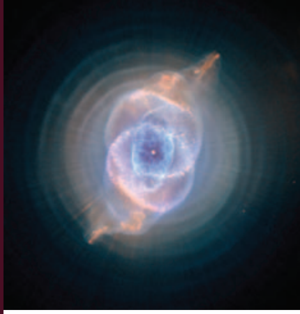
Presolar History Recorded in Extraterrestrial Materials



Hubble Space Telescope image of the Cat's Eye Nebula with an evolved AGB star at the center. Image credit: ESA, NASA, HEIC, and the Hubble Heritage Team (STScI/AURA)

Ann N. Nguyen[1,2] and Scott Messenger[1]

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Extraterrestrial samples include a rich variety of materials with different histories. Among the array of Solar System materials are tiny grains with extremely anomalous isotopic compositions—records of nucleosynthetic processes that occurred deep within their now extinct parent stars. The isotopic and mineralogical characterization of these presolar grains in the laboratory provides unprecedented insight into stellar and galactic evolution, nucleosynthesis, and dust formation and processing. The discovery of presolar grains has opened up a pivotal new dimension in the field of astrophysics. Coupled with astronomical observations and astrophysical studies, stardust analyses bring nanometer-scale detail to the history of our immense Galaxy.

Keywords: circumstellar and interstellar dust, stellar evolution and nucleosynthesis, galactic evolution, Solar System formation, nanoscale analytical techniques

INTRODUCTION

The origins and inner workings of stars have long been a source of fascination. Until recently, the only means of studying these fantastically distant objects was through their faint specks of light. The introduction of spectroscopy in the 1850s enabled the composition of stars to be measured for the first time. With a new perspective from modern physics, it was shown that stars live, evolve, and die according to nuclear reactions in their deep interiors (Burbidge et al. 1957). Nuclear fusion reactions in stellar interiors provide the energy to make stars shine and are the primary origin of all elements heavier than helium in the Universe. But, the very source of energy that powers stars also leads to their undoing: once the fuel is exhausted, stars die gradually as red giants or in spectacular fashion as exploding supernovae. As a result of both of these fates, vast amounts of stellar detritus—grains of stardust—are flung into the Galaxy to form the feedstock for the next generation of stars.

In 1987, Lewis and coworkers made a remarkable discovery that would revolutionize the study of stars and of our own Solar System: they identified *bona fide* pristine pieces of stardust surviving in ancient meteorites (Lewis et al. 1987). These "presolar grains" originated from dying stars and were some of the original building blocks of the Solar System. They were shown to be stardust by their highly unusual and wide ranging isotopic compositions, which could only be explained by nucleosynthetic processes in stars. The laboratory study of stardust has opened a new window into the inner mechanics of stars and the ancient history of the Galaxy.

Dust grains that condense in the stellar atmospheres of evolved red giant (RG) and asymptotic giant branch (AGB) stars and in the ejecta of novae and supernovae (SNe) are ejected into the interstellar medium (ISM) and incorporated into molecular clouds that are the birthplaces of stars, including our Sun. Most of the Solar System starting materials were destroyed during the formation of the Sun and planets. However, some minimally altered primitive extraterrestrial materials, such as chondritic meteorites and interplanetary dust particles, preserve these presolar grains. The unique chemical and isotopic makeup of each tiny (up to a few micrometers in diameter) piece of stardust reflects a history of its formation, travel through the ISM, and incorporation into asteroids and comets. As direct samples of stars, these grains are sensitive probes of the chemical evolution of the Galaxy, stellar evolution and nucleosynthesis, and dust condensation processes.

Red giant (RG) and asymptotic giant branch (AGB) stars – Red giant stars have exhausted all the hydrogen in their cores through nuclear reactions, and some of the H-burning products are brought to the stellar envelope by convective mixing. After helium in the core is exhausted, stars of less than ~8 solar mass ($M_\odot$) evolve to the asymptotic giant branch (AGB) phase where H-burning and He-burning resume in thin shells around the inert core. Further convective mixing enriches the stellar envelope with the nucleosynthetic products.

Nova – A nova occurs when envelope material from a companion star is accreted onto the surface of a white dwarf star, causing an onslaught of nuclear reactions and explosion of the accreted layer.

Supernova (SN) – A star more massive than 8 $M_\odot$ continues burning elements in the core until it is mainly comprised of iron and nuclear fusion is no longer energetically favorable. The core then collapses and recoils, producing a shock wave that expels the stellar matter.

Traditional astronomy and laboratory studies of stardust operate on fundamentally different scales. By astronomical methods, the dust around an evolved star can be considered within the context of other properties of the star (size, temperature, pulsation, mass loss) and its surroundings. Spectroscopic observations of stars reveal major and minor element abundances and the major mineralogy, but this technique has limited ability to identify specific minerals and measure isotopic ratios. Here, laboratory analysis of

1 Robert M. Walker Laboratory for Space Science, ARES
NASA Johnson Space Center, Houston, Texas 77058, USA

2 ESCG/Jacobs Technology, Houston, Texas 77058, USA
E-mail: lan-anh.n.nguyen@nasa.gov; scott.r.messenger@nasa.gov

stardust has a big advantage. Recent advances in nanoscale and microscale technology enable high-precision isotopic measurements and mineralogical characterization of individual stardust grains. This capability is important because each grain possesses distinct isotopic and chemical properties. Multielement isotopic analyses of individual grains can provide strong constraints on their origins, rigorously test nucleosynthetic models, and even investigate mixing of SN ejecta (Travaglio et al. 1999; Hoppe et al. 2000; Nittler et al. 2008; Nguyen et al. 2010). Laboratory studies of stardust mineralogy by transmission electron microscopy (TEM) have revealed new details on the physical and chemical conditions during grain condensation and on dust processing in the ISM and Solar System. Some stardust grains contain even smaller grains of carbide and metal in their interiors (Bernatowicz et al. 2005), providing a direct record of the dust condensation sequence in stellar atmospheres.

The varying survival rates of presolar grains in extraterrestrial samples also serve as measures of the processing that primitive materials have experienced early in Solar System history. Silicates are the most abundant, but also the most easily destroyed, type of stardust. Because these grains are so sensitive to processing in the ISM and on the parent body, their concentrations have been used to provide a direct comparison of the primitiveness of different meteorites.

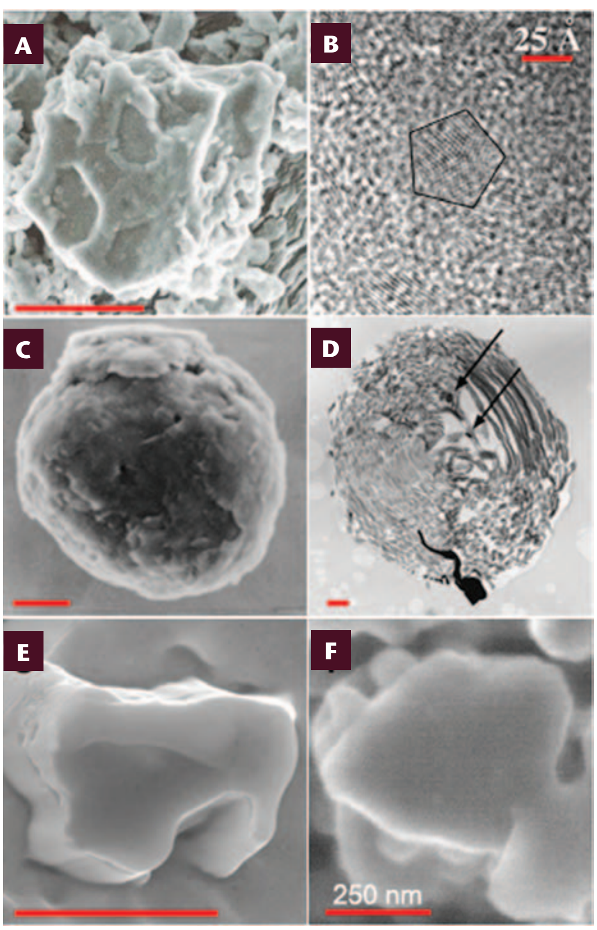

FIGURE 1 Images of presolar grain phases. Scale bars are 1 µm unless otherwise noted. (**A**) Silicon carbide; (**B**) high-resolution TEM image of presolar nanodiamonds (one of which is outlined) dispersed on amorphous C film; (**C**) graphite; (**D**) titanium carbide grains (arrows) within a graphite slice; (**E**) corundum; (**F**) silicate. The corundum and silicate grain surfaces are smooth from sputtering in the NanoSIMS ion probe. PHOTOS COURTESY OF TOM BERNATOWICZ (A), TYRONE DAULTON (B), SACHIKO AMARI (C), KEVIN CROAT (D), LARRY NITTLER (E), ANN NGUYEN (F)

Though this field of laboratory astrophysics is relatively new, the advances are too numerous to be covered in detail in this article. Here we highlight the most recent and exciting scientific developments and discuss the analytical techniques that made them possible. The interested reader is directed to recent, more detailed reviews (Lodders and Amari 2005; Meyer and Zinner 2006; Zinner 2007).

Types and Abundances of Presolar Grains

Presolar grains include a variety of high-temperature minerals with a range in morphologies and sizes (FIG. 1). The abundances, sizes, and stellar sources of hitherto identified presolar phases are given in FIGURE 2. Grains are typically submicrometer in size, with abundances on the order of parts per million, though presolar silicates have been identified at the percent level in rare samples (Busemann et al. 2009). The isotopic compositions of the grains show that most originated from AGB stars of <2 $M_\odot$, but some originated from 2–4 $M_\odot$ AGB stars, stars with nonsolar metallicities (i.e. proportion of elements heavier than He compared to that of the Sun), and exotic sources including SNe, novae, and possibly massive Wolf-Rayet stars (supermassive stars, >20 $M_\odot$, that have very strong stellar winds, resulting in huge mass loss).

The isolation of presolar grains from meteorites was first achieved by harsh chemical-dissolution treatments that removed the bulk of the meteorite material and concentrated acid-resistant phases into residues. Using this preparation, the first presolar phases identified were nanodiamonds and grains of silicon carbide (SiC) and graphite. SiC grains are by far the best studied presolar phase because essentially all SiC grains are presolar, they can be chemically isolated from the meteorite matrix material, they have high trace element concentrations, and they include unusually large grains. These grains have been analyzed individually for many isotopic systems, such as Si, C, and N, and they exhibit anomalies in essentially all isotopic ratios measured relative to any Solar System material. Conversely, despite their high concentrations, nanodiamonds (~2 nm in size) are the least well characterized because they cannot be measured individually, but some portion carries an exotic noble gas component (Huss 2005). Presolar graphite grains exist in various morphologies, and the isolated low- and high-density fractions appear to have different origins. Presolar Si_3N_4 and oxides were identified by ion microprobe analyses of acid residues. Si_3N_4 is rare and likely formed in SNe. Presolar oxide phases identified include corundum, spinel, hibonite, and TiO_2.

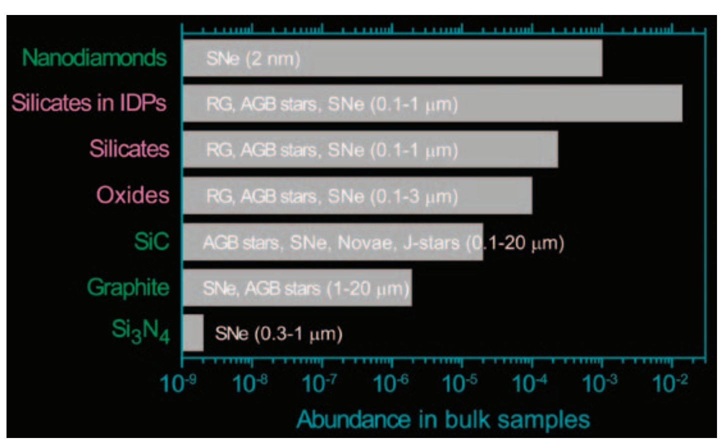

FIGURE 2 Abundances, sizes, and stellar sources of presolar phases in bulk meteorite samples. Note: 10^{-6} = 1 part per million; 10^{-2} = 1%. SNe = supernovae; IDPs = interplanetary dust particles; SiC = silicon carbide; RG = red giant; AGB = asymptotic giant branch

For many years, presolar silicates—the major condensate around diverse types of O-rich evolved stars and pervasive throughout the ISM—were missing from the inventory of presolar grains. Presolar silicates were hidden among an enormous number of Solar System grains of similar mineralogy. Indeed, the main component of meteorites and interplanetary dust particles (IDPs) are silicates that formed in the early solar nebula. The small size of presolar silicates, just a few hundred nanometers on average, made their detection even more challenging. Thus to find these grains, hundreds of thousands of submicrometer-sized silicates from chemically untreated samples (physically separated meteorite matrix grains, meteorite sections, IDPs) have to be measured for their isotopic compositions. This gargantuan task became feasible when a new-generation ion "nano"-probe, capable of isotopic imaging at the necessary scale (described in the next section), was introduced. This led to one of the most exciting breakthroughs of the past decade: the discovery of presolar silicates, including olivine, pyroxene, and nonstoichiometric grains. In addition to being ubiquitous, presolar silicates hold special importance and potential for tracing the lifecycle of dust in the Galaxy because they display a greater range of mineralogy and chemical compositions than other presolar grain types. Being more susceptible to alteration than the more refractory stardust phases, presolar silicates may preserve evidence of processing during their journey through interstellar space (i.e. radiation processing, thermal annealing) and in Solar System bodies (thermal and aqueous metamorphism). These characteristics make silicate stardust unique probes of essentially all the astronomical topics previously mentioned.

TOOLS OF THE TRADE: METHODS OF LABORATORY INVESTIGATION

Isotopic Analysis

The study of presolar grains is also a story of technological advances. Traditional laboratory methods, such as thermal ionization mass spectrometry and inductively coupled plasma mass spectrometry, only allow for the study of bulk samples. Yet key to constraining the stellar sources of these grains and astrophysical models is the analysis of individual grains, and thus individual stars, for multiple isotopic systems. Single-grain analysis reveals the true extent of isotopic variation among these grains and has played an integral role in the identification of new presolar grain types. The first-generation secondary ion mass spectrometry (SIMS) instruments were indispensable to the study of stardust, but they consumed relatively large amounts of material, had a spatial resolution not better than one micrometer, and could only measure multiple isotopic systems in the largest grains. Most presolar grains were simply too small to measure in sufficient detail to determine their stellar sources or to resolve them from adjacent materials.

The Cameca NanoSIMS ion probe revolutionized the field of laboratory astrophysics by offering an order of magnitude improvement in both spatial resolution (50–200 nm) and sensitivity for isotopic measurements. These attributes paved the way for multiple analyses in single, submicrometer grains. Presolar silicates were discovered by rastering the primary ion beam over sample areas to rapidly analyze large numbers of grains (Messenger et al. 2003; Nguyen and Zinner 2004) (Fig. 3). Other achievements gained with the NanoSIMS include the measurement of abundant submicrometer presolar spinel grains and the isotopic analysis of <200 nm inclusions within presolar graphite.

Another significant technological advancement is laser ablation and resonance ionization mass spectrometry (RIMS). This instrument can measure heavy trace elements (part-per-million concentration level) in single grains larger than one micrometer, while eliminating isobaric interferences. These measurements have played a significant role in the study of slow neutron capture (s-process) nucleosynthesis isotopes, which are produced in AGB stars and SNe.

Mineralogical Studies

Scanning electron microscopy (SEM) images of presolar grains show their varied histories—some SiC grains have retained delicate primary growth features (Fig. 1a), while others appear coated, fractured, or eroded (Bernatowicz et al. 2003). However, the internal crystal structures and chemical compositions of presolar grains determined by TEM reveal much greater detail about their origins and histories. TEM studies have shown that SiC occurs in two polytypes and that graphite grains contain abundant internal grains. The preparation of electron-transparent samples for TEM analysis is not easy and includes slicing individual grains, producing slices of entire interplanetary dust particles, and extracting grains using a novel application of the focused ion beam (FIB; Zega et al. 2007). These TEM analyses are often coupled with isotopic analyses, thereby producing a richer spectrum of information on individual grains and their parent stars.

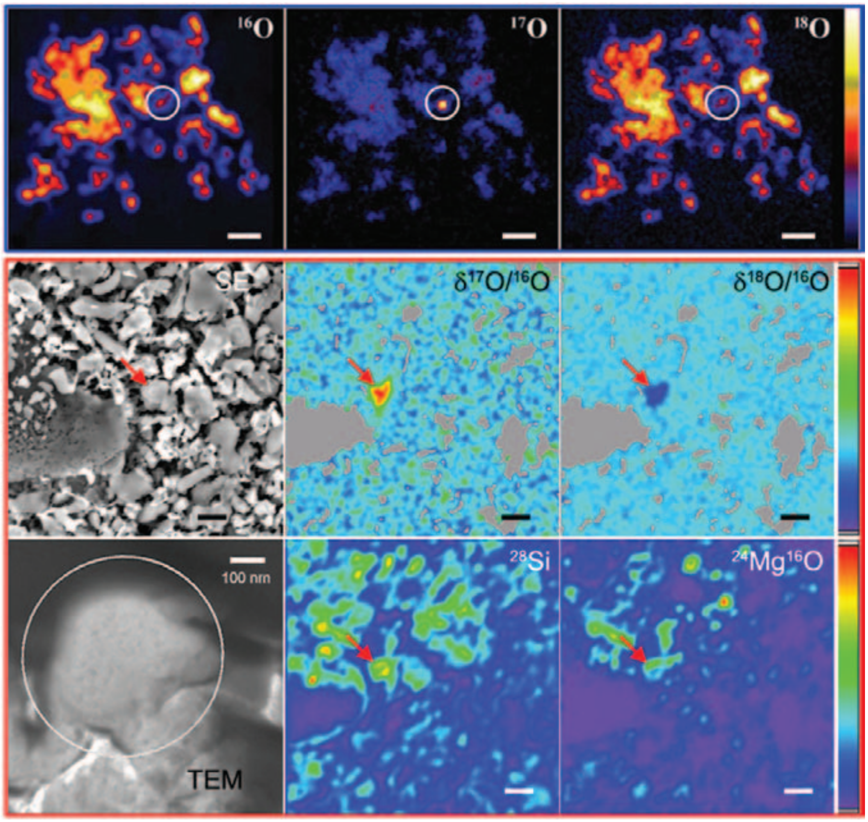

Figure 3 **Top panels:** NanoSIMS isotopic images of an interplanetary dust particle containing the first presolar silicate ever identified (circled). This olivine grain is highly enriched in ^{17}O. **Middle and bottom panels:** NanoSIMS and TEM images of meteorite matrix grains. The presolar silicate indicated by the arrows is enriched in ^{17}O and depleted in ^{18}O. The correlated ^{28}Si and $^{24}Mg^{16}O$ ion images show the grain is rich in Si and Mg. TEM analysis determined that the grain is amorphous. Scale bars are 1 μm unless otherwise noted.

Chemical Analysis

The sample-preparation methods for TEM studies described above are destructive, and sample loss, especially with the FIB technique, is possible. Thus, it is ideal to obtain chemical information on the presolar grains by nondestructive techniques before conducting mineralogical studies. Energy dispersive X-ray spectroscopy with an SEM only accurately determines the chemical composition of grains larger than 1 µm because of the large excitation volume. SIMS measurements provide a first estimate of the grain chemistry, but contaminating signals from adjacent particles limit its usefulness in characterizing submicron grains. Auger spectroscopy has a lateral resolution of tens of nanometers and measures just the near-surface chemical compositions, making it an ideal choice for analysis of submicrometer presolar grains (Stadermann et al. 2009). The Auger Nanoprobe is the most recent addition to the collection of advanced laboratory instruments that provide in-depth information on stardust.

STARDUST IN THE LABORATORY: RECORDS OF PRESOLAR HISTORY

Tracers of Nucleosynthesis and Mixing Processes in Evolved Stars

Nuclear reactions occur in stellar interiors where the temperatures and pressures are sufficiently high. The isotopic compositions of the stellar envelopes of low- and intermediate-mass stars (1–8 $M_\odot$) become enriched with fusion products when material from the interior is dredged up to the surface by convection. The O isotope compositions of evolved stellar envelopes and dust condensates deviate dramatically from the initial stellar compositions as the fusion of hydrogen in the stellar core produces ^{17}O while exhausting ^{18}O. The O isotope composition of the stellar surface depends upon the initial composition and the depth of mixing, which is dependent on the stellar mass.

Presolar silicate and oxide grains are identified by large deviations of their O isotope ratios from "solar" compositions (Fig. 4). Whereas the range of O isotope compositions of Solar System materials is only ~5%, stardust samples have orders of magnitude larger isotopic variations,

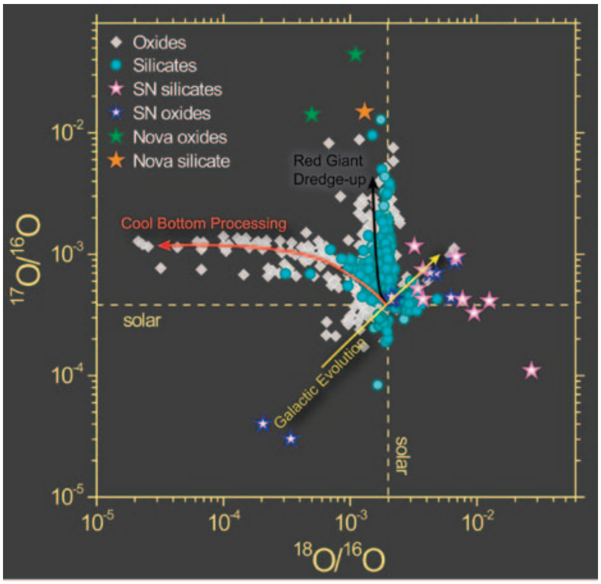

Figure 4 Oxygen isotope ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) of presolar silicate and oxide grains span several orders of magnitude. The huge variations in grain compositions can be explained by nuclear reactions and mixing processes that occurred in the grains' parent stellar sources, which include red giant stars, asymptotic giant branch stars, supernovae, and novae. The dashed lines indicate solar isotopic compositions.

produced by the different nucleosynthetic processes that stars undergo at various stages of their lives. The aforementioned stellar mechanisms are recorded in presolar silicate and oxide grains that have $^{17}O/^{16}O$ ratios larger than the solar value (indicated in Figure 4) and small to modest depletions in ^{18}O ($^{18}O/^{16}O$ between 0.001 and solar). The range of $^{17}O/^{16}O$ ratios agrees quite well with astrophysical models of low-mass stars and with the observed O isotope ratios of red giant and AGB stars.

New types of mixing mechanisms were invoked to explain isotopic observations that did not fit the standard models of AGB stars (Boothroyd and Sackmann 1999). In one such mixing process, termed "cool bottom processing," material from the stellar envelope undergoes partial H-burning when it is cycled to the hot interior, resulting in the production of ^{13}C and ^{26}Al and rapid destruction of ^{18}O. The latter two signatures are observed in presolar silicates and oxides with large ^{18}O depletions ($^{18}O/^{16}O < 0.001$) and higher-than-solar $^{17}O/^{16}O$ (Fig. 4). Many of these grains also show the high, inferred $^{26}Al/^{27}Al$ ratios predicted for cool bottom processing in low-mass AGB stars. These grain data, and also those for presolar SiC, provide additional constraints on this extra mixing process. For example, while ^{13}C production and ^{18}O destruction are dependent on the circulation rate, ^{26}Al production is dependent on the temperature reached by the envelope material.

Chemical Evolution of the Galaxy

As generations of stars are born and die, the material that they eject into interstellar space becomes progressively enriched in the heavier elements and isotopes. The stellar metallicity therefore increases over time, and many isotopic ratios are predicted to change accordingly. Presolar grains can be used to study the evolution of multiple isotopic systems. The predicted galactic evolutionary trend for oxygen, which reflects the range of initial stellar compositions, is shown in Figure 4. The subsequent nucleosynthesis and mixing processes previously discussed shift the grain data from these initial compositions. For AGB stars that have not undergone extensive cool bottom processing, the initial stellar metallicity is manifested in the $^{18}O/^{16}O$ ratios of presolar silicates and oxides. The spread in the ratios indicates condensation from stars of varying stellar metallicities.

The Si (and C) isotope compositions of presolar SiC grains originating from AGB stars reflect a range of parent stellar metallicities (Nittler et al. 2005; Zinner et al. 2006), and these grain data have demanded revisions of existing galactic chemical evolution models. Presolar silicates should better represent the galactic evolution of Si because they are less affected by s-process nucleosynthesis than SiC grains that form at a later stage of stellar evolution. However, Si isotope measurements of presolar silicates are confounded by the small size of the latter and by isotopic dilution with surrounding Solar System materials. Future endeavors to more accurately determine the Si isotope ratios in silicates are therefore important.

Supernova Dust: Nucleosynthesis and Mixing

Stars more massive than 8 $M_\odot$ end their lives in spectacular supernova explosions. Just prior to the explosion, these stars are made up of concentric shells that have experienced different stages of nucleosynthesis and have distinct chemical and isotopic compositions. Astronomical models (Herant and Woosley 1994) and observations (Hughes et al. 2000) predict extensive and deep mixing of the SN zones during the explosion. Some presolar grains have isotopic signatures consistent with SN nucleosynthesis, including evidence for ^{44}Ti, which is fused only in SNe. The combined chemical and isotopic properties of these

SN grains require large-scale mixing of the stellar shells before the grains formed.

For some time, the stellar sources for silicate and oxide grains falling along the galactic evolution trend (FIG. 4) have been enigmatic. While originally postulated to come from stars of lower or higher metallicity than our Sun, recent isotopic measurements of multiple elements in single grains suggest instead that these grains may have condensed in the winds of SNe (Nittler et al. 2008). For example, ^{18}O-rich presolar silicates do not have the ^{29}Si- and ^{30}Si-rich isotopic compositions predicted for high-metallicity stars. Moreover, the mostly ^{25}Mg-poor and ^{26}Mg-rich compositions of ^{18}O-rich presolar oxides and silicates are again inconsistent with galactic chemical evolution trends, which predict large enhancements in both ^{25}Mg and ^{26}Mg (Nittler et al. 2008; Nguyen et al. 2010). The multiple isotope ratios of these SN dust grains can strongly constrain SN mixing scenarios, with each grain requiring a distinct mixture.

Comparison of presolar grain data with models of SN compositions raised the possibility that all ^{18}O-rich grains could have condensed from a single supernova (Nittler et al. 2008). One intriguing discovery was the clustering of four probable SN silicates and one SiC grain from a SN in a ~5 µm-sized IDP (Busemann et al. 2009). The four silicates have similar isotopic compositions ($^{17}O/^{16}O \approx 2.8 \times 10^{-5}$; $^{18}O/^{16}O \approx 1.8 \times 10^{-4}$) and could have condensed from a single SN, lending support to the theory that a SN shock triggered the collapse of the molecular cloud to form the Solar System and that a SN polluted the nascent solar nebula with short-lived radionuclides. Clearly, the study of presolar grains of SN origin has provided an unprecedented look into the details of SN dynamics at a level that cannot be achieved in any other way.

Indicators of Parent-Body Processing

The abundances of presolar silicate grains are quite variable (from just a few parts per million to nearly 2%) among different types of meteorites, interplanetary dust particles, and Antarctic micrometeorites, and provide a gauge for the degree of nebular and parent-body processing. The highest abundances are associated with IDPs that have escaped hydration, and these particles thus preserve the most pristine Solar System materials. The highest abundance of presolar silicates ever identified was in an IDP collected during Earth's passage through the dust stream of comet Grigg-Skjellerup (Busemann et al. 2009). This IDP also shows other highly primitive characteristics, making a cometary origin very likely. The extremely primitive meteorite Queen Elizabeth Range 99177, in which amorphous silicates prevail and secondary alteration phases are nonexistent, has the highest concentration of presolar silicates found thus far in meteorites (Floss and Stadermann 2009). Lower concentrations of presolar silicates in more altered meteorites demonstrate the consequence of parent-body alteration on presolar silicate survival.

Heavy Element Isotopic Analysis: SiC Stardust

S-process nucleosynthesis produces heavy element isotopes and mainly occurs in AGB stars. Single-grain measurements of Mo, Zr, Sr, and Ba by RIMS in presolar SiC and graphite attest to low-mass AGB sources for grains that display the s-process nucleosynthetic patterns predicted by stellar models (Lugaro et al. 2003). Recent measurements of SiC stardust indicate excesses in ^{99}Ru from the decay of ^{99}Tc (Savina et al. 2004), which have been observed in the spectra of AGB stars. The s-process isotopic patterns are influenced by the stellar mass, metallicity, temperature, neutron density, neutron source, and neutron-capture cross sections. All of these stellar conditions can thus be constrained by the s-process patterns found in the laboratory.

Surprising results have been obtained from trace heavy element isotopic analysis of SiC type X grains of purported SN origin. Measurement of Mo showed a very unique isotopic pattern (Meyer et al. 2000) inconsistent with s-process nucleosynthesis, but also with r-process (rapid neutron capture) and p-process (which produces proton-rich nuclei) reactions predicted to occur in SNe. Instead, the Mo isotope compositions can be explained by a "neutron-burst" model where neutron capture briefly occurs at very high neutron densities (Meyer et al. 2000). The Mo and Ru isotope compositions of one rare SiC grain revealed the first evidence for p-process nucleosynthesis in presolar grains (Savina et al. 2007). The enhancements observed for this grain are not predicted by current models of core-collapse SN, and other possible scenarios do not reproduce all measured isotope ratios for this grain. This unique grain will certainly stimulate further analyses and reconsideration of stellar models to determine the stellar source.

DUST CONDENSATION

Evolved stars undergo mass loss when material from the outer envelope is ejected into space. Dust grains begin to condense when this ejected gas cools with time and distance from the star. The types of dust species and mineral structures to condense are highly dependent on the C/O ratio of the circumstellar atmosphere, as well as on the pressure and temperature. Whereas O-rich phases condense when $C/O < 1$ during the earlier stages of an AGB star's life, carbonaceous phases condense in the later thermally pulsing phase when $C/O > 1$. In SN outflows, different mixtures of SN zones will yield different chemical compositions and C/O ratios. Mineralogical studies of presolar grains thus provide information about the evolving chemistry of the stellar atmospheres, as well as the pressure and temperature conditions, gas densities, and cooling rates during grain condensation. Possible secondary alteration in space or in the Solar System can also be surveyed.

The crystal structures of circumstellar SiC grains inferred from astronomical spectra are not well constrained. TEM studies of presolar SiC grains reveal that they exist only as two main polytypes (Daulton et al. 2002), consistent with equilibrium grain condensation calculations at low temperatures. This finding was surprising considering that hundreds of SiC polytypes form in the laboratory. Whereas SiC grains from AGB stars are primarily single crystals, those that accreted in SN outflows are comprised of many small crystals, indicating shorter condensation timescales.

Graphite grains of both AGB and SN origin are quite different from SiC grains in that the former show an assortment of textures with varying degrees of disorder and often contain internal grains (FIG. 1D; Bernatowicz et al. 2006; Croat et al. 2008). These subgrains are most commonly titanium carbide (TiC), but metal grains, oxides, and other carbides, including rare SiC, have also been identified. Variations in the density, location, size, and chemical composition of the internal grains record the condensation sequence and the physical and chemical evolution of the stellar atmosphere during accretion. Isotopic analyses of these inclusions help to constrain the stellar origins.

The mineralogy of very few presolar oxides is known, but crystalline hibonite, spinel, and corundum have been identified, as well as one amorphous Al_2O_3 grain (Stroud et al. 2004). While most presolar grains are crystalline and stoichiometric, the current inventory of presolar silicate mineralogy displays a rich variety of minerals and chemical compositions. Half the presolar silicate grains are amorphous to weakly crystalline, with a large range of nonstoichiometric compositions. Many of the grains are more

Fe-rich than expected and show fine-scale compositional heterogeneity. Some of these silicates, termed "GEMS" (glass with embedded metal and sulfide; Bradley 1994), contain Fe–Ni metal and sulfide grains and are also major constituents of IDPs. In addition, a few crystalline species, mainly Mg-rich olivine, have been identified as single crystals, crystal aggregates, and dispersed crystals in amorphous material. A preponderance of nonstoichiometric and Fe-rich compositions has also been observed in hundreds of silicate grains analyzed by Auger spectroscopy (e.g. Floss and Stadermann 2009).

The mineralogy and chemical compositions of silicate stardust are in stark contrast to expectations from astronomical spectra and thermodynamic calculations, both of which suggest a prevalence of amorphous material with the composition of stoichiometric Mg-rich olivine and pyroxene. The source of this discrepancy is unclear, but possible explanations are that these silicate grains condensed under nonequilibrium conditions, or that secondary alteration in the ISM and in the Solar System changed the grain chemistry without erasing the anomalous isotopic signatures. The lower proportion of crystalline species in the ISM than in young and evolved stars indicates some silicate grains were likely altered from their original form. Spectral fits to nonstoichiometric grains, laboratory annealing and irradiation of silicates, and nonequilibrium condensation models and experiments will help constrain the silicate stardust formation processes.

CONCLUDING REMARKS

This is a tremendously exciting time to be involved in astromaterials research. A unique window has been opened with the discovery of surviving stardust grains, relics from ancient stars. These grains chronicle the history of the Galaxy up to their incorporation into our Solar System. The detailed information gleaned from the laboratory study of stellar samples is truly remarkable and complementary to observational and theoretical astronomy. Presolar-materials research is a rapidly developing frontier that will offer new insight into our ancient past as new analytical capabilities emerge and new samples become available.

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