1.02
Presolar Grains

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1.02.1 INTRODUCTION

Traditionally, astronomers have studied the stars by using, with rare exception, electromagnetic radiation received by telescopes on and above the Earth. Since the mid-1980s, an additional observational window has been opened in the form of microscopic presolar grains found in primitive meteorites. These grains had apparently formed in stellar outflows of late-type stars and in the ejecta of stellar explosions and had survived the formation of the solar system. They can be located in and extracted from their parent meteorites and studied in detail in the laboratory. Their stellar origin is recognized by their isotopic compositions, which are completely different from those of the solar system and, for some elements, cover extremely wide ranges, leaving little doubt that the grains are ancient stardust.

By the 1950s it had been conclusively established that the elements from carbon on up are produced by nuclear reactions in stars and the classic papers by Burbidge et al. (1957) and Cameron (1957) provided a theoretical framework for stellar nucleosynthesis. According to these authors, nuclear processes produce elements with very different isotopic compositions, depending on the specific stellar source. The newly produced elements are injected into the interstellar medium (ISM) by stellar winds or as supernova (SN) ejecta, enriching the
1.02.2 HISTORICAL BACKGROUND

Although the work by Burbidge et al. (1957) and Cameron (1957) and subsequent work by nuclear astrophysicists made it clear that many different stellar sources must have contributed to the material that formed the solar system and although astronomical observations indicate that some of this material was in the form of interstellar (IS) grains (e.g., Mathis, 1990), it was generally believed that it had been thoroughly homogenized in a hot solar nebula (Cameron, 1962). The uniform isotopic composition of all available solar system material seemed to confirm this opinion.

The first evidence for isotopic heterogeneity of the solar nebula and a hint of the survival of presolar grains came from hydrogen (Boato, 1954) and the noble gases xenon (Reynolds and Turner, 1964) and neon (Black and Pepin, 1969; Black, 1972), but it was only after the discovery of anomalies in oxygen, a rock-forming element (Clayton et al., 1973), that the concept of survival of presolar material in primitive meteorites was widely accepted. The finding of 16O excesses was followed by the detection of isotopic anomalies in other elements such as magnesium, calcium, titanium, chromium, and barium in refractory inclusions (CAIs for calcium-, aluminum-rich inclusions) (Wasserburg, 1987; Clayton et al., 1988; Lee, 1988). Also, large anomalies in carbon (Halbout et al., 1986) and nitrogen (Lewis et al., 1983) indicated the presence of presolar grains. However, it was the pursuit of the carriers of the “exotic” (i.e., isotopically anomalous) noble gas components of neon and xenon (Figure 1) by Ed Anders and his colleagues at the University of Chicago that led to their ultimate isolation (see Anders and Zinner, 1993).

The approach taken by these scientists, “burning down the haystack to find the needle,” consisted of tracking the noble gas carriers through a series of increasingly harsher chemical dissolution and physical separation steps (Tang and Anders, 1988b; Amari et al., 1994). Their effort culminated in the isolation and identification of diamond, the carrier of Xe-HL (Lewis et al., 1987), silicon carbide, the carrier of Ne-E(H) and Xe-S (Bernatowicz et al., 1987; Tang and Anders, 1988b), and graphite, the carrier of Ne-E(L) (Amari et al., 1990).

Once isolated, SiC and graphite (for diamond see below) were found to be anomalous in all their isotopic ratios and it is this feature that identifies them as presolar grains. This distinguishes them from other materials in meteorites such as CAIs that also carry isotopic anomalies in some elements but, in contrast to bona fide stardust, formed in the solar system. They apparently inherited their anomalies from incompletely homogenized presolar material. Another distinguishing feature is that anomalies in presolar grains are up to several orders of magnitude larger than those in CAIs and match those expected for stellar atmospheres (Zinner, 1997).
1.02.3 TYPES OF PRESOLAR GRAINS

Table 1 shows the types of presolar grains identified so far. It also lists the sizes, approximate abundances, and stellar sources. In addition to the three carbonaceous phases that were discovered because they carry exotic noble gas components (Figure 1) and which can be isolated from meteorites in almost pure form by chemical and physical processing, presolar oxides, silicon nitride (Si$_3$N$_4$), and silicates were identified by isotopic measurements in the ion microprobe and the number of such grains available for study is much smaller than for the carbonaceous phases. Most oxide grains are spinel (MgAl$_2$O$_4$) and corundum (Al$_2$O$_3$), but hibonite (CaAl$_2$O$_4$), and possibly titanium oxide have also been found (Hutcheon et al., 1994; Nittler et al., 1994; Nittler and Alexander, 1999; Choi et al., 1998; Zinner et al., 2003b). While all these grains as well as presolar Si$_3$N$_4$ (Nittler et al., 1995) were located by single grain analysis of acid residues, presolar silicates were discovered by isotopic imaging of chemically untreated interplanetary dust particles (IDPs) (Messenger et al., 2003) and meteoritic grain size separates and polished sections (Nguyen and Zinner, 2004; Nagashima et al., 2004).

Finally, titanium-, zirconium-, and molybdenum-rich carbides, cohenite ((Fe,Ni)$_3$C), kamacite (Fe-Ni), and elemental iron were found as tiny subgrains inside of graphite spheres (Bernatowicz et al., 1991, 1996; Croat et al., 2003). While TiC inside of a SiC grain (Bernatowicz et al., 1992) could have formed by exsolution, there can be little doubt that interior grains in graphite must have formed prior to the condensation of the spherules.

1.02.4 ANALYSIS TECHNIQUES

Although the abundance of carbonaceous presolar grains in meteorites is low, once they are identified, almost pure samples can be prepared and studied in detail. Enough material of these phases can be obtained for “bulk” analysis, that is, analysis of collections of large numbers of grains either by gas mass spectrometry (GMS) of carbon, nitrogen, and the noble gases (Lewis et al., 1994; Russell et al., 1996, 1997), by thermal ionization mass spectrometry (TIMS) of strontium, barium,
neodymium, samarium, dysprosium (Ott and Begemann, 1990; Prombo et al., 1993; Richter et al., 1993, 1994; Podosek et al., 2004) or secondary ion mass spectrometry (SIMS) (Zinner et al., 1991; Amari et al., 2000). Isotopic ratios of barium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, yttrium, and hafnium on SiC-rich bulk samples have recently been obtained by inductively coupled plasma mass spectrometry (ICP-MS) (Yin et al., 2006). While only averages over many grains are obtained by bulk analysis, it allows the measurement of trace elements such as the noble gases and heavy elements that cannot be analyzed otherwise.

However, because presolar grains come from different stellar sources, information on individual stars is obtained by the study of single grains. This challenge has been successfully taken up by the application of a series of microanalytical techniques. For isotopic analysis, the ion microprobe has become the instrument of choice. While most SIMS measurements have been made on grains 1 μm in size or larger, a new type of ion probe, the NanoSIMS, allows measurements of grains an order of magnitude smaller (e.g., Zinner et al., 2003b). Ion probe analysis has led to the discovery of new types of presolar grains such as corundum (Hutcheon et al., 1994; Nittler et al., 1994) and silicon nitride (Nittler et al., 1995). It also has led to the identification of rare subpopulations of presolar dust such as SiC grains of type X (Amari et al., 1992) and type Y (Hoppe et al., 1994). Searches for presolar oxide grains and rare subpopulations of SiC profited from the application of isotopic imaging in the ion probe, which allows the rapid analysis of a large number of grains (Nittler et al., 1997; Nittler and Alexander, 2003). Whereas earlier analyses have been made on well-separated grains, isotopic imaging of tightly packed grains, of polished sections of meteorites, and of samples pressed into a metal foil allows the automatic analysis of many thousands of grains (Nguyen et al., 2003) and has been essential in the discovery of presolar silicate grains (Messenger et al., 2001, 2002; Croat et al., 2001, 2002; Croat et al., 2003).

The surface morphology of grains has been studied by secondary electron microscopy (SEM) (Hoppe et al., 1995). Such studies have been especially useful for pristine SiC grains that have not been subjected to any chemical treatment (Bernatowicz et al., 2003; Tizard et al., 2005). Finally, the transmission electron microscope (TEM) played an important role in the discovery of presolar SiC (Bernatowicz et al., 1987) and internal TiC and other subgrains in graphite (Bernatowicz et al., 1991). Electron diffraction analysis in the TEM allow the determination of the crystal structure of grains (Bernatowicz et al., 1987; Stroud et al., 2004a). The TEM also has been successfully applied to the study of diamonds (Daulton et al., 1996) and of polytypes of SiC (Daulton et al., 2002, 2003).

1.02.5 ASTROPHYSICAL IMPLICATIONS OF THE STUDY OF PRESOLAR GRAINS

There are many stages in the long history of presolar grains from their stellar birth to their incorporation into primitive meteorites and, in principle, the study of the grains can provide information on all of them.

The isotopic composition of a given circumstellar grain reflects that of the stellar atmosphere from which the grain condensed. The atmosphere’s composition in turn is determined by several factors: (1) by the galactic history of the material from which the star itself formed, (2) by nucleosynthetic processes in the star’s interior, and (3) by mixing episodes in which newly synthesized material is dredged from the interior into the star’s envelope. In supernovae, mixing of different layers with different nucleosynthetic history accompanies the explosion and the ejection of material. The isotopic compositions of grains provide information on these processes.

Grain formation occurs when temperatures in the expanding envelope of red giants (RGs) or in SN ejecta are low enough for the condensation of minerals. Many late-type stars are observed to be surrounded by dust shells of grains whose mineral compositions reflect the major chemistry of the gas (e.g., Little-Marenin, 1986). The study of morphological features of pristine grains, of internal grains, and of trace element abundances can give information on the physical and chemical properties of stellar atmospheres (Bernatowicz et al., 1996, 2005; Amari et al., 1995a; Lodders and Fegley, 1998; Kashy et al., 2001, 2002; Croat et al., 2003).

After their formation as circumstellar grains or as SN condensates, grains enter a long
journey through the ISM. They should be distinguished from true IS grains that form in the ISM (e.g., in dense molecular clouds). Grains of stellar origin are most likely to be covered by mantles of IS cloud material. During their IS history, grains are subjected to a variety of destructive processes, such as evaporation in SN shocks and sputtering by shocks and stellar winds. They are also exposed to galactic cosmic rays that leave a record in the form of cosmogenic nuclides (Tang and Anders, 1988a; Ott and Begemann, 2000; Ott et al., 2005).

Grains might go in and out of IS clouds before some were finally incorporated into the dense molecular cloud from which our solar system formed. The final step in the complex history of stellar grains is the formation of planetesimals and of the parent bodies of the meteorites in which we find these presolar fossils. By far the largest fraction of the solids, even in primitive meteorites, formed in the solar system and the fraction of surviving presolar grains is small (see Table 1). Primitive meteorites experienced varying degrees of metamorphism on their parent bodies and these metamorphic processes affected different types of presolar grains in different ways. The abundance of different grain types can thus give information about conditions in the solar nebula and about parent-body processes (Huss and Lewis, 1995; Mendybaev et al., 2002).

1.02.6 SILICON CARBIDE

Silicon carbide is the best-studied presolar grain type. It has been found in carbonaceous, unequilibrated ordinary, and enstatite chondrites with concentrations ranging up to ~10 ppm (Huss and Lewis, 1995). Most SiC grains are <0.5 µm in diameter. Murchison is an exception in that grain sizes are, on average, much larger than those in other meteorites (Amari et al., 1994; Huss et al., 1997; Russell et al., 1997). This difference is still not understood but it, and the fact that plenty of Murchison is available, is the reason that by far most measurements have been made on Murchison SiC. Many SiC grains show euhedral crystal features (Figure 2) but there are large variations. Morphological studies by high-resolution SEM (Bernatowicz et al., 2003; Stroud and Bernatowicz, 2005) reveal detailed crystallographic features that give information about growth conditions. Such information is also obtained from TEM studies (Stroud et al., 2003, 2004b; Stroud and Bernatowicz, 2005; Hynes et al., 2006). Electron diffraction measurements in the TEM show that only the cubic (3C) (~80%) and hexagonal (2H) polytypes are present, indicating low pressures and condensation temperatures in stellar outflows (Bernatowicz et al., 1987; Daulton et al., 2002, 2003). A preponderance of cubic SiC has been observed astronomically in carbon stars (Speck et al., 1999).

The availability of >1 µm SiC grains and relatively high concentrations of trace elements (Amari et al., 1995a; Kashiv et al., 2002) allow
the isotopic analysis of the major and of many trace elements in individual grains. In addition to the major elements carbon and silicon, isotopic data are available for the diagnostic (in terms of nucleosynthesis and stellar origin) elements nitrogen, magnesium, calcium, titanium, iron, the noble gases, and the heavy refractory elements strontium, zirconium, molybdenum, ruthenium, barium, neodymium, samarium, and dysprosium. Refractory elements such as aluminum, titanium, vanadium, and zirconium are believed to have condensed into SiC (Lodders and Fegley, 1995, 1997, 1999). However, Verchovsky and coworkers (Verchovsky et al., 2004; Verchovsky and Wright, 2004) argued on the basis of the grain-size dependence of elemental concentrations that implantation played a major role not only for noble gases but also for relatively refractory elements such as strontium and barium. These authors identified two components with different implantation energies: the low-energy component is implanted from the stellar wind and has the composition of the asymptotic giant branch (AGB) envelope, the high-energy components is implanted during the planetary nebula phase from the hot remaining white dwarf star and has the composition of helium-shell material. The \(^{134}\text{Xe}/^{138}\text{Xe} \) ratio found in the grains confirms their conclusion that most s-process xenon in SiC originated in the envelope (Pignatari et al., 2004a).

Carbon, nitrogen, and silicon isotopic as well as inferred \(^{26}\text{Al}/^{27}\text{Al} \) ratios in a large number of individual grains (Figures 3–5) have led to the classification into different populations (Hoppe and Ott, 1997): mainstream grains (~93% of the total), and the minor subtypes A, B, X, Y, Z, and nova grains. Most of presolar SiC is believed to have originated from carbon stars, late-type stars of low mass (1–2 \( M_{\odot} \)) in the thermally pulsing (TP) AGB phase of evolution (Iben and Renzini, 1983). Dust from such stars has been proposed already one decade prior to identification of SiC to be a minor constituent of primitive meteorites (Clayton and Ward, 1978; Srinivasan and Anders, 1978; Clayton, 1983a). Several pieces of evidence point to such an origin. Mainstream grains have \(^{12}\text{C}/^{13}\text{C} \) ratios similar to those found in carbon stars (Figure 6), which are considered to be the most prolific injectors of carbonaceous dust grains into the ISM (Tielens, 1990). Many carbon stars show the 11.3 \( \mu \text{m} \) emission feature typical of SiC (Treffers and Cohen, 1974; Speck et al., 1997). Finally, AGB stars are believed to be the main source of the s-process (slow neutron capture nucleosynthesis) elements (e.g., Busso et al., 2001), and the s-process isotopic patterns of the heavy elements exhibited by mainstream SiC provide the most convincing argument for their origin in carbon stars (see below).

1.02.6.1 Mainstream Grains

Mainstream grains have \(^{12}\text{C}/^{13}\text{C} \) ratios between 10 and 100 (Figure 3). They have carbon and nitrogen isotopic compositions (Zinner et al., 1989; Stone et al., 1991; Virag et al., 1992; Alexander, 1993; Hoppe et al., 1994, 1996a; Nittler et al., 1995; Huss et al., 1997; Amari et al., 2002a; Nittler and Hoppe, 2005, and Barzyk et al. (2006a).
Envelope, increases the $^{12}\text{C}/^{13}\text{C}$ ratio from the low values resulting from the first dredge-up and, by making $\text{C}_4\text{O}$, causes the star to become a carbon star.

Envelope $^{12}\text{C}/^{13}\text{C}$ ratios predicted by canonical stellar evolution models range from $\sim 20$ after first dredge-up in the RG phase to $\sim 300$ in the late TP-AGB phases of solar-metallicity stars (El Eid, 1994; Gallino et al., 1994; Amari et al., 2001b) and to several thousand in low-metallicity stars (Nittler et al., 2005c; Zinner et al., 2006b). Predicted $^{14}\text{N}/^{15}\text{N}$ ratios are $600$–$1,600$ (Becker and Iben, 1979; El Eid, 1994), falling short of the range observed in the grains. However, the assumption of deep mixing (“cool bottom processing”) of envelope material to deep hot regions close to the H-burning shell in $M<2.5M_\odot$ stars during their RG and AGB phases (Charbonnel, 1995; Wasserburg et al., 1995; Langer et al., 1999; Nollett et al., 2003) results in partial hydrogen burning, with higher $^{14}\text{N}/^{15}\text{N}$ and lower $^{12}\text{C}/^{13}\text{C}$ ratios in the envelope than in canonical models (see also Huss et al., 1997).

Two other isotopes that are a signature for AGB stars are $^{26}\text{Al}$ and $^{22}\text{Ne}$. Figure 5 shows inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios in different types of SiC grains. The existence of the short-lived radioisotope $^{26}\text{Al}$ ($T_{1/2} = 7.3 \times 10^5$ years) is inferred from large $^{26}\text{Mg}$ excesses. Aluminum-26 is produced in the H-shell by proton capture on $^{25}\text{Mg}$ and mixed to the surface by the third dredge-up (Forestini et al., 1991; Mowlavi and Meynet, 2000; Karakas and Lattanzio, 2003). It can also be produced during “hot bottom burning” (Lattanzio et al., 1997) but this

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**Figure 4** Silicon isotopic ratios of different types of presolar SiC grains plotted as $\delta$-values, deviations in permil (‰) from the solar ratios: $\delta^{28}\text{Si}/^{28}\text{Si} = \frac{1}{2} \left( \frac{\text{Meas}}{\text{Solar}} - 1 \right) \times 1,000$. Mainstream grains plot along a line of slope 1.4 (solid line). Symbols are the same as those in Figure 3. Sources same as in Figure 3 as well as Lin et al. (2002), Nittler and Alexander (2003), and Zinner et al. (2003a).
process is believed to prevent carbon-star formation (Frost and Lattanzio, 1996). Neon-22, the main component in Ne-E, is produced in the helium-shell by $^{14}\text{N} + 2x$. The neon isotopic ratios measured in SiC bulk samples (Lewis et al., 1990, 1994) are very close to those expected for He-shell material (Gallino et al., 1990). In contrast to krypton and xenon and heavy refractory elements, neon as well as helium and argon, show very little dilution of helium-shell material with envelope material, indicating a special implantation mechanism by an ionized wind (Verchovsky et al., 2004; Verchovsky and Wright, 2004). Another piece of evidence that the Ne-E(H) component originated from the helium-shell of AGB stars and not from the decay of $^{22}\text{Na}$ (Clayton, 1975) is the fact that in individual grains, of which only $\sim 5\%$ carry $^{22}\text{Ne}$, it is always accompanied by $^{4}\text{He}$ (Nichols et al., 1995; Heck et al., 2005). Excesses in $^{21}\text{Ne}$ in SiC relative to the predicted He-shell composition have been interpreted as being due to spallation by galactic cosmic rays (Tang and Anders, 1988a; Lewis et al., 1990, 1994), which allows the determination of grain lifetimes in the IS medium. Inferred exposure ages depend on grain size and range from 10 to 130 Myr (Lewis et al., 1994). However, this interpretation has been challenged (Ott and Begemann, 2000) because recoil loss of neon from SiC grains is higher than assumed. Ott et al. (2005) recently determined recoil losses of xenon isotopes and concluded that most of spallation xenon (from barium) is retained in 1 $\mu$m large SiC grains. Based on the amount of $^{126}\text{Xe}$ present in $>1$ $\mu$m grains, they conclude that exposure ages of such grains are smaller than 40 Myr and are smaller than $\sim 175$ Myr for sub-micrometer grains, much shorter than theoretically expected lifetimes of IS grains (Jones et al., 1997).

The silicon isotopic compositions of most mainstream grains are characterized by enrichments in the heavy silicon isotopes of up to 200% relative to their solar abundances (Figure 4). In a silicon three-isotope plot the data fall along a line with slope 0.2–0.5 line in a $\delta$-value
silicon three-isotope plot (Gallino et al., 1990, 1994; Brown and Clayton, 1992; Lugaro et al., 1999; Amari et al., 2001b; Nittler and Alexander, 2003; Zinner et al., 2006b). Predicted excesses are only on the order of 20% in low-mass AGB stars of close-to-solar metallicity (metallicity is the abundance of all elements heavier than He). This led to the proposal that many stars with varying initial silicon isotopic compositions contributed SiC grains to the solar system (Clayton et al., 1991; Alexander, 1993) and that neutron-capture nucleosynthesis in these stars only plays a secondary role in modifying these compositions. Several explanations have been given for the initial silicon ratios in the parent stars, which in their late stages of evolution became the carbon stars that produced the SiC. One is the evolution of the silicon isotopic ratios through galactic history as different generations of supernovae produced silicon with increasing ratios of the secondary isotopes $^{28}$Si and $^{30}$Si to the primary $^{26}$Si (Gallino et al., 1994; Timmes and Clayton, 1996; Clayton and Timmes, 1997a, b). Clayton (1997) addressed the problem that most SiC grains have higher-than-solar $^{29}$Si/$^{28}$Si and $^{30}$Si/$^{28}$Si ratios by considering the possibility that the mainstream grains originated from stars that were born in central, more metal-rich regions of the galaxy and moved to the molecular cloud from which our Sun formed. Alexander and Nittler (1999), alternatively, suggested that the Sun has an atypical silicon isotopic composition. Lugaro et al. (1999) explained the spread in the isotopic compositions of the parent stars by local heterogeneities in the galaxy caused by the stochastic nature of the admixture of the ejecta from supernovae of varying type and mass. Finally, Clayton (2003) invoked merger of our galaxy, assumed to have high metallicity, with a satellite galaxy of low metallicity some time before solar-system formation to account for the silicon isotopic ratios of mainstream grains. A detailed discussion of the role of galactic chemical evolution for the silicon isotopic ratios in SiC grains from AGB stars is found in Nittler and Dauphas (2006).

Titanium isotopic ratios in single grains (Ireland et al., 1991; Hoppe et al., 1994; Alexander and Nittler, 1999) and in bulk samples (Amari et al., 2000) show excesses in all isotopes relative to $^{48}$Ti, a result expected of neutron capture in AGB stars. However, as for silicon, theoretical models (Lugaro et al., 1999) cannot explain the range of ratios observed in single grains. Furthermore, titanium ratios are correlated with those of silicon, also indicating that the titanium isotopic compositions are dominated by galactic evolution effects (Alexander and Nittler, 1999). However, local heterogeneity cannot explain the correlations between titanium isotopic ratios and the correlations between titanium and silicon isotopic ratios imply that at most 40% of the range of isotopic ratios in the grains can be accounted for by heterogeneous mixing of SN ejecta (Nittler, 2005). Excesses of $^{44}$Ca and $^{46}$Ca relative to $^{40}$Ca observed in bulk samples (Amari et al., 2000) agree with predictions for neutron capture. Large $^{44}$Ca excesses are apparently due to the presence of type X grains (see below).

All heavy elements measured so far show the signature of the s-process (Figure 7, see also Figure 10). They include the noble gases krypton and xenon (Lewis et al., 1990, 1994) but also the heavy elements strontium (Podosek et al., 2004), barium (Ott and Begemann, 1990; Zinner et al., 1991; Prombo et al., 1993), neodymium and samarium (Zinner et al., 1991; Richter et al., 1993), and dysprosium (Richter et al., 1994). Although most measurements were made on bulk samples, it is clear that mainstream grains dominate. Single grain measurements of strontium (Nicolussi et al., 1998b), zirconium (Nicolussi et al., 1997), molybdenum (Nicolussi et al., 1998a), ruthenium (Savina et al., 2004a), and barium (Savina et al., 2003a) have been made with RIMS, and of barium with the NanoSIMS (Marhas et al., 2006a). From systematic excesses in $^{99}$Ru in single SiC grains Savina et al. (2004a) concluded that the grains contained short-lived $^{99}$Tc ($T_{1/2} = 2.1 \times 10^5$ years) when they condensed. Large enrichments of certain heavy elements such as yttrium, zirconium, barium, and cerium in single mainstream grains also indicate large overabundances of s-process elements in the parent stars (Amari et al., 1995a; Kashiv et al., 2002). Kashiv et al. (2006) interpreted large Nb/Zr ratios compared to those expected from the condensation of these elements into SiC grains in the envelope of AGB stars as evidence for the initial presence of short-lived $^{97}$Zr ($T_{1/2} = 1.5 \times 10^6$ years). For all the isotopic compositions of the elements listed above there is good agreement with theoretical models of the sprocess in low-mass AGB stars (Gallino et al., 1993, 1997; Arlandini et al., 1999; Lugaro et al., 2003, 2004; Fazio et al., 2003; Pignatari et al., 2003, 2004b). Discrepancies with earlier model calculations were caused by incorrect nuclear cross-sections and could be resolved by improved experimental determinations (e.g., Guber et al., 1997; Wisshak et al., 1997; Koehler et al., 1998). An exception is dysprosium, for which the data show large discrepancies with AGB models. However, ICP-MS analysis of dysprosium (Yin et al., 2006) gives much better agreement with models for the isotopes 161–164 and indicates that the TIMS results might be in error.
The s-process isotopic patterns observed in grains allow the determination of different parameters affecting the s-process such as neutron exposure, temperature, and neutron density (Hoppe and Ott, 1997). Since these parameters depend in turn on stellar mass and metallicity as well as on the neutron source operating in AGB stars, they allow information to be obtained about the parent stars of the grains. For example, the barium isotopic ratios indicate a neutron exposure that is only half of that inferred for the solar system (Ott and Begemann, 1990; Gallino et al., 1993). Another example is provided by the abundance of $^{96}$Zr in single grains, which is sensitive to neutron density because of the relatively short half-life of $^{95}$Zr ($\sim 64$ d). While the $^{13}$C($n,n'$) source with its low neutron density destroys $^{96}$Zr, activation of the $^{22}$Ne($n,n'$) source during later thermal pulses in AGB stars restores some of this isotope, whose abundance thus varies with pulse number. Some grains have essentially no $^{96}$Zr, indicating that the $^{22}$Ne($n,n'$) source was weak in their parent stars, pointing to low-mass AGB stars as the source of mainstream grains (Lugaro et al., 2003).

### 1.02.6.2 Type Y and Z Grains

Type Y grains have $^{12}$C/$^{13}$C $> 100$ and silicon isotopic compositions that lie to the right of the mainstream correlation line (Figures 3 and 4b) (Hoppe et al., 1994; Amari et al., 2001b; Nittler and Alexander, 2003). Type Z grains have even larger $^{30}$Si excesses relative to $^{28}$Si and, on average, lower $\delta^{29}$Si values than Y grains. However, they are distinguished from Y grains by having $^{12}$C/$^{13}$C $< 100$ (Alexander, 1993; Hoppe et al., 1997; Nittler and Alexander, 2003). Comparison of the carbon, silicon, and titanium isotopic ratios of Y grains with models of nucleosynthesis indicates an origin in low-to-intermediate-mass AGB stars with approximately half the solar metallicity (Amari et al., 2001b). Such stars dredge up more $^{12}$C, and silicon and titanium that experienced neutron capture, from the helium shell (see also Lugaro et al., 1999). According to their silicon isotopic ratios Z grains came from low-mass stars of even lower (approximately one-third solar) metallicity (Hoppe et al., 1997). This interpretation is in agreement with the large depletions in $^{46}$Ti, $^{47}$Ti, and $^{48}$Ti relative to $^{46}$Ti that are correlated with depletions in $^{28}$Si (Amari et al., 2005a; Zinner et al., 2005a). The relative excesses in $^{30}$Si and $^{50}$Ti are explained by the effects of neutron capture, which are more pronounced in low-metallicity AGB stars (Zinner et al., 2005a, 2006b). In order to achieve the relatively low $^{12}$C/$^{13}$C ratios of Z grains, the parent stars must have experienced cool bottom processing (Wasserburg et al., 1995; Nollett et al., 2003) during their RG and AGB phase (Nittler et al., 2005c; Zinner et al., 2006b). However, inferred $^{26}$Al/$^{27}$Al ratios in Z grains (Hoppe et al., 2004; Zinner et al., 2005a) are not higher than those in mainstream SiC grains (Figure 5), and are much lower than those in many presolar oxide grains, for which cool bottom processing has been invoked (see Section 1.02.9 and Figure 14). The parametric model for cool bottom processing by Nollett et al. (2003) assumes two independent parameters, the circulation rate of material from the (cool) bottom of the convective envelope to deep hot regions and the temperature reached by this material. The former affects mostly the production of $^{13}$C and destruction of $^{18}$O, the latter mostly the production of $^{26}$Al, which requires a much higher temperature. Accordingly, cool bottom processing in the parent stars of Z grains must have occurred with a high circulation rate but low temperature.

Nittler et al. (2005c) and Zinner et al. (2006b) compared the carbon and silicon isotopic compositions of mainstream, Y, and Z grains with new theoretical models of AGB nucleosynthesis. They concluded that cool bottom burning on the AGB was necessary to explain the carbon ratios and that the recent silicon neutron capture cross section by Guber et al. (2003) yield a better fit to the silicon isotopic ratios. From the theoretically inferred metallicities and average silicon isotopic ratios of mainstream, Y, and Z grains Zinner et al. (2001, 2006b) and Nittler et al. (2005c) derived the galactic evolution of the silicon isotopic ratios as function of metallicity. This evolution differs from the results of galactic evolution models based on the yields of supernovae (Timmes and Clayton, 2000).

![Figure 7](image-url) Isotopic patterns measured in bulk samples and individual grains of SiC extracted from the Mu- richson meteorite. Isotopic ratios are relative to the reference isotope plotted as a solid circle and are normalized to the solar isotopic ratios. Plotted are the pure s-process ratios, also called the G-component, that exist in the helium shell of AGB stars. The ratios measured in SiC are a mix of the G- and the N-components; the N-component is similar to but not exactly the same as the solar isotopic composition of a given element. For details see Hoppe and Ott (1997). Data are from Lewis et al. (1994) (Kr and Xe), Podosek et al. (2004) (Sr), Prombo et al. (1993) (Ba), Richter et al. (1993) (Nd and Sm), Richter et al. (1994) (Dy), Lugaro et al. (2003) (Mo), and Savina et al. (2004a) (Ru).
and has important implications concerning the relative contributions from type II and Ia supernovae during the history of our galaxy.

### 1.02.6.3 Type A+B Grains

Grains of type A+B have $^{12}\text{C}/^{13}\text{C}<10$, but their silicon isotopic ratios plot along the mainstream line (Figures 3 and 4). In contrast to mainstream grains, many A+B grains have lower than solar $^{14}\text{N}/^{15}\text{N}$ ratios (Hoppe et al., 1995, 1996a; Huss et al., 1997; Amari et al., 2001c; Nittler and Alexander, 2003). On average, they have higher $^{26}\text{Al}/^{27}\text{Al}$ ratios than mainstream, Y, and Z grains (Figure 5). While the isotopic ratios of the latter grains find an explanation in nucleosynthetic models of AGB stars, a satisfactory explanation of the data in terms of stellar nucleosynthesis is more elusive for the A+B grains. The low $^{12}\text{C}/^{13}\text{C}$ ratios of these grains combined with the requirement for a carbon-rich environment during their formation indicate helium burning followed by limited hydrogen burning in their stellar sources. However, the astrophysical sites for this process are not well known. There might be two different kinds of A+B grains with corresponding different stellar sources (Amari et al., 2001c). Grains with no s-process enhancements (Amari et al., 1995a; Pellin et al., 2000b; Savina et al., 2003c) probably come from J-type carbon stars that also have low $^{12}\text{C}/^{13}\text{C}$ ratios (Lambert et al., 1986). Unfortunately, J stars are not well understood and there are no astronomical observations of nitrogen isotopic ratios in such stars. Furthermore, the low $^{14}\text{N}/^{15}\text{N}$ ratios observed in some of the grains as well as the carbon-rich nature of their parent stars appear to be incompatible with the consequences of hydrogen burning in the CNO cycle, which seems to be responsible for the low $^{12}\text{C}/^{13}\text{C}$ ratios of J stars and the grains. A+B grains with s-process enhancements might come from post-AGB stars that undergo a very late thermal pulse. An example of such a star is Sakurai’s object (e.g., Asplund et al., 1999; Herwig, 2001, 2004). However, grains with low $^{14}\text{N}/^{15}\text{N}$ ratios pose a problem. Huss et al. (1997) proposed that the currently used $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction rate is too low by a factor of 1,000. This would result in low $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$ ratios if an appropriate level of cool bottom processing is considered. One A+B grain shows excesses in the p-process isotopes $^{92}\text{Mo}$, $^{94}\text{Mo}$, $^{98}\text{Ru}$, $^{98}\text{Ru}$ and in the r-process isotopes $^{100}\text{Mo}$ and $^{104}\text{Ru}$ (Savina et al., 2003c, 2004b), and another grain shows a molybdenum isotopic pattern similar to those found in X grains (Figure 10), indicating a neutron burst. While these signatures indicate a SN origin, the carbon and silicon isotopic ratios of A+B grains are difficult to reconcile with such an origin. The authors suggest material transfer in a binary star system.

### 1.02.6.4 Type X Grains

Although SiC grains of type X account for only 1% of presolar SiC, a fairly large number can be located by ion imaging (Nittler et al., 1997; Hoppe et al., 1996b, 2000; Lin et al., 2002; Besmehn and Hoppe, 2003) or automatic isotopic measurements (Nittler and Alexander, 2003). X grains are characterized by mostly $^{12}\text{C}$ and $^{15}\text{N}$ excesses relative to solar (Figures 3 and 6), excesses in $^{26}\text{Si}$ (Figure 4) and very large $^{26}\text{Al}/^{27}\text{Al}$ ratios, ranging up to 0.6 (Figure 5). About 10–20% of the grains show large $^{44}\text{Ca}$ excesses, which must come from the decay of short-lived $^{44}\text{Ti}$ ($T_{1/2} = 60$ years) (Amari et al., 1992; Hoppe et al., 1996b, 2000; Nittler et al., 1996; Besmehn and Hoppe, 2003). Inferred $^{44}\text{Ti}/^{48}\text{Ti}$ ratios range up to 0.6 (Figure 8). In contrast to presolar graphite, which contains subgrains of TiC, titanium in SiC seems to occur in solid solution and radiogenic $^{44}\text{Ca}$ is uniformly distributed in most of the grains. There is only one X grain with a pronounced isotopic heterogeneity, which points to a titanium-rich subgrain (Besmehn and Hoppe, 2003). Because $^{44}\text{Ti}$ can only be produced in SN explosions (Timmes et al., 1996), grains with evidence for $^{44}\text{Ti}$, and by implications all X grains, must have a SN origin. In type II supernovae $^{44}\text{Ti}$ is produced in the nickel- and silicon-rich inner zones (see Figure 9) (Woosley and Weaver, 1995; Timmes et al., 1996). Silicon in the Si/S zone consists of almost pure $^{28}\text{Si}$. Also the other isotopic signatures of X grains are compatible with an origin in type II supernovae: high $^{13}\text{C}/^{12}\text{C}$ and low $^{14}\text{N}/^{15}\text{N}$ ratios are the signature of silicon burning (Figure 9) and high $^{26}\text{Al}/^{27}\text{Al}$ ratios can be reached in the He/N zone by hydrogen burning.

However, these isotopic signatures occur in massive stars in very different stellar zones, which experienced different stages of nuclear burning before the SN explosion (Figure 9) (e.g., Woosley and Weaver, 1995; Rauscher et al., 2002). The isotopic signatures of the X grains suggest deep and inhomogeneous mixing of matter from these different zones in the SN ejecta. While the titanium and silicon isotopic signature of the X grains requires contributions from the Ni, O/Si, and Si/S zones, which experienced silicon-, neon-, and oxygen-burning, significant contributions must also come from the He/N and He/C zones that
experienced hydrogen and incomplete helium burning in order to achieve $C>0$, the condition for SiC condensation (Larimer and Bartholomay, 1979; Lodders and Fegley, 1997). Furthermore, addition of material from the intermediate oxygen-rich layers must be severely limited. Astronomical observations indicate extensive mixing of SN ejecta (e.g., Ebisuzaki and Shibazaki, 1988; Hughes et al., 2000) and hydrodynamic models of SN explosions predict mixing in the ejecta initiated by the formation of Rayleigh–Taylor instabilities (e.g., Herant et al., 1994). However, it still has to be seen whether mixing can occur on a microscopic

Figure 8  $^{44}$Ti/$^{48}$Ti ratios inferred from $^{44}$Ca excesses in SiC grains of type X and graphite grains are plotted against silicon isotopic ratios. Except for one graphite, all grains with evidence for $^{44}$Ti have $^{28}$Si excesses. Data are from Amari et al. (1992, unpublished), Hoppe et al. (1994, 1996b, 2000), Nittler et al. (1996), and Besmehn and Hoppe (2003).

Figure 9  Schematic structure of a massive star before its explosion as a type II supernova. Such a star consists of different layers, labeled according to their most abundant elements that experienced different stages of nucleosynthesis. Indicated are dominant nuclear reactions in some layers and the layers in which isotopes abundant in grains of an inferred SN origin are produced. Source: Woosley and Weaver (1995).
scale and whether these instabilities allow mixing of matter from nonneighboring zones while excluding large contributions from the intermediate oxygen-rich zones. Clayton et al. (1999) and Deneault et al. (2003, 2006) suggested condensation of carbonaceous phases in type II SN ejecta even while C\textless O because of the destruction of CO in the high-radiation environment of the ejecta. While this might work for graphite, it is doubtful whether SiC can condense from a gas with C\textless O (Ebel and Grossman, 2001). Even for graphite, the presence of subgrains of elemental iron inside of graphite grains whose isotopic signatures indicate a SN origin argues against formation in an oxygen-rich environment (Croat et al., 2003).

Although multizone mixing models can qualitatively reproduce the isotopic signatures of X grains (Yoshida and Hashimoto, 2004), several ratios, in particular the large $^{15}$N excesses and excesses of $^{28}$Si over $^{30}$Si found in most grains, cannot be explained quantitatively and indicate deficiencies in the existing models. The latter is a long-standing problem: SN models cannot account for the solar $^{29}$Si/$^{30}$Si ratio (Timmes and Clayton, 1996). Studies of SiC X grains isolated from the Qingzhen enstatite chondrite (Lin et al., 2002) suggest that there are two populations of X grains with different trends in the silicon isotopic ratios, the minor population having lower-than-solar $^{29}$Si/$^{30}$Si ratios (see also Nittler and Alexander, 2003). Clayton et al. (2002) and Deneault et al. (2003) have tried to account for isotopic signatures from different SN zones by considering implantation into newly condensed grains as they pass through different regions of the ejecta, specifically through zones with reverse shocks.

Some SiC X grains also show large excesses in $^{49}$Ti (Amari et al., 1992; Nittler et al., 1996; Hoppe and Besmehn, 2002). The correlation of these excesses with the V/Ti ratio (Hoppe and Besmehn, 2002) indicates that they come from the decay of short-lived $^{49}$V ($T_{1/2} = 330$ days) and that the grains must have formed within a few months of the explosion. Vanadium-49 is produced in the Si/S zone, which contains almost pure $^{28}$Si. RIMS isotopic measurements of iron, strontium, zirconium, molybdenum, ruthenium, and barium have been made on X grains (Pellin et al., 1999, 2000a, 2006; Davis et al., 2002b). The most complete and interesting are the molybdenum measurements, which reveal large excesses in $^{95}$Mo and $^{97}$Mo. Figure 10 shows the molybdenum isotopic patterns of a mainstream and an X grain. The mainstream grain has a typical s-process pattern, in agreement with bulk measurements of other heavy elements such as xenon, barium, and neodymium (Figure 7). The molybdenum pattern of the X grain is completely different and indicates neutron capture at much higher neutron densities. While it does not agree with the pattern expected for the r-process, it is successfully explained by a neutron-burst model (Meyer et al., 2000). In the type II SN models by Rauscher et al. (2002) an intense neutron burst is predicted to occur in the oxygen layer just below the He/C zone, accounting for the molybdenum isotopic patterns observed in X grains. The isotopic patterns in other elements, such as large excesses in $^{58}$Fe, $^{88}$Sr, $^{90}$Zr, and $^{138}$Ba, and depletions in $^{90}$Zr and $^{108}$Ru (Pellin et al., 2006), are consistent with a neutron-burst origin.

Type Ia supernovae offer an alternative explanation for the isotopic signature of X grains. In the model by Clayton et al. (1997) nucleosynthesis takes place by explosive helium burning of a helium cap on top of a white dwarf. This process produces most of the isotopic signatures of the SN grains. The isotopes $^{12}$C, $^{15}$N, $^{26}$Al, $^{28}$Si, and $^{44}$Ti are all made by helium burning during the explosion, which makes the transport of $^{28}$Si and $^{44}$Ti through the massive oxygen-rich zone into the overlying carbon-rich zones of a type II SN.
unnecessary. Mixing is limited to material from helium burning and to matter that experienced CNO processing. The best match with the X grain data, however, is achieved for mixing scenarios that yield O > C (Amari et al., 1998). Other problems include the questions of whether high-energy gas densities can be achieved in the ejecta for the condensation of micrometer-sized grains and whether type Ia supernovae can generate a neutron burst necessary for the molybdenum isotopic pattern. More work is needed to decide whether a type Ia SN origin for X grains is a realistic alternative.

TEM studies of X grains (Stroud et al., 2004b; Hynes et al., 2006) indicate a polycrystalline composition with crystallite sizes ranging from 10 to 200 nm. This is in marked contrast to the structure of most mainstream grains, which consist of single, twinned, or otherwise defect-laden crystals (Daulton et al., 2002, 2003; Stroud et al., 2004b).

1.02.6.5 Nova Grains

A few grains have isotopic ratios that are best explained by a nova origin (Amari et al., 2001a). These grains have low 12C/13C and 14N/15N ratios (Figure 3), large 28Si excesses (Figure 4), and high 26Al/27Al ratios (Figure 5). All these features are predicted to be produced by explosive hydrogen burning taking place in classical novae (e.g., Kovetz and Prialnik, 1997; Starrfield et al., 1998; José et al., 1999, 2003, 2004), but the predicted anomalies are much larger than those found in the grains, and the nova ejecta have to be mixed with material of close-to-solar isotopic compositions. A comparison of the data with the models implicates ONe novae with a white dwarf origin (Amari et al., 2001a). Nittler and Hoppe (2005) identified a SiC grain with carbon and nitrogen isotopic ratios within the range spanned by nova candidate grains (Figure 3). However, this grain has a large 28Si and 49Ti excess and an 26Al/27Al ratio of 0.4 (Figure 5) and is almost certainly a SN grain. Another grain with small carbon and nitrogen isotopic ratios has a large 28Si depletion and 30Si excess, a 47Ti excess and a high 26Al/27Al ratio. It might be a SN grain as well but in Figures 3–5 it is plotted as a question mark.

1.02.6.6 Grain-Size Effect

Grain-size distributions of SiC have been determined for several meteorites and while grain sizes vary from 0.1 to 20 µm, the distributions are different for different meteorites. Murchison appears to have, on average, the largest grains (Amari et al., 1994), while SiC from Indarch (Russell et al., 1997) and Orgueil (Huss et al., 1997) is much finer grained. Various isotopic and other properties vary with grain size. Both the 22Ne/E(H)/130Xe-S and the 86Kr/82Kr (Figure 7) ratios increase with grain size (Lewis et al., 1994) and the first ratio has been used as a measure for the average grain size in meteorites for which no detailed size distributions have been determined (Russell et al., 1997). The 86Kr/82Kr ratio is a function of neutron exposure and the data indicate that exposure decreases with increasing grain size. The 86Sr/88Sr and 138Ba/136Ba ratios also depend on grain size (Figure 7), but the dependence of neutron exposure on grain size inferred from these isotopic ratios is just the opposite of that inferred from the 86Kr/82Kr ratio. This puzzle has not been resolved. A possible explanation is a different trapping mechanism for noble gases and refractory elements, respectively (Zinner et al., 1991), or different populations of carrier grains if, as for neon (Nichols et al., 1995), only a small fraction of the grains carry krypton. Excesses in 21Ne relative to the predicted helium-shell composition, interpreted as being due to spallation by galactic cosmic rays, increase with grain size (Tang and Anders, 1988a; Lewis et al., 1990, 1994). However, the correlation of the 21Ne/22Ne ratio with the s-process 86Kr/82Kr ratio (Hoppe and Ott, 1997) and the recent determination of spallation recoil ranges (Ott and Begemann, 2000) cast doubt on a chronological interpretation. Other grain-size effects are, on average, larger 14N/15N ratios for smaller grains (Hoppe et al., 1996a) and an increasing abundance of Z grains among smaller SiC grains (Hoppe et al., 1996a, 1997; Zinner et al., 2006b). There are also differences in the distribution of different grain types in SiC from different meteorites: whereas the abundance of X grains in SiC from Murchison and other carbonaceous chondrites is ~1%, it is only ~0.1% in SiC from the enstatite chondrites Indarch and Qingshen (Besmehn and Hoppe, 2001; Lin et al., 2002).

1.02.7 SILICON NITRIDE

Presolar silicon nitride (Si3N4) grains are extremely rare (in Murchison SiC-rich separations ~5% of SiC of type X) but automatic ion imaging has been successfully used to detect those with large 28Si excesses (Nittler et al., 1998; Besmehn and Hoppe, 2001; Lin et al., 2002).
The carbon, nitrogen, aluminum, and silicon isotopic signatures of these grains are the same as those of SiC grains of type X, that is, large $^{15}$N and $^{28}$Si excesses and high $^{26}$Al/$^{27}$Al ratios (Figure 12). Although so far no resolvable $^{44}$Ca excesses have been detected (Besmehn and Hoppe, 2001) the similarity with X grains implies a SN origin for these grains. While Si$_3$N$_4$ grains in SiC-rich residues from Murchison are extremely rare and, if present, are of type X, enstatite chondrites contain much higher abundances of Si$_3$N$_4$ (Alexander et al., 1994; Besmehn and Hoppe, 2001; Amari et al., 2002a). Most of them have normal isotopic compositions. Recent measurements of small (0.25–0.65 μm) grains from Indarch revealed several Si$_3$N$_4$ grains with carbon and nitrogen isotopic ratios similar to those of mainstream SiC grains but contamination from attached SiC grains cannot be excluded (Amari et al., 2002a; Zinner et al., 2003a).

1.02.8 GRAPHITE

Graphite, the third type of carbonaceous presolar grains, was isolated because it is the carrier of Ne-E(L) (Amari et al., 1990, 1995b). Subsequent isotopic measurements of individual grains revealed anomalies in many different elements.

1.02.8.1 Physical Properties

Only grains $\geq$1 μm in diameter carry Ne-E(L) and only round grains, which range up to 20 μm in size, appear to be of presolar origin (Amari et al., 1990; Zinner et al., 1995). Presolar graphite has a range in density (1.6–2.2 g cm$^{-3}$) and four different density fractions from the Murchison meteorite have been isolated (Amari et al., 1994). Average sizes of these grains decrease with increasing density and density fractions differ in the distribution of their carbon and noble gas isotopic compositions (Amari et al., 1995b; Hoppe et al., 1995). SEM studies revealed two basic morphologies (Hoppe et al., 1995): dense aggregates of small scales (“cauliflowers,” Figure 2b) and grains with smooth or shell-like platy surfaces (“onions,” Figure 2c). Graphite from Orgueil differs from Murchison graphite in that the average size increases with density and that no cauliflower grains are found (Jadhav et al., 2006). TEM analysis of microlomed sections of graphite spherules (Bernatowicz et al., 1991, 1996) found the surface morphology reflected in the internal structure of the grains. Cauliflower consist of concentrically packed scales of poorly crystallized carbon whereas onions either consist of well-crystallized graphite throughout or of a core of tightly packed graphene sheets of only several atomic layers surrounded by a mantle of well-crystallized graphite. Most graphite spherules contain small (20–500 nm) internal grains of mostly titanium carbide (TiC) (Bernatowicz et al., 1991); however, also zirconium- and molybdenum-rich carbides have been found (Bernatowicz et al., 1996; Croat et al., 2005b). Studies of low-density graphite spherules whose oxygen and silicon isotopic compositions indicated a SN origin (see below) did not detect Zr–Mo-rich carbides but revealed internal kamacite, cohenite, and iron grains in addition to TiC (Croat et al., 2003). A high-density graphite whose stellar origin is uncertain contains many SiC grains and a few Fe–Ni grains (Croat and Stadermann, 2006). Both cauliflowers and onions contain internal grains, which must have condensed before the graphite and were apparently captured and included by the growing spherules. Some onions show TiC grains at their center that apparently acted as condensation nuclei for the graphite (Figure 11). Sizes of internal grains and graphite spherules and their relationship and

Figure 11 Transmission electron micrograph of a slice through a presolar graphite grain (onion). The grain in the center is TiC and apparently acted as condensation nucleus for the growth of the graphite spherule. Photo courtesy of Thomas Bernatowicz.
chemical compositions provide information about physical properties such as pressure, temperature, and C/O ratio in the gas from which the grains condensed (Bernatowicz et al., 1996, 2005; Croat et al., 2003, 2005b).

1.02.8.2 Isotopic Compositions

Noble gas measurements were made on bulk samples of four density fractions from Murchison (Amari et al., 1995b) and in single grains (Nichols et al., 1995). In contrast to SiC, a substantial fraction of Ne-E in graphite seems to come from the decay of short-lived ($T_{1/2} = 2.6$ years) $^{22}$Na (Clayton, 1975), most likely produced in supernovae (Amari, 2003, 2006; Amari et al., 2005c). This is supported by the low $^{4}$He/$^{22}$Ne ratios measured in individual grains (Nichols et al., 1995). Krypton in graphite has two s-process components with apparently different neutron exposures, residing in different density fractions (Amari et al., 1995b). Krypton in low-density graphite seems to have a SN origin, while that in high-density graphite seems to have originated in low-metallicity AGB stars (Amari et al., 1995b, 2006).

Ion microprobe analyses of single grains revealed the same range of $^{12}$C/$^{13}$C ratios as in SiC grains, but the distribution is quite different (Figure 6). Most anomalous grains have $^{12}$C excesses, similar to SiC X grains. A substantial fraction has low $^{12}$C/$^{13}$C ratios like SiC A+B grains. Most graphite grains have close-to-solar nitrogen isotopic ratios (Hoppe et al., 1995; Zinner et al., 1995; Jadhav et al., 2006). In view of the enormous range in carbon isotopic ratios these normal nitrogen ratios cannot be intrinsic and most likely are the result of isotopic equilibration, either on the meteorite parent body or in the laboratory. Apparently, elements such as nitrogen are much more mobile in graphite than in SiC. An exception are graphite grains of low density ($\leq 2.05$ g cm$^{-3}$), which have anomalous nitrogen (Figure 12). Low-density (LD) graphite grains have in general higher trace-element concentrations than those with higher densities and for this reason have been studied for their isotopic compositions in detail (Travaglio et al., 1999; Jadhav et al., 2006). Those with nitrogen anomalies have $^{15}$N excesses (Figure 12). Many LD grains have large $^{18}$O excesses (Amari et al., 1995c; Stadermann et al., 2005a; Jadhav et al., 2006) and high $^{26}$Al/$^{27}$Al ratios that almost reach those of SiC X grains (Figure 12) and are much higher than those of mainstream SiC grains (Figure 5). Oxygen-18 excesses are correlated with $^{12}$C/$^{13}$C ratios. Many low-density grains for which silicon isotopic ratios could be determined with sufficient precision show $^{28}$Si excesses, although large $^{26}$Si and $^{30}$Si excesses are also seen. The similarities of the isotopic signatures with those of SiC X point to a SN origin of LD graphite grains. The $^{18}$O excesses are compatible with such an origin. Helium burning produces $^{18}$O from $^{14}$N, which dominates the CNO isotopes in material that had undergone hydrogen burning via the CNO cycle. As a consequence, the H/C zone in pre-SNII massive stars (see Figure 9), which experienced partial helium burning, has a high $^{18}$O abundance (Woosley and Weaver, 1995). Wolf-Rayet stars during the WN–WC transitions are predicted to also show $^{12}$C, $^{15}$N, and $^{18}$O excesses and high $^{26}$Al/$^{27}$Al ratios (Arnould et al., 1997) but also large excesses in $^{29}$Si and $^{30}$Si and are therefore excluded as the source of LD graphite grains with $^{26}$Si excesses.

There are additional features that indicate a SN origin of LD graphite grains. A few grains show evidence for $^{44}$Ti (Nittler et al., 1996), others have large excesses of $^{41}$K, which must be due to the decay of the radioisotope $^{41}$Ca ($T_{1/2} = 1.05 \times 10^5$ years) (Amari et al., 1996). Inferred $^{41}$Ca/$^{40}$Ca ratios are much higher (0.001–0.01) than those predicted for the envelopes of AGB stars (Wasserburg et al., 1994; Zinner et al., 2006a) but are in the range expected for the carbon- and oxygen-rich zones of type II supernovae, where neutron capture leads to the production of $^{41}$Ca (Woosley and Weaver, 1995). Measurements of calcium isotopic ratios in grains without evidence for $^{44}$Ti show excesses in $^{42}$Ca, $^{43}$Ca, and $^{44}$Ca, with $^{43}$Ca having the largest excess (Amari et al., 1996; Travaglio et al., 1999). This pattern is best explained by neutron capture in the He/C and O/C zones (Figure 9) of type II supernovae. In cases where titanium isotopic ratios have been measured (Amari et al., 1996; Nittler et al., 1996; Travaglio et al., 1999; Stadermann et al., 2005a) they show large excesses in $^{49}$Ti and smaller ones in $^{50}$Ti. This pattern also indicates neutron capture and is well matched by predictions for the He/C zone (Amari et al., 1996). However, large $^{49}$Ti excesses in grains with relatively low (10–100) $^{12}$C/$^{13}$C ratios can only be explained if contributions from the decay of $^{49}$V are considered (Travaglio et al., 1999). Stadermann et al. (2005a) measured oxygen isotopic ratios of individual TiC sub-grains in mictomote slices of a graphite spherule with SN signatures. These grains had variable $^{18}$O excesses that were substantially larger than those in the graphite. Either they formed in a different region of the SN ejecta before accretion onto the growing graphite or they retained their original oxygen isotopic composition.
Figure 12 Nitrogen, oxygen, carbon, and aluminum isotopic ratios measured in individual low-density graphite grains. Also shown are data for presolar Si$_3$N$_4$ and SiC grains of type X. Figure from Zinner (1998a) with additional data from Nittler and Hoppe (2005) and Jadhav et al. (2006).
better than the graphite during partial equilibration with isotopically normal oxygen.

Nicolussi et al. (1998c) have reported RIMS measurements of zirconium and molybdenum isotopic ratios in individual graphite grains from the highest Murchison density fraction (2.15–2.20 g cm$^{-3}$), in which no other isotopic ratios had been measured. Several grains show s-process patterns for zirconium and molybdenum, similar to those exhibited by mainstream SiC grains, although two grains with a distinct s-process pattern for zirconium have normal molybdenum. Two grains have extreme $^{96}$Zr excesses, indicating a SN origin, but the molybdenum isotopes in one are almost normal. Molybdenum, like nitrogen, might have suffered isotopic equilibration in graphite. High-density graphite grains apparently come from AGB stars as previously indicated by the krypton data (Amari et al., 1995b) and from supernovae. It remains to be seen whether LD grains also have multiple stellar sources.

In order to obtain better constraints on theoretical models of SN nucleosynthesis, Travaglio et al. (1999) tried to match the isotopic compositions of LD graphite grains by performing mixing calculations of different type II SN layers (Woosley and Weaver, 1995). While the results reproduce the principal isotopic signatures of the grains, there remain several problems. The models do not produce enough $^{15}$N and yield too low $^{28}$Si/$^{30}$Si ratios. The models also cannot explain the magnitude of $^{26}$Al/$^{27}$Al, especially if SiC X grains are also considered, and give the wrong sign in the correlation of this ratio with the $^{14}$N/$^{15}$N ratio. Furthermore, large neutron-capture effects observed in calcium and titanium can be only achieved in a mix with O $> C$. Clayton et al. (1999) and Deneault et al. (2006) proposed a kinetic condensation model that allows formation of graphite in the high-radiation environment of SN ejecta even when O $> C$, which relaxes the chemical constraint on mixing. However, it remains to be seen whether SiC and Si$_3$N$_4$ can also form under oxidizing conditions. Additional information about the formation environment of presolar graphite is, in principle, provided by the presence of indigenous polycyclic aromatic hydrocarbons (PAHs) (Messenger et al., 1998). PAHs with anomalous carbon ratios show different mass envelopes, which indicate different formation conditions.

Evidence has been mounting that most high-density graphite grains have an origin in low-metallicity AGB stars. High concentrations of the s-process elements zirconium, molybdenum, and ruthenium found in TiC subgrains (Bernatowicz et al., 1996; Croat et al., 2005a, b) agree with the expected and observed large overabundance of these elements in the envelope of AGB stars. Many high-density grains have large $^{28}$Si excesses and these excesses are correlated with high $^{12}$C/$^{13}$C ratios (Amari et al., 2003, 2004a, 2005b; Jadhav et al., 2006). These signatures point to parent stars of low metallicity. Nucleosynthesis models of AGB stars predict $^{28}$Si/$^{30}$Si and $^{12}$C/$^{13}$C ratios in such stars to be much higher than in stars of solar metallicity (Zinner et al., 2006). These models also predict high C/O ratios. Under these conditions graphite is expected to condense before SiC (Lodders and Fegley, 1997) and this is the likely reason that SiC grains with the C and Si isotopic compositions of high-density graphite grains are not found.

A few graphite grains appear to come from novae. Laser extraction GMS of single grains show that, like SiC grains, only a small fraction contains evidence for Ne-E. Two of these grains have $^{20}$Ne/$^{22}$Ne ratios that are lower than ratios predicted to result from helium burning in any known stellar sources, implying decay of $^{22}$Na (Nichols et al., 1995). Furthermore, their $^{22}$Ne is not accompanied by $^4$He, expected if neon was implanted. The $^{12}$C/$^{13}$C ratios of these two grains are 4 and 10, in the range of SiC grains with a putative nova origin. Another graphite grain with $^{12}$C/$^{13}$C = 8.5 has a large $^{28}$Si excess of 760‰ (Amari et al., 2001a).

In summary, low-density graphite grains seem to have a SN origin and most high-density graphite an origin in low-metallicity AGB stars. However, the apparent isotopic equilibration of elements such as nitrogen and oxygen and the generally low abundance of trace elements in many cases makes it difficult to obtain enough diagnostic isotopic signatures to unambiguously identify the parent stars of presolar graphite grains.

### 1.02.9 OXYGEN-RICH GRAINS

#### 1.02.9.1 Oxide Grains

In contrast to the carbonaceous presolar phases, presolar oxide grains apparently do not carry any “exotic” noble gas component. They have been identified by ion microprobe oxygen isotopic measurements of single grains from acid residues free of silicates. In contrast to SiC, essentially all of which is of presolar origin, most oxide grains found in meteorites formed in the solar system and only a small fraction is presolar. The oxygen isotopic compositions of the most abundant presolar oxide minerals are plotted in Figure 13a. They
include 219 corundum grains (Huss et al., 1994; Hutcheon et al., 1994; Nittler et al., 1994, 1997, 1998, 2001, 2005a; Nittler and Alexander, 1999; Strebel et al., 1996; Choi et al., 1998, 1999; Krestina et al., 2002), 57 spinel grains (Nittler et al., 1997, 2001, 2003, 2005a; Choi et al., 1998; Zinner et al., 2003b, 2005b), and 26 hibonite grains (Choi et al., 1999; Krestina et al., 2002; Nittler et al., 2005a). (The identification of minerals is based entirely on their elemental compositions. TEM analysis of presolar Al₂O₃ (Stroud et al., 2004a) has shown that it occurs in both crystalline and amorphous form.) In addition, five presolar chromite grains (Nittler et al., 2005b) and three presolar titanium oxide grains (Nittler and Alexander, 1999; Nittler et al., 2005a) have been identified.

These numbers, however, cannot be used to infer relative abundances of these mineral phases. Analyses were made on grains of different size with instruments having different spatial resolution and sensitivity. Furthermore, searches for presolar oxide grains have been made in different types of residues, some containing spinel, others not. Another complication is that more than half of all presolar corundum grains have been found by automatic direct ¹⁸O/¹⁶O imaging searches in the ion microprobe (Nittler et al., 1997), a method that does not detect grains with anomalies in the ¹⁷O/¹⁶O ratio but with close-to-normal ¹⁸O/¹⁶O. The oxygen isotopic distribution of corundum in Figure 13a therefore does not reflect the true distribution. Figure 13a does not include sub-micrometer oxide grains that were found by NanoSIMS oxygen isotopic raster imaging of tightly packed grain separates or polished sections (Nguyen et al., 2003; Nguyen and Zinner, 2004; Mostefaoui and Hoppe, 2004). Because of beam overlap onto adjacent, isotopically normal grains, the oxygen isotopic ratios of small grains analyzed in this way are diluted. Raster imaging of small grains from the Murray CM2 chondrite led to the identification of 252 presolar spinel and 32 presolar corundum grains (Nguyen et al., 2003). Additional small oxide grains have been detected during imaging searches for presolar silicates (Nguyen and Zinner, 2004; Nagashima et al., 2004; Mostefaoui and Hoppe, 2004; Stadermann and Floss, 2004; Nguyen, 2005). The abundance of presolar oxide grains varies greatly from meteorite to meteorite. The highest abundances have been found in the most primitive meteorites, in the ungrouped carbonaceous chondrite Acfer 094 (~110 ppm) and the CO3 chondrite ALH 77037 (~80 ppm) (Mostefaoui and Hoppe, 2004; Nguyen, 2005; Vollmer et al., 2006). This contrasts with an abundance of only 1.2 ppm for spinel and ~0.15 ppm for corundum in the CM2 meteorite Murray (Zinner et al., 2003b) and upper limits of a few parts per million in ordinary chondrites (Mostefaoui et al., 2003, 2004; Tonotani et al., 2006).

Nittler et al. (1997) have classified presolar oxide grains into four different groups according to their oxygen isotopic ratios. Grains with ¹⁷O/¹⁶O > solar (3.82 x 10⁻⁵) and
$0.001 < {^{18}\text{O}}/{^{16}\text{O}} < \text{solar}$ (2.01 $\times$ 10$^{-3}$), comprising group 1, have oxygen isotopic ratios similar to those observed in RG and AGB stars (Harris and Lambert, 1984; Harris et al., 1987; Smith and Lambert, 1990), indicating such an origin also for the grains. These compositions can be explained by hydrogen burning in the core of low-to-intermediate-mass stars followed by mixing of core material into the envelope during the first dredge-up (also second dredge-up in low-metallicity stars with $M > 3M_\odot$) (Boothroyd et al., 1994; Boothroyd and Sackmann, 1999). Variations in $^{17}\text{O}/^{16}\text{O}$ ratios mainly correspond to differences in stellar mass while those in $^{18}\text{O}/^{16}\text{O}$ can be explained by assuming that stars with different metallicities contributed oxide grains to the solar system. According to galactic chemical evolution models, $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios are expected to increase as a function of stellar metallicity (Timmes et al., 1995). Grains with depletions in both $^{17}\text{O}$ and $^{18}\text{O}$ (group 3) could thus come from low-mass stars (producing only small $^{17}\text{O}$ enrichments) with lower-than-solar metallicity (originally having lower-than-solar $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios). The oxygen isotopic ratios of group 3 grains have been used to obtain an estimate of the age of the galaxy (Nittler and Cowsik, 1997). Group 2 grains have $^{17}\text{O}$ excesses and large $^{18}\text{O}$ depletions ($^{18}\text{O}/^{16}\text{O} < 0.001$). Such depletions cannot be produced by the first and second dredge-up but have been successfully explained by an extra mixing mechanism (cool bottom processing) of low-mass ($M < 1.65M_\odot$) stars during the AGB phase that circulates material from the envelope through hot regions close to the hydrogen-burning shell (Wasserburg et al., 1995; Denissenkov and Weiss, 1996; Nollett et al., 2003). Group 4 grains have both $^{17}\text{O}$ and $^{18}\text{O}$ excesses. If they originated from AGB stars they could either come from low-mass stars, in which $^{18}\text{O}$ produced by helium burning of $^{14}\text{N}$ during early pulses was mixed into the envelope by third dredge-up (Boothroyd and Sackmann, 1988) or from stars with high metallicity. More likely for the grains with the largest $^{18}\text{O}$ excesses is a SN origin as suggested by Choi et al. (1998) if $^{18}\text{O}$-rich material from the He/C zone can be admixed to material from oxygen-rich zones.

There is only one grain that has the typical isotopic signature expected for SN condensates, namely a large $^{16}\text{O}$ excess (labeled SN in Figure 13a) (Nittler et al., 1998). All oxygen-rich zones (O/C, O/Ne, and O/Si—see Figure 9) are dominated by $^{16}\text{O}$ (Woosley and Weaver, 1995; Thielemann et al., 1996; Rauscher et al., 2002). The paucity of such grains, whose abundance is expected to dominate that of carbonaceous phases with a SN origin, remains an unsolved mystery. It has been suggested that oxide grains from supernovae are smaller than those from RG stars but recent measurements of submicron grains have not uncovered any additional oxides with large $^{16}\text{O}$ excesses (Zinner et al., 2003b; Nguyen et al., 2003; Mostefaoui and Hoppe, 2004; Nguyen, 2005; Vollmer et al., 2006). Two corundum grains with high $^{17}\text{O}/^{16}\text{O}$ and low $^{18}\text{O}/^{16}\text{O}$ ratios do not fit into the four groups. These grains could come from stars with $\geq 5M_\odot$ that experienced hot bottom burning, a condition during which the convective envelope extends into the hydrogen-burning shell (Boothroyd et al., 1995; Lattanzio et al., 1997).

Some but not all grains in the four groups show evidence for initial $^{26}\text{Al}$ (Figure 14) (Nittler et al., 1997, 2005a; Choi et al., 1998, 1999; Krestita et al., 2002; Zinner et al., 2003b, 2006a). Aluminum-26 is produced in the hydrogen-burning shell (Forestini et al., 1991), and dredge-up of material during the TP AGB phase is required. Thus grains without $^{26}\text{Al}$ must have formed before their parent stars reached this evolutionary stage. However, shell hydrogen burning can account only for $^{26}\text{Al}/^{27}\text{Al}$ ratios of up to $\sim 3 \times 10^{-3}$ (Forestini et al., 1991; Mowlavi and Meynet, 2000; Karakas and Lattanzio, 2003) and cool bottom processing has to be invoked for grains with higher ratios (Nollett et al., 2003). Although group 2 grains generally have higher $^{26}\text{Al}/^{27}\text{Al}$ ratios there is no simple correlation between $^{26}\text{Al}/^{27}\text{Al}$ and $^{18}\text{O}/^{16}\text{O}$ ratios. This is not surprising, because in the theory of cool bottom

![Figure 14](https://example.com/figure14.png) **Figure 14** Inferred aluminum isotopic ratios in presolar oxide grains are plotted against their oxygen isotopic ratios. Data are from Nittler et al. (1997, 2005a), Choi et al. (1998, 1999), Nguyen and Zinner (2004), and Zinner et al. (2005b, 2006a).
processing by Nollett et al. (2003) the two parameters (maximum temperature and circulation rate) affecting these ratios are almost completely decoupled. It should be noted that most SiC grains from AGB stars (mainstream, Y, and Z grains) have $^{26}\text{Al}/^{27}\text{Al}$ ratios that agree with models of shell hydrogen burning in AGB stars (see Figure 5). Carbon stars, the parent stars of SiC, follow oxygen-rich stars, the parents of oxide grains, in their evolutionary sequence. It could be that cool bottom processing, which is responsible for the high $^{26}\text{Al}/^{27}\text{Al}$ ratios in oxide grains, prevents oxygen-rich stars from becoming carbon stars.

Titanium isotopic ratios have been determined in presolar corundum, hibonite, and titanium oxide grains (Choi et al., 1998; Nittler et al., 2005a). Isotopic patterns vary from a V-shaped pattern with excesses in all titanium isotopes relative to $^{48}\text{Ti}$ to the inverse of it. The observed $^{58}\text{Ti}$ excesses agree with those predicted to result from neutron capture in AGB stars. The range of patterns indicates that, just as for SiC grains, galactic evolution affects the isotopic compositions of the parent stars of oxide grains. The identification of presolar hibonite grains (Choi et al., 1999; Krestina et al., 2002; Nittler et al., 2005a) provides the opportunity to measure calcium isotopic ratios and to look for $^{44}\text{K}$ excesses from $^{41}\text{Ca}$ decay. Inferred $^{43}\text{Ca}/^{40}\text{Ca}$ ratios range up to $2 \times 10^{-4}$ (Choi et al., 1999; Nittler et al., 2005a; Zinner et al., 2006a), within the range of values predicted for the envelope of AGB stars (Wasserburg et al., 1994; Zinner et al., 2006a). One grain has a ratio of $4.3 \times 10^{-4}$, but other isotopic signatures indicate that it has a SN origin.

1.02.9.2 Silicate Grains

Several attempts to identify presolar silicates in primitive meteorites have been unsuccessful (Nittler et al., 1997; Messenger and Bernatowicz, 2000). This situation has changed with the advent of the NanoSIMS and its capability of analyzing a large number (tens of thousands) of sub-micrometer grains for their oxygen isotopic compositions by raster imaging (Nguyen et al., 2003). This capability has also been achieved with the Cameca IMS 1270 equipped with a SCAPS (stacked CMOS-type active pixel sensor) device (Yurimoto et al., 2003), which allows direct imaging of the sample surface in a given isotope with high sensitivity. The first method has better spatial resolution and thus a higher detection efficiency of anomalous grains as fraction of all analyzed grains. The second method makes it possible to analyze a larger area in a given time but has lower spatial resolution, which leads to a lower detection efficiency and greater dilution of the isotopic ratios by contributions from adjacent grains than is the case for NanoSIMS analysis.

The first presolar silicates were discovered in IDPs (Messenger et al., 2003), followed by the discovery of presolar silicates in meteorites (Nguyen and Zinner, 2004; Nagashima et al., 2004; Mostefaoui and Hoppe, 2004) and Antarctic micrometeorites (AMMs) (Yada et al., 2005, 2006). With a few exceptions (ranging up to 1 μm), these grains are smaller than 0.5 μm in size. As of early 2006, close to 200 presolar silicates have been identified in IDPs (Messenger et al., 2003, 2005; Floss et al., 2006), meteorites (Nguyen and Zinner, 2004; Mostefaoui et al., 2004; Mostefaoui and Hoppe, 2004; Nagashima et al., 2004, 2005; Nguyen 2005; Kobayashi et al., 2005; Ebata et al., 2006; Mathas et al., 2006b; Tonotani et al., 2006; Vollmer et al., 2006), and AMMs (Yada et al., 2005, 2006). Figure 13b shows the oxygen isotopic ratios of presolar silicates analyzed in the NanoSIMS. A comparison with the oxygen isotopic ratios of presolar oxide grains (Figure 13a) shows that, on average, the isotopic compositions of the silicate grains are closer to normal. The reason for this difference is most probably the fact that the silicate grains are small and were analyzed in polished section or tightly packed grain separates where the overlap of the primary Cs$^+$ onto adjacent grains diluted the isotopic compositions. This effect has been demonstrated during the separated-grain and raster imaging analysis of small presolar spinel grains (Nguyen et al., 2003). As a consequence, the anomalies in the grains plotted in Figure 13b should be considered lower limits. Isotopic dilution effects are even larger for silicate grains identified by SCAPS analysis. In spite of this limitation, the isotopic analysis of presolar silicates yielded some interesting results. Three grains, one from an IDPs and two from Acfer 094, have $^{18}\text{O}/^{16}\text{O}$ ratios that are larger than any found in oxide grains (see Figure 13). The grain from the IDP has also a large depletion in $^{17}\text{O}$. This composition can be interpreted as a large $^{18}\text{O}$ and an even larger $^{18}\text{O}$ excess and has been considered to be the signature of a SN origin (Messenger et al., 2005). The two $^{18}\text{O}$-rich grains from Acfer 094 (Mostefaoui and Hoppe, 2004; Stadermann et al., 2005b) probably have a SN origin as well.

Uncertainties in the detection efficiency of small anomalous grains in thin section or tightly packed aggregates affect estimates of the abundances of presolar silicates in various extraterrestrial objects. Nguyen (2005) assumed a detection efficiency of 50% in her NanoSIMS analyses and arrived at an abundance of...
180 ppm in Acfer 094 and of 140 ppm in ALH 77037. Mostefaoui and Hoppe (2004) and VOLLMER et al. (2006) arrive at similar estimates for Acfer 094. The efficiency of 50% used by Nguyen was derived from raster imaging analysis of Murray spinel grains whose average diameter is 0.45 μm (Nguyen et al., 2003). However, most presolar silicates are smaller, which makes the above abundance estimates lower limits. Because of limited statistics and because the detection efficiency of SCAPS analysis is essentially unknown, abundance estimates for other meteorites are even more uncertain. With the possible exception of the ungrouped carbonaceous chondrite Adelaide (KOBAYASHI et al., 2005) and the CO3 chondrite Y-81025 (KOBAYASHI et al., 2005; MARHAS et al., 2006b), presolar silicate abundances are lower in the other meteorites that have been analyzed. Abundances in group 3 ordinary chondrites are on the order 20–30 ppm and are probably smaller in the C2 carbonaceous chondrites Murchison (CM2) and Tagish Lake (CI2) (NAGASHIMA et al., 2005; MARHAS et al., 2006b). Abundance estimates are ~375 ppm for a class of primitive IDPs (FLOSS et al., 2006) and ~50 ppm for AMMs (YADA et al., 2006). Because these authors make no corrections for the detection efficiency, these values are strictly lower limits.

Attempts to determine the mineralogy of presolar silicates have been made difficult by the small size of these grains. X-ray analysis in the SEM or electron microprobe suffers from the problem that the volume excited by the electron beam is usually larger than that of the grains and X-rays are thus also obtained from adjacent or underlying grains (NGUYEN and ZINNER, 2004). In Auger spectroscopy the signal (Auger electrons) is obtained only from the first few atomic layers and this method appears to be better suited to the determination of the elemental composition of sub-micrometer grains (FLOSS et al., 2005; STADERMANN et al., 2005c). The method of choice is analytical transmission electron microscopy because it allows the determination of the grains’ crystalline structure via electron diffraction analysis, but the preparation of samples is very labor intensive (MESSINGER et al., 2003, 2005; NGUYEN et al., 2005). Based on different analytical methods, the identification of olivine, pyroxene, and GEMS as well as nonstoichiometric amorphous grains has been claimed among presolar silicates (MESSINGER et al., 2003, 2005; NGUYEN and ZINNER, 2004; NAGASHIMA et al., 2004; MOSTEFAOUI et al., 2004; NGUYEN et al., 2005). However, only TEM analysis can provide unambiguous mineral identification (MESSINGER et al., 2003, 2005; NGUYEN et al., 2005). While astronomical observations indicate that circumstellar dust around evolved stars is magnesium-rich (e.g., WATERS et al., 1996; DEMYK et al., 2000; MOLSTER and WATERS, 2003), many presolar silicates are surprisingly iron-rich (NGUYEN and ZINNER, 2004; FLOSS et al., 2005; MESSENGER et al., 2005; NGUYEN et al., 2005).

Silicon isotopic ratios have been measured in 20 presolar silicates from Acfer 094 and an IDP (MOSTEFAOUI and HOPPE, 2004; NGUYEN et al., 2005; MESSENGER et al., 2005). In a silicon three-isotope diagram the measured ratios plot on a line parallel to the mainstream line of presolar SiC grains (see Figure 4) that goes approximately through the origin (normal isotopic composition). The silicate grains’ compositions most likely reflect the initial compositions of the parent stars because during the oxygen-rich phase of RG and AGB stars not enough material that experienced neutron-capture nucleosynthesis is mixed into the envelope by the third dredge-up to change its silicon isotopic composition. An exception is the grain in the IDP that was identified to have a SN origin (MESSENGER et al., 2005). It has a large 26Si depletion, in agreement with such an origin. NGUYEN and ZINNER (2004) measured the magnesium isotopic ratios of one silicate grain, identified as a group 2 grain according to its oxygen isotopic composition (Figure 13), and found a 26Mg excess of 12% and an inferred 26Al/27Al ratio of 0.12. This ratio is second only to that of one corundum grain (Figure 14). Such a high ratio implies cool bottom processing at a temperature of almost $6 \times 10^7$ K.

1.02.10 DIAMOND

Although diamond is the most abundant presolar grain species (~1,400 ppm) and was the first to be isolated (LEWIS et al., 1987), it remains the least understood. The only presolar isotopic signatures (indicating a SN origin) are those of Xe-HL and tellurium (Richter et al., 1998), to a marginal extent also those of strontium and barium (LEWIS et al., 1991). However, the carbon isotopic composition of bulk diamonds is essentially the same as that of the solar system (RUSSELL et al., 1991, 1996) and diamonds are too small (the average size is ~2.6 nm—hence nanodiamonds) to be analyzed as single grains. At present, it is not known whether or not this normal carbon isotopic composition is the result of averaging over grains that have large carbon isotopic anomalies, and whether all nanodiamonds are of presolar origin. Nitrogen shows a 15N depletion of 343% but isotopically light nitrogen is produced by the CN cycle in all stars and is therefore not very diagnostic. More recent
measurements have shown that the nitrogen isotopic ratio of Jupiter (Owen et al., 2001) is very similar to that of the nanodiamonds, which therefore is not necessarily a presolar signature. Furthermore, the concentration of Xe-HL is such that only one diamond grain in a million contains a xenon atom. To date, all attempts to separate different, isotopically distinct, components among nanodiamonds have met with only limited success. Stepped pyrolysis indicates that nitrogen and the noble gas components Xe-HL and Ar-HL are decoupled, with nitrogen being released at lower temperature (Verchovsky et al., 1993a, b) and it is likely that nitrogen and the exotic gases are located in different carriers. A solar origin of a large fraction of the nanodiamonds remains a distinct possibility (Dai et al., 2002).

The light and heavy isotope enrichment in Xe-HL has been interpreted as being due to the p- and r-processes, and thus requires a SN origin (Heymann and Dziczkaniec, 1979, 1980; Clayton, 1989). In one model Xe-H is made by a short neutron burst, with neutron densities intermediate between those characteristic for the r- and s-processes (Clayton, 1989; Howard et al., 1992). Ott (1996) kept the standard r-process but proposed that xenon is separated from iodine and tellurium precursors on a time scale of a few hours after their production. Measurements of tellurium isotopes in nanodiamonds show almost complete absence of the isotopes $^{120}\text{Te}$, $^{122-126}\text{Te}$, and a slight excess of $^{128}\text{Te}$ relative to $^{130}\text{Te}$ (Richter et al., 1998). This pattern agrees much better with a standard r-process and early element separation than with the neutron burst model. Clayton and co-workers (Clayton, 1989; Clayton et al., 1995) have tried to attribute also the diamonds and their carbon and nitrogen isotopic compositions to a type II supernova. This requires mixing of contributions from different SN zones. In contrast, Jørgensen (1988) proposed that diamond and Xe-HL were produced by different members of a binary system of low-mass (1–2$M_\odot$) stars, diamond in the winds of one member, a carbon star, while Xe-HL by the other, which exploded as a type Ia supernova. However, at present we do not have an unambiguous identification of the origin of the Xe-HL and tellurium, and of the diamonds (in case they have a different origin).

1.02.11 CONCLUSION AND FUTURE PROSPECTS

The study of presolar grains has provided a wealth of information on galactic evolution, stellar nucleosynthesis, physical properties of stellar atmospheres, and conditions in the solar nebula and on meteoritic parent bodies. However, there are still many features that are not well understood with existing models of nucleosynthesis and stellar evolution and stellar structure. Examples are the carbon and nitrogen isotopic compositions of SiC A+B grains, $^{15}\text{N}$ and $^{29}\text{Si}$ excesses in SN grains, and the paucity of oxide grains from supernovae. The grain data, especially correlated isotopic ratios of many elements, thus provide a challenge to nuclear astrophysics in tightening constraints on theoretical models.

Continuing instrumental developments allow us to make new and more measurements on the grains and likely lead to new discoveries. For example, the NanoSIMS features high spatial resolution and sensitivity, making isotopic analysis of small grains possible, and this capability has already resulted in the discovery of presolar silicate grains in IDPs, meteorites, and AMMs (Messenger et al., 2003; Nguyen and Zinner, 2004; Nagashima et al., 2004; Mostefaoui and Hoppe, 2004; Yada et al., 2006) and the identification of a large number of presolar spinel grains (Zinner et al., 2003b; Nguyen et al., 2003). The NanoSIMS also makes it possible to analyze internal grains that have been studied in detail in the TEM (Stadermann et al., 2005a). Another example is the application of RIMS to grain studies. As the number of elements that can be analyzed is being expanded (e.g., to the rare-earth elements), unexpected discoveries such as the molybdenum isotopic patterns in SiC X grains (Pellin et al., 1999) will probably result. RIMS measurements can also be made on grains, such as SiC and graphite, for which the isotopic ratios of many elements are measured with the ion microprobe. Recently, ICP-MS has been added to the arsenal of analytical instruments applied to the analysis of presolar grains (Yin et al., 2006).

It is clear that the discovery of presolar grains and their detailed study in the laboratory have opened a new and fruitful field of astrophysical research. In our effort to understand the distant stars the microscope successfully complements the telescope.

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