Published in final edited form as:

Meteorit Planet Sci. 2018 November ; 53(11): 2327–2342. doi:10.1111/maps.13129.

Neon isotopes in individual presolar low-density graphite grains from the Orgueil meteorite

Philipp R. HECK^{1,2,*}, Manavi JADHAV^{1,2}, Matthias M. M. MEIER³, Teruyuki MARUOKA⁴, Sachiko AMARI⁵, Ernst K. ZINNER^{5,†}, Henner BUSEMANN³, Colin MADEN³, Frank GYNGARD⁵, Heinrich BAUR³, and Rainer WIELER³

¹Department of Science and Education, Robert A. Pritzker Center for Meteoritics and Polar Studies, The Field Museum of Natural History, 1400 South Lake Shore Drive, Chicago, Illinois 60605, USA ²Chicago Center for Cosmochemistry and Department of the Geophysical Sciences, The University of Chicago 60637, Chicago, Illinois, USA ³Institute of Geochemistry and Petrology, ETH Zurich, Zurich, Switzerland ⁴Graduate School of Life and Environmental Sciences, University of Tsukuba, Ibaraki, Japan ⁵Laboratory for Space Sciences and the Physics Department, Washington University, St. Louis, Missouri 63130, USA

Abstract

We present He and Ne isotopes of individual presolar graphite grains from a low-density separate from Orgueil. Two grain mounts were analyzed with the same techniques but in a different sequence: The first one was measured with NanoSIMS followed by noble gas mass spectrometry, and the second one in reverse order. No grain contained ⁴He and only one grain on the second mount contained ³He. On the first mount, the grains had been extensively sputtered with NanoSIMS ion beams prior to noble gas analysis; we found only one grain out of 15 with presolar ²²Ne above detection limit. In contrast, we found presolar ²²Ne in six out of seven grains on the second mount that was not exposed to an ion beam prior to noble gas analysis. All 22 grains on the two mounts were imaged with scanning electron microscopy (SEM) and/or Auger microscopy. We present evidence that this contrasting observation is most likely due to e-beam–induced heating of the generally smaller grains on the first mount during SEM and Auger imaging, and not primarily due to the NanoSIMS analysis. If thermal contact of the grains to the substrate is absent, such that heat can only be dissipated via radiation, then the smaller, sputter-eroded grains are heated to higher temperatures such that noble gases can diffuse out. We discuss possible gas loss mechanisms and suggest solutions to reduce heating during e-beam analyses by minimizing voltages, beam currents, and dwell times. We also found small amounts of ²¹Ne in five grains. Using isotope data we determined that the dominant sources of most grains are core-collapse supernovae, congruent with earlier studies of low-density presolar graphite from Murchison. Only two of the grains are most likely from AGB stars, and two others have an ambiguous origin.

*Corresponding author. prheck@fieldmuseum.org.

†Deceased.

INTRODUCTION AND MOTIVATION

Presolar grains condensed in the outflows and ejecta of evolved stars, before the formation of the solar system. They are the tiny fraction of solid material that survived the formation of the solar system intact and can be found in primitive solar system materials, such as unequilibrated meteorites, interplanetary dust particles, and cometary dust (Davis 2011; Zinner 2014; Nittler and Ciesla 2016). Since their discovery (Lewis et al. 1987), laboratory studies of presolar grains have provided unprecedented information regarding the types of stellar sources that contributed materials to the early solar system. Furthermore, they have yielded new insights into nucleosynthesis, mixing, and condensation processes in their stellar sources, mainly Asymptotic Giant Branch (AGB) stars and core-collapse supernovae (SN). The isotopic compositions of the major and minor elements, used to classify presolar grains, reflect the distinct nucleosynthetic outputs of their stellar sources. Presolar graphite grains were first discovered in the CM2 meteorite Murchison by Amari et al. (1990). Individual presolar graphite grains from the CI1 chondrite Orgueil were first analyzed by Jadhav et al. (2006). Interestingly, the isotopic compositions and, hence, the origins of presolar graphite grains, generally vary with grain density. Based on bulk noble gas analyses of millions of grains at a time (Amari et al. 1995) and ion probe measurements of isotope ratios of major, minor, and trace elements in individual grains (Hoppe et al. 1995) from different density fractions, Amari et al. (1995) concluded that high-density (HD) grains ($> 2.0 \text{ g cm}^{-3}$) are predominately from AGB stars, whereas low-density (LD) grains ($< 2.0 \text{ g cm}^{-3}$) are mainly condensates from core-collapse supernovae (CCSNe). Subsequent studies of helium and neon in HD graphite from Murchison showed that the grains originate from a mix of stellar sources (Heck et al. 2009a; Meier et al. 2012). This is similar to what was observed by NanoSIMS ion probe studies of presolar graphite grains from Orgueil: a majority of the LD grains have signatures of CCSNe nucleosynthesis, while the HD grains originate from multiple stellar sources (Jadhav et al. 2006, 2008, 2013a). A large number of HD grains originate from low-metallicity AGB stars, but grains from CCSNe and post-AGB stars are also observed (Jadhav et al. 2006, 2008, 2013a, 2013b).

In conjunction with ion probe analyses, light noble gas isotopic analyses of individual presolar graphite grains have provided information on processes such as mixing and ion trapping in stellar ejecta and winds (Nichols et al. 1992, 1994; Kehm et al. 1996; Heck et al. 2009a; Meier et al. 2012). These earlier analyses were performed exclusively on grains from the CM2 chondrite Murchison. Here, we present the first helium and neon isotopic analyses of individual LD presolar graphite grains from the CI1 chondrite Orgueil to characterize their light noble gas inventories and to determine the nature of their presolar gas acquisition processes.

SAMPLES AND METHODS

We studied 22 presolar graphite grains (between 2 and 12 μm diameter) from an Orgueil specimen from the National Museum of Natural History in Paris. The grains were extracted from the 24.16 g meteorite specimen by acid dissolution and density separation and were identified by Jadhav et al. (2006) with SEM and energy-dispersive X-ray spectroscopy (EDS). They belong to the low-density separate “OR1d” ($1.75\text{--}1.92 \text{ g cm}^{-3}$ density range).

Two mounts were prepared by transferring grains with a micromanipulator onto a gold substrate attached to an 8 mm diameter aluminum SEM stub. The grains on each mount were widely spaced, with a minimum distance of 100 μm between each grain. In both cases, the grains were not pressed into the gold substrate. The first mount (“4m”) with 15 grains (ranging from 2 to 5 μm initial pre-NanoSIMS diameter) was studied in the following analytical sequence: secondary electron (SE) imaging and EDS—NanoSIMS—SE imaging—noble gas mass spectrometry—SE imaging. The second mount (“8m”) with seven mostly larger grains (5–12 μm initial pre-NanoSIMS diameter) was analyzed as follows: SE imaging and EDS—noble gas mass spectrometry—SE imaging—NanoSIMS—SE imaging. Secondary electron imaging before and after each of the mass spectrometric analyses is necessary to document sample erosion and to assess the extent of melting due to laser heating for noble gas extraction.

Noble gas data were collected during two sessions. The grains on mount 4m were analyzed in 2010 and those on mount 8m during a second session, 4 yr later.

In detail, Jadhav et al. (2013a) analyzed grains on the first mount (4m) first by EDS with a JEOL-840A SEM followed by NanoSIMS for isotopes of C, N, O, Al-Mg, Si, K, Ca, and Ti and subsequently imaged with the Auger Nanoprobe, all at Washington University in St. Louis. The results were presented and discussed in Jadhav et al. (2013a). The Auger Nanoprobe was simply used to image the grains at high spatial resolution and no compositional data were acquired. The conditions used with electron beam instruments are shown in Table 1. We selected the 15 largest grains on this mount (diameters of 2–5 μm) for the subsequent He and Ne analysis because the smaller ones had been considerably eroded due to extensive ion sputtering during the prolonged NanoSIMS isotope analyses. This increased the probability of grains still containing gas amounts above our detection limits (Fig. 1).

The Zeiss Evo 60 SEM at the Field Museum of Natural History in Chicago was used to image all 22 grains on both mounts before and after noble gas extraction. At this point, we used short electron beam dwell times (Table 1) to minimize heating and damage to graphite (e.g., Egerton et al. 2004; Teweldebrian and Balandin 2009) prior to noble gas mass spectrometry.

After SE imaging at the University of Hawai’i and at the Field Museum (Table 1), the second mount (8m) with the seven larger grains was analyzed for He and Ne isotopes at ETH Zurich, followed by NanoSIMS analyses of C and O isotopes in St. Louis and SE imaging in Chicago. Compared to our previous study of KFB1 graphite from Murchison (Heck et al. 2009a), mount 8m had considerably lower amounts of melt residue of the grains after noble gas measurements due to the higher laser energy density used during the extraction process. The insufficient grain quantities left over limited the number of isotope systems that could be analyzed by NanoSIMS to only C and O.

Noble Gas Analysis

To extract and measure ^3He , ^4He , ^{20}Ne , ^{21}Ne , and ^{22}Ne , we used an infrared (IR) laser (Nd:YAG with a wavelength of 1064 nm; for 210 to 240 s at 70–100% of the continuously

adjustable output power; 100% = 16 W max; laser beam spot diameter ~50 μm) and an extraction line coupled to an ultrahigh-sensitivity noble gas mass spectrometer equipped with a compressor ion source at ETH Zurich. This instrument and method is currently optimized for He and Ne isotopes and results in a two-orders-of-magnitude better sensitivity compared to the same instrument without the compressor (Baur 1999). The extraction line is described in Heck et al. (2007). The grain mounts were loaded into the IR laser extraction chamber of the mass spectrometer a few days before analysis to obtain a low pressure in the extraction line ($\sim 10^{-9}$ mbar) at the beginning of the analysis session.

The use of a low-blank extraction line and a molecular-drag pump, which concentrates the gas into the ion source, allows us to measure very small amounts of He and Ne. Figure 2 shows the ^{22}Ne and ^{21}Ne gas amounts measured in all blank and sample analyses, respectively, ordered according to the analysis sequence (see Fig. S1 in supporting information for ^3He , ^4He and Fig. S2 for ^{20}Ne). For the duration of each extraction and measurement, the extraction line is in static vacuum and open to the mass spectrometer. We measured “hot” blanks in the same way as samples with the exception that the laser was fired at a sample-free area of the mount. We also measured “cold” blanks without firing the laser at all but otherwise using the same protocol as for samples and “hot” blanks. The two types of blanks were indistinguishable and in the following we refer to them simply as “blanks.” The analysis procedures were carried out as described in detail by Heck et al. (2007). Briefly, for each noble gas isotope, we subtracted the prelaser-heating background signal from the postlaser-heating signal. Both signals were approximated with best-fit techniques and extrapolated to the time of the start of laser heating. This data reduction method corrects for the increase in spectrometer background signals (“noble gas memory”) during the course of each individual measurement. Figure 2 and the corresponding figures in the supporting information show the cleanliness of the system. In detail, most individual blanks overlap within twice their internal error with zero, with negative values being about as frequent as positive values. This is expected due to ion counting statistics and the errors of the extrapolations of the ion beam currents in time. In all cases, the mean blank overlaps with zero within twice its standard error (Table 2). We correct all isotopes in both runs for the corresponding mean blank, although in most of these cases the correction is negligible. Taking into account that mean blanks may be slightly different from zero, we define the detection limit (DL) to be twice the standard deviation (2SD) of all blanks of a run added to the mean blank value ($\text{DL} = \text{mean_blank} + 2\text{SD_blank}$, Table 2; Fig. 2c). For calibration we used an artificial gas mixture with amounts known to about 2% accuracy, as determined by laboratory cross-calibrations (see section 2.5 in Heber et al. 2009). We determined the reproducibility of the calibrations within each of the two sessions to be $\sim 2\%$.

The data analysis method (described above) differs from the one we presented in our preliminary report of this study (Heck et al. 2010) but is now similar to previous studies (Heck et al. 2007, 2009a, 2009b; Meier et al. 2012).

Noble gas concentrations of individual grains were calculated by using an assumed mean bulk graphite density of 1.835 g cm^{-3} (Jadhav et al. 2006) and dimensions measured on SE images taken immediately before noble gas analysis. These are listed together with gas amounts, concentrations, and isotope ratios in Table 3. Bulk concentrations were calculated

by dividing the sum of all ^{22}Ne amounts by the sum of the masses of all grains in the respective run. These bulk concentrations are lower limits of their original values because the grains presumably lost noble gases due to e-beam heating (see Discussion section). Grain volumes and their uncertainties were calculated based on grain shapes determined from SE images. We used spheres, ellipsoids, spheres with a hole due to the NanoSIMS primary beam sputtering erosion through their centers, prisms, or a combination of these shapes for grains with irregular morphologies, to estimate the grain volumes (for details see supporting information). The depth dimension is not visible on the images and, for most grains, we assume that the depth is equal to the smallest axis of the two-dimensional grain image. Therefore, gas concentrations in grains that were not exposed to a NanoSIMS ion beam prior to noble gas extraction (mount 8m) should be more accurate because the assumption that their geometries are similar in the third dimension is more reliable. Generally, there is an unknown error in the determination of the grain sizes, which could be as large as some tens of percent. However, this error is not propagated into the data presented in the following discussion. The error in the mass only affects the concentration error but not to an extent that changes the results. All data on isotope ratios, limits, amounts and noble gas components detected remain unaffected by the mass error.

Pre-NanoSIMS grain diameters on mount 4m were 2.0–5.4 μm and on mount 8m were 5.0–11.8 μm . The average mass of the grains on mount 8m (0.098–1.6 ng) is about six times higher than that of the pre-noble gas analysis grains on mount 4m (0.0007–0.13 ng). This has implications for the detectability of gas amounts from the smaller grains and is addressed in the Discussion section.

RESULTS

Mount 4m

On the first mount (OR1d4m), only 1 of the 15 presolar LD graphite grains from Orgueil had ^{22}Ne above detection limit (given in Table 2). One grain (4m-18) had a nominal ^{22}Ne amount just 0.2 σ above detection limit (Fig. 2a). Remarkably, the small mass of this grain leads to an extremely large ^{22}Ne concentration of $(4.2 \pm 1.8) \times 10^{-3} \text{ cm}^3 \text{ STP g}^{-1}$ (Fig. 3; Table 3). We found one grain (4m-1) with a ^{21}Ne amount 1.7 σ above detection limit (Fig. 2) and two grains (4m-13, 4m-15) with ^{21}Ne amounts just barely (0.3 σ) above detection limit (Fig. 2c; Table 3). No grain contained ^4He amounts above detection limit.

Mount 8m

In contrast to the first mount, a majority of the grains (six out of seven; ~86%) contained detectable amounts of ^{22}Ne ranging from 2.2×10^{-15} to $6.0 \times 10^{-12} \text{ cm}^3 \text{ STP}$ (Fig. 2; Table 3). The concentrations of ^{22}Ne range from 1.6×10^{-5} to $1.9 \times 10^{-2} \text{ cm}^3 \text{ STP g}^{-1}$ (Fig. 3; Table 3, and full data table in supporting information). The bulk ^{22}Ne concentration of the ^{22}Ne -containing grains is determined to be $3.1 \times 10^{-3} \text{ cm}^3 \text{ STP g}^{-1}$ (total amount of ^{22}Ne detected/total mass of all 8m grains). The ^{22}Ne detection limit was about five times better than in the previous mount 4m session (Table 2). Grain 8m-1 was the largest of all grains and was, therefore, heated a second time with the laser using the same conditions as for the first step. During the second extraction, more ^{22}Ne above the detection limit was released.

We found two grains (8m-13 and 8m-1) with a ^{21}Ne amount just above detection limit (0.3σ and 0.1σ , respectively). We did not find ^{20}Ne or ^4He above detection limits in grains from this mount. Besides neon, grain 8m-1 contained ^3He ($[1.8 \pm 0.8] \times 10^{-7} \text{ cm}^3 \text{ STP g}^{-1}$) 1.1σ above the detection limit and is the only grain in this study where ^3He was detected.

High ^{22}Ne concentrations (as in grains 4m-18, 8m-6, and 8m-7) were determined for a large part of the grain mass range (Fig. 3). Intermediate ^{22}Ne concentrations (as in grains 8m-1, 8m-8, and 8m-16) were detectable down to $\sim 0.06 \text{ ng}$ in session 4m and down to $\sim 0.01 \text{ ng}$ during session 8m (because of different detection limits in the two sessions; Fig. 3). These mass ranges encompass $\sim 50\%$ of the analyzed 4m grains and all 8m grains. Low ^{22}Ne concentrations (as barely detected in grain 8m-13) would not be detectable in grains of the size range analyzed in session 4m but would be detected in the entire grain mass range from session 8m.

NanoSIMS Analysis

NanoSIMS analyses of the thin melt residues on mount 8m did not reveal large C and O isotopic anomalies except in Ne-rich grain 8m-1 ($^{12}\text{C}/^{13}\text{C} = 12 \pm 2$; Fig. 4a). Grains 4m-1 and 4m-13 from mount 4m had low $^{16}\text{O}/^{18}\text{O}$ ratio of ~ 140 and ~ 150 , respectively. As reported by Jadhav et al. (2013a), several grains have ^{28}Si excesses along with radiogenic ^{26}Mg from the decay of radioactive ^{26}Al (Fig. 4b). The C and O isotopic ratios in the grains from this study are similar to those obtained for other low-density graphite grains from Orgueil (see Fig. 4a).

DISCUSSION

Implications of Grain Masses and Detection Limits

Neon-22 was detected in several grains and will, hence, be the preferred isotope used to discuss implications of grain masses and limits on noble gas detectability.

A detectable amount of ^{22}Ne was found in only one grain (out of 15) on mount 4m, but ^{22}Ne was detected in six out of seven grains on mount 8m. There is no reason to believe that grains from mounts 4m and 8m are completely different in their initial gas concentrations, as they are from the same Orgueil density separate, and it is unlikely that they represent different grain populations. The smaller 4m grain sizes and five times higher ^{22}Ne detection limits could be a reason that no ^{22}Ne was detected in any of the 4m grains. However, if the individual masses of the 4m grains are multiplied by the bulk ^{22}Ne concentration of the 8m grains (Table 3), then 12 out of the 15 grains (80%) should contain detectable amounts of ^{22}Ne , even with the higher detection limit during the 4m analysis session, and nine grains (60%) should have gas amounts at least an order of magnitude above the detection limit. Assuming that 60% of the 4m grains contain detectable ^{22}Ne (9 out of 15 grains), then the probability p of randomly picking 12 grains that contain no ^{22}Ne out of a big pool of sufficiently large grains containing detectable amounts of ^{22}Ne is exceedingly small ($p = 2 \times 10^{-5}$). The probability is even smaller to pick grains with gas below the ^{22}Ne detection limit from an ensemble of grains where 85% (six out of seven grains) have ^{22}Ne amounts above detection limit ($p = 7 \times 10^{-11}$). We are, therefore, led to the conclusion that gas was lost

from the grains on the 4m mount at a stage prior to noble gas analysis, such as during the extensive SEM or NanoSIMS analyses.

Possible Mechanisms for Gas Loss from 4m Grains

We discuss possible gas loss-causing mechanisms for the 4m grains.

First we consider the release of He and Ne during grain erosion by the NanoSIMS ion beam. This will inevitably decrease the amount of gas available to be released from the grain, but because the amount of gas released should correlate with the volume of material sputtered, the gas concentrations in the grains should remain the same. Therefore, although ion sputtering will reduce the total amount of gas, it should not lower the gas concentrations ($\text{cm}^3 \text{ STP g}^{-1}$) of the 4m grains compared to the 8m grains.

Smaller gas concentrations require that noble gases were lost from the grains, for example by diffusion. Could the NanoSIMS ion beam release noble gases from the portion of the grain that is not sputtered? Neon can occur intercalated between the graphene sheets of the grain (e.g., Amari 2009). Lattice vibrations (phonons) caused by the impact of Cs^+ or O^- ions during NanoSIMS sputtering could potentially mobilize the gas atoms such that they could escape through lattice defects in the graphite without heating the grain. We are not aware that such an effect exists and the studies known to us have found no noticeable diffusion of Ne in graphite (e.g., Kim et al. 2002; Lindner et al. 2006). Therefore, we will not discuss this possibility any further.

Next, we consider simple heating of a graphite grain by ion (NanoSIMS) and electron (SEM and Auger Nanoprobe) beam irradiation as a cause of gas loss in the 4m grains. Diffusive loss of He and Ne to the surrounding vacuum is possible if the grain is heated to a sufficiently high temperature. The amounts of noble gases released will not be large enough to be detected as a discernible increase in vacuum chamber pressure during NanoSIMS or SEM analysis. Heating is caused by the transformation of kinetic energy carried by the ions or electrons into thermal energy by collision of the primary particles with the atoms in the grain. Given the higher power delivered by electron beams (approximately 100 pA at 20 kV = 2 μW) compared to the NanoSIMS ion beam (approximately 10 pA at 16 kV = 0.16 μW ; <1 pA for Cs^+ beam; ~20 pA for O^- beam; Jadhav et al. 2013a), it seems plausible that sample heating is stronger during SEM and Auger imaging compared to NanoSIMS analysis. However, the exact temperature reached is difficult to quantify as it strongly depends on the sample geometry and its ability to effectively transfer heat to the substrate (e.g., Egerton et al. 2004; Volkert and Minor 2007; Teweldebrhan and Balandin 2009). An upper limit to the grain temperature can be determined by assuming all the energy delivered by an ion/electron beam has been dissipated by radiation (i.e., no heat conduction to the substrate). Given that thermal contact between individual objects in vacuum is generally almost nonexistent, this assumption is justified. We have developed a model of grain heating, taking into account beam energy, size of the beam energy deposition volume, dwell time, perimeter (the distance covered by the electron beam on the substrate, on either side of the grain during the scanning process of SEM imaging), and the thermal properties of graphite. The full model is provided in supporting information (also see Fig. S3 and associated text). In the size range of the graphite grains studied here, the efficiency of heat loss by radiation

could also be a function of grain size, and thus, might deviate from the Stefan–Boltzmann law, resulting in lower temperatures (e.g., García-García 2008). We have ignored this effect because it would allow the grain to radiate energy more efficiently and therefore, lower the temperature of a grain.

The results of our model, which assumes graphite grains are situated on a polished substrate, are summarized in Fig. 5. The estimated upper limits depend on the heating power delivered by the SEM electron beam or the SIMS ion beam, as well as the grain size, with larger grains reaching lower temperatures than smaller ones. We can define a “safe zone” where the temperature of the grain will certainly stay below 500 °C (the lowest temperature at which low-density presolar graphite has been observed to release Ne-E/R, e.g., Amari et al. 1995), and an “unsafe zone” where the temperature might rise above 500 °C, if some conditions are met. With the possible exception of grain 4m-18, all gas-rich grains plot within the “safe zone” (for a perimeter = 1 on each side, given in units of the corresponding grain diameter, and a radiating surface fraction $f = 0.5$, i.e., only the upper side of the grain is radiating away from the substrate). A large fraction of the gas-poor grains plot within the “unsafe” zone. While not conclusive, this clearly suggests grain heating by SEM and Auger imaging is a possible Ne loss process for small individual presolar graphite grains.

Due to the high thermal conductivities of graphite and gold, a contact area as low as 10 ppm of the total grain surface area is sufficient to keep the grain within a few degrees of the substrate temperature during electron bombardment. As a result, there would be no diffusive loss of noble gases due to grain heating. However, with smaller or no contact area and sufficient heating power, the grains get heated to temperatures high enough to degas. We can imagine that a grain without or with very little thermal contact to the substrate in a high-power electron beam would get heated initially, degas, and then melt together with the gold, thus forming a larger contact area that would keep the grain at cooler temperatures and prevent it from evaporating. It is clear from Fig. 5 that all samples that were analyzed with the Auger Nanoprobe had some thermal contact with the substrate, otherwise they would have evaporated.

The visually most extreme case of erosion is seen in grain 4m-18 (Fig. 1) where only a few islands of graphite remain on the gold mount. This grain contained enough ^{22}Ne (it had the third highest ^{22}Ne concentration of all grains analyzed in this study) that it was just about detectable, despite heavy erosion. It is conceivable that grain 4m-18 was in thermal contact with the substrate, and was, therefore, able to retain a comparably large amount of ^{22}Ne despite its very small size and the extensive NanoSIMS analysis and SE imaging prior to noble gas analysis. If this were indeed the reason why grain 4m-18 retained some gas, then one would have to conclude that most of the grains had essentially no thermal contact to the substrate.

Stellar Sources of the Graphite Grains in This Study

The isotopic analyses with the NanoSIMS help to constrain the origin of the graphite grains in this study. For grains from CCSNe, O, and Si isotope ratios are particularly diagnostic along with the detection of an excess of the radiogenic nuclide ^{26}Mg due to the decay of ^{26}Al (e.g., Hoppe et al. 1995). The limits of Ne isotope ratios are used to further constrain

the stellar sources of the grains and the mechanism by which Ne got incorporated into the grains. In the following section, we discuss the plausible stellar sources for the graphite grains in the study in light of the new Ne isotope data (in conjunction with C and O), particularly in grains from mount 8m, as they most likely preserved their original gas concentrations. Stellar sources of 4m grains where we did not detect noble gases are discussed in detail in Jadhav et al. (2013a).

Supernova Grains

Six of the seven grains from mount 8m and one grain from mount 4m contain ^{22}Ne but no detectable ^{20}Ne or ^4He (Table 3). Upper limits of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios for three of the seven grains (8m-1, 8m-6, and 8m-7) are below the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio for Ne from the He-shell of AGB stars (“Ne-G”; Lewis et al. 1990), and therefore, are inconsistent with an AGB star origin (Fig. 6). The Ne isotopic ratios of all seven ^{22}Ne -containing grains do not overlap with model predictions of Ne produced by nucleosynthesis in a CCSNe (Rauscher et al. 2002). This most widely used CCSNe model yields very high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios (>10) for the relevant $^{12}\text{C}/^{13}\text{C}$ range and plots outside the range shown in Fig. 6. The Ne isotopic ratios are, therefore, inconsistent with implantation of CCSNe-produced Ne.

The same applies for ^3He , because of the measured $^3\text{He}/^{22}\text{Ne}$ ratios, and for the upper limit of $^{20}\text{Ne}/^{22}\text{Ne}$ of grain 8m-1. This nonnucleosynthetic ^3He is possibly cosmogenic. We tested this by calculating an exposure age by assuming all ^3He in the grain 8m-1 was produced during the meteoroid phase of Orgueil, that is, while exposed to galactic cosmic rays in interplanetary space during the time period from the ejection from its parent body to its fall in France. We used the model from Leya and Masarik (2009) and assumed reasonable shielding conditions in a carbonaceous chondrite (radius = 25 cm; depth = 10 cm); and a pure O target as the best proxy for C, resulting in a $^3\text{He}_{\text{cos}}$ production rate of $2.07 \times 10^{-8} \text{ cm}^3 (\text{g Ma})^{-1}$. We found an exposure age of $9 \pm 4 \text{ Ma}$ (1σ), which is below the $\sim 16 \text{ Ma}$ exposure age of Orgueil (Nishiizumi et al. 1993) and can be explained by $46 \pm 25\%$ of ^3He loss. This confirms that the measured ^3He is cosmogenic. The detection of ^3He was possible because this was the largest of all analyzed grains. Part of the ^{21}Ne measured in this grain could be also cosmogenic, recoiled from the surrounding matrix: using the same model and parameters, the $^{21}\text{Ne}_{\text{cos}}$ production rate is $1.81 \times 10^{-9} \text{ cm}^3 (\text{g Ma})^{-1}$ and would result in a gas amount of $\sim 4 \times 10^{-18} \text{ cm}^3 \text{ STP}$, which is only 5% of the measured gas amount. Correction for the 5% cosmogenic recoil contribution results in a $^{21}\text{Ne}/^{22}\text{Ne}$ ratio of $(5.4 \pm 2.9) \times 10^{-3}$, which is below the ratio predicted for nucleosynthetic CCSNe neon of ~ 0.07 at this $^{12}\text{C}/^{13}\text{C}$ composition (Fig. S4 in supporting information). However, we argue in the next paragraph that much of the ^{22}Ne is not nucleosynthetic but rather radiogenic, pure ^{22}Ne . We would need only a nucleosynthetic ^{22}Ne contribution of 0.5% to obtain a $^{21}\text{Ne}/^{22}\text{Ne}$ ratio for 8m-1 compatible with CCSNe nucleosynthetic neon.

The low $^{20}\text{Ne}/^{22}\text{Ne}$ ratios and no detected ^{20}Ne for grains 8m-6, 8m-7, and also from 8m-1 (Fig. 6) can be best explained with the Ne being pure ^{22}Ne , known as radiogenic Ne (Ne-R) from the decay of the radioactive nuclide ^{22}Na ($t_{1/2} = 2.6 \text{ a}$) that was extant in the grains when they formed. Stellar sources of ^{22}Na include core-collapse supernovae and novae (e.g., Clayton 1975a). Although novae have long been regarded as an important source of ^{22}Na

due to the presence of astronomically observed gamma ray lines (e.g., Clayton and Hoyle 1974), only a small number of presolar grains have been classified as putative nova grains, mainly based on C and N isotopic compositions (e.g., José and Hernanz 2007). The C isotopic compositions (we did not measure N isotopes for 8m grains to minimize grain erosion for the noble gas study) of grains 8m-1, 8m-6, and 8m-7 are inconsistent with both CO and ONe nova models ($^{12}\text{C}/^{13}\text{C} < 10$; José and Hernanz 2007). Therefore, a nova origin can be excluded. However, the C isotopic compositions are compatible with CCSNe as $^{12}\text{C}/^{13}\text{C}$ in ejecta of a typical CCSNe span a large range from below 10 to $>10^3$ (Rauscher et al. 2002). Astronomical observations and nucleosynthetic models suggest CCSNe are a major source of ^{22}Na (e.g., Clayton 1975b). Sodium-22 can have a peak abundance of almost 10% in the He-shell of the CCSNe of a $25 M_{\odot}$ solar metallicity star (Pignatari et al. 2015). Astronomical observations show that dust forms within 1–2 yr of the explosion (e.g., Sugerman et al. 2006). It has been suggested earlier that the Ne-R in graphite condensed as radioactive ^{22}Na during graphite condensation to form intercalated Na within the graphite in the stellar ejecta (Amari 2009; Heck et al. 2009a); various such intercalated C-Na compounds can be produced in the laboratory (e.g., Dresselhaus and Dresselhaus 2002; Sangster 2007). In such a scenario, the radioactive sodium decays ($\tau_{1/2} = 2.6$ yr) within the graphite grains into the pure ^{22}Ne that comprises the Ne-R component. The in situ decay would result in a more or less homogeneous distribution of ^{22}Ne throughout the grain volume. This scenario would explain why essentially pure ^{22}Ne was measured in the grains with the lowest limits of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios (<0.002 , <0.007 , and <0.05 in 8m-7, 8m-6, and 8m-1, respectively) of all samples in this study without requiring any implantation of neon into the grains. No conceivable stellar sources other than CCSNe could explain our observations of these three grains.

Grains 4m-1, 4m-13, and 4m-15 originate from a CCSNe based on the following arguments. Grain 4m-1 is enriched in ^{28}Si (Fig. 4b) more than any other analyzed LD graphite grain from Orgueil (Jadhav et al. 2013a) and similar to presolar silicon carbide grains of type X from CCSNe (Hoppe et al. 1994). The ^{28}Si excess in grain 4m-13 is smaller than in 4m-1 but still significant and consistent with X grains. Both grains are also enriched in ^{15}N and ^{18}O (Fig. 4a), relative to terrestrial atmospheric composition, and contain a large ^{26}Mg excess (Table 4) indicating the initial presence of extinct radioactive ^{26}Al . Jadhav et al. (2013a) reported that grain 4m-13 has a ^{49}Ti anomaly; although small, it is still a diagnostic nucleosynthetic feature of CCSNe. The limits of $^{21}\text{Ne}/^{22}\text{Ne}$ ratios in grains 4m-1 and 4m-13 are consistent with nucleosynthetic CCSNe-Ne and inconsistent with an AGB star origin (Fig. S4). The ^{21}Ne that was detected in grain 4m-13 could not have been produced by spallation in graphite alone because of the very low abundance of target elements in the suitable mass range. To evaluate a cosmogenic origin further, we assumed all ^{21}Ne of 4m-13 is cosmogenic obtained from nuclear recoil from the surrounding matrix in the meteorite as for 8m-1. With the same assumption and production rate as for grain 8m-1, we calculated that only 0.5% of the measured ^{21}Ne amount can be explained by recoiled cosmogenic ^{21}Ne from the surrounding meteorite matrix. The remaining ^{21}Ne from 4m-13 is likely nucleosynthetic neon and shifts the limit for the $^{21}\text{Ne}/^{22}\text{Ne}$ ratio corrected for the cosmogenic contribution by only 0.8%, leaving it consistent with a CCSNe origin (Fig. S4). A match with the CCSNe model requires that the amount of nucleosynthetic ^{22}Ne is the

same as the nucleosynthetic ^{21}Ne . This still allows the majority of the measured ^{22}Ne to be Ne-R (up to 95% in order to stay below our ^{22}Ne detection limit). All these observations combined are strong evidence for an origin of grains 4m-13 and 4m-1 from a CCSNe (e.g., Amari et al. 1992; Hoppe et al. 1994; Davis 2011; Zinner 2014) and exclude other stellar sources.

Unlike grains 4m-1 and 4m-13, grain 4m-15 does not have a ^{26}Mg excess; nevertheless, its Si isotopic composition (Fig. 4b) and $^{21}\text{Ne}/^{22}\text{Ne}$ limit is consistent with a CCSNe origin, and an AGB star origin is excluded.

AGB Star Grains 4m-18 and 8m-13

The low $\delta^{29}\text{Si}$ values and high $\delta^{30}\text{Si}$ values of grain 4m-18 are similar to those found in presolar SiC grains of type Z from low-mass, low-metallicity AGB stars (Hoppe et al. 1997). There are negative anomalies of $\delta^{25}\text{Mg}/^{24}\text{Mg}$ (-45 ± 12) and $\delta^{26}\text{Mg}/^{24}\text{Mg}$ (-37 ± 11) in this grain. The other isotope ratios of this grain do not show any anomalies (Table 4) (Jadhav et al. 2013a): The $^{12}\text{C}/^{13}\text{C}$ ratio of this grain falls in the upper range of ratios observed in Z grains (Hoppe et al. 1997). This ratio is also identical to those in a large fraction of graphite grains from Murchison (Hoppe et al. 1995) with terrestrial or close-to-terrestrial $^{12}\text{C}/^{13}\text{C}$ ratios, and is roughly consistent with model predictions of envelope compositions of low-mass ($<2.3 M_{\odot}$) and low-metallicity ($\sim 0.5 Z_{\odot}$) AGB stars (Hoppe et al. 1997; Heck et al. 2007). The $^{14}\text{N}/^{15}\text{N}$ ratio of grain 4m-18 is equal within uncertainty to the terrestrial value of 272 as for many presolar graphite grains, whereas the $^{14}\text{N}/^{15}\text{N}$ ratios of all SiC Z grains are above solar (441; Marty et al. 2011). Contamination with solar system (normal) N in the laboratory or parent body can explain the normal N isotopic composition in this and other graphite grains (e.g., Hoppe et al. 1995). Limits of $^{20}\text{Ne}/^{22}\text{Ne}$ of grain 4m-18 are consistent with model predictions for He-shells of AGB stars (Fig. 6). Neon and He isotope data from previous studies of presolar mainstream SiC grains (Lewis et al. 1990, 1994; Heck et al. 2007) and HD graphite grains (Amari et al. 1995; Heck et al. 2009a) from AGB stars provide evidence for the hypothesis proposed by Gallino et al. (1990). In this scenario, first described for circumstellar SiC grains from close-to-solar metallicity AGB stars, the Ne, predominantly consisting of ^{22}Ne (Ne-G), was implanted into circumstellar grains during the planetary nebula phase from a hot wind emanating from the exposed He-shell of the central star. While this scenario is consistent with the majority of the HD presolar graphite grains from Murchison, it is also a plausible explanation for the origin of the LD Orgueil graphite grain 4m-18 in this study.

The limit of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio ($^{20}\text{Ne}/^{22}\text{Ne} \leq 5$), the $^{21}\text{Ne}/^{22}\text{Ne}$ ratio (0.05 ± 0.04) of grain 8m-13, and its C isotopic composition ($^{12}\text{C}/^{13}\text{C} = 98 \pm 5$) are consistent with a low-to-intermediate mass, solar to subsolar metallicity AGB star origin. The Ne data are inconsistent with a mixture of Ne-R and CCSNe-Ne to obtain a $^{21}\text{Ne}/^{22}\text{Ne}$ ratio below CCSNe model predictions. In addition, the concentration of ^{22}Ne is unusually low for grains that would contain Ne-R. Measured O isotopic compositions are also consistent with an AGB star origin but in the case of 4m-13, the $^{16}\text{O}/^{18}\text{O}$ ratio is not unique for AGB stars. In this case, however, it is the Ne isotopic data for this grain that indicate a most likely AGB star origin.

The origins of grains 8m-8 and 8m-16 are not as well-constrained due to the lack of Si, Mg, and other isotope measurements. The $^{20}\text{Ne}/^{22}\text{Ne}$ upper limits measured in these grains and their C and O isotopic compositions are consistent with either a CCSNe or an AGB star origin for both grains.

Comparison with Literature Data

The measured gas concentrations of ^{22}Ne in our LD Orgueil graphite grains are similar to the range of values detected in individual KFB1 and KFC1 Murchison high-density graphite grains (Heck et al. 2009a; Meier et al. 2012). The isotope ratios and ratio limits obtained here are similar to what was found in these previous studies. The bulk concentration of grains on mount 4m (Table 3) is lower than the value in LD presolar graphite (KE1 $\sim 6.9 \pm 10^{-5} \text{ cm}^3 \text{ STP g}^{-1}$) from Murchison determined by Amari et al. (1995). The nominal bulk concentration of grains on mount 8m, which were not degassed significantly, is ~ 45 times higher than the bulk value from Amari et al. (1995). A detailed comparison of Orgueil and Murchison graphite based on the NanoSIMS data and morphologies is presented in Jadhav et al. (2013a). Jadhav et al. (2013a) concluded that LD graphite from Orgueil predominantly originated from CCSNe. A similar conclusion was reached by Amari et al. (2014) on LD graphite from Murchison where 76% originate from CCSNe. The findings of our study are consistent with the concept that the Orgueil and Murchison parent bodies formed from a relatively homogeneous mixture of presolar grains in the solar nebula. This concept was brought up by several authors and confirmed in independent studies. Varying abundances of presolar grains in different meteorites were explained as the result of thermal metamorphism (affecting mainly SiC, graphite, and diamond) and aqueous alteration (affecting mainly silicates) on the parent bodies (e.g., Huss and Lewis 1995; Davidson et al. 2014).

SUMMARY AND CONCLUSIONS

Only 1 of the 15 grains that were heavily sputtered (mount 4m) contained amounts of ^{22}Ne slightly above the detection limit. This is in contrast to mount 8m, which was not sputtered prior to Ne extraction, where six out seven of grains have detectable ^{22}Ne . After accounting for the dissimilar detection limits for both runs and reduced particle and gas volumes due to the large sputter losses during preceding NanoSIMS analysis of mount 4m grains, some further variation in detected gas amounts remain between the two mounts. These differences between grains from the same Orgueil density separate can at best be partly explained by varying initial concentrations, and most likely due to the loss of trapped Ne through heating by electron beams. We conclude that during electron beam analyses, beam currents, voltages, and beam dwell times should be minimized. This is a requirement to obtain useful helium and neon isotope data. N, O, Al-Mg, and Si isotope data obtained with NanoSIMS helped constrain stellar sources of the grains in this study. Of the grains displaying detectable amounts of Ne, three contain Ne-R from a CCSNe origin (8m-1, 8m-6, and 8m-7) and three additional grains possibly contain nucleosynthetic ^{21}Ne implanted from CCSNe ejecta (4m-1, 4m-13, and 4m-15). One grain with detected ^{22}Ne (4m-18) most likely originated from a low-mass, low-metallicity AGB star and another one (8m-13) originated in a low-to-intermediate mass, solar to subsolar metallicity AGB star. Despite the heating-induced degassing of grains on mount 4m, useful neon isotope data including isotope ratio

limits could be obtained for a small subset of grains. Almost all grains on mount 8m (the mount that was not subjected to much heating) contained detectable amounts of neon. We conclude that these presolar LD graphite grains from Orgueil formed predominantly in core-collapse supernovae, similar to what was found by NanoSIMS studies of Orgueil LD graphite (Jadhav et al. 2013a) and Murchison LD graphite (Amari et al. 2014). Data for each individual presolar grain where neon was detected provide quantitative information on the isotope ratios or ratio limits of the sampled reservoir of its specific parent star. Such information is not possible to obtain with bulk analyses, which measure mixtures of grains from different stars and any data will be just averages.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments—

The authors thank Associate Editor Katherine Joy, Gary Huss, Jan Leitner, and an anonymous reviewer for their thorough reviews and constructive comments that helped improve the manuscript. This research is supported by NASA Grants NNX11AG77G and NNX15AC53G to P.R.H., NNX16A31G to S.A., NNX11AH14G to E.Z., NNX15AF78G (to A.M. Davis) and grants by the Swiss National Science Foundation to R.W. and M.M. This work has partially been carried out within the framework of the NCCR PlanetS supported by the Swiss NSF (H.B.). The Robert A. Pritzker Center for Meteoritics and Polar Studies was established through funding by the Tawani Foundation. We thank Betty Strack for support of the Field Museum SEM laboratory.

REFERENCES

- Amari S 2009 Sodium-22 from supernovae: A meteorite connection. *The Astrophysical Journal* 690:1424–1431.
- Amari S, Anders A, Virag A, and Zinner E 1990 Interstellar graphite in meteorites. *Nature* 345:238–240.
- Amari S, Hoppe P, Zinner E, and Lewis RS 1992 Interstellar SiC with unusual isotopic compositions: Grains from a supernova? *The Astrophysical Journal* 394:L43–L46.
- Amari S, Lewis RS, and Anders E 1995 Interstellar grains in meteorites: III. Graphite and its noble gases. *Geochimica et Cosmochimica Acta* 59:1411–1426.
- Amari S, Zinner E, and Gallino R 2014 Presolar graphite from the Murchison meteorite: An isotopic study. *Geochimica et Cosmochimica Acta* 133:479–522.
- Baur H 1999 A noble-gas mass spectrometer compressor source with two orders of magnitude improvement in sensitivity. *EOS Transactions AGU* 46: Abstract F1118.
- Clayton DD 1975a ^{22}Na , Ne-E, extinct radioactive anomalies and unsupported ^{40}Ar . *Nature* 257:36–37.
- Clayton DD 1975b Gamma-ray lines: A ^{22}Na radioactive diagnostic of young supernovae. *The Astrophysical Journal* 198:151–152.
- Clayton DD and Hoyle F 1974 Gamma-ray lines from novae. *The Astrophysical Journal* 187:L101–L103.
- Davidson J, Busemann H, Nittler LR, Alexander CMD, Orthous-Daunay FR, Franchi IA, and Hoppe P 2014 Abundances of presolar silicon carbide grains in primitive meteorites determined by NanoSIMS. *Geochimica et Cosmochimica Acta* 139:248–266.
- Davis AM 2011 Stardust in meteorites. *Proceedings of the National Academy of Sciences* 108:19,142–19,146.
- Dresselhaus MS and Dresselhaus G 2002 Intercalation compounds of graphite. *Advances in Physics* 51:1–186.

- Egerton RF, Li P, and Malac M 2004 Radiation damage in the TEM and SEM. *Micron* 35:399–409. [PubMed: 15120123]
- Gallino R, Busso M, Picchio G, and Raiteri CM 1990 On the astrophysical interpretation of isotope anomalies in meteoritic SiC grains. *Nature* 348:298–302.
- García-García AM 2008 Finite-size corrections to the blackbody radiation laws. *Physical Review A* 78:023806.
- Heber VS, Wieler R, Baur H, Olinger C, Friedmann TA, and Burnett DS 2009 Noble gas composition of the solar wind as collected by the Genesis mission. *Geochimica et Cosmochimica Acta* 73:7414–7432.
- Heck PR, Marhas KK, Hoppe P, Gallino R, Baur H, and Wieler R 2007 Presolar He and Ne isotopes in single circumstellar SiC grains. *The Astrophysical Journal* 656:1208–1222.
- Heck PR, Amari S, Hoppe P, Baur H, Lewis RS, and Wieler R 2009a Ne isotopes in individual presolar graphite grains from the Murchison meteorite together with He, C, O, Mg–Al isotopic analyses as tracers of their origins. *The Astrophysical Journal* 701:1411–1425.
- Heck PR, Gyngard F, Ott U, Meier MMM, Ávila JN, Amari S, Zinner EK, Lewis RS, Baur H, and Wieler R 2009b Interstellar residence times of presolar SiC dust grains from the Murchison carbonaceous meteorite. *The Astrophysical Journal* 698:1155.
- Heck PR, Jadhav M, Meier MMM, Amari S, Zinner E, Baur H, and Wieler R 2010 Radiogenic and nucleosynthetic neon-22 from individual presolar Orgueil graphites (abstract #5396). *Meteoritics & Planetary Science* 45(Supplement).
- Hoppe P, Amari S, Zinner E, Ireland T, and Lewis RS 1994 Carbon, nitrogen, magnesium, silicon, and titanium isotopic compositions of single interstellar silicon carbide grains from the Murchison carbonaceous chondrite. *The Astrophysical Journal* 430:870–890.
- Hoppe P, Amari S, Zinner E, and Lewis RS 1995 Isotopic compositions of C, N, O, Mg, and Si, trace element abundances, and morphologies of single circumstellar graphite grains in four density fractions from the Murchison meteorite. *Geochimica et Cosmochimica Acta* 59:4029–4056.
- Hoppe P, Annen P, Strebel R, Eberhardt P, Gallino R, Lugaro M, Amari S, and Lewis RS 1997 Meteoritic silicon carbide grains with unusual Si-isotopic compositions: Evidence for an origin in low-mass, lowmetallicity asymptotic giant branch stars. *The Astrophysical Journal* 487:L101–L104.
- Huss GR and Lewis RS 1995 Presolar diamond, SiC, and graphite in primitive chondrites: Abundances as a function of meteorite class and petrologic type. *Geochimica et Cosmochimica Acta* 59:115–160.
- Jadhav M, Amari S, Zinner E, and Maruoka T 2006 Isotopic analysis of presolar graphite grains from Orgueil. *New Astronomy Reviews* 50:591–595.
- Jadhav M, Amari S, Marhas KK, Zinner E, Maruoka T, and Gallino R 2008 New stellar sources for high-density, presolar graphite grains. *The Astrophysical Journal* 682:1479–1485.
- Jadhav M, Zinner E, Amari S, Maruoka T, Marhas KK, and Gallino R 2013a Multi-element isotopic analyses of presolar graphite grains from Orgueil. *Geochimica et Cosmochimica Acta* 113:193–224.
- Jadhav M, Pignatari M, Herwig F, Zinner E, Gallino R, and Huss GR 2013b Relics of ancient post-AGB stars in a primitive meteorite. *The Astrophysical Journal Letters* 777: L27.
- José J and Hernanz M 2007 The origin of presolar nova grains. *Meteoritics & Planetary Science* 42:1135–1143.
- Kehm K, Amari S, Hohenberg CM, and Lewis RS 1996 $^{22}\text{Ne-E(L)}$ measured in individual KFC1 graphite grains from the Murchison meteorite. *Proceedings, 27th Lunar and Planetary Science Conference* pp. 657–658.
- Kim YM, Philipps V, Rubel M, Vietzke E, Pospieszczyk A, Unterberg B, and Jaspers R 2002 Retention of neon in graphite after ion beam implantation or exposures to the scrape-off layer plasma in the TEXTOR tokamak. *Journal of Vacuum Science & Technology A* 20:138–145.
- Lewis RS, Ming T, Wacker JF, Anders E, and Steel E 1987 Interstellar diamonds in meteorites. *Nature* 326:160–162.
- Lewis RS, Amari S, and Anders E 1990 Meteoritic silicon carbide—Pristine material from carbon stars. *Nature* 348:293–298.

- Lewis RS, Amari S, and Anders E 1994 Interstellar grains in meteorites: II. SiC and its noble gases. *Geochimica et Cosmochimica Acta* 58:471–494.
- Leya I and Masarik J 2009 Cosmogenic nuclides in stony meteorites revisited. *Meteoritics & Planetary Science* 44:1061–1086.
- Lindner P, Brix M, Mertens Ph, Pospieszczyk A, Samm U, Schweer B, and Unterberg B 2006 Velocity distribution of helium and neon atoms released from graphite and tungsten limiters in TEXTOR. *Journal of Nuclear Materials* 348:282–293.
- Marty B, Chaussidon M, Wiens RC, Jurewicz AJG, and Burnett DS 2011 A ^{15}N -poor isotopic composition for the solar system as shown by Genesis solar wind samples. *Science* 332:1533–1536. [PubMed: 21700869]
- Meier MMM, Heck PR, Amari S, Baur H, and Wieler R 2012 Graphite grains in supernova ejecta—Insights from a noble gas study of 91 individual KFC1 presolar graphite grains from the Murchison meteorite. *Geochimica et Cosmochimica Acta* 76:147–160.
- Nichols RH, Jr., Hohenberg CM, Hoppe P, Amari S, and Lewis RS 1992 ^{22}Ne -E(H) and 4He in single SiC and ^{22}Ne -E(L) in single Ca. of known C-isotopic compositions. *Proceedings, 23rd Lunar and Planetary Science Conference* pp. 989–990.
- Nichols RH, Jr., Kehm K, Brazzle R, Amari S, Hohenberg CM, and Lewis RS 1994 Ne, C, N, O, Mg, and Si isotopes in single interstellar graphite grains: Multiple stellar sources for Neon-E(L). *Meteoritics* 29:510–511.
- Nishiizumi K, Arnold JR, Caffee MW, Finkel RC, Southon JR, Nagai H, Honda M, Sharma P, Imamura M, and Kobayashi K 1993 Exposure ages of carbonaceous chondrites. *Proceedings, 24th Lunar and Planetary Science Conference* pp. 1085–1086.
- Nittler LR and Ciesla F 2016 Astrophysics with extraterrestrial materials. *Annual Review of Astronomy and Astrophysics* 54:53–93.
- Pignatari M, Zinner E, Hoppe P, Jordan CJ, Gibson BK, Trappitsch R, Herwig F, Fryer C, Hirschi R, and Timmes FX 2015 Carbon-rich presolar grains from massive stars: Subsolar $^{12}\text{C}/^{13}\text{C}$ and $^{14}\text{N}/^{15}\text{N}$ ratios and the mystery of ^{15}N . *The Astrophysical Journal Letters* 808:43.
- Rauscher T, Heger A, Hoffman RD, and Woosley SE 2002 Nucleosynthesis in massive stars with improved nuclear and stellar physics. *The Astrophysical Journal* 576:323–348.
- Sangster J 2007 C-Na (carbon-sodium) system. *Journal of Phase Equilibria and Diffusion* 28:571–579.
- Sugerman B, Ercolano B, Barlow MJ, Tielens AGGM, Clayton GC, Zijlstra AA, Meixner M, Speck A, Gledhill TM, Panagia N, Cohen M, Gordon KD, Meyer M, Fabbri J, Bowey JE, Welch DL, Regan MW, and Kennicutt RC, Jr. 2006 Massive-star supernovae as major dust factories. *Nature* 313:196–200.
- Teweldebhran D and Balandin AA 2009 Modification of graphene properties due to electron-beam irradiation. *Applied Physics Letters* 94:013101.
- Volkert CA and Minor AM 2007 Focused ion beam microscopy and micromachining. *MRS Bulletin* 32:389–395.
- Zinner E 2014 Presolar grains In *Meteorites, comets, and planets*, edited by Davis AM, Holland HD, and Turekian KK *Treatise in Geochemistry*, vol. 1, 2nd ed. Oxford: Elsevier pp. 1–33.

Fig. 1.

Secondary electron images of six presolar graphite grains before noble gas analysis. The 4m grains have been eroded to varying degrees by the preceding analysis with a primary NanoSIMS ion beam. The 8m grains were not exposed to an ion beam before noble gas analysis.

Fig. 2.

Detected amounts of ^{22}Ne (a, b) and ^{21}Ne (c, d) from graphite grain samples and blanks. Negative amounts result from our data analysis method described in the “Samples and Methods” section and by Heck et al. (2007). The extraction system has an average blank of almost zero cm 3 STP (dotted line). Error bars are 1σ .

Fig. 3.

Concentrations of ^{22}Ne and ^{21}Ne as a function of mass with detection limits drawn for the two different sessions. The shaded and hatched areas below the detection limits show mass–concentration combinations with undetectable gas amounts. Nominally negative concentrations indicate no detected gas (see the Methods section for details). Concentrations shown here are based on amounts that were subtracted by the mean blank. Error bars are 1σ and shown if larger than symbol. (Color figure can be viewed at wileyonlinelibrary.com.)

Fig. 4.

(a) Neon-rich OR1d graphite grains containing detectable amounts of Ne (large black circles) shown in a C and O isotope ratio diagram together with grains from Jadhav et al. (2013a) which were not analyzed for noble gases. Error bars are 1σ and shown if larger than symbol. Dashed lines represent the terrestrial ratios. (b) Silicon isotope ratios of OR1d4m graphite grains. Grains labeled Ne had detectable amounts of ^{22}Ne or ^{21}Ne . Error bars are 1σ and shown if larger than symbol. Dashed lines represent the terrestrial ratios. (Color figure can be viewed at wileyonlinelibrary.com.)

Fig. 5.

Summary figure for heating model for graphite grains on flat polished substrate (see main text and supporting information for explanations). a) Maximum nominal grain temperature as a function of grain size and primary beam power for scanning mode analysis, e.g., as during SEM imaging (the perimeter parameter is constant and in units of the corresponding grain diameter). b) Same as for (a), but with a static primary beam continuously focused onto the grain. The heating power of the NanoSIMS in (b) is shown for comparison purposes. Solid symbols are samples with detected Ne, empty symbols are samples without

detected Ne. Data points can be shifted in the vertical direction to illustrate the heating effect of varying beam power.

Fig. 6. $^{12}\text{C}/^{13}\text{C}$ ratios and upper limits of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios of ^{22}Ne -containing graphite grains from this study (solid triangles) compared with model predictions (star symbols) for AGB stars of 1.5 and 2 solar masses with solar and half solar metallicities from Heck et al. (2007). Model $^{12}\text{C}/^{13}\text{C}$ ratios are for AGB star envelopes, the C-rich reservoir from which circumstellar graphite condensed; model $^{20}\text{Ne}/^{22}\text{Ne}$ ratios are for AGB star He-shell ^{22}Ne -rich stellar wind (Ne-G) that got implanted into circumstellar graphite grains. Core-collapse supernova produced Ne and C model isotopic ratios plot outside of the range as shown in this diagram. (Color figure can be viewed at wileyonlinelibrary.com.)

Table 1.

Electron beam instrument conditions used for single grain secondary electron (SE) imaging and energy-dispersive X-ray spectroscopy (EDS) prior to noble gas analyses.

Mount	Instrument and technique	Accelerating voltage	Probe current	Maximum dwell times
4m	JEOL 840A EDS at WUSTL	15 kV	~10 nA ^a	20 s per grain
4m	PHI 700 Auger Nanoprobe SE imaging at WUSTL	20 kV	10 nA	60 s per grain
4m	Zeiss Evo 60 SE imaging FMNH	5 kV	0.1 nA	~40 ms μm^{-2}
8m	JEOL JSM-5900LV SEM EDS at UH	15 kV	~10 nA ^a	20 s per grain
8m	JEOL SEM SE imaging at UH	7 kV	~2 nA ^a	90 s per grain
8m	Zeiss Evo 60 SE imaging at FMNH	20 kV	0.1 nA	~40 ms μm^{-2}

^aThe JEOL SEMs used at WUSTL and UH did not provide a record of the beam current at the time of analysis. The stated numbers are typical conditions for grain analyses from previous analyses determined on the WUSTL JEOL SEM with a Faraday Cup (Floss, personal communication).

WUSTL = Washington University in St. Louis; UH = University of Hawai'i at M noa; FMNH = Field Museum of Natural History, Chicago.

Table 2.

Mean blank amounts, detections limits (see text for definition), and mean, blank-corrected sample amounts with standard errors (SE). Rounded amounts are given in cm³ at standard temperature and pressure (STP). Taking into account that mean blanks may be slightly different from zero, we define the detection limit to be 2SD of all blanks of a run above the mean blank value.

In cm ³ STP	³ He 10 ⁻¹⁷	⁴ He 10 ⁻¹³	²⁰ Ne 10 ⁻¹⁵	²¹ Ne 10 ⁻¹⁷	²² Ne 10 ⁻¹⁶
Mean blanks ± 2SE; 2SD					
Mount 4m (<i>n</i> = 35)	n.m.	1 ± 1; 5	8 ± 5; 29	-7 ± 7; 39	4 ± 13; 75
Mount 8m (<i>n</i> = 11)	3 ± 4; 13	3 ± 3; 10	2 ± 3; 10	-1 ± 3; 10	2 ± 4; 13
Detection limits					
Mount 4m	n.m.	6	36	32	79
Mount 8m	16	13	12	8	15
Mean samples ± 2SE					
Mount 4m (<i>n</i> = 15)	n.m.	0.3 ± 0.8	0.03 ± 4.83	16 ± 13	25 ± 16
Mount 8m (<i>n</i> = 7)	7 ± 9	3 ± 3	-0.1 ± 2.1	0.7 ± 5.0	11500 ± 16700

n.m. = not measured.

Table 3.

Gas amounts, concentrations, and Ne isotope ratios of OR1d 4m and 8m graphite grains with Ne above detection limits. Calculated “bulk” values are given in the last two rows (see text for explanation). No value is shown if the amount is below detection limit and if no limit could be calculated for an isotope ratio. See electronic supplement for geometric models used to calculate masses. All errors are 1σ and are dominated by counting statistics. Mean blanks were subtracted from gas amounts.

Grain OR 1d-	Diameter or geometric mean (μm)	Mass (ng)	^{21}Ne (10^{-16} cm ³ STP)	^{22}Ne (10^{-16} cm ³ STP)	^{21}Ne (10^{-5} cm ³ STP g ⁻¹)	^{22}Ne	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$
4m-1	5.0	0.103	5.6 ± 1.4	b.d.	0.54 ± 0.14	-	-	>0.07
4m-13	2.0	0.000742	4.0 ± 2.2	b.d.	54 ± 35	-	-	>0.05
4m-15	2.1	0.026	4.2 ± 3.8	b.d.	3.2 ± 3.4	-	-	>0.05
4m-18	2.0	0.021	b.d.	86 ± 40	-	416 ± 177	<4.2	-
8m-1	11.8	1.6	0.9 ± 0.7	2321 ± 16	0.00054 ± 0.00045	14.7 ± 2.3	<0.05	0.0004 ± 0.0003
8m-6	5.0	0.12	b.d.	17776 ± 16	-	1480 ± 235	0.007	-
8m-7	6.8	0.31	b.d.	59569 ± 8	-	1940 ± 306	<0.002	-
8m-8	6.2	0.23	b.d.	706 ± 10	-	30.2 ± 4.8	<0.2	-
8m-13	5.2	0.14	1.0 ± 0.7	22 ± 8	0.08 ± 0.06	1.6 ± 0.5	<5	0.05 ± 0.04
8m-16	5.2	0.097	-	347 ± 10	-	35.6 ± 5.7	<0.3	-
“Bulk” 4m		0.8 ^a	23 ± 7	375 ± 129	0.27 ± 0.08	4.3 ± 1.5	<1.7	0.06 ± 0.03
“Bulk” 8m		2.6 ^a	0.5 ± 1.6	80700 ± 170	0.002 ± 0.006	310 ± 1	<0.001	<0.00003

^aTotal mass of all measured grains of a mount.
b.d. = below detection limit.

Table 4.

Isotopic compositions of graphite grains measured by NanoSIMS. All errors are 1σ and are based on counting statistics. Delta-values are isotope ratios relative to terrestrial standards given in parts per thousand.

Grain ORId	$^{12}\text{C}/^{13}\text{C}$	$^{14}\text{N}/^{15}\text{N}$	$^{16}\text{O}/^{18}\text{O}$	$\delta^{25}\text{Mg}/^{24}\text{Mg}$	$\delta^{26}\text{Mg}/^{24}\text{Mg}$	$[\text{}^{26}\text{Al}/^{27}\text{Al}]_{\text{inferred}}$	$\delta^{29}\text{Si}/^{28}\text{Si}$	$\delta^{30}\text{Si}/^{28}\text{Si}$	Possible source
Grains with neon above the detection limit									
4m-1	64.4 ± 0.6	72.7 ± 0.6	144.4 ± 2.1	87 ± 19	83834 ± 618	0.620 ± 0.005	-451 ± 5	-660 ± 5	CCSN
4m-13	106.7 ± 1.0	161.3 ± 1.6	149.0 ± 1.6	79 ± 21	89976 ± 702	0.141 ± 0.001	-54 ± 11	-56 ± 15	CCSN
4m-15	90.4 ± 0.9	270.4 ± 2.7	536.2 ± 10.5	103 ± 12	-2 ± 10	-	-44 ± 14	0 ± 19	CCSN
4m-18	89.6 ± 0.9	274.0 ± 2.8	535.3 ± 11.6	-45 ± 12	-37 ± 11	-	-80 ± 14	84 ± 19	AGB
8m-1	12.0 ± 2.2	n.m.	495.9 ± 6.8	n.m.	n.m.	-	n.m.	n.m.	CCSN
8m-6	91.5 ± 1.0	n.m.	503.2 ± 9.3	n.m.	n.m.	-	n.m.	n.m.	CCSN
8m-7	77.2 ± 7.3	n.m.	494.7 ± 19.6	n.m.	n.m.	-	n.m.	n.m.	CCSN
8m-8	94.5 ± 0.9	n.m.	500.6 ± 15.9	n.m.	n.m.	-	n.m.	n.m.	CCSN or AGB
8m-13	98.0 ± 5.0	n.m.	509.4 ± 18.8	n.m.	n.m.	-	n.m.	n.m.	AGB
8m-16	99.8 ± 3.5	n.m.	503.3 ± 8.6	n.m.	n.m.	-	n.m.	n.m.	CCSN or AGB
Grains with neon below detection limit									
4m-2	18.1 ± 0.2	265.7 ± 2.1	526.7 ± 8.6	-23 ± 7	-32 ± 6	-	13 ± 8	-18 ± 11	
4m-3	2280 ± 22.9	248.9 ± 4.3	56.6 ± 0.7	-44 ± 15	10150 ± 83	0.104 ± 0.009	-8 ± 19	-261 ± 20	
4m-5	150.5 ± 1.5	269 ± 3	538.5 ± 7.9	-25 ± 9	-45 ± 8	-	-4 ± 8	-15 ± 12	
4m-6	90.9 ± 0.9	268.4 ± 4.4	540.5 ± 12.2	-48 ± 55	-36 ± 53	-	-40 ± 18	1 ± 23	
4m-9	110.6 ± 1.1	259.3 ± 2.5	444.4 ± 6.4	-15 ± 16	1780 ± 29	0.011 ± 0.001	-111 ± 11	-132 ± 15	
4m-10	108.6 ± 1.1	244.8 ± 4	145.2 ± 2.3	-43 ± 15	2450 ± 33	0.078 ± 0.006	18 ± 12	-45 ± 15	
4m-11	89.5 ± 0.9	310.2 ± 1.9	551 ± 10.9	-54 ± 22	-25 ± 21	-	-6 ± 19	-6 ± 24	
4m-12	26.3 ± 0.3	267.2 ± 2.9	544.1 ± 9.8	-41 ± 11	-24 ± 10	-	-17 ± 12	-40 ± 16	
4m-16	103.9 ± 1	182.6 ± 1.4	113.1 ± 1.2	1 ± 18	613260 ± 4270	0.572 ± 0.048	-59 ± 9	-27 ± 12	
4m-17	90.5 ± 0.9	290.9 ± 5.6	546.1 ± 17.6	-48 ± 18	-37 ± 17	-	-10 ± 23	-6 ± 28	
4m-19	8.6 ± 0.1	247.3 ± 3.8	441.7 ± 6.3	-45 ± 17	6220 ± 64	0.029 ± 0.002	-19 ± 12	8 ± 16	
8m-5	96 ± 1.5	500.4 ± 15.8	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	

n.m. = not measured. Stellar sources: CCSN = Core-collapse supernova; AGB = Asymptotic giant branch star. NanoSIMS data for 4m grains are published in Jadhav et al. (2013a) (refer to this publication for complete data set).