, V. S.**, Rahul, K. K., Thombre, R., Hill, H., ... & Sivaraman, B. (2020). Sticking dust and micrometeorite particles on to ices at high impact velocities -Implications for astrochemical ice enrichment. *Planetary and Space Science*, *190*, 104972. (https://doi.org/10.1016/j.pss.2020.104972) (**Not included in thesis)**