Chapter 1

Meteoritic Presolar Grains and Their Significance

One of the most fascinating discoveries of the last fifty years is that much of the material that constitutes our world and ourselves came from the stars. All elements heavier than hydrogen and helium are produced in stellar interiors where temperatures of several million degrees allow nuclear fusion reactions to occur (*nucleosynthesis*) [47, 50, 131, 287]. At the end of the life of a star the newly formed elements are ejected into the interstellar medium from which new stars are born. Material in the Universe is processed in a continuous cycle and the chemical composition of galaxies evolves (Fig. 1.1), so that different compositions are present within a galaxy at different times and locations. The birth of the theories of stellar nucleosynthesis and Galactic chemical evolution owed much to the availability of spectroscopic observations of the abundances of the elements in stars [184, 185], and to the first compilation of the distribution of the abundances of the elements in the solar system compiled in 1956 [267].

Until a few decades ago it was believed that the abundances of the different isotopes of each element[1] in the solar system were completely homogenised, because all the material present in the protosolar nebula – the planetary disk formed during the gravitational collapse from which the solar system originated – was very well mixed. The abundances of different *elements* do vary in different locations of the solar system depending on their chemical properties, such as their ability to form molecules and condense into solids, and on the thermal conditions at which different solar-system bodies were formed. For example, the amount of iron (Fe) condensed into rocks on Earth is much higher than the amount of Fe that remained as a gas in the atmosphere, because Fe can condense into solid material. The

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[1] Nuclei belonging to the same element, i.e. characterised by a given number of protons, but with different numbers of neutrons

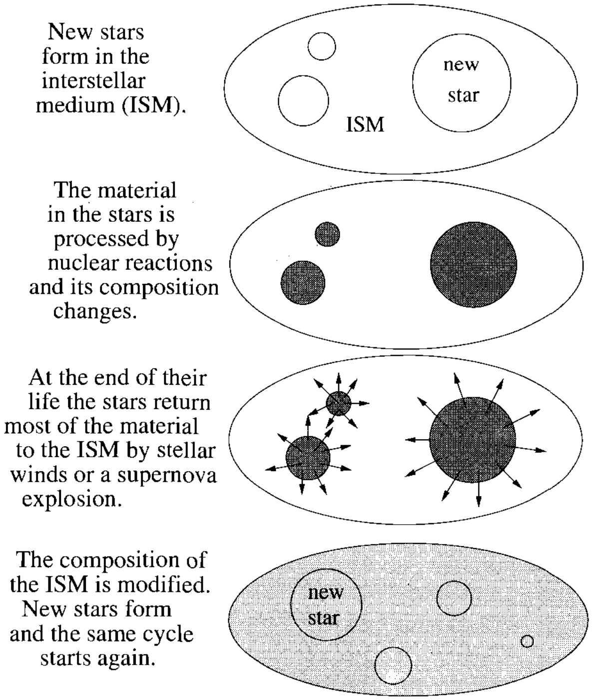

Fig. 1.1 Schematic representation of the recycling of material in a galaxy and the resulting evolution of the composition of stars and the interstellar medium.

amount of the noble gas Xe, instead, is much higher in the atmosphere since this gas does not easily condense into solids.

However, if complete homogenisation of the solar material is assumed, then the fraction of Fe, or any other element, made up by each of its stable *isotopes*: ^{54}Fe, ^{56}Fe, ^{57}Fe, and ^{58}Fe is the same in every corner of the solar system (with, for example, ^{56}Fe representing 92% of all Fe in the solar system, and ^{58}Fe only accounting for 0.3% of it). This is because the chemical reactions and physical processes that produced the material in the solar system occurred at temperatures of at most a few thousand degrees, and could have changed the isotopic composition of an element only at the level of a few parts per thousand. Observed variations much larger than that can only be present if the material was *originally* anomalous in its isotopic compositions. Large isotopic anomalies, in fact, can only be produced by nuclear reactions, occurring at temperatures of million degrees, by which the structure of the atomic nucleus, i.e. the number of neutrons present in the nucleus, is modified.

Recently, the idea of a completely uniform isotopic composition in the solar system has been challenged by the discovery of small amounts of material that have "anomalous" or "exotic" isotopic compositions, i.e. differing from that commonly observed in the solar system. This material is mostly recovered from meteorites, relatively small extra-terrestrial rocks that fall onto the Earth. Since the observed large variations in the isotopic composition of such anomalous material cannot have been produced during the formation of the solar system, it is believed that this exotic material carries the signature of processes that predated the formation of the protosolar nebula, and it is hence labelled as "presolar".

In the next section, different types of presolar material are presented, and the rest of this chapter is focused on one particular type of presolar material: *stardust*, the meteoritic stellar grains that are the topic of this book. A brief history of their discovery is told in Sec. 1.2, the different types of stellar grains recovered so far from meteorites are introduced in Sec. 1.4. In the last section, 1.5, the many different types of information that can be derived from the study of presolar stellar grains are summarised.

1.1 Presolar isotopic signatures and their carriers

There are several types of presolar isotopic signatures, which are summarised in Table 1.1. The first type are represented by some meteoritic solids showing the consequences of the radioactive decay of unstable nuclei such as ^{26}Al, ^{41}Ca, ^{60}Fe and ^{107}Pd, which have relatively long half-lives[2], between 0.1 and 100 million years. The signature of the presence of radioactive nuclei in the early solar system shows up today in excesses of the abundance of their daughter nuclei, i.e. those they decay into. For example, large excesses in ^{26}Mg with respect to solar system material, but not in ^{24}Mg and ^{25}Mg, have been measured in small clumps of calcium- and aluminium-rich material, Ca- and Al-rich inclusions (CAIs, see Fig. 1.4) from the Allende meteorite [165]. These ^{26}Mg excesses are attributed to radioactive decay of the unstable nucleus ^{26}Al that must have been initially present in the solar system and incorporated into CAIs at the time of their formation.

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[2] The time by which the abundance of a radioactive nucleus decreases by half of its initial abundance because of the decaying process.

Table 1.1 Types of presolar isotopic signatures.

anomaly	carrier	source
1) excesses of nuclei produced by radioactive decay	Ca- and Al-rich inclusions (CAIs) in primitive meteorites	presence of radioactive nuclei in the early solar system
2) small isotopic anomalies (order 10^{-4})	CAIs	small inhomogeneities in the solar nebula, or *chemical effects*
3) anomalies of deuterium and ^{15}N	primitive meteorites and Interplanetary Dust Particles (IDPs)	chemical processes in the molecular cloud where the Sun formed.
4) isotopic anomalies of many elements, up to four orders of magnitude	stellar grains recovered from primitive meteorites	stellar nucleosynthesis

Interesting questions are posed regarding where these radioactive nuclei have come from and their origin is still much debated. Initial abundances derived for radioactive nuclei with relatively long half-lives – higher than about 10 million years – are explained as the result of the evolution of the abundances in the interstellar region where the Sun was born due to equilibrium between Galactic production in stars and radioactive decay [192, 248]. Some light nuclei with shorter half-lives could have been generated during the active early phases of the formation of the Sun by some sort of interaction with accelerated particles (solar cosmic rays) [166], in which case the origin of these nuclei is not truly "presolar". Beryllium-10, in particular, could have been produced by this type of process, but occurring before the formation of the Sun, by interaction with Galactic cosmic rays [84]. Alternatively, some of these nuclei could have been produced by an event that occurred close to and just before the formation of the Sun and polluted the protosolar nebula with radioactive material, such as a supernova explosion [53, 192] or the winds of a red giant star [290]. If some of these nuclei came via stellar winds or explosion ejecta, then such an event could also be related to the triggering of the formation of the solar system. Interstellar shock waves could have initiated the collapse of the presolar gas cloud to form the Sun [43]. The study of these anomalies can ultimately shed light on the dynamical sequence of events that produced our Sun and Earth.

When material with anomalous composition is mixed and diluted with non-anomalous material, the sign of the early presence of *unstable* nuclei discussed above is not lost because it shows up in excesses of the abundances of the stable daughter nuclei they decay into. On the contrary, it is much more difficult to recover anomalies in the composition of *stable* nuclei, when anomalous material is mixed and heavily diluted with material having composition like that of the bulk of the solar system.

Small anomalies in the composition of stable nuclei of calcium, titanium, and iron are shown by CAIs [73] (presolar material of type 2 listed in Table 1.1). The first accepted sign of the presence of presolar material in meteorites was an observed +4% deviation from the abundance of solar ^{16}O in CAIs [72]. However, there is the possibility that this anomaly could have been produced in the solar system by chemical effects [275].

The third type of presolar material is identified by anomalous abundances of deuterium (D=^{2}H) and ^{15}N observed in primitive meteorites as well as in Interplanetary Dust Particles (IDPs), i.e. tiny meteorites (diameter $< 50\mu$m) collected in the stratosphere. Observed D/H ratios are up to 10 times higher than in terrestrial rocks [189, 186]. These anomalies are within the range observed in some molecular clouds, which are cool and dense regions of the interstellar medium where atoms tend to combine into molecules. High D/H ratios are due to isotopic fractionation occurring during chemical reactions between ions and molecules at very low temperature, and to the fact that the relative mass difference between D and H is very high [277]. Also ^{15}N excesses of up to 50% of the terrestrial standard are observed in IDPs, which can also associated with chemical fractionation, if reactions take place at very low temperatures.

The fourth type of presolar material is that which is discussed in the rest of this book: *stardust*, also called stellar, or presolar, dust grains. These grains have isotopic compositions very different to those commonly measured in the solar system: they display enormous anomalies of up to four orders of magnitude in their isotopic compositions. These are too large to be attributed to chemical or physical fractionation and could only have been produced by nuclear reactions, which occur in stars. After being ejected into the interstellar medium presolar stellar grains were incorporated in the protosolar nebula and then survived the formation of the solar system without being destroyed. These grains existed in their current form before the solar system was born and have kept their own individuality and composition until today. General reviews on presolar stellar grains can be found in Refs. [21, 68, 171, 301, 302], while a large number of detailed reviews on a variety of related subjects are collected in Ref. [28].

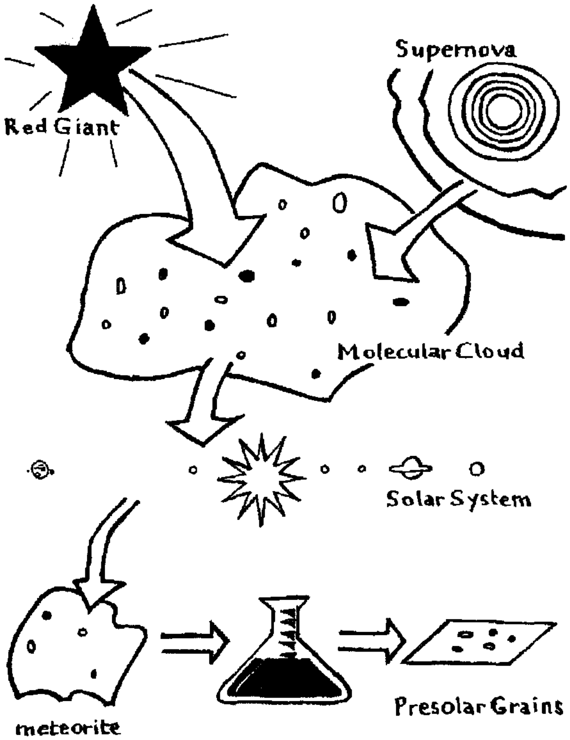

Fig. 1.2 Schematic representation of the journey of presolar grains from their site of formation around stars to the laboratory (courtesy Larry Nittler).

A schematic representation of the journey of stellar presolar grains from their circumstellar site of formation to the laboratory is shown in Fig. 1.2. It begins with their birth, as dust grains forming in the gas surrounding stars. For example, favourable locations for the formation of dust are the wind-driven extended envelopes of red giant stars, and apparently the majority of known presolar grains came from these stars. The outer regions of giant stars, or circumstellar shells, are cool enough ($\simeq$ 1500 K) for the gas to condense into grains. The presence of heated dust in circumstellar shells, which is observationally associated with strong mass loss from the star, was known and studied well before the discovery of stellar grains in meteorites, as it causes the infrared excess seen in the spectrum of many giant stars: the dust makes the circumstellar shells opaque so that the light coming from the star is absorbed and re-emitted in the infrared. Other sites where dust can form are in the cooled ejecta of nova and supernova explosions.

The stellar dust, together with most of the gas that formed the star, is ejected into the interstellar medium by the stellar winds or the nova or supernova explosion. About 1% of the mass of the interstellar medium is made up of this *cosmic dust*, which causes interstellar extinction, i.e. the dimming of light from stars. When the Sun formed in a molecular cloud, some of the grains present in the protosolar nebula were trapped in asteroids. Fragments resulting from the impact of smaller rocks on an asteroid can have their course deflected in such a way that they reach the surface of the Earth. These extra-terrestrial pieces of rock are the meteorites from which presolar grains are recovered today[3]. Since presolar grains carry the signature of the composition of the gas that surrounds stars, the laboratory analysis of their composition and structure provides invaluable information on the stars, the astrophysical site of their origin.

The discovery of stellar grains in meteorites has created a new field of astronomy, where scientists from different disciplines, from nuclear physics to astronomy and chemistry, are required to work together. In this new field information and constraints on theories of Galactic evolution and stellar nucleosynthesis come from measurements on dust grains performed in the laboratory.

While the bulk of the solar material came from many different stars because of Galactic chemical evolution, each presolar grain carries the signature of its site of formation around its parent star. Hence the composition of stellar grains gives us a unique opportunity to study the composition of a single star, rather than a mixture of them. Thus, data from presolar grains are similar to the spectroscopic observations of stellar atmospheres, however, they are conceptually and practically different in several ways. While stellar observations usually deal with elemental abundances, and only in rare cases yield the isotopic composition of the star, the laboratory analysis of presolar material yield data on isotopic compositions. Theories have thus to be tested against information about isotopic compositions, which presents more detailed constraints than elemental data. Moreover, the laboratory measurements of presolar material, with error bars in some cases as low as a few percent, are typically much more precise than spectroscopic observations, with typical error bars of a factor of two.

On the other hand, while we do know from which star spectroscopic observations are derived, and hence we automatically have information such

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[3] Other types of meteorites came from the Moon and Mars.

as its spectral type and luminosity, that allows us to classify the star in our theoretical framework, we do not know *a priori* in which astrophysical site the grain was produced. The first challenge of measured presolar compositions is to understand which conditions made them possible. Only after this is reasonably well established can the data be used to constrain the theories. Stellar observations and the analysis of presolar material complement each other in bringing new challenges to our knowledge of the stars and our Galaxy.

1.2 The discovery of presolar stellar grains

The first hint of the existence of presolar stellar grains appeared in the 1960s from the analysis of the composition of the noble gases neon (Ne) and xenon (Xe) in primitive meteorites. In spite of the fact that noble gases have very low concentrations in other materials, hence they are also known as *rare* gases[4], they are found as trapped or implanted bubbles inside materials and can be extracted during heating experiments. Analysis of the composition of Xe [233] and Ne [33] in old carbonaceous meteorites showed the presence of "exotic" components with isotopic compositions completely different from the bulk of solar system material.

Two exotic components were found for Xe: Xe-HL, which stands for Xe *heavy* and *light* [233], and Xe-S, which stands for Xe *s process* [260] (see Fig. 1.3). In the case of Xe-HL, the light isotopes ^{124}Xe and ^{126}Xe and the heavy isotopes ^{134}Xe and ^{136}Xe are especially enhanced with respect to the solar composition. The production of these isotopes is related to two nucleosynthesis processes: the *proton*-capture process (p process, see Sec. 2.5.3) for ^{124}Xe and ^{126}Xe, and the *rapid* neutron-capture process (r process, see Sec. 2.5.2) for ^{134}Xe and ^{136}Xe. In the case of Xe-S, instead, ^{128}Xe and ^{130}Xe are the most enhanced isotopes. Their production is related to the *slow* neutron-capture process (s process, see Sec. 2.5.1).

Anomalous Ne was found to be very much enriched in ^{22}Ne with respect to solar material with ^{22}Ne/^{20}Ne and ^{22}Ne/^{21}Ne ratios up to a thousand times higher than in the Sun. This component was named Ne-E (as the letters A, B, C and D were already taken for other Ne components), and further distinguished in two types: Ne-E(L) and Ne-E(H) because of differ-

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[4] Noble gases He, Ne, Ar, Kr and Xe, are the most volatile elements, they do not form any chemical compounds and condense only at extremely low temperatures. This is because their atomic structure is very stable and hence they do not react easily with other atoms.

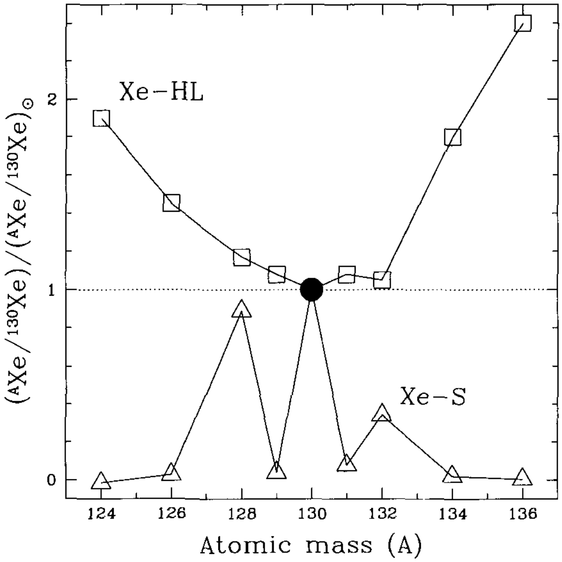

Fig. 1.3 Isotopic composition of the two Xe exotic components present in meteorites. All isotopic ratios are calculated with respect to ^{130}Xe and divided by the corresponding ratios in the solar system, so that data for ^{130}Xe always equals 1 (full circle). In the case of Xe-HL (open squares) all isotopes are more abundant than ^{130}Xe, with respect to solar, particularly at the two endpoints of the isotopic range. In contrast, in the case of Xe-S (open triangles) ^{130}Xe is the most abundant isotope, followed by ^{128}Xe.

ences in the heating temperature (*lower* or *higher* than 1200 ^{o}C) at which they are released. Also, the density of the type of grains that host them turned out to be lower or higher than 2.3 g/cm^3 for the two components, respectively.

These anomalous compositions were not plausibly explained as a product of processes that occurred in the solar system, but seemed rather to be the product of nuclear reactions in stellar interiors. This led to the quest of the isolation of these components, so to identify their carriers inside the meteorites.

It took approximately ten years for Anders and his colleagues at the University of Chicago to identify and extract the minerals within the meteorites responsible for carrying the exotic noble gas components [12, 270]. In the case of Xe-S and Ne-E(H) the carrier was found to be silicon carbide (SiC) grains [30, 306] and in the case of Xe-HL the carrier was found to be diamond [169] (see also Ref. [270]). In the case of Ne-E(L) the carrier was found to be graphite [6]. The final isolation process has been described by Anders as "burning down the haystack to find the needle", as it involves dissolving the meteoritic rock using appropriate harsh acids until only the presolar dust remains (as will be described in Sec. 3.1). Fortunately, many presolar grains are made of hard and resistant material, able to survive all these destructive processes. On the other hand, they are microscopic and their abundance relative to the other minerals composing the meteorites is very small, typically of the orders of parts per million (by mass).

1.3 Meteorites carrying stellar grains

Presolar stellar grains have been found in all classes of primitive *chondrite* meteorites. Chondrite meteorites represent more than 80% of all meteorite falls and are characterised by the presence of *chondrules*, small spheres of average diameter $\simeq$ 1 mm of previously melted minerals that have come together with other mineral matter to form a solid rock (see Fig. 1.4).

The abundance of presolar grains in a chondrite meteorite correlates with the percentage of the rock that is composed by the *matrix*, the amalgam of amorphous material and crystals of very small dimensions, of the order of 10^{-6} m, not visible with an optical microscope. This implies that presolar grains are situated in the matrix, representing some of the microcrystals of which the amalgam is formed. The types of chondrite meteorites that are mostly composed of matrix and hence contain the largest abundance of presolar grains, are the subgroups CI and CM2 belonging to the rare class of *carbonaceous* chondrites, of which examples are Orgueil (CI, France 1964) and Murchison (CM2, Australia 1969). These meteorites contain carbon, of which some is in the form of organic compounds, and are believed to be the oldest stones formed in the solar system. Their bulk composition is almost identical with that of the Sun, thus they represent a most reliable source from which to derive standard solar abundances of elements and isotopes (see e.g. [20]).

The abundance of presolar grains in different chondrites normalised to their matrix content depends on the grade of *metamorphism* of the meteorite, i.e. how much the meteorite has endured processes characterised by variations in temperature, pressure and the presence of fluids, which can cause a variation of the structure and composition of the rock. Meteorites of types CI and CM2 are also the least metamorphosed type of chondrites hence they contain the largest absolute number of presolar grains.

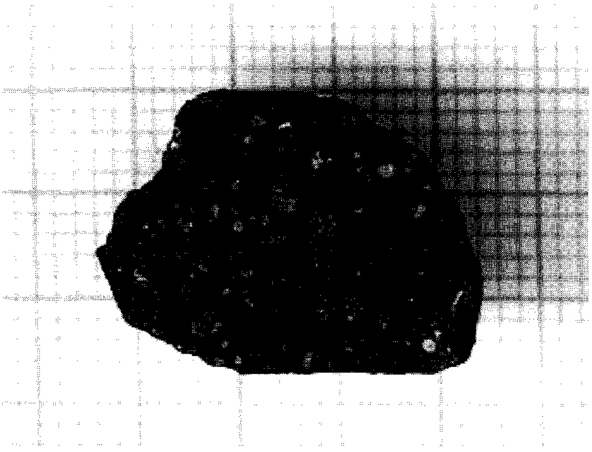

Fig. 1.4 Photograph of a stone from the Allende meteorite, which fell in Mexico in 1969. The small squares in the background grid have 1 mm size (courtesy Eric Twelker). Allende is a carbonaceous chondrite of class CV3. Chondrules with size of the order of mm (10^{-3} m) stand out against the darker matrix, where presolar grains of the size of μm (10^{-6} m) are located. The clumps of white material are calcium-aluminium-rich inclusions (CAIs) where the signature of the early presence of the radioactive nucleus ^{26}Al has been discovered (Sec. 1.1).

1.4 Types of presolar grains

In Table 1.2 is presented a list of the types of presolar grains recovered so far and their abundances in the Murchison meteorite, in units of parts per million (ppm). The most abundant type is diamond, other relatively abundant carbon-bearing minerals are silicon carbide and graphite. Silicate grains are probably the second most abundant presolar grains, though data are not yet available for the Murchison meteorite since these grains have only very recently (in 2004) been discovered in the Acfer 094 and North West Africa 530 meteorites. In some meteorites, oxide grains such as corundum are more abundant than silicon carbide, thus the order in which the grains are listed in Table 1.2, which is only based on available analysis of the Murchison meteorite, should be considered as indicative. The question of which type of presolar grains are in general more abundant will only be settled through further analysis.

Graphite and SiC grains also contain tiny subgrains of Ti, Zr, Mo, Ru and Fe-carbides [29] as well as subgrains of Fe-Ni metals [75]. Also polycyclic aromatic hydrocarbon (PAH) molecules have been found in many graphite grains [187].

Presolar grains are all refractory, which means that, at high temperatures, roughly between 1300 and 2000 K, they can condense directly from the gas phase. The condensation sequence of minerals depends on the initial composition of the gas, and indeed mainly on the C/O ratio. If $C/O < 1$, all the carbon is locked up in carbon monoxide (CO) molecules, which have a very strong bond and are stable at high temperature, and the condensed minerals are mostly oxides and silicates. If $C/O > 1$, instead, all the oxygen is locked up in CO molecules and carbon compounds can condense, such as graphite and carbides. Since in the solar system $C/O \simeq 0.4$, carbon bearing minerals could not have condensed in the protosolar nebula. Hence, these types of meteoritic grains are virtually all of presolar origin.

Table 1.2 Types of presolar grains, abundance in the Murchison meteorite [132], and typical size.

type	abundance (ppm)	size (μm)
diamond	$>750^a$	0.002
silicates	$—^b$	0.1 – 0.5
silicon carbide (SiC)	9^a	0.1 – 20
spinel ($MgAl_2O_4$)	1^c	0.5
graphite	$>2^d$	0.8 – 28
corundum (Al_2O_3)	$\sim 0.005^e$	0.5 – 4
silicon nitride (Si_3N_4)	$>0.002^f$	~ 1

[a] Found and measured in $\simeq$ 40 chondritic meteorites. Abundances vary with the matrix content and metamorphic degree of the meteorite.

[b] Identified in the Acfer 094 and North West Africa 530 meteorites with contrasting abundance estimations of $\simeq$ 25 ppm [200], 30 ppm [199] and 75 ppm [194].

[c] Also identified in other chondritic meteorites such as Murray, Orgueil and Acfer 094.

[d] Also identified in nine other chondritic meteorites.

[e] Also identified in four other chondritic meteorites, with abundance up to 0.2 ppm.

[f] Inaccurately known, also identified in four other chondritic meteorites.

1.4.1 *Diamonds*

The most abundant presolar grains are very small diamonds of the size of nanometers (10^{-9} m), hence they are called *nanodiamonds.* These grains are far more abundant than any other presolar grain. For example they constitute almost 6% of the total carbon in the Murchison meteorite. Presolar diamonds carry the exotic Xe-HL component related to p- and r-process nucleosynthesis [270]. Since these processes are predicted to occur in massive stars exploding as supernovæ, presolar diamonds probably have a supernova origin. The implications of this origin will be discussed in Sec. 6.1. The presence of the Xe-HL component, and their Te and Pd compositions, are the only information from the nanodiamonds that points to their presolar origin. However, this origin can be strictly applied only to a small fraction of the diamond grains because the concentration of Xe is extremely low so that only about one nanodiamond in each million contains an atom of anomalous Xe. Moreover, because diamond nanocrystals are too small to be analysed one by one, their carbon isotopic composition can be measured only in bulk, i.e. in collections of large numbers of grains. In this way it is only possible to obtain data on the carbon composition averaged on millions of grains, which happens to be very close to solar [239]. Of course, this does not necessarily mean that all the grains have solar carbon composition, because extreme compositions would cancel each other out in the averaging process. The $^{14}N/^{15}N$ ratio is on average about 35% higher than the terrestrial value, but in agreement with the ratio observed in Jupiter [221] . As for noble gases in meteoritic diamonds, a detailed study of the different components and the implications for their origin can be found in Ref. [134].

The favoured mechanism for the formation of nanodiamonds has been identified in a chemical vapour-deposition-like process occurring at low pressure [78], by which material in a vapour state condenses through chemical reactions, rather than a high-pressure shock-induced metamorphism that produced, for example, diamonds in meteorite craters. This is consistent with condensation in cool stellar atmospheres. For the inclusion of noble gases in the diamonds, ion implantation is the most likely mechanism, which would also be consistent with the fact that the concentration of noble gases increases with the grain size [285].

In summary, it is not known which fraction of the diamond grains are actually presolar. Some of them could have formed in the inner regions of the solar system [76]. This is suggested by the fact that nanodiamonds are mostly absent in Interplanetary Dust Particles of cometary origin, and comets are thought to have formed further out in the early solar system and to be older than asteroid parent bodies. Moreover diamonds are detected within the accretion discs of young stars.

1.4.2 *Silicate grains*

Before 2004, the inability to find presolar silicate grains in meteorites was puzzling. This was because the major oxide phases observed around red giant stars are silicates, represented by SiO, other Si-based minerals such as olivine and pyroxene, and amorphous silicate grains [80, 291]. However, no presolar silicates were to be found in meteorites. Problems are that silicates are more likely to be destroyed by chemical processing during the life of the meteorite, and that presolar silicate are very difficult to locate among the abundant silicate of solar origin that constitute the main part of meteorites. Moreover, silicates were destroyed by most of the chemical treatments used to prepare meteoritic residues. Presolar silicates were also difficult to detect because of their small size.

Thanks to the advent of the NanoSIMS instrument (Sec. 3.3.2) it is now possible to identify and analyse presolar grains of smaller sizes than was possible before. The existence of presolar silicate grains in the solar system has thus been confirmed by their discovery within Interplanetary Dust Particles [188], where they are quite abundant: $\simeq$ 5500 ppm in cluster IDPs, and also in the carbonaceous chondrites Acfer 094 and North West Africa 530 [194, 199, 200]. The estimated abundance of silicates in these meteorites varies from $\simeq$ 25 to $\simeq$ 75 ppm, exceeding that of any other presolar material, except diamond. It is foreseen that by using improved techniques many more of these grains will be collected from various sources in the near future.

1.4.3 *Silicon carbide grains*

Silicon carbide grains (SiC) are large enough to allow the analysis of single grains, since their size varies from a fraction to a few tens of μm. They are also relatively easy to extract from meteorites, with respect to the other types of presolar grains, and thus several thousands of them have been analysed to date. SiC grains typically have shapes bounded by crystal planes, with more or less pitted surfaces, likely due to the harsh treatments

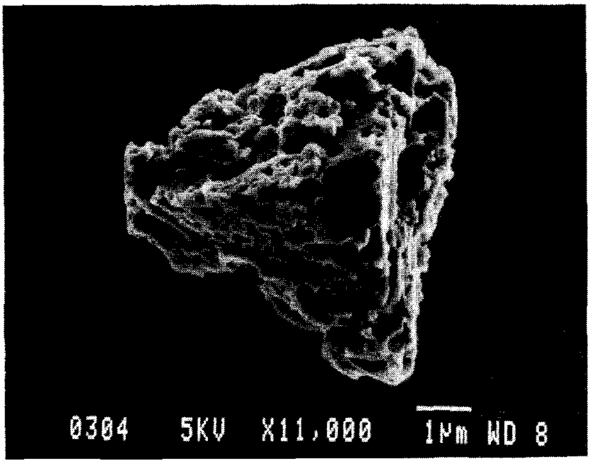

Fig. 1.5 High-resolution scanning electron microscope image of a presolar SiC grain of size $\simeq$ 6 μm from the Murchison meteorite. The $^{12}C/^{13}C$ ratio of this grain is 55, while in the solar system is 89 (courtesy Sachiko Amari).

to which they were exposed during the extraction (Fig. 1.5[5]). Even if SiC can crystallise in many different ways, 80% of presolar SiC grains have cubic form (β-SiC, as opposed to α-SiC, which refers to a variety of different structures) and the remaining 20% have hexagonal form [77].

Since their discovery, presolar SiC grains have been extensively studied (see e.g. [122, 127]) and a relatively large amount of information is available, which will be discussed in detail in Chapters 4 and 5. Based on their C and Si composition, SiC grains have been classified into several populations, the largest of which (*mainstream* SiC) comprises more than 90% of the grains. The remaining SiC grains are classified in other five small populations: A, B, X, Y and Z (Sec. 4.8). Presolar SiC contains impurities dominated by N, Al and Ti, and trace elements with low concentrations such as Mg, Ca, Zr, Mo, Ru, Ba, Nd.

These grains are the carriers of the Xe-S exotic component, which is produced by s-process nucleosynthesis. Enhancements in the elements produced by the s-process are observed in red giant stars on the Asymptotic Giant Branch (AGB), and therefore most SiC grains are believed to have formed in the carbon-rich envelopes of AGB stars. In fact, the emission line

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[5] Reprinted from Chemie der Erde, Lodders & Amari, Presolar grains from meteorites: Remnants from the early times of the solar system, to appear, Copyright(2005), with permission from Elsevier.

at 11 μm – characteristic of β-SiC – is observed spectroscopically in these stars [74, 258, 259, 282]. The fact that SiC grains are the carriers of the Ne-E(H) component also fits into this scenario as theoretical models predict that the envelopes of AGB stars are also enriched in ^{22}Ne (see Sec. 4.4).

1.4.4 *Graphite grains*

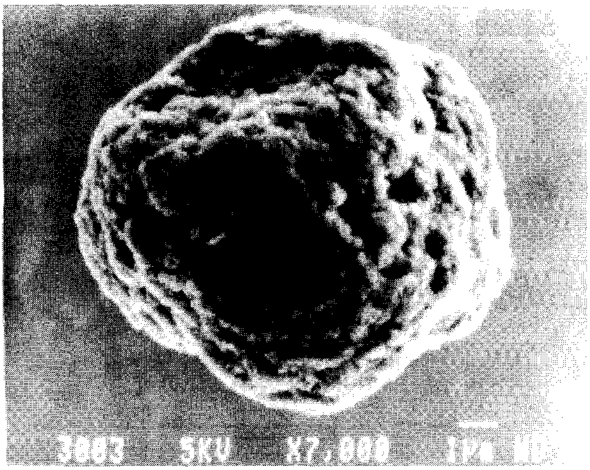

Fig. 1.6 High-resolution scanning electron microscope image of a presolar graphite grain of cauliflower-like morphology and size ≃ 6 μm from the Murchison meteorite. Presolar graphite grains always show spherical appearance (courtesy Sachiko Amari).

Like SiC grains, graphite grains are large enough to be analysed singularly. However, their extraction procedure is more complex than that of other grains, because graphite has chemical and physical properties similar to those of other carbonaceous compounds present in the meteorite. Moreover, trace elements are present in extremely low abundances, which makes their analysis challenging. A few hundreds graphite grains have been analysed to date and have been classified according to their morphologies and densities. Round grains, which comprise more than 90% of graphite grains, have isotopically anomalous carbon and hence are clearly of stellar origin. Their density is in the range 1.6–2.2 g/cm^3 and they have two different external appearances: cauliflower-like, consisting of aggregates of smaller grains (Fig. 1.6) and more abundant among grains of low density, and onion-like, consisting of concentric layers of graphitised carbon and more abundant among grains of high density. About one third of all presolar graphite grains have low densities (1.6–2.05 g/cm^3) and appear to have originated from supernova explosions [123, 281]. Higher-density grains could have originated from a range of stellar environments. Details on this type of grains and their origin are presented in Sec. 6.2.

1.4.5 *Oxide grains*

Until 2003, corundum (sapphire and ruby, Al_2O_3) was believed to be the most abundant presolar oxide grain. However, with the NanoSIMS instrument (Sec. 3.3.2) it is now possible to identify and analyse presolar grains of smaller sizes, and it has been recently found out that spinel ($MgAl_2O_4$) is the most abundant presolar oxide grain [304]. This result was missed before because spinel grains have average sizes smaller than corundum grains. A few hibonite grains (with composition $CaAl_{12}O_{19}$) and one titanium oxide grain (TiO_2) of presolar origin have also been recovered [58, 59, 212]. Oxide grains are resistant to the chemical treatments used to isolate the carbonaceous grains and they are present in meteoritic residues together with SiC grains. However, presolar oxide grains are more difficult to locate because the majority of oxide grains in meteorites formed in the solar system, where $C/O < 1$. Only a small fraction of oxide grains are of presolar origin and special techniques are needed to recognise them (see Sec. 3.4). These types of grains have not been traced through the presence of noble gases, but have been recognised during analysis of acid-resistant meteoritic residues because of their anomalous composition.

Oxide grains have been separated into distinct groups, based on their oxygen and aluminium isotopic ratios. The $^{26}Al/^{27}Al$ is derived for the time when the grain formed by estimating the initial presence of ^{26}Al from the radiogenic abundance of ^{26}Mg. The composition of most of these grains suggests that they have formed around red giant and AGB stars, as will be discussed in Sec. 6.3.

1.4.6 *Silicon nitride grains*

Also silicon nitride grains (Si_3N_4) have been identified during analysis of meteoritic residues because of their anomalous composition [215]. The condensation of silicon nitride requires $C/O > 1$ and a high nitrogen concentration. The composition of these type of grains is very similar to that of SiC grains belonging to the X population (Sec. 4.8.3) and points to a supernova origin of Si_3N_4 grains.

1.5 New information from presolar grains

When considering the different astronomical sites through which presolar grains journey, as represented in Fig. 1.2, it is clear why these grains represent not only a new field of astronomy, where dust from stars is analysed in the laboratory, but also a new scientific field requiring the common effort of scientists from very different disciplines. These disciplines range from nuclear physics, to theoretical astrophysics, observational astronomy, cosmochemistry and the laboratory analysis of materials. The information that we can extract from presolar grains is summarised in Table 1.3 and discussed in the rest of this section.

Table 1.3 Information from presolar grains relating to their site of formation and their journey through space.

site	information
Circumstellar regions	- initial composition of the star (Galactic Chemical Evolution) - stellar thermal structure, nucleosynthesis and nuclear reaction rates - mixing processes inside red giant stars and during nova and supernova explosions - physical and chemical properties of the gas around stars
Interstellar medium	- destruction processes of cosmic dust - exposure to Galactic cosmic rays
Molecular cloud	- cloud and grain chemistry
Solar system	- survival of presolar material in the early solar system
Meteorite	- metamorphism processes of meteorites

1.5.1 *Stellar evolution, nucleosynthesis and mixing*

The very precise analysis of the isotopic composition of presolar grains represents a breakthrough in the field of stellar evolution and nucleosynthesis. During the chemical process of formation of molecules and grains around stars, isotopic fractionation effects, i.e. preferences in incorporating different isotopes of a given element, could have only produced very small isotopic anomalies, at a level of a few parts per thousand. Thus, the enormous range of variation in the isotopic compositions observed in presolar grains is an extremely precise record of the isotopic composition of their site of formation and must be explained by models of nucleosynthesis and mixing in stars.

The composition of the parent star of a grain is determined both by the initial composition of the star and the nucleosynthesis occurring inside the star itself. The initial composition is a complex function of the age of the star and the place where the star was born and can be predicted by Galactic chemical evolution calculations. These calculations model the continuous recycling of matter represented in Fig. 1.1, from the interstellar medium into new stars in which the matter is processed and transformed by nuclear reactions, and from the stars back into the interstellar medium. The aim of such studies is to follow the evolution of the composition of matter in various regions of a galaxy and in many generations of stars. Predictions are usually compared with observations of the composition of stars of different ages, and of the interstellar medium. Because some elements are not modified by nucleosynthesis in the parent stars of presolar grains, their composition in presolar grains is believed to record the initial composition of the parent stars, thus providing detailed constraints on models of the evolution of the Galaxy (see e.g. Sec. 4.6).

The stellar composition is further modified by the nucleosynthesis occurring inside the star itself. These modifications depend on the initial mass, composition and evolutionary phase of the star (see Chapter 2). Modifications are due to nuclear reactions and usually take place in the hot stellar interiors. They depend crucially on the thermodynamic structure of the star and the efficiency of nuclear reactions. Temperatures and densities of the different region of the star are computed using theoretical models of stellar evolution, while nuclear reaction rates are measured in the laboratory, or calculated theoretically. The composition of many elements in presolar grains show large variations due to the nucleosynthesis that occurred in their parent stars. The analysis of these effects provides constraints on the thermal structure of the stars and on nuclear reaction rates.

In order for the nucleosynthesis occurring in the hot deep layers of the star to be relevant to the composition of the dust grains forming in the much cooler outer regions, some mixing mechanism must be at work so that the processed material is carried from those deep layers to the surface of the star. In red giant stars this mechanism is referred to as *dredge-up* (see Secs. 4.2.1 and 4.3) because the envelope of the star, where most of the stellar mass is located and where the transport of energy occurs by convection (fluid circulation), periodically extends to deeper regions of the star and brings material to the surface. Other mechanisms by which processed material is mixed to the surface of red giant stars are known as *hot bottom burning* (see Sec. 4.2.1) and *extra mixing* or *cool bottom processing* (see Sec. 4.3). In this cases the mixing occurs continuously because the nuclear processes occur at, or just below, the base of the convective envelope.

Mixing processes in stars are related to the general astrophysical problem of the treatment of turbulent convection in stellar interiors, and can also be connected to structural asymmetries, stellar rotation and the presence of magnetic fields. A current limitation of the theoretical models of red giant stars is that they are performed in one dimension. This allows us to make the computation feasible and obtain a good description of the basic properties of the star, but does not represent a realistic way of modelling mixing phenomena. The composition of presolar grains give us constraints that can help us to better understand such complex mixing processes.

In supernovæ the mixing of material from inner to outer layers can be achieved prior to or during the explosion. For example, the trend shown by observations of the variation with time of the light from the very bright supernova SN1987A can only be explained if, because of hydrodynamical instabilities (turbulence), "fingers" of material from the inner regions, in particular the radioactive nucleus ^{56}Ni, were shot to the outer regions [108, 294]. Microscopic mixing of different supernova regions is required to explain the composition of presolar graphite and SiC-X grains, which show the signature of the nucleosynthesis occurring in supernovæ of type II [281], i.e. they are produced by the explosion of massive stars (see Sec. 2.4). In these grains are found nucleosynthesis products both from the inner supernova regions, such as ^{44}Ti and ^{28}Si, together with those from the outer regions, such as ^{15}N and ^{26}Al (Secs. 4.8.3 and 6.2). The mixing issue is also strongly connected to the mechanism by which the grains condensed. Two- and three-dimensional hydrodynamical calculations involving a large computational effort are needed to attempt to produce realistic models of the pre-supernova and supernova stages [24]. The existence and the composition of presolar grains from supernovæ can be used as a road map in the difficult task of understanding mixing phenomena in supernovæ.

1.5.2 *Physical and chemical properties of the gas around stars and supernovæ*

From the structural features and the elemental composition of presolar grains it is possible to obtain constraints on the properties of the circumstellar gas in which they formed. For example, smaller dust particles of Ti, Zr, and Mo carbides are found inside larger graphite and SiC grains. These crystals can form within initially homogeneous SiC grains, but not within graphite grains. They must have thus condensed before graphite. On the other hand, the fact that no SiC particles have been found trapped in graphite grains indicates that SiC grains must have formed after graphite [29]. The elemental abundances of various trace elements in SiC grains give information on the chemical composition of the gas around stars and its thermal properties. Refractory elements, which condense from gas into solids at high temperature, such as Zr and Nd, are believed to have condensed together with SiC, while volatile elements, such as noble gases, which condense from gas into solids at low temperature, are believed to have been ionised, accelerated and implanted into the grains. Implantation models have provided independent constraints on the velocities of the material around red giant stars and planetary nebulae [286], as will be briefly discussed in Sec. 5.3.

Condensation models assuming thermochemical equilibrium around red giant stars, combined with simple grain growth models, have shown that it is possible to achieve the required condensation sequence in a carbon-rich gas (from Ti, Zr, and Mo carbides to graphite and SiC) and have set limits on the pressure of the gas, which should be in the range of 0.1 to 100 dyne/cm^2, and on the C/O ratio, which should be in the range of 1.05 to 1.2, to obtain the observed grain sizes [172, 252]. These models have also been successful in explaining the observed condensation patterns of refractory trace heavy elements in SiC grains [173]. However, the densities required to form TiC before graphite and to produce grains of the observed size are much higher than those predicted to characterise the dust-forming regions in red giant stellar atmospheres. This might mean that around these stars there are regions of a higher density than predicted. Another possibility is that large grains preferably form in long-living disks around interacting binary systems rather than around single stars [150, 151].

Moreover, in stellar outflows thermochemical equilibrium is a simple approximation because of the dynamic role played by the expanding and cooling matter, and the heating effect of possible shock waves. Several studies consider red giant envelopes as places of pronounced non-equilibrium, both in their thermodynamic and chemical features (e.g. [57, 222, 250]). These models attempt to include all the processes involved in the production of the grains, from the formation of the molecules to the growth of the dust itself. The theory is complicated by the fact that there is not yet a clear and satisfactory description of the observed mass loss through stellar winds shown by red giant stars, which, together with the treatment of mixing, represents a major uncertainty in stellar evolution models of red giant stars. The observed mass loss is up to ten orders of magnitude higher than that of the Sun: from 10^{-8} solar mass ($M_\odot$) per year for stars on the first red giant branch (see Sec. 4.2.1), to 10^{-7} $M_\odot$/yr during the Asymptotic Giant Branch phase, and up to 10^{-4} $M_\odot$/yr in the final phases of the life of the star. Dust formation certainly plays a role as it is believed that one of the mechanisms responsible for the mass loss is radiation pressure on dust grains, which then drag the gas along with them.

Supernovæ are also believed to be one of the major producers of dust in our Galaxy, but many problems are still open on how the dust condensation physically occurs. The existence of graphite and SiC-X grains with the nucleosynthetic signature of supernova nucleosynthesis is a challenge to the theoretical modelling of mixing and dust formation during supernova explosions. From the observational point of view, dust has been observed in the cooled ejecta of the supernova SN1987A [44, 294] and in supernova remnants [87]. The study of dust formation around supernovæ, in particular in relation to presolar grains from meteorites, has barely begun. It is a complex task since the condensation of dust cannot in principle be decoupled from the mixing phenomena occurring in supernovæ. Both processes working together are likely to have determined the composition observed in the grains. The condition $C/O > 1$ is possibly not strictly necessary to form carbon-rich minerals in a supernova environment because CO molecules can be disrupted by energetic electrons produced by radioactivity in the supernova [67, 69]. A recent analysis of the impact of supernova shocks on the formation and composition of SiC-X from supernovæ can be found in [81], together with a detailed analysis of the issues involved, as well as the many unsolved problems.

Dust formation has also been associated with nova outbursts [263]. A few SiC and graphite grains have been recovered showing the signature of nova nucleosynthesis [7] thus giving further proof that dust production occurs also around novæ.

1.5.3 *The interstellar medium, molecular clouds and early solar system*

Before the discovery of presolar grains the study of cosmic dust was based only on its effects on starlight. The detailed laboratory observation of the structure and the appearance of presolar grains, as well as the relative abundance of the different types of presolar grains complement astronomical observations in the study of the interstellar dust, its propagation and its survival in the interstellar medium [147]. During their time in the interstellar medium dust grains are subjected to destructive processes such as sputtering by shocks and stellar winds, and are also likely to interact with Galactic cosmic rays, which are ions, mostly protons, that travel across the Galaxy and are probably accelerated by supernova shocks. This interaction can result in nuclear spallation reactions, i.e. the detachment of nucleons or small nuclei from larger nuclei as a result of the impact of energetic particles, which would thus modify the composition of the grains. While such modifications are yet to be observed unambiguously, they could reveal information on the age of presolar grains since their effect would depend on how long the grains have resided in the interstellar medium (see Sec. 4.4).

The survival of presolar grains during the formation of the solar system, and inside the solar-system bodies where they have been trapped, also represents a precious piece of information for the understanding of the formation of the solar system. The different types of presolar grains could have been destroyed to various degrees by potentially destructive processes occurring during the formation of the Sun (see e.g. [183]). In the early phases the grains were exposed to the thermal radiation of the collapsing cloud. Subsequently, the grains suffered an accretion shock produced by the dissipation of the energy of the material falling from the original cloud onto the nebula [54].

Since presolar grains have been found in all primitive meteorites studied they must have been initially present in the protosolar nebula all through the region of formation of meteorites. However, variations in the relative abundance of different types of grains in different classes of chondrites are found. For example, the abundance of SiC in enstatite ($Mg_2Si_2O_6$) chondrites is higher that that of diamond, with respect to the Orgueil and Murchison meteorites, while the abundance of diamond is higher that that of SiC in chondrites of type CV3. These data are of great importance for probing the properties of the protosolar nebula in which meteorite parent bodies formed, because the relative abundance of different types of grains depends on the temperature and composition of the surrounding environment [132]. More experimental data are necessary both on the abundances of the grains as well as on the destruction criteria of different types of grains in different conditions.

1.6 Outline

In Chapter 2 some basics of stellar nucleosynthesis are given, which will serve as a tool for the understanding of the chapters to follow. In Chapter 3 the various laboratory techniques currently used to extract and analyse presolar grains are described.

Constraints derived from presolar grain data and applied to theoretical nucleosynthetic models of the composition of their parent stars, are discussed in detail in Chapters 4, 5 and 6. In particular, Chapters 4 and 5 focus on the information from presolar SiC grains, which are the best-studied type of presolar grains and have been widely analysed. In Chapter 6 the constraints arising from the other types of presolar grains, diamond, graphite and oxide grains, are presented.

1.7 Exercises

(1) How many atoms are present in two presolar grains of radius 0.01 μm and 1 μm, respectively?
(2) How many milligrams of diamond, SiC and graphite grains are present in one gram of the Murchison meteorite?
(3) How many atoms of anomalous Xe are present among ten billion atoms constituting presolar diamonds?