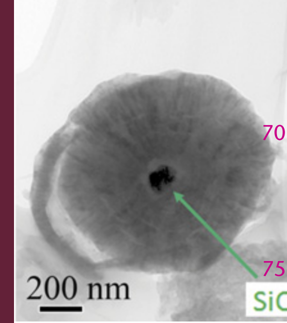
Presolar Graphitic Carbon Spherules: Rocks from Stars



Graphitic carbon spherule formed around a Si carbide grain

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Graphitic carbon spherules found in primitive meteorites have large carbon isotope anomalies, indicating that they are carbonaceous stardust (also known as presolar grains) expelled from dying stars prior to the formation of the Sun. Presolar spherules show varying degrees of graphitization, ranging from poorly graphitic, turbostratic layers in low-density spherules to well-crystallized graphitic outer shells in high-density ones, and some spherules also contain a polycrystalline phase in their core. Within the spherules, grains of other refractory phases (including carbides and metals) are common, and these assemblages can be studied as one would study a rock. The isotopic and microstructural information available from these presolar graphitic assemblages gives insights into nucleosynthesis and grain condensation in late-stage carbon-rich stars.

Keywords: presolar grains, graphite, transmission electron microscopy, ion probe, AGB stars, supernovae

INTRODUCTION

A quarter of a century ago, chemical dissolution experiments were performed on primitive carbonaceous meteorites in the hope of concentrating the carriers of poorly understood neon and xenon isotope anomalies observed in those meteorites. This led to the discovery of microscopic grains of stardust in the acid residues (Lewis et al. 1979). Several different chemically resistant minerals of preserved ("presolar") carbonaceous stardust—nanodiamonds, silicon carbide (SiC), and graphitic carbon (C)—were identified in these initial dissolution and size-separation experiments (Amari et al. 1994). Presolar graphitic carbon grains occur as micrometer-sized spherules with an enormous range in $^{12}C/^{13}C$ isotope ratios (from ~1 to 10,000); by way of comparison, the solar ratio is 92 and varies by only a few percent in Solar System materials. The C isotope compositions of the spherules reflect contributions to the Solar System of C from a variety of stars older than the Sun. The most important of these stars are asymptotic giant branch (AGB) carbon stars (a late evolutionary stage of many 1–5 solar mass stars) and core-collapse supernovae (the final explosive phase of massive stars exceeding 8 solar masses). These stars produce C primarily through the fusion of He nuclei. Stellar carbon is expelled from a star as gas and dust at the end of the star's life. Some of this carbonaceous stardust survived Solar System formation and occurs as minute spherules in primitive meteorites and interplanetary dust particles. While carbonaceous stardust around stars has been traditionally studied via remote observations of its absorption and emission spectra, it is now possible to make high-precision, isotopic, chemical, and microstructural measurements on actual stardust in the laboratory. These results can be used to test and refine stellar models of nucleosynthesis (e.g. Bernatowicz et al. 2006; Zinner 2014).

Presolar graphitic spherules, which range from ~0.3 to ~10 µm in diameter, exhibit a range of crystallographic order and a corresponding range of density. Higher-density (HD) spherules (2.0–2.3 g/cm^3) tend to be smooth, whereas lower-density (LD) types (1.6–2.0 g/cm^3) commonly have scaly surfaces, leading to the convenient labels of "onion" and "cauliflower" types, respectively (Hoppe et al. 1995). The LD cauliflowers often lack long-range crystallographic order and are thus not graphite in the strict mineralogical sense (as will be discussed below). Transmission electron microscopy (TEM) of spherule cross sections uncovers significant structural differences in the length scales and degree of perfection of the graphene layers comprising HD and LD presolar spherules. Some HD spherules have unusual polycrystalline carbon cores that appear to be aggregates of naturally occurring graphene (Bernatowicz et al. 1996; Lazzeri and Barreiro 2014 this issue). Presolar spherules are a rich source of information on stellar environments because they are not single mineral grains but rather mineral assemblages that have survived largely unaltered since their condensation. Embedded within the spherules are mineral subgrains that were ubiquitous in regions of graphitic carbon formation, both in stellar winds from carbon stars and in C-rich supernova ejecta. The study of these "rocks from stars" using methods familiar to geologists (e.g. Croat et al. 2003) can yield detailed insights into the stars that produced starting materials for the Solar System.

ISOTOPIC ANOMALIES IN PRESOLAR GRAPHITE

All elements heavier than lithium are produced by nucleosynthesis in stars. The elements synthesized, and their isotopes, depend on the nucleosynthetic reactions that occur, and these reactions vary depending on the metallicity, mass, and age of the star. Metallicity is a measure of a star's metal content (with "metals" defined as all elements except H and He): the overall metallicity of the galaxy increases with time as stars create elements heavier than H

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and He that did not exist right after the Big Bang. A star's initial mass (and metallicity) determines its lifetime as well as its ultimate fate after consuming its nuclear fuel. Stellar age is also an important parameter for stardust formation, since stars typically produce and eject large quantities of stardust only after exhausting most of their nuclear fuel (Gail et al. 2009).

We know that presolar graphitic spherules condensed as stardust around ancient stars based on their very large isotopic anomalies relative to solar values; these anomalies are mainly in C, but trapped minor elements such as O and Si are commonly isotopically anomalous. Figure 1 shows the distribution of $^{12}C/^{13}C$ and $^{16}O/^{18}O$ ratios and Si isotope compositions from both HD and LD spherules (Jadhav et al. 2013a). While similar in their C isotope range, the HD and LD spherules (HDs and LDs) show pronounced differences in minor element isotopic anomalies, with LDs commonly having significant excesses of ^{18}O and/or ^{28}Si. The ^{28}Si excesses in many LD spherules are so large that only the O-burning layers of massive stars, such as supernovae, can produce them (Amari et al. 1995). While supernovae do produce massive amounts of ^{16}O, the C-rich outer layers where the spherules condense have excess ^{18}O. Other diagnostic isotopic anomalies shown by LDs are carried by internal titanium carbide (TiC) subgrains, which show large ^{44}Ca excesses from the decay of radioactive ^{44}Ti. This ^{44}Ti is formed by explosive He burning during a supernova explosion and, with a half-life of only 60 years, it is a smoking gun for a supernova origin (Nittler et al. 1996). TiC subgrains often carry anomalies more extreme than those of their host spherules (e.g. the ^{18}O-enriched TiCs in Fig. 1a). The combinations of isotopic anomalies observed in LD spherules demonstrate that most formed from matter in the outer layers of supernovae. Astronomical observations provide evidence for dust condensation in supernova ejecta (typically occurring within a few years of the explosion), but detailed information about the nature of this dust is difficult to discern from supernova spectra (Gall et al. 2011). Presolar graphitic spherules and their internal grains provide unique samples of supernova dust for laboratory analysis.

HD graphitic spherules lack the large O and N anomalies found in LD spherules, which suggests a different stellar origin for these grains. Their C isotope distribution is skewed towards more ^{12}C-rich compositions relative to LDs, with ~75% of spherules showing isotopically light C (i.e. $^{12}C/^{13}C > 92$; Fig. 1a). The large ^{12}C enrichments, accompanied by ^{29}Si and ^{30}Si enrichments, are consistent with a low-metallicity AGB carbon star origin for many HDs (Zinner et al. 2006). Further evidence of an AGB origin comes from the high Zr, Mo, and Ru contents in internal carbides within HDs (Croat et al. 2005). These elements are produced in high abundances only by AGB stars through the nuclear s-process, which creates certain heavy isotopes through slow neutron capture by iron seed nuclei. Whereas many HDs are produced by AGB stars, others can be produced only by massive stars such as supernovae, including rare HDs that contain internal SiC grains with very large ^{29}Si and ^{30}Si excesses (Fig. 1b; Croat et al. 2010). Along with the prodigious carbon-producing stars mentioned above, novae (a type of nuclear explosion that can occur in some binary star systems; Amari et al. 2001; Heck et al. 2009) and born-again carbon stars (which late in their evolution undergo a thermal pulse that reignites He burning; Jadhav et al. 2013b) are thought to produce spherules with rare isotopic compositions. Once the likely stellar origin of a given spherule has been determined, its precise isotopic values can be tested against predictions from stellar nucleosynthesis models and against astronomical observations, and any discrepancies found can be used to improve these models.

PRESOLAR GRAPHITIC CARBON STRUCTURE AND MORPHOLOGY

Examination of ultramicrotome sections of spherules using TEM techniques, such as electron diffraction and imaging, has revealed their structure in great detail (Croat et al. 2008). Graphite is constructed from stacks of two-dimensional hexagonal sheets of sp^2-bonded carbon (termed graphene), which are weakly bound to each other by Van der Waals forces (Lazzeri and Barreiro 2014). The weak interlayer bonding between adjacent graphene sheets allows for considerable structural variation and varying degrees of graphitization, leading to diverse and interesting forms of carbonaceous grains. Across the range of densities from LD to HD, we observe a continuum of presolar spherules in different stages of graphitization, from the poorly graphitized carbon that comprises cauliflowers (Fig. 2a, c; often called "turbostratic" graphite; Oberlin 1989) to well-ordered onions showing concentric graphitic layering (Fig. 2b, d). Several techniques have been used to characterize presolar graphitic spherules, including TEM, Raman spectroscopy, and X-ray absorption near edge spectrometry (XANES), all of which provide distinct but complementary perspectives on their structures.

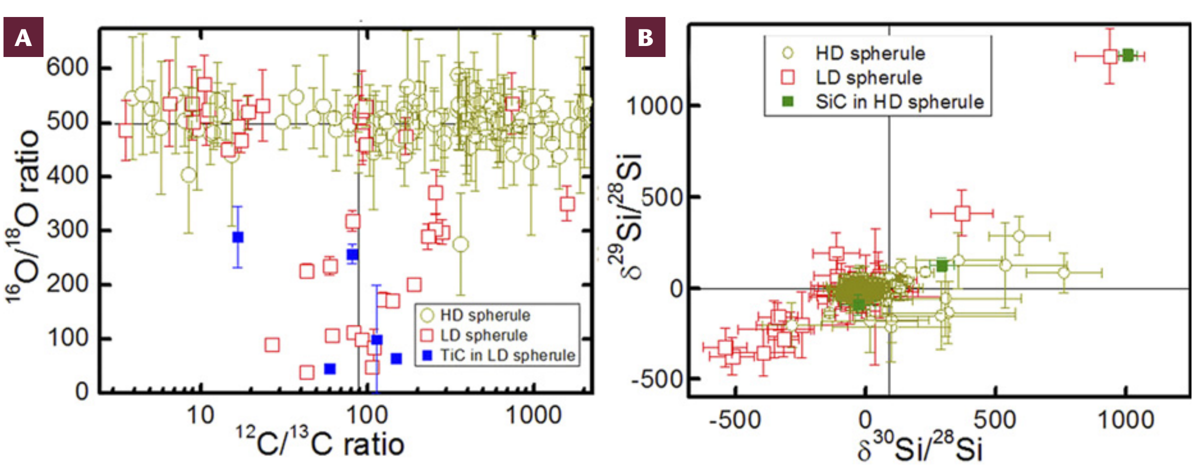

Figure 1 (**A**) C and O isotope ratios and (**B**) Si isotope compositions from secondary ion mass spectrometry of high-density (HD) and low-density (LD) spherules and the more anomalous internal Ti carbide and Si carbide grains commonly found within them (the vertical and horizontal lines show the mean of terrestrial matter). Si anomalies are in delta notation: $\delta^{i}Si$ (‰) = $[(^{i}Si/^{28}Si)_{measured} / (^{i}Si/^{28}Si)_{solar} - 1] \times 1000$ (for i = 29, 30). Error bars are 2σ.

Structural ordering in graphitic carbon can be characterized by the root mean area of the graphene sheet (L_a), by the stacking height (L_c, which depends on the number of graphene sheets in a stack), and by the interplanar spacing between the stacked graphene sheets (d_{002}). The L_a dimension of presolar graphitic carbon has been inferred from Raman spectra as being ~3 nm for cauliflowers and ~13 nm for onions, with L_c/L_a ratios near unity (Wopenka et al. 2013). The interplanar spacings (d_{002}) can be determined from diffraction patterns (such as in Fig. 2e), and these spacings vary due to the weak bonding of the graphene sheets, from d_{002} = 3.35 Å for perfect crystalline graphite to ~3.9 Å as stacking disorder increases. The outer layers of HD spherules show strong {002} diffraction rings from preferential stacking of graphene sheets tangent to the sphere's outer surface (like the layers of an onion). HD onion spherules have d_{002} = 3.49 ± 0.05 Å, whereas LDs show slightly larger values (d_{002} = 3.60 ± 0.05 Å; Croat et al. 2008). The ranges of d_{002} values and L_a/L_c dimensions of presolar spherules generally indicate that they are composed of poorly crystalline graphite.

Changes in structure are also seen within single onion spherules, such as that in Figure 2d which shows a minimally ordered polycrystalline core surrounded by a well-graphitized outer shell. Diffraction patterns from the outer shells (Fig. 2e) show {002} and {004} arcs that indicate alignment and stacking of adjacent graphene sheets, whereas patterns from the core (Fig. 2f) show only the in-plane {100} and {110} rings, and these differences are clearly seen in the extracted diffraction line profiles (Fig. 2g). Modeling of TEM diffraction data suggests that the cores are aggregates of graphene sheets with 3 nm < L_a < 4 nm but with no appreciable {002} stacking (Bernatowicz et al. 1996). This may indicate that the core graphene sheets are curled due to pentagonal configurations within the hexagonal graphene nets (Lazzeri and Barreiro 2014). In addition, modeling the shape of core diffraction profiles indicates that as much as one-quarter of the core may be in the form of polycyclic aromatic hydrocarbons (PAHs), which are typically four to seven attached C rings with H at the edges.

Raman spectra of the spherules have narrow D (disorder) and G (graphite) peaks whose ratio provides a useful bulk comparative measure of the degree of graphitization (Wopenka et al. 2013). The disordered D peak is absent from highly crystalline graphite, but grows in magnitude in the presence of structural defects and impurities. In Raman spectra collected from ~100 HD and LD spherules, Wopenka et al. (2013) found a range of spectral types, including well-ordered graphite (D/G > 0. 5), disordered graphite (0. 5 < D/G < 1. 1), and glassy carbon (D/G > 1. 1). HD spherules were predominantly classified as well-ordered graphite, whereas LDs were either disordered graphite or even glassy carbon. Other rare spectral types were also found among presolar spherules, including kerogen-type material with broad D and G peaks and unusual sp^2-bonded carbon with abnormally intense second-order peaks.

Along with copious H in PAHs, presolar spherules contain significant concentrations of other heteroatoms, such as N and O. From studies of terrestrial and synthetic graphite, the sizes of coherent diffraction domains are known to be influenced by the presence of heteroatoms such as O and S (Oberlin 1989). The heteroatoms can cause cross-linking between adjacent graphene sheets, which prevents them from rearranging into more perfectly ordered graphite. The higher degree of graphitization in onions from

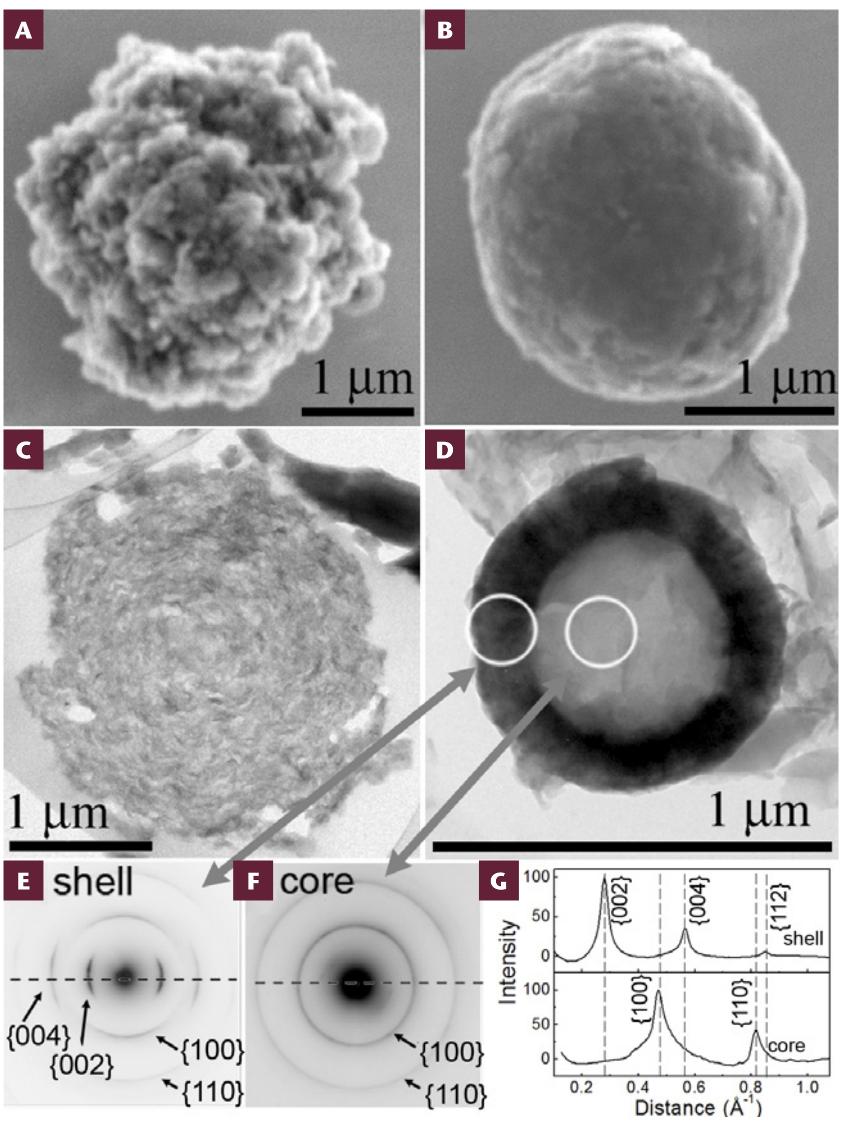

Figure 2 Scanning electron microscope images of (**A**) a cauliflower, low-density spherule and (**B**) an onion, high-density spherule. Images courtesy of S. Amari. Transmission electron microscope cross-section images of (**C**) a cauliflower and (**D**) an onion spherule with a polycrystalline core. Also shown are selected area diffraction patterns from (**E**) the shell and (**F**) the core, and (**G**) intensity profiles along dotted lines in (E) and (F).

AGB carbon stars likely indicates formation from a more C-rich environment than that of cauliflowers formed from supernova (which may have C/O closer to unity; Croat et al. 2008). XANES spectra have confirmed the presence of strong aromatic C peaks (from the rings of C that comprise the graphene sheets) in LD and HD spherules (Groopman et al. 2014). These spectra are also sensitive to the presence of heteroatoms and can even determine the types of chemical bonds that are present. Polycrystalline core regions match the spectra expected from 2–4 nm graphene sheets, whereas the turbostratic regions show peaks resulting from C=O bonds, consistent with higher O content in these more disordered regions (Groopman et al. 2014). Thus, XANES spectra provide complementary information that reinforces structural determinations made with TEM and Raman studies.

Presolar graphitic spherules and the other exotic carbonaceous grains (i.e. nanodiamonds and silicon carbide stardust) are present only at parts-per-million-level concentrations and are thus very minor components of the C-rich matter in carbonaceous meteorites. These primitive meteorites typically contain several weight percent C, most of which is organic matter along with small amounts of carbonates. The insoluble organic matter is predominantly unstructured and heterogeneous kerogen-like material, but it also includes features such as hollow nanoglobules, flakes, and tubes (Pizzarello et al. 2006). Soluble organic matter, including hydrocarbons and amino acids, is also present. The organic matter contains some regions with large H and N isotope anomalies, which may reflect an origin in cold molecular clouds (Messenger et al. 2006). However, the diverse isotopic and structural properties seen in organic matter complicate its interpretation, and it may have also formed in the outer Solar System (Alexander et al. 2007).

SUBGRAINS WITHIN PRESOLAR GRAPHITIC CARBON SPHERULES

A range of mineral species condense in the heavy-element-rich dusty envelopes and stellar winds of late-evolutionary-stage stars. Mineral grains that condensed at higher temperatures than the graphitic carbon can become encapsulated in spherules as subgrains. Once shielded in the interior of spherules, subgrains survive largely unaltered, protected from subsequent chemical processing in the interstellar medium, the solar nebula, and their meteorite parent body, as well as during laboratory separation from the host meteorite. Single 10 µm diameter supernova spherules can contain up to ~1000 grains of other phases, predominantly Ti carbides (Fig. 3a; Croat et al. 2003). In many cases, a central carbide appears to have served as a nucleation center for the surrounding spherule (Fig. 3b). Most of the subgrains in supernova spherules (~90%) exhibit variable degrees of "weathering" of otherwise well-defined euhedral to subhedral surfaces. One of the most striking features observed is that most subgrains have a 3–15 nm thick, amorphous to highly disordered surface rim (Fig. 3c), partially or completely enveloping the grain (Daulton et al. 2012). The atomic microstructures of these rims are consistent with particle irradiation damage and were likely created by collisions between dust grains and parcels of gas moving at different relative velocities.

While TiC represents the dominant subgrains in presolar spherules, other refractory carbonaceous phases are also found: Ti(Zr,Mo,Ru) carbides, titanium carbonitrides, SiC, nickel and iron silicides, refractory metal nuggets (RMNs), iron-rich metal (FeNiSi), and intergrowths of these (Bernatowicz et al. 2006). In many cases, the other phases form as coatings or subgrains on existing TiC surfaces. Sometimes multiple iron-rich metal subgrains grow onto

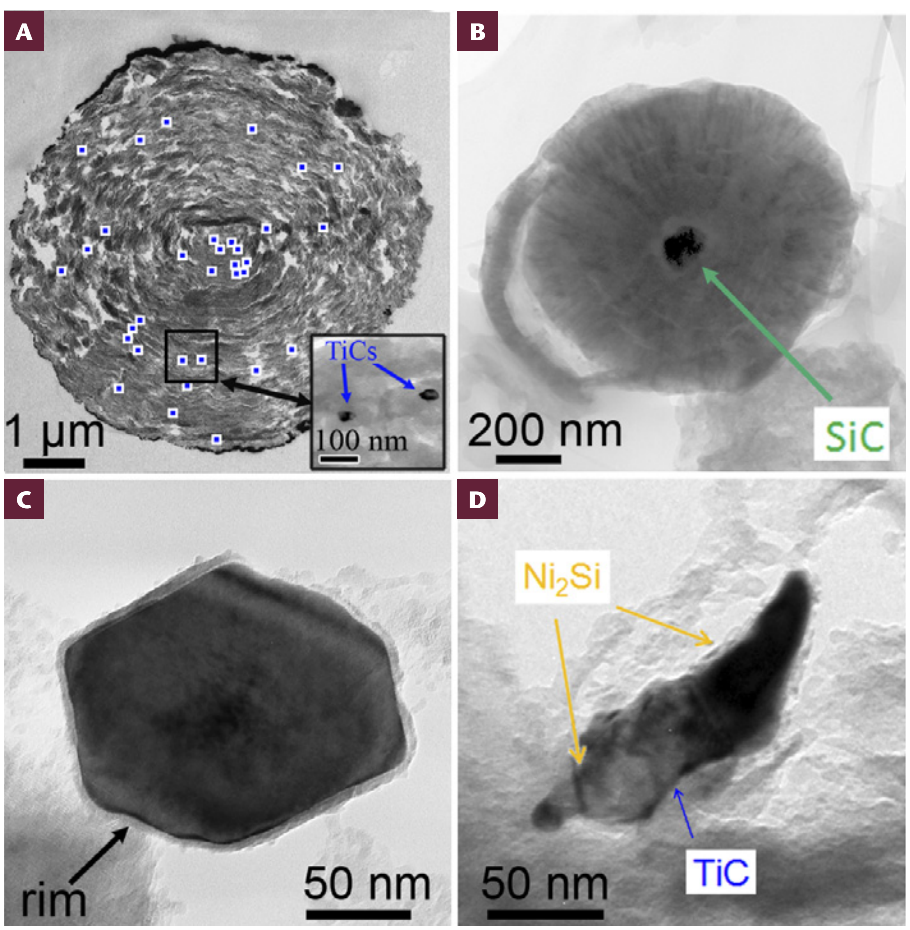

Figure 3 Transmission electron microscope images of (**A**) a low-density supernova spherule with TiC subgrain locations marked, (**B**) a high-density spherule with an unusually ^{29,30}Si-rich central SiC subgrain acting as its nucleation site, (**C**) a TiC subgrain with an amorphous rim in a supernova spherule, and (**D**) a TiC subgrain with multiple epitaxially attached nickel silicide grains in a low-density spherule.

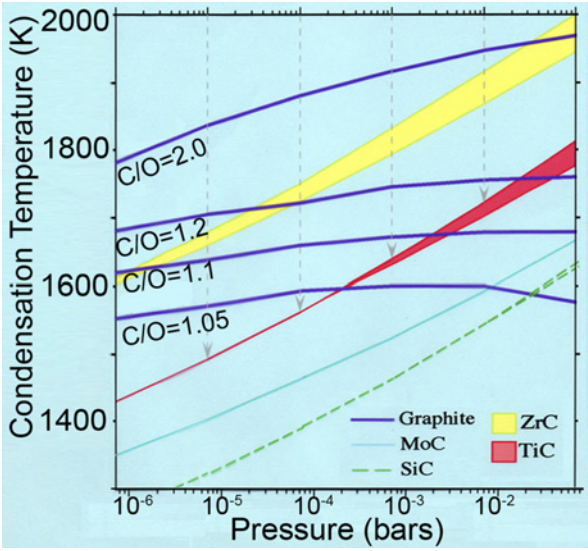

FIGURE 4 Predicted condensation temperatures from thermodynamic models of graphite and various carbides as a function of gas pressure and C/O ratio for an asymptotic giant branch carbon star. FIGURE ADAPTED FROM BERNATOWICZ ET AL. (1996) AND BASED ON DATA FROM LODDERS AND FEGLEY (1995)

different faces of the same TiC grain (FIG. 3D), and the structure of these assemblages makes the phase-condensation sequence clear (e.g. TiC → metal → graphite; Croat et al. 2003). These observed phase-condensation sequences can act as important tests for thermodynamic models of grain condensation. Such models are used to predict the condensation temperatures of various carbonaceous phases as a function of temperature, pressure, and C/O ratio (FIG. 4). Many features observed in HD spherules (such as ubiquitous TiC grains but rare SiC grains) are consistent with these models: at the pressure and C/O ratios expected in AGB carbon stars (which are $4 \times 10^{-4} < P < 4 \times 10^{-2}$ bars and $1.05 < C/O < 1.2$), TiC condenses at a higher temperature than graphite and thus can be incorporated during spherule growth, whereas SiC in general forms at lower temperatures after spherules have already formed (Lodders and Fegley 1995; Bernatowicz et al. 1996). The chemical compositions of internal RMNs, which are metal grains highly enriched in platinum-group elements, provide an independent means to estimate the graphite condensation temperature, and these estimates are in reasonable agreement with thermodynamic model predictions (Croat et al. 2013). The RMN compositions, which range from osmium-rich at higher temperatures to platinum-rich at lower temperatures, can be used to infer the temperature at which RMNs fall out of equilibrium with nebular gas, a temperature that likely coincides with the condensation temperature of the host graphite spherule (e.g. Berg et al. 2009). The RMN compositions predict 1400–1800 K as the range for spherule growth, with HDs condensing at considerably higher temperatures than LDs.

Thermodynamic modeling is considerably more complex for supernovae (Fedkin et al. 2010) than for AGB stars (Lodders and Fegley 1995), due to the wide chemical and isotopic heterogeneity in different layers of their ejecta (Travaglio et al. 1999). Isotopic constraints coupled with supernova nucleosynthesis models restrict the starting compositions used as input into thermodynamic calculations. Such efforts yield detailed predictions of the condensation sequence for a plethora of C-rich phases, and the results match very well with actual observations of supernova spherules. For example, Fedkin et al. (2010) predicted the formation of TiC, SiC, iron–nickel silicide, iron–nickel metal, and graphite from the C-rich zones in the ejecta of a supernova, and grains of each of these phases were later observed within a single LD supernova spherule. Despite these successes, the complex processes operating in supernova environments, such as intense radiation and grain–gas collisions, make it unclear whether models based on thermodynamical equilibrium are valid. It is even possible that intense supernova radiation can break up CO molecules, leading to unexpected results, such as graphite condensation from O-rich environments (Clayton et al. 1999).

A spherule's internal grains often yield new and unique insights into the stellar source of the stardust grain. For example, the Ti carbides found within most HDs show large s-process element enrichment, with Mo/Ti ratios often ~100× or more above the mean of the Solar System (Croat et al. 2005). Since extensive chemical fractionation is not expected for (Mo,Ti)C condensation, the s-process-enriched compositions reflect their formation environment and are inconsistent with supernovae but consistent with s-process-enriched AGB stars. Grains within spherules, with their different chemistries, offer a wide selection of elements on which to perform isotopic measurements. In most cases, supernova carbides have more extreme ^{18}O and ^{15}N enrichments than their host spherules. This can be explained by dilution of minor element anomalies by graphite (which more freely exchanges isotopes with the rest of the meteorite) and by a higher retention within carbides (Stadermann et al. 2005). Most SiC grains within HDs show unusually large $^{29,30}Si$ enrichments, of a type only expected from a massive star (Croat et al. 2010). FIGURE 5 shows NanoSIMS ratio images of $^{12}C/^{13}C$, $^{28}Si/^{29}Si$, and $^{28}Si/^{30}Si$ from an SiC-containing spherule, a visual representation of the large Si isotope anomalies present in the SiC. Such SiC–C grains are very rarely found in the overall presolar SiC distribution (Hoppe et al. 2010) but are relatively common inside HDs.

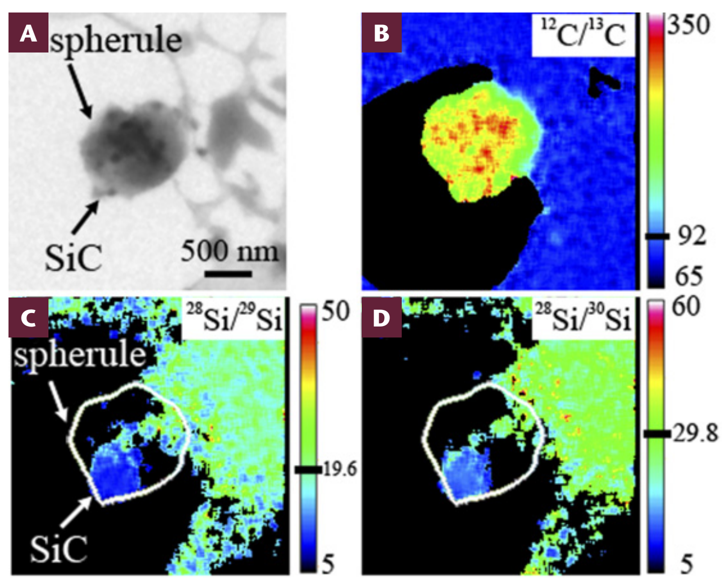

FIGURE 5 (**A**) Transmission electron microscope image of a small (~250 nm) SiC subgrain at the edge of a ~1 µm spherule, and (**B**–**D**) NanoSIMS $^{12}C/^{13}C$, $^{28}Si/^{29}Si$, and $^{28}Si/^{30}Si$ ratio images of same. (**B**) shows a uniformly ^{12}C-enriched spherule and an indistinguishable SiC grain, but (**C**) and (**D**) show strong ^{29}Si and ^{30}Si enrichments in the SiC subgrain but not in the spherule (blue color indicates ~2× higher $^{29,30}Si$ than expected). The black regions have undefined ratios due to insufficient counts, and the black lines on color bars correspond to the solar isotopic ratios. The white closed curves in (C) and (D) show the perimeter of the spherule.

SUMMARY AND OUTLOOK

Laboratory analyses of presolar graphitic carbon spherules provide direct information from ancient stardust that predates the Solar System. Detailed studies of these grains give insight into stellar nucleosynthesis and grain condensation processes around carbon-rich stars. As microanalytical instrumentation further progresses into the nanometer regime, many more discoveries will likely be made by studying tiny grains of stardust. With each new discovery we come closer to a thorough understanding of their origins and their role in the early Solar System.

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