Zr AND Mo ISOTOPES IN SINGLE PRESOLAR GRAPHITE GRAINS: A RECORD OF STELLAR NUCLEOSYNTHESIS*

G. K. Nicolussi[1,2], M. J. Pellin[1], A. M. Davis[2],
R. S. Lewis[2], and R. N. Clayton[2,3,4]

1Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439
2Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637
3Department of Chemistry, The University of Chicago, Chicago, IL 60637
4Department of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637

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Zr AND Mo ISOTOPES IN SINGLE PRESOLAR GRAPHITE GRAINS: A RECORD OF STELLAR NUCLEOSYNTHESIS; G. K. Nicolussi[1,2], M. J. Pellin[1], A. M. Davis[2], R. S. Lewis[2], and R. N. Clayton[2,3,4], [1]Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, IL 60439; [2]Enrico Fermi Institute, [3]Department of Chemistry, [4]Department of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637.

Abstract. Thirty-two individual graphite grains from the Murchison meteorite were analyzed for their Mo and/or Zr isotopic compositions by laser ablation resonant ionization mass spectrometry. $^{96}Zr/^{94}Zr$ ratios range from 0.074 times to 10 times the solar value. Five grains have depletions in ^{96}Zr, suggestive of the *s*-process, and two grains have extraordinary enrichments in ^{96}Zr, suggestive of the *r*-process. Most graphite grains have close-to-terrestrial Mo isotopic composition, but five have *s*-process Mo nucleosynthesis signatures.

Introduction. Circumstellar dust grains recovered from meteorites provide important constraints on nucleosynthesis theory [1]. These "stardust" grains condense from stellar outflows or from stellar explosion ejecta, survive potentially destructive processes in the interstellar medium and the solar system, and can be isolated from a variety of types of primitive meteorites [2].

Thus far, our heavy element isotopic analyses of individual presolar grains have focused on SiC [3,4]. Most SiC grains have light element isotopic compositions consistent with formation around AGB stars [5]. The large and variable *s*-process enrichments in Zr and Mo seen in presolar SiC grains are entirely consistent with mixing of *s*-process material from the He-intershell into the initially isotopically normal H-envelopes of AGB stars in repeated third dredge-up episodes [3,4,6]. Our data on Zr and Mo isotopic compositions of 25 individual presolar SiC grains [3,4] show only *s*-process enrichments. There are, however, two major types of presolar grains that have C, N, O, Mg, Si, Ca and Ti isotopic signatures indicating a supernova origin: (1) X-type SiC grains, which comprise about 1% of the SiC presolar grain population [7]; and (2) low-density graphite grains [8,9,10,11]. In hopes of finding evidence of nucleosynthetic processes thought to have occurred in supernovae (*r*- or *p*-processes), we have extended our single-grain Zr and Mo isotopic measurements to presolar graphite. For a variety of reasons, our first effort was on high-density graphite. These grains have received less attention than those from the low-density fraction, because high-density graphite grains tend to be smaller and have lower concentrations of minor and trace elements.

Experimental. Mo and Zr isotopic compositions of grains were measured on the CHARISMA instrument located at Argonne National Laboratory, in which laser-desorbed neutral atoms are resonantly ionized and counted with a time-of-flight mass spectrometer [3,4,12,13]. The key advantages of this technique for analysis of presolar grains are its high useful yield (a few percent) and its relative immunity to isobaric interferences. Both Zr and Mo were resonantly ionized using two overlapped tuned dye laser beams. For Zr, 319.121 nm and 388.75 nm beams resonantly ionized the atom ($a^3F_2 \rightarrow w^3G^o_3 \rightarrow$ ionization continuum); for Mo, 313.26 nm and 388.2 nm beams were used ($a^7S_3 \rightarrow y^7P^o_4 \rightarrow$ionization continuum). These excitation schemes had extremely low yields of isobaric ions, with the Zr scheme significantly better than one we had used previously (but at the expense of somewhat lower useful yield).

The graphite grains used here are from the Murchison high-density fraction KFC1 (ρ=2.15-2.20 g/cm^3); the grains were typically 2–4 μm in diameter. The grains were mounted on a gold mount and all graphite grains on the mount were imaged with a scanning electron microscope prior to isotopic analysis. Zr and Mo are known to occur in some presolar graphite grains in the form of tiny ZrC-TiC-MoC subgrains [14], but graphite with supernova isotopic signatures appears to contain only TiC subgrains [15]. The overall concentration of Mo and Zr is <10 ppm for most grains measured based on our sensitivity. For most grains, Mo was analyzed first and the grain was consumed. One grain was analyzed for Zr only, and for eight grains both elements were analyzed.

Zr isotopes. Zr has four isotopes predominantly produced by *s*-process nucleosynthesis, ^{90}Zr, ^{91}Zr, ^{92}Zr, and ^{94}Zr, and one predominantly *r*-process isotope, ^{96}Zr. ^{96}Zr can also be produced by the *s*-process at neutron densities $>10^8$ cm^{-3}, because of the relatively long half-life of ^{95}Zr (64d). An enormous range of isotopic anomalies was observed for Zr. In Fig. 1, raw mass spectra of two extreme graphite grains are compared with a terrestrial standard. Grain 3.05 has virtually no ^{96}Zr ($\delta^{96}Zr$= –926±35‰, normalized to ^{94}Zr) whereas in grain 5.01, ^{96}Zr is the most abundant isotope ($\delta^{96}Zr$=9377±1251‰).

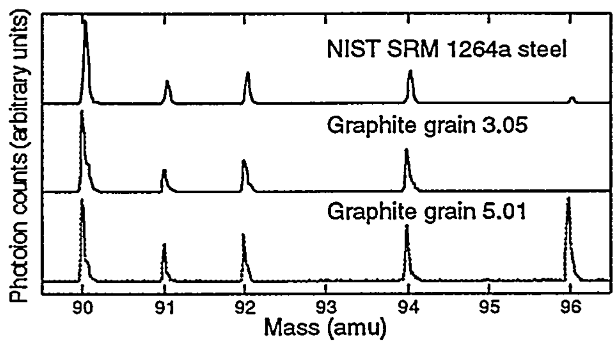

Fig. 1. Resonant ionization mass spectra of a terrestrial standard and two Murchison graphite grains.

^{94}Zr-normalized Zr isotopic compositions of graphite and SiC are compared in 3-isotope plots in Fig. 2. Five graphite grains show progressively larger depletions in ^{92}Zr, ^{91}Zr, and ^{90}Zr and have $\delta^{96}Zr < -500$‰. These patterns resemble those seen in individual SiC grains [3], but the graphite grains tend to have lower $\delta^{90}Zr$, $\delta^{91}Zr$, and $\delta^{92}Zr$. Both these graphite grains and the SiC grains are enriched in *s*-process Zr and probably formed around low-mass (<5 solar mass) thermally pulsing asymptotic giant branch (TP-AGB) stars [6], but the two types of grains may come from different populations of stars. In the TP-AGB stage (part of normal stellar evolution of low mass stars), *s*-process material synthesized in the He-intershell is episodically mixed into the initially near-solar isotopic composition H-envelope.

Two grains have large ^{96}Zr excesses (Fig. 2 right side). The most likely explanation for large ^{96}Zr enrichments is the *r*-process, which is thought to occur in core-collapse supernovae. It is also possible to produce ^{96}Zr in the *s*-process if the neutron density is high enough. Since solar system Zr is a mixture of *r*-process and *s*-process components, the solar system-normalized isotopic patterns should be complementary. Since *s*-process graphite grains have low $\delta^{90}Zr$, $\delta^{91}Zr$, and

δ^{92}Zr and very low δ^{96}Zr values, *r*-process Zr should have enhancements in these δ values. Grain C.14 has δ^{90}Zr, δ^{91}Zr, and δ^{92}Zr enhancements and high δ^{96}Zr, as expected for *r*-process Zr, but its δ^{96}Zr is not as large as predicted for pure *r*-process Zr. Grain 5.01 has a light Zr isotope pattern like the *s*-process grains, but a spectacular δ^{96}Zr of nearly 10,000 ‰. Perhaps *s*-process Zr mixed with extreme, almost monoisotopic ^{96}Zr *r*-process Zr from different zones of supernova ejecta. A second possibility is that Zr in this grain is the product of a special *s*-process nucleosynthesis at unusually high neutron density. Grain 5.01 has about as extreme a ^{96}Zr enrichment as is allowed by neutron capture cross sections. One grain, C.10, has the low δ^{90}Zr, δ^{91}Zr, and δ^{92}Zr of the *s*-process grains, but normal δ^{96}Zr, and could also be an *s*-process grain produced at an enhanced neutron density.

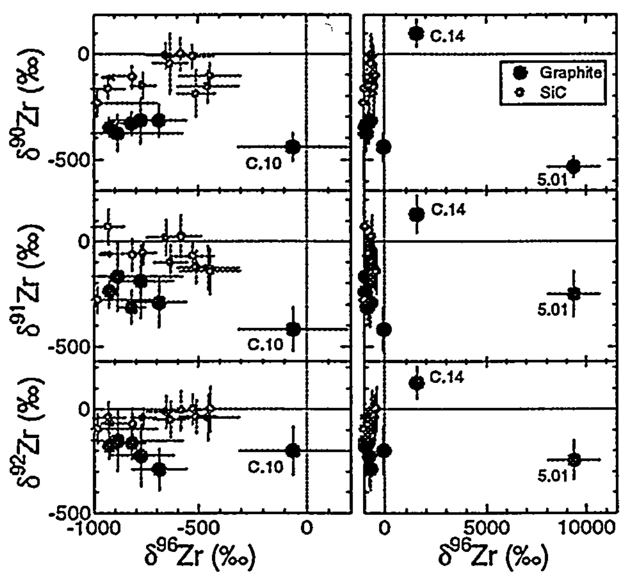

Fig. 2. Zr isotopic compositions of individual presolar graphite and SiC grains, ±2σ. Note the greatly expanded δ^{96}Zr scale on the right side.

Mo isotopes. Mo has two *p*-process isotopes, ^{92}Mo and ^{94}Mo, which are shielded from the *s*- and *r*-processes. ^{96}Mo is a pure *s*-process isotope, shielded from the *r*-process by ^{96}Zr. ^{100}Mo is a pure *r*-process isotope, which cannot be produced in substantial amounts by the *s*-process because of the short half-life of ^{99}Mo ($T_{1/2}$~66h). The remaining stable isotopes, ^{95}Mo, ^{97}Mo, and ^{98}Mo are produced in different proportions by both the *r*- and *s*-processes.

^{96}Mo-normalized Mo isotopic compositions of graphite and SiC are compared in 3-isotope plots in Fig. 3. Both types of presolar grain show the same correlations among Mo isotopes. The strongest depletions are observed for the *p*-process ^{92}Mo and ^{94}Mo and *r*-process ^{100}Mo, which are destroyed in the *s*-process. The isotopes ^{95}Mo, ^{97}Mo and ^{98}Mo show lesser depletions relative to solar system Mo, because solar Mo has both *r*- and *s*-process contributions. The correlations point to a stellar environment in which mixing of *s*-process material with material of near-solar composition occurred, most likely in the H-envelopes of low mass TP-AGB stars [6]. The distributions of SiC and graphite along the correlation lines in Fig. 2 are quite different: SiC grains are generally more than 50% of the way towards the pure *s*-process endmember at δ^{92}Mo= −1000‰, whereas only 5 of 26 graphite grains plot significantly away from the origin.

Zr and Mo isotopes. The correlations between Zr and Mo in graphite grains in which both elements were analyzed are quite interesting (Fig. 3 lower right). Three grains have *s*-process patterns in Zr and Mo, characterized by large depletions in δ^{96}Zr and δ^{92}Mo. For 4 graphite grains, very small, if any, variations in δ^{92}Mo, δ^{94}Mo, and δ^{100}Mo accompany large positive or negative δ^{96}Zr values. Due to the large fraction of presolar graphite grains with nonsolar Zr and near-solar Mo isotopic compositions, the possibility of dilution with solar Mo in the laboratory or in nature must be considered. A solar system contribution to graphite would have a greater effect than for SiC, because of the observed lower trace element content of presolar graphite.

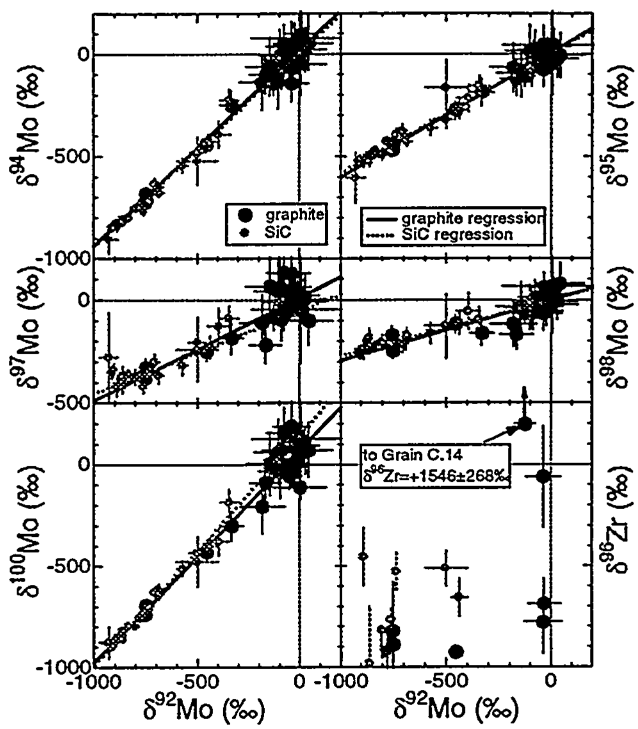

Fig. 3. Mo isotopic compositions of individual presolar graphite and SiC grains, ±2σ, with weighted linear regressions through each type of grain.

Conclusions. The Zr and Mo isotopic compositions of presolar graphite reveal a rich variety of stellar heavy element nucleosynthesis products. In addition to sampling what appears to be a different population of AGB stars than is sampled by mainstream SiC grains, there are grains that appear to have sampled stars in which the *r*-process and/or an unusually neutron-rich *s*-process at occurred.

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