Diamonds in Space:

Messengers from the stars

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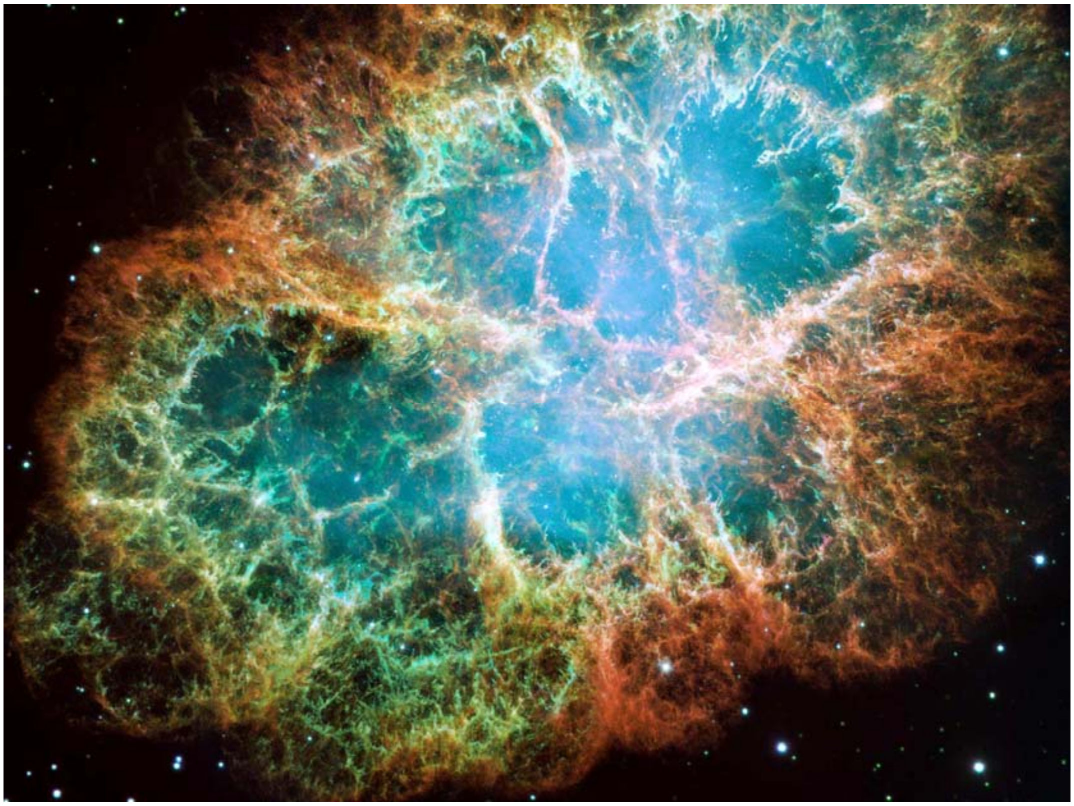

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1. Introduction

Diamonds do not just capture the hearts of many young and old women alike; also scientists have been known to have a keen eye on these pristine stones.

Our solar system is an extraordinary being. Not just because it houses our blue planet and our source of warmth; it is the result of something far greater. Many billions of years ago the Big Bang ejected a huge amount of hydrogen, helium and lithium atoms into deep space. After a long period of cooling down, galaxies were created, containing an immense amount of stars.

As these first generation stars were eventually dying, paving the way for the development of our own galaxy, the gas ejected from these objects formed a huge molecular cloud together with other atomic compounds. Essentially being a mix of products from the Big Bang and subsequent star chemistry, this huge clump of molecular matter gravitationally collapsed and a central star was formed. Following the creating of our main energy source, other solid objects like planets, moons, comets and asteroids were created.

Originally, it was thought that all matter present was homogenized in the hot swirling cloud of gas present in the center during its gravitational collapse. All record of presolar chemical and isotopical origin would have been destroyed as all solid were vaporized by the intense heat in the center of the cloud and mixed together with the presolar gases to form one homogenous solar nebula. In the outer colder fringes of our solar system, smaller bodies like meteorites, comets and Pluto were formed.

In the 1950's and 60's there were indications that the solar nebula was not homogenous after all. In meteorites Baoto and Briggs found deuterium enrichments that could not be explained by mass-fractionation [1] [2]. Besides deuterium, large ^{13}C enrichments were found by Clayton in carbonate material from the Orgueil meteorite [3]. Besides these early examples, many more elements with an anomalous isotopic signature were found inside different meteorites, signifying the possibility of presolar material present in meteorites.

It was not up until Lewis discovered and isolated presolar grains [4] from the Allende meteorite in 1987, that a new window of astronomy was opened. After Lewis successfully isolated diamond, SiC was discovered by Bernatowicz [5] and later graphite by Amari [6].

A part of these dust grains seem to have survived the initial onslaught, perhaps in the colder outer fringes of our solar system, during the formation of our solar nebula. These grains somehow were implanted into meteorites and interstellar dust particles, which carried them eventually to our planet and indirectly into our laboratories. These sources of material survived the formation of the solar system without being seriously affected by isotope homogenization in the center of the hot solar nebula.

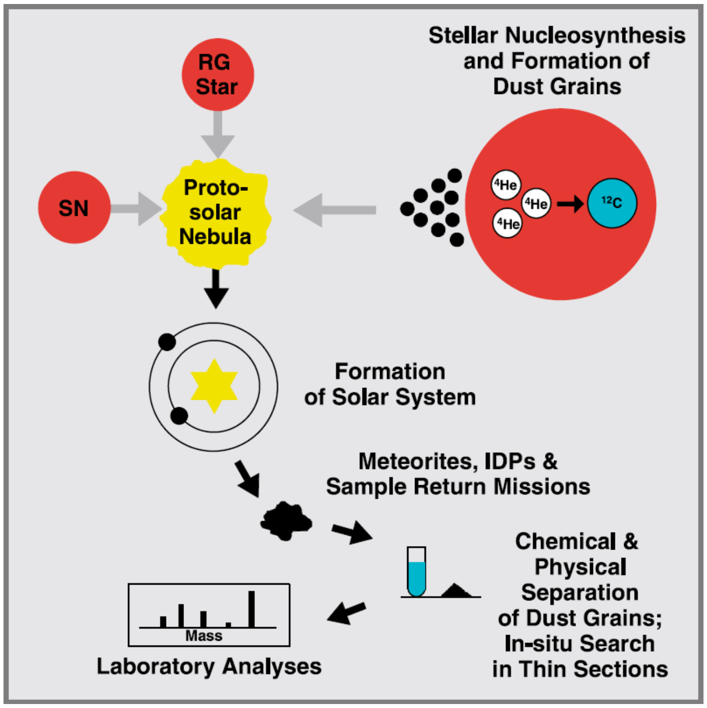


Figure 1: Schematic depiction of route of formation to analyses of presolar grains [7].

The amount of information these tiny grains give us, is enormous. These small objects have stood against the test of time and their morphologies and compositions may have been formed during their creation in other stellar systems. They can be seen as frozen fragments of individual star systems. By looking at their physical, chemical and isotopic characteristics, we gain a great amount of knowledge about the creation of solar systems (including our own), the interstellar medium, nucleosynthesis in stars and Galactic Chemical Evolution.

Amongst presolar grains like graphite, silicon carbide etc., diamond grains are the most abundant compounds present in meteorites, even though most nanodiamonds consist of a mere 1000 atoms. Many of the carbon structures house different trace elements with often anomalous isotopic signatures, which tell us a lot of their presolar origin.

Since the discovery of presolar diamond in meteorite samples by Lewis et al.[4] in 1987, there was no evidence that every could have a solar origin. In 2002 however, Dai made an important contribution by stating that nanodiamonds could have originated in the early solar system. By studying interplanetary dust particles or IDPs, he suggested that a part of these nanodiamonds were actually formed in our inner solar nebula, not in a presolar environment [8].

Although he did not propose a mechanism, Kouchi et al. provided in 2005 a suitable diamond formation route [9]. In his paper, Kouchi supplied two possible mechanisms, one being the formation of diamond on parent bodies of carbonaceous chondrites (see chapter 4.2 for more information). This formation route supports the conclusion of Dai, signifying the importance of this argument to the scientific field of nanodiamond formation in space.

In this review I shall discuss the latest development on the study of nanodiamonds, spanning from their isolation and identification, up to their formation and possible origins in the depths of space.

2. Diamonds in meteorites: isolation, analysis and structure

2.1 Isolation of nanodiamonds: burning down the haystack to find the needle

After the discovery and isolation of presolar diamond by Lewis et al.[4], Amari developed an effective separation method in 1994, isolating SiC, graphite and diamond [10]. Generally, the major part of stony meteorites (silicates), is removed by HF. Organic matter, mainly aromatic polymers, are destroyed by oxidants. Up till this point nearly 99% of the meteorite is destroyed. From the remaining residue, diamonds are collected by colloidal separation.

Figure 2: Nanodiamonds precipitate as a cloudy white gel from acidic solution [11].

For many years, scientists applied the same method to isolate nanodiamonds. But until 2003, Merchel et al. updated and sped up the process significantly, allowing the isolation of nanodiamonds from primitive meteorites in just a week [11] [12]. The time of isolating these nanometer sized objects is largely dictated by the duration of dissolving the major minerals with strong acids in order to isolate the so called "Q phase" (a phase consisting of isotopically normal noble gases). Not being interested in this specific phase, Merchel et al. used oxidizing agents at the beginning of the treatment. These oxidizing agents destroy this specific phase at the initial stages of the isolation procedure, instead of collecting it. Thus the number of necessary steps was drastically reduced. Furthermore the microwave digestion technique, developed by Kingston and Jassie [13] was used, eventually yielding an overall shorter isolation time.

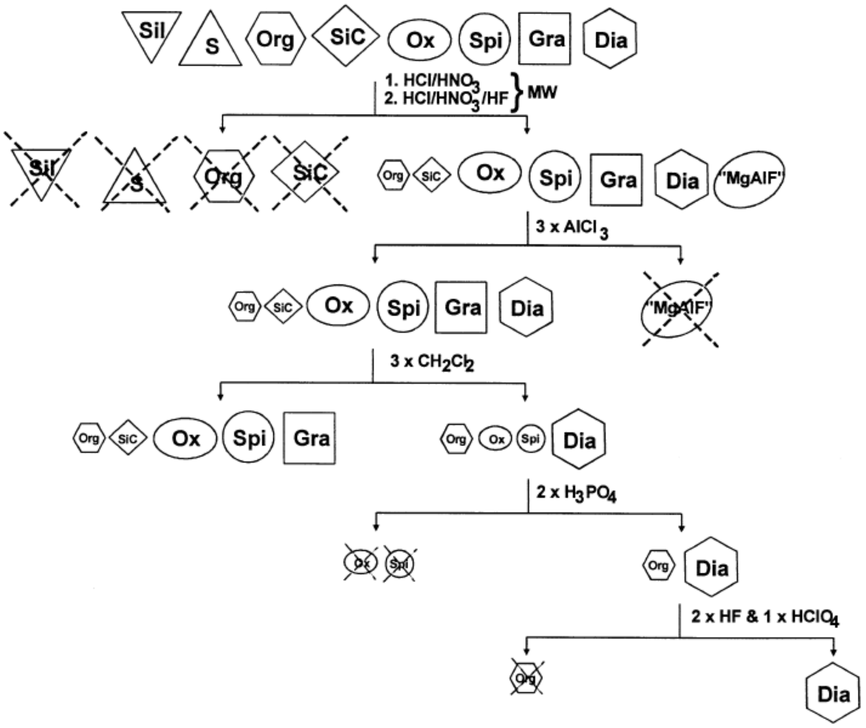


Figure 3: Schematic depiction of nanodiamond isolation procedure developed by Merchel et al. [11]

Besides collecting nanodiamonds through chemical processes, a non-destructive isolation method was developed by Verchovsky et al. in 1998 [14]. The technique comprises of the standard isolation procedure developed by Amari et al. [10], yielding colloids, followed by using ultracentrifugation. Verchovsky managed to isolate 2 – 4 nm nanodiamonds by different grain size. In 2006, he used this technique to discover the presence of Xe-S in presolar diamonds [15] (a xenon compound with a specific isotopic configuration), which is not found in diamond samples treated by the standard chemical procedure.

There are indications that the destructive chemical treatments could influence the physical properties of the nanodiamonds and even might dissolve unknown components. The isolation of Xe-S by ultracentrifugation is such an example. Perhaps in the future with the development of more advanced isolation techniques, new components could be discovered, which previously were not found due to destruction by chemical isolation.

2.2 Analysis Techniques

The problem with these tiny diamonds from meteorites is their minute size. These nanodiamonds consist of about 1000 atoms, which means that it is almost impossible to measure them individually. Therefore, a single measurement of many diamonds is taken, which tells us something about the average isotopic composition and other properties. On the other hand, individual grains can be studied by high resolution electron microscopes like TEM and SEM.

First of all, for structural analysis a lot of **X-ray** and **electron diffraction techniques** are being used to identify the crystal structure, space group etc. of the crystalline nanodiamond.

Secondly, **Raman spectroscopy** is a powerful method to study carbonaceous material. The power of this method is to easily identify different forms of carbon such as diamond, graphite, fullerene, amorphous carbon etc. Also information about crystal sizes, stresses and structural perfection can be obtained by looking at the broadening and shifts of the peaks [16].

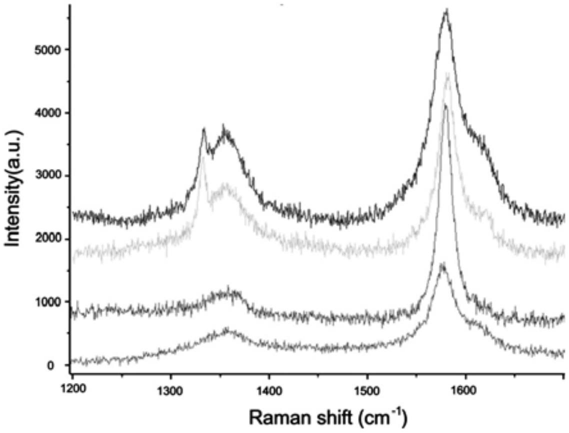


Figure 4: First-order Raman spectra of carbon phases at four different places in the NWA XXX ureilite found in 2006 in Morocco, the Raman bands at 1332 cm^{-1} indicate the presence of diamond [16].

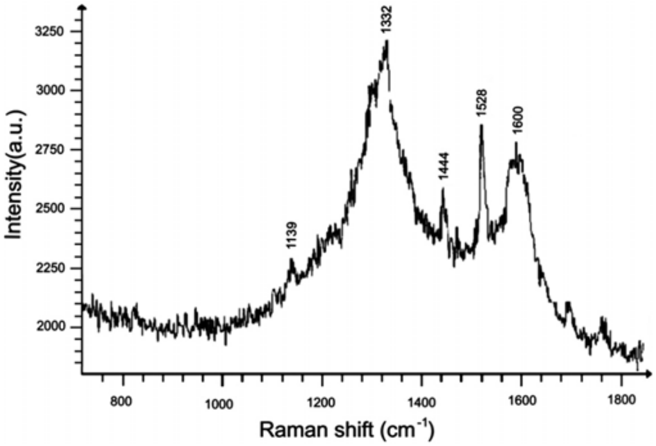


Figure 5: Raman spectra of Nanocrystalline Diamond Coating (NCD) obtained in laboratory by the RF PACVD method [16].

SEM (Scanning Electron Microscopy) is used to characterize surface morphology and bulk elemental make-up of grains. **TEM (**Transmission Electron Microscopy) is used to study crystal structures, defects on a nanometer scale and to search for subgrains within individual grains. These features make this technique highly useful for locating nanodiamonds within meteoric samples.

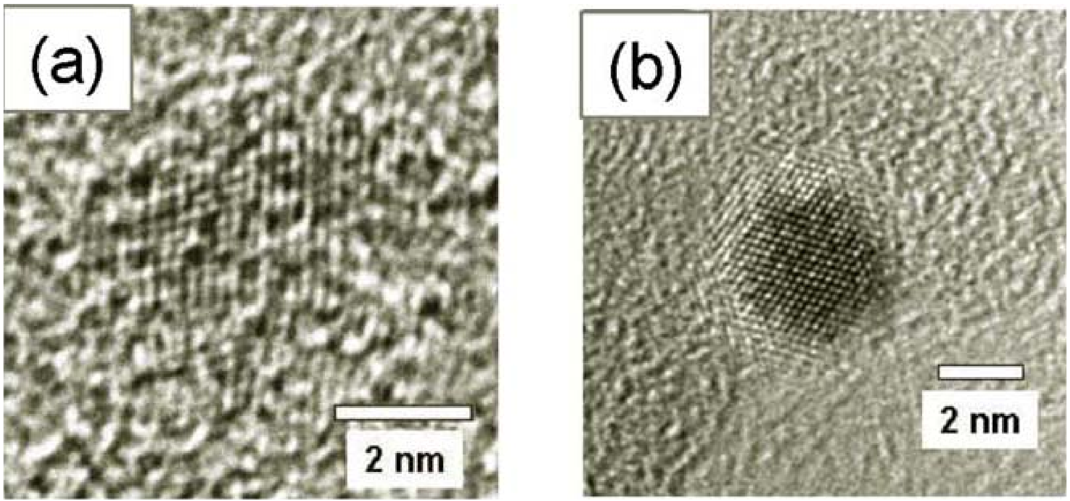


Figure 6: TEM images showing the crystal lattices of (a) Allende and (b) synthetic diamond [17].

NanoSIMS 50, designed in 1993, is the successor of SIMS and a big step forward in the study of presolar grains since its introduction in the scientific field of extraterrestrial material research in 2001 [18]. Secondary ions are produced by bombardment of the sample with either O^- or Cs^+ primary ions, and transported to a mass spectrometer. It has a higher lateral resolution and a much higher sensitivity for secondary ions compared to its predecessor, SIMS (see Figure 7). It is one of the most important tools in cosmochemistry. A couple of achievements of the Nanosims 50 are: (i) the discovery of silicate stardust in interplanetary dust particles and primitive meteorite,; (ii) the extension of isotopic studies to submicrometer-sized presolar SiC and spinel grains separated from primitive meteorites by chemical and physical treatments; (iii) identification of isotopic heterogeneities within micrometer-sized presolar grains; (iv) coordinated NanoSIMS-TEM studies made it possible to obtain simultaneous information on the mineralogy, structure, and isotopic composition of grains.

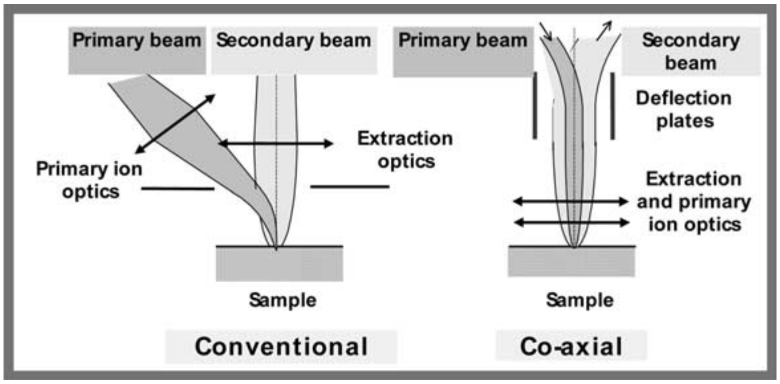


Figure 7: Ion optics of the NanoSIMS 50 (right) in comparison with the conventional design (left) [18].

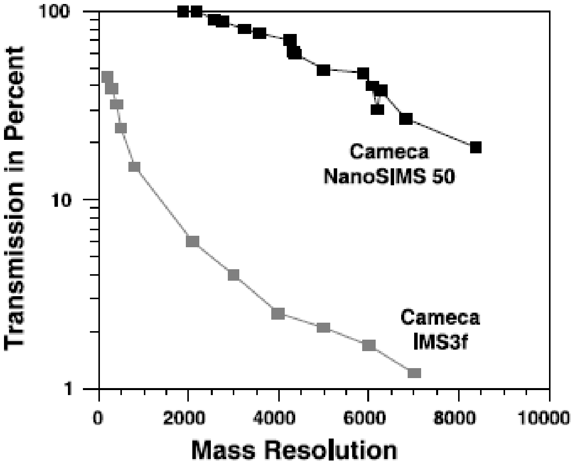


Figure 8: Transmission of the NanoSIM 50 as a function of mass resolution, in comparison with the IMS 3f ion microprobe [18].

TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) [19] is comparable to the NanoSIMS 50. It is a higher resolution than the standard SIMS, although not as high as the NanoSIMS 50. The advantage of TOF-SIMS over NanoSIMS 50 is that data over a whole mass range can be obtained. Therefore it is an excellent method to study surface features, abundances of elements and their distribution. On the other hand NanoSIMS 50 is far superior in specific and precise isotope measurements.

RIMS (Resonance ionization mass spectrometry) [20] is also one of the mostly used analytical techniques used for presolar material research. With RIMS, material is desorbed from sample using a laser beam. A tunable laser is used to resonantly ionize a specific element of interest in the desorbed plume, which is then analyzed by a mass spectrometer. This technique enables the detection of heavy elements and their isotopic composition at trace levels within individual grains. The NanoSIMS 50 is a better alternative if the specific elements are easily ionized and not compromised by isobaric interference, i.e. when different elements have the same mass due to certain isotopic compositions.

AMS (Accelerator Mass Spectrometry) [19] also overcomes isobaric interference and has a larger flexibility in switching between elements compared to RIMS, although it is not as sensitive. An example in which AMS is highly useful is in the case of analyzing trace elements incorporated in nanodiamonds from meteorite samples. On average, a nanodiamond consists of around a 1000 atoms, but only a few contain a trace element. Therefore a lot of diamonds need to be measured to find these components, which can easily be done using AMS.

EELS (Electron Energy Loss Spectrometry) [21] is a useful technique which allows the measurement the electronic structure (i.e. bonding) in materials with subnanometer spatial resolution. With this method information can be obtained of which types of carbon are present at the surface of nanodiamonds, for example graphite, diamond etc. The specific transitions (e.g. 1s , 1p) are deducted from the minute energy loss measured after a primary electron beam has penetrated a sample. Furthermore, EELS is used in combination with TEM, which allows for very local measurements.

2.3 Structural Analysis

Terrestrial and extraterrestrial diamonds have different structures. While terrestrial diamonds are mostly cubic, diamonds from space have several structural forms known, including several cubic, hexagonal and rhombohedral. The polytypes of these diamond structures are 3C, 2H, 4H, 6H, 8H, 10H, 15R, 21 R [22].

The most common presolar diamond is polytype 2H, also known as Lonsdaleite.

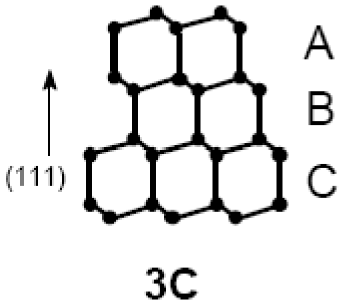
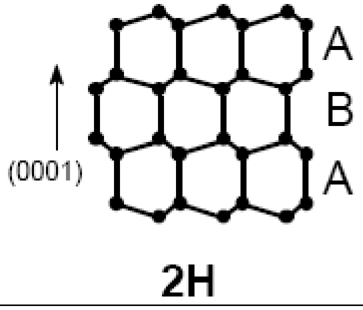
Polytype	**3C: Diamond from Earth**	**2H: Lonsdaleite**
Crystal lattice		
Hybridization	Face Centered Cubic (FCC)	Hexagonal
Stacking sequence	ABC ABC ABC	AB AB AB
Binding distance	1,54 Å	1,52 Å
Lattice constant	a = 3,56 Å	a = 2,52 Å, c = 4,12 Å
Characteristic Raman peeks	^{12}C / ^{13}C 1332 cm^{-1} / 1284 cm^{-1}	1320 ± 5 cm^{-1}
Density	3,52 g/cm^{3}	2,22 – 2,33 g/cm^{3} *

Figure 9. Table of characteristics of 3C and 2H diamond polytypes [22].
*: the density of lonsdaleite presolar diamond is low because one nanodiamond consists of only around 1000 atoms, which leads to a low density because of its high surface energy compared to the bulk.

Nanodiamonds consist of merely around 1000 atoms per grain and measure 2-3 nm. Therefore a large amount of carbon atoms are present at the surface, which means its physical and chemical properties are different from larger diamonds, in which most atoms are in the bulk of the crystal.

2.3.1. Carbonado diamond

In 2006, Garai [23] hypothesized about a possible extraterrestrial origin of Carbonado diamonds. Carbonado diamonds are black to dark grey polycrystalline cuboid diamond, found in Brazil and the Central African Republic. On closer inspection however, many of the characteristics did not comply with a deep earth environment, so further studies were carried out. It is assumed that Carbonado is a product of a large meteorite impact [24]. It has also been suggested to be a meteorite, possibly from a fragmented carbon-type asteroid [25]. By using synchrotron infrared radiation, the spectra conjured was almost identical to spectra of CVD and presolar diamonds, leading to the conclusion that these diamonds are likely formed in outer space.

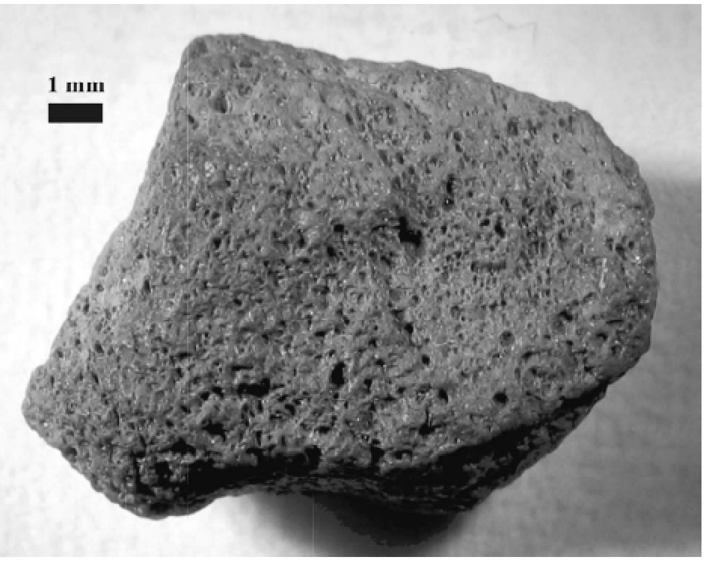


Figure 10: A typical black and highly porous polycrystalline carbonado-diamond (5.3 cts) from Lencois, State of Bahia, Brazil [21].

2.4 Isotopic Analysis

As far as 1964, years before the discovery and isolation of presolar grains, Reynolds and Turner found anomalous isotopic signatures for xenon in meteorites [26]. As more isotopic compositions of different elements were found, which did not comply with the solar abundance, the scientific community was puzzled for it was thought that before the creation of our solar system, all matter was homogenized in the large hot swirling cloud of gas.

As Lewis discovered presolar grains in meteorites [4], it all fell into place, or so it seemed. After careful analyses of collected meteorite samples, trace elements were found present in the diamond grains of these meteorite samples. These diamond grains appear to be the perfect protection cages for certain trace atoms. These findings consequently initiated a completely new scientific area since trace elements act as beacons which signify that a part of the grains are of presolar origin. Consequently, this gives an incredible amount of information about nucleosynthesis, Galactic Chemical Evolution and the creation of our solar system and others alike.

For a long time it was believed that nanodiamonds found in meteorites had no solar origin. However in 2002, when Dai stated that nanodiamonds could have originated in the early solar system [8], the assumption about the origin of nanodiamonds present in space changed.

Because of the current technical limitations of measuring isotopic compositions of minute nanodiamonds, no diamond grain can be measured individually. Therefore only bulk samples can be measured, meaning possible solar and presolar nanodiamonds can not be distinguished from each other.

2.4.1. Xenology

The xenon component Xe-HL was found as the prime beacon for presolar diamond grains. This form of xenon is partly enriched in both light (Xe-L, p-process, 124 and 126 isotopes) and heavy (Xe-H, r-process, 134 and 136 isotopes). [27] Xenon-HL also comprises of Xe-S (s-process, 128 and 130 isotopes), which is often accompanied by Kr-S. [28]

Xe-H and Xe-L are correlated; the higher the former, the higher the latter (see Figure 11). This correlation has been found in many diamond grains within different kinds of meteorites. This phenomenon is somewhat odd, since both types of isotopes (p- and r-process) are produced in different physical settings.

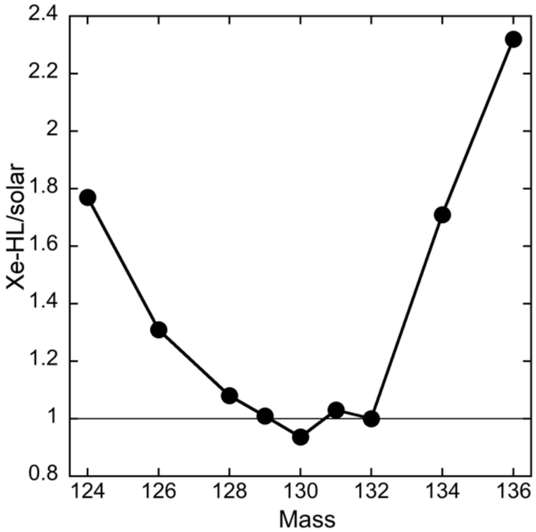


Figure 11: The Xe-HL pattern of xenon isotopes are normalized by 132Xe and the solar ratios. Excesses in the p-process only isotopes and the r-process only isotopes are always observed together. [29].

The p-process is considered to occur in O/Ne zone in supernovae [30], while the r-process is said to most likely occur in neutrino-driven winds from the neutron star of core-collapsed supernovae [31].

Furthermore, the ratios found for p- and r-process xenon found in diamond grains do not comply with the ratio of solar abundance xenon (see Figure 12).

	Xe-L ratio ($^{124}Xe/^{126}Xe$)	Xe–H ratio ($^{134}Xe/^{136}Xe$)
Presolar Diamond	**2.205**	**0.699**
Solar System Abundance	**1.157**	**1.207**

Figure 12: Ratios of p- and r-process xenon found in presolar diamonds and in our own solar system [32].

In an attempt to explain the appearance of the ratios of Xe-L and Xe-H, which are non-compliant to the solar abundance, Howard proposed that the anomalous isotopes were produced by an intense neutron burst, before being implanted into the diamond [33].

Also, Ott et al. proposed a "rapid separation scenario", in which unstable precursors with different half-lives are separated from Xe at a proper time to produce the Xe-H pattern. Ott used the same approach to explain Xe-L [34]. However, this process requires a very precise timing of the separation. Presolar diamonds in meteorites are undoubtedly formed in more than one supernova. Therefore, the separation should have taken place at the "right" time in most supernovae that produced diamonds in meteorites. Realistically, it is highly unlikely that most supernovae experienced the same "separation" time.

Another scenario is proposed by Ott et al. In order to explain the Xe-H pattern, Ott states that the origin of the anomalous heavy isotope composition is due to a mix of neutron-burst material and solar Xe [34]. Unfortunately, this scenario could not answer the anomalous Xe-L isotopic composition.

Besides Xe-HL, two xenon components have been identified: Xe-P3 and Xe-P6, which is minutely present compared to the other two components [35].

Through stepwise combustion, the first fraction released is Xe-P3 at low temperature (500 ^{0}C). Except for Ne, the rest of the isotopic ratios of the noble gasses in this fraction are close to the solar abundance. A mixture of Xe-P3 and Xe-HL is released at intermediate temperature. Xe-HL consists of more fractionated isotopic compositions relative to solar abundance [12]. Finally, at high temperatures, a mixture of Xe-HL and Xe-P6 is released [36]. The release of different components over different temperatures points to the fact that these components probably have been implanted in different events and/or into a separate diamond population [37] [38]. Besides these findings, the carbon release patterns (observed by stepwise heating) and the C/N ratios found, also indicate this possibility. It is also possible that another phase remained in the diamond separate after chemical and physical isolation [39].

Another important issue is why one component is thermally more easily released (Xe-P3) than the other Xe-HL. Lodders arguments that, because Xe-P3 and nitrogen concentrations are higher in CI- and CM-chondrites than in CV-, ordinary-, and enstatite chondrites, the diamonds containing the P3-component could have more nitrogen as an impurity in solid solution, which might lead to a crystal structure which is less stable to thermal destruction [12].

In 2006, Verchovsky states that the minor fraction of diamonds which have Xe-S present (an s-process isotope), point to an AGB-star origin [15].

These noble gas components and maybe even other trace elements with a presolar isotopic composition, seem to have been incorporated by ion implantation [37]. Also the abundances of noble cases seem to be linked to grain size [14]. Finally, it is virtually impossible to determine the age of the trace elements in diamond grains since these systems involve the decay of rare constituents, which decay into other rare elements with uncertain non-radiogenic compositions [40].

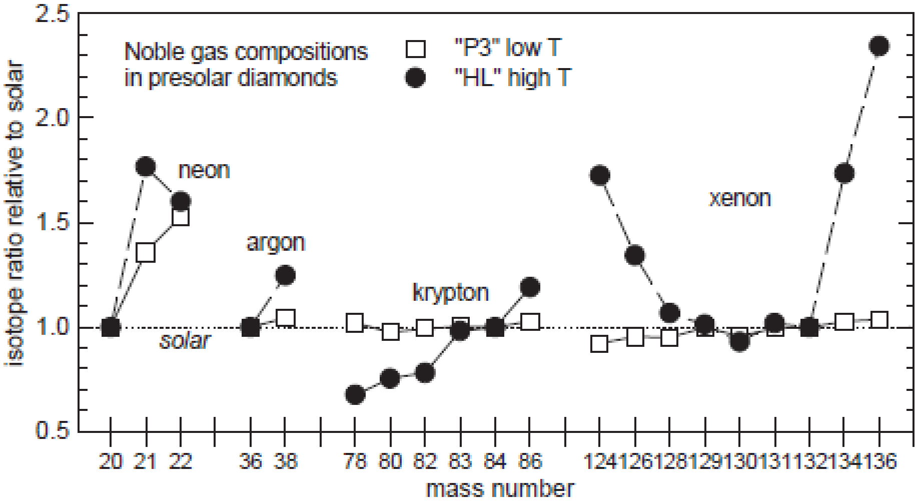


Figure 13: Noble gas isotopic composition in presolar diamonds [29] [41].

2.4.2. Other elements

Besides the large anomalous isotopic composition deviations of xenon, those of other heavy elements are very small. Amongst them, tellerium [42] and palladium [43] show smaller anomalies compared to xenon, but nonetheless they can successfully be applied to the rapid separation and the neutron burst model [44].

Furthermore, the isotopic ratio of carbon is very close to the solar ratio [4]. The isotopic range of nitrogen [4 39,] present in nanodiamonds, is higher than the values observed in different types of meteorites, but according to Owen et al. it is close to the isotopic composition ratio of Jupiter [45]. This specific ratio is a better representation for the solar system than the terrestrial atmosphere, since it is influenced by atmospheric escape processes [12].

The overall similarity of carbon and nitrogen isotopes of nanodiamond grains supports the argument that most diamonds in meteorites originate from within the solar system. This is in correspondence with Dai et al. who investigated interstellar dust particles and suggested the same [8].

One big problem that remains is that individual diamond grains can not be measured individually for its isotopic composition. Therefore it might be possible that there are indeed specific isotopic compositions present within nanodiamonds that point to a solar or presolar origin.

For example, it could be possible that there is indeed an anomalous presolar isotopic composition for carbon and nitrogen but that these signatures are masked by the huge amount of solar carbon and nitrogen present in more abundant grains present in meteorites. On the other hand, p- and r-processes of noble gases point to the contribution of supernovae to the formation of diamonds, which would mean that the highly variable C-isotopic compositions average out to give a $^{12}C/^{13}C$ ratio close to the solar ratio [12]. Also, xenon is sparsely present in diamond (1 out of 10^6 nanodiamonds) [15] and bulk samples are taken to measure its isotopic ratios. Therefore a huge isotopic anomaly in Xe-HL within a small grain fraction can easily dominate the overall observed Xe-isotopic composition.

Up till today, there is no definite answer as to why Xe-L and Xe-H are correlated and why the ratios of both isotopes differ significantly from the solar system abundance. The findings of different xenon components with different thermal stabilities related to different diamond populations is also not fully understood as of yet. Furthermore there could be populations of anomalous isotopic signatures for carbon and nitrogen present in nanodiamond, in line with the observations for xenon, giving indications of their solar or presolar origin. These are major problems which have been present for decades. Advances in analysis techniques which would allow for isotopic measurements in individual diamond grains and further studies might help finally cracking this puzzle.

3. Diamonds in space: spectroscopy

3.1 Discovery of diamonds in space

The discovery of presolar nanodiamonds opened up a world of possibilities. Before the time in which isotopic ratios of noble gasses in meteorites were linked to the presolar origin of their carriers, scientists were mostly relying on telescopes and electromagnetic radiation for doing research about our solar system and beyond. After the discovery of Lewis et al. [4] it became possible to conduct extensive laboratory studies in order to find out more about these beacons from outer space. These unaltered particles from other stars provided a wealth of information for scientists to study.

Spectroscopic methods have evolved substantially throughout the years due to technological advances and better know-how of the studied samples. Although nanodiamonds were found in several different types of meteorites and studied extensively in laboratories, for a long time there had not been one single definitive observation of diamond outside of our planet.

Since the 1980's the scientific community was puzzled by the infrared emission features at 3.43 μm and 3.53 μm observed in the spectra of several Herbig Ae/Be stars (very young stars developed by a protoplanetary disk) [46 47]. After a long time of speculation, Guillois finally identified what was responsible for the 3.53 μm infrared band: the C-H stretch of the surface of nanodiamonds present in the dusty envelopes surrounding stars [48]. This discovery meant the first observation of diamond outside our planet.

Up till today there are four stars known to have the 3.53 μm signature [49]: three Herbig Ae/Be stars: HD 97048 [46], Elias 1 [47], MWC 297 [50] and HR 4049, a post AGB-object [51].

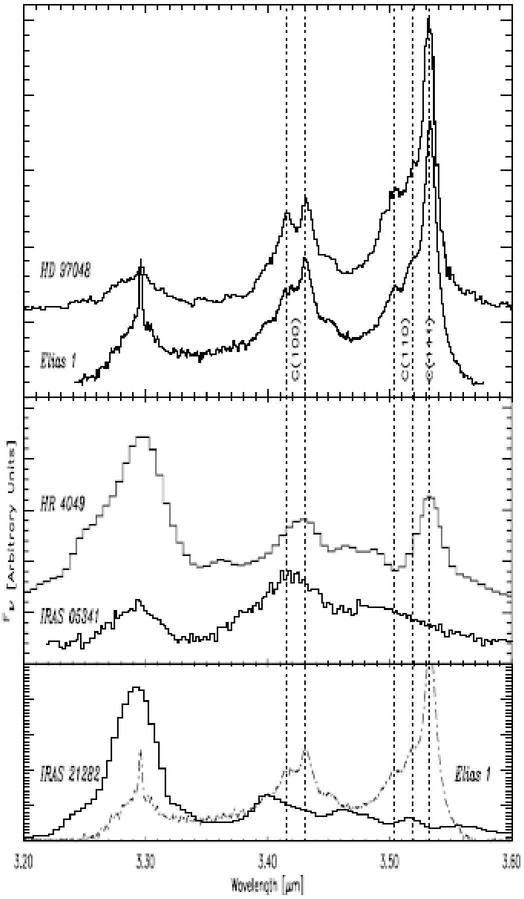


Figure 14: The 3 µm spectra of HD 97048 and Elias 1 (top panel) and of HR 4049 and IRAS 05341 (middle panel). A comparison of the 3 µm m spectra of Elias 1 and the planetary nebula, IRAS 21282 is shown in the bottom panel [51].

Scientists have been looking constantly for new stars which share the same specific infrared band. Acke et al. started a survey of 60 stars in 2006 but it did not yield any new stars with the same emission feature but he did find some possible candidates like TY CrA, V 921 Sco and HD 163296 [52]. Furthermore, there are several findings of a relatively weak 3.53 µm feature of different stars, for example HD 142527 [53] and HD 100546 [54]. The intensities of these 3.53 µm emissions are very low compared to the three Herbig Ae/Be stars.

These stars, which clearly show the 3.53 µm infrared band, are birth grounds for nanodiamonds. So far no other convincing identification feature has been found for diamond detection in space.

3.2 Diamond formation models and sizes of nanodiamonds

After the discovery of nanodiamonds present near certain stars, the scientific community was trying to find answers as to how these diamonds are formed and what their physical properties are.

It seems that a protoplanetary disk, a hot central star and a stellar companion emitting hard X-rays [49] are the perquisites for nanodiamond formation in outer space, responsible for the 3.53 µm emission feature. Temperatures around 1000 K have been observed around HD 97048 by Kerckhoven et al. [51] and coincide with the experimental findings of 800 K by Banhart [55]. This temperature (due to strong UV fluxes) is high enough to induce a process of nanodiamonds formation in space similar to Chemical Vapor Deposition (CVD) [56]. For more information on CVD, read chapter 4.

Dai linked his findings of a solar origin of meteoric nanodiamonds to the detection of diamond within the accretion discs of other young stars [8 51]. Years later, Kouchi supported Dai's conclusion by coming up with a suitable formation route of diamond produced on parent bodies of carbonaceous chondrites (see chapter 4.2) [9]. In the same paper, Kouchi suggested another diamond formation model [9]. He experimentally found out that a diamond precursor can nucleate under UV photolysis of interstellar ice mixtures in molecular clouds and can manage to grow with further UV irradiation in diffuse clouds. Applying this discovery to their own research of interstellar diamondoid molecules, Pirali et al. implied that the growth of small diamondoids would take place on the surfaces of the grains/ices, acting as substrates [57]. The frozen water would sublimate in the inner planet forming disks around protostars, liberating these small diamondoids into the gas phase. Furthermore it is possible that the intense far-UV field in HD 97048 and Elias 1 would convert the less stable into the more stable symmetric diamondoids which dominate the 3 µm spectra.

The debate about the size of the nanodiamonds is still ongoing. In 2002, Kerckhoven et al. determined that the size of presolar diamonds (observed from the infrared spectra of the Herbig Ae / Be stars) is about 1 – 10 nm [51]. On the other hand, Sheu et al 2002 produced CVD synthesized nanodiamonds and found that only the CVD diamonds between the size of 25 – 50 nm are responsible for the specific emission feature at 3.53 µm [56].

In 2004, Jones et al. surface-cleaned and hydrogenated nanodiamonds (from the Orgueil meteorite) of different sizes, followed by infrared measurements to study the 3 µm bands [58]. It became apparent that the mean size of the nanodiamond particles strongly influences the CH-stretching pattern. Most importantly the distinct 3.53 µm infrared band appeared only for diamonds larger than 50 nm.

It became apparent that the mean size of the nanodiamond particles strongly influences the CH-stretching pattern. Extending the discussion about the size of the observed diamonds in space, a study by Pirali et al, in which different diamondoid molecules were synthesized and their infrared frequencies measured, showed the presence of the 3.53 µm infrared pattern for diamondoids with a size smaller than 50 nm [57]. Consequently, they state the distinct possibility that the 3.43 µm and 3.53 µm emission features in HD 97048 and Elias 1 could be assigned to smaller diamondoids a few nanometers in size. Finally, in 2009 Goto et al determinded the size the nanodiamonds present for Elias 1 to be as large as 100 nm [49].

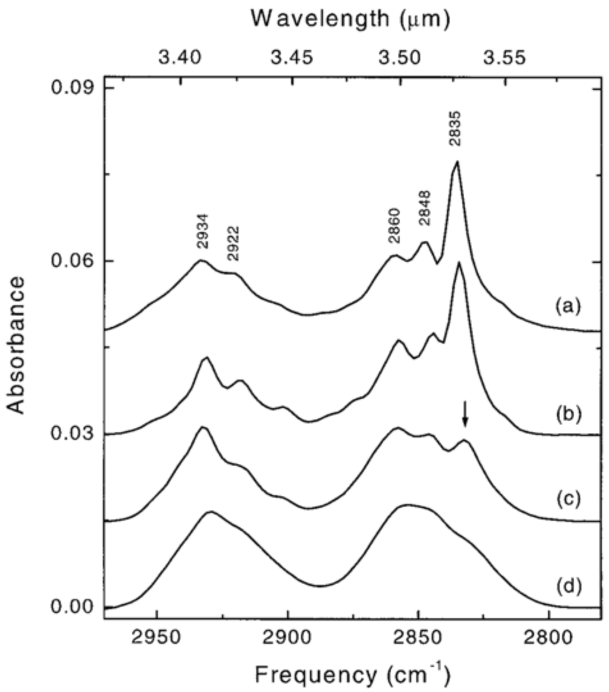


Figure 15: Comparison of the infrared spectra of diamond particles with a size of (*a*) 700 nm, (*b*) 100 nm, (*c*) 25–50 nm, and (*d*) less than 5 nm. The diamond nanoparticles are all derived from the same source and are H-etched using the same CVD type hot-filament method. All the spectra are taken at room temperature. The arrow in (*c*) indicates the emergence of the characteristic feature at 2835 cm^{-1} (i.e. 3.53 μm) [56].

Apparently there is a limit on the sizes of nanodiamonds which are responsible for the particular infrared band observed. What this limit is, is still not very clear. Rati and Gally studied in 2003 the stability of nanodiamonds and their results show that as the size of diamond is reduced to about 3 nm, it is energetically more favourable for this material to have bare, reconstructed surfaces than hydrogenated surfaces [59]. If there is no hydrogen present at the surface, there will be no C-H stretch visible for these components. Overall there is a good possibility that nanodiamonds, which do not have the specific size requirements (either by their lack of hydrogen at the surface or by other factors), are indeed present in space but can not be detected as of today by infrared measurements.

The question remains in what way nanodiamonds are formed in outer space and how they are responsible for the 3.53 μm emission feature in HD 97048 and Elias 1. Furthermore it is unclear how nanodiamonds observed in space are related to presolar diamonds found in meteorites, CVD produced nanodiamonds and other diamondoids, and how the findings of the authors mentioned above are significant to the understanding of this specific emission feature and the deducted size of the true diamonds in space.

3.3 Carbon onion as a pressure cell for diamond creation

Besides possible formation sites and the size of these nanodiamonds in space, a lot of discussion is going on about the morphology of the specific diamond particles.

Banhart et al. proved in 1996 experimentally that by electron irraditation, nanometer sized carbon onions were formed and that by further applying high-electron beams, the cores of the carbon onions transformed into the lattice of the diamond within an hour [55]. This discovery was later linked to the observations of the 3.53 μm band by Goto et al, who proposed a diamond formation route using carbon onions as a high pressure cell [49]. In protoplanetary disks it is difficult to maintain a high enough pressure to allow diamonds to form over the energetically more favored graphite. Goto et al. state that carbon onions are possibly formed in these disks and due to the continuously peeling of the outers shells (because of electron irradiation), the inner shells experienced enormous pressures, leading to diamond formation from the inside out [49].

Carbon onions have been found in meteorites [60 61], in modeling experiments [62 63] and in laboratory experiments [55 64]. So far there are some indications of their presence in the interstellar medium, although no conclusive evidence has been published as of yet.

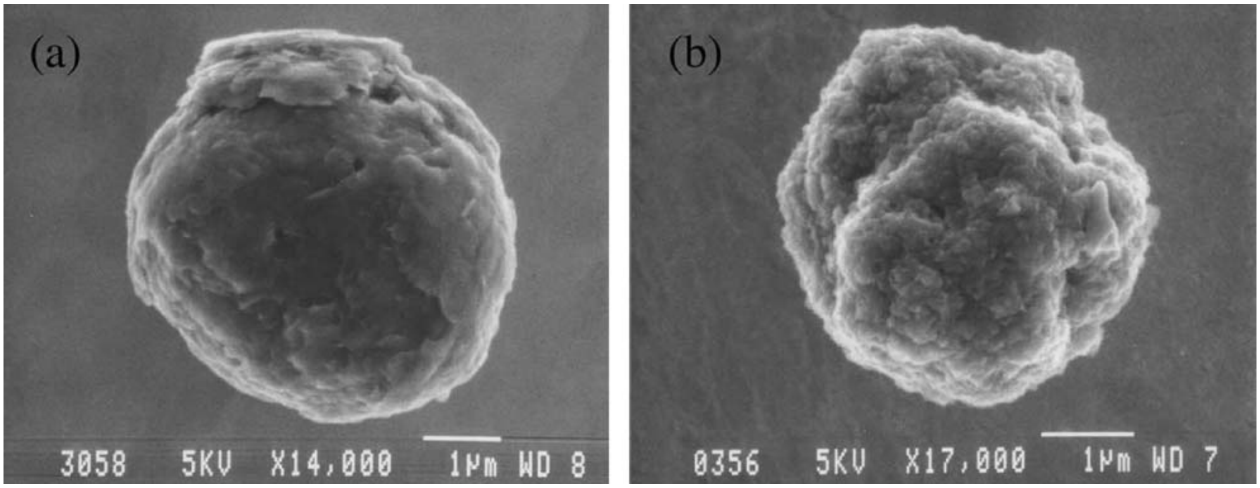


Figure 16: Presolar graphite grains show two morphologies: (a) a graphite grain of the ‘‘onion’’ type, with a layered surface structure; and (b) a graphite grain of the ‘‘cauliflower’’ type, which appears as aggregates of small grains [12].

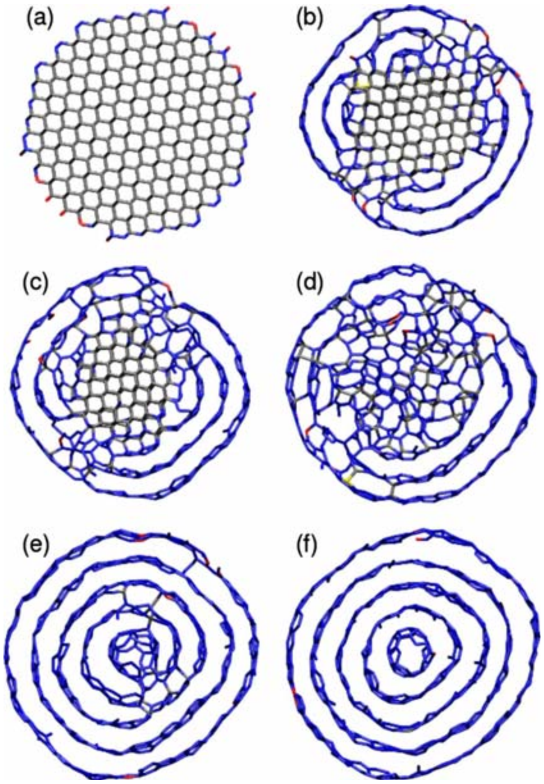


Figure 17: Atomistic simulations of the formation of multiwall fullerenes from nanodiamonds. 6 Å-thick slices as a function of time (a: 0 ps, b: 50 ps, c: 100 ps, d: 200 ps, e: 800 ps, and f: 1600 ps) illustrating the graphitization

mechanism of a 3 nm UDD at 3000 K. Atoms are colored according to their coordination (red: twofold, blue: threefold, gray: fourfold, yellow: other) [65].

Unfortunately carbon onions show a continuous absorption consisting of no bands or lines due to some functional groups [49]. Despite the presence of diamond cores inside carbon onions, the specific surface feature of nanodiamonds at 3.53 μm would not be seen as it would be shielded by carbon layers on the outside.

Combining the facts of their existence, together with the limits of detection, the presence of diamonds in space, created specifically through the formation from these carbon onions, remains a promising suggestion.

3.4 Extended Red Emission

Besides the discovery of nanodiamonds through infrared spectroscopy, ERE (Extended Red Emission) is seen as a possible candidate for detecting diamonds in space. ERE is the 500 to 1000 nm spectral range of emission, which is excited by ultraviolet photons irradiating specific components. It is an important property of interstellar dust and it is still unclear as to which component is responsible for the ERE band. In 2006, Chang and Chen published a paper in which they state the possibility that nanodiamond may be the possible carrier for the Extended Red Emission (ERE) band by luminescence [66]. If this assumption would be correct (although it is far from definite as of today), ERE could become the second method to detect the presence of these diamonds in space. Having different properties, ERE could find new birthgrounds for these tiny carbon particles and give more information about their existence and creation.

4. Diamond formation

After the discovery of interstellar diamond grains in meteorites by Lewis et al in 1987 [4], the scientific community was seeking definite answers in which way these diamonds have been formed over the ages. Diamonds are incredible resistant to temperature, radiation and chemical treatment. Therefore their original growth features such as morphology, polymorphic modifications and lattice defects are readily preserved since their formation in space until the descent and impact on our planet.

In the early sixties, meteoric diamonds were believed to have been formed in the interior of planetary bodies due to pressure and temperature processes [16]. With the rise of the development of shockwave produced synthetic diamonds, it was implied that the same mechanism was responsible for the formation of meteoric diamonds. Strong shockwaves generated by exploding supernovae, were believed to transform interstellar graphite or amorphous carbon into diamond by grain-grain collisions [67]. Also the fact that the same lonsdaelite structure (as found in meteoric diamonds) could be created by this shock explosion process, enhanced the popularity of this theory.

After the development of several low-pressure methods of diamond formation (Chemical Vapor Deposition or CVD) and the discovery of interstellar diamond, the CVD theory quickly gained popularity among the scientific community. Chemical Vapor Deposition is a process in which carbon species are activated and subsequently deposited as diamond at the solid interface in the carbon-hydrogen system at low pressure and high temperature [68].

After Dai’s suggestion that nanodiamonds might also have originated in our own solar system [8], Kouchi came up with an interesting model for solar nanodiamond formation on parent bodies of carbonaceous chondrites [9].

Up till today the shockwave and CVD theory (as well as the suggestion of Dai for solar nanodiamond formation) have been the contenders for the title of which method is mainly responsible for the creation of nanodiamonds in outer space.

There have been some more specific models proposed, such as UV annealing of carbonaceous grains and radiation-induced mechanism [12 69 70], but they are not as widely accepted as the other formation routes as of yet and it is unclear whether these models will become just as recognized as these theories in due time.

4.1 Presolar nanodiamond formation: CVD versus Shock

In the same paper in which Lewis et al. published about their new discovery of presolar diamonds in meteorites, they implied that it was improbable that these diamonds were produced by some sort of shock mechanism as the meteorites showed no strong shock stress [4]. Also it puzzled them that only the diamond grains containing Xe-HL had been transformed, leaving the bulk of carbon without the inclusion of this noble gas unaffected. They stated also the possibility of a “metastable formation of diamond from a hot gas at low pressure”. This CVD-like process requires the same low-pressure conditions as seen in the circumstellar atmosphere of carbon stars.

Soon after this discovery, Tielens et al [67] proposed a shock metamorphism of amorphous carbon or graphite driven by high collision in interstellar shock waves, associated with supernovae, as a possible mechanism for interstellar diamond formation.

Several theories, modifications and hypothesis about the subject followed. Daulton made an important contribution in 1996 by comparing nanodiamonds produced by CVD, shock and samples from the Murchison and Allende meteorites [68]. He used high resolution transmission electron microscopy to investigate the different nanodiamonds by looking at several micro- and nanostructural growth features including morphology, polymorphic dislocations and lattice defects. He concluded that presolar nanodiamonds have been formed by a low-pressure CVD process.

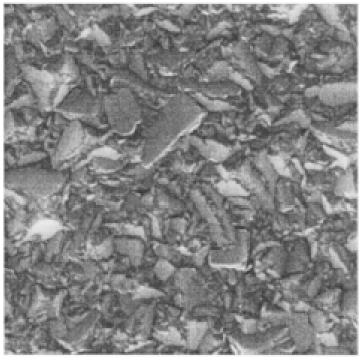


Figure 18: SEM image of a typical diamond thin film prepared by using the HFCVD method [60].

By looking at the size of the observed nanodiamonds from meteorites, both shockwave produced [71] and CVD nanodiamonds [72] [73] have about the same size as diamonds found in meteorites.

Furthermore, the size mass distribution of nanodiamonds was investigated by Maul [17]. Nanodiamonds of the Murchison and Allende meteorites were compared with synthetic produced ones by shock detonation. All the nanodiamonds investigated showed a log-normal mass distribution, similar to as is seen in CVD (see Figure 19).

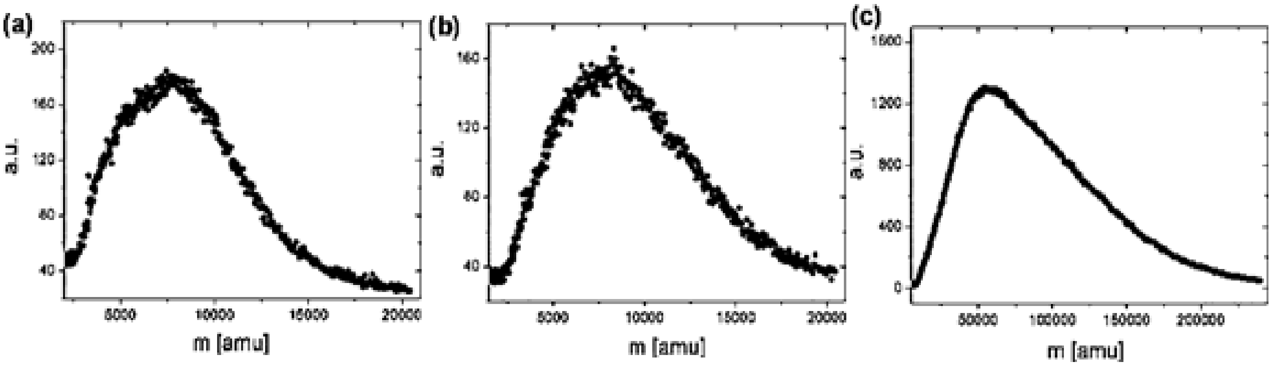


Figure 19: Laser ablation/ionization time-of-flight mass spectra from the different nanodiamond samples: (a) Murchison, (b) Allende, and (c) synthetic diamonds. Each spectrum clearly exhibits a significantly asymmetric shape, as it is typical for lognormal size distributions [17].

Raty and Galli looked at thermodynamics and surface properties to understand the similar size distribution of meteoric nanodiamonds, compared to nanodiamonds produced by CVD or shock processes [59]. The calculations made, showed that at about 3 nm, and for a broad range of pressures and temperatures, particles with bare, reconstructed surfaces become thermodynamically more stable than those with hydrogenated surfaces, thus preventing the formation of larger grains.

Besides looking at the size of terrestrial and extraterrestrial diamonds, observations of nanodiamonds in space indicated a strong preference for CVD. The findings of Guillois in 1999, who concluded that the 3.53 µm emission feature found around three Herbig Ae / Be stars points to small nanodiamonds [48], combined with the later studies by Chen [74], Shen [56] and Jones [57], showed that there is a great possibility that nanodiamonds in these areas are produced by a CVD-like process. The temperature around these stars is high enough to induce a process of nanodiamond formation in space similar to a CVD process [56]. Providing a viable mechanism for nanodiamond production under these circumstances, Kouchi et al. identified in 2005 a new CVD formation route for producing diamond in interstellar clouds [9] (chapter 3.2).

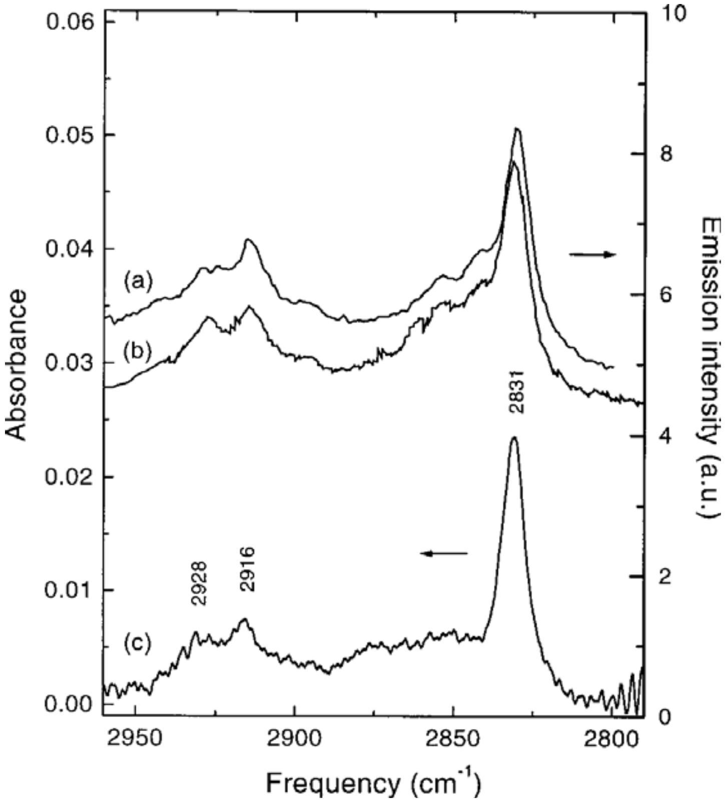


Figure 20: Comparison of the spectra of infrared emission from the stars (a) Elias 1 and (b) HD 97048 and the infrared absorption spectrum of (c) 100-nm diamonds H-etched by MWCVD in laboratory [74].

4.2 Solar nanodiamond formation

In that same paper, Kouchi performed experiments simulating aqueous alteration and subsequent thermal metamorphism for parent bodies of carbonaceous chondrites [9]. Using TEM, Kouchi found both graphite and diamond present in the product (see Figure 21). The conditions are similar to those in the parent bodies of carbonaceous chondrites, because aqueous alteration occurs at temperatures between 270 and 470 K and thermal metamorphism at temperatures lower than 1000 K. Kouchi et al. proposed that this is a suitable formation route for nanodiamond production in our own solar system, supporting Dai’s suggestion that that nanodiamonds could have originated in the early solar system [8].

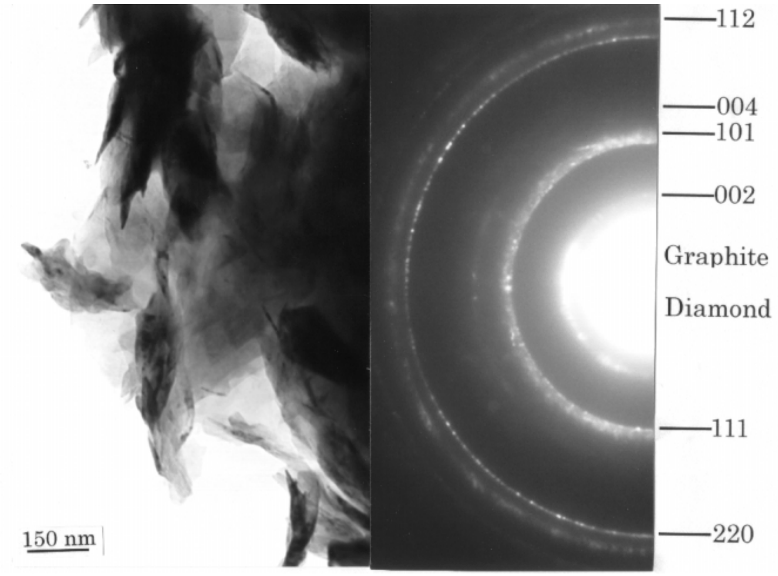


Figure 21: TEM image and electron diffraction pattern of a residue that is the result of experiments simulating aqueous alteration and subsequent thermal metamorphism for parent bodies of carbonaceous chondrites by Kouchi et al. [9]

Dai et al. observed that the amount of diamond in interplanetary dust from meteoritic parent bodies is larger than those from comets [8]. Kouchi explains this observation by considering that the material from meteoritic parent bodies contains diamonds of both interstellar and parent body origin, whereas the material from comets contains those of interstellar or presolar origin only [9].

On the other hand, Aoki et al. has some doubts considering the claims of Kouchi et al [75]. They believe that TEM identification of Kouchi et al. of nanodiamonds needs to be more clearly verified, and their model for the formation of the nanodiamonds under low-pressure is still debatable. Furthermore, their study revealed that nanodiamond grains occur even in thermally unmetamorphosed cabonaceous chondrites, which implies to them that the theory of presolar origin is more probable than that of parent-body origin.

4.3 Relation of carbon onions to current formation models

Carbon onions have been found in meteorites [60 61], in modeling experiments [62 63] and in laboratory experiments [55 64] and are being discussed as possibly playing a big role in diamond formation. In laboratory experiments they have been produced by CVD [76] and by shock [77]. The discovery of the 3.53 μm emission band has been attributed to nanodiamonds in the vicinity of stars, which have the right properties suitable for a CVD-like process [56]. Therefore carbon-onions can be linked *in situ* to the CVD process for diamond formation in space.

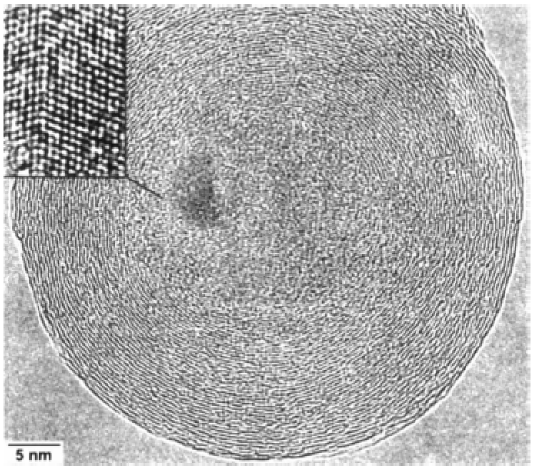


Figure 22: Onion within a diamond core, formed under irradiation at 700 °C and cooled to room temperature. A twinned diamond crystallite is seen almost in <110> projection (shown enlarged in the inset) [55].

Later in 2008, Karchmeszka used Raman spectroscopy in order to investigate nanodiamonds, both artificial and extraterrestrial [16]. The Raman spectrum showed the presence of graphite and diamond in shockwave produced diamonds, which could indicate the same onion-like structures as proposed by Raty and Galli [59].

4.4 Shock transformation within meteorites

Although there is no concrete evidence so far that the shock wave theory is responsible for the creation of interstellar diamonds, there are examples of nanodiamond present in meteorites which have been transformed by shock inside these large objects. The diamonds for example of the Canyon Diablo meteorite were transformed by shock impact due to collision with the Earth [78]. Secondly, the nanodiamonds of the Goalpara meteorite were transformed from crystallized graphite into diamond by a collision in space [78]. Also other intergrowths of graphite and diamond have been found in the Havero meteorite and other ureilites [79], which indicates that a portion of the original graphite was transformed into its polymorphs, diamond and lonsdaleite by shock.

4.5 Is there a winner?

Overall it appears that CVD is the main formation process of nanodiamonds outside our solar system. Diamonds collected from meteorites show many growth features similar to CVD created nanodiamonds [67] and no stresses (which is typical for shock produced ones [4]). The same log-normal size distribution has been observed for both diamonds from meteorites and CVD diamonds [17 71 72 73]. Furthermore, the discovery of nanodiamonds in outer space showed that the surroundings of these discovered objects have similar growth conditions (high temperature, low pressure, carbon and hydrogen present) as in a CVD process [56].

On the other hand, shockwave produced diamond has some similarities to interstellar ones and the process is quite realistic as high energy shockwaves are frequently produced by supernovae [67]. Compared to the weight of the evidence which points to CVD, the shock wave theory is down but not out. Perhaps in the future, more evidence will shed new light into what extent both models responsible for the creation of interstellar diamond.

On the solar nanodiamond production front, Kouchi identified a promising new formation route in parent bodies of carbonaceous chondrites [9], supporting the suggestion of Dai that a part of the nanodiamonds were formed within our own solar nebula [8]. However, it remains unclear as to what extent this formation route can be responsible for interstellar diamond formation and if it can compete with the CVD and shockwave theory.

5 Nanodiamond birth grounds in space

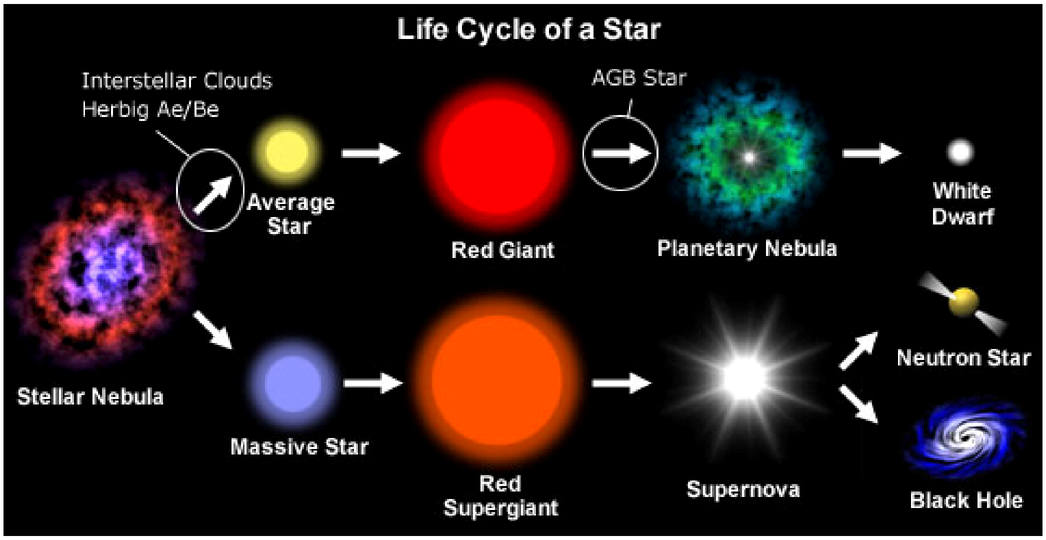


Figure 23: Life cycle of a star.

Throughout the years many possible birth grounds have been proposed.

The solar system

A possible birth ground closest to us is our solar system itself. In 2002, Dai et al. studied interplanetary dust particles and suggested that a part of these nanodiamonds were actually formed in our inner solar nebula [8]. At a later staqe, Kouchi et al. supported this suggestion by proposing a diamond formation route in parent bodies of carbonaceous chondrites [9].

Herbig Ae/Be stars and interstellar clouds

Herbig Ae/Be stars are so called pre-main sequence stars of 2 – 8 solar mass. These stars are considered young for they have not entered the main sequence. In other words, they have not yet developed into a stabile stationary condition.

These stars have been proposed as possible places of origin for nanodiamonds when the 3.53 μm infrared band was finally attributed to these objects by Guillois in 1999 [48].

These diamonds have most likely been formed by a type of CVD process, because the surroundings of these stars have the right high temperature, low pressure conditions present [56]. A possible formation route in interstellar clouds was discovered by Kouchi et al., who experimentally found out that a diamond precursor can nucleate under UV photolysis of interstellar ice mixtures in molecular clouds and can manage to grow with further UV irradiation in diffuse clouds [9].

Asymptotic Giant Branch Stars

AGB stars are stars of a mass of 0.6 – 10 solar mass, which have evolved from a Red Giant in the later stages of their lives, just before the formation of a planetary nebula.

In 2006, Verchovsky et al. isolated (through a non-destructive ultracentrifugation process) nanodiamonds and found that a minor fraction of these particles have Xe-S present (an s-process xenon isotope), which indicates an AGB-star origin since these stars are known to be important sources for these isotopes [15]. Furthermore, the formation of the nanodiamonds is most likely through a CVD process in the atmosphere of these stars.

Red Giants

Red Giants are stars of 0.5 – 10 solar masses in the late stages of their lives. These stars are yellow-orange to red in appearance and their large size is due to the hydrogen burning of the outer shells, since the hydrogen in the inner core has already been depleted. Some of these Red Giants are rich in carbon. Therefore it is believed that nanodiamonds condensate from these carbon rich expanding atmospheres under low pressure, high temperature conditions as in CVD processes [4].

Supernovae type II

When in the core of a Red Supergiant, the nuclear fusion has transformed progressively light material into heavy metals. The electromagnetic forces repelling the atomic nuclei cannot sustain the gravitational forces anymore. This results in a collapse of the core, followed by a supernovae explosion. These supernovae generate huge shockwaves which could be responsible for nanodiamond formation [67]. Furthermore p-process and r-process isotopes of xenon have been found in presolar diamonds, which are produced in supernovae, linking these sites as the birth ground for diamonds.

Neutron star/Black hole

If a Red Supergiant under 20 solar masses turns into a supernova, its core collapses and forms a neutron star. These stars are incredibly small, heavy, are very hot and consist almost entirely of neutrons. If a star is heavier than 20 solar masses, the core collapses into a black hole. The r-process isotope of xenon is believed to occur in the neutrino driven winds from the neutron star, formed after a supernovae event. There are also other possible candidates like the "hot bubble (high entropy)" region, which is believed to appear just after the creation of a newly-born proto-neutron star in the core-collapse supernova explosion. Also neutron star – neutron star binaries, and neutron star – black hole binaries are named as possible candidates [31] [80]. Binary systems are two objects which are so close together in space that their gravitational interaction causes them to orbit around a common centre of mass. Being possible formation sites of r-processes makes them also candidates for presolar nanodiamond formation.

White dwarfs

Red Giants with a small mass evolve into a white dwarf. Jørgensen implied that for a number of binary systems, mass from a carbon-rich giant star is transferred onto a white dwarf, which then explodes as a type Ia supernova. In this event, Xe-HL is formed, which is implanted into presolar diamond [81].

Novae

In 1995, Clayton proposed novae as possible birth sites for nanodiamond formation [82]. Novae, another type of nuclear explosions, are the result of accretion of hydrogen on the surface of a white star from a larger companion in a binary star system.

Wolf Rayet stars

Wolf Rayet stars are massive stars which have over 20 solar masses. During their life time they lose mass very rapidly in the form of strong stellar winds. It is thought that very massive stars become WR stars before they explode as a supernovae. Tielens [83] and Arnould [84] have proposed that nanodiamond might origin for these stars.

6. Summary and outlook

6.1 Summary

Discovery

The discovery of presolar diamonds, by Lewis in 1987, lead to a great boost in this particular astronomical area. By looking at their physical, chemical and isotopic characteristics, we gain a great amount of knowledge about the creation of solar systems (including ours), the interstellar medium, nucleosynthesis in stars and Galactic Chemical Evolution. In 2002, Dai made an important contribution by stating that nanodiamonds could have originated in the early solar system.

Isolation

Amari introduced a general separation method in 1994, relying on chemical isolation. This model was enhanced by Merchel et al. in 2003, who were able to significantly speed up the isolation time. Besides chemical isolation of nanodiamonds, Verchovsky used a physical isolation method, in which he was able to collect presolar diamonds through centrifugation. Furthermore he isolated Xe-S, which was not found in diamonds collected through chemical isolation.

Structure

As for structural analysis, X-ray and electron diffraction techniques are used together with Raman spectroscopy, TEM and SEM.

Furthermore advanced techniques have been developed over the years in order to investigate nanodiamonds, which only contain around a 1000 atoms. Examples of these techniques are NanoSIMS 50 (a heavily improved SIMS), TOF-SIMS, RIMS, AMS and EELS, identifying mainly surface features, element abundance and distribution.

Diamonds crystallize in different space groups. Terrestrial diamonds have mostly a cubic structure. Diamonds from space have several structural forms known, including several cubic, hexagonal and rhombohedral.

Xenon

Trace elements in nanodiamonds are of great importance of understanding the origin of these stones, since diamonds act as a perfect protection cage against time, temperature, radiation and more hazards. As far as in 1964, Reynolds and Turner found anomalous isotopic signatures for xenon in meteorites, which did not comply with solar abundance. The discovery of presolar diamonds by Lewis showed that the xenon anomaly signified their presolar origin.

For a long time it was believed that every nanodiamond present in meteorites, was of a presolar origin. However in 2002, when Dai stated that nanodiamonds could have originated in the early solar system, the assumption about the presolar origin of meteoric nanodiamonds changed.

Because of the current technical limitations of measuring isotopic compositions of minute nanodiamonds, no diamond grain can be measured individually. Therefore only bulk samples can be measured, meaning possible solar and presolar nanodiamonds can not be distinguished from each other.

Xenon-HL is the prime element of interest in presolar nanodiamond. It is enriched in enriched in both light (Xe-L, p-process, 124 and 126 isotopes) and heavy (Xe-H, r-process, 134 and 136 isotopes). Xenon-HL also comprises of Xe-S (s-process, 128 and 130 isotopes).

Xe-H and Xe-L are correlated; the higher the former, the higher the latter, which is strange considering that both types of isotopes (p- and r-process) are produced in different physical settings. Also the ratios found for p- and r-process xenon in presolar diamond grains do not comply with the ratio of solar abundance xenon.

To try to understand this deviation, Howard and Ott proposed different models, though not one model fully explains this anomaly.

Besides Xe-HL, Xe-P3 and Xe-P6 have been discovered, which are released at different temperatures with a technique called stepwise combustion. This points to the fact that these phases have been implanted at different stages. Their different stabilities however, is not fully understood as of yet.

These elements have entered the crystal structure of nanodiamonds due to ion implantation. Finally it is not possible to determine the age of xenon and other trace elements since these systems use decay of rare constituents decaying in other rare elements with uncertain non-radiogenic compositions.

Besides xenon, other elements show only a small deviation in isotopic composition, like tellurium and palladium.

Carbon and Nitrogen

The ratios of carbon and nitrogen are close to solar abundance and support the argument that most diamonds in meteorites originate from our solar system. This is also supported by Dai, who investigated interstellar dust particles and came to the same conclusion. It could be that the presence of a possible anomalous ratio of carbon and nitrogen (signifying a presolar origin) is masked by the overly abundant solar carbon and nitrogen.

Discovery in Space

In 1999, Guillois discovered the presence of nanodiamonds in space. He attributed the 3.53 µm infrared band to the C-H stretch of the surface of nanodiamonds present in the dusty envelopes surrounding stars.

Up till today there are four stars known to contain the 3.53 µm stars: three Herbig Ae/Be stars: HD 97048, Elias 1 , MWC 297 and HR 4049, a post AGB-object. More candidates have been found, but till today only these four are confirmed to contain nanodiamonds in their vicinities.

It seems that a protoplanetary disk, a hot central star and a companion emitting hard X-rays are the perquisites for nanodiamond formation in outer space, responsible for the 3.53 µm emission feature, which has been confirmed in different types of experiments.

Dai linked his findings of a solar origin of meteoric nanodiamonds to the detection of diamond within the accretion discs of other young stars. In 2005, Kouchi experimentally found out that a diamond precursor can nucleate under UV photolysis of interstellar ice mixtures in molecular clouds and can manage to grow with further UV irradiation in diffuse clouds, linking this model to the observations of the 3.53 µm emission feature.

There is a debate going on as to how large these nanodiamonds actually are. Sheu proposed 25-50 nm, while Jones believed the diamonds to be larger than 50 nm. Goto found a size of 100 nm during his own studies.

Rati and Galli studied the stability of these diamonds and found that for sizes lower than 3 nm, the diamonds contain bare non-hydrogenated surface structures, meaning that C-H stretch would not be visible through infrared emission for these sizes. This implies that there might be smaller than 3 nm diamonds present in space, but these can not be detected as of yet through infrared emission.

Carbon Onions

Carbon onions have been proposed as a model for diamond creation in outer space. Carbon onions might be formed around stars and due to electron irradiation the shells start to peel off. The core then experiences an enormous pressure, due to the shrinking of the outer shells, leading to diamond formation in the centre.

This has been reproduced experimentally and by modeling experiments. Furthermore, these carbon onions have been found in meteorites. A possible presence of diamond cores inside carbon onions in space can not be identified since the outer carbon shells show a continuous absorption around the region of 3.53 μm.

Extended Red Emission

Besides infrared measurements, ERE (Extended Red Emission) is seen as a possible candidate for detecting diamonds in space. If this would be confirmed, it would yield a second method to identify diamonds in space.

Diamond Formation Models

Up till today there are two models which are believed to be responsible for presolar nanodiamond production in space, Chemical Vapor Deposition (CVD) and shock waves.

Chemical Vapor Deposition is a process in which metastable diamond is deposited on a solid interface in an activated carbon-hydrogen system at low pressure and high temperature. On the other hand, strong shock waves generated by exploding supernovae, are believed to transform interstellar graphite or amorphous carbon into diamond by grain-grain collisions.

Daulton made a big contribution to the discussion of which of the two models is mainly responsible for nanodiamond formation in space. Using high resolution TEM he analyzed nanodiamond samples made by shock, CVD and from meteorites and came to the conclusion that CVD diamonds show the biggest resemblance to meteorite nanodiamonds for many growth features.

Furthermore, the size mass distribution of nanodiamonds was investigated by Maul. Nanodiamonds of the Murchison and Allende meteorites were compared with synthetic produced ones by shock detonation. All the nanodiamonds investigated showed a log-normal mass distribution, similar to as is seen in CVD.

Importantly, observations of nanodiamonds in space indicated a strong preference for CVD. The temperature around the stars, where nanodiamonds have been found, is high enough to induce a process to form nanodiamonds in space similar to a CVD process.

Carbon onions are shown to be produced by both CVD and shock.

Although there is no concrete evidence so far that the shock wave theory is responsible for the creation of interstellar diamonds, there are examples of nanodiamonds present in meteorites which have been transformed by shock inside these large objects.

It seems that that CVD is the main formation process in which interstellar nanodiamonds are formed. The shock wave theory has some strong points though, but still it is unsure as to what extent shockwaves and CVD are responsible for nanodiamond formation in space.

Kouchi identified a promising new formation route in parent bodies of carbonaceous chondrites, supporting the suggestion of Dai that a part of the nanodiamonds were formed within our own solar nebula. It remains unclear as to what extent this formation route can be responsible for diamond formation outside our solar system and if it can compete with the CVD and shockwave theory.

Nanodiamond Birth Grounds

There are many possible birth grounds for presolar diamonds. These include: our own solar system, Herbig Ae/Be stars, interstellar clouds, AGB stars, Red Giants, Supernovae type I/II, Neutron stars/black holes, White Dwarfs, Novae, Wolf Rayet stars.

6.2 Remaing questions and outlook

There are still many problems present that need to be solved in order to fully understand the formation of nanodiamonds in our universe.

First of all, the development of alternative isolation techniques in the future could perhaps identify new phases in presolar diamond grains. Verchovsky showed that by using a method based on centrifugal isolation, he could identify Xe-S, which is not found when using the standard chemical isolation procedure to collect nanodiamonds.

Secondly, the extent as to the contribution of a solar and presolar nanodiamond is one of the biggest outstanding problems in this scientific field. The current range of analysis equipment is still limited in the sense that single diamonds grains can not be studied individually on isotopic compositions. Therefore only bulk samples can be measured, meaning possible solar and presolar nanodiamonds can not be distinguished from each other. For example an anomalous presolar isotopic composition for carbon and nitrogen could be masked by the more abundant solar isotopes of those elements. Advances in these techniques could crack the puzzle and thus gives us much more detailed information about certain isotopic compositions, pointing to either a solar or presolar origin for these nanodiamonds.

The solar nanodiamond formation route developed by Kouchi on parent bodies of carbonaceous chondrites is an interesting addition to the discussion as to where nanodiamonds are formed. In time, it will become clear as to how this model is responsible for the nanodiamond formation in our solar system (and maybe even outside) and if other realistic models will be proposed.

Furthermore, the correlation between Xe-L and Xe-H is not yet fully understood. Also the current models developed by Howard and Ott do not fully explain the ratios found for p- and r-process xenon in presolar diamond grains, which do not comply with the ratio of solar abundance xenon.

The findings of different xenon components with different thermal stabilities related to different diamond populations is also not fully understood as of yet.

Solving these trace element riddles would give indirectly a huge amount of information about our understanding of nucleosynthesis, Galactic Chemical Evolution and the creation of our solar system and others alike.

Considering the 3.53 µm emission feature, there still is lots of debate about the sizes of the nanodiamonds in space and formation models. Also the relation of carbon onions to diamond formation is space is very promising but it is still not entirely concluded in how exactly it is linked.

Besides infrared emission, ERE is seen as a possible candidate for nanodiamond detection in space. More research could promote this candidacy into a clear and evident identification feature.

The question in what way CVD and shock waves are ultimately responsible for presolar diamond formation is not fully defined. CVD seems to be the most prominent method so far.

The Stardust mission from Nasa, which goal is to collect material from comet Wild 2, is expected to yield many different circumstellar grains. Comets are formed in the outer fringe of our solar system and over time they have incorporated primitive solar system matter. Up till today one circumstellar grain was identified [7] and it is expected that more grains will be found, hopefully also diamond grains.

7. References

1. Boato, G. *Geochim. Cosmochim. Acta* **1954**, *6*, 209
2. Briggs. *Nature* **1963**, *197*, 1290
3. Clayton, R.N. *Science* **1963**, *140*, 192
4. Lewis R.S.; Ming T.; Wacker J.F.; Anders E.; Steel E. *Nature* **1987**, *326*, 160-162
5. Bernatowicz, T.; Fraundorf, G.; Tang, M.; Anders E.; Wopenka, B.; Zinner, E.; Fraundorf P. *Nature* **1987**, *330*, 728–730
6. Amari, S.; Anders, E.; Virag, A.; Zinner, E. *Nature* **1990**, *345*, 238-240
7. Hoppe, P. *Space Science Reviews* **2008**, *138*, 43-57
8. Dai Z.R.; Bradley J.P.; Joswiak D.J.; et al. *Nature*, **2002**, *418*, 218-221
9. Kouchi, A.; Nakano, H.; Kimura, Y.; Kaito, C. *Astrophys. J.*, **2005**, *626*, L129-L132
10. Amari, S.; Lewis R.S.; Anders, E. *Geochim. Cosmochim. Acta*, **1994**, *58*, 459-470
11. Merchel, S.; Ott U.; Herrmann S. *Geochim. Cosmochim. Acta*, **2003**, *67*, 4949-4960
12. Lodders, K.; Amari, S. *Chem. Erde*, **2005**, *65*, 93-166
13. Kingston, H.M.; Jassie, L.B. *J. Res. Nat. Inst. Stand. Technol.*, **1988**, *93*, 269-274
14. Verchovsky A.B.; Fisenko A.V.; Semjonova L.F.; Wright I.P.; Lee M.R.; Pillinger C.T. *Science*, **1998**, *281*, 1165-1168
15. Verchovsky A.B.; Fisenko A.V.; Semjonova L.F.; Bridges J .; Lee M.R. *Astrophys. J.*, **2006**, *651*, 481-490
16. Karczemska A.; Szurgot M.; Kozanecki M.; et al. *Diamond and Relat. Mater.*, **2008**, *17*, 1179-1185
17. Maul J.; Marosits E.; Sudek C.; et al. *Phys. Rev. B*, **2005**, *72*, 245401
18. Hoppe P. *Appl. Surf. Sci.*, **2006**, *252*, 7102-7106
19. Ott U.; Hoppe P.; Lugmair G.W. *New Astron. Rev.*, **2004**, *48*, 165-169
20. Nittler L.R. *Earth Planet. Sci. Let.*, **2003**, 209, 259-273
21. Egerton R.F. *Rep. Prog. Phys.*, **2009**, *72*, 016502
22. Schoutsen M. *Interstellaire Diamanten*, Vaste Stof Chemie, Katholieke Universiteit Nijmegen, 2001
23. Garai J.; Haggerty S.E.; Rekhi S.; et al. *Astrophys J.*, **2006**, *653*, L153-L156
24. J. V. Smith and J. B. Dawson, *Geology*, **1985**, *13*, 342
25. Haggerty E. *Proceedings of the 5th International Symposium on Advanced Materials*, **1998**, 39-42
26. Reynolds, J.H.; Turner, G. *J. Geophys. Res.*, **1964**, *69*, 3263
27. Lewis R.S.; Srinivasan B.; Anders E, *Science*, **1975,** *190*, 1251-1262
28. Srinivasan B.; Anders E, *Science*, **1978,** *201*, 51-56
29. Huss G.R.; Lewis R.S. *Meteorit. Planet. Sci.*, **1994**, *29*, 791-810
30. Rayet, M.; Arnould, M.; Hashimoto, M.; et al. *Astron. Astrophys.*, **1995**, *298*, 517-527
31. Wanajo S, Kajino T, Mathews GJ, et al. *Astrophys. J.*, **2001**, *554*, 578-586
32. Ott U. *Astrophys. J.*, **1996**, *463*, 344-348
33. Howard, W.M.; Meyer, B.S.; Clayton, D.D. *Meteorit. Planet. Sci.*, **1992**, *27*, 404-412
34. Ott U. *New Astron. Rev.*, **2002**, *46*, 513-518
35. Tang, M.; Anders, E.; *Geochim. Cosmochim. Acta*, **1988**, *52*, 1235–1244.
36. Ott, U. *Space Sci. Rev.*, **2003**, *106*, 33-48
37. Koscheev A.P.; Gromov M.D.; Mohapatra R.K.; et al. *Nature*, **2001**, *412*, 615-617
38. Gilmour J.D.; Verchovsky A.B.; Fisenko A.V. *Geochim. Cosmochim. Acta*, **2005**, *69*, 4133-4148
39. Russell, S.S. *Meteorit. Planet. Sci.*, **1996**, *31*, 343
40. Ott, U. *Space Sci. Rev.*, **2007**, *130*, 87-95
41. Wieler, R. *Rev. Mineral. Geochem.*, **2002**, *47*, 21-70
42. Richter S.; Ott, U.; Begemann, F. *Nature*, **1998**, *391*, 261
43. Maas, R.; Loss, R.D.; Rosman, K.J.R.; et al. *Meteorit. Planet. Sci.*, **2001**, *36*, 849-858
44. Amari, S. Outstanding problems of presolar diamonds in meteoritics, In *Origin of Matter and Evolution of Galaxies,* Suda T.; et al.; Eds.; AIP Conf. Proceedings 1016, 2008; pp 389-393
45. Owen T, Mahaffy PR, Niemann HB, et al. *Astrophys. J.*, **2001**, *553*, L77-L79
46. Whittet, D.C.B.; Bode M.F.; Longmore A.J.; Baines D.W.T.; Evans, A. *Nature*, **1983**, *303,* 218-221
47. Whittet, D.C.B.; McFadzean A.D.; Geballe T.R.; *MNRAS*, **1984**, *211,* P29-P31
48. Guillois O.; Ledoux G.; Reynaud C. *Astrophys. J.*, **1999**, *521*, L133-L136
49. Goto M.; Henning T.; Kouchi, A.; et al. *Astrophys. J.*, **2009**, *693*, 610-616
50. Terada, H.; Imanishi, M.; Goto M.; et al. *Astron. Astrophys.*, **2001**, *377*, 994-998
51. Van Kerckhoven C.; Tielens A.G.G.M.; Waelkens C.; *Astron. Astrophys.*, **2002**, *384*, 568-584

52. Acke, B.; Van den Ancker, M.E., *Astron. Astrophys.*, **2006**, *457*, 171-U124
53. Waelkens, C.; Waters, L.B.F.M.; De Graauw, M.S.; et al. *Astron. Astrophys.*, **1996**, *315*, L245-L248
54. Malfait K.; Waelkens C.; Walters, L.B.F.M.; Vandenbussche, B.;Huygen, E.; De Graauw, M. S. *Astron. Astrophys.*, **1998**, *318*, 879
55. Banhart, F.; Ajayan, P.M. *Nature*, **1996**, *382*, 433-435
56. Sheu, S.Y.; Lee, I.P.; Lee Y.T.; et al. *Astrophys. J.*, **2002**, *581*, L55-L58
57. Pirali, O.; Vervloet, M.; Dahl, J.E.; et al. *Astrophys. J.*, **2007**, *661*, 919-925
58. Jones, A.P.; d'Hendecourt, L.B.; Sheu, S.Y.; et al. *Astron. Astrophys.*, **2004**, *416*, 235-241
59. Raty, J.Y.; Galli, G. *Nature Mater.*, **2003**, *2*, 792-795
60. Amari, A.; Zinner, E.; Lewis, R.S. *Meteorit. Planet. Sci.*, **1993**, *28*, 316
61. Smith, P.P.K.; Buseck, P.R. *Science*, **1981**, *212*, 322-324
62. Henrard, L.; Lambin, P.; Lucas, A.A. *Astrophys. J.*, **1997**, *487*, 719-727
63. Tomita, S.; Fujii M.; Hayashi, S. *Astrophys. J.*, **2004**, *609*, 220-224
64. Jager, C.; Henning, T.; Schlogl, R.; et al. *J Non-Cryst. Solids*, **1999**, *258*, 161-179
65. Los, J.H.; Pineau, N.; Chevrot, G.; Vignoles, G.; Leysalle, J-M. *Phys. Rev. B.*, **2009**, *80*, 155420
66. Chang, H.C.; Chen K.W.; Kwok, S. *Astrophys. J.*, **2006**, *639*, L63-L66
67. Tielens, A.G.G.M.; Seab, C.G.; Hollenbach D.J; et al. *Astrophys. J.*, **1987**, *319*, L109-L113
68. Daulton, T.L.; Eisenhour, D.D.; Bernatowicz T.J.; et al *Geochim. Cosmochim. Acta* **1996**, *60*, 4853-4872
69. Szurgot, M.; Karczemska, A.; Kozanecki, M.; *Nanodiam*; Mitura, S, Niedzielski, P., Walkowiak, B., Eds.; PWN, Warsaw, 2006; pp 259
70. Norton, O.R.*The Cambridge Encyclopedia of Meteorites*, Cambridge Univ., Cambridge, 2002
71. Greiner, N.R.; Philips, D.S.; Johnson, J.D.; Volk, F. Nature, **1988**, *333*, 440-442
72. Jiao, S; et al. *J. Appl. Phys.*, **2001**, *90*, 118-122
73. Krauss, A.R.; et al. *J. Appl. Physics,* **2001**, *89*, 2958-2967
74. Chen, C.F.; Wu, C.C.; Cheng, C.L.; et al. *J. Chem. Phys.*, **2002**, *116*, 1211-1214
75. Aoki, T.; Akai, J. J. Mineral. Petrol. Sci., 2008, 103, 173-182
76. Chen, X.H.; Deng, F.M.; Wang, J.X.; et al. *Chem. Phys. Lett.*, ***2001***, *336*, 201-204
77. Yamada, K.; Kunishige, H.; Sawaoka, A.B. *Naturwissenschaften*, 1991,*78*, 450
78. Haneman, R.E.; Strong, H.M.; Budny, F.P. *Science*, **1967**, *155*, 995
79. McSween Jr., *Meteorites and Their parent Planets*, Cambridge University Press, Cambridge, 1999
80. Meyer, B.S.; Mathews, G.J.; Howard, W.M.; et al. *Astrophys. J.*, **1992**, *399*, 656-664
81. Jorgensen, U.G. *Nature*, **1988**, *332*, 702-705
82. Clayton, D.D.; Meyer B.S.; Sanderson C.I. *Astrophys. J.*, **1995**, *447*, 894-905
83. Tielens, A.G.G.M. Carbon Stardust – From Soot to Diamonds, In *Carbon in the Galaxy: Studies from Earth and Space*, 1990; 3061, pp 59
84. Arnould, M. Wolf-Rayet stars and their nucleosynthetic signatures in meteorites, A*strophysical Implications of the Laboratory Studies of Presolar Materials*, 1997; 179