

INTERSTELLAR EXPOSURE AGES OF LARGE PRESOLAR SiC GRAINS FROM THE MURCHISON METEORITE

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ABSTRACT

We report the Li isotopic compositions of nine large, greater than 5 μm , presolar SiC grains from the Murchison (CM) meteorite. Most of the SiC grains analyzed are isotopically similar in C and Si and morphologically distinct from other presolar SiC grains. Their ${}^7\text{Li}/{}^6\text{Li}$ ratios range from ~ 9.3 to the solar value (~ 12). The ${}^6\text{Li}$ enrichments observed in the grains can only arise from galactic cosmic ray spallation off C atoms during travel through the interstellar medium (ISM) and before incorporation into the meteorite parent body. Using appropriate production rates, we calculate recoil-loss-corrected individual exposure ages of eight grains with ${}^6\text{Li}$ excesses that range from 40 Myr to about 1 Gyr. The long exposure ages (>500 Myr) are consistent with calculations of grain survival lifetimes in the ISM, while the shorter ages (<100 Myr) of two grains are more consistent with previous cosmogenic noble gas studies. Although the sample size is only eight grains, there appears to be little evidence for clustering of exposure ages and no obvious correlation between exposure age and grain size.

Key words: circumstellar matter – cosmic rays – ISM: kinematics and dynamics – shock waves – stars: winds, outflows

1. INTRODUCTION

Some dust grains found in many carbonaceous meteorites and interplanetary dust particles represent the most primitive materials in the solar system (SS). Identified by highly anomalous isotopic compositions compared to the bulk of SS matter, these grains, termed “presolar,” are stellar condensates from the atmospheres of asymptotic giant branch (AGB) stars or the ejecta of Type II supernovae (SNe) that predate the isotopic homogenization of the early SS, and are therefore the oldest material that can be analyzed in terrestrial laboratories. Types of presolar grains discovered so far include C-rich phases, such as diamond, SiC, and graphite; O-rich phases, such as Al_2O_3 , MgAl_2O_4 , and silicates; and Si_3N_4 . The reader is referred to Zinner (2007) for a comprehensive account of the various presolar grain types and their discovery. Presolar grain studies have contributed significantly to our understanding of nucleosynthesis and stellar evolution, dust growth in stellar outflows, and the chemical evolution of the galaxy.

While presolar grains must have formed before the SS, the time of their formation is largely unknown. Precise ages would have important astrophysical implications for models of grain destruction in the interstellar medium (ISM) and the incorporation of dust into the protosolar cloud. A large population of grains with short ages (<10 Myr) would be evidence in support of the suggestion that a nearby SN or AGB star triggered the formation of the SS (Boss & Foster 1997; Cameron & Truran 1977; Ouellette et al. 2007). On the other hand, a prevalence of grains over 500 Myr old could confirm theoretical studies of dust destruction mechanisms (Jones et al. 1997), and would cast doubt on the viability of the SN or AGB star trigger hypothesis. For the very oldest meteoritic materials, such as Ca–Al-rich inclusions (CAIs), the decay scheme of U–Th–Pb, for example, has been very successfully applied. For absolute ages, typically the chronometer system needs radioactive parent nuclides with half-lives somewhat comparable to the age of the SS, thus allowing for relatively precise age determinations. For instance, the application of the

Pb–Pb system (a special version of the U–Th–Pb scheme, in which two radiogenic isotopes of U both decay to two stable isotopes of Pb) to one CAI from the CV chondrite Allende has led to a remarkably precise absolute age of 4567.60 ± 0.36 Myr (Jacobsen et al. 2008), commonly accepted as the formation age of the SS. Assuming no isotopic disturbance, these absolute chronometers essentially record the amount of time between isotopic closure—in which the particle cools, becomes a solid, and experiences no further modification of parent or daughter isotope except for radioactive decay—and the present. The ability to calculate absolute ages requires (along with accurately known half-lives) that believable determinations of both the initial isotopic compositions of the parent element and the radiogenic element can be made. In the case of presolar grains, these compositions are fundamentally uncertain, and require model-dependent estimates based on a likely stellar origin (i.e., AGB star or SN) in order to separate radiogenic contributions from nucleosynthetic ones. From an experimental perspective, presolar grains are exceedingly small and contain such low abundances of any of the elements used in these radiometric dating schemes that application to presolar materials is technically difficult, although some first exploratory attempts with the U–Th–Pb system have been made (Avila et al. 2007).

Of all presolar materials, SiC offers the best chance for accurate age determinations, because it can have large grain sizes (in excess of 20 μm in some rare cases) and trace elements are more easily incorporated into the SiC crystal lattice structure than in other presolar grain types, such as Al_2O_3 . As an alternative to the complications of radiometric dating procedures, previous studies (Lewis et al. 1994; Ott et al. 2005; Tang & Anders 1988) have focused on estimating galactic cosmic ray (GCR) exposure ages of aggregates of SiC grains (“bulk samples”). Bombardment of presolar SiC grains by GCRs, predominantly composed of protons and alpha particles, can produce spallation products in the grains. These spallation nuclides are mostly formed by the breakup of C and Si nuclei (but also sometimes from heavier trace elements, such as Ba) during travel through the ISM—up until incorporation

into meteoritic parent bodies. Measurement of the concentrations of the spallation products, combined with knowledge of the appropriate production rates, allows determination of exposure ages of the grains. Ages derived in this manner from the purported presence of cosmogenic ^{21}Ne (Lewis et al. 1994) have been invalidated by the consideration of spallation recoil loss (Ott & Begemann 2000), in which almost all of the spallation-produced ^{21}Ne would have escaped the grains. However, the low limits on cosmogenic ^{126}Xe in bulk samples of SiC led Ott et al. (2005) to infer short (probably <50 Myr) cosmic ray (CR) exposure ages. Recently, CR-produced ^3He and/or ^{21}Ne in large, individual SiC grains (from the same fractions, LS+LU, as those of this study, although not the same grains) were measured with a high-sensitivity noble gas mass spectrometer (Heck et al. 2008). Although the uncertainties are large, most reported recoil-corrected exposure ages are between ~ 2 and 400 Myr, shorter than theoretical expectations.

SN shockwaves are the primary cause for the destruction of dust grains in the ISM, and calculations of grain lifetimes are in apparent contrast with most of the ages inferred from the ^3He , ^{21}Ne , and ^{126}Xe analyses. Jones et al. (1997) estimated interstellar lifetimes to range from ~ 500 Myr up to ~ 1.5 Gyr for interstellar SiC grains. In addition, grains that have spent considerable time in the ISM should retain evidence of their transit on their surfaces; however, “pristine” SiC grains show little indication of pitting due to sputtering by gas atoms or fragmentation from grain–grain collisions (Bernatowicz et al. 2003). The surface features of these chemically untreated grains, which often exhibit crystallographic faces, seem to imply short interstellar residence times, consistent with the noble gas studies.

Here we report Li isotopic measurements made on nine large ($5\text{--}40\ \mu\text{m}$) presolar SiC grains from the Murchison CM chondritic meteorite. Large enrichments in ^6Li were found in eight of the grains, and by assuming that these excesses are due to CR spallation, we can infer lower limits on the length of time individual presolar SiC grains spent in the ISM. Preliminary reports of this study have previously appeared in Gyngard et al. (2007a, 2007b).

2. EXPERIMENTAL DETAILS

The procedure used to chemically isolate the SiC grains used in this study has been described in detail by Amari et al. (1994). Essentially, 88 g of fusion-crust bearing chips from the Murchison meteorite were treated with progressively harsher reagents in order to remove unwanted mineral phases, resulting in residues with relatively high concentrations of SiC grains. Grains from the LS and LU separates (LS+LU) were deposited from isopropanol suspensions onto microscope slides. Approximate grain sizes for LS and LU range from roughly $2\text{--}10\ \mu\text{m}$ to $>10\ \mu\text{m}$, respectively. The L-series was used for development of the now standard SiC chemical separation process, resulting in samples apparently lower in yields and purity of SiC compared to subsequent chemical separations, such as the K-series (Amari et al. 1994). With an optical microscope, the slides were scanned for SiC grains, and likely candidates were picked with a micromanipulator and placed onto a clean gold foil. The grains were pressed into the foil with a quartz disk, and from the subsequent energy dispersive X-ray analysis, 40 grains were identified as SiC.

The large grains of the LS+LU separates have previously been shown (Virag et al. 1992) to be morphologically distinct from smaller SiC grains. The grains identified in this study can

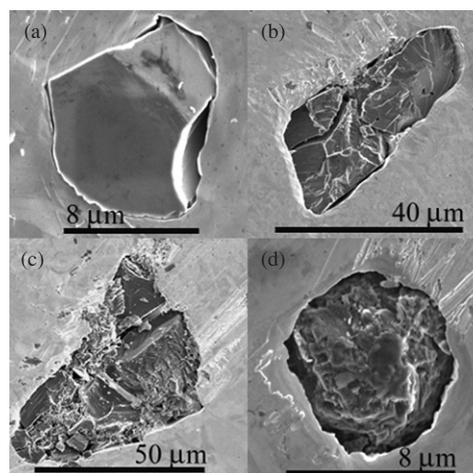


Figure 1. SEM images of grains representing the three morphology classes observed in LS+LU SiC. (a) Grain d3-4 shows a very smooth, flat surface with conchoidal fractures. (b) and (c) Grains a3-3 and d3-1 are very large and irregularly shaped. The large cracks along the surfaces are likely to be artifacts from pressing the grains into the gold substrate. (d) Grain d3-4 is an example of a large euhedral grain, similar to most smaller SiC.

be roughly grouped into three classes: (1) very flat, smooth anhedral grains (Figure 1(a)), often exhibiting conchoidal fracture features indicative of fissure from a larger crystal. (2) Very large, irregularly shaped grains with at least one dimension greater than $30\ \mu\text{m}$, two of which are shown in Figures 1(b), (c). No grains this large were seen in the previous study by Virag et al. (3) Euhedral, round grains (Figure 1(d)) similar to most presolar SiC grains identified so far, except larger ($5\text{--}10\ \mu\text{m}$). Morphological types (1) and (2) are unique to grains from the LS+LU separates and have not been seen in any further searches for presolar SiC, whether in chemical separates or in situ.

The isotopic compositions of nine large and morphologically interesting SiC grains, typically morphological types 1 and 2, were obtained with the Washington University NanoSIMS. Negative secondary ions were produced by bombarding the grains with a Cs^+ primary beam. Carbon and Si isotopes were measured simultaneously, with synthetic SiC grains used for normalization. In a separate measurement sequence, an O^- primary beam (which greatly enhances the secondary ion yields of electropositive elements compared to Cs^+) was used to produce positive secondary ions of $^6,7\text{Li}$, $^{10,11}\text{B}$, and ^{30}Si , which were measured together in multicollection. It should be noted here that the test tubes used in the chemical treatment process (for both the L and K series) contained significant concentrations of Li and B, which may have leached out of the glassware onto the grain surfaces. In fact, some Li and B contamination was evident on both the grains and sample mount, so analyzed regions were small (often much less than the grain diameter) and away from the edges of the grains in order to minimize contributions from isotopically normal material that may be present either in or on the surface of the gold foil nearby. Also, Li and B hotspots, identified as very bright spots—which often quickly sputtered away—in real-time ion images taken briefly before the actual measurements, were seen in many places on the grain surfaces, and measurement locations were chosen to avoid these locations. Measurement times were long in order to obtain statistically meaningful data. A polished glass standard (NBS 610) was used for normalization of the Li and B isotopes. Because Li concentrations were very low, the electronic noise in each electron multiplier, along with background from scattered

Table 1
Isotopic Compositions of the Nine LS+LU Grains Measured for Li Isotopes ($\pm 1\sigma$)

Grain Label	Diameter ^a (μm)	$^{12}\text{C}/^{13}\text{C}$	$\delta^{29}\text{Si}/^{28}\text{Si}^{\text{b}}$ (‰)	$\delta^{30}\text{Si}/^{28}\text{Si}^{\text{b}}$ (‰)	$^7\text{Li}/^6\text{Li}^{\text{c}}$
a3-3	37	47.5 \pm 0.4	45 \pm 4	73 \pm 7	9.3 \pm 0.4
a4-2	8	55.7 \pm 0.4	70 \pm 4	75 \pm 7	10.7 \pm 0.2
a4-4	23	48.0 \pm 0.4	51 \pm 4	74 \pm 7	9.8 \pm 0.4
a4-5	43	47.4 \pm 0.4	36 \pm 4	57 \pm 7	10.9 \pm 0.4
a5-1	5	47.5 \pm 0.4	57 \pm 4	71 \pm 7	10.5 \pm 0.2
b3-2	18	48.0 \pm 0.4	55 \pm 4	65 \pm 7	10.8 \pm 0.3
d3-1	20	47.9 \pm 0.4	57 \pm 4	66 \pm 7	9.7 \pm 0.2
d3-4	8	90.8 \pm 0.7	15 \pm 3	21 \pm 7	11.3 \pm 0.3
b5-1	5	47.4 \pm 0.4	54 \pm 4	76 \pm 7	11.4 \pm 0.4

Notes. Uncertainties on the C and Si isotopic results are mostly derived from the scatter in measurements on standards, whereas for Li, the errors are entirely governed by counting statistics.

^a Calculated geometric mean of estimates of each dimension, as discussed in the text.

^b Values given in so-called “delta” notation, defined as $\delta^i\text{X}/^j\text{X} = [(^i\text{X}/^j\text{X})_{\text{measured}} / (^i\text{X}/^j\text{X})_{\odot} - 1] \times 1000$.

^c The solar $^7\text{Li}/^6\text{Li}$ ratio is taken to be 12.06.

ions in the mass spectrometer, was monitored and corrected. These contributions were negligible to the subsequent results. Although sensitivity factors for Li and B were measured from the NBS standard, an intrinsic uncertainty exists in the reporting of elemental ratios. This uncertainty arises from the fact that we did not have a SiC standard with known Li and B elemental concentrations (or of any other trace elements for that matter) and matrix effects between the SiC grains and the NBS standard may produce some elemental fractionation. This effect is further discussed below.

3. RESULTS

The measured isotopic compositions and grain sizes are reported in Table 1. All nine grains show enrichments in $^{29,30}\text{Si}$, eight of which also show depletions in ^{12}C , relative to normal SS ratios. The C and Si isotopic compositions of the grains identify them as mainstream grains (Figure 2), as defined previously (Hoppe et al. 1994; Hoppe & Ott 1997). However, in a Si three-isotope plot of $\delta^{29}\text{Si}/^{28}\text{Si}$ versus $\delta^{30}\text{Si}/^{28}\text{Si}$ (delta notation: $\delta^i\text{X}/^j\text{X} = [(^i\text{X}/^j\text{X})_{\text{measured}} / (^i\text{X}/^j\text{X})_{\odot} - 1] \times 1000$), the Si isotopic compositions of eight of the grains are slightly shifted to the right of the mainstream correlation line of slope 1.37 (Zinner et al. 2007) by $\sim 10\%$. Interestingly, six of the grains have roughly the same C and Si isotopic composition within two sigma (2σ) errors, possibly implying formation in the same stellar environment or, more speculatively, fragmentation from a larger grain. Further comparisons between the isotopic characteristics of the grains analyzed here and the thousands of other SiC grains measured so far are outside the scope of this paper.

Eight out of the nine grains show enrichments in ^6Li of more than 2σ , up to $\sim 300\%$, relative to the Li isotopic ratio of SS material. Three grains also show anomalous B isotopic compositions slightly more than 2σ from solar, with enrichments (up to $\sim 140\%$ in one case, albeit with large errors) in ^{10}B . Boron abundances are very low, typically a few ppm, while Li abundances are in general an order of magnitude smaller than those for B. These very low abundances in the large and morphologically distinct LS+LU SiC grains, compared to grains from other chemical separations, are consistent with previous results that showed very low abundances of other trace elements in large SiC from Murchison (Virag et al. 1992). This may be a size selection effect, since for the K-series, Amari et al. (1995) found lower trace element abundances in KJH SiC

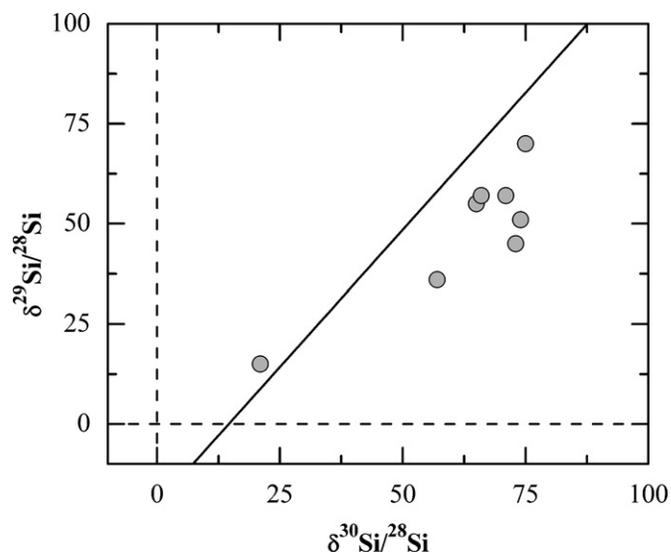


Figure 2. Plot of the Si isotopic ratios of the eight Li anomalous grains of this study expressed as δ -values, or deviations from solar isotopic ratios in parts per thousand (‰). Also shown is the so-called mainstream correlation line of $\delta^{29}\text{Si} = 1.37 \times \delta^{30}\text{Si} - 20$ (Zinner et al. 2007).

grains (size range 3.4–5.9 μm) than in smaller fractions. The majority of the grains (at least 5) of this study roughly fall into cluster II, as defined in Virag et al., characterized by trace element patterns roughly similar to the KJH grains and having $\delta^{29}\text{Si}/^{28}\text{Si}$ and $\delta^{30}\text{Si}/^{28}\text{Si}$ values of about 45%.

Few previous Li isotopic measurements have been performed on individual presolar SiC grains. Huss et al. (1997) measured $^7\text{Li}/^6\text{Li}$ ratios in six small ($< 10 \mu\text{m}$), individual SiC grains from the Orgueil (CI) carbonaceous chondrite, and observed no isotopic anomalies within analytical uncertainties. Li concentrations ranged from ~ 5 to ~ 140 ppm, several orders of magnitude greater than those observed in the current study. However, the low spatial resolution of the IMS 3f, used in the Huss et al. study, may make it difficult to preclude significant contribution from Li contamination. Lyon et al. (2007) measured Li isotopes in 21 SiC grains, 10 of which were isolated with a gentle separation procedure (Tizard et al. 2005) that avoids the usage of harsh chemicals, which may alter the initial grain surfaces, and 11 grains from the Murchison KJG separate (size range 1.5–3.0 μm), prepared by standard chemical procedures.

For these measurements, a time-of-flight SIMS instrument with a reported spatial resolution of ≈ 300 nm was used; however, no Li isotopic anomalies ($>2\sigma$) were observed in any of the grains. Interestingly, very high Li/Si ratios of up to $\sim 10^{-2}$ were reported for the surfaces of the grains, decreasing to $\sim 10^{-5}$ in the grain interiors. With Li concentrations this high, it is unlikely that any anomalous Li would remain detectable, as any significant terrestrial Li contribution (either in the laboratory or elsewhere) would erase any expected isotopic anomalies. The authors attribute the source of their high Li abundances and solar isotopic composition to ion implantation from shock waves in an isotopically homogenized (in Li at least), dense molecular cloud.

4. DISCUSSION

Presolar SiC grains have been found to have anomalies in all the elements analyzed to date (Zinner 2007). Thus, it should not be surprising that Li isotopic ratios in SiC grains are anomalous. However, in contrast to isotopic anomalies in other elements, the observed Li ratios in the LS+LU grains cannot be explained as a stellar signature because ${}^6\text{Li}$ and ${}^7\text{Li}$ are destroyed in stars at temperatures around 2×10^6 and 2.5×10^6 K, respectively, by proton captures (Pagel 1997). However, the situation is not quite this simple, as explained below.

The story of lithium in the universe is unique. This element can be created by three very different processes: big bang nucleosynthesis, production by spallation reactions from GCR bombardment, and nucleosynthesis reactions in stars. Combinations of these three production channels, as well as stellar destruction, determine the Li abundances we see in the universe. The interstellar ${}^7\text{Li}/{}^6\text{Li}$ ratio in the solar neighborhood is ~ 12 (Knauth et al. 2003), virtually identical to the meteoritic value, as discussed below. For a comprehensive study of the sources and evolution of ${}^7\text{Li}$ in the Galaxy, see Travaglio et al. (2001).

It should be noted that, similar to the isotopic ratios of most other elements, the accepted solar isotopic ${}^7\text{Li}/{}^6\text{Li}$ ratio is taken to be its meteoritic value of 12.06 (Seitz et al. 2007), markedly different from what is expected in the Sun's photosphere. The overall Li abundance in the Sun's photosphere is reduced by approximately two orders of magnitude compared to the chondritic value. Nuclear burning processes in the Sun (as well as other stars), discussed in further detail below, are expected to preferentially destroy ${}^6\text{Li}$. Few direct measurements of the ${}^7\text{Li}/{}^6\text{Li}$ ratio in the Sun exist; however, a lower limit of ${}^7\text{Li}/{}^6\text{Li} = 33$ has been estimated based on detections of ${}^6\text{Li}$ in sunspots (Ritzenhoff et al. 1997). Lunar soil measurements of implanted solar wind yield ${}^7\text{Li}/{}^6\text{Li} = 31 \pm 4$ (Chaussidon & Robert 1999), consistent with theoretical expectations. Quantitative predictions from nuclear burning at the base of the Sun's convective zone yield ${}^7\text{Li}/{}^6\text{Li}$ ratios (from a few hundred to a few thousand) several orders of magnitude higher than the measured ratios in the implanted solar wind samples or in sunspots. Although uncertainties remain, the most probable solution to this discrepancy is ${}^6\text{Li}$ production from spallation of C and O atoms in the Sun's photosphere by protons from solar flares. Regardless of the uncertainty of the Li isotopic composition of the Sun, the meteoritic value of 12.06 (Seitz et al. 2007) is assumed here to best represent the initial Li isotopic composition of the protoplanetary disk from which the SS formed. All references to "solar" Li in this paper correspond to the meteoritic value, and the Li isotopic composition of the Sun will not be discussed further.

For low-mass ($1\text{--}3 M_{\odot}$) C-rich AGB stars, thought to be the parent stars of mainstream SiC grains, the abundance of Li at the stellar surface (close to where the grains condense) is expected to be reduced by 2–4 orders of magnitude compared to the ISM abundance of $\log \varepsilon({}^7\text{Li}) \sim 3.3$, where $\log \varepsilon({}^7\text{Li}) \equiv \log [n({}^7\text{Li})/n(\text{H}) + 12]$ (Sackmann & Boothroyd 1999). Under some special circumstances, it is possible to create ${}^7\text{Li}$ by the Cameron–Fowler mechanism (Cameron & Fowler 1971), in which the reaction ${}^3\text{He}(\alpha, \gamma){}^7\text{Be}(e^-, \nu){}^7\text{Li}$ can produce significant amounts of ${}^7\text{Li}$. Spectra of high-luminosity ($M_{\text{bol}} \sim -6$ to -7), intermediate mass ($4\text{--}8 M_{\odot}$) AGB stars exhibit high Li abundances (Smith & Lambert 1990), quantitatively consistent with predictions for AGB stars that experience hot bottom burning (HBB). During HBB, the star's convective envelope dips down into the top of the H-burning shell. The ${}^3\text{He}(\alpha, \gamma){}^7\text{Be}$ reaction requires temperatures greater than 10^7 K to operate, and thus an efficient method of moving the ${}^7\text{Li}$ (or rather its precursor ${}^7\text{Be}$) produced at the top of the H-burning shell out into the cooler envelope must exist. While in intermediate-mass AGB stars this is accomplished by HBB, in lower mass ($<4 M_{\odot}$) stars on the red giant branch (RGB), deep mixing processes, invoked to explain observed low ${}^{12}\text{C}/{}^{13}\text{C}$ ratios, may provide the necessary transport mechanism for significant ${}^7\text{Li}$ buildup in their stellar envelope (Charbonnel 1995; Sackmann & Boothroyd 1999). Calculations of first and second dredge-up with deep mixing produce significant ${}^7\text{Li}$, in agreement with observations of some Li-rich K giants (de la Reza et al. 1997). In contrast to ${}^7\text{Li}$, ${}^6\text{Li}$ is not produced by any known nucleosynthetic process, not even big bang nucleosynthesis, and thus, ${}^6\text{Li}$ excesses are not expected in any stellar environment. In fact, in any stellar environment in which ${}^7\text{Li}$ is destroyed, ${}^6\text{Li}$ should be consumed as well, as it is susceptible to proton captures at a lower temperature. For a thorough discussion, see Clayton (2003).

In general, ${}^6\text{Li}$ is only formed by spallation nuclear reactions in which ${}^6\text{Li}$ nuclei are spalled off mostly from C or O atoms, and the ${}^7\text{Li}/{}^6\text{Li}$ ratio expected to be produced from CR bombardment is ~ 2 (Meneguzzi et al. 1971; Reedy 1989). In contrast to the previous Li measurements in presolar SiC, the large grains analyzed here have ${}^7\text{Li}/{}^6\text{Li}$ ratios from 9.3 to 11.4, likely to be the result of two component mixing between "normal" Li and CR-produced Li. However, the ~ 2 Ma time of the Murchison meteorite (Herzog et al. 1997) during transit to Earth is much too short to allow for significant ${}^6\text{Li}$ enrichments from GCR exposure. Rather, the observed effects can only be generated through GCR bombardment of the grains themselves during interstellar transit.

Evidence for an intense irradiation in the protosolar nebula by an early active Sun has been suggested by the detection of extinct ${}^{10}\text{Be}$ in CAIs (McKeegan et al. 2000); however, it is unlikely that such an irradiation produced the ${}^6\text{Li}$ excesses observed in the grains, for several reasons. The Li isotopic variability observed in most CAIs is in general limited to enrichments in ${}^6\text{Li}$ of up to 50% (except for a few rare cases), whereas seven out of eight of the grains analyzed here show ${}^6\text{Li}$ enrichments greater than 50%, even up to 300% in one case. The higher percentage of SiC grains showing large isotopic effects indicates that it is unlikely that the same physical process, in this case irradiation in the early SS, is responsible for the isotopic signatures in both the grains and CAIs.

Further proof that local irradiation processes are unlikely to be able to explain the isotopic signatures in these presolar SiC grains is given by noble gas concentrations in Murchison

olivine grains. In only a few percent of these olivines, higher cosmogenic ^{21}Ne concentrations than can be explained by GCR irradiation on the parent body hint that these grains may have been exposed to an energetic particle irradiation (Hohenberg et al. 1990). As argued by Tang & Anders (1988), the fact that only such a small fraction of these olivines, which compose $\sim 10\%$ of the meteorite itself, show signs of intense irradiation, implies that for such an underabundant mineral as SiC (~ 6 ppm total), only a preferential targeting of this particular mineral could account for any sizeable number of grains being irradiated, and would be highly improbable.

It is unlikely that any substantial amount of indigenous Li from the grains' parent stars condensed into the grains. Note, also, that it is improbable that any Li was implanted in the grains we measured—either in the stellar outflows from which the grains condensed or in the ISM—as no clear evidence for changes in elemental or isotopic ratios were seen as a function of depth in the grains. Although, in principle, deep mixing in RGB and AGB stars may bring some ^7Li , produced by the Cameron–Fowler process, to the stars' surface, if this were in fact the case, any amount of original Li is expected to have ^7Li excesses and not the ^6Li enhancements observed in the grains. In addition, SiC grains from the LS+LU fractions have been shown to have very low trace element abundances, so it is even less likely that significant amounts of Li condensed into these particular grains. Because of its volatility, Li does not tend to be incorporated into grains, in which more refractory elements are thought to condense, and is more likely to be left over in the stellar atmospheres of carbon stars (Lodders & Fegley 1997). Therefore, we assume that the grains' "normal" composition probably comes from contamination, either in the lab or on the meteoritic parent body. The measured signal for each isotope of Li can be expressed as

$$^7\text{Li}_{\text{measured}} = ^7\text{Li}_{\text{spallation}} + ^7\text{Li}_{\text{solar}} \quad (1)$$

and

$$^6\text{Li}_{\text{measured}} = ^6\text{Li}_{\text{spallation}} + ^6\text{Li}_{\text{solar}} \quad (2)$$

This assumption of "solar" Li as the nonspallogenic endmember in our calculation means that we may actually underestimate the amount of spallation Li (and in turn the exposure age) if any Li from the grains' parent stars actually condensed into the grains. Combining Equations (1) and (2), the fractional amount of spallation produced ^6Li can be expressed as

$$^6f_{\text{spallation}} = \frac{\left(\frac{^7\text{Li}}{^6\text{Li}}\right)_{\text{measured}} - \left(\frac{^7\text{Li}}{^6\text{Li}}\right)_{\text{solar}}}{\left(\frac{^7\text{Li}}{^6\text{Li}}\right)_{\text{spallation}} - \left(\frac{^7\text{Li}}{^6\text{Li}}\right)_{\text{solar}}} \quad (3)$$

The relevant production ratio of Li isotopes from C atoms by GCRs—the $(^7\text{Li}/^6\text{Li})_{\text{spallation}}$ term in Equation (3)—has been calculated by Reedy (1989) for small ($\lesssim 1$ cm), pure C targets. No comparable rates exist for the production of Li atoms by spallation of Si on small targets, and are therefore not included in the calculations here. However, according to Reedy (1989) and Leya et al. (2000), the production of ^{10}Be from Si is about an order of magnitude smaller than that from C (in dpm kg^{-1} of pure target element), corresponding to an overall factor of two or less. By analogy, production of Li from Si will be considerably smaller than that for spallation from C, though we may nevertheless be underestimating the total production rate. GCRs are composed of $\sim 12\%$ α -particles (Simpson 1983),

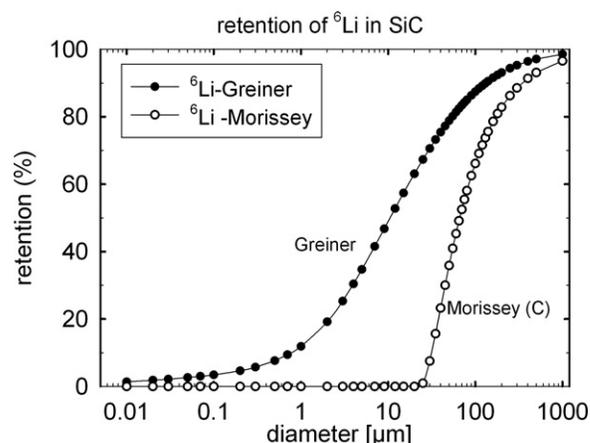


Figure 3. Plot of ^6Li retention as a function of grain diameter for two different recoil energy data sets. For reasons discussed in the text, we prefer the retention curve calculated from the Greiner et al. (1975) data.

and irradiation by interstellar α -particles is expected to be responsible for $\approx 25\%$ of the cosmogenic Li produced from C (Reedy 1989). The exposure ages calculated here take into account Li production from both proton and α -particle spallation reactions. With Equation (3) and the atomic abundance of Li in the grains, we can use the production rates to calculate the amount of time it would take for GCR irradiation to produce the observed ^6Li enrichments.

Knowledge of retention of the recoiling ^6Li during the spallation reaction in the grains is important for estimating exposure ages. Experimental determination of the retention of spallogenic ^{21}Ne was performed on irradiated terrestrial samples of SiC, indicating recoil lengths of $2\text{--}3 \mu\text{m}$ (Ott & Begemann 2000). To our knowledge, no similar experiments have been performed in order to determine the recoil retention of spallation Li produced in SiC grains. Here we present an analysis of the Li recoil range in SiC, in order to estimate the effect of recoil loss on our exposure age calculations. To do so, we consider experimental data for the energy distribution of spallation recoil ^6Li in conjunction with range energy relations using the SRIM code (Ziegler 2004). For a more detailed discussion of the problem of retention of light spallation products, in particular ^3He , see Huss et al. (2008).

Figure 3 shows our calculated ^6Li retention as a function of grain diameter. Two different inputs were considered for the recoil energies. The Morrissey (1989) case uses the average recoil energy (for ^{12}C as a target and ^6Li as the product) determined from a fit to the average momentum observed in a number of different recoil experiments as shown in his Figure 3 and described in the footnote to this figure. This energy was then used as the input into the SRIM code for calculating stopping ranges. The retention curve was generated using a simple geometric relationship for spheres (see Equation (1) of Ott & Begemann (2000)).

Close inspection of the data in Morrissey's Figure 3, however, reveals that the empirical relation fails to reproduce the results most relevant for our problem, which were obtained by Greiner et al. (1975) by studying the breakup of high-energy ^{12}C and ^{16}O projectiles leading to, among others, fragments of ^6Li . Hence we prefer the original Greiner et al. (1975) experimental data set, for which the resulting retention is shown by the second curve in Figure 3. An important additional advantage compared to the Morrissey case is that in this approach we make use of the energy distribution rather than an average. This is especially

Table 2
Calculated Exposure Ages, Corrected for Recoil Loss, of the 8 Li Anomalous Grains

Grain Label	Diameter ^a (μm)	Li/Si (atom/atom)	⁶ Li Retention (%)	Age ^b (Myr)	Corrected Age ^b (Myr)
a3-3	37	2.38E-07	74	640	860
a4-2	8	3.66E-07	44	430	980
a4-4	23	1.23E-08	65	30	40
a4-5	43	3.59E-08	77	40	50
a5-1	5	1.72E-07	35	230	660
b3-2	18	1.76E-07	61	190	310
d3-1	20	4.75E-08	63	110	170
d3-4	8	3.01E-07	43	180	420

Notes.

^a Calculated geometric mean of estimates of each dimension, as discussed in the text.

^b Relative errors are about 50% and absolute errors are probably at least a factor of 2. See the text for a discussion of the uncertainties associated with these ages.

important for small grains, where use of an average energy will result in significant underestimation of retention. In detail, zero retention is predicted in the Morissey case for grains $< 23 \mu\text{m}$, which is obviously not the case.

For our calculations based on the Greiner et al. (1975) data, we used the mean of the three data sets for the momentum distribution of ⁶Li, but the results do not differ significantly among the individual data sets. The resulting energy distribution was then used, as in the Morissey case, as the input into SRIM code for calculating stopping ranges and finally for calculating retention as a function of grain size.

In principle, knowledge of ⁶Li retention as a function of grain diameter should be enough to correct for recoil loss. Unfortunately though, for most of the large and irregularly shaped grains of this study, precise determination of the exact sizes of the grains is difficult, and a simple geometric mean of length and width determined from SEM images is not appropriate for grains in which one dimension is much smaller than the others, as is the case for many of these thin, platy LS+LU grains. The situation is further complicated by the fact that all information about the third dimension of the grains was effectively lost by pressing them into the gold foil. In order to provide an upper limit on recoil-loss-corrected exposure ages, we approximated the dimensions of each grain from SEM images and subsequently calculated their geometric mean. At best, the geometric mean is only approximately correct for grains that are not roughly equant; however, for determining an estimate to the sensitivity to recoil loss, this assumption should suffice.

Calculated CR exposure ages (corrected for recoil loss) of the eight Li anomalous grains range from 40 Myr to 1 Gyr (Table 2 and Figure 4). Two grains have irradiation times of less than 50 Myr, three grains of between 100 Myr and 500 Myr, and three grains have ages greater than 500 Myr. Any calculation incorporating both theoretical and experimental techniques often contains many sources of possible uncertainties, and estimating the magnitude of the errors associated with these age calculations is difficult. Without an SiC standard having a known Li elemental concentration, we do not know whether matrix effects between the SiC grains and the NBS standard could systematically influence our results. From a theoretical perspective, the dominant sources of uncertainty arise from poor knowledge of the interstellar flux of GCRs and lack of detailed knowledge of the correct reaction cross-sections in the regimes in which we are interested. Typical uncertainties in the cross-sections are $\sim 20\%$ (Reedy 1989); however, more recent

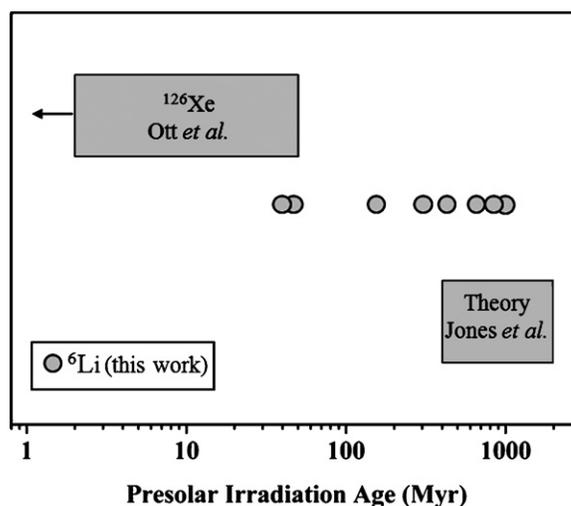


Figure 4. Comparison of experimentally determined CR exposure ages (recoil corrected) with expected grain lifetimes. The ages inferred from ⁶Li calculations span both the short ages inferred from bulk analyses of ¹²⁶Xe and model predictions of SiC grain lifetimes in the ISM.

Voyager 1 and 2 data (Webber et al. 2002) suggest a revision in the Read & Viola (1984) cross-sections used by Reedy to better match satellite observations. The situation is even more complicated, however, if one tries to estimate the interstellar flux of CRs more than 4.5 Ga ago, and in fact, many spectral shapes and intensities may be possible, as described in Reedy (1987). Specifically, the four spectra from which production rates of Li were calculated from are the $M = 0$ case of Castagnoli & Lal (1980), with M corresponding to the amount of solar modulation; Webber & Yushak (1983); Ip & Axford (1985); and the $R^{-2.65}$ power-law estimate of the rigidity (momentum per unit charge) of the proton spectrum at the GCR source. A geometric mean of the resultant production rates was then taken. While some features of Reedy's (1989) calculation may need updating, we nevertheless prefer to use his production rates, as the targets used in Reedy's calculation are small ($< 1 \text{ cm}$) and thus more realistic in simulating GCR exposure on presolar grains. Taking the uncertainties into consideration, we attach relative errors of about 50% to our exposure ages and absolute errors of at least a factor of 2.

The prescription outlined above for calculating exposure ages from Li isotopes could, in principle, also be applied to

the three grains with ^{10}B excesses; however, the situation for B is apparently more complex than for Li. The $^{11}\text{B}/^{10}\text{B}$ CR production ratio is ~ 2.5 (Meneguzzi et al. 1971; Reedy 1989), lower than the solar value of ~ 4 . Therefore, CR production of B has a smaller effect on the B isotopic ratio than that of Li on the Li isotopic ratio, where the production rate is ~ 2 and the solar value is ~ 12 . In addition, B atomic concentrations are roughly an order of magnitude larger than those for Li, likely due to contamination and not indigenous to the grains themselves, even further diluting the CR signature in B. Finally, the B isotopic ratios of three anomalous grains are only 2.4, 2.2, and 2.5 σ away from the solar ratio. It is difficult to say with certainty whether we are dealing with B anomalies, especially in view of the fact that only three of nine grains show marginal hints of B isotopic anomalies, whereas eight of the same grains show (much larger) anomalies in Li. For these reasons, we do not report any ages calculated from B, and the isotopic and elemental composition of B will not be discussed any further.

The best previous attempt to infer exposure ages of presolar SiC grains was made by Ott et al. (2005), who investigated the possible presence of spallation Xe in previously analyzed SiC bulk samples (Lewis et al. 1994). With Ba concentrations ranging from 130 to 440 ppm (Zinner et al. 1991), depending on the size fraction of the K-series separation (Amari et al. 1994), it was expected by Ott & Begemann (2000) that spallation Xe produced from Ba would be present at detectable levels. After careful determination of the recoil range of spallation Xe from Ba, Ott et al. (2005) argued that no spallogenic contribution is required to explain the ^{126}Xe abundance in the Lewis et al. (1994) bulk SiC data. Realistic upper limits of spallogenic Xe composition constrain the exposure ages of the grains to be less than about 50 Myr, markedly shorter than theoretically calculated times for SiC grain survival in the ISM (Jones et al. 1997). However, at best this method can only produce gross averages of the compositions of individual grains, thereby possibly rendering any smaller subset of older grains hidden.

Only two grains in this study have Li inferred ages less than or about 50 Myr, consistent with the previous Xe analyses. However, the wide range of ages reported here is for grains both morphologically and isotopically distinct from the K-series grains used in the bulk measurements. As noticed previously (Virag et al. 1992), the Si isotopic composition of many of these L-series grains places them into three distinct groups: (1) grains with close to solar Si isotopic ratios, thought perhaps to be contamination; (2) grains with enrichments in ^{29}Si and ^{30}Si of about 40%–60%; and, (3) grains with Si anomalies greater than 80%. New NanoSIMS Si isotopic measurements of more than 100 LS+LU grains (unpublished data from our laboratory) point to a blurring of this somewhat facile division into three groups; however, at least five of the grains in this study fall roughly into the second group (cluster II). Five of the grains measured here have virtually identical $^{12}\text{C}/^{13}\text{C}$ ratios of ~ 47 –48, comparable to the peak in the distribution seen previously for LS+LU grains. While it is tempting to postulate that some of these grains condensed from the same star at the same time, it is highly unlikely, since the grains have dissimilar morphologies and drastically different exposure ages. Although, if some of the grains were part of a larger aggregate, the recoil corrections performed in this study would overestimate the actual amount of ^6Li lost, and the calculated exposure ages reported here would then be too high. Unfortunately, determining the validity of such a scenario is virtually impossible.

As mentioned above, the morphology of most LS+LU SiC is markedly different from those of the K-series (and similarly produced) grains analyzed previously. Most LS+LU series grains have sizes between 5 and 20 μm (with some rare grains reaching 60 μm in one dimension), often with smooth, platy surfaces sometimes exhibiting conchoidal fracture features. Lithium isotopic measurements on some KJG (mean diameter $\sim 3 \mu\text{m}$) SiC grains yielded no isotopic anomalies, as the measurements were largely compromised by terrestrial Li contamination. Regardless, the smaller (several μm) K-series grains are likely to be too small to retain substantial spallation-produced Li, at most up to 20% (Figure 3).

To first order, one might expect a positive correlation between grain size and exposure age, as grains much larger than a few microns would be mostly unaffected by interstellar shocks due to a paucity of sufficiently large collision partners and their large mass (Jones et al. 1997); however, we see no obvious relationship. In addition, the grains with very smooth surfaces show no evidence of surface erosion or pitting from travel through the ISM. Two of the largest grains have the shortest exposure ages, and the grain with an exposure age of 1 Gyr is only about $\sim 8 \mu\text{m}$ in size. For only eight grains, statistically meaningful comparisons between isotopic compositions and exposure ages are difficult to make. More grains need to be measured for Li isotopes and have their exposure histories determined in order to make any inferences on whether there is a preferential nominal age of presolar SiC.

5. CONCLUSION

We have found large SiC grains enriched in ^6Li relative to the SS Li isotopic composition. Only by significant contribution from GCR spallation can such enrichments be possible. We have used these ^6Li excesses, along with appropriate production rates and corrections for recoil loss, to infer cosmogenic exposure ages of individual grains. Two grains have nominal exposure ages of 50 Myr or less, three grains have ages between 100 and 500 Myr, and three grains have ages greater than 500 Myr, with one grain having an age close to 1 Gyr.

Long exposure ages are consistent with expected timescales for grain destruction in SN shockwaves, which dust is likely to encounter during interstellar transit. These ages represent the first realistic determination of individual presolar grain lifetimes that have been reported; however, future work remains to be done. Li isotopic measurements need to be performed on additional grains, in order to give better statistics on whether grains tend to cluster around an age and to better refine the age distribution. In particular, correlated studies of inferred exposure ages from both Li and noble gases (in particular ^3He and ^{21}Ne) in the same grains need to be performed in order to independently verify the validity of each technique. The large sizes of these LS+LU grains allow for substantial ^3He and ^{21}Ne to be retained, and measurements of the noble gas compositions in the same grains measured for Li are planned. Finally, new and updated models of grain survival should also be developed, taking into account that at least a portion of presolar grains have short exposure ages.

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REFERENCES

- Amari, S., Hoppe, P., Zinner, E., & Lewis, R. S. 1995, *Meteoritics*, **30**, 679
- Amari, S., Lewis, R. S., & Anders, E. 1994, *Geochim. Cosmochim. Acta*, **58**, 459
- Avila, J. N., Ireland, T. R., Holden, P., Gyngard, F., Bennett, V., Amelin, Y., & Zinner, E. 2007, in Workshop on the Chronology of Meteorites and the Early Solar System Lunar Planet. Sci., ed. A. N. Krot & E. R. D. Scott (League City, TX: LPI), 26
- Bernatowicz, T. J., Messenger, S., Pravdivtseva, O., Swan, P., & Walker, R. M. 2003, *Geochim. Cosmochim. Acta*, **67**, 4679
- Boss, A., & Foster, P. 1997, in Astrophysical Implications of the Laboratory Study of Presolar Materials, ed. T. J. Bernatowicz & E. Zinner (New York: AIP), 649
- Cameron, A. G. W., & Fowler, W. A. 1971, *ApJ*, **164**, 111
- Cameron, A. G. W., & Truran, J. W. 1977, *Icarus*, **30**, 447
- Castagnoli, D., & Lal, D. 1980, *Radiocarbon*, **22**, 133
- Charbonnel, C. 1995, *ApJ*, **453**, L41
- Chaussidon, M., & Robert, F. 1999, *Nature*, **402**, 270
- Clayton, D. 2003, *Handbook of Isotopes in the Cosmos* (Cambridge: Cambridge Univ. Press)
- de la Reza, R., Drake, N. A., da Silva, L., Torres, C. A. O., & Martin, E. L. 1997, *ApJ*, **482**, L77
- Greiner, D. E., Lindstrom, P. J., Heckman, H. H., Cork, B., & Bieser, F. S. 1975, *Phys. Rev. Lett.*, **35**, 152
- Gyngard, F., Amari, S., Zinner, E., Gallino, R., & Lewis, R. S. 2007a, in Lunar Planet. Sci., XXXVIII, ed. S. J. Mackwell (League City, TX: LPI), Abstract 1338
- Gyngard, F., Amari, S., Zinner, E., & Lewis, R. S. 2007b, *Meteorit. Planet. Sci.*, **42**, A61
- Heck, P. R., et al. 2008, *Lunar Planet. Sci.*, XXXIX, ed. S. J. Mackwell (League City, TX: LPI), Abstract 1239
- Herzog, G. F., et al. 1997, *Meteorit. Planet. Sci.*, **32**, 413
- Hohenberg, C. M., Nichols, R. H., Jr., Olinger, C. T., & Goswami, J. N. 1990, *Geochim. Cosmochim. Acta*, **54**, 2133
- Hoppe, P., Amari, S., Zinner, E., Ireland, T., & Lewis, R. S. 1994, *ApJ*, **430**, 870
- Hoppe, P., & Ott, U. 1997, in Astrophysical Implications of the Laboratory Study of Presolar Materials, ed. T. J. Bernatowicz & E. Zinner (New York: AIP), 27
- Huss, G. R., Hutcheon, I. D., & Wasserburg, G. J. 1997, *Geochim. Cosmochim. Acta*, **61**, 5117
- Huss, G. R., Ott, U., & Koscheev, A. P. 2008, *Meteorit. Planet. Sci.*, **43**, 1811
- Ip, W. H., & Axford, W. I. 1985, *A&A*, **149**, 7
- Jacobsen, B., et al. 2008, *Earth Planet. Sci. Lett.*, **272**, 353
- Jones, A., Tielens, A., Hollenbach, D., & McKee, C. 1997, in Astrophysical Implications of the Laboratory Study of Presolar Materials, ed. T. J. Bernatowicz & E. Zinner (New York: AIP), 595
- Knauth, D. C., Federman, S. R., & Lambert, D. 2003, *ApJ*, **586**, 268
- Lewis, R. S., Amari, S., & Anders, E. 1994, *Geochim. Cosmochim. Acta*, **58**, 471
- Leya, I., Lange, H.-J., Neumann, S., Wieler, R., & Michel, R. 2000, *Meteorit. Planet. Sci.*, **35**, 259
- Lodders, K., & Fegley, B., Jr. 1997, in Astrophysical Implications of the Laboratory Study of Presolar Materials, ed. T. J. Bernatowicz & E. Zinner (New York: AIP), 391
- Lyon, I. C., Tizard, J. M., & Henkel, T. 2007, *Meteorit. Planet. Sci.*, **42**, 373
- McKeegan, K. D., Chaussidon, M., & Robert, F. 2000, *Science*, **289**, 1334
- Meneguzzi, M., Audouze, J., & Reeves, H. 1971, *A&A*, **15**, 337
- Morrissey, D. J. 1989, *Phys. Rev. C*, **39**, 460
- Ott, U., Altmair, M., Herpers, U., Kuhnemann, J., Merchel, S., Michel, R., & Mohapatra, R. K. 2005, *Meteorit. Planet. Sci.*, **40**, 1635
- Ott, U., & Begemann, F. 2000, *Meteorit. Planet. Sci.*, **35**, 53
- Ouellette, N., Desch, S. J., & Hester, J. J. 2007, *ApJ*, **662**, 1268
- Pagel, B. E. J. 1997, *Nucleosynthesis and Chemical Evolution of Galaxies* (Cambridge: Cambridge Univ. Press)
- Read, S. M., & Viola, V. E., Jr. 1984, *At. Data Nucl. Data Tables*, **31**, 359
- Reedy, R. C. 1987, *J. Geophys. Res.*, **92**, E697
- Reedy, R. C. 1989, *Lunar Planet. Sci.*, **20**, 888
- Ritzenhoff, S., Schroter, E. H., & Schmidt, W. 1997, *A&A*, **328**, 695
- Sackmann, I.-J., & Boothroyd, A. I. 1999, *ApJ*, **510**, 217
- Seitz, H.-M., Brey, G. P., Zipfel, J., Ott, U., Weyer, S., Durali, S., & Weinbruch, S. 2007, *Earth Planet. Sci. Lett.*, **260**, 582
- Simpson, J. A. 1983, *Annu. Rev. Nucl. Part. Sci.*, **33**, 323
- Smith, V. V., & Lambert, D. L. 1990, *ApJ*, **361**, L69
- Tang, M., & Anders, E. 1988, *ApJ*, **335**, L31
- Tizard, J. M., Lyon, I. C., & Henkel, T. 2005, *Meteorit. Planet. Sci.*, **40**, 335
- Travaglio, C., Randich, S., Galli, D., Lattanzio, J., Elliott, L. M., Forestini, M., & Ferrini, F. 2001, *ApJ*, **559**, 909
- Virag, A., Wopenka, B., Amari, S., Zinner, E., Anders, E., & Lewis, R. S. 1992, *Geochim. Cosmochim. Acta*, **56**, 1715
- Webber, W. R., Lukasiak, A., & McDonald, F. B. 2002, *ApJ*, **568**, 210
- Webber, W. R., & Yushak, S. M. 1983, *ApJ*, **275**, 391
- Ziegler, J. F. 2004, *Nucl. Instrum. Methods Phys. Res. B*, **219**, 1027
- Zinner, E. 2007, in Treatise on Geochemistry Update, ed. H. D. Holland, K. K. Turekian, & A. Davis (Oxford: Elsevier), 1.02 (online update only), 1
- Zinner, E., Amari, S., & Lewis, R. S. 1991, *ApJ*, **382**, L47
- Zinner, E., et al. 2007, *Geochim. Cosmochim. Acta*, **71**, 4786