The Laboratory Study of Ancient Stardust

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Où finit le télescope, le microscope commence. Lequel des deux a la vue la plus grande? Choisissez.

Victor Hugo *Les Misérables* Tome IV, Livre troisième, Chapitre III

Introduction

In the last stages of their lives, stars lose some or most of their mass through a continuous ejection of gases in stellar winds, or sometimes, in the case of very massive stars, violently through supernova explosions. The ejected gaseous material expands and cools, partly forming tiny mineral grains, which are literally "stardust." To some astronomers this dust is merely a nuisance because it obscures the line of sight to astronomical objects of interest. But to others, the dust itself is a worthy object of study. First, the dust that forms in the mass outflow of a star couples to the star's radiant energy, which propels the grains outward. These grains, in turn, push gas molecules away from the star, thus driving its mass loss and determining the subsequent evolution of the star. Second, collections of gas and dust are the building materials for new stars and planetary systems like our own. Indeed, except for H and He, all of the elements in our bodies—e.g., the Ca in our bones and the Fe in our blood—were made in the nuclear furnaces of ancient stars. And third, the stardust itself is, in effect, a relic of grain formation around ancient stars. Its isotopic composition, morphology, chemistry and mineralogy contain detailed information about nuclear processes occurring within stars, as well as the physical and chemical conditions that prevail in the star's mass outflow during grain formation. Remote astronomical observations can give us limited information about some of these things, but to get really detailed information we would need to study these grains in the laboratory—figuratively speaking, to do astronomy with a microscope instead of a telescope. Is this really possible? Remarkably, the answer is "yes."

Primitive Meteorites of the Solar System – Le Régne Minéral No3 2013 pp. 41-46.

Some History

By the early 1970s, after the Apollo and Luna sample return missions from the Moon, cosmochemists had three kinds of solids from the Solar System that could be analyzed: terrestrial rocks, meteorites, and lunar rocks. For nearly all of the major elements, the isotopic compositions of these materials were identical to high precision, and for those elements that showed variations (e.g., several percent variations in C isotopic ratios), the cause could be ascribed plausibly to nuclear, chemical or biological processes operating in the Solar System. Thus arose the idea that when the Sun and the planets formed from the cloud of gas and dust known as the "solar nebula," the cloud had become so hot that all previous stardust grains were vaporized and destroyed, completely erasing evidence of them and their individual prior histories, and making the isotopic composition of the solar nebula a homogeneous average. It was realized that if any grains of ancient stardust survived, they would probably have isotope compositions markedly different from this average Solar System composition, which would reflect the particular nuclear processes operating in their stellar sources. Although isotope anomalies in the major element oxygen had been discovered in the early 1970s, and were thought to be evidence of the presence of surviving stardust, it turned out that the solids containing the O-anomalies had really formed in the Solar System.

The real discovery of ancient stardust in meteorites (now referred to as "presolar grains"), came from the search for the mineral carriers of unexplained isotope anomalies in the noble gases Ne and Xe. Edward Anders and Roy Lewis at the University of Chicago had discovered that one could dissolve away 99% of a piece of a primitive carbonaceous meteorite like Murchison (Figure 1) in a mixture of the acids HF and HCl, and yet the anomalies remained! Thus began a heroic, decade long search for the mineral carriers of the anomalies, analogous to the effort to isolate radium by Marie and Pierre Curie. This work led, in 1987, to the discovery of the carrier of Xe anomalies—nanometer-sized diamonds. Additional work that same year, in collaboration with the authors' laboratory (which had a secondary ion mass spectrometer or SIMS capable of determining the isotopic compositions in tiny mineral grains), led to the discovery of micrometer-sized grains of silicon carbide (SiC) stardust as one of the carriers of Ne

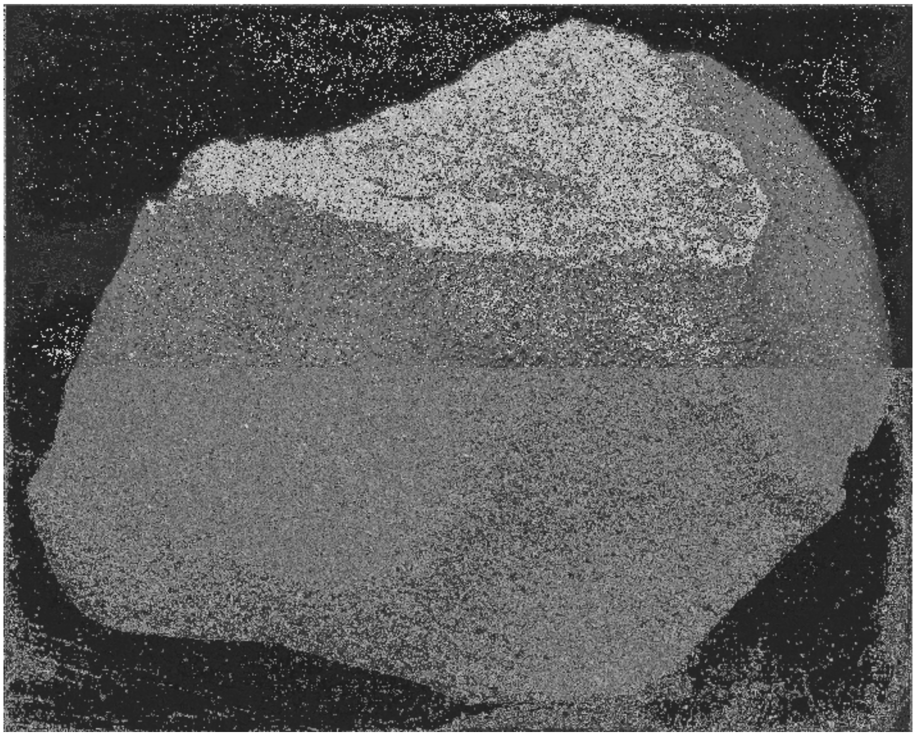


Fig. 1: The Murchison CM2 chondrite, which is a type of primitive meteorite that contains many presolar grains. Murchison, Australia; 7.7 x 4.5 x 4.0 cm; Fell on Nov. 28, 1969: MNHN (No 2436) – Photo: L. D. Bayle

anomalies. The other Ne anomaly carrier, later isolated by Sachiko Amari at the University of Chicago, was micrometer-sized graphite spherules, a third type of ancient stardust. Chemical isolation also aided in the discovery of presolar oxide grains like corundum, but the discovery of silicate stardust grains (known from astronomical observation to exist in the interstellar medium) could not be achieved this way, since presolar silicates dissolve just like the Solar System silicates that make up the bulk of primitive meteorites. Their discovery in the early 2000s had to await the development of automated instrumentation that could efficiently detect these tiny grains, which are present at abundances of at most a few hundred ppm in meteorites. That instrument is the NanoSIMS (= nanoscale SIMS; Figure 2). The isotopic anomalies measured in the NanoSIMS that establish a given grain as presolar also give information about the kinds of stars that gave birth to them and the nuclear processes taking place in those stars. For both C- and O-rich presolar grains, the isotopic ratios of their major elements can be

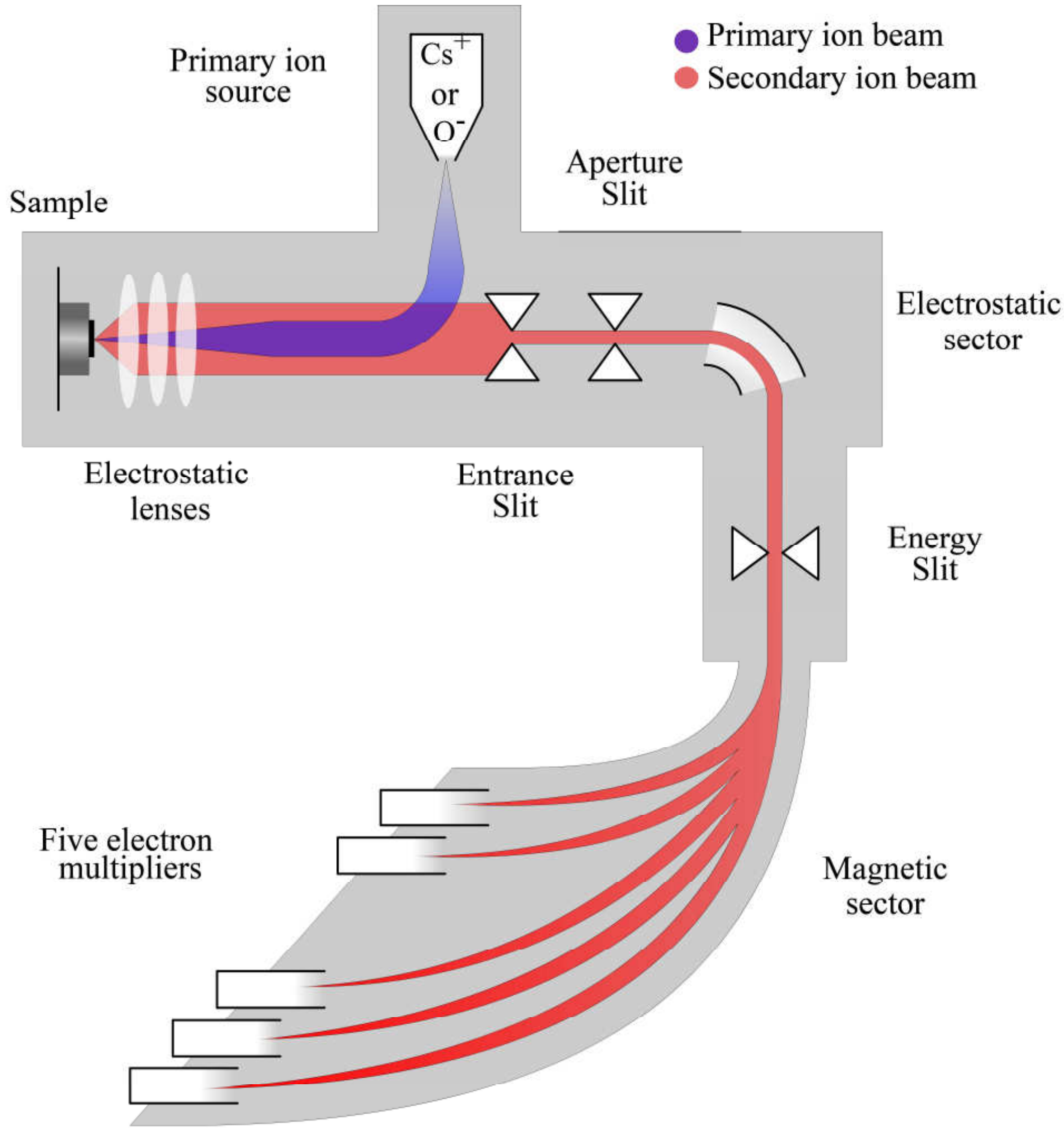


Fig. 2: In an ion microprobe, the implantation of a species of primary ions into a given sample leads to the emission of secondary ions which are then sent through a mass spectrometer. Technological advances in secondary ion mass spectrometry (SIMS), continually pioneered by Georges Slodzian of the University of Paris-Sud, have allowed an increased ability to isotopically analyze grains on the sub-micron scale. Typical ion microprobes, for instance the Cameca IMS-f series, employ an off-axis, oblique, primary ion beam to generate secondary ions by sputtering the sample surface. Prof. Slodzian realized that placing the extraction lenses of the secondary ions much closer to the sample surface, by incorporating co-axial primary and secondary ion optics, would allow for greater spatial resolution (on the order of ~50 nm) and significantly higher ionization yields, even at high mass-resolving-power.

compared to theoretical models of nucleosynthesis in dust-forming stars such as asymptotic giant branch and red giant branch stars (AGB and RGB, respectively), and Type II supernovae (SNe). For instance, a comparison of the $^{12}C/^{13}C$ ratios in presolar SiC grains with those measured in C-rich AGB stars reveals a striking similarity (Figure 3), which is interpreted as proof of their extra-solar source. The vast majority of all presolar grains can be assigned to origins in two different astrophysical settings: giant branch stars of various masses and metallicities, or SNe. Presolar grains are minerals, so once they have been identified isotopically, their composition and atomic structure can be analyzed by conventional experimental methods, such as transmission electron microscopy (TEM). Such studies yield a wealth of information about the physical and chemical conditions in the mass outflows of highly evolved stars.

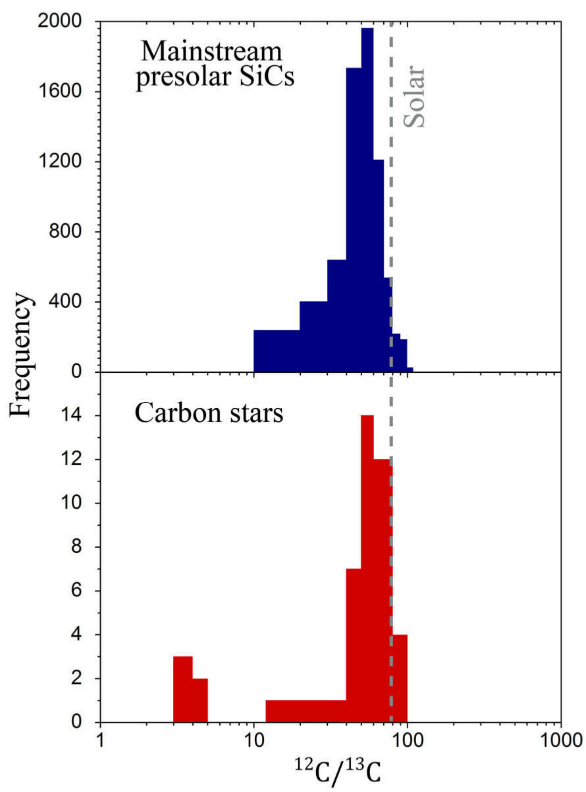


Fig. 3: The distribution of $^{12}C/^{13}C$ ratios in presolar SiC mainstream grains compared to astronomical values measured by spectroscopic methods in N-type (cool C-rich) AGB stars as a function of number. The striking similarity of the two distributions, with peaks at values of ~55, combined with the fact that both distributions clearly do not have compositions representative of the Sun or the Solar System average ($^{12}C/^{13}C$ = 89) is conclusive evidence that not only are the grains presolar, but that they condensed in mass outflows of AGB stars having close-to-solar masses and metallicities. Also, the spread of their $^{12}C/^{13}C$ ratios is indicative that the grains come from many presolar C stars, not a single one.

Oxide and silicate presolar grains

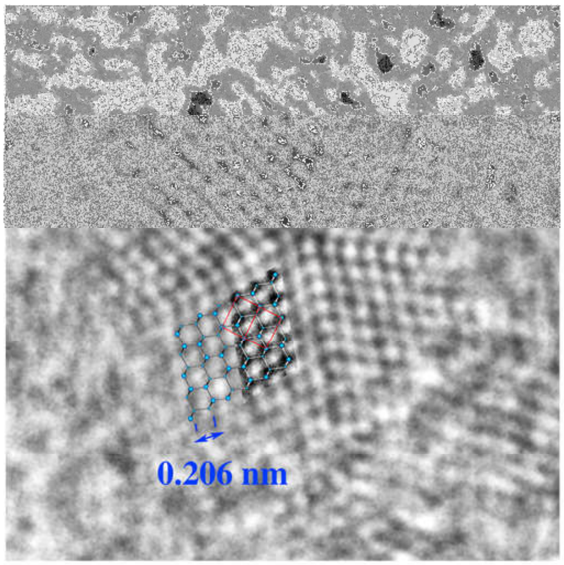
O-rich presolar grains including alumina (Al_2O_3), spinel ($MgAl_2O_4$), hibonite ($CaAl_{12}O_{19}$) and silicates are now known to be the most abundant presolar grains in meteorites. Based on their O isotopic compositions, most presolar O-rich grains (both oxides and silicates) have been assigned to four groups, thought to reflect origins in distinct types of stars. The isotopic signatures of most Group 1-3 grains are consistent with models of envelope compositions of low-mass ($M \lesssim 3M_{\odot}$), close-to solar metallicity RGB and AGB stars, while the enigmatic Group 4 grains have been theorized to be possible SN condensates. There is some evidence that many (or all) of the Group 4 grains, and perhaps some of the Group 3 grains, may come from a single supernova; however, this is not yet firmly established.

Nanodiamonds

Nanometer-sized diamonds are the most abundant refractory carbonaceous material in chondrites (Figure 4). Although they were the first presolar minerals to be discovered, the origin of the bulk of them is still unknown. Careful high-resolution TEM analysis has shown that typical nanodiamond microstructures most closely resemble those of nanodiamonds produced by chemical vapor deposition rather than shock. This suggests that the nanodiamonds formed by low-pressure condensation from a C-rich vapor. The average C isotopic composition is normal, but evidence for a supernova origin of at least some of the diamonds comes from anomalous Xe and Te isotopic compositions. Even if individual diamonds have very different C isotope compositions and originated in a wide variety of stellar sources, the most sensitive isotopic measurements to date still require thousands of diamonds, which might effectively average their isotopic compositions to yield a solar-like mean. Alternatively, most of them might have been produced from a gas of solar-like C isotopic composition, perhaps even early in the Solar System.

Presolar graphite

Presolar graphite generally comes in micrometer-sized spherules of two basic kinds: a high density (HD) form with an external morphology resembling an onion (Figures 5a and 5b) and a lower density (LD) form resembling a cauliflower. When sliced into cross-sections a few hundred atoms thick, TEM studies of graphites reveal additional high-temperature mineral grains (predominantly Ti, Si, Zr, and Mo carbides) sequestered inside, making these presolar grains, in reality, tiny polymineralic rocks. Some TiCs served as nuclei for graphite condensation (Figure 5c), allowing determination of the order in which phases condense. The types of mineral phases present and their condensation order in these assemblages permit thermodynamic models to be used to



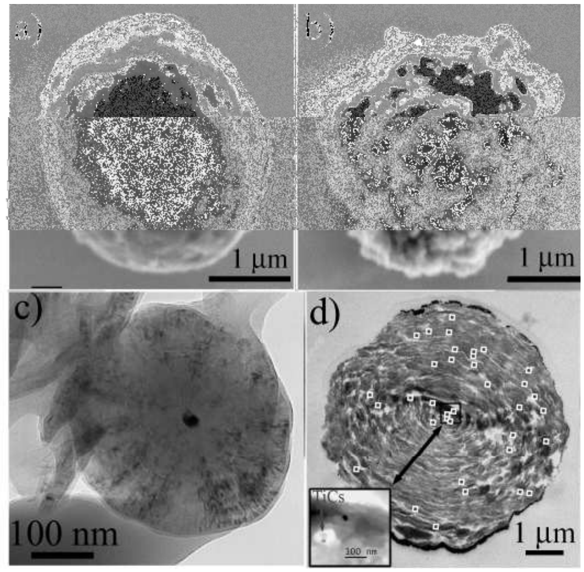


Fig. 4: High resolution transmission electron microscope (TEM) image of a nanodiamond from the meteorite Allende, showing five-fold symmetry due to twinning (courtesy of Tyrone Daulton).

Fig. 5: Scanning electron microscope (SEM) images of a) presolar graphite grain with a "cauliflower" morphology and b) with an "onion" morphology (both courtesy of Sachiko Amari); c) TEM image of 70nm thick ultramicrotome slices of an onion-type presolar graphite spherule from an AGB star with a 30 nm TiC crystal at its center that served as a nucleation center for condensation of the graphite; and d) TEM image of graphite spherule from a supernova showing the locations of many TiC crystals (see inset) accreted by the graphite during its growth.

determine the range of temperatures and pressures under which onion graphites formed. Their noble gas isotopic compositions and the degree of s-process enrichment in their internal carbides both suggest that most HD graphites form in AGB stars. Most LD graphite spherules (~5 micrometers average diameter) contain large ^{18}O and ^{28}Si enrichments that could only have been produced by massive stars such as SNe. Stellar models and astronomical observations suggest that outer SN layers are sufficiently C-rich to enable graphite condensation, and these layers also contain isotopic anomalies (e.g., enrichments of ^{18}O, ^{15}N) that are consistent with those measured in LD SN graphites. In contrast to the HD graphites, the TiCs in SN graphites lack s-process elements but instead sometimes have overgrowths of other phases, such iron-nickel metal, nickel silicides and

SiC. In some cases, a single graphite captured and preserved hundreds of such subgrains during its growth (e.g., Figure 5d), and here chemical and size trends in the internal grain properties can reveal details about the evolution of the gas from which they condensed. While formation of carbonaceous dust has been observed astronomically around SNe, the relatively featureless spectra from these grains yield little additional information. Thus, these graphite assemblages offer a unique means to study nucleosynthesis, mixing and grain condensation in SN ejecta.

Presolar silicon carbide (SiC)

Primarily based on their C, N, and Si isotopic compositions, presolar SiC have been categorized into different populations, termed mainstream, AB, X, Y, Z, and nova (Figure 6). Comparison of the isotopic compositions of these different grain types to the compositions both measured in and predicted for various astrophysical settings has led to well accepted origin scenarios for most SiC grain types. Mainstream, type Y, and type Z grains have been attributed to an origin in low-mass (1–3 $M_{\odot}$) AGB stars of approximately close-to-solar, half-solar, and one-third-solar metallicity, respectively. Type X grains often have large inferred $^{26}Al/^{27}Al$ ratios and large enrichments in ^{44}Ca from the decay of ^{44}Ti, indicative of condensation in the ejecta of a SN explosion.

For a compound consisting of only two elements, the microscopic structure of SiC is fascinatingly complex. This comes from the fact that the fundamental stacking layers of Si and C planes can each have one of three rotational positions (A, B or C) and the repetitive sequence of these layers produces different crystal forms called “polytypes.” For example, the sequence ABCABCABC…gives rise to the unique cubic polytype (called 3C), and the sequence ABABAB… gives rise to 2H, the simplest of the many hexagonal and rhombohedral polytypes (Figure 7a). More than two hundred different SiC polytypes are known from laboratory syntheses, but TEM studies have shown that only the two simplest polytypes, 3C and 2H, and intergrowths of these two forms, occur as presolar SiC. These generally condense from vapor at lower temperatures (1500 K - 1700 K) than the other polytypes, and such condensation temperatures are consistent with predictions based on equilibrium thermodynamic models of grain formation, for example around AGB stars.

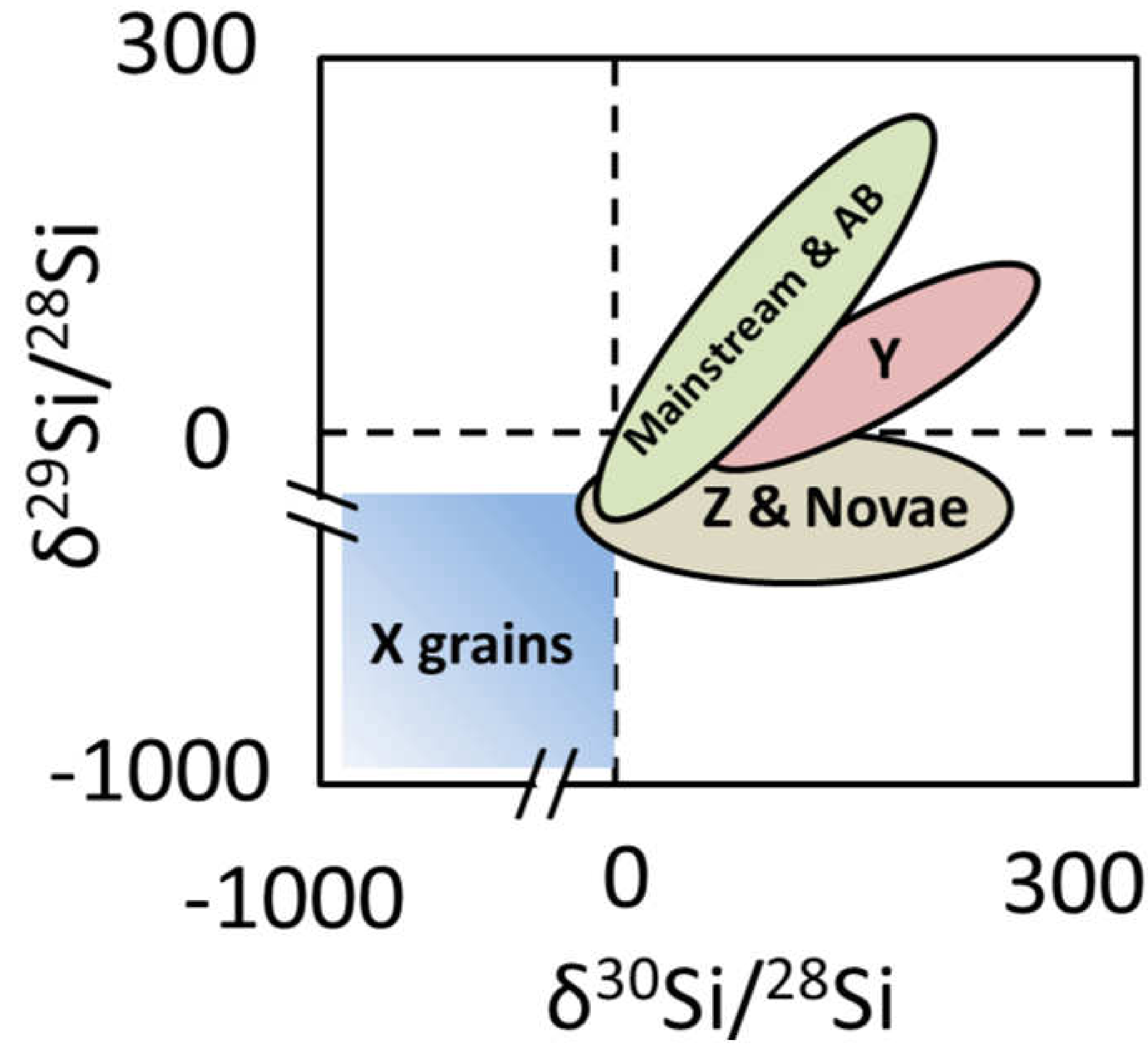


Fig. 6: Schematic diagram of the Si 3-isotope compositions of presolar SiC grains, expressed as per mil deviations (i.e., δ-values) from solar ratios, for the various grain types described in the text. Mainstream, type Y, and type Z grains come from low-mass AGB stars of varying metallicities. Type X grains are thought to condense in stellar outflows of Type II SNe; however, the astrophysical origins of Type AB and nova grains are more enigmatic. Type AB grains likely originate in J-type C stars or born-again AGB stars, while nova grains probably formed in binary star systems.

Presolar SiC grains that came from AGB stars have had a complicated history: they condensed in the expanding atmospheres of these stars; they were expelled by stellar radiation pressure into the interstellar medium where they may have resided for hundreds of millions of years; during this time they acted as substrates for the condensation of ices which were continually processed by ultraviolet radiation, forming coatings of complex organic molecules; they were accreted into the solar nebula 4.6 billion years ago, becoming constituents of asteroids, pieces of which ultimately fell onto the Earth. Is it possible that the SiC grains have recorded any evidence of this fantastic journey? To answer this question we could not study SiC that has been concentrated by chemical processing, because this would have already damaged the surfaces of the grains. Instead we had to conduct laborious scanning electron microscope searches for "pristine" SiC, present only at the level of a few parts per million in primitive carbonaceous meteorites. We found some pristine SiC grains with exquisitely detailed polygonal surface features that reflect incomplete convergence of growth fronts caused by cessation of quick grain growth (Figure 7b). No evidence was discovered of coatings of minerals like silicates, which would have formed subsequent to SiC, suggesting that the growth of such minerals was inhibited by rapidly falling gas pressures as SiC grains were propelled away from their parent stars. We do, however, sometimes observe other internal minerals like TiC and CaS within SiC that formed by exsolution as temperatures fell. Some pristine SiC grains appear to have amorphous carbonaceous coatings whose origin is unknown (Figure 7c). One intriguing possibility is that these coatings are the residues of evaporated ices that coated the SiC grains in the interstellar medium. Evidence for this origin may be carried by H, C and N isotopes in the coatings, and studies of these are currently underway in our laboratory.

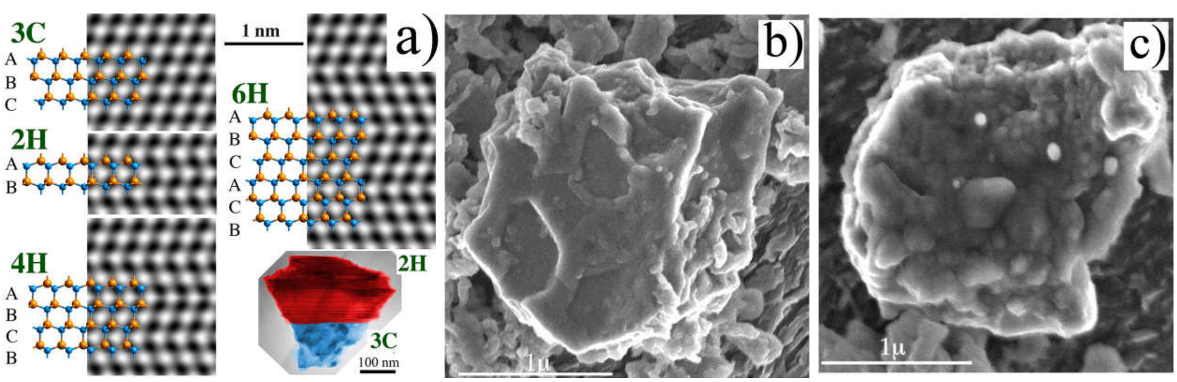


Fig. 7: a) The molecular structure of several polytypes of SiC (both ball and stick models and simulated TEM images), plus a false color image of a composite presolar SiC grain from the Murchison meteorite consisting of 2H and 3C polytypes on either side of a twin plane boundary (courtesy of Tyrone Daulton). b) SEM image of a pristine SiC grain from an AGB star showing polygonal features resulting from arrested growth of surface atomic layers; c) SEM image of a pristine SiC grain with an amorphous coating of carbonaceous material, possibly of interstellar origin.