

# Stardust in meteorites

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**Primitive meteorites, interplanetary dust particles, and comets contain dust grains that formed around stars that lived their lives before the solar system formed. These remarkable objects have been intensively studied since their discovery a little over twenty years ago and they provide samples of other stars that can be studied in the laboratory in exquisite detail with modern analytical tools. The properties of stardust grains are used to constrain models of nucleosynthesis in red giant stars and supernovae, the dominant sources of dust grains that are recycled into the interstellar medium by stars.**

presolar grains | AGB stars | silicon carbide | graphite | diamond

One of the great discoveries in cosmochemistry in the last century was the fact that primitive meteorites contain tiny mineral grains that condensed around dying stars. These grains survived a myriad of destructive environments, including the immediate surroundings of their parent stars, the interstellar medium, the molecular cloud that collapsed to form the solar system, the solar nebula, meteorite parent bodies, breakup of those bodies, and atmospheric entry. There were a number of hints of the presence of these grains over the years, mainly from strange isotopic patterns of the noble gases, and a nearly two-decade search for the hosts of the anomalous isotopic patterns culminated in the discovery of diamond (1), silicon carbide (2, 3), and graphite (4) in carbonaceous chondrites in the late 1980s. These grains are commonly referred to as “presolar grains,” although the more evocative name “stardust” is often used. The latter term will be used here, because it is now clear that these grains formed around individual stars with little apparent subsequent modification in the interstellar medium. Note that the name is also used for the National Aeronautics and Space Administration (NASA)’s Stardust mission, which returned dust grains from Comet Wild 2 (surprisingly little actual stardust has been detected so far) and from the contemporary interstellar medium (not yet confirmed).

The mineralogy, textures, chemistry, and isotopic composition of stardust from meteorites provide direct evidence of processes that occurred in individual stars and complement observations by more traditional astronomical methods. Stardust from meteorites samples a number of different types of stars, including asymptotic giant branch (AGB) stars, part of the normal stellar evolution of stars 1.5 to 4 times the Sun’s mass, as well as core-collapse supernovae and novae. Diamond, silicon carbide, and graphite are common types of stardust but are thermodynamically unstable in the solar nebula, so their survival places constraints on physicochemical conditions in the solar nebula.

Stardust grains are small: although the largest grains can reach a few tens of  $\mu\text{m}$  in diameter, such grains are very rare, and most grains are  $\mu\text{m}$ -sized or less. For this reason, laboratory study of stardust has driven advances in analytical technology and progress depends on further improvements in spatial resolution and analytical sensitivity.

Here, we begin with a brief description of stardust types, followed by a discussion of the stellar sources of stardust and some recent advances in the field. This review is necessarily relatively brief. Several more extensive reviews have been published in recent years (5, 6).

## Types

**Reduced Phases. Diamond.** The first type of presolar grain recognized was diamond, identified by X-ray diffraction and by an unusual xenon isotopic pattern enriched in both the light *p*-process and heavy *r*-process isotopes (Xe-HL) (1) and *r*-process tellurium (7), yet it is not clear that all of the nanodiamonds recovered from primitive meteorites are presolar. For many years, not much progress was made on deeper understanding of diamond, because individual diamonds are so small that they cannot be studied individually. Typical meteoritic nanodiamonds have sizes of 2–4 nm (8). A diamond with a diameter of 2.8 nm, the median of the size distribution, contains  $\sim 1,800$  atoms of carbon and  $\sim 18$  atoms of nitrogen, but there is only about one xenon atom per million diamond grains. On average, meteoritic nanodiamond has the terrestrial (and likely solar)  $^{12}\text{C}/^{13}\text{C}$  ratio of 89 and a nitrogen isotopic composition that is different from that of the Earth’s atmosphere,  $^{14}\text{N}/^{15}\text{N} = 272$ , but similar to the recently determined solar nitrogen isotope ratio,  $^{14}\text{N}/^{15}\text{N} = 441$  (9). The solar nitrogen and carbon isotopic composition raises the possibility that rare xenon-bearing nanodiamonds are from supernovae, but that most diamonds formed in the solar system (10), although how diamonds, a reduced carbon phase, could form in an oxidized solar nebula remains unclear.

There has been some recent progress. A newly developed aberration-corrected scanning transmission electron microscope has allowed study of carbon bonding in meteoritic nanodiamond separates and revealed that there are actually two carbon phases present, crystalline nanodiamond and a spatially distinct disordered carbon phase with  $\text{sp}^2$  bonding (11). Either disordered carbon, nanodiamond, or both could be carriers of supernova xenon. Another advanced technique, atom probe tomography (12), which allows the mass and position of atoms in a sample to be determined with about 50% efficiency, has recently been applied to meteoritic nanodiamond. Sample preparation is the most difficult aspect of this technique, but individual nanodiamonds have recently been imaged (13, 14) and further advances may lead to carbon isotopic measurements of individual nanodiamonds. Because the solar  $^{12}\text{C}/^{13}\text{C}$  ratio is 89, a typical nanodiamond with 1,800 atoms of carbon should have about 20 atoms of  $^{13}\text{C}$ . Although  $^{13}\text{C}$ -poor nanodiamonds will be difficult to detect,  $^{13}\text{C}$ -rich ones should be readily apparent. Supernova SiC and graphite have a wide range of carbon isotopic compositions, so supernova diamonds might be expected to show a similar range.

**Silicon carbide.** Silicon carbide was the second presolar phase recognized in meteorites (2), and continues to be the most extensively studied. Presolar SiC grains range in size from a few nm to a few tens of  $\mu\text{m}$  in size and are easily studied individually by microbeam techniques (12). A database compiling literature data (15) shows over 40,000 individual carbon, nitrogen, or silicon isotopic analyses of individual SiC grains. Grains one  $\mu\text{m}$  or larger in diameter were extensively characterized in the 1990s and more advanced instruments like the NanoSIMS (12) are now concen-

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trating on the smallest analyzable SiC grains (16, 17) as well as rare very large ones (18, 19). Classification of SiC into different groups is based on its isotopic composition, primarily that of carbon, nitrogen, and silicon. Among individual SiC grains,  $^{12}\text{C}/^{13}\text{C}$  and  $^{14}\text{N}/^{15}\text{N}$  ratios cover an astounding four orders of magnitude, dwarfing the range of a few percent that these ratios vary over in natural terrestrial materials (Fig. 1). Silicon isotopic compositions are also quite variable, with  $^{29}\text{Si}/^{28}\text{Si}$  and  $^{30}\text{Si}/^{28}\text{Si}$  ratios covering a range of a factor of 15, again dwarfing the  $\sim 1\%$  range among terrestrial materials (Fig. 2). About 90% of SiC grains are thought to come from low-mass AGB stars of approximately solar metallicity. Type X grains are from core-collapse Type II supernovae and have been subdivided into Types X0, X1, and X2 based on silicon isotopic compositions and several other isotopic systems (20). Types Y and Z grains are from low metallicity AGB stars (21, 22). The origin of Type AB grains is not clear and several alternatives have been suggested (23). Very  $^{29}\text{Si}$ -,  $^{30}\text{Si}$ -rich SiC grains have been known for a while, but were only recently named Type C grains; they come from supernovae (17, 24–27). A few SiC grains have isotopic compositions characteristic of novae (28) and a few others don't fit into the major groups of grains. The isotopic compositions of many other elements have been measured in presolar SiC and some of these data will be discussed below.

**Graphite.** Graphite grains are perhaps the most complex of presolar grains, as transmission electron microscopy of microtomed thin sections of graphite shows that they often contain inclusions of refractory carbides and metal enclosed in graphite (29–32). In other words, graphite grains are tiny sedimentary rocks, which preserve textural, chemical, and isotopic evidence of the environments in which they formed. Whereas analyses of whole graphite grains were done in the 1990s, more recent efforts have concentrated on identification and even isotopic analysis of subgrains within graphite (24, 33). Graphite has quite variable carbon and nitrogen isotope ratios, but there is a tendency towards atmospheric nitrogen isotopic composition (Fig. 1), likely because of contamination with terrestrial nitrogen during the harsh chemical processing needed to extract graphite from primitive meteorites

(34). About 60% of graphite grains come from core-collapse supernovae, 30% from low-mass AGB stars, and the remainder from other types of carbon-rich stars (35).

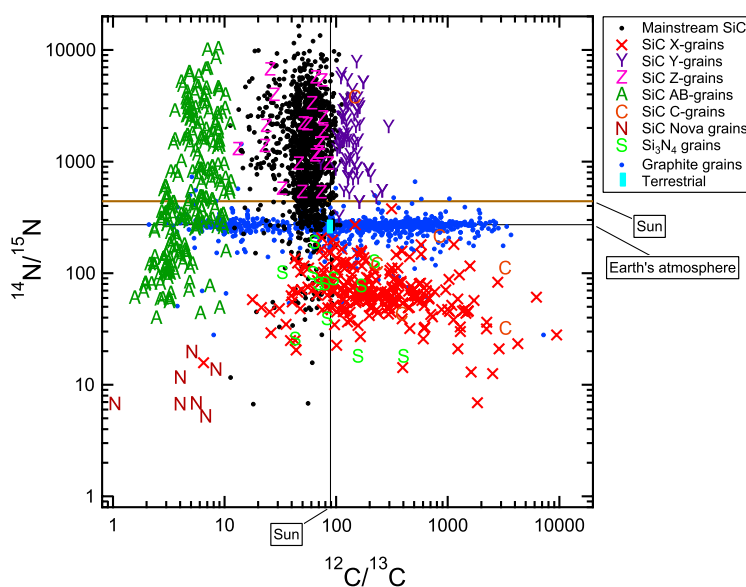
**Silicon nitride.** Diamond, silicon carbide, and graphite are the major reduced presolar grain types, but  $\text{Si}_3\text{N}_4$  has also rarely been found as a separate phase (20, 36). Silicon nitride has similar isotopic properties to Type X SiC grains (Figs. 1 and 2) and is likely formed in the ejecta of core-collapse supernovae.

**Oxidized Phases. Oxides.** Presolar oxide grains, principally aluminum oxide and hibonite, have been known since the mid-1990s, but with advanced techniques that can identify sub- $\mu\text{m}$  presolar grains, the list has expanded to include spinel, chromite, and  $\text{TiO}_2$ . All of these minerals also formed within the solar system and are commonly found in the same meteorites where presolar grains are found. The presolar oxide grains can only be identified by their anomalous oxygen isotopic composition and are found by oxygen isotopic mapping with ion microprobes (12). The oxygen isotopic compositions of presolar oxides show a wide range (Fig. 3). These oxides have been classified into four different groups, each of which is thought to have formed in different stellar environments (37). Approximately 90% of presolar oxides come from AGB stars and 10% from core-collapse supernovae (35).

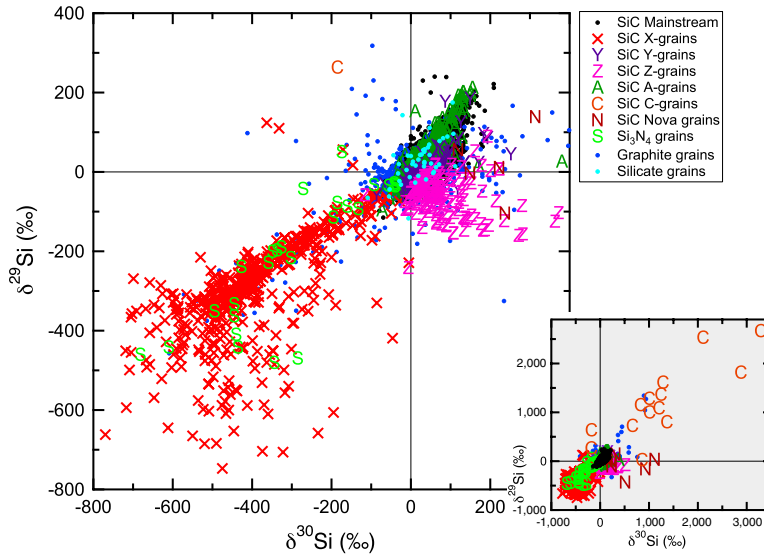
**Silicates.** For a long time, it was considered a great puzzle in the field that reduced phases such as silicon carbide and graphite were easy to identify in primitive meteorites, but no silicate phases were found. The development of the NanoSIMS, an advanced ion microprobe that allowed oxygen isotopic mapping with a spatial resolution of  $\sim 100$  nm (12), led to the discovery of presolar silicates in interplanetary dust particles (38) and primitive meteorites (39) in the early 2000s. Presolar silicates show the same oxygen isotopic range and fall into the same isotopic groups as presolar oxides (Fig. 3).

#### Isotopic Measurement of Minor and Trace Elements

The mineral chemistry of these presolar grains dictates abundances of minor and trace elements, whose isotopic patterns can



**Fig. 1.** Carbon and nitrogen isotopic compositions of presolar SiC, graphite, and  $\text{Si}_3\text{N}_4$ . Grains plot in distinct groups, depending on their stellar origins. Note that the entire range of natural isotopic variation on Earth is a tiny cyan square in the center. The recently measured solar nitrogen isotopic composition (9) is distinctly different from that of the Earth's atmosphere. Data from the Presolar Grain Database (15) with a few updates from recent literature (17, 24–27).



**Fig. 2.** Silicon isotopic compositions of presolar SiC, graphite, and silicates. The full range of isotopic compositions is shown in the inset. The solid lines denote terrestrial silicon isotopic composition, presumed to be the same as solar composition. Data from the Presolar Grain Database (15) with a few updates from recent literature (17, 24–27).  $\delta^{xx}\text{Si} = [({}^{xx}\text{Si}/{}^{28}\text{Si})_{\text{sample}}/({}^{xx}\text{Si}/{}^{28}\text{Si})_{\text{Earth}} - 1] \times 1000$ .

be used to study stellar nucleosynthesis. One of the reasons that SiC is so widely studied is that its crystal structure accepts a number of minor and trace elements. In addition to silicon, carbon and nitrogen, the isotopic compositions of neon, magnesium, calcium, titanium, chromium, iron, nickel, strontium, zirconium, molybdenum, ruthenium, and barium have been measured in individual presolar SiC grains. While some of these elements have been measured by ion microprobe, advanced techniques such as resonant ionization mass spectrometry (12, 40) are needed to measure many of the heavy elements. Graphite is also widely studied, because inclusions of refractory carbides allow measurement of individual graphite grains and, with the highest resolution instruments, even

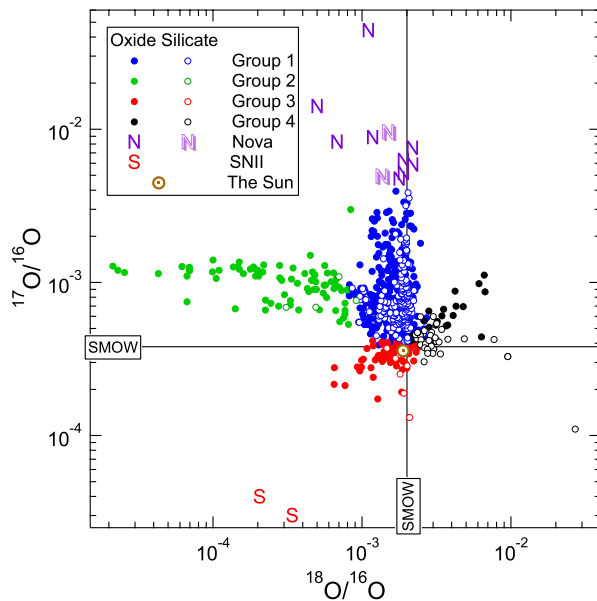
individual subgrains within graphite. Oxides are somewhat more difficult to fully isotopically characterize. The most common minerals among presolar silicates are olivine and low-calcium pyroxene, which tend to have very low concentrations of elements other than their major constituents (oxygen, magnesium, silicon, and iron).

Presolar grains often show the effects of decay of extinct radionuclides. Among the short-lived radionuclides whose presence has been inferred are  ${}^{26}\text{Al}$  ( $T_{1/2} = 7.1 \times 10^5$  y),  ${}^{41}\text{Ca}$  ( $T_{1/2} = 1.03 \times 10^5$  y),  ${}^{44}\text{Ti}$  ( $T_{1/2} = 59$  y),  ${}^{49}\text{V}$  ( $T_{1/2} = 331$  d),  ${}^{93}\text{Zr}$  ( $T_{1/2} = 1.5 \times 10^6$  y),  ${}^{99}\text{Tc}$  ( $T_{1/2} = 2.13 \times 10^5$  y), and  ${}^{135}\text{Cs}$  ( $T_{1/2} = 2.3 \times 10^6$  y). The inferred presence of  ${}^{49}\text{V}$  in supernova SiC grains is particularly interesting, as it implies grain condensation within a couple of years of the explosion (41), but is also equivocal. Early condensation of dust has been observed around supernova 1987A, but the  ${}^{49}\text{Ti}$  excesses used to infer the presence of  ${}^{49}\text{V}$  in presolar grains may have other origins within supernovae (20).

### Stellar Sources

Types, abundances, sizes, and stellar sources of stardust are shown in Table 1. Information comes from similar tables in recent reviews (35, 42).

**Asymptotic Giant Branch Stars.** About 90% of presolar SiC grains have isotopic characteristics suggesting formation around AGB stars. These stars represent a late phase of the normal stellar evolution of stars with initial masses of 1.5 to 4 solar masses. At this point, low-mass stars have burned hydrogen and helium to yield an inert core of carbon and oxygen, over which are layers that burn hydrogen to helium and helium to carbon. Outside of these burning layers is an extended stellar envelope. AGB stars produce carbon and *s*-process elements. Most of the time, these stars burn hydrogen at the base of the envelope. Eventually, helium builds up and reaches temperatures and pressures high enough to initiate the triple- $\alpha$  reaction, in which helium is burned to carbon. The latter burning phase occurs episodically, causing a thermal pulse that dredges freshly made  ${}^{12}\text{C}$  and *s*-process heavy elements into the well-mixed envelope (43). Stars also lose significant mass during the AGB phase. Mainstream SiC, graphite with heavy element carbides, and group I oxide and silicate grains have the isotopic, chemical, and textural characteristics expected from ejecta from AGB stars. Enrichments in *s*-process isotopes of heavy elements are in excellent agreement with models of



**Fig. 3.** Oxygen isotopic compositions of presolar oxides and silicates. The recently measured solar oxygen isotopic composition, although distinctly different from that of the Earth, Moon, and most meteorites (59), is seen to be only slightly displaced from SMOW (Standard Mean Ocean Water) on this log-log plot. Data from the Presolar Grain Database (15).

Table 1. Types, abundances, sizes, and sources of stardust (after 33,40)

Mineral	Type	Abund* (ppm)	Size (μm)	Isotopic signature	Stellar source <sup>†</sup>	Relative contribution
Diamond		1400	0.002	Solar $^{12}\text{C}/^{13}\text{C}$ , $^{14}\text{N}/^{15}\text{N}$ ; Xe-HL	SNII; solar system?	
SiC	mainstream	30	0.3–50	low $^{12}\text{C}/^{13}\text{C}$ ; high $^{14}\text{N}/^{15}\text{N}$ ; <i>s</i> -elements	AGB (1.5–3 $M_{\odot}$ )	90%
				very low $^{12}\text{C}/^{13}\text{C}$ ; high $^{14}\text{N}/^{15}\text{N}$	J-stars; born-again AGB	<5%
				high $^{12}\text{C}/^{13}\text{C}$ ; very high $\delta^{29,30}\text{Si}$ ; extinct $^{26}\text{Al}$ , $^{44}\text{Ti}$ , $^{49}\text{V}$	SNII	0.1%
	X0			low $^{14}\text{N}/^{15}\text{N}$ , negative $\delta^{29,30}\text{Si}$ , high $^{29}\text{Si}/^{30}\text{Si}$ ; extinct $^{26}\text{Al}$ , $^{44}\text{Ti}$ , $^{49}\text{V}$	SNII	0.2%
	X1			low $^{14}\text{N}/^{15}\text{N}$ , neg. $\delta^{29,30}\text{Si}$ , midrange $^{29}\text{Si}/^{30}\text{Si}$ ; extinct $^{26}\text{Al}$ , $^{44}\text{Ti}$ , $^{49}\text{V}$	SNII	1%
	X2			low $^{14}\text{N}/^{15}\text{N}$ , neg. $\delta^{29,30}\text{Si}$ , low $^{29}\text{Si}/^{30}\text{Si}$	SNII	0.3%
	Y			high $^{12}\text{C}/^{13}\text{C}$ ; high $^{14}\text{N}/^{15}\text{N}$	~1/2 solar metallicity AGB	few %
	Z			low $^{12}\text{C}/^{13}\text{C}$ ; high $^{14}\text{N}/^{15}\text{N}$ ; mostly neg. $\delta^{29}\text{Si}$ ; high $\delta^{30}\text{Si}$	~1/4 solar metallicity AGB	few %
	nova			low $^{12}\text{C}/^{13}\text{C}$ ; high $\delta^{30}\text{Si}$ ; Ne-E(L) <sup>‡</sup>	novae	0.1%
	Graphite		10	1–20	low $^{14}\text{N}/^{15}\text{N}$ , high $^{18}\text{O}/^{16}\text{O}$ ; extinct $^{26}\text{Al}$ , $^{41}\text{Ca}$ , $^{44}\text{Ti}$ , $^{49}\text{V}$	SNII
<i>s</i> -elements low $^{12}\text{C}/^{13}\text{C}$					AGB (1.5–3 $M_{\odot}$ ) J-stars; born-again AGB	30% <10%
low $^{12}\text{C}/^{13}\text{C}$ ; high $\delta^{30}\text{Si}$ ; Ne-E(L) <sup>‡</sup>					novae	<10%
$\text{Si}_3\text{N}_4$		0.002	≤1	low $^{14}\text{N}/^{15}\text{N}$ , $\delta^{29,30}\text{Si}$ , extinct $^{26}\text{Al}$	SNII	100%
Oxides		50	0.1–2			
Silicates		200	≤1	high $^{17}\text{O}/^{16}\text{O}$ ; low or normal $^{18}\text{O}/^{16}\text{O}$	AGB (1–2.2 $M_{\odot}$ )	70%
				high $^{17}\text{O}/^{16}\text{O}$ ; very low $^{18}\text{O}/^{16}\text{O}$	AGB (<1.8 $M_{\odot}$ ; CBP)	15%
				low $^{17}\text{O}/^{16}\text{O}$ , $^{18}\text{O}/^{16}\text{O}$	AGB (low mass & metallicity); SNII	5%
				low $^{17}\text{O}/^{16}\text{O}$ , $^{18}\text{O}/^{16}\text{O}$ ; extinct $^{44}\text{Ti}$	SNII	10%
				very high $^{17}\text{O}/^{16}\text{O}$ ; low $^{18}\text{O}/^{16}\text{O}$	novae	<1%

\*Abund—abundance by weight in CM chondrites.

<sup>†</sup>AGB—asymptotic giant branch stars; SNII—Type II supernovae; CBP—cool-bottom processing, a process that can occur at the base of the envelope of low mass AGB stars.

<sup>‡</sup>Ne-E(L) is a component of neon highly enriched in  $^{22}\text{Ne}$ , likely from the decay of  $^{22}\text{Na}$ .

nucleosynthesis in AGB stars (44, 45) and the inferred presence of  $^{99}\text{Tc}$  ties mainstream SiC grains to the major site for the *s*-process (46). Low-mass stars likely are oxygen-rich while on the main sequence and become carbon-rich as  $^{12}\text{C}$  is mixed into the envelope during the AGB phase. Thus, during the earlier stages AGB stars condense oxides and silicates and in the later stages they condense SiC and graphite. AGB stars are also the source of Type Y and Z grains, but lower metallicity is needed to explain the enhanced  $^{30}\text{Si}$  in these grains. AGB stars also produce about one third of all graphite grains and the majority of oxide and silicate grains.

**Supernovae.** Supernovae grains were the first type of SiC grains discovered after mainstream grains and comprise about 2% of all SiC grains, about two-thirds of all graphite grains, all  $\text{Si}_3\text{N}_4$  grains, and about 10% of oxide and silicate grains. These grains are thought to come from Type II supernovae. Such stars have an initial mass of 8 to 40 solar masses. These massive stars evolve rapidly and develop an onion-shell structure with increasing degrees of nuclear burning towards the core. Eventually the core burns to iron and then collapses on itself, leading to an explosion that throws off the outer layers and leaves a neutron star as a remnant. A wide variety of nucleosynthesis environments occur in these stars, both before the explosion and due to shock waves passing through the ejecta. Presolar grains do not randomly sample this material, but appear to require mixing of different layers of ejecta. For example, the  $^{28}\text{Si}$ -rich silicon in the grains is unlikely to come from the same region as the  $^{12}\text{C}$ -rich carbon. It is likely that SiC forms from a carbon-rich gas, but Type X SiC often contains molybdenum with a peculiar isotopic signature resulting

from the explosion that occurs in an oxygen-rich layer of ejecta (47, 48). Models that mix different layers of ejecta from stellar evolution calculations with a full nuclear network (49) have achieved some success in explaining the isotopic and chemical properties of supernova stardust (50–52), but some problems remain in explaining observations of supernova grains. It is clear that a deeper understanding of mixing and chemical behavior in supernova ejecta is needed.

**Other Sources.** A few SiC and graphite as well as silicate and oxide grains have the isotopic characteristics of novae (26, 53), which include low  $^{12}\text{C}/^{13}\text{C}$  and  $^{14}\text{N}/^{15}\text{N}$  (Fig. 1) or very high  $^{17}\text{O}/^{16}\text{O}$  (Fig. 3). Although Type Ia supernovae produce about two-thirds of all of the iron in the galaxy, no grains from such sources have been unambiguously identified. Type AB SiC grains have extremely low  $^{12}\text{C}/^{13}\text{C}$  ratios that may or may not have enrichments in *s*-process elements. J-type carbon stars and born-again AGB stars have been proposed for normal and *s*-process-enriched AB grains, respectively (23).

### Recent Advances

1. It has been known for many years that leaching of primitive meteorites with progressively harsher reagents dissolves material that is enriched or depleted in  $^{54}\text{Cr}$ . A search of nearly 20 y for the actual carrier of this isotope anomaly culminated in the discovery of spinel grains with  $^{54}\text{Cr}/^{52}\text{Cr}$  ratios several times the terrestrial ratio (54, 55).
2. Stardust grains in meteorites are known to be presolar, because they have exotic properties and are contained in meteor-



ites that formed early in solar system history, but it has proven difficult to determine how old the grains are. Long-lived radionuclides are not useful for the most part, because presolar grains do not have favorable parent-daughter ratios, but there is hope that the uranium-lead system can be used to date grains. For now, the best constraints come from rare isotopes produced in grains by galactic cosmic rays. The interstellar residence times inferred for large presolar SiC grains are 40 to 1,000 My based on  $^6\text{Li}$  (18) and 3 to 1,100 My based on cosmogenic helium and neon (19).

3. The application of multiple techniques to the same stardust grain, with analyses done in order of increasing destructive-

ness has led to a number of advances and this approach will grow in the future to get the maximum information from each grain. As an example, the development of focused ion beam milling for preparation of transmission electron microscopy samples has allowed detailed structural analyses to be combined with ion microprobe isotopic measurements, so that conditions of formation of presolar grains can be studied in unprecedented detail (e.g., 56–58).

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