

Frontiers

Presolar stardust in meteorites: recent advances and scientific frontiers

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Abstract

Grains of stardust that formed in stellar outflows prior to the formation of the solar system survive intact as trace constituents of primitive meteorites. The presolar origin of the grains is indicated by enormous isotopic ratio variations compared to solar system materials. Identified presolar phases include diamond, silicon carbide, graphite, silicon nitride, corundum, spinel, hibonite, titanium oxide, and, most recently, silicates. Sub-grains of refractory carbides (e.g. TiC), and Fe–Ni metal have also been observed within individual presolar graphite grains. Isotopic compositions indicate that the grains formed in red giants, asymptotic giant branch (AGB) stars, supernovae and novae; thus they provide unique insights into the evolution of and nucleosynthesis within these environments. Some of the isotopic variations also reflect the chemical evolution of the galaxy and can be used to constrain corresponding models. Presolar grain microstructures provide information about physical and chemical conditions of dust formation in stellar environments; recent studies have focused on graphite grains from supernovae as well as SiC and corundum from AGB stars. The survival of presolar grains in different classes of meteorites has important implications for early solar system evolution. Recent analytical developments, including resonance ionization mass spectrometry, high spatial resolution secondary ion mass spectrometry and site-selective ion milling, should help solve many outstanding problems but are likely to also introduce new surprises.

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1. Introduction

Almost all of the isotopes of the chemical elements heavier than He are synthesized by nuclear reactions in the interiors of stars. The freshly syn-

thesized isotopes, often condensed into dust grains, are expelled into the interstellar medium by stellar winds or explosions and become part of the raw material from which new generations of stars are born. As a result, the bulk elemental and isotopic composition of the solar system is due to a mixture of material from a vast number of stellar sources. Most of this material was homogenized either in the interstellar medium or early solar system, with the result that isotopic

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ratios in diverse solar system materials (the Sun, planets, etc.) are highly uniform. One of the most remarkable recent discoveries in space science was that primitive meteorites contain tiny (nm to μm) dust grains that escaped this large-scale isotopic homogenization. Isotopic variations in these grains can span several orders of magnitude, too large to be explained by physical or chemical fractionations, which are typically of order percent or smaller. In fact, the only viable explanation for the isotopic compositions is nuclear reactions occurring within stars, indicating that the grains are preserved presolar stardust. Each grain is essentially a frozen piece of a single star that ended its life before the formation of the solar system. Fig. 1 shows example images of presolar grains and their formation environments.

Prior to the discovery of meteoritic stardust, essentially all information about stars came from the electromagnetic radiation that they emit. Moreover, our knowledge of interstellar dust was based solely on how it affects background starlight. Presolar grains are exciting because they bring bona fide stellar materials into the laboratory, where the full battery of modern micro- and nano-analytical techniques can be brought to bear on them. Although astronomical spectroscopy can reveal chemical (and in rare cases isotopic) information about stars, both the number of measurable elements and the achievable precision is much more limited than can be attained in a modern geochemistry laboratory, even on micron-sized dust particles. Thus, models of stellar evolution and nucleosynthesis can be tested more stringently than previously possible. Furthermore, direct laboratory observations of dust reveal far more about its properties than can be obtained by inference from its effects on starlight. As reviewed here, the grains provide information com-

plementary to astronomical observations on a wide array of subjects, including the chemical evolution of the galaxy, stellar nucleosynthesis and mixing, dust formation in stellar environments, dust processing in the interstellar medium and the formation of the solar system.

In this brief review, I highlight some recent advances in presolar grain research and suggest where new insights might come. A recurrent theme is how progress in this field has gone hand in hand with the development of new analytical techniques. There have been several reviews of the subject over the last decade [1–3] and the reader is referred to these and the current literature for more details on the topics discussed here.

2. Isolation and analysis of presolar grains

Hints that presolar grains might be present in meteorites surfaced in the 1960s, but it was the development of both new chemical dissolution techniques and new isotopic microanalysis techniques, especially secondary ion mass spectrometry (SIMS), that finally led to their successful isolation and identification as presolar stardust in the late 1980s. The history of this discovery has been reviewed by [2]. The known types of presolar grains are summarized in Table 1; example micrographs are shown in Fig. 1.

It is fortuitous that among the mineral phases that condense in stars are tough, acid-resistant phases like SiC and Al_2O_3 , enabling their isolation from meteorites by essentially dissolving away everything else in harsh acids. This has often been likened to burning down a haystack to find a hidden needle and immediately raises the crucial issue of sampling bias. There are probably other presolar phases present in meteorites,

Fig. 1. Images of presolar grains and their stellar sources. (a) 3- μm presolar SiC grain. (b) 0.8- μm presolar spinel grain (this grain has been sputtered by an ion beam and is sitting atop a gold pedestal). (c) 5- μm presolar graphite grain. (d) TEM image of a ~ 100 -nm-thick slice of a ~ 1 - μm presolar graphite grain. The dotted ellipse indicates a cluster of tiny TiC crystals that probably served as a nucleation center for the growing graphite spherule. (e) *Hubble Space Telescope* image of planetary nebula NGC 6751, a cloud of gas and dust thrown off by a dying star. (f) *Chandra X-ray Observatory* image of SN remnant Cassiopeia A, the remains of a massive star that exploded $\sim 10\,000$ years ago. Red, green and blue correspond to X-rays of low, medium, and high energy, respectively, and indicate that material has been mixed in the SN ejecta. Most presolar grains are believed to have originated in stellar environments like those in panels e and f. Photo credits: (a) Rhonda Stroud; (b) author; (c,d) Tom Bernatowicz; (e) Hubble Heritage Team (STScI/AURA); (f) NASA/CXC/SAO/Rutgers/J. Hughes.

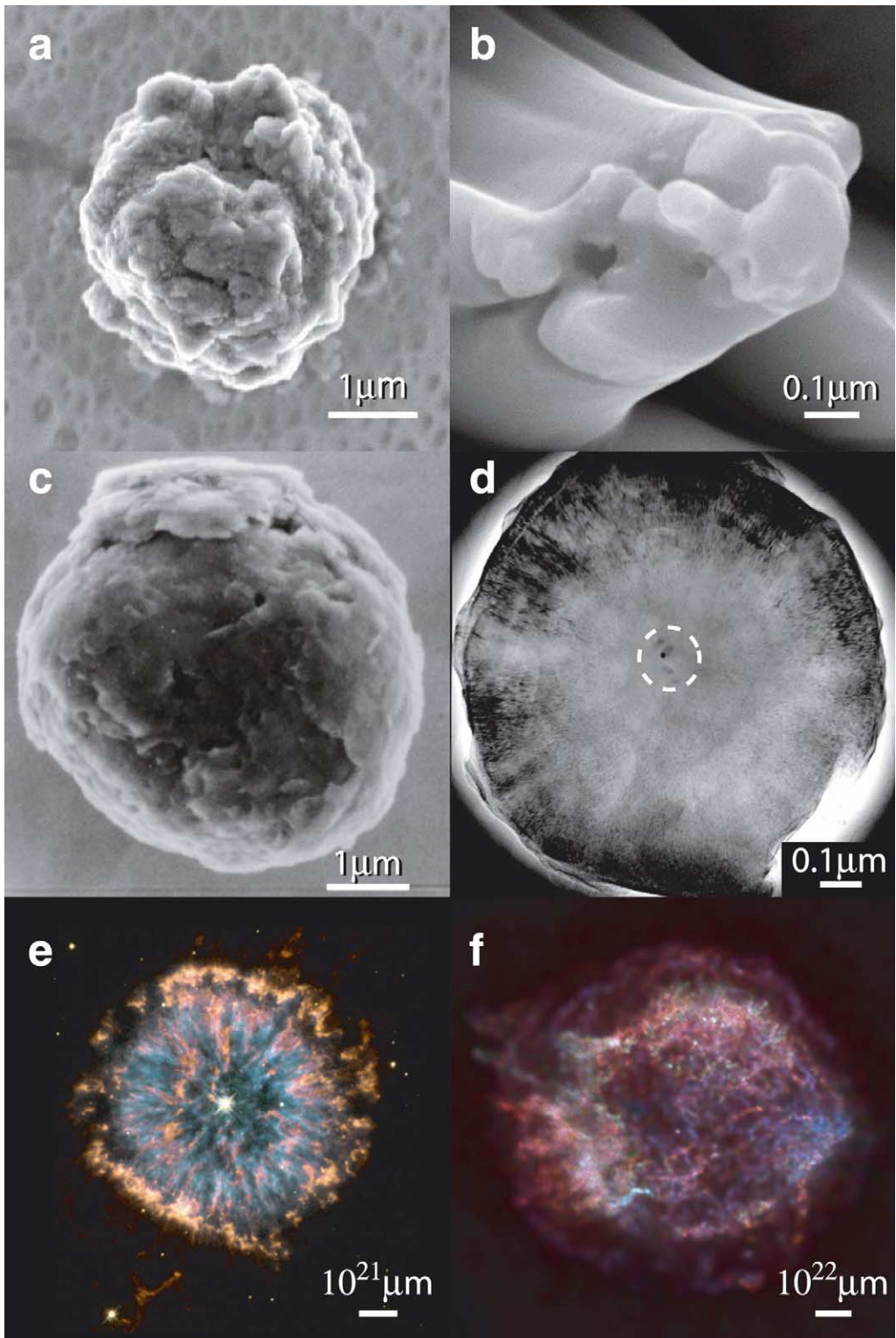


Table 1
Types of presolar grains in meteorites

Phase	Abundance (ppm)	Size
Nanodiamond	1400 ^a [71]	2 nm
SiC	14 ^a [71]	0.1–20 μm
Graphite	10 ^a [71]	1–20 μm
TiC, ZrC, MoC, RuC, FeC, Fe–Ni metal	? (sub-grains within presolar graphite) [12]	5–220 nm
Si ₃ N ₄	> 0.002 ^b [21]	~ 1 μm
Corundum (Al ₂ O ₃)	~ 0.05 ^c [16]	0.5–3 μm
Spinel (MgAl ₂ O ₄)	≤ 0.05 ^c [16,20,58]	0.1–3 μm
Hibonite (CaAl ₁₂ O ₁₉)	0.002 (three grains) ^c [17]	~ 2 μm
TiO ₂	? (one grain) ^c [18]	~ 1 μm

^a Abundance from: Orgueil (CI1).

^b Abundance from: Murchison (CM2).

^c Abundance from: unequilibrated ordinary chondrites.

especially silicates, which are dissolved in the procedures currently used to concentrate presolar grains. An additional bias comes from grain size: most work on individual presolar grains has been on particles at least 1 μm in diameter. In contrast, typical circumstellar and interstellar grain sizes inferred from astronomical observations are closer to 0.1 μm.

Ultimately, obtaining a representative sample of the presolar solid materials that went into forming the solar system will require new chemical and/or microanalytical techniques, many of which are under development. Two recent advances discussed here are resonance ionization mass spectrometry (RIMS), which allows measurement of ppm-level trace elements in micron-sized grains with elimination of isobaric interferences, and the new Cameca NanoSIMS 50 ion probe, which allows isotopic measurements of major and minor elements to be made on a 50–200 nm scale, compared with the 1 μm scale of previous SIMS instruments. As a dramatic example of the new frontier opened by the NanoSIMS, Messenger et al. [4] recently reported the in situ discovery of sub-micron presolar silicates in interplanetary dust particles.

3. Types of presolar grains

Nanodiamonds (~2.5 nm diameter) are the most abundant, but least understood type of pre-

solar grains. They are identified as presolar on the basis of containing highly unusual Xe and Te isotopic ratios, which seem to reflect nucleosynthetic processes in supernovae (SN) [5,6]. However, their small size precludes isotopic measurement of individual grains and the average C isotopic composition (determined by measurements of large aggregates of grains) is indistinguishable from that of the solar system. Making matters worse is the fact that the Xe abundance is such that only about one in a million diamond grains contains a single Xe atom! Nitrogen is much more abundant and has a ¹⁵N/¹⁴N ratio some 35% lower than the terrestrial atmosphere, apparently arguing for a presolar origin as well. However, a recent measurement of the N isotopic composition of Jupiter [7] suggests that the solar ¹⁵N/¹⁴N ratio is very similar to that observed in the meteoritic nanodiamonds. 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 SN explosions (see also [8]).

SiC is the best-studied type of presolar grain [9]. Isotopic measurements of both single grains and aggregates of many grains have revealed anomalous isotopic compositions in essentially every major, minor and trace element that has been measured. Figs. 2 and 3 show the observed distributions of Si (given as permil variations from solar values), C, and N isotopic ratios in individual presolar SiC grains. A significant fraction of the grains also contains elevated ²⁶Mg/

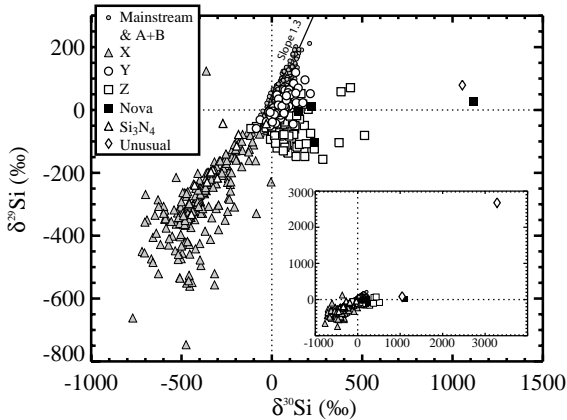


Fig. 2. Silicon isotopic ratios of presolar SiC and Si₃N₄ grains in meteorites, expressed as delta values: $\delta^i\text{Si} = 10^3 \times [(^{i}\text{Si}/^{28}\text{Si})_{\text{grain}} / (^{i}\text{Si}/^{28}\text{Si})_{\text{Sun}} - 1]$. Data are from [9] and references therein, [21,43,44,46,47,59], and unpublished from the author's laboratory. The grains have been divided into subgroups on the basis of their Si, C and N isotopic ratios; 90% of the grains belong to the mainstream group. Dashed lines indicate solar isotopic ratios in this and subsequent figures. The mainstream grains form a line with slope 1.3, in contrast to the line of slope ~ 0.5 expected for evolution in an AGB star.

²⁴Mg ratios, indicating that they contained live radioactive ²⁶Al (half-life = 720 000 years) when they formed. The grains have been divided into several groups on the basis of having similar isotopic compositions. Some 90% of the grains be-

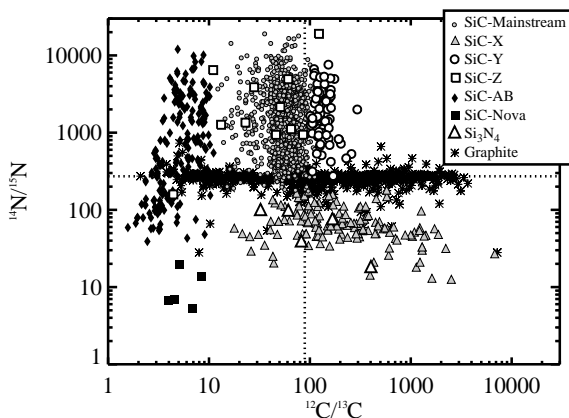


Fig. 3. Carbon and nitrogen isotopic ratios of presolar SiC, Si₃N₄ and graphite grains. Graphite data are from [11]; see Fig. 1 for other data sources. Solar system ranges are $< 10\%$ for C, $< \text{factor of } 2$ for N.

long to the 'mainstream' population; the other groups and ungrouped grains make up the remainder. Comparison of the observed isotopic distributions with both astronomical observations and theoretical models has allowed identification of particular types of stars as the sources of most of the grain groups. For example, as discussed in greater detail later, mainstream grains are inferred to have formed in AGB stars (see Section 4) and X-grains in SN. Note that the data shown in Figs. 2 and 3 were acquired on grains larger than 1 μm . Recent NanoSIMS measurements of sub-micron SiC grains show very similar ranges of C and N isotope ratios [10], but Si measurements have not been reported.

Presolar graphite is less well understood than presolar SiC. Both round and non-round graphite grains have been found in meteorite residues, but only the round grains have isotopic signatures unambiguously pointing to a circumstellar origin (e.g. [11]). Refractory carbides and metal have also been found as tiny sub-grains within individual presolar graphite grains [12–14], many probably served as nucleation seeds for the graphite condensation. It is apparent from Fig. 3 that the isotopic distributions of SiC and graphite are distinct: most SiC grains have isotopically heavy C, whereas a majority of the graphite grains has light C. The ¹⁴N/¹⁵N ratios in graphite are largely similar to the terrestrial value, probably reflecting contamination¹. About one-third of presolar graphite grains have relatively low density ($\rho < 2.15 \text{ g/cm}^3$) and have somewhat higher trace-element contents than the denser grains. The isotopic signatures of these grains are in many ways similar to those observed in the rare SiC X-grains and probably originated in SN [15]. The higher-density grains are believed to have originated from a range of stellar environments including AGB stars, SN and novae.

In contrast to the thousands of measured indi-

¹ High-density presolar graphite has very low trace-element contents and hence is more susceptible to contamination than other presolar grain types, e.g. SiC. Nevertheless, in many cases, the true presolar grain isotopic signatures, especially for minor and trace elements, might be even more extreme than the measured values.

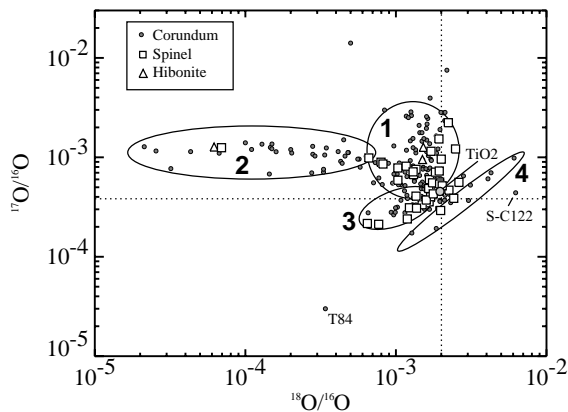


Fig. 4. Oxygen isotopic ratios measured in presolar oxide grains from meteorites. Data are from [19] and references therein, [16,17,57,58], and unpublished from the author's laboratory, Washington University, and Caltech. Ellipses indicate grain groups defined by [16].

vidual SiC and graphite grains, only ~ 200 presolar oxides (mostly corundum and spinel) have been identified to date in meteorite acid residues [16–19]. The difficulty in locating such grains 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 microanalysis techniques. O isotopic ratios span several orders of magnitude in the presolar oxide grains (Fig. 4). Many of the grains also show evidence for high initial $^{26}\text{Al}/^{27}\text{Al}$ ratios when they formed and a handful of grains have been analyzed for N, K and/or Ti as well. The oxide grains have been divided into four groups (labeled ellipses in Fig. 4), on the basis of their O isotopic ratios [16]. 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, though a SN origin has been suggested for a few grains and there is still no satisfactory explanation for several grains, including Group 4. Significant recent advances in presolar oxide grain studies were the discovery of two new phases, hibonite [17] and TiO_2 [18]. Also, recent NanoSIMS measurements have indicated that sub-micron presolar

lar spinel is much more abundant than spinel of $> 1 \mu\text{m}$ in size [20].

A few presolar silicon nitride grains have also been found in meteorite residues [21,22]. These grains have isotopic compositions similar to those of the rare SiC X-grains and, like those, probably formed in SN.

4. Stellar evolution and nucleosynthesis

Understanding presolar grains requires some basic concepts of stellar evolution and nucleosynthesis, so I will briefly review this subject (see e.g. [3] or the many available textbooks for more details). Stars are powered by nuclear reactions and over the course of their lives, light nuclei are fused into heavier ones. There are several distinct astrophysical processes of nucleosynthesis that occur in different types of stars during different evolutionary stages. All stars spend most of their lives fusing hydrogen into helium (H-burning) in their cores. When core H is exhausted in its core, a star cools and expands, becoming a red giant. During this phase, convective mixing of some of the products of H-burning into the stellar envelope changes the surface isotopic composition (the 'first dredge-up').

Following the red giant phase is a period of core He-burning, when helium nuclei are fused into ^{12}C , some of which gets further converted into ^{16}O . Eventually, the core He is exhausted; at this point the evolution of low- and intermediate-mass stars ($M < 8M_{\odot}$) diverges from that of more massive stars. In the lighter stars, core pressures and temperatures are not high enough for further fusion reactions to occur and the core remains an inert ball of gas. The outer layers expand, however, and the star becomes a red giant again, this time known as an asymptotic giant branch (AGB) star. During this phase, H-burning and He-burning continue in thin shells just outside the core. The shell-burning produces large amounts of ^{12}C and many heavy elements that are synthesized by slow capture of neutrons by lighter nuclei (*s*-process nucleosynthesis). Periodic convection episodes (third dredge-up) mixes shell material into the envelope [23], gradually increas-

ing the envelope abundances of ^{12}C and *s*-process isotopes. When the envelope C/O ratio exceeds unity, the star becomes known as a carbon star and carbonaceous dust such as SiC and graphite is observed to condense². Large stellar winds ultimately lead to the loss of the outer stellar layers, forming a planetary nebula (e.g. Fig. 1e), with the core ending its life as a white dwarf star.

Following He-burning, stars more massive than $8M_{\odot}$ continue to fuse heavier and heavier elements in their cores. The result is an onion-like structure with each layer having experienced a more extensive nuclear burning history than the outwardly adjacent layer. Once the inner core is primarily composed of iron, nuclear fusion can produce no more energy and the core collapses and rebounds. The resulting shock wave ejects most of the stellar material into the interstellar medium, an event known as a SN explosion of type II (SNII). The shock wave also heats the material, causing further nuclear reactions to synthesize new nuclei (explosive nucleosynthesis). SNII are the major sources of many of the elements heavier than He in the galaxy [24]. In particular, many elements heavier than iron are made by photodisintegration and proton capture (*p*-process) and rapid neutron capture (*r*-process).

The endpoint of evolution of binary stars can differ strongly from that for single stars. Most notably, if one star of a binary pair has evolved to the white dwarf stage, it can gravitationally accrete material from its partner. As the accreted material builds up on the surface of the white dwarf, instabilities eventually lead to an explosion as a nova or SN of type Ia (SNIa). In novae, only the H-rich accreted layer explodes; the high-temperature H-burning that results may be an important contributor to some nuclei in the galaxy, including ^{13}C , ^{15}N , and ^{17}O . In SNIa, the entire white dwarf is disrupted in a thermonuclear explosion. These stars are believed to be the primary sources of ^{56}Fe and a few other isotopes in the galaxy.

A key parameter in studies of abundances in the cosmos is ‘metallicity’, defined as the mass fraction of material composed of elements heavier than He (known as ‘metals’ to astronomers). Solar metallicity is $\sim 2\%$. The nucleosynthetic yields of stars depend strongly on metallicity, so that elemental and isotopic abundances change with time (and location) in the galaxy as generations of stars are born, live their lives and expel newly synthesized material into the interstellar medium. The theory of Galactic Chemical Evolution describes this process (e.g. [25]).

5. Frontiers in presolar grain research

5.1. Nucleosynthesis in low- and intermediate-mass stars

It is now well established that the majority of presolar SiC grains originated in C-rich AGB stars and most of the oxide grains formed in O-rich red giants and AGB stars. The strongest evidence for both conclusions is the similarity of measured isotope distributions (C in SiC, O in oxides) with direct spectroscopic isotope measurements of the stars (e.g. [26,27]). Infrared spectroscopic features of SiC and corundum have also been observed around such stars [28,29]. Moreover, the ranges of many isotopic ratios observed in the grains are in good quantitative agreement with theoretical predictions for these types of stars [9,16,30]. The agreement extends to trace elements in SiC: measurements of Ne, Xe, Kr, Sr, Ba, Nd, Sm and Dy in bulk aggregates of grains show excesses of isotopes believed to be produced by the *s*-process [9], associated with AGB stars as discussed above.

One of the most exciting recent advances has been the development of the RIMS technique, which allows isotopic analysis of heavy trace (ppm-level) elements in micron-sized grains. RIMS has now been successfully applied to determine Mo, Zr, Sr, Ba and Fe isotopic ratios in individual presolar SiC and graphite grains [31–37]. Some SiC and graphite Mo isotopic data are plotted in Fig. 5. The mainstream SiC grains and some high-density graphite grains show the iso-

² The very stable CO molecule controls condensation chemistry in thermodynamic equilibrium: if $C < O$, O-rich phases form, if $C > O$, reduced ones do.

topic patterns expected for AGB star nucleosynthesis; namely enrichment of the *s*-process only ^{96}Mo , relative to isotopes produced in part by other processes (*r*-process for $^{95,97}\text{Mo}$). For the most part, these data, as well as that for the other Mo isotopes and several other analyzed elements, are in excellent agreement with theoretical models of AGB stars [23,38]. Beyond just confirming an AGB origin, the trace-element data can be used to constrain still-uncertain parameters in the stellar models and to constrain the masses of the parent stars. In contrast to Mo and Zr, the first Fe isotope data of individual mainstream SiC grains [33] do not agree well with predictions, suggesting that the nuclear history of this element is not yet well understood [39].

Although many isotopic ratios observed in the grains are well explained by standard stellar mod-

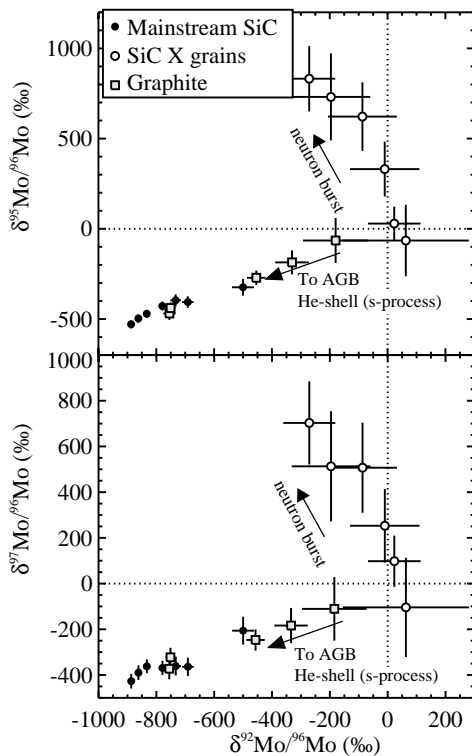


Fig. 5. Mo isotopic ratios of individual presolar SiC and high-density graphite grains, measured by RIMS [32,34,35]. Mainstream grains show patterns expected for *s*-process nucleosynthesis in parent AGB stars. The SN-derived SiC X grains show patterns well explained by a neutron-burst model [55].

els, some of the notable exceptions have yielded new insights into stellar evolution. For example, there are important differences in detail between the observed SiC C and N isotopic ratios and those predicted by standard AGB models. These differences provide support to the hypothesis that an ‘extra’ mixing process (beyond that predicted by standard hydrodynamical stellar models) occurs in low-mass red giants, resulting in partial H-burning of the star’s envelope material. This process (termed cool-bottom processing (CBP) by [40]) had previously been invoked to explain anomalous astronomical observations [30] but the grain data provide additional information about this still-enigmatic process (e.g. [41]). Moreover, CBP has been shown to be a likely explanation for the very low $^{18}\text{O}/^{16}\text{O}$ and high inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios of Group 2 presolar oxide grains [19,40,42]. In fact, the presolar grain data provide strong evidence that CBP probably occurs in low-mass AGB stars in addition to red giants, a result not previously known from astronomical observations.

SiC Y grains ($\sim 2\%$) and Z grains ($\sim 2\text{--}3\%$) differ from mainstream grains in their C and Si isotopic compositions (Figs. 2 and 3). Recent studies indicated that these grains most likely also originated in AGB stars, but the Y grain progenitors had to have had initial metallicities a factor of ~ 2 lower than the Sun [43], and Z grain parent stars even lower metallicity (\sim one-third solar) [44]. Thus, presolar grains can be used to probe nucleosynthesis in stars with a considerable range of chemical compositions.

The stellar origin of the A+B SiC grains ($\sim 5\%$, defined as having $^{12}\text{C}/^{13}\text{C} < 10$) is ambiguous. There are a few classes of C-rich stars with similar observed C-isotope signatures, including J, R and CH stars, and so-called ‘born-again’ AGB stars [45]. Isotopic and trace-element data from a large number of A+B grains suggest a connection to J stars and ‘born-again’ AGB stars [46], but the evolution of these stars is unfortunately still poorly understood.

5.2. Nucleosynthesis in SN

SiC of type X, low-density graphite, and preso-

lar Si_3N_4 grains are all believed to have originated in SN [15]. A SN origin has also been suggested for a ‘singular’ SiC grain [47] with huge $^{29,30}\text{Si}$ excesses (Fig. 2, inset). Many of the isotopic signatures of these grains (e.g. heavy N, light C, ^{28}Si excesses, very high inferred $^{26}\text{Al}/^{27}\text{Al}$) are qualitatively consistent with SN models, but the smoking gun for a SN origin came in the form of excess ^{44}Ca , attributable to in situ decay of radioactive ^{44}Ti [48]. This isotope has a half-life of 60 years and is synthesized only in SN. Recent NanoSIMS measurements indicating the initial presence of live ^{49}V (half-life = 330 days) in several SiC X grains [49] provide further strong evidence for a SN origin. Both SNII and SNIa have been considered as potential sources [15,50].

Attempts to quantitatively reproduce isotopic compositions of the SN grains have met with some success [51,52]. A SNII origin requires selective microscopic mixing of material from the various onion layers. Extensive mixing in SN ejecta is both theoretically expected [53] and observed [54] (see also Fig. 1f), but neither astronomical observations nor theory can yet address the mixing scales required by the grain data. A SNIa origin relaxes some of the mixing requirements, but introduces difficulties of its own [52].

Additional clues to the origin of SN grains come from trace-element isotopic measurements by RIMS. Mo, Zr, Sr, Ba, and Fe have all been measured in individual SiC X grains [34,39]. As expected, these data are clearly distinct from those in mainstream grains (Fig. 5). They are also distinct from prior expectations that SN grains should show isotopic characteristics of the r - and/or p -process. Rather, the data seem to point toward a novel nucleosynthetic process, a ‘neutron burst’ [55]. The physical location within a SN explosion of the neutron burst is unknown, but its identification would help better constrain the origin of the SN grains and the mixing processes responsible for their compositions. Note that many of the isotopic signatures are much less extreme than expected for pure SN material. Clayton et al. [56] recently suggested that this puzzle might be explained by a model in which a freshly condensed grain passes at high velocity through the SN ejecta, with subsequent implanta-

tion of atoms from the ambient gas and dilution of the original isotope signatures.

A SN origin has also been suggested for two presolar corundum grains (Fig. 4). Oxide grain T84 has close to pure ^{16}O and is likely a condensate from the inner ^{16}O -rich SN zones [57]. Corundum grain S-C122 has a $3\times$ solar $^{18}\text{O}/^{16}\text{O}$ ratio and has been suggested to have formed from a mixture of outer H- and He-rich SNII layers [58]. This grain has a $^{17}\text{O}/^{16}\text{O}$ ratio smaller than predicted for such a mixture and no other compelling SNII isotope signatures. Nonetheless, this suggestion raises the intriguing possibility that the ^{18}O -enriched Group 4 oxides formed from SNII. These grains form a linear array on the O 3-isotope plot (Fig. 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 [24], though some fairly selective mixing of layers would have to occur to make it work quantitatively.

5.3. Nucleosynthesis in novae

Amari et al. [59] reported five SiC grains and one graphite grain with very low $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$ ratios, high inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios and large ^{30}Si enrichments. These compositions point unambiguously to an origin in nova explosions. Neon data for a few graphite grains also suggest a nova origin [60]. Detailed comparison with models suggests an origin in O,Ne-rich novae, rather than C,O-rich ones. This conclusion is tempered by large uncertainties in current models, but it is clear that the grains have great potential for constraining models of nucleosynthesis in novae.

5.4. Galactic chemical evolution

Although evolution in individual parent stars can explain many presolar grain compositions, there are notable exceptions. For example, the Si isotopic ratios of mainstream SiC grains do not follow the expected trend for mixing in AGB stars. Current models predict that Si isotopes in a single AGB star should evolve along a line of slope ~ 0.4 – 0.8 on a Si 3-isotope plot [61], in stark conflict with the slope 1.3 line that

the data actually form (Fig. 2). Similar behavior was found for Ti isotopes, which also correlate with Si ratios [9,62]. It is now believed that the Si and Ti data reflect ranges of initial compositions of the parent stars, with little modification during stellar evolution [61–63]. A natural explanation for these variations comes from the theory of galactic chemical evolution (GCE, see Section 4), which predicts that many isotopic ratios, including $^{29,30}\text{Si}/^{28}\text{Si}$, will increase in the galaxy over time [25]. The GCE model of [63] in fact predicts a slope of unity on the Si plot, not too different from observed. The difference between observed and predicted slope probably is due to errors in nucleosynthesis and GCE models and it is hoped that the relatively precise grain data can help improve the models (e.g. [62]). Recently, GCE was also invoked to explain unusual $^{54}\text{Fe}/^{56}\text{Fe}$ isotopes in SiC grains [39] and has played a crucial role in the interpretation of presolar oxide grain data [16,19]. The presolar grain data also show promise for helping to constrain how homogeneously ejecta from individual stars is mixed in the interstellar medium [61,64].

5.5. Dust formation in stars

Presolar grains are gas-to-solid condensates from cooling stellar outflows and the conditions of their formation are recorded in their structures. This was dramatically shown by Bernatowicz et al. [12], who used a diamond knife to cut ultrathin slices of individual graphite grains. Transmission electron microscopy (TEM) of the slices revealed a range of microstructures and sub-grains of TiC and other refractory carbides. The TEM data, together with equilibrium and kinetic models, were used to put tight constraints on C/O ratios, pressures, and mass-loss rates in the grains' parent stars.

SN are profoundly radioactive and dust formation in such environments must occur in strongly non-equilibrium conditions. For example, Clayton et al. [65] suggested that in SN, graphite dust can form even with $\text{O} \gg \text{C}$, since the CO molecule is destroyed by radiation. This model has great difficulty accounting for SiC condensation, however [66]. Recent TEM analyses of SN

graphites have revealed sub-grains of Fe–Ni metal with amorphous rims, apparently reflecting sputtering prior to the sub-grains being captured by the growing graphite [67]. Further, Croat et al. [13,14] recently found large numbers of corroded TiC crystals, some with metallic Fe condensed onto them, within a SN graphite grain. Variations in sub-grain compositions and properties suggest that this graphite samples material from distinct SN gas parcels that are turbulently mixed.

SiC occurs in a huge number of polytypes, depending on formation conditions. TEM analyses of sub-micron SiC grains have now shown that presolar SiC almost exclusively occurs as one of two polytypes: a cubic phase and the 2H hexagonal phase [68]. The cubic phase is much more abundant, consistent with inferences from infrared spectroscopy of AGB stars [29]. A very small fraction of SiC grains apparently have disordered structures, but it is not known if these are related to a specific SiC isotopic sub-group.

Presolar oxide grains also show promise for inferring dust formation processes in O-rich stars. Recently, Stroud et al. [69] used a novel ion beam technique to prepare for the first time an ultrathin section from a presolar oxide grain. The TEM study revealed this grain to have the thermodynamically stable corundum structure, in contrast to some astronomical observations suggesting that circumstellar Al_2O_3 grains in AGB stars are amorphous [28]. Spinel is rare among micron-sized presolar oxide grains and the grains that have been found typically have Al/Mg ratios higher than that of stoichiometric MgAl_2O_4 . This led to the suggestion [58] that the spinels formed by back-reaction of precondensed Al_2O_3 with Mg in the circumstellar gas. The recent discovery that presolar spinel is more abundant at 0.1- μm grain sizes [27] might help shed light on this issue.

5.6. Presolar grains and the early solar system

The pristine, unprocessed nature of presolar grains makes them most useful as probes of their formation environments. However, they have also provided useful information about the early solar system. Their very existence in meteorites has extremely important implications for physical con-

ditions in the solar nebula, since phases like SiC will oxidize very quickly at high temperatures in a nebular gas [70]. Moreover, the abundances of presolar grains in different classes of meteorites have proven to be useful as probes of both nebular and parent-body processes [71].

A major unsolved problem in planetary science is the origin of large ^{16}O excesses in the most primitive meteoritic materials [72,73]. A favored hypothesis for nearly three decades has been the partial preservation of a reservoir of presolar ^{16}O -rich refractory dust, presumably from a SN. However, it is clear from the known presolar grains (Fig. 4) that presolar oxides are preferentially rich in ^{17}O , not ^{16}O , and this result applies to presolar silicates as well [4]. Thus, the presolar grain data seem to favor a chemical, rather than nuclear, origin for the ^{16}O -rich component in the early solar system [74,75].

6. Outlook

Microscopic presolar dust grains are clearly an exciting new source of important information about cosmic objects tens of orders of magnitude larger than themselves (Fig. 1). However, there are still many unsolved problems, some of them fundamental, some in the details. I have touched on some puzzles in this brief review (e.g. the still uncertain origins of nanodiamonds, high-density graphite, A+B SiC and Group 4 oxide grains) but there are of course others, including the origin of ^{15}N enrichments in SN grains [48,52] and the paucity of presolar oxides relative to C-rich presolar grains [16]. Although many of these problems will undoubtedly be solved, we are certain to encounter both new surprises and new puzzles in the future. Some of the most promising routes to interesting new insights are given below.

6.1. Searches for new types of presolar grains

The recent discovery of presolar silicates [4] and still-unexplained isotope anomalies in bulk meteorites [76] suggest that we have probably only scratched the surface of the presolar materials

present in meteorites. Novel analytical (e.g. NanoSIMS mapping) and chemical (e.g. [77]) techniques will likely result in identification of new and perhaps more representative samples of presolar grains.

6.2. Combined chemical and microstructural investigations

With the advent of NanoSIMS isotopic imaging and site-selective TEM sample preparation techniques, it is now possible to simultaneously characterize the microstructural, isotopic, and elemental properties of individual presolar grains on a sub-micron scale. This has great potential for investigating dynamical processes of stellar evolution and circumstellar dust formation. For example, isotopic heterogeneity within grains or sub-grains would indicate formation at different times within the stellar gas, and correlations with structure could tie physical conditions (pressure, temperature, etc.) directly with nucleosynthetic processes. Such studies of SN grains could provide fundamental information about both large- and small-scale processes in the ejecta of exploding stars [78].

6.3. Complete isotopic analysis of individual grains

Since the composition of each presolar grain is a ‘snapshot’ of a particular star at a particular point in its evolution, knowing the isotopic ratios for many elements (major, minor, and trace) in single grains provides the tightest constraints on stellar models. Development of new ultrahigh sensitivity RIMS instrumentation [79] will soon bring us closer to the ultimate goal of counting every atom in single micron-sized grains. Extension of the RIMS technique to new elements (e.g. U for possible age-dating) is also highly desirable.

Finally, significant progress depends on strengthening the collaborations between meteoriticists and researchers in related fields, especially nuclear astrophysics theory and observational astronomy. Developments in these fields can contribute to the better understanding of presolar stardust, and vice versa.

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