Review

Recent Progress in Presolar Grain Studies

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Presolar grains are stardust that condensed in stellar outflows or stellar ejecta, and was incorporated in meteorites. They remain mostly intact throughout the journey from stars to the earth, keeping information of their birthplaces. Studies of presolar grains, which started in 1987, have produced a wealth of information about nucleosynthesis in stars, mixing in stellar ejecta, and temporal variations of isotopic and elemental abundances in the Galaxy. Recent instrumental advancements in secondary ion mass spectrometry (SIMS) brought about the identification of presolar silicate grains. Isotopic and mineralogical investigations of sub- μm grains have been performed using a combination of SIMS, transmission electron microscopy (TEM) and focused ion beam (FIB) techniques. Two instruments have been developed to study even smaller grains (~ 50 nm) and measure isotopes and elements of lower abundances than those in previous studies.

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INTRODUCTION

Our solar system formed from a molecular cloud that contained dust and gas expelled from dying stars 4.6 billion years ago. Until the late 1960s it was believed that the solar system was isotopically homogeneous because all dust grains in the molecular cloud were evaporated and material in the molecular cloud was well mixed during the formation. However, when Black and Pepin¹⁾ analyzed Ne in primitive meteorites, they found a ^{22}Ne -rich component contained in the meteorites ($^{20}\text{Ne}/^{22}\text{Ne} < 3.4$, $^{20}\text{Ne}/^{22}\text{Ne}_{\text{Air}} = 9.8$). The enrichment was so large that it could not be explained by the processes occurring in the solar system and its stellar origin was proposed: meteorites contain a small amount of stardust that survived the solar system formation and subsequent processes in meteorite parent bodies.²⁾ Isotopically anomalous Kr and Xe components were also detected in meteorite residues processed by HF–HCl.^{3,4)} Kr–S, for *s*-process (slow neutron capture process) Kr, and Xe–S, for *s*-process Xe, are enriched in even-numbered isotopes relative to the solar ratios. Xe–HL is enriched in light, *p*-process (proton capture process) only isotopes 124 and 126, and heavy, *r*-process (rapid neutron capture process) only isotopes 134 and 136.³⁾ Since the main *s*-process takes place in asymptotic giant branch (AGB) stars and the *p*- and *r*-processes are believed to take place in supernovae, these anomalies reinforced the idea that stardust was hidden in meteorites.

The identification and isolation of the carrier minerals that contained these anomalous noble gases was performed by Edward Anders, Roy S. Lewis and their colleagues at

The University of Chicago.^{5–8)} A historical account has been described by Anders.⁹⁾ They dissolved more than 99% of meteorites they started with during the separation. Diamond was the first mineral type that was isolated in meteorites in 1987,⁵⁾ followed by SiC^{6,10)} and graphite.¹¹⁾ Interestingly, they all are carbonaceous and quite resistant to chemicals, and that was the reason why they could be concentrated using chemicals. These grains also show isotopic anomalies in elements other than noble gases, proving their stellar origin. These grains are now called presolar grains, which are stardust that formed in stellar outflows or ejecta, remained mostly intact throughout their journey in space, and were eventually incorporated into meteorites.

Mineral types of presolar grains include diamond,⁵⁾ SiC,^{6,10)} graphite,¹¹⁾ Si_3N_4 ,¹²⁾ oxides,^{13–15)} silicates^{16–19)} and refractory carbides inside SiC²⁰⁾ and graphite.²¹⁾ Their abundances range from a few ppb (nanograms/gram) to a few hundred ppm (micrograms/gram) relative to bulk samples of undifferentiated chondrites^{7,8,22)} (Table 1).

Before presolar grains were discovered in meteorites, spectroscopic observations of stars were the only available observations of isotopic ratios in stars. The data obtained this way often have large uncertainties. Presolar grains, on the other hand, can be studied in the laboratory using the state-of-the-art instruments with much higher precision. Studies of presolar grains have yielded a wealth of information about nucleosynthesis in stars, mixing in stellar ejecta, and Galactic chemical evolution (the temporal variation of isotopic and elemental abundances in the Galaxy). There are many aspects of presolar grain studies, which are discussed in detail in review papers.^{29–32)} In this paper we will focus on recent progress that has been made in presolar grain studies

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Abbreviations: AGB, asymptotic giant branch; FIB, focused ion beam; RIMS, resonance ionization mass spectrometry; SIMS, secondary ion mass spectrometry; TEM, transmission electron microscopy; TIMS, thermal ionization mass spectrometry; TOF, time-of-flight

Table 1. Presolar grains in meteorites.

Mineral	Year of discovery	Size	Abundance*	References
Diamond	1987	Average: 30 nm	~500 ppm	5,7,23)
SiC	1987/1988	Mostly <1 μm , up to 50 μm (rare)	5.9 ppm	7)
Graphite	1990	>1 μm	0.88 ppm	7,24)
Refractory carbides (as subgrains)	1991	Up to a few hundred nm	(Present in host graphite/ SiC grains)	21,25,26)
Oxides	1994	Mostly <1 μm , up to a few μm	1–3 ppm**	13–15,22,27)
Si ₃ N ₄	1995	Up to a few μm	A few ppb	12)
Silicates	2004	<1 μm	29–57 ppm**	17–19,22,27)

* These numbers are relative to bulk samples of undifferentiated chondrites. The abundances of diamond, SiC and graphite are those in the Murchison meteorite (CM2).

** 100–200 ppm of silicates+oxides are a matrix-normalized abundance.²²⁾ In CO and CR chondrites where many of the abundance data have been obtained, the matrix comprise 30 vol% and 30–50 vol% of meteorites, respectively.²⁸⁾ Taking 30 vol% for the average and assuming that the matrix and the rest of the meteorites have the same density, the abundance of silicates+oxides relative to a bulk meteorite would be 30–60 ppm. The average ratio of silicates to oxides in CR chondrites is 22.²⁷⁾

during the last 10–15 years.

IDENTIFICATION OF PRESOLAR SILICATE GRAINS

Presolar SiC and, to lesser extent, graphite have been extensively studied using noble gas mass spectrometry, thermal ionization mass spectrometry (TIMS), and SIMS. There are two ways to analyze presolar grains. One way is to analyze a large number of grains at the same time (bulk analysis) and the other way is to analyze grains one by one. Most of the single grain data were obtained using SIMS. Since each presolar grain might have formed in a different star, single grain analysis would be best suited for presolar grains. A drawback is that these analyses require relatively large grains (>1 μm) and high elemental abundances in the grains. Isotopic ratios of C, N, Si, Mg–Al, Ca and Ti in SiC grains analyzed with SIMS³³⁾ and those of Kr, Xe, Sr, Ba with noble gas mass spectrometry^{34–36)} and TIMS^{37–39)} indicate that most SiC grains (~93% of the total SiC grains) formed in AGB stars.^{40–42)}

Carbon-rich stars produce carbonaceous grains while O-rich stars produce oxides and silicates (silicates can still form in C-rich conditions but mainly form in O-rich conditions). Studies of presolar oxides and silicates would give us much information of O-rich stars. The difficulty is, however, how to find presolar oxides and silicates in meteorites.

Carbonaceous grains are chemically resistant thus it is possible to use chemicals, such as hydrofluoric acid (HF) and dichromate solution ($\text{Cr}_2\text{O}_7^{2-}$), to remove the other phases to concentrate the carbonaceous grains. Since oxides are also chemically resistant, we could concentrate them together with these carbonaceous grains. The difference between C-rich and oxide grains is that most of the oxide grains in meteorites formed in the solar system. We needed a method to efficiently locate presolar oxides from the sea of solar oxide grains. Ion Imaging techniques were developed to find rare types of grains in low abundances from overwhelmingly abundant normal grains.¹³⁾ Isotopic images of a 100×100 μm area, where oxide grains are dispersed, are taken using a defocused beam. Grains are defined from a grain-definition algorithm and isotopic ratios of the grains are calculated from the images. This method enables us to quickly locate presolar oxides, which comprise much less

than 1% of the oxide grains in meteorites.

The search for presolar silicates was much more labor intensive. Most of the bulk meteorites were dissolved to concentrate oxide grains to search for presolar oxides. This method was out of question in the search for presolar silicates. Silicates are rock-forming minerals and meteorites consist mostly of silicates. If we dissolved solar silicates, presolar silicates would have been equally destroyed. Therefore, either meteorite thin sections or dispersed meteorite materials were examined. Ion imaging techniques had been also applied to search for presolar silicate grains using the CAMECA IMS-3f at Washington University in Saint Louis in the late 1990s with no avail.⁴³⁾ In hindsight, the spatial resolution of the CAMECA IMS-3f was not enough to locate presolar silicates because the diameter of a Cs^+ primary beam of the CAMECA IMS-3f was a few μm . In addition, the sensitivity was not high enough to obtain high signal to noise ratios. We had to wait until a new type of SIMS was constructed and delivered.

The CAMECA NanoSIMS was developed in the late 1990s and the first NanoSIMS was delivered at Washington University in December 2000. A Cs^+ primary beam diameter can be as small as 50 nm and this made it possible to find isotopic anomalies in much smaller grains/areas in meteorites than previously possible.⁴⁴⁾ The NanoSIMS is equipped with 4 moveable and one fixed electron multipliers that can simultaneously detect five ions up to mass 30. Together with the ion optics, the sensitivity of the NanoSIMS is much higher than that of the CAMECA IMS-3f. Presolar silicate grains were first found in interplanetary dust particles¹⁶⁾ followed by their discovery in meteorites.^{17–19)} Silicate grains have been located in various types of meteorites that had experienced the least amount of aqueous alteration.²²⁾ Their O isotopic distribution is similar to that of oxide grains (see Fig. 14 by Zinner³²⁾ for the O isotopic distribution of oxides): grains are classified into four groups according to their O isotopic ratios⁴⁵⁾ (Fig. 1). Group 1 grains show ^{17}O excesses and close-to-solar $^{18}\text{O}/^{16}\text{O}$ ratios. Group 2 grains have ^{17}O excesses and ^{18}O deficits and the latter are more pronounced than the former. Group 3 grains show ^{16}O excesses whereas Group 4 grains show ^{17}O and ^{18}O excesses. Grains of Groups 1, 2 and 3 formed in red giants or AGB stars⁴⁵⁾ and those of Group 4 most likely formed in supernovae.^{46,47)} With the identification of presolar silicate grains, major types of

Fig. 1. Oxygen isotopic ratios of presolar silicate grains. Data are from the Presolar Grain Database⁴⁸⁾ (http://presolar.wustl.edu/PGD/Presolar_Grain_Database.html). The grains are classified into four groups based on their O isotopic ratios (see the text). The dotted lines indicate the solar ratios.

presolar grains formed in both C-rich and O-rich stars have been identified in meteorites.

STUDIES BY THE COMBINATION OF DIFFERENT TYPES OF INSTRUMENT

Isotopic analyses of presolar grains are essential for presolar grain studies. To establish the presolar origin of grains, isotopic anomalies in at least one element have to be present. NanoSIMS analyses consume less material than previous analyses by the CAMECA IMS-3f, thus leaving more material for subsequent measurements by other types of instrument. The crystal structure and presence of subgrains inside host carbonaceous grains have been examined using TEM.^{21,25,26,49,50)} The presence of subgrains and their elemental compositions in graphite grains revealed formation conditions of the subgrains and their host graphite grains.²⁵⁾ Isotopic analyses of subgrains in thin (~70 nm) slices of graphite grains^{51,52)} could be also performed. Titanium isotopic ratios of TiC subgrains (<~500 nm) in a graphite grain of supernova origin agreed with those measured in the host graphite grain and were consistent with their supernova origin.⁵¹⁾ Silicon carbide subgrains with ²⁹Si/²⁸Si and ³⁰Si/²⁸Si excesses (up to 2 times solar ²⁹Si/²⁸Si and ³⁰Si/²⁸Si ratios) were identified in two graphite grains.⁵²⁾ Such high excesses could only be explained by C-burning and/or Ne-burning in massive stars (>8 M_{sun}). Croat *et al.*⁵²⁾ suggested that these SiC grains were later incorporated into the graphite grains, either in supernova ejecta or in the colliding winds of Wolf-Rayet binaries.

TEM, in combination with the FIB technique, has been widely used to examine presolar silicate grains. Normal silicate grains usually surround presolar silicate grains. Even with a small primary beam with the NanoSIMS, signals from nearby grains cannot be totally excluded. Oxygen isotopic ratios, which are used to locate presolar silicate grains, are usually vastly different from the solar ratios thus the interference from nearby solar grains has little effect on locating these grains. However, other isotopic ratios, such

as those of Mg and Si, of presolar silicates are usually not so different from the solar ratios. To precisely determine isotopic ratios of these other elements, it is necessary to remove surrounding grains. Nguyen and Messenger⁵³⁾ placed a Pt cap to protect a silicate grain of interest and milled surrounding grains to analyze Mg, Si and Fe isotopic ratios (see Fig. 1 by Nguyen and Messenger⁵³⁾). From isotopic analyses of the 11 grains measured this way, they estimated ~12% and 1% of presolar silicates have supernova and nova origins, and the rest originated from red giants and AGB stars.

The structures of presolar grains reflect condensation conditions of these grains as well as subsequent processing histories. Observations using the ISO SWS (Infrared Space Observatory Short-Wavelength Spectrometer) indicates that a widespread presence of crystalline silicates in the envelopes of evolved stars.⁵⁴⁾ It is assumed that a portion of freshly condensed amorphous silicate grains is converted into crystalline silicates by thermal annealing in the circumstellar shell.⁵⁵⁾ TEM examinations have been carried out for both presolar oxide and silicate grains. Corundum (Al₂O₃),⁵⁶⁾ hibonite (CaAl₁₂O₁₉),^{27,57)} and spinel (MgAl₂O₄ and Fe- and Cr-rich with varied amounts of Mg and Al)⁵⁸⁾ have been investigated using FIB and TEM techniques. Except for one amorphous Al₂O₃ grain and an assemblage of three Fe-Cr-rich crystalline grains, they are single crystal grains. One highly crystalline orthopyroxene (MgSiO₃) grain with a high Al content (1.8±0.5 at.%), and an amorphous Ca-Si rich grain, with hibonite nanocrystallites (< 20 nm) embedded in one region, have been found in the Acfer 094 meteorite.⁵⁹⁾ Vollmer *et al.*⁵⁹⁾ suggested that the complex assemblage of the latter indicated the fast cooling and changing chemical environments where the grain had formed.

FUTURE DIRECTIONS

Presolar grain studies are a relatively new field, starting in 1987.⁵⁾ Progress has been made in many aspects such as nucleosynthesis in AGB stars and supernovae, mixing in supernova and nova ejecta, and the Galactic chemical evolution. There are still a few aspects yet to be explored.

There are most likely other presolar-grain minerals that have not been isolated/identified in meteorites. Besides the major mineral types of presolar grains identified to date [diamond, SiC, graphite, oxides, silicates, Si₃N₄, refractory carbides (TiC, Mo- and Zr-rich carbides) as subgrains], condensation calculations predict sulfides would form in sufficiently reducing stellar environments.⁶⁰⁾ Sulfides are dissolved during an alternate treatment with HF-HCl and HCl in the chemical separation procedure. Thus, some other methods to remove other phases are needed to concentrate presolar sulfides, if they exist. How to effectively concentrate minerals of interest poses a challenge to identify new phases. Besides the difficulty of concentrating the new phases, their low abundances, probably on the order of a few ppm (micrograms/gram) or less relative to bulk meteorites, make the task even more challenging.

Another aspect is to analyze isotopic ratios of heavy elements in single grains. Isotopic ratios of heavy elements were analyzed mostly on bulk samples.^{34–39,61)} Although high precision data were obtained, a large number of grains were analyzed at the same time and it was hard to correlate

isotopic ratios of multiple elements even if aliquots of the same fraction were used for analyses. SIMS, used to acquire isotopic ratios of single grains, has been mostly used to analyze isotopic ratios of light to intermediate elements such as C, N, O, Mg, Si, Ca, Ti, Fe and Ni.^{24,33,62)} It is very hard to analyze isotopic ratios of heavy elements using SIMS because extremely high mass resolving power ($M/\Delta M$) is necessary to separate interferences in the mass region of heavy elements: to separate ^{96}Mo and ^{96}Zr , a $M/\Delta M$ of 22,120 is required and this would considerably reduce sensitivity. In addition, abundances of elements heavier than Fe are quite low in nature.⁶³⁾

Isotopic ratios of heavy elements are important to decipher nucleosynthesis in stars. The *s*-process takes place in AGB stars and massive stars ($>8M_{\text{sun}}$) and isotopic yields of elements affected by *s*-process branching are good indicators of neutron density, neutron exposure (*i.e.*, the total number of neutrons) and temperature. Thus these pieces of information would provide us with nucleosynthetic conditions in the stars. Other processes that synthesize heavy elements are the *p*-process and *r*-process and they are thought to take place in supernovae. The *p*-process is a photo-disintegration processes [(γ, n) , (γ, p) and (γ, α)] of pre-existing neutron-rich nuclei under high temperature ($T > \sim 2 \times 10^9 \text{ K}$). The *r*-process is thought to occur in neutrino-driven winds from the neutron star of core-collapse supernovae.⁶⁴⁾ Other candidate locations include the “hot bubble (high entropy)” region, which is believed to appear just after the creation of a newly-born proto-neutron star in the core-collapse supernova explosion, neutron star—neutron star binaries, and neutron star—black hole binaries. These processes can be better understood when isotopic ratios of heavy elements in supernova presolar grains are analyzed with high precision.

Isotopic ratios of heavy elements in a few graphite and SiC grains have been analyzed using resonance ionization mass spectrometry (RIMS). Atoms, desorbed from samples with a laser, are resonantly ionized with several tuned lasers. Thus only elements of interest are ionized. These ions are analyzed by a time-of-flight (TOF) mass spectrometer. An advantage is that RIMS has higher ionization yields than SIMS. Useful yields, defined as the number of detected ions to the number of sputtered atoms, are a few % (up to 25%) in the former, while they are less than 1% in the latter.

Isotopic ratios of Mo and Zr,^{65–69)} Sr,^{70,71)} Ba,^{71,72)} and Ru⁷³⁾ in single SiC and graphite grains have been analyzed using the RIMS, CHARISMA instrument (Chicago-Argonne Resonant Ionization Spectrometer for Mass Analysis), at Argonne National Laboratory, USA.⁷⁴⁾ These isotopic analyses of mainstream SiC grains, which comprise $\sim 93\%$ of the total SiC grains, have shown signatures of *s*-process in low-mass ($1\text{--}3M_{\text{sun}}$) AGB stars of close-to-solar metallicity (metallicity indicates the mass fraction of elements heavier than He). Silicon carbide grains of Type X, comprising 1% of total SiC, are considered to originate from supernovae. Molybdenum and Zr isotopic ratios of X grains^{65,71)} show signature of neutron burst, or mini *r*-process that takes place in the He-rich zone during the passage of the shock wave from the core.⁷⁵⁾ In neutron burst, neutron exposure τ is estimated to be $0.07\text{--}0.08 \text{ mbarn}^{-1}$ at $T_{\text{max}} = 10^9 \text{ K}$ ⁷⁵⁾ and most neutrons are captured by seed nuclei, resulting in a few neutrons captured per nucleus. In the *r*-process, neutron exposure τ is calculated to be $\sim 1.2 \times 10^{10} \text{ mbarn}^{-1}$ at $T = 10^9 \text{ K}$ (Meyer,

personal communication), but most of the neutrons are lost via the (γ, n) reaction and ~ 100 neutrons per nucleus are captured in the end.

A few high-density graphite grains have shown signatures of *s*-process in AGB stars.⁶⁹⁾ Ruthenium isotopic analysis of SiC grains⁷³⁾ is particularly interesting: Savina *et al.*⁷³⁾ have found a ^{99}Ru anomaly that is explained by the *in situ* decay of ^{99}Tc ($T_{1/2} = 213,000 \text{ a}$) in SiC grains. Technetium has been spectroscopically observed in AGB stars.⁷⁶⁾ Since there are no stable Tc isotopes, the observation has been taken as evidence that nucleosynthesis is taking place in stars. Both the grain analysis and the observation of stars agreed with each other and proved nucleosynthesis takes place in stars.

Although CHARISMA has produced new insights into nucleosynthesis in stars from these isotopic measurements, the grains measured in the above analyses were at least a few μm in size. The effort has been made to analyze isotopic and elemental abundances with much higher precision and in much smaller (down to a nanometer range) grains and areas. Two instruments have been developed. CHILI (The Chicago Instrument for Laser Ionization), under construction at The University of Chicago, USA, is a newer version of RIMS.⁷⁷⁾ The goal is to have a useful yield of $\sim 40\%$. A liquid metal ion gun is used to analyze $\sim 10 \text{ nm}$ scale samples. Six tunable lasers will simultaneously ionize up to three elements.

Another instrument, LIMAS (Laser Ionization Mass Nanoscope), is located at Hokkaido University, Japan. The prototype was developed at Osaka University in collaboration with Hokkaido University, Kyushu University, Hitachi High-Tech Science Corporation, and JEOL in Japan.⁷⁸⁾ A liquid metal Ga ion source is used for a primary beam. Atoms are desorbed and are non-resonantly ionized by a femtosecond laser, which is capable of yielding very high-power densities. The femtosecond laser is focused at a point $100 \mu\text{m}$ above the surface of a sample.⁷⁹⁾ High-mass resolution power is needed to eliminate interferences after non-resonant ionization of samples. A multi-turn TOF mass spectrometer, MULTUM II, can achieve mass resolving power of 250,000 when ions are focused in both space and time.⁸⁰⁾ The prototype is at Osaka University and is in the process of modification to optimize the performance. The main focus would be to optimize post ionization efficiencies and tuning of the MULTUM II to minimize the loss of ions.⁸¹⁾

Although it will take some time before these instruments are in full operation, we expect isotopic and elemental abundances of extra-terrestrial materials will be analyzed in unprecedented precisions. In the past, improvements of instrument always bring some new insights and it remains to be seen what kind of new information these instruments will reveal.

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