

FIRST FOUR-ISOTOPE MEASUREMENTS OF CHROMIUM IN PRESOLAR SiC GRAINS. J. Levine^{1,2,♦}, M. R. Savina^{1,3}, N. Dauphas^{1,2,4}, A. M. Davis^{1,2,4}, B. H. Isselhardt^{5,6}, K. B. Knight^{1,2,6}, R. S. Lewis^{1,4}, M. J. Pellin^{1,3}, T. Stephan^{1,2}, ¹Chicago Center for Cosmochemistry, ²Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, USA, ³Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA, ⁴Enrico Fermi Institute, University of Chicago, Chicago, Illinois 60637, USA, ⁵Department of Nuclear Engineering, University of California, Berkeley, California 94720, USA, ⁶Lawrence Livermore National Laboratory, Livermore, California 94550, USA, ♦Present address: Space Sciences Laboratory, University of California, Berkeley, California 94720, USA (jlevine@ssl.berkeley.edu).

Introduction: Recent improvements to the CHARISMA instrument at Argonne National Laboratory have enabled the first four-isotope measurements of Cr in presolar SiC grains. Resonance ionization mass spectrometry (RIMS), which uses tuned lasers to excite and ionize atoms of a single element of interest from a cloud of desorbed neutral atoms, permits the unambiguous detection ⁵⁰Cr and ⁵⁴Cr without interference from ⁵⁰Ti, ⁵⁰V, ⁵⁴Fe or molecules. The technique also affords the extremely high sensitivity necessary to detect Cr in presolar SiC grains, where its abundance is typically hundreds to thousands of parts per billion [1]. Because the nucleosynthetic anomalies expected for Cr isotopes are much smaller [2,3] than those we have measured previously among Sr, Zr, Mo, Ru, and Ba isotopes [4-9], this work employs all the high precision capabilities we have developed recently [10], and some additional enhancements that we report here for the first time. In particular, to obtain the highest possible precision, we use mounts upon which presolar SiC grains have been interspersed with grains of terrestrial Cr₃C, large sample holders that flatten the electric field near the specimen, and motorized steering mirrors to raster the desorption laser beam.

Experimental setup: Previously the reproducibility of Cr isotope measurements obtained with CHARISMA on terrestrial materials was limited to a few tens of permil. Most of this systematic error was eliminated when we compared measurements taken less than ~300 μm apart on the same sample stub. We adopted two strategies to mitigate this source of error. First, we dispersed a suspension of synthetic Cr₃C grains over a mapped sample mount of presolar SiC grains, so that the distance between any SiC grain and the nearest possible standard was ~300 μm or less. Second, we potted the 8 mm sample stub in the center of a 75 mm holder, instead of the 25 mm holders formerly used. Ion paths through the time-of-flight mass spectrometer depend sensitively on the electric field above the target where the desorbed atoms are photoionized. The larger holder ensures that atoms desorbed from anywhere on the sample are photoionized far from the edge of the target electrode, and therefore in a more nearly uniform electric field.

Another source of error is the geometry of the grains themselves. When an ion beam is used to sputter atoms from the sample, analytical spots can be as small as 350 nm. We found that spot analyses at different points on the same ~5 μm Cr₃C grains had isotopic reproducibility limited to ~15%, even though repeated analyses on single spots were identical within 4%. By contrast, rastering the ion beam over a small area including the entire Cr₃C grain yielded reproducible results with Poisson-limited uncertainties at the 4% level. Trace-element isotopic analyses in presolar grains require higher sample erosion rates than we can obtain by ion sputtering, and we therefore use a pulsed laser to desorb atoms from the sample. In this mode, spot-to-spot variations due to sample geometry are compounded by the non-uniform profile of the desorption beam. We therefore used motorized steering mirrors to raster the 1 μm laser spot over a 5–10 μm field centered on each 3–6 μm grain.

Samples: The SiC grains we examined were isolated from the Murchison chondrite according to the procedure of [11], except that no Cr₂O₇ was used to oxidize organic matter. (The samples were also prepared to be free of W contamination by avoiding use of Na₆(H₂W₁₂O₄₀) for density separation.) The diameter of each grain is nominally 3–6 μm. The grains were identified as SiC by secondary electron microscopy and energy dispersive x-ray spectroscopy, but have not been isotopically analyzed for C, N, or Si. Nevertheless, we assume that most of the grains are from the mainstream population, which formed around asymptotic giant branch (AGB) stars.

Results: We report Cr isotopic abundances in 18 presolar SiC grains. We were unable to obtain reliable measurements of ⁵²Cr on four grains because of high count rates which led to undercounting. Measured isotope ratios, normalized to ⁵⁰Cr and to the Cr₃C standard (assumed to be of terrestrial isotopic composition), are presented in Figures 1 and 2 in δ notation.

We observe significant enrichments of ⁵²Cr relative to ⁵⁰Cr, with the measurements on individual grains distributed around a mean of +90%. Only 4 of 14 grains have δ⁵²Cr consistent with zero at the 1σ confidence level. The spread in the measurements is some-

what larger than would be expected from statistical fluctuations within a single population ($\chi^2 = 2.4$ per degree of freedom). Count rates on both the Cr_3C and SiC grains were low enough that the positive $\delta^{52}\text{Cr}$ anomalies cannot have been an artifact of undercounting ^{52}Cr in the Cr_3C standards. Likewise, elevated $\delta^{52}\text{Cr}$ cannot be a spallation signature, because production of all Cr isotopes by ^{56}Fe spallation would reduce the relative abundance of the major isotope ^{52}Cr . Finally, elevated $\delta^{52}\text{Cr}$ excludes the possibility that SiC grains are responsible for the Cr isotope anomalies observed in meteoritic leachates [e.g., 12].

Although cosmic ^{52}Cr and ^{53}Cr are produced together in Type II supernovae [e.g., 13], our measurements of $\delta^{53}\text{Cr}$ are unlike those of $\delta^{52}\text{Cr}$. Observed values of $\delta^{53}\text{Cr}$ are centered on zero, with 8 negative and 10 positive values, and with 11 of 18 measurements consistent with zero at the 1σ confidence level. Once again, the spread of measurements is slightly larger than would be expected from statistical fluctuations alone ($\chi^2 = 2.3$ per degree of freedom).

^{54}Cr is the only Cr isotope that is significantly overproduced during s -process nucleosynthesis, with the models of [2,3] predicting $\delta^{54}\text{Cr}$ values between +120‰ and +240‰ for the material ejected during thermal pulses of carbon-rich AGB stars. Our statistical uncertainties are too large to unambiguously test the model predictions, especially if s -processed Cr is mixed with Cr from another source [e.g. 9]. Measured $\delta^{54}\text{Cr}$ values are centered around +40‰; ten of 18 grains have $\delta^{54}\text{Cr}$ within 1σ of zero, and 8 of 18 are consistent with $\geq +120$ ‰ at the same level of confidence. The spread of measurements is hardly larger than expected from statistical fluctuations alone ($\chi^2 = 1.5$ per degree of freedom).

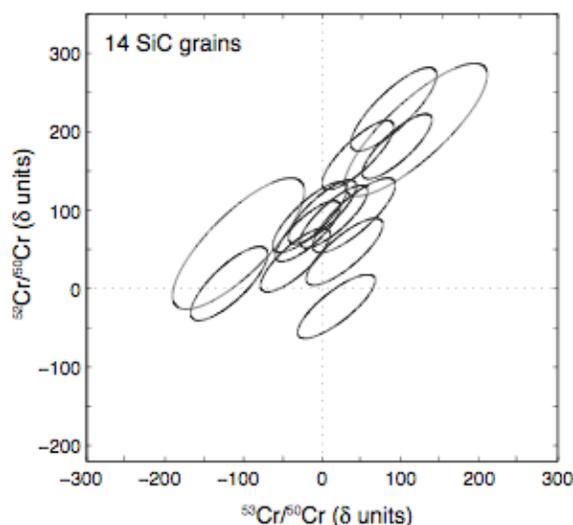


Figure 1: Measured $^{52/53}\text{Cr}/^{50}\text{Cr}$ ratios in presolar SiC grains. Ellipses contour 1σ . Dashed lines represent terrestrial values.

Discussion and Conclusions: Because nucleosynthesis in the AGB stars where most SiC grains are formed does not greatly affect the abundances of $^{50,52,53}\text{Cr}$, our observed enrichments in $\delta^{52}\text{Cr}$ are likely an isotopic signature inherited from an earlier generation of stars. A similar explanation is invoked for Si and Ti isotopes in mainstream presolar SiC [14]. Similarly, the dearth of appreciable $\delta^{53}\text{Cr}$ anomalies in these grains argues that galactic dust two stellar generations ago had a comparable $^{53}\text{Cr}/^{50}\text{Cr}$ ratio to that of terrestrial materials. The very different results we obtain for $\delta^{52}\text{Cr}$ and $\delta^{53}\text{Cr}$ requires the decoupling of these two quantities in (pre)history of Solar System Cr.

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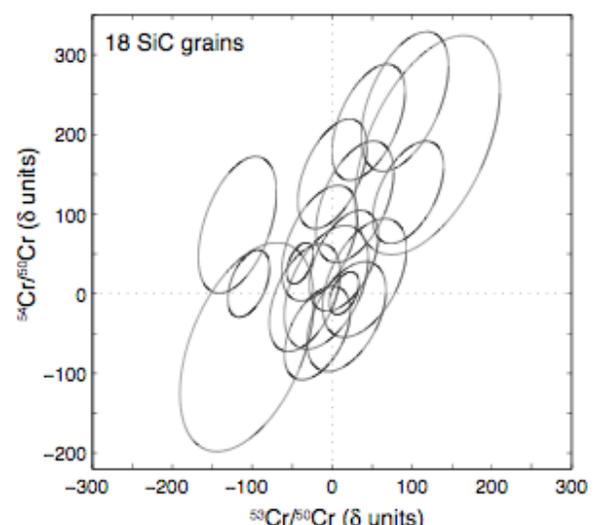


Figure 2: As in Figure 1, but with $^{53}\text{Cr}/^{50}\text{Cr}$ and $^{54}\text{Cr}/^{50}\text{Cr}$ ratios.