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ASTROPHYSICS WITH PRESOLAR STARDUST

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■ **Abstract** Meteorites and interplanetary dust particles contain presolar stardust grains: solid samples of stars that can be studied in the laboratory. The stellar origin of the grains is indicated by enormous isotopic ratio variations compared with Solar System materials, explainable only by nuclear reactions occurring in stars. Known presolar phases include diamond, SiC, graphite, Si_3N_4, Al_2O_3, $MgAl_2O_4$, $CaAl_{12}O_{19}$, TiO_2, $Mg(Cr,Al)_2O_4$, and most recently, silicates. Subgrains of refractory carbides (e.g., TiC), and Fe-Ni metal have also been observed within individual presolar graphite grains. We review the astrophysical implications of these grains for the sciences of nucleosynthesis, stellar evolution, grain condensation, and the chemical and dynamic evolution of the Galaxy. Unique scientific information derives primarily from the high precision (in some cases $<1\%$) of the measured isotopic ratios of large numbers of elements in single stardust grains. Stardust science is just now reaching maturity and will play an increasingly important role in nucleosynthesis applications.

1. INTRODUCTION

Presolar grains of stardust are solid samples of stars that can be studied in terrestrial laboratories. They condensed during cooling of gases in ancient stellar outflows and became part of the interstellar medium (ISM) from which our Solar System formed some 4.6 billion years ago. These grains survived destruction processes in the ISM and early Solar System and have survived to this day trapped in asteroids and comets. They are now identified as minor or trace constituents of asteroidal and cometary samples collected on the earth in the form of primitive meteorites and interplanetary dust particles. The word "stardust" distinguishes these grains from the much larger mass of interstellar dust that formed in other ways. Although stardust grains are rare, the ability to study bona fide stellar materials in the laboratory has opened new scientific frontiers in astrophysics.

Presolar grains are recognized as such by their highly unusual isotopic compositions relative to all other materials available for laboratory study. Their isotopic variations, in essentially every element that they contain, can span several orders of magnitude, much too large to be explained by chemical or physical fractionation processes. Rather, most of the observed variations clearly point to nuclear reactions that occur in stars, and it is believed that individual grains are indeed essentially pure samples of individual stars. It may strain credibility that a presolar stardust grain is indeed composed only of atoms from the single donor star despite the lengthy residence time of the grains within the ISM prior to their incorporation into the solar accretion disk. Do not high-energy interstellar ions implant within the grains as well as sputter them? Can interstellar chemistry add more atoms to the mineralized grains? What about grain ejection from a protostellar disk after chemically adding to it within the hot dense disk structure? Such doubts are reasonable considering the incomplete knowledge of these and other processes.

The grains themselves provide the best answers. They largely consist of high-temperature minerals with well-ordered crystal structures, consistent with expectations for condensation within cooling gases but not for low-temperature accretion within the ISM. The dramatic isotopic ratios within individual stardust grains, obtained as they are from their nearly homogeneous samples of large numbers of atoms (10^6 to 10^{12}, for instance), strongly suggests that the condensation was from a gas having that isotopic composition. For example, presolar SiC grains, the best-studied presolar grain type, were assembled from C atoms having observed isotopic ratios between $^{12}C/^{13}C = 3$ to 5000 (e.g., Hoppe & Ott 1997), whereas hot chemistry in an accretion disk would rapidly shift ratios toward interstellar norms, $^{12}C/^{13}C = 89$ in the case of the solar accretion disk. Similar evidence appears in isotopic compositions of N, and Si, to name the most studied elements. Similarly, presolar oxide Al_2O_3 grains (e.g., Nittler et al. 1997) exhibit four orders of magnitude variation in their O isotope ratios, ruling out any growth within a mixed ISM. Even more stunning is the almost pure isolated s-process compositions found in presolar SiC and graphite grains (Lugaro et al. 2003a; Nicolussi et al. 1997, 1998c; Srinivasan & Anders 1978). Such evidence abounds in the sections of this review to follow. It is only by careful consideration of the entirety of the known properties of grains that one becomes confident that they are indeed solid samples of presolar stars.

Quite a large literature exists documenting the discovery of presolar stardust and their scientific consequences, including recent reviews by Zinner (1998) and Nittler (2003). A comprehensive discussion of the astrophysical implications of presolar grains is beyond the scope of any reasonably sized review paper (see Bernatowicz & Zinner 1997 for a review volume). Our purpose here is to provide an overview of the field from the points of view of both a theorist and an observer and to indicate the types of arguments and conclusions that presolar grains have uniquely brought to astrophysics. We cite key papers on the way, but the reader is also referred to the above cited reviews and to the current literature for many more details.

2. STARDUST IDENTIFICATION AND ANALYSIS

Presolar diamonds and SiC were first isolated in 1987 (Bernatowicz et al. 1987, Lewis et al. 1987, Zinner et al. 1987), following some two decades of attempts to identify the mineral carriers of isotopically anomalous noble gases measured in bulk meteorites. The history of this long road to discovery is described in some detail by Anders & Zinner (1993). Most stardust grains have been found in residues of extensive acid dissolution of bulk meteorites, a process often likened to burning a haystack to find a hidden needle. SiC grains have also been found in situ in polished sections of meteorites using electron microscopic techniques (Alexander et al. 1990b), but this required a priori knowledge of the existence of the grains from work with acid residues. The standard chemical treatments certainly introduce a selection bias in the data set; acid-soluble presolar phases (e.g., silicate minerals) are dissolved along with the host meteorites. Recently, new chemical techniques and instrumentation have allowed identification of new presolar minerals that would be destroyed in the traditional dissolution techniques (Messenger et al. 2003, Nittler & Alexander 2003b).

The full scientific exploitation of presolar grains is only made possible by the development of advanced instrumentation for chemical, isotopic, and mineralogical microanalysis of very small samples. Of all these stardust telescopes, perhaps the most important technique has been secondary ion mass spectrometry (SIMS) in which a solid sample is bombarded by a finely focused beam of ~20 keV ions. Sputtered ions from the sample are transported through a mass spectrometer that determines their masses using electric and magnetic fields. The high sensitivity of SIMS allows for isotopic measurements of many major and minor elements in individual tiny dust grains. Until recently, the practical lower limit for individual grain measurements was $\sim 1\ \mu$m. A new generation SIMS instrument, the NanoSIMS (manufactured by Cameca Instruments, France), allows measurements of smaller samples (down to $\sim 0.1\ \mu$m) with higher sensitivity than that of previous devices. The development of the NanoSIMS has opened a new door on presolar grain studies, enabling both new sorts of studies (Messenger et al. 2003, Stadermann et al. 2003) and the analysis of more astrophysically typical grain sizes (e.g., Zinner et al. 2003b).

Another relatively recent analytical technique providing exciting results in presolar grain studies is resonance ionization mass spectrometry, or RIMS (Nicolussi et al. 1997, Savina et al. 2003c). In RIMS, material is desorbed from samples using a laser beam. A tunable laser is used to resonantly ionize a specific element of interest in the desorbed plume, which is then analyzed in a mass spectrometer. This technique has allowed for isotopic determination of heavy elements present at trace levels in individual presolar grains, with important astrophysical implications as discussed later in this review. This technique has also been used to selectively ionize and characterize polycyclic aromatic hydrocarbon molecules from individual presolar grains (Messenger et al. 1998).

Mineralogical and microstructural investigations of presolar grains have also provided new information about the stellar sources of the grains. Scanning electron microscopy (see Figure 1) is routinely used to characterize surface morphology and bulk elemental makeup of grains. Transmission electron microscopy (TEM) is used to characterize crystal structures and defects on a nanometer scale and to search for subgrains within individual stardust grains. TEM requires very thin samples (<100 nm) and large grains are sliced using either a diamond knife attached to

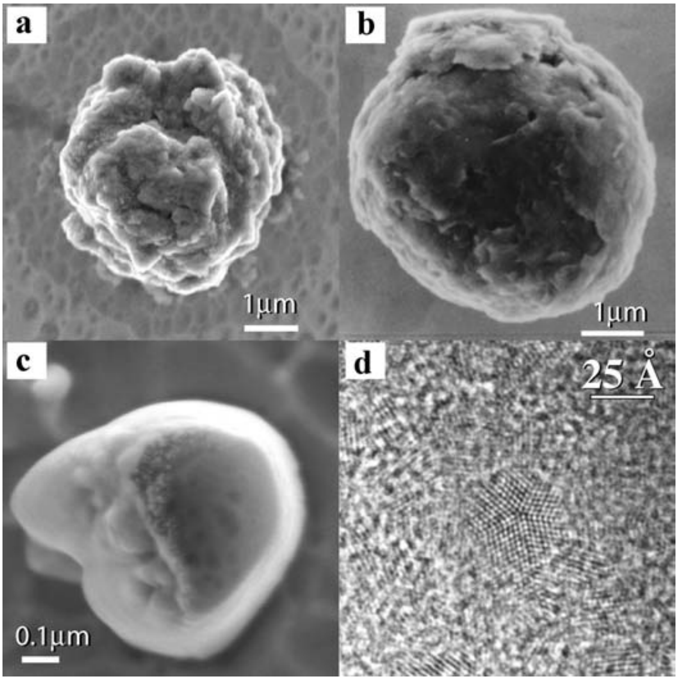

Figure 1 (*a*) Scanning electron (SE) micrograph of 3 μm presolar SiC grain (courtesy R. Stroud). (*b*) SE image of 5 μm presolar graphite grain (courtesy S. Amari). (*c*) SE image of 0.5 μm presolar Al_2O_3 grain. (*d*) High-resolution transmission electron microscope image of presolar nanodiamonds (courtesy T. Daulton).

an ultramicrotome (Bernatowicz et al. 1996) or ion beam techniques (Stroud et al. 2002b).

Additional laboratory techniques that have been applied to presolar grains include laser-ablation noble gas mass spectrometry (Nichols et al. 1992), thermal ionization mass spectrometry (Prombo et al. 1993, Richter et al. 1998), laser Raman spectroscopy (Virag et al. 1992, Zinner et al. 1995), time-of-flight SIMS (Fahey & Messenger 2001, Stephan 2001), and various other spectroscopies (e.g., Braatz et al. 2000).

3. TYPES OF PRESOLAR STARDUST

Basic properties of the known types of presolar stardust are described in this section. Example electron micrographs of some of these are shown in Figure 1. In the following sections, we shall discuss in more detail some of the astrophysical consequences of the grains, focusing on specific types of stellar sources.

Silicon carbide (*SiC*) is the best-studied type of presolar grain (Hoppe & Ott 1997). Grain sizes range from ~0.1 μm up to more than 20 μm, and its abundance in meteorites is roughly 10 ppm. Isotopic measurements of both single grains and aggregates of many grains have revealed highly anomalous isotopic compositions, relative to solar, in essentially every major, minor, and trace element, including C, Si, N, Mg, Ca, Ti, Ne, Xe, Kr, Ba, Nd, Sr, Sm, Dy, Mo, Zr, and Ru. The distributions of Si, C, and N isotopes in individual presolar SiC grains are shown in Figures 2 and 3. A significant fraction of the grains also contain elevated $^{26}Mg/^{24}Mg$ ratios, indicating that they contained live radioactive ^{26}Al (half-life = 720,000 years) when they formed, which subsequently decayed in situ to ^{26}Mg. Note that Si, C, and N form a four-dimensional isotopic space, within which each grain occupies a unique position. This space is mostly empty, but filled volumes enable identification of clustered grains and isotopic trends. Isotopically related grains form the basis of a classification system, illustrated by the different symbols on Figures 2 and 3. The significance of such classification systems for extracting useful scientific information from stardust grains can be likened to the significance of stars of

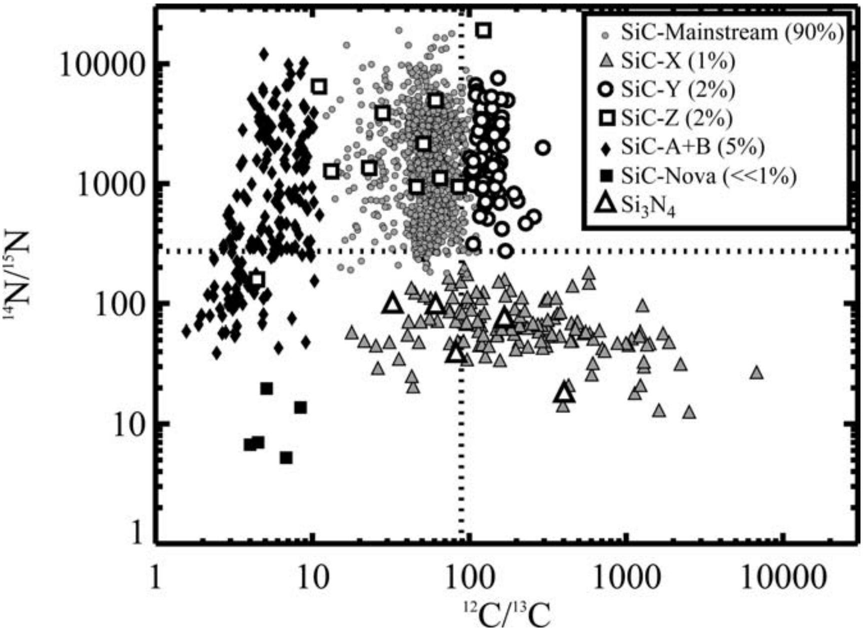

Figure 2 C and N isotopic ratios measured in individual presolar SiC and Si_3N_4 grains (Hoppe & Ott 1997 and references therein; Hoppe et al. 2000, Huss et al. 1997, Nittler et al. 1995). Dotted lines indicate the terrestrial isotope ratios here and in subsequent figures. Different symbols indicate a classification system developed for SiC grains based on multiple isotopic ratios. Percentages indicate fraction of total SiC grains found in meteorites (>0.5 μm).

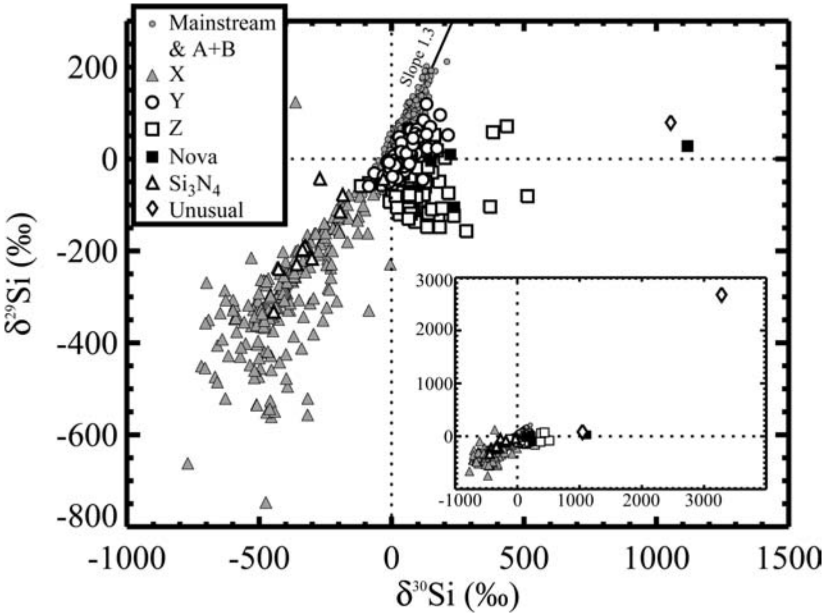

Figure 3 Silicon isotopic ratios of presolar SiC and Si_3N_4 grains in meteorites, expressed as delta values: $\delta^{i}Si = 10^3 \times [(^{i}Si/^{28}Si)_{grain}/(^{i}Si/^{28}Si)_{Sun} - 1]$ (Data from Amari et al. 1999, 2001a,b,c; Hoppe & Ott 1997; Hoppe et al. 1997; Nitter & Alexander 2003a; Nittler et al. 1995). The grains have been divided into subgroups on the basis of their Si, C, and N isotopic ratios; 90% of meteoritic SiC grains belong to the mainstream group. The mainstream grains form a line with slope 1.3.

spectral types and the Hertzprung-Russell diagram. Below, we show that various stellar parents can be assigned to the different grain groups on the basis of the details of the nucleosynthesis processes that occur in various stellar types.

The largest family of SiC grains, some 90% of the total, has been termed the mainstream population; the other groups and ungrouped grains make up the remainder. As discussed in greater detail below, mainstream grains are inferred to have formed in C-rich asymptotic giant branch (AGB) stars (see Section 5.1.) and X grains in supernovae (Section 4). Note that the data shown in Figures 2 and 3 were acquired on grains larger than 1 μm, but most circumstellar and interstellar dust is inferred from astronomical measurements to be smaller. Recent NanoSIMS measurements of submicron SiC grains show very similar ranges of Si, C, and N isotope ratios (Amari et al. 2002, Zinner et al. 2003a), indicating that the larger grains for which we have the most information are not atypical in their isotopic compositions. Also, the fraction of X grains is constant at ~1% for a wide range of grain sizes (Hoppe et al. 2000), indicating that AGB stars and supernovae produce closely similar size distributions of SiC grains. This is remarkable, given the likely very different nature of grain formation processes in these environments.

Graphite has similar abundance and grain size to SiC but is less well understood (Amari et al. 1990, 1993; Hoppe et al. 1995). Presolar graphite grains are round and typically larger than 1 μm. They largely fall into one of two morphologies: "onions" (Figure 1*b*) consist of concentric layers of relatively well-graphitized C, whereas "cauliflowers" appear to be aggregates of submicron grains. The $^{12}C/^{13}C$ ratios of presolar graphite grains span a similar range to that observed in SiC, from $\sim$2 to 7000, but the distribution is quite distinct: Most SiC grains have $^{12}C/^{13}C$ ratios lower than solar, whereas a majority of the graphite grains has higher-than-solar $^{12}C/^{13}C$. Like SiC, the graphite grains often contain relatively high concentrations of minor and trace elements, allowing isotopic measurements of several elements to be made on single grains. This is especially true for the $\sim$one-third of presolar graphite grains of relatively low density ($\rho < 2.15$ g cm^{-3}). The isotopic signatures of these grains are in many ways similar to those observed in the rare SiC X grains and, like those, probably originated in supernovae (Section 4) (Amari & Zinner 1997, Travaglio et al. 1999). The higher-density grains are somewhat more ambiguous, mainly because multi-element data are sparser and lower trace-element contents make terrestrial contamination a concern. However, isotopic evidence suggests that these grains originated from a range of stellar environments including AGB stars, supernovae and novae.

TEM studies of individual graphite grains, sliced with a diamond knife, have revealed the common presence of subgrains of refractory carbides (Bernatowicz et al. 1996), including TiC and MoC, as well as Fe-Ni metal (Croat et al. 2003). In some cases, the subgrains clearly formed as nucleation sites for graphite growth and in other cases appear to have been captured by growing graphite grains. Polycyclic aromatic hydrocarbons (PAHs) have been identified within many graphite grains as well, using a laser mass spectrometric technique (Messenger et al. 1998). In some cases, individual PAH molecules have the same C isotopic ratio as the host grain, indicating that they most likely originated during the circumstellar formation of the grain.

In contrast to the thousands of measured individual SiC and graphite grains, only a few hundred presolar *oxides* have been identified to date in meteorites (Choi et al. 1999; Huss et al. 1994; Nittler 1997; Nittler & Alexander 1999a,b; Nittler et al. 1997; Zinner et al. 2003b). The most common types are corundum (Al_2O_3) and spinel ($MgAl_2O_4$), but hibonite ($CaAl_{12}O_{19}$), TiO_2, and $Mg(Cr,Al)_2O_4$ have been reported as well. The difficulty in locating O-rich stardust reflects a large background of isotopically normal oxide grains of Solar System origin in the residues. In fact, most of the known grains were found with the aid of automated and semiautomated microanalysis techniques. O isotopic ratios span several orders of magnitude in the presolar oxide grains (Figure 4), in contrast to the $\sim$10% relative range in these ratios for materials formed in the Solar System. Many of the grains also show evidence for high initial $^{26}Al/^{27}Al$ ratios when they formed and a small number of grains have been analyzed for N, K, Ti, and/or Cr as well. As for SiC, the oxide grains have been classified according to clustering in multidimensional isotope space. Most grains are defined as belonging to one of four groups (labeled

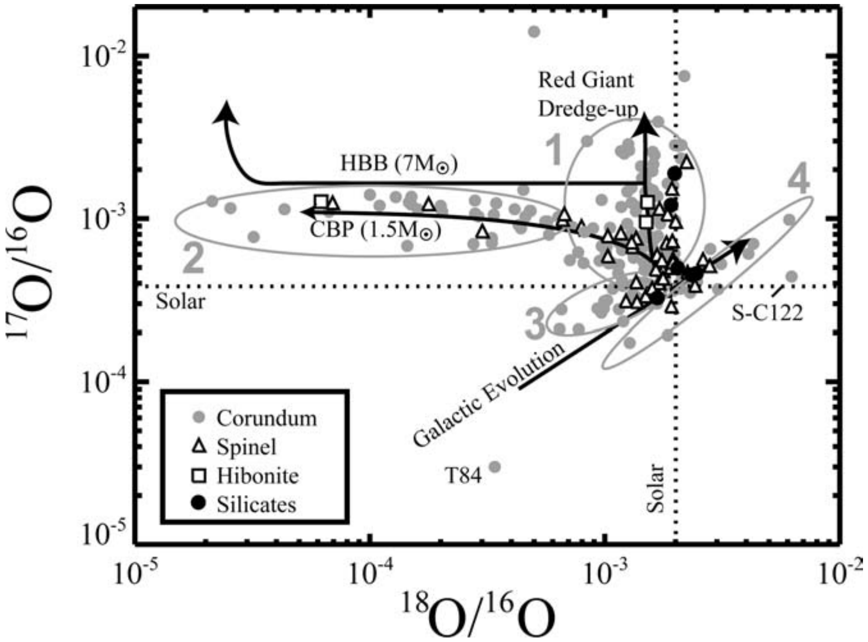

Figure 4 O isotopic ratios measured in presolar oxide stardust (Choi et al. 1998, 1999; Messenger et al. 2003; Nittler 1997; Zinner et al. 2003b). Gray ellipses indicate grain groups defined by Nittler et al. (1997). Theoretical expectations for Galactic evolution (Timmes et al. 1995), red giant dredge-up (Boothroyd & Sackmann 1999), cool-bottom processing (CBP) (Nollett et al. 2003, Wasserburg et al. 1995), and hot-bottom burning (HBB) (Boothroyd et al. 1995) are schematically shown.

ellipses in Figure 4), on the basis of their O isotopic ratios (Nittler et al. 1997). As for SiC, comparison of oxide grain isotopic distributions with astronomical observations and theory allows identification of specific stellar source types with grain groups. Most of the grains (Groups 1–3) are believed to have originated in O-rich red giant stars, although a supernova origin has been suggested for a few grains, and there is still no satisfactory explanation for several grains, including those belonging to Group 4.

Until recently, presolar spinel appeared to be rarer than in meteorites than presolar Al_2O_3, but this observation was based on measurements of grains larger than 1 μm. Recent NanoSIMS measurements of submicron meteoritic oxide grains (Zinner et al. 2003b) have indicated that presolar spinel is considerably more abundant ($\sim$1 ppm) than previously recognized; in fact, it is significantly higher than presolar Al_2O_3($\sim$200 ppb).

Messenger et al. (2003) recently used the new NanoSIMS instrument to identify six submicron presolar *silicate* grains within interplanetary dust particles (essentially, meteorites with <50-μm diameter) collected by NASA in the stratosphere. The reported abundance ($\sim$5500 ppm) is much higher than that of presolar phases in meteorites. Identified phases include forsterite (Mg_2SiO_4) and glass with embedded metal and sulfides (GEMS) (Bradley 1994). O isotopic ratios of the presolar grains fall into the ranges observed in more refractory presolar oxide phases (Figure 4), indicating an origin in similar types of stars. No Mg or Si data have yet been reported for presolar silicate grains, but such data could be very powerful both in identifying stellar sources and in relating O-rich presolar dust to C-rich dust.

A few presolar *silicon nitride* grains have also been found in meteorite residues (Besmehn & Hoppe 2001, Nittler et al. 1995). These grains have sizes and isotopic compositions similar to those of the rare SiC X grains and, like those, probably formed in supernovae. Their abundance is $\sim$10 ppb in meteorites.

Nanodiamonds are by far the most abundant of suspected presolar grains in meteorites. But their origin is also the least understood because they are too small ($\sim$2.5 nm in diameter, Lewis et al. 1989) to allow isotopic-ratio measurements on individual grains. The diamonds constitute about 0.14% of the mass of a carbonaceous meteorite, which is about 3% of all carbon in the carbonaceous meteorites. This amounts to an astonishing 10^{19-20} diamonds per gram of carbon. If that fraction applies to the ISM as well, nanodiamonds are by far the most abundant known interstellar solid, certainly abundant enough to influence interstellar opacity (Lewis et al. 1989). Allamandola et al. (1993) reported evidence of abundant diamonds in interstellar clouds.

The size distribution and microstructures of the diamonds support an origin via condensation by a chemical-vapor-deposition-like process, rather than by fragmentation or shock (Daulton et al. 1996, Frenklach et al. 1989, Lewis et al. 1989). Prior to the discovery of meteoritic nanodiamonds, Saslaw & Gaustad (1969) had suggested that diamonds might be possible in astrophysics because the energy difference between diamond and graphite, the ground state of solid carbon, is so small that condensation from a hot cooling gas might produce the metastable diamonds. Clayton et al. (1995) argued the case for this in mixing regions between the He shell and the H envelope of supernovae on the basis of a postulated need for hydrogen in the chemical-vapor-deposition cycles and from C and N isotopic ratios in bulk diamonds, but their argument is weakened by not knowing isotopic ratios in individual diamonds. Because a single nanodiamond contains but 10 or so ^{13}C atoms, measurement of C isotopes of the diamonds individually would be plagued by counting statistics and efficiency. In bulk, the diamonds are within the range observed for Solar System materials (Russell et al. 1996), casting doubt on the idea that all are supernova particles. Abundant nitrogen in the diamonds has a $^{15}N/^{14}N$ ratio some 35% lower than the terrestrial atmosphere, apparently arguing for a presolar origin. However, a recent measurement of the N isotopic composition of Jupiter (Owen et al. 2001) suggests that the solar $^{15}N/^{14}N$ ratio is very similar to that observed in the meteoritic nanodiamonds. Thus, a presolar origin is not required by the isotopic composition of the two most abundant elements, C and N. Moreover, based on the presence or absence of diamonds in certain types of interplanetary dust particles, Dai et al. (2002) have argued that most diamonds condensed in the solar accretion disk. The presence of diamonds in diverse geophysical samples (Haggerty 1999) casts further confusion over the origin of meteoritic nanodiamonds.

Evidence that at least a portion of the meteoritic nanodiamonds could be presolar grains arose from showing that in bulk they carry the isotopically anomalous Xe gas (Tang & Anders 1988) that had long been known to exist in meteorites (Reynolds & Turner 1964). That Xe component, called Xe-HL because it is enriched in both heavy (H) and light (L) Xe isotopes, has been interpreted as originating from *r* (Xe-H) and *p* (Xe-L) processes within supernovae (Clayton 1989, Heymann & Dziczkaniec 1979, Howard et al. 1992). Tellurium anomalies in bulk diamond residues also show evidence for a supernova *r* process (Richter et al. 1998). Ott (1996) has interpreted the Xe and Te data in terms of a supernova *r* process and a very rapid separation (within a few hours) of the radioactive precursors to some isotopes. This model gives a good match to the data, but it is not clear that the required chemical separation could take place within hours of a supernova explosion. It must be noted that the Xe abundance in the nanodiamonds is such that only about one in a million diamond grains contains a single Xe atom! Thus, it is possible that most of the diamonds in fact formed in the Solar System, with only a tiny fraction having an origin in presolar supernova explosions.

4. SUPERNOVA GRAINS

4.1. History and Isotopic Characteristics

With the realization that computer models of massive supernovae generate large mass shells of abundant intermediate-mass elements, Hoyle & Wickramasinghe (1970) argued that the adiabatic expansion and cooling of these newly synthesized nuclei within the supernova interior should be accompanied by condensation of a potentially large amount of silicate dust. Their goal had been to account for the interstellar dust mass of silicates and of graphite. Clayton (1975a,b, 1978) seized on that idea to demonstrate that grains from this process would be identifiable by the extreme isotopic signatures inherited from those supernova shells. As an initial possibility for detecting the effects of such grains in the solar accretion disk, a chemical memory (e.g., Clayton 1982) of such precursor grains during the chemical growth of the larger solids stored in meteorites was described. This work primarily aimed at explaining several isotopic anomalies, especially ^{16}O-enrichments (R.N. Clayton et al. 1973), observed in high-temperature inclusions in meteorites. D.D. Clayton (1975a) attributed the ^{16}O anomalies to presolar grains that had condensed deep within expanding supernova interiors. However, modern evidence does not favor this interpretation of the ^{16}O excess in refractory Solar System solids because O-rich stardust that has been discovered in meteorites is largely ^{17}O-rich, not ^{16}O-rich (Nittler et al. 1997). Nonetheless, the existence of isotopic anomalies in a major element within meteoritic solids provided a decade of motivation for the search for supernova stardust. Clayton & Wickramasinghe (1976), Clayton (1979), and Kozasa et al. (1989) showed that grains larger than one micrometer could grow in expanding supernova interiors. None of these works was so optimistic as to assert that individual supernova grains could be found today intact within the meteorites, but they did establish ideas by which those discoveries could be recognized.

Today at least five different presolar minerals in meteorites have been identified as originating in supernovae: diamond, SiC of type X, low-density graphite (including subgrains of TiC and Fe-Ni metal), Si_3N_4, and a small number of presolar Al_2O_3 grains. Amari & Zinner (1997) and Zinner (1998) have reviewed in depth the isotopic characteristics of most of these grain types. The ambiguous nature of the meteoritic nanodiamonds was described in Section 3, so we do not discuss them further. Here, after a brief overview of the remaining types, we concentrate on some specific astrophysical implications of the supernova grains.

SiC X grains were originally identified as a rare (~1%) and unusual population during early SIMS measurements of individual grains from meteoritic residues (Alexander et al. 1990a, Amari et al. 1992). Unlike the dominant mainstream population (see Sections 3 and 5.1), they are depleted in heavy Si isotopes (Figure 3), and ^{13}C (most grains), and they are highly enriched in ^{15}N. The development of an automated SIMS ion imaging technique made it possible to identify large numbers of X grains relatively efficiently, and several hundred have now been analyzed for various isotopic signatures (Hoppe et al. 1996b, 2000; Nittler et al. 1995, 1996). Several grains of silicon nitride with isotopic signatures closely similar to the X grains have also been identified in the same meteorite residues (Besmehn & Hoppe 2001, Hoppe et al. 1996a, Nittler et al. 1995). In addition to having unusual Si, C, and N compositions (Figures 2 and 3), they are also usually highly enriched in ^{26}Mg, attributable to in situ decay of radioactive ^{26}Al, with inferred ^{26}Al/^{27}Al ratios greater than 0.1 (Figure 5). In fact, in some grains, the Mg is essentially monoisotopic ^{26}Mg, in strong contrast to the terrestrial ^{26}Mg/^{24}Mg ratio of 0.13932.

The smoking gun for a supernova origin (Clayton 1975b) for SiC X grains is the presence in some grains of large excesses of ^{44}Ca, relative to ^{40}Ca and the terrestrial isotopic ratio (Hoppe et al. 1996b, Nittler et al. 1996). Other stable Ca isotope ratios are normal in the grains, and a monoisotopic effect like this usually indicates radioactive decay. In this case, the parent specie was certainly ^{44}Ti, with a half-life of ~50 years. Because the grains had live ^{44}Ti when they formed, and this isotope is synthesized only in supernovae, the conclusion that the grains formed in supernovae is inescapable. Using measured Ti/Ca elemental ratios, initial ^{44}Ti/^{48}Ti ratios can be inferred for the grains. These range from $\sim 10^{-2}$ to ~0.6 and are correlated with Si isotopes in the sense that the grains with highest ^{44}Ti/^{48}Ti ratios are also the most ^{28}Si rich (Figure 6). This correlation is consistent with the grains containing material from the innermost ^{28}Si-rich zones of a Type II supernova

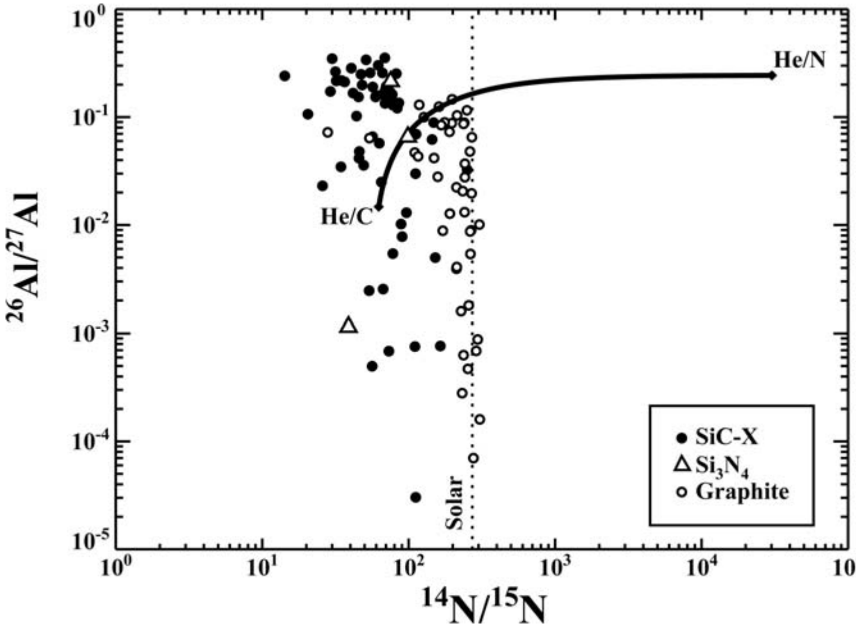

Figure 5 Inferred $^{26}Al/^{27}Al$ ratios plotted against $^{14}N/^{15}N$ ratios for supernova SiC, graphite and Si_3N_4 grains. Also shown are typical ratios predicted for two zones of a type II supernova (Meyer et al. 1995) and a mixing curve between them.

(SNII), where ^{44}Ti is synthesized during an alpha-rich freezeout (Woosley et al. 1973).

Similar to the case of ^{44}Ca excesses, ^{49}Ti excesses correlated with V/Ti ratios in some grains clearly point to the in situ decay of live ^{49}V (Hoppe & Besmehn 2002), whose 330-day half-life indicates that the grains formed within months of the parent stars' explosions. Additional isotope measurements reported for X grains include ^{41}K excesses from decay of ^{41}Ca (Amari & Zinner 1997), boron measurements (Hoppe et al. 2001), and the heavy elements Sr, Zr, Mo, Ba, and Fe (Davis et al. 2002, Pellin et al. 2000). The heavy element data are discussed in more detail below.

The lowest density (1.6–2.15 g/cm^3) fraction of presolar graphite isolated by Amari et al. (1994) also has isotopic signatures pointing to a supernova origin. As for SiC X grains, the signature most diagnostic of a supernova origin is ^{44}Ca excesses from in situ decay of ^{44}Ti (Nittler et al. 1996). Many of the grains show ^{28}Si and ^{15}N excesses similar to X grains as well, inferred initial $^{26}Al/^{27}Al$ ratios up to $\sim$0.1, a huge range of $^{12}C/^{13}C$ ratios, and large ^{18}O enrichments, with $^{18}O/^{16}O$ ratios up to 200 times the terrestrial ratio. TEM investigation of supernova graphite grains has also revealed the presence of tiny internal subgrains of TiC and Fe-Ni metal (Croat et al. 2003). Isotopic measurements of individual TiC crystals within

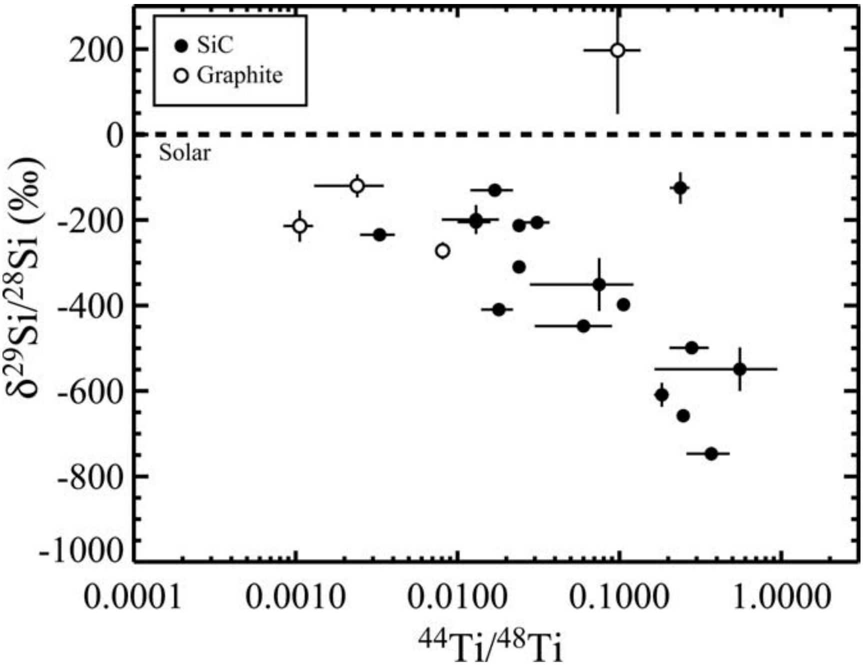

Figure 6 δ^{29}Si values plotted versus inferred ^{44}Ti/^{48}Ti ratios for supernova SiC and graphite grains (Besmehn & Hoppe 2003, Hoppe et al. 2000, Nittler et al. 1996). The presence of extinct ^{44}Ti in the grains proves a supernova origin.

a single supernova graphite grain have revealed a large range of ^{18}O/^{16}O ratios, but homogeneous Ti isotopic composition, similar to that observed in SiC X grains (Stadermann et al. 2003). These observations have important consequences for how these grains condensed within their parent supernovae, as discussed below.

Although a special Type Ia supernova model was proposed to explain many of the observed isotopic signatures of supernova SiC, graphite, and Si_3N_4 grains (Clayton et al. 1997), it now appears to be most likely that the bulk of these grains formed in Type II supernovae (SNII). As discussed in detail by Amari & Zinner (1997), Zinner (1998), and Hoppe et al. (2000), most of the major isotope signature observed in the grains are at least qualitatively consistent with models of SNII. Of key importance is the observation that the grains carry the isotopic signatures of different mass zones of the parent supernovae. For example, ^{28}Si excesses and high ^{44}Ti/^{48}Ti ratios are expected for the innermost zones, low ^{14}N/^{15}N ratios are expected in the He-burning zone, and high ^{26}Al/^{27}Al ratios are only produced by H-burning in outer layers of the parent stars. Thus, the data imply the need for extensive and selective mixing of material from different layers. This result has profound implications for processes of gas transport and dust nucleation and growth within SNII ejecta, as discussed below in Section 4.3.

The vast majority of presolar oxide grains are believed to originate in red giants and AGB stars (see Section 5.3. and, e.g., Nittler et al. 1997). However, Nittler et al. (1998) reported an Al-rich oxide grain, T84, whose O consists of almost pure ^{16}O (Figure 4). Because this is by far the most abundant isotope ejected by SNII, T84 almost certainly formed in such an environment. Unfortunately, the grain was completely consumed during the O measurement, so no additional isotope data are available, and such grains appear to be very rare in meteorites. Choi et al. (1998) reported a highly ^{18}O-enriched Al_2O_3 grain, S-C122, which they also proposed to have originated in a SNII. The O isotope signature of this grain is qualitatively consistent with a mixture of material from the He-burning shell and the H-rich envelope of a SNII, but the $^{17}O/^{16}O$ ratio is lower than predicted for such a mixture and the other isotopic ratios measured in the grain (Mg and Ti) do not point compellingly to a SNII origin. Nonetheless, this suggestion raises the intriguing possibility that the ^{18}O-enriched Group 4 oxides formed from SNII. These grains roughly form a linear array on the O 3-isotope plot (Figure 4), extending into the ^{16}O-rich quadrant. This line is suggestive of mixing and the ^{16}O-rich and ^{16}O-poor end-members could in principle arise in SNII (Rauscher et al. 2002), though some fairly selective mixing of layers would have to occur to make it work quantitatively.

4.2. New Nucleosynthesis with Supernova Stardust

Although the isotopic signatures of the supernova grains are, in general, qualitatively consistent with prior expectations for nucleosynthesis within SNII, there are some difficulties in quantitatively explaining the data and the grains have also provided some surprises. We discuss a few illustrative examples of how presolar supernova grains provide new information about nucleosynthesis in SNII.

4.2.1. SILICON AND NITROGEN ISOTOPES Two long-recognized problems in reconciling the supernova grain data with SNII models are related to the Si and N isotopic ratios. Most of the SiC X grains and Si_3N_4 grains lie on a Si 3-isotope plot near a line consistent with mixing of a highly ^{28}Si-rich composition with a composition close to solar (Figure 3). However, the implied ^{28}Si-rich end member has a $^{29}Si/^{30}Si$ ratio higher than the solar ratio, but supernova models (e.g., Woosley & Weaver 1995) predict lower-than-solar $^{29}Si/^{30}Si$ ratios for the ^{28}Si- (and ^{44}Ti-) rich inner zones. In fact, as discussed in detail by Timmes & Clayton (1996), chemical evolution calculations using the Woosley & Weaver (1995) supernova models fail to explain the solar $^{29}Si/^{30}Si$ ratio, implying that real SNII produce either more ^{29}Si or less ^{30}Si than predicted by the models. Thus, both the grains, which sample specific regions of supernova ejecta, and the solar isotopic composition, sampling mixed bulk ejecta from many supernovae, point to a problem with the relative production of ^{29}Si and ^{30}Si in supernovae. One possible solution to the grain Si isotope puzzle has been proposed as part of a new condensation model for SiC X grains (Deneault et al. 2003), discussed in more detail below in Section 4.3.

Nitrogen-15 is produced in SNII models primarily by neutrino spallation from ^{16}O in inner mass zones (Woosley & Weaver 1995). Presolar supernova stardust grains typically have large ^{15}N excesses coupled with isotopic signatures of H burning (e.g., high ^{26}Al/^{27}Al ratios) (Figure 5). This has posed a significant problem for quantitatively explaining the grain data, since H-burning produces abundant ^{14}N-rich N. Grain data, predictions for the H-burning ("He/N") and He-burning ("He/C") zones of a 15$M_\odot$ Type II supernova (Woosley & Weaver 1995), and a mixing curve between these zones are shown in Figure 5. The measured ^{14}N/^{15}N ratios in most of the SiC X grains are clearly lower than can easily be explained by SNII mixing models, especially if $C > O$ is assumed to be required for SiC or graphite condensation (Hoppe et al. 2000, Travaglio et al. 1999). Relaxing the $C > O$ restriction might allow for SiC formation in the ^{15}N- and ^{16}O-rich inner mass zones (Deneault et al. 2003), possibly helping to alleviate the problem. Alternatively, the grains might indicate that supernovae produce much more ^{15}N than predicted by current models. This is supported both by recent observational measurements of N isotopes in extragalactic systems (Chin et al. 1999) and by massive star models incorporating rotation (Heger et al. 1998).

4.2.2. NEUTRON-BURST NUCLEOSYNTHESIS The development of the RIMS technique (Section 2) has made possible the measurement of trace heavy elements in individual stardust grains. Pellin et al. (2000) and Davis et al. (2002) reported Sr, Zr, Mo, Ba, and Fe isotopic compositions for several SiC X grains. The isotopic patterns observed for these elements are not only distinct from those measured in grains from other stellar sources (e.g., Section 5), but also from the *r*-process composition commonly associated with SNII. Molybdenum in the grains is particularly interesting, with large excesses of ^{95}Mo and ^{97}Mo, relative to the *s*-only ^{96}Mo and the solar isotopic composition. Meyer, Clayton & The (2000) showed that the X-grain Mo and Zr isotope patterns could be well-explained by a new kind of neutron burst nucleosynthesis, occurring when a large flux of neutrons are released as the supernova shock wave passes through the He shell. The neutron burst model also qualitatively explains the Sr, Zr, Ba, and Fe isotopic patterns observed in the grains. Although this process is apparently a minor contributor to bulk abundances of the relevant isotopes in the Solar System in comparison to the *s* and/or *r* processes, unknown reasons exist for its preferential enrichment in trace elements in SiC grains from supernovae. This result clearly shows the power of presolar grains for probing conditions and processes in localized regions of SNII ejecta.

4.3. Special Condensation Issues in Supernovae

The ejected mantle above the collapsed supernova core offers a unique laboratory for condensation physics. It guarantees that chemistry begins with gaseous atoms, with no trace of previous molecules or grains. But persistent questions concerning how the condensation physically occurs are only slowly being answered. Because the supernova core is hydrogen-free, chemical condensation routes utilizing abundant H are not relevant. Polycyclic aromatic hydrocarbons, for example, do not come into play except in the envelope, but 90–95% of the mass of ejected Mg, Al, and Si exists in the H-free core. And yet abundant dust condensation is observed to have occurred in SN 1987a (Colgan et al. 1994, Wooden et al. 1993), in Cas A (Arendt et al. 1999, Dunne et al. 2003), and in the Kepler remnant (Morgan et al. 2003). Apparently a few solar masses condensed in Cas A and one solar mass in Kepler, requiring high condensation efficiency for Mg, Al, and Si and even for carbon and establishing supernovae as a major contributor to the budget of thermally condensed interstellar grain cores, as expected (Clayton 1982).

One approach to core condensation has been to assume that chemical equilibrium holds during the expansion and temperature decline of the supernova interior and to calculate the equilibrium condensed masses of differing minerals (Ebel & Grossman 2001, Lattimer et al. 1978). This approach is moot when questions of grain size are asked because it yields only the total condensed masses; moreover, it suffers from the wide departures from equilibrium among solids actually expected in the expanding supernova matter. The equilibrium approach may be regarded at best as a guideline for identifying the solids expected if the expansion were so slow that condensed atoms can maintain equilibrium vapor pressure capable of moving them from one solid phase into another as the temperature declines. Because of the rapid fall of density and temperature during the expansion of the ejecta, almost all thermal condensation must be accomplished within about two years, too fast to maintain equilibrium. A nonequilibrium theory of condensation based on nucleation theory followed by subsequent growth has been developed by Kozasa and others (Kozasa & Hasegawa 1987; Kozasa et al. 1989, 1991; Todini & Ferrara 2001). Their method identifies a "key molecular species" whose abundance controls the condensation (Kozasa & Hasegawa 1987). Applying their method to dust condensation in SN 1987a, Kozasa et al. (1989) showed that carbon grains condense first, then Al_2O_3, Mg silicates, and Fe_3O_4 condense in that order as the gas cools, but in physically distinct mass zones. However, their assumptions concerning molecular mixing and an outdated role of the CO molecule (see below) render their results of questionable value today.

Key physical questions for supernova condensation involve a large disequilibrium of gas phase abundances, especially of the CO molecule, and the nature of mixing indicated by the isotopic compositions measured in the supernova stardust. The nucleosynthesis problems posed by isotopic ratios in supernova grains cannot be decoupled from physical questions about their condensation. As discussed above, the isotope data indicate contributions from more than one supernova mass zone, indicating some sort of physical mixing (Amari & Zinner 1997, Hoppe et al. 2000, Travaglio et al. 1999), but it is not physically clear whether that mixing represents molecular mixing in the very young remnant or transport of a growing grain from one composition zone into another. Intimately related is an elemental composition question; namely, whether the requirement that the C abundance be greater than O abundance in order to condense SiC and graphite within supernovae is a valid requirement. For their discussion of supernova stardust, Travaglio et al. (1999) took the view that mixing occurs at the molecular level, prior to condensation, and that only portions with $C > O$ support condensation of carbon. They arbitrarily mixed regions that had $C < O$ with the He shell that had $C > O$ to find mixing fractions that retained $C > O$ overall and reproduced isotopic trends observed in the grains. Kozasa et al. (1989) and Todini & Ferrara (2001) performed similar thought experiments. Such treatment is deeply flawed, however, because it is physically highly unlikely that gases could mix at the molecular level within a few years time [see Section 2.1 (Deneault et al. 2003) and Section 6 (Fryxell et al. 1991)]. The mixing expected for SNII ejecta, at least from current observations and hydrodynamical models, instead represents fluids of one composition exchanging places in the homologous expansion with overlying fluids of another composition.

Clayton, Liu & Dalgarno (1999) and Clayton, Deneault & Meyer (2001) attacked the often assumed requirement that C/O be greater than unity in order for carbon to condense by calling upon the fast Compton electrons caused by supernova radioactivity to dissociate the CO molecules. Otherwise those CO molecules represent C traps, removing C atoms from thermal condensation. These authors advanced a kinetic theory of graphite growth and calculated its consequences in detail after advocating a specific nucleation model (namely, linear carbon chain molecules C_n isomerized at sufficiently large n (near $n = 14$) to C_n rings, followed by free C association with C_n faster than oxidation can be brought about by free oxygen). The last point is equivalent to this: Small graphite particles in a hot gas of C and O will associate with C faster than their oxidation reactions by more abundant O, so that even though oxidation is the ultimate end, given adequate time, the expansion will terminate the chemistry after approximately two years with remaining large graphite grains. Ebel & Grossman (2001) attempted to finesse the CO molecular trap by simply postulating that CO was not stable and then computing the equilibrium masses of various species as before. Their procedure confirmed that graphite is a stable early condensate under such assumptions provided that $C/O > \sim 0.5$.

The condensation theory of Clayton, Liu & Dalgarno (1999) and Clayton, Deneault & Meyer (2001) built on the finding that supernova 1987 A ejected only $10^{-3}\ M_\odot$ of CO molecules instead of the $0.1\ M_\odot$ of CO molecules that is originally formed by association reactions in the hot gas (Gearhart et al. 1999; Liu & Dalgarno 1994, 1995). However, the theory is far from complete and as yet has not addressed the new constraints arising from recent structural and isotopic studies of supernova graphite grains. For example, Croat et al. (2003) have recently shown that supernova graphite grains commonly contain subgrains of TiC and Fe-Ni metal, which clearly condensed prior to the graphite condensation. Moreover, the ^{44}Ti, ^{49}Ti, and ^{18}O enrichments in the TiC subgrains (Nittler et al. 1996, Stadermann et al. 2003) clearly point to variable mixing of material from different mass zones prior to graphite condensation, especially given the wide range of $^{18}O/^{16}O$ ratios observed among TiC crystals from a single graphite grain. The O isotopic compositions of the TiC grains suggest they could not have formed in the highly ^{16}O-rich zones where graphite is postulated to form in this theory.

Similar issues surround the condensation mechanisms of supernova SiC dust, i.e., X grains. It seems plausible that radioactive liberation of free C atoms from CO molecules could also facilitate the condensation of SiC in O-rich gas. Although a kinetic route to SiC condensation has not been laid out, Deneault, Clayton & Heger (2003) have formulated a physical description of the ejecta enabling them to make several relevant conclusions derived from the starting assumption that the radioactive CO-disruption mechanism is the correct key to SiC growth. In their model, a reverse shock generated by the increasing value of ρr^3 as a function of r in the H envelope causes, after about a month, a dense shell in an inner layer of the supernova, where ^{28}Si and ^{16}O are the most abundant isotopes (though some C remains, indicating that SiC could condense there). Because Si is much more abundant than C in this layer, ^{28}Si-rich SiC condenses preferentially to graphite, aided by radiation-induced dissociation of CO and SiO molecules. Mixing of a new type during condensation occurs if the reverse shock from the presupernova wind arrives at the condensation zone between six months to a year after the explosion, because that shock slows the gas and forces the partially condensed SiC grains to propel forward through the decelerating gas into regions with different isotopic compositions. At this stage, larger SiC grains could slowly overtake more rapidly decelerating smaller ones, perhaps leading to grain agglomerates with associated isotopic mixing. After $\sim 10^3$ years, a third reverse strong shock from the ambient ISM propels SiC grains forward through overlying ejecta at high speed (typically 500 km/s) such that other atoms are implanted into the grains, perhaps accounting for some trace isotopes, as suggested for Mo and Fe (Clayton et al. 2002). Velocity-mixing instabilities prior to these reverse shocks will result in a spectrum of overlying column compositions so that grains from different supernovae (or different regions of a given supernova) could have a diversity of compositions.

Such physical modeling suggests that SiC X grains provide new sampling techniques of supernovae structure, but it remains to be seen if the ideas will withstand the scrutiny of more detailed models. Especially threatening is the possibility that the first shock from the presupernova wind is too strong and may destroy the initial SiC particles, either thermally or by sputtering by O atoms (Deneault et al. 2003), so a key point becomes the spectrum of wind masses that accompany Type II supernovae, for those masses provide the mass of the shock-generating obstacle. To avoid O sputtering (most atoms in the zones overlying the ^{28}Si-rich layers are ^{16}O), Deneault et al. (2003) suggest that some interior ^{28}Si-rich mass zones were exchanged by Rayleigh-Taylor instabilities (Fryxell et al. 1991) with initially overlying O zones. They suggest that the relative rarity of SiC X grains reflects the rarity of that velocity exchange, providing a measure of that probability. Especially needed are two- and three-dimensional hydrodynamic calculations of the reverse shocks and of instability-induced velocity mixing by the primary outgoing shock and a detailed study of molecular mixing to ascertain the degree to which microscopic mixing can be called upon during the first year.

Despite these many questions, or perhaps because of these many questions, it now appears certain that supernova grains studied by isotopic analysis will provide, through details of condensation chemistry, a new sampling spectrum of young supernova interiors, just as have gamma-ray lines and hard X rays. The radioactivity that causes each type of sampling raises fundamental chemical questions as well. The meaning of the supernova stardust for supernova physics depends on the treatment of these many questions.

5. PRESOLAR STARDUST FROM LOW-MASS STARS

Most of the presolar SiC (Figures 2 and 3) and oxide grains (Figure 4) and a significant fraction of high-density graphite grains are believed to originate in the strong winds from late stages of low-mass ($<5\ M_\odot$) stars. The O-rich dust formed in red giants and O-rich asymptotic giant branch stars (AGB, e.g., spectral types MS and S) whereas the C-rich phases condensed in C-rich AGB stars (e.g., N stars). There are several lines of evidence for this conclusion. First and strongest is the similarity of measured isotope compositions ($^{12}C/^{13}C$ in the case of SiC and some graphite; $^{17,18}O/^{16}O$ for oxides) with direct spectroscopic measurements of the stars (e.g., Harris & Lambert 1984, Smith & Lambert 1990). Second, the ranges of many isotopic ratios observed in the grains are in quantitative agreement with theoretical models of evolution and nucleosynthesis in red giants or AGB stars, but not with other types of dust-producing stars. This is true for both light elements (e.g., C, N, O) and heavy trace elements (e.g., Mo, Ba), as discussed in more detail below. Third, the abundance patterns of many trace elements measured in individual grains are in good agreement with predictions for condensation in C-star atmospheres (Amari et al. 1995, Lodders & Fegley 1995). Fourth, infrared spectra from these types of stars are commonly interpreted to show evidence for C, SiC, and oxide dust (Gilman 1969; Speck et al. 1999, 2000; Treffers & Cohen 1974).

5.1. SiC FROM AGB STARS

5.1.1. AGB NUCLEOSYNTHESIS The initial surface compositions of AGB stars, and of dust that condenses in their outflows, are modified by a series of convective dredge-up episodes. The "first dredge-up" occurs shortly after a star leaves the main sequence to become a red giant and results in the ashes of CNO-cycle H burning being mixed to the surface (e.g., Boothroyd & Sackmann 1999). Additional H-burnt material is mixed during the "second dredge-up" (only in stars $>\sim 2.3\ M_\odot$) early in the AGB phase (following core He-burning). Later on the AGB, periodic thermal pulses occur in which H- and He-burning alternately ignite in thin shells above an inert C-O white dwarf core. Recurrent convective episodes (known collectively as the "third dredge-up") mix processed material into the envelope (e.g., Iben &

Renzini 1983). A key result of the third dredge-up is to enrich the surface in ^{12}C (ultimately resulting in the transition to a C-star when C > O) and the products of *s*-process nucleosynthesis. That this occurs is well documented by observations (Abia et al. 2002, Busso et al. 2001, Smith & Lambert 1990).

The isotopic ratios of most presolar SiC grains (the mainstream, Y and Z classes indicated in Figures 2 and 3) clearly show the results of these dredge-up episodes. The ^{12}C/^{13}C ratio of most of the grains reflects an initial drop in this ratio to $\sim$20 during the first dredge-up followed by a gradual increase as the third dredge-up mixes pure ^{12}C into the envelope. The ^{14}N/^{15}N ratio is increased by the first dredge-up, owing to the production of pure ^{14}N in the CNO cycles. Although the range of ^{12}C/^{13}C ratios of most of the SiC grains is within that expected for AGB stars (e.g., Boothroyd & Sackmann 1999, El Eid 1994), the range of ^{14}N/^{15}N ratios exceeds predictions, both higher and lower. One possible explanation for this discrepancy is an extra mixing process not predicted by standard stellar evolutionary calculations. Such a process, termed cool-bottom processing (CBP) by Wasserburg, Boothroyd & Sackmann (1995), requires transport of envelope material to deep regions where it is directly processed by H-burning reactions before being mixed back out into the convective envelope. Although the physical mechanism for the mixing has not been identified, CBP has been implicated in anomalously low ^{12}C/^{13}C ratios observed in low-mass red giant stars (Boothroyd & Sackmann 1999, Charbonnel 1994, Denissenkov & VandenBerg 2003, Gilroy & Brown 1991, Sweigart & Mengel 1979). Moreover, O isotopes observed in some stars and, especially, in presolar oxide grains (see Section 5.2) indicate that this mixing occurs in AGB stars as well (Nollett et al. 2003, Wasserburg et al. 1995). CBP in the SiC parent stars could result in the high ^{14}N/^{15}N ratios observed, and if certain reaction rates are modified could also explain grains with low ^{14}N/^{15}N ratios (Huss et al. 1997). Alternatively, low ^{14}N/^{15}N ratios might reflect third dredge-up in low-mass AGB stars (Lugaro et al. 2003b).

Particularly striking and illustrative of the potential of presolar grains for astrophysics is the nearly pure *s*-process composition of heavy elements in the SiC grains. This is true both for elements measured in bulk samples of many grains (Hoppe & Ott 1997, Prombo et al. 1993, Srinivasan & Anders 1978) and those measured in individual grains (e.g., Nicolussi et al. 1997, 1998a; Savina et al. 2003a,b). Moreover, in many cases, the compositions include branchings unique to AGB stars (Gallino et al. 1997, Lugaro et al. 2003a). Note that for decades the existence of the *s* and *r* processes of neutron capture nucleosynthesis was an act of theoretical faith, based on deconvolution of the Solar System abundance distribution (Clayton & Fowler 1961, Käppeler et al. 1982, Seeger et al. 1965). The identification of nearly pure *s*-process Xe gas in a meteorite acid residue (Srinivasan & Anders 1978) followed by the many other isotope systems measured in SiC since then, not only demonstrated that the *s* process occurs in nature, but the grain data now allow for subtle differences in the *s* process in different stars to be identified. Figure 7 (reproduced from figure 8 of Lugaro et al. 2003a) compares Zr and Mo isotopic ratios measured by RIMS in individual SiC grains (each from an

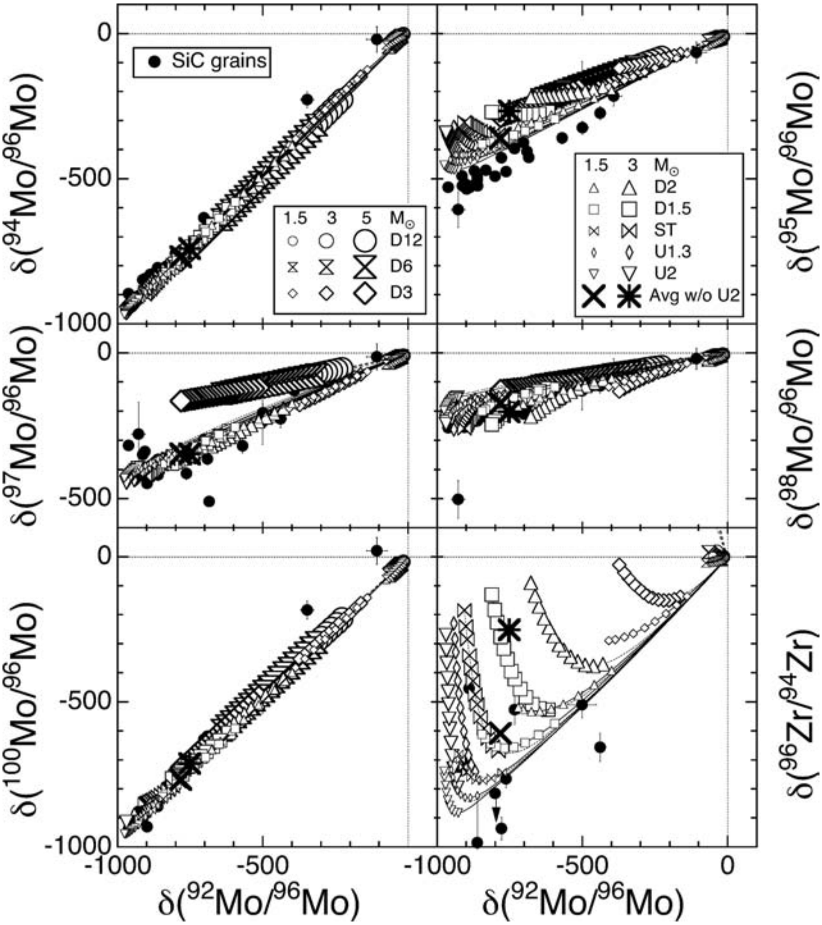

Figure 7 Mo and Zr isotopic ratios (expressed as delta values, see Figure 3 for definition) in individual SiC grains from AGB stars. Superimposed on data are theoretical calculations of nucleosynthesis for AGB stars of different masses and amount of ^{13}C mixed into the He shell. Figure is reprinted from Lugaro et al. (2003a, figure 8) with permission from the AAS.

individual AGB star) with recent models of AGB star nucleosynthesis. The different symbols indicate AGB models of different masses and sizes of the "^{13}C pocket," a free parameter in the models corresponding to the amount of ^{13}C available to release neutrons by the $^{13}C(\alpha,n)^{16}O$ reaction (see Gallino et al. 1998 for more details). The SiC grains have large depletions in all Mo isotopes relative to the *s*-only isotope ^{96}Mo, indicating nearly pure *s*-process composition. Moreover, detailed comparisons like this of theory with data can be used both to constrain the origins of the grains (range of progenitor masses, for example) and to point

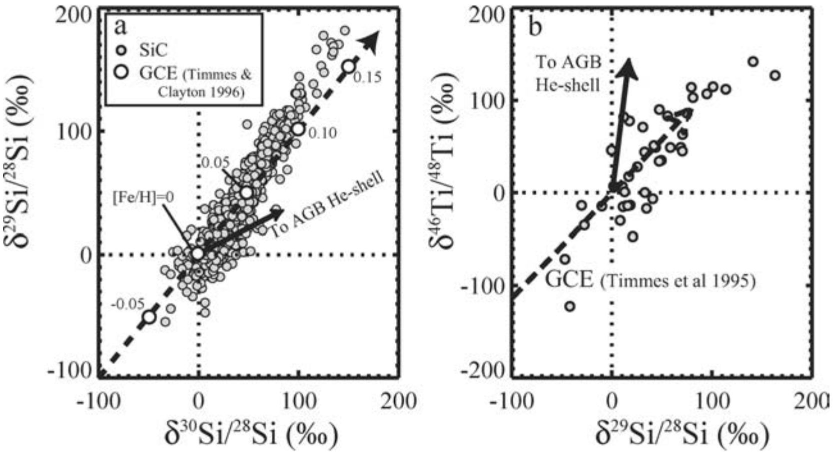

Figure 8 Si and Ti isotope δ-values (see Figure 3 for definition) of mainstream SiC grains. The grain data are correlated in both plots, but the slopes are different from expectations for dredge-up in single AGB stars (Lugaro et al. 1999). Also shown are Galactic chemical evolution (GCE) calculations for isotopic evolution (Timmes & Clayton 1996, Timmes et al. 1995); metallicity values are indicated in (*a*).

out problems in the stellar evolutionary and nucleosynthesis models. Because it is unlikely that astronomical observations will ever allow high-precision isotopic compositions of heavy elements to be determined in AGB stars, presolar grains are clearly a key tool for testing models of these stars.

In addition to Zr and Mo isotopes, RIMS has also been used to study Sr (Nicolussi et al. 1998b), Fe (Tripa et al. 2002), Ba (Savina et al. 2003a) and, most recently, Ru isotopes (Savina et al. 2003b) in AGB SiC. In the latter case, most of the measured ratios were in good agreement with AGB models, but the ^{99}Ru/^{100}Ru ratios could only be well explained if live ^{99}Tc was incorporated into the grains during their formation. The discovery of extinct Tc in SiC from AGB stars is historically resonant, as the observation of Tc spectral lines in AGB stars (Merrill 1952) provided the first direct evidence that elements are made in stars.

5.1.2. SILICON AND TITANIUM ISOTOPES IN AGB SiC The good agreement of AGB models with mainstream SiC isotope signatures does not extend to the 50% of the grains' atoms that are Si. As shown in Figures 3 and 7*a*, the Si isotope ratios of the grains, expressed as permil deviations from the solar ratios, are aligned on the 3-isotope plot. The slope of the best-fit line to the data is 1.3, considerably steeper than the slope expected for third dredge-up of *s*-processed Si in AGB stars (0.4–0.8; Lugaro et al. 1999). Moreover, the total range of Si isotopic compositions (~25%) is much larger than both individual grain errors (<1%) and that expected for AGB nucleosynthesis (~2%). It is now generally accepted that the Si correlation line indicates a spread in the initial isotopic compositions of the parent stars with only a minor contribution from the *s* process in the parents themselves (Alexander 1993, Alexander & Nittler 1999, Timmes & Clayton 1996). A similar conclusion has been drawn for Ti isotopes in the SiC mainstream (Alexander & Nittler 1999, Hoppe et al. 1994) because these are strongly correlated with Si isotopes and the slope and extent of variations are different from expectations for *s*-process dredge-up in individual stars (Figure 7*b*).

Galactic chemical evolution (GCE) should correlate $^{29}Si/^{28}Si$ and $^{30}Si/^{28}Si$ ratios within stars of different metallicities (Clayton 1988), given the secondary nature of the nucleosynthesis of ^{29}Si and ^{30}Si, if both the Sun and the AGB donor stars formed within the temporal evolution of a well-mixed single-zone interstellar medium (ISM) (Timmes & Clayton 1996). However, there are significant problems with a GCE interpretation of the SiC data, illustrated in Figure 7*a*. First, the slope of the mainstream line is 1.3, steeper than the slope-1 line predicted by GCE theory (Timmes & Clayton 1996). Second, most of the grains are enriched in the secondary, neutron-rich isotopes relative to the Sun, but formed in stars born 1–2 Gyr earlier than the Sun. In a one-zone GCE model that produces the Sun, older stars should have $^{29,30}Si/^{28}Si$ ratios lower than the Sun. Finally, taking the Timmes & Clayton (1996) GCE calculation at face value, the range of Si isotopes of the mainstream SiC compositions requires a difference of about 5 Gyr to explain the range of Si isotopes from the bottom to the top of the mainstream. There is much evidence pointing to a relatively narrow range of parent masses for the majority of mainstream SiC grains (Lugaro et al. 1999, 2003a), so this time difference would indicate a large range in ages of the grains themselves. This hardly seems credible, making a simple temporal interpretation of the Si data implausible. Even if a temporal interpretation is discarded, the grains still appear to have originated in donor AGB stars with higher initial metallicities than the Sun and the problem of the 1.3 slope remains. A number of attempts have been made to resolve these problems.

5.2. Nontemporal Proposals for the Donor-AGB-Star Composition Spread

One explanation of the SiC mainstream that discards temporal evolution was advanced by Clayton (1997). He proposed that the low-mass grain parent stars formed on nearly circular orbits interior to the position of solar birth could scatter from massive molecular clouds into orbits that become considerably more elongated and thus be found at the end of their lives (their AGB phases) at larger galactocentric radii than their birthplaces. Because metallicity gradients exist in the Galactic disk, these stars could have higher metallicities than the Sun, despite forming earlier. A semianalytic model by Nittler & Alexander (1999b), using astronomically derived parameters, indicates that such outward orbital diffusion of stars probably would not result in the observed Si isotopic distribution of the SiC grains. Moreover, unpublished Monte Carlo calculations by one of us (DDC) do not indicate large-scale outward scattering of presolar AGB stars. However, Sellwood & Binney (2002) have given support to the general idea by calculating radial migration of low-mass stars as a result of scattering from spiral density waves (rather than from molecular clouds).

A second approach gives a nontemporal interpretation to the Solar Si isotopes, regarding them as atypical for the Sun's age and galactocentric radius, but keeps the temporal interpretation of initial AGB abundances (Clayton & Timmes 1997). This approach regards only the Sun as peculiar. These authors concluded that the sun must lie far to the right (^{30}Si-rich) side of the initial AGB (GCE) line in Figure 7*a*. However, in this case dredge-up of He-shell material in the parent AGB stars would have to increase the surface ^{30}Si/^{28}Si ratio so much that the final (observed mainstream) line falls, as if by a miracle, very near the Sun's abnormal composition. Moreover, such a large increase of ^{30}Si/^{28}Si in AGB stars is not regarded as possible, based both on the grains' C-isotopic ratios (Alexander & Nittler 1999) and on AGB nucleosynthesis calculations (Lugaro et al. 1999).

A third explanation discarding the temporal evolution restriction was advanced by Lugaro et al. (1999), who attempted to interpret the correlations of the initial compositions as being attributable to inhomogeneous chemical evolution of the ISM when non-uniformly polluted by supernovae of varying masses. Their Monte Carlo model for galactic gas enriched by random supernovae was able to reproduce the range and slope of Si isotopic ratios in the mainstream SiC. However, Nittler (2002) extended this model to Ti and O isotopes and showed that it could explain neither the high degree of correlation between Si and Ti isotopes in the grains nor the range of O isotopic compositions observed in presolar oxide grains. It is also highly unlikely that any model of this sort could account for the Si-Ti correlations because the isotopes of these elements are made in different types and/or masses of supernovae. In fact, the observed Si-Ti isotope correlations might allow the degree of heterogeneity in galactic chemical evolution of the Solar neighborhood to be estimated with higher precision than currently attainable by astronomy (Nittler 2002, Reddy et al. 2003).

A fourth explanation is that the true ISM Si isotope evolution actually occurs along a line of steeper than unity slope. Based on a fit to the Si and Ti isotope SiC data, Alexander & Nittler (1999) concluded that the true Si GCE slope is closer to 1.5 than to 1. One possibility to obtain such a slope would be a changing initial mass function with time in the Galaxy, since high-mass supernovae models produce Si with ^{29}Si/^{30}Si $>$ solar and low-mass ones produce ^{29}Si/^{30}Si $<$ solar (Woosley & Weaver 1995). Alternatively, a faster evolution of ^{29}Si than ^{30}Si near solar metallicity would imply a faster evolution of ^{30}Si at low metallicity. Thus, if there were a large source of ^{30}Si relative to ^{29}Si at low metallicity, the required steep slope on the Si 3-isotope plot might be obtained. There is no hint of an "extra" source of ^{30}Si in low-metallicity supernova calculations, but other possibilities include ONe novae and low-metallicity AGB stars. Recent calculations of each of these stellar types indicate relatively large production factors of ^{30}Si and smaller or no production of ^{29}Si (Amari et al. 2001b, José & Hernanz 1998). GCE calculations taking these sources into account are needed to test this idea.

5.3. A Mixing Proposal for the AGB-Star Spread

Clayton (2003b) has recently proposed that the mainstream-grain Si-isotope correlation line compositions was the result of star formation during the mixing of a high-metallicity gas with a low-metallicity gas. A useful property of three-isotope plots like those in Figures 3 and 7*a* is that mixtures of distinct reservoirs appear along lines connecting the reservoir compositions. The idea is that the Si-isotope correlation line is in fact such a two-component mixing line between Galactic-disk gas (high Z) and that of a satellite galaxy (low Z) having significant interstellar gas that was cannibalized by the Milky Way about 5.5 to 6.5 Gyr ago. Stars born amid this starburst-inducing merger inherited their initial compositions from this variable mixture, and many later evolved to the AGB phase shortly before the Solar System formed. This suggestion should not be viewed as improbable, being the current view of how much of the mass of the Galaxy was acquired (e.g., Shetrone et al. 2003, Wyse 2003). The gaseous mixing would have occurred along hydrodynamic streams generated by the gaseous collision. As this merger progressed, vigorous star formation was induced by its hydrodynamic shock waves. Turbulence along those collision fronts mixed the gases of the two galaxies to variable degrees, so that new stars formed at that time did so from linear admixtures of the two end points. Approximately 1 to 2 Gyr later many evolved to AGB stars, outnumbering those that would have been present without the induced starburst, whereupon they donated to the local ISM the SiC particles that we find present in the early solar system. Because the sun formed in the same region, it incorporated its own mix of the two galaxies as well as the local ejecta of stars that occurred between the time of merger and that of solar birth. That ejecta included specifically the young mainstream SiC grains and the bulk ejecta of the supernovae caused by the starburst.

This model is illustrated in Figure 9. Clayton (2003b) takes the upper end of the gaseous mixing line in the Si three-isotope plot to be the Milky Way disk composition near the solar birth radius at the time of the merger (“G”) and the lower end of the mixing line to represent the Si composition of the gas in the satellite dwarf-galaxy (“S”). The point S' represents the most S-rich star formed after the S gas was diluted by the G gas of the Galaxy. The satellite companion may have been similar to, though not as distant as, the familiar clouds of Magellan. The mixing-line end members, G and S, can lie anywhere beyond the extremities of the actual stars formed during the mixing. The most extreme AGB stars formed lie, according to his hypothesis, near the ends of the parallel mainstream line formed by the data points from the presolar mainstream SiC grains. The extreme gaseous mixtures that actually appeared in the stars formed, namely G' and S', are translated to G'' and S'' by the *s*-process neutron irradiation of initial Si in the AGB stars, which later become the donors of the mainstream grains. That neutron irradiation translates each initial composition (3–4%) rightward and 1–2% upward in this graph (e.g., Lugaro et al. 1999). That translation is small compared with the extent of the mainstream line. As a consequence, the mainstream-grain line parallels the initial-stellar-composition line but is slightly to the right of it.

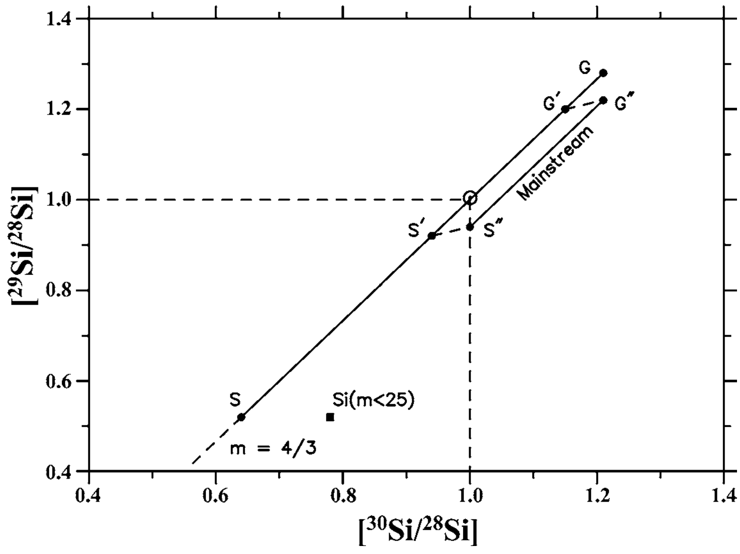

Figure 9 Schematic illustration of galactic merger mixing model for explanation of mainstream SiC Si-isotope data. Figure is reprinted from Clayton (2003b, figure 2) with permission from the AAS. See text for details.

This model has many attractions, including explanations for the tight correlation between SiC Si and Ti isotope ratios, the placement of the Sun at the bottom of the SiC mainstream, and the unusual ^{18}O/^{17}O ratio of the Sun, compared with the local ISM (Penzias 1981). However, it clearly needs critical scrutiny by assorted scientific disciplines before it can be accepted. We note that a galactic merger is not the only scenario in which the proposed mixing might occur. Alternative dynamic reasons may be found for sudden large-scale mixing events associated with starburst activity within the Milky Way. Considering the galactic metallicity gradient d[Fe/H]/dR = –0.1 dex kpc^{-1}, sudden radial mixing of 1–2 kpc between gases that had previously evolved separately might suffice.

5.3.1. DENSITY OF STARDUST ALONG THE MAINSTREAM It is natural to examine the density of SiC grains along the mainstream correlation line. Figure 10 shows a histogram of mainstream SiC Si isotopic ratios, constructed by summing two-dimensional Gaussian probability distributions for each grain (for details, see figure 12 in Nittler & Alexander 2003a). This result is the spectral shape of the mainstream, in some ways complementary to distributions of stars in a Hertzsprung-Russell diagram. From this plot, it is clear that the most abundant mainstream grains lie near the middle (~50%) rather than near the ends of the range. Moreover, there are preferred compositions where local peaks in the distribution occur. Huss et al. (1997) noticed some of these peaks and proposed that some of them correspond to multiple grains from single AGB stars, though in fact differences in C and Ti

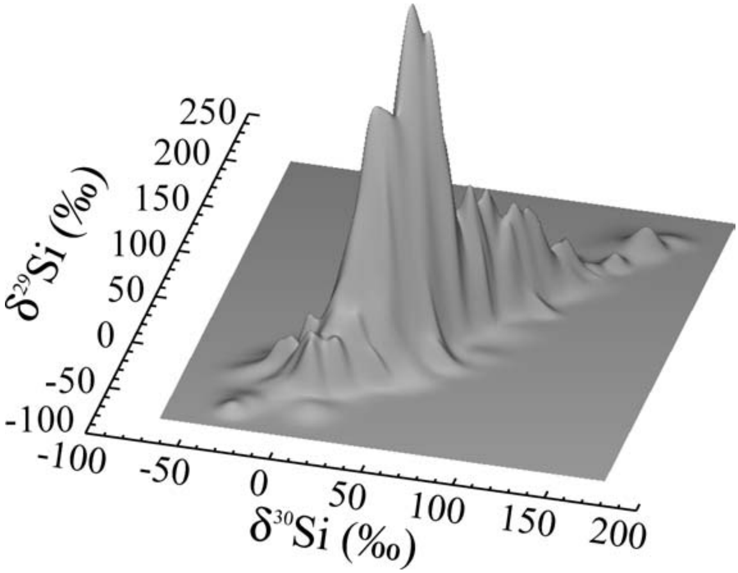

Figure 10 Shaded surface representation of probability distribution of mainstream SiC Si isotopic compositions generated by summing Gaussian distributions corresponding to measurement uncertainties for individual grains (see figure 12 in Nittler & Alexander 2003a).

isotope compositions rule this out for most of the grains within the peaks (Nittler & Alexander 2003a, Smith & Huss 2002).

If the grains live forever, the spectrum reflects the spectrum of the mainstream grain production in the solar neighborhood. More realistically, if the grains have a natural lifetime in the ISM, the spectrum measures (in steady state) the numbers of grains produced during the last mean lifetime of the grains. So the population decline toward the ends of the range may reflect either lower production or shorter lifetime. In the picture based on homogeneous temporal chemical evolution of the galaxy, the abundance peak near the spectral center can be viewed as peaked star formation in the past combined with lifetime loss of the oldest grains (which would be at the metal-poor end). From the galactic-merger picture the peak in the middle would be interpreted in terms of the mixing fractions of the two masses producing more stars having comparable amounts of both end members than the numbers dominated by either end member. Such arguments are important but have not yet been developed. Such arguments also illustrate another way of testing astrophysical questions with the grain data.

5.3.2. SIC GRAINS OF TYPE Y, Z, AND AB The rare SiC subgroups called Y and Z grains (Figures 2 and 3) are also believed to have originated in AGB stars. The Y grains are defined as having $^{12}C/^{13}C > 100$ and Si and N isotope ratios distinct from those of the X grains (Section 4). A detailed study of a large number of Y grains (Amari et al. 2001b) found that they most likely originated in AGB stars of about one-half solar metallicity and probably somewhat higher masses than the mainstream donor stars (3–5 $M_\odot$, compared to $<\sim 2.5\ M_\odot$). The high $^{12}C/^{13}C$ ratios reflect more extensive third dredge-up in such stars than in low-mass solar metallicity stars, as do ^{30}Si excesses relative to the mainstream grains. The Y grains might provide some support for the galactic merger model outlined above (Clayton 2003b). The initial Si isotopic compositions of most Y grains are inferred to lie near the lower end of the mainstream line. Moreover, there is a smooth and rapid increase in the fraction of SiC grains with high $^{12}C/^{13}C$ ratios (a rough proxy for AGB mass) with decreasing $^{29}Si/^{28}Si$ ratios (Nittler & Alexander 2003a). Because more massive stars evolve faster than less massive ones, these results imply a more recent formation for the parent stars of grains near the bottom of the mainstream compared with those with higher $^{29,30}Si/^{28}Si$ ratios. This runs counter to the expectations for the temporal galactic evolution interpretation of the mainstream line, but is compatible with the physical mixing model, assuming that the mixing fraction of the exotic S material increases with time during the merger event.

SiC Z grains have $^{12}C/^{13}C$ ratios similar to the mainstream, but relatively large ^{30}Si enrichments, relative to the mainstream. Hoppe et al. (1997) reported isotopic data for several Z grains and argued that they most likely formed in AGB stars of even lower metallicity than the Y grains, perhaps ∼1/3 solar. This conclusion is also supported by recent Ti data for two Z grains (Amari et al. 2003). Z grain Si isotopic ratios indicate significant dredge-up of *s*-process material. However, the fact that the grains have $^{12}C/^{13}C$ ratios lower than the Y grains despite their parent stars having experienced more extensive AGB dredge-up requires that their parent stars underwent CBP (see Section 5.1.1) while on the AGB (Hoppe et al. 1997, Nittler & Alexander 2003a).

Type A and B grains (hereafter AB), defined as having $^{12}C/^{13}C < 10$, make up about 5% of presolar meteoritic SiC. Although their Si isotopic compositions are similar to mainstream grains, they form a slope 1.5 line on the Si 3-isotope plot, slightly steeper than the mainstream slope 1.3 line (Nittler & Alexander 2003a). Their low $^{12}C/^{13}C$ ratios are similar to those observed in several types of C-rich stars, including J, CH, and R stars and born-again AGB stars (e.g., Sakurai's object; Asplund et al. 1999). Amari et al. (2001c) reported isotopic and trace-element data for a large number of these grains and suggested that J stars and born-again AGB stars are the most likely sources. Unfortunately, these types of ^{13}C-rich C stars are not well understood theoretically, and there are few models with which to confront the grain data. A remarkable recent result is the observation that one AB grain (out of ∼10 measured grains) contains molybdenum with a *p*-process isotope pattern (Savina et al. 2003d). The astrophysical site of the *p* process is still not well established, although Type Ia and II supernovae are often invoked. Although both supernova types have difficulty explaining the global *p*-process distribution, there is no question that O- and Ne-burning shells within them produce locally a *p*-process isotopic signature within individual elements (Arnould 1976).

5.4. O-Rich Dust from Red Giants and AGB Stars

The majority of presolar O-rich grains identified to date are also believed to have formed in low mass giant stars. In particular, the O isotopic ratios of the dominant Group 1 grains (Figure 4) are consistent both with spectroscopic observations of O-rich red giants and AGB stars (Harris & Lambert 1984) and with model calculations of dredge-up processes in these stars (labeled curve in Figure 4) (Boothroyd & Sackmann 1999, Dearborn 1992, El Eid 1994). The isotopic compositions of the Group 3 grains are also explained by dredge-up models if it is assumed that their parent stars had initial compositions enriched in ^{16}O, owing to Galactic chemical evolution (GCE, analogous to above discussion of Si in SiC). The range of ^{17}O/^{16}O ratios in the grains requires a range of masses of the parent stars ($\sim$1.2–5 $M_{\odot}$), whereas the range of ^{18}O/^{16}O ratios requires a range of initial compositions owing to GCE (Boothroyd et al. 1994, Huss et al. 1994, Nittler et al. 1997). A large fraction of the Group 1 and a few of the Group 3 grains also have ^{26}Mg excesses indicating that they formed with high abundances of live ^{26}Al. The inferred ^{26}Al/^{27}Al ratios ($\sim 10^{-3}$) are in reasonably good agreement with expectations for AGB stars (Busso et al. 1999, Mowlavi & Meynet 2000), though the theoretical predictions are plagued by large uncertainties. The presence or absence of ^{26}Al in presolar Al-rich grains can be used as a diagnostic for when the grains formed. Grains with clear evidence for ^{26}Al must have formed in AGB stars undergoing third dredge-up episodes, whereas grains without ^{26}Al must have formed earlier, either on the red giant branch or early on the AGB.

Some 10% of presolar oxide grains (Group 2, Figure 4) have lower ^{18}O/^{16}O ratios and higher inferred ^{26}Al/^{27}Al ratios than can be explained by standard stellar evolutionary models, indicating partial H-burning of the parent stars' envelopes. Two proposed mechanisms for this processing are CBP (see Section 5.1.1) (Figure 4) in low-mass stars and hot-bottom burning (HBB) in more massive ($>$4–5 $M_{\odot}$) AGB stars (Boothroyd et al. 1995). Calculations by Nollett et al. (2003) strongly favor a CBP explanation for most of the Group 2 oxides and indicate that the grain compositions can constrain mixing rates and temperatures of the processing (see Figure 11). Thus, the stardust grains reveal that CBP occurs in AGB stars as well as red giants, and it is hoped that the grain data will help identify the still-unknown physical mechanism(s) driving the extra mixing. HBB is ruled out for most of the Group 2 oxide grains, because it can explain neither grains with intermediate ^{18}O/^{16}O ratios nor grains with ^{17}O/^{16}O ratios $<$0.001 (Boothroyd et al. 1995). However, Nittler et al. (2003) found an extreme Group 2 $MgAl_2O_4$ grain with very high ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg ratios. The composition of this grain is most consistent with an origin in a $\sim$4–5 $M_{\odot}$ AGB star undergoing HBB. This result indicates that intermediate-mass stars were dust contributors to the protosolar cloud. Moreover, it emphasizes the importance of using multiple elements in individual grains to better constrain stellar origins.

The distribution of ^{18}O/^{16}O ratios observed in Group 1 and 3 oxide grains is in good agreement with expectations for GCE (Nittler et al. 1997). Thus, the

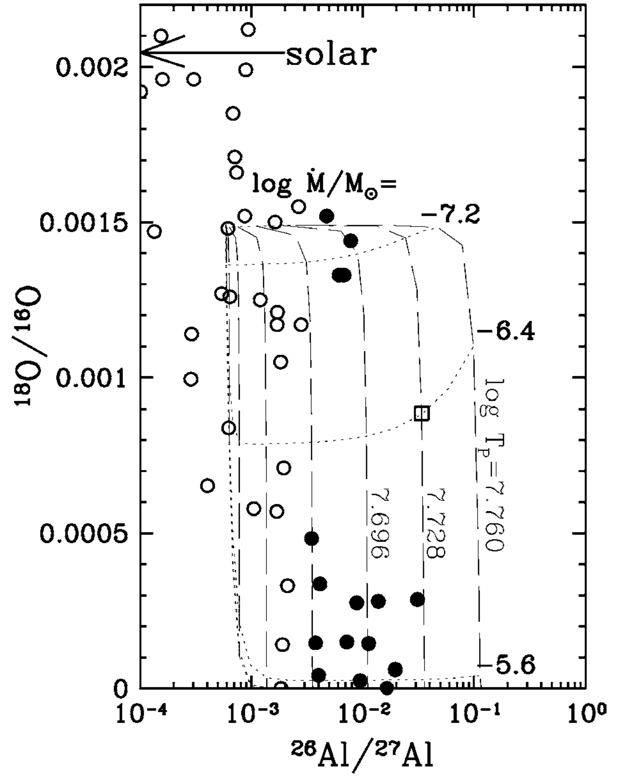

Figure 11 $^{18}O/^{16}O$ ratios plotted against inferred initial $^{26}Al/^{27}Al$ ratios in presolar oxide stardust (*circles*). Superimposed are model calculations for cool-bottom processing (CBP) in low-mass AGB stars with different values of the mass-circulation rate and CBP temperature parameters. Reprinted from figure 6 of Nollett et al. (2003) with permission from the AAS; see original paper for more details.

metallicities of parent stars can be inferred from grain O-isotope ratios and theoretical models. The grains can then be used to trace evolutionary histories of other isotope systems. For example, NanoSIMS measurements of $^{25}Mg/^{24}Mg$ ratios in presolar spinel and corundum grains (Nittler et al. 2003) suggest that this ratio evolves slowly near solar metallicity, consistent both with astronomical observations (Gay & Lambert 2000) and recent GCE models taking into account new AGB star Mg isotope yields (Fenner et al. 2003). Ti isotopes in a few corundum grains also seem to reflect Galactic chemical evolution (Choi et al. 1998, Hoppe et al. 2003). Finally, Nittler & Cowsik (1997) used the inferred masses and metallicities of the parent stars of Group 3 grains to put bounds on the age of the Milky Way. The age they derived (14 Gyr) has large systematic uncertainties, but is remarkably consistent with other estimates, considering it was derived in a fundamentally new way.

5.5. Dust Condensation in Red Giants and AGB Stars

The great binding of the CO molecule (11.3 eV) causes it to form and remain stable at temperatures higher than those required for stability of solids. Because CO is almost inert it removes the lesser abundance of C or O from further reactions. The basis for the carbon-star transition observed in AGB stars rests on this property. When dredge-up of newly synthesized C from the He-burning shell has enriched surface C to the extent that its abundance exceeds that of O, the stellar spectra shift from oxides (e.g., TiO) to carbides (TiC). By the same token, solids that condense within the cooling gas as it moves away from the photosphere will shift from oxides and silicates to carbides (Lodders & Fegley 1995, Sharp & Wasserburg 1995). Oxide and silicate stardust is expected prior to the C-star transition and carbide dust (PAH, graphite, SiC, TiC, etc.) after that transition. Infrared emission features associated with specific dust species are observed around many evolved stars, including silicate and oxide features in O-rich stars (Speck et al. 2000, Waters et al. 1996) and an 11.3 μm SiC feature in many C stars (Blanco et al. 1998, Speck & Hofmeister 2004, Treffers & Cohen 1974). A 21-μm emission feature in preplanetary nebulae has also been attributed to both TiC and to SiC (Speck & Hofmeister 2004). Only tiny clusters (25–127 atoms) of TiC reveal this feature strongly (Helden et al. 2000). Other candidates for that 21-μm emission feature are well reviewed by Speck & Hofmeister (2004).

Because isotopic evidence indicates that many of the presolar stardust grains originated in AGB stars, they provide a new method of testing astronomical identifications of circumstellar mineralogy and theoretical ideas about AGB dust condensation. For example, a broad feature at $\sim$11 μm in O-rich stars is commonly associated with amorphous Al_2O_3 particles (Speck et al. 2000). The cause of a sharp feature at 13 μm is controversial, but popular candidates are crystalline Al_2O_3 and $MgAl_2O_4$ (Posch et al. 1999, Sloan et al. 1996). Interestingly, the TEM observations of two presolar Al_2O_3 grains have, in fact, found that one is crystalline and one is amorphous (Stroud et al. 2002a; R. Stroud, unpublished data), indicating that both types of Al_2O_3 are formed in AGB stars. Also, SiC is known to exist in over 100 different crystal structures (polytypes) in the laboratory. In contrast, TEM (Section 2) analysis of several hundred individual presolar SiC grains found only two polytypes, a cubic phase and the 2H hexagonal phase (Daulton et al. 2002), with the cubic type dominating. These two phases are the ones formed at lowest temperatures in the laboratory and are consistent with expected condensation temperatures for AGB star outflows. Detailed analysis of the 11.3-μm SiC emission line indicates that the cubic phase also dominates the SiC dust forming around present-day AGB stars (Speck et al. 1999). Most TEM analyses of individual SiC grains have found no evidence for subgrains of different minerals (Daulton et al. 2002), but TiC (Bernatowicz et al. 1992) and graphite subgrains (Stroud et al. 2002b) have been reported in two SiC grains.

Glassgold (1996) reviews circumstellar photochemistry around an AGB star and describes five zones of changing circumstances during radial mass flow. For issues of condensation the density and temperature of both gas and solids are relevant.

Spherical symmetry is usually assumed, in which case the number density declines as r^{-2} for constant wind speed, but its magnitude depends on the rate of mass loss, observed in the range 10^{-7} to 10^{-4} $M_\odot$ yr^{-1} (Olofsson 1994), and on the wind speed (Glassgold 1996). The temperature follows from a complete thermal model, or as is more often assumed, from an adiabatic condition assumed within the wind. Usually $T(r)r^p$ = constant, where the exponent p ranges from one-half to one.

In this framework various approaches have been applied to the condensation of dust within these winds. One approach (Allamandola et al. 1989, Cherchneff et al. 1992, Frenklach & Feigelson 1989) attempts a kinetic description of the formation of polycyclic aromatic hydrocarbons (PAH), graphene-like fragments terminated by H on their edges, which then collide and stick together in the buildup of larger soot-like carbon particles. Observed graphite stardust particles from C stars (Bernatowicz et al. 1996) studied in the TEM (Section 2) reveal cores of randomly oriented graphene fragments, which are overlain by graphitized carbon, which supports such agglomeration of large PAH molecules as cores followed by later vapor deposition of hot C gas that coated them with graphite. The pioneering prediction of stardust graphite by Hoyle & Wickramasinghe (1962) had utilized nucleation theory followed by graphite growth from vapor carbon in their paper on graphite from C stars. Bernatowicz et al. (1996) did the same in their penetrating analysis of graphite growth and comparison with the observed graphite particles. Salpeter (1974) utilized more detailed nucleation theory in a similar approach.

The simplest approach, or idealization, is that of assuming that the gas and solids are in thermodynamic equilibrium, which can, given enough time, partition each element between gas and various solids according to free energies. Although this approach can identify stable solids, it will not in itself yield grain sizes. This equilibrium approach to C stars has been studied most thoroughly by Sharp & Wasserburg (1995) and Lodders & Fegley (1995) and applied to laboratory stardust by Bernatowicz et al. (1996). This approach has found good agreement both in the abundance patterns of trace elements in SiC grains and in the order of dust condensation (e.g., TiC before graphite before SiC) inferred from presolar grain properties.

In their study of graphite stardust, Bernatowicz et al. (1996) found frequent TiC subgrains near the center of graphite grains. They concluded that TiC condensed first and was occluded by overgrowth of graphite after Ti exhaustion from the gas. Equilibrium calculations showed that at higher temperature TiC could be more stable than graphite, but only if C abundance slightly exceeded O abundance (to raise the ratio of Ti to that C not bound in CO) and if the ambient pressure was surprisingly high for AGB winds. They also showed by numerical integrations within the wind that larger pressure was required to grow the large TiC crystals in the allotted wind time. They speculated that a very high mass-loss-rate superwind near the end of AGB phase might provide sufficiently high density to meet the time constraint for TiC growth. We would add the possibility that the wind may not be uniform (spherically symmetric) and that some grains might spend longer than average time in the growth zone before their gaseous parcel is picked up by the wind forces. It may also be worthwhile to reconsider the approximation that the AGB photosphere is of uniform composition during dredge-ups, considering that the dredge-up channels are local and require time to mix with the entire photosphere; however, we know of no cases in which TiC and TiO molecules have been found in the same AGB atmosphere.

6. NOVA GRAINS

Possible isotopic identifiers of presolar nova grains arose as part of the initial speculations about isotopically abnormal stardust. Clayton & Hoyle (1976) discussed the special nucleosynthesis in the nova thermonuclear runaway with an eye toward the condensation of carbon grains during the expansion phase, and predicted several isotopic characteristics of such grains. They focused on extinct radioactivity ^{22}Na and ^{26}Al within the rapidly condensed grains, leading to fossil excesses of ^{22}Ne and ^{26}Mg in the grains, and on the large excesses of ^{13}C, ^{15}N, and ^{30}Si that are produced in the explosions and that would also characterize and identify the condensates (Gehrz et al. 1998; José & Hernanz 1998; José et al. 1997,1999; Starrfield et al. 1974,1998). Clayton & Wickramasinghe (1976) modeled the condensation in a time-dependent way, considering only graphite as the prototype of carbon dust, although SiC condensation should also be present. They were inspired by an infrared observation of rapid dust condensation within nova Serpentis 1970 (Geisel et al. 1970). More recent infrared observations indicate that most novae produce dust and in fact evidence for silicates, SiC, C, and/or Fe dust exists for several systems (see Gehrz et al. 1998 and references therein).

Regardless of these predictions for novae dust, such grains have proven to be quite rare in the total population of presolar grains in meteorites. Fewer than ten grains of SiC and graphite have been reported with isotopic signatures strongly pointing to a nova origin (Amari et al. 2001a, Nittler & Alexander 2003a). Amari et al. (2001a) provide a thorough description of what is known about six candidate nova grains and of the nova context for their condensation. A common diagnostic of most nova nucleosynthesis models is very low ^{12}C/^{13}C and ^{14}N/^{15}N ratios due to high-temperature H-burning and four SiC nova candidate grains showing these isotope signatures are visible in Figure 2. The grains are explained by nova models as long as the white-dwarf mass is as great as $1.25M_\odot$, in order to yield thermonuclear runaways hot enough to produce the observed (Figure 3) ^{30}Si richness (José & Hernanz 1998, Starrfield et al. 1998). In addition, Nichols et al. (2004) found ^{22}Ne excesses, not accompanied by He, in $\sim$20 individual presolar graphite grains measured by laser-ablation noble gas mass spectrometry. These ^{22}Ne excesses are best explained as arising from in situ decay of ^{22}Na (2.75 yr) as originally predicted for nova dust by Clayton (1975b) and Clayton & Hoyle (1976). However, no individual SiC grains have been identified with this isotope signature.

Predictions of nova grain properties are hampered by multiple uncertainties concerning the realism of the hydrodynamic nova models, which are usually one dimensional: For example, What is the pre-explosion history and mixing leading up to the thermonuclear runaway? What is the thermal history of its ejected mass? By what processes does condensation occur? Does interaction with an accretion disk play a role? Gallagher & Starrfield (1978) have provided a good description of the many uncertain aspects of novae as a phenomenon. Abundant H must certainly play a role in the condensation chemistry (Frenklach et al. 1989), unlike within the inner zones of supernova, where the chemical kinetics are H free (Clayton et al. 1999, 2001). It seems possible that the CO molecule is not sufficiently stable during the condensation epoch (several weeks) to remove carbon from condensation in those circumstances where it is less abundant than oxygen. Nova radioactivity and an intense UV radiation field may disrupt CO faster than the expansion rate (Evans 1998), but this must be modeled for novae as it has been for supernovae (Clayton et al. 1999, Liu & Dalgarno 1995). Many approaches to condensation theory can be found (Cherchneff & Millar 1998 and references therein; Gail & Sedlmayr 1999, Salpeter 1977). Amari et al. (2001a) present reasons why their six isotopically appropriate grains are not from other types of stellar death and therefore are most likely from the novae that provide an isotopic match. But we remark that uncertainty over the condensation processes for other SiC grains still leaves ambiguity in the expectations of their isotopic properties. Although no supernova zone, or gaseous mix thereof, has the observed properties of ^{15}N richness, ^{13}C richness, and ^{30}Si richness found in ONe novae, dynamic histories following the reverse shocks within young supernova interiors may afford realistic alternatives (Deneault et al. 2003). For example, small grains of ^{15}N-rich and ^{30}Si-rich Si_3N_4 from the interior zones (a known refractory supernova grain) could perhaps be propelled forward into ^{13}C-rich envelope gas following a reverse shock that slows the gas, perhaps even while condensation still occurs. To consider this would require thermal histories of the changing composition of the growing grain as it evolves toward SiC. Such complicated dynamic histories have barely been considered to date.

7. CONCLUDING REMARKS

Presolar stardust has rapidly emerged as a new area of astronomy. In just 15 years, their existence has evolved from a bewildering new discovery into the best of all techniques available for measuring isotopic abundance ratios with high precision in stars. And it is the only way to observe abundance ratios in stars that evolved and died prior to the birth of the Solar System. Such stars have special significance to the evolution of the Milky Way. Their precisely measured isotopic ratios in many chemical elements endows these gemlike refractory minerals with applications to stellar structure and evolution, to the chemical evolution of the Milky Way, mostly 7–5 Gyr ago, to new nucleosynthesis insights, and to otherwise unmeasurable details of kinetic condensation chemistry. This rich harvest is compromised only by the fact that the donor stars cannot be seen, as they have been gone this past 4.7 Gyr or more. Their stardust bears no label, save that of measurable properties. The nature and evolutionary state of the donor stars must be ascertained from the detailed properties, mostly isotopic and structural, of each grain and of the way each grain fits into the spectrum of several thousand stardust grains that have been analyzed to date. The rapidly growing numbers of analyzed grains allows evolutionary trends within their distinct families to be identified. To the reader wishing to build better familiarity we recommend two books, *Astrophysical Implications of the Laboratory Study of Presolar Materials* (Bernatowicz & Zinner 1997) and *Handbook of Isotopes in the Cosmos* (Clayton 2003a).

The study of myriad presolar stardust properties has been made possible by development of a huge number of microanalytical tools and techniques (see Section 2). Those laboratories that have specialized in the micron-scale characterizations have achieved levels of technical mastery unanticipated a decade ago. To date, the grains studied have been those expected when hot atomic gas cools slowly enough for condensation to occur thermally. Local thermodynamic equilibrium provides the first approximation to the theoretical expectations, and in broad strokes, the grains found are those anticipated on the basis of that theoretical idea. This confirms stellar mass loss as their sites of origin. And the isotopic ratios are so extreme that mixing of stellar ejecta with interstellar matter prior to condensation is all but ruled out for almost all grains. These facts have led to the current belief that we do indeed examine solid samples of individual stars. The stardust grains may be thought of as measurements of individual stars made prior to solar birth. Laboratory measurements develop that ancient "film."

Presolar dust clearly constitutes a much more diverse collection of interstellar chemistry. Grains formed by low-temperature interstellar chemistry have been largely destroyed by the search procedures used to isolate the stardust grains, but one can anticipate that these too will be found by future nondestructive techniques. For this reason, we recommend that the term stardust, rather than presolar grains, be used for the families of particles that we know of today, namely the small fraction of interstellar dust that has condensed thermally within individual stars.

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