

Presolar Grain Studies: Recent Progress and Development

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Abstract. Since the discovery of presolar grains, a wealth of information on nucleosynthesis in stars and mixing in stellar ejecta has been accumulated from studies of these grains. The progress in the studies of presolar grains has been made by developments of new techniques and new types of instruments. We will review the advances that brought about these progresses and consider future directions of the studies.

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INTRODUCTION

Presolar grains were dust formed in stellar outflow or stellar ejecta and were subsequently incorporated into meteorites. Since primitive meteorites formed when the solar system was born, presolar grains must have formed before the solar system, hence they are called *presolar*. During the end of stars' lifetimes, they expel gas and dust into space. Mass loss rates are accelerated in the end of third dredge-up of the asymptotic giant branch phase. More massive stars ($> 8M_{\text{sun}}$) explode as supernovae. Such material from stars was eventually incorporated into molecular clouds. Our solar system formed from such a molecular cloud 4.6 billion years ago. Since dust grains in molecular clouds were produced in various types of stars, there should have been isotopic variations among those grains. However, it was thought that during the solar system formation, all the solid materials were evaporated and that the solar system became isotopically uniform.

However, a piece of evidence that suggested otherwise emerged in 1969 when Black and Pepin [1] analyzed Ne released from a fragment of the Orgueil meteorite. At high temperatures (800-1100°C), a ²²Ne-rich component was released, bringing the ²⁰Ne/²²Ne ratios down to ~ 4 (air: 9.8). An upper limit of ²⁰Ne/²²Ne of the component was estimated to be 3.4. Subsequent studies showed that the ²⁰Ne/²²Ne ratio of the component was even lower and that there were two kinds of Ne-E, Ne-E(H) and Ne-E(L) [2]. Since it was difficult to explain such a huge isotopic anomaly by the processes occurring in the solar system, they started to wonder whether there might be stardust hidden in meteorites [3]. Other isotopically noble gas components were

identified in acid residues from meteorites in the subsequent years. Xe-HL, the component that is enriched both *heavy*, r-process only isotopes (134 and 136) and *light*, p-process only isotopes (124 and 126) were found in acid residues of the Allende meteorite [4]. Xe-S, or s-process Xe, was identified in residues from the Murchison meteorite [5], with elevated $^{130}\text{Xe}/^{132}\text{Xe}$ ratios above the 1000°C fraction. Kr-S, or s-process Kr, was also observed in meteoritic residues [5]. Minerals that contain these noble gas components turned out to be stardust.: the quest for these minerals ultimately led to the identification of presolar grains in meteorites. In this paper, we will review how presolar grain studies have been evolved since they started.

DISCUSSION

Separation of carbonaceous grains

The isotopically anomalous noble gas components hinted the presence of presolar grains in meteorites. However, the amount of these grains was expected to be very low because most of these anomalies could not be detected in bulk meteorites with overwhelmingly abundant solar system minerals. Furthermore, there were very few clues as to what kind of mineral phases carried these noble gas components. It took more than 15 years before the first mineral type of presolar grains, diamond, was isolated from meteorites. Drs. Edward Anders, Roy S. Lewis and their colleagues at the University of Chicago carried out the separation (see [6] for detailed history). Their method was “to burn a haystack to find the needle”: they removed minerals one by one starting from silicates that comprised 96 % of the meteorites. During the quest, the isotopically anomalous noble gas components served as a beacon to guide the separation. Presolar diamond, the carrier of Xe-HL, was finally separated in 1987 [7], followed by SiC with Xe-S, Kr-S and Ne-E(H) [8, 9] and graphite with N-E(L) [10]. Interestingly, all the minerals that carried the noble gases were carbonaceous and were resistant to chemicals. Therefore, it was possible to concentrate these minerals from meteorites using a chemical separation procedure [7, 9, 11, 12]. Diamond is most abundant with its abundance ranging from 500-1000 ppm. Silicon carbide comprises a few ppm of meteorites, and graphite does only one ppm or less in primitive meteorites [13].

With the establishment of the separation procedure of the carbonaceous presolar grains, analyses of these grains in laboratory using various types of state-of-the-art instruments have become possible. The three carbonaceous types of grains, diamonds, SiC and graphite, are the only minerals that were analyzed as bulk (aggregates of grains). Even so, most data have been obtained using secondary ion mass spectrometry (SIMS). Although the major part of SiC grains in meteorites are submicron in size, there are large ($>1\ \mu\text{m}$) grains that can be analyzed for isotopic ratios of several elements. Graphite grains are usually $1\ \mu\text{m}$ or larger. Therefore, SiC and graphite have been examined with SIMS. An exception is diamond whose the average grain size is 3nm.

Single grain analyses of SiC grains indicate that SiC grains are classified into several populations based on their C, N and Si isotopic ratios [14, 15] (Fig. 1). Mainstream grains, having isotopically heavy $^{12}\text{C}/^{13}\text{C}$ and light $^{14}\text{N}/^{15}\text{N}$ ratios than solar (air for N), comprise more than 90% of SiC grains in meteorites. Y grains, defined as having $^{12}\text{C}/^{13}\text{C}$ ratios > 100 , light $^{14}\text{N}/^{15}\text{N}$ ratios and ^{30}Si excesses relative to the mainstream correlation line, comprise about 1% of the total SiC [16], while Z grains, with similar C and N isotopic ratios as those of mainstream grains but with pronounced ^{30}Si excesses relative to the mainstream correlation line and close-to-normal or lower $^{29}\text{Si}/^{28}\text{Si}$ ratios than solar [17], become more abundant in smaller grain-size fractions. Mainstream, Y and Z grains are believed to have formed in AGB stars with a range of metallicities: the metallicities of grains' parent stars range from close-to-solar to a-third-of-solar metallicities (mainstream $> Y > Z$) [18]. X grains, characterized by isotopically light C, heavy N and ^{28}Si excesses, are considered to have formed in core-collapse supernovae [19-21].

A+B grains, defined as grains having $^{12}\text{C}/^{13}\text{C}$ ratios lower than 10, comprise 3-4% of the total SiC. A+B grains show a wide range of $^{14}\text{N}/^{15}\text{N}$ ratios. Some A+B grains show an enhancement in the s-process elements, while other grains show the solar abundance of those elements [22]. Since no single stellar source can explain the range of the N isotopic ratios, multiple sources have been proposed. J-stars are invoked to explain grains with no enrichment in the s-process elements. Born-again AGB stars have been proposed as a source for the grains with the s-process enrichment.

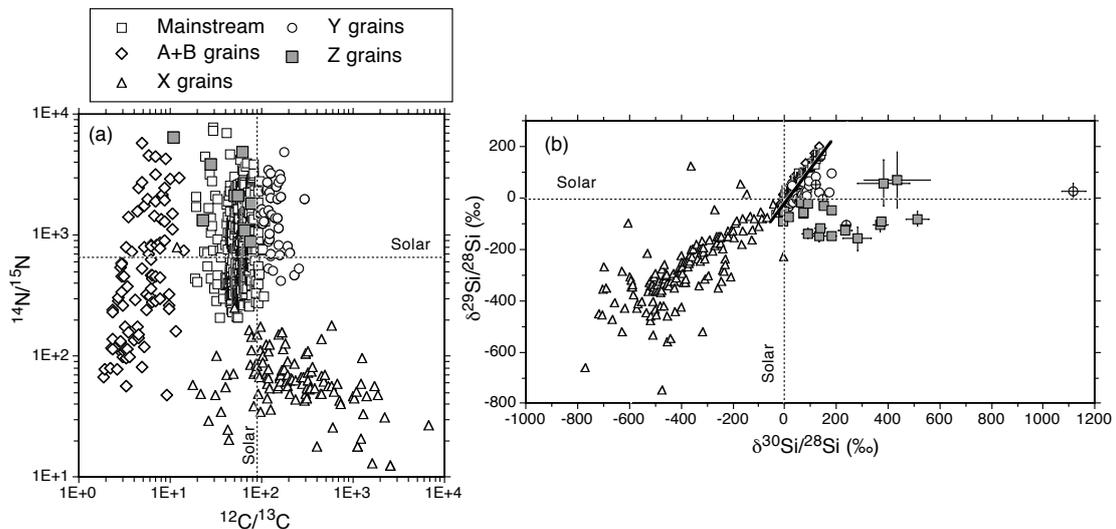


FIGURE 1. (a) Carbon and N isotopic ratios of SiC grains. (b) Silicon isotopic ratios of SiC grains. The thick line is the mainstream correlation line. Data are from [14, 16, 17, 19, 21-23].

Graphite grains have a range of density ($1.6\text{-}2.2\text{ g/cm}^3$). One of the interesting characteristics of presolar graphite is that isotopic and elemental properties depend on density. There are more grains with lower $^{12}\text{C}/^{13}\text{C}$ ratios than solar in low-density grains ($1.65\text{-}2.10\text{ g/cm}^3$), while many high-density grains have higher $^{12}\text{C}/^{13}\text{C}$ ratios than solar ($2.15\text{-}2.20\text{ g/cm}^3$). Many low-density graphite grains have the isotopic signature similar to that of X grains and are considered to have formed in supernovae [24]. The high $^{12}\text{C}/^{13}\text{C}$ ratios of high-density graphite grains indicate that their parent

stars did not experience cool bottom processing, indicating the stars' masses are higher than $3M_{\text{sun}}$, whereas pronounced $^{46}\text{Ti}/^{48}\text{Ti}$ and $^{49}\text{Ti}/^{48}\text{Ti}$ ratios than solar in a few grains indicate that metallicities of the parent stars are lower than solar [25].

The origin of diamond is still not clear. The presence of Xe-HL indicates that the Xe was acquired in supernovae because of the enrichment in *p*- and *r*-process only isotopes. However, a bewilderingly close-to-normal C isotopic ratios ($^{12}\text{C}/^{13}\text{C} = 93$, solar = 89) and the $^{14}\text{N}/^{15}\text{N}$ ratio (407-420) close to those of Jupiter (435 ± 57) [26] and the implanted solar wind onto the GENESIS sample ($443 \pm 131, 2\sigma$) [27] suggest that there are multiple stellar sources for diamonds.

Identification of oxide grains

Carbonaceous grains form in the outflow of carbon stars or C-rich stellar ejecta, thus they contain information of these environments. In the Galaxy, there are more O-rich stars than C-rich stars. Oxide and silicate grains form in the O-rich environments, although a small amount of silicates also form in the C-rich environment. To better understand O-rich stars, presolar oxide and silicate grains would provide us valuable data. The problem of studying oxide grains was that the majority of oxide grains in meteorites were of solar origin. Thus, a very small amount of presolar oxide grains had to be located and identified in meteoritic oxide grains, where most of them were isotopically normal.

Ion imaging was developed to find rare types of grains using the secondary ion mass spectrometry [28]. Isotopic images were taken with a defocused beam and isotopic ratios of the grains in the image are calculated after the grains are defined. Nittler et al. [28] classified presolar oxide grains into four groups using their O isotopic ratios [Fig. 2(a)]. Group 1 grains, characterized with ^{17}O excesses and moderate ^{18}O depletions relative to solar, and Group 3 grains, having solar or lower $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios, have signatures of O-rich red giant stars, which experienced the first dredge-up. Grains with the evidence of ^{26}Al in these groups formed in thermally pulsing AGB stars before the envelope turned C-rich. Group 2 grains, having ^{17}O excesses and large ^{18}O depletions, most likely formed in low-mass AGB stars, which experienced cool bottom processing. The origin of Group 4 grains was not clear, although recently their supernova origin has been proposed [29]. We note that ion imaging has been also applied to search for rare types of SiC grains of types A+B, X, Y, and Z.

Identification of silicate grains

Silicate grains have been spectroscopically observed in stars. However, until recently, it was not known whether or not presolar silicate grains existed in meteorites, having survived the events during the solar system formation and in the meteorite parent bodies. Search for presolar silicate grains posed serious challenges. Since silicates were major constituents of primitive meteorites, essentially bulk meteorites had to be searched. Although presolar oxide grains also had to be located among a vast

amount of normal oxide grains, oxide grains could be concentrated from meteorites using a chemical separation procedure. Search for presolar silicates were conducted from the late nineties using ion imaging without success [30]. In hindsight, it was because the primary beam diameter of the ion probe (CAMECA IMS-3f), a few μm in size, was too big to locate presolar silicate grains, most of which were submicron in size. Even if there were presolar silicate grains, the isotopic anomalies must have been diluted by surrounding grains. Furthermore, the sensitivity of the ion probe was not quite up to the task to detect diluted isotopic anomalies.

In December 2000, the NanoSIMS, a new type of the ion probe, was delivered at Washington University, and half an year later another NanoSIMS was installed at Max-Planck Institute in Mainz, Germany. The NanoSIMS has a much higher spatial resolution due to a small primary beam (as small as 50 nm) and a higher sensitivity at high mass resolution. In addition, it is capable to simultaneously detect five ions with 5 electron multipliers.

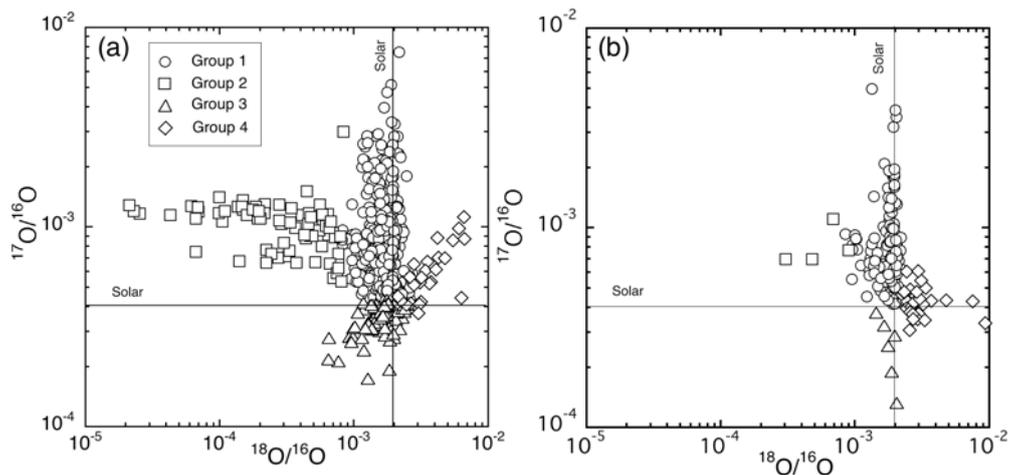


FIGURE 2. Oxygen isotopic ratios of (a) oxide grains and (b) silicate grains. Data are from the presolar grain database (<http://presolar.wustl.edu/~pgd/>). For the details of the database, see [31].

Messenger et al. [32] identified first presolar silicate grains in an interplanetary dust particle (IDP) using the NanoSIMS. It was soon followed the discovery of presolar silicates in meteorites [33-35]. At present presolar silicates are observed in meteorites of different compositional groups and they have become the most abundant type of presolar grains second to diamond.

The O isotopic distribution of presolar silicates is very similar to that of presolar oxides (Fig. 2). However, the numbers of grains in groups 2 and 3 are smaller for silicate grains than for oxide grains. It is probably due to the dilution from normal oxygen affects more to the minor isotopes than to the major isotope.

Future directions

There are other minerals that are predicted to condense in stellar envelopes. Lodders and Amari [36] predicted minerals that are expected to condense from both M-stars and C-stars (Table 9 in their paper). For example, sulfur compounds (MgS, CaS, FeCr₂S₄) are not yet identified in meteorites. New mineral types of presolar grains would certainly be a welcome addition to the presolar grain inventory of meteorites. However, development of new techniques will be needed to take this direction. For example, since sulfur compounds are dissolved in acids, it is necessary to concentrate them to efficiently examine their isotopic ratios.

Another direction is to analyze isotopic ratios of heavy elements. Presolar grains have been extensively studied with secondary ion mass spectrometry. If grains are a few μm in size, we are able to analyze isotopic ratios of a few elements. However, it is difficult to analyze isotopic ratios of elements beyond iron. First of all, abundances of heavy elements themselves are low. Furthermore, when atomic number increases, higher mass resolution power is required to separate interferences, which results in a significant reduction of sensitivity.

Resonant ionization mass spectrometry has been used to analyze isotopic ratios of heavy elements such as Zr, Mo, and Ba in SiC [37-40] and graphite grains [41]. Samples are abraded by a laser to produce neutral atoms, elements of interest are selectively ionized by two to four lasers and the ions are analyzed by a time-of-flight mass spectrometer. Two resonant ionization mass spectrometers operated by Michael Pellin, Michael Savina and their colleagues at Argonne National Laboratory have useful yields (= ions detected/atoms removed) of 2% for CHARISMA (Chicago Argonne Resonance Ionization Spectrometer for Microbeam Analysis) and up to 25% for SARISA (Surface Analysis by Resonant Ionization of Sputtered Atoms). A new RIMS that is dedicated to presolar grain studies is under construction at the University of Chicago [42]. A liquid metal ion gun will be used to focus the beam to a few nm for CHILI (The Chicago Instrument for Laser Ionization). Also a used yield is expected to be 50%. An ultra-high-sensitive TOF (time of flight)-SIMS has been also developed in collaboration with Osaka University and Hokkaido University in Japan. A Ga ion beam is used to achieve high spatial resolution and a femtosecond laser will be used for post-ionization to increase the sensitivity.

The development of these new types of SIMS will undoubtedly help explore new aspects of presolar grain studies: With high-precision isotopic analyses of heavy elements, we will be able to gain a better insight into nucleosynthetic processes in stars.

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