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Geochimica et Cosmochimica Acta 76 (2012) 147–160

Geochimica et Cosmochimica Acta

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Graphite grains in supernova ejecta – Insights from a noble gas study of 91 individual KFC1 presolar graphite grains from the Murchison meteorite

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Received 2 February 2011; accepted in revised form 4 October 2011; available online 20 October 2011

Abstract

We have measured helium and neon concentrations, elemental and isotopic ratios of 91 individual presolar graphite grains from the KFC1 density separate of the Murchison meteorite. Eleven grains contain measurable amounts of either ^{4}He, ^{20}Ne, ^{21}Ne or ^{22}Ne, or a combination thereof. We report the first detection of ^{21}Ne from an individual presolar graphite grain and the first detection of ^{4}He and ^{20}Ne in individual KFC1 graphite grains. Six of the gas-rich grains originate from asymptotic giant branch (AGB) stars, while another five are likely derived from core-collapse supernovae. The mono-isotopic ^{22}Ne detected in one supernova grain is either radiogenic and compatible with condensation in the O/Ne zone, or nucleosynthetic and derived from the He/C zone. Two grains with ^{20}Ne and ^{12}C/^{13}C <10 are consistent with condensation and Ne acquisition in a ~80:20 mixture of material from the H envelope and He/N zone. The isotopic ratios of a single grain with ^{21}Ne and ^{22}Ne, and a further grain with ^{20}Ne and ^{22}Ne are compatible with condensation and Ne acquisition in the C/O zone. We discuss the implications of our study on the understanding of processes in supernova ejecta.

1. INTRODUCTION

Apart from the interstellar grains collected by the stardust probe, presolar grains from interplanetary dust particles and primitive meteorites are the only samples of stellar matter available for laboratory analysis on Earth. As such, they can provide ground truth to astrophysical models of evolved stars like asymptotic giant branch (AGB) stars, supernovae and novae. Specific pressures, temperatures, and initial elemental and isotopic compositions allow different nucleosynthetic reactions and mixing processes to take place and give each source a distinct "fingerprint" in the elemental and isotopic ratios of the condensing dust grains (Meyer and Zinner, 2006). Presolar grains, found in primitive meteorites which were never subjected to substantial thermal metamorphism (e.g., the CM2 chondrite Murchison), essentially preserve these isotopic signatures to the present day.

Over the years, a large number of presolar mineral phases have been identified by their extremely large isotopic anomalies, for example nanodiamond residues (Lewis et al., 1987), silicon carbide (Bernatowicz et al., 1987), graphite (Amari et al., 1990), silicon nitride (Nittler et al., 1995), oxides (Nittler et al., 1994; Hutcheon et al., 1994) and silicates (Messenger et al., 2003; Nagashima et al., 2004; Nguyen and Zinner, 2004).

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doi:10.1016/j.gca.2011.10.027

Noble gases have played a major role in the identification and characterization of presolar grains. Xenon enriched in the heaviest and lightest isotopes (called Xe-HL) was the first presolar noble gas component identified (Reynolds and Turner, 1964) and was later attributed to nanodiamond (Lewis et al., 1987). Black and Pepin (1969) identified an anomalous component of neon (then called Ne-E), with a very low $^{20}Ne/^{22}Ne$-ratio of <3.4, released at high temperatures from carbonaceous chondrites. Clayton (1975) proposed that Ne-E was in fact pure ^{22}Ne from the decay of radioactive ^{22}Na ($t½ = 2.6$ a), a component that is now called Ne-R (for radiogenic). However, two sub-components of Ne-E were later identified: Ne-E(H), released at higher temperature (>900 °C) steps from high-density carriers, and Ne-E(L), released at lower temperatures from low-density carriers. Ne-E(H) is today called Ne-G (for "Giant"/"AGB"), as it is thought to originate from the He-shell of AGB stars, where ^{22}Ne is produced by α-capture on ^{14}N, and is found in presolar graphite and silicon carbide. Amari et al. (1990) isolated and analyzed the first presolar graphite grains, and identified presolar graphite as the sole carrier phase of Ne-E(L). Amari et al. (1995) showed later that Ne-E(L) is itself a mixture of Ne-G and Ne-R, with the relative contributions of the two components depending on the density of the graphite grains.

The first noble gas analysis of single presolar graphite grains was done by Nichols et al. (1992). They were extracted from the CM2 chondrite Murchison, where presolar graphite has an overall abundance of about 4.7 ± 0.5 ppm (Huss et al., 2003). The details of the procedure for the isolation of presolar SiC, graphite and diamond are described in Amari et al. (1994). So far, the number of noble gas studies of individual presolar graphite grains has remained rather limited. Most of them have been done on three different density and size fractions of Murchison (KE3: 1.6–2.05 g/cm^3, KFB1: 2.10–2.15 g/cm^3; >1 μm, KFC1: 2.15–2.20 g/cm^3; >1 μm). Nichols et al. (1992) found 14 grains with measurable ^{22}Ne in KFB1, out of 49 grains analyzed. Nichols et al. (1994) found 9 (out of 21) gas-rich grains from KE3, and Kehm et al. (1996) found 3 (out of 46) gas-rich grains in KFC1. In these studies, only ^{22}Ne was found, with no ^{20}Ne, ^{21}Ne or ^{4}He above the respective detection limits. Heck et al. (2009) reported 11 gas-rich among 51 KFB1 grains analyzed, including the first presolar graphite grains to contain measurable ^{4}He and ^{20}Ne. Recently, graphite from the meteorite Orgueil was separated (Jadhav et al., 2008) and initial results of He and Ne isotope measurements of 15 individual low-density grains were reported by Heck et al. (2010). Four of these grains were gas-rich in ^{22}Ne.

There are at least two possible mechanisms that can incorporate Ne into presolar graphite grains in an expanding supernova ejecta cloud. The presence of Ne-R is best explained by the condensation of the parent nuclide ^{22}Na together with graphite (Clayton, 1975; Amari, 2009; Heck et al., 2009). The presence of ^{4}He, ^{20}Ne, ^{21}Ne and nucleosynthetic ^{22}Ne needs another mechanism, as the typical temperatures in regions where presolar grains condense are higher than the condensation temperatures of He and Ne (for the solar nebula at 10^{-4} bar total pressure, condensation temperatures are <3 and 9.3 K, respectively: Lodders, 2003). Ion implantation was proposed as the mechanism to implant nucleosynthetic Ne-G into SiC grains from AGB stars by Gallino et al. (1990) and Lewis et al. (1990). Verchovsky et al. (2004) proposed two ion implantation regimes for these grains, an initial one during the "quiet" AGB phase, and a later, more energetic implantation to larger depths during the post-AGB-phase.

Ion implantation may also work for supernova graphite grains. The implantation depth of Ne ions can be calculated using the SRIM code (Ziegler et al., 2010, http://www.srim.org). A relative velocity between the ions and the grains of 130–350 km/s results in an implantation depth of 6–30 nm for ^{20}Ne (Amari, 2009), while implantation depths on the order of ~1 μm are reached for relative velocities of ~2700 km/s, typical for the reverse shock region (Heck et al., 2009). During passage of the grains through this region, they become dynamically decoupled from the gas. Throughout the reverse shock, the H-rich regions beyond the reverse shock and in the interstellar medium (ISM), they are sputtered by hot H ions. However, for relative velocities of up to 3000 km/s, a 1 μm graphite grain will not lose significantly more than 0.7%, or 7 nm of its diameter in the reverse shock, and no more than 20%, or 20 nm of its diameter in the ISM (Nozawa et al., 2007). Therefore, while ions implanted at very low velocities have probably been sputtered away in the reverse shock or the ISM, ions putatively implanted at higher velocities would be detectable. The detection of nucleosynthetic Ne in supernova graphite grains is therefore a clear sign that ion implantation takes place in the expanding ejecta of supernovae, giving us the opportunity to learn more about nature's biggest explosions.

2. SAMPLES AND METHODS

2.1. Grain preparation and selection

The KFC1 graphite grain density separate (2.15–2.20 g/cm^3) is part of the K-series of presolar grains extracted at the University of Chicago from the Murchison CM2 carbonaceous chondrite in the 1990s (Amari et al., 1994). For this study, the KFC1 grains were suspended in a drop of isopropanol–water solution, and deposited on a gold foil attached to a standard Al scanning electron microscope (SEM) sample holder. The grains were then briefly imaged with the SEM at Washington University in St. Louis and subsequently analyzed for their C and Si isotopic composition ($^{12}C^-$, $^{13}C^-$, $^{28}Si^-$, $^{29}Si^-$, $^{30}Si^-$) in multicollection with a rastering Cs^+-beam of the Washington University Cameca NanoSIMS 50 ion micro-probe with a typical rastering-size of 2 μm. The measured carbon isotopic ratios have typical analytical errors of 1–2%, while the Si isotope ratios, with a typical Si abundance of only ~100 to 10,000 ppm (Hoppe et al., 1995), have much higher errors of up to ~10%. This limits their diagnostic use, but nevertheless allows us to recognize rare grains with large Si anomalies. Interestingly, grains with significant Si isotopic anomalies are much less abundant in graphite than in SiC grains (Hoppe et al., 1995), implying that some equilibration with isotopically

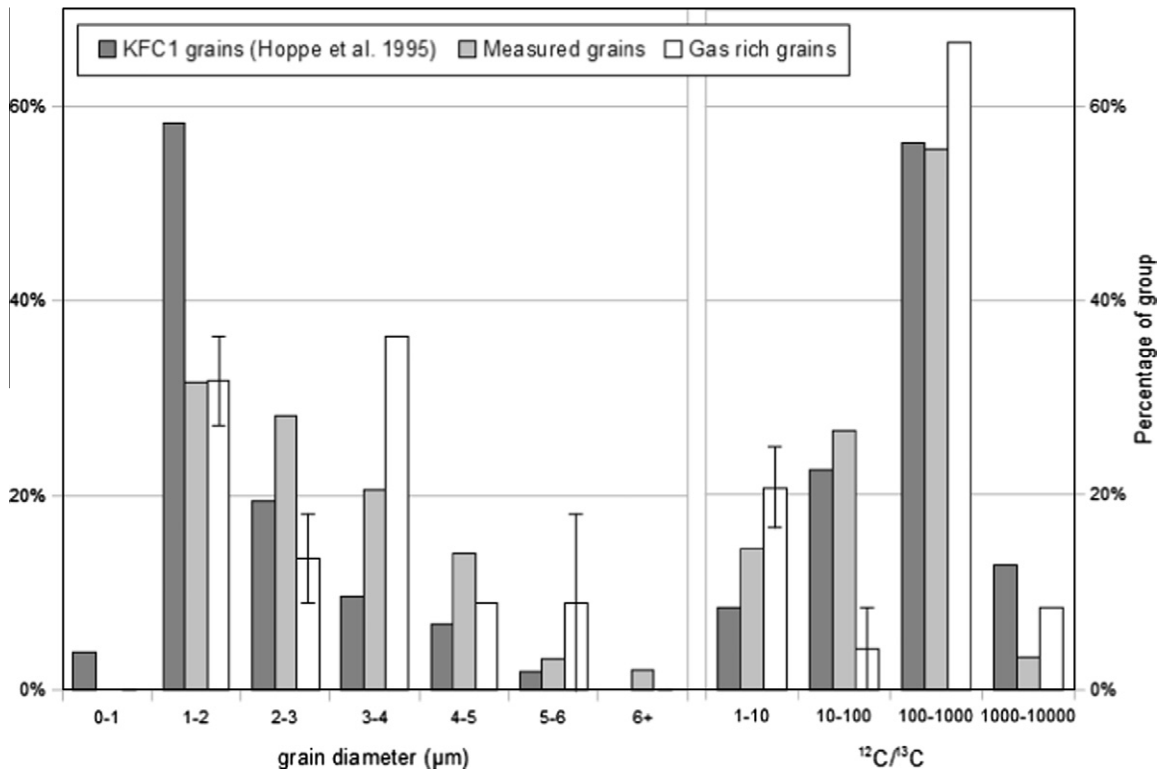

Fig. 1. The diameter and $^{12}C/^{13}C$ ratio distributions for KFC1 grains measured by Hoppe et al. (1995), all grains measured for this study, and the 11 gas-rich grains (the error bars denoting the uncertainty induced by the co-extraction of grains). Small grains with diameters below 2 μm are under-represented in this study, and the resulting relative over-representation of larger grains is largest for grains in the 3–4 μm bin. Grains with a $^{12}C/^{13}C$ ratio <10 are over-represented by about a factor of ~2.

normal material has taken place, probably from the meteorite matrix, further limiting the diagnostic value of Si.

Only grains with diameters above ~1.2 μm (measured from SEM images) were selected for noble gas analysis at ETH Zurich, as most smaller grains presumably yield amounts that are below detection limits. Grains with large diameters (above 2 μm) are thus overrepresented compared to the KFC1 size distribution reported by Hoppe et al. (1995) (see Fig. 1). The first 42 grains were selected based on their distance (>~200 μm) to neighboring grains. This was done to avoid multiple extractions by the laser beam, which has a spot size of about 50–100 μm. Thirty-six grains were selected based on extreme isotopic ratios ($^{12}C/^{13}C$ <20 or $^{12}C/^{13}C$ >200, or more than 100‰ away from solar Si composition), and 14 were selected based on their large size (measured diameter >2.5 μm). For the latter two groups of grains, somewhat closer spacings (down to ~100 μm) to neighboring grains were deemed acceptable.

2.2. Calibrations and blanks

A total of 22 calibration measurements were done, with a known amount of calibration gas (essentially atmospheric in Ne isotopic composition and slightly higher than atmospheric or "air-like" in $^{3}He/^{4}He$, as discussed in Heber et al. (2009)) processed as in a sample analysis. The spectrometer sensitivity determined with these calibrations remained nearly constant: for all species, the 2σ variation was within ~1–2%. For the first ~30 samples, each grain extraction was bracketed by cold blank measurements. During a cold blank, the laser was not fired, but otherwise, the analysis was carried out just as for a sample. As it became clear after the first ~20 cold blanks that the blank was very stable and essentially zero within error (see below), fewer cold blanks were measured. In total, 50 cold blanks were measured. In addition, seven hot blanks were measured, where the laser was aimed at an empty spot on the sample-holder and operated for the same time as during a typical grain extraction. Cold and hot blanks agree within analytical uncertainty, indicating no significant increase in background gases from laser operation or heating of the sample-holder gold foil.

2.3. Noble gas extraction and data reduction

Extraction of the noble gases was done by heating the grains with a 1024 nm Nd:YAG-Laser operated in CW (continuous wave) mode. The glowing of the heated grains during the individual extractions was monitored on a video screen. An extraction was considered successful when a grain identified on the SEM map was seen glowing on the screen. Whenever necessary, we attempted to aim the laser beam off-center to the side facing away from the next neighboring grain(s), but in some cases, neighboring grains were nevertheless heated, as indicated by their glowing on the screen. In the following, to be on the safe side, we will treat all co-heated (glowing) grains as if they had been co-extracted. Because of the very low amounts of gas expected, we used a low-blank extraction line and an ultra-high-sensitivity mass spectrometer, where a molecular drag pump concentrates the gases almost quantitatively into the ion source, as described by Baur (1999). Prior to admission into the mass spectrometer, the gases where cleaned with metal-oxide getters and activated-charcoal traps cooled with liquid N_2, in order to remove chemically active and/or interfering species. Remaining contributions of the interfering species were between one and two orders of magnitude smaller than typical ion counting errors of the affected species and were therefore neglected (except for calibration measurements) in the data reduction procedure. We used the analytical method developed by Heck et al. (2007, 2009). No valves are operated between the gas extraction and the admission of the noble gases into the mass spectrometer. After the closure of the pump valve, laser chamber and extraction line are directly connected to the mass spectrometer. The increase of spectrometer "memory" on all isotopes of interest ($^3He^+$, $^4He^+$, $^{20}Ne^+$, $^{21}Ne^+$, $^{22}Ne^+$), as well as the background of interfering species ($H_2^+ \rightarrow HD^+$ on mass 3, $H_2{}^{16}O^+ \rightarrow H_2{}^{18}O^+$ on mass 20, $^{40}Ar^+ \rightarrow {}^{40}Ar^{++}$ on mass 40 and $CO_2^+ \rightarrow CO_2^{++}$ on mass 44) is then monitored for four cycles in peak-jumping mode, prior to sample gas extraction. After extraction and one additional cycle (~5 min), the spectrometer was separated from the extraction line, and the latter was pumped in preparation for the next analysis. During that time, the isotopes of interest and the interfering species in the spectrometer were measured again in six additional peak-jumping mode cycles. The "memory" gases from within the mass spectrometer show a steady increase, as exemplified in Fig. 2 by ^{20}Ne, that looks just like a blank measurement in this extraction. In a blank run, we do not expect the measured signal to show a step or jump at time zero, the moment we start the laser. A forward extrapolation of the four data points measured prior to the laser extraction should result in the same value as a backward extrapolation of the seven data points obtained after the moment of extraction. The difference between the two extrapolated signals will thus scatter around zero, and the detection limit of a species is defined to plot two standard deviations above the average of this scatter (Heck et al., 2007). Our blank (the noble gas amount measured in an empty run) is therefore essentially zero, and each extraction has its own blank attributed to it, in the form of the forward extrapolation of the first four measurements prior to the laser extraction. For a more detailed description of this procedure, see Heck et al., 2007. The detection limits for all interesting isotopes are as follows (in units of 10^{-15} ccSTP, cm^3 at standard temperature and pressure, where 1 ccSTP = 2.687×10^{19} atoms): ^3He: 0.46, ^4He: 430, ^{20}Ne: 29.9, ^{21}Ne: 0.60, ^{22}Ne: 5.53. In the following we will call

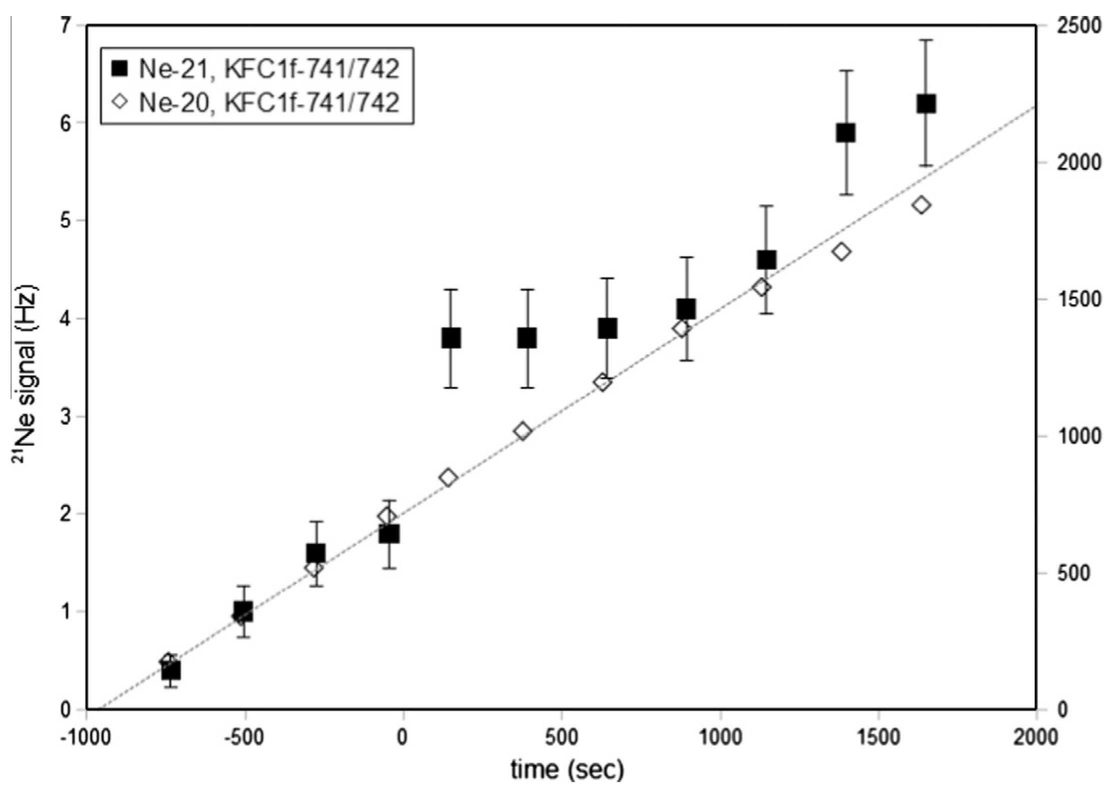

Fig. 2. The recorded ^{20}Ne and ^{21}Ne-signals (represented by white diamonds and black squares, respectively) during the extraction of grains KFC1f-741/742, plotted against time. For the ^{21}Ne signal, 2σ-Poisson-counting errors are shown. Time 0 indicates the beginning of laser extraction. The gray dotted line represents the (linear) forward extrapolation of the first four ("blank") measurements of the ^{21}Ne signal. Note that the ^{21}Ne signal always plots above this line after extraction. See the Electronic Annex for a discussion of the significance of the ^{21}Ne-signal at time 0.

each grain having a measured gas amount above the detection limit a "gas-rich" grain. A measurement sequence for a single "gas-rich" grain, KFC1f-741/742, is shown in Fig. 2. Within a few seconds after extraction, the signal jumps to a higher value, and further shows a linear increase, essentially with the same slope as the line from the first four measurements (see the Electronic Annex for a more thorough discussion). Upper or lower limits of isotope ratios, where given, are defined as the ratio between a measured concentration and a detection limit as defined above (or vice versa). This definition is essentially identical to those used by Heck et al. (2009) and similar to Nichols et al. (1992, 1994), but more conservative than the one used by Kehm et al. (1996). A total of 92 grains were degassed in 76 extractions (10 double, three triple extractions). One extraction was discarded, as it released a comparatively large amount of noble gases of atmospheric composition, probably pointing to some terrestrial contamination. This leaves us with a total of 91 presolar graphite grains extracted.

3. RESULTS

The grain diameters, C and Si isotopic ratios, He and Ne concentrations, and elemental or isotopic ratios or upper/lower limits, where applicable, for all gas-rich grains are shown in Table 1. The masses of the grains were calculated by assuming that they are spheres with radius ($d_{meas}/2$), where d_{meas} is the average diameter measured from the SEM-image, and a density corresponding to the average density of the KFC1 density separate, i.e., 2.18 g/cm^3. Grains with sub-solar $^{12}C/^{13}C$ are over-represented in our study, compared to the average distribution (Fig. 1) as reported by Hoppe et al. (1995). Most of the Si isotope ratios of the grains plot within error on the "mainstream line" as defined by SiC data (Zinner et al., 2007), and are therefore of limited diagnostic use (see Fig. EA-1-1 in the Electronic Annex).

The grains rich in either ^{4}He, ^{20}Ne, ^{21}Ne or ^{22}Ne from all runs are also displayed in Fig. 3. None of the grains contained ^{3}He above the detection limit, but two grains contained ^{4}He: KFC1f-251 and -312. These are the first ^{4}He-rich grains reported for the density separate KFC1. Heck et al. (2009) reported the first ^{4}He measured in a presolar graphite grain in the lower-density separate KFB1. Neither of the two ^{4}He-rich grains presented here showed ^{20}Ne, ^{21}Ne or ^{22}Ne above detection limit.

In three further extractions, ^{20}Ne was detected. In two of the grains (KFC1f-315 and -711), ^{20}Ne was the only detected noble gas isotope. In a third extraction (KFC1f-342), both ^{20}Ne and ^{22}Ne were found above detection limit, with a measured ^{20}Ne/^{22}Ne ratio of 5.2 ± 3.1. In another extraction, both ^{21}Ne and ^{22}Ne were detected, with a ^{21}Ne/^{22}Ne ratio of 0.046 ± 0.022. This is the first detection of ^{21}Ne in a presolar graphite grain. In the Electronic Annex, we analyze this detection, discuss and finally reject alternative explanations. In the extraction yielding ^{21}Ne, two grains (KFC1f-741 and KFC1f-742) were heated simultaneously, so that the ^{21}Ne and ^{22}Ne cannot be clearly attributed to one of the two grains, but given the low abundance of gas-rich grains in KFC1, it is unlikely ($p = (^{11}/_{91})^2 = \sim 1.5\%$) that both contributed to the observed Ne. However, the two grains are clearly distinct in terms of C and Si isotope ratios, and we will consider the attribution of the Ne to one of the two grains in the discussion section.

In four single-grain extractions (KFC1f-134, -302, -323 and -422), ^{22}Ne was the only isotope significantly above the detection limit. A fifth single-grain extraction (KFC1f-701, not shown in Table 1) also showed ^{22}Ne just above the detection limit, but as the ion counting error of this measurement is so large it encompasses zero and the average blank, data from this grain was discarded. In the simultaneous extraction of the three grains KFC1f-531, -532 and -533, a small amount of ^{22}Ne was measured, close to the detection limit.

4. DISCUSSION

4.1. Inferred bulk concentrations

In a $\sim$7 μg bulk sample of KFC1, Amari et al. (1995) measured a ^{22}Ne concentration of 5.1×10^{-5} ccSTP/g and ^{20}Ne/^{22}Ne, ^{21}Ne/^{22}Ne ratios of 0.063 and 0.00025, respectively (corresponding to a ^{20}Ne concentration of 3.2×10^{-6} ccSTP/g, and a ^{21}Ne concentration of 1.3×10^{-8} ccSTP/g). In the course of our project, we have extracted 91 grains with a total mass of $\sim$3.8 ng (assuming spheres with a density of 2.18 g/cm^3). They sum up to a total ^{22}Ne concentration of 2.7×10^{-5} ccSTP/g, or about half the value observed by Amari et al. (1995). On the other hand, the KFC1 single-grain analyses by Kehm et al. (1996), where three out of 46 grains were found to be gas-rich, yield an inferred ^{22}Ne concentration of $\sim 9 \times 10^{-5}$ ccSTP/g or about a factor of $\sim$3 higher than our value. The data of Kehm et al. (1996) and our own study taken together (weighted average from 133 individual grains with an inferred total mass of $\sim$10 ng) thus result in an inferred bulk concentration of $\sim 6.6 \times 10^{-5}$ ccSTP/g, close to the value given by Amari et al. (1995). This suggests that the few ^{22}Ne-rich grains found in the single-grain studies indeed represent the major fraction of ^{22}Ne in bulk KFC1.

Our inferred bulk amounts of ^{20}Ne (2.9×10^{-5} ccSTP/g) and ^{21}Ne (1.6×10^{-7} ccSTP/g) are higher (by a factor of $\sim$9 and $\sim$13, respectively) than the values given by Amari et al. (1995). This factor could be explained if large grains or grains with isotopic anomalies, which were preferred in our selection, were also more likely to be rich in ^{21}Ne and ^{20}Ne. This tentative explanation is supported by the fact that all grains rich in ^{21}Ne or ^{20}Ne from our study are either large (>4 μm diameter) or have a low $^{12}C/^{13}C$ ratio (<10).

4.2. Identification of stellar sources

In the following paragraphs we discuss the stellar sources for the gas-rich grains listed in Table 1. We consider five different stellar sources: AGB stars, born-again AGB stars, J-type carbon stars, novae and core-collapse supernovae.

Asymptotic giant branch (AGB) stars are low- and intermediate-mass stars (1–8 $M_\odot$), essentially in the last evolution stage driven by nuclear burning. Hydrogen and Helium are fused in separate, alternating shells above a

Table 1
Results for all gas-rich grains.

Grain	ϕ (μm)	$^{12}C/^{13}C$	$\delta^{29}Si$ (‰)	$\delta^{30}Si$ (‰)	^{4}He	^{20}Ne	^{21}Ne	^{22}Ne	$^{4}He/^{20}Ne$	$^{4}He/^{22}Ne$	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	Stellar source
KFC1f-251	3.1	699 ± 6	−6 ± 15	−7 ± 18	7000 ± 2100				>76	>410			$Z/Z_{\odot} = 1/3$, 5 $M_{\odot}$ AGB star. No He loss?
KFC1f-312	3.6	146 ± 1	−8 ± 16	−30 ± 19	810 ± 170				>15	>79			$Z/Z_{\odot} = 1/2 - 1$, 2–3 $M_{\odot}$ AGB star. No He loss?
KFC1f-315	1.4	7.07 ± 0.04	130 ± 80	46 ± 88		1000 ± 300			<12		>6.1		SN (C/O 45.1%, He/N 54.9%, or H envelope 71.9%, He/N: 28.1%) Or J type carbon star?
KFC1f-711	1.4	7.62 ± 0.04	−83 ± 45	−69 ± 54		1400 ± 500			<9.6		>7.5		SN (C/O 48.3%, He/N 51.7%, or H envelope 77.0%, He/N: 23.0%) Or J type carbon star?
KFC1f-134	3.6	1557 ± 23	5 ± 53	−23 ± 61				12 ± 1		<60	<4.6	<0.088	$Z/Z_{\odot} = 1/6$, 1.5–2 $M_{\odot}$ AGB star. He loss >64%
KFC1f-302	3.5	104 ± 1	−4 ± 17	−25 ± 20				66 ± 7		<13	<0.96	<0.019	$Z/Z_{\odot} = 1/2 - 1$, 2–3 $M_{\odot}$ AGB star. He loss >91%
KFC1f-323	1.3	313 ± 2	−46 ± 46	−121 ± 52				970 ± 250		<16	<1.2	<0.023	$Z/Z_{\odot} = 1/3$, 1.5 $M_{\odot}$ AGB star, He loss >89%? Or SN (He/C or O/Ne 98.6%, He/N 1.4%)?
KFC1f-422	2.4	211 ± 1	11 ± 32	−83 ± 35				88 ± 27		<30	<2.2	<0.043	$Z/Z_{\odot} = 1/2 - 1$, 2–3 $M_{\odot}$ AGB star. He loss >79%
KFC1f-531*	5.4	11.3 ± 0.1	−31 ± 18	−39 ± 22				3.4 ± 1.0		<66	<5.0	<0.096	Born-again AGB star? SN? CO nova?
KFC1f-532*	1.7	638 ± 5	−140 ± 90	320 ± 130				110 ± 30					$Z/Z_{\odot} = 1/3$, 2–3 $M_{\odot}$ AGB star, (similar to SiC Z grains?) probable carrier grain for this extraction.
KFC1f-533*	2.7	5.30 ± 0.03	−11 ± 10	−32 ± 12				27 ± 8					Born-again AGB star? SN? CO nova?
KFC1f-342	5.2	202 ± 1	37 ± 35	−23 ± 40		21 ± 10		4.1 ± 1.5	<12.1	<63	5.2 ± 3.1	<0.092	SN (C/O 97.8%, He/N 2.2%)
KFC1f-741**	4.1	479 ± 4	−50 ± 17	−60 ± 20			0.80 ± 0.28	17 ± 6		<30	<2.3	0.046 ± 0.022	SN (C/O or He/C, 99.1%, He/N 0.9%), probable carrier grain for this extraction.
KFC1f-742**	4.3	108 ± 1	−39 ± 29	−1 ± 36			0.67 ± 0.24	15 ± 5					SN (condensation: C/O or He/C, 95.9%, He/N 4.1%)
Inferred bulk[a]	–	–	–	–	~82	2.9	0.016	2.7	–	–	–	–	–

All noble gas concentrations and given in units of 10^{-5} ccSTP/g.
SN = supernova.
*,** Co-extractions, He and Ne concentrations calculated, and stellar sources assigned, as if the measured gas amount resulted from the respective grain.
[a] Note that the inferred bulk may be biased from the preferential selection of large and isotopically anomalous grains.

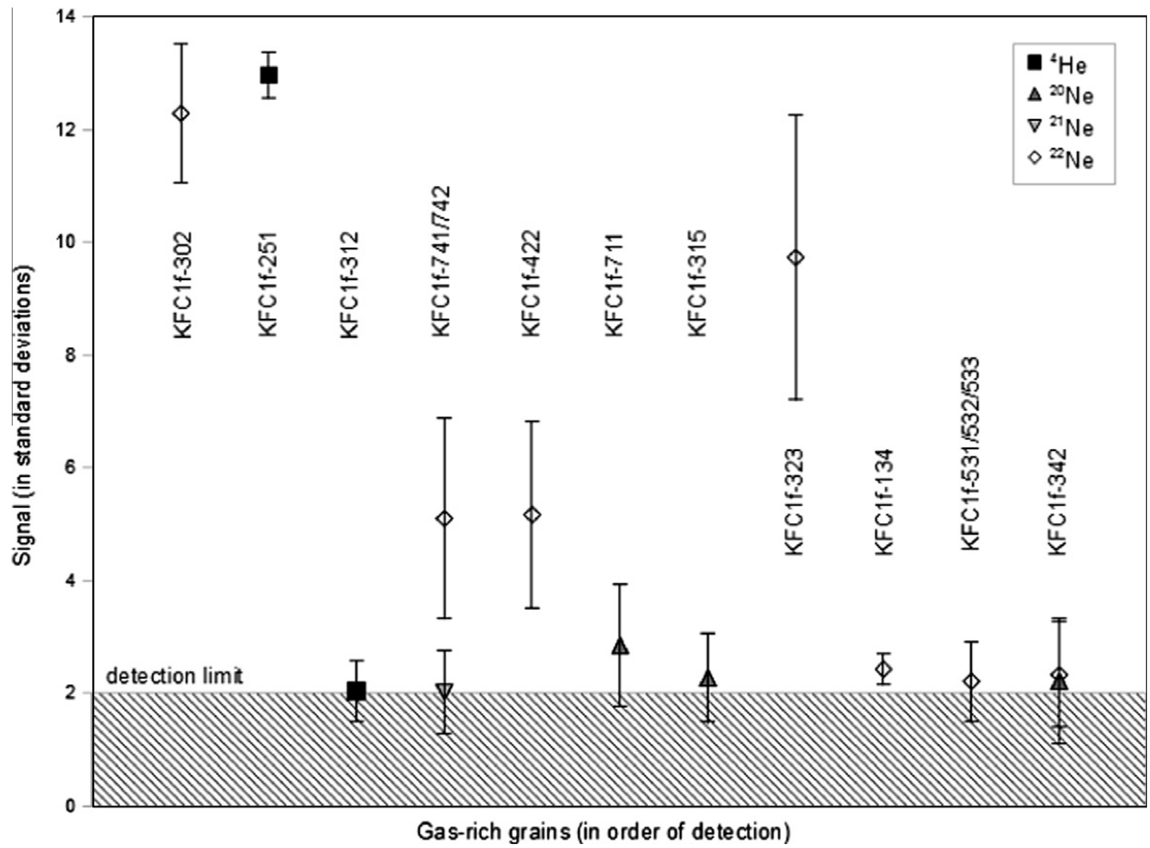

Fig. 3. Measured noble gas amounts (and corresponding 1σ errors) of the 11 gas-rich grains, expressed in multiples of the standard deviation from the average blank for the respective isotope. For example, the measured ^{22}Ne amount of grain KFC1f-302 plots ~12 standard deviations (from the average blank) above the average blank for ^{22}Ne. Two standard deviations define the detection limit for all species.

degenerated core, which leads to instabilities resulting in thermal pulsing and an associated dredge-up of nuclear ashes into the photosphere ("third dredge-up events"; e.g., Herwig, 2005). Due to their strong stellar winds and abundance, AGB stars are the main contributors of stardust to the ISM, and are also important drivers of galactic chemical evolution (e.g., Arnone et al., 2003). Presolar graphite condenses in the extended envelopes of these stars. A majority of isotopic signatures of presolar graphite grains can be matched with AGB star model predictions. Such models were first published by Gallino et al. (1990) and have been updated in Heck et al. (2007). *Born-again AGB stars* and *J-type carbon stars* are two types of evolved stars with low ^{12}C/^{13}C-ratios (<15), which are enriched (Asplund et al., 1999, and references therein), and solar-like (Abia and Isern, 2000), in their s-process element abundances, respectively. So far, no detailed model predictions for the yields of all Ne and He isotopes exist for these two objects, although the work by Herwig et al. (2011) is a promising first step in this direction. A high abundance of the neutron-seed isotope ^{22}Ne, and therefore a low ^{20}Ne/^{22}Ne-ratio, similar to those in AGB stars, have been suggested for born-again AGB stars (Heck et al., 2007), while for J-type carbon stars, high ^{20}Ne abundances from hot α-capture, and therefore a high ^{20}Ne/^{22}Ne-ratio are expected (Abia and Isern, 2000; Deupree and Wallace, 1987). *Novae* are recurring thermonuclear explosions on the surface of white dwarfs, fed by H and He accreting from the expanded atmosphere of an evolved companion star. The modeled ^{12}C/^{13}C ratios of novae are also very low (0.3–1.8), while the ^{20}Ne/^{22}Ne depends on the composition of the involved white dwarf (carbon, oxygen (CO) or oxygen, neon, magnesium (ONe), José et al., 2004). *Core-collapse supernovae* mark the death of massive stars (>8 $M_{\odot}$, e.g., Leonard, 2010). Prior to the supernova, they go through a series of nuclear burning stages (H, He, C, Ne, O and finally Si burning), where the ashes of the most recent stage become the fuel for the next one. Whenever a new stage starts in the center of the star, the last stage continues to burn in a shell around the innermost core. The stellar core develops an onion-shell structure, with the ashes of the last, Si burning stage accumulating as an inert Fe/Ni-core in the center, and all of the earlier burning stages going on in separated shells (or zones) above the core (zones from core to surface: Fe/Ni, Si/S, O/Si, O/Ne, C/O, He/C, He/N, and H envelope, Meyer et al., 1995). Finally, the core partially collapses into a neutron star, producing a fierce neutrino wind, upon which the collapsing star rebounds and explodes outward, initiating explosive burning in all shells while accelerating the shell material outward (Meyer and Zinner, 2006). As the ejecta of 25 $M_{\odot}$ supernovae are considered representative of the total supernova contribution to the ISM

(Woosley and Weaver, 1995), we will use a supernova model (s25a28d) of a 25 $M_\odot$ star by Rauscher et al. (2002).

For the identification of the most likely stellar source of a grain we work with Figs. 4 and 5. Using the $^{12}C/^{13}C$ and Ne isotopic ratios (or upper/lower limits thereof), it is usually straightforward to identify which of the stellar sources are compatible, since the four non-supernova sources usually occupy well-defined regions in the two diagrams. If several sources provide possible fits, this is pointed out in the discussion. If the data of a grain does not fit any of the source regions, but can be explained by mixtures of supernova zone-averages, we assume that it is of supernova origin. We then attempt to reproduce its $^{12}C/^{13}C$ composition from mixtures of material from the carbon-rich (C/O >1) He/C and He/N supernova zones, where the condensation of graphite is likely. If this is not possible, we consider all other supernova zones. The five grains of supernova origin found in this study (~50%) are to first order compatible with the finding of Hoppe et al. (1995) that more than 60% of all graphite grains are derived from supernovae (or Wolf–Rayet stars), implying that supernova grains are about equally likely to be gas-rich as grains from other sources. Our data for grains from AGB stars provide further confirmation of existing models, which is why we will discuss them first, and address the supernova grains in the later paragraphs.

4.3. Grains from AGB stars

In grains *KFC1f-251* and *KFC1f-312*, ^{4}He was above detection limit. As no other noble gas isotope was above detection limit in these two extractions, we can only give lower limits to the $^4He/^{22}Ne$ ratio. This ratio and the C, Si isotopic composition can be matched with models of AGB stars of 2–5 $M_\odot$ and $Z/Z_\odot = {}^1/_3 - 1$, by assuming that the grains condense in the stellar winds (thus acquiring the C and Si isotopic ratios of the H envelope) and are irradiated by He and Ne ions originating in the He shell (Heck et al., 2007). Together with the grain KFB1 g-34-4 reported by Heck et al. (2009), these are the only known graphite

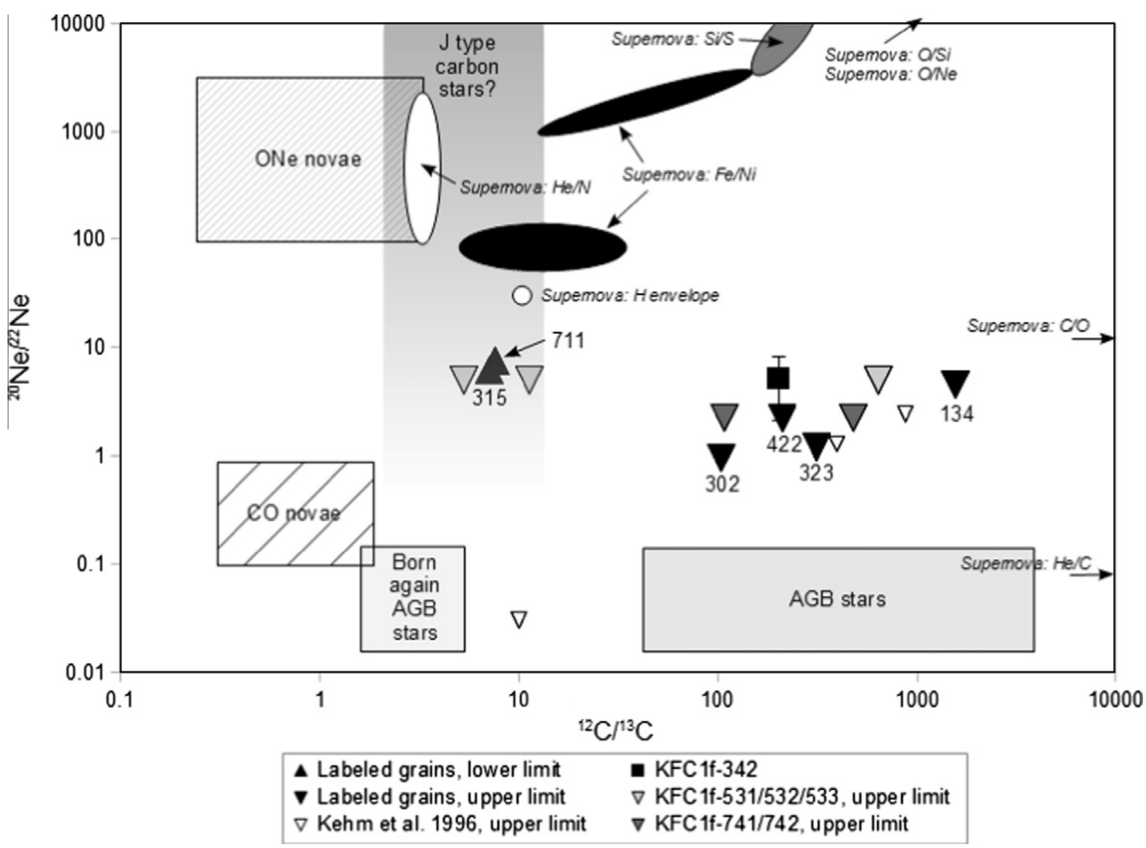

Fig. 4. Measured $^{20}Ne/^{22}Ne$ ratio of KFC1f-342 (black square, error bars are 1σ) and upper or lower limits (down-, and upward facing triangles, respectively) of $^{20}Ne/^{22}Ne$ ratios of all other ^{20}Ne- or ^{22}Ne-rich grains (including three grains from Kehm et al., 1996, for comparison), with predicted nucleosynthetic yields for CO, ONe novae (José et al., 2004), AGB stars (a synthesis of He-shell/envelope values, according to Heck et al., 2007), born-again AGB stars ($^{12}C/^{13}C$: Asplund et al., 1999, $^{20}Ne/^{22}Ne$: same as for AGB stars, Herwig et al., 2011), J-type carbon stars ($^{12}C/^{13}C$: Abia and Isern, 2000, no bounds are known on the $^{20}Ne/^{22}Ne$ ratio, but it is assumed to be high: Heck et al., 2007) and the Fe/Ni, Si/S, He/N and H envelope zones of a 25 $M_\odot$ supernova, with arrows indicating the position of the O/Ne, O/Si, He/C and C/O zones outside the plot area (based on model s25a28d from Rauscher et al., 2002). The upper limits on the $^{20}Ne/^{22}Ne$ ratio for most grains are compatible with an AGB star origin, but for grains KFC1f-323, -315, -711, -332/342 and -741/742, a supernova origin is proposed (see discussion). Carbon isotopic ratios for these grains can be produced by mixing material from the carbon-rich (C/O >1) He/N and He/C regions, and the C/O region (C/O ~0.25–0.5). See Fig. EA-1-2 for a colored version.

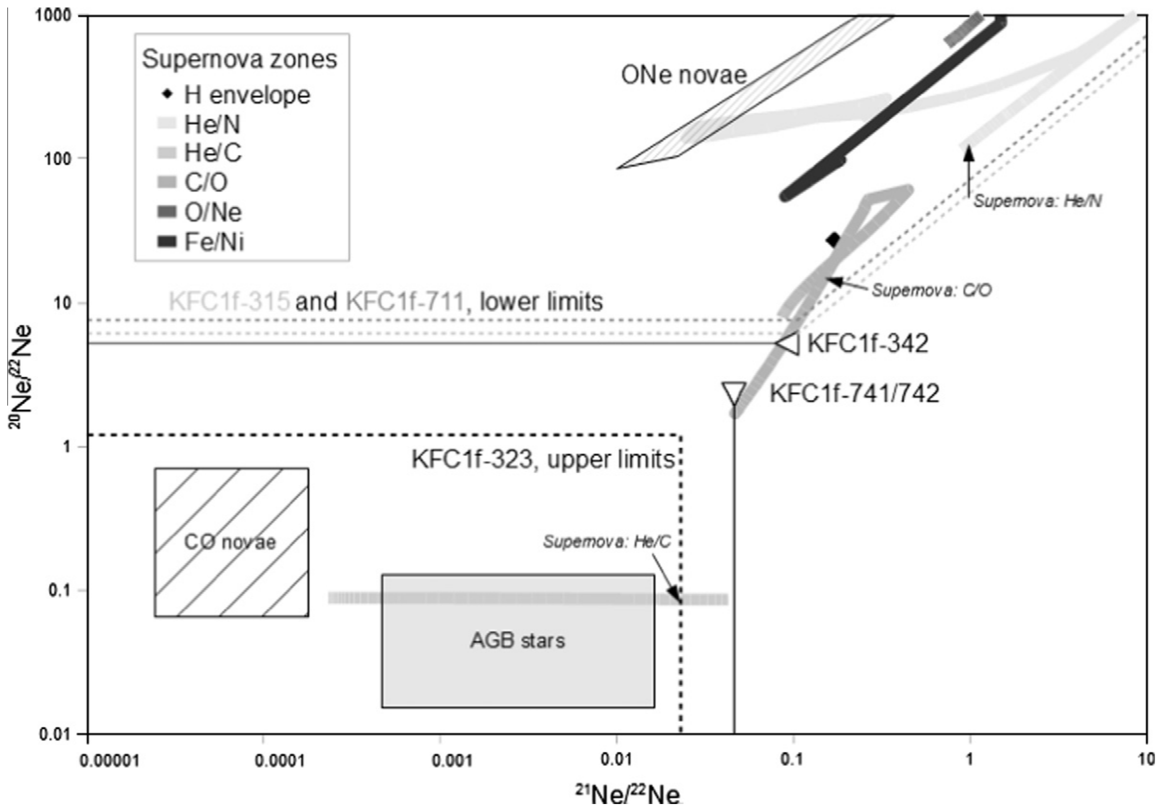

Fig. 5. The five proposed supernova grains, with predictions by Rauscher et al. (2002) for the Ne-composition of different zones within a 25 $M_\odot$ supernova (model s25a28d) after the decay of all short-lived radio-activities (including ^{22}Na), with six different nucleosynthetic zones shown (the O/Si and Si/S zones plot outside the area), AGB stars (He shell, Heck et al., 2007; Gallino et al., 1990), CO and ONe novae (José et al., 2004). As there are no detailed nucleosynthetic models of born-again AGB stars and J-type carbon stars, these sources are not displayed here. For two supernova grains (KFC1f-342 and KFC1f-741/742), a measured ratio is known, and from the detection limit of the third, undetected Ne isotope, an upper limit can be calculated. Therefore, the true Ne ratios of these grains must plot somewhere on the solid lines concluded by white triangles. Both grains are compatible with the C/O zone, while KFC1f-741/742 is also compatible with the He/C zone. For grains KFC1f-315 and KFC1f-711, only ^{20}Ne was detected, therefore upper limits on the ^{20}Ne/^{22}Ne and ^{20}Ne/^{21}Ne ratios constrain the true ratio to an area to the top and left of the grey short-dashed lines (e.g., compatible with the He/N zone) For grain KFC1f-323, only ^{22}Ne was detected, constraining its ^{20}Ne/^{22}Ne and ^{20}Ne/^{21}Ne ratios to an area to the bottom-left of the black short-dashed lines, compatible with the He/C zone, but also with AGB stars. See Fig. EA-1-3 for a colored version.

grains with a measured ^{4}He/^{22}Ne compatible with AGB models. In grains *KFC1f-134*, *KFC1f-302*, *KFC1f-422*, only ^{22}Ne was above detection limit, therefore we can only give an upper limit to the ^{20}Ne/^{22}Ne ratio for these grains. Together with the C, Si isotopic composition, these upper limits are in accordance with models of sub-solar to solar metallicity ($Z/Z_\odot = {}^1/_6 - 1$), low- to intermediate (1.5–3 $M_\odot$) mass AGB stars (Heck et al., 2007). To explain the non-detection of ^{4}He in these grains, we have to assume a minimum amount of He loss for each grain (Table 1). Grains *KFC1f-531*, *KFC1f-532* and *KFC1f-533* were co-heated in the same extraction. It is therefore not possible to attribute the measured ^{22}Ne unequivocally to any of the three grains. However, grain KFC1f-532 was at the center of the laser beam and is therefore considered the most likely grain to have released the measured ^{22}Ne. The Si isotopes of this grain (δ^{29}Si: -135 ± 85, δ^{30}Si: 317 ± 128) resemble the ones from presolar SiC "Z grains", which are thought to originate from low-metallicity AGB stars. The C isotopic ratio matches a low metallicity ($Z/Z_\odot = ⅓$), 2–3 $M_\odot$ AGB star (Heck et al., 2007). The two other grains heated in the same extraction both have a very low ^{12}C/^{13}C-ratio, which would indicate a born-again AGB star, a supernova or a CO nova as origin. Grain KFC1f-323, which is discussed with the supernova grains below, could also originate in a $Z/Z_\odot = ⅓$, 1.5 $M_\odot$ AGB star.

4.4. Grains from supernovae

While the grain *KFC1f-323* has a measurable amount of ^{22}Ne and a ^{12}C/^{13}C ratio compatible with an origin in an AGB star (Heck et al., 2007), this grain also shows a small excess of ^{28}Si (δ^{29}Si: -46 ± 46, δ^{30}Si: -121 ± 56), which calls for a discussion. In case of a supernova origin, the ^{22}Ne measured in this grain could either be radiogenic (Ne-R from the decay of ^{22}Na), or nucleosynthetic, probably from the He/C zone (see Fig. 5). The ^{12}C/^{13}C ratio of 313 ± 2, taken at face value, would imply condensation somewhere in the Si/S zone (see Fig. 4). Condensation of graphite grains outside the carbon-rich (C/O >1) He/C and He/N zones is possible according to a model proposed by Clayton et al. (1999). In the model of Ebel and Grossman (2001), graphite may condense down to the O/Si zone (where C/O $\sim 1.6 \times 10^{-3}$) if the formation of any kind of gaseous molecule (e.g., CO, SiO, H_2O, etc.) is somehow suppressed, which is certainly not expected from our current understanding of supernova ejecta clouds. Graphite can however never condense in the Fe/Ni and Si/S zones, as these innermost zones are dominated by metals (predominantly Fe, Si and some amount of Ti), which will quickly bind all the available C to form carbides, predominantly TiC. TiC sub-grains ($\sim$15–500 nm) in presolar graphite grains are common and show C isotopic ratios that are identical to the C ratio of the surrounding graphite (Stadermann et al., 2005). The abundance of these TiC sub-grains in graphite is so low (200–2500 ppm by mass) that equilibration of core-derived TiC with graphite material derived from another zone would not significantly alter the C isotopic composition of the grain (in the case of KFC1f-323, even the addition of $\sim$1% of material from the Fe/Ni zone to a grain condensed in any of the possible mixing zones would only lower its $^{12}C/^{13}C$ ratio to $\sim$4800). The observed $^{12}C/^{13}C$ ratio in the graphite grain *KFC1f-323* can however also be reached by condensing the grain from a mixture of material from the carbon-rich He/C (98.58%) and He/N (1.42%) zones (with the average atomic $^{12}C/^{13}C$ ratio being $\sim 9.27 \times 10^5$ in the He/C zone and $\sim$3.45 in the He/N zone). Alternatively, the ^{22}Ne could be of radiogenic (Ne-R) origin. In that case, the grain would probably have condensed in the ^{22}Na-rich O/Ne zone, a conclusion that was also reached by Amari (2009) for graphite grains from the low-density separate KE1. An origin in the O/Ne zone is compatible with the $^{12}C/^{13}C$ ratio if the admixture of small amounts (1.42% or 3.80%, respectively) of material from the He/N zone or the H envelope is allowed. Nucleosynthetic Ne from the O/Ne zone (with a $^{21}Ne/^{22}Ne$-ratio of $\sim$3.5) can then be constrained to <0.1% of the total Ne inventory.

In both grains *KFC1f-315* and *KFC1f-711*, ^{20}Ne was found, with no other noble gas isotope above the detection limit. Both grains have a very low $^{12}C/^{13}C$-ratio of 7.07 ± 0.04 and 7.62 ± 0.04, respectively, excluding AGB stars as a possible source (Fig. 4). Interestingly, they are also of virtually identical size ($\sim$1.4 µm). Silicon isotopes for both grains are solar within two standard deviations (see Table 1 or Fig. EA-1-1 in the Electronic Annex). This excludes an ONe nova, which would be expected to produce grains with low $^{12}C/^{13}C$-ratios alongside large ^{29}Si and/or ^{30}Si anomalies. Although the Si-isotopes in the KFC1 presolar graphite grains have been partially equilibrated with isotopically normal material, in this case, solar material contributions of >80% are necessary to "hide" a putative ONe nova provenance. Based on the lower limit on the $^{20}Ne/^{22}Ne$ ratio, we can also exclude a CO nova and a born-again AGB star as origin (see Fig. 4). J-type carbon stars would be a possible source as they have been observed to have low $^{12}C/^{13}C$-ratios (Abia and Isern, 2000) and are expected to have high $^{20}Ne/^{22}Ne$ ratios (Heck et al., 2007), but so far, there are no detailed nucleosynthetic models of J-type carbon stars. As we will show below, the grains can be attributed to a specific zone of the Rauscher et al. (2002) supernova model, which is therefore our preferred interpretation. Nittler and Hoppe (2005) suggested that some presolar grains with low $^{12}C/^{13}C$ ratios might originate from supernovae, based on the observation of high excesses of ^{28}Si, ^{49}Ti, ^{44}Ca and inferred ^{26}Al in one grain that had previously been classified as a nova grain due to its very low $^{12}C/^{13}C$ ratio. They point out that a possible explanation for the low $^{12}C/^{13}C$ ratio is proposed by Langer et al. (1998), where the rotation of the pre-supernova star induces mixing between a ^{13}C-rich layer next to the ^{12}C-rich He shell. In the Rauscher et al. (2002) supernova model, $^{12}C/^{13}C$ ratios at or below the value observed in these two grains are found in two nucleosynthetic zones (Fe/Ni and He/N). As explained above, the Fe/Ni zone is excluded, so any supernova zone-mixing scenario must include some material from the He/N zone. Beside the two core zones, we also exclude the O/Si zone for its very low C/O-ratio as explained before, and the O/Ne zone for the absence of Ne-R in these grains. The $^{12}C/^{13}C$ ratios of the two grains can then be reached by mixing either $\sim$50% He/N material with material from the He/C and C/O zones, or $\sim$20% He/N material with $\sim$80% H envelope material. In Fig. 5, grains KFC1f-315 and -711 are included only with lower limits (from Table 1) for $^{20}Ne/^{22}Ne$ (horizontal short-dashed lines on the left side of the figure) and $^{20}Ne/^{21}Ne$ (sloped short-dashed lines on the right side of the figure, derived from the non-detection of ^{21}Ne and the ratio of the ^{21}Ne, ^{22}Ne detection limits). The true isotopic Ne ratio of the grains must thus plot in the area on top and left of the horizontal and sloped lines, excluding the He/C zone and the part of the C/O zone. The grains can therefore only have formed in mixtures of either 50% He/N + 50% C/O, or 20% He/N + 80% H envelope. It is interesting to note that KFC1f-711 and -315 are nearly identical grains with respect to size (1.4 µm), $^{12}C/^{13}C$ ratio ($\sim$7) and a measurable ^{20}Ne concentration of $\sim 1 \times 10^{-3}$ ccSTP/g. In future work, measuring a relatively high $^{21}Ne/^{22}Ne$-ratio of $\sim$0.3–0.7 in such a grain would further corroborate their supernova origin and might make it possible to distinguish between a He/N + C/O, or He/N + H envelope condensation.

The extraction of grain *KFC1f-342* is the only one where both ^{20}Ne and ^{22}Ne were above the detection limit. The $^{12}C/^{13}C$ ratio is 202.3 ± 1.2, and the Si isotope ratio plots close to the mainstream line. The C isotopic ratio clearly excludes a born-again AGB star, J-type carbon star and a nova as origin (Fig. 4). The measured $^{20}Ne/^{22}Ne$ ratio is 5.2 ± 3.1. While within 2σ, this ratio is consistent with AGB star model predictions ($^{20}Ne/^{22}Ne$ <0.13; Heck et al., 2007, see Fig. 4), this is nevertheless an unlikely explanation, as the maximum amount of ^{20}Ne expected from the product of the measured amount of ^{22}Ne (6.37×10^{-15} ccSTP) and the AGB star He-shell $^{20}Ne/^{22}Ne$ ratio of <0.13, is still far below the ^{20}Ne detection limit (2.99×10^{-14} ccSTP), i.e., if the Ne of this grain was of AGB He-shell origin, we would not have seen any ^{20}Ne above the detection limit. If we however accept the detection of ^{20}Ne, we can give a lower limit of >4.69 (>$2.99 \times 10^{-14}/6.37 \times 10^{-15}$) to the $^{20}Ne/^{22}Ne$ ratio for this grain, derived from the ratio of the ^{20}Ne detection limit and the measured ^{22}Ne. As shown in Figs. 4 and 5, the only supernova zone compatible with the measured $^{20}Ne/^{22}Ne$ ratio is the C/O zone (model range of values: 1.7–60), and fittingly, a mixture of 97.8% C/O material and 2.2% He/N material (zone-averages) yields the $^{12}C/^{13}C$-ratios observed in this grains.

Grains *KFC1f-741* and *KFC1f-742* were co-heated in the same extraction. In this extraction, both ^{21}Ne and ^{22}Ne were above the detection limit. This is the first detection of ^{21}Ne in a presolar graphite grain. While the $^{12}C/^{13}C$ ratio of both grains is compatible with an AGB star origin (and incompatible with a nova, born-again AGB and J-type carbon star origin; see Fig. 4), we do not expect high amounts of ^{21}Ne to be found in any type of grain from an AGB star (see Fig. 5). Gallino et al. (1990) predict $^{21}Ne/^{22}Ne$ ratios for AGB stars of different metallicities between $\sim 5 \times 10^{-4}$ and 0.014, Karakas et al. (2008) predict $^{21}Ne/^{22}Ne\text{-G} = 0.0033$ for the maximum $^{18}F(\alpha,p)^{21}Ne$ rate, and from the most ^{22}Ne-rich presolar SiC grain of the mainstream group (SiC166) measured by Heck et al. (2007), an upper limit to the $^{21}Ne/^{22}Ne$-ratio of ~ 0.0055 can be calculated. All these values are well below 0.046 ± 0.022, the value measured in grain KFC1f-741/742. KFC1f-741 is the only gas-rich grain that shows a robust 2σ excess of ^{28}Si (with $\delta^{29}Si = -50 \pm 17‰$ and $\delta^{30}Si = -60 \pm 20‰$), and enrichments in ^{28}Si are expected in grains from supernovae. This makes KFC1f-741 the likely carrier of the measured ^{21}Ne. If the $^{12}C/^{13}C$ ratio of 479 ± 4 for this grain is not a mixing product, this ratio plots somewhere in the O/Si zone. Both the C/O and the He/C supernova zone are fitting – within 2σ-errors – the Ne ratios (see Fig. 5), and indeed the $^{12}C/^{13}C$ ratio can also be reproduced with mixing 99.1% material from the C/O or He/C zones with 0.9% from the He/N zone.

In summary, we have one possible supernova grain (KFC1f-323) with a ^{22}Ne inventory that is either nucleosynthetic if the grain condensed from material from the He/C and He/N zones, or radiogenic if it condensed in the O/Ne zone. We find two probable supernova grains (KFC1f-315 and KFC1f-711), remarkably similar in size, $^{12}C/^{13}C$ ratio and ^{20}Ne concentration, that are compatible with condensation and Ne acquisition from either a 80:20 mixture of H envelope and He/N, or a 50:50 mixture of C/O and He/N zone material, respectively. Finally, supernova grain KFC1f-342 condensed and acquired its nucleosynthetic ^{20}Ne, ^{22}Ne inventory predominantly from the C/O zone, while supernova grain KFC1f-741 condensed and acquired its nucleosynthetic ^{21}Ne, ^{22}Ne inventory predominantly from either the C/O or the He/C zone.

4.5. Contributions of radiogenic ^{22}Ne?

While ^{20}Ne and ^{21}Ne from supernova grains has to be of nucleosynthetic origin, ^{22}Ne can also be of radiogenic origin, from the decay of ^{22}Na (Ne-R). This is of no concern for the grains KFC1f-315 and KFC1f-711, where no ^{22}Ne was found. But for the other three supernova grains, we have to investigate a possible contribution of Ne-R. Sodium-22 reaches its highest abundance in the O/Ne zone ($\sim 1.8 \times 10^{-6}$; Rauscher et al., 2002) and is one to four orders of magnitude less abundant in most parts of the C/O, He/C and He/N zones. In a small part of the He/N zone, the ^{22}Na-abundance may reach values of up to $\sim 8.4 \times 10^{-7}$, similar to those in the O/Ne zone. However, this ^{22}Na-"spike" in the He/N zone may also be a computational artifact, as it is not as pronounced in lower mass supernova models from Rauscher et al. (2002) and does not show up in the supernova model of Chieffi and Limongi (2004). Although ^{22}Na is less abundant than ^{22}Ne in most supernova zones, Na can be intercalated into graphite (see Amari, 2009, and references therein) while noble gases cannot, thus possibly resulting (during the life-time of ^{22}Na) to a Ne-R contribution that is larger than would be expected from the atomic Na/Ne ratio in the supernova ejecta gas alone. For grain KFC1f-323, where only ^{22}Ne was above detection limit, even pure Ne-R cannot be excluded, and the grain is consistent with condensation in both the He/C (implying nucleosynthetic ^{22}Ne) or O/Ne (implying radiogenic ^{22}Ne) zone. For the other two grains where some ^{22}Ne was measured (KFC1f-342 and KFC1f-741), the detection of ^{20}Ne or ^{21}Ne, respectively, already requires a significant contribution of nucleosynthetic Ne. But the attempt to attribute the measured Ne composition directly to a specific nucleosynthetic supernova zone would be meaningless if there is also a significant contribution of Ne-R.

Figuratively speaking, we can imagine the contribution of Ne-R in Fig. 5 to constitute a slope 1 "shadow" cast by a nucleosynthetic zone, if illuminated from the top right (^{22}Ne-poor) corner of Fig. 5. Any grain having a Ne-composition possibly plotting within the shadow of a ^{22}Na-rich zone (or all zones, when accounting for possible mixtures) can be suspected to have a significant Ne-R contribution, while such a contribution can be excluded for grains having a Ne-composition plotting outside of all possible shadows. For grain KFC1f-342, where we only have an upper limit to the $^{21}Ne/^{22}Ne$ ratio, a possible true $^{21}Ne/^{22}Ne$ ratio within the shadow of a zone is not excluded. While we therefore cannot exclude a contribution from Ne-R for grain KFC1f-342, we still consider this unlikely, given that both the Ne and C isotopic composition match the ^{22}Na-poor C/O zone (in a part that is not itself in the shadow of another zone). For grain KFC1f-741, both the Ne and C isotopic compositions match the C/O or He/C zones. Here, we have a measured value for the $^{21}Ne/^{22}Ne$ ratio, which places this grain with high probability outside of any shadows (see Fig. 5).

One might ask whether the uncertainties of these nucleosynthetic models do not preclude the precise prediction of these Ne-R "shadows". However, the main uncertainty in this kind of supernova models lies in the ^{22}Ne production rate (Rauscher et al., 2002) and not necessarily the $^{20}Ne/^{22}Ne$, $^{21}Ne/^{22}Ne$ ratios. A variation in the ^{22}Ne-production rate will therefore move the predicted zonal compositions parallel to the shadows, with no consequences for the argumentation presented here.

4.6. Condensation and ion implantation in supernova ejecta

In infrared observations of the Cassiopeia A supernova ejecta cloud with the Spitzer Space telescope (Rho et al., 2008), supernova dust grains have been observed to condense in the expanding ejecta. These observations show the nucleosynthetic zones remain essentially intact.

However, previous work on presolar grains from supernovae (Travaglio et al., 1999; Lin et al., 2010; Hoppe et al., 2010) has shown that it is not possible to reproduce the observed supernova grains without mixing of material from several different zones. The disentangling of the different zones becomes increasingly complex if many isotope systems are measured in the same grains. The five probable KFC1 supernova grains found in this study can however be explained by a simple two-component mixture of zone-averages. All five grains have a Ne isotopic composition compatible with the zone of condensation as implied by their $^{12}C/^{13}C$ ratio, in accordance with a previous finding in supernova graphite grains from the KE3 density separate (Amari, 2009). The detection of nucleosynthetic Ne, however, constitutes an interesting difference to the work by Amari (2009), where all the observed ^{22}Ne found in these low-density presolar graphite grains is derived from the decay of ^{22}Na. As ^{22}Na can be intercalated into graphite, no special acquisition mechanism for nucleosynthetic Ne is needed. In fact, as Amari (2009) pointed out, the complete absence of ^{20}Ne in the KE3 graphite grains speaks against any significant nucleosynthetic Ne addition in these grains. Since ^{20}Ne and ^{22}Ne are much more abundant than ^{22}Na in the O/Ne zone, where most of the ^{22}Na is produced, even a very small addition of nucleosynthetic Ne would shift the $^{20}Ne/^{22}Ne$ ratio to the high values typical for that zone. Amari (2009) proposed that either the relative velocities between gas and grains in the expanding supernova ejecta are so small that no implantation takes place, or that Ne is indeed implanted, but is later sputtered away again by hot H ions when the grains pass through the reverse shock and into the interstellar medium (ISM). In this context, we can give two possible (but mutually non-exclusive) explanations as to why grains of higher density would be more likely to retain nucleosynthetic Ne: The high-density grains may either have formed in another environment, where the relative gas velocity is higher, so that the Ne ions can be implanted deep into the grains. Or, high-density grains may be more resilient against sputtering by hot ions and thus able to retain their implanted nucleosynthetic Ne. In future work, when more supernova graphite grains with nucleosynthetic inventories have been identified, it will become possible to establish whether the nucleosynthetic Ne is surface- or volume correlated, thereby giving constraints on typical ion implantation velocities in the different supernova zones.

5. SUMMARY AND CONCLUSIONS

- We have analyzed C, Si, He and Ne isotopes from 91 individual presolar graphite grains from the KFC1 density separate of the Murchison meteorite. Eleven grains showed measurable gas amounts in one or more of the measured He and Ne isotopes (Table 1). Integrated Ne concentrations and abundances of gas-rich grains are similar to values determined in earlier studies by Amari et al. (1995) (bulk) and Kehm et al. (1996) (single grains) of the KFC1 density separate. This implies that the few Ne-rich KFC1 grains carry the major fraction of Ne in bulk KFC1 grains.
- By comparing the grain isotope data with published nucleosynthetic model predictions for AGB stars, born-again AGB stars, J type carbon stars, novae and supernovae, we have attributed all the gas-rich grains to their most probable stellar sources. In six out of 91 grains, the data best matches model predictions of AGB stars with subsolar to solar ($Z/Z_{\odot} = {}^{1}/_{6}$ to 1) metallicities and a few (1.5–5) solar masses (Table 1). This is in line with the interpretation of isotopic signatures of KFC1 graphite by Amari et al. (1995) and Hoppe et al. (1995). Two grains from AGB stars have retained most of their He and show a lower limit to the $^{4}He/^{22}Ne$ ratio in agreement with model predictions. For the other grains attributed to AGB stars, no ^{4}He was detected, indicating a He loss of at least 64–91%, compared to these model predictions.
- Five of the gas-rich grains likely formed in core-collapse supernovae (Table 1). The C and Ne isotopic compositions of these grains are consistent with condensation in (mixtures of) the C/O, He/C, He/N and H envelope zones of a model supernova with 25 $M_{\odot}$. We report the first detection of nucleosynthetic ^{20}Ne (KFC1f-315, KFC1f-711, KFC1f-342) and ^{21}Ne (KFC1f-741/742) in KFC1 presolar graphite grains, sometimes measured together with ^{22}Ne (KFC1f-342 and KFC1f-741/742). One grain (KFC1f-323) released only ^{22}Ne, which could be explained either with nucleosynthetic Ne from the He/C and He/N zones, or with radiogenic Ne from intercalation of ^{22}Na in the O/Ne zone.
- We can exclude a significant contribution of ^{22}Ne from the decay of co-condensed ^{22}Na ($t_{1/2} = 2.6$ years) for three (KFC1f-315, KFC1f-711, KFC1f-741/742) of the five supernova grains from KFC1. This, and the detection of nucleosynthetic Ne, contrasts with KE3 graphite grains where all measured ^{22}Ne is radiogenic (Amari, 2009). We propose that the differences between the KE3 and KFC1 graphites are best explained by either formation in regions of the supernova with higher ion energies, or by higher resilience of high-density grains to sputtering in the reverse shock and the interstellar medium.

ACKNOWLEDGMENTS

This work was funded by the Swiss National Science Foundation (MMMM) and NASA grant NNX08AG56G (SA). The Robert A. Pritzker Center (PRH) is supported by the Tawani Foundation. We thank Roy S. Lewis for preparing the graphite mounts, Falk Herwig and Marco Pignatari for a discussion on the details of AGB star models, and Carl Alwmark for helpful comments on the manuscript. We also thank the two reviewers Ulrich Ott and Peter Hoppe, whose careful and thorough reviews have significantly increased the quality of this manuscript.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.10.027.

REFERENCES

Abia C. and Isern J. (2000) The chemical composition of carbon stars. II. The J-Type stars. *Astrophys. J.* **536**, 438–449.

Amari S. (2009) Sodium-22 from supernovae: a meteorite connection. *Astrophys. J.* **690**, 1424–1431.

Amari S., Anders A., Virag A. and Zinner E. (1990) Interstellar graphite in meteorites. *Nature* **345**, 238–240.

Amari S., Lewis R. S. and Anders E. (1994) Interstellar grains in meteorites. I – Isolation of SiC, graphite, and diamond; size distributions of SiC and graphite. *Geochim. Cosmochim. Acta* **58**, 459–470.

Amari S., Lewis R. S. and Anders E. (1995) Interstellar grains in meteorites: III. Graphite and its noble gases. *Geochim. Cosmochim. Acta* **59**, 1411–1426.

Arnone E., Travaglio C., Gallino R. and Straniero O. (2003) Galactic chemical contribution to CNO and Ne isotopes by AGB stars. In *CNO in the universe, Proceedings of a conference held in Saint-Luc, Valais, Switzerland, 10–14 September 2002* (eds. C. Charbonnel., D. Schaerer and G. Meynet). ASP Conference Series 304, Astronomical Society of the Pacific, San Francisco. pp. 327–329.

Asplund M., Lambert D. L., Kipper T., Pollacco D. and Shetrone M. D. (1999) The rapid evolution of the born-again giant Sakurai's object. *Astron. Astrophys.* **343**, 507–518.

Baur H. (1999) A noble-gas mass spectrometer compressor source with two orders of magnitude improvement in sensitivity. *EOS Trans.* AGU 46, Abstract F1118.

Bernatowicz T., Fraundorf G., Tang M., Anders E., Wopenka B., Zinner E. and Fraundorf P. (1987) Evidence for interstellar SiC in the Murray carbonaceous meteorite. *Nature* **330**, 728–730.

Black D. C. and Pepin R. O. (1969) Trapped neon in meteorites – II. *Earth Planet. Sci. Lett.* **6**, 395–405.

Chieffi A. and Limongi M. (2004) Explosive yields of massive stars from $Z = 0$ to $Z = Z_{\odot}$. *Astrophys. J.* **608**, 405–410.

Clayton D. D. (1975) ^{22}Na, Ne-E, extinct radioactive anomalies and unsupported ^{40}Ar. *Nature* **257**, 36–37.

Clayton D. D., Liu W. and Dalgarno A. (1999) Condensation of carbon in radioactive supernova gas. *Science* **283**, 1290–1292.

Deupree R. G. and Wallace R. K. (1987) The core helium flash and surface abundance anomalies. *Astrophys. J.* **317**, 724–732.

Ebel D. S. and Grossman L. (2001) Condensation from supernova gas made of free atoms. *Geochim. Cosmochim. Acta* **65**, 469–477.

Gallino R., Busso M., Picchio G. and Raiteri C. M. (1990) On the astrophysical interpretation of isotope anomalies in meteoritic SiC grains. *Nature* **348**, 298–302.

Heber V. S., Wieler R., Baur H., Olinger Ch., Friedmann T. A. and Burnett D. S. (2009) Noble gas composition of the solar wind as collected by the Genesis mission. *Geochim. Cosmochim. Acta* **73**, 7414–7432.

Heck P. R., Marhas K. K., Hoppe P., Gallino R., Baur H. and Wieler R. (2007) Presolar He and Ne isotopes in single circumstellar SiC grains. *Astrophys. J.* **656**, 1208–1222.

Heck P. R., Amari S., Hoppe P., Baur H., Lewis R. S. and Wieler R. (2009) 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. *Astrophys. J.* **701**, 1411–1425.

Heck P. R., Jadhav M., Meier M. M. M., Amari S., Zinner E., Baur H. and Wieler R. (2010) Radiogenic and nucleosynthetic neon-22 from individual presolar orgueil graphites. 73rd Annual Meeting of the Meteoritical Society, held July 26–30, 2010 in New York, New York. Published in *Meteorit. Planet. Sci.* 45(Suppl.), Abstract 5396.

Herwig F. (2005) Evolution of asymptotic giant branch stars. *Annu. Rev. Astron. Astrophys.* **43**, 435–479.

Herwig F., Pignatari M., Woodward P. R., Porter D. H., Rockefeller G., Fryer C. L., Bennett M. and Hirschi R. (2011) Convective-reactive Proton-^{12}C combustion in Sakurai's Object (V4334 Sagittarii) and implications for the evolution and yields from the first generation of stars. *Astrophys. J.* **727**, 89.

Hoppe P., Leitner J., Gröner E., Marhas K. K., Meyer B. S. and Amari S. (2010) NanoSIMS studies of small presolar SiC grains: new insights into supernova nucleosynthesis, chemistry, and dust formation. *Astrophys. J.* **719**, 1370–1384.

Hoppe P., Amari S., Zinner E. and Lewis R. S. (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. *Geochim. Cosmochim. Acta* **59**, 4029–4056.

Huss G. R., Meshik A. P., Smith J. B. and Hohenberg C. M. (2003) Presolar diamond, silicon carbide, and graphite in carbonaceous chondrites: implications for thermal processing in the solar nebula. *Geochim. Cosmochim. Acta* **67**, 4823–4848.

Hutcheon I. D., Huss G. R., Fahey A. J. and Wasserburg G. J. (1994) Extreme ^{26}Mg and ^{17}O enrichments in an Orgueil corundum: identification of a presolar oxide grain. *Astrophys. J. Lett.* **425**, L97–L100.

Jadhav M., Amari S., Marhas K. K., Zinner E., Maruoka T. and Gallino R. (2008) New stellar sources for high-density, presolar graphite grains. *Astrophys. J.* **682**, 1479–1485.

José J., Hernanz M., Amari S., Lodders K. and Zinner E. (2004) The imprint of nova nucleosynthesis in presolar grains. *Astrophys. J.* **612**, 414–428.

Karakas A. I., Lee H. Y., Lugaro M., Görres J. and Wiescher M. (2008) The impact of the 18F(α, p)21Ne reaction on asymptotic giant branch nucleosynthesis. *Astrophys. J.* **676**, 1254–1261.

Kehm K., Amari S., Hohenberg C. M. and Lewis R. S. (1996) ^{22}Ne-E(L) measured in individual KFC1 graphite grains from the Murchison meteorite. *Lunar Planet. Sci.* **27**, 657–658.

Langer N., Heger A., Woosley S. E. and Herwig F. (1998) The first supernovae. In *Nuclei in the Cosmos V* (eds. N. Prantzos and S. Harissopulos). Edition Frontières, Paris, pp. 129–135.

Leonard D. C. (2010) On the progenitors of core-collapse supernovae. *Astrophys. Space Sci.*. doi:10.1007/s10509-010-0530-8.

Lewis R. S., Tang M., Wacker J. F., Anders E. and Steel E. (1987) Interstellar diamonds in meteorites. *Nature* **326**, 160–162.

Lewis R. S., Amari S. and Anders E. (1990) Meteoritic silicon carbide: pristine material from carbon stars. *Nature* **348**, 293–298.

Lin Y., Gyngard F. and Zinner E. (2010) Isotopic analysis of supernova SiC and Si_3N_4 grains from the Qingzhen (EH3) chondrite. *Astrophys. J.* **709**, 1157–1173.

Lodders K. (2003) Solar system abundances and condensation temperatures of the elements. *Astrophys. J.* **591**, 1220–1247.

Messenger S., Keller L. P., Stadermann F. J., Walker R. M. and Zinner E. (2003) Samples of stars beyond the solar system: silicate grains in interplanetary dust. *Science* **300**, 105–108.

Meyer B. S. and Zinner E. (2006) Nucleosynthesis. In *Meteorites and the Early Solar System II* (eds. D. S. Lauretta and Jr. H. Y. McSween). University of Arizona Press, Tucson, pp. 69–108.

Meyer B. S., Weaver T. A. and Woosley S. E. (1995) Isotope source table for a 25 $M_{\odot}$ supernova. *Meteoritics* **30**, 325–334.

Nagashima K., Krot A. N. and Yurimoto H. (2004) Stardust silicates from primitive meteorites. *Nature* **428**, 921–924.

Nguyen A. N. and Zinner E. (2004) Discovery of ancient silicate stardust in a meteorite. *Science* **303**, 1496–1499.

Nichols, Jr., R. H., Kehm K., Brazzle R., Amari S., Hohenberg C. M. and Lewis R. S. (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.

Nichols R. H., Hohenberg C. M., Hoppe P., Amari S. and Lewis R. S. (1992) ^{22}Ne-E(H) and ^{4}He in single SiC and ^{22}Ne-E(L) in single Cα of known C-isotopic compositions. *Lunar Planet. Sci.* **23**, 989–990.

Nittler L. and Hoppe P. (2005) Are presolar silicon carbide grains from novae actually from supernovae? *Astrophys. J. Lett.* **631**, L89–L92.

Nittler L. R., Alexander C. M. O'D., Gao X., Walker R. M. and Zinner E. K. (1994) Interstellar oxide grains from the Tieschitz ordinary chondrite. *Nature* **370**, 443–446.

Nittler L. R., Hoppe P., Alexander C. M. O'D., Amari S., Eberhardt P., Gao X., Lewis R. S., Strebel R., Walker R. M. and Zinner E. (1995) Silicon nitride from supernovae. *Astrophys. J. Lett.* **453**, L25–L28.

Nozawa T., Kozasa T., Habe A., Dwek E., Umeda H., Tominaga N., Maeda K. and Nomoto K. (2007) Evolution of dust in primordial supernova remnants: can dust grains formed in the ejecta survive and be injected into the early interstellar medium? *Astrophys. J.* **666**, 955–966.

Rauscher T., Heger A., Hoffman R. D. and Woosley S. E. (2002) Nucleosynthesis in massive stars with improved nuclear and stellar physics. *Astrophys. J.* **576**, 323–348.

Reynolds J. H. and Turner G. (1964) Rare gases in the chondrite Renazzo. *J. Geophys. Res.* **69**, 3263–3281.

Rho J., Kozasa T., Reach W. T., Smith J. D., Rudnick L., DeLaney T., Ennis J. A., Gomez H. and Tappe A. (2008) Freshly formed dust in the Cassiopeia A supernova remnant as revealed by the Spitzer space telescope. *Astrophys. J.* **673**, 271–282.

Stadermann F. J., Croat T. K., Bernatowicz T. J., Amari S., Messenger S., Walker R. M. and Zinner E. (2005) Supernova graphite in the NanoSIMS: carbon, oxygen and titanium isotopic compositions of a spherule and its TiC sub-components. *Geochim. Cosmochim. Acta* **69**, 177–188.

Travaglio C., Gallino R., Amari S., Zinner E., Woosley S. and Lewis R. S. (1999) Low-density graphite grains and mixing in type II supernovae. *Astrophys. J.* **510**, 325–354.

Verchovsky A. B., Wright I. P. and Pillinger C. T. (2004) Astrophysical significance of asymptotic giant branch stellar wind energies recorded in meteoritic SiC grains. *Astrophys. J.* **607**, 611–619.

Woosley S. E. and Weaver T. A. (1995) The evolution and explosion of massive stars. II. Explosive hydrodynamics and nucleosynthesis. *Astrophys. J.* **101**(Suppl.), 181–235.

Ziegler J. F., Ziegler M. D. and Biersack J. P. (2010) SRIM – The stopping and range of ions in matter. *Nucl. Instr. Meth. Phys. Res. B* **268**, 1818–1823.

Zinner E., Amari S., Guinness R., Jennings C., Mertz A. F., Nguyen A. N., Gallino R., Hoppe P., Lugaro M., Nittler L. R. and Lewis R. S. (2007) NanoSIMS isotopic analysis of small presolar grains: Search for Si_3N_4 grains from AGB stars and Al and Ti isotopic compositions of rare presolar SiC grains. *Geochim. Cosmochim. Acta* **71**, 4786–4813.

Associate editor: Bernard Marty