Strontium Isotopic Composition in Individual Circumstellar Silicon Carbide Grains: A Record of s-Process Nucleosynthesis

G. K. Nicolussi,[1,2,*] M. J. Pellin,[2] R. S. Lewis,[1] A. M. Davis,[1,3] R. N. Clayton,[1,3,4] and S. Amari[1,5]
[1]*Enrico Fermi Institute, University of Chicago, Chicago, Illinois 60637*
[2]*Materials Science & Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois 60439*
[3]*Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637*
[4]*Department of Chemistry, University of Chicago, Chicago, Illinois 60637*
[5]*McDonnell Center for the Space Sciences, Washington University, St. Louis, Missouri 63130*
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Twenty six individual circumstellar SiC grains extracted from the Murchison meteorite were analyzed for their strontium isotopic compositions by resonant ionization mass spectrometry. Large abundance deficits were found for the p-process isotope ^{84}Sr. The measured grains had ^{87}Sr/^{86}Sr ratios indistinguishable from the primordial solar value, but several grains differed in their ^{88}Sr/^{86}Sr ratios as a consequence of the branch point at ^{85}Kr. The Sr isotopic data are consistent with s-process nucleosynthesis at moderate neutron densities. [S0031-9007(98)07435-3]

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Various mineral phases with isotopic compositions radically different from solar-system values have been found in small amounts in several primitive meteorites over the last decade [1]. These so-called *presolar* or *circumstellar* grains predate the formation of our solar system. Circumstellar dust ("stardust") condensed from stellar outflows or from stellar explosion ejecta and provides important constraints on nucleosynthesis theory [2,3]. Silicon carbide is the most widely studied presolar mineral phase found in primitive meteorites. The isolated SiC grains are typically not larger than a few micrometers in size [4]. Small grains (<1 μm) are usually studied as aggregates of many grains; larger grains can be studied individually for their chemical and isotopic compositions. To obtain information from individual stars, it is essential to measure individual grains since aggregates contain grains from many different stellar sources and are contaminated with solar-system matter.

The vast majority of single SiC grains have isotopic signatures consistent with s-process nucleosynthesis (neutron capture on a *slow* time scale compared to β decay). These grains are often referred to as "mainstream" SiC grains and it is now generally believed that they formed around asymptotic giant branch (AGB) red giant stars [5]. In previous analyses we have measured isotopic abundances of Zr and Mo in mainstream SiC [6,7]. The large and variable s-process enrichments in Zr and Mo seen in these SiC grains are consistent with grain formation in the hydrogen envelope of low-mass AGB stars [$M \sim (1\text{–}3)M_\odot$] [8,9]. Strontium is also synthesized in AGB stars; ^{88}Sr, with its extremely low neutron capture cross section, acts as a "bottleneck" and therefore plays a critical role in s-process nucleosynthesis of elements with $A \geq 90$, the so-called *main* component [8,10]. Strontium isotopes have been measured previously, but only in aggregates of SiC grains from the Murchison meteorite. These measurements have shown large depletions in the ^{84}Sr/^{86}Sr ratios and very small deviations from solar in the ^{87}Sr/^{86}Sr and ^{88}Sr/^{86}Sr ratios [11–13]. In this letter we report the first measurements of Sr isotopes in individual circumstellar SiC grains.

Strontium has four stable isotopes at masses 84, 86, 87, and 88. ^{84}Sr is a p-process isotope which is shielded from the s- and r-processes. In the r-process, neutron capture occurs on a *rapid* time scale compared to β decays. As a result, the r-process involves very neutron-rich nuclei far from β stability. The p-process, on the other hand, is responsible for the nucleosynthesis of proton-rich isotopes (such as ^{84}Sr) by proton capture or (γ, n) photodisintegration reactions. ^{86}Sr is a pure s-process isotope, shielded from the r-process by ^{86}Kr. ^{87}Sr is also an s-process isotope; it is shielded from the r-process by ^{87}Rb. Because of its long half-life (48×10^9 yr), ^{87}Rb can be considered a stable nuclide on the time scale of nucleosynthesis. ^{88}Sr, on the other hand, has some minor r-process contribution but it is predominantly an s-process isotope.

In Fig. 1, the important region of the chart of the nuclides for s-process nucleosynthesis of Sr is shown. The possible s-process paths of neutron captures and

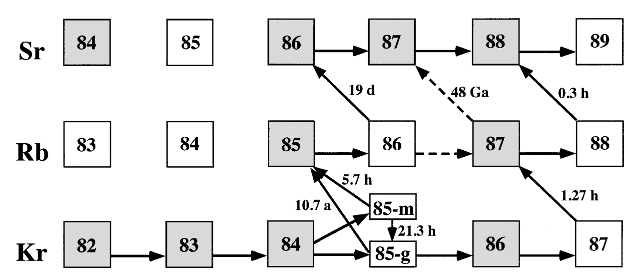

FIG. 1. The Kr-Rb-Sr region of the chart of the nuclides. Stable isotopes are in shaded boxes, unstable isotopes in open boxes. The major and minor channels for neutron capture and β decays are indicated by arrows (solid and dashed).

β decays are indicated by arrows. The synthesis of Sr is affected by the relative probabilities of neutron capture and β decay of short-lived ^{85}Kr ($T_{1/2} \approx 10.7$ yr). The actual branching ratio is further complicated by an isomeric state of ^{85}Kr with a very short half-life of 5.7 h. A detailed analysis of the operation of the ^{85}Kr branch is given by Lambert *et al.* [14]. These authors have also estimated a critical neutron density for the ^{85}Kr branch of $N(n)_c \approx 1.1 \times 10^8$ cm^{-3}, defining $N(n)_c$ as the neutron density for which the probability of ground state ^{85}Kr decay is equal to the probability that ^{85}Kr will capture a neutron to form ^{86}Kr. From Kr isotopic measurements on aggregates of SiC grains [15], it is known that the ^{86}Kr/^{82}Kr ratios vary dramatically among different size fractions and increase steadily with the grain size, suggesting that SiC comes from carbon stars representing a range of neutron densities. The ^{85}Kr branch yields two principal pathways for s-process nucleosynthesis of Sr: (1) $^{85}\text{Kr} \rightarrow {}^{85}\text{Rb} \rightarrow {}^{86}\text{Rb} \rightarrow {}^{86}\text{Sr} \rightarrow {}^{87}\text{Sr} \rightarrow {}^{88}\text{Sr}$ and (2) $^{85}\text{Kr} \rightarrow {}^{86}\text{Kr} \rightarrow {}^{87}\text{Kr} \rightarrow {}^{87}\text{Rb} \rightarrow {}^{88}\text{Rb} \rightarrow {}^{88}\text{Sr}$. "Path 1" as well as "path 2" synthesize ^{88}Sr; ^{86,87}Sr are only produced by path 1 and ^{84}Sr is not synthesized either way. Note that neutron capture on ^{86}Rb does not play an important role since the critical neutron density for the ^{86}Rb branch is much higher than for the ^{85}Kr branch.

Presolar SiC grains were recovered from the Murchison meteorite by methods described by Amari *et al.* [4]. In this study, grains from a specific size fraction with typical diameters of 2.1–4.5 μm (KJG size fraction) were analyzed for their Sr isotopic compositions. Because of the limited number of Sr atoms available in single grains, isotopic analyses are challenging and require ultrasensitive techniques such as time-of-flight resonant ionization mass spectrometry (TOF-RIMS). The methods used in our measurements have been described in previous papers [7,16,17]. In short, a pulsed desorption laser focused to a spot size of ~ 2 μm is utilized to atomize the grains in a UHV chamber. After each desorption pulse, laser radiation from two or three tunable lasers is used for stepwise excitation, and finally ionization, of a specific element. As a result, a certain element can be selectively detected in the time-of-flight mass spectrometer. The capabilities of this method are unique and we are now able to perform isotopic analysis of trace elements at the low ppm level in μm-sized grains.

For resonant ionization of Sr, a two-color ionization scheme was applied. Laser radiation of 460.73 nm pumps the prominent $5s^2(^1S_0) \rightarrow 5s5p(^1P_1^0)$ transition. A 421.32 nm photon further excites the Sr atoms from the $^1P_1^0$ level into a Rydberg state which ionizes in the extraction field of the time-of-flight mass spectrometer. As a solar-system reference material, we used SRM 855a from the National Institute of Standards and Technology. This standard is an aluminum casting alloy with a certified Sr concentration of 0.018 wt %. The isotopic composition (in atom percent) of such a terrestrial Sr sample is typically 0.56% ^{84}Sr, 9.86% ^{86}Sr, 7.00% ^{87}Sr, and 82.58% ^{88}Sr [18]. The Sr isotopic ratios obtained from this standard by TOF-RIMS were used in order to normalize the grain data to solar-system values.

About 40 individual SiC grains from the Murchison KJG fraction were probed for their Sr content. For a total of 26 individual SiC grains, we found enough Sr for the determination of the isotopic ratios with reasonable accuracy. Based on our experimental sensitivity, we estimate a Sr concentration in the low ppm regime for these 26 grains; this is similar to the values reported by Amari *et al.* [19]. The experimental uncertainties are largely determined by the total number of Sr atoms detected for a specific isotope. In many cases, the entire grain was consumed in the course of a measurement.

In Table I the results for these individual SiC grains are given as δ values, i.e., permil (0.1% [‰]) deviations from the isotopic ratios obtained from the terrestrial standard ($\delta^i\text{Sr}[‰] = \{(^i\text{Sr}/^{86}\text{Sr})_{\text{grain}}/(^i\text{Sr}/^{86}\text{Sr})_{\text{terr}} - 1\} \times 1000$). ^{86}Sr was chosen for normalization since it is a pure s-process isotope. In Fig. 2 the correlations among the isotopic ratios are shown in the form of three-isotope plots. Very large deficits in the abundance of the p-process isotope ^{84}Sr were found, ranging from solar-system values ($\delta^{84}\text{Sr} \equiv 0‰$) down to $\delta^{84}\text{Sr} < -800‰$

TABLE I. Sr isotopic composition in δ values for 26 individual SiC grains (Murchison KJG fraction, average grain size ≈ 3 μm in diameter); quoted errors are $\pm 2\sigma$, based on counting statistics.

Grain No.	δ^{84}Sr	δ^{87}Sr	δ^{88}Sr
106-C2	-843 ± 140	88 ± 138	281 ± 118
106-D6	-809 ± 123	16 ± 95	-24 ± 68
106-E2	-552 ± 546	-137 ± 152	9 ± 116
106-E9	<-786	41 ± 171	-34 ± 106
106-E18	-503 ± 323	-59 ± 118	-170 ± 74
106-G4	-852 ± 455	56 ± 189	280 ± 158
106-H5	<-533	53 ± 204	49 ± 127
106-H7	-659 ± 228	-80 ± 107	36 ± 87
106-I1	-715 ± 173	115 ± 129	20 ± 88
106-I2	-824 ± 172	-86 ± 124	-7 ± 96
106-I5	-84 ± 483	-73 ± 120	-23 ± 88
106-I9	-226 ± 366	-76 ± 130	82 ± 107
106-I10	-572 ± 506	72 ± 185	124 ± 137
106-I12	-212 ± 522	-33 ± 144	61 ± 109
106-J2	-531 ± 352	-71 ± 155	-87 ± 104
106-J4	-49 ± 481	-108 ± 139	135 ± 121
106-J5	-249 ± 396	-16 ± 130	1 ± 94
106-J7	-478 ± 395	50 ± 152	158 ± 119
106-J8	-216 ± 519	8 ± 149	25 ± 105
106-J9	-553 ± 353	162 ± 159	190 ± 118
106-J10	-309 ± 427	-4 ± 154	11 ± 109
106-K4	-829 ± 269	47 ± 128	30 ± 90
106-L9	74 ± 686	88 ± 175	37 ± 118
106-L10	-635 ± 165	-18 ± 107	-41 ± 76
106-L13	94 ± 656	93 ± 189	185 ± 144
106-M3	-307 ± 319	8 ± 135	5 ± 96

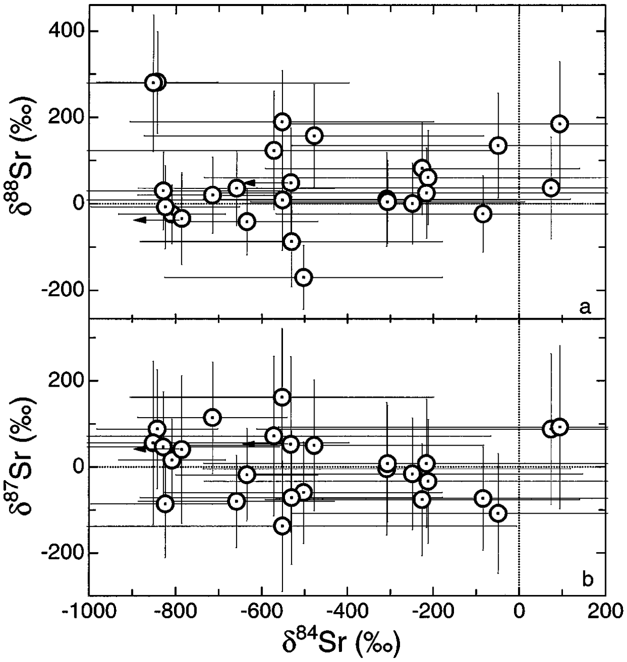

FIG. 2. Sr three-isotope plots of 26 SiC grains: δ^{88}Sr vs δ^{84}Sr (a) and δ^{87}Sr vs δ^{84}Sr (b). For the majority of grains, the ^{84}Sr/^{86}Sr ratio is highly depleted. The ^{87}Sr/^{86}Sr ratios, on the other hand, are indistinguishable from the solar value. Within the $\pm 2\sigma$ uncertainty, most grains are also normal in ^{88}Sr/^{86}Sr, but seven grains are anomalous with respect to the solar ratio. Six grains have significantly enhanced ^{88}Sr abundances and one grain is distinguished by a depletion in ^{88}Sr.

for several grains. Generally, grains with large deficits in ^{84}Sr had higher Sr concentrations [20]. This observation has a simple explanation: a large deficit in the p-isotope ^{84}Sr indicates a high degree of s-process nucleosynthesis in the parent star and, as a result, a large overproduction of the s-process isotopes ^{86}Sr, ^{87}Sr, and ^{88}Sr. The δ^{87}Sr values have a mean of 5 ± 30‰, not significantly different from solar. The spread in these δ values has a reduced χ^2 of 1.17, indicating no detectable variation from the average. The absence of a detectable deviation in the ^{87}Sr/^{86}Sr ratio is also consistent with higher precision Sr measurements on SiC aggregates [11]. Conversely, the δ^{88}Sr values have a mean of 51 ± 41‰ (2σ deviation in the mean). Furthermore, the spread in the δ^{88}Sr values from this mean have a reduced χ^2 of 3.85, indicating $\gg$99.9% likelihood of significant variation.

The SiC grains analyzed in this study show large depletions in the ^{84}Sr/^{86}Sr ratio, as expected for the s-process. The almost constant ^{87}Sr/^{86}Sr ratio reflects the fact that this ratio depends only on the relative neutron capture cross sections for steady state conditions; it is not affected by the branching ratio at ^{85}Kr. However, synthesis of ^{86}Sr and ^{87}Sr requires that the s-process path runs at least to some extent via path 1. The situation for the ^{88}Sr/^{86}Sr ratios is more complicated since ^{88}Sr can be produced via path 1 or path 2; hence, the ^{88}Sr/^{86}Sr ratio should reveal information on the s-process branching at ^{85}Kr. At neutron densities $N(n) < 10^7$ cm^{-3}, essentially all ^{85}Kr will decay (path 1 only), producing ^{88}Sr/^{86}Sr ratios lower than solar. We found one grain (106-E18) with a significant ^{88}Sr depletion and conclude that the neutron density in the parent star must have been low. For s-process nucleosynthesis with neutron densities approaching the critical value, a substantial amount of ^{88}Sr is produced by path 2. ^{88}Sr/^{86}Sr ratios higher than solar are then expected since the ^{86}Sr (and ^{87}Sr) synthesis is reduced. These conditions are achieved in later stages of thermally pulsating AGB (TP-AGB) stellar evolution. Since the envelope of the star is then dominated by s-process nucleosynthesis products, very low δ^{84}Sr is expected when δ^{88}Sr is high. Six SiC grains have a significant enhancement in ^{88}Sr (106-C2, -G4, -J4, -J7, -J9, -L13) but only two of them have the expected low δ^{84}Sr values (106-C2 and -G4). The solar-like ^{88}Sr/^{86}Sr ratios found in many SiC grains suggest predominant β decay at the ^{85}Kr branch, indicating that the neutron densities in the parent stars were lower than the critical density. The average ^{88}Sr/^{86}Sr ratio is slightly higher than the solar value and the magnitude of the shift in the average ^{88}Sr/^{86}Sr ratio is comparable to those measured in size-separated SiC aggregates [11]. The r-process nucleosynthesis can also produce an enhanced ^{88}Sr/^{86}Sr ratio, as ^{88}Sr can be made in the r-process and ^{86}Sr cannot. One likely site for r-process nucleosynthesis is supernovae. However, only ~1% of SiC grains, the so-called X-grains, from the Murchison meteorite have major element isotopic compositions that are consistent with a supernova origin [5]. Also, X-grains have lower trace element contents than mainstream SiC grains [19]. Thus, it is unlikely that an r-process grain is among the select 26 SiC grains that had high enough Sr to measure isotopic ratios.

The ^{87}Sr abundance in presolar SiC grains may also have a contribution from the decay of ^{87}Rb since grain formation. For example, the present solar system ^{87}Sr/^{86}Sr ratio of ~0.755 is about 8.1% higher than it was at the formation of the solar system 4.6×10^9 years ago [21]. If the ^{87}Rb/^{87}Sr ratio and the age of the SiC grains were known, the contribution to the total ^{87}Sr abundance could be calculated. For aggregates of SiC grains, Podosek *et al.* [11] found that the Rb/Sr ratios are highly depleted compared to the solar value. As a result, the additional ^{87}Sr abundance due to ^{87}Rb decay must be very small for most grains, even if these presolar grains were as old as our galaxy. However, an aggregate measurement could easily mask a small fraction of SiC grains with unusually high Rb/Sr ratios. The 26 single SiC grains in this study have δ^{87}Sr values and uncertainties which resemble a Gaussian error distribution (see above). As a result, there is no statistical evidence for an enhanced ^{87}Sr/^{86}Sr ratio. Even the 2.04σ deviation from the solar value in grain 106-J9 is (from a statistical point of view) not uncommon since a Gaussian distribution has a $\sim 5\%$ probability for a value outside $\pm 2\sigma$.

Over the past decade, meteoritic, astronomical, and nuclear data, as well as theoretical considerations, have provided strong evidence that thermally pulsing AGB stars are the site of the main component s-process nucleosynthesis. During this stage of stellar evolution, neutrons are produced in the He-burning shell by reactions such as $^{13}C(\alpha, n)^{16}O$ and $^{22}Ne(\alpha, n)^{25}Mg$. Strontium, especially ^{88}Sr, is expected to be overproduced in TP-AGB with large enhancement factors [8]. However, Sr concentrations measured previously in large circumstellar SiC grains were found to be low ($\sim$9 ppm on average) compared to those of Y and Zr, which are also overproduced in TP-AGB stars [19]. This depletion is thought to occur because Sr has a lower condensation temperature than Y and Zr [22].

Recently, the Sr isotopic composition in stellar atmospheres of TP-AGB stars was modeled by Gallino *et al.* [9]. Similar to our experimental results, large depletions in ^{84}Sr and relatively small effects for the $^{87}Sr/^{86}Sr$ ratios were found in these theoretical calculations. On the other hand, larger variations in the $\delta^{88}Sr$ values (ranging from -300 to $+1000‰$) were predicted, depending upon the amount of ^{13}C and ^{22}Ne available in the He-burning shell. The largest effects were observed for the grains 106-C2 ($\delta^{88}Sr = 281 \pm 118‰$), and 106-G4 ($\delta^{88}Sr = 280 \pm 158‰$). This enhancement in ^{88}Sr suggests neutron capture on ^{85}Kr which bypasses the synthesis of ^{86}Sr and ^{87}Sr but would produce ^{88}Sr, as mentioned above. The required higher neutron density can occur in low-mass TP-AGB stars due to the activation of the $^{22}Ne(\alpha, n)^{25}Mg$ neutron source in late thermal pulses [9]. The ^{22}Ne source becomes more important with increasing stellar mass since the higher Coulomb barrier requires somewhat higher temperatures, in excess of $\sim 3 \times 10^8$ K. For most SiC grains, the measured Sr isotopic data are consistent with an s-process at low neutron densities since the nucleosynthesis of Sr is dominated by β decay of short-lived ^{85}Kr; therefore, the $^{13}C(\alpha, n)^{16}O$ reaction must be the principal neutron source. The observation of the enhanced $^{88}Sr/^{86}Sr$ ratios in several SiC grains indicates that the $^{22}Ne(\alpha, n)^{25}Mg$ neutron source may have been activated in some of the parent stars.

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*Electronic address: gunther_nicolussi@qmgate.anl.gov

[1] G. R. Huss and R. S. Lewis, Geochim. Cosmochim. Acta **59**, 115 (1995).
[2] E. Anders and E. Zinner, Meteoritics **28**, 490 (1993).
[3] E. Zinner, Annu. Rev. Earth Planet. Sci. **26**, 147 (1998).
[4] S. Amari, R. S. Lewis, and E. Anders, Geochim. Cosmochim. Acta **58**, 459 (1994).
[5] P. Hoppe, S. Amari, E. Zinner, T. Ireland, and R. S. Lewis, Astrophys. J. **430**, 870 (1994).
[6] G. K. Nicolussi, A. M. Davis, M. J. Pellin, R. S. Lewis, R. N. Clayton, and S. Amari, Science **277**, 1281 (1997).
[7] G. K. Nicolussi, M. J. Pellin, R. S. Lewis, A. M. Davis, S. Amari, and R. N. Clayton, Geochim. Cosmochim. Acta **62**, 1093 (1998).
[8] R. Gallino, C. Arlandini, M. Busso, M. Lugaro, C. Travaglio, O. Straniero, A. Chieffi, and M. Limongi, Astrophys. J. **497**, 388 (1998).
[9] R. Gallino, M. Busso, and M. Lugaro, in *Neutron Capture Nucleosynthesis in AGB Stars*, edited by T. J. Bernatowicz and E. K. Zinner, Astrophysical Implications of the Laboratory Study of Presolar Material (American Institute of Physics, New York, 1997), pp. 115–153.
[10] D. D. Clayton, *Principles of Stellar Evolution and Nucleosynthesis* (McGraw-Hill, New York, 1986).
[11] F. A. Podosek, C. A. Prombo, S. Amari, and R. S. Lewis, Astrophys. J. (to be published).
[12] U. Ott and F. Begemann, Lunar Planet. Sci. **21**, 920 (1990).
[13] S. Richter, U. Ott, and F. Begemann, Lunar Planet. Sci. **23**, 1147 (1992).
[14] D. L. Lambert, V. V. Smith, M. Busso, R. Gallino, and O. Straniero, Astrophys. J. **450**, 302 (1995).
[15] R. S. Lewis, S. Amari, and E. Anders, Geochim. Cosmochim. Acta **58**, 471 (1994).
[16] Z. Ma, R. N. Thompson, K. R. Lykke, M. J. Pellin, and A. M. Davis, Rev. Sci. Instrum. **66**, 3168 (1995).
[17] G. K. Nicolussi, M. J. Pellin, W. F. Calaway, R. S. Lewis, A. M. Davis, S. Amari, and R. N. Clayton, Anal. Chem. **69**, 1140 (1997).
[18] E. Anders and N. Grevesse, Geochim. Cosmochim. Acta **53**, 197 (1989).
[19] S. Amari, P. Hoppe, E. Zinner, and R. S. Lewis, Meteoritics **30**, 679 (1995).
[20] The Sr concentration (or any other trace element concentration) cannot be determined by our technique on an absolute scale. However, based on the observed TOF-RIMS signal (for a given ablation laser power), we can estimate relative Sr concentrations among grains.
[21] D. W. Mittlefehldt and G. W. Wetherill, Geochim. Cosmochim. Acta **43**, 201 (1979).
[22] K. Lodders and B. Fegley, Jr., Meteoritics **30**, 661 (1995).