Mote of Dust Suspended in Shock Waves

A thesis submitted in partial fulfilment of

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Doctor of Philosophy

by

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Taking the guidance from

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Discipline of Physics

Indian Institute of Technology, Gandhinagar, India

2023

Dedicated to My Parents

+

In memory of Vikram. A. Sarabhai and Carl Sagan

+

Those words of Carl Sagan's Valentine with the Earth

".....on a mote of dust suspended in a Sunbeam"

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 taken when needed.

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CERTIFICATE

It is certified that the work contained in the thesis titled **"Mote of Dust Suspended in Shock Waves"** by **Mr. Arijit Roy** (Roll no: 18330004) has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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Date: 9-04-2024

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Abstract:

Interstellar dust grains, nanometer to submicron sizes, are thought to form in the extended envelope of the evolved stars, such as Asymptotic Giant Branch (AGB) stars. The elemental abundance of these stars significantly affects the chemical compositions of these dust grains, especially the C/O abundance ratio, as these two elements are major after the hydrogen and helium of these stars. For the case of C/O <1, the dust grains are mostly oxides like olivine, pyroxene, spinel etc.; for the possibility of C/O >1, dust grains are carbonaceous like SiC, C₆₀, and other carbon allotropes. Astronomers used multi-wavelength observation techniques to understand the chemical composition of these tenuous dust grains.

Despite the joint effort of various laboratory and theoretical works on the formation pathways of interstellar dust grains, it is still poorly understood. Currently, two well-known formation pathways exist: the bottom-up formation route, which involves dust formation from the atomic scale, and the top-down formation route, where smaller dust grains are produced due to the destruction of larger pre-existing dust grains by energetic processes in the Interstellar Medium (ISM).

The shock wave is a known and important energetic source in the ISM. Violent shock waves from the Super Nova (SN) explosions can destroy the dust grains in its path. The role of relatively low velocity (< 10 km s⁻¹) shock waves in the interstellar chemical enrichment processes is still the least explored. It is observationally shown that nova shocks can initiate dust formation. At the same time, it has been proposed that the low-velocity shock processing of silicate dust precursors in the early solar nebula may lead to the formation of mineral dust in comets and the chondrules detected in various chondritic meteorites. Therefore, there is a growing need to carry out experiments by mimicking the low-velocity shock processing of different cosmic dust analogues.

A shock tube can be employed to replicate low-velocity interstellar shocks. The use of shock tubes in astrochemistry is limited to date. In this thesis, we take advantage of the High-Intensity Shock Tube for Astrochemistry (HISTA) housed at the Physical Research Laboratory (PRL), Ahmedabad. By utilizing the HISTA this thesis explores the formation and processing of various astrophysically relevant dust analogues. Different cosmic dust analogue samples were subjected to extreme shock conditions with Mach around 5.3 to 5.6 M and gas temperature around 6400 – 7300 K for 2 ms, respectively. The processed and unprocessed samples were analysed using different material characterization techniques such as ATR-FTIR spectroscopy, Raman spectroscopy, FE-SEM analysis, HR-TEM imaging, and EDX spectroscopy.

Shock processing of amorphous carbon with and without hydrogen shows the structural transformation to diverse carbon nanostructures such as carbon nanoribbons, carbon nanotubes, nano onion, fullerene, graphene, quantum dots, and nanodiamond. These findings suggest the possibility of these nanostructures in different C-rich shock-processed regions in the ISM. Shock processing of amorphous carbon and silicon nanodust mixtures paves an alternative formation pathway of SiC nanodust in interstellar conditions. The exposure of diamagnetic ferrocene to extreme shock turns it into the ferromagnetic iron carbide composite and amorphous carbon. Such drastic transformations from non-magnetic to magnetic dust induced by shocks can play a significant role in interstellar polarization. Shock processing of various silicate dust analogue mixtures shows the formation of forsterite, MgO, especially MgO quantum dots, olivine, and magnetite quantum dots. The results from these experiments suggest that olivine class cosmic dust can grow behind the shock front in interstellar space and in the presolar nebula. The presence of ferromagnetic dust, such as magnetite, can influence the dust aggregation process in the presence of a magnetic field in the ISM.

This thesis demonstrates that low-velocity shock waves can play a significant role in interstellar dust formation. It also highlights the potential of shock tubes as valuable tools for laboratory astrochemistry and astrophysics, particularly in simulating low-velocity ISM shocks. Results from this thesis help us propose new physical structures of cosmic dust, including carbon nanoribbons, graphene, graphene quantum dots, carbon nanotubes, MgO quantum dots, and magnetite quantum dots, some of which are not yet considered as components of interstellar dust. In addition, the magnetization of dust particles after shock processing of non-magnetic dust has to be considered in ISM dust modelling. Future work will involve studying various elemental and molecular mixtures under different shock strengths and gas temperatures to explore the impact of other thermodynamic parameters on dust grain composition and structures.

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List of Abbreviations

AFM	Atomic Force Microscopy
AGB	Asymptotic Giant Branch
ATR	Attenuated Total Reflectance
ATR-FTIR	Attenuated Total Reflectance -Fourier Transform Infrared Spectroscopy
AU	Astronomical Unit
CNC	Carbon Nano Cone
CNG	Closed Network Growth
CNN	Cyano Naphthalene
CNO	Carbon Nano Onion
CNT	Carbon Nanotube
CODID	Crystallographic Open Database ID
COSmIC	COsmic SImulation Chamber
CSM	Circumstellar Medium
CW	Continuous Wave
DFT	Density Functional theory
DIB	Diffuse Interstellar Band
EDS	Energy Dispersive X-ray Spectroscopy
EDX	Electron Dispersive X-Ray
EELS	Electron Energy Loss Spectroscopy
ERE	Extended Red Emission
FE-SEM	Field Emission Scanning Electron Microscopy
FFT	Fast Fourier Transformed
FIR	Far Infrared
FTIR	Fourier Transform Infrared Spectroscopy
GQD	Graphene Quantum Dot
HAADF	High-Angle Angular Dark Field
HAC	Hydrogenated Amorphous Carbon
HISTA	High-Intensity Shock Tube for Astrochemistry

HR-TEM	High-Resolution Transmission Electron Microscopy
IOM	Insoluble Organic Molecule
IR	Infrared
ISM	Interstellar Medium
ISO	Infrared Space Observatory
LDIMS	Laser Desorption Ionization Mass Spectrometry
MIR	Mid-Infrared
MR	Magnetic retentivity
MWCNT	Multi-walled carbon nanotubes
NMR	Nuclear Magnetic Resonance
OES	Optical Emission Spectroscopy
PAH	Polycyclic Aromatic Hydrocarbon
PNe	Planetary Nebula
PPE	Personal Protective Equipment
PRL	Physical Research Laboratory
QD	Quantum Dots
QMS	Quadrupole Mass Spectrometry
R-H	Rankine-Hugoniot
RBM	Radial Breathing Mode
RGB	Red Super Giant stars
RY-SG	Red and Yellow supergiant starts
S-G	Savitzky–Golay
SEM	Scanning Electron microscopy
SNR	Supernova Remnant
SOT	Silicon Oxygen Tetrahedron
STM	Scanning Tunnelling Microscopy
TMC-1	Taurus Molecular Cloud
TNT	Trinitrotoluene
TOFMS	Time of Flight Mass Spectrometer
UV	Ultraviolet

- VSM Vibrating Sample Magnetometry
- VUV Vacuum Ultra Violet
- WD white dwarf
- WR Wolf Rayet
- XRD X-Ray Diffraction

Chapter 1 Introduction

Chapter overview:

This chapter provides an elementary introduction and overview of the thesis. It begins with a short description of the Interstellar Medium (ISM), its different phases and the distribution of gas and dust in those regions. It also briefly describes the history of dust detection in the ISM. Much emphasis has been given to the spectroscopic observation of dust in different parts of the ISM using telescopes like ISO, Spitzer, and JWST, data from which offer a hint of the chemical composition of dust. A short description of various types of dust detected in meteorites known as presolar grain has also been covered. Interstellar dust is known to be either carbonaceous or oxide, so the structures of both carbonaceous and oxide dust are discussed in detail. These dust grains' formation pathways in the evolved stars' expanding envelope have also been covered briefly. The life cycle of cosmic dust and its processing by various energetic sources such as UV, cosmic rays, electrons, and shock waves in the ISM have been discussed. As the primary focus of this thesis is the experimental investigation of the shock-induced formation and processing of various interstellar dust analogues. A review relevant to various experiments performed on the formation of interstellar dust analogues (both carbonaceous and oxides) in the laboratory has been added. This bridges the motivation of the thesis, which explains why laboratory shock processing of interstellar dust analogue is essential. The chapter concludes with a clear statement of the thesis objectives and an outline of the thesis structure, providing a roadmap for the subsequent chapters.

1.1 The Interstellar Medium and its Phases:

The Interstellar Medium (ISM) refers to the vast region between stars and stellar systems, which contains an inhomogeneous mixture of gas, dust, and radiation. The advent of infrared and sub-millimetre astronomy, especially in the last five decades, has greatly transformed our perception of the interstellar medium (ISM) (Tielens 2005). Stars play a key role in the evolution of the ISM. Violent events such as harsh radiation, stellar winds, and explosive from the stars deeply impacted morphology, dynamics and chemical composition of the ISM. Based on the pressure, temperature, and state of its hydrogen content, the ISM can be classified into three different phases; these are cold ISM, warm ISM, and Hot ISM. The cold

ISM has two components: a molecular cloud with a densities of 10^2 to 10^6 cm, a temperature ranges of 10 K to 30 K, and the state of hydrogen being molecular. The other component of the cold ISM is a cold neutral medium with a density of 10^3 cm⁻³ and a temperature of approximately 50 K to 100 K, and the state of hydrogen being neutral atomic. The warm ISM has three components with a temperature range of 10^4 K to 10^5 K, and the state of hydrogen in the warm neutral medium is neutral atomic.

In contrast, the warm ionised medium, is ionized atomic, and the number density (-0.1 cm^{-3}) of this region is similar to what we see for the case of warm neutral medium. The third component of the warm ISM are HII regions, with a much higher number density ($\sim 10^4$ cm⁻³) than the previous two components. The third phase is the hot coronal gas region; its temperature range is around 10⁶ K, with the state of the hydrogen being ionized atomic (Tielens 2005). The specifications of different phases of ISM are tabulated in Table 1.1. To date, about 300 molecules are known to be present in different parts of the ISM (CDMS (Müller et al. 2005)), and the list keeps increasing. The matter distribution in the ISM is such that 99% consists of gas, and dust accounts for only 1% of the mass budget. Despite its minimal contribution to the interstellar mass budget, dust plays a key role in various processes that occur in ISM, such as molecular enrichment process, energy balance, interstellar extinction of starlight, polarization and scattering of starlight (Tielens 2005). A significant amount of heavy elements (in astronomy, elements beyond He are treated as metals) have been proposed to be locked up in the form of dust.

Phases	Component	State of the	Pressure	Temperature
		hydrogen	(cm ⁻³)	(K)
Cold	Molecular Cloud	Molecular	10 ² -10 ⁶	10-30
	Cold neutral medium	Neutral atomic	~ 10	50-100
Warm	Warm neutral medium	Neutral atomic	~ 0.1	~10 ⁴ -10 ⁵
	Warm ionized medium	Ionized atomic	~ 0.1	~10 ⁴
	HII region	Ionized atomic	10 ² -10 ⁴	~ 10 ⁴
Hot	Hot ionized medium	Ionized atomic	10-4-10-2	~10 ⁶

Table 1.	1: Different phases of ISM are classified based on the	state of hydrogen,
pressure	, and temperature (Data taken from (Wilkins & Blake	2021)).

Interstellar Dust:

1.2.1 Historical Background:

For a considerable period, the dark patches observed at night in the Milky Way's were regarded as starless 'voids' or 'holes' (Kwok 2007). In 1785, Sir William Herschel described these regions as "holes in the heavens" or starless areas. In the early 20th century, astronomers began considering these regions to be composed of 'dark obscuring masses' capable of absorbing stellar radiations (Kwok 2007). During this time, Vesto Slipher discovered Reflection Nebulae while studying the spectrum of the nebulosity in the Pleiades cluster. It was proposed that the nebulosity resulted from the scattering of starlight by materials present in the nearby Interstellar Medium (ISM). In 1920, Anton Pannekoek suggested that the scattering of starlight from ISM materials couldn't be caused by Rayleigh scattering from gas alone, as it would require unrealistic mass around the stars

(Kwok 2007). The decisive evidence for the presence of solid interstellar particles was presented in 1930 by Robert J Trumpler (Trumpler 1930). His team observed that many stars on the galactic plane appeared much redder than expected in their observations of 100 open clusters. This phenomenon, known as selective extinction, involves a higher degree of extinction (combination of absorption and scattering) at shorter wavelengths due to solid dust particles. These solid dust particles can also reflect and scatter background starlight, resulting in the visibility of Reflection Nebulae. Additionally, these dust particles absorb stellar radiation, aiding in our understanding of the chemical composition of the dust in the ISM (Kwok 2007). The other important feature of the ISM dust is its ability to polarize the interacting starlight (Kwok 2007). A brief discussion of the various events which provide evidence of the presence of dust grains in interstellar space is given below.

1.2.2 Interstellar extinction:

In principle, extinction is defined as the absorption and scattering of light propagating through a medium (Kwok 2007). In the ISM, the absorption of starlight by dust particles leads to a decrease in intensity, causing the star to appear dimmer. The scattering of light by dust particles causes the starlight to change direction, leading to a phenomenon known as reddening, where shorterwavelength light (such as blue and ultraviolet) is scattered more than longerwavelength light (such as red and infrared) (Draine 2003). Astronomers use the pairing method to study interstellar extinction, wherein they conduct spectrophotometry of two similar spectral classes of stars, one with very low matter density, and the other encased by a very thick dust shell. This causes a difference in the intensity of the detected light from these two stars. By observing changes in the spectrum astronomers were able to quantify the extinction at different wavelengths and study the properties of the intervening dust (Draine 2003). Fig 1.1 shows a typical interstellar extinction curve for the Milky Way galaxy. This curve is shown in the wavelength range from the far UV (~ 100 nm) to the NIR region (~ 1- 20 μ m). This curve has a robust feature (bump) around 220 nm or 4.6 μ m⁻¹, and the curve was found to rise more in the far UV range (Draine 2003). In the visible wavelength range, extinction is found to vary with
$1/\lambda$ where λ is the wavelength of the light. This almost linear portion of the extinction curve can hint at the dimension of the dust grains in the light path, which is of the order of the wavelength of the incident light (Draine 2003).



Fig 1. 1: A typical interstellar extinction curve for the Milky Way galaxy. The extinction at a wavelength λ , A_{λ} is normalized with respect to the extinction at a wavelength V = 550 nm plotted against frequency in the form of $1/\lambda$, where λ is in μ m (Image adapted from the book 'The Physics of the Interstellar Medium' third edition by J E Dyson D A Williams. 2021).

1.2.3 Interstellar Polarization:

Apart from absorbing and scattering starlight, the interstellar dust grains can also polarize the starlight. This phenomenon was first reported by Hiltner & Hall (Hiltner 1949, Hall 1949). The polarization of starlight occurs due to the preferential scattering of light by non-spherical, elongated dust grains aligned with the interstellar magnetic field. This scattering process causes the electric field vectors of the light waves to become aligned in a particular direction, resulting in polarized light. The degree and direction of polarization depend on the properties of the dust grains and the orientation of the interstellar magnetic field (Draine 2003, Krügel 2003). Interstellar polarization thus suggests that cosmic dust grains are non-spherical, although the spherical dust grains are possible. Instead cosmic dust is elongated and aligned towards a preferential direction, specifically along the direction of the galactic magnetic field (Draine 2003).

1.2.4 Scattering by dust grains:

The Milky way galaxy is illuminated by diffuse light that, which has not directed from any specific source (Draine 2003, Krügel 2003, Dyson & Williams 2020). This light is the result of starlight being scattered by some mechanism. Other physical processes do not seem to explain the origin of this diffuse light, as scattering by atoms and molecules would not be sufficient to account for it. The diffuse light is argued to result from the starlight's scattering by interstellar grains. Consequently, this scattered light carries valuable information about the properties of these grains. Specifically, it provides insights into the reflectivity and the phase factor, which describes the preferred direction of light scattering by the grains, either forward or backwards (Draine 2003, Krügel 2003, Dyson & Williams 2020). Another crucial evidence for the scattering of starlight can be seen in Reflection Nebula. A reflection nebula is a cloud consisting of dust and gas and usually appears blue. The primary reason for this blue colour is associated with the Rayleigh scattering of the starlight by the dust grains present in the nebula (Draine 2003, Krügel 2003, Dyson & Williams 2020).

1.2.5 Depletion of Heavy elements:

In the ISM, the abundance of heavy elements (Z > 2), where Z is the atomic number) is reduced compared to their cosmic abundance. This is referred to as the depletion of heavy elements that occurs due to the formation of dust grains ((Savage & Sembach 1996), (Li 2005)). The elements found to be depleted more than the other elements are Mg, Fe, Ni, Al Ti, and Ca (Savage & Sembach 1996, Li 2005). The extent of depletion can be correlated with the depleted elements' condensation temperature (Tc) (Savage & Sembach 1996, Li 2005). The elements with high T_c such as Fe and Mg, condensate early and therefore are depleted more. However, the elements which have low T_c, such as C, and O, will be available for reaction in the gas phase and are less depleted. Fig 1.2 shows a typical interstellar depletion pattern of the elements measured towards the star ζ Oph where the relative abundance of various elements is plotted against their respective condensation temperature. It suggests that the refractory elements with $T_c > 1200$ K are depleted substantially(Blain et al. 2004). The study of interstellar depletion patterns provided vital information about the elemental composition of the dust grains.



Fig 1. 2: Interstellar depletion pattern measured towards ζ Oph where the relative abundance of the elements are plotted with respect to condensation temperature (Blain et al. 2004). It suggests that the relatively heavy elements such as Mg, Fe, Ni, Al Ti, and Ca have been heavily depleted, whereas, for elements like C, O, the extent of depletion is relatively less.

1.2.6 Emission from micron size dust grains:

Dust grains can also emit electromagnetic waves. Large grains with size in microns in thermodynamic equilibrium with the local radiation field can self-emit radiation in the mid to far IR ranges. Using the Plank's law, we can understand the temperature of these grains, which usually fall within 10 to 100 K (Blain et al. 2004). The dust grains located close to any star forming region have much more interaction with the stellar radiation and usually have a higher temperature, around 300 K, and the peak wavelength is around 10 μ m. When the dust grains have become dimensionally very small (~ submicron to nm), then single UV photo absorption can provide an energy which is much higher than the internal specific heat capacity of the dust particles. Thus, these dust grains get heated up instantaneously, and cool down much faster rates (Draine & Li. 2001, Blain et al. 2004) than larger grains. So the temperature profile of the tiny grains is very much time-dependent, where we observe rapid heating by absorbing a UV photon and

cooling by near IR continuum thermal emission (Draine & Li. 2001, Blain et al. 2004). Also, electric dipole emission from the spinning charged dust grains has also been considered a source of so-called anomalous microwave emission in the ISM (Kogut et al. 1996, Hoang, Lazarian, & Draine. 2011).

1.3. Chemical Composition of Dust:

Submicron to nanometer size dust grains are ubiquitously detected in various parts of interstellar space and in our Solar System. The chemical composition of dust in different parts of the ISM as well as in our Solar System, has been probed using space-borne Infrared (IR) telescopes like the Infrared Space Observatory (ISO), followed by Spitzer and airborne observatories like the Stratospheric Observatory for Infrared Astronomy (SOFIA) (Krügel 2003). At the same time, laboratory analysis on meteorites has revealed morphological information and isotopic composition of the dust (Krügel 2003). Solid matter in interstellar space can be divided into three broad categories: first, refractory mineral dust such as olivine, pyroxene, and other metal oxides. Second, solid carbonaceous dust, such as SiC, and other carbon allotropes, such as diamond, graphite, amorphous carbon, and hydrogenated amorphous carbon. The third and final member of this classification is molecular ice, which is composed of volatile abundant molecules such as CO, H₂O, CH₄, and other organic molecules (Dartois 2019). Fig 1.3 provides a pictorial representation of the above discussion and shows the present scenario with regard to the chemical composition of the dust grains detected in different parts of ISM and our Solar System. In the upcoming paragraph, details of carbonaceous molecules, carbonaceous dust, and mineral dust will be addressed.



Fig 1. 3: Combined effort of multi-wavelength astronomical observations, theoretical studies, and analysis of the meteorite and samples from different sample return missions has given information about the chemical composition of the interstellar dust grains. A large fraction of interstellar dust grains is found to be amorphous silicate dust with olivine and pyroxene stoichiometry, whereas the 2nd most abundant dust class are carbonaceous dust which includes different carbonaceous allotropes, such as nano diamond, graphite, fullerenes, and SiC. Crystalline silicate dust only accounts for a small fraction of interstellar dust mass budget along with other oxide dust (Numbers are taken from Tielens, Waters, and Bernatowicz. 2005).

1.3.1 Interstellar Carbonaceous molecules and dust:

Molecules have been routinely detected in different parts of our Universe, and to date, more than 300 molecules (CDMS) (Müller et al. 2005) are known to be present. A larger fraction of these molecules contains carbon (C), signifying carbon's important role in our Universe's chemical enrichment processes. Unlike H and He, C originates from the stellar nucleosynthesis at the core of intermediate-mass stars. The reaction in which three ⁴He nuclei fuse to form ¹²C in the core of a star (Asymptotic Giant Branch (AGB), red giant star) is known as the triple-alpha process (Burbidge *et al.* 1957). Later, C is transported into the outer envelope of stars by the convection-induced degrade-up mechanism, and a tussle between O and C is initiated. The least abundant element between them is considered locked up in the form of CO, whereas the abundant one contributes to the formation of varieties of molecules are mostly carbonaceous, whereas in the opposite case, oxides are known to dominate (Höfner & Olofsson 2018). The abundance of C available for the formation of carbonaceous dust is usually measured by taking the difference between the cosmic abundance of C to H [C/H]^c and the gas

phase abundance of C to H $[C/H]^{g}$ (Henning & Salama 1998). To date, the known cosmic C abundance is around 85 C atoms per 10^{6} H atoms, whereas, for Sun's photosphere, it is about 250 C atoms per 10^{6} H atoms (Henning & Salama 1998).

Carbon, with its ability to make different kinds of bonds, has contributed to ISM's molecular enrichment, especially by synthesising organic molecules. Targeted multi-wavelength astronomical observations towards different astrophysical sites reveal the presence of various organic and inorganic carbonaceous molecules and radicals. These range from the simplest diatomic molecule CO to the polyatomic aliphatic sp³ bonded alkanes like CH₄, sp²-bonded alkenes such as C₂H₄; the sp bonded linear C₂H₂ to the long chain hydrocarbons such as polyenes and cyano-polyenes. The presence of large aromatic molecules in different parts of ISM was proposed in the mid-80's, and their signatures have been found in various astrophysical objects (Tielens 2008). Signatures of benzene in stellar envelopes have been detected almost two decades ago (Cernicharo et al. 2001a). Large molecules made of multiple benzene rings, called Polycyclic Aromatic Hydrocarbon (PAH), where almost 20 % of the cosmic carbon is thought to be locked up in such molecules (Tielens 2008). However, detecting specific PAHs in the ISM has been difficult, at least until recently, when benzonitrile was discovered in the dark molecular cloud TMC-1(McGuire et al. 2018). Since then, many other smaller PAH molecules have also been reported to be present at TMC-1; these include 1-cyanonapthlane, 2-cyanonapthlane (McGuire et al. 2021), and indene (Burkhardt et al. 2021, Cernicharo et al. 2021b). A detailed survey of different molecules and radicals which are reported to be present in the ISM, CSM and extragalactic environment can be found in the recent census carried out by McGurie and co-workers (McGuire 2022). Many carbon-bearing molecules (gas phase) are thought to be potential carriers of different unknown spectroscopic features detected in other parts of ISM. The well-known Unidentified Infrared Emission (UIE) features have the most robust IR features around 3.3, 6.2, 7.7-7.9, 8.6, 11.3, and 12.7 µm. These bands are called aromatic infrared bands (AIB) and are attributed to PAHs (Tielens 2008), (Candian et al. 2019, Van Diedenhoven et al. 2004). One of the challenging task still remains for the astronomers is to finding a suitable carrier for the Diffuse Interstellar Band (DIB). DIB is a weak absorption feature spanning in between 400 to 1200 nm, often observed in different parts of the ISM. On the basis of different experimental and theoretical studies various potential carries of DIB has been proposed

so far. These include different carbonaceous molecules such as PAHs, carbon chains, fullerene (Salama et al 1996, Freivogel et al 1994, Tulej et al 1998, Ehrenfreund & Foing 1996, Foing 1996, Foing & Ehrenfreund 1997). Apart from large carbonaceous molecules, ionic species such as C_7^- (Tulej et al 1998), C_{60}^+ (Foing & Ehrenfreund (1997)) has also been proposed as a carrier of DIB. However, Ionic fullerene (C_{60}^+) may solve this interstellar puzzle. The experiment conducted by Campbell et al. 2015 and Linnartz et al. 2020 showed that two of the DIB's bands, around 9632.7 Å and 9577 Å are due to C_{60}^+ . Formation pathways of carbonaceous molecules is still an evolving topic and beyond the scope of this paper and can be found elsewhere in the literature by Henning and Salama (Henning & Salama 1998) and the references there.

Carbon can formulate different kinds of allotropes like diamonds, graphite, fullerene, PAHs, graphene, and carbon nanotube. Interstellar carbonaceous nanoparticles or nanoclusters are one of the possible candidates of interstellar dust responsible for the UV-VIS extinction (Li, 2005, Yastrebov and Smith, 2009). It is thought that solid Hydrogenated Amorphous Carbon (HAC) is one of the main reservoirs of carbonaceous material in our Galaxy; they are detected through 3.4 μ m absorption along the line of sight toward the center of our Galaxy (Allen & Wickramasinghe 1981, Duley & Williams 1983).

Fullerenes are the recent addition to the interstellar carbonaceous molecular inventory. Kroto et al., (Kroto *et al.* 1985b) performed a series of experiments to understand the carbon chemistry in Asymptotic Giant Branch (AGB) stars and discovered a new stable form of carbon: Buckminster fuller, C₆₀. Soon after this discovery astronomer carried out targeted spectroscopic observations to detect the signature of fullerenes in space. The first unambiguous detection of all four IR - active modes of C₆₀ at 7.0, 8.5, 17.4, 18.9 µm resulted from the analysis of Spitzer IRS spectra of the Planetary nebula Tc1 (Cami *et al.* 2010). The same spectral features were also detected in reflection nebula (Sellgren *et al.* 2010, Peeters *et al.* 2017), the diffuse ISM (Berné *et al.* 2017), and in young stellar objects and Herbig Ae/Be stars (Roberts *et al.* 2012). The corresponding IR features due to the fullerene cations, C₆₀⁺, at 6.4, 7.1, 8.2 and 10.5 µm have been reported as well (Berne *et al.* 2013, Walker *et al.* 2015, Cordiner *et al.* 2019). Recently (Campbell *et al.* 2015) and (Linnartz *et al.* 2020) experimental evidence pointed that C₆₀⁺ is the carrier of two

Diffuse Interstellar Bands (DIB) at 9632.7 Å and 9577.5 Å.

Amongst the possible carbon allotropes, graphene has become very popular in the last decade for its scientific and technological importance. It was discovered in 2004 by A. Geim and K. S. Novoselov, where they were able to extract a single layer of graphite (monolayer of atoms) from three-dimensional graphite using the micromechanical cleavage technique (Geim & Novoselov 2007). Graphene is considered to play an important role in the formation of carbon allotropes like fullerene and carbon nanotube (Chuvilin et al. 2010, Berné & Tielens 2012). Graphene could be present in the ISM as it could be formed via photochemical processing of PAH (Berné & Tielens 2012) and benzonitrile (Rahul et al. 2020a). Despite all of these studies, still we are not much sure about the presence of graphene in interstellar and the circumstellar medium. The possible presence of graphene in the various planetary nebula (PNe) in the Milky Way and at the Magellanic Clouds has been proposed by García-Hernández et al., (García-Hernández et al. 2011a). They assigned a set of unusual IR emission features at 6.6, 9.8, and 20 µm as planar C₂₄ graphene. From different experimental and theoretical studies, it is clear that graphene has a strong electronic absorption band near 2755 Å or 4.5 eV, but this band is undetected in the ISM. P.J.Sarre (Sarre 2019) proposed that the Extended Red Emission (ERE) features that are observed around various astrophysical environments (Cohen et al. 1975, Vijh et al. 2004b, Witt 2013, Lai et al. 2017) could be due to the photoluminescence of graphene oxide nanoparticles. The presence of different carbon allotropes and carbonaceous molecules in various astrophysical regions has indicated sensational possibilities of the presence of Carbon Nanotube (CNT), Carbon Nano Onion (CNO) i.e. multishell fullerene (de Heer & Ugarte 1993) in the ISM. The other spectroscopic feature in IR, which shows the presence of carbonaceous dust around C-rich stars, is the 11.3 µm feature, which has been attributed to the SiC (Speck et al. 1997). A detailed description of the known carbonaceous dust detected in space can be found in the review article by Dartois (Dartois 2019).

Signatures of interstellar carbon dust are also detected in primitive meteorites as presolar grains. Presolar grains originated well before our Solar System's formation and contained information about their respective birth site. The most abundant carbonaceous presolar dust is nanodiamond, and the 2nd most is SiC and then comes Graphite (Ott 2010). The isotopic anomalies present in the presolar grains make it unique from other Solar System grains. By studying the isotopic anomalies of Xe and Kr present in Allende meteorite C3V chondrites, cosmochemists were able to detect presolar nanodiamond (Lewis *et al.* 1987). Later Chang et al (Chang *et al.* 1995), and Guillois et al (Guillois *et al.* 1999) reported the presence of nanodiamonds around intermediate-mass stars. They attributed the 3.43, 3.53 µm IR features to the C-H stretching motion of the hydrogenated nanodiamonds. The signature of presolar SiC was first detected in Murray carbonaceous chondrites (Bernatowicz *et al.* 1987).

1.3.2 Silicate Dust in the ISM:

In interstellar space, silicate dust is characterised based on its mid-infrared (MIR) features at 10 and 20 µm (Jäger et al. 1998, Colangeli et al. 2003). These features arise from the silicate dust grains' Si-O stretching and O-Si-O bending motions (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). The IR spectra of the silicate dust are largely influenced by factors like chemical composition, grain size, morphology of the grains, temperature etc. (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). As Fig 1.3 suggests, a larger fraction of the interstellar silicate dust is found to be amorphous in nature, and they betray their presence by showing a broad 10 and 20 µm emission or absorption feature (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). However, crystalline silicate dust showed very sharp and prominent IR active features both in MIR as well as in the FIR region of their IR spectra (Jäger et al. 1998, Colangeli et al. 2003, Molster et al. 2002). Signatures of crystalline silicate dust have been detected in the stellar envelope of the AGB stars, Herbig Ae/Be stars, and T Tauri stars (Molster et al. 2002, Henning 2010). Signatures of crystalline silicate dust have also been detected in our Solar System bodies such as comets (Wooden 2008, Kelley & Wooden 2009, Hanner & Zolensky 2010) and asteroids (Feierberg et al. 1983& Lebofsky. 1983, and Cruikshank et al. 2006). In the upcoming paragraph, we will discuss the structural properties of silicate dust grains.

Although silicon and carbon are the nearest neighbours in the periodic table, unlike carbon, which can form various bonds and allotropes, silicon primarily forms single bonds. The core principle of silicon chemistry lies in its strong affinity for oxygen (Colangeli et al. 2003). When silicon and oxygen combine, they form a highly stable Si-O bond, leading to the formation of $[SiO_4]^{4-}$ tetrahedra, which serve as the

fundamental building blocks of silicate dust, as shown in Fig 1.4(a). The Si-O bond derives its exceptional stability from sharing oxygen's nonbonding electron pair with the empty d shell of silicon. This bonding arrangement results in remarkable stability in the [SiO⁴]⁴⁻ tetrahedron. To maintain charge neutrality, these tetrahedra can link with other $[SiO_4]^{4-}$ tetrahedra through their corner oxygen atoms or remain isolated. In the case of isolated [SiO₄]⁴⁻ tetrahedra, the corner oxygen atoms can associate with abundant astrophysical cations such as Mg²⁺ and Fe²⁺ to achieve charge balance. This leads to the formation of olivine-type silicate dust, including minerals like forsterite and fayalite (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). Alternatively, suppose the $[SiO^4]^4$ - tetrahedra are able to form chains or arrays by utilizing their corner oxygen atoms. In that case, it forms pyroxene-type silicate dust, such as minerals like enstatite. Silicate dust can be categorized into different types based on the interactions of $[SiO_4]^{4-1}$ tetrahedra with other cations or $[SiO_4]^{4-}$ tetrahedra (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). These classifications include nesosilicate, inosilicate, and phyllosilicate. Nesosilicates consist of isolated tetrahedral anions ([SiO₄]⁴⁻), while inosilicates form single chain structures ($[SiO_3]^2$) where tetrahedra share two oxygen atoms. Phyllosilicates are characterized by continuous sheets ([Si₂O₅]²⁻) in which the tetrahedra share three oxygen atoms (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010).

Interstellar silicates exhibit diverse compositions and are often characterized as solid solutions. In this context, a solid solution refers to a homogeneous mixture of multiple substances in a solid state. The formation of a solid solution occurs when atoms, ions, or molecules from one component, known as the solute, are incorporated into the crystal lattice of another component, called the solvent. This integration results in forming a single, continuous phase with uniform distribution of solute species throughout the solvent matrix (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). As a result, the solid solution possesses consistent properties throughout its structure. The composition of a solid solution can vary within a specific range, allowing for a continuum of compositions between the pure end-members (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). A suitable example of such a solid solution is the olivine class of dust; its primary structure is shown in **Fig 1.4(b)**. Olivine is usually defined as $Mg_{(2-x)}Fe_{2x}SiO_4$, where x denotes the proportion of iron in it. When x=0, the end member is Mg-rich forsterite (Mg₂SiO₄); for x=2, it is iron-rich fayalite (Fe₂SiO₄). An

example of an olivine solid solution that includes both endmembers is $Mg_{1.8}Fe_{0.2}SiO_4$ ((Jäger et al. 1998), (Colangeli et al. 2003), (Henning 2010)). Another example of an



Fig 1. 4: (a) shows a Silicon Oxygen Tetrahedron (SOT), which is the primary building block of interstellar silicate dust (Figure adapted from Henning. 2010). (b) Structure of the crystalline olivine dust, where the tetrahedron represents the SOT, the green colour balls represent Mg^{2+} Cations, and the red colour balls represent the Fe^{2+} cations. (c) structure of the crystalline pyroxene class dust where the tetrahedrons represent the SOT, the green balls show the presence of abundant Mg^{2+}/Fe^{2+} cations (Image taken from: <u>https://opentextbc.ca/geology/chapter/2-4-silicate-minerals/</u>).

astronomically relevant solid solution is the pyroxene class of dust, and its structure is shown in **Fig 1.4(c)**. It is defined as $Mg_{(1-x)}Fe_xSiO_3$, where x denotes the proportion of iron in it. It also has two end members, and these two are Mg-rich enstatite (MgSiO₃) and ferrosilite (FeSiO₃) ((Jäger et al. 1998), (Colangeli et al. 2003), (Henning 2010)).

Interstellar silicate dust is predominantly amorphous (Henning 2010). Unlike crystalline mineral dust, these amorphous grains lack a long-range periodic structural order. They exhibit wide distributions of bond angles and bond lengths, as well as a random orientation of $[SiO_4]^4$ tetrahedra. These structural characteristics contribute to their isotropic nature and give rise to broad spectral features in the infrared (IR) spectra within the 10 to 20 µm wavelength region (Jäger et al. 1998, Colangeli et al. 2003, Henning 2010). The presence of metal cations within the silicate network causes a partial disruption of the O bridges and the creation of non-bridging oxygen sites. These void spaces accommodate cations' coordination by bridging and non-bridging oxygen atoms. However, small cations, such as Mg^{2+} , can act as network formers by replacing

the Si atom in the SiO₄ clusters. Amorphous silicate dust forms when a melt solidifies faster than the crystallization rate (Henning 2010). A key parameter involved in this process is the glass transition temperature. It is the temperature above which a given compound turns into a crystalline state, provided the annealing time scale is way higher than the cooling time. Interstellar crystalline silicates typically bear signatures of prolonged heating at their formation sites. However, when ejected into the interstellar medium (ISM), surface destruction caused by ion and electron bombardment leads to the formation of amorphous silicate dust (Henning 2010).

1.4 Dust formation in interstellar space:

Stars are the main sources of dust in the ISM. Dust is known to be produced in the extended envelope of stars. These include low to intermediate-mass (0.8 to 10 solar mass) stars like Asymptotic Giant Branch (AGB) stars, red giants and supergiant stars. Fig 1.5 shows a pie chart illustrating the contribution of various kinds of starts to the dust input to the ISM (SedImayr 2005). At the end phase of stellar evolution, these stars make extended cool envelopes where the dust-forming elements (C, O, Mg, Si, Fe etc.) are mixed according to their abundance (Ferrarotti & Gail 2006), (Gail & Sedlmayr 2014). The condensation of dust within the stellar envelope is a very complex process, which starts from molecular mixtures in the gas phase, and molecular clusters are made after a series of chemical reactions. The subsequent growth of molecular clusters makes a solid dusty seed, which provides a finite surface for further dust growth (Gail & SedImayr 2014). The thermodynamic conditions, elemental mixing, metallicity and stellar radiation field influence the sequence of dust condensations, which in turn affect the structure, morphology and spectral properties of dust grains. A combined effort of theoretical and experimental studies is required to understand the entire formation pathway of dust, including information about the molecular precursor, intermediate products, and various possible end products.



Fig 1. 5: Mass ejection from various stellar sources contributes to the interstellar dust budget. Asymptotic Giant Branch (AGB) stars are the major contributors of interstellar dust. The other sources of interstellar dust are supernova explosions, Red Super Giant stars (RGB), Wolf Rayet (WR) starts, Red and Yellow supergiant starts (RY-SG), and Main sequence stars (M). The photospheric abundance of C and O decides whether the dust will be oxide type (C/O < 1) or it will be carbonaceous (C/O > 1) (Data taken from SedImayr 1994, Tielens. 2021).

To date, there exist two different formation pathways of interstellar carbonaceous nanodust. These are 'bottom-up' formation routes that mimic dust formation from the atomic and small molecular precursors and 'top-down' routes-where dust formation happens because of the destruction of larger molecular clusters. Each of these processes has advantages and limitations.

1.5 Laboratory production of cosmic dust analogues via the bottomup formation pathway:

Experiments dealing with the bottom-up formation process of carbonaceous dust grains in interstellar space mostly mimic gas phase condensation events in a simulated circumstellar environment. Principally these kinds of experiments are done in two segments. The first step is the production of vapour of any atomic or molecular precursor material through pyrolysis or sublimation. This can be done using various energetic sources like a laser, arc discharge technique, and shock tubes. In the second step, the produced vapour can settle on a substrate or can be directly quenched in a cool inert gas environment (Jäger *et al.* 2009, Contreras & Salama 2013, Sciamma-O'Brien & Salama 2020). A pictorial representation of the possible pathways of carbonaceous dust formation can be seen in **Fig 1.6**.



Fig 1. 6: Different formation routes of interstellar carbonaceous dust. Bottom-up formation routes are the main pathway when using laser ablation (Kroto, Heath, 1985), laser-induced pyrolysis, and gas-phase condensation of hydrocarbon (Jäger et al. 2009), or arc discharges (Iijima, 1991, Krätschmer et al., 1990). In such experiments, Closed Network Growth (CNG) leads to the bottom-up formation of fullerenes by insertion of C and C2 in existing smaller cages (Dunk et al., 2012). Similar bottom-up routes lead to the formation of CNTs (Liu et al., 2009). The self-assembly of atomic carbon C and C2 units into higher-order clusters has been theoretically investigated by (Cruz-Silva et al., 2016, and Irle et al., 2006) (Image taken from A. Roy et al. 2023).

1.5.1 Laser-induced and graphite reactor-based pyrolysis:

Laser--induced pyrolysis of the gaseous precursor is a promising technique to produce a cosmic carbon nanodust analogue. In this method, the gas phase precursors molecules are rapidly heated and dissociated using either continuous wave (CW) or pulsed laser. To do so, the precursor molecule or molecular mixtures should absorb the laser radiation; else, a sensitizer like sulphur hexafluoride SF_6 (for CO_2 laser) is usually used. The soot particles produced from the pyrolysis of the precursor can be collected using particle filters or allowed to nucleate on any substrate far from the reaction zone. A flow of inert gas like Ar and N₂ has been used to move the produced dust particles. The presence of a well-defined and relatively small reaction zone and sharp thermal gradient helps to control nucleation rate and laser interaction time. This provides an advantage over conventional techniques such as the plasma-heated gas phase process or furnace-based technique (Cannon *et al.* 1982), (Herlin *et al.* 1998). The factors which influenced the nature of the carbon dust produced in this method are the nature of the precursor, the pressure of the reaction chamber, laser intensity and the residence time

of the gas phase molecules in the laser beam, which depends on the mass flow rate of the gas mixture.

Using this technique, the condensation of diamond nanoparticles in low pressure (1000 mbar) and temperature (500- 550 °C) has been investigated by Buerki et al. (Buerki & Leutwyler 1991). They used two sets of gas mixtures, pure C₂H₄ and mixtures of C₂H₄, H₂, and SiH₄ and decomposed these mixtures using a CO₂ laser (10.6 μ m, 6000-8000 W cm⁻²). The diamond's cubic and hexagonal phases and polymeric hydrocarbon species, amorphous carbon and graphite were observed. Nucleation of nanodiamonds in the low-pressure condition can complement the diamond formation theory in the ISM suggested by authors like Lewis et al. (Lewis et al. 1987), E. Anders (Anders & Fitch 1962), Jørgensen, U.G (Jørgensen 1988).

The formation of carbon nano grains mimicking the thermal decomposition of C_2H_2 in the evolved carbon star atmosphere has been experimentally investigated by Herlin et al. (Herlin et al. 1998). A continuous wave CO₂ laser operating at a wavelength of 10.6 µm and power ranging from 200 to 1000 W was focused perpendicularly on two different molecular beams of C_2H_4 and C_4H_6 . The range of parameters used in this experiment was gas flow rate ~ 30-540 cc min⁻¹, pressure ~ 700 -900 torr, laser power 280- 450 W, and the estimated temperature range was around 1200 – 1500 K. TEM analysis of the high-temperature condensate (~ 1500 K) revealed the presence of spherical particles (20- 40 nm) with organized internal structure and their IR spectra showed the presence of strong continuum. This suggests that these high-temperature condensate is mainly dominated by amorphous carbon, and its IR spectra have features of aromatic –CH and –C-C vibrational motions (Herlin et al. 1998).

Unlike Herlin et al (Herlin *et al.* 1998), who used a continuous wave CO₂ laser, Schnaiter et al (Schnaiter *et al.* 1999) used a pulsed CO₂ laser to study the formation of interstellar carbon dust analogues from C₂H₂. As C₂H₂ does not absorb 10.6 μ m radiation, they mixed the gas with sulfur hexafluoride (SF₆) as a sensitizer with different concentrations, which plays a key role in determining reaction temperature up to as high as 2000 K. The produced soot particles were extracted using a mass filter attached to the pumping line. The produced materials have been analyzed using a technique like IR Spectroscopy, TEM imaging, Electron Energy Loss Spectroscopy (EELS), and Time of Flight (TOF) mass spectrometry. One of the major findings from this experiment was the growth of PAH during the nucleation of amorphous soot particles.

Biennier and co-workers (Biennier et al. 2009) produced carbonaceous dust by pyrolysis of gaseous precursor acetylene in a chamber of a reduced dimension known as a circumstellar carbon analogue source. It is a high-temperature reactor, and its dimension reduction was achieved by using a heated porous graphitic rod. This rod can be heated electrically to a temperature of the order of 2000 K. Because of its porosity, it has a large exchange area, allowing for efficient heat transfer from the rod to the gas flowing through it. The thermodynamic conditions under which acetylene pyrolysis occurred are comparable to those in circumstellar shells. The condensed particles were analysed using Nuclear Magnetic Resonance (NMR) spectroscopy, XRD, and IR spectroscopy. The NMR result showed the presence of smaller aromatics in the soluble components of the pyrolysis product. XRD analysis of the bulk samples showed the presence of amorphous chemical networks, which contain small organized aromatic islands composed of two graphene layers and connected by aliphatic groups. The IR spectra of the condensate showed aromatic features around 3.29, 6.30, 11.36, 11.98, and 13.31µm. The broad 7.7 to 10 µm feature has also been assigned to the aromatic CC and CH plane deformation motions. Signatures of aliphatic groups were also observed at 3.42 and 3.50 µm. The aromatic-to-aliphatic almost remained at 3.2 µm for the entire sample. The IR spectra of the condensate showed a good amount of resemblances with some IR emission spectra of the post-AGB stars observed by Dartois et al. (2007).

1.5.2 Laser ablation of graphite:

Laser ablation of solids is another technique routinely used to produce cosmic dust analogues in laboratory conditions. The vapour produced in this method can be rapidly quenched in a low-pressure (1- 25 mbar) inert gas atmosphere (He/Ar) with a rate as high as 10⁴ K s⁻¹. This leads to the formation of soot particles, which can be extracted from the laser ablation chamber by making a molecular beam using a nozzle and skimmer. The condensate's physicochemical nature depends on the laser pulse energy and quenching gas's thermodynamic properties. Different experiments have been carried out using various precursors and the parameters such as chamber pressure, laser intensity and wavelength.

One path-breaking experiment using the laser ablation technique was carried out by Kroto et al (Kroto *et al.* 1985a) and led to the discovery of a new carbon allotrope *viz.* fullerene (C_{60}). This experiment aimed at understanding the formation mechanism of long carbonaceous chains in the envelope of the evolved AGB stars. Graphite was vaporized using Nd: YAG laser with pulse energy ~ 30 mJ. While expanding with supersonic speed, the vapour was photo-ionized utilizing an excimer laser and analysed using TOF mass spectrometry. Pressure played a key role in this experiment. When the quenching gas pressure was low (less than 10 torr), wide ranges of carbon clusters were detected, starting from C₃₀ to C₁₂₀. At a pressure of ~ 760 torr, both C₆₀ and C₇₀ peaks were visible and distinguishable. Under the same experimental conditions, passing the carbon vapour through an integration cup caused He- cluster, cluster- cluster collision and only the stable clusters survived. The mass distribution in this condition was dominated by C₆₀ (50%) and C₇₀ (5%) as the surviving clusters. The structure of C₆₀ was predicted to be like a football, and later it was spectroscopically confirmed by Krätschmer et al (Krätschmer *et al.* 1990), Dennis et al (Dennis *et al.* 1991).

Laser-induced ablation of graphite in He, He + H_2 environment was experimentally studied by Jäger et al (Jäger et al. 2009). The pressure of the quenching gas varied between 3.3 to 26.7 mbar, and the laser-produced plasma with a temperature range between 4000 to 6000 K was produced. Fullerene and fullerene-like soot were observed in the high-temperature condensates.

Fulvio and co-workers (Fulvio *et al.* 2017) have studied the low-temperature formation of carbonaceous grains from graphite. With the help of a Nd: YAG laser (wavelength 532 nm, 10 pulses per second, 10 mJ of energy), graphite pellets were ablated. Vapours coming out because of laser ablation were allowed to settle in the cold (~ 10 K) KBr substrate directly or in an Ar ice matrix. The chemical composition of the condensate grown on top of the KBr substrate or isolated within the Ar ice matrix was probed using UV and Mid IR (MIR) spectroscopy, and the morphology of the condensate was studied using Field Emission Scanning Electron Microscope (FESEM) and High-Resolution Transmission Electron Microscope (HRTEM). This confirmed the presence of carbon clusters with different size starting from C₂ to C₁₃, a few oxidized species like CO and C₃O, and possible contaminations from H₂O and CO₂ has also been noticed (Fulvio et al. 2017). The FE-SEM images of the condensate showed the presence of a meshed structure with a dimension of the order of a few μ m. The HR- TEM images demonstrated a fullerene-like structure with different sizes and shapes. In the second part of this work, they carried out successive Vacuum Ultra Violet (VUV) irradiation on the condensate to understand the effect of energetic processing on the dust grains during their growth in interstellar conditions. As a VUV source, they employ a hydrogen discharge lamp with two prominent spectral features at 122 nm and 160 nm. The effect of VUV irradiation on the physicochemical properties of the condensates was probed using MIR spectroscopy, FE-SEM, and HR-TEM imaging technique. A drop in the intensity of MIR bands corresponding to different carbon chains and clusters has been observed. This showed that under VUV irradiation, these carbon chains and clusters were fragmented. These fragmented products reacted with themselves and made fullerene-like structure, observed in HR-TEM images. These fullerene-like structures were much more ordered than those observed in the non-irradiated condensate (Fulvio et al. 2017). The presence of a chain-like structure in the lowtemperature condensate has been previously reported in a high-temperature condensate by Jäger et al. 2009. These chain-like structures were also proposed to serve as an intermediate product for the fullerene and fullerene-like particle growth in the atmosphere of Wolf Rayet stars (Cherchneff et al. 2000).

1.5.3 Dust production using combustion in flames:

Combustion of gas phase hydrocarbon mixed with oxygen is another method of producing cosmic carbon dust analogues. The nature of the soot particle produced in this technique depends on various factors such as chamber pressure, the flame's temperature, the precursor molecules used, the C/O ratio and the construction of the burner (Mansurov 2005). In this technique, soot particles can nucleate at low pressure and can be extracted using a quartz cone or nozzle (Pino *et al.* 2008). This technique uses different types of hydrocarbon to produce carbon dust e.g. CH_4 , C_2H_2 , C_2H_4 , C_3H_6 , and C_6H_6 . These hydrocarbons were decomposed in different C/O ratio environments (0.5 to 2), and the flame temperature was as high as 2500 K (Homann 1998). A range of end products has been reported to form, including long carbon chains, PAHs, and fullerene-like particles (Homann 1998).

Carpentier *et al.* (2012) have also investigated the structural and spectroscopic properties of the cosmic carbonaceous dust analogues produced from precursors like ethylene and propylene using the same setup used by Pino et al. 2019 Here both the precursors were burned using a flat flame in a fuel-rich environment, where the C/O

ratio was in the range of 1.1, 1.4, and 1.6 for all three sets of experiments. Soot particles were allowed to deposit on a stainless steel substrate and analysed using Fourier Transform Infrared Spectroscopy (FTIR), Raman spectroscopy and HR-TEM imaging technique. Variations observed in the IR absorption feature, especially in the 6.2 μ m and 7.7 μ m region of the soot particles, have also been reported to be present in the IR spectra of the interstellar carbon dust. This could be due to defects and polyaromatic structures in the soot particles, verified using techniques like HR-TEM imaging and Raman spectroscopy. Based on these results, authors proposed a plausible scenario for carbonaceous dust growth in the ISM, which can be found in detail in Carpentier et al. (2012).

1.5.4 Microwave, Radio and Arc discharge technique:

Condensation of carbonaceous dust can also be studied using the microwave discharge plasma technique. In this technique, gas-phase molecular precursors such as CH₄ fill a quartz tube exposed to a magnetron's microwave field. This causes methane dissociation, and the ionized gas is passed into a vacuum chamber, where it condenses into black soot particles. X-Ray (XRD) diffraction, and UV spectroscopic analysis of the condensate reveals the presence of Quenched Carbonaceous Composites (QCC). UV spectra correlate well with the interstellar extinction curve, peaking around 2200 Å (Sakata et al. 1992). Using the radio frequency plasma technique, spherical carbonaceous grains have also been produced from C₂H₂ (Kovačević et al. 2005). The arc discharge technique has also been utilized to produce carbon nanoparticles. One of the important results of this kind of experiment is the discovery of carbon nanotubes by Iijima (Iijima 1991). Mass production of fullerene has been developed using this technique (Krätschmer et al. 1990). In such experiments, Closed Network Growth (CNG) leads to the bottom-up formation of fullerenes by inserting C and C2 in smaller cages (Dunk et al. 2012). Similar bottom-up routes lead to the formation of CNTs also (Liu et al. 2009).

1.5.5 Production of cosmic grain analogues from gas phase molecular precursors using plasma chemistry:

The formation and evolution of cosmic carbonaceous dust analogues, can also be studied experimentally under simulated interstellar and circumstellar conditions by using NASA's COsmic SImulation Chamber (COSmIC) (Contreras & Salama 2013). COSmIC has three major components: a pulsed Discharge Nozzle (PDN) capable of producing microscopic particulates by exposing a supersonically fast Ar jet seeded with precursor molecules like PAH and other hydrocarbons to a plasma discharge. The products generated in this hot plasma experience rapid cooling over a very short distance as the plasma expands. Second, a cavity ring breakdown spectrometer is attached to the system to probe the spectroscopic information of the products. Third is the orthogonal reflection Time of Flight Mass Spectrometer (TOFMS) for studying particulates' mass and structural information (Contreras & Salama 2013).

Using COSmIC, Contreras and Salama investigated the formation of circumstellar carbonaceous dust analogues from different aliphatic and aromatic molecular precursors. These include methane, ethane, ethylene, and acetylene representing aliphatic precursors. For the aromatics, the precursors were benzene, toluene, pyridine, and different PAHs. These molecules have gone through fragmentation accompanied by loss of H, CH and acetylene radicals. Results from these experiments showed that the nature of the end product has a high dependency on the molecular nature of the precursors. This fact has to be considered in the theoretical models dealing with dust formation in circumstellar conditions. The fragments generated from aliphatic precursors and small ring molecules like benzene, toluene and pyridine have shown the tendency to recombine and enhance molecular complexity via ion-molecular reactions. These molecular growths can lead to grains forming in the circumstellar environment via chain growth and ring formation (Contreras & Salama 2013). Homogeneous (naphthalene, 1-methylnaphthalene, and acenaphthene) and heterogeneous (quinoline, benzofuran, and thianaphthene) PAHs used in this experiment showed better stability and did not contribute to any chemical reaction which led to the formation of dust grains (Contreras & Salama 2013). Results from this experiment were found to support the assumptions considered in the models (Cherchneff 2011) made to describe PAH formation in the circumstellar environment, where the interaction among the propargyl (C_3H_3) radicals led to the formation of benzene and then the growth of larger aromatic molecules started via the so-called hydrogen abstraction and acetylene addition (HACA) mechanism (Frenklach et al. 1985).

Using the COSmIC facility, Gavilan and Salama (Marin et al. 2020) explored the low-temperature (< 200 K) formation pathway of carbonaceous dust from PAH, starting from benzene, naphthalene, anthracene, phenanthrene, and pyrene. Condensate generated separately from these PAHs was collected on a substrate (graphite bar) and analysed using laser desorption mass spectrometry. Mass spectra obtained from these condensates showed the fragmented part of the precursor molecule and the signature of the larger complex organic molecules. Pyrene, its isomers, and its methylated series were the most abundant product in all condensates originating from the above mention PAHs. This indicated a favourable pathway for the formation of larger PAHs and solid grains via the formation of stable PAHs such as pyrene and its isomers. The dust formation yield was maximum for anthracene, whereas for benzene, it was minimum. The absence of heavy masses (> 400 m/z) showed that the solids grains were not refractory; instead, they were mostly made of organic molecules, mainly medium size aromatics, connected via aliphatic bonds. As the residence time of the precursor molecule in the plasma was limited by a few microseconds so, the growth and the formation of molecules within these solid grains could be a good representative of the early PAH growth mechanism. This work has also studied the effect of the precursor's structure on PAH growth. This was accomplished with anthracene and phenanthrene, where anthracene dissociated more effectively in the plasma and phenanthrene demonstrated greater thermal stability. The dust production yield in the case of anthracene was almost six times that compared to phenanthrene. However, the mass spectra of the condensate from these two isomers were nearly similar, indicating that dust generated from these two isomers followed the same kinds of growth mechanism and was independent of the precursor's dissociation cross-section. A comparison of the mass spectra between the condensate from anthracene and Murchison meteorite showed a preponderance of pyrene, its isomers and methylated products in both instances. This suggests a possible low-temperature formation of PAHs in the parent body of the Murchison meteorite (Marin et al. 2020). Also, it is important to note the growth of small and medium size PAHs within the solid grains, which could save them from extreme interstellar energetics later; these PAHs can be released in the gas phase by various dust destruction processes like stuttering.

Sciamma-O'Brien & Salama (Sciamma-O'Brien & Salama 2020) studied the morphology of the dust grains produced in the COSmIC facility using the precursors such as methane and acetylene. The grown carbonaceous grains were collected on a Quantefoil grid and analysed using the FE-SEM technique. The size and shape of the carbonaceous grains were found to be different for different precursors. For the methane, the grains were in the diameter range from 15 to 385 nm, having an average density of ~ 2.1 grains μ m⁻². Whereas for the acetylene, the grains showed much spherical structure compared to grains formed from methane, and these grains had a diameter in the range of 40 to 650 nm with an average density of ~ 3.5 grains μ m⁻². This morphological change of the carbonaceous grains can be linked with the different stages of dust growth at low temperatures. The planer structure grows first and then coagulates into a spherical form (Sciamma-O'Brien & Salama 2020).

Raman spectroscopy is now an integral part of many ongoing and future planetary exploration missions. PAHs have delocalized pi-electron, which enhances their polarizability and makes it an excellent target to probe using Raman spectroscopy. Gavilan and co-workers carried out a Raman spectroscopic study of microcrystalline pyrene and the dust particles derived from pyrene (Gavilan et al. 2022). These dust particles were synthesized by exposing gaseous pyrene seeded in a carrier gas Ar to a pulsed (300 µs) plasma discharge (~ 1000 V) in the COSmIC facility. The Raman spectra of the microcrystalline pyrene consist of many narrow bands and showed a good match with the previous studies on the single crystal and powder form of pyrene. The Raman spectra of the dust particles showed a broad G band around 1580 cm^{-1,} indicating the presence of graphitic structures. Its D band has multiple components assigned to the defects present in the disordered carbonaceous dust. The authors compared several Raman parameters, such as peak position, Full Width Half Maxima (FWHM), and peak intensity ratio of D to G band (I_D/I_G) , between the produced carbonaceous grains and various cosmically impotent carbonaceous dust, such as Insoluble Organic Molecule (IOM) from meteorites, soot, and hydrogenated amorphous carbon. (HAC). This comparison revealed that the produced carbonaceous dust grains were more crystalline than HAC, and their crystallite size was smaller than soot particles. However, a good match was observed in the crystallite size of IOM from the Allende meteorite and generated carbonaceous grains, indicating a probable low-temperature pathway of IOM in the Allende meteorite (Gavilan et al. 2022).

1.5.6 Low-pressure gas phase condensation technique:

Martinez and co-workers (Martínez et al. 2020) have studied the formation of cosmic carbonaceous dust analogue from gas phase carbon atoms and molecular hydrogen with different ratios similar to the atmosphere of AGB stars. The experiment was carried out in a setup known as Stardust (Martínez et al. 2018), which is an UHV system capable of mimicking the thermodynamic conditions observed in the dust formation zone of many evolved stars like AGB stars and allows one to study the formation, evolution of dust in those conditions. Here atomic carbon was produced by means of sputtering of graphite target using Ar ion, and this atomic carbon were reacted with molecular hydrogen in a gas aggregation zone, where the gas temperature was around < 1000 K. Two different molecular hydrogen concentration 1.5×10^{10} molecules cm⁻³, referred as low density and 1.5×10^{12} molecules cm⁻³, referred as high density were used in this experiment and the reactions were monitored with the help of Optical Emission Spectroscopy (OES) technique. The gaseous reactant and products were extracted to another chamber with a differential pressure using a nozzle. Here the solids present in the extracted gas were collected on a substrate, and the product remaining in the gas phase were analysed using Quadrupole Mass Spectrometry (QMS) technique. The morphology of solid aggregates was analysed using Atomic Force Microscopy (AFM) and Scanning Tunnelling Microscopy (STM). Whereas the chemical composition of these solid grains was studied using Laser Desorption Ionization Mass Spectrometry (LDIMS) technique. The OES results for the low hydrogen density case showed the formation of C₂, whereas its signature was missing in the case of the high hydrogen density case. The absence of C₂ in the high hydrogen concentration case suggested that most of the C₂ was consumed in a chemical reaction C₂ + H₂ \rightarrow CCH+H. For the low hydrogen density QMS, the result showed the signatures of aliphatic hydrocarbons like C₂H₂ and fragments of C₂H₄, C₂H₆, and other larger molecules. An increment in the abundance of these above mentioned molecules was observed with the increase in the hydrogen density. Notably, no signatures of fullerene and PAHs were noticed. AFM images of the solid particles showed a spherical shape with an average height of ~ 9 nm. STM images of the condensates showed various amorphous carbon nanostructures with height ranges from 1 Å to 5 Å. Signatures of individual molecules with five carbon atoms were also observed. The LDIMS analysis showed a larger abundance of CH clusters for low hydrogen density. The largest aromatic molecule

detected in a trace amount was $C_{16}H_{10}$, suggesting that the condition in which these grains formed was unsuitable for PAH or larger carbonaceous molecules to grow. Although signatures of benzene and naphthalene were detected after the annealing of the carbonaceous grains at a temperature of more than 355 K, suggesting a possible surface catalytic reaction between smaller hydrocarbons. Such annealing of nano grains can occur in ISM upon UV photon absorption and can lead to PAH formation through grain surface reactions (Martínez *et al.* 2020).

1.5.7 Formation of carbon clusters in the ice phase:

Molecular ices play a key role in the chemical enrichment processes of the interstellar medium. These ices are made of volatile molecules like H₂O, CH₃OH, CH₃CH₂OH, CH₄, NH₃, C₂H₂, and PAHs (Bernstein et al. 1999). In cold, dense interstellar clouds (~ 10 K), these molecules are accreted on top of a refractory core made of silicates/ carbonaceous materials. These molecular ices have gone through various non-energetic (thermal chemistry and atom addition chemistry) and energetic processing (shock chemistry, photochemistry, radiation chemistry) (Arumainayagam et al. 2019) in interstellar space. Irradiation of UV photons on the top of the ice surface can initiate photochemistry, forming new molecules and refractory organic residues (Bernstein et al. 1999). Thermal processing of dust grains can sublime these ices and enrich interstellar space by releasing molecules. In contrast, the refectory organic residue can stay on the dust surface until a much higher temperature and contribute to the growth of dust grains. To understand the extent of molecular complexity forming on the top of the dust surface in the ice phase, different groups across the globe have conducted extensive lab-based work on the energetic processing of ice. A detailed review of these works can be found elsewhere in the literature by Bernstein et al. (1999), and Sandford et al. (2020).

Lin *et al.* (2014) have experimentally studied the formation of hydrocarbon and carbon clusters of different sizes from methane ice. Using a synchrotron, pure CH₄ ice and CH₄ in Ne ice matrices at ratios (CH₄: Ne) 1:100 to 1: 10000 at 3K were irradiated using photons having a wavelength of less than 165 nm. The IR spectra of the irradiated ice showed the presence of multiple hydrocarbon species, such as CH₃, C₂H₂, C₂H₄, C₂H₆, C₄H₂, C₄H₄, C₅H₂, C₈H₂, C_nH (n= 1-5), and bare carbon clusters C_n (n= 1- 20). The yield of the hydrocarbon chain growth is found to be dependent on the energy of the irradiating VUV photon, especially when it is more than the dissociation energy of

 CH_4 . The efficiency of the agglomeration of the carbon clusters has also been reported to be influenced by the concentration of CH_4 and the mixing of H_2 in small proportions.

Knowledge of the physical structure of the organic refractory residue made on the surface of dust grains due to the energetic processing of ice has been limited. However, Rahul *et al.* (2020b) have shown that the physical structure of the residue made on the dust surface can have a wide range of structures and shapes, from flakes to cubes to the elongated triangular prism. For example, benzene deposited on a cold (~ 4 K) LiF substrate and irradiated with 9 eV VUV photons for 9 and 25 hours. Which followed by the heating of the ice containing residue with a ramp rate of 5 K min⁻¹ up to 300 K, showed a variety of structures and shapes. At 300 K temperature, most volatile organics are expected to be sublimated, and only the residue will stick on the substrate. VUV spectroscopy of the residue showed the presence of benzene derivatives such as aromatics and side carbon chains. FE- SEM images of the residue showed flakes, cubes, and spherical particles. After 25 hours of irradiation, the observed structures are cubes, T-shaped rods and many elongated prisms-like structures. These results can help our understanding of the physical shapes and bottom-up growth of the mixed aliphatic-aromatic dust produced on top of the pre-existing dust grains in ISM.

Recently benzonitrile has been discovered in the molecular cloud TMC-1 (McGuire *et al.* 2018). These small molecules are believed to play a vital role in forming larger PAHs in the interstellar medium. The fate of benzonitrile in the cold interstellar icy conditions (4 K) exposed to the VUV photons has been experimentally investigated by Sivaraman et al (Sivaraman *et al.* 2023). Irradiation of benzonitrile ice at 4 K using 9 eV photons produced refectory organic residues, which remain on the substrate even after heating up to 300 K. HR-TEM, Electron Dispersive X-Ray (EDX) analysis of the residue has shown the presence of N doped graphene and graphene quantum dots. The fact which makes this experiment unique is that it showed carbon nano dust graphene, and quantum dots could be made in cold icy conditions. These results can also be relevant for the atmospheric chemistry of Titan, where nitrogen and PAHs are known to be present.

The simultaneous formation of carbonaceous and silicate grains in cryogenic conditions on a pre-existing dust surface was experimentally studied by Rouillé *et al.* (2020). In Ne ice matrices, atomic (Mg, Fe) and molecular precursors (SiO, SiO₂) of

silicates and carbonaceous dust (C_n , n= 1- 20) were initially doped. By annealing, these doped atomic and molecular precursors interact with each other, which showed the evolution of a Si-O stretching feature around 10 µm, below 13 K. A broad 10 µm feature showed the presence of amorphous silicates. TEM, EDX analysis of the solid refractory residue showed that amorphous carbon and silicate are condensed together, although they are chemically different. These experimental results validate that silicates and carbonaceous materials can be reformed in cold interstellar conditions.

1.6 Top-down formation pathways:

While bottom-up formation routes can produce large quantities of fullerenes, PAHs, other astrophysically relevant carbon allotropes and carbon nanodust, they require high temperatures and densities. The another well-known formation pathway of interstellar dust is Top-down formation pathway. As the name suggests, this formation pathway can be started with the larger PAH molecules (> 50 C atoms) (Berné & Tielens 2012, Berné *et al.* 2015) or graphene (Chuvilin et al. 2010) or HAC (Scott *et al.* 1997), (Micelotta *et al.* 2012), SiC (Merino *et al.* 2014, Bernal *et al.* 2019). A pictorial representation of the various known/proposed top-down formation route of carbon dust in the ISM can be found in **Fig 1.7**.



Fig 1. 7: Top-down formation route of interstellar carbonaceous dust. Top-down routes start with larger molecules like PAH (Berné et al., 2015, Berné and Tielens, 2012, Zhen et al., 2014) or Graphene (Chuvilin, Kaiser, 2010) or HAC (Scott et al., 1997); (Micelotta et al., 2012). Experimentally, (Chuvilin, Kaiser, 2010), showed that bombardment of graphene by high-energy electrons (more than 85 KeV) leads to the formation of fullerenes, essentially by removing a carbon atom from a hexagonal ring; the resulting pentagonal ring causes the initial curvature and in short timescales, fullerene cages are the result. When starting from large PAHs, a similar process can be induced by using UV photons that first strip the PAHs of their hydrogen atoms; the resulting bare carbon cluster then isomerizes into a cage structure. Such processes were first speculated to be possible in the ISM (Berné and Tielens, 2012), and were then shown experimentally to take place as well (Zhen, Castellanos, 2014). Similar UV photo processing of HAC grains also showed the formation of fullerene and others carbon nanoclusters (Scott, Duley, 1997). The surface destruction of SiC dust using ions or by the application of high temperature can also lead to the formation of carbonaceous dust (Bernal et al. 2019, 2022) (Image taken from A. Roy et al. 2023).

Direct formation of fullerene from graphene was first experimentally demonstrated by Chuvilin and co-workers (Chuvilin *et al.* 2010). In this experiment, graphene was placed in an aberration-corrected TEM and irradiated using an 80 keV electron beam. Exposure of the graphene to the energetic electron beam led to the removal of C atoms from its edge. At the same time, these high-energy electrons also destroy the graphene sheets producing many small graphene flakes by means of energy transfer to the carbon atoms. As time progressed, more energy was deposited on these small flakes, and their shapes started changing to round shapes. The end product is often observed to be perfect fullerene. The sequence of the transformation of graphene to fullerene can be understood in 4 steps. In the first step, the carbon atoms at the edges of the graphene sheet were removed. During the second stage, the formation of the

pentagon structure commenced, driven by the goal of minimizing the energy associated with the dangling bonds. In the subsequent step, multiple pentagons joined together, creating bowl-shaped structures. Finally, these bowl-like structures fused, ultimately resulting in the formation of fullerene.

Berné and Tielens (Berné & Tielens 2012) proposed the top-down formation of cosmic carbon dust, especially fullerenes, by photochemical processing of larger PAHs. Spritzer observations of the PNe NGC 7023 showed the co-existence of PAHs and C₆₀, where the calculated abundance of fullerene was seen to increase and PAH abundance to decrease towards the central star. These observations can be explained by the photo destruction of PAH and the formation of C₆₀. The possible formation pathway of C₆₀ from PAH can be simplified into a few steps. First, the UV photons bombarded on the PAH initiate dehydrogenation. Once all the H is removed from the edges, it makes graphene sheets. Upon absorption of UV photons, graphene can be fragmented into small flakes. Energy deposited on these small flakes can remove C atoms and minimize the dangling bond energy, so the pentagon starts to appear. This leads to the formation of curvature and, subsequently, a bowl-like structure being formed, which are then zipped together and to make fullerenes. The other proposed structures are small cages, rings, and chains. This proposal was later experimentally verified by Zhen *et al.* (2014), and Berné *et al.* (2015).

Photo processing of HAC is an alternative pathway for the formation of carbon dust like fullerene. Scott et al (Scott et al. 1997) studied the photodecomposition of HAC using the UV laser (308 nm). HAC thin films were grown on the Cu and Al substrates and then irradiated with different fluences (0.09 to 0.5 J m⁻²). The gaseous product was analyzed using TOF mass spectrometry. This experiment aimed to study the combined effect of thermal, mechanical and photochemical processing of HAC dust. HAC dust can encounter similar energetics under interstellar shock conditions (Scott *et al.* 1997). The analysis of the gaseous product showed the presence of molecular clusters with a wide mass distribution. For low fluence (0.13 J cm⁻²) irradiation, molecular clusters, including C_{50} , C_{60} , and C_{70} , have been observed, but after exposure to many UV pulses, C_{40} became the most dominant cluster. This indicates the sequential decomposition of HAC, where small molecules and molecular fragments were produced before larger molecular clusters. For high fluence (0.2 J cm⁻²) irradiation, both low and high-mass molecular clusters were observed even for a single pulse application. After multiple UV pulse applications, the authors claimed the tentative detection of dehydrogenated PAHs like chrysene (C_{18}), anthracene (C_{14}), and naphthalene (C_{10}) in their gaseous product. Results from these experiments can aid an understanding of the formation of carbon dust like PAHs and C60 from HAC, decomposed by interstellar shocks.

Destruction of SiC through energetic processing can be another possible route to produce carbon nanodust. SiC has been routinely detected around carbon-rich AGB stars, and is the 2nd most abundant carbon dust found in presolar grains. Despite that, its spectroscopic detection in the ISM is very rare. The possible reason behind that can be the destruction of SiC grains due to extreme energetic processing. Bernal et al. (2019) showed the formation of C_{60} by bombarding energetic ions on the cubic SiC. In vacuum, the SiC particles deposited on a SiN film consist of a microelectromechanical system, which allows the rapid heating of the sample up to 1300 K and then bombarded with 150 keV Xe ions. The combination of fast heating followed by ion irradiation mimics ISM shock heating of dust grains. The processed samples were later analysed using Scanning Transmission Electron Microscope (STEM), EDX and EELS spectroscopy. From TEM imaging, it was observed that after energetic processing, the SiC crystal had undergone structural modifications. Signatures of graphitization have been found around the edges of SiC crystal. A hemispherical structure with a diameter of around 0.7 nm was observed, which they assigned as fullerene. These results can be applied to understand the formation pathways of fullerene in a hydrogen-poor, carbon dust-rich environment like PNe Tc1.

Recently Bernal *et al.* (2022) have also studied the thermal decomposition of SiC. In this experiment, SiC was initially heated up to 800 °C with a ramp rate of 25.7 °C min⁻¹, then heated up to 1500 °C at a ramp rate of 4.2 °C min⁻¹, and then remained isothermal for 13 min. In situ TEM observations showed that at temperature ~ 1000 °C, an increment in the surface graphitization of SiC has been observed. In contrast, around 1050 °C, a hemispherical fullerene-like structure started growing, and multi-walled carbon nanotubes (MWCNT) were also detected. It was also noticed that as the isothermal state continued, the MWCNT became much more ordered. To date, the largest carbonaceous molecule known to be present in ISM are fullerenes, HAC and PAHs but this experiment suggests that CNTs can also be a component of interstellar dust.

Merino *et al.* (2014) experimentally investigated the top-down formation pathway of PAHs in a simulated interstellar condition. They exposed graphene terminated cubic SiC surface to atomic hydrogen at an elevated temp ~ 1000 - 1300 K. This led to the erosion of the graphene, and graphene flakes of different sizes came out, which in a hydrogenous atmosphere turned into PAHs.

Pino *et al.* (2019) have experimentally studied the effect of cosmic ray bombardment on pre-existing cosmic carbonaceous dust analogue. The carbonaceous dust analogue was produced from ethylene by burning it in a flame using the same experimental set up previously used Pino *et al.* (2019)and Carpentier *et al.* (2012). 4.8 MeV u⁻¹ swift heavy ${}^{48}Ca^{n+}$ ion was used to irradiate the carbonaceous dust analogue, which was placed at an angle of 45° to the direction of the incident ion beam. The ion matter interaction leaves many ionic and neutral molecular fragments whose mass was recorded using TOFMS technique. Large PAH with a number of carbon atoms up to 50 and cationic fullerene were detected in the molecular fragments. This experiment suggests that swift heavy ion bombardment on the carbonaceous dust in the ISM can also produce large carbonaceous molecule like fullerene and PAHs.

1.7 Laboratory Production of cosmic Silicate dust analogue:

Several methods are employed to produce cosmic silicate dust analogues in the laboratory. These methods aim to mimic the composition, structure, and physical properties of silicate grains found in various astrophysical environments. These methods are melt and quench technique, Sol-gel technique, gas phase condensation technique, laser ablation, and cold condensation technique. A brief summary of these various experimental technique can be found in the following section. **Fig 1.8** represents a pictorial summary of various abatable experimental technique for the production of cosmic mineral dust analogue.



Fig 1. 8: Different formation pathways of cosmic silicate dust. These include melt and quench, Sol-gel, gas phase condensation, laser ablation, and cold condensation techniques. Also, a new shock-induced formation pathway of silicate dust has been highlighted.

1.7.1 Melt and Quench Technique:

It is one of the simplest techniques to produce an amorphous silicate dust analogue in the laboratory. In this technique, a dust precursor mixture of cosmic silicate, and dust analogue is gradually heated with a ramp rate of ~ 10 K s⁻¹ to a high temperate ~ 1700 K using platinum cubicles. This produces a melt from these precursors, and the melt remains at a high temperature for around ~ 1 hour. After that, the melt was allowed to cool rapidly with a cooling rate of ~ 10^3 K s⁻¹. This rapid cooling can be achieved using a rotating copper roller, where the melt gets pressed and compacted with a dimension of ~ few mm. Despite a very rapid cooling, some degree of crystallization can happen, and that part can be removed with the help of a magnifying glass, as described in Dorschner *et al.* (1995).

Using this technique J. Dorschner and co-workers (Dorschner *et al.* 1995) produce pyroxene and olivine class of solid solution with wide verities of compositions. Magnesium carbonate, ferrous oxalate, and silicon dioxide were put in the platinum cubical. With the help of the resistive heating technique, the mixture gradually heated up to 1900 K and remained fixed for about an hour. This produces a melt from the above-described mixture. The melt was quenched rapidly with a rate of ~ 10^3 K s⁻¹ to make the glass state, using the same method described in the previous paragraph. The

condensate was later analysed using IR reflectance spectroscopy, XRD, SEM imaging and EDX analysis techniques. One of the main advantages of this technique is that it can produce condensate in bulk (thin sheet). After polishing it, it can be used to measure optical constant using IR reflectance and transmission spectroscopy. Because the melting was performed in the ambience, preventing iron (Fe²⁺) from getting oxidized was difficult in this method. When iron content is more in the melt than Mg, then a tendency of phase separation and crystallization was observed. Also, for the olivine stoichiometry mixture, the presence of Mg in the precursor increased the melting point of the mixture above the melting point of the platinum cubical. Similar kinds of work were also carried out by Mohr *et al.* 2013, where they produced a melt from a similar mixture used by Dorschner *et al.* (1995).

1.7.2 Sol-Gel Technique:

The Sol-Gel technique is a relatively low-temperature formation technique of interstellar dust analogue in the laboratory compared to the melt and quench technique. The sol-gel technique provides a way to overcome the challenges associated with synthesizing materials that exhibit thermal and thermodynamic instability in other laboratory methods (Burlitch *et al.* 1991). In this technique, the cosmic dust analogue precursors are suspended or dissolved in a solvent like water or alcohol, and the reaction usually starts by mixing either acid or base into the solvent. Molecular clusters or micron size particles can be grown in the liquid environment (sol) with the help of chemical reaction such as hydrolysis. Due to the small particle size range of approximately 1-1000 nm, the interactions between the formed particles primarily occur through van der Waals, coulombic, and steric forces. This results in the growth of solid particles throughout the sol, forming a gel consisting of two phases: a solid phase filled with the solvent. The liquid solvent is evaporated and released into the air through the pores of the solid particles by subjecting the material to elevated temperatures, typically reaching several hundred kelvins.

Jäger *et al.* (2003) utilized the Sol-Gel technique to synthesize amorphous cosmic silicate dust with varying Mg/Si ratios in their study. They employed tetraethoxysiloxane (TEOS) and magnesium methylate Mg (OCH₃)₂ as metalorganic precursors for the cosmic silicate dust analogue. To promote the formation of amorphous silicate dust, they introduced hydrogen peroxide (H₂O₂) into the solution, which acted as a catalyst for the hydrolysis reaction by providing additional protons.

To ensure a contamination-free environment, the experiment was conducted in an argon (Ar) atmosphere, preventing the formation of insoluble Mg(OH)(OCH₃) and inhibiting further phase separation of MgO. Subsequently, the solvent in the solution was removed using a rotary evaporation technique. The collected solid particles were then heated to increase their density and reduce porosity. The resulting structure and chemical composition of the silicate dust grains were examined using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The samples were pressed and polished to determine the optical constants, allowing for IR reflectance and transmission spectroscopy analysis. The obtained IR emission spectra of two AGB stars, TY Draconis and R Cassiopeiae, showed a good match with the synthesized amorphous Mg-rich silicate dust, suggesting the significance of such dust in understanding the structure of AGB circumstellar shells. Additionally, the authors conducted annealing experiments on the amorphous silicate dust grains, observing a decrease in the crystallization temperature with an increase in the Si-OH concentration. Similar effects were also noticed when the iron content in the sample was increased.

1.7.3 Gas phase condensation:

Interstellar dust is arguably formed at the extended envelope of the evolved stars via the gas phase condensation process. The formation of dust can simply be understood in two steps, nucleation and growth. In a suitable thermodynamic condition, a supersaturated vapour mixed with atoms, ions and molecules started to nucleate and make clusters of new molecular composition, leading to solid submicron size particles formed by various dust growth mechanisms. Laboratory-based gas phase condensation methods have been routinely used to produce amorphous cosmic silicate dust analogue, known as 'smoke' (Day 1979, Nelson *et al.* 1989, Rietmeijer *et al.* 1999). Gas phase condensation experiments are typically conducted using two methods. In the first method, solid condensates are produced by allowing various species in vapour phase to collide with a substrate held at an extremely low temperature. Alternatively, condensation can occur by rapidly cooling the system in an inert atmosphere, promoting interactions among the atoms and molecules in a cooling environment (Williams & Cecchi-Pestellini 2015).

Using the NASA GSFC's Dust generator facility J Nuth and co-workers have been routinely producing cosmic silicate dust analogue. In this part, we will only summarise a few crucial results from this facility, and a detailed discussion of such experiments and results can be found in, (NUTH III et al. 2002, Rietmeijer et al. 2013) and references therein. Solid condensate is produced by combusting from a gaseous mixture of silane (SiH₄), iron pentacarbonyl (Fe(CO)₅), and trimethyle aluminium $((CH_3)_3Al)$ in an atmosphere of H₂ with chamber pressure ~ 90 torr and in the temperature range from 500 to 1500 K. An oxidant like O₂ was separately introduced just before the combustion. Metals like Mg, Ca, Na, and K can also be introduced separately simultaneously. The flow velocity in the furnace is usually maintained within the range of 10-20 cm s⁻¹. Using a high flow rate in the gas phase condensation process ensures that the solid condensate spends minimal time in the vicinity of the combustion zone, thereby minimizing the duration of nucleation and growth stages. This high-speed flow carries this mixture of hot gas, and the freshly produced condensate to another chamber followed by quenching and deposition on an aluminium substrate, usually kept at a temperature of 300 K - 350 K, which is relatively lower than the combusting temperature. The chemical composition of these grains can be predicted stochastically from the chemical composition of the precursor vapour. These grains are found to be fluffy, and it is found that hundreds of individual grains aggregate to form larger grains with a particle size of around 20 to 30 nm (NUTH III et al. 2002). Rietmeijer, Nuth, and the co-workers (Rietmeijer et al. 1999) studied the condensation of Mg or Fe-rich dust grains from the vapour of Mg-Fe-SiO-H₂-O₂. SEM analysis of these condensates suggests that no significant amount of condensate with a mixed MgFeSiO composition exists under definite conditions. It is well known that the crystalline silicate observed around the evolved stars is Mg-rich. Results from this experiment show a good agreement with this observation.

1.7.4 Laser Ablation:

Like for the case of carbonaceous dust, laser ablation materials can also be utilized to produce cosmic silicate dust analogue. Laser ablation involves the use of high-energy lasers to vaporize and ionize a target material, which then condenses and solidifies to form nanoparticles. This method allows for precise control over the produced dust analogues' size, composition, and crystallinity (Brucato *et al.* 2002). Brucato and colleagues (Brucato *et al.* 2002) utilized the laser ablation technique to synthesize Mg-rich amorphous pyroxene class dust in their study. The experiment involved exposing a pellet of bulk pure silicate mineral to a Q-switched Nd: YAG laser at an angle of 45° , with the resulting plumes collected normally to the pellet's surface. The entire process was conducted in a 10 mbar O₂ environment. Subsequently, the amorphous grains obtained underwent thermal annealing to induce their transformation into crystalline solids. These solid condensates' morphology and chemical composition were characterized using FE-SEM and EDX analysis techniques. The phase transition from amorphous to crystalline due to annealing was monitored through IR spectroscopy. The size distribution of these condensates followed a log-normal pattern. The findings from this study imply that crystalline silicate dust observed in comets may originate from the thermal annealing of amorphous silicate grains during the precometary phase.

In their study, Sabri and colleagues (Sabri et al. 2013) employed the laser ablation technique to synthesize amorphous cosmic silicate dust analogues. They utilized metallic targets with stoichiometry corresponding to olivine and pyroxene and amorphous materials with compositions resembling olivine and pyroxene. One can find the details of the experimental procedure in Sabri et al. 2013. The plume which came out from the target surface because of laser irradiation was allowed to quench in an atmosphere with a He to O_2 ratio which was maintained around 3:1. The newly produced solid particles were later extracted adiabatically into the second chamber with a pressure of $\sim 10-3$ m bar where they got decoupled from the carrier gas and deposited on a substrate. These solid condensates were subjected to various analytical techniques, including HR-TEM, FE-SEM, EDX spectroscopy, Atomic Force Microscopy (AFM), and IR spectroscopy. The analyses revealed that the solid particles consisted of amorphous forsterite and fayalite. Furthermore, the researchers conducted thermal annealing experiments on these solid condensates, resulting in their transformation into crystalline forsterite and fayalite. Additionally, the authors conducted investigations to elucidate the formation of H₂ on the surface of these dust analogues.

1.7.5 Low-temperature formation of silicate dust:

Experimental investigations have been conducted to study the condensation process of complex silicates with compositions resembling pyroxene and olivine under conditions found in molecular clouds, and details of these experimental results can be found in the work by Rouillé *et al.* (2014), and by Krasnokutski *et al.* (2014). The condensation of atoms and molecules in the ISM at extremely low temperatures of ~10 K is believed to occur on the surfaces of dust grains, which are, remaining as a result

of various dust destruction processes such as sputtering and shattering. In a study by Krasnokutski *et al.* 2014, the low-temperature condensation of SiO, one of the abundant molecules in the ISM, was investigated using He droplet and Ne matrix isolation techniques. The researchers observed the growth of SiO clusters at very low temperatures (~10 K) through a series of barrierless reactions, providing insights into a potential growth mechanism for refractory silicate dust in cold interstellar conditions.

The formation of Mg and Fe-rich silicate dust on a pre-existing cold dust surface has also been explored by Rouillé *et al.* 2014. In the first phase of this experiment, laserproduced vapour comprised of the composition of olivine and pyroxene was allowed to condense into Ne matrix and cooled to a temperature similar to cold ISM, ~6 K. In the second phase, the condensate was subjected to thermal annealing at around 13 K, causing the sublimation of Ne and leaving behind the remaining condensates. These grains were subsequently analysed using techniques such as UV spectroscopy, IR spectroscopy, and HR-TEM imaging. The analyses revealed the presence of nanometersized spherical grains with flexible structures. The IR features of these grains showed a significant correlation with those of cosmic silicate dust, particularly in the 10 and 20 μ m spectral region.

1.8 Motivation of the thesis:

The formation and evolution of cosmic dust grains continues to remain an evolving research topic. To address this problem, varieties of laboratory work has been carried out, which involved the production of cosmic dust analogues under controlled space-simulated environments, followed by the analysis of the dust analogues generated. Details of different experiments focusing on the formation of cosmic dust analogues in the laboratory have been discussed in sections 1.5 - 1.7. Dust grains in the ISM have gone through various energetic and non-energetic processing. These include photo processing by the VUV radiation from the stars, high energy cosmic ray bombardment on the dust grains, electron bombardment, and shock processing (Arumainayagam *et al.* 2019). A pictorial representation of different energetic processing occurring on the surfaces of dust grains in the ISM is shown in **Fig 1.9**. Amongst the different energetic processing of dust grains, shock processing. To the best of our knowledge, laboratory shock processing of interstellar dust analogues is limited only to a handful of studies. One such has been carried out by Carmer &
Frenklach (1989), and Frenklach *et al.* (1989) where they studied the formation of SiC from the gaseous mixture of SiH₄ and CH₄ using a shock tube. Recently Biennier *et al.* (2017) also studied the energetic processing of fullerene by employing a shock tube. This thesis has tried to shed some light on the least explored frontier of dust evolution by subjecting different cosmic dust analogues to shock waves. The other relevant aspects which motivated this thesis work are listed below,

- Finding an alternative formation pathway of cosmic carbonaceous dust : In 2010 astronomers first detected the signature of fullerene in the ISM, specifically in the planetary nebula PNe Tc1 (Cami *et al.* 2010). This planetary nebula is particularly hydrocarbon poor; even the signatures of the simplest hydrocarbon molecules, such as acetylene, ethylene, and methane, are found to be absent (Cami *et al.* 2010). Later fullerene has also been detected in another hydrocarbon-poor planetary nebula, PNe Lin-49 (Otsuka *et al.* 2016). These findings raised questions about the efficiency of the top-down (Berne and Tielens. 2012) formation route of fullerene, which usually starts form large PAH molecules with more than 50 C atoms. To address the formation of fullerene and other carbon nanostructures in a hydrocarbon deficient environment there is a need to carry out a new set of experiment which is independent to the known hydrocarbon based formation route.
- Understanding the fate of amorphous carbon behind shock fronts: The amorphous carbon, especially hydrogen-free amorphous carbon, has been detected in the envelope of the AGB stars (Gauba & Parthasarathy 2004), PNe (Cami *et al.* 2010) using their feature less IR emissions. The evolution pathways of the hydrogen-poor amorphous carbon compared to its hydrogenated counterpart are least explored (Dartois. 2019). Shock processing of amorphous carbon in different environments may induce physicochemical changes in it, which can be helpful in understanding and adding more value to the least explored evolution tracks of amorphous carbon in the ISM. Apart from the structural refinement, in the high-temperature shock processing, amorphous carbon can also be involved in various chemical reactions

with another abundant element like Si. Thus there is an urgent need to carry out laboratory shock processing of amorphous carbon under controlled space-simulated environments.

- Understanding the physicochemical evolution of organometallic dust induced by shock: The discovery of the simplest metallocene molecule, ferrocene, back in 1951 started a new branch of chemical science known as organometallic chemistry (Heinze K., Lang H. 2013). Since then, verities of organometallic molecules have been discovered. Because of their unique structure, these organometallics play a vital role in different chemical reactions that start from catalytic reactions, charge transfer processes, and polymer reactions (Heinze K., Lang H. 2013). The recent discovery of cyclopentadiene in the ISM has drawn the attention of astrochemist investigating he role of organometallics in ISM chemist (Cernicharo *et al.* 2001b, Cernicharo *et al.* 2021b). Despite the importance of organometallics in earth-based chemistry, its importance in interstellar chemistry has been least explored to date. Thus, shock processing of the simplest organometallic molecule may improve our understanding of the interstellar dust enrichment process.
- Shock-induced formation route of cosmic mineral dust: A large fraction of the cosmic mineral dust is thought to form in the extended envelope of the AGB stars (Gail *et al.* 2009, Zhukovska & Henning 2013, Gail *et al.* 2016). Various experiments have been carried out to understand the formation pathways of mineral dust in different astrophysics regions, and we have already discussed such experiments in section 1.7. Methods like the sol-gel technique, and the melt and quench technique are dedicated mainly to the production of the bulk grains in thermodynamic equilibrium. *The grains produced in these methods are homogeneous and mostly used for the measurement of optical constants (Henning. 2014, Williams and Pestellini. 2016). The production technique of these grains does not mimic the real scenario in which dust grains originate in stellar envelopes (Henning. 2014, Williams and Pestellini. 2016).* Signatures of crystalline dust have been detected in comets like Hale-Bopp (Crovisier *et al.* 1997, 2000) and

Comet NEAT (Wooden *et al.* 2004). The formation pathways of crystalline dust in comets are largely unexplored experimentally. The dust grains produced in conventional gas phase condensation techniques are mostly amorphous, and further heating is required to turn them into the crystalline form (NUTH III *et al.* 2002, Rietmeijer *et al.* 2013), and the references therein). Shocks in the early solar nebula could produce the flash heating of the amorphous silicate precursors and lead to crystalline silicate dust formation (Haker and Desch. 2002, Nuth *et al.* 2006). Therefore, laboratory experiment mimicking such nebular shock processing of silicate dust precursors is required in understanding various formation pathways of crystalline silicate dust in comets.



Fig 1. 9: Submicron to nm size interstellar dust grains consists of a core which is made of silicate or carbonaceous refectory materials. In the cold, (~ 10 K) interstellar medium, volatile gas-phase molecules are usually deposited on top of the core, in the form of ice. In the ISM, dust grains are subjected to various energetic processing, including photo processing by the harsh VUV radiation, cosmic ray bombardment, electron bombardment and shock process (Arumainayagam et al. 2019).

1.9 Thesis Objective:

The objectives of this thesis work are listed below:

1. Carrying out laboratory shock processing of interstellar dust analogues using the High-Temperature Shock Tube for Astrochemistry (HISTA) facility at PRL.

- 2. Characterization of the pre and post-shocked materials by analysing their crystallographic structure, chemical composition, phase transitions, and physical properties such as porosity, density, and magnetic behaviour.
- **3.** Understanding the evolution of interstellar dust analogues under simulated low-velocity interstellar shocks (1-2 km s⁻¹) in the laboratory. This includes the formation of new compounds, destruction and fragmentation of dust grains and subsequent effects on the overall composition and characteristics of interstellar circumstellar dust.
- **4.** By correlating the results of laboratory investigations with observational data from telescopes and astrophysical models, this thesis aims to bridge the gap between experimental simulations and the real astrophysical environment.

1.10 Thesis Structure:

The Chapters in the thesis are arranged in the following order.

- Chapter 1: Provides an introduction to interstellar dust and reviews different laboratory experiments carried out to produce cosmic dust analogues by different groups across the globe. This chapter also discussed the motivation behind the thesis work and also describes the objectives of this thesis.
- Chapter 2: Provides details about, shock waves in the ISM and its importance to cosmic dust chemistry. This chapter also discusses the working principle of shock tubes and their role in chemical kinetics.
- Chapter 3: Gives detailed information about the experimental methodology used in this thesis, which includes a detailed description of the shock tube used, experimental procedure, sample preparation, collection and various analysis techniques employed to characterize the pre and post-shocked samples.
- Chapter 4: discusses the effect of shock processing of carbon nanopowder in a hydrogen deficient environment and its implications for the formation of dust in interstellar space.
- Chapter 5: provides the results from shock processing of amorphous carbon nanopowder in the presence of hydrogen and also discusses the implication of the outcome to the condensation of dust grains in the interstellar space.

- Chapter 6 discusses the effect of shock processing of amorphous carbon and silicon nanopowder mixtures in the presence of hydrogen. It also tries to imply the results out of this experiment to the formation of SiC dust in interstellar space.
- Chapter 7: discusses the fate of the organometallic dust when subjected to extreme shock in the laboratory. This chapter also discusses the implications of the results to interstellar elemental recycling and interstellar polarization.
- Chapter 8: Shows the instantaneous shock-induced formation pathways of the cosmic olivine class dust.
- Chapter 9: Provides a summary of the thesis and a future outlook based on the findings.

Chapter 2 Physics of Shock Waves and Shock Tube

Chapter overview:

This chapter starts with a basic introduction to shock waves and their occurrence in nature. The mathematical formulation of shock waves, including the continuity equation and Rankin Hugoniot jump equation, which describes the change of medium properties such as pressure and temperature across the shock front, are discussed. The formation of shock waves in different parts of ISM, such as outflows from evolved stars, cloud-cloud collisions, and supernova explosions, have been explored. One of the main objectives of this thesis is to understand the impact of shock waves on the physicochemical and structural properties of interstellar dust analogues. Therefore, various processes associated with the interaction of shock waves with matter are discussed. A brief discussion of the various techniques used to produce shock waves in the laboratory are provided in this chapter to highlight their advantages and limitations. Additionally, the use of a shock tube as a chemical reactor is discussed, including its working principle, the Rankine-Hugoniot jump equations applied to shock tube operation, and the description of various parameters associated with shock tube experiments. The chapter concludes with a description of how shock tubes can be used to simulate low-velocity interstellar shock waves in the laboratory. This sets the stage for the next chapter, which focuses on the experimental methodology employed in the thesis.

2.1 Shock Waves:

Shock waves are rapid and intense disturbances propagating through a medium, causing a sudden and abrupt change in pressure, temperature, and density (Gaydon & Hurle 1963). These waves are characterized by a steep front, known as the shock front, where the properties of the medium experience a sharp jump over a very short distance (Gaydon & Hurle 1963, Jagadeesh 2008). The typical thickness of such a shock front at normal atmospheric pressure is around a few Å, much smaller than the characteristic length scale associated with the fluid propagation (Jagadeesh 2008). The typical thickness of the shock front

depends on the properties of the medium. For monoatomic gas, the thickness is about four times the mean free path; for polyatomic gases, the thickness is much larger (Jagadeesh 2008). Shock waves are different from sound waves in many ways. Sound waves are characterized by relatively small amplitudes, while shock waves exhibit four distinct and remarkable features. Firstly, shock waves have a supersonic velocity of propagation that depends on the pressure of the medium. Secondly, they create a sharp wavefront with sudden and drastic changes in all thermodynamic quantities. Thirdly, in the case of nonplanar shock waves, their velocity of propagation decreases significantly as the distance from the point of origin increases. Lastly, shock waves demonstrate non-linear superposition properties, including reflection and interaction with other waves (Jagadeesh 2008). These unique attributes distinguish shock waves from ordinary sound waves and make them notable phenomena in various fields of science and engineering. When a sound wave propagates through a gas, it induces oscillations in the pressure and density of the gas along an adiabatic path, representing a reversible process. On the other hand, when a shock front travels through the gas, it causes a sudden and irreversible jump in the state of the gas along its path (Gaydon & Hurle 1963, Jagadeesh 2008). Unlike electromagnetic waves, shock waves cannot travel in a vacuum, and therefore, require a medium to propagate. In nature, any sudden dissipation of energy (with a time scale around a few µs) manifests itself in the form of shock waves, as it is the most efficient way for energy release in nature known so far (Jagadeesh 2008). Shock waves can occur under various natural and artificial scenarios, such as explosions, supersonic flight, astrophysical events such as supernova explosions, cloud collision, expansion of HII regions, and high-velocity impacts between planetary bodies (Gaydon & Hurle 1963, Jagadeesh 2008). Fig 2.1 shows different events that occurred on Earth and in interstellar space where shock wave formation was detected. The energy carried by shock waves makes them capable of inducing significant changes in the materials and environments they encounter, leading to a wide range of physical and chemical effects.



Fig 2. 1: shows various events that occur in nature that are associated with shock waves. (a) shock front, shown in white colour, due to 90 Tonnes of TNT exploding and travelling (https://gizmodo.com.au/2014/07/100-tons-of-tnt-one-awesome-explosionoutward shock-wave/). (b)Sonic Boom generated by an *F-16* fighter jet (https://theaviationist.com/2021/09/07/listen-to-the-sonic-boom-generated-by-an-f-16flying-supersonic-over-oshkosh/). (c) Image of a Supernova Remnant (SNR) with a blue coloured boundary edge representing the shock wave propagating outward in the interstellar space (https://www.princeton.edu/news/2017/07/20/scientists-create-firstlaboratory-generation-high-energy-shock-waves-accelerate/). (d) Shock front attached with the Saturn-V rocket during separation of one of its stages (https://www.sciencelearn.org.nz/images/407-saturn-v-stage-separation/). (e)Shock wave bullet attached to moving with supersonic а speed (https://en.wikipedia.org/wiki/Shock wave).

2.2 Generation of Shock Wave and its mathematical formulation:

To create a shock wave in a medium, one needs to introduce a supersonic displacement or perturbation in the medium. A simple thought experiment using a piston and a gas tube can help us understand how a shock wave forms, as suggested by Kumar *et al.* (2014). We assume that the piston can be accelerated to a speed greater than the sound speed in the gas medium inside the tube, and there are no leakages or friction on the tube walls. At time t=0, the piston is at rest. Over a short time, interval δt , the piston is accelerated to a velocity δV . For a shock wave to form, this velocity must exceed the sound speed (a) in the gas medium, which is related to the temperature (T) as $a=\sqrt{(\gamma RT)}$, where R

is the universal gas constant and γ is the ratio of the specific heat of the gas at constant pressure to the specific heat of the gas at constant volume.

With each incremental movement of the piston, weak compression waves are generated, compressing the gas medium and causing a small increase in temperature (δT). This temperature increment leads to a corresponding increase in the gas's sound velocity (δa). As the piston gains further velocity δV , additional compression waves are produced. Each successive compression wave propagates through the gas medium with an increased velocity compared to the previous one as the gas temperature progressively rises due to the cumulative effect of the compression waves.

As time progresses, multiple compression waves travel through the gas, each faster than the preceding one, eventually merging into a single strong wave known as a shock wave. This shock wave moves through the medium with a velocity of Vs and is characterized by abrupt pressure, temperature, and density changes across its front. This process is illustrated in **Fig 2.2**, where successive panels (a) to (e) depict the stages of shock wave formation as the piston accelerates and compression waves combine to form the final shock wave.



Fig 2. 2: Schematic diagram of the different stages of the thought experiment to produce a shock wave. (a) shows the piston is just displaced from its rest position at a time t=0. (b) Shows that the generation of the 1st compression wave in the gas medium because of the movement of the piston. (c) –(d) shows the generation of many compression waves, which eventually coalesce to form a strong shock wave, shown in (e). The idea of this figure is adapted from Kumar et al. (2014).

Thus, based on the thought experiment, it becomes evident that when an object is accelerated from its rest position to a velocity V greater than the speed of sound in the medium, it can form shock waves. As the shock wave propagates through the medium, there are abrupt alterations in the pressure, temperature, and density across the shock front. These rapid changes in fluid parameters can be mathematically described using the continuity equation (Gaydon & Hurle 1963, Kumar *et al.* 2014).

Let's consider a one-dimensional flow of an inviscid fluid along the x-axis as shown in **Fig 2.3**. The shock wave is assumed to be a thin discontinuity propagating through the fluid at velocity V_s . The pre-shock state is denoted by the subscript "1," and the post-shock state is denoted by the subscript "2."



Fig 2. 3: Shows a shock front marked by a red arrow travelling through a medium where the blue arrow indicates its propagation direction. The region across the shock front will experience rapid changes in the fluid parameters such as pressure, temperature and particle density. The shock-processed region is marked by subscript 2, and the unshocked region is marked by subscript 1.

Conservation of Mass:

The conservation of mass states that the mass flow rate into a control volume must equal the mass flow rate out of the control volume. In mathematical form, it can be expressed as follows:

$$u_2 \rho_2 = u_1 \rho_1 \tag{2.1}$$

where ρ_1 and ρ_2 are the pre-shock and post-shock densities, respectively, and u_1 and u_2 are the pre-shock and post-shock velocities, respectively.

Conservation of Momentum:

The conservation of momentum along the x-axis states that the net force acting on the fluid in the x-direction within a control volume must be equal to the rate of change of momentum. In mathematical form, it can be expressed as follows:

$$P_2 + \rho_2 \, u_2^2 = P_1 + \rho_1 u_1^2 \qquad 2.2$$

where P_1 and P_2 are the pre-shock and post-shock pressures, respectively.

Conservation of Energy (First Law of Thermodynamics):

The first law of thermodynamics states that the change in total energy within a control volume is equal to the net energy flux across the control surface. For an inviscid fluid, the energy flux comprises kinetic and internal energy. In mathematical form, it can be expressed as follows:

$$2H_2 + u_2^2 = 2H_1 + u_1^2 2.3$$

Where H_1 and H_2 are the specific internal energies of the fluid in the pre-shock and postshock states, respectively.

Shock Jump Conditions:

To obtain the jump conditions, we need to express the post-shock variables (ρ_2 , u_2 , P_2) in terms of the pre-shock variables (ρ_1 , u_1 , P_1) and the shock velocity Vs. These jump conditions are obtained by solving the above equations for the post-shock variables.

For a perfect gas (an idealized fluid obeying the ideal gas law), the specific internal energy *H* is given by $H = C_P T$, where C_P is the specific heat at constant pressure and T is the temperature. By assuming a polytropic relation between pressure and density ($P \propto \rho^{\gamma}$), where γ is the adiabatic index, and using the perfect gas law ($P = \rho RT$), the specific internal energy can be expressed as

$$H = C_P T = \frac{\gamma}{\gamma - 1} \frac{P}{\rho}$$
 2.4

After solving these four equations, the jump conditions for a one-dimensional shock wave can be expressed as follows:

$$\frac{T_2}{T_1} = \frac{\left(\gamma M_1^2 - \frac{\gamma - 1}{2}\right) \left(\frac{\gamma - 1}{2} M_1^2 + 1\right)}{\left(\frac{\gamma + 1}{2}\right)^2 M_1^2}$$
2.5

$$\frac{P_2}{P_1} = \frac{2\gamma M_1^2 - (\gamma - 1)}{\gamma + 1}$$
 2.6

$$\frac{\rho_2}{\rho_1} = \frac{M_1^2(\gamma+1)}{(\gamma-1)M_1^2+2}$$
 2.7

where:

 $M_1 = u_1 / a_1$ is the Mach number of the pre-shock flow,

 $a_1 = \sqrt{(\gamma P_1/\rho_1)}$ is the speed of sound in the pre-shock state,

Equations 2.5 to 2.7 are known as the Rankine-Hugoniot Jump equations for onedimensional shock waves. They are specifically applicable to calorically perfect gases, where the ratio of specific heat remains constant with changes in temperature. For instance, if we consider an inert monoatomic gas like Argon (Ar), these equations can accurately describe the gas behaviour up to temperatures of around 8300 K. However, at temperatures beyond this point, the presence of electronic excitation and ionization starts to alter the theoretical values predicted by these equations (Gaydon & Hurle 1963, Kumar *et al.* 2014).

2.3 Shock Tube and its working principle:

A shock tube is a device capable of generating shock waves with different intensities in a controlled and reproducible manner. Before going into the details of the shock tube working principles, we will discuss some historical aspects of shock tube research that happened across the globe. In the 17th century, Sir George Stokes reported about finite discontinuities in sound waves. French engineer Paul Vieille developed the first practical shock tube, the "shock apparatus" in the late 19th century (Gaydon & Hurle 1963). Vieille used this apparatus to study the detonation of explosives, and it laid the groundwork for further developments in shock wave research. In the early 20th century, Swedish engineer and physicist Gustav De Laval made significant contributions to the advancement of the shock tube. De Laval designed a shock tube to study engine supersonic flow and combustion processes. He successfully demonstrated the formation of shock waves in a controlled environment and furthered the understanding of gas dynamics (Gaydon & Hurle 1963, Kumar et al. 2014). One of the early pioneers in shock tube research was the Hungarian-American physicist Theodore von Kármán, who utilized shock tubes to study supersonic flows and combustion processes. His work and that of many others during this period significantly contributed to the development and applications of shock tubes (RANNE 1963). Soon after the 2nd world War, there was a growing interest in the development of shock tubes, driven by growing development in the field of gas dynamics, aerodynamics and space exploration (Gaydon & Hurle 1963, Kumar et al. 2014). In the 21st century, shock tube is being used in different science fields, including aerospace

engineering, combustion research, material science and chemistry, astrophysics, planetary science, and medical science (Kumar et al. 2014). Several shock tube types are used in different experimental setups and research applications. Some of the common types of shock tubes include:

- 1. Inert gas-driven shock tube: In this kind of shock tube high, pressure inert gas such as helium is used to generate shock waves.
- 2. Explosive-driven shock tube: In this setup, an explosive charge is placed at one end of the shock tube. When the explosive is detonated, it rapidly releases a large amount of energy, creating a high-pressure shock wave that travels through the tube.
- 3. Combustion driven shock tube: In this kind of shock tube, the high pressure required for the shock wave generation is created by a controlled combusting explosion using a mixture of helium, hydrogen and oxygen.
- 4. Free-Piston driven shock tube: Here heavy piston is used to generate the high pressure required for the shock generation.
- 5. Electrically driven Shock tube: In this type of shock tube, shock waves are generated by using electrical discharge heated gas. These shock tubes are diaphragm-less shock tubes and contain no high pressure chamber. Details of these different kinds of shock tubes used for different scientific and industrial applications can be found in (Kumar *et al.* 2014).

2.3.1 Working Principle of Shock Tube:

The shock tube consists of two sections: driver section which holds high pressure gas and driven section which usually kept at very low pressure. A diaphragm separates these two sections. A schematic diagram of a conventional shock tube is shown in **Fig 2.4(a)**. We can understand the different events which take place inside the shock tube during and after the shock formation with the help of a wave diagram as shown in **Fig 2.4(b)**.



Fig 2. 4: Shows a schematic diagram of a shock tube. This consists of a high pressure section known as driver section and a relatively large low pressure section known as the driven section, and these two sections are separated by a diaphragm. (b) The x-t diagram of the shock tube operation shows how different events take place inside the shock tube with time once the diaphragm ruptures. (c) Shows the variation of pressure inside the shock tube before and after the shock formation. (d) Shows the variation of the temp erature inside the shock tube before the shock formation and after the shock formation.

In shock tube theory, the high-pressure driven section is conventionally referred to as region 4. Whereas, the driven section is referred as region 1 (Gaydon & Hurle 1963, Kumar et al. 2014). Because of the continuous filling of high-pressure gas in region 4, at a time t=0 the diaphragm gets ruptured at a particular bursting pressure, referred to as P4. The sudden rupture of the diaphragm release of high-pressure gas into the low-pressure driven gas. And the high-pressure driver gas will start to expand with a particular speed in the driven section. This is a similar scenario to what we described as a motion of a piston in a gas medium in section 2.2. The expansion of high-pressure gas in the driven section will generate multiple compression waves. These compression waves will eventually coalesce to form a strong shock wave at a particular distance from the diaphragm, known as shock formation distance. The value of the shock formation distance depends on the diaphragm opening time, the more rapid the opening less the shock formation distance (Gaydon & Hurle 1963, Kumar et al. 2014). The shock formation length usually has values about 5 to 6 times to the internal diameter of the shock tube. As the shock wave travels through the driven section, it will keep increasing the driven gas's both pressure and temperature (Gaydon & Hurle 1963, Kumar et al. 2014). The shock processed driven section is referred as region 2 and the thermodynamic properties of the fluid parameters across the shock front between region 1 and 2 can be calculated using the R-H jump condition (eq 2.5 -2.7). Note that the shock wave is propagating with a speed much higher than the expansion speed of the high-pressure gas. The moving boundary between the expanding driver gas and the just shock-processed driven gas is called as contact surface, and it will be chasing the shock wave with a speed equal to the speed of sound in that medium (Gaydon & Hurle 1963, Kumar *et al.* 2014) as shown in **Fig 2.4(b)**. The region behind the contact surface is referred to as region 3. The pressure and velocity of the gas on both sides of the contact surface remains the same, but there will be a rapid gradient in the temperate between these two regions, as shown in **Fig 2.4(c-d)**.

When diaphragm ruptures a shock wave is generated and travels towards the pressure section to equalize the pressure in the system. For speeding up this process multiple expansion waves also propagates though the driver section, opposite to the direction of shock wave (Gaydon & Hurle 1963, Kumar *et al.* 2014) as shown in **Fig 2.4(b)**. Unlike shock waves these expansions wave travels with the local speed of sound and cools down the driver section (Gaydon & Hurle 1963, Kumar *et al.* 2014). There will be series of expansion waves propagating through the driver section and because of cooling the velocity of the nth expansion wave will be lesser than the velocity of the (n-1) th expansion wave (Gaydon & Hurle 1963, Kumar *et al.* 2014).

If the shock tube's driven section is closed, the primary shock wave will be reflected back from the end flange and travel back into the driven section, as shown in **Fig 2.4(b)**. The shock wave is now referred to as reflected shock, and the region processed by the reflected shock is referred as region 5. The driven gas which was dragged by the primary shock now becomes stagnant. The incident shock initially heated the driven gas, and the reflected shock will further rise the gas temperature, and pressure to an elevated level (Gaydon & Hurle 1963, Kumar *et al.* 2014). This high pressure and temperature state persists until the arrival of the contact surface and this persistence time is known as dwell time (Gaydon & Hurle 1963, Kumar *et al.* 2014), as shown in **Fig 2.4(a)**. The relation between the pressure and temperature of the drive gas across the reflected shock front can be expressed in terms of incident shock Mach number (M₁) and initial pressure and temperature of the driven gas. Considering that the velocity of the gas behind the reflected shock is zero, and utilizing eqns 2.5-2.7 and doing successive iteration for the different region we can reach to the set of mathematical relation between P_5 , P_1 and T_5 , T_1 (Gaydon & Hurle 1963, Kumar et al. 2014). These relations can be expressed as:

$$\frac{P_5}{P_1} = \left(\frac{2\gamma M_1^2 - (\gamma - 1)}{\gamma + 1}\right) \left[\frac{(3\gamma - 1)M_1^2 - 2(\gamma - 1)}{(\gamma - 1)M_1^2 + 2}\right]$$
2.8

$$\frac{T_5}{T_1} = \frac{\left[(2\gamma - 1)M_1^2 + (3 - \gamma)\right]\left[(3\gamma - 1)M_1^2 - 2(\gamma - 1)\right]}{(\gamma + 1)^2 M_1^2}$$
2.9

The Mach number can be measured experimentally and the details of shock velocity measurement technique can be found in Chapter 3. The two equations above also have some limitations, which are adapted from (Gaydon & Hurle 1963, Kumar *et al.* 2014):

- Validity for Perfect Gas: The jump equations are specifically applicable to a calorically perfect gas, where the ratio of specific heats (γ) remains constant with temperature changes. For real gases with varying γ, the jump equations may not accurately predict shock wave properties, especially at high temperatures and pressures.
- One-Dimensional Assumption: The jump equations are derived based on the assumption of one-dimensional shock waves. In reality, shock waves can be complex and multi-dimensional, and the jump equations might not fully capture the behavior of oblique or curved shock fronts.
- Shockwave Strength: The jump equations are suitable for moderate shockwave strengths. For extremely strong shockwaves, other effects such as ionization, dissociation, and radiation can significantly influence the shock wave properties, making the jump equations less accurate.
- Non-Ideal Effects: The jump equations do not consider non-ideal gas behavior, chemical reactions, or phase changes in the gas. In cases where these effects are significant, the jump equations may not provide accurate predictions.
- Limited Temperature Range: The jump equations are generally applicable up to a certain temperature range where the assumption of a perfect gas is reasonable. At very high temperatures, electronic excitation and ionization start to affect the gas properties, and the jump equations become less applicable.

• Shock Tube Geometry: The jump equations assume a straight, uniform shock tube. In practical shock tubes, various geometries and conditions can affect the shock wave dynamics, which may not be captured accurately by the jump equations.

2.3.2 A few Facts about the shock tube operation:

<u>Dependence of shock strength</u>: The strength of the shock wave generated in the shock tube depends on the pressure ratio on both sides of the diaphragm and the thermo-physical properties of the driver and the driver gas (Gaydon & Hurle 1963, Kumar *et al.* 2014). The strength of the shock wave is usually expressed in terms of Mach number. For a calorically perfect gas, the relation between the Mach number of the primary shock (M_1) and the pressure ratio on both side of the diaphragm can be expressed as eq:

$$\frac{P_4}{P_1} = \frac{2\gamma_1 M_1^2 - (\gamma_1 - 1)}{\gamma_1 + 1} \left[1 - \frac{\gamma_4 - 1}{\gamma_1 + 1} \cdot \frac{a_1}{a_4} \left(M_1 - \frac{1}{M_1} \right) \right]^{-\left(\frac{2\gamma_4}{\gamma_4 - 1}\right)}$$
2.10

Where γ_1, γ_4 are the ratio of specific heat of the driven and driver gas, respectively. In the above equation, we have control on the P_4 , and P_1 . A particular P_4 can be archived by using the suitable diaphragm and the pressure of the driven side can be controlled with the help of a vacuum pump. Now for a fixed P_4 to P_1 ratio eqn 2.10 reveals that the Mach number of the primary shock wave depends on the specific heat ratio and the speed of sound of the driver gas. The maximum intense shock formation is possible when the LHS of the eqn 2.10 become infinity. This can only be possible when

$$1-\frac{\gamma_4-1}{\gamma_1+1}\cdot\frac{a_1}{a_4}\left(M_1-\frac{1}{M_1}\right)\to 0$$

Further

$$M_1 \rightarrow \frac{\gamma_4 - 1}{\gamma_1 + 1} \cdot \frac{a_4}{a_1} \tag{2.11}$$

The above relation suggests that the strongest shock wave can be generated if we use a driver gas with very high speed of sound, and low specific heat ratio and a driven gas with relatively low speed of sound in it. If we recall the relation between the speed of sound at a particular pressure and temperature and the molecular weight of the gas, it shows inverse

square relation. This drives experimentalist to select light gases as a potential candidate of driver gas and relatively heavy gases as a driven gas (Gaydon & Hurle 1963, Kumar *et al.* 2014). Hydrogen is the best known candidate for a driver gas but dealing with hydrogen in high temperature can be hazardous. Thus the, helium is routinely used as a driver gas in shock tubes (Gaydon & Hurle 1963, Kumar *et al.* 2014).

Various other ways exist to increase the shock tube's strength. One such way is to heat the driver's gas. This will increase the sound speed in the driver gas and hence increase the shock strength (Gaydon & Hurle 1963, Kumar *et al.* 2014).

Shock tube length and dwell time: The dwell time in a shock tube is the duration of time that the test gas experiences the reflected shock wave (Gaydon & Hurle 1963, Kumar et al. 2014). A longer dwell time allows the gas to interact more extensively with the shock wave, leading to better equilibration and higher temperatures and pressures. The duration of the shock wave in a shock tube is mainly determined by the time it takes for the contact surface to reach the end station of the shock tube. Increasing the distance between the diaphragm and the end station can extend this time by creating a larger separation between the shock front and the contact surface (Gaydon & Hurle 1963, Kumar et al. 2014). However, simply increasing the shock tube length is insufficient to achieve a longer test time. The presence of the shock wave depends on the driving force behind it, which is provided by the highpressure driver gas. As the driver gas expands and its pressure drops below the pressure of the shock wave, the driving force diminishes. This occurs when the reflected rarefaction wave overtakes the contact surface (Gaydon & Hurle 1963, Kumar et al. 2014). The duration of the shock wave depends on the initial conditions and the dimensions of the shock tube. The test time can be controlled by carefully adjusting these parameters to achieve the desired experimental duration.

2.4 Astrophysical Shock:

Shock waves are ubiquitous in space. Stars are the main sources of shock waves in the ISM (McKee & Hollenbach 1980). Strong stellar winds excite and, ionize part of their surroundings and create a rapid pressure gradient in their neutral surroundings thereby generating shock waves (Spitzer Jr 1978). The other known sources of shock waves in the ISM are supernova explosions, cloud-cloud collisions, and expansion of HII regions (Spitzer Jr 1978). The strongest source of shock waves in the ISM are supernova explosions (McKee & Hollenbach 1980). Shock waves produced by the supernova remnants (SNR) can have velocity up to 10^4 km s⁻¹, and capable of generating X –rays (McKee & Hollenbach 1980).

Interstellar shocks can have wide ranges of parameters. Velocities of interstellar shocks range from 1 to 10^4 km s⁻¹ while the pre-shock density ranges from 10^{-2} to 10^7 cm⁻³ and the post-shock temperature may rise from 10^2 to 10^9 K (McKee & Hollenbach 1980). For dense clouds, shock velocities are typically few tens of km s⁻¹ and the density is around 10^4 to 10^6 cm⁻³. The strength of the interstellar shock can go as high as 10^3 times of the laboratory produced shock (McKee & Hollenbach 1980). Interstellar shock waves have magnetic field associate with it. The presence of a magnetic field influences both the configuration of the shock front and contributes to the determination of the shock wave's Mach number (McKee & Hollenbach 1980).

The interaction of the shock wave and dust gains in the ISM is a complex process. Based on its strength the shock wave can induce various kinds of physicochemical changes in the dust grains (Jones *et al.* 1996). **Fig 2.5** shows a pictorial representation of the propagation of a shock wave in the ISM and the associated phenomena which happened because of the interaction of the shock wave and the propagating medium. The details of such process can be as follows.



Fig 2. 5: shows the propagation of a shock wave in the interstellar space generated by a star placed at the centre of the figure. The strength of the shock wave is very high close to the star and the matter, especially dust present in that area marked in blue colour will be destroyed by phenomena such as shattering, sputtering, grain charging. Whereas, the shock wave will keep moving outwards and will keep damped away. At the outer envelope of the circumstellar shell the strength of the shock wave will be drastically reduced. This low velocity shock wave does not have sufficient energy to ionize or destroy the dust and molecules present there. Rather it will thermally process the materials and molecules present in that medium and chemically enrich the surrounding medium. The numbers in this figure are taken from the book 'The Physics and Chemistry of the Interstellar Medium' (Kwok 2007)

2.4.1 Sputtering of dust grains:

When a shock wave passes through the interstellar medium (ISM) or circumstellar medium (CSM), it can accelerate charged particles to high velocities, creating a population of high-speed ions and atoms. These fast ions and atoms can then impact dust grains present in the medium. When a high-speed ion collides with a dust grain, it transfers some of its energy to the surface atoms of the grain. If the transferred energy exceeds the binding energy of the surface atoms, those atoms can be sputtered, i.e., ejected from the grain into the surrounding medium (Seab & Shull 1983, McKee 1989, Tielens *et al.* 1994, Draine 2009, Jones 2005, Draine 1995, Jones & Nuth 2011, Zhu *et al.* 2019, Jones *et al.* 1996). Sputtering can lead to the destruction of dust grains in the ISM. It can initiate chemical reaction on the grain surface and enrich the chemical complexities in the surrounding medium (Draine 1995, Draine 2009). Sputtering can alter the composition and structure of dust grains, affecting the infrared and ultraviolet emission and absorption features observed in astrophysical environments (Jones *et al.* 1996).

2.4.2 Shattering of Dust grains:

Shattering is a process in which solids such as dust grains or particles are fragmented in to smaller pieces due to the applications of mechanical forces. In interstellar space, dust grains can be shattered in to small fragments when they are exposed to the high velocity shock waves (Jones *et al.* 1996). Dust grains in the ISM can collide with each other due to their relative velocities. These collisions can lead to the fragmentation of larger dust particles into smaller ones (Jones *et al.* 1996). Shattering contributes to the evolution of dust size distribution in the ISM. It produces a population of small dust grains that can have different properties and effects on various astrophysical processes, including extinction, scattering, and thermal emission (Jones *et al.* 1996).

2.4.3 Grain Charging in shock waves:

When shock waves propagate in the ISM, based on its strength it can ionize atoms and molecules present in the medium and lead up to the formation of plasma. (Jones et al. 1996, McKee & Hollenbach 1980). The interaction of the dust grains presents in the medium with plasma can lead to the charging of the duat grains (McKee & Hollenbach 1980). The charging of dust grains in shock waves has significant implications for various astrophysical phenomena, including the coupling between dust and gas, the dynamics of dusty plasmas, and the role of dust in radiation and energy transfer processes. It also affects the behavior of dust grains in magnetic fields, their alignment with magnetic field lines, and their contribution to polarization of starlight (Draine & Hensley 2013).

2.4.4 Direct vaporization of dust grains:

High intensity shocks in the ISM can directly vaporize dust grains leading to its complete destruction and this process in turn maintains a balance the between gas to dust ratio in the ISM (McKee & Hollenbach 1980). The vaporized dust releases its constituent atoms and molecules into the surrounding gas. This enrichment can contribute to the chemical evolution of the interstellar medium, providing building blocks for the formation of new stars and planets (McKee & Hollenbach 1980).

2.4.5 Low velocity Shocks in the ISM and its importance:

Observations suggest that early type stars can also drive relatively low-velocity shock waves into the ISM with velocities < 10 km s⁻¹ (Spitzer Jr 1978). These low-velocity shock waves are also known to be present in the outer envelope of red giant stars (Ludwig & Kučinskas 2012). These low-velocity shock waves do not have sufficient energy to ionize the gas medium through which they propagate; they thermally process the molecules and dust present in the medium and enrich the medium chemically (Rudnitskij 1997). Extensive research by authors such as Jones et al. (1996) and Guilliet et al. (2011) has focused on studying the evolution of molecules and dust under high-velocity interstellar shocks. However, understanding dust particle behaviour when exposed to low-velocity interstellar shocks (3 < M < 10, where M represents the Mach number) is still in its early stages. To shed light on the formation and evolution of interstellar dust grains in the lowvelocity ISM shock regime, it is crucial to conduct rigorous laboratory experiments using various interstellar dust analogue precursors.

2.5 Shock tube and its applications to Astrochemistry:

Low-velocity shock waves can be routinely produced in the laboratory using shock tubes. Shock tubes are capable of rapid uniform heating, followed by very fast quenching of the processed materials. This provides an excellent opportunity for the laboratory astrochemist to study the condensation and growth of dust grains from the vapour phase (Carmer & Frenklach 1989, Frenklach et al. 1989). Shock tube also offers the advantage of easily achieving high-temperature conditions, which are often challenging to attain in other experimental setups like conventional heat reactors (Bhaskaran and Roth. 2002). Additionally, shock tubes provide a cleaner and more controlled environment, making them ideal for conducting chemical studies (Bhaskaran and Roth. 2002). To the best of our knowledge, one of the first experiments devoted to the field of astrochemistry is associated with the study of the formation of SiC from its gas phase precursor using a shock tube, was carried out by (Carmer & Frenklach 1989). A gaseous mixture of SiH₄, CH₄, H₂ and Ar was shocked with the reflected shock temperature ranging from 800 K to 3650 K. TEM analysis of the shock-processed residue has shown the presence of Cubic SiC having particle size ~ 20-50 nm. No signature of SiC has been observed below the reflected shock temperature of 800 K. This experiment showed that SiC formation could be extreme, and

its formation rate can be increased with the increase in reflected shock temperature. Its growth rate can be as high as $10^6 \,\mu m \, h^{-1}$.

Biennier *et al.* (2017) studied the energetic processing of fullerenes by employing a shock tube. Shock processing of C_{60} in H₂ was investigated up to a reflection temperature of ~3900 K. The processed solid residues were collected and analyzed using a XRD, IR, Raman spectroscopy, TEM imaging, and scanning electron microscopy. The gaseous product was analyzed using gas chromatography and cavity ring-down spectroscopy. The nature of the solid-state residue is amorphous, with some aliphatic bonds observed. In the gas phase, the detected molecules were CH₄, C₂H₂, C₂H₄, and C₂H₆. Results from this experiment demonstrated the top-down formation of simple hydrocarbon molecules and amorphous carbon dust.

The above discussion explains the capabilities and importance of shock tubes in the field of astrochemistry. In this thesis we tried to utilize the shock tube as a tool to mimic low velocity ISM shock waves in a controlled environment, and tried to understand the formation and evolution of cosmic dust grain analogues behind the shock front. In the next chapter, a detailed discussion on the shock tube set up used in this thesis will be discussed along with various analysis techniques that we used to examine both the shocked and the unshocked dust analogues.

Chapter 3 Experimental Methodology

Chapter overview:

This chapter describes the instrument used to carry out shock processing of interstellar dust analogues and various analysis techniques used to characterize both pre and post-shocked samples. All the experiments described in this thesis were conducted using the High-Intensity Shock Tube for Astrochemistry (HISTA) housed at Physical Research Laboratory, Ahmedabad, India. Much emphasis has been given on HISTA's specifications, sample depositions and the extraction technique, measurement of shock parameters such as Mach number, and the calculation of the reflection shock temperature and quenching rate. Furthermore, this thesis chapter covers various analysis techniques utilized to explore the pre- and post-shocked samples. These techniques include ATR-FTIR Spectroscopy, Raman spectroscopy, X-ray Diffraction (XRD), Vibrating Sample Magnetometry (VSM), Field Emission Scanning Electron Microscopy (FE-SEM), and High-Resolution Transmission Electron Microscopy (HR-TEM). The applications and advantages of each technique are discussed, highlighting their contributions to the characterization of the shock-processed samples.

3.1 The High Intensity Shock Tube for Astrochemistry (HISTA):

The High Intensity Shock Tube for Astrochemistry (HISTA) is a piston less single pulse gas driven shock tube dedicated for the astrochemistry research. This shock tube is capable to mimic the low velocity interstellar shocks, especially shocks observed around Mira variable, pulsation driven shock from AGB stars and impact induced shocks observed in different airless solar system bodies (Carmer & Frenklach 1989, Biennier *et al.* 2017). A schematic diagram of the HISTA is shown in Fig 3.1. It is a 7 m long, gas-driven shock tube that has two different sections separated by a metal (Aluminium) diaphragm. The high-pressure (driver) section is 2 m long whereas the low-pressure (driven) section is 5 m long, and can be extended by another 3 m. Both ends of the HISTA are usually closed using thick metal (steel) flanges, serving as a shock reflector and shock absorber. The entire shock tube is made of stainless steel and mounted horizontally with the help of metallic mount. The

inner diameter of the HISTA is around 82 mm and the outer diameter is around 115 mm. The driven section of the HISTA is equipped with two piezoelectric pressure sensors separated by 30 cm. Also, a pumping system is connected to the driven section and we load the sample at the end of the driven section and spread across the lower part of the inner wall as shown in **Fig 3.2**.



Fig 3. 1: The experimental setup shown above is a schematic of the High-Intensity Shock Tube for Astrochemistry (HISTA) at the Physical Research Laboratory (PRL), Ahmedabad. The driver section contains high-pressure helium (He), while the driven section is filled with low-pressure argon (Ar). The sample to be tested is loaded at the end of the shock tube, indicated in black. Two Piezo electric dynamic-pressure sensors, labelled as Sensor 1 and Sensor 2, are positioned 30 cm apart at the end of the driven section to measure shock speed (A. Roy et al. 2022, A. Roy et al. 2022 a).

3.2 Experimental procedure to conduct Shock Experiment:

The inner walls of HISTA is cleaned with ethanol; C_2H_5OH before every experiment to reduce the chances of contamination from any previously performed experiment. About 0.1 g of the powder (high purity) sample is placed at the end of the driven section inner wall and spread out radially on the inner surface of the tube as shown in **Fig 3.2.** Immediately afterwards the metal end flanges at both ends of HISTA were closed and the shock tube was pumped up the order of 10^{-2} m bar. Afterward, the driven section undergoes purging of argon (Ar) and is then filled with ultra-high purity argon (Ar) at a desired pressure, estimated before the experiment. In this thesis we used Ar pressure of 0.1 bar for all the experiments. The Al diaphragm which separates the driven section from the driver section has a crucial role in the generation of shock waves. These Al diaphragms have different grove depth, with a particular grove depth being selected to achieve the required shock strength and reflected shock temperature. Since we aimed to generate a very high temperature we used an Al diaphragm with the minimum groove depth (0.5 mm). Like in the driven section, the driver section also pumped down to the order of 0.01 bar using a rotary pump and purged using He. Following this we filled the driver section with very high pressure He with a very high flow rate, ~ 1.69 E-3 m^3s^{-1} . This ultimately led to the rupture of the Al diaphragm. The sudden exposure of the high pressure He to the low pressure Ar generates a shock wave which propagates through the driven section at a speed greater than the speed of sound in Ar at room temperature. This shock wave is called the primary shock wave which will be reflected back from the metal end flange at the end of the driven section and therefore called as reflected shock. The sample placed at the end of the driven section inner walls is usually lifted by the primary shock whereas it is processed by the reflected shock. Two PCB PIEZOTRONICS dynamicpressure sensors (Voltage sensitivity 0.4949 mV/PSI, Bias voltage 10.71 V) are positioned at the end of the driven section. Their separation is around 30 cm and they are connected to a digital storage oscilloscope where the pressure signal is traced for the shock velocity measurement. High intensity shocks may induce physio-chemical changes in the sample and it is very likely that a significant amount of the powder sample would have transformed into the gas phase after the processing. To avoid any loss of processed sample we left the entire shocked gas alone for a couple of hours so as to settle the residual sample inside the shock tube. During the settle down period, the internal static pressure of HISTA was around 18 bar, we then slowly removed the shocked gas to the atmosphere using a leak valve. While doing this we allow the shocked gas to pass through a Teflon filter where sub-micron size processed particles were trapped, as shown in Fig 3.2. Once the shock tube's internal pressure became equal to the atmospheric pressure we opened the end flange of the driven section and collected the rest of the processed samples in the vicinity to the end flange area. The amount of processed sample collected was approximately 30% of the original mass. Therefore, a significant amount of sample was lost while removing the shocked processed gas. Details of the different samples used, strength of shock wave, and the processing temperature can be found in Table 3.1.

Table 3.1: Details of different sample used in this thesis along with their particle size, amount, driver gas pressure, driven has pressure, shock Mach number, and reflected shock temperature.

Sample	Particle	Amount	Driver	Driven	Mach	Reflected
Details	Size	(gm)	Gas (He)	gas (Ar)	Number	Shock
			pressure	pressure	(M)	Temperature
			(bar)			(K)
Amorphous	< 100 nm	0.1	68	0.1	5.6	~ 7300
Carbon						
(a-C)						
a-C in H ₂	< 100 nm	0.1	67.5	0.15 (0.1	5.3	~ 6400
				bar Ar +		
				0.05 bar		
				H ₂)		
a-C + Si	< 100 nm	0.1	67	0.15 (0.1	5.3	~ 6400
(2:1) in H ₂	for both			bar Ar +		
				0.05 bar		
				H ₂)		
Ferrocene	< 100 nm	0.1	68.6	0.1	5.6	~ 7300
Mg+ SiO ₂	< 100 nm	0.1	67	0.1	5.6	~ 7300
(M1) (1:1)						
M1+Fe	µm size	0.1	68	0.1	5.6	~ 7300
(M2) (1:1)	iron					
	particle					
Fe+ SiO ₂	µm size	0.1	68	0.1	5.6	~ 7300
(M3)	iron					
	particle					



Fig 3. 2: (a) shows the sample spread in the lower part of the driven section inner wall. (b) shock processed sample collected on the Teflon while letting the high pressure gas out. (c) shock processed sample deposited on the end flange.

3.3 Measurement and calculation of various shock parameters:

In the shock tube, most of the thermodynamic parameters are usually expressed in terms of the Mach number (M). As explained in the previous section, two piezoelectric pressure sensors provide the pressure response created because of the arrival of the incident shock, and the pressure response curve is recorded in a digital oscilloscope. A typical shock pressure response curve is shown in **Fig 3.3**.

The velocity of the shock wave (V_s) is calculated by determining the time taken (Δt) for the shock wave to travel the distance (Δx) between the pressure sensors, using the recorded pressure signal as shown in **Fig 3.3**. Once the shock velocity is calculated, one can calculate the Mach number of the shock wave using the following relation:

Mach Number (Ms)
$$=\frac{v_s}{a}$$
 3.1

Where a is the local speed of sound. By employing the calculated value Ms in the R-H Jump equation one can determine the reflected shock temperature (T_5) and the reflected shock pressure (P_5) as described in **Chapter 2**. In the shock tube, a direct measurement of the reflected shock temperature is very challenging as the high temperature and pressure state persists only for around ~ 2 ms. Hence we try to estimate the reflected shock temperature using the R-H jump equation. The estimated reflected shock

temperature obtained using the R-H jump equation may have an error of up to 5-6 % of the calculated value. A platinum resistance thermometer can be employed close to the driven section end flange to measure the heat conversion rate. As discussed in **Chapter** 2, shock parameters such as P_5 , T_5 depends on both Ms and ratio of the specific heat γ of the gas present in driven section. The strength of the shock wave has also depended on the pressure ratio of driver to the driven side (P_4/P_1) , and the groove depth of the Al diaphragm and, play a key role in the determination of the bursting pressure (Gaydon and Hurle. 1963). In this thesis we used an Al diaphragm with 2 mm thickness with a grove depth of 0.5 mm. This configuration is capable of producing shock Mach number, Ms= 5.6, bursting pressure $P_4 \sim 68.8$ bar where $P_1 \sim 0.1$ bar, and $T_5 \sim 7300$ K. By changing the Al diaphragm groove depth, and driven gas such as Xe, Kr, and driven gas pressure, shock waves with various strengths can be obtained. To date, HISTA is capable of producing a wide range of reflected shock temperatures ranging from 3000 K to 16000 K using different groove depths and different driven gases with different γ values, respectively. In a shock tube experiment, the heating and cooling rate plays a key role in the conversion process. In HISTA we reached 7300 K reflected shock temperature from the room temperature in less than a second suggesting rapid heating of the Ar with a heating rate ~ 10^6 K s⁻¹. As discussed above, the high temperature and pressure condition persists about 2 ms. Soon after that the shock phenomena started to decay via rapid cooling. The cooling rate can be calculated by considering isentropic cooling as suggested by (Hall & Herrin 1976) and it is around 10⁵ K s⁻¹ for the shock wave with M ~ 5.6 and reflected shock temperature ~ 7300 K.



Fig 3. 3: The response curve from the two piezoelectric pressure sensors placed at the end of the shock tube indicates the arrival of the incident shock (inset) and the reflected shock, as recorded using a digital storage oscilloscope (Roy et al. 2022a).

3.3 Precautions:

Safety is a crucial aspect of shock tube operation to ensure the protection of personnel, equipment, and the environment. Some important safety aspects that were incorporated include:

- Pressure and Vacuum Safety: Properly rated pressure vessels, vacuum pumps, and relief valves should be used to handle the high-pressure and vacuum conditions in the shock tube. Regular inspection and maintenance of pressure vessels are essential to prevent any leaks or failures.
- 2. Gas Handling: Proper handling and storage of gases, especially high-pressure gases, are critical to avoid accidents. Adequate ventilation and gas monitoring systems should be in place to detect any leaks or abnormal gas concentrations.

- 3. Electrical Safety: Electrical components, such as high-voltage power supplies and instrumentation, must be properly insulated and grounded to prevent electrical hazards.
- 4. Personal Protective Equipment (PPE): Operators and researchers involved in shock tube experiments should wear appropriate PPE, including safety goggles, lab coats, gloves, and hearing protection, depending on the specific experimental conditions.
- Emergency Response Plan: An emergency response plan should be established and communicated to all personnel involved in the experiment. It should include procedures for handling emergencies such as gas leaks, equipment failures, or accidents.
- 6. Training and Awareness: All personnel operating or working near the shock tube should receive proper training on the equipment and safety procedures. Regular safety briefings and reminders help maintain safety awareness.
- 7. Controlled Environment: Shock tube experiments should be conducted in controlled environments with restricted access to authorized personnel only.
- 8. Safety Interlocks: Implementing safety interlocks and emergency shut-off systems can help prevent accidents by automatically stopping the experiment if certain safety parameters are breached.
- 9. Risk Assessment: Before starting any experiment, a thorough risk assessment should be conducted to identify potential hazards and implement appropriate safety measures.
- 10. Safety Regulations and Compliance: Ensure compliance with relevant safety regulations, standards, and guidelines to create a safe working environment.

3.4 Sample Analysis Techniques:

The collected, shocked solid samples were examined under ambient conditions using different experimental techniques such as ATR-FTIR Spectroscopy, Raman Spectroscopy, X-ray Diffraction analysis, Vibrating Sample Magnetometry (VSM) Field Emission Scanning Electron Microscopy (FE-SEM), High-Resolution Transmission Electron Microscopy (HR-TEM). Details of these above mention sample analysis is as follows:

3.4.1 ATR-FTIR Spectroscopy:

Attenuated Total Reflectance Fourier Transform Infrared (ATR FTIR) spectroscopy is a valuable analytical tool for studying carbonaceous molecules. It provides detailed information about the molecular structure, functional groups, and chemical composition of carbon-containing, and silicate compounds. In ATR FTIR spectroscopy, a beam of infrared light is directed onto the surface of the sample in contact with an ATR crystal. As the infrared light interacts with the sample, certain frequencies are absorbed by the molecule, causing molecular vibrations. These vibrations produce characteristic absorption bands in the infrared spectrum, which can be used to identify the types of bonds present in the sample. The non-destructive nature of ATR FTIR spectroscopy makes it an ideal technique for analysing carbonaceous molecules in their native form, without the need for extensive sample preparation. Note that our pre and post shocked sample are always in powder form, so ATR spectroscopy is very useful for the powder sample as suggested by Chu and Li (Chu & Li 2006).

In this thesis the ATR-FTIR spectroscopy of the shocked and unshocked sample was carried out using a diamond attenuated total reflectance module attached to the Nicolet IS50 FTIR spectrometer. Using a Polaris IR source (9600 – 10 cm⁻¹), in conjunction with a solid substrate beam splitter (> 1000 – 10 cm⁻¹), and a DLaTGS-KBr detector (12500 – 350 cm⁻¹), we retrieved the MIR to FIR (up to 35 μ m) spectra of the sample. Also, throughout spectra collection, the spectrometer's resolution was 2 cm⁻¹, the acquisition time was 1 minute 32 secs, and the pressure applied to the sample during the analysis was approximately 60 lbs.

3.4.2 Raman Spectroscopy:

Like IR spectroscopy, Raman spectroscopy is also a non-destructive technique for sample analysis and is particularly useful for those molecules which are not IR active such as hydrogen free amorphous carbon (Ferrari & Robertson 2004). In Raman spectroscopy, a monochromatic laser light is directed onto the sample, and the scattered light is collected and analysed. The frequency shifts of the scattered light (Raman shift) is caused by the interaction of the incident light with the molecular vibrations and lattice vibrations of the sample. This shift is unique to the specific molecular bonds and crystal structures present in the material, allowing for detailed identification and characterization (Ferrari & Robertson 2004). For carbonaceous molecules, Raman spectroscopy is particularly useful

in investigating the presence of carbon-carbon bonds, aromatic rings, double bonds, and other functional groups. It can distinguish between different forms of carbon, such as amorphous carbon, graphite, and carbon nanotubes, based on their characteristic Raman spectra (Ferrari & Robertson 2004).

In this thesis, we utilized the LabRAM HR (UV) Raman spectrometer, which offers exceptional spectroscopic resolution and a wide wavelength range, providing a combination of excellent performance and versatility. The LabRAM HR enables efficient collection of Raman images over large areas through its X, Y, and Z mapping features, with rapid acquisition times in seconds to minutes. For Raman spectroscopy, we prepared the pre and post-shocked samples on a glass plate, and then exposed the samples to a 532 nm laser for irradiation. The Raman spectrometer recorded the scattered light from the samples, allowing us to analyse the molecular vibrations and obtain valuable information about the sample's composition, structure, and changes induced by shock processing.

3.4. 3 X-Ray Diffraction (XRD) Analysis:

X-ray Diffraction (XRD) is a powerful and widely used technique in the analysis of powder samples due to its importance in various scientific and industrial applications. One of the primary applications of XRD is phase identification. It allows researchers to determine the different crystalline phases present in a sample, even at trace levels. XRD is also vital in studying crystal structure. It provides precise data about the arrangement of atoms in the crystal lattice, helping researchers understand the material's properties, behaviour, and potential applications. It also helps us to study the Polymorphism present in the sample.

In this thesis we used the D8 DISCOVER X-ray diffractometer by Bruker which offers a versatile platform with various features. It is capable of performing Powder X-ray Diffraction (XRD) and Thin-Film XRD, making it suitable for a wide range of applications. Additionally, it includes Small Angle XRD capability for analysing biological samples. One of its notable capabilities is high-temperature XRD, with a temperature range from room temperature up to 1200 degrees Celsius, enabling investigations of materials at elevated temperatures. The instrument is particularly useful for determining lattice parameters, phase identity, and phase purity of samples, as well as providing insights into crystallinity, crystal structure, and percent phase composition. For the indexing of the different peaks in the XRD pattern we compared our experimental data with the standard
data available in the Crystallographic Open Database (COD). Unlike other well-known commercial crystallographic data base COD is an open access data base. The COD provides crystallographic data, including atomic coordinates, unit cell parameters, symmetry information, and other relevant data necessary for studying the structure of crystals. Researchers can access this data to analyse crystal structures, perform theoretical calculations, and gain insights into the properties and behaviour of various materials (Gražulis *et al.* 2011).

3.4.4 Field Emission Scanning Electron Microscopy (FE-SEM):

FE-SEM (Field Emission Scanning Electron Microscopy) analysis plays a crucial role in the comprehensive characterization of powder samples, carbon nano materials (Chu & Li 2006) and silicon based materials (Colangeli et al. 2003). Its high-resolution imaging capabilities allow researchers to visualize the morphology, size, and shape of individual particles within the sample. The FE-SEM provides valuable insights into the surface topography, enabling the observation of microstructural features, such as cracks, fractures, and agglomeration, that could influence the material's properties. Moreover, the ability to perform elemental analysis through Energy Dispersive X-ray Spectroscopy (EDS) complements the imaging, providing information about the chemical composition and elemental distribution within the particles.

In this thesis we used the JSM7600F microscope by Jeol which is a highly versatile instrument equipped with secondary and back-scattered electron modes, offering valuable insights into various sample characteristics. Its resolution capabilities of 1.0 nm (at 15 kV) and 1.5 nm (at 1 kV) make it suitable for studying particle morphology, size, and distribution. The microscope also incorporates Energy Dispersive X-ray Spectroscopy (EDX) through the Oxford INCA Energy 250 EDS system, enabling elemental analysis of the samples. With a magnification range from 25x to an impressive 1,000,000x, it allows for detailed investigations of micro-cracks, fractures, thin-film thickness, and oxide layers.

3.4.5 High-Resolution Transmission Electron Microscopy (HR-TEM) technique:

High-Resolution Transmission Electron Microscopy (HR-TEM) analysis plays a crucial role in the study of carbon nanostructures and mineral samples, offering unprecedented insights into their structural and compositional characteristics at the atomic scale. For carbon nanostructures, HR-TEM allows direct visualization of their lattice

arrangements, crystal defects, and grain boundaries, enabling a comprehensive understanding of their unique electronic, mechanical, and thermal properties (Chu & Li 2006). Similarly, HR-TEM analysis of mineral samples provides invaluable information about crystallographic orientations, phase identification, and the presence of nanoinclusions, offering fundamental insights into their geological evolution and potential industrial uses (Xing *et al.* 2023). Furthermore, HR-TEM combined with elemental analysis techniques, such as electron energy-loss spectroscopy (EELS) and energydispersive X-ray spectroscopy (EDS), enables the identification and quantification of elemental compositions within these samples, facilitating comprehensive material characterization.

HR-TEM analysis of the shocked processed samples was carried out using Titan Themis 300 S/TEM from Thermo. The samples were ultra-sonicated in ethyl alcohol for 15 minutes, then drop cast on a quantefoil grid and allowed to dry in a chemically inserted atmosphere overnight. Before the imaging analysis started, these drop casted grids were plasma cleaned using Ar-O₂ plasma to reduce any changes of further contamination. Throughout the analysis, the HR-TEM was operated at 300 KeV operating voltage.

Chapter 4 Shock processing of Amorphous Carbon nanodust

Chapter overview:

This chapter describes the experimental results obtained from the shock processing (5.6 M, 7000 K) of amorphous carbon nanopowder (particle size < 100 nm). Shock processing was conducted using HISTA as described in the previous chapter, and the pre and post shocked samples were analysed using techniques like Raman spectroscopy and HR-TEM analysis. Results from this analysis: We have found compelling evidence for the formation of carbon nanotubes, graphene, and various other carbon nanostructures induced by the shock. Our results show that shocks in the interstellar medium can provide important chemical pathways for the formation of fullerenes and suggests that other carbonaceous structures may be present as well.

4.1 Introduction:

Carbon because of its electronic structure, can formulate several types of bonds and allotropes such as diamond, graphite, carbon chains, PAHs, fullerenes, graphene, and carbon nanotubes. In the ranking of elements in the Universe, carbon is the 4th most abundant after H, He and O. To date, carbon signatures have been detected in different parts of Interstellar medium (ISM), Circumstellar Medium (CSM), in our Solar system as well as in the galactic and extragalactic environments. Interstellar carbonaceous dust manifests its presence through various spectroscopic features in different wavelengths, and their morphology, internal structure, and the nature of chemical bonds influence their spectral properties. In the UV, the presence of carbon-containing dust can be traced by studying the interstellar extinction feature around 217.5 nm (Fitzpatrick & Massa 1986),(Draine 1989). The UV absorption feature around 240 to 250 nm observed in different H-poor objects is also attributed to the π to π^* electronic transition of hydrogenpoor carbonaceous dust (Hecht 1991), (Drilling *et al.* 1997). Signatures of H-poor

amorphous carbon dust are also found around many carbon stars by studying the featureless continuum infrared emission (Gauba & Parthasarathy 2004). The extended red emission feature peaked at 650 and 700 nm (ERE), has been detected around different interstellar objects (Cohen et al. 1975), (Lai et al. 2017), (Vijh et al. 2004a), (Witt 2013). The UV-induced luminescence of Hydrogenated Amorphous Carbon (HAC) has also been suggested for this emission feature. A recent experimental result by (Sarre 2019) has shown that graphene oxide nanoparticles could also contribute to the ERE features. Although graphene has not been detected in interstellar space, the presence of C₂₄ planer sheets is claimed in the planetary nebula (García-Hernández et al. 2011a). In addition a recent experiment that irradiated a benzonitrile ice film at 4K using 9 eV photons, followed by gradual warming to room temperature demonstrated the formation of nitrogen doped graphene sheets, suggesting a possible pathway for the formation of graphene in the ISM (Sivaraman et a. 2023). The prominent infrared plateau emission features at 6 to 9 µm and the 3.4 µm absorption features have long been associated with hydrocarbon dust particles. While the presence polycyclic aromatic hydrocarbon (PAH) molecules are often attributed to these infrared features, an alternative hypothesis has been proposed. It suggests that Mixed Aliphatic Aromatic Organic Nanoparticles (MAONs), which consist of various combinations of sp² and sp³ bonded hydrocarbon networks, can also account for the observed emission/absorption features (Kwok & Zhang 2011). Fullerene is the most recently detected component of cosmic carbon dust. Its infrared active features around 7.0, 8.5, 17.4, 18.5 µm have been detected around planetary nebula (Cami et al. 2010), reflection nebula (Sellgren et al. 2010), (Peeters et al. 2017), diffuse ISM (Berné et al. 2017), and around young stellar objects like Herbig Ae/Be stars (Roberts et al. 2012).

The formation pathways of these carbon nanostructures is still not clear. There are two distinct formation pathways: bottom-up formation starting from smaller units or topdown formation where the process starts from larger dust grains or molecules. Bottomup formation routes are the main pathway when using laser ablation (Kroto et al. 1985b), laser-induced pyrolysis, and gas-phase condensation of hydrocarbon (Jäger et al. 2009), or arc discharges (Krätschmer et al. 1990, Iijima 1991), and plasma chemistry (Contreras & Salama 2013). In such experiments, Closed Network Growth (CNG) leads to the bottom-up formation of fullerenes by insertion of C and C₂ in existing smaller cages (Dunk et al. 2012). Similar bottom-up routes lead to the formation of Carbon Nanotubes (CNTs) (Liu et al. 2009). The self-assembly of atomic carbon C and C₂ units into higherorder clusters has been theoretically investigated by (Irle et al. 2006, Cruz-Silva et al. 2016). While bottom-up formation routes deals the synthesis of carbonaceous dust from the atomistic level, the top-down formation route synthesizes carbonaceous dust by breaking preexisting larger molecules like PAH (Berné & Tielens 2012, Zhen et al. 2014, Berné et al. 2015) or Graphene (Chuvilin et al. 2010) or HAC (Scott et al. 1997); (Micelotta et al. 2012). Experimentally, (Chuvilin et al. 2010), showed that bombardment of graphene by high-energy electrons (more than 85 KeV) leads to the formation of fullerenes, essentially by removing a carbon atom from a hexagonal ring; the resulting pentagonal ring causes the initial curvature and in short timescales, fullerene cages are the result. When starting from large PAHs, a similar process can be induced by using UV photons that first strip the PAHs of their hydrogen atoms; the resulting bare carbon cluster then isomerizes into a cage structure. Such processes were first speculated to be possible in the ISM (Berné & Tielens 2012), and were then shown experimentally to take place as well (Zhen et al. 2014). Similar UV photo processing of HAC grains also showed the formation of fullerene and others carbon nanoclusters (Scott et al. 1997).

To date, our knowledge about the chemical evolution of (H-poor) amorphous carbon in interstellar space is limited (Dartois 2019) compared to the evolution of HAC dust (Jones et al. 2013, Chiar et al. 2013). Amorphous carbon dust can be detected through their featureless blackbody-like continuum emission spectrum near the ejecta of carbon stars (Martin & Rogers 1987, Volk et al. 2001, Gauba & Parthasarathy 2004, Groenewegen et al. 2009, Chen et al. 2010). García-Hernández et al. (García-Hernández et al. 2010, García-Hernández et al. 2011b) observed the presence of fullerenes in various Planetary Nebula (PNe) along with PAHs. Based on their observations and the possible presence of shock waves in young PNe, they proposed shock induced decomposition of HAC as a possible mechanism for C_{60} formation in young PNe. However, the PNe Tc -1 and Lin-49, where the C₆₀ and C₇₀ (only in Tc-1) were observed, have at most very weak PAH emission (Cami et al. 2010, Otsuka et al. 2016). Therefore, apart from the known pathways from hydrocarbons or PAHs to C₆₀ and C₇₀, it is of interest to consider whether amorphous carbon dust (possibly in hydrogen deficient environments) can evolve to create carbon nanostructures by shock processing. It was experimentally shown that laser ablation of graphite can make C_{60} (Kroto et al. 1985b).

However, amorphous carbon dust undergoing shock processing is different from laser ablation of graphite (which is crystalline).

Owing to the importance of low-velocity shock waves in interstellar chemistry, we have mainly explored low-velocity (1-2 km s-1) shock processing of amorphous carbon powder in this work. In the low-velocity shock wave region, thermal processing dominates over grain destruction processes like sputtering and vaporization (Rudnitskij 1997). A high-intensity shock tube can be used to recreate shock conditions in the laboratory akin to those in the ISM to study dust processing (Biennier et al. 2017). However, to the best of our knowledge, experimental studies on the evolution of carbon nanopowder in a hydrogen-deficient environment) are limited. Here, we experimentally investigate the shock (M ~ 5.6) induced thermal processing of carbon nanopowder in a hydrogen-deficient where temperature reaches up to ~ 7300 K for about 2 ms. Post shock solid residues have been collected and investigated using Raman spectroscopy and High Resolution-Transmission Electron Microscope (HR-TEM).

4.2 Experimental Methodology:

Shock processing of the amorphous carbon nanopowder (particle size < 100 nm) was carried out using the HISTA. Helium was used as the driver gas, argon used as a driven gas. The experimental parameters employed are provided in **Table 4.1.** Further information regarding the experimental procedure, the technique employed to measure the shock speed from the pressure response curve, and the estimation of the reflected shock temperature (T_5) using the R-H jump equation can be found in **Chapter 3** of this thesis. Following the shock processing, solid residues were collected and analyzed using various techniques, including Raman Spectroscopy and, HR-TEM imaging techniques.

Table	4. 1: Det	ails of the	sample u	sed in this	s chapter	along w	vith its p	rocessing	temperature,
Mach	number	of the sho	ck wave, l	bursting p	pressure,	and dri	ven sect	ion pressi	ıre.

Amount	0.1 g
Driven Pressure (P ₁)	0.1 bar of Ar
Bursting Pressure (P ₄)	68.5 bar
Mach Number (M)	~ 5.3
Reflected Shock Temp (T ₅)	~ 7300 K

4.3 Results and Discussion:

4.3.1 Raman Spectroscopy:

Carbon nanopowder which had been shocked to temperatures of a few thousand Kelvin was collected from the end of the shock tube where the samples were initially loaded. In addition, we also collected samples using a Teflon filter while letting the high-pressure gas out of the shock tube. The samples collected using a filter, and at the end of the shock tube, all appeared to be blackish, similar in color to the pre-shock sample. We loaded the samples onto a glass plate for Raman Spectroscopy. The Raman spectra of the unshocked samples show the well-known D and G bands (Tuinstra & Koenig 1970) at 1350 cm⁻¹ and 1598 cm⁻¹ respectively. The G band is associated with the doubly degenerate E_{2g} mode of the carbon atoms in the hexagonal lattice of graphene. This mode involves the in-plane stretching of the carbon-carbon bonds in the sp² hybridized carbon atoms (Ferrari & Basko 2013b). The D band arises due to defects and disorder in the carbon lattice. It is associated with the breathing mode of sp^2 carbon atoms in rings with six-membered hexagons and pentagons. The presence of defects, such as vacancies, adatoms, or grain boundaries, leads to the activation of this mode (Ferrari & Basko 2013b). In the case of shocked sample these bands are shifted to 1348 cm⁻¹ and 1585 cm⁻¹, and additionally, reveal broad bands around 72 cm⁻¹ (extending up to 130 cm⁻¹) and 2668 cm⁻¹ as shown in Fig 4. 1. The I(D)/I(G) ratio of both shocked and unshocked samples is measured by taking the ratio of the band area under the D and G bands as suggested by (Cançado et al. 2007). For the shocked sample, the ratio is around 1.50 and for the unshocked sample it is 1.62. A higher ratio shows a less crystalline sample. As the I(D)/I(G) ratio is inversely related to the crystallite size (Tuinstra & Koenig 1970) an increment in the crystallite size of the post shocked sample is expected. The calculated crystallite size using the Tunistra and

Koing formula for unshocked and shocked samples is 11.87 nm and 12.82 nm. Thus, the decrement in the I(D)/I(G) ratio and the shrinkage of the D, G band's bandwidth in the shocked sample is the indication of the shock-induced graphitization. The band at 2668 cm⁻¹ may correspond to the G' band of graphene (Ferrari & Basko 2013a) and CNT (Dresselhaus *et al.* 2005, DiLeo *et al.* 2007, Lehman *et al.* 2011). In addition, G' band has also been observed in graphitized carbon (Lee *et al.* 2016), defected multilayered graphene (Milenov *et al.* 2017), and also in bitumen (Jehlička *et al.* 2003). However, the intense G band, observed at 1585 cm⁻¹ may be due to the presence of sp² bonded carbon clusters and other nanostructures of carbon, along with graphene. The G' band exhibits multiple peak components at both sides of G' showing that the graphene is stacked in a Bernal manner i.e. two successive layers of graphene stacked in such a way where the carbon atoms in the upper layer sit on the top of the empty space of the lower layer (Ferrari 2007). The presence of a broadband observed until 130 cm⁻¹ (Fig 4. 1) could be from the CNT's, arising from the Radial Breathing Mode (RBM) a characteristic feature from the CNT's (Dresselhaus et al. 2005, Costa *et al.* 2008).



Fig 4. 1: Raman spectra of the unshocked (black) and shocked sample (red). Here the RBM stands for Radial Breathing Mode which is one of the characteristics mode of the Multi Wall Carbon Nanotube (MWCNT) (Roy et al. 2022b).

4.3.2 HR-TEM Analysis:

For HR-TEM analysis, we loaded the collected samples onto a quantifoil grid. Using HR-TEM, bright field and high-resolution images were taken for both pre and post-

shock samples. From the HR-TEM images, we can see that the unshocked carbon possesses non-graphitic structure i.e. they don't have a long order structure (**Fig 4. 2**). HR-TEM images of the shocked samples on the other hand show highly ordered structures and a wide variety of carbon nanostructures (**Fig 4. 3 - 7**).



Fig 4. 2: HR-TEM image of the unshocked carbon nanopowder.

HR- TEM images of the shock processed carbon are shown in **Fig 4. 3** – **7**. Compared to the HR-TEM images of the unshocked carbon, a wide variety of carbon nanostructures can be seen in the shocked sample. **Fig 4. 3(a)** shows carbon nanoribbons (marked with white arrows) having various degrees of graphitization (Terrones *et al.* 2010). **Fig 4. 3(b)** shows the presence of Carbon Nano Onion (CNOs) marked by white arrows (Ugarte 1992). The estimated internal diameter of the CNO is around 4.5 nm and the intershell spacing is around 0.33 nm. Fig 4. (6) is suggesting a possible presence of CNT (Iijima 1991), especially a Multi-Walled CNT (MWCNT) (Lehman et al. 2011). The internal diameter of the present MWCNT is of the order of ~ 5 nm and the estimated d spacing of the wall (marked by red rectangle) is around 0.41 nm. This falls well within the predicted range of MWCNT's d spacing as reported by Kharissova & Kharisov 2014 (Kharissova & Kharisov 2014). Whereas, the measured d spacing of the nano structure within the blue rectangle turned out to be around 0.33 nm which indicates the presence of Graphitic carbon nanoribbons (Kim *et al.* 2016). **Fig 4. 5** shows the possible presence of a two-dimensional graphene sheet marked by red arrows in inset 1. Fast Fourier Transformed (FFT) image of

the selected area marked by red rectangle is shown in inset 2. The measured lattice parameter is 0.22 nm which is very close to the (1100) lattice fringe of graphene (Habiba *et al.* 2013). **Fig 4. 6(a)** reveals two types of carbon nanostructure a carbon ribbon and at the edges of the ribbon, it has the fullerene-like (~ 0.7 nm) structure attached with the walls of the ribbon. This kind of structure has also been reported as fullerene previously by Duan *et al.* (2017), and by Bernal *et al.* (2019). **Fig 4. 6(b)** reveals that the conical structure has a diameter of the order of ~ 4 nm. We assign this structure to Carbon Nano Cone (CNC) (Terrones et al. 2010). **Fig 4. 7** shows the presence of Graphene Quantum Dot (GQD) in the area marked by a red rectangle. Inset 1 is the zoomed version of marked area where we found GQD and inset 2 is the FFT image of inset 1 which shows good crystallinity of GQDs. The lattice parameter is around 0.232 nm, which matches well to the (1120) lattice fringe of GQD (Peng *et al.* 2012).



Fig 4. 3: HR-TEM images of the shocked sample. (a) carbon nanoribbons indicated by white arrow. (b) carbon nano-onion indicated by white arrow.



Fig 4. 4: HR-TEM image of the shocked sample showing the presence of MWCNT (indicated by white arrows) with internal diameter about 5 nm. The red and the blue boxes show the places from where we obtained the d spacing of the MWCNT and carbon nanoribbons.



Fig 4. 5: HR-TEM image of graphene observed in the post shock sample, Inset1 is the zoomed version of the area marked by red round rectangle. Inset 2 is the FFT of the selected area shown in inset 1.



Fig 4. 6: HR-TEM images of the post-shock carbon nanopowder containing (a) fullerenelike structure (inset marked by red arrow) having diameter round 0.7 nm attached with the walls of carbon nanoribbons and (b) carbon nanocone/nanodiamond.



Fig 4. 7: HR-TEM Image of the graphene quantum dot found in the area marked by a red rounded rectangle. Inset 1 is the zoomed version of that area and inset 2 in the FFT image of inset 1.

The presence of fullerene-like structure, observed in the HR-TEM image, in the post-shock sample is surprising as its characteristic bands (273, 434, 496, 710, 774, 1100, 1250, 1426, 1470, 1576 cm⁻¹ (Meilunas *et al.* 1991) were not present in the Raman

Spectrum of the same sample. The main reason for this is that the Raman scattering crosssection of fullerene in the optical wavelength (we use 532 nm laser) is almost 10^6 times less than the carbon nanotube Raman scattering cross-section (Merlen *et al.* 2017).

There could be several possible formation pathways of the different carbon nanostructures from amorphous carbon nanopowder under high-intensity shock conditions (reflected-shock temperature ~ 7300 K, 2 ms). In the shock conditions employed in our experiment, carbon nanopowder should be in the vapor phase (Bundy 1989). After 2 ms, the reflected shock temperature started to drop from its maximum, and then nucleation might have taken place, leading to the formation of various carbon nanostructures. Suggested mechanisms to date are based on the PAHs, top-down pathway (Berné & Tielens 2012, Merino et al. 2014, Chen et al. 2020), and hydrocarbon under laser ablation (Hatta & Murata 1994, Scott et al. 1997, Jäger et al. 2009, Kroto et al. 1985b). García-Hernández et al. (2011b) proposed that pure carbon grain-grain collisions might lead to C_{60} and Cami et al. (2018) suggested high-temperature dust formation followed by shock processing could lead to C₆₀ formation. Quantum chemical molecular dynamics simulation is another way to understand the formation pathway of different carbon clusters (Zheng et al. 2005, Irle et al. 2006, Zheng et al. 2007). Starting from hot carbon vapor (Zheng et al. 2005, Irle et al. 2006, Zheng et al. 2007) showed a two-step pathway of carbon clusters; in the first step self-assembly of carbon atoms in a hot carbon vapor gives rise to giant multi-cell fullerene structures. Since the multi-cell fullerene, CNO, are in higher vibrational excited sates, this excess energy should release by means of physical processes like unimolecular dissociations and collisional relaxations (Irle et al. 2006). This leads to the formation of smaller fullerenes. Sinitsa et al. (2017) who also discussed a possible mechanism for the transformation of amorphous carbon under high temperatures and microsecond time scales using molecular dynamics simulations. They concluded that the formation of fullerenes from amorphous carbon takes place in two steps. In the first step, the amorphous carbon is shaped into hollow sp^2 bonded shells with attached carbon chains. Due to the constant insertion of carbon chains, a C₆₀ structure is then formed within it. These structures form from amorphous carbon clusters by the self-assembly of carbon atoms driven by thermodynamical instabilities (Sinitsa et al. 2017). The time scale of fullerene formation in those studies (a few microseconds) is much faster than our experimental shock exposure time scale (around 2 ms).

It has been shown that for some of the structures like C_{60} and CNT, graphene may be one of the intermediate structures (Chuvilin *et al.* 2010, Pietrucci & Andreoni 2014, Neng *et al.* 2014). Repeated C₂ addition to hemisphere-like fullerene caps may also result in the formation of CNT (Cruz-Silva *et al.* 2016). Carbon atoms may assemble to produce nanoribbons (Dai 2002). Subsequent rolling/twisting of the nanoribbons can make CNT (Jiang *et al.* 2011, Kit *et al.* 2012, Lim *et al.* 2013). Conversely, unzipping of CNT can also result in making nanoribbons (Jiao *et al.* 2009, Kosynkin *et al.* 2009). In our work, nanoribbons are one of the products in the shocked sample, therefore, the formation and unzipping pathways to make and convert the CNT, respectively, may exist. In the case of CNOs (multi-shell fullerenes), and for CNC the formation pathways may be independent of the graphene route and maybe rather associated with buckyball formation. While CNC could subsequently form either C_{60} / C_{70} or might lead to the formation of CNOs. The formation of all of these carbon nanostructures observed could have also formed simultaneously from the carbon nanopowder.

4.4 Astrophysical Significance:

To date, some of the carbon structures we detect in our experiments, such as nanoribbons and nanocone, are not considered as a component of Interstellar dust. However, our experiments clearly show that there are conditions in shocked gas that result in the formation of these structures alongside graphene, C₆₀ and CNT's. From our experimental results, we thus encourage a search of these species in astronomical observations where carbon might be found in other forms in the interstellar dust. In addition, shock-induced synthesis of such structures of carbon may explain the observation of fullerene-like carbon nanostructures observed in the Allende meteorite (Harris et al. 2000), where it is proposed that the carbon present in the meteorite could have experienced rapid heating by few 1000's of Kelvin such that these structures could have been made when the parent body was subject to impact-induced shock condition. Onion-like carbonaceous dust has been proposed as a constituent of cosmic carbon dust based on experiments conducted by researchers such as Ijima 1980, Ugrate 1992, and Kuznetsov et al. 1994. These studies demonstrated that onion-like carbon dust can form in highly energetic environments. Furthermore, it has been argued that these dust grains may serve as carriers of interstellar extinction features (Wada et al. 1999).

Fullerene has been detected in various regions of the interstellar medium (ISM), including hydrocarbon-poor regions such as the planetary nebula Tc1 and Lin 49. Because of hydrocarbon deficiency, the top-down formation pathway which started from PAH or HAC to fullerene may not be efficient in those hydrocarbon-poor regions. Planetary nebula Tc1 is known to contain amorphous carbon (Cami *et al.* 2010). Also, this planetary nebula is thought to have gone through late thermal pulsation, which caused mass loss followed by the formation of circumstellar shell where fullerene is detected (Cami *et al.* 2010). Therefore, the shock processing of precursor materials, such as amorphous carbon, can also contribute to the formation of fullerene in Tc1. Our work demonstrated that carbon nanostructures like carbon nanobuds and nano onions along with other carbon nanostructure can be formed by shock processing of amorphous carbon nanodust in a hydrogen-poor condition. Based on our findings, we may conclude that the shock processing of amorphous carbon nanostructures in regions of the ISM with minimal hydrocarbon concentration.

4.4 Conclusions:

Our results provide evidence that in a carbon-rich environment, shock processing of carbon dust can synthesize a wide variety of carbon nanostructures. Fullerenes have been observed in the ISM but there may be several other structures made of carbon that are awaiting discovery, especially carbon nanoribbons, graphene, MWCNT's, CNC, and CNO. In fact, carbon nanoribbons were observed to be the major product that could be the base for other carbon nanostructures to form. In future experiments, we aim to shock carbon nanopowder in the presence of hydrogen gas to understand the influence of hydrogen on the formation of carbon nanostructures.

Chapter 5 Shock processing of Amorphous Carbon nanodust in the presence of Hydrogen

Chapter overview:

This chapter describes the experimental results obtained from the shock processing of amorphous carbon nanodust (particle size < 100 nm) in H_2 . One of the primary objectives of this experiment is to understand the condensation of different carbon nanostructures in the presence of hydrogen. Shocked processed samples were collected and analysed using Raman spectroscopy and HR-TEM imaging technique; these results are documented in this chapter. A significant change in dust morphology has been observed, especially the presence of graphite and nanodiamond.

5.1 Introduction:

Almost 99 % of the interstellar gas comprises H and He, and 70 % of H is present either in atomic or molecular form (Ferrière 2001). Hydrogen is also reported to be present in the envelope of the AGB stars, where dust condensation takes place from the gas phase. Also, hydrogen is known to be present in different fullerene-containing planetary nebula. Interstellar carbonaceous dust particles can also be subjected to collision with hydrogen atoms and molecules in the ISM. Hence hydrogen can play a vital role in the condensation process of cosmic carbon dust.

Cosmic carbonaceous dust is predominately amorphous (Sorrell 1990). These dust grains are also thought to be a potential component of the carbonaceous dust present in the envelope of the C-rich AGB stars and late-type variable stars (Anderson Höfner, and Loidl. 2002). The evolution trajectories of the amorphous carbon, while subjected to different energetic conditions in the ISM, have been least explored to date (Dartois 2019). In Chapter 4, we studied the fate of the amorphous carbon by subjecting it to 5.6 M shock, where the gas temperature was raised to about 7300 K and remained at that temperature for 2 ms. In continuation to the work carried out in the previous chapter, here we study the shock processing of amorphous carbon in the presence of hydrogen. This study's primary

objective is to understand the effect of hydrogen effect in the condensation process of carbonaceous dust.

5.2 Experimental Methodology:

In this chapter, we investigated the shock processing of amorphous carbon nanopowder (particle size < 100 nm) in the presence of hydrogen. Helium was used as the driver gas, while a mixture of argon and hydrogen was used in the driven section. The experimental parameters employed are provided in **Table 5.1**. Further information regarding the experimental procedure, the technique employed to measure the shock speed based on the pressure response curve, and the estimation of the reflected shock temperature (T_5) using the R-H jump equation can be found in **Chapter 2 and 3** of this thesis.

Table 5: 1: Details of the experimental parameters used to include the shock bursting pressure (P_4) Mach number (M), reflected shock temperature (T_5) .

Amount	0.1 g			
Driven Pressure	0.15 Bar (0.1 bar Ar, 0.05 bar H ₂)			
Bursting Pressure (P ₄)	68.5 bar			
Mach Number (M)	~ 5.3			
Reflected Shock Temp (T ₅)	~ 6450 K			

5.3 Results and Discussion:

5.3 1 Raman Spectroscopy:

The Raman spectra of both pre and post-shocked samples are in **Fig 5.1**. Before plotting, these spectra were normalized in to the same scale and an offset applied for the

visual clarity. The spectra coloured in black represents the amorphous carbon with its characteristic D and G band at 1350 cm⁻¹ and 1598 cm⁻¹ (Roy et al. 2022b). The origin of G and D band has already been discussed in Chapter 4 and hence there is no separate discussions here on this. The spectrum coloured in blue is the Raman spectra of the shocked sample in the presence of H₂. Here, the D and G bands' peak positions are around 1341 and 1397 cm⁻¹. Notable, the band area of the D and G bands gets reduced compared to the unshocked sample. This suggests that the shock processing of the amorphous carbon in the presence of H₂ has gone through the crystallisation process, which can be referred to as shock-induced crystallisation (Roy et al. 2022b). We also observed the presence of a new band around 2650 cm⁻¹, which is usually referred to as the G' band. The presence of the G' band in the shocked sample suggests the possible presence of graphene and MWCNT. Further, we also observe the broad band close to the Rayleigh tale, marked by the red arrow. This could be the radial breathing mode associated with the radial vibration of the C atoms in MWCNT (Costa et al., 2008, Dresselhaus, Dresselhaus, 2005). The spectra coloured in red are the Raman spectra of the shock-processed C in the absence of Hydrogen (Roy et al. 2022b), which we have already discussed in Chapter 4. Notice that the Raman spectroscopic features of the shocked sample with and without hydrogen are almost similar.



Fig 5. 1: Raman Spectra of the pre and post shocked samples. The red arrow indicates the presence of Radial Breathing Mode (RBM) present in the both with and without hydrogen shocked samples.

5.3.2 HR-TEM imaging:

The HR-TEM images of the shocked sample of amorphous carbon nanodust can be found in **Fig 4. 2** in Chapter 4. The HR-TEM images of the shocked sample of the $C + H_2$ is in Fig 5. 2 -6. Fig 5. 2 is a relatively low magnification image with a scale up to 500 nm showing the presence of solid carbonaceous dust condensates with different shapes and sizes. The Inset of Fig 5.2 shows the zoomed view of the area in the red bracket. It consists of carbonaceous sheets with ribbons-like structures. Fig 5. 3(a) shows carbon nanoribbons with d spacing around 0.36 nm. Fig 5. 3(b) shows the presence of a hollow carbonaceous shell with a diameter of around 120 nm. It is mainly made of carbon nanoribbons with d spacing around 0.36 nm. Fig 5. 4 (a) indicates the presence of MWCNT (Lehman et al. 2011) with an inner diameter of around 5 nm, marked by red arrows. Fig 5. 4 (b) contains multi-shell Carbon Nano onions (CNO) (Ugarte, 1992), with the innermost shell having a diameter of around 6.5 nm and the outermost shell having a diameter of around 23 nm. Fig 5. 5 (a) contains two different carbon nanostructures. The white arrow in Fig 5. 5 (a) indicates an amorphous carbon shell. Inside the shell, there also exists another crystalline carbon nanostructure marked by a red box. Its electron diffraction pattern can be seen in the inset. The calculated d spacing of the crystalline structure within the red box is around 0.26 nm, indicating that it is graphene (Habiba et al. 2013). Fig 5.5 (b) shows the presence of another carbon nanostructure within the red box. The inset of this figure describes the zoomed view of the region within the red box. The electron diffraction pattern of this nanostructure shows that it is crystalline, and its d spacing is found to be around 0.21 nm, assigned to the (2 0 0) plane of a hexagonal diamond (Kim et al. 2016). These kinds of nanodiamond grains could be a possible nucleation site for further diamond growth, as suggested by Lifshitz et al (Lifshitz et al. 2002, Lifshitz et al. 2004). Fig 5. 6 contains a part of the shocked sample consisting of carbon nanostructures with different orientations. The electron diffraction pattern of the area in the yellow box shows that these structures are crystalline. The calculated d spacing is found to be around 0.37 nm which indicates the presence of a graphite (200) plane, indicated by a red arrow in the inset.



Fig 5. 2:HR-TEM image of the shocked sample with lower magnification. inset of this image shows the zoomed view of the area marked by a red bracket.



Fig 5. 3: *HR-TEM images of the shocked sample show the presence of carbon nanoribbons* (*a*), *and a hollow carbonaceous shell made of carbon nanoribbons.*



Fig 5. 4: HR-TEM images of the shocked sample show the presence of (a) MWCNT, and (b) CNO.



Fig 5. 5: HR-TEM images of the shocked sample. (a) indicating the possible presence of graphene within the area marked by a red box, encapsulated by an amorphous carbon shell, and the inset shows the electron diffraction pattern of the above-described area. (b) shows diamond QD within the area marked by the red box, and the inset in the LHS shows the zoomed view of the region within the red box.



Fig 5. 6: HR-TEM image of the shocked sample. The inset shows the electron diffraction pattern of the area within the yellow box, and its calculated d spacing is around 0.37 nm, which matches well with the lattice spacing of graphite's (2 0 0) plane.

The shock processing (5.3 M) of the amorphous carbon nanodust (particle size < 100 nm) about an estimated gas temperature around 6400 K for 2 ms in the presence of hydrogen gives rise to various kinds of carbon nanostructures such as carbon nanosheets, nanoribbons, CNO, MWCNT, graphene, nanodiamond, and graphite. Such structures have also been reported in Chapter 4, where we studied the shock processing of amorphous carbon in hydrogen-less conditions. The high-temperature formation pathway of various carbon nanostructures has already been discussed in Chapter 4. In this section, we will only focus on the role of hydrogen in the formation of various crystalline forms of carbon.

There exist various ways to graphitise the amorphous carbon, which include (1) catalytic active transition metals, (2) laser irradiation, (3) ion irradiation, (4) mechanical shear forces, and (5) high-temperature annealing with high-pressure (Loh & Baillargeat 2013). The incorporation of hydrogen in the shock process plays a crucial role in transforming amorphous carbon into these diverse carbon nanostructures. During the shock heating up to temperature 6400 K, H₂ present in the driven gas will be dissociated via the following reaction suggested by Patch et al. (Patch 1962).

$$H_2 + Ar \rightarrow 2H + Ar \qquad 5.1$$

Also, the amorphous carbon present there will also be thermally excited by the collision with the shock-heated Ar atoms via the following reaction:

$$C + Ar \rightarrow C^* + Ar$$
 5.2

Where the * sign shows the thermally excited state. The atomic hydrogen produced because of the shock heating is much more reactive than the molecular hydrogen, and it acts as a catalyst reducing the graphitisation barrier during the transformation of amorphous carbon into graphite by promoting the formation of sp^2 bond (Wang et al. 1995). The graphitisation process involves rearranging carbon atoms into a highly ordered, layered structure characteristic of graphite. However, defects, impurities, and irregular bonding in amorphous carbon often hinder this transformation, creating a high energy Barrier that prevents efficient graphitisation. Hydrogen facilitates removing defective carbon bonds during shock processing or high-temperature conditions (Wang et al. 1995). It preferentially reacts with dangling bonds and carbon radicals, leading to the stabilisation of graphitic layers. Because of high thermal conductivity, the presence of hydrogen in the driven gas mixture can make it a better quencher than the presence of only inert Ar (Wang et al. 1995). Although a more significant fraction of the observed structures in the shocked sample were found to be graphitic, signatures of nanodiamonds have also been reported. The presence of hydrogen can also play a significant role in the formation of nanodiamonds. During diamond growth, H can remove the unwanted sp² bond and saturate the dangling bonds from the nanodiamond surface (Sorkin et al. 2008).

The condensation of the carbonaceous grains in a hydrogen atmosphere was previously studied by Jäger et al (Jäger *et al.* 2009), where they ablated graphite using a laser where the laser-produced plasma temperature range was between 4000 to 6000 K. The analysis of the solid condensate shows the presence of fullerene and fullerene-like soot particles. Our experiment is different from the laser ablation done by Jäger *et al.* (2009), and here we started from amorphous carbon, not graphite. The analysis of the shocked sample also showed varieties of carbon nanostructures that are not limited to the fullerene-like soot particles. From the study of the shocked sample, we have not seen the presence of the PAH molecule. However, we identified graphene in the shocked sample. Graphene is considered a primary building block of various carbon nanostructures such as fullerene and graphite, and it can also be considered a fully dehydrogenated PAH (Berné & Tielens 2012). We have not analysed the shocked processed gas, so the molecules produced in the gas phase because of shock processing are largely unknown in this experiment.

4. Conclusions:

The results from the shock processing of amorphous carbon in hydrogen suggests that carbon nanostructures such as carbon nanoribbons, nano onions, MWCNT, graphene, graphite, and nanodiamond can preferentially condense from very high temperature in the presence of hydrogen. This outcome suggests that such carbon nanostructures can also be grown in the different parts of the ISM where high-temperature condensation is feasible in the vicinity of hydrogen, which is the most likely scenario as hydrogen is present in the chemically active zone of the ISM. One possible site for such high-temperature condensation could be the stellar envelope of AGB stars, notable the photospheric region, where atomic and molecular hydrogen are often found along with other hydrocarbon and organosilicon molecules (Cherchneff 2000). Such high temperature dust condensation zone has also been reported about a distance twice of the photospheric diameter of the Mira variable stars, where low velocity shocks have been reported (Rudnitskij 1997). Amorphous carbon has also been proposed to be present in the AGB star's envelope and considered as a potential contributor to the infrared excess detected around these stars (Groenewegen 1995). Pulsation-driven low-velocity shocks (< 10 km s⁻¹) can process the amorphous carbon and dissociate molecular hydrogen present in those regions of AGB stars (Cherchneff et al. 1992). This could lead to various carbon nanostructures such as carbon nanoribbons, carbon nano onions, MWCNT, graphene etc.

4. Conclusions:

Chapter 6 Shock induced formation of Silicon Carbide (SiC) nanodust

Chapter overview:

This chapter describes the experimental results obtained from the shock processing of amorphous carbon nanodust and silicon nanopowder (2:1) in the presence of hydrogen. The pre and post-shocked samples were examined using techniques like ATR-FTIR spectroscopy, XRD, and HR-TEM imaging and the outcome of these analyses is documented here in this chapter. These results show the presence of polycrystalline SiC and various carbon nanostructures such as carbon nanoribbons, carbon nanotubes and nanobuds. This helps us conclude that shock waves, especially low-velocity shock waves, in the ISM/CSM, can induce a chemical reaction between elemental C and Si which could make polycrystalline SiC and various other forms of carbon.

6.1 Introduction

Silicon Carbide (SiC) is one of the important components of interstellar mineral dust (Speck et al. 2009). Based on molecular equilibrium calculations, its presence as a condensate in the outflow of carbon stars has been predicted by authors like Gilman (Gilman 1969), Friedemann (Friedemann 1969), and McCabe (McCabe 1982). Hackwell (Hackwell 1972), Treffers & Cohen (Treffers & Cohen 1974), and Goebel (Goebel et al. 1980), are those authors who attributed first SiC as a potential carrier of the 11.2 µm infrared emission feature observed around carbon-rich AGB stars. Also, the same kinds of absorption features of SiC are observed in numerous extreme carbon stars (Jones et al. 1978, Speck et al (Speck et al. 1997), (Speck et al. 2009). Besides dust, sub-mm observations on the stellar envelope of IRC+10216 (CW Leo) reveal the presence of many silicon carbon-based molecules and radicals. These are the SiC radical (Cernicharo et al. 1989), closed-shell ionic ring SiC₂ (Thaddeus et al. 1984), (Cernicharo et al. 2010) a wellknown carrier of the Merrill and Sanford band, rhomboidal SiC_3 (Apponi *et al.* 1999), the linear chain molecule SiC₄ (Ohishi et al. 1989) and in the last decade Si₂C (Cernicharo et al. 2015). Despite the presence of SiC as dust and many Si-C-based molecules and radicals in circumstellar envelopes, SiC dust in the diffuse ISM has not been detected. The reason

behind the absence of a 11.2 μ m band in the diffuse ISM is still not apparent. However, one possible explanation could be the destruction of SiC grains by O atoms. Once SiC is injected into the ISM, they lead to silicate formation (Whittet *et al.* 1990, Chen *et al.* 2022).

Presolar grains extracted from primitive meteorites are identified by their isotopic anomalies compared to solar system standards. As the name suggests, these grains are older than the solar system and contain imprints of their respective stellar origins (Zinner et al. 2005, Lodders & Amari 2005, Hoppe et al. 2010, Ott 2010). SiC is the most studied and the 2nd most abundant carbonaceous grain after nano diamonds which have been detected in presolar grains (Ott 2010). The presence of SiC was first detected in the Murry carbonaceous chondrites by analysing the isotopic anomalies of the noble gas trapped within it (Bernatowicz et al. 1987). Presolar SiC can be distributed into different categories based on the isotopic proportion of the elements like C, N, Si and Al (Ott 2010). Amongst them, the most abundant grains (90%) are known as mainstream grains, and the other types are classified as A, B, X, Y, and Z (Ott 2010). Isotopic analysis of the mainstream grains shows the presence of excess ¹³C and ¹⁵N isotopes as compared to the standard solar system isotopic composition. This helps one to conclude that most of these grains are formed in the outflows of the AGB stars (Hoppe et al. 1996). This claim is also supported by the presence of s process signature detected in trapped noble gases and the heavy trace elements in those grains (Hoppe et al. 1997). The A and B grains are characterized by their low $^{12}C/^{13}C$ ratio (< 10), and the approximate range of $^{12}C/^{13}C$ for A grains is between 2 to 3.5, whereas for B grains, it is around 3.5 to 10 (Zinner 1998, Amari et al. 2001). To date, the sources of A and B grains are still not well known. It has been proposed that J-type carbon stars and born-again AGB stars could be possible sites for their formation (Amari et al. 2001b). Y, Z type grains are thought to be produced in AGB stars having metallicity lower than solar metallicity (Hoppe et al. 1997, Amari et al. 2001a), and some may also have originated from novae (Zinner 1998). The X grains only contain 1% of the presolar SiC population, and the presence of ⁴⁴Ti in these grains suggests that these grains are generated in supernova explosions (Timmers et al. 1996, Zinner 1998, Zinner et al. 2005, Amari & Lodders 2006). In nature, SiC has been identified in 250 different polytypes. However, samples extracted from meteorites only showed the presence of cubic (β -SiC) and hexagonal (α -SiC) phases, in which β -SiC is the most abundant phase (Daulton *et al.* 2003, Bernatowicz et al. 2005). These grains follow a log-normal size distribution (Amari et al. 1994). In the 90s, the known grain size was limited to the range 0.3 to 3 μ m (Amari *et al.* 1994). However, in the era of NanoSIMS, more fine-grained samples have been analysed $(0.2 - 0.5 \ \mu\text{m})$ and revel that submicron to nanometre size grains are more abundant than micron size grains (Gyngard *et al.* 2010, Hoppe *et al.* 2010, Amari 2014). The above discussion can be summarizing in a tabular format in **Table 6.1**.

Table 6.1: Classifications of presolar SiC grains based on their abundance, ${}^{12}C/{}^{13}C$ isotopic ratio, ${}^{14}N/{}^{15}N$ isotopic ratio, and their primary sources (Hoppe et al. 2010).

Group	Abundance (%)	¹² C/ ¹³ C	¹⁴ N/ ¹⁵ N	Sources/Signatures	
Mainstream	87–94	10–100	50-20,000	AGB stars (s - process signature)	
A	2	2-3.5	40-600	J stars for s process rich grains and 'born again' stars for the s process poor grains	
В	2-2.5	3.5-10	70-12000	Same as A grains	
Y	1-2	18–7,000	13–180	Low mass solar metallicity AGB Star	
Z	0-3	140–260	400–5,000	Low mass low metallicity AGB stars	
X	1	8–180	1,100– 19,000	Supernova explosion (⁴⁴ Ti)	

SiC is thought to play a crucial role in the interstellar molecular enrichment process. Once injected into the ISM, they are exposed to harsh energetic processing, which leads to subsequent mass loss and enriches the chemical complexity in the ISM. In planetary nebula, high-velocity outflows generate shock waves, which process the dust by rapid heating up to several thousands of Kelvin (Sevenster & Chapman 2001, Van de Steene & Van Hoof 2003). These nebular shocks also contain ions which bombard dust grains and implant themselves on their surface (Heck *et al.* 2009). Laboratory experiments simulating stellar shock heating (up to 1300 K) followed by ion bombardment (150 KeV of Xe) on the SiC grains shows the formation of carbon nanostructures like fullerene, and graphite (Bernal et al. 2019). Also, the thermal decomposition of SiC has been found to make carbon nanostructures like hemispherical fullerene and CNT (Kusunoki *et al.* 1997, Watanabe *et al.* 2001, Bernal et al. 2022). Experiments have also shown that the exposure of graphitized SiC surface to atomic H, in a simulated interstellar condition, led to the formation of Polycyclic Aromatic Hydrocarbon (PAH) molecules (Merino et al. 2014). This suggests that SiC works as a catalyst in interstellar chemistry.

Like other carbonaceous dust the formation pathway of SiC dust in circumstellar conditions is still an evolving topic (Speck et al. 2009). Shock processing of dust precursors could lead to the formation of dust in various astrophysical events, such as in Nova V2891 Cyg (Kumar et al. 2022). A high-intensity shock tube can be used to simulate the low velocity circumstellar shock conditions in the laboratory. In recent years there has been a growing interest in shock tubes in the field of high-temperature astrochemistry and astrobiology. A recent review by Roy et al. (2023) covers various results obtained using shock tubes in the area of laboratory astrochemistry by different research groups. In light of the significance of low-velocity shock processing in interstellar dust chemistry, this study delved into the bottom-up shock-induced formation pathway of SiC. We processed the mixture of amorphous carbon and Silicon nanopowder into the high-intensity shock ~ 5.3 Mach, reflected shock temperature ~ 6400 K for 2 ms in the presence of Hydrogen (H₂) in a high-intensity shock tube. The shock-processed samples were later analyzed using ATR-FTIR spectroscopy, XRD, HR-TEM imaging, and EDX mapping. One of the primary reasons for choosing amorphous carbon in this experiment is associated with the fact that carbonaceous dust in different astrophysical regions is predominately amorphous rather than graphitic (Sorrell 1990). Whereas H₂ is the most abundant molecule observed in the different parts of ISM and can play a key role in the nucleation process of dust grains (Cherchneff 2000).

6.2 Experimental Methodology:

In this chapter, we investigated the shock processing of mixtures consisting of amorphous carbon nanopowder (particle size < 100 nm) and Si nanopowder using the

HISTA. Helium was used as the driver gas, while a mixture of argon and hydrogen was used in the driven section. The experimental parameters employed are provided in **Table 6.2**. Further information regarding the experimental procedure, the technique employed to measure the shock speed based on the pressure response curve, and the estimation of the reflected shock temperature (T_5) using the R-H jump equation can be found in **Chapters 2** and 3 of this thesis.

Amount	0.1 g (C + Si (2:1))			
Driven Pressure	0.15 bar (0.1 bar Ar, 0.05 bar H ₂)			
Bursting Pressure (P ₄)	68.5 bar			
Mach Number (M)	~ 5.3			
Reflected Shock Temp (T ₅)	6450 K			

Table 6. 2: Details of the experimental parameters used to generate the shock bursting pressure (P_4) Mach number (M), reflected shock temperature (P_5) .

6.3 Results and Discussion:

6.3.1 ATR- FTIR Spectroscopy:

The ATR – FTIR Spectroscopy of the pre and post-shocked sample in the wavelength range between 7 to 20 μ m is shown in **Fig 6.1**. The details of the specifications of the spectrometer used in this analysis are provided in **Chapter 3**. The spectra were acquired using a Nicolet iS50 FTIR spectrometer with a resolution of 2 cm⁻¹. The spectra of the unshocked sample, marked by black colour in Fig 6. 2, have a broad plateau-like feature spanning between 8.2 and 10.3 μ m. This band is assigned to the Si-O-Si asymmetric stretching motion (Jäger et al. 2003a), where O is an impurity as silicon has good surface activity.

The IR spectra of the shocked sample coloured in red and blue in the left hand panel of **Fig 6.1** taken from two parts of the same sample. These two spectra in the left hand panel are almost identical and have two very distinct IR features. One is between 8.2 to 10.3 μ m, also present in the unshocked sample due to surface reaction between Si and atmospheric O. The other one has a sharp asymmetric Gaussian feature that peaked around 12.6 μ m. This peak represents silicon carbide's fundamental resonance absorbance feature in the IR (Spitzer *et al.* 1959). From the resonance absorbance band, it is difficult to tell about the structure of silicon carbide as both hexagonal and cubic phases have similar IR features (Spitzer *et al.* 1959).



Fig 6. 1: ATR FTIR Spectra of both the pre and post-shocked sample. The right hand panel, indicated by a red dash-dot-dash arrow is a close-in view of the shaded 12 to 14 μ m region in the left hand panel, which contains the IR active mode of SiC. The unshocked sample remains featureless in this spectral window.

6.3.2 XRD analysis:

XRD pattern of both pre and post-shocked mixtures of Si plus C (1:2) is shown in **Fig 6. 2**. These patterns are normalised in the same scale before plotting, and offset is applied for visual clarity. Braggs equation has been employed to calculate the interplanar spacing (d) of different XRD peaks. **Fig 6. 2(a)** represent the XRD patterns of the unshocked sample. The broad feature around 26°, marked by a black star, shows amorphous carbon. The other peaks marked by orange colour stars are the well-known diffraction pattern of silicon (CODID: 1526655).

Fig 6. 2(b) shows the XRD patterns of the shocked sample. It has many new peaks compared to its unshocked counterpart. Some new peaks are marked by a blue circle and a pentagon, and some by a blue triangle. Also we can also see the presence of both silicon

and amorphous carbon in the shocked sample, and an orange star and a black star mark their corresponding peaks. Those peaks marked by a blue triangle show the presence of Al, which comes from the Al diaphragm used in HISTA. The peaks marked by a blue pentagon are around 35.86°,41.62°, 60.20°, and 72°. We compared these peak positions with the synthetic XRD pattern of cubic SiC (β) shown in **Fig 6.2(c)** and found a good match. This synthetic XRD pattern of cubic SiC (β) was generated using VESTA, and its unit cell information was taken form CODID:1011031. A less intense peak around 33.86°, marked by a blue circle is assigned to the Hexagonal SiC phase. One can find the details of the crystallographic information of the shocked sample, such as Millar indices, interplanar d spacing and comparison of d spacing with the standard data in **Table 6.2**. We also noticed that the band peaked around 26° in **Fig 6.2(b)** gets sharper compare to the band present at around 26° in **Fig 6.2(a)**. This suggests that the amorphous carbon in the unshocked sample has undergone a graphitisation process induced by shock processing.



Fig 6. 2: (a) XRD Pattern of the unshocked sample, (b) XRD pattern of the shocked sample, and (c) synthetic XRD pattern of cubic SiC (β).

So shock processing of Si plus C in H_2 gives rise to dual-phase silicon carbide, where its cubic phase is more dominant, as seen from the intensities. Also, we see possible indications of shock-induced graphitisation. Notable, the peaks of the Si in the shocked sample are sharper compared to the unshocked sample. This observation indicates that an increase in the crystallite size of Si induced by shock processing ultimately leads to crystal growth in the shocked sample.

Table 6. 3: XRD peaks observed in the shocked sample along with their corresponding dspacing values and assignments to different crystalline phases (β -SiC, Hexagonal SiC, C, and Si).

		Assignment (Millar indices (d spacing in Å))					
2θ (°)	θ (°)	d (Å) (Experiment al)	β- SiC CODID:1011031	Hexagonal SiC	Carbon	Si CODID: 1526655	
					200		
26.06	13.03	3.42			(3.42)		
						111	
28.66	14.33	3.11				(3.11)	
				101			
33.83	16.92	2.65		(2.65)			
35.86	17.93	2.5	1 1 1 (2.51)				
41.62	20.81	2.17	2 0 0 (2.17)				
						220	
47.52	23.76	1.91				(1.90)	
						311	
56.33	28.17	1.63				(1.62)	
60.2	30.1	1.54	2 2 0 (1.53)				
69.36	34.68	1.35	4 0 0 (1.34)				
71.99	36	1.31	3 1 1 (1.31)				
75.74	37.87	1.25	2 2 2 (1.25)				
						331	
76.58	38.29	1.24				(1.23)	
78.17	39.09	1.22					
88.18	44.09	1.11				4 2 2 (1.09)	

6.3.3 HR-TEM imaging:

HR-TEM analysis of the shock processed samples was carried out using Titan Themis 300 S/TEM from Thermo. The samples were ultra-sonicated in ethyl alcohol for 15 minutes, then drop cast on a quantefoil grid and allowed to dry in a chemically inert atmosphere overnight. Before the imaging analysis started, these drop cast grids were plasma cleaned using Ar-O₂ plasma to reduce any changes of further contamination. Throughout the investigation, the HR-TEM was operated at 300 keV.

HR-TEM images of the shocked samples are in Fig 6. 3(a-g). Fig 6. 3(a) shows the low magnification image of the shocked sample (up to 200 nm scale size). It shows the presence of a sheet-like structure. Fig 6. 3(b) shows the presence of numerous solid condensates. These particles have a maximum size of ~90 nm to a minimum of ~ 17 nm. Fig 6. 3(c) shows the presence of two distinct crystalline phases. Inset 1 of Fig 6. 3(c) contains information about the reciprocal lattice orientation of the area marked by a red box. The calculated interplanar d spacing of this region is around 0.25 nm, and it is assigned to the (1 1 1) plane of β -SiC (CODID:1011031). Inset 2 of Fig 6. 3(c) contains information about the reciprocal lattice orientation of the area marked by a yellow box. The calculated interplanar d spacing is around 0.34 nm, corresponding to graphite's (200) plane (Li et al. 2007). Fig 6. 3(d) indicates the presence of many randomly oriented elongated particles, a few of these structures can be recognised as Multiwall Carbon Nanotube (MWCNT) marked by a red arrow in Fig 6. 3(d). The inset shows the close-in view of the region marked by a yellow box in Fig 6. 3(d), which contains MWCNT with an internal diameter of around 5 nm. Fig 6. 3(e) shows the presence of a MWCNT with an inner diameter of approximately 5 nm marked by red a red arrow. At its bottom is a hemispherical structure marked by a yellow arrow. The inset of Fig 6. 3(e) shows a close view of the hemispherical object, and its diameter is around 0.7 nm. This kind of structure is usually called a carbon nanobud, where a fullerene (marked by a yellow arrow in the inset of Fig 6. 3(e) is found to be attached to the outer wall of a carbon nanotube (Duan et al. 2017, Bernal et al. 2017, Roy et al. 2022). Fig 6. 3(f) shows the presence of a crystalline domain and its corresponding reciprocal lattice orientation can be found in the inset. The inter planer d spacing of this crystalline domain was found to be around 0.25 nm, and it was assigned to the $(1 \ 1 \ 1)$ plane of β -SiC (CODID:1011031). Fig 6. 3(g) shows the presence of three different crystalline domains marked by a blue box, a red box, and a yellow box. Inset 1 shows the reciprocal lattice orientation of the region within the blue box, and the calculated Interplanar d spacing is ~ 0.25 nm, corresponding to the (1 1 1) plane of β -SiC (CODID:1011031). Inset 2 shows the reciprocal lattice orientation of the region with the red box, and its interplanar d spacing is around 0.31nm, and it corresponds to the (1 1 1) plane of Si (CODID: 1526655). Inset 3 shows the reciprocal lattice orientation of the region within the yellow box and has d spacing around 0.27 nm, which shows the presence of hexagonal SiC.

Fig 6. 3(h) shows the High-Angle Annular Dark Field (HAADF) image of the shocked sample. Since the HAADF technique is sensitive to the atomic number (Z) of the element present in the sample, those areas that appeared bright in the image contain high Z value elements compared to those in the relatively less bright area. **Fig 6. 3(i)** indicates the elemental distribution (C, Si) of the structure shown in **Fig 6. 3(h)**. This elemental mapping suggests that the relatively bright spots in **Fig 6. 3(h)** are made of Si, and the less bright area contains C, which is further confirmed by the individual elemental mapping of the C in **Fig 6. 3(i)** and Si in **Fig 6. 3(k)** as shown in.




Fig 6. 3: (a-h) HR-TEM images of the shocked sample with different magnifications showing the presence of sheets like structure (a), graphite (b), MWCNT (D), nanobud (e), β - SiC (f) and different crystalline phases of SiC and Si (g). (h) HAADF image of the shocked sample, (i) elemental distribution of C and Si of (h). (j, k) individual elemental distribution of C and Si of the structure showed in (i).

We synthesised SiC dust by subjecting mixtures of amorphous carbon nanopowder and Si nanopowder in a proportion of 2:1 in the presence of H₂ to an extreme shock wave with Mach 5.3 and estimated reflected shock temperature ~ 6400 K. Cubic SiC is found to be the dominant component compared to hexagonal SiC. Apart from the SiC, we also see the presence of various carbon nanostructures such as carbon nanosheets, nanoribbons, carbon nanotube, nanobuds, and graphite. Previously, the shock tube has been used to synthesise SiC from aseous precursors, such as the mixtures of SiH₄ and CH₄ in the temperature range from 800 – 3600 K, and the pressure range 0.46 to 4.16 atm (Carmer & Frenklach 1989). Similarly, Frenklach et al. (1989) showed the formation of SiC grains by shock processing of the gaseous mixtures of SiH₄, CH₄ and almost 60% of H₂. They explored the temperature range between 1200 and 2000 K and the pressure between 1.07 and 1.56 atm. These aboveexplained experiments can be considered as a top-down pathway of SiC dust formation where shock induced destruction of SiH₄ provides Si and CH₄ as a source of C. In our work, we explored the bottom-up formation route of SiC starting from the element C and Si. Also, we explored a high-temperature formation route ~6400 K for 2 ms mimicking low-velocity circumstellar shock processing of cosmic carbonaceous dust analogue.

By combining the results from the IR spectroscopy, XRD, and HR-TEM analysis, and considering the thermodynamic parameters such as reflected shock temperature (T₅) and reflected shock pressure (P₅), we tried to formulate a possible formation pathway of SiC and other carbon nanostructures in this experiment. At T₅ ~ 6400 K, shock-heated Ar atoms collide with the H₂ present in the driven gas and can lead to the dissociation of H₂ (Patch 1962) via the following reaction:

$$H_2 + Ar \rightarrow 2H + Ar \tag{6.1}$$

C and Si will also be vibrationally heated due to the collision with shock-heated Ar atoms. According to their corresponding phase diagram, C (Bundy 1989) will be into the vapour phase at a gas temperature of ~ 7300 K and pressure of ~ 25 Bar, whereas Si (Bundy 1964) will also melt at this high temperature and pressure.

$$C + Ar \rightarrow C^* + Ar \tag{6.2}$$

$$\operatorname{Si} + \operatorname{Ar} \rightarrow \operatorname{Si}^* + \operatorname{Ar}$$
 (6.3)

The '*' denotes the thermally excited state of C and Si. The vibrationally excited C can react with another excited C atom and make C_2 , and this reaction will continue towards forming of n numbers of larger carbon clusters (C_n).

$$C + C + Ar \rightarrow C_2 + Ar \rightarrow n C_n$$
(6.4)

At high temperatures, C_2 can react with the molecular hydrogen and produce C_2H . Although a significant amount of H_2 will dissociate at a high temperature, recombination is still possible via a third body/ surface reaction.

$$C_2 + H_2 \rightarrow C_2 H + H \tag{6.5}$$

This is a high enthalpy reaction (~ 100 kJ mol⁻¹) and only possible above the temperature of ~ 550 K (Pitts *et al.* 1982). Hence, eq (6.5) is likely to occur in our experimental conditions. C₂H can further react with H₂ and form acetylene (C₂H₂). Also, it can react with atomic carbon and form C₃ (Santoro *et al.* 2020), which can again contribute to the formation of larger carbon clusters. In the high-temperature formation of sp² bonds are energetically favourable (Derjaguin *et al.* 1977). Therefore, we see most of the observed structures in the TEM images (**Fig 6. 3 (c-e**)) of the shocked samples are either graphitic such as carbon nanoribbons, MWCNT or polycrystalline graphite. The possible reactions hence can be written as

$$C_2H + H_2 \rightarrow C_2H_2 + H \tag{6.6}$$

$$C_2H + C \rightarrow C_3 + H_2 \tag{6.7}$$

Acetylene can again react with the C, form C_3 , and release molecular hydrogen. Also at the same time, it can also react with the shock-heated Si atoms and produce SiC₂H (MacKay & Charnley 1999) The following reactions can be written as

$$C_2H_2 + C \rightarrow C_3 + H_2 \tag{6.8}$$

$$C_2H_2 + Si \rightarrow SiC_2H + H \tag{6.9}$$

The SiC₂H can further react with C and can form SiC₃ (MacKay & Charnley 1999) via the following reaction:

$$SiC_2H + C \rightarrow SiC_3 + H$$
 (6.10)

 SiC_3 can contribute to the formation of larger $(SiC)_n$ clusters. Whereas in the gas phase, both Si and C can react and form SiC.

$$C + Si \rightarrow SiC$$
 (6.11)

There are also possibilities of forming various gas phase hydrocarbon and organosilicon molecules by the reactions amongst the excited C, Si and H₂ (Accolla *et al.* 2021, Martínez *et al.* 2020, Santoro *et al.* 2020). However, in this present study, we have not analysed the gas phase products. Hence no separate discussion has been carried out on the gas phase molecules in the shocked gas.

6.4. Astrophysical Implications:

The C-rich AGB stars show strong infrared excess, which can be attributed to the combined presence of amorphous carbon and SiC (Groenewegen 1995). The gas in the inner region of AGB stars comprises H₂, H, He, CO, C₂H₂, CH₄, and organosilicon molecules such as SiH₄, SiC₂, Si₂C, SiC₃, SiC₄, SiCN, SiH₃CN, CH₃SiH₃ etc. (Accolla et al. 2021, and the reference therein). Pulsations from the AGB stars can create shock waves which propagate away from its photosphere and subsequently alter the layer of the gas in the propagating medium (Bowen 1988, Cherchneff et al. 1992). These pulsation-created shock waves usually have a velocity of around < 20 km s⁻¹ and do not have sufficient energy to ionise the atoms and molecules present in the medium. However, these low-velocity shocks can thermalize the gas and dust in its path (Fox & Wood 1985). This in turn can produce vibrationally and electronically excited C and Si atoms from the amorphous carbon, hydrocarbon molecules and organosilicon molecules. These excited atoms can react with the hydrocarbon molecules or radicals via eqns (6.9-10), as suggested by McKay & Charnley (1999) and leading to the formation of Si-C bonds, which served as a basic building block of the SiC dust. Our work shows that in extreme shock conditions, ~ 5.3 M and reflected shock temperatures of ~ 6400 K, elements C and Si can react to make biphase SiC dust along with various other carbon nanostructures such as carbon nanoribbons, MWCNT, nanobud, and graphite in the presence of hydrogen. This finding suggests that the presence of low-velocity shocks within the envelopes of carbon-rich AGB stars can trigger the formation of SiC and various types of carbon allotropes.

6.5 Conclusions:

We studied the fate of a mixture of amorphous carbon (particle size < 100 nm) and Si nanopowder under extreme shock conditions (5.3 M, 6400 K) in the presence of hydrogen. The analysis of the shocked sample showed the presence of bi-phase SiC, both cubic (β) and hexagonal phase, with the dominance of β - SiC. Also, we observed the presence of various carbon nanostructures such as carbon nanoribbons, MWCNT, nanobud, and graphite. Results from this experiment suggest that SiC and other graphitic carbon nanostructures could be an abundant and early high-temperature condensate product in the low-velocity shock-processed region of C-rich AGB stars. In the future, we will explore the formation route of other astrophysically relevant organosilicon molecules, such as SiCN, Si₂C, SiH₃CN etc., via shock processing.

Chapter 7 Shock Processing of an organometallic Dust: Ferrocene

Chapter overview:

This chapter reports the experimental results of shock processing of a cosmic organometallic dust analogue, ferrocene. The primary objective of this work was to investigate the fate of organometallic dust when they are exposed to the extreme ISM shocks. Both pre and post shocked samples were analysed using techniques like XRD, Raman Spectroscopy, ATR-FTIR Spectroscopy, HR-TEM, EDX spectroscopy and VSM. The results from our analysis show that a non-magnetic dust composed of molecules containing transition metals undergoing shock processing in the ISM can dissociate and synthesize dust that is then magnetic. Such drastic transformations from non-magnetic to magnetic dust, induced by shocks, might be of importance in influencing interstellar polarization.

7.1 Introduction:

Organometallics have been considered to be one of the important components of interstellar and cometary dust (Serra *et al.* 1992). In general, any organometallic compound is defined as [$TM_nL_mAr_o$], where *n*, *m*, *o* are the integers and *TM* is any transition metal like Fe, Ni, Cr, and *L* is any type of ligand molecule such as a hydrocarbon chain, CO, etc., which serves as an electron source and, *Ar* is any aromatic molecule (Fioroni 2016). Signatures of organics are widely present at various parts of the ISM as well as in our solar system bodies (Kwok 2011). Depending on the abundance of the organic ligand molecules and aromatics, various kinds of iron-bearing organometallic molecules have been proposed to be present in the ISM as well as in the solar system (Serra *et al.* 1992, Klotz *et al.* 1996). The presence of various polyynes ($-C \equiv C -$)_n have been reported in the ISM (Broten *et al.* 1978, Galazutdinov *et al.* 2001) and CSM (Souza & LUTz 1977, Bernath *et al.* 1989, Hinkle *et al.* 1988, Fonfría *et al.* 2018). Iron in the form of clusters could also be attached to polyynes and form a particular class of molecule known as iron pseudocarbyne (Tarakeshwar *et al.* 2019). Carbonyls group can also serve as a ligand in which nascent

iron could be locked up. Iron pentacarbonyl (Fe(CO)₅) has also been proposed as an important component of cometary dust (Huebner 1970).

Collisions between the larger Polycyclic Aromatic Hydrocarbon (PAHs) found in the ISM (Li 2020, Candian et al. 2019, Tielens 2013, Tielens 2008) and in the solar system bodies (Moreels et al. 1994) and Fe ions in the gas phase are postulated to lead to the formation of a stable Fe- PAH complex (Serra et al. 1992). Experiments have also shown the formation of a stable organometallic cluster due to the collisions between the PAHs precursors like benzene, and smaller PAHs naphthalene, and iron cations in the gas phase (Boissel 1994, Szczepanski et al. 2006, Boissel et al. 1995). Recently cyclopentadiene has been detected in the dark molecular cloud TMC-1 along with two other hydrocarbons viz. cyclopropenylidene and indene (Cernicharo et al. 2021a). Cyclopentadiene under terrestrial conditions is known to react with iron cations in the gas phase and can make the simplest organometallic molecule ferrocene ($Fe(C_5H_5)_2$) (McKee 1992). It has a sandwich-like structure in which an iron atom is trapped in between two pentagonal hydrocarbon rings (Wilkinson et al. 1952). In the ISM, the formation of any molecule depends on the energetic of the reactions involved processing and rates between the abundant elements/atoms/molecules. Reactions leading to the formation of ferrocene in space, both in the gas phase or mediated by solid-phase processes are not known. Also, the dipole moment of ferrocene is "Zero" (Mohammadi et al. 2012). It therefore cannot be detected using sub-mm observations. Considering all the factors discussed in this paragraph, we contemplate ferrocene as a proxy of organometallic dust in the ISM.

Ferrocene first discovered in the laboratory in the 1950s, and ferrocene-based molecules have an enormous impact on organometallic chemistry due to their involvement in catalytic reactions, charge transfer processes, and polymer reactions (Heinze & Lang 2013). In nanotechnology, ferrocene has been used as a catalyst and a source of carbon for the growth of carbon nanostructures (Barreiro *et al.* 2006, Moisala *et al.* 2006). Photoprocessing followed by heating of ferrocene has been shown to form iron-bearing carbon nanostructures (Elihn *et al.* 2007). High pressure (8 GPa) and high temperature (500 to 1200 K) processing of ferrocene has also been shown to result in the formation of iron-carbide nanostructures (Davydov *et al.* 2014, Baskakov *et al.* 2018). However, despite its importance in terrestrial organometallic chemistry, the role of ferrocene in organometallic astrochemistry has received little attention. Owing to the importance of organometallics in

astrochemistry, there is a need to carry out a series of experiments to understand their evolution under extreme conditions.

In **Chapter 2**, we discussed the importance of low-velocity shock waves (3 < M < 10) in the interstellar and circumstellar dust and molecular enrichment process. Here, we investigated the effects of low-velocity shock processing on ferrocene nano powder (~ 1.8 km s⁻¹). The ferrocene powder precursor was exposed to shock waves with a magnitude of approximately 5.6 M for a duration of 2 ms, resulting in an estimated reflected shock temperature of around 7300 K.

7.2 Experimental Methodology:

Shock processing of the cosmic organometallic dust analogue, ferrocene was carried using the HISTA which has been described in **Chapter 3**. Helium was used as the driver gas, while argon was used as a driven gas. The experimental parameters employed are shown in **Table 7.1**. Further information regarding the experimental procedure, the technique employed to measure the shock speed from the pressure response curve, and the estimation of the reflected shock temperature (T_5) using the R-H jump equation can be found in **Chapter 2, and 3** of this thesis. Following the shock processing, solid residues were collected and subjected to analysis using various techniques, including Raman Spectroscopy, XRD analysis, HR-TEM imaging technique, EDX spectroscopy, IR Spectroscopy, VSM analysis.

Amount	0.1 g	
Driven Pressure (P ₁)	0.1 bar of Ar	
Bursting Pressure (P ₄)	68.5 bar	
Mach Number (M)	~ 5.3	
Reflected Shock Temp (T ₅)	7300 K	

Table 7.1: Details of the experimental parameters used to include the shock bursting pressure (P_4) Mach number (M), reflected shock temperature (P_5) .

7.3 Results and Discussion:

7.3.1 XRD Analysis:

The XRD pattern of ferrocene is shown in **Fig 7.1(a)**, we can observe all of the intense peaks within the small-angle value of $2\theta \sim 10^{\circ} - 30^{\circ}$. This indicates that the patterns originated due to X-ray diffraction from the planes with larger inter-planar spacing. From crystallography, it is known that the ferrocene molecular crystal belongs to P2₁/a space group and it has a monoclinic unit cell with lattice parameter, a= 9.00 Å, b= 7.52 Å, c=5.94 Å, β =92.5° (Eiland & Pepinsky 1952). In the work by Baskakov et al. 2018, they observe a broad low-intensity pattern of ferrocene around 45°. In our XRD pattern, such a feature is missing. A possible reason for this was the X-Ray source used in our analysis. We used the Cu Ka radiation source, which produces X-ray fluorescence while interacting with iron-based systems (Klug & Alexander 1974, Mos *et al.* 2018). Baskakov et al. 2018 used a Co Ka radiation source to record the XRD pattern. Co Ka doesn't produce fluorescence emission while interacting with Iron-based materials (Klug & Alexander 1974, Mos *et al.* 2018). That is the reason in our case, the low-intensity peak of ferrocene around 45° could be suppressed because of the presence of fluorescence.

Fig 7. 1 (b) shows the XRD pattern of the shocked processed (5.6 M, 7300 K) sample which was smoothed using a robust Savitzky–Golay (S-G) algorithm (Savitzky & Golay 1964) that can preserve features of the input distribution such as maxima and minima while effectively suppressing noise. These features are generally flattened by other smoothing technique (Savitzky & Golay 1964). In our case, the S-G method was used with a 2nd order polynomial, and a smoothing window of 25. There are very well-separated peaks in the $2\theta \sim 30^{\circ} - 70^{\circ}$. The peaks marked by blue arrows are assigned to the Fe-Fe₃C composite (JCPDS Card Files, No. 89-2867, (Bagramov et al. 2012, Baskakov et al. 2018) where the most intense peak is around 43.5° and the peak around 64° are two wellrecognized peaks of α -Fe. A few low-intensity peaks of iron carbide can be seen around the intense peak, about 43.5°, marked by blue arrows. α -Fe is the most stable form amongst the allotropes of iron. Features of Fe₃C, including the low-intensity peaks, which we observe as shoulder peaks, are quite prominent in the XRD pattern shown by Bagramov et al. (2012), and Baskakov et al. (2018). This again is because of the type of X-ray sources (high back ground in our case) used by us. We find the crystallinity of iron carbide produced by Baskakov et al. 2018 is better which contributes to differences in the XRD pattern (formation pathway used by them is different from ours). Here our objective was not to produce good quality iron carbide; instead, our interest was in understanding the evolution of the organometallic dust analogue ferrocene when subjected to a low-velocity ISM like shock produced in the lab. From the crystallographic point of view Fe₃C, known as cementite belongs to the Pnma space group, and has an orthorhombic unit cell with the parameters a=5.059 Å, b= 6.07 Å, c= 4.500 Å (Baskakov *et al.* 2018). In our sample, the broad pattern around 26°, as marked by a black filled circle in the upper panel of Fig. 7.1, indicates the possible presence of carbon (JCPDS Card Files, No. 75-1621) having different degrees of graphitization, which can be seen in the HR-TEM images (**Fig 7.3**). In the work by Baskakov *et al.* (2018) they observed a sharp peak around 30°, which they assigned to graphite (002). The peaks around 38.3°, 44.6°, 64° indicate the presence of Al in the shock processed sample, which originates from the rupture of the Al diaphragm in the shock tube. Hence, from our XRD analysis, it is clear that shock-processing turned ferrocene in to carbon and iron carbide composite systems.



Fig 7. 1: (a) the XRD pattern of the ferrocene in Fig 7. (b) is the XRD pattern of the shock processed (5.6 M, 7300 K) sample. The blue arrows show the presence of Fe $-Fe_3C$ composite, the black circle indicates the graphite-like carbon feature and, the stars show the presence of Al in the shock processed sample (A. Roy et al. 2022a).

7.3.2 Raman Spectroscopy:

Raman spectra of the pristine ferrocene (marked as black) and its shock processed counterpart are shown in **Fig 7. 2**. From the symmetry of the molecule, it is known that ferrocene has 15 Raman active vibration modes (Bodenheimer *et al.* 1969) that are either inter-ring or intra -ring vibrations. In **Fig 7. 2**, we can see a doublet appears around 350 cm⁻¹. This feature corresponds to the inter-ring vibrational motion, where the most intense peak is around 314 cm⁻¹ due to the symmetric ring metal stretching mode (Long & Huege 1968). The relatively less intense doublet around 395 cm⁻¹ represents the symmetric tilt of the ring (Long & Huege 1968). The peak around 1074 cm⁻¹ is due to the symmetric ring breathing motion (Long & Huege 1968). A relatively less intense peak is seen around 1424 cm⁻¹ which is assigned to the symmetric stretching vibration of carbon atoms in the ring (Long & Huege 1968). The intense spectral feature around 3130 cm⁻¹ is due to the -CH symmetric stretching motion (Long & Huege 1968).

In Fig 7. 2, we also show two Raman spectra of shock processed sample recorded from two different places of the same sample. These spectra have the same features and fewer bands than their un-shocked counterparts. Two broad spectral features exist, around 1348 cm⁻¹ and about 1593 cm⁻¹. The broadband around 1348 cm⁻¹ is known as the D band. This band appears due to the defect present in the carbon system. The broad band around 1593 cm⁻¹ is designated as the G band. This G band corresponds to the in-plane vibration of the sample's sp² bonded (graphite-like) carbon atoms. We can compare our Raman spectra with the single-phase Fe₃C Raman spectra obtained by Zhang (Zhang et al. 2015). In their ranges, the D band is around 1350 cm⁻¹, and the G band is about 1590 cm⁻¹. This is a very good agreement with our results, where D is about 1348 cm⁻¹, and the G band is around 1593 cm⁻¹. These observations are consistent with our XRD results. The formation of α-Fe and Fe₃C composites could be a direct consequence of the shockinduced bond destruction as the signature of the various bonds present in the unshocked ferrocene are absent in the shocked sample. The destruction of the metal-ring bond might liberate Fe from the ferrocene, whereas the destruction of other bonds, such as the C-H, releases carbon (C) and hydrogen (H) atoms to the gas phase, where the C atoms later combine with iron to form iron carbide composites. The G band position suggests that the graphite-like carbon present in our shocked sample could be nano-crystalline graphite

(Ferrari & Robertson 2004). From Raman spectra of the shocked sample, it is difficult to conclude the morphology of the nanostructure in the sample. To obtain structural information of the shock processed sample on the nm scale, we used HR-TEM imaging.



Fig 7. 2: Raman spectra of the ferrocene and the post shocked sample. The shaded region around 350 cm⁻¹ is the signature of ring-metal and ring tilt vibrational modes present in ferrocene but absent in the shocked sample. Both spectra from different positions of a shocked sample have the same spectral features with broad D, and G bonds (A. Roy et al. 2022 a).

7.3.3 HR-TEM imaging:

HR-TEM analysis of the shocked processed samples was carried out using Titan Themis 300 S/TEM form thermo. The samples were ultrasonicated in ethyl alcohol for 15 minutes, then drop cast on a quantefoil grid and allowed to dry in a chemically inert atmosphere overnight. Before the imaging analysis started, these drop casted grids were plasma cleaned using Ar-O₂ plasma to reduce any changes of further contamination. Throughout the investigation, the HR-TEM was operated at 300 keV.

HR – TEM images of the shock processed samples are shown in Fig 7. 3. Fig 7.
3(a) shows the bright field image of the shock processed sample whereas Fig 7. 3(b-e) shows high-resolution images of the processed sample. The energy-dispersive X-ray (EDX) spectra of the processed sample used for elemental analysis are shown in Fig 7. 3(e),

indicating that most of the nanostructures in the sample are made of carbon and iron. In **Fig 7. 3(b)** we see evidence of iron carbide nano-sheets. In **Fig 7. 3(c)**, we can see carbon nanoribbons with various degrees of graphitization (marked by red arrows) attached with iron matrices (marked by blue arrows). There is also a lot of free amorphous carbon, marked by saffron-coloured arrows. **Fig 7. 3(d)** shows the presence of an iron encapsulated carbide nanostructure which has a compact iron core (d-spacing ~ 2.1 Å) of diameter ~ 10 nm, and is surrounded by the onions like carbon shells (d-spacing ~ 3.4 Å) with thickness of ~ 4 nm.

XRD and Raman spectroscopic observations show the possibility of iron carbide and free graphite-like carbon being present in the shock processed sample. HR – TEM images and EDX spectroscopy of the shock processed sample support these conclusions. From the EDX spectra, we could not find any trace of the presence of Al in the sample whose presence was observed in the XRD results. This means the contribution of Al, if any, in forming nanostructure as an impurity is negligible.



Fig 7. 3: HR- TEM images of the shocked sample with different scale (a-d) and EDX spectra (e) of the shock processed sample (Roy et al. 2022a).

7.3.4 Infrared Spectroscopy:

The Attenuated Total Reflectance (ATR) mid-infrared spectra of both pre and postshocked samples were collected at room temperature using Nicolet IS 50 FTIR Spectrometer. During the spectra collection, we set the resolution of the spectrometer at 2 cm⁻¹ and the average scanning period was around 1.26 mins. The spectra of both ferrocene and shocked samples are shown in **Fig 7. 4.** For the ferrocene, we can see multiple prominent peaks around 3.2, 7.10, 9.05, 10, 12.31, 12.69, 20.57, and at 21.2 μ m. These are very well-known IR features of ferrocene (Lippincott & Nelson 1958). But for the shocked processed sample, its IR spectra remain featureless. This shows that almost all of the ferrocene sample was converted to Iron carbide- carbon composite. This observation is also consistent with Raman and XRD results which reveal that ferrocene turned to iron carbide composites and graphite like carbon is confirmed by G and D bands appeared in Raman spectra after shock processing.



Fig 7. 4: ATR-FTIR Spectra of the Solid ferrocene (black) and the shocked sample (red) at room temperature (Roy et al. 2022 a).

7.3.5 Magnetic Response:

We have studied the magnetic response of both shocked and unshocked samples. Initially the magnetic response of the ferrocene sample before and after the shock was observed by video recording in the presence of a bar magnet (**c.f. Supplementary video** - **1**). It was observed that the initial ferrocene samples did not respond to the magnetic field because of its diamagnetic nature, whereas shocked processed residue of ferrocene showed a strong response. In order to quantify the magnetic properties of the shocked sample, we used a VSM. About 30 mg of shocked sample was placed in the VSM to obtain the magnetic properties at room temperature. The response of the shocked sample in an external magnetic field up to 2 T or 20,000 Oe has been traced as a hysteresis loop as shown in **Fig 7. 5**, the results are typical of a sample demonstrating ferromagnetism. The measured parameters associated with a ferromagnetic sample such as Saturation Magnetization (M_s), Remnant magnetization (M_R), and Coercivity (H_c) are listed in **Table 7. 2**.

Parameters	Values		
Saturation Magnetization (Ms)	$0.887 \text{ A} \text{ m}^2 \text{ kg}^{-1}$		
Remnant Magnetization (M _R)	$0.154 \text{ A} \text{ m}^2 \text{ kg}^{-1}$		
Coercivity (H _c)	423 x10 ⁻⁴ T		

Table 7. 2: Magnetic properties of the Shocked Sample (Roy et al. 2022 a)

This response curve (**Fig 7. 5**) supports the conclusions based on the results obtained from XRD, HRTEM imaging, and the Raman spectra showing the possible presence of Iron carbide systems, which are known to show ferromagnetic behaviour (Sajitha *et al.* 2004). A finite area of our hysteresis loop indicates that our sample has no superparamagnetic constituents, as superparamagnetic particles do not have any coercivity (Huber 2005). Iron contributes most to the magnetization of the iron carbide systems. Its presence can be seen in the EDX spectra in **Fig 7. 3(e).** The magnetic properties of the iron nanoparticles can be influenced by its chemical surroundings (Huber 2005). It has been reported (Wang *et al.* 2017, Wu *et al.* 2011, Sajitha *et al.* 2007, Sajitha et al. 2004) that

wrapping of carbon on iron or iron carbide nanoparticle leads to the reduction of saturation magnetization. In our shocked sample, the major product is carbon. HR-TEM images of our shocked sample showed the presence of carbon encapsulated iron nanoparticles (Fig 7. 3 c, d), where surface reactions with iron and carbon atoms might have taken place. Any bond made due to the interaction via the d orbital has a directional dependency. So when an iron atom at the surface of an iron nanoparticle make any bond with any other atoms or molecules, it leads to the freezing of its spins in a particular direction. Because of that when an external magnetic field is applied to that system, those atoms won't be able to orient their spins towards the filed direction and ultimately reduce the magnetization (Huber 2005). Also, low iron carbide content in the shocked sample can be another reason for low saturation magnetization for our shocked sample. Very low saturation magnetization and high coercivity of our sample as compared to the iron carbide sample prepared from ferrocene (Sajitha et al. 2007, Sajitha et al. 2004), indicates that we produce hard ferromagnetic iron carbide – carbon composite using shock processing.



Fig 7. 5: The magnetization curve of the shock-processed sample (Roy et al., 2022a) is depicted in the figure. The top solid arrow indicates the magnetic saturation (M_s) , while the blue-colored arrow represents the magnetic retentivity (M_R) , and the dash-dot black arrow denotes the magnetic coercivity (H_c) .

In the shock tube, the processing time is limited; in our system, it is around 2 ms. So, the reflected shock pressure and temperature play a vital role in the conversion from the reactant to the product (Bhaskaran & Roth 2002). The conversion rate from the reactant to the product in the shock tube varies with the processing temperature (Bhaskaran & Roth 2002). Ferrocene's vapor pressure is 1.296 Pa at room temperature (Monte et al. 2006), and it will start sublimating during the arrival of the incident shock front, which raises the temperature to around 2000 K, later it is also processed to the elevated reflected shock temperature (around 7300 K). The conversion process can be tracked using the optical technique suggested by Sommer et al. (1996) and the references therein. In our experimental set-up, we did not employ any optical measurement system, so any in-situ measurement related to the efficiency of the entire conversion process is difficult to calculate. However, we tried to understand the conversion using XRD, IR, and Raman spectroscopic techniques. From those analyses, we can conclude that shock processing of ferrocene leads to formation of iron carbide -carbon composites, which have an iron core of 10 nm and are surrounded by onion-like carbon shells of around 4 nm. The carbon shell around the iron nanoparticles provides better stabilization of its magnetic property by minimizing the flipping of the magnetic moments caused by thermal fluctuations (Wu et al. 2011). This structure also acts as anti-oxidation layer to the iron core and enhances its chemical stability (Wu et al. 2011). We also observe the presence of carbon nanoribbons, an iron carbide nano-sheet, and amorphous carbon in the shock processed sample. Previously these kinds of structures were synthesized from ferrocene at very high pressure and temperature (8 GPa, 500 -1220 K) and exposures of 20 secs in each temperature zone (Davydov et al. 2012, Baskakov et al.2018). These experiments have shown the transformation of amorphous iron carbide composite to its crystalline form Fe_7C_3 and then its transformation to crystalline Fe₃C with the isobaric stepwise increment of temperature. However, in our experiment ferrocene was subjected to an intense shock (5.6 M) for 2 ms resulting in a reflected shock temperature of up to 7300 K. Hence the shocked dust samples are the product of ultra-fast (2 ms) thermal processing from room temperature to ~ 7300 K at the rate of $\sim 10^6$ K s⁻¹, compared to, the multistep formation pathway showed by Davydov et al. (2012) and Baskakov et al.(2018) by thermally processing the sample up to ~ 2000 K by slow heating rate using a toroidal high pressure cell in a graphite heater.

Elihn *et al.* (2007) have shown the formation of iron carbide composite using 193 nm, 15 ns pulse duration ArF excimer laser ablation. To understand the shock-induced

thermal decomposition of ferrocene we can refer to the molecular dynamics simulations and DFT calculations obtained by K. Elihn and Larsson (Elihn & Larsson 2004); According to these DFT calculations the energies of various bonds present in ferrocene are 492 kJ mol ¹ (C-H), 602 kJ mol⁻¹ (C-C), and 1480 kJ mol⁻¹ (Fe-C ring). Hence in high intensity shocks, we can expect a sequence of bond breaking resulting in the decomposition of ferrocene. First, at 2000 K, the C-H bonds will break apart and release hydrogen into the gas phase. A large amount of carbon will be released due to the destruction of C-C bonds in the rings and then, later, the metal ring bonds will break and release iron. The entire process can take place within 300 fs (Elihn & Larsson 2004), much faster than our experimental shock exposure time scale (2 ms). The carbon produced due to the destruction of C-C bonds should be placed into the vapour phase during the shock wave exposure (Bundy 1989) but when the temperature drops below 4000 K the carbon present in the vapour will start to nucleate (Bundy 1989) to form the complex carbon nanostructures as seen at Fig 7. 3. Nucleation of carbon from its shocked processed vapour phase can give rise to different carbon nanostructures starting from Carbon nanoribbons to fullerene, carbon nanotubes to graphene (Roy et al. 2022b), where carbon nanoribbons are the most dominant component. Here in our TEM images in Fig 7. 3 we observed the presence of carbon nanoribbons, carbon nano sheets, and amorphous carbon too. The role of iron as catalyst during the growth of carbon nano structure can't be ignored. The presence of graphitic shells around iron nanoparticle as shown in Fig 7. 3d can be the consequences of metal mediated crystallization process (Ramirez et al. 1999).

7.4 Astrophysical Significance:

The results obtained in this experiment have some implications for dust recycling in the ISM. Dust throughout its life cycle moves back and forth between various forms and phases (Jones 2004). This experiment shows that shock processing of the organometallic dust analogue, ferrocene, results in the formation of Fe – Fe₃C composites and graphitelike carbon. Iron carbide composites have been considered as a component of ISM dust (Moseley 1980). The presence of Fe₃C in the shock processed sample is therefore an indication of a possible transformation pathway from one phase of dust to another phase. We also have α -Fe and the amorphous carbon in the shock processed sample. This is a clear indication of shock-induced elemental recycling in the ISM. From our experiments, it is also clear that organometallics not only play a role as a catalyst but it can also serve as a source of carbon during the growth of carbon dust in ISM. Apart from the extinction of background starlight, dust present in ISM can also manifest itself through its ability to polarize incident light. The well-accepted reason for interstellar polarization is the collective alignment of elongated dust grains along a particular direction (Shapiro 1975). This can be either magnetic alignment or radiative alignment (Krügel 2002). Various iron-bearing molecules starting from iron oxides sulphides (Draine & Hensley 2013, Draine & Lazarian 1999) and hydrides (Bilalbegović *et al.* 2017) have been proposed as a potential candidate for magnetic dust. These kinds of dust can orient themselves along the galactic magnetic field lines and could contribute to interstellar polarization. In our experiment, we have shown shock-induced transformation from diamagnetic ferrocene to ferromagnetic iron carbide composites. This implies that if organometallics, like ferrocene, present in ISM are exposed to the shock conditions, they produce iron-bearing ferromagnetic composites which can then orient themselves and so contribute to the interstellar polarization.

Observations of 20 different comets in various regions of our solar system, spanning heliocentric distances from 0.68 AU to 3.8 AU, have revealed the presence of neutral iron and nickel atoms (Manfroid et al. 2021). Previously, iron signatures were only observed in two sungrazing comets: the 'Great Comet of 1882' (Burke-Gaffney 1968) and comet 'C/1965 SI (Ikeya-Seki)' (Thackeray et al. 1966). Interestingly, the presence of iron and nickel signatures was detected in comets located at a considerable distance from the Sun (~3.8 AU). At such distances, the temperature of cometary nuclei is not high enough to sublime refractory dust containing iron. Organometallic molecules have been proposed as a component of cometary dust (Serra et al. 1992). The impact of hypervelocity micrometeorites on a cometary organometallic molecular matrix can raise the temperature to several thousand Kelvin, leading to the ejection of attached metal atoms (Manfroid et al. 2021). Our study demonstrates that shock processing (5.6 M, 7300 K) of the organometallic dust ferrocene can effectively release α - Fe through the disruption of its the ring metal bond. This finding can be a good complement to the proposed mechanism of impact induced release of neutral Fe (Manfroid et al. 2021) from the organometallic molecules present in distant comets, such as in comet 103P/Hartley.

7.5 Conclusion:

Through high-intensity shocks (~ 5.6 M, estimated ~ 7300 K), we investigated the behaviour of ferrocene as a representative of organometallic dust in the interstellar medium

(ISM), and circumstellar medium (CSM). Analysis of the post-shocked samples revealed the presence of composite materials, including α -Fe and Fe₃C, in conjunction with graphitelike carbon. Furthermore, we observed the formation of nanostructures consisting of carbon nanoribbons and carbon-encapsulated iron nanoparticles. These findings suggest that organometallic compounds such as ferrocene can contribute to the formation of carbon nanostructures in regions of the ISM and CSM that have undergone shock processing.

Additionally, our study demonstrated the transformation of diamagnetic ferrocene into magnetic α -Fe and Fe₃C through shock processing. Dust particles with magnetic properties are known to play a significant role in the polarization of starlight, aligning themselves with galactic magnetic field lines. Therefore, the sudden change in magnetic properties induced by shock fronts may contribute to dynamic changes in light polarization in the ISM.

Furthermore, our findings provide additional support for the proposed mechanism of impact shock-induced release of neutral iron into the cometary coma of distant comets.

Chapter 8 Shock Induced Formation of Interstellar Mineral Dust

Chapter overview:

Signatures of minerals are often detected in different parts of our galaxy and our solar system. Cosmic mineral dusts have been thought to be produced in the outflows of evolved stars via gas phase condensation. In this chapter explores the formation of astrophysically relevant mineral dust, such as olivine, MgO behind the shock front. A shock tube was used to create low-velocity shock conditions ($< 10 \text{ km s}^{-1}$) typically observed in the atmospheres of early type stars. Using a high-intensity shock tube, we studied the processing of different cosmic mineral dust precursors with shock strength ~ 5.6 M and temperature ~ 7300 K. The analysis of the processed samples showed the presence of Mg-rich olivine, MgO, and magnetite. This result suggests that shock waves can also induce dust formation in the interstellar space. Additionally, the results of this work also showed that shock processing could create crystalline silicate dust in comets and cause the formation of chondrules observed in the chondritic meteorite.

8.1 Introduction:

Silicate-type mineral dust has been detected for decades in different astrophysical regions using their 10 μ m and 20 μ m IR spectral features corresponding to Si-O stretching and O-Si-O bending vibrations (Henning 2010). These spectral signatures have also been observed in comets (Wooden 2008, Kelley & Wooden 2009), Hanner & Zolensky 2010), and asteroids (Feierberg *et al.* 1983, and Cruikshank *et al.* 2006), and in the interplanetary medium as Interplanetary Dust Particles (IDP) (Bradley 2010). A large fraction of observed interstellar silicate dust grains has been proposed to be amorphous with pyroxene or olivine stoichiometry (Gürtler & Henning 1986, Chiar & Tielens 2006, Min *et al.* 2007, Van Breemen *et al.* 2011). Crystalline silicate dust only accounts for < 5 % of the entire interstellar silicate dust population (Kemper *et al.* 2004).

The backbone of silicate class dust is the $[SiO_4]^{4-}$ tetrahedra (Jäger et al. 1998). To achieve charge neutrality, it interacts with fellow SiO₄ tetrahedrons or can react with abundant cations such as Mg²⁺, Fe²⁺ etc. Astrophysically-relevant silicate dust, olivine is usually expressed by a general formula Mg_{2x}Fe_{1-x}SiO₄, where x is the concentration of Mg in the system, and when x=0, it makes Fayalite (Fe₂SiO₄), whereas, for x=1 it makes forsterite (Mg₂SiO₄). Here the isolated SiO₄ tetrahedrons are linked with the divalent cations. For pyroxene, the SiO₄ tetrahedrons are linked with each other and make a much more complex structure than olivine. The pyroxene class of dust is usually defined as Mg_xFe_{1-x}SiO₃, where x varies between 0 and 1. For x=0, the iron-rich end member is called ferrosilite (FeSiO₃), and the Mg-rich end member (x=1) is called enstatite (MgSiO₃) (Henning 2010). SiO₂ is a special case where all the corner O atoms in the SiO₄ tetrahedra are linked with the nearby SiO₄ tetrahedra, and no cations are used for charge neutrality (Henning 2010). A detailed discussion on the structural properties and its influence on the spectral properties of the silicate dust can be found in **Chapter 1**.

Formation pathways of interstellar silicate dust grains are still in an evolving phase and various experiments and theory-based formation pathways have attempted to understand the formation of interstellar silicate dust. Dorschner et al. (1995) synthesized pyroxene and olivine-type composite silicate glasses using a melting and quenching technique. Using the Sol-Gel method, Jäger et al. (2003) successfully synthesized interstellar silicate dust by polymerizing silicate in the liquid phase at low temperatures. Koike et al. (2003), and Chihara et al. (2002) applied a crystal growth technique to prepare an astrophysically relevant silicate dust analogue. Research groups like Day (1979), Nuth III et al. (1986), Scott & Duley (1996), showed a formation pathway of interstellar silicate dust using gas phase condensation experiments. Laser-induced pyrolysis and laser ablation techniques has also been explored to prepare ISM silicate dust analogues. Sabri et al. (2013) produced pyroxene and olivine-type silicate dust analogue using laser pyrolysis from a pyroxene and olivine-type stoichiometric mixture. Rouillé et al. (2014) investigated the formation of Mg and Fe-rich silicate dust on a cold dust surface by condensing laserproduced vapour and followed by thermal annealing. The grains produced in this method have a spherical shape with nm order diameter, and it exhibit IR features similar to cosmic silicate dust in the 10 and 20 µm spectral regions. Nevertheless, ion-induced processing of dust grains in different regions of ISM can play a significant role in the interstellar dust life cycle. Jäger et al (Jäger et al. 2016) investigated ion-induced processing of amorphous

silicate grains using protons and Ar⁺ ions with different energies. The results of these ion bombardments on the silicate grains lead to the formation of glassy grains with embedded metals often observed in IDPs and meteorites.

In the previous chapters, we have investigated the formation (**Chapter 4-6**) and processing (**Chapter 7**) of cosmic carbonaceous dust analogues by exposing dust precursors to low-velocity shocks with speeds around 1.8 km s⁻¹. Owing to the importance of the low velocity shocks in interstellar chemical enrichment processes, which we have already discussed in the **Chapter 2**, this chapter focuses on investigating the shock-induced formation pathway of cosmic mineral dust. Our study involves the examination of low-velocity (1.8 km/s, 5.6 M) shock processing of stoichiometric mixtures of cosmic silicate dust analogues, namely Mg + SiO₂ (1:1) referred to as M1, M1 + Fe (1:1) referred to as M2, and Fe + SiO₂ (1:1) referred to as M3.

8.2 Methodology:

The High-Intensity Shock Tube for Astrochemistry (HISTA) developed inhouse at Physical Research Laboratory, Ahmedabad, has been used to carry out shock processing of the stoichiometric mixtures like interstellar silicate dust analogue samples named M1, M2, and M3. Details of the composition of M1, M2, and M3 dust analogues can be found in **Table 8.1**. Details description of HISTA, its working principles and procedure, sample preparation, Mach number measurement technique, reflection shock temperature and pressure calculation are documented in detail in Chapter 3. About 0.1 gm of M1, M2 and M3 samples were separately shock processed using shock wave with Mach 5.6 and reflected shock temperature ~ 7300 K for 2 ms. Details of the experimental parameters such as diaphragm bursting pressure (P₄), driven pressure (P₁), Mach Number (M), and reflected shock temperature (T₅) used in this experiment can also be found in Table 8.1.

After the shock processing, the samples were carefully collected both the inner walls of the HISTA, and from its end flange. These collected samples were analyzed using techniques like Attenuated Total Reflectance (ATR) FTIR Spectroscopy, X-ray Diffraction analysis (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), and High-Resolution Transmission Electron Microscopy (HR-TEM) Technique.

Sample Details	Bursting Pressure (bar) (He as driver gas)	Driven gas (Ar) Pressure (bar)	Mach (M)	Reflected Shock Temperature (T ₅) (K)
$\begin{array}{rrr} M1 = & Mg & + \\ SiO_2 (1:1) & & \end{array}$	68.5	0.1	5.6	~ 7300
M2= M1+ Fe (1:1)	68.9	0.1	5.6	~ 7400
M3=Fe+SiO ₂ (1:1)	67.8	0.1	5.6	~ 7340

 Table 8. 1: Sample details along with experimental parameters.

8.3 Results and Discussions

FT-IR Spectroscopy:

ATR-FTIR spectroscopy can provide valuable insights into the samples' composition, molecular vibrations, and structural changes, both before and after exposure to a shock. The comparison between the unshocked and shocked samples' spectra can help identify the effects of the shock wave on the material's molecular and structural characteristics. The ATR-FTIR spectroscopy of the shocked and unshocked sample was carried out using a diamond attenuated total reflectance module attached to the Nicolet IS50 FTIR spectrometer. Using a Polaris IR source (9600 – 10 cm⁻¹), solid substrate beam splitter (> 1000 – 10 cm⁻¹), and a DLaTGS-KBr detector (12500 – 350 cm⁻¹), we retrieved the MIR to FIR (up to 35 μ m) spectra of the sample. Throughout spectra collection, the spectrometer's resolution was 2 cm⁻¹, the acquisition time was 1 minute 32 secs, and the pressure applied to the sample during the analysis was approximately 60 lbs.

Sample M1:

The ATR – FTIR spectra of both the shocked and unshocked samples of M1 are in **Fig 8.1**. The lower panel **Fig 8.1(a)** represents the unshocked mixture's IR spectra which have peaks around 8.4 μ m, 9.4 μ m, 10.5 μ m, 12.5 μ m, and around 22.2 μ m. The feature around 9.4 μ m is assigned to the Si-O stretching vibration, the feature around 12.5 μ m can be due to the symmetric stretching of the Si-O-Si bond (Fluxi 1979, Brinker & Scherer 1990), and the broad feature around 22.2 μ m is associated to the bending motion of O-Si-

O network. The broad peak around 9.4 μ m and around 22.2 μ m suggests that the mixture contains amorphous SiO₂ (Jäger et al.2003a).

Fig 8. 1(b) shows the MIR to FIR spectra of the shocked sample. The shocked sample's IR spectra were less intense than the unshocked sample and shifted towards a higher wavelength. It consists of many new prominent sharp features in MIR and the FIR region. The drop in the intensity for the shocked sample compared to the unshocked sample suggests shock-induced destruction of Si-O bonds of SiO₂ present in the unshocked sample. The MIR region of the spectra can be divided into two parts, from 8 to 14 μ m and 14 to 28 μm. In the 8 to 14 μm region, the two most prominent, sharp and well-spaced peaks are around 9.9 µm and about 11.1 µm. The sharp feature, around 9.9 µm, is accompanied by a shoulder band at 10.2 µm and another broad feature around 9 µm. The other sharp and intense 11.1 µm feature is also accompanied by two relatively less intense peaks around 10.4 µm and around 12 µm. The peaks mentioned above can be assigned to different asymmetric and symmetric stretching motions of Si-O bonds. The peaks within 14 to 28 μm region are at 16.2 μm, 19.7 μm, 23.8 μm, 25 μm and around 28 μm. The peaks around 16.2 µm and 19.7 µm correspond to the asymmetric and symmetric bending motion of the O-Si-O network. Whereas the peak around 23.8 µm could be due to the translation motion of metallic ion in the SiO₄ matrices. In the FIR region, an intense and narrow feature around 33 µm exists. This band is assigned to the Mg - O translation motion (Jäger et al.1998, Hennig.2010).

The factors like temperature, particle size, grain morphology and chemical composition greatly influence the IR spectra of the silicate dust. Different sharp features in the MIR and FIR region suggest that the shock-processed sample contains crystalline silicate dust. The red shift observed (inset 1 of **Fig 8. 1(b)**) in the stretching vibration of the shocked sample (~ 9.9 μ m) compared to the unshocked sample (~ 9.4 μ m) could be due to the inclusion of Mg cation into the SiO₄ network and lead to the formation of new solid solutions. A similar trend of Si-O stretching red band shift due to Mg inclusion into silicate network has already been shown by Jäger et al.2003. The Si-O-Si symmetric stretching feature around 12.5 μ m in the unshocked sample was found to be missing in the shocked sample IR spectra. This can be associated with the significant presence of MgO in the shocked sample (Jäger *et al.*2003). The broadening (inset 2 of **Fig 8. 1(b**)) of the O-Si-O bending motion band beyond 20 μ m of the shocked sample could be because of the coupling of Si-O bending and Mg-O stretching vibrations (Gervais *et al.* 1987).

Olivine dust is known to produce asymmetric stretching vibrations of the Si-O bond at 10 to 12.6 μ m and Si-O-Si and O-Si-O bending bands at 16, 20, and 23 μ m. Metal oxide translation motion dominates the FIR region between 33 and 40 μ m. The pyroxene class of dust exhibited far more complicated IR characteristics, which are substantially impacted by the degree of polymerization of SiO₄. To determine the type of solid solutions in the shocked sample, we compared our IR spectra to crystalline forsterite (Mg₂SiO₄) and enstatite (MgSiO₃) IR spectra from Jäger *et al.* (1998). This comparison suggests our shocked sample includes crystalline forsterite along with MgO. Details of the different peaks present in the shocked sample and their assignment can be found in Table 2.



Fig 8. 1: IR spectra of the unshocked sample of M1(a) and a shocked sample of M1 (b). **Sample M2:**

The ATR – FTIR spectra of both the shocked and unshocked samples of M2 are in **Fig 8. 2. Fig 8. 2(a)** represent the IR spectra of the unshocked sample containing a mixture of Mg, Fe and SiO₂ (1:1:1). Its spectral features are almost identical with the unshocked sample IR spectra of M1as Mg, and Fe powder does not show any prominent IR active bands.

The IR spectra of the shocked sample of M2 are shown in **Fig 8. 2(b)**. Compared to the unshocked sample, the IR spectra of the shocked sample show the presence of many well-spaced sharp bands both in the MIR and the FIR region. Like in the case of M1 here, we also noticed that the shock-processed sample IR spectra have shifted towards the higher

wavelength, and its intensity dropped significantly compared to the unshocked counterpart. From the 8 to 14 μ m region of MIR, the well-spaced peaks are around 9.9 μ m, 10.2 μ m, 10.4 μ m, 11.3 μ m, and 12 μ m. These bands represent different asymmetric and symmetric vibrations of Si-O bonds. From 14 to 20 μ m, the peaks are around 16.4 μ m, 18.9 μ m, 19.8 μ m, and they correspond to different asymmetric and symmetric bending motions of O-Si-O bonds. In the range beyond 20 to 28 μ m, the peaks are around 21.5 μ m, 23.5 μ m, 25.3 μ m. These features may arise because of the translation of metallic cations present in the sample. The sharp feature at 33 μ m is due to Mg-O stretching vibration.

The above discussion clearly hints metallic inclusion into the SiO₄ network and the formation of new solid solutions because of shock processing. The shock-induced metallic



Fig 8. 2: IR spectra of the unshocked sample of M2(a) and shocked sample of M2 (b).

inclusion into the SiO₄ network can cause a band shift towards a higher wavelength which we have already observed (Inset 1 and 2 of **Fig 8. 2**). Like in the case of M1 here, we also noticed that the 12.5 μ m Si-O-Si symmetric stretching feature of SiO₂ gets disappeared in the shocked sample IR spectra, and the reason behind such phenomena could be associated with the presence of MgO (Jäger *et al.*2003). The presence of a broad feature between 23 to 28 μ m may arise due to the coupling of O-Si-O bonds and the Mg-O stretching bond. The presence of well-spaced and sharp bands both in MIR and FIR regions suggest that the produced solid solution might have a crystalline structure, especially olivine type, as these peaks reside close to the well-known IR active bands of olivine (Jäger *et al.*1998). The sharp and intense 33 μ m feature suggests that the shock-processed sample contains Mgrich olivine dust (Jäger *et al.*1998, Henning 2010). To find out the chemical composition of the solid solution present in our shocked sample, we compared the IR spectra of our shocked sample with the crystalline Mg-rich olivine (Mg_{1.8} Fe_{0.2} SiO₄) IR spectra from Jäger *et al.*(1998), and it showed good agreement between two spectra. Details of this comparison along with the assignment of different bands, can be found in Table 3. This comparison indicates that the level of iron inclusion in the SiO₄ network is much less than Mg, but this has to be verified using techniques like EDX spectroscopy.

Sample M3:

The ATR-FTIR spectra of both the unshocked and shocked sample of the mixture M3 is shown in **Fig 8. 3**. The spectral feature of the unshocked sample showed in **Fig 8**. **3**(a) is almost identical to the unshocked sample of M1 and M2 and nothing much to discuss here in this section.

Compared to the unshocked sample, shocked sample IR spectra (**Fig 8. 3(b**)) do not show much variety in their spectral feature both in MIR and the FIR region. A drop in the absorbance could be due to the shock-induced destruction of the Si-O network present SiO₂. From the IR spectra of the shocked sample, it is complicated to predict what kind of solid



solution was made after shock processing of the mixture of Fe and SiO₂.

Fig 8. 3: IR spectra of the unshocked (a) and shocked sample (b) of M3.

Table 8. 2: Relative comparison between the IR active peaks present in shocked sample of M1 and the IR active peaks of Forsterite (Mg_2SiO_4) from Jäger et al. 1998.

Peak position (µm) Shocked Sample (M1)	Peak Position of Forsterite (µm) Jäger et al. 1998	Assignment
9	9.3	
9.9	10	Asymmetric stretching of Si-O bond
10.1	10.2	do
10.4	10.4	do
11.1	11.2	do
12.9	11.9	Symmetric stretching of Si-O bond
16.2	16.3	Asymmetric bending of Si-O-Si bond
19.7	19.5	Symmetric bending of Si-O-Si
23.8	23.5	Translation of Mg ²⁺
25	24.7	
27.8	27.5	
33	33.5	Mg-O stretching

Table 8.	3: Relative	comparison	between th	he IR a	ctive peaks	present in	the shocked	sample
of M2 an	d the IR act	ive peaks of	natural o	livine (I	$Mg_{1.8}Fe_{0.2}S$	iO4) from	Jäger et al.1	998.

Peak position (µm) Shocked Sample (M2)	Peak Position of Natural Olivine (μm) Jäger et al. 1998	Assignment
9		
9.9	10	Asymmetric stretching of Si-O bond
10.2	10.2	do
10.4	10.5	do
11.3	11.3	do
12	11.9	Symmetric stretching of Si-O bond
16.4	16.4	Asymmetric bending of Si-O-Si bond
18.9	18.3	
19.8	19.5	Symmetric bending of Si-O-Si
21.5	21.6	Rotation of SiO ₄
23.9	23.9	Translation of Metal cation
25.3	25.3	
33	33.5	Mg-O stretching

XRD Analysis:

Sample M1:

We carried out the X-Ray Diffraction (XRD) analysis of unshocked and shocked samples. The XRD Pattern of both shocked and unshocked sample M1 is shown in **Fig 8**.

4(a). These patterns are normalized in the same scale before plotting, and offset is used for visual clarity. Braggs equation has been employed to calculate the interplanar spacing (d) of different XRD peaks. The diffraction pattern of the unshocked sample, coloured in black, consists of a broad feature spread between 20 ° to 30 ° marked by a blue star. This indicates the presence of amorphous SiO₂. Apart from that, many well-spaced distinct peaks are marked by green stars at 32.57 °, 34.63 °, 36.82 °, 48.04 °, 57.58 °, 63.23 °, 67.60 °, 68.96 °, 70.34 °, 72.84 °, and at 78.14 °. These peaks are attributed to the Mg, which has a hexagonal lattice structure belonging to P63/mmC space group, and the corresponding lattice planes are (100), (002), (101), (102), (120), (103), (200), (122), (201), (004), and (202) (CODID: 9008506).

The XRD pattern of the shocked sample, coloured in red in Fig 8. 4(d), has many new peaks compared to its unshocked counterpart. The blue circle marks the new peaks showing the presence of forsterite (CODID: 900319). For proper indexing of those peaks, we compared our shocked sample XRD pattern with the calculated XRD pattern of forsterite, as shown in Fig 8. 4(c). This theoretical XRD pattern of forsterite was calculated using VESTA software and the unit cell information was taken from CODID: 900319. Details of Millar indices and the d spacing values of forsterite from both our shocked sample and from CODID: 900319 are shown in Table 8. 4. From the crystallographic perspective, it is well known that forsterite belongs to an orthorhombic crystal system with lattice parameters a= 4.75 Å, b=10.19 Å, c=5.98 Å, and $\alpha=\beta=\gamma=90^{\circ}$ (Downs et al, 1993). Because of its large unit cell, there can be many possible planes of reflections, which makes indexing difficult for the high 20 values (Swanson & Tatge 1951), especially after 65°. Besides forsterite, MgO is another crystalline phase observed in the shocked sample. The new peaks in the shocked sample marked by a magenta colour circle indicate the presence of MgO (CODID: 100053). Here also, we examined the MgO's observed peaks by comparing it with its calculated XRD pattern, as shown in Fig 8. 4(b). This comparison also reveals that MgO present in our sample has a cubic unit cell with a=b=c= 4.21 Å, $\alpha = \beta = \gamma = 90^{\circ}$ and belongs to Fm-3m space group. Details of the Millar indices and corresponding d spacing of MgO present in our sample can be found in Table 4. Peaks marked by yellow circles at 28.86 °, 47.59 °, and 56.40 ° are assigned to Si (CODID: 1526655), which suggests shock-induced bond destruction of SiO₂. One can also find the Millar indices and d spacing of Si in Table 4. The peaks at 38.6 ° and 44.87 °, marked by a black triangle, show Al's presence in the shocked sample, which came from the Al diaphragm used in HISTA. The presence of Mg can also be seen in the shocked sample, and green stars mark the peaks corresponding to Mg. Notice that in the shocked sample XRD in **Fig 8. 4(d)**, many peaks are marked as common for different crystalline phases. These peaks are around 32.5° , 36.8° , 62.5° ; they are shaded and denoted by 1, 2, and 3 in **Fig 8. 4(d)**. In the right-hand side of **Fig 8. 4**, three inset plots show the zoomed view of the shaded region 1,2,3. From these inset plots, it is clear that those shaded peaks are not a single peak; instead, they have multiple peaks components on both sides of the central peak. This suggests that the observed peaks may be attributed to blended reflection features resulting from the presence of numerous crystalline phases in the sample. XRD of the shocked processed sample showed the presence of Mg-rich end members of olivine, forsterite, metal oxide MgO, Si, and Mg. Amongst these crystalline phases, signatures of forsterite and MgO have already been predicted by IR spectroscopy, and XRD analysis added more values to that information. The shocked sample does not show phases like Mg₂Si, or the simplest Mg-rich pyroxene class dust enstatite (Mg₃SiO₄).



Fig 8. 4: (a) XRD Pattern of the unshocked mixture of M1, (b) synthetic XRD pattern of MgO, (c) synthetic XRD pattern of forsterite (Mg_2SiO_4), (d) XRD pattern of the shocked sample. Insets 1, 2, and 3 showed the close in view of the region marked by 1, 2 and 3 in (d).

Sample M2:

Fig 8. 5 depicts the XRD patterns of both unshocked and shocked samples of a mixture of M2 (M1+ Fe (1:1)) ranging from 20° to 90°. **Fig 8. 5(a)** shows the XRD pattern of the unshocked M2 sample. Because we combined Fe with M1 (1:1), the XRD pattern of the unshocked M2 sample has Fe peaks at 45 °, 65 °, and 82.5 °, marked by a blue triangle, and the remaining features are almost identical to what we saw in the case of M1 in **Fig 8. 5(a)**.

In Fig 8. 5(d), the shocked sample shows much more complex patterns than the unshocked sample. This shows the presence of new crystalline phases produced after the shock processing of M2. We compare the XRD of shocked M2 shown in Fig 8. 5(d) to the calculated XRD pattern of olivine shown in Fig 8. 5(c). The XRD pattern of the olivine was calculated using VESTA software, and the unit cell information was taken from CODID-1010497. From this comparison, we assigned many peaks marked by the blue circle in Fig 8. 5(d) to olivine with the formula Fe_{0.2}Mg_{1.8}SiO₄. Table 8.5 contains crystallographic data such as Millar indices and d spacing related to distinct lattice planes present in shock-produced olivine. Here we also found the signature of crystalline MgO in the shocked sample, and its XRD peaks are marked by a magenta colour circle shown in Fig 8. 5(d). The calculated XRD pattern of MgO (CODID; 1000053) can be found in Fig 8. 5(b). we compare the peaks marked by a magenta colour circle in Fig 8. 5(d) with Fig 8. 5(b). The details of the Millar indices and the d spacing of MgO present in shocked sample of M2 are tabulated in Table 5. The other peaks observed here are due to Mg, marked by green stars, and iron, marked by the blue triangle. Signatures of Al are also present and marked by a black star in Fig 8. 5(d), which comes due to the rupture of the Al-made diaphragm used in HISTA.

We observe the presence of new crystalline phases of olivine and MgO in the shocked sample of M2. The comparison with the XRD data from CODID-1010497 showed that shock-produced olivine is Mg-rich, and the extent of iron inclusion is significantly less. Here we can not observe any presence of compounds like Iron oxides and pyroxene class of dust.



Fig 8. 5: (a) XRD pattern of the unshocked sample of M2, (b) calculated XRD pattern of the MgO, (c) calculated XRD pattern of Olivine ($Mg_{1.8}Fe_{0.2}SiO_4$), (d) XRD pattern for the shocked sample of M2.

Sample M3:

The XRD pattern of both the pre and post-shocked mixture of M3 (Fe and SiO₂ (1:1)) is shown in **Fig 8.6**. The lower panel contains the XRD pattern of the unshocked mixture. As the stoichiometric composition of the mixtures suggests, here we see the presence of amorphous SiO₂, marked by a blue triangle, whereas the peaks marked by the blue circle are assigned to Fe.

The upper panel XRD pattern of the shocked sample does not show any change in the sample's chemical composition. Here we can locate the presence of iron's three most intense peaks at the same position as observed in the unshocked sample. Additional peaks around 38.6°, 44.8° and 65° are assigned to Al, which comes from the diaphragm. A hump around 25° is also there, which is because of SiO₂. No signatures of iron-rich olivine or pyroxene class of dust are observed. These observations are also consistent with the IR spectroscopic result of the same sample.


Fig 8. 6: XRD pattern of the unshocked and shocked sample of the mixtures of Fe and SiO_2 (1:1).

Assignment (Millar indices (d spacing in Å))								
2 θ (deg)	θ	d spacing (Å)	Forsterite (Mg ₂ SiO ₄)	MgO	Mg	Si		
			CODID: 9000319	CODID:1000053	CODID: 9008506	CODID:		
						1526655		
17.65	8.83	5.02	2 0 0 (5.10)					
23.12	11.56	3.84	0 2 1 (3.88)					
24.13	12.07	3.69	101(3.72)					
25.74	12.87	3.46	1 1 1 (3.49)					
28.76	14.38	3.1				111		
						(3.10)		
30.05	15.03	2.97	0 0 2 (2.99)					
32.43	16.22	2.76	1 3 0 (2.76)					
32.57	16.29	2.75			1 0 0 (2.77)			
34.63	17.32	2.59			002 (2.60)			
35.97	17.99	2.49	1 3 1 (2.51)					
36.82	18.41	2.44	1 1 2 (2.45)	1 1 1 (2.43)				
37.16	18.58	2.42			1 0 1 (2.45)			
38.64	19.32	2.33						
39.92	19.96	2.26	1 2 2 (2.26)					
40.32	20.16	2.24	1 4 0 (2.24)					
42.04	21.02	2.15	2 1 1 (2.15)					
43.15	21.58	2.09		2 0 0 (2.10)				
44.86	22.43	2.02						
47.57	23.79	1.91				200		
						(1.90)		
48.04	24.02	1.89			1 0 2 (1.90)			
52.49	26.25	1.74	2 2 2 (1.74)					
56.44	28.22	1.63				311		
						(1.62)		

Table 8. 4: XRD peaks observed in the shocked sample of M1, along with their corresponding d-spacing values and assignments to different crystalline phases (Forsterite, MgO, Mg, and Si).

1 1 0 (1.60)
2 0 (1.49)
103 (1.47)
1 1 2 (1.36)
1 1 (1.27)
2 2 (1.21)

Table 8. 5: XRD peaks observed in the shocked sample of M2, along with their corresponding d-spacing values and assignments to different crystalline phases (Olivine, MgO, Mg, and Fe).

Assignment (Millar indices (d spacing in Å))						
2θ (deg)	θ (deg)	d (Å)	Olivine (Mg _{1 8} Fe₀ ₂ SiO₄)	MgO	Mg	Fe
			CODID:1010497	CODID:1000053	CODID: 9008506	
17.41	8.71	5.09	2 0 0 (5.10)			
22.94	11.47	3.87	2 0 1(3.88)			
23.97	11.99	3.71	0 1 1 (3.72)			
25.56	12.78	3.48	3.49 (1 1 1)			
29.93	14.97	2.98	0 2 0 (2.99)			
32.31	16.16	2.77	3 0 1 (2.76)		100(2.77)	
34.49	17.25	2.6			0 0 2 (2.60)	
36.68	18.34	2.45	1 2 1 (2.45)		1 0 1 (2.45)	
36.89	18.45	2.43		1 1 1 (2.43)		
38.51	19.26	2.34	4 1 0 (2.34)			
39.72	19.86	2.27	2 2 1 (2.26)			
40.17	20.09	2.24	4 0 1 (2.24)			
41.85	20.93	2.16	1 1 2 (2.15)			

43	21.5	2.1		2 0 0 (2.10)		
						111
44.47	22.24	2.04				(2.01)
45.48	22.74	1.99				
47.93	23.97	1.9				
52.43	26.22	1.74	2 2 2 (1.74)			
52.76	26.38	1.73	4 0 2 (1.73)			
56.96	28.48	1.62	6 1 0 (1.63)			
57.43	28.72	1.6			1 1 1 (1.6)	
62.01	31.01	1.5	040(1.49)			
62.34	31.17	1.49		2 2 0 (1.49)		
62.83	31.42	1.48	6 2 0 (1.48)			
63.09	31.55	1.47			1 0 3 (1.47)	
						211
65.18	32.59	1.43				(1.44)
68.74	34.37	1.36			1 1 2 (1. 36)	
69.79	34.9	1.35	2 2 3 (1.35)			
70.08	35.04	1.34			2 0 1 (1.34)	
77.8	38.9	1.23	1 3 3 (1.23)			
78.76	39.38	1.21		2 2 2 (1.21)		
						211
82.54	41.27	1.17				(1.17)

FE SEM and EDX Analysis:

By combining FE-SEM imaging and EDX spectroscopy, a comprehensive understanding of the morphological changes and the variations in the chemical composition of the cosmic dust analogues induced by the shock processing can be obtained. The imaging and EDX spectroscopy of both pre and post-shocked samples was carried out using a JEOL JSM-7900F Schottky Field Emission FE-SEM. A conductive coating of Pt was applied to all the samples for 1.5 minutes to minimize electron-induced charging effects during imaging. For imaging, an operating voltage of 5 keV was employed, and for the EDX spectroscopy, it was 15 keV.

Sample M1:

The FE SEM images of the unshocked sample of M1 with different length scales up to 100 nm are in **Fig 8.7(a-b)**. These images suggest the M1 mixture contains porous grains of different shapes and sizes.



Fig 8. 7: FE-SEM images of the unshocked sample of M1.

The FE SEM images of the shocked samples of M1 are shown in **Fig 8. 8**. **Fig 8. 8(a)** indicates a spherical dust particle with a diameter of around 15 μ m. On top of these larger grains, there are many small grains. **Fig 8. 8(b)** represents the close-in view of the region marked by a red box in **Fig 8. 8(a)**, which shows many tiny spherical particles mostly having a diameter in the sub-micron range. The Inset of **Fig 8. 8(c)** shows the EDX spectra of the spherical condensate from the area marked by a red box in **Fig 8. 8(c)**. This spectrum tells that these spherical condensates are made of Mg, Si and O with weight percentages around 46 %, 12.7 %, and 41 %.



Fig 8. 8: FE-SEM images of the shocked sample of M1shows the presence of a spherical particle (a) with a diameter of about $15 \mu m$. (b) represents the close-in view of the area marked by a red box in (a), and it consists of sub-micron size spherical particles. (C) shows the EDX spectra of the spherical particles with in the red box.

Sample M2:

FE SEM images of the unshocked mixture of M2 are in **Fig 8.9**. Like in the case of M1, the morphology of the unshocked mixture of M2 are almost similar; porous grains with different shapes and size.



Fig 8. 9: FE-SEM images of the unshocked samples of M2. (a) is showing a large grain, and (b) represents the close view of the area marked by a red box in (a), which contains small dust grains of different shapes and sizes.

FE SEM images of the shocked sample of M2 are shown in **Fig 8. 10**. Compared to its unshocked counterpart, an apparent change in the morphology of the shocked sample can be observed. **Fig 8. 10(a)** shows the presence of spherical dust particles having sizes around 9.4 μ m, 12.3 μ m, and 18.7 μ m. **Fig 8. 10(b)** represents another part of the sample where the small dust particle is grown up on top of relatively large grains. **Fig 8. 10(c)** shows a much close-in view of the region marked by a red box in **Fig 8. 10(b)**. It suggests that these smaller aggregates are spherical in nature and have a typical size range of 300 nm to 30 nm. The EDX spectra of these smaller spherical dust particles are in **Fig 8.10(d)**. EDX spectra of these grains indicate that they are mostly made of Mg-rich silicates and metallic oxide.



Fig 8. 10: FE-SEM images of the shocked sample of M2. (a) shows the presence of spherical particles with diameters around 18.7 μ m, 12 μ m, and 9.4 μ m. (b) shows a large dust grain; on top of that, relatively small grains are aggregated. (c) shows the area marked by a red box in (b), which contains smaller spherical dust particles with diameter ranges in between 30 to 300 nm. (d) shows the EDX spectra of the area with in the red box in (c).

Sample M3:

FE SEM images of the unshocked mixture of sample M3 are in **Fig 8. 11(a-b)**. These images indicate that the morphology of the unshocked M3 sample is very similar to that of the unshocked M1 and M2 samples.

For the shocked sample, an apparent change in the morphology compared to the unshocked sample can be seen in **Fig 8. 12**. **Fig 8. 12(a-c)** indicates the presence of a spherical particle with a diameter of around 12 μ m and much smaller dust aggregates on top of it. **Fig 8. 12(b)** shows these aggregated dust grains from the area marked by the red box in **Fig 8. 12(a)**. They consist of many relatively small spherical grains with different diameters. **Fig 8. 12(c)** indicates another spherical condensate grown on top of the larger spherical particle in **Fig 8. 12(a)** and is marked by a blue box. **Fig 8. 12(d)** showed the EDX spectra of the

spherical condensate, suggesting that they are made of iron-rich oxides and silicates. Although from the IR and XRD analysis of the shocked M3 sample, we are unable to see any presence of iron-rich oxide and silicate dust there.



Fig 8. 11: FE-SEM images of the unshocked samples of M3 with two different scale sizes, 5 μ m (a), and 1 μ m (b).



Fig 8. 12: FE-SEM images of the shocked samples of M3. (a) shows a large grain with a diameter of around $12 \mu m$. (b) shows the close view of the area marked by a red box in (a). (c) shows isolated spherical particles grown on top of a large grain, marked by a blue box in (a). (d) shows the EDX spectra of the spherical dust with in the red box in (c).

HR-TEM analysis:

HR-TEM analysis of the shocked processed samples was carried out using Titan Themis 300 S/TEM form thermo. The samples were ultrasonicated in ethyl alcohol for 15 minutes, then drop cast on a quantefoil grid and allowed to dry in a chemically inserted atmosphere overnight. Before the imaging analysis started, these drop casted grids were plasma cleaned using Ar-O₂ plasma to reduce any changes of further contamination. Throughout the analysis, the HR-TEM was operated at 300 keV.

Sample M1:

HR-TEM images of the shock-processed sample of M1 are depicted in Fig 8. 13(ae). Fig 8. 13(a) represents a low magnification (1 µm scale size) image of the shocked sample showing an overall view of the aggregated dust particle produced by shock processing. Fig 8. 13(b) shows the zoomed view of the region marked by a red rectangle in Fig 8. 13(a). This region contains many spherical dust particles with a particle size range lies in between 285 nm to 40 nm. The inset of Fig 8. 13(b) shows the particle size distribution of these spherical dust particles. Fig 8. 13(c) describes the zoomed view of the region marked by the yellow rectangle in Fig 8. 13(b). This region consists of many crystalline domains with different orientations, as suggested by their electron diffraction pattern (shown by the red arrow adjacent to each domain). The measurement of the lattice spacing from the selected area of each domain, marked by the yellow rectangle, indicates that they consist of forsterite (Mg_2SiO_4). The domain located at the top left of **Fig 8. 13(c)** exhibits a lattice spacing of approximately 0.39 nm, which corresponds to the (0 2 1) plane of forsterite (COD ID: 9000319). The domain at the bottom left has a d spacing of ~ 0.52nm and can be assigned to the (2 0 0) plane of forsterite (CODID: 9000319). The domain at the bottom right of Fig 8. 13(c) has a d spacing of ~ 0.22 nm, and it corresponds to the (1 2 2) plane of forsterite (CODID: 9000319). The domain at the right top has d spacing ~ 0.25 nm, showing the (1 3 1) plane of forsterite (CODID: 9000319). Fig 8. 13(d) shows a single crystalline domain and, in the inset, its electron diffraction pattern taken from the area marked by a red rectangle. Interplanar spacing of this domain d is ~ 0.39 nm which shows the presence of (0 2 1) plane of forsterite (CODID: 9000319). Fig 8. 13(e) shows the presence of many nanometer size small domains. The Inset of Fig 8. 13(e) shows the particle size distribution of these small domains with a maximum particle size of ~ 3.5 nm and a minimum of ~ 1.2 nm. The interplanar d-spacing (0.21 nm) measurement in these small domains indicates that they are composed of MgO (200) crystal planes. Furthermore,

their nanometer-sized dimensions suggest they can be classified as MgO quantum dots (QD).

Fig 8. 13(f) is the HAADF image of the spherical dust particles produced by shock processing. The HAADF imaging technique is sensitive to the atomic number (Z) of the element present in the sample, so the structures in **Fig 8. 13(f)**, which appeared bright made of a high Z value element compared to the elements present in the structure appeared less bright. **Fig 8. 13(g-i)** show the distribution of Mg, Si and O in these dust particles.





Fig 8. 13: HR-TEM images of the shocked sample of M1 with different scale sizes (a-e) showing the presence of different crystalline phases. (f) shows the HAADF image of the shocked sample. (g-i) depicts the elemental mapping of the specks of dust present in the (f).

Sample M2:

HR-TEM images of the shocked processed samples of the M2 with different magnifications are in **Fig 8. 14(a-d)**. **Fig 8. 14(a)** showed the presence of spherical dust grains with a maximum particle size of around 280 nm and a minimum particle size of approximately 35 nm. The Inset of **Fig 8. 14(a)** shows the particle size histogram of these spherical dust particles. **Fig 8. 14(b)** shows the high magnification image of the area marked by a red rectangle in **Fig 8. 14(a)**. This area consists of two distinct crystalline phases marked by a yellow rectangle at the top and a red rectangle at the low right corner. Inset 1 of **Fig 8. 14(b)** shows the reciprocal lattice plane orientation of the area marked by

a yellow rectangle, and the Interplanar d spacing of this area is ~ 0.21 nm, which corresponds to $(2\ 0\ 0)$ plane of MgO (CODID-1000053). Inset 2 of **Fig 8. 14(b)** indicates the reciprocal lattice orientation of the area marked by a red rectangle. This region's calculated interplanar d spacing is ~ 0.38 nm and corresponds to the $(0\ 2\ 1)$ plane of olivine (CODID-1010497). **Fig 8. 14(c)** also shows two distinct crystalline phases and their corresponding reciprocal lattice plane arrangement can be found in insets 1 and 2, respectively. For the inset 1, its d spacing is ~ 0.39 nm suggesting the presence of $(0\ 2\ 1)$ plane of olivine (CODID-1010497). For inset 2, its corresponding d spacing is ~ 0.24 nm, and assigned to the $(1\ 1\ 2)$ plane of olivine (CODID-1010497). **Fig 8. 14(d)** displays the presence of numerous nanometer-sized domains, and their particle size distribution can be observed in Inset 2. The particle sizes range from 5.1 nm to 1.7 nm. Inset 1 of **Fig 8. 14(d)** describes the reciprocal lattice plane orientation of such a nanometer-size domain marked by a red rectangle. Its Interplanar d spacing is ~ 0.21 nm which suggests the presence of (2 0 0) plane of MgO (CODID-1000053), and their nanometer order dimension indicates that they could be MgO (QD).

Fig 8. 14(e) shows the HAADF image of the same spherical dust grains showed in **Fig 8. 14(e)**. In the HAADF methods, the contrast of any image depends on the atomic number (Z) value; more brightness suggests the presence of a high Z-value element compared to the elements present in the relatively less bright region. Notably, the core region of the spherical structures marked by a red arrow, as shown in **Fig 8. 14(e)**, is more intense than the encompassing shell, indicating its made of an element with a higher Z value relative to the parts containing the shell. **Fig 8. 14(d)** shows the elemental mapping of the spherical olivine dust grains. **Fig 8. 14(i, j)** shows the distribution of the Fe, Mg, O and Si elements in these dust grains. Furthermore, **Fig 8. 14(g)** suggests the presence of a compact iron core within these dust grains, upon which dust growth has subsequently occurred, incorporating Mg, O, and Si.









Fig 8. 14: HR-TEM images of the shocked sample of M2 with different scale sizes (a-d) showing the presence of different crystalline phases. (e) shows a HAADF image of the shocked sample with a core-shell structure marked by red arrows. (f-j) depicts the elemental mapping of the dust present in (e).

Sample M3:

The HR-TEM images of the shocked samples of M3 are shown in Fig 8. 15(a-e). Fig 8. 15(a) is a relatively low resolution image up to scale size 200 nm and shows the presence of shock produced aggregates which has a preponderance of spherical particles with particle size ranges from 10 to 200 nm. Inset 1 of Fig 8. 15(a) shows the zoomed view of the region marked by a red box. The red arrow in the inset shows a core-shell structure with a dense core having a diameter around ~ 102 nm, and surrounded by a shell with a dimeter around 140 nm. The Inset 2 shows the HAADF images of the core shell structure along with the elemental mapping. This suggest that the core is made of iron and the shell made of Si and O. On top of this core shell structure many smaller spherical structure has also been grown up. Observations from the Fig 8.15 (a) are very much consistent with the observations of the FE-SEM images of the shocked samples of M3. Fig 8. 15(b) shows the HAADF image of the spherical dust particles present in the shocked sample of M3. it descripts that the core of the spherical dust particles is made of relatively heavy elements, in this case it is Fe. Whereas the shell is made of Si and O. Fig 8. 15(c) is a high resolution image of the shocked sample with scale size up to 5 nm. Inset of this images shows the electron diffraction patter of the area marked by a red box. The calculated d spacing is around 0.31nm, can be ascribed to the (1 1 1) plane of Si. Fig 8. 15(d) shows the presence of polycrystalline domains. Two of such domains are marked by a red box and by a yellow box, and their corresponding electron diffraction patterns can be found in inset 1 and 2 respectively. The d spacing of the structure within the red box is around 0.25 nm, assigned to the (3 1 1) plane of the magnetite (Fe₃O₄) (Noval & Carriazo 2019). Whereas the d spacing of the structure with in the yellow box is around 0.2 nm and it shows the presence of Fe's (1 1 1) plane. Fig 8. 15(e) shows the area of the shocked sample consists of three different crystalline phases, marked by a red, white and a yellow box. Their corresponding electron diffraction pattern can be found in the inset 1, 2 and 3 respectively. The d spacing of the crystalline domain present with in the red box is around 0.31nm, assigned to the (1 1 1) plane of the Si. The crystalline domain present with in the white box has a d spacing around 0.29 nm which we assigned to the (2 2 0) plane of Fe₃O₄. The d spacing of the crystalline structure present with in yellow box is around 0.25 nm and assigned to the (3 1 1) plane of Fe₃O₄. These kinds of structures were previously assigned as magnetite QD by authors like Lin et al. 2011. Although the formation pathway they use to synthesized such QD are different than us. The absence of clear signatures of crystalline Si, magnetite, and magnetite quantum dots (QD) in the XRD (Fig 8. 6) pattern of the shocked sample of M3 can be attributed to the use of a Cu K α source in the XRD machine. It is known that the energy associated with Cu K α radiation (~ 8 keV) is higher than the K absorption edge of iron. As a result, it can induce X-ray fluorescence from iron (Klug & Alexander 1974; Mos et al. 2018), which may subsequently suppress or mask the peaks corresponding to Si and Fe₃O₄ in the XRD pattern.







Fig 8. 15: HR-TEM image of the shocked sample of M3. (a) shows the presence of spherical dust grains with a dense core surrounded by relatively dense shell. (b) HAADF image of the spherical dust grains shows that they the core of these dust rains are made of high Z value element and the shell is made of relatively low Z value element. (c) Nano crystalline Si. (d) shows the presence of polycrystalline phases such as iron with in the yellow box and magnetite with in the red box. (e) polycrystalline phase consists of Si, with in the red box, (311) plane of magnetite with in the yellow box, and (2 0 0) plane of Fe₃O₄ with in the magnetite.

We studied the shock processing (5.6 M) of interstellar silicate dust analogue precursors M1, M2, and M3 up to a reflected shock temperature of about 7300 K and a reflected shock pressure of about 25 bar for the 2ms. Under these circumstances, the sample will experience flash heating with a heating rate of about 10^{6} K s⁻¹, and the heating usually persists for around 2 ms, followed by a rapid quenching with a rate of about 10^{5} K s⁻¹ (Roy *et al.* 2022b, Roy *et al.* 2022a). In the shock tube, the processing time is limited, so the reflected shock pressure and temperature play a vital role in the conversion process (Bhaskaran & Roth 2002). Also, the conversion rate from the precursors to the final product in shock tube operation depends on the properties of the precursor, such as their melting point/sublimation temperature (Bhaskaran & Roth 2002). Notably, in this conversion process, the precursors dissociated or ionized based on the energy applied during the heating phase. The high pressure and temperature generated by the reflected shock create a supersaturation state consisting of the precursor fragments. As the high pressure started to release, the supersaturated vapour nucleated, and tiny solid grains were deposited on top

of the shock tube's inner walls and the end flange of the shock tube (Bhaskaran & Roth 2002). In HISTA, we don't have any in-situ measurement facility to monitor different phases of the entire conversion process. However, we used excite analysis techniques such as ATR-FTIR spectroscopy, XRD, FE-SEM, HR-TEM imaging, and EDX imaging to understand the conversion process.

For sample M1, it contains the mixtures of amorphous SiO₂ nanopowder and Mg nanopowder (1:1). The phase diagram of the Mg (Gieseke *et al.* 2016) suggest that it will start to melt upon the arrival of the incident shock, which can raise the gas temperature around 2400 K, whereas it will be fully melted at the reflected shock temperature around 7300 K for the 2 ms. Similarly, SiO₂ will also go into the vapour phase (Melosh 2007). Using hydrocode modelling, they tried to understand the variation in abundance of different decomposition products of SiO₂ over a wide range of temperatures and pressure. Gas phase species like SiO and O₂ dominated the vapour phase of SiO₂. As the temperature increases, the composition of the gas phase shifts to predominantly consist of monoatomic Si and O gases (Melosh 2007). Although we have not used any insitu observation technique to monitor different chemical reactions that occurred behind the shock front, we tried to frame a set of possible reactions by combining the results from the hydrocode modelling of Melosh (Melosh 2007), results from the work of Toguri and Pidegon (Toguri & Pidgeon 1961), and results from the analysis of our shocked samples. The possible reactions which lead to the formation of forsterite and MgO can be as follows:

$$Mg + Ar \rightarrow Mg^* + Ar$$
 (8.1)

$$SiO_2 + Ar \rightarrow SiO + O + Ar$$
 (8.2)

$$Mg+O+Ar \rightarrow MgO+Ar$$
 (8.3)

$$2Mg + 4SiO + Ar \rightarrow Mg_2SiO_4 + 3Si + Ar$$
(8.4)

The reaction involving the formation of MgO and forsterite (equations 3 and 4) is accompanied by the release of heat, which facilitates the conversion of the reactants into their respective solid phases. He et al (He *et al.* 2021) showed a non-classical two-stage particle attachment mechanism could be used to understand the crystallization from hightemperature melt or extreme metamorphic phases. This process starts with the formation of multi-ion complexes. In the first stage, nanoparticles are formed, which undergo oriented aggregation. During this aggregation process, the building blocks of the crystals may exhibit a common crystallographic orientation or have slight rotations relative to each other. **Fig 8. 13(c)** indicates a scenario where different crystalline domains consist of various phases of forsterite, and MgO oriented themselves in relatively different directions. In the second stage, the grains undergo coarsening through the attachment of the nano-flakes. In this step, the individual nano-flakes can have varying orientations, and the attachment process helps grow larger grains. **Fig 8. 13(a)** and **Fig 8. 13(f)** indicate that individual spherical grains with 30 to 300 nm particle sizes try to agglomerate and make larger grains.

Analysis of the shocked sample of M2 showed new crystalline phases such as polycrystalline olivine (Mg_{1.8}Fe_{0.2}SiO₄) and MgO. The olivine showed a significantly lower extent of iron inclusion. However, the HAADF image (**Fig 8. 14(e)**) of the core-shell structure in the shocked sample shows that iron provides a finite area on which silicate dust growth happens. During the shock processing, the shock-heated Ar will transfer the heat to the Mg, Fe and SiO₂. At the shock-heated gas temperature ~ 7300 K, most of the Mg and Fe (Söderlind *et al.* 1996) will be in the melt phase and start to react with the SiO and O, which comes out because of the destruction of SiO₂ according to eq (8.2). In these circumstances, the MgO formation pathways can be similar to what we see in the case of M1 via eq (8.4). MgO will starts condenssing below 2500 K but Mg will still be available and will again react with the available SiO and Fe, which leads to the formation of olivine via the following equation suggested by Gail *et al.* (2016):

$$Mg + SiO + Fe + Ar \rightarrow [MgFeSiO_4] + Ar$$
 (8.5)

Here [MgFeSiO₄] is the solid solution of silicate dust. **Fig 8.16** gives a pictorial representation of different process happening during the shock heating and cooling of the mineral dust precoursours. The less inclusion of iron in the olivine or absence of iron-rich crystalline phase of silicate dust in the shocked sample can be associated with the particle size of the iron powder used in this experiment. Here we used iron powder with an average particle size of about 40 μ m (325 mesh), whereas both the Mg and SiO₂ have particle sizes in the nm range. Because of reduced particle size, Mg will react more than iron with oxygen and silicon, making Mg-rich olivine dust and MgO.



Fig 8.16: Pictorial representations of different processes and reactions takes place during shock heating and cooling.

For sample M3, we observe the presence of crystalline Si, Fe, and magnetite QDs. Iron will be in the melt phase during the shock heating up to a gas temperature of about 7300 K (Söderlind *et al.* 1996), whereas SiO₂ will dissociate into species like SiO, O, and Si (Melosh 2007). The reaction between shock-heated Fe and SiO₂ can lead to FeO and FeSi forming via the following reaction suggested by Dubrovinsky et al. 2003.

$$3 \text{ Fe} + \text{SiO}_2 \rightarrow 2 \text{ FeO} + \text{FeSi}$$
 (8.6)

FeSi and FeO can further oxidize, leading to the fortin of Fe₂O₃ via the following reaction.

$$4 \operatorname{FeSi} + 7 \operatorname{O}_2 \xrightarrow{} 2 \operatorname{Fe}_2 \operatorname{O}_3 + 4 \operatorname{SiO}_2 \tag{8.7}$$

4 FeO + O₂
$$\rightarrow$$
 2 Fe₂O₃ (8.8) (Kress and Carmichael 1991)

 Fe_2O_3 can further be oxidized to Fe_3O_4 via the reaction suggested by Salmon (Salmon 1961).

$$Fe_2O_3 \iff Fe + Fe_3O_4$$
 (8.9)

As dust cools, the varying melting points of its constituent elements shape its structure. In Figure **8.15(a)**, Insets 1 and 2 reveal that iron (Fe) forms the core of the dust grains, encapsulated by a shell composed of silicon (Si) and oxygen (O). This core-shell structure likely arises from the differing melting points of Fe, Si, and O. Iron has

significantly higher melting point, causing it to condense first, providing a surface upon which Si and O can react and form the surrounding thick shell.

8.4 Astrophysical Significance:

We have observed the presence of Mg-rich olivine and MgO signatures in both shocked samples of M1 and M2. According to Gail & Sedlmayr (1999), a fraction of MgO is expected to condense along with iron grains during the growth of silicate dust. Therefore, the presence of MgO in both shocked samples of M1 and M2 aligns well with the theoretical predictions. Furthermore, observations of crystalline dust in various circumstellar regions have shown a prevalence of Mg-rich compositions rather than iron, despite the similar abundance of Mg and iron in stellar envelopes (Millar 2016). The results from the shock processing of M2 indicate that starting from a mixture with an equal abundance of Mg and Fe, the formation of Mg-rich crystalline silicate dust, particularly in the olivine class, is the most probable outcome, as opposed to pyroxene or iron-rich silicate dust. For sample M3, the newly formed phases are crystalline Si and magnetite (Fe₃O₄) QD. Magnetite is commonly referred to as permanent magnet material and ferrimagnetic below 580 ° C (Ponomar 2018). The origin of such magnetic behaviours of magnetite is associated with its crystal structure where both Fe^{2+} and Fe^{3+} ions are arranged in inverse spinel cubic structure (Ponomar 2018). This arrangement leads to electron spins aligning within the material, resulting in a net magnetic moment (Ponomar 2018). Magnetic nanoparticles such as magnetite has been considered as a potential carrier of the cosmic anomalous microwave emission (Draine & Hensley 2013). These magnetic cosmic grains tend to align towards the galactic magnetic field and contribute to interstellar polarization (Shapiro 1975). Also, they can influence the dust growth process as the collisional efficiency of the magnetically aligned grains is different than the non-magnetic grains; hence the rate of dust growth will also be different (Andersson et al. 2015). Also, the shape and compactness of the coagulated grains from the magnetically aligned grains have also been proposed to be different from those coagulated from the non-aligned grains (Hoang 2022). The magnetically aligned dust grains could preferentially stick together and form elongated and compact grains. In contrast, the elongation of coagulated grains formed from the nonaligned grains is proposed to be less (Hoang 2022).

8.4.1 Implications to the formation of Silicate dust induced by stellar pulsation:

Stellar pulsations can generate shock waves within a star's stellar envelope, leading to various dynamic phenomena. A star's periodic expansion and contraction during the pulsation phase create pressure waves propagating through its layers. When these pressure waves become sufficiently strong, they can create shock fronts, which are rapid changes in pressure and temperature. Propagation of shock through the circumstellar shell can lift the gas and compress it, raising its temperature to thousands of kelvins. Soon after the passage of these shocks, the heated and compressed gas starts to cool down following the condensation of dust grains (Höfner & Olofsson 2018).

The signature of dust formation in the classical novae is well-known. However, it is still a topic of research that molecules and dust grains survive such an extreme condition, especially the ionizing radiation coming out from the central white dwarf (WD). A simple one-zone model has been developed to study the thermodynamic evolution of fluid elements following their passage through a shock (Derdzinski et al. 2017). This model considers essential factors such as radiative cooling and irradiation from the central WD. Applying a simplified molecular chemistry network and utilizing density/temperature trajectories has demonstrated that efficient dust formation, including carbonaceous and forsterite, can occur within shock-processed gas. The shocked gas's high density (~ 10^{14} particles per cm⁻³) takes the abundant CO into saturation and enhances the dust nucleation, flowing submicron size dust growth, which they explained using classical nucleation theory. Shock-induced dust formation in novae has been observationally studied by Kumar et al (Kumar et al. 2022). The author conducted a comprehensive study of the Fe II class Nova V2891 Cygni, which exhibited significant reddening. This study spanned a duration of 15 months, during which the nova's behaviour was observed and analyzed across optical and near-infrared wavelengths. The analysis indicates a dust mass ranging from approximately 0.83 to 1.25×10^{-10} solar masses. Compelling evidence suggests the origin of the coronal lines is shock heating not the photoionization. The coexistence of dust and coronal lines, exhibiting varying velocity shifts, further supports the notion that dust formation is induced by shocks.

In our own experiment, we investigated the effects of low-velocity shock waves (~ 1.8 km s^{-1}) on mixtures of amorphous SiO₂ and Mg (in equal proportions) and mixtures of

amorphous SiO₂, Mg, and Fe (in equal proportions). These mixtures were processed at a gas temperature of approximately 7300 K for about 2 ms. The results demonstrate that in low-velocity ISM shock the mixtures transform into crystalline Mg-rich olivine and MgO.

8.4.2 Implications to the formation of Crystalline dust in Comets:

Comets are thought to originate from the cool outer periphery of the presolar nebula and comprise unaltered interstellar materials (Bailey et al. 1986). IR spectra of Comets like Hale-Bopp (Crovisier et al. 2000, Crovisier et al. 1997) in Comet NEAT (Wooden 2008) show the presence of crystalline silicate dust in it. Formation pathways of crystalline silicate dust in Comets are still a topic of discussion. Greenburg et al. 1996 proposed that crystalline silicate observed in Comets originated because of the thermal annealing of amorphous dust grains during multiple passages around the Sun. But, IR spectra of crystalline silicate dust in relatively young Comets like Mueller (Hanner et al. 1994) raised questions about the applicability of this above-described proposal. The crystalline dust in Comets can also originate due to the thermal annealing of amorphous silicate grains present in the inner zone of the presolar nebula (Nuth III 1999). Which then transported to the outer part of the nebula via winds which are blowing in both above and below the disc and deposit these crystalline grains into the region where dust and ice mix to build up Comets (Nuth et al. 2000, Nuth III et al. 2000, Hill et al. 2001). The possible sources of such winds might be magneto hydrodynamic interaction proposed by Shu et al (Shu et al. 1996), and nebular turbulence-induced winds can also be responsible for such material transport (Prinn 1990, Stevenson 1990). However, observational shreds of evidence of such wind-driven transportation of crystalline dust beyond the snowline of a presolar nebula are still not sound. Direct incorporation of crystalline silicate stardust grains into Comets has also been proposed (Wooden 2000). Still, a significant amount of crystalline silicate dust must survive their journey from the circumstellar environment to the presolar nebula. Crystalline silicate dust accounts for only about 5% of the observed interstellar silicate population (Kemper et al. 2004). It is a very well-accepted fact that these crystalline grains, when they are subjected to the extreme ISM condition, turned to amorphous (Krätschmer & Huffman 1979, Demyk et al. 2001, Brucato et al. 2004). Another constrain to the stardust inclusion in the Comet hypothesis is it is still not clear whether silicate dust condensed in the circumstellar environment as a crystal or they are the product of thermal annealing of amorphous silicate dust (Demyk et al. 2000)? The current models present are not much capable of giving an insight about the structure of condensed circumstellar silicate dust (Demyk et al. 2001). Also, according to (Sogawa & Kozasa 1999), the formation of crystalline grains in the circumstellar region is improbable. Instead, they originated due to the thermal annealing of heterogeneously condensed silicate grains. Notable, amorphous grains were found to crystalize more rapidly than the conventional crystal growth rate in the circumstellar environment of AGB stars (Sogawa & Kozasa 1999). The shock processing of amorphous silicate dust through high-velocity shock waves in the outer regions (~ 10 AU) of the solar nebula can lead to the formation of crystalline silicate dust, which may subsequently be incorporated into comets (Harker & Desch 2002, Nuth III & Johnson 2006). According to their calculation, a shock wave with velocity ~ 5 km s⁻¹ propagating through a medium with pre-shock density ~ 5×10^{-10} g cm⁻³ can do flash heating to the amorphous micron size dust grains up to temperature ~ 1000 K, and this sharp thermal spike will remain in the grain for ~ 2 s, subsequently do the annealing (Harker & Desch 2002, Nuth III & Johnson 2006). The exact sources of such shock waves in the outermost part of the presolar nebula are still a topic of ongoing discussion. However, according to Boss and Durisen 2004, a spiral density wave in a gravitationally unstable disk could form a shock wave with a velocity of ~ 10 km s⁻¹, which can thermally process amorphous silicate dust and convert it to crystalline silicate dust. We synthesized polycrystalline forsterite, olivine and periclase along with other crystalline phases like Si by shock processing (5.6 M, 7000 K, for 2 ms) of the mixture of amorphous silica and Mg (M1) in equal ratio, combinations of M1 and Fe (1:1) (M2). Our experiment's results can complement such a shock-induced crystalline silicate formation hypothesis in Comet.

8.4.3 Implications to the formation of chondrules:

Chondrules are the millimetre size spherical metallic particles found in the primitive chondritic meteorite. Formation pathways of these chondrules are still a matter of presentday research. Shock-induced flash heating of the chondrules precursors in the presolar can lead to the formation of chondrules (Boss & Durisen 2005). Different sources of the shock waves in the presolar nebula have been proposed for the desired heating of the chondrule precursors. These include accretion shock at the nebular surface (Wood 1984, Ruzmaikina & Ip 1994), shocks due to infalling clumps (Boss & Graham 1993, Hood & Kring 1996), bow shocks driven by planetesimals of the order of a thousand km, and shock waves linked with the non-axisymmetric disc structure such as spiral wave (Hood & Horanyi 1991, Wood 1996). Amongst these four types of shock waves, Boss and Durisen (Boss & Durisen 2005) showed that the shock wave associated with the spiral wave shock driven by gravitational instability in the presolar nebula is the most suitable for the thermal processing of chondrule precursors. The fate of chondrule precursors subjected to such spiral wave associates shock waves has been computationally explored by authors like (Iida *et al.* 2001; Desch *et al.* 2002; Ciesla & Hood 2002). These studies showed that a shock wave with a velocity of 5 to 9 km s⁻¹ is sufficient enough to raise the temperature up to 4000 K, which is sufficient to melt the available chondrule precursors and follow the condensation of chondrule behind the shock front (Ciesla & Hood 2002).

In this work, we subjected various chondrule precursor analogues M1, M2, and M3 to shock waves with Mach 5.6 and reflected shock temperature ~ 7300 K for 2ms. FE-SEM and HR-TEM images of the shocked samples show spherical particles with particles ranging between 30 and 300 nm. The EDX spectra of these particles show similarities with the EDX spectra of the chondrules, and the IR spectra and XRD of these shocked samples reveal that they are made of Mg-rich olivine and MgO. So this experiment showed that chondrule precursors exposed to low-velocity shock (5.6 M in this case) could lead to the formation of chondrules, which has been studied theoretically by authors like (Iida et al. 2001; Desch et al. 2002; Ciesla & Hood 2002).

8.5 Conclusions:

We studied the formation of mineral dust by subjecting different cosmic mineral dust precursors to a shock wave with a velocity of ~ 5.6 M and reflected shock temperature of ~ 7300 K for 2 ms. Analysis of the post-shocked sample showed the presence of a Mgrich olivine class of dust for both the cases of M1 and M2. A significant presence of MgO has also been observed in the shock-processed samples for both the case of M1 and M2. Another notable finding from these two (M1 & M2) shocked samples is the presence of MgO QD. This suggests that MgO QD could be a component of interstellar silicate dust generated by shock processing. The available data collected from the shock-processed samples of M3 showed the presence of crystalline Si and magnetite QD. Spherical grains with metallic core found to be the most dominant component in all three sets of shocked samples. We cannot see the presence of the pyroxene class dust in shocked processed samples from all three samples, and for the shocked sample of M3, we have not seen any signatures of iron-rich silicate dust. Our results show that shock processing of the silicate dust precursors can be a viable route to produce silicate dust grains in different astrophysical environments especially in the case of Nova and in the circumstellar environment of early type of stars where low-velocity shock (< 10 km s⁻¹) processing is possible. We extend the implications of this work to the crystalline silicate dust formation in the comets, where it has been

proposed that low-velocity nebular shock processing of the amorphous silicate dust or silicate dust precursors can lead to the formation of crystalline silicate dust. Results from this work also show a good agreement with the hypothesis that shock processing of chondrules precursors in the presolar nebula can be an alternative route leading to the formation of chondrules, which is observed in the different chondritic meteorites. Furthermore, shock processing can also lead to the formation of magnetic dust grains such as magnetite, which can contribute to various astrophysical processes such as interstellar polarization and anomalous microwave emission, and it can size influence the shape and morphology of the aggregated dust grains. In the future, we will continue exploring the role of shock strength on the physicochemical properties of the silicate grains by subjecting their respective precursors to various shock strengths and stoichiometric ratios.

Chapter 9 Summary and Future Work

Chapter overview:

This chapter offers a summary of the entire thesis and highlights its significant aspects and findings. Furthermore, the chapter concludes with a tentative future research plan based on the current thesis's insights and outcomes.

9.1 Summary of the Thesis:

One of the primary objectives of this thesis is to carry out laboratory shock processing of the cosmic dust analogues and understand the physicochemical changes that take place in those dust analogues due to the shock. This can be useful for the astrochemistry community to better understand the evolution of dust in the ISM.

In **Chapter 1** we discussed the history of dust detection in the ISM, various spectroscopic features of the interstellar dust, its chemical compositions. Different formation pathways of interstellar dust which include both bottom – up and top- down formation route has been covered in details. Laboratory experiment carried out worldwide to date for a better understanding of cosmic dust grains has also been covered. The essence for carrying out new set of laboratory experiment to understand the formation of dust in the ISM has also been discussed. The chapter ends with a description of the thesis objective as well as thesis structure.

The **Chapter 2** starts with a basic description of physics of shock waves and its mathematical formulations. Then we discussed the working principle of shock tube and few scientific facts associated with the shock tube operations. Details discussions on the formation of shock waves in the astrophysical conditions, and its interaction with dust and molecules in the ISM have also been covered in this chapter. The limited use shock tube and its capabilities in the field of astrochemistry has also been discussed in this chapter.

In **Chapter 3**, we discussed in detail the shock tube setup (HISTA) used in this thesis, with its specifications, associated experimental procedure, data collection and analysis. We showed that HISTA could routinely mimic low velocity $(1-2 \text{ km s}^{-1})$ interstellar shock waves, allowing us to study the fate of various interstellar dust analogues behind the shock front. This chapter also describes various analysis techniques for characterizing the shocked and unshocked samples. Prior to this study, numerous attempts

have been made by laboratory astrochemists to simulate astrophysical shock conditions in the lab, involving diverse methods such as lasers, impactors, heat reactors, electron guns, accelerators, and synchrotrons to examine the impact of shock on the formation and evolution of dust grains. However, our thesis demonstrates that the shock tube emerges as a promising tool, capable of replicating low-velocity astrophysical shocks within a limited timeframe, thereby establishing itself as a valuable tool in laboratory astrochemistry.

In **Chapter 4**, we studied the fate of amorphous carbon nanodust in shock waves in a hydrogen-free environment. Our findings present a convincing indication that within a carbon-rich environment, shock processing of carbon dust can facilitate the synthesis of a diverse array of carbon nanostructures. While fullerenes have been previously observed in the gas phase in the interstellar medium (ISM), our study suggests the possibility of the formation of several other carbon-based structures for solid particles that await discovery, including carbon nanoribbons, graphene, graphene quantum dots, multi-walled carbon nanotubes (MWCNTs), carbon nanocone/ nanodiamond (CNCs), and carbon nano-onions (CNOs). Particularly important are carbon nanoribbons which were identified as the predominant product, serving as potential building blocks for the formation of other carbon nanostructures.

Based on the findings of **Chapter 4**, in **Chapter 5**, we further explored the fate of amorphous carbon behind the shock front in the presence of hydrogen. Results from this experiment suggest that carbon nanostructures such as carbon nanoribbons, graphene, MWCNT, CNO, nanodiamond, and graphite can preferentially grow in the presence of hydrogen. Hydrogen is an abundant molecule in the universe, and the formation of different carbon nanostructures in the presence of hydrogen indicates that these carbon nanostructures may be present in various carbon-rich, shock-processed regions of interstellar space.

In **Chapter 6**, we studied the shock-induced bottom-up formation route of SiC from the mixture of amorphous carbon and Si nanoparticles in the presence of hydrogen. Analysis of the post-shocked sample showed the presence of both β - SiC (cubic) and hexagonal SiC, along with other carbon nanostructures such as carbon nanoribbons, graphite, MWCNT, and fullerene (nanobuds). The findings from this chapter indicate that low-velocity shocks can play a vital role in forming refractory carbonaceous dust, especially in the envelope of

the C-rich AGB stars where amorphous carbon, SiC and hydrogen are both reported to be present.

In **Chapter 7**, we investigated the behaviour of ferrocene, representing organometallic dust in the ISM and CSM, under high-intensity shocks. Post-shock analysis revealed the presence of composite materials like α -Fe and Fe3C, along with graphite-like carbon. Additionally, we observed the formation of nanostructures, including carbon nanoribbons and carbon-encapsulated iron nanoparticles. These findings indicate that organometallic compounds, like ferrocene, can contribute to forming carbon nanostructures in shockprocessed regions of the ISM and CSM. Furthermore, our study demonstrated the transformation of diamagnetic ferrocene into magnetic α -Fe and Fe₃C during shock processing. Magnetic dust particles play a significant role in the polarization of starlight, by aligning along the direction of galactic magnetic field lines. Consequently, the sudden change in magnetic properties induced by shock fronts may contribute to dynamic changes in light polarization in the ISM. Moreover, our findings provide additional support for the proposed mechanism of shock-induced impact release of neutral iron into the coma of distant comets. These results advance our understanding of the role of organometallic dust and the formation of carbon nanostructures in astrophysical environments.

Signatures of minerals are often detected in different parts of our galaxy and our solar system. In **Chapter 8**, we studied the formation of mineral dust by subjecting cosmic mineral dust precursors to shock waves. We found that shock processing can produce Mgrich olivine class of dust, MgO QD, crystalline Si, and magnetite QD. The morphology analysis revealed that a considerable proportion of the dust grains generated from all three sample sets exhibited a spherical shape with a metallic core. The results from this work suggest that shock processing of silicate dust precursors can be a viable route to produce silicate dust grains in different astrophysical environments, such as novae and the circumstellar environment of early-type stars. We extend the implications of this work to the crystalline silicate dust formation in comets and the formation of chondrules in the presolar nebula. Magnetic mineral dust present in the shocked sample can influence the shape and morphology of aggregated dust grains, and they can also contribute to various astrophysical processes, such as interstellar polarization and anomalous microwave emission in the dust growth process in the ISM.

9.2 Future direction:

The findings from this thesis work will pave the way for future research in several key areas. Moving forward, we plan to investigate the following research topics based on the outcomes of this study:

- In this thesis, we successfully demonstrated that HISTA is a powerful tool for generating and mimicking low-velocity interstellar shocks. Throughout our research, we operated HISTA within a Mach number range of 3 to 5.6. However, for future investigations, we plan to push HISTA beyond its current capabilities by utilizing much higher Mach numbers, resulting in significantly higher reflected shock temperatures. To achieve this, we will employ xenon (Xe) as the driven gas and use diaphragms with much smaller groove depths. By extending the operating limits of HISTA, we aim to explore the fate of cosmic dust grains subjected to much higher temperatures than those examined in this thesis. This enhanced capability will provide valuable insights into the behaviour of dust under more extreme astrophysical conditions such as supernova remnant, shocks associated with bi-polar high velocity out flow regions, and turbulence induced shocks in the early solar nebula contributing to a deeper understanding of dust evolution and processing in the ISM.
- Hydrogenated Amorphous Carbon (HAC) has been recognized as a significant component of interstellar carbonaceous dust (Jones et al., 1990; Dartois et al., 2004, 2007; Dartois & Muñoz-Caro, 2007; Pino et al., 2008). Its presence in the interstellar medium (ISM) has been studied by examining its infrared (IR) active features located at approximately 3.4, 6.8, and 7.2 µm, which correspond to the C-H stretching vibration and C-H bending motions in HAC (Chiar et al., 2000; Pendleton & Allamandola, 2002). Additionally, HAC has been proposed as a potential carrier of the Emission of the Extended Red Emission (ERE) phenomenon (Duley and Williams, 1988, 1990). Dust grains in the ISM undergo various energetic processes, enriching the chemical complexity of the ISM (Arumainayagam et al. 2019). Photoprocessing of HAC grains can lead to structural modifications by breaking the C-H bonds. UV-irradiated HAC grains have also been considered to be potential carriers of the interstellar 4.6 µm⁻¹ features (Mannella et al., 1996; Gadallah et al., 2011). Moreover, photo processing of HAC can give rise to carbon nanostructures such as PAHs and

fullerenes (Scott et al., 1997). In the last decade, astronomers have detected signatures of HAC in various astrophysical regions, including planetary nebulae that also contain fullerenes (García-Hernández et al. 2011a). To explain the formation pathway of fullerene in these planetary nebulae, (García-Hernández et al. 2011a) proposed that shock-induced thermal decomposition of HAC could lead to the formation of fullerene and graphene. However, laboratory shock processing of HAC grains behind the low-velocity interstellar shocks is currently limited. Therefore, studying the shock processing of HAC grains can provide valuable insights into the formation of different carbon nanostructures in the ISM.

Recently McGuire et al. 2021 identified the radio signatures of the two Nbearing PAH molecules, 1-cyano naphthalene (1-C₁₀H₇CN, 1-CNN) and 2cyano naphthalene (2-C₁₀H₇CN, 2-CNN) in the dark molecular cloud TMC-1. The evolution tracks of these two molecules in the ISM are still in evolving phase. Stockett et al. 2023 reported the findings on unimolecular dissociation and radiative cooling rate coefficients of the cationic form of 1-CNN isomer in their study. Their results are derived from measurements of the time-dependent emission rate of neutral products and kinetic energy release distributions obtained from a group of internally excited 1-CNN⁺ molecules. These experiments were conducted in an environment that closely resembles the conditions found in interstellar clouds. Their findings explain the unusual abundance of CNN in TMC-1 and question the commonly held notion of the rapid destruction of small PAHs in space (Stockett et al., 2023). Recently Ramachandran et al. 2023 conducted an infrared spectroscopic investigation of 1- and 2-CNN molecular ices under simulated interstellar conditions, exploring their temperature-dependent behaviour. Both 1-CNN and 2-CNN molecular ices were found to be amorphous at 7 K, and changes in their infrared spectral features were observed upon heating. Interestingly, these molecular ices demonstrated a tendency to remain in the amorphous state even when warmed to their respective sublimation points, which are higher than the sublimation point of water. This suggests that these molecules can exist on pre-existing dust surfaces under a wide range of thermodynamic conditions. While some laboratory experiments have been conducted by Stockett et al. (2023) and Ramachandran et al. (2023), there remains a lack of similar experiments exploring 1-CNN and 2-CNN molecules under simulated interstellar conditions. Understanding the fate of these molecules behind shock fronts in the ISM could shed light on the formation of various carbon nanostructures. We are eager to investigate the shock-induced evolution pathways of 1-CNN and 2-CNN molecules in future studies.

• In this thesis, we have studied the formation of the mineral dust, especially silicate-type mineral dust and magnetic dust. In future, we will explore the chemical reactions and transformations occurring in different cosmic mineral dust precursors under varying shock conditions. By analysing the post-shocked samples, we aim to identify additional mineral dust types and nanostructures that can form in the presence of different shock strengths and temperatures.

In this thesis 'Mote of dust Suspended in shock waves' we utilized shock tube very first time to probe the formation and evolution of cosmic dust grains, which has been least explored to date. We observed comprehensive evidences of the formation of different carbon nanostructures such as carbon nanoribbons, nano onions, fullerene, MWCNT, nanodiamond. We observed that interaction of shock front with the organometallic diamagnetic dust turned in to ferromagnetic dust. Mineral dust such as SiC, olivine, MgO QD, magnetite QD. These findings suggest that shocks especially the low velocity shocks can enrich its propagating medium by making different dust grains. In future we will be keep exploring the fate of different organic and inorganic dust grains behind the shock fronts.
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List of Publications:

1. Arijit Roy, Surendra Vikram Singh, M. Ambresh, D. Sahu, J.K. Meka, R. Ramachandran, P. Samarth, S. Pavithraa, V. Jayaram c, H. Hill e, J. Cami, B.N. Rajasekhar, P. Janardhan, Anil Bhardwaj, N.J. Mason, B. Sivaraman "Shock processing of amorphous carbon nanodust". Advances in Space Research 70.8(2022): 2571-2581. (https://doi.org/10.1016/j.asr.2022.06.068).

2. Arijit Roy, Surendra V. Singh, J. K. Meka, R. Ramachandran, D. Sahu, A. Gautam, T. Vijay, Jayaram Vishakantaiah, P. Janardhan, B. N. Rajasekhar, Anil Bhardwaj, N. J. Mason, and B. Sivaraman. "Shock-induced transformation of non-magnetic to magnetic ISM dust analogue." Monthly Notices of the Royal Astronomical Society 517.4 (2022): 4845-4855. (https://doi.org/10.1093/mnras/stac2637).

3. Arijit Roy, V. S. Surendra, R. Ramachandran, J. K. Meka, S. Gupta, P. Janardhan, B. N. Rajasekhar, H. Hill, Anil Bhardwaj, N. J. Mason, and B. Sivaraman. "Interstellar Carbonaceous Dust and Its Formation Pathways: From an Experimental Astrochemistry Perspective." Review Article Published in Journal of the Indian Institute of Science. (https://doi.org/10.1007/s41745-023-00393-6).

4. R Ramachandran, K K Rahul, J K Meka, S Pavithraa, A Roy, B N Rajasekhar, P Janardhan, Anil Bhardwaj, N J Mason & B Sivaraman. "Stability and morphology of cyanonaphthalene icy mantles on ISM cold dust analogues". (https://doi.org/10.1007/s12039-023-02192-z)

5. Venkataraman V; Arijit Roy; Ramachandran R; Quitian-Lara H M; Hill H; Raja Sekhar B N; Bhardwaj Anil; Mason N J; Sivaraman B. "Detection of polycyclic aromatic hydrocarbons on a sample of comets". (<u>https://doi.org/10.1007/s12036-023-09977-1</u>).

Manuscripts Under Preparations:

1. Arijit Roy et al. "Shock Induced Formation of Cosmic Mineral Dust Analog in Laboratory using High Intensity Shock Tube for Astrochemistry."

2. Arijit Roy et al. "Shock induced Formation of Cosmic Silicon Carbide dust analogue."

Awards/recognitions/travel grant:

- American Chemical Society (ACS) poster prize for the poster "*Shock Processing of Carbon Nanopowder*" in 3rd National Conference on Chemistry, held in IIT Gandhinagar from 12th to 13th February 2020.
- InterCat Travel Grant to attend the CosmicPAH meeting at Aarhus University, Denmark from 4th to 9th September, 2022.

- **Best Poster prize** for the poster "*Shock Induced Formation of Mineral Dust in the Interstellar Space*" in the 60th Annual Convention of Chemists (ACC) held in IIT Delhi from 20th to 21st December 2023.
- Jon Hougen Memorial Award to attend the 77th International Symposium on Molecular Spectroscopy, from June 17-21, 2024, in University of Illinois, Urbana-Champaign, U.S.A.

International Scientific Visit:

Visited Planetary Spectroscopy Laboratory (PSL), DLR, Berlin, Germany from 9th to 13th October 2023 for performing bi directional reflectance spectroscopic studies of shock processed interstellar and planetary dust analogues.

Conference, Workshop Details:

2023-2024 Academic Year:

1. 'Shock processing of smaller PAHs', at Meteoroids, Meteors and Meteorites: Messengers from Space (MetMess), 2023 from 1 to 3rd November 2023, PRL, Ahmedabad.

(Oral presentation)

2. 'Shock-Induced Formation of Mineral Dust in the Interstellar Space', in 60th Annual Convention of Chemist (ACC), from 20 to 21st December, 2023, IIT Delhi, New Delhi, India. (**Poster**)

3. 'Fate of Organics and Organometallics behind the Shock Front' in the 1st Symposium on genesis and evolution of organics in space, from 18 to 20th January, 2024, IIST, Thiruvananthapuram, India (**Invited Talk**).

4. 'Fate of PAHs behind the Shock Front' in the 22nd National Space Science Symposium' from 26th February to 1st of March 2024, Goa University, Goa, India. (**Poster and Oral representation**)

2022- 2023 Academic Year:

1. Bottom-up PAH Synthesis via Shocked Carbon Nanodust in The life cycle of Cosmic PAH, Aarhus, Denmark held on 5 - 9 September 2022. (**Poster**)

2. Shock Induced formation of SiC nanodust in Meteoroids, Meteors and Meteorites: Messengers from Space, PRL held on November 24-25, 2022. (**Online Oral Presentation**)

3. Organometallic Astrochemistry: a new frontier in Chemical Science in the XXXXI conference of the Indian Council of Chemists (ICC) organized by Indian Council of Chemists (ICC) from 27-29 December - 2022 at Dr. Bhimrao Ambedkar University, Agra. (**Poster**)

4. Minerals in the ISM are made in an instant in 7th National Symposium on Shock Waves (NSSW 2023), PRL on February 15-17, 2023. (**Oral Presentation**)

5. Shock Induced Formation of Cosmic Mineral Dust Analog in Laboratory using High-Intensity Shock Tube for Astrochemistry accepted in 54th Lunar and Planetary Science Conference (LPSC 2023) Organized by Lunar and Planetary Institute and NASA, from March 13–17, 2023, Houston, Texas, U.S.A. (**Poster**)

6. Shock Induced Formation of Cosmic Mineral Dust Analog in Laboratory using High-Intensity Shock Tube for Astrochemistry at 4th Indian Planetary Science Conference (IPSC) 2023, PRL held from March 22-24, 2023. (**Poster**)

2021- 2022 Academic Year:

- "Spectroscopic investigation of Comet 46P Wirtanen at UV wavelengths", European Planetary Science Congress (EPSC 2021), 13-24 September 2021. (Online Oral Presentation)
- "Minerals in the ISM are Made in an Instant", online symposium on Meteoroids, Meteors, Meteorites: Messenger from space (MetMeSS 2021), 29 & 30 November 2021. (Online Oral Presentation)
- **3.** "Minerals in the ISM are Made in an Instant", 21st National Space Science Symposium (NSSS-2022), 31 Jan 4 Feb 2022. (**Online Oral Presentation**)
- **4.** "Shock Processing of Organometallic Dust Ferrocene", 3rd Indian Planetary Science Conference (IPSC-2022), 14-16 March 2022. (**Online Oral Presentation**)

2020-2021 Academic Year:

- 1. Chandrayan 2 Data Workshop, 6-7 January, 2020, ISSDC, ISRO, Bangalore. (Attended)
- 2. "Shock Processing of Amorphous Carbon nano powder" at 3rd National Conference on Chemistry, 12-13th February,2020, IIT Gandhinagar. (Poster)
- **3.** "Shock Processing of Amorphous Carbon nano powder" at 1st Indian Planetary Science Conference (IPSC 2020), 19-21February,2020, PRL, Ahmedabad. (**Poster**)

- "Fate of Carbon Nanoparticles in Interstellar Medium" at National Shock Wave Symposium(NSSW2020), 26 -28 February,2020, IIT MADRAS, Chennai. (Oral presentation)
- "Shock processing of carbon nanopowder" in the European Planetary Science Congress (EPSC 2020), Virtual meeting from 21 September – 9 October 2020. (Poster).
- 6. "From smaller to laager PAH via shock processing in ISM." In the 2nd Indian Planetary Science Conference (IPSC 2020), 19-21February,2020, PRL, Ahmedabad. (Poster)

<u> 2019 – 2020 Academic Year:</u>

- 1. "Experimental Low Temperature Astrochemistry." In International Conference On the Infrared Astronomy and the Astrophysical Dust(IRAAD) 22-25 October,2019, IUCAA, Pune. (Poster)
- 2. 150th year of Periodic table, Chemical elements of our Universe: Origin and Evolution. 16-19 December, 2019, IIA, Bangalore, India. (Attended)