TRACE ELEMENT DETERMINATIONS IN PRESOLAR SiC GRAINS BY SYNCHROTRON X-RAY FLUORESCENCE: COMMENCEMENT OF A COORDINATED MULTIMETHOD STUDY.

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Introduction: Presolar SiC grains are robust remnants of stellar matter ejected from stars. They survived processing in the early solar system and retain the nucleosynthetic fingerprints of their stellar progenitors. As such, they represent unique physical probes of the interiors of stars. Presolar SiC grains are commonly analyzed by mass spectrometric techniques that determine isotopic compositions and, to some degree, elemental concentrations. These techniques, however, are destructive, and can be subject to matrix effects. Elemental composition data on presolar grains remain scarce and affected by contamination and analytical artifacts. In addition, contamination has plagued isotopic characterization of some elements such as Mo and Ba [1].

We determined trace element compositions of individual ~1–3 μm presolar SiC grains from the Murchison CM chondrite using nondestructive synchrotron X-ray fluorescence (SXRF). Samples included the KJG fraction [2], and a second KJG fraction that underwent additional cleaning. As every cleaning step results in some grain loss, one goal of this study was to justify additional cleaning of grains. Six KJG grains and 26 additionally cleaned KJG grains were analyzed, with location and identities of individual grains noted for future correlated isotopic study.

Technique: This study follows work of Kashiv [3], but with reduced contamination, reduced analytical scatter and improved detection limits. Also, in [3] the location of individual grains on the mount was not recorded, preventing correlative elemental and isotopic studies. Recleaned samples were treated with $HClO_4$ followed by a combination of HF and HCl with the aim of removing contaminants including Li, Cr, W and Pb. Grains from the recleaned and normal KJG fractions were then deposited onto separate 1 μm thick substrates of high-purity SiN.

A 12 nm coating of high-purity aluminum oxide was applied via atomic layer deposition (ALD) [4] to prevent loss of grains from the substrate surfaces. Sample mounts were then examined using a JEOL JSM-5800LV SEM under low vacuum conditions using a 10 kV accelerating voltage. Energy-dispersive x-ray microanalysis (EDX) allowed positive identification of SiC grains and generation of a map of all grain locations on the sample mounts, essential for relocating and tracking grains for SXRF and intended isotopic analyses.

SXRF analyses were done at the Advanced Photon Source (APS) synchrotron on the GeoSoilEnviroCARS beam line, using a monochromatic 22 keV primary X-ray beam, sufficient to excite fluorescence from most trace elements expected to be present in ppm concentrations or greater. The beam diameter was adjusted to ~2.5 μm, comparable in size to the SiC grains. Elements detected include Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Zr, Nb. Mo and W. We also searched for Os, Pt, Au, Tl, Pb and Th in spite of detection challenges due to low abundances and peak overlaps. Silicon in the grains could not be quantified or used as an internal reference because of the high and variable contribution from the SiN substrate.

Two NIST standard glasses (SRM 1832 and 1833) were analyzed to calibrate peak energies of select elements. Analyses of the set-up without the sample mounts were taken to determine baselines at the start and finish of the experiment. Background substrate analyses were taken near each grain, and subtracted from the relevant SiC grain spectra. Substrate background spectra showed minimal variations in time and position.

Fluorescence peaks in the SiC spectra were fitted by developing a peak-fitting scheme based on the NIST standard analyses, and then applying these fit parameters (with some peak additions) to the background-subtracted grain spectra. Since the SiN substrate prevented the use of Si as an internal reference element, we used a Cameca SX-50 electron microprobe (EPMA) to determine the Ti concentration of individual grains following SXRF analyses. Using a 15 kV accelerating voltage with 50 nA of current on the sample, we determined Ti concentrations relative to the Kakanui augite standard. These EPMA Ti concentrations were then used as grain-specific internal references, which together with relative sensitivities determined from the NIST standard spectra, allowed peak intensities in the SXRF spectra to be converted to concentrations. Sensitivities for elements absent in the

NIST standards were determined by interpolation and extrapolation. This Ti internal reference normalization procedure was a primary source of uncertainty in the determination of absolute trace element abundances

Results: Comparison between cleaned and normal KJG SiC grains shows significant removal of at least two contaminant elements of particular interest, W and Pb. Previous SXRF observation of W in SiC [5] grains is clearly dominated by contamination. KJG grains yield ~50 microgram/gram (ppm) W, while all but one cleaned KJG grains have undetectable (<0.5 ppm) W. Lead, in contrast, remains present in the cleaned grains, although reduced by an order of magnitude in concentration from precleaning levels. The removal of contaminants is crucial for future isotopic study of these grains.
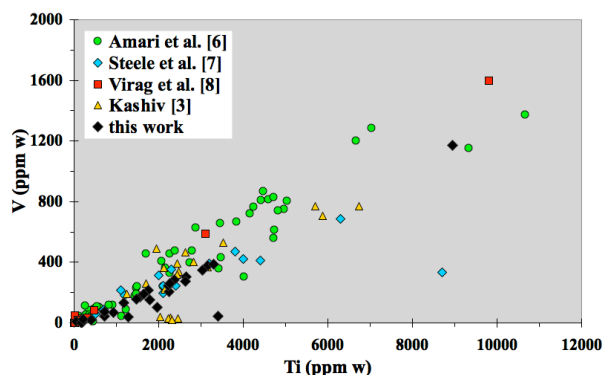

Fig. 1: *Ti and V compositions of presolar SiC from this and other [3,6-8] studies, determined by multiple techniques.*

Comparison of these data with data from other studies [3,6–8] shows good agreement between different data sets obtained using different techniques, although few elements have so far been measured by multiple techniques. A plot of Ti and V concentrations (Fig. 1) shows roughly similar trends in all five data sets, with the very tight behavior of the SXRF data likely due to the lack of matrix-dependent artifacts and removal of contaminants. Several studies [3,6,8] have also determined Zr and Fe concentrations (Fig. 2). We show this plot to illustrate one strong discrepancy between these new data and previous studies, an offset in Fe concentrations. Our data, as well as results reported by [3] and [8] support Fe concentrations orders of magnitude smaller than those reported in [6]. Other element concentrations suggest generally good correlation between previous data, as can be seen by the similar spread in Zr concentrations.

Conclusions: While EMPA studies are relatively straightforward [7, this work], they are useful for a limited number of elements, generally only Si, Al and Ti. SIMS analyses [6,8], while having lower detection limits, suffer from lack of appropriate SiC standards and

may be subject to matrix effects. TOF-SIMS analyses [9–11] and NanoSIMS analyses can be less destructive, but are dependent on matrix and surface morphology, and have a spatial resolution generally unsuited to bulk composition determinations in individual SiC grains. Thus far, studies of individual presolar SiC grains have suggested some correlations between grain isotopic and elemental composition [6,11] but further investigation is clearly needed. Presently, SXRF offers the best combination of detection limit and sample preservation for determining elemental compositions of presolar SiC.
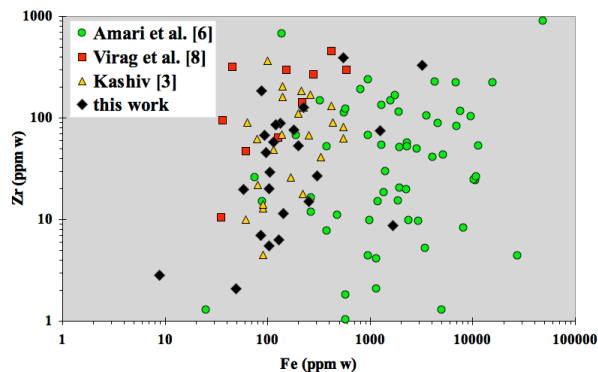

Fig. 2: *Order of magnitude variations in Fe and Zr compositions of SiC reported in this and other [3,6,8] studies.*

Future work will use CVD diamond as the mounting substrate to allow Si to be used as the internal reference element for SXRF trace element analyses. These measurements will be part of a consortium study on individual grains including isotopic analysis of a range of elements. Together, these multi-method results will permit detailed investigation of the relative roles of chemistry and nucleosynthesis in controlling trace element abundances in presolar grains.

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